Therasiaite, $(NH_4)_3KNa_2Fe^{2+}Fe^{3+}(SO_4)_3CI_5$, a new sulfate chloride from La Fossa Crater, Vulcano, Aeolian islands, Italy

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ABSTRACT

The new mineral therasiaite, ideally (NH₄)₃KNa₂Fe²⁺Fe³⁺(SO₄)₃Cl₅, was found in a mediumtemperature (~250°C) intracrater active fumarole at La Fossa crater, Vulcano, Aeolian Islands, Sicily, Italy. It occurs on a pyroclastic breccia as brown to dark brown equant to short prismatic crystals up to 0.1 mm in length, in association with salammoniac, kremersite and adranosite. The mineral is monoclinic, space group: Cc (no. 9) with a = 18.284(4), b = 12.073(2), c = 9.535(2) Å, $\beta = 108.10(3)^\circ$, V = 2000.6(7) Å³ and Z = 4. The six strongest reflections in the X-ray powder diffraction pattern are: $[d_{obs} \text{ in } \mathring{A}(I)(h \ k \ l)] 2.812(100)(\bar{2} \ 2 \ 3), 2.664(77)(\bar{5} \ 1 \ 3), 3.297(28)(3 \ 3 \ \bar{1}), 3.208(14)(\bar{5} \ \bar{1} \ 2), 3.008(12)(0 \ \bar{1} \ \bar{1}), 3.208(14)(\bar{5} \ \bar{1} \ 2), 3.008(12)(0 \ \bar{1}))$ 4 0), 2.942(11)(3 3 1). The empirical formula (based on 17 anions per formula unit (p.f.u.)) is $(NH_4)_{2.68}K_{1.32}Na_{2.04}Fe_{1.76}Al_{0.12}Mn_{0.12}S_{2.98}O_{11.95}Cl_{5.05}$. The measured density is 2.41(1) g cm⁻³, d_{calc} = 2.395 g cm⁻³. The mineral is biaxial (-) with α = 1.585(3) β = 1.615(3) and γ = 1.630(3) (white light). Using single-crystal diffraction data, the structure was refined to a final R(F) = 0.0240 for 5574 independent observed reflections $[I > 2\sigma(I)]$. The structure of the asiaite displays a novel topology and contains two independent, distorted octahedral Fe sites, with the Fe atoms in oxidation state 3+ and 2+, respectively, each surrounded by three Cl atoms and three oxygens of the sulfate ions. The Fe octahedra and the three independent sulfate anions are connected to form chains running along [001]. Voids between the chains are occupied by three independent ammonium ions (partially replaced by K^+), one K^+ and two Na⁺ ions. The formula resulting from the structure refinement is [(NH₄)_{2,25}K_{0,75}]KNa₂Fe₂(SO₄)₃Cl₅.

Keywords: therasiaite, new mineral species, fumarole sublimate, crystal structure, ammonium, sulfate, chloride, Vulcano island, Italy.

Introduction

ANHYDROUS sulfate chlorides are not common and amount to about a dozen species (see for instance rruff.info/ima/). Among these, those containing ammonium are rare and seem to have been found to date only at Vulcano Island, Aeolian Islands, Sicily, Italy (Campostrini *et al.*, 2011), i.e. adranosite (Demartin *et al.*, 2010) and adranosite-(Fe) (Mitolo *et al.*, 2013).

* E-mail: francesco.demartin@unimi.it DOI: 10.1180/minmag.2014.078.1.14 Therasiaite, $(NH_4)_3KNa_2Fe^{2+}Fe^{3+}(SO_4)_3Cl_5$, is another new ammonium sulfate chloride recently found in the same locality. It was approved as a new species by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (No. 2013-050). The name is for the type locality, Therasia, one of the ancient names for Vulcano island (from the Greek $\theta\eta\rho\alpha\sigma\tau\alpha$, warm earth).

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

Occurrence, morphology, chemical data and physical properties

Therasiaite was found on a pyroclastic breccia in an active, medium-temperature (~250°C) intracrater fumarole (fumarole FA in the La Fossa crater). It is associated with salammoniac, kremersite and adranosite. The mineral was observed only on one fragment of breccia, from which, after trimming, five significant specimens were recovered. Therasiaite forms aggregates of brown to dark brown equant to short prismatic crystals up to 0.1 mm in length (Figs 1 and 2). No twinning is apparent. The most common forms observed are: $\{012\}$, $\{210\}\{101\}\{\overline{1}01\}$ and $\{010\}$, an attribution derived from comparison of computer-generated crystal drawings with the morphology observed.

The mineral decomposes in the open air after a couple of weeks, in a few hours after grinding, but it remains stable if stored under nitrogen. The streak is brown and the lustre is vitreous. Cleavage and fracture were not observed. No fluorescence was observed under either shortwave or longwave ultraviolet radiation.

The density measured by flotation in a diiodomethane-benzene mixture is 2.41(1) g cm⁻³, and that calculated from the empirical formula and the X-ray data is 2.397 g cm⁻³. The mineral is biaxial (-) with $\alpha = 1.585(3) \beta = 1.615(3)$ and $\gamma = 1.630(3)$ (white light) and non-pleochroic; the compatibility index $[1 - (K_P/K_C)]$ is -0.017, which is superior according to Mandarino (1981).

Quantitative chemical analyses (12) were carried out in Energy Dispersive Spectroscopy



FIG. 1. Backscatter scanning electron microscope image of crystals of therasiaite.

(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). This analytical method was chosen because the sample would be severely damaged by using the wavelength dispersive spectroscopy technique, even with a low voltage and a largediameter beam. Element concentrations were measured using the $K\alpha$ lines for Fe, S, K, Na and Cl. The presence of N was also evident in the EDS spectrum; however, the uncertainties of the measurements were considered too large for a quantitative estimation of this element. Therefore the $(NH_4)_2O$ content was calculated by stoichiometry, taking into account its partial replacement by K (see later). The presence of ammonium was also established from crystal structure-analysis and confirmed by the Fourier transform infrared spectrum, recorded on a Jasco IRT-3000 spectrometer, which shows strong absorption peaks at 3205 and 1410 cm^{-1} , consistent with the presence of this ion (Fig. 3). The mean analytical results are reported in Table 1. The empirical formula





FIG. 2. (*a*) Backscatter scanning electron microscope image of crystals of therasiaite. (*b*) Idealized drawing of a crystal of Fig. 2*a* with indexing of the faces.



FIG. 3. Infrared spectrum of therasiaite.

(based on 17 anions p.f.u.) is $(NH_4)_{2.68}K_{1.32}$ Na_{2.04}Fe_{1.76}Al_{0.12}Mn_{0.12}S_{2.98}O_{11.95}Cl_{5.05}. The idealized formula is $(NH_4)_3KNa_2Fe_2(SO_4)_3Cl_5$, which requires $(NH_4)_2O$ 10.91, Na₂O 8.65, K₂O 6.58, FeO 10.03, Fe₂O₃ 11.15, SO₃ 33.53, Cl 24.74, total 100.00 wt%.

The holotype material is deposited in the Reference Collection of the Dipartimento di Chimica, Università degli Studi di Milano, specimen number 2013-01.

X-ray data

X-ray powder diffraction data (Table 2) were obtained using a Philips PW1830 diffractometer, with $CuK\alpha$ radiation. Due to the small amount of available material and its instability after grinding in a mortar, the polycrystalline sample was affected by preferred orientation as can be inferred by the difference between the observed and calculated intensities of some reflections. The

Constituent	Wt.%	Range	SD	Probe standard
(NH ₄) ₂ O*	9.64			
K ₂ O	8.61	8.02-9.12	0.15	KCl
Na ₂ O	8.72	7.32-9.10	0.22	Natural albite
FeO**	8.75			
Fe ₂ O ₃ **	9.72	17.50-19.05	0.20	Natural almandine garnet
MnO	1.21	0.22-1.29	0.20	Natural almandine garnet
Al_2O_3	0.87	0.77 - 0.95	0.15	Natural almandine garnet
SO ₃	32.93	32.02-33.19	0.13	Synthetic anhydrite
Cl	24.70	24.22-26.13	0.23	KCl
O = Cl	-5.58			
Total	99.57			

TABLE 1. Chemical composition of therasiaite.

* by stoichiometry; $**Fe^{2+}/Fe^{3+} = 1$ in accord with the structure determination.

h k l	I _{obs}	I_{calc}^{**}	d_{obs} (Å)	d_{calc1} (Å)*	d_{calc2} (Å)**
1 1 0	6	26	9.99	9.913	9.915
111	8	100	7.36	7.378	7.372
3 1 0	6	22	5.22	5.236	5.223
0 0 2	6	2	4.513	4.514	4.531
4 0 0	6	12	4.375	4.360	4.345
312	4	4	4.049	4.045	4.026
1 3 0	3	4	3.928	3.914	3.921
4 2 0	6	12	3.511	3.532	3.526
331	28	26	3.297	3.303	3.299
512	14	17	3.208	3.204	3.180
ī 3 2	8	9	3.068	3.068	3.073
040	12	12	3.008	3.012	3.018
3 3 1	11	52	2.942	2.935	2.942
041	6	25	2.859	2.857	2.864
<u>2</u> 23	100	58	2.812	2.809	2.811
1 1 3	9	8	2.749	2.744	2.757
513	77	21	2.664	2.688	2.672
7 1 0	5	6	2.438	2.440	2.432
204	5	12	2.374	2.378	2.380
<u>2</u> 24	6	12	2.212	2.212	2.214
8 0 4	4	7	1.911	1.902	1.888

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

* Calculated from the unit cell: a = 18.415(3), b = 12.048(2), c = 9.531(1) Å, $\beta = 108.71(2)^{\circ}$ obtained from least-squares refinement of the above data using the program *UNITCELL* (Holland and Redfern, 1997). ** Calculated from single-crystal data.

indexing of the powder-diffraction pattern was made by comparison with the pattern calculated after the structure determination. The following unit-cell parameters a = 18.415(3), b = 12.048(2),c = 9.531(1) Å, $\beta = 108.71(2)^{\circ}$ were obtained from least-squares refinement from the above data using the program UNITCELL (Holland and Redfern, 1997). There is a significant difference (greater than 3σ) between the values obtained in this way and those derived from single-crystal data, 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.

The unit-cell parameters obtained from 7440 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 10,373 intensities corresponding to a

complete scan of the reciprocal lattice up to $2\theta =$ 62.86° were collected from a crystal $(0.05 \text{ mm} \times 0.05 \text{ mm} \times 0.03 \text{ mm})$ 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 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 effects. An absorption correction ($\mu = 2.894 \text{ mm}^{-1}$, $T_{min} = 0.897$) was applied using the SADABS program (Sheldrick, 2000). After averaging the symmetry-related reflections (Friedel opposites not merged, $R_{int} = 0.0129$), 5956 independent data were obtained. Systematic absences indicated the two possible space groups C2/c and Cc; the choice of the non-centrosymmetric space group Cc was suggested by statistical tests on the distribution of the E values $[|E^2-1| = 0.760]$ and confirmed by the subsequent satisfactory structure solution and refinement. Furthermore the absence of additional missed symmetry was confirmed by the PLATON program (Spek, 2003) after the final structure refinement. 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 one of the sulfate anions (the one containing S1) were present, due to a small rotation of the tetrahedron about the O1-S1 vector. A refinement of the occupancies of the three disordered O atoms gave values of ~0.70 and ~0.30 for the two conformations, respectively. These values were kept fixed in the final stages of the refinement. The oxygens with minor occupancy were refined with an isotropic displacement parameter, whereas all the other atoms of the structure were allowed to vibrate anisotropically. A refinement of the occupancies of the N sites revealed significant substitution of the ammonium ions by K^+ as shown in Table 4, whereas no occupancy was refined for the Fe sites, due to only small amounts of Mn and Al replacing Fe. The formula resulting from the structure refinement is $[(NH_4)_{2,25}K_{0,75}]$ KNa₂Fe₂(SO₄)₃Cl₅. The positions of all the H atoms of the ammonium ion could not be detected from a difference fourier map due to local disorder. The Flack parameter is 0.000(18), confirming the correctness of the absolute structure. The final R is 0.0240 for 5574 observed reflections $[I > 2\sigma(I)]$. The coordinates and displacement parameters of the atoms are reported

Crystal system	Monoclinic
Space Group	Cc (no. 9)
a (Å)	18.284(4)
b (Å)	12.073(2)
<i>c</i> (Å)	9.535(2)
β (°)	108.10(3)
$V(\text{\AA}^3)$	2000.6(7)
a:b:c ratio	1.515:1:0.790
Ζ	4
Radiation	MoK_{α}
$\mu (mm^{-1})$	2.894
$D_{\text{calc}} (\text{g cm}^{-3})$	2.395
Measured reflections	10373
Independent reflections	5956
Observed reflections $[I > 2\sigma(I)]$	5574
Parameters refined	269
Final $R [I > 2\sigma(I)]$ and wR2 (all data)	0.0240, 0.0884
S	1.171

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

 $R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; \ wR2 = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]\}^{1/2};$

 $w = 1[\frac{g}{(r_c^2)} (\frac{1}{r_c^2}) (10.0535q)^2] \text{ where } q = [\max(0, F_c^2) + 2F_c^2]/3;$ $S = \{\Sigma[w(F_c^2 - F_c^2)]/(n-p)\}^{1/2} \text{ where } n \text{ is the number of reflections and } p \text{ is the number of refined parameters.}$

in Table 4; selected interatomic distances, angles and bond valence calculations are listed in Table 5. Observed and calculated structurefactors tables have been deposited with the Principal Editor of Mineralogical Magazine and are available at http://www.minersoc.org/pages/ e journals/dep mat mm.html.

Description of the structure and discussion

The structure of therasiaite contains two independent, distorted octahedral iron sites, Fe1 and Fe2, each surrounded by three Cl atoms and three oxygens of the sulfate ions, with the following average distances (Å): Fe1-O 1.993, Fe1-Cl 2.400, Fe2-O 2.101, Fe2-Cl 2.531. These values suggest that the Fe1 and Fe2 sites are exclusively occupied by Fe^{3+} and Fe^{2+} , respectively, a situation also confirmed by a bond-valence calculation (Brese and O'Keeffe, 1991) that gives 2.92 and 1.96 vu for Fe1 and Fe2, respectively.

The two Fe ions form dimeric octahedral units sharing a common vertex (Cl2) bridged by two sulfate anions (S2 and S3). A third sulfate anion (S1) is instead coordinated to Fe1 by one vertex only (O1). In addition sulfate S3 acts as a bridge between adjacent dimeric octahedral units through O12 giving rise to infinite chains extending along [001] (Figs 4 and 5). Therefore the S1-containing sulfates interact with the Fe ions by one vertex only, those with S2 and S3 by two and three vertices respectively, the remaining vertices being involved in the coordination of the alkaline cations or in H bonds with the ammonium ions located in the voids between the chains (three independent ammonium ions, partially replaced by K⁺, one K⁺ and two Na⁺ ions, see Figs 6, 7). In the three sulfate anions, the S–O distances range from 1.434(4) to 1.506(3) Å with an average value of 1.469 Å (excluding in the computation those belonging to the minor disordered conformation) that is in accord with the grand <S-O> distance reported by Hawthorne et al. (2000) of 1.473 A.

The two Na sites display sevenfold and sixfold coordination, with average Na-O distances of 2.443 and 2.419 Å and average Na-Cl distances of 3.011 and 2.940 Å, respectively. The average distances are consistent with the different coordination numbers for the two Na⁺ cations. The site occupied exclusively by potassium (K4) is 9-coordinated, with average K-O and K-Cl distances of 2.969 and 3.142 Å, respectively.

The three sites occupied by the ammonium ions (partially replaced by K⁺ cations) are surrounded by 8 to 10 close neighbours. Considering that the ionic radius for the ammonium ion has been

Atom	Occupancy	x/a	y/b	z/c	$U_{ m eq}$
Fel	1	0.61710(3)	0.24642(4)	0.30691(5)	0.01405(9)
Fe2	1	0.78831(3)	0.16054(4)	0.13411(5)	0.01475(10)
S1	1	0.47523(4)	0.07746(7)	0.31396(8)	0.01514(15)
S2	1	0.76294(4)	0.40549(6)	0.28569(8)	0.01261(14)
S3	1	0.77323(5)	0.09989(6)	0.46880(8)	0.01358(14)
01	1	0.53705(16)	0.1328(3)	0.2652(3)	0.0272(6)
02	0.70	0.4079(3)	0.1480(5)	0.2522(7)	0.0559(17)
03	0.70	0.4931(3)	0.0760(5)	0.4714(4))	0.0320(10)
04	0.70	0.4662(4)	-0.0346(4)	0.2548(6)	0.0456(14)
02'	0.30	0.4038(6)	0.0790(10)	0.1987(12)	0.033(2)
03'	0.30	0.4691(11)	0.1313(16)	0.441(2)	0.070(5)
04′	0.30	0.5021(13)	-0.0326(19)	0.328(2)	0.084(6)
05	1	0.70649(14)	0.3489(2)	0.3467(3)	0.0186(5)
06	1	0.80393(15)	0.3215(2)	0.2249(3)	0.0227(5)
07	1	0.81787(15)	0.4604(2)	0.4110(3)	0.0228(5)
08	1	0.72171(17)	0.4824(2)	0.1702(3)	0.0301(6)
60	1	0.68928(15)	0.1269(2)	0.4232(3)	0.0228(5)
010	1	0.79577(19)	0.0777(3)	0.3360(3)	0.0306(6)
011	1	0.81836(17)	0.1890(2)	0.5545(3)	0.0306(6)
012	1	0.7838(2)	-0.0009(2)	0.5568(4)	0.0361(7)
CII	1	0.93292(5)	0.16126(8)	0.19391(10)	0.02456(18)
CI2	1	0.64268(5)	0.17794(7)	0.08040(9)	0.01930(16)
Cl3	1	0.59703(5)	0.31622(8)	0.51999(9)	0.02348(18)
Cl4	1	0.76610(5)	0.24305(8)	-0.11708(9)	0.02282(17)
CI5	1	0.53540(5)	0.38191(7)	0.15459(10)	0.02331(17)
Nal	1	0.77669(9)	0.35490(13)	0.62489(18)	0.0242(3)
Na2	1	0.88338(9)	0.38624(13)	0.05359(19)	0.0285(4)
N1/K1	0.738(9)/0.262(9)	0.62181(19)	0.4170(3)	-0.1233(4)	0.0544(12)
N2/K2	0.839(7)/0.161(7)	0.62577(16)	0.0736(2)	0.7045(3)	0.0370(10)
N3/K3	0.677(8)/0.323(8)	0.91055(14)	-0.0961(2)	0.3440(3)	0.0451(9)
K4	1	0.94411(6)	0.31507(8)	0.46801(10)	0.0336(2)

TABLE 4. Atomic coordinates and displacement parameters [Ueq/ U_{ij} , Å²] for the rasiaite. F. DEMARTIN ET AL.

(13(18)	0.0145(2)	0.0172(2)	-0.00070(15)	0.00536(15)	-0.00246(15)
69(2)	0.0128(2)	0.0152(2)	-0.00209(17)	0.00578(16)	-0.00146(17)
08(3)	0.0204(4)	0.0138(3)	0.0018(3)	0.0031(3)	-0.0039(3)
13(3)	0.0093(3)	0.0177(3)	-0.0001(3)	0.0051(3)	-0.0016(2)
[83(3)	0.0104(3)	0.0124(3)	0.0017(2)	0.0054(3)	0.0026(3)
256(14)	0.0334(16)	0.0284(14)	-0.0120(11)	0.0170(11)	-0.0194(11)
20(2)	0.065(4)	0.080(4)	0.038(3)	0.011(3)	0.021(2)
35(2)	0.054(3)	0.0091(15)	-0.0037(17)	0.0088(15)	-0.022(2)
72(4)	0.029(2)	0.049(3)	-0.025(2)	0.038(3)	-0.033(2)
180(11)	0.0189(11)	0.0206(12)	-0.0006(9)	0.0087(10)	-0.0069(9)
198(12)	0.0217(13)	0.0304(14)	-0.0104(10)	0.0135(11)	-0.0018(10)
183(12)	0.0187(12)	0.0311(14)	-0.0123(10)	0.0070(10)	-0.0070(9)
285(14)	0.0226(14)	0.0351(15)	0.0181(12)	0.0041(12)	0.0024(11)
182(12)	0.0240(13)	0.0270(13)	0.0079(10)	0.0082(10)	0.0033(10)
388(16)	0.0400(17)	0.0173(12)	0.0066(11)	0.0150(11)	0.0173(13)
288(15)	0.0229(14)	0.0326(15)	-0.0085(11)	-0.0014(12)	0.0008(11)
471(18)	0.0196(13)	0.0390(16)	0.0175(12)	0.0098(14)	0.0059(13)
175(4)	0.0283(4)	0.0282(4)	-0.0037(3)	0.0075(3)	0.0027(3)
165(3)	0.0249(4)	0.0174(49	-0.0002(3)	0.0066(3)	-0.0007(3)
263(4)	0.0255(4)	0.0214(4)	-0.0068(3)	0.0114(3)	-0.0031(3)
(233(4))	0.0274(4)	0.0186(4)	0.0035(3)	0.0076(3)	-0.0007(3)
194(4)	0.0218(4)	0.0264(4)	0.0008(3)	0.0038(3)	0.0037(3)
283(8)	0.0212(7)	0.0243(7)	-0.0028(6)	0.0102(6)	0.0031(6)
268(9)	0.0262(8)	0.0310(8)	0.0064(7)	0.0070(7)	-0.0038(6)
537(18)	0.0499(19)	0.060(2)	0.0058(14)	0.0177(14)	0.0035(13)
381(16)	0.0240(14)	0.0415(17)	0.0053(10)	0.0016(11)	-0.0065(10)
410(14)	0.0486(15)	0.0492(15)	0.0064(10)	0.0192(10)	0.0047(9)
306(5)	0.0398(5)	0.0268(4)	-0.0015(4)	0.0035(3)	0.0090(4)

THERASIAITE, A NEW SULFATE CHLORIDE FROM LA FOSSA CRATER, VULCANO

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Fe1-O1	1.954(3)	0.590	Fe2-O10	2.135(3)	0.338
Fe1-O9	2.035(3)	0.474	Fe2-O12	2.057(3)	0.418
Fe1-O5	1.990(2)	0.536	Fe2-O6	2.111(3)	0.361
Fe1-Cl2	2.489(1)	0.340	Fe2-Cl1	2.526(1)	0.284
Fe1-Cl3	2.331(1)	0.521	Fe2-Cl2	2.559(1)	0.260
Fe1-Cl5	2.381(1)	0.455	Fe2-Cl4	2.508(1)	0.298
		$\Sigma = 2.917$			$\Sigma = 1.959$
S1-01	1.506(3)	1.376			
S1-O2	1.462(5)	1.549	S1-O2'	1.42(1)	
S1-O3	1.434(4)	1.671	S1-O3'	1.41(2)	
S1-O4	1.455(4)	1.579	S1-O4'	1.41(2)	
	1.464	$\Sigma = 6.175$			
\$3-09	1.496(3)	1.413	S2-O5	1.498(2)	1.406
S3-O10	1.473(3)	1.504	S2-06	1.481(2)	1.472
S3-011	1.445(3)	1.622	S2-07	1.459(3)	1.562
S3-012	1.456(3)	1.575	S2-08	1.458(3)	1.566
~~ ~ ~ ~	1 468	$\Sigma = 6.110$		1 474	$\Sigma = 6.010$
Na1-O2	2 328(5)	0 240	Na2-03	2 414(5)	0 1 9 0
Na1-05	2.520(3) 2.564(3)	0.127	Na2-04	2.254(6)	0.293
Na1-07	2.702(3)	0.087	Na2-O6	2.620(3)	0.110
Na1-08	2.308(3)	0.253	Na2-07	2387(3)	0.205
Na1-011	2.300(3) 2.315(3)	0.249	Na2-Cl1	3.039(2)	0.090
Na1-Cl3	3.157(2)	0.070	Na2-Cl4	2.840(2)	0.155
Na1-Cl4	2 865(2)	0.145		2.010(2)	$\Sigma = 1.040$
itur ori	2.005(2)	$\Sigma = 1.170$			2 1.010
K4-O1	2.884(3)	0.130	K4-07	2.814(3)	0.157
K4-O2	3.016(7)	0.091	K4-011	3.076(3)	0.078
K4-O3	3.273(5)	0.046	K4-Cl1	3.160(2)	0.177
K4-O4	2.846(5)	0.144	K4-C15	3.124(2)	0.195
K4-O6	2.873(3)	0.134			$\Sigma = 1.152$
Shortost distance	a of the ammonium	ions to their nois	hbourg		
N1/K105	3 277(4)	ions to their heig	N2/K209	3,300(4)	
N1/K108	2.935(5)		N2/K2C12	3.308(3)	
N1/K108	3304(5)		N2/K2 C12	3.373(3)	
N1/K1Cl1	3.301(3) 3.481(4)		N2/K2 = C13 N2/K2 = C14	3.379(3)	
N1/K1Cl2	3,434(3)		N2/K2····CI4	3.208(7)	
N1/K1Cl2	3 506(3)		N3/K3010	2.952(4)	
N1/K1Cl3	3.500(3) 3.582(3)		N3/K3011	2.932(4) 2.971(4)	
N1/K1Cl/	3 358(3)		N3/K3012	2.971(4) 3.208(4)	
N1/K1C15	3 285(3)		N3/K3C11	3.208(+) 3.407(3)	
N1/K1Cl5	3.507(3)		N3/K3C11	3.797(3)	
N2/K201	3.307(3) 3.124(4)		N3/K3C12	3.527(3) 3.465(3)	
N2/K202	2.124(4) 2.724(5)		N3/K3. C14	3,207(2)	
N2/K2 04	2.734(3) 2.126(7)		N2/K2 C15	3.297(3)	
N2/K209	3.130(7) 3.170(4)		1NJ/KJCIJ	5.552(5)	
112/ K2···O3	5.1/0(+)				

TABLE 5. Selected interatomic distances (Å), angles (°) and bond valences (vu) in therasiaite.

estimated at ~1.65–1.66 Å (Khan and Baur, 1972) and that the crystal radius of O^{2-} is 1.24 Å and that of Cl is 1.67 Å, distances of ~3.0 Å are to be expected for N···O hydrogen-bonds and of ~3.3 Å for the N···Cl ones. The corresponding interactions observed in therasiaite are slightly

larger than those predicted, indicating weak and disordered H bonds, explaining why the location of the corresponding hydrogens could not be determined.

Therasiaite belongs to the group of sulfates containing infinite chains made by octahedra and



FIG. 4. Perspective view of the structure of therasiaite seen along [100]. Fe: green octahedra; SO_4^{2-} : yellow tetrahedra; Na: orange spheres; NH_4^+ : blue spheres; K^+ : pink spheres.

tetrahedra, but has a novel topology. Within this group a comparison can be made only with

copiapite, $Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2\cdot 20H_2O,$ where there are chains containing dimeric octahedral



FIG. 5. A portion of the $[Fe_2(SO_4)_3Cl_5^{6-}]_n$ chain extending along [001]. Fe: green octahedra; SO_4^{2-} : yellow tetrahedra.

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FIG. 6. Perspective view of the structure of therasiaite seen along [001]. Colours are the same as in Fig. 4.

units that share a common vertex and are bridged by two sulfate anions (Fanfani *et al.*, 1973; Majzlan and Michallik, 2007). However, in the chains of copiapite, Fe is always in the 3+oxidation state, and polymerization of the dimeric units occurs through a sulfate ion that shares two vertices only instead of three as in therasiaite.

Another comparison can be made with xitieshanite, $Fe^{3+}(SO_4)Cl\cdot 6H_2O$, (Zhou Jingliang *et*



FIG. 7. Perspective view of one chain showing the arrangement of the Na^+ , NH_4^+ and K^+ cations. Colours are the same as in Fig. 4.

al., 1988), which is the only other example of a sulfate species where Cl is coordinated to Fe. However in xitieshanite, Fe is present only in the 3+ oxidation state, with an average Fe–O distance of 2.032 Å and a unique Fe–Cl distance of 2.243 Å which can be compared with the average values of the Fe1–O and Fe1–Cl distances in therasiaite, 1.993 and 2.400 Å, respectively. This difference is due to the different number of chlorides and sulfates present in the coordination sphere as well as to a different coordination about Cl.

Therasiaite is an additional example confirming the uniqueness of the geochemical conditions that occur in the fumaroles at La Fossa Crater that has led to it becoming, in recent years, one of the most prolific localities for new mineral species in the world.

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