ACMONIDESITE, A NEW AMMONIUM SULFATE CHLORIDE FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

The new mineral acmonidesite, $(NH_4, K, Pb^{2+}, Na)_9Fe_4^{2+}(SO_4)_5Cl_8$, was found in an active fumarole (fumarole FA, temperature about 250 °C) at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. It occurs on a pyroclastic breccia as brown prismatic crystals up to 0.10 mm in length, in association with salammoniac, alunite and adranosite. The mineral is orthorhombic, space group: $C222_1$ (no. 20) with a = 9.841(1), b = 19.448(3) c = 17.847(3) Å, V = 3415.7(9) $Å^3$ and Z = 4. The six strongest reflections in the X-ray powder diffraction pattern are: [d_{obs} in Å(*I*)(*h k l*)] 8.766(100)(1 1 0), 1.805(88)(3 9 0), 5.178(45)(1 3 1), 4.250(42)(2 2 1), 2.926(42)(3 3 0), 2.684(32)(2 6 1). The empirical formula (based on 28 anions *pfu*) is $(NH_4)_{5.77}K_{1.42}Pb_{0.62}Na_{1.24}Fe_{3.96}Mn_{0.08}S_{5.04}O_{20.16}Cl_{7.97}Br_{0.08}$. The idealized formula is $(NH_4, K, Pb^{2+}, Na)_9Fe_4^{2+}(SO_4)_5Cl_8$. The calculated density is 2.551 g cm^{-3}. Using single-crystal diffraction data, the structure was refined to a final $R(F)$ = 0.0363 for 4614 independent observed reflections [$I > 2\sigma(I)$]. The structure contains two independent, distorted octahedral iron sites, Fe1 and Fe2, with the iron

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atoms in the 2+ oxidation state, as confirmed by the interatomic distances and bond valence calculations (2.06 and 1.94 *vu*, respectively). Fe1 is surrounded by two chlorine atoms and four oxygens of the sulfate ions, with the following average distances (Å): Fe1-O 2.125, Fe1-Cl 2.472; Fe2 is surrounded by three chlorine atoms and three oxygens of the sulfate ions, with the following average distances (Å): Fe2-O 2.110, Fe2-Cl 2.531. Three independent sulfate anions are also present and are connected with the iron polyhedra to form a tridimensional structure containing voids occupied by four independent ammonium ions (two of them partially replaced by K^+) , one Na^+/Pb^{2+} site and one Cl^- ion.

Keywords: acmonidesite, new mineral species, volcanic sublimate, crystal structure, Vulcano island, Italy.

INTRODUCTION

Ammonium sulfate chlorides are quite rare (see for instance rruff.info/ima/), the only examples known to date seem to have been found as sublimates only at Vulcano Island, Aeolian Islands, Sicily, Italy (Campostrini *et al.*, 2011), i.e. adranosite (Demartin *et al.*, 2010), adranosite-(Fe) (Mitolo *et al.*, 2013) and therasiaite (Demartin *et al.*, 2014). Acmonidesite $(NH_4, K, Pb^{2+}, Na)_9Fe_4^{2+}(SO_4)_5Cl_8$, is an additional new mineral of this kind recently found in the fumaroles at the same locality. This mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2013-068). The name is from Acmonides (from the Greek Ακμωνιδης), cited by Ovidius as one of the Cyclops, who were helpers of Hephaistos, the mythological god of fire whose forge was alleged to be located at Vulcano.

This paper deals with the description of the new mineral, together with its crystal structure determination.

OCCURRENCE, CHEMICAL DATA AND PHYSICAL PROPERTIES

Acmonidesite is a volcanic sublimate found at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy, in an active fumarole [fumarole FA, reported in Borodaev *et al.* (2000) and Pinto *et al.* (2006)] that occurs on a pyroclastic breccia as brown prismatic crystals up to 0.10 mm in length, in association with salammoniac NH_4Cl, alunite $KAl_3(SO_4)_2(OH)_6$ and adranosite $(NH_4)_4NaAl_2(SO_4)Cl(OH)_2$, (Figure 1). The most commonly observed forms are: {1 0 0}, {1 2 0}, {0 1 1}, {0 1 0}and {1 0 2}; such an indexing has been obtained by comparison of computer-generated drawings of the crystals. No twinning is apparent. The *a*:*b*:*c* ratio calculated from the unit-cell parameters is 0.5060:1:0.9177 (single-crystal data). The streak is light brown and the lustre is vitreous. Cleavage and fracture were not observed. No fluorescence was observed both under SW and LW ultraviolet radiation. A measurement of the density, obtained by flotation in a diiodomethane-benzene solution, gives the value of 2.56(1) g cm^{-3}. The density calculated using the empirical formula and single-crystal unit-cell data is 2.551 g cm^{-3}.

Acmonidesite is biaxial (+) with α= 1.580(2), β = 1.590(2) γ = 1.635(2) (white light), measured with a spindle stage. 2V(meas) = 53(3)°, 2V(calc) = 51.6°. Orientation $X = c$, $Y = b$, $Z = a$. Taking into account the empirical chemical formula and the density based on it, the calculated mean refractive index is 1.602, using the Gladstone-Dale constants of Mandarino (1976, 1981). The compatibility index $1-(K_p/K_c) = 0.033$ is rated as excellent. Dispersion could not be observed because of the intense brown color of the mineral.

Quantitative chemical analyses (8) were carried out in EDS mode using a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe (20 kV excitation voltage, 10 pA beam current, 2 μm beam diameter). The analytical method was chosen because it was impossible to prepare a flat polished sample and the crystal is severely damaged by using the WDS technique, even with a low voltage and current and a large diameter beam. Element concentrations were measured using the $K\alpha$ lines for S, K, Na, Fe, Mn, and Cl, the $L\alpha$ line for Br and the $M\alpha$ line for Pb. The presence of ammonium was established from crystal structure analysis, confirmed by the FT infrared spectrum (Figure 2) as well as by the EDS spectrum (Figure 3). The

IR spectrum was recorded on a Jasco IRT-3000 spectrometer and shows strong absorption bands related to the presence of ammonium at 3214 (broad), 2921, 2851 and 1395 cm^{-1}, together with typical sulfate absorptions at 740, 1005, 1083, 1137 and 1218 cm^{-1}. Minor absorptions at 1620 and 1730 cm^{-1} may be due to partial replacement of Cl^- by OH^-. The $(NH_4)_2O$ content was deduced from structure solution, taking into account its partial replacement by K^+ (see later). The mean analytical results are reported in Table 1. The empirical formula (based on 28 anions *pfu*) is $(NH_4)_{5.77}K_{1.42}Pb_{0.62}Na_{1.24}Fe_{3.96}Mn_{0.08}S_{5.04}$ $O_{20.16}Cl_{7.97}Br_{0.08}$. The simplified formula is $(NH_4, K, Pb^{2+}, Na)_9Fe_4^{2+}(SO_4)_5Cl_8$. Holotype material is deposited in the Reference Collection of the Dipartimento di Chimica, Università degli Studi di Milano, specimen number 2013-02.

X-RAY DATA

X-ray powder-diffraction data (Table 2) have been obtained using a Rigaku DMAX II diffractometer, with graphite monochromatized Cu*K*α radiation. The indexing of the powder-diffraction pattern was made by comparison with the pattern calculated after the structure determination. The following unit-cell parameters a = 9.840(1), b = 19.455(2), c = 17.847(2) Å, V= 3416.6(5) $Å^3$ were derived from least-squares refinement from the above data using the program UNITCELL (Holland and Redfern, 1997).

Single-crystal diffraction data were collected using a Bruker Apex II diffractometer with Mo*K*α radiation (λ = 0.71073 Å). Some 17663 intensities were measured up to 2θ = 63.03°, of which 5336 were unique (R_{int} 0.0501). A SADABS absorption correction was applied (Sheldrick, 2000) (μ = 5.95 mm^{-1}). On the basis of systematic absences the space group $C222_1$ (no. 20) was unambigously selected, in agreement also with statistical tests on the distribution of the E values [$|E^2$-1| = 0.781] and confirmed by satisfactory structure solution and refinement. The structure was solved by direct methods and refined using the *SHELXL-2017* program (Sheldrick, 2008) implemented in the *WinGX* suite (Farrugia, 1999) to a final R = 0.0363 for 4614 observed reflections [$I > 2\sigma(I)$]. A refinement of the occupancies of the N and Na sites revealed in two of them a significant substitution of the ammonium ions by K^+ and of Na^+ by Pb^{2+}, as shown in Table 4, whereas no occupancy was refined for the Fe and Cl sites, due to only small amounts of Mn and Br replacing Fe and Cl, respectively. The formula resulting from the structure refinement is

$(NH_4)_{5.77}K_{1.22}Pb_{0.64}Na_{1.36}Fe_4(SO_4)_5Cl_8$ (corresponding to 17.63 positive charges for the cations and 18 negative charges for the anions). It seems satisfactory in view of the approximations introduced for the atomic scattering factors of mixed sites. The positions of all the hydrogen atoms of the ammonium ion could not be detected from a difference Fourier map due to local disorder. The value of the Flack parameter, 0.228(8), confirms the correctness of the absolute structure, in view with the fact that the crystal is partially twinned and a TWIN refinement was carried out (twin matrix -1 0 0, 0 -1 0, 0 0 -1 and components ratio 0.772(8)/0.228(8)). The coordinates and displacement parameters of the atoms are reported in Table 4; selected interatomic distances are listed in Table 5. The crystallographic files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of acmonidesite (Figure 4) contains two independent, distorted octahedral iron sites, Fe1 and Fe2, with the iron atoms in the 2+ oxidation state, as confirmed by the range of interatomic distances and bond valence calculations (2.06 and 1.94 vu, respectively). Fe1 is surrounded by two chlorine atoms and four oxygens of the sulfate ions, with the following average distances: Fe1-O 2.125 Å, Fe1-Cl 2.472 Å; Fe2 is surrounded by three chlorine atoms and three oxygens of the sulfate ions, with the following average distances: Fe2-O 2.111 Å, Fe2-Cl 2.531 Å. The structural type of acmonidesite is unprecedented and displays finite clusters made by four iron vertex-sharing distorted octahedra and sulfate tetrahedra (Figure 5), interacting each other only through the sulfate anions. Fe octahedra linked *via* vertices to form infinite chains ancased from both sides by SO_4 tetrahedra are also present in parabutlerite (Plášil et al. 2017), however in acmonidesite each couple of adjacent octahedral is bridged by two sulfate anions instead of by one. The three independent sulfate anions, one of which located on a two-fold axis (S3), are connected to the iron polyhedra and to the other cations as shown in Figure 6. The S1 sulfate shares two vertices of the tetrahedron with two symmetry-related Fe1 polyhedra of the same cluster. The S2 sulfate shares two vertices with Fe1 and Fe2 polyhedra of the same cluster and one with a Fe2 of an adjacent cluster. The S3 one shares two of the four vertices with Fe1and Fe2 octahedra of the same cluster and the other two with the corresponding Fe1 and Fe2 polyhedra related by two-fold symmetry. Voids within the three-dimensional framework determined by the arrangement of these clusters are occupied by four independent ammonium ions (two of them partially replaced by K^+), by one Na^+ cation, partially substituted by Pb^{2+} and one Cl^- anion (Cl5). The larger voids are those occupied by ammonium only (average radius of the cage 3.32-3.46 Å) or by ammonium plus potassium (average radius 3.12-3.14 Å). The smallest (average radius 2.79 Å) are occupied by Na^+ and Pb^{2+}, as expected by the ionic radii of these cations. Bond valence calculations (Table 5) are in agreement with the structure model proposed. The value of 1.421 vu obtained for the Na/Pb site accounts for the presence of an amount of the divalent Pb^{2+} cation.

The ammonium ions interact with the surrounding sulfate oxygens and chloride ions via hydrogen bonds. The three sulfate anions display S-O distances ranging from 1.448(5) to 1.483(4) Å with an overall average distance of 1.465 Å, not significantly different from the grand mean S-O distance reported by Hawthorne *et al*. (2000).

In spite of the similar chemical composition with adranosite-(Fe) and therasiaite, no topological relationship of acmonidesite with them is evident. In adranosite-(Fe) iron is present only in the 3+ oxidation state, and its polyhedron does not contain chlorine which is instead coordinated to Na; the $FeO_4(OH)_2$ distorted octahedra and sulfate tetrahedra are linked to form helicoidal chains extending along [001]. Two different oxidation states for iron are instead present in therasiaite, where three chlorides and three oxygens of the sulfate anions are octahedrally coordinated to the metal centre thus forming $[Fe_2(SO_4)_3Cl_5^{6-}]_n$ infinite chains along [001].

The occurrence of acmonidesite in the fumaroles at La Fossa Crater, together with other rare and unique minerals containing ammonium, is an additional example of the singularity of this locality and provides further information in the study of the overall geochemical context of this environment. The presence of this minerals as volcanic sublimates emphasizes an high activity of free ammonia and volatile chlorides in the gas phase that prevent dissociation of such minerals, which would be otherwise unstable at the observed temperature.

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Supplementary material

To view supplementary material for this article, please visit https://doi.org/

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Table 1. Analytical data for acmonidesite (average of 8 analyses).

Constituent	wt%	Range	SD	Probe Standard
$(NH_4)_2O$*	11.05			
K_2O	4.91	4.28 – 6.14	0.27	KBr
Na_2O	2.82	2.28 – 3.54	0.22	Natural albite
FeO	20.93	19.51 – 21.88	0.25	Natural almandine garnet
MnO	0.42	0.15 – 1.24	0.10	Natural almandine garnet
PbO	10.25	7.03 – 12.23	0.99	phosgenite
SO_3	29.67	27.46 – 32.51	0.37	Synthetic anhydrite
Cl	20.80	18.42– 23.46	0.50	phosgenite
Br	0.45	0.36 – 0.51	0.20	KBr
O = Cl	-4.75			
Total	96.55			

* From structure solution

The empirical formula (based on 28 anions *pfu*) is $(NH_4)_{5.77}K_{1.42}Pb_{0.62}Na_{1.24}Fe_{3.96}Mn_{0.08}S_{5.04}$ $O_{20.16}Cl_{7.97}Br_{0.08}$. The simplified formula is $(NH_4, K, Pb^{2+}, Na)_9Fe_4^{2+}(SO_4)_5Cl_8$.

Table 2. X-ray powder diffraction data for acmonidesite.

h k l	I_{rel}	d_{obs} (Å)	d_{calc} (Å)*
0 2 0	12	9.704	9.727
0 0 2	37	9.049	8.924
1 1 0	100	8.766	8.781
0 2 1	1	8.544	8.541
1 1 1	14	7.860	7.879
0 2 2	22	6.570	6.576
1 3 1	45	5.178	5.182
0 4 0	9	4.850	4.864
2 2 1	42	4.250	4.263
0 2 4	13	4.044	4.056
0 4 3	1	3.776	3.765
1 5 0	25	3.605	3.618
1 3 4	14	3.449	3.443
2 4 1	8	3.407	3.396
0 2 5	26	3.346	3.351
0 4 4	9	3.275	3.288
3 1 0	23	3.230	3.234
0 6 1	29	3.203	3.190
1 5 3	21	3.085	3.091
1 3 5	18	2.983	2.980
0 0 6	24	2.969	2.975
3 3 0	42	2.926	2.927
3 1 3	10	2.833	2.842
1 5 4	13	2.804	2.810
2 6 1	32	2.684	2.677
3 3 4	5	2.444	2.447
4 2 2	2	2.304	2.304
2 0 7	27	2.266	2.264
0 2 8	9	2.175	2.174
0 8 4	2	2.136	2.135
4 0 5	3	2.023	2.026
2 2 8	2	1.992	1.989
2 6 7	13	1.858	1.856
1 9 5	10	1.814	1.817
3 9 0	88	1.805	1.805
3 9 1	24	1.797	1.796
4 4 6	2	1.768	1.766
5 5 3	4	1.683	1.684
4 8 3	9	1.662	1.661
6 0 2	2	1.615	1.613

*Calculated from the unit cell a = 9.840(1), b = 19.455(2), c = 17.847(2) Å, V= 3416.6(5) Å^3, obtained from least-squares refinement of the above data using the program UNITCELL (Holland and Redfern, 1997).

Table 3. Single-crystal diffraction data and refinement parameters for acmonidesite

Crystal system	orthorhombic
Space Group	$C222_1$ (no. 20)
a (Å)	9.841(1))
b (Å)	19.448(3)
c (Å)	17.847(3)
V (Å^3)	3415.7(9)
Z	4
Radiation	Mo$K\alpha$
μ (mm^{-1})	5.95
D_{calc} (g cm^{-3})	2.551
Measured reflections	17663
R_{int}	0.0501
Independent reflections	5336
Observed reflections [$I > 2\sigma(I)$]	4614
Parameters refined	214
Final R [$I > 2\sigma(I)$] and wR2 (all data)	0.0363, 0.0945
S	1.037

Notes: $R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$;

$w=1/[\sigma^2(Fo^2)+(0.0563q)^2]$ where $q = [\max(0, Fo^2)+2Fc^2]/3$;

$S=\{\Sigma[w(Fo^2-Fc^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

Table 4. Final atom coordinates and equivalent isotropic displacement parameters (Å^2).

Atom	Wyckoff site	occupancy	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq
Fe1	8*c*	1	0.06089(8)	0.09769(4)	0.14882(4)	0.01876(18)
Fe2	8*c*	1	0.32631(7)	0.15792(4)	-0.00614(5)	0.01962(17)
S1	8*c*	1	0.19697(12)	0.00302(8)	0.28715(7)	0.0218(3)
S2	8*c*	1	-0.01601(12)	0.18634(6)	-0.00283(7)	0.0165(2)
S3	4*a*	1	0.16498(15)	0	0	0.0138(3)
O1	8*c*	1	0.3439(5)	0.0072(4)	0.2850(3)	0.0652(19)
O2	8*c*	1	0.1430(5)	0.0169(2)	0.2111(2)	0.0314(10)
O3	8*c*	1	0.1508(6)	-0.0668(3)	0.3071(3)	0.0521(15)
O4	8*c*	1	0.1425(4)	0.0534(2)	0.3402(2)	0.0309(9)
O5	8*c*	1	0.1255(4)	0.2045(3)	-0.0185(3)	0.0431(13)
O6	8*c*	1	-0.1040(5)	0.2458(2)	-0.0174(3)	0.0373(11)
O7	8*c*	1	-0.0601(7)	0.1307(3)	-0.0515(3)	0.0499(14)
O8	8*c*	1	-0.0306(5)	0.1659(3)	0.0756(3)	0.0403(12)
O9	8*c*	1	0.2498(5)	0.0580(2)	-0.0234(3)	0.0445(14)
O10	8*c*	1	0.0781(4)	0.0199(2)	0.0631(2)	0.0266(8)
Cl1	8*c*	1	0.29077(14)	0.14689(7)	0.13413(8)	0.0259(3)
Cl2	4*b*	1	0	0.17900(10)	0.25	0.0295(4)
Cl3	8*c*	1	0.3433(2)	0.16197(9)	-0.14856(9)	0.0400(4)
Cl4	8*c*	1	0.55827(13)	0.10510(7)	0.00109(9)	0.0299(3)
Cl5	4*b*	1	0	-0.21271(12)	0.25	0.0408(5)
Na/Pb	8*c*	0.68(1)/0.32(1)	0.07476(6)	-0.10348(3)	0.15782(3)	0.0251(2)
N1/K1	4*a*	0.74(1)/0.26(1)	-0.1854(4)	0	0	0.0304(14)
N2/K2	8*c*	0.52(1)/0.48(1)	0.43348(19)	0.00093(12)	-0.13237(11)	0.0288(7)
N3	8*c*	1	0.1904(6)	0.3092(3)	0.1455(3)	0.0367(13)
N4	8*c*	1	-0.3063(6)	0.1870(3)	0.1444(3)	0.0348(12)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	0.0211(4)	0.0192(4)	0.0159(3)	0.0004(3)	0.0005(3)	0.0014(3)
Fe2	0.0188(3)	0.0135(3)	0.0265(4)	0.0005(3)	0.0002(3)	-0.0024(2)
S1	0.0175(5)	0.0299(7)	0.0180(5)	0.0047(6)	0.0000(4)	0.0030(6)
S2	0.0197(5)	0.0120(5)	0.0179(5)	0.0015(5)	-0.0001(5)	0.0030(4)
S3	0.0144(6)	0.0115(6)	0.0154(6)	-0.0010(7)	0	0
O1	0.019(2)	0.135(6)	0.041(3)	-0.015(4)	-0.005(2)	0.002(4)
O2	0.043(2)	0.032(2)	0.0191(18)	-0.0001(16)	-0.0069(17)	0.0071(19)
O3	0.058(3)	0.028(3)	0.070(4)	0.016(3)	0.022(3)	0.007(2)
O4	0.027(2)	0.040(3)	0.025(2)	-0.0069(18)	-0.0004(17)	0.0030(19)
O5	0.022(2)	0.041(3)	0.065(4)	0.027(2)	0.009(2)	0.0043(19)
O6	0.036(2)	0.020(2)	0.057(3)	0.0018(19)	-0.007(2)	0.0120(18)
O7	0.078(4)	0.025(2)	0.047(3)	-0.013(2)	-0.021(3)	0.003(3)
O8	0.038(2)	0.056(3)	0.027(2)	0.021(2)	0.0080(19)	0.017(2)
O9	0.053(3)	0.026(2)	0.055(3)	-0.015(2)	0.029(2)	-0.025(2)
O10	0.029(2)	0.031(2)	0.0197(17)	-0.0094(15)	0.0048(16)	-0.0067(17)
Cl1	0.0251(6)	0.0237(6)	0.0289(7)	-0.0002(5)	-0.0012(5)	-0.0023(5)
Cl2	0.0455(12)	0.0206(9)	0.0225(9)	0	0.0078(8)	0
Cl3	0.0568(11)	0.0327(8)	0.0304(8)	0.0040(6)	-0.0020(7)	0.0097(8)

Cl4	0.0226(5)	0.0294(7)	0.0375(7)	-0.0006(7)	-0.0006(6)	0.0043(5)
Cl5	0.0432(13)	0.0323(12)	0.0469(13)	0	0.0120(10)	0
Na/Pb	0.0262(3)	0.0234(3)	0.0256(3)	-0.0053(2)	-0.0012(2)	0.0006(2)
N1/K1	0.0213(19)	0.033(2)	0.037(2)	-0.007(2)	0	0
N2/K2	0.0265(10)	0.0298(11)	0.0302(11)	-0.0014(9)	0.0049(7)	0.0018(10)
N3	0.037(3)	0.027(3)	0.046(3)	0.003(2)	-0.005(3)	0.002(2)
N4	0.039(3)	0.025(3)	0.040(3)	-0.006(2)	-0.001(2)	0.002(2)

The anisotropic displacement factor exponent takes the form:

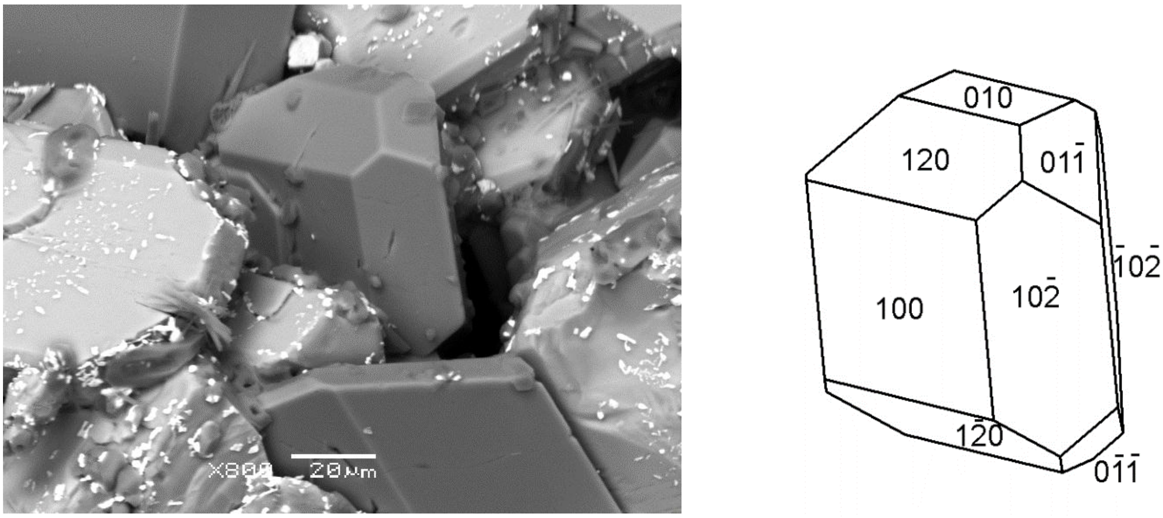
$-2\pi^2(U_{11}h^2(a^*)^2+...+2U_{12}hka^*b^*+...)$; U_{eq} according to Fischer and Tillmans (1988)

Table 5. Selected interatomic distances (Å) and bond valences* (vu) in acmonidesite.

Fe1-O2	2.086(4)	0.386	Fe2-O5	2.185(4)	0.296
Fe1-O4[a]	2.188(4)	0.293	Fe2-O6[b]	2.039(4)	0.438
Fe1-O8	2.068(4)	0.405	Fe2-O9	2.107(4)	0.365
Fe1-O10	2.158(4)	0.318	Fe2-Cl1	2.537(2)	0.275
Fe1-Cl1	2.470(2)	0.330	Fe2-Cl3	2.549(2)	0.267
Fe1-Cl2	2.474(2)	0.327	Fe2-Cl4	2.507(1)	0.299
<Fe1-φ>	2.241	Σ= 2.059	<Fe2- φ>	2.321	Σ= 1.940
N1/K1-O7	2.970(6)	0.122	Na/Pb-O2	2.615(4)	0.160
N1/K1-O7[c]	2.970(6)	0.122	Na/Pb-O3	2.857(6)	0.091
N1/K1-O4[f]	3.064(4)	0.095	Na/Pb-O10	2.935(4)	0.076
N1/K1-O4[g]	3.064(4)	0.095	Na/Pb-O3[a]	2.414(6)	0.258
N1/K1-O10	2.853(5)	0.166	Na/Pb-O5[c]	3.207(6)	0.040
N1/K1-O10[c]	2.853(5)	0.166	Na/Pb-O7[c]	2.375(6)	0.282
N1/K1-O8[c]	3.814(6)	0.013	Na/Pb-O9[c]	3.084(6)	0.053
N1/K1-Cl4[d]	3.247(3)	0.167	Na/Pb-Cl3[c]	2.882(2)	0.259
N1/K1-Cl4[e]	3.247(3)	0.167	Na/Pb-Cl5	2.786(2)	0.202
<N1/K1-φ>	3.120	Σ=1.113	<Na/Pb-φ>	2.795	Σ= 1.421
N2/K2-O1[h]	2.646(5)	0.261	N3-O3[i]	2.996(8)	0.123
N2/K2-O1[c]	2.868(5)	0.147	N3-O5	3.623(8)	0.023
N2/K2-O2[c]	3.204(5)	0.062	N3-O6[b]	3.235(8)	0.064
N2/K2-O9	2.878(5)	0.143	N3-O7[b]	3.195(8)	0.072
N2/K2-O9[c]	3.508(6)	0.029	N3-O8	3.749(8)	0.016
N2/K2-Cl3	3.268(3)	0.146	N3-Cl1	3.313(6)	0.153
N2/K2-Cl4	3.359(3)	0.118	N3-Cl2	3.661(6)	0.060
N2/K2-Cl1[c]	3.200(3)	0.171	N3-Cl3[m]	3.733(6)	0.049
N2/K2-Cl4[c]	3.354(3)	0.119	N3-Cl3[j]	3.462(6)	0.103
<N2/K2-φ>	3.143	Σ= 1.196	N3-Cl4[j]	3.363(6)	0.134
			N3-Cl5[n]	3.598(6)	0.071
N4-O1[a]	3.736(10)	0.017	N3-Cl5[i]	3.598(6)	0.071
N4-O4[a]	3.071(7)	0.100	<N3-φ>	3.460	Σ= 0.939
N4-O5[j]	3.153(7)	0.080			
N4-O6	3.688(8)	0.019	S1-O1	1.448(5)	1.609
N4-O8	3.006(7)	0.120	S1-O2	1.483(4)	1.464
N4-Cl3[j]	3.286(6)	0.165	S1-O3	1.475(5)	1.492
N4-Cl4[d]	3.294(6)	0.162	S1-O4	1.464(4)	1.541
N4-Cl5[k]	3.315(6)	0.153	<S1-O>	1.468	Σ= 6.106
N4-Cl5[l]	3.315(6)	0.153			
<N4-φ>	3.318	Σ= 0.969	S2-O5	1.464(4)	1.541
			S2-O6	1.467(4)	1.529
S3-O9	1.463(4)	1.545	S2-O7	1.455(5)	1.579
S3-O10	1.466(4)	1.533	S2-O8	1.462(4)	1.549
S3-O9[c]	1.463(4)	1.545	<S2-O>	1.462	Σ= 6.198
S3-O10[c]	1.466(4)	1.533			
<S3-O>	1.465	Σ= 6.156			

Symmetry codes: a = -x, y, 1/2-z; b = x+1/2, 1/2-y, -z; c = x, -y, -z; d = x-1, y, z; e = x-1, -y, -z; f = -x, -y, z–1/2; g = -x, y, 1/2-z; h = 1-x, -y, z-1/2; i = 1/2-x, y+1/2, 1/2-z; j = x-1/2, 1/2-y, -z; k= x-1/2, y+1/2, z; l = -x-1/2, y+1/2, 1/2-z, m = 1/2-x, 1/2-y, z+1/2, n = x+1/2, y+1/2, z.

* Bond-valence parameters from Brown and Altermatt (1985), and Brown (2009).



(a) **(b)**

Figure 1. SEM-BSE image of crystals of acmonidesite with alunite (a) and a crystal drawing with indexing of the faces (b).

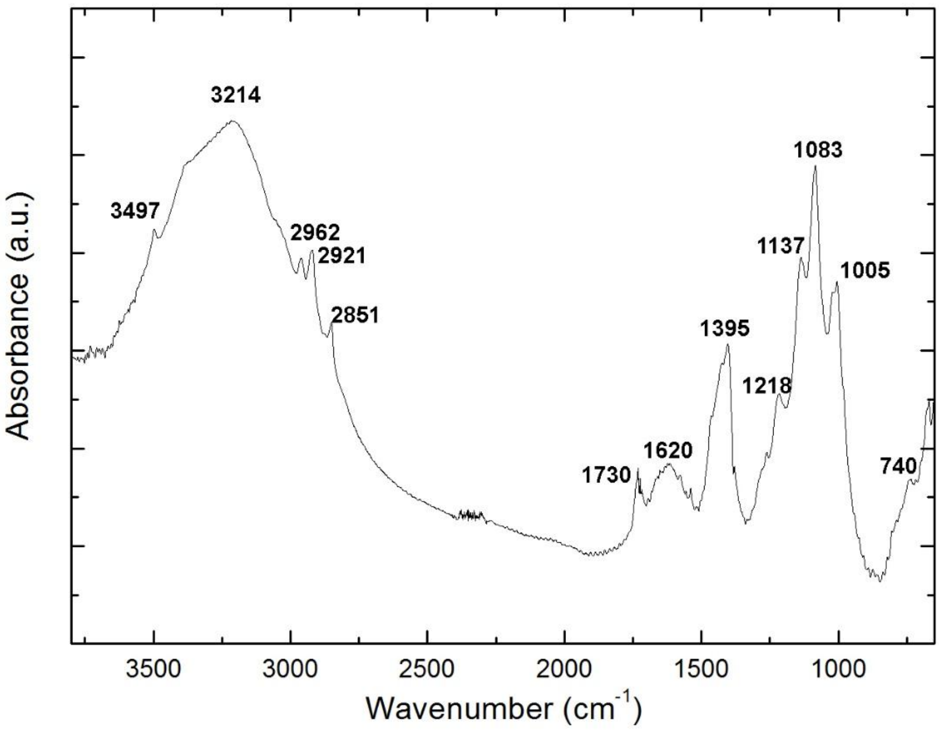


Figure 2. Infrared spectrum of acmonidesite.

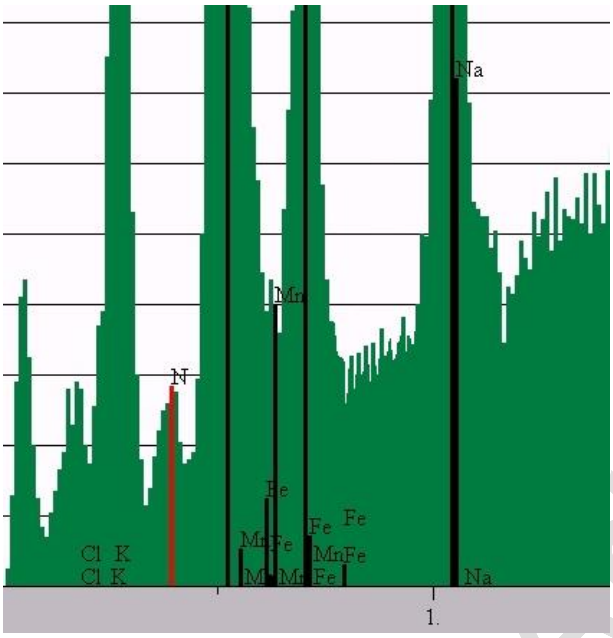


Figure 3. A portion of the EDS spectrum, where the presence of the ammonium nitrogen is evident.

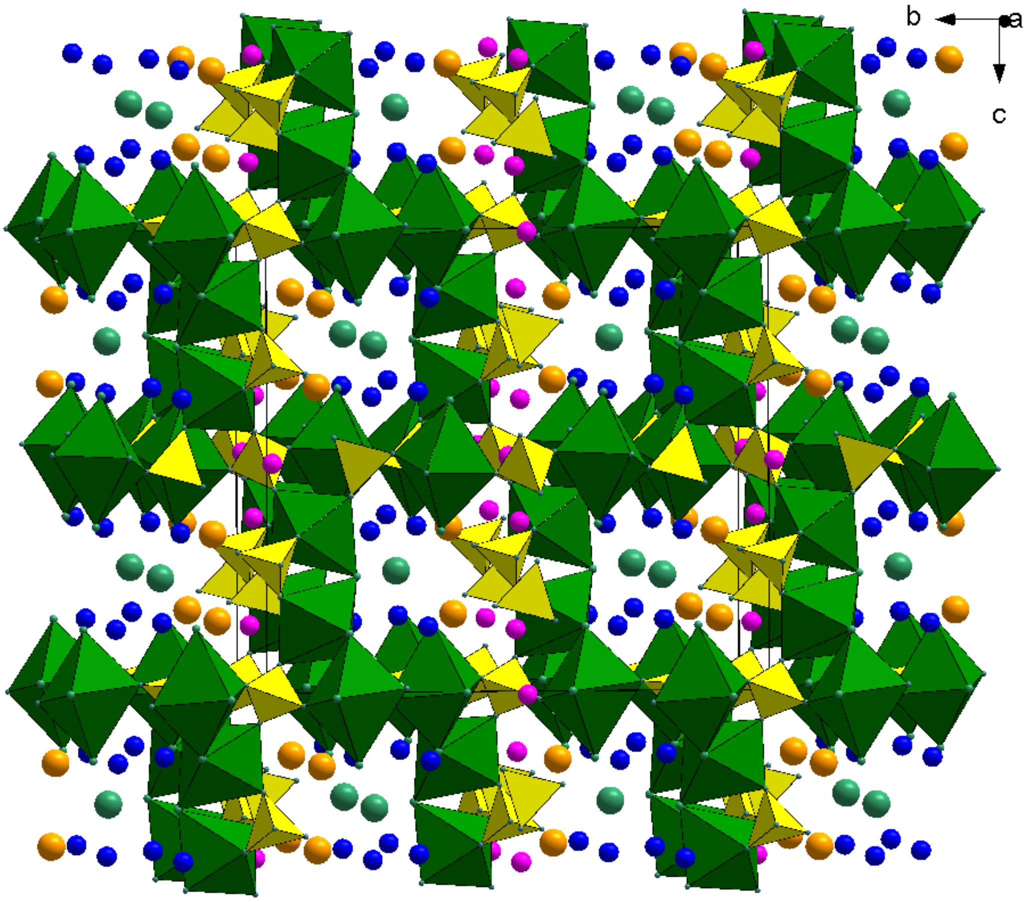


Figure 4. Perspective view of the structure of acmonidesite seen almost along [100]. Fe^{2+}: green octahedra; SO_4^{2-}: yellow tetrahedra; NH_4^+: blue spheres; Na^+/Pb^{2+}: orange spheres; NH_4^+/K^+: magenta spheres; Cl5: green spheres.

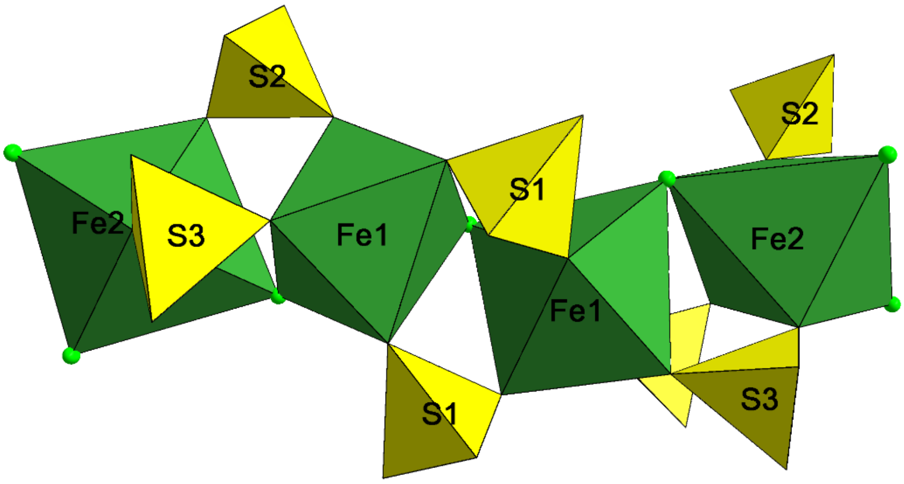
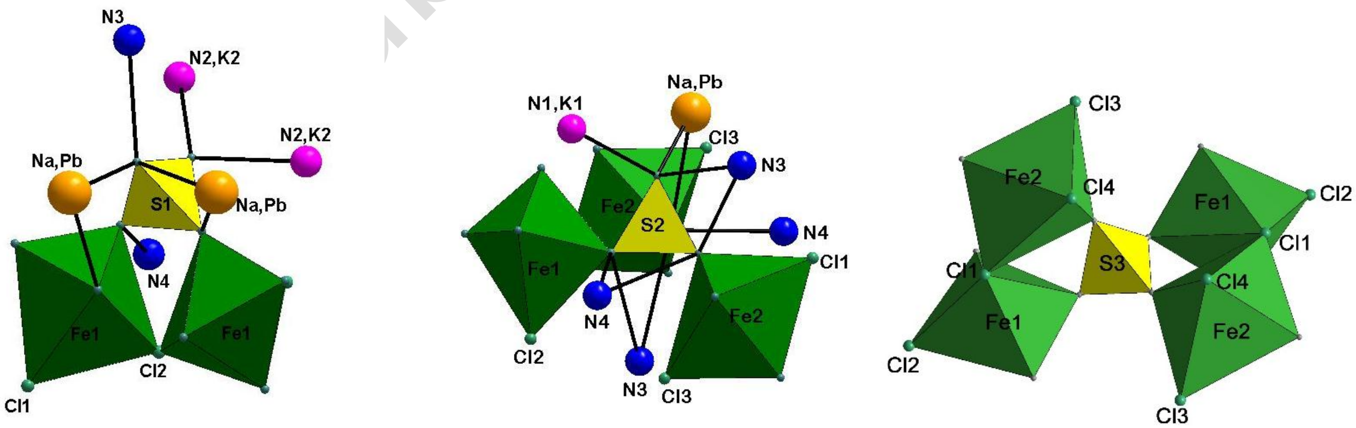


Figure 5. Perspective view of the discrete cluster of iron and sulfate polyhedra observed in acmonidesite.



(a) **(b)** **(c)**

Figure 6. The environment about the three independent sulfate anions.