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

Cristian Biagioni1,*, Daniela Mauro1, Marco Pasero1, Elena Bonaccorsi1, Giovanni Orazio Lepore2†, Federica Zaccarini3, and Henrik Skogby4

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 \((K_{0.73}Tl_{0.28}Fe_{0.34}Al_{0.24}O_{2}·18H_2O\)) \(\Sigma 4.17\). The crystal structure was refined down to \(R = 0.0351\) 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 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 \((K_{1.98}Tl_{0.02}Fe_{0.22}Al_{0.53}O_{2}·18H_2O\)) \(\Sigma 3.83\) and \((K_{2.01}Tl_{0.02}Fe_{0.22}Al_{0.53}O_{2}·18H_2O\)) \(\Sigma 3.83\). The crystal structure was refined down to \(R = 0.0344\) 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

INTRODUCTION

Thallium \((Z=81)\) is a toxic heavy element, classified as one of the 13 priority metal pollutants (Keith and Tellier 1979) and having an average concentration in the upper continental crust of 0.75 μg/g (Wedepohl 1995). Thallium occurs in two different oxidation states, i.e., Tl+ and Tl3+. Monovalent Tl has both a lithophile and chalcophile geochemical behavior, being enriched in K-bearing minerals as well as in several chalcogenides. In particular, the ionic radius of Tl+ is close to that of K+ and Rb+ (e.g., Shannon 1976). Indeed, the only three secondary Tl3+-minerals known up to now as products of sulfide weathering, i.e., dorallcharite, TiFe3(SO4)(OH)6 (Balić-Žunic et al. 1994), lamnuchangite, \(TlAl(SO_4)·12H_2O\) (Chen and Wang 2001), and thalliumpharmacosiderite, \(TlFe_4(AsO_4)(OH)_4·4H_2O\) (Runsey et al. 2014), are the counterparts of the K-minerals jarosite, alum-(K), and pharmacosiderite, respectively. Götz et al. (1968) described “monsmedite” as a new K-Tl3+ sulfate, with approximate chemical formula \(Tl_2O_7·K_2O·8SO_3·15H_2O\). This species was later discredited by the then IMA-CNMMN (Grice and Ferraris 2003), and the reinvestigation of several samples and co-type material by some authors (e.g., Johan et al. 2009; Kovács-Pálffy et al. 2011) showed that “monsmedite” is simply Tl-bearing voltaite.

The identification of the thallium-rich nature of the pyrite ore deposits of the southern Apuan Alps (northern Tuscany, Italy), with up to more than 4000 μg/g Tl (Biagioni et al. 2013; George et al. 2018), gave rise to a series of mineralogical and geochemical studies that led to the description of the dispersion of thallium in the environment (D’Orazio et al. 2017; Biagioni et al. 2017; Perotti et al. 2018; Ghezzi et al. 2019). Sulfate assemblages play a major role in the control of the release of heavy metals in the environment, and their mineralogical characterization is being currently undertaken. Our attention is mainly focused on the assemblages found in the Fornovolasco mining complex, where

*D E-mail: cristian.biagioni@unipi.it
† Orcid 0000-0002-7984-3099.