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First occurrence of close-to-ideal kirkiite at Vulcano (Aeolian Islands, Italy): chemical data and single-crystal X-ray study

DANIELA PINTO[1], TONCI BALIĆ-ŽUNIĆ[2], ANNA GARAVELLI[1], CARLO GARBARINO[3], EMIL MAKOVICKY[2] and FILIPPO VURRO[1], *

[1]Dipartimento Geomineralogico, University of Bari, Via E. Orabona 4, I-70125 Bari, Italy
*Corresponding author, e-mail: f.vurro@geomin.uniba.it
[2]Department of Mineralogy, Geological Institute, University of Copenhagen, Østervoldgade 10, DK-1350 Copenhagen K, Denmark
[3]Dipartimento di Geoingegneria e Tecnologie Ambientali, University of Cagliari, Piazza d'Armi, I-09123 Cagliari, Italy

Abstract: Samples of kirkiite from the high temperature fumaroles of La Fossa crater of Vulcano (Aeolian islands, Italy) were chemically and structurally investigated in this work. Associated minerals are vurroite, bismuthinite, galenobismutite, cannizzarite, lillianite, heyrovskýite, galena, and other less characterized Pb(Bi)-sulfochlorides. Electron-microprobe analyses gave the average chemical formula $Pb_{10.00}Bi_{3.01}As_{3.01}(S_{18.47}Se_{0.44}Cl_{0.06})_{\Sigma=18.97}$, which is very close to the ideal composition of kirkiite, $Pb_{10}Bi_3As_3S_{19}$, and indeed significantly closer than the composition of the type specimen, $Pb_{10.08}Bi_{2.55}Sb_{0.13}As_{2.91}S_{19}$. Lattice parameters are: a = 8.700(2) Å, b = 26.237(6) Å, c = 8.774(3) Å, β = 119.653(4)°, V = 1740.2(9) Å^3. A twinned structure was refined using single-crystal data (Mo$K\alpha$ X-ray diffraction, CCD detector). The refinement converges to R = 0.074 for 1443 reflections with $F_o > 4\sigma(F_o)$. The structure of the close-to-ideal kirkiite from Vulcano has been compared with the structure of the type specimen.

The comparison reveals a variation in As-Bi substitution, with samples from Vulcano probably being close to the maximum possible Bi and the minimum As content for this structure type. This is reflected in more regular and symmetric coordination polyhedra than in the holotype, as well as in the overall regularity of the structure. The increased Bi:As ratio produces an elongation of the a and b lattice periods, and a shortening of the c period, and increases the frequency of twinning in kirkiite.

Key-words: kirkiite, sulfosalts, crystal structure, twinning, Vulcano fumaroles.

Introduction

Kirkiite with composition $Pb_{10.08}Bi_{2.55}Sb_{0.13}As_{2.91}S_{19}$, ideally $Pb_{10}Bi_3As_3S_{19}$, was first described by Moëlo *et al.* (1985) from the Aghios Philippos deposit near Kirki (Greece). Notwithstanding the compositional differences, it was considered as the natural analogue of the synthetic Phase A in the system PbS-Bi_2S_3-As_2S_3 (Walia & Chang, 1973). The crystal structure of type kirkiite has recently been determined (Makovicky *et al.*, 2006). It consists of octahedral slabs (010), three octahedral layers thick, mutually related by a mirror plane situated in the intervening layer of prisms. This structure can be alternatively described as composed of slabs based on a transitional PbS/SnS archetype, with tightly-bonded layers parallel to (083) of kirkiite; the slabs are unit-cell twinned on (010) mirror planes (Makovicky *et al.*, 2006). The structure of kirkiite forms a pair of homologues with the crystal structure of jordanite $Pb_{28}As_{12}S_{46}$ (Ito & Nowacki, 1974). The homology of these structures was suggested by Moëlo *et al.* (1985) as well as by Makovicky (1989), and confirmed by the structure determination (Makovicky *et al.,* 2006). In the latter work, the general formula of the potential kirkiite homologous series was defined as $Pb_{8N-4}Me^{3+}_{12}S_{8N+14}$, where N represents the number of octahedral layers in the (010) octahedral slabs. Kirkiite and jordanite represent respectively the homologues N = 3 and N = 4 of this series.

Borodaev *et al*. (1998) described the occurrence of kirkiite from the high temperature fumarole deposit of La Fossa crater, Vulcano island, Aeolian archipelago, Italy. The crystals were collected in 1993 from the deepest part of the fumarole F11 (T = 470 °C). The average composition was $Pb_{9.97}(Bi_{2.61}As_{3.35})_{\Sigma=5.96}(S_{18.65}Se_{0.42})_{\Sigma=19.07}$. The higher content of As, the presence of Se, as well as the absence of Sb make it compositionally different from the holotype (Moëlo *et al.*, 1985).

A new occurrence of kirkiite was found at Vulcano in 1998. The new crystals revealed an unusual composition, very close to the ideal $Pb_{10}Bi_3As_3S_{19}$. This suggested to perform more detailed crystal-chemical and structural investigations. The results of this study are listed and discussed herein.

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