

UDC 553

## RECENT CONTRIBUTION TO MINERALOGICAL AND GEOCHEMICAL STUDIES IN THE CARPATHIANS

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Samples of rocks, minerals and the organic matter were taken for mineralogical, petrological and geochemical studies from the tectonic mélange zone in the vicinity of Jabłonki–Rabe and Cisna in the Bieszczady Mts., situated in south-easternmost part of the Polish Outer Carpathians. Analytical procedures comprised sampling and preparation; microscopic evaluation of the material from the point of view of inclusions, organic matter and minerals; detailed microscopic determinations and auxiliary studies. Fluid inclusion analysis was performed on double-sided polished thin sections prepared based on the cold techniques. The minerals analyzed in SEM correspond to calcite, Mn-calcite, dolomite, Mn-dolomite, ankerite and pyrite. XRD studies of black organic aggregates in the form of lenses point to the presence of the following minerals: quartz, dolomite, calcite, clay minerals, gypsum with anhydrite admixture, traces of pyrite and siderite. Feldspars are also present.

The pyrolytic Rock-Eval analysis of samples from the Jabłonki region showed a variable TOC in the interval from 0,77 to 35,83 % TOC, generally between 0,77 and 4,44 %, with a low HI (from 30 to 116 mg HC/g TOC). Samples display high degree of thermal evolution, which corresponds to the end of generation processes (the end of the oil window). In the composition of the extractable organic matter, the saturated hydrocarbons constitute a majority of 61,3 % that points to adsorption of the generated or migrating oil. Due to the fluid inclusion studies conducted under the microscope in thin sections (calcite) and in glued wafers or loose crystals (quartz – the Marmarosh “diamonds”), inclusions were characterized in minerals.

*Key words:* quartz, Marmarosh “diamonds”, calcite, organic matter, inclusions, tectonic mélange, Carpathians.

Recognition of the character of mineralization of tectonic mélanges, which are one of many types of the chaotic complexes recognized recently in the Outer Carpathians, is the objective of the present paper. In this area the mélange zones are frequently outcropped in bands of a variable width.

The studies on minerals filling the veins in the Carpathians have been conducted for many years in different aspects. That mostly concerns the quartz. J. Tokarski [41] studied morphology of the so called the Marmarosh diamonds, L. Mastella and I. Kojzar [33] concerned them as bound with the process of bituminization of the Podhale area. Thermometric and cryometric studies [31] showed a presence of methane and most probably nitrogen. Ł. Karwowski and I. Dorda [30] characterized an environment of formation of the Marmarosh “diamonds” in the Mszana Dolna tectonic window in the Krosno beds from beneath of the Inoceramus Cretaceous deposits of the Magura unit as well as in the Mszanka and Raba basins with tributaries and in the Dunajec basin. Studies on the Marmarosh diamonds in the central part of the Polish Carpathians were conducted by

A. Kozłowski with co-auth. (1995, oral information). The Marmarosh “diamonds” have been gaining an interest in last decades since in Ukraine the hydrocarbon inclusions have been concerned as the indicators of hydrocarbon migration and accumulation in the folded Carpathians. Papers of some authors as e.g. [5, 36, 45] may be quoted here.

More and more frequently, the problematic of hydrocarbon migration has been connected with the fluid inclusion studies. These inclusions occur mostly in the quartz of euhedral crystal habit (so called the Marmarosh diamond) and in the minerals of the calcite-quartz-bitumen veins in the Carpathian units (e.g. [11, 30, 43] and Matkovskiy, 1961). It results from numerous papers in the Polish and Ukrainian areas that a majority of the hydrocarbon inclusions in the minerals in the Carpathians co-occurs with the aqueous inclusions [2, 5, 28, 29, 44].

Last studies on the material filling the calcite-quartz veins as well of bitumens and fluid inclusions were conducted in the eastern part of the Polish Carpathians and in the western part of Ukraine [6, 19, 20, 22]. In the Slovak territory in the Western Carpathians V. Hurai with co-auth. [10, 12] studied the origin of the methane in the quartz.

The mineralogical research has been till present conducted in the distinguished mélange zones in the Bieszczady region. First relations come from last years [15, 23, 24].

Recognition of the character of mineralization in the Outer Carpathians, conducted in recent years, concerns zones of the tectonic mélange, which are one of many types of the chaotic complexes recently recognized [14 et al.].

In the Tatra Mts. area, Jurewicz studied *shear zones* in the granitoid body and its cover [25–27]. The aim of the present paper is to determine a character of mineralization in the mélange in the eastern part of the Carpathians and to approximate mineralogical and geochemical conditions of mineral formation in the south-easternmost part of the territory of Poland, mainly in the region between Jabłonki and Ustrzyki Górne (fig. 1). It should be underlined here that observations were conducted also more westwards, in the western Bieszczady and in Beskid Niski, the mélange zones discovered there do not display such a rich mineralization as in the area under a present description.

The observation and sampling area lies in the south-easternmost part of the Polish Outer Carpathians. Traditionally, three tectonic-facial units have been distinguished there. The so called Dukla unit is the southernmost one. Its profile comprises the deposits from the Upper Cretaceous to Oligocene.

The Inoceramus beds are the oldest beds in the sequence, being deposited from Upper Cretaceous to Palaeocene; their profile has been completed by the so called Majdan beds of the Palaeocene age. The Inoceramus beds of his unit are developed slightly different from those in other regions – two facies of different percentage of sandstones may be distinguished here.

The Łupków facies lies lower in the profile, being more typical; thin and medium banded sandstones and schists dominate in its lithology. The Cisna facies, of a predominance of thick sandstones is higher in the profile. Still higher, in the Eocene part of the Dukla unit, there is a complex of variegated schists with sandstone interlayers either of the Przybyszów or Ciężkowice sandstones lithotypes. The hieroglyph beds, typically developed as thin sandstones and schists are the highest part of the Eocene deposits.

The results shown in the present paper have a mineralogical, geochemical and petrological character and are an example of a combination of these analyses with field and cartographic works.

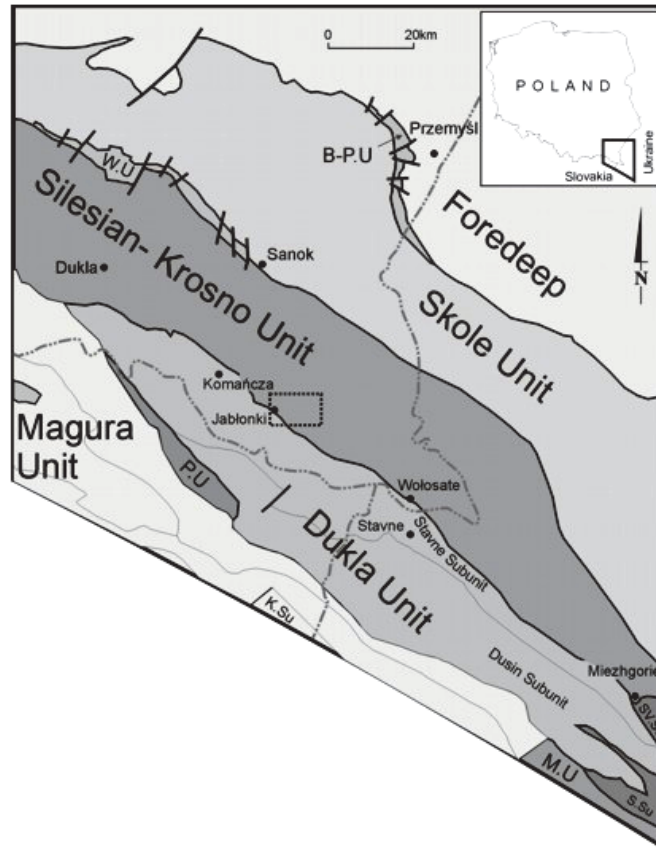


Fig. 1. Tectonic sketch of the border area of Poland, Slovakia and Ukraine, after [17].

Redactions: B-P.U – Boryslaw-Pokuttia unit; W.U – Weglowka unit; P.U – Papin unit; M.U – Maramuresh unit; Sv.Su – Svidovec subunit; S.Su – Sukhov subunit; K.Su – Krynica subunit. Point's rectangle – sampling area in melange zone.

A distinct change in the sedimentation occurs at the Eocene–Oligocene boundary. The complex of the Mszanka sandstones appears which has been recently ascribed to the lower part of the menilite beds. The complex of the menilite beds, mainly in its lower part, forms a Lower Oligocene part of the profile. Black schists of hornstones and marls are interbedded with lenses of sandstones of different thickness (known as the Cergowa sandstones). The profile of the Dukla unit has been completed by the Krosno beds complex with thick schists at the top.

The so called fore-Dukla folds may be traditionally distinguished at the Dukla unit foreland, being generally ascribed to the Silesian unit. Their profile has been in general not different from that of the Silesian unit. Still a total tectonic evenement in his region is so called the Bystre slice. A whole profile of the Silesian unit starting from the Lower Cretaceous deposits to the Oligocene Krosno beds is present there. The Lower Cretaceous Cieszyn beds developed as the complex of dark schists, sandstones and marls or even limestones occur in the lowermost part of the profile. The Grodziskie beds, not thick, occur higher, being overlain by a twice folded, rather thick complex of the Lgota

beds, completed by the Upper Cretaceous variegated schists. The complex of the Itebna sandstones and schists of the Upper Cretaceous/ Palaeocene age and the Ciężkowice sandstones surrounded by the Eocene variegated schists lie higher in the profile. Similarity to the Dukla unit, the Upper Eocene is here represented by the Hieroglyphic beds. The profile has been completed by the menilite-Krosno series similarly to other Carpathian tectonic units.

The so called Central Carpathian Depression, which contacts with the fore-Dukla folds, is filled with the Krosno beds, strongly deformed and with a complicated geometry of the thrusts.

Field observations – mainly mapping of the *mélange* zones – were held in a distinct area of the south-eastern part of the Polish Carpathians and in the adjacent zone of the Ukrainian Carpathians. Sets of profiles perpendicular to the run of main tectonic units were studied, resulting in distinguishing the *mélange* zones, previously not shown on the maps [4, 9, 39].

The main zone under observation, followed at the distinct Bieszczady Mts. and Beskid Niski area, stretches from the territory of Ukraine through the Bieszczady region, being seen in numerous outcrops. The *mélange* outcrops are seen at the Polish side of the Bieszczady Mts. west of Ustrzyki Górne (in the Bystry stream), further westwards the *mélange* zone may be seen in the left tribute of the Prowcza stream. Still westwards, the *mélange* outcrops occur in the upper run of the Wetlinka stream (under the Wyżnia pass) as well as in Smerek.

The most beautiful *mélange* outcrops in the Bieszczady area are present in the Jablonki region (the Jablonki stream). This zone runs through Kołonicze, is well seen in the Rabski stream (near the “Gołoborze” Natural Reserve), turning westwards through Huczvice. It is also outcropped in Kalnica. A potential prolongation of this *mélange* zone towards the west demands further observations.

The *mélange* zone in the Jablonki and Kolonice regions is built here by deposits which represent a lithotype of the menilite and Krosno beds – this zone was earlier treated as a so called transition zone [38]. Apart from the fragments typical for the menilite and Krosno beds, other rock types may be observed in the deformed complexes, e. g. limestones or siderites not seen in typical profiles. The *mélange* seen in the outcrop displays features of the tectonic *mélange* described above.

A strong mineralization of this zone is, however, restricted only to the Bieszczady area and is manifested in the accumulation of the minerals in a genetic sequence. Extremely distinct are accumulations in the caverns and fissures gradually filled. The observations in the Beskid Niski Mts. and in the northern part of the Polish Carpathians point to band-like zones of the tectonic *mélange*, which, however, do not display mineralization as strong as in the Bieszczady region.

43 samples of rocks, minerals and the organic matter were taken for mineralogical, petrological and geochemical studies from the tectonic *mélange* zones described above. Sampling sites are shown in figure (see fig. 1), while detailed methods applied, mostly basing on the equipment of the Polish Geological Institute, Warsaw, are described below. Analytical procedures comprised several stages, as: sampling and preparation; microscopic evaluation of the material from the point of view of inclusions, organic matter and minerals; detailed microscopic determinations; auxiliary studies. The microscopic analyses in detail corresponded to the similar steps as described by [15]. Fluid inclusion analy-

sis was performed on double-sided polished thin sections prepared based on the cold techniques [18].

General description and standard petrological studies comprised observations in the polarization microscope (Nikon-Optiphot). The character of the rocks in the mélange zones was determined in samples further analysed. The cathodoluminescence (CL) studies were the auxiliary element. Being somehow limited in the fluid inclusion studies (Jarmolowicz-Szulc, 1998). The CL studies were conducted on twin sections to those studied microthermometrically. They were mostly performed in carbonates timing at their sequence. The CD analysis was conducted by use of CCL 8200 mk 3 (Cambridge Image Technology Ltd.) mounted on Nikon-Optiphot microscope. The analysis was photographically registered. Fluorescence studies were conducted under the quartz lamp in uV Nikon device with filters (uV – 365 nm, blue – 480 nm). Samples were analysed in two directions aiming at rock, mineral and fluid inclusion diagnosis. The observations of luminescence were conducted consequently in one magnitude (eye-piece 15<sup>×</sup> Nikon, objective 10<sup>×</sup> Nikon), which ensures an evaluation of fluorescence colours always in the same conditions.

Microthermometric studies of fluid inclusions were conducted using Fluid Inc. System mounted on the Leitz Orthoplan microscope. The system was calibrated against international standards [35]. Fluid inclusions were analyzed in the freezing and heating moods in the range of temperatures from –196 to +250 °C. The homogenization of HCFI was conducted prior to the homogenization of the aqueous inclusions. Homogenization temperatures were measured prior to freezing to avoid a potential change in the inclusion volume.

Characteristic values were measured in the heating after freezing in that *freezing point depression* [1]. The analytical results were calculated using computer programs (Flincor – [3]) for AQFI and methane systems. That resulted in fluid density, character and composition. A method of crossing isochors was used to estimate trapping temperature and pressure of HCFI and AQFI pairs.

The analysis of content of saturated hydrocarbons was performed aiming at composition of the organic matter in the mélange zones and at comparison of those described in the other formations. These determinations were done both in the Institute of Oil and Gas in Cracow and in PGI in Warsaw. Determinations were performed by use of GS/MSD Hewlett Packard. Contents of n-alkanes and isoprenoids were determined using the external detector and the biomarker qualitative analysis performed. Bitumens from the lenses in the mélange zones and samples of rocks and minerals were analysed (Rock-Eval) according to the well-known procedures (e. g. [6, 7, 32 et al.]).

The pirolitic analysis was conducted by use of Vinci Technologies Rock-Eval 6. XRD determinations were performed by powder method with a use Philipps X' Pert PW 3020 in respect to the international standards (JCPDS). The reflectance of the organic matter was determined both in the double-sided polished sections (approximate data) and in the polished slabs. SEM analyses were conducted in 10 samples from the tectonic mélange. Studies were performed by use of two electron scanning microscopes: JSM-35, JEOL and 1430, LEO, combined with EDS ISIS. Uncovered carbon-plated thin sections with were analysed.

As it has been already described by K. Jarmolowicz-Szulc and L. Jankowski (2004), sampling took place in the mélange zone in the vicinity of Jablonki-Rabe and Cisna in the Bieszczady Mts. (see fig. 1). In black, schistous rocks of the mélange, larger and

smaller blocks (“block-in-matrix”), clasts and lenses occur. Fragments of clasts are varied in size, from some tens of centimetres to some meters. They are fractured. The fractures are filled with mineralization which is the object of the petrological, mineralogical and geochemical studies. Grey or beige sandstones and limestones cut with veins or nests with mineralization have the following characteristics: micosparite limestones with admixture of quartz and black schliers; quartz arenites with a carbonate cement, often co-occurring with nest aggregates of the coarse crystalline calcite spar; quartz arenites with carbonate-clayey or with quartz-carbonate-clayey cements.

Clay-carbonate rocks with veinlets and nests of quartz-carbonate-bitumen filling and iron-clayish interlayers are also observed. The structure of these rocks is generally random, sometimes directional, being shown by undulated mica flakes.

Hydrocarbon and the aqueous inclusions were distinguished due to fluorescence and microthermometry studies. The methane inclusions either do not show fluorescence or a dull-blue one. The fluid inclusions mostly show white-blue to yellow luminescence in the uV-light.

The fillings of the veins in the sandstone rocks in the Jabłonki and Kalnica regions show a yellow-red luminescence colours in CL for carbonates and violet-blue for quartz. The organic matter showed no fluorescence. The minerals fill smaller and larger veins and aggregates and occur either together or separately there.

Due to the detailed SEM analysis, the chemical composition of minerals was determined in eight samples and a diagnosis of the minerals done (table 1; fig. 2). The minerals analyzed in SEM correspond to calcite, Mn-calcite, dolomite, Mn-dolomite, ankerite and pyrite.

Table 1

Analysis of composition of vein filling in the mélange rocks  
in the Jabłonki–Kalnica region

Element	Samples							
	14/05		F-4		09/05			
	1	2	1	2	1	2	3	4
C	12,60	12,08	12,05	12,07	12,56	12,53	12,44	12,03
Mg	8,23	0,26	0,60	0,57	9,19	8,28	6,63	0,00
Ca	21,78	38,75	37,65	37,62	22,93	22,92	21,58	38,40
Mn	0,69	1,01	0,81	0,82	–	0,27	0,14	0,18
Fe	6,15	0,46	0,26	0,86	4,42	5,14	9,24	1,26
O	50,52	48,33	47,86	48,17	50,57	50,28	50,11	47,96
Σ	99,97	100,90	99,23	100,13	99,67	99,42	100,13	99,82
Mineral	Dolomite	Calcite	Calcite	Calcite	Dolomite	Dolomite with Mn	Dolomite	Calcite

XRD studies of black organic aggregates in the form of lenses point to the presence of the following minerals: quartz, dolomite, calcite, clay minerals, gypsum with anhydrite admixture, traces of pyrite and siderite. Feldspars are also present, what is seen in X-ray diagrams.

The pyrolytic Rock-Eval analysis of twelve samples from the Jabłonki region showed a variable TOC in the interval from 0,77 to 35,83 % TOC, with a low HI (from 30 to 116 mg HC/g TOC). Such a wide interval results from the presence of one extreme sample (B7, 35,83 % TOC), while the values of other samples generally lie between 0,77 and 4,44 %. Samples display high degree of thermal evolution, which corresponds to the end

of generation processes (the end of the oil window). In the composition of the extractable organic matter, the saturated hydrocarbons constitute a majority of 61,3 % that points to adsorption of the generated or migrating oil.

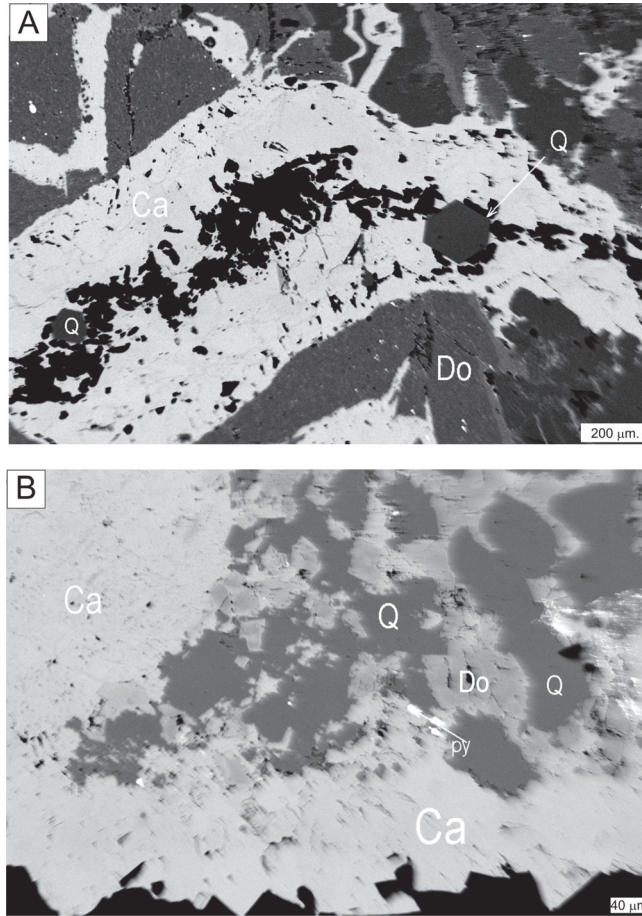


Fig. 2. BEI image from electron microscope:

*A* – filling with minerals: calcite, dolomite, quartz and bitumens, sample B3; *B* – calcite I growing up on the wall of fissure in the sandstone, sample Ja 09/05.

Due to the fluid inclusion studies conducted under the microscope in thin sections (calcite) and in glued wafers or loose crystals (quartz – the Marmarosh “diamonds”), inclusions can be characterized in minerals.

Small, primary aqueous inclusions and secondary hydrocarbon inclusions (in fissures cutting cleavage planes) were observed in calcite. These last ones display fluorescence in blue-white colours, which proves a presence of higher hydrocarbons – petroleum.

Brine and different hydrocarbon inclusions occur in the quartz. They are single, bi- or multiphase. Some of them do not fluoresce, some other – dull blue or white-blue colour. Microthermometric results were partly reported [15, 24]. Based on the types of the filling, the following assemblages of inclusions may be distinguished: primary liquid-gas inclusions filled with brine of low salinity and homogenization temperatures from 150 to

184 °C; primary single phase inclusions filled with methane and homogenization temperatures from –75 to –90 °C; decrepitation of these inclusions occurs between 85 and 95 °C; primary liquid-gas and gas-liquid hydrocarbon inclusions showing white-blue fluorescence; secondary liquid-gas brine inclusions.

The tectonic mélange recently distinguished and described by L. Jankowski occur in different localities of the eastern part of the Polish Western Carpathians and in the adjacent territory of Ukraine and Slovakia. Only some of them, however, are mineralized in the rocks of the character “block-in-matrix”. Among numerous mélange occurrences within the Polish boundaries, the mineralization occurs in the Cisna–Kalnica and Jabłonki–Rabe regions. This is the carbonate-quartz mineralization and distinct accumulations of bitumens. These last ones, but one lens in the Jabłonki region of a very high TOC, display a similar character to the accumulations in the Silesian and Dukla units (compare: [6, 7, 22]).

The characteristic feature of the mélange is an occurrence of the carbonate-quartz mineralization with bitumens filling fissures and cavers and nests and in form of veinlets, brushes and nests. The mutual relations of these components are seen both in the macroscopic and microscopic scale together with a differentiated chemical composition.

In the calcite mass there occur occasionally dolomite crystals; calcite is often overgrown with the quartz. Dolomite and calcite display two types – “pure” and with a manganese admixture (e. g. in the Jabłonki region the manganese dolomite contains from 0,13 to 0,27 % Mn). As it is seen from the SEM and CL images, the calcite filling in the dolomite (calcite I) is earlier than the bitumens and authigenic quartz (the Marmarosh “diamond” type 0). Small veinlets prove the occurrence of the earlier crystalline quartz prior to the white calcite.

The organic matter (bitumens) described in bibliography as e. g. asphaltite (Karwowski, Dorda, 1982), or anthraxolite (Dudok et al., 2005) fills in general the central part of the fissures. The quartz crystallizes as fine crystals on the fissure walls and distinct authigenic, transparent crystals within the bitumens and/or carbonates.

The character of the organic matter oscillates from primary, weak mature liptinite material to vitrinite-type substance. The values of the vitrinite reflectance index lie in the interval from 0,96 to 1,54 %, while the averages oscillate from 1,0 to 1,43 %. Temperatures calculated based on these values change from 122 °C to 191 °C, the averages are in the interval between 146 and 182 °C (table 2).

Similar values were obtained from homogenization of brine inclusions in quartz. That is the minimum estimation of temperatures, in which the rocks remained.

Table 2

Vitrinite reflectance index and temperature\*

Sample	$R_o$ -interval, %	Average $R_o$ , %	$T$ -interval, °C	Average temperature, °C
14/2005	0,96–1,19	1,07	142–164	153
B 2		1,00	122–158	146
B 3	1,20–1,54	1,42	165–191	182
Jabłonki 1	1,02–1,06	1,03	148–152	149
Cisna 1	0,94–1,14	1,07	139–159	153
Cisna 2	0,94–1,14	1,07	139–159	153

\* Temperature calculated from the vitrinite reflectance index after the formula [19]:  $T = (\ln R_o + 1,4) : 0,0096$ .



Due to the biomarker analysis for saturated and aromatic fractions, values of ratios as pristane/phytane from 1,92 to 2,55, pristane/C17 from 0,30 to 2,02 and phytane/C18 from 0,15 to 0,73 have been determined (table 3). The source material was deposited in oxygen conditions with bacterial activity.

Table 3

## Exemplary results of analysis of biomarkers

Sample	Pristane/phytane	Pristane/C17	Phytane/C18
B7, 25/05/1 I	1,92	1,48	0,73
Me 7, 25/05/5 I	1,76	0,38	0,22
Me11, 25/05/7 I	2,10	0,30	0,15
Me 13, 25/05/9 I	1,53	0,38	0,24
Ja 2, 24/04/05	2,55	2,02	0,70

Among pentacyclic terpanes a peak from oleanane may be distinguished, which suggests a continental component of Tertiary or younger age within the organic matter trapped in the rock (I. Matyasik, oral information). The dimethylphenantrene and methylphenantrene compounds with isomers of the more stable configuration (2-MP i 3-MP) predominate in the distribution of the aromatic fraction. Values of vitrinite reflectance calculated based on the MPI-1 factor prove a high thermal alteration adequate to  $R_o = 1,24$  %. That corresponds to the temperature of about 168 °C (see table 2). Following the discussion from above, the concordance of the independent analytical results of the organic matter dispersed in the rocks and of aromatic fraction of bitumens in the mélange zone may be concluded.

On the base of earlier mineralogical studies and fluid inclusion analysis in the tectonic mélange zones, it may be concluded that the mélange in the Jabłonki region is the hydrocarbon migration path. Hydrocarbons were generated from the terrigenous organic matter which corresponds to the menilite schists, studied many times in the Silesian unit [24].

Hydrocarbons are trapped as inclusions mostly in the Marmarosh “diamonds”, while brine or gas-liquid inclusions are more frequent in calcite. Primary inclusions with hydrocarbons may be divided into three phase groups: solid, liquid and gas. *Homogenic* inclusions are those solid ones which contain different bitumens; liquid ones, which occur mostly in the outer growth parts of crystals and contain either one or two immiscible fluids; gas inclusions contain methane with admixture of higher hydrocarbons. *Heterogenic* inclusions display the following compositions – gas + liquid hydrocarbon + brine; gas + liquid hydrocarbon + brine + solid bitumens; liquid hydrocarbons + solid bitumens. Solid bitumens are occasionally observed in the quartz in such amounts that it causes macroscopically almost black colour of the mineral. What is interesting, such black crystals are usually long prismatic. Similar crystals were observed by Karwowski in the Mszana Dolna region in Poland (personal communication), in very rare cases, however. Similar quartz has been recently noticed also in the Pavlovka vicinity in Ukraine.

The chemical composition of inclusions in calcite is similar despite the age of the rocks, namely chlorite-sulphide-carbonate (compare: [5]).

Introductory estimation of pressures based on the fluid inclusion studies are about 1,5 kbar, being analogical to those referred by E. Jurewicz, A. Kozłowski [26] for the Tatra region. The hitherto obtained temperatures are, however, lower.

Consequently, it is possible to draw such conclusions on the basis of the expounded materials:

- strong mineralization of these zones is mostly the Bieszczady region phenomenon;

- following minerals have been stated in the zones: calcite, Mn-calcite, dolomite, Mn-dolomite, fine crystalline quartz, coarse crystalline quartz, ankerite and pyrite;
- the organic matter occurs in the association with minerals as vein and cavern filling as well as material dispersed in the rocks;
- fine crystalline quartz is genetically earlier or contemporary to calcite; the authigenic coarse crystalline quartz occurs after calcite and is later or contemporary to the organic matter;
- the following mineral sequence may be presented in the mélange zone in the Jabłonki–Cisna–Kalnica region: calcite I/dolomite I; quartz I; calcite II/dolomite II; organic matter; quartz (Marmarosh “diamonds”).

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## НОВІ ДАНІ З МІНЕРАЛОГІЇ ТА ГЕОХІМІЇ ПОРІД КАРПАТСЬКОГО РЕГІОНУ

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Для мінералогічних, петрологічних і геохімічних досліджень відібрано зрізці гірських порід, мінералів та органічної речовини з тектонічної меланжевої зони Яблонки–Рабе та Цісна (Бескиди), розташованої в південно-східній частині Польських Карпат. Виконано підготовку зрізців, мікроскопічне оцінювання матеріалу щодо наявності включень, органічної речовини й мінералів, детальні мікроскопічні та допоміжні дослідження. Флюїдні включення вивчали у відполірованих тонких пластинках. Мінерали, проаналізовані на SEM, відповідають кальциту, Mn-кальциту, доломіту, Mn-доломіту, анкериту і піриту. Дифрактометричне вивчення чорних органічних агрегатів у формі лінз засвідчило наявність таких мінералів, як кварц, доломіт, кальцит, глинисті мінерали, гіпс з домішкою ангідриту, сліди піриту й сидериту. Виявлено також польові шпати.

Піролітичний Rock-Eval аналіз зрізців з регіону Яблонки засвідчив змінне значення ТОС в інтервалі від 0,77 до 35,83 % ТОС, звичайно між 0,77 та 4,44 %, за низького значення НІ (від 30 до 116 мг НС/г ТОС). Зрізцям притаманні ознаки термальної еволюції високого ступеня, який відповідає завершенню генераційного процесу. У складі екстрагованої органічної речовини насичені вуглеводні становлять загалом близько 61,3 %, що є доказом адсорбції нафти, генерованої або такої, що мігрує. Включення в мінералах схарактеризовано завдяки дослідженню флюїдних включень під мікроскопом у шліфах (кальцит) та окремих кристалах (кварц – мармароські “діаманти”).

*Ключові слова:* кварц, мармароські “діаманти”, кальцит, органічна речовина, включення, тектонічний меланж, Карпати.

## НОВЫЕ ДАННЫЕ О МИНЕРАЛОГИИ И ГЕОХИМИИ ПОРОД КАРПАТСКОГО РЕГИОНА

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Для минералогических, петрологических и геохимических исследований отобраны образцы горных пород, минералов и органического вещества из тектонической меланжевой зоны Яблонки–Рабе и Цисна (Бескиды), расположенной в юго-восточной части Польских Карпат. Проведены подготовка образцов, микроскопическая оценка материала на наличие включений, органического вещества и мине-

ралов, детальные микроскопические и вспомогательные исследования. Флюидные включения изучали в тонких полированных пластинках. Минералы, проанализированные на SEM, соответствуют кальциту, Mn-кальциту, доломиту, Mn-доломиту, анкериту и пириту. Дифрактометрическое изучение черных органических агрегатов в форме линз показало наличие таких минералов, как кварц, доломит, кальцит, глинистые минералы, гипс с примесью ангидрита, следы пирита и сидерита. Обнаружены также полевые шпаты.

Пиролитическим Rock-Eval анализом образцов из региона Яблонки выявлено переменное значение ТОС в интервале от 0,77 до 35,83 % ТОС, обычно между 0,77 и 4,44 %, и низкое значение НІ (от 30 до 116 мг НС/г ТОС). В образцах зафиксированы признаки термальной эволюции высокой степени, которая соответствует завершению генерационного процесса. В составе экстрагированного органического вещества насыщенные углеводороды составляют около 61,3 %, что является доказательством адсорбции генерированной или мигрирующей нефти. Включения в минералах охарактеризованы с помощью исследования флюидных включений под микроскопом в шлифах (кальцит) и отдельных кристаллах (кварц – мармарошские “диаманты”).

*Ключевые слова:* кварц, мармарошские “диаманты”, кальцит, органическое вещество, включения, тектонический меланж, Карпаты.

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