

Sb⁵⁺ and Sb³⁺ substitution in segnitite: A new sink for As and Sb in the environment and implications for acid mine drainage

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ABSTRACT

A sample of Sb-rich segnitite from the Black Pine mine, Montana, U.S.A., has been studied by microprobe analyses, single-crystal X-ray diffraction, and μ -EXAFS and XANES spectroscopy. Linear combination fitting of the spectroscopic data provided Sb⁵⁺:Sb³⁺ = 85(2):15(2), where Sb⁵⁺ is in octahedral coordination substituting for Fe³⁺ and Sb³⁺ is in tetrahedral coordination substituting for As⁵⁺. Based upon this Sb⁵⁺:Sb³⁺ ratio, the microprobe analyses yielded the empirical formula Pb_{1.02}H_{1.02}(Fe_{2.36}Sb_{0.41}Cu_{0.27})_{Σ3.04}(As_{1.78}Sb_{0.07}S_{0.02})_{Σ1.88}O₈(OH)_{6.00}. The crystal structure refinement and bond valence analysis are consistent with these cation site assignments. The formation of Sb-rich segnitite opens new possibilities for Sb sinks within the supergene zone. Segnitite may, in fact, be an ideal host for the sequestering of several toxic elements for pH < 2. At higher pH values, As is more likely to be incorporated into schwertmannite and ferrihydrite.

Keywords: μ -EXAFS, XANES, crystal structure, segnitite, antimony, valency, alunite supergroup, oxidized zone