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PYRACMONITE, $(NH_4)_3Fe(SO_4)_3$, A NEW AMMONIUM IRON SULFATE FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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Abstract

The new mineral species *pyracmonite*, ideally $(NH_4)_3Fe(SO_4)_3$, was found in a medium-temperature (~250°C) active intracrater fumarole at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. It occurs on a pyroclastic breccia as colorless to white prismatic crystals up to 0.2 mm in length, in association with salammoniac and kremersite. The mineral is trigonal, space group $R3c$ (no. 161) with a 15.2171(14), c 8.9323(8) Å, V 1791.3(3) $Å^3$ and $Z = 6$. The strongest six reflections in the X-ray powder-diffraction pattern [d_{obs} in Å(I)(hkl)] are: 7.596(100)(110), 3.320(30)(122), 3.371(26)(131), 4.358(23)($12\bar{1}$), 2.829(14)(312), and 2.863(8)(321). The empirical formula, based on 12 anions, is $[(NH_4)_{2.74}K_{0.23}]_{\Sigma 2.97}(Fe_{0.94}Al_{0.04})_{\Sigma 0.98}S_{3.02}O_{12}$, and the simplified formula $(NH_4,K)_3(Fe,Al)(SO_4)_3$. The measured density is 2.22(1) g/cm^3, and D_{calc} is 2.228 g/cm^3. The mineral is uniaxial, and the average index of refraction index is 1.562(3) (λ = 589 nm). Using single-crystal X-ray-diffraction data, the structure was refined to a final $R(F) = 0.039$ for 1010 independent observed reflections [$I > 2\sigma(I)$]. The mineral is identical to the synthetic compound $(NH_4)_3Fe(SO_4)_3$ and is isostructural to the high-temperature phase of the synthetic compound $(NH_4)_3In(SO_4)_3$. Building blocks of the structure are $(Fe,Al)O_6$ octahedra and SO_4 tetrahedra, which are linked together to form infinite columns $[(Fe,Al)(SO_4)_3]_\infty$ along [001]. The two independent (Fe,Al)–O distances are 1.959(1) and 1.998(1) Å; in the sulfate anion, the S–O distances range from 1.415(2) to 1.485(1) Å. The ammonium ions, only partly replaced by K^+ ions, interact with the oxygen atoms of the sulfate groups *via* hydrogen bonds.

Keywords: pyracmonite, new mineral species, crystal structure, ammonium sulfates, iron sulfates, Vulcano Island, Italy.

Sommaire

Nous avons découvert la nouvelle espèce minérale *pyracmonite*, de composition idéale $(NH_4)_3Fe(SO_4)_3$, dans une fumerolle active de température moyenne (~250°C) au sein du cratère La Fossa, à Vulcano, îles Éoliennes, en Sicile, Italie. Elle se présente en cristaux prismatiques incolores ou blancs atteignant une longueur de 0.2 mm sur des fragments bréchifiés pyroclastiques en association avec salammoniac et kremersite. C'est un minéral trigonal, groupe spatial $R3c$ (no. 161) avec a 15.2171(14), c 8.9323(8) Å, V 1791.3(3) $Å^3$ et $Z = 6$. Les six raies les plus intenses du spectre de diffraction X, méthode des poudres [d_{obs} en Å(I)(hkl)] sont: 7.596(100)(110), 3.320(30)(122), 3.371(26)(131), 4.358(23)($12\bar{1}$), 2.829(14)(312), et 2.863(8)(321). La formule empirique, fondée sur 12 anions, est $[(NH_4)_{2.74}K_{0.23}]_{\Sigma 2.97}(Fe_{0.94}Al_{0.04})_{\Sigma 0.98}S_{3.02}O_{12}$, et la formule simplifiée est $(NH_4,K)_3(Fe,Al)(SO_4)_3$. La densité mesurée est 2.22(1) g/cm^3, et la densité calculée est 2.228 g/cm^3. Il s'agit d'un minéral uniaxe, et l'indice de réfraction moyen est 1.562(3) (λ = 589 nm). Nous en avons affiné la structure sur monocristal par diffraction X jusqu'à un résidu final $R(F)$ de 0.039 pour 1010 réflexions observées indépendantes [$I > 2\sigma(I)$]. Le minéral est identique au composé synthétique $(NH_4)_3Fe(SO_4)_3$, et il possède la même structure que la forme de haute température du composé $(NH_4)_3In(SO_4)_3$. Les éléments structuraux sont les octaèdres $(Fe,Al)O_6$ et les tétraèdres SO_4, qui sont connectés pour former des colonnes infinies $[(Fe,Al)(SO_4)_3]_\infty$ le long de [001]. Les deux distances (Fe,Al)–O indépendantes sont 1.959(1) et 1.998(1) Å; dans le groupe anionique sulfate, les distances S–O vont de 1.415(2) à 1.485(1) Å. Les ions ammonium, remplacés en partie seulement par les ions K^+, interagissent avec les atomes d'oxygène des groupes sulfate grâce aux liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: pyracmonite, nouvelle espèce minérale, structure cristalline, sulfates d'ammonium, sulfates de fer, île de Vulcano, Italie.

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INTRODUCTION

In the last few years, a systematic investigation of the fumarole system at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy, has led to the discovery of several rare and new minerals (see for details Garavelli *et al.* 2005, Campostrini *et al.* 2008, Demartin *et al.* 2009a, 2009b, 2009c, 2009d, 2010a). In particular, the medium- to low-temperature intracrater fumaroles have led to a suite of unusual ammonium-bearing sulfates. One of these, the new species pyracmonite $(NH_4)_3Fe(SO_4)_3$ is described in the present work, together with its crystal structure.

The mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2008–029). The name is after the Greek words πνρ = "fire" and ακμων = "anvil"; it recalls the mythical Hephaistos's workshop, which allegedly was located on the Island of Vulcano. Holotype material is deposited in the Reference Collection of the Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, specimen number 2008–04.

OCCURRENCE, CHEMICAL DATA AND PHYSICAL PROPERTIES

Pyracmonite occurs in an active medium-temperature (~250°C) intracrater fumarole developed on a pyroclastic breccia. It is associated with salammoniac, kremersite, $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$, and other new sulfates and halides currently under investigation. The mineral forms aggregates of colorless to white elongate hexagonal prismatic crystals up to 0.2 mm in length (Fig. 1). No twinning is apparent. The *c:a* ratio calculated from the unit-cell parameters is 0.587. The mineral is not hygroscopic and is stable in air. The streak is white, and the luster is vitreous. Cleavage and fracture were not observed. No fluorescence was observed both under short- and long-wavelength ultraviolet radiation.

The density, measured by flotation in a tribromomethane–trichloromethane mixture, is 2.22(1) g/cm^3; the density calculated on the basis of the empirical formula and the X-ray data is 2.228 g/cm^3. The mineral is uniaxial; the average index of refraction is 1.562(3) (589 nm); the corresponding Gladstone–Dale value calculated using Mandarino's constants (1981) is 1.562, leading to a compatibility index $[1 - (K_P/K_C)] = 0.022$ (excellent).

Quantitative chemical analyses (12) were carried out in energy-dispersion 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 $K\alpha$ lines for Fe, Al, K and S. The presence of ammonium was established from crystal-structure analysis and was also confirmed by microchemical tests using the Nessler reaction. The infrared spectrum shows the following absorption peaks at 3203(vs), 3064(s) and 1430(vs) cm^{-1}, consistent with the presence of the ammonium ion. The mean analytical results are reported in Table 1. The empirical formula (based on 12 anions) is: $[(NH_4)_{2.74}K_{0.23}]_{\Sigma 2.97}(Fe_{0.94}Al_{0.04})_{\Sigma 0.98}S_{3.02}O_{12}$ corresponding to a simpli-

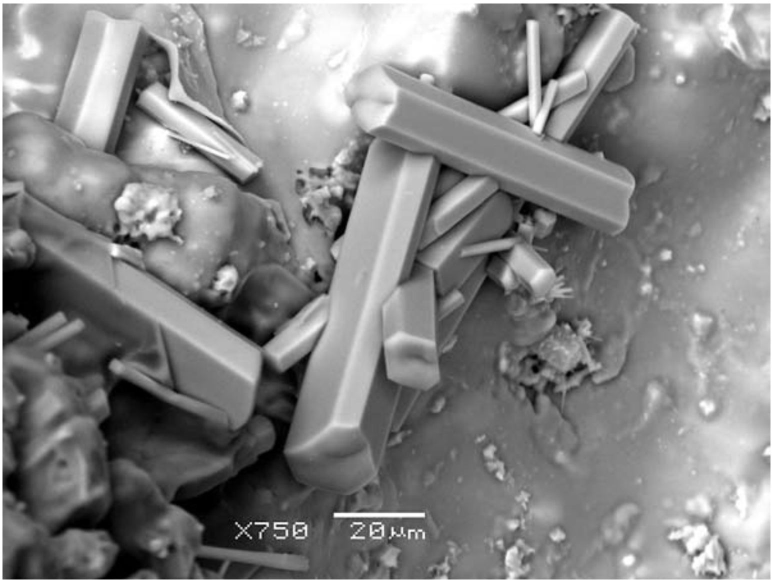

FIG. 1. SEM–BSE image of crystals of pyracmonite.

fied formula $(NH_4,K)_3(Fe,Al)(SO_4)_3$. The end-member formula is $(NH_4)_3Fe(SO_4)_3$, which requires: $(NH_4)_2O$ 19.62, Fe_2O_3 20.05, SO_3 60.33, total 100.00 wt.%.

X-RAY DATA

X-ray powder-diffraction data (Table 2) have been obtained using a Bruker D8 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. We obtained the following parameters *a* 15.218(2), *c* 8.937(1) Å of the trigonal unit-cell in the hexagonal setting from a least-squares refinement from the above data using the program UNITCELL (Holland & Redfern 1997).

The unit-cell parameters obtained from 2730 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 5148 intensities corresponding to a complete scan of the reciprocal lattice up to 2θ = 59.22° were collected from a crystal (0.12 × 0.02 × 0.02 mm) using a Bruker Apex II diffractometer equipped with a 2K CCD detector and Mo*K*α radiation (λ = 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 ($\mu = 1.78$ mm^{-1}, T_{min} 0.84) was applied using the SADABS program (Sheldrick 2000). After averaging the symmetry-related reflections (R_{int}= 0.029), 1064 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). The occupancy of the iron site, which is partly replaced by aluminum, and that of the ammonium site, which is partly replaced by potassium, were also refined. 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 atomic displacement parameters, whereas anisotropic displacement parameters were considered instead for all the other atoms. The final *R* is 0.039 for 1010 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. Tables of observed and calculated structure-factors may be obtained from The Depository of Unpublished Data on the MAC website [document Pyracmonite CM48_307].

TABLE 1. CHEMICAL COMPOSITION OF PYRACMONITE

Constituent	wt.%	Range	Probe standard
$(NH_4)_2O$*	17.85	-	
K_2O	2.77	2.65 – 2.91	KCl
Fe_2O_3	18.70	18.02 – 19.13	Almandine
Al_2O_3	0.50	0.10 – 0.92	Almandine
SO_3	60.47	59.60 – 61.40	Synthetic anhydrite
Total	100.29		

* Obtained from the occupancy of the site in the crystal-structure refinement.

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR PYRACMONITE AND COMPARISON WITH SYNTHETIC $(NH_4)_3Fe(SO_4)_3$ AND $(NH_4)_3Al(SO_4)_3$#

pyracmonite						$(NH_4)_3Fe(SO_4)_3$		$(NH_4)_3Al(SO_4)_3$	
h	*k*	*l*	*I/Io*	d_{obs} (Å)	d_{calc} (Å)*	d_{obs} (Å)	*I/Io*	d_{obs} (Å)	*I/Io*
1	1	0	100	7.596	7.609	7.60	100	7.50	100
0	3	0	5	4.384	4.393				
1	2	$\bar{1}$	23	4.358	4.351	4.34	15	4.30	50
0	1	2	5	4.247	4.232	4.12	4	4.19	20
0	2	$\bar{2}$	2	3.691	3.698	3.71	10		
1	3	1	26	3.371	3.383				
1	2	2	30	3.320	3.326	3.34	40	3.32	83
3	2	1	8	2.863	2.864	2.85	15	2.81	20
3	1	2	14	2.829	2.829				
1	1	3	5	2.771	2.774			2.74	13
0	4	2	4	2.656	2.652	2.65	8	2.64	4
2	3	2	5	2.508	2.504	2.50	8	2.46	5
1	5	$\bar{1}$	3	2.290	2.288	2.29	4	2.26	10
0	6	0	2	2.196	2.196	2.17	3		
1	5	2	5	2.092	2.092	2.10	8	2.07	4
1	3	4	3	1.906	1.906	1.91	2	1.93	5
1	7	0	5	1.746	1.745	1.75	4		
2	5	3	5	1.722	1.722			1.72	5
0	5	4	4	1.704	1.704	1.71	2	1.68	13
1	5	$\bar{4}$	5	1.625	1.625	1.63	4	1.60	5

* Calculated from the unit cell : *a* 15.218 (2), *c* 8.937(1) Å, obtained from least-squares refinement from the above data using the program UNITCELL (Holland & Redfern 1997).

\# ICDD PDF–2 entries 00–003–0043 and 00–003–0045; data provided by the Dow Chemical Co., Midland, Michigan, U.S.A., as a private communication to the PDF–2 database.

TABLE 3. SINGLE-CRYSTAL DIFFRACTION DATA AND REFINEMENT PARAMETERS FOR PYRACMONITE

Crystal system	trigonal	Space group	*R*3*c* (no. 161)
a (Å)	15.2171(14)	Radiation	Mo*K*α
c (Å)	8.9323(8)	μ (mm^{-1})	1.87
V (Å^3)	1791.3(3)	D_{calc} (g/cm^3)*	2.243
Z	6		
Measured reflections		5148	
Independent reflections		1064	
Observed reflections [$I > 2\sigma(I)$]		1010	
Parameters refined		76	
Final *R* and *wR*2 (all data)		0.039, 0.101	
S		1.103	

Notes: $R = \Sigma ||Fo| - |Fc|| / \Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (0.0572q)^2 + 6.9446q]$, 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.

* Density calculated using the composition derived from the occupancy refinement.

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS [$U_{EQ}/U_{(I,J)}$] OF ATOMS IN PYRACMONITE

Atom	Site occupancy	X/a	Y/b	Z/c	U_{eq}/U
(Fe,Al)	Fe 0.893(2) Al 0.107(2)	0	0	0.13800(4)	0.01631(6)
S	1	0.16913(2)	0.14291(2)	0.38360(3)	0.02027(7)
(N,K)	N 0.867(2) K 0.133(2)	0.07773(6)	0.30174(6)	0.24189(11)	0.0322(2)
O(1)	1	0.1198(1)	0.0934(1)	0.5215(1)	0.0585(5)
O(2)	1	0.09084(8)	0.11849(7)	0.2668(1)	0.0299(3)
O(3)	1	0.2218(1)	0.2516(1)	0.4072(2)	0.0693(6)
O(4)	1	0.2384(1)	0.1128(1)	0.3339(2)	0.0730(4)
H(1)	0.867*	0.031(2)	0.307(2)	0.264(3)	0.059(7)
H(2)	0.867*	0.113(1)	0.342(2)	0.169(3)	0.047(7)
H(3)	0.867*	0.066(2)	0.244(2)	0.207(4)	0.077(9)
H(4)	0.867*	0.112(2)	0.332(2)	0.323(4)	0.091(10)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
(Fe,Al)	0.01909(7)	0.01909(7)	0.0107(1)	0	0	0.00954(4)
S	0.01528(9)	0.02044(10)	0.0189(1)	-0.0021(1)	0.0006(1)	0.00431(7)
(N,K)	0.0315(3)	0.0324(3)	0.0330(4)	0.0048(3)	-0.0011(3)	0.0163(2)
O(1)	0.0390(6)	0.0803(8)	0.0184(5)	0.0180(5)	0.0043(5)	0.0013(6)
O(2)	0.0384(4)	0.0252(4)	0.0216(4)	-0.0034(3)	-0.0095(4)	0.0126(3)
O(3)	0.0732(9)	0.0238(5)	0.0685(8)	-0.016(6)	-0.0324(8)	-0.0075(6)
O(4)	0.0513(4)	0.1238(7)	0.0721(8)	-0.0514(6)	-0.0266(5)	0.0650(3)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(U_{11}h^2(a^*)^2 + ... + 2U_{12}hka^*b^* + ...)$; $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$. * The occupancy of the H atoms was constrained to be equal to that of the N atom.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN PYRACMONITE

(Fe,Al) – O(1) × 3	1.959(1)	O(1) – (Fe,Al) – O(1) × 3	94.38(4)
(Fe,Al) – O(2) × 3	1.998(1)	O(1) – (Fe,Al) – O(2) × 3	88.15(6)
<(Fe,Al) – O>	1.979	O(1) – (Fe,Al) – O(2) × 3	87.22(6)
		O(1) – (Fe,Al) – O(2) × 3	176.90(5)
S – O(1)	1.443(1)	O(2) – (Fe,Al) – O(2) × 3	90.17(4)
S – O(2)	1.485(1)	O(1) – S – O(2)	109.05(7)
S – O(3)	1.448(1)	O(1) – S – O(3)	108.58(9)
S – O(4)	1.415(2)	O(1) – S – O(4)	112.1(1)
<S – O>	1.448	O(2) – S – O(3)	107.74(8)
		O(2) – S – O(4)	109.43(8)
N – H(1)	0.78(3)	O(3) – S – O(4)	109.83(9)
N – H(2)	0.87(2)	<O – S – O>	109.45
N – H(3)	0.86(4)		
N – H(4)	0.88(3)		

Hydrogen bonds and N···O short interactions

N···O(3)^{a}	2.894(2)	N – H(1)···O(3)^{a}	158(3)
N···O(4)^{b}	2.909(2)	N – H(2)···O(4)^{b}	172(2)
N···O(2)	2.902(2)	N – H(3)···O(2)	140(3)
N···O(4)^{c}	3.096(2)	N – H(4)···O(4)^{c}	169(3)
N···O(1)^{d}	3.379(2)	N···O(3)^{d}	3.082(2)
N···O(3)	3.040(2)	N···O(4)^{e}	2.914(1)

Symmetry codes: a = x – 1/3, x – y +1/3, z – 1/6; b = y – x + 1/3, –x + 2/3, z – 1/3; c = –y +1/3, –x + 2/3, z + 1/6; d = y – x, y, z – 1/2; e = –y, x – y, z.

DESCRIPTION OF THE STRUCTURE

A projection of the cystal structure along [001] is shown in Figure 2. The structure contains infinite $[(Fe^{3+},Al)(SO_4)_3]_\infty$ columns made of slightly distorted $(Fe^{3+},Al)O_6$ octahedra, which share all their corners with sulfate tetrahedra (Fig. 3). Each column is arranged about a three-fold axis, where the (Fe^{3+},Al) atoms reside, and therefore all the sulfate ions are crystallographically equivalent. The voids located between these parallel colums host the ammonium ions (with only minor replacement by potassium ions); the hydrogen atoms are ordered and interact *via* H-bonds with the neighboring oxygen atoms of the sulfate ions. Although the crystal structures of the synthetic Fe and Al counterparts have not been determined yet, this structure type was observed for the first time in the high-temperature phase of $(NH_4)_3In(SO_4)_3$ (Jolibois *et al.* 1981). On looking at the structure down [001], a small twisting of adjacent octahedra about the three-fold axis can be observed. Infinite $[Fe(SO_4)_3]_\infty$ columns similar to those found here are also present in ferrinatrite, $Na_3Fe(SO_4)_3•3H_2O$ (Scordari 1977, Scordari & Ventruti 2009) and in aluminocoquimbite $AlFe(SO_4)_3•9H_2O$ (Demartin *et al.* 2010b). The (Fe^{3+},Al)-centered octa-

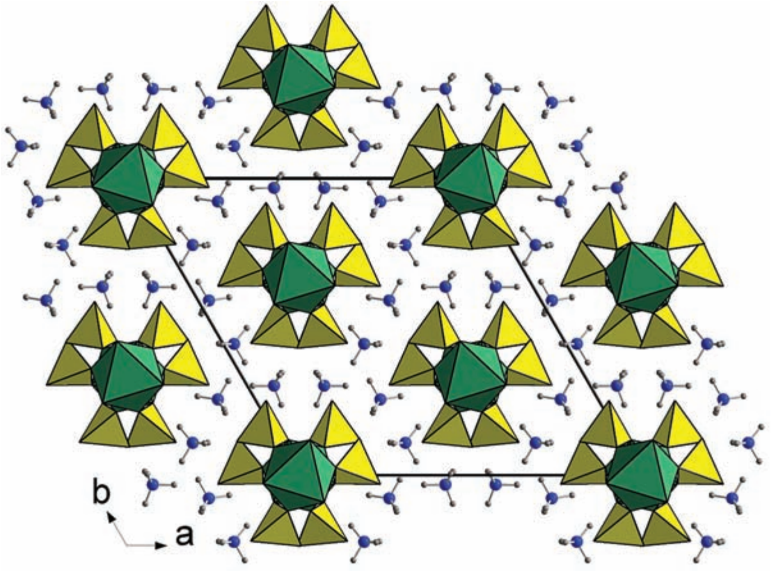

FIG. 2. The crystal structure of pyracmonite seen along [001]. The (Fe,Al)O_6 octahedra are shown in green, the sulfate anions in yellow, the N atoms of the NH_4^+ ions in blue.

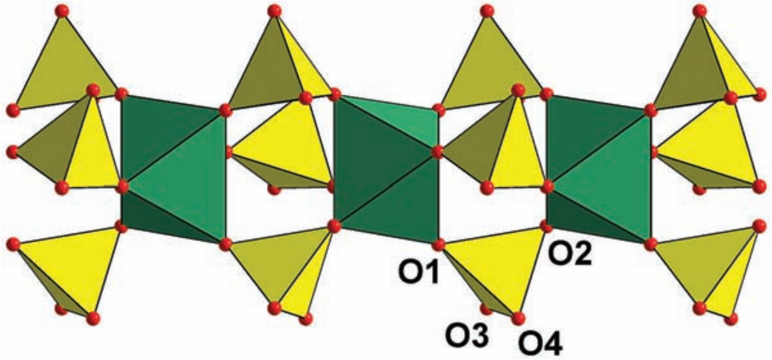

FIG. 3. Portion of the columns consisting of the (Fe,Al)O_6 distorted octahedra (green) and SO_4 tetrahedra (yellow).

hedron is slightly flattened and displays three short metal–oxygen distances [1.959(1) Å] and three longer ones [1.998(1) Å]. Because of partial replacement of iron by aluminum in pyracmonite, the average value of these distances, 1.979 Å, is slightly shorter than a typical value for Fe^{3+}–O distances, which can be observed for instance in ferrinatrite (1.995 Å).

The average S–O distance, 1.448 Å, can be compared with that found in $(NH_4)_3In(SO_4)_3$ (1.451 Å); it is slightly shorter than the averages found in most hydrated sulfates, which fall in the range 1.47–1.48 Å (Palmer *et al.* 1972, and references therein, Hawthorne *et al.* 2000). This shortening is an indirect consequence of the weaker O···H–N hydrogen-bond interactions between the oxygen atoms of the sulfate ions and the ammonium ion with respect to the O···H–O interactions between the sulfate ions and H_2O. A significant example in this respect is provided once again by ferrinatrite, $Na_3Fe(SO_4)_3$•$3H_2O$ (Scordari 1977, Scordari & Ventruti 2009). Here, similar $[Fe(SO_4)_3]_\infty$ columns are present, but the sulfate ions interact instead with H_2O molecules rather than ammonium ions, and the average S–O bond length is 1.480 Å.

In a survey of ammonium-containing structures, Khan & Baur (1972) have pointed out that the number of contacts of the N atoms ranges from four to nine. Where 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. Where the CN is instead larger, 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 about 1.65–1.66 Å with CN 7 or 8. Considering that the radius of O^{2-} is 1.37 Å, distances of about 3.1 Å are to be expected for N···O hydrogen-bond interactions, and O···H–N angles near 180°. In pyracmonite, the ammonium ion is surrounded by eight atoms of oxygen at distances in the range 2.894(2) – 3.379(2) Å, and therefore displays CN 8 or 7+1, considering that seven of these distances are below 3.09 Å. Among these, only four interactions correspond to "regular" hydrogen bonds (Fig. 4), whereas the others can be considered as short contacts arising from polyfurcated hydrogen bonds, where the same hydrogen atom of the ammonium ion bridges two different oxygen atoms. In view of such a situation, the ammonium ion displays a dual behavior, intermediate between that of an ordered hydrogen-bonding donor group and that of a large alkaline cation (Catti & Franchini-Angela 1976).

Anhydrous natural or synthetic ammonium iron sulfates are not common. Among them, sabieite $NH_4Fe(SO_4)_2$, whose structure is not known, has been described as trigonal, with space group $P32_1$ on the basis of the powder-diffraction pattern (ICDD PDF–2 entry 00–024–0044). The same chemical formula is reported for another rhombohedral phase, space group $R\overline{3}$, whose structure has been deposited in the ICSD database as a private communication (Entry 413817). It contains infinite layers made by iron-centered octahedra held together by sulfate tetrahedra that share three corners with three adjacent octahedra, the fourth corner being involved in hydrogen bonding with the ammonium ions; the latter are disordered and display two centrosymmetric orientations. An additional cubic phase with formula $(NH_4)_2Fe_2(SO_4)_3$ is reported in the PDF–2 database (ICDD PDF–2 entry 00–018–1105), but no structure information is given. No papers concerning all these phases have been found in the literature. It is interesting to note that the synthetic compound $(NH_4)_3Fe(SO_4)_3$ corresponding to pyracmonite was prepared by the Dow Chemical Co., Midland, Michigan, USA (private communication to the ICDD PDF–2 database) by dissolving and evaporating a $(NH_4)_2SO_4{\bullet}Fe_2(SO_4)_2 + 2(NH_4)_2SO_4$ mixture and heating at 250°C to obtain the anhydrous phase;

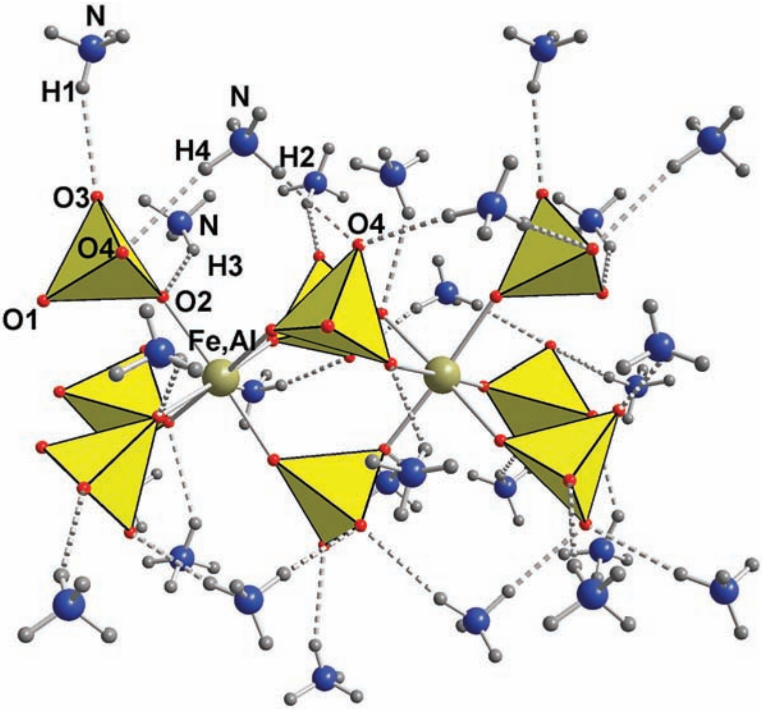

FIG. 4. The pattern of the "regular" hydrogen-bonds in pyracmonite (see text).

these temperature conditions correspond to those at the fumarole where pyracmonite was collected.

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