Delhayelite and Mountainite Mineral Families: Crystal Chemical Relationship, Microporous Character and Genetic Features

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Many minerals show the properties commonly named "zeolitic": ion exchange and leaching, sorption of gases and organic molecules, reversible hydration, *etc*. The most well-known examples are aluminosilicate zeolites, clay minerals and pyrochlores. Besides them, several other large groups of minerals are now in focus of research as potential microporous materials or their prototypes. First, there are Ti-, Zr-, Nb-silicates with heteropolyhedral frameworks. This paper is devoted to other minerals of this interest. There are two related families of natural silicates with structures based on Si,O or Al,Si,O tetrahedral layers and columns of edge-shared Ca-centered octahedra.

The delhayelite mineral family can be distinguished within the rhodesite mero-plesiotype series (Ferraris and Gula 2005; Cadoni and Ferraris 2009) as its aluminosilicate branch that includes delhayelite, fivegite and hydrodelhayelite (Table 1). The idealized formula of delhayelite earlier presented as $K_7Na_3Ca_5[AlSi_7O_{19}]_2F_4Cl_2$ ($Z = 1$) (Cannillo et al. 1969) was recently refined: $K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl$ ($Z = 2$) (Pekov et al. 2009). Its crystal structure is based upon the double-layer tetrahedral blocks $[(Al,Si)_4Si_{12}O_{38}]$ linked by the columns of Ca octahedra (Fig. 1a). Zeolite-like channels inside the tetrahedral blocks host K^+ and Cl^- ions whereas the channels in the interlayer space, between Ca columns, host Na^+ and F^- (Cannillo et al. 1969; Pekov et al. 2009). Fivegite, $K_4Ca_2[AlSi_7O_{17}(O_{2-x}OH_x)][(H_2O)_{2-x}OH_x]Cl$ ($x = 0$–2) (Pekov et al. 2010a), and hydrodelhayelite, $KCa_2[AlSi_7O_{17}(OH)_2]\cdot(6\text{-}x)H_2O$ (Pekov et al. 2009; Ragimov et al. 1980), have the same Ca,Al,Si,O structure motif (rigid 3D part of the structure, $Ca_2[AlSi_7O_{17}\varnothing_2]$, slightly distorted as compared with delhayelite, with protonated "pendent" vertices Ø of Si tetrahedra) but different contents of the channels (Cannillo et al. 1969; Pekov et al. 2009) (Fig. 2). We consider this Ca,Al,Si,O motif as

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Table 1 Comparative data for minerals of the delhayelite family

	Delhayelite	Fivegite	Hydrodelhayelite[a]
Mineral formula	$K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl$	$K_4Ca_2[AlSi_7O_{17}(O_{2-x}OH_x)][(H_2O)_{2-x}OH_x]Cl$	$KCa_2[AlSi_7O_{17}(OH)_2](H_2O)_{6-x}$
Crystal system space group	Orthorhombic *Pmmn*	Orthorhombic $Pm2_1n$	Orthorhombic $Pm2_1n$
a, Å	24.58	24.34	23.85
b, Å	7.06	7.04	7.07
c, Å	6.58	6.54	6.65
V, $Å^3$	1,142	1,120	1,121
Z	2	2	2
References	(Cannillo et al. 1969; Pekov et al. 2009)	(Pekov et al. 2010a)	(Pekov et al. 2009; Ragimov et al. 1980)

[a] Hydrodelhayelite unit cell is given in the setting with tetrahedral layers perpendicular to the *a* axis (with corresponding space group), like other minerals in this table

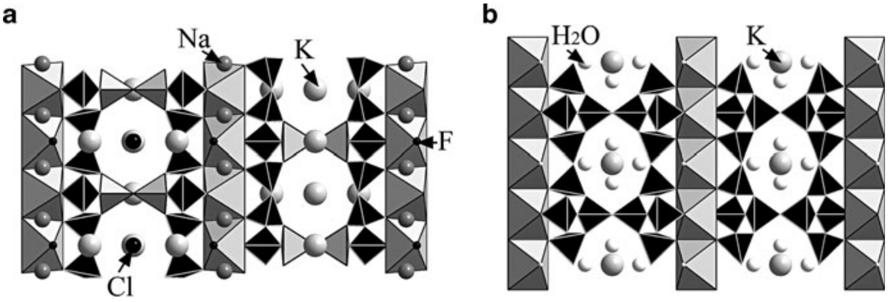

Fig. 1 Crystal structures of delhayelite (**a**): drawn based on the data from Pekov et al. (2009) and rhodesite (**b**): drawn based on the data from Hesse et al. (1992)): *ab* projections. Ca octahedral columns and the tetrahedral motifs are shown in polyhedra; Si tetrahedra are *black*, (Al,Si) tetrahedra in delhayelite are *gray*

a heteropolyhedral quasi-framework. If we do not take into account Ca octahedra then delhayelite-family members could be presented as phyllosilicates. However it seems more correct, from both physical and chemical viewpoints, to include Ca octahedral columns to the main building unit of these minerals.

The Ca,Al,Si,O quasi-framework remains stable in natural transformation series delhayelite → fivegite → hydrodelhayelite (Pekov et al. 2010a) and in products of our experiments with delhayelite for ion leaching, cation exchange and hydration in aqueous systems (Turchkova et al. 2011). Thus the delhayelite family is a new, specific family of natural microporous aluminosilicates with zeolitic properties that is, in fact, intermediate between phyllo – and tecto-aluminosilicates. Its representatives delhayelite and fivegite differ from other microporous minerals by the presence of mobile halogen anions in the same channels as alkali cations. These ions are ordered in accordance with widths of the channels (Figs. 1 and 2). The hydrothermal alteration of delhayelite occurs step-by-step and shows different mobility of ions located in different structural sites: first leaching of F^- and Na^+ from the interlayer space occurs and

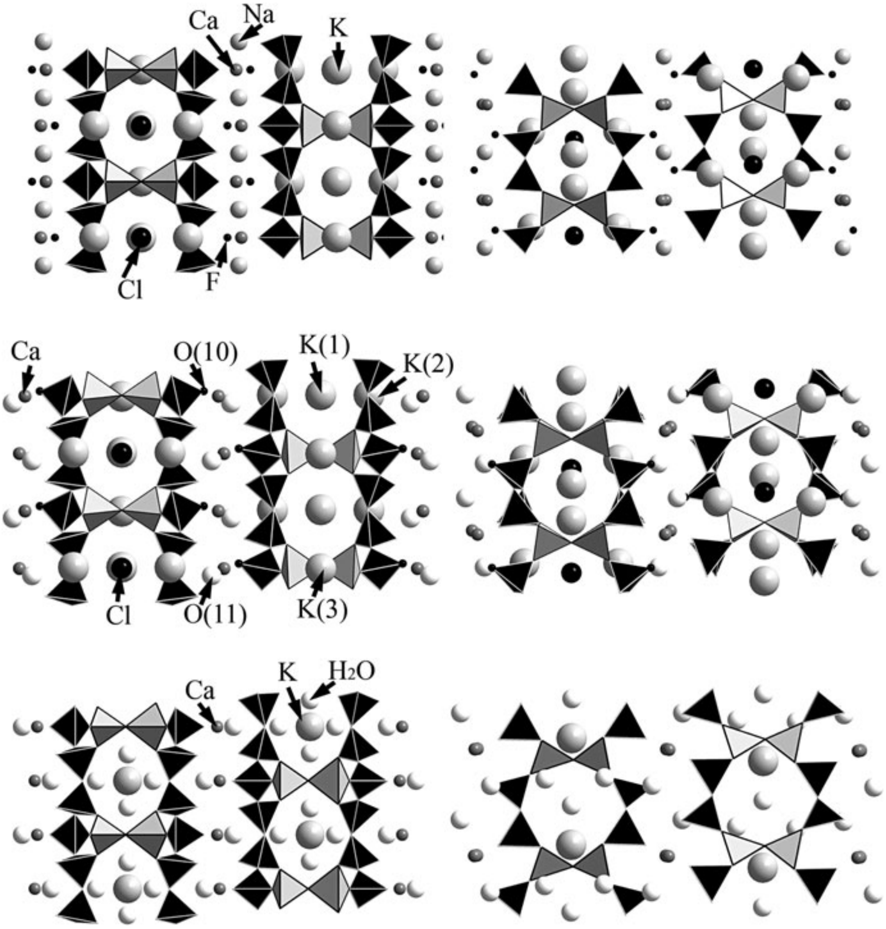

Fig. 2 Crystal structures (from *top* to *bottom*) of delhayelite, fivegite and hydrodelhayelite. Si tetrahedra are *black*, (Al,Si) tetrahedra are *gray*. *Left* column – *ab* projections, *right* column – *ac* projections, in the unified setting (see Table 1)

further Cl^- and K^+ leave their sites within the tetrahedral block. These processes can be presented as following reactions:

(1) Delhayelite $K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl + 2H_2O \rightarrow$ fivegite $K_4Ca_2[AlSi_7O_{17}(O_{2-x}OH_x)][(H_2O)_{2-x}OH_x]Cl + 2Na^+ + 2F^-$;

(2) Fivegite + $(5-x)H_2O \rightarrow$ hydrodelhayelite $KCa_2[AlSi_7O_{17}(OH)_2](H_2O)_{6-x}$ + 3 $K^+ + Cl^-$.

Delhayelite, fivegite and hydrodelhayelite are individual, well-stoichiometric minerals and transformations from one to other have discrete character: boarders between the initial and replacing phases in this evolution series are sharp (Pekov et al. 2010a).

Table 2 Comparative data for minerals of the mountainite family

Mineral formula	Mountainite $KNa_2Ca_2[Si_8O_{19}(OH)] \bullet 6H_2O$	Shlykovite KCa $[Si_4O_9(OH)] \bullet 3H_2O$	Cryptophyllite K_2Ca $[Si_4O_{10}] \bullet 5H_2O$
Crystal system space group	Monoclinic $P2/c$	Monoclinic $P2_1/c$	Monoclinic $P2_1/n$
a, Å	13.70	6.49	6.49
b, Å	6.58	7.00	6.99
c, Å	13.75	26.71	32.09
β,°	105.75	94.60	94.68
V, Å^3	1,193	1,209	1,452
Z	2	4	4
References	(Gard et al. 1957; Zubkova et al. 2009)	(Pekov et al. 2010b)	(Pekov et al. 2010b)

In our experiments on cation exchange (that is accompanied by significant hydration), leaching of contents of the interlayer space and channels shows the same sequence as simple hydration: first F and Na, further Cl and K. These facts indicate high selectivity of "zeolitic" characteristics of delhayelite-family minerals that makes them (and related synthetic compounds) promising as technologically usable microporous materials.

Rhodesite, $KCa_2[Si_8O_{18}(OH)] \cdot (6-x)H_2O$, the structural analogue of hydrodelhayelite with Si instead of Al in corresponding tetrahedral sites (Pekov et al. 2009; Hesse et al. 1992) (Fig. 1b), can be considered as a "bridge" between aluminosilicates of the delhayelite family and crystal chemically related Al-free silicates of the mountainite family of natural phyllosilicates recently defined in (Pekov et al. 2010b).

The mountainite family includes three minerals (Table 2) with unique, different one from others but related structures. The structure of mountainite, a mineral known since 1957 (Gard et al. 1957), was solved in 2008 and its crystallochemically correct formula was determined: $KNa_2Ca_2[Si_8O_{19}(OH)] \cdot 6H_2O$ ($Z = 2$) (Zubkova et al. 2009). Shlykovite, $K_2Ca_2[Si_8O_{18}(OH)_2] \cdot 6H_2O$, and cryptophyllite, $K_4Ca_2[Si_8O_{20}] \cdot 10H_2O$, are new minerals discovered in 2009 in the Khibiny alkaline complex, Kola Peninsula, Russia (Pekov et al. 2010b).

The main structural unit of all three minerals is *TOT* block consisting of two identical tetrahedral Si layers (*T*) $[Si_8O_{18}(O,OH)_2]$ and an octahedral component (*O*), formed by columns of edge-sharing Ca octahedra sandwiched between them (Fig. 3). Single *T*-layer in shlykovite and cryptophyllite is topologically the same as half of the double-layer block of rhodesite, $[Si_{16}O_{36}(OH)_2]$, or delhayelite, $[(Al,Si)_4Si_{12}O_{38}]$ (Fig. 4). *T*-layer in mountainite is very similar and differs from that of shlykovite and cryptophyllite only by the orientation of some Si tetrahedra that causes the difference in configuration of the Ca octahedral columns in these minerals. K^+ cations are located in channels within *TOT* blocks in all three minerals, like delhayelite-family members that also contain only the largest K^+ cations in channels within the tetrahedral block.

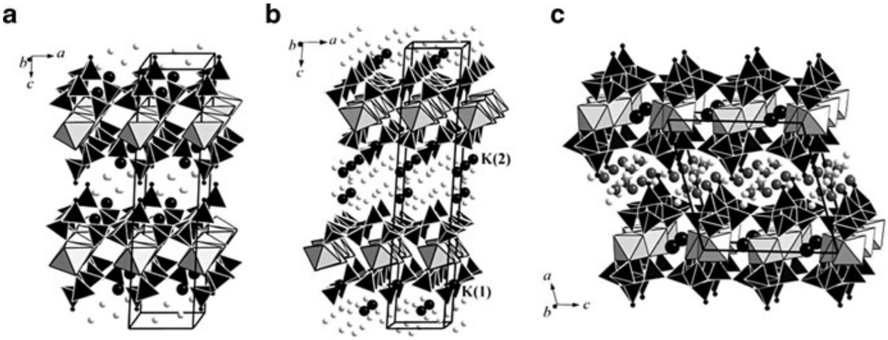

Fig. 3 Crystal structures of shlykovite (**a**), cryptophyllite (**b**), and mountainite (**c**), SiO_4 tetrahedra are *black*, Ca octahedra are *light grey*. K cations are shown as *large black circles*, O atoms of H_2O molecules – as *small grey circles*. Na atoms in mountainite are marked as *large grey spheres*. Positions of OH-groups in shlykovite and (O, OH) in mountainite are shown as *small black circles*

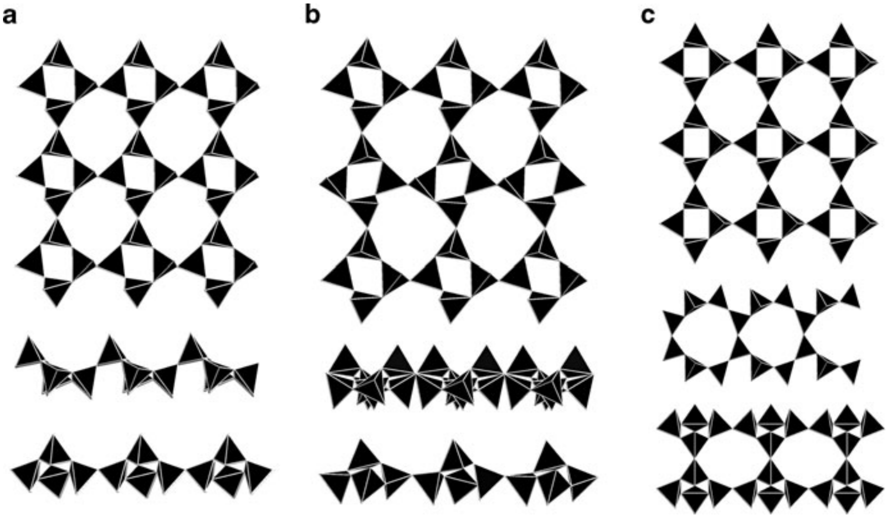

Fig. 4 Silicate layer formed by 4- and 8-membered rings in the structures of shlykovite and cryptophyllite (**a**), mountainite (**b**), and rhodesite (**c**)

Unlike rhodesite mero-plesiotype series minerals with heteropolyhedral quasi-frameworks, members of the mountainite family are true phyllosilicates: *TOT* blocks are isolated from each other and only H_2O molecules (shlykovite) or H_2O molecules and alkali cations (K^+ in cryptophyllite, Na^+ in mountainite) are located between them (Fig. 3). An important feature of the mountainite family is the variability of the distance between *TOT* blocks (that determines the basal parameter of unit cell) in accordance with interlayer contents: $(H_2O)_4$ in shlykovite ($c = 26.7$ Å), $K_2(H_2O)_8$ in cryptophyllite ($c = 32.1$ Å) or $Na_2(H_2O)_4$ in mountainite ($2a = 27.5$ Å).

This variability and significant hydration capacity indicate great potential of mountainite-family minerals as new microporous materials suitable to the exchange of large cations and, probably, their immobilization after heating for H_2O removal and structure contraction.

Minerals of both the delhayelite and the mountainite families were only found in the alkaline formation. Common feature of all of them is species-defining role of K (Tables 1 and 2) and they occur in potassium-enriched rocks or their derivatives. Delhayelite, the only anhydrous mineral among six representatives of these families, is formed under high-temperature conditions in K-rich peralkaline rocks and related pegmatites. All other discussed minerals have hydrothermal origin. The Al-bearing species, fivegite and hydrodelhayelite, are known only as products of transformation of delhayelite with preservation of its stable Ca,Al,Si,O heteropolyhedral quasi-framework whereas Al-free minerals (mountainite family) crystallize directly from low-temperature hydrothermal solutions just as rhodesite. The minerals with single and double tetrahedral layers are formed under the same conditions, sometimes together. Intimate intergrowths of mountainite and rhodesite were found in hydrothermally altered kimberlitic rock at Bultfontein, South Africa (Gard et al. 1957). In one pegmatite body at Mt. Rasvumchorr in Khibiny, we have observed five of six minerals (except mountainite) of both discussed families. In the late-stage, low-temperature hydrothermal assemblage hydrodelhayelite, occurring as partial or complete pseudomorphs after fivegite (that partially or completely replaced delhayelite), is associated with shlykovite and cryptophyllite typically forming intimate intergrowths in cracks and cavities of this pegmatite.

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