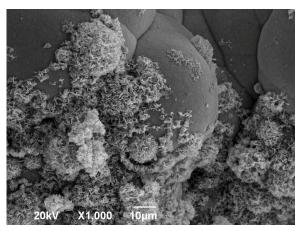
## STUDY OF SECONDARY MINERALS OF ABANDONED Cu DEPOSIT ĽUBIETOVÁ-PODLIPA (SLOVAKIA)

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This study presents preliminary results of detailed mineralogical investigation of sulphide oxidation products at abandoned Cu-Fe deposit at the L'ubietová-Podlipa (Central Slovakia). Our research goal is to determine release, migration and precipitation of metallic and non-metallic compounds under weathering conditions at the deposit. The Cu-Fe ore district L'ubietová has rich mining history and is nowadays famous as an interesting mineralogical locality. Environmental issues on this deposit comprise mainly oxidation of primary sulphides and forming of secondary phases such as those under this study. Our investigation was focused on Fe-oxy-hydroxides (known as good scavengers of many elements), Mn-oxides and supergene minerals of Cu by means of XRD, SEM-EDS, WDS.

The goethite of several generations and morphological types was recovered from the dump debris. It was identified as the main component of massive hard Feoxy-hydroxides ("limonite"). Usually it occurs in assemblage with libethenite, pseudomalachite, malachite and occasionally with hematite or Mn-oxides. Visible growth zoning corresponds to variation of main and trace elements in alternating layers. Fe content ranges from 30.43 to 52.43 wt% with minor concentration of Cu (< 6.89 wt%), P (< 2.49 wt%), Al (< 0.67 wt%), rarely Bi (< 5.70 wt%), Mn (< 0.19 wt%) and Si (< 1.06 wt%), traces of Co, Sb, As occur. The XRD study shows well ordered crystal structure of goethite. Bioxide (bismite?) was found in association with goethite. It forms irregular aggregates with skeletal texture or impregnations along growth zones within goethite. Covellite, idiomorphic natropharmacosiderite and pharmacosiderite were determined in microcracks, cavities and rims of tennantite. Covellite with goethite and chalcocite also replace primary chalcopyrite. Isolated grains of  $Ag_2S$  (< 5 µm) are frequently found in cavities and matrix of goethite and Cu secondary minerals. Studied Mn-oxides form fine grained aggregates in cavities of goethite, secondary Cu-phases and on quartz, or they occur as an interface between pseudomalachite and goethite. Several characteristic morphologies have also distinctive chemical composition: (1) aggregates of subtle acicular and fibrous crystals up to 1  $\mu m$  show Mn (< 43.87 wt%), Ba (< 8.60 wt%), Cu (< 7.25 wt%), Fe (< 6.47 wt%), Co (< 1.84 wt%) and Ca, Ni, K, Al < 1 wt%; (2) chaotically arranged platy crystals, up to 5  $\mu$ m, with Mn (< 28.02 wt%), Cu (< 16.89 wt%), Co (< 10.18 wt%), Fe (< 4.99 wt%) and Al, P, Ba, Ca, K < 1 wt%; (3) fine-grained porous aggregates with variable concentration of Mn, Cu, Co, Ba, Fe (EDS). The XRD revealed presence of romanèchite, hollandite and cryptomelane. These phases exhibit poorly defined (diffuse) diffraction maxima of low intensity characteristic of low degree of structural ordering and small size of diffraction domains. Definitive identification and refinement of crystal chemistry will be further performed by vibrational spectroscopy on well-defined mineral separates. Systematically increased contents of heavy metals in the Fe-oxy-hydroxides (goethite) and Mn-oxides suggest, that on the studied deposit they act as "natural" chemical barriers.



**Fig. 1.** Platy crystals of Mn-oxides growing on goethite (SEM).

During the study focused on secondary minerals, the ore minerals were also discovered. Some of them were already known (chalcopyrite, tetrahedrite, pyrite), others were expected (Ag<sub>2</sub>S, gold, tennantite, bismuthinite, gersdorffite), but presence of others is surprising (cinnabar, cassiterite).

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