Crystal chemistry of uranyl arsenates and phosphates from the Rabejac deposit, Lodève, France

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Located on the meridional border of the Central Massif, France, the Permian sedimentary basin of Lodève is well-known for its abundance of uranium minerals species. The uranium ore is mainly located in Autunian, Saxonian and Thuringian sandstones, pelites and conglomerates. This basin can be divided in several mining districts such as Mas d'Alary, Saint-Jean-de-la-Blaquière, les Mares, Usclas-du -Bosc, Riviéral, La Plane and Rabejec. The district of Mas d'Alary is the type locality of two uranyl sulfates: deliensite and leydetite. The district of Riviéral is the type locality of a rare uranyl arsenate named metalodèvite, and the distric of Rabejac has provided three new uranyl mineral species: fontanite, rabejacite and seelite.

The Rabejac deposit is also well-known for the occurence of many uranyl arsenates and phosphates. However, detailed chemical and crystallographic data on these minerals are still missing. Electron-microprobe analyses were performed on metauranocircite, nováčekite, uranospinite, and single-crystal X-ray diffraction measurements were performed on zeunerite and arsenuranospathite. Zeunerite, is tetragonal, $P4/nnc$, with a = 7.183(1), c = 20.872(2) Å and V = 1076.1(1) Å^3. Arsenuranospathite, is orthorhombic, $Pnn2$, with a = 29.926(1), b = 7.132(1), c = 7.186(1) Å, and V = 1533.9 (1) Å^3.

As the other members of the autunite group, the basic structural unit of zeunerite and arsenuranospathite is the corrugated autunite-type sheet. This sheet consists of corner-sharing UO_6 square bipyramids and $T^{5+}O_4$ tetrahedra (T^{5+} = As or P), and shows the composition $[(UO_2)(T^{5+}O_4)]^-$. The negative charge of the sheets is balanced by mono-, di- or trivalent cations and H_2O molecules located in the interlayer space. The interlayer space of zeunerite is occupied by one Cu atom occuring in a Jahn-Teller distorted octahedron, which connects together two successive uranyl arsenate sheets. The Cu atom shares two long bonds with the $(UO_2)^{2+}$ uranyl cation and four shorter bonds with H_2O molecules (O3) positioned in a square planar arrangement. One symmetrically independent H_2O molecule (O5) also occurs in the zeunerite interlayer space. Four of these molecules are connected to each other by H-bonding to form a square-planar group. The oxygen shared by the UO_6 square bipyramids and AsO_4 tetrahedra (O4) is also connected by H-bonding to the independent H_2O group (O5). The structure of natural zeunerite is identical to that of synthetic zeunerite and to that of torbernite.

The interlayer arrangement of arsenuranospathite is far away more complicated than in other minerals from the autunite group, with one Al atom and eleven symmetrically independent H_2O molecules. These water molecules can be divided in to three sets: the first set contains three H_2O molecules which form an octahedron around Al atoms; the second set contains four H_2O molecules connected in square-planar groups by H-bonding; and the third set contains four H_2O groups. Al atoms are completely isolated from the uranyl arsenate sheets while the H_2O molecules from the first set show H-bonds with oxygens occuring in the uranyl arsenate sheets. Arsenuranospathite is isostructural with the P-analogue mineral named uranospathite.