

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

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The delhayelite mineral family can be distinguished within the rhodesite mero-plesiotype series (Cadoni and Ferraris 2009) as its aluminosilicate branch that includes delhayelite, fivegite and hydrodelhayelite. 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: $K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl$ ($Z = 2$) [3]. Its crystal structure is based upon the double-layer tetrahedral blocks $[(Al,Si)_4Si_{12}O_{38}]$ linked by the columns of edge-shared Ca octahedra. 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; Cadoni and Ferraris 2009). Fivegite, $K_4Ca_2[AlSi_7O_{17}(O_{2-x}OH_x)][(H_2O)_{2-x}OH_x]Cl$ ($x = 0-2$), and hydrodelhayelite, $KCa_2[AlSi_7O_{17}(OH)_2] \cdot (6-x)H_2O$, have the same CaAlSiO structure motif (rigid 3D part of the structure, $Ca_2[AlSi_7O_{17}O_2]$, slightly distorted as compared with delhayelite, with protonated “pendent” vertices \emptyset of Si tetrahedra) but different contents of the channels (Pekov et al. 2009, 2010a). We consider this CaAlSiO motif as a heteropolyhedral quasi-framework. It remains stable in natural transformation series delhayelite \Rightarrow fivegite \Rightarrow hydrodelhayelite (Pekov et al. 2010a) and in products of our experiments with delhayelite for ion leaching, cation exchange (NH_4^+ , Rb^+ , Cs^+ and Ba^{2+}) and hydration in aqueous systems. Thus the delhayelite family is a new, specific family of natural microporous aluminosilicates with zeolitic properties that is 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. 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 further Cl^- and K^+ leave their sites within the tetrahedral block. It indicates high selectivity of zeolitic characteristics of delhayelite-family minerals that makes them (or related synthetic compounds) promising as technologically usable microporous materials.

Rhodesite, $KCa_2[Si_8O_{18}(OH)] \cdot (6-x)H_2O$, the Al-free structural analogue of hydrodelhayelite (Pekov et al. 2009), can be considered as a “bridge” between the delhayelite family (and, generally, the rhodesite mero-plesiotype series) and chemically and structurally related mountainite mineral family, a new family of natural phyllosilicates recently defined by us.

The mountainite family includes three minerals 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. Single *T*-layer in

shlykovite and cryptophyllite is topologically the same as half of the double-layer block of rhodesite, $[\text{Si}_{16}\text{O}_{36}(\text{OH})_2]$, or delhayelite, $[(\text{Al},\text{Si})_4\text{Si}_{12}\text{O}_{38}]$. *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.

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. 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: $(\text{H}_2\text{O})_4$ in shlykovite ($c = 26.7 \text{ \AA}$), $\text{K}_2(\text{H}_2\text{O})_8$ in cryptophyllite ($c = 32.1 \text{ \AA}$) or $\text{Na}_2(\text{H}_2\text{O})_4$ in mountainite ($2a = 27.5 \text{ \AA}$). 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 water removal and structure contraction.

Minerals of both the delhayelite and the mountainite families occur in the alkaline formation. 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 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 CaAlSiO 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 [5]. In Khibiny, we observe late-stage, low-temperature hydrothermal association of hydrodelhayelite, occurring as partial or complete pseudomorphs after fivegite (that replaced delhayelite), with shlykovite and cryptophyllite typically forming intergrowths in cracks and cavities of a pegmatite.

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