Sb$^{5+}$ and Sb$^{3+}$ 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 Sb$^{5+}$:Sb$^{3+} = 85(2):15(2)$, where Sb$^{5+}$ is in an octahedral coordination substituting for Fe$^{3+}$ and Sb$^{3+}$ is in tetrahedral coordination substituting for As$^{3+}$. Based on this Sb$^{5+}$:Sb$^{3+}$ ratio, the microprobe analyses yielded the empirical formula Pb$_{5.02}$H$_{1.02}$(Fe$^{3+}_{0.36}$Sb$_{0.64}$Cu$_{0.01}$)$_{3.04}$(As$^{3+}_{0.07}$Sb$_{0.93}$)$_{2.04}$(OH)$_{6.80}$-OH$^{-}$. 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. Seginitite may, in fact, be an ideal host for the sequestration of several toxic elements for pH < 2. At higher pH values, As is more likely to be incorporated into schwertmannite and ferricyanide.

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

INTRODUCTION

Seginitite, ideally PbFe$_3^+(\text{AsO}_4)_2(\text{OH},\text{H}_2\text{O})_6$ (Birch et al., 1992), is the Pb Fe-rich member of the dussertite group, within the alunite supergroup (Mills et al. 2009a; Bayliss et al., 2010). It forms solid-solution series with both kintoreite and beudantite (e.g., Rattray et al. 1996; Jambor 1999; Mills 2007), and it has been observed at more than 100 localities worldwide (www.mindat.org).

Minerals in the alunite supergroup have the general formula $AB_3(TO_4)_2X_n$, where the A-site can be occupied by monovalent (Na$^+$, K$^+$, Ag$^+$, NH$_3$, or H$_2$O$^-$), divalent (Pb$^{2+}$, Ca$^{2+}$, or Ba$^{2+}$), or trivalent (Bi$^{3+}$ or REE$^{3+}$) cations; the B-site can be occupied by either Fe$^{3+}$, Al$^{3+}$, or Ga$^{3+}$, while the T cation site can be occupied by P$^{5-}$, S$^{2-}$, or As$^{5+}$ (e.g., Jambor 1999). The supergroup has always been of significant interest to mineral scientists especially because of its relevance to acid mine drainage (e.g., Nordstrom et al., 2000; Welch et al. 2007, 2008, 2009) and the mobility of toxic elements (e.g., Kolitsch and Pring 2001) and because of its structural variability (e.g., Grey et al. 2008; Mills et al. 2008). To date, however, there has been only one reported example of Sb substitution within a member of the supergroup. Kolitsch et al. (1999) reported the structure of “antimonian” dussertite from the Clara mine, Germany, and attributed all of the Sb to Sb$^{3+}$ substituting for Fe$^{3+}$ within the octahedral site. The find of an unusual Sb-rich segnitite from the Black Pine mine, Montana, U.S.A., has prompted further investigation by us into the valency and structural role of Sb within members of the alunite supergroup.

EXPERIMENTAL METHODS

Sample

The Sb-rich segnitite occurs at the Black Pine mine, 14.5 km NW of Philipsburg, Granite Co., Montana, U.S.A. (46°26′52″N, 113°21′56″W), and was discovered by John Dagenais of Vancouver, British Columbia, Canada. The mineral occurs as flattened, tabular or rhombohedral yellowish crystals up to about 100 μm across. Crystals are commonly intergrown to form botryoidal groups up to about 0.3 mm across and also form as coatings lining quartz vughs and on quartz crystals. Associated minerals are hidalgoite and tetrahedrite. The Black Pine mine is the type locality for philipsburgite (Peacock et al. 1985), joëlbruggerite (Mills et al. 2009a), and auriacusite (Mills et al. 2010). The studied specimen has been deposited in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County, catalog number 64096.

X-ray absorption spectroscopy

Sb K-edge (30491 eV) X-ray absorption near edge structure (XANES) and micro-extended X-ray absorption fine structure (μ-EXAFS) spectra were measured at beamline 13-ID-C (GSE-CARS) at the Advanced Photon Source (APS), at Argonne, U.S.A. The APS is a 7 GeV ring and operates in top-up mode with a current of 102 mA. 13-ID-C is an undulator beamline with a Si(111) monochromator and an energy resolution (∆E/E) of 1.4 × 10^-4 at 10 keV. A focused beam size of 5 μm$^2$ was used. A 16-element solid-state Ge detector was used for detecting fluorescence data. XANES and μ-EXAFS data were analyzed with the HORAEE package (Ravel and Newville 2005), calculations being performed using FEFF version 9 (Rehr et al., 2010). Self-absorption effects were checked for the fluorescence data using the SABCOR (Booth and Bridges 2005) correction routine that is incorporated into ATHENA (part of the HORAEE package) and were found to be negligible. The data

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