A new type of carbonate-hosted Au mineralization at Dúbrava near Rochovce, Western Carpathians

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Abstract: A unique metallogenic type of Au mineralization was discovered in Mesozoic carbonates belonging to the Bôrka nappe accretion mélange near Rochovce. The mineralization is structurally controlled by faults formed during several stages of Alpine deformation. Widespread dolomitization, along with sericite and pyrite alteration of marbles, indicate extensive hydrothermal activity along the Lubeník – Margecany thrust fault. The earlier period of Au mineralization is linked to N – S structures, hosting coarse-grained zonal gold accompanied by minor silicification. This indicates that the mineralization differs from typical Carlin style deposits. Zonal textures of gold with inward Ag diffusion, together with aurostibite inclusions, indicate a sulphur-deficient environment during the late stages of hydrothermal evolution. Later base-metal mineralization is related to the NE – SW fault zones displacing the Au-bearing structures. The presence of various assemblages of Pb-Zn-Sb-As secondary minerals (segnitite, mimetite, oxyplumboroméite, arsendescloizite, austinite) originated from slightly acidic fluids as a result of pyrite oxidation. The studied locality is geochemically similar to other gold and polymetallic occurrences within 5 km of the Rochovce granite, which can be interpreted as intrusion-related and/or heat energy driven types of mineralization. However, this type of mineral association in carbonate host rock with specific alterations is quite unusual. **Key words:** Rochovce granite, gold, aurostibite, adelite group minerals, roméite group minerals, mimetite, segnitite

1. INTRODUCTION

Ochtiná and Rochovce villages in eastern Slovakia are famous for mining of magnesite and metasomatic siderite ore in the past. Well-known here is also the occurrence of Cretaceous granite intrusion, which is unique in the area of the Western Carpathians. Near to the intrusion, there are rich accumulations of various types of ores present. The porphyry W-Mo mineralization is the most important, with the economically promising resources. Besides, this intrusion is considered to be responsible for the formation of numerous Pb, Zn, Sb, Fe and As mineralizations, located along the Lubeník-Margecany fault structure (Slavkay et al., 2004). First notes about Au occurrence in this area (specifically in Drábska) are reported by Gargulák et al. (1995) who found the Au grade of 1.36 g/t. Later discoveries mention Au from Dubiná, north of the village of Rochovce (Maťová & Kusein, 2001).

In this study, preliminary results of exploration activities from the proximity of the Rochovce intrusion carried out by Rodinia Company are reported. New Au occurrences and polymetallic mineralization are described. The focus is put on the mineralization at Dúbrava located in Mesozoic carbonates of the Bôrka nappe.

2. BACKGROUND

Gold mining activities at Rochovce are only briefly mentioned in local memorials (Miklôšik, 1961). Based on the findings of iron picks at Dúbrava, mining activities can be dated here back to the Middle Ages. The first note in literature is from the mid-19th century where the occurrence of Pb-Zn at the Mária-Margita site is reported (Eisele, 1907). At the end of 19th century, the Mária-Margita deposit was owned by a Prussian businessman T. Lange, but he has stopped all mining activities in 1911. In 1930's, the exploration was led by A.K. Horal, who sold the mining rights in 1937 to the Bata Company (Horal, 1971). Besides the Mária-Margita deposit, the exploration activities were focused on the area of Dubiná-Drábska with Pb-Zn mineralization. Mining period lasted until the Second World War (with a few closure periods). Exploration from 1949 to 1954 was restored by the Východoslovenský rudný prieskum Company. In the Margita adit, 2070 t of ore containing 8.73 wt. % Zn, 3.08 wt. % Pb, 0.37 wt. % Cu, 99 g/t Ag and 0.02 g/t Au was estimated (Ilavský et al., 1956). In the Ilona adit, stockwork with pyrite-arsenopyrite mineralization and local occurrence of Pb-Zn mineralization were detected (Abonyi & Ševčík, 1958). At the end of 1990's, further exploration activities were undertaken by the Aurex Company (Maťová & Kusein, 2001). In Dubiná, an Au anomaly was defined by soil geochemistry and 15 holes with the total depth of 632 m were drilled here. The richest mineralization was found in the VVS-25 drillhole at the depth of 13 - 18 m with the average Au concentration of 2.2 g/t (max. 5.3 g/t Au at 16.5 - 17 m).

At the Mária-Margita deposit, geochemical and metallogenic research was performed by Pouba (1953), Ilavský & Beňo (1958), Kozlovský (1977), Václav (1962, 1963, 1965, 1981). Primary mineralization was studied by Hraško et al. (2005) and Števko et al. (2009). Secondary minerals from the Mária-Margita deposit were also studied by Mrázek & Ďuďa (1983) and recently by Števko & Bálintová (2008). The area of Dubiná-Drábska was investigated by Gargulák et al. (1995), who distinguished there three generations of mineralization.

3. GEOLOGY

The studied area is adjacent to the contact zone of the Lubeník-Margecany line (LML), located between the Veporic and Gemeric Superunits (Fig. 1). These units represent two collided terrains with different origin and geology: the West-Carpathians and the African micro-plates, which were tectonically overlain by allochthonous Mesozoic nappes during the Cretaceous Eo-Alpine convergence (Plašienka et al., 1997). The Gemeric Superunit (African micro-plate) overrode the Veporic Superunit. As a result of this collision, a large-scale overprint of both superunits occurred and extensive shear zones developed along the thrust zone (Németh et al., 2001; Grecula et al., 2011). The lithology of the contact zone consists of the Veporic clastic meta-sediments in the footwall (Revúca Group) and Gemeric dark chlorite phyllites in the hanging wall (Ochtiná Group). The Bôrka nappe occurs as a tectonic outlier lying on the Gemeric Superunit as a member of the Meliata subduction-accretionary complex of the Jurassic age (Faryad & Henjes-Kunst, 1997). The rock composition corresponds to different types of metabasalts in association with metacarbonates and metapelites.

An extensional tectonic regime that followed the nappestack led to the emplacement of the Upper Cretaceous Rochovce granite, which caused contact-metamorphism of the Upper Palaeozoic metasediments and metavolcanics of the Gemeric and Veporic superunits. It was classified as an I-type granite of calc-alkaline, subaluminious to peraluminious character. The magmatic body consists of first stage coarse-grained monzogranite with granite porphyry in its apical part and the second stage medium- to fine-grained leucogranite and leucogranite porphyry (Határ et al., 1989; Kohút et al., 2013). According to geophysical data, the intrusion follows LML (Fig. 1) and the NE block of intrusion was sunken by the younger NW - SE Štítnik fault system (Filo et al., 1991). Continued extension of the contact zone resulted in emplacement of several vein mineralizations types, including Au, As, Pb, Zn, Sb, Mo, and W (Fig. 1). Occurrences of ore mineralization near to the studied locality are typically accompanied by intensive pyritization along mineralized subvertical



Fig. 1 Simplified geological map of the Lubeník – Margecany line in the area close to the village of Rochovce. Pyritization and localities with different types of ore mineralization are spatially related to the underlying Rochovce granite intrusion. Pyritization zone possibly continues to the southwest and to the north – not verified. 1 – Dúbrava, 2 – Mária-Margita, 3 – Dubiná, 4 – Dubiná-Drábska, 5 – Oriešok, 6 – Slavošovce-Za Hôrkou, 7 – Lašanka, 8 – Ochtiná, 9 -Hrádok, 10 – Jelšava-Galmajka, 11 – Kopráš-Skaličná, 12 – Mníšany-Karol, 13 – Chyžné-Kubej, Herichová.

fractures forming stockwork or breccia at some places. Pyritization also forms a characteristic alteration halo around the W-Mo Ochtiná porphyry deposit and other sulphidic occurrences close to the Rochovce granite intrusion (Slavkay et al., 2004). These mineral occurrences represent the northernmost continuation of mineralization associated with the Cretaceous calc-alkaline magmatism within the Alpine-Balkan-Carpathian-Dinaride metallogenic belt (Kohút et al., 2013).

4. METHODS

Reconnaissance and mapping of the locality and surrounding area (approx. 2 km radius) was focused on lithology, structural mapping (foliation, faults, joints) and zones of alteration. Detailed mapping was performed in underground historic stopes. Obtained data were digitized in ArcMap 10.6 and structural measurements were processed in Orient 3.9.1 software (Vollmer, 2019).

Samples for the mineralogical study were collected from waste dumps of old workings at Dúbrava. Gold with the heavy fraction was obtained by panning of waste rock in a nearby stream. Several types of secondary minerals and gold were separated, and the polished sections were prepared. Standard thin sections $(30 \,\mu m)$ of representative carbonate host rock were studied in transmitted and reflected light. Electron microprobe analyses (EMPA) of native Au, carbonates and secondary minerals were performed on a JEOL JXA 8530FE microprobe in a wavelengthdispersive mode (WDS) at the Earth Sciences Institute of Slovak Academy of Sciences in Banská Bystrica under the following conditions: gold – accelerating voltage 20 kV, probe current 20 nA, beam diameter $2 - 3 \mu m$; carbonates – accelerating voltage 15 kV, probe current 16 nA, beam diameter 8 µm; secondary minerals - accelerating voltage 15 kV, probe current 15 nA, beam diameter 2 – 8 µm, ZAF correction, counting time 10 s on peak, 5 s on background. The following standards were used: Au(Ma) – pure Au, Ag(La) – pure Ag, S(Ka) – pyrite, Cu(Ka) and $Fe(K\alpha)$ – chalcopyrite, $Hg(M\alpha)$ – cinnabar, $Bi(L\alpha)$ – Bi2S3, Te(La) - CdTe, Sb(La) - stibnite, Ni(Ka) - pentlandite. For carbonates: $Ca(K\alpha)$ and $Mg(K\alpha)$ – diopside, $Sr(L\alpha)$ – celestite, $Mn(K\alpha)$ – rhodonite, $Ba(L\alpha)$ – barite, $Fe(K\alpha)$ – hematite. For secondary minerals: $As(L\alpha) - GaAs$, $Pb(M\beta) - crocoite$, $Ca(K\alpha)$ - diopside, $Cu(K\alpha)$ - cuprite, $Zn(K\alpha)$ - gahnite, $Mn(K\alpha)$ - rhodonite, $Fe(K\alpha)$ – hematite, $Sb(L\alpha)$ – stibnite, $Sr(L\alpha)$ – celestite, $Ba(L\alpha)$ and $S(K\alpha)$ – barite, $P(K\alpha)$ – apatite, $Al(K\alpha)$ – corundum, Na(Ka) – albite, Si(Ka) – quartz, V(Ka) – ScVo4, Cl(Ka) – tugtupite, $F(K\alpha)$ – fluorite, $K(K\alpha)$ – orthoclase. Energy-dispersive mode (EDS) was used to identify pyrite.

Raman spectroscopy analyses were performed with a Horiba Jobin-Yvon LabRAM HR 800 spectrometer at the Earth Science Institute of Slovak Academy of Sciences in Banská Bystrica. The Raman spectrometer was equipped with a Czerny-Turner monochromator, 600 gr/mm grating, a Peltier-cooled CCD detector Synapse (Horiba Jobin-Yvon), coupled with an Olympus BX51 microscope with a long working distance 100×/0.8 objective. Samples were irradiated by He-Ne (633 nm) and Nd:YAG (532 nm) lasers with power of about 3 mW on a sample. Rayleigh line (0 cm^{-1}) and Teflon standard were used for calibration. The spectra were collected in two acquisitions in the range of $70-4000 \text{ cm}^{-1}$ lasting 50 s per spectral window. Obtained spectra were processed (baseline correction, normalization) using the LabSpec 5 software (Horiba Jobin-Yvon).

All composite or rock chip samples selected for whole rock analyses were sent to ALS Global Rosia Montana laboratory (Romania). The samples were weighed, dried and milled so that minimum 70 % of each sample was in fraction < 2 mm. Later, quartered parts of samples with weight of 250 g were milled so that minimum 85 % of each sample has reached the grain size < 0.075 mm. Gold was analyzed in 30 g of sample using fire assay by AAS (methodology code Au-AA25). The detection limit of this method is 0.01 ppm. Other elements were analyzed in the Lougrea Laboratory (Ireland) using 0.5 g of sample by Aqua Regia digestion with ICP-MS finish (analytical code ME-MS41). Detection limits for this method are available at https:// www.alsglobal.com/en/services-and-products/geochemistry/ geochemistry-downloads.

5. RESULTS

The Au and Pb-Zn-Sb-As mineralization at Dúbrava is located in dolomitized marbles of the Bôrka nappe, Meliata Unit. Dolomitized carbonates form a non-continuous 15 km long zone from Dúbrava (close to Jelšava town), Hrádok, Dúbrava (close to Rochovce village), Vysoká Hora to Kobeliarovo village. The thickness of altered carbonates is from a few cm to 250 – 300 m. Several ore mineralization occurrences were described in the nearby area (Fig. 1), but in this paper, we will discuss only the localities adjacent to Dúbrava hill.

The Au-Ag and base metal mineralization at Mária-Margita is hosted by altered carbonate rocks, similar to the Dúbrava locality, which is situated 800 m north. Mineralization follows N – S and NW – SE fault structures and contact of metabasics with dolomitized marble. According to recent sampling, the mineralization at the Mária-Margita deposit is enriched in Au (mostly 0.X ppm with the maximum grade of 1.74 ppm), Ag (max. 582 ppm), Zn (max. 38.67 wt. %), Pb (max. 11.75 wt. %), Cu (max. 1.04 wt. %), Sb (> 1.00 wt. %), Hg (max. 0.13 wt. %), Cd (> 1000 ppm). The As grades are quite low (max. 79.9 ppm).

In SE direction approximately 1400 m from the Dúbrava locality, close to the village of Roštár, a new undescribed occurrence of polymetallic mineralization in dolomitized carbonates, similar to the mineralization at Dúbrava, was found.

There is a group of exploration pits located 400 m north of the Dúbrava locality, probably to check the carbonate stockwork containing pyrite and gold in mylonitized phyllites of the Ochtiná Group. Furthermore, a 100 – 200 m long adit in NE direction confirmed the continuation of this mineralization but panning showed only low amounts of Au in mylonitic graphitic phyllites.

At the Dubiná-Drábska locality, situated 650 m west of Dúbrava hill, Pb-Zn and Au-As mineralization is located on the LML contact zone between the Ochtiná group phyllites and the Verporic Rimava formation meta-arkoses. Typical ore is represented by the stockwork with abundant pyrite, sphalerite, galena and locally sulphosalts and arsenopyrite. Au grades reach up to 1.19 ppm and mineralization is also enriched in Zn (max. 4.32 wt. %), Pb (max. 3.51 wt. %), As (> 1.00 wt. %) and Ag (max. 158 ppm). The concentrations of other metals are relatively low.



Fig. 2 Detailed geological map of Dúbrava hill on Lidar base map showing the shaded relief. Mineralized structures are interpreted according to old workings visible on Lidar and the mineralogical, geochemical and structural observations.

5.1. General characteristics of the mineralization

5.1.1. Au mineralization

Based on the extent of historical workings, the ore structures at Dúbrava reach the length of 320 m (Fig. 2). The mineralization follows N - S strike and it is present in 3 parallel zones which are 35 – 75 m apart from each other. The largest stopes are in the northern part of the locality, close to the transition zone between altered and non-altered marbles (Fig. 3). The thickness of mined structure reaches here up to 1 - 1.5 m. Relatively extensive mining is apparent also in the southern part of the locality at the contact zone between metabasics and altered marble and intersections of N - S and NE - SW structures with Pb-Zn-Sb-As mineralization. Based on these findings, it is assumed that the Au mineralization has a bonanza character with several ore shoots. The stopes in the northern part of the locality indicate the presence of a high-grade ore shoot dipping 40 – 500 south. The maximum depth of the old workings is unknown; however, it reaches at least to 25 m accessible depth. It is estimated that 3000 – 3500 tons of ore were mined here (15 to 17 kg Au at 5 ppm Au cut-off).

The large diameter of the historical shafts in the south and the middle part of the locality indicates their minimal depth of 20 m. The estimation of the mined ore volume in this part is complicated because of missing data.

The ore in stopes is hosted by dolomite stockwork to initial breccia of dolomized and sericitized marble (Fig. 4) and locally by monomict breccias with subangular clasts. The most common alteration mineral is pyrite and locally quartz. The amount of pyrite varies, from weak disseminations to rich impregnations with more than 10 % of pyrite. At the transition zone of altered marbles with non-altered marbles in the north part of the locality, coarse-grained calcite occurs in the form of veins and zones parallel to foliation or N – S structures. Metabasites at the contact zone with dolomitized marble are sericitized and carbonatized but barren. Dolomitized marble in the contact zone also locally hosts a quartz stockwork, with veins up to tens



Fig. 3 Detail map of stopes and geological and tectonic setting of the northern part of the Dúbrava locality.



Fig. 4 Typical texture of altered marble from the Dúbrava locality. Thin veinlets of dolomite II and calcite II intersect the dolomite I matrix.

of centimeters of NE – SW direction. The amount of quartz reaches here > 50 %. The thickness of the high intensity quartz stockwork zone is 14 m.

Whole rock assays of waste piles belonging to the N – S gold bearing structure range from 0.0X ppm to 58 ppm Au (average 2.86 ppm out of 26 samples). The amount of Ag is low, maximum 0.32 ppm. Concentrations of As reach up to 593 ppm and Mn up to 0.2 wt. %. Maximum contents of Pb, Zn, and Sb are 47 ppm, 55 ppm and 34 ppm, respectively. Concentration of other metal elements is very low (Cu up to 4.2 ppm, Hg 0.2 ppm, Bi 0.2 ppm, Mo 1.0 ppm, W 0.2 ppm, etc.) in contrast to adjacent localities with sulphidic mineralization.

5.1.2. Pb-Zn-Sb-As mineralization

The study of primary mineralization on NE – SW structures was complicated because the rock was strongly oxidized. Therefore, only the secondary mineral assemblage was studied. The waste pile material consists of friable dolomite and ore minerals could be obtained only by panning. Exceptionally, dolomites with druses of thin quartz crystals and oxyplumboroméite are present. The average Au content in 15 samples is 1.1 ppm. Six samples were analyzed for multi elements with average values 13.7 ppm Ag, 0.60 % Zn, 1.03 % Pb, 0.33 % Sb, 0.10 % Cu, and 0.60 % As. Concentrations of other elements were not anomalously increased.

5.2. Structural data

This study is focused on fault structures, since the mineralization is present as fault-related veins or stockwork zones. The most important tectonic regional feature is the LML of N - Sdirection. Based on our observations, the oldest structures are represented by N - S faults, which also host the Au mineralization at Dúbrava. The strike of the main mineralization in stopes is 185° with 82° dip to the west. North-south extension structures are filled with Fe-dolomite, calcite, and pyrite. At Dubiná-Drábska, structures are filled mostly with pyrite, less galena and sphalerite. Usually N - S structures in approx.



Fig. 5 a, b, c Structural measurements of the three main fault systems of the Dúbrava locality vicinity (approx. 2 km radius).

2 km radius around the Dúbrava locality are quite steep, and the general dip direction is difficult to determine (Fig. 5a).

N-S structures are distorted by younger, generally steep (~ 80°) NW – SE faults, dipping to NE following the Štítnik and Rochovce faults (Fig. 5b). At the Mária-Margita deposit, the Pb-Zn-Cu-Ag-Sb ± Au mineralization is hosted by several parallel structures of NW – SE direction, and also karstification on the west slope of Dúbrava hill.

NE – SW faults are another important brittle tectonic structure. Their dip is subvertical to 35°, oriented towards NW and SE (Fig. 5c). At Dúbrava, these fault structures host Pb-Zn-Sb-As mineralization and cut the main N – S oriented Au mineralization, as observed in underground workings.

Subhorizontal faults were observed in stopes only at Dúbrava. These faults cause a local step-like displacement (tens cm up to 2 m) of the main Au-bearing N – S structure to the west (Fig. 3). Succession of NW – SE and NE – SW faults is unclear.

5.3. Mineralogy

5.3.1. Primary phases

Gold and electrum in the heavy-mineral concentrate occur as free anhedral grains usually up to 300 μ m in size, maximum of 2 mm. Aggregates of gold are cemented by carbonates (calcite, dolomite) and gangue quartz. Gold also penetrates fractures and replaces Fe oxyhydroxides representing pseudomorphs after pyrite (Fig. 6a). Chemically, the gold grains are very heterogeneous (Fig. 6b) and 3 different Au-Ag alloys were distinguished (Fig. 7). Au-I represents a relatively homogenous Au-Ag alloy, usually containing 12 – 19 at. % Ag. This phase is the most abundant, commonly distributed in the central part of Au aggregates (Fig. 6b) and contains up to 0.54 at. % Hg. Au-II and Au-III usually forms diffuse zones filling interstices of Au-I aggregates or rims around Au-I grains with diffusive, but locally sharp contacts (Fig. 6b). Low-fineness Au-II alloy reach the concentration of Ag 42 - 50 at. % (electrum) and have the highest Hg content up to 1.35 at. %. Au-III represents a highfineness native gold usually contain < 3.84 at. % of Ag and have the lowest Hg content maximum 0.34 at. %. All analytical data from gold grains are plotted in a ternary Au-Ag-Sb diagram in Fig. 7. The content of other trace elements (Cu, Bi, Sb, Te) analyzed by EPMA is below or close to detection limits in both Au generations (Tab. 1).

Tab. 2. Chemical composition of aurostibite from the Dúbrava locality, formula is based on 3 apfu.

Wt. %			DUB-1		
Ag	0.02	0.02	0.03	0.00	0.02
Sb	53.31	53.30	53.26	53.37	54.00
Ni	0.00	0.00	0.02	0.02	0.00
Au	45.96	46.09	46.00	46.49	43.85
Bi	0.05	0.03	0.00	0.18	0.20
S	0.02	0.00	0.02	0.00	0.00
Hg	0.00	0.00	0.00	0.42	0.94
Total	99.37	99.44	99.33	100.48	99.02
Atoms pe	er formula uni	it			
Ag	0.00	0.00	0.00	0.00	0.00
Sb	1.95	1.95	1.95	1.94	1.98
Ni	0.00	0.00	0.00	0.00	0.00
Au	1.04	1.04	1.04	1.05	0.99
Bi	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00
Hg	0.00	0.00	0.00	0.01	0.02
Total	2 00	2 00	2 00	2 01	2 00
iotai	2.99	2.99	2.99	5.01	2.99

Tab. 1. Chemical composition of gold from the Dúbrava locality.

Wt. %		Au I			Au II			Au III	
Ag	7.68	8.32	9.82	31.76	34.84	35.49	0.69	1.59	2.41
Sb	0.00	0.00	0.01	0.09	0.24	0.19	0.01	0.00	0.01
Ni	0.00	0.01	0.01	0.00	0.00	0.01	0.03	0.03	0.01
Fe	0.02	0.03	0.00	0.19	0.01	0.02	0.10	0.00	0.04
Те	0.04	0.08	0.01	0.08	0.08	0.08	0.00	0.00	0.00
Au	92.05	90.59	90.81	66.30	63.78	62.78	98.53	98.11	97.59
Bi	0.16	0.24	0.04	0.38	0.00	0.14	0.00	0.10	0.08
S	0.04	0.02	0.00	0.02	0.03	0.01	0.01	0.03	0.00
Hg	0.50	0.59	0.46	1.18	1.80	1.48	0.20	0.20	0.07
Total	100.47	99.86	101.16	99.98	100.78	100.20	99.57	100.06	100.20
Atoms per form	nula unit								
Ag	0.13	0.14	0.16	0.46	0.49	0.50	0.01	0.03	0.04
Sb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Те	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	0.86	0.85	0.83	0.52	0.49	0.48	0.98	0.97	0.95
Bi	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
s	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hg	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Tetal	0.00	1 00	0.00						



Fig. 6 BSE images of mineralization at the Dúbrava locality. a – Allotriomorphic aggregate of gold (white) associated with Fe-oxyhydroxides (grey), representing pseudomorphoses after pyrite. b Intragranular texture and chemical heterogeneity of gold grains. c – Inclusion of aurostibite (AuSb₂) associated with dolomite (Dol) in gold (AuIII). d – Fracture in dolomite I (Dol I) filled with zoned crystals of dolomite II (Dol II), corroded by Fe oxyhydroxides (white). The latest phase is calcite II (Cal II). e – Zonal aggregates of mimetite (Mim) associated with segnitite (Seg). f – Detail of radial crystalline aggregates of prismatic crystals of adelite group minerals.

Aurostibite forms tiny inclusions in Au-III, up to 10 μ m in size (Fig. 6c). Its composition is homogeneous, and contents of trace elements are below detection limits. Only two inclusions showed an elevated Hg content (up to 0.02 apfu). Its crystallochemical formula is close to ideal: Au_{0.99-1.04}Sb_{1.94-1.98} (Tab. 2). The analytical data are plotted in the ternary Au–Ag–Sb diagram in Fig. 7.

In the heavy mineral concentrate from gold bearing structure, scheelite occurs as rare allotriomorphic grains up to 0.5 mm together with cinnabar, forming irregular grains up to 0.1 mm.

Pyrite is the most common ore mineral in the studied area, and it occurs as impregnations (up to 1 mm in size) in dolomite



Fig. 7 The Au-Ag-Sb ternary plot of EMPA analyses from the Dúbrava locality.

II and often in calcite II veinlets. Less common is the form of thin veinlets (up to 2 mm thick) in cataclazed dolomite I. In gold bearing structures, the amount of pyrite does not exceed 1 %; however, in alteration zones with dolomite and muscovite there is sometimes more than 10 % of pyrite. EDS analyses did not confirm trace elements in pyrite. Gold is often associated by Fe oxyhydroxide pseudomorphs after pyrite (Fig. 6a).

Based on their chemical composition (Tab. 3) and textural evidence, carbonates form at least four generations. The oldest carbonate is represented by white fine- to coarse-grained marble (calcite I) replaced by dolomite I and muscovite. An irregular distribution is typical for dolomite I, with dolomite zones thickness ranging from 0.5 to 300 m. Its composition corresponds to pure dolomite (Fig. 8). Tectonic fractures, cracks, and veins in matrix of dolomite I are filled by dolomite II (Fig. 4). Dolomite II forms idiomorphic aggregates and crystals with a typical oscillatory zoning (Fig. 6d). Dolomite II is enriched in Fe (up to 0.16 apfu) and the zones previously rich in Fe carbonates are locally



Fig. 8 Projection of EPMA analyses for carbonates from the Dúbrava locality in the system CaO-MgO-FeO-CO₂.

replaced by Fe oxyhydroxides. The latest carbonate generation is represented by calcite II, which cements and corrodes the crystals of dolomite II.

Two types of quartz were observed at the Dúbrava locality. Quartz I occurs as stockwork zones (locally with veins up to tens of cm thick) in altered marble at the contact zone with metabasites. Commonly it has a massive texture; rarely, it forms druses of short prismatic crystals. No ore minerals were observed in quartz I. Quartz II occurs as idiomorphic long prismatic crystals up to 1 mm long in carbonate veinlets.

5.3.2. Secondary phases (associated to Pb-Zn-Sb-As mineralized structures)

Mimetite, a member of the pyromorphite group, was found as white or white-yellow aggregates up to several mm long, rarely composed of idiomorphic hexagonal crystals up to 600 μ m long, or prismatic needle-shape crystals up to 50 μ m long. Mimetite fills quartz fissures and it is rarely associated with

	RD-1	RD-3	RD-3	RD-1	RD-3	RD-3	RD-1	RD-3
Wt. %	Dolomite I			Dolomite II			Calcite II	
CaO	29.55	30.55	30.07	29.63	30.03	29.46	53.65	53.72
MnO	0.10	0.03	0.03	0.18	0.23	0.21	0.04	0.28
MgO	21.13	22.10	21.69	17.64	16.63	16.65	1.79	1.98
FeO	0.57	0.10	0.24	5.62	6.75	7.10	0.06	0.10
SrO	0.01	0.05	0.02	0.02	0.01	0.09	0.00	0.00
CO ₂	46.68	48.21	47.54	46.08	46.02	45.82	44.12	44.58
Total	98.05	101.04	99.65	99.18	99.69	99.33	99.69	100.69
			Atoms per	formula unit				
Ca ²⁺	0.91	0.91	0.91	0.94	0.96	0.95	0.95	0.94
Mn ²⁺	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Mg ²⁺	1.07	1.09	1.08	0.92	0.88	0.88	0.05	0.06
Fe ²⁺	0.01	0.00	0.01	0.13	0.15	0.16	0.00	0.00
Sr ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	2.00	2.00	2.00	2.00	2.00	2.00	1.00	1.00

Tab. 3. Chemical composition of carbonates from the Dúbrava locality, formula for dolomite is based on 2 apfu, for calcite on 1 apfu.

Tab. 4. Chemical composition of mimetite from the Dúbrava locality,

formula is based on 5 apfu.											
Wt. %	DUB-4	DUB-4	DUB-2	DUB-2	DUB-2	DUB-3					
P ₂ O ₅	0.04	0.03	0.12	0.21	0.00	0.00					
As ₂ O ₅	21.41	21.84	23.44	24.43	24.54	23.86					
V ₂ O ₅	0.02	0.00	0.05	0.06	0.11	0.03					
CaO	0.29	1.38	3.19	4.09	4.13	4.17					
SrO	0.00	0.00	0.00	0.00	0.05	0.17					
BaO	0.06	0.07	0.00	0.00	0.00	0.00					
PbO	76.77	73.97	71.67	70.03	69.27	69.21					
ZnO	0.00	0.193	0.09	0.00	0.00	0.01					
CuO	0.00	0.00	0.00	0.00	0.03	0.00					
MnO	0.16	0.06	0.17	0.03	0.12	0.05					
FeO	0.16	0.06	0.11	0.10	0.00	0.16					
CI	2.52	2.39	2.77	2.88	2.76	2.83					
Total	101.46	99.98	101.60	101.80	101.00	100.49					
		Atoms	per formu	ıla unit							
P ⁵⁺	0.01	0.00	0.02	0.04	0.00	0.00					
As ⁵⁺	2.99	3.00	2.97	2.96	2.98	3.00					
V ⁵⁺	0.00	0.00	0.01	0.01	0.02	0.00					
ΣΤ	3.00	3.00	3.00	3.00	3.00	3.00					
Ca ²⁺	0.07	0.34	0.74	0.94	0.95	0.96					
Sr ²⁺	0.00	0.00	0.00	0.00	0.01	0.02					
Ba ²⁺	0.01	0.01	0.00	0.00	0.00	0.00					
Pb ²⁺	4.86	4.60	4.19	4.04	4.02	3.98					
Zn ²⁺	0.00	0.03	0.01	0.00	0.00	0.00					
Cu ²⁺	0.00	0.00	0.00	0.00	0.00	0.00					
Mn ²⁺	0.03	0.01	0.03	0.00	0.02	0.01					
Fe ²⁺	0.03	0.01	0.02	0.02	0.00	0.03					
ΣΜ	5.01	5.01	5.00	5.00	5.00	5.00					
CI-	1.01	0.94	1.02	1.05	1.01	1.03					
ΣΧ	1.00	1.00	1.00	1.00	1.00	1.00					

other secondary minerals segnitite (Fig. 6e) and oxyplumboroméite.

A distinct heterogeneity of mimetite was observed in BSE images. The heterogeneity is caused by Pb \Leftrightarrow Ca substitutions (Fig. 9), ranging from pure mimetite to Ca-bearing mimetite



Fig. 9 Projection of the main substitutional trend in mimetite from the Dúbrava locality.

Tab. 5. Chemical composition of segnitite from the Dúbrava locality,
formula is based on 4 apfu. $\rm H_2O$ content was calculated from stoichiometric

constraints. The general formula is $DG_3(TO_4)_2(OH)_6$.									
Wt. %		DUB-2							
CaO	0.59	0.59	0.60						
PbO	29.90	29.83	29.94						
FeO	31.06	31.09	32.39						
ZnO	0.23	0.28	0.09						
CuO	0.50	0.59	0.55						
SO ₃	1.12	1.20	1.21						
P ₂ O ₅	0.04	0.01	0.07						
As ₂ O ₅	26.86	27.60	27.01						
SiO ₂	0.01	0.07	0.06						
H ₂ O _{calc}	8.33	8.42	8.53						
Total	98.89	99.68	100.55						
Atoms per forn	nula unit								
Ca ²⁺	0.08	0.08	0.08						
Pb ²⁺	1.01	1.00	0.99						
ΣD	1.09	1.08	1.07						
Fe ³⁺	2.94	2.92	3.00						
Zn ²⁺	0.02	0.03	0.01						
Cu ²⁺	0.05	0.06	0.05						
ΣG	3.01	3.00	3.06						
S ⁶⁺	0.11	0.11	0.11						
P ⁵⁺	0.00	0.00	0.01						
As ⁵⁺	1.77	1.80	1.74						
Si ⁴⁺	0.00	0.01	0.01						
ΣΤ	1.88	1.92	1.86						

(Fig. 10). The Ca content varies from 0.07 to 0.96 apfu. The substitution at the anion position is very weak and the highest detected amount is only 0.04 apfu P. The crystallochemical formula of Ca-bearing mimetite can be expressed as $(Ca_{0.96Sr0.02}Pb_{3.98}Fe_{0.03)4.99(AsO4)3Cl1.03}$ (Tab. 4).

Segnitite was found in association with mimetite as allotriomorphic aggregates with a typical size up to 50 μ m, usually replacing mimetite (Fig. 6e). Its inhomogeneity is caused by the presence of non-stoichiometric Fe_(AsO4)OH, H₂O compound,



Fig. 10 Compositions of mimetite from the Dúbrava locality in the classification diagram of Pb-Ca phosphates and arsenates of the pyromorphite group minerals (atomic proportions).

which could not be measured because of small dimensions. Segnitite is a member of the alunite supergroup, which includes trigonal (rhombohedral) sulphates, phosphates, and arsenates with the general formula of $DG_{3(TO4)2(OH)6}$, where the speciesdefining constituents are as follows: tetrahedrally coordinated $T = S^{6+}, P^{5+}, As^{5+}$; octahedrally coordinated cations $G = Al^{3+}, C^{5+}$ Fe^{3+} , V^{3+} , Ga^{3+} , Cu^{2+} , Zn^{2+} ; and large cations $D = K^+$, Na^+ , Tl^+ , Ag⁺, H₃O⁺, Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺, REE³⁺, Bi³⁺, Th⁴⁺. The ideal formula of segnitite is $PbFe_{3+3(AsO4)2(OH)6}$. At the Dúbrava locality segnitite chemical composition is quite simple with no distinct substitutions. The D position is almost fully occupied by Pb, which is partially substituted by Ca (0.08 apfu). The G position is dominantly occupied by Fe^{3+} , and partially by Zn (0.03 apfu) and Cu (0.05 apfu). The T position is occupied by As and only a minor content of S was observed (0.11 apfu). The crystallochemical formula of segnetite can be written as $^{D}(Pb_{1,0}Ca_{0.08})_{\Sigma 1.08}$ ${}^{G}(Fe^{3+}_{2.95}Zn_{0.02}Cu_{0.05})_{\Sigma 3.02}{}^{T}[(AsO_{4})_{1.77}(SO_{4})_{0.11}]_{\Sigma 1.88}OH_{6}$ (Tab. 5).

Rare members of the adelite group minerals arsendescloizite and austinite are also present at the Dúbrava locality (Fig. 11). Adelite group represents orthorhombic arsenates or vanadates



Fig. 11 Composition of austinite and arsenodescloizite from the Dúbrava locality in the Pb/(Pb+Ca) versus Zn/(Zn+Ca) classification diagram of the adelite group minerals (atomic proportions).

Tab. 6. Chemical composition of arsendescloizite and austenite of the adelite group from the Dúbrava locality. Formula is based on 2 *apfu*, H₂O content was calculated from stoichiometric constraints. The general formula is (AB)(TO₄)(OH).

					DUB-4				
Wt. %	arsendescloisite austinite							stinite	
SO ₃	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.00	0.00
P ₂ O ₅	0.04	0.06	0.00	0.06	0.06	0.03	0.06	0.06	0.11
As ₂ O ₅	29.41	28.69	28.41	29.27	29.75	33.76	33.29	34.88	34.82
Al ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.10
V ₂ O ₃	0.10	0.06	0.06	0.00	0.04	0.09	0.09	0.02	0.06
CaO	3.49	3.62	3.58	4.73	4.98	9.38	9.41	9.89	11.80
SrO	0.00	0.00	0.18	0.11	0.00	0.00	0.00	0.03	0.00
BaO	0.00	0.00	0.00	0.31	0.00	0.00	0.07	0.00	0.12
PbO	42.93	44.12	44.35	40.50	40.56	28.99	29.64	27.57	24.11
MnO	0.00	0.14	0.09	0.30	0.18	0.07	0.06	0.09	0.08
FeO	0.11	0.33	0.12	0.00	0.19	0.10	0.07	0.03	0.16
ZnO	21.98	21.89	21.73	18.31	18.18	19.41	20.72	19.67	21.96
CuO	1.15	0.01	0.98	4.25	4.36	6.40	5.47	6.79	5.30
H_2O_{calc}	2.40	2.37	2.39	2.42	2.44	2.74	2.76	2.80	2.90
Total	101.60	101.28	101.89	100.27	100.75	100.98	101.67	101.85	101.54
Atoms per fe	ormula unit								
S ⁶⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P ⁵⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As⁵⁺	0.96	0.95	0.93	0.95	0.95	0.96	0.95	0.97	0.94
V ³⁺	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σт	0.97	0.96	0.94	0.95	0.96	0.97	0.95	0.98	0.95
Al ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Ca ²⁺	0.23	0.25	0.24	0.31	0.33	0.55	0.55	0.57	0.65
Sr ²⁺	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Ba ²⁺	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Pb ²⁺	0.72	0.75	0.75	0.67	0.67	0.43	0.43	0.40	0.34
Mn ²⁺	0.00	0.01	0.00	0.02	0.01	0.00	0.00	0.00	0.00
Fe ²⁺	0.01	0.02	0.01	0.00	0.01	0.00	0.00	0.00	0.01
Zn ²⁺	1.01	1.02	1.01	0.84	0.82	0.78	0.83	0.78	0.84
Cu ²⁺	0.05	0.00	0.05	0.20	0.20	0.26	0.22	0.27	0.21
ΣМ	2.03	2.04	2.06	2.05	2.04	2.03	2.05	2.02	2.05

with a general formula of $(AB)(TO_4)(OH)$, where A can be Ca or Pb, B includes a wide variety of divalent transition metals such as Cu and Zn, and T is either As or V (Gaines et al., 1997). At Dúbrava, these minerals form light grey, grey-white collomorphic, radial aggregates up to 1 cm in diameter that consist of prismatic crystals up to 40 µm in size (Fig. 6f). Rarely, they fill fissures in oxyplumboroméite aggregates and show a strong oscillatory and sector chemical zoning (Fig. 6f). The strong heterogeneity is caused by an extensive Pb \Leftrightarrow Ca and Zn \Leftrightarrow Cu substitutions (Fig. 12a,b). A wide compositional range from Ca-bearing arsendescloizite with up to 0.33 apfu Ca to Pb-bearing austinite with up to 0.43 apfu Pb was observed. The B site is predominantly occupied by Zn with a significant amount of Cu (up to 0.27 apfu). The T position is predominantly occupied by As, without detectable P, S, V contents (Tab. 6).

Oxyplumboroméite is another rare mineral from the Dúbrava locality. It belongs to the roméite-group of minerals of the pyrochlore supergroup with the general formula $A_2B_2O_6X$, where: A = Na, Ca, Ag, Mn, Sr, Ba, Fe²⁺, Pb, Sn²⁺, Sb³⁺, Bi³⁺, Y, REE, Sc, U, Th, or vacancy ; B = Ta, Nb, Ti, Sb⁵⁺, W, V⁵⁺, Sn⁴⁺, Zr, Hf, Fe³⁺, Mg, Al, and Si; and X = O, OH, plus maybe F, H₂O (Atencio et al., 2010). Currently, there are four valid minerals of the roméite group: oxycalcioroméite (Ca₂Sb₂O₇), oxyplumboroméite (Pb₂Sb₂O₇), fluorcalcioroméite [(Ca, Na)Sb₂O₆F] and hydroxycalcioroméite $[(Ca, Sb^{3+})_2(Sb, Ti^{4+})_2O_6F]$. At the Dúbrava locality, oxyplumboroméite occurs as light yellow to brown-orange massive aggregates up to 1 cm large, consisting of lamellar needle-like crystals reaching up to 100 µm. Cracks and empty cavities in oxyplumboroméite are filled with adelite group minerals, often containing relics of mimetite. The B position is dominantly occupied by Sb5+. Considerable amount of Si4+ was found in studied oxyplumboroméite which was assigned to the B position. Pb is usually the dominant cation occupying the A position (the maximal content is 1.2 apfu). The A position contains also variable proportions of Ca (max. 0.39 apfu) and Sr (0.28 apfu). Iron (presumed ferrous) was assigned to the A position, since the assignment of Fe to the B sites results in a significant imbalance between the amount of A and B cations. Fe content varies from 0.16 to 0.4 apfu. Other cations in the A position include Mn, Ba, Zn, and Na. The average structural formula can be expressed as $^{A}(Pb_{1.05}Sr_{0.26}Ca_{0.25}Fe^{2+}_{0.29}Sb^{3+}_{0.11}Zn_{0.03}Na_{0.01})_{\Sigma^{2}}^{B}(Sb^{5+}_{1.82}Si_{0.17})_{\Sigma^{2}}$ $As_{0.01})_{\Sigma_2} (O_{6Y}(O_{0.9}OH_{0.1})_{\Sigma_1})$

Tab. 7. Chemical composition of oxyplumboroméite from the Dúbrava locality. Formula is based on 4 *apfu*. *Sb³⁺ and H₂O were calculated from stoichiometric constraints. The general formula isA₂B₂O₆X.

Wt. %	DUB-4	DUB-2	DUB-2	DUB-2	DUB-2	DUB-2	DUB-2	DUB-2
PbO	39.54	33.61	33.41	36.93	37.53	35.70	38.58	41.56
CaO	1.75	3.37	3.55	2.20	2.81	2.30	2.04	1.39
SrO	4.09	4.60	4.53	4.32	4.53	4.78	4.34	4.21
FeO	2.04	4.97	3.97	5.20	2.07	4.00	4.78	4.31
MnO	0.00	0.08	0.05	0.05	0.00	0.06	0.04	0.01
ZnO	1.16	0.05	0.11	0.25	0.07	0.10	0.12	0.04
BaO	0.11	0.05	0.00	0.24	0.00	0.24	0.14	0.00
Na₂O	0.02	0.04	0.05	0.05	0.02	0.02	0.00	0.04
Sb ₂ O ₅	49.31	51.22	50.82	50.51	50.13	53.64	49.15	48.21
As ₂ O ₅	0.41	-	-	-	-	-	-	-
SiO ₂	2.32	1.86	1.89	1.15	1.87	1.04	1.36	1.26
*H ₂ O _{calc}	0.14	0.15	0.15	0.15	0.14	0.15	0.14	0.14
Total	101.06	99.99	98.55	101.06	99.24	102.04	100.70	101.18
Atoms per for	mula unit							
Pb ²⁺	1.11	0.90	0.91	1.02	1.06	0.98	1.08	1.19
Ca ²⁺	0.20	0.36	0.39	0.24	0.32	0.25	0.23	0.16
Sr ²⁺	0.25	0.27	0.27	0.26	0.28	0.28	0.26	0.26
Fe ²⁺	0.16	0.37	0.30	0.40	0.16	0.31	0.37	0.34
Mn ²⁺	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.00
Zn ²⁺	0.09	0.00	0.01	0.02	0.01	0.01	0.01	0.00
Ba ²⁺	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.00
*Sb ³⁺	0.19	0.08	0.11	0.04	0.16	0.15	0.04	0.04
Na⁺	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01
ΣΑ	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Sb⁵⁺	1.72	1.82	1.81	1.88	1.80	1.89	1.86	1.87
As ⁵⁺	0.02							
Si ⁴⁺	0.24	0.19	0.19	0.12	0.20	0.11	0.14	0.13
Al ³⁺	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ΣΒ	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
он	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
0	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
ΣΧ	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00



Fig. 12 a, b Main substitutional trends in the adelite group of minerals from the Dúbrava locality.

Raman spectra of our samples show a pattern similar to other minerals of the roméite group (e.g., Lafuente et al., 2015; Atencio et al., 2013; Hålenius & Bosi, 2013; Frost & Bahfenne, 2010; Fig. 13). Positions of Raman bands in the representative spectra of oxyplumboroméite from Dúbrava are as follows (intense sharp bands are highlighted in bold): 128, 149, 300, 350, 403, 513, 569, 605, 749, 823 cm⁻¹. Nevertheless, in our spectra, the Raman bands are slightly shifted likely due to substitutions at A, B, and Y positions. The intense band between 505 and 522 cm-1 is assigned to Sb–O stretching (e.g., Lafuente et al., 2015; Atencio et al., 2013; Hålenius & Bosi, 2013; Frost & Bahfenne, 2010). In studied samples, Sb (the B position) is partly substituted by Si (0.11 to 0.24 apfu) probably causing the shift of the band between 507 and 514 cm⁻¹. The band shifts are sometimes accompanied by the band broadening. The broad band in the OH stretching region with center at 3415 cm⁻¹ (Fig. 13 inset) is an apparent feature in the Raman spectra. Hereby with missing band at around 1600 cm⁻¹ (H₂O bending), it confirms the presence of OH groups quantified from stoichiometric constraints from EPMA to 0.16-0.17 apfu (Tab. 7).

6. DISCUSSION

Gold mineralization at the Dúbrava locality is linked to faults and breccia zones hosted by dolomitized marble. This type of Au mineralization is quite unique not just in the Gemeric Superunit, but it also differs from a typical sediment-hosted gold deposit in the world recognized as Carlin-type deposits. Carlin-type gold deposits, with the most prominent examples near Carlin, Nevada (USA), are characterized by very finely disseminated gold in gold-rich arsenian pyrite, associated with Sb, Hg, and Tl, hosted by silicified decarbonated limestones ("jasperoids") (e. g., Hofstra & Cline, 2000). Ore deposition took here from relatively low-temperature (150 - 250 °C), moderately saline, low pH fluids, most likely of distal magmatic origin (Large et al., 2016), although in some districts (e.g., Guizhou in China) metamorphic origin is proposed (Su et al., 2009). At Dúbrava, silicification is just minor and the gold-bearing zones are accompanied by dolomitization, which indicates different fluid properties and fluid sources compared to typical Carlin-style deposits. Although we do not have any data on palaeofluids yet, it is clear that dolomitization was here an important factor for an efficient penetration of fluids, as dolomitization reactions involve a significant loss of volume (6 to 13 %, Morrow, 1982), further enhanced by active brecciation along fault zones.

Near the Dúbrava locality, a relatively large area is covered by metasomatically dolomitized marbles, however, they are not recognized on modern geological maps as a separate lithology. Václav et al. (1983) mentioned dolomitization at surrounding localities, which should be related to the same metasomatic processes that has formed magnesite lenses in the area of the



Fig.13. Representativ e Raman spectra of oxyplumboroméite from the Dúbrava locality, compared to "bindheimite" and "roméite" from RRUFF database (Lafuente et al. 2015). Based on their chemical composition, minerals correspond to oxyplumboroméite and fluorocalcioroméite respectively, according to nomenclature of the pyrochlore supergroup (Atencio et al. 2010). Inset shows OH stretching vibrations. All spectra were normalized according to the most intense band (~510 cm⁻¹).

LML. Dolomites were mapped only during the state prospection of metallogeny of the contact zone between the Veporic and Gemeric superunits (Snopko et al., 1985). Dolomitic replacement of marbles was also observed in the nearby Ochtiná Aragonite Cave (Zimák et al., 2004), but compared to Dúbrava, this carbonate has a higher amount of FeO (~ 12 wt. %). Dolomitized carbonates were observed as a host-rock of several Pb-Zn mineral occurrences as Mária-Margita, Dúbrava (close to Jelšava town) or Roštár.

The steep N – S structures hosting the studied Au-mineralization at Dúbrava are related to Alpine deformation and extension processes, which have also resulted in the emplacement of the Rochovce granite porphyry intrusion (Vojtko et al., 2016). This collapse phase is linked to the unroofing of the Veporicum unit, after the Gemericum unit overrode the Veporicum unit (Hók et al., 1993; Plašienka, 1993; Jeřábek et al., 2012; Vojtko et al., 2016). The step-like character of N – S structures in stopes probably originated as a rejuvenation of flat faults that are parallel to the detachment fault in the basement (Fig. 3, cross section). The base metal mineralization is related either to NE – SW structures (Dúbrava locality) or to NW – SE structures (Mária-Margita deposit), while the NE – SW structures are possibly younger.

Mineralogy of gold bearing structures from the Dúbrava locality is quite unique in Western Carpathians due to zoned gold grains and associated aurostibite inclusions. However, the absence of host rock and other primary ore minerals makes the interpretation of this assemblage problematic. Similar textural features of gold and association with aurostibite were also described and interpreted by Zachariáš & Němec (2017) from the Krásna Hora Au-Ag-Sb deposit. Similar to the Dúbrava locality, the early high-fineness gold is replaced by a later generation that forms rims along the early gold with variable Au/Ag ratio. This later gold shows a gradual increase in Ag towards the grain core similar to the gold textures at Dúbrava (Fig. 5b). They interpreted this feature as the result of the reaction with the Ag-rich fluid, with the source of Ag in the earlier generation of gold being replaced by aurostibite with almost absent Ag. The preferential formation of Ag-rich Au-Ag alloy by an inward diffusion of Ag is the result of low activity of sulphur and possibly low contents of base metals in the fluid. By analogy, a similar scenario could have also occurred at Dúbrava; however, this interpretation requires further mineralogical study.

Zonal gold with inwards decreasing Ag was not described from the Western Carpathians yet. However, the presence of aurostibite was already published from the Zlatá Idka Au-Ag-Sb deposit (Pršek & Lauko, 2009). At Zlatá Idka, aurostibite occurs as inclusions in tetrahedrite together with sphalerite, chalcopyrite, gold, and berthierite and it is significantly enriched in Ni (up to 6.63 wt. %) and Cu (up to 1.66 wt. %). At the Krásna Hora deposit, aurostibite is associated with miargyrite and various Au-Ag-Sb alloys in addition to zonal gold and it corresponds almost to ideal AuSb₂ formula (Zachariáš & Němec, 2017), which is similar to the Dúbrava locality.

All secondary minerals at the Dúbrava locality are hosted by NE – SW faults and contain variable contents of Pb, Ca, Zn, Sb \pm Cu, Fe in cation positions and As in the anion position. Surprising is the lack of PO₄, SO₄ or VO₄ in their structure and the absence of carbonates containing base metals despite the host rock is dolomitized marble. The source of As probably comes from arsenopyrite. Members of the adelite group minerals arsendescloizite and austinite have been firstly identified in the Western Carpathians. Arsendescloizite was reported from the Caldbeck lead mine in UK (Neall et al., 2006). Števko et al. (2018) recently identified minerals of the adelite group (conichalcite-duftite series) with extensive Pb \Leftrightarrow Ca substitution from the abandoned Drienok carbonate-hosted base metal deposit near Poniky. The Pb \Leftrightarrow Ca and Cu \Leftrightarrow Zn substitution was also found at the Dúbrava locality. In the adelite group, mimetite and oxyplumboroméite Pb ↔ Ca substitution is the main substitutional trend with the source of cations in weathered primary sulphides or sulphosalts. There was no significant substitution observed in segnitite from the Dúbrava locality. In our sample of oxyplumboroméite, the Pb content was up to 1.21 apfu, which is close to a sample from the Långban Mn-Fe deposit in Central Sweden, where the most Pb-rich oxyplumboroméite was found with 1.42 apfu (Christy & Gatedal, 2005).

Data from Dúbrava hill can be compared to two closest localities with Pb-Zn mineralization. First is the Mária-Margita deposit hosted by NW - SE and N - S structures in altered carbonates. Mineral succession reported by Števko et al. (2009) follows in the sequence: pyrite \rightarrow sphalerite \rightarrow galena \rightarrow chalcopyrite \rightarrow tetrahedrite \rightarrow meneghinite \rightarrow bournonite. Secondary minerals from the Mária-Margita deposit were also studied by Števko & Bálintová (2008), who reported aurichalcite, azurite, cerussite, bindheimite, malachite, linarite, hydrozincite, smithsonite, and gypsum. The Mária-Margita deposit contains various Pb-Zn sulphides and sulphosalts, carbonates, and sulphates, but no arsenates, so both primary and secondary mineralization differ significantly from the Dúbrava sulphidic mineralization. As pyrite is just a minor mineral at Mária-Margita, only secondary minerals precipitating at higher pH are present (Pb-Zn carbonates) in contrast to Dúbrava where mimetite and austinite are stable at lower pH (Bowell, 2014), corresponding to intensive pyritization. Compared to Dúbrava, Mária-Margita also differs geochemically by lower grades of Au and As and higher grades of Ag, Cu, Hg, Cd, and Zn/Pb ratio.

Second locality compared is Dubiná-Drábska situated on the LML contact zone between the Ochtiná group phyllites and the Rimava formation meta-arkoses. These host rocks contain arsenopyrite, as well as abundant pyrite in addition to base metal sulphides and sulphosalts, filling the fractures of all the strikes described from Dúbrava (Fig. S). Dubiná-Drábska also differs geochemically by lower Au grade but the As content is similar to Dúbrava.

Genesis of the Dúbrava mineralization is not clear yet. As the occurrence is a part of numerous mineralized localities and extensive alteration surrounding the Rochovce granite porphyry intrusion, there is undoubtedly a link to this magmatic intrusion, hosting the Ochtiná W-Mo porphyry deposit. However, two contrasting scenarios can be considered. Either the link could be magmatic-hydrothermal, in case the surrounding mineralized systems were governed mostly by cooling magmatic fluids escaping from the porphyry system. Alternatively, they were governed by heated meteoric waters, deeply convecting in the vicinity of the thermal anomaly of the intrusive center and remobilizing metals from wall rocks. Furthermore, combination of the two models is also possible.

The first alternative represents an analogue to the intrusion related (IR) type of deposits (e.g., Lang & Baker, 2001; Hart, 2007) with the typical examples of Kidston, Queensland, Australia (Thompson et al., 1999), Logtung, Yukon Territory (Noble et al., 1984), Fire Tower Zone, New Brunswick (Kooiman et al., 1986) or Ryan Lode, Alaska (Sillitoe & Thompson, 1998). Veins rich in arsenopyrite and gold are typically adjacent to the parental intrusion and more distal Ag-Pb-Zn veins occur up to 3 km from the intrusive contacts (Thompson et al., 1999). However, such a clear zonal arrangement of Au-As \pm Sb (Dúbrava, Dubiná) and Pb-Zn \pm Ag \pm Sb (Dúbrava, Mária-Margita, Dubiná-Drábska, etc.) occurrences cannot be observed (Fig. 1).

The second alternative corresponds to leaching of metals from favorable wall rocks, such as gold from metabasic rocks and Sb from black phyllites of the Gemeric Superunit. The lack of silicification, but extensive dolomitization of carbonates at Dúbrava could be related to buffering of hydrothermal fluids by surrounding metabasites, providing Mg and Au, but a little silica. However, the source of Pb-Zn is less clear in the studied area. World examples of systems with heat energy provided by deep-seated large intrusions are swarms of polymetallic veins in the Edmund and Collier Basin in Western Australia (Pirajno, 2014) or Sabies-Pilgrims Rest district in South Africa, where numerous Au with minor base metal lodes are related to the heat of the Bushweld Igneous Complex (Anderson et al., 1992; Boer et al., 1995).

7. CONCLUSIONS

New occurrence of Au mineralization at Dúbrava hill is unique in the Western Carpathians by its character, mineral composition, association of secondary minerals in oxidation zone and specific alteration of carbonates. Widespread dolomitization together with sericite and pyrite alteration of marbles indicate an extensive hydrothermal activity. Mineralization and alteration around the village of Rochovce occurred in numerous successive and spatially overlapping stages, which were structurally controlled by faults formed during Alpine deformation. At Dúbrava, the earlier phase is represented by Au mineralization present as coarse gold unlike the Carlin style mineralization. Zonal textures of gold with inward diffusion of Ag result from the sulphur deficient environment, as the late Ag-rich fluid was not able to precipitate Ag-rich sulphides and sulphosalts. Pb-Zn-Sb-As mineralization occurred as a later event cutting the Au structure. However, the character of primary mineralization is unknown, but the secondary minerals association suggests an As-rich Pb, Zn, Sb ± Cu ore. This unusual assemblage of secondary minerals in carbonate host rock is probably related to slightly acidic waters resulting from decomposition of widespread pyrite. The genesis of the mineralization at Dúbrava hill can be related to either magmatichydrothermal fluids, escaping from the Ochtiná intrusive center, and/or deeply circulating meteoric fluids, driven by the heat of the intrusive center and buffered by favorable host rocks.

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