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ADRANOSITE, $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$, A NEW AMMONIUM SULFATE CHLORIDE FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

The new mineral species adranosite, $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$, 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 sprays of prismatic crystals up to 0.3 mm in length, in association with aiolosite, alunite, anhydrite, bismuthinite, sassolite, demicheleite-(Br), demicheleite-(Cl), panichiite and IMA 2009–049. The mineral is tetragonal, space group: $I4_1/acd$ (no. 142) with a 18.118(3), c 11.320(3) Å, V 3715.5(13) Å^3 and $Z = 8$. The strongest six reflections in the X-ray powder-diffraction pattern [d_{obs} in Å(I)(hkl)] are: 2.980(100)(152), 2.265(87)(080), 4.530(86)(040), 6.398(80)(220), 3.020(65)(060) and 3.202(47)(440). The average result of chemical analyses (wt.%) is: Na_2O 5.88, Al_2O_3 17.40, K_2O 0.90, $(NH_4)_2O$ 16.52, SO_3 51.31, Cl 5.68, H_2O 2.99, –O=Cl –1.28, for a total of 99.40. The empirical formula (based on 19 anions) is: $[(NH_4)_{3.89}K_{0.12}]_{\Sigma 4.01}Na_{1.16}Al_{2.09}S_{3.93}O_{15.99}Cl_{0.98}(OH)_{2.03}$. The end-member formula is $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$. The measured density is 2.15(1) g/cm^3, and D_{calc} is 2.176 g cm^{-3}. The mineral is uniaxial (–) with $\omega = 1.55(1)$, $\varepsilon = 1.54(1)$ ($\lambda = 589$ nm). Using single-crystal diffraction data, the structure was refined to a final $R = 0.0355$ for 596 independent observed reflections [$I > 2\sigma(I)$]. Adranosite is isostructural with the $(NH_4)_4NaFe_2(SO_4)_4Cl(OH)_2$ phase found in a burning coal dump. Building blocks of the structure are AlO_6 octahedra [Al–O in the range 1.862(1)–1.923(1) Å] and SO_4 tetrahedra, which are linked together to form spiraling chains parallel to [001]. There are also NaO_4Cl_2 square tetragonal bipyramids [Na–O 2.360(1), Na–Cl 2.830(1) Å], linked together by sharing the Cl atoms at the corners. The ammonium ions occupy the voids in the resulting framework and interact with the neighboring atoms *via* hydrogen bonds.

Keywords: adranosite, new mineral species, crystal structure, ammonium sulfates, Vulcano, Aeolian Islands, Italy.

SOMMAIRE

Nous décrivons une nouvelle espèce minérale, l'adranosite, $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$, provenant d'une fumerolle active à environ 250°C au cratère La Fossa, à Vulcano, dans les îles Éoliennes, en Sicile, Italie. Le minéral se présente en gerbes de cristaux prismatiques blancs à incolores atteignant 0.3 mm de longueur sur une brèche pyroclastique, dans une association avec aïolosite, alunite, anhydrite, bismuthinite, sassolite, demicheleïte-(Br), demicheleïte-(Cl), panichiite, et une nouvelle espèce approuvée par l'IMA, #2009–049. Il s'agit d'un minéral tétragonal, groupe spatial $I4_1/acd$ (no. 142), ayant a 18.118(3), c 11.320(3) Å, V 3715.5(13) Å^3 et $Z = 8$. Les six raies les plus intenses du spectre de diffraction, méthode des poudres [d_{obs} en Å(I)(hkl)] sont: 2.980(100)(152), 2.265(87)(080), 4.530(86)(040), 6.398(80)(220), 3.020(65)(060), et 3.202(47)(440). Le résultat moyen des analyses chimiques (en %, poids) est: Na_2O 5.88, Al_2O_3 17.40, K_2O 0.90, $(NH_4)_2O$ 16.52, SO_3 51.31, Cl 5.68, H_2O 2.99, –O=Cl –1.28, pour un total de 99.40. La formule empirique, fondée sur 19 anions, est: $[(NH_4)_{3.89}K_{0.12}]_{\Sigma 4.01}Na_{1.16}Al_{2.09}S_{3.93}O_{15.99}Cl_{0.98}(OH)_{2.03}$. La formule du pôle est $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$. La densité mesurée est 2.15(1) g/cm^3, et D_{calc} est égal à 2.176 g cm^{-3}. Le minéral est uniaxe négatif, avec $\omega = 1.55(1)$, $\varepsilon = 1.54(1)$ ($\lambda = 589$ nm). Au moyen de données diffractométriques obtenues sur monocristal, nous en avons affiné la structure, jusqu'à un résidu final R égal à 0.0355 pour 596 réflexions indépendantes observées [$I > 2\sigma(I)$]. L'adranosite est isostructurale avec la phase $(NH_4)_4NaFe_2(SO_4)_4Cl(OH)_2$ découverte dans des haldes brulées de charbon. Les éléments fondamentaux de la structure sont des octaèdres AlO_6 [liaisons Al–O dans l'intervalle 1.862(1)–1.923(1) Å] et les tétraèdres SO_4, qui sont interconnectés pour former des chaînes en spirales parallèles à [001]. Il y a aussi des bipyramides tétragonales carrées NaO_4Cl_2 [Na–O 2.360(1), Na–Cl 2.830(1) Å], connectées par partage d'atomes Cl aux coins. Les ions d'ammonium se trouvent dans les lacunes de la charpente, et interagissent avec les atomes avoisinants par un réseau de liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: adranosite, nouvelle espèce minérale, structure cristalline, sulfates d'ammonium, Vulcano, îles Éoliennes, Italie.

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Introduction

In the last few years, an evolution of the environmental conditions of the fumarole system at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy, has led to the formation of a number of rare minerals, among them new species (for details, see for instance Garavelli *et al*. 2005, Campostrini *et al*. 2008, Demartin *et al*. 2009a, 2009b, 2009c, 2010a, 2010b, Mitolo *et al*. 2009, and references therein). During our systematic investigations of these minerals in the years 2007–2008, the new species adranosite, $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$, was discovered. We report here the description of the mineral and the determination of its structure.

The mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2008–057). The mineral is named after the ancient god of fire Adranos (Αδρανος), father of the Palicis, which reflects the origin of the mineral and a link to Hephaistos ("Ηφαιιιστος, Vulcanus for the Aetruscans and the Latins), who had his forges in the bowels of Vulcano Island (or Etna). Holotype material is deposited in the Reference Collection of the Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, Via G. Venezian 21, I–20133 Milano, Italy, specimen number 2008–06.

Occurrence, Chemical Data and Physical Properties

Adranosite occurs in an active medium-temperature (~250°C) intracrater fumarole on pyroclastic breccia, in association with aiolosite (Demartin *et al*. 2010a), alunite, anhydrite, bismuthinite, sassolite, demicheleite-(Br), demicheleite-(Cl) and IMA 2009–049. In addition, in the same environment, other very unusual species containing ammonium also are present, such as godovikovite $(NH_4)Al(SO_4)_2$, pyracmonite $(NH_4)_3Fe(SO_4)_3$ (Demartin *et al*. 2010b), and several other new minerals, some of which are still under investigation. Besides sulfates, there are also ammonium-bearing complex chlorides that contain heavy metals, for instance panichiite $(NH_4)_2SnCl_6$, brontesite $(NH_4)_3PbCl_5$ (Demartin *et al*. 2009a, 2009d) and an ammonium bismuth chloride.

Adranosite forms aggregates of colorless to white acicular crystals up to 0.3 mm in length (Fig. 1), with pointed terminations. The habit is tetragonal, the most common forms being {100}, {110}, and {111}. No twinning is apparent. The *c : a* ratio calculated from the unit-cell parameters is 0.625. The mineral is not hygroscopic and is stable in open air. The streak is white, and the luster is vitreous. Cleavage and fracture were not observed. No fluorescence was observed both under SW and LW ultraviolet radiation.

The density, measured by flotation in a tribromomethane–trichloromethane mixture, is 2.15(1) g/cm^3; that calculated from the empirical formula and the X-ray data is 2.176 g/cm^3. The mineral is uniaxial (–) with ω 1.55(1), ε 1.54(1) (589 nm); the corresponding Gladstone–Dale value calculated using Mandarino's constants (1981) is 1.547, leading to a compatibility index $[1 - (K_P/K_C)] = -0.018$ (superior).

Quantitative chemical analyses (six) were carried out in wavelength-dispersion mode, using a JEOL JXA

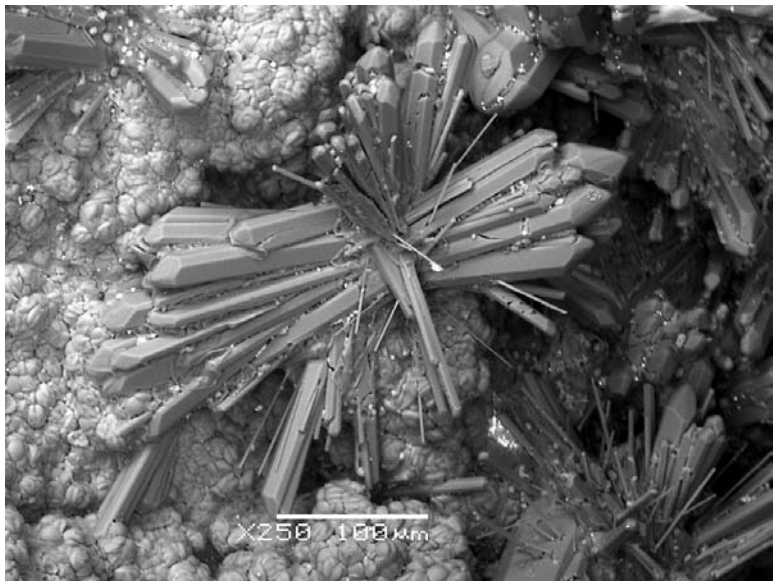


Fig. 1. SEM–BSE image of crystals of adranosite.

8200 electron microprobe operated under the following conditions: 15 kV excitation voltage, 4×10^{-9} A beam current, and a beam diameter of 10 μm. Element concentrations were measured using the *K*α lines for Na, Al, K, S and Cl. The H_2O content was deduced from the results of crystal-structure analysis. The presence of ammonium was established from crystal-structure analysis and confirmed by microchemical tests using the Nessler reaction; its content was deduced from the difference between the theoretical value of the site (4 *apfu*) and the K content. The mean analytical results are reported in Table 1.

The empirical formula (based on 19 anions) is: $[(NH_4)_{3.89}K_{0.12}]_{\Sigma 4.01}Na_{1.16}Al_{2.09}S_{3.93}O_{15.99}Cl_{0.98}(OH)_{2.03}$. The end-member formula is $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$, which requires $(NH_4)_2O$ 17.29, Na_2O 5.14, Al_2O_3 16.91, SO_3 53.12, Cl 5.88 H_2O 2.99, subtotal 101.32, less O=Cl –1.33, for a total of 100.00 wt%.

X-Ray Data

The X-ray powder-diffraction data were obtained using a Philips PW1830 diffractometer, with graphite-monochromated Cu*K*α radiation (Table 2).The unit-cell parameters, *a* 18.105(3), *c* 11.320(1) Å, were obtained by least-squares refinement from the above data using the program Unitcell (Holland & Redfern 1997).

The unit-cell parameters obtained from 741 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 17231 intensities corresponding to a complete scan of the reciprocal lattice up to $2\theta = 58.62°$ were collected from a single crystal ($0.012 \times 0.018 \times 0.175$ 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 ($\mu = 0.873$ mm^{-1}) was applied using the Sadabs program (Sheldrick 2000). After averaging the symmetry-related reflections (R_{int}= 0.083), 1248 independent data were obtained.

The structure was solved by direct methods and refined using the ShelxL97 program (Sheldrick 2007) implemented in the WinGX program (Farrugia 1999). 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 atomic-displacement parameters were considered instead for all the other atoms. The final *R* is 0.0355 for 596

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

h	*k*	*l*	*I*/*I*o	d_{obs}	d_{calc} #	*h*	*k*	*l*	*I*/*I*o	d_{obs}	d_{calc} #
0	2	0	5	9.055	9.053	0	8	0	87	2.265	2.263
1	2	1	18	6.574	6.586	4	7	1	12	2.203	2.203
2	2	0	80	6.398	6.401	3	6	3	10	2.192	2.195
1	1	2	5	5.163	5.177	6	6	0	11	2.134	2.134
0	4	0	86	4.530	4.526	0	6	4	10	2.062	2.064
2	4	0	28	4.052	4.048	2	9	1	13	1.936	1.935
1	3	2	19	4.019	4.025	1	8	3	14	1.931	1.930
3	4	1	11	3.446	3.449	4	8	2	44	1.902	1.906
3	3	2	22	3.402	3.407	2	9	3	24	1.746	1.742
2	4	2	24	3.264	3.293	4	10	0	15	1.681	1.681
2	5	1	27	3.248	3.223	6	9	1	6	1.655	1.656
4	4	0	47	3.202	3.201	4	9	3	5	1.652	1.653
0	6	0	65	3.020	3.018	8	8	0	5	1.601	1.600
1	5	2	100	2.980	3.008	3	9	4	10	1.581	1.582
2	6	0	29	2.864	2.863	0	12	0	6	1.507	1.509
0	0	4	16	2.820	2.830	2	12	0	19	1.490	1.488
3	5	2	36	2.739	2.722	3	7	6	5	1.481	1.478
0	6	2	7	2.665	2.663	4	10	4	5	1.445	1.445
3	4	3	7	2.603	2.613	6	11	1	5	1.433	1.433
4	6	0	15	2.509	2.511	0	0	8	12	1.414	1.415
5	5	2	17	2.330	2.333	2	2	8	5	1.384	1.382
						5	9	6	11	1.287	1.286

Calculated from the unit cell: *a* = 18.105(3), *c* = 11.320(1) Å, obtained from least-squares refinement from the above data using the program Unitcell (Holland & Redfern 1997). Conditions of data collection: step width 0.02°, time per step 10 s. Divergence slit 0.25°, soller slit 0.04 rad, antiscatter slit 0.5°. The values of *d* are quoted in Å.

TABLE 1. CHEMICAL COMPOSITION OF ADRANOSITE

Constituent	wt%	Range	Probe standard
Na_2O	5.88	5.06–6.40	Albite
K_2O	0.90	0.87–1.01	KCl
Al_2O_3	17.40	16.74–18.21	Albite
SO_3	51.31	50.67–54.34	Synthetic anhydrite
Cl	5.68	5.52–5.94	KCl
H_2O*	2.99		
$(NH_4)_2O$*	16.52		
	100.68		
Less –O=Cl	–1.28		
Total	99.40		

* Calculated value from structure determination assuming full occupancy of the N and O(5) sites.

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

Crystal system	tetragonal	Space group	$I4_1/acd$ (no. 142)
a (Å)	18.118(3)	Z	8
c (Å)	11.320(3)	Radiation	Mo*K*α
V (Å^3)	3715.5(13)	μ (mm^{-1})	0.873
D_{calc} (g/cm^3)	2.176		
Measured reflections		17231	
Independent reflections		1248	
Observed reflections [$I > 2\sigma(I)$]		596	
Parameters refined		88	
Final *R* and w*R*2		0.0355, 0.0575	
S		0.788	

Notes: $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (0.0209q)]$, where $q = (Fo^2 + 2Fc^2)/3$.
$S = \{\Sigma[w(Fo^2 - Fc^2)]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

observed reflections [$I > 2\sigma(I)$]. The final coordinates and displacement parameters of the atoms are reported in Table 4, and interatomic distances, in Table 5. Tables of observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, on the MAC web site [document Adranosite CM48_315].

Description of the Structure

Perspective views of the structure of adranosite are reported in Figures 2 and 3. This structure type has already been encountered by Kolitsch & Brandstätter (2007) in the iron analogue of this mineral, $(NH_4)_4NaFe_2(SO_4)_4Cl(OH)_2$, described as a salt-inclusion phase and found in a burning coal dump at Anna mine, North Rhine-Westphalia, Germany. The structure contains infinite...Na–Cl–Na–Cl... chains and helicoidal chains of composition $[AlO_4(OH)_2SO_4]_n$ (Fig. 4), both running along [001]. The former can be described as formed by NaO_4Cl_2 square tetragonal bipyramids, linked through their opposite Cl corners. Similar chains, formed by alkali or alkaline-earth ions, are found in minerals of the cancrinite–davyne types (Ballirano *et al*. 1996, 1998, and references therein).

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS [Ueq,Ui,j] OF ATOMS IN ADRANOSITE

Atom	Wyckoff notation	*X/a*	*Y/b*	*Z/c*	U_{eq}, *U*
Na	8*a*	1/2	1/4	1/8	0.0164(3)
Al	16*f*	0.30294(2)	0.55294(2)	1/8	0.0147(2)
S	32*g*	0.37582(1)	0.39982(2)	0.13783(3)	0.0167(1)
Cl	8*b*	1/2	1/4	3/8	0.0309(2)
N	32*g*	0.32267(7)	0.23391(6)	0.3765(1)	0.0269(4)
O(1)	32*g*	0.37981(5)	0.48138(5)	0.11043(9)	0.0185(3)
O(2)	32*g*	0.31502(9)	0.36716(6)	0.07200(9)	0.0295(3)
O(3)	32*g*	0.36366(5)	0.39176(5)	0.26733(8)	0.0191(3)
O(4)	32*g*	0.44711(5)	0.36856(6)	0.10786(9)	0.0280(3)
O(5)	16*e*	0.26221(7)	1/2	1/4	0.0157(4)
H(1)	32*g*	0.3013(3)	0.2837(2)	0.3907(5)	0.100(7)
H(2)	32*g*	0.3677(2)	0.2362(4)	0.3278(4)	0.142(10)
H(3)	32*g*	0.3311(4)	0.2075(3)	0.4526(3)	0.129(9)
H(4)	32*g*	0.2835(2)	0.2044(3)	0.3307(4)	0.185(13)
H(5)	16*e*	0.2127(3)	1/2	1/4	0.028(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	0.0142(3)	0.0142(3)	0.0209(6)	0	0	0
Al	0.0156(2)	0.0156(2)	0.0127(3)	0.0007(2)	0.0007(2)	-0.0004(3)
S	0.0188(2)	0.0177(2)	0.0136(2)	-0.0013(2)	0.0006(2)	0.0028(2)
Cl	0.0320(3)	0.0320(3)	0.0286(4)	0	0	0.0016(4)
N	0.0361(8)	0.0217(7)	0.0229(7)	0.0012(7)	0.0071(8)	0.0079(6)
O(1)	0.0189(5)	0.0150(6)	0.0216(6)	0.0031(4)	0.0040(5)	0.0007(5)
O(2)	0.0332(6)	0.0276(7)	0.0276(6)	-0.0077(5)	-0.0130(5)	-0.0022(6)
O(3)	0.0224(6)	0.0207(5)	0.0143(5)	0.0026(4)	0.0050(4)	0.0039(4)
O(4)	0.0265(6)	0.0276(6)	0.0300(6)	0.0054(6)	0.0124(5)	0.0125(5)
O(5)	0.0143(7)	0.0161(8)	0.0165(7)	0.0046(7)	0	0

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 helicoidal chains consist of $AlO_4(OH)_2$ distorted octahedra linked to each other through the corners occupied by the OH groups [O(5)–H(5)] and by sulfate ions bridging two adjacent octahedra through the atoms O(1) and O(3). Of the remaining two oxygen atoms at the corners of the sulfate ion, one [O(4)] is shared with the Na^+ ion, and another [O(2)] is involved in hydrogen bonding with the NH_4^+ ions (Fig. 5). The Al–O distances range from 1.862(1) to 1.923(1) Å, the shortest distance being that with the OH group.

In the sulfate ion, the average of all S–O distances (1.477 Å) is close to that observed in an accurate redetermination of the structure of gypsum by neutron diffraction (Pedersen & Semmingsen 1982) and is comparable with that found in most sulfates (Palmer *et al*. 1972, and references therein). Following Brown & Altermatt (1985), the total charge on the sulfur atom (5.96 valence units, *vu*) is close to that expected. In particular, the "bridging" S–O(1) and S–O(3) bonds [1.511(1) and 1.490(1) Å, respectively], imply 1.357 and 1.436 *vu*. These two bonds are significantly longer than their "non-bridging" counterparts S–O(2) and S–O(4) [1.456(1) and 1.451(1) Å, corresponding to 1.575 and 1.596 *vu*, respectively].

The framework resulting from the sharing of the sulfate ions between the different chains displays cages in which the nine-coordinated ammonium ions are hosted. The range (2.87–3.42 Å) of NH_4–(O,Cl) distances indicates the presence of hydrogen bonding; as in pyracmonite (Demartin *et al*. 2010b), these H bonds render the position of the hydrogen atoms in the ammonium ion ordered.

In the contribution by Kolitsch & Brandstätter (2007), where the iron analogue of this mineral and this kind of crystal structure were first described, the authors considered the possibility that these substances be ascribed to the so-called "salt-inclusion compounds". However, most of true "salt-inclusion compounds" show a porous framework with considerably larger cavities (5 Å or much more in diameter) where the salt is hosted and can even be exchanged, like in zeolites. In the structure of adranosite, instead, the diameter of the corresponding cavities is smaller (~4.7 Å), the

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

Na –O(4) ×2	2.360(1)	O(1)–S–O(2)	109.18(6)
Na –O(4) ×2	2.360(1)	O(1)–S–O(3)	107.75(6)
Na –Cl ×2	2.8299(7)	O(1)–S–O(4)	106.93(6)
Al –O(1) ×2	1.910(1)	O(2)–S–O(3)	110.61(6)
Al –O(3) ×2	1.923(1)	O(2)–S–O(4)	113.29(6)
Al –O(5) ×2	1.862(1)	O(3)–S–O(4)	108.88(6)
S –O(1)	1.511(1)	<O–S–O>	109.44
S –O(2)	1.456(1)		
S –O(3)	1.490(1)		
S –O(4)	1.451(1)		
<S–O>	1.477		

FIG. 2. The crystal structure of adranosite, as seen along [001]. The SO_4^{2-} tetrahedra are represented in red, the Al-centered octahedra in sky-blue, the Na-centered bipyramids in yellow, and the N atoms of the NH_4^+ ions in blue.

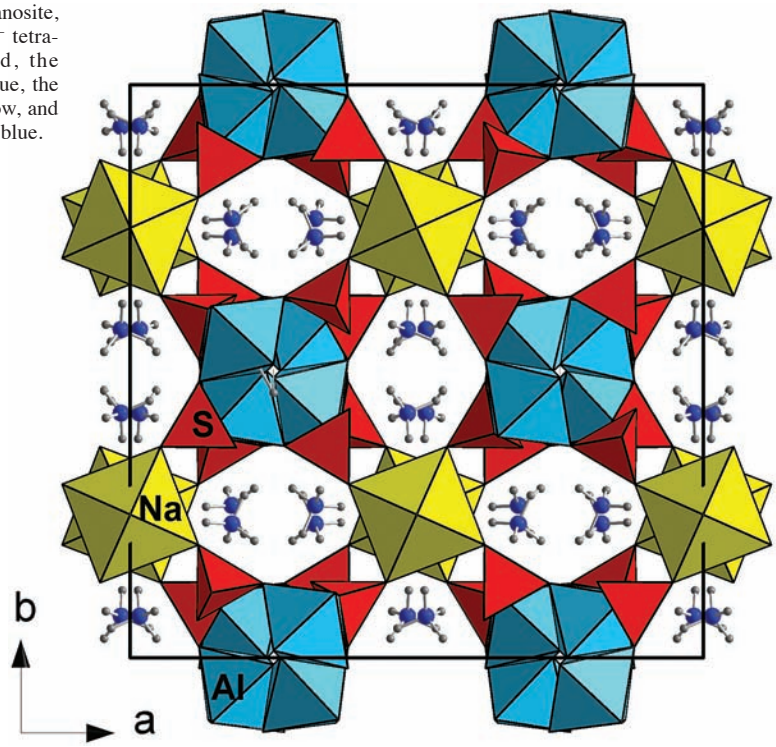
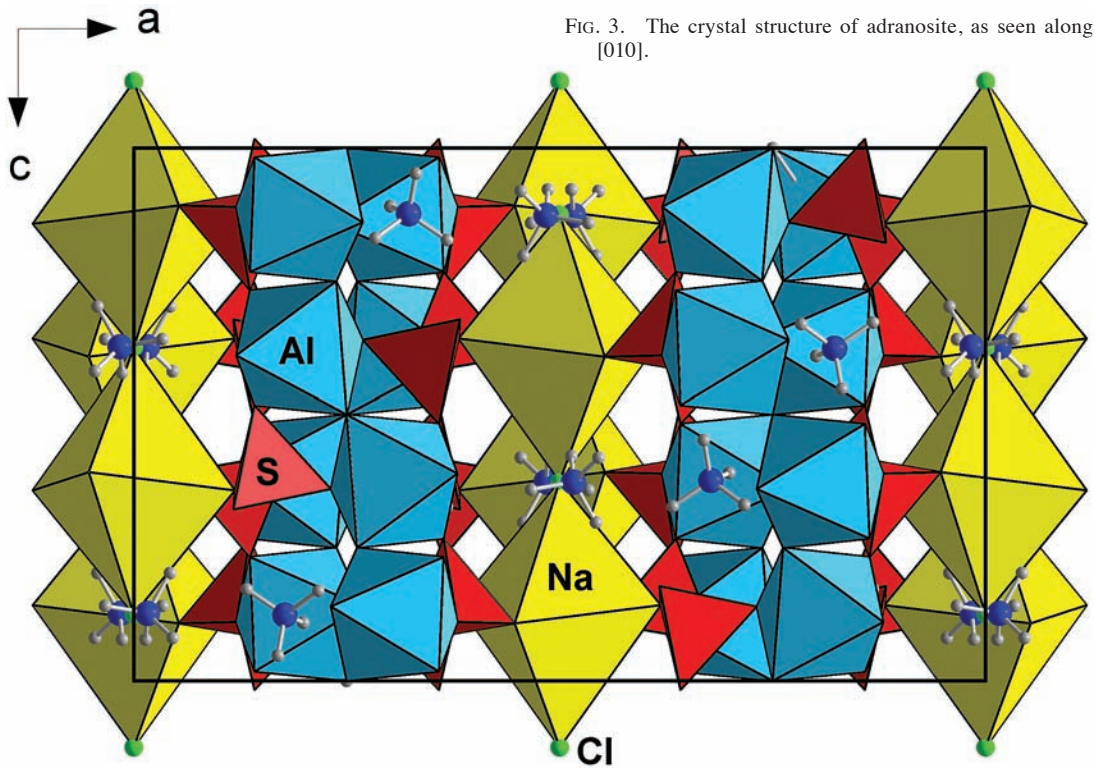


FIG. 3. The crystal structure of adranosite, as seen along [010].



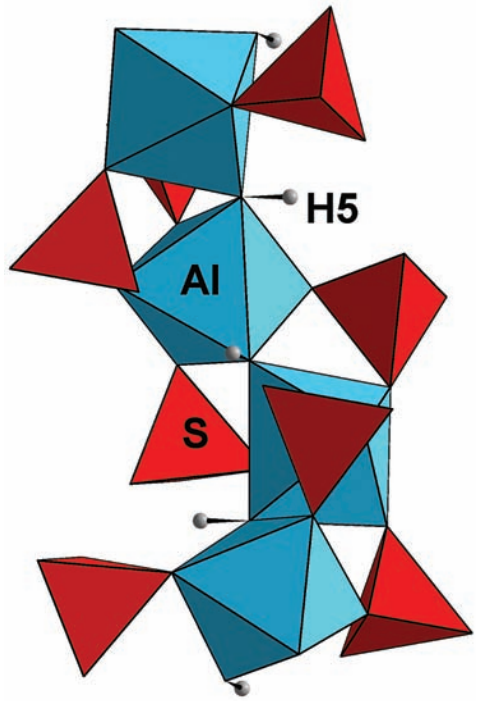


FIG. 4. The helicoidal chains made by Al-centered octahedra and SO_4 tetrahedra.

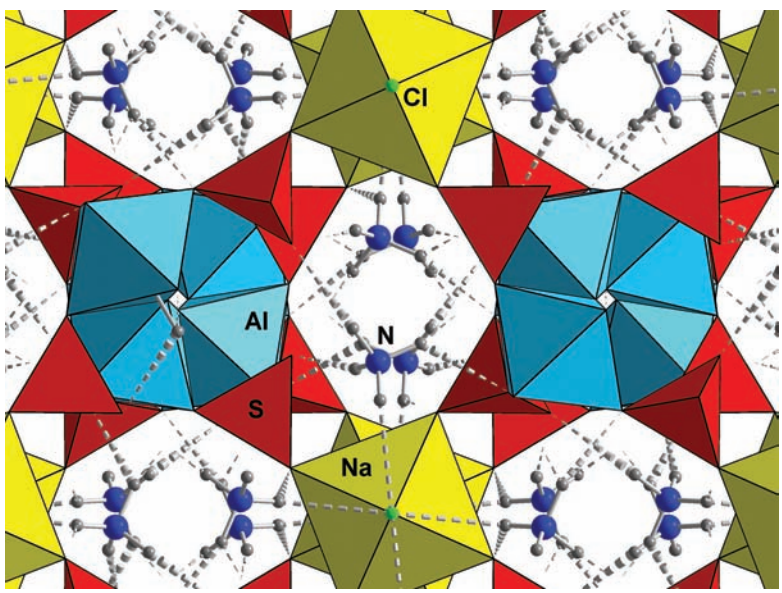


FIG. 5. The hydrogen-bond pattern involving the ammonium ions.

largest cavities being instead the ones containing the ammonium ions.

Conclusions

The discovery of adranosite accompanied by other rare and generally unique minerals containing ammonium adds a further important detail in the study of the overall geochemical context of La Fossa crater. The presence of these minerals in the fumaroles emphasizes a considerably high activity of free ammonia and of volatile metal chlorides in the gas to prevent the dissociation of such compounds, which would not otherwise be stable, even at moderately high temperature.

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