

Krasheninnikovite, $\text{KNa}_2\text{CaMg}(\text{SO}_4)_3\text{F}$, a new mineral from the Tolbachik volcano, Kamchatka, Russia

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ABSTRACT

A new mineral krasheninnikovite, ideally $\text{KNa}_2\text{CaMg}(\text{SO}_4)_3\text{F}$, is found in the sublimates of an active fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with tenorite, thenardite, hematite, euchlorine, blöditite, vergasovaite, and fluorophlogopite. Krasheninnikovite forms long-prismatic to acicular crystals up to 3 mm long and up to 20 μm thick. The crystals are combined in sheaf-like, radiating or open-work matted aggregates forming nests up to several cm^3 or crusts. Krasheninnikovite is transparent, colorless in individuals and white in aggregates. The luster is vitreous. The mineral is brittle; the thinnest needles are flexible and elastic. The Mohs hardness is $2\frac{1}{2}$ –3. Cleavage was not observed. D_{meas} is 2.68(1), D_{calc} is 2.67 g/cm^3 . Krasheninnikovite is optically uniaxial (–), $\omega = 1.500(2)$, $\epsilon = 1.492(2)$. The IR spectrum is unique. The chemical composition (wt%, electron microprobe data) is: Na_2O 15.48, K_2O 6.92, CaO 11.51, MgO 9.25, MnO 0.15, FeO 0.04, Al_2O_3 0.23, SO_3 53.51, F 3.22, Cl 0.16, $-\text{O}=(\text{F},\text{Cl})_2$ –1.39, total 99.08. The empirical formula, calculated on the basis of 13 (O+F+Cl) apfu, is: $\text{K}_{0.67}\text{Na}_{2.27}\text{Ca}_{0.93}\text{Mn}_{0.01}\text{Mg}_{1.04}\text{Al}_{0.02}(\text{SO}_4)_{3.04}\text{F}_{0.76}\text{Cl}_{0.02}\text{O}_{0.06}$. Krasheninnikovite is hexagonal, space group $P6_3/mcm$, $a = 16.6682(2)$, $c = 6.9007(1)$ Å, $V = 1660.36(4)$ Å³, $Z = 6$. The strongest reflections of the X-ray powder pattern [d , Å $I(hkl)$] are: 4.286 22(121); 3.613 24(040); 3.571 17(221); 3.467 42(131); 3.454 43(002); 3.153 100(140), 3.116 22(022), 2.660 39(222), 2.085 17(440). The crystal structure was solved on a single crystal and refined on a powder sample by the Rietveld method, $R_{\text{wp}} = 0.0485$. The krasheninnikovite structure is unique. It is based upon a heteropolyhedral pseudo-framework consisting of CaO_6 octahedra, MgO_6F octahedra, and SO_4 tetrahedra; K and Na cations are located in cavities. Krasheninnikovite is named in honor of the Russian geographer, ethnographer, and naturalist S.P. Krasheninnikov (1711–1755), one of the first scientists who researched Kamchatka. The type specimen is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow.

Keywords: Krasheninnikovite, new mineral, sulfate, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka

INTRODUCTION

Sulfate minerals are typical products of fumarolic activity. Sulfates can be deposited directly from the gaseous phase (volcanic sublimates) or formed through complex reactions of gas-rock interaction around fumaroles. In both cases, minerals can be anhydrous or possess associated water (Quisefit et al. 1989; Taran et al. 2001; Zelenski and Bortnikova 2005). When the temperature of a fumarole decreases, numerous secondary hydrous sulfates are formed as products of the alteration of early mineralization due to the exposure to atmospheric water. Most often, fumarolic sulfates contain only rock-forming elements (Na, K, Mg, Ca, Al, and Fe) as main cations.

Sulfates are abundant and most diverse among the minerals formed in fumaroles of the Tolbachik volcano in the Kam-

chatka Peninsula, Far East Asia, Russia. The fumarole fields of Tolbachik, born by the Great Tolbachik Fissure Eruption in 1975–1976 (Fedotov and Markhinin 1983), are still active. The Tolbachik fumaroles are an outstanding mineralogical object producing numerous minerals (Vergasova and Filatov 1993). As of 2011, more than 100 mineral species are known in fumarole sublimates and products of their alteration at Tolbachik, including 38 species first found in nature. Fourteen of these 38 minerals contain SO_4^{2-} as the species-defining anion, namely piypite $\text{K}_2\text{Cu}_2\text{O}(\text{SO}_4)_2$ (Vergasova et al. 1984), atlasovite $\text{KCu}_6\text{Fe}^{3+}\text{Bi}^{3+}\text{O}_4(\text{SO}_4)_5\text{Cl}$, nabokoite $\text{KCu}_7(\text{Te}^{4+}\text{O}_3)\text{O}(\text{SO}_4)_5\text{Cl}$ (Popova et al. 1987), fedotovite $\text{K}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ (Vergasova et al. 1988a), kamchatkite $\text{KCu}_3\text{O}(\text{SO}_4)_2\text{Cl}$ (Vergasova et al. 1988b), klyuchevskite $\text{K}_3\text{Cu}_3\text{Fe}^{3+}\text{O}_2(\text{SO}_4)_4$ (Vergasova et al. 1989), alumoklyuchevskite $\text{K}_3\text{Cu}_3\text{AlO}_2(\text{SO}_4)_4$ (Gorskaya et al. 1995), vlodavetsite $\text{Ca}_2\text{Al}(\text{SO}_4)_2\text{F}_2\text{Cl}\cdot 4\text{H}_2\text{O}$ (Vergasova et al.

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1995), vergasovaite $\text{Cu}_3\text{O}(\text{MoO}_4)(\text{SO}_4)$ (Bykova et al. 1998), meniaylovite $\text{Ca}_4(\text{SO}_4)\text{F}(\text{SiF}_6)(\text{AlF}_6) \cdot 12\text{H}_2\text{O}$ (Vergasova et al. 2004), pauflerite $(\text{V}^{4+}\text{O})(\text{SO}_4)$ (Krivovichev et al. 2007), and three species approved by the IMA CNMNC in 2011: steklite $\text{KAl}(\text{SO}_4)_2$ (earlier known only as the technogenic phase in burnt coal dumps and first found in natural environment: Murashko et al. 2012), calciolangbeinite $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ (Pekov et al. 2012), and krasheninnikovite $\text{KNa}_2\text{CaMg}(\text{SO}_4)_3\text{F}$, a mineral described in the present paper.

Krasheninnikovite (Cyrillic: крашенинниковит) is named in honor of the famous Russian geographer, ethnographer, and naturalist Stepan Petrovich Krasheninnikov (1711–1755), one of the first scientists who researched the Kamchatka Peninsula. During his long Kamchatka expedition (1737–1741), Krasheninnikov collected and systematized unique material on the nature, history, and aboriginal population of the peninsula, including studies of active volcanoes and mineral resources. His encyclopedic book *Opisanie Zemli Kamchatki* (Description of the Kamchatka Land), first published in Russian in 1755 and later translated into English, German, French, and Dutch, was for many years the only serious publication on Kamchatka.

The new mineral and its name have been approved by the IMA CNMNC, No. 2011-044. The type specimen of krasheninnikovite is deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow; the registration number is 4112/1.

OCCURRENCE AND GENERAL APPEARANCE

Krasheninnikovite was found in 2008 by one of the authors (M.E.Z.) in an unnamed active fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano. This scoria cone, formed in 1975 (Fedotov and Markhinin 1983), is 300 m high and approximately 0.1 km^3 in volume. In 2010, several gas vents with temperatures of up to 480°C , were observed at the apical parts of the cone. Tolbachik fumarolic gases are compositionally close to atmospheric air, with the contents of $<1 \text{ vol}\%$ water vapor and $<0.1 \text{ vol}\%$ acid species, mainly CO_2 , HF, and HCl (data by M.E.Z.).

Krasheninnikovite was collected from a 2 m long fracture, cross-cutting massive basalt and basaltic scoria. The origin of the mineral is unclear. At the time of sampling, the temperature was $120\text{--}150^\circ\text{C}$. However, the measured temperature is likely insufficient to ensure effective gaseous transport of K, Na, Ca, and Mg. The two latter elements have very low volatilities in such post-volcanic systems even at moderate temperatures up to $400\text{--}500^\circ\text{C}$ (Symonds and Reed 1993). Presumably, the mineral could have been deposited directly from the gaseous phase at some earlier time (Mg, Ca, Na, and K were carried by gas), or could have been formed through gas-rock interaction where basalt served as a source of metals, whereas volatiles (S and F) originated from volcanic gases. Some combination of both processes is also possible. A detailed study of the depositional conditions falls outside the scope of the present paper.

Krasheninnikovite forms long-prismatic to acicular crystals elongated along [001], with hexagonal or, typically, more complicated cross section. The prismatic zone of the crystals (symmetry class $6/mmm$) displays hexagonal prisms {100} and {110} and dihexagonal prisms.

Crystals are typically terminated by the pinacoid {001}, sometimes with knobby relief. In addition, some crystals also show well-formed, complex terminations that include hexagonal and dihexagonal dipyrramids (Figs. 1a–1d). Individuals with polygonal cross section (Figs. 1e and 1f) are also observed. Krasheninnikovite crystals are usually up to 1 mm long (rarely reaching 3 mm long), and typically not more than $5 \mu\text{m}$, rarely up to $20 \mu\text{m}$ thick. They are combined in sheaf-like, radiating or open-work matted aggregates (Figs. 1f and 1g) and form nests up to several cubic centimeters in volume filling cavities. In some cases, dense columnar aggregates of krasheninnikovite (consisting of near-parallel individuals: Fig. 1f) up to $1 \times 2 \text{ mm}$ are observed.

Krasheninnikovite, tenorite (black elongate and lamellar crystals, typically strongly distorted, and their clusters up to several millimeters), and thenardite (white thin crusts) overgrow thin crusts of fluorophlogopite and hematite, partially covering the surfaces of basalt fragments inside the fumarole. Minor blödite (colorless aggregates up to 0.5 mm) is a secondary mineral in this assemblage. Krasheninnikovite also occurs as “fluffy” crusts (up to several cm^2) of hair-like crystals up to 1 mm long covering porous scoria in association with euchlorine (crusts of green, euhedral tabular crystals up to 0.5 mm), hematite (iron-black globs up to 0.3 mm) and subordinate tenorite (black clusters of coarse crystals up to 3 mm) and vergasovaite (brown prismatic crystals, perfectly shaped or divergent, up to 0.2 mm).

PHYSICAL PROPERTIES AND OPTICAL DATA

Krasheninnikovite is transparent, colorless in separate crystals and white in aggregates. The streak is white. The luster is vitreous. The mineral is non-fluorescent under ultraviolet rays or an electron beam. It is brittle; the thinnest needles are flexible and elastic. The Mohs hardness is $2\frac{1}{2}\text{--}3$. Cleavage and parting were not observed, the fracture is uneven. Density measured by flotation in heavy liquids ($\text{CHBr}_3 + \text{ethanol}$) is $2.68(1) \text{ g/cm}^3$, the calculated density is 2.67 g/cm^3 . Krasheninnikovite slowly dissolves in H_2O at room temperature.

Krasheninnikovite is optically uniaxial (–), $\omega = 1.500(2)$, $\epsilon = 1.492(2)$. Elongation is negative. Under the microscope, the mineral is colorless.

INFRARED SPECTROSCOPY

Krasheninnikovite powder was mixed with anhydrous KBr (the KBr:mineral ratio is 100:1), pelletized, and analyzed (16 scans) using an ALPHA Fourier transform infrared (FTIR) spectrometer (Bruker Optics) at the resolution of 4 cm^{-1} . The infrared (IR) spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectrum of krasheninnikovite (Fig. 2) is unique and can be used as a good diagnostic tool. Wavenumbers at the maxima of absorption bands (in cm^{-1} , s = strong band) and their assignments are: 1169s, 1130s, 1107s (asymmetric S-O stretching vibrations of SO_4^{2-} groups, degenerate mode), 1008 (symmetric S-O stretching vibrations of SO_4^{2-} groups, non-degenerate mode), 673, 662, 638, 612s, 605 (bending vibrations of SO_4^{2-} groups), 508, 470, 442 (Mg-F, Mg-O, and possibly Ca-O stretching vibrations). The presence of the band of symmetric S-O stretching vibrations at 1008 cm^{-1} indicates a distortion of SO_4 tetrahedra.

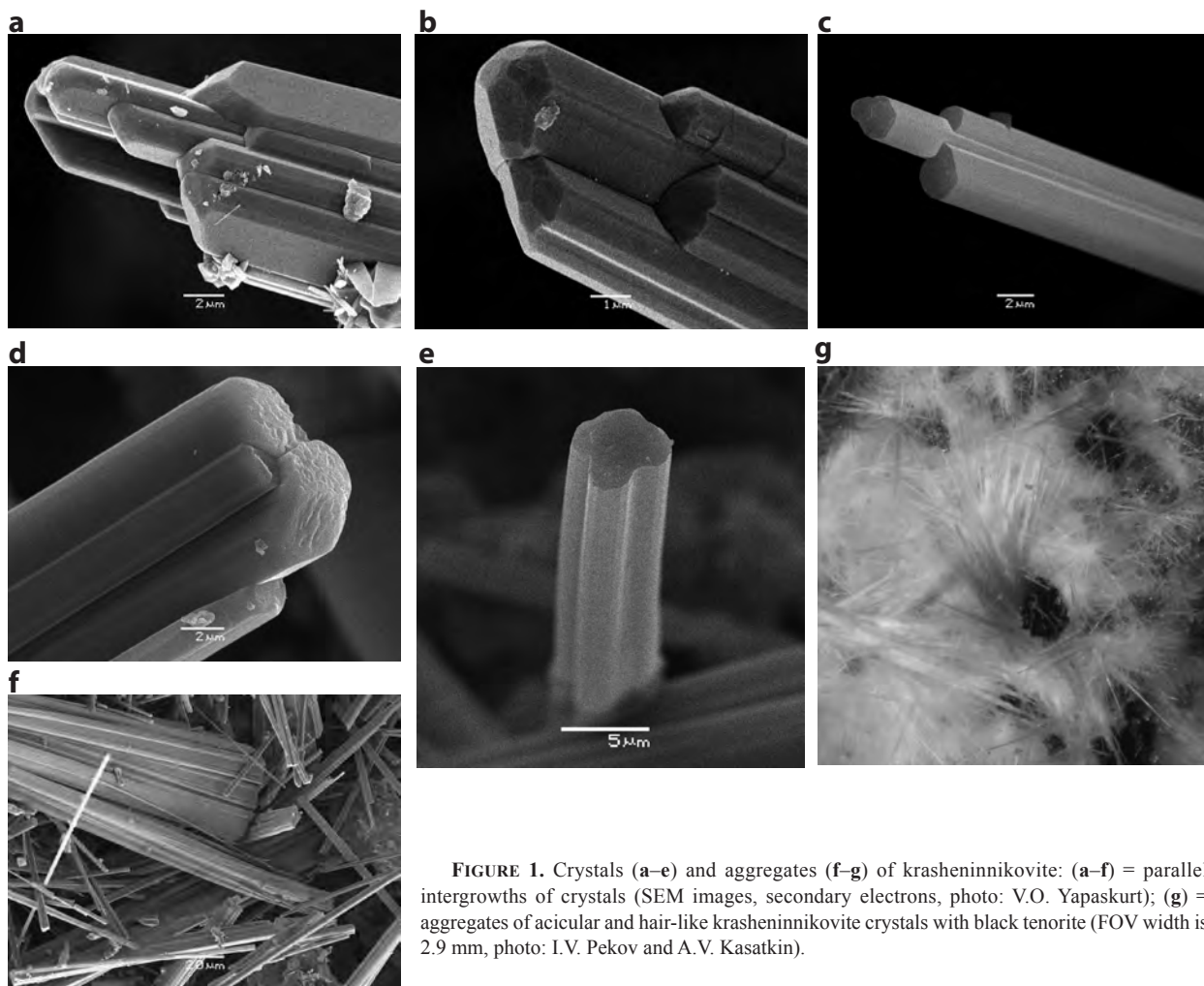


FIGURE 1. Crystals (a–e) and aggregates (f–g) of krashennikovite: (a–f) = parallel intergrowths of crystals (SEM images, secondary electrons, photo: V.O. Yapaskurt); (g) = aggregates of acicular and hair-like krashennikovite crystals with black tenorite (FOV width is 2.9 mm, photo: I.V. Pekov and A.V. Kasatkin).

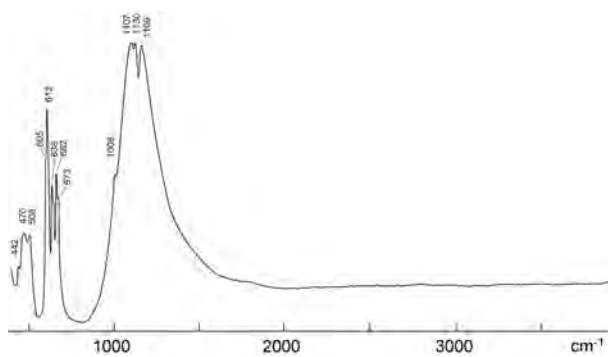


FIGURE 2. IR spectrum of krashennikovite.

Multiple narrow bands corresponding to O–S–O bending vibrations ($600\text{--}680\text{ cm}^{-1}$) reflect a high degree of ordering of cations coordinated by oxygen atoms of SO_4^{2-} groups. Bands of H-, B-, C- and N-bearing groups (in the range $1200\text{--}3800\text{ cm}^{-1}$) are absent in the IR spectrum. Bands in the range $700\text{--}800\text{ cm}^{-1}$ that could belong to BeO_4 tetrahedra are also absent.

CHEMICAL COMPOSITION

Chemical data were obtained using an electron microprobe with combined wavelength-dispersive spectroscopy (WDS) (for F) and energy-dispersive spectroscopy (EDS) (for other elements) modes. A JEOL JSM-6480LV scanning electron microscope (SEM) equipped with an INCA-Energy 350 EDS and an INCA-Wave 500 WDS were used, with an accelerating voltage of 20 kV, a beam current of 1 nA, and a $3\text{ }\mu\text{m}$ beam diameter. The following standards were used: albite (Na, Al), orthoclase (K), anorthite (Ca), MgF_2 (Mg, F), MnO (Mn), olivine (Fe), BaSO_4 (S), and scapolite (Cl). For F, the detection limit is 0.2 wt%. The following program package was used for correct combination of WDS and EDS data: INCA Suite version 4.08 the Microanalysis Suite Issue 17a + SP1 (Oxford Instrument).

The average (5 analyses) chemical composition of krashennikovite (wt%, ranges are in parentheses) is: Na_2O 15.48 (14.0–16.1), K_2O 6.92 (6.6–7.4), CaO 11.51 (10.2–12.3), MgO 9.25 (8.4–9.8), MnO 0.15 (0.05–0.2), FeO 0.04 (0.00–0.07), Al_2O_3 0.23 (0.1–0.4), SO_3 53.51 (52.2–54.2), F 3.22 (3.0–3.6), Cl 0.16 (0.05–0.4), $-\text{O}=(\text{F,Cl})_2$ –1.39, total 99.08. Contents of other elements with atomic numbers >8 are below their detection limits.

The empirical formula of krasheninnikovite, calculated on the basis of 13 anions (O+F+Cl) apfu, is $K_{0.67}Na_{2.27}Ca_{0.93}Mn_{0.01}Mg_{1.04}Al_{0.02}(SO_4)_{3.04}F_{0.76}Cl_{0.02}O_{0.06}$. The idealized formula, taking into account the structure data, is $KNa_2CaMg(SO_4)_3F$, which requires Na_2O 13.57, K_2O 10.31, CaO 12.28, MgO 8.83, SO_3 52.60, F 4.16, $-O=F_2$ -1.75, total 100.00 wt%.

The correctness of the determination of chemical composition, refractive indexes and density of the mineral is confirmed by the very low value of the Gladstone-Dale compatibility index: $1 - (K_p/K_c) = 0.001$ (*superior*).

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

A crystal 1 mm long and 15 μm thick was used for single-crystal studies of krasheninnikovite and its structure model determination. The measurements were carried out at room temperature with an Xcalibur S diffractometer equipped with a CCD detector (MoK α radiation, $\lambda = 0.71073$ Å). A total of 36 947 reflections were obtained in the θ range 2.45 to 30.94°. The hkl range was: $-23 \leq h \leq 23$, $-23 \leq k \leq 23$, $-9 \leq l \leq 9$. The following

dimensions of hexagonal unit cell were found: $a = 16.630(2)$, $c = 6.882(1)$ Å, $V = 1648.2(3)$ Å³, $Z = 6$. Space group $P6_3/mcm$ (no. 193) was determined on the basis of systematic absences. The structure was solved using direct methods and refined with the use of SHELX software package (Sheldrick 2008). Unfortunately, the acicular shape of the crystal did not allow a good agreement between observed and calculated F values [final $R_{hkl} = 0.2908$ for $867 I > 2\sigma(I)$] and further refinement of the structure was performed by the Rietveld method using the model obtained from the single-crystal data.

X-ray powder diffraction data for krasheninnikovite were collected using a STOE-STADI MP diffractometer equipped with a primary curved Ge(111) monochromator (CuK α_1 radiation, $\lambda = 1.54056$ Å). The XRD pattern of the mineral (Table 1) is unique. A total angular scan range of $8.00 \leq 2\theta \leq 89.98^\circ$ was measured using a STOE linear position sensitive detector with exposure time of 4200 s per 5° (2θ). Data treatment and the Rietveld structural analysis were carried out using the Wyriet program package (Schneider 1989). A total of 4100 observed intensity

TABLE 1. XRD data of krasheninnikovite

l_{obs}	d_{obs} (Å)	l_{calc}	d_{calc} (Å)	hkl	l_{obs}	d_{obs} (Å)	l_{calc}	d_{calc} (Å)	hkl
3	8.356	3	8.334	110	5	1.805	5	1.804	080
4	7.234	4	7.217	020	1	1.786	1	1.785	451
1	5.465	2	5.456	120	11	1.771	6, 5	1.770, 1.770	072, 352
12	5.324	12	5.315	111	1	1.764	1	1.764	270
1	4.819	1	4.812	030	2	1.759	2	1.759	243
22	4.286	22	4.280	121	11	1.732	10	1.731	262
6	4.172	6	4.167	220	10	1.726	11	1.725	004
6	4.009	6	4.003	130	5	1.722	4	1.721	153
24	3.613	24	3.609	040	6	1.709	6	1.709	271
17	3.571	17	3.567	221	5	1.673	5	1.673	172
42	3.467	42	3.463	131	3	1.668	3	1.667	550
43	3.454	43	3.450	002	3	1.652	3	1.652	343
5	3.359	6	3.356	012	4	1.642	4	1.641	181
5	3.315	5	3.312	230	1	1.631	1	1.630	253
6	3.191	6	3.188	112	1	1.630	1	1.629	452
100	3.153	100	3.150	140	3	1.625	3	1.624	370
22	3.116	21	3.113	022	3	1.605	3	1.604	090
14	2.988	14	2.986	231	1	1.600	1	1.599	082
4	2.919	3	2.916	122	2	1.591	3	1.590	163
13	2.806	13	2.804	032	3	1.585	2	1.584	134
14	2.780	14	2.778	330	2	1.582	3	1.581	371
3	2.730	3	2.728	240	2	1.557	2	1.556	044
39	2.660	39	2.658	222	4	1.514	4	1.513	144
7	2.616	7	2.614	132	2	1.502	1	1.501	552
2	2.579	2	2.577	331	2	1.493	3	1.493	462
4	2.408	5	2.406	060	1	1.470	1	1.469	372
4	2.375	5	2.373	340	1	1.466	1	1.466	334
1	2.328	1	2.326	142	1	1.463	1	1.463	471
12	2.246	12	2.244	341	3	1.459	3	1.458	244
5	2.203	4	2.201	160	1	1.455	1	1.454	092
14	2.165	15	2.164	332	1	1.444	1	1.444	010, 0
1	2.141	1	2.140	242	9	1.433	9	1.433	282
6	2.121	5	2.120	123	1	1.423	1	1.422	290
1	2.099	2	2.097	161	2	1.403	2	1.402	064
17	2.085	17	2.084	440	4	1.400	4	1.400	273
2	2.074	2	2.073	152	7	1.394	7	1.393	291
2	2.063	1, 1	2.062, 2.062	070, 350	2	1.365	2	1.364	480
7	1.996	7	1.994	133	1	1.362	1	1.362	183
4	1.977	4	1.976	351	1	1.358	1	1.358	164
2	1.975	2	1.973	062	1	1.356	1	1.356	571
1	1.924	1	1.923	261	2	1.339	2	1.338	481
1	1.921	1	1.920	252	2	1.329	2	1.329	444
1	1.913	1	1.912	170	4	1.327	4	1.327	373
6	1.890	6	1.889	233	2	1.324	1, 1	1.323, 1.323	074, 354
5	1.857	5	1.856	162	1	1.311	1	1.310	391
1	1.849	1	1.848	450	1	1.305	1	1.305	135
2	1.844	2	1.843	171	1	1.274	1	1.274	235
2	1.820	2	1.819	360					

points were used in the refinement. The profiles were modeled using a Pearson VII function limited to six FWHM on each side of the peak maximum. The effect of preferential orientation of acicular particles of the mineral on the (001) direction was corrected using the March-Dollase function. The refinement of the krashennikovite structure involved 42 parameters including 8 profile parameters. The (K,Na) position was restrained to be fully occupied. From the data obtained, krashennikovite is hexagonal, with space group $P6_3/mcm$, $a = 16.6682(2)$, $c = 6.9007(1)$ Å, $V = 1660.36(4)$ Å³, $Z = 6$. Final agreement factors are $R_p = 0.0363$, $R_{wp} = 0.0485$, $R_B = 0.0427$, and $R_F = 0.0537$. The structure model of krashennikovite obtained during the single-crystal study was completely confirmed. Atomic coordinates, isotropic displacement parameters, and site multiplicities in the structure are given in Table 2, selected interatomic distances in Table 3. Figure 3 shows observed and calculated powder XRD diagrams for krashennikovite.

The krashennikovite structure (Fig. 4) is based upon a heteropolyhedral pseudo-framework consisting of Ca-centered octahedra, Mg-centered octahedra, and SO₄ tetrahedra. Monovalent cations K and Na are located in cavities of this quasi-framework. MgO₅F octahedra are connected through common vertices occupied by F anions to form chains along [001]. The linkage in the chains is reinforced by the S2O₄ tetrahedra. Pairs of sevenfold Na-centered polyhedra, connected to each other via a common face [O5-F-O5] (Fig. 5), are linked with the chain of MgO₅F octahedra through common edges (Fig. 6). Isolated CaO₆ octahedra share all vertices with SO₄ tetrahedra, two with S2O₄ and four with S1O₄. S1O₄ tetrahedra have a common O5-O5

TABLE 2. Atomic coordinates, isotropic displacement parameters (Å²) and Wyckoff positions in the structure of krashennikovite

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{iso}	Position
Mg	0.5	0	0	0.009(5)	6 <i>f</i>
Ca	0	0.2371(6)	0.25	0.012(4)	6 <i>g</i>
Na	0.7038(8)	0.1158(8)	0.25	0.025(5)	12 <i>j</i>
K	0	0	0	0.027(7)	2 <i>b</i>
(K,Na) = K _{0.72(1)} Na _{0.28(1)} *	2/3	1/3	0	0.053(6)	4 <i>d</i>
S1	0.8117(8)	0	0.25	0.013(5)	6 <i>g</i>
S2	0.5371(8)	0.6843(6)	0.25	0.015(3)	12 <i>j</i>
F	0.5577(13)	0	0.25	0.019(9)	6 <i>g</i>
O1	0.4706(13)	0.7139(11)	0.25	0.014(7)	12 <i>j</i>
O2	0.5237(10)	0.6263(10)	0.4234(19)	0.052(6)	24 <i>i</i>
O3	0.6271(15)	0.7632(15)	0.25	0.052(8)	12 <i>j</i>
O4	0.8230(11)	-0.0789(11)	0.25	0.022(8)	12 <i>j</i>
O5	0.7559(11)	0	0.086(3)	0.025(7)	12 <i>k</i>

* From the structure refinement.

TABLE 3. Selected interatomic distances (Å) in the structure of krashennikovite

Ca octahedron	K polyhedron
Ca-O3 2.27(2) x2	K-O4 3.09(2) x12
Ca-O4 2.31(3) x2	
Ca-O5 2.318(18) x2	(K,Na) polyhedron
<Ca-O> 2.30	(K,Na)-O1 2.65(2) x6
Mg octahedron	S1 tetrahedron
Mg-F 1.98(3) x2	S1-O4 1.42(2) x2
Mg-O2 2.01(2) x4	S1-O5 1.47(2) x2
Na polyhedron	
Na-F 2.226(17)	S2 tetrahedron
Na-O3 2.41(3)	S2-O1 1.42(3)
Na-O1 2.52(2)	S2-O2 1.483(15) x2
Na-O2 2.552(16) x2	S2-O3 1.42(2)
Na-O5 2.73(2) x2	

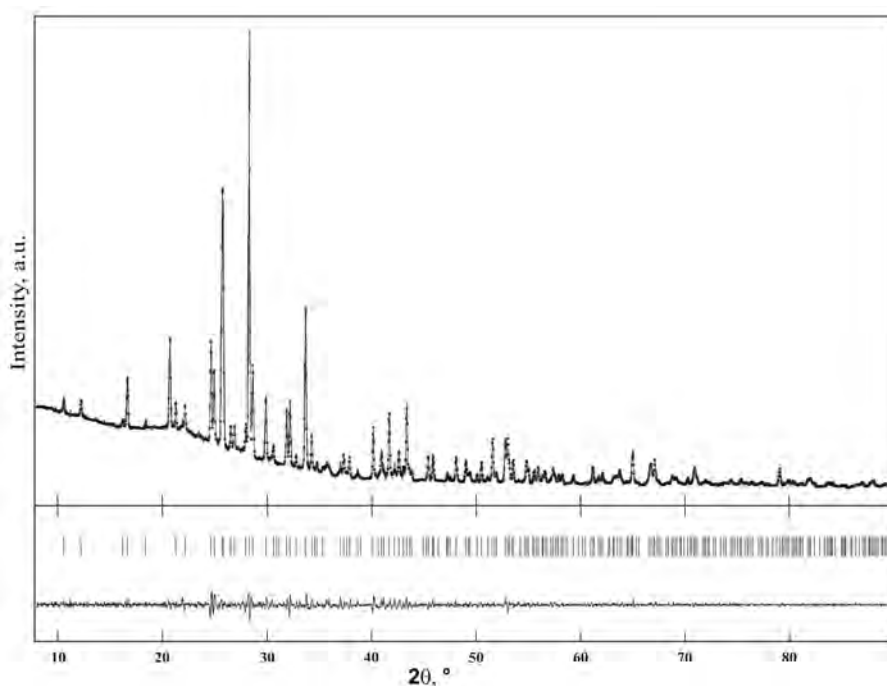


FIGURE 3. Observed and calculated powder XRD patterns of krashennikovite. The crosses are the calculated data, the solid line is the observed pattern, and vertical bars mark all possible Bragg reflections. The difference between the observed and calculated patterns is shown at the bottom.

edge with NaO_6F polyhedra. Potassium cations are located in channels along the c axis. Hexagonal KO_{12} prisms connected to each other by common faces and distorted $(\text{K},\text{Na})\text{O}_6$ octahedra form columns of two types (Fig. 7).

DISCUSSION

The stoichiometry of krashennikovite, $\text{KNa}_2\text{CaMg}(\text{SO}_4)_3\text{F}$, is the same as that of apatite-supergroup minerals: $M_5(\text{TO}_4)_3X$ with species-defining $M = \text{Ca}^{2+}, \text{Pb}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Mn}^{2+}, \text{Na}^+, \text{REE}^{3+}, \text{Bi}^{3+}$; $T = \text{P}^{5+}, \text{As}^{5+}, \text{V}^{5+}, \text{Si}^{4+}, \text{S}^{6+}, \text{B}^{3+}$; $X = \text{F}^-, (\text{OH})^-, \text{Cl}^-$ (Pasero et al. 2010). Krashennikovite crystallizes in the hexagonal system (the most common for apatite-type compounds) but its space group is $P6_3/mcm$, i.e., krashennikovite is more highly symmetric in comparison with the apatite structure archetype (space group $P6_3/m$). The unit-cell dimensions also show the relationship of krashennikovite to apatite supergroup members; the dimension of the c parameter (6.90 Å) is within the typical range of the c parameter of apatites, whereas the a parameter (16.68 Å) can be represented as $a'\sqrt{3}$, from which calculated $a' = 9.63$ Å that is within typical range of the c parameter of apatites (White et al. 2005). Moreover, the synthetic compound $(\text{Cd},\text{Mn})_5(\text{PO}_4)_3\text{OH}$ (space group $P6_3$) with the superstructure based upon the apatite-type structure has unit-cell dimensions close to those of krashennikovite: $a = 16.20$, $c = 6.65$ Å (Hata and Marumo 1983).

However the comparison of crystal structures of krashennikovite and apatite-type compounds, including $(\text{Cd},\text{Mn})_5(\text{PO}_4)_3\text{OH}$,

clearly shows that their relationship is very remote. Figure 8 demonstrates that their anion sublattices (arrangements of tetrahedra $[\text{TO}_4]$ and additional anions X) are quite different. The similarity in unit-cell parameters is caused only by the similar arrangement of the positions of the largest cations $[\text{K}$ and $(\text{K},\text{Na})]$ in krashennikovite and X anions in apatite-type compounds. Figure 9 shows the arrangements of X anions in fluorapatite ($X^- = \text{F}$: Hughes et al. 1990) and $(\text{Cd},\text{Mn})_5(\text{PO}_4)_3\text{OH}$ ($X^- = \text{OH}$: Hata and Marumo 1983) in comparison with the arrangement of the largest cations occupying two different sites $[\text{K}$ and $(\text{K},\text{Na})]$ in krashennikovite (Table 2, Fig. 4) and the relations between their unit cells. In this aspect, the structural motif of krashennikovite can be considered as an “antiapatite motif”: the X anion sublattice of apatites is close to the K cation sublattice of krashennikovite (Fig. 7). No other common crystal-chemical features between the new mineral and apatite-type compounds were found. The X-ray powder-diffraction patterns of krashennikovite and apatite-like minerals and synthetic compounds are quite different, especially in relative intensities of reflections.

Thus, krashennikovite is unique in its crystal structure, and there are no close examples among minerals and synthetic compounds. One of its most remarkable features is the ordering

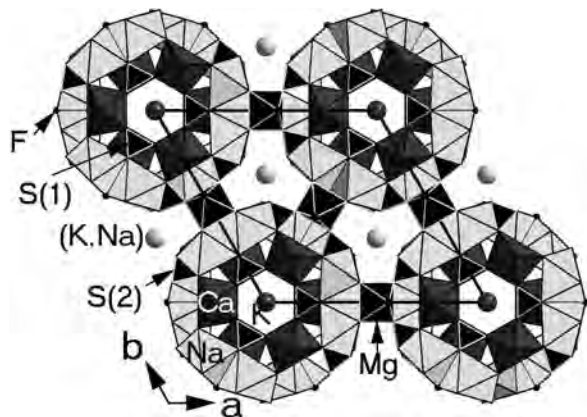


FIGURE 4. Crystal structure of krashennikovite (a - b projection). The unit cell is outlined.

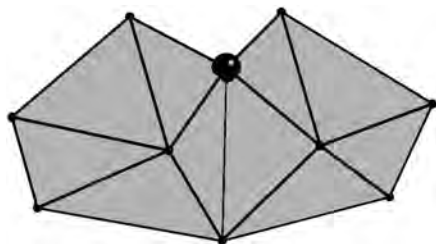


FIGURE 5. Pair of face-connected NaO_6F polyhedra (the $\text{Na}_2\text{O}_{10}\text{F}$ group) in the structure of krashennikovite. The F atom is shown as a sphere.

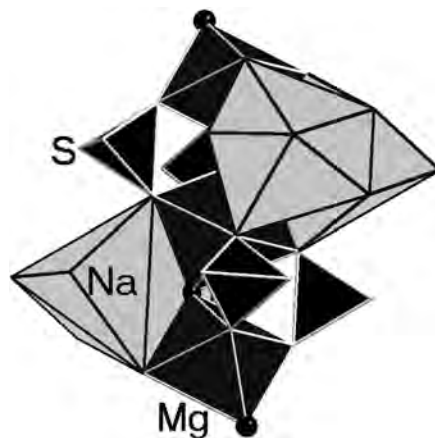


FIGURE 6. Fragment of the structure of krashennikovite formed by S_2O_4 tetrahedra, chains of MgO_5F octahedra and pairs of NaO_6F polyhedra. F atoms are shown as spheres.

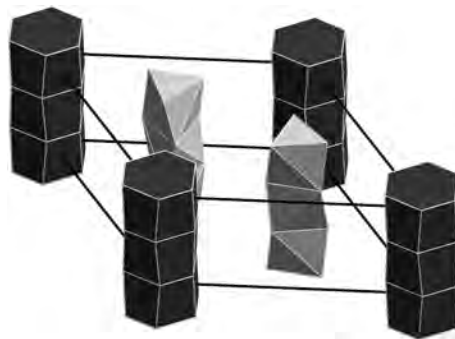


FIGURE 7. Columns of face-connected, distorted hexagonal KO_{12} prisms and columns of edge-connected distorted $(\text{K},\text{Na})\text{O}_6$ octahedra in the structure of krashennikovite. The unit cell is outlined.

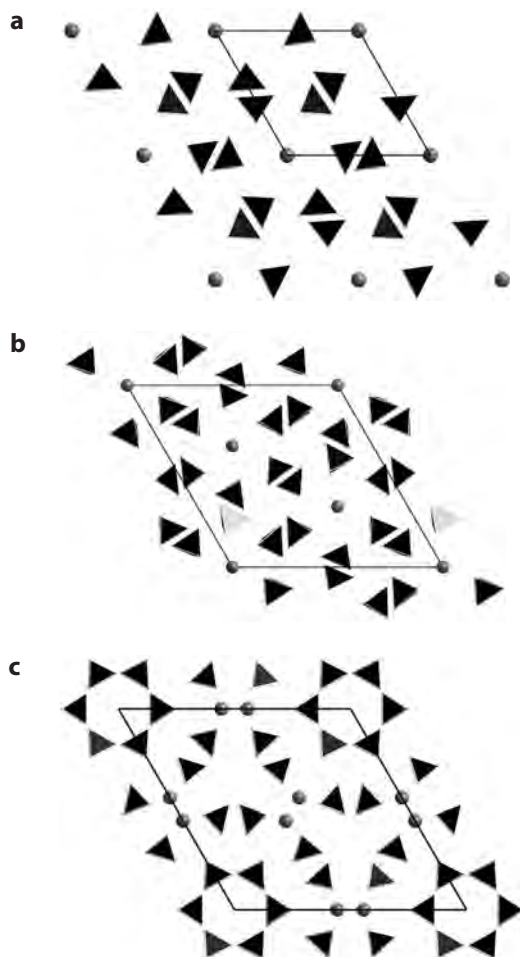


FIGURE 8. Anion sublattices of fluorapatite (a) drawn from the data by Hughes et al. (1990), $(\text{Cd,Mn})_5(\text{PO}_4)_3\text{OH}$ (b) drawn from the data by Hata and Marumo (1983), and krasheninnikovite (c) in the a - b projection. PO_4^{3-} or SO_4^{2-} anions are shown as tetrahedra, F^- or OH^- anions as circles. The unit cells are outlined; the a unit-cell parameter values for fluorapatite, $(\text{Cd,Mn})_5(\text{PO}_4)_3\text{OH}$ and krasheninnikovite are 9.46, 16.20, and 16.68 Å, respectively.

of four types of metal cations in five sites with different coordination numbers, coordination polyhedra and cation-anion distances (Table 3; Figs. 4–7). No other natural and synthetic sulfates of K, Na, Ca, and Mg with ordered distribution of all these cations have been found in the literature and databases. In conclusion, note that space group $P6_3/mcm$ is extremely rare for minerals.

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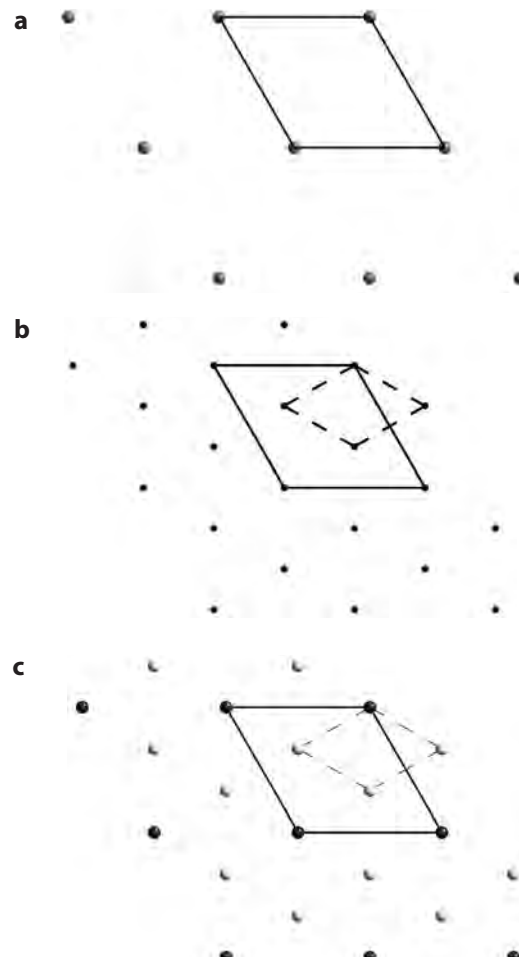


FIGURE 9. The X anion sublattices of fluorapatite (a) $X^- = \text{F}$, drawn from the data by Hughes et al. (1990), and $(\text{Cd,Mn})_5(\text{PO}_4)_3\text{OH}$ (b) $X^- = \text{OH}$, drawn from the data by Hata and Marumo (1983), and the largest cations sublattice of krasheninnikovite (c). Potassium sites are shown as dark circles; (K,Na) sites as light circles in the a - b projection. The unit cells are outlined. Dotted line shows the pseudo-cells corresponding to the apatite-type unit cell for $(\text{Cd,Mn})_5(\text{PO}_4)_3\text{OH}$ and krasheninnikovite.

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