

Argesite, $(\text{NH}_4)_7\text{Bi}_3\text{Cl}_{16}$, a new mineral from La Fossa Crater, Vulcano, Aeolian Islands, Italy: A first example of the $[\text{Bi}_2\text{Cl}_{10}]^{4-}$ anion

FRANCESCO DEMARTIN,* ITALO CAMPOSTRINI, CARLO CASTELLANO, AND
CARLO MARIA GRAMACCIOLI

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, via Venezian 21, I-20133 Milano, Italy

ABSTRACT

The new mineral argesite, ammonium bismuth chloride $(\text{NH}_4)_7\text{Bi}_3\text{Cl}_{16}$, was found in a medium-temperature ($\sim 250^\circ\text{C}$) active fumarole at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. The mineral occurs on a pyroclastic breccia as pale-yellow crystals up to 0.15 mm in length, in association with bismuthinite, adranosite, brontesite, demicheleite-(Br), demicheleite-(Cl), and panichiite. Argesite is trigonal, space group: $R\bar{3}c$ (no. 167) with $Z = 18$; the unit-cell parameters are (single-crystal data): $a = 13.093(1)$, $c = 102.682(1)$ Å, and $V = 15245(2)$ Å³. The six strongest reflections in the X-ray powder diffraction pattern are: $[d_{\text{obs}}(\text{Å}) (I) (hkl)]$ 3.164 (100) (0 3 18), 3.808 (44) ($\bar{2}$ 2 20), 2.742 (78) ($\bar{2}$ 4 21), 6.14 (16) ($\bar{1}$ 2 6), 1.906 (16) (0 0 $\bar{5}$ 4), 1.686 (13) ($\bar{5}$ 6 34). The mineral is uniaxial (–), with $\omega = 1.731(2)$, $\epsilon = 1.725(2)$ (589 nm). The IR spectrum shows absorptions at 3188(vs), 3060(s), and 1397(vs) cm^{-1} , in agreement with the presence of the ammonium ion. Chemical analyses obtained by EDS electron microprobe gave (average wt%) Bi 42.26, Cl 32.57, Br 13.06, I 0.95, K 2.46, Tl 0.88, NH_4 7.82 (by difference) total 100.00, corresponding to the empirical formula: $[(\text{NH}_4)_{6.29}\text{K}_{0.91}\text{Tl}_{0.06}]_{\Sigma 7.26}\text{Bi}_{2.93}(\text{Cl}_{13.33}\text{Br}_{2.37}\text{I}_{0.11})_{\Sigma 15.81}$. The measured density is 2.88(1) g/cm^3 . The structure was refined, using single-crystal diffraction data, to a final $R = 0.0345$ for 1289 independent observed reflections [$I > 2\sigma(I)$]. It contains $\text{Bi}_2\text{Cl}_{10}^{4-}$ and BiCl_6^{3-} anions where the Bi atoms are octahedrally coordinated, and NH_4^+ cations are partially replaced by K^+ and Tl^+ ions.

Keywords: Argesite, new mineral species, crystal structure, ammonium bismuth chloride, bismuth(III) complexes, sublimates, Vulcano, Italy

INTRODUCTION

The fumarole system at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy, is subject to a wide mineralogical variability depending on the geochemical conditions, which may change considerably even in a very brief span of time. The peculiar chemistry of the fluids discharged from the area, as well as the wide range of fumarole temperatures, favor the deposition of an extensive variety of minerals, whose formation and association are highly influenced by the flow rates of the gases emitted from the vents at the time of deposition (Garavelli et al. 1997; Cheynet et al. 2000).

Notable quantities of ammonium minerals such as salammianic are present in this environment; this mineral was at times so abundant to be commercially exploited, especially in the last centuries (Campostrini et al. 2011, and references therein). Besides this salt, there are several ammonium-bearing sulfates, which were completely absent during the thermal crisis, which occurred in the area in the years 1988–1997. These products, such as adranosite $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$ (Demartin et al. 2010a), mascagnite $(\text{NH}_4)_2\text{SO}_4$, and the very rare pyracmonite $(\text{NH}_4)_3\text{Fe}^{3+}(\text{SO}_4)_3$ (Demartin et al. 2010b), were found only in the last few years. Particularly interesting is also the presence of some ammonium-bearing minerals containing heavy elements in

the form of chloride complexes, such as panichiite $(\text{NH}_4)_2\text{SnCl}_6$ (Demartin et al. 2009a) and brontesite $(\text{NH}_4)_3\text{PbCl}_5$ (Demartin et al. 2009b).

In the course of systematic investigations on minerals at Vulcano, the new mineral argesite $(\text{NH}_4)_7\text{Bi}_3\text{Cl}_{16}$, an ammonium bismuth chloride, has also been discovered in the year 2007; this mineral had previously been mentioned as an unknown species by Campostrini et al. (2011) as “UKI-fo-05-(Cl: NH_4 Bi).” Here we report the description of the new species and its structure determination. The mineral was approved by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2011-072). The name is after Uranus’s son Arges, one of the three Cyclops who were helpers of Hephaistos, the ancient Greek god of fire (Vulcanus for the ancient Romans) whose workshops were alleged to be located at Vulcano island (or Etna). The holotype is deposited (no. 2011-04) in the Reference Collection of the Dipartimento di Chimica Strutturale e Stereochimica Inorganica at the Università degli Studi di Milano.

OCCURRENCE, PHYSICAL PROPERTIES, AND CHEMICAL DATA

Argesite occurs in an active medium-temperature ($\sim 250^\circ\text{C}$) intracrater fumarole [labeled as fumarole FA in Borodaev et al. (2000) and in Pinto et al. (2006)] on a pyroclastic breccia, in close association with bismuthinite, adranosite, brontesite, demicheleite-(Br) (Demartin et al. 2008), demicheleite-(Cl)

* E-mail: francesco.demartin@unimi.it

(Demartin et al. 2009c), and panichiite. The mineral is not hygroscopic and is stable in open air. The crystals range up to 0.15 mm in size; their habit is almost tabular [according to the {001} pinacoid] and in most cases is very complex, due to the presence of various rhombohedra and bipyramids (Fig. 1). The *c*:*a* ratio calculated from the unit-cell parameters is 7.843. The color is pale yellow, the luster is vitreous, and the streak is white. A cleavage was not observed, the fracture is conchoidal. No fluorescence was observed under either short-wave or long-wave ultraviolet radiation.

The density, measured by flotation in a diiodomethane-toluene mixture, is 2.88(1) g/cm³; that calculated from the empirical formula and the unit-cell data reported in Table 3 is 2.843 g/cm³.

The mineral is uniaxial (–) with $\omega = 1.731(2)$, $\epsilon = 1.725(2)$ (589 nm) determined by immersion in bromonaphthalene-diiodomethane mixture. The average index of refraction, calculated according to the Gladstone–Dale relationship is 1.729, providing an excellent agreement (Mandarino 1981).

The infrared spectrum, recorded on a Jasco IRT-3000 spectrometer, shows absorption bands at 3188(vs), 3060(s), 2803(ms), and 1397(vs) cm⁻¹, in agreement with the presence of the ammonium ion (Farmer 1974) (Fig. 2). The presence of a shoulder at about 3500 cm⁻¹ is due to atmospheric water absorbed by the powdered crystals before the IR spectrum recording.

Due to the very small size of the crystal used for the structure determination, the chemical analyses were carried out on a different crystal picked from the same specimen. However, a screening carried out on additional specimens has shown a notable variation in the Br content, in some cases even leading to prevalence of Br over Cl [see Campostrini et al. 2011, UKI-fo01-(Br: BiNH₄) p. 257]; for this reason the composition derived from chemical analysis may not be fully consistent with that obtained from structure refinement. To avoid sample decomposition under an intense beam of electrons, quantitative chemical analyses (6) were carried out using a JEOL JSM-5500 LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe (20 kV, 10⁻¹¹ A, 2 μm beam diameter). Element concentrations were measured using the *Kα* lines for Cl and K, the *Lα* lines for Br, and the *Mα* lines for Bi, I, and Tl.

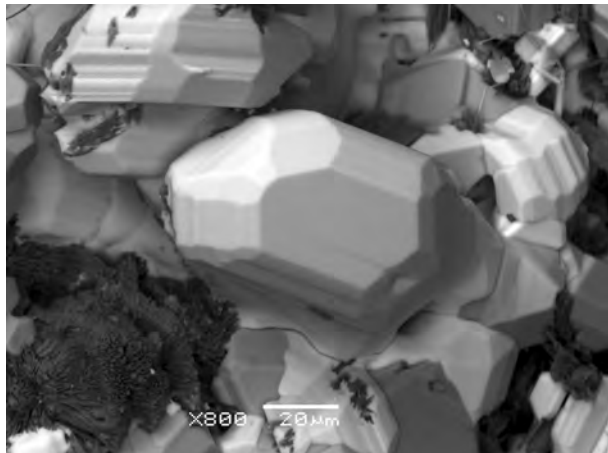


FIGURE 1. SEM-BSE image of crystals of argesite.

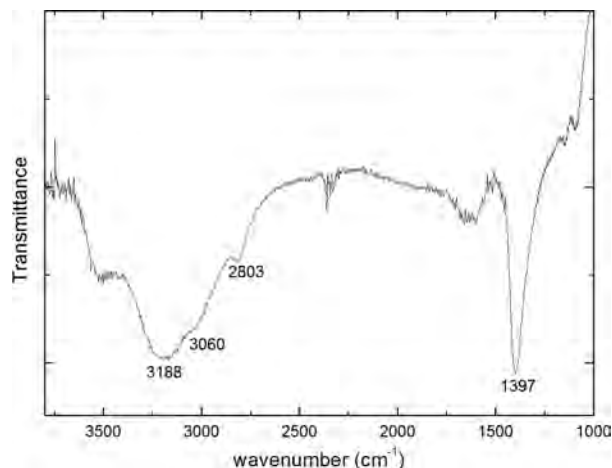


FIGURE 2. Infrared spectrum of argesite.

The ammonium content was deduced by difference in the total weight. The mean analytical results are reported in Table 1. The empirical formula obtained in this way (based on 26 apfu) is: [(NH₄)_{6.29}K_{0.91}Tl_{0.06}]_{Σ7.26}Bi_{2.93}(Cl_{13.33}Br_{2.37}I_{0.11})_{Σ15.81}. The simplified formula is (NH₄)₇Bi₃Cl₁₆, which requires: NH₄ 9.56, Bi 47.48, Cl 42.96, total 100.00 wt%.

X-RAY DATA

X-ray powder diffraction data were collected using a Rigaku D-MAXII diffractometer with CuK α radiation (Table 2). A least-squares fit of these data has provided the unit-cell parameters: $a = 13.055(1)$, $c = 102.72(11)$ Å, and $V = 15163(2)$ Å³.

The unit-cell parameters obtained from 3613 single-crystal reflections with $I > 5\sigma(I)$ are reported in Table 3, together with other details concerning the data collection and refinement. A total of 19 521 diffraction maxima corresponding to a complete scan of the reciprocal lattice up to $2\theta = 62.50^\circ$ were collected, using a Bruker Apex II diffractometer equipped with a 2 K CCD detector and MoK α radiation ($\lambda = 0.71073$ Å). A one-minute frame-time and 0.5° frame width were used. The intensity data were reduced using the program SAINT (Bruker 2001), and corrected for Lorentz, polarization, and background. An absorption correction ($\mu = 18.524$ mm⁻¹, minimum transmission factor 0.638) was applied using the SADABS program (Sheldrick 2000). After averaging the symmetry-related (space group 167, *R3c*) reflections ($R_{int} = 0.075$), 1851 independent data were obtained. The structure was solved by direct methods and refined using the SHELXL97 program (Sheldrick 2008) implemented in the WinGX suite of software (Farrugia 1999). In agreement with the indications of chemical analysis, a partial replacement of some nitrogen atoms (N2 to N4) and of some chlorine atoms (Cl4 and Cl6) by heavier elements was indicated during the refinement by their physically implausible atomic displacement parameters. Therefore, the corresponding occupancies were refined (Table 4), considering the possible partial replacement of nitrogen by potassium and of chlorine by bromine and neglecting the presence of minor contents of iodine

TABLE 1. Analytical data for argesite

Constituent	wt%*	Range	S.D.	Probe standard	wt%† crystallographic
Bi	42.26	41.24–43.34	0.5	Bi ₂ Se ₃	44.67
K	2.46	2.32–2.65	0.1	K-feldspar	3.34
Br	13.06	12.46–14.49	0.6	TlBr	7.40
Cl	32.57	30.93–33.11	0.5	scapolite	37.13
I	0.95	0.69–1.30	0.2	KI	
Tl	0.88	0.51–1.12	0.1	TlBr	
NH ₄	7.82				7.46
Total	100.00				100.00

* The derived empirical formula (based on 26 apfu) is: [(NH₄)_{6.29}K_{0.91}Tl_{0.06}]_{Σ7.26}Bi_{2.93}(Cl_{13.33}Br_{2.37}I_{0.11})_{Σ15.81}.

† The formula derived from structure refinement is: [(NH₄)_{5.79}K_{1.21}Tl_{0.03}Bi₃(Cl_{14.58}Br_{1.42})_{Σ16.00}].

TABLE 2. X-ray powder-diffraction data for argesite

<i>I</i> _{rel}	<i>d</i> _{obs}	<i>d</i> _{calc} [*]	<i>hkl</i>
11	6.46	6.41	$\bar{1} 2 3$
16	6.14	6.10	$\bar{1} 2 6$
11	5.71	5.71	0 0 $\bar{1} 8$
4	4.31	4.32	$\bar{1} 1 22$
44	3.808	3.801	$\bar{2} 2 20$
3	3.664	3.680	$\bar{3} 3 6$
4	3.600	3.600	0 2 22
3	3.284	3.287	$\bar{1} 2 27$
4	3.263	3.264	$\bar{2} 4 0$
100	3.164	3.145	0 3 18
3	3.136	3.134	$\bar{1} 4 1$
6	3.112	3.112	$\bar{1} 4 4$
3	2.877	2.900	$\bar{1} 3 26$
4	2.854	2.853	0 0 $\bar{3} 6$
3	2.802	2.810	$\bar{1} 2 33$
24	2.742	2.715	$\bar{2} 4 21$
4	2.617	2.614	$\bar{1} 2 36$
10	2.555	2.554	$\bar{3} 5 7$
4	2.492	2.493	$\bar{1} 4 25$
8	2.471	2.477	$\bar{2} 4 27$
3	2.456	2.456	$\bar{3} 4 26$
3	2.348	2.348	$\bar{3} 4 29$
4	2.206	2.203	$\bar{4} 5 21$
7	2.159	2.158	$\bar{3} 6 6$
6	2.089	2.092	$\bar{2} 6 10$
16	1.906	1.902	0 0 $\bar{5} 4$
5	1.886	1.884	0 6 0
4	1.831	1.836	$\bar{3} 6 30$
3	1.824	1.825	$\bar{3} 5 40$
5	1.818	1.820	$\bar{5} 6 25$
13	1.686	1.685	$\bar{5} 6 34$

Note: The experimental error for the *d*-spacings is about ±0.02 Å for low-angle values and ±0.003 Å for high-angle values.

* Calculated from the unit cell *a* = 13.055(1), *c* = 102.72(11) Å obtained from least-squares refinement of the above data using the program UNITCELL (Holland and Redfern 1997).

and thallium, owing to the practical impossibility of accurately determining the population of a site with more than two occupants. The composition deduced from the structure refinement is reported in the last column of Table 1 and is different from that indicated by the chemical analysis, since different crystals were used in these procedures (see above). For instance, the refined atomic Cl/Br ratio, averaged on *all sites*, is 14.7/1.3 = 11.3 instead of 0.92/0.16 = 5.75 (chemical data); similarly, the corresponding NH₄/K ratio is 5.8/1.2 = 4.8 instead of 0.43/0.06 = 7.2. (CIF¹ is available on deposit.)

The hydrogen atoms of the ammonium ion did not show up clearly in a difference-Fourier map and therefore they were not included in the final refinement. The final *R* is 0.0345 for 1289 observed reflections [*I* > 2σ(*I*)]. The final

TABLE 3. Crystal data and structure refinement details for argesite

Empirical formula [*]	[(NH ₄) _{5.79} K _{1.21}] _{27.00} Bi ₃ (Cl _{14.58} Br _{1.42}) _{216.00}
Crystal system	Trigonal
Space group	$R\bar{3}c$ (no. 167)
Unit-cell dimensions	<i>a</i> = 13.093(1) Å <i>c</i> = 102.682(9) Å <i>V</i> = 15245(2) Å ³
<i>Z</i>	18
Density (calculated)	2.763 g/cm ³
Absorption coefficient	18.524 mm ⁻¹
<i>F</i> (000)	11398
Crystal size	0.08 × 0.08 × 0.04 mm
Wavelength	0.71073 Å
θ range for data collection	1.19 to 31.25°
Index ranges	−19 ≤ <i>h</i> ≤ 19, −19 ≤ <i>k</i> ≤ 19, −147 ≤ <i>l</i> ≤ 147
Reflections collected	19521
Independent reflections	1851 [<i>R</i> _{int} = 0.075]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/parameters	1289/110
Goodness-of-fit on <i>F</i> ²	1.070
Final <i>R</i> indices†	<i>R</i> ₁ = 0.0345, <i>R</i> _w = 0.0933 [1289 reflections with <i>I</i> > 2σ(<i>I</i>)]
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0619, <i>R</i> _w = 0.0993

* Obtained from structure refinement.

† The weighting scheme used was $w = 1/[\sigma^2(F_o)^2 + (0.0496P)^2]$ where $P = [\text{Max}(F_o)^2 + 2(F_c)^2]/3$ as defined by SHELX-97 (Sheldrick 2008).

coordinates and displacement parameters of the atoms are reported in Table 4; relevant interatomic distances are listed in Table 5.

RESULTS AND DISCUSSION

A perspective view of the crystal structure of argesite is shown in Figure 3. It contains layers parallel to (001) made by isolated octahedral BiCl₆³⁻ anions (octahedra centered on Bi2 and Bi3 shown in Figs. 4a and 4b, respectively), with bioctahedral Bi₂Cl₁₀⁴⁻ anions (Fig. 4c) sandwiched between these layers. The NH₄⁺ cations occupy the voids between the anions (Fig. 5) and some of them are partially replaced by K⁺ or Tl⁺ ions. Of the two BiCl₆³⁻ anions, one is located on a threefold axis (Bi2) and is heavily distorted forming three longer Bi-Cl distances [2.805(1) Å] and three shorter ones [2.656(1) Å], the average Bi-Cl being 2.731 Å; the other anion (centered on Bi3) is more regular, being located on a 6*b* Wyckoff site ($\bar{3}$ site) with six Bi-Cl distances 2.723 Å long. All these bond lengths are comparable with the overall average Bi-Cl distance (2.717 Å) found in stropesite Tl₃BiCl₆, another bismuth-chloride complex from the same locality (Demartin et al. 2009d), minor differences being most probably due to partial replacement of Cl by Br. Six Bi-Cl distances between 2.464 and 3.235 Å (average 2.867 Å) have been observed in BiCl₃; however the coordination of the bismuth atom is not octahedral and the distortion of the coordination polyhedron clearly shows the effect of the stereochemically active lone pair (Bartl 1982). The Bi₂Cl₁₀⁴⁻ anion, made by two edge-sharing distorted octahedra, is located on a twofold axis normal to [001] and passing through the Cl15 and Cl16 atoms. The longest Bi-Cl distances are those with the bridging Cl15 and Cl16 atoms (average 2.948 Å); the shortest ones are those in position *trans* to Cl16 (average 2.637 Å), in agreement with bond-valence requirements. Of the six independent ammonium ions, three are located on threefold axes (N4, N5, and N6 on site 12*c*) and are surrounded by nine chlorine atoms of the complex anions. This arrangement forms a tricapped-trigonal prismatic cavity, with N-Cl distances ranging from 3.284 to 3.822 Å. Two additional ammonium ions (centered on N1 and N3) are in general position and are surrounded by eight chlorine atoms with N-Cl distances ranging from 2.849 to 3.977 Å. The remaining one (N2) is located on a twofold axis (on site 18*e*) and displays seven distinguishable N-Cl distances ranging from 3.127 to 3.297 Å. Of particular interest is the arrangement of some of these cations with respect to the octahedra centered by Bi2 and Bi3 as shown in Figure 6. The nitrogen atoms N1, N4, and N6, located in the cages between the anions, lie above the six triangular faces of each octahedron. However, in the case of Bi2 an additional very short interaction of 2.849 Å with N3 is present, which is responsible for the heavy distortion of the coordination polyhedron. Therefore this deformation is not due to the presence of a stereochemically active lone pair of Bi but is due instead to steric factors. Such a feature is in agreement with a general behavior of bismuth(III), which forms numerous halo-complexes where the lone pair is only slightly

¹ Deposit item AM-12-052, CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 4. Final atom coordinates and displacement parameters for argesite

Atom	Wyckoff site	Occupancy	x/a	y/b	z/c	U _{eq}
Bi1	36f	1	0.66697(3)	0.66628(4)	0.061525(1)	0.03218(2)
Bi2	12c	1	1/3	2/3	0.001711(1)	0.02618(4)
Bi3	6b	1	1/3	2/3	1/6	0.03851(8)
Cl1	36f	1	0.42424(5)	0.53716(5)	0.061762(6)	0.0338(2)
Cl2	36f	1	0.90924(5)	0.77942(5)	0.061746(6)	0.0333(2)
Cl3	36f	1	0.66682(5)	0.50816(5)	0.044966(7)	0.0392(2)
Cl4/Br4	36f	0.778(2)/0.222(2)	0.66707(6)	0.79390(6)	0.042206(7)	0.0623(2)
Cl5	18e	1	2/3	0.51733(7)	1/12	0.0310(2)
Cl6/Br6	18e	0.686(2)/0.314(2)	2/3	0.81028(6)	1/12	0.0573(2)
Cl7/Br7	36f	0.667(2)/0.333(2)	0.37243(6)	0.51729(5)	0.015372(10)	0.0865(3)
Cl8	36f	1	0.34075(6)	0.83637(6)	-0.015537(8)	0.0458(2)
Cl9	36f	1	0.19199(7)	0.47653(7)	0.18176(1)	0.0843(4)
N1	36f	1	0.3378(4)	0.9918(3)	0.011783(15)	0.0460(4)
N2/K2	18e	0.643(3)/0.357(3)	2/3	1.0491(1)	1/12	0.0426(4)
N3/K3	36f	0.738(2)/0.262(2)	0.33370(11)	0.95776(9)	-0.038254(13)	0.0395(3)
N4/K4	12c	0.508(5)/0.492(5)	1/3	2/3	0.04085(3)	0.0735(7)
N5	12c	1	1/3	2/3	0.08236(6)	0.0252(6)
N6	12c	1	0	0	0.04037(4)	0.0461(11)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Bi1	0.01539(2)	0.04562(3)	0.02683(2)	-0.0010(2)	-0.0005(1)	0.00872(3)
Bi2	0.03031(3)	0.03031(3)	0.01793(8)	0	0	0.01515(2)
Bi3	0.01684(6)	0.01684(6)	0.0818(2)	0	0	0.00842(3)
Cl1	0.0268(2)	0.0458(2)	0.0356(3)	0.0010(2)	0.0014(2)	0.0233(2)
Cl2	0.0270(2)	0.0286(2)	0.0325(3)	-0.0019(2)	0.0014(2)	0.0051(2)
Cl3	0.0154(2)	0.0379(2)	0.0571(3)	-0.0304(2)	0.0004(2)	0.0079(2)
Cl4/Br4	0.0869(3)	0.0590(3)	0.0483(3)	0.0141(3)	0.0003(3)	0.0421(2)
Cl5	0.0219(4)	0.0304(3)	0.0378(4)	-0.0004(2)	-0.0009(3)	0.0111(2)
Cl6/Br6	0.0930(7)	0.0482(3)	0.0456(4)	-0.0015(2)	-0.0031(5)	0.0465(3)
Cl7/Br7	0.0721(3)	0.0598(2)	0.1442(7)	0.0151(4)	0.0129(4)	0.0456(2)
Cl8	0.0466(2)	0.0532(3)	0.0509(4)	-0.0028(3)	-0.0084(3)	0.0351(2)
Cl9	0.0406(3)	0.0367(3)	0.1736(11)	-0.0044(5)	0.0183(5)	0.0177(2)

Note: The anisotropic displacement factor exponent takes the form: $-2\pi^2[U_{11}h^2(a^*)^2 + \dots + 2U_{12}hka^*b^* + \dots]$; $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE 5. Relevant interatomic distances and hydrogen-bond interactions below 4.0 Å in argesite

Bi1--Cl1	2.754(1)	Bi2--Cl7 ×3	2.656(1)
Bi1--Cl2	2.749(1)	Bi2--Cl8 ×3	2.805(1)
Bi1--Cl3	2.678(1)		
Bi1--Cl4	2.593(1)	Bi3--Cl9 ×6	2.723(1)
Bi1--Cl5	2.968(1)		
Bi1--Cl6	2.929(1)		
N1--Cl4	3.531(3)	N3--Cl1	3.412(1)
N1--Cl7	3.550(3)	N3--Cl2	3.414(2)
N1--Cl7	3.214(5)	N3--Cl3	3.391(2)
N1--Cl8	3.477(3)	N3--Cl3	3.393(1)
N1--Cl8	3.668(4)	N3--Cl4	3.282(2)
N1--Cl8	3.977(3)	N3--Cl7	3.378(1)
N1--Cl9	3.626(4)	N3--Cl8	2.849(2)
N1--Cl9	3.387(5)	N3--Cl9	3.433(2)
N2--Cl1 ×2	3.297(1)	N4--Cl1 ×3	3.305(2)
N2--Cl2 ×2	3.295(1)	N4--Cl4 ×3	3.822(1)
N2--Cl5 ×2	3.270(1)	N4--Cl7 ×3	3.455(3)
N2--Cl6	3.127(2)		
N5--Cl1 ×3	3.284(4)	N6--Cl2 ×3	3.338(3)
N5--Cl2 ×3	3.418(4)	N6--Cl4 ×3	3.815(1)
N5--Cl6 ×3	3.393(1)	N6--Cl9 ×3	3.428(3)

if at all stereochemically active (Cotton and Wilkinson 1980).

It is worth mentioning that argesite represents the first known occurrence of the Bi₂Cl₁₀⁴⁻ anion, both in minerals and in synthetic phases. Other discrete bioctahedral Bi₂Cl_n⁽ⁿ⁻⁶⁾⁻ complex anions are known, however they show a different topology from that of Bi₂Cl₁₀⁴⁻. For instance the Bi₂Cl₈²⁻ present in [N(CH₃)₄]₃Bi₂Cl₉ (Ishihara et al. 1993) consists of two face-sharing BiCl₆ octahedra, whereas the Bi₂Cl₁₁³⁻ anion is found in [NH₃(CH₃)₅]₂Bi₂Cl₁₁ (Lefebvre et al. 1991) and consists of two BiCl₆ octahedra sharing one vertex only.

ORIGIN OF THE MINERAL

The La Fossa Crater fumaroles at Vulcano are rich in bismuth minerals, especially sulfides and sulfosalts among which bismuthinite is the most common. Bismuth halides or sulfosalts were observed for the first time within silica tubes inserted in the fumaroles (see, for instance, Garavelli et al. 1997; Cheynet et al.

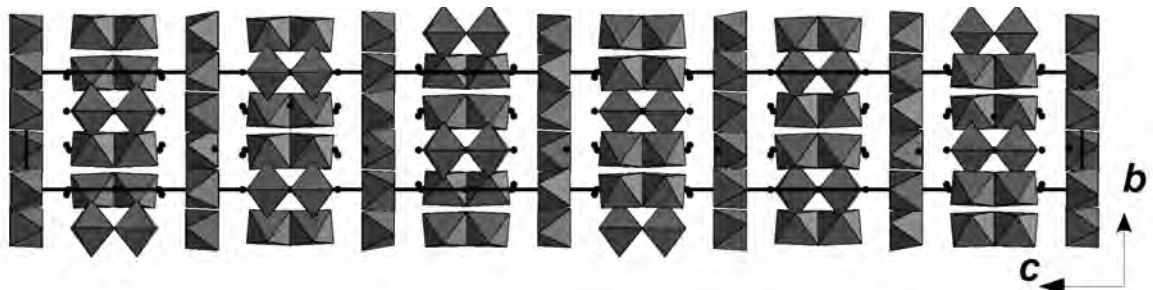


FIGURE 3. Perspective view of the structure of argesite seen along [1 0 0]. Bismuth polyhedra are shown in gray, ammonium nitrogen/potassium atoms are shown as black spheres.

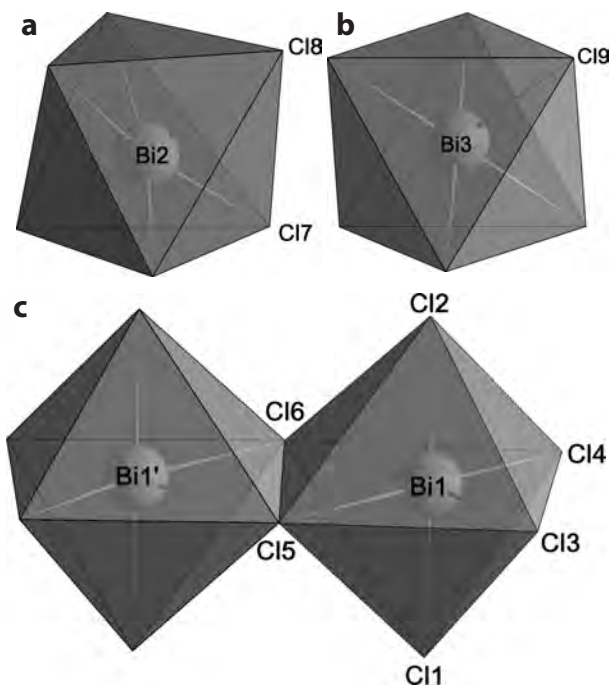


FIGURE 4. (a) The distorted octahedral BiCl_6^{2-} anion, located on a threefold axis. (b) The regular octahedral BiCl_6^{2-} anion, located on a $\bar{3}$ site. (c) The dioctahedral $\text{Bi}_2\text{Cl}_{10}^{4-}$ anion. The twofold axis passes through atoms Cl15 and Cl16.

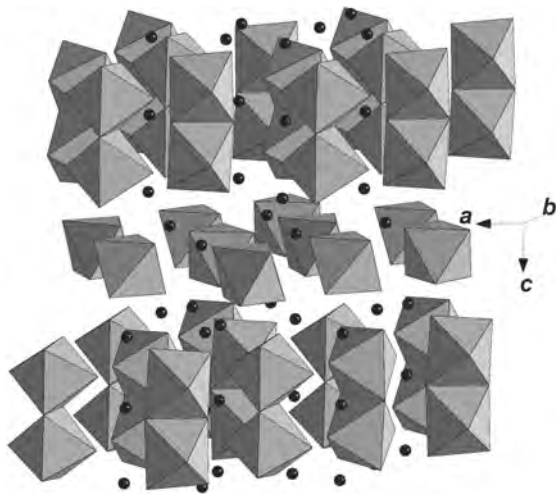


FIGURE 5. A portion of the structure of argesite showing the location of the ammonium/potassium ions.

2000). Later on, bismoclite BiOCl and complex bismuth halides or sulfohalides have also been observed as minerals deposited at the rim of the crater (Campostrini et al. 2011; Demartin et al. 2008, 2009b, 2009c, 2010c).

In the complex equilibria taking place in volcanic vapors bismuth is generally in the form of sulfides or halides (Cheynet et al. 2000). The covalent and relatively volatile compound BiCl_3 (b.p. 447 °C) is a most plausible candidate in the presence of notable concentrations of hydrochloric acid. In the presence of

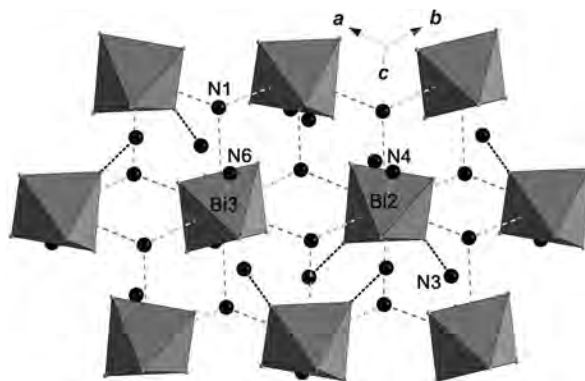


FIGURE 6. The Bi_2/Bi_3 -containing sheet showing the arrangement of the ammonium/potassium ions around the BiCl_6^{2-} anions. The short interactions of the $\text{Bi}_3\text{Cl}_6^{2-}$ anion with N3 are shown with black-dashed lines.

water this halide easily tends to hydrolyze to the non-volatile oxychloride (bismoclite BiOCl) or instead, if sufficient concentrations of H_2S are present, it forms demicheleite-(Cl) BiSCl or even bismuth sulfides such as bismuthinite.

While the relatively hygroscopic BiCl_3 as such has not been found as a mineral yet, the chloride complexes of bismuth are more stable, especially those with large cations. For this reason the presence of alkali metals, ammonium, or thallium can lead to the formation of stable minerals (see also steropesite). Ammonium salts have a tendency to dissociate even at moderate temperature, and the formation of ammonium-rich complexes is only possible in the presence of a sufficiently high concentration (activity) of ammonia in the vapor and a not too high temperature. Therefore, the extreme rarity of minerals like argesite is related to the very restricted field of stability of these ammonium complexes.

ACKNOWLEDGMENTS

The authors are most indebted to the referees Filippo Vurro and Stefan Graeser for useful suggestions. We also thank Silvia Bruni for the FTIR measurements.

REFERENCES CITED

- Bartl, H. (1982) Messzeitersparnis durch Profilauswertung bei der Registrierung von neutronene-inkristallreflexen. Die Kristallstruktur von Wismuth trichlorid, BiCl_3 . Fresenius' Zeitschrift fuer Analytische Chemie, 312, 17–18.
- Borodaev, Y.S., Garavelli, A., Garbarini, C., Grillo, S.M., Mozgova, N.N., Organova, N.I., Trubkin, N.V., and Vurro, F. (2000) Rare sulfosalts from Vulcano, Aeolian Islands, Italy. III. Wittite and cannizzarite. Canadian Mineralogist, 38, 23–34.
- Bruker (2001) SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin.
- Campostrini, I., Demartin, F., Gramaccioli, C.M. and Russo, M. (2011) Vulcano. Tre secoli di mineralogia. Associazione Micro-mineralogica Italiana ed., Cremona-Italy, 344 p.
- Cheyne, B., Dall'Aglia, M., Garavelli, A., Grasso, M.F., and Vurro, F. (2000) Trace elements from fumaroles at Vulcano Island (Italy): rates of transport and a thermochemical model. Journal of Volcanology and Geothermal Research, 95, 273–283.
- Cotton, F.A. and Wilkinson, G. (1980) Advanced Inorganic Chemistry. A comprehensive text. 4th ed. Wiley-Interscience, New York.
- Demartin, F., Gramaccioli, C.M., Campostrini, I., and Orlandi, P. (2008) Demicheleite, BiSBr , a new mineral from La Fossa crater, Vulcano, Aeolian Islands, Italy. American Mineralogist, 93, 1603–1607.
- Demartin, F., Campostrini, I., and Gramaccioli, C.M. (2009a) Panichiite, natural ammonium hexachlorostannate, $(\text{NH}_4)_2\text{SnCl}_6$, from La Fossa crater, Vulcano, Aeolian Islands, Italy. Canadian Mineralogist, 47, 367–372.
- Demartin, F., Gramaccioli, C.M., and Campostrini, I. (2009b) Brontesite,

- $(\text{NH}_4)_3\text{PbCl}_5$, a new product of fumarolic activity from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Canadian Mineralogist*, 47, 1237–1243.
- (2009c) Demicheleite-(Cl), $\text{Bi}_2\text{S}_2\text{Cl}_2$, a new mineral from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *American Mineralogist*, 94, 1045–1048.
- (2009d) Steropesite, $\text{Tl}_3\text{Bi}_2\text{Cl}_6$, a new thallium bismuth chloride from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Canadian Mineralogist*, 47, 373–380.
- (2010a) Adranosite, $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, a new ammonium sulfate chloride from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Canadian Mineralogist*, 48, 315–321.
- (2010b) Pyracmonite, $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$, a new ammonium iron sulfate from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Canadian Mineralogist*, 48, 307–313.
- (2010c) Demicheleite-(I), Bi_2S_2 , a new mineral from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Mineralogical Magazine*, 74, 141–145.
- Farmer, V.C. (1974) The infrared spectra of minerals. Monograph 4: Mineralogical Society, London.
- Farrugia, L.J. (1999) WinGX suite for small-molecule single-crystal crystallography. *Journal of Applied Crystallography*, 32, 837–838.
- Garavelli, A., Laviano, R., and Vurro, F. (1997) Sublimate deposition from hydrothermal fluids at the Fossa crater-Vulcano, Italy. *European Journal of Mineralogy*, 9, 423–432.
- Holland, T.J.B. and Redfern, S.A.T. (1997) Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine*, 61, 65–77.
- Ishihara, H., Yamada, K., Okuda, T., and Weiss, A. (1993) The structures of M_2X_3^- ($\text{M}=\text{Bi}$; $\text{X}=\text{Cl}, \text{Br}$) ions determined by Rietveld analysis of X-ray powder diffraction data. *Bulletin of the Chemical Society of Japan*, 66, 380–383.
- Lefebvre, J., Carpentier, P., and Jakubas, R. (1991) Structures and phase transition in the ferroelectric crystal of pentakis(methylammonium) undecachlorodibismuthate(III): $[\text{NH}_3(\text{CH}_3)]_5\text{Bi}_2\text{Cl}_{11}$. *Acta Crystallographica*, B, 47, 228–234.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship. IV. The compatibility index and its application. *Canadian Mineralogist*, 19, 441–450.
- Pinto, D., Balić Žunić, T., Garavelli, A., Garbarino, C., Makovický, E., and Vurro, F. (2006) First occurrence of close-to-ideal kirkiite at Vulcano (Aeolian Islands, Italy): chemical data and single crystal X-ray study. *European Journal of Mineralogy*, 18, 393–401.
- Sheldrick, G.M. (2000) SADABS Area-Detector Absorption Correction Program, Bruker AXS Inc., Madison, Wisconsin.
- (2008) A short history of *SHELX*. *Acta Crystallographica*, A64, 112–122.

MANUSCRIPT RECEIVED NOVEMBER 17, 2011

MANUSCRIPT ACCEPTED APRIL 3, 2012

MANUSCRIPT HANDLED BY FERNANDO COLOMBO