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Genetic relationship of minerals to fluid circulation in the Polish Carpathians – the Bystre Slice case study

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Fieldwork conducted in the area of the Bystre Slice of the Polish Carpathians has allowed the recognition and mapping of mineral assemblages with respect to a mélange zone. Ore mineralization in the Cretaceous and Paleogene zones of the Bystre Slice, analyzed geochemically, petrographically and mineralogically, includes epigenetic minerals such as realgar, orpiment and cinnabar, here characterized and their parageneses described. Fluid inclusions are distinguished in newly discovered realgar crystals, and microthermometric results allow a mineralogical sequence in the study area to be proposed. The new mineral goyazite, previously not described in the Carpathians, occurs as solid inclusions in the realgar crystals, co-occurring with kaolinite. The mineralization likely relates to a magmatic anomaly present in the NE part of Slovakia in the Western Carpathians south of Dukla in Poland, and a possible sub-surface subvolcanic body that deepens towards the E, the inferred top of which lies at a depth of ~1 km. The mineralization may be connected with dislocations in the rock units.

Key words: Carpathians, the Bystre Slice, realgar, goyazite, cinnabar, orpiment, fluid inclusions.

INTRODUCTION

For many decades the Polish part of the Carpathian chain (Fig. 1) has been intensively prospected and mined for hydrocarbons and metal ores. Iron, copper and manganese ores and even gold have been exploited in the flysch Carpathians and in the Tatra Mts. in the past. At present, the mining has a mostly historical significance. However, ores remain and reflect the geological processes that led to the formation of these mineral accumulations.

After World War II, the search for resources resulted in the discovery of manganese, copper and arsenic ores (Gruszczyk, 1958), and signs of different kinds of mineralization have been found at the surface (e.g., Gaweł, 1970; Wieser, 1994; Jebrak, 2012; Nieć et al., 2016). A need to search at greater depth has been expressed, especially as regards the tectonic mélange zones in the Carpathians (e.g., Jankowski, 2015a, b). The Bystre Slice appears to be a suitable area for the continuation of such research (Wieser, 1994; Nieć, 2010).

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Mineral studies in the Carpathians at the beginning of the 21st century have concentrated on determination of the mineral character (Dudok and Jarmołowicz-Szulc, 2000; Dudok et al., 2002; Jarmołowicz-Szulc and Dudok, 2005; Jankowski and Jarmołowicz-Szulc, 2009), and on the petrographic analysis of the rocks within the flysch deposits (e.g., Leśniak et al., 2009). Intensive field research and mapping has been conducted parallel to these studies (Jankowski, 2004, 2007, 2015a; Jankowski and Probulski, 2011).

For many years, associations of sulphides and other minerals have been studied in the area of the Bystre Slice (e.g., Gaweł, 1970; Wieser, 1994). Wilczyńska-Michalik and Michalik (2000) suggested that associations of sulphides and kaolinite-barite may point to a variability in the chemical composition of the mineralizing solutions. The origin of such fluids is, however, unknown. The migration of solutions from the distinct depth may be involved, perhaps related to magmatic events, or to local fluid circulation and dissolution of components from the flysch deposits. Diagenetic influence may be also considered. Wilczyńska-Michalik and Michalik (2000) stated a need for detailed studies of fissure-filling minerals and of the surrounding rocks aiming at explaining the origin of the solutions and the conditions of mineral formation. Such research has been recently undertaken and partly reported (Jarmołowicz-Szulc et al., 2023), together with fluid inclusion studies.

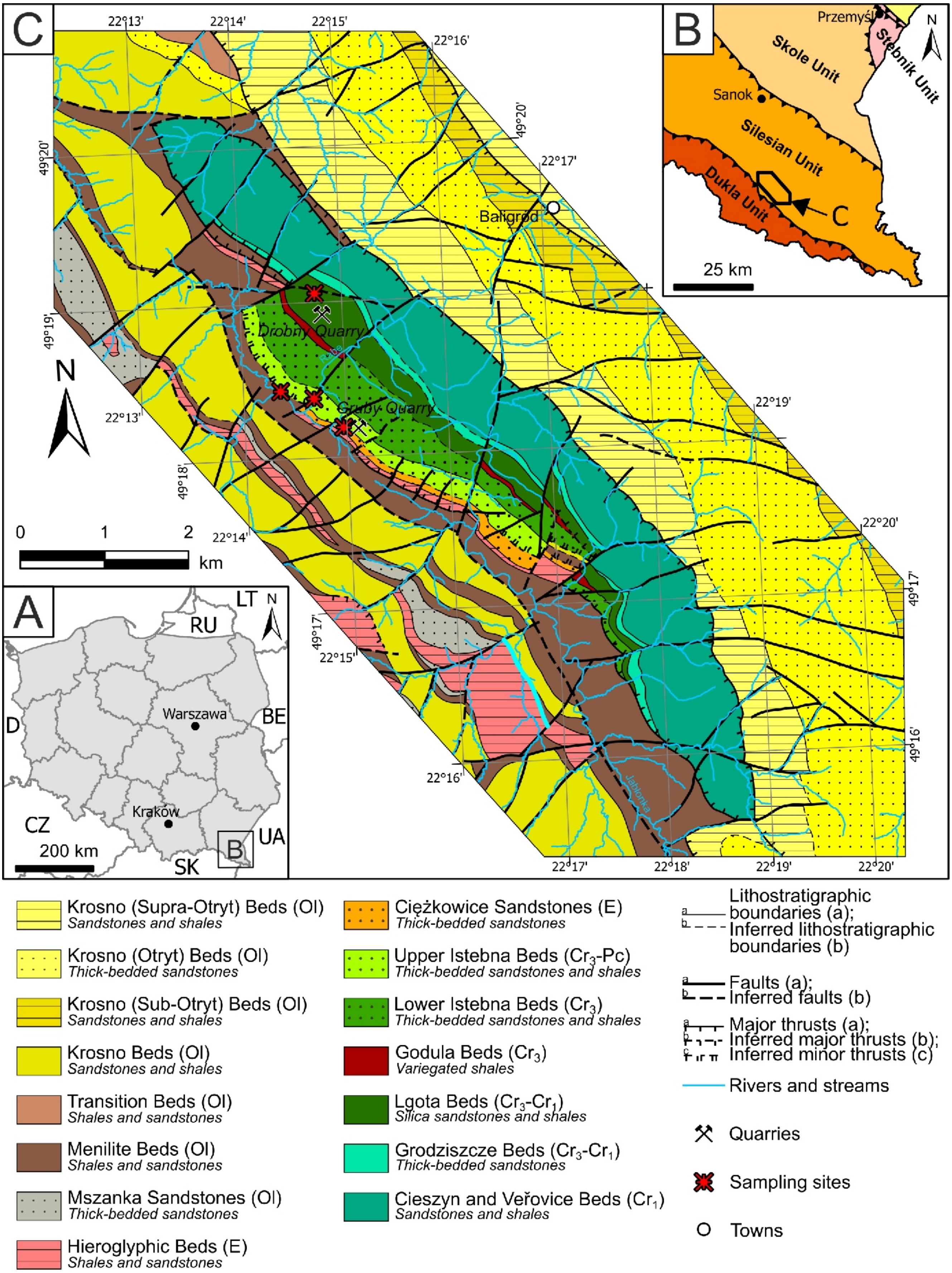

Fig. 1. Location of the study area

A – location of the study area on a map of Poland; **B** – location of the study area on a simplified geological map of Outer Carpathian units in SE Poland; **C** – geological map of the Bystre Slice (Ślączka, 1958; Jankowski and Ślączka, 2000; Jankowski, 2001; Malata, 2001; Jarmołowicz-Szulc et al., 2023, modified)

Application of fluid inclusion (FI) studies in minerals in sedimentary basins may provide much data needed for reconstruction of conditions involving the presence of hydrocarbons, of the composition of gas phases, of migration processes, and so on (e.g., Jarmołowicz-Szulc and Jankowski, 2011; Jarmołowicz-Szulc et al., 2012; Jarmołowicz-Szulc, 2016).

Previous FI studies have been carried out on the Ukrainian side of the Carpathians (Vityk et al., 1996) with some data from the Polish side (Karwowski and Dorda, 1984). Newer microthermometric data described by Świerczewska et al. (1999), Tokarski et al. (1999) and Hurai et al. (2002) have indicated an increase in pressure and temperature values estimated from FIs from minerals in the Magura nappe towards the Dukla zone. High values have been obtained in the central part of the Carpathians and very deep burial is suggested there. At the border Polish-Ukrainian area, the P-T values seem to be lower (Jarmołowicz-Szulc and Dudok, 2005). Altogether, the microthermometric data in the border area show a distinct differentiation as regards data from quartz (Dudok and Jarmołowicz-Szulc, 2000 and bibliography therein; Jarmołowicz-Szulc, 2000, 2001, 2009; Jarmołowicz-Szulc and Dudok, 2001, 2005; Jankowski and Jarmołowicz-Szulc, 2009; Jarmołowicz-Szulc et al., 2012).

GEOLOGICAL STRUCTURE OF THE REGION

The Carpathians form part of the Alpine orogen, extending for >1300 km from the Vienna Forest to the Iron Gate on the Danube. In the west, the Carpathians are linked with the Eastern Alps, and in the east they pass into the Balkan chain (Oszczypko, 2004). The traditional, commonly used subdivision of the Polish segment of the Carpathians is based on a distinction between the Inner Carpathians, that comprise the Tatra Massif, the Pieniny Klippen Belt and the Podhale Basin, and the Outer Carpathians, divided into the Magura, Dukla, Silesian, Skole, Zgłobice and Stebnik units. The Silesian unit (nappe) is divided into two minor parts: the Central Carpathian Depression and the Fore-Dukla sub-unit in Poland (e.g., Oszczypko et al., 1989; Rubinkiewicz, 2000, 2007). The Outer Carpathians are composed of marine sedimentary rocks that have been deposited in the a basin (Jankowski, 2015a), or in one of the sub-basins of the Tethys Ocean in the Late Jurassic to the Early Miocene interval (e.g., Sikora, 1976; Golonka, 2004; Oszczypko, 2004). The deposits of the Tethys Ocean are mainly turbidites of prograding submarine fans (Dżułyński, 1959; Unrug, 1963; Leszczyński, 1989).

In the Outer Carpathians, a fold-overthrust structure is visible, associated with stages of compressional deformation (Csontos et al., 1992; Oszczypko, 2004). In the Early Neogene, andesite-basalt volcanism occurred as follows. Andesite-basalt-rhyolite volcanism (Wieser, 1994) was a result of contraction of the ALCAPA – Tisza-Dacia microplates in the region of north-eastern Slovakia and in the Ukrainian Transcarpathia. Alkaline Miocene magmas in the south of the area were replaced by more acidic Pliocene magmas to the north (Wieser, 1994). The resulting solutions were saturated with elements or compounds of mercury (Hg), arsenic (As), antimony (Sb), copper (Cu) and other metals, as indicated by the mineralization documented (Nieć, 2010; Radwanek-Bąk et al., 2015; Nieć et al., 2016).

In the Polish part, the Carpathians were overthrust onto the western European platform which is divided into the Brunovistulicum and the Małopolska blocks separated by a tectonic zone (*vide* Żelaźniewicz et al., 2011). These geological units are mainly documented by boreholes (e.g., Buła and Habryn, 2008). The depth of the blocks, known from boreholes, varies from a few hundred metres in the marginal part of the foredeep up to >7000 m beneath the Carpathian overthrust (Oszczypko, 2004). The western European platform is built of a Paleozoic-Mesozoic sedimentary cover overlying Precambrian metasedimentary, metamorphic and igneous basement rocks (Ryłko and Tomaś, 2005). In the study area the basement structure beneath the Silesian Unit is poorly understood. Attempts to describe it in this area have been made mainly on the basis of geophysical and magnetotelluric methods (Młynarski et al., 1982; Stefaniuk, 2001; Ryłko and Tomaś, 2005).

The present research was carried out south-east from Baligród village within the tectonic structure called the Bystre Slice (Fig. 1; Ślączka, 1958). The geological succession of the Bystre Slice (BS) comprises formations ranging from Lower Cretaceous to the Oligocene or even lower Miocene, typical of the Silesian Unit (Ślączka, 1958; Rubinkiewicz, 1998; Jankowski and Ślączka, 2000). The most important of these are the Cretaceous Cieszyn and Grodziszcze sandstones, the Lgota beds, the Godula shales, the lower Istebna and the Paleocene upper Istebna beds (Ślączka, 1958; Jankowski and Ślączka, 2000; Jankowski and Jarmołowicz-Szulc, 2009). Moreover, the BS also includes the Eocene Hieroglyphic and the Ciężkowice beds, and the Oligocene Krosno and the Menilite beds (Ślączka, 1958; Jankowski and Ślączka, 2000; Jankowski and Jarmołowicz-Szulc, 2009).

The BS has a sigmoidal shape and it is overthrust onto the Oligocene Krosno beds towards the NE. At the southern margin of the BS Jankowskiand Jarmołowicz-Szulc (2004) described a large NW–SE oriented mélange zone (e.g., Jankowski and Jarmołowicz-Szulc, 2004). The SW margin of the BS likely also includes reverse and thrust faults. The main faults in the NW and central parts of the BS have a NE–SW strike, while those in the SE part are close to E–W. A characteristic feature of the BS is the overturned attitude of beds with the azimuth of the angle directed mainly towards the NE. The most intense tectonic deformation can be seen in the Cieszyn and Lgota beds, seen mainly as shear zones associated with numerous folds.

Mineralization was observed throughout the geological succession (Fig. 2). It mostly includes calcite and quartz as well as bituminous impregnations. In the area of the BS it is common to observe calcareous sinter (travertine), most often in stream sections. The present research is focused on the mineral realgar (AsS) and its parageneses (Jarmołowicz-Szulc et al., 2023). Field research and the search for mineralization were carried out in the Rabe Stream, and the Gruby and the Drobny quarries and surrounding area. The fieldwork detailed documentation of the geological succession and taking samples for laboratory analyses. Sulphide mineralization was collected from the Lgota Beds in the Drobny Quarry (Huczwice), from the Upper Istebna shales and Upper Istebna sandstones (the Gruby Quarry), in the exposure above the Rabe Stream's main scarp, as well as in a new site located in a small tributary of the Rabe Stream, in the Oligocene Menilite Beds. The sampling site of realgar in the Rabe Creek scarp is located within siltstones and sandstones.

SAMPLING AND ANALYSES

After review of the available literature (e.g., Wieser, 1994; Rubinkiewicz, 2000; Jankowski and Ślączka, 2000; Nieć et al., 2016) and geological maps (Ślączka, 1958; Oszczypko, 2004), several sampling locations were determined (Fig. 3). Samples were taken from the Drobny Quarry (Huczwice), the Gruby Quarry, the slope at the Rabe Stream, and in a tributary of the

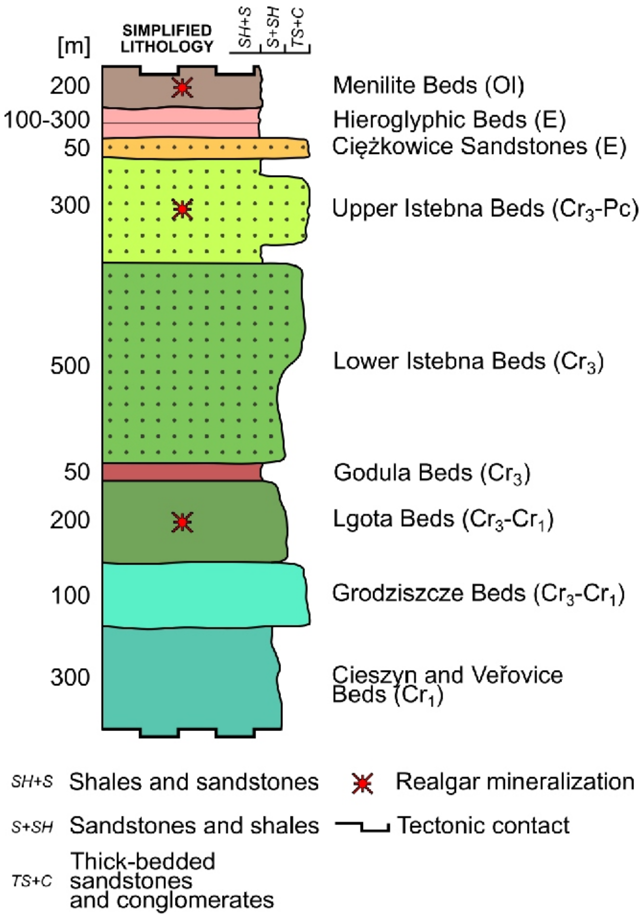

Fig. 2. Simplified lithostratigraphic profile of the Bystre Slice (Rubinkiewicz, 1998; Jankowski and Ślączka, 2000, modified)

Rabe Stream (Table 1 and Fig. 3). Samples were collected using the point method.

The Gruby Quarry is located south of the Rabe–Huczwice road. The quarry wall exposes very thick grey sandstones and conglomerates, with occasionally thin mudstone interbeds. In the western part of the quarry, a bright red coating is common on the surface of the fractured sandstone beds. In the Gruby Quarry, samples for further analyses were taken within the Upper Istebna beds (Fig. 3A).

The Drobny Quarry is located north of the Rabe–Huczwice road and has three mining levels. The quarry is dominated by thin-bedded sandstones. One interbed of dark shales several metres thick was observed. A red coating is common on the surface of the fractured sandstone layers. In the Drobny Quarry, the material for study was collected within the Lgota beds which are exposed in longwalls (Fig. 3B).

Mineralization was also observed within natural exposures. One site is located on a scarp near the water intake (Fig. 3C) and a second one is located in a tributary of the Rabe Stream ~200 m to the south-west of the water intake.

The first site exposes thick-bedded sandstones and conglomerates of the Upper Istebna beds. Realgar was observed both within weathered sandstone and in tectonic fractures in the sandstones and conglomerates. Realgar crystals in the weathering layers are up to several mm in length and display a tabular crystal habit. They have a glassy lustre. On slickensides, realgar occurs in the form of nests and veins.

In the second exposure, sandstones and shales of the Menilite beds are present. Locally abundant arsenic mineralization was found there within a mudstone tectonic breccia, while loose, washed-out realgar crystals (of the same development as in the first locality) occur in fluvial sediments. In the tectonic breccia, the realgar occurs in form of nests, lenses and also forms varnishes within druses (Fig. 3D). The crystals reach up to 1–3 cm in length. Abundant orpiment was found together with realgar at this location.

METHODS

Sampling points at the four localities within the BS, around Baligród near Rabe, are shown in Figure 1C. A range of microscopic analyses were used to analyze the samples, correspond to those described elsewhere (e.g., Jankowski and Jarmołowicz-Szulc, 2009, and references therein; Jarmołowicz-Szulc and Toboła, 2021; Toboła and Jarmołowicz-Szulc, 2023, and references therein). The procedures included sampling and preparation; microscopic evaluation of the material; detailed microscopic study, analysis of organic matter, minerals and inclusions; and auxiliary studies, such as Raman, SEM or XRD analyses. Forty thin and thick sections were analyzed using a *Optiphot 2Pol* (Nikon) polarization microscope. XRD analyses were performed by a *X'Pert PW 3020* X-ray diffractometer by Philips to study the mineral assemblages (Polish Academy of Science, Kraków). The phase analysis was conducted on powdered samples (grains to 0.063 mm). Diffractograms were registered at angle interval 5 ÷ 60 2 and identified based on ICDD tests (e.g., Środoń et al., 2001).

The Raman analyses performed on new samples were conducted using *Thermo Scientific* ™*DXR* equipment with a Nd-YAG laser (wave length 532 nm). Details of the measurements have been recently described by Toboła and Jarmołowicz-Szulc (2023). The laser strength was 1–2 mW in case of the organic matter, and 5 m W for fluid and stable inclusions. The analyses were conducted at AGH University in Kraków.

Fluid inclusion analyses were performed on 30 two-sided-polished wafers at the PGI in Warsaw. Fluid inclusions were analyzed using a *Nikon Linkam* freezing-heating stage. Observations were made using a polarization micro-

Table 1

Sampling localations in the Bystre Slice

Localization	GPS	Geology	Lithology	Sample numbers
Drobny Quarry	N 49°19.02; E 22°14.44	Lgota Beds	sandstone/shale	DR3, DR3.3, DBX3
Gruby Quarry	N 49°18.18; E 22°14.58	Istebna Beds	sandstone/mudstone	Gru IX
Rabe Stream scarp	N 49°18.23; E 22°14.41	Istebna Beds	sandstone	PK, PK1–PK3, PK-3.1, PK4, PK4.1, RapV
Rabe Stream left-bank tributary	N 49°18.25; E 22°14.23	Menilite Beds	mudstone tectonic breccia	PK-7, PK-8, PK-10, PK-11

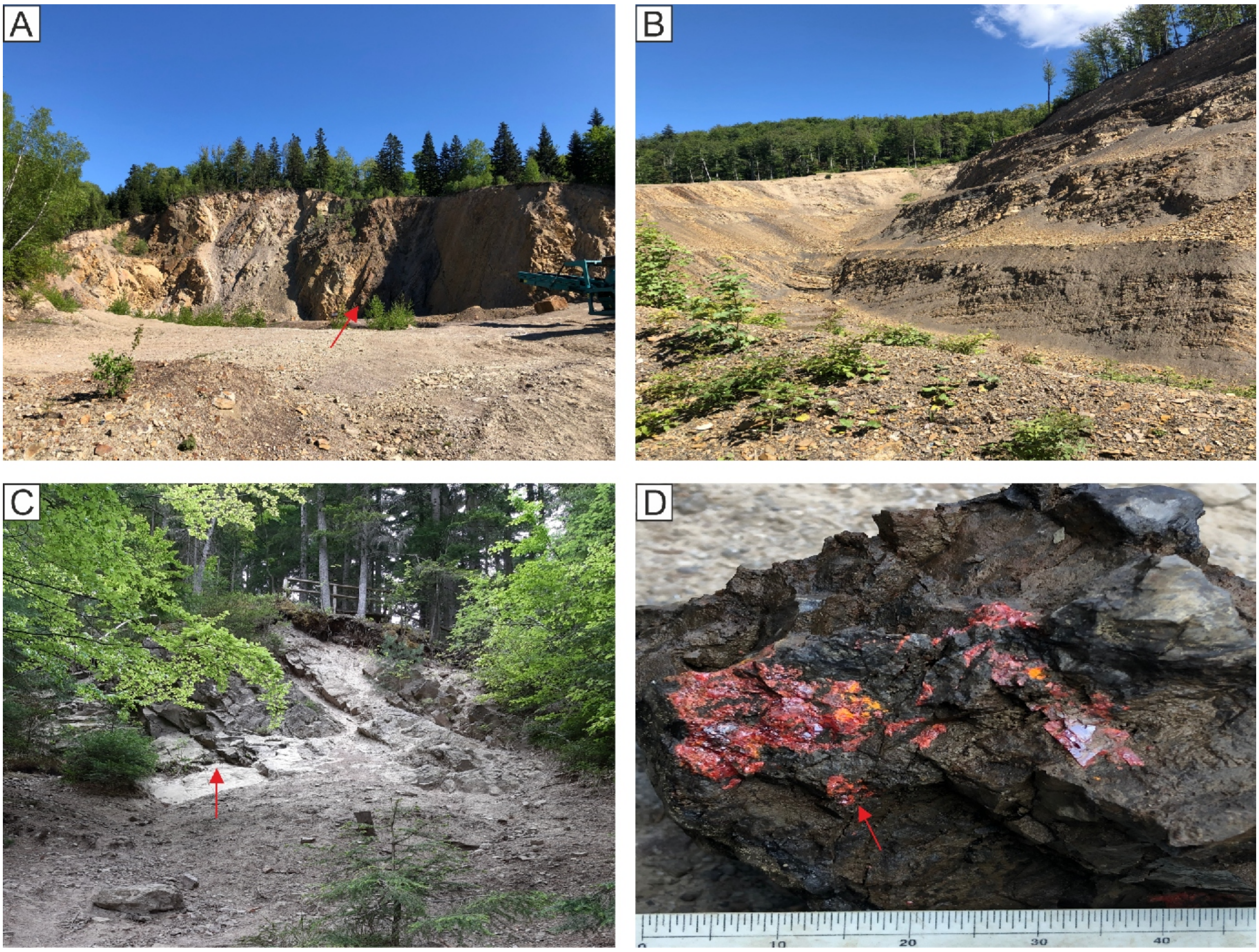

Fig. 3. Three sampling locations (A, B, C) and close-up of a specimen with the richest realgar mineralization at the fourth location (D)

A – the Gruby Quarry; **B** – the Drobny Quarry; **C** – the scarp near a water intake; **D** – "pockets" filled with realgar mineralization in tectonic breccia in samples from a tributary of the Rabe Stream; in photographs A, C, D the occurrence of realgar is shown with red arrows

scope, both in transmitted and reflected light (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 based on the criteria of Roedder (1984) and Goldstein et al. (2003).

Studies of the inclusions were conducted using a *Nikon Eclipse* microscope with a fluorescent device. Apart from the "fluid inclusion petrography", the inclusions were analyzed by mercury lamp in the ultraviolet and blue ranges. The hydrocarbons fluorescence was induced by ultraviolet reflected light in the plates prepared for fluid inclusion microthermometric studies.

FI analyses were performed on realgar, goyazite, carbonates and the quartz. Similar analytical steps were carried out. For carbonates and carbonate cements, heating took place prior to freezing as suggested by Goldstein and Reynolds (1994); for quartz and goyazite the procedure was reversed. Calculations of microthermometric results (isochores, salinity and other fluid parameters) were made using the *FLINCOR* program (Brown, 1989) for complex chemical systems. The interpretation of microthermometric results was performed applying Bakker's packages (e.g., Bakker, 2003). All calculations were conducted for simplified chemical systems and referred to the NaCl weight percent equivalent.

SEM analyses were performed in PGI in Warsaw to establish mineral composition, using a *1430 LEO* electron scanning microscope, combined with EDS ISIS. Uncovered carbon-coated thin sections were analyzed.

RESULTS

Rocks occur in the Baligród region comprise sandstones (lithic, sublithic and subarkosic arenites and lithic wackes), conglomerates and limestones. The mineralization, however, is mostly restricted to the sandstones and/or tectonic breccia. Analysis of recently collected rock samples corroborates published examples (Jarmołowicz-Szulc, 2001a, 2009, 2016; Leśniak et al., 2009). Cements in the sandstones are represented by quartz and calcite, by a clayey-calcareous matrix (with Fe hydroxides) and by the a clayey-quartz cement. The grain fabric of the sandstones is built of quartz, feldspars (mainly potassium feldspars, rare plagioclases) and lithic clasts. Glauconite, micas (frequent muscovite, rare biotite),

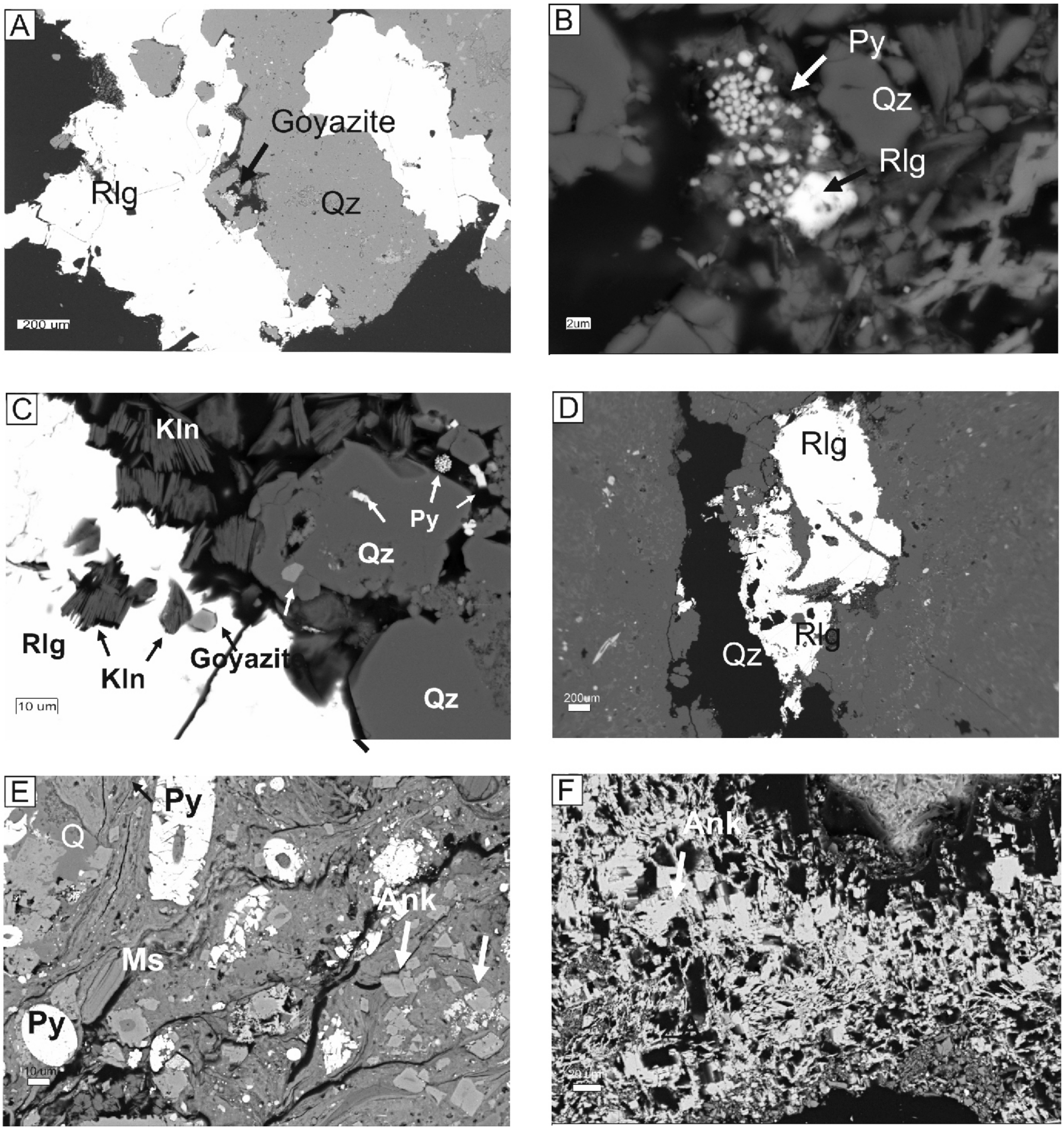

Fig. 4. SEM images

A, **B** – co-occurrence of quartz (Qz), realgar (Rlg) and goyazite in sample PK 4; **C** – realgar (Rlg), kaolinite (Kln), quartz (Qz) and goyazite in sample PK 3.1; **D** – realgar and quartz filling a veinlet in a carbonate rock; **E**, **F** – minerals recognized in a calcareous rock in sample PK 4

heavy minerals, and accessory tourmaline and zircon, are occasionally present.

The rocks are deformed and cut by a network of micro- and mesofissures. They are filled with mineral and bitumen in different mutual proportions. Field and microscope observations and published studies (e.g., Jankowski and Jarmołowicz-Szulc, 2004, 2009; Jarmołowicz-Szulc, 2009; Jarmołowicz-Szulc et al., 2012) show that at least two types of calcite, quartz and bitumen (hydrocarbons) fill the fissures and druses within the rocks. Narrow fissure associations, often parallel, within only a few exposures are commonly filled with realgar. In the field, occasional traces of oil may be seen on the surface of caverns, outside the sampling points.

Crystals of realgar were analyzed in thin and special thick sections. These samples contain layered rocks cut with white veins with red realgar accumulations. The rocks have bright and dark parts. The dark rock displays a clayey and iron-rich character, while the bright rock contains quartz, carbonates and much glauconite.

The minerals were studied by means of SEM (Fig. 4). Their chemical content is given in Table 2.

Table 2

Chemical composition of minerals based on SEM analyses

Sample	Oxides/ sulphides	Content [wt.%]	Ions	Remarks
PK-4				
Pkt. 1-2 Dark part	CO_2 MgO CaO MnO FeO O	44.63 10.20 29.73 3.36 12.05	2.01 0.50 1.09 0.38 0.33 6.00	Ankerite
	Na_2O MgO Al_2O_3 SiO_2 K_2O TiO_2 MnO FeO O	0.94 0.20 35.97 47.13 9.60 0.75 0.08 0.88	0.26 0.04 6.09 6.77 1.76 0.08 0.01 0.11 12.00	Muscovite
	CO_2 MgO CaO MnO FeO O	41.30 8.60 2.80 1.57 46.50	2.00 0.46 0.11 0.05 1.38 6.00	Siderite
	S Fe	52.70 47.02	66.12 33.88	Pyrite
	Al_2O_3 P_2O_5 CaO SrO BaO	31.60 30.85 0.00 22.20 0.96	1.11 0.78 0.00 0.38 0.01	Goyazite
Rabe PK-10				
	Na_2O MgO Al_2O_3 SiO_2 K2O CaO TiO_2 FeO O	0.33 1.50 18.31 45.27 3.23 1.22 0.33 8.80	0.11 0.39 3.79 6.77 0.72 0.23 0.04 1.29 24.00	Fe , K Alum-silicate
	CO_2 MgO CaO MnO FeO O	43.81 0.23 55.89 0.01 0.57	1.99 0.01 1.99 0.00 0.02 6.00	Calcite, columnar form
	CO_2 MgO CaO MnO FeO O	44.15 0.45 54.99 0.03 0.61	2.00 0.02 1.96 0.00 0.02 6.00	Vein calcite
	CO_2 MgO CaO FeO O	43.98 0.44 54.79 0.70	2.00 0.02 1.96 0.02 6.00	Columnar calcite
PK /10	S As	30.25 69.92	50.27 49.73	Realgar

The analyses show that the dark accumulations correspond to clay minerals with pyrite and micas. No bitumen has been observed. Elongate, opaque veinlets are filled with siderite. Biogenic fragments within the quartz and ankerite (as rhombohedra) are pyritized and contain traces of TiO_2, muscovite and feldspars. The pyrite is nodular. Rosettes of kaolinite are common in association with the realgar.

The realgar has a pure arsenic composition. White small crystal accumulations within the realgar and in association with quartz and kaolinite have the composition of strontium phosphate: goyazite (Fig. 4A, C).

Results of the XRD determinations are shown in Table 3.

The main minerals determined in the rocks analyzed were quartz, ankerite, kaolinite, pyrite/marcasite, muscovite and calcite/dolomite. The realgar in sample PK8 is accompanied by quartz, ankerite, kaolinite and muscovite, less frequently by siderite, nacrite, plagioclase and pyrite/marcasite, dickite and carbonates (calcite, dolomite).

Some rock samples from the BS and the Jabłonki mélange zone were studied by means of Raman spectroscopy. Dark accumulations in the mélange zone contain organic matter (OM) that occurs in form of compact accumulations of ~50 μm thick at the boundaries of the calcite and quartz grains and as fine intergrowths in the crystals. The Raman spectra both for OM and for calcite and quartz are very homogeneous and similar. The temperature calculated for them using the method of Kouketsu et al. (2014) is ~175°C (Toboła and Jarmołowicz-Szulc, 2023).

In a sample from the Drobny Quarry (DR3), quartz with fluid inclusions and evident quartz peaks was seen (Fig. 5A). The Raman analysis failed here to prove gas in these inclusions. The OM is weak, coalified and not suitable for temperature calculations (Fig. 5B). Pyrite is occasionally present, as shown by peaks in the Figure 5C.

In a sandstone sample from the BS, different minerals appear in the Raman spectra (PK4). Brownish-red aggregates that at the first glance appear to be realgar consist of cinnabar, hematite, lepidocrockite and pyrite (Toboła and Jarmołowicz-Szulc, 2023). Larger red cinnabar crystals (up to ~20 μm) appear less frequently, but may be also noticed at microscopic scale. Different Raman spectra of OM in form of aggregates and interlayers in the dolomitic sandstone were observed. Some display 'washed out' GL and D3 peaks without a clear D1 peak, which means a weak coalification. The spectra for the most coalified OM are shown in Figure 5D. The calculations point to a mean temperature of coalification of ~148.8°C (Table 4). The distribution of the Raman spectra suggests that different hydrocarbons migrated into the area. They display a varied coalification degree and most probably they originate from different sources. One measurement in another sample (PK10) from the Bystre slice showed calcite (or perhaps rhodochrosite or aragonite).

Fluid inclusions are present in different minerals (Figs. 6 and 7). In the realgar crystals they have been distinguished for the first time in the area. FIs in the realgar display pseudo-secondary and secondary character. They form two or even three distinct fluid inclusion assemblages (FIAs), as seen in photomicrographs (Fig. 6). Most inclusions are monophase, slightly elongated and display the characteristic shape of libellae (Fig. 6A). One group contains small dark inclusions arranged on a distinct plane (pseudo-secondary?).The second is formed by linearly arranged bright inclusions. The third group is formed by large, stretched inclusions. The diagnosis of these inclusions is difficult due to their small sizes and the intense red colour of realgar (Fig. 6E, F). Fluorescence of inclusions in the realgar was not observed. Microthermometric analyses were also difficult due to the size of the inclusions, the red colour of the mineral itself and dark colour of the inclusion infill. However, some monophase libellae in the realgar from the Rabe region formed

Table 3

Results of XRD analyses (analyses performed by Szczerba and Ciesielczuk, 2022, archival materials)

Sample	Locality	Minerals [wt.%]
pK2 D	Rabe	quartz (66.5), ankerite (13.9), kaolinite (5.4), pyrite/marcasite (4.6), muscovite (2.5), siderite (1.1), dolomite (0.5), calcite (0.3)
PK7	Rabe	quartz (66.8), calcite(17), ankerite (6) , muscovite (1.2)
PK8	Rabe	quartz (54.7), ankerite (7.9), kaolinite (6.1), muscovite (4.5), plagioclase (1.3), siderite (2.3), pyrite/marcasite (1.2) , nacrite (2.3), dickite (1.6) , calcite (1) , dolomite (1)
RaP V	Rabe	quartz (77.4), muscovite 2M1 (5.9), muscovite 1M (3.7), kaolinite (2.6), anatase (0.3)
GRU IX	Rabe–Gruby Quarry	quartz (87.6), kaolinite (3.7), muscovite (3.2), goethite (2.9), calcite (0.2)
Ja 2-2021	Jabłonki	quartz (38.7), muscovite (14.8), calcite (19.8), plagioclase (9.2), dolomite (5.6), ankerite (3.5), pyrite/marcasite (0.3)

a contraction bubble during freezing that gave a chance of homogenization during subsequent heating. The microthermometric results for this realgar are: homogenization temperature T_h = +66.1°C, ice melting temperature T_m = –3.5°C.

Fluid inclusions are also present in other minerals as shown in Figure 7: goyazite, quartz and carbonates. Those in goyazite, although very small, revealed some homogenization at >150°C.

Based on temperature results obtained from different minerals, a sequence of mineral crystallization in the BS may be proposed (Fig. 8).

This figure does not take into account the cinnabar indicated by the Raman spectra analysis. There are still no temperature data for this mineral to put it into the genetic sequence. The cinnabar may be, however, genetically related to the fluids responsible for the realgar formation.

DISCUSSION

Recent mapping of the geology of the BS, where the minerals under discussion occur, recognized also a mélange zone.

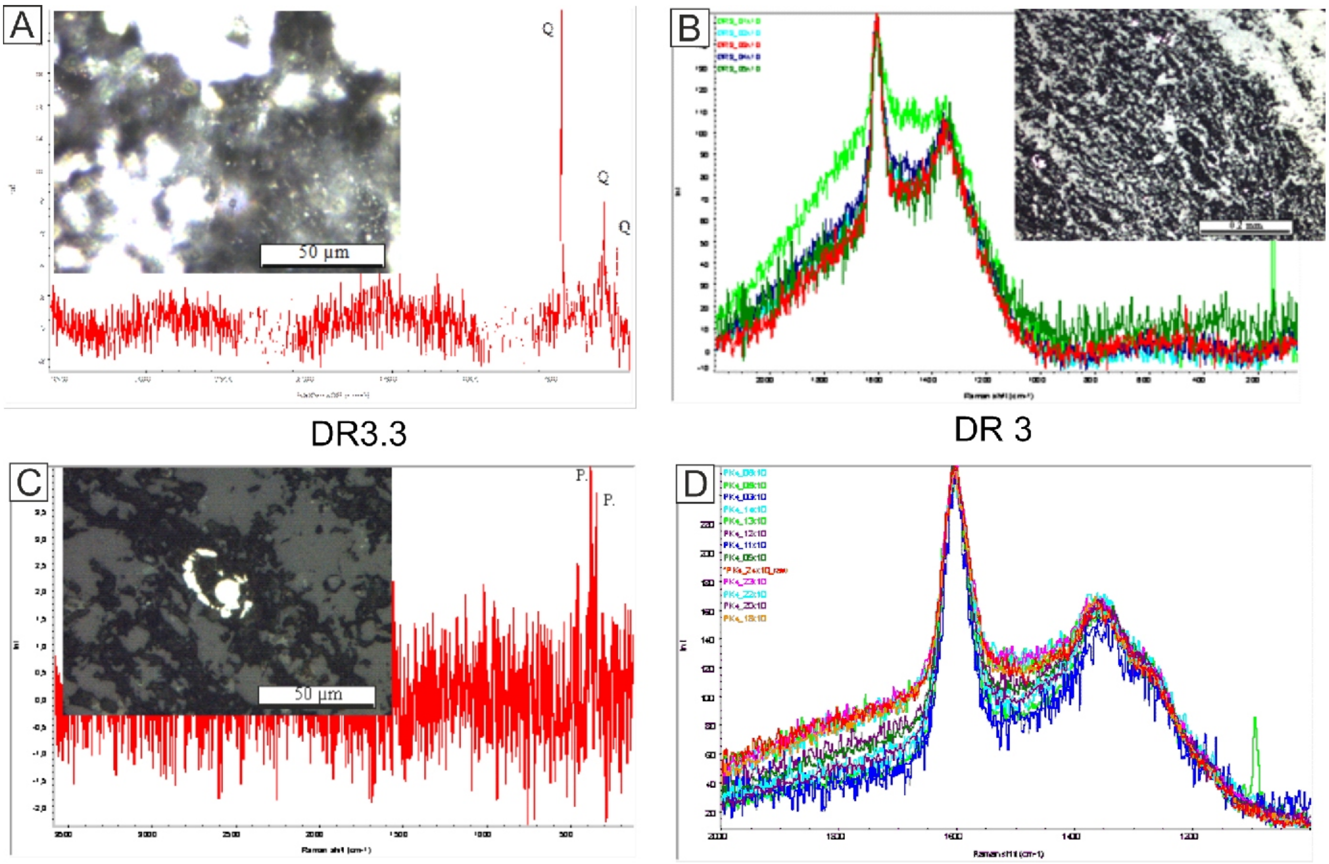

Fig. 5. Raman spectra and sample images

A – quartz with fluid inclusions, sample DR3.3, the Drobny Quarry, image in reflected light, Raman spectrum with evident quartz (Q) peaks; **B** – an image and Raman spectra of the organic matter, sample DR3, the Drobny Quarry, image in reflected light, peaks in the interval 1000–2000 cm^{-1} indicate a low maturity of the OM; **C** – pyrite image and its Raman spectrum; D – consistent Raman spectrum of low maturity OM (sample PK 10)

Table 4

Values of parameters of basic peaks for OM and coalification temperatures calculated following Kouketsu et al. (2014) sample PK4.1.

Number	Half width of peaks (FWHH)				Temperature [°C]
	D4 (1250)	D1 (1350)	D3 (1500)	GL (1600)	
PK4_03x10	113.63	143.50	217.84	49.17	169.47
PK4_05x10	147.33	142.60	237.61	54.25	171.40
PK4_06x10	116.61	142.36	239.38	52.99	171.94
PK4_09x10	129.10	145.66	247.76	52.62	164.84
PK4_11x10	98.02	157.44	221.97	50.99	139.50
PK4_12x10	118.60	151.61	182.18	52.56	152.04
PK4_13x10	120.91	147.09	167.66	51.70	161.75
PK4_14x10	135.06	153.89	200.99	55.09	147.13
PK4_18x10	114.22	155.28	148.18	57.76	144.14
PK4_20x10	120.26	162.34	136.55	54.73	128.98
PK4_22x10	115.83	159.49	139.31	57.16	135.09
PK4_23x10	119.88	173.36	132.23	57.75	105.28
PK4_24x10	114.14	155.91	140.46	57.40	142.79
Min.	98.02	142.36	132.23	49.17	105.28
Max.	147.33	173.36	247.76	57.76	171.94
Medium	120.28	153.12	185.55	54.17	148.8
Standard deviation	11.83	9.04	44	2.8	19.43
Differentiation coefficient	9.83	5.9	23.71	5.17	13.06

The newest geological map is based on the earlier maps of Ślączka (1958) and the results of later fieldwork (Malata and Marciniec, 1997; Jankowski and Ślączka, 2000; Malata, 2001; Jankowski, 2007). Sampling localities are shown on that newest map (Fig. 1). Realgar was sampled at two localities, although also found at microscopic scale in petrographic wafers from the Gruby and Drobny quarries.

The rocks in the Baligród region – sandstones (lithic, sublithic and subarcosic arenites and lithic wackes), conglomerates and limestones – correspond to those earlier reported (Jarmołowicz-Szulc, 2001a, 2009, 2016; Leśniak et al., 2009). Cements in the sandstones are represented by quartz and calcite, by a clayey-carbonate matrix (with Fe hydroxides) and by a clayey-quartz cement. The sandstone grain fabric comprises quartz, feldspars (mainly potassium feldspars, rare plagioclases) and lithic clasts. Glauconite, micas (frequent muscovite, rare –biotite) and heavy minerals including tourmaline and zircon are occasionally present.

The rocks of the BS consist of quartz, carbonates, the realgar, and clayey-iron and ore aggregates. Bitumen is less frequent. Other minerals as dolomite, anhydrite and pyrite are also present in quartz–carbonate veinlets. In a paragenesis with Marmarosh diamonds and calcite, ore mineralization is present at some locations as e.g., in the Rabe region, as described by Ślączka (1958) and Wieser (1982 a, b, 1994, 2001), including realgar, orpiment, antimonite, cinnabar, metacinnabarite and native mercury. The present study shows realgar, orpiment, cinnabar and non-ore goyazite and gypsum. The quartz-carbonate-bitumen paragenesis (Jarmołowicz-Szulc and Jankowski, 2011; Jarmołowicz-Szulc et al., 2012) is seemingly related to the tectonic mélange zones while the ore mineralization is generally connected with fissures and dislocations. This mineralization has an epigenetic character. According to Rybak (2000), the epigenetic mineralization is not only related to the dislocations but also to the fissures of the transverse joint assemblage T, less frequently of the longitudinal L or diagonal D2 joints. We consider that there is no basis to establish such a detailed relationship between the ore mineralization and the joints.

The relation between mineralization and fluid circulation in the BS is complicated. First of all, the co-occurrence of quartz – calcite – bitumen must be concerned, with respect to the presence of realgar (Jarmołowicz-Szulc and Jankowski, 2021). Several generations of quartz and calcite are present, and also different types of bitumen. As shown above, the sequence of the filling of voids (“pockets” with mineralization and bitumen) might have been as follows: fine crystalline quartz I – calcite I – hydrocarbons (oil) (Dudok and Jarmołowicz-Szulc, 2000; Jarmołowicz-Szulc and Dudok, 2005). A further sequence might be: calcite II – hydrocarbon fluid inclusions (HCFI 1) – quartz II. The Marmarosh diamonds represent the youngest quartz generation. The realgar itself is later than the MD; it contains no fluorescent hydrocarbons. It co-occurs with kaolinite, goyazyte, pyrite and cinnabar. The organic matter is present in different associations with calcite, quartz and pyrite in the mélange zones (Jarmołowicz-Szulc et al., 2023). A direct relation between OM and the realgar has not be noticed.

Field observations and XRD and SEM analyses show that the red realgar is accompanied by quartz and carbonates. It occurs as layers, lenses and/or impregnations. The rocks contain quartz, ankerite/calcite, kaolinite, illite/smectite and pyrite/marcasite. In the rocks with distinct amounts of the realgar, abundant glauconite is observed, this not yet being explained. The quartz that occurs with the realgar in the same site has the character of “Marmarosh diamonds”, with hydrocarbons trapped as inclusions. That is especially characteristic for the locality on the scarp in Rabe close to mineral water pump. Pure realgar occurs there as a distinct layer 1–2 cm thick at the top of the scarp. Quartz is there, too, mostly loose at the scarp base, i.e. not in the same layer.

The realgar in the Bystre Slice sandstones is a pure arsenic sulphide displaying the composition As 68.76–70.03 wt.% and S 29.93–30.33 wt.% (sum 100.06 wt.%). This mineral was simi-

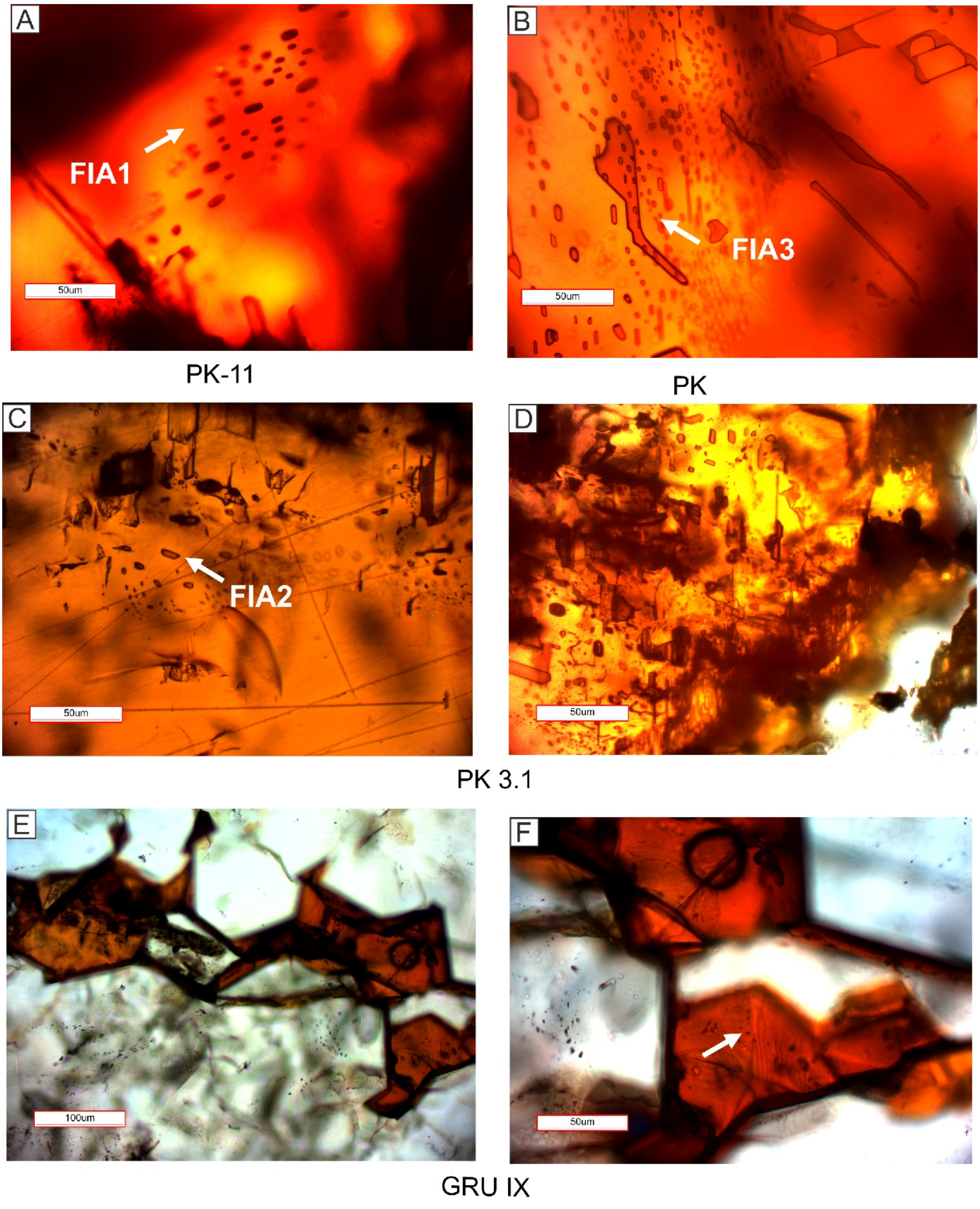

Fig. 6. Realgar from the Bystre Slice

A–**D** – fluid inclusion assemblages in realgar in different samples; three assemblages marked: FIA 1 (sample PK-11), FIA2 (sample PK), FIA 3 (sample PK 3.1); **E**, **F** – fluid inclusions in realgar and associated quartz in the sample GRU-IX from the Gruby Quarry

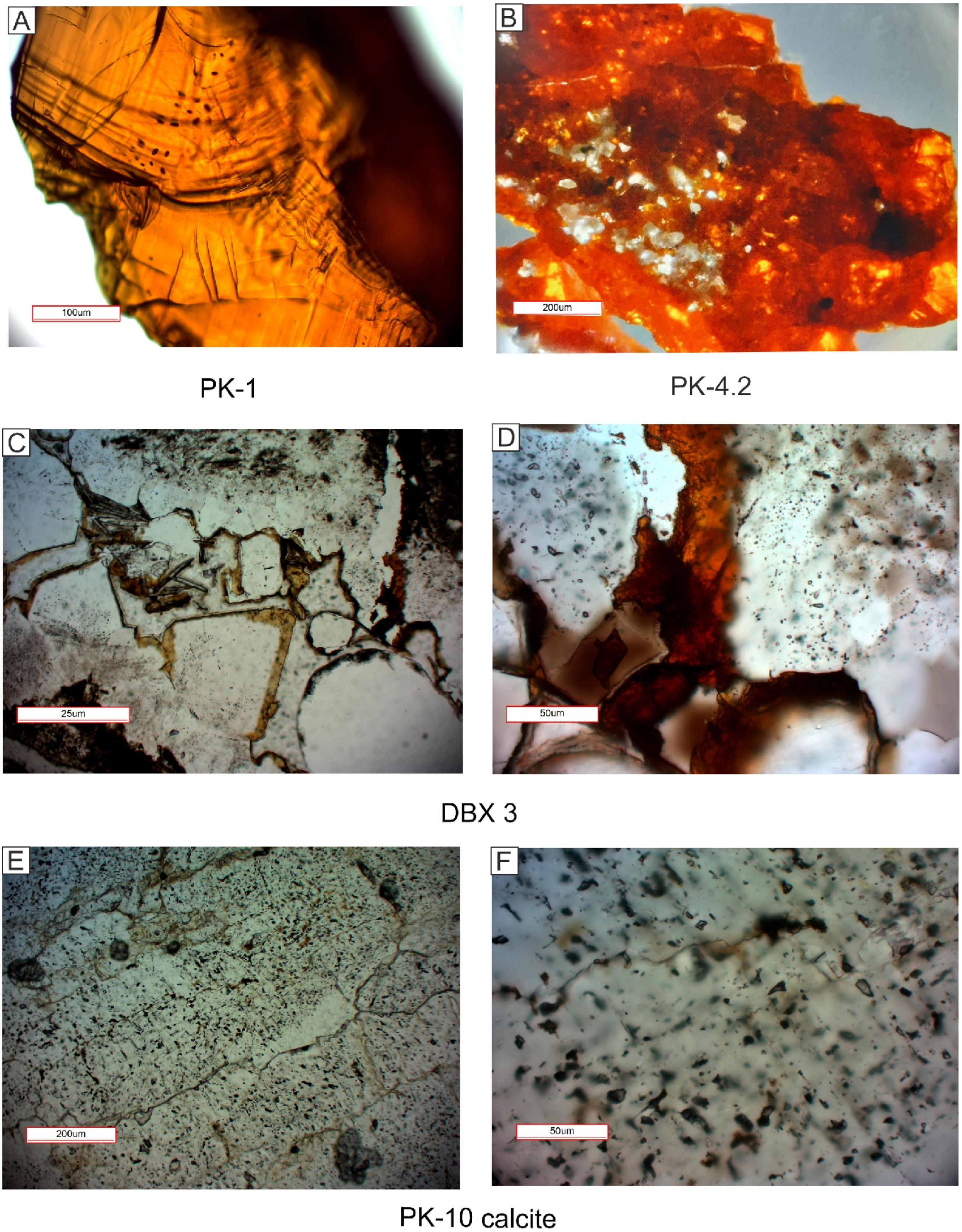

Fig. 7. Fluid inclusions in various minerals

A – realgar, sample PK-1, transparent light; **B** – FI-containing goyazite in a realgar crystal; **C**, **D** – quartz, realgar and fluid inclusions in sample DBX 3, transmitted light; **E**, **F** – fluid inclusions in calcite, sample PK-10, transmitted light

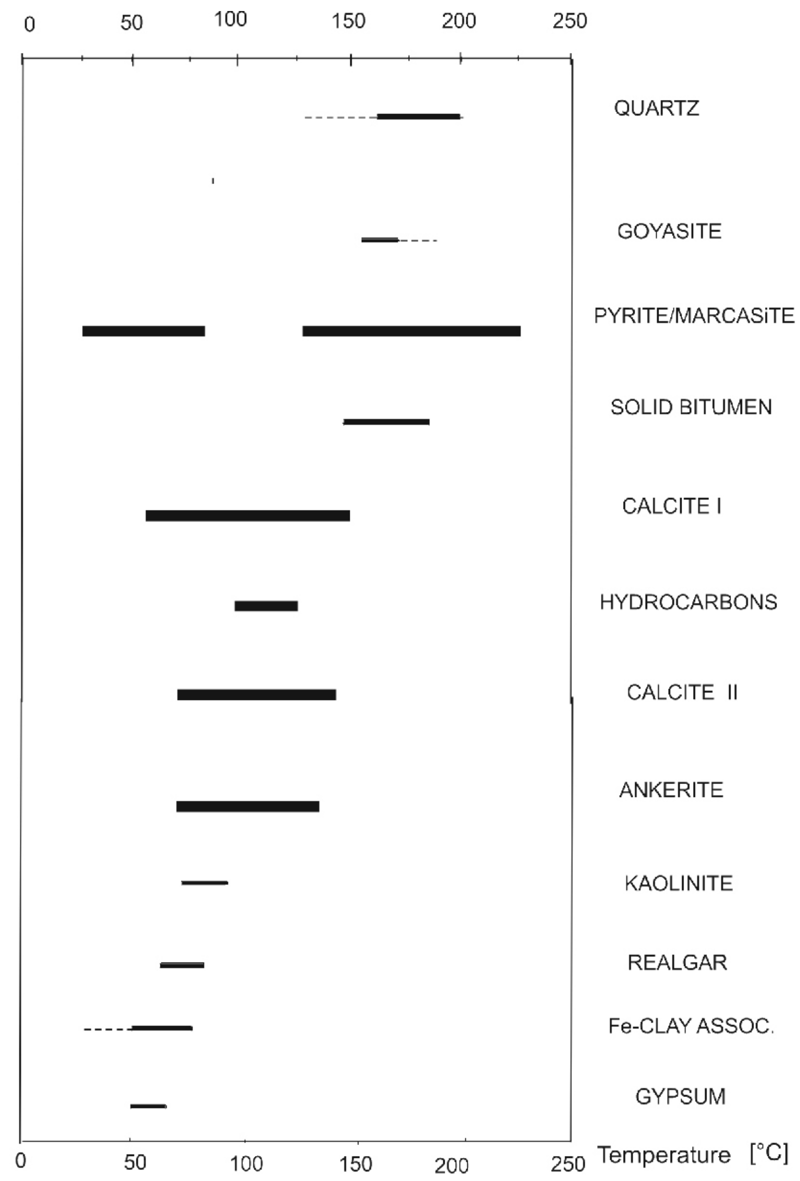

Fig. 8. Sequence of mineral crystallization in the BS based on homogenization temperatures

larly characterized by other authors (Ostrowicki, 1958; Ślączka, 1958; Kita-Badak, 1971). According to Kamiński (1937) the chemical composition of this realgar is almost identical: As 69.90 wt.% and S 30.13 wt.% (sum 100.033 wt.%), while the density of the realgar from Baligród is 3.56 g/cm^3. According to Ostrowicki (1958) the spectral analysis of this realgar showed traces of Sb.

Gaweł (1970) studied the geochemical relationship and accumulation trends of Cu and As. According to his observations, the arsenic is connected with pyrite concrections in greyish-green claystones at top of the Cretaceous spotted schists. The content of arsenic shows an increasing tendency from the Monasterec region to the Baligród vicinity (in the present research) in contrast to the Cu/As ratio (Table 5). We tried to find out the relationship between As and Cu. Although copper occurrences are mentioned in some papers on mineralization in the Carpathians (Gaweł, 1970; Nieć et al., 2016), we did not sample any copper mineralization.

According to Gaweł (1970), the copper distribution is inverse to that of arsenic in the pyrite. Pyrite is abundant in the Rabe–Jabłonki area, but was not geochemically studied in the present research. New microscopic observations from the Gruby Quarry show the co-occurrence of a red arsenic mineral – realgar – and (most probably) black opaque pyrite (Fig. 6E, F).

Another type of the ore mineral has been presently identified.

Mercury sulphide (cinnabar) was identified in the Raman spectra, in a red mineral originally thought to be realgar (Toboła and Jarmołowicz-Szulc, 2023). That means that mercury co-occurs with arsenic in the study area.

The carbonates are white or yellow with a granoblastic and crustification texture. Pure carbonate veins co-occur with veinlets of yellow calcite, in the middle of which quartz crystals

Table 5

Relationship between Cu and As concentrations in the eastern part of the Polish Carpathians (after Gaweł, 1970)

Locality	Cu [ppm]	As [ppm]	Atomic content Cu	Atomic content As	Cu/As Ratio
Bezmiechowa near Monasterec	85	90	1.33	1.3	1.10
Bystre near Baligród	105	170	2.59	2.26	1.14
Jabłonka near Baligród	93	195	1.40	2.60	0.57
Rabe	105	260	12.65	3.47	0.47

accumulate. That suggests calcite formation earlier than the quartz. Calcite is a primary mineral here, filling veins and/or forming impregnations. Large crystals of this mineral form rhombohedra (calcite I), while other forms are seen in the central parts of the veins (scalenohedra, calcite II). Crystal size varies up to ~20 mm. In the Silesian zone, the calcite is occasionally covered by a thin film of bitumen, and chemically has varying manganese concentrations.

As observed in the neighbourhood of the realgar, the calcite habit is locally very characteristic. It not only fills veinlets but also displays a character of a 'ropy calcite' manifested as a "columnar" habit. These crystals are very distinct, and often seen together with the realgar and pyrite.

The organic matter fills spaces between the calcite crystals, forms 'impregnations' and, in the central parts of the veins, forms rims around the quartz crystals. Earlier studies showed a high hydrogen index in relation to the $(H/C)_{at}$ ratio (Dudok et al., 2002). The R_o values are between 0.5% and 1.35%, close to the determinations of Matyasik (1994), the average of which is 1.24%, that corresponds to a temperature of ~168°C (Jarmołowicz-Szulc et al., 2023).

Kaolinite and barite intergrowths are often observed in the region studied. Our observations show that these intergrowths can be observed both in the macroscale and microscale. Wilczyńska-Michalik and Michalik (2000) related the presence of kaolinite and barite to the association with quartz, realgar and orpiment in the flysch Carpathians sandstones in the Rabe Stream in the Baligród region, but did not specify which beds they found them in. Generally these authors considered that the non-ore minerals post-date the tectonic movements. Barite and kaolinite crystallized simultaneously. Neither temperatures of crystallization of these minerals, nor of others, have been determined in the Rabe Stream material. Based on the quartz-realgar relationship Wilczyńska-Michalik and Michalik (2000) suggested that crystallization of realgar post-dated that of quartz, and we agree with this suggestion, as it is consistent with microscopic evidence. The realgar from two sites in the BS contains fluid inclusions, seemingly monophase and dark, some displaying a libellae form (see Fig. 6). Microthermometric analyses of these inclusions yielded a temperature of homogenization for the realgar of T_h = 66.1°C, close to the suggestions of Goldstein and Reynolds (1994) on the formation of monophase inclusions in minerals in sedimentary rocks at low temperatures (50–60°C). This value also corresponds to the results obtained for arsenic sulphide from realgar-bearing veins in Turkey (50–120°C; Kuşçu, 1995). The difference, however, is that the realgar in Turkey is evidently associated with calcite while that in the rocks in the BS co-occurs with quartz. The salinity of the fluid is low – ~7 wt.% NaCl eq.

Apart from the realgar and cinnabar in the BS, the presence of another mineral, goyazite, is notable, as this has not previously been found in the Carpathians (Gucwa and Pelczar, 1986).

Latest SEM analyses have shown the existence of strontium and phosphorus in tiny, white crystals within the realgar accumulations. The formula of goyazite is $SrAL_3(PO_4)(PO_3OH)(OH)_6$ (Jarmołowicz-Szulc et al., 2023). It forms inclusions in the realgar crystals (Figs. 4 and 7B), and co-occurs with kaolinite. Microthermometric evidence shows that the formation temperature of goyazite could have been rather high (>150°C), while the aqueous fluid salinity is low (~7 wt.% NaCl eq.). It seems that the goyazite crystallized earlier than the realgar, so its small crystals form stable inclusions within the realgar crystals.

The goyazite has been described by various authors and from different localities. Many studies were performed in the Athabasca Basin, Saskatchewan, Canada. They showed there the presence of a Th-rich aluminophosphate which belongs to the solid solution series of the crandallite group, including crandallite and goyazite. According to Mwenifumbo et al. (2004) the development of the diagenetic and alteration minerals there is believed to be associated with hydrothermal alteration which operated during the formation of uranium deposits in the Athabasca Basin.

Hoshino et al. (2016) considered that the uranium deposits in this basin include REE prospects characterized by the presence of xenotime with goyazite, hematite and clay minerals disseminated in sandstone.

In general, the crandallite group minerals form in highly acidic environments and are associated with clay minerals such as illite.

According to Zhang et al. (2012), apatite and crandallite group minerals often indicate volcanic input, sometimes being found in tonsteins within coal seams (e.g., Kokowska-Pawłowska and Nowak, 2013).

As regards the origin of the minerals presently analyzed in the area of the BS, Wieser (1994), in his reconstruction of the development of the Carpathians, showed that Miocene lavas in the south are gradually substituted by more acidic Pliocene lavas. Fluids which contained mercury, arsenic, antimony, copper and so on migrated into the Polish flysch Carpathians (e.g., in the Krynica, Męciny and Baligród areas), explaining the presence of these elements in the BS area. Kucharič et al. (2013) showed that a magnetic anomaly is present in NE Slovakia in the Western Carpathians. It lies south of Dukla in Poland where the Racza, Dukla and Silesian units outcrop (Woźnicki and Šucha in: Poprawa and Nemčok, 1988–1989). This anomaly is interpreted to reflect a sub-surface subvolcanic body that deepens towards the NE, the top of this body being inferred at a depth of ~1 km. The Zboj-1 borehole lies close to this anomaly. The fluids there display a varied composition and a temperature range of 130–220°C for inclusions in quartz (Kucharič et al., 2013). That interval is concordant with the temperatures obtained from re-calculation of vitrinite reflectance values (128–178°C). The composition of these fluids as well as the temperatures are analogous to the present results from the BS and those from the wider area of the Outer Carpathians according to Jarmołowicz-Szulc and Jankowski (2011) and Jarmołowicz-Szulc et al. (2012). This sub-surface subvolcanic body may be a source of different elements contributing to mineralization in the study area (including realgar and goyazite) and may be responsible for the warm, mineralized waters present in this region (Paczyński and Sadurski, 2007). As-rich waters may result from hydrothermal leaching of this element from mineral accumulations in the subsurface.

This hypothesis is supported by analogy to ore accumulations reported elsewhere (e.g., Schneiderhöhn, 1962; Urabe and Ayoki, 1992; Kuşçu, 1995; Mwenifumbo et al., 2004; Zhang et al., 2012), as well as exactly from the Bystre region (Nieć, 2010; Radwanek-Bąk et al., 2015; Nieć et al., 2016).

CONCLUSIONS

Mineralization observed in the BS has either a primary (pyrite, marcasite, galena) or epigenetic (realgar, orpiment, cinnabar) character.

Realgar in the BS was found in the Lgota Beds (Lower-Upper Cretaceous), the Istebna Beds (Upper Cretaceous-Paleocene) and the Menilite Beds (Oligocene). It occurs as veins, lenses and/or impregnations in tectonic deformation zones and tectonic breccias.

The realgar is a pure arsenic sulphide composed of As 68.76–70.03 wt.% and S 29.93–30.33 wt.%. It includes up to 3 assemblages of monophase fluid inclusions and may have formed at low temperature (e.g., T_h = 66.1°C).

Values of temperatures for the organic matter obtained by the Raman method are relatively high, reaching 175°C. That suggests high temperatures in the BS in the Rabe-Jabłonki Stream area for the origin of the quartz-calcite-bitumen association there.

Our research has provided new data for minerals already known in the area (realgar, orpiment and cinnabar) and discovered goyazite, previously undescribed from the BS area. Fluorescence of inclusions has not been observed in the realgar and the goyazite, suggesting that no liquid hydrocarbons have been trapped in these minerals. The lack of fluorescence and monophase (?) inclusions in realgar does not exclude the presence of methane, although not confirmed by microthermometry.

This mineralization is probably the result of migration of low-temperature hydrothermal solutions, probably related to the origin of an inferred sub-volcanic body in NE Slovakia, in the vicinity of the Zboj-1 borehole. These volcanic processes likely took place in the Miocene, coevally with the tectonic deformation of the study area. This is consistent with the occurrence of the highest realgar concentrations in post-diagenetic tectonic fractures and breccias. In this context, future research might be extended into the Fore-Dukla zone, and the Dukla and Silesian Nappes.

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