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RARE SULFOSALTS FROM VULCANO, AEOLIAN ISLANDS, ITALY.
III. WITTITE AND CANNIZZARITE

YURI S. BORODAEV

Department of Geology, Moscow State University, Moscow, 119899, Russia

ANNA GARAVELLI

Dipartimento Geomineralogico, University of Bari, Via E. Orabona 4, I-70125 Bari, Italy

CARLO GARBARINO AND SILVANA M. GRILLO

Dipartimento di Geoingegneria e Tecnologie Ambientali, University of Cagliari, Piazza d'Armi, I- 09123 Cagliari, Italy

NADEZHDA N. MOZGOVA, NATALIA I. ORGANOVA AND NIKOLAY V. TRUBKIN

IGEM RAS, Staromonetny 35, Moscow, 109017, Russia

FILIPPO VURRO[§]

Dipartimento Geomineralogico, University of Bari, Via E. Orabona 4, I-70125 Bari, Italy

ABSTRACT

Wittite and cannizzarite, two rare and structurally related nonstoichiometric sulfosalts belonging to the system Pb–Bi–S–Se, were found together around high-temperature fumaroles at La Fossa crater, Vulcano island, Italy. This occurrence makes a comparative study by different methods possible (scanning electron microscope, electron microprobe, and X-ray and electron diffraction). We discuss once more the question whether or not they are distinct mineral species. Cannizzarite was found in samples collected from 1990 to 1995 in assemblages with bismuthinite and galenobismutite (mostly), in some cases with lillianite, heyrovskiite, Se-bearing galena, kirkiite, and the new species mozgovaite. Wittite was revealed only in samples collected in 1995 around the fumarole vent F11 in association with bismuthinite. Both minerals form aggregates of very tiny sheaves of slightly divergent, bladed crystals (cannizzarite up to 0.5 mm in length and 0.07 mm in width; wittite up to 2 mm in length). The electron-microprobe data obtained (141 analyses) show significant variations in proportions of the main elements. In terms of Bi/(Bi + Pb), the range of composition is 3.14 at.%; the Se content varies from less than 1 to 14.65 wt%. The composition field of the minerals under consideration may be described by the general empirical chemical formula $Pb_{3+x}Bi_{4-x}(S_{9-y}Se_{y})_{9-x/2}$ or $Pb_{3}(Bi_{4-x}Pb_{x})_{4}(S_{9-y}Se_{y})_{9-x/2}$, with $0.04 \leq x \leq 0.28$, and $0.5 \leq y \leq 3.5$. Electron-diffraction data and X-ray investigations of a sample of wittite containing ~8.5 wt% Se confirm that cannizzarite and wittite have the same structure. Measured unit-cell parameters show that volumes of the H and Q subcells both vary in direct proportion to Se content. No chemical discontinuity between cannizzarite and wittite series has been observed up to 40 at.% Se; consequently, wittite may be validated or discredited as a distinct mineral species only when a definitive crystallographic work will prove that Se exceeds S in the H layers.

Keywords: cannizzarite, wittite, Pb–Bi sulfosalts, fumaroles, Vulcano Island, Italy.

SOMMAIRE

La wittite et la cannizzarite, deux sulfosels rares et structuralement apparentés du système Pb–Bi–S–Se, se présentent ensemble autour de fumerolles de haute température au cratère de La Fossa, île de Vulcano, en Italie. Cet exemple permet enfin une étude comparative par diverses méthodes (microscopie électronique à balayage, microsonde électronique, et diffraction électronique). Nous évaluons de nouveau s'il s'agit d'espèces distinctes ou non. Nous avons prélevé la cannizzarite entre 1990 et 1995, associée surtout à bismuthinite et galénobismutite, avec dans quelques cas lillianite, heyrovskiite, galène sélénifère, kirkiite, et la nouvelle espèce mozgovaïte. La wittite est présente seulement dans des échantillons prélevés en 1995 autour de la fumerolle F11 en association avec bismuthinite. Les deux minéraux se présentent en aggrégats de très petites lames légèrement divergentes,

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[§] *E-mail address*: f.vurro@geomin.uniba.it

jusqu'à 0.5 mm de long et 0.07 mm de large dans le cas de la cannizzarite, et jusqu'à 2 mm de long dans le cas de la wittite. Les données à la microsonde électronique (141 analyses) montrent des variations importantes des proportions des éléments essentiels. En termes de Bi/(Bi + Pb), les compositions varient selon une marge de 3.14% (proportions atomiques); la teneur en Se va de moins de 1 à 14.65% (en poids). L'intervalle de compositions de ces minéraux répond à la formule chimique empirique générale $Pb_{3+x}Bi_{4-x}(S_{9-y}Se_y)_{9-x/2}$ ou bien $Pb_3(Bi_{4-x}Pb_x)_4(S_{9-y}Se_y)_{9-x/2}$, avec $0.04 \le x \le 0.28$, et $0.5 \le y \le 3.5$. D'après nos observations en diffraction électronique et en diffraction X d'un échantillon de wittite contenant ~8.5% Se (en poids), la cannizzarite et la wittite posséderaient la même structure. Les paramètres réticulaires mesurés montrent que le volume des modules H et Q varie dans les deux cas en proportion directe de la teneur en Se. Il ne semble pas y avoir de discontinuité chimique entre les séries cannizzarite et wittite jusqu'à une teneur de 40% Se (proportion atomique). Par conséquent, il ne sera possible de valider la wittite, ou de la discréditer comme espèce minérale distincte, que suite à une étude cristallographique définitive visant à établir que la proportion de Se dépasse la proportion de S dans les couches H.

(Traduit par la Rédaction)

Mots-clés: cannizzarite, wittite, sulfosels de Pb–Bi, fumerolles, île de Vulcano, Italie.

INTRODUCTION

Both wittite and cannizzarite, two rare Pb–Bi sulfosalts, were first described in 1924: wittite was found at Falun, Sweden (Johansson 1924), and cannizzarite was found in high-temperature fumaroles at Vulcano, Italy (Zambonini *et al.* 1924). The minerals have had a complex history (Graham *et al*. 1953, Johan & Picot 1976, Mumme 1976, 1980, Mozgova 1985, Mozgova *et al.* 1985, Efimov *et al.* 1988, Garavelli 1994). There was a time when both minerals had been discredited, wittite as Se-rich hammarite (Strunz 1982, Povarennykh 1972) or as a mixture of minerals (Sindeeva 1964), and cannizzarite as galenobismutite (Palache *et al.* 1944). Subsequent detailed studies re-established them as valid mineral species (Graham *et al.* 1953, Mumme 1976, 1980, Johan & Picot 1976). Actually, they are described in recent handbooks of mineralogy (Gaines *et al.* 1997, Anthony *et al.* 1990) with different formulas: $Pb_3Bi_4(S,Se)_9$ for wittite (Pb/Bi = 0.75, *Me*/S = 0.778), and $Pb_4Bi_6S_{13}$, the formula of a high-Bi variety of cannizzarite (Mozgova 1985, Mozgova *et al.* 1984, 1988), for cannizzarite (Pb/Bi = 0.667, *Me*/S = 0.769).

The close relationship between wittite and cannizzarite was first revealed by Mumme (1980), who showed that wittite and cannizzarite differ mainly in their selenium content (greater than 8 wt% for wittite), and that both of them share the same non-commensurate layer structure previously established in cannizzarite (Graham *et al.* 1953, Matzat 1972, 1979). Despite their established similarity, wittite and cannizzarite, as stated above, were described in recent texts of mineralogy (Gaines *et al.* 1997, Anthony *et al.* 1990) as being unrelated to each other. This situation may have been due to the different occurrences of these minerals; they previously had not been found together in the same deposit, and thus had been investigated independently of each other. A few occurrences of cannizzarite in addition to Vulcano are known: Santa Maria mine, Switzerland (Nowacki & Stalder 1969), Visokogorskoe deposit, Far East, former USSR (Litavrina *et al.* 1978, Mozgova 1985), and the Shumilovskoe deposit, West Transbaikal, former USSR (Mozgova *et al.* 1988). Falun was the only known locality for wittite until 1988, when a second occurrence of wittite (Se from 9.5 to 16.5 wt%) was found in the Nevskoe tin deposit, northeastern Siberia (Efimov *et al.* 1988, Mozgova *et al.* 1992).

Here we report the first occurrence of wittite and cannizzarite together among the products of sublimation in high-temperature fumaroles at Vulcano. The chemical investigations, performed on a large number of samples, and the X-ray data obtained, allow us to discuss the wittite–cannizzarite problem once more, in order to contribute to the knowledge of relations existing between these two rare Pb–Bi sulfosalts, and to discuss if they are or they are not two distinct species.

OCCURRENCE

Vulcano is an island off the northern coast of Sicily (Fig. 1). The geological setting, the La Fossa crater fumarole system, and the mineralogy of the area were described in Borodaev *et al.* (1998).

Samples of sulfosalts investigated in this work were collected between 1990 and 1995 from selected high-temperature fumaroles in the crater (FF, FA, F5AT, F11 in Fig. 1). Deposition of cannizzarite around fumarole vents, characterized by temperature values ranging from 400° to 600°C, was continuous during the time interval investigated. Wittite, however, was found only at fumarole F11, at a temperature of sampling of about 450°C, in June 1995.

The sulfosalts at Vulcano occur as aggregates of tiny acicular, tabular and leafy crystals, among which the largest are less than 5 mm in length. All minerals are silvery grey and have a metallic luster. Cannizzarite is abundant in some of these aggregates. The association is most commonly with bismuthinite (Bi_2S_3) and galenobismutite ($PbBi_2S_4$), and less commonly with lillianite ($Pb_3Bi_2S_6$), heyrovskiite ($Pb_6Bi_2S_{9,}$) and Se-bearing galena (Mozgova *et al.* 1985, Garavelli *et al.* 1997).

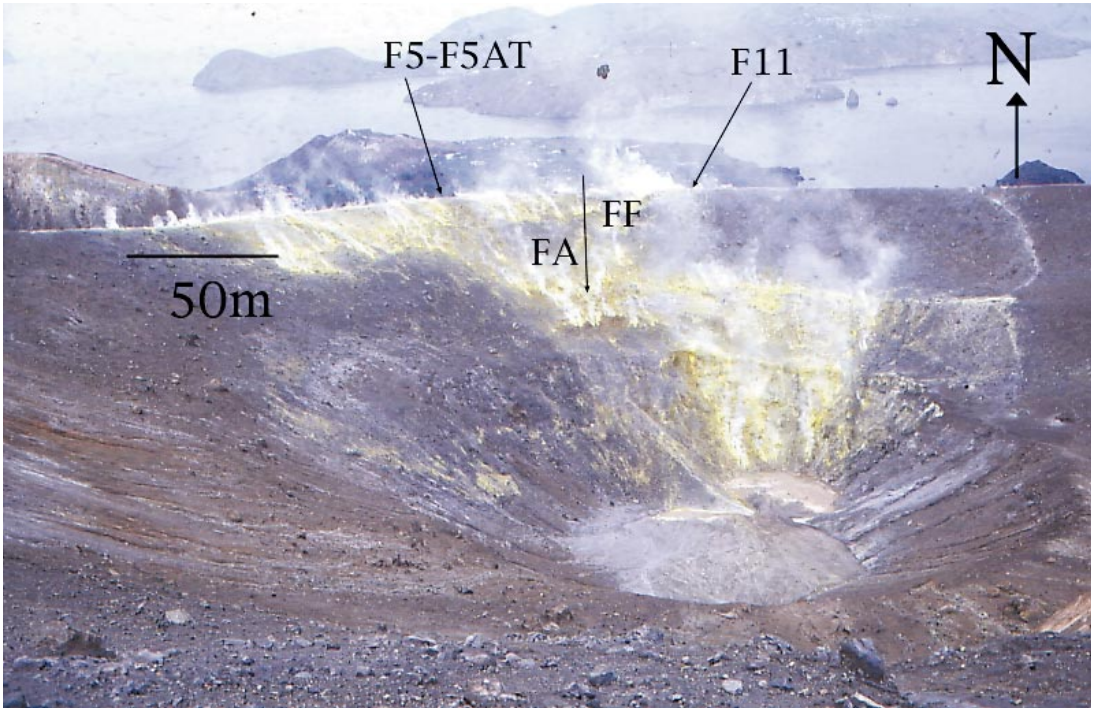

FIG. 1. Location of fumaroles at La Fossa crater from which cannizzarite and wittite were sampled.

Rarely present are kirkiite $Pb_{10}(Bi,As)_6(S,Se)_{19}$ (Borodaev *et al.* 1998) and, in only one case, mozgovaite, $PbBi_4(S,Se)_7$, a new mineral species (Vurro *et al.* 1999). All these minerals contain Se, the amount of which varies with the year of deposition and the specific fumarole around which the minerals were collected. The sole occurrence of wittite, which is associated with bismuthinite, is evidently due to the contemporaneous presence of the most favorable values of $f(S_2)$, $f(Se)$, and temperature values occurring in June 1995 around the F11 fumarole vent.

MORPHOLOGY AND ASSOCIATIONS OF THE WITTITE AND CANNIZZARITE CRYSTALS

The morphology of wittite and cannizzarite and their associations were studied under the scanning electron microscope (CamScan 4DV). Both minerals form similar aggregates up to a few millimeters in diameter. The monomineralic aggregates consist of tiny tabular and leafy crystals, some of which are beautiful and characteristic (Fig. 2). Individual crystals of cannizzarite are 0.5–0.7 mm in length and 0.01–0.07 mm in width; leaves of wittite attain 2 mm in length (Figs. 3a, b). The crystals of wittite are extremely thin and fragile, are typically strongly striated parallel to their elongation (Fig. 4), and are easily twisted, bent, and split into thin bright plates.

In polymineralic aggregates, wittite and cannizzarite show various relations with bismuthinite. Some are intergrown in microdruses (Fig. 5a); more commonly, however, clusters of thin elongate flakes of these sulfosalts grow on the surface of bismuthinite (Fig. 5b). Tiny crystals of Se-bearing galena occur sparingly on some of the wittite (Fig. 6). In assemblages with kirkiite, leaves of cannizzarite partly covered these crystals together with scarcer sphalerite. In polymineralic associations with kirkiite and bismuthinite, cannizzarite is the last mineral to have formed during the sequence of deposition: kirkiite – bismuthinite – cannizzarite (Fig. 7).

Cannizzarite and wittite display microscopic thread-like cross-sections of leaves (Borodaev *et al.* 1998). They are white in reflected light, with a high reflectance, similar to that of selenian bismuthinite. The anisotropism is distinct, with colors from grey-brown to dark brown when polars are not fully crossed. Polysynthetic twinning, described by Johan & Picot (1976) and Mozgova *et al.* (1992) in wittite from the Nevskoe deposit, was not observed. The extremely small size of the thread-like cross-sections of leaves did not allow us to investigate the optical properties of these sulfosalts in more detail.

FIG. 2. Aggregate of cannizzarite leaves (Se ≈ 2.3 wt%). CamScan 4DV scanning electron microscope. Scale bar: 100 μm.

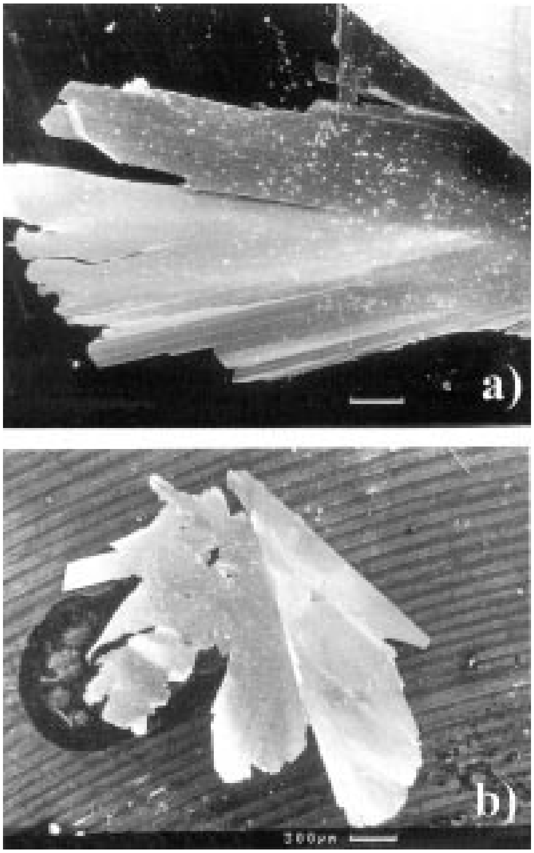

FIG. 3. Morphology of wittite crystals (Se content ranging from ~8 to ~14 wt %. Variation of color is due to the Se contents; the highest Se contents are in the darkest portions. a) Leaves, scale bar: 100 μm, b) elongate tabular crystals, scale bar: 300 μm.

CHEMICAL DATA

The samples investigated in this paper were collected from various fumaroles of Vulcano between 1990 and 1995. The most of analyses were obtained with a ARL–SEMQ–95 electron microprobe at the Centro Studi Geominerari e Mineralurgici, CNR, in Cagliari. Operating conditions were: voltage 20 kV, beam current 20 nA, standards: PbS (Pb*M*α, S*K*α), Bi_2S_3 (Bi*M*α, S*K*α), $FeAsS_2$ (As*L*α), Cu_2S (Cu*K*α), metallic selenium (Se*L*α). Detection limits were: S 0.02, Se 0.04, Pb 0.10, Bi 0.10, As 0.075 wt% . In addition, seven analyses were obtained with a CAMEBAX SX–50 electron microprobe (Moscow State University) under the following conditions: voltage 20 kV, beam current 30 nA, standards (element, emission line): PbS (Pb*M*α, S*K*α), Bi metal (Bi*M*α), GaAs (As*L*α), ZnSe (Se*L*α).

We obtained 141 electron microprobe compositions of wittite–cannizzarite sulfosalts (Fig. 8). As is usual for sulfosalts from Vulcano, the analyzed samples typically contain only Pb, Bi, S and Se, and only a few of them contain additional small amounts of other minor elements.

The Se content varies continuously up to 14.65 wt%, and Se/(Se + S) attains 39.1 at.%. Significant variations of Se contents, from 8.65 to 9.99 wt%, were also revealed across single grains (Fig. 6). Despite the strong variation of Se/(S + Se) value, the Bi/(Bi + Pb) value varies within narrow limits, from 53.43 to 56.57 at.%, and the composition interval of the minerals studied, expressed in terms of the atomic ratio Bi/(Bi + Pb), is 3.14 at.%. On the other hand, this far exceeds the interval of 0.3 at.% supposed by Makovicky (1981) for the theoretically possible end-member homologues of cannizzarite: $Pb_{12}Bi_{14}S_{33}$ [100Bi/(Bi + Pb) = 53.84], and $Pb_{17}Bi_{20}S_{47}$ [100Bi/(Bi + Pb) = 54.05].

Obviously, the interval established for the minerals from Vulcano includes the instrumental error, that is about 1 at.% in terms of Bi/(Bi + Pb). The observed variation of the atomic ratio Bi/(Bi + Pb) is in good agreement with the known nonstoichiometry of these phases, which is caused particularly by a disordered distribution of elements that have different valences (Pb^{2+} and Bi^{3+}) but occur at the same structural sites.

No correlation between the atomic ratios Bi/(Bi + Pb) and Se/(Se + S) was found ($R^2 = 0.007$), although some trends may be observed in Figure 8. These trends were caused by a continuous geochemical variation of Pb, Bi and Se in fluids discharging from different fumaroles during the years in which sulfosalts were collected.

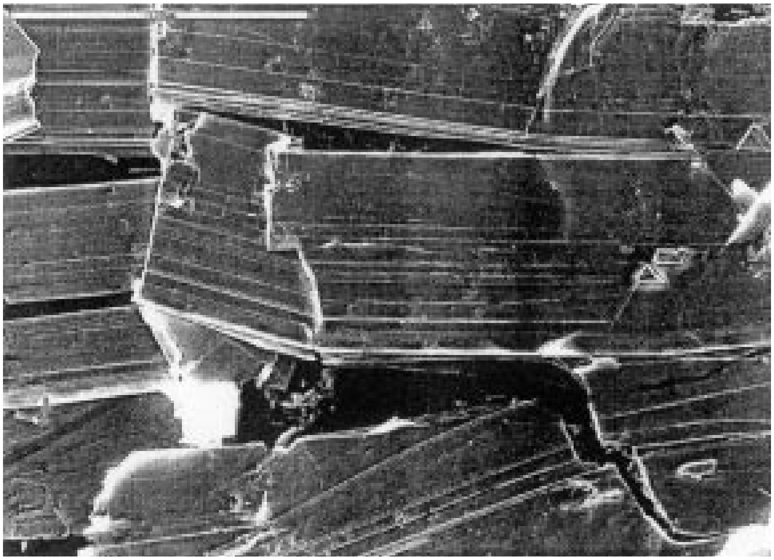

FIG. 4. Striated elongate crystals of wittite (Se ≈ 10 wt%) with small crystals of galena on the surface. CamScan 4DV scanning electron microscope. Scale bar: 100 μm.

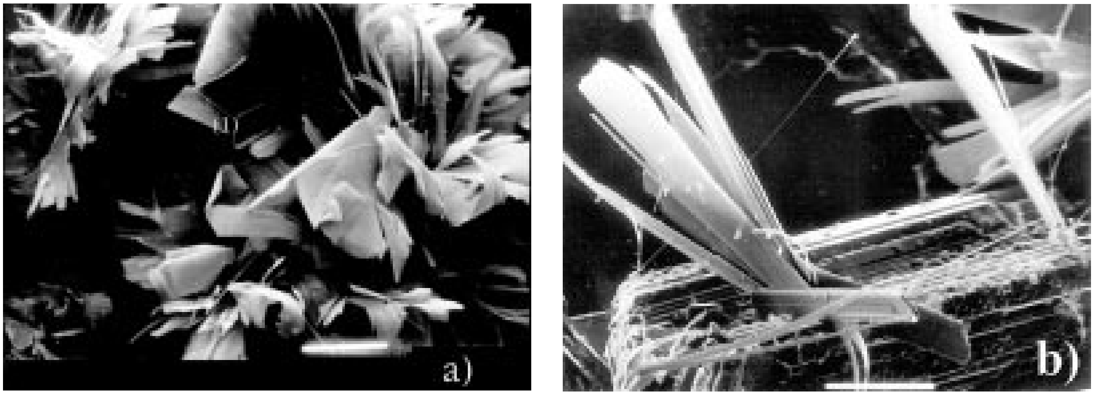

FIG. 5. Relation between cannizzarite (Se ≈ 3 wt%) and bismuthinite. a) Idiomorphic prismatic bismuthinite crystals (1) among the cannizzarite leaves, scale bar: 100 μm, b) clusters of cannizzarite leaves on a large crystal of bismuthinite, scale bar: 50 μm. CamScan 4DV scanning electron microscope.

The absence of correlations between Bi/(Bi + Pb) and Se/(S + Se) in cannizzarite–wittite samples from Vulcano is in agreement with the conclusion concerning wittite from Nevskoe that these ratios are not related to each other (Mozgova *et al.* 1992).

Thirty-eight microprobe compositions from the 141 obtained are shown in Table 1. All of them have been obtained from samples collected in June 1995 from the F11 fumarole (T = 450°C). The analyses were calculated on the basis of seven cations in correspondence with the chemical formula of wittite given in the recent compilations (Gaines *et al.* 1997, Clark 1993, Anthony *et al.* 1990).

Although all the compositions are for samples collected at the same time and from the same fumarole, they show a great variability in the Se/(Se + S) values (from 6.1 to 39.1 at.%), and cover the entire range of variation in Bi/(Bi + Pb). The compositional field of these minerals is reflected by their empirical chemical formulas. Taking into account the deviations from inte-

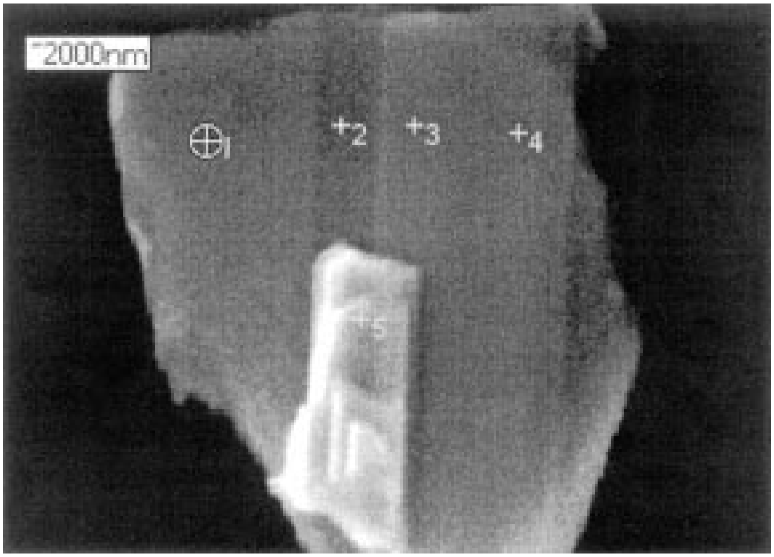

FIG. 6. Se-bearing galena (11.4–11.8 Se wt%) on the surface of wittite. The spots indicate different Se contents in wittite : 1) 8.65 wt%, 2) 8.45%, 3) 9.62%, 4) 9.99 % .

ger values, these may be expressed as follows: $Pb_{3+x}Bi_{4-x}(S_{9-y}Se_y)_{9-x/2}$ or $Pb_3(Bi_{4-x}Pb_x)_4(S_{9-y}Se_y)_{9-x/2}$, with $0.04 \le x \le 0.28$, and $0.5 \le y \le 3.5$.

DIFFRACTION DATA

The cannizzarite–wittite structure has been discussed by Matzat (1972, 1979), Mumme (1980), Makovicky &

FIG. 7. Polimineralic aggregate of sulfosalts; clusters of cannizzarite leaves, prismatic crystals of bismuthinite based on an aggregate of small isometric crystals of kirkiite. Scale bar: 50 μm.

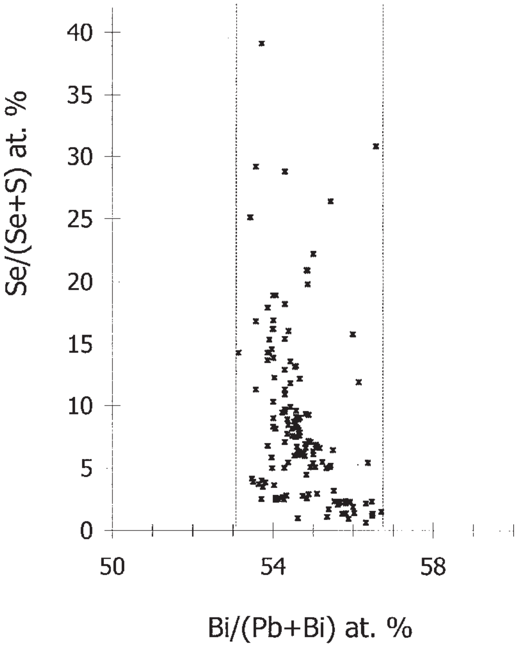

FIG. 8. Relation between Se/(S + Se) and Bi/(Bi + Pb), both in at.% in 141 analyzed samples of cannizzarite–wittite.

TABLE 1 .
ELECTRON-MICROPROBE DATA ON WITTITE AND CANNIZZARITE FROM VULCANO

N	Pb	Bi	S	Se	Total	Formula based on 7 cations	A	B
1	34.94	41.01	9.26	14.65	99.86	$(Pb_{3.24}Bi_{3.76})_{\Sigma 7}(S_{5.54}Se_{3.56})_{\Sigma 9.10}$	39.1	53.71
2	33.59	44.32	10.47	11.49	100.00	$(Pb_{3.02}Ag_{0\cdot 02}Bi_{3.96})_{\Sigma 7}(S_{6.09}Se_{2.71})_{\Sigma 8.80}$	30.8	56.57
3	35.80	42.76	11.02	10.96	100.54	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{6.38}Se_{2.57})_{\Sigma 8.95}$	28.7	54.29
4	35.24	40.97	10.55	10.74	97.52	$(Pb_{3.25}Bi_{3.75})_{\Sigma 7}(S_{6.29}Se_{2.60})_{\Sigma 8.89}$	29.2	53.57
5	35.10	44.11	11.04	9.74	99.99	$(Pb_{3.12}Bi_{3.88})_{\Sigma 7}(S_{6.34}Se_{2.27})_{\Sigma 8.61}$	26.4	55.43
6	36.55	42.37	11.51	9.52	99.95	$(Pb_{3.26}Bi_{3.74})_{\Sigma 7}(S_{6.63}Se_{2.23})_{\Sigma 8.86}$	25.2	53.43
7	34.75	42.75	11.68	8.22	97.50	$(Pb_{3.15}Bi_{3.85})_{\Sigma 7}(S_{6.85}Se_{1.96})_{\Sigma 8.81}$	22.2	55.00
8	35.90	43.49	12.43	8.11	100.10	$(Pb_{3.16}As_{0.04}Bi_{3.80})_{\Sigma 7}(S_{7.07}Se_{1.87})_{\Sigma 8.94}$	20.9	54.86
9	36.03	44.19	12.63	7.70	100.55	$(Pb_{3.16}Bi_{3.84})_{\Sigma 7}(S_{7.16}Se_{1.77})_{\Sigma 8.93}$	19.8	54.86
10	36.42	42.71	12.81	7.36	99.49	$(Pb_{3.22}As_{0.04}Bi_{3.74})_{\Sigma 7}(S_{7.31}Se_{1.71})_{\Sigma 9.02}$	18.9	54.00
11	36.09	43.23	12.76	6.99	99.07	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{7.31}Se_{1.63})_{\Sigma 8.94}$	18.2	54.29
12	37.30	43.58	12.87	6.89	100.64	$(Pb_{3.23}Bi_{3.77})_{\Sigma 7}(S_{7.23}Se_{1.57})_{\Sigma 8.80}$	17.8	53.86
13	36.69	43.55	13.04	6.52	99.80	$(Pb_{3.22}Bi_{3.78})_{\Sigma 7}(S_{7.39}Se_{1.50})_{\Sigma 8.89}$	16.9	54.00
14	37.12	43.16	13.05	6.49	99.82	$(Pb_{3.25}Bi_{3.75})_{\Sigma 7}(S_{7.39}Se_{1.49})_{\Sigma 8.88}$	16.8	53.57
15	37.31	44.18	13.15	6.26	100.90	$(Pb_{3.22}Bi_{3.78})_{\Sigma 7}(S_{7.33}Se_{1.42})_{\Sigma 8.75}$	16.2	54.00
16	37.17	44.50	13.38	6.00	101.05	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{7.45}Se_{1.36})_{\Sigma 8.81}$	15.4	54.29
17	37.53	44.29	13.39	5.52	100.73	$(Pb_{3.23}Bi_{3.77})_{\Sigma 7}(S_{7.44}Se_{1.24})_{\Sigma 8.68}$	14.3	53.86
18	36.74	43.46	13.62	5.41	99.23	$(Pb_{3.22}Bi_{3.78})_{\Sigma 7}(S_{7.72}Se_{1.25})_{\Sigma 8.97}$	13.9	54.00
19	37.06	43.63	13.78	5.41	99.88	$(Pb_{3.23}Bi_{3.77})_{\Sigma 7}(S_{7.76}Se_{1.24})_{\Sigma 9.00}$	13.8	53.86
20	36.94	44.47	13.58	5.26	100.25	$(Pb_{3.19}Bi_{3.81})_{\Sigma 7}(S_{7.58}Se_{1.19})_{\Sigma 8.77}$	13.6	54.43
21	36.68	43.92	13.92	5.07	99.59	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{7.85}Se_{1.16})_{\Sigma 9.01}$	12.9	54.29
22	36.57	44.16	14.12	4.66	99.51	$(Pb_{3.19}Bi_{3.81})_{\Sigma 7}(S_{7.95}Se_{1.06})_{\Sigma 9.01}$	11.8	54.43
23	35.51	45.73	13.92	4.62	99.78	$(Pb_{3.07}Bi_{3.93})_{\Sigma 7}(S_{7.79}Se_{1.05})_{\Sigma 8.84}$	11.9	56.14
24	37.54	43.67	14.18	4.46	99.85	$(Pb_{3.25}Bi_{3.75})_{\Sigma 7}(S_{7.93}Se_{1.01})_{\Sigma 8.94}$	11.3	53.57
25	37.36	44.62	14.18	4.43	100.59	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{7.86}Se_{1.00})_{\Sigma 8.86}$	11.3	54.29
26	37.10	44.43	14.30	4.31	100.14	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{7.97}Se_{0.98})_{\Sigma 8.95}$	10.9	54.29
27	36.93	43.85	14.30	4.04	99.12	$(Pb_{3.22}Bi_{3.78})_{\Sigma 7}(S_{8.05}Se_{0.92})_{\Sigma 8.97}$	10.3	54.00
28	36.72	44.27	14.42	3.88	99.29	$(Pb_{3.19}Bi_{3.81})_{\Sigma 7}(S_{8.09}Se_{0.88})_{\Sigma 8.97}$	9.8	54.43
29	36.90	44.16	14.40	3.82	99.28	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{8.08}Se_{0.87})_{\Sigma 8.95}$	9.7	54.29
30	37.24	44.52	14.38	3.70	99.84	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{7.99}Se_{0.84})_{\Sigma 8.83}$	9.5	54.29
31	37.24	45.00	14.15	3.70	100.09	$(Pb_{3.18}Bi_{3.82})_{\Sigma 7}(S_{7.82}Se_{0.83})_{\Sigma 8.65}$	9.6	54.57
32	37.43	44.45	14.76	3.62	100.26	$(Pb_{3.22}Bi_{3.78})_{\Sigma 7}(S_{8.19}Se_{0.82})_{\Sigma 9.01}$	9.1	54.00
33	37.19	45.13	14.46	3.55	100.33	$(Pb_{3.18}Bi_{3.82})_{\Sigma 7}(S_{7.99}Se_{0.80})_{\Sigma 8.79}$	9.1	54.57
34	36.82	44.52	14.65	3.28	99.27	$(Pb_{3.18}Bi_{3.82})_{\Sigma 7}(S_{8.19}Se_{0.74})_{\Sigma 8.93}$	8.3	54.57
35	37.77	44.66	14.58	3.27	100.28	$(Pb_{3.22}Bi_{3.78})_{\Sigma 7}(S_{8.04}Se_{0.73})_{\Sigma 8.77}$	8.3	54.00
36	37.53	44.88	14.69	2.76	99.86	$(Pb_{3.20}Bi_{3.80})_{\Sigma 7}(S_{8.10}Se_{0.62})_{\Sigma 8.72}$	7.1	54.29
37	37.61	44.26	15.08	2.73	99.68	$(Pb_{3.23}Bi_{3.77})_{\Sigma 7}(S_{8.37}Se_{0.62})_{\Sigma 8.99}$	6.9	53.86
38	37.49	46.09	14.92	2.40	100.90	$(Pb_{3.15}Bi_{3.85})_{\Sigma 7}(S_{8.11}Se_{0.53})_{\Sigma 8.64}$	6.1	55.00

The analytical results are quoted in weight %.
Analyses N. 1, 2, 4-7, 10 : CAMEBAX SX-50 electron microprobe. Other Analyses : ARL-SEMQ-95 electron microprobe. Totals include: an. 2. Cu 0.04, Ag 0.09 wt % ; an. 4. Sb 0.02 wt % ; an. 7. Sb 0.10 wt % ; an. 8. As 0.17 wt % ; an. 10. As 0.19 wt % .

$$A = \frac{Se}{(S+Se)} * 100 \qquad B = \frac{Bi}{(Pb+Bi)} * 100$$

Hyde (1981), Makovicky (1981), and others. According to Makovicky (1997a, b), the structure consists of pseudotetragonal (Q type) layers of (Pb,Bi)S, which are two atomic layers (*i.e.*, ½ *a* PbS) thick (space group $P2_1/m$), and pseudohexagonal (H type) layers $(Bi,Pb)S_2$, which are double-octahedra thick (space group $C2/m$). These alternating layers differ in the *c* subcell parameter (~7 Å in H subcell and ~ 4 Å in Q subcell) and have the other parameters similar (*b* is about 4.1 Å, *a* is about 15.5 Å). The formula of cannizzarite $Pb_{46}Bi_{54}S_{127}$ (Pb/Bi = 0.852, *Me*/S = 0.787) was derived from the crystal structure (Matzat 1979), which consists of alternating layers *A* $[(Pb,Bi)_{46}S_{46}]$ and *B* $[(Pb,Bi)_{54}S_{81}]$ parallel to (001). Fine-scale changes in stoichiometry and dimensions of the layers lead to the variable-fit homologues of the cannizzarite series (Makovicky & Hyde 1981, Mozgova *et al.* 1984, 1988, Organova 1989, Makovicky 1997a, b).

Electron-diffraction data for wittite (Se content 8.5 wt% determined by energy dispersion) were obtained with a JEM–100C microscope. Selected-area electron-diffraction (SAED) patterns from different microcrystals and different inclinations of the electron beam are shown in Figure 9. The arrangements of reflections along the *X** axis are irregular because of the incommensurate structure of the mineral. Strong reflections in Figure 9a display regularity and correspond to the H subcell. Reflections corresponding to the Q subcell are

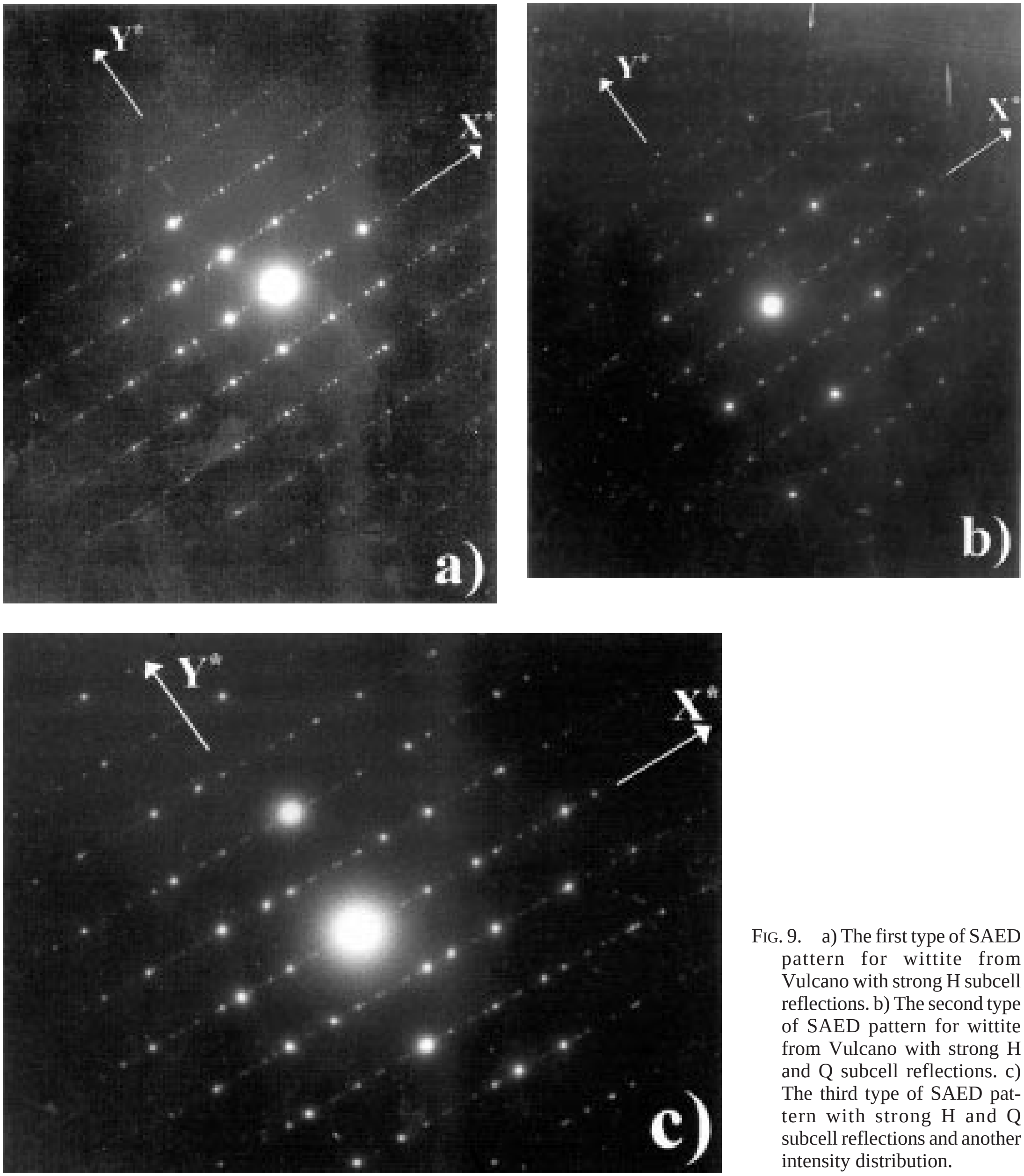

FIG. 9. a) The first type of SAED pattern for wittite from Vulcano with strong H subcell reflections. b) The second type of SAED pattern for wittite from Vulcano with strong H and Q subcell reflections. c) The third type of SAED pattern with strong H and Q subcell reflections and another intensity distribution.

less strong. In Figures 9b and 9c, there are H and Q subcells but with a different distribution of intensities. Variation of intensity may be dependent on different orientation of particles studied in regard to the electron beam as well as on slight differences in composition. Numerical evaluation of SAED obtained for three microcrystals from Vulcano (Fig. 9) gave a range of the ratio C(H):C(Q) from 1.710 to 1.725. It is close to value (1.734) calculated from the X-ray-diffraction data (Table 2).

X-ray powder-diffraction data for the same sample analyzed by SAED were obtained using a Debye–Scherrer camera 114 mm in diameter (unfiltered Cu radiation, Si as a standard); the relative intensities of lines were visually estimated. The results (Table 2) are similar to those for wittite from Nevskoe (Organova 1989,

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR WITTITE AND CANNIZZARITE

Cannizzarite Vulcano (1)		Wittite Vulcano (2)		Q subcell (calc)		H subcell (calc)		Wittite Nevskoe (3)		Q subcell (calc)		H subcell (calc)	
d(hkl)	I/I_0	*d(hkl)*	I/I_0	*d(hkl)*	*hkl*	*d(hkl)*	*hkl*	*d(hkl)*	I/I_0	*d(hkl)*	*hkl*	*d(hkl)*	*hkl*
		7.8	4	7.7	200	7.7	200	7.8	1	7.6	200	7.6	200
5.12	1	5.12	4	5.13	300	5.12	300	5.2	2br	5.12	300	5.12	300
4.21	1	4.26	2w	4.17	$\bar{1}01$			4.16	1	4.16	$\bar{1}01$		
								4.06	0.5	4.10	001		
		3.96	2	3.95	110	3.94	110			3.96	110		
3.84	6	3.85	10	3.85	400	3.85	400	3.88	10br	3.84	400	3.84	400
								3.79	0.5	3.78	101		
3.64	2	3.64	4	3.61	210	3.60	210	3.64	3br	3.62	210		
3.53	2	3.53	5	3.55	$\bar{3}01$	3.54	011	3.53	3w	3.55	$\bar{3}01$	3.55	011
								3.45	3				
3.40	5							3.42	3			3.40	111
		3.38	7w			3.37	102					3.38	102
								3.35	4w	3.35	201		
3.32	2	3.31	7			3.30	$\bar{2}11$	3.309	4			3.32	$\bar{2}11$
3.195	2	3.20	3	3.19	310	3.20	401	3.21	2br	3.20	310	3.20	401
3.14	0.5	3.13	2	3.12	$\bar{4}01$	3.13	211	3.13	1	3.124	$\bar{4}01$	3.14	211
								3.076	8	3.07	500	3.07	500
3.02	10	3.004	10			3.009	$\bar{3}11$	3.005	9			3.017	$\bar{3}11$
2.90	10	2.886	10	2.88	011			2.90	9	2.89	011		
								2.87	0.5	2.85	$\bar{1}12$		
2.79	2	2.79	5	2.80	410	2.79	$\bar{4}10$	2.815	2br	2.805	410	2.801	$\bar{4}10$
								2.769	2br	2.781	111		
2.70	2	2.696	7	2.72	$\bar{5}01$	2.69	501	2.702	7	2.720	$\bar{5}01$	2.726	501
								2.637	1	2.67	$\bar{3}11$		
2.60	1	2.576	1	2.566	600	2.565	600	2.589	4br	2.564	600	2.563	600
2.48	1	2.479	2br	2.485	$\bar{4}11$	2.483	$\bar{3}12$	2.453	2	2.477	$\bar{4}11$	2.486	$\bar{3}12$
2.41	2	2.409	2	2.393	$\bar{6}01$	2.404	$\bar{5}11$	2.412	1			2.405	$\bar{5}11$
								2.386	2	2.386	311		
								2.283	7	2.272	511		
2.25	5	2.247	6			2.248	511	2.237	6br			2.250	511
2.20	1	2.202	1	2.197	700	2.198	700	2.198	3	2.197	700	2.197	700
		2.118	2	2.115	$\bar{7}01$			2.114	5	2.115	$\bar{7}01$		
2.05	9	2.039	10br	2.050	020	2.039	020	2.051	9br	2.052	020	2.049	020
1.914	1	1.920	1br	1.923	800	1.924	800	1.923	10	1.922	800	1.922	800

(1) Mozgova *et al.* 1985 : (2) This study : (3) Organova 1989.

Mozgova *et al.* 1992) and cannizzarite from Vulcano (Mozgova *et al.* 1985). The (*hkl*) indexes are given separately for the H and Q subcells. Some overlaps of *d* values from the two subcells cause a rather low accuracy in the unit-cell values.

The cell parameters, refined by method of least squares, are given in Table 3. Figure 10 shows that volumes of both subcells (V_Q and V_H) vary directly with Se content and allow us to assume that Se enters both types of layers. It will be necessary to carry out single-crystal investigations of wittite, however, to get more reliable information concerning Se sites in the structure.

DISCUSSION

The results of the electron-microprobe analyses of minerals under consideration from Vulcano reveal a continuous isomorphic S–Se substitution: the amount of Se in the samples studied varies continuously from values less than 1 wt% up to 14.65 wt%, and even in a single grain. According to Gaines *et al.* (1997) and Anthony *et al.* (1990), these compositions correspond to Se-bearing cannizzarite as well as wittite (Se ≥ 7.7 wt%).

All analytical data are satisfactorily calculated on the simplified formula of wittite accepted in the handbooks cited. It should be stressed that all samples studied were collected in the same deposit, the minerals contain only the principal elements (Pb, Bi, S, Se) without noticeable admixtures of other elements, and the majority of the electron-microprobe analyses were conducted under the same conditions. The diffraction data obtained for a sample with ~8.5 wt% Se from Vulcano indicate a non-commensurate layer structure known for cannizzarite and wittite. Thus, the data given in this paper allow us to hypothesize that there is no chemical or structural discontinuity between cannizzarite and wittite in this series up to 40 at.% Se.

In addition to the isomorphic S–Se substitution, there is also a heterovalent Pb–Bi substitution in this series, which results in the nonstoichiometric formulas of members of the series. It is not as extensive as the first one, but exceeds several times the analytical error as well as the composition field assumed earlier by Makovicky (1981). Existence of this compositional field is also supported by its limited variation with changing condition of deposition of these minerals (in different fumaroles and different years of collection). Both types of substitution of the series change independently of each other, and the relation between them has not been revealed. In general, the compositional field may be described by the formula $Pb_{3+x}Bi_{4-x}(S_{9-y}Se_y)_{9-x/2}$ or $Pb_3(Bi_{4-x}Pb_x)_4(S_{9-y}Se_y)_{9-x/2}$, with $0.04 \leq x \leq 0.28$, and $0.5 \leq y \leq 3.5$, which was obtained on the basis of the known simplified chemical formula of wittite. The range of formulas of cannizzarite and wittite given by various authors may be explained by existence of a compositional field in connection with the scheme of substitution discussed here.

The data reported in this paper show up once more the chemical and structural resemblances of wittite and cannizzarite. Even if one assumes that all Se enters in H layers, only where it exceeds 14 wt% does the composition exceed the 50% mark needed to consider wittite as a valid selenium-dominant species. It is evident that wittite will be validated or discredited with certainty only when the full details of its crystal structure are finally deduced.

The very dynamic environment in fumaroles generates non-equilibrium conditions of mineral formation. The heterogeneous distribution of Se contents in minerals studied, even on a microscopic scale, evidently results from this situation. Non-equilibrium conditions of mineral formation are also responsible for the disorder in the sequence of deposition of minerals in cannizzarite–wittite assemblage noted above.

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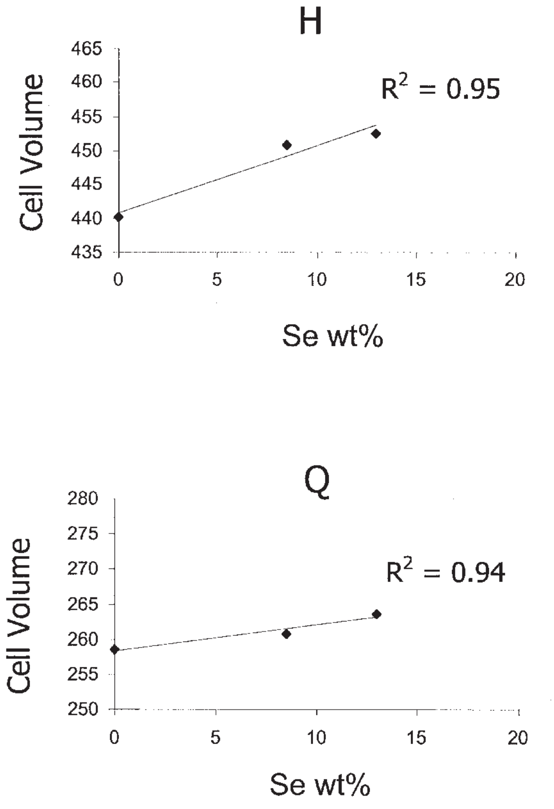

FIG. 10. Volumes (Å^3) of the H and Q subcells increase with increase in Se content in cannizzarite and wittite.

TABLE 3 . UNIT SUBCELL VALUES OF WITTITE AND CANNIZZARITE

	H- subcell	*Q- subcell*	*Se (wt %)*
Cannizzarite *(1)*	a = 15.46(0) Å b = 4.09(0) Å c = 7.03(0) Å β = 98.00(0)° V = 440.19 Å^3	a = 15.48(0) Å b = 4.09(0) Å c = 4.13(0) Å β = 98.56(0)° V = 258.57 Å^3	0.0
Wittite – Vulcano *(2)*	a = 15.53(3) Å b = 4.07(1) Å c = 7.18(1) Å β = 97.83(1)° V = 449.60 (1) Å^3	a = 15.70(4) Å b = 4.08(0) Å c = 4.14(1) Å β = 101.34(1)° V = 260.01(1) Å^3	8.5
Wittite – Nevskoe *(3)*	a = 15.53(0) Å b = 4.09(1) Å c = 7.19(2) Å β = 97.79(9)° V = 452.48(1) Å^3	a = 15.68(1) Å b = 4.10(1) Å c = 4.18(1) Å β = 101.20(3) V = 263.61(1) Å^3	13.0

(1) Matzat, 1979; *(2)* This study ; *(3)* Organova, 1989.

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