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RARE SULFOSALTS FROM VULCANO, AEOLIAN ISLANDS, ITALY. VI. VURROITE, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, A NEW MINERAL SPECIES

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Abstract

Vurroite, ideally $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, is a new mineral species from the modern Pb–Bi epithermal deposit of La Fossa crater, on Vulcano Island, Italy. It occurs as a volcanic encrustation deposited around high-temperature fumaroles (400–600°C) located both on the rim and on the inner slope of the active crater. The mineral consists of slender, needle-shaped crystals up to 0.4 mm long and 0.01 mm across, which generally form fibrous aggregates. Associated minerals are bismuthinite, lillianite, kirkiite, heyrovskýite, galena, and other less-well-characterized sulfochlorides of Pb(Bi), some of which contain traces of Tl, Sn or As. The color of vurroite is silver-gray, with a metallic luster. In reflected plane-polarized light, it is white, without distinct bireflectance or pleochroism. Anisotropism is weak, without color effects. The measured values of reflectance in air for a single grain are 34.25 (470 nm), 32.95 (546 nm), 32.60 (589 nm), 31.05% (650 nm); values for 400–800 nm are tabulated. Electron-microprobe analyses yield the following ranges of concentrations (wt.%): Pb 39.92–41.80 (ave. 40.92), Bi 27.51–29.11 (ave. 28.30), As 7.59–9.03 (ave. 8.38), Sn 1.33–1.78 (ave. 1.60), Tl 0.00–0.34 (ave. 0.06), S 17.64–8.64 (ave. 18.28), Se 0.09–0.25 (ave. 0.18), Cl 1.74–2.02 (ave. 1.85), Br 0.23–0.25 (ave. 0.24). The empirical chemical formula, calculated on the basis of 44 cations, is $Pb_{18.95}Sn_{1.30}(Bi_{12.99}As_{10.73}Tl_{0.03})_{\Sigma 23.75}(S_{54.71}Se_{0.22}Cl_{5.00}Br_{0.29})_{\Sigma 60.22}$. Single-crystal X-ray-diffraction data reveal a pseudo-orthorhombic symmetry, space group *F2mm*, with *a* 45.824(6), *b* 8.368(2), *c* 53.990(6) Å, *V* 20702(6) $Å^3$ and $Z = 8$. The calculated density is 6.15 g/cm^3. The strongest powder-diffraction lines [*d* in Å(I)(*hkl*)] are: 2.07(100)(18.2.8), 3.34(80)(8.2.2), 2.85(80)(16.0.2), 2.69(80)(12.2.6), 2.10(70)(0.4.0), 3.17(60)(18.2.2), 2.17(60)(8.2.6), and 2.04(50)(20.0.12). Vurroite is the second Pb–As–Bi sulfosalt mineral known (kirkiite, $Pb_{10}Bi_3As_3S_{19}$, is the other), and it is the first mineral of the system $PbS–Bi_2S_3–$

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As_2S_3 to contain Cl and Sn. The name of this new mineral species (IMA 2003–027) honors of Filippo Vurro, Professor of mineralogy at the University of Bari, specialist in the mineralogy and geochemistry of modern volcanic deposits.

Keywords: vurroite, Pb–Bi–As sulfosalts, chlorosulfide, tin, fumaroles, Vulcano island, Italy.

SOMMAIRE

La vurroïte, de composition idéale $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, est une nouvelle espèce minérale du gisement épithermal contemporain à Pb–Bi du cratère de La Fossa, île de Vulcano, en Italie. Elle se présente en encroûtements volcaniques déposés par des fumeroles de haute température (400–600°C), situées en bordure et sur la pente interne du cratère actif. Il s'agit de fins cristaux aciculaires atteignant une longueur de 0.4 mm pour une épaisseur de 0.01 mm, généralement en aggrégats fibreux. Lui sont associés bismuthinite, lillianite, kirkiite, heyrovskýite, galène, ainsi que des chlorosulfures de Pb(Bi) moins bien caractérisés, dont certains contiennent des traces de Tl, Sn ou As. La vurroïte est gris-argent, avec un éclat métallique. En lumière réfléchie polarisée, la vurroïte est blanche, sans biréflectance distincte ni pléochroïsme. L'anisotropie est faible, sans teintes de polarisation. Les valeurs principales de réflectance mesurée dans l'air sont 34.25 (470 nm), 32.95 (546 nm), 32.60 (589 nm), et 31.05% (650 nm). Les analyses à la microsonde électronique ont donné les intervalles de concentration suivants (% pondéraux): Pb 39.92–41.80 (moy. 40.92), Bi 27.51–29.11 (moy. 28.30), As 7.59–9.03 (moy. 8.38), Sn 1.33–1.78 (moy. 1.60), Tl 0.00–0.34 (moy. 0.06), S 17.64–8.64 (moy. 18.28), Se 0.09–0.25 (moy. 0.18), Cl 1.74–2.02 (moy. 1.85), Br 0.23–0.25 (moy. 0.24). La formule chimique empirique, calculée sur une base de 44 cations, est $Pb_{18.95}Sn_{1.30}(Bi_{12.99}As_{10.73}\ Tl_{0.03})_{\Sigma 23.75}(S_{54.71}Se_{0.22}\ Cl_{5.00}Br_{0.29})_{\Sigma 60.22}$. Les données en diffraction X obtenues sur monocristal révèlent une symétrie pseudo-orthorhombique, groupe spatial *F2mm*, *a* 45.824(6), *b* 8.368(2), *c* 53.990(6) Å, *V* 2070.2(6) Å^3 et *Z* = 8. La densité calculée est 6.15 g/cm^3. Les raies les plus intenses du spectre de diffraction [*d* en Å(I)(*hkl*)] sont: 2.07(100)(18.2.8), 3.34(80)(8.2.2), 2.85(80)(16.0.2), 2.69(80)(12.2.6), 2.10(70)(0.4.0), 3.17(60)(18.2.2), 2.17(60)(8.2.6), et 2.04(50)(20.0.12). La vurroïte est le second sulfosel de Pb–As–Bi connu, après la kirkiite, $Pb_{10}Bi_3As_3S_{19}$); c'est le premier minéral du système $PbS–Bi_2S_3–As_2S_3$ à contenir Cl et Sn. Le nom choisi pour la nouvelle espèce (IMA 2003–027) honore Filippo Vurro, professeur de minéralogie à l'Université de Bari, spécialiste de la minéralogie et la géochimie des gisements volcaniques modernes.

(Traduit par la Rédaction)

Mots-clés: vurroïte, sulfosels à Pb–Bi–As, chlorosulfure, étain, fumeroles, île de Vulcano, Italie.

INTRODUCTION

In spite of the relative abundance of sulfosalt species containing Pb and Bi, or Pb and As, the sulfosalts of Pb–As–Bi are extremely rare. Up to now, the sole natural representative of this group of sulfosalts is the mineral kirkiite, $Pb_{10}Bi_3As_3S_{19}$. It was first discovered at the Aghios Philippos lead–zinc deposit near Kirki, Greece, by Moëlo *et al.* (1985) and found later in the high-temperature fumarole deposits of Vulcano, Aeolian Islands, Italy (Borodaev *et al.* 1998). Here, we describe the second natural representative of Pb–As–Bi sulfosalts, vurroite, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$. The new mineral was discovered during the systematic investigation of rare sulfosalts from Vulcano; they constitute the products of high-temperature fumaroles at the La Fossa crater (Garavelli *et al.* 1997, Borodaev *et al.* 1998, 2000, 2001, Vurro *et al.* 1999). It is the third new mineral species, together with barberiite (Garavelli & Vurro 1994) and mozgovaite (Vurro *et al.* 1999), to be found at Vulcano as a result of the last thermal event.

The new mineral is named after Filippo Vurro (b. 1940), Professor of mineralogy at the University of Bari, in recognition of his important contributions to the knowledge of the mineralogy and geochemistry of modern volcanic deposits. Both the mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA (No. 2003–027). The holotype is deposited in the mineralogical museum of the University of Bari (No. 6/nm).

OCCURRENCE AND PARAGENESIS

The occurrence at Vulcano of both kirkiite (Borodaev *et al.* 1998) and vurroite is related both to the high fugacity of sulfur and the high halogen contents of the fumarolic fluids, which play an important role in the transport of arsenic and other metalloids and metals, and in the deposition of their compounds (Garavelli *et al*. 1997, Cheynet *et al*. 2000).

For the most part, sulfosalts from Vulcano belong to the system Pb–Bi–S (cannizzarite, lillianite, heyrovskýite, galenobismutite, mozgovaite) and usually contain traces of selenium substituting for sulfur. They occur as crusts and aggregates of tiny crystals, covering the brecciated and altered rocks. Vurroite crystals can be easily recognized because they consist of very tiny needle-shaped crystals forming thin layers and fibrous aggregates randomly accreted in holes and fissures of the rock.Three samples of vurroite have been found in distinct locations (Fig. 1) at Vulcano, where it is intimately admixed with bismuthinite, lillianite, kirkiite, heyrovskýite, galena and other less-well-characterized sulfochlorides of Pb(Bi), occasionally containing traces of K, Sn, As or

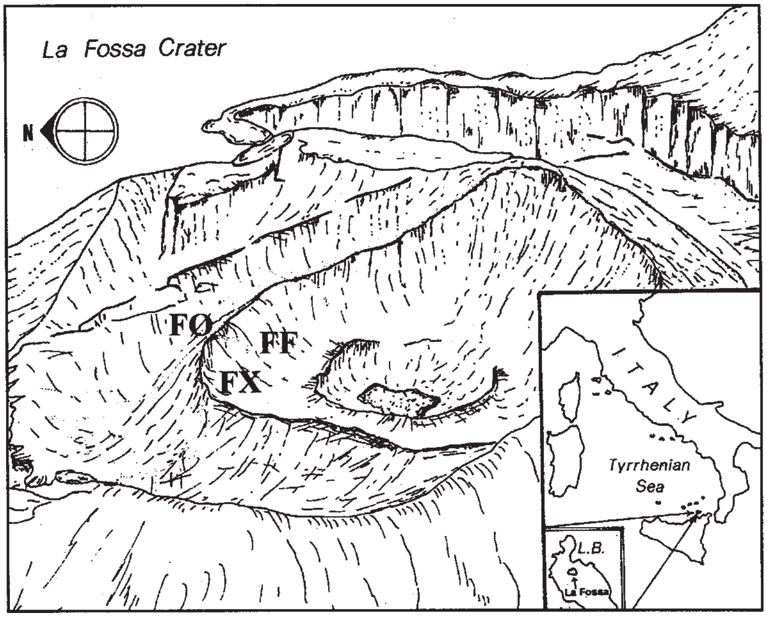

FIG. 1. Summit of "La Fossa crater", Vulcano Island (Italy). Map of the fumarole field and location of sampling sites of vurroite.

Tl. Pb–Bi–As sulfosalts and Pb(Bi) sulfochlorides are generally present as small crystals at the base of the aggregates of Pb–Bi minerals, which are usually better crystallized.

Vurroite was first observed during an SEM investigation as rare and small crystals intergrown with Pb–Bi sulfosalts in samples collected in 1995 from fumarole FX (Fig. 1, T = 430°C). Unfortunately, the size and the rarity of the crystals permitted only a qualitative analysis of the new mineral, and no additional or more detailed investigations could be performed. Later, an appreciable amount of very tiny and slender crystals of vurroite was found in samples collected in 1998 from the fumarole F0 (Fig. 1, T = 406 °C). X-ray powder-diffraction investigations indicated the existence of a new mineralogical phase, but the small size of the crystals allowed only four good chemical analyses, which were obtained from a single larger crystal. Finally, during the re-examination of samples collected in 1991 from the fumarole FF (Fig. 1, T = 607°C), suitable crystals of vurroite were found, and chemical, physical and structural investigations were performed. Therefore, vurroite from fumarole FF is considered and described in this paper as the holotype.

MORPHOLOGY AND PHYSICAL PROPERTIES

Vurroite occurs as slender, needle-shaped crystals, up to 0.4 mm long and 0.01 mm across, which generally form fibrous aggregates (Fig. 2). The crystals are silver-gray in color, with a metallic luster. The density, calculated from results of electron-microprobe analyses and unit-cell volume of the holotype, is 6.15 g/cm^3. Under reflected light, vurroite is white. Bireflectance and pleochroism were not observed. Between crossed polars, the anisotropism is weak, without color effects. The reflectance spectrum in air was measured from 400 to 800 nm on three distinct elongate crystals, with the polarization direction perpendicular to the elongation (Table 1, Fig. 3).

CHEMICAL DATA

Electron-probe micro-analyses (EPMA) of vurroite were performed in two laboratories using a CAMECA SX–50 instrument (Table 2). Crystals from the holotype (sample FF91) were investigated at the BRGM–CNRS–University common laboratory (Orléans, France). Operating conditions were as follows: voltage 20 kV, beam current 20 nA; standards [element (emission line), counting time for one spot-analysis]: PbS (Pb$M\alpha$, 20 s), SnS (Sn$L\alpha$, 20 s), Bi metal (Bi$M\alpha$, 20 s), FeS_2 (S$K\alpha$, 20 s), AsGa (As$L\alpha$, 20 s), ZnS (Zn$K\alpha$, 20 s), Cu metal (Cu$K\alpha$, 20 s), $TlAsS_2$ (Tl$M\alpha$, 10 s), Se metal (Se$L\alpha$, 20 s), $Pb_5(VO_4)_3Cl$ (Cl$K\alpha$, 20 s), $Li_2B_4O_7$ doped with 1.84 wt.% Br (Br$L\alpha$, 20 s). Iodine was sought, but not detected. Analyses were also conducted at the Moscow State University on a crystal of vurroite from a specimen collected in 1998 from fumarole F0. Operating conditions: voltage 15 kV, beam current 30 nA; standards (element, emission line): PbS (Pb$M\alpha$), SnS (Sn$L\alpha$), Bi_2S_3 (Bi$M\alpha$, S$K\alpha$), $AgAsS_2$ (As$L\beta$), Bi_2Se_3 (Se$L\alpha$), $Pb_5(VO_4)_3Cl$ (Cl$K\alpha$).The combined results are given in Table 2.

The holotype of vurroite clearly contains significant amounts of Br, up to 0.29 atoms per formula unit (*apfu*), Se (up to 0.31 *apfu*) and Tl (up to 0.16 *apfu*), in addition to the major constituents Pb (18.57–19.21 *apfu*), Bi (12.54–13.60 *apfu*), As (9.92–11.43 *apfu*), Sn (1.06–1.44 *apfu*), S (53.88–55.30 *apfu*) and Cl (4.67–5.40 *apfu*). The amount of Bi varies inversely with As, indicating that these elements substitute for one another in the structure (Fig. 4a). Similarly, the negative correlation between Pb or Sn and (As + Bi + Tl) (Figs. 4b, c) suggests the partial replacement of Sn and Pb by (As + Bi + Tl) and *vice versa*. Conversely, the correlation between Sn and Pb (Fig. 4d), as well as stereochemical considerations (Pinto 2004, Pinto *et al.*, in prep.) and charge-balance indications suggest two distinct positions for Sn and Pb in vurroite, with the tin in a tetravalent state.

On the basis of a total of 44 cations per formula unit, according to the structural data (Pinto 2004, Pinto *et al.*, in prep.), the mean chemical formula of vurroite (holo-

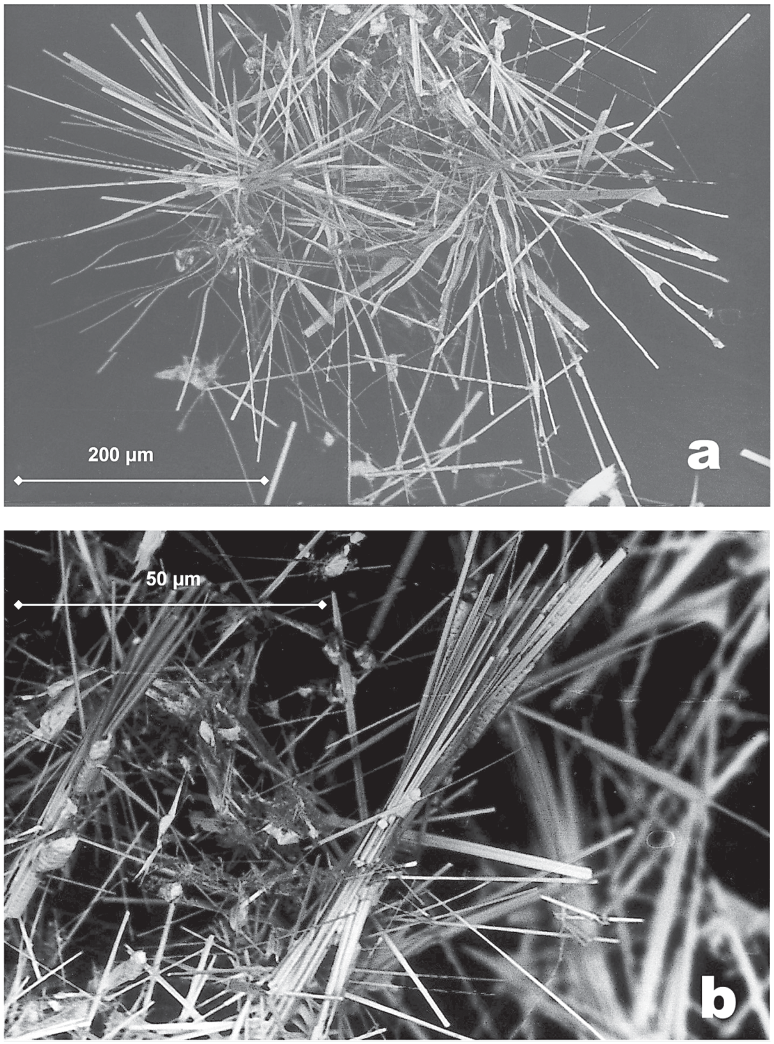

FIG. 2. Scanning electron photomicrographs of vurroite aggregates: a) general view; b) detail.

type) is $Pb_{18.95}Sn_{1.30}$ $(Bi_{12.99}As_{10.73}Tl_{0.03})_{\Sigma 23.75}$ $(S_{54.71}Se_{0.22}Cl_{5.00}Br_{0.29})_{\Sigma 60.22}$. Taking into account the substitutions of Sn and Pb for Bi, as well as the occupancy factors derived from the crystal-structure refinement (Pinto 2004, Pinto *et al.*, in prep.), the empirical structural formula can be written: $(Pb_{18.95}Bi_{1.05})_{\Sigma 20.00}(Sn_{1.30}Bi_{0.70})_{\Sigma 2.00}$ $(Bi_{11.24}As_{10.73}Tl_{0.03})_{\Sigma 22.00}(S_{54.71}Se_{0.22}Cl_{5.00}Br_{0.29})_{\Sigma 60.22}$. This formula is very close to the ideal one, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, in which Cl was determined on the basis of charge balance. This composition requires Pb 43.86, Sn 2.51, As 8.72, Bi 24.33, S 18.33, Cl 2.25, or a total of 100.00 wt.%.

Electron-microprobe analyses of the vurroite crystal from sample FØ98 (Table 2) showed it to be chemically similar to the holotype. The empirical chemical formula of this sample of vurroite, $Pb_{20.96}Sn_{1.12}$ $(Bi_{10.92}As_{10.99})_{\Sigma 21.91}$ $(S_{51.18}Se_{0.95}Cl_{7.04})_{\Sigma 59.17}$, is significantly enriched in Pb and Cl, and depleted in Bi and S with respect to the holotype.

As a general rule, the compositional variation of vurroite from Vulcano seems to be governed by the mutual substitutions $Sn^{4+} + S^{2-} \Rightarrow (As,Bi)^{3+} + Cl^-$ and $Pb^{2+} + Cl^- \longrightarrow (As,Bi)^{3+} + S^{2-}$, which act together in order to maintain charge balance. This compositional variability of vurroite can be expressed by the general empirical structural formula $Pb_{20-x}Sn_{2-y}$ $(Bi,As)_{22+x+y}$ $(S_{54+x-y}Cl_{6-x+y})_{\Sigma 60}$, with $-1.59 < x < 1.43$ and $0.57 < y < 0.97$.

CRYSTALLOGRAPHIC DATA

Samples of vurroite were investigated by single-crystal and powder X-ray-diffraction techniques. A single crystal of holotype vurroite (sample FF91) was mounted in the beamline 5.2 R (X-ray diffraction) at the Elettra synchrotron facility (Basovizza–Trieste, Italy). The wavelength of the radiation was set to 1.0 Å. A 165 mm MarCCD detector was placed 50 mm from the crystal. In this configuration, the resolution is about 1.05 Å. The data were processed by means of the HKL package of programs (XDISP, DENZO and SCALEPACK; Otwinowsky & Minor 1997). The 90 frames, collected with a rotation angle $\Delta\varphi = 2°$, were indexed, and the unit cell refined. The X-ray pattern of the new mineral is characterized by strong reflections pointing to an orthorhombic cell with *a* 22.912(3), *b* 4.184(1), *c* 26.995(3) Å. However, many weak reflections are present, which can be indexed only by assuming the doubling of all three cell parameters. If this new orthorhombic supercell is chosen, the reflections showing odd $(h + k)$, $(h + l)$, or $(k + l)$ values are systematically absent, indicating that the lattice is *F*-centered. As the diffraction pattern does not reveal any other systematic absences, the possible space-groups of vurroite are reduced to five: *F*222, *F*2*mm*, *Fm*2*m*, *Fmm*2 and *Fmmm*. After several trials, the crystal structure was solved and refined in the space group *F*2*mm* (Pinto 2004, Pinto *et al.,* in prep.). The refined orthorhombic supercell is $a = 45.824(6) = 2a_{\text{sub}}$, $b = 8.368(2) = 2b_{\text{sub}}$, $c = 53.990(6)$ Å $= 2c_{\text{sub}}$, $V = 20702(6)$ Å^3, $Z = 8$. However, the structural refinement points to the possible occurrence of twinning, and the real symmetry of vurroite could actually be monoclinic.

X-ray powder-diffraction data for the holotype of vurroite (Table 3) were obtained using a Gandolfi camera (diameter 114.6 mm, Cu*K*α radiation). The indexing was done taking into account the findings of the single-crystal study, and assuming an orthorhombic symmetry. Unit-cell parameters refined from the X-ray powder pattern are *a* 45.836(9), *b* 8.386(2), *c* 53.97(1) Å, *V* 20743(7) Å^3, in excellent agreement with the data obtained from the single-crystal investigation. The description of the structure is discussed in detail in the Ph.D. thesis of Pinto (2004), and will be published separately (Pinto *et al.*, in prep.).

TABLE 1. REFLECTANCE* IN AIR
OF VURROITE HOLOTYPE, VULCANO, ITALY

λ	*R*	λ	*R*
400 nm	33.75%	600 nm	32.05%
420	35.30	620	31.95
440	34.70	640	31.40
460	34.25	**650**	**31.05**
470	**34.25**	660	30.85
480	34.05	680	30.10
500	33.80	700	29.50
520	33.30	720	28.60
540	33.00	740	27.80
546	**32.95**	760	26.50
560	32.85	780	24.65
580	32.75	800	25.10
589	**32.60**		

* Leica DMR microscope, objective FLUOTAN 20×/0.50 POL, standard SiC (NPL no. 50). Microphotometer Leica MPV–SP, monochromator resolution: λ = 2 nm.

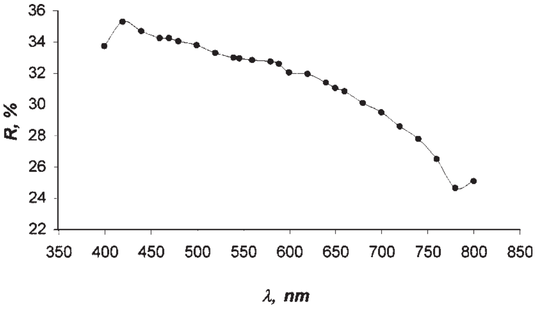

FIG. 3. Reflectance spectrum for vurroite in air.

TABLE 2. CHEMICAL COMPOSITION OF VURROITE FROM VULCANO

Sample		*Sn*	*Pb*	*Tl*	*Bi*	*As*	*S*	*Se*	*Cl*	*Br*	*Total*	Val Bal
Crst FF91/6b	1	1.71	40.35	0.00	29.03	7.59	17.64	0.25	1.83	0.24	98.64	0.55
Crst FF91/6c	2	1.72	41.13	0.00	29.00	7.86	18.19	0.24	1.78	0.23	100.15	-0.66
	3	1.54	40.78	0.00	29.11	7.86	17.95	0.19	1.75	0.24	99.42	0.10
Crst FF91/6d	4	1.51	39.92	0.00	28.52	8.58	18.39	0.18	1.96	0.23	99.29	-1.72
	5	1.58	40.51	0.00	28.00	8.38	18.10	0.18	1.79	0.23	98.77	-0.45
	6	1.72	41.02	0.00	28.27	8.24	18.24	0.21	1.83	0.24	99.77	-0.68
Crst FF91/6c	7	1.74	41.18	0.00	28.06	8.28	18.40	0.20	1.84	0.24	99.94	-1.43
	8	1.78	41.80	0.20	27.51	8.44	18.33	0.16	1.74	0.23	100.19	-0.02
	9	1.78	40.99	0.00	28.09	8.37	18.36	0.22	1.85	0.24	99.90	-1.00
Crst FF91/8e	10	1.45	41.42	0.00	28.16	9.02	18.56	0.09	1.86	0.25	100.81	-0.13
	11	1.33	41.26	0.34	27.78	8.95	18.59	0.12	1.94	0.24	100.55	-1.25
	12	1.37	40.72	0.20	28.11	9.03	18.64	0.12	2.02	0.25	100.46	-1.53
Average	1-12	1.60	40.92	0.06	28.30	8.38	18.28	0.18	1.85	0.24		
Minimum		1.33	39.92	0.00	27.51	7.59	17.64	0.09	1.74	0.23		
Maximum		1.78	41.80	0.34	29.11	9.03	18.64	0.25	2.02	0.25		
St. Dev.		0.16	0.51	0.12	0.51	0.47	0.28	0.05	0.09	0.01		
Crst F098	13	1.27	46.50	n.d.	21.03	9.11	16.65	0.71	2.90	n.d.	98.17	1.74
	14	1.42	46.09	n.d.	21.53	8.99	16.85	0.71	2.96	n.d.	98.55	0.79
	15	1.41	43.53	n.d.	25.61	7.90	17.05	0.79	2.19	n.d.	98.48	0.55
	16	1.38	42.23	n.d.	25.44	7.84	16.8	0.86	2.22	n.d.	96.77	0.07
Average	13-16	1.37	44.59	-	23.40	8.46	16.84	0.77	2.57	-		
Minimum		1.27	42.23	-	21.03	7.84	16.65	0.71	2.19	-		
Maximum		1.42	46.50	-	25.61	9.11	17.05	0.86	2.96	-		
St. Dev.		0.07	2.05	-	2.46	0.68	0.17	0.07	0.42	-		

Empirical chemical formulas based on 44 cations

1.	$Pb_{19.07}Sn_{1.41}\ (Bi_{13.60}As_{9.92})_{\Sigma 23.52}\ (S_{53.88}Se_{0.31}Cl_{5.05}Br_{0.29})_{\Sigma 59.53}$
2.	$Pb_{19.13}Sn_{1.40}\ (Bi_{13.37}As_{10.11})_{\Sigma 23.48}\ (S_{54.67}Se_{0.29}Cl_{4.84}Br_{0.28})_{\Sigma 60.07}$
3.	$Pb_{19.07}Sn_{1.26}\ (Bi_{13.50}As_{10.17})_{\Sigma 23.67}\ (S_{54.26}Se_{0.23}Cl_{4.78}Br_{0.29})_{\Sigma 59.57}$
4.	$Pb_{18.57}Sn_{1.23}\ (Bi_{13.16}As_{11.04})_{\Sigma 24.20}\ (S_{55.30}Se_{0.22}Cl_{5.33}Br_{0.28})_{\Sigma 61.13}$
5.	$Pb_{18.92}Sn_{1.29}\ (Bi_{12.97}As_{10.82})_{\Sigma 23.79}\ (S_{54.64}Se_{0.22}Cl_{4.89}Br_{0.28})_{\Sigma 60.02}$
6.	$Pb_{19.03}Sn_{1.39}\ (Bi_{13.00}As_{10.57})_{\Sigma 23.58}\ (S_{54.69}Se_{0.26}Cl_{4.96}Br_{0.29})_{\Sigma 60.20}$
7.	$Pb_{19.09}Sn_{1.41}\ (Bi_{12.89}As_{10.61})_{\Sigma 23.51}\ (S_{55.11}Se_{0.24}Cl_{4.98}Br_{0.29})_{\Sigma 60.63}$
8.	$Pb_{19.21}Sn_{1.43}\ (Bi_{12.54}As_{10.73}Tl_{0.09})_{\Sigma 23.36}\ (S_{54.45}Se_{0.19}Cl_{4.67}Br_{0.27})_{\Sigma 59.59}$
9.	$Pb_{18.97}Sn_{1.44}\ (Bi_{12.89}As_{10.71})_{\Sigma 23.60}\ (S_{54.90}Se_{0.27}Cl_{5.00}Br_{0.29})_{\Sigma 60.46}$
10.	$Pb_{18.82}Sn_{1.15}\ (Bi_{12.69}As_{11.34})_{\Sigma 24.03}\ (S_{54.51}Se_{0.11}Cl_{4.94}Br_{0.29})_{\Sigma 59.86}$
11.	$Pb_{18.87}Sn_{1.06}\ (Bi_{12.59}As_{11.32}Tl_{0.16})_{\Sigma 24.07}\ (S_{54.94}Se_{0.14}Cl_{5.18}Br_{0.28})_{\Sigma 60.55}$
12.	$Pb_{18.63}Sn_{1.09}\ (Bi_{12.75}As_{11.43}Tl_{0.09})_{\Sigma 24.27}\ (S_{55.12}Se_{0.14}Cl_{5.40}Br_{0.30})_{\Sigma 60.97}$
Average formula 1-12 (*vurroite holotype*)	$Pb_{18.95}Sn_{1.30}\ (Bi_{12.99}As_{10.73}Tl_{0.03})_{\Sigma 23.75}\ (S_{54.71}Se_{0.22}Cl_{5.00}Br_{0.29})_{\Sigma 60.22}$
13.	$Pb_{21.59}Sn_{1.03}\ (Bi_{9.68}As_{11.70})_{\Sigma 21.38}\ (S_{49.96}Se_{0.87}Cl_{7.87})_{\Sigma 58.70}$
14.	$Pb_{21.40}Sn_{1.15}\ (Bi_{9.91}As_{11.54})_{\Sigma 21.45}\ (S_{50.56}Se_{0.86}Cl_{8.03})_{\Sigma 59.45}$
15.	$Pb_{20.54}Sn_{1.16}\ (Bi_{11.98}As_{10.31})_{\Sigma 22.29}\ (S_{52.00}Se_{0.98}Cl_{6.04})_{\Sigma 59.02}$
16.	$Pb_{20.30}Sn_{1.16}\ (Bi_{12.12}As_{10.42})_{\Sigma 22.54}\ (S_{52.19}Se_{1.08}Cl_{6.24})_{\Sigma 59.51}$
Average formula 13-16	$Pb_{20.96}Sn_{1.12}\ (Bi_{10.92}As_{10.99})_{\Sigma 21.91}\ (S_{51.18}Se_{0.95}Cl_{7.04})_{\Sigma 59.17}$

n.d.: not determined.

Relationship with Synthetic Phases

Vurroite represents the second natural sulfosalt with Pb, Bi and As as major elemental constituents, kirkiite being the other. Experimental studies on the system $PbS–Bi_2S_3–As_2S_3$ (Walia & Chang 1973) showed the presence of only two pseudoternary phases: Phase A, with compositions ranging from $27PbS•7(As_{0.75}Bi_{0.25})_2S_3$ to $27PbS•7(As_{0.65}Bi_{0.35})_2S_3$, and Phase B, $Pb_2(As_{0.60}Bi_{0.40})_2S_5$.

The natural homologue of Phase A is kirkiite, $Pb_{10}Bi_3As_3S_{19}$ (Moëlo *et al.* 1985). Phase B has no natural equivalent, and no crystallographic data are available in the literature. Recalculation of the chemical

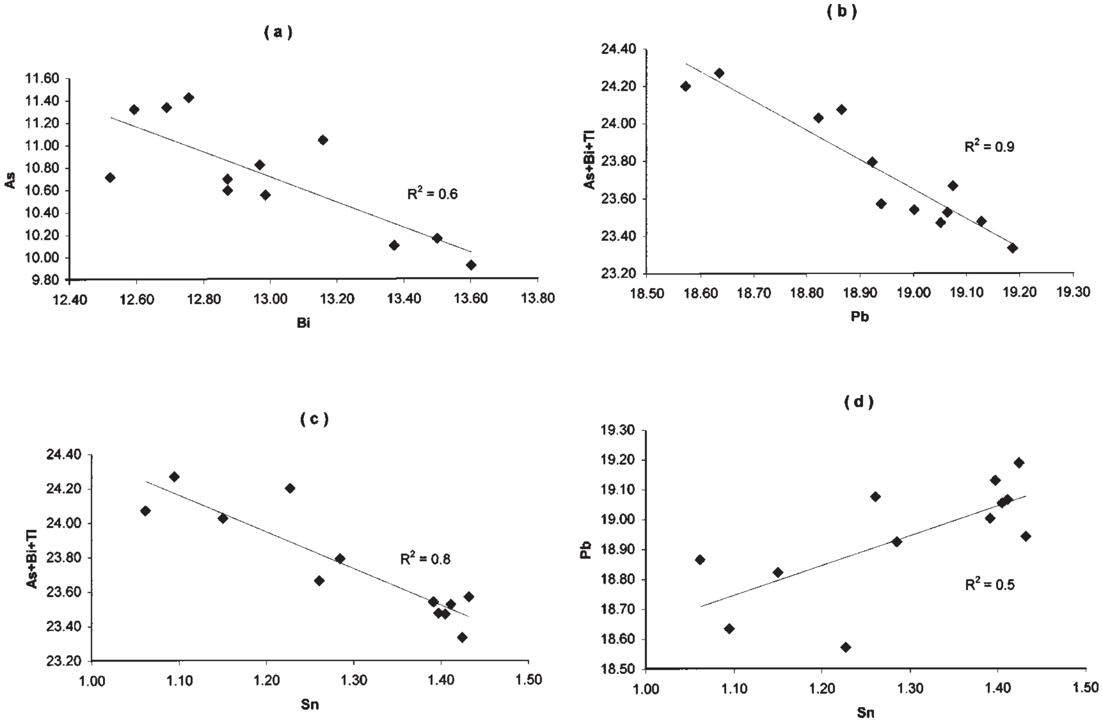

FIG. 4. Covariance relationships among various cations (*apfu*) in vurroite. a) Negative correlation between Bi and As, b) negative correlation between Pb and (As + Bi + Tl), c) negative correlation between Sn and (As + Bi + Tl), and d) slight positive correlation between Sn and Pb.

composition of synthetic Phase B on the basis of 44 cations leads to the chemical formula $Pb_{22}(As_{13.2}Bi_{8.8})_{\Sigma 22}S_{55}$, which shows similarities with the empirical chemical formula of vurroite, $(Pb_{18.95}Bi_{1.05})_{\Sigma 20.00}$ $(Sn_{1.30}Bi_{0.70})_{\Sigma 2.00}$ $(Bi_{11.24}As_{10.73}Tl_{0.03})_{\Sigma 22.00}$ $(S_{54.71}Se_{0.22}Cl_{5.00}Br_{0.29})_{\Sigma 60.22}$. The main chemical difference between them is the presence of tin and chlorine in vurroite from Vulcano. Nevertheless, vurroite and Phase B cannot confidently be compared, as reliable indexes, unit-cell parameters and *Z* value for Phase B are not known. As regards their structural features, it is worth noting that some significant discrepancies exist between the X-ray powder-diffraction data of vurroite and synthetic Phase B (Table 3), suggesting that these phases do not show structural similarities.

DISCUSSION

Vurroite is a new example of a multicomponent sulfosalt in which two minor chemical components, Sn and Cl, act as essential constituents, together with Pb, Bi, As and S. The presence of Cl allows it to be considered a chlorosulfosalt, together with ardaite ($Pb_{10}Sb_6S_{17}Cl_4$: Breskovska *et al.* 1982), dadsonite ($Pb_{23}Sb_{25}S_{60}Cl$: Moëlo 1979), pillaite ($Pb_9Sb_{10}S_{23}ClO_{0.5}$: Orlandi *et al.* 2001) and pellouxite [$(Cu,Ag)_2Pb_{21}Sb_{23}S_{55}ClO$: Orlandi *et al.* 2004]. The presence of minor Br substituting for Cl is unique among sulfosalts and, up to now, such a substitution was known only among mercury halogenosulfides of the corderoite–arzakite and capgaronnite–perroudite groups (Strunz & Nickel 2001).

Considered particularly interesting also is the presence of trace amounts of Tl in vurroite, because it is the first time that it has been found in sulfosalts at Vulcano. As pointed out by Garavelli (1994), Garavelli *et al.* (1997) and Cheynet *et al.* (2000), the thallium content of fumarolic fluids discharging from high-temperature fumarole vents at Vulcano is relatively high. According to Cheynet *et al.* (2000), thallium and arsenic are transported in these fluids as gaseous TlCl and AsF_3, respectively. The tendency of these elements to remain as volatile compounds explains their extreme rarity in solid phases condensed from fumarole fluids. Thallium chloride bromide and thallium bromide have been identified only in sublimates deposited on altered rocks from high-temperature fumarole FØ (T > 300–350°C,

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR VURROITE AND SYNTHETIC PHASE B

	Vurroite			Phase B	
hkl	d_{calc}	d_{obs}	$I/I_{0\,obs}$	d_{obs}	$I/I_{0\,obs}$
10 0 4	4.340	4.27	20		
10 0 6	4.084	4.09	8		
4 2 0	3.938	3.98	8	3.934	10
12 0 0	3.820	3.82	12	3.850	10
12 0 4	3.675	3.71	45	3.738	25
6 2 2	3.642	3.64	13	3.633	13
6 2 4	3.546	3.54	5	3.548	50
2 2 8	3.519	3.49	5	3.493	13
8 2 2	3.357	3.34	80	3.293	100
6 2 8	3.228	3.23	9		
8 2 6	3.167	3.17	60	3.121	15
14 0 6	3.077			3.079	13
10 2 4	3.015	3.02	25	3.016	75
14 0 8	2.946			2.940	13
12 0 12	2.911	2.92	5		
8 0 16	2.908 }			2.894	15
4 0 18	2.901				
16 0 2	2.849	2.85	80	2.849	10
4 2 14	2.754	2.77	14	2.780	10
16 0 6	2.730			2.741	30
12 2 6	2.694	2.69	80		
16 0 8	2.637	2.63	5	2.652	8
2 2 16	2.611			2.611	8
12 2 8	2.605			2.585	8
10 2 12	2.549	2.55	20		
16 0 12	2.416	2.42	5		
12 0 18	2.358	2.36	5		
12 2 14	2.278	2.28	5	2.269	15
8 2 18	2.244	2.24	35		
12 0 20	2.204			2.196	40
18 2 2	2.169	2.17	60		
14 2 14	2.144			2.136	8
0 4 0	2.096	2.10	70		
18 2 8	2.071	2.07	100	2.071	25
20 0 12	2.042	2.04	50	2.027	6
10 1 0	2.011 }			2.012	10
2 2 3	2.010				
8 2 22	1.986	1.977	8		
12 2 20	1.951	1.951	9		
6 2 24	1.918	1.917	30		
18 2 14	1.895	1.892	5	1.902	25
10 4 4	1.888 }			1.8806	8
20 2 10	1.884				
0 2 26	1.860			1.8597	40
8 4 10	1.849	1.846	20		
10 0 28	1.777	1.780	40	1.7712	10
10 4 12	1.755 }			1.7529	13
8 4 14	1.753				
14 0 26	1.753				
10 0 10	1.747 }			1.7460	10
2 2 28	1.746				
26 0 8	1.706	1.707	35	1.7098	5
20 2 18	1.670			1.6709	5
22 2 0	1.649 }			1.6474	8
2 2 30	1.649				
8 4 18	1.646				
18 4 0	1.619	1.621	20	1.6234	6
10 0 32	1.583	1.584	15		
4 2 32	1.550			1.5505	6
22 2 24	1.436			1.4357	10
30 2 8	1.404			1.4041	8
24 4 8	1.382			1.3822	8
10 6 6	1.319 }			1.3195	13
32 0 16	1.319				

Fulignati & Sbrana 1998), whereas As has been found as metastable As–S–Cl compounds in sublimates collected on the inner walls of silica sampling tubes (Garavelli *et al.* 1997). Cheynet *et al.* (2000) have suggested that the As–S–Cl compounds react with gaseous H_2S to form more stable As–S reduced phases, like kirkiite and vurroite. The discovery of the presence of Tl in vurroite suggests that the same depositional process can act also on the Tl–Br–Cl compounds to fix this element in the structure of vurroite. In addition, traces of bromine in vurroite suggest that it, as well as chlorine, could play a significant role not only in the transport of metals, but also in the condensation processes of sulfides and sulfosalts.

Like all the other sulfosalts from the contemporary epithermal deposit of Vulcano, vurroite contains traces of Se, ranging between 0.09 and 0.86 wt.%. The presence of this element, which is typical for the locality, is ascribed to the high Se content in fumarole fluids discharging from the vents.

Although the metallogenic processes are quite different, the high fugacities of sulfur present at Vulcano (fumarolic-type deposit) and Kirki (endogenous, subvolcanic hydrothermal process) permitted the simultaneous deposition of As^{3+} and Sn^{4+} together with Pb and Bi. At Kirki, these two cations were fixed in different sulfosalts (As^{3+} in kirkiite and tennantite, Sn^{4+} in lévyclaudite: Moëlo *et al.* 1990), whereas at Vulcano, they were partly fixed in the same phase, vurroite.

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