MANGANESE MINERALS FROM THE OXIDATION ZONE OF BANSKÁ ŠTIAVNICA DEPOSIT

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The interesting and varied manganese and iron mineral association was described within the southern subsurface parts of the Terézia vein, which represent probably the oxidation zone of the Banská Štiavnica deposit. Besides the manganese oxide – todorokite, cryptomelane and pyrolusite have also been identified. The presence of vernadite, feroxyhyte and woodruffite is also assumed but these minerals have not been determined undoubtedly. Aggregates of these minerals are closely connected with the central cavities of the vein, where they fill up empty area among quartz crystals, but more often they form coatings on mineral surfaces, which suggest their formation in oxidizing conditions supported by bacteria activity (HÁBER *et al.*, 2003).

Within the primary vein filling sphalerite, galena, chalcopyrite, pyrite, tetrahedrite–tennantite, acanthite, polybasite–pearceite, gold–electrum, silver and hematite are present in substantial amounts. Pyrrhotite, marcasite, bornite, Cu-Ag-S mineral phases, chalcocite, gersdorffite, magnetite, ilmenite and rutile are present only as accessory minerals. With regard to non-metallic and secondary minerals, quartz, carbonates (calcite, dolomite, ankerite, siderite, kutnohorite, cerussite, smithsonite, witherite), rhodonite, anglesite, covellite, chlorites, clinozoisite, epidote, barite, gypsum, clay minerals (kaolinite, illite, illite/smectite) and hydroxides of iron are present (HÁBER *et al.*, 2002). The association of manganese and iron oxides and hydroxides represent the relatively youngest constituents of the vein fillings. Bright silver-grey, euhedral, tabular pyrolusite crystals form 1-2 mm thick crusts on the quartz surface. Pyrolusite crystals occur on the rims of globular aggregates composed of Mn and Fe minerals. Cryptomelane usually fills interstices in the quartz aggregates in the form of black masses.

The chemical composition of pyrolusite and cryptomelane was investigated using a CAMECA SX 100 electron microprobe. EDS spectra showed that pyrolusite contained Mn (60.67–61.53 wt%) and O. In cryptomelane K (3.10–3.82 wt%) and also Na, Zn, Ca, Mg and Fe contents were determined besides Mn (56.03–60.05 wt%) and O. The empirical formula of cryptomelane is as follows: $(Na_{0.10}K_{0.72}Ca_{0.02}Zn_{0.05})_{0.91}Mn_{8.03}O_{16}$.

X-ray study of pyrolusite and of cryptomelane was realised using a DRON-2 diffractometer and an RKG-86 Debye-Scherrer camera (Fe radiation, diameter of the sample 0.3 mm). Strongest lines observed on the Debye-Scherrer film (pyrolusite – 3.109 (10), 2.386 (9), 2.101 (4), 1.618 (7), 1.552 (3), 1.426 (1), cryptomelane – 6.96 (8), 4.81 (6), 3.109 (9), 2.39 (10), 1.54 (5)) and on the diffractogram (pyrolusite – 3.113 (100), 2.401 (15), 2.111 (4), 1.620 (27.5), 1.557 (19.5), 1.433 (1.5)) agree with the characteristic reflections of the cryptomelane and pyrolusite standards (MIKHEEV, 1957). X-ray study of the analysed homogenous grains of supposed vernadite and feroxyhyte samples was inconclusive because some characteristic reflections necessary for unambiguous identification have been missing. Probably insufficiently recrystallized amorphous phases, resp. X-ray amorphous phases of aggregates were investigated; the assumption that the samples contain probably vernadite and feroxyhyte is supported by the electron microscopic study (using JEOL JSM-840) and by the chemical composition of the grains in question.

We suppose, that within the oxidation zone of the upper part of Terézia vein, a stromatolitic texture with higher content of Mn minerals has been formed, by gradual growth of altered spongy soil tissues. Similarly to normal stromatolites, after they became gradually mineralised, mainly by Mn hydroxides. As the presence of unmineralized basidia and idiomorphic rhombohedral crystals of up to now unidentified Ca-Mg carbonates have been found in the studied samples, we suppose that this process has been going on up to the present.

Todorokite formations similar to those described from Terézia vein at Banská Štiavnica had been found by BOSTON *et al.* (2001) in New Mexico, USA. They described sinter coatings on walls and hanging-walls from Hidden Cave, Lechuguilla and Spider Caves. By means of SEM they found that the peculiar forms were built by microorganisms, which are composed of, besides other minerals, mixture of todorokite, buserite and amorphous Mn oxides ("filamentous manganese snow").

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