

THERMESSAITE, $K_2[AlF_3SO_4]$, A NEW INO-ALUMINOFLUORIDE–SULFATE FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

Thermessaite, ideally $K_2[AlF_3SO_4]$, is a new ino-aluminofluoride-sulfate found in active medium- to high-temperature fumaroles (300–350°C) at the rim of La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy. The mineral occurs as sharp translucent crystals up to 0.25 mm in an altered pyroclastic breccia, together with alunite, sassolite, anhydrite and metavoltine. It is orthorhombic (*mmm*), space group *Pbcn*, with *a* 10.810(2), *b* 8.336(2), *c* 6.822(1) Å, *V* 614.8(2) Å³, *Z* = 4; the crystal habit is prismatic, with {110} and the pinacoid {100} as the dominant forms, terminated by minor faces of the bipyramid {111}. The mineral is colorless to white; the streak is white, the luster, vitreous, and the tenacity, brittle. It is nonfluorescent. Cleavage and fracture were not observed. The calculated density is 2.790 g/cm³, the observed density is 2.77(2) g/cm³, and the mean index of refraction is 1.445. The chemical analysis leads to the empirical formula $K_{2.02}[Al_{1.05}F_{3.17}S_{0.94}O_{3.83}]$, corresponding to the ideal formula $K_2[AlF_3SO_4]$. The structure was refined to a final *R* = 0.0286 for 685 observed reflections [*I* > 2σ(*I*)]. It contains chains of corner-sharing AlF_4O_2 octahedra running along [001]; these octahedra share two vertices with SO_4 tetrahedra [Al–F distances 1.752(1) × 2 and 1.844(1) Å × 2, and Al–O 1.906(1) Å × 2]; this structural motif is new for aluminofluoride minerals. The K^+ ions are surrounded by five oxygen atoms [$\langle K-O \rangle$ 2.642(2)–3.247(2) Å] and by four fluorine atoms [$\langle K-F \rangle$ 2.682(2)–2.926(2) Å]. The strongest six lines in the X-ray powder-diffraction pattern [d_{obs} in Å(*I*)/*hkl*] are: 2.983(100)(311), 2.702(82)(130), 6.631(70)(110), 1.712(58)(530), 2.208(30)(330) and 3.317(28)(310). The mineral is named after Thermessa (θερμῆσσα), an ancient Greek name of the Island of Vulcano meaning “the warm island”. Both the mineral and the mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2007–030).

Keywords: thermessaite, new mineral species, aluminofluorides, sulfates, crystal structure, Vulcano Island, Aeolian Islands, Italy.

SOMMAIRE

Nous décrivons la thermessaïte, de composition idéale $K_2[AlF_3SO_4]$, ino-aluminofluorure–sulfate récemment découvert dans des fumerolles de température moyenne à élevée (300–350°C) en bordure du cratère La Fossa, île de Vulcano, dans l'archipel Eolien, en Sicile, Italie. Le minéral se présente en cristaux translucides bien définis, atteignant 0.25 mm dans une brèche pyroclastique altérée, avec alunite, sassolite, anhydrite et métavoltine. Il est orthorhombique (*mmm*), groupe spatial *Pbcn*, avec *a* 10.810(2), *b* 8.336(2), *c* 6.822(1) Å, *V* 614.8(2) Å³, *Z* = 4. Les cristaux sont prismatiques, avec les formes dominantes {110} et le pinacoidé {100}, avec terminaisons bipyramidales {111} mineures. Le minéral est incolore à blanc; sa rayure est blanche, son éclat, vitreux, et sa tenacité, cassante. Il n'est pas fluorescent. Nous n'avons décelé aucun clivage et aucune fracture. La densité calculée est 2.790 g/cm³, la densité observée est 2.77(2) g/cm³, et l'indice de réfraction moyen est 1.445. L'analyse chimique mène à la formule empirique $K_{2.02}[Al_{1.05}F_{3.17}S_{0.94}O_{3.83}]$, ce qui correspond à la formule idéale $K_2[AlF_3SO_4]$. La structure a été affinée jusqu'à un résidu final *R* de 0.0286 pour 685 réflexions observées [*I* > 2σ(*I*)]. Elle contient des chaînes d'octaèdres AlF_4O_2 à coins partagés alignées selon [001]; ces octaèdres partagent deux sommets avec des tétraèdres SO_4 [distances Al–F 1.752(1) × 2 et 1.844(1) Å × 2, et distance Al–O 1.906(1) Å × 2]; ce motif structural n'a jamais été signalé parmi les minéraux aluminofluorés. Les ions K^+ sont entourés par cinq atomes d'oxygène [$\langle K-O \rangle$ 2.642(2)–3.247(2) Å] et par quatre atomes de fluor [$\langle K-F \rangle$ 2.682(2)–2.926(2) Å]. Les six raies les plus intenses du spectre de diffraction prélevé sur poudre [d_{obs} en Å(*I*)/*hkl*] sont:

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2.983(100)(311), 2.702(82)(130), 6.631(70)(110), 1.712(58)(530), 2.208(30)(330) et 3.317(28)(310). Le nom du minéral vient de Thermessa (θερμессα), un ancien nom grec de l'île de Vulcano qui veut dire "île chaude". Le minéral et son nom ont reçu l'approbation de la Commission sur les Nouveaux Minéraux, la Nomenclature et la Classification de l'IMA (no. 2007-030).

(Traduit par la Rédaction)

Mots-clés: thermessaïte, nouvelle espèce minérale, aluminofluorures, sulfates, structure cristalline, île de Vulcano, archipel Eolien, Italie.

INTRODUCTION

The fumaroles at La Fossa crater, Vulcano, Aeolian Islands, have long been the object of mineralogical investigation. Recently, several new species have been discovered (*e.g.*, Garavelli *et al.* 2005, Camprostrini *et al.* 2008, and references therein). Characteristic of the locality are Pb and Bi sulfides and sulfosalts (in some cases with significant amounts of halogens), Pb and Tl chlorides and complex fluorides (fluorosilicates or silicofluorides and fluoroborates or borofluorides). Here, we describe a new species found in an active medium- to high-temperature fumarole (300–350°C) at the rim of La Fossa crater, as small colorless to white prismatic crystals up to 0.25 mm, associated with alunite, sassolite, anhydrite and metavoltine. The mineral has been named thermessaïte after Thermessa (θερμессα), *i.e.*, "the warm island", an ancient Greek name of the Island of Vulcano. Both the mineral and the mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2007-022). The type specimen is deposited (no.

2007-2) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

PHYSICAL PROPERTIES AND CHEMICAL DATA

The crystal habit is prismatic, with {110} and the pinacoid {100} as the dominant forms, terminated by minor faces of the bipyramid {111} (Figs. 1, 2). The mineral is colorless to white; the streak is white, the luster, vitreous and the tenacity, brittle. Cleavage and fracture were not observed. No fluorescence was observed both under short-wave and long-wave ultraviolet radiation. The calculated density is 2.790 g/cm³, the observed density is 2.77(2) g/cm³ (from flotation at 25°C in bromoform–chloroform). By immersion in a mixture of petroleum oil and turpentine, the indices of refraction of several fragments were all found to be close to 1.445. The compatibility index with a Gladstone–Dale calculation (Mandarino 1981) is –0.02, which can be regarded as excellent.

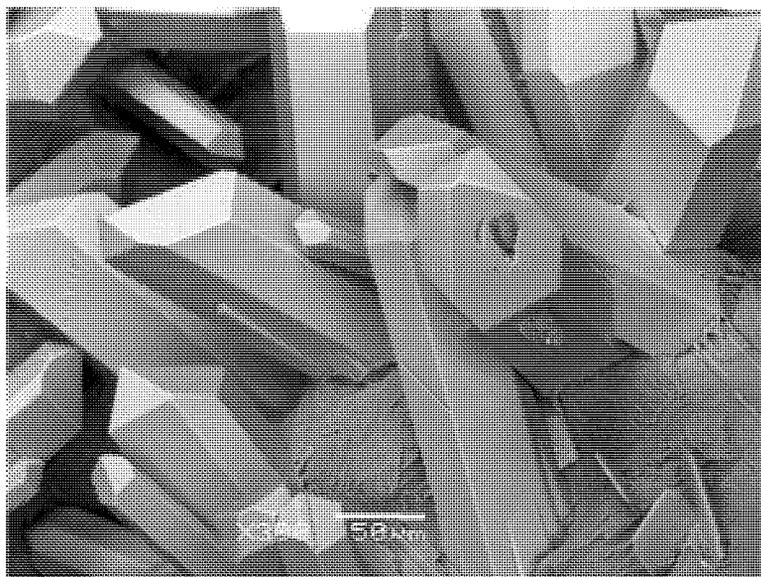


FIG. 1. BSE image of thermessaite crystals.

Chemical analyses were carried out by means of a JEOL JXA 8200 electron microprobe under the following conditions: 15 kV excitation voltage, 4.04×10^{-9} A beam current, 10 μm beam diameter. Element concentrations were measured using the $K\alpha$ line in wavelength-dispersive spectrometry (WDS). The mean analytical results (average on seven analyzed points) are reported in Table 1. The empirical formula obtained (based on seven anions *pfu*) is: $\text{K}_{2.02}[\text{Al}_{1.05}\text{F}_{3.17}\text{S}_{0.94}\text{O}_{3.83}]$. The idealized formula is $\text{K}_2[\text{AlF}_3\text{SO}_4]$, which requires: K_2O 36.48, Al_2O_3 19.74, SO_3 31.01, F 22.07, $-\text{O}=\text{F}$ -9.30, for a total of 100.00 wt.%. This content is in line with the result of the crystal-structure refinement (see below).

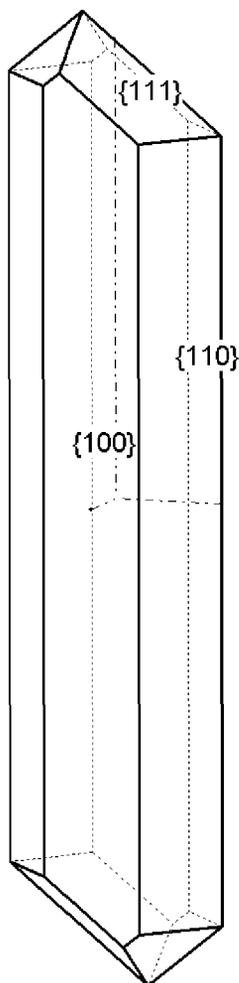


FIG. 2. Idealized drawing of a typical crystal of thermessaite.

X-RAY DATA

X-ray powder-diffraction data have been obtained using a Rigaku DMAX-II diffractometer, with $\text{CuK}\alpha$ radiation (Table 2). A least-squares fit of these data provided the following orthorhombic unit-cell parameters: a 10.8345(7), b 8.3600(6), c 6.8476(5) Å, V 620.23(6) Å³. Single-crystal diffraction data were collected from a crystal fragment ($0.20 \times 0.09 \times 0.08$ mm) with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å), using a Bruker Apex II diffractometer equipped with a 2K CCD detector. A one-minute frame-time and 0.3° frame width were used. A total of 5180 reflections, corresponding to a complete scan of the reciprocal lattice up to $2\theta_{\text{max}} = 58.80^\circ$, were measured; of these, 821 were found to be unique ($R_{\text{int}} = 0.0355$). The unit-cell dimensions were refined by least-squares from 1601 reflections with $I > 5\sigma(I)$; the refined values are given in Table 3, together with other details concerning the data collection and refinement. The data were reduced using the Bruker program SAINT, and corrected for Lorentz, polarization, and background. An absorption correction was applied (minimum transmission factor 0.845) using

TABLE 1. CHEMICAL COMPOSITION OF THERMESSAITE

Constituent	wt.%	Range	Stand. dev.	Probe standard
K_2O	36.19	35.61 – 36.55	0.8	K-feldspar
Al_2O_3	20.42	19.99 – 20.95	0.4	anorthite
SO_3	28.74	28.17 – 29.26	0.4	SrSO_4
F	22.89	21.52 – 23.77	0.9	RbMnF_3
$-\text{O} = \text{F}$	-9.64			
Total	98.6			

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

<i>l</i> / <i>h</i>	<i>d</i> (obs.)	<i>d</i> (calc.) ⁵	<i>h</i>	<i>k</i>	<i>l</i>	<i>l</i> / <i>h</i>	<i>d</i> (obs.)	<i>d</i> (calc.) ⁵	<i>h</i>	<i>k</i>	<i>l</i>
70	6.631	6.619	1	1	0	3	1.967	1.965	1	4	1
14	5.429	5.417	2	0	0	7	1.951	1.950	2	4	0
7	4.762	4.759	1	1	1	10	1.877	1.879	2	2	3
5	4.182	4.180	0	2	0	2	1.854	1.852	5	2	1
3	3.574	3.568	0	2	1	4	1.833	1.831	5	0	2
28	3.317	3.315	3	1	0	5	1.808	1.806	6	0	0
2	3.171	3.168	0	1	2	2	1.783	1.789	5	1	2
14	3.04	3.041	1	1	2	2	1.72	1.712	0	4	4
100	2.983	2.984	3	1	1	58	1.712	1.711	5	3	0
2	2.96	2.980	2	2	1	3	1.707	1.709	4	1	3
82	2.702	2.699	1	3	0	1	1.69	1.691	1	0	4
14	2.648	2.649	0	2	2	5	1.66	1.660	5	3	1
3	2.573	2.573	1	2	2	9	1.656	1.657	1	1	4
3	2.415	2.412	4	1	1	1	1.53	1.530	5	3	2
5	2.331	2.330	2	3	1	3	1.523	1.522	7	1	0
6	2.275	2.273	4	2	0	2	1.518	1.517	3	5	0
30	2.208	2.206	3	3	0	1	1.492	1.492	6	2	2
6	2.101	2.100	3	3	1	2	1.485	1.488	1	5	2
9	2.06	2.059	4	1	2	7	1.482	1.489	7	1	1
4	2.008	2.006	5	1	1	3	1.444	1.446	1	3	4
2	2.003	1.999	0	4	1	5	1.393	1.393	0	6	0

⁵ Calculated from the powder-diffraction data using UNITCELL (Holland & Redfern 1997). The unit-cell parameters derived from powder data: a 10.8345(7), b 8.3600(6), c 6.8476(5) Å, V 620.23(6) Å³. The values of *d* are expressed in Å.

the SADABS program (Sheldrick 2000). The structure was solved by direct methods with SIR97 (Altomare *et al.* 1999) and refined with the SHELXL97 program (Sheldrick 1997) implemented in the WINGX suite (Farrugia 1999). The structure was refined to a final $R = 0.0286$ for 685 observed reflections [$I > 2\sigma(I)$]. The final coordinates and displacement parameters of the atoms are reported in Table 4. A table of observed and calculated structure-factors may be obtained from The Depository of Unpublished Data on the MAC website [document Thermessaite CM46_693].

RESULTS AND DISCUSSION

Two projections of the crystal structure of thermessaite are shown in Figures 3 and 4. Selected interatomic distances and angles are reported in Table 5, together with the bond-valence estimates (Brese & O'Keefe 1991). There are chains of corner-sharing AlF_4O_2 octahedra running along [001] (Fig. 5). These octahedra

are joined to each other by sharing two fluorine atoms at opposite vertices [$\langle \text{Al-F}_2 \rangle 1.844(1) \text{ \AA}$]; the non-bridging Al-F1 distances are shorter [$1.752(1) \text{ \AA}$]. The two oxygen atoms at the vertices are shared with SO_4 tetrahedra [Al-O $1.906(1) \text{ \AA}$].

This structural motif is new for aluminofluoride minerals: if the classifications of Hawthorne (1984) or Strunz & Nickel (2001) are followed, the new mineral should be placed among "compound aluminofluorides" or "aluminofluorides with CO_3 , SO_4 , PO_4 ", respectively, like bøggildite $\text{Sr}_2\text{Na}_2\text{Al}_2(\text{PO}_4)\text{F}_9$. However, the chains in bøggildite (Hawthorne 1982) contain phosphate groups as the only elements linking the Al-centered octahedra, whereas in thermessaite, the octahedra are directly connected to each other by sharing fluorine

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

Crystal system	orthorhombic	Space group	<i>Pbcn</i> (no. 60)
<i>a</i> (Å)	10.810(2)	F_{000}	504
<i>b</i> (Å)	8.336(2)	Radiation	MoK α
<i>c</i> (Å)	6.822(1)	μ (mm ⁻¹)	2.047
<i>V</i> (Å ³)	614.8(2)	D_{calc} (g/cm ³)	2.79
<i>Z</i>	4		
Measured reflections	5180		
Independent reflections	821		
Observed reflections [$I > 2\sigma(I)$]	685		
Parameters refined	54		
Final <i>R</i> and <i>wR2</i>	0.0286, 0.0673		
<i>S</i>	0.909		

Notes: $R = \sum |F_o| - |F_c| / \sum |F_o|$; $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$; $w = 1/(\sigma^2(F_o^2) + (0.0424p)^2)$, where $p = (F_o^2 + 2F_c^2)/3$; $S = (\sum [w(F_o^2 - F_c^2)](n - p))^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

TABLE 4. THERMESSAITE: ATOM COORDINATES AND DISPLACEMENT PARAMETERS

Atom	X/a	Y/b	Z/c	U _{eq}
K	0.69572(5)	0.32309(7)	0.20090(8)	0.0232(2)
S	0	0.18950(8)	0.39450	0.0125(2)
Al	½	0	0	0.0102(2)
F1	0.8438(1)	0.4474(2)	0.4773(2)	0.0174(3)
F2	½	0.0840(2)	¼	0.0155(4)
O1	-0.1002(2)	0.0950(2)	0.3301(2)	0.0245(4)
O2	-0.0528(1)	0.2958(2)	0.0936(2)	0.0146(3)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
K	0.0212(3)	0.0237(3)	0.0246(3)	-0.0082(2)	-0.0043(2)	0.0027(2)
S	0.0165(4)	0.0102(4)	0.0108(3)	0	0.0004(3)	0
Al	0.0117(4)	0.0116(4)	0.0074(4)	0.0000(3)	0.0002(3)	-0.0004(3)
F1	0.0128(6)	0.0203(6)	0.0191(7)	-0.0013(5)	-0.0015(5)	-0.0023(5)
F2	0.0240(10)	0.0148(9)	0.0077(8)	0	0.0010(7)	0
O1	0.0309(10)	0.0215(9)	0.0211(9)	0.0058(7)	0.0012(7)	-0.0118(7)
O2	0.0189(8)	0.0124(7)	0.0125(7)	0.0021(6)	-0.0026(6)	-0.0014(6)

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

TABLE 5. THERMESSAITE: INTERATOMIC DISTANCES (Å), BOND VALENCES (*vu*) AND BOND ANGLES (°)

K-F1	2.682(1)	0.15	Al-F1 ^o	1.752(1)	0.57	F1-Al-F1	180.00(11)
K-F1 ^b	2.755(1)	0.13	Al-F1 ^a	1.752(1)	0.57	F1-Al-F2 × 2	90.76(4)
K-F1 ^a	2.924(1)	0.08	Al-F2	1.844(1)	0.45	F1-Al-F2 × 2	89.24(4)
K-F2	2.926(1)	0.08	Al-F2 ^b	1.844(1)	0.45	F2-Al-F2	180
K-F _(average)	2.824		Al-F _(average)	1.798		F1-Al-O2 × 2	92.04(6)
K-O1 ^c	2.642(2)	0.25	Al-O2 ^l	1.906(1)	0.5	F1-Al-O2 × 2	87.96(6)
K-O1 ^d	2.816(2)	0.16	Al-O2 ^j	1.906(1)	0.5	F2-Al-O2 × 2	91.68(7)
K-O1 ^e	3.043(2)	0.08		Σ=3.04		F2-Al-O2 × 2	88.32(7)
K-O2 ^e	2.824(2)	0.15	S-O1	1.446(2)	1.62	O2-Al-O2	180.00(9)
K-O2 ^f	3.247(2)	0.05	S-O1 ^k	1.446(2)	1.62	O1-S-O1	114.0(2)
K-O _(average)	2.914	Σ=1.13	S-O2	1.500(1)	1.4	O1-S-O2 × 2	109.8(1)
			S-O2 ^k	1.500(1)	1.4	O1-S-O2 × 2	107.8(1)
			S-O _(average)	1.473	Σ=6.04	O2-S-O2	107.6(1)

Symmetry codes: **a** = 3/2 - *x*, ½ - *y*, *z* - ½; **b** = *x*, 1 - *y*, *z* - ½; **c** = ½ - *x*, ½ + *y*, *z*; **d** = ½ - *x*, ½ - *y*, *z* - ½; **e** = *x* + 1, *y*, *z*; **f** = ½ - *x*, ½ - *y*, *z* + ½; **g** = *x* - ½, *y* - ½, ½ - *z*; **h** = 1 - *x*, -*y*, -*z*; **i** = ½ - *x*, *y* - ½, *z*; **j** = ½ + *x*, ½ - *y*, -*z*; **k** = -*x*, *y*, ½ - *z*. The sum of bond valences for F1, F2, O1 and O2 is 0.93, 1.05, 2.11 and 2.10 *vu*, respectively.

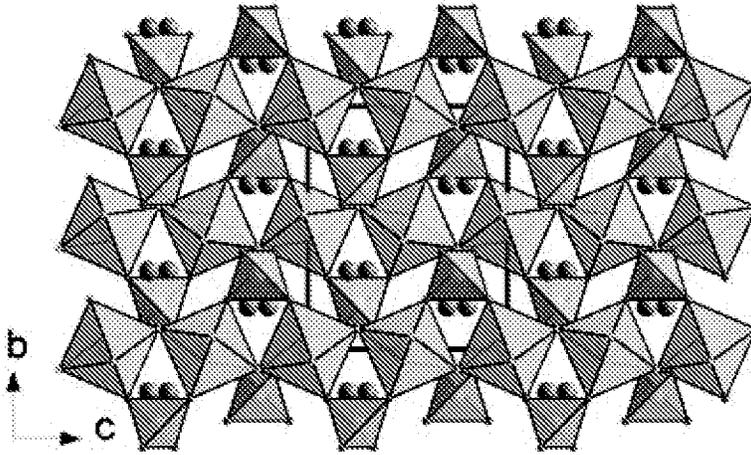


FIG. 3. A view of the crystal structure of thermessaite seen along [100]. The K atoms are represented as gray spheres, the AlF_4O_2 octahedra are shown in turquoise, and the SO_4 tetrahedra in gold.

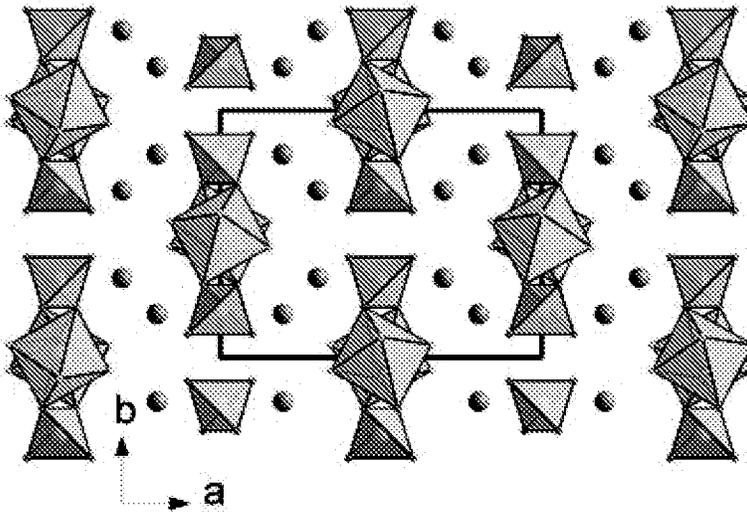


FIG. 4. A view of the crystal structure of thermessaite seen along [001]. The scheme of colors is the same as in Figure 3.

atoms at the corners; further linking is ensured through the sulfate groups, which also connect the AlF_4O_2 octahedra by sharing all the oxygen atoms at the remaining corners. If only the Al-centered octahedra are considered, edge-sharing chains can also be found in "simple aluminofluorides" such as prosopite, $\text{CaAl}_2(\text{OH},\text{F})_8$ (Giacovazzo & Menchetti 1969), and rosenbergite, $\text{AlF}[\text{F}_{0.5}(\text{H}_2\text{O})_{0.5}]_4 \cdot \text{H}_2\text{O}$ (Olmi *et al.* 1993), where

triangular or tetrahedral groups such as CO_3^{2-} or SO_4^{2-} connecting these octahedra are lacking. The sulfate ion present in creedite, $\text{Ca}_5\text{Al}_2\text{F}_8(\text{OH})_2(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ (Giuseppetti & Tadini 1983) does not play any role in linking the Al-centered octahedra; these polyhedra are joined in couples sharing one edge made of two oxygen (OH) atoms, whereas hydrogen bonds play an important role in connecting the SO_4 tetrahedra with the Ca-centered

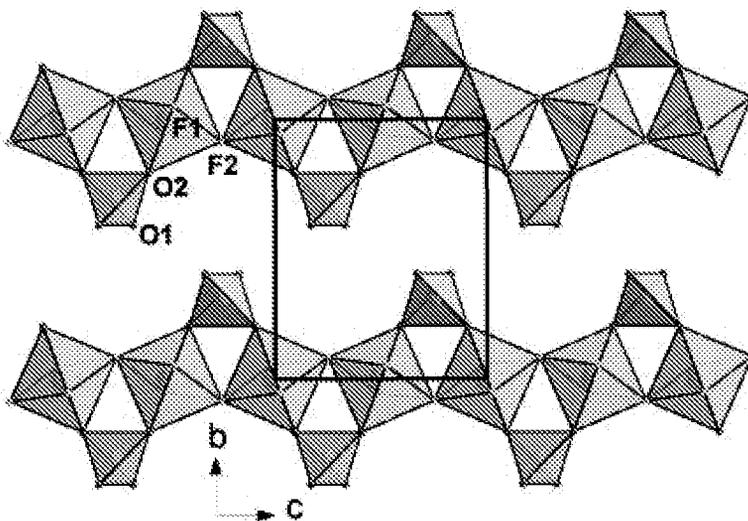


FIG. 5. The aluminofluoride chains in thermessaite.

polyhedra. In thermessaite, however, an important point is the absence of H_2O groups, unlike creedite and many other aluminofluorides, where hydrogen bonds are essential in establishing the type of crystal structure. In the sulfate ion, the “bridging” S–O1 bond [1.500(1) Å] is significantly longer than the other [1.446(2) Å], in agreement with theory. The average of these distances virtually coincides with that observed in an accurate redetermination of the structure of gypsum by neutron diffraction (Pedersen & Semmingsen 1982).

In the AlF_4O_2 octahedra, the only oxygen atoms are those shared with the sulfate groups, similarly to what happens for phosphates and carbonates in other “compound aluminofluorides” such as bøgildite and stenorite (Hawthorne 1982, 1984).

The presence of the fluorosulfate ion has been reported in a single natural example in reederite-(Y), which occurs in an alkaline environment at Mont-Saint-Hilaire, Quebec (Grice *et al.* 1995). At Vulcano and in other volcanos, the formation of such substances should be even more likely, because of the reaction: $\text{HF} + \text{HSO}_4^- \rightarrow \text{SO}_3\text{F}^- + \text{H}_2\text{O}$, which is favored by the high activity of hydrogen fluoride in the strongly acidic environment of the fumaroles. Notwithstanding this possibility, no fluorine atoms directly bonded to sulfur are present in our mineral; in this case, the distinction between oxygen and fluorine atoms is also clearly in agreement with bond-valence estimates (see Table 5).

The nine-coordinate K^+ ions are surrounded by five oxygen atoms [K–O distances in the range 2.642(2)–3.247(2) Å] and by four fluorine atoms [K–F distances in the range 2.682(2)–2.926(2) Å] forming a very irregular coordination polyhedron.

CONCLUSIONS

Another rare fluoride has been discovered in the fumaroles at Vulcano. With the exception of gearksutite, which was found to occur there a long time ago (Bernauer 1941) and not in the immediate proximity of the fumaroles, but as a “deposit”, the other fluorides known so far in this locality [*i.e.*, hieratite, K_2SiF_6 (Cossa 1881–1882, 1882, 1884), barberite, NH_4BF_4 (Garavelli & Vurro 1994), demartinite, K_2SiF_6 (Gramaccioli & Campostrini 2007), knasibite, $\text{K}_3\text{Na}_4[\text{SiF}_6]_3[\text{BF}_4]$ and avogadrite, KBF_4 (Demartin *et al.* 2008)] contain boron and silicon in the form of complex anions, but do not contain aluminum.

Alkali fluorides and those of boron (BF_3) and silicon (SiF_4) are volatile at relatively low temperatures, as is the case with other anhydrous halides such as ferric chloride Fe_2Cl_6 or aluminum chloride Al_2Cl_6 , which are molecular. On the contrary, in the inorganic chemistry literature, anhydrous aluminum trifluoride (AlF_3) is reported to be ionic and to volatilize only above 1200°C. On this basis, we might reasonably expect that aluminum-containing fluorides are not formed immediately from deposition of fumarolic gases, but they derive instead from action of both HF and SO_3 present in the gases on the volcanic wallrock materials; such a material at Vulcano belongs to the calc-alkaline suite (Chiodini *et al.* 1995). These authors and Garavelli *et al.* (1996) proposed that the fumarolic system of the La Fossa crater is fed by mixing of the gases released by a magma body and a “shallower” vapor deriving from fluids having a marine origin. The presence of hydrofluoric acid as such is well known as a component

of the fumaroles (see, for instance, Mazor *et al.* 1988, and references therein), or else it may derive from hydrolysis of other fluorides owing to the action of water vapor. The absence of H₂O groups in the mineral might indicate that it was formed at moderately high temperature.

Our conclusions about the formation of the mineral contradict the opinion of some authors (Oskarsson 1981, Rosenberg 1988), who affirmed that “although AlF₃ has never been positively identified as a mineral, the gaseous molecule may be present as an initial constituent of the volcanic plume at Mount Hekla, in Iceland” and in other localities such as Mount Erebus in Antarctica. In any case, the alleged presence of anhydrous AlF₃ in the mixture of sublimates for these volcanos was suggested by only three reflections in the X-ray powder pattern.

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