

Alexkhomyakovite, $K_6(Ca_2Na)(CO_3)_5Cl \cdot 6H_2O$, a new mineral from the Khibiny alkaline complex, Kola peninsula, Russia

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Abstract: The new mineral alexkhomyakovite $K_6(Ca_2Na)(CO_3)_5Cl \cdot 6H_2O$ (IMA2015-013) occurs in a peralkaline pegmatite at Mt. Koashva, Khibiny alkaline complex, Kola peninsula, Russia. It is a hydrothermal mineral associated with villiaumite, natrite, potassic feldspar, pectolite, sodalite, biotite, lamprophyllite, titanite, fluorapatite, wadeite, burbankite, rasvumite, djerfisherite, molybdenite and an incompletely characterized Na–Ca silicate. Alexkhomyakovite occurs as equant grains up to 0.2 mm, veinlets up to 3 cm long and up to 1 mm thick and fine-grained aggregates replacing delhayelite. Alexkhomyakovite is transparent to translucent, colourless, white or grey, with vitreous to greasy lustre. It is brittle, the Mohs hardness is *ca.* 3. No cleavage was observed, the fracture is uneven. $D_{meas} = 2.25(1)$, $D_{calc} = 2.196 \text{ g cm}^{-3}$. Alexkhomyakovite is optically uniaxial (–), $\omega = 1.543(2)$, $\varepsilon = 1.476(2)$. The infrared spectrum is reported. The chemical composition [wt%, electron microprobe data, CO_2 and H_2O contents calculated for 5 (CO_3) and 6 (H_2O) per formula unit (*pfu*), respectively] is: Na_2O 4.09, K_2O 35.72, CaO 14.92, MnO 0.01, FeO 0.02, SO_3 0.11, Cl 4.32, CO_2 28.28, H_2O 13.90, $-O=Cl$ –0.98, total 100.39. The empirical formula calculated on the basis of 9 metal cations *pfu* is $K_{5.90}Ca_{2.07}Na_{1.03}(CO_3)_5(SO_4)_{0.01}O_{0.05}Cl_{0.95} \cdot 6H_2O$. The numbers of CO_3 groups and H_2O molecules are based on structure data. Alexkhomyakovite is hexagonal, $P6_3/mcm$, a 9.2691(2), c 15.8419(4) Å, V 1178.72(5) Å³ and $Z = 2$. The strongest reflections of the powder X-ray diffraction pattern [d Å(hkl)] are: 7.96(27)(002), 3.486(35)(113), 3.011(100)(114), 2.977(32)(211), 2.676(36)(300), 2.626(42)(213, 115), 2.206(26)(311) and 1.982(17)(008). The crystal structure (solved from single-crystal X-ray diffraction data, $R = 0.0578$) is unique. It is based on (001) heteropolyhedral layers of pentagonal bipyramids $(Ca,Na)O_5(H_2O)_2$ interconnected *via* carbonate groups of two types, edge-sharing ones and vertex-sharing ones. Ca and Na are disordered. Ten-fold coordinated K cations centre $KO_6Cl(H_2O)_3$ polyhedra on either side of the heteropolyhedral layer. A third type of carbonate group and Cl occupy the interlayer. The mineral is named in honour of the outstanding Russian mineralogist Alexander Petrovich Khomyakov (1933–2012).

Key-words: alexkhomyakovite; new mineral; potassium carbonate hydrate; crystal structure; peralkaline pegmatite; Koashva apatite deposit; Khibiny alkaline complex; Kola peninsula.

1. Introduction

Unlike sodium-bearing carbonates which are numerous in nature and for some of them form large deposits, carbonate minerals with species-defining potassium are very rare and represented by a small number of mineral species. Only eight such minerals were reported until now as valid species, namely baylissite $K_2Mg(CO_3)_2 \cdot 4H_2O$, bütschliite $K_2Ca(CO_3)_2$ (trigonal), fairchildite $K_2Ca(CO_3)_2$ (hexagonal),

kalicinite $KHCO_3$ and four uranyl-bearing species: agricoloite $K_4(UO_2)(CO_3)_3$, grimselite $K_3Na(UO_2)(CO_3)_5 \cdot H_2O$, línekite $K_2Ca_3[(UO_2)(CO_3)_3]_2 \cdot 7H_2O$, and braunerite $K_2Ca_3[(UO_2)(CO_3)_3]_2 \cdot 7H_2O$ (IMA-CNMNC list of minerals, 2017). All the potassium-uranyl carbonates are known in the oxidation zone of complex deposits belonging to the famous Jáchymov ore district in Bohemia, Czech Republic (Plášil *et al.*, 2017). Three of them are Jáchymov endemics, only grimselite is also known from another locality, the

Gerstenegg-Sommerloch cable tunnel in the Grimsel area in Switzerland. At Gerstenegg-Sommerloch, grimselite was found together with baylissite and both of these are secondary minerals in fractures of granodiorite (Walenta, 1976). The majority of occurrences of U-free K-bearing carbonates in nature are reported from the mineral-forming systems related to plants or animals: ash of burned trees, cave deposits, *etc.* (Anthony *et al.*, 2003). The K^+ and CO_3^{2-} ions are abundant constituents in many alkaline rocks and their derivatives, however, among potassium carbonates only kalincite was mentioned for alkaline formations, as a minor, likely supergene phase for three carbonatite localities: St.-Honoré in Québec, Canada (Fournier, 1993), Oldoinyo Lengai volcano in Tanzania (Zaitsev & Keller, 2006), and Alnö in Sweden (Sandström *et al.*, 2010).

This paper is devoted to the first potassium carbonate found in a mineral assemblage of undoubtedly endogenous origin. This new mineral species was found in a peralkaline pegmatite in the Khibiny alkaline complex in Kola peninsula and named alexkhomyakovite (Cyrillic: алексомяковит) in honour of the outstanding Russian mineralogist Alexander Petrovich Khomyakov (1933–2012), a well-known specialist in the mineralogy of alkaline rocks and, especially, pegmatites and hydrothermal assemblages related to peralkaline rocks. He worked in the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements (IMGRE) in Moscow. Dr. Khomyakov made a great contribution to the mineralogy of the Khibiny and Lovozero alkaline complexes of Kola peninsula. During 45 years of his studies on Khibiny and Lovozero, Dr. Khomyakov discovered in these two alkaline complexes 73 (!) new mineral species as a senior author and co-authored the description of another 12 new minerals from Khibiny and Lovozero. Dr. Khomyakov is the author of a fundamental monograph on the mineralogy of hyperagpaitic alkaline rocks based mainly on his studies of Khibiny and Lovozero and published both in Russian (Khomyakov, 1990) and in English (extended and revised edition: Khomyakov, 1995).

The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2015-013). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 95005.

2. Occurrence and general appearance

The new mineral was identified in the material collected by the authors (IVP and ISL) in June 2014 in the southern area of the Koashva open pit situated at Mt. Koashva, in the south-east part of the Khibiny alkaline complex. This huge open pit, belonging to the Vostochnyi (Eastern) mine of the Apatit JSC, operates the Koashva apatite deposit. From the mineralogical point of view, Koashva is famous for the numerous peralkaline pegmatites mainly located on the margin between urtite and nepheline-apatite rocks. These pegmatites demonstrate very diverse and specific mineralogy: more than 160 minerals are found there, including 27

species for which Koashva is the type locality. Data on these pegmatites were summarized by Pekov & Nikolaev (2013).

Alexkhomyakovite was found in several pegmatite lumps. Unfortunately, we could not observe this pegmatite body *in situ*: it was uncovered in the zone of active mining operations. The new mineral is associated with villiaumite, natrite, potassic feldspar, pectolite, sodalite, biotite, lamprophyllite, titanite, fluorapatite, wadeite, burbankite, rasvumite, djerfisherite, molybdenite and an incompletely characterized Na–Ca silicate. White powdery aggregates of thermonatrite, villiaumite, fluorite and sylvite are products of the supergene alteration of natrite, alexkhomyakovite and primary red villiaumite, which are unstable under atmosphere conditions.

Alexkhomyakovite occurs mainly inside massive polymineralic pseudomorphs after large (up to $3 \times 5 \times 15$ cm in size) delhayelite crystals. Delhayelite was completely replaced by other minerals, however, the nature of the proto-phase of these pseudomorphs is undoubtedly determined due to their characteristic morphology and bulk chemistry (Pekov *et al.*, 2012). Alexkhomyakovite is an important constituent of these pseudomorphs: in some areas (up to 2×4 cm) it makes up 30–40 vol% (Fig. 1); in all studied samples the new mineral occurs in intimate intergrowths with other phases, mainly pectolite, villiaumite, potassic feldspar and an incompletely characterized Na–Ca silicate (Fig. 2). Monomineralic areas of alexkhomyakovite in such aggregates, even the richest in it, are typically not larger than 10×20 μ m.

Massive veinlets (up to 3 cm long and up to 1 mm thick) with alexkhomyakovite as the major component are observed in the border zone of some abovementioned pseudomorphs after delhayelite, usually at their contact with natrite nests (Fig. 3). These veinlets contain at least 15–20 vol% of inclusions of fine-grained villiaumite and fibrous lamprophyllite (Fig. 4) or/and pectolite.

In nests of beige or yellowish granular natrite, alexkhomyakovite was found as separate grains and their clusters, sporadically abundant, included in massive natrite. Both alexkhomyakovite individuals (up to 0.2 mm, rarely up to 1 mm across) and natrite matrix are saturated with microinclusions of pectolite, lamprophyllite (Fig. 5), and/or villiaumite.

Well-shaped crystals of alexkhomyakovite were not observed. Sections of some grains of the new minerals included in natrite show contours corresponding to coarse prismatic, equant or tabular individuals (Fig. 5). Most commonly alexkhomyakovite occurs as massive fine-grained aggregates forming intimate intergrowths with other minerals (Figs. 1–4).

3. Physical properties and optical data

Alexkhomyakovite is transparent to translucent, colourless in individuals and white or grey in massive aggregates, with a white streak and a vitreous to greasy lustre. The mineral is brittle, with a Mohs hardness of *ca.* 3. No cleavage or parting was observed and the fracture is uneven. Density

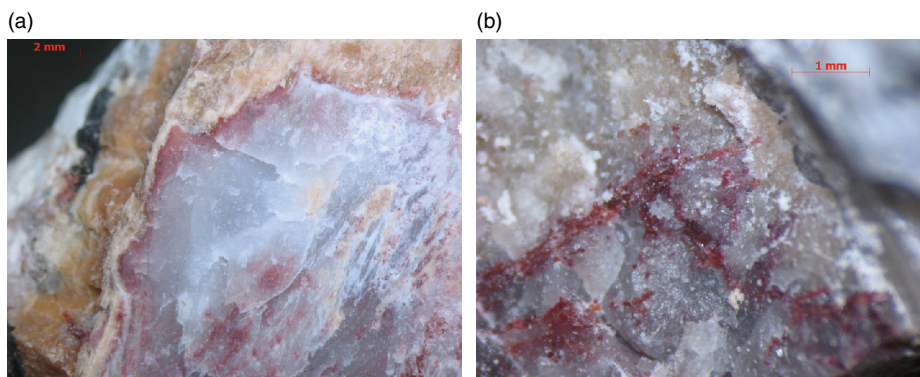


Fig. 1. Massive, fine-grained aggregates of alexkhomyakovite intimately associated with other minerals inside pseudomorphs after delhayelite: a – pale greyish nest consisting mainly of alexkhomyakovite, pectolite and potassic feldspar and rimmed by red villiaumite and beige-yellowish natrite; b – grey aggregate of alexkhomyakovite saturated by micro-inclusions of fibrous lamprophyllite (see Fig. 4) and cross-cut by red villiaumite veinlets. Field of view (FOV): a – 14 mm, b – 5.7 mm. Photo: I.V. Pekov & A.V. Kasatkin.

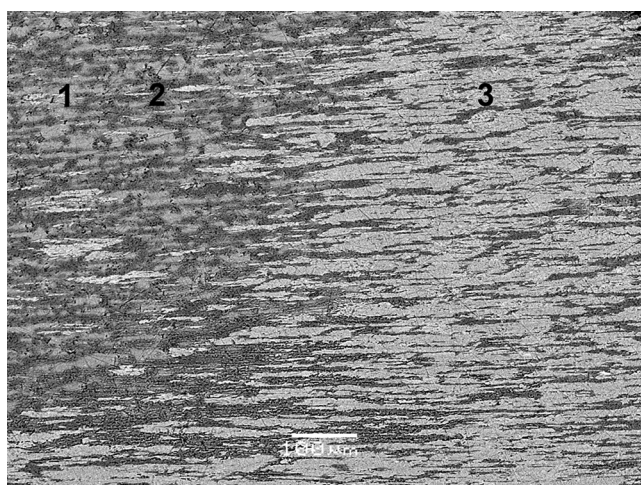


Fig. 2. Massive aggregate of alexkhomyakovite (1: medium grey), villiaumite (2: dark grey) and an incompletely characterized Na–Ca silicate (3: light grey) replacing delhayelite. Polished section, SEM (BSE) image. FOV: 2.2 mm.

measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.25(1), and the density calculated using the empirical formula and single-crystal unit-cell data is 2.196 g cm^{-3} . The difference between measured (higher) and calculated density values could be caused by the presence in the studied sample of micro-inclusions of silicate minerals with higher densities than alexkhomyakovite.

The new mineral is optically uniaxial (–), $\omega = 1.543(2)$, $\varepsilon = 1.476(2)$ (589 nm). Under the microscope alexkhomyakovite is colourless and non-pleochroic. Distinct pseudo-absorption is observed in plane-polarized light with the colour change from colourless to greyish. This is a result of the large birefringence (0.067) of the mineral.

4. Infrared spectroscopy

In order to obtain an IR absorption spectrum, alexkhomyakovite powder was mixed with anhydrous KBr, pelletized, and analysed using an ALPHA FTIR spectrometer (Bruker

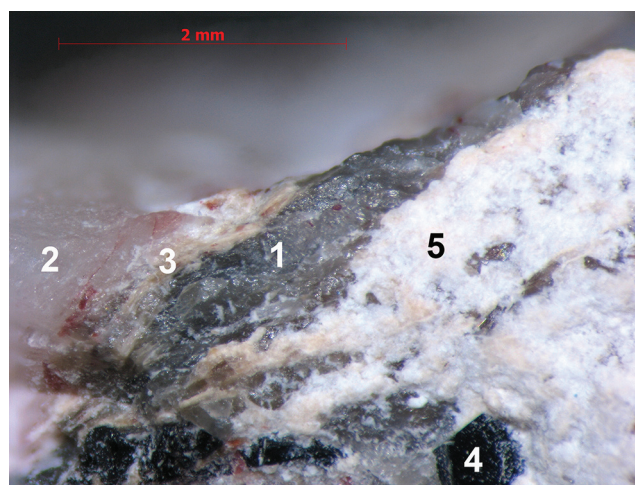


Fig. 3. Grey veinlet consisting mainly of alexkhomyakovite (1) on the border between a pseudomorph after delhayelite and surrounding natrite aggregate. The pale greyish substance (2) in the pseudomorph consists mainly of alexkhomyakovite, pectolite and potassic feldspar (see also Fig. 1a). Beige banded areas (3) are strongly saturated by fibrous lamprophyllite, which also forms abundant inclusions in the alexkhomyakovite veinlet (1): see Fig. 4. Black spots (4) are biotite crystals. White area (5) is a natrite aggregate covered by white efflorescence of the supergene thermonatrite. FOV: 4.4 mm. Photo: I.V. Pekov & A.V. Kasatkin.

Optics) at a resolution of 4 cm^{-1} ; 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectrum of alexkhomyakovite (Fig. 6) significantly differs from the IR spectra of all other carbonate minerals and can be a good diagnostic tool. Bands in the range $2900\text{--}3400 \text{ cm}^{-1}$ correspond to O–H-stretching vibrations of H_2O molecules forming rather strong hydrogen bonds. Most probably, the strongest bands in this region (at 2920 and 3156 cm^{-1}) correspond to symmetric and antisymmetric vibrations of symmetric H_2O molecules coordinating Ca^{2+} . The shoulder at 1600 cm^{-1} is assigned to H–O–H bending vibrations of H_2O molecules. Strong bands of the

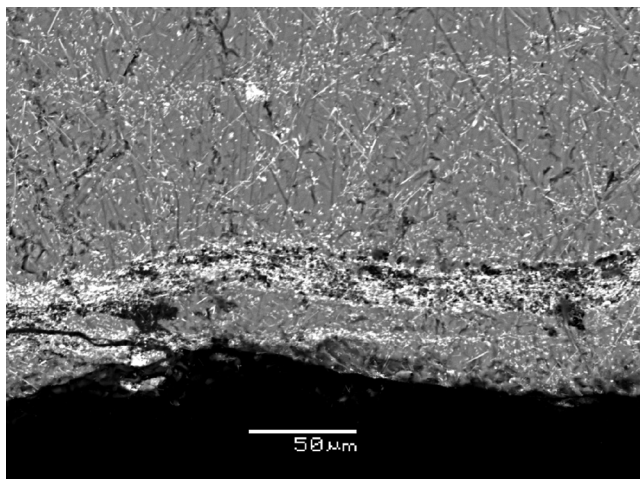


Fig. 4. Fragment of an alexkhomyakovite veinlet (see Fig. 3, area 1) with abundant micro-inclusions of lamprophyllite (white phase). Polished section, SEM (BSE) image.

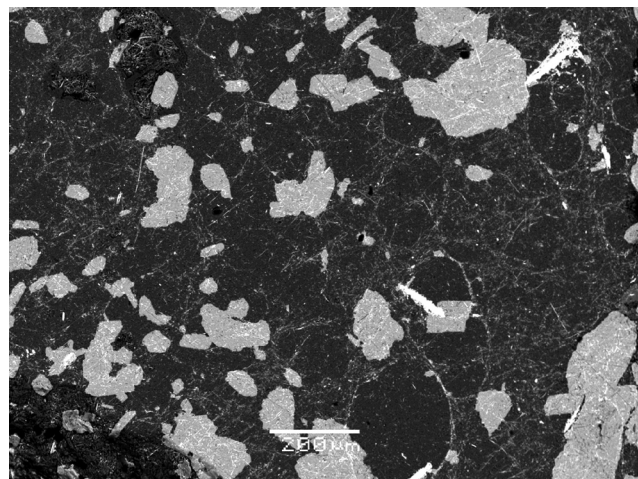


Fig. 5. Massive, granular aggregate of natrite (dark grey) with numerous inclusions of alexkhomyakovite (light grey). Abundant micro-inclusions of lamprophyllite (white phase) are present in both carbonates. Polished section, SEM (BSE) image. FOV: 1.4 mm.

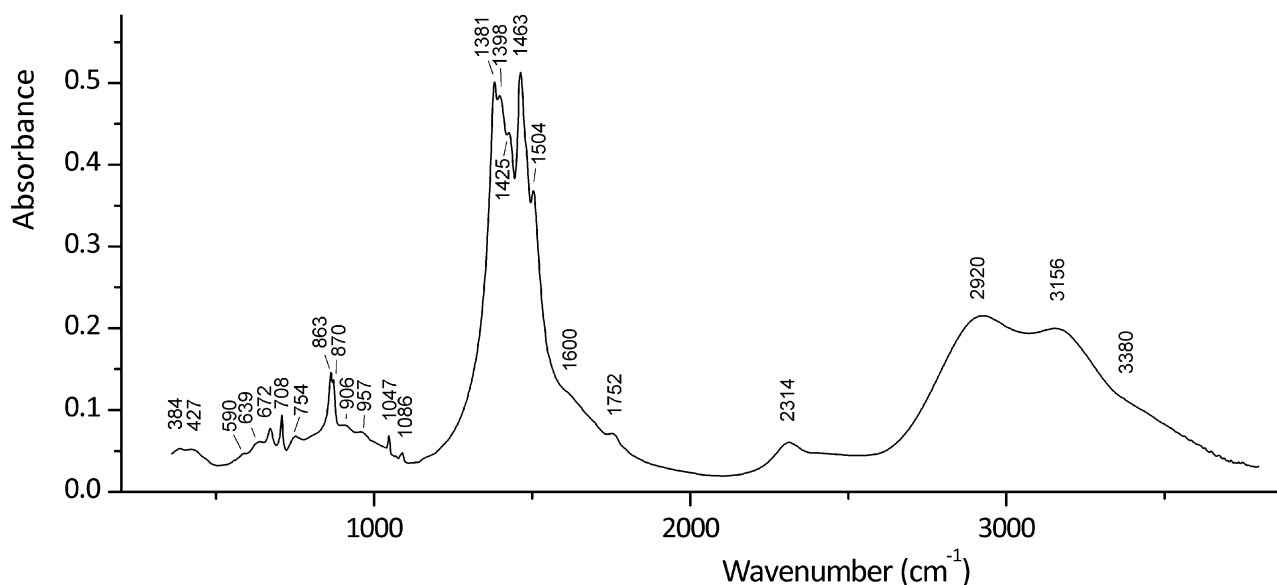


Fig. 6. The IR spectrum of alexkhomyakovite.

degenerate antisymmetric C–O-stretching vibrations are in the range from 1300 to 1550 cm^{-1} and weak bands of the non-degenerate symmetric C–O-stretching vibrations are centered at 1047 and 1086 cm^{-1} .

Bands in the ranges from 860 to 870 and from 670 to 760 cm^{-1} are to be assigned to in-plane and out-of-plane bending vibrations of CO_3^{2-} anions, respectively. Bands at 957, 906, 639 and 590 cm^{-1} are assigned to librational vibrations of H_2O molecules. Low-frequency bands (below 430 cm^{-1}) correspond to lattice modes involving Ca–O-stretching vibrations. The band at 2314 cm^{-1} could be explained by a superposition of combination modes involving antisymmetric C–O-stretching and in-plane bending vibrations of CO_3^{2-} anions. The weak band at 1752 cm^{-1}

corresponds to the overtone of out-of-plane bending vibrations of CO_3^{2-} anions.

5. Chemical data

The chemical composition of alexkhomyakovite was studied using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA and a beam diameter of 3 μm . The following standards were used: NaCl (Na, Cl), microcline (K),

Table 1. Powder X-ray diffraction data (d in Å) of alexkhomyakovite.

I_{obs}	d_{obs}	I_{calc}^*	d_{calc}^{**}	hkl
27	7.96	19	7.921	002
1	4.629	0.5	4.635	110
12	3.981	4, 7	4.000, 3.960	112, 004
11	3.558	2, 8	3.580, 3.552	202, 104
35	3.486	34	3.483	113
100	3.011	100	3.011	114
32	2.977	36	2.980	211
6	2.829	5, 4	2.833, 2.819	212, 204
36	2.676	44	2.676	300
42	2.626	8, 27, 34	2.640, 2.631, 2.616	006, 213, 115
1	2.513	0.5	2.508	106
12	2.411	17	2.409	214
3	2.319	5	2.317	220
4	2.298	5	2.294	116
2	2.219	5	2.217	304
26	2.206	3, 35	2.206, 2.205	206, 311
2	2.144	3	2.143	312
5	2.123	7	2.122	223
1	2.049	0.5	2.051	313
10	2.006	15, 1	2.007, 2.000	400, 224
17	1.982	26	1.980	008
8	1.942	4, 10	1.945, 1.941	402, 314
4	1.873	2, 8	1.879, 1.870	306, 225
11	1.827	16, 4	1.829, 1.822	321, 315
7	1.814	10	1.814	217
1	1.790	1	1.790	404
2	1.745	2, 0.5	1.742, 1.741	226, 411
2	1.707	1, 3	1.710, 1.702	412, 316
6	1.674	12	1.670	324
12	1.594	12	1.592	308
7	1.588	12	1.587	317
1	1.576	1	1.573	502
1	1.545	1	1.545	330
1	1.537	0.5	1.538	331
2	1.524	2	1.523	219
3	1.515	3, 0.5, 0.5	1.517, 1.516, 1.510	420, 332, 326
1	1.491	0.5, 0.5	1.490, 1.488	422, 504
2	1.462	1, 1	1.460, 1.458	416, 423
2	1.440	0.5	1.442	510
4	1.434	5, 6	1.436, 1.428	511, 327
4	1.412	8	1.410	408
1	1.393	2	1.391	513
2	1.384	3	1.381	319
2	1.379	3	1.375	1.1.11
2	1.357	6	1.355	514
2	1.319	1	1.320	430
1	1.286	1	1.285	520
3	1.223	1, 5, 2	1.223, 1.223, 1.221	2.2.11, 524, 611
1	1.209	1, 1	1.211, 1.210	2.1.12, 612

Notes: *For the calculated pattern, only reflections with intensities ≥ 0.5 are given;

**For the unit-cell parameters calculated from single-crystal data.

CaMoO₄ (Ca), Mn (Mn), and CuFeS₂ (Fe, S). The contents of other elements with atomic numbers higher than carbon are below detection limits. The absence of Li, Be and B in detectable amounts is confirmed by both structure data and IR spectrum.

Although the new mineral is common in the pegmatite, it is impossible to separate pure material in the amount sufficient for direct quantitative determinations of CO₂ and

H₂O; in all examined samples alexkhomyakovite forms intimate intergrowths with other minerals and monomineralic or almost monomineralic areas are tiny (Figs. 2, 4 and 5). Consequently, the contents of CO₂ and H₂O were calculated based on the crystal-structure data (see below). These calculated values demonstrate a good agreement with the analytical total derived from the constituents measured using the electron microprobe. The correctness of the calculation is

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

Idealized formula	$K_6(Ca_2Na)(CO_3)_5Cl \cdot 6H_2O$
Formula mass*	780.66
Temperature, K	293(2)
Radiation and wavelength, Å	MoK α ; 0.71073
Crystal system, space group, Z	Hexagonal, $P6_3/mcm$; 2
Unit-cell dimensions, Å	$a = 9.2691(2)$, $c = 15.8419(4)$
V , Å ³	1178.72(5)
Absorption coefficient μ , mm ⁻¹ *	1.760
F_{000} *	783
Crystal size, mm ³	0.09 × 0.18 × 0.20
Diffractometer	Xcalibur S CCD
θ range for data collection, °	4.40–28.26
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-21 \leq l \leq 21$
Reflections collected	18 372
Independent reflections	557 ($R_{int} = 0.0866$)
Independent reflections $I > 2\sigma(I)$	555
Absorption correction	Gaussian [Numerical correction based on Gaussian integration over a multifaceted crystal model]
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	45
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0578$, $wR2 = 0.1565$
R indices (all data)	$R1 = 0.0581$, $wR2 = 0.1568$
GoF	1.217
Largest diff. peak and hole, e/Å ³	0.68 and -0.86

Note: *Calculated on the basis of (Ca,Na) position occupied by 0.65Ca and 0.35Na, according to structural data.

Table 3. Coordinates and equivalent displacement parameters (U_{eq} , in Å²) of atoms and site multiplicities (Q) for alexkhomyakovite.

Site	x	y	z	U_{eq}	Q
(Ca,Na)=Ca _{0.655(10)} Na _{0.35}	0.6119(2)	0.0	0.25	0.0117(6)	6
K	0.0	0.72353(18)	$-0.12352(9)$	0.0280(5)	12
C(1)	0.3333	0.6667	0.0	0.024(2)	4
C(2)	0.3333	0.6667	0.25	0.0144(19)	4
C(3)	0.0000	0.0000	0.75	0.014(3)	2
O(1)	0.4830(5)	0.6910(6)	0.25	0.0203(10)	12
O(2)	0.2526(3)	0.7474(3)	0.0	0.0354(13)	12
O(3)	0.8623(7)	0.0	0.25	0.0290(17)	6
O(4)=O _w	0.6030(7)	0.0	0.3955(3)	0.0325(13)	12
H*	0.563(7)	$-0.0849(12)$	0.4279(13)	0.035(17)**	24
Cl	0.0	0.0	0.0	0.0247(9)	2

Notes: *The position of H atom was found from difference Fourier synthesis, freely refined and at the last stages of refinement the O(4)–H distance was restrained at 0.85 Å;

** U_{iso} .

also indicated by a low Gladstone-Dale compatibility index value (Mandarino, 1981): $1 - (K_p/K_c) = -0.019$, superior, if $D(\text{meas.})$ is used, or -0.044 , good, if $D(\text{calc.})$ is used.

The chemical composition of alexkhomyakovite (average of 17 spot analyses; wt%, with range/standard deviation given in parenthesis) is: Na₂O 4.09 (3.73–4.48/0.19), K₂O 35.72 (35.20–36.33/0.33), CaO 14.92 (14.49–15.34/0.28), MnO 0.01 (0.00–0.03/0.01), FeO 0.02 (0.00–0.06/0.02), SO₃ 0.11 (0.00–0.38/0.11), Cl 4.32 (4.17–4.40/0.06), CO₂ (calc.) 28.28, H₂O (calc.) 13.90, $-O=Cl$ -0.98 , total 100.39 wt%. CO₂ and H₂O contents were calculated for 5 (CO₃) and 6 (H₂O) per formula unit (*pfu*), respectively.

The empirical formula calculated on the basis of 9 metal cations *pfu* is K_{5.90}Ca_{2.07}Na_{1.03}(CO₃)₅(SO₄)_{0.01}O_{0.05}Cl_{0.95}·6H₂O. We avoid to use an anionic basis of calculation because of the absence of reliable quantitative data on the minor constituents probably substituting Cl⁻ in its position: O²⁻, OH⁻ or H₂O⁰. In this calculation scheme, we assumed these to be O²⁻.

The idealized formula is K₆(Ca₂Na)(CO₃)₅Cl·6H₂O, which requires Na₂O 3.97, K₂O 36.16, CaO 14.35, Cl 4.54, CO₂ 28.16, H₂O 13.84, $-O=Cl$ -1.02 , total 100 wt%.

Alexkhomyakovite readily dissolves in dilute HCl at room temperature, with strong effervescence. The mineral slowly decomposes (hydrolyses) in H₂O at room temperature: the

Table 4. Selected interatomic distances (Å) in the structure of alexkhomyakovite.

(Ca,Na)–O(4)	$2.306(5) \times 2$
–O(3)	2.321(7)
–O(1)	$2.488(5) \times 2$
–O(1)	$2.491(5) \times 2$
K–O(1)	$2.899(3) \times 2$
–O(2)	$2.974(4) \times 2$
–O(3)	$2.9900(15) \times 2$
–O(4)	3.042(7)
–Cl	3.2243(16)
–O(4)	$3.281(5) \times 2$
C(1)–O(2)	$1.295(5) \times 3$
C(2)–O(1)	$1.289(4) \times 3$
C(3)–O(3)	$1.276(7) \times 3$

surface of the colourless, transparent grain becomes white, dull and rough after 2 h of exposure in water.

6. X-ray crystallography

Powder X-ray diffraction data of alexkhomyakovite (Table 1) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector (radius 127.4 mm) using Debye-Scherrer geometry, Co $K\alpha$ radiation (rotating anode with Vari-MAX microfoc optics), 40 kV, 15 mA, and 15 min exposure. Angular resolution of the detector is 0.045 2 θ (pixel size 0.1 mm). The data were integrated using the software package Osc2Tab (Britvin *et al.*, 2017). The hexagonal unit-cell parameters refined from the powder data are: $a = 9.269$ (1), $c = 15.888$ (4) Å and $V = 1182.1$ (5) Å³.

The single-crystal X-ray diffraction study of alexkhomyakovite was carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. The measured intensities were corrected for Lorentz, background, polarization and absorption effects. Data reduction was performed using CrysAlisPro Version 1.171.35.21 (Agilent, 2012). The crystal structure of alexkhomyakovite was solved by direct methods and refined using the SHELX-97 software package (Sheldrick, 2008) to $R = 0.0578$ for 555 independent reflections with $I > 2\sigma(I)$. The crystal data and the experimental

details are presented in Table 2, atom coordinates and displacement parameters in Table 3, selected interatomic distances in Table 4, and bond valence calculations in Table 5.

7. Discussion

7.1. Crystal structure

The crystal structure of alexkhomyakovite (Fig. 7) is unique. It is based on (001) heteropolyhedral layers of (Ca,Na)-centred pentagonal bipyramids (Ca,Na)O₅(H₂O)₂ interconnected *via* triangular carbonate groups C(2)O₃ and C(3)O₃ (Fig. 8). These groups play different roles in the construction of the heteropolyhedral layer: the C(2)-centred triangle shares all three edges with three (Ca,Na)-centred pentagonal bipyramids, whereas the C(3)-centred one shares three vertices with the (Ca,Na)-centred polyhedra. The Ca and Na atoms are disordered in their site and the Ca:Na atomic ratio is very close to 2:1 (Table 3), which is probably caused by the general charge-balance requirement. The H atoms of H₂O molecules involved in the formation of the (Ca,Na)-centred polyhedra are oriented towards the interlayer space where the C(1)O₃ triangles are located. Thus the system of hydrogen bonds O(4)–H...O(2) with an O(4)–O(2) distance of 2.624(4) Å is formed (Table 4, Fig. 9). The K cations occur between the H₂O molecules located at the vertices of the (Ca,Na)-centred polyhedra on both sides of the heteropolyhedral layer and occupy KO₆Cl(H₂O)₃ polyhedra in ten-fold coordination. The C(1)O₃ groups and Cl occupy the interlayer.

No mineral or synthetic compound related to alexkhomyakovite in terms of both chemistry and structure was found in literature and databases.

7.2. Notes on genesis

Alexkhomyakovite is a hydrothermal mineral crystallized at a late stage of formation of a potassium-rich peralkaline (hyperagpaitic) pegmatite. This hydrous chlorocarbonate mainly occurs in polymineralic aggregates pseudomorphic after completely altered crystals of delhayelite. The latter is widespread in K-rich hyperagpaitic pegmatites in Khibiny. In the hydrothermally altered bodies, partial to complete

Table 5. Bond valence calculations for alexkhomyakovite.

	Ca _{0.65} Na _{0.35}	K	C(1)	C(2)	C(3)	Σ	H-bonding	Σ
O(1)	0.21 ^{x2↓} 0.21 ^{x2↓}	0.12 ^{x2↓ x2→}		1.31 ^{x3↓}		1.97		1.97
O(2)		0.10 ^{x2↓ x2→}	1.29 ^{x3↓}			1.49	+0.27 × 2	2.03
O(3)	0.34	0.10 ^{x2↓ x4→}			1.36 ^{x3↓}	2.10		2.10
O(4)	0.35 ^{x2↓}	0.08 0.04 ^{x2↓ x2→}				0.51	–0.27 × 2	–0.03
Cl		0.15 ^{x6→}				0.90		0.90
Σ	1.88	0.95	3.87	3.93	4.08			

Note: Bond-valence parameters are taken from Brese & O'Keeffe (1991) and, for hydrogen bonding, from Ferraris & Ivaldi (1988).

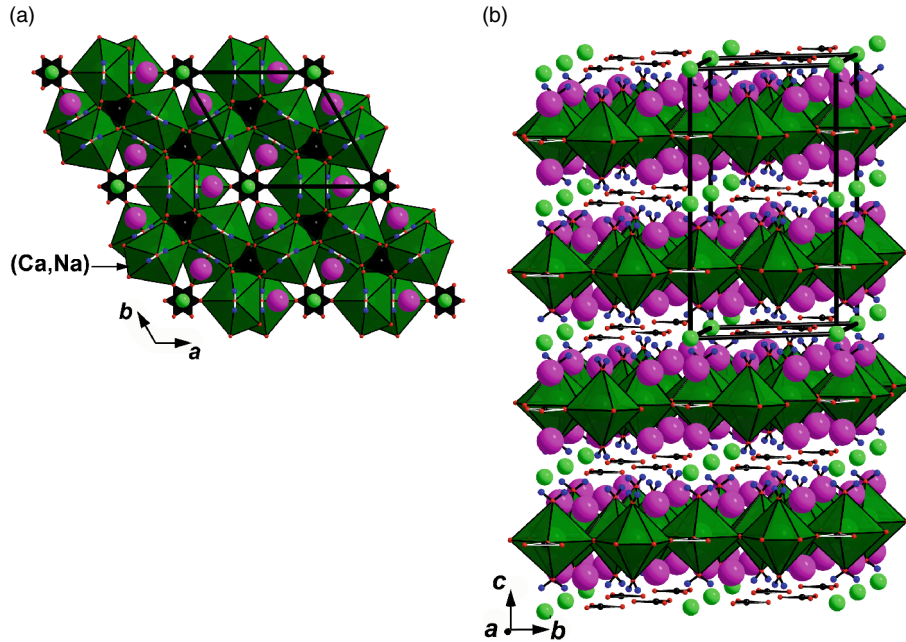


Fig. 7. The crystal structure of alexkhomyakovite in the *ab* (a) and close to *bc* (b) projections. CO₃ groups are black triangles, K cations are big purple spheres, Cl anions are light green spheres, O anions are small red spheres and H atoms are small blue spheres. The unit cell is outlined.

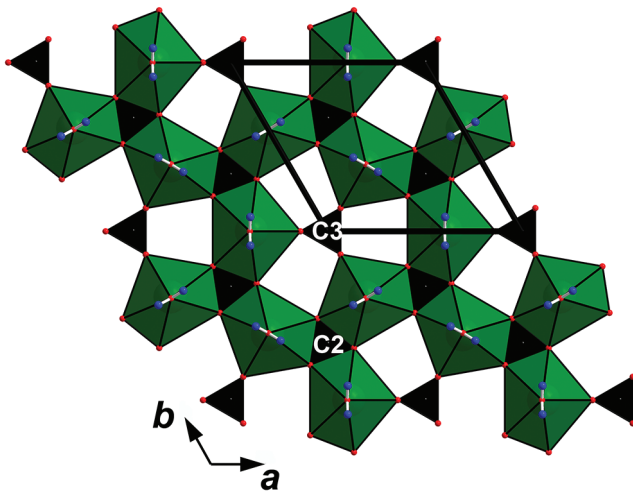


Fig. 8. Heteropolyhedral layer formed by (Ca,Na)O₅(H₂O)₂ pentagonal bipyramids and C(2)O₃ and C(3)O₃ triangles in the crystal structure of alexkhomyakovite. The unit cell is outlined. For legend see Fig. 7.

pseudomorphs after delhayelite are common and diverse in mineral composition (Pekov *et al.*, 2012). In the pegmatite bearing alexkhomyakovite, the early, high-temperature, anhydrous mineral delhayelite K₄Na₂Ca₂(AlSi₇O₁₉)F₂Cl (Pekov *et al.*, 2009) most likely underwent the influence of peralkaline hydrothermal solutions strongly enriched in Na, CO₂, and F and was altered to aggregates of alkali silicates, alkali carbonates and villiaumite. The natrite–villiaumite aggregations (nests and veinlets) were formed between pseudomorphs of delhayelite and aggregates of unaltered, more stable primary pegmatitic minerals (potassic feldspar, soda-

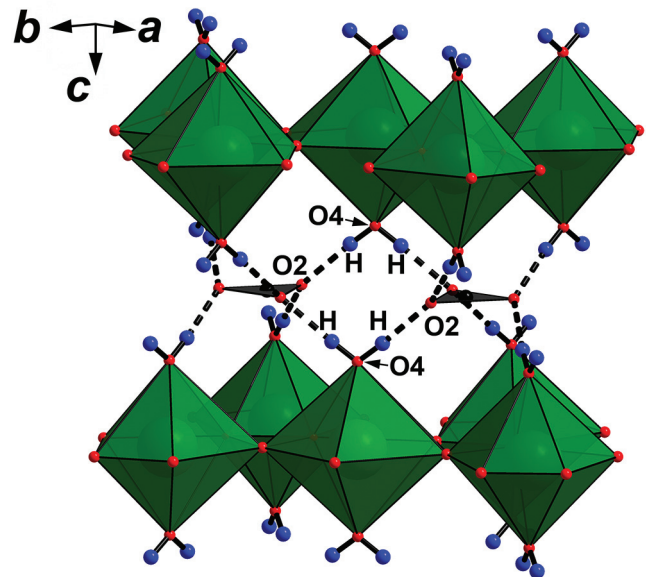


Fig. 9. The system of hydrogen bonds (shown as dashed lines) in alexkhomyakovite. The C(1)O₃ triangles located in the interlayer space are shown. For legend see Fig. 7 and Table 3.

lite, biotite, lamprophyllite, titanite and coarse-grained pectolite) probably at the same stage. The process of the hydrothermal alteration of delhayelite in this pegmatite can be schematically represented as follows: delhayelite K₄Na₂Ca₂(AlSi₇O₁₉)F₂Cl + [H₂O, Na⁺, CO₃²⁻, F⁻] → alexkhomyakovite K₆(Ca₂Na)(CO₃)₅Cl·6H₂O + pectolite (secondary, fibrous) NaHCa₂(Si₃O₉) + potassic feldspar (secondary, fine-grained) K(AlSi₃O₈) + villiaumite

NaF + natrite Na_2CO_3 . Metal cations and chlorine for alexkhomyakovite could be directly inherited from delhayelite.

Acknowledgements: We thank referees Joel D. Grice and Gerald Giester for valuable comments. This study was supported by the Russian Science Foundation, grant no. 14-17-00048 (spectroscopic study), and the Russian Foundation for Basic Research, grant no. 15-05-02051 (crystal structure study). The technical support by the SPbSU X-Ray Diffraction Research Resource Center in the powder X-ray diffraction studies is acknowledged.

References

- Agilent Technologies (2012): CrysAlisPro Software system, version 1.171.35.21. Agilent Technologies UK Ltd, Oxford, UK.
- Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C. (2003): Handbook of Mineralogy, Vol. V. Borates, Carbonates, Sulfates. Mineral Data Publishing, Tucson, AZ.
- Breese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.*, **B47**, 192–197.
- Britvin, S.N., Dolivo-Dobrovolsky, D.V., Krzhizhanovskaya, M.G. (2017): Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zapiski RMO*, **146**, 104–107 (in Russian).
- Ferraris, G. & Ivaldi, G. (1988): Bond valence vs. bond length in O...O hydrogen bonds. *Acta Crystallogr.*, **B44**, 341–344.
- Fournier, A. (1993): Magmatic and hydrothermal controls of LREE mineralization of the St.-Honoré carbonatite, Québec. M.Sc. thesis, McGill University, Montreal.
- IMA-CNMNC, the Official List of Mineral Names (2017): Updated list of IMA-approved minerals, November 2017. *The official website of the IMA Commission on New Minerals*, ima-cnmnc.nrm.se/imalist.htm
- Khomyakov, A.P. (1990): Mineralogy of Hyperagpaitic Alkaline Rocks. Nauka Publishing, Moscow (in Russian).
- Khomyakov, A.P. (1995): Mineralogy of Hyperagpaitic Alkaline Rocks. Oxford, Clarendon Press.
- Mandarino, J.A. (1981): The Gladstone-Dale relationship. Part IV. The compatibility concept and its application. *Can. Mineral.*, **14**, 498–502.
- Pekov, I.V. & Nikolaev, A.P. (2013): Minerals of the pegmatites and hydrothermal assemblages of the Koashva deposit (Khibiny, Kola peninsula, Russia). *Mineral. Almanac*, **18** (2), 6–65.
- Pekov, I.V., Zubkova, N.V., Chukanov, N.V., Sharygin, V.V., Pushcharovsky, D.Yu. (2009): Crystal chemistry of delhayelite and hydrodelhayelite. *Doklady Earth Sci.*, **428** (7), 1216–1221.
- Pekov, I.V., Zubkova, N.V., Chukanov, N.V., Turchkova, A.G., Filinchuk, Ya.E., Pushcharovsky, D.Yu., Krivovichev, S.V. (2012): Delhayelite and mountainite mineral families: crystal chemical relationship, microporous character and genetic features. *Minerals as Advanced Materials II*, Springer Verlag, Berlin, 213–219.
- Plášil, J., Čejka, J., Sejkora, J., Hloušek, J., Škoda, R., Novák, M., Dušek, M., Císařová, I., Němec, I., Ederová, J. (2017): Línekite, $\text{K}_2\text{Ca}_3[(\text{UO}_2)(\text{CO}_3)_3]_2 \cdot 8\text{H}_2\text{O}$, a new uranyl carbonate mineral from Jáchymov, Czech Republic. *J. Geosci.*, **62**, 201–213.
- Sandström, F., Binett, T., Wiklund, C., Vikström, J. (2010): Alnöområdet geologi och mineralogi. *Litiofilen*, **27**, 14–42.
- Sheldrick, G.M. (2008): A short history of SHELX. *Acta Crystallogr.*, **A64**, 112–122.
- Walenta, K. (1976): Baylissit, ein neues Karbonatmineral aus den Schweizer Alpen. *Schweiz. Mineral. Petrogr. Mitt.*, **56**, 187–194.
- Zaitsev, A.N. & Keller, J. (2006): Mineralogical and chemical transformation of Oldoinyo Lengai natrocarbonatites, Tanzania. *Lithos*, **91**, 191–207.

Received 30 April 2018

Modified version received 1 June 2018

Accepted 2 June 2018