

Table 39. Corrected structure data for Zr_4Al_3 (original data from ACCRA 13 56)

(191) $P6/mmm$, $a = 5.433$, $c = 5.390$ Å.						
		x	y	z	PP	Old
Al	3(f)	$\frac{1}{2}$	0	0		
Zr(1)	2(e)	0	0	$\frac{1}{2}$		1
Zr(2)	2(d)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$		2,3

Structures reported in the correct space group and which may be considered as isotypic, anti-types ($PuGa_3$ HT, $ZrAl_3$), representatives of structure-type branches ($MnHg$ LT, WC), or site-ordering variants ($CoMnSb$, $PuBr_3$) of the structure types discussed here, are indicated in the last column of Table 1. The coordinates of $NaSbS_2$ refined in space group $P\bar{1}$ become, after transformation, very similar to those of $NaSbS_2$ previously reported with a $KSbS_2$ -type structure. The deviations from the data refined in $C2/c$ (see Table 24) are only slightly outside the e.s.d. ranges indicated for this structure, and the fact that this work was not known to the authors of the refinement in $P\bar{1}$ makes the existence of a triclinic deformation variant under these conditions unlikely. Among the compounds crystallizing with an Na_2HgO_2 -type structure, some were reported in the incorrect space group $I422$, some refined in space group $I4/mmm$ but were identified as isotypic (e.g.

Na_2PdH_2), and some were published in space group $I4/mmm$ without being recognized as isotypic (e.g. U_2IrC_2).

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The Importance of Accurate Crystal Structure Determination of Uranium Minerals. I. Phosphuranylite $KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \cdot 8H_2O$

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Abstract

On the basis of accurate crystal structure determination, the mineral phosphuranylite corresponds to the chemical formula $KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \cdot 8H_2O$.

$Cmcm$, $a = 15.778$ (3)– 15.899 (2), $b = 13.702$ (2)– 13.790 (5), $c = 17.253$ (3)– 17.330 (3) Å, $Z = 4$, $D_x = 4.575$ – 4.631 g cm⁻³, $\mu = 287.6$ – 291.1 cm⁻¹. The presence of potassium (about 1.80 wt% K_2O), overlooked until now, has been confirmed by microprobe

analysis on samples from four different localities. The best data for structure determination have been obtained by single-crystal X-ray diffraction on specimens from Capoterra, Sardinia, and Bois Noirs, France; here 1453 and 1254 independent reflections, respectively, were used in the refinement, and the corresponding final *R* index is 0·036 and 0·048. The structure consists of layers of phosphate groups connected with hexagonal, pentagonal and tetragonal dipyramids centered on the U atoms. The Ca and K atoms are located within channels in the uranylphosphate framework, together with water molecules, with statistical distribution of the Ca atoms over two symmetrically related sites. The U—O distances are of two kinds: two bonds are very short (1·77 to 1·80 Å) and make an angle close to 180°, in agreement with the conformation of the uranyl ion UO₂⁺; the others range from 2·23 to 2·68 Å.

Introduction

Some time ago, thanks to the courtesy of friend collectors, we obtained a suite of samples of phosphuranylite, a rare uranium phosphate. Structural data for this mineral have already been published (Shashkin & Sidorenko, 1974) for a sample from an unstated locality (presumably in the Soviet Union). These data are questionable however because of the high final *R* index (0·157) and the unacceptable atom—atom distances involving uranium. This obscures most details regarding the lighter atoms.

Unit-cell and space-group data were obtained by single-crystal X-ray diffraction on samples from four different localities. The unit-cell parameters (see the first four columns in Table 1) were obtained for each crystal from a least-squares fit of 25 reflections with 2θ ranging between 32 and 36°. Most of the differences observed here between the various specimens are likely to be due to the large absorption coefficient, combined with the unfavourable crystal shape and with possible slight variations in chemical composition (see Table 2). Whereas the values of the unit-cell parameters for our samples show a general agreement with the literature, the Laue symmetry and the extinction rule ($h0l: l = 2n + 1$) are consistent with the space group *Cmcm* (or the non-centro-

symmetric *Cmc2*₁), instead of *C222*₁, as found by Shashkin & Sidorenko (1974); our results are in agreement with the earlier observations by Hogarth & Nuffield (1954) and with the recent data obtained by Piret & Piret-Meunier (1991, see below). This again indicated that a reinvestigation of the crystal structure was needed.

Crystal structure determination

In order to determine the crystal structure of phosphuranylite, rectangular tablets measuring about 0·20 × 0·05 mm and about 0·010 mm thick (taken from the samples from Sardinia and France, which gave the best crystals) were mounted on an Enraf-Nonius CAD-4 diffractometer. A data set for each crystal was measured up to $2\theta = 55^\circ$ at room temperature, using a conventional ω - 2θ scan mode, with graphite-monochromated Mo *K* α radiation ($\lambda = 0\cdot71073$ Å). 4835 and 4615 reflections were measured for the Sardinian and French crystals, respectively, by exploring the reciprocal lattice with $0 \leq h \leq 20$, $0 \leq k \leq 16$, $-22 \leq l \leq 22$. The scan speed was determined from pre-scans, requiring $I > 0\cdot5\sigma(I)$ for a reflection to be considered observed and for a final scan to be performed, with a maximum time of 120 s. After averaging the symmetry-related data, the number of independent reflections was 2324 and 2303, respectively; of these, 1453 and 1254 with $I > 3\sigma(I)$ were used in the structure determination. An absorption correction was introduced for each crystal according to North, Phillips & Mathews (1968), using six reflections with χ values near 90° (minimum relative transmission factors 0·17 and 0·27, respectively, for the two samples); after this correction the disagreement in intensity between symmetrically equivalent reflections was 2·3 and 3·1%, respectively.

The structure was solved by direct methods on the data from the Sardinian crystal using the *MULTANII* routine (Main *et al.*, 1980). A first *E* map led to location of all the U atoms; from subsequent difference Fourier maps the P, Ca and O atoms were also readily located. A peak of $17\text{ e } \text{Å}^{-3}$ was in agreement with the electron density and the steric requirements of a K atom. The presence of

Table 1. Unit-cell data for phosphuranylite (Å)

Standard deviations, in parentheses, refer to the last digit.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
<i>a</i>	15·899 (2)	15·778 (3)	15·890 (6)	15·862 (6)	15·95 (2)	15·85 (10)	15·835 (5)
<i>b</i>	13·740 (2)	13·769 (2)	13·790 (5)	13·702 (5)	13·75 (2)	13·76 (10)	13·724 (4)
<i>c</i>	17·300 (3)	17·330 (3)	17·322 (5)	17·253 (7)	17·38 (4)	17·42 (10)	17·326 (6)

Notes: (1) Our data; sample from S. Leone di Capoterra, Sardinia. (2) Our data; sample from Bois Noirs, France. (3) Our data; sample from Peveragno, Cuneo, Piemonte, Italy. (4) Our data; sample from Zambia. (5) Data for phosphuranylite from Shashkin & Sidorenko (1974). (6) Data from Hogarth & Nuffield (1954) on a sample from Urgeiriça, Portugal. (7) Data from Piret & Piret-Meunier (1991) on a sample from Margnac, France.

Table 2. *Analytical data for phosphuranylite (wt%)*

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
UO ₃	72.59	76.58	76.4	79.3	78.1	77.8	79.1
PbO	—	—	Trace	0.5	0.2	0.6	1.4
BaO	—	—	—	—	—	0.1	0.5
CaO	4.74	2.14	2.3	2.0	2.1	1.9	2.5
K ₂ O	—	1.80	—	2.2	2.5	2.8	1.9
P ₂ O ₅	12.01	10.86	11.1	10.9	10.3	10.4	9.8
H ₂ O	10.66	8.61	8.4	(5.1)	(6.8)	(6.4)	(4.8)
Ins	—	—	1.8	—	—	—	—
	100.00	100.00	100.0	100.0	100.0	100.0	100.0

Notes: (1) Theoretical composition for phosphuranylite, derived from the formula proposed by Shashkin & Sidorenko (1974). (2) Theoretical composition for phosphuranylite, derived from our structure analysis. (3) Analysis reported by Hallowell in Frondel (1950) for a 200 mg sample from Rosmaneira, Portugal. (4) Results from our microprobe analysis on phosphuranylite from Sardinia (average of three analyses for UO₃, two for PbO, and 14 for the oxides of all the other elements). (5) Results from our microprobe analysis on phosphuranylite from France (average of six analyses). (6) Results from our microprobe analysis on phosphuranylite from Peveragno, Cuneo (average of five analyses, and three for Ba). (7) Results from our microprobe analysis on phosphuranylite from Zambia (average of four analyses for UO₃ and BaO, and eight for all the other elements).

potassium was later confirmed by a complete microprobe analysis (see below and Tables 2, 3).

The structure was refined by full-matrix least squares separately for each sample, minimizing the function $\sum_i w_i (|F_o| - k|F_c|)^2$ and using, for each crystal, the corresponding unit-cell and intensity data; in this procedure, no attempt was made to account for H atoms in the structure-factor calculations. Therefore, these atoms will be considered here only to the extent of balancing the chemical formula and of satisfying the bond-valence criterion; their presence is also in agreement with a possible set of hydrogen bonds, on the basis of acceptable O—O distances (see below). Anisotropic thermal parameters were used for all the atoms in the Sardinian crystal; for the French crystal (owing to the slightly inferior quality and size of the collected data set) isotropic thermal parameters were assigned to the O atoms.

The final weighting scheme was $w = 1/\sigma^2(F_o)$ where $\sigma(F_o) = [\sigma^2(I)_{cs} + (kI)^2]^{1/2}/2F_oLp$, in which $\sigma(I)_{cs}$ is the standard deviation for each reflection as derived from counting statistics, k ($=0.04$) is a coefficient for improving the goodness-of-fit and Lp is the Lorentz-polarization coefficient. Scattering factors for the neutral atoms according to Cromer & Waber (1974) have been used; anomalous-scattering effects for all the atoms were accounted for according to Cromer (1974), using the real and imaginary parts. In most cases, the site-occupancy factors ($=p$) essentially converged to unity in the first stage of the refinement, and they were kept fixed at this value in the final stage. The only exceptions, where p is different from unity, are Ca, O(16) and K; here the values of p were refined even in the last cycles and

converged to 0.49 ± 0.01 , 0.50 ± 0.02 and 0.88 ± 0.02 , respectively.* The values of the final disagreement factor were 0.036 and 0.048 for the Sardinian and the French crystals, respectively, and the weighted disagreement factor 0.049 and 0.061. All the positional parameters in the two samples agree within 0.03 \AA , even for the O atoms with very high thermal motion or low occupancy. The final difference Fourier maps showed residual peaks of the order of 2 and $3 e \text{ \AA}^{-3}$ for the two crystals, respectively; the highest were in the proximity of the U atoms. $(\Delta/\sigma)_{\max}$ was 0.01 and the goodness-of-fit was 1.69 for the Sardinian and 2.06 for the French sample.

In order to provide every kind of information for comparison with other specimens of phosphuranylite considered in the literature, the X-ray diffraction powder pattern was calculated, using the program *POWLS80* (Will, 1979). The results are virtually coincident with the powder diffraction file JCPDS 19-898 (1974) for phosphuranylite and are deposited.

From the residuals and the inverse matrix of the final cycles of the least-squares refinement, an estimate of the uncertainty in the positions of the U atoms of about 0.001 \AA , or even smaller, can be derived. This value is so small that the uncertainty in the unit-cell parameters (here not quite negligible) sensibly contributes to the uncertainty in the distances between the U atoms. The comparatively large uncertainty in the unit-cell parameters is probably one reason why there is a difference (up to 0.003 \AA) between the French and the Sardinian crystals in the corresponding positions of the U atoms in the unit cell.

For the position of the K and Ca atoms, the uncertainty, as derived from the last least-squares cycle, is about 0.01 \AA ; for P, it amounts to about 0.004 \AA , and for the O atoms it ranges from 0.015 \AA (in most cases) up to 0.04 \AA for the atoms affected by disorder or high thermal motion. Therefore, our results correspond to a particular case of high precision (and presumably accuracy) obtained for an X-ray structure determination of a uranium mineral. This situation is due to the favourable occurrence of good crystals and to the efficiency of the ψ -scan method for absorption correction.

Chemical analysis

Electron-microprobe analyses were performed on polished grain-mounts by using the ARL-SEMQ instrument of the Italian National Research Council (CNR) at Centro di Studio per la Stratigrafia e

* The relatively low value of the temperature factor of O(13) and the coordination polyhedron around this atom could support at least a partial substitution by a metal atom such as K or Ca; however, the refined p value (0.99 ± 0.03) rules out this possibility.

Table 3. Conditions and standards for electron microprobe analysis

Accelerating voltage	20 kV
Sample current on brass	10 nA
Beam spot diameter	~15 μm
Counting time at peak position	10 s
Counting time at both backgrounds	2 s
Analyzing crystal	PET
Characteristic lines	U Mα, Pb Mα, Ba Lα, Ca Kα, K Kα, P Kα
Analytical standards	
P	Apatite, USNM 104021 (Jarosewich, Nelen & Norberg, 1980)
Ca, K	Kaersuhte, natural standard
Pb	Anglesite, natural standard
Ba	Celsian, natural standard
U	Synthetic uranium oxide 99.80 wt% UO ₂
Correction method	MAGICIV (Colby, 1968)

Petrografia delle Alpi Centrali, Milan. To determine the content of U, Ca, K, Pb, Ba and P, a series of natural and synthetic standards was employed (see Table 3). The data were corrected using a modified version of the MAGICIV computer program (Colby, 1968). As is well known, the potassium lines *Kα* and *Kβ* are liable to suffer from interference from the uranium lines *Mβ* and *Mγ*, respectively. In our wavelength-dispersion instrument, however, the peaks are perfectly separated (see Fig. 1), and an empirical correction for partial overlap has been applied as in our work regarding analysis of rare-earth elements (Mannucci, Diella, Gramaccioli & Pilati, 1986; Bianchi, Pilati, Diella, Gramaccioli & Mannucci, 1988; Demartin, Pilati, Diella, Donzelli & Gramaccioli, 1991). The analytical results are reported in Table 2, where they are shown to be in good agreement with the theoretical composition resulting from structure determination and, apart from the presence of potassium, with Hallowell's analysis reported in Frondel (1950). As in their crystal structure determination, Piret & Piret-

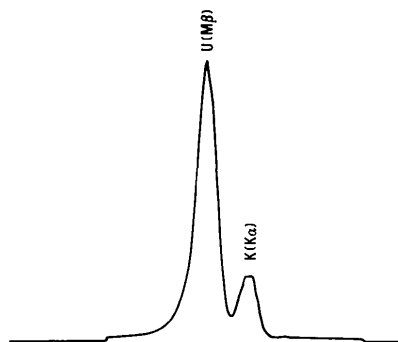


Fig. 1. An intensity versus wavelength plot of the uranium *Mβ* peak, together with the potassium *Kα* peak, as given by our instrument ARL-SEM-Q with a phosphuranylite specimen. The resolution of the two peaks at the operating conditions is clearly shown.

Table 4. Atomic coordinates and equivalent isotropic thermal parameters

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta) \times B(1,3) + bc(\cos\alpha)B(2,3)]$.

Wyckoff		x	y	z	$B_{eq}(\text{Å}^2)$
letter					
U(1)	(h)	0.24363 (4)	0.87219 (3)	0.63876 (3)	1.155 (9)
U(2)	(g)	0.20815 (6)	0.61435 (5)	0.750	1.14 (1)
U(3)	(b)	0.000	0.500	0.500	1.30 (2)
Ca	(f)	0.000	0.9680 (7)	0.5800 (7)	2.5 (2)
K	(c)	0.000	0.4196 (8)	0.750	5.7 (4)
P	(h)	0.1896 (3)	0.6210 (2)	0.5614 (2)	1.07 (6)
O(1)	(h)	0.1379 (8)	0.9179 (8)	0.6323 (7)	2.1 (2)
O(2)	(h)	0.3474 (9)	0.8228 (8)	0.6433 (7)	3.0 (3)
O(3)	(g)	0.318 (1)	0.631 (1)	0.750	2.7 (4)
O(4)	(g)	0.097 (1)	0.602 (1)	0.750	1.7 (3)
O(5)	(f)	0.000	0.542 (1)	0.4035 (9)	1.9 (3)
O(6)	(h)	0.1000 (8)	0.6111 (7)	0.5281 (6)	2.1 (2)
O(7)	(h)	0.1944 (8)	0.7095 (7)	0.6155 (6)	1.9 (2)
O(8)	(h)	0.2062 (9)	0.5362 (7)	0.6175 (6)	2.1 (2)
O(9)	(h)	0.2530 (8)	0.6249 (7)	0.4967 (6)	1.7 (2)
O(10)	(f)	0.270 (1)	0.954 (1)	0.750	2.5 (4)
O(11)	(g)	0.190 (1)	0.7870 (9)	0.750	2.0 (3)
O(12)	(g)	0.000	0.783 (1)	0.577 (1)	3.0 (4)
O(13)	(f)	0.000	0.242 (1)	0.583 (1)	2.2 (3)
O(14)	(h)	0.086 (1)	0.906 (1)	0.450 (1)	9.1 (5)
O(15)	(c)	0.000	0.221 (3)	0.750	9 (1)
O(16)	(f)	0.000	1.005 (3)	0.780 (2)	5 (1)
O(17)	(c)	0.000	0.795 (3)	0.750	9 (1)

Meunier (1991) found no potassium in their microprobe analysis of the mineral; however, they state that their own quantitative results are not coherent due to several difficulties, and they have limited themselves to only qualitative tests. Accordingly, the potassium could easily be overlooked, both in view of this situation and also in view of the interference with the uranium lines, which is critical, especially if an instrument with small dispersion is used.

Discussion

Atomic positional parameters (Table 4), and bond distances and angles (Table 5) are reported here only for the Sardinian crystal, whose data are the best.* In any case, the differences in bond distances and angles between the Sardinian and French crystals are irrelevant with respect to the following discussion. The motive of interconnected polyhedra around U(1), U(2), U(3) and P seen along the *a*, *b* and *c* axes is given in Figs. 2, 3 and 4, respectively; the motive of interconnecting water chains and cations like K⁺ and Ca²⁺ is represented in Fig. 5.

* Lists of atomic coordinates for the French (Bois Noirs) sample, observed and calculated structure-factor amplitudes and anisotropic thermal parameters for both samples, and the calculated powder diffraction pattern have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53961 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. Bond distances (Å) and angles (°) for phosphuranylite

Standard deviations, given in parentheses, refer to the last digit.

Pentagonal bipyramid around U(1)

U(1)—O(1)	1.80 (1)	U(1)—O(2)	1.79 (1)	U(1)—O(7)	2.403 (9)
U(1)—O(8) ^a	2.418 (2)	U(1)—O(9) ^b	2.344 (8)	U(1)—O(10)	2.268 (6)
U(1)—O(11)	2.410 (7)				

O(1)—O(7)	3.02 (1)	90.6 (4)	O(2)—O(7)	2.93 (1)	87.4 (4)
O(1)—O(8) ^a	2.98 (1)	88.5 (4)	O(2)—O(8) ^a	3.09 (1)	93.3 (4)
O(1)—O(9) ^b	2.89 (1)	87.3 (4)	O(2)—O(9) ^b	2.99 (1)	91.7 (4)
O(1)—O(10)	2.97 (2)	92.9 (5)	O(2)—O(10)	2.86 (1)	89.0 (5)
O(1)—O(11)	2.84 (1)	83.5 (5)	O(2)—O(11)	3.15 (2)	96.2 (5)
O(7)—O(9) ^b	3.11 (1)	81.7 (3)	O(7)—O(11)	2.56 (1)	64.3 (3)
O(8) ^a —O(9) ^b	3.06 (1)	79.9 (3)	O(8) ^a —O(10)	2.58 (1)	66.8 (3)
O(10)—O(11)	2.63 (2)	68.2 (4)	O(1)—O(2)		177.8 (4)

Hexagonal bipyramid around U(2)

U(2)—O(3)	1.77 (1)	U(2)—O(4)	1.77 (1)	U(2)—O(7) × 2	2.677 (8)
U(2)—O(8) × 2	2.531 (8)	U(2)—O(10) ^c	2.23 (1)	U(2)—O(11)	2.39 (1)

O(3)—O(7) × 2	3.23 (1)	90.9 (3)	O(4)—O(7) × 2	3.16 (1)	88.1 (3)
O(3)—O(8) × 2	3.19 (1)	93.9 (3)	O(4)—O(8) × 2	3.01 (1)	86.9 (3)
O(3)—O(10) ^c	2.81 (2)	88.6 (6)	O(4)—O(10) ^c	2.93 (2)	93.3 (6)
O(3)—O(11)	2.96 (2)	89.4 (6)	O(4)—O(11)	2.94 (2)	88.7 (5)
O(7)—O(8) × 2	2.39 (1)	54.5 (3)	O(7)—O(11) × 2	2.56 (1)	60.4 (2)
O(8)—O(10) ^c × 2	2.58 (1)	65.4 (2)	O(3)—O(4)		178.1 (6)

Tetragonal bipyramid around U(3)

U(3)—O(5) × 2	1.77 (1)	U(3)—O(6) × 4	2.26 (1)
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O(5)—O(6) × 4	2.84 (1)	88.9 (4)	O(5)—O(6) ^d × 4	2.89 (1)	91.1 (4)
O(6)—O(6) ^e × 2	3.18 (2)	89.5 (5)	O(6)—O(6) ^d × 2	3.21 (2)	90.5 (5)
O(5)—O(5) ^f		180			

Tetrahedron around P

P—O(6)	1.542 (9)	P—O(7)	1.537 (8)	P—O(8)	1.540 (8)
P—O(9)	1.507 (9)				

O(6)—O(7)	2.52 (1)	110.0 (5)	O(6)—O(8)	2.51 (1)	109.1 (5)
O(6)—O(9)	2.50 (1)	110.1 (5)	O(7)—O(8)	2.39 (1)	101.9 (5)
O(7)—O(9)	2.54 (1)	113.1 (5)	O(8)—O(9)	2.53 (1)	112.4 (5)

Coordination polyhedron around Ca

Ca—O(1) × 2	2.47 (1)	Ca—O(12)	2.54 (2)	Ca—O(14) ^f × 2	2.26 (2)
Ca—O(14) × 2	2.77 (2)	Ca—O(16) ^g	2.48 (3)		

Polyhedron around K

K—O(2) ^h × 4	3.33 (1)	K—O(4) × 22.94 (1)	K—O(5) ^d × 2	2.71 (1)
K—O(15)	2.73 (3)			

Oxygen—oxygen contacts suggesting H-bond formation

O(13) ^h ...O(14) ^d × 2	2.52 (2)	O(13) ^h ...O(15)	2.91 (1)
O(14) ^d ...O(14) ^f	2.73 (3)	O(16) ^g ...O(17)	2.92 (5)
O(9) ^b ...O(14) ^h	2.76 (2)	O(5) ^d ...O(13)	2.96 (2)
O(12) ^h ...O(13) ^d	2.78 (2)	O(6) ^e ...O(12)	2.97 (2)
O(2) ^h ...O(13) ^h	2.87 (1)	O(12) ^h ...O(17)	3.00 (2)

Symmetry code: (a) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (b) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (c) $\frac{1}{2} - x, -\frac{1}{2} + y, z$; (d) $x, 1 - y, 1 - z$; (e) $-x, y, z$; (f) $x, 2 - y, 1 - z$; (g) $-x, y, \frac{1}{2} - z$; (h) $\frac{1}{2} + x, \frac{1}{2} + y, z$.

In this structure, the crystal chemistry of the various elements follows their general behaviour. In line with Shashkin & Sidorenko's observations, the U atoms are surrounded by hexagonal bipyramids [around U(2)], or by pentagonal bipyramids [around U(1)]; however, in disagreement with these authors, we find U atoms [U(3)] situated at the centre of tetragonal bipyramids, reminiscent of the corresponding coordination in the autunite group (Ross

& Evans, 1964; Ross, Evans & Appleman, 1964). In all these polyhedra, the U—O bond lengths are of two kinds: two bonds are noticeably shorter than the others (1.77 to 1.80 Å), and make an angle always close to 180°, in agreement with the interpretation as UO_2^{2+} ions. The remaining bonds are nearly perpendicular to the two shortest ones, and are noticeably longer (2.23 to 2.68 Å).

Each Ca atom is surrounded by eight O atoms forming an irregular polyhedron, and the Ca—O distances range from 2.26 to 2.77 Å. The K atom is situated at the centre of another irregular polyhedron, formed by nine O atoms, and the K—O

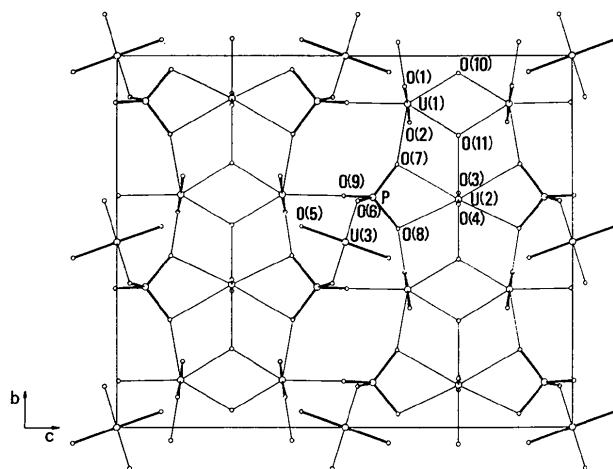


Fig. 2. ORTEP (Johnson, 1976) view of the uranylphosphate framework seen along the *a* axis. P—O and short U—O bonds are represented as thick segments.

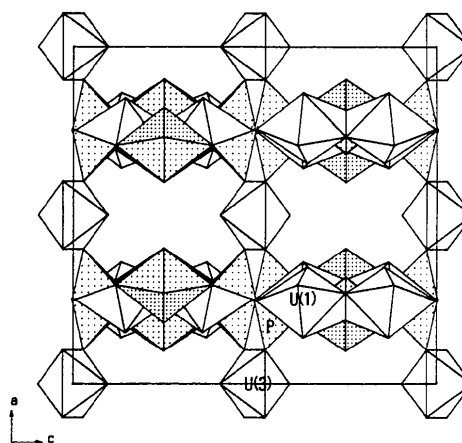


Fig. 3. A view of the polyhedra constituting the uranylphosphate framework seen along the *b* axis, obtained by the program POLIEDRI (Pilati, 1990). For clarity the tetragonal and pentagonal bipyramids around U(3) and U(1) and their equivalents are not shaded; the tetrahedra and the hexagonal bipyramids around P and U(2) and their equivalents are shaded.

distances range from 2.71 to 3.33 Å: these distances are in line with the steric requirements of potassium and are distinctive, especially with respect to the possibility of extensive replacement by O atoms (as H₃O⁺). This is particularly evident on considering the average O...O distance (2.57 Å) around the oxonium ion reported in the literature (Lundgren & Olovsson, 1976).

Following the bond-valence concept (see Brown, 1980, and references therein), the sum of bond valences at the Ca and K atoms is 2.03 and 0.92, respectively: this fully confirms our interpretation.

Some of the O atoms are very tightly bonded to U or P atoms, or to both of them; others are bonded to

Ca, or K atoms only, with bonds of essentially ionic character. The remaining O atoms are not directly bonded to any heavier atom, and their short O—O distances (see Table 5) show them to be linked to other O atoms, as a part of a hydrogen-bonded network.

The geometry of the phosphate ions is also consistent with its crystal chemistry: the P—O bond lengths range from 1.51 to 1.54 Å, and the PO₄ group is tetrahedral, the O—P—O angles ranging from 102 to 113°. The seven- and eightfold-coordinated U atoms are linked together by phosphate groups and form puckered layers of composition (UO₂)₃(PO₄)₂O₂, as was described by Shashkin & Sidorenko. These layers are approximately parallel to the borders of a diamond-shaped primitive cell and are linked together by the sixfold-coordinated U atoms (see Figs. 3, 4), thereby constituting the walls of a 'honeycomb' structure, with comparatively large tubular cavities, substantially similar to zeolites: as in these minerals, inside the cavities water and metal ions like Ca²⁺ and K⁺ are found. This situation accounts for the high value of some temperature factors (especially for the K atom and for some water molecules), which are similar to those observed in zeolites.

The apparent coordination around the Ca atom is particularly interesting: besides eight O atoms, there is another Ca atom situated at 2.90 Å from the central atom and derived from it by the symmetry operation $x, -y, -z$. This distance is too short to be reasonable; also one O atom bonded to Ca [here called O(16)] is situated at an unreasonable distance (1.07 Å) from an O atom derived from it through another symmetry operation $(-x, y, \frac{1}{2}-z)$. This anomalous situation can be explained by considering the partial site occupancies of these atoms: *i.e.* of the two symmetry-related atomic positions which are situated at such a short distance, one (at least) must be empty. It is useful to note that these alternatively occupied positions are lying in the same tubular ('zeolitic') cavity. Since O(16) is only bound to calcium (besides the hydrogen bonds), this implies that the site is occupied only when the adjacent position of the Ca atom is actually occupied by the metal.

The present model of partial substitution in the Ca position implies strong correlation between the occupancy of these sites: absence of some symmetry operations (in particular those connecting each of these atoms with its symmetrically related one) might also be suggested as a possibility. From the set of the *Cmcm* space group, if such operations are omitted, the *C_{2h}* (*P2₁/c*) space-group symmetry would result. However, the hypothesis of lower symmetry would imply additional correlation between a cavity and its neighbours, *i.e.* the presence of the Ca atom in one

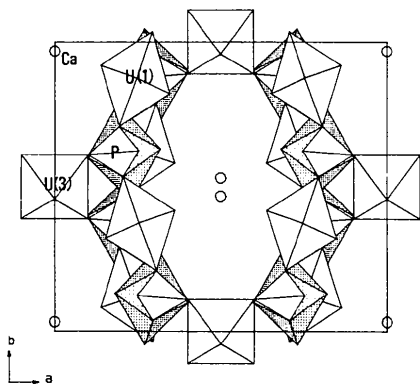


Fig. 4. *POLIEDRI* plot of the uranylphosphate framework along the *c* axis. Here only the hexagonal bipyramids around U(2) are shaded; the sites statistically occupied by Ca atoms are represented by circles. A primitive unit cell, whose corners correspond to U(3) atoms (*i.e.* they are midway between the corners of the C-centered unit cell represented here) can be clearly seen.

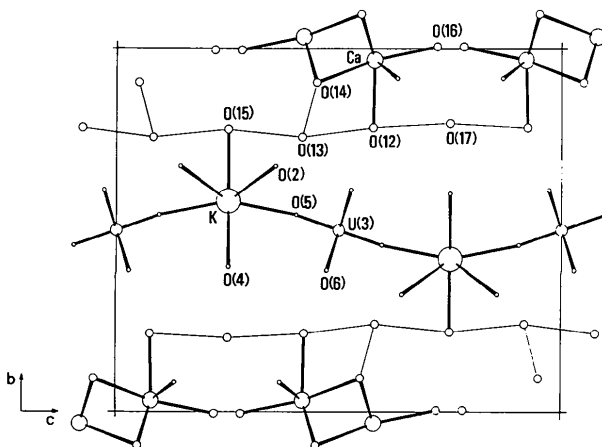


Fig. 5. *ORTEP* view of the atomic chains lying on the mirror plane at $x=0$. These chains are made up of K, O and U atoms (around $y=0.5$), or O atoms of water molecules connected by hydrogen bonds (thin segments). The numbered atoms either correspond or are symmetry-related to those in Table 4.

of the two equivalent sites of a single cavity (which corresponds to a primitive unit cell in projection: see Fig. 4) should be correlated to the occupation of the corresponding sites in the adjacent unit cells. Owing to the 'screening' effect of the uranylphosphate sheet, however, the presence of the Ca atom in one such position should not substantially influence the behaviour of the corresponding Ca atoms in the neighbouring unit cells, since their positions on the upper or on the lower site would be almost equally acceptable. For this reason, the choice of orthorhombic symmetry due to statistical disorder is the best in our opinion.

A systematic search of cavities in this structure was also performed using the program *OPEC* (Gavezzotti, 1983), but none were found. Therefore, the proposed structural model corresponds to an optimum space filling.

The bond-valence concept (Brown, 1980) is also useful for establishing the number of H atoms bonded to each O atom in the structure. For instance, the sum of the bond valences at O(1) down to O(10) ranges from 1.91 to 2.20, and this excludes the presence of directly bonded H atoms; for O(11) it is 1.54, which might also meet the requirement of an OH group; however, this would lead to non-bonded U—H distances shorter than 2.7 Å. For O(12) to O(17), the bond-valence sum ranges between zero and 0.28, essentially in agreement with the requirement of water molecules.

Considering the number of atoms located in the structure, their multiplicity and occupation factor, and the number of water molecules derived above, the charge balance in the structure requires the presence of three additional H atoms per formula unit.

The water at O(13) can be considered to be an oxonium ion (H_3O^+), on account of two very short hydrogen bonds (2.52 Å): taking account of its multiplicity, this would imply two H atoms per formula unit. The remaining H atom is very difficult to locate: we suggest a statistical distribution of it (as H_3O^+) with respect to the remaining water molecules. As an alternative, since there is an infinitely extended chain of hydrogen-bonded water molecules at O(12'), O(17), O(12), O(13), O(15) and O(13'') in sequence (see Fig. 5), a charge on O(17) would result in alternation of H_3O^+ ions and neutral water molecules.

When our paper was being written, we became aware of a parallel structure determination on phosphuranylite from Margnac (France) by Piret & Piret-Meunier (1991). The description of the uranylphosphate framework and of the statistical Ca-atom distribution is essentially similar to ours, thereby contradicting Shashkin & Sidorenko (1974), but the K atom is taken as an oxygen atom [O(15) in

their labelling]. Such an exchange between two atoms so widely different in atomic number should lead to a dramatic difference in temperature factors, which is not evident (3.9 against 5.7 Å²); however, a peak of $7\text{ e } \text{Å}^{-3}$ has been observed by Piret & Piret-Meunier in their final difference Fourier close to this atom (0.41 Å) (explained in terms of a partial substitution of the water molecule by a Pb atom). The mistaking of potassium for oxygen may have been facilitated by the poorer quality of the data [the final *R* index is 0.089 for 983 observed reflections with $I > 2.5\sigma(I)$]; moreover, these authors state that their least-squares refinement was not satisfactory. This may be due to considering some symmetry-related atoms as independent [see, for instance, the couples O(20)—O(21), O(22)—O(23) and O(25)—O(26) in their numbering, corresponding to our O(12), O(14) and O(13), respectively].

Concluding remarks

Our experimental results show the ideal chemical composition and the crystal structure of phosphuranylite to be different from what is described in the literature: the potassium content, until now unsuspected, is in essential agreement with the widespread occurrence of this mineral in pegmatites (type phosphuranylite has been discovered in a North Carolina pegmatite: see Genth, 1879) or in other rocks rich in potassium.

According to our data, the chemical formula for phosphuranylite is $\text{KCa}(\text{H}_3\text{O})_3(\text{UO}_2)_7(\text{PO}_4)_4\text{O}_4 \cdot 8\text{H}_2\text{O}$; therefore it is considerably different from the currently accepted one of $\text{Ca}(\text{UO}_2)_3(\text{PO}_4)_2 \cdot (\text{OH})_2 \cdot 6\text{H}_2\text{O}$ based on Shashkin & Sidorenko's crystal structure determination or $\text{Ca}(\text{UO}_2)_3[(\text{UO}_2)_3(\text{OH})_2(\text{PO}_4)_2]_2 \cdot 12\text{H}_2\text{O}$ based on Piret & Piret-Meunier's conclusions. Apart from the presence of potassium, which only corresponds to 1.8 wt% K_2O , our new formula is also in excellent agreement with Hallowell's analysis of a sample from Urgeiriça, Portugal (see columns 2 and 3 in Table 2). This analysis is the most accurate reported in the work by Frondel (1950), and probably represents the best which has been attained so far with traditional methods.

For these reasons, we think we have given a practical example of the capital importance of using highly accurate crystal data and careful refinement in establishing the chemical composition of crystalline substances containing very heavy elements such as uranium.

We are indebted to Dr Peter and Giuse Frank (Zürich) and to Mr Franco Soi (Piedimulera, Ossola) for having provided us with suitable samples of the mineral, to Mr Stefano Conforti for considerable

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Pb²⁺ Cation Ordering in Pb₃(Mo₄O₆)₄

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Abstract

The commensurately modulated structure of lead molybdenum oxide, Pb₃(Mo₄O₆)₄, has been determined by single-crystal X-ray diffraction. The Pb/Pb repulsion leads to a four-cell superlattice along the *c*-axis direction. Commensurate ordering of Pb²⁺ ions in the supercell was taken into account in the structure refinement. Crystal data are: *M*_r = 2540.6, tetragonal, *P4/mnc* (No. 128), *a* = 9.615 (1), *c* = 11.362 (3) Å, *V* = 1050.4 (3) Å³, *Z* = 2, *D*_x = 8.033 Mg m⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 33.21 mm⁻¹, *F*(000) = 2220, *T* = 297 K, *R* = 0.030, *wR* = 0.032 for 409 unique reflections. Refinement of the occupancy numbers of the Pb²⁺ sites in the supercell leads to the formula Pb₃(Mo₄O₆)₄, which reflects an ordering of Pb²⁺ in three of four sites in the tunnel. Each Pb²⁺ has a coordination environment of eight O atoms in a tetragonal arrangement.

The supercell is characterized by an ordering of the lead ions and vacancies in the tunnel following the sequence ...Pb—Pb—Pb—Δ... The Mo—Mo bond lengths parallel to the tunnel direction are regular.

Introduction

The structure of the reduced ternary molybdenum oxide NaMo₄O₆ (Torardi & McCarley, 1979) is comprised of infinite molybdenum metal cluster chains based on edge-shared Mo₆O₁₂ building blocks with the ternary metal cation in the tunnels formed by four metal cluster chains cross-linked by Mo—O bonds. The tunnels are parallel to the fourfold rotation axis of the tetragonal space group. Several compounds containing different ternary metal cations were found to adopt this structure type. It was noted that the stoichiometry of the cation *A* in A_xMo₄O₆ (*x* ≤ 1) depends upon its valency and size. When *A* is a small univalent cation, there is one

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