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Crystal structures of shlykovite and cryptophyllite: comparative crystal chemistry of phyllosilicate minerals of the mountainite family

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Abstract: We solved the crystal structures of the phyllosilicates shlykovite, $KCaSi_4O_9(OH)\cdot 3H_2O$, and cryptophyllite, $K_2CaSi_4O_{10}\cdot 5H_2O$, two minerals recently discovered in the Khibiny alkaline complex (Kola Peninsula, Russia). Both minerals are monoclinic with close values of the a, b and β parameters but significantly different c parameters: shlykovite $a = 6.4897(4)$, $b = 6.9969(5)$, $c = 26.714(2)$ Å, $\beta = 94.597(8)°$, $V = 1209.12(15)$ Å^3, sp. gr. $P2_1/c$, Z = 4; cryptophyllite $a = 6.4934(14)$, $b = 6.9919(5)$, $c = 32.087(3)$ Å, $\beta = 94.680(12)°$, $V = 1451.9(4)$ Å^3, sp. gr. $P2_1/n$, Z = 4. The structures were solved from synchrotron diffraction data collected on the same intergrown crystal and refined anisotropically to $R(F) = 0.0960$ for 1147 unique reflections with $I > 2\sigma(I)$ (shlykovite) and $R(F) = 0.0856$ for 1667 unique reflections with $I > 2\sigma(I)$ (cryptophyllite). Shlykovite and cryptophyllite are representatives of two new, closely related structure types. The main structural units of both minerals are *TOT* blocks consisting of tetrahedral Si layers (*T*) and an octahedral component (*O*), sandwiched between them. Each *T*-layer consists of 4- and 8-membered rings of SiO_4-tetrahedra and can be considered as a half of a double layer described in the structures of the members of the rhodesite mero-plesiotype series. A topologically closely related Si layer also forming *T*-fragments of *TOT* blocks was recently discovered in mountainite, $KNa_2Ca_2[Si_8O_{19}(OH)]\cdot 6H_2O$. The *O*-fragment of the *TOT* blocks in shlykovite and cryptophyllite is formed by columns of edge-sharing Ca-centred octahedra $CaO_5(H_2O)$. In both minerals K cations are located in the voids of the Si layer. The content of the interlayer space is different in each mineral: only H_2O molecules in shlykovite, K atoms and H_2O molecules in cryptophyllite. Mountainite, shlykovite and cryptophyllite are closely related in configuration of the *TOT* blocks, their main structure unit, and could be used to define the mountainite structural family.

Key-words: shlykovite, cryptophyllite, mountainite, mountainite family, phyllosilicates, crystal structure, synchrotron radiation.

1. Introduction

Natural phyllosilicates are numerous and characterized by a very wide diversity of tetrahedral layers. Discoveries of new structural types of these minerals and even topological types of layers formed by SiO_4-tetrahedra are not so rare in both new mineral species and earlier described minerals with unknown structures.

Recently, we solved the crystal structure of the hydrous K,Na,Ca-silicate mountainite (Zubkova *et al.*, 2009) which remained unknown for more than half of a century, since the first description of this mineral (Gard *et al.*, 1957). It was found that this phyllosilicate is not only a representative of a new structural type but it also reveals a new topological type of tetrahedral layer. Later on, the IMA Commission on New Minerals, Nomenclature and Classification approved, from our proposals, two new minerals, shlykovite (IMA 2008–062) and cryptophyllite (IMA 2008–061). They represent two new mountainite-related structural types that allow us to propose to join these three mineral species into the mountainite structural family. We avoid the term ‘‘mountainite group’’ because mountainite, shlykovite and cryptophyllite are not isotypic, which is the accepted condition for the majority of mineral groups in present-day mineralogical nomenclature (Mills *et al.*, 2009): the term ‘‘mountainite family’’ accentuates only the close crystallochemical relationship between its members.

The present paper has two aspects. First, it presents the crystal structures of shlykovite and cryptophyllite studied using synchrotron radiation on a sample consisting of an oriented intergrowth of single crystals of both minerals. The second aspect is a comparison of the crystal chemistry of these two new species, mountainite and related phyllosilicates.

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2. Shlykovite and cryptophyllite: experimental data

2.1. Brief mineralogical and chemical data

Full mineralogical description of shlykovite and cryptophyllite is given in the paper by Pekov *et al.* (2010a). In the present paper, we briefly summarize the major results.

Shlykovite and cryptophyllite were found at Mountain Rasvumchorr in the south part of the Khibiny alkaline intrusion (Kola Peninsula, Russia), the world-largest alkaline complex. They were found in a peralkaline pegmatite uncovered by open pit of the Tsentral'nyi (Central) Mine of the Apatit JSC operating for apatite. Minerals of the pegmatite can be subdivided into products of three stages (only major minerals are listed): (1) the earliest, high-temperature pegmatitic assemblage with potassic feldspar, nepheline, sodalite, alkali pyroxene (Ca- and Mg-bearing aegirine) and amphibole, lamprophyllite, eudialyte, ilmenite, fluorapatite; (2) a peralkaline (hyperagpaitic) pegmatitic assemblage with aegirine, lomonosovite, shcherbakovite, magnesium astrophyllite, villiaumite, pectolite, fenaksite, zirsinalite, kazakovite, natisite, phosinaite-(Ce), clinophosinaite, nacaphite, rasvumite, djerfisherite; (3) a peralkaline (hyperagpaitic) low-temperature hydrothermal assemblage with lovozerite, tisinalite, shafranovskite, ershovite, megacyclite, revdite, shlykovite, cryptophyllite.

Shlykovite occurs as lamellae up to 0.02 × 0.2 × 0.5 mm or fibres up to 0.5 mm long typically combined in aggregates up to 3 mm, crusts or parallel-columnar veinlets. Cryptophyllite, forming lamellae up to 0.02 × 0.1 × 0.2 mm, was found only as intergrowths with shlykovite, both oriented on {001} or chaotic. Individuals of both minerals are typically curved and/or split; lamellae show perfect, mica-like cleavage. Shlykovite and cryptophyllite are transparent, colourless in individuals; their aggregates are white, beige, brownish, pale cream-coloured or pale yellowish-greyish.

Chemical composition of both minerals was determined by electron microprobe (EDS mode, 15.7 kV, 0.5 nA, scanning a 16 × 16 μm^2 area to minimise sample damage; probe standards: Na – albite, K, Al and Si – microcline, Ca – wollastonite). Using the WDS mode, which needs high beam current, was impossible because of sample damage even with a scanning beam. H_2O contents were calculated from total difference. Chemical composition of shlykovite (wt%) is: Na_2O 0.68, K_2O 11.03, CaO 13.70, SiO_2 59.86, H_2O 14.73, total 100.00, the empirical formula (based on 13 O atoms; OH/H_2O from charge balance) is: $(K_{0.96}Na_{0.09})_{\Sigma 1.05}Ca_{1.00}Si_{4.07}O_{9.32}(OH)_{0.68}\cdot 3H_2O$, the idealized formula is: $KCaSi_4O_9(OH)\cdot 3H_2O$. Chemical composition of cryptophyllite (wt%) is: Na_2O 1.12, K_2O 17.73, CaO 11.59, Al_2O_3 0.08, SiO_2 50.24, H_2O 19.24, total 100.00, the empirical formula (based on $(Si,Al)_4(O,OH)_{10}$; OH/H_2O from charge balance) is: $(K_{1.80}Na_{0.17})_{\Sigma 1.97}Ca_{0.99}Al_{0.01}Si_{3.99}O_{9.94}(OH)_{0.06}\cdot 5.07H_2O$, the idealized formula is: $K_2CaSi_4O_{10}\cdot 5H_2O$.

2.2. X-ray crystallography and crystal-structure data

A crystal of a potentially new mineral, later named cryptophyllite, (~12 × 84 × 96 μm) was initially tried for structure determination at room temperature with an in-house Xcalibur S diffractometer (Mo*K*α-radiation, $\lambda = 0.71073$ Å) equipped with a CCD detector. A data set of 6106 reflections was obtained in the θ-range from 2.94 to 26.42°. A monoclinic unit cell (space group $P2_1/n$ was determined on the basis of the systematic absences) with $a = 6.495(2)$, $b = 6.9931(7)$, $c = 32.1000(14)$ Å and $\beta = 94.705(14)°$ was revealed. A model of the crystal structure was found by direct methods and refined with the use of SHELX software package (Sheldrick, 1997a, b) in sp. gr. $P2_1/n$. Unfortunately, the small dimensions of the crystal and the presence of a set of unindexed diffraction spots did not permit to obtain good agreement between observed and calculated F values. As it was found later, these additional reflections originated from another related mineral, later named shlykovite, which forms oriented intergrowth with cryptophyllite in this crystal; the presence of two related phases in studied aggregates was already clear from the X-ray powder-diffraction data (Pekov *et al.*, 2010a). The final value of R(F) was 0.2025. At the same time, all atoms except H were located, bond valence sums calculations (Brese & O'Keeffe, 1991) allowed us to identify O-atoms of H_2O molecules and the model seemed to be reliable. Therefore, it was decided to carry out a structural study of the crystal using synchrotron radiation.

The same crystal has been measured at the Swiss-Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Diffraction data were collected at 296 K using the MAR345 Image Plate detector, at the wavelength 0.69978 Å and the crystal-to-detector distance of 130 mm. All diffraction intensities were indexed by assuming two intergrown phases, each possessing a primitive monoclinic lattice with very close values of a and b parameters as well as β and significantly different c parameters: for one phase (cryptophyllite) the unit-cell parameters were close to those obtained earlier (see above) $a = 6.4934(14)$, $b = 6.9919(5)$, $c = 32.087(3)$ Å, $\beta = 94.680(12)°$; the second phase (shlykovite) gave the smaller cell with $a = 6.4897(4)$, $b = 6.9969(5)$, $c = 26.714(2)$ Å, $\beta = 94.597(8)°$. The lattices of these minerals are related by ~180° rotation around the b-axis, thus a significant overlapping of reflections was revealed. According to the average reflections intensity obtained during the integration process, it was found that ~60 % of shlykovite and ~40 % of cryptophyllite fractions are present in the studied sample. A total of 10514 and 15118 diffraction intensities were integrated using the CrysAlis software (Oxford Diffraction, 2006) for shlykovite and cryptophyllite, respectively. The data were corrected for Lorentz and polarization effects. Absorption correction and scaling of frames for the decaying intensity of the synchrotron beam were performed using SADABS (Sheldrick, 1997c). Only non-overlapping reflections were used in structure solution and refinement.

Space groups $P2_1/c$ for shlykovite and $P2_1/n$ for cryptophyllite were determined on the basis of the systematic absences. The structures were solved and refined anisotropically using SHELX (Sheldrick, 1997a, b) to $R = 0.0960$ for 1147 unique reflections with $I > 2\sigma(I)$ (shlykovite) and $R = 0.0856$ for 1667 unique reflections with $I > 2\sigma(I)$ (cryptophyllite). High values of R are resulting from some reflections partly affected by an overlap and a problem of background estimation which remains in such cases, as well as the poor quality of the crystals. Further details of the data collection and structure refinement of shlykovite and cryptophyllite are given in Table 1.

The structure model of cryptophyllite confirmed the structure obtained using laboratory diffraction data. PLATON (Spek, 2003) did not detect higher metric or crystallographic symmetry for both studied minerals. The refinements indicated the following idealized structural formulae: $KCa[Si_4O_9(OH)]\cdot3H_2O$ ($Z = 4$) for shlykovite and $K_2Ca[Si_4O_{10}]\cdot5H_2O$ ($Z = 4$) for cryptophyllite.

Atomic coordinates, displacement parameters, selected interatomic distances and bond-valence sums (Brese & O'Keeffe, 1991) are reported in Tables 2–4, respectively, for shlykovite; in Tables 3, 5, and 6, for cryptophyllite. Their crystal structures are shown on Fig. 1a, b.

3. Discussion

Shlykovite and cryptophyllite are representatives of two new structure types closely related to each other (Fig. 1a, b). The main structural units of both minerals are *TOT* blocks consisting of tetrahedral silicate layers (*T*-layers) and an octahedral component (*O*), formed by columns of edge-sharing Ca octahedra, sandwiched between two *T*-layers. Each *T*-layer consists of 4- and 8-membered rings of Si tetrahedra. In cryptophyllite, the *T*-layers have the composition $[Si_4O_{10}]^{\infty}$, in shlykovite $[Si_4O_9(OH)]^{\infty}$. The apical vertices of the Si tetrahedra (O(4) in Table 3) that do not participate in the bridging Si–O–Si and Si–O–Ca bonds in shlykovite were interpreted as OH group. Its bond valence sum (1.01 without possible hydrogen bonds contribution) could be increased only to 1.47 v.u. by the contribution of +0.27 v.u. from water molecule Ow(3) and +0.19 v.u. from Ow(2) in the case when O(4) is an acceptor (we can only speculate on the possible role of O(4) as well as Ow(2) and Ow(3) without the localized H-positions). In this case O(4) should be considered as O,OH and the formula of shlykovite is not balanced. Note also that the IR spectrum of shlykovite shows two distinct bands at 3250 and 3090 cm^{-1} (resonance doublet) which correspond to stretching vibrations

Table 1. Crystal data, data-collection information and refinement details for shlykovite and cryptophyllite.

Crystal data	Shlykovite	Cryptophyllite
Formula	$KCa[Si_4O_9(OH)]\cdot3H_2O$	$K_2Ca[Si_4O_{10}]\cdot5H_2O$
Formula weight	405.59	480.72
Space group, Z	$P2_1/c$, 4	$P2_1/n$, 4
Unit-cell dimensions (Å, °)	$a = 6.4897(4)$	$a = 6.4934(14)$
	$b = 6.9969(5)$	$b = 6.9919(5)$
	$c = 26.714(2)$	$c = 32.087(3)$
	$\beta = 94.597(8)$	$\beta = 94.680(12)$
V (Å^3)	1209.12(15)	1451.9(4)
$F(000)$, ρ_{calc} ($g\cdot cm^{-3}$)	820, 2.228	976, 2.199
μ (mm^{-1})	1.325	1.412
Crystal dimensions (μm)	84 × 96 × 12	
Data collection	MAR345 Image plate	
Radiation and wavelength (Å)	synchrotron, 0.69978 Å	
Temperature (K)	296(1)	
Crystal-detector dist. (mm)	130	
Total no. of frames	359	
θ range for data collection (°)	3.10–26.00	
h, k, l ranges	$-7 \le h \le 7, -8 \le k \le 8, -33 \le l \le 33$	$-7 \le h \le 7, -8 \le k \le 8, -40 \le l \le 40$
Reflections collected	10514	15118
Unique reflections	1721 ($R_{int} = 0.0967$)	2224 ($R_{int} = 0.0852$)
Reflections with $I > 2\sigma(I)$	1147	1667
Structure solution	Direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.1888, 0.8167	0.0678, 23.5684
Number of refined parameters	174	201
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0960$, $wR2 = 0.2438$	$R1 = 0.0856$, $wR2 = 0.1922$
R indices (all data)	$R1 = 0.1287$, $wR2 = 0.2735$	$R1 = 0.1092$, $wR2 = 0.2056$
GoF	1.066	1.112
$(\Delta/\sigma)_{max}$	0.001	0.001
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	−0.883, 0.882	−0.719, 0.774

Table 2. Fractional atomic coordinates and displacement parameters (in Å^2) for shlykovite.

Atom	*x*	*y*	*z*	U_{eq}
Ca	0.0189(3)	0.8392(3)	0.24336(7)	0.0210(6)
K	−0.2533(5)	0.8663(4)	0.37057(10)	0.0391(8)
Si(1)	0.0011(4)	0.8447(4)	0.08283(9)	0.0190(7)
Si(2)	0.2318(4)	0.0640(4)	0.35444(9)	0.0205(7)
Si(3)	0.4083(4)	0.8447(4)	0.15613(10)	0.0215(7)
Si(4)	0.2350(4)	0.6265(4)	0.35640(9)	0.0196(7)
O(1)	−0.0897(15)	0.0496(13)	0.1005(3)	0.043(2)
O(2)	0.5482(13)	0.6525(11)	0.1562(3)	0.0317(18)
O(3)	0.1468(13)	0.1689(10)	0.4040(2)	0.0285(17)
O(4)=OH	−0.0340(14)	0.1558(12)	−0.0233(3)	0.0332(19)
O(5)	0.2810(11)	0.8491(10)	0.3730(2)	0.0230(16)
O(6)	0.1256(13)	0.6019(10)	0.3012(3)	0.0259(17)
O(7)	0.3315(13)	0.8941(11)	0.2101(3)	0.0277(18)
O(8)	0.0649(13)	0.0753(11)	0.3073(2)	0.0297(18)
O(9)	0.2270(13)	0.8010(14)	0.1136(3)	0.039(2)
O(10)	0.5390(11)	0.0191(10)	0.1335(3)	0.0273(16)
Ow(1)	−0.3252(15)	0.7724(14)	0.2731(3)	0.042(2)
Ow(2)	−0.265(3)	0.601(3)	−0.0265(4)	0.116(7)
Ow(3)	0.3528(13)	0.6823(14)	−0.0143(3)	0.039(2)

Note: Numbers in parentheses are e.s.d.'s referred to the last digit.

Table 3. Selected interatomic distances (Å) for the coordination polyhedra in shlykovite and cryptophyllite.

Shlykovite				Cryptophyllite			
Ca–O(7)	2.311(8)	Si(1)–O(3)	1.617(8)	Ca–O(6)	2.305(6)	Si(1)–(3)	1.571(6)
–O(8)	2.328(8)	–O(4)	1.620(7)	–O(1)	2.356(6)	–O(2)	1.631(7)
–O(6)	2.336(7)	–O(1)	1.634(8)	–O(3)	2.357(6)	–O(10)	1.634(7)
–O(6)	2.345(7)	–O(9)	1.650(8)	–O(1)	2.358(6)	–O(9)	1.646(6)
–O(8)	2.378(7)	Av.	1.630	–O(3)	2.369(6)	Av.	1.620
–Ow(1)	2.475(10)			–Ow(1)	2.458(7)		
Av.	2.362	Si(2)–O(8)	1.595(8)	Av.	2.367	Si(2)–O(1)	1.578(6)
		–O(2)	1.602(9)			–O(7)	1.621(7)
K–Ow(1)	2.689(8)	–O(5)	1.607(7)	K(1)–Ow(1)	2.699(6)	–O(5)	1.641(6)
–Ow(2)	2.767(12)	–O(3)	1.646(7)	–Ow(5)	2.764(8)	–O(2)	1.645(7)
–O(2)	2.823(8)	Av.	1.612	–O(7)	2.828(8)	Av.	1.621
–O(5)	3.031(8)			–O(2)	3.031(7)		
–O(10)	3.052(8)	Si(3)–O(9)	1.599(8)	–O(10)	3.062(7)	Si(3)–O(6)	1.586(6)
–O(9)	3.074(10)	–O(7)	1.600(7)	–O(1)	3.120(7)	–O(8)	1.616(7)
–O(8)	3.133(8)	–O(2)	1.622(8)	–O(8)	3.124(8)	–O(7)	1.636(7)
–O(1)	3.191(10)	–O(10)	1.629(7)	–O(9)	3.248(8)	–O(10)	1.637(6)
–O(3)	3.413(9)	Av.	1.612	Av.	2.984	Av.	1.619
Av.	3.02						
		Si(4)–O(6)	1.593(7)	K(2)–Ow(4)	2.683(9)	Si(4)–O(4)	1.584(6)
		–O(1)	1.637(7)	–Ow(3)	2.696(12)	–O(5)	1.625(7)
		–O(5)	1.640(7)	–Ow(3)	2.757(9)	–O(9)	1.627(7)
		–O(10)	1.651(8)	–Ow(5)	2.772(9)	–O(8)	1.631(7)
		Av.	1.630	–Ow(2)	2.812(14)	Av.	1.617
				–O(2)	2.970(6)		
				–O(5)	3.323(7)		
				Av.	2.86		

of silanol groups Si–OH located close to each other (Pekov *et al.*, 2010a). Thus O(4) in the shlykovite structure is OH.

Topologically similar $[Si_8O_{18}(O,OH)_2]^{\infty}$ layers also forming *T*-fragment of *TOT*-blocks were recently discovered in the structure of mountainite, $KNa_2Ca_2[Si_8O_{19}(OH)]\cdot 6H_2O$, with space group *P*2/*c* and unit-cell dimensions: $a = 13.704$, $b = 6.576$, $c = 13.751$ Å, $\beta = 105.75°$ (Zubkova *et al.*, 2009) (Fig. 1c). *T*-layers in shlykovite and cryptophyllite are practically identical while in mountainite they are slightly different. Each 4-membered ring in all three minerals contains one tetrahedron whose apical vertex looks in opposite direction with respect to the other three tetrahedra. In shlykovite and cryptophyllite (Fig. 2a) the orientation of the 4-membered rings is the same in both

Table 4. Bond order calculations for shlykovite.

	Ca	K	Si(1)	Si(2)	Si(3)	Si(4)	Σ	H-bonds contribution	Σ_{total}
O(1)		0.06	0.97			0.96	1.99		1.99
O(2)		0.15		1.06	1.00		2.21		2.21
O(3)		0.03	1.02	0.94			1.99		1.99
O(4)=OH			1.01				1.01		1.01*
O(5)		0.09		1.05		0.96	2.10		2.10
O(6)	0.37 0.36					1.09	1.82		1.82
O(7)	0.39				1.07		1.46	+0.23(Ow(1)) +0.18(Ow(1))	1.87
O(8)	0.38 0.33			1.08			1.79		1.79
O(9)		0.08 0.07	0.93		1.07		2.15		2.15
O(10)		0.08			0.99	0.93	2.00		2.00
Ow(1)	0.25	0.22					0.47	−0.23(O(7)) −0.18(O(7))	0.06
Ow(2)		0.18					0.18		0.18*
Ow(3)							0.00		0.00*
Σ	2.08	0.96	3.93	4.13	4.13	3.94			

Note: Parameters taken from Brese & O'Keeffe (1991) and Ferraris & Ivaldi (1988).
*Bond valence sums for water molecules Ow(2), Ow(3) and O(4)=OH are given without hydrogen bonds contribution.

Table 5. Fractional atomic coordinates and displacement parameters (in Å^2) for cryptophyllite.

Atom	*x*	*y*	*z*	U_{eq}
Ca	0.2275(3)	0.8469(2)	0.24478(5)	0.0101(4)
K(1)	−0.0773(4)	0.3757(4)	0.14911(7)	0.0267(6)
K(2)	0.4642(5)	0.3655(5)	0.05485(8)	0.0458(8)
Si(1)	0.4166(4)	0.1350(4)	0.16108(6)	0.0097(5)
Si(2)	0.4156(4)	0.5747(3)	0.16335(6)	0.0091(5)
Si(3)	−0.2152(4)	0.8568(4)	0.17356(6)	0.0101(5)
Si(4)	0.1402(4)	0.8539(4)	0.11015(6)	0.0102(5)
O(1)	0.2820(10)	0.5798(9)	0.20226(16)	0.0134(13)
O(2)	0.4557(10)	0.3556(9)	0.14722(17)	0.0141(12)
O(3)	0.3399(11)	0.1097(9)	0.20594(19)	0.0171(14)
O(4)	0.0613(10)	0.8522(10)	0.06211(17)	0.0168(13)
O(5)	0.3051(11)	0.6837(10)	0.12212(18)	0.0192(15)
O(6)	−0.1077(10)	0.9049(9)	0.21850(18)	0.0141(13)
O(7)	0.6464(11)	0.6611(10)	0.17274(19)	0.0202(14)
O(8)	−0.0513(11)	0.8194(11)	0.13918(19)	0.0221(15)
O(9)	0.2518(11)	0.0558(10)	0.12330(19)	0.0206(15)
O(10)	−0.3636(10)	0.0301(9)	0.15437(17)	0.0140(13)
Ow(1)	0.5913(12)	0.7909(10)	0.26910(18)	0.0203(15)
Ow(2)	−0.3397(17)	0.007(2)	0.0629(3)	0.064(3)
Ow(3)	0.4071(15)	0.7198(16)	0.0228(3)	0.047(2)
Ow(4)	0.1115(15)	0.2050(12)	0.0224(2)	0.035(2)
Ow(5)	−0.1236(14)	0.4715(12)	0.0653(2)	0.036(2)

Note: Numbers in parentheses are e.s.d.'s referred to the last digit.

directions while in mountainite (Fig. 2b) these rings have the same orientation in one direction (*b*-axis) and the opposite one along the *c*-axis.

The *T*-layers in the structures of the three minerals can be compared with those in the apophyllite-group minerals, $ACa_4(Si_8O_{20})X{\cdot}8H_2O$ with A = K, Na and X = F, OH, where all tetrahedra in the 4-membered rings are oriented in one direction (Taylor & Naray-Szabo, 1931), in cavansite, $Ca(VO)(Si_4O_{10}){\cdot}4H_2O$, with similar layers but with the pairs of tetrahedra in each 4-membered ring oriented in opposite directions (Evans, 1973) and with a group of minerals and synthetic compounds with topologically closely related corrugated layers formed by 4- and 8-membered rings of tetrahedra: ekanite, $ThCa_2[Si_8O_{20}]$ (Szymanski *et al.*, 1982), gillespite, $BaFe[Si_4O_{10}]$ (Pabst, 1943), cuprorivaite, $CaCu[Si_4O_{10}]$ (Pabst, 1959), effenbergerite, $BaCu[Si_4O_{10}]$ (Giester & Rieck, 1994), and wesselsite, $SrCu[Si_4O_{10}]$ (Chakoumakos *et al.*, 1993; Knight

Table 6. Bond order calculations for cryptophyllite.

Atom	Ca	K(1)	K(2)	Si(1)	Si(2)	Si(3)	Si(4)	Σ	H-bonds contribution	Σ_{total}
O(1)	0.35 0.35	0.07			1.13			1.90		1.90
O(2)		0.09	0.10	0.98	0.94			2.11		2.11
O(3)	0.35 0.34			1.15				1.84		1.84
O(4)							1.11	1.11	+0.18(Ow(4)) +0.18(Ow(3)) +0.18(Ow(2)) +0.16(Ow(4)) +0.15(Ow(5))	1.96
O(5)			0.04		0.95		1.00	1.99		1.99
O(6)	0.40					1.11		1.51	+0.21(Ow(1)) +0.20(Ow(1))	1.92
O(7)		0.15			1.01	0.97		2.13		2.13
O(8)		0.07				1.02	0.98	2.07		2.07
O(9)		0.05		0.94			0.99	1.98		1.98
O(10)		0.08		0.97		0.96		2.01	+0.14(Ow(2))	2.15
Ow(1)	0.26	0.21						0.47	−0.21(O(6)) −0.20(O(6))	0.06
Ow(2)			0.16					0.16	−0.18(O(4)) +0.17(Ow(3)) −0.14(Ow(2))	0.01
Ow(3)			0.22 0.18					0.40	−0.18(O(4)) −0.17(Ow(2)) −0.18(O(4))	0.05
Ow(4)			0.22					0.22	−0.16(O(4)) +0.15(Ow(5))	0.03
Ow(5)		0.18	0.18					0.36	−0.15(Ow(4)) −0.15(O(4))	0.06
Σ	2.05	0.90	1.10	4.04	4.03	4.06	4.07			

Note: Parameters taken from Brese & O'Keeffe (1991) and Ferraris & Ivaldi (1988).

et al., 2010). Detailed comparison of the layers formed by 4- and 8-membered rings of SiO_4-tetrahedra in natural and synthetic phyllosilicates was made by Zubkova *et al.* (2009).

Among the thirteen K,Ca synthetic silicates known so far, the cationic composition and the single silicate layers make the structures of shlykovite and cryptophyllite close to synthetic potassium calcium silicate $K_2Ca_4Si_8O_{21}$ (Arroyabe *et al.*, 2009). However, unlike the members of mountainite family, the layers of $K_2Ca_4Si_8O_{21}$ are characterized by a complex arrangement of 6-, 8-, 10- and 12-membered tetrahedral rings. An interrupted silicate framework with the same Si:O ratio as in the layers of shlykovite, cryptophyllite and mountainite was recently revealed in the structure of another K,Ca silicate, $K_8CaSi_{10}O_{25}$ (Kahlenberg *et al.*, 2006).

It is worthy of note that the silicate complexes described in the members of the rhodesite mero-plesiotype series (Cadoni & Ferraris, 2009) reveal more similarities with those in shlykovite and cryptophyllite than with the tetrahedral layers in mountainite. This series now includes seven minerals, rhodesite, $HK_{1-x}Na_{x+2y}Ca_{2-y}[Si_8O_{19}]\cdot(6\text{-}z)H_2O$ (Hesse *et al.*, 1992), macdonaldite, $BaCa_4[Si_8O_{18}(OH)]_2\cdot 10H_2O$ (Cannillo *et al.*, 1968), monteregianite-(Y), $K_2Na_4Y_2[Si_8O_{19}]_2\cdot 10H_2O$ (Ghose *et al.*, 1987), seidite-(Ce), $Na_4(Ce,Sr)_2\{Ti(OH)_2[Si_8O_{18}]\}$ $(O,OH,F)_4\cdot 5H_2O$ (Ferraris *et al.*, 2003), delhayellite, $K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl$ (Cannillo *et al.*, 1970; Pekov *et al.*, 2009), hydrodelhayelite, $KCa_2[AlSi_7O_{17}(OH)_2]\cdot 6\text{–}x(H_2O)$ (Dorfman & Chiragov, 1979; Ragimov *et al.*, 1980) and the recently discovered fivegite, $K_4Ca_2[AlSi_7O_{17}(O_{2-x}OH_x)][(H_2O)_{2-x}OH_x]Cl$ (IMA 2009-067: Pekov *et al.*, 2010b), and seven synthetic compounds: AV-5, $KNa_2Ce[Si_8O_{19}]\cdot 5H_2O$ (Rocha *et al.*, 2000), Eu-AV-9, $KNa_2Eu[Si_8O_{19}]\cdot 5H_2O$ and Tb-AV-9, $KNa_2Tb[Si_8O_{19}]\cdot 5H_2O$ (Ananias *et al.*, 2001), Er-AV-9 $KNa_2Er[Si_8O_{19}]\cdot 5H_2O$ (Ananias *et al.*, 2004), TR03, $KNaCa_2[Si_8O_{19}]\cdot 5H_2O$ and TR04, $KNa_3Sr[Si_8O_{19}]\cdot 4.3H_2O$ (Cadoni & Ferraris, 2009), CAS-1, $(|(Ca_4K_4(H_2O)_8)|\ [Si_{16}O_{38}])$ (Jorda *et al.*, 2005). All these phyllosilicates are characterized by the presence of a double Si or (Si,Al) (in delhayelite, hydrodelhayelite and fivegite) layer formed by two single *T*-layers topologically very close to those found in shlykovite and cryptophyllite and connected via common vertices (Fig. 2c). Corrugated double silicate layers similar to those described in rhodesite were found in the structure of synthetic microporous silicate $Cs_3ScSi_8O_{19}$ (Kolitsch & Tillmanns, 2004).

Like in mountainite, the *O*-fragment of the *TOT*-blocks in shlykovite and cryptophyllite is formed by columns of edge-sharing $CaO_5(H_2O)$ octahedra. The main difference

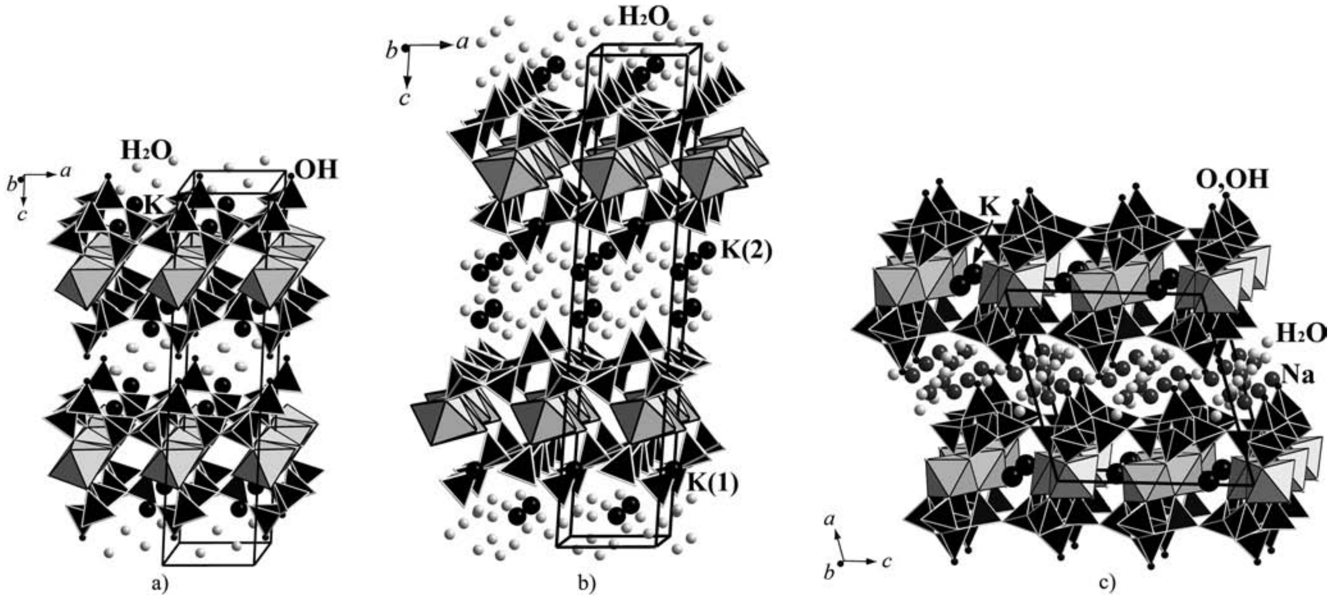


Fig. 1. Crystal structures of shlykovite (a), cryptophyllite (b) and mountainite (c). SiO_4 tetrahedra are black, Ca octahedra are light grey. K cations are shown as large black circles, O atoms of H_2O molecules as small grey circles. Na atoms in mountainite are marked as large grey spheres. Positions of the OH-groups in shlykovite and (O,OH) in mountainite are shown as small black circles.

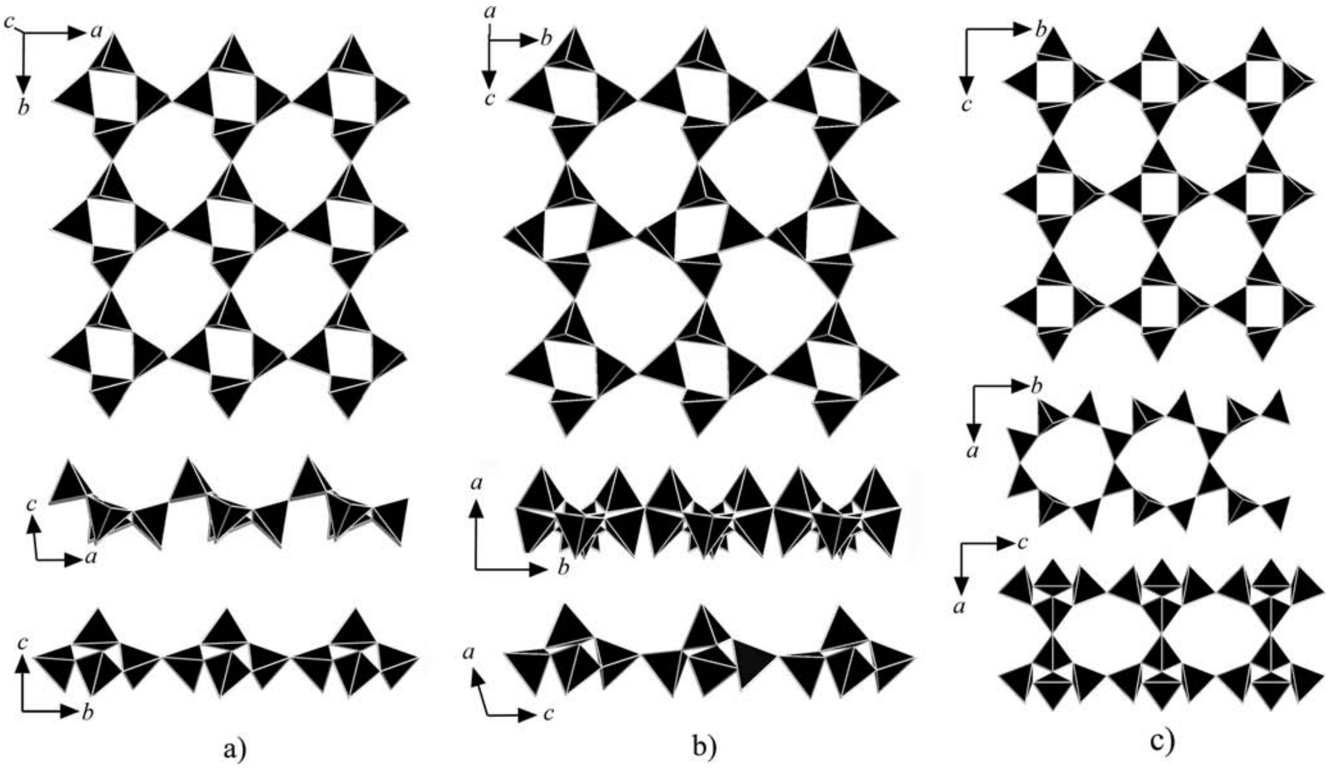
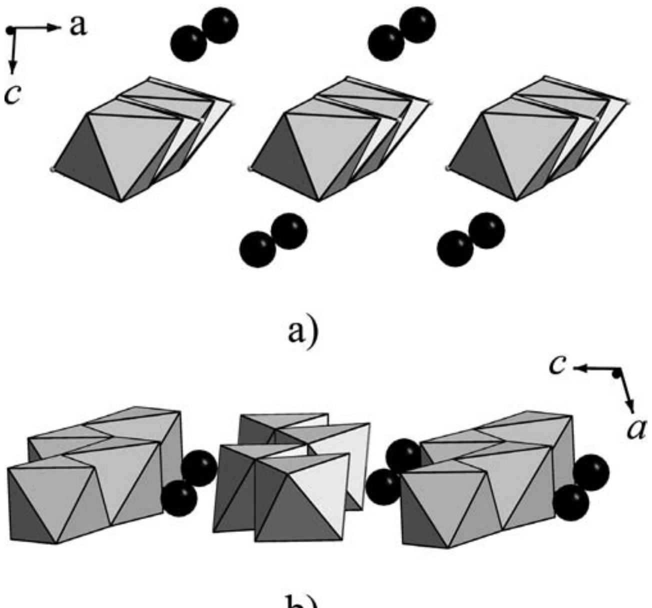


Fig. 2. Silicate layer formed by 4- and 8-membered rings in the structure of shlykovite (a), mountainite (b) and rhodesite (c).

in this structural fragment between mountainite and the two new minerals is in the configuration of these columns: in mountainite it is similar to the fragment of the octahedral framework in the structure of α-PbO_2, *i.e.* the *O*-fragment in mountainite contains zig-zag columns of Ca-centred octahedra (Zubkova *et al.*, 2009), while in shlykovite and cryptophyllite these columns are straight. Similar configurations of the *O*-fragment were found in rhodesite and several other members of the rhodesite mero-plesiotype series (Cadoni & Ferraris, 2009). Location of the K atoms inside the *TOT*-blocks in mountainite (between the columns of Ca-centred octahedra, *i.e.*, between the two



a)

b)

Fig. 3. The columns of Ca octahedra and the position of K cations inside the *TOT* blocks in shlykovite (a) and mountainite (b).

silicate layers forming one block) is also quite different from those in shlykovite and cryptophyllite, where the K cations are located in the voids of the silicate layer. Figure 3a, b shows the configurations of the columns of Ca octahedra and the position of K cations inside the *TOT* blocks in shlykovite and mountainite, respectively.

The content of the interlayer space between *TOT* blocks is characteristic for each mineral: only H_2O molecules in shlykovite, K atoms and H_2O molecules in cryptophyllite and Na atoms and H_2O molecules in mountainite (Zubkova *et al.*, 2009). The arrangement of alkali cations and vacancies (φ) in the *O*-layer and in the interlayer space, respectively, is as follows ($Z = 1$): $[K_2\varphi_2][Na_4]$ – mountainite, $[K_4][\varphi_4]$ – shlykovite, $[K_4][K_4]$ – cryptophyllite.

In spite of the differences in space groups and unit-cell dimensions between mountainite, shlykovite and cryptophyllite, these three minerals are closely related in the configuration of the *TOT*-blocks, the main structure unit for this family. At the same time, their relationship to other phyllosilicates is significantly more distant. Thus, mountainite, shlykovite and cryptophyllite could be united to form the mountainite structural family.

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