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Aluminopyracmonite, $(NH_4)_3Al(SO_4)_3$, a new ammonium aluminium sulfate from La Fossa crater, Vulcano, Aeolian Islands, Italy

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ABSTRACT

The new mineral aluminopyracmonite, ideally $(NH_4)_3Al(SO_4)_3$, was found in a medium-temperature (~250ºC) intracrater active fumarole at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. It occurs on a pyroclastic breccia as colourless to white prismatic crystals up to 0.2 mm long, in association with adranosite, mascagnite, alunite and salammoniac. The mineral is identical to the synthetic compound $(NH_4)_3Al(SO_4)_3$. It is trigonal, space group: $R\bar{3}$ (no. 148) with a = 15.0324(8), c = 8.8776(5) Å, V = 1737.3(2) Å^3 and Z = 6. The six strongest reflections in the X-ray powder diffraction pattern are: [d_{obs} in Å(I)(hkl)] 3.336(100)(131), 7.469(62)(1 1 0), 3.288(60)(122), 4.289(45)($\bar{2}$31), 2.824(29)($\bar{3}$51), 4.187(27)(012). The empirical formula based on 12 anions is $[(NH_4)_{2.89}K_{0.10}]_{\Sigma 2.99}(Al_{1.18}Fe_{0.01})_{\Sigma 1.19}S_{2.91}O_{12}$, and the simplified formula $(NH_4,K)_3Al(SO_4)_3$. The measured density is 2.12(1) g/cm^3, calculated density 2.143 g/cm^3. The mineral is uniaxial(–) with ω = 1.545(3) and ε = 1.532(3) (λ = 589 nm). Using single-crystal diffraction data, the structure was refined to a final $R(F)$ = 0.0258 for 998 independent observed reflections [$I > 2\sigma(I)$]. In spite of having unit-cell parameters comparable with those of pyracmonite, the two minerals are not isostructural; the difference is related to a disordered conformation of the sulfate anions about the two independent Al^{3+} ions in aluminopyracmonite.

Keywords: aluminopyracmonite, new mineral species, crystal structure, ammonium sulfates, aluminium sulfates, Vulcano island, Italy.

Introduction

The medium-to-low-temperature intracrater fumaroles at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy, are the source of a suite of new sulfates that were discovered during our systematic investigations of fumarole minerals (Campostrini *et al.*, 2011; Demartin *et al.*, 2010*a*,*b*,*c*; 2011, 2012). Aluminopyracmonite, $(NH_4)_3Al(SO_4)_3$ was found recently in the same locality and was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2012-075). The name was chosen on the basis of the chemical analogy with pyracmonite $(NH_4)_3Fe^{3+}(SO_4)_3$ and similarity of the unit-cell parameters of the two minerals. However the space group is different, being $R\bar{3}$ instead of $R3c$, and the two species are not isostructural. This paper deals with the description of the new mineral aluminopyracmonite, together with its crystal structure.

Occurrence, chemical data and physical properties

Aluminopyracmonite occurs in an active, medium-temperature (~250ºC) intracrater fumarole developed on a pyroclastic breccia. It is associated with adranosite, mascagnite, alunite and salammoniac. About 20 specimens of this mineral were recovered. Aluminopyracmonite

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forms aggregates of colourless to white, elongate, hexagonal prismatic crystals up to 0.2 mm long (Fig. 1). No twinning is apparent. The *c*:*a* ratio calculated from the unit-cell parameters is: 1:0.591. The mineral is not hygroscopic and is stable in the open air. The streak is white and the lustre is vitreous. Cleavage and fracture were not observed. No fluorescence was observed under SW or LW ultraviolet radiation.

The density measured by flotation in a tribromomethane-trichloromethane mixture is 2.12(1) g/cm^3, that calculated from the empirical formula and the X-ray data is 2.143 g/cm^3. The mineral is uniaxial (−) with ω = 1.545(3) and ε = 1.532(3) (λ = 589 nm) and non-pleochroic; the compatibility index [1 − (K_P/K_C)] is −0.010, which is superior according to Mandarino (1981).

Quantitative chemical analyses (12) 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). Element concentrations were measured using the *K*α lines for Al, Fe, K and S. The presence of ammonium was established from crystal-structure analysis and was also confirmed by the infrared spectrum that shows absorption peaks at 3208(vs), 3048(s) and 1421(vs) cm^{-1}. The mean analytical results are reported in Table 1. The empirical formula (based on 12 anions) is $[(NH_4)_{2.89}K_{0.10}]_{\Sigma 2.99}(Al_{1.18}Fe_{0.01})_{\Sigma 1.19}S_{2.91}O_{12}$ corresponding to a simplified formula $(NH_4,K)_3Al(SO_4)_3$. The idealized formula is $(NH_4)_3Al(SO_4)_3$, which requires: $(NH_4)_2O$ 21.15, Al_2O_3 13.81, SO_3 65.04, total 100.00 wt.%. Holotype material is deposited in the Reference Collection of the Dipartimento di Chimica, Università degli Studi di Milano, specimen number 2012-01.

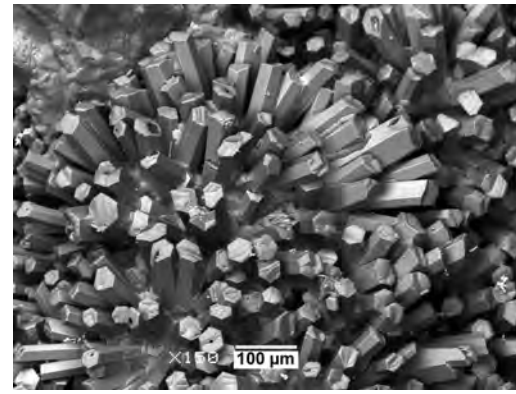

FIG. 1. SEM-BSE image of crystals of aluminopyracmonite.

X-ray data

X-ray powder-diffraction data (Table 2) were obtained using a Philips PW1830 diffractometer, with Cu*K*α radiation. The indexing of the powder-diffraction pattern was achieved by comparison with the pattern calculated after the structure determination. The following parameters *a* = 15.009(1), *c* = 8.863(1) Å of the trigonal unit cell in the hexagonal setting were obtained from least-squares refinement from the above data using the program *UNITCELL* (Holland and Redfern, 1997). There is a significant difference between the values obtained in this way and those from single-crystal data (greater than 3σ), that may be due to small differences in the chemical composition of the bulk material used for recording the powder pattern with respect to the single crystal as well as to a possible underestimation of the estimated standard deviations obtained by refinement programs.

TABLE 1. Chemical composition of aluminopyracmonite.

Constituent	Wt.%	Range	SD	Probe standard
$(NH_4)_2O$*	20.15			
K_2O	1.26	1.12–1.45	0.05	KCl
Fe_2O_3	0.30	0.22–0.40	0.06	Almandine garnet
Al_2O_3	16.07	14.69–17.63	0.12	Almandine garnet
SO_3	62.22	60.76–63.46	0.18	Synthetic anhydrite
Total	100.00			

* by difference

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

h k l	I_{rel}	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)*	d_{obs} (Å)**	I_{rel}**
1 1 0	62	7.469	7.504	7.500	100
0 3 0	5	4.364	4.333		
$\bar{2}$ 3 1	45	4.289	4.297	4.300	50
0 1 2	27	4.187	4.194	4.190	20
1 3 1	100	3.336	3.339	3.320	83
1 2 2	60	3.288	3.291		
$\bar{4}$ 4 1	9	3.042	3.051	3.060	3
$\bar{3}$ 5 1	29	2.824	2.826	2.810	20
$\bar{3}$ 4 2	26	2.796	2.797		
1 1 3	21	2.748	2.749	2.740	13
0 3 3	11	2.441	2.441	2.460	5
2 2 3	6	2.321	2.321	2.310	3
$\bar{6}$ 5 1	16	2.257	2.258	2.260	10
$\bar{5}$ 5 2	9	2.242	2.242		
$\bar{2}$ 7 0	6	2.080	2.081	2.070	4
1 4 3	5	2.046	2.046		
$\bar{1}$ 7 1	8	1.934	1.934	1.930	5
$\bar{1}$ 8 0	9	1.722	1.722	1.720	5
$\bar{5}$ 8 2	5	1.713	1.713		
$\bar{6}$ 5 4	7	1.608	1.607	1.600	5
$\bar{4}$ 8 3	9	1.585	1.584	1.590	1

* Calculated from the unit cell a = 15.009(1), c = 8.863(1) Å, obtained from least-squares refinement from the above data using the program *UNITCELL* (Holland and Redfern, 1997).
** Synthetic $(NH_4)_3Al(SO_4)_3$; non-indexed pattern from ICDD entry 00-003-0045.

TABLE 3. Single-crystal diffraction data and refinement parameters for aluminopyracmonite.

Crystal system	Trigonal
Space Group	$R\bar{3}$(no. 148)
a (Å)	15.0324(8)
c (Å)	8.8776(5)
V (Å^3)	1737.3(2)
Z	6
Radiation	Mo$K\alpha$
μ (mm^{-1})	0.788
D_{calc} (g/cm^3)	2.143
Measured reflections	6156
Independent reflections	1229
Observed reflections [$I > 2\sigma(I)$]	998
Parameters refined	104
Final R [$I > 2\sigma(I)$] and wR2 (all data)	0.0258, 0.0754
S	1.082

$R = \Sigma||Fo|-|Fc||/ \Sigma|Fo|$;
w$R2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(Fo^2)+(0.0452q)^2 + 0.2800q]$
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.

The unit-cell parameters obtained from 3057 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 6156 intensities corresponding to a complete scan of the reciprocal lattice up to 2θ = 63.26° was collected from a crystal (0.08 mm × 0.03 mm × 0.02 mm) using a Bruker Apex II diffractometer equipped with a 2K CCD detector and Mo$K\alpha$ radiation (λ = 0.71073 Å). A one-minute frame-time and a 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 = 0.788 mm^{-1}, T_{min} 0.955) was applied using the *SADABS* program (Sheldrick, 2000). After averaging the symmetry-related reflections (R_{int} = 0.0202), 1229 independent data were obtained. The structure was solved by direct methods and refined using the *SHELXL97* program (Sheldrick, 2008) implemented in the *WinGX* suite (Farrugia, 1999). During the structure solution it was evident that two possible conformations of the sulfate anions about the Al^{3+} cations were present. A refinement of the occupancies of the three disordered oxygen atoms gave values of about 0.67 and 0.33 for the two conformations, respectively. The location of the H atoms from the NH_4^+ ion were identified in the difference-fourier map and were included in the final refinement, with isotropic atomic displacement parameters, whereas anisotropic displacement parameters were used for all other atoms. The final R is 0.0258 for 998 observed reflections [$I > 2\sigma(I)$]. The final coordinates and displacement parameters of the atoms are reported in Table 4; selected interatomic distances and angles are listed in Table 5. Observed and calculated structure-factors tables have been deposited with the Editor and are available for download at: http://www.minersoc.org/pages/e_journals/dep_mat_mm.html

Description of the structure

Projections along [001] of the crystal structures of aluminopyracmonite and pyracmonite are shown in Figs 2*a* and 2*b*. It is evident that the two minerals

TABLE 4. Atomic coordinates and displacement parameters [U_{eq}/U_{ij}), Å^2] for aluminopyracmonite.

Atom	Wyckoff notation	Occupancy	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Al1	3*a*	1	2/3	1/3	1/3	0.01316(6)
Al2	3*b*	1	2/3	1/3	1/6	0.01003(6)
S	18*f*	1	0.52228(1)	0.17358(1)	0.08077(1)	0.01605(3)
O1	18*f*	1	0.54994(2)	0.24610(2)	0.04809(3)	0.01907(8)
O2a	18*f*	0.673	0.41032(3)	0.11292(4)	0.08097(6)	0.0263(2)
O2b	18*f*	0.327	0.41553(8)	0.13008(9)	0.12312(13)	0.0351(4)
O3a	18*f*	0.673	0.55285(3)	0.24001(3)	0.21654(5)	0.0229(1)
O3b	18*f*	0.327	0.59127(8)	0.21516(7)	0.21467(10)	0.0250(3)
O4a	18*f*	0.673	0.57239(3)	0.11529(3)	0.07087(6)	0.0286(1)
O4b	18*f*	0.327	0.54211(8)	0.08949(7)	0.02667(13)	0.0301(3)
N	18*f*	1	0.26073(3)	0.09755(3)	0.05993(5)	0.0259(1)
H1	18*f*	1	0.2330(5)	0.0949(6)	0.0210(11)	0.083(3)
H2	18*f*	1	0.3052(5)	0.0405(5)	0.0609(9)	0.057(2)
H3	18*f*	1	0.2812(6)	0.1340(6)	0.0593(11)	0.080(3)
H4	18*f*	1	0.2247(5)	0.1034(5)	0.1300(9)	0.065(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al1	0.01596(8)	0.01596(8)	0.0076(1)	0	0	0.00798(4)
Al2	0.01000(7)	0.01000(7)	0.0101(1)	0	0	0.00500(3)
S	0.01542(3)	0.01439(3)	0.01444(4)	0.00109(3)	0.00068(3)	0.00453(2)
O1	0.0173(1)	0.0198(1)	0.0205(1)	0.0064(1)	0.0034(1)	0.00907(7)
O2a	0.0186(2)	0.0213(2)	0.0297(2)	0.0025(2)	0.0048(2)	0.0029(1)
O2b	0.0155(4)	0.0419(5)	0.0354(6)	0.0153(5)	0.0095(4)	0.0048(4)
O3a	0.0250(2)	0.0289(2)	0.0146(2)	–0.0054(2)	–0.0046(2)	0.0134(1)
O3b	0.0313(4)	0.0211(4)	0.0146(4)	–0.0033(3)	–0.0048(4)	0.0069(3)
O4a	0.0320(2)	0.0224(2)	0.0377(3)	0.0056(2)	0.0050(2)	0.0182(1)
O4b	0.0465(5)	0.0180(3)	0.0284(5)	–0.0030(4)	–0.0088(4)	0.0181(3)
N	0.0249(1)	0.0230(1)	0.0297(2)	–0.0029(1)	0.0049(1)	0.0119(1)

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

display similar features but are not isostructural, the difference being related to the conformation of the sulfate anions. The structure contains two independent Al^{3+} ions located on different $\bar{3}$ symmetry elements, octahedrally coordinated by sulfate anions. The latter are arranged with two possible conformations about Al1, with occupancy 0.67 (conformation **a**) and 0.33 (conformation **b**), whereas the coordination of O1 about Al2 is fixed. These different conformations can be appreciated in Fig. 3, where two projections of the infinite $[Al(SO_4)_3]_\infty$ chains made by the AlO_6 octahedra which share all their corners with sulfate tetrahedra are shown.

The prevailing conformation **a**, where all the Al-centred octahedra are eclipsed looking down the [001] direction, is different from that observed in pyracmonite and in other sulfates containing topologically similar $[Fe(SO_4)_3]_\infty$ arrangements, like ferrinatrite, $Na_3Fe(SO_4)_3{\cdot}3H_2O$ (Scordari, 1977; Scordari and Ventruti, 2009) and aluminocoquimbite $AlFe(SO_4)_3{\cdot}9H_2O$ (Demartin *et al.*, 2010*d*,*e*), where the octahedra are staggered instead, due to a twisting about the [001] direction, as for conformation **b** in the present structure.

The voids located between these parallel chains extending along [001] host the ammonium ions that are hydrogen-bonded with the neighbouring oxygen atoms of the sulfate ions not involved in the coordination with Al (Fig. 4).

The average S–O distance, calculated considering both conformations of the sulfate anions is

TABLE 5. Selected interatomic distances (Å) and angles (º) in aluminopyracmonite.

Al1−O3a ×6	1.8895(4)	Al2−O1 ×6	1.8989(3)
Al1−O3b ×6	1.8806(9)		
<Al−O>	1.891		
S−O1	1.4889(3)		
S−O2a	1.4592(4)	S−O2b	1.447(1)
S−O3a	1.4840(4)	S−O3b	1.4937(9)
S−O4a	1.4153(6)	S−O4b	1.515(1)
<S−O>	1.474		
N−H1	0.841(9)		
N−H2	0.780(6)		
N−H3	0.750(11)		
N−H4	0.800(8)		
Hydrogen bonds			
N···O2a	2.826(1)	N−H2···O2a	172.7(7)
N···O2b	3.078(1)	N−H2···O2b	164.5(7)
N···O1[a]	2.999(1)	N−H3···O1	147.9(8)
N···O2a[b]	3.078(1)	N−H1···O2a[b]	157.9(8)
N···O2b[b]	2.775(1)	N−H1···O2b[b]	163.2(9)
N···O4a[c]	2.752(1)	N−H4···O4a[c]	162.8(8)
N···O4b[c]	2.936(1)	N−H4···O4b[c]	175.9(8)

Symmetry codes: $a = y, -x+y, -z$; $b = -y+1/3, x-y-1/3, z-1/3$; $c = x - y -1/3, x -2/3, -z+1/3$

1.474 Å, and can be compared with those found in most hydrated sulfates, which fall in the range 1.47−1.48 Å (Hawthorne *et al.*, 2000) but is slightly larger than that found in pyracmonite (1.448 Å), which is in line with the values usually found in anhydrous sulfates. This lengthening, therefore, seems unusual and can probably be attributed to the presence of disorder in the sulfates. However, considering the prevailing conformation **a**, i.e. that determined with greater accuracy, an average value of 1.461 Å is obtained, which is closer to the typical values observed in anhydrous sulfates. Also the Al1−O and Al2−O distances are slightly, but significantly, different, probably for the same reason; however, their overall average is in line with that found in $Al_2(SO_4)_3$, where bridging sulfates are also present (Dahmen and Gruehn, 1993).

We have checked whether the disorder of the sulfate anions is real or is the effect of a structure determination carried out in an incorrect space group. This possibility was suggested by the existence of a trigonal-to-monoclinic ferroelastic transition in some $M^{I}_3M'^{III}(XO_4)_3$ compounds (M^{I} = NH_4^+, Tl^+; M'^{III} = In^{3+}) (Jolibois *et al.*, 1981), which can be accomplished by a slight tilting of the SO_4 tetrahedra in adjacent chains with symmetry reduction. The same authors state, on the basis of micro DTA and X-ray measurements, that such a transition occurs in two steps as they have observed an intermediate phase of point symmetry $\bar{3}$. Our X-ray diffraction data led us to rule out a monoclinic pseudorhombohedral phase for aluminopyracmonite and to suggest that we are dealing with an analogous intermediate disordered rhombohedral phase as hypothesized by Jolibois *et al.* (1981). In addition we have also tried a structure refinement in the non-centrosymmetric space group *R*3, however the disorder remains and the *R* index is worse.

A systematic investigation on ammonium-containing structures by Khan and Baur (1972) showed that the number of contacts of the N atoms with their surroundings ranges from four to nine. When the coordination number (CN) of NH_4^+ is four, then four hydrogen bonds are usually formed with a roughly tetrahedral arrangement and almost linear donor-H-acceptor interactions. For larger CN values, either the ammonium ion is disordered, or polyfurcated hydrogen bonds may be present. The same authors suggest that the ionic radius for the ammonium ion is

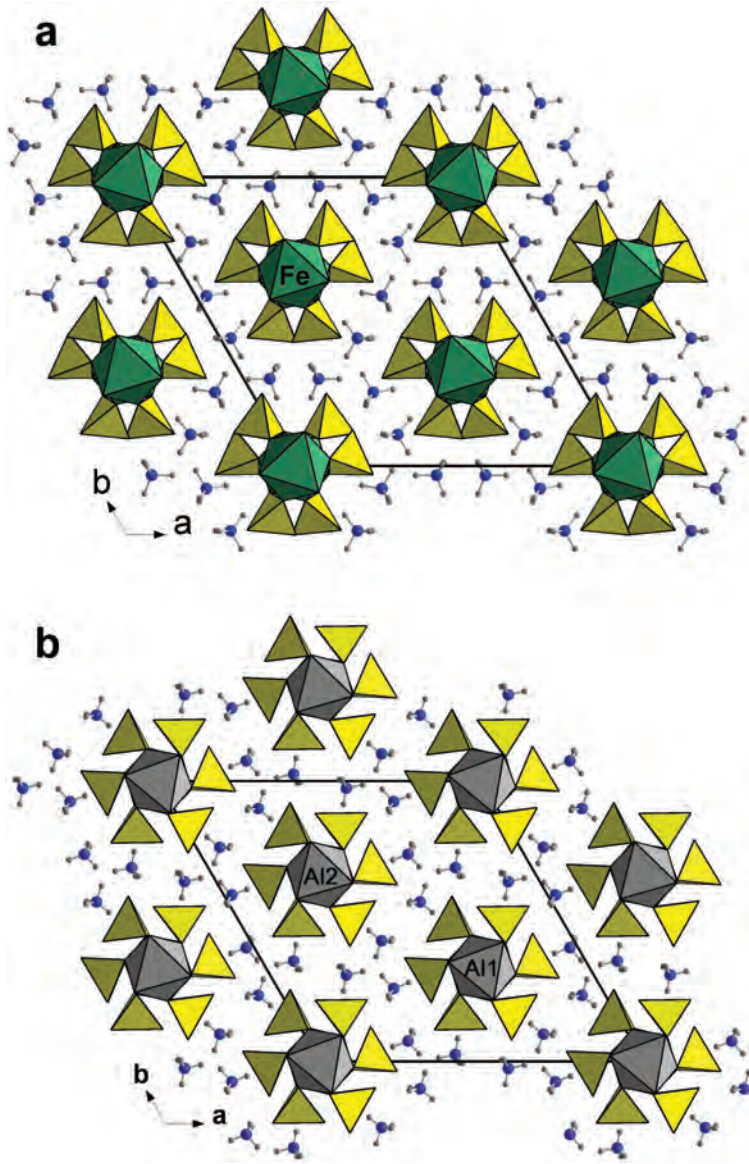

FIG. 2. A comparison of the crystal structures of pyracmonite (*a*) and aluminopyracmonite (*b*) seen along [001]. The prevalent conformation of the sulfate anions for aluminopyracmonite is shown (see above). SO_4^{2-} tetrahedra are represented in yellow and N atoms of the NH_4^+ ions in blue. Unit cell outlined.

~1.65–1.66 Å and as the radius of O^{2-} is 1.37 Å, distances of ~3.1 Å are to be expected for N···O hydrogen-bond interactions and O···H–N angles near 180º. Considering the prevailing conformation for the sulfate ions, in aluminopyracmonite the ammonium ion is surrounded by four oxygens at distances in the range 2.752(1)–3.078(1) Å corresponding to 'regular' hydrogen bonds (Fig. 4).

Anhydrous natural or synthetic ammonium aluminium sulfates are very rare. Among them the only known mineral was godovikovite $NH_4(Al,Fe^{3+})(SO_4)_2$, where Al is partly replaced by minor Fe, that was found for the first time as a

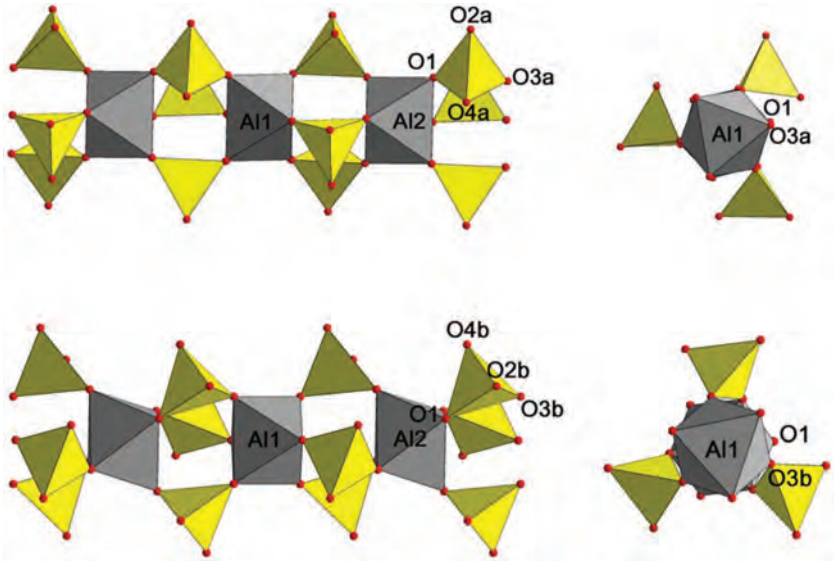

FIG. 3. Comparison of the two conformations (**a**) and (**b**) of the sulfate anions in the chains consisting of the AlO_6 distorted octahedra.

product of anthropogenic activity in the burning coal dumps at Kopeisk, Chelyabinsk Oblast, southern Urals, Russia (Shcherbakova *et al.*, 1988), and for the first time in a geological context at Vulcano (Campostrini *et al.*, 2011). The structure solution of the corresponding synthetic "anhydrous alum" $NH_4Al(SO_4)_2$, obtained on heating hydrous alum at 400ºC, was performed by Rietveld refinement from the powder-diffraction pattern and reported (Boujelben *et al.*, 2008).

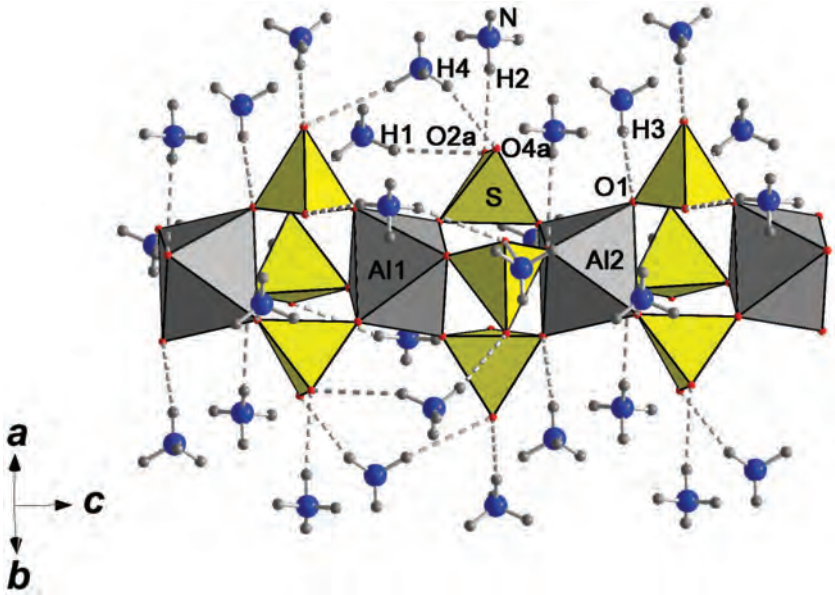

FIG. 4. The pattern of hydrogen-bonds in aluminopyracmonite. Only conformation (**a**) of the sulfate anions is shown.

Aluminopyracmonite is therefore the second known anhydrous ammonium aluminium sulfate mineral. It is interesting to note that the synthetic compound $(NH_4)_3Al(SO_4)_3$ corresponding to aluminopyracmonite was prepared by the Dow Chemical Co., Midland, Michigan, USA (private communication to the ICDD PDF-2 database, Entry #00-003-0045) by dissolving and evaporating a $(NH_4)_2SO_4{\cdot}Al_2(SO_4)_3$ + $2(NH_4)_2SO_4$ mixture and heating at 250ºC to obtain the anhydrous phase; these temperature conditions correspond to those detected at the fumarole where aluminopyracmonite was collected.

Aluminopyracmonite and pyracmonite represent additional examples of sulfate minerals having analogous chemical formulae and similar unit-cell parameters but are not isostructural, other examples being aluminocoquimbite and coquimbite (Demartin *et al*., 2010*d*,*e*) and the copiapite group minerals (Majzlan and Michallik, 2007).

Acknowledgements

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Table S1. Observed and calculated structure factors for aluminopyracmonite

h	k	l	10Fo	10Fc	10σ	h	k	l	10Fo	10Fc	10σ	h	k	l	10Fo	10Fc	10σ	h	k	l	10Fo	10Fc	10σ	h	k	l	10Fo	10Fc	10σ
-1	2	0	2082	2024	2	-10	7	1	629	655	2	-12	17	1	50	8	50	-19	12	2	110	93	22	-3	6	3	88	27	6
0	3	0	60	63	8	-7	7	1	827	802	2	-9	17	1	565	567	5	-16	12	2	327	321	7	0	6	3	50	35	14
-2	4	0	652	701	1	-4	7	1	836	800	2	-6	17	1	239	231	11	-13	12	2	433	448	6	3	6	3	478	484	3
-4	5	0	152	122	3	-1	7	1	1467	1452	2	-3	17	1	495	500	8	-10	12	2	664	688	4	6	6	3	200	202	7
-1	5	0	184	182	3	2	7	1	24	37	24	0	17	1	567	539	8	-7	12	2	891	902	3	-11	7	3	1646	1648	3
-3	6	0	575	600	2	5	7	1	282	277	5	3	17	1	282	271	17	-4	12	2	898	897	3	-8	7	3	86	114	10
0	6	0	481	521	2	-15	8	1	485	486	5	-17	18	1	358	358	8	-1	12	2	316	326	5	-5	7	3	54	57	14
-5	7	0	628	594	2	-12	8	1	935	957	3	-14	18	1	73	65	33	2	12	2	224	231	9	-2	7	3	552	547	2
-2	7	0	874	916	2	-9	8	1	62	25	12	-11	18	1	756	754	6	5	12	2	465	465	8	1	7	3	204	189	4
-7	8	0	1317	1279	2	-6	8	1	154	145	4	-8	18	1	82	94	28	8	12	2	367	371	10	4	7	3	362	360	4
-4	8	0	401	422	4	-3	8	1	386	423	3	-5	18	1	197	194	14	-21	13	2	213	203	16	7	7	3	63	47	25
-1	8	0	1506	1500	2	0	8	1	391	399	3	-2	18	1	166	161	17	-18	13	2	523	516	6	-13	8	3	459	469	5
-6	9	0	123	132	6	3	8	1	538	518	3	1	18	1	21	57	20	-15	13	2	247	238	8	-10	8	3	698	704	3
-3	9	0	349	331	3	6	8	1	148	148	8	-19	19	1	105	117	48	-12	13	2	29	14	29	-7	8	3	113	107	7
0	9	0	1004	969	2	-17	9	1	151	149	12	-16	19	1	0	27	1	-9	13	2	24	16	24	-4	8	3	1766	1771	3
-8	10	0	916	901	2	-14	9	1	795	800	4	-13	19	1	65	61	64	-6	13	2	235	232	6	-1	8	3	29	39	29
-5	10	0	210	210	5	-11	9	1	546	559	4	-10	19	1	293	272	9	-3	13	2	27	13	26	2	8	3	688	712	3
-2	10	0	236	226	4	-8	9	1	927	939	2	-7	19	1	276	268	11	0	13	2	123	119	15	5	8	3	69	72	20
-10	11	0	44	81	34	-5	9	1	1118	1145	2	-4	19	1	537	518	9	3	13	2	604	596	6	8	8	3	60	57	39
-7	11	0	1207	1209	2	-2	9	1	93	77	7	-1	19	1	94	105	67	6	13	2	239	250	14	-15	9	3	677	674	4
-4	11	0	619	624	3	1	9	1	528	528	3	-15	20	1	58	30	57	-20	14	2	39	5	38	-12	9	3	1266	1297	3
-1	11	0	0	54	1	4	9	1	106	105	11	-12	20	1	83	103	38	-17	14	2	346	333	8	-9	9	3	802	809	3
-9	12	0	420	420	4	7	9	1	842	840	4	-9	20	1	86	77	35	-14	14	2	233	229	8	-6	9	3	623	638	3
-6	12	0	1496	1513	3	-19	10	1	179	186	11	-6	20	1	135	144	21	-11	14	2	398	391	6	-3	9	3	576	579	3
-3	12	0	125	128	8	-16	10	1	558	554	5	-14	21	1	46	7	45	-8	14	2	534	532	4	0	9	3	558	565	3
0	12	0	540	539	5	-13	10	1	15	5	15	-11	21	1	395	368	13	-5	14	2	542	553	4	3	9	3	354	355	5
-11	13	0	222	215	7	-10	10	1	612	603	3	-8	21	1	121	93	36	-2	14	2	414	419	7	6	9	3	103	103	17
-8	13	0	1594	1599	3	-7	10	1	290	287	5	0	1	2	1671	1719	2	1	14	2	548	564	6	9	9	3	225	221	10
-5	13	0	347	346	5	-4	10	1	457	444	3	-2	2	2	567	474	1	4	14	2	136	114	20	-17	10	3	339	328	8
-2	13	0	640	670	4	-1	10	1	248	249	5	1	2	2	2351	2304	2	7	14	2	73	32	72	-14	10	3	136	137	10
-13	14	0	318	310	7	2	10	1	110	85	10	-4	3	2	1723	1710	6	-19	15	2	422	400	9	-11	10	3	410	423	4
-10	14	0	422	423	5	5	10	1	59	69	29	-1	3	2	1693	1662	3	-16	15	2	262	282	8	-8	10	3	767	765	3
-7	14	0	785	774	4	8	10	1	641	630	5	2	3	2	37	16	21	-13	15	2	328	321	7	-5	10	3	691	698	3
-4	14	0	142	144	9	-21	11	1	223	237	19	-6	4	2	305	281	3	-10	15	2	561	554	5	-2	10	3	388	409	4
-1	14	0	734	727	5	-18	11	1	28	38	28	-3	4	2	1297	1311	3	-7	15	2	498	499	5	1	10	3	694	692	3
-12	15	0	324	298	7	-15	11	1	522	515	5	0	4	2	774	784	1	-4	15	2	187	190	10	4	10	3	634	630	5
-9	15	0	0	19	1	-12	11	1	247	257	6	3	4	2	1070	1056	2	-1	15	2	211	186	10	7	10	3	315	311	9
-6	15	0	173	176	9	-9	11	1	965	938	3	-8	5	2	152	160	4	2	15	2	268	259	10	10	10	3	0	51	1
-3	15	0	674	671	5	-6	11	1	158	159	6	-5	5	2	1372	1379	2	5	15	2	322	290	11	-19	11	3	79	63	43
0	15	0	23	49	22	-3	11	1	877	900	3	-2	5	2	1124	1132	2	-18	16	2	375	372	8	-16	11	3	436	421	7
-14	16	0	128	120	15	0	11	1	602	605	4	1	5	2	757	702	2	-15	16	2	309	320	8	-13	11	3	74	83	23

-11	16	0	405	399	7	3	11	1	701	704	4	4	5	2	1143	1158	2	-12	16	2	439	441	7	-10	11	3	661	651	4
-8	16	0	220	218	8	6	11	1	506	512	7	-10	6	2	1181	1170	2	-9	16	2	634	648	5	-7	11	3	29	14	29
-5	16	0	164	167	12	9	11	1	23	4	23	-7	6	2	915	967	2	-6	16	2	622	613	5	-4	11	3	1349	1369	3
-2	16	0	250	221	8	-20	12	1	0	27	1	-4	6	2	299	304	3	-3	16	2	130	136	19	-1	11	3	125	131	10
-16	17	0	142	160	15	-17	12	1	195	177	11	-1	6	2	693	634	2	0	16	2	524	532	8	2	11	3	28	47	28
-13	17	0	172	184	11	-14	12	1	26	62	25	2	6	2	1018	1002	2	3	16	2	0	50	1	5	11	3	0	1	1
-10	17	0	101	102	20	-11	12	1	0	7	1	5	6	2	0	15	1	-20	17	2	97	104	41	8	11	3	260	250	11
-7	17	0	150	158	12	-8	12	1	387	408	5	-12	7	2	211	212	6	-17	17	2	469	475	7	-21	12	3	132	137	32
-4	17	0	97	116	23	-5	12	1	421	421	4	-9	7	2	196	179	4	-14	17	2	149	158	13	-18	12	3	146	137	16
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-15	18	0	546	556	6	1	12	1	420	428	6	-3	7	2	67	80	10	-8	17	2	353	335	7	-12	12	3	341	343	7
-12	18	0	209	215	11	4	12	1	247	241	8	0	7	2	613	641	2	-5	17	2	433	423	9	-9	12	3	461	468	5
-9	18	0	0	21	1	7	12	1	230	229	12	3	7	2	1077	1053	2	-2	17	2	518	521	8	-6	12	3	455	473	4
-6	18	0	398	412	8	-19	13	1	112	124	21	6	7	2	973	997	4	1	17	2	346	343	12	-3	12	3	1145	1162	4
-3	18	0	192	182	14	-16	13	1	52	83	51	-14	8	2	438	434	5	-19	18	2	162	172	22	0	12	3	340	347	7
0	18	0	27	5	26	-13	13	1	45	61	44	-11	8	2	1144	1142	3	-16	18	2	285	281	10	3	12	3	573	575	7
-17	19	0	63	96	63	-10	13	1	129	127	10	-8	8	2	291	308	4	-13	18	2	52	51	51	6	12	3	0	12	1
-14	19	0	833	831	6	-7	13	1	155	153	8	-5	8	2	1427	1395	2	-10	18	2	440	438	7	9	12	3	203	208	31
-11	19	0	56	17	55	-4	13	1	144	160	8	-2	8	2	275	306	3	-7	18	2	160	139	16	-20	13	3	0	9	1
-8	19	0	784	787	6	-1	13	1	209	229	8	1	8	2	62	66	13	-4	18	2	661	648	8	-17	13	3	192	203	11
-5	19	0	241	252	12	2	13	1	520	534	5	4	8	2	489	486	4	-1	18	2	150	153	19	-14	13	3	184	211	10
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-16	20	0	568	579	10	8	13	1	359	366	13	-16	9	2	536	545	5	-15	19	2	470	458	8	-8	13	3	178	192	8
-13	20	0	255	252	10	-21	14	1	115	94	31	-13	9	2	840	841	4	-12	19	2	183	186	15	-5	13	3	94	107	16
-10	20	0	234	235	11	-18	14	1	341	352	8	-10	9	2	547	534	3	-9	19	2	49	55	48	-2	13	3	190	192	8
-7	20	0	698	682	8	-15	14	1	178	164	10	-7	9	2	411	409	3	-6	19	2	0	56	1	1	13	3	131	125	13
-4	20	0	205	211	15	-12	14	1	728	744	5	-4	9	2	897	898	2	-3	19	2	184	163	16	4	13	3	148	155	17
-12	21	0	195	176	15	-9	14	1	158	164	9	-1	9	2	429	413	3	-17	20	2	226	227	29	7	13	3	90	61	35
-9	21	0	568	549	10	-6	14	1	638	657	4	2	9	2	1049	1058	3	-14	20	2	212	185	14	-19	14	3	245	232	11
-11	22	0	0	46	1	-3	14	1	174	179	9	5	9	2	224	221	6	-11	20	2	300	296	11	-16	14	3	211	205	10
-1	1	1	265	262	1	0	14	1	324	323	7	8	9	2	470	472	6	-8	20	2	387	377	10	-13	14	3	158	155	11
-3	2	1	1338	1288	2	3	14	1	123	124	18	-18	10	2	145	146	13	-5	20	2	242	257	13	-10	14	3	401	393	6
0	2	1	384	370	1	6	14	1	212	201	16	-15	10	2	671	685	4	-13	21	2	275	269	21	-7	14	3	154	157	10
-5	3	1	935	968	2	-20	15	1	49	78	49	-12	10	2	307	291	6	-10	21	2	264	252	17	-4	14	3	68	65	27
-2	3	1	1547	1507	3	-17	15	1	205	201	10	-9	10	2	1105	1124	2	0	0	3	826	837	5	-1	14	3	168	186	12
1	3	1	3142	3196	3	-14	15	1	549	546	6	-6	10	2	979	972	2	1	1	3	1514	1499	3	2	14	3	209	209	12
-7	4	1	202	170	3	-11	15	1	474	475	6	-3	10	2	623	632	3	-1	2	3	1252	1234	2	5	14	3	233	215	13
-4	4	1	715	745	2	-8	15	1	319	315	6	0	10	2	670	663	3	2	2	3	724	798	2	-18	15	3	391	364	8
-1	4	1	1865	1867	2	-5	15	1	902	904	4	3	10	2	505	503	4	-3	3	3	996	972	1	-15	15	3	267	279	8
2	4	1	973	956	2	-2	15	1	108	117	16	6	10	2	362	370	7	0	3	3	1169	1141	2	-12	15	3	737	748	6
-9	5	1	557	580	2	1	15	1	265	256	9	9	10	2	87	74	33	3	3	3	478	444	2	-9	15	3	222	218	8
-6	5	1	1991	1917	3	4	15	1	118	111	24	-20	11	2	229	222	13	-5	4	3	791	725	2	-6	15	3	703	704	5
-3	5	1	1995	2041	4	-19	16	1	237	206	11	-17	11	2	151	145	12	-2	4	3	867	919	2	-3	15	3	157	154	13
0	5	1	718	690	2	-16	16	1	471	473	7	-14	11	2	158	153	10	1	4	3	719	748	2	0	15	3	428	434	9
3	5	1	266	296	3	-13	16	1	346	345	8	-11	11	2	997	1010	4	4	4	3	1445	1450	2	3	15	3	271	265	11
-11	6	1	95	97	10	-10	16	1	526	528	5	-8	11	2	861	856	3	-7	5	3	511	487	3	-17	16	3	338	337	9
-8	6	1	51	47	13	-7	16	1	310	314	7	-5	11	2	513	503	3	-4	5	3	227	272	4	-14	16	3	106	111	21

-5	6	1	69	39	7	-4	16	1	151	176	13	-2	11	2	596	587	3	-1	5	3	637	608	2	-11	16	3	206	208	9
-2	6	1	274	263	2	-1	16	1	41	4	40	1	11	2	536	536	4	2	5	3	506	491	2	-8	16	3	71	50	28
1	6	1	489	470	2	2	16	1	527	502	8	4	11	2	711	687	5	5	5	3	999	1002	2	-5	16	3	403	402	7
4	6	1	1396	1388	2	-18	17	1	259	249	9	7	11	2	219	229	12	-9	6	3	70	59	11	-2	16	3	107	120	25
-13	7	1	11	3	11	-15	17	1	275	272	8	10	11	2	252	239	18	-6	6	3	284	283	4	1	16	3	765	727	8
-19	17	3	199	224	17	-14	12	4	1017	1007	4	-11	8	5	1095	1086	3	-1	2	6	244	218	4	-14	16	6	523	517	9
-16	17	3	577	571	7	-11	12	4	62	74	26	-8	8	5	576	584	3	2	2	6	1146	1142	3	-11	16	6	598	599	6
-13	17	3	187	180	12	-8	12	4	792	797	4	-5	8	5	1068	1070	3	-3	3	6	1228	1228	2	-8	16	6	383	392	8
-10	17	3	299	298	8	-5	12	4	457	464	5	-2	8	5	454	471	4	0	3	6	324	333	4	-5	16	6	232	241	10
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