American Mineralogist, Volume 109, pages 949–959, 2024

Znucalite, the only known zinc uranyl carbonate: Its crystal structure and environmental implications

Gwladys Steciuk[1], Juraj Majzlan[2], Jan Rohlíček[1], Radek Škoda[3], Jiří Sejkora[4], and Jakub Plášil[1,*]

[1]Institute of Physics of the CAS, Na Slovance 1999/2, 182 00 Prague 8, Czech Republic
[2]Institute of Geosciences, Friedrich-Schiller University, Burgweg 11, Jena, 07749, Germany
[3]Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, 611 37, Brno, Czech Republic
[4]Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, 193 00 Prague 9-Horní Počernice, Czech Republic

Abstract

Znucalite is a zinc uranyl-carbonate mineral that was until recently only partially characterized with a formula originally given as $Zn_{12}Ca(UO_2)(CO_3)_3(OH)_{22}\cdot 4H_2O$, with an unknown crystal structure and ambiguous symmetry determinations. We have reinvestigated this mineral using three-dimensional electron diffraction (3D ED) and powder X-ray diffraction and revealed for the first time its structural details. Znucalite is unambiguously monoclinic, $P2_1/m$, with a = 10.722(2) Å, b = 6.259(1) Å, c = 25.355(1) Å, β = 101.13(1)°, and V = 1669.54(9) Å^3. The structure refinement of the 3D ED data using the dynamical approach (R_{obs} = 0.1594 for 3579 observed reflections and 244 parameters) provided the following structure model. Znucalite possesses a layered structure, with a $[Zn_{10}(OH)_{14}(CO_3)_2]$ double sheet (with Zn^{2+} both in octahedra and tetrahedra), which is connected to a thick interlayer that hosts U^{6+}, Ca^{2+}, and H_2O molecules. The linkage between structural units and the interlayer occurs via the vertices of ZnO_4 tetrahedra protruding from the sheet. In the interlayer, differences in ordering between U and Ca take place and likely cause the difficulties encountered during the attempts to solve the structure. The refined structural formula of znucalite, $Zn_{10}Ca_{0.828}[UO_2]_{0.828}[CO_3]_4(OH)_{15.312}(H_2O)_{5.484}$, corresponds well to the composition obtained from the electron-microprobe analyses, $(Zn_{9.84}Al_{0.16})_{\Sigma 10.00}Ca_{0.83}(UO_2)_{0.80}[(CO_3)_{3.96}(SO_4)_{0.04}]_{\Sigma 4.00}(OH)_{15.42}(H_2O)_{5.48}$. Raman spectroscopy evidenced the presence of several non-equivalent CO_3 groups, as well as OH and H_2O. The U-O bond lengths obtained from the stretching frequencies of UO_2^{2+} vibrations are in line with the structural model. A discussion on the environmental importance of znucalite is appended, based on geochemical calculations with an estimate of the solubility product for this mineral.

Keywords: Znucalite, uranyl carbonate, crystal structure, 3D electron diffraction, Rietveld refinement, conditions of formation, uranium immobilization