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PETROGRAPHIC CHARACTERISTIC OF THE MIDDLE MIOCENE SEDIMENTS IN THE UKRAINIAN SEGMENT OF THE CARPATHIAN FOREDEEP

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Abstract: The Upper Badenian and Sarmatian strata from thirteen wells situated in the Ukrainian part of the Carpathian Foredeep were petrographically analysed. The studies were performed using a polarizing microscope (standard petrographic analysis, cathodoluminescence studies – CL), SEM and EDS ISIS. Moreover, the XRD was conducted, isotopic ratios of light isotopes of carbon and oxygen in carbonate cements determined, and porosimetric measurements performed on selected samples of sandstones. Claystones, mudstones and sandstones were distinguished among the studied rocks. The sandstones were examined in great detail. The following sandstone varieties were distinguished: unequal-grained, fine-, and rare medium-grained. They are classified as arenites and subarkosic, locally sublithic and quartz wackes. Quartz and feldspars (K-feldspars, plagioclases) are main components of the grain fabric of mudstones and sandstones. Rock fragments (of sedimentary, less common effusive rocks, individual fragments of granitoids and/or metamorphic rocks) occur in the sandstones, too. Micas (mainly muscovite), glauconite, rare bioclasts, fine plant remnants, and accessory zircons are present. The cement is composed of allogenic-and authigenic clay minerals (illite, smectite, chlorites, kaolinite), carbonates (Fe-calcite, dolomite, ankerite), authigenic quartz and, sporadically, authigenic feldspar and anhydrite. Effects of diagenetic processes, mainly of mechanical compaction, cementation, dissolution, and less significant replacement and alteration have been recorded in the sediments studied. The compaction and cementation have almost an equal influence on reduction of porosity and permeability of the analysed rocks. Abundant sandstone packages, however, display very good reservoir properties (porosity amounts to 30%, and permeability is over 200 mD).

Key words: siliciclastic rocks, diagenesis, pore space, Upper Badenian, Sarmatian, Carpathian Foredeep, Ukraine.

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INTRODUCTION

As opposed to the rocks from the Polish Carpathian Foredeep area (Kozłowska *et al.*, 2011, with references herein), the Miocene strata in the Ukrainian segment of the Carpathian Foredeep basin have not been the subject of a complex petrographic analysis yet. Still, they are equally interesting from the oil and gas prospection point of view (Kurovets *et al.*, 2004). The Miocene siliciclastic rocks from the following wells were studied: Bortiatyn 1, Yuryiv 1, Lanivka 1, Makuniv 1, Moryantsi 1, Mosty 1, Nyklovychi 26, Pyatnychany 1, Pivnichne Hirs'ke 1, Podil'tsi 1, Skhidne Dovge 3, Susoliv 5, and Voloscha 1 (Fig. 1). These rocks are included into the Kosiv and Dashava (Lower and Upper) formations (Petryczenko *et al.*, 1994; Andreyeva-Grigorovich *et al.*, 1997). According to micropalaeontological results, the rocks are of Late Badenian and Sarmatian age (Peryt, 1999; Garecka & Olszewska, 2011). Determination of mineral content of deposits, recognition of main diagenetic processes in the rocks as well as of the influence of diagenesis on the evolution of their porosity were main goals of our study.

GEOLOGICAL SETTING AND DEPOSITIONAL ENVIRONMENTS

The Ukrainian Carpathian Foredeep is a part of the large sedimentary basin, which developed along the Carpathian front from the Danube River in Vienna to the Iron Gate in Romania and is about 1,300 km long (Oszczypko *et al.*, 2006). The early to middle Miocene Carpathian Foredeep has been developing as a foreland basin in response to the Carpathian front movement towards the northeast. The basin is filled predominantly with siliciclastic sediments, such as a claystones, mudstones and sandstones, the thick-

Fig. 1. Location of the investigated wells

ness of which in the Ukrainian part reaches 6 km (Kurovets *et al.*, 2004), whereas in the Polish part is does not exceed 3 km (Oszczypko *et al.*, 2006). The sedimentary record represents in majority Sarmatian strata that formed in a variety of depositional environments, from deep marine (basin plain) to shallow marine successions (Lis & Wysocka, in press). Usually, the section consists of mudstones and fine-grained sandstones deposited predominantly from gravity flows. Proximal facies contain sandstones in metre-scale packages; the distal ones are dominated by fine-grained sediments with only thin, centimetre-scale sandstone beds. Like in the Polish Carpathian Foredeep basin, the main source area for the deposited material was the orogen. Both source and reservoir rocks are localized in the Miocene deposits.

METHODS

The analysis of thin sections cut from rocks and partly stained with a blue epoxy resin and performed using the polarizing microscope was the main analytical method. Uncovered surfaces of thin sections were stained applying the Evamy solution, aiming at preliminary recognition of carbonates. Sandstones and selected mudstones underwent counting using a counter PRIOR model G. Selected polished thin sections underwent the CL studies in a device Cambridge Image Technology Ltd., model CCL 8200 mk^3, mounted on the microscope Optiphot 2.

The SEM equipment (1430 LEO) with EDS ISIS was used in identification of cement components and recognition of architecture of the filling of the pore space. Microareas for the quantitative XRD analyses were selected and the chemical composition of carbonates was determined.

XRD analyses of selected claystone and mudstone samples were conducted using X-ray diffractometer Philips PW 1840, with an automatic, computer system of powder identification APD 1877.

Stable isotope (oxygen and carbon) analysis in calcites and dolomites was performed by the team of Prof. S. Hałas, using the modified mass spectrometer MI in the Mass Spectrometry Laboratory at the Maria Curie-Skłodowska University in Lublin.

Sandstone porosity was determined dually – in thin sections under the microscope and in the selected samples in the laboratory of the Oil and Gas Institute in Kraków.

RESULTS

Lithofacies and rock components

Claystones (the most rare), mudstones and sandstones were distinguished in the studied siliciclastic rocks. Claystones form thin interlayers in abundant mudstones. Sandstones form packages and small layers of different thickness within thick mudstone complexes.

Claystones are often represented by varieties displaying a pellitic-aleuritic texture and a parallel structure. Detrital

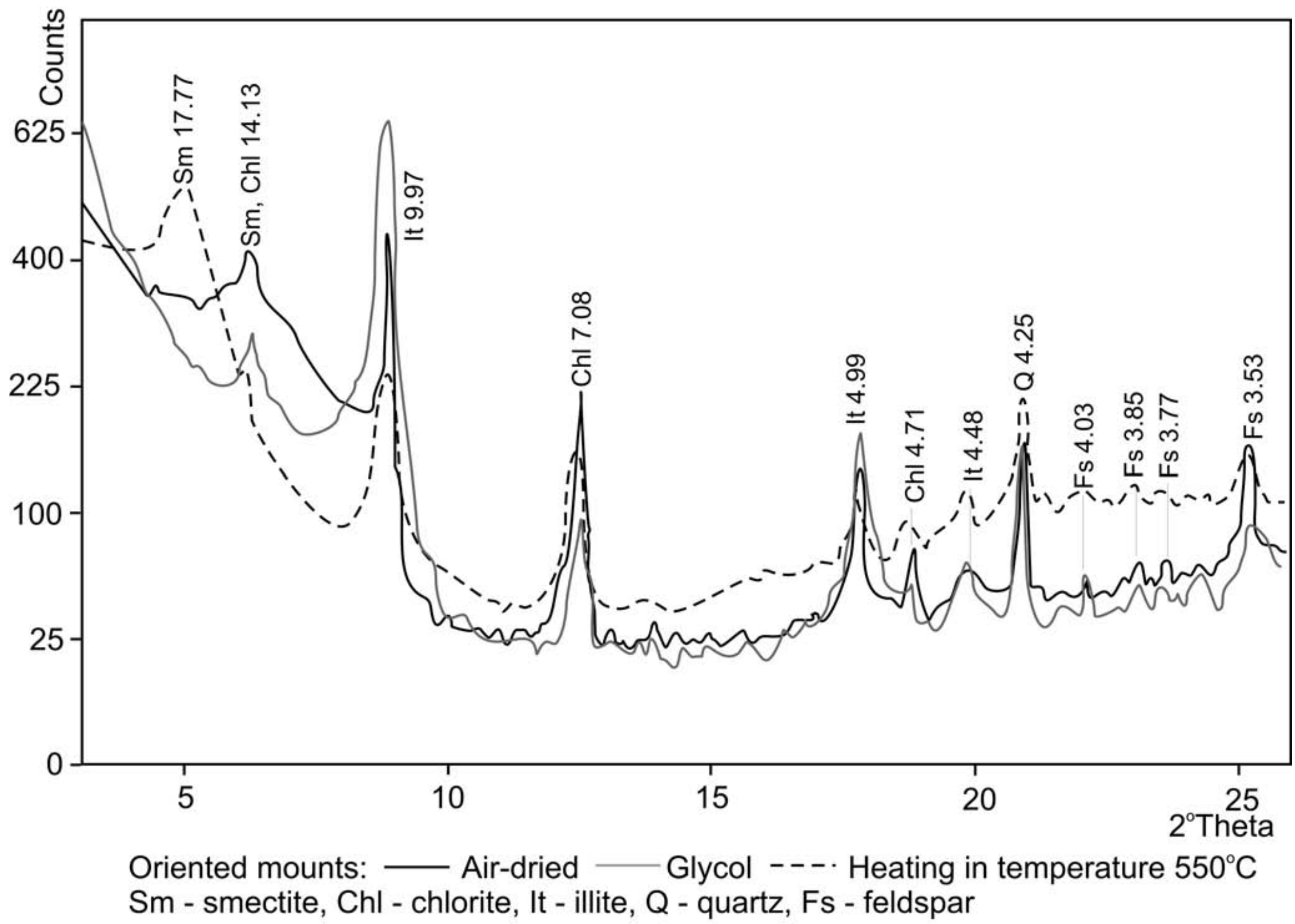

Fig. 2. XRD of mudstone from Pivnichne Hirs'ke 1 well, depth 1,395.0 m

flakes of clay minerals (illite, illite/smectite, smectite) are here the main component. Quartz silt and sand as well as mica flakes occur occasionally, whereas feldspar grains are subordinate. Iron hydroxides and carbonate micrite are present, too. The mudstones are predominantly grey, weakly bound rocks, which have an aleuritic or aleuritic-pellitic texture, locally with the psammitic fraction. They display a directional structure underlined by parallel arrangement of mica flakes, occasionally accompanied by iron hydroxides or organic matter. The mudstones compose complexes of a distinct thickness in particular well sections. Quartz, mostly monocrystalline and weakly rounded, is a component of the fabric. There also occur relatively abundant mica flakes (mostly muscovite, less frequently biotite), subordinate feldspar and glauconite grains. The mudstones are cemented by clay minerals. Chlorite, illite and smectite have been identified in XRD (Fig. 2). Calcite, gypsum and anhydrite, iron hydroxides and the organic matter were also found.

The sandstones are fine- and very fine-grained, unequal, exceptionally medium-grained. The average quartz grain diameter changes from 0.07 mm to about 0.32 mm. The degree of sorting of detrital material, expressed as the ratio of maximum to average diameters of quartz grains, changes from 2.5 to 6.2; most frequently it is 3.0. The sandstones display psammitic, psammitic-aleuritic, sporadically psammitic-pellitic texture. According to the Pettijohn *et al.*'s (1972) nomenclature, arenites and subarkosic wackes, locally sublithic and quartz wackes (Fig. 3), have been distinguished there.

Quartz is the main component of all types of sandstones. It occurs most frequently as monocrystalline (13.0–57.0 vol. %), less frequently polycrystalline grains (1.3–15.0 vol. %). Fragments of quartzites and cherts were also assigned to the polycrystalline grains. Quartz grains often have sharp edges, only grains of the fraction of 0.25 mm are partly rounded. The quartz displays a brown or dark-blue luminescence in CL.

Feldspars (1.0–9.3 vol. %) have been observed in all samples. In general, their grains have sharp edges; occasionally they are half-rounded. Potassium feldspars (microcline, orthoclase), display a blue luminescence in CL, while more rarely occurring plagioclases (albite – oligoclase) are green. Many feldspar grains are partly altered into clay minerals, only some are albitized. Some grains underwent a partial or total calcitization. Authigenic feldspar rims on the detrital feldspar grains have been noticed.

Lithoclasts occur in the studied sandstones in amounts up to 10 vol. %. These are mainly sedimentary rock fragments (mudstones, very fine-grained sandstones, claystones, carbonate rocks). Less frequent are volcanic (individual fragments of intermediate chemical composition),

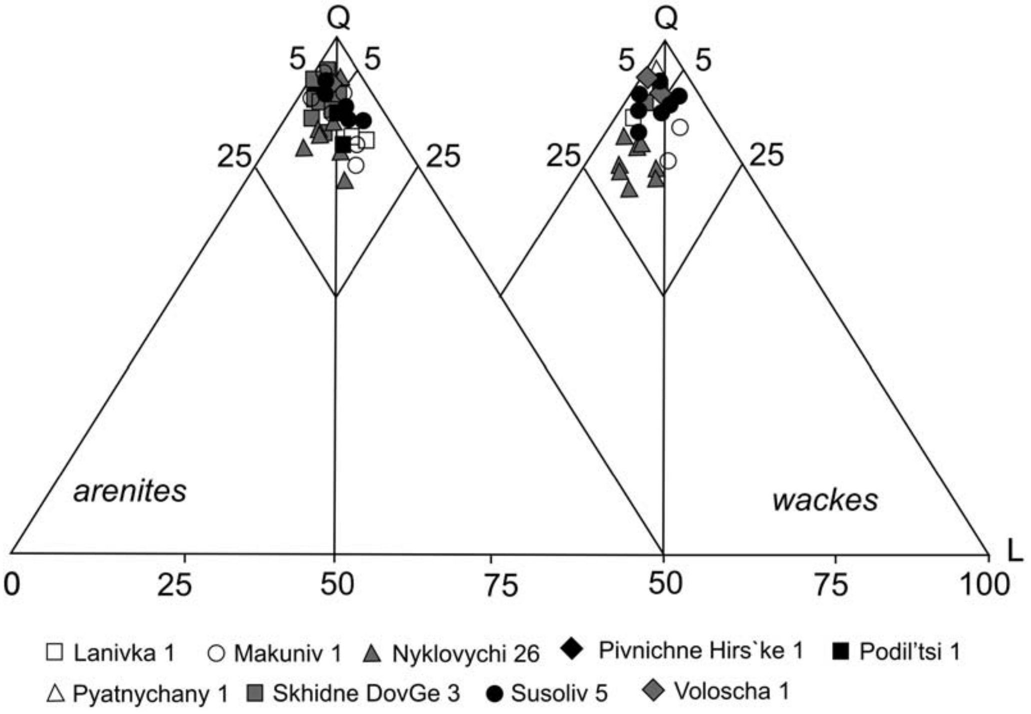

Fig. 3. Miocene sandstones according to classification triangles of Pettijohn *et al.* (1972)

granitoid and metamorphic rock fragments (quartz-mica schists). The lithic varieties of the sandstones predominate in the Makuniv 1 and Susoliv 5 wells.

Micas are represented by muscovite, occasionally by biotite. They occur in low percentage, only occasionally attaining over 10 vol. % (*e.g.*, Nyklovychi 26, depth 1,450.4 m).

Glauconite is frequent. Its content does not exceed 4 vol. %. It forms oval, often chloritized grains. Random bioclasts are noticed in the sandstones, too (foraminifer shells, fragments of bivalve shells, bryozoan branches). The elements of skeletons are in general composed of calcite (Fe-calcite as shown by staining with the Evamy solution). Moreover, fine plant fragments and accessory zircons occur.

The matrix, authigenic clay minerals, carbonates, authigenic quartz and sporadic authigenic feldspar and anhydrite have been noticed in the cements of sandstones under description. The matrix is composed of fine grains of quartz mud and detrital flakes of clay minerals. Locally, it is impregnated by iron hydroxides, organic matter or pyrite. Illite, sometimes smectite and chlorite, are present in the clay pellite. The matrix content over 15 vol. % indicates that some sandstones are wackes after Pettijohn *et al.* (1972) (Fig. 3). This rock type occurs in the Makuniv 1, Nyklovychi 26 and Susoliv 5 wells that are characterized by abundant clay minerals. It may be presumed, however, that a part of these minerals may have an authigenic origin.

Among the authigenic clay minerals, fine chlorite aggregates are noticed. Locally, they form structures in the form of "honeycomb". Kaolinite is also recognised in the polarizing and scanning microscopes. It occurs as pseudohexagonal crystallites in the form of booklets. The kaolinite fills in intergranular space, occasionally the intragranular space. Fibrous illite – a product of alteration of chlorites or kaolinite – is least frequent.

Among the carbonates which constitute the cement, calcite, dolomite and ankerite were distinguished. The results of chemical analyses of carbonates in the micro-area are shown in Table 1.

The calcite shows in majority anhedral forms. Crystals which display their own habit are rare and may be noticed only under the electron microscope. The analysed calcites are red or pink-violet when stained with the Evamy solution, pointing to an admixture of iron Fe^{2+}. Low admixtures of manganese and magnesium are present, too (Fig. 4). Their content in the calcite structure, the Mn/Fe ratio as well, influence the intensity of the luminescence colour of the mineral in CL – from yellow to light orange or red. The distribution of iron and manganese in the calcite is in general homogeneous. A similar calcite cement was described in Miocene sandstones from the Vienna Basin (Gier *et al.*, 2008). Apart from calcite, dolomite is also present. It forms rhombohedrons of different size, sometimes anhedral or subhedral ones, that fill in the pore space. Chemical analyses in the micro-area in dolomite show a presence of iron and manganese (Table 2). The dolomite displays luminescence in red-brown colours depending on the admixture of iron Fe^{2+} that muffles luminescence. Iron concentration in edge zones causes a zonality of the dolomite structure (Fig. 5). Quite often, the outer parts of crystals have, therefore, an ankeritic composition. The ankerite is rather rare as an individual component of the cements. It does not show luminescence in CL, while it is stained blue or dark blue by the Evamy solution. The carbonates under description often replace grains of quartz, feldspars and lithoclasts, forming partial or total pseudomorphs.

The petrographic studies have shown that the majority of the sandstones is cemented either with the calcite and dolomite or only with calcite.

Table 1

Chemical composition based on microprobe analysis

Borehole	Point of analysis	Depth [m]	Mg	Ca	Mn	Fe	$MgCO_3$ % mol	$CaCO_3$ % mol	$MnCO_3$ % mol	$FeCO_3$ % mol	Carbonate type
Nyklovychi 26	1	1,249.7	0.26	37.87	0.32	1.52	0.90	95.3	0.7	3.1	Fe-calcite
	4		5.60	22.91	0.90	9.99	19.6	57.6	1.9	20.8	ankerite
	5		9.89	22.86	0.46	4.02	34.3	56.5	1.0	8.2	dolomite
	1	1,990.3	0.42	37.41	0.61	1.17	1.50	94.7	1.4	2.4	Fe/Mn-calcite
	2		11.28	21.40	0.46	3.21	39.3	53.2	1.0	6.5	Fe-dolomite
	3		5.35	22.45	1.05	8.53	19.7	59.2	2.4	18.7	ankerite
Lanivka 1	1	1,580.4	0.09	39.96	0.00	0.16	0.3	99.4	0	0.3	calcite
	2		12.87	21.65	0.00	0.37	45.0	54.2	0	0.8	dolomite
	3		0.16	38.46	0.97	0.73	0.6	95.9	2.0	1.5	Fe-calcite
	4		10.13	21.77	1.00	4.12	35.3	54.1	2.1	8.5	Fe-dolomite
	5		7.15	23.75	0.50	6.25	25.4	60.5	1.0	13.1	ankerite
	6		11.83	23.62	0.08	0.43	40.8	58.1	0.2	0.9	dolomite
Skh. Dovge 3	1	1,702.5	0.58	37.63	0.58	1.80	2.0	93.1	1.2	3.7	Fe-calcite
	3		0.62	36.88	0.96	1.75	2.2	92.2	2.0	3.6	Fe-calcite
	1	1,726.9	11.79	22.89	0.11	0.21	41.7	57.7	0.2	0.4	dolomite
	2		9.00	22.55	0.26	5.55	31.5	56.5	0.5	11.5	ankerite
	3		0.18	37.87	0.53	1.43	0.6	95.3	1.1	3.0	Fe-calcite
Susoliv 5	1	2,515.1	0.72	37.45	0.58	1.35	2.5	93.5	1.2	2.8	Fe-calcite
	1	2,809.8	0.27	38.28	0.42	1.18	0.9	95.8	0.9	2.4	Fe-calcite
	1	2,950.3	0.33	38.49	0.54	1.08	1.2	95.6	1.1	2.1	Fe-calcite
	2		12.36	22.33	0.00	0.17	43.5	56.1	0	0.4	dolomite
	3		0.18	39.86	0.00	0.07	0.6	99.3	0	0.1	calcite
Voloscha 1	1	2,091.2	0.46	37.22	0.46	1.93	1.6	93.4	1.0	4.0	Fe-calcite
	2		0.35	37.81	0.52	1.41	1.2	94.8	1.1	2.9	Fe-calcite
	3		0.65	37.88	0.32	1.42	2.3	94.1	0.7	2.9	Fe-calcite

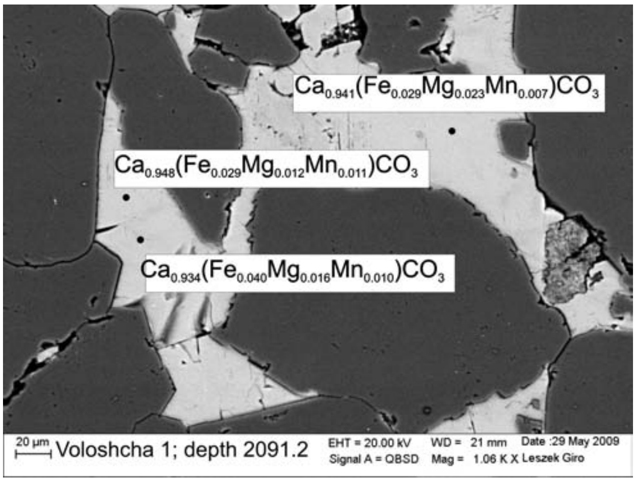

Fig. 4. Calcite cement in sandstone. BSI image; Voloscha 1 well, depth 2,091.2 m

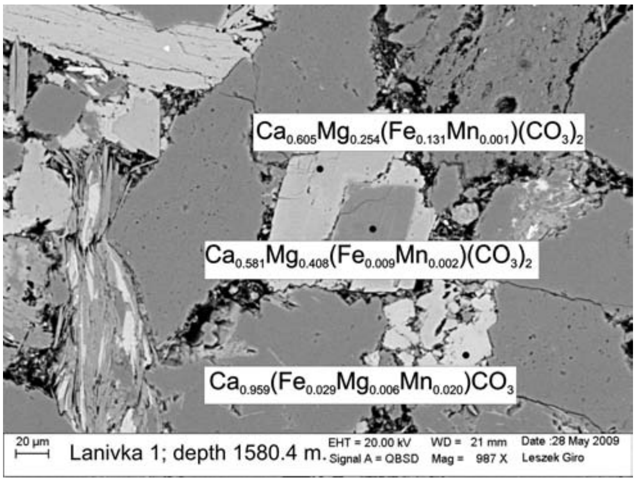

Fig. 5. Crystal of dolomite with ankerite rim in cement and calcite cement in sandstone. BSI image. Lanivka 1 well, depth 1,580.4 m

Samples selected for oxygen and carbon isotopic analyses have an almost monomineral cement or one of the components (calcite or dolomite) in a distinct predominance. Moreover, the samples are depleted in lithoclasts of carbonate rocks and bioclasts. The results of $\delta^{18}O$ and $\delta^{13}C$ determinations are shown in Tables 2 and 3. The $\delta^{18}O$ values in the calcite cement fall into the interval from –8.8 to –3.5‰ VPDB, most frequently from about –8.0 to –4.0‰ VPDB

Table 2

Isotopic ratios in calcite cement

Borehole	Depth [m]	$\delta^{13}C$ [‰ VPDB]	$\delta^{18}O$ [‰ VPDB]
Bortiatyn 1	1,594.5	-2.61	-4.27
Lanivka 1	1,456.3	-2.40	-5.76
Makuniv 1	1,847.0	-5.55	-7.66
	1,920.0	-5.09	-7.06
	2,506.0	-7.22	-8.62
	2,515.0	-4.50	-7.40
Moryantsi 1	1,704.2	-1.74	-3.65
	1,919.5	-2.57	-4.16
Nyklovychi 26	1,249.7	-5.80	-7.20
	1,250.5	-1.30	-4.66
	1,352.8	-4.22	-6.71
	1,450.4	-2.92	-6.02
	1,691.2	-1.58	-4.24
	1,701.3	-4.39	-7.19
	1,840.3	-3.04	-6.43
	1,873.5	-1.74	-4.34
	1,880.2	-2.53	-5.47
	2,102.3	-1.70	-5.90
Pyatnychany 1	1,034.0	-4.39	-6.03
	1,135.0	-1.67	-3.46
Pivn. Hirs'ke 1	904.8	-2.02	-4.16
Podil'tsi 1	1,217.0	-2.79	-4.94
	1,231.8	-5.95	-7.24
	1,233.0	-1.28	-4.26
	1,402.1	-1.03	-4.38
	1,721.2	-1.91	-4.28
Skh. Dovhe 3	1,702.5	-2.22	-3.48
	1,714.3	-7.76	-8.27
	1,726.9	-6.56	-8.80
	1,770.2	-1.71	-3.66
Susoliv 5	2,100.5	-1.95	-6.11
	2,528.2	-2.78	-6.09
	2,531.6	-2.66	-5.63
	2,624.7	-3.78	-6.56
	2,809.8	-4.11	-6.61
	2,950.1	-3.96	-6.51
Voloscha 1	2,079.8	-1.97	-4.53
	2,082.2	-2.61	-4.22
	2,091.2	-6.91	-5.59

(Fig. 6). The $\delta^{18}O$ values in the dolomite cement are between –8.2 and –1.7‰ VPDB (Table 3), most frequently from –4.0 to –2.0‰ VPDB (Fig. 7).

Authigenic quartz is very rare in the rocks studied. It forms thin overgrowths on the detrital quartz grains. Locally, as it was noticed under the electron microscope, the fine crystals of the authigenic quartz occur in the pore space of the sandstone.

Table 3

Isotopic ratios in dolomite cement

Boreholes	Depth [m]	$\delta^{13}C$ [‰ VPDB]	$\delta^{18}O$ [‰ VPDB]
Moryantsi 2	1,704.2	1.01	-2.26
Nyklovychi 26	1,691.2	0.19	-3.23
	1,701.3	-0.11	-3.81
	1,840.3	0.25	-4.05
	1,880.2	0.58	-4.62
	2,102.3	0.66	-8.25
Podiltsi 1	1,217.0	0.24	-3.95
	1,231.8	-0.59	-4.17
	1,233.0	0.35	-3.47
	1,402.1	-0.04	-2.87
	1,721.2	0.19	-2.85
Skh. Dovhe 3	1,702.5	0.09	-1.70
Susoliv 5	2,100.5	1.48	-2.46
	2,528.2	1.74	-2.49
	2,531.6	1.61	-2.86
	2,624.7	1.49	-3.13
	2,809.8	2.11	-2.38
Voloscha 1	2,079.8	1.51	-2.47

Feldspar overgrowths on the detrital feldspar grains and individual anhydrite and barite occurrences represent the least frequent cement components.

Petrophysical properties of rocks

Porosity and permeability studies were conducted on 25 sandstone samples (Table 4). The samples were selected after introductory microscopic analysis, which excluded measurements in claystones and mudstones. Low porosity, not exceeding 1%, mainly of fissure character, was noticed in the deposits with a predominance of the aleuritic fraction. The results of laboratory determinations of porosity factor oscillate from 0.88 to 30.31%. Curves of capillary pressure were constructed and a threshold diameter determined (from 0 to 30 µm). Values below 3 µm prove very low properties, while higher values point to good or very good filtration abilities of the analysed sandstones. For each sample, curves for decreasing and increasing pressures were drawn. Their mutual position is a proof for a dimension of deviation of a real pore space from the cylinder model. The value of the hysteresis effect is a numerical dimension of the distance between the curves. In the case of the studied rocks, this value changes from 43 to 82%. Due to the analysis of these values some regularity in development of the pore space may be noticed. The percentage of pores with a diameter larger than 1 µm is differentiated and changes from 0 to 90%, exceeding 50% in most samples.

The porosity measured in thin sections (planimetric analysis) varies from 0 to 19.3 vol. %. It has been observed that it is mainly a primary intergranular porosity. The secondary intragranular or intercrystalline porosity was also observed.

Table 4

Results of petrophysical studies from selected Miocene sandstones (studied and developed by G. Leśniak and the team)

Borehole	Depth [m]	Grain density [g/cm^3]	Total porosity [%]	Bulk density [g/cm^3]	Porosimeter density [g/cm^3]	Effective porosity [%]	Average diameter [µm]	Specific surface [m^2/g]	Pores >1 um [%]	Threshold diameter [µm]	Hysteresis [%]	Permeability [mD]
Lanivka 1	1,450.2	2.65	24.52	2.61	1.99	23.58	0.48	0.98	78	30	43	177.93
Makuniv 1	2,506.0	2.69	3.34	2.67	2.58	3.27	0.04	1.16	12	0.2	56	np.
Nyklovychi 26	1,253.7	2.71	12.28	2.63	2.33	11.37	0.05	4.17	7	1	64	0.43
	1,452.5	2.67	11.72	2.68	2.36	11.84	0.08	2.36	7	0.9	65	1.56
	1,514.4	2.66	19.97	2.56	2.10	18.15	0.22	1.56	66	8	79	9.92
	1,882.9	2.67	15.96	2.63	2.23	15.35	0.17	1.60	34	2	72	0.76
	1,930.5	2.68	0.88	2.23	2.21	0.61	0.00	0.00	n.o.	n.o.	n.o.	0.10
	2,103.5	2.67	14.66	2.64	2.26	14.23	0.19	1.34	30	2	57	0.77
	2,113.5	2.69	10.93	2.64	2.36	10.41	0.07	2.67	4	0.8	60	0.19
Pivn. Hirs'ke 1	884.0	2.64	30.31	2.57	1.84	28.33	0.40	1.52	90	20	46	294.40
Podiltsi 1	968.0	2.67	21.59	2.51	2.04	18.61	0.32	1.16	76	9	81	37.57
	973.0	2.65	29.48	2.63	1.87	28.90	0.55	1.13	86	20	65	226.85
Skh. Dovhe 3	1,637.9	2.67	5.26	2.64	2.50	5.11	0.06	1.26	14	1	50	0.10
	1,703.2	2.66	17.45	2.60	2.17	16.46	0.21	1.46	77	8	78	2.37
	1,711.2	2.66	16.15	2.59	2.20	15.09	0.11	2.45	42	7	71	5.47
	1,723.8	2.63	19.50	2.62	2.11	19.31	0.15	2.45	64	10	75	23.71
	1,728.5	2.64	21.36	2.57	2.06	19.96	0.30	1.28	81	15	82	80.78
	1,736.1	2.65	14.79	2.58	2.22	13.82	0.15	1.68	59	10	74	37.75
Susoliv 5	2,525.3	2.64	17.72	2.51	2.12	15.68	0.11	2.59	51	7	69	3.23
	2,556.5	2.67	9.23	2.62	2.39	8.79	0.07	2.19	7	0.8	58	0.16
	2,588.4	2.67	10.06	2.58	2.34	9.23	0.07	2.42	7	0.6	55	0.10
	2,649.1	2.67	10.72	2.60	2.34	10.01	0.13	1.27	16	2	61	0.22
	2,856.5	2.67	8.71	2.68	2.44	8.80	0.06	2.58	10	0.5	49	0.10
Voloscha 1	2,076.6	2.68	13.28	2.58	2.27	12.07	0.07	3.08	7	0.9	54	0.13

n.o. – not determined; np. – not permeable

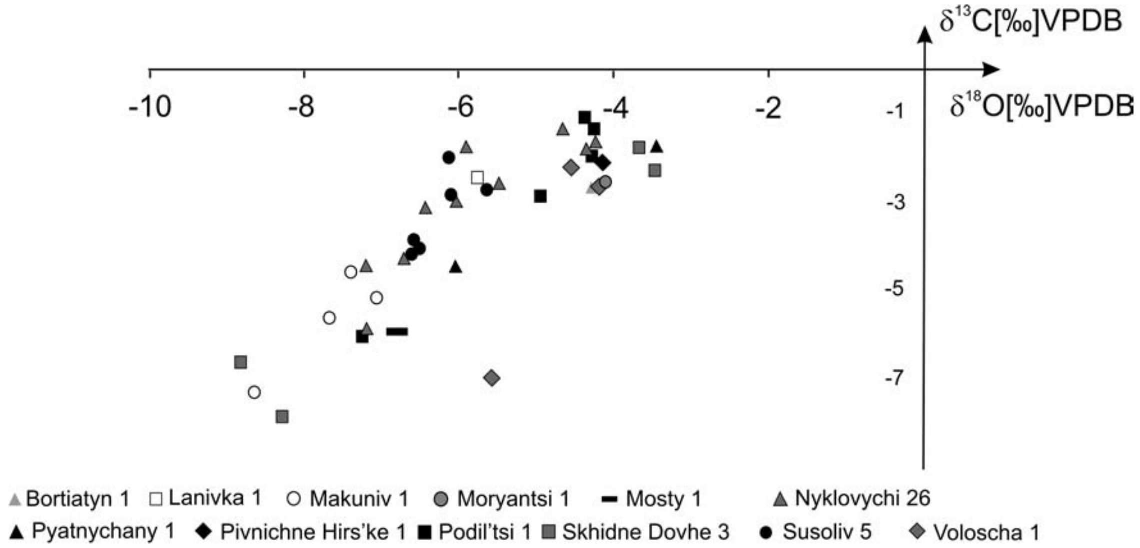

Fig. 6. Projection points of δ^{18}O and δ^{13}C in calcite cement of sandstones

The majority of the studied samples display a low permeability – below 1 mD (Table 4). In some samples, the permeability is of some dozens mD, occasionally over 200 mD. The low permeability is related to strongly developed carbonate cementation. High values were noticed in the samples bearing a primary intergranular porosity.

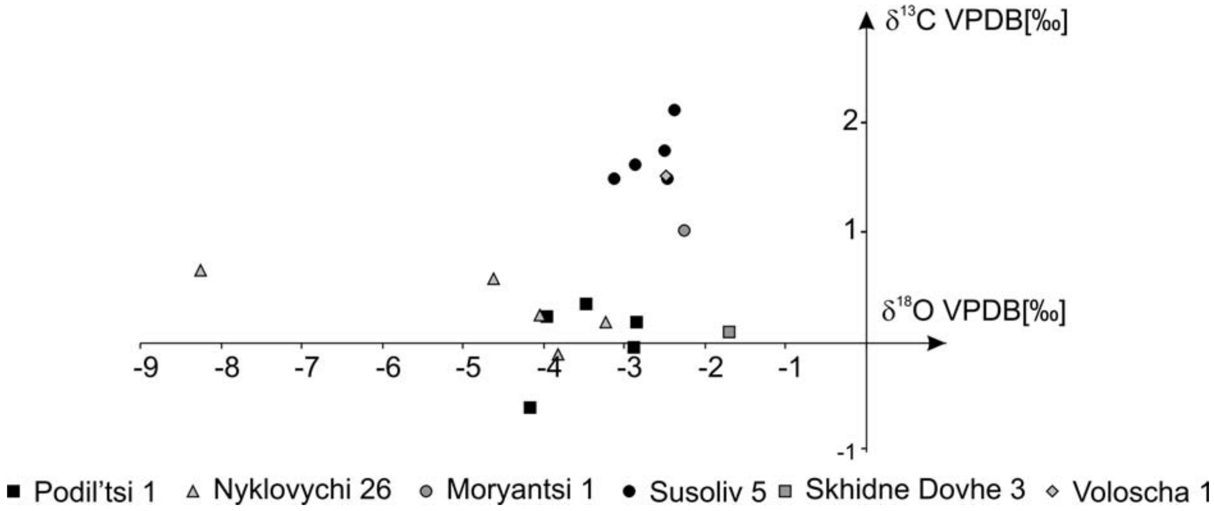

Fig. 7. Projection points of $\delta^{18}O$ and $\delta^{13}C$ in dolomite cement of sandstones

INTERPRETATION AND DISCUSSION

Diagenetic processes and porosity

The compaction, cementation, dissolution and diagenetic alteration were regarded as the most significant post-depositional processes, which have influenced the Middle Miocene deposits in the Ukrainian part of the Carpathian Foreland (*cf.* Lyzun *et al.*, 2004). These processes had a differentiated intensity and in a different manner influenced the pore space of the rocks under description. The effects of these processes were observed both in the detrital grains and in the cements.

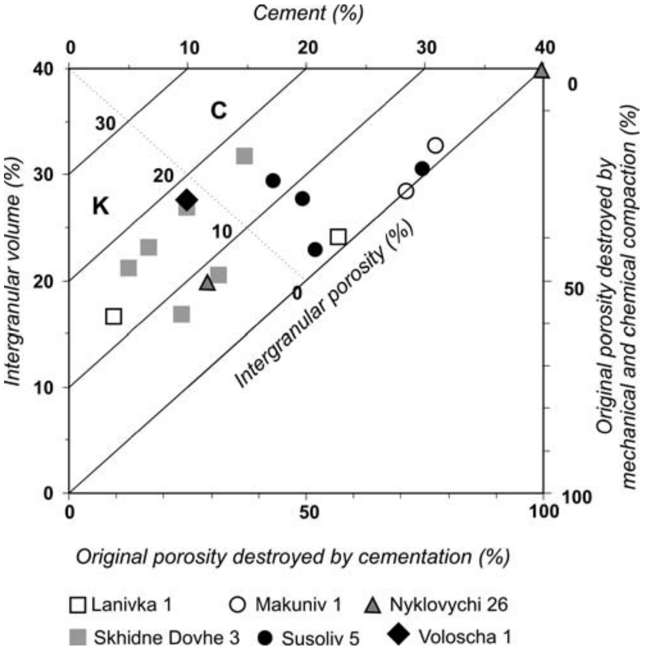

Fig. 8. Diagram of Houseknecht (1987) showing the effect of compaction and cementation on primary porosity of Middle Miocene sandstones: C – cementation predominance; K – compaction predominance

Mechanical compaction resulted in an increase in parking of the grain fabric. Point and linear contacts were observed in the sandstones. Both in the sandstones, mudstones and claystones mica flakes undulated or deformed due to mechanical compaction may be observed. No traces of chemical compaction were seen. Despite the unequal reach of the cementation processes, the effects are common. In some samples a low percentage of the orthochemical cements was observed (about 3–5 vol. %), while some sandstone layers are strongly calcium – bearing (about 49 vol. % – sample at a depth of 1,250.5 m, Nyklovychi 26 well).

The position of points in the Houseknecht's (1987) diagram suggests that the reduction of the primary porosity of the sandstones was connected with both compaction and cementation (Fig. 8). Both processes have caused the significant reduction, locally exceeding 30%.

The diagenetic replacement was connected with cementation. The effects of partial or total replacement of feldspars or lithoclasts by calcite, sometimes by dolomite, were noticed.

As it was mentioned above, both compaction and cementation have influenced on the porosity of the studied sandstones. The process of diagenetic dissolution, which combined mineral grains (Fig. 9) and cement components (Fig. 10) resulting in intergranular and/or intragranular porosities, had some influence on creation of the secondary porosity. Fine secondary pores may be seen in fine mica flakes and clay mineral aggregates.

History of diagenesis

In the present paper, a classification of stages of diagenesis has been applied after Choquette and Pray (1970) who distinguished the eo- and mesodiagenesis. The early diagenesis (eodiagenesis), corresponds to the period from the end of deposition to burial to a certain depth, at which the influence of surface components is stopped. The stage of mesodiagenesis corresponds to the period of progressing burial.

Formation of clay overgrowths, mostly chlorite rims on the detrital grains, and the mechanical compaction, ob-

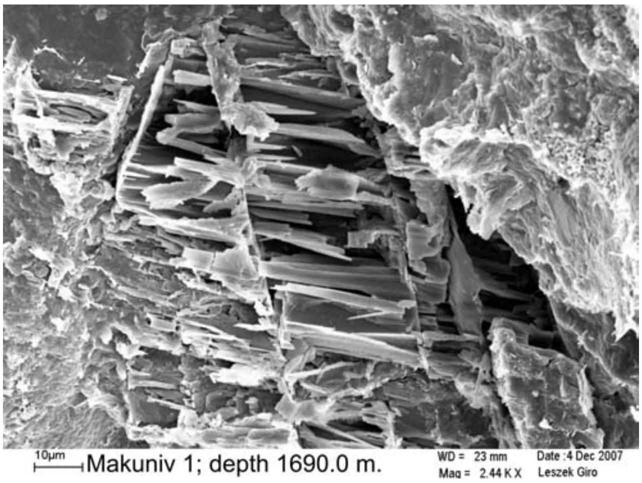

Fig. 9. Relics of feldspar formed due to dissolution. SEM image; Makuniv 1 well; depth 1,690.0 m

Fig. 10. Dissolution traces (arrows) of dolomite. SEM image; Pyatnychany 1 well; depth 1,034.0 m

served as undulated mica flakes or as local increase in parking of the grain fabric, were the earliest diagenetic processes. At this stage, the crystallization of the calcite micrite started. Due to the later recrystallization, this micrite formed strongly calcium-bearing sandstone interlayers with a coarse crystalline cement. During the eodiagenesis, preliminary alteration stages of unstable components of the grain fabric (such as micas and feldspars) took place, which led to kaolinite formation. Temperatures of the kaolinite formation may be determined as 25–50°C (Osborne *et al.*, 1994). At this temperature, a precipitation of silica may also start. With an increase in temperature and pressure, authigenic quartz overgrowths over the detrital grains and pore cements could have been formed. With a progress in diagenesis, feldspar overgrowths on the detrital feldspar grains were formed, that most probably preceded the crystallization of calcite cements. Taking the $\delta^{18}O$ results for dolomites and calcites into account (Tables 2, 3) and applying the $\delta^{18}O$ SMOW of the pore water for the Badenian and Sarmatian between –3.0 and 0.0‰ (Sheppard, 1986; Lear *et al.*, 2000), the formulae after Epstein *et al.* (1953) were used to calculate the hypothetic temperatures of the cement-crystallizing fluids. These temperatures did not exceed 60°C. The meteoric or mixed, meteoric and marine, waters could have been a source of the carbonates. Czapowski (1976), Hałas (1982) and Kurzawa (1990) have already reported on selective carbonate cementation in the Miocene deposits in Poland. The $\delta^{13}C$ results in the calcite and dolomite in the studied samples (Tables 2, 3) in general point to inorganic source of the carbon (Longstaffe, 1989). The lowest negative values $\delta^{13}C$ may either suggest the organic origin, that is from the decay of the organic matter during diagenetic processes in burial conditions (Ayalon & Longstaffe, 1995), or the fact that the carbon could have been connected with methanogenesis (Kotarba, 1999). It may be assumed, however, that the carbon may have originated from cement dissolution in older strata.

The dissolution of the earlier calcite cements or plagioclases may have been a source of calcium (Milliken, 1998; Morad, 1998), while illitization of the smectite was one of the possible iron sources (Boles & Franks, 1979).

The microscopic observations of a relationship of dolomite and ankerite occurrence suggest their late diagenetic origin. In progressive mesodiagenesis, the dissolution of feldspars, lithoclasts and components of the earlier cements continued. That is how the secondary, intergranular and intragranular, porosity was created. Moreover, very random effects of the process of illitization of chlorites and kaolinites, were observed. All these processes were accompanied by mechanical compaction of a limited intensity.

CONCLUSIONS

The Upper Badenian and Sarmatian siliciclastic rocks from the Ukrainian part of the Carpathian Foredeep, represented by claystone, mudstone and sandstone lithofacies, were the subject of petrographic studies. The thick sets of mudstones are separated by claystone and sandstone layers of variable thicknesses.

Claystone is most often a pellitic-aleuritic rock that is composed primarily of clay mineral flakes (illite, illite/smectite, smectite) and an admixture of silt or quartz sand and micas. Mudstones have an aleuritic structure, sometimes with an admixture of pellitic or psammitic fraction. Their grain fabric contains quartz, single feldspars, mica flakes and glauconite. The cement of sandstones is composed of a mixture of clay minerals, such as chlorite, illite and smectite. Sandstones, represented primarily by arenite or subarkosic, sublithic or quartz wackes, are most important for search for hydrocarbon deposits. Detrital components have been divided into mono- and polycrystalline quartz, potassium feldspars and plagioclases, pieces of sedimentary, volcanic, plutonic and metamorphic rocks, micas, glauconite, and single bioclasts. It has been shown that the cements of sandstones contain matrix, authigenic clay minerals (chlorite, kaolinite), carbonate (Fe/Mn calcite, dolomite, ankerite), quartz, authigenic feldspar and, occasionally, anhydrite.

The described rocks revealed signs of mechanical compaction and cementation, dissolution and diagenetic alteration. Compaction and cementation affected the sandstone porosity, which has decreased even by 30%. Diagenetic dissolution of grain components and cements was the key factor to develop secondary porosity in deposits. The laboratory determinations of porosity and permeability confirmed that some sandstones reveal very good reservoir and filtration properties: the porosity reaches over 30%, and permeability varies from a few dozens to over 200 mD.

The diagenetic processes and changes in the architecture of pore space occurred in the deposit during eo- and mesodiagenesis, *i.e.*, from the moment of deposition through consecutive burial stages, with a changing chemistry of pore waters, temperature and pressure as well. The isotopic analysis has shown, among others, that the waters which crystallized into sandstone cements were of meteoric and/or mixed – meteoric and marine nature. Their formation temperatures (especially the formation temperature of carbonate cements) oscillated around 60°C. The occasional occurrence of fibrous illite implies slightly higher temperatures reaching 100°C.

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REFERENCES

Andreyeva-Grigorovich, A. S., Kulchytsky, Y. O., Gruzman, A. D., Lozynyak, P. Yu., Petrashkevich, M. I., Portnyagina, L. O., Ivanina, A. V., Smirnov, S. E., Trofimovich, N. A., Savitskaya, N. A. & Shvareva, N. J., 1997. Regional stratigraphic scheme of Neogene formations of the Central Paratethys in the Ukraine. *Geologica Carpathica*, 48: 123–136.

Ayalon, A. & Longstaffe, F. J., 1995. Stable isotope evidence for the origin of diagenetic carbonate minerals from Lower Jurassic Inmar Formation, Southern Israel. *Sedimentology*, 42: 147–160.

Boles, J. R. & Franks, S. G., 1979. Clay diagenesis in Wilcox sandstones of Southwest Texas: implications of smectite diagenesis on sandstones cementation. *Journal of Sedimentary Petrology*, 49: 55–70.

Choquette, P. W. & Pray, L. C., 1970. Geologic nomenclature and classification of porosity in sedimentary carbonates. *American Association of Petroleum Geologists Bulletin*, 54: 207–220.

Czapowski, G., 1976. Several kinds of carbonate cementation in Miocene sediments in the vicinity of Sandomierz (Holy Cross Mts., Central Poland). *Bulletin de l'Academie Polonaise des Sciences, Série de les Sciences de la Terre*, 24: 83–92.

Epstein, S., Buchsbaum, R., Lowenstam, H. A. & Urey, H. C., 1953. Revised carbonate – water isotopic temperature scale. *Geological Society of America Bulletin*, 64: 1315–1326.

Garecka, M. & Olszewska, B., 2011. Correlation of the Middle Miocene deposits in SE Poland and West Ukraine based on foraminifera and calcareous nannoplankton. *Annales Societatis Geologorum Poloniae*, 81: 309–330.

Gier, S., Worden, R. H., Hohns, W. D. & Kurzweil, H., 2008. Diagenesis and reservoir quality of Miocene sandstones in the Vienna Basin, Austria. *Marine and Petroleum Geology*, 25: 681–695.

Hałas, S., 1982. Badania izotopowe siarczanów, węglanów oraz wody krystalizacyjnej gipsów w utworach miocenu Przedkarpacia. (In Polish). *Przegląd Geologiczny*, 30: 73–76.

Houseknecht, D. W., 1987. Assessing the relative importance of compaction processes and cementation to reduction of porosity in sandstones. *American Association of Petroleum Geologists Bulletin*, 71: 633–642.

Kotarba, M. J., 1999. Generation and accumulation of hydrocarbons and geochemical characteristics of organic matter in autochthonous Miocene strata of the Carpathian Foredeep. (In Polish, English summary) *Prace Państwowego Instytutu Geologicznego*, 168: 277–295.

Kozłowska A., Kuberska M., Lis, P. & Maliszewska, A., 2011. Diagenesis and reservoir properties of the Middle Miocene sandstones in the Polish segment of the Carpathian Foredeep. *Annales Societatis Geologorum Poloniae*, 81: 87–103

Kurovets, I., Prytulka, G., Shpot, Y. & Peryt, T. M., 2004. Middle Miocene Dashava Formation sandstones, Carpathian Foredeep, Ukraine. *Journal of Petroleum Geology*, 27: 373–388.

Kurzawa, M., 1990. The early diagenesis influence on forming of physical properties of Miocene biodetrital limestones from Roztocze hills. (In Polish, English summary). *Kwartalnik Geologiczny*, 34: 369–392.

Lear, C. H., Elderfield, P. A. & Wilson, P. A., 2000. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science*, 287: 269–272.

Lis, P. & Wysocka, A., in press. Sedimentological characteristics of Miocene deposits of the Carpathian Foredeep: Implications for hydrocarbon reservoirs. *Annales Societatis Geologorum Poloniae*.

Longstaffe, F. J., 1989. Stable isotopes as tracers in clastic diagenesis. In Hutcheon, I. E. (*ed.*), *Short Course in Burial Diagenesis, Mineralogical Association of Canada. Short Course Handbook*, 15: 201–277.

Lyzun, O., Kurovets, I., Prystulka, G., Sheremeta, O. & Zybko, O., 2004. Petrofizychni vlastyvosti porid-kolektoriv. In: Kolodiy, V. V., Boyko, G. Y., Boychevs'ka, L. E., Bratus', M. D.& Velychko, N. S., (*eds.*), 2004. *Karpats'ka naftogazonosna provintsiya*. (In Ukrainian). Ukrains'kyi Vydavnychyi Tsentr, Lviv–Kyiv: 130–146.

Milliken, K. L., 1998. Carbonate diagenesis in non-marine foreland sandstones at the western edge of the Alleghanian overthrust belt, Southern Appalachians. In: Morad, S. (*ed.*), *Carbonate Cementation in Sandstones. International Association of Sedimentologists, Special Publication*, 26: 87–105.

Morad, S., 1998. Carbonate cementation in sandstones: distribution patterns and geochemical evolution. In: Morad, S. (*ed.*), *Carbonate Cementation in Sandstones. International Association of Sedimentologists, Special Publication*, 26: 1–26.

Oszczypko, N., Krzywiec, P., Papadyuk, I. & Peryt, T., 2006. Carpathian Foredeep Basin (Poland and Ukraine) – its sedimentary, structural and geodynamic evolution. In: Golonka,

J. & Picha, F. J. (*eds*), *The Carpathians and their Foreland: Geology and Hydrocarbon Resources. American Association of Petroleum Geologists Memoir*, 84: 293–350.

Osborne, M., Haszeldine, R. S. & Fallick, A. E., 1994. Variation in kaolinite morphology with growth temperature in isotopically mixed pore – fluids, Brent Group, UK North Sea. *Clay Minerals*, 29: 591–608.

Peryt, D., 1999. Calcareous nannoplankton assemblages of the Badenian evaporites in the Carpathian Foredeep. *Biuletyn Państwowego Instytutu Geologicznego*, 387: 158–161.

Petryczenko, O. I., Panow, G. M., Peryt, T. M., Srebrodolski, B. I., Pobereżski, A. W. & Kowalewicz ,W. M., 1994. Zarys geologii mioceńskich formacji ewaporatowych ukraińskiej części zapadliska przedkarpackiego. (In Polish). *Przegląd Geologiczny*, 42: 734–737.

Pettijohn, F. J., Potter, P. E. & Siever, R., 1972. *Sand and Sandstone*. New York, Springer Verlag, 618 pp.

Sheppard, S. M. F., 1986. Characterization and isotopic variation in natural waters. In: Valley, J. W., Taylor, H. P. Jr. & O'Neill, J. R. (*eds*), *Stable Isotopes in High Temperature Geological Processes. Reviews in Mineralogy*, 16: 165–181.