The Canadian Mineralogist
Vol. 45, pp. 1275-1280 (2007)
DOI : 10.2113/gscanmin.45.5.1275

DEMARTINITE, A NEW POLYMORPH OF K_2SiF_6 FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

Carlo Maria GRAMACCIOLI[§] and Italo CAMPOSTRINI

Dipartimento di Chimica Strutturale e Stereochimica Inorganica,
Università degli Studi di Milano, via Venezian 21, I-20133 Milano, Italy

Abstract

Demartinite, ideally K_2SiF_6, is a new hexagonal polymorph of potassium fluorosilicate, found in a fumarole at the rim of La Fossa crater, Vulcano Island, Aeolian Archipelago, Sicily, Italy. The mineral occurs as colorless hexagonal pyramidal crystals up to 0.3 mm across on a fragment of altered pyroclastic breccia, together with hieratite, avogadrite and knasibfite, a recently approved tetrafluoroborate-hexafluorosilicate of Na and K. The mineral is hexagonal (6*mm*), space group $P6_3mc$, with *a* 5.6461(8) and *c* 9.2322(18) Å, *V* 254.88(7) Å^3 . The crystals are sharp hexagonal pyramids {112}, terminated by the $\{00\bar{1}\}$ pedion. The crystal structure has been refined to a final R index of 0.018; its SiF_6^{2-} groups have the same geometry as in the other natural fluorosilicates known. There are two independent twelve-coordinated K sites, displaying distorted cuboctahedral and hexagonal cuboctahedral coordination, respectively. The K–F distances are in the range 2.800(2) – 3.087(2) Å, with an average of 2.885 Å. The Si–F distances in the octahedral SiF_6^{2-} anion range from 1.681(2) to 1.689(2) Å, with an average of 1.685 Å. The chemical analysis obtained by EDS microprobe gave (wt%) K 35.1, Si 12.4, F 51.0, Na 0.2, total 98.7, corresponding to the empirical formula $(K_{2.00}Na_{0.02})_{\Sigma 2.02}Si_{0.99}F_{5.99}$, based on nine atoms per formula unit. The calculated density is 2.87 g cm^{-3}, the measured density obtained by flotation in heavy liquids is 2.85 g cm^{-3}. The indices of refraction are: ω 1.350 ± 0.005; ε 1.340 ± 0.005 (589 nm). Demartinite is uniaxial (–) and nonpleochroic (colorless). The strongest six lines in the X-ray powder-diffraction pattern [d_{obs} in Å(I) *hkl*] are: 2.301(100)(004), 4.62(75)(002), 2.155(54)(022), 4.32(43)(011), 4.90(25)(010) and 2.358(22)(021). The mineral is named in honor of Prof. Francesco Demartin (b. 1953), who has made significant contributions to the chemistry of metallic clusters and to the crystal structure of Alpine rare-earth minerals and uranium minerals. Both the mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA (No. 2006–034).

Keywords: demartinite, new mineral species, hieratite, crystal structure, Vulcano Island, Aeolian Islands, Italy.

Sommaire

La demartinite, nouvelle espèce minérale de composition idéale K_2SiF_6, est un polymorphe hexagonal du fluorosilicate de potassium, découvert dans une fumerolle en bordure du cratère La Fossa, île de Vulcano, archipel aéolien, en Sicile, Italie. Le minéral se présente en cristaux incolores hexagonaux et pyramidaux atteignant 0.3 mm recouvrant un fragment de brèche pyroclastique altérée, accompagné de hiératite, avogadrite et knasibfite, un tétrafluoroborate-hexafluorosilicate de Na et K récemment approuvé. Il s'agit d'un minéral hexagonal (6*mm*), groupe spatial $P6_3mc$, avec *a* 5.6461(8) et *c* 9.2322(18) Å, et *V* 254.88(7) Å^3 . Les cristaux ont une forme pyramides hexagonales {112} aigues, terminées par le pédion $\{00\bar{1}\}$. Nous en avons affiné la structure jusqu'à un résidu R de 0.018. Les groupes SiF_6^{2-} possèdent la même géométrie que dans les autres fluorosilicates naturels connus. Il y a deux sites K à coordinence 12, cuboctaédrique difforme dans un cas et cuboctaédrique hexagonale difforme dans l'autre. Les distances K–F sont entre 2.800(2) et 3.087(2) Å, et en moyenne, 2.885 Å. Les distances Si–F des octaèdres SiF_6^{2-} sont entre 1.681(2) et 1.689(2) Å, et en moyenne, 1.685 Å. Une analyse chimique obtenue par dispersion d'énergie a donné K 35.1, Si 12.4, F 51.0, Na 0.2, pour un total de 98.7% (poids), ce qui correspond à la formule empirique $(K_{2.00}Na_{0.02})_{\Sigma 2.02}Si_{0.99}F_{5.99}$, fondée sur neuf atomes par formule unitaire. La densité calculée est 2.87 g cm^{-3}, la densité mesurée par flottation dans une liqueur dense est 2.85 g cm^{-3}. Les indices de réfraction sont: ω 1.350 ± 0.005, ε 1.340 ± 0.005 (589 nm). La demartinite est uniaxe (–) et non pléochroïque (incolore). Les six raies les plus intenses du spectre de diffraction, méthode des poudres [d_{obs} en Å(I) *hkl*] sont: 2.301(100)(004), 4.62(75)(002), 2.155(54)(022), 4.32(43)(011), 4.90(25)(010) et 2.358(22)(021). Le nom est choisi pour honorer Francesco Demartin, né en 1953, professeur, responsable de contributions importantes à la chimie des groupements métalliques et à la documentation de structures cristallines de minéraux alpins contenant les terres rares et l'uranium. Le minéral et le nom ont reçu l'approbation de la Commission des Nouveaux Minéraux et des Noms de Minéraux de l'IMA (no. 2006–034).

(Traduit par la Rédaction)

Mots-clés: demartinite, nouvelle espèce minérale, hiératite, structure cristalline, île de Vulcano, îles Aéoliennes, Italie.

[§] *E-mail address*: carlo.gramaccioli@unimi.it

INTRODUCTION

More than one century ago, Alfonso Cossa, in his investigation of the minerals of Vulcano, Aeolian Islands, in Sicily, Italy, discovered two new minerals, cannizzarite and hieratite (Cossa 1881–1882, 1882, 1884). The first of these new minerals, a lead–bismuth sulfosalt, occurs together with bismuthinite and galenobismuthite, and the second is a potassium hexafluorosilicate, K_2SiF_6, found in cubic crystals. Hieratite was later found also at Vesuvius (Zambonini & Carobbi 1926).

In recent times, there has been a renewed interest in the rare minerals occurring in the fumarole system at the La Fossa crater, leading to the discovery of further lead–bismuth sulfosalts, including new species such as vurroite, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, and mozgovaite, $PbBi_4(S,Se)_7$ (Vurro *et al.* 1999, Garavelli *et al.* 2005, and references therein). In addition, a new complex fluoride, barberiite, NH_4BF_4, (Garavelli & Vurro 1994) and thallium chloride, lafossaite (Roberts *et al.* 2006), were observed in nature for the first time.

Demartinite is a newly discovered hexagonal polymorph of K_2SiF_6; it was collected in April 2006 from a fumarole at the rim of the La Fossa crater, Vulcano Island, Aeolian Archipelago.

Demartinite is named after Francesco Demartin (b. 1953), Professor of General and Inorganic Chemistry at the State University of Milan in recognition of his significant contributions to the chemistry of metallic clusters in organometallic compounds and to the crystal structure of Alpine rare-earth minerals and uranium minerals. Both the mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA (No. 2006–034). The holotype is deposited (no. 2006–1) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

PHYSICAL PROPERTIES

The mineral occurs as colorless hexagonal pyramidal crystals (Fig. 1) up to 0.3 mm across on a fragment (4 × 3 × 1.5 cm) of altered pyroclastic breccia, together with hieratite, avogadrite and knasibfite, a new tetrafluoroborate-hexafluorosilicate, $K_3Na_4[SiF_6]_3[BF_4]$, recently approved as a new species by the IMA Commission on New Minerals and Mineral Names (IMA 2006–042). The observed forms are the pedion $\{00\bar{1}\}$ and the hexagonal pyramid {112}. Demartinite is isostructural with the artificial compound $(NH_4)_2SiF_6$ described by Fábry *et al.* (2001).

TABLE 1. CHEMICAL COMPOSITION OF DEMARTINITE

	wt%	Range, eight analyses	Standard deviation	Probe standard
K	35.1	34.8-35.6	0.1	KF
Si	12.4	12.3-12.7	0.1	Si
F	51.0	50.8-52.0	0.2	KF
Na	0.2	0.0-0.4	0.1	NaF
Total	98.7			

The mineral is not hygroscopic; the calculated density is 2.87 g cm^{-3}, and the measured density is 2.85 g cm^{-3} obtained by flotation in heavy liquids. The indices of refraction are: ω 1.350 ± 0.005, ε 1.340 ± 0.005 (589 nm). The mineral is uniaxial (–) and nonpleochroic (colorless).

CHEMICAL DATA

An initial energy-dispersion spectrum (EDS) obtained with a scanning electron microscope showed K, Si, and F to be the only important constituents. Therefore, chemical analyses were carried out by means of an EDS-equipped electron microscope (20 kV, 10^{-11}A, 2 μm beam diameter). The mean analytical results are reported in Table 1.

The empirical formula (based on 9 atoms per formula unit) is: $(K_{2.00}Na_{0.02})_{\Sigma 2.02}Si_{0.99}F_{5.99}$; the simplified formula is: K_2SiF_6, which requires: K 35.50, Si 12.75, F 51.75, total 100.00 wt.%.

A wavelength-dispersion (WDS) analysis was attempted, but the results were poor, owing to the difficulty in obtaining an adequate polish of the sample and to volatilization under the electron beam. In both EDS and WDS scans, no trace of Rb, Cs, and Tl was detected.

X-RAY DATA AND STRUCTURE REFINEMENT

We acquired the X-ray powder-diffraction data using a Gandolfi camera 114.6 mm in diameter, with Cu$K\alpha$ radiation (Table 2). A least-squares fit of these data provided the following unit-cell parameters (hexagonal cell): *a* 5.621(5), *c* 9.235(11) Å, and *V* 252.6(5) Å^3.

Single-crystal diffraction data were collected from a pyramidal crystal (0.15 × 0.12 × 0.10 mm) with Mo$K\alpha$ radiation (λ = 0.71073 Å), using a BRUKER Apex II diffractometer equipped with a 2K CCD detector. A one-minute frame-time and 0.2° frame width were used. A total of 2380 reflections were measured up to 2θ = 58.32° (2146 individual reflections belonging to the Ewald sphere), of which 296 are unique. The unit-cell dimensions were refined by least squares from 1604 reflections with $I > 5\sigma(I)$; the refined values are given in Table 3, together with other details concerning the collection and refinement of data. An absorption correction was applied using the SADABS program (Sheldrick 2000). The distribution of E-values and the morphology of the crystals strongly suggested that demartinite is non-centrosymmetric and polar, and the possible space-group $P6_3mc$ was confirmed by structure solution. 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). An extinction parameter x was refined to the value of 0.031(6), where F_c is multiplied by $k\ [1+ 0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, in which expression k is the overall scale-factor. The final coordinates and displacement parameters of the atoms are reported in Table 4. A projection of the crystal structure along [001] is provided as Figure 2a, whereas a side view perpendicular to the hexagonal axis is shown in Figure 2b.

A comparison of demartinite with the other natural and synthetic ammonium and potassium hexafluorosilicates is reported in Table 5. A table of observed and calculated structure-factors may be obtained from The Depository of Unpublished Data on the MAC web site [document Demartinite CM45_xxx].

RESULTS AND DISCUSSION

The structure contains two independent twelve-coordinated K sites, displaying hexagonal cuboctahedral (K1) and distorted cuboctahedral (K2) coordination, respectively. The first of these polyhedra is entirely different from that occurring in hieratite; in contrast, the second one is very similar. A comparison of these polyhedra with the cuboctahedron in hieratite is shown in Figure 3. Selected interatomic distances are reported in Table 6. For the first potassium atom (K1), the K–F distances are in the range 2.800(2)–2.895(2) Å, with an average of 2.842 Å; for the second (K2), the range is 2.858(2)–3.087(2) Å, with an average of 2.928 Å. In hieratite, the corresponding distances (all equal) are 2.897(1) Å. The Si–F distances in the octahedral SiF_6^{2-} anionic group range from 1.681(2) to 1.689(2)

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

I/Io*	I/Io**	*d* (Å) (obs.)	*d* (Å) (calc.)	*h*	*k*	*l*	I/Io*	I/Io**	*d* (Å) (obs.)	*d* (Å) (calc.)	*h*	*k*	*l*
25	**m**	**4.90**	**4.890**	**0**	**1**	**0**	3			1.678	0	2	4
75	**s**	**4.62**	**4.616**	**0**	**0**	**2**	3			1.605	0	3	1
43	**s**	**4.32**	**4.321**	**0**	**1**	**1**	1			1.584	1	2	3
7	w	3.36	3.357	0	1	2	4	w	1.540	1.539	0	0	6
7	w	2.825	2.823	1	1	0	5			1.473	0	2	5
1			2.605	0	1	3	1			1.468	0	1	6
7	w	2.450	2.445	0	2	0	1			1.443	1	2	4
22	**m**	**2.358**	**2.363**	**0**	**2**	**1**	3			1.440	0	3	3
100	**vs**	**2.301**	**2.308**	**0**	**0**	**4**	**13**	**m**	**1.403**	**1.412**	**2**	**2**	**0**
54	**s**	**2.155**	**2.161**	**0**	**2**	**2**	1			1.351	1	1	6
3			2.087	0	1	4	1			1.350	2	2	2
14	**m**	**1.909**	**1.914**	**0**	**2**	**3**	1			1.331	0	3	4
1			1.812	1	2	1	1			1.306	1	2	5
1			1.787	1	1	4	2			1.302	0	2	6
1			1.716	1	2	2	2			1.204	2	2	4

* The numerical values of relative intensity have been calculated using the atomic positions and displacement parameters obtained from the crystal-structure refinement.

** Visually estimated from the measured peaks in the Gandolfi pattern: vs: very strong, s: strong, m: medium, w: weak.

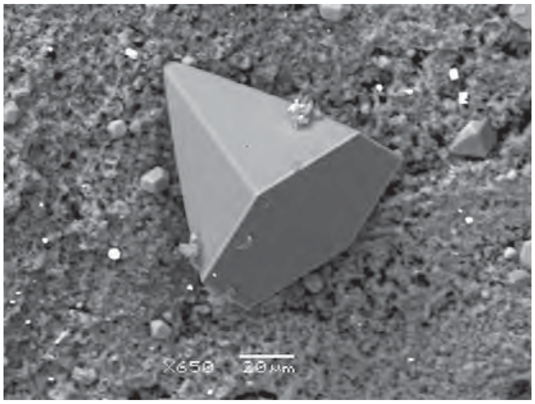

FIG. 1. A SEM image of a demartinite crystal.

TABLE 3. SINGLE-CRYSTAL DATA FOR DEMARTINITE

Formula	K_2SiF_6	*a* (Å)	5.6461(8)
Formula weight (*amu*)	220.29	*c* (Å)	9.2322(18)
Crystal system	hexagonal	*V* (Å^3)	254.88(7)
Space group	*P*6$_3$*mc* (no. 186)	*Z*	2
D calc. (g cm^{-3})	2.870	Scan mode	ω
μ (Mo*K*α) (mm^{-1})	2.134		
θ range (°)	4.17–29.16		
Measured reflections	2380		
Temperature (K)	293(2)		
Independent reflections	296		
Observed reflections [I > 2σ(I)]		291	
Minimum transmission-factor		0.767	
Parameters refined		23	
Final *R* and *wR*2 [§]		0.0182, 0.0519	
Largest diff. peak and hole (*e* Å^{-3})		0.191, –0.466	

[§] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

TABLE 4. DEMARTINITE: FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS

Atom	*X/a*	*Y/b*	*Z/c*	Site symmetry
K(1)	0.66667	0.33333	1.09275(9)	3*m*.
K(2)	0.00000	0.00000	0.81199(13)	3*m*.
Si	0.33333	0.66667	0.97559(12)	3*m*.
F(1)	0.61751(30)	0.80875(15)	1.07798(20)	.*m*.
F(2)	0.05287(39)	0.52644(20)	0.86889(15)	.*m*.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	0.0188(3)	0.0188(3)	0.0210(5)	0	0	0.0094(2)
K(2)	0.0244(3)	0.0244(3)	0.0294(6)	0	0	0.0122(2)
Si	0.0134(3)	0.0134(3)	0.0142(5)	0	0	0.0067(2)
F(1)	0.0185(7)	0.0242(6)	0.0248(7)	-0.0040(4)	-0.0079(8)	0.0093(4)
F(2)	0.0184(9)	0.0260(7)	0.0240(8)	-0.0034(3)	-0.0068(6)	0.0092(5)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(U_{11}\,h^2(a^*)^2 + \ldots + 2U_{12}hka^*b^* + \ldots)$.

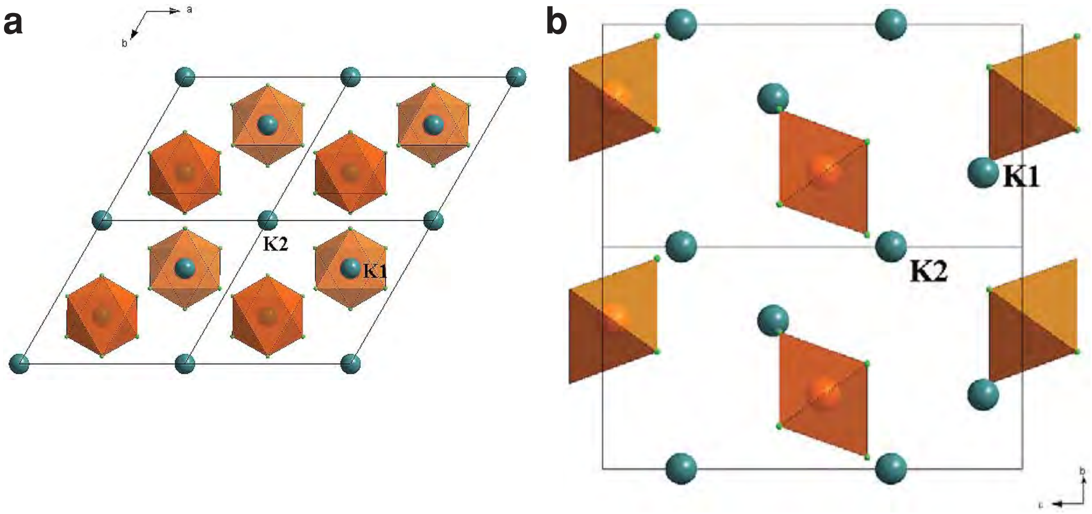

FIG. 2. A projection of the crystal structure of demartinite along the *c* axis (a, left) and a view (b, right) perpendicular to the *c* axis (here horizontal). The octahedra are SiF_6 polyhedra.

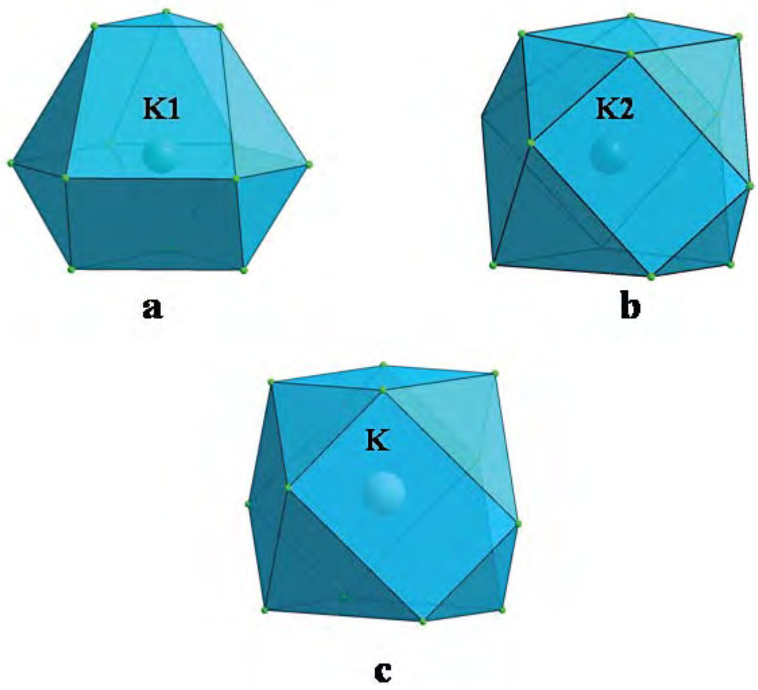

FIG. 3. Coordination polyhedra of the K atoms in demartinite (a, b) and hieratite (c).

TABLE 5. CRYSTAL DATA FOR SOME FLUOROSILICATES

	Hieratite K_2SiF_6 (1)	Demartinite K_2SiF_6 (2)	Cryptohalite $(NH_4)_2SiF_6$ (3)	Bararite $(NH_4)_2SiF_6$ (4)	Synthetic $(NH_4)_2SiF_6$ (5)
System	cubic	hexagonal	cubic	trigonal	hexagonal
Space group	$Fm\bar{3}m$	$P6_3mc$	$Fm\bar{3}m$	$P\bar{3}m1$	$P6_3mc$
a (Å)	8.1419(3)	5.6461(8)	8.395	5.784(5)	5.8955(10)
c (Å)		9.2322(18)		4.796(6)	9.599(1)
$c : a$		1.635 (×0.5 = 0.818)		0.829	1.628 (×0.5 = 0.814)
V (Å^3)	539.73	254.88(7)	591.65	138.95	288.93(8)
V/Z	134.93	127.44	147.91	138.95	144.46
Z	4	2	4	1	2
M^+–F (Å) [*]	2.897(1)	2.885 (ave.)	2.996(2)	3.030 (ave.)	3.043 (ave.)
Range M^+–F (Å)	all equal	2.800(2)–3.087(2)	all equal	2.970–3.206	2.962–3.241
Si–F (Å) [*]	1.683(2)	1.685 (ave.)	1.688(3)	1.694	1.697 (ave.)

[*] Here, all the values are uncorrected for thermal motion. References: (1) Hester *et al.* (1993), (2) this work, (3) Schlemper *et al.* (1966), (4) Schlemper & Hamilton (1966), (5) Fábry *et al.* (2001).

TABLE 6. DEMARTINITE: INTERATOMIC DISTANCES (Å) AND ANGLES (°) [*]

	SiF_6^{2-} polyhedra		
Si-F(1) ×3	1.681(2)	F(1)-Si-F(2) ×3	178.54(7)
Si-F(2) ×3	1.689(2)	F(1)-Si-F(1) ×3	91.46(10)
Si-F (average)	1.685	F(1)-Si-F(2) ×6	89.56(6)
		F(2)-Si-F(2) ×3	89.40(10)
	Coordination of the K^+ ions		
K(1)-F(1) ×6	2.837(2)	K(2)-F(1) ×3	2.858(2)
K(1)-F(2) ×3	2.800(2)	K(2)-F(1) ×3	3.087(2)
K(1)-F(2) ×3	2.895(2)	K(2)-F(2) ×6	2.883(2)
K(1)-F(average)	2.842	K(2)-F(average)	2.928

[*] All these values are uncorrected for thermal motion.

Å, with an average of 1.685 Å, which is identical with that of hieratite (within 1σ). The reason for the polar symmetry is shown in Figures 2a and 2b. At least at first sight, the side view (Fig. 2b) seems to show the presence of glide planes perpendicular to the *c* axis, but the two K atoms are not at all equivalent, as is clearly shown in Figure 2a.

The analogy with the synthetic isostructural hexagonal $P6_3mc$ ammonium compound (Table 5) suggests isomorphism, just as may also be inferred for the corresponding cubic $Fm\bar{3}m$ modifications hieratite K_2SiF_6 and cryptohalite $(NH_4)_2SiF_6$ (Ketelaar 1935). In line with the larger size of the NH_4^+ ion, with respect to that of K^+, the unit-cell volumes of the ammonium compounds are larger than those of the corresponding potassium compounds, a phenomenon reflected in the longer NH_4–F distances with respect to the K–F distances (the Si–F distances in the ammonium compounds are also slightly longer than in the potassium compounds).

An *artificial* hexagonal polymorph of K_2SiF_6 (named "camermanite") has long been reported (Gossner 1903, Denaeyer & Ledent 1950, 1952). However, the crystals were found to be unsuitable for X-ray diffraction, even for obtaining powder data, and the only available crystallographic information is morphological, the habit consisting of small hexagonal crystals, tabular on {001}, slightly modified by {201} faces; the angles were difficult to measure adequately. From such data, Gossner (1903) deduced the *c: a* ratio to be 0.8003. This ratio is reasonably close to the *c: 2a* ratio in demartinite (0.818), but it is not too far from the *c:a* ratio (0.829) of bararite $(NH_4)_2SiF_6$, a mineral for which an isostructural K-analogue might also exist (Table 5).

For this reason, and also in view of the distinctive, markedly pyramidal habit of demartinite, we cannot at present confirm the identity of "camermanite" with our mineral. It may be interesting to note that Palache *et al.* (1951) reported that "a hexagonal modification [of K_2SiF_6] *isostructural with bararite* is known only as an artificial compound", but no detailed indications about the real nature of this phase were given.

In view of the smaller molar volume, demartinite and all the trigonal or hexagonal polymorphs of these fluorosilicates should be more stable at higher pressures than the cubic phases, but the apparent conditions at the surface of fumaroles rather suggest their formation as metastable products. With respect to temperature, Denaeyer & Ledent (1952) seemed to suggest that hieratite is formed at a higher temperature (say, 100–150°C) than the hexagonal phase(s), but no precise data are available, and the formation of all such fumarolic minerals may not correspond to chemical equilibrium.

Acknowledgements

The courtesy of Prof. Paolo Orlandi from the Università di Pisa in providing the Gandolfi camera pattern is gratefully acknowledged. The authors are indebted to Prof. Robert F. Martin, to the Associate Editor Dr. Dana T. Griffen and to the referees J. Fábry and J.H. Lochlin for useful criticism.

References

Altomare, A., Burla. M.C., Camalli, M., Cascarano, G., Giacovazzo, C., Gagliardi, A., Moliterni, A.G., Polidori, G., & Spagna, R. (1999): SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **32**, 115-119.

Cossa, A. (1881–1882): Sulla hieratite, nuova specie mineralogica. *Transunti dell'Accademia dei Lincei*, *Ser.* 3, **6**, 141-142.

Cossa, A. (1882): Sur la hiératite, espèce minérale nouvelle. *Bull. Soc. Fr. Minéral.* **5**(2), 61-62.

Cossa, A. (1884): Hieratit, ein neues Mineral. *Z. Kristallogr.* **8**, 305.

Denaeyer, M.E. & Ledent, D. (1950): Sur la présence de la modification hexagonale de la hiératite (camermanite) dans des incrustations de sels potassiques d'une cheminée d'usine. *Bull. Soc. fr. Minéral. Cristallogr.* **73**, 483.

Denaeyer, M.E. & Ledent, D. (1952): Sur la présence de la modification hexagonale de la hiératite (camermanite) dans des incrustations de sels potassiques d'une cheminée d'usine. *Bull. Soc. fr. Minéral. Cristallogr.* **75**, 231-236.

Fábry, J., Chval, J. & Petříček, V. (2001): A new modification of diammonium hexafluorosilicate, $(NH_4)_2[SiF_6]$. *Acta Crystallogr.* **E57**, i90-i91.

Farrugia, L.J. (1999). WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32**, 837-838.

Garavelli, A., Mozgova, N.N., Orlandi, P., Bonaccorsi, E., Pinto, D., Moëlo, Y. & Borodaev, Yu.S. (2005): Rare sulfosalts from Vulcano, Aeolian Islands, Italy. VI. Vurroite $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, a new mineral species. *Can. Mineral.* **43**, 703-711.

Garavelli, A. & Vurro, F. (1994): Barberiite, NH_4BF_4, a new mineral from Vulcano, Aeolian Islands, Italy. *Am. Mineral.* **79**, 381-384.

Gossner, B. (1903): Untersuchung polymorpher Körper *Z. Kristallogr.* **38**, 109-168.

Hester, J.R., Maslen, E.N., Spadaccini, N., Ishizawa, N. & Satow, Y. (1993): Accurate synchrotron radiation $\Delta\rho$ maps for K_2SiF_6 and K_2PdCl_6. *Acta Crystallogr.* **B49**, 967-973.

Ketelaar, J.A.A. (1935): Die Kristallstruktur von K-, Rb-, Cs-, und Tl- Silico-fluoride und von $LiMnO_4{\bullet}3H_2O$. *Z. Kristallogr.* **92**, 155-156.

Palache, C., Berman, H. & Frondel, C. (1951) *The System of Mineralogy of J.D. Dana and E.S. Dana* **2** (7th ed.). John Wiley & Sons, New York, N.Y.

Roberts, A.C., Venance, K.E., Seward, T.M., Grice, J.D. & Paar, W.H. (2006): Lafossaite a new mineral from the La Fossa Crater, Vulcano, Italy. *Mineral. Rec.* **37**, 165-168.

Schlemper, E.O. & Hamilton, W.C. (1966): On the structure of trigonal ammonium fluorosilicate. *J. Chem. Phys.* **45**, 408-409.

Schlemper, E.O., Hamilton, W.C. & Rush, J.J. (1966): Structure of cubic ammonium fluosilicate: neutron-diffraction and neutron-inelastic-scattering studies. *J. Chem. Phys.* **44**, 2499-2505.

Sheldrick, G.M. (1997): SHELXL97: *Program for Crystal Structure Refinement*. University of Göttingen, Göttingen, Germany.

Sheldrick, G.M. (2000): SADABS *Area-Detector Absorption Correction Program*. Bruker AXS Inc., Madison, Wisconsin, U.S.A.

Vurro, F., Garavelli, A., Garbarino, C., Moëlo, Y. & Borodaev, Yu. S. (1999): Rare sulfosalts from Vulcano, Aeolian Islands, Italy. II. Mozgovaite $PbBi_4(S,Se)_7$, a new mineral species. *Can. Mineral.* **37**, 1499-1506.

Zambonini, F. & Carobbi, E. (1926): Sulla presenza del fluosilicato sodico e di quello di potassio tra i prodotti dell'attuale attività del Vesuvio. *Atti R. Accad. Naz. Lincei, ser. 6, Rend. Cl. Sci. Fis. Mat. Nat.* **2**(5-6), 171-175.

Received December 18, 2006, revised manuscript accepted March 28, 2007.