

NEW MINERALS, NOMENCLATURE,
AND CLASSIFICATION

**Shlykovite $\text{KCa}[\text{Si}_4\text{O}_9(\text{OH})] \cdot 3\text{H}_2\text{O}$ and Cryptophyllite
 $\text{K}_2\text{Ca}[\text{Si}_4\text{O}_{10}] \cdot 5\text{H}_2\text{O}$, New Mineral Species from the Khibiny
Alkaline Pluton, Kola Peninsula, Russia¹**

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Abstract—New minerals, shlykovite and cryptophyllite, hydrous Ca and K phyllosilicates, have been identified in hyperalkaline pegmatite at Mount Rasvumchorr, Khibiny alkaline pluton, Kola Peninsula, Russia. They are the products of low-temperature hydrothermal activity and are associated with aegirine, potassium feldspar, nepheline, lamprophyllite, eudialyte, lomonosovite, lovozerite, tisinallite, shcherbakovite, shafraonovskite, ershovite, and megacyclite. Shlykovite occurs as lamellae up to $0.02 \times 0.02 \times 0.5$ mm in size or fibers up to 0.5 mm in length usually combined in aggregates up to 3 mm in size, crusts, and parallel-columnar veinlets. Cryptophyllite occurs as lamellae up to $0.02 \times 0.1 \times 0.2$ mm in size intergrown with shlykovite being oriented parallel to {001} or chaotically arranged. Separate crystals of the new minerals are transparent and colorless; the aggregates are beige, brownish, light cream, and pale yellowish-grayish. The cleavage is parallel to (001) perfect. The Mohs hardness of shlykovite is 2.5–3. The calculated densities of shlykovite and cryptophyllite are 2.444 and 2.185 g/cm³, respectively. Both minerals are biaxial; shlykovite: $2V_{\text{meas}} = -60(20)^\circ$; cryptophyllite: $2V_{\text{meas}} > 70^\circ$. The refractive indices are: shlykovite: $\alpha = 1.500(3)$, $\beta = 1.509(2)$, $\gamma = 1.515(2)$; cryptophyllite: $\alpha = 1.520(2)$, $\beta = 1.523(2)$, $\gamma = 1.527(2)$. The chemical composition of shlykovite determined by an electron microprobe (H_2O determined from total deficiency) is as follows, wt %: 0.68 Na₂O, 11.03 K₂O, 13.70 CaO, 59.86 SiO₂, 14.73 H₂O; the total is 100.00. The empirical formula calculated on the basis of 13 O atoms (OH/H₂O calculated from the charge balance) is $(\text{K}_{0.96}\text{Na}_{0.09})_{\Sigma 1.05}\text{Ca}_{1.00}\text{Si}_{4.07}\text{O}_{9.32}(\text{OH})_{0.68} \cdot 3\text{H}_2\text{O}$. The idealized formula is $\text{KCa}[\text{Si}_4\text{O}_9(\text{OH})] \cdot 3\text{H}_2\text{O}$. The chemical composition of cryptophyllite determined by an electron microprobe (H_2O determined from the total deficiency) is as follows, wt %: 1.12 Na₂O, 17.73 K₂O, 11.59 CaO, 0.08 Al₂O₃, 50.24 SiO₂, 19.24 H₂O, the total is 100.00. The empirical formula calculated on the basis of (Si,Al)₄(O,OH)₁₀ (OH/H₂O calculated from the charge balance) is $(\text{K}_{1.80}\text{Na}_{0.17})_{\Sigma 1.97}\text{Ca}_{0.99}\text{Al}_{0.01}\text{Si}_{3.99}\text{O}_{9.94}(\text{OH})_{0.06} \cdot 5.07\text{H}_2\text{O}$. The idealized formula is $\text{K}_2\text{Ca}[\text{Si}_4\text{O}_{10}] \cdot 5\text{H}_2\text{O}$. The crystal structures of both minerals were solved on single crystals using synchrotron radiation. Shlykovite is monoclinic; the space group is $P2_1/n$; $a = 6.4897(4)$, $b = 6.9969(5)$, $c = 26.714(2)$ Å, $\beta = 94.597(8)^\circ$, $V = 1209.12(15)$ Å³, $Z = 4$. Cryptophyllite is monoclinic; the space group is $P2_1/n$; $a = 6.4934(14)$, $b = 6.9919(5)$, $c = 32.087(3)$ Å, $\beta = 94.680(12)^\circ$, $V = 1451.9(4)$ Å³, $Z = 4$. The strongest lines of the X-ray powder patterns (d , Å– I , [hkl] are: shlykovite 13.33–100[002], 6.67–76[004], 6.47–55[100], 3.469–45[021], 3.068–57[121], 3.042–45[121], 2.945–62[123], 2.912–90[025, 212, 211]; cryptophyllite 16.01–100[002], 7.98–24[004], 6.24–48[101], 3.228–22[109], 3.197–27[0.0.10], 2.995–47[122], 2.903–84[123, 204, 124, 211], 2.623–20[028, 208, 126]. Shlykovite and cryptophyllite are members of new related structural types. Their structures are based on a two-layer packet consisting of tetrahedral Si layers linked with octahedral Ca chains. Mountainite, shlykovite and cryptophyllite could be combined into the mountainite structural family. Shlykovite is named in memory of Russian geologist V. G. Shlykov (1941–2007); the name cryptophyllite is from the Greek words meaning *concealed* and *leaf* that allude to its layered structure (phyllosilicate) in combination with a lamellar habit and intimate intergrowths with visually indistinguishable shlykovite. Type specimens of the minerals are deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow.

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INTRODUCTION

In recent years the Khibiny pluton in the Kola Peninsula, the world's largest alkaline complex, also became number one for new mineral species discovered within a single compact geological object passing out the neighboring Lovozero pluton that had retained the world record in this respect for a long time. In this article we describe two other minerals from Khibiny, K–Ca hydrous phyllosilicates, which are similar in chemical components and structure of octahedral–tetrahedral (Ca,Si,O) motif. At the same time, these minerals, being members of two new structural types, differ from each other and from all previously known natural and synthetic compounds in the number and arrangements of K⁺ cations and H-bearing groups.

The new mineral of $\text{KCa}[\text{Si}_4\text{O}_9(\text{OH})] \cdot 3\text{H}_2\text{O}$ composition has been named *shlykovite* in memory of Russian geologist Valerii Georgievich Shlykov (1941–2007), a specialist in X-ray studies of phyllosilicates, mineralogy of sedimentary rocks, lithology, and pedology. V.G. Shlykov, a scientist and lecturer, worked at the Geology Faculty of Moscow State University.

The name of the second mineral comprised of $\text{K}_2\text{Ca}[\text{Si}_4\text{O}_{10}] \cdot 5\text{H}_2\text{O}$ has been derived from the Greek words *κρυπτος* (*concealed*) and *φυλλον* (*leaf*), which emphasize its layered structure (phyllosilicate) in combination with a lamellar habit and intimate intergrowths with visually indistinguishable shlykovite commonly dominant in these aggregates. The appearance of superfluous reflections in the X-ray powder diffraction patterns of two shlykovite samples, including strong reflections with $d \approx 16.0$ and 8.0 \AA , which could not be indexed in its unit cell, was the first indication of the occurrence of a second mineral, future cryptophyllite, in these samples. Then, it was identified by an optical method in immersion preparations and extracted for a further examination.

The type specimens are deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow; their registration numbers are 3753/1 (shlykovite) and 3753/2 (cryptophyllite).

OCCURRENCE AND GENERAL DESCRIPTION

Shlykovite and cryptophyllite were found in hyperalkaline pegmatite at the southern wall of the open pit (level +640 m) of the apatite Central Mine at Mount Rasvumchorr. This pegmatitic body currently destroyed by mining operations was irregularly-shaped and hosted in urtite close to the contact with the nepheline–apatite rock. It was more than 10 m long and more than 1 m thick in swells. The pegmatite was devoid of a clear zoning and was characterized by a diversity of minerals. Assemblages corresponding to the three major mineralization stages were distinguished in the pegmatite. The earliest of them are potassium feldspar, nepheline, sodalite, alkaline

pyroxene (aegirine–salite), amphibole, eudialyte, lamprophyllite, ilmenite, and fluorapatite. The second assemblage, which may be called dry hyperalkaline, is dominated by anhydrous or almost anhydrous minerals: acicular green aegirine (predominant), magnesioastrophyllite, lomonosovite, shcherbakovite, barytolamprophyllite, villiaumite, fenaksite, delhayelite, phosinaite-(Ce), clinophosinaite, natisite (replacing ilmenite), zirsinalite (rims and complete pseudomorphs after eudialyte) kazakovite, pectolite, nakaphite (replacing fluorapatite), sidorenkite, djerfisherite, rasvumite, sphalerite, and molybdenite. The third hydrothermal stage characterized by high-alkaline solutions and a low temperature (probably not higher than 200–250°C) gave birth to the minerals with a low-density structure, including those replacing the anhydrous hyperalkaline phases, for example, lovozerite after zirsinalite, tisinialite after kazakovite, and aggregates of hydrodelhayelite, late pectolite, and kalborsite replacing delhayelite. Other products of this later stage that occur in fractures and small cavities are shafranovskite, ershovite, megacyclite, revdite, grumantite, shlykovite, cryptophyllite, and unidentified K,Na-zeolite. Abundant, poorly crystallized and highly hydrous Na-, K-, Fe-, Mn-, and Ti-bearing silicates occur as pockets and crusts and make up poly-component pseudomorphs after earlier phases.

The new minerals described in this article are the latest in the pegmatite and they are observed only in fractures and cavities.

Shlykovite is more abundant than cryptophyllite and occurs as monomineralic segregations and intergrowths with cryptophyllite. Thin sheets or lamellae up to $0.02 \times 0.2 \times 0.5 \text{ mm}$ in size (sporadically up to $0.03 \times 0.3 \times 1 \text{ mm}$) and flattened parallel to {001} are most frequent. Fine fibers up to 0.5 mm long are less frequent. Both lamellar and fibrous mineral individuals are curved, split, and combined in nearly parallel bunches, radiated or chaotic aggregates. Monomineralic parallel-columnar veinlets of shlykovite up to 2 cm long and 0.3 mm thick composed of oblong lamellae fill the fractures cutting segregations of earlier minerals (Fig. 1a). Soft aggregates (up to 3 mm) of curved shlykovite fibers (Fig. 1b) and extremely rare crystals as oblique-angled lamellae up to 0.4 mm thick (Fig. 1c) occur in cavities. Pinacoid {001} is the major habit form; lateral faces are poorly developed.

Cryptophyllite occurs as curved and/or split lamellae up to $0.02 \times 0.1 \times 0.2 \text{ mm}$ in size. The mineral was found only in the form of intergrowths with shlykovite, where the mineral grains are intergrown parallel to {001} or oriented irregularly. As a rule, shlykovite is predominant in these bimineral aggregates occupying 60–90% of their volume; intergrowths, which are dominated by cryptophyllite (up to 60%), are less abundant. The crusts coating fracture walls and composed of clusters of parallel shlykovite and cryptophyllite intergrown sheets (Fig. 1d) are most typical. They

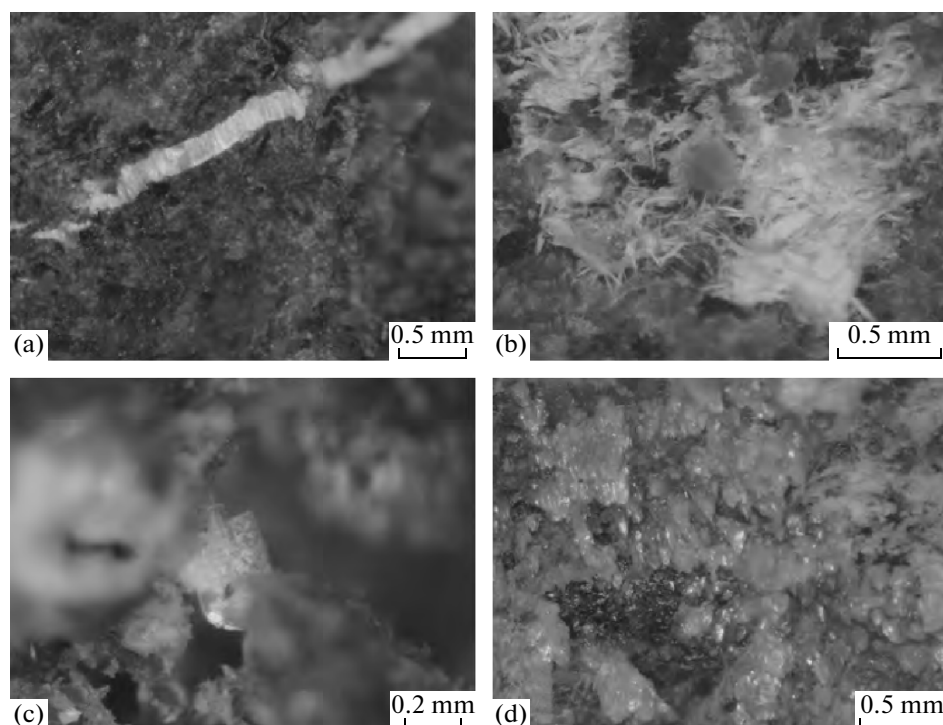


Fig. 1. Segregations of shlykovite and cryptophyllite. Photos by I.V. Pekov and A.V. Kasatkin: (a) parallel-columnar veinlet of a shlykovite cutting massive aggregate of tisinallite and unidentified poor-crystallized K, Na, Fe, and Mn hydrous silicates; (b) fibrous aggregate of shlykovite in a cavity within yellowish brown ershovite; (c) colorless tabular crystal of shlykovite in a cavity within tisinallite; (d) crust formed by intimately intergrown lamellae of visually indistinguishable shlykovite and cryptophyllite.

reach 1.5×1.5 cm in area and rarely exceed 0.2 mm in thickness. Rosette-shaped cryptophyllite–shlykovite intergrowths up to 1 mm across and rounded segregations up to $0.5 \times 1 \times 1$ mm in size composed of chaotic aggregates of both minerals are known. Aggregates of shlykovite and cryptophyllite occasionally contain microinclusions of unidentified K, Na-zeolite and K, Na, and Ti silicates.

PHYSICAL PROPERTIES AND OPTICAL PARAMETERS

The separate crystals of the new minerals are colorless and transparent, whereas aggregates are translucent to dull, white, beige, brownish, light cream, or pale yellowish–greyish. The lamellar segregations have a nacreous luster, whereas fibrous aggregates are silky. Shlykovite and cryptophyllite are not luminescent in UV and cathode rays. The cleavage of both minerals is perfect parallel to (001). Their mineral individuals are flexible but inelastic. The Mohs hardness of shlykovite is 2.5–3; the determination of the cryptophyllite hardness was not successful. The measured density of the new minerals was incorrect because of the porous aggregates and numerous inclusions. The calculated densities of shlykovite and cryptophyllite are 2.244 and 2.185 g/cm³, respectively.

Visually identical shlykovite and cryptophyllite are clearly distinguished by optical parameters. Both minerals are biaxial, but shlykovite is negative, whereas cryptophyllite is positive. The refractive indices of shlykovite are: $\alpha = 1.500(3)$, $\beta = 1.509(2)$, $\gamma = 1.515(2)$. Cryptophyllite has a higher refraction: $\alpha = 1.520(2)$, $\beta = 1.523(2)$, $\gamma = 1.527(2)$. The measured $2V$ of shlykovite is $60(20)^\circ$, the calculated value is 78° . The measured $2V$ of cryptophyllite is more than 70° and $2V_{\text{calc}} = 82^\circ$. The dispersion of the optical axes of shlykovite is medium, $r < v$ and is not observed for cryptophyllite. Under a microscope, both minerals are colorless and nonpleochroic. Their optical orientation is $X = c$.

CHEMICAL COMPOSITION

The cation composition of new minerals was determined on a MV2300 CamScan digital SEM equipped with a YAG detector of secondary and back-scattered electrons and a Link INCA Energy EDS with a semiconductor (Si–Li) detector operating at accelerating voltage 15.7 kV, current 0.5 nA, and scanning area $16 \times 16 \mu\text{m}$ (analyst K.V. Van). Such conditions allowed for the avoidance of damage to these high-hydrous minerals unstable under an electron beam. The following standards were used: microcline (K, Si, Al), wollastonite (Ca), and albite (Na). The concentrations of other elements with an atomic number higher than Be

were below the detection limits. The absence of Li and Be is verified by XRD. The water content was not determined due to the small amount of pure material.

The average composition (7 point analyses) of shlykovite (H_2O is calculated from the total deficiency, the range of the contents is given in parentheses) is as follows, wt %: 0.68 (0.4–0.9) Na_2O , 11.03 (10.6–12.0) K_2O , 13.70 (13.6–13.9) CaO , 59.86 (59.2–60.8) SiO_2 , 14.73 $\text{H}_2\text{O}_{\text{calc}}$, total is 100.00. The empirical formula of the mineral is $(\text{K}_{0.96}\text{Na}_{0.09})_{\Sigma 1.05}\text{Ca}_{1.00}\text{Si}_{4.07}\text{O}_{9.32}(\text{OH})_{0.68} \cdot 3\text{H}_2\text{O}$. In line with structural data (see below), this formula was calculated on the basis of 13 O atoms and $\text{OH}/\text{H}_2\text{O}$ was calculated from the charge balance. The idealized formula is $\text{KCa}[\text{Si}_4\text{O}_9(\text{OH})] \cdot 3\text{H}_2\text{O}$; the corresponding theoretical contents of the components are as follows, wt %: 11.58 K_2O , 13.79 CaO , 59.12 SiO_2 , 15.51 H_2O , the total is 100.00.

The average composition (4 point analyses) of cryptophyllite (H_2O calculated from the total deficiency, the range of contents is given in parentheses) is as follows, wt %: 1.12 (0.8–1.3) Na_2O , 17.73 (17.5–18.2) K_2O , 11.59 (11.3–11.9) CaO , 0.08 (0.00–0.15) Al_2O_3 , 50.24 (49.0–51.1) SiO_2 , 19.24 $\text{H}_2\text{O}_{\text{calc}}$, the total is 100.00. The empirical formula is $(\text{K}_{1.80}\text{Na}_{0.17})_{\Sigma 1.97}\text{Ca}_{0.99}\text{Al}_{0.01}\text{Si}_{3.99}\text{O}_{9.94}(\text{OH})_{0.06} \cdot 5.07\text{H}_2\text{O}$. The formula was calculated on the basis of $(\text{Si,Al})_4(\text{O,OH})_{10}$ in compliance with incorporation of OH groups into the apices of Si tetrahedra in the structurally similar shlykovite; $\text{OH}/\text{H}_2\text{O}$ was calculated from the charge balance. The idealized formula is $\text{K}_2\text{Ca}[\text{Si}_4\text{O}_{10}] \cdot 5\text{H}_2\text{O}$; the corresponding theoretical contents of the components are, wt %: K_2O 19.60, CaO 11.67, SiO_2 49.99, H_2O 18.74, the total is 100.00.

The composition and properties compatibility index $(1 - K_p/K_C)$ calculated from the Gladstone–Dale equation is -0.001 (superior) for shlykovite and -0.036 (excellent) for cryptophyllite.

CRYSTALLOGRAPHY

The crystal structures of both new minerals were studied on single crystals with synchrotron radiation (wavelength 0.70000 Å) at the Laboratory of Swiss–Norwegian Beam Lines at European Synchrotron Radiation Facility (SNBL at ESRF) in Grenoble, France. The diffraction data were collected using a MAR 345 image plate detector at 296 K.

Shlykovite is monoclinic, the space group is $P2_1/c$; the unit-cell dimensions are $a = 6.4897(4)$, $b = 6.9969(5)$, $c = 26.714(2)$ Å, $\beta = 94.597(8)^\circ$, $V = 1209.12(15)$ Å³, $Z = 4$.

Cryptophyllite is monoclinic, the space group is $P2_1/n$; the unit-cell dimensions are $a = 6.4934(14)$, $b = 6.9919(5)$, $c = 32.087(3)$ Å, $\beta = 94.680(12)^\circ$, $V = 1451.9(4)$ Å³, $Z = 4$.

The X-ray powder diffraction patterns of shlykovite and cryptophyllite are individualized. The X-ray powder diffraction pattern of shlykovite (Table 1) was

recorded with a STOE STADI MP diffractometer equipped with a CCD detector ($\text{CuK}_{\alpha 1}$ radiation). The monoclinic unit-cell dimensions calculated on the basis of these data are $a = 6.505(4)$, $b = 6.988(5)$, $c = 26.72(2)$ Å, $\beta = 94.64(8)^\circ$, $V = 1211(3)$ Å³. The X-ray powder diffraction pattern of cryptophyllite (Table 2) was recorded using a STOE IPDS II single crystal diffractometer equipped with an image plate detector and allowing recording X-ray powder diffraction patterns from a very small sample according to the principle used in the Gandolfi camera. The monoclinic unit-cell dimensions calculated on the basis of these data are $a = 6.486(5)$, $b = 6.997(4)$, $c = 32.11(2)$ Å, $\beta = 94.91(6)^\circ$, $V = 1452(3)$ Å³.

The crystal structures of the minerals studied and their crystal chemistry are described in a separate article (Zubkova et al., in press). Here, we briefly characterize their structures and relationship to other phyllosilicates.

Shlykovite and cryptophyllite belong to the previously unknown related structural types. These structures (Fig. 2) are based on a *TOT*-packet consisting of two similar *T*-layers of Si-tetrahedra and sandwiched edge-shared chains of Ca-octahedra (*O*). Each *T*-layer consists of 4- and 8-member rings of Si tetrahedra. In cryptophyllite, the layer consists of $[\text{Si}_4\text{O}_{10}]^\infty$, whereas in shlykovite one out of ten oxygen atoms (pendant apex not involving in Si–O–Si and Si–O–Ca bridges) is substituted by an OH group. Thus, the tetrahedral layer of shlykovite is composed of $[\text{Si}_4\text{O}_9(\text{OH})]^\infty$. The identical structure of *TOT*-packet is determined by the very close values of the *a* and *b* parameters, as well as of the β angle of the unit cells of shlykovite and cryptophyllite.

The new minerals substantially differ from each other in the number and arrangement of K^+ cations and water molecules. In shlykovite, K^+ cations are located only in voids (windows) within tetrahedral layers and only H_2O molecules are identified within the interlayer space (Fig. 2a). Cryptophyllite is enriched in potassium and water. In its structure, K^+ cations occupy two types of sites in the windows of the tetrahedral layer, K(1), and together with water molecules in the interlayer space, K(2) (Fig. 2b). Such discrepancies in the concentration of potassium and water determine the substantial (5.4 Å) difference in the *c* parameter of the shlykovite (26.7 Å) and cryptophyllite (32.1 Å) cells and, hence, in their X-ray powder patterns (Tables 1–3).

The tetrahedral layer in the structures of the described minerals is topologically close to that recently established in mountaineite with a formula ($Z = 2$) $\text{KNa}_2\text{Ca}_2[\text{Si}_8\text{O}_{19}(\text{OH})] \cdot 6\text{H}_2\text{O}$ (Zubkova et al., 2009). This is a new type of Si-layer, to some extent, similar to the well-known sheet in the structure of apophyllite, which also consists of 4- and 8-member rings of Si-tetrahedra (Rouse et al., 1978). Apophyllite and

Table 1. X-ray powder-diffraction data of shlykovite

I_{meas}	$d_{\text{meas}}, \text{\AA}$	I_{calc}	$d_{\text{calc}}, \text{\AA}$	hkl
100	13.33	100	13.314	002
76	6.67	64	6.657	004
55	6.47	20	6.469	100
24	6.01	5	6.011	$\bar{1}02$
11	5.65	2	5.643	102
26	4.835	10	4.837	$\bar{1}04$
22	4.717	5	4.724	$\bar{1}11$
2	4.552	1	4.559	$\bar{1}12$
17	4.447	3, 2	4.464, 4.438	104, 006
9	4.290	1	4.294	$\bar{1}13$
24	4.113	9	4.089	113
36	3.978	11	3.979	$\bar{1}14$
27	3.790	8, 8	3.805, 3.763	$\bar{1}06, 114$
37	3.529	25	3.530	106
45	3.469	6	3.468	021
20	3.337	5, 19	3.342, 3.329	017, 008
13	3.215	6	3.202	$\bar{2}02$
2	3.143	5	3.152	116
11	3.084	3, 2	3.097, 3.087	024, 202
57	3.068	15, 1	3.070, 3.061	$\bar{1}21, \bar{1}08$
45	3.042	16, 4	3.044, 3.024	121, $\bar{1}22$
32	2.996	1, 18	3.006, 3.005	018, $\bar{2}04$
62	2.945	17, 4	2.942, 2.942	$\bar{1}23, \bar{2}11$
90	2.912	10, 15, 10	2.924, 2.920, 2.895	025, $\bar{2}12, 211$
24	2.877	2, 19	2.887, 2.874	117, 123
17	2.830	5, 1, 4	2.824, 2.822, 2.805	212, 204, $\bar{1}18$
10	2.756	1, 1, 2	2.761, 2.754, 2.747	$\bar{2}14, 124, 026$
12	2.718	5, 6	2.720, 2.710	$\bar{2}06, \bar{1}25$
5	2.654	2	2.653	118
7	2.623	3	2.621	125
12	2.573	3, 3	2.575, 2.575	$\bar{1}26, 027$
10	2.540	5	2.535	$\bar{2}16$
5	2.494	3, 5	2.495, 2.489	215, 0.1.10
7	2.438	8	2.438	$\bar{1}27$
3	2.318	1	2.329	$\bar{2}23$
6	2.252	4, 2, 3	2.256, 2.246, 2.232	029, 217, 208
1	2.220	2	2.218	$\bar{2}25$

Table 1. (Contd.)

I_{meas}	$d_{\text{meas}}, \text{\AA}$	I_{calc}	$d_{\text{calc}}, \text{\AA}$	hkl
3	2.190	1, 1	2.192, 2.182	$\bar{1}$ 31, 131
6	2.157	2, 1	2.156, 2.155	300, 132
2	2.122	1, 1	2.101, 2.093	$\bar{3}$ 04, 129
8	2.062	1, 1, 1	2.065, 2.061, 2.048	036, 310, $\bar{2}$.1.10
12	2.003	4, 1	2.005, 2.004	304, $\bar{3}$ 06
2	1.902	3	1.902	$\bar{2}$.0.12
1	1.886	1, 2	1.881, 1.880	231, $\bar{3}$ 08
13	1.874	4, 1, 1	1.868, 1.868, 1.861	1.2.11, $\bar{1}$.0.14, 232
18	1.835	5, 1, 2	1.840, 1.836, 1.835	$\bar{3}$ 21, 320, 0.1.14
5	1.827	2	1.823	321
7	1.771	2, 1	1.765, 1.756	2.0.12, 235
27	1.748	4, 5, 4	1.749, 1.747, 1.745	040, $\bar{2}$.2.11, 041
4	1.730	2	1.726	$\bar{2}$ 37
2	1.694	1	1.700	325
2	1.665	1	1.671	$\bar{2}$.2.12
2	1.650	1	1.647	2.2.11
6	1.616	1, 2, 1	1.619, 1.617, 1.611	145, 400, 327
3	1.590	2, 3	1.598, 1.586	$\bar{2}$.2.13, $\bar{3}$ 31
5	1.544	1	1.543	$\bar{3}$ 35
8	1.520	1, 1, 1	1.526, 1.523, 1.518	$\bar{2}$ 43, $\bar{4}$ 16, $\bar{1}$.3.13
4	1.514	1, 2	1.513, 1.512	$\bar{3}$.2.11, $\bar{2}$ 44
3	1.496	1, 1	1.493, 1.488	$\bar{2}$ 45, 3.0.12
10	1.419	1, 1	1.431, 1.418	$\bar{3}$ 39, $\bar{1}$.2.17
1	1.392	1	1.390	425
5	1.340	2	1.337	427

mountainite layers are, however, markedly different in ring configuration of and tetrahedron orientation.

The shlykovite layer may also be interpreted as a half of a double rhodesite-type layer $[\text{Si}_{16}\text{O}_{34}(\text{O},\text{OH})_4]^\infty$. Such a double layer has been established in the structures of rhodesite, macdonaldite, monteregianite-(Y), related aluminosilicates, delhayellite and hydrodelhayellite (the composition of the layer is $[(\text{Al},\text{Si})_2\text{Si}_{14}\text{O}_{34}(\text{O},\text{OH})_4]^\infty$), and some synthetic compounds (Cadoni and Ferraris, 2009). As follows from Table 3, the a and b parameters (mainly affected by the character of TOT -packets) of monoclinic unit cells of shlykovite, mountainite, and rhodesite are close or divisible. Among the structurally related synthetic

K,Ca-silicates, CAS-1 synthesized at 493 K deserves mentioning. Its formula is $\text{K}_4\text{Ca}_4[\text{Si}_{16}\text{O}_{38}] \cdot 8\text{H}_2\text{O}$. The monoclinic (the space group is $C2$) unit-cell parameters (in arrangement, where Si-layers are on the plane ab) are $a = 6.482$, $b = 7.016$, $c = 24.158 \text{ \AA}$, $\beta = 95.19^\circ$. The tetrahedral layer in its structure is double, rhodesite-like (Jordá et al., 2005), and the atomic ratio Si:Ca : K = 4 : 1 : 1 is the same as for shlykovite.

Mountainite differs in the arrangement of Ca atoms in a TOT -packet from shlykovite and cryptophyllite (Zubkova et al., 2009). In combination with the differences in the composition and arrangement of alkali cations and water molecules, this leads to a dif-

Table 2. X-ray powder-diffraction data of cryptophyllite

I_{meas}	$d_{\text{meas}}, \text{\AA}$	I_{calc}	$d_{\text{calc}}, \text{\AA}$	hkl
100	16.01	100	15.990	002
24	7.98	19	7.995	004
48	6.24	11	6.245	101
8	5.83	1	5.847	013
16	5.33	6	5.330	006
14	4.752	3	4.749	110
16	4.651	2	4.658	111
18	4.338	5	4.374	105
3	4.229	4, 2	4.245, 1.195	113, $\bar{1}$ 14
2	3.918	4, 5	3.927, 3.885	$\bar{1}$ 15, $\bar{1}$ 07
5	3.716	1	3.708	115
9	3.656	2	3.656	$\bar{1}$ 16
14	3.484	5, 2	3.475, 3.470	021, 018
22	3.228	10	3.228	$\bar{1}$ 09
27	3.197	11	3.198	0.0.10
9	3.163	3	3.168	019
15	3.121	9	3.122	202
17	3.068	2, 4	3.076, 3.067	120, 025
8	3.043	5	3.042	$\bar{1}$ 22
47	2.995	12	2.999	122
16	2.938	2, 4	2.937, 2.931	210, $\bar{1}$ 19
84	2.903	3, 5, 13, 6	2.925, 2.918, 2.909, 2.905	123, 204, $\bar{1}$ 24, 211
18	2.877	7	2.886	$\bar{2}$ 13
16	2.843	5, 2	2.851, 2.834	212, 124
3	2.765	1, 2	2.779, 2.776	213, 027
8	2.709	2	2.710	$\bar{1}$ 26
20	2.623	2, 2, 9	2.632, 2.622, 2.620	028, $\bar{2}$ 08, 126
3	2.578	2	2.575	1.0.11
6	2.479	1, 2	2.492, 2.490	029, 0.1.12
6	2.394	2, 2	2.416, 2.393	1.1.11, 128
14	2.349	2, 2	2.351, 2.348	$\bar{2}$ 19, $\bar{2}$ 23
2	2.283	2	2.289	223
4	2.240	2	2.235	0.2.11
10	2.190	2, 2	2.193, 2.180	130, $\bar{1}$ 32
2	2.101	1, 1	2.092, 2.082	$\bar{1}$ 35, 303
4	2.013	2	2.015	$\bar{3}$ 07
1	1.990	1, 1	1.994, 1.979	2.1.11, 2.0.12
5	1.876	2	1.869	$\bar{1}$ 2.14
8	1.842	4	1.838	$\bar{3}$ 22
4	1.795	1	1.798	2.0.14
7	1.746	2, 1	1.748, 1.745	040, 041
3	1.656	4	1.660	2.2.13
4	1.527	1	1.525	242
1	1.496	1	1.499	244
3	1.394	1	1.397, 1.394	1.2.20, $\bar{4}$ 29
4	1.360	2	1.352	$\bar{4}$ 2.11

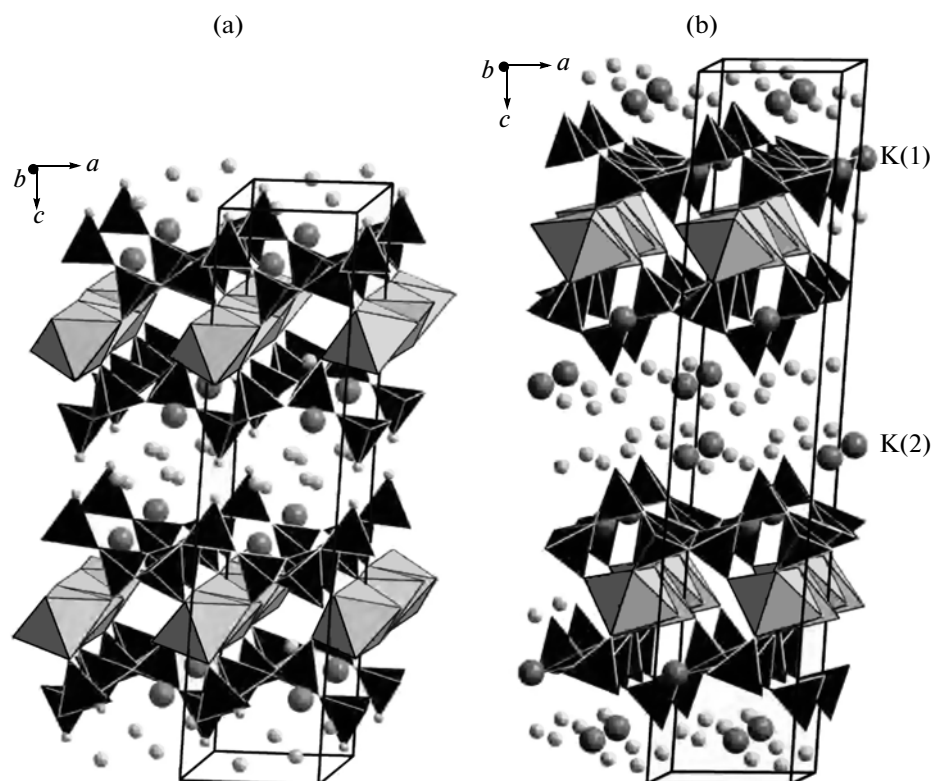


Fig. 2. Crystal structures of (a) shlykovite and (b) cryptophyllite. Si-tetrahedra, Ca-octahedra, K atoms (large dark gray circles), and water molecules (small light gray circles) are shown. In the structure of shlykovite, OH groups arranged in pendant apices of Si-tetrahedra are marked as the smallest light gray circles.

ference in the space groups and unit-cell metrics of these minerals (Table 3).

INFRARED SPECTROSCOPY

The IR spectrum of shlykovite was recorded with a Specord-75-IR spectrophotometer using a standard technique of pelleting with KBr. Recording of the IR spectrum of cryptophyllite was unsuccessful due to a deficiency in the pure matter.

Wavenumbers of the band peaks in the IR spectrum of shlykovite (Fig. 3) and their assignment are as follows (cm^{-1} ; s is a strong band; sh is a shoulder): 3585, 3250 3090sh (stretching vibrations of O–H); 1680, 1660sh, 1585 (bending vibrations of water molecules); 1135s, 1097s, 1024s, 999s, 962s (stretching vibrations of Si–O); 880sh, 795, 760sh, 690sh, 680, 590 (mixed vibrations of the tetrahedral sheet); and 470sh, 455, 432s, 420sh (bending vibrations of Si–O–Si).

The bands at 3250 and 3090 cm^{-1} indicate strong hydrogen bonds typical of weak-acid OH groups. Taking into account the structural data, these bands may be assigned to the stretching vibrations of silanol Si–O–H groups. Splitting of the band of nondegenerate bending vibrations H–O–H (region of 1585–1680 cm^{-1}) suggests the occurrence of different types of H_2O molecules in the mineral.

The IR spectra of mountainite, rhodesite, and apophyllite-(OH) (hydroxyapophyllite) related to shlykovite are also shown in Fig. 3 for comparative purposes. As is seen, the spectrum of shlykovite is individualized and differs from the IR spectra of these and other phyllosilicates. The pronounced strong band in the region of 680–700 cm^{-1} is characteristic of minerals with Si-tetrahedral layers of rhodesite and mountainite types, whereas it is not observed in the spectra of apophyllite.

In contrast to shlykovite and mountainite, cognate minerals with a rhodesite-type double Si-tetrahedral sheet (rhodesite, monteregianite-(Y), macdonaldite) are characterized by a high-frequency shift $\Delta v_{\text{Si-O}}$ of Si–O stretching mode bands. This is consistent with the well-known positive correlation between $\Delta v_{\text{Si-O}}$ and the condensation degree of the Si-tetrahedral motif (Chukanov, 1995).

DISCUSSION

The close structure of the tetrahedral layer and the general structural similarity of mountainite, shlykovite, and cryptophyllite (Zubkova et al., in press) allow us to combine these three hydrous alkali–calcium silicates into the mountainite structural family. To a lesser degree, they are related (Table 3) to the mem-

Table 3. Comparative data of shlykovite, cryptophyllite, and related phyllosilicates

Parameter	Shlykovite $\text{KCa}[\text{Si}_4\text{O}_9(\text{OH})] \cdot 3\text{H}_2\text{O}$	Cryptophyllite $\text{K}_2\text{Ca}[\text{Si}_4\text{O}_{10}] \cdot 5\text{H}_2\text{O}$	Mountaineite $\text{KNa}_2\text{Ca}_2[\text{Si}_8\text{O}_{19}(\text{OH})] \cdot 6\text{H}_2\text{O}$	Rhodesite $\text{KCa}_2[\text{Si}_8\text{O}_{18}(\text{OH})] \cdot (6-x)\text{H}_2\text{O}$	Apophyllite-(OH) $\text{KCa}_4[\text{Si}_8\text{O}_{20}(\text{OH}) \cdot 8\text{H}_2\text{O}$
Symmetry	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Tetragonal
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Pnmm$	$P4/mnc$
<i>a</i> , Å	6.490	6.493	13.704	7.01–7.06	8.98
<i>b</i> , Å	6.997	6.992	6.576	6.54–6.59	8.98
<i>c</i> , Å	26.714	32.087	13.751	23.4–23.8*	15.83
β , deg	94.60	94.68	105.75	90	90
<i>V</i> , Å ³	1209	1452	1193	1082–1098	1277
<i>Z</i>	4	4	2	2	2
Major components, wt %					Ideal composition
K_2O	11.0	17.7	5.8–7.0	5.2–6.0	5.2
Na_2O	0.7	1.1	6.5–7.9	1.2–5.2	0.0
CaO	13.7	11.6	13.4–14.0	14.8–15.1	24.8
SiO_2	59.9	50.2	58.2–58.5	61.6–64.3	53.1
H_2O	14.7	19.2	13.4–14.7	12.3–12.6	16.9
$\text{Ca}/(\text{K} + \text{Na})$ (atom.)	1:1	1:2	1:1.5	2:1	4:1
Strongest reflections in the X-ray powder pattern, <i>d</i> , Å ⁻¹	13.33–100 6.67–76 6.47–55 3.469–45 3.068–57 3.042–45 2.945–62 2.912–90 2.205(calc)	16.01–100 7.98–24 6.24–48 3.228–22 3.197–27 2.995–47 2.903–84 2.623–20 2.185(calc)	6.70–45 6.59–41 4.697–23 3.198–21 3.038–33 2.961–100 2.944–33 1.876–21 2.36–2.38	6.55–100 6.30–32 5.90–34 5.032–28 4.386–47 2.864–25 2.762–23	7.90–13 7.82–13 4.554–23 3.965–100 2.990–67 2.494–22 1.588–26
Density, g/cm ³	1.500	1.520	1.500–1.504	2.27–2.36	2.37
α	1.509	1.523	1.505–1.510	1.501–1.504	1.536–1.542 (ω)
β	1.515	1.527	1.513–1.519	1.505–1.508	1.537–1.543 (ϵ)
Optical sign, 2 <i>V</i>	(–)60°	(+) >70°	(+) medium to large	(+) 57–68° (calc.)	(+) uniaxial
Source	This study	This study	Gard et al., (1957); Bussen et al. (1973); Zubkova et al., (2009)	Hesse et al., (1992); <i>Mineraly</i> ..., (1992)	Dunn et al., (1978); Rouse et al., (1978)

Notes: * Unit cell of rhodesite is given in arrangement, where Si-tetrahedra are coplanar to the *ab* plane similarly to the other minerals presented in the table.

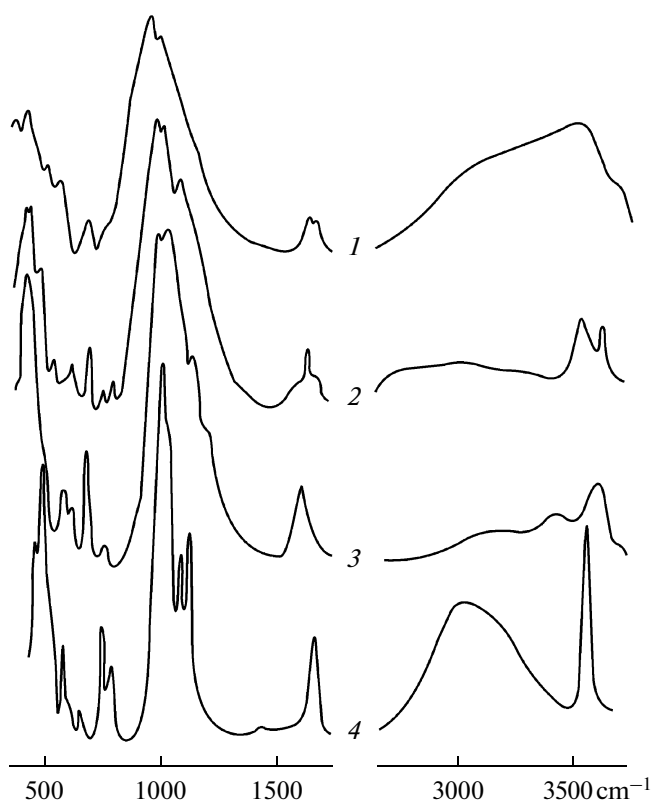


Fig. 3. The IR spectra of (1) shlykovite and (2) mountainite, the Yubileiny pegmatitic body, Lovozero pluton, Russia, (3) rhodesite, Bultfontein Mine, South Africa, and (4) apophyllite-(OH), Mount Bol'shoi Kermen, Bakhchisarai district, Crimea, Ukraine.

bers of the apophyllite group and the rhodesite meroplesiotype series (Cadoni and Ferraris, 2009).

The scarcity of shlykovite and cryptophyllite composed of abundant chemical elements is apparently caused by special formation conditions of these high-K and highly hydrous silicates, almost Al-free and containing only a small admixture of Na.

The extremely low alumina content is a special feature of the late-stage mineralization in the pegmatite, where shlykovite and cryptophyllite have been found. In contrast to the majority of other Khibiny pegmatites, aluminosilicates, including zeolites, are extremely rare in the hydrothermal assemblage of this pegmatite, though purely alkali silicates occur, for example, megacyclite $\text{KNa}_8\text{Si}_9\text{O}_{18}(\text{OH})_9 \cdot 19\text{H}_2\text{O}$, the rarest mineral, which turned out to be unexpectedly abundant as a later phase here (Zubkova et al., 2007), as well as revdite and grumantite. The development of such mineralization, characteristic of the hyperalkaline rocks of the Lovozero pluton but unusual of Khibiny, is also resulting from the very low CO_2 activity at the later stages (Pekov et al., 2008). Another feature of the described pegmatite is abundant high-K low-tem-

perature phases indicating an elevated K/Na ratio of the late hydrothermal fluid even in the Khibiny pluton generally enriched in K. The activity of potassium in this fluid was apparently much higher than that of calcium, because instead of apophyllite $\text{K}_2\text{Ca}_4[\text{Si}_8\text{O}_{20}]M \cdot 8\text{H}_2\text{O}$ ($M = \text{OH}, \text{F}$), which is widespread in nature, other phyllosilicates with a similar set of elements but different Ca/Na atomic ratio 1/1 (shlykovite) and 1/2 (cryptophyllite) appeared here.

It is suggested that cryptophyllite enriched in K and water and having a longer distance between TOT-packets (Fig. 2b) is less stable than shlykovite. This may be the reason why it occurs only as an epitactic mineral on the crystals of its more stable relative.

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