PŮVODNÍ PRÁCE/ORIGINAL PAPER

Supergénne minerály z kremeňovej žily s Mo-W mineralizáciou pri Ochtinej, Spišsko-gemerské rudohorie (Slovenská republika)

Supergene minerals from quartz vein with Mo-W mineralization near Ochtiná, Spišsko-gemerské rudohorie Mts. (Slovak Republic)

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Abstract

An interesting association of supergene minerals, represented by ferrimolybdite, hydrotungstite, jarosite, sulphur and tungstite has been recently identified at the outcrop of quartz vein with Mo-W mineralization (Mg-rich ferberite to huanzalaite, molybdenite and pyrite are dominant primary ore minerals) near the Ochtiná village, Spišsko-gemerské rudohorie Mts., Slovak Republic. Ferrimolybdite is a dominant supergene mineral and it forms pale to bright yellow crystalline coatings covering areas up to 400 cm^2 or radial and fibrous aggregates with silky lustre in fissures and cavities of quartz with rich impregnations of molybdenite. Coatings and aggregates of ferrimolybdite consist of individual acicular crystals up to 6 mm in size. It occurs predominantly separately, only infrequently it is directly associated together with sulphur, hydrotungstite and tungstite. It was identified by PXRD and its refined unit-cell parameters (for the orthorhombic space group *Pmmm*) are: *a* 6.670(3) Å, *b* 15.409(7) Å, *c* 28.924(7) Å and *V* 3075.6(2) $Å^3$. All studied samples of ferrimolybdite tend to be rather unstable in interaction with the electron beam, so complete quantitative chemical data of ferrimolybdite were not obtained, but except of dominant contents of Fe and Mo, also minor amounts of Ca (up to 0.4 wt.% CaO) and W (up to 1.2 wt. % WO_3) were detected. Hydrotungstite is common supergene phase and its occurrence is always closely constrained to accumulations of weathered ferberite. It mostly forms greenish-yellow to bright yellow fine-crystalline pseudomorphs after aggregates and crystals of ferberite or coatings on altered ferberite, in both cases very often associated with tungstite. Rare are well developed tabular crystals of hydrotungstite up to 4 mm in size growing on altered ferberite in drusy cavities of quartz. The unit-cell parameters of hydrotungstite refined from the powder X-ray diffraction data (for the monoclinic space group *P*2/*m*) are: *a* 7.392(5) Å, *b* 6.898(4) Å, *c* 3.765(4) Å, *β* 90.4(3)° with *V* 191.9(3) $Å^3$. Chemical composition of hydrotungstite from Ochtiná is close to ideal empirical formula $WO_2(OH)_2 \cdot H_2O$, only infrequent minor contents of Fe and Ca (both up to 0.01 *apfu*) were detected. Jarosite occurs as soft, yellowish-orange to yellowish-brown, fine-crystalline to powdery aggregates and fillings of drusy cavities and caverns after weathered pyrite up to several cm in size. Aggregates of jarosite consists of individual trigonal tabular crystals up to 15 μm in size. It occurs separately, predominantly in the parts of the vein which are rich in pyrite. Its unit-cell parameters refined from the powder X-ray data (for trigonal space group *R*-3*m*) are: *a* 7.296(3) Å, *c* 17.2202(3) Å and *V* 793.8(4) $Å^3$. Jarosite from Ochtiná contain uncommon concentrations of Mo and W (both up to 0.08 *apfu*), with average (n=10) empirical formula corresponding to $[K_{0.82}Na_{0.04}(H_3O)_{0.14}]_{\Sigma 1.00}(Fe_{2.89}Al_{0.01})_{\Sigma 2.90}[(SO_4)_{1.89}(MoO_4)_{0.06}(WO_4)_{0.05}]_{\Sigma 2.00}(OH)_{5.64}Cl_{0.03}$ on the basis of (S+Mo+W) = 2 *apfu*. Sulphur is common mineral and it forms pale yellow brittle crystalline aggregates and fillings of cavities up to several cm in size, which consists of rounded, often skeletal crystals up to 3 mm in size. It was identified by PXRD and its refined unit-cell parameters (for the orthorhombic space group *Fddd*) are: *a* 10.472(4) Å, *b* 12.864(6) Å, *c* 24.498(10) Å and *V* 3300.1(3) $Å^3$. Tungstite is common mineral, always closely associated with altered ferberite. It forms orange to brownish-yellow fine-crystalline coatings or pseudomorphs after ferberite, often associated together with hydrotungstite. Rare are crystalline crusts and aggregates of tungstite, which consists of well developed pyramidal crystals up to 40 μm in size. The unit-cell parameters of tungstite refined from the powder X-ray diffraction data (for the orthorhombic space group *Pmnb*) are: *a* 5.245(1) Å, *b* 10.727(2) Å, *c* 5.130(2) Å with *V* 288.6(1) $Å^3$. Two types of tungstite can be distinguished according to chemical composition, first has average

(n=5) empirical formula $(W_{0.98}Fe_{0.01}Ca_{0.01})_{\Sigma 1.00}O_3 \cdot H_2O$ based on (W+Fe+Ca) = 1 *apfu*. The second type is Fe enriched and its average (n=8) empirical formula is $(W_{0.74}Fe_{0.24}Ca_{0.02})_{\Sigma 1.00}O_3 \cdot H_2O$ based on (W+Fe+Ca) = 1 *apfu*. Described supergene mineral association is product of *in-situ* alteration of molybdenite and ferberite under the rather acidic conditions, which were induced by the weathering of abundant pyrite.

Key words: *supergene minerals, supergene zone, Mo-W mineralization, ferrimolybdite, hydrotungstite, jarosite, sulphur, tungstite, X-ray powder data, chemical composition, Ochtiná, Slovak Republic*

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