

Article



Interpretation of Mineralization in the Western Carpathians (Polish Segment)—A Tectonic Mélange Approach

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Abstract: Quartz, carbonates and other minerals as e.g., realgar are present in veins and caverns in sedimentary rocks in the Western Carpathians. In the Polish segment, they have been characterized from the mineralogical, petrologic, and geochemical points of view, as well as fluid inclusions. Their characters are discussed from perspective of a description of particular types of chaotic complexes—the tectonic mélange zones, distinguished in the Western Carpathian area over the last two decades. The mélange zones are considered to be geochemical systems open to fluid flow, a site for mineral crystallization and/or migration zones of hydrocarbons and mineralized waters. In this context the tectonic mélange in the Jabłonki/Rabe vicinity (SE Poland, the Bieszczady region) in comparison to that of the Mszana Dolna tectonic window area are proposed as the examples. The trapping conditions of fluids (brine and methane) in the minerals in the mélange zones appear to have been 180–205 °C and ~550–570 bars, and 220 °C and 500 bars for calcite and quartz, respectively. The general trend of the increase in temperatures and pressures from west towards east and south-east in the mélange zones points to an increase in the degree of exhumation of different parts of the Carpathians.

Keywords: Carpathians; tectonic mélange; mineralization; quartz; calcite; fluid inclusions; mineral waters

1. Introduction

The tectonic mélange represents one of the types of chaotic complexes—the sediments which display a lithology of "blocks in the matrix". Numerous mélange zones are present in the Western Carpathians in the south of Poland and contain different minerals. They have been gradually discovered in the field by Jankowski in the last 20 years ([1,2], and references therein) and presented on the geological maps of the Carpathians (e.g., [3,4], and references therein). The formation of the mélange zones may be referred to the stages of the tectonic evolution of the Carpathians [5,6]. The tectonic mélange may be deep-rooted and may reach the Carpathian basement related to the pre-Alpian tectonic structures. The main accumulations of the Carpathian hydrocarbons are displayed along the widespread mélange zones in the Carpathians. Recognition of the tectonic mélange zones is, significant for the reconstruction of additional stages of tectonic deformation (strike-slip faults and the orogenic collapse) and for an explanation of mineralization zones, as well as the hydrocarbon migration. Therefore, they should be studied with different methods. Studies of mineralization are one of the important tools. For many years, the relatively rich mineralization present in the Carpathians has been an object of mineralogical and geochemical studies (e.g., [7–10]), with its origin being further related to the mélange zones (e.g., [11-13] and references therein). The present authors believe that there exists a strong correlation between mineral enrichment and the tectonic mélange zones. Mineral occurrences, mostly of quartz and carbonates, are abundant in the tectonic mélange zones or in their aureoles. Different types of fluids that migrate from depth are responsible for the mineralization of rocks and mineral waters [8,11,13–16].



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2. Geological Setting and Mineralogy

The Carpathians, which extend for over 1300 km across Central and Eastern Europe, were formed in the Tertiary by a NE/E-ward migration of an accretionary wedge in front of the Alcapa and Tisza Dacia microplates (e.g., [17,18]). This study focuses on the Polish sector of the Outer Carpathians, a thin-skinned thrust and fold belt, which constitutes the accretionary wedge of the Carpathian orogen. The Carpathian orogen is formed of different nappes (tectonic units), as the Magura, Silesia, Dukla and Skole units (Figure 1), which are largely composed of strata from the Lower Cretaceous to the Lower Miocene. The origin of these nappes (oceanic or continental) is still disputed. It is generally accepted that the main stage of primary contractional deformation and thrusting occurred in this region between the Oligocene and the Middle–Late Miocene, and that its direction progressively shifted from NW to NE (e.g., [19–21]).



Figure 1. Geological Map of the Outer Carpathians in Poland (after [4], modified).

Several tectonic mélange zones are present in different positions in the Carpathian geometry (Figure 1). The tectonic mélange represents one of the important structures that delineates the main tectonic zones and documents numerous deformation stages, which are primarily connected with the out-of-sequence thrust, gradually re-activated and then enlarged in additional stages of the tectonic deformation (Figure 2). The deposits reach a large width in the outcrops. The process of the enlargement results from the consecutive re-activation of the tectonic zones formed at the primary stage of the formation of the Carpathian orogen. The formation and the orientation of the mélange zones is independent of the orientation of main tectonic units. It postdates the formation of these units. The formation of the mélange zones may be referred to the stages of the tectonic evolution of the Carpathians—the process of strike-slip fault formation, or orogenic collapse ([5,6,22]). These processes are confirmed by thermochrononometric studies [23].



Figure 2. Explanation of formation of tectonic mélange zone. (**A**) Primary stage with out-of-sequence thrust; (**B**) Re-activation and formation of flower structure; (**C**) Final stage—tectonic mélange zone (based on [2]).

The main mélange zone under geological and mineralogical research stretches from the territory of Ukraine (in the East, outside Polish borders) through the Bieszczady region, as it is seen in numerous outcrops in Poland (the area of Jabłonki-Rabe-Cisna (JRC)). The area of the Mszana Dolna tectonic window (MD), where the Dukla unit is exposed tectonically within the Magura unit (Figure 1), has been under present investigation, in some earlier studies, too (e.g., [11,16]). In every localization, the recognized mélange zones are saturated with mineralization. The mineralization processes remain in co-relation with the tectonic deformation of the Carpathians. In general, a filling of the mélange zone with mineralization has been occurring at the post-folding stages during successive stages of tectonic deformation of the Carpathians in the extension regime (strike-strip and collapse stages) from Miocene up to recent times.

The character of fluids in vein minerals has been studied by the authors and referred to fluid migration [11–13,24].

3. Materials and Methods

Samples of rocks, minerals and the organic matter were taken for mineralogical, petrologic and geochemical studies from different tectonic mélange zones, in that from two main regions pointed out above. The sampling areas lie in the Polish part of the Western Carpathians and are shown in Figure 1. They are localized in the western part of the mountain chain—near Mszana Dolna (MD) and in the eastern part—near Jabłonki-Cisna-Rabe (JCR) settlements. For the purpose of the present paper a new sampling was carried out in the MD area, new isotopic analyses performed and fluid inclusion studies were conducted in carbonates. The attempt at an isochore graph interpretation of fluid inclusion results in both study areas is also a new methodic achievement.

The microscopic analyses corresponded to those described elsewhere (e.g., [13], and references therein; [25], and references therein). The procedures comprised several technical and analytical stages (sampling and preparation; microscopic evaluation of the material; detailed microscopic research on inclusions, organic matter and minerals; auxiliary studies, such as CL, Raman or XRD analyses, and stable isotope analyses). In detail, 40 thin sections were petrographically analyzed in the Optiphot 2Pol (Nikon, Warsaw, Poland) polarization microscope. Cathodoluminescence analysis (CL) was performed on all the samples using a CCL 8200 mk³ equipment with a cold cathode produced by Cambridge Image Technology Ltd. attached to a Nikon Optiphot microscope. CL observations were used in the analysis of a detrital material and cements, as well as the textural features of the rocks. X-ray analyses were performed using X-ray diffractometer X'Pert PW 3020 by Philips to study the types of minerals (PGI, Warsaw, Poland). Phase analysis was conducted on powder samples (grains to 0.063 mm). Diffractograms were registered at angle interval $5^{\circ} \div 60^{\circ}$ 20 and identified based on ICDD tests. Oxygen and carbon isotopic determinations were conducted in Germany, in GeoZentrum Nordbayern at the Friedrich-Alexander University Erlangen-Nürnberg for 6 samples in the carbonates. Carbonate powders were reacted with 100% phosphoric acid at 70 °C using a Gasbench II connected to a ThermoFisher Delta V Plus mass spectrometer [26]. All values are reported in per mille

relative to Vienna-Pee Dee Belemnite (V-PDB) (Joachimski, 2020, personal communication [26]). Reproducibility and accuracy were monitored by replicate analysis of laboratory standards calibrated by assigning a δ^{13} C of +1.95‰ to NBS19 and -47.3‰ to IAEACO9 and a δ^{18} O of -2.20‰ to NBS19 and -23.2‰ to NBS18. Reproducibility for δ^{13} C and δ^{18} O was ± 0.03 and ± 0.06 (1 std. dev., respectively, op. cit.). Fluid inclusion analyses were performed in 30 two-sided-polished wafers. Fluid inclusions were analyzed using a Nikon Linkam freezing-heating stage. Observations were conducted by applying a polarization microscope to both transmitted and reflected lights (UV). Microthermometric analyses were calibrated against melting temperatures of pure chemicals and phase transitions in synthetic fluid inclusions (Synflinc standards). The uncertainty limits of freezing-heating modes are 0.2 °C below -100 °C, 0.1°C, between -100 °C and +100 °C, and 1 °C above 100 °C until the equipment's temperature threshold. FI petrography was held based on the criteria of [27,28].

Studies on the character of inclusions were conducted using Nikon Eclipse microscope with a fluorescent device. Apart from the so called "inclusion petrography", the inclusions were analyzed in the light of the Mercury lamp in the ultraviolet and blue ranges. The fluorescence of hydrocarbons was induced by ultraviolet reflected light in the plates prepared for fluid inclusion microthermometric studies and observed in the reflected light. Fluid inclusion analyses were performed in carbonates and quartz. Similar analytical steps were carried out. For carbonates, heating conducted was prior to freezing as suggested by [29]. Calculations of microthermometric results (isochores, salinity and other fluid parameters) were conducted using the FLINCOR program [30], which comprises uncomplicated chemical systems. The interpretation of microthermometric results was also performed applying tables by [31]. All calculations were conducted for simplified chemical systems.

Raman analyses performed on new samples were conducted using Thermo Scientific ™DXR equipment at AGH University of Science and Technology, Cracow, Poland with a Nd-YAG laser (wave length of 532 nm). Details of measurements are described by [25]. The laser strength was 1–2 mW for the organic matter, and 5 mW for fluid and stable inclusions.

4. Results

The mélange documented by the authors lies in the Jabłonki—Rabe—Cisna region (the Jabłonki stream)—the JRC area (Figure 1). Further the zone runs through Kołonice, it is well seen in the Rabski stream, turning westwards through Huczwice. It is also outcropped in Kalnica settlement [32]. Sampling proceeded in the distinct mélange zones, as e.g.,: in the vicinity of Jabłonki—Rabe and Cisna (JRC) region in the Bieszczady Mts. [13], and in the west, in the area of the Mszana Dolna tectonic window (MD). Fractured blocks ("block-in-matrix"), clasts and lenses occur in black, schistose rocks in the mélange there. The fractures are filled with mineralization (mostly quartz and carbonates) and bitumen (Figure 3). Other minerals are observed in the field and under the microscope. The rocks were: microsparite limestones with quartz and black aggregates; quartz arenites with a carbonate cement, often with nest aggregates of the coarse crystalline calcite spar; quartz arenites cemented by carbonates and clays, or by quartz-carbonates—clays. The fillings of the veins in the sandstones show yellow–red luminescence for carbonates and violet–blue colors for quartz in CL.



Figure 3. The occurrence of the tectonic mélange in the field and mineralogical samples in MD and JRC areas. (**A**) The outcrop in the Mszana Dolna region; (**B**) Calcite veins sampled; (**C**) Methane inclusions in quartz; (**D**) Image and Raman spectrum of assemblage of quartz (Q), organic matter and pyrite (P); (**E**) Fluid inclusions in calcite; (**F**) The outcrop in the wall of the Jabłonki stream (JRC area); (**G**) Assemblage of sampled calcite (Ca) and quartz (Q); (**H**) One phase gas-filled inclusions in quartz; (**I**) Raman spectra showing presence of methane and nitrogen in inclusions. (a) Ru 8-C, (b) Ra 2-C.

The organic matter displays no luminescence. The minerals and bitumen infill smaller and larger veins and form aggregates. The SEM chemical composition of these veins points mostly to carbonates, such as calcite, Mn-calcite, dolomite, Mn-dolomite, ankerite, and to pyrite. XRD studies of black organic aggregates in lenses show the presence of quartz, dolomite, calcite, clay minerals, gypsum with anhydrite, feldspars, traces of pyrite and siderite, i.e., a whole fan of minerals. The chemical composition of some carbonate samples in JRC is presented in Table 1, following data from [14]. In the Rabe vicinity (in JRC), other minerals as e.g., realgar are also present, the character of which is shown microscopically in Figure 4. The presence of yellow-red mineralization was noticed in the MD area, this was not sampled, however.

Sample	Ba	Cr	Cu	La	Mn	Мо	Ni	Sr	Ti	V	Zr
U1	<5	14	<5	<5	1207	<2	4	589	84	<5	9
PD4	99	16	<5	<5	1163	<2	5	1304	93	<5	11
D9	<5	15	<5	<5	1066	<2	5	694	88	<5	5
PD21	<5	3	<5	<5	704	<2	<3	865	75	<5	6
W13	<5	11	<5	<5	1102	<2	5	916	80	<5	6
PS1	487	9	<5	<5	1078	<2	3	631	143	5	7
PS2	<5	8	<5	6	1007	<2	5	773	115	<5	6

Table 1. XRF analyses of vein calcite (ppm) (from [14]).





Figure 4. The photomicrograph of realgar within the tectonic mélange in the JRC area (Rabe point). A sample due to the courtesy of T. Wieser [33]. (**A**) Polarizing microscope image. The arrow points to a bi-phase inclusion. (**B**) UV image. No characteristic features.

The rocks from the JRC region show a variable values of Total Organic Carbon (TOC—mostly between 0.77 and 4.44%), with a low Hydrogen Index (HI),—from 30 to 116 mg HC/g TOC). The calcite and quartz fillings contain different hydrocarbon (HCFI) and aqueous (AQFI) inclusions (Figure 3; Figure 3A–E for MD; Figure 3F–I for JRC). One phase, methane filled, inclusions occur in central parts of quartz. In MD they are often broken. They either do not show fluorescence, or are dull-blue. Small, two phase primary aqueous inclusions (AQFI)) in calcite do not fluoresce, the secondary hydrocarbon inclusions (HCFI in fissures cutting cleavage planes) display fluorescence in blue–white colors. The following FI assemblages 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 that homogenize at temperatures ranging from -75 to -90 °C (decrepitation between +85 and +95 °C); primary or secondary (Figure 5) liquid–gas and gas-liquid hydrocarbon inclusions showing white–blue fluorescence; secondary liquid-gas brine inclusions. Microthermometric results are reported elsewhere (e.g., [7,13,14,24,25,32]). Table 2 presents some of these data.

Sample ¹	Locality	Mineral/FI Type	Ice Melting Temperature T _m (°C)	Homogenization Temperature T _h (°C) ²	Homogeni Zation Temperature T _h (°C) ³	Homogeni Zation Temperature T _h (°C) ⁴	Salinity NaCl (wt % eq.)
UG-16/08-6	Ustrzyki Górne	Quartz/ AQFI HCFI	-0.1	-95.1	+14.3	+117.3 +125.0 +145.3 +146.0 +132.0	0.166
MD2/08-1	Mszana Dolna	Quartz/ HCFI		82.2 77.8 103 87.5	57.6 60.0 56.6	+8.5 +16.8 +13.2 +16.0	
MD 2A/08	Mszana Dolna	Quartz/ HCFI		-103 -87.5			
Ru 4/09	Jabłonki	Quartz/ HCFI	-0.6		-61.2	+128.7	0.172
Ru 8/07	Jabłonki	Quartz/ AQFI HCFI	-1.3 -2.1	-90.7	-77.4	+183.9 +19.2 +22.1	2.14 3.49
Ka-13	Kalnica	Calcite/ AQFI	-5.6	-77.4		+199.9	8.6
Ra-1/07-1	Rabe	Quartz/ AQFI HCFI	$-1.1 \\ -1.8$	-88.8 -88.8		+175.9	1.80 2.96
Ja 7/03 *	Jabłonki	Quartz/ AQFI HCFI	-1.1	-91.4		+173.0	1.80
Ja-10 *	Jabłonki	Quartz/ AQFI HCFI	-1.3	$-80 \\ -75$	-58.0 -56.7	n.d.	

Table 2 Results of fluid inclusion studies in a	martz from fissures in the	MD and IRC regions
Table 2. Results of fluid inclusion studies in c	juartz from fissures in the	e MD and JKC regions.

	Table 2. Cont.								
Sample ¹	Locality	Mineral/FI Type	Ice Melting Temperature T _m (°C)	Homogenization Temperature T _h (°C) ²	Homogeni Zation Temperature T _h (°C) ³	Homogeni Zation Temperature T _h (°C) ⁴	Salinity NaCl (wt % eq.)		
B-2002 *	Jabłonki	Quartz/ AQFI HCFI	n.d.	-92.0 -90.0		+150.0 +172			
B-8 *	Jabłonki	Quartz/ HCFI		-77.0 -76.6		Decr.+85 +95			
Wo-12/07	Wołosa-te	Quartz/ HCFI		$-88.6 \\ -84.9$					
We 20	Wetlina	Quartz/ HCFI				+79.7 +77.9			

¹ Numbers of selected samples as in [14]. Additional appendices mean crystal numbers. Data with *—quoted from [12]; ² Temperatures of homogenization of inclusions, dull-blue or not fluorescent in UV, one phase in room conditions; ³ Temperatures of homogenization of one phase inclusions, one phase in room conditions; ⁴ Temperatures of homogenization of two phase inclusions, not florescent and/or white-blue fluorescing individuals. n.d.—not determined.



Figure 5. Secondary assemblages of bi-phase fluid inclusions in quartz in the Jabłonki settlement (JRC area). (**A**) Polarizing microscope, one polarizer, transparent light; (**B**) Polarizing microscope, UV, reflected light.

The results of recent and earlier stable isotope determinations (presented as $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB}$, and $\delta^{13}C_{PDB}$ and $\delta^{18}O_{PDB}$ values, respectively) for both regions are shown in Table 3, with recalculation to $\delta^{18}O_{SMOW}$, while the regional distribution of data ($\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$) is presented in Figure 6 against the background of other Carpathian regions in Poland, Ukraine and Slovakia.

Sample ID	Locality	Position **	δ ¹³ C ‰ (PDB)	δ ¹⁸ Ο ‰ (PDB)	δ ¹⁸ O * ‰ (SMOW)
	Area: JRC ***				
Ka 15/07	Kalnica, PL		-0.05	-8.31	+22.29
Cisna 3/06	Cisna, PL		-0.11	-7.51	+23.12
Cisna 10/07	Cisna, PL	49°13.383″ 22°21.217″	-0.19	-6.67	+23.98
Kalnica 13	Kalnica, PL		-1.02	-8.42	+22.18
Ru 9/07	Jabłonki, PL		-2.89	-9.73	+20.83
Sample ID	Locality	Position **	δ ¹³ C ‰ (VPDB) ±0.06	δ ¹⁸ O ‰ (VPDB) ±0.03	δ ¹⁸ O * ‰ (SMOW)
	Area: MD				
Szcz4/2020	Szczawa		-0.07	-7.99	+22.62
MD 22/08	Mszana Dolna region		-0.90	-8.97	+21.61
MD 2/08	Mszana Dolna region		-4.53	-9.44	+21.13
MD 201/2020	Mszana Dolna	49°35.9699′ N 20°03.87549′ E	-5.38	-10.85	+19.68
MD 203A/2020	Mszana Dolna	49°40.4229′ N 20°07.2976′ E	-6.05	-11.41	+19.06

Table 3. Stable isotope results for vein calcite in JRC and MD.

* Re-calculations according to the O' Neil formula: δ^{18} O (SMOW) = 1.03086 δ^{18} O (PDB) + 30.86 [34]; ** Exact geographic localization not available in some places; *** JRC—Sampled between 2007–2010.



As shown in the table, δ^{13} C values change from -0.05 to -2.89% _{PDB} and -0.5 to -6.05% _{PDB}, while δ^{18} O vary from -6.67 to -9.73% _{PDB} in the JRC region and from -7.46 to -11.41% (VPDB) in the MD region, respectively.

Figure 6. Stable isotope results in the Mszana Dolna area and the Jabłonki-Rabe-Cisna region on the background of data for other parts of the Carpathians (the background after [10]).

5. Discussion

The tectonic mélange zones recently distinguished and described by Jankowski [1,2] occur in different localities of the Western Carpathians. The JRC area covers the most significant mélange zone, while the MD area corresponds to the tectonic window outcropping an analogic geological unit. The mélange zones are mostly mineralized in the rocks of the "block-in-matrix" character (Figure 3A). Among the numerous mélange zones the carbonate—quartz mineralization and distinct accumulations of bitumen are predominant [13]. The characteristic feature of the discussed mélange zone (JRC) (Figure 3B) is the occurrence of the carbonate-quartz mineralization with bitumen filling fissures, caverns, and nests, and as veinlets, brushes and accumulations. The veins are filled with quartz, carbonates and bitumen in different spatial relationships. The spatial relations of these components are seen at macroscopic and microscopic scales together with a differentiated chemical composition. Quartz often fills the center part of the vein, being overgrown with bitumen (Figure 3C) and carbonates. In the calcite mass there occur occasionally dolomite crystals. Carbonates display two types—"pure" and with a manganese admixture (e.g., in the JRC region, the manganese dolomite contains from ~ 0.1 to $\sim 0.3\%$ Mn; Table 1). The calcite that fills the dolomite (calcite I) is earlier than the bitumen accumulations and the authigenic quartz (the Marmarosh diamond type). Small veinlets prove the occurrence of the earlier crystalline quartz prior to the white calcite. The organic matter (bitumen) described as e.g., asphaltite (MD, [16]), or anthraxolite (JRC, [35]) often fills the central part of the fissures (JRC), or forms impregnations (MD). Quartz and bitumen aggregates were seen in the field, and their presence is also proved at the microscale by Raman spectra and results of microscopic analyses (Figure 3D).

According to [13] in JRC and its neighbourhood, the mélange zone represents the area where the thermal kerogen maturity points to the early "gas window". In the composition of the extractable organic matter, the saturated hydrocarbons constitute a majority (~61%), which points to the adsorption of the generated or migrating oil. The quartz crystallizes as fine crystals on the fissure walls and forms distinct authigenic, transparent crystals within the bitumen 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% (comparewith [14]). The calculated temperatures change from 122 to 191 °C; the averages are between 146 and 182 °C. This is in a real coincidence with the analysis of 33 Raman spectra of the organic matter [25], which point to a temperature of thermal alterations in the interval between 159 °C and 196 °C (the Kouketsu et al. method [36]). Similar values were obtained from the homogenization of brine inclusions in the quartz [14]. This is the minimum estimation of temperatures at which the rocks remained in the geological history of the area. These values correspond to the data shown in the bibliography (e.g., [11,14]).

Recent stable isotope data of the carbonate veins (calcite) in MD and earlier results by [14] for JRC point to a diversity of data (Table 2). Their spatial distribution suggests an increase in oxygen analytical results from the west (MD) to the east (JRC), and at least two types of calcite both in MD and JRC confirming the characteristics presented above (Figure 5). These results are compared with the data by [13,14].

Due to the biomarker analysis for saturated and aromatic fractions, pristane/phytane ratios from 1.92 to 2.55, pristane/C17 ratios from 0.30 to 2.02 and phytane/C18 ratios from 0.15 to 0.73 have been determined [13,14]. The source material was deposited in oxygen conditions with bacterial activity. 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 (Matyasik, personal communication [37]). The dimethylophenantrene and methylophenantrene compounds with isomers of the more stable configuration (2-MP and 3-MP) predominate in the distribution of the aromatic fraction. The values of vitrinite reflectance, calculated based on the MPI-1 factor, evidence a high thermal alteration adequate to Ro = 1.24%. This corresponds at minimum to a temperature of ~168 °C. Following the discussion from above, the concordance of the independent analytical results of the organic matter dispersed in the rocks and the aromatic fraction of bitumen in the mélange zone may be considered (compare: [14]). It can be concluded that the mélanges in the JRC and MD regions are the evident hydrocarbon migration paths [14,16], which is important from the perspective of hydrocarbon deposits. Hydrocarbons were generated from the terrigeneous organic matter which may correspond to the menilite schists, or to another source.

Hydrocarbons as inclusions are mostly trapped in the "Marmarosh diamonds" (at the late stage of vein/fissure filling), while brine or gas-liquid inclusions are more frequent in calcite. The fluorescent HCFI (Figure 5) prove a presence of higher hydrocarbonspetroleum fluids trapped in minerals, while not fluorescent gas inclusions contain methane with admixture of other components (Figure 3H,I). The solid bitumen in the quartz is occasionally abundant, that results in macroscopically black color of the mineral. It is interesting, that such black crystals are usually long and prismatic. Such crystals were observed both in JRC and in the MD regions. A similar quartz type was also noticed in the Pavlovka vicinity in Ukraine; however, no detailed analysis was conducted [10].

Detailed studies on bitumen-enriched quartz varieties, and other minerals found in the Carpathians (as e.g., realgar, orpiment) may be a future analytical research direction.

Fluids in quartz in AQFI are brines of low composition [13]. The chemical composition of brines in inclusions in calcite is chlorite-sulfide-carbonate. In cases of brine co-occurrence with methane, conditions of co-trapping of these fluids estimated from crossing isochores appear to be in carbonate of ~180–205 °C and ~550–570 bars (MD201 sample, MD: AQFI $T_h = 148.5-173.7$ °C, $T_m = -1.9$ °C, HCFI, $T_h = -83.0$ °C; Figure 7a) and in quartz of 220 °C and 500 bars (Ra-5 sample, JRC: AQFI $T_h = 180.1$ °C, $T_m = -6.6$ °C; HCFI, $T_h = -82.6$ °C; Figure 7b), assuming that the brine and the methane were trapped simultaneously. For the isochore calculations, equations for not complex chemical systems were used (NaCl–H₂O and CH₄ systems, FLINCOR program [30]). Using this program, isochores for certain pairs of inclusions (AQFI and HCFI) were calculated and adequate lines drawn in the P-T graph. The coordinates of the point at which the isochores cut, represent the trapping conditions.





Figure 7. P-T trapping conditions for brine and methane in inclusions: (**a**) in carbonate (calcite) in MD, (**b**) in quartz in JRC. Isochores were calculated using FLINCOR program [30].

In the MD area, if $T_h = 148.5$ °C for calcite is used to the oxygen isotope diagram (Figure 8) in the $\delta^{18}O_{W VPDB}^{\infty}$ range between -11.41 and -7.46 (see: Table 2), the isotopic composition of the formation water will correspond to $\delta^{18}O$ between 5.5 and 9% _{SMOW}. The isotopic composition of the water for JRC is slightly shifted towards higher positive values ($\delta^{18}O$ of about 7–9% _{SMOW}). Generally, the isotopic composition of the formation water for JRC.



Calcite

Figure 8. Temperature and δ^{18} O relationship for calcite in both regions. Lines were calculated using formula in [38]. MD—range of isotopic values for the MD area; JRC—range of isotopic values for the JRC area.

The hitherto related, published data on mineralization in the Western Carpathians mostly pertain to quartz (a special type called "the Marmarosh diamonds"—[10,13,14,34,35], less frequently to calcite. This quartz mostly contains brine and hydrocarbon inclusions. In the MD region, the previously cited authors [34,35] estimated fluid pressures of about 0.99 MPa and diversified salinities from 1.5 to 11.5 weight % NaCl eq. The earlier estimations point to an interval between 0.49 and 1.3 kbar in the Beskidy Zachodnie area, i.e., the Mszana Dolna region, and to an interval between 0.56 and 2.2 kbar in the Bieszczady Mts., i.e., the Jabłonki-Rabe-Cisna area and further eastwards and south-eastwards. The increase in pressures from the west to the east (toward Ukraine) and the south-east (toward Slovakia) may derived from comparisons of present and bibliographic results in the tectonic mélange context. That is summarized in Table 4 with the generalized results from Ukraine and Slovakia.

Table 4. Variation in temperature, pressure and brine salinity in the area of the Polish part of the Carpathians and outside Polish frontiers.

Characteristics	Beskidy Zachodnie *	Bieszczady *	Eastern and South-Eastern Directions	References
Temperature (°C)	$ \begin{array}{c} 75137 \\ \rightarrow \end{array} $	$\begin{array}{c} 116196 \\ \rightarrow \end{array}$	110–230	[7,10,25,39,40]
Pressure (kbar)	0.49–1.3 Mszana Dln about 0.99 MPa \rightarrow	$\begin{array}{c} 0.56-2.2\\ \text{Rabe-Wołosate}\\ 0.8-1.5\\ \rightarrow\end{array}$	0.5–2.7 Stavne-Volovec (Ukraine) 1.4–2.7 Dara (Slovakia) 1.65–2.06	[41]
Brine salinity (weight % NaCl eq.)	1.5–11.5	4–14 3–4		

* Arrows (\rightarrow) suggest a general trend of an increase in values from the west towards east and south-east.

The observed trend of increasing temperature-pressure values of minerals from the west to the east and south-east may be a result of the tectonic relations of the areas. This suggests differences in the exhumation of the particular regions (the mélange zones) from the west eastwards and south-eastwards. The deep-rooted mélange zone in the east (i.e., the JRC region) could have been deeper than that in the west (i.e., the MD region). Additionally, the presence of minerals such as realgar or orpiment may suggest that the mélange's foundation is on the boundaries of huge blocks in the Carpathian basement.

The thermal and mineralized waters in the Outer Carpathians occur both in the flysch formation and in the underlying rocks. The complicated geological structure is the cause that the waters are recognized in privileged zones, related mostly to the tectonic zones. They may also be concerned as fluids expelled tectonically (compare with [15]). The present paper's authors are of the opinion that the origin of these waters should be referred to the mélange. In the vicinity of the JRC mélange zone described above, the mineralized waters occur in the Rabe and Polańczyk settlements. The waters there are highly mineralized and display the following chemical composition: 0.2–0.3% HCO₃–Cl–Ca, CO₂ (Rabe) and 0.24 HCO₃-Na (Polańczyk IG-1) and 0.89% Cl-HCO₃-Na (Polańczyk IG-2), showing weak or no reproducing ability. It seems that the flysch is a low prospective collector for the thermal waters [42,43]. The zone of conditions prospective for mineral waters appears to be present in the Rabka-Zdrój and Poreba Wielka, that is exactly in the area of the MD tectonic window. The water parameters there are: up to 16.1 m^3/h water with mineralization of 24–28 g/dm³ and of temperature of 28–42 °C at the outlet (the Rabka IG-2 and Poreba IG-1 wells). If we compare the composition of brines in FI in carbonates in the MD area (chlorate-sulfide-carbonate composition) with the chemical character of mineral waters in the neighborhood, it seems that they really may be related. However, the relationship between mineralization and mineral waters in the tectonic zones demands detailed analyses, and this will be a further research direction.

6. Conclusions

The following conclusions may be drawn from the combined geological and mineralogical research:

- The tectonic mélange zones occur in different localities of the Western Carpathians;
- The mineralization in the mélange zones occurs in veins and accumulations in the rocks of the "block-in-matrix" character;
- The veins are mostly filled with quartz, carbonates and bitumen in different spatial relationship with the presence of other minerals (e.g., realgar, orpiment, pyrite);
- The deep rooting of the mélange zones enables fluid migration from the relatively high depth of the Carpathians, even from their basement;
- The mélange zones represent open geochemical systems which enable both hydrocarbon (in that—also oil seepages) and mineral water migration;
- The mélange zones represent one of the most significant elements of the Carpathian hydrocarbon system;
- Tectonically expelled fluids are responsible both for the mineralization of the rocks and for mineral waters;
- The trapping conditions of fluids (brine and methane) in the minerals in the present studied mélange zones appear to have been of 180–205 °C and ~550–570 bars (in MD) and 220 °C and 500 bars (in JRC) for calcite and quartz, respectively;
- A general trend of increasing temperatures and pressures from W to E and SE may be observed which suggests different degrees of exhumation of the mélange zones;
- The deep-rooted mélange zone in the east (e.g., the JRC region) appears to have been deeper than that in the west (e.g., the MD region);
- The repeating processes of mineralization are connected with the re-opening of the adequate systems as a result of the orogenic collapse events.

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