

BRONTESITE, $(\text{NH}_4)_3\text{PbCl}_5$, A NEW PRODUCT OF FUMAROLIC ACTIVITY FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

The new mineral species *brontesite*, ammonium lead chloride $(\text{NH}_4)_3\text{PbCl}_5$, was found in a medium-temperature (~250°C) active fumarole at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. The mineral occurs on a pyroclastic breccia as colorless to white tabular crystals up to 0.1 mm in length, in association with bismuthinite, godovikovite, demicheleite-(Cl), demicheleite-(Br), alunite, IMA 2008–057, $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, and IMA 2009–049, BiSi. The mineral is orthorhombic, space group *Pnma* (no. 62), with *Z* = 4; the unit-cell parameters are: *a* 8.434(1), *b* 15.759(2), *c* 8.462(1) Å, *V* 1124.7(2) Å³. The strongest six reflections in the X-ray powder-diffraction pattern [*d*_{obs} in Å(*I*)(*hkl*)] are: 3.067(100)(132), 2.020(80)(342), 2.710(78)(241), 1.910(78)(134), 2.421(75)(152) and 1.491(75)(373). Chemical analyses made with an electron microprobe in EDS mode gave, on average, Pb 47.8, Cl 36.1, Br 3.7, K 1.1, NH₄ 11.3 (by difference), for a total of 100.0 wt.%, corresponding to the empirical formula: $[(\text{NH}_4)_{2.87}\text{K}_{0.13}]_{\Sigma 3.00}\text{Pb}_{1.09}(\text{Cl}_{4.79}\text{Br}_{0.21})_{\Sigma 5.00}$. The measured density is 2.72(1) g/cm³. The average index of refraction *n* is 1.70(3) (λ = 589 nm). Using single-crystal diffraction data, the structure was refined to a final *R* = 0.0238 for 1463 independent observed reflections [*I* > 2σ(*I*)]. The coordination polyhedron of the independent eight-coordinated Pb atom is a bicapped trigonal prism with Pb–Cl distances ranging from 2.777(1) to 3.724(1) Å. The Pb polyhedra are connected by sharing edges to form chains running along [100]. There are also two independent sites occupied by ammonium ions whose environment corresponds nearly exactly to that of the Rb atoms in Rb₃PbCl₅. It is essentially similar to that of the lead atom, *i.e.*, the chlorine atoms are also arranged at the corners of bicapped trigonal prisms. There is some substitutional disorder involving the Pb²⁺ and NH₄⁺ ions, similar to that occurring for Pb²⁺ and K⁺ in the high-temperature modification of KPb₂Cl₅. The mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (IMA #2008–014); it is named after Brontes (Βρόντης), one of the three Cyclops (Κύκλωπες) and a son of Uranus.

Keywords: brontesite, new mineral species, crystal structure, ammonium lead chloride, Vulcano, Italy.

SOMMAIRE

Nous avons découvert la brontesite, nouvelle espèce minérale, chlorure d'ammonium et de plomb ayant la formule idéale $(\text{NH}_4)_3\text{PbCl}_5$, dans une fumarolle active de température moyenne (~250°C) au cratère La Fossa, Vulcano, îles Aeoliennes, en Sicile, Italie. Le minéral forme des cristaux incolores à blancs atteignant 0.1 mm en longueur sur une brèche pyroclastique, en association avec bismuthinite, godovikovite, demicheleite-(Cl), demicheleite-(Br), alunite, IMA 2008–057, $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, and IMA 2009–049, BiSi. La brontesite est orthorhombique, groupe spatial *Pnma* (no. 62), avec *Z* = 4; ses paramètres réticulaires sont: *a* 8.434(1), *b* 15.759(2), *c* 8.462(1) Å, *V* 1124.7(2) Å³. Les six réflexions les plus intenses du spectre de diffraction X (méthode des poudres) [*d*_{obs} en Å(*I*)(*hkl*)] sont: 3.067(100)(132), 2.020(80)(342), 2.710(78)(241), 1.910(78)(134), 2.421(75)(152) et 1.491(75)(373). Les analyses chimiques effectuées avec une microsonde électronique en dispersion d'énergie ont donné, en moyenne, Pb 47.8, Cl 36.1, Br 3.7, K 1.1, NH₄ 11.3 (par différence), pour un total de 100.0% (poids), ce qui correspond à la formule empirique $[(\text{NH}_4)_{2.87}\text{K}_{0.13}]_{\Sigma 3.00}\text{Pb}_{1.09}(\text{Cl}_{4.79}\text{Br}_{0.21})_{\Sigma 5.00}$. La densité mesurée est 2.72(1) g/cm³. L'indice de réfraction moyen *n* est 1.70(3) (λ = 589 nm). Nous nous sommes servis de données prélevées sur monocristal pour affiner la structure jusqu'à un résidu *R* final de 0.0238 pour 1463 réflexions indépendantes observées [*I* > 2σ(*I*)]. Le polyèdre autour de l'atome Pb à coordination huit est un prisme trigonal en chape; les distances Pb–Cl vont de 2.777(1) à 3.724(1) Å. Les polyèdres Pb sont connectés par partage d'arêtes pour former des chaînes le long de [100]. Il y a aussi deux sites indépendants occupés par les ions ammonium; leur environnement correspond presque exactement à celui des atomes Rb dans le composé Rb₃PbCl₅. Il est aussi semblable à celui de l'atome de plomb, ce qui veut dire que les atomes de chlore sont aussi disposés aux coins de prismes trigonaux en chape. Il y a un degré de désordre impliquant le Pb²⁺ et les ions NH₄⁺, tout comme celui qui implique le Pb²⁺ et le K⁺ dans la forme de KPb₂Cl₅ stable à température élevée. Le minéral a été approuvé comme

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espèce nouvelle par la Commission des nouveaux Minéraux, de Nomenclature et de Classification de l'IMA (#2008–014); son nom rappelle Brontes (Βρόντης), un des trois cyclopes (Κύκλωπες) et fils d'Uranus.

(Traduit par la Rédaction)

Mots-clés: brontesite, nouvelle espèce minérale, structure cristalline, chlorure d'ammonium et de plomb, Vulcano, Italie.

INTRODUCTION

In the last few years, a renewed mineralogical interest in the fumarole system at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy has led to the discovery of a number of rare and new minerals [for details, see for instance Garavelli *et al.* (2005), Camprostrini *et al.* (2008), Demartin *et al.* (2009), Mitolo *et al.* (2009), and references therein]. During a systematic sampling carried out in the years 2007–2008, the new species *brontesite* $(\text{NH}_4)_3\text{PbCl}_5$, an ammonium lead chloride, was also discovered. We report here the description of the mineral and its structure determination.

The mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2008–039). The name is after Brontes (Βρόντης), one of the three Cyclops (Κύκλωπες) and a son of Uranus. These mythological half-gods were helpers of Hephaistos (Ηφαίστος), the ancient Greek god of fire, whose workshops were alleged to be located at Vulcano (or Etna). The holotype is deposited (no. 2008–03) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

OCCURRENCE, CHEMICAL DATA AND PHYSICAL PROPERTIES

Brontesite occurs in an active medium-temperature ($\sim 250^\circ\text{C}$) intracrater fumarole on a pyroclastic breccia, in close association with bismuthinite, godovikovite, demicheleite-(Cl), demicheleite-(Br), alunite, IMA 2008–057 $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, and IMA 2009–049 BiSI.

Our mineral forms aggregates of colorless to white tabular crystals up to 0.1 mm in length (Figs. 1, 2). The habit is pseudotetragonal, tabular on $\{010\}$; the other most common forms are $\{110\}$, $\{011\}$, and $\{121\}$; no twinning is apparent from the morphology. The $a:b:c$ ratio calculated from the unit-cell parameters is: 0.5348:1:0.5354. The mineral is not hygroscopic and is stable in the open air; the streak is white, and the luster is vitreous. Cleavage and fracture were not observed. No fluorescence was observed both under short-wave and long-wave ultraviolet radiation.

The density, measured by flotation in a tribromomethane–trichloromethane mixture, is $2.72(1) \text{ g/cm}^3$; that calculated corresponding to the empirical formula and to the X-ray data is 2.728 g/cm^3 . The mineral is

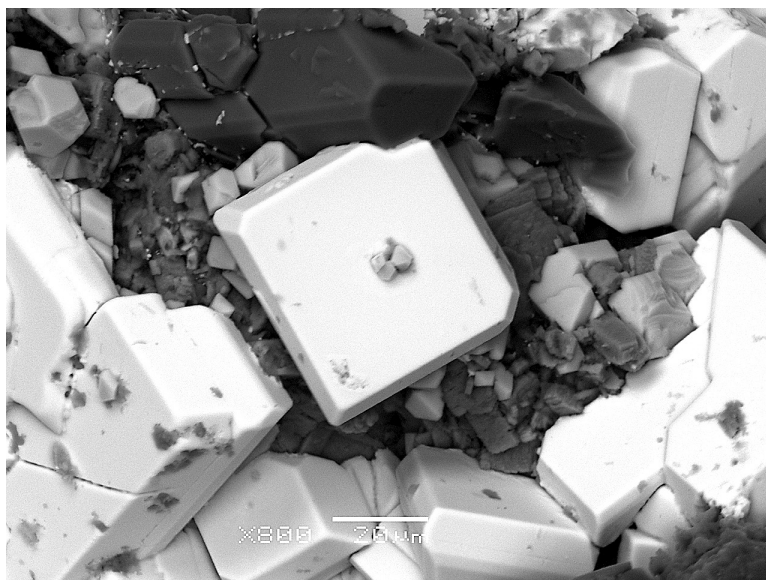


FIG. 1. SEM–BSE image of crystals of brontesite; the dark crystals at the top of the photo are alunite.

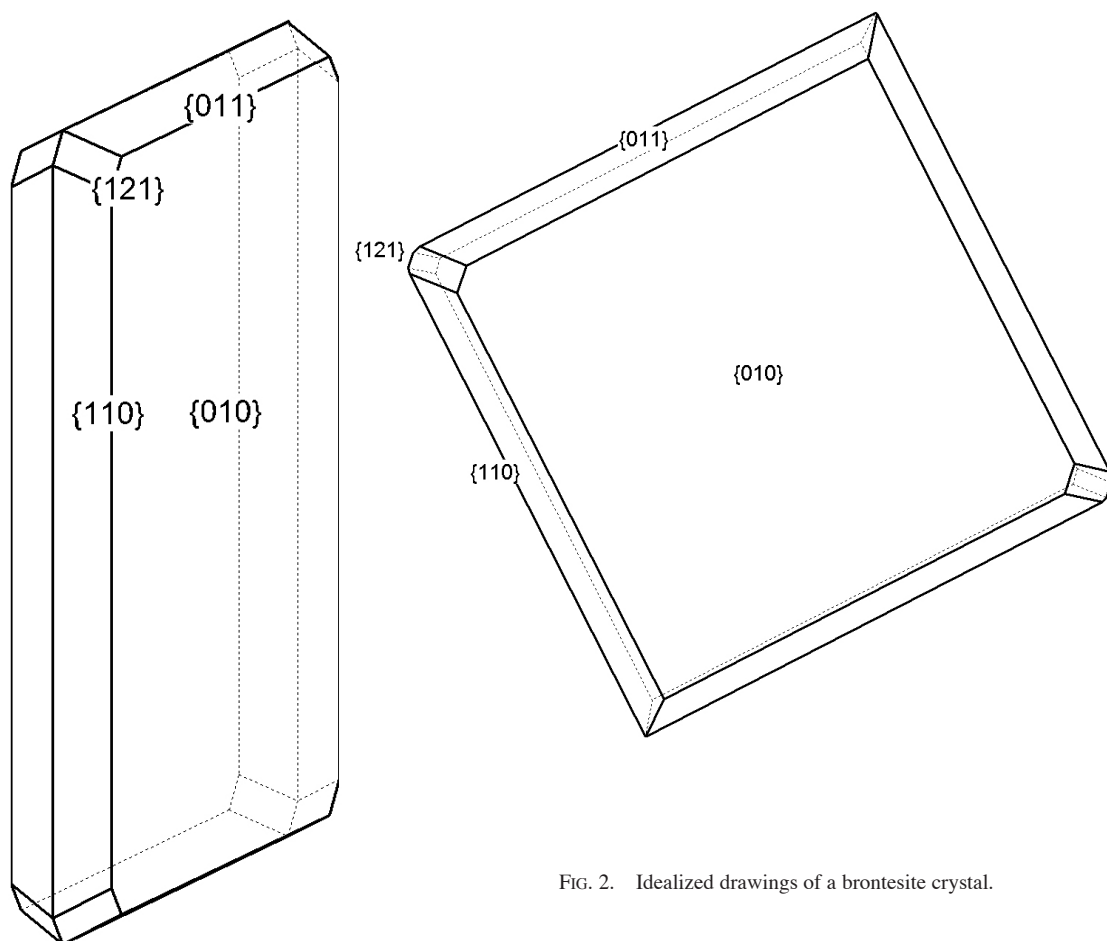


FIG. 2. Idealized drawings of a brontesite crystal.

biaxial, the average index of refraction n measured by immersion in α -monobromo-naphthalene – methylene iodide is 1.70(3) (589 nm); the corresponding Gladstone–Dale value calculated using Mandarino’s constants (1981) is 1.693, leading to a compatibility index $[1 - (K_p/K_C)] = -0.011$, which is considered as “superior”.

In order 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 μ m beam diameter). Element concentrations were measured using the $K\alpha$ lines for Cl and K, the $L\alpha$ lines for Br, and the $M\alpha$ lines for Pb. The presence of ammonium was established from crystal-structure analysis, and its content was deduced from the total theoretical value of the sites (3 *apfu*) minus that of the K content (0.13 *apfu*) obtained from the chemical analysis; the mean analytical results are reported in Table 1.

The empirical formula obtained, based on 5 *apfu* for (Cl + Br) and 3 *apfu* for (NH₄ + K) is: $[(\text{NH}_4)_{2.87}\text{K}_{0.13}]_{\Sigma 3.00}\text{Pb}_{1.09}(\text{Cl}_{4.79}\text{Br}_{0.21})_{\Sigma 5.00}$; the idealized formula is $(\text{NH}_4)_3\text{PbCl}_5$, which requires: NH₄ 12.32, Pb 47.25, Cl 40.43, total 100.00 wt.%. The infrared spectrum shows the following absorption peaks at 3165(vs), 3039(s) and 1401(vs) cm^{-1} , in agreement with the presence of ammonium (Farmer 1974); these results were confirmed by microchemical tests using the Nessler reaction. No peaks due to H₂O or OH⁻ are present. The estimates of the composition were also calculated using crystallographic data only (see Table 1): although the potassium content was neglected because it could not be evaluated in this way, the agreement with the microprobe results remains acceptable, being within the uncertainty of the experimental data. Some improvement in the charge balance can be further achieved if vacancies are assumed to be present, but in view of the very high energy involved, we are reluctant to consider such a possibility. Since in absence of

vacancies stoichiometry should be respected, the only way to have five positive charges with a total of four atoms is the presence of one atom only with 2+ charge and three with one positive charge each. On this basis, the Pb content should be exactly 1 *apfu*.

X-RAY DATA

The X-ray powder-diffraction data were obtained using a Bruker D8 diffractometer, with CuK α radiation (Table 2). A least-squares fit of these data provided the unit-cell parameters: *a* 8.434(1), *b* 15.759(2), *c* 8.462(1) Å, *V* 1124.7(2) Å³. The unit-cell parameters obtained from 3613 single-crystal reflections with *I* > 5 σ (*I*) are reported in Table 3, together with other details concerning the data collection and refinement. A total of 11176 diffraction maxima corresponding to a complete scan of the reciprocal lattice up to 2 θ = 60.14° were collected from a crystal (0.08 × 0.08 × 0.04 mm) using a Bruker Apex II diffractometer equipped with a 2K CCD detector and MoK α radiation (γ = 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 (μ = 16.84 mm⁻¹) was applied using the SADABS program (Sheldrick 2000). After averaging the symmetry-related reflections (R_{int} = 0.027), 1739 independent data were obtained.

The structure was solved by direct methods and refined using the SHELXL97 program (Sheldrick 1997) implemented in the WINGX suite of software (Farrugia 1999). During the refinement, a partial replacement of the ammonium ions by a heavier substituent such as Pb was indicated by the exceedingly low values of their atomic displacement parameters (from here onward, ADPs) and by residual peaks of opposite sign in the Fourier synthesis around the N and the Pb atoms. This NH₄⁺ → Pb²⁺ disorder is a consequence of the similar coordination of these atoms (see below) and shows analogies with the structure of other lead chlorides, such as for instance that of the high-temperature modification of KPb₂Cl₅, which is also partially disordered (Velázquez *et al.* 2006).

TABLE 1. CHEMICAL COMPOSITION OF BRONTESITE

Constituent	wt.%	Range	<i>apfu</i>	Probe standard	wt.% from structure determination	<i>apfu</i> *
K	1.1(6)	0.9–1.2	0.13	KCl	–	–
Pb	47.8(5)	46.9–49.1	1.09	phosgenite	48.10	1.07
Cl	36.1(6)	35.2–36.7	4.79	phosgenite	36.62	4.76
Br	3.7(5)	3.1–4.2	0.21	TlBr	4.16	0.24
NH ₄ ⁺	11.3		2.87		11.11	2.84
Total	100.0		9		99.99	8.91

* In the refinement, no restraints concerning the total number of atoms were introduced. † By difference (see text).

Accordingly, the occupancy parameters of the Pb and N atoms in the crystal structure were refined, without restraints. For similar reasons, in view of the non-negligible presence of bromine and because the ADP of the Cl(1) atom only was too small if compared with those of the other Cl atoms, the occupancy of this site was also refined with no restraints; the overall occupancy of Cl and Br in the site Cl(1) [0.93(1) + 0.12(1) = 1.05] remained reasonably close to unity. On applying such considerations, the residual *R* dropped from 0.076 to 0.024. All the hydrogen atoms of the ammonium ion showed up clearly in a difference-Fourier map and were included in the final refinement, with isotropic ADPs, whereas anisotropic temperature-factors were considered instead for all the other atoms. The final *R* is 0.0238 for 1463 observed reflections [*I* > 2 σ (*I*)]. The final coordinates and displacement parameters of the atoms are reported in Table 4; interatomic distances (below 4 Å) are listed in Table 5. Observed and calculated structure-factors tables may be obtained from The Depository of Unpublished Data on the MAC web site [document Brontesite CM47_1237].

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR BRONTESITE

<i>h k l</i>	<i>l/l_o</i>	<i>d</i> (Å) obs.	<i>d</i> (Å) calc. #	<i>h k l</i>	<i>l/l_o</i>	<i>d</i> (Å) obs.	<i>d</i> (Å) calc. #
0 2 0	21	7.920	7.879	0 7 1	27	2.177	2.176
0 1 1	37	7.460	7.455	3 4 2	80	2.020	2.013
1 0 1	6	5.980	5.974	0 8 0	40	1.972	1.970
1 1 1	5	5.550	5.586	1 3 4	78	1.910	1.911
1 2 1	19	4.759	4.760	2 1 4	37	1.874	1.877
0 3 1	17	4.463	4.463	3 3 3	38	1.850	1.862
2 0 0	5	4.218	4.217	4 4 1	60	1.816	1.816
2 1 0	20	4.064	4.074	3 6 2	55	1.748	1.748
1 1 2	27	3.672	3.677	3 7 1	38	1.722	1.721
2 2 1	44	3.404	3.404	5 1 2	42	1.558	1.559
1 3 2	100	3.067	3.069	2 2 5	55	1.550	1.540
2 4 1	78	2.710	2.725	3 8 2	40	1.508	1.507
3 1 1	55	2.630	2.631	3 7 3	75	1.491	1.492
1 2 3	45	2.529	2.533	2 4 5	65	1.457	1.459
1 5 2	75	2.421	2.421	5 2 3	60	1.430	1.424
3 0 2	30	2.340	2.342	5 2 4	40	1.403	1.402
3 2 2	57	2.235	2.245	6 1 1	30	1.381	1.381
1 4 3	60	2.211	2.213	1 10 3	30	1.358	1.358
				2 6 5	30	1.347	1.348

* Calculated from the unit cell: *a* 8.434(1), *b* 15.759(2), *c* 8.462(1) Å, *V* 1124.7(2) Å³, obtained from least-squares refinement from the above data using the program UNITCELL (Holland & Redfern 1997).

TABLE 3. SINGLE-CRYSTAL DATA AND REFINEMENT PARAMETERS FOR BRONTESITE

Crystal system	orthorhombic	μ (mm ⁻¹)	16.84
Space group	<i>Pnma</i> (no. 62)	D_{calc} (g/cm ³)	2.728
<i>a</i> (Å)	8.4351(9)	Measured reflections	11176
<i>b</i> (Å)	15.7732(17)	Independent reflections	1739
<i>c</i> (Å)	8.4446(4)	Observed reflections	1463
<i>V</i> (Å ³)	1123.5(8)	[<i>I</i> > 2 σ (<i>I</i>)]	
<i>Z</i>	4	Parameters refined	80
Radiation	MoK α	Final <i>R</i> and wR2	0.0238, 0.0454
		<i>S</i>	1.05

Notes: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.225q)^2 + 0.4839q]$, where $q = (F_o^2 + 2F_c^2) / 3$; $S = \{\sum [w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS [$U_{eq}U(i,j)$] OF ATOMS IN BRONTESITE

Atom	X/a	Y/b	Z/c	U_{eq}	Site occupancy [†]
Pb	0.08521(1)	0.25	0.84823(1)	0.02880(3)	0.94(Pb) + 0.08(N)
N(1)	-0.5706(1)	0.25	1.1515(1)	0.0345(2)	0.90(N) + 0.11(Pb)
N(2)	-0.2369(1)	0.4519(1)	1.0375(2)	0.0483(4)	0.96(N) + 0.02(Pb)
Cl(1)	-0.05060 (5)	0.11727(3)	0.67683(5)	0.0436(1)	0.93(Cl) + 0.12(Br)
Cl(2)	0.11853(6)	0.37741(3)	1.12905(6)	0.0354(1)	
Cl(3)	-0.21660(7)	0.25	0.97949(8)	0.0324(1)	
H11	-0.5012(9)	0.25	1.2475(5)	0.14(1)	
H12	-0.4951(7)	0.25	1.0567(5)	0.13(1)	
H13	-0.6172(7)	0.3112(3)	1.1365(9)	0.13(1)	
H21	-0.2801(8)	0.4504(5)	1.1488(4)	0.13(1)	
H22	-0.1321(4)	0.4247(4)	1.0305(10)	0.15(1)	
H23	-0.2443(10)	0.5082(2)	0.9884(8)	0.11(1)	
H24	-0.3191(7)	0.4129(4)	0.9728(8)	0.23(2)	

[†] All these values were refined independently, with no restraints.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	0.02789(5)	0.02904(5)	0.02946(5)	0	-0.00501(4)	0
N(1)	0.0333(3)	0.0354(3)	0.0346(3)	0	-0.0050(3)	0
N(2)	0.0548(7)	0.0348(6)	0.0553(8)	0.0102(5)	0.0117(6)	0.0037(5)
Cl(1)	0.0472(2)	0.0448(2)	0.0389(2)	-0.0124(2)	0.0044(2)	-0.0175(2)
Cl(2)	0.0385(2)	0.0306(2)	0.0371(2)	0.0013(2)	-0.0012(2)	-0.0036(2)
Cl(3)	0.0285(3)	0.0317(3)	0.0368(3)	0	0.0028(3)	0

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. INTERATOMIC DISTANCES AND HYDROGEN BOND INTERACTIONS BELOW 4.0 Å IN BRONTESITE

Pb–Cl(1)	2.7911(5)	Pb–Cl(2)	3.1211(6)
Pb–Cl(1) ^a	2.7911(5)	Pb–Cl(2) ^a	3.1211(6)
Pb–Cl(1) ^b	3.7236(4)	Pb–Cl(3)	2.7766(7)
Pb–Cl(1) ^c	3.7236(4)	Pb–Cl(3) ^c	3.2332(7)
N(1)...Cl(1) ^a	3.4781(7)	N(2)...Cl(1) ^b	3.3867(13)
N(1)...Cl(1) ^b	3.4781(7)	N(2)...Cl(1) ^a	3.5968(13)
N(1)...Cl(2) ^a	3.3092(8)	N(2)...Cl(1) ^c	3.3766(13)
N(1)...Cl(2) ^b	3.1652(7)	N(2)...Cl(2) ^a	3.1975(13)
N(1)...Cl(2) ^c	3.3092(8)	N(2)...Cl(2) ^b	3.3114(13)
N(1)...Cl(3)	3.3204(10)	N(2)...Cl(3)	3.2266(12)
N(1)...Cl(3) ^d	3.3509(10)		

Symmetry codes: a = $x - 1/2, y, 3/2 - z$; b = $x - 1/2, 1/2 - y, 3/2 - z$; c = $x - 1/2, 1/2 - y, z$; d = $x - 1/2, 1/2 - y, 5/2 - z$; e = $x - 1, y, z$; f = $x + 1/2, 1/2 - y, 3/2 - z$; g = $x, 1/2 - y, z$; h = $x + 1/2, y, 3/2 - z$; i = $-x - 1/2, y + 1/2, z + 1/2$; j = $-x, 1 - y, 2 - z$.

RESULTS AND DISCUSSION

The mineral is isostructural with the synthetic compound Rb_3PbCl_5 (Beck *et al.* 1999), not a surprising consequence of the close similarity between the ionic radii of NH_4^+ and Rb^+ (about 1.47 Å for both); on the other hand, it is not isostructural with the best characterized modification of Tl_3PbCl_5 (Keller 1977); a different

crystal-chemical behavior between Tl^+ and the alkali ions has already been noticed for thallium–bismuth halides (Demartin *et al.* 2009).

The structure contains one independent eight-coordinated Pb atom located on a *m*. symmetry site; the coordination polyhedron is a bicapped trigonal prism with Pb–Cl distances ranging from 2.777 to 3.724 Å. The Pb polyhedra are connected by shared edges to form chains running along [100] (Fig. 3). There are also two independent sites (with symmetry *m*. and 1, respectively) occupied by the ammonium ions (Fig. 4). The environment of such ions corresponds nearly exactly to that of the Rb atoms in Rb_3PbCl_5 and is similar to that of the lead atom, *i.e.*, the coordinating chlorine atoms are arranged in the same way at the corners of bicapped trigonal prisms. The similarity between the coordination polyhedra of the Pb^{2+} and NH_4^+ ions accounts for the presence of minor disorder concerning the mutual replacement of these ions (see above and Table 4).

Some N...Cl distances, ranging from 3.17 to 3.48 Å for N(1) and from 3.20 to 3.39 Å for N(2), indicate the presence of weak N–H...Cl hydrogen bonds, thereby preventing rotational disorder of the ammonium groups.

In view of disorder, the refined values of the occupancy of the Pb and N atoms are reasonable (see

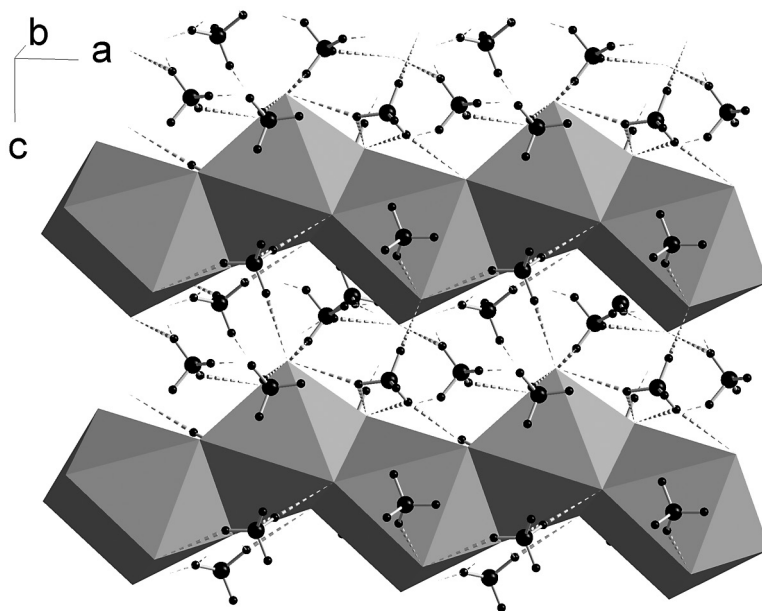


FIG. 3. A view of the crystal structure of brontesite showing the chains made by the PbCl_5 polyhedra. The hydrogen bonds involving the NH_4^+ ions are shown as dashed lines.

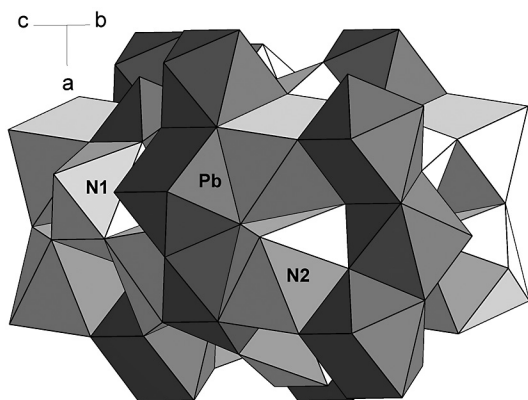


FIG. 4. A view of the coordination polyhedra around the lead atoms (dark gray) and the nitrogen atoms of the NH_4^+ ions (light gray).

Table 4), the overall occupations of Pb and NH_4^+ in the Pb, N(1) and N(2) sites being close to unity (1.02, 1.01 and 0.98, respectively). Bond-valence calculations might be interesting to perform; however, the partial substitution of Cl by Br and the disorder concerning Pb renders such results not particularly appropriate for a detailed discussion, and for this reason they are omitted.

The $\text{Pb}^{2+} \rightarrow \text{NH}_4^+$ disorder occurring in brontesite is analogous with the $\text{Pb}^{2+} \rightarrow \text{K}^+$ disorder in the high-temperature polymorph of KPb_2Cl_5 (Velázquez *et al.* 2006). However, the difference occurring between the ionic radii of NH_4^+ (1.42 Å) and Pb^{2+} (1.20 Å) is still greater than that between K^+ (1.33 Å) and Pb^{2+} . Therefore, if lead is replaced by ammonium (and *vice versa*), here a considerable increase in ΔH , of the energy of packing (enthalpy), should occur. Therefore, in order to maintain the free-energy variation $\Delta F = \Delta H - T\Delta S$ negative for sake of stability, an appropriately high value of temperature T is needed to raise the $T\Delta S$ contribution, where ΔS is the entropy of mixing.

However, ammonium salts are usually unstable at high temperature because of their tendency to dissociate by releasing NH_3 . In reality, ammonium salts are not equally volatile: for instance, salammoniac (ammonium chloride, a common product in the fumaroles at Vulcano) can be very easily volatilized, and probably for this reason it is not present in the immediate environment of brontesite; instead, less volatile ammonium-bearing sulfates such as tschermigite and godovikovite occur. Therefore, a restricted field of stability for brontesite can be inferred, characterized by a moderately high temperature and a strong activity of ammonia in the fumarolic gases to prevent dissociation by a mass-action process.

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