

## Shuvalovite, $K_2(Ca_2Na)(SO_4)_3F$ , a new mineral from the Tolbachik volcano, Kamchatka, Russia

IGOR V. PEKOV<sup>1,\*</sup>, NATALIA V. ZUBKOVA<sup>1</sup>, SERGEY N. BRITVIN<sup>2,3</sup>, NIKITA V. CHUKANOV<sup>4</sup>,  
VASILII O. YAPASKURT<sup>1</sup>, EVGENY G. SIDOROV<sup>5</sup> and DMITRY Y. PUSHCHAROVSKY<sup>1</sup>

<sup>1</sup> Faculty of Geology, Moscow State University, Vorobievsky Gory, 119991 Moscow, Russia

\*Corresponding author, e-mail: igorpekov@mail.ru

<sup>2</sup> Department of Crystallography, St Petersburg State University, Universitetskaya Nab. 7/9, 199034 St Petersburg, Russia

<sup>3</sup> Nanomaterials Research Center, Kola Science Center of Russian Academy of Sciences, Fersman Str. 18,  
184209 Apatity, Russia

<sup>4</sup> Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

<sup>5</sup> Institute of Volcanology and Seismology, Far Eastern Branch of Russian Academy of Sciences, Piip Boulevard 9, 683006  
Petropavlovsk-Kamchatsky, Russia

**Abstract:** The new mineral shuvalovite, ideally  $K_2(Ca_2Na)(SO_4)_3F$ , was found in sublimates of the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is closely associated with calciolangbeinite, tenorite, hematite, orthoclase, fluorophlogopite and fluorite. Shuvalovite occurs as coarse lamellar to tabular (flattened on [100]), rectangular, octagonal or irregular crystals up to  $0.05 \times 0.7 \times 0.9$  mm combined in open-work groups or crusts up to  $1 \times 1$  cm on basalt scoria. Shuvalovite is transparent, colourless, and has a vitreous lustre. The mineral is brittle, with Mohs' hardness *ca.* 3. Cleavage was not observed, the fracture is uneven.  $D_{\text{calc}} = 2.64 \text{ g cm}^{-3}$ . Shuvalovite is optically biaxial (–),  $\alpha = 1.493(1)$ ,  $\beta = 1.498(1)$ ,  $\gamma = 1.498(1)$  and  $2V_{\text{meas}} \leq 20^\circ$ . The IR spectrum is reported. The chemical composition (average of 22 analyses) is: Na<sub>2</sub>O 7.37, K<sub>2</sub>O 19.33, CaO 21.39, SO<sub>3</sub> 49.49, F 3.78, O = F – 1.59, total 99.77 wt%. The empirical formula calculated on the basis of 13 (O + F) *apfu* is: Na<sub>1.16</sub>K<sub>2.01</sub>Ca<sub>1.86</sub>S<sub>3.02</sub>O<sub>12.03</sub>F<sub>0.97</sub>. Shuvalovite is orthorhombic, *Pnma*,  $a = 13.2383(4)$ ,  $b = 10.3023(3)$ ,  $c = 8.9909(4)$  Å,  $V = 1226.22(7)$  Å<sup>3</sup> and  $Z = 4$ . The strongest reflections of the powder X-ray diffraction pattern [ $d, \text{Å}(I)(hkl)$ ] are: 4.245(45)(102, 121), 3.963(62)(301), 3.281(100)(122), 3.210(30)(031), 3.144(84)(302, 321), 3.112(67)(131, 401), 3.016(78)(222) and 2.785(52)(420). The crystal structure, solved from single-crystal X-ray diffraction data ( $R = 0.067$ ), contains two crystallographically inequivalent isolated SO<sub>4</sub> tetrahedra. For the S(2) site, a disordered arrangement of coordinating O atoms is found that defines two possible orientations of the S(2)O<sub>4</sub> tetrahedron. The Ca(1) cations occupy CaO<sub>7</sub>F polyhedra whereas Ca(2) cations occupy CaO<sub>5</sub>F or CaO<sub>6</sub>F polyhedra, depending on the presence or absence of the half-occupied O(6) site split around the mirror plane. The K(1) and K(2) cations are nine-fold coordinated. All Ca and K sites contain admixed Na, the majority of which is located in the Ca(2) site. The comparative crystal chemistry of structurally different sulfates with the general formula  $M_5(SO_4)_3X$  (shuvalovite, krashennikovite and apatite-type compounds) is discussed. Shuvalovite is named in honour of the Russian nobleman and statesman Ivan Ivanovich Shuvalov (1727–1797), an enthusiastic patron of the sciences, arts and literature, one of the founders of the Moscow University in 1755.

**Key-words:** shuvalovite; new mineral; potassium calcium fluoride sulfate; crystal structure; fumarole; Tolbachik volcano; Kamchatka.

### Introduction

This paper provides the mineralogical description and crystal chemistry of a new fluorosulfate species of fumarolic origin. It is named shuvalovite (Cyrillic: шуваловичит) in honour of the Russian nobleman and statesman Ivan Ivanovich Shuvalov (1727–1797), an enthusiastic patron of the sciences, arts and literature. Along with Academician Mikhail Vasil'evich Lomonosov, he founded

Moscow University in 1755 (since 1940, Lomonosov Moscow State University). Ivan Shuvalov became the first curator of Moscow University and very actively promoted its development in all aspects, including the natural sciences.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014-057). The type specimen is deposited in the collections of the Fersman Mineralogical

Museum of the Russian Academy of Sciences, Moscow, with the registration number 4549/1.

## Occurrence

The only specimen of shuvalovite was collected by us in July 2013 in the Arsenatnaya fumarole located at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (GTFE), Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41'N 160°14'E, 1200 m asl). This scoria cone, a monogenetic volcano about 300 m high and approximately 0.1 km<sup>3</sup> in volume, was formed in 1975 during the first phase of the GTFE (Fedotov & Markhinin, 1983). Its fumarole fields are still active; gas vents with temperatures up to 430 °C are abundant at the summit of the cone. The Arsenatnaya fumarole was first uncovered by us in July 2012 and described in detail by Pekov *et al.* (2014). It is undoubtedly one of the world's most prolific mineralogical occurrences linked to volcanic exhalation. Almost ninety mineral species, mainly sulfates and arsenates, are found in Arsenatnaya, including seventeen new minerals.

Shuvalovite was found in a richly mineralized pocket in the southern part of the Arsenatnaya fumarole, at the depth of 0.5 m below day surface. The temperature measured (using chromel-alumel thermocouple) inside the pocket immediately after its uncovering was 370 ± 10 °C. Walls of the pocket were covered by sublimate incrustations. Their major minerals are hematite, tenorite, orthoclase (including its As-bearing variety), fluorophlogopite, langbeinite, apthitalite, anhydrite, lammerite, johillerite and tilasite. Krashennikovite, euchlorine, alumoklyuchevskite, calciolangbeinite, vanthoffite, arcanite, wulfite (IMA2013-035), fluorborite, urusovite, svabite, lammerite-β, bradaczekite, ericlxmanite, kozyrevskite, popovite (IMA2013-060), alarsite, halite, gahnite (Cu-bearing variety), corundum, shuvalovite and fluorite are subordinate and rare constituents of this assemblage.

Shuvalovite is a fumarolic mineral formed at temperatures not lower than 360–380 °C, but the mechanism of its crystallization is not completely clear. Calcium has very low volatility in such post-volcanic systems even at temperatures of about 400–500 °C (Symonds & Reed, 1993). Shuvalovite could have precipitated early, directly from the gaseous phase at higher temperatures, or it could have been formed through gas–rock interaction where basalt served as a source of metals, Ca in particular, whereas volatiles, SO<sub>3</sub> and F (and possibly K and Na), originated from volcanic gas. The latter scenario seems more probable for the formation of shuvalovite and other high-temperature Ca- and/or Mg-bearing oxysalts with the additional anion F<sup>-</sup> that occur in the Arsenatnaya fumarole, namely fluorophlogopite  $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})\text{F}_2$ , krashennikovite  $\text{KNa}_2\text{CaMg}(\text{SO}_4)_3\text{F}$ , fluorborite  $\text{Mg}_2(\text{BO}_3)\text{F}_3$ , tilasite  $\text{CaMg}(\text{AsO}_4)\text{F}$ , svabite  $\text{Ca}_5(\text{AsO}_4)_3\text{F}$  and kononovite  $\text{NaMg}(\text{SO}_4)\text{F}$  (Pekov *et al.*, 2015).

## General appearance, physical properties and optical data

Shuvalovite forms coarse lamellar to tabular (flattened on [100]), rectangular, octagonal or irregular crystals up to 0.05 × 0.7 × 0.9 mm. The dominant crystal form is the pinacoid {100}, lateral faces are assumed to be the pinacoids {010} and {001} and the unspecified orthorhombic prisms {0kl}. They are combined in open-work groups or crusts (Fig. 1) up to 1 × 1 cm in area overgrowing, together with calciolangbeinite and tenorite, the surface of basalt scoria “sprinkled” with small crystals of hematite, orthoclase and fluorophlogopite. Besides the above described crystals, shuvalovite occurs as imperfect, sometimes curved, pillow-like individuals occasionally overgrown by tiny distorted cubo-octahedra of fluorite (Fig. 2). Both crystals and “pillows” of the new mineral are micro-cavernous. On the surface of some crystals, a second generation of shuvalovite forms long prismatic to acicular, typically divergent microcrystals up to 0.05 mm long and up to 3 μm thick, and dendrite-like aggregates (Fig. 3).

Shuvalovite is transparent, colourless, with white streak and vitreous lustre. It is non-fluorescent under ultraviolet light or an electron beam. The mineral is brittle. Its Mohs' hardness is *ca.* 3. Cleavage or parting was not observed and the fracture is uneven. Attempts to measure density were unsuccessful because of the micro-cavernous character of the crystals. The density calculated based on the empirical formula is 2.641 g cm<sup>-3</sup>.

Shuvalovite is optically biaxial (-),  $\alpha = 1.493(1)$ ,  $\beta = 1.498(1)$ ,  $\gamma = 1.498(1)$  (589 nm),  $2V_{\text{meas}} \leq 20^\circ$  and  $2V_{\text{calc}} = 0^\circ$ . Dispersion of optical axes was not observed. Under the microscope the mineral is colourless and non-pleochroic.

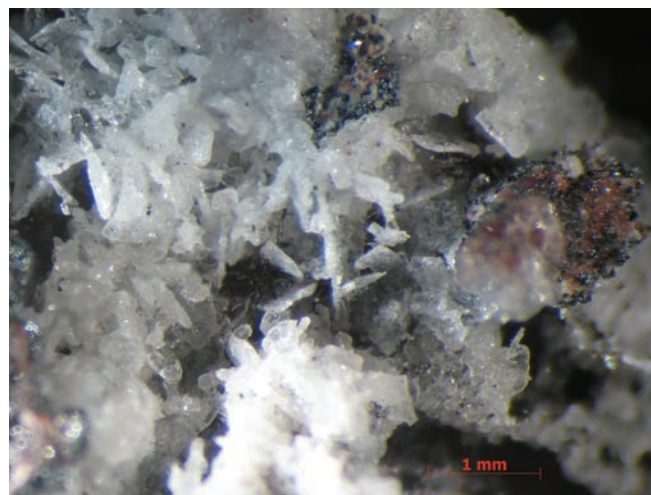


Fig. 1. Open-work aggregates of lamellar crystals of shuvalovite forming a crust on scoria “sprinkled” with small iron-black hematite crystals. Field of view: 5.8 mm. Photo: I.V. Pekov & A.V. Kasatkin.

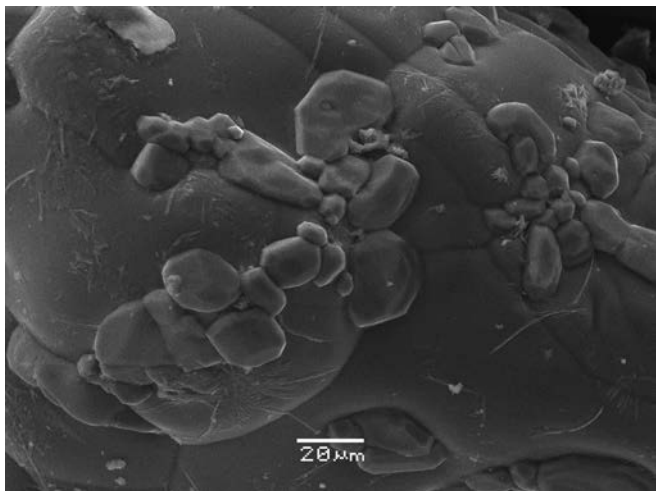


Fig. 2. Surface of pillow-like individuals of shuvalovite with overgrowing small, distorted cubo-octahedral fluorite crystals. Scanning-electron microscope image (secondary electrons).

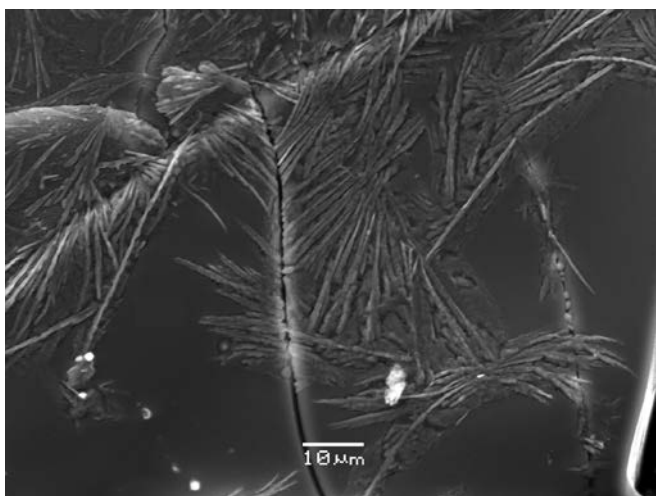


Fig. 3. A second generation of shuvalovite forming long prismatic to acicular, divergent microcrystals and their dendrite-like aggregates on the surface of a crystal belonging to the first, main generation of the mineral. SEM (SE) image.

### Infrared spectroscopy

The infrared (IR) absorption spectrum of shuvalovite was recorded for a powdered sample mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of  $4\text{ cm}^{-1}$ . The number of sampling scans was 16. The IR spectrum of a pure KBr disc was subtracted from the overall spectrum.

The absorption bands in the IR spectrum of shuvalovite (Fig. 4(a)) and their assignments are ( $\text{cm}^{-1}$ , s – strong band, w – weak band, sh – shoulder): 1165sh, 1125s [ $\nu_3(F_2)$  – asymmetric stretching vibrations of  $\text{SO}_4^{2-}$  anions], 993w [ $\nu_1(A_1)$  – symmetric stretching vibrations

of  $\text{SO}_4^{2-}$  anions), 643, 627, 612 [ $\nu_4(F_2)$  – bending vibrations of  $\text{SO}_4^{2-}$  anions], 474w (overtone or librational vibrations of  $\text{SO}_4^{2-}$  anions). The presence of a rather weak  $\nu_1(A_1)$  band (at  $993\text{ cm}^{-1}$ ) indicates moderate distortion of the  $\text{SO}_4$  tetrahedra. Characteristic bands of  $\text{BO}_3^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$  and hydrogen-bearing groups are absent in the IR spectrum.

The IR spectrum of shuvalovite is similar to that of the apatite-super group sulfate mineral cesanite,  $\text{Ca}_2\text{Na}_3(\text{SO}_4)_3(\text{OH})$  (Fig. 4(b)). This may be due to a remote similarity between the environments of tetrahedral anionic groups in shuvalovite and in compounds with apatite-like structures (see below). However, the IR spectrum of krashennikovite (Fig. 4(c)), another sulfate mineral with the same general stoichiometry,  $M_5(\text{SO}_4)_3X$ , substantially differs from those of shuvalovite and cesanite in that it exhibits a stronger splitting of the bands of stretching and bending vibrations of  $\text{SO}_4^{2-}$  anions. This specific feature of the IR spectrum of krashennikovite may be due to the interaction of the S(2)–O(2) bond with  $\text{Mg}^{2+}$ , a cation with higher force characteristics than K, Na and Ca (see Pekov *et al.*, 2012).

### Chemical composition

The chemical composition of shuvalovite was studied using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 15 nA, and a  $5\text{ }\mu\text{m}$  beam diameter. The following standards were used: albite (Na), orthoclase (K),  $\text{CaWO}_4$  (Ca),  $\text{BaSO}_4$  (S) and  $\text{MgF}_2$  (F).

The chemical composition of shuvalovite (average of 22 spot analyses for 10 crystals, wt%, range/standard deviation are in parentheses) is:  $\text{Na}_2\text{O}$  7.37 (4.70–9.09/1.19),  $\text{K}_2\text{O}$  19.33 (18.01–20.19/0.57),  $\text{CaO}$  21.39 (20.26–23.21/0.60),  $\text{SO}_3$  49.49 (47.90–50.98/0.77), F 3.78 (3.41–4.33/0.19), O = F – 1.59, total 99.77. Contents of other elements with atomic numbers higher than carbon are below their detection limits.

The empirical formula calculated on the basis of 13 (O + F) anions *pfu* is:  $\text{Na}_{1.16}\text{K}_{2.01}\text{Ca}_{1.86}\text{S}_{3.02}\text{O}_{12.03}\text{F}_{0.97}$ . The idealized formula is  $\text{K}_2(\text{Ca}_2\text{Na})(\text{SO}_4)_3\text{F}$ , which requires  $\text{Na}_2\text{O}$  6.34,  $\text{K}_2\text{O}$  19.28,  $\text{CaO}$  22.96,  $\text{SO}_3$  49.17, F 3.89, O = F – 1.64, total 100.00 wt%.

The Gladstone-Dale compatibility index is:  $1 - (\text{K}_p/\text{K}_c) = 0.025$  (“excellent”).

### X-ray crystallography and crystal structure

Powder X-ray diffraction data of shuvalovite (Table 1) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image-plate detector using Debye-Scherrer geometry ( $\text{CoK}\alpha$

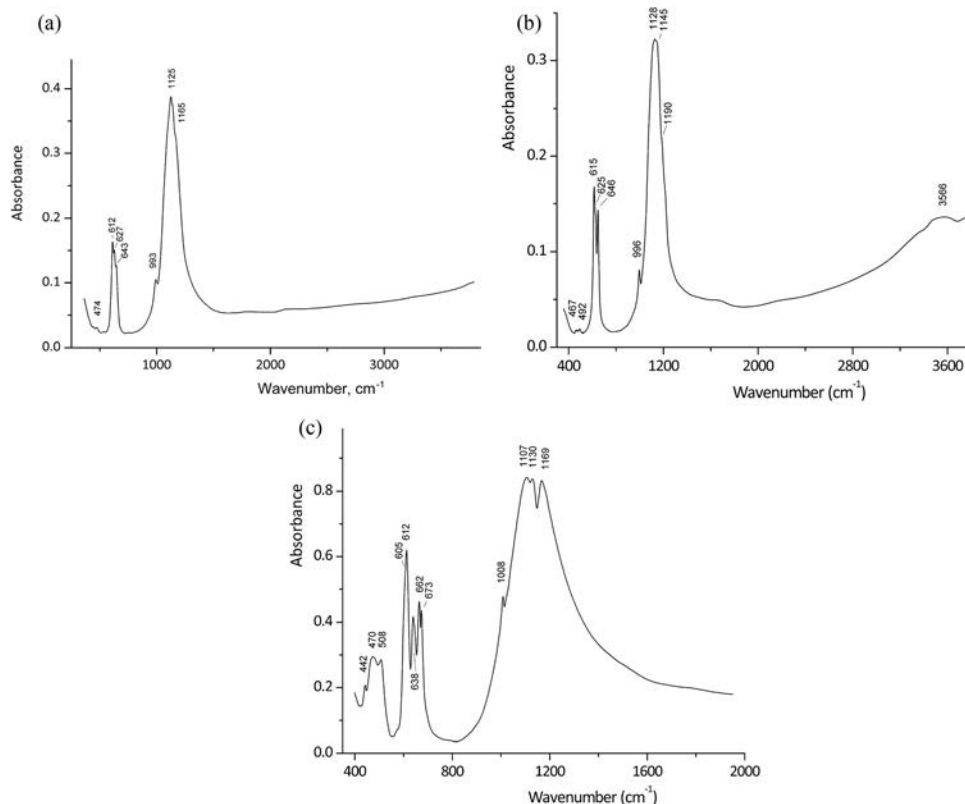


Fig. 4. Powder IR spectra of shuvalovite (a), cesanite from Cesano I geothermal well, Cesano, Latium, Italy (b), and krashennikovite from the Glavnaya Tenoritovaya fumarole, Second scoria cone of the Northern Breakthrough of the GTFE, Tolbachik volcano, Kamchatka, Russia (c).

radiation,  $d = 127.4$  mm). The orthorhombic unit-cell parameters refined from the powder data are:  $a = 13.248(3)$ ,  $b = 10.306(3)$ ,  $c = 8.989(3)$  Å and  $V = 1227.2(9)$  Å<sup>3</sup>.

Single-crystal X-ray studies of shuvalovite were carried out using an Xcalibur S diffractometer equipped with a CCD detector. An absorption correction was applied based upon the shape of the crystal. The crystal structure of the new mineral was solved by direct methods and refined using the SHELX-97 software package (Sheldrick, 2008) to  $R = 0.067$ . The unit-cell parameters and the experimental details are presented in Table 2, atom coordinates, displacement parameters and site occupancies in Table 3, and selected interatomic distances in Table 4.

In the crystal structure of shuvalovite (Fig. 5(a)), sulfur atoms occupy two crystallographically inequivalent positions and form isolated tetrahedral  $\text{SO}_4^{2-}$  anions. The S(1) atom occupies a nearly regular tetrahedron with S(1)–O distances varying from 1.436(4) to 1.459(6) Å (Table 4). For the S(2) site, a disordered arrangement of coordinating O atoms is found that defines two possible orientations of the S(2)O<sub>4</sub> tetrahedra (Figs 5(a) and 6). The Ca(1) site is surrounded by seven O atoms and one F atom; the Ca(1)O<sub>7</sub>F polyhedron has a short Ca(1)–F distance of 2.270(5) Å and longer Ca(1)–O distances in the range 2.355(9) to 2.644(7) Å (Table 4). The Ca(2) site occupies six- or seven-fold coordinated polyhedra. The coordination polyhedra for Ca(2), K(1) and K(2) can be described taking

into account the splitting of the oxygen sites O(5), O(6), O(7), and O(7') and the impossibility of the simultaneous occupancy of their sub-sites characterized by s.o.f. of 0.5 (Tables 3 and 4; Fig. 6). The involvement of the seventh vertex in the coordination of Ca(2) depends on the presence or absence of the O(6) site, which is split around the mirror plane, each subsite being half-occupied. Note that when O(6) atoms occupy the 4c position, the Ca(2)–O(6) distance is too long ( $\sim 3.24$  Å) and thus the Ca(2) cation occupies a six-fold polyhedron. The K(1) and K(2) cations occupy nine-fold polyhedra. All Ca(1), Ca(2), K(1) and K(2) sites contain subordinate (admixed) Na. Most Na is located in the Ca(2) site (Table 3), so that the idealized formula of shuvalovite can be given as  $\text{K}_2(\text{Ca}_2\text{Na})(\text{SO}_4)_3\text{F}$ .

In the frame of the general structural systematics of sulfates, the shuvalovite structure, formed by isolated  $\text{SO}_4$  tetrahedra and  $\text{MO}_n$  polyhedra with  $M$ –O bond strengths incomparable with those of S–O bonds, belongs to the “group” category (Pushcharovsky *et al.*, 1998).

## Discussion

No mineral structurally similar to shuvalovite is known, but there are several structurally similar synthetic compounds.  $\text{Pb}_4\text{Bi}(\text{PO}_4)_3\text{O}$  (Moore *et al.*, 1982),  $\text{K}_2\text{Bi}_3(\text{PO}_4)_3\text{O}$  (Debreuille-Gresse *et al.*, 1986),  $\text{Bi}_{1.5}(\text{Pb}_{7.3}\text{Mn}_{0.7})(\text{PO}_4)_6\text{O}_{1.3}$  (Wang *et al.*, 2003) and  $\text{Pb}_5(\text{CrO}_4)(\text{PO}_4)_2\text{O}$  (Mao *et al.*, 2009)

Table 1. Powder X-ray diffraction data of shuvalovite.

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$
27	7.44	20	7.438	101
22	6.62	18	6.619	200
3	5.576	1	5.569	210
3	5.335	2	5.330	201
3	5.154	2	5.151	020
5	4.736	3	4.734	211
11	4.492	7	4.495	002
45	4.245	17, 24	4.257, 4.235	102, 121
13	4.065	7	4.065	220
62	3.963	46	3.961	301
15	3.929	10	3.934	112
18	3.713	5, 2	3.719, 3.704	202, 221
13	3.499	7	3.498	212
100	3.281	100	3.281	122
30	3.210	30	3.208	031
84	3.144	33, 53	3.149, 3.140	302, 321
67	3.112	33, 37	3.118, 3.106	131, 401
78	3.016	82	3.015	222
12	2.976	8	2.974	411
15	2.923	10	2.923	103
22	2.884	7, 4	2.887, 2.878	231, 013
52	2.785	59	2.784	420
13	2.733	10	2.730	203
11	2.672	9	2.673	132
16	2.639	19	2.639	213
17	2.578	1, 16	2.580, 2.576	412, 040
2	2.544	0.5	2.542	123
6	2.523	3	2.523	232
5	2.475	1, 0.5	2.479, 2.466	303, 511
10	2.412	10, 1	2.412, 2.410	223, 313
6	2.370	4	2.367	422
6	2.305	6	2.303	431
3	2.280	1	2.278	521
8	2.221	6, 7	2.226, 2.216	133, 104
6	2.205	0.5, 4	2.206, 2.204	600, 142
4	2.173	3	2.172	413
3	2.159	1	2.159	341
7	2.128	7	2.128	204
6	2.119	5	2.117	242
6	2.099	1, 6	2.105, 2.098	432, 611
5	2.087	2, 3	2.086, 2.084	522, 214
3	2.058	2	2.060	024
9	2.035	2, 4, 6	2.042, 2.036, 2.033	531, 124, 440
12	2.008	7, 7, 6	2.010, 2.008, 2.003	333, 051, 304
27	1.982	7, 5, 12, 18, 8	1.986, 1.984, 1.983, 1.981, 1.978	151, 503, 441, 602, 621
3	1.949	3	1.948	513
12	1.933	9	1.932	143
2	1.901	1	1.900	532
5	1.866	2, 2, 2, 1	1.873, 1.867, 1.865, 1.862	243, 324, 433, 134
19	1.852	17, 14	1.852, 1.851	523, 701
7	1.821	3, 4	1.822, 1.818	711, 631
6	1.802	7	1.802	252
4	1.772	0.5, 5	1.777, 1.771	603, 015
5	1.750	0.5, 6	1.751, 1.749	613, 450
7	1.717	2, 7, 3, 2	1.718, 1.717, 1.717, 1.714	533, 060, 451, 504
7	1.683	13, 4	1.684, 1.680	125, 144
2	1.665	3	1.665	305
7	1.646	0.5, 8, 3	1.647, 1.645, 1.644	641, 253, 225
6	1.627	15	1.626	524
2	1.609	2	1.608	811
8	1.573	1, 2, 3, 7	1.578, 1.575, 1.572, 1.570	633, 820, 543, 642

(Continued)

Table 1. Continued

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$
5	1.560	1, 2, 1	1.562, 1.559, 1.556	415, 262, 614
6	1.554	1, 6	1.553, 1.552	802, 821
2	1.526	0.5, 2	1.529, 1.524	552, 460
4	1.509	2, 3, 1	1.511, 1.509, 1.508	425, 154, 362
3	1.503	2, 1	1.503, 1.503	741, 461
3	1.486	1, 2	1.488, 1.485	505, 651
2	1.465	1, 0.5	1.465, 1.463	145, 643
2	1.452	1	1.452	071
3	1.445	3, 2	1.444, 1.444	171, 742
3	1.432	1, 2, 2, 3	1.435, 1.431, 1.430, 1.429	435, 634, 126, 553
2	1.407	3, 0.5	1.406, 1.406	226, 316
3	1.398	2	1.398	345
4	1.368	1, 2, 1	1.372, 1.368, 1.368	562, 272, 326
2	1.358	1	1.359	743
2	1.345	3	1.345	470
3	1.333	3, 3	1.333, 1.331	372, 752
2	1.322	1	1.321	073
2	1.311	1	1.310	10.0.1
3	1.299	2, 2	1.298, 1.297	563, 662
3	1.292	2, 2, 1	1.292, 1.290, 1.290	635, 850, 824
4	1.280	3, 4, 1	1.282, 1.279, 1.277	10.2.0, 923, 851

\*For the calculated pattern, only reflections with intensities  $\geq 0.5$  are given. \*\*For the unit-cell parameters calculated from single-crystal data.

Table 2. Crystal data, data collection information and structure refinement details for shuvalovite.

Temperature, K	293(2)
Radiation and wavelength, Å	MoK $\alpha$ ; 0.71073
Crystal system, space group, Z	Orthorhombic, <i>Pnma</i> , 4
Unit-cell dimensions, Å	$a = 13.2383(4)$ $b = 10.3023(3)$ $c = 8.9909(4)$
$V, \text{Å}^3$	1226.22(7)
Crystal size, mm	0.05 $\times$ 0.12 $\times$ 0.17
Diffractometer	Xcalibur S CCD
$\theta$ range for data collection, °	2.74–27.48
Index ranges	$-17 \leq h \leq 17, -13 \leq k \leq 13, -11 \leq l \leq 11$
Reflections collected	17529
Independent reflections	1479 ( $R_{\text{int}} = 0.065$ )
Independent reflections with $I > 2\sigma(I)$	1379
Structure solution	direct methods
Refinement method	full-matrix least-squares on $F^2$
Number of refined parameters	120
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.067, wR2 = 0.126$
$R$ indices (all data)	$R1 = 0.073, wR2 = 0.129$
GoF	1.146
Largest diff. peak and hole, $e/\text{Å}^3$	1.164 and $-0.635$

have similar unit-cell parameters and the same space group *Pnma*. Moreover, the last three compounds are characterized by disordered arrangement of one of the  $TO_4$  tetrahedra. The compound  $K_3Ca_2(SO_4)_3F$  is chemically most similar to shuvalovite. It has similar unit-cell parameters ( $a = 13.415, b = 10.493, c = 9.127$  Å) but the non-centrosymmetric space group *Pn2<sub>1</sub>a*, and shows partial disorder of its  $SO_4$  tetrahedra. On the basis of the interatomic distances in some cation-centred polyhedra, partial disorder of K and Ca was assumed for this synthetic fluorosulfate (Fayos *et al.*, 1987); thus, its

simplified formula could be presented as  $K_2(Ca_2K)(SO_4)_3F$ , by analogy with the new mineral.

Shuvalovite has the same general stoichiometry  $M_5(TO_4)_3X$  as the apatite-supergroup members (with species-defining constituents  $M = Ca, Pb^{2+}, Ba, Sr, Mn^{2+}, Na, REE^{3+}, Bi^{3+}; T = P, As^{5+}, V^{5+}, Si, S^{6+}; X = F, OH, Cl$ ; Pasero *et al.*, 2010) and krashennikovite  $KNa_2CaMg(SO_4)_3F$ , a mineral recently discovered at the Second scoria cone of the GTFE (Pekov *et al.*, 2012). However shuvalovite, krashennikovite and apatite-like

Table 3. Atom coordinates, isotropic displacement parameters ( $U_{\text{eq}}$ , in  $\text{\AA}^2$ ), site occupancies (s.o.f.) and site multiplicities ( $Q$ ) for shuvalovite.

Atom	$Q$	$x$	$y$	$z$	$U_{\text{eq}}$	s.o.f.
K(1)	4	0.21405(14)	0.75	0.1522(2)	0.0319(7)	$\text{K}_{0.810(8)}\text{Na}_{0.19}$
K(2)	4	0.77308(16)	0.75	0.8055(3)	0.0441(8)	$\text{K}_{0.878(8)}\text{Na}_{0.12}$
Ca(1)	4	0.01003(12)	0.25	0.48431(17)	0.0207(5)	$\text{Ca}_{0.831(7)}\text{Na}_{0.17}^*$
Ca(2)	8	0.07503(10)	0.04723(13)	0.80963(15)	0.0276(4)	$\text{Ca}_{0.650(6)}\text{Na}_{0.35}^*$
S(1)	8	0.15444(10)	0.96882(12)	0.43452(16)	0.0269(4)	1
S(2)	4	0.02276(16)	0.75	-0.0829(2)	0.0315(5)	1
O(1)	8	0.1335(5)	0.9185(7)	0.5831(7)	0.080(2)	1
O(2)	8	0.1465(4)	0.3922(4)	0.4333(7)	0.0610(16)	1
O(3)	8	0.7473(3)	0.4284(5)	0.6160(7)	0.0650(17)	1
O(4)	8	0.0759(4)	0.5895(6)	0.3428(6)	0.0634(16)	1
O(5)	8	-0.0616(10)	0.8158(14)	-0.0218(19)	0.123(6)**	0.5
O(6)	8	0.5012(9)	0.1996(9)	0.2709(9)	0.063(3)	0.5
O(7)	8	0.0469(8)	0.8651(10)	0.0068(11)	0.051(3)	0.5
O(7')	8	0.1084(12)	0.8331(13)	-0.0891(18)	0.100(5)	0.5
F	4	0.0966(4)	0.25	0.7022(5)	0.0371(12)	1

\*The electron-microprobe data show that Ca could be slightly substituted by K.

\*\* $U_{\text{iso}}$ .

Table 4. Selected interatomic distances ( $\text{\AA}$ ) in the structure of shuvalovite.

Ca(1) – F 2.270(5)	S(2) – O(5) 1.417(9)
– O(6) 2.355(9)/O(6) 2.355(9)*	– O(7') 1.422(12)
– O(2) 2.371(5) $\times$ 2	– O(6) 1.449(9)
– O(4) 2.539(6) $\times$ 2	– O(7) 1.469(10)
– O(1) 2.644(7) $\times$ 2	K(1) – F 2.547(5)
Ca(2) – F 2.319(2)	– O(7') 2.720(13)/O(7) 2.831(10)*
– O(5) 2.379(15)/O(7) 2.479(10)*	– O(3) 2.825(6) $\times$ 2
– O(3) 2.390(5)	– O(7) 2.831(10)/O(7') 2.720(13)*
– O(7') 2.427(13)/O(7) 2.608(11)*	– O(4) 3.003(6) $\times$ 2
– O(4) 2.462(6)	– O(2) 3.070(6) $\times$ 2
– O(1) 2.551(7)	K(2) – O(1) 2.726(6) $\times$ 2
– O(6) 2.758(10)	– O(5) 2.768(17)/O(5) 2.768(17)*
S(1) – O(2) 1.436(4)	– O(2) 2.808(6) $\times$ 2
– O(3) 1.440(4)	– O(7') 3.04(2)/O(7') 3.04(2)*
– O(4) 1.456(5)	– O(6) 3.049(13)/O(6) 3.049(13)*
– O(1) 1.459(6)	– O(3) 3.354(7) $\times$ 2

\*Pairs of statistically occupied oxygen sites that cannot be occupied simultaneously.

compounds demonstrate three quite different types of crystal structures and are very different in unit-cell dimensions and powder X-ray diffraction patterns; nevertheless, it seems interesting to compare them. For this comparison, we chose the Ca-Na sulfate cesanite as a representative of the apatite supergroup (Table 5; Fig. 5). Note that all three sulfate minerals of the apatite supergroup, namely cesanite  $\text{Ca}_2\text{Na}_3(\text{SO}_4)_3(\text{OH})$ , caracolite  $\text{Na}_2(\text{Pb}_2\text{Na})(\text{SO}_4)_3\text{Cl}$  and aiolosite  $\text{Na}_2(\text{Na}_2\text{Bi})(\text{SO}_4)_3\text{Cl}$ , are Na-rich and belong to the hedyphane group (Pasero *et al.*, 2010).

The apatite structure archetype and its derivatives are well-known (Hughes *et al.*, 1989; White *et al.*, 2005; Pasero *et al.*, 2010). A remote relationship between the above-mentioned synthetic compound  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ , which is structurally related to shuvalovite, and fluorapatite  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  ( $P6_3/m$ ) was noted by Fayos *et al.* (1987). For comparison, both structures could be described in terms of the packing of cation-polyhedral cages enclosing

the  $\text{SO}_4^{2-}/\text{PO}_4^{3-}$  and  $\text{F}^-$  anions. The similarity between the structures is demonstrated in the arrangement of the columns of F-centred cages running along the  $a$  axis in  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$  and the  $c$  axis in apatite, surrounded by triads of  $M$  cages centred by  $\text{SO}_4/\text{PO}_4$  tetrahedra and containing  $\text{Ca}^{2+}$  and  $\text{K}^+$  cations (only Ca in apatite) at vertices. The  $\text{F}^-$  anions centre  $\text{FCa}_2\text{K}_2$  tetrahedra in  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ , while in apatite the F-centred triangles  $\text{FCa}_3$  are observed. In  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$ , the anion-centred  $\text{FCa}_2\text{K}_2$  tetrahedron is repeated every 6.74  $\text{\AA}$ , while in apatite the period between  $\text{FCa}_3$  triangles is 3.5  $\text{\AA}$ , *i.e.* almost a half of the period in  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$  (Fayos *et al.*, 1987). All features discussed here for  $\text{K}_3\text{Ca}_2(\text{SO}_4)_3\text{F}$  are the same for shuvalovite.

Krashennikovite is hexagonal, like most apatite-type compounds, but more highly symmetric ( $P6_3/mcm$ ) as compared to the apatite structure archetype ( $P6_3/m$ ). The unit-cell parameter  $c$  (6.90  $\text{\AA}$ ) of krashennikovite is within the

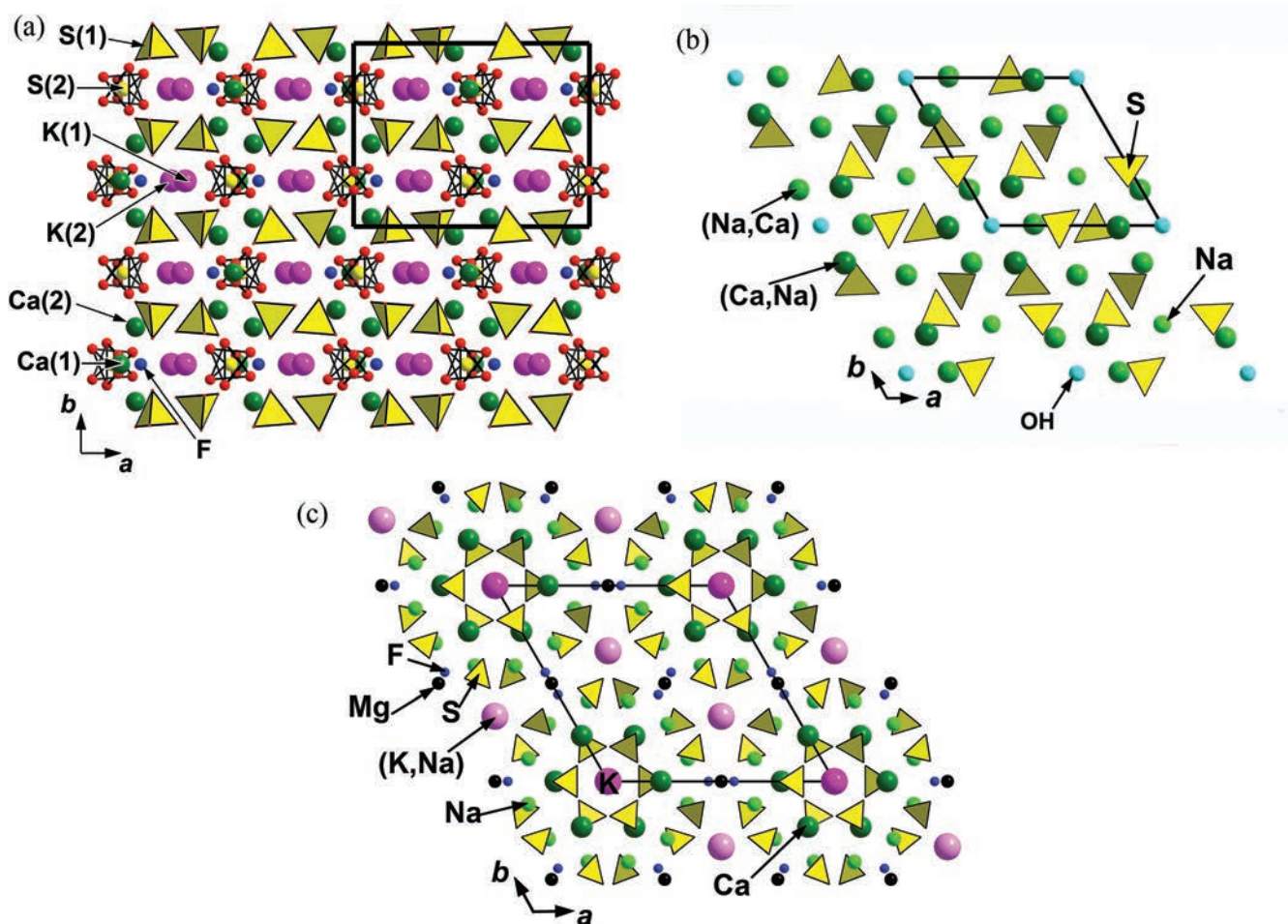


Fig. 5. Crystal structures of minerals with the same general formula  $M_5(\text{SO}_4)_3X$  but belonging to quite different structure archetypes: *a* – shuvalovite  $\text{K}_2(\text{Ca}_2\text{Na})(\text{SO}_4)_3\text{F}$  [*ab* projection; two possible orientations of the  $\text{S}(2)\text{O}_4$  tetrahedra are shown], *b* – cesanite  $\text{Ca}_2\text{Na}_3(\text{SO}_4)_3(\text{OH})$  [*ab* projection; drawn after Piotrowski *et al.*, 2002], *c* – krashennikovite  $\text{KNa}_2\text{CaMg}(\text{SO}_4)_3\text{F}$  [*ab* projection; Pekov *et al.*, 2012]. The unit cells are outlined.

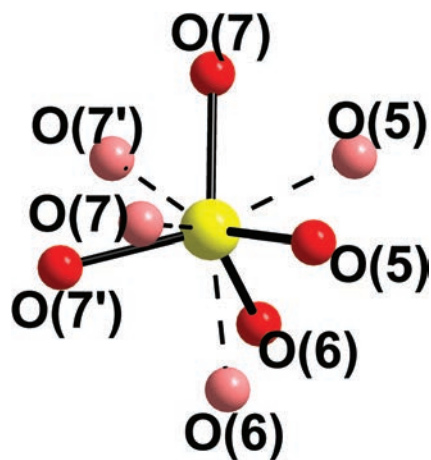


Fig. 6. Two possible orientations of the  $\text{S}(2)\text{O}_4$  tetrahedron in shuvalovite. The  $\text{S}(2)$  atom is shown as a central circle. Simultaneously existent O ligands are given in the same colour.

typical range of the  $c$  parameter of apatites, whereas the  $a$  parameter (16.68 Å) can be represented as  $a'\sqrt{3}$  (9.63 Å) which is within typical range of the  $a$  parameter of apatites (White *et al.*, 2005). Moreover, the synthetic  $(\text{Cd},\text{Mn})_5(\text{PO}_4)_3\text{OH}$  compound ( $P6_3$ ) with the superstructure based on the apatite-type structure has unit-cell dimensions close to those of krashennikovite:  $a = 16.20$ ,  $c = 6.65$  Å (Hata & Marumo, 1983). However, the similarity in unit-cell parameters is caused only by the similar arrangement of the positions of the largest cations [K and (K,Na)] in krashennikovite  $[\text{K}_2(\text{K},\text{Na})_4\text{Na}_{12}\text{Ca}_6\text{Mg}_6(\text{SO}_4)_{18}\text{F}_6, Z = 1]$  and  $X$  anions in apatite-type compounds (Figs 5(b) and (c)). For this reason, we consider the structural motif of krashennikovite as an “antiapatite motif”: the  $X$  anion sublattice of apatites is close to the K cation sublattice of krashennikovite (Pekov *et al.*, 2012).

Thus, the similarity between shuvalovite, krashennikovite and apatite-type compounds is very weak, in spite of the same stoichiometry  $M_5(\text{TO}_4)_3X$ . Compared to shuvalovite and krashennikovite, cesanite, as well as other



Table 5. Comparative data for shuvalovite, cesanite and krashennikovite, which share the same general formula  $M_5(\text{SO}_4)_3\text{X}$  but belong to quite different structure archetypes.

Mineral	Shuvalovite	Cesanite	Krashennikovite
Ideal formula	$\text{K}_2(\text{Ca}_2\text{Na})(\text{SO}_4)_3\text{F}$	$\text{Ca}_2\text{Na}_3(\text{SO}_4)_3(\text{OH})$	$\text{KNa}_2\text{CaMg}(\text{SO}_4)_3\text{F}$
Structure archetype	$\text{Pb}_4\text{Bi}(\text{PO}_4)_3\text{O}$	Apatite	Krashennikovite
Crystal system	Orthorhombic	Hexagonal	Hexagonal
Space group	<i>Pnma</i>	<i>P</i> -6	<i>P6</i> <sub>3</sub> / <i>mcm</i>
<i>a</i> , Å	13.238	9.443	16.668
<i>b</i> , Å	10.302		
<i>c</i> , Å	8.991	6.886	6.901
<i>V</i> , Å <sup>3</sup>	1226	532	1660
<i>Z</i>	4	2	6
Strongest reflections of the X-ray powder pattern: <i>d</i> , Å <sup>-1</sup>	4.245–45 3.963–62 3.281–100 3.144–84 3.112–67 3.016–78 2.785–52	3.896–66 3.448–87 2.822–60 2.727–100 2.636–49 2.269–47 1.844–71	4.286–22 3.613–24 3.467–42 3.454–43 3.153–100 3.116–22 2.660–39
Strongest bands of the IR spectrum, cm <sup>-1</sup>	1165, 1125, 643, 627, 612	1145, 1128, 646, 625	1169, 1130, 1107, 1008, 673, 662, 638, 612, 605
<i>D</i> , g cm <sup>-3</sup>	2.64 (calc.)	2.79–2.83	2.67–2.68
References	this work	Cavarretta <i>et al.</i> (1981); Piotrowski <i>et al.</i> (2002); Chukanov (2014)	Pekov <i>et al.</i> (2012)

apatite-type compounds, is characterized by a more compact (dense) structure, which results in a lower unit-cell volume (*pfu*) and a higher density (Table 5).

Both shuvalovite and krashennikovite contain species-defining potassium prevailing in some structural positions or occupying them completely, whereas no apatite-supergroup mineral with species-defining K is known. Moreover, among numerous and chemically various synthetic apatite-like compounds, only a few K-bearing phases are known. White *et al.* (2005) reported the crystal data for more than four hundreds apatite-type salts and only nine of them contain potassium, namely  $\text{K}_8\text{Na}_2(\text{VO}_4)_6$ ,  $\text{Pb}_8\text{K}_2(\text{PO}_4)_6$ ,  $\text{Pb}_9\text{K}(\text{AsO}_4)_5(\text{SiO}_4)$ ,  $\text{Pb}_6\text{KNa}_2\text{Bi}(\text{PO}_4)_6$ ,  $\text{Pb}_6\text{K}_4(\text{PO}_4)_4(\text{SO}_4)_2$ ,  $\text{Pb}_6\text{K}_4(\text{PO}_4)_4(\text{SeO}_4)_2$ ,  $\text{KNd}_9(\text{SiO}_4)_6\text{O}_2$  (space group *P6*<sub>3</sub>/*m*),  $\text{K}_6\text{Sn}_4(\text{SO}_4)_6\text{Cl}_2$  and  $\text{K}_6\text{Sn}_4(\text{SO}_4)_6\text{Br}_2$  (*P6*<sub>3</sub>). These statistics demonstrate that the apatite structure archetype has in general low affinity for the  $\text{K}^+$  ion, probably because of its very large ionic radius and its monovalence (unlike large bivalent Ba and Pb, very common cations of apatite-type compounds). This, we believe, is the main reason that potassium-bearing phases with the general formula  $M_5(\text{TO}_4)_3\text{X}$  do not assume the apatite structure.

Note that representatives of all three above-discussed structure archetypes are found in the Arsenatnaya fumarole: krashennikovite, shuvalovite and svabite  $\text{Ca}_5(\text{AsO}_4)_3\text{F}$ , an arsenate analogue of fluorapatite, occur in the same pocket.

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