

FERRO-FLUORO-EDENITE, A NEW AMPHIBOLE ENDMEMBER FROM VULCANO ISLAND (SICILY, ITALY)

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ABSTRACT

Ferro-fluoro-edenite, ideally $\text{NaCa}_2\text{Fe}^{2+}_5(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2$, was found as prismatic crystals up to 1.00 mm inside cavities in ejecta of the 1873 eruption at La Fossa crater, Vulcano Island, Aeolian Archipelago, Sicily, Italy. It is associated with quartz, magnetite, and vonsenite. Crystals are dark brown to black, transparent or semitransparent with vitreous luster, and non fluorescent. The Mohs hardness is 5–6. Cleavage is fair on {110} and fracture is uneven. Density (calc.) is 3.358 g cm^{-3} using the empirical formula and single-crystal cell data. The mineral is biaxial negative, $\alpha = 1.629(2)$, $\beta = 1.659(2)$, $\gamma = 1.667(2)$, $2V$ (calc.) = -53.8° , $Y = b$. Dispersion is weak to very weak, $r < v$, pleochroism not visible. Ferro-fluoro-edenite is monoclinic, space group $C2/m$, $a = 9.9132(10)$, $b = 18.1736(19)$, $c = 5.2943(6) \text{ \AA}$, $\beta = 104.85(1)^\circ$, $V = 922.0(2) \text{ \AA}^3$, $Z = 2$. The strongest X-ray diffraction peaks in the powder pattern are $[d(I, hkl)]$: 8.54(100, 1 1 0), 4.506(16, 0 4 0), 3.154(52, 3 1 0), 2.833(43, 3 3 0), 2.057(14, 2 0 2), 1.910(12, 5 1 0), 1.662(15, 4 6 1). The FTIR spectrum shows a broad band at about 950 cm^{-1} and no bands in the OH stretching region. The structure refinement led to a final $R = 0.0210$ for 1444 observed reflections with $I > 2\sigma(I)$ and allowed cation site assignment and ordering. Microprobe analysis gave the following empirical formula calculated on the basis of 24 (O + F + Cl) apfu: $(\text{Na}_{0.69}\text{K}_{0.23}\square_{0.08})(\text{Ca}_{1.69}\text{Mg}_{0.16}\text{Mn}_{0.10}\text{Na}_{0.05})_{\Sigma 2}(\text{Fe}^{2+}_{2.86}\text{Mg}_{2.04}\text{Ti}_{0.10})_{\Sigma 5}(\text{Si}_{6.93}\text{Al}_{1.05}\text{Ti}_{0.02})_{\Sigma 8}\text{O}_{22}(\text{F}_{1.89}\text{Cl}_{0.09}\text{OH}_{0.02})_{\Sigma 2}$.

Keywords: ferro-fluoro-edenite, amphibole supergroup, single-crystal structure refinement, Vulcano Island.

INTRODUCTION

In the last two decades, in connection with the increased activity of the fumaroles at La Fossa crater, Vulcano Island, Aeolian Archipelago, Sicily, Italy, results of important investigations on this locality have been published in the fields of volcanology and geochemistry (see Campostrini *et al.* 2011, and references therein). At the same time, renewed interest in the rare minerals occurring in this area, mainly as sublimate products of the fumarolic activity, led to the discovery of a total of 33 mineral species for which Vulcano Island is the locality.

However, less attention has been devoted to rock-forming minerals that are present in the volcanic ejecta; crystal-chemical studies and structural data for these minerals are rare and were carried out with the aim of obtaining geobarometric information and exploring implications for the structure of volcanic plumbing systems (see, e.g., Nazzareni *et al.* 2001 and references therein).

During our investigations of some minerals present in cavities in the ejecta of the 1873 eruption, we happened to find the new mineral ferro-fluoro-edenite, ideally $\text{NaCa}_2\text{Fe}^{2+}_5(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2$, recently approved as a new species by the IMA Commission on New

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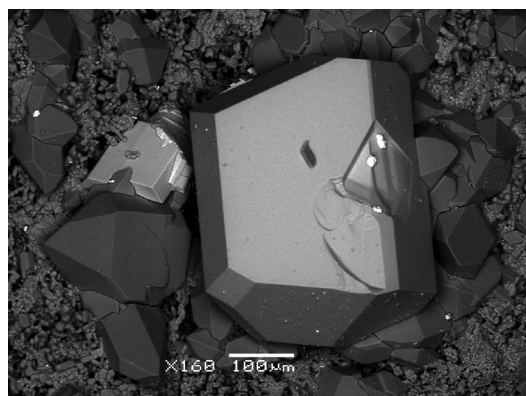


FIG. 1. SEM-BSE image of a crystal of ferro-fluoro-edenite associated with quartz.

Minerals, Nomenclature and Classification (No. 2020-058). The mineral belongs to the amphibole supergroup, $W(\text{OH}, \text{F}, \text{Cl})$ -dominant amphibole group, calcium amphibole subgroup, edenite root-name (Hawthorne *et al.* 2012, Hawthorne & Oberti 2007b). Ferro-fluoro-edenite is classified as 9.DE.15 in the classification of Strunz (9 silicates, D inosilicates, E inosilicates with 2-periodic double chains Si_4O_{11}). In the Dana classification it belongs to the 16.22 class (16 silicates containing aluminum and other materials, 22 aluminosilicates of Fe, Ca, and alkalis). Ferro-fluoro-edenite does not correspond to any valid unnamed mineral (Smith & Nickel 2007). The possible existence of this endmember was predicted on the basis of compositions, close to the ideal stoichiometry, of specimens from several occurrences (see below).

Part of the holotype of ferro-fluoro-edenite is deposited in the Reference Collection of Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133 Milan, Italy, sample number 2020-01. Another part of the holotype is deposited in the mineralogical collection of the Museo Civico di Storia Naturale, corso Venezia 55, 20121 Milan, Italy, catalogue number M38989.

PHYSICAL AND OPTICAL PROPERTIES

Ferro-fluoro-edenite occurs as dark brown to black prismatic crystals (Figs. 1–2), transparent or semi-transparent, up to 1.00 mm, inside cavities in ejecta at La Fossa crater, Vulcano Island, Aeolian Archipelago, Sicily, Italy. It is associated with quartz, magnetite, and vonsenite and probably crystallized during a late-stage hydrothermal phase. The most commonly observed forms are $\{0\ 1\ 0\}$, $\{1\ 1\ 0\}$, $\{2\ 1\ 0\}$, $\{0\ 2\ 1\}$, $\{0\ 0\ 1\}$, $\{1\ 0\ 0\}$ and $\{2\ 1\ 1\}$; indexing was done



FIG. 2. A 1.0 mm prismatic crystal of ferro-fluoro-edenite associated with quartz.

using computer-generated drawings of the crystals (Fig. 3).

The $a:b:c$ ratio calculated from the unit-cell parameters is 0.5455:1:0.2913 (single-crystal data). No twinning is apparent. The streak is light brown and the luster is vitreous. Cleavage is fair on $\{110\}$ and fracture is uneven. No fluorescence was observed under either short wave or long wave ultraviolet radiation. The crystal slowly sinks into diiodomethane ($d = 3.32\text{ g/cm}^3$). The density calculated using the empirical formula and single-crystal unit-cell data is 3.358 g/cm^3 .

Ferro-fluoro-edenite is biaxial ($-$) = 1.629(2), β = 1.659(2), γ = 1.667(2) (white light), $2V$ (calc.) = -53.8° , $Y = b$. Dispersion is weak to very weak, $r < v$, pleochroism not visible. From the empirical chemical formula and the density based on it, the calculated mean refractive index is 1.660, using the Gladstone-Dale constants of Mandarino (1976, 1981). The compatibility index, $1 - (K_p/K_c) = 0.013$, is rated as superior.

The FTIR spectrum was recorded with a Jasco IRT-3000 spectrometer (Fig. 4) and shows a strong and broad absorption band at about 950 cm^{-1} in the region of the Si–O stretching vibrations and no bands in the OH region.

CHEMICAL COMPOSITION

Quantitative chemical analyses (5) were carried out using a Jeol JXA-8200 WDS electron microprobe and a polished fragment of a crystal found close to that used for single-crystal X-ray diffraction. The acceleration voltage was 15 kV, beam current was 5 nA, and beam diameter was 5 μm . Element concentrations were measured using the $K\alpha$ lines. The mean analytical results and calibration reference materials are reported in Table 1. The empirical

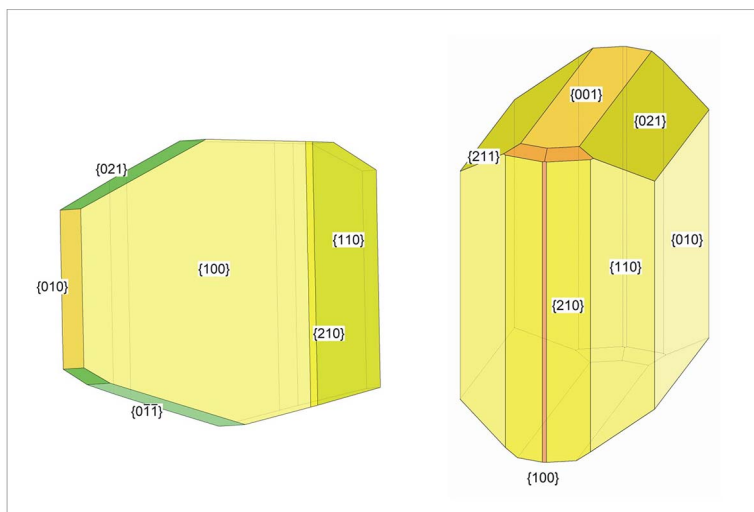


FIG. 3. Idealized drawings of crystals of ferro-fluoro-edenite.

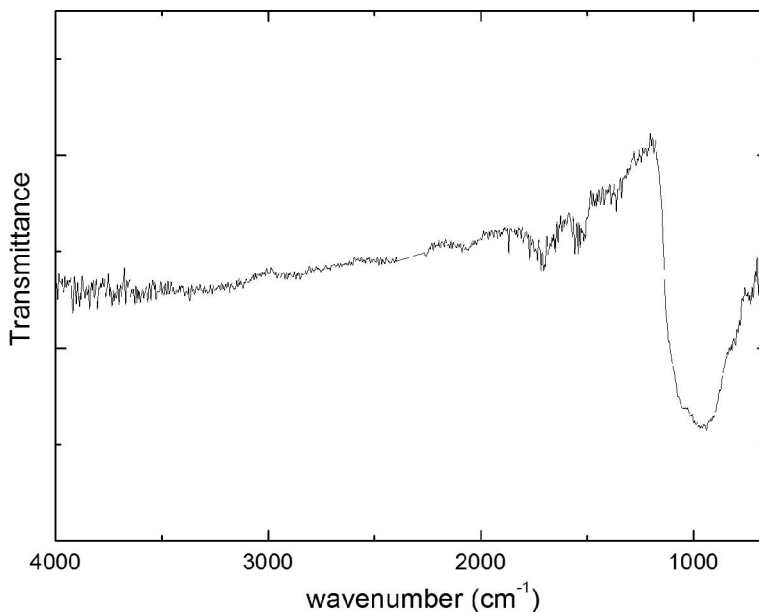


FIG. 4. FTIR spectrum of ferro-fluoro-edenite.

formula calculated on the basis of 24 (O + F + Cl) *apfu* is: $(\text{Na}_{0.69}\text{K}_{0.23}\square_{0.08})(\text{Ca}_{1.69}\text{Mg}_{0.16}\text{Mn}_{0.10}\text{Na}_{0.05})_{\Sigma 2}(\text{Fe}^{2+}_{2.86}\text{Mg}_{2.04}\text{Ti}_{0.10})_{\Sigma 5}(\text{Si}_{6.93}\text{Al}_{1.05}\text{Ti}_{0.02})_{\Sigma 8}\text{O}_{22}(\text{F}_{1.89}\text{Cl}_{0.09}\text{OH}_{0.02})_{\Sigma 2}$. The simplified and ideal formula is: $\text{NaCa}_2\text{Fe}^{2+}_5(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2$, which requires Na_2O 3.12, CaO 11.27, FeO 36.08, Al_2O_3 5.12, SiO_2 42.20, and F 3.82 wt.%, $-\text{O}=\text{F}$ 1.61, total 100 wt.%.

X-RAY DATA

X-ray powder diffraction data, collected using a Rigaku Miniflex powder diffractometer with graphite-monochromated $\text{CuK}\alpha$ radiation, are listed in Table 2 together with the pattern calculated from the crystal structure using VESTA (Momma & Mizumi 2011).

TABLE 1. CHEMICAL DATA (IN wt.%)

Constituent	Mean [§]	Range	Stand. Dev. (σ)	Standard Material
SiO ₂	44.86	(44.50–45.44)	(0.38)	Grossular
TiO ₂	1.03	(0.96–1.07)	(0.05)	Ilmenite
Al ₂ O ₃	5.74	(5.26–6.00)	(0.29)	Grossular
FeO	22.13	(20.79–22.73)	(0.78)	Fayalite
MnO	0.74	(0.66–0.79)	(0.05)	Rhodonite
CaO	10.21	(10.07–10.35)	(0.10)	Grossular
MgO	9.56	(9.22–10.19)	(0.39)	Forsterite
K ₂ O	1.15	(1.09–1.21)	(0.04)	K-feldspar
Na ₂ O	2.47	(2.29–2.59)	(0.11)	Omphacite
F	3.87	(3.77–3.96)	(0.08)	Hornblende Hbl-123
Cl	0.32	(0.26–0.38)	(0.05)	Scapolite
Sum	102.11			
–O = F	–1.63			
–O = Cl	–0.07			
Total	100.41			

[§] Average of five analyses.

Unit-cell parameters refined from the powder data using the program UNITCELL (Holland & Redfern 1997) are as follows: $a = 9.9285(11)$, $b = 18.1406(25)$, $c = 5.3098(7)$ Å, $\beta = 104.678(14)^\circ$, $V = 925.13(14)$ Å³.

Intensity data corresponding to a complete scan of the Ewald sphere were collected using a Bruker Apex II diffractometer equipped with a 2K CCD detector and MoK α radiation ($\lambda = 0.71073$ Å). A total of 5380 reflections were measured up to $2\theta = 63.00^\circ$. After intensity integration using the program SAINT (Bruker 2001), the data were corrected for Lorentz, polarization, and background effects. A SADABS (Sheldrick 2000) absorption correction was applied ($\mu = 3.436$ mm^{–1}); finally, 1506 unique reflections were obtained ($R_{\text{int}} = 0.0109$). The structure was refined with SHELXL-2017, starting from the atomic positions known for amphiboles (Gianfagna & Oberti 2001). Site scattering was modeled using the scattering factors for Fe and Mg for the $M(1)$, $M(2)$, and $M(3)$ sites. After the first stage of the refinement the presence of residual electron density close to the $M(4)$ and O(3) positions (7.42 and 3.13 e/Å³, respectively) prompted us to consider a splitting of these sites. For the $M(4)$ site the situation is similar to that observed in fluoro-edenite, and the electron density in the cavity was modeled by refining Ca at the $M(4)$ site and minor amounts of Mn at the nearby $M(4)'$ site. The electron density residual at the O(3) site was accounted for by refining the occupation of the O(3) site by fluorine and that of the O(3)' site by minor amounts of chlorine. The best fit of the electron density corresponding to the disordered A site was obtained with the A2 site partially occupied by K and the Am site partially occupied by Na (see below).

The occupancy of the T sites was modeled using the scattering factor of Si; this was kept fixed and not refined to avoid strong correlation during the final structure refinement. The final R was 0.0210 for 1444 observed reflections [$I > 2\sigma(I)$]. The chemical formula obtained from the structure refinement is (Na_{0.57}K_{0.21}□_{0.22})(Ca_{1.84}Mn²⁺_{0.16})_{Σ2}(Fe²⁺_{2.56}Mg_{2.44})_{Σ5}Si₈O₂₂(F_{1.92}Cl_{0.08})_{Σ2}. Selected crystallographic information, together with details concerning the data collection and refinement, are reported in Table 3. Coordinates of the atoms and equivalent isotropic displacement parameters are given in Table 4. Anisotropic displacement parameters are given in Table 5. Refined distances are given in Table 6. Tables of observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, on the MAC website¹.

RESULTS AND DISCUSSION

The crystal structure of ferro-fluoro-edenite conforms with the $C2/m$ amphibole structure (Hawthorne & Oberti 2007a). It consists of double chains of corner-sharing tetrahedra and strips of edge-sharing octahedra both running parallel to the c axis. In the double chains there are two topologically distinct types of tetrahedra that are designated $T(1)$ and $T(2)$; in the strips there are three distinct types of octahedra that are designated $M(1)$, $M(2)$, and $M(3)$ (Figs. 5 and 6).

¹ Supplementary Data are available from the Depository of Unpublished Data on the MAC website (<http://mineralogicalassociation.ca/>), document "Ferro-fluoro-edenite, CM59, 20-00118".

TABLE 2. EXPERIMENTAL AND CALCULATED X-RAY POWDER DIFFRACTION DATA (d IN Å)

l_{meas}	d_{meas}	$d_{\text{calc}}^{\text{S}}$	l_{calc}^{**}	hkl
4	9.16	9.070	23	0 2 0
100	8.54	8.488	99	1 1 0
2	4.813	4.908	16	1 1 $\bar{1}$
16	4.506	4.535	15	0 4 0
8	4.255	4.244	14	2 2 0
2	3.404	3.403	64	1 3 1
8	3.307	3.297	34	2 4 0
52	3.154	3.153	30	3 1 0
2	2.962	2.962	47	2 2 1
43	2.833	2.829	19	3 3 0
		2.751	32	3 3 $\bar{1}$
10	2.718	2.722	100	1 5 1
3	2.585	2.606	55	0 6 1
	2.550	2.549	69	2 0 $\bar{2}$
8	2.403	2.400	6	3 5 0
6	2.353	2.353	37	3 5 $\bar{1}$
		2.313	14	1 7 $\bar{1}$
		2.288	19	3 1 $\bar{2}$
		2.174	40	2 6 1
14	2.057	2.058	20	2 0 2
		2.028	17	3 5 1
12	1.910	1.910	10	5 1 0
4	1.821	1.831	5	5 3 0
15	1.662	1.662	28	4 6 1
2	1.628	1.625	13	1 11 0
3	1.596	1.587	23	1 5 3
4	1.545	1.543	12	5 7 0
11	1.517	1.521	24	2 6 $\bar{3}$
		1.449	32	6 6 $\bar{1}$
		1.370	12	5 1 2
5	1.323	1.321	5	7 5 $\bar{1}$
		1.301	14	2 12 $\bar{2}$

^S Calculated from the unit cell $a = 9.9285(11)$, $b = 18.1406(25)$, $c = 5.3098(7)$ Å, $\beta = 104.678(14)^\circ$, $V = 925.13(14)$ Å³ obtained from least-squares refinement of the above data using the program UNITCELL (Holland & Redfern 1997). ^{**} Calculated from the crystal structure using VESTA (Momma & Mizumi 2011).

One larger eightfold $M(4)$ site is located at the junction of the strips of octahedra and the chains of tetrahedra, and an even larger A site is below the hexagonal ring of tetrahedra at the center of a large cavity defined by 12 oxygen atoms (Figs. 5 and 6). The structure of ferro-fluoro-edenite shows features comparable to that of the fluoro-edenite described by Gianfagna & Oberti (2001), with the main exception being the O(3) (W) site, occupied by F and Cl, that is split into two close positions. This splitting is common to all the amphiboles that incorporate chlorine (Oberti *et al.* 1993) and is due to the different ionic radii of these two elements. The values of the refined occupancy,

TABLE 3. SINGLE-CRYSTAL DATA AND REFINEMENT DETAILS

Crystal Data	
Simplified chemical formula	$\text{NaCa}_2\text{Fe}^{2+}_5(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2$
a (Å)	9.9132(10)
b (Å)	18.1736(19),
c (Å)	5.2943(6)
β (°)	104.85(1)
V (Å ³)	921.96(29)
Z	2
Data Collection	
Instrument	APEX II CCD diffractometer
Absorption correction	Empirical (SADABS, Sheldrick 2000)
Radiation, wavelength (Å)	MoK α , 0.71073
μ (mm ⁻¹)	3.436
Min. θ (°)	2.241
Max. θ (°)	31.500
Measured reflections	5380
R_{int}	0.0109
Independent reflections	1506
Observed reflections [$I > 2\sigma(I)$]	1444
Refinement	
Parameters refined	113
Final R [$I > 2\sigma(I)$] and $wR2$ (all data)	0.0210 and 0.0595
GoF	1.115
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.83, -0.69

Notes: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0285q)^2 + 1.9042q]$ where $q = (F_o^2 + 2F_c^2)/3$; $\text{GoF} = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.

0.960(5) and 0.040(5) for F and Cl, respectively, correspond to 1.92 *apfu* F and 0.08 *apfu* Cl and are in agreement with the chemical composition.

The presence of F at the O(3) position significantly reduces the size of the $M(1)$ and $M(3)$ sites and promotes ordering of Fe^{2+} at the $M(2)$ site that usually accepts the smaller high charge cations and has a lower preference for ferrous iron (Oberti *et al.* 2007). Owing to a higher content of Fe^{2+} , the $M(2)$ polyhedron is significantly larger than in fluoro-edenite, with an $\langle M(2)\text{-O} \rangle$ distance of 2.111 *versus* 2.079 Å. Titanium (0.10 *apfu*) is also ordered at the $M(2)$ site, in agreement with the bond-valence sum of 2.138 *vu*, which indicates the presence of high-charge cations at

TABLE 4. REFINED POSITIONAL AND ISOTROPIC ATOM DISPLACEMENT PARAMETERS ($\text{\AA}^2$)

Site	Occupancy	x	y	z	U_{iso}
<i>M</i> (1)	Mg 0.627(3) Fe 0.373(3)	0	0.08932(2)	0.5	0.00824(16)
<i>M</i> (2)	Mg 0.250(4) Fe 0.750(4)	0	0.17763(2)	0	0.00672(11)
<i>M</i> (3)	Mg 0.684(5) Fe 0.316(5)	0	0	0	0.0067(2)
<i>M</i> (4)	Ca 0.918(6)	0	0.27759(9)	0.5	0.01174(16)
<i>M</i> (4)'	Mn 0.082(6)	0	0.2554(7)	0.5	0.0117(15)
<i>T</i> (1)	1	0.28120(4)	0.08395(2)	0.29846(7)	0.00725(10)
<i>T</i> (2)	1	0.29036(4)	0.17071(2)	0.80462(7)	0.00671(9)
<i>O</i> (1)	1	0.11052(10)	0.08513(5)	0.21901(19)	0.00897(19)
<i>O</i> (2)	1	0.12147(10)	0.17166(6)	0.72191(19)	0.00954(19)
<i>O</i> (3)	0.960(5)	0.1060(2)	0	0.7131(3)	0.0140(3)
<i>O</i> (3)'	0.040(5)	0.170(2)	0	0.743(3)	0.011(5)
<i>O</i> (4)	1	0.36541(11)	0.24753(6)	0.7885(2)	0.0133(2)
<i>O</i> (5)	1	0.34738(10)	0.13515(6)	0.09984(19)	0.0129(2)
<i>O</i> (6)	1	0.34613(10)	0.11751(6)	0.59625(19)	0.0126(2)
<i>O</i> (7)	1	0.34180(16)	0	0.2873(3)	0.0142(3)
<i>Am</i>	Na 0.286(9)	0.0412(6)	0.5	0.0909(12)	0.0248(15)
<i>A2</i>	K 0.105(5)	0	0.4878(3)	0	0.019(2)

this site. The *M*(1) and *M*(3) sites, where the content of Fe is higher than in fluoro-edenite, show the same trend in the increase of the M–O distances, to a minor extent: the $\langle M(1)–O \rangle$ distance is 2.080 *versus* 2.059 Å and the $\langle M(3)–O \rangle$ distance is 2.060 *versus* 2.046 Å. The refined total site scattering at the *C* site is 95.84 *epfu*, which is slightly lower than that calculated from the chemical formula, 101.04 *epfu*.

The larger *M*(4) site, as happens in fluoro-edenite, is split into two close positions, *M*(4) and *M*(4)', the former occupied by Ca and the latter by Mn with

relative refined occupancies of 0.918(6) and 0.082(6), respectively. This yields 40.82 *epfu* at the *B* site, to be compared to the value from the chemistry of 38.77 *epfu*.

Analysis of the experimental Fourier maps and bond-strength considerations confirmed that Na orders at the *Am* site in fluoroamphiboles but distributes between the *Am* and *A2* sites in OH-dominant amphiboles (Hawthorne & Oberti 2007a). On the other hand, when potassium is a major *A* cation, it is generally ordered at the *Am* site. In ferro-fluoro-

TABLE 5. REFINED ANISOTROPIC ATOM DISPLACEMENT PARAMETERS ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
<i>M</i> (1)	0.0079(2)	0.0110(2)	0.0061(2)	0	0.00240(15)	0
<i>M</i> (2)	0.00696(16)	0.00655(16)	0.00699(16)	0	0.00241(11)	0
<i>M</i> (3)	0.0082(3)	0.0052(3)	0.0060(3)	0	0.0005(2)	0
<i>M</i> (4)	0.0142(2)	0.0102(4)	0.0138(2)	0	0.00914(16)	0
<i>T</i> (1)	0.00686(17)	0.00742(17)	0.00714(17)	–0.00020(11)	0.00123(12)	–0.00044(11)
<i>T</i> (2)	0.00614(16)	0.00755(17)	0.00618(16)	0.00038(11)	0.00111(12)	–0.00095(11)
<i>O</i> (1)	0.0080(4)	0.0102(4)	0.0086(4)	–0.0007(3)	0.0021(3)	–0.0012(3)
<i>O</i> (2)	0.0063(4)	0.0124(4)	0.0097(4)	0.0001(3)	0.0016(3)	0.0000(3)
<i>O</i> (3)	0.0138(10)	0.0152(6)	0.0129(6)	0	0.0032(5)	0
<i>O</i> (4)	0.0146(5)	0.0105(5)	0.0143(5)	–0.0002(4)	0.0028(4)	–0.0047(4)
<i>O</i> (5)	0.0095(4)	0.0182(5)	0.0103(4)	0.0052(4)	0.0016(4)	–0.0004(4)
<i>O</i> (6)	0.0093(4)	0.0167(5)	0.0117(5)	–0.0040(4)	0.0026(4)	0.0010(4)
<i>O</i> (7)	0.0112(6)	0.0103(6)	0.0201(7)	0	0.0024(5)	0

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2(U^{11}h^2(a^*)^2 + \dots + 2U^{12}hka^*b^* + \dots)$$

TABLE 6. REFINED DISTANCES (Å) AND BOND VALENCES*

	Distance	BV (vu)		Distance	BV (vu)
<i>T</i> (1)–O(1)	1.6357(11)	0.970	<i>T</i> (2)–O(2)	1.6184(11)	1.015
<i>T</i> (1)–O(5)	1.6599(11)	0.912	<i>T</i> (2)–O(4)	1.5946(11)	1.079
<i>T</i> (1)–O(6)	1.6588(11)	0.914	<i>T</i> (2)–O(5)	1.6514(11)	0.932
<i>T</i> (1)–O(7)	1.6463(7)	0.944	<i>T</i> (2)–O(6)	1.6644(11)	0.901
< <i>T</i> (1)–O>	1.6501	Σ = 3.740	< <i>T</i> (2)–O>	1.6322	Σ = 3.927
<i>M</i> (1)–O(1) (×2)	2.0626(11)	0.375 (×2)	<i>M</i> (2)–O(1) (×2)	2.1724(11)	0.307(×2)
<i>M</i> (1)–O(1) (×2)	2.0844(11)	0.357 (×2)	<i>M</i> (2)–O(2) (×2)	2.1303(11)	0.338 (×2)
<i>M</i> (1)–O(3) (×2)	2.0986(14)	0.255 (×2)	<i>M</i> (2)–O(4) (×2)	2.0292(11)	0.424(×2)
<i>M</i> (1)–O(3)' (×2)	2.454(15)	0.014 (×2)	< <i>M</i> (2)–O>	2.1106	Σ = 2.138
< <i>M</i> (1)–O>	2.0819	Σ = 2.002			
<i>M</i> (3)–O(1) (×4)	2.0705(11)	0.366 (×4)	<i>M</i> (4)–O(2) (×2)	2.4106(17)	0.292 (×2)
<i>M</i> (3)–O(3) (×2)	2.0562(17)	0.283 (×2)	<i>M</i> (4)–O(4) (×2)	2.3166(13)	0.367(×2)
<i>M</i> (3)–O(3)' (×2)	2.424(17)	0.016 (×2)	<i>M</i> (4)–O(5) (×2)	2.7658(16)	0.122 (×2)
< <i>M</i> (3)–O>	2.0657	Σ = 2.062	<i>M</i> (4)–O(6) (×2)	2.5728(17)	0.196(×2)
			< <i>M</i> (4)–O>	2.5165	Σ = 1.954
<i>Am</i> –O(5) (×2)	2.974(2)		<i>A2</i> –O(5) (×2)	3.186(4)	
<i>Am</i> –O(6) (×2)	2.757(4)		<i>A2</i> –O(5) (×2)	2.823(4)	
<i>Am</i> –O(7) (×2)	2.458(4)		<i>A2</i> –O(6) (×2)	2.981(3)	
<i>Am</i> –O(7) (×2)	2.558(4)		<i>A2</i> –O(7) (×2)	2.459(2)	
< <i>Am</i> –O>	2.7885		< <i>A2</i> –O>	2.8356	

* Bond-valence parameters involving oxygen from Gagné & Hawthorne (2015), those involving halogens from Brese & O'Keeffe (1991).

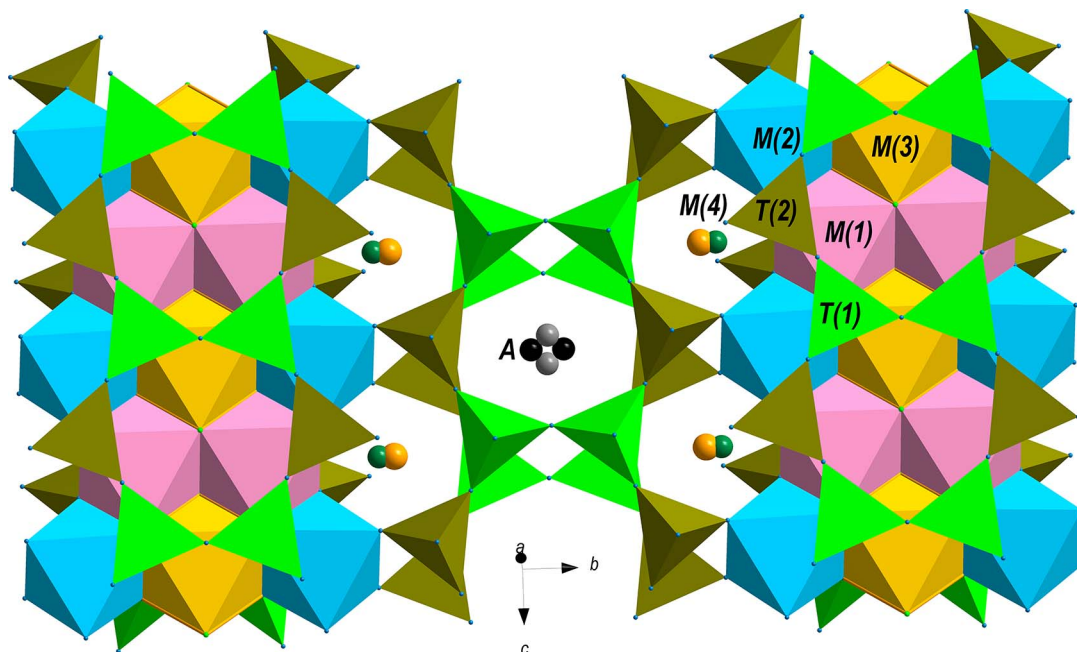


FIG. 5. Perspective view of the structure of ferro-fluoro-edenite seen almost along [100]. Orange spheres: *M*(4) sites, green spheres: *M*(4)' sites, black spheres: *Am* sites, gray spheres: *A2* sites.

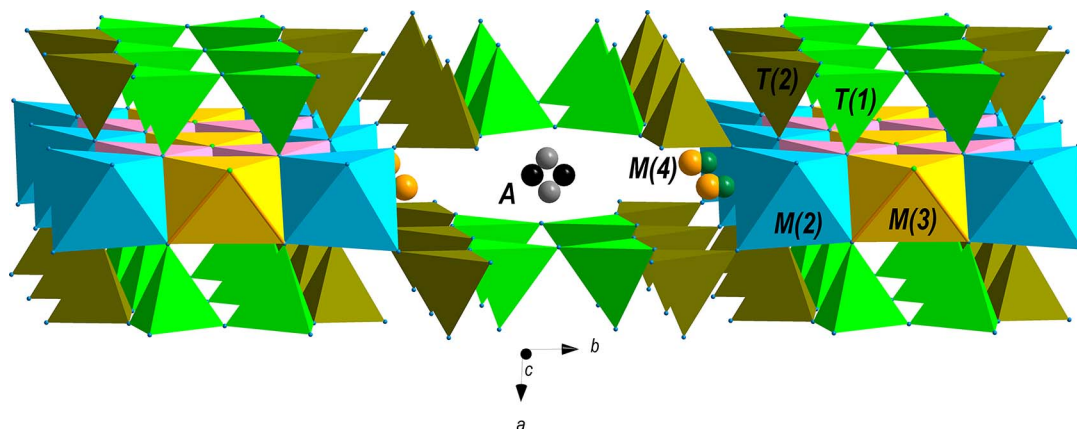


FIG. 6. Perspective view of the structure of ferro-fluoro-edenite seen almost along [001].

edenite, where sodium prevails over potassium, the former is located at the *Am* site and the latter at the *A2* site. This yields 10.26 *epfu* at the *A* site compared to 11.96 *epfu* by chemical formula. Perhaps the lower scattering obtained at the *A* site is related to the use of an isotropic split-sites model.

As for the two tetrahedral sites, *T*(1) and *T*(2), the former is on average slightly larger: $\langle T(1)-O \rangle$ 1.650 versus $\langle T(2)-O \rangle$ 1.632 Å. This feature and the bond-valence calculations (3.740 *vu*) clearly indicate the ordering of Al at the *T*(1) site and the virtual absence of Ti^{4+} in the tetrahedra (Oberti *et al.* 1992). The value of 1.05 *apfu* of Al, calculated using the regression relation $\overline{n(1)Al} (apfu) = [\langle T(1)-O \rangle - 1.6193] \times 34.2199$ proposed by Oberti *et al.* (2007), is the same as obtained from the chemistry.

CONCLUSIONS

In “*Contributo allo studio dei minerali dell’Isola di Vulcano*” Panichi (1914) reported the presence of well-formed crystals of an amphibole in association with acicular ilvaite (“breislakite”), quartz, and magnetite. At that time, the nature of “breislakite” was not well defined, and it seems to correspond to what has actually been determined to be vonsenite. It is surprising that no further investigation has been carried out on this amphibole.

Until now the existence of ferro-fluoro-edenite was suggested but only one composition close to the endmember was found. Petersen *et al.* (1982) discussed the presence of fluorine in micas and amphiboles and cited one analysis carried out by Borley & Frost (1963) among analytical data on hastingsites (reported in Table III sample A.25) with a composition corresponding to a ferro-fluoro-edenite. An Fe-rich fluoro-edenite from pyroxene-hornblende

andesites in the Ishigamiyama, Kumamoto Prefecture, Japan, was reported by Tomita *et al.* (1994). Moreover, in the amphibole database built up at the CNR-Centro di Studio per la Cristallografia e Cristallografia, which presently contains more than 1,000 structure refinements, there is only one sample of ferro-edenite, which also has a significant F content (around 0.80 *apfu*) (Gianfagna & Oberti 2001).

The occurrence at Vulcano Island of ferro-fluoro-edenite is additional evidence of the peculiar geochemical situation occurring in the volcanic apparatus of this island.

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