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First occurrence of iodine in natural sulfosalts: The case of mutnovskite, $Pb_2AsS_3(I,Cl,Br)$, a new mineral from the Mutnovsky volcano, Kamchatka Peninsula, Russian Federation

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Abstract

Mutnovskite, ideally $Pb_2AsS_3(I,Cl,Br)$, is a new mineral from the high-temperature fumaroles of the Mutnovsky volcano, Kamchatka Peninsula, Russian Federation. It occurs as microscopic ruby-colored short-prismatic crystals up to 100 μm across, closely associated with halogen-sulfosalts of Pb, Bi, and As, Cd-Pb-Bi sulfosalts, pyrite, anhydrite, and cristobalite. Mutnovskite is transparent in thin fragments with a dark-red to blue color. The crystals are soft and fragile. Cleavage and fracture were not observed and the Mohs hardness is approximately 2. In reflected light mutnovskite is silvery lead-grey in color with an iridescent tarnish. Pleochroism and anisotropy are not visible because of the strong orange internal reflections, especially in immersion. Reflectance percentages measured in air in the range 400–700 nm were tabulated. Reflectance percentages (R_{min} and R_{max}) for the four COM wavelengths are 34.2, 34.6 (470 nm), 33.2, 33.5 (546 nm), 32.5, 32.7 (589 nm), and 31.4, 31.7 (650 nm), respectively. A mean of four electron microprobe analyses gave Pb 62.0(3), As 11.0(4), Bi 0.6(1), S 14.4(2), Se 0.2(3), I 8.9(3), Cl 2.44(9), Br 1.1(7), Cu 0.03(2), Fe 0.01(1), total 100.7 wt%, corresponding, on the basis of a total of 7 atoms, to $Pb_{1.99}(As_{0.98}Bi_{0.02})_{\Sigma 1.00}(S_{2.98}Se_{0.02})_{\Sigma 3.00}(I_{0.47}Cl_{0.46}Br_{0.09})_{\Sigma 1.02}$. The nine strongest powder-diffraction lines [*d* in Å (I/I_0) (*hkl*)] are: 4.69 (32) (002); 4.37 (67) (210); 3.34 (73) (020); 3.19 (100) (212); 2.715 (61) (022); 2.648 (66) (410); 2.539 (31) (213); 2.455 (29) (402); 1.894 (30) (232). Mutnovskite is orthorhombic, space group *Pnma*, with $a = 11.543(1)$, $b = 6.6764(7)$, and $c = 9.359(1)$ Å, $V = 721.3(1)$ Å^3, $Z = 4$. The crystal structure was solved and refined to $R = 4.14\%$. It consists of three independent cation positions: Pb1 and Pb2 have tricapped trigonal prismatic coordinations with S and I atoms (completed with one As atom in the case of Pb2), while As has threefold coordination with S atoms, which form the base of a trigonal pyramid with As at the apex. Pairs of Pb1-Pb2 prisms are connected in columns which extend along **c**. AsS_3 coordinations are isolated from each other. S atoms and half of the Pb atoms form wavy close-packed layers. Two kinds of channels parallel to **b** occur between the layers. The smaller channels host As atoms close to the channel walls, with their lone-electron pairs occupying the median part, while the bigger ones accommodate rows of alternating halogen and Pb atoms. The new mineral is named after the type locality, the Mutnovsky volcano, Kamchatka Peninsula, Russian Federation.

Keywords: Mutnovskite, chemical composition, new mineral, X-ray data, crystal struture, Kamchatka Peninsula, Mutnovsky volcano