

**FLUORVESUVIANITE, $\text{Ca}_{19}(\text{Al}, \text{Mg}, \text{Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{F}, \text{OH})_9$,
A NEW MINERAL SPECIES FROM PITKÄRANTA, KARELIA,
RUSSIA: DESCRIPTION AND CRYSTAL STRUCTURE**

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ABSTRACT

Fluorvesuvianite was found in the abandoned Lupikko iron mine, Pitkäranta, Karelia, Russia. It occurs in cavities of chloritized diopside skarn, as radiating aggregates of acicular crystals in calcite. Crystals (up to 1.5 cm long and 5–20 μm across) are elongate along [001]; the dominant forms are {100} or {110}. Associated minerals are sphalerite and clinocllore. Single crystals of fluorvesuvianite are colorless and transparent, aggregates are white with silky luster, and the mineral is non-fluorescent. The Mohs hardness is 6. The mineral is brittle, and no cleavage or parting was observed. D_{meas} is 3.46(3) g/cm^3 , and D_{calc} is 3.43 g/cm^3 . In immersion liquids, the mineral is colorless and non-pleochroic. Fluorvesuvianite is uniaxial (–), ω 1.702(1), ε 1.699(1) for $\lambda = 589$ nm. Chemical composition (electron microprobe, H_2O by TGA, F by ion-selective electrode, wt.%): CaO 36.1, MgO 1.9, MnO 0.1, FeO 2.8, Al_2O_3 17.9, SiO_2 36.6, H_2O 0.5, F 4.6, $-\text{O}=2\text{F}$ 1.94, Total 98.56. The empirical formula based on 50 cations per formula unit is $\text{Ca}_{19.03}(\text{Al}_{10.38}\text{Mg}_{1.39}\text{Fe}^{2+}_{1.15}\text{Mn}^{2+}_{0.04})_{\Sigma 12.96}\text{Si}_{18.01}\text{O}_{68.00}(\text{F}_{7.16}\text{OH}_{1.64}\text{O}_{0.80})_{\Sigma 9.60}$, which corresponds to the ideal formula $\text{Ca}_{19}(\text{Al}, \text{Mg}, \text{Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{F}, \text{OH})_9$. The bands in the IR spectrum are: 3625, 3555, 3400, 3170, 1650, 1575, 1080 shoulder, 1021, 983, 905, 870 shoulder, 800, 710 shoulder, 636, 605, 577, 490, 444, 411, 395 cm^{-1} . The strongest eight lines in the X-ray powder-diffraction pattern [d in \AA (1)(hkl)] are: 4.74(20)(202), 3.465(30)(420), 3.040(30)(510), 2.945(35)(004), 2.743(90)(432,440), 2.589(50)(224,522), 2.453(100)(620), and 1.619(30)(526,922). Fluorvesuvianite is tetragonal, space group $P4/nmc$, unit-cell parameters refined from the powder data: a 15.516(2), c 11.772(3) \AA , V 2834(1) \AA^3 , $Z = 2$. The crystal structure has been refined to $R_1 = 0.043$, calculated for 1108 unique observed reflections ($|F_o| \geq 4\sigma(F_o)$). The structure refinement demonstrates that most of the fluorine is at the F(11) position [the refined site-occupancy is $\text{F}_{0.72}(\text{OH})_{0.28}$]. The elongate $\langle \text{Si}(1)-\text{O} \rangle$ bond length (1.664 \AA) and the Si(1) site-occupancy factor, 0.803(8), suggest substitution according to the

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scheme $(\text{SiO}_4)^{4-} \leftrightarrow 4\text{F}^-$. If $\text{Ca}_{19}(\text{Al,Mg,Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{OH})_9$ is considered the formula of vesuvianite, the end-member composition of fluorvesuvianite is $\text{Ca}_{19}(\text{Al,Mg,Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{F})_9$. In other words, a vesuvianite-group specimen with more than 4.5 F *apfu* is named fluorvesuvianite.

Keywords: fluorvesuvianite, new mineral species, crystal structure, Pitkäranta, Karelia, Russia.

SOMMAIRE

La fluorvésuvianite a été découverte à la mine de fer abandonnée de Lupikko, Pitkäranta, Karélie, Russie. On la trouve dans des cavités d'un skarn à diopside chloritisé, en amas fibroradiés dans la calcite. Les cristaux, jusqu'à 1.5 cm de long et 5–20 μm de diamètre, sont allongés le long de [001]; les formes dominantes sont {100} et {110}. Lui sont associés sphalérite et clinocllore. Les monocristaux de fluorvésuvianite sont incolores et transparents, les agrégats sont blancs avec un éclat soyeux, et le minéral est non-fluorescent. La dureté de Mohs est 6. C'est un minéral cassant, sans clivage ou plan de séparation. La densité mesurée est 3.46(3) g/cm^3 , et la densité calculée, 3.43 g/cm^3 . Dans les liquides d'immersion, le minéral est incolore et non-pléochroïque. La fluorvésuvianite est uniaxe (-), ω 1.702(1), ϵ 1.699(1) pour $\lambda = 589 \text{ nm}$. Sa composition chimique (microsonde électronique, H_2O par analyse thermogravimétrique, F par électrode à ion sélectif, résultats en %, poids): CaO 36.1, MgO 1.9, MnO 0.1, FeO 2.8, Al_2O_3 17.9, SiO_2 36.6, H_2O 0.5, F 4.6, $-\text{O}=2\text{F}$ 1.94, total 98.56. La formule empirique fondée sur 50 cations par unité formulaire est $\text{Ca}_{19.03}(\text{Al}_{10.38}\text{Mg}_{1.39}\text{Fe}^{2+}_{1.15}\text{Mn}^{2+}_{0.04})_{\Sigma 12.96}\text{Si}_{18.01}\text{O}_{68.00}(\text{F}_{7.16}\text{OH}_{1.64}\text{O}_{0.80})_{\Sigma 9.60}$, ce qui correspond à une formule idéale $\text{Ca}_{19}(\text{Al,Mg,Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{F,OH})_9$. Les bandes du spectre d'absorption infra-rouge sont: 3625, 3555, 3400, 3170, 1650, 1575, 1080 épaulement, 1021, 983, 905, 870 épaulement, 800, 710 épaulement, 636, 605, 577, 490, 444, 411, 395 cm^{-1} . Les huit raies les plus intenses du spectre de diffraction, méthode des poudres [d en $\text{Å}(I)(hkl)$] sont: 4.74(20)(202), 3.465(30)(420), 3.040(30)(510), 2.945(35)(004), 2.743(90)(432,440), 2.589(50)(224,522), 2.453(100)(620), et 1.619(30)(526,922). La fluorvésuvianite est tétragonale, groupe spatial $P4/nmc$, paramètres réticulaires affinés à partir du spectre sur poudre: a 15.516(2), c 11.772(3) Å , V 2834(1) Å^3 , $Z = 2$. Nous avons affiné la structure cristalline jusqu'à un résidu $R_1 = 0.043$, calculé pour 1108 réflexions uniques observées ($|F_o| \geq 4\sigma |F_c|$). L'affinement démontre que la plupart du fluor se situe au site F(11), dont l'occupation affinée est $\text{F}_{0.72}(\text{OH})_{0.28}$. La liaison $\langle \text{Si}(1)-\text{O} \rangle$ légèrement allongée (1.664 Å) et le facteur d'occupation du site Si(1), 0.803(8), témoigneraient de la substitution $(\text{SiO}_4)^{4-} \leftrightarrow 4\text{F}^-$. Si la formule de la vésuvianite s'écrit $\text{Ca}_{19}(\text{Al,Mg,Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{OH})_9$, celle du pôle fluorvésuvianite serait $\text{Ca}_{19}(\text{Al,Mg,Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{F})_9$. En d'autres mots, un échantillon du groupe de la vésuvianite ayant plus de 4.5 F atomes par unité formulaire mérite le nom fluorvésuvianite.

(Traduit par la Rédaction)

Mots-clés: fluorvésuvianite, nouvelle espèce minérale, structure cristalline, Pitkäranta, Karélie, Russie.

INTRODUCTION

There are three known mineral species in the vesuvianite group of minerals: vesuvianite itself, $\text{Ca}_{19}\text{Al}_{10}(\text{Mg,Fe})_3\text{Si}_{18}\text{O}_{69}(\text{OH,F})_9$, known since 1795, and two new recently described species: wiluite, $\text{Ca}_{19}(\text{Al,Mg,Fe,Ti})_{13}(\text{B,Al})_5\text{Si}_{18}\text{O}_{68}(\text{O,OH})_{10}$ (Groat *et al.* 1998), and manganvesuvianite, $\text{Ca}_{19}\text{Mn}^{3+}(\text{Al,Mn}^{3+},\text{Fe}^{3+})_{10}(\text{Mg,Mn}^{2+})_2\text{Si}_{18}\text{O}_{69}(\text{OH})_9$ (Armbruster *et al.* 2002). The crystal chemistry of vesuvianite is rather complex, and considerable efforts have been undertaken by many authors in order to characterize its variations in symmetry and chemical compositions (see Groat *et al.* 1992a, b, 1994a, b, 1995, 1998; Armbruster & Gnos 2000a, b, c; Armbruster *et al.* 2002, and references therein). The general formula of vesuvianite-group minerals can be written as $X_{18}X'Y_{12}Y'Z_{18}O_{69}W_9$ where X , Y and Z are fully or almost fully occupied cation sites; X' and Y' are cations in sites that are half-occupied, and W is usually OH or F occupying two anion sites. The X' and Y' sites form polar strings along the fourfold axis and the schemes of order [interpreted by Armbruster & Gnos (2000c) as a 'rod' polytypism] determine the symmetry of the structure, with the possible space-groups $P4/nmc$ (disordered arrangement), $P4/n$ and $P4nc$ (ordered arrangements).

In a detailed study, Groat *et al.* (1992b) examined possible mechanisms of incorporation of fluorine into the vesuvianite structure. However, among their samples, there were no crystals with prevalence of F over OH and O in the W additional anion sites. In the summer of 1999, unusual acicular crystals of vesuvianite were found by the first author in a boulder of chloritized diopside–calcite skarn of the Lupikko mine, Pitkäranta ore field, Karelia, Russia. The low indices of refraction and the high density of these crystals in comparison to the usual vesuvianite prompted us to study the sample in more detail. Chemical analyses demonstrated that the mineral is enriched in fluorine and in fact is a fluorine-dominant analogue of vesuvianite. The mineral was named *fluorvesuvianite* according to its chemical composition, and it is the fourth known mineral species of the vesuvianite group. Both the mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA No. 2000–037). The holotype specimen is deposited at the Mineralogical Museum of the Department of Mineralogy, St. Petersburg State University, St. Petersburg, Russia (catalogue number 1/18619). Our aim in this paper is to report a description of fluorvesuvianite and the results of a refinement of its structure.

LOCALITY AND OCCURRENCE

The Pitkäranta ore field is an old mining region located on the northeastern coast of Ladoga Lake, Karelia (Trüstedt 1907) (Fig. 1). It had been intensively exploited since the late 17th century, with more than 30 mines operated for Fe, Sn, Zn, Cu and Ag. By the beginning of the 20th century, most of the orebodies had been mined out, and the mines have been abandoned since 1940. Despite the intensive mining, little is known about the mineralogy of the area. A detailed mineralogical characterization was undertaken in the 1970s by E.I. Nefedov, but the report was never published (Nefedov 1977).

The Lupikko mine of the Pitkäranta ore field (Fig. 1) was operated for magnetite ore in the 17th Century and consisted of five shafts. At the present time, small ore dumps can be observed with vesuvianite–magnetite and diopside–magnetite skarns that were severely altered by late hydrothermal processes, leading to the pervasive formation of fluorite, calcite and chlorite. In the Lupikko skarns, vesuvianite as a rock-forming mineral forms coarse-grained aggregates of brown, centimeter-sized prismatic crystals. The chemical composition of the Lupikko vesuvianite of this type was studied by Groat *et al.* (1992a).

Crystals of fluorvesuvianite were found in a piece of a coarse-grained chloritized diopside skarn with cavities up to 3 cm filled by white calcite. Fluorvesuvianite occurs in calcite as radiating aggregates of colorless acicular crystals, 5–30 μm thick and up to 1.5 cm long (Fig. 2), associated with clinocllore and sphalerite. These fluorvesuvianite whiskers emerge out of clusters of relatively thick (~30–150 μm) composite crystals of vesuvianite. Figure 3 schematically shows a (001) cross-section of one of these composite crystals. Its inner biaxial zone, $(-)\alpha \approx 10^\circ$, consists of two intergrown sectors with optical orientations perpendicular to each other. The chemical composition of these sectors has been studied by electron microprobe, and they were found to be a fluorine-bearing vesuvianite (F content of about 1.5–2.5 wt.%). The very thin whiskers (3–5 μm) are optically homogeneous and uniaxial. The latter crystals constitute the fluorvesuvianite, with an F content of about 3–5 wt.%.

PHYSICAL AND OPTICAL PROPERTIES

Fluorvesuvianite is white and has a vitreous silky luster. The prism faces are probably {100} and {110}. The mineral is non-fluorescent. Fluorvesuvianite, with a Mohs hardness 6, is brittle, and without cleavage or parting observed. The density measured by sink–float in diluted Clerici solution is 3.46(3) g/cm^3 . The density calculated on the basis of the structure refinement is 3.40 g/cm^3 .

In immersion liquids, fluorvesuvianite is colorless and non-pleochroic. No anomalous interference-colors

have been observed with crossed polarizers. The mineral is uniaxial, optically negative, ω 1.702(1), ϵ 1.699(1) for $\lambda = 589 \text{ nm}$.

The Gladstone–Dale compatibility (Mandarino 1979) is -0.016 (superior).

CHEMICAL COMPOSITION

The chemical composition of fluorvesuvianite (Table 1) was determined using a Camebax wavelength-dispersion microprobe operated at 20 kV acceleration voltage and 20 nA beam current. Diopside, spessartine and almandine were used as analytical standards. No other elements except those given were detected. No measurable amounts of Li (<0.01 wt.%), Be (<0.02 wt.%) or B (<0.1 wt.%) were detected by inductively coupled plasma (ICP) analysis. Infrared (IR) spectroscopy demonstrated the absence of carbon- and nitrogen-bearing anions. The fluorine concentration was determined by an ion-selective electrode from a sample weighing 12.7 mg.

The empirical formula calculated on the basis of 50 cations per formula unit is $\text{Ca}_{19.03}(\text{Al}_{10.38}\text{Mg}_{1.39}\text{Fe}^{2+}_{1.15}\text{Mn}^{2+}_{0.04})\Sigma_{12.96}\text{Si}_{18.01}\text{O}_{68.00}(\text{F}_{7.16}\text{OH}_{1.64}\text{O}_{0.80})\Sigma_{9.60}$, which is close to the ideal formula, $\text{Ca}_{19}(\text{Al,Mg,Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{F,OH})_9$.

THERMAL ANALYSIS

Thermogravimetric analysis (TGA) was performed using a vacuum thermograph M–10 at the Institute of Chemical Physics, Russian Academy of Sciences. To remove adsorbed water, the sample was first dried in a vacuum chamber at 70°C. Then the sample (66 mg) was heated to 990°C in vacuum at a constant rate of 20°C/min, followed by annealing at this temperature for 1 h. Whereas typical vesuvianite dehydrates in one stage at 1050°C (Chukhrov 1972), the TGA curve for fluorvesuvianite has three steps of weight loss (at 380, 630

TABLE 1. THE CHEMICAL COMPOSITION OF FLUORVESUVIANITE, wt.%

Component	Analysis #				Average
	1	2	3	4	
CaO	36.6	35.6	35.9	36.4	36.1
MgO	1.7	2.0	1.5	2.3	1.9
MnO	0.1	0.4	0.0	0.0	0.1
FeO	2.3	4.1	2.3	2.5	2.8
Al ₂ O ₃	17.5	17.0	18.7	18.3	17.9
SiO ₂	37.1	35.9	36.9	36.4	36.6
H ₂ O					0.50
* F					4.6
-O=2F					1.94
Total					98.56

* Fluorine measured by ion-selective electrode

Empirical formula: $\text{Ca}_{19.03}(\text{Al}_{10.38}\text{Mg}_{1.39}\text{Fe}^{2+}_{1.15}\text{Mn}^{2+}_{0.04})\Sigma_{12.96}\text{Si}_{18.01}\text{O}_{68.00}(\text{F}_{7.16}\text{OH}_{1.64}\text{O}_{0.80})\Sigma_{9.60}$

Ideal formula: $\text{Ca}_{19}(\text{Al,Mg,Fe}^{2+})_{13}[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4\text{O}(\text{F,OH})_9$

and 950°C) with a total loss of 6.6 wt.%. The weight loss involves H₂O and F (the latter presumably as SiF₄). To establish the amount of fluorine, a separate sample (10.5 mg) was annealed at 1000°C for two hours. The residual was found to contain 0.3 wt.% F (in comparison with 4.6 wt.% in a fresh sample). These results show that 4.3 wt.% of F (corresponding to 6.1 wt.% SiF₄) was released by the annealing. The rest of the total weight loss, 0.5 wt.%, is related to the release of H₂O. This value is in a good agreement with the results of the electron-microprobe analyses.

INFRARED SPECTROSCOPY

The IR-spectrum of fluorvesuvianite (Fig. 4) was measured from a powdered sample embedded in a KBr pellet, using a Specord 85 scanning IR-spectrometer. In the principal hydroxyl-stretching region (3800–3000 cm⁻¹), characteristic bands related to O–H stretching vibrations are poorly resolved owing to the limitations of sample quality, but they may be interpreted as unresolved doublets, studied in detail by Groat *et al.* (1995). Band 3625 cm⁻¹ in the spectrum of fluorvesuvianite thus corresponds to unresolved bands *B* (3635) and *C* (3596), band 3555 cm⁻¹, to *D* (3567) and *E* (3524), band 3400 cm⁻¹, to *G* (3430) and *H* (3383), and band 3170 cm⁻¹, to *J* (3210) and *K* (3156). Band 3170 cm⁻¹ corresponds to the OH(10)–O(10) hydrogen bond, which is in agreement with the results of the crystal-structure refinement (see below).

X-RAY POWDER DIFFRACTION

Powder-diffraction data for fluorvesuvianite were obtained with a DRON 2.0 powder diffractometer operated at 20 kV and 35 mA using CuK α radiation and a quartz monochromator. The intensities of the *hk0* reflections are enhanced owing to the unavoidable orientation of acicular crystals elongate along [001]. The X-ray powder-diffraction pattern is given in Table 2, where it is compared with the theoretical pattern calculated from the crystal-structure data using PowderCell for Windows 1.0 (Kraus & Nolze 1997). The unit-cell parameters refined from powder data (space group *P4/nnc*) are: *a* 15.516(2), *c* 11.772(3) Å, *V* 2834(1) Å³, *Z* = 2.

CRYSTAL STRUCTURE

Experimental

For the structure analysis, a crystal of fluorvesuvianite was mounted on a Bruker PLATFORM goniometer equipped with an APEX SMART CCD detector with a crystal-to-detector distance of 5 cm. The data were collected using MoK α X-radiation and frame widths of 0.3° in ω , with 180 s used to acquire each frame. A hemisphere of three-dimensional data was collected. The unit-cell dimensions were refined on the basis of 762 reflections (Table 3). The data were reduced using the Bruker program SAINT. A semi-empirical absorption-correction based upon the intensities of equivalent reflections was applied, and the data were

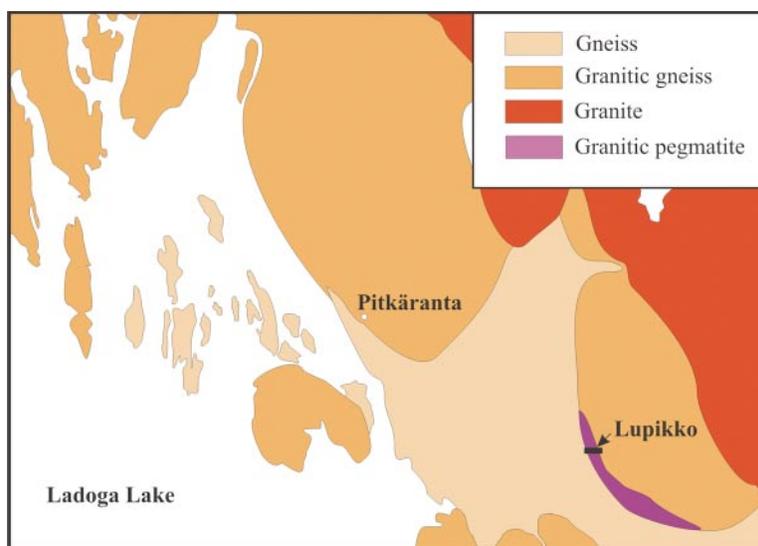


FIG. 1. The scheme of geological structure of the Pitkyaranta ore field. Modified from Trüstedt (1907).



FIG. 2. Acicular crystals of fluorvesuvianite in a calcite matrix. The horizontal dimension of the field of view is 12 mm.

corrected for Lorentz, polarization, and background effects. A total of 29165 intensities was measured; there were 3006 unique reflections, with 1108 classified as observed ($F_o > 4\sigma F_o$).

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5.1 system of programs was used for the refine-

ment of the crystal structure on the basis of F^2 . The reflection statistics and systematic absences were found to be consistent with the space group $P4/nnc$. The structure was refined on the basis of the atom coordinates of Groat *et al.* (1992a, b). Refinement of all atom-position parameters, allowing for anisotropic displacement of all atoms except H, and the inclusion of a weighting scheme of the structure factors, resulted in a final agreement-index ($R1$) of 0.043, calculated for the unique observed

reflections, and a goodness-of-fit (*S*) of 0.824. The final atom-parameters are listed in Table 4, selected interatomic distances are presented in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Bond-valence analysis

The bond-valence calculations were performed using Al³⁺-O, Al³⁺-F, Ca²⁺-O, Fe²⁺-O and Si⁴⁺-O bond-valence curves from Brown & Altermatt (1985). The bond-valence sums for cations are: 3.59, 3.81, 3.98, 1.85, 3.06, 2.77, 2.39, 2.25, 1.92 and 2.27 *vu* (valence units) for Si(1), Si(2), Si(3), Fe(1), Al(2), Al(3), Ca(1), Ca(2), Ca(3) and Ca(4), respectively. The bond-valence sums for anions are: 2.04, 1.98, 2.00, 1.93, 2.09, 2.22, 1.81, 2.15, 2.12, 1.05 and 0.96 *vu* for O(1), O(2), O(3), O(4), O(5), O(6), O(7), O(8), O(9), (O,OH)(10) and F(11), respectively.

Cation positions

The general formula for vesuvianite-group minerals is usually written as X₁₈X'Y₁₂Y'Z₁₈O₆₈W₁₀. In fluorvesuvianite, the X sites are Ca(1), Ca(2) and Ca(3), and these sites are fully occupied by Ca. The Ca(1), Ca(2) and

Ca(3) positions are coordinated by eight, eight and nine anions, respectively, if two long bonds [Ca(2)-O(6) = 2.899 Å, Ca(3)-O(6) = 2.998 Å], are taken into account. The Y sites are Al(2) and Al(3). The Al(2) position is octahedrally coordinated and is fully occupied by Al [*<*Al(2)-φ = 1.902 Å]. The Al(3) site has octahedral coordination as well, but the *<*Al(3)-φ> bond length is

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR FLUORVESUVIANITE

<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> _{meas}	<i>d</i> _{meas}	<i>I</i> _{calc}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> _{meas}	<i>d</i> _{meas}	<i>I</i> _{calc}	<i>d</i> _{calc}
1	1	0	20	10.93	18	10.972	5	4	3	5	2.058	4	2.062
0	0	2	8	5.89	8	5.886	5	2	4			2	2.059
2	2	0	5	5.49	3	5.486	7	1	2			3	2.056
2	0	2	20	4.74	8	4.689	7	3	0	18	2.037	9	2.037
2	1	2			5	4.489	6	4	2	5	2.021	6	2.021
2	2	2	8	4.02	9	4.013	7	3	1	8	2.008	6	2.008
4	0	0	10	3.877	6	3.879	6	3	3	7	1.993	12	1.993
3	1	2	3	3.770	1	3.769	6	5	1	7	1.959	7	1.959
4	2	0	30	3.465	9	3.470	6	1	4	7	1.929	2	1.928
4	0	2	10	3.236	7	3.239	7	3	2			2	1.925
3	1	3			4	3.065	7	1	3	12	1.913	5	1.915
5	1	0	30	3.040	11	3.043	2	0	6	7	1.903	5	1.902
4	3	1	10	2.997	8	3.001	7	4	1			2	1.899
4	2	2			7	2.989	8	1	1			1	1.899
0	0	4	35	2.945	60	2.943	6	5	2	15	1.881	1	1.882
3	2	3	5	2.898	4	2.900	8	2	0			6	1.882
1	1	4	6	2.841	4	2.843	7	1	4	8	1.759	14	1.759
4	3	2	90	2.743	100	2.745	9	1	0	10	1.713	5	1.714
4	4	0			29	2.743	7	3	4	7	1.675	15	1.675
5	3	0	8	2.660	5	2.661	4	3	6	12	1.659	26	1.658
2	2	4	50	2.589	31	2.593	5	2	6	30	1.619	26	1.622
5	2	2			68	2.588	9	2	2			34	1.618
3	1	4	5	2.522	8	2.524	7	7	0	10	1.568	9	1.567
6	1	1	5	2.493	2	2.493	6	0	6	8	1.564	1	1.563
4	4	2			1	2.486	6	1	6	8	1.554	10	1.555
6	2	0	100	2.453	44	2.453	6	6	4			10	1.553
5	0	3	10	2.435	8	2.434	7	5	4	5	1.539	5	1.538
5	4	1	6	2.369	3	2.373	10	2	0	10	1.522	6	1.522
6	0	2			5	2.368	6	5	5	7	1.519	1	1.518
4	0	4	5	2.342	9	2.345	8	5	3			1	1.517
6	1	2			4	2.341	10	2	1	7	1.508	1	1.509
5	2	3	7	2.319	3	2.322	9	5	0			4	1.507
4	1	4			7	2.318	6	3	6	6	1.495	3	1.496
3	3	4	3	2.292	5	2.293	8	4	4			9	1.494
6	3	1	4	2.270	5	2.270	10	1	2			3	1.493
4	2	4	2	2.245	1	2.244	0	0	8	3	1.472	6	1.472
2	1	5	2	2.230	2	2.230	11	1	0	3	1.405	1	1.405
5	3	3			5	2.202	7	7	4	4	1.384	11	1.383
7	1	0	6	2.193	6	2.194	10	0	4	4	1.371	1	1.373
7	0	1	6	2.177	4	2.178	8	6	4			2	1.373
7	1	1	7	2.157	6	2.157	8	8	0			2	1.371
3	0	5	3	2.139	3	2.143	9	2	5			1	1.369
6	1	3			1	2.139	8	7	3			2	1.368
4	3	4			2	2.135	10	5	2	4	1.353	2	1.351
3	1	5	15	2.119	14	2.123	9	5	4	5	1.343	14	1.341
6	4	1			10	2.117	4	4	8	8	1.294	7	1.297
7	2	1	2	2.097	1	2.097	11	4	2			8	1.293
6	2	3	5	2.080	8	2.080							

TABLE 3. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR FLUORVESUVIANITE

<i>a</i> (Å)	15.5295(10)	Crystal size (mm)	0.06 × 0.005 × 0.005
<i>c</i> (Å)	11.7808(11)	Radiation	MoKα
<i>V</i> (Å ³)	2841.1(4)	Total reflections	29165
Space group	<i>P4/mnc</i>	Unique reflections	3006
<i>F</i> ₀₀₀	2885	Unique <i>F</i> _{hkl} = 4 <i>G</i> _{<i>h</i>²+<i>k</i>²+<i>l</i>²}	1108
<i>Z</i>	2	<i>R</i> ₁	0.043
<i>μ</i> (cm ⁻¹)	28.14	<i>wR</i> ₂	0.063
<i>D</i> _{calc} (g/cm ³)	3.40	<i>S</i>	0.824

Note: *R*₁ = Σ||*F*_{hkl}|| - |*F*_{hkl}|| / Σ|*F*_{hkl}||; *wR*₂ = {Σ[w(*F*_o² - *F*_c²)²] / Σ[w(*F*_o²)]}^{1/2}; *w* = 1/[σ²(*F*_o²) + (*aP*)² + *bP*], where *P* = (*F*_o² + 2*F*_c²)/3; *s* = {Σ[w(*F*_o² - *F*_c²)] / (*n* - *p*)^{1/2}, where *n* is the number of reflections and *p* is the number of refined parameters.

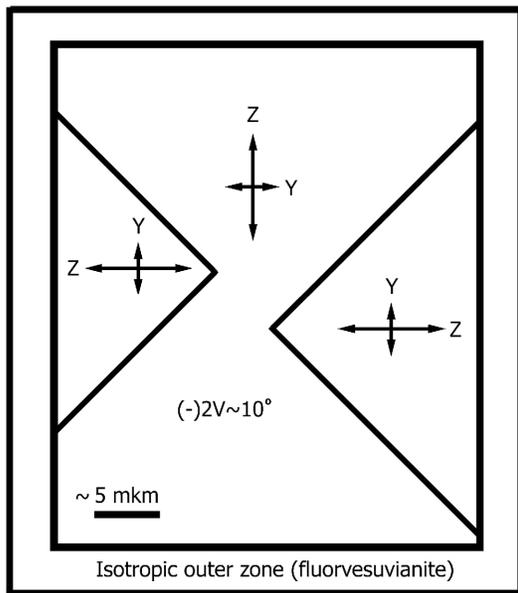


Fig. 3. Schematic representation of the internal structure of the composite fluorian vesuvianite crystals from which acicular crystals of fluorvesuvianite originate.

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (\AA^2) FOR FLUORVESUVIANITE

Atom	s.o.f.	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	0.803(8)	¼	¼	0	0.0031(8)	0.0029(11)	0.0029(11)	0.0034(14)	0	0	0
Si(2)	1	0.81894(9)	0.04068(8)	0.87126(12)	0.0097(3)	0.0093(7)	0.0104(7)	0.0095(6)	0.0007(6)	0.0007(6)	0.0004(5)
Si(3)	1	0.91766(9)	0.84952(8)	0.36457(12)	0.0102(3)	0.0135(7)	0.0081(7)	0.0091(6)	0.0008(5)	0.0002(6)	-0.0012(5)
Ca(1)	1	¼	¼	¼	0.0113(4)	0.0131(11)	0.0099(10)	0.0108(9)	0	0	0
Ca(2)	1	0.81096(6)	0.04346(6)	0.37980(9)	0.0111(2)	0.0095(5)	0.0128(5)	0.0109(4)	0.0001(4)	-0.0002(4)	0.0010(4)
Ca(3)	1	0.89923(6)	0.82022(6)	0.88711(9)	0.0156(2)	0.0132(5)	0.0130(5)	0.0207(6)	-0.0026(5)	-0.0057(5)	0.0020(4)
Ca(4)	0.50	¼	¼	0.1428(3)	0.0140(9)	0.0140(13)	0.0140(13)	0.014(2)	0	0	0
Fe(1)	0.50	¼	¼	0.0500(3)	0.0255(8)	0.0141(10)	0.0141(10)	0.048(2)	0	0	0
Al(2)	1	0	0	0	0.0103(4)	0.0095(10)	0.0067(10)	0.0148(10)	0.0003(9)	0.0019(9)	0.0013(8)
Fe(3)	0.046(4)	0.88813(9)	0.12071(9)	0.12691(13)	0.0080(4)	0.0087(7)	0.0084(7)	0.0070(6)	-0.0001(6)	0.0017(6)	0.0004(5)
Al(3)	0.780(4)	0.88813(9)	0.12071(9)	0.12691(13)	0.0080(4)	0.0087(7)	0.0084(7)	0.0070(6)	-0.0001(6)	0.0017(6)	0.0004(5)
Mg(3)	0.17	0.88813(9)	0.12071(9)	0.12691(13)	0.0080(4)	0.0087(7)	0.0084(7)	0.0070(6)	-0.0001(6)	0.0017(6)	0.0004(5)
O(1)	1	0.7811(2)	0.1714(2)	0.0869(3)	0.0111(7)	0.010(2)	0.014(2)	0.009(2)	-0.0042(14)	-0.002(1)	-0.0006(14)
O(2)	1	0.8835(2)	0.1594(2)	0.2785(3)	0.0096(7)	0.012(2)	0.008(2)	0.009(2)	0.0016(13)	-0.001(1)	-0.0005(13)
O(3)	1	0.9504(2)	0.2782(2)	0.4233(3)	0.0104(7)	0.014(2)	0.009(2)	0.009(2)	-0.0034(13)	-0.0027(1)	-0.0025(13)
O(4)	1	0.1067(2)	-0.0627(2)	0.0296(3)	0.0106(7)	0.010(2)	0.009(2)	0.012(2)	0.0021(14)	-0.0004(14)	-0.0033(13)
O(5)	1	0.8305(2)	0.0148(2)	0.1782(3)	0.0121(7)	0.009(2)	0.012(2)	0.015(2)	0.0008(14)	0.0037(14)	0.0061(14)
O(6)	1	0.8823(2)	0.7288(2)	0.0590(3)	0.0148(8)	0.021(2)	0.010(2)	0.014(2)	0.0025(14)	0.003(2)	0.0034(14)
O(7)	1	0.0564(2)	0.1750(2)	0.3221(3)	0.0122(7)	0.011(2)	0.013(2)	0.013(2)	0.0031(14)	-0.0002(14)	0.0016(14)
O(8)	1	0.0906(2)	0.0610(2)	0.5661(3)	0.0104(7)	0.010(2)	0.009(2)	0.012(2)	-0.0028(13)	-0.0008(13)	-0.0008(13)
O(9)	1	0.8554(2)	0.8554(2)	¼	0.0109(10)	0.0115(15)	0.0115(15)	0.010(2)	0.0017(14)	-0.0017(14)	-0.002(2)
O,OH(10)	1	¼	¼	0.8642(6)	0.0146(15)	0.014(2)	0.014(2)	0.015(4)	0	0	0
F(11)	0.72(5)	-0.0047(2)	0.0620(2)	0.1374(2)	0.0166(10)	0.016(2)	0.020(2)	0.014(2)	-0.0030(13)	-0.0010(14)	-0.0006(13)
O(11)	0.28(5)	-0.0047(2)	0.0620(2)	0.1374(2)	0.0166(10)	0.016(2)	0.020(2)	0.014(2)	-0.0030(13)	-0.0010(14)	-0.0006(13)
H(1)	1	¼	¼	¼	0.080						

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. SELECTED BOND LENGTHS (\AA) IN THE STRUCTURE OF FLUORVESUVIANITE

Si(1)-O(1)	1.664(3)	4x	Ca(1)-O(1)	2.326(3)	4x
<Si(1)-O>	1.664		Ca(1)-O(2)	2.528(3)	4x
			<Ca(1)-O>	2.43	
Si(2)-O(7)	1.617(4)				
Si(2)-O(3)	1.634(3)		Ca(2)-O(8)	2.318(3)	
Si(2)-O(2)	1.642(3)		Ca(2)-O(5)	2.343(3)	
Si(2)-O(4)	1.677(3)		Ca(2)-O(3)	2.377(3)	
<Si(2)-O>	1.64		Ca(2)-O(5)	2.435(3)	
			Ca(2)-O(2)	2.436(3)	
Si(3)-O(6)	1.609(3)		Ca(2)-O(4)	2.439(3)	
Si(3)-O(8)	1.617(3)		Ca(2)-O(1)	2.480(3)	
Si(3)-O(5)	1.618(4)		Ca(2)-O(6)	2.899(3)	
Si(3)-O(9)	1.663(2)		<Ca(2)-O>	2.47	
<Si(3)-O>	1.63				
			Ca(3)-O(7)	2.364(3)	
Fe(1)-O(6)	2.084(3)	4x	Ca(3)-O(3)	2.461(3)	
Fe(1)-O,OH(10)	2.190(8)		Ca(3)-F(11)	2.472(3)	
<Fe(1)- ϕ *>	2.11		Ca(3)-O(7)	2.480(3)	
			Ca(3)-O(6)	2.487(3)	
Al(2)-O(8)	1.867(3)	2x	Ca(3)-O(7)	2.560(3)	
Al(2)-F(11)	1.884(3)	2x	Ca(3)-O,OH(10)	2.576(1)	
Al(2)-O(4)	1.954(3)	2x	Ca(3)-O(8)	2.597(3)	
<Al(2)- ϕ *>	1.902		Ca(3)-O(6)	2.998(3)	
			<Ca(3)- ϕ *>	2.56	
Al(3)-O(2)	1.886(3)				
Al(3)-O(1)	1.899(3)		Ca(4)-O(6)	2.304(4)	4x
Al(3)-F(11)	1.902(3)		Ca(4)-O(9)	2.636(4)	4x
Al(3)-O(3)	1.937(3)		<Ca(4)-O>	2.47	
Al(3)-O(5)	1.968(4)				
Al(3)-O(4)	2.054(3)				
<Al(3)- ϕ *>	1.941				

* ϕ = O, F

slightly longer (1.941 \AA). The occupancy for this site is $\text{Al}_{0.78}\text{Mg}_{0.17}\text{Fe}_{0.05}$ (the amount of Mg was fixed during refinement on the basis of the chemical data, whereas

the Al:Fe ratio was refined). The X' and Y' sites are half-occupied by Ca(4) and Fe(1), respectively, and are on the fourfold axis ($x = y = \frac{3}{4}$). The Ca(4)-Fe(1) distance is 1.093(5) \AA . The Ca(4) site is coordinated by eight anions, whereas the coordination of Fe(1) is five-fold (tetragonal pyramid with equatorial Fe-O bonds of 2.084 \AA and an apical Fe-O bond of 2.190 \AA). The Z positions, Si(1), Si(2) and Si(3), are tetrahedrally coordinated by four O atoms each. The Si(1)O₄ and Si(2)O₄ tetrahedra are isolated, whereas the Si(3)O₄ tetrahedra share the O(9) atom to form Si₂O₇ double tetrahedra.

Fluorine position and hydrogen bonding

Groat *et al.* (1992b) studied F-for-OH substitutions in samples of vesuvianite and reported the OH(11) and O(10) positions as possible hosts for fluorine. Occupancy refinement for fluorvesuvianite indicates that most of the fluorine is incorporated at the OH(11) [= F(11)] site. The refined content of this site is $\text{F}_{0.72}(\text{OH})_{0.28}$. The bond-valence sum for the F(11) site is 0.96 *vu* using the bond-valence curves for F and 1.22 *vu* using the bond-valence curves for O.

Groat *et al.* (1992b) showed that incorporation of fluorine at the O(10) site induces positional disorder at this site, or at least a highly asymmetrical shape of the atom-displacement ellipsoid, which is smeared parallel to the *c* axis. In fluorvesuvianite, no disorder is observed, and O(10) exhibits almost isotropic behavior.

The only H site found in this study is located at special position ($\frac{3}{4}$ $\frac{3}{4}$ $\frac{3}{4}$), and is 1.345 Å away from two O(10) sites. This geometry is characteristic of a symmetrical hydrogen bond. However, the most probable configuration is an H position that is disordered over two sites related by the symmetry center at ($\frac{3}{4}$ $\frac{3}{4}$ $\frac{3}{4}$), as reported for *P4/nnc* vesuvianite by Lager *et al.* (1999) on the basis of a combined neutron-diffraction study and infrared (IR) spectroscopy. As a consequence, (O,OH)(10) is occupied equally by OH and O. The strong O(10)...H-O(10) hydrogen bond is responsible for the pronounced IR absorption band $\sim 3100\text{--}3200\text{ cm}^{-1}$. In fluorvesuvianite, there is a well-defined band 3170 cm^{-1} that is consistent with the (O,OH)(10) site being equally occupied by OH and O. The occupancy of the O(10) site by equal amounts of O and OH would result in an expected bond-valence sum in the order of 1.5–1.6 *vu*, whereas in fluorvesuvianite, it is 1.05 *vu*. It is noteworthy that the same observation also holds for the *P4/nnc* vesuvianite studied by Lager *et al.* (1999). In their case, the bond-valence sum for the O(10) site is 1.22 *vu*, which is again more consistent with OH. Furthermore, the H positions in the sample studied by Lager *et al.* (1999) have been confirmed by neutron-diffraction data. It is very likely that in this case, the direct bond-valence calculations are not applicable, as they correspond to atom arrangements that are averages of two disordered ar-

rangements. In a similar way, ionic radii are not applicable for the disordered sites, as the cation–anion distances for these sites are usually longer than for fully occupied ones (Shannon 1976).

Vacancies at the Si(1) site

The mean $\langle\text{Si}(1)\text{--O}\rangle$ bond length in fluorvesuvianite is 1.664 Å, which results in the Si(1) bond-valence sum of 3.59 *vu*. In the samples of F-bearing vesuvianite studied by Groat *et al.* (1992b), the $\langle\text{Si--O}\rangle$ bond lengths for SiO₄ tetrahedra were invariably shorter than 1.648 Å. Occupancy refinement for the Si(1) site in fluorvesuvianite provides the value of 0.803(8). Similar results [$\langle\text{Si--O}\rangle$ bond lengths of ~ 1.66 Å and occupancies of $\sim 0.80\text{--}0.85$ for the Si(1) site] have been observed by Armbruster & Gnos (2000b) for Mn-bearing vesuvianite and have been interpreted as evidence of a hydrogarnet-like substitution: $(\text{SiO}_4)^{4-} \leftrightarrow (\text{O}_4\text{H}_4)^{4-}$. However, owing to the high F content of our sample, another scheme of substitution may be proposed: $(\text{SiO}_4)^{4-} \leftrightarrow 4\text{F}^-$.

Structural formula and definition of fluorvesuvianite

On the basis of a structure refinement, the simplified structural formula for fluorvesuvianite should be written as $\text{Ca}_{19}(\text{Al,Mg,Fe})_{13}(\text{SiO}_4, \text{O}_4\text{H}_4)_2(\text{SiO}_4)_8$

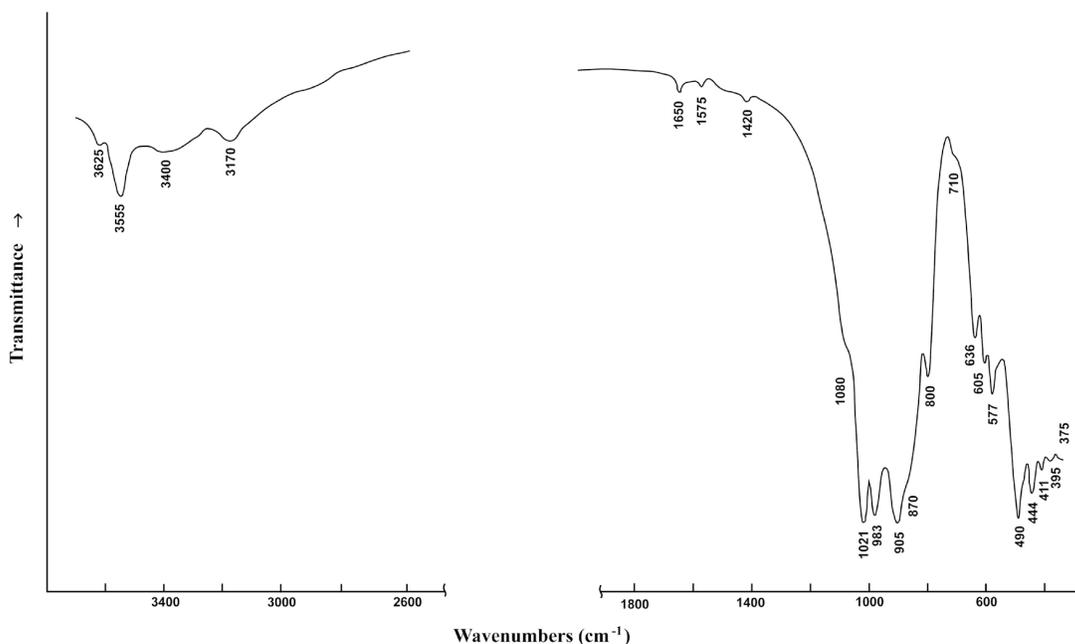


FIG. 4. Infrared absorption spectrum of fluorvesuvianite.

(Si₂O₇)₄(OH)O(F,OH)₈ if a hydrogarnet-like substitution is proposed, and Ca₁₉(Al,Mg,Fe)₁₃(SiO₄,F₄)₂(SiO₄)₈(Si₂O₇)₄(OH)O(F,OH)₈ if the substitution scheme (SiO₄)⁴⁻ ↔ 4F⁻ is present. Considering the general formula of a vesuvianite-group mineral as X₁₈X'Y₁₂Y'Z₁₈O₆₉W₉, fluorvesuvianite is defined as a mineral species with prevalence of fluorine at W [*i.e.*, in the sum of O,OH(10) and OH(11) sites].

ORIGIN OF THE MINERAL AND CRITERIA FOR ITS IDENTIFICATION

Fluorvesuvianite is a late-stage hydrothermal mineral, and its origin is not related to the formation of rock-forming vesuvianite, which is widespread at the Lupikko mine. The formation of fluorvesuvianite is most probably due to the late carbonate and fluorine metasomatism of the Lupikko orebodies. However, this process certainly occurred below 400–800°C, the temperature range suggested by Allen & Burnham (1992) as typical conditions of formation for *P4/nnc* vesuvianite, whereas the *P4nc* and *P4/n* types of vesuvianite are believed to be characteristic of low-temperature processes (<300°C). It is highly unusual to find fluorine-rich vesuvianite formed at a low temperature, and it is also striking that these crystals possess *P4/nnc* symmetry, indicating string disorder. This obvious contradiction may be explained by: (1) epitactic growth of low-temperature fluorvesuvianite whiskers on pre-existing nuclei of high-temperature *P4/nnc*-vesuvianite; thus the string disorder was inherited from the nuclei. (2) Low-temperature fluorine metasomatism led to a specific process of growth leading to whisker formation and string disorder. Growth conditions and processes of vesuvianite in fluorine-rich environments are still enigmatic and not explored experimentally.

The major criterion with which to identify fluorvesuvianite and F-bearing vesuvianite lies in its low indices of refraction, which are in accordance with the Gladstone–Dale relationship (Mandarino 1979).

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