

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 $\text{Sb}^{5+}:\text{Sb}^{3+} = 85(2):15(2)$, where Sb^{5+} is in octahedral coordination substituting for Fe^{3+} and Sb^{3+} is in tetrahedral coordination substituting for As^{5+} . Based upon this $\text{Sb}^{5+}:\text{Sb}^{3+}$ ratio, the microprobe analyses yielded the empirical formula $\text{Pb}_{1.02}\text{H}_{1.02}(\text{Fe}_{2.36}\text{Sb}_{0.41}\text{Cu}_{0.27})_{\Sigma 3.04}(\text{As}_{1.78}\text{Sb}_{0.07}\text{S}_{0.02})_{\Sigma 1.88}\text{O}_8(\text{OH})_{6.00}$. 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 $\text{pH} < 2$. 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