

OUTCROPS AS ONE OF THE KEYS IN RECONSTRUCTION OF PETROLEUM SYSTEM OF THE POLISH OUTER CARPATHIANS

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Abstract: A petroleum system was recognized in the Gorlice–Bóbrka region of the Outer Carpathians in Poland. Three tectonic units (Dukla, Silesian and Magura) in the area of study are most important for petroleum industry. Several types of sandstone with reservoir potential belong to these units, but only the Istebna and Ciężkowice sandstones from the Silesian Unit were investigated in boreholes. Carefully chosen outcrop sandstones as well as some samples from available boreholes were gathered in the database. Porosity, permeability, capillary pressure investigations, petrography and computer analyses of microscopic images were performed for outcrops and borehole samples. Artificial Neural Net simulation using the whole database gave very good permeability fit for all kinds of sandstones (also from outcrops). It means that all types of sandstones are petrophysically very similar. Detailed investigations show only an insignificant porosity increase for outcrop samples. Petrography investigation provides an explanation for this fact. Circulations of meteoric waters dissolve sand grains, whereas pore throat is not changed. Correlation matrix method was applied to share factors steering petrophysical properties in sandstones from the investigated region. Source rocks *responsible for generation* of hydrocarbons in the area of study have been identified. Outcrop samples (157) were taken from deposits of the Dukla and Silesian units. Generally, outcrop samples were taken from the Menilite beds located along anticlines in the analysed area. Finally, hydrocarbon potential of the region was evaluated. The weathering effect was taken into consideration.

Key words: outcrops, pore space properties, maturity, petrography.

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INTRODUCTION

For correct modelling of petroleum system in the Outer Carpathians it is essential to characterize its key elements, such as source rocks, reservoir rocks, carrier beds and seals. These characteristics should be based on a representative population of samples. In the Carpathian “flysch” it is very difficult to collect samples, which represent full stratigraphic section, because of tectonic deformation, numerous erosion gaps and in sufficient amount of core samples received from drilling. Basin analysis, the final effect of which is the reconstruction of basin’s evolution, is a modern instrument used in hydrocarbons generation modelling. This reconstruction can only be carried out with sufficient amount of geological, geochemical and petrophysical data. Amount of data from Carpathians allows only for fragmentary reconstruction. Complementary analyses are possible to carry out on outcrops in those areas, where source rocks crop out on the surface and can be correlated with core samples. The main interest of geochemical research in the Polish Outer Carpathians (*e.g.* Matyasik & Dziadzio, 2006;

Kotarba & Koltun, 2006 and references therein) is focused on Menilite beds, which are considered to be the main source for generation of hydrocarbons, supplying the discovered accumulations of hydrocarbons in Silesian and Dukla units. In the last years, many different parameters have been received from outcrops research, particularly concerning the degree thermal maturity. Maturity criterion (similarly to richness in organic substance) determinates, whether it is meaningful to search in a concrete petroleum basin (Bordenave, 1993; Brooks & Welte, 1993). Research has been carried out also for source samples, collected from exposures, which could correlate with core samples – *e.g.* Draganowa well. Influence of external factors (erosion, water, biodegradation), which can disturb values of particular parameters was taken into consideration. Estimation of weathering effect on geochemical parameters value in this study is based on data from published papers (Philp *et al.*, 1992; Burns *et al.*, 1999). It allowed correlating different measurements of the same maturity feature.

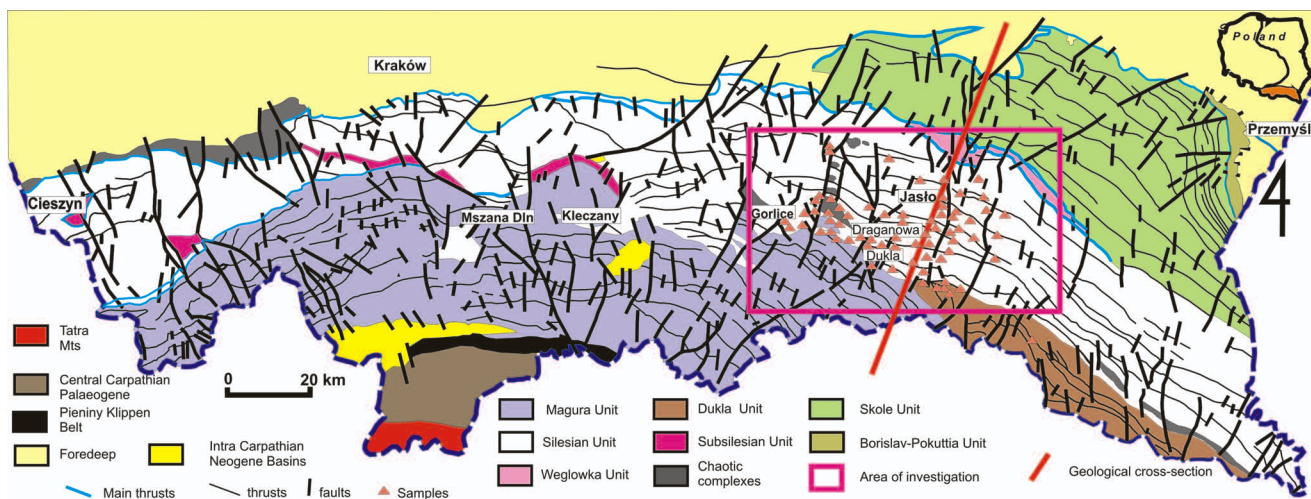


Fig. 1. Area of investigation (after Jankowski, 2004)

Potential reservoir rocks, such as the Istebna sandstones, Ciężkowice sandstones, Krosno beds, Inoceranium beds, Cergowa beds and Magura beds as well as shales within flysch packages, which constitute seal element of petroleum system, were investigated with the use of correlation of petrologic investigations and artificial neural network applied to petrophysical properties. No significant differences were observed.

The aim of this study was to show, basing on large population of samples, that properly collected samples from surface exposures can be representative for stratigraphic levels and useful for analysis of petroleum systems in the Carpathians, taking into consideration the weathering effect.

STUDY AREA

The area of interest is located in the central part of the Polish Outer Carpathians (Fig. 1). The sedimentary basins of the Outer Carpathians were created on the disintegrated southern edge of the European Platform (Wieczorek, 1993; Golonka *et al.*, 2000, 2006 and references therein). The sequence of deposits of the Outer Carpathian basins began to form during the Late Jurassic times (Książkiewicz, 1974; Ślącza *et al.*, 2006; Oszczypko *et al.*, 2008 and references therein). The sedimentary basins of the Outer Carpathians had existed until the foredeep basin was created, before Early Miocene. The shortening processes of the basin brought about inversion and change of the architecture of the basin. New investigations (Jankowski, 2004, 2007; Dziadzio *et al.*, 2006;) indicate a possibility of deposition in half-graben-type subbasins. Geometry of sand-bodies (e.g. Ciężkowice and Istebna beds) shows deposition in this type of subbasins, which existed perhaps since the Late Cretaceous. Half-graben-type subbasins were separated by ridges of tectonic origin (traditionally called “cordilleras”). The arrangement and architecture of Carpathian basins was probably connected with the pre-existing, older than Alpine orogen, structures of the basement of the Carpathians. The process of inversion brought a change in geometry of the sub-

basins (the change of direction of axis, absorption of tectonic edges) as well as a shift of the centre of deposition towards the European Platform. The shortening process of sedimentary basin in this area is revealed in tectonic structures (syndimentary thrusts, especially in the Menilite beds). Moreover, relative changes of the sea-level exerted essential influence on architecture of the sedimentary basin and facies (Jankowski, 2004; Dziadzio *et al.*, 2006; Poprawa *et al.*, 2006). This was particularly visible during the Eocene and Palaeocene times when basin floor, fan-type sand-bodies appeared. The occurrence of these sand-bodies was connected with the sea-level fall, probably forced, by local tectonics (Jankowski, 2004, 2007; Dziadzio *et al.*, 2006). It is possible to distinguish several facies strongly connected with relatively high sea level, for example the widespread Menilite beds – the main source rock of the Outer Carpathians. In the last stage of existence of the Carpathian basin, during sedimentary systems collapse, gravitational sliding was very important (Jankowski, 1997, 2007; Cieszkowski *et al.*, 2009). The Carpathian thrust belt has been traditionally interpreted (e.g., Ślącza *et al.*, 2006; Oszczypko *et al.*, 2008 and references therein) as an accretionary wedge, which represents a sub-horizontal detachment, termed “sole thrust”. The geometry of such types of thrust belts has been termed “thin-skinned”. Recent fieldwork investigations show that the final stage of tectonic deformation took place both in the thrust belt and the Carpathian basement (Jankowski, 2004, Jankowski & Jarmołowicz-Szulc, 2004; Golonka *et al.*, 2009). Some surfaces of overthrusts in the Carpathian orogen can be deeply rooted in the basement. Recently discovered some kinds of out-of-sequence thrusts support this theory (Jankowski, 2007). The deformation of the basement of the Carpathians together with the thrust belt has the essential significance for recognition of the architecture of the thrust belt. The pre-Alpine tectonic structures of the basement, existing before overthrusting of the Carpathians were reactivated. The basement influence was proved by seismic survey and wells in the western part of the Polish Outer Carpathians (Golonka *et al.*, 2009).

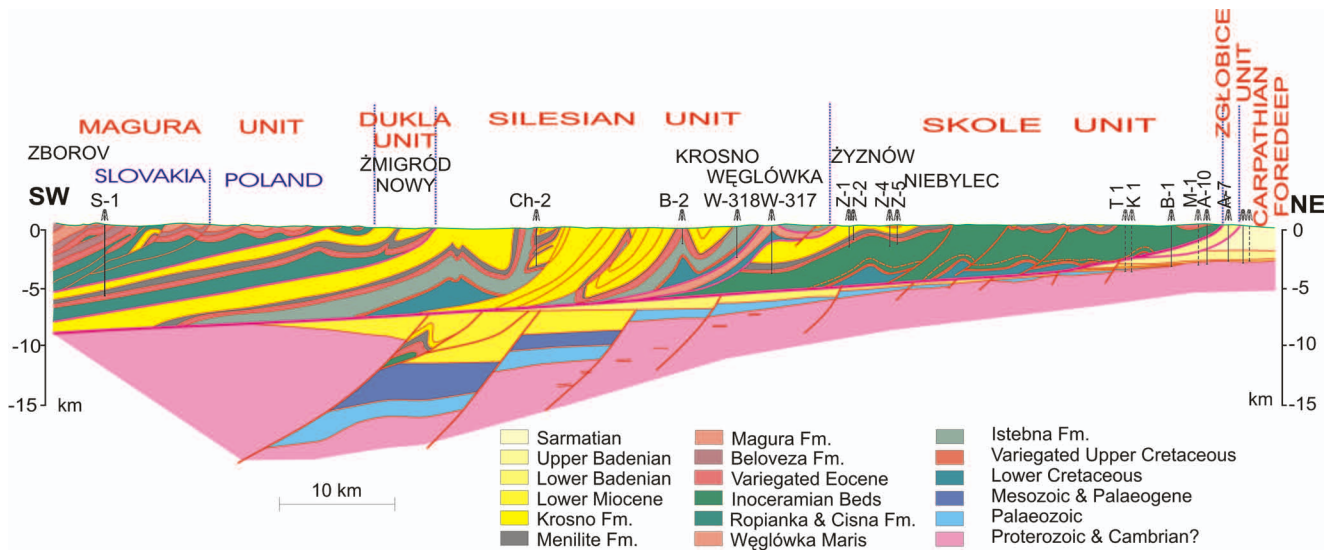


Fig. 2. Geological cross-section (location in Fig. 1). After Ślącza *et al.* (2006)

Gravitational sliding had the essential meaning in the process of emplacement of the most southern tectonic elements in structures of the mountain belt (e.g., Magura Unit). In the Outer Carpathian thrust belt, several tectono-sedimentary units (nappes) were distinguished (Książkiewicz, 1974). In the studied area, we can distinguish five, main tectono-sedimentary units. The Lower Cretaceous deposits are common for all units and reveal unification of the Outer Carpathian's basin in the Early Cretaceous times. Later, differentiation occurs as a result of the occurrence of several half-graben-type subbasins in extensional regime. The most southern nappe is the Magura Unit. Towards the north we can distinguish the Dukla Unit, the Silesian Unit, the Subsilesian Unit (called also Węglówka Unit) and the marginal part of the Carpathian thrust belt called the Skole Unit (Fig. 2). The Upper Cretaceous–Palaeogene Magura Unit consists probably of deposits of the southernmost half-graben subbasin lying on the common for the whole Carpathians Lower Cretaceous sequences. In the Magura Unit, samples were taken from the Magura Sandstones and Supramagura beds (Fig. 3). The Dukla Unit contains slope facies and, moreover, sedimentary cover of the temporarily existing intrabasinal ridge (Silesian “cordillera”), separating the Magura basin from the Silesian basin. In the Dukla Unit, samples were taken from the Menilite beds and Cisna sandstones (Fig. 3). The Silesian Unit consists mainly of deposits of the Silesian basin, which constituted the most central part of the Carpathian basins. In the Silesian Unit samples were taken from the Istebna beds, Ciężkowice sandstones, Menilite beds, and Krosno beds (Fig. 3). The Subsilesian Unit (Węglówka Unit) contains sedimentary facies (Węglówka marls) of the temporarily existing intrabasinal ridge (horst) separating the Silesian and Skole basins. The Skole Unit contains sedimentary facies deposited within the outer Skole basin. It is a strongly imbricated, most external part of the Carpathian thrust belt.

The latest, Miocene history of tectonic deformation of the Outer Carpathians is very complicated – it is possible to

recognize a few stages of tectonic deformation (Rubinkiewicz, 2007; Mazzoli *et al.*, in press). Several tectonic elements (traditionally called “folds”) are distinguished in this area. They represent slice-type “horses” with reduced northern limbs. The Lower Cretaceous limestones, shales and sandstones form the oldest facies elements in this area. The youngest elements are represented by the Krosno beds and Menilite beds (Oligocene–lower Miocene).

PETROLOGIC INVESTIGATIONS

Petrologic investigations were performed using 94 thin sections prepared from outcrops and boreholes. Samples for petrologic study represented the Istebna beds, Ciężkowice beds, Krosno, Menilite and Magura sandstones. For all samples, granulometric analyses, computer analysis of microscopic images and petrographic investigations were performed. Diagenetic processes were described. The main goal of petrographic investigations was to reveal all factors affecting reservoir and filtration properties.

Grain-size analysis

Granulometric analyses using microscopic technique were performed. Frequency diagrams of grain density shows four types of grain distribution: one bimodal and three monomodal ones, which differ in the degree of sorting. (Fig. 4). Mean diameter covers the range of 0.75–4.65 Φ (Fig. 5), the sorting cover the range 0.32–1.25 (Fig. 6). These parameters allow for classification of the investigated sandstones from fine-grained to siltstones. The sorting varies from poor to very good.

Computer analyses of microscopic images

These types of analysis provided digital parameterization of pore space as well as rock grains. During analysis,

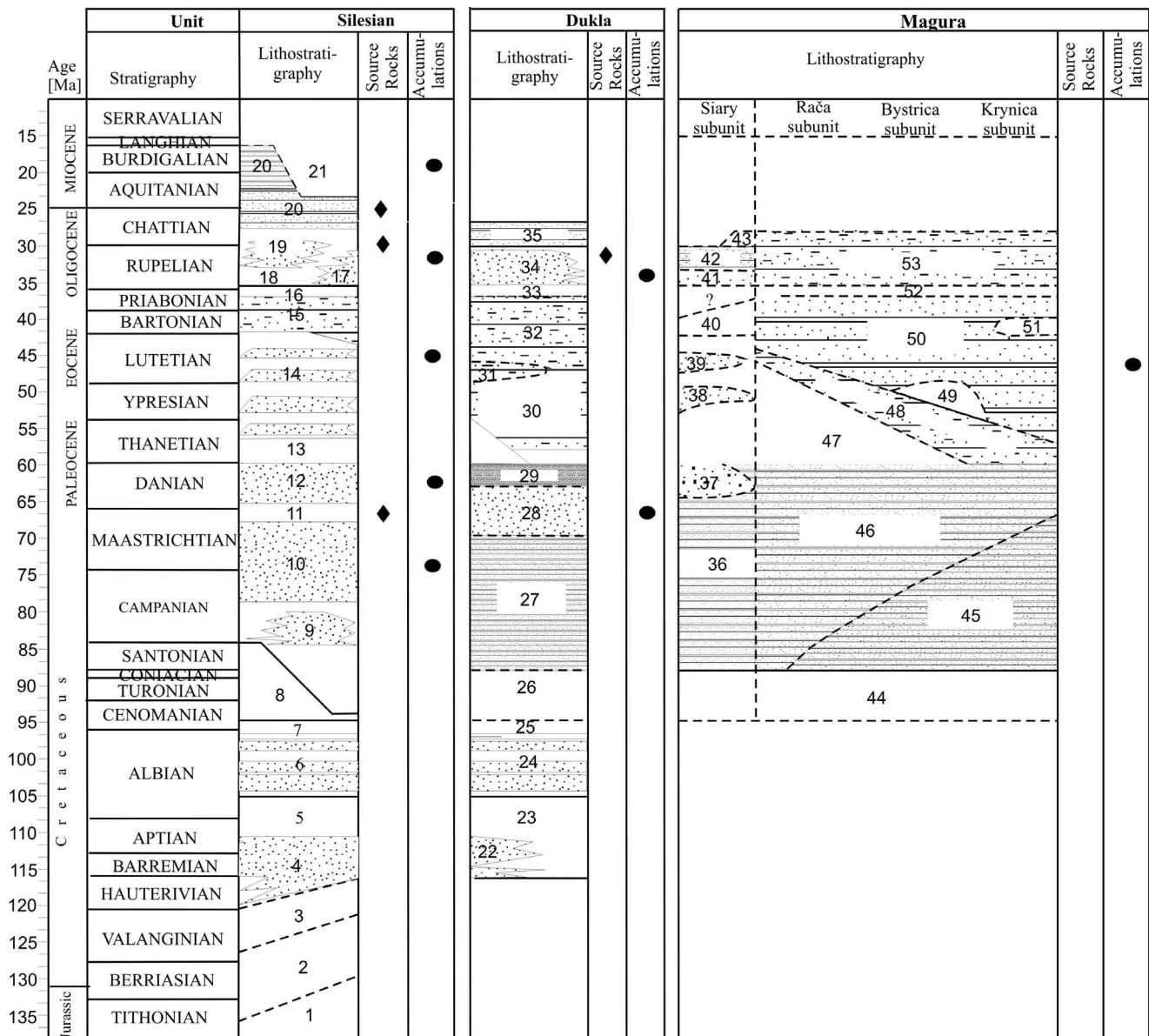


Fig. 3. General lithostratigraphic column showing position of examined samples (compilation by Dziadzio *et al.*, 2001, after Koszarski *et al.*, 1985). SILESIAAN UNIT: 1 – lower Cieszyn shales, 2 – Cieszyn limestones, 3 – upper Cieszyn shales, 4 – Grodziszczce sandstones, 5 – Veřovice beds, 6 – Lgota sandstones with shales, 7 – Gaize beds, 8 – Variegated shales, 9 – Godula beds, 10 – Lower Istebna sandstones, 11 – Lower Istebna shales, 12 – Upper Istebna sandstones, 13 – Upper Istebna shales, 14 – Ciężkowice sandstones with variegated shales, 15 – Hieroglyphic beds, 16 – Globigerina marls, 17 – Cergowa sandstones, 18 – Menilite beds, 19 – Magdalena sandstones, 20 – Krosno beds, 21 – Gorlice beds (olistostromes), DUKLA UNIT: 22 – Grodziszczce sandstones, 23 – Veřovice shales, 24 – Lgota beds, 25 – Gaize beds, 26 – Variegated shales, 27 – Łupków beds, 28 – Cisna sandstones, 29 – Majdan beds, 30 – Hieroglyphic beds with Green shales, 31 – Przybyszów sandstones, 32 – Hieroglyphic beds with Green shales, 33 – Globigerina marls, 34 – Cergowa sandstones, 35 – Krosno beds, MAGURA UNIT: 36 – Inoceramian beds, 37 – Mutne sandstones, 38 – Ciężkowice sandstones, 39 – Pasierbiec sandstones, 40 – sub-magura beds, 41 – Wątkowa sandstones, 42 – supra-Magura beds, 43 – Gładyszów beds, 44 – Malinowa shales (variegated shales), 45 – Szczawina sandstones, 46 – Inoceramian beds, 47 – variegated shales, 48 – Hieroglyphic and Beloveža beds, 49 – Łącko marls, 50 – Magura sandstones, 51 – variegated shales, 52 – Globigerina marls, 53 – Malcov beds

the following parameters were measured: EqDiameter, VolumeEqSphere, VolumeEqCylinder, Perimeter, MeanChord, Length, Width, MaxFerret, MinFerret, Circularity, Elongation (Leśniak, 1999). The results were mathematically prepared by discrimination of micropores with the diameter lower than 5 mm. Then, pore parameterization was performed (min, max, average pore diameter and the content of pores with diameter larger than 0.005 mm).

Petrographic investigations

The investigated sandstones were classified as sublithic arenites, lithic arenites, subarcose arenites, arcose arenites, sublithic wackes and lithic wackes (Pettijohn *et al.*, 1972). Grain skeleton of all samples (Table 1) is highly similar. Mono and polycrystalline quartz dominates. Roundness and sorting differ highly. Fine-grained sandstones are character-

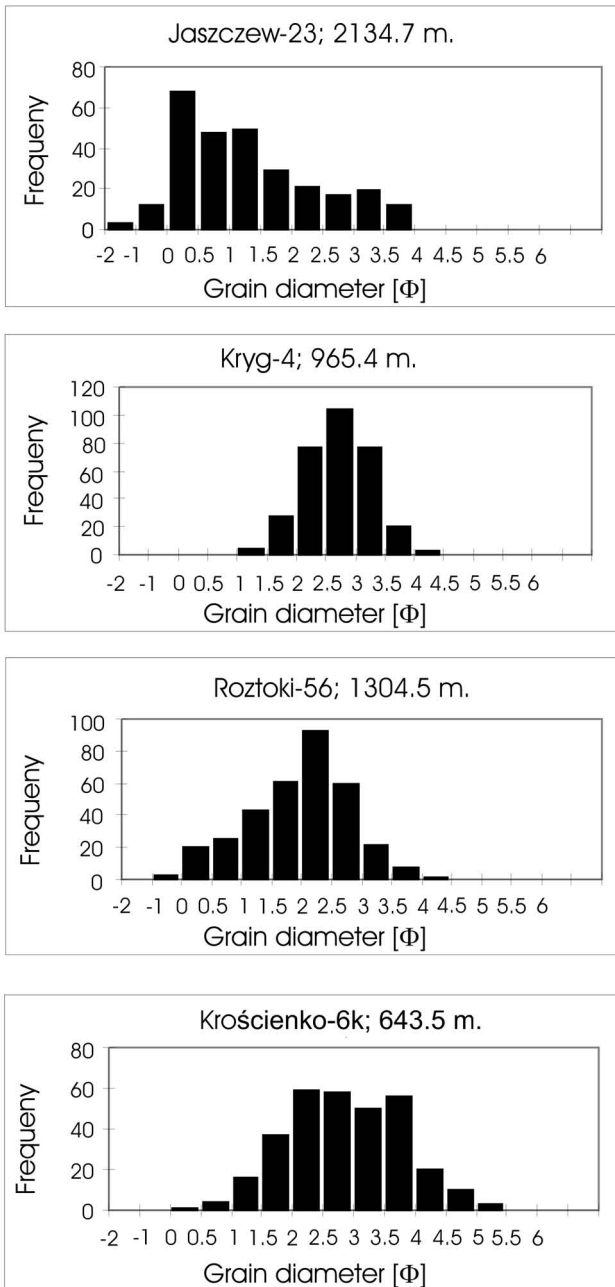


Fig. 4. Frequency diagrams of typical grain density

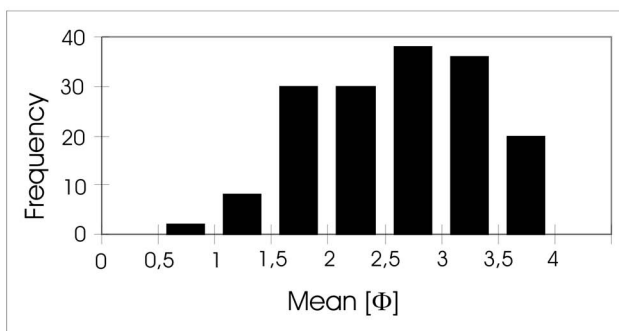


Fig. 5. Histogram of mean diameter

Table 1

Mineralogical composition of the investigated sandstones

Sandstones	Quartz [%]	Feldspar [%]	Rocks fragments [%]	Micas [%]	Glauconite [%]	Cements [%]
Istebna	19-69	3-22	1-23	0-18	0.3-1.6	2.8-38.5
Ciężkowice	39-68	10-29	2-22	0-6	0-1.6	5-31.7
Intra-Menilite	23-78	3-24.2	0-34.9	0-6	0-7.7	5-37
Krosno	22-53	6-20	5-38	0-12.5	0-3.5	8.3-32.6
Magura	42-58	6-16.8	1.4-13	0-4	0-5.8	11-29

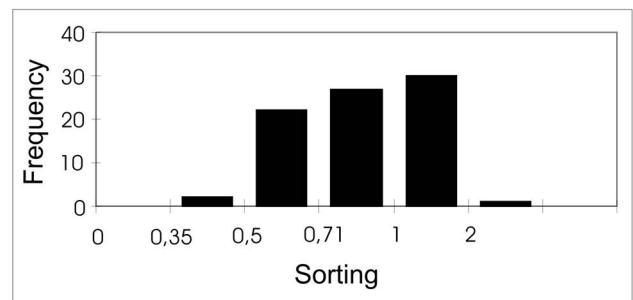


Fig. 6. Histogram of sorting

ized by worse roundness. In cathodoluminescence, quartz grains gleam brown and purple (pointing to metamorphic and magmatic origin) and rarely red (volcanic origin) (Goetze & Zimmerle, 1994).

Feldspars are represented mainly by K-feldspar, the number of plagioclase reaches a maximum of 12% of all feldspars. Feldspars show various degrees of transformation. Rock fragments consist of magmatic, metamorphic, carbonate fragments, clay clasts, bioclasts and sandstone fragments. Micas are formed as muscovite, and rarely biotite. Glauconite is present in the form of conglomerations between grains, mostly with the traces of piritization and transformation to iron hydroxides.

Matrix consists of quartz or carbonates and clay minerals, as well as iron hydroxide. Clay minerals are represented by kaolinite, chlorite, illite/smectite and illite. Cements are represented by authigenic quartz and calcite cement. Quartz cement exists as a typical contact cement or authigenic overgrowth. Calcite cement reveals basal or contact pores. Carbonate cements are represented by manganese or iron calcite, more seldom by dolomite and ankerite. The style of cement development and its distribution varies. In each sample, we can observe all types of cement.

Diagenetic processes

General diagenetic processes are very similar in all types of the analysed sandstones (Leśniak, 2004). Greater differences are observed within a single formation rather than between various ones in one borehole. The main diagenetic processes present in the investigated sandstones

Table 2

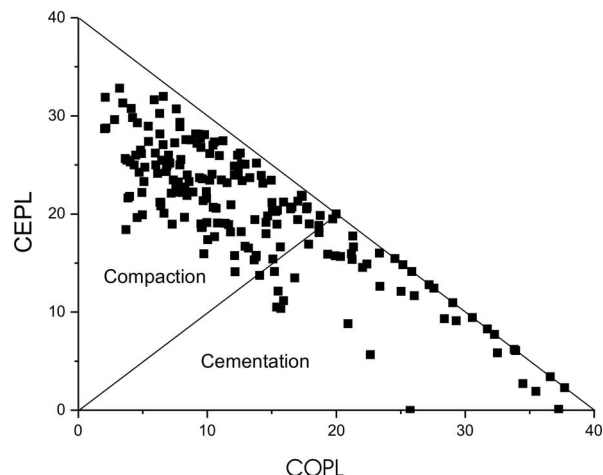


Fig. 7. Primary porosity loss (after Lundegard, 1992)

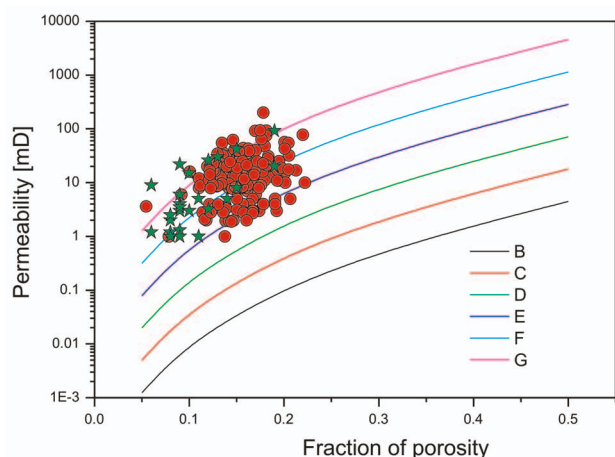


Fig. 8. Cross plot porosity permeability coupled with Global Hydraulic Unit (GHU)

are: accretion, dissolution, neomorphism, transformation as well as compaction and cementation.

Compaction and cementation dominate. Compaction always decreases initial porosity. In cementation processes two stages were observed. In the first stage, quartz overgrowths were created. The rocks became more rigid and initial porosity is conserved. The second stage was carbonate cementation and drastic initial porosity reduction.

In order to provide quantitative estimation of initial porosity loss due to compaction and cementation processes, the formulae elaborated by Lundegard (1992) were used. Analysis for all sandstone samples was made. Lundegard elaborated the formula (1), which makes possible estimating the percentage of initial porosity loss due to mechanical compaction.

$$\text{COPL} = P_i - ((100 - P_i) \times P_{mc})(100 - P_{mc}) \quad (1)$$

$$P_{mc} = P_o + C;$$

where: P_i – initial porosity (%), P_o – total optical porosity from microscope observation (%), C – volume percentage of pore filling cement.

Parameters of similarity classes

Number	Porosity [%]	Permeability [mD]	Threshold diameter [mm]	Fractal dimension	Description
I	13-25	>10	>20	2.98-2.96	the best rocks
II	13-25	3-60	15-20	2.96-2.94	good
III	8-25	1-20	8-15	2.96-2.92	moderate
IV	8-25	<3	4-8	2.94-2.9	poor

Taking into consideration factors responsible for initial porosity reduction (with exception of compaction), the formula (2) elaborated by Lundegard (1992) was used and initial porosity reduction caused by cementation processes was estimated:

$$\text{CEPL} = (P_i - \text{COPL}) \times (C/P_{mc}) \quad (2)$$

Also ICOMPACT was calculated (3) to consider the compaction factor:

$$\text{ICOMPACT} = \text{COPL}/(\text{COPL} + \text{CEPL}) \quad (3)$$

If ICOMPACT value is equal 1, the compaction is fully responsible for total initial porosity reduction. If ICOMPACT value is equal 0, the cementation effects total initial porosity reduction. Valid use of Lundegard (1992) formula for sandstone samples with initial porosity equal 40 and 45% requires the following conditions: loamy matrix content (<10%), porosity and cement content sum (?45%), and allogenic origin of cement.

The results are presented in Fig. 7. Most of these results are located in the field assigned to initial porosity reduction as a result of compaction. Samples located in the field, assigned to initial porosity reduction, contain high amount of carbonate cement. It is necessary to highlight that initial porosity reduction, either as a result of cementation or compaction, was leading to relatively high porosity maintenance. Clear dominance of compaction over cementation processes resulting in initial porosity reduction in the Itebna beds and Ciężkowice sandstones can be observed, whereas in the Krosno, Menilite, and Magura beds cementation is a dominating process, which results in initial porosity reduction.

PETROPHYSICAL INVESTIGATIONS

155 oil samples from 15 boreholes and 41 outcrops were examined. Samples were taken from the Itebna sandstones, Ciężkowice sandstones, Krosno beds, Inocera- mian beds, Cergowa beds, Menilite and Magura beds. Analyses of porosity and capillary pressure were executed for all samples. Gas permeability was investigated for the rocks for which it was possible to cut plug samples (Such, 2002).

Cross plot porosity – permeability combined with the Global Hydraulic Unit (GHU) was prepared (Corbett & Potter, 2004). It is shown in Fig. 8. Green stars signify outcrop samples, the red ones deep – seated rocks. As it is shown in Fig. 8, both outcrop and deep seated samples occupied the

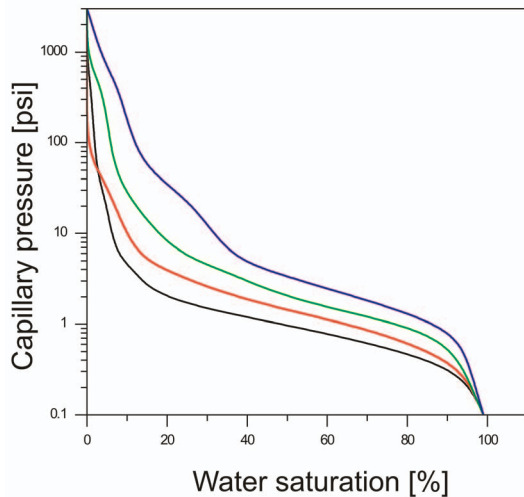


Fig. 9. Average capillary pressure curves for classes of similarity

same GHU. This fact induces treatment of the whole database with all types of sandstones from the Silesian and Dukla units as a single file to find factors steering the reservoir and filtration properties and to describe the way of estimating these properties in deep-seated rocks on the base of petrophysical properties of outcrops rocks.

Fractal dimension was calculated for all samples and the database was divided into classes of similarity (Such, 2002; Peveraro *et al.*, 2004). Porosity, permeability, threshold diameter and fractal dimension were used as parameters. A sketch of classes of similarity is shown in Table 2.

Figure 9 presents average capillary pressure curve for the shared classes. Finally, it is checked that filtration parameters are steered only by threshold diameter and fractal dimension. In other words, petrographically they signify spatial distribution of grains, their diameters, and content of the wall as the kind of cements.

Artificial Neural Network (ANN) was used to confirm similarity of all types of sandstones as well as that between outcrops and deep-seated ones. Neural Works professional II/plus software was used. In calculations, multi-layer, one-dimensional, with back propagation algorithm was applied (Darlak *et al.*, 2006). This type of simulation requires teaching file. Finally, permeability calculation was performed. Fortunately, about 50% of samples belong to the Istebna sandstones. Hence, in the first stage of simulation, it was only the Istebna sandstones that were examined. In the second stage, simulation was done using the whole database. Then the calculated values of permeability were compared with experimental data. The quality of fitting in both cases was practically the same. The research results indicate no significant difference between various types of sandstones or between outcrops and subcrop rocks.

CORRELATION ANALYSES

All measured parameters of rocks (petrophysical, pore space parameters, grain-size distribution, and computer analyses of microscopic images) were used in correlation

work. Correlation matrix method was applied. It was treated as a method to check similarity of various types of the Carpathian sandstones and that between outcrop and subcrop rocks within the same type of sandstone.

Petrographic investigations show that rocks from different stratigraphic beds have very similar structure of grain skeleton, similar cements, and that diagenetic processes were very similar. This confirms the results of petrophysical investigation indicating that the main factors affecting reservoir and filtration properties consist in space distribution of these two components.

Intense processes of dissolution were observed in outcrop rocks. Dissolution occurs both in cements (quartz and carbonate) and detritic grains (feldspars, fragments quartz). Petrophysical data allow us to check that these processes generally increase porosity or conserve porosity (in vicinity of carbonate cements), but practically do not affect filtration properties. It means that factors affecting values of permeability (grain diameter, space distribution of grains and cements) were not disturbed in outcrop samples. Correlation analyses of petrophysical parameters and the parameters obtained with the use of computer analyses of microscopic image indicate that:

- petrophysical parameters depend on the sum of cements,
- for all shared groups (grain diameter, cement content), correlation matrixes show the same trends,
- in the rocks with cement contents greater than 15%, carbonate cements decrease pore space parameters, but quartz cements increase them,
- small quantity of cement content always decreases petrophysical parameters,
- for very fine-grained and fine-grained rocks, a strong correlation was observed for geometrical parameters of pores calculated with the use of computer analysis of images and petrophysical parameters; there was also strong dependence on the sum of cements. These correlations became weaker for greater grain diameters. It means that the increase of grain diameter is connected with more chaotic development of pore space.

GEOCHEMICAL INVESTIGATIONS

Special attention in geochemical research in the Polish Outer Carpathians is focused on the source Menilite beds, which are now treated as the main source of hydrocarbon generation, especially in the Silesian and Dukla units. These sediments show great facies variability of source potential as well as the degree of maturity (Kotarba *et al.*, 1999; Kuśmierk *et al.*, 1995, 1996; Kotarba & Koltun, 2000; Matyasik & Dziadzio, 2006; Matyasik, 2006). The first investigations of Menilite beds recognized them as enriched in organic matter rocks but not mature enough. Finally, systematic works made for PGNiG Corp and Medusa Oil & Gas, using samples taken from tectonic windows of the Dukla Unit show that these rocks have reached a high level of thermal evolution (Matyasik *et al.*, 2001). Further investigations of Menilite beds were performed in Gorlice, Folsz and Ropa regions. The results of research confirm

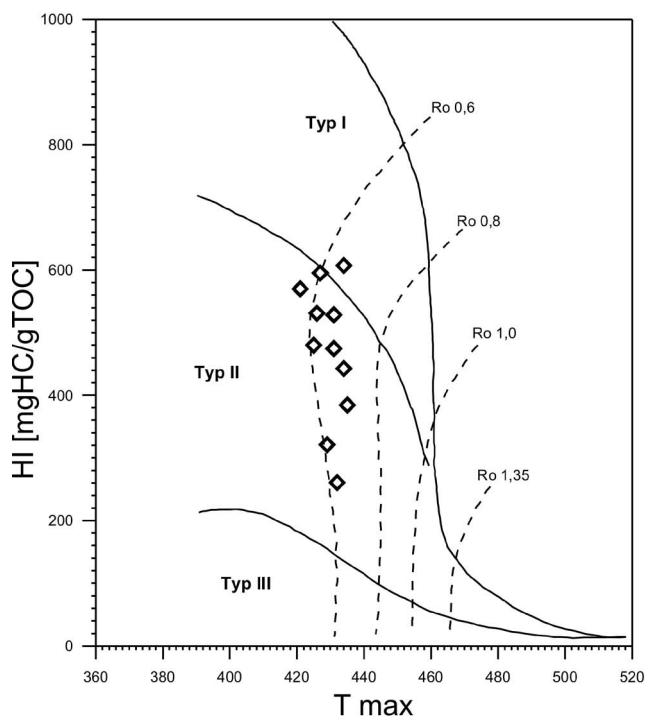


Fig. 10. Plot of hydrogen index vs. Rock-Eval T_{max} temperature for the Menilite outcrops

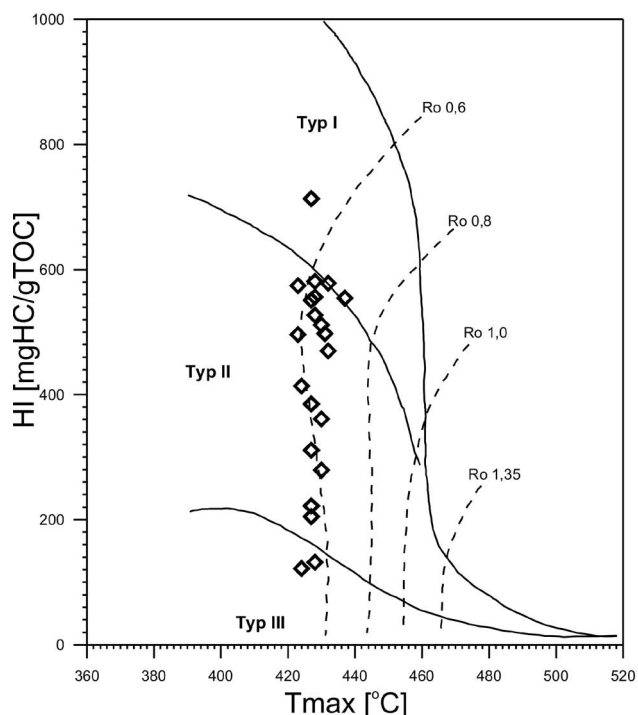


Fig. 11. Plot of hydrogen index vs. Rock-Eval T_{max} temperature for the Menilite samples from Draganowa well

the significant role of the hydrocarbon expelled from Menilite source rocks in filling reservoir traps. Now, a new set of investigations for outcrop samples was conducted.

The obtained results revealed inconsistency in geochemical parameters of these rocks. Especially, the results

of thermal maturity reveal considerable variance comparing parameters obtained using different types of methods. According to the reports from comparative investigation conducted for source rocks using outcrops parallel with core samples from wells, an attempt was made at estimating the impact of weathering effect on T_{max} value (from RockEval analysis), vitrinite reflectance and biomarker indices (Petres & Moldovan, 1991; Philp *et al.*, 1992; Burns *et al.*, 1999; Chang & Berner, 1999; Petsch *et al.*, 2000).

Changes of parameters related to erosion were minimalised by correlation results obtained for outcrop samples and samples from equivalent formation from boreholes. Samples collected from outcrops in the Iwonicz fold area and cores from Draganowa well (Matyasik & Słoczyński, 2007) provide the best example for correlation work. Decrease of n-alkanes content was observed for outcrop samples. Biodegradation due to bacterial activity provides another explanation for n-alkanes drop. Because isoprenoids are more resistant to degradation, it is impossible to calculate the factor of deposition environment Pr/nC_{17} and Ph/nC_{18} , which is usually used to correlate and classify source rocks and oils.

Disintegration of steranes and hopanes is the next element related to the weathering effect. It is revealed by the presence of isomers characteristic for samples with high degree of maturity (high concentration of pregnanes and bb steranes), in spite of low value of vitrinite reflectance on a level of $VR = 0.37\%$. Weathering effect could be also reflected in the shift of $\delta^{13}C$ of aromatic fractions towards heavier isotopes (Philp *et al.*, 1992). In Rock Eval analyses weathering effect can be seen in the decrease of S_1 peak. It is related to the so-called hydrocarbons removal.

Sixty samples, mainly derived from the Menilite beds, were examined. Outcrop samples and rocks from four boreholes were collected from the Dukla and Silesian units. Menilite samples were taken from all tectonic elements of the investigated units. Rock Eval, bitumen extraction, gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GCMS) analyses were performed. In the first step, the age and stratigraphic position were established. Geochemical interpretation was focused on maturation parameters. The results obtained from outcrops and buried (taken from boreholes) samples were compared (Figs 10, 11). The impact of weathering effect was evaluated as a minimal (lower value of S_1 peak for outcrop sample). Saturated hydrocarbon chromatograms exhibit very similar distribution suggesting the same organic matter input and that bottom waters were not anoxic at the time of deposition (Didyk *et al.*, 1978). Biomarker distribution of aromatic fraction is also very similar for both types of samples. It shows that outcrop samples can be used in geochemical research. This result is supported by correlation between outcrops and buried samples from a very close area (Fore-Dukla fold).

The results of Rock Eval for these outcrops are shown in Fig. 10. They supported the assumed similarity of geochemical features for both kinds of samples; taken from exposures as well as from borehole.

Using high resolution geochemical methods such as: mass spectrometry of biomarkers and gas chromatography, the analogy of genetic characteristics of both groups of sam-

ples was confirmed. These samples contain the same characteristic elements, such as steranes, hopanes and oleanane. Distribution of these compounds shows a low maturity level. Similar parameters and compounds of both outcrops and borehole samples give us possibility to estimate geochemical parameters of subcrop layers using results from outcrop samples.

CONCLUSIONS

1. All types of the investigated Carpathian sandstones reveal similar reservoir and filtration properties depending on the threshold diameter and fractal dimension. It means that reservoir parameters of sandstones in the whole Carpathian flysch are steered by diagenesis processes.

2. No evident differences between outcrops and borehole samples were observed.

3. Only the dissolution processes are more intense in outcrops rocks. These processes affect only porosity and not permeability.

4. It is possible to estimate all enhancements and properly evaluate the petroleum system in the Silesian and Dukla units using outcrop samples.

5. The Menilite beds in the Draganowa well showed good correlation with outcrops taken from Fore-Dukla fold. Both sets of samples are characterized by same thermal maturity.

6. The results of geochemical study have permitted the reconstruction of development of the hydrocarbon generation history for this part of the Carpathians.

REFERENCES

- Bordenave, M. L., 1993. *Applied Petroleum Geochemistry. Editions Technip*, 517 pp.
- Brooks, J. & Welte, D., 1984. *Advances in Petroleum Geochemistry. Academic Press London*: 337 pp.
- Burns, K. A., Codi, S., Pratt, C. & Duke, N.C., 1999. Weathering of hydrocarbons in mangrove sediments: testing the effects of using dispersants to treat oil spills. *Organic Geochemistry*, 30: 1273–1286.
- Chang, S. B. & Berner, R. A., 1999. Coal weathering and the geochemical carbon cycle. *Geochimica et Cosmochimica Acta*, 63: 3301–3310.
- Cieszkowski, M., Golonka, J., Krobicki, M., Ślącza, A., Oszczytko, N., Waśkowska, A. & Wendorff, M., 2009. The Northern Carpathians plate tectonic evolutionary stages and origin of olistoliths and olistostromes. *Geodynamica Acta*, 22(1-2): 1–26.
- Corbett, P. W. M. & Potter, D. K., 2004. Petrotyping: a Basemap and Atlas for Navigating through Permeability and Porosity Data for Reservoir Comparison and Permeability Prediction. *Society of Core Analysts Papers*, 30: 385–396.
- Darłak, B., Malaga, M. & Włodarczyk, M., 2006. An application of artificial neural Network and geostatistics In oil and gas reservoir parametrisation. (In Polish, English summary). *Prace Instytutu Nafty i Gazu*, 135: 1–54.
- Didyk, B. M., Simoneit, B. R. T., Brassel, S. C. & Eglinton, G., 1978. Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature*, 272: 216–222.
- Dziadzio, P. S., Enfield, M. A., Watkinson, M. P. & Porębski, S. J., 2006. The Cieczkowice Sandstone: Examples of basin-floor fan-stacking patterns from the main (upper Paleocene to Eocene) reservoir in the Polish Carpathians. In: Golonka, J. & Picha, F. (eds), *The Carpathians and their foreland: Geology and hydrocarbon resources. American Association of Petroleum Geologists, Memoir*, 84: 375–376 and CDROM.
- Dziadzio P., Jankowski L. & Kopciowski, R., 2001. Field trip guidebook. *Carpathian Petroleum Conference – Application of modern exploration methods in a complex petroleum system*. Wysowa 27-30.06. 2001: 1–48.
- Golonka, J., Oszczytko, N. & Ślącza, A., 2000. Late Carboniferous–Neogene geodynamic evolution and paleogeography of the circum-Carpathian region and adjacent areas. *Annales Societatis Geologorum Poloniae*, 70:107–136.
- Golonka, J. Gahagan, L., Krobicki, M., Marko, F., Oszczytko, N. & Ślącza, A., 2006. Plate Tectonic Evolution and Paleogeography of the Circum-Carpathian Region. In: Golonka, J. & Picha, F. (eds), *The Carpathians and their foreland: Geology and hydrocarbon resources. American Association of Petroleum Geologists, Memoir*, 84: 11–46.
- Golonka, J., Pietsch, K., Marzec, P., Stefaniuk, M., Waśkowska, A. & Cieszkowski, M., 2009. Tectonics of the western part of the Polish Outer Carpathians. *Geodynamica Acta*, 22(1-2): 81–97.
- Gotze, J. & Zimmerle, W., 1994. Provenance of quartz in siliciclastic sediments. *Second International Conference on the Geology of Siliciclastic Shelf Seas, Program with Abstracts*, Gent, p. 55–56.
- Jankowski, L., 1997. Warstwy z Gorlic – najmłodsze utwory południowej części jednostki śląskiej (In Polish). *Przegląd Geologiczny*, 45: 305–308.
- Jankowski, L., 2004. Rozwój karpackiej przyzmy akrecyjnej – ujęcie koncepcyjne. (In Polish). *LXXV Zjazd Polskiego Towarzystwa Geologicznego, Iwonicz*, Polskie Towarzystwo Geologiczne, Kraków: 98–99.
- Jankowski, L., 2007. Chaotic complexes in Gorlice region (Polish Outer Carpathians). *Polish State Geological Institute Bulletin*, 426: 27–52.
- Jankowski, L. & Jarmołowicz-Szulc, K., 2004. Wstępna charakterystyka mineralogiczna melanży tektonicznych w Bieszczadach. (In Polish). *LXXV Zjazd Polskiego Towarzystwa Geologicznego, Iwonicz*, Polskie Towarzystwo Geologiczne, Kraków: 122.
- Kotarba, M. J. & Koltun, Y. V., 2006. The origin and habitat of hydrocarbons of the Polish and Ukrainian Parts of the Carpathian Province. In: Golonka, J. & Picha, F. J. (eds), *The Carpathians and their foreland: geology and hydrocarbon resources. American Association of Petroleum Geologists Memoir*, 84: 395–442.
- Kotarba, M., Kosakowski, P., Więclaw, D. & Kowalski, A., 1999. Potencjał węglowodorowy skał macierzystych jednostki skolskiej Karpat fliszowych. (In Polish). *Karpacka Konferencja Naukowa. Przemysł Naftowy i nauka razem w XXI wiek. Raba Niżna, maj 1999*, p. 143–152.
- Książkiewicz, M., 1972. Tectonics of the Carpathians. In: Pożaryski, W., (ed.), *Geology of Poland, vol IV Tectonics*. Wydawnictwa Geologiczne Publishing House, Warszawa: 476–620.
- Kuśmierk, J., 1996. Zastosowanie zintegrowanych modeli geodynamicznych i petrofizycznych dla prognozowania potencjału naftowego. (In Polish) Unpublished report: Proj. cel. 1025/C.S 6-9/94, PGNiG Warszawa.
- Kuśmierk, J. (ed.), 1995. Ewolucja a ropogazoność Karpat Polskich. Interpretacja zintegrowanych modeli systemu

- naftowego wschodniej części jednostek allochtonicznych. (In Polish, English summary). *Prace Geologiczne PAN*, 38: 1–92.
- Leśniak, G., 1999. Application of computer analysis of microscopic images in petrophysical investigations. *Przegląd Geologiczny*, 47: 644–651.
- Leśniak, G., 2005. The diagenesis of sandstones in eastern part of the Silesian nappe and a hydrocarbon migration. *Prace Instytutu Nafty i Gazu*, 131: 1–70.
- Lundegard, P. D., 1992. Sandstone porosity loss – a “Big picture” view of the importance of compaction. *Journal of Sedimentary Petrology*, 62: 250–260.
- Matyasik, I., 2006. Hydrocarbon potential of Skole Unit in Flysch Carpathians, Poland. (In Polish, English summary). *Prace Instytutu Nafty i Gazu*, 135: 1–97.
- Matyasik, I. & Dziadzio, P. S., 2006. Reconstruction of petroleum systems based on integrated geochemical and geological investigations: Selected examples from the middle Outer Carpathians in Poland. In: Golonka, J. & Picha, F. (eds), *The Carpathians and their foreland: Geology and hydrocarbon resources. American Association of Petroleum Geologists, Memoir*, 84: 377–378 and CDROM.
- Matyasik, I. & Słoczyński, T., 2007. Possibilities and limitations of using outcrop samples for geochemical evaluation of source rock. *Nafta – Gaz*, 6: 371–387.
- Matyasik, I., Słoczyński, T., Steczko, A. & Halik, A., 2001. Hydrocarbon potential of the Menilite formation in the Carpathian tectonic windows and their relationship with oils accumulated in the Gorlice – Krosno area. Unpublished report. *Archiwum Instytutu Nafty i Gazu*, Kraków.
- Mazzoli, S., Jankowski, L., Szaniawski, R. & Zattin, M., (in press). Low-T thermochronometric evidence for post-thrusting (<11 Ma) exhumation in the western Carpathians, Poland. *Comptes Rendus de l'Académie des Sciences - Series IIA - Earth and Planetary Science*.
- Oszczypko, N., Ślaczka, A. & Żytko, K., 2008. Tectonic subdivision of Poland: Polish Outer Carpathians and their foredeep. (In Polish, English summary). *Przegląd Geologiczny*, 56: 927–935.
- Peters, K. E. & Moldowan, J. M., 1991. Effects of source, thermal maturity and biodegradation on the distribution and isomerisation of homohopanes in petroleum. *Organic Geochemistry*, 17: 47–61.
- Petsch, S. T., Berner, R. A. & Eglinton, T. I., 2000. A field study of the chemical weathering of ancient sedimentary organic matter. *Organic Geochemistry*, 31: 475–487.
- Pettijohn, F. J., Potter, P. D. & Siever, R., 1972. *Sand and Sandstone*. Springer Verlag, Berlin, 618 pp.
- Pevearo, R., van Delden, S., Holwart, J., Geselle, L., Haberland, J., Kloas, F., Lingnau, R., Gupta, R., Larijani, R., Sementsov, A. & Charreyron, Y., 2004. The development of an integrated reservoir description and simulation model: organization, data integration, development of a shared-earth model, preliminary results and the way ahead. *Prace Instytutu Nafty i Gazu*, 110: 129–135.
- Philp, R. P., Junhong, Chen., Galvez-Sinibaldi, A., Huaida Wang, & Allen, J. D., 1992. Effects of Weathering and Maturity on the Geochemical Characteristics of the Woodford Shale. *Oklahoma Geological Survey Circular*, 93: 106–121.
- Poprawa, P., Malata, T., Oszczypko, N., Słomka, T., Golonka, J. & Krobicki, M., 2006. Tectonic activity of sediment source areas for the Western Outer Carpathian basins – constraints from analysis of sediment deposition rate. (In Polish, English summary). *Przegląd Geologiczny*, 54: 878–887.
- Rubinkiewicz, J., 2007. Fold-thrust-belt geometry and detailed structural evolution of the Silesian nappe – eastern part of the Polish Outer Carpathians (Bieszczady Mts.). *Acta Geologica Polonica*, 57: 479–508.
- Such, P., 2002a. Investigations of pore space of reservoir rocks with the use of the fractal approach. *Prace Instytutu Górnictwa Naftowego i Gazownictwa*, 115: 28.
- Such P., 2002b. Pore space investigations in reservoir rocks. (In Polish, English summary). *Prace Instytutu Górnictwa Naftowego i Gazownictwa*, 113: 78.
- Ślaczka, A., Kruglow, S., Golonka, J., Oszczypko, N. & Popadyuk, I., 2006. The General Geology of the Outer Carpathians, Poland, Slovakia, and Ukraine. In: Golonka, J. & Picha, F. (eds), *The Carpathians and their foreland: Geology and hydrocarbon resources. American Association of Petroleum Geologists, Memoir*, 84: 221–258.
- Wieczorek J., 1993. Pasywne brzegi Tetydy – zagadnienia ogólne (In Polish). *Technika Poszukiwań Geologicznych Geosynoptyka i Geotermia*, 4: 31–50.