

Article

Copper-Bearing Mineralisation in the Upper Devonian Limestones: A Case Study from the Historical Teresa Adit in the Świętokrzyskie Mountains, Poland

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Abstract: The studied copper ore deposit is located in Miedzianka Mountain (Świętokrzyskie Mountains, central Poland). This deposit was exploited from the 13th century to the 1950s; therefore numerous historical adits are currently present. One of these is Teresa adit (established in 1805), consisting of underground mining corridors and natural cave developed in the Upper Devonian limestones, partially transformed by mining works. Samples of copper- and rock-forming minerals in limestones collected at seven sites within the richest copper-bearing mineralisation in this adit were studied with petrographic investigation of thin sections, micro-area chemical analysis (EDS), and XRD. This study shows the presence of various minerals: (a) Cu-Fe sulphides (relics of chalcopyrite) and Cu sulphides (covellite, chalcocite), (b) Cu-Fe oxides (cuprite and hematite), (c) Ca and Cu carbonates (calcite, azurite, and malachite), (d) clay minerals (Fe-Mg illite), and (e) micro-crystalline silica (quartz). For the first time in the studied deposit, we described chalcopyrite relics in cuprite pseudomorphosis, hematite with admixture of vanadium in pinkish-creme veins in limestones, and the presence of an admixture of Fe-Mg illite and microcrystalline silica within cracks of limestones. In addition, for the first time, unit cell parameters of malachite and azurite from Miedzianka Mountain were determined, indicating very low substitutions of atoms other than Cu in their structures. We suppose that the minerals studied were formed during three types of copper mineralisation processes: (a) hydrothermal (relics of chalcopyrite), (b) secondary weathering (chalcocite, covellite, cuprite, hematite), and (c) adsorptive mineralisation (azurite, malachite). The latter stage is related to residuum, which consists of a mixture of Fe-Mg illite and micro-crystalline quartz, which was formed during the dissolution of limestones in karst processes in some crevices. We proposed a model of the formation of copper carbonates in the adsorption stage of the copper-bearing mineralisation in Miedzianka Mountain deposits. Two generations of calcite veins (older—red calcite and younger—crème-pinkish calcite) were also detected. Mineralogical–petrographical studies of samples revealed a high scientific and educational value. Due to the fact that the Teresa adit is planned to be made available to geotourists, this work is worth presenting to the public either in the adit and/or in a local museum in Miedzianka village.

Keywords: Miedzianka Mountain deposit; mining heritage; copper minerals; azurite; malachite



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1. Introduction

Miedzianka Mountain is located in the southeastern part of Poland, about 20 km west of Kielce (Figure 1). The massif lies in the southwestern part of the Świętokrzyskie Mountains, in the northwest part of the Chęciński range. It consists of two rocky peaks: the eastern one, the higher of the two, 354 m above sea level, and the lower, western

one, 350 m.a.s.l., separated by a mountain pass (Figure 2a,b). At the foot of Miedzianka Mountain lies Miedzianka village.



Figure 1. Position of Miedzianka Mountain in Poland.

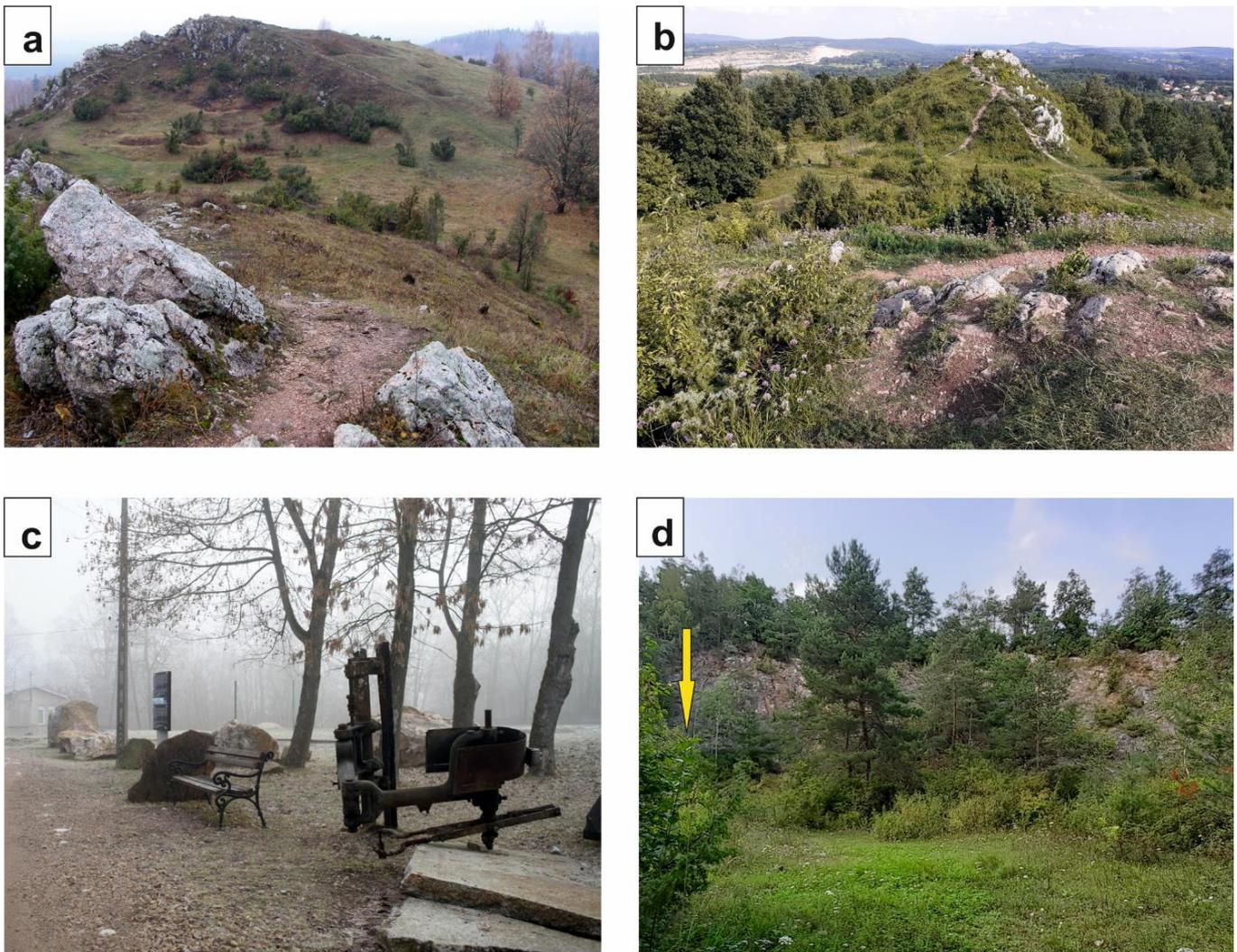


Figure 2. Field photos showing historical mining activities in Miedzianka Mountain: (a) the summit of the mountain with shallow morphological depressions, which are the remains of collapsed mining excavations (funnels); a view towards the northwest; (b) peak of Miedzianka Mountain, with visible excavation remnants; a view towards the east; (c) an exposition of rocks, mining instruments, and machines in the Museum Chamber of Ore Mining in Miedzianka; (d) abandoned Devonian limestone quarry on the southeast slope of Miedzianka Mountain, showing the entrance (yellow arrow).

Miedzianka Mountain was a thriving centre of ore mining (copper, silver) since the 13th century [1]. Currently the deposit has not been exploited since 1958, when the Miedzianka Mountain Reserve was formed in the mountain and adjacent area. The history, geology, tectonics, and mineralogy of Miedzianka Mountain deposit have been studied for almost 200 years, e.g., [1–7]. Forty minerals have been found in this deposit so far [8]. Two adits named Teresa and Zofia located on Miedzianka Mountain are planned to be opened for tourists [9]. Recent exploration of the Teresa adit has shown that it has unique geological, mining, mineralogical, and historical features [10]. This work is a comprehensive study of the minerals in the Teresa adit, which could constitute an important educational and scientific contribution, especially when this adit is made publicly available.

The aim of this study was mineralogical and petrographical investigation of copper and accompanying minerals at selected points in the Teresa adit. A comprehensive documentation of the minerals in the Teresa adit is presented in the context of making it available to tourists and constructing the mineralogical museum's collection. For the first time in this adit, in situ samples were collected from seven selected points with the richest mineralisation, and then studied using petrographic investigation of thin sections, micro-area chemical analysis (EDS), and XRD analysis. The results presented in this study are a significant supplement to the information for the proposed geotourist route in the Teresa adit [10,11].

2. Outline of the History of Mineral Investigation in the Miedzianka Mountain Deposit

2.1. Exploitation of the Deposit

Historical sources indicate that Miedzianka Mountain was an important source of copper and silver in Poland through the centuries [1]. For example, according to Czarnocki [5], from 1820 to 1840 almost 18 thousand (17.623) tons of Cu ores were excavated here. The copper content in this deposit was 1%–4% [5]. Later data showed that from 1915 to 1918 about 1360 tons of copper ore were extracted [5]. At present, numerous traces of old mining activity, including buried shafts, mine craters, and heaps, are observed on Miedzianka Mountain (Figure 2a,b). There are also three adits: Zofia, Teresa, and Łaszczynscy, as well as the Austrian shaft. The Teresa and Zofia adits were actively operated from the beginning of the 19th century to the 1920s and are currently unavailable.

Due to the historical importance of this place, its legal protection was planned from the 1950s. Finally in 1958 Miedzianka Mountain was granted the status of an inanimate nature reserve. The area of the Miedzianka Mountain Reserve is approx. 0.25 km². There is also the Museum Chamber of Ore Mining in Miedzianka, where, among other exhibits, the old mining machines (Figure 2c) and the Piotr shaft tower are presented. This reserve is located in the Kielce-Chęciny Landscape Park and is one of the most beautiful points of the Świętokrzyski Archaeological and Geological Trail. Already in the 19th century, there were plans to open the adits for tourism. In 2017, preliminary research on making underground workings available for geotourism (geotouristic path) were published [9]. Miedzianka Mountain is also one of the geological sites located in the Świętokrzyski Geopark (Holy Cross Mountains Geopark) which in the 2021 was granted UNESCO Global Geopark status.

2.2. Minerals Described from the Deposit

The first general descriptions of the Miedzianka Mountain deposit and copper mineralisation were made by Stanisław Staszic [2], who is named the father of geology in Poland, due to his precursor geological and deposit research in Poland. In 1841, a monograph on the deposits and their exploitation was published [12]. From the mid-19th century, the copper ore deposit on Miedzianka Mountain was abandoned for economic and political reasons. At the beginning of the 20th century, operations were resumed by the mining company of the Łaszczynski brothers. In the first half part of the 20th century three new phases were described by Morozewicz: “staszicite” [3], “lubekite” [4], and “miedziankite” [13]. They were not accepted by IMA CNMNC (International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification). Detailed

studies in the 21st century showed that the “staszicite” is a zincian variety of conicalcrite (formula: $\text{CaCu}(\text{AsO}_4)(\text{OH})$) [14], “lubeckite” is an admixture of a cuprian–cobaltian wad (formula: $(\text{Mn,Cu,Co})_x\text{O}_y$) [8], whereas “miedziankite” is Zn-rich tennantite-Cu (formula: $(\text{Cu,Zn})_{12}(\text{As,Sb})_4\text{S}_{13}$) [15].

Mineralogical studies on minerals in the Miedzianka Mountain deposit were later carried out by Łaszkiwicz [16]. In 1928, Czarnocki [17] described the relationship between tectonics and copper mineralisation. After the Second World War, the research was continued; however, in the 1950s it was decided that the Miedzianka Mountain ore was not suitable for mining for economic reasons. Despite the fact that the ore deposit is no longer exploited, mineralogical, geochemical, and geological studies are still being carried out e.g., [1,6–8,10,11,18–23].

Recently, for the purposes of mineralogical and geochemical research, samples are usually taken from heaps, but occasionally from underground adits, e.g., [8,18]. Forty minerals from this deposit have been described so far [8] and references therein. They are mainly copper ore minerals (sulphides, sulphosalts, oxides, and carbonates), but also very rare minerals (such arsenates, vanadates, and phosphates) [6,7,18,19,24–27].

2.3. The Origin of the Deposit

The origin and age of mineralisation in the Miedzianka Mountain deposit were discussed in many papers. It is assumed that the Miedzianka Mountain deposit has a hydrothermal origin, related to migration of low-temperature fluids (epithermal) [6,28] or high-temperature ones [7]. Kozłowski [8] suggested the primary mineral assemblages are of meso- to (mostly) epithermal origin; many of the mineral assemblages are of the tele-thermal type. The deposit was probably formed during the Variscan movements in the Lower Permian [29] and before the Upper Permian because there is no copper mineralisation in the Buntsandstein sandstones and Zeichstein conglomerates. The ore concentration in the oxidation and weathering zone of the primary copper deposit was described by Urban [30] as impregnations in tectonic zones and/or vein ores.

Ore mineralisation in the Miedzianka Mountain deposit is described as a complex process consisting of three stages [6]. According to Rubinowski [6], the first hydrothermal stage of the formation of primary copper ore in Devonian rocks is associated with hydrothermal solutions. The presence of such solutions was associated with the intrusion of diabase and lamprophyre glands into the Cambrian and Lower Devonian rocks in the area of the Świętokrzyskie Mountains [6,31–33]. Based on the geological position of these rocks in the exposures and drill cores, it was assumed that their intruded age and the formation of ore-bearing hydrothermal solutions are Upper Carboniferous/Lower Permian [31,33,34]. This primary mineralisation is related to the older longitudinal fault parallel to the axis of the Chęciny anticline [28] and forms a vein deposit located in the tectonic fractures. New data [35] using K-Ar and Ar-Ar methods for diabbases and lamprophyres showed that these rocks are between 391.7 and 254.5 Ma (Lower Devonian–Permian).

The formation of secondary copper sulphides and the second stage of ore mineralisation were linked by Rubinowski [6] with the processes of primary deposit weathering and called the weathering stage. The third adsorption stage [6] was related to the “capture” of copper ions by the clay and carbonate residue resulting from the karstification process of Devonian limestones, which led to the formation of copper carbonates.

Minerals that occur in the primary ore zone belonging to the primary paragenesis are chalcopyrite (CuFeS_2), Zn-rich tennantite-Cu [$(\text{Cu, Zn})_{12}(\text{As,Sb})_4\text{S}_{13}$], and galena (PbS) [7]. “Miedziankite” oxidises quickly, and the unoxidised mineral phase can only be observed at the mining site on the sides of the adit tunnels [18]. The “Miedziankite” phase is also called grey copper ore (so-called “szaromiedniak”) [36].

Kozłowski [8] also included native gold as a primary mineral of the Miedzianka Mountain deposits. It was probably also an admixture of sulphides (chalcopyrite) or Cu-sulphosalts (tennantite series). Chemical weathering of primary ores resulted in the

release of gold from their crystal lattice and its secondary accumulation in hypergenic minerals—Fe oxides and hydroxides and malachite [7,8,37,38].

Secondary minerals related to the oxidation zone described in the Miedzianka Mountain deposit [6–8,39] are copper carbonates (malachite and azurite), chalcocite (Cu_2S), covellite (CuS), bornite (Cu_5FeS_4), cuprite (Cu_2O), tenorite (CuO), and iron oxides. Secondary minerals are found in veins/veinlets as well as in karst funnels into Devonian limestones.

In the primary zone of the deposit, there is also chalcocite (Cu_2S), which, according to Rubinowski [6], is the dominant mineral in the Miedzianka deposit. The origin of this mineral is still under discussion. Rubinowski [6] described that this chalcocite occurs in a rhombus-shaped modification (the so-called β -chalcocite) and its formation was associated with the weathering process of the deposit. On the other hand, Balcerzak et al. [7] suggested that chalcocite occurs in veins in the zone of primary ores, but it cannot be ruled out that these veins were formed as a result of chalcocite migration from the ore zone changed by distention solutions. These authors reported that chalcocite occurs in two overgrown forms that are crystallographically related and do not take up relics of bornite and chalcopyrite.

Gold found in some minerals, i.e., hematite and malachite, was also described from this copper deposit [3,7,8,38,40]. As suggested by Balcerzak et al. [7] gold was formed during the hypergenic processes and is located in the lower part of weathering ores. In the 16th century, gold and silver were extracted from malachite and other Cu-bearing minerals that were mined at Miedzianka Mountain. Extracted gold was used to make the golden dome of Sigismund's Chapel (a funerary chapel for the last kings of the Jagiellonian dynasty) in the Wawel Cathedral in Kraków, Poland [41].

3. Study Area

Miedzianka Mountain is located in the Świętokrzyskie Mountains (Kielce zone) in the south wing of the Chęciny anticline (Czarnocki vide Konon [42]). It is composed of Devonian massive organogenetic limestones (Upper Givetian, Frasnian) and plate limestones (Frasnian–Famennian [6]). On the southern slopes there are Triassic sediments that inconsistently lie on the Palaeozoic formations [21]. In the east part, clay-mudstone Cambrian rocks occur, and build the core of the Chęciny anticline (Figure 3). The contact between the Palaeozoic series is tectonic because the Devonian rocks are overlapped by the Cambrian rocks [6].

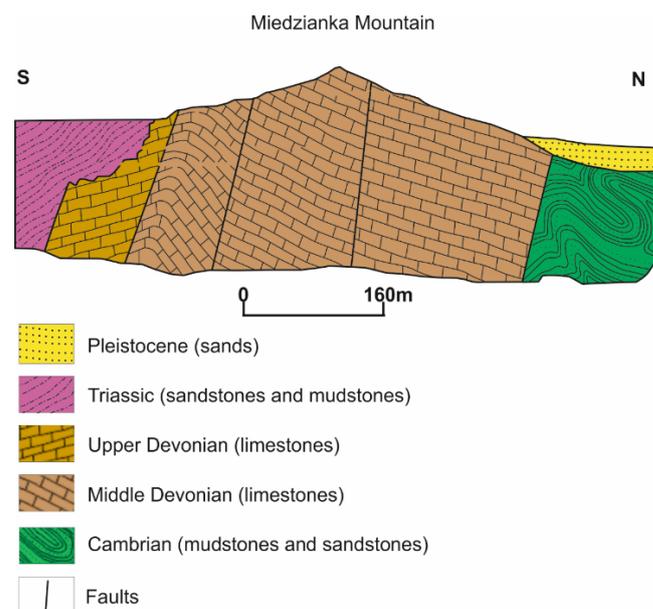


Figure 3. Geological cross-section of Miedzianka Mountain [28], simplified.

Our investigations were carried out in the Teresa adit, which is located on the eastern slope of Miedzianka Mountain. It is hollowed out within the Upper Devonian (Frasnian–

Famennian) limestones, which are cut by cherry, marly shales (Famennian) [6]. The entrance is located in the eastern part an abandoned quarry (Figure 2d). The Teresa adit is a 523 m system of underground corridors including 270 m of natural karst caves, altered by mining works (Figure 4). There are also two shafts that are inaccessible. Detailed descriptions of the Teresa adit are included in a paper published by Ciurej et al. [10].

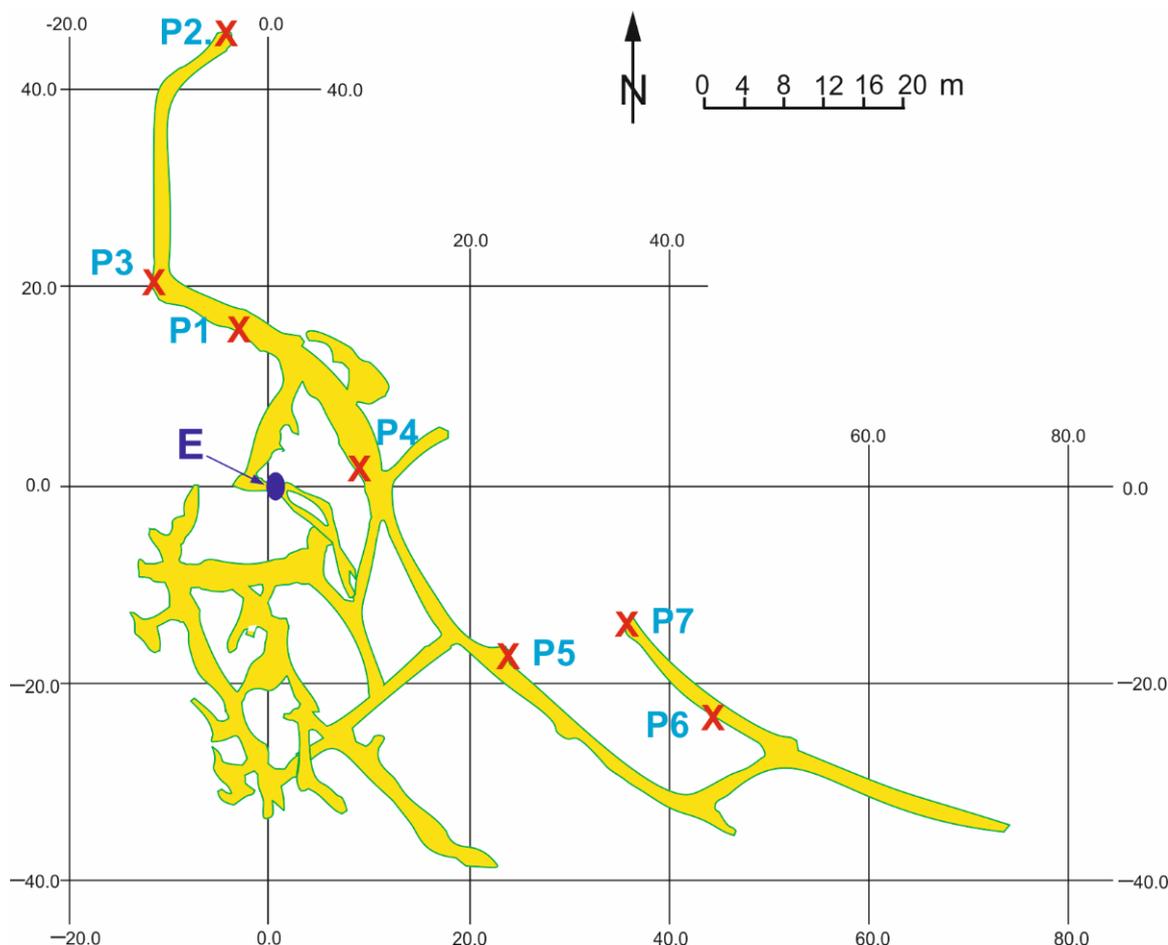


Figure 4. Simplified map of the cave in the Teresa adit inside Miedzianka Mountain [43], with the location of the studied sites and samples collected for mineralogical studies. X—location of studied sites and E—entrance.

4. Research Methods

The Teresa adit is not publicly available and it was necessary to obtain permission in order to explore and collect samples from the Regional Director for Environmental Protection in Kielce. The study of the Teresa adit took place during winter 2018/2019, by a team of specialists in the fields of geology and speleology. Exploration covered 150 m of the adit's natural caves, corridors, and underground galleries. Two shafts were not examined, because they are collapsed and their exploration could be associated with high risk. Seven representative sites with symbols P1–P7 were selected for detailed examination and laboratory studies (Figure 4). For detailed descriptions of the studied sites see Ciurej et al. [10]. In total, twenty-three rock samples were obtained. The samples were chipped (detached) with a hammer and also drilled using a core drill with a diameter of 2.5 cm and 5 cm (Figure 5). Twenty-four petrographic, uncovered thin sections of about 5 cm × 3 cm size were made. All thin sections were observed with a Nikon Eclipse LV100N POL (Japan) polarizing optical microscope with a photographic camera and NIS-Elements BR (ver. 4.30) software located at the Department of Geology, Pedagogical University in Krakow.

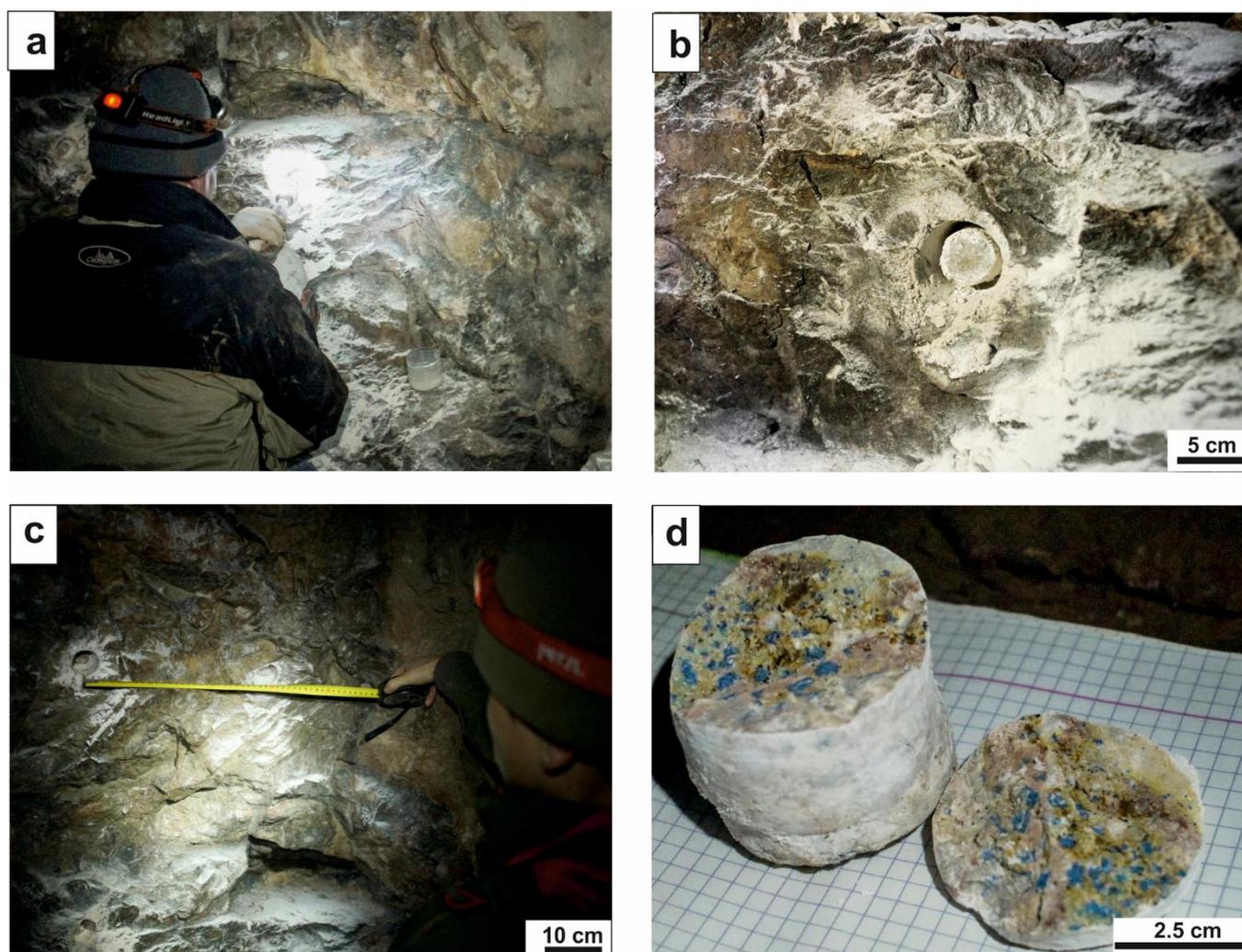


Figure 5. Sampling procedure: (a) drilling a sample with a core drill in dead end walkway, site P7; (b) sample P3A1-2 drilled in the sidewalk wall, site P3; (c) pulling out the core of sample P7A1-1 from the sidewalk wall, site P7; (d) core of sample P6A1-1 obtained by using a core drill, note distinct deep blue colour of azurite mineral dispersed in rock, site P6.

The chemical composition of ore minerals was determined using the SEM-EDS method. Ten selected samples, including thin sections and rock chips of about 5 cm × 3 cm size, were examined. Carbon-coated polished thin sections and rock chips of the studied samples were analysed using a HITACHI S 4700 (Japan) microscope with a Vantage (NORAN EDX) spectrometer. The time of analysis was 100 s for point at an acceleration voltage of 20 kV. The ZAF correction algorithm was used. The study was carried at the Laboratory with Field Scanning Emission Microscopy and Microanalysis at the Institute of Geological Sciences of the Jagiellonian University, Krakow, Poland.

The mineralogy of five selected samples was determined on randomly oriented powder specimens. The material was precisely extracted with a dental scalpel and the aim was to obtain information on minerals from selected crusts. The samples were then milled in an agate mortar. X-ray diffraction measurements were carried out using a Bruker D8 diffractometer (USA) located in the Clay Minerals Laboratory in the Institute of Geological Sciences, Polish Academy of Sciences, Kraków, Poland. Diffractograms were recorded with Co radiation in the range of 4–85° 2 Θ , with a step size of 0.014°, registered every 3 s. BGMN/Profex (ver. 4.3) software was used for quantitative analysis. The range below 8° or 10° 2 Θ was excluded from fitting due to high background at lower angles and artificial peaks caused by diffraction of X-rays that were not fully filtered by Fe foil. Peak posi-

tions were corrected by assuming sample displacement. All major phases were calculated with corrections for crystallite sizes, microstrain, as well as preferred orientation. A LaB₆ crystallite size standard (SRM 660a) was used as a test for correct instrumental function calculation. Unit cell parameters of the identified Cu-bearing phases were determined and compared with parameters of these minerals from the American Mineralogist Crystal Structure Database (AMCSD).

The samples are archived at the Institute of Geography, Geology Department, Pedagogical University of Krakow, Podchorążych 2, 30-084 Kraków, Poland; Collection reference: Góra Miedzianka, 2019/ P1-P7.

5. Results

Devonian limestones with calcite (Figure 6a) and copper (Figure 6b) mineralisation were collected for this study. The presence of secondary copper minerals—secondary copper sulphides, copper oxides—and carbonates—malachite (Figure 6c) and azurite (Figure 6d)—as well as iron minerals (Fe-oxides) and a mixture of Fe-Mg illite with microcrystalline quartz/silica (in karst fractures) were found.

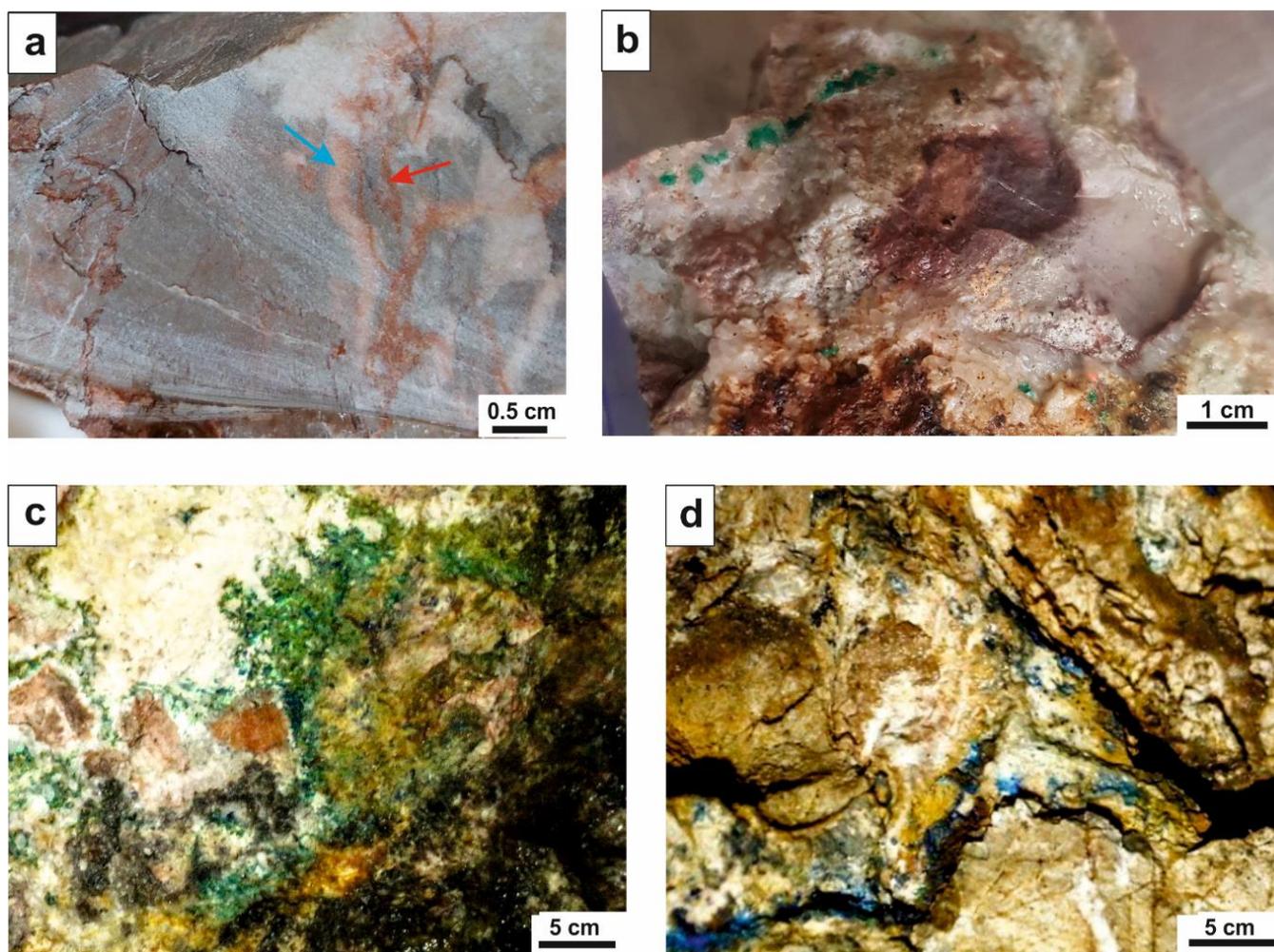


Figure 6. Devonian limestone with various styles of mineralisation in the Teresa adit: (a) fine-grained micrite limestones with different-colour calcite (rosa-like calcite type) vein: old—red (red arrow) and young—creme-pinkish (blue arrow) generations, sample P3A3-1; (b) breccia of Devonian limestones cut with veins of red calcite and malachite, sample P1A1; (c) underground photo showing the malachite (green colour) and black mineralisation in creme-pinkish calcite vein, site P7; (d) underground photo showing the nest azurite (blue colour) mineralisation in creme-pinkish calcite vein, site P6.

XRD tests showed the presence of the above mentioned minerals (Figure 7, Tables 1 and 2). The determined unit cell parameters show that azurite is within precision, practically identical to the one from the database, indicating a lack or small substitutions of Cu in the structure. For malachite the unit cell parameters are also very close to those from the database, but the a and b parameters are slightly lower, while c is slightly higher than in the AMCSD.

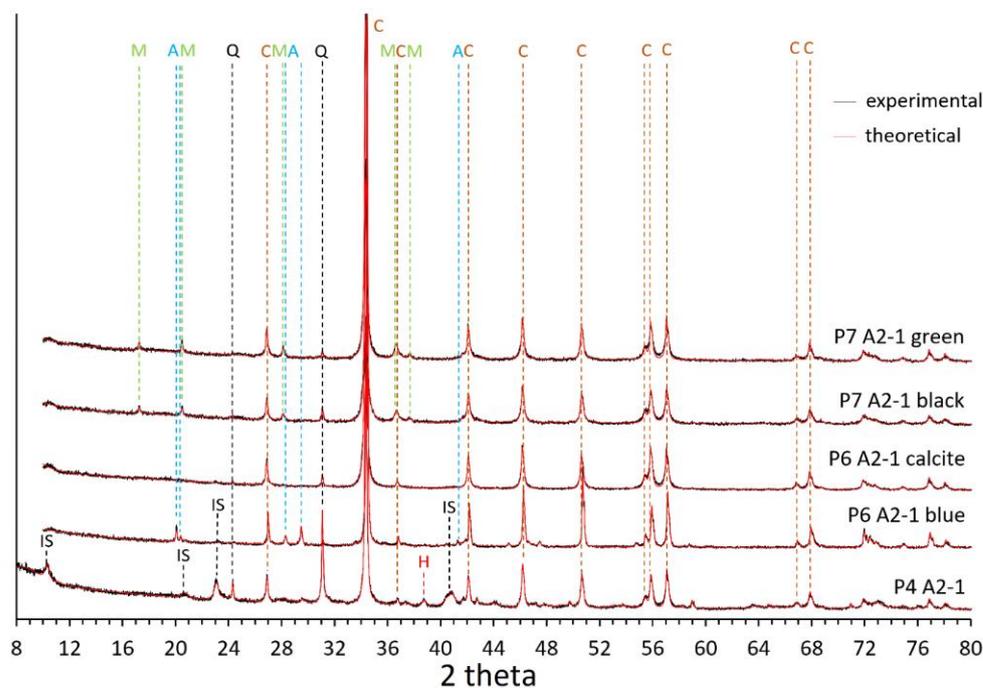


Figure 7. Comparison of experimental (black) and calculated (red) diffractograms of selected samples. C—calcite, Q—quartz, A—azurite, M—malachite, IS—mica/illite, H—hematite.

Table 1. Quantitative composition of precisely extracted crusts. Optimised unit cell parameters of copper-bearing phases are expressed in Å and degrees. For sample P4A2-1, unit cell parameters are not shown because of the low content of this phase, and thus its low precision. Unit cell values in brackets are from the AMCSD database [44,45].

Sample	Quartz	Calcite	Azurite	Malachite	Mica/illite	Hematite	Siderite	SUM
P4A2-1	8.1	40.3	0.8		47.7	2.5	0.6	100.0
P6A2-1 calcite	2.5	97.5						100.0
P6A2-1 blue	0.4	85.5	8.8 a = 5.0150 ± 0.0063 (5.011) b = 5.8482 ± 0.0092 (5.850) c = 10.349 ± 0.012 (10.353) β = 92.48° ± 0.10 (92.41)		5.3			100.0
P7A1-1 green	1.3	87.9		10.8 a = 9.492 ± 0.027 (9.502) b = 11.946 ± 0.025 (11.974) c = 3.2441 ± 0.0082 (3.240) β = 98.56° ± 0.20 (98.75)				100.0
P7A1-1 black	3.0	89.0		8.0 a = 9.493 ± 0.038 (9.502) b = 11.943 ± 0.033 (11.974) c = 3.243 ± 0.012 (3.240) β = 98.55° ± 0.30 (98.75)				100.0

Table 2. Reflections used for qualitative analysis of copper-bearing phases.

Phase	2 Theta (Co)	Relative Intensity	D-Spacing	hkl
Malachite	17.18	48.11	5.9870	020
	20.41	67.53	5.0484	120
	28.02	68.15	3.6948	220
	36.51	100.00	2.8556	−201
	37.57	43.29	2.7777	−211
Azurite	19.92	61.54	5.1719	002
	20.23	29.12	5.0921	011
	28.17	55.14	3.6753	−102
	29.33	100.00	3.5336	111
	41.14	26.31	2.5460	022

Malachite was found in both samples: P7 green and P7 black, based on XRD analysis (Figure 7, Table 1). The black mineralisation in the sample P7 black was not detected by XRD. The difference in colour in both samples can be related to admixtures of other minerals; sample P7 black can contain cuprite, that is below the sensitivity of XRD.

5.1. Characteristics of Devonian Limestones

Ore mineralisation occurs in host Middle Devonian limestones. The limestones are light grey to grey, fine-grained (Figure 6a), and contain fauna (e.g., *Amphipora* sp.; *Stromatopora* sp., *Megalodon* sp., *Lexonema* sp., *Tetracorallia* sp.) [11,46]. The studied limestone was described as biolithite/boundstone and biostrome [47,48]. The calcite in the limestone is fine-grained and occurs in the micrite variety (Figure 8a). Micro-area chemical analysis of the micrite calcite showed that it is a calcite with an admixture of magnesium (MgO from 0.6 to 0.5 wt.%) (Figure 9a—sample P6A1).

The limestones are strongly tectonically fractured and cut by numerous veins and veinlets (0.5–0.1 cm). The veins and veinlets are of various colours (white, pink, black, brown, blue, and green—Figures 6a,b and 9b) because they are filled with different minerals—white and creme: pinkish calcite (Figures 8a and 9c); black: Cu oxides (tenorite?) (Figure 8b) and cuprite (Figure 8c,d); blue and green: Cu carbonates—azurite (Figure 8e) and malachite (Figure 8f); red-brown, red Fe hydroxides (Figure 8f) and oxides (hematite) (Figure 8g,h).

In thin sections, the studied limestones are micritic (Figure 8a) with stylolite seams (Figure 8b). The rocks are cut by numerous veins and veinlets. The carbonates from white and pink veins and veinlets contain sparitic, colourless calcite (Figure 8a). In transmitted light, this mineral has variable relief, low to high ($n_{\omega} = 1.640\text{--}1.660$, $n_{\epsilon} = 1.86$), high birefringence ($\delta = 0.154\text{--}0.174$) [49], and high-order interference colour. In fine-grained aggregates (micritic aggregates), the rhombohedral cleavage is not observed, while in the veins, rhombohedral cleavage is visible in the sparitic calcite crystals (coarse grains) as well as polysynthetic lamellar twinning in two directions (Figure 8a). These twins form as a result of relatively low mechanical stress during the tectonic deformation of rocks.

In karst nests, which were formed due the weathering processes in the Permian/Early Triassic, the Fe-Mg illite blasts and micro-crystalline quartz grains occurred. The presence of these minerals in the studied limestones was confirmed by the XRD data (Figure 7—sample P4A2-1, Table 1) as well as the EDS investigations (Figure 9d–f—sample P6A1). The small broadening of $\sim 10^{\circ}$ 2Θ peak of illite indicates a low percentage of the smectitic component (10%–20%).

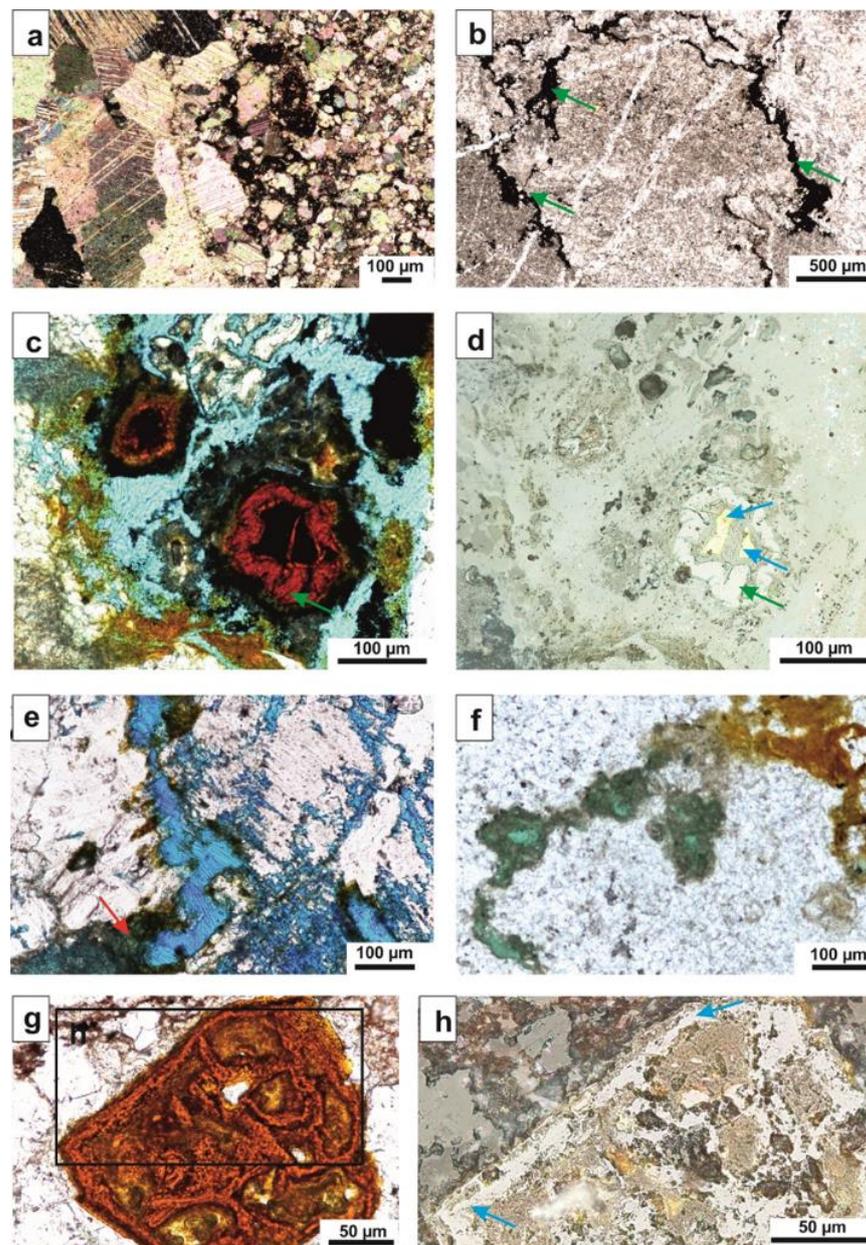


Figure 8. Minerals in optical microscope views: (a) host micritic Devonian limestone (right part) cut by veinlet of sparite, creme-pinkish calcite (left part), sample P1A1 (transmitted light XPL); (b) stylolite impregnated by the so-called “black/tarry copper ore” (green arrows), sample P3A1 (transmitted light PPL); (c) cuprite (cochineal red colour, green arrow, left) in azurite nests (blue colour) in the centre of the pseudomorphosis chalcopyrite relics (black), sample P6A1-1 (transmitted light PPL); (d) cuprite (bluish white colour, green arrow) in azurite nests (light gray). In the centre can be observed yellow chalcopyrite relics (blue arrows), which are replaced by cuprite, sample P6A1-1 (reflected light, PPL); (e) fibrous azurite (deep blue) locally turns into malachite (red arrow), sample P6A1-1, (transmitted light PPL); (f) fibrous malachite (green colour) nests/veinlets (left) and secondary Fe-hydroxide (goethite) (brown colour), on the right side, sample P6A1-1 (transmitted light PPL); (g) hematite (red-brown colour) pseudomorphosis (called “kidney ore”) after primary sulphides, sample P1A1 (transmitted light PPL); (h) greyish-white hematite (blue arrows) in pseudomorphosis after primary sulphides, sample P1A1, enlarged from (g) (reflected light, PPL).

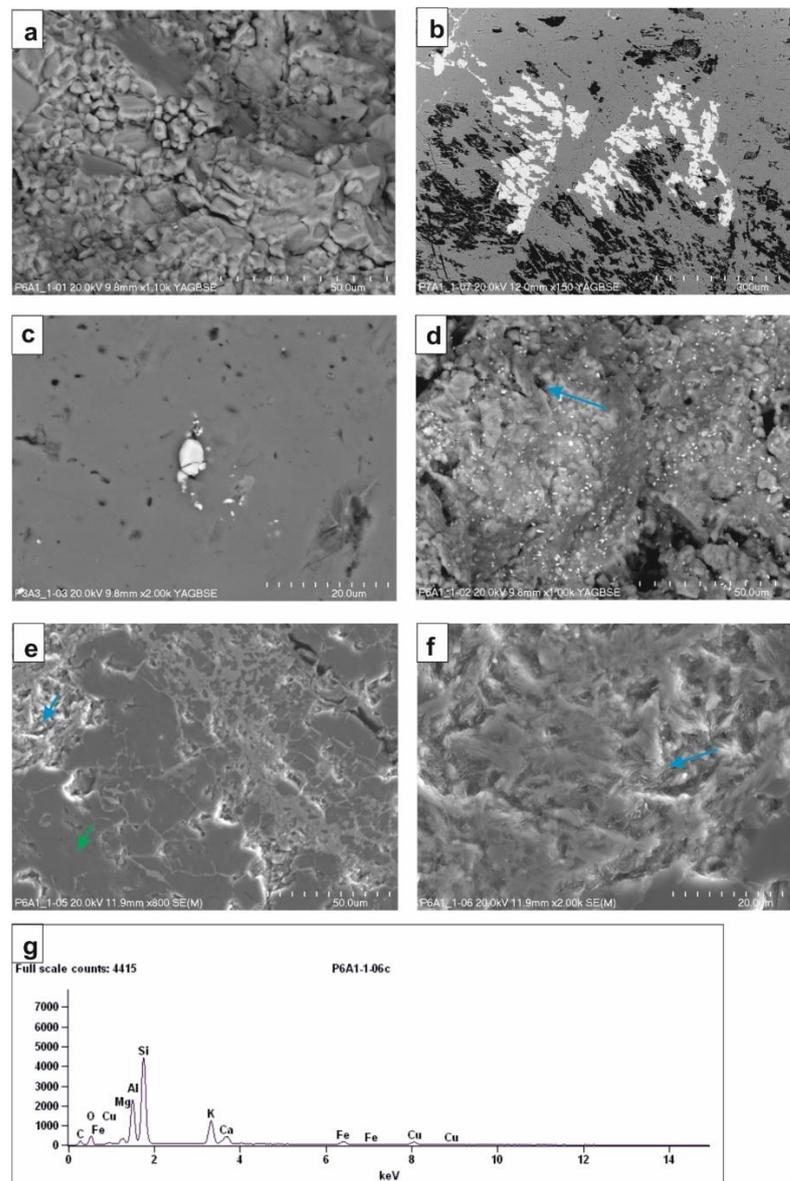


Figure 9. SEM images of secondary minerals in the oxidised zones: (a) host Devonian limestones—calcite with admixture of magnesium, sample P6A1; (b) azurite nest (white) in limestone (gray), (black is an artefact), sample P7A1; (c) scattered hematite crystals with admixture of V₂O₅ 0.6 wt.% (limit detection for EDS \pm 0.05) in creme-pinkish calcite, sample P3A3; (d) host Devonian limestones—Fe-Mg illite nests (blue arrow) and scattered Fe oxides (light) in calcite, sample P6A1; (e) Mg-Fe illite nests (blue arrow) in calcite (green arrow), sample P6A1; (f) calcite with Fe-Mg illite nests (blue arrow); blue arrow also marks the EDS analyses, shown in (g), sample P6A1, (g) microprobe analyses of Fe-Mg illite, taken from site marked with blue arrow in (f).

5.2. Characteristics of Minerals from the Teresa Adit

5.2.1. Primary Minerals—Ore Mineralisation

In the samples studied from the Teresa adit only relics of primary chalcopyrite are visible in sample P6A1-1 (Figure 8c,d). This mineral has a yellow colour in reflected light. In the other samples (P1A1, P3A3, P7A1), the pseudomorphoses after primary sulphides are filled by Fe oxides (hematite), calcite, Fe-Mg illite (Figure 8g,h (sample P1A1) and 10a (sample P3A3)), as well as azurite (Figure 10b sample P7A1).

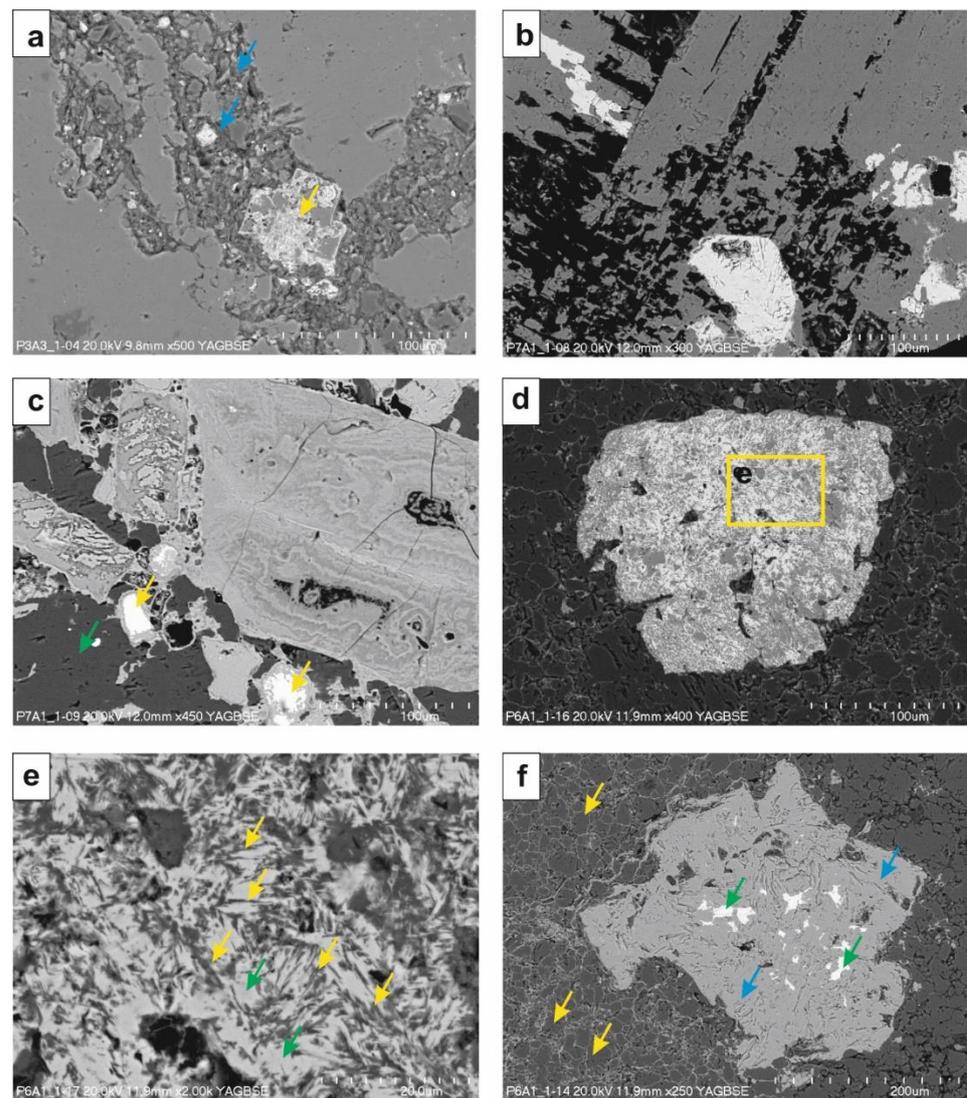


Figure 10. SEM images of primary and secondary sulphide minerals in the oxidised zones: (a) pseudomorphosis after primary sulphide (pyrite) (marked by yellow arrow) filled with a mixture of calcite, hematite, and Fe-Mg illite is present in cracks (blue arrows), sample P3A3; (b) pseudomorphosis after primary sulphide (pyrite) filled with azurite, sample P7A1; (c) pseudomorphosis (right side) after primary sulphide (pyrite) and sulfosalt (Zn-rich tennantite-Cu) filled with a mixture of Fe oxide and conicalcrite. Covellite (yellow arrows), calcite (green arrow), sample P7A1; (d) replacement of Cu sulphide (chalcocite) by azurite, enlarged in (e), sample P6A1; (e) enlarged view from (d) of replacement of Cu sulphide (chalcocite, green arrows) by azurite (yellow arrows), sample P6A1; (f) secondary sulphide relics (covellite, green arrows) in azurite (blue arrows) pseudomorphosis and host calcite (yellow arrows), sample P6A1.

5.2.2. Secondary Minerals in the Oxidised Zones

During the research performed in the present study the minerals Cu sulphide minerals chalcocite (Cu_2S) and covellite (CuS) were detected. They were identified in the studied samples (P6A1-1 and P7A1) using micro-area chemical analysis (Figure 10c–f). The size of these minerals is small (a few microns to 10–25 μm). They appear as relics in the secondary Cu carbonates (mainly azurite). We have to remark here that the primary or secondary origin of chalcocite in this Miedzianka deposit is still under debate (see Section 2.3).

Cuprite— Cu_2O . This mineral forms octahedral crystals or less often cubic crystals; more common are massive, compact varieties (Figure 8c,d). Its colour is dark red to cochineal red, sometimes black; compact varieties are brown-red. In transmitted light, thin

and small crystals of cuprite are translucent and have cochineal red colour (Figure 8c). It has exceptionally high relief ($n = 2.849$), is isotropic, and has no birefringence but sometimes exhibits anomalous birefringence [47]. Its colour in reflected light is bluish-white with internal blood-red reflections (Figure 8d). Cuprite is commonly formed as an oxidation product of copper sulphides in the upper zone of veins. In the studied samples it is often associated with azurite (Figure 8c). In the Teresa adit this mineral occurs in sample P6A1-1. Earthy and massive clusters of cuprite with Fe hydroxides formed the so-called “orange-red (brick colour) copper ore” [50], while the mixture of earthy clusters of cuprite, tenorite, and Fe oxide and hydroxide with silica formed the so-called “black (tarry colour) copper ore” [50] (Figure 8b).

Azurite— $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$. This mineral is typically found as tabular to prismatic crystals of a deep blue (“azure blue”) colour [18]. In the Teresa adit it occurs as fine-grained massive aggregates or earthy clusters (Figure 8c) as well as fibrous aggregates (Figures 8e and 10d). In transmitted light, azurite is transparent or translucent and has a blue colour (Figure 8c,e). The mineral has high surface relief ($n_\alpha = 1.730$, $n_\beta = 1.758$, $n_\gamma = 1.830$) and high birefringence ($\delta = 0.108$). Its pleochroism is visible in blue tones (in plane-polarised light) [49]. Azurite often fills pseudomorphoses after primary and secondary sulphides (Figure 10d–f) and secondary Cu oxides (Figure 8c). This mineral also occurs in veinlets (Figure 8e). XRD data of azurite (the sample P6A2-1 blue) are presented in Tables 1 and 2, and Figure 7. Optimized/calculated unit cell parameters of azurite from the Teresa adit (sample P6A2-1 blue) follow, and are identical to the parameters of the standard from the AMCSD database:

- $a = 5.0150 \pm 0.0063$
- $b = 5.8482 \pm 0.0092$
- $c = 10.349 \pm 0.012$
- $\beta = 92.48^\circ \pm 0.10$

These data indicate a lack of significant atomic substitutions in the mineral structure.

Malachite— $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$. Similar to azurite, malachite is formed as a result of the oxidation of copper ore. In the samples studied from the Teresa adit, malachite is rare compared to azurite. This mineral occurs as massive, compact, or earthy clusters in veinlets in Devonian limestones (Figure 8f). Crystalline, radiate clusters of malachite are uncommon in the studied samples. Small crystals are rarely observed [6]. In transmitted light it is transparent and has a green colour (Figure 8f). Pleochroism is visible: X—nearly colourless, Y—yellowish green, Z—deep green. Surface relief is very high ($n_\alpha = 1.655$, $n_\beta = 1.875$, $n_\gamma = 1.909$); birefringence is also very high ($\delta = 0.254$) [49].

XRD data of malachite (samples P6A1-1 green and P6A1-1 black) are presented in Tables 1 and 2, and Figure 7. Calculated unit cell parameters of malachite from the Teresa adit (samples P7A2-1 green and P7A2-1 black) are as follows:

Sample P7A2-1 green:

- $a = 9.492 \pm 0.027$
- $b = 11.946 \pm 0.025$
- $c = 3.2441 \pm 0.0082$
- $\beta = 98.56^\circ \pm 0.20$

Sample P7A2-1 black:

- $a = 9.493 \pm 0.038$
- $b = 11.943 \pm 0.033$
- $c = 3.243 \pm 0.012$
- $\beta = 98.55^\circ \pm 0.30$

Both are very close to the standards from AMCSD. Small admixtures of bigger atoms of Ag or Au in the structure can lead to slight deformations of the unit cell and thus a decrease in a and b parameters with an increase in the c parameter in comparison to the values from AMCSD.

Hematite— Fe_2O_3 . Fe oxide is an opaque mineral that has brown to reddish-brown colours (Figure 8g,h). This mineral occurs as fibrous masses, sometimes radiating or in reniform masses with a smooth fracture “kidney ore” (Figure 8g). It is frequently in earthy masses in veinlets or in stylolite seams in Devonian limestones. Hematite has very high surface relief ($n_\omega = 3.150$ – 3.220 , $n_\epsilon = 2.870$ – 2.940) and high birefringence ($\delta = 0.280$) [49]. In transmitted light, pleochroism is weak from brownish-red to yellowish-red (Figure 8g).

In reflected light this mineral is white to greyish-white with a bluish tint (Figure 8h). The mineral filled the pseudomorphoses after primary sulphides and occurs in veinlets (Figures 8g,h and 10a). It also occurs in the pseudomorphoses after primary sulphides accompanied by primary sulphide pyrite and sulfosalt Zn-rich tennantite-Cu (historical name “miedziankite”) Figure 10c. XRD investigations showed the presence of hematite in sample P4A2-1 (Table 1, Figure 7). Very small crystals of hematite are scattered in limestones (sample P6A1, Figure 9d) and in creme-pinkish calcite veinlets (sample P3A3, Figure 9c). Sometimes, hematite has the admixture of V_2O_5 0.6 wt.% (limit of detection for EDS \pm 0.05) as shown in the microprobe chemical analysis of sample P3A3.

Illite flakes occur in nests in Devonian limestones (Figure 9e,f). They are very small in size, up to 3 μ m. Illite together with calcite and micro-crystalline quartz/silica is found in fractures in limestones (Figure 10a). XRD investigations showed the presence of illite in sample P4A2-1 (Table 1, Figure 7). Based on the microprobe chemical analysis, it was found that the composition of this mineral includes FeO 3.3 wt.% (limit of detection for EDS \pm 0.03) and MgO 3.0 wt.% (limit of detection for EDS \pm 0.04). The occurrence of this mineral in nest and karst fractures in Devonian limestones is connected to the weathering processes and the development of karst on the exposed limestone surface during the Permian/Early Triassic.

6. Discussion

The Teresa adit is one of the oldest adits in Miedzianka Mountain. It was hollowed in 1805 by the Austrians, then expanded many times and was finally connected to the natural cave system. A preliminary description of the Teresa adit exploration was presented by Borowiecki et al. [9], which focused on technical issues related to safety and adaptation for tourism purposes. Furthermore, in the work of Ciurej et al. [10] there is a description of the adit, its pavements, and the natural corridors of the cave.

In the Miedzianka Mountain copper deposit, 40 minerals, both primary and secondary, have been described [8]. Paragenesis of primary ore minerals was described in the works of researchers for over 100 years [6,7,22,24–27,33,37] and include the chalcopyrite, tennantite variety (“miedziankite”), and galena.

In the samples collected in the Teresa adit, only one mineral of this paragenesis was found, unfortunately in the form of relics of the primary chalcopyrite in a pseudomorphosis filled with secondary cuprite (Figure 8d). Relics of primary chalcopyrite surrounded by cuprite in the Miedzianka deposits was for the first time described in this paper. In this study, the copper sulphides covellite (Figure 10f) and chalcocite (Figure 10e,d) were found.

The origin of the chalcocite is still not clear, whether it is a primary or secondary mineral, as was mentioned in Section 2.3. According to Rubinowski [6,51], the formation of these minerals is related to the stage of weathering of the primary deposit, the so-called weathering stage. Balcerzak et al. [7] described that chalcocite occurs in the veins in the primary zone, which could suggest its primary origin, although they do not exclude the possibility of the formation of this mineral as a result of chalcocite migration from the altered ores (oxidised and karstic secondary ores) and by distention solutions. Balcerzak et al. [7] determined that chalcocite was formed at a temperature not higher than 103 °C. Chalcocite is formed in reducing conditions as the first sulphide mineral in the secondary sulphide cementation zone [41]. Covellite is also related to the secondary sulphide paragenesis, but it is formed later during cementation processes.

During this stage, apart from the formation of secondary copper sulphides, copper oxides, mainly cuprite, were formed, which was described in our work. In sample P6 (Figure 8c,d) a pseudomorphosis filled with cuprite with relics of primary chalcopyrite was found. Cuprite is formed at a lower partial pressure of O_2 than tennantite [41].

The release of iron during primary chalcopyrite weathering is indicated by the presence of veins of goethite (Figure 8f) and hematite (Figures 7 and 8g,h) in the limestones. Also, the two generations of rosa-like calcite (older (red) and younger (creme-pinkish) veins) found in limestones are coloured with diffused hematite pigment (Figures 8a and 9c).

Copper carbonate mineralisation (azurite and malachite) is visible in many thin veins (Figure 6c,d), and can also be found in the creme-pinkish veins of calcite (Figure 6d). The formation of these minerals is related to the last stage of cupriferous mineralisation—the adsorption stage [6,51]. Then, the clay residue, formed after the dissolution of the limestones in the karsting process, became a medium carrying copper ions, which was facilitated by the network of cracks in the limestones. It was then that nests were created in unchanged/partially karstic Devonian limestones filled with copper carbonates (azurite and malachite—Figure 6c,d). Azurite forms in the oxidation zone initially. This mineral precipitates under slightly acid conditions (pH ca. 6.95 [52]), and then locally turns into malachite. We can observe such a process in Figure 8e. Malachite forms under neutral to slightly basic pH conditions [52] during the neutralization of acidic supergene solutions by Devonian limestones. In samples taken from the Teresa adit it can be observed that azurite not only forms nests in the limestones (Figure 6d), but also occurs in pseudomorphoses, where relics of copper sulphides can still be observed: chalcocite (Figure 10d,e) and covellite (Figure 10f) as well as the copper oxide cuprite (Figure 8c). Malachite, similarly to azurite, occurs in the form of fibrous aggregates (Figure 8e,f).

Devonian limestones in the Miedzianka Mountain deposit are strongly tectonically fractured and cut by numerous veins of different colours (Figure 6a). Fragments of red veins strongly stained with hematite can be observed (Figure 6a,b). Calcite veins with hematite in limestones and their mechanism of formation were described by Bąk et al. [53] and Bąk et al. [54]. Rubinowski [6] described two generations of veins. The oldest generation of calcite is of a rosa-like calcite type. Creme-pinkish calcite veins can be observed in the studied Devonian limestones from the Teresa adit (Figures 6a and 8a), and belong to the younger generation of calcite [6]. According to Migaszewski et al. [55], it is the so-called younger post-Variscan mineralisation. This calcite is the most common in the Miedzianka Mountain deposit and was formed in conditions typical of the terrestrial environment, characterised by strongly developed karst processes, as determined by isotope studies (C, O, and Sr) carried out by Migaszewski et al. [55]. Micro-area chemical analysis of the calcite from the creme-pinkish vein revealed the presence of scattered very small grains of hematite with V_2O_5 admixture. The presence of hematite containing vanadium, which occurs in creme-pinkish calcite veins in Devonian limestones, was for the first time described in this paper. The colour of calcite is related to various amounts of disseminated hematite. The oxidation of iron minerals in limestones occurs during the processes of weathering and karsting, and results in the appearance of a red colour in limestones and veins caused by the presence of small grains of hematite [56].

Rubinowski [6] described the occurrence of clay residuum in Devonian limestones in the Miedzianka Mountain deposit, and suggested that it was a medium that transferred copper ions into fractured Devonian limestones and was responsible for the formation of copper carbonates. This author also believed that this process was related to the adsorption stage in the evolution of the copper deposit on Miedzianka Mountain [6]. During our study of Devonian limestones we managed to find the clay residuum in limestone microcracks, and we have defined its mineral composition. Our research showed that the residuum, formed after the dissolution of limestones during the karsting process, is composed of a mixture of Fe-Mg illite and micro-crystalline quartz/silica (Figures 7, 9f and 10a). In addition, isolated azurite nest was found in limestones (Figure 10b), which might be evidence of the transfer by clay minerals (illite) of copper ions in the limestones. Taking into account Rubinowski's hypothesis [6] concerning the adsorption stage of copper-bearing mineralisation as well as our results, we proposed a model of the formation of copper carbonates in the adsorption stage of copper-bearing mineralisation in the Miedzianka Mountain deposit, presented in Figure 11.

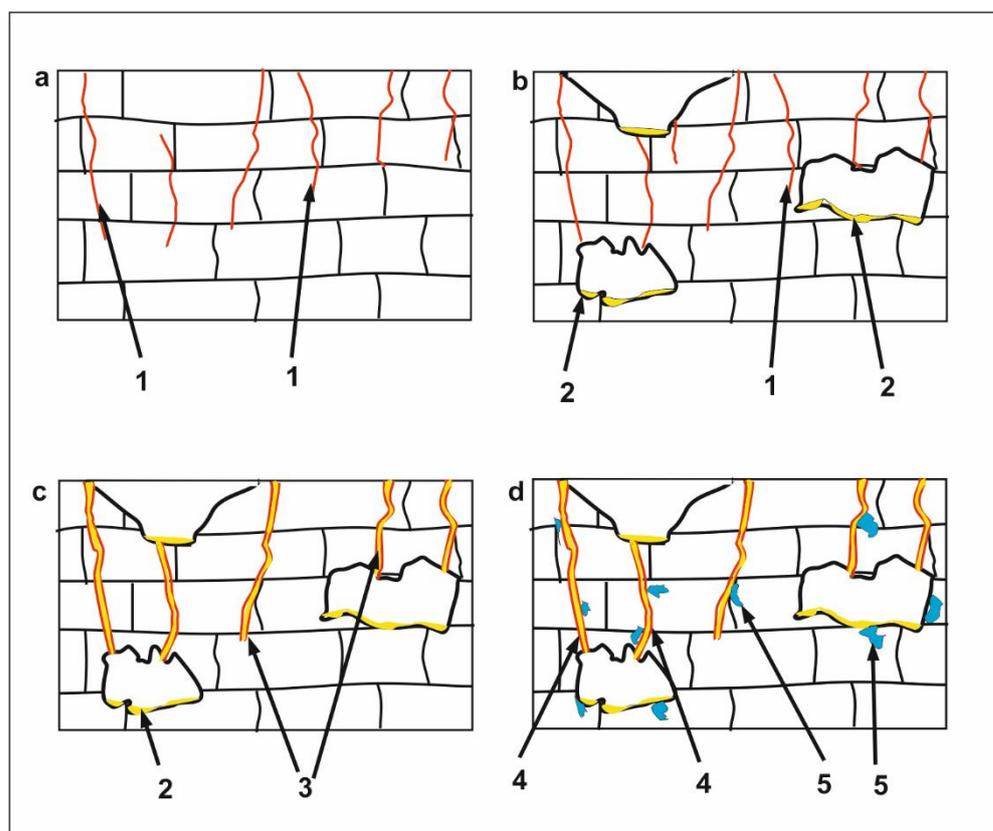


Figure 11. Scheme of formation of azurite nests, Fe-Mg illite, and fine crystalline silica within microcracks in Devonian limestones in the adsorption stage (see [6]). Not to scale. (a,b)—stages of dissolution of limestones during karstification; (c,d)—stages of adsorptive mineralisation. Legend: 1—microcracks in limestones; 2—karst voids with residuum of clay minerals and microcrystalline silica; 3—microcracks with residuum of clay minerals (illite) + solution with ions of Cu^{2+} and Fe^{2+} ; 4—Fe-Mg illite and microcrystalline silica in microcracks (see Figure 10a); 5—nests of azurite (see Figure 9b).

7. Summary

Our investigation of the Teresa adit shows that mineralisation occurs as veins of irregular shapes with various minerals. The minerals detected in the studied samples are copper minerals (primary and secondary) and rock-forming minerals.

The primary minerals occurring only as relics of chalcopyrite were developed during hydrothermal mineralisation (the first stage of mineralisation). Secondary minerals are developed during: (a) weathering and karstification processes (the second stage of mineralisation), namely, secondary copper sulphides, copper oxides, and iron oxides including chalcocite, covellite, cuprite, and hematite; and (b) adsorptive mineralisation (the third stage of mineralisation), namely, azurite and malachite.

Our investigations show for the first time the presence of secondary cuprite with relics of primary chalcopyrite in the studied deposit. Moreover, the disseminated hematite with admixture of vanadium, which occurs in younger creme-pinkish calcite veins, was not described previously in this deposit. Although clay minerals (illite) are common minerals in sedimentary rocks, it has not been described in limestones in the Miedzianka deposit previously. We found Fe-Mg illite together with fine-grained silica in cracks in limestones (Figures 9f and 10a). We proposed a model of the formation of copper carbonates in the adsorption stage of copper-bearing mineralisation in the Miedzianka Mountain deposit (Figure 11). In addition, for the first time unit cell parameters of malachite and azurite from Miedzianka Mountain were determined. The data indicated very low substitutions of atoms other than Cu in their structures (Table 1), probably silver and gold.

The presence of the minerals described in the Miedzianka deposit suggest that it is a deeply weathered deposit of copper sulphide with Pb-Zn hydrothermal veins. These minerals' parageneses are known from the Mississippi Valley deposit types.

The collected samples together with the detailed results described in this paper will be donated to the Museum Chamber of Ore Mining in Miedzianka located in Miedzianka village. The aim of our work was to enlarge the museum's collection of mineralogical specimens from the Teresa adit in the Miedzianka Mountain deposit. We are convinced that the set of samples collected in the Teresa adit and studied in this paper will certainly enrich the scientific and educational activity of this public institution.

The described minerals from samples in situ collected at seven points in the Teresa adit may constitute the basis for the graphic design of information boards in the planned underground geotourist route in the Teresa adit on Miedzianka Mountain [9].

Our research leads to the conclusion that, despite the fact that the Miedzianka Mountain deposit is already exhausted and not exploited, and has been studied in various aspects for almost 200 years, it still has great scientific potential. Findings of paragenesis of various minerals in heaps and in adits are still being described. Therefore, the study of old deposits usually extends knowledge with new scientific aspects, as presented in many works on various ore and historical deposits in Europe, e.g., Lavrion Mines in Greece [57], the Sulcis, Sardinia, Italy [58], Eastern Liguria, Italy [59], Wieliczka Salt Mine [60], Jachymoc, Czech Republic [61], Freiberg, Germany [62], and Zemplín, Slovakia [63].

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