American Mineralogist, Volume 105, pages 1088–1098, 2020

Crystal-chemistry of sulfates from the Apuan Alps (Tuscany, Italy). VI. Tl-bearing alum-(K) and voltaite from the Fornovolasco mining complex

Cristian Biagioni[1,*], Daniela Mauro[1], Marco Pasero[1], Elena Bonaccorsi[1], Giovanni Orazio Lepore[2,†], Federica Zaccarini[3], and Henrik Skogby[4]

[1]Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy
[2]CNR-IOM-OGG c/o ESRF, 71 Avenue des Martyrs CS 40220 F-38043 Grenoble Cedex 9, Grenoble, France
[3]Department of Applied Geological Sciences and Geophysics, University of Leoben, Peter Tunner Str. 5, A-8700 Leoben, Austria
[4]Department of Geosciences, Swedish Museum of Natural History, Box 50007, SE-10405 Stockholm, Sweden

Abstract

Thallium-bearing samples of alum-(K) and voltaite from the Fornovolasco mining complex (Apuan Alps, Tuscany, Italy) have been characterized through X-ray diffraction, chemical analyses, micro-Raman, infrared (FTIR), Mössbauer, and X-ray absorption spectroscopy (XAS). Alum-(K) occurs as anhedral colorless grains or rarely as octahedral crystals, up to 5 mm. Electron-microprobe analysis points to the chemical formula $(K_{0.74}Tl_{0.10})_{\Sigma 0.84}(Al_{0.84}Fe_{0.14})_{\Sigma 0.98}S_{2.03}O_8 \cdot 12H_2O$. The occurrence of minor NH_4^+ was detected through FTIR spectroscopy. Its unit-cell parameter is a = 12.2030(2) Å, V = 1817.19(9) Å^3, space group $Pa\bar{3}$. Its crystal structure has been refined down to R_1 = 0.0351 for 648 reflections with $F_o > 4\sigma(F_o)$ and 61 refined parameters. The crystal structure refinement agrees with the partial substitution of K by 12 mol% Tl. This substitution is confirmed by XAS data, showing the presence of Tl^+ having a first coordination shell mainly formed by 6 O atoms at 2.84(2) Å. Voltaite occurs as dark green cubic crystals, up to 1 mm in size. Voltaite is chemically zoned, with distinct domains having chemical formula $(K_{1.94}Tl_{0.28})_{\Sigma 2.22}(Fe^{2+}_{3.57}Mg_{0.94}Mn_{0.55})_{\Sigma 5.06}Fe^{3+}_{3.06}Al_{0.98}S_{11.92}O_{48} \cdot 18H_2O$ and $(K_{2.04}Tl_{0.32})_{\Sigma 2.36}(Fe^{2+}_{3.83}Mg_{0.91}Mn_{0.29})_{\Sigma 5.03}Fe^{3+}_{3.05}Al_{0.97}S_{11.92}O_{48} \cdot 18H_2O$, respectively. Infrared spectroscopy confirmed the occurrence of minor NH_4^+ also in voltaite. Its unit-cell parameter is a = 27.2635 Å, V = 20265(4) Å^3, space group $Fd\bar{3}c$. The crystal structure was refined down to R_1 = 0.0434 for 817 reflections with $F_o > 4\sigma(F_o)$ and 87 refined parameters. The partial replacement of K by Tl is confirmed by the structural refinement. XAS spectroscopy showed that Tl^+ is bonded to six O atoms, at 2.89(2) Å. The multi-technique characterization of thallium-bearing alum-(K) and voltaite improves our understanding of the role of K-bearing sulfates in immobilizing Tl in acid mine drainage systems, temporarily avoiding its dispersion in the environment.

Keywords: Alum-(K), voltaite, thallium, XAS, crystal structure, Fornovolasco, Apuan Alps, Tuscany, Italy