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## FLUORAPOPHYLLITE-(Cs), CsCa<sub>4</sub>(Si<sub>8</sub>O<sub>20</sub>)F(H<sub>2</sub>O)<sub>8</sub>, A NEW APOPHYLLITE-GROUP MINERAL FROM THE DARAI-PIOZ MASSIF, TIEN-SHAN, NORTHERN TAJIKISTAN --Manuscript Draft--

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<b>Article Type:</b>	Regular
<b>Abstract:</b>	<p>Fluorapophyllite-(Cs) (IMA 2018-108a), ideally CsCa<sub>4</sub>(Si<sub>8</sub>O<sub>20</sub>)F(H<sub>2</sub>O)<sub>8</sub>, is an apophyllite-group mineral from the moraine of the Darai-Pioz glacier, Tien-Shan, Northern Tajikistan. Associated minerals are quartz, pectolite, baratovite, aegirine, leucosphenite, pyrochlore, neptunite, fluorapophyllite-(K), reedmergnerite.</p> <p>Fluorapophyllite-(Cs) is a hydrothermal mineral. It is colourless, it has a vitreous luster and a white streak. Cleavage is perfect, it is brittle and has a stepped fracture. Mohs hardness is 4.5–5. D<sub>meas.</sub> = 2.54(2) g/cm<sup>3</sup>, D<sub>calc.</sub> = 2.513 g/cm<sup>3</sup>. Fluorapophyllite-(Cs) is uniaxial (+) with refractive indices (λ = 589 nm) ω = 1.540(2), ε = 1.544(2). It is non-pleochroic. Chemical analysis by electron microprobe gave SiO<sub>2</sub> 48.78, Al<sub>2</sub>O<sub>3</sub> 0.05, CaO 22.69, Cs<sub>2</sub>O 10.71, K<sub>2</sub>O 1.13, Na<sub>2</sub>O 0.04, F 1.86, H<sub>2</sub>O<sub>calc.</sub> 14.61, –O=F<sub>2</sub> –0.78, sum 99.09 wt.%, H<sub>2</sub>O was calculated from crystal-structure analysis. The empirical formula based on 29 (O + F) apfu, H<sub>2</sub>O = 8 pfu, is (Cs<sub>0.75</sub>K<sub>0.24</sub>)Σ<sub>0.99</sub>(Ca<sub>3.99</sub>Na<sub>0.01</sub>)Σ<sub>4</sub>(Si<sub>8.01</sub>Al<sub>0.01</sub>)Σ<sub>8.02</sub>O<sub>20.03</sub>F<sub>0.97</sub>(H<sub>2</sub>O)<sub>8</sub>, Z = 2. The simplified formula is (Cs,K)(Ca,Na)<sub>4</sub>(Si,Al)<sub>8</sub>O<sub>20</sub>F(H<sub>2</sub>O)<sub>8</sub>. Fluorapophyllite-(Cs) is tetragonal, space group P4/mnc, a 9.060(6), c 15.741(11) Å, V 1292.10(19) Å<sup>3</sup>. The crystal structure has been refined to R<sub>1</sub> = 4.31% based on 498 unique (Fo &gt; 4σF) reflections. In the crystal structure of fluorapophyllite-(Cs), there is one [4]T site occupied solely by Si, &lt;T–O&gt; = 1.615 Å. SiO<sub>4</sub> tetrahedra link to form a (Si<sub>8</sub>O<sub>20</sub>)<sub>8</sub>-sheet perpendicular to [001]. Between the Si–O sheets, there are two cation sites: A and B. The A site is coordinated by eight H<sub>2</sub>O groups [O(4) site], A–O(4) = 3.152(4) Å; the A site contains Cs<sub>0.75</sub>K<sub>0.24</sub>o<sub>0.01</sub>, ideally Cs apfu. The Cs–O bondlength of 3.152 Å is definitely larger than the K–O bondlength of 2.966–2.971 Å in fluorapophyllite-(K), KCa<sub>4</sub>(Si<sub>8</sub>O<sub>20</sub>)F(H<sub>2</sub>O)<sub>8</sub>. The [7]B site contains Ca<sub>3.99</sub>Na<sub>0.01</sub>, ideally Ca<sub>4</sub> apfu; &lt;B–φ&gt; = 2.420 Å (φ = O, F, H<sub>2</sub>O). The Si–O sheets connect via A and B polyhedra and hydrogen bonding; two H atoms have been included in the refinement. Fluorapophyllite-(Cs) is isostructural with fluorapophyllite-(K). Fluorapophyllite-(Cs) is a</p>

	Cs-analogue of fluorapophyllite-(K).
<b>Keywords:</b>	fluorapophyllite-(Cs); new mineral; apophyllite group; Darai Pioz, Tien Shan, Northern Tajikistan; electron microprobe analysis; crystal structure
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Dear Lee:

I am returning the revised manuscript No. CANMIN-D-19-00038:  
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MINERAL FROM THE DARAI-PIOZ MASSIF, TIEN-SHAN, NORTHERN TAJIKISTAN".

We found comments and suggestions made by Associate Editor James Evans and an anonymous reviewer constructive and corrected the manuscript accordingly.

Best Regards,

A handwritten signature in black ink that reads "E. Sokolova".

Elena Sokolova,  
Professor, Mineralogy

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## ABSTRACT

Fluorapophyllite-(Cs) (IMA 2018-108a), ideally  $\text{CsCa}_4(\text{Si}_8\text{O}_{20})\text{F}(\text{H}_2\text{O})_8$ , is an apophyllite-group mineral from the moraine of the Darai-Pioz glacier, Tien-Shan, Northern Tajikistan. Associated minerals are quartz, pectolite, baratovite, aegirine, leucosphenite, pyrochlore, neptunite, fluorapophyllite-(K), reedmergnerite. Fluorapophyllite-(Cs) is a hydrothermal mineral. It is colourless, it has a vitreous luster and a white streak. Cleavage is perfect, it is brittle and has a stepped fracture. Mohs hardness is 4.5–5.  $D_{\text{meas.}} = 2.54(2) \text{ g/cm}^3$ ,  $D_{\text{calc.}} = 2.513 \text{ g/cm}^3$ . Fluorapophyllite-(Cs) is uniaxial (+) with refractive indices ( $\lambda = 589 \text{ nm}$ )  $\omega = 1.540(2)$ ,  $\varepsilon = 1.544(2)$ . It is non-pleochroic. Chemical analysis by electron microprobe gave  $\text{SiO}_2$  48.78,  $\text{Al}_2\text{O}_3$  0.05,  $\text{CaO}$  22.69,  $\text{Cs}_2\text{O}$  10.71,  $\text{K}_2\text{O}$  1.13,  $\text{Na}_2\text{O}$  0.04,  $\text{F}$  1.86,  $\text{H}_2\text{O}_{\text{calc.}}$  14.61,  $-\text{O}=\text{F}_2$   $-0.78$ , sum 99.09 wt.%,  $\text{H}_2\text{O}$  was calculated from crystal-structure analysis. The empirical formula based on 29 (O + F) *apfu*,  $\text{H}_2\text{O} = 8$  *pfu*, is  $(\text{Cs}_{0.75}\text{K}_{0.24})_{\Sigma 0.99}(\text{Ca}_{3.99}\text{Na}_{0.01})_{\Sigma 4}(\text{Si}_{8.01}\text{Al}_{0.01})_{\Sigma 8.02}\text{O}_{20.03}\text{F}_{0.97}(\text{H}_2\text{O})_8$ ,  $Z = 2$ . The simplified formula is  $(\text{Cs},\text{K})(\text{Ca},\text{Na})_4(\text{Si},\text{Al})_8\text{O}_{20}\text{F}(\text{H}_2\text{O})_8$ . Fluorapophyllite-(Cs) is tetragonal, space group *P4/mnc*,  $a$  9.060(6),  $c$  15.741(11) Å,  $V$  1292.10(19) Å<sup>3</sup>. The crystal structure has been refined to  $R_1 = 4.31\%$  based on 498 unique ( $F_o > 4\sigma F$ ) reflections. In the crystal structure of fluorapophyllite-(Cs), there is one <sup>[4]</sup>T site occupied solely by Si,  $\langle \text{T}-\text{O} \rangle = 1.615$  Å.  $\text{SiO}_4$  tetrahedra link to form a  $(\text{Si}_8\text{O}_{20})^{8-}$  sheet perpendicular to [001]. Between the Si–O sheets, there are two cation sites: A and B. The A site is coordinated by eight  $\text{H}_2\text{O}$  groups [O(4) site],  $\text{A}-\text{O}(4) = 3.152(4)$  Å; the A site contains  $\text{Cs}_{0.75}\text{K}_{0.24}\square_{0.01}$ , ideally Cs *apfu*. The Cs–O bondlength of 3.152 Å is definitely larger than the K–O bondlength of 2.966–2.971 Å in fluorapophyllite-(K),  $\text{KCa}_4(\text{Si}_8\text{O}_{20})\text{F}(\text{H}_2\text{O})_8$ . The <sup>[7]</sup>B site contains  $\text{Ca}_{3.99}\text{Na}_{0.01}$ , ideally  $\text{Ca}_4$  *apfu*;  $\langle \text{B}-\varphi \rangle = 2.420$  Å ( $\varphi = \text{O}, \text{F}, \text{H}_2\text{O}$ ). The Si–O sheets connect via A and B polyhedra and hydrogen bonding; two H atoms have been included in the refinement. Fluorapophyllite-(Cs) is isostructural with fluorapophyllite-(K). Fluorapophyllite-(Cs) is a Cs-analogue of fluorapophyllite-(K).

**Keywords:** fluorapophyllite-(Cs), new mineral, apophyllite group, Darai-Pioz, Tien-Shan, Northern Tajikistan, electron microprobe analysis, crystal structure.

## INTRODUCTION

Fluorapophyllite-(Cs), ideally  $\text{CsCa}_4(\text{Si}_8\text{O}_{20})\text{F}(\text{H}_2\text{O})_8$ , is a new mineral of the apophyllite group (Dunn & Wilson 1978, Hatert *et al.* 2013) from the moraine of the Darai-Pioz glacier, Tien-Shan, Northern Tajikistan. This locality is well-known for Cs-bearing minerals. Fluorapophyllite-(Cs) is named in accord with the current nomenclature of the apophyllite-group minerals (Hatert *et al.* 2013). The new mineral species and its name were approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2018–108a). The holotype specimen of fluorapophyllite-(Cs) has been deposited in the collections of the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow, Russia, registration number 5280/1. Here we report the description and crystal structure of fluorapophyllite-(Cs), a new mineral.

## OCCURRENCE AND MINERAL ASSOCIATION

Fluorapophyllite-(Cs) was found at the moraine of the Darai-Pioz glacier (39° 30' N and 70° 40' E), the Alai mountain range, Tien-Shan, Rashtskii district, N. Tajikistan. The multiphase Darai-Pioz massif belongs to the Upper Paleozoic Alaysky (Matchaisky) intrusive complex. The area of outcrop of the massif is about 16 km<sup>2</sup>. Most of the massif rocks are covered by moraine or glaciers, and/or are difficult to access. In the north, the massif intrudes Silurian limestones and slates, and in the south, it intrudes terrigenous slates of Late Carboniferous age. The outer zone of the massif consists of subalkaline biotite granite, often tourmalinized (300–290 Ma), surrounding a discontinuous ring of biotite granites and granosyenites. The central part of massif comprises quartz and aegirine syenites. In the northeast part of the massif, there is a stock of cancrinite and nepheline foyaite (247±6 Ma). There are veins of syenite pegmatites and aegirine-potassium feldspar-quartz rocks containing polyolithionite (286±7 Ma) and rare-metal and boron mineralization. Veins of calcite carbonatites and syenite carbonatites (Faiziev *et al.* 2010) are widespread. Much of the rock is fenitized to different degrees. Detailed descriptions of the petrography and mineralogy of the Darai-Pioz massif can be found in Moskvina (1937), Dusmatov (1968, 1971), Semenov & Dusmatov (1975), Belakovskiy (1991) and Reguir *et al.* (1999).

This locality is known for Cs-bearing minerals. Kupletskite-(Cs) was the first Cs-bearing mineral described from Darai-Pioz (Yefimov *et al.* 1971, Cámara *et al.* 2010). In the last five years, five Cs-bearing minerals have been described from Darai-Pioz: odigitriaite,  $\text{CsNa}_5\text{Ca}_5[\text{Si}_{14}\text{B}_2\text{O}_{38}]\text{F}_2$  (IMA 2015-028, Agakhanov *et al.* 2017a); mendeleevite-(Nd),  $(\text{Cs}, \square)_6(\square, \text{Cs})_6(\square, \text{K})_6(\text{REE}, \text{Ca})_{30}(\text{Si}_{70}\text{O}_{175})(\text{OH}, \text{H}_2\text{O}, \text{F})_{35}$  (IMA 2015-031, Agakhanov *et al.* 2017b); two Cs-micas: garmite,  $\text{CsLiMg}_2(\text{Si}_4\text{O}_{10})\text{F}_2$  (IMA 2017-008, Pautov *et al.* 2017) and gorbunovite,  $\text{CsLi}_2(\text{Ti}, \text{Fe})(\text{Si}_4\text{O}_{10})(\text{F}, \text{OH}, \text{O})_2$  (IMA 2017-040, Agakhanov *et al.* 2017c); fluorapophyllite-(Cs),  $\text{CsCa}_4(\text{Si}_8\text{O}_{20})\text{F}(\text{H}_2\text{O})_8$  (IMA 2018-108a, this work).

Fluorapophyllite-(Cs) is a hydrothermal mineral. It was found in a quartz-pectolite aggregate in quartzolite boulders. Associated minerals are quartz, pectolite, baratovite, aegirine, leucosphenite, pyrochlore, neptunite, fluorapophyllite-(K) and reedmergnerite.

#### APPEARANCE AND PHYSICAL PROPERTIES

In the quartz-pectolite aggregate, fluorapophyllite-(Cs) occurs as separate grains up to 0.08 mm across (Fig. 1) and as zones in grains of fluorapophyllite-(K) (grains of fluorapophyllite-(K) are up to 0.2 mm across). Individual grains of fluorapophyllite-(Cs) are irregular in shape.

Fluorapophyllite-(Cs) is colourless, it has a vitreous luster and a white streak. Cleavage is perfect; it is brittle and has a stepped fracture. The microhardness of fluorapophyllite-(Cs) is  $\text{VHN}_{100} = 480$   $\text{kg}/\text{mm}^2$  (with the range of 468–502) which corresponds to a Mohs hardness of 4.5–5.  $D_{\text{meas.}} = 2.54(2)$   $\text{g}/\text{cm}^3$  as determined by floatation in Clerici liquid;  $D_{\text{calc.}} = 2.513$   $\text{g}/\text{cm}^3$  (from the empirical formula). Fluorapophyllite-(Cs) is uniaxial (+) with refractive indices ( $\lambda = 589$  nm)  $\omega = 1.540(2)$ ,  $\varepsilon = 1.544(2)$ . It is non-pleochroic. The compatibility index  $(1 - \text{Kp}/\text{Kc}) = -0.002$  (for  $D_{\text{calc.}}$ ) and 0.010 (for  $D_{\text{meas.}}$ ), and is rated as superior (Mandarino 1981).

#### CHEMICAL COMPOSITION

A grain of fluorapophyllite-(Cs) was analyzed with a JEOL 773 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 20 kV, a specimen current of 20 nA, and a

beam diameter of 3  $\mu\text{m}$ . The following standards were used: Si, Al, K: microcline USNM 143966; Na: omphacite USNM 110607; Ca: anorthite USNM 110607; Cs:  $\text{Cs}_2\text{Nb}_4\text{O}_{11}$ ; F: fluoro-phlogopite. The data were reduced and corrected by the *PAP* method of Pouchou & Pichoir (1985). Table 1 gives the chemical composition of fluorapophyllite-(Cs), (mean of 10 points). The empirical formula based on 29 (O + F) *apfu* ( $\text{H}_2\text{O} = 8$  *pfu* was calculated from crystal-structure refinement) is  $(\text{Cs}_{0.75}\text{K}_{0.24})_{\Sigma 0.99}(\text{Ca}_{3.99}\text{Na}_{0.01})_{\Sigma 4}(\text{Si}_{8.01}\text{Al}_{0.01})_{\Sigma 8.02}\text{O}_{20.03}\text{F}_{0.97}(\text{H}_2\text{O})_8$ ,  $Z = 2$ . The simplified formula is  $(\text{Cs},\text{K})(\text{Ca},\text{Na})_4(\text{Si},\text{Al})_8\text{O}_{20}\text{F}(\text{H}_2\text{O})_8$ . The ideal formula is  $\text{CsCa}_4\text{Si}_8\text{O}_{20}\text{F}(\text{H}_2\text{O})_8$  which requires  $\text{SiO}_2$  48.03,  $\text{CaO}$  22.41,  $\text{Cs}_2\text{O}$  14.07,  $\text{H}_2\text{O}$  14.40, F 1.90,  $-\text{O}=\text{F}_2$  -0.80 total 100 wt.%.

### DATA COLLECTION AND STRUCTURE REFINEMENT

Single-crystal X-ray data for fluorapophyllite-(Cs) were collected with a Bruker D8 QUEST ECO CMOS diffractometer equipped with a fine-focus tube ( $\text{MoK}\alpha$ ) and a PHOTON 50 detector. The crystal does not diffract very well and that is why we cut the data at  $2\Theta = 47.95^\circ$  (collected up to  $2\Theta = 60.00^\circ$ ). X-ray powder diffraction data were obtained by collapsing the experimental single-crystal data into two dimensions (Table 2). Unit-cell parameters from the single-crystal data were determined by least-squares refinement of 5962 reflections with  $I > 10\sigma I$  and are given in Table 3, together with miscellaneous information on data collection and structure refinement. For fluorapophyllite-(Cs), the intensities of 10527 reflections were measured using 60 s per  $0.5^\circ$  frame. An absorption correction was done using the SADABS program (Sheldrick 2015). All calculations were done with the Bruker SHELXTL-2014/3 (version 3) system of programs (Sheldrick 2015).

The crystal structure of fluorapophyllite-(Cs) was refined using the atom coordinates of fluorapophyllite-(K) (Stähl *et al.* 1987) as a starting model. The crystal structure of fluorapophyllite-(Cs) was refined to  $R_1 = 4.31\%$  based on 498 unique reflections with  $(F_o > 4\sigma F)$ . Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson 1992). Site-scattering values were refined for the A and B sites with the scattering curves of Cs and Ca, respectively. For the final refinement, the D(donor)–H(1,2) distances were softly constrained to 0.98 Å.



Final atom coordinates and anisotropic displacement parameters are listed in Table 4, selected interatomic distances and Si–O–Si angles are given in Table 5, refined site-scattering and assigned site-populations for selected cation and anion sites are given in Table 6, details of hydrogen bonding are given in Table 7 and bond-valence values in Table 8. A Crystallography Information File (CIF) may be obtained from The Depository of Unpublished Data on the MAC website [documents Fluorapophyllite-(Cs) CM\_XXX].

### STRUCTURE DESCRIPTION

In the crystal structure of fluorapophyllite-(Cs), there is one *T* site occupied solely by Si and tetrahedrally coordinated by O atoms,  $\langle T-O \rangle = 1.615 \text{ \AA}$ . SiO<sub>4</sub> tetrahedra link to form a (Si<sub>8</sub>O<sub>20</sub>)<sup>8-</sup> sheet perpendicular to [001]; in a sheet, SiO<sub>4</sub> tetrahedra form 4- and 8-membered rings (Fig. 2). Between the Si–O sheets, there are two cation sites: *A* and *B*. The Cs-dominant *A* site is coordinated by eight H<sub>2</sub>O groups [O(4) site], with A–O(4) = 3.152(4) Å (Table 5); the *A* site contains Cs<sub>0.75</sub>K<sub>0.24</sub>□<sub>0.01</sub>, ideally Cs<sub>1</sub> *apfu* (Table 6). The Cs–O bondlength of 3.152 Å is definitely larger than the K–O bondlength of 2.966–2.971 Å in fluorapophyllite-(K) (Table 9). The Ca-dominant <sup>[7]</sup>*B* site contains Ca<sub>3.99</sub>Na<sub>0.01</sub>, ideally Ca<sub>4</sub> *apfu*; the *B* site is coordinated by four O atoms, two H<sub>2</sub>O groups and one F atom, with  $\langle B-\varphi \rangle = 2.420 \text{ \AA}$  ( $\varphi = O, F, H_2O$ ) (Tables 5,6). The Si–O sheets connect via *A* and *B* polyhedra and hydrogen bonding (Fig. 2). The geometry of hydrogen bonding is in accord with the geometry of hydrogen bonding in fluorapophyllite-(K) (Chao 1971, Ståhl *et al.* 1987).

We write the ideal formula of fluorapophyllite-(Cs) as the sum of cation and anion sites (Table 6), CsCa<sub>4</sub>(Si<sub>8</sub>O<sub>20</sub>)F(H<sub>2</sub>O)<sub>8</sub>, *Z* = 2. Fluorapophyllite-(Cs) is isostructural with fluorapophyllite-(K) and is a Cs-analogue of fluorapophyllite-(K) (Table 9).

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## FIGURE CAPTIONS

Fig. 1. BSE image of fluorapophyllite-(Cs) (1) in quartz (2) - pectolite (3) aggregate.

Fig. 2. General view of the crystal structure of fluorapophyllite-(Cs). Si tetrahedra and Ca-dominant polyhedra are orange and pale blue; Cs atom (*A* site) is shown as a large pink sphere; F atom is shown as a small yellow sphere, O atom of the H<sub>2</sub>O group at the O(4) site is shown as a medium red sphere and H atoms as small gray spheres. Bonds O(4)–H and H-acceptor are shown as black solid and dashed lines, respectively. Thin black lines show the unit cell.

TABLE 1. CHEMICAL COMPOSITION AND UNIT FORMULA\* FOR FLUORAPOPHYLLITE-(Cs)

Constituent	wt. %	Range		<i>apfu</i>
SiO <sub>2</sub>	48.78	48.25–49.08	Si	8.01
Al <sub>2</sub> O <sub>3</sub>	0.05	0.00–0.12	Al	0.01
CaO	22.69	22.32–22.83	Ca	3.99
Cs <sub>2</sub> O	10.71	9.67–11.81	Cs	0.75
K <sub>2</sub> O	1.13	0.72–1.46	K	0.24
Na <sub>2</sub> O	0.04	0.00–0.09	Na	0.01
H <sub>2</sub> O	14.61**			
F	1.86	1.65–2.18	F	0.97
F=O	<u>-0.78</u>		H <sub>2</sub> O	8.00
Total	99.09			

\*formula unit calculated on 29 (O + F) *pfu*;

\*\*calculated from crystal-structure analysis: H<sub>2</sub>O = 8 *pfu*.

TABLE 2. X-RAY POWDER DIFFRACTION DATA\* FOR FLUORAPOPHYLLITE-(Cs)

$I_{\text{est.}}$	$d_{\text{calc}}(\text{\AA})$	$h$	$k$	$l$	$I_{\text{est.}}$	$d_{\text{calc}}(\text{\AA})$	$h$	$k$	$l$
100	7.8705	0	0	2		2.0259	4	2	0
	7.8522	1	0	1	14	1.9662	2	1	7
10	6.4064	1	1	0		1.9639	3	2	5
38	4.5405	1	0	3		1.9619	4	2	2
	4.5300	2	0	0	6	1.9185	4	1	4
100	3.9352	0	0	4	25	1.8012	4	2	4
	3.9261	2	0	2		1.8001	5	0	1
	3.9239	2	1	1		1.8001	4	3	1
55	3.6024	2	1	2	25	1.7700	2	1	8
28	3.3532	1	1	4		1.7689	3	1	7
24	3.2069	2	1	3		1.7658	4	3	2
	3.2032	2	2	0	13	1.7173	1	0	9
84	2.9738	1	0	5		1.7144	4	0	6
	2.9669	2	2	2		1.7127	5	0	3
	2.9659	3	0	1		1.7127	4	3	3
12	2.8650	3	1	0	10	1.6766	2	2	8
11	2.8229	2	1	4		1.6729	5	2	1
	2.8187	3	1	1	15	1.6220	3	1	8
37	2.6922	3	1	2		1.6194	5	1	4
73	2.5146	3	1	3	20	1.6058	2	1	9
71	2.4860	2	1	5		1.6035	4	2	6
	2.4842	2	2	4		1.6021	5	2	3
19	2.4278	1	1	6		1.6016	4	4	0
25	2.1825	1	0	7	13	1.5741	0	0	10
	2.1794	3	0	5		1.5704	5	0	5
	2.1767	4	0	2	16	1.5538	5	3	0
42	2.1189	3	1	5		1.5492	3	2	8
	2.1179	3	2	4		1.5470	5	2	4
14	2.0609	3	3	2	7	1.5135	3	0	9
45	2.0296	2	2	6		1.5100	6	0	0

\*Powder data were obtained by collapsing experimental single-crystal data into two dimensions. The most intense reflection (101) was covered by the beam stop. Therefore intensity of (101) was calculated from the refined crystal structure and all intensities rescaled accordingly. Reflections with  $I_{\text{est}} < 5$  are not listed.



TABLE 3. MISCELLANEOUS REFINEMENT DATA FOR FLUORAPOPHYLLITE-(Cs)

$a$ (Å)	9.060(6)
$c$	15.741(11)
$V$ (Å <sup>3</sup> )	1292.10(19)
Space group	$P4/mnc$
$Z$	2
Reflections ( $I > 10\sigma I$ )	5962
Absorption coefficient (mm <sup>-1</sup> )	2.41
$F(000)$	973.9
$D_{\text{calc.}}$ (g/cm <sup>3</sup> )	2.513
Crystal size (mm)	0.045 x 0.040 x 0.030
Radiation/monochromator	MoK $\alpha$ /graphite
2 $\theta$ -range for data collection (°)	60.00, 47.95*
$h^*$	$-10 \leq h \leq 10$
$k^*$	$-10 \leq k \leq 10$
$l^*$	$-18 \leq l \leq 18$
$R(\text{int})$	0.0564*
Reflections collected	10527*
Independent reflections	539*
$F_o > 4\sigma F$	498*
Refinement method	Full-matrix least squares on $F^2$ , fixed weights proportional to $1/\sigma F_o^2$
Final $R(\text{obs})$	
$R_1(F_o > 4\sigma F)$	0.0431
$R_1$	0.0487
$wR_2$	0.0851
Highest peak, deepest hole (e Å <sup>-3</sup> )	0.42, -0.52
Goodness of fit on $F^2$	1.276

\*structure refinement (see text).



TABLE 5. SELECTED INTERATOMIC DISTANCES (Å)  
AND ANGLES (°) FOR FLUOROAPOPHYLLITE-(Cs)

A–O(4) <sub>a</sub> x8	3.152(4)	T–O(3)	1.587(3)
		T–O(1)	1.616(2)
B–O(3) x4	2.395(3)	T–O(2) <sub>b</sub>	1.626(3)
B–F	2.415(2)	T–O(2)	1.631(3)
B–O(4) x2	2.473(4)	<T–O>	1.615
<B–φ>	2.420		
		T–O(1)–T <sub>c</sub>	141.5(3)
		T–O(2)–T <sub>c</sub>	140.1(2)
		<T–O–T>	140.8

\*φ = O, F, H<sub>2</sub>O.

Symmetry operators: a:  $-x+1/2, y-1/2, -z+1/2$ ;

b:  $y, -x, z$ ; c:  $-y, x, z$ .

TABLE 6. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR FLUOROAPOPHYLLITE-(Cs)

Site*	Refined site-scattering (epfu)	Site population (apfu)	Calculated site-scattering (epfu)	$\langle \text{Ct}-\phi \rangle_{\text{obs.}}$ (Å)*	Ideal composition (apfu)
Cations					
<sup>[8]</sup> A	45.0(3)	Cs <sub>0.75</sub> K <sub>0.24</sub> □ <sub>0.01</sub>	45.81	3.152	Cs
<sup>[7]</sup> B	80.0	Ca <sub>3.99</sub> Na <sub>0.01</sub>	79.91	2.420	Ca <sub>4</sub>
<sup>[4]</sup> T	112.0	Si <sub>8.00</sub>	112.00	1.615	Si <sub>8</sub>
Anions and H <sub>2</sub> O groups					
<sup>[2,2,4]</sup> O(1,2,3)		O <sub>20</sub>			O <sub>20</sub>
<sup>[4]</sup> F		F <sub>0.97</sub> □ <sub>0.03</sub>			F
O(4)		(H <sub>2</sub> O) <sub>8</sub>			(H <sub>2</sub> O) <sub>8</sub>

\*Ct = cation, φ = O, F, H<sub>2</sub>O.

TABLE 7. HYDROGEN BONDING IN FLUOROAPOPHYLLITE-(Cs)

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	∠DHA (°)	∠HDH (°)
O(4)-H(1)...O(2)a	0.98(1)	2.23(1)	3.186(5)	167(4)	111(4)
O(4)-H(1)...O(3)b	0.98(1)	1.81(1)	2.769(5)	167(4)	

a:  $x^{-1/2}$ ,  $-y+1/2$ ,  $z+1/2$ ; b:  $y$ ,  $-x+1$ ,  $z$ .

TABLE 8. BOND-VALENCE VALUES\* FOR FLUOROAPOPHYLLITE-(Cs)

Atom**	A	B	T	H(1)	H(2)	$\Sigma$
O(1)			1.02 <sup>x2→</sup>			2.04
O(2)			0.99 0.98	0.09		2.06
O(3)		0.30 <sup>x4↓ x2→</sup>	1.10		0.19	1.89
O(4)	0.14 <sup>x8↓</sup>	0.25 <sup>x2↓</sup>		0.91	0.81	2.11
F		0.23 <sup>x4→</sup>				0.92
$\Sigma$	1.10	1.93	4.09	1.00	1.00	

\* bond-valence parameters ( $\nu$ ) are from Brown (1981), except Brown & Altermatt (1985) for H–O;

\*\* A = Cs; B = Ca; T = Si; O(4) = O atom of an H<sub>2</sub>O group.

TABLE 9. COMPARISON OF F-MEMBERS OF THE APOPHYLLITE GROUP

Mineral	Fluorapophyllite-(Cs)	Fluorapophyllite-(K)		Fluorapophyllite-(Na)
End-member formula, Z = 2	$\text{CsCa}_4(\text{Si}_8\text{O}_{20})\text{F}(\text{H}_2\text{O})_8$	$\text{KCa}_4(\text{Si}_8\text{O}_{20})\text{F}(\text{H}_2\text{O})_8$		$\text{NaCa}_4(\text{Si}_8\text{O}_{20})\text{F}(\text{H}_2\text{O})_8$
Crystal system	Tetragonal	Tetragonal		Orthorhombic
Space group	<i>P4/mnc</i>	<i>P4/mnc</i>		<i>Pnm</i>
<i>a</i> (Å)	9.060	8.965*	8.970**	8.875
<i>b</i>	9.060	8.965*	8.970**	8.881
<i>c</i>	15.741	15.767*	15.792**	15.79
<i>V</i> (Å <sup>3</sup> )	1292.1	1267.2*	1270.6**	1236.9
A-site dominant cation	Cs	K	K	Na
A-H <sub>2</sub> O (Å)	3.152 x 8	2.971* x 8	2.966** x 8	2.763 x 4; 2.854 x 4
Optical data	Uniaxial (+) $\omega = 1.540$ $\epsilon = 1.544$	Uniaxial (+) $\omega = 1.530\text{--}1.536$ $\epsilon = 1.532\text{--}1.538$		Biaxial (–) $\alpha = 1.536$ $\beta = 1.538$ $\gamma = 1.544$
<i>D</i> <sub>meas.</sub> (g cm <sup>-3</sup> )	2.54	2.33–2.37		2.50
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	2.513	2.37		2.30
References	This work	*Chao (1971); **Ståhl <i>et al.</i> (1987); Anthony <i>et al.</i> (1995)		Matsueda <i>et al.</i> (1981)

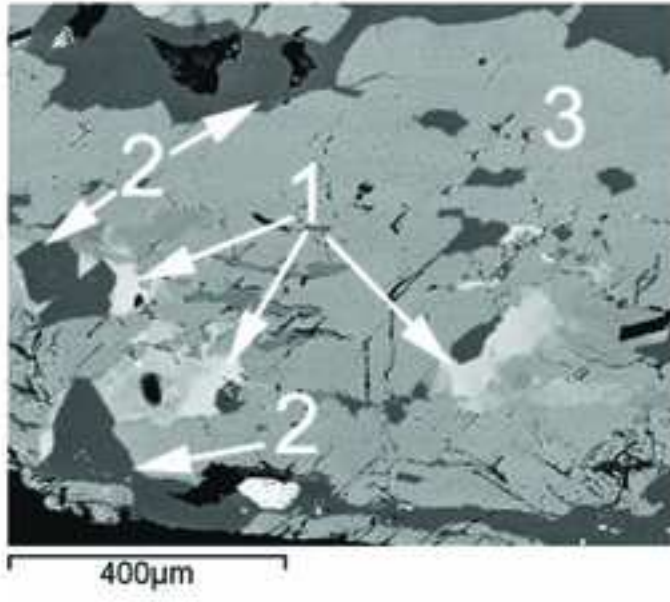


Fig. 1



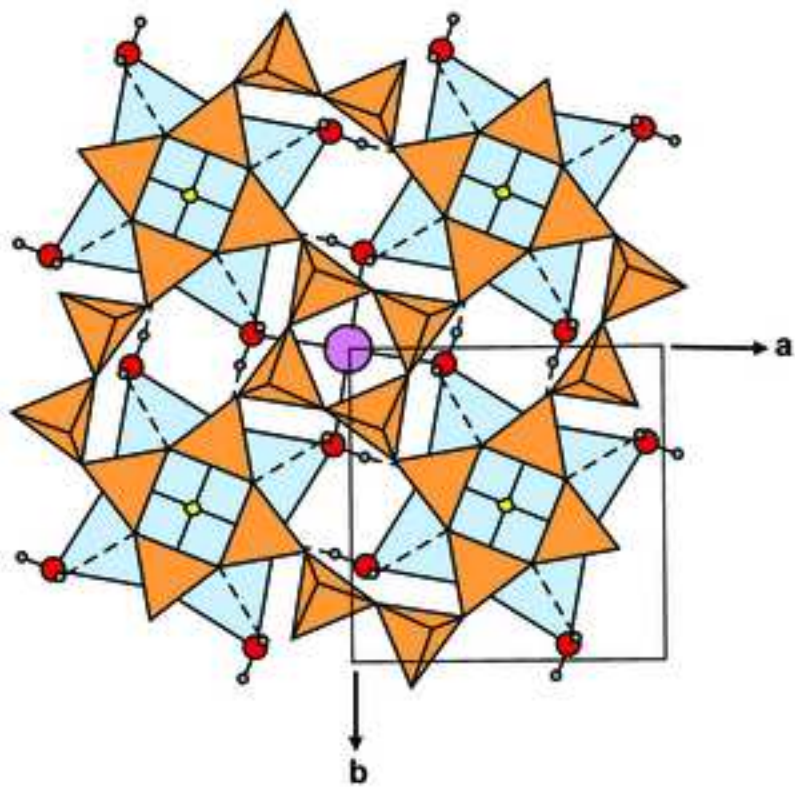


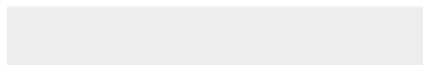
Fig. 2



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