Crystal structure of arsenuranospathite from Rabejac, Lodève, France

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Abstract: The crystal structure of the natural aluminium uranyl arsenate hydrate arsenuranospathite, ideally $Al[(UO_2)(AsO_4)]_2F(H_2O)_{20}$, from the Rabejac deposit, Lodève, France, was solved for the first time. Arsenuranospathite is orthorhombic, space group $Pnn2$, $Z = 2$, $a = 29.9262(7)$, $b = 7.1323(1)$, $c = 7.1864(1)$ Å, and $V = 1533.9(1)$ Å^3. The crystal structure was refined from single-crystal X-ray diffraction data to $R_1 = 0.0373$ for 3348 unique observed reflections, and to $wR_2 = 0.0768$ for all 3833 unique reflections. The mineral is isostructural with its P-analogue uranospathite, $Al[(UO_2)(PO_4)]_2F(H_2O)_{20}$; both minerals contain the autunite-type sheet $[(UO_2)((As,P)O_4)]-$ constituted by corner-sharing UO_6 square bipyramids and $(As,P)O_4$ tetrahedra. Aluminium is linked with water molecules to form an $Al(H_2O)_6$ octahedron located in the interlayer of the structure. Eight independent and isolated water molecules are also located in the interlayer. A very complex network of H-bonds links the water molecules together, to the Al octahedra and to the uranyl-arsenate sheets. Fluorine was not accurately located by the current structure model and is supposed to replace some of the H_2O molecules in the $Al(H_2O)_6$ octahedron. The crystal-chemical formula, calculated on the basis of $(As + P + Si + S) = 2$ cations per formula unit is $(Al_{1.02}Cu_{0.01})[(U_{0.98}O_2)(As_{0.89}P_{0.08}Si_{0.02}S_{0.01})O_4]_2(F_{0.77}OH_{0.05})(H_2O)_{20.18}$.

Key-words: arsenuranospathite; crystal structure; uranospathite; autunite group; aluminium uranyl arsenate hydrate; Rabejac; France.

Introduction

Uranyl phosphates and arsenates constitute the most diverse group of uranyl minerals, with more than 70 species described to date. Among the uranyl phosphates and arsenates, more than 41 mineral species containing autunite-type sheets are already reported in the literature (Krivovichev & Plášil, 2013). However, structural data are still missing for few members of the autunite group such as uranocircite, $Ba[(UO_2)(PO_4)]_2(H_2O)_{10}$ (Weisbach, 1877; Locock *et al.*, 2005a), uranospinite, $Ca[(UO_2)(AsO_4)]_2(H_2O)_{11}$ (Weisbach, 1873; Mrose, 1953), and bassetite, $Fe^{2+}[(UO_2)(PO_4)]_2(H_2O)_8$ (Hallimond, 1915; Vochten *et al.*, 1984). Furthermore, the autunite group can be assumed to be incomplete with some species remaining to discover in nature such as the hypothetical P analogues of metalodèvite, $Zn[(UO_2)(AsO_4)]_2(H_2O)_8$ (Agrinier *et al.*, 1972; Plášil *et al.*, 2010), metakirchheimerite, $Co[(UO_2)(AsO_4)]_2(H_2O)_8$ (Walenta, 1958; Plášil *et al.*, 2009), and rauchite, $Ni[(UO_2)(AsO_4)]_2(H_2O)_{10}$ (Pekov *et al.*, 2012).

Uranyl phosphates have a wide distribution in nature due to the presence of dissolved phosphate in many geological environments (Finch & Murakami, 1999). Both uranyl phosphates and uranyl arsenates generally occur in the oxidation zone of uranium deposits. The investigation of these minerals is of interest because they are controlling the mobility and the solubility of uranium in many geological environments. Due to their very low solubility, uranyl phosphates and arsenates can behave as a trap for uranium in oxidized uranium deposits (Murakami *et al.*, 1997), in soils contaminated by actinides (Buck *et al.*, 1996; Roh *et al.*, 2000), and in groundwater and wastewater systems (Fuller *et al.*, 2002; Jerden & Sinha, 2003; Grabias *et al.*, 2014).

The name arsenuranospathite was first used by Walenta (1963) to describe the As analogue of uranospathite discovered by Hallimond (1915). The first samples of arsenuranospathite were found in the Menzenschwand deposit, Black Forest (Schwarzwald) massif, Germany. Further investigations of Walenta (1978) indicated that arsenuranospathite from the type locality has the same optical and physical properties than other members of the autunite group. On the basis of micro-chemical and spectrochemical analysis, the ideal formula for the As-dominant species was given as $(HAl)_{0.5}[(UO_2)(AsO_4)]_2 \cdot 20H_2O$. The unit-cell parameters derived from the X-ray powder diffraction pattern of arsenuranospathite are $a = 7.16$ Å and $c = 30.37$ Å, with the probable space group $P4_2/n$ (Walenta, 1978). However, due to the observation of a biaxial interference figure under the polarizing microscope, Walenta (1978) suggested that the true symmetry

of the mineral is orthorhombic. Recently, the crystal structure of uranospathite from Vénachat, Haute-Vienne, France, was reported by Locock *et al.* (2005b). Single-crystal X-ray diffraction data indicate that uranospathite is orthorhombic, pseudo-tetragonal; the structure was refined in the non-centrosymmetric space group $Pnn2$, with $a = 30.020(4)$, $b = 7.0084(9)$, $c = 7.0492(9)$ Å, $Z = 2$. The similarity of the unit-cell dimensions and of the X-ray powder diffraction patterns of uranospathite and arsenuranospathite, as well as the general isotypism of uranyl phosphates and uranyl arsenates belonging to the (meta-) autunite group, suggest that arsenuranospathite is certainly isostructural with uranospathite (Walenta, 1978). Taking into account qualitative energy-dispersive X-ray spectrometric analysis and crystal-structure refinement data, Locock *et al.* (2005b) propose a new hypothetical general formula for uranospathite, given as $Al_{1-x}[]_x[(UO_2)(PO_4)]_2(H_2O)_{20+3x}F_{1-3x}$, in which [] is a vacancy, and x varies in general between 0 and 0.33. The electron-microprobe analysis performed by Chukanov *et al.* (2009) shows that the Al content in arsenuranospathite from the type locality is always close to 1 and they consequently suggest the simplified formula $Al[(UO_2)(AsO_4)]_2(F,OH)(H_2O)_{20}$.

The goal of the present paper is to describe the crystal structure of arsenuranospathite for the first time, in order to confirm the ideal formula of this mineral. The structural features are discussed in detail, as well as the chemical composition of arsenuranospathite. These data are also compared to those of other members of the autunite group.

Occurrence, physical and optical properties

Located on the southern border of the Central Massif, France, the Permian sedimentary basin of Lodève is well known for its abundance of uranium-bearing minerals species. The uranium ore (pitchblende) is mainly set in the Autunian, Saxonian and Thuringian sandstones, pelites and conglomerates. The geology and metallogeny of the uranium deposits of the Lodève basin have been described in detail by Mathis *et al.* (1990). 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 Rabejac. The district of Mas d'Alary is the type locality of two uranyl sulphates: deliensite, $Fe^{2+}[(UO_2)_2(SO_4)_2(OH)_2](H_2O)_7$ (Vochten *et al.*, 1997), and leydetite, $Fe^{2+}(UO_2)(SO_4)_2(H_2O)_{11}$ (Plášil *et al.*, 2013). The district of Riviéral is the type locality of a rare uranyl arsenate named metalodèvite, $Zn[(UO_2)(AsO_4)]_2(H_2O)_8$ (Agrinier *et al.*, 1972; Plášil *et al.*, 2010), and the district of Rabejac has provided three new uranyl mineral species: fontanite, $Ca[(UO_2)_3O_2(CO_3)_2](H_2O)_6$ (Deliens & Piret, 1992), rabejacite, $Ca(UO_2)_4(SO_4)_2(OH)_6(H_2O)_6$ (Deliens & Piret, 1993), and seelite, $Mg[(UO_2)(AsO_3)_x(AsO_4)_{1-x}]_2(H_2O)_7$ (Bariand *et al.*, 1993).

The arsenuranospathite sample analyzed in this study was collected in the Rabejac deposit and belongs to the collections of the Natural History Museum of Luxembourg (sample VC2135). Arsenuranospathite forms light-green to yellow-greenish transparent bladed crystals showing the {100}, {010} and {001} forms. The crystals can reach up to 0.5 mm in length. A perfect (001) cleavage plane is observed, as well as two other weaker cleavage planes parallel to (100) and (010). Optical examinations under the polarizing microscope indicate that the mineral has a positive elongation, and is biaxial negative. Emerald-green platy crystals of zeunerite are associated with arsenuranospathite; these two minerals form intimate intergrowths which probably mean that both species have crystallized simultaneously. An undetermined powdery yellowish mineral is also occurring in close association with arsenuranospathite and zeunerite. Energy-dispersive X-ray spectrometric analysis shows that this compound contains high amounts of U, S and Ca, as well as a low amount of Fe; it may correspond to rabejacite. Several crystals of arsenuranospathite are completely coated by these yellowish crystals, indicating that this mineral crystallized during a later stage.

Chemical composition

Quantitative chemical analyses were performed with a Cameca SX-100 electron microprobe (Laboratoire Magmas et Volcans, Université Blaise Plascal, Clermont-Ferrand, France) operating in the wavelength-dispersion mode, with an accelerating voltage of 15 kV, a beam current of 2 nA, and a beam diameter of 10–20 μm. The following standards and lines were used: GaAs (As$L\alpha$); Al_2O_3 (Al$K\alpha$); UO_2 (U$M\beta$); $BaSO_4$ (S$K\alpha$, Ba$L\alpha$); apatite (P$K\alpha$, Ca$K\alpha$); chalcopyrite (Cu$K\alpha$); fayalite (Fe$K\alpha$); albite (Na$K\alpha$); MgO (Mg$K\alpha$); CaF_2 (F$K\alpha$); and wollastonite (Si$K\alpha$). Counting time was 10–20 s on peak depending on the element, and 50 % of that time for the background. Arsenuranospathite is prone to electron-beam damage, even under the soft conditions described above. Elevated analytical totals can be accounted for by water evaporation due to the high vacuum or to the heating of the analyzed area by the electron beam. This phenomenon is quite common with minerals containing a very large amount of hydroxyl groups or structural water.

The empirical formula of arsenuranospathite was calculated on the basis of $(As + P + Si + S) = 2$ atoms per formula unit (*apfu*) (Table 1). The OH-content was calculated in order to maintain the charge balance, and the number of H_2O molecules was calculated, according to structural observations and in order to have $21(H_2O + F + OH)$ per formula unit. The empirical formula of the studied arsenuranospathite is $(Al_{1.02}Cu_{0.01})[(U_{0.98}O_2)(As_{0.89}P_{0.08}Si_{0.02}S_{0.01})O_4]_2(F_{0.77}OH_{0.05})(H_2O)_{20.18}$.

A part of As in the tetrahedra is replaced by P, thus confirming the classical substitution between these cations in tetrahedral coordination. The F content reaches 0.77 *apfu*, the U content is close to 2 *apfu*, and the Al content is close to 1 *apfu*. The other cations (Fe, Mg, Ca, Ba and Na) occur in very low amounts and play no significant

Table 1. Chemical composition of arsenuranospathite from Rabejac, France.

	VC2135	Range	SD
n	20		
SO_3 wt %	0.08	0.00–0.23	0.06
SiO_2	0.22	0.00–0.51	0.26
As_2O_5	21.3	20.5–23.5	1.3
P_2O_5	1.27	0.85–1.80	0.46
Al_2O_3	5.44	4.83–6.32	0.33
CuO	0.11	0.00–0.80	0.18
FeO	0.02	0.00–0.08	0.03
MgO	0.01	0.00–0.05	0.02
CaO	0.05	0.00–0.18	0.05
BaO	0.02	0.00–0.19	0.05
Na_2O	0.05	0.00–0.13	0.04
UO_3	58.8	55.2–63.1	2.8
F	1.52	1.22–1.89	0.18
H_2O*	19.30		
O=F	–0.64		
Total	107.57		
Formula based on As + P + Si + S = 2 *apfu*			
S	0.013		
Si	0.036		
As	1.779		
P	0.172		
ΣT site	2.000		
Al	1.024		
Cu	0.013		
Fe^{2+}	0.003		
Mg	0.002		
Ca	0.008		
Ba	0.001		
Na	0.015		
ΣA site	1.066		
U^{6+}	1.975		
F	0.768		

n: number of point analyses performed.
* H_2O content was calculated on the basis of $(H_2O + F + OH) = 21$.

crystal-chemical role in the structure. Nevertheless, according to the light greenish colour of the crystals of arsenuranospathite and the Cu-bearing mineral (zeunerite) associated with arsenuranospathite, it may be possible that a small amount of Cu occurs in the interlayer space of arsenuranospathite.

Single-crystal X-ray diffraction

Single-crystal X-ray study of arsenuranospathite was carried out on an Agilent Technologies Xcalibur four-circle diffractometer (kappa geometry), using the $MoK\alpha$ radiation ($\lambda = 0.71073$ Å, 40 kV, 40 mA), and equipped with an EOS CCD area detector, on a $0.17 \times 0.16 \times 0.05$ mm crystal fragment (sample VC2135). Arsenuranospathite is orthorhombic, $Pnn2$, with $a = 29.926(1)$, $b = 7.1323(1)$, $c = 7.1864(1)$ Å, and $V = 1533.91(6)$ Å^3 (Table 2). The data were corrected for Lorentz, polarization and

absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED package (Agilent Technologies, 2012). At the opposite of uranospathite (Locock *et al.*, 2005b), no dehydration process was observed during the data collection.

The crystal structure of arsenuranospathite was solved by direct methods and subsequently refined using SHELXS and SHELXL softwares (Sheldrick, 2008). The reflection conditions and statistics clearly indicate the non-centrosymmetric orthorhombic space group *Pnn*2. Scattering curves for neutral atoms and anomalous dispersion correction were taken from the *International Tables for X-ray Crystallography, Vol. C* (Wilson, 1992). The relative occupancies of Al and As were refined on the Al and As sites, respectively. The refined occupancies are in good agreement with the chemical composition obtained from the electron-microprobe analyses. The refinements were completed using anisotropic-displacement parameters for all atoms except for O4 and hydrogen atoms (Table 3). Hydrogen atoms were located using constraints on bond lengths, 0.85 Å with a weight of 0.01, resulting in O-H lengths from 0.83(1) to 0.86(1) Å; their isotropic displacement parameters were set to 0.058 Å^2 (Tables 4 and 5). The stuctural model was completed by applying an inversion twin law [−100/0–10/00−1], with a refined inversion-twin-component scale factor of 0.61(3). The refinement converged with the final indices of agreement $R_1 = 0.0454$, $wR_2 = 0.0768$ for all data using the structure-factor weights assigned during least-squares refinement. Selected interatomic bond distances and the bond-valence sums are given in the Tables 6 and 7, respectively. Bond-valence sums were calculated with the parameters of Brown & Altermatt (1985) for Al and As, and those of Burns *et al.* (1997) for U^{6+}. The bond-valence sums for Al, U and As sites are 3.07, 5.96 and 5.07 valence units (*vu*), respectively. The bond-valence sums for the oxygen atoms range from 1.72 to 2.26 *vu*, and the bond-valence sums for hydrogen atoms vary from 0.87 to 1.18 *vu*.

Discussion

Structural features

As the other members of the autunite and meta-autunite groups, the main structural feature of arsenuranospathite is the corrugated autunite-type sheet (Beintema, 1938). In the present case, these sheets consist of corner-sharing $U^{6+}O_6$ square bipyramids and $As^{5+}O_4$ tetrahedra, and show the composition $[(U^{6+}O_2)(As^{5+}O_4)]-$ (Fig. 1). In the case of arsenuranospathite the negative charge of the sheets is balanced by one Al atom and eleven symmetrically independent H_2O groups located in the interlayer space. Al is connected to the three different H_2O groups and forms an $Al(H_2O)_6$ octahedron (Fig. 2).

Table 2. Experimental details for the single-crystal X-ray diffraction study of arsenuranospathite from Rabajec, France.

Ideal structural formula	$Al[(UO_2)(AsO_4)]_2F(H_2O)_{20}$
a (Å)	29.9262(7)
b (Å)	7.1323(1)
c (Å)	7.1864(1)
V (Å^3)	1533.9(1)
Space group	*Pnn2*
Z	2
D_{calc} (g.cm^{-3})	2.651
Absorption coefficient (mm^{-1})	12.83
$F(000)$	1136
Radiation	Mo$K\alpha$, 0.71073Å
Crystal size (mm)	$0.17 \times 0.16 \times 0.05$
Colour and habit	pale-green plate
Temperature (K)	293(2)
θ range ($^\circ$)	2.92–28.81
Reflection range	$-40 \le h \le 40; -9 \le k \le 9; -9 \le l \le 9$
Total no. of reflections	34167
Unique reflections	3833
Observed reflections, $|F_o| \ge 4\sigma(F)$	3348
Refined parameters	239
$R_1, |F_o| \ge 4\sigma(F)$	0.0373
R_1, all data	0.0454
wR_2 (F^2), all data	0.0768
GoF obs/all	1.192/1.186
$\Delta\sigma_{min}, \Delta\sigma_{max}$ (e/Å^3)	2.33, –1.69

As in the structure of uranospathite (Locock *et al.*, 2005b), the independent water molecules located in the interlayer can be classified into three groups. The first group contains O10, O11, O12 and O13 which are linked together by H-bonds to form a square-planar set (Fig. 2, Table 5), and show a H-bonds mean length of 2.11 Å. These water molecules are also connected to the uranyl-arsenate sheets (H-bonds O10 to O3, O11 to O4, O12 to O5, and O13 to O6; mean bond length 2.02 Å), and to the $Al(H_2O)_6$ octahedra (O11 to O14 and O12 to O9; mean bond length 2.17 Å). The second group of water molecules contains O7, O8 and O9 which form, with their symmetry equivalent, an octahedron around Al. Hydrogen bonds link O7 with O14 and O17, O8 with O9 and O14, and O9 with O12 and O16. As shown on Fig. 2, the water molecules of this second group are mainly connected to the isolated water molecules of the interlayer, and to water molecules from the square-planar set. The third group of water mocules contains O14, O15, O16 and O17, which are located in the interlayer and connect the $Al(H_2O)_6$ octahedra with the water molecules forming the square-planar set. H-bonds connect O14 with O11 and O15, O15 with O13, O14 and O17, O16 with O8 and O15, and twice O17 with O7. The H-bonds toward the oxygens from the square-planar sets and the $Al(H_2O)_6$ octahedra are on average shorter (1.96 Å) than those toward oxygens from the third group of water molecules (2.08 Å).

According to the empirical correlations between the O-H stretching frequencies and O–H $\cdots$ O hydrogen bond lengths in minerals (Libowitzky, 1999), Chukanov *et al*. (2009) derived O $\cdots$ O distances of 3.1, 2.81, 2.74 and 2.68 Å for corresponding hydrogen bonds in arsenuranospathite, calculated from experimental infrared spectral data. The last three distances are in good agreement with the O $\cdots$ O distances (2.60–2.88 Å) observed in the

Table 3. Atom coordinates and anisotropic displacement parameters (Å^2) for arsenuranospathite from Rabejac, France.

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al*	0.5	0	1.1484(8)	0.027(2)	0.025(3)	0.031(3)	0.020(2)	0	0	0.003(2)
U	0.28124(1)	0.24021(4)	0.4397(2)	0.01439(8)	0.0205(1)	0.0112(1)	0.0117(1)	0.0064(2)	0.0003(4)	−0.0001(1)
As*	0.24956(2)	−0.2605(1)	0.4408(5)	0.0142(2)	0.0224(4)	0.0101(3)	0.0100(3)	0.0093(5)	0.001(2)	−0.0002(3)
O1	0.2222(2)	0.2402(8)	0.423(5)	0.024(4)	0.023(3)	0.035(3)	0.014(9)	0.009(5)	−0.004(4)	−0.001(3)
O2	0.3405(2)	0.2390(8)	0.441(4)	0.027(1)	0.029(3)	0.027(3)	0.025(3)	0.003(4)	0.016(8)	0.003(2)
O3	0.2837(2)	−0.4419(8)	0.3932(8)	0.017(2)	0.024(3)	0.013(3)	0.015(5)	−0.007(2)	0.002(3)	0.003(2)
O4†	0.2830(2)	−0.0766(8)	0.469(1)	0.016(2)	–	–	–	–	–	–
O5	0.2842(4)	0.204(1)	0.113(2)	0.021(2)	0.025(5)	0.026(5)	0.011(4)	−0.002(4)	−0.001(3)	0.007(4)
O6	0.2165(4)	−0.225(1)	0.249(2)	0.022(2)	0.035(5)	0.026(5)	0.006(4)	−0.007(4)	0.000(4)	0.005(4)
O7	0.4741(3)	−0.153(1)	0.973(1)	0.035(2)	0.038(4)	0.032(4)	0.036(6)	−0.008(3)	−0.008(4)	0.010(3)
O8	0.4799(3)	−0.162(1)	1.332(1)	0.037(2)	0.038(5)	0.036(4)	0.035(4)	−0.003(4)	0.006(4)	0.000(4)
O9	0.4459(3)	0.143(1)	1.139(1)	0.044(2)	0.038(5)	0.031(4)	0.063(6)	−0.015(5)	−0.012(5)	0.002(4)
O10	0.3620(3)	−0.359(1)	0.186(1)	0.032(2)	0.024(4)	0.041(5)	0.032(5)	0.003(4)	0.008(4)	0.001(3)
O11	0.1408(3)	0.339(1)	0.177(1)	0.038(2)	0.034(5)	0.034(5)	0.047(6)	0.001(4)	0.002(4)	0.006(4)
O12	0.3661(4)	0.007(1)	0.036(1)	0.036(2)	0.024(5)	0.042(5)	0.041(5)	−0.005(4)	−0.001(4)	−0.001(4)
O13	0.3616(3)	0.477(1)	0.832(1)	0.039(2)	0.028(5)	0.041(5)	0.047(5)	−0.019(4)	−0.005(4)	−0.008(4)
O14	0.0572(3)	0.467(1)	0.142(1)	0.046(2)	0.052(6)	0.043(5)	0.043(5)	−0.005(5)	−0.002(5)	0.001(4)
O15	0.4362(3)	0.354(1)	0.661(1)	0.043(2)	0.035(5)	0.036(5)	0.058(6)	−0.004(4)	0.013(5)	0.004(4)
O16	0.4399(3)	0.493(1)	0.303(1)	0.042(2)	0.032(5)	0.035(5)	0.059(6)	−0.009(4)	−0.007(4)	−0.001(4)
O17	0.5	−0.5	0.870(2)	0.039(3)	0.041(7)	0.027(5)	0.049(7)	0	0	0.003(5)

* Al occupancy = 0.98(2); As occupancy = 0.961(3).
† O4 atom was refined isotropically.

Table 4. Hydrogen atoms coordinates for arsenuranospathite from Rabejac, France.

	x	y	z	U_{eq}*
H7a	0.479(3)	−0.270(3)	0.97(2)	0.058
H7b	0.449(2)	−0.130(8)	0.93(2)	0.058
H8a	0.501(1)	−0.18(1)	1.409(8)	0.058
H8b	0.458(2)	−0.11(1)	1.39(1)	0.058
H9a	0.428(3)	0.08(1)	1.20(1)	0.058
H9b	0.452(3)	0.245(9)	1.19(1)	0.058
H10a	0.359(5)	−0.242(5)	0.17(2)	0.058
H10b	0.342(3)	−0.39(1)	0.26(1)	0.058
H11a	0.121(3)	0.26(1)	0.16(2)	0.058
H11b	0.136(4)	0.40(2)	0.28(1)	0.058
H12a	0.385(3)	0.09(1)	0.08(2)	0.058
H12b	0.340(1)	0.04(2)	0.07(2)	0.058
H13a	0.339(2)	0.42(2)	0.80(1)	0.058
H13b	0.358(3)	0.51(2)	0.944(6)	0.058
H14a	0.084(1)	0.43(1)	0.13(2)	0.058
H14b	0.056(4)	0.582(6)	0.17(2)	0.058
H15a	0.434(5)	0.236(4)	0.64(2)	0.058
H15b	0.418(4)	0.39(1)	0.75(1)	0.058
H16a	0.424(3)	0.49(1)	0.40(1)	0.058
H16b	0.455(4)	0.59(1)	0.30(1)	0.058
H17	0.504(4)	−0.597(3)	0.937(3)	0.058

* Constrained value.

structure of arsenuranospathite (Table 5); however, the O · · · O distance of 3.1 Å is significantly longer. The O · · · H distances calculated by Chukanov *et al.* (2009) from the infrared spectrum of arsenuranospathite are 2.20, 1.94,

1.86 and 1.77 Å; these distances are also in good agreement with those observed in the structure of arsenuranospathite (1.89–2.51 Å; Table 5).

Fluorine location and substitution mechanism

The distinction between F and O in the structure model is often difficult due to the small difference in X-ray scattering power of these two atoms. In the present case, F cannot be accurately located in the model; however, the maximum F amount in the stucture of arsenuranospathite is 1 *apfu*, according to the ideal formula (0.77 *apfu* in the studied sample). In the structure of uranospathite, Locock *et al.* (2005) state that F substitutes partially for H_2O group of O7 and O8 as these positions have the Al–O interatomic distances the most similar to the ideal Al–F bond length (1.865 Å; Shannon, 1976). The same assumption can be done for arsenuranospathite, in which the Al–O7 (1.838(8) Å) and Al–O8 (1.854(9) Å) interatomic distances are close to the ideal Al–F bond length.

Comparison with previous data on arsenuranospathite and uranospathite

Firstly investigated by Hallimond (1915) and Walenta (1978), uranospathite and arsenuranospathite were supposed to be tetragonal species; however, optical properties indicate an orthorhombic symmetry for these minerals. This assumption was confirmed by Locock *et al.* (2005b)

Table 5. Hydrogen-bond geometry in the structure of arsenuranospathite from Rabejac, France.

Bond	O–H (Å)*	H · · · O (Å)	O · · · O (Å)	O–H · · · O (°)
O7–H7a · · · O17	0.85	1.89	2.70	157.9
O7–H7b · · · O14	0.85	2.16	2.69	121.2
O8–H8a · · · O9	0.85	2.51	2.60	85.74
O8–H8b · · · O14	0.86	1.97	2.65	135.1
O9–H9a · · · O12	0.85	2.15	2.70	122.0
O9–H9b · · · O16	0.85	1.94	2.75	158.0
O10–H10a · · · O12	0.85	2.05	2.83	153.6
O10–H10b · · · O3	0.84	2.04	2.84	157.2
O11–H11a · · · O14	0.85	2.42	2.67	97.92
O11–H11a · · · O13	0.85	2.41	2.81	109.7
O11–H11b · · · O4	0.83	2.04	2.80	140.2
O11–H11b · · · O12	0.83	2.01	2.84	171.7
O12–H12a · · · O9	0.83	1.92	2.68	147.7
O12–H12b · · · O5	0.85	2.05	2.88	165.4
O13–H13a · · · O6	0.86	1.96	2.82	171.7
O13–H13b · · · O10	0.84	1.98	2.81	167.3
O14–H14a · · · O11	0.86	1.81	2.67	170.5
O14–H14b · · · O15	0.84	1.99	2.76	153.5
O15–H15a · · · O14	0.86	1.94	2.77	165.0
O15–H15b · · · O13	0.84	2.22	2.67	114.1
O15–H15b · · · O17	0.84	2.29	2.63	105.3
O16–H16a · · · O15	0.85	2.10	2.77	134.3
O16–H16b · · · O8	0.85	1.89	2.74	170.8
O17–H17 · · · O7	0.85	1.92	2.70	151.0

* Restrained to 0.85 ±0.01 Å.

Table 6. Selected interatomic distances (Å) for arsenuranospathite from Rabejac, France.

U–O1	1.770(6)		
U–O2	1.773(6)		
U–O3	2.293(6)		
U–O4	2.270(6)	Al–O7	1.838(8)
U–O5	2.362(12)	Al–O7[i]	1.838(8)
U–O6	2.237(12)	Al–O8	1.854(9)
$\langle U–O_{ap}\rangle$	1.77	Al–O8[i]	1.854(9)
$\langle U–O_{eq}\rangle$	2.29	Al–O9	1.916(9)
		Al–O9[i]	1.916(9)
As–O3	1.683(6)	$\langle Al–O\rangle$	1.87
As–O4	1.663(6)		
As–O5	1.619(12)		
As–O6	1.717(13)		
$\langle As–O\rangle$	1.67		

Symmetry code: (i) 1-*x*, -*y*, *z*

for uranospathite, and by the present work for arsenuranospathite.

The unit-cell parameters reported for these mineral species are in the same range and indicate an unusual large interlayer distance for minerals of the autunite group (Table 8). The unit-cell parameters *b* and *c*, which reflect the dimensions of the $[(UO_2)((P,As)O_4)]–$ sheets, increase from uranospathite to arsenuranospathite; this increase is in good agreement with the replacement of PO_4 by AsO_4. The unit-cell parameter *a* is similar for both species.

During their investigations, Hallimond (1915) and Walenta (1978) did not consider the presence of fluorine as a way to compensate the excess of cationic charges produced by the insertion of Al^{3+}. Energy-dispersive X-ray spectrometric analyses performed by Locock *et al.* (2005b) on uranospathite indicate the presence of fluorine in the mineral; electron-microprobe analyses performed on arsenuranospathite have also confirmed the presence of fluorine in this species (Chukanov *et al.*, 2009; this study). The structural data obtained by Locock *et al.* (2005b) on natural uranospathite, and the synthesis of the compound $Al_{0.67}[]_{0.33}[(UO_2)(PO_4)]_2(H_2O)_{15.5}$ from a F-free solution, seem to indicate that the amount of F is positively correlated with the amount of Al located in the interlayer. Chemical analyses provided by Chukanov *et al.* (2009) on samples with one Al *pfu* and nearly one F *pfu* confirm this assumption. However, the structural data obtained in the present study indicate that the Al site is nearly fully occupied, while the electron-microprobe data indicate that the F content is 0.77 *apfu* on average. This lower F content, in regard to the Al content, can be explained by the poor accuracy of the F measurement, due to the very beam-sensitive behaviour of arsenurano-pathite. By the way, the possible replacement of a water molecule by an OH group, instead of F, is difficult to highlight in the structural model and, therefore, cannot be ruled out.

It is also interesting that no significant Al substitutions were reported for both uranospathite and arsenuranos-pathite. Walenta (1978) has reported traces of Fe, Cu, and Co for uranospathite and, in the case of arsenuranospathite

Table 7. Bond-valence table (*vu*) for arsenuranospathite from Rabejac, France.

	Al	U	As*	H7a	H7b	H8a	H8b	H9a	H9b	H10a	H10b	H11a	H11b	H12a	H12b	H13a	H13b	H14a	H14b	H15a	H15b	H16a	H16b	H17	Σ
O1		1.72																							1.72
O2		1.71																							1.71
O3		0.63	1.22								0.21														2.06
O4		0.66	1.29											0.21											2.15
O5		0.55	1.45												0.21										2.21
O6		0.70	1.11													0.23									2.04
O7	0.55 ×2↓			0.74	0.74																	0.24			2.28
O8	0.53 ×2↓					0.74	0.73																0.25		2.25
O9	0.45 ×2↓				0.13	0.13		0.74	0.74																2.30
O10										0.74	0.75						0.22								1.71
O11												0.74	0.76					0.27							1.77
O12								0.19		0.21			0.25	0.74	0.76										2.11
O13												0.15				0.73	0.75			0.18	0.17				1.80
O14							0.23					0.14						0.73	0.75						2.22
O15																			0.17	0.73	0.75			0.24	1.88
O16									0.23													0.74	0.74		1.72
O17				0.24 ×2→																	0.16			0.74 ×2→	2.12
Σ	3.06	5.96	5.07	0.98	0.87	0.87	0.96	0.93	0.97	0.95	0.96	1.03	1.01	0.95	0.96	0.97	1.00	0.97	0.92	0.92	1.08	0.91	0.99	0.98	

* Bond-valence sum was calculated according to the occupancy 0.93 As^{5+}+0.07 P^{5+}.
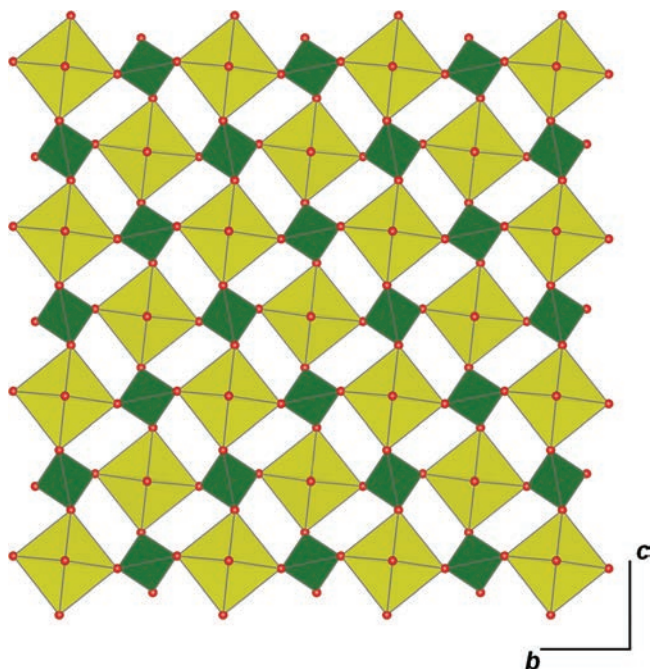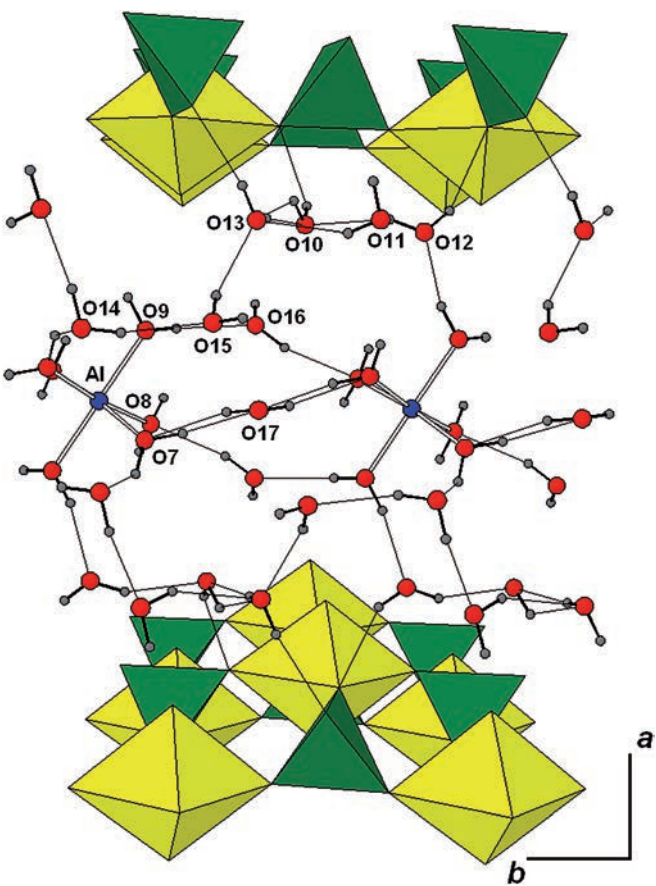
Fig. 1. View of the autunite-type sheet in the arsenuranospathite, projected along [100] (Atoms software; Dowty, 1993). Arsenate tetrahedral are green and uranyl square bipyramids are yellow. Red spheres represent oxygen atoms. (online version in colour)

from Rabejac, electron-microprobe analyses show traces of Cu and Na. However, in both cases, the oxide content is well below 1 wt.%, and is consequently not significant.

Structural comparisons with other aluminium uranyl phosphates and arsenates

To date, fifteen Al-bearing uranyl phosphates and arsenates are reported in the literature: five species in the (meta-)autunite group, four species in the phosphuranylite group, and six species which do not belong to any mineral group (coconinoite, furongite, kamitugaite, moreauite, ranunculite and triangulite). Among these minerals, only

Fig. 2. Detailed view of the interlayer space of arsenuranuspathite, projected along [001] (Atoms software; Dowty, 1993). Arsenate tetrahedral are green and uranyl square bipyramids are yellow. Blue spheres represent Al atoms, red spheres represent oxygen atoms, and dark grey spheres represent hydrogen atoms. Thin lines show the H-bonds network. (online version in colour)

six species have a known crystal structure: phuramulite, $Al_2(UO_2)_3(PO_4)_2(OH)_6(H_2O)_{10}$ (Piret *et al.*, 1979), thread-goldite, $Al(UO_2)_2(PO_4)_2(OH)(H_2O)_8$ (Khosrawan-Sazedj, 1982), upalite, $Al(UO_2)_3(PO_4)_2O(OH)(H_2O)$ (Piret & Declercq, 1983), althupite, $AlTh^{4+}(UO_2)[(UO_2)_3O(OH)$

Table 8. Comparison of the crystallographic parameters for uranospathite and arsenuranospathite.

| Mineral	Uranospathite	Uranospathite	Arsenuranospathite	Arsenuranospathite	Arsenuranospathite
Simplified formula	$(HAl)_{0.5}[(UO_2)(PO_4)]_2(H_2O)_{20}$	$Al_{0.86}[(UO_2)(PO_4)]_2F_{0.58}(H_2O)_{20.42}$	$(HAl)_{0.5}[(UO_2)(AsO_4)]_2(H_2O)_{20}$	$H_{0.07}Al_{0.97}[(UO_2)(AsO_4)_{0.76}(PO_4)_{0.24}]_2F_{0.98}(H_2O)_{19.28}$	$Al_{1.06}[(UO_2)(AsO_4)_{0.87}(PO_4)_{0.09}]_2(F_{0.73}OH_{0.27})(H_2O)_{20}$
a (Å)	7.00	30.020(4)	7.16	30.070	29.9262(7)
b (Å)	–	7.0084(9)	–	7.147	7.1323(1)
c (Å)	30.02	7.0492(9)	30.37	7.193	7.1864(1)
V (Å^3)	1470.98	1483.1(3)	1556.93	1545.8	1533.9(1)
Space group	$P4_2/n$	$Pnn2$	$P4_2/n$	$Pnn2$	$Pnn2$
Z	2	2	2	2	2
Locality	Cornwall, UK	Vénachat, France	Menzenschwand, Germany	Menzenschwand, Germany	Rabejac, France
Reference	Walenta, 1978	Locock *et al.*, 2005b	Walenta, 1978	Chukanov *et al.*, 2009	This study
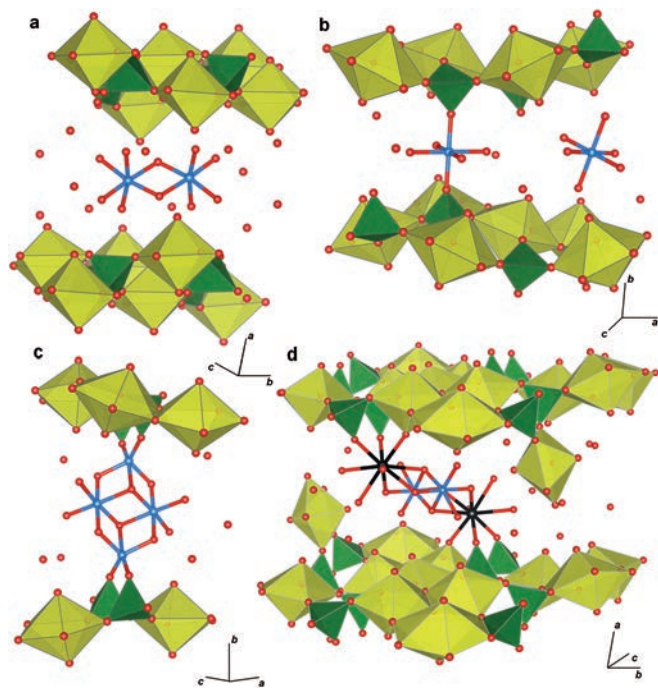
Fig. 3. View of the interlayer arrangement of threadgoldite (a), upalite (b), phuralumite (c) and althupite (d) (VESTA 3 software; Momma & Izumi, 2011). Green tetrahedra, PO4; yellow polyhedra, UO6, UO7 and UO8; blue spheres, Al atoms; red spheres, O atoms and H2O molecules; black spheres, Th atoms. The references for the atomic coordinates are given in the text. (online version in colour)

$PO_4)_2]_2(OH)_3(H_2O)_{15}$ (Piret & Deliens, 1987), uranospathite (Locock *et al.*, 2005b) and arsenuranospathite (this work). Despite a similar chemical composition and a similar structural topology of the uranyl-phosphate sheets, the arrangement of the Al polyhedra in the interlayer is completely different for each mineral.

The simplest arrangement occurs in uranospathite and arsenuranospathite, where Al occurs in $Al(H_2O)_6$ octahedra which are not directly linked to the adjacent sheets (Fig. 2). Threadgoldite, $Al(UO_2)_2(PO_4)_2(OH)(H_2O)_8$, is characterized by a dimer of edge-sharing octahedra of composition $[Al_2(OH)_2(H_2O)_8]$ (Fig. 3a). The dimers are isolated from the uranyl-phosphate sheets but they are probably connected to some oxygens of the uranyl-phosphate sheets by H-bonds. The interlayer complex of upalite, $Al(UO_2)_3(PO_4)_2O(OH)(H_2O)_7$, is defined by the presence of two distinct and unconnected Al octahedra: $AlO_2(H_2O)_4$ and $Al(H_2O)_6$ (Fig. 3b). The first octahedron is connected to the apical oxygens of the PO_4 tetrahedra of two successive phosphuranylite-type sheets. The equatorial H_2O groups of this octahedron are also connected the phosphuranylite-type sheets and to the isolated water molecules by H-bonds. The $Al(H_2O)_6$ octahedron is only connected by H-bonds to adjacent water molecules and to the sheets. Note that this octahedron is tilted, as well as the $Al(H_2O)_6$ octahedron in the structure of uranospathite and arsenuranospathite. The stucture of phuralumite, $Al_2(UO_2)_3(PO_4)_2(OH)_6(H_2O)_{10}$, is characterized by a remarkable $[Al_4O_{14}]$ group which is formed by two $Al(H_2O,OH)_6$ octahedra and two $Al(H_2O,OH)_5$ trigonal

bipyramids (Fig. 3c). The two Al octahedra are connected together by edge sharing to form a dimer. The Al trigonal bypyramids are connected to three oxygens from the Al dimers and to two apical oxygens from the PO_4 tetrahedra of the phosphuranylite-type sheets. The $[Al_4O_{14}]$ group is also connected by H-bonds to the adjacent water molecules and to the uranyl-phosphate sheets. Finally, althupite, $AlTh^{4+}(UO_2)[(UO_2)_3O(OH)PO_4)_2]_2(OH)_3(H_2O)_{15}$, shows one of the most complex interlayer arrangement (Fig. 3d). The Al octahedra form a dimer of $Al_2(OH)_6(H_2O)_4$ composition. This dimer shares six oxygens with thorium in 9-fold coordination, to form a complex with the composition $[(Th(H_2O)_3O_3)(OH)_3(Al_2(H_2O)_4)(OH)_3(Th(H_2O)_3O_3)]$. Thorium polyhedra are sharing two oxygens with the PO_4 tetrahedra and one oxygen with the UO_7 pentagonal bypyramids from the uranyl-phosphate sheets. In addition, interstitial UO_7 pentagonal bypyramids are also occurring in the interlayer and are connected to two oxygens from the PO_4 tetrahedra. The plane formed by the five equatorial oxygens of the uranyl bypyramids is nearly perpendicular to the plane of the uranyl-phosphate sheets.

As demonstrated in the present study, the Al-bearing uranyl phosphates and arsenates show a wide type of structural arrangements. The structural data are still missing for nine of these minerals and, therefore, new types of structural models are likely to be discovered in the future.

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