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Pyradoketosite, a new, unexpected, polymorph of Ag_3SbS_3 from the Monte Arsiccio mine (Apuan Alps, Tuscany, Italy)

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Abstract

Although everything seemed clear about the Ag-Sb-S compounds belonging to one of the more deeply studied experimental systems, nature allowed us to discover a new polymorph of Ag_3SbS_3, which could represent a compound for assessing new technological potentialities. The new mineral species pyradoketosite, Ag_3SbS_3 (IMA 2019-132), was discovered in the pyrite + baryte + iron oxide ore deposit of the Monte Arsiccio mine, Apuan Alps, Tuscany, Italy. It occurs as brittle orange acicular crystals, up to 200 μm in length and 25 μm in thickness, with adamantine luster. Under reflected light, pyradoketosite is slightly bluish-gray, with abundant orange internal reflections. Bireflectance is weak, and anisotropism was not observed, being masked by abundant internal reflections. Minimum and maximum reflectance data for the wavelengths recommended by the Commission on Ore Mineralogy [R_{min}/R_{max} (%) (λ, nm)] are 32.8/32.9 (470), 30.2/30.7 (546), 29.0/29.6 (589), and 27.5/28.4 (650). Electron microprobe analysis gave (mean of 6 spot analyses, in wt%): Ag 59.81, Sb 22.63, S 17.78, total 100.22. On the basis of (Ag+Sb) = 4 atoms per formula unit, the empirical formula of pyradoketosite is $Ag_{2.996(11)}Sb_{1.004(11)}S_{2.996(15)}$. Pyradoketosite is monoclinic, space group $P2_1/n$, with a = 13.7510(15), b = 6.9350(6), c = 19.555(2) Å, β = 94.807(4)°, V = 1858.3(3) Å^3, Z = 12. The crystal structure was solved and refined to R_1 = 0.063 on the basis of 2682 unique reflections with $F_o > 4\sigma(F_o)$ and 191 refined parameters. The structure of pyradoketosite can be described as formed by the alternation of {101} layers: an Sb-rich layer, Sb_3AgS_3, and two distinct Ag_8S_6 layers. This layered organization allows identifying structural relationships with the wittichenite-skinnerite pair. Pyradoketosite is associated with pyrargyrite, tetrahedrite-(Hg), valentinite, and probable pyrostilpnite in baryte + dolomite + quartz veins embedded in metadolostone. Its name derives from the old Greek words "πυρ" (fire) and "άδόκητος" (unforeseen), because of the unexpected occurrence of this third polymorph of the compound Ag_3SbS_3.

Keywords: Pyradoketosite, silver, antimony, sulfosalt, crystal structure, new mineral, Monte Arsiccio mine, Apuan Alps, Tuscany, Italy