



Article

Fluorapophyllite-(NH₄), NH₄Ca₄(Si₈O₂₀)F·8H₂O, a new member of the apophyllite group from the Vevec quarry, eastern Slovakia

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Abstract

The new mineral fluorapophyllite-(NH₄), ideally NH₄Ca₄(Si₈O₂₀)F·8H₂O, was found at the Vevec andesite quarry located near Vevec village, Vranov nad Topľou Co., Prešov Region, Slovak Republic. It occurs in cavities of quartz–illite–saponite–tobelite xenolith embedded in pyroxene andesite. Fluorapophyllite-(NH₄) is associated with calcite, tridymite, pyrite, chabazite-Ca and heulandite-Ca. It forms clusters, aggregates or crystalline crusts consisting of individual, well-developed crystals up to 4 mm in size, exhibiting the forms {110}, {101} and {001}. The mineral is colourless to light pink and translucent with white streak and vitreous to pearly lustre; it is non-fluorescent under ultraviolet radiation. The Mohs hardness is ~4½ to 5, tenacity is brittle, fracture is irregular, and there is perfect cleavage on {001}. The calculated density is 2.325 g cm⁻³. Fluorapophyllite-(NH₄) is optically uniaxial (+) with ω = 1.5414(5) and ε = 1.5393(8) (λ = 589 nm). It is non-pleochroic. The empirical formula (based on 29 O + F apfu) is [(NH₄)_{0.55}K_{0.32}Na_{0.07}Ca_{0.06}]_{Σ1.00}(Ca_{4.01}Mg_{0.02})_{Σ4.03}Si_{7.97}O₂₀[F_{0.84}(OH)_{0.16}]_{Σ1.00}·8H₂O. Fluorapophyllite-(NH₄) is tetragonal, space group *P4/mnc*, *a* = 8.99336(9) Å, *c* = 15.7910(3) Å, *V* = 1277.18(3) Å³ and *Z* = 2. The seven strongest X-ray powder diffraction lines are [*d*_{obs} in Å, (I, %)(*hkl*)]: 7.897(32)(002), 7.812(13)(101), 4.547(14)(103), 3.946(100)(004), 2.985(39)(105), 2.4841(11)(215) and 1.5788(12)(00.10). The crystal structure of fluorapophyllite-(NH₄), refined to *R*₁ = 0.0299 for 743 unique (*I* > 3σ*I*) observed reflections, confirmed that the atomic arrangement is very similar to that of the other members of the apophyllite group. The new mineral is named according to the current nomenclature scheme for apophyllite-group minerals and is an NH₄ dominant analogue of fluorapophyllite-(K), fluorapophyllite-(Na) and fluorapophyllite-(Cs).

Keywords: fluorapophyllite-(NH₄), new mineral, apophyllite group, phyllosilicates, Raman spectroscopy, xenoliths, Vevec, Slovakia

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Introduction

Fluorapophyllite-(NH₄), ideally NH₄Ca₄(Si₈O₂₀)F·8H₂O, is a new member of apophyllite group. It was found at the Vevec andesite quarry located 2.8 km SW of the Vevec village, Vranov nad Topľou Co., Prešov Region, Slovak Republic.

Fluorapophyllite-(NH₄) is named according to the current nomenclature scheme of apophyllite-group minerals (Hatert *et al.*, 2013), and is an NH₄ dominant analogue of fluorapophyllite-(K), KCa₄Si₈O₂₀F·8H₂O, fluorapophyllite-(Na), NaCa₄Si₈O₂₀F·8H₂O and fluorapophyllite-(Cs), CsCa₄Si₈O₂₀F·8H₂O (Dunn and Wilson, 1978; Dunn *et al.*, 1978; Hatert *et al.*, 2013; Agakhanov *et al.*, 2019). The new mineral and the name has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2019-083, Števkó *et al.*, 2020). The holotype specimen of fluorapophyllite-(NH₄) is deposited in the collections of the Department of Mineralogy and Petrology, National Museum in Prague, Cirkusová 1740, 19300 Praha 9, Czech Republic under the catalogue number P1P 44/2019.

Occurrence

The first (holotype) samples with fluorapophyllite-(NH₄) were collected on September 30, 2018, by one of the authors (MŠ not MS) from the fresh blast pile on the lowest level of the Vevec andesite quarry (48°51'9.58"N, 21°36'12.10"E). More specimens with fluorapophyllite-(NH₄) were later collected at the same level of the Vevec quarry in April and June of 2019.

The Vevec quarry is situated in the central neck of the parasitic andesite volcano of Miocene (Sarmatian) age, which is a part of the Makovica stratovolcano in the Slanské vrchy Mts. volcanic range (Kaličiak, 1991). This quarry is well-known for the occurrence of tridymite, cristobalite, calcite, aragonite and various zeolites (mainly phillipsite-Ca, phillipsite-K, chabazite-Ca and stilbite-Ca), which fill cavities and fractures in pyroxene andesite (Ďuďa *et al.*, 1981, 2001; Števkó *et al.*, 2019). The Vevec quarry andesites also contain numerous xenoliths of Neogene and Paleogene sedimentary as well as metamorphic basement rocks with very variable composition. An interesting association of minerals was described from these xenoliths including quartz, corundum, cordierite–sekaninaite, sanidine, spinel, magnesioferrite, arsenopyrite, pyrite, pyrrhotite, chlorites, diopside, richterite, ferrisepiolite, plagioclase, phlogopite, ilmenite, calcite, ankerite, dolomite, siderite, wollastonite, gyrolite, tobermorite, jennite, fluorapophyllite-(K), stilbite-Na, titanite, chlorapatite and graphite (e.g. Ďuďa *et al.*, 1981, 1993, 2001;

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Košuth, 1999; Košuth and Marcinčáková, 2010; Marcinčáková and Košuth, 2011; Myšlan et al., 2018).

Fluorapophyllite-(NH₄) occurs in cavities of a quartz–illite–saponite–tobelite xenolith embedded in pyroxene andesite. The xenolith containing the holotype specimens was 35 cm × 20 cm × 12 cm with an irregular shape. Minerals associated with fluorapophyllite-(NH₄) are calcite, tridymite, pyrite, chabazite-Ca and heulandite-Ca. Fluorapophyllite-(NH₄) is a hydrothermal mineral, which was formed at the late stage of an (auto)-hydrothermal alteration of the xenoliths together with calcite and zeolites. The protolith of the xenolith was a basement sedimentary rock (most probably from the underlying Neogene evaporite sequences), which contained minor amounts of NH₄.

Physical and optical properties

Fluorapophyllite-(NH₄) occurs as clusters or crystalline crusts consisting of individual, well developed crystals up to 4 mm in size (Figs 1, 2) on the surface of the cavities, which occurs mostly in the central part of the xenolith. Crystals of fluorapophyllite-(NH₄) are mostly prismatic with pyramidal or flat terminations, with the crystals forms: {110}, {101} and {001}. Individual crystals are frequently grouped in aggregates or hypo-parallel groups. Fluorapophyllite-(NH₄) is colourless to light pink, translucent, with a white streak, a vitreous to pearly lustre and it is non-fluorescent in shortwave and longwave ultraviolet light. The Mohs hardness is estimated at ~4½ to 5 based on scratch tests and by analogy to other apophyllite-group minerals. Fluorapophyllite-(NH₄) crystals show perfect cleavage on {001} and are brittle; fracture is irregular. A density of 2.325 g cm⁻³ was calculated using the empirical formula and unit-cell volume refined from single-crystal X-ray diffraction (SCXRD) data. Fluorapophyllite-(NH₄) is uniaxial (+) with refractive indices ($\lambda = 589$ nm) $\omega = 1.5414(5)$ and $\epsilon = 1.5393(8)$ without apparent pleochroism. The Gladstone–Dale compatibility (Mandarino, 2007), $1 - (K_p/K_c)$ is 0.000 (superior) using the ideal formula, and -0.005 (superior) using the empirical formula.

Raman and infrared spectroscopy

The Raman spectrum of fluorapophyllite-(NH₄) (Fig. 3) was collected in the range 4000–40 cm⁻¹ using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal



Fig. 1. Clusters of pinkish crystals of fluorapophyllite-(NH₄) from the Vechec quarry. Field of view is 14 mm. Photo: Pavel Škácha, specimen in private collection.



Fig. 2. Pyramidal crystal of fluorapophyllite-(NH₄) associated with calcite. Field of view is 6.2 mm. Photo: Pavel Škácha, specimen in private collection.

Olympus microscope. The Raman signal was excited by an unpolarised red 633 nm He–Ne gas laser and detected by a CCD detector. The experimental parameters were: 100× objective, 60 s exposure time, 100 exposures, 50 μm pinhole spectrograph aperture and 8 mW laser power level. The spectra were repeatedly acquired from different grains in order to obtain a representative spectrum with the best signal-to-noise ratio. The eventual thermal damage of the measured point was excluded by visual inspection of the excited surface after measurement, by observation of possible decay of spectral features in the start of excitation and checking for thermal downshift of Raman lines. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser-frequency calibration) and standardised white-light sources (intensity calibration). Spectral manipulations were performed using the *Omnisc 9* software (Thermo Scientific).

The main bands observed are (in wavenumbers): 3565, 3556, 3540, 3204, 3119, 3034, 1689, 1462, 1114, 1059, 1008, 854, 792, 763, 662, 586, 551, 486, 431, 373, 340, 321, 300, 271, 229, 208, 165, 141, 108, 91 and 54 cm⁻¹. The presence of the ammonium cation is shown by a weak band at 1462 cm⁻¹ (bending vibrations of NH₄). The N–H stretching vibrations together with the O–H stretching vibrations of H₂O molecules were observed in the range 3600–2800 cm⁻¹. A weak band at 1689 cm⁻¹ is connected with ν_2 (δ) H₂O-bending vibrations of hydrogen-bonded water molecules. The complex bands below 1200 cm⁻¹ are attributed to ν (Si–O) vibrations, libration and translation modes of water molecules, Ca²⁺ translation modes and framework vibrations and their assignment is not unambiguous (Adams et al., 1981).

The infrared (IR) vibrational spectrum of fluorapophyllite-(NH₄) was recorded by the attenuated total reflection (ATR) method with a diamond cell on a Nicolet iS5 spectrometer. Spectra over the 4000–400 cm⁻¹ range were obtained by the co-addition of 64 scans with a resolution 4 cm⁻¹ and a mirror velocity of 0.4747 cm/s. Spectra were co-added to improve the signal-to-noise ratio.

The main bands in the infrared spectrum of fluorapophyllite-(NH₄) from the Vechec quarry are indicated in Fig. 4. The presence of an (NH₄) group in fluorapophyllite-(NH₄) is confirmed by a distinct band at 1464 cm⁻¹ with a shoulder at 1440 cm⁻¹ connected with bending vibrations of the ammonium cation. The possible representation of N–H stretching vibrations in the range 3300–3100 cm⁻¹ is overlapped by O–H stretching vibrations of H₂O molecules observed

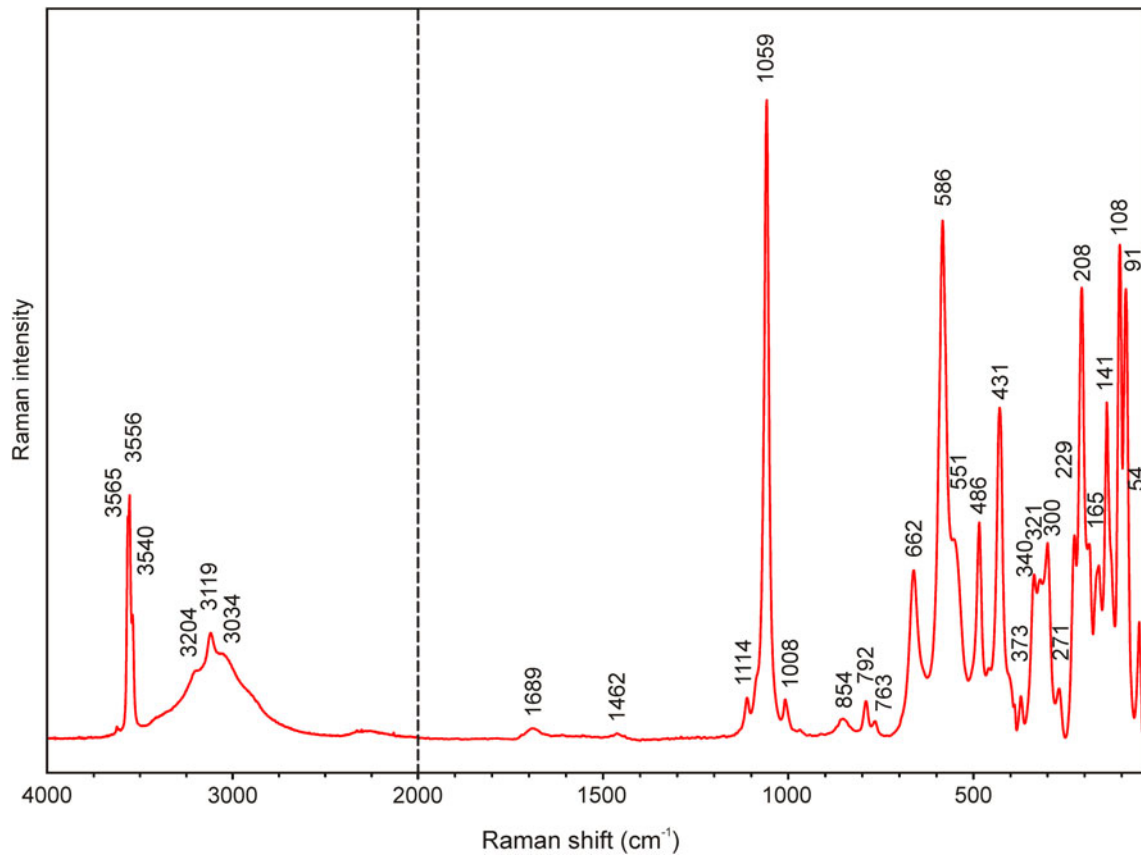


Fig. 3. Raman spectrum of fluorapophyllite-(NH₄) from the Vehec quarry, full range (split at 2000 cm⁻¹).

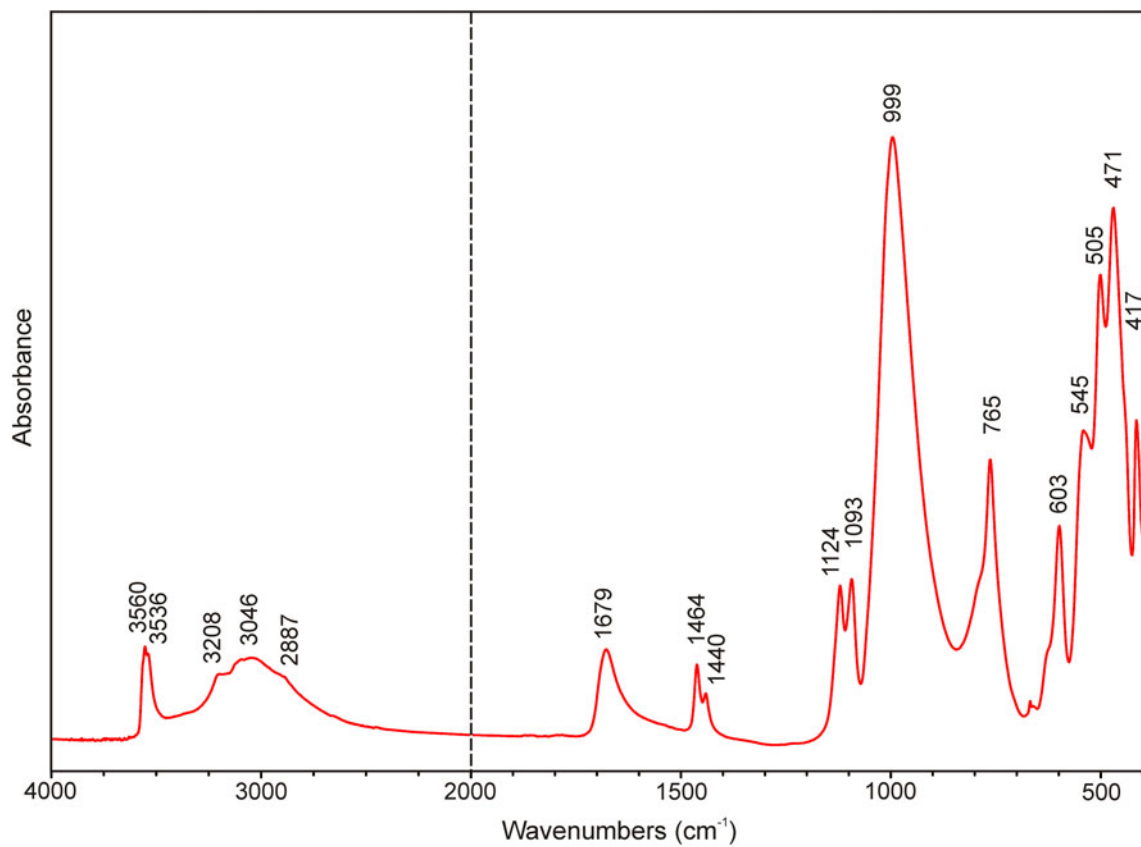


Fig. 4. Infrared spectrum of fluorapophyllite-(NH₄) from the Vehec quarry, full range (split at 2000 cm⁻¹).

in the range 3600–2800 cm⁻¹. A band at 1679 cm⁻¹ is connected with $\nu_2(\delta)$ H₂O bending vibrations of hydrogen-bonded water molecules. The bands below 1200 cm⁻¹ are attributed to ν (Si–O) vibrations, libration and translation modes of water molecules, Ca²⁺ translation modes and framework vibrations and their assignment is not unambiguous (Adams *et al.*, 1981).

Chemical composition

Quantitative chemical analyses (11 points) of fluorapophyllite-(NH₄) were performed at the Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic on the Cameca SX100 electron microprobe (EMPA) equipped with five wavelength-dispersive spectrometers (WDS). Analytical conditions were the following: 15 kV accelerating voltage, 5 nA beam current, 10 μ m beam diameter and WDS mode. Concentrations of other measured elements (Al, Ba, Cl, Cs, Fe, Mn, P, Rb, S and Sr) were below detection limits (*ca.* 0.03 to 0.05 wt.%). Raw X-ray intensities were corrected for matrix effects with a $\varphi(\rho z)$ algorithm (Pouchou and Pichoir, 1991). Due to the limited amount of material available, the H₂O content was not measured directly and is instead calculated by stoichiometry with respect to the crystal structure; the presence of water was also confirmed by spectroscopic (Raman and infrared) study. Analytical data for fluorapophyllite-(NH₄) as well as standards used are given in Table 1.

The empirical formula of fluorapophyllite-(NH₄) based on 29 O + F atoms per formula unit (apfu) is [(NH₄)_{0.55}K_{0.32}Na_{0.07}Ca_{0.06}] $\Sigma_{1.00}$ (Ca_{4.01}Mg_{0.02}) $\Sigma_{4.03}$ Si_{7.97}O₂₀[F_{0.84}(OH)_{0.16}] $\Sigma_{1.00}$ ·8H₂O. The ideal formula is NH₄Ca₄(Si₈O₂₀)F·8H₂O, which requires (NH₄)₂O 2.94, CaO 25.31, SiO₂ 54.24, F 2.14, H₂O 16.27, total 100 wt.%. Some of the studied crystal fragments of fluorapophyllite-(NH₄) from the Večec quarry show a wide range of NH₄–K (Fig. 5) and F–OH (Fig. 6) substitutions. Importantly, in the fragment used for the SCXRD study, the NH₄ content (0.50–0.59 apfu) clearly predominates over the K content (0.28–0.42 apfu) with an associated significant F content (0.80–0.95 apfu), which is consistent with the resulting crystal chemical formula.

X-ray crystallography and structure refinement

Powder X-ray diffraction data of fluorapophyllite-(NH₄) were recorded using a Bruker D8 Advance diffractometer equipped with a solid-state LynxEye detector and secondary monochromator producing CuK α radiation housed at the Department of Mineralogy and Petrology, National Museum, Prague, Czech Republic. The instrument was operating at 40 kV and 40 mA.

Table 1. Chemical composition (in wt.%) of fluorapophyllite-(NH₄).

Constituent	Mean	Range	S.D.	Standard
Na ₂ O	0.23	0.00–1.01	0.31	Albite
K ₂ O	1.67	1.48–2.14	0.19	Sanidine
(NH ₄) ₂ O	1.62	1.48–1.76	0.08	BN
CaO	25.74	25.16–26.11	0.29	Wollastonite
MgO	0.11	0.00–0.35	0.14	Diopside
SiO ₂	53.97	52.44–55.31	0.77	Sanidine
F	1.80	1.72–1.99	0.08	LiF
H ₂ O*	16.41			
O = F ₂	–0.76			
Total	100.79			

H₂O* – calculated on the basis 8 H₂O and F + OH = 1 apfu
S.D. = standard deviation

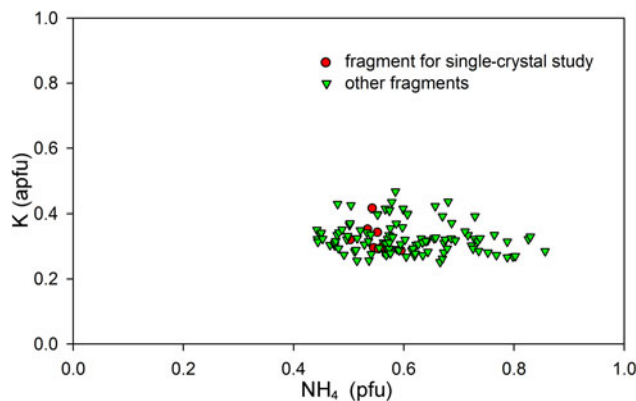


Fig. 5. The NH₄ (pfu) vs. K (apfu) plot for studied fluorapophyllite-(NH₄) from the Večec quarry.

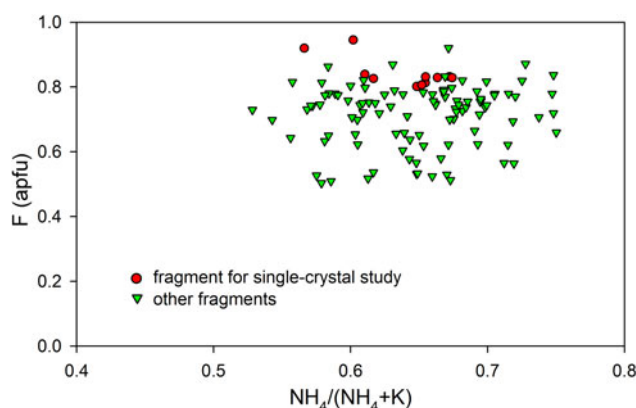


Fig. 6. The NH₄/(NH₄+K) vs. F (apfu) plot for studied fluorapophyllite-(NH₄) from the Večec quarry.

Table 2. Powder X-ray diffraction data of fluorapophyllite-(NH₄) from the Večec quarry; the seven strongest diffractions are reported in bold.

l_{meas}	d_{meas}	d_{calc}	$h k l$
31.5	7.897	7.900	0 0 2
12.8	7.812	7.815	1 0 1
2.0	6.355	6.358	1 1 0
13.9	4.547	4.545	1 0 3
4.1	4.494	4.496	2 0 0
100.0	3.946	3.950	0 0 4
3.7	3.895	3.897	2 1 1
8.7	3.583	3.584	2 1 2
6.6	3.357	3.355	1 1 4
7.0	3.178	3.179	2 2 0
38.6	2.985	2.981	1 0 5
1.6	2.946	2.945	3 0 1
1.0	2.818	2.818	2 1 4
7.4	2.501	2.502	3 1 3
11.0	2.4841	2.4847	2 1 5
3.2	2.4339	2.4330	1 1 6
1.3	2.2041	2.2030	2 1 6
0.9	2.1877	2.1893	1 0 7
4.3	2.1140	2.1137	3 1 5
1.2	2.1096	2.1088	3 2 4
10.4	2.0105	2.0106	4 2 0
2.0	1.7670	1.7679	3 1 7
4.6	1.7247	1.7231	1 0 9
12.4	1.5788	1.5801	0 0 10
0.9	1.5493	1.5483	3 2 8
0.8	1.4933	1.4938	3 1 9

Table 3. Data collection and structure refinement details for fluorapophyllite-(NH₄).

Crystal data	
Formula	[(NH ₄) _{0.656} K _{0.344}] _{Σ1.00} [Ca _{3.956} Mg _{0.044}] _{Σ4.00} (Si ₈ O ₂₀)F·8H ₂ O
Crystal size (μm)	90 × 68 × 90
Crystal system, space group	Tetragonal, <i>P4/mnc</i>
Temperature (K)	297
Unit-cell dimensions (Å)	<i>a</i> = 8.99336(9), <i>c</i> = 15.7910(3)
<i>V</i> (Å ³)	1277.18(3)
<i>Z</i>	2
Density (for above formula) (g cm ⁻³)	2.314
Absorption coefficient (mm ⁻¹)	1.43
Data collection	
Diffractometer	Rigaku SuperNova with Atlas S2 CCD
X-ray radiation/power	MoKα (λ = 0.71075 Å)/40 kV, 30 mA
<i>F</i> (000)	907
θ range (°)	3.20 to 28.45
Reflections collected/unique	14709/816; <i>R</i> _{int} = 0.037
Reflections with <i>I</i> > 3σ	743
Completeness to θ = 28.20°	98.0%
Index ranges	-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -20 ≤ <i>l</i> ≤ 19
Refinement	
Refinement method	Full-matrix least-squares on <i>F</i> ²
Param./restraints/constraints	58/3/12
GoF	1.84
Final <i>R</i> indices [<i>I</i> > 3σ]	<i>R</i> = 0.0299, <i>wR</i> = 0.0918
<i>R</i> indices (all data)	<i>R</i> = 0.0365, <i>wR</i> = 0.0957
Weighting scheme	based on measured s.u.'s; <i>w</i> = 1/(σ ² (<i>I</i>) + 0.0012959999/ <i>I</i> ²)
Δρ _{max} , Δρ _{min} (e ⁻ Å ⁻³)	+1.94/-0.97

In order to minimise background, powder samples were placed on the surface of a flat silicon wafer. Powder patterns were collected in Bragg-Brentano geometry in the range 3–75°2θ CuKα, with 0.01° step and counting time of 30 s per step (total duration of experiment was ca. 3 days). The positions and intensities of diffractions were found and refined using the Pearson VII profile-shape function of the ZDS program package (Ondruš, 1993) and the unit-cell parameters were refined by the least-squares program of Burnham (1962). The powder X-ray diffraction data of fluorapophyllite-(NH₄) presented in Table 2 show good agreement with the pattern calculated from the structure determination. Unit-cell parameters of fluorapophyllite-(NH₄) refined for the tetragonal space group *P4/mnc* are: *a* = 8.992(2) Å, *c* = 15.800(3) Å, *V* = 1277.5(6) Å³ and *Z* = 2.

Single-crystal X-ray studies of fluorapophyllite-(NH₄) were carried out using a Rigaku SuperNova single-crystal diffractometer with an Atlas S2 CCD detector and monochromatised

Table 5. Selected interatomic distances (in Å) in the structure of fluorapophyllite-(NH₄).

Ca/Mg–F	2.4185(6)	Si–O1	1.6206(16)
Ca/Mg–O3	2.3899(18)	Si–O2	1.6388(19)
Ca/Mg–O3 ⁱⁱ	2.4014(18)	Si–O3 ⁱⁱⁱ	1.6272(19)
Ca/Mg–O3 ^v	2.3899(18)	Si–O3	1.5842(17)
Ca/Mg–O3 ^{vii}	2.4014(18)	<Si–O>	1.618
Ca/Mg–O4	2.4875(18)		
Ca/Mg–O4 ^v	2.4875(18)	K1–O4	3.0052(18) × 8
<Ca/Mg–φ>	2.425		

<i>D</i> –H... <i>A</i>	<i>D</i> –H (Å)	H... <i>A</i> (Å)	<i>D</i> ... <i>A</i> (Å)	∠ <i>DHA</i> (°)
O4–H1O4...O3 ^{xix}	0.920(18)	1.87(2)	2.764(3)	164(2)
O4–H2O4...O2 ^{xi}	0.936(16)	2.304(18)	3.180(2)	156(2)

Symmetry codes: (i) –*x*, –*y*, *z*; (ii) –*y*, *x*, *z*; (iii) *y*, –*x*, *z*; (iv) –*x*, –*y*, –*z*; (v) *x*, *y*, –*z*; (vi) *y*, –*x*, –*z*; (vii) –*y*, *x*, –*z*; (viii) –*y*+½, –*x*+½, –*z*+½; (ix) –*x*+½, *y*–½, *z*+½; (x) *y*, –*x*+1, *z*.
D – donor; *A* – acceptor

Table 6. Bond-valence analysis for fluorapophyllite-(NH₄)*.

	Ca/Mg	N/K	Si	H1O4	H2O4	Σ
O1			1.01 ^{x2→}			2.02
O2			0.96; 0.99		0.04	1.99
O3	(0.30; 0.30) ^{x21}		1.11	0.10		1.81
O4	0.24 ^{x21}	0.11 ^{x81}		1.00	1.00	2.35
F	0.28 ^{x4→}					1.12
Σ	1.96	0.88	4.07	1.10	1.04	

*All values in valence units; bond-valence parameters used: Ca²⁺–O, Mg²⁺–O, K⁺–O, Si⁴⁺–O and H⁺–O from Gagné and Hawthorne (2015), NH₄⁺–O from Garcia-Rodriguez *et al.* (2000), Mg²⁺–F from Brown and Altermatt (1985)

MoKα radiation from the microfocus X-ray tube. The fragment investigated by single-crystal X-ray studies was separated from a polished section of an aggregate pre-analysed by means of electron microprobe. The *CrysAlis Pro* software package was used for processing the structure data. The empirical absorption correction (multi-scan) was applied to the data in *CrysAlis* during the data reduction process. The *Jana2006* program (Petříček *et al.*, 2014) was used for the refinement of the structure retrieved from the diffraction data using the *SHELXT* program (Sheldrick, 2015). All non-hydrogen atoms were refined with anisotropic displacement parameters while the water molecule H atoms (as located in difference-Fourier maps) were refined using a riding model with soft restraints on the O–H distances and with *U*_{iso} values set at 1.2× the *U*_{eq} of the bonded O atom (O4). Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, respectively, and

Table 4. Atom coordinates, displacement parameters (Å²) and occupation factors for the structure of fluorapophyllite-(NH₄).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}	Occupancy	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ¹²	<i>U</i> ¹³	<i>U</i> ²³
F	0	0	0	0.0163(8)		0.0099(11)	0.0099(11)	0.029(2)	0	0	0
N1/K1	0	0	½	0.02 [#]	0.656(6)/0.344(6)	0.02	0.02	0.02	0	0	0
Ca/Mg	0.10851(7)	0.24605(7)	0	0.0087(2)	0.989(11)/0.011(11)	0.0087(4)	0.0095(4)	0.0080(4)	0.0009(2)	0	0
Si	0.22506(6)	0.08732(6)	0.18999(4)	0.0069(2)		0.0069(3)	0.0067(3)	0.0071(4)	–0.00028(19)	–0.0011(2)	–0.0008(2)
O1	0.36230(16)	0.13769(16)	¼	0.0095(4)		0.0094(6)	0.0094(6)	0.0098(10)	–0.0005(7)	–0.0024(6)	–0.0024(6)
O2	0.08336(16)	0.19015(17)	0.21767(11)	0.0134(5)		0.0089(7)	0.0134(8)	0.0178(9)	0.0029(6)	–0.0012(6)	–0.0025(6)
O3	0.26281(17)	0.10287(17)	0.09236(10)	0.0122(5)		0.0146(8)	0.0135(8)	0.0085(8)	0.0001(6)	–0.0009(6)	–0.0003(5)
O4	0.210(2)	0.4491(2)	0.09004(11)	0.0232(5)		0.0361(11)	0.0151(9)	0.0184(9)	0.0000(8)	–0.0005(8)	–0.0043(7)
H1O4	0.193(3)	0.5499(19)	0.0913(14)	0.0279 [*]							
H2O4	0.214(3)	0.421(2)	0.1474(11)	0.0279 [*]							

constrained to 0.02 Å².

Table 7. Comparison of the physical properties for a valid members of the apophyllite group.

Mineral	Fluorapophyllite-(NH ₄)	Fluorapophyllite-(K)	Fluorapophyllite-(Na)	Fluorapophyllite-(Cs)	Hydroxyapophyllite-(K)
Formula	NH ₄ Ca ₄ Si ₈ O ₂₀ F·8H ₂ O	KCa ₄ Si ₈ O ₂₀ F·8H ₂ O	NaCa ₄ Si ₈ O ₂₀ F·8H ₂ O	CsCa ₄ Si ₈ O ₂₀ F·8H ₂ O	KCa ₄ Si ₈ O ₂₀ (OH)·8H ₂ O
Crystal system	Tetragonal	Tetragonal	Orthorhombic	Tetragonal	Tetragonal
Space group	<i>P4/mnc</i>	<i>P4/mnc</i>	<i>Pnmm</i>	<i>P4/mnc</i>	<i>P4/mnc</i>
<i>a</i>	8.99336(9)	8.963-8.970	8.875(4)	9.060(6)	8.978(3)
<i>b</i>			8.881(6)		
<i>c</i>	15.7910(3)	15.767-15.804	15.79(1)	15.741(11)	15.83(1)
<i>V</i>	1277.18(3)	1267-1271	1236.9	1292.1	1276
<i>Z</i>	2	2	2	2	2
Optical data	Uniaxial (+) ω = 1.5414(5) ε = 1.5393(8)	Uniaxial (+) ω = 1.530-1.536 ε = 1.532-1.538	Biaxial (-) α = 1.536(2) β = 1.538(2) γ = 1.544(2)	Uniaxial	Uniaxial (+) ω = 1.543 ε = 1.542
Data source	[1]	[2], [3], [4], [5]	[6]	[7]	[8]

References: [1] this work; [2] Chao (1971); [3] Ståhl *et al.* (1987); [4] Marriner *et al.* (1990); [5] Anthony *et al.* (1995); [6] Matsueda *et al.* (1981); [7] Agakhanov *et al.* (2019); [8] Dunn *et al.* (1978).

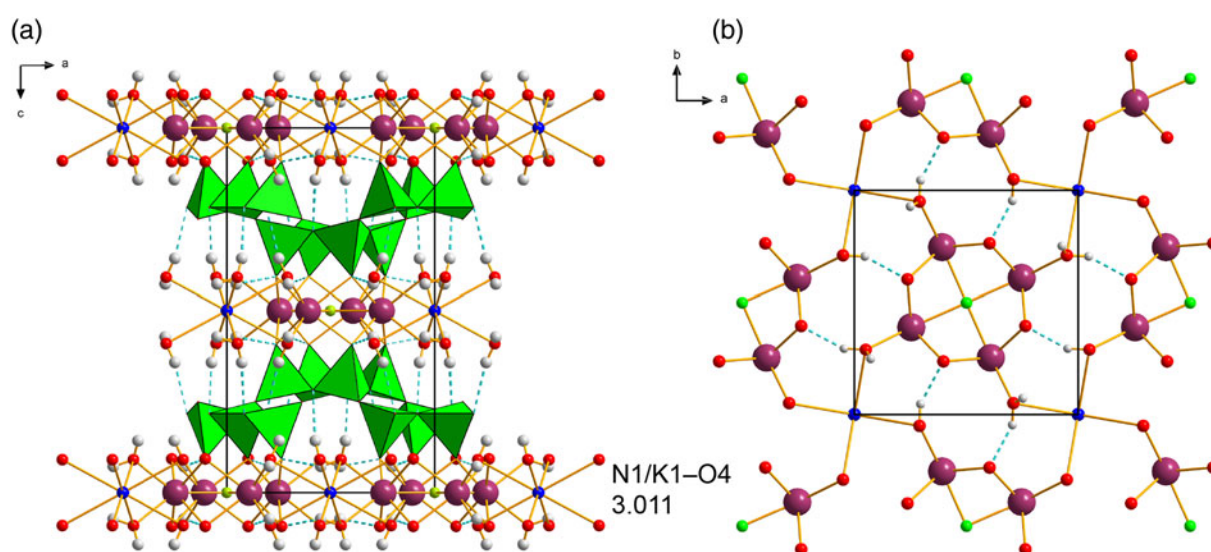


Fig. 7. Crystal structure of fluorapophyllite-(NH₄) (a) viewed down **b**, and (b) down **c** showing the coordination of interlayer cations and part of hydrogen bonding network. Si tetrahedra are green, Ca atoms plum, N1/K1 site dark blue, F atoms are light green (located at the origin), O atoms are red, H atoms are grey and corresponding H-bonds (emanating from molecular H₂O) are displayed as blue dashed lines. Unit-cell edges are outlined by black lines; interatomic distance is given in Å.

selected bond distances in Table 5. Results of bond-valence analysis are given in Table 6. The crystallographic information files have been deposited with the Principal Editor of Mineralogical Magazine and are available as Supplementary material (see below).

The SCXRD study of fluorapophyllite-(NH₄) shows it to be isostructural with fluorapophyllite-(K) (Stahl, 1993), but with the mineral defining 8-coordinate cation site now occupied predominantly by NH₄⁺. Given the significantly mixed nature of this site as indicated by the EMPA, refinement of the site scattering based on N and K (as a proxy for the non-ammonium content) was considered appropriate and confirmed the predominance of NH₄ over (significant) K, while still allowing for the minor amounts of Na and Ca, and was in good agreement with the EMPA. The structure of fluorapophyllite-(NH₄) is displayed in Fig. 7. The site occupied by K⁺ in fluorapophyllite-K was found to be occupied by nitrogen and therefore refined as a mixed site. The site-scattering refinement confirmed the predominance of N over K at the site.

Unfortunately, it was not possible to localise H atoms associated with the NH₄ moiety from the difference-Fourier maps, probably due to some degree of freedom (rotation) of NH₄ in the structure, bonded by the relatively weak H bonds (corresponding Donor...Acceptor distance, N...O, ~3 Å).

Relationship to the known species

Fluorapophyllite-(NH₄), NH₄Ca₄(Si₈O₂₀)F·8H₂O, is the NH₄ dominant analogue of fluorapophyllite-(K), KCa₄Si₈O₂₀F·8H₂O, fluorapophyllite-(Na), NaCa₄Si₈O₂₀F·8H₂O and fluorapophyllite-(Cs), CsCa₄Si₈O₂₀F·8H₂O, and belongs to the apophyllite group (Dunn and Wilson, 1978; Dunn *et al.*, 1978; Hatert *et al.*, 2013; Agakhanov *et al.*, 2019). Marriner *et al.* (1990) discussed the existence of an NH₄-enriched variety ('ammonian apophyllite') of fluorapophyllite-(K) in samples from Mexico, with up to 25% of stoichiometric K⁺ replaced by NH₄⁺. A comparison of the physical properties of valid mineral species of the apophyllite group is shown in Table 7.

In the Nickel–Strunz classification system Fluorapophyllite-(NH₄) fits in subdivision 9.EA.15 (Phyllosilicates with single nets of tetrahedra with 4-, 5-, (6-), and 8-membered rings.

Supplementary material. To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2020.44>

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