Hydrothermal scheelite associated with upper Cretaceous intrusions in Romania: A mineralogical insight to the W metallogenesis

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Hydrothermal scheelite from three Romanian occurrences was analyzed in order to ascertain its structural, optic, vibrational, paragenetic and crystal-chemical peculiarities, as an important tool for characterize the metallogenetic behavior and facilitate the ore-processing. All the three occurrences, *i.e.*, Ciclova (Ci) and Oravița (Or) in Banat and Băița Bihor (BB) in Bihor Mountains are related to skarn deposits developed at the contact of Upper Cretaceous granodioritic bodies with Mesozoic calcareous deposits. The host rocks are carbonated veins hosted by endoskarns at Ciclova and Oravița and magnesian exoskarns at Băița Bihor. Typical crystals show {001}, {111} and {101} forms and are up to 15 mm across. The structure was successfully refined as tetragonal, space group $I4_1/a$, with R_1 = 0.0165 (Ci), 0.0204 (Or) and 0.0237 (BB), respectively. The cell parameters refined for the same samples are a = 5.2459(10) Å and c = 11.3777(5) Å at Ciclova, a = 5.2380(2) Å and c = 11.3679(8) Å at Oravița, and a = 5.2409(2) Å and c = 11.3705(6) Å at Băița Bihor. The mean crystal-chemical formulae based on EMP analyses are $(Ca_{0.994}Mn_{0.001}Mg_{0.001}Fe_{0.002}Pb_{0.001}Cu_{0.001})(W_{0.981}Mo_{0.019})O_4$ (Ci), $(Ca_{0.996}Mg_{0.001}Fe_{0.002}Pb_{0.001})(W_{0.981}Mo_{0.019})O_4$ (Or), and $(Ca_{0.097}Mg_{0.001}Fe_{0.001}Pb_{0.001})(W_{0.983}Mo_{0.017})O_4$ (BB), respectively. The low contents of powellite that can be deduced from these formulas (up to 1.9 mol.%) perfectly agree with the blue tints of fluorescence in short-wave UV radiation (254 nm). Up to 0.1 mol% stolzite can be deduced from the chemical formulae, whereas the contents in Cu, Fe and Mn could be due to submicronic inclusions of cuprotungstite or even wolframite in the analyzed crystals, as a result of weathering or immiscibility. The multiplicity of bands in the infrared absorption spectrum ($2\nu_3 + 1\nu_1 + 2\nu_2 + 2\nu_4$) is consistent with the S_4 punctual symmetry of the tungstate anion, agreeing with the structural data. The most common associated sulfides are pyrite, chalcopyrite and gersdorffite at Ciclova and Oravița and chalcopyrite and galena at Băița Bihor. The abundance of F-bearing mineral species in the scheelite ore (i.e., fluorite and fluorapatite at Ciclova and Oravița and norbergite, clinohumite, fluorapatite and fluorite at Băița Bihor) is consistent with the precipitation of W from fluorine- and phosphorous-bearing fluids.