



NEW CRYSTALLOGRAPHIC DATA ON SEVERAL URANYL MINERALS

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INTRODUCTION

The importance of uranium minerals as alteration products of uraninite and nuclear fuels has led to an increase of studies about U mineralogy and crystal chemistry^[1]. In order to provide new crystallographic data, several secondary uranyl minerals from different localities have been investigated.

Firstly, samples from the Rabejac deposit, Lodève, France, have been examined. The Rabejac deposit contains several uranyl arsenates from the autunite group (zeunerite, nováčekite, uranospinite, heinrichite and arsenuranospathite), for which some of the crystallographic data are still missing. Secondly, bassetite samples from the type locality (Basset Mines, Cornwall, United Kingdom) have been reinvestigated in order to determine the water content of bassetite and its relationship with other minerals of the autunite group. Finally, new studies have been performed on samples from the Kobokobo pegmatite, Mwenga, South Kivu, Democratic Republic of Congo. The Kobokobo pegmatite is well known for

its unusual assemblage of aluminium uranyl minerals, with more than ten Al-U⁶⁺-bearing phosphates reported. However, the crystal structure is known for only four of them. The reinvestigation of material from this pegmatite allows the authors to find single crystals suitable for X-ray crystallographic studies on furongite and phuralumite.

STRUCTURE OF ARSEURANOSPAPHITE

The crystal structure of arsenuranospathite,

$\text{Al}[(\text{UO}_2)(\text{AsO}_4)]_2\text{F}(\text{H}_2\text{O})_{20}$, from Rabejac was solved for the first time^[2]. Arsenuranospathite is orthorhombic, *Pnn*2, $a = 29.926(1)$, $b = 7.132(1)$ and $c = 7.186$ Å. The structure is based on typical $[(\text{UO}_2)(\text{AsO}_4)]^-$ autunite-type sheets and on $\text{Al}(\text{H}_2\text{O})_6$ octahedra located in the interlayer. A very complex network of H-bonds links the $\text{Al}(\text{H}_2\text{O})_6$ octahedra to the uranyl arsenate sheets. Fluorine was not accurately located in the structure model.

Comparison with uranospathite^[3,4] confirms that both minerals are isostructural. Recent studies^[5] highlight the substitution of fluo-

rine by hydroxyl groups in arsenuranospathite, and indicate that the presence of fluorine seems to be restricted to Al-bearing members of autunite group with high water content (uranospathite and arsenuranospathite).

STRUCTURE OF BASSETITE

Bassetite, $\text{Fe}^{2+}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{10}$ is one of the oldest known uranyl phosphates^[6]. Crystals of bassetite from the Basset Mines were used to solve the crystal structure. Bassetite is monoclinic, $P2_1/n$, $a = 6.961(1)$, $b = 20.039(2)$, $c = 6.974(1)$ Å, $\beta = 90.46(1)^\circ$, and is isostructural with the Mg-analogue named saléeite. As other members of the autunite group, the structure is based upon the autunite-type sheets. Fe^{2+} cations are located between the sheets and are coordinated by six water molecules to form $\text{Fe}(\text{H}_2\text{O})_6$ octahedra. Two symmetrically independent and isolated H_2O groups are also occurring in the inter-layer space of the structure. Energy-dispersive X-ray spectroscopy measurements, as well as refined site occupancy factor for the Fe site, indicate that Fe^{2+} is partially replaced by Mg.

STRUCTURE OF FURONGITE

Finally, the crystal structure of furongite, $\text{Al}_2(\text{UO}_2)_2(\text{PO}_4)_3(\text{OH})(\text{H}_2\text{O})_{14}$ ^[7], from the Kokoboko pegmatite, has been refined for the first time. Furongite is triclinic, $P-1$, $a = 12.168(1)$, $b = 14.158(1)$, $c = 17.788(1)$ Å, $\alpha = 79.82(1)$, $\beta = 77.64(1)$ and $\gamma = 67.29(1)^\circ$. The structure is made of sheets of U^{6+}O_7 pentagonal bipyramids and PO_4 tetrahedra connected together by corner- and edge-sharing. Al atoms are occurring in octahedral coordination

and form two distinct clusters; $\text{Al}_2(\text{O},\text{OH},\text{H}_2\text{O})_{11}$ and $\text{Al}_4(\text{O},\text{OH},\text{H}_2\text{O})_{20}$. These Al clusters cross perpendicularly the uranyl-phosphate sheets and are connected to the sheets via corner-sharing. The sheets are only connected together by H-bonds. Investigation of the topological arrangement of anions within the sheets indicates that furongite has a sheet anion topology very close to that of uranophane. However the uranophane anion topology is deeply modified in order to incorporate the Al clusters.

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