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Silurian black shales of Western Ukraine: petrography and mineralogy

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Abstract. Organic-rich Silurian black shale, stretching along the western margin of the East European Platform from the Baltic Sea to the Black Sea, represent a potential target for conventional and unconventional hydrocarbon exploration. In Western Ukraine, these strata occur in the most deeply buried part of the platform and their thickness reaches 1000–1500 m. On the basis of petrographic investigations of rocks enriched with total organic carbon (TOC) (up to 2.16 wt%), their mineral composition has been established and four types of rocks have been distinguished: mudstones, clayey mudstones, limy marlstones and marlstones. In these rocks quartz (30–60%) significantly (1.5 to 2 times) prevails over the clay minerals. They contain a large amount of carbonates (calcite, dolomite): from 5–15% in mudstones and limy mudstones to 51% in marlstones. It was established that quartz grains, by their size correspond to the very fine sand (0.125–0.062 mm) and coarse silt (0.062–0.031 mm) fractions. Such a proportion of minerals in the rocks and the quartz grain size indicates their high brittleness, and consequently, the possibility of the efficient hydraulic fracturing within these strata. X-ray diffraction investigations were used in order to obtain the quantitative estimate of the mineral composition of the rocks with the highest TOC content – mudstones and limy mudstones. Additionally, it was established that the clay fraction was represented by chlorite and illite. These minerals are present in the rocks in different proportions, depending on the depth and the area of occurrence. Illite content decreases, while chlorite content increases with depth, contributing over 30% of the clay fraction. Smectite and mixed-layered minerals are lacking in the clay fraction of the rocks, which provides favourable conditions for their eventual hydraulic fracturing.

Key words: Silurian, black shale, petrography, mineral composition, total organic carbon, X-ray diffraction.

INTRODUCTION

The Silurian sequence of the East European Platform has become of interest as one of the European potential targets for shale gas exploration over the past decade. It covers a large area stretching from the Baltic Sea to the Black Sea. The Silurian deposits of Western Ukraine are the main subject of this study. They represent a continuation of the coeval deposits on the Polish territory, whose shale gas potential has been widely discussed (e.g., Poprawa 2010; Sachsenhofer & Koltun 2012). Even though the challenging forecast of large-scale shale gas potential resources have not yet been proven, these deposits still are of significant interest for further investigations, due to their great thickness and the possibility of ‘sweet spots’ within separate tectonic units. As a result, the Silurian black shale sequence of Western Ukraine can be regarded as a potential unconventional natural gas resource, and may therefore become an important supplement to the conventional energy sources in the future.

The petrographic features and mineralogical composition of black shales serve as one of the major non-tectonic factors which influence the fracture development of the rocks and control the gas accumulation conditions (Ding et al. 2012). The mineralogical and petrographic composition of Silurian black shales of Western Ukraine has not yet been analysed with regard to shale gas prospecting and this study represents the first attempt in this field.

Based on the analyses of data from the existing wells, in particular, well-log data, core samples, thin section and X-ray diffraction (XRD) analyses, data on the petrography and mineralogical composition of the rocks as well as the content of clay and non-clay minerals in the rocks, different types of rocks and their distribution within the area of Silurian occurrence will be discussed.

GEOLOGICAL BACKGROUND

The area under study is the southwestern margin of the East European Platform (Fig. 1). The sedimentary cover of this territory rests on the Archaean–Proterozoic basement made up of magmatic and metamorphic rocks. The basement crops out at the surface within the Ukrainian Shield and monoclinally dips westwards towards the Teisseyre–Tornquist Zone. The maximum thickness of the sedimentary cover reaches 10 km (Kruglov & Tsypko 1988; Chebanenko et al. 1990). The sedimentary succession is represented by the Neo-Proterozoic (Tonian, Cryogenian and Ediacaran), Palaeozoic (Cambrian, Ordovician, Silurian, Devonian and Carboniferous), Mesozoic (Jurassic and Cretaceous) and Cenozoic (Palaeogene, Neogene and Quaternary) strata.

At the beginning of the Silurian, the entire territory of the southwestern margin in the Ukrainian part of the East European Platform was uplifted and underwent an intense denudation. As a result, Silurian deposits rest upon the eroded surfaces of Ordovician, Cambrian and Vendian deposits (Chebanenko et al. 1990).

Silurian strata stretch along the southwestern margin of the East European Platform from the Baltic Sea to the Black Sea. The thickness of the Silurian increases regularly from the Ukrainian Shield westwards towards the Teisseyre–Tornquist Zone, reaching a maximum thickness of over 1300 m (borehole Dublyany-4). Cross-sections I–I[1] (Fig. 2**I**) and II–II[1] (Fig. 2**II**) (see Fig. 1 for location) display the entire sedimentary cover of the study area, as well as the occurrence of the Silurian strata and the location of the wells under investigation.

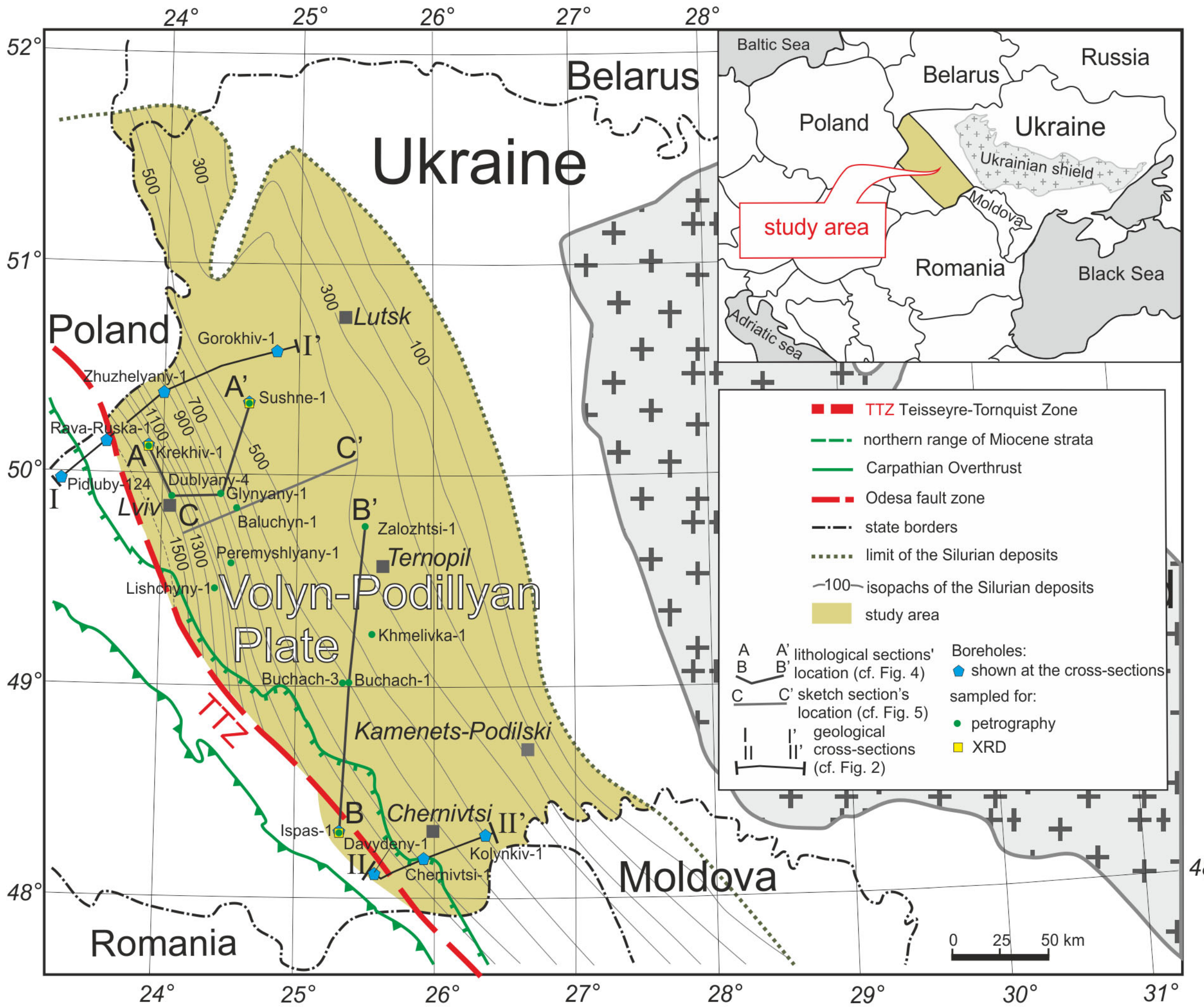

Fig. 1. Location map, showing the generalized distribution and thickness of the Silurian within Western Ukraine and the studied boreholes.

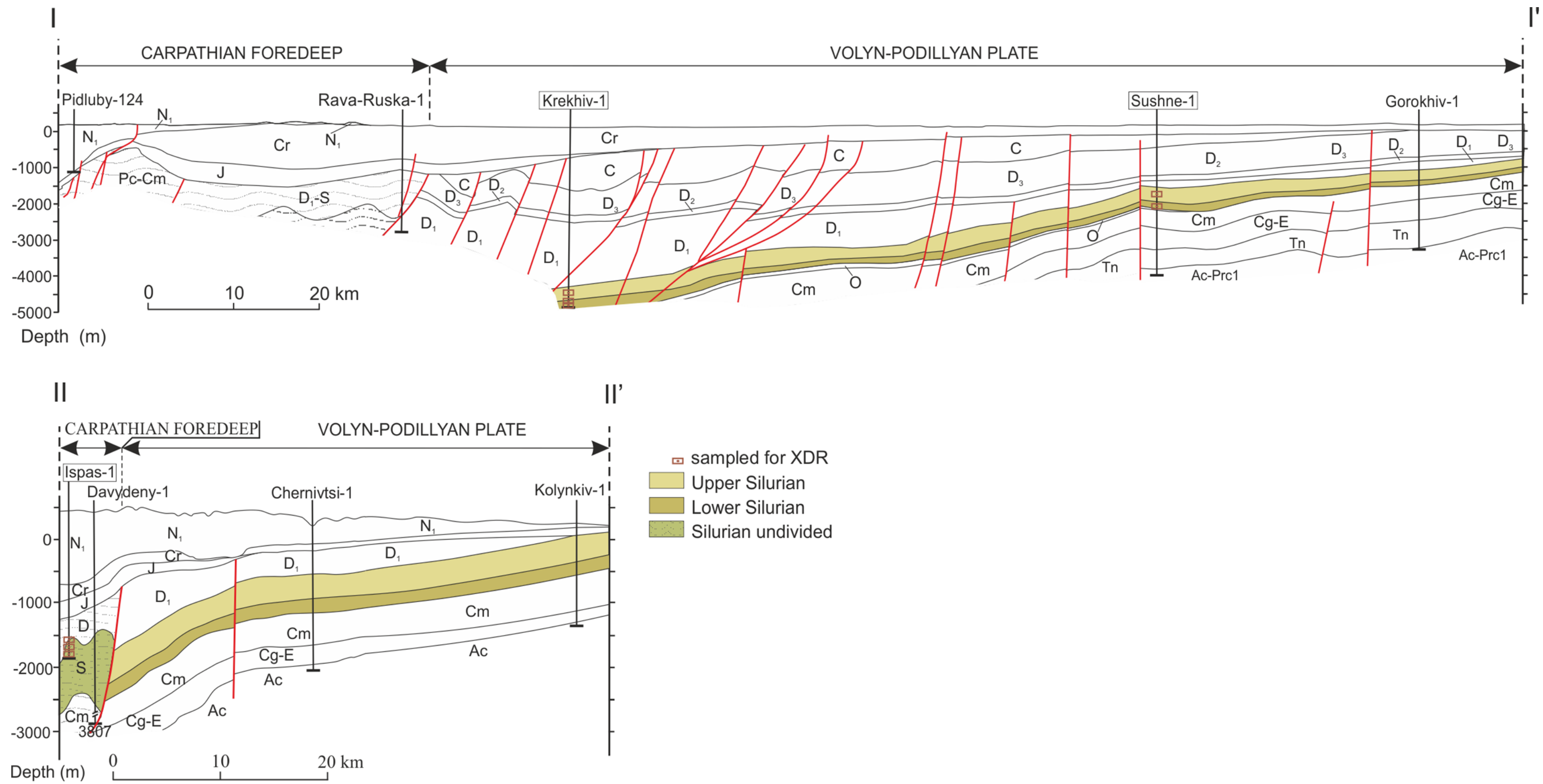

Fig. 2. Geological cross-sections **I–I'** and **II–II'** through the Carpathian Foredeep and Volyn-Podillyan Plate (see Fig. 1 for location) (modified after Vashchenko et al. 2007). Ac, Archaean; Ac-Prc1, Archaean and Lower Proterozoic; Tn, Tonian; Cg-E, Cryogenian–Ediacaran; Pc-Cm, Precambrian–Cambrian; Cm, Cambrian; O, Ordovician; D_1-S, Lower Devonian and Silurian undivided; D_1, Lower Devonian; D_2, Middle Devonian; D_2 Upper Devonian; C, Mississippian and Pennsylvanian; J, Jurassic; Cr, Cretaceous; N_1, Miocene. Boreholes at cross-section **I–I'**: projections of Sushne-1 and Krekhiv-1 about 17 and 16 km from the NW, respectively. Borehole at cross-section **II–II'**: projection of Ispas-1 about 31 km from the SE.

Within the southwestern margin of the East European Platform, the Silurian system is represented by the Lower and Upper Silurian. It has been established that the Lower Silurian platform strata of Poland and Lithuania comprise the Llandovery and Wenlock (Verniers et al. 2008; Modliński & Podhalańska 2010). There are different opinions regarding the completeness of the Lower Silurian stratigraphic succession throughout the Ukrainian territory. Tsegelnyuk et al. (1983) and Drygant (2000) stated that the Lower Silurian is represented here by both the Llandovery and Wenlock. Nikiforova et al. (1972) expressed doubts about the presence of the Llandovery in the Silurian sequence and assumed that these Lower Silurian strata should be considered as Wenlock. In this study we used the stratigraphic scheme of Rizun et al. (2007), which states that within the Ukrainian territory, the Lower Silurian platform strata are represented only by the Wenlock (Kytayhorod and Bagovytsya stages). The Upper Silurian covers the entire time range and includes the Malynivtsi stage of the Ludlow and the Skala stage of the Pridoli (Fig. 3).

METHODOLOGY

Rock sampling sites and petrographic analyses

The study is based on the analysis of well-logs, core samples and thin sections. Thirty-nine representative core samples of Silurian deposits (mudstones, limy mudstones, clayey marlstones, marlstones, clayey biodetrital limestones, biolithites) were selected for petrographic examination (Table 1). The samples come from the following boreholes: Baluchyn-1, Buchach-1, Buchach-3, Dublyany-4, Ispas-1, Glynyany-1, Khmelivka-1, Krekhiv-1, Lishchyny-1, Peremyshlyany-1, Zalozhtsi-1 (see Fig. 1 for boreholes locations).

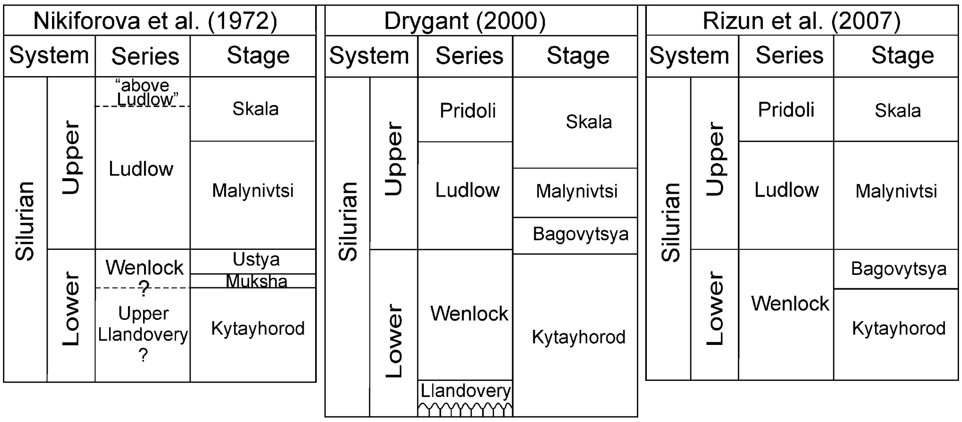

Fig. 3. Stratigraphic scheme of the Silurian deposits of the Volyn-Podillyan Plate (modified after Nikiforova et al. 1972; Drygant 2000; Rizun et al. 2007).

Table 1. Petrographic composition of the Silurian rocks

Lithology	Number of samples	Minerals content of rock (%)				
		Clay	Quartz	Feldspar	Carbonate	TOC (wt%)
Mudstones	8	24–35	41–64	3.2–5.8	3.8–5.2	0.2–2.16
		29	59	4.7	5	0.8
Limy mudstones	8	22–45	45–60	3.2–6	5.2–15	0.2–1.12
		28	57	4.5	10.5	0.6
Clayey mudstones	7	20–31	35–56	2.9–5.5	16–40	0.2–0.82
		25	43	4.1	31	0.5
Marlstones	7	16–20	23–30	2.1–3.3	04–55	0.2–0.8
		17	29	3	51	0.4
Clayey biodetrital limestones	5	5.5–10	7–15	0.5–2.9	56–79	<0.6
		8.2	14.5	1.1	77	
Biolithites	4	1–7	2–11	0.5–1.2	80–98	<0.4
		3.8	5.5	0.7	92	

TOC, total organic carbon. The range of minerals content is given as the numerator, the median value as the denominator.

The $CaCO_3$, $CaMg(CO_3)_2$ and clayey material rock content was calculated from chemical analyses, which was performed in the Institute of Geology and Geochemistry of Combustible Minerals of the NAS of Ukraine (Lviv, Ukraine). Thin sections were examined under a polarizing microscope. Well-log data along with the results of analytical and petrographic analyses of the rocks were used for lithostratigraphic correlation of the examined sections. The total organic content (TOC) in the rock samples was measured using Rock-Eval pyrolysis, according to the standard procedure in Montanuniversitaet Leoben, Austria.

Rock sampling sites and X-ray diffraction analytical procedure

Core samples of mudstones and limy mudstones were collected from three boreholes: Ispas-1, Krekhiv-1 and Sushne-1. Samples were taken from several depth intervals from each well (see Figs 1, 2 for location and Table 2).

The XRD study was performed in the laboratory of the Institute of Geology and Geochemistry of Combustible Minerals of NAS of Ukraine, Lviv, Ukraine, by means of standard methods (Frank-Kamenetskiy 1983; Moore & Reynolds 1997), using an ADP-2.0 diffractometer. The XRD system operated under the following conditions: 34 kV, 14 mA, Mn-filtered Fe radiation, at 0.025° 2Θ/step using the counting time of 1.5 s (3.0 s for the 30–45° 2Θ interval). Oriented (≤2 µm) preparations were examined. In order to determine the clay mineral associations, the XRD patterns of oriented air-dried preparations of clay fraction (≤2 µm) were analysed. The mineral composition of the rocks was studied using the diffractograms of the powder (without separation, mechanically ground) and the oriented (after separation gravity precipitated fraction less than ≤2 µm) preparations.

The disintegration of samples was performed for the determination of the mass fraction Total Clay (≤4 µm) and investigation of clay minerals in it. Rock samples were disintegrated by decarbonization and long-duration multiple rinsing. The particles of samples crushed to 1–3 mm were dissolved with a 10% solution of acetic acid (CH_3COOH). During decarbonization periodically, in order to increase the active area, big flocculent particles were crushed by a rubber finger (Frank-Kamenetskiy 1983, p. 112). Complete disintegration of the rock lasted about six months. After that the sand fraction was removed. The silt fraction was separated from the clay fraction by centrifugation (Moore & Reynolds 1997, p. 211), whereas the latter was used to identify the clay minerals.

The minerals with the labile structure (smectite group) were identified in oriented preparations saturated with ethylene glycol. The quantitative distribution of clay minerals in the pelitic fraction was determined by the simulation of 1-dimensional XRD patterns of disordered layered minerals using PyXRD software (BSD-2 Clause 2016).

The quantitative content of non-clay minerals, previously identified in the diffractograms of the powder preparations, was determined by two methods. The quartz content of all samples was found by the method of the 'internal standard', using albite as a standard. The main lines of albite in the diffractograms occur side by side (0.334 and 0.318 nm), whereas their absorption mass factors differ by less than 15%. The contents of other non-clay minerals in the association were determined by the formula, which takes into account the known quartz

Table 2. Mineral composition of the Silurian rocks, determined by XRD

Borehole	Depth (m)	Chronostratigraphy	Lithology	Non-clay minerals content of rocks (%)						Minerals content of clay fraction (%)		
				Q	Ca	Dl	Fs	Pr	TOC (wt%)	Ch	It	Total
Krekhiv-1	4406.7–412.7	Ludlow	Limy mudstones	59.89	5.79	2.48	4.69	1.56	0.68	23	77	24.91
Krekhiv-1	4689.5–4693.7	Wenlock	Mudstones	63.54	2.52	2.09	5.4	1.84	0.7	27	73	23.91
Krekhiv-1	4825–4830	Wenlock	Limy mudstones	43.51	4.95	1.78	2.97	1.62	0.42	27	73	44.75
Sushne-1	2047–2055	Ludlow	Limy mudstones	49.2	9.68	3.65	3.17	2.32	0.24	18	82	31.74
Sushne-1	2335–2345	Wenlock	Clayey marlstones	38	9.23	7.28	2.36	7.8	0.4	20	80	34.93
Ispas-1	1403–1409	Pridoli	Limy mudstones	47.04	9.35	3.91	4.66	6.9	0.58	30	70	27.56
Ispas-1	1505–1515	Pridoli	Limy mudstones	46.65	5.66	2.11	4.11	2.01	0.6	27	73	38.86
Ispas-1	1599–1605	Pridoli	Limy mudstones	55.46	12.89	2.67	4.2	1.46	0.61	28	72	22.71

Q, quartz; Ca, calcite; Dl, dolomite; Fs, feldspar; Pr, pyrite; TOC, total organic carbon; Ch, Chlorite; It, Illite.

concentration in the sample and the correlation of intensities of the main maxima of quartz and the mineral, whose quantity is being determined in the experimental diffractogram to their correlations in the diffractograms of the binary solutions (1:1) of their pure phases (Zevin & Zavyalova 1977 p. 35). In calculations the averaged value of intensity was used. For quantitative determination of non-clay minerals the powder preparations of the samples studied and binary mixtures with pure phases (quartz and the mineral whose quantity was being determined) were scanned in the interval of 30–45° 2Θ with a threefold repeat.

In order to make an oriented preparation, 1 g of clay fraction (≤4 μm) was macerated in distilled water. The obtained homogeneous suspension was then transferred into a test-tube where it was washed with distilled water several times to reach stability. The test-tube was then shaken up and left to settle for 30 min. Several droplets from the top 5 cm layer of the suspension (particles ≤2 μm) were deposited onto an object-plate with an eye dropper. The final drying was conducted at room temperature. The resulting film density was 3 mg/cm^2.

The determination of expanding minerals and mixed-layered species with an expanding constituent involved solvation with ethylene glycol.

RESULTS AND DISCUSSION

Correlation of borehole sections and petrographic characteristics

Clayey dark-coloured Silurian deposits with the TOC content from 0.2 to over 2.16 wt% (Table 1) occur within the most subsided part of the study area in the entire Wenlock to Pridoli succession. Towards the northwest (Drygant 2000; Radkovets 2015), the thickness of the Silurian sequence decreases and the lithological composition changes from clayey and carbonate-clayey to carbonate and carbonate-sulphate rocks. However, the boundary between the carbonate and clayey deposits was not stable during the Silurian, and as a result, shifted depending on numerous transgressions or regressions which occurred during that time (Radkovets 2015).

Figure 4 displays the location of the typical Silurian borehole sections, which give the best insight into the lithological features of the strata. The lithological sections of the boreholes, located within the area of the deepest Silurian occurrences, show the greatest thicknesses: Ispas-1, Krekhiv-1 and Dublyany-4 are made up of black clayey rocks and are enriched with dispersed organic matter. The lithological sections of the boreholes Glynyany-1 and Buchach-1 indicate a decrease in Silurian thickness; these are located further away from the Teisseyre–Tonquist Zone and comprise dark-coloured clayey deposits as well as clayey-carbonate and carbonate ones, the latter representing the reef facies. The lithological sections with the smallest Silurian thickness occur in Sushne-1 and Zalozhtsi-1, where the minimum of dark-coloured clayey deposits is found. The facies distribution of Silurian deposits within the study area is discussed by Radkovets (2015).

The sketch-section in Fig. 5 demonstrates changes in the lithological composition of the Silurian succession from its maximum to minimum thickness. The mudstones and limy mudstones within the most subsided region have minimum $CaCO_3$ and $CaMg(CO_3)_2$ and maximum TOC contents. For example, the samples from the borehole Krekhiv-1, located within the deeply buried part of the platform, show significantly higher TOC and lower carbonate contents than the ones from the borehole Sushne-1, which has penetrated the Silurian in its shallower occurrence (Table 1).

According to petrographic data, mudstones (Fig. 6A) show a low content of carbonates (calcite, dolomite), reaching a maximum of 5–6%. The TOC content of these rocks ranges mainly between 0.2 and 2.16 wt% (Table 1). The matrix of the rock is made up of illite, chlorite, fine of mica and sub-parallel streaks of organic matter. Large amounts of silt-size quartz grains, relicts of calcareous bioclasts as well as muscovite are observed. The carbonate content of mudstones is not stable. It often reaches up to 15%, forming limy mudstones (Figs 6B; 7A, B). At carbonate content of 15–40%, clayey marlstones (Fig. 7A) and 40–55%, marlstones are formed (Fig. 6D). The latter are represented by dark-grey, clayey, pyritized, dolomitized, fine- and microlaminated due to the distribution of small pyrite grains, lenticular accumulations of organic matter and calcareous bioclast debris. Marlstones consist of carbonate and terrigenous-clayey material which forms the matrix. The admixture of quartz grains of 0.01–0.08 mm, calcareous bioclast debris of 0.1–0.8 mm (sometimes >1 mm) and possibly strongly recrystallized bioclasts are present.

Rocks containing 55–75% $CaCO_3$ and $CaMg(CO_3)_2$ are biodetrital limestones (Fig. 6E), which are represented by rounded and non-rounded biolithite debris with clayey matrix. The TOC of limestones is insignificant, reaching < 0.4 wt% (Table 1). According to chemical analysis, carbonate content is highest within biolithites (Fig. 6F), ranging between 80% and 90%, and reaching a maximum of 98%. The TOC content of these rocks is negligible. The reef facies started to develop in the Wenlock and it formed a boundary behind which deeper-water clayey sediments were deposited (Radkovets 2015). The presence of the oxygen-minimum layer resulted

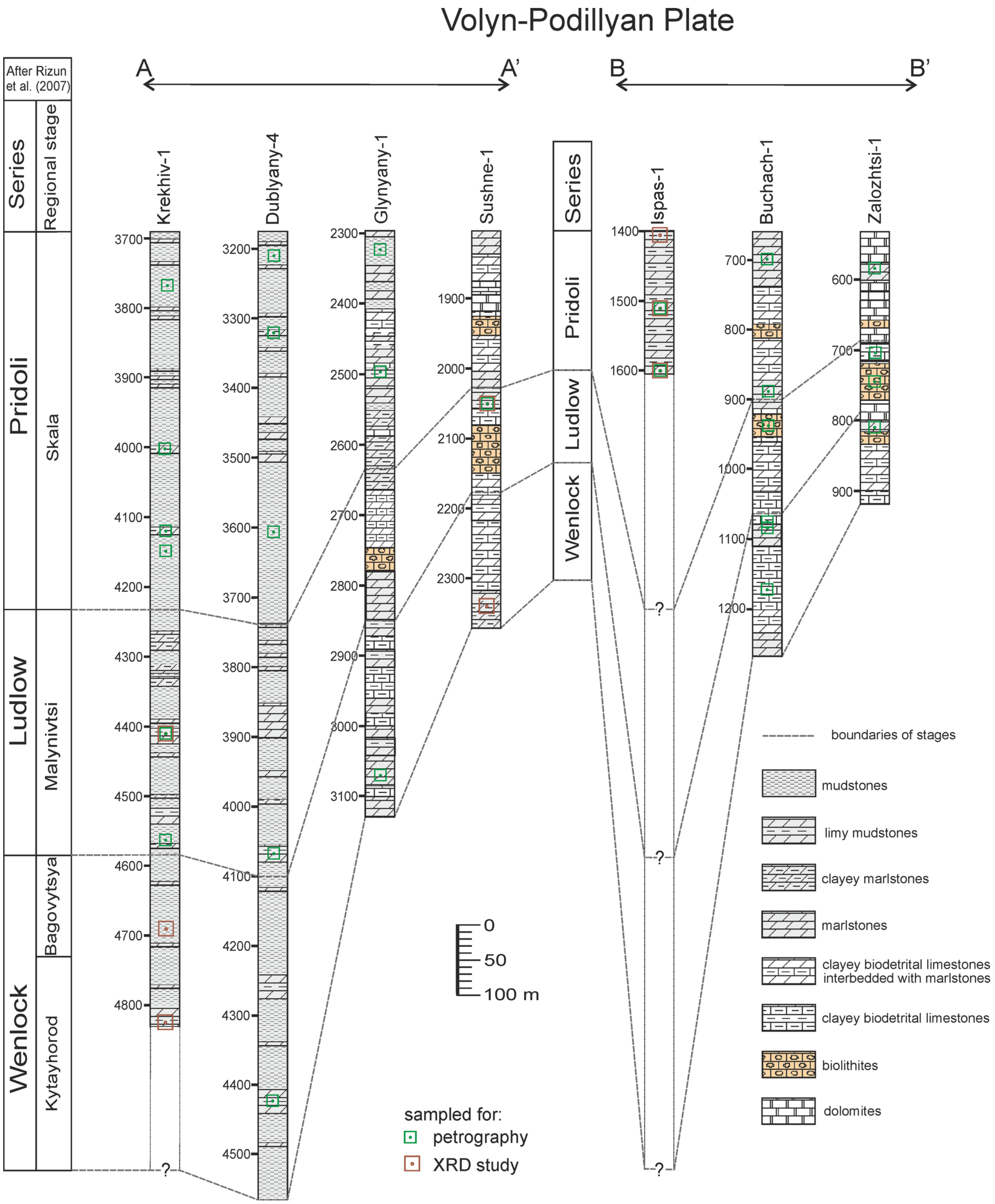

Fig. 4. Lithological sections **A–A'** and **B–B'** through the Silurian succession in the Volyn-Podillyan Plate (see Fig. 1 for location).

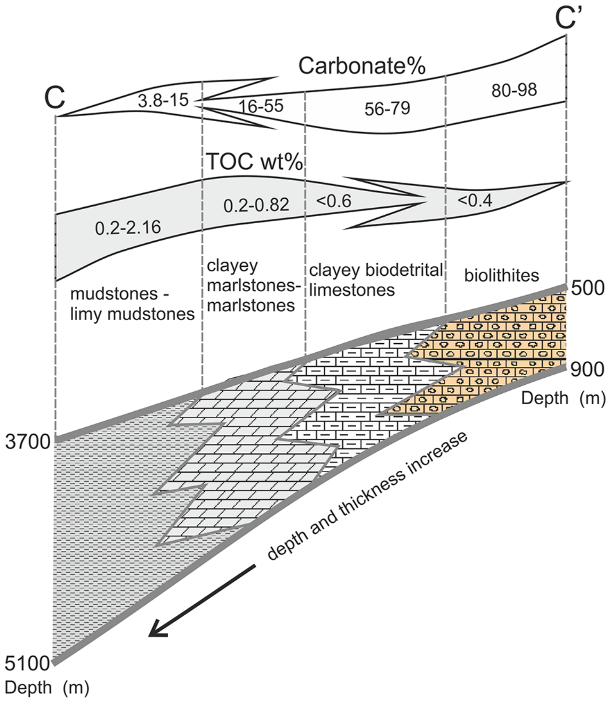

Fig. 5. Sketch-section **C–C'** of the Silurian deposits showing the interdependent changes in the lithological composition, depth of occurrence, thickness, carbonates and TOC contents (see Fig. 1 for location).

in the enhanced fossilization of organic matter with simultaneous dissolution of the planktonic carbonate material. However, the debris of carbonate fauna is always present in these clayey sediments, accounting for 2–5% to 15% in mudstones and limy mudstones, and reaching 30% in marlstones.

Mineral composition

Petrographic investigations of the Silurian organic-rich dark-coloured clayey rocks led to a selection of characteristic types of rocks from different parts of the study area for further quantitative investigation of their mineral composition using the XRD method (Table 2).

Figure 8 presents the results of XRD analysis of the sampled rocks (Table 1) and the circle diagrams showing the mineral contents, which were established by the XRD results. The lines, observed in the XRD pattern of the powder preparations (Fig. 8**A**I–III), allowed the identification of the mineral composition of the rocks from the boreholes Ispas-1 (Fig. 8**AI, B**I), Krekhiv-1 (Fig. 8**A**II**, B**II) and Sushne-1 (Fig. 8**A**III, **B**III), respectively. A set of lines indicates the association of quartz, calcite, dolomite, plagioclase and pyrite. Fine quartz grains (> 0.1 mm) were identified on peaks 0.424, 0.334, 0.245, 0.228, 0.212 and 0.1812 nm, calcite on 0.302 nm, dolomite on 0.289 nm, plagioclase on 0.321 nm and pyrite on 0.270 nm. Here also the reflexes are present, by which the layered aluminosilicates can be indicated: mica (1.0, 0.49, 0.45 and 0.256 nm) and chlorite (1.38, 0.71 and 0.354 nm).

Detailed investigations of the clay fraction in the oriented preparations (initial, Fig. 8**Ba**I–III; saturated with ethylene glycol, Fig. 8**Bb**I–III showed that the clay fraction of all the samples under study is represented by chlorite and illite, which have been identified by the characteristic maxima that do not change their positions after saturation with ethylene glycol. This indicates the lack of smectite or mixed-layered minerals with the swelling components. Peaks of low (commensurable to the background) intensity in the range of low angles (up to 8°) and in the range of 22–32° angles 2Θ are caused by the sorption of organic matter by clay particles.

Samples from the borehole Ispas-1 indicate different proportions of chlorite and illite. Chlorite content is much lower, making 28–30%, while illite reaches 73%. Samples from the borehole Krekhiv-1, where Silurian strata occur at depths of over 4000 m, also display a predominance of illite over chlorite. Illite content reaches 77% of the clay fraction. Samples from the borehole Sushne-1, where Silurian strata occur significantly shallower than in the borehole Krekhiv-1 (at depths of 2000–2300 m), show that chlorite content is essentially lower (up to 20%), while illite reaches 82%.

An increased TOC content of up to 2.16 wt% (Tables 1, 2) was established in four lithological types of Silurian rocks: mudstones, limy mudstones, clayey marlstones and marlstones. Our investigations have shown that in all these rocks quartz (38–64%) essentially prevails over clay minerals (23–39%). The rocks also contain significant amounts of carbonates (from 5–15% in mudstone-limy mudstone to 51% in marlstones) as well as small amounts of feldspar (3–6%) (Fig. 8). As stated in Decker et al. (1992), Curtis (2002) and Jarvie (2003), if quartz, carbonate and feldspar in a rock are 1.5–2 times as abundant as clay minerals, the organic-rich rock becomes highly brittle and suitable for efficient hydraulic fracturing, which is a standard operation for shale gas recovery. Grain size is another important factor, as rocks with finer grain size become more favourable for fracturing than rocks with coarser grain size. Quartz grains in the rocks under study belong to the coarse silt to very fine sand grains with the size of 0.031 to 0.125 mm, which provides favourable conditions for fracturing. The results of XRD analysis indicate that clay minerals, depending on the depth and the area of their occurrence, are represented by chlorite and illite

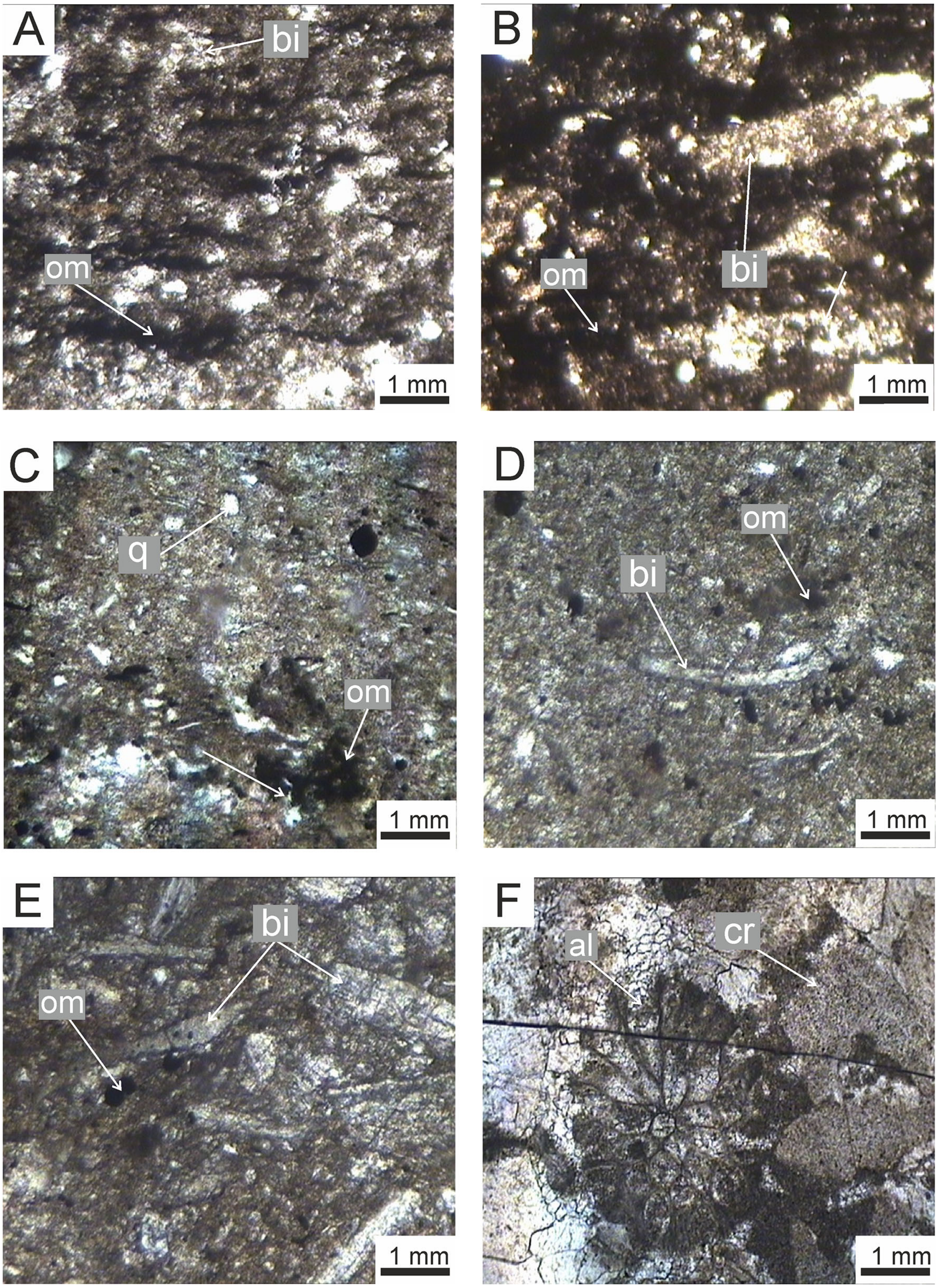

Fig. 6. Photomicrographs of the Silurian rocks; Volyn-Podillyan Plate. **A**, mudstones from borehole Krekhiv-1, depth interval 4146–4151 m. **B**, **C**, limy mudstones: B, from borehole Krekhiv-1, depth interval 4406.7–4412.2 m; C, from borehole Sushne-1, depth interval 2047–2055 m. **D**, marlstones from borehole Buchach-1, depth interval 4406.7–4412.2 m. **E**, clayey biodetrital limestone from borehole Buchach-1, depth interval 1075–1080 m. **F**, biolithites from borehole Zalozhtsi-1, depth interval 729–761 m. Abbreviations: al, algae; bi, calcareous bioclasts; cr, fragment of crinoid; om, organic matter; q, quartz.

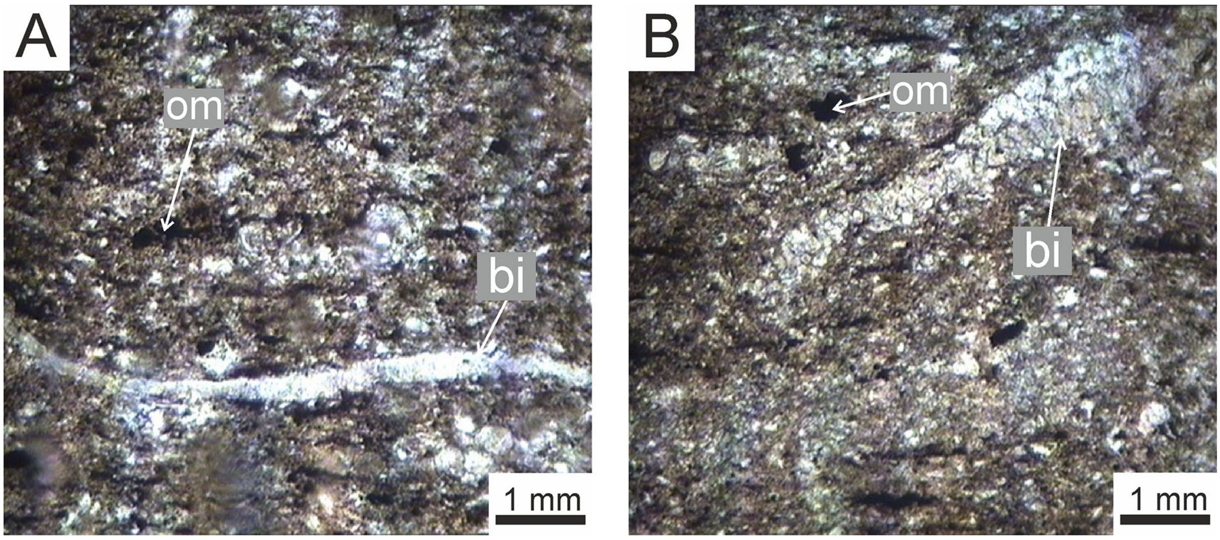

Fig. 7. Photomicrographs of the Silurian rocks. Carpathian Foredeep. **A**, **B**, limy mudstones from borehole Ispas-1: A, depth interval 1505–1515 m; B, depth interval 1599–1605 m; om, organic matter; bi, calcareous bioclasts.

in different ratios. Smectite or mixed-layered minerals with the swelling components were not revealed, which is another positive feature (Burtner & Warner 1986) of these rocks in respect of the eventual hydraulic fracturing.

CONCLUSIONS

The thickness of the Silurian strata of Western Ukraine regularly increases in a western direction, from the Ukrainian Shield towards the TTZ, reaching a maximum value of over 1300 m. The lithological composition of rocks changes from carbonate-sulphate and carbonate to carbonate-clayey and clayey rocks in the same direction.

The investigations of different lithological types of the Silurian rocks, namely biolithites, biodetrital limestones, marlstones, clayey marlstones, limy mudstones and mudstones, showed a decrease in $CaCO_3$ and $CaMg(CO_3)_2$ and an increase in the TOC content of rocks from the shallower to deeper occurrences. Carbonate-clayey and clayey dark-coloured deposits: marlstones, clayey marlstones, limy mudstones and mudstones, occuring in the most subsided region, displayed the maximum values of TOC content. In marlstones and clayey marlstones, carbonate content was 16–55% and maximum TOC content was 0.82 wt% with average values of 0.5 wt%, while in mudstones and limy mudstones carbonate content was 3.8–15% and TOC content reached a maximum value of 2.16 wt% with an average of 0.8 wt%.

The investigations of the mineral composition of Silurian rocks with a maximum TOC content – clayey marlstones and marlstones, using the XRD method, showed the following percentages: quartz, 38–64%; calcite, 2.5–13%; dolomite, 1.8–7%; feldspar, 2.4–5.4% and pyrite, 1.5–7.8%. Clay fraction content was 23–45%. Detailed investigations of the clay fraction in the oriented preparations, saturated with ethylene glycol, showed that all samples under study were represented by illite (70–82%) and chlorite (18–30%), which were identified by the characteristic peaks, which did not change their position after saturation with ethylene glycol. This indicates a lack of smectite or mixed-layered minerals with the swelling components. Illite and chlorite were present in the rocks in different proportions, depending on the depth and the area of occurrence. Illite content decreases, while chlorite content increases with depth in a western direction towards the Teisseyre–Tornquist Zone, and contributes over 30% of the clay fraction.

It was established that in Silurian organic-rich rocks quartz prevailed over the clay minerals by a factor of 1.5 to 2 and was represented by coarse silt to very fine sand grains with the size of 0.031 to 0.125 mm. The rocks contained a significant amount of carbonates, while no smectite was found in the clay fraction. These characteristics indicate a high brittleness for the rocks, making them suitable for the efficient hydraulic fracturing.

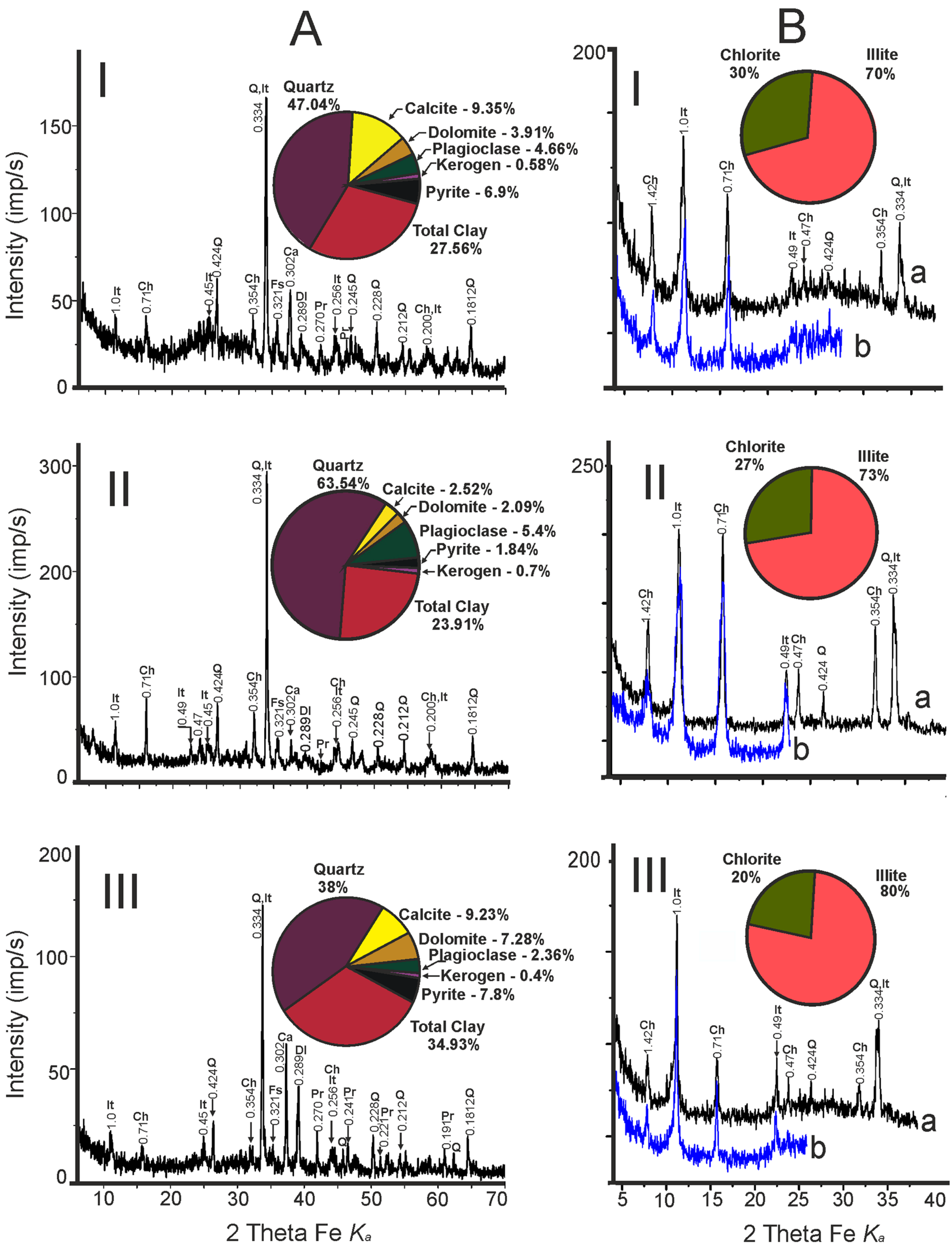

Fig. 8. Diffraction patterns and mineral composition of Silurian rocks. **A**, non-oriented preparation (fraction finer than 0.01 mm). **B**, oriented preparations (fraction finer than 0.002 mm): **a**, non-treated (air-dried); **b**, ethylene glycole solvated. Minerals: Q, quartz; Ca, calcite; Dl, dolomite; Fs, feldspar; Pr, pyrite; TOC, total organic carbon; Ch, Chlorite; It, Illite. **I**, limy mudstones from borehole Ispas-1, Pridoli, depth interval 1403–1409 m; **II**, mudstones from borehole Krekhiv-1, Wenlock, depth interval 4689.5–4693.7 m; **III,** clayey marlstones from borehole Sushne-1, Wenlock, depth interval 2335–2345 m.

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Siluri mustad kildad Lääne-Ukrainas: petrograafia ja mineraloogia

Natalia Radkovets, Johannes Rauball ja Iaroslava Iaremchuk

Siluri orgaanikarikkad mustad kildad Ida-Euroopa platvormi lääneservas levivad Baltikumist kuni Musta mereni ja on potentsiaalne sihtobjekt traditsiooniliste ning mittetraditsiooniliste süsivesinike otsinguteks. Lääne-Ukrainas esinevad need kihid platvormi sügavale mattunud 1000–1500 m paksuses osas. Orgaanikarikaste (kuni 2,16 wt%)

kivimite petrograafiliste uuringute käigus on kindlaks tehtud kivimite mineraalne koostis ja eristatud neli kivimitüüpi: mudakivimid, savikad mudakivimid, lubimerglid ning merglid. Kõigis neis kivimites domineerib kvarts (30–60%) 1,5–2 korda savimineraalide üle. Kivimid sisaldavad karbonaatseid mineraale (kaltsiiti ja dolomiiti): 5–15% mudakivimites ja karbonaatsetes mudakivimites ning kuni 51% merglites. Kvartsitera suurus on põhiliselt vahemikus 0,125–0,062 ja 0,062–0,031 mm, mis vastab peenliivale ning jämealeuriidile. Selline mineraalide vahekord kivimis ja kvartsitera suurus osutab, et kivimid on märkimisväärselt haprad ning neis võib esineda efektiivset hüdraulilist mõranemist. Kõrgeima orgaanikasisaldusega kivimite, mudakivimite ja karbonaatsete mudakivimite mineraalne koostis on mõõdetud röntgendifraktomeetriliselt. Selgus, et savimineraalid on esindatud illiidi ja kloriidiga. Illiidi kontsentratsioon väheneb ja kloriidi oma kasvab kivimite lasumussügavuse suurenedes, ületades 30% savifraktsioonist. Smektiiti ja segakihilisi savimineraale ei esine, mis on kivimite hüdraulilise mõranemise heaks eelduseks.