

**Delhayelite: ion leaching and ion exchange**

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Delhayelite, ideally  $K_4Na_2Ca_2[AlSi_7O_{19}]F_2Cl$  ( $Z = 2$ ), can be considered as a mineral structurally intermediate between phyllosilicates and silicates with heteropolyhedral frameworks. Its crystal structure is based upon the two-layer tetrahedral blocks, or double layers,  $[(Al,Si)_4Si_{12}O_{38}]$ , linked by the columns of edge-shared Ca-centered octahedra [1, 2]. These two main building units form a heteropolyhedral quasi-framework with zeolite-like channels of two types: 1) inside the tetrahedral blocks, hosting  $K^+$  and  $Cl^-$ ; 2) in the interlayer space, between Ca columns, hosting  $Na^+$  and  $F^-$ . Such ordering of three large cations and two halogen anions is a feature of delhayelite making it unique among minerals. Products of the step-by-step hydrothermal alteration of delhayelite in peralkaline pegmatites of the Khibiny alkaline complex (Kola Peninsula, Russia) are fivegite,  $K_4Ca_2[AlSi_7O_{17}(O_{2-x}OH_x)][(H_2O)_{2-x}OH_x]Cl$  ( $x = 0-2$ ), and hydrodelhayelite,  $KCa_2[AlSi_7O_{17}(OH)_2] \cdot (6-x)H_2O$ , preserving the stable  $CaAlSiO$  motif of the structure [2, 3]. It was a reason for us to assume its zeolitic properties and check them experimentally. It seems important that, unlike other known microporous silicate minerals showing easy mobility of weakly-bonded cations, delhayelite hosts also halogen anions in the same zeolitic channels.

Grains (0.5–3 mm) of delhayelite from Khibiny were placed in 1N aqueous solutions of  $(NH_4)_2SO_4$ ,  $Na_2SO_4$ ,  $K_2SO_4$ ,  $RbNO_3$ ,  $CsNO_3$ ,  $SrCl_2$ ,  $BaCl_2$ ,  $Pb(NO_3)_2$  and  $CuSO_4$  at 80–90°C and 1 atm for 3 hours and in distilled  $H_2O$  under the same conditions for 500 hours. Samples after the experiments were examined by IRS, SEM and EMPA. In acidic solution ( $CuSO_4$ ), delhayelite partially dissolves and its rest shows no signs of Cu absorption. The mineral remains unaltered in solutions of Na, K, Sr and Pb salts but absorbs  $NH_4$ , Rb, Cs and Ba with decrease of K, Na, Cl and F contents. The experiment with  $H_2O$  showed partial leaching of Na and F resulting in the formation of a fivegite-like phase. All processes of ion leaching and ion exchange in delhayelite are accompanied by its hydration. The IR spectra show the appearance of H-bearing groups of two kinds:  $H_2O$  molecules and strongly H-bonded weak-acidic hydroxyls, probably forming silanol groups Si-OH, as it was found in fivegite [3]. Ratios of Si, Al and Ca remain constant in all cases that confirms stability of the  $CaAlSiO$  motif in delhayelite-like phases (members of the rhodesite mero-pleisotype series [4]) considered by us as a quasi-framework.  $SO_4$  is typical anionic admixture in initial delhayelite (probably substituting Cl); however in our experiments there are no signs of absorption of additional  $SO_4$ , as well as  $NO_3$  or additional Cl anions. Among all tested cations, this mineral demonstrates the strongest affinity to  $Cs^+$ . The most Cs-enriched form of delhayelite obtained in our experiments is Na-, F- and Cl-free and has the following composition:  $Cs_{1.67}K_{0.16}Ca_{1.85}Al_{1.06}Si_{6.94}O_{17.47}(OH)_{1.53}(H_2O)_n$ . The distribution of cation-exchanged areas in delhayelite crystals is uneven.

Our data show that the first stage of delhayelite alteration in aqueous solutions is partial or complete leaching of  $Na^+$  and  $F^-$  from the interlayer space accompanying by hydration. The second stage is leaching of univalent ions from channels inside the tetrahedral block:  $K^+$  (partially or almost completely) and  $Cl^-$  (partially or completely) with additional hydration and/or absorption of large cations (Rb, Cs, Ba) from a solution. The second stage can start when the first stage is still not finished in other parts of a crystal.

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