Supergene Au mineralization at Divín – Divínsky háj locality (Slovenské rudohorie Mts., Veporic Unit)

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Abstract: Six occurrences of Medieval mine workings are known in the area of Divínsky háj hill between Divín and Lovinobaňa villages. The major one in the area of 500 × 10–130 m was a subject of drilling of 14 diamond and RC holes. Supergene gold mineralization is hosted in faulted and folded argillized and limonitized Permian to Triassic schists, sandstones, and quartzites of the Veporic Unit. The ore bodies are irregular, related to crossing of NW–SE trending tectonic zones dipping 40–60° to NE and metamorphic foliation, mainly close to contact of schists with quartzites and with barren quartz veins. The thickness of ore bodies varies between 1 and 15 m. The grade in holes ranges from 0.01 to 8.86 ppm of Au. Oxidation zone reaches up to 40–50 m. Gold is of high fineness, 950 in average. Except clays and limonite, barite is the only mineral accompanying supergene gold. The character of primary mineralization and the source of Au are unknown.

Key words: gold mineralization, supergene enrichment, Medieval mines, Divín, Veporic Unit

1. INTRODUCTION

A gold mines at Divín village (Fig. 1) are situated (coordinates: UTM 34U 393700, 5367100) 15 km NW from Lučenec district town and belong to the largest one in the western part of Slovenské rudohorie Mts. According to dimensions of old mining activities it is one of the biggest occurrences of supergene Au mineralization in the Western Carpathians with economic potential. Main target of the present exploration works was verifying the extent and the ore potential of the oxidation zone. Primary mineralization was not site of the interest yet. Paper summarizes results of the present state of exploration knowledge on this exceptional locality. Unusual type of this mineralization and its geological setting increase metallogenetic potential of the Veporic Unit as well as increase potential of the small obscure Au anomalies in the other regions of the Western Carpathians.

Fig. 1. Schematic geological map of the southwestern part of the Veporic Unit (modified after Bezák et al., 1999). Legend: 1–4) crystalline basement of the Veporic Unit (Early Palaeozoic–Proterozoic?): 1) ortho- and paragneisses, phyllites, mica schists; 2) metabasics; 3) hybrid granitoids changed to migmatites; 4) granites and aplites, granodiorites; 5) metasediments, metavolcanics, and metavolcanoclastic deposits of the Slavín and Rimava formations (Late Palaeozoic) and the Föderat Group (Mesozoic); 6) Gemic Unit, carbonates, metasediments, metavolcanics, and metavolcanoclastic deposits of the Late Palaeozoic; 7) Neogene volcanites (andesites and their pyroclastic rocks); 8) Neogene and Quaternary sediments of the Pöltar Formation; 9) faults; 10) main nappes; 11) occurrences of supergene Au mineralization: 1 – Divín - Divínsky háj; 2 – Uderíná; 3 – Katarínska Huta; 4 – České Brezovo - Kečka.
2. HISTORIC OVERVIEW

The beginning of gold mining at Divín village is unknown as well as in many other localities in the Western Carpathians. The most intense exploitation of the gold deposit can be dated between 13th and 15th century. Archeologist E. Hrašková dated the findings of so-called “white ceramics” found in the old shafts waste dumps to the 13th and first half of the 14th century (personal information). Same ceramics was dated by archeologist M. Kvetok to the 14th and first half of the 15th century (personal information).

The oldest written note about gold in Divín village is connected with a visit of controller clerk F. Heinz from bureau of mines. He was mandated by Main Chamber Count office (Banská Štiavnica) in 1766 for a report compilation about mining activities at Divín (Zilák, 1993). Before any exploration works, F. Heinz recommended study of old reports (dated to Rákoczy uprising 1680–1708) in mining archive. The map of the western part of Slovenskú rudohorie Mts. shows gold placers between Divín and Lovinobaňa (Hvozdára, 1999). Michálek et al. (2010) reports small but contrast Au anomaly in the west slope of Divinsky háj hill. They found 66 gold flakes from 2 dry panning samples from the old exploitation pits. However, the detailed exploration was made by AQUA SYM Ltd. during 2012 and 2013 on this locality.

3. METHODS

GPS was used for mapping of an old mining works (accuracy ± 10 m). During the first phase of the exploration 65 litho-geochemical samples were taken dominantly from the old dump material. During the second phase, 4 shallow holes were drilled with the total length of 162 m and 11 holes with 335 m total length in the third phase.

Gold from litho-geochemical samples was analysed by ALS CHEMEX Company in Rosia Montana (Romania) laboratory from the sample weight about 30 g by fire assay method following Au detection by AAS. The analytical range of this method is 0.01–100 ppm. Samples were homogenized, quartz and sent for analysing of the rest of elements to ALS CHEMEX in Perth (Australia) laboratory (determined by ICP method) with the following analytical ranges: Ag (0.5–100 ppm), Al (0.01–50 %), As (5–10000 ppm), Ba (10–10000 ppm), Be (0.5–1000 ppm), Ca (0.01–50 %), Cd (0.5–1000 ppm), Co (1–100000 ppm), Cr (1–10000 ppm), Cu (1–10000 ppm), Fe (0.01–50 %), Ga (10–100000 ppm), K (0.01–5 %), La (10–10000 ppm), Li (10–10000 ppm), Mg (0.01–50 %), Mn (5–10000 ppm), Mo (1–10000 ppm), Na (0.01–10 %), Ni (1–10000 ppm), P (10–100000 ppm), Pb (2–100000 ppm), Rb (10–100000 ppm), S (0.01–5 %), Sb (5–10000 ppm), Sc (1–10000 ppm), Sr (1–10000 ppm), Th (20–100000 ppm), Ti (0.01–10 %), Tl (10–100000 ppm), U (10–100000 ppm), V (1–100000 ppm), W (10–100000 ppm), Zn (2–10000 ppm), Zr (5–10000 ppm).

Drill holes DH-1 to DH-4 were realized in 2012 by self-propelled mobile drilling rig. Diameter of diamond bit was PQ3 and HQ3 with wire-line technology. Double core barrel was used for the maximum yield of drill core. Drill holes DH-5 to DH-14 were drilled in 2013 using RC method (reverse circulation). Every meter of rock chips was collected to plastic bags. A half of the drill core and a quart of the rock chips were sent for analyses. Core was sampled in 1 m intervals. The rock chips from RC holes were sampled in 1–3 m intervals. Samples were dried and milled (70 % < 2 mm) in the laboratory. Later the samples were quartered and sample weight 250 g was milled (min 85 % < 0.075 mm). Core and rock chips were analysed only for Au (ALS CHEMEX Rosia Montana, Romania), sample weight 50 g by “fire assay” method with following Au detection by AAS (analytical range 0.01–100 ppm). Despite of higher weight of analytical sample, compared to standard one, a strong nugget effect was determined. Repeated analyses (3×) achieved max ± 74 % deviation. Accuracy of analyses was controlled by high grade Au standards and deviation shown was only up to 5.4 %.

Gold for mineralogical study was panned from dumps of old pits. Electron microscope JEOL JSM-6390LV (Earth Science Institute, SAS, Banská Bystrica) was used for BSE images and qualitative analyses of gold. Following condition was used: EDS detector (OXFORD INSTRUMENTS INCA x-act), acc. voltage 15 kV, WD 10 mm, probe current 15 nA, beam diameter 1 µm.

4. GEOLOGICAL SETTING

Area between the Tuhár and Kriváň creeks was studied by Gregor (1951, 1964). He recognized Permian formation (arkoses, sericitic and chloritic-sericitic schists) in footwall of Lower Triassic quartzites and the same lithological succession he also found in Divinsky háj hill. Epideite-zoisite schist occurring to the south of Divinsky háj hill, described by Gregor (1. c.), was later unified (Vass et al., 1992; Bezák et al., 1999) with metasediments of the Rimava Formation belonging to the Foederata cover sequence of the Veporic Unit.

Plašienka (1983) studied area between Ružiná and Tuhár villages. The Tuhár succession of the Divín synform as a part of the Foederata cover sequence is composed of Upper Permian metaarkoses and schists (Rimava Fm.) with the thickness up to 50 m. The upper part of the Tuhár succession is formed by the Lower Triassic metaquartzites with interlayers of sandy schists (Lúžna Fm.) with the thickness up to 100 m. Sandy schists (thickness up to 50 m) predominantly occur in the upper portion of the Lúžna Fm., and the uppermost part of the Foederata cover sequence contains Middle to Upper Triassic mainly carbonate deposits. In structural point of view, Mesozoic members form fan-like structures with NE–SW direction of fan axis. Sequence is dipping to NW with sharp termination on the Divín Fault.

According to Bezák et al. (1989) Divinsky háj area is built only by Lower Triassic quartzites of the Foederata cover sequence and rauwackes. Their contact has NNW–SSE trend. According to Vass et al. (1992) the underlying strata of the Triassic quartzites in the south of Divinsky háj hill are built by metasediments of the Rimava Formation (metamorphosed arkoses, arkose greywackes, schists, and silicic conglomerates) belonging to Permian (VozárOVÁ & Vozár, 1982, 1988). Alpine deformed crystalline basement (mica schist, amphibolites, and hybrid
granitoids) belonging to Lovinobaňa complex (Bezák, 1982) occurs in the SE part of Divínsky háj hill.

Plašienka (1983) defined Alpine deformation stages D₁ (A₁) characterized by evolution of the Alpine metamorphic foliation between Ružíná and Tuhár villages. Subvertical fault-slip-related cleavage or jointing (deformation stage D₃, S₃ planes) with the strikes in NW–SE direction represents axial plane cleavage of the kink-bend folds.

5. RESULTS

5.1. Zones of old mining works

Old mining works occur at 6 places (Fig. 2, working nomenclature A, B, C, D, E, and F) on the Divínsky háj site. They are concentrated to the NW–SE zones.

A) Western zone (most important) is 500 m long, 130 m wide in NW end and 10–30 m wide in SE end (Fig. 3). The presence of 110–115 massive craters after buried shafts is characteristic for the western zone. Their diameter ranges between 5–10 m with the present depth of 2–5 m. Adits are rare despite appropriate field morphology in the SE end of the locality. Waste dumps of these small exploration adits (3–4) contains up to 10 m³ of material. Size of the shafts, volume of the waste dumps and width of mining area are decreasing in SE direction and mining works come into exploration character. Mining works in NW part shows exploitation character, shafts are often ordered in lines 40–70 m long and are spaced 10–30 m. The volume of waste dumps near these shafts is usually more than 1000 m³. 100,000 ton of gangue is approximately overall volume of waste dumps. Material from the waste dumps is fine-grained, bigger pieces show marks after hammer and chisel crafted.

B) Middle zone (less important) with several 30–100 m gaps is 600 m long. This zone is only few metres wide and contains 45–50 craters after buried shafts and open pits. Dimensions and shape of the mining works suggest only exploration character. Exploitation character (several hundred tons of material) is evident only on the top of the Divínsky háj hill (384 m a.s.l.) the diameter of the craters after collapsed shafts is 2–3 m and their present depth is 1–2 m. Waste dumps near shafts are small (up to tens of m³).

C) Similar type of Au mineralization occurs at the east foothill of Divínsky háj (384 m a.s.l.). Mineralized zone was confirmed in several dozen m² large area by shallow shafts.

D) The next group of old mining works is located on the ridge approx. 850 m SE of Divínsky háj hill (384 m a.s.l.) with dominant 30 x 40 m large open pit of max. depth of 5 m. Two other pits have trench shape, 30 m long and 5–10 m wide. Their azimuth is NE–SW to ENE–WSW. Shallow shafts and excavations are

Fig. 2. Map of old workings in the area between Divín and Lovinobaňa.
Fig. 3. Map of old workings, localization of drill-holes and rock-chips samples with a distribution of Au at the Divín - Divínsky háj locality (detail of zones A and B from Fig. 2).
also visible in the field. At least 1500 tons of material could be mined here.

E) The group of 4 small exploration shafts is located about 500 m SE from previous group. The biggest shaft is up to 10 m deep.

F) Shaft located 1.2 km NW from Divinsky haj hill (384 m a.s.l.).

5.2. GEOLOGY OF ORE ZONES

Mineralization was studied in the western zone (A) and middle zone (B). Mineralized zones in Divinsky haj hill are following system of main fault zones of NW–SE direction. These mineralized structures are parallel to faults geomorphologically represented by valleys of Krivansky potok creek, Bansky potok creek near Cinobaňa village, Ipeľ creek near Malinec village, etc. Other important structures are thrusting planes of Mesozoic rocks slices belonging to Southern Veporic Unit (Fig. 4A). The ore body dips 40–60° to NE (Fig. 4B). Thickness of the mineralized structure ranges between 1 and 15 m, in average 2–5 m. The lithological marker of the sequence – quartizes of the Lûžna Formation (Fig. 5A) is several metres thick with the maximum thickness of 20 m. Quartizes are mostly crumbled; massive layers are rare (max. 1–2 m thick layers in drill holes). Argillized and limonitized shists (Fig. 5B) are in hanging wall position. Quartz-sericite shales, sandstones, and quartizes are forming the base of the slices as well as footwall of the ore body. The sandstones are dominantly sheared in semiductile style (Fig. 5C) and have less cataclastic texture. Hangingwall shales with sandstone interbeds are intensively faulted, folded, and sliced. Fold hinge radius ranges from few centimetres up to several metres (Fig. 5D). The zones of lithological boundaries contain tectonic breccias (Fig. 5E) with maximum thickness up to 15 m. Breccias are formed by fragments of quartzites and hydrothermal quartz (most probably of metamorphic origin). Breccias are cemented by red-brown plastic clay derived from crushed limonitized schists. White lenticular quartz veins are related to lithological contact of shales and quartzites. These quartz veins are most probably of metamorphic origin. Their thickness is variable (0.3–1.5 m). These rejuvenated structures were suitable also for origin of younger white-grey quartz veinlets (1–5 cm thick) followed by crystallization of carbonate veinlets with thickness up to 1 cm (Fig. 5F). The depth of the oxidation zone is at least 50 m according to the deepest drill hole DH-3.

Gold distribution is controlled by structural traps at the studied locality. The most significant are NW–SE trending fault intersections with quartzite and shale beds (Fig. 5G). Other important features are cataclazed footwall and hanging-wall of pre-mineralization quartz veins. Less important Au mineralization is locally also related to hanging-wall blocks of plastic argillized shales (Fig. 5H). Au content ranges between 0.0X and 8.86 ppm in samples from drill holes. Bonanza gold accumulations that were object of historic mining occur within these zones. The quality of bonanzas is documented with litho-geochemical sample from waste dump containing 60.4 ppm of Au. The mined-out stopes were intersected in 9 of 14 drill holes (Tab. 1).

Gold forms often isometric grains (Fig. 6A, B), strips, and tufted aggregates with morphology resembling negative-forms of host minerals (Fig. 6C–F). Gold intergrows with limonite and rock-forming minerals (Fig. 6G, H). Limonitized carbonates, limonitized pyrite, barite, and zircon are dominating minerals in heavy fraction of heavy-mineral concentrate. Limonite (pseudomorphoses after pyrite and carbonate) and rarely barite were found in the fragments of quartz-carbonate veins from the waste dumps. Barite forms clusters of white fine-grained aggregates associated with limonite and quartz. Barium content in samples from waste dumps ranges from 100 ppm to few % (0.14 % in average). Other elements show low concentrations. The ore contains in average 2.9 % Fe (max. in limonite sample 18.5 %), < 5 ppm As (max. in limonite sample 49 ppm), 30 ppm Zn (max. 56 ppm), 14 ppm Pb (max. 28 ppm), < 5 ppm Sb (max. 105 ppm in limonite sample), 15 ppm Ni (max. in limonite sample 138 ppm),
10 ppm Cu (max. in limonite sample 990 ppm), 8.6 ppm Co (max. in limonite sample 306 ppm). Moreover, Bi and Te were not confirmed in the ore. The Ag content in the ore is dependent on the Au content. Maximal Ag content is 6.4 ppm, in average is below detection limit of used method (< 0.5 ppm).

Gold at Divín locality has high fineness. Based on EDX analyses of 15 separated gold grains the gold contains in average 95.15 wt % Au (93.01–97.15 %) and 4.08 % Ag (1.54–6.09 %). Content of other admixtures is around 1 % (Cu, Bi, Sb, Pd, Cd). Bismuth shows highest but variable concentrations (0–1.14 %). Hg was not found in the gold from Divín.

The average Au content of 56 lithological samples taken from waste dumps of ore bodies A and B is 1.91 ppm. The amount of extracted ore in the past can be estimated from 25000 to 75000 tons (Tab. 2), what represents production of 125–1500 kg Au with average grade 5–20 g/t Au.
6. DISCUSSION AND CONCLUSION

The footwall of the quartzites at Divinsky háj locality is built by metaarkoses, metasandstones, and green schists belonging to Late Permian (verucano in the terms of Gregor, 1951). On the base, they are covered by siliciclastic sediments with silicious conglomerates and quartzites. Upper parts have interlayers of metabelites. Lithological relationships are modified by tectonic lines of the NW–SE and NNW–SSE direction that caused tectonic shortening of the middle Triassic carbonates (rauwackes). Divinsky háj locality probably represents a relict of the south wing of the Tuhár fan (shallowly dipping to the NNW). Gold mineralization is bound to the contact between rheologically contrasting beds (schists and metaquartzites). The trend of ore zone is coincident with trend of young fault (NW–SE) related to Alpine deformation stage D3. These structures served for incursion of meteoritic waters that in the end led to formation of deep oxidation zones.

We suppose supergene origin of gold at Divín locality due to character of mineralization, chemical composition of gold and ore and mineralogical composition of ore. Besides Divín locality four occurrences of supergene Au-mineralization were described in the Veporic Unit. Uderíná is the best known locality (Maťo & Matová, 1993), the most explored locality of supergene Au-mineralization is at Pohronská Polhora (Knešl & Knešlová, 2002), small occurrence was mined in Middle Age at Katařinska Huta (Ferenc et al., 2006) and probably also in České Brezovo – Keľa with limited knowledge. Supergene Au mineralization is known also from Tatic Unit of Tribeč Mts. (Bakos & Zitňan, 2001).

Dozens more occurrences can be assumed in the Veporic Unit according to amount of heavy-mineral concentrate anomalies (Hvožďara, 1999). Old mining works focused to barren-seeming sulphides-free structures can be the next indicator of the presence of supergene gold mineralization occurrences.

All supergene gold mineralization occurrences show characteristic common features, which affect exploration methods and eventually their economic importance. Supergene enriched ore bodies are usually structurally controlled. The depth of the enrichment depends on palaeogroundwater level (several metres to more than 50 metres underneath the surface). Mineralization occurs in whichever rock type and metallogenetic types, gold distribution is irregular, economic potential ranges from several kg up to first tons of Au, and mineralization occurs in whichever rock type and metallogenetic types (Butt, 1998).

The basic geological factors controlling supergene Au mineralization are following: intense brittle-tectonic reworking (localized deformation), tropical or sub-tropical (semi-arid) climatic conditions, presence of a geochemical barrier for Au precipitation and terrain with relatively flat relief. The Au remobilization processes take place in two basic environments: Low-fineness gold in neutral-alkaline environment under the control of thiosulphate complexes and high-fineness gold in acid saline environment under the control of chlorine complexes (Webster & Mann, 1984). Most common geochemical barrier for Au redeposition are tectonic zones with presence of Fe-oxides and hydroxides (Gao et al.,

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**Tab. 1. Results of exploration drilling at Divín – Divínsky háj locality.**

<table>
<thead>
<tr>
<th>Drill hole</th>
<th>Comments</th>
<th>From (m)</th>
<th>To (m)</th>
<th>Interval (m)</th>
<th>Au (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td>6</td>
<td>11</td>
<td>6</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>Including</td>
<td>41</td>
<td>43</td>
<td>2</td>
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</tr>
<tr>
<td></td>
<td>Mined out</td>
<td>27.5</td>
<td>28.5</td>
<td>1</td>
<td>?</td>
</tr>
<tr>
<td>DH-2/35m</td>
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<td>23</td>
<td>30</td>
<td>7</td>
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</tr>
<tr>
<td></td>
<td>Including</td>
<td>26</td>
<td>28.2</td>
<td>2.2</td>
<td>4.14</td>
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<td></td>
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<td>40</td>
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<td>&lt;0.01</td>
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<td>11</td>
<td>3</td>
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<td>14</td>
<td>4</td>
<td>?</td>
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<tr>
<td></td>
<td>Mined out</td>
<td>28</td>
<td>31</td>
<td>3</td>
<td>?</td>
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<td>9</td>
<td>2</td>
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<tr>
<td>DH-10/37m</td>
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<td>3</td>
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<tr>
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<td>Including</td>
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<tr>
<td></td>
<td>Mined out</td>
<td>16</td>
<td>17</td>
<td>1</td>
<td>?</td>
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**Tab. 2. Various estimations of total gold production at Divín – Divínsky háj locality.**

<table>
<thead>
<tr>
<th>Average Au grade</th>
<th>1 m thickness of ore body</th>
<th>2 m thickness of ore body</th>
<th>3 m thickness of ore body</th>
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<tr>
<td>5 ppm Au</td>
<td>125 kg Au</td>
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<td>7 ppm Au</td>
<td>175 kg Au</td>
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<td>525 kg Au</td>
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<td>10 ppm Au</td>
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<td>750 kg Au</td>
</tr>
<tr>
<td>20 ppm Au</td>
<td>500 kg Au</td>
<td>1000 kg Au</td>
<td>1500 kg Au</td>
</tr>
</tbody>
</table>
1995), less common are barriers with Fe silicates, Mn oxides, and hydroxides or clay minerals (Milési et al., 1999).

We assume that gold from the Divín locality was remobilized in acid saline environment from the meteoric waters similar as Sarmatian – Panonian kaolinite weathering in the SW part of Veporic Unit (Kraus, 1989). Supergene Au mineralization in Divín is supposed to originate during 20 Ma at least according to other analogous deposits world-wide (Darke et al., 1997; Sillitoe & McKee, 1996). The depth of supergene kaoline alteration at Divín locality is min. 50 m. Supergene allunite indicate the depth of oxidation from 60 to 250 m in the Paradise Peak (Nevada) deposit (Sillitoe & Lorson, 1994). Depth of supergene alteration reached 30–50 m (max. 120 m in the central part) at Detva – Biely vrch Au porphyry deposit (Hanes et al., 2010).

Ore mineralization with Au described in the Veporic Unit, e.g., near Ozdín (Ferenc & Maťo, 2003), Uderiná (Maťo & Maťová, 1993), Pohronská Polhora (Knésl & Knéslová, 2002), Katarínska Huta (Ferenc et al., 2006) represents vein-stockwork quartz and carbonate mineralization (± small portion of Fe, As, Cu, Sb, Pb, Zn, Ni sulphides). Similar quartz stockwork with limonitized carbonates occurs at Divín locality (related to the Paradise Peak (Nevada) deposit (Sillitoe & Lorson, 1994). Depth of supergene alteration reached 30–50 m (max. 120 m in the central part) at Detva – Biely vrch Au porphyry deposit (Hanes et al., 2010).

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contact zone of schists vs. quartzites). Sporadically increased content of Cu, Sb, As, Ni, Co in limonite samples indicates that primary mineralization contained sulphides of above-mentioned metals. It could be expected that primary source of Au at Divín locality was quartz-carbonate mineralization with small portion of Cu, Sb and Ni, Co sulphides.

From the economic point of view, this type of ore body could be extracted in small extent by open pit without blasting operation. Gold could be obtained by gravity processing plant. Considering the high content of clay in ore, waste after Au extraction could be used as clay-material in building industry. If we compare projects like this with those at Kremnica or Detva deposits, this project has incomparably lesser impact on the environment, has higher chance get final approval of mining licence and in financial point of view is more accessible to domestic investors.

Acknowledgement: This work was financed by company AQUA SYM Ltd. Authors also thank Jiri Zacharia, Stefan Ferenc and Rastislav Vojtko for their detailed reviews.

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