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Three members of the mayenite mineral-supergroup from UHT-LP skarns, Upper Chegem caldera, North Caucasus, Russia

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The proposed mayenite supergroup can be defined on the basis of the simplified chemical formula $X_{12}T_{14}O1_{24}O2_8W_6$, where X – Ca polyhedral site, T tetrahedron, W – center of a large structural cage, which is partially occupied by additional anions (Galuskin et al., 2012). The supergroup consists of mayenite- and wadalite groups including mayenite, ideal formula $Ca_{12}Al_{14}O_{33}$ (Hentschel, 1964), brearleyite, $Ca_{12}Al_{14}O_{32}Cl_2$ (Ma et. al., 2011), wadalite, $Ca_{12}Al_{10}Si_4O_{32}Cl_6$ (Tsukimura et al., 1993; Mihajlovic et al., 2004), eltyubyuite, $Ca_{12}Fe^{3+}_{10}Si_4O_{32}Cl_6$ (Galuskin et al., 2011).

Wadalite, eltyubyuite and a potential new mineral "chlormayenite" $Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$ (Galuskin et al., 2009) were discovered in altered silicate - carbonate xenoliths in the Upper Chegem caldera, Kabardino Balkaria, North Caucasus, Russia. They occur in ignimbrite where they are formed by contact metamorphism at temperatures above 800^{o}C at low pressure. They are associated with typical high-temperature minerals and their reaction products: periclase, larnite, spurrite, cuspidine, chegemite, rondorfite, reinhardbraunsite, lakargiite, perovskite, elbrusite-(Zr), megawite, srebrodolskite, hydroxylellestadite, hydrogrossular, ettringite-thaumasite group minerals, and hydrocalumite. With mayenite as reference there are several types of substitution, which define three end-members: $O^{2-} = 2Cl^-$, Al^{3+} (Fe^{3+}) = $Si^{4+} + Cl^-$, $2Al^{3+}$ (Fe^{3+}) = $Si^{4+} + Mg^{2+}$ and $Ca^{2+} + Al^{3+}$ (Fe^{3+}) = $Na^+ + Si^{4+}$ (Bailau et al., 2010). Based on electron-microprobe analyses following empirical formulas were calculated: wadalite - $Ca_{12.073}(Fe^{3+}_{0.829}Al_{9.108}Si_{3.839}Ti^{4+}_{0.051}Mg_{0.100})_{\Sigma 13.927}O_{32.030}Cl_{5.656} \approx Ca_{12}(Fe^{3+}Al_9Si_4)_{\Sigma 14}O_{32}Cl_6$, eltyubyuite - $Ca_{12.222}(Fe^{3+}_{9.407}Al_{1.259}Si_{2.963}Ti^{4+}_{0.112}Mg_{0.037})_{\Sigma 13.778}O_{31.889}Cl_{5.038} \approx Ca_{12}(Fe^{3+}_{10}AlSi_3)_{\Sigma 14}O_{32}Cl_5$, "chlormayenite" - $Ca_{11.978}(Al_{12.987}Fe^{3+}_{0.823}Si_{0.179}Ti^{4+}_{0.033})_{\Sigma 14.022}[O_{31.908}(OH)_{0.092}]_{\Sigma 32}[(H_2O)_{3.582}Cl_{2.326}]_{\Sigma 5.908} \approx Ca_{12}Al_{14}O_{32}[(H_2O)_4Cl_2]$. Raman investigation of mayenite shows an intensive band at 777 cm^{-1} representing stretching vibrations of $[AlO_4]^{5-}$. One intensive band near 700 cm^{-1} in the eltyubyuite spectrum and several bands near 700-710 cm^{-1}in wadalite spectra correspond to stretching vibrations of $[Fe^{3+}O_4]^{5-}$. In the high-wavenumber region specific of OH and H_2O vibrations, there are characteristic bands in wadalite spectra but no bands in the eltyubyuite spectrum. Formula calculations on electron-microprobe results for "chlormayenite" indicate that a neutral molecule may be hosted in the structural cages. Spectroscopic studies suggest that the deviation of the analytical total from 100% is related to H_2O which occupies W - sites in the structural cages. Furthermore, "chlormayenite" spectra have no marker bands of other molecules beside molecular H_2O. Structural data suggest that the W site is fully occupied: 3.62(2)O *pfu* + 2.38(2)Cl *pfu*, close to the results obtained by calculation of H_2O and Cl content from electron-probe microanalyses: W = 3.582O *pfu* + 2.326Cl *pfu*. Structure investigations indicate that "chlormayenite" is a new mineral, the H_2O analog of brearleyite, $Ca_{12}Al_{14}O_{32}Cl_2$. The chemical composition of all three members confirms two main trends: continuous solid solution between mayenite – wadalite and a solid solution between wadalite – eltyubyuite with a big gap.

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