

Contribution to the mineralogy of acid drainage of Uranium minerals: Marecottite and the zippeite-group

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ABSTRACT

Sulfate-rich acid waters produced by oxidation of sulfide minerals enhance U mobility around U ores and U-bearing radioactive waste. Upon evaporation, several secondary uranyl minerals, including many uranyl sulfates, precipitate from these waters. The zippeite-group of minerals is one of the most common and diverse in such settings. To decipher the nature and crystal chemistry of the zippeite-group, the crystal structure of a new natural hydrated Mg uranyl sulfate related to Mg-zippeite was determined. The mineral is named marecottite after the type locality, the La Creusaz U prospect near Les Marécottes, Western Swiss Alps.

Marecottite is triclinic, $P\bar{1}$, with $a = 10.815(4)$, $b = 11.249(4)$, $c = 13.851(6)$ Å, $\alpha = 66.224(7)$, $\beta = 72.412(7)$, and $\gamma = 69.95(2)^\circ$. The ideal structural formula is $\text{Mg}_3(\text{H}_2\text{O})_{18}[(\text{UO}_2)_4\text{O}_3(\text{OH})(\text{SO}_4)_2]_2(\text{H}_2\text{O})_{10}$. The crystal structure of marecottite contains uranyl sulfate sheets composed of chains of edge-sharing uranyl pentagonal bipyramids that are linked by vertex-sharing with sulfate tetrahedra. The uranyl sulfate sheets are topologically identical to those in zippeite, $\text{K}(\text{UO}_2)_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. The zippeite-type sheets alternate with layers containing isolated $\text{Mg}(\text{H}_2\text{O})_6$ octahedra and uncoordinated H_2O groups. The uranyl sulfate and Mg layers are linked by hydrogen bonding only.

Magnesium-zippeite is redefined as $\text{Mg}(\text{H}_2\text{O})_{3.5}(\text{UO}_2)_2(\text{SO}_4)_2$, based on comparison of the powder X-ray diffraction pattern of micro-crystalline co-type material with the pattern of a synthetic phase. Magnesium-zippeite contains zippeite-type uranyl sulfate sheets with Mg located between the layers, where it is in octahedral coordination. In Mg-zippeite, distorted Mg octahedra are linked by sharing vertices, resulting in dimers. The apices of the Mg octahedra correspond to two O atoms of uranyl ions, and four H_2O groups.

Magnesium-zippeite and marecottite co-exist, sometimes in the same sample, at Lucky Strike no. 2 mine, Emery County, Utah (type locality of Mg-zippeite), at Jáchymov, Czech Republic, and at La Creusaz. This study provides insight into the complexity of the zippeite-group minerals containing divalent cations, where different arrangements in the interlayers result in different unit cells and space groups.