RARE SULFOSALTS FROM VULCANO, AEOLIAN ISLANDS, ITALY.
VII. Cl-BEARING GALENOBISMUTITE

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ABSTRACT

Cl-bearing galenobismutite (with Cl ranging from 0.12 to 1.45 wt.%), discovered among high-temperature fumarole incrustations at "La Fossa" crater , Island of Vulcano, Italy, has been chemically and structurally investigated. The mineral is commonly associated with bismuthinite, cannizzarite, lillianite, heyrovskýite and galena, and rarely with kirkiite, vurroite and other less well characterized Pb(Bi)-sulfochlorides. Electron-microprobe investigations show that Cl-bearing galenobismutite from Vulcano has a wide compositional field (Pb:Bi atomic ratio ranging from 0.52 to 0.72). The statistical analysis of chemical data shows correlations between the main elements and chlorine, positive Pb *versus* Cl and negative Bi *versus* Cl, according to the coupled heterovalent substitution scheme: $Pb^{2+} + Cl^- \rightleftharpoons Bi^{3+} + S^{2-}$. The compositional variation of Cl-bearing galenobismutite can be represented by the general empirical formula $Pb_{1+x}Bi_{2-x}(S_{4-x-y}Cl_xSe_y)$, with $0 < x < 0.3$ and $0 < y < 0.2$, indicating the extent of departure from the ideal composition $PbBi_2S_4$ toward an increase of the Pb content and a decrease of Bi. The phase

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IV, synthetic analogue of galenobismutite in the system Pb–Bi–S, has the compositional field extending from ideal composition toward decreasing Pb (Pb:Bi atomic ratio in the range 0.50–0.39). It reflects another type of substitution: $3Pb^{2+} \rightarrow 2Bi^{3+} + \square$. single-crystal X-ray investigations were performed on two selected crystals of Cl-bearing galenobismutite from Vulcano. The composition of galenobismutite controls the a and b unit-cell parameters, which increase with the increase of the Cl content. The structural refinements converge to R values of 3.10% for 840 reflections [$F_o > 4\sigma(F_o)$] and 1.49% for 376 reflections [$F_o > 4\sigma(F_o)$], respectively. The structure of Cl-bearing galenobismutite is topologically identical to that of Cl-free galenobismutite. The excess of Pb observed in Cl-bearing galenobismutite is incorporated in the trigonal prismatic $M2_{gb}$ and $M3_{gb}$ sites. No Pb-for-Bi substitution was observed at the octahedral position $M1_{gb}$. We do not find evidence of a preferential distribution of Cl among the anion positions.

Keywords: Cl-bearing galenobismutite, Pb–Bi sulfosalt, crystal structure, fumaroles, Vulcano Island, Italy.

SOMMAIRE

La galénobismutite porteuse de Cl (les teneurs en Cl allant de 0.12 à 1.45%, poids), découverte comme incrustations fumerol-liennes de haute température au cratère "La Fossa", île de Vulcano, en Italie, a fait l'objet d'une étude chimique et structurale. Lui sont associés bismuthinite, cannizzarite, lillianite, heyrovskýite et galène, et moins habituellement, kirkiite, vurroïte et autres sulfochlorures de Pb(Bi) moins bien caractérisés. Les données obtenues avec une microsonde électronique montrent que la galé-nobismutite chlorée de Vulcano possède un champ de composition assez large (rapport atomique Pb:Bi allant de 0.52 à 0.72). L'analyse statistique des données chimiques montrent des corrélations entre les éléments principaux et le chlor, positive dans le cas de Pb *versus* Cl et négative dans le cas de Bi *versus* Cl, selon le schéma de substitution hétérovalente couplée $Pb^{2+} + Cl^- \rightleftharpoons Bi^{3+} + S^{2-}$. On peut représenter la variation en compositions dans la galénobismutite chlorée par la formule générale empirique $Pb_{1+x}Bi_{2-x}(S_{4-x-y}Cl_xSe_y)$, avec $0 < x < 0.3$ et $0 < y < 0.2$, indiquant la portée de l'écart de la composition idéale $PbBi_2S_4$ en direc-tion d'une augmentation du Pb et d'une diminution de la teneur en Bi. La phase IV, analogue synthétique de la galénobismutite dans le système Pb–Bi–S, possède un champ compositionnel allant de la composition idéale dans la direction d'une diminution du Pb (rapport atomique Pb:Bi dans l'intervalle 0.50–0.39). Il s'agit d'une autre substitution: $3Pb^{2+} \rightarrow 2Bi^{3+} + \square$. Nos études par diffraction X sur monocristal ont porté sur deux cristaux de galénobismutite chlorée. La composition régit les dimensions a et b de la maille, qui augmentent avec la teneur en Cl. Les affinements de la structure ont convergé à des valeurs du résidu R de 3.10% pour 840 réflexions [$F_o > 4\sigma(F_o)$] et 1.49% pour 376 réflexions [$F_o > 4\sigma(F_o)$], respectivement. La structure de cette variante est topologiquement identique à celle de la galénobismutite dépourvue de Cl. L'excédent de Pb observé dans la galénobismutite chlorée occupe les sites prismatiques trigonaux $M2_{gb}$ et $M3_{gb}$. Nous n'avons pas d'évidence d'une substitution de Pb pour Bi au site octaédrique $M1_{gb}$ ou d'une distribution préférentielle du Cl parmi les sites anioniques.

(Traduit par la Rédaction)

Mots-clés: galénobismutite chlorée, sulfosel de Pb–Bi, structure cristalline, fumerolles, île de Vulcano, Italie.

INTRODUCTION

Galenobismutite, $PbBi_2S_4$, is the natural analogue of the synthetic Phase IV in the system $PbS–Bi_2S_3$ (Otto & Strunz 1968, Salanci & Moh 1969). It was first described from the Kogrufvan deposit, Nordmark, Sweden, by Sjögren (1878), who derived the composi-tion $PbS•Bi_2S_3$. The type specimen was re-investigated by Berry (1940) and, successively, by Wickman (1951) and Iitaka & Nowacki (1962), who determined the crystal structure. Makovicky (1977) interpreted the crystal structure of galenobismutite to be an incomplete lillianite-like structure $^{2,-}L$. Two-thirds of this structure represents, in fact, a distorted, contracted set of the lillianite linkage pattern. Recently, a re-investigation of the crystal structure of galenobismutite has been performed on a sample with a close-to-ideal composi-tion from the high-temperature fumaroles at "La Fossa" crater of Vulcano, Aeolian Archipelago, Italy (Pinto 2004, Pinto *et al*. 2006).

At Vulcano, the system of fumaroles is famous for its assemblage of rare Pb–Bi sulfosalts described in previous papers (Mozgova *et al*. 1985, Garavelli 1994, Garavelli *et al*. 1997, 2005, Vurro *et al*. 1999, Borodaev *et al*. 1998, 2000, 2001, 2003, Pinto 2004). At Vulcano, galenobismutite, a very abundant mineral, is commonly associated with bismuthinite, cannizzarite, lillianite, heyrovskýite, galena and vurroite, the newly recognized Pb–Bi–As halogen-bearing sulfosalt. As the other sulfo-salts from Vulcano, galenobismutite invariably contains selenium as a substituent for sulfur, but its distinctive feature is the remarkable chlorine content, generally present in samples collected from various fumaroles from 1991 onward. The presence of Cl in Pb–Bi sulfo-salts is only rarely encountered. At Vulcano, chlorine was previously reported as traces in lillianite (Borodaev *et al*. 2001) and, as an essential constituent in vurroite, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$ (Garavelli *et al*. 2005).

In this paper, we report a detailed study of Cl-bearing galenobismutite from Vulcano. This mineral represents the first example of natural pure Pb–Bi sulfosalt significantly enriched in chlorine.

Preliminary Study:
Samples FX Collected in 1995

Cl-bearing galenobismutite was first discovered in samples collected in June 1995 around the fumarole FX (T = 523°C) located in the North inner slope of the crater (Fig. 1). Preliminary SEM investigations revealed the presence of tiny acicular crystals of galenobismutite commonly intergrown in microdruses. The most interesting assemblage consists of a relatively large (about 200×25 μm) crystal of bismuthinite surrounded by a fine-grained radial aggregate of slender crystals, fringed by a tiny heterogeneous border (Fig. 2a). Minute (about 10 μm in length) needle-like crystals of Cl-bearing galenobismutite were found in the inner part of the radial aggregate, as well as in the thin border. Investigations using energy-dispersion spectroscopy (EDS) showed the presence of chlorine in some of the needles analyzed. X-ray maps of the distribution of Pb, Cl and Se for the assemblage reported in Figure 2a are shown in Figures 2b, c, d. The X-ray map for Cl (Fig. 2c) shows that the thin external border is particularly enriched in the halogen. The highest concentrations of chlorine were found in small grains of chlorides and sulfochlorides, which are abundant in the border. The paragenetic sequence and age relationships between bismuthinite and associated minerals indicate that the deposition of Cl-free bismuthinite occurred earlier than the deposition of Cl-bearing minerals, suggesting that the chlorine concentration in the fluid phase increased with time.

In order to quantify the Cl content in galenobismutite, polished sections have been accurately prepared without heating. Electron-microprobe investigations (EPMA) were performed at the Moscow State University (Camebax SX–50) and at the Centro Studi Geominerari e Mineralurgici, CNR, Cagliari (ARL–SEMQ–95). The results obtained are quite comparable.

Results of ten selected analyses are reported in Table 1 and compared with the theoretical composition $PbBi_2S_4$. Formulas calculated on the basis of seven atoms per formula unit (*apfu*) also are given. The chemical analyses show that the Pb(Zn) : Bi(As) ratios are invariably greater than 0.5, the expected value. A plot of the data (Fig. 3) shows a relationship between Pb(Zn) and Cl. A similar tendency is shown by Bi(As) and S(Se). In Cl-bearing galenobismutite, therefore, the coupled heterovalent substitution $Pb^{2+} + Cl^- \rightleftharpoons Bi^{3+} + S^{2-}$ evidently takes place. This mechanism of substitution is similar to that observed in lead – antimony – chlorine sulfosalts by Mozgova (1985). Unfortunately, the small size of the crystals as well as their fine intergrowths did not allow us to perform other types of analyses on these samples.

Subsequently, a re-examination of sulfosalts collected in 1991 from the fumaroles FF and FS (samples FF–1991 and FS–1991) led to the discovery of larger crystals of Cl-bearing galenobismutite, particularly enriched in the halogen, so that mineralogical, chemical and crystal-structure investigations could be performed. The results of these studies are presented and discussed below.
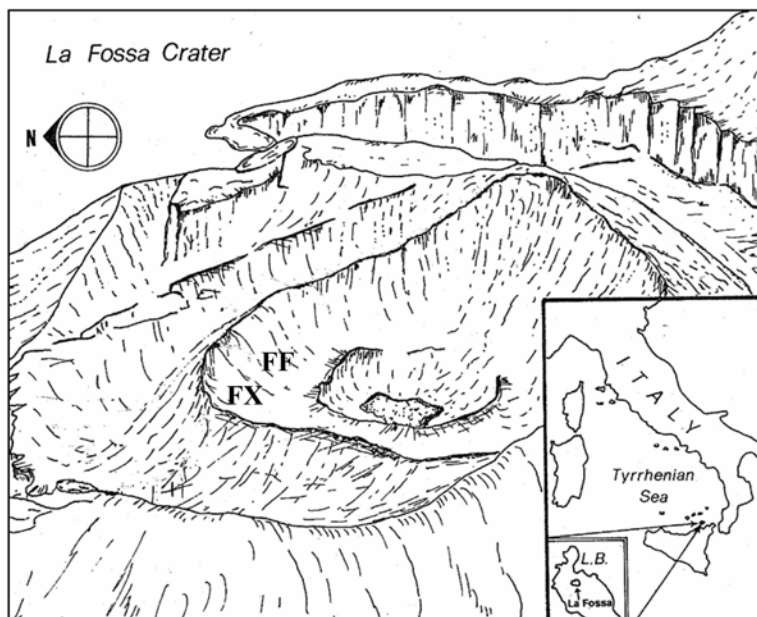

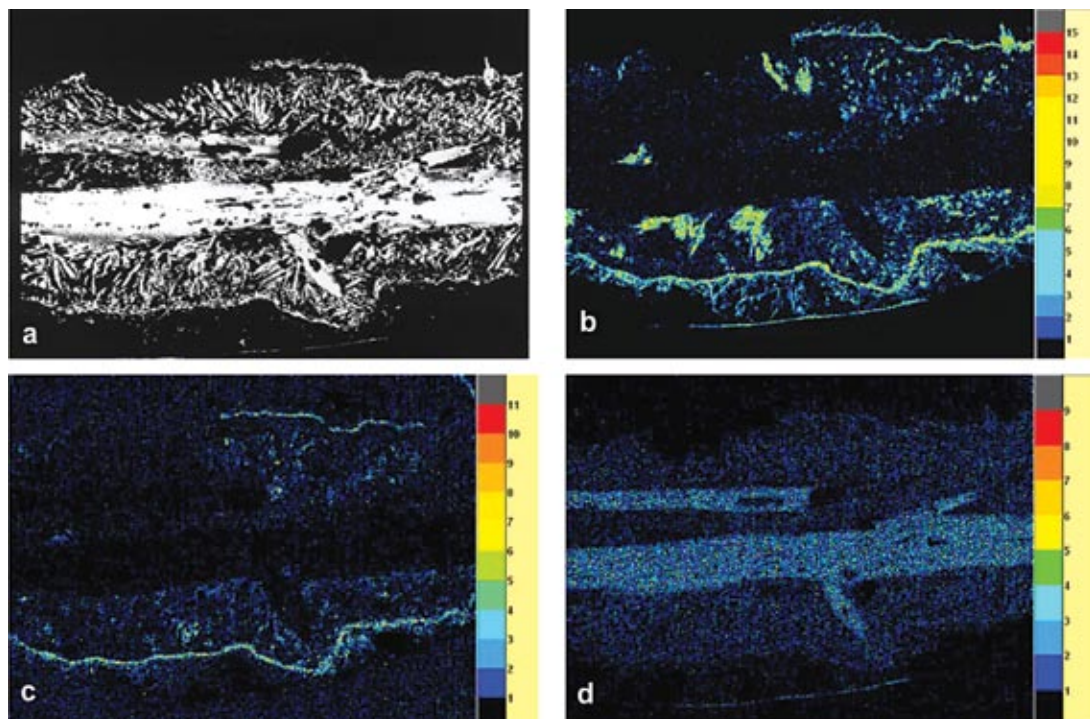Fig. 1. Map of the fumarole field and location of sampling sites.

FIG. 2. Cl-bearing galenobismutite and chlorides surrounding a relatively large crystal of Cl-free bismuthinite (sample FX–1995): (a) back-scattered-electron image; (b), (c) and (d): X-ray element-distribution maps, which show the distributions of Pb$M\alpha$, Cl$K\alpha$, and Se$L\alpha$, respectively. Color variations represent differences in concentration of the elements.

DESCRIPTION OF THE SAMPLES

The crystals of Cl-bearing galenobismutite collected in 1991 were recovered from the exhalative area around fumaroles FF and FS (T ≈ 600°C), in the inner North slope of the crater (Fig. 1). Associated minerals are kirkiite, vurroite and less well characterized Pb–Bi sulfochlorides, occasionally containing traces of K, Sn, As and Tl. The Cl-bearing minerals, vurroite and Pb–Bi sulfochlorides form crusts and aggregates directly on the wallrock face (Fig. 4a), suggesting an earlier condensation of the chlorine-bearing minerals. The crystals of Cl-bearing galenobismutite are usually prismatic, about 400 μm in length and less than 30 μm in width (Fig. 4b). Slender needle-like crystals, which generally form parallel aggregates, have been observed as well (Fig. 4c).

CHEMICAL DATA

Chemical investigations on samples FF and FS have been conducted with an ARL–SEMQ–95 electron microprobe (Centro Studi Geominerari e Mineralurgici, CNR, Cagliari). Operating conditions were: accelerating voltage 20 kV, beam current 20 nA, standards (element, emission line): PbS (Pb$M\alpha$, S$K\alpha$), Bi$_2$S$_3$ (Bi$M\alpha$), CdS (Cd$L\alpha$), ZnS (Zn$K\alpha$), metallic Ag (Ag$L\alpha$), CuS (Cu$K\alpha$), FeAsS$_2$ (As$L\alpha$), metallic selenium (Se$L\alpha$) and KCl (Cl$K\alpha$). Detection limits are: Pb 0.10, Cd 0.14, Bi 0.10, As 0.08, S 0.02, Se 0.04, Cl 0.03, Ag 0.05, Cu 0.04, Zn 0.05 wt% at a confidence level of 99%.

The electron-microprobe results are summarized in Table 2, and compared with the theoretical composition PbBi$_2$S$_4$. The ranges of concentrations of the main components are as follows (in wt%): Pb 28.15–34.94 (ave. 31.37, σ 1.67), Bi 47.36–55.34 (ave. 50.56, σ 1.95), S 14.72–16.60 (ave. 15.98, σ 0.35). As in the other sulfosalts from Vulcano, all the samples investigated contain selenium (from 0.40 to 1.03 wt%, ave. 0.86, σ 0.14). Small amounts of Zn (up to 0.22 wt%), Cu (up to 0.10 wt%), Ag (up to 0.23 wt%) and As (up to 0.23 wt%) have also been sporadically observed. Chlorine is invariably present, reaching concentrations of 1.45 wt%.

In Table 2, the empirical formulae, calculated on the basis of seven atoms per formula unit, also are given. The balance of valences is rather good: deviations do not exceed 2.5% in absolute value. Chemical N values

TABLE 1. ELECTRON-MICROPROBE DATA AND CHEMICAL FORMULAE
FOR Cl-BEARING GALENOBISMUTITE FROM SAMPLE FX–1995

	Pb	Zn	Bi	As	S	Cl	Se	Total	Bal. val.	Pb(Zn) Bi(As)
1	28.15	0.13	53.08	0.00	15.96	0.18	1.62	99.13	-0.43	0.54
2	28.43	0.13	53.46	0.00	16.14	0.14	1.68	99.98	-0.71	0.54
3	27.10	1.06	53.45	0.00	16.28	0.13	1.51	99.53	0.31	0.57
4	30.48	0.00	53.03	0.00	16.46	0.34	0.58	100.89	0.42	0.58
5	30.09	0.07	52.83	0.00	16.22	0.23	0.53	99.97	1.86	0.58
6	29.97	0.11	52.14	0.00	16.15	0.24	0.49	99.10	1.41	0.59
7	31.08	0.00	51.64	0.11	16.11	0.61	0.48	100.04	1.10	0.60
8	31.68	0.00	52.35	0.08	16.40	0.53	0.52	101.48	0.58	0.61
9	31.92	0.00	49.97	0.07	16.26	0.87	0.34	99.43	-1.83	0.64
10	32.10	0.00	50.26	0.07	16.35	0.87	0.34	99.99	-1.80	0.64
11	27.50		55.47		17.02			100.00		0.50

Compositions are quoted in wt%. Samples 1, 3, 7, 9: ARL–SEMQ 95 electron microprobe. Operating conditions: voltage 20 kV, beam current 20 nA, standards (element, emission line): PbS (Pb$M\alpha$, S$K\alpha$), Bi$_2$S$_3$ (Bi$M\alpha$), CdS (Cd$L\alpha$), ZnS (Zn$K\alpha$), FeAsS$_2$ (As$L\alpha$), metallic selenium (Se$L\alpha$) and KCl (Cl$K\alpha$). Samples 2, 4–6, 8, 10: Camebax SX–50 electron microprobe. Operating conditions: voltage 15 kV, beam current 30 nA, standards (element, emission line): PbS (Pb$M\alpha$, Bi$_2$S$_3$ (Bi$M\alpha$, S$K\alpha$), AgSAsS$_2$ (As$L\beta$), Bi$_2$Se$_3$ (Se$L\alpha$), Pb$_5$(VO$_4$)$_3$Cl (Cl$K\alpha$). 11. Theoretical composition of galenobismutite. Balance of valences (Bal. val.) has been calculated from the empirical formulae.

Empirical formulae based on 7 atoms

1 (Pb$_{1.04}$Zn$_{0.01}$)$_{\Sigma1.05}$Bi$_{1.94}$(S$_{3.81}$Cl$_{0.04}$Se$_{0.16}$)$_{\Sigma4.01}$
2 (Pb$_{1.04}$Zn$_{0.02}$)$_{\Sigma1.06}$Bi$_{1.94}$(S$_{3.82}$Cl$_{0.03}$Se$_{0.16}$)$_{\Sigma4.01}$
3 (Pb$_{0.98}$Zn$_{0.12}$)$_{\Sigma1.06}$Bi$_{1.92}$(S$_{3.81}$Cl$_{0.03}$Se$_{0.14}$)$_{\Sigma3.98}$
4 Pb$_{1.11}$Bi$_{1.91}$(S$_{3.86}$Cl$_{0.07}$Se$_{0.06}$)$_{\Sigma3.99}$
5 (Pb$_{1.11}$Zn$_{0.01}$)$_{\Sigma1.12}$Bi$_{1.93}$(S$_{3.86}$Cl$_{0.05}$Se$_{0.05}$)$_{\Sigma3.96}$
6 (Pb$_{1.11}$Zn$_{0.01}$)$_{\Sigma1.12}$Bi$_{1.91}$(S$_{3.86}$Cl$_{0.05}$Se$_{0.05}$)$_{\Sigma3.96}$
7 Pb$_{1.14}$(Bi$_{1.87}$As$_{0.01}$)$_{\Sigma1.88}$(S$_{3.80}$Cl$_{0.13}$Se$_{0.05}$)$_{\Sigma3.98}$
8 Pb$_{1.14}$Bi$_{1.87}$(S$_{3.82}$Cl$_{0.11}$Se$_{0.05}$)$_{\Sigma3.98}$
9 Pb$_{1.16}$(Bi$_{1.80}$As$_{0.01}$)$_{\Sigma1.81}$(S$_{3.82}$Cl$_{0.18}$Se$_{0.03}$)$_{\Sigma4.03}$
10 Pb$_{1.16}$(Bi$_{1.80}$As$_{0.01}$)$_{\Sigma1.81}$(S$_{3.82}$Cl$_{0.18}$Se$_{0.03}$)$_{\Sigma4.03}$
11 PbBi$_2$S$_4$

Fig. 3. Samples FX–1995: trends representing the variation of concentration (in *apfu*) of S(Se), Bi(As), Pb(Zn) and Cl in the crystals analyzed.

(N$_c$), calculated for each composition using the formula of the lillianite homologues (Makovicky & Karup-Møller 1977a, b, Makovicky 1977), also are reported. The values are non-integral and are invariably higher than the crystallographically defined theoretical value (N = 2).

Results obtained for samples FF and FS are in agreement with those given in Table 1; they confirm a linear positive correlation between Pb and Cl (Fig. 5a), as well as a negative correlation between Bi and Cl (Fig. 5b). No relationships are observed in plotting Pb and Bi *versus* selenium (Figs. 5c, d), as well as Cl *versus* Se (Fig. 5e). The positive correlation observed between N$_c$ and Cl (Fig. 5f) is related to the variation of Pb:Bi ratio driven by the incorporation of chlorine, according to the mechanism of substitution Pb^{2+} + Cl$^-$ $\rightleftharpoons$ Bi^{3+} + S^{2-}.

X-Ray Diffraction and Structure Refinement

Two needle-like crystals of Cl-bearing galenobismutite from fumarole FF (FF–1991a and FF–1991b) were selected for structural investigations. Only pre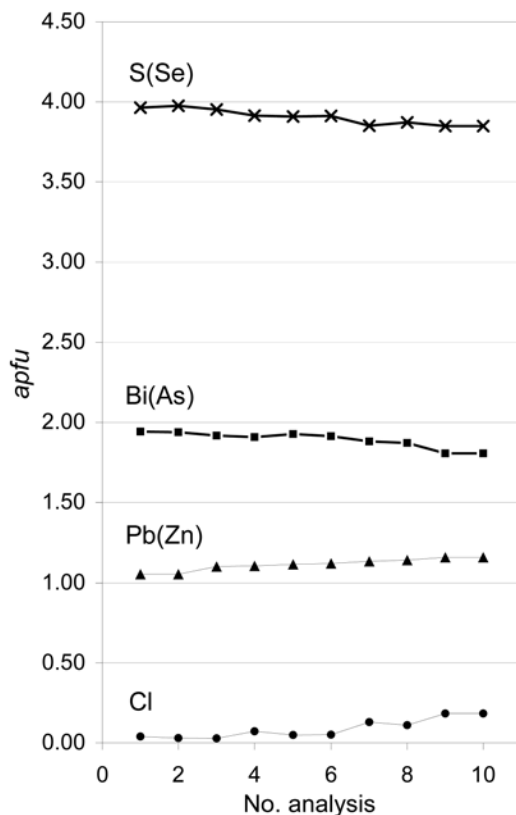liminary measurements were performed on a third needle-like crystal of Cl-bearing galenobismutite (sample FF–1991c). The crystals FF–1991a and FF–1991c were chemically analyzed (Table 2). The crystals are homogeneous, with average composition Pb$_{1.14}$Bi$_{1.85}$(S$_{3.75}$Se$_{0.09}$Cl$_{0.17}$)$_{\Sigma4.01}$ and Pb$_{1.17}$Bi$_{1.80}$(S$_{3.70}$Se$_{0.09}$Cl$_{0.22}$)$_{\Sigma4.01}$, respectively. No satisfactory microprobe data could be obtained on sample FF–1991b because of the small diameter of the crystal (~10 μm).

The crystal FF–1991a was analyzed with a Bruker AXS four-circle diffractometer equipped with CCD 1000 area detector (6.25 cm × 6.25 cm active detection-area, 512 × 512 pixels) using graphite-monochromatized Mo$K\alpha$ radiation. The sample-to-detector distance was fixed at 4 cm. A total of 2240 frames was collected with an exposure time of 20 seconds per frames (0.3° rotation width). The SMART (Bruker AXS 1998) system of programs was used for unit-cell determination and data collection, SAINT PLUS (Bruker AXS 1997a) for the calculation of integrated intensities, and XPREP (Bruker AXS 1997b) for face-indexed absorption correction.
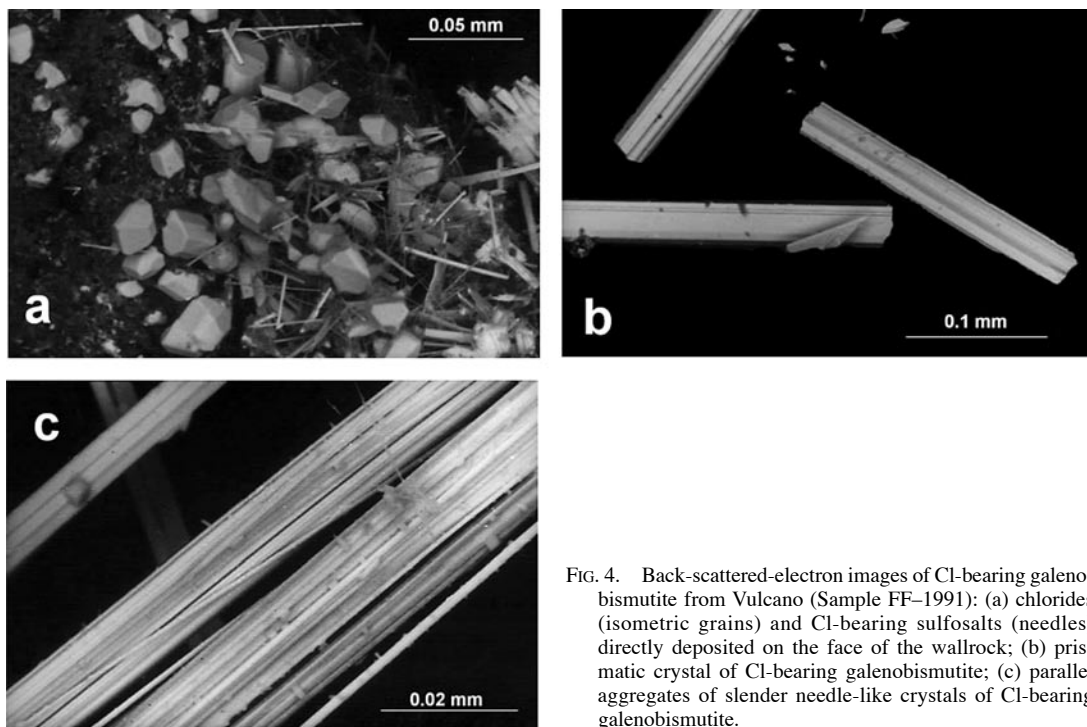
FIG. 4. Back-scattered-electron images of Cl-bearing galeno-bismutite from Vulcano (Sample FF–1991): (a) chlorides (isometric grains) and Cl-bearing sulfosalts (needles) directly deposited on the face of the wallrock; (b) prismatic crystal of Cl-bearing galenobismutite; (c) parallel aggregates of slender needle-like crystals of Cl-bearing galenobismutite.

The crystal FF–1991b was tested on a conventional diffractometer, but owing to its small size, not enough intensity for a structural investigation could be obtained. The same crystal was therefore measured on the beamline 5.2 R (X-ray diffraction) at the Elettra synchrotron facility (Basovizza – Trieste, Italy). The wavelength of the radiation was set at 1.0 Å, and the crystal was placed at a distance of 5 cm from the 165 mm MarCCD detector. Data reduction including intensity integration, background, and Lorentz-polarization corrections, was carried out using the HKL package of programs (XDISP, DENZO and SCALEPACK, Otwinowsky & Minor 1997).

The structure refinements were performed in space group *Pnam*, starting from the atom coordinates of natural Cl-free galenobismutite (Iitaka & Nowacki 1962), using the full-matrix least-squares program SHELXL–97 (Sheldrick 1997). Unit-cell parameters are listed in Table 3 and compared with those reported for a sample of Cl-free galenobismutite from Vulcano (Pinto *et al.* 2006). Unit-cell parameters obtained on the crystal FF–1991c are reported in Table 3 as well. No further structural data are available for this crystal.

Owing to the negligible difference in the scattering powers of Pb and Bi, the distribution of these elements over the metal positions in the structure was investigated by means of an analysis of the coordination polyhedra, and no refinement of occupancies was performed. Similarly, because of the similar numbers of electrons of sulfur and chlorine, the potential ordering of chlorine was investigated only by the analysis of the coordination characteristics of anion positions.

The occupancies of the S sites were unconstrained during the first refinements. This allowed us to identify the positions showing higher density of electrons, which, subsequently, were refined as mixed (S,Se) sites in order to investigate the distribution of selenium in the structure (Table 4). In the final refinements, anisotropic displacement parameters were used for all the atoms.

The structure refinement of sample FF–1991a converged to a final value of $R = 3.10\%$ for 840 reflections $[F_o > 4\sigma(F_o)]$ and $R = 5.23\%$ for all the 1202 unique reflections; the refinement of sample FF–1991b converged to $R = 1.49\%$ for 376 reflections $[F_o > 4\sigma(F_o)]$, $R = 1.50\%$ for all the 380 unique reflections.

Fractional coordinates and displacement parameters of atoms are listed in Table 4; the details of data collections and refinement procedures are reported in Table 5; selected *Me*–S bond distances, compared with bond lengths of Cl-free galenobismutite from Vulcano (Pinto *et al.* 2006), are reported in Table 6. Observed and calculated structure-factors for samples FF–1991a and FF–1991b are listed in Table 7 and Table 8, respectively; these tables are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0E8, Canada.

TABLE 2. ELECTRON-MICROPROBE DATA AND CHEMICAL FORMULAE
OF Cl-BEARING GALENOBISMUTITE FROM SAMPLES 1991

No.	Sample*	Pb	Zn	Bi	As	Cu	Ag	S	Cl	Se	Total	Nc	Bal. val.	Pb(Zn) Bi(As)
1	FS-1991	30.22	0.00	52.57	0.00	0.00	0.00	16.04	0.60	0.86	100.28	2.16	0.7	0.58
2	FS-1991	30.18	0.00	52.86	0.12	0.00	0.00	15.95	0.46	0.89	100.47	2.14	2.4	0.57
3	FS-1991	29.02	0.11	53.18	0.00	0.00	0.00	16.60	0.39	0.90	100.20	2.11	-2.1	0.56
4	FS-1991	28.41	0.00	55.34	0.00	0.00	0.00	16.59	0.12	0.84	101.30	2.04	0.9	0.52
5	FS-1991	28.66	0.22	53.39	0.00	0.00	0.00	16.39	0.24	0.93	99.83	2.11	-0.3	0.55
6	FF-1991	32.49	0.00	48.89	0.00	0.00	0.00	15.77	1.06	0.96	99.17	2.34	-2.2	0.67
7	FF-1991	32.81	0.00	48.41	0.00	0.00	0.00	15.73	1.11	0.90	98.95	2.37	-2.3	0.68
8	FF-1991	28.64	0.00	52.16	0.00	0.00	0.00	15.94	0.81	0.83	98.37	2.11	-1.3	0.55
9	FF-1991	28.15	0.12	52.81	0.00	0.00	0.00	16.29	0.30	0.91	98.57	2.09	-1.3	0.54
10	FF-1991	31.83	0.12	48.86	0.17	0.07	0.00	15.84	1.08	0.87	98.84	2.34	-2.0	0.66
11	FF-1991	31.47	0.00	50.77	0.00	0.00	0.09	15.81	0.80	0.97	99.91	2.27	0.0	0.63
12	FF-1991	31.50	0.00	51.04	0.00	0.00	0.11	15.97	0.83	0.99	100.43	2.27	-0.7	0.62
13	FF-1991	30.94	0.00	51.68	0.00	0.00	0.00	16.12	0.81	0.87	100.42	2.21	-1.0	0.60
14	FF-1991	30.86	0.00	51.19	0.00	0.00	0.08	15.86	0.83	0.95	99.77	2.23	-0.3	0.61
15	FF-1991	32.77	0.07	49.46	0.18	0.10	0.00	15.92	1.02	0.98	100.51	2.37	-0.9	0.67
16	FF-1991	31.27	0.00	49.95	0.00	0.00	0.00	15.93	0.85	0.88	98.87	2.26	-2.0	0.63
17	FF-1991	31.53	0.00	50.59	0.16	0.00	0.00	15.85	0.84	0.91	99.88	2.25	0.2	0.62
18	FF-1991	32.10	0.00	47.36	0.20	0.00	0.00	14.72	1.45	0.87	96.68	2.35	1.7	0.68
19	FF-1991	33.32	0.00	48.08	0.23	0.00	0.00	15.64	1.37	0.87	99.51	2.38	-1.4	0.69
20	FF-1991	34.94	0.00	48.13	0.21	0.00	0.00	15.93	1.35	0.72	101.26	2.45	-1.3	0.72
21	FF-1991	33.89	0.00	48.38	0.19	0.00	0.00	15.67	1.16	0.91	100.19	2.40	-0.4	0.70
22	FF-1991	31.45	0.00	50.64	0.18	0.00	0.00	16.22	0.78	1.03	100.28	2.24	-2.1	0.62
23	FF-1991	31.64	0.00	50.94	0.00	0.00	0.23	16.16	0.79	0.99	100.74	2.30	-1.6	0.63
24	FF-1991	32.09	0.00	49.35	0.16	0.00	0.00	15.96	0.94	0.93	99.44	2.30	-2.0	0.65
25	FF-1991	31.36	0.00	49.66	0.00	0.00	0.00	15.97	0.81	0.85	98.65	2.27	-2.4	0.64
26	FF-1991	32.29	0.00	51.03	0.00	0.00	0.00	16.34	0.92	0.58	101.25	2.30	-1.4	0.64
27	FF-1991	31.67	0.00	50.26	0.00	0.00	0.00	16.15	0.95	0.57	99.60	2.27	-2.0	0.64
28	FF-1991	32.92	0.00	48.59	0.18	0.00	0.07	15.99	1.26	0.40	99.40	2.37	-1.9	0.68
29		27.11	0.00	55.55	0.00	0.00	0.03	16.25	0.00	1.12	100.06	1.99	1.7	0.49
30		27.50	–	55.47	–	–	–	17.02	–	–	100.00	2.00	0.0	0.50

Empirical formulae based on 7 atoms

1 $Pb_{1.10}Bi_{1.90}(S_{3.78}Cl_{0.13}Se_{0.08})_{\Sigma 3.99}$

2 $Pb_{1.11}(Bi_{1.92}As_{0.01})_{\Sigma 1.93}Bi_{1.93}(S_{3.78}Cl_{0.10}Se_{0.09})_{\Sigma 3.97}$

3 $(Pb_{1.05}Zn_{0.01})_{\Sigma 1.06}Bi_{1.90}(S_{3.87}Cl_{0.08}Se_{0.09})_{\Sigma 4.04}$

4 $Pb_{1.03}Bi_{1.99}(S_{3.88}Cl_{0.03}Se_{0.08})_{\Sigma 3.99}$

5 $(Pb_{1.04}Zn_{0.02})_{\Sigma 1.06}Bi_{1.93}(S_{3.86}Cl_{0.05}Se_{0.09})_{\Sigma 4.00}$

6 $Pb_{1.19}Bi_{1.77}(S_{3.72}Cl_{0.23}Se_{0.09})_{\Sigma 4.04}$

7 $Pb_{1.20}Bi_{1.76}(S_{3.72}Cl_{0.24}Se_{0.09})_{\Sigma 4.05}$

8 $Pb_{1.05}Bi_{1.90}(S_{3.79}Cl_{0.17}Se_{0.08})_{\Sigma 4.04}$

9 $(Pb_{1.04}Zn_{0.01})_{\Sigma 1.05}Bi_{1.93}(S_{3.87}Cl_{0.06}Se_{0.09})_{\Sigma 4.02}$

10 $Pb_{1.16}Zn_{0.01}Cu_{0.01})_{\Sigma 1.18}(Bi_{1.76}As_{0.02})_{\Sigma 1.78}(S_{3.73}Cl_{0.23}Se_{0.08})_{\Sigma 4.04}$

11 $(Pb_{1.15}Ag_{0.01})_{\Sigma 1.16}Bi_{1.84}(S_{3.74}Cl_{0.17}Se_{0.09})_{\Sigma 4.00}$

12 $(Pb_{1.14}Ag_{0.01})_{\Sigma 1.15}Bi_{1.84}(S_{3.74}Cl_{0.18}Se_{0.09})_{\Sigma 4.01}$

13 $Pb_{1.12}Bi_{1.85}(S_{3.77}Cl_{0.17}Se_{0.08})_{\Sigma 4.02}$

14 $(Pb_{1.13}Ag_{0.01})_{\Sigma 1.14}Bi_{1.85}(S_{3.74}Cl_{0.18}Se_{0.09})_{\Sigma 4.01}$

15 $(Pb_{1.18}Zn_{0.01}Cu_{0.01})_{\Sigma 1.20}(Bi_{1.77}As_{0.02})_{\Sigma 1.79}(S_{3.73}Cl_{0.21}Se_{0.09})_{\Sigma 4.01}$

16 $Pb_{1.15}Bi_{1.82}(S_{3.77}Cl_{0.18}Se_{0.09})_{\Sigma 4.04}$

17 $Pb_{1.15}(Bi_{1.83}As_{0.02})_{\Sigma 1.85}(S_{3.74}Cl_{0.18}Se_{0.09})_{\Sigma 4.01}$

18 $Pb_{1.21}(Bi_{1.77}As_{0.02})_{\Sigma 1.79}(S_{3.59}Cl_{0.32}Se_{0.09})_{\Sigma 4.00}$

19 $Pb_{1.21}(Bi_{1.73}As_{0.02})_{\Sigma 1.75}(S_{3.67}Cl_{0.29}Se_{0.08})_{\Sigma 4.04}$

20 $Pb_{1.25}(Bi_{1.71}As_{0.02})_{\Sigma 1.73}(S_{3.68}Cl_{0.28}Se_{0.07})_{\Sigma 4.03}$

21 $Pb_{1.23}(Bi_{1.74}As_{0.02})_{\Sigma 1.76}(S_{3.68}Cl_{0.25}Se_{0.09})_{\Sigma 4.02}$

22 $Pb_{1.13}(Bi_{1.81}As_{0.02})_{\Sigma 1.83}(S_{3.78}Cl_{0.16}Se_{0.10})_{\Sigma 4.04}$

23 $(Pb_{1.14}Ag_{0.02})_{\Sigma 1.16}Bi_{1.82}(S_{3.76}Cl_{0.17}Se_{0.09})_{\Sigma 4.02}$

24 $Pb_{1.17}(Bi_{1.78}As_{0.02})_{\Sigma 1.80}(S_{3.75}Cl_{0.20}Se_{0.09})_{\Sigma 4.04}$

25 $Pb_{1.15}Bi_{1.81}(S_{3.79}Cl_{0.17}Se_{0.08})_{\Sigma 4.04}$

26 $(Pb_{1.14}Ag_{0.01})_{\Sigma 1.17}Bi_{1.81}(S_{3.78}Cl_{0.19}Se_{0.05})_{\Sigma 4.02}$

27 $Pb_{1.15}Bi_{1.81}(S_{3.79}Cl_{0.20}Se_{0.05})_{\Sigma 4.04}$

28 $Pb_{1.19}(Bi_{1.74}As_{0.02})_{\Sigma 1.76}(S_{3.74}Cl_{0.27}Se_{0.04})_{\Sigma 4.05}$

29 $Pb_{1.00}Bi_{2.03}(S_{3.87}Se_{0.11})_{\Sigma 3.98}$
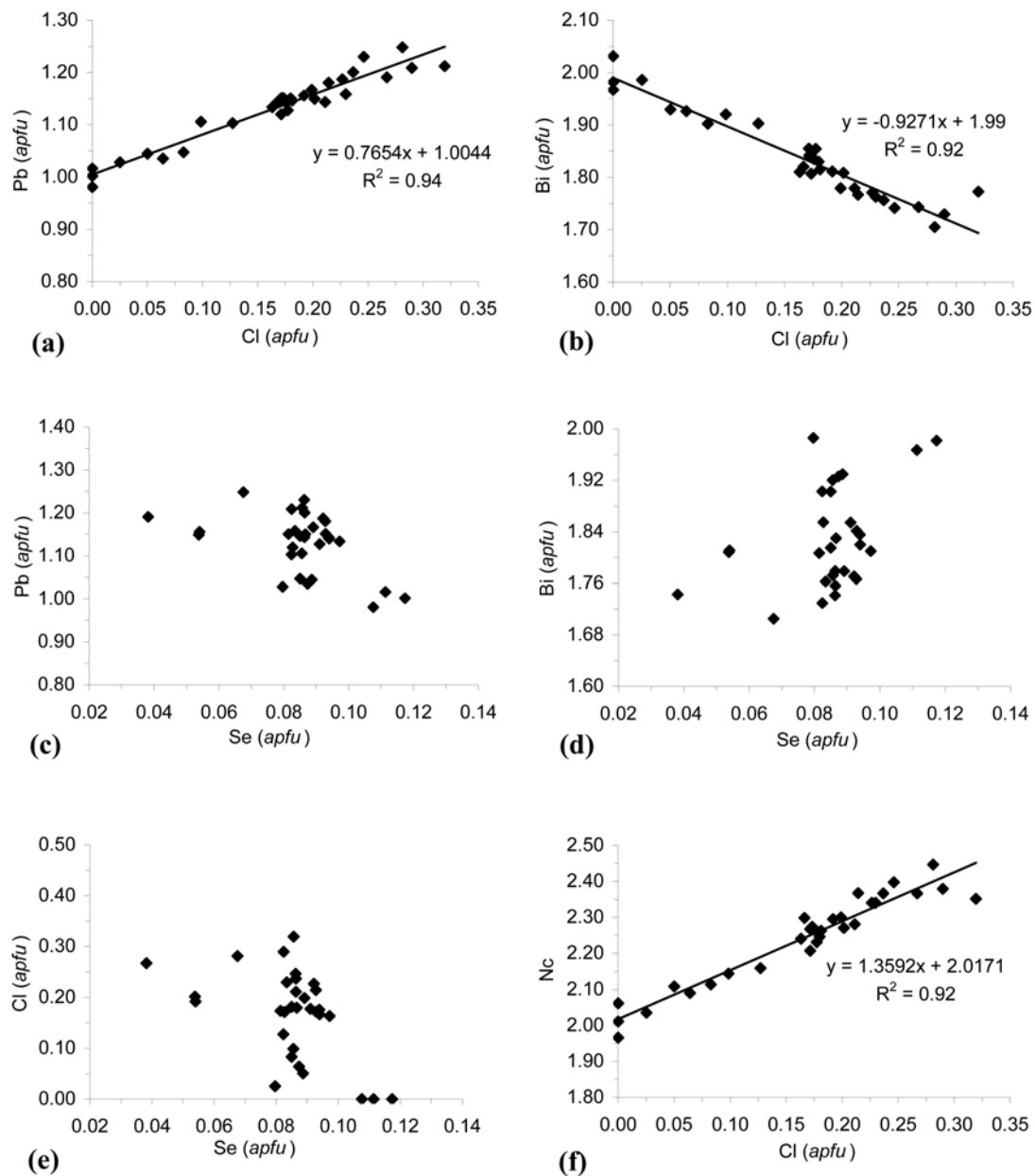
30 $PbBi_2S_4$

Fig. 5.   Samples FF and FS–1991: relationship between Cl and other elements: (a) Pb *versus* Cl, (b) Bi *versus* Cl, (c) Pb *versus* Se, (d) Bi *versus* Se, (e) Cl *versus* Se, (f) N_c *versus* Cl.

TABLE 3. UNIT-CELL PARAMETERS OF SAMPLES OF Cl-BEARING AND Cl-FREE GALENOBISMUTITE

Sample	Composition	Space group	a (Å)	b (Å)	c (Å)	V (Å³)	References
FS-1991	$Pb_{1.00}Bi_{2.03}(S_{3.87}Se_{0.11})_{\Sigma3.98}$	$Pnam$	11.814(2)	14.593(2)	4.0814(6)	703.7(2)	Pinto *et al.* (2006)
FF-1991a	$Pb_{1.14}Bi_{1.85}(S_{3.75}Se_{0.09}Cl_{0.17})_{\Sigma4.01}$	$Pnam$	11.832(1)	14.640(2)	4.0817(4)	707.0(1)	This study
FF-1991b	$Pb_{1.15}Bi_{1.82}(S_{3.60}Se_{0.20}Cl_{0.20})_{\Sigma4.00}$	$Pnam$	11.846(4)	14.667(5)	4.085(1)	709.7(4)	This study
FF-1991c	$Pb_{1.17}Bi_{1.80}(S_{3.70}Se_{0.09}Cl_{0.22})_{\Sigma4.01}$	$Pnam$	11.856(6)	14.687(9)	4.092(3)	712.5(8)	This study

FF-1991a: Composition based on the average result of analyses 11–14 in Table 1.
FF-1991b: Composition derived from the unit-cell parameters (see text).
FF-1991c: Unit-cell values obtained by preliminary single-crystal X-ray measurements. Composition based on the average of analyses 15–18 in Table 1.

CRYSTAL STRUCTURE

General features

The structural arrangement in Cl-bearing galenobismutite from Vulcano is substantially the same as that of galenobismutite with close-to-ideal composition (Iitaka & Nowacki 1962, Pinto *et al.* 2006). The discrepancy in atom coordinates affects the third decimal place (Table 4).

A comparison between the sets of the unit-cell parameters obtained in this study and those reported in the literature for Cl-free galenobismutite (Pinto *et al.* 2006) shows that the cell volume increases in samples of Cl-bearing galenobismutite. This is mainly connected with the variation of the unit-cell parameters a and b, which increase as well; no significant elongation of the parameter c with composition is observed. The variations are related to the increase of the Pb:Bi ratio in the Cl-bearing galenobismutite, which is driven by the incorporation of chlorine according to mechanism of substitution $Pb^{2+} + Cl^- \rightleftharpoons Bi^{3+} + S^{2-}$. Taking into account the positive linear correlation between the a and b unit-cell parameters (Fig. 6), as well as the previously discussed substitution $Pb^{2+} + Cl^- \rightleftharpoons Bi^{3+} + S^{2-}$, the variation of the a and b parameters with composition is expected to be linear. In Figure 7, the a and b parameters of Cl-bearing galenobismutite and Cl-free galenobismutite from Vulcano are plotted against the concentrations of Pb, Bi and Cl. The correlations observed do not deviate much from the expected linear relation. Unfortunately, three points are too few to permit a precise estimate of the trend.

The potential influence of selenium on the unit-cell size has been disregarded owing to the predominant effect of Pb on the increase of cell parameters, as well as to the very low and comparable concentrations of Se in the samples investigated.

Considering the relationship discussed between composition and unit-cell parameters, an attempt to calculate the unknown chemical composition of the sample FF–1991b was made. The a and b cell parameters refined for this sample (Table 3) were inserted in the equations obtained from the relations in Figure 7. The resulting derived composition is $Pb_{1.15}Bi_{1.82}(S_{3.60}Se_{0.20}Cl_{0.20})_{\Sigma4}$, where Se was obtained from the refinement.

Cation distribution

The crystal structure of galenobismutite consists of three independent cation positions: $M1_{gb}$ (distorted octahedron), $M2_{gb}$ ("lying down" monocapped trigonal prism) and $M3_{gb}$ (standing bicapped trigonal prism). Pinto *et al.* (2006) showed that the $M1_{gb}$ site of galenobismutite is exclusively a Bi position, whereas some evidence of Pb–Bi mixed occupancy has been observed in both the $M2_{gb}$ (Bi-dominated) and $M3_{gb}$ (Pb-dominated) positions. However, definite proof of this chemical disorder could not be provided.
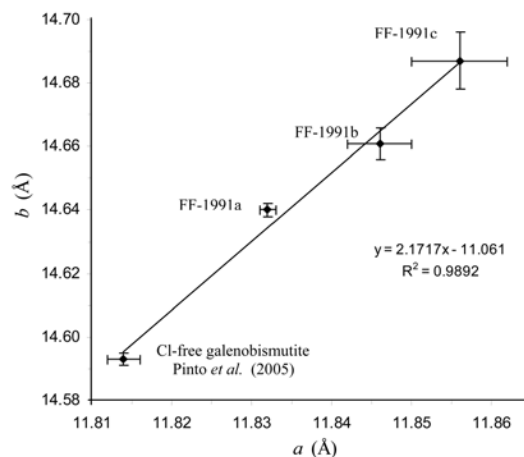

FIG. 6. Linear correlation between a and b unit-cell parameters for samples of galenobismutite.

TABLE 4. ATOM COORDINATES AND ANISOTROPIC DISPLACEMENT PARAMETERS
FOR Cl-BEARING GALENOBISMUTITE FROM VULCANO

	x/a	y/b	z/c	sof	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
				FF-1991a					
$M1_{gb}$	0.06735(5)	0.38982(3)	¼	1*	0.0207(3)	0.0177(3)	0.0220(2)	0.0018(2)	0.0201(1)
$M2_{gb}$	0.10188(5)	0.90348(4)	¼	1*	0.0308(3)	0.0148(3)	0.0349(3)	-0.0020(2)	0.0268(2)
$M3_{gb}$	0.24859(6)	0.65368(4)	¼	1*	0.0349(4)	0.0233(3)	0.0322(3)	0.0101(2)	0.0301(2)
S1	0.33714(3)	0.01493(2)	¼	0.937(5)**	0.024(2)	0.019(2)	0.023(2)	0.003(1)	0.022(1)
Se1	0.33714(3)	0.01493(2)	¼	0.063(5)	0.024(2)	0.019(2)	0.023(2)	0.003(1)	0.022(1)
S2	0.2592(3)	0.29667(2)	¼	1**	0.018(2)	0.012(1)	0.018(1)	0.001(2)	0.0157(6)
S3	0.0564(3)	0.0931(2)	¼	0.987(5)**	0.020(2)	0.017(2)	0.019(2)	0.001(1)	0.019(1)
Se3	0.0564(3)	0.0931(2)	¼	0.013(5)	0.020(2)	0.017(2)	0.019(2)	0.001(1)	0.019(1)
S4	0.0177(3)	0.7120(2)	¼	0.982(4)**	0.018(2)	0.014(2)	0.020(2)	-0.004(1)	0.017(1)
Se4	0.0177(3)	0.7120(2)	¼	0.018(4)	0.018(2)	0.014(2)	0.020(2)	-0.004(1)	0.017(1)
				FF-1991b					
$M1_{gb}$	0.06725(3)	0.38979(3)	¼	1*	0.0284(4)	0.0263(4)	0.0271(4)	0.0022(2)	0.0273(3)
$M2_{gb}$	0.10207(4)	0.90320(3)	¼	1*	0.0410(4)	0.0400(4)	0.0252(4)	-0.0023(2)	0.0354(3)
$M3_{gb}$	0.24865(4)	0.65379(3)	¼	1*	0.0446(4)	0.0374(4)	0.0330(4)	0.0102(2)	0.0383(3)
S1	0.3375(2)	0.0150(1)	¼	0.905(5)**	0.031(2)	0.027(2)	0.025(2)	0.001(1)	0.028(1)
Se1	0.3375(2)	0.0150(1)	¼	0.095(5)	0.031(2)	0.027(2)	0.025(2)	0.001(1)	0.028(1)
S2	0.2592(2)	0.2966(2)	¼	0.957(4)**	0.020(2)	0.021(2)	0.018(2)	-0.0007(9)	0.020(1)
Se2	0.2592(2)	0.2966(2)	¼	0.043(4)	0.020(2)	0.021(2)	0.018(2)	-0.0007(9)	0.020(1)
S3	0.0569(2)	0.0929(2)	¼	0.941(4)**	0.024(2)	0.022(2)	0.029(2)	0.001(1)	0.025(1)
Se3	0.0569(2)	0.0929(2)	¼	0.059(4)	0.024(2)	0.022(2)	0.029(2)	0.001(1)	0.025(1)
S4	0.0181(2)	0.7120(2)	¼	0.936(4)**	0.027(2)	0.021(2)	0.022(2)	-0.002(1)	0.023(1)
Se4	0.0181(2)	0.7120(2)	¼	0.064(4)	0.027(2)	0.021(2)	0.022(2)	-0.002(1)	0.023(1)

Note : U_{13} and U_{23} are equal to 0.00.   * A crystal-chemical analysis shows $M1_{gb}$ to be a pure Bi site, and $M2_{gb}$ and $M3_{gb}$ to be mixed Pb + Bi sites, with a strong preference of Bi for $M2_{gb}$ and Pb for $M3_{gb}$. The contents of $M2_{gb}$ + $M3_{gb}$ are estimated as 1.14 Pb + 0.85 Bi and 1.15 Pb + 0.82 Bi in FF–1991a and FF–1991b, respectively. ** A crystal-chemical analysis suggests a statistical distribution of Cl + S at all sites labeled S. The estimated Cl:S ratios are 0.17 : 3.75 and 0.20 : 3.60 for FF–1991a and FF–1991b, respectively. In the structure refinement, the scattering factors for neutral Bi atoms were used for all sites labeled M; the factors for neutral S atoms were used for sites labeled S, and those for neutral Se atoms were used for sites labeled Se. We provide further details in the text.

A comparison of the interatomic distances in the structures of Cl-bearing galenobismutite and Cl-free galenobismutite (Pinto *et al.* 2006) is given in Table 6. The distances $M2_{gb}$–S3, $M2_{gb}$–S1 and $M3_{gb}$–S1, as well as the shortest distance $M3_{gb}$–S4, are significantly longer in the Cl-bearing, Pb-rich samples of galenobismutite than in the Cl-free galenobismutite (Pinto *et al.* 2006). The regular increases of the bond lengths can be explained by the increase of Pb substituting for Bi in both the $M2_{gb}$ and $M3_{gb}$ sites of Cl-bearing, Pb-rich galenobismutite. This is also confirmed by the analysis of coordination parameters reported in Table 9. The volume of the $M2_{gb}$ and $M3_{gb}$ polyhedra increases from Cl-free to the Cl-bearing, Pb-rich galenobismutite, whereas the variation in volume of $M1_{gb}$ is in the range of analytical error (Fig. 8). The volume eccentricities (ECC$_v$) decrease from the Cl-free galenobismutite

to the Cl-bearing, Pb-rich galenobismutite (Table 9), suggesting a decreasing influence of the element with the more active lone-electron pairs (Bi) on the distance from centroid to central atom.

No evidence of incorporation of Pb at the $M1_{gb}$ site is observed, *i.e.*, the variation of coordination parameters of $M1_{gb}$ from Cl-free to Cl-bearing, Pb-rich galenobismutite is very small, and the values of parameters describing the coordination of $M1_{gb}$ in all the structures of galenobismutite agree with full occupancy by Bi (Table 9).

The assumption that Pb can increase in the $M3_{gb}$ site of Cl-bearing, Pb-rich samples of galenobismutite suggests that usually this position is not occupied only by Pb in galenobismutite, but small amounts on Bi are invariably present. As a consequence, the $M2_{gb}$

site ought to have a mixed (Pb,Bi) occupancy even for galenobismutite with ideal composition, and this demonstrates the mixed (Pb,Bi) character of both the $M2_{gb}$ and $M3_{gb}$ sites of galenobismutite.

Se and Cl order

In spite of the very low concentrations of selenium in the samples of Cl-bearing, Pb-rich galenobismutite investigated, the high quality of the collected X-ray data allowed accurate refinements, which suggest a pattern of distribution for Se in both the structures investigated. The results (Table 4) are consistent with the data on Cl-free galenobismutite (Pinto *et al.* 2006): S1 is the position with the highest Se-for-S substitution, whereas S2 accommodates the lowest concentration of Se (down to
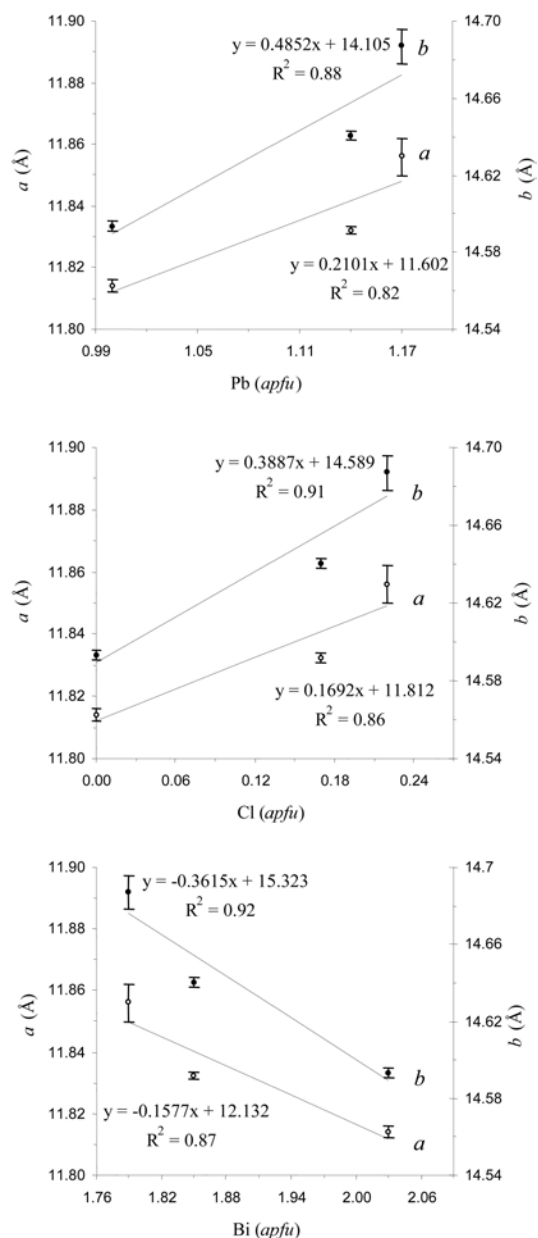
TABLE 5. EXPERIMENTAL DETAILS OF DATA COLLECTIONS FOR SAMPLES OF Cl-BEARING GALENOBISMUTITE

Sample label	Conventional X-ray source FF – 1991a	Synchrotron radiation source FF – 1991b
X-ray power	40 kV, 37 mA	
Wavelength of radiation	0.71073 Å	1 Å
Temperature	294 K	293 K
Detector to sample distance	4 cm	5 cm
Active detection-area	6.25 × 6.25 cm²	16.5 × 16.5 cm²
Crystal size (mm)	0.07 × 0.015 × 0.162	0.009 × 0.010 × 0.12
Number of frames	2240	63
Rotation width per frame	0.3°	3°
Measuring time	20 s	dose = 60
Maximum covered 2θ	61.12 (d = 0.699 Å)	57.68 (d = 1.037 Å)
Unique reflections	1202	380
Reflections $I > 2\sigma_I$	840	376
R_{int} before absorption correction	8.4%	2.88%
R_{int} after absorption correction	6.9%	2.61%
$R_\sigma [F_o > 4\sigma (F_o)]$	5.59%	2.17%
Range of h, k, l	-16 ≤ h ≤ 16	-10 ≤ h ≤ 11
	-20 ≤ k ≤ 20	-14 ≤ k ≤ 14
	-5 ≤ l ≤ 5	-3 ≤ l ≤ 3
$R [F_o > 4\sigma (F_o)]$	3.10%	1.49%
R (all data)	5.23%	1.50%
wR (on F_o^2)	6.02%	3.85%
wR (all data)	6.47%	3.85%
Goof	0.846	0.896
Number of least-squares parameters	46	47

TABLE 6. SELECTED BOND-LENGTHS FOR SAMPLES OF Cl-BEARING AND Cl-FREE GALENOBISMUTITE

		FF-1991a	FF-1991b	FS-1991
$M1_{gb}$	- S2	2.648(3)	2.653(2)	2.646(5)
$M1_{gb}$	- S1	2.966(2) × 2	2.968(2) × 2	2.965(2) × 2
$M1_{gb}$	- S4	2.719(2) × 2	2.723(2) × 2	2.731(3) × 2
$M1_{gb}$	- S1	3.061(3)	3.059(2)	3.075(5)
$M2_{gb}$	- S3	2.770(2) × 2	2.778(2) × 2	2.762(3) × 2
		2.827(3)	2.833(2)	2.793(4)
$M2_{gb}$	- S4	2.976(3)	2.975(2)	2.979(5)
$M2_{gb}$	- S2	3.051(2) × 2	3.052(2) × 2	3.061(3) × 2
$M2_{gb}$	- S1	3.226(3)	3.235(2)	3.193(5)
$M3_{gb}$	- S2	2.925(2) × 2	2.926(2) × 2	2.925(3) × 2
$M3_{gb}$	- S1	3.053(2) × 2	3.058(2) × 2	3.026(3) × 2
$M3_{gb}$	- S3	3.206(3) × 2	3.205(2) × 2	3.217(4) × 2
$M3_{gb}$	- S4	3.743(3)	3.749(2)	3.760(5)
		2.862(4)	2.862(2)	2.834(5)
		This study	This study	Pinto *et al.* (2006)

FIG. 7. Correlation between the *a* and *b* unit-cell parameters and composition in samples of galenobismutite.

0 in sample FF–1991a). In sample FF–1991a, the total amount of selenium resulting from the structural refinement is 0.10(1) atoms per formula unit (*apfu*), a value close to that indicated by the chemical analysis. Electron-microprobe data are not available for the sample FF–1991b. Considering the very low residual *R* factor

FIG. 8. Variation of the volumes (Vp) of polyhedra with the increase of Cl in galenobismutite.

(about 1.5%), the refined values are considered reliable. The concentration of Se in that sample, 0.203(9) *apfu*, was estimated only from the structure refinement.

The investigation of the distribution of chlorine among the anion positions of the crystal structures of sulfosalts is normally performed only with difficulty. This is mainly due to the impossibility to obtain information directly from the refinement. In the case of Cl-bearing galenobismutite, the quite low concentration of chlorine in the samples, as well as the presence of selenium, further complicates the situation.

In Table 10, the coordinations of the S positions obtained for the two structures of Cl-bearing galenobismutite are compared with those calculated for the structure of galenobismutite without Cl (Pinto *et al.* 2006). No evidence for any preference of Cl at some anion positions of Cl-bearing galenobismutite can be derived from this comparison. Bond-valence sums for S1 are smaller than the value expected for a full occupancy by sulfur (Table 10). As the same evidence is observed in the sample of Cl-free galenobismutite, this result cannot be considered indicative of the presence of chlorine in the site S1. Bond-valence calculations, which usually may help to discern chlorine in the sulfur sites, do not provide any information in this case.

In the absence of evidence for an ordered scheme of Cl, a statistical distribution among the anion positions of Cl-bearing galenobismutite is assumed.

DISCUSSION AND CONCLUSIONS

In this study, we describe the first occurrence of Cl-bearing galenobismutite. It is the first example of a significant concentration of chlorine in natural sulfosalts in the system PbS–Bi$_2$S$_3$.

The presence of chlorine in galenobismutite from Vulcano is due to the chemical composition of fumarole fluids discharging from the vents, which are simultaneously enriched in HCl, H$_2$S and SO$_2$ (Cheynet *et al.* 2000). All the ore-forming elements (Pb, Bi, but also S, Se and Cl) are transported in the steam, partly from the magma degassing and partly from the hydrothermally altered rocks of the crater. Under these conditions, the deposition of sulfosalts is mainly controlled by the chemical composition, temperature and flux rates of the fumarole fluids, which have been found to fluctuate (Cheynet *et al.* 2000). The deposition happens because of the rapid drop in temperature taking place at the fumaroles, similar to the quenching procedure in the synthesis of phases in laboratory experiments. The crystals form very quickly, and this led to the formation of a great number of very small, homogeneous individual grains lacking traces of decomposition. The mineralization forms a thin crust with aggregates of several tiny crystals of sulfosalts covering fragments of wallrocks, with no clear order in the sequence of deposition or relevant paragenetic sequence of deposition. This explains the different mineralogical association and paragenesis
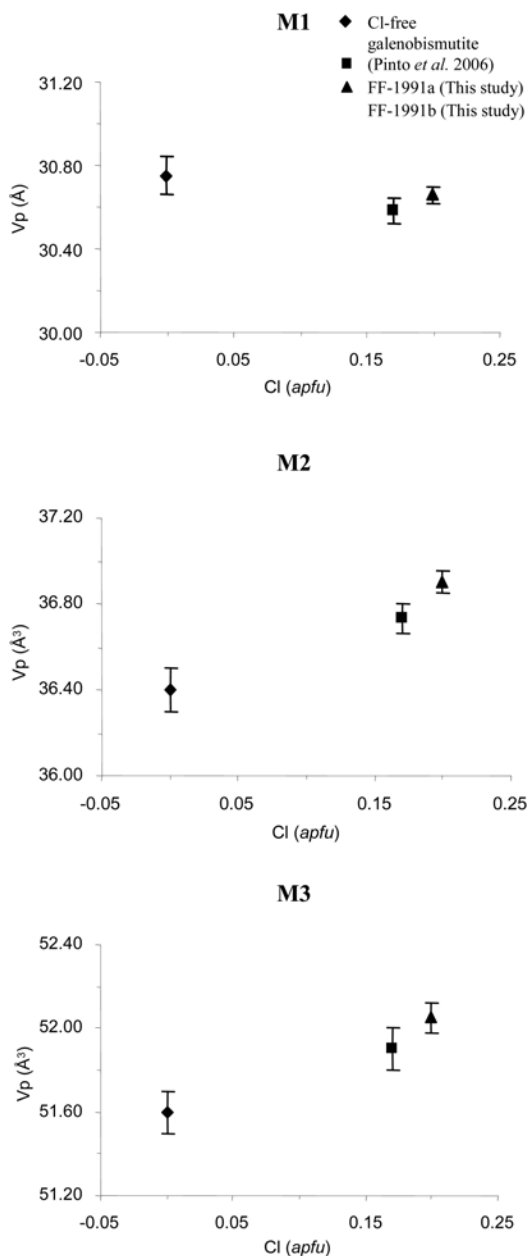
TABLE 9. COORDINATION PARAMETERS* OF CATION POSITIONS
IN SAMPLES OF Cl-BEARING AND Cl-FREE GALENOBISMUTITE

	CN	$<d>$	d min	d max	r_s	Vs	Vp	υ	ECCv	SPHv	Val.
FF-1991a											
$M1_{gb}$	6	2.8 (2)	2.648 (3)	3.061 (3)	2.85(1)	97.223	30.58(6)	0.0117	0.2676	0.9882	2.98
$M2_{gb}$	7	3.0 (2)	2.770 (2)	3.226 (3)	2.96(6)	108.201	36.73(7)	0.1030	0.2394	0.9437	2.59
$M3_{gb}$	8	3.1 (3)	2.861 (4)	3.744 (3)	3.1(2)	125.624	51.9(1)	0.0465	0.3096	0.8261	2.06
FF-1991b											
$M1_{gb}$	6	2.8 (2)	2.650 (2)	3.058 (2)	2.85(1)	97.421	30.66(4)	0.0113	0.2658	0.9898	3.03
$M2_{gb}$	7	3.0 (2)	2.778 (2)	3.236 (2)	2.96(6)	108.720	36.90(5)	0.1030	0.2374	0.9422	2.64
$M3_{gb}$	8	3.1 (3)	2.859 (2)	3.752 (3)	3.1(2)	125.930	52.05(7)	0.0464	0.3105	0.8242	2.09
Pinto _et al._ (2006)											
$M1_{gb}$	6	2.9 (2)	2.646 (5)	3.075 (5)	2.86(1)	97.888	30.75 (9)	0.0132	0.2693	0.9880	2.94
$M2_{gb}$	7	2.9 (2)	2.762 (3)	3.193 (5)	2.95(5)	107.099	36.4(1)	0.1021	0.2453	0.9504	2.68
$M3_{gb}$	8	3.1 (3)	2.834 (3)	3.761 (5)	3.1(2)	124.668	51.6(1)	0.0462	0.3311	0.8284	2.13

$<d>$: average bond distance, r_s: radius of the circumscribed sphere, Vs: volume of the circumscribed sphere, Vp: volume of the coordination polyhedron, υ: volume distortion, ECCv: volume-based eccentricity of the coordination, SPHv: volume-based sphericity of the coordination, Val.: valence.
* The polyhedron parameters for atom coordinations are defined in Balić-Žunić & Makovicky (1996) and in Makovicky & Balić-Žunić (1998). Bond-valence calculations made use of the parameters of Brese & O'Keeffe (1991). All the calculations were done by means of the program IVTON (Balić-Žunić & Vicković 1996).

TABLE 10. COORDINATION PARAMETERS* FOR S POSITIONS
IN SAMPLES OF Cl-BEARING AND Cl-FREE GALENOBISMUTITE

	CN	$<d>$	d min	d max	Vs	Vp	υ	ECCv	SPHv	Val.
FF-1991a										
S1	6	3.05(9)	2.966(2)	3.226(3)	119.704	37.77(4)	0.0086	0.0981	0.9330	1.63
S2	5	2.9(2)	2.648(3)	3.051(2)	104.615	19.00(4)	0.1215	0.2757	1.000	2.01
S3	5	3.0(2)	2.770(2)	3.206(3)	109.277	18.82(3)	0.1671	0.2968	1.000	1.93
S4	5	3.0(4)	2.719(2)	3.743(3)	113.819	21.12(2)	0.1024	0.4248	0.7442	2.03
FF-1991b										
S1	6	3.06(9)	2.968(2)	3.235(2)	120.168	37.913(7)	0.0088	0.1031	0.9333	1.64
S2	5	2.9(2)	2.653(2)	3.052(2)	104.758	19.035(5)	0.1211	0.2726	1.0000	2.04
S3	5	3.0(2)	2.778(2)	3.205(2)	109.699	18.928(5)	0.1655	0.2914	1.0000	1.95
S4	5	3.0(4)	2.723(2)	3.749(2)	114.102	21.169(5)	0.1026	0.4259	0.7435	2.11
Pinto _et al._ (2006)										
S1	6	3.04(9)	2.965(3)	3.193(5)	118.173	37.32(6)	0.0079	0.0710	0.9303	1.67
S2	5	2.9(2)	2.646(5)	3.061(3)	105.011	19.05(6)	0.1227	0.2829	1.000	2.02
S3	5	3.0(1)	2.762(3)	3.217(4)	109.165	18.53(4)	0.1789	0.3164	1.000	2.01
S4	5	3.0(4)	2.731(3)	3.760(5)	114.219	21.19(4)	0.1028	0.4352	0.7505	2.07

Definitions of symbols: see Table 9.

observed in samples of Cl-bearing galenobismutite collected in different years from different fumaroles, and reflects the nonequilibrium conditions of formation, typical of high-temperature fumaroles at Vulcano (Borodaev *et al.* 2001, 2003, Garavelli *et al.* 2005).

The broad compositional field of Cl-bearing galenobismutite [Pb(Zn):Bi(As) atomic ratio ranging from 0.52 to 0.72] is expressed by the general empirical formula $Pb_{1+x}Bi_{2-x}(S_{4-x-y}Cl_xSe_y)$ with $0 < x < 0.3$ and $0 < y < 0.2$, which indicates the extent of departure from the ideal composition $PbBi_2S_4$ toward an excess of Pb and a deficiency of Bi. This compositional field differs substantially from that ascribed to the synthetic analogue of galenobismutite, Phase IV of the system $PbS–Bi_2S_3$, which starts from the ideal composition and extends toward an increase in Bi content (Pb:Bi atomic ratio ranging from 0.50 to 0.39).

If we use the chemical formula of galenobismutite $Pb_{1-x}Bi_{2x/3}S•Bi_2S_3$ proposed by Salanci & Moh (1969), the variation in composition of Phase IV is reflected in x values ranging from 0 to 0.17. However, the Cl-bearing galenobismutite from Vulcano is characterized by negative values of x, which range from –0.3 to –0.25. The discrepancy is evidently due to the different schemes of substitution operating at Vulcano and in chlorine-free synthesis in the laboratory. As indicated by the formula, the dominant mechanism of substitution in Cl-bearing galenobismutite from Vulcano is $Pb^{2+} + Cl^- \rightleftharpoons Bi^{3+} + S^{2-}$, which occurs because of the high partial pressure of chlorine in fumarole fluids discharging from the vents, as opposed to the scheme of substitution acting in synthetic Phase IV, $3Pb \rightarrow 2Bi + \square$ ($\square$: vacancy).

The structure of Cl-bearing galenobismutite refined here differs only in details from that of Cl-free galenobismutite (Iitaka & Nowacki 1962, Pinto *et al.* 2006). A comparison of structural data for Cl-bearing galenobismutite with that for Cl-free galenobismutite suggests that both the $M2_{gb}$ and $M3_{gb}$ sites in the structure of Cl-bearing, Pb-rich galenobismutite incorporate the excess Pb, which is related to the heterovalent substitution $Pb^{2+} + Cl^- \rightleftharpoons Bi^{3+} + S^{2-}$. No Pb-for-Bi substitution is observed at the octahedral position $M1_{gb}$. This finding supports the conclusion that in the structure of galenobismutite, only $M1_{gb}$ is exclusively occupied by Bi, whereas the other two sites are partly mixed sites, but with a strong preference of Bi for $M2_{gb}$ and Pb for $M3_{gb}$. No evidence of a preferential distribution of Cl among anion positions was observed.

Acknowledgements

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