The Canadian Mineralogist
Vol. 36, pp. 1105-1114 (1998)

RARE SULFOSALTS FROM VULCANO, AEOLIAN ISLANDS, ITALY. I. Se-BEARING KIRKIITE, $Pb_{10}(Bi,As)_6(S,Se)_{19}$

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ABSTRACT

This note reports the first occurrence of a Se-bearing variety of kirkiite, a rare lead – bismuth – arsenic sulfosalt, from the deepest part of fumarole F11, La Fossa crater, island of Vulcano, Italy. Small crystals of sphalerite and aggregates of cannizzarite occur sporadically on the kirkiite crystals. Optical properties, X-ray powder-diffraction data and the results of electron-microprobe analyses are compared with those of kirkiite from type locality as well as of phase A, the synthetic analogue. An electron-microdiffraction study revealed the presence of three structural varieties of kirkiite. The Se content ranges from 0.73 to 1.16 wt%. As and Bi concentrations vary from 6.49 to 7.98 wt% and from 14.32 to 16.84 wt%, respectively. The composition field of kirkiite from Vulcano can be described by the formula $Pb_{10}(As_{6-x}Bi_x)_{\Sigma 6}(S_{19-y}Se_y)_{\Sigma 19}$, where $2.3 \leq x \leq 2.8$ and $0.3 \leq y \leq 0.5$, which is close to the ideal formula $Pb_{10}(As,Bi)_6(S,Se)_{19}$. Kirkiite and its associated minerals at Vulcano crystallized at a high fugacity of sulfur and a high temperature (470°C, direct measurements). This temperature is in agreement with that known for the synthetic analogue, stable at 400°C .

Keywords: kirkiite, cannizzarite, Pb–Bi–As sulfosalts, Pb–Bi sulfosalts, fumarolic incrustations, Vulcano Island, Italy.

SOMMAIRE

Nous décrivons pour la première fois un exemple d'une variété sélénifère de kirkiite, sulfosel rare de plomb, bismuth et arsenic, provenant de la partie la plus profonde de la fumerolle F11 du cratère La Fossa, île de Vulcano, en Italie. On trouve aussi de façon sporadique des petits cristaux de sphalérite et des agrégats de cannizzarite sur les cristaux de kirkiite. Les propriétés optiques, les données de diffraction X et les résultats d'analyses à la microsonde électronique sont comparés avec ceux de la kirkiite de la localité type et de la phase A, équivalent synthétique. Une étude par microdiffraction des électrons a révélé la présence de trois variantes structurales de la kirkiite. Les teneurs en Se vont de 0.73 à 1.16% en poids. Les teneurs en As and Bi varient de 6.49 à 7.98% et de 14.32 à 16.84%, respectivement. L'intervalle de compositions de la kirkiite de Vulcano répond à la formule $Pb_{10}(As_{6-x}Bi_x)_{\Sigma 6}(S_{19-y}Se_y)_{\Sigma 19}$, dans laquelle $2.3 \leq x \leq 2.8$ et $0.3 \leq y \leq 0.5$, ce qui se rapproche de la formule idéale, $Pb_{10}(As,Bi)_6(S,Se)_{19}$. La kirkiite et les phases associées ont cristallisé à une fugacité élevée du soufre et à une température élevée (470°C, mesures directes). Cette température concorde bien avec le fait que l'équivalent synthétique est stable à 400°C .

(Traduit par la Rédaction)

Mots-clés: kirkiite, cannizzarite, sulfosels de Pb–Bi–As, sulfosels de Pb–Bi, incrustations fumerolliennes, île de Vulcano, Italie.

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INTRODUCTION

Kirkiite, the first representative of As–Bi sulfosalts, was first discovered at the Aghios Philippos lead–zinc deposit near Kirki, in Greece, by Moëlo *et al.* (1985). An ideal formula $Pb_{10}Bi_3As_3S_{19}$ was proposed by considering an ordered distribution of Bi and As atoms in it. The exact structure of kirkiite has remained unknown until now, but on the basis of its structural resemblance to jordanite, $Pb_{10}(As,Sb)_6S_{23}$, it was classified with the jordanite homologous series. The *a* and *c* dimensions of the pseudohexagonal cell were determined to be 8.69 and 26.06 Å, respectively. Moëlo *et al.* (1985) considered kirkiite as the natural analogue of phase A (Walia & Chang 1973).

In the Greek deposit, kirkiite is associated with cosalite, bismuthinite, Bi-bearing jordanite (up to 4.6 wt% Bi), galena and seligmannite, in a matrix of sphalerite and pyrite. Epitactic growth of jordanite grains around kirkiite crystals was documented. Later, kirkiite with a very high Sb content [Sb/Bi (atomic) >1.0] was found in the same deposit, and the new mineral species lévyclaudite, $Pb_8Sn_7Cu_3(Bi,Sb)_3S_{28}$, a member of cylindrite series, was established in the association (Moëlo *et al.* 1990).

In this paper, we report the first occurrence of Se-bearing kirkiite. The mineral was collected from fumaroles at Vulcano, Aeolian Islands, Italy. It is the first As–Bi-bearing mineral to be found in fumaroles.

OCCURRENCE

The island of Vulcano (Fig. 1) lies off the northern coast of Sicily. Presently fumarolic activity is mainly located at La Fossa crater. Keller (1980) and Frazzetta *et al.* (1983) provided details of the geological setting. A description of the fumaroles and of the mineralogy of the area was given by Garavelli (1994) and Garavelli *et al.* (1997).

It has been noted that sulfosalts and sulfides appeared only during thermal anomalies, when the temperature of fumaroles increased up to 400°C. The first took place in 1923–1927, and only one sulfosalt mineral, cannizzarite, was discovered (Zambonini *et al.*

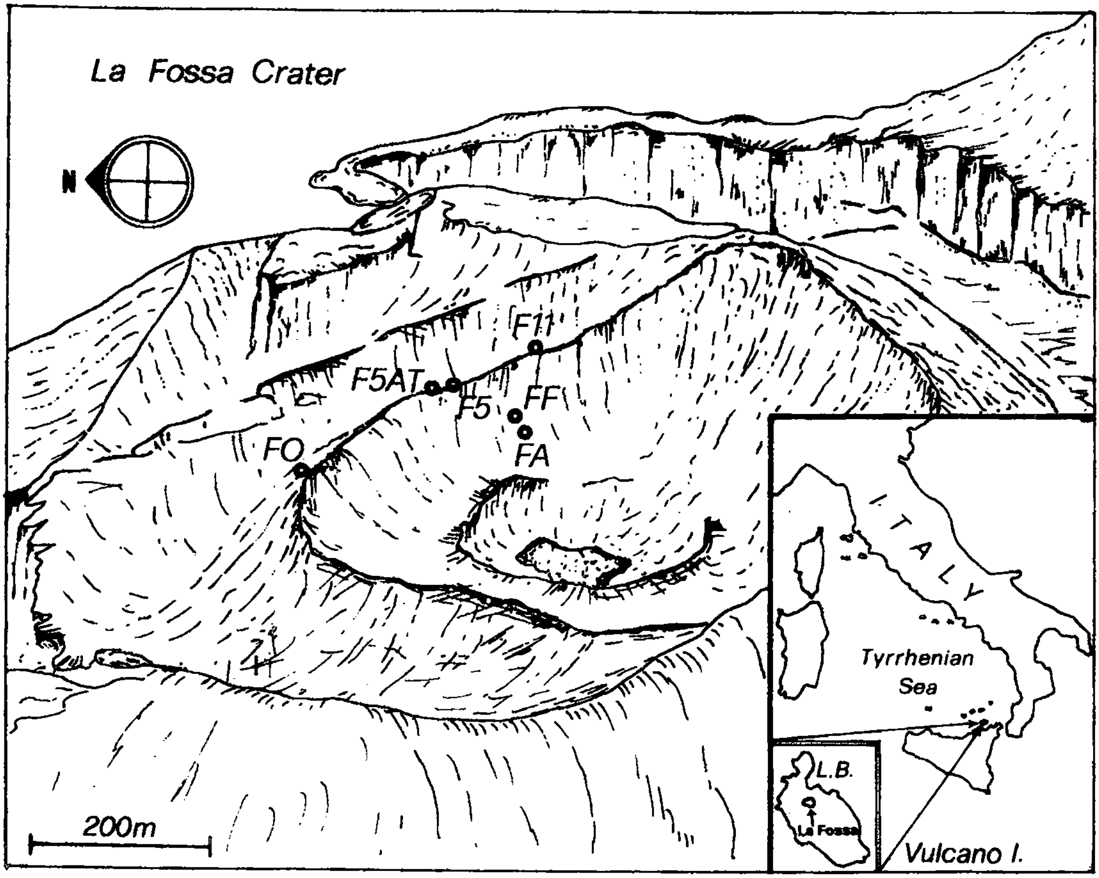

FIG. 1. Location of the La Fossa crater fumaroles and sampling sites at Vulcano.

1925). Later, in museum samples of "cannizzarite", five minerals belonging to the Pb–Bi–S(Se) system were identified (Mozgova *et al.* 1985). In 1990, sulfides and sulfosalts appeared again around the hottest fumaroles FA and FF (Fig. 1), located inside the crater, for which a temperature of 595° and 607°C, respectively, was measured. The deposition of these phases was continuous since 1990 up to 1996. Beginning in June 1993, owing to the temperature increase, sulfides and sulfosalts appeared also on the crater rim, around the F5AT and F11 fumarolic vents. As in the period 1923–1927, the minerals of the system Pb–Bi–S(Se) (Table 1) occur as minute crystals covering rock surfaces from the deepest part of the hottest fumaroles (T > 400°C).

TABLE 1. PUBLISHED DATA ON INCRUSTATION MINERALS BELONGING TO THE Pb-Bi-S SYSTEM COLLECTED AROUND HIGH TEMPERATURE FUMAROLES AT VULCANO.

Minerals	*Formulae*	*References*
Galena	PbS	1
"Goongarite"	$Pb_{10}Bi_5S_{18}$	1
Lillianite	$Pb_3Bi_2S_6$	1-2
Bursaite	$Pb_5Bi_4S_{11}$	2
Cosalite	$Pb_2Bi_2S_5$	1-2
Cannizzarite	$Pb_4Bi_{5-x}S_{11.5-1.5x}$	1-2
Galenobismutite	$PbBi_2S_4$	1-2
Bismuthinite	Bi_2S_3	2

References :
1. Mozgova et al. (1985); 2. Garavelli (1994), Garavelli et al. (1997).

Geochemical investigations showed the particular abundance of selenium and arsenic among the products from the La Fossa crater fumarolic area (Garavelli *et al.* 1997). Selenium was established in sulfosalts as a substituent for sulfur (Mozgova *et al.* 1985, Garavelli *et al.* 1993); As–S–Cl compounds were the predominant solid phases containing arsenic identified as sublimates on the inner part of silica tubes inserted as deep as possible into the fumarolic vents (Garavelli *et al.* 1997). On the ground, arsenic was identified only as an amorphous phase containing sulfur as well (Garavelli 1958).

The samples investigated in this work were collected in 1993 from the deepest part of fumarole F11, where there was a very little interaction between fumarolic fluids and atmosphere. The sampling temperature, measured by means of a thermocouple manually inserted into the fumarolic vent, was about 470°C. The chemical composition of fluids discharged from fumarole F11 in the same period of kirkiite sampling is given in Table 2.

MORPHOLOGY AND ASSOCIATION OF THE KIRKIITE CRYSTALS

Kirkiite was found in the sample (7 × 10 cm) consisting of brecciated altered rock covered by a thin crust of sulfosalt aggregates characterized by a metallic luster. The crust predominantly consists of kirkiite aggregates in places covered in turn by flakes of cannizzarite. These minerals differ slightly in color: kirkiite is steel grey (resembles arsenopyrite), in some cases covered by a blue film, whereas cannizzarite is bluish lead grey (resembles molybdenite).

TABLE 2. CHEMICAL COMPOSITION OF FUMAROLIC FLUIDS DISCHARGING FROM FUMAROLE F11 DURING THE SAMPLING OF KIRKIITE *

Date	T(°C)	H_2O	CO_2	S_{tot}	HCl	HF
13.06.93	428	888700	95230	10648	2854	1478
16.09.93	487	927560	57710	8855	1977	2708

* Data are expressed in μmol/mol (Chiodini et al. 1996)

Under the scanning microscope (CamScan 4DV), the individual crystals are characterized by short pseudohexagonal prisms measuring up to 100 μm in length and in width (Fig. 2a). The basal face of the crystals is usually even, but the others have stepped surfaces. In fact, the prismatic crystals seem to be formed of parallel layers of hexagonal platelets (Fig. 2b). Small tetrahedral crystals of sphalerite occur sporadically on the kirkiite

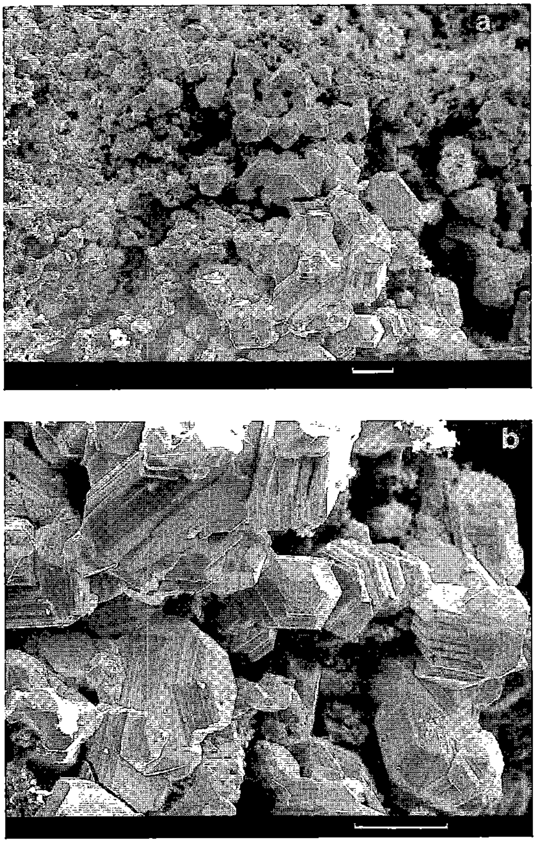

FIG. 2. The crystals of kirkiite. a. General view of the coating of kirkiite crystals on aggregates of Si- rich phases. b. Pseudohexagonal short-prismatic crystals of kirkiite (detail of lower part of Fig. 2a). CamScan 4DV scanning electron microscope. Scale bar: 30 μm in each case.

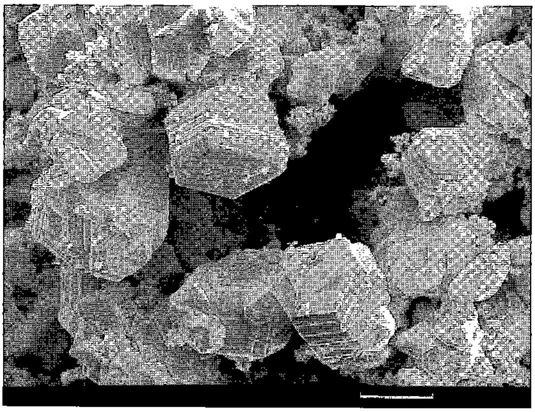

FIG. 3. Crystals of kirkiite with sporadic small crystals of sphalerite on their surface. CamScan 4DV scanning electron microscope. Scale bar: 30 μm.

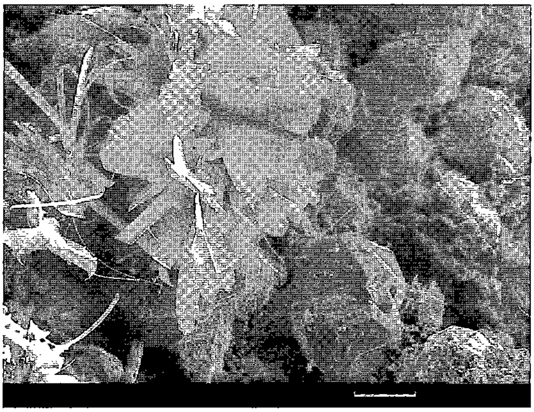

FIG. 4. Aggregates of cannizzarite leaves on crystals of kirkiite. CamScan 4DV scanning microscope. Scale bar: 30 μm.

prisms (Fig. 3). Very striking aggregates of cannizzarite "leaves" locally grow on the kirkiite crystals (Fig. 4).

In polished sections, pseudohexagonal sections of crystals of kirkiite are displayed; they are partially rimmed by a thin layer and blebs of sphalerite (Fig. 5). Very thin thread-like cannizzarite (cross-sections of the leaves) grow on kirkiite crystals (Figs. 5, 6).

OPTICAL PROPERTIES AND MICROHARDNESS

Under reflected light, kirkiite is light grey. The bireflectance is very weak, and noticeable only on the contacts of differently oriented grains. Reflection pleochroism is absent. Anisotropy is strong, but without color effect. Very fine polysynthetic twins, invariably observed in type kirkiite, here were seen in only one grain. No internal reflections are present.

Reflectivity was measured in air on a randomly oriented grain using an automatic polarization microspectrophotometer unit MSFU–312L (LOMO, Saint-Petersburg), with Si as reflectance standard and a 20 × 0.40 objective (Table 3). The spectral curves over the wavelength range 420–700 nm for both R_1 and R_2, along with previously published data for kirkiite from the type locality, are plotted in Figure 7. The reflectance curves and the bireflectance are close to those reported by Moëlo *et al.* (1985), but the values of reflectance of kirkiite from Vulcano are less intense.

The microhardness of kirkiite from Vulcano is 117 kg/mm^2 (indentation-hardness tester PMT–3M with

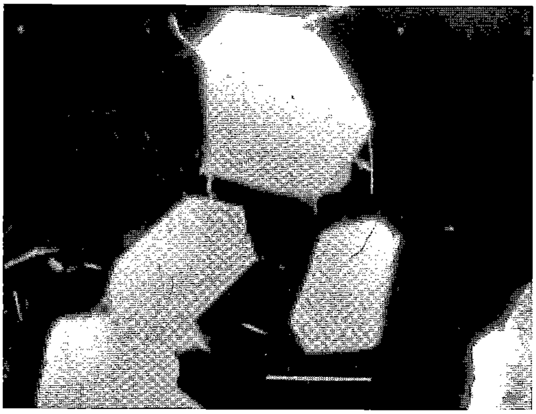

FIG. 5. Pseudohexagonal sections of crystals of kirkiite partially rimmed by sphalerite (dark gray) and cannizzarite (thread-like cross-sections of leaves). Polished section. Scale bar: 50 μm.

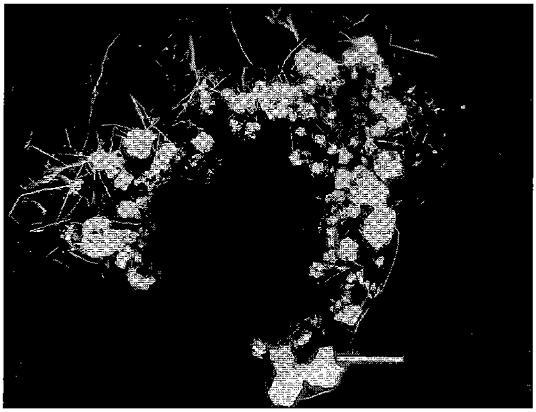

FIG. 6. Aggregate of small grains of kirkiite surrounded by cannizzarite (thread-like cross-sections of leaves). Polished section. Scale bar: 100 μm.

TABLE 3. REFLECTANCE DATA FOR KIRKIITE FROM VULCANO*

nm	R_1	R_2	nm	R_1	R_2
420	44.2	38.5	580	40.8	36.0
440	43.1	37.9	600	40.7	35.8
460	42.1	37.4	620	40.2	35.5
480	42.3	37.3	640	39.8	35.0
500	42.5	37.0	660	39.7	34.9
520	42.0	36.9	680	39.2	34.6
540	41.6	36.4	700	39.1	34.1
560	40.8	36.1			

*Standard : Si.
Reflectance data are expressed in %

a load of 5 g), which is less than the microhardness of type-locality kirkiite (VHN_{100} = 150 kg/mm^2) (Moëlo *et al.* 1985). The observed differences in reflectance and microhardness can be interpreted as due to differences in chemical composition or orientation of the grains studied.

DIFFRACTION DATA

A microdiffraction study was performed using an electron microscope JEM–100C. The results are displayed in Figure 8. Under the electron microscope (Fig. 8a), kirkiite appears as elongate platy particles (0.5–1.5 μm). They give three different selected-area electron-diffraction patterns (SAED). As a first approximation, the first type (Figs. 8b, c) appears to have a hexagonal unit-cell with a = 8.69 Å, c = 26.06 Å and space group $P6_322$ (Fig. 8c) because of the absence of $00l$ reflections with $l = 2n + 1$. A closer inspection of these pictures for reflections of larger magnitude of g_{hk0} has revealed some small differences in their values. This sample can be considered to be monoclinic, with a = 8.4 ± 0.6 Å, b = 7.8 ± 0.6 Å, c = 26.0 ± 0.1 Å, γ = 118 ± 1%, in concordance with the published observations (Moëlo *et al.* 1990). The space group is $P2_1$, corresponding to the absence of the $00l$ odd reflections.

The second type of SAED (Fig. 8d) is the same as the first one, except for the diffuse streaks with $h = 2n + 1$ that are parallel to c^*. It can be related to systematic disordered displacements of (100) layers with value $\pm a/2$. Such a structural variety was noted at the type locality (Moëlo *et al.* 1990) as a subcell of kirkiite, with $a' = a/2$ and $c' = c$.

The third type of SAED (Figs. 8e, f) shows $B2/m$, Bm or $B2$ symmetry. The unit cell has a double c value, whereas a and b are the same. The presence of the last type can be missed with XRD because of the small proportion of these domains (such a pattern may show supplementary and weak reflections compared to ordinary crystals).

The main part of the microcrystals corresponds to the first two types in the ratio approximately 1:1.

X-ray powder-diffraction data for kirkiite from Vulcano were obtained using an 86-mm Debye–Scherrer camera and unfiltered Fe-radiation; the relative intensities of lines were visually estimated. The results are given in Table 4 with the two different refinements, for the hexagonal and monoclinic cases (starting unit-cell values were given above) and are compared to those of kirkiite from Greece (Moëlo *et al.* 1990) and of synthetic phase A (Walia & Chang 1973). The refinement results gave: a = 8.70 ± 0.05 Å, b = 8.70 ± 0.05 Å, c = 25.97 ± 0.1 Å, γ = 120°, for space group $P6_3/m$ and a = 8.47 ± 0.05 Å, b = 7.84 ± 0.05 Å, c = 25.97 ± 0.1 Å, γ = 118.03° for $P2_1/m$. The comparison shows that data obtained for the material with hexagonal symmetry are close to those previously published. On the other hand, the results of refinements show the better fit between experimental and calculated spacings for the monoclinic variant ($\Delta_{mon.} < \Delta_{hex.}$; our comparison has been carried out for d with the closest values to d_{exp}).

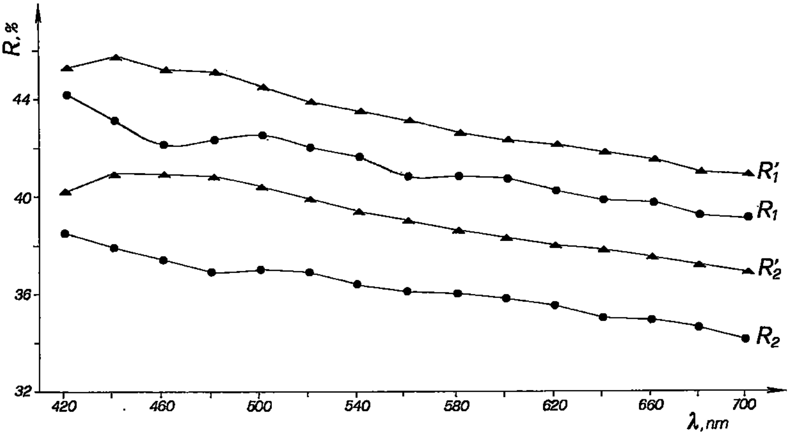

FIG. 7. Reflectance spectra for kirkiite in air from Vulcano (R_1, R_2) and Aghios Philippos (R'_1 and R'_2, after Moëlo *et al.* 1985).

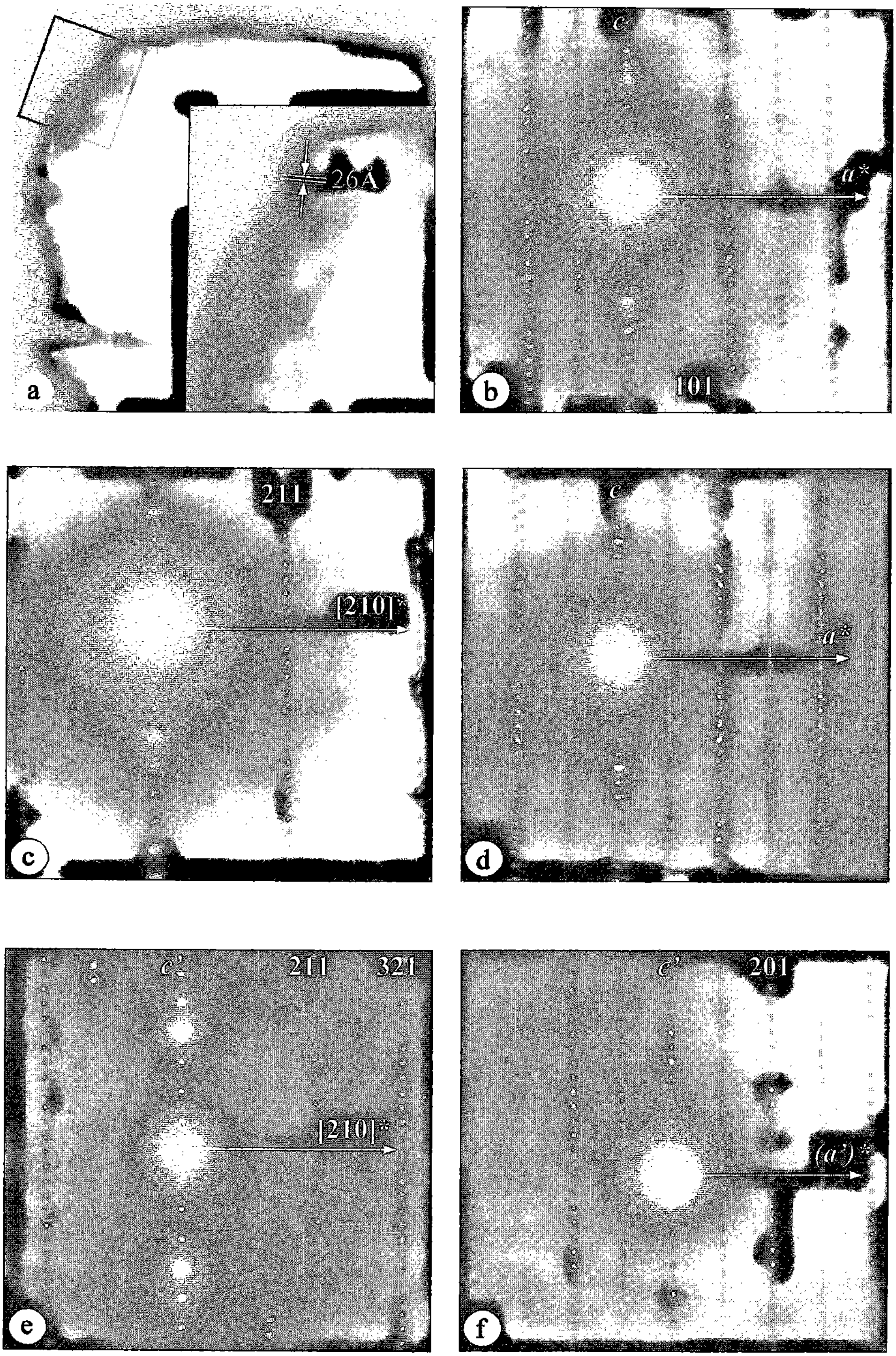

FIG. 8. Electron-microdiffraction pictures of kirkiite. a. Lattice image obtained by transmission electron microscopy; the inset shows direct image of (001) planes. b–e. Selected-area electron diffraction photographs of different modifications of kirkiite. b–c. Primitive structure with $c = 26$ Å. d. Disordered structure. e–f. Face-centered structure with $c' = 2c$.

TABLE 4. X-RAY POWDER DIFFRACTION DATA FOR KIRKIITE AND SYNTHETIC PHASE A

I		II		III		IV		V	
I	d_{meas}	d_{calc}	*h k l*	d_{calc}	*h k l*	*I*	d_{meas}	*I*	d_{meas}
1	7.50	7.53	1 0 0	7.47	1 0 0	-	-	-	-
0.5	6.50	6.49	0 0 4	6.49	0 0 4	-	-	-	-
1	4.33	4.328	0 0 6	4.328	0 0 6	<10	4.33	-	-
2	(3.96)	-	-	-	-	-	-	-	-
3	3.81*	-	-	-	-	<10	3.81	-	-
8	3.59	3.618	2 0 2	3.592	2 0 2	50	3.65	55	3.633
-	-	-	-	-	-	-	-	23	3.550
9w	3.43	3.452	2 0 3	3.432	2 0 3	60	3.475	70	3.477
-	-	-	-	-	-	-	-	13	3.388
10	3.24	3.246	0 0 8	3.246	0 0 8	100	3.260	100	3.277
0.5	(3.127)	-	-	-	-	-	-	-	-
10	3.052	3.050	2 0 5	3.053	2 0 5	70	3.070	100	3.068
4	2.948*	-	-	-	-	-	-	17	2.978
9	2.843	2.842	2 0 6	2.829	2 0 6	60	2.854	70	2.858
0.5w	2.715	2.705	1 2 3	2.716	$3\ \bar{2}\ 0$	<10	2.715	13	2.740
4	2.631	2.643	2 0 7	2.633	2 0 7	<10	2.636	13	2.623
2w	2.500	2.500	3 0 0	2.500	3 0 0	<10	2.505	10	2.517
4	(2.390)	2.405	3 0 3	2.391	3 0 3	<10	2.410	6	2.414
1	(2.353)	2.342	3 0 4	2.352	3 0 4	-	-	4	2.356
3	2.296	2.291	0 2 9	2.297	$0 3 1 ; 0 \bar{3} 1$	<10	2.286	4	2.309
8	2.190	2.175	2 2 0	2.192	$3\ \bar{2}\ 7$	50	2.190	70	2.190
6	2.139	2.138	2 0. 10	2.133	2 0. 10	30	2.135	23	2.155
7	2.087*	-	-	-	-	-	-	8	2.103
8	2.008	2.006	2 2 5	2.009	$4\ \bar{1}\ 3$	40	2.003	30	2.014
1	1.951*	-	-	-	-	-	-	-	-
0.5	1.894	1.894	3 0 9	1.894	$3\ \bar{4}\ 1$	30	1.879	23	1.8879
5	1.880	1.879	4 0 1	1.880	$0 \bar{3} 8 ; 0 3 8$	-	-	15	1.8697
9	1.816	1.815	1 1. 13	1.816	$1\ \bar{4}\ 4$	50	1.815	55	1.8180
3	1.786*	-	-	-	-	-	-	-	-
4	1.770	1.771	4 0 5	1.770	$4\ \bar{2}\ 8$	20	1.773	23	1.7780
-	-	-	-	-	-	-	-	8	1.7430
3	1.706	1.706	1 1. 14	1.707	$4\ \bar{4}\ 3$	<10	1.699	6	1.6808
2	1.671	1.670	2 3 4	1.671	0 4 4	<10	1.664		
								10	1.6372
5	1.631	1.631	1 4 2	1.631	$5 \bar{3} 3 ; 2 2.10$	20	1.626	4	1.6130
1	1.575	1.577	0 4 9	1.574	$4 1 4 ; 4 \bar{2}.11$	<10	1.586	-	-
-	-	-	-	-	-	<10	1.562	-	-
2	1.528	1.528	0 0. 17	1.528	1 2. 14	<10	1.532	6	1.5325
4	1.476	1.479	1 2. 15	1.476	$1\ \bar{4}.\ 11$	<10	1.474	10	1.4796
2	(1.442)	1.441	3 3 2	1.443	0 0. 18	-	-	-	-
4	1.423	1.423	5 0 6	1.423	$1 \bar{2}.\ 17$	<10	1.425	12	1.4260
1	1.397	1.397	3 3 5	1.397	3 3 0 ; 0 2.17	-	-	12	1.3973
2	1.379	1.375	3 3 6	1.375	$6\ \bar{3}\ 4$	<10	1.378	12	1.3786
3	1.361	1.363	0 3. 16	1.361	4 5 8	-	-	8	1.3627
5	1.325	1.325	1 5 4	1.325	$1 \bar{5} 9 ; 3 1.15$	<10	1.353	8	1.3576
6	1.309	1.309	1 4. 12	1.310	5 1 4	-	-	15	1.3099
-	-	-	-	-	-	20	1.306	12	1.3068
1	1.291	-	-	-	-	-	-	-	-
3	1.257	-	-	-	-	-	-	10	1.2552
	Δ (Å)	0.0053		0.0035					
	a (Å)	8.70 ± 0.05		8.47 ± 0.05					
	b (Å)	8.70 ± 0.05		7.84 ± 0.05					
	c (Å)	25.97 ± 0.1		25.97 ± 0.1					
	γ	120°		118.03°					
Space group		$P6_3/m$		$P2_1/m$					

I-II-III from Vulcano. I : w- wide lines, ( ) - reflections from β-radiation, * - possible admixture of Pb-Bi-sulfosalts ; II- indexed on the basis of the hexagonal cell ($P6_3/m$) ; III- indexed on the basis of the monoclinic cell ($P2_1/m$) ; IV- from Kirki (Moëlo et al. 1985) ; V- phase A (Walia & Chang 1973). $\Delta = \Sigma\left|\left(\left|d_m\right| - \left|d_c\right|\right)\right| / n$, where n is the reflection number

Thus, the results of the diffraction study of kirkiite from Vulcano are in agreement with the early assumption of its possible true monoclinic symmetry (Moëlo *et al.* 1990), and reveal the existence here of at least three structural variants of the mineral.

CHEMICAL DATA

Twelve electron-microprobe analyses were carried out on kirkiite from Vulcano with a CAMEBAX SX–50 electron microprobe under the following conditions: voltage 20 kV, beam current 30 nA, with the following standards (and analytical lines): PbS (PbM), pure Bi metal (Bi$M\alpha$), Sb_2S_3 (Sb$L\alpha$), $AgAsS_2$ (As$L\alpha$), Cu_3VS_4 (S$K\alpha$), and ZnSe (Se$L\alpha$). The results obtained are shown in Table 5 in comparison with published data.

Kirkiite from Vulcano contains a rather high Se content (0.73–1.16 wt %), and this serves to distinguish it from the type-locality samples. Sb was not found in our samples. As and Bi concentrations range noticeably: from 6.49 to 7.98 wt% and from 14.32 to 16.84 wt%, respectively. The ratio As/Bi varies from 1.098 to 1.557, with a negative correlation between As and Bi contents (r = –0.727, p (the statistical significance) = 0.007 for 12 cases; Fig. 9). These data evidently indicate that despite the large difference in ionic size between bismuth and arsenic, these elements can substitute for each other in the structure of the mineral, as it does in phase A, according to Walia & Chang (1973).

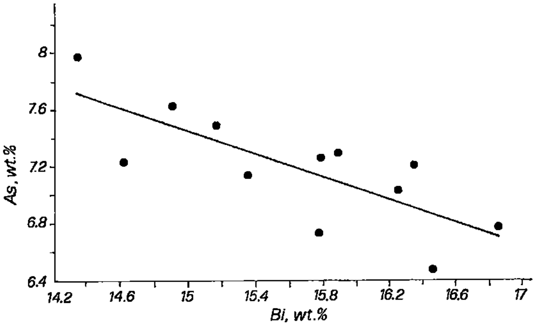

FIG. 9. Concentration of Bi *versus* that of As (wt%). Line corresponds to linear regression equation.

Structural formulae calculated from the analytical data on the basis of 35 atoms are given in Table 5. Taking into account the evidence given above, As and Bi were combined in the formulae. As shown in Table 5, the composition of kirkiite from Vulcano ranges between $Pb_{10}(As_{3.2}Bi_{2.8})_{\Sigma 6}(S_{18.7}Se_{0.3})_{\Sigma 19}$ and $Pb_{10}(As_{3.7}Bi_{2.3})_{\Sigma 6}(S_{18.5}Se_{0.5})_{\Sigma 19}$, in approximate terms, and a general formula may be expressed as follows: $Pb_{10}(As_{6-x}Bi_x)_{\Sigma 6}(S_{19-y}Se_y)_{\Sigma 19}$, where $2.3 \le x \le 2.8$, $0.3 \le y \le 0.5$. The average formula is $Pb_{9.97}(As_{3.35}Bi_{2.61})_{\Sigma 5.96}(S_{18.65}Se_{0.42})_{\Sigma 19.07}$, which is close to the ideal formula $Pb_{10}(As,Bi)_6(S,Se)_{19}$. The projec-

TABLE 5. CHEMICAL COMPOSITION OF KIRKIITE (ELECTRON-MICROPROBE ANALYSES) AND SYNTHETIC PHASE A

N	Pb	As	Sb	Bi	Se	S	Total	Formulae (based on 35 atoms)
Vulcano								
1	58.29	6.49	-	16.46	1.01	17.31	99.56	$Pb_{9.85}(As_{3.03}Bi_{2.76})_{\Sigma 5.79}(S_{18.90}Se_{0.45})_{\Sigma 19.35}$
2	59.62	6.74	-	15.46	1.01	16.97	99.80	$Pb_{10.14}(As_{3.17}Bi_{2.61})_{\Sigma 5.78}(S_{18.64}Se_{0.45})_{\Sigma 19.09}$
3	57.94	6.79	-	16.84	1.16	17.29	100.02	$Pb_{9.74}(As_{3.16}Bi_{2.81})_{\Sigma 5.97}(S_{18.78}Se_{0.51})_{\Sigma 19.13}$
4	58.53	7.04	-	16.26	1.01	17.02	99.86	$Pb_{9.91}(As_{3.30}Bi_{2.73})_{\Sigma 6.03}(S_{18.62}Se_{0.45})_{\Sigma 19.07}$
5	60.32	7.15	-	15.35	1.00	17.18	101.00	$Pb_{10.11}(As_{3.31}Bi_{2.55})_{\Sigma 5.86}(S_{18.59}Se_{0.44})_{\Sigma 19.03}$
6	59.56	7.22	-	16.36	1.00	16.88	101.02	$Pb_{10.05}(As_{3.37}Bi_{2.74})_{\Sigma 6.11}(S_{18.41}Se_{0.44})_{\Sigma 18.85}$
7	60.24	7.24	-	14.60	0.87	17.21	100.16	$Pb_{10.13}(As_{3.36}Bi_{2.43})_{\Sigma 5.79}(S_{18.69}Se_{0.39})_{\Sigma 19.08}$
8	58.34	7.27	-	15.79	0.94	16.95	99.29	$Pb_{9.91}(As_{3.41}Bi_{2.66})_{\Sigma 6.07}(S_{18.60}Se_{0.42})_{\Sigma 19.02}$
9	59.54	7.31	-	15.90	0.91	17.29	100.95	$Pb_{9.94}(As_{3.38}Bi_{2.63})_{\Sigma 6.01}(S_{18.65}Se_{0.40})_{\Sigma 19.05}$
10	58.93	7.50	-	15.16	0.85	16.95	99.39	$Pb_{9.97}(As_{3.51}Bi_{2.54})_{\Sigma 6.05}(S_{18.60}Se_{0.38})_{\Sigma 18.98}$
11	60.50	7.63	-	14.90	1.00	17.36	101.39	$Pb_{10.03}(As_{3.50}Bi_{2.45})_{\Sigma 5.95}(S_{18.59}Se_{0.43})_{\Sigma 19.02}$
12	59.17	7.98	-	14.32	0.73	17.34	99.54	$Pb_{9.89}(As_{3.69}Bi_{2.37})_{\Sigma 6.06}(S_{18.73}Se_{0.32})_{\Sigma 19.05}$
mean	59.25	7.20	-	15.62	0.96	17.15	100.18	$Pb_{9.97}(As_{3.35}Bi_{2.61})_{\Sigma 5.96}(S_{18.65}Se_{0.42})_{\Sigma 19.07}$
Kirkii								
13	59.40	6.20	0.50	15.20	-	17.40	98.70	$Pb_{10.15}(As_{2.93}Sb_{0.14}Bi_{2.57})_{\Sigma 5.64}S_{19.21}$
14	61.26	7.56	4.81	7.02	-	18.26	98.91	$Pb_{9.95}(As_{3.39}Sb_{1.33}Bi_{1.13})_{\Sigma 5.85}S_{19.20}$
15	61.78	8.49	3.71	6.43	-	18.51	98.92	$Pb_{9.94}(As_{3.76}Sb_{1.02}Bi_{1.02})_{\Sigma 5.80}S_{19.26}$
Phase A								
16	64.67	9.09	-	8.45	-	17.79	100.00	$Pb_{10.62}(As_{4.13}Bi_{1.37})_{\Sigma 5.50}S_{18.88}$
17	63.30	7.71	-	11.58	-	17.41	100.00	$Pb_{10.62}(As_{3.58}Bi_{1.92})_{\Sigma 5.50}S_{18.88}$

13 : average from 6 analyses ; 0.2% Zn was excluded as analytical pollution due to sphalerite microinclusions (Moëlo et al. 1985) ;

14-15 : antimonoan kirkiite; 14-K1 : average from 10 analyses (Moëlo et al. 1990) ; 15-K2 : average from 4 analyses (Moëlo et al. 1990) ;

16-17 : terminal members of compositional field of synthetic phase A calculated from the formulae given by Walia & Chang (1990).

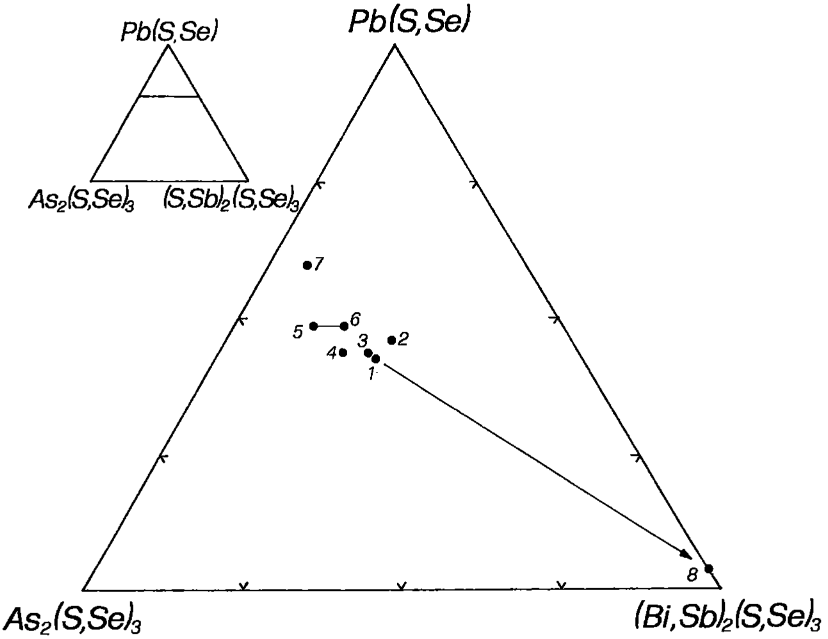

FIG. 10. Projection in the pseudoternary system Pb(S,Se) – $As_2(S,Se)_3$ – $(Bi,Sb)_2(S,Se)_3$ showing chemical composition (in mol.%) of kirkiite and associated sulfosalts. Legend: 1–2: kirkiite, 1 from Vulcano, average composition from 12 analyses, 2 from Aghios Philippos, average composition from six analyses (Moëlo *et al.* 1985), 3: antimonoan kirkiite from Aghios Philippos, average composition from 10 analyses, 4: antimonoan kirkiite from Aghios Philippos, average composition from four analyses (Moëlo *et al.* 1990), 5–6: terminal members of compositional field of synthetic phase A (Walia & Chang 1990), 7: bismuthoan jordanite from Aghios Philippos (Moëlo *et al.* 1990), 8: cannizzarite, average composition from eight analyses (Mozgova *et al.* 1985). Arrow: trend of kirkiite – cannizzarite crystallization at Vulcano.

tion of the mean composition in terms of Pb(S,Se) – $As_2(S,Se)_3$ – $(Bi,Sb)_2(S,Se)_3$ lies near those of kirkiite and antimonoan kirkiite from the type locality (Fig.10).

DISCUSSION

The data obtained show that the compositional field of kirkiite resulted from As-for-Bi substitution, and it is close to that of phase A (Fig. 10).

In a discussion of conditions of formation of kirkiite and its paragenesis from the Aghios Philippos deposit, Moëlo *et al.* (1985) noted that the geochemical association Bi–As–Pb is common in some types of hypothermal sulfide deposits, but there, As usually plays the role of an anion owing to the high temperature and low fugacity of sulfur. According to those authors, the appearance of kirkiite and its assemblage at the Aghios Philippos deposit is due to a low temperature and high fugacity of sulfur during its crystallization. They also noted that the sequence of mineral formation is classified in order of increasing Pb/(Bi + As), as is rather common in sulfide deposits.

The occurrence of kirkiite in Vulcano implies also high fugacity of sulfur; the calculated $f(S_2)$ at 600°C ranges between 10^{-1} and 10^{-4} atm. (Garavelli & Vurro 1997). In addition, the high halogen acid contents in fumarolic fluids (Table 2) play an important role in the transport and deposition of arsenic (Garavelli *et al.* 1997). On the other hand, the temperature of kirkiite formation at Vulcano was rather high, about 470°C according to direct measurements. This temperature is in agreement with that known for phase A, which is stable at 400°C (Walia & Chang 1973). It is known also that orpiment As_2S_3 and realgar AsS are stable at low temperatures in this system, whereas the stability field of sulfosalts is usually located at higher temperatures (Vaughan & Craig 1978). Growth of cannizzarite on the kirkiite crystals in fumarole incrustations is evidence of a decrease in the Pb/(Bi + As) value during the crystallization of this assemblage.

ACKNOWLEDGEMENTS

The authors thank I.A Brizgalov and O. Doynikova for analytical support, D.K. Shcherbachev for the measurements of the reflectivity and microhardness. Useful discussions with Prof. A.I. Gorshkov are gratefully acknowledged. In addition, we are most grateful to Drs. R.F. Martin and L.L.Y. Chang for their efforts to improve the quality of presentation of this paper. This research was carried out with the partial financial support of the National Group for Volcanology, Italy.

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Received October 17, 1997, revised manuscript accepted May 9, 1998.