

ADRANOSITE-(Fe), $(\text{NH}_4)_4\text{NaFe}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, A NEW AMMONIUM SULFATE CHLORIDE FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

The new mineral adranosite-(Fe), ideally $(\text{NH}_4)_4\text{NaFe}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, is the Fe^{3+} -analogue of adranosite. It was found on a pyroclastic breccia in two different fumaroles at “La Fossa” crater of Vulcano, Aeolian Islands, Italy, and corresponds to an anthropogenic product previously observed in a burning coal dump at the Anna mine, near Aachen, Germany. The mineral is tetragonal, space group $I4_1/acd$ (no. 142), with $a = 18.261(2)$, $c = 11.562(1)$ Å, $V = 3855.5(7)$ Å³ (single-crystal data), and $Z = 8$. The six strongest reflections in the X-ray powder diffraction pattern are [d_{obs} in Å(I)(hkl)]: 9.134(100)(020), 4.569(83)(040), 3.047(79)(152), 6.462(36)(220), 3.232(29)(251), and 2.891(11)(004). The average chemical composition of the holotype is (wt.%): Na₂O 5.01, Fe₂O₃ 15.77, Al₂O₃ 5.11, K₂O 0.82, (NH₄)₂O 15.76, SO₃ 50.96, Cl 3.71, H₂O 2.75, –O≡Cl –0.84, total 99.05; the corresponding empirical formula is: $[(\text{NH}_4)_{3.89}\text{K}_{0.11}]_{\Sigma 4.00}\text{Na}_{1.04}[\text{Fe}_{1.27}\text{Al}_{0.64}]_{\Sigma 1.91}\text{S}_{4.10}\text{O}_{16.40}\text{Cl}_{0.67}(\text{OH})_{1.96}$. Adranosite-(Fe) forms aggregates of pale yellow acicular crystals up to 1 mm in length, the most common forms most probably being {100}, {110}, and {111}. The measured density is 2.18(1) g/cm³, and the calculated density is 2.195 g/cm³. Adranosite-(Fe) is uniaxial (–) with $\omega = 1.58(1)$, $\epsilon = 1.57(1)$ ($\lambda = 589$ nm). Using single-crystal X-ray diffraction data from the holotype, the structure was refined to a final $R(F) = 0.0415$ for 670 independent observed reflections [$I > 2\sigma(I)$]. Adranosite-(Fe) is isostructural with its Al-analogue adranosite and contains NaO₄Cl₂ square tetragonal bipyramids, linked through their opposite Cl corners and

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helicoidal chains with composition $[\text{FeO}_4(\text{OH})_2\text{SO}_4]_n$, both extending along [001]. The framework resulting from the sharing of the sulfate ions between the different chains displays cages in which the nine-coordinated hydrogen-bonded NH_4^+ ions are hosted.

Keywords: adranosite-(Fe), new mineral species, sublimates, fumaroles, crystal structure, ammonium sulfates, Vulcano, Aeolian Islands, Italy, Anna Mine

INTRODUCTION

A systematic investigation on the sublimate minerals from Vulcano, Aeolian Islands, Italy (see Garavelli *et al.* 1997 for more detailed geological settings) has been carried on for about 17 years by two different research groups from Bari and Milano Universities, respectively. These investigations permitted explanation of the high variability of the mineralogy of the area (Garavelli 1994, Garavelli *et al.* 1997, Cheynet *et al.* 2000), therefore contributing to the knowledge of the volcanic system and to its surveillance (Ferrara *et al.* 1995, Coradossi *et al.* 1996). Furthermore, these long-term studies led to the discovery of a considerable number of new mineral phases and to improved characterization of some others (Garavelli & Vurro 1994, Vurro *et al.* 1999, Borodaev *et al.* 1998, 2000, 2001, 2003, Garavelli *et al.* 2005, Pinto *et al.* 2006a,b, Campostrini *et al.* 2008, Demartin *et al.* 2009a,b,c,d, Mitolo *et al.* 2009, Demartin *et al.* 2010a,b,c, Campostrini *et al.* 2011, and references therein). The peculiar chemistry of the fluids discharged from the area, as well as the wide range of fumarole temperatures, favor the deposition of an extensive variety of minerals, whose formation and association are highly influenced by the flow rates of the gases emitted from the vents and thermodynamic conditions at the time of deposition (Garavelli *et al.* 1997, Cheynet *et al.* 2000). At Vulcano, these conditions are highly variable, since temperature and gas composition may change considerably even in a very brief span of time. Thus, it is no wonder that sublimate samples collected at the same time and from the same fumarole area show different mineralogical associations, and, conversely, samples collected at different times and from different vents may contain analogous minerals.

The history of the discovery of adranosite-(Fe), $(\text{NH}_4)_4\text{NaFe}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, is well framed in this context and exemplifies this situation. The new mineral was independently and simultaneously identified by the two different research groups in samples collected in different years and from around different fumaroles. The millimeter-sized crystals used for the full characterization of the species (holotype specimen) were collected at fumarole F11 in 2007 and were studied at the University of Milano. The micrometer-sized crystals investigated at the University of Bari (hereafter the cotype specimen) were instead collected in 1996 at the intracrater fumarolized area IC (Fig. 1). An identical anthropogenic product has been characterized (Kolitsch & Brandstätter 2007) from a burning coal dump at the

Anna mine, near Aachen, North Rhine-Westphalia, Germany.

The mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2011-006) and was named as the Fe^{3+} analogue of adranosite, $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, which was also discovered at Vulcano (Demartin *et al.* 2010c). The type material is deposited in the Reference Collection of the Dipartimento di Chimica, Università degli Studi di Milano, specimen number 2010-02. The cotype specimen has been deposited at the Museum "C.L. Garavelli", Dipartimento di Scienze della Terra e Geoambientali, Università di Bari, Italy, under the catalogue number 10/nm-V28. The studied anthropogenic material is stored in the collection of the Natural History Museum, Vienna, Austria (specimen no. N 9389).

OCCURRENCE, CHEMICAL DATA, AND PHYSICAL PROPERTIES

On the holotype specimen, adranosite-(Fe) is associated with thermessaite, pseudocotunnite and bismuthinite. On the cotype specimen the association is with barberiite, salammontiac, anhydrite, sassolite, and sulfur. The anthropogenic adranosite-(Fe) from the burning coal mine is mainly accompanied by the ammonium salts clairite, tschermigite, rostitite/khademite, and boussingaultite/mohrite (Kolitsch & Brandstätter 2007). Adranosite-(Fe) forms aggregates of pale yellow acicular crystals up to 1 mm in length (Figs. 2-4). The habit is tetragonal, the most common forms most likely being {100}, {110}, and {111}, an attribution derived from comparison of the crystal drawings with the morphology shown in Figure 3. No twinning is apparent. The $c:a$ ratio calculated from the unit-cell parameters is 0.633. The mineral is not hygroscopic and is stable in open air. The streak is white and the luster is vitreous. A perfect cleavage is observed on {001}. The mineral is not fluorescent under either SW- or LW-ultraviolet radiation. The density, measured by flotation in a tribromomethane-trichloromethane mixture using the holotype specimen, is 2.18(1) g/cm³; the density calculated from the empirical formula and the X-ray data (holotype specimen) is 2.195 g/cm³. The mineral is uniaxial (−) with $\omega = 1.58(1)$, $\epsilon = 1.57(1)$ (589 nm); the corresponding Gladstone-Dale value calculated using Mandarino's (1981) constants is $n = 1.577$, leading to a compatibility index $[1 - (K_p/K_c)] = -0.012$ (superior).

Quantitative chemical analyses of the holotype specimen (mean of 12 analyses) were carried out by

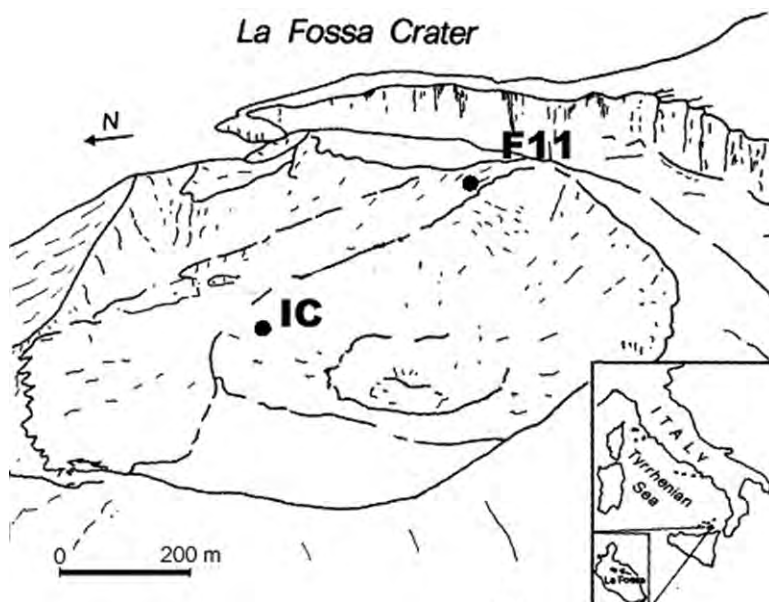


FIG. 1. Summit of the "La Fossa" crater, Vulcano Island (Italy). Location of sampling sites.



FIG. 2. A spray 1 mm across of adranosite-(Fe) crystals (holotype specimen).

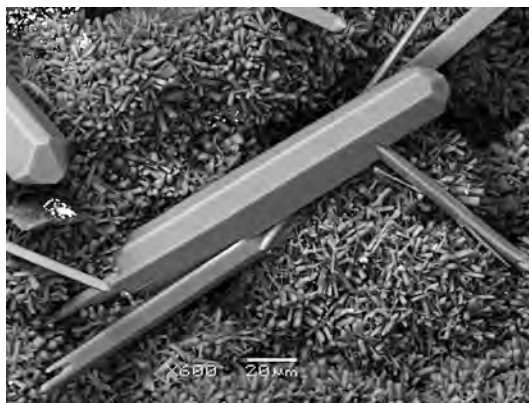


FIG. 3. SEM-BSE image of crystals of adranosite-(Fe) grown on thermessaite (holotype specimen).

means of a JEOL JSM 5500LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe (conditions: 20 kV, 10^{-11} A and 2 μ m beam diameter) (Table 1). Element concentrations were measured using the $K\alpha$ lines for Na, Fe, Al, K, S, and Cl. The H_2O content was calculated by stoichiometry from the results of the crystal-structure analysis. The presence of ammonium was evident from crystal-structure analysis and was 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 holotype empirical formula, calculated on the basis of 19 anions per formula unit (*pfu*), is: $[(NH_4)_{3.89}K_{0.11}]_{\Sigma 4.00}Na_{1.04}(Fe_{1.27}Al_{0.64})_{\Sigma 1.91}(SO_4)_{4.10}Cl_{0.67}(OH)_{1.96}$. Chemical data from the cotype specimen were obtained by SEM-EDS analysis, using a S 360 Cambridge scanning electron microscope coupled with an Oxford-Link Ge ISIS EDS

equipped with a Super Atmosphere Thin Window[®], since this allows better detection of light elements. The SEM was operated at 15 kV accelerating potential, 500 pA probe current, 2,500 cps as average count rate for the whole spectrum, and counting time 100 s. X-ray intensities were converted to wt.% by the ZAF4/FLS quantitative analysis software of Oxford-Link Analytical (U.K.). The standards employed were: albite (Na), almandine (Fe), corundum (Al), barite (S), and halite (Cl). The range of composition (five different analyses from different spots) is (wt.%): Na₂O 3.06–5.78, Fe₂O₃ 20.98–24.76, Al₂O₃ 0.52–4.41, SO₃ 38.07–52.31, and Cl 3.89–5.18. These results are comparable to those of the holotype, the major differences being the higher Fe/Al and Cl/OH ratios and the absence of potassium. The ideal formula of adranosite-(Fe) is (NH₄)₄NaFe³⁺₂(SO₄)₄Cl(OH)₂, which requires (NH₄)₂O 15.77, Na₂O 4.69, Fe₂O₃ 24.18, SO₃ 48.18, Cl 5.37, H₂O 2.73, –O=Cl –1.21, total 100.00 wt.%.

X-RAY DATA

X-ray powder-diffraction data (Table 2) were recorded from the holotype specimen using a Philips PW1830 diffractometer, with graphite-monochromated CuK α radiation. The unit-cell parameters, $a = 18.272(1)$, $c = 11.558(1)$ Å, and $V = 3859.0(5)$ Å³, were obtained by least-squares refinement from the above data using the program UNITCELL (Holland & Redfern 1997). For the cotype specimen, X-ray powder-diffraction data were recorded using a PANalytical X'Pert Pro MPD diffractometer with Bragg-Brentano geometry, using CuK α radiation and a secondary-beam graphite monochromator. The unit-cell parameters, $a = 18.259(2)$, $c = 11.571(1)$ Å, and $V = 3857.7(8)$ Å³, obtained with the program CELREF (Laugier & Bochu 2003), are close to those of the holotype specimen.

Owing to the small crystal size of the cotype specimen, single-crystal diffraction data were obtained only for the holotype specimen. A total of 1821 reflections with $I > 5\sigma(I)$ were used to derive the unit-cell parameters reported in Table 3. Details concerning the data collection and refinement are reported in the same table, where they are compared with those obtained by Kolitsch & Brandstätter (2007) from the anthropogenic material. A total of 17,242 intensities corresponding to a complete scan of the reciprocal lattice up to $2\theta = 52.26^\circ$ were collected from a single crystal ($0.18 \times 0.03 \times 0.03$ mm) using a Bruker Apex II diffractometer equipped with a 2K CCD detector and MoK α radiation ($\lambda = 0.71073$ 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 effects. An absorption correction ($\mu = 2.098$ mm⁻¹) was applied using the SADABS program (Sheldrick 2000). After averaging the symmetry-related reflections ($R_{\text{int}} = 0.038$), 976 independent data were obtained.

Single-crystal X-ray diffraction data were obtained from a crystal of the anthropogenic material with dimensions $0.02 \times 0.02 \times 0.36$ mm using a Nonius Kappa CCD diffractometer with MoK α radiation. An absorption correction was applied to the intensities according to the multi-scan procedure of Otwinowski *et al.* (2003).

The structure of adranosite-(Fe) was refined using the SHELXL-97 program (Sheldrick 2008) implemented in the WinGX program (Farrugia 1999), beginning with the atomic coordinates of adranosite (Demartin *et al.* 2010c). All the hydrogen atoms of the ammonium ion showed up clearly in a difference-Fourier map and were included in the final refinement without constraints and with isotropic atomic displacement parameters, whereas anisotropic displacement parameters were considered

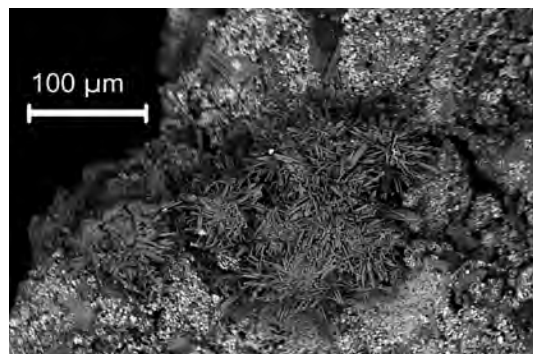


FIG. 4. SEM-BSE image of aggregates of adranosite-(Fe) (cotype specimen).

TABLE 1. CHEMICAL COMPOSITION OF ADRANOSITE-(Fe)

Constituent	Holotype (wt.%)	Range	SD
Na ₂ O	5.01	4.42–5.48	0.19
K ₂ O	0.82	0.75–0.91	0.18
Fe ₂ O ₃	15.77	15.01–16.45	0.27
Al ₂ O ₃	5.11	4.93–5.44	0.29
SO ₃	50.96	50.38–51.69	0.11
Cl	3.71	3.67–4.09	0.34
H ₂ O*	2.75		
(NH ₄) ₂ O*	15.76		
	99.89		
O = Cl	–0.84		
Total	99.05		

* Calculated value from crystal-structure determination.

Note: The standards employed for the holotype were: coquimbite (for Fe) and adranosite (for all the other elements).

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR ADRANOSITE-(Fe)^a

Holotype specimen (fumarole F11)					Cotype specimen (fumarole IC)			
<i>hkl</i>	<i>I</i> _{calc} ^b	<i>I</i> _{obs}	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å) ^c	<i>hkl</i>	<i>I</i> _{obs}	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å) ^d
0 2 0	14	100	9.134	9.136	0 2 0	100	9.15	9.13
1 2 1	8	3	6.665	6.672	1 2 1	62	6.66	6.66
2 2 0	81	36	6.462	6.460	1 1 2	43	5.25	5.26
0 4 0	37	83	4.569	4.568	2 3 1	20	4.62	4.62
1 4 1	9	10	4.135	4.138	0 4 0	21	4.55	4.54
2 4 0	65	5	4.088	4.086	1 4 1	15	4.13	4.11
3 4 1	100	3	3.486	3.484	2 4 0	13	4.07	4.06
2 5 1	3	29	3.232	3.256	3 4 1	10	3.45	3.45
4 4 0	5	2	3.211	3.230	2 5 1	14	3.23	3.22
1 5 2	90	79	3.047	3.045	4 4 0	13	3.20	3.20
0 0 4	25	11	2.891	2.890	1 5 2	16	3.01	3.01
2 0 4	12	2	2.757	2.755	0 0 4	10	2.86	2.86
5 5 2	40	4	2.359	2.359	2 0 4	9	2.72	2.72
0 8 0	8	6	2.285	2.284	5 5 2	6	2.32	2.32
1 8 1	5	3	2.225	2.224	0 8 0	6	2.27	2.28
6 6 0	12	7	2.156	2.153	1 8 1	6	2.24	2.24
6 7 1	5	1	1.955	1.953				
1 5 6	8	7	1.697	1.697				
4 9 3	3	2	1.673	1.672				
8 8 0	3	2	1.617	1.615				
1 11 2	7	1	1.591	1.590				
0 12 0	5	3	1.524	1.523				
5 10 3	6	2	1.503	1.505				
0 0 8	7	4	1.445	1.445				
1 10 5	3	2	1.428	1.429				

^a Owing to the small amount of pure material available and the unfavorable crystal shape, it was impossible to prepare a sample for X-ray powder diffraction with no preferential orientation. Therefore some intensities in the powder diffraction pattern are affected by preferred orientation.

^b Calculated from the refined crystal structure.

^c Calculated from the unit cell with $a = 18.272(1)$, $c = 11.558(1)$ Å, obtained from least-squares refinement of the data using the program UNITCELL (Holland & Redfern, 1997).

^d Calculated from the unit cell with $a = 18.259(2)$, $c = 11.571(1)$ Å, obtained from least-squares refinement of the data using the program CELREF (Laugier & Bochu, 2003).

instead for all the other atoms. The final $R(F)$ was 0.0415 for 670 observed reflections [$I > 2\sigma(I)$]. The final coordinates and displacement parameters of the atoms are reported in Table 4 and the interatomic distances in Table 5 (where they are compared with the data for the anthropogenic material). Observed and calculated structure-factors tables may be obtained from The Depository of Unpublished Data, on the MAC web site [document Adranosite-(Fe) CM51_57].

RESULTS AND DISCUSSION

Adranosite-(Fe) is isostructural to its Al-analogue adranosite, $(\text{NH}_4)_4\text{NaAl}_2(\text{SO}_4)_4\text{Cl}(\text{OH})_2$, whose structural details were previously illustrated and discussed in Demartin *et al.* (2010c). A perspective view of the atomic arrangement of adranosite-(Fe) is shown in Figure 5. The structure contains NaO_4Cl_2 square tetragonal bipyramids, linked through their opposite

Cl corners and helicoidal chains with composition $[\text{FeO}_4(\text{OH})_2\text{SO}_4]_n$, both extending along $[001]$. The helicoidal chains are built of $\text{FeO}_4(\text{OH})_2$ distorted octahedra linked to each other through the corners occupied by the OH groups $[\text{O}(5)-\text{H}(5)]$ 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 $[\text{O}(4)]$ is shared with the Na^+ ion, and another $[\text{O}(2)]$ is involved in weak hydrogen-bonding to the NH_4^+ ions (Table 5). The Fe–O distances range from 1.929(1) to 2.034(1) Å, the shortest distance being that with the OH group.

In the sulfate ion, the average of all S–O distances (1.473 Å) is identical to the corresponding grand mean value reported for sulfate minerals (1.473 Å, Hawthorne *et al.* 2000). The framework resulting from the sharing of the sulfate ions between the different chains displays cages in which the nine-coordinated NH_4^+ ions are hosted. The range (2.91–3.52 Å) of the N–(O,Cl)

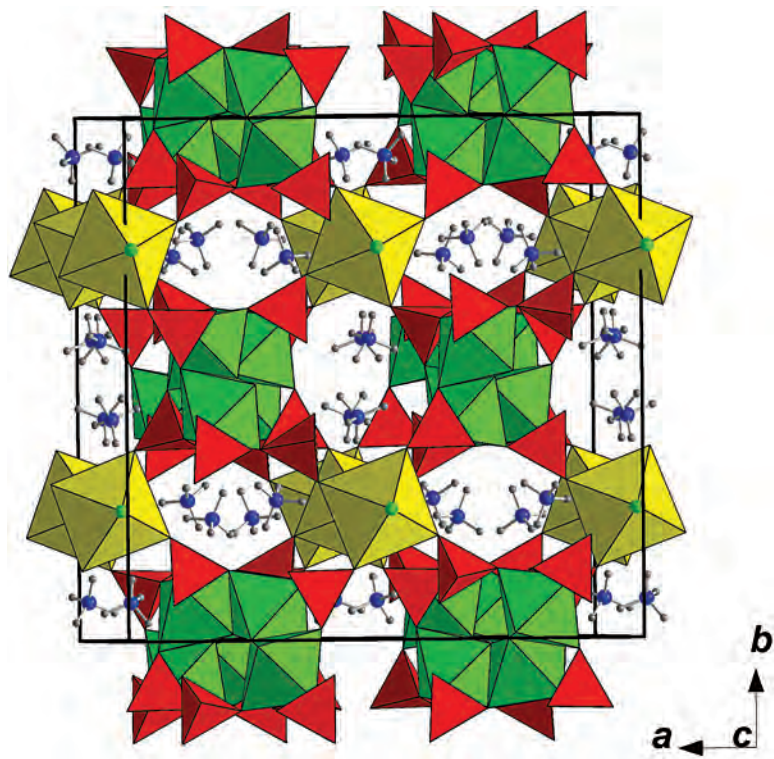


FIG. 5. Perspective view of the crystal structure of adranosite-(Fe). The SO_4^{2-} tetrahedra are shown in red, the Fe-centered octahedra in green, the Na-centered bipyramids in yellow, the N atoms of the NH_4^+ ions as blue spheres, and the Cl atoms as green spheres.

TABLE 3. SINGLE-CRYSTAL DATA AND REFINEMENT PARAMETERS

	Adranosite-(Fe)	Anthropogenic material
Crystal system	tetragonal	
Space group	$I4_1/acd$ (no. 142)	
<i>a</i> (Å)	18.261(2)	18.259(3)
<i>c</i> (Å)	11.562(1)	11.557(2)
<i>V</i> (Å ³)	3855.5(7)	3853.0(11)
<i>Z</i>	8	
Radiation	MoK α	
μ (mm ⁻¹)	2.098	
2 θ_{max} (°)	52.26	60.00
Measured reflections	17242	5229
Independent reflections	976	1414
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	670	951
Parameters refined	90	81
Extinction coefficient	-	0.00019(6)
Final <i>R</i> and <i>wR</i> 2	0.0415, 0.0997	0.0438, 0.0998
Weighting scheme	$w=1/[\sigma^2(\text{Fo}^2)+(0.0388q)^2+23.050q]$	$w=1/[\sigma^2(\text{Fo}^2)+(0.038q)^2+11q]$
<i>S</i>	1.012	1.086
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ eÅ ⁻³	-0.62, 0.68	-0.48, 0.53

Notes: $R = \sum ||\text{Fo}| - |\text{Fc}|| / \sum |\text{Fo}|$; $wR2 = \{\sum [w(\text{Fo}^2 - \text{Fc}^2)^2] / \sum [w(\text{Fo}^2)^2]\}^{1/2}$; $q = [\max(0, \text{Fo}^2) + 2\text{Fc}^2] / 3$; $S = \{\sum [w(\text{Fo}^2 - \text{Fc}^2)] / (n - p)\}^{1/2}$ where *n* is the number of reflections and *p* is the number of refined parameters

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (U_{eq}/U_{iso}) FOR ADRANOSITE-(Fe)

Atom	Wyckoff letter	x/a	y/b	z/c	$U_{eq}/U_{iso}^{\S}$	
Na	8a	1/2	1/4	1/8	0.0192(4)	
Fe	16f	0.30466(2)	0.55466(2)	1/8	0.0139(1)	
Al	16f	0.30466(2)	0.55466(2)	1/8	0.0139(1)	
S	32g	0.37858(3)	0.39769(3)	0.13582(4)	0.0163(1)	
Cl	8b	1/2	1/4	3/8	0.0288(3)	
N	32g	0.32456(11)	0.23263(9)	0.37804(15)	0.0375(6)	
K	32g	0.32456(11)	0.23263(9)	0.37804(15)	0.0375(6)	
O(1)	32g	0.38441(8)	0.47904(7)	0.11353(12)	0.0185(4)	
O(2)	32g	0.31686(9)	0.36867(10)	0.07216(14)	0.0344(5)	
O(3)	32g	0.36733(8)	0.38742(8)	0.26199(12)	0.0205(4)	
O(4)	32g	0.44810(9)	0.36554(9)	0.10319(14)	0.0311(4)	
O(5)	16e	0.26100(10)	1/2	1/4	0.0164(5)	
H(1)	32g	0.3047(3)	0.2833(2)	0.3920(5)	0.1170(15)	
H(2)	32g	0.3695(2)	0.2355(4)	0.3292(4)	0.162(18)	
H(3)	32g	0.3347(4)	0.2077(3)	0.4527(3)	0.060(9)	
H(4)	32g	0.2858(2)	0.2040(3)	0.3344(4)	0.172(19)	
H(5)	16e	0.2117(3)	1/2	1/4	0.098(18)	
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	0.0145(4)	0.0145(4)	0.0286(8)	0	0	0
Al/Fe	0.0136(1)	0.0136(1)	0.0145(2)	0.0016(1)	-0.0016(1)	0.0012(2)
S	0.0183(2)	0.0151(2)	0.0155(2)	-0.0005(2)	0.0009(2)	0.0028(2)
Cl	0.0290(3)	0.0290(3)	0.0285(4)	0	0	0.0006(5)
N/K	0.0534(12)	0.0281(10)	0.0309(10)	0.0019(9)	0.0050(10)	0.0072(9)
O(1)	0.0164(7)	0.0152(7)	0.0238(7)	0.0039(6)	0.0026(6)	0.0012(6)
O(2)	0.0343(9)	0.0306(9)	0.0382(9)	-0.0099(8)	-0.0137(8)	-0.0062(8)
O(3)	0.0234(7)	0.0206(8)	0.0175(7)	0.0036(6)	0.0040(6)	0.0047(6)
O(4)	0.0310(8)	0.0292(8)	0.0332(9)	0.0048(7)	0.0138(7)	0.0174(7)
O(5)	0.0131(9)	0.0167(10)	0.0195(9)	0.0075(8)	0	0

[§] The anisotropic displacement factor exponent takes the form:

$$-2\pi^2(U_{11}h^2(a^*)^2 + \dots + 2U_{12}hka^*b^* + \dots); U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$$

Occupancies different from unity: Fe = 0.910(2); Al = 0.090(2); N, H(1), H(2), H(3), H(4) = 0.973(2); K = 0.027(2).

distances and the well-defined H atom positions indicate that the ammonium ion is ordered due to the presence of hydrogen bonding.

The occurrence of adranosite-(Fe) in both natural fumaroles and fumarole-like vents in a burning coal dump, within fairly different mineral assemblages, indicates that the phase has a wide stability range. The same structure type may also be shown by the Rb^+ , V^{3+} , Cr^{3+} , or SeO_4^{2-} synthetic analogues. The formula obtained from the structure refinement, $[(NH_4)_{3.89}K_{0.11}]_{\Sigma 4.00}Na(Fe_{1.82}Al_{0.18})_{\Sigma 2.00}(SO_4)_4Cl(OH)_2$, is distinctly more Fe-rich than that obtained from the EPMA data, $[(NH_4)_{3.89}K_{0.11}]_{\Sigma 4.00}Na_{1.04}(Fe_{1.27}Al_{0.64})_{\Sigma 1.91}(SO_4)_{4.10}Cl_{0.67}(OH)_{1.96}$, thus evidencing some variability of the Fe/Al ratio within the holotype material and suggesting the existence of an isomorphous series with isotypic adranosite. The anthropogenic adranosite-(Fe) is even more Fe-rich, but has more K^+ substituting for NH_4^+ : $[(NH_4)_{3.59}K_{0.41}]_{\Sigma 4.00}Na(Fe_{1.88}Al_{0.12})_{\Sigma 2.00}(SO_4)_4Cl(OH)_2$; single-crystal laser-Raman spectra confirmed the presence of considerable NH_4^+ , and also indicated somewhat variable NH_4^+/K^+ ratios (Kolitsch & Brandstätter 2007, this work).

As previously discussed (Kolitsch & Brandstätter 2007, Demartin *et al.* 2010c), adranosite and adranosite-(Fe) have some structure relationships with the so-called "salt inclusion compounds". These composite materials, which have attracted much attention due to their potential applications, contain mixed ionic and covalent sublattices, where the alkaline halogenide salts reside in the structure channels and can be removed by washing, leaving nanopores in the remaining framework (*e.g.*, Liao *et al.* 2005, Mo *et al.* 2005, Lee *et al.* 2009, Queen *et al.* 2011). However, most of these materials usually contain a more stable framework, similar to that of zeolites with larger cavities or channels, than those entrapping NaCl in adranosite and adranosite-(Fe).

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

	Adranosite-(Fe), holotype	Anthropogenic material*	
Na—O(4) ×4	2.327(2)	2.336(3)	
Na—Cl ×2	2.8905(3)	2.8893(5)	
NH ₄ /K—O2	2.912(2)	2.893(5)	
NH ₄ /K—O4	2.957(2)	2.958(4)	
NH ₄ /K—O1	2.994(2)	3.005(4)	
NH ₄ /K—O3	3.099(2)	3.109(4)	
NH ₄ /K—O2	3.228(3)	3.230(5)	
NH ₄ /K—O3	3.225(2)	3.234(4)	
NH ₄ /K—O1	3.461(2)	3.475(4)	
NH ₄ /K—O4	3.529(2)	3.519(5)	
NH ₄ /K—Cl	3.220(2)	3.209(4)	
Fe/Al—O(1) ×2	2.011(1)	2.009(2)	
Fe/Al—O(3) ×2	2.034(1)	2.020(2)	
Fe/Al—O(5) ×2	1.929(1)	1.9416(15)	
<Fe/Al—O>	1.991	1.990	
S—O(1)	1.512(1)	1.509(2)	
S—O(2)	1.447(1)	1.450(3)	
S—O(3)	1.485(2)	1.490(2)	
S—O(4)	1.449(1)	1.446(2)	
<S—O>	1.473	1.474	
Hydrogen bonds			
	Adranosite-(Fe), holotype	Anthropogenic material*	
N—H(1)	1.005(4)		
N—H(2)	0.997(4)		
N—H(3)	0.993(4)		
N—H(4)	1.014(5)		
N···O(1) ⁱ	2.994(2)	N···O(1) ⁱ	2.893(5)
N···O(3) ⁱⁱ	3.099(2)	N···O(3) ⁱⁱ	3.109(4)
N···O(4) ⁱⁱⁱ	2.957(2)	N···O(4) ⁱⁱⁱ	3.005(4)
N···O(2) ^{iv}	2.912(2)	N···O(2) ^{iv}	2.958(4)
O(5)—H(5)	0.900(5)		
O(5)···O(1) ^{vii}	2.884(1)	O(5)···O(1) ^{vii}	2.961(4)
O(5)···O(2) ^{vii}	2.990(2)		
N—H(1)···O(1) ^j	152.0(3)	N—H(1)···O(1)	unknown**
N—H(1)···O(3) ⁱⁱ	128.1(3)	N—H(1)···O(3)	unknown**
N—H(2)···O(4) ⁱⁱⁱ	128.3(3)	N—H(2)···O(4) ^{vi}	167(4)
N—H(3)···O(2) ^{iv}	153.3(3)	N—H(3)···O(2)	unknown**
O(5)—H(5)···O(1) ^{vii}	83.52(3)	O(5)—H(5)···O(1) ^{vii}	139.4(12)
O(5)—H(5)···O(2) ^{vii}	139.0(4)		

Symmetry codes: i = y−1/4, 3/4−x, 1/4+z; ii = 3/4−y, 3/4−x, 3/4−z; iii = 3/4−y, x−1/4, 1/4−z; iv = x, 1/2−y, 1/2+z; v = 3/4−y, −3/4+x, −1/4+z; vi = 1/4+y, 3/4−x, 1/4−z; vii = y−1/4, 1/4+x, 1/4−z

* From burning coal dump at the Anna mine, near Aachen, Germany (Kolitsch & Brandstätter 2007)

** Only two of the H positions could be located.

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