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

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Abstract

Znucalite is a zinc uranyl-carbonate mineral that was until recently only partially characterized with a formula originally given as Zn₁₋₂Ca(UO₂)(CO₃)₃(OH)₃·₄H₂O, 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, P2₁/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) Å³. The structure refinement of the 3D ED data using the dynamical approach (R_{damped} = 0.1594 for 3579 observed reflections and 244 parameters) provided the following structure model. Znucalite possesses a layered structure, with a [Zn₉₀(OH)₆(CO₃)₃] double sheet (with Zn²⁺ both in octahedra and tetrahedra), which is connected to a thick interlayer that hosts U⁶⁺, Ca²⁺, and H₂O molecules. The linkage between structural units and the interlayer occurs via the vertices of ZnO₆ 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, Zn₁₋₂Ca₀.₈₂[UO₂]₀.₈₂[CO₃]₀.₈₂(OH)₀.₈₂(H₂O)₅.₄₈, corresponds well to the composition obtained from the electron-microprobe analyses, (Zn₀.₉₆Al₀.₁₄)[UO₂]₀.₈₀[CO₃]₀.₂₀(SO₄)₀.₀₁₂[H₂O]₀.₄₆(Al₂O₃)₀.₁₂. Raman spectroscopy evidenced the presence of several non-equivalent CO₃ groups, as well as OH and H₂O. The U-O bond lengths obtained from the stretching frequencies of UO₅²⁻ 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

Introduction

Znucalite is the only uranyl carbonate containing zinc as an essential constituent. It was first described from the waste dump of the Lill mine in the Březové Hory base-metal deposit in Příbram, Central Bohemia, Czech Republic (Ondruš et al. 1990). The description of the new mineral was based on powder X-ray diffraction data as znucalite from the type locality forms only powdery aggregates and efflorescences on the gangue deposited as mining waste in the old dump. Ondruš et al. (1990) reported the mineral to be triclinic and determined that its chemical formula is Zn₁₋₂Ca(UO₂)(CO₃)₃(OH)₃·₄H₂O. Later on, Chiappero and Sarp (1993) reported on a new znucalite occurrence from the Mas d’Alary uranium deposit in Lodève (France). Based on the precession X-ray diffraction, they inferred znucalite to be orthorhombic and, thus, following the density change, having a different formula from the original one, Zn₁₋₀Ca(UO₂)(CO₃)₃(OH)₃·₄H₂O. Since then, znucalite has been reported from a few other localities worldwide. Nevertheless, since the work of Chiappero and Sarp (1993), no additional detailed crystallographic study has been undertaken, and the structure of znucalite remains unknown.

Here we report on the first determination of the crystal structure of znucalite based on three-dimensional electron diffraction (3D ED) techniques and Rietveld refinement from powder X-ray diffraction data.

Znucalite occurrence in Jáchymov (Czech Republic)

The znucalite occurrence in Jáchymov was first reported by Ondruš et al. (1997) from the Jan Evangelista and Ondřej veins within the Svornost mine. The original material was discovered and collected in the 1980s. Nevertheless, we found the site as the detailed information was communicated to us by the late Jan Hloušek. Fortunately, his brief description helped us find the site and collect the samples directly in underground spaces. Thus, all solid and liquid samples used in this study come from the Jan Evangelista vein (the south mining field nearby the crossing with Ondřej vein) at the so-called Adit level (approximately 224 m under the surface) of the Svornost mine in Jáchymov. The Jan Evangelista is one of the “midnight” veins (with northwest-southeast strike) and was one of the most economically important veins at this Bi-Co-Ni-Ag-U deposit. After World War II, it was intensively exploited for its U mineralization (Škácha et