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PHURCALITE FROM PERUS, SÃO PAULO, BRAZIL, AND REDETERMINATION OF ITS CRYSTAL STRUCTURE

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ABSTRACT

Phurcalite has been found filling fractures in the tourmaline-bearing granitic pegmatite of Perus, in the northwestern part of São Paulo city, Brazil. It forms aggregates of radiating euhedral crystals up to 5 mm in length. The crystal structure of phurcalite, $Ca_2(UO_2)_3O_2(PO_4)_2{\cdot}7H_2O$, orthorhombic, space group *Pbca*, *a* 17.415(2), *b* 16.035(3), *c* 13.598(3) Å, *V* 3797(2) Å^3, *Z* = 8, has been solved by single-crystal X-ray-diffraction methods and refined to an *R* of 3.8% using 2065 observed [$I > 3\sigma(I)$] reflections. The structure consists of $[(UO_2)_3O_2(PO_4)_2]_n^{4n-}$ layers, parallel to (010), which are connected by Ca^{2+} ions and H_2O. The coordination polyhedra are: for U(1) a hexagonal bipyramid, for U(2) and U(3) pentagonal bipyramids, for Ca(4) and Ca(5) a capped trigonal prism and a triangulated dodecahedron, respectively, and for P(6) and P(7), tetrahedra. As a consequence of this work, the structural formula of phurcalite, previously reported as $Ca_2(UO_2)_3(PO_4)_2(OH)_4{\cdot}4H_2O$, must be changed to $Ca_2(UO_2)_3O_2(PO_4)_2{\cdot}7H_2O$. The analytical formula, derived from microprobe data, is $(Ca_{1.97}K_{0.05})_{\Sigma 2.02}(UO_2)_{2.87}O_{1.93}[(PO_4)_{1.90}(SiO_4)_{0.04}]_{\Sigma 1.94}{\cdot}7.57H_2O$.

Keywords: phurcalite, hydrous calcium uranyl oxyphosphate, pegmatite, crystal structure, X-ray diffraction, physical and chemical characterization, Perus, São Paulo, Brazil.

SOMMAIRE

Nous avons trouvé la phurcalite le long de fissures dans une pegmatite granitique à tourmaline de Perus, dans la partie Nord-Ouest de la ville de São Paulo, au Brésil. Les agrégats fibroradiés de cristaux idiomorphes atteignent 5 mm en longueur. La phurcalite est orthorhombique, groupe spatial *Pbca*, *a* 17.415(2), *b* 16.035(3), *c* 13.598(3) Å, *V* 3797(2) Å^3, *Z* = 8. Sa structure cristalline a été affinée par diffraction X, sur cristal unique, jusqu'à un résidu *R* de 3.8% en utilisant 2065 réflexions observées [$I > 3\sigma(I)$]. La phurcalite contient des feuillets $[(UO_2)_3O_2(PO_4)_2]_n^{4n-}$ parallèles à (010), et liés par des ions Ca^{2+} et des molécules d'eau. Les polyèdres de coordination comprennent un bipyramide hexagonal pour U(1), des bipyramides pentagonaux pour U(2) et U(3), un prisme trigonal à capuchon pour Ca(4), un dodécaèdre à faces triangulées pour Ca(5), et des tétraèdres pour P(6) et P(7). La formule structurale, interprétée comme étant $Ca_2(UO_2)_3(PO_4)_2(OH)_4{\cdot}4H_2O$ auparavant, devient $Ca_2(UO_2)_3O_2(PO_4)_2{\cdot}7H_2O$. Les analyses à la microsonde électronique ont donné $(Ca_{1.97}K_{0.05})_{\Sigma 2.02}(UO_2)_{2.87}O_{1.93}](PO_4)_{1.90}(SiO_4)_{0.04}]_{\Sigma 1.94}{\cdot}7.57H_2O$.

(Traduit par la Rédaction)

Mots-clés: phurcalite, oxyphosphate hydraté de calcium et d'uranyl, pegmatite, structure cristalline, diffraction X, caractérisation physique et chimique, Perus, São Paulo, Brésil.

INTRODUCTION

Phurcalite occurs in the Perus district, São Paulo city, Brazil, and corresponds to "mineral X" of Camargo (1965), also quoted as "unnamed uranyl phosphate" by Fleischer (1974) and Fleischer *et al.* (1984). The other recorded occurrences of phurcalite are at Nisa, Alto Alentejo, Portugal (Lencastre & Vairinho 1970, Braithwaite *et al.* 1989), Bergen an der Trieb, Vogtland, Saxony, Germany (Deliens & Piret 1978), Streuberg, near Bergen an der Trieb (PDF 30-285), Shinkolobwe, Shaba, Zaire (Deliens & Comblain 1978), Kern County, California (Pemberton 1983, Braithwaite *et al.* 1989), Riverside County, California (Chew 1982) and Dartmoor, southwestern England (Braithwaite *et al.* 1989).

New data are presented here to better define the properties of the mineral, and to document at the same time a chemical formula that shows a better agreement with new structural information. The crystal structure of phurcalite was solved by Piret & Declercq (1978). The formula given was $Ca_2(UO_2)_3(PO_4)_2(OH)_4{\cdot}4H_2O$, with a final residual index *R* of 12%. However, there are problems with their structure. Bond-valence considerations derived from the bond lengths determined by Piret & Declercq (1978) clearly suggest that (i) O(14) and O(17) are isolated O^{2-} anions and not $(OH)^-$ groups, (ii) O(24) to O(29) are all H_2O groups, and (iii) an additional oxygen atom linked to Ca(5) might exist.

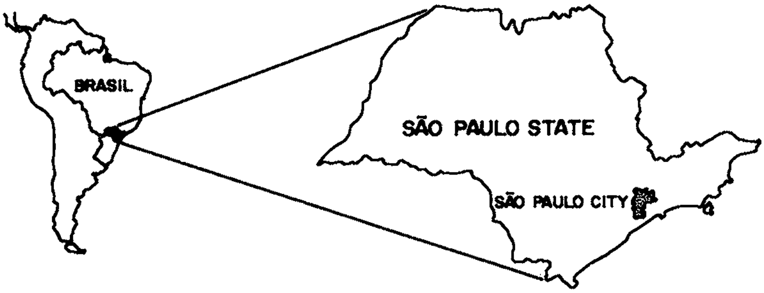

FIG. 1. Location map.

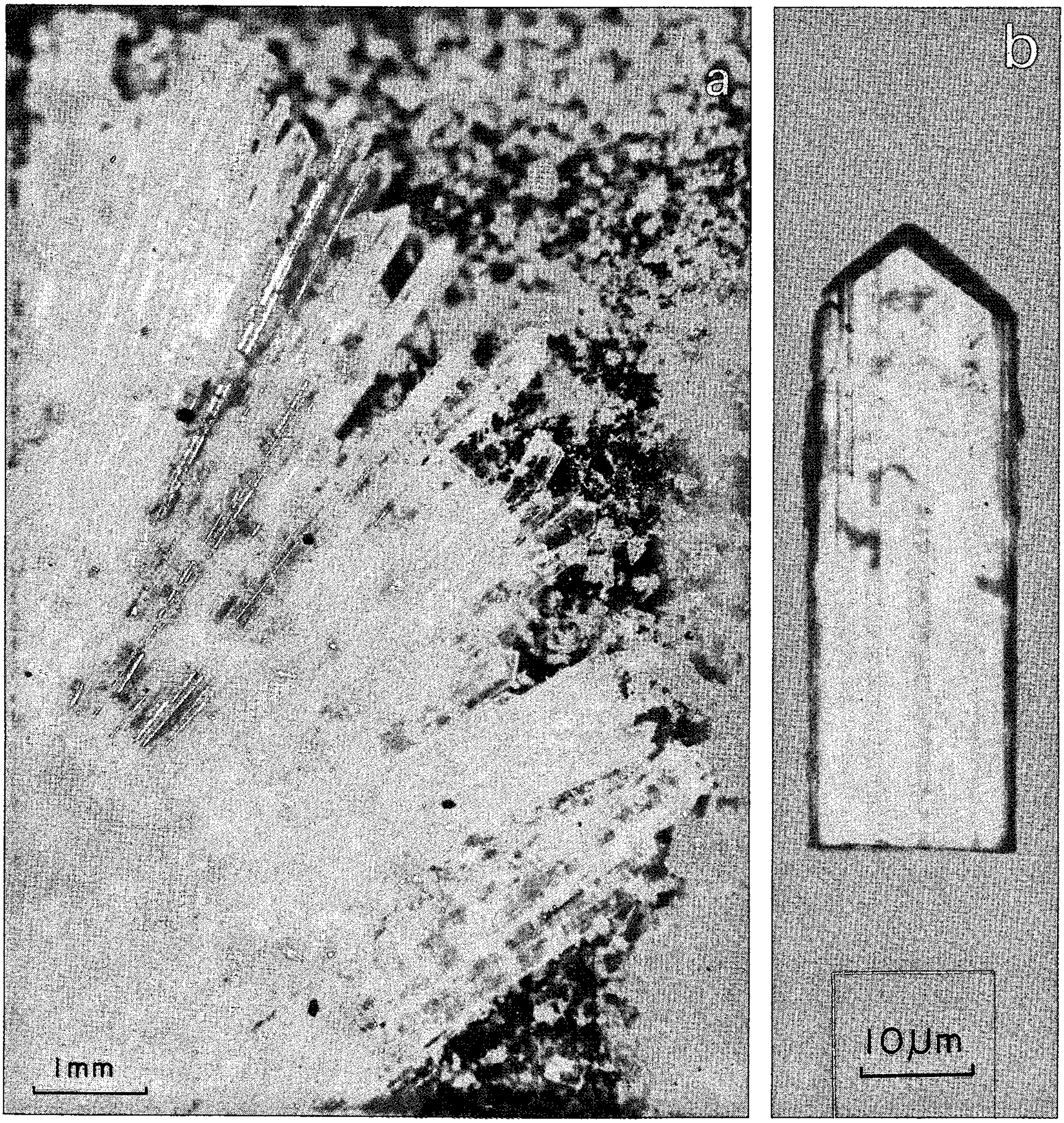

FIG. 2. Phurcalite: a) an aggregate of radiating crystals; b) an individual crystal from Perus.

To resolve these points, a new structural study of phurcalite was undertaken using a crystal from the occurrence at Perus.

OCCURRENCE AND PARAGENESIS

Phurcalite fills in fractures of the tourmaline-bearing granitic pegmatite at Perus, a district in the northwestern part of São Paulo city, Brazil (Fig. 1). Only one hand specimen with this material was obtained, which served as a basis for this study. No other uranium mineral is directly associated with phurcalite in this hand specimen, but several other uranium minerals occur in the pegmatite fractures: autunite, meta-autunite, chernikovite, torbernite, metatorbernite, phosphuranylite, uranophane, uranophane-beta and haiweeite. For background information on the geology and mineralogy of the Perus area, see Camargo & Coutinho (1960), Hasui (1963), Gabelman (1963), Camargo (1965), Camargo & Svisero (1969), Svisero (1976), Coelho (1980), Madureira *et al.* (1986) and Atencio (1988).

Phurcalite is interpreted as a secondary mineral, product of hydrothermal activity. DTA and TGA data (see below) suggest that the temperature of formation did not exceed 150°C.

HABIT AND PHYSICAL PROPERTIES

Phurcalite from Perus forms aggregates of radiating euhedral crystals, tabular according [010] and elongate following [001] (Fig. 2). Morphological studies by Camargo (1965) showed the presence of pinacoids {010} and {100}, rhombic prism {110} and rhombic dipyramid {111} (Fig. 3). The crystals studied are up to 5 mm in length, whereas those first described by Camargo (1965) and all the others cited in the literature have a maximum length of 1 mm.

Phurcalite is bright yellow, transparent and displays a vitreous luster, grading to adamantine in the largest crystals and to silky in the fine aggregates. The streak is pale yellow. The crystals in this study do not fluoresce in short- (254 nm) or long-wave (366 nm) ultraviolet radiation. Camargo (1965) noted weak pale green fluorescence only under short-wave ultraviolet radiation. Phurcalite has good cleavages on {001} and {100}, and a perfect cleavage on {010}. It is brittle, with a conchoidal fracture. Hardness measurements were carried out with a Vickers microhardness tester. Two indentations (5 g load) gave VHN values of 86 and 95 (average 90.5) corresponding (Young & Millman 1964) to a Mohs hardness of 2.4.

The density determination was carried out on crystals using Clerici solution diluted with distilled water. The resulting average of four determinations is 4.22(4) g/cm^3. The calculated density is 4.220 g/cm^3.

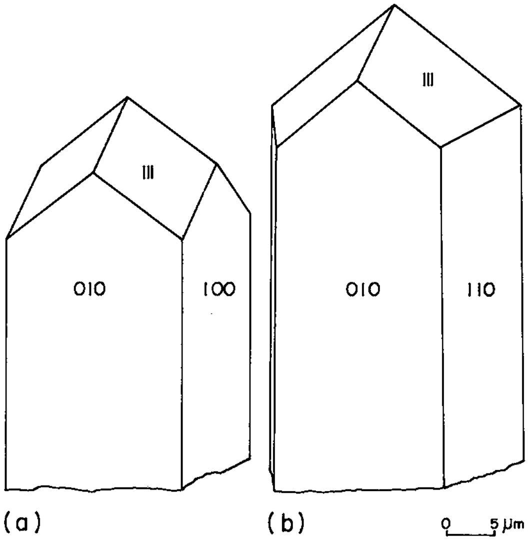

FIG. 3. Habit of phurcalite from Perus (modified from Camargo 1965): a) the most frequent habit; b) the rarest habit. Faces (010) and (100) were interchanged to agree with the orientation proposed by Deliens & Piret (1978).

TABLE 1. OPTICAL PROPERTIES OF PHURCALITE

	1	2	3	4	5
α	1.690(calc.)	1.670(5)	1.670	1.680	1.677(2)
β	1.730(1)	1.720(5)	1.725	1.732	1.732(2)
γ	1.749(1)	1.770(5)	1.775	1.775	1.766(2)
Biref.	0.059	0.100	0.105	0.095	0.089
$2V_x$meas.	68°	84°	82(2)°	80°	75°
$2V_x$calc.	-	90°	84.4°	84(3)°	74°
Pleoc. X	colorless	pale yellow	pale yellow	colorless	pale yellow
Pleoc. Y	pale yellow	pale yellow	pale yellow	yellow	yellow
Pleoc. Z	bright yellow	dark yellow	dark yellow	golden yellow	golden yellow

1. Bergen an der Trieb, Vogtland, Saxony, Western Germany (Deliens & Piret 1978)
2. Nisa, Alto Alentejo, Portugal (Lencastre & Vairinho 1970)
3. Merrivale quarry, Dartmoor, Southwest England (Braithwaite *et al.* 1989)
4. Perus, São Paulo, Brazil (Camargo 1965)
5. Perus, São Paulo, Brazil (this paper)

TABLE 2. CHEMICAL DATA FOR PHURCALITE

	1	2	3	4
CaO wt%	9.06	8.3	8.7	9.40 (8.73- 9.87)
K_2O	-	-	-	0.20 (0.16- 0.24)
UO_3	69.30	70.9	72.0	69.88 (68.56-71.73)
P_2O_5	11.46	11.5	9.4	11.52 (10.97-12.05)
As_2O_5	-	-	1.4	-
SiO_2	-	-	-	0.23 (0.13- 0.39)
H_2O	10.18	(9.3)	8.5(5)	11.62
Total	100.00	(100.0)	100.0	102.85

1. Theoretical formula, $Ca_2(UO_2)_3O_2(PO_4)_2.7H_2O$
2. Bergen an der Trieb, Vogtland, Saxony, West Germany (Deliens & Piret 1978)
3. Merrivale quarry, Dartmoor, Southwest England (Braithwaite *et al.* 1989)
4. Perus, São Paulo, Brazil (this paper, average of 19 analyses)

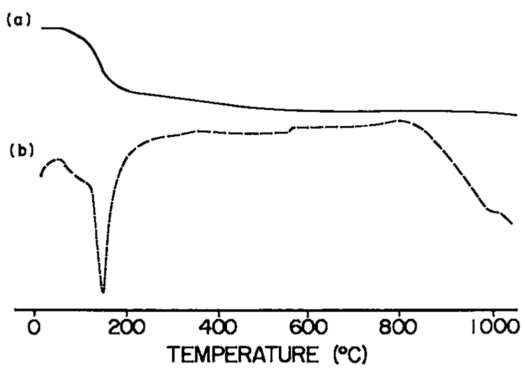

FIG. 4. Thermal data for phurcalite from Perus: a) thermogravimetric curve; b) differential thermal curve.

Optical data were determined in white light. Phurcalite is biaxial negative, dispersion $r > v$ medium, orientation $X = b$, $Y = a$ and $Z = c$, absorption $X < Y < Z$, positive elongation. Other optical properties for phurcalite are presented in Table 1.

CHEMICAL DATA

Nineteen analyses of two crystals were carried out in the Institute of Mineralogy, University of Berne, Switzerland, by means of an ARL–EMX automated electron microprobe fitted with an energy-dispersion analyzer. The operating voltage was 15 kV, and the sample current 3 nA. The COMIC.ED program, 1981 version, was used for corrections. The following standards were used: metallic uranium (U), wollastonite (Ca and Si), apatite (P), adularia (K) and pyrrhotite (S). Metallic uranium was polished and recoated shortly before analysis in order to avoid oxidation. The results demonstrate a homogeneous chemical composition. No other elements with atomic number greater than 10 were found by energy-dispersion X-ray fluorescence. A separate hand-picked sample was used to determine concentration of hydrogen on a Perkin–Elmer Model 240B Elemental Analyzer, recalculated to H_2O. The average results of the chemical analyses of phurcalite from Perus (with ranges in brackets) are compared with those from other occurrences in Table 2. Only at one point was 0.04% SO_3 detected. The empirical formula for phurcalite from Perus (based on 23 atoms of oxygen) is $(Ca_{1.97}K_{0.05})_{\Sigma 2.02}(UO_2)_{2.87}O_{1.97}[(PO_4)_{1.90}(SiO_4)_{0.04}]_{\Sigma 1.94}{\cdot}7.57H_2O$.

The differential thermal curve shows an intense endothermic peak with a maximum at 150°C, corresponding to loss of H_2O, as confirmed by the thermogravimetric curve. A small irregularity in the DTA curve at about 550°C may correspond to a slow volatilization of oxide from above about 500°C, as suggested from a TGA curve obtained by Braithwaite *et al.* (1989). No further change takes place until about 900°C, when melting begins (Fig. 4).

A more detailed infrared-absorption spectrum than that given by Camargo (1965) was obtained (Fig. 5). The following absorption maxima (in cm^{-1}) were observed: 3400, 1615, 1140, 1055, 960, 885, 575, 540, 385 and 255. The very broad band centered at 3400 cm^{-1} is due to the stretching vibration of H_2O. The band at 1615 cm^{-1} is a consequence of the bend vibration of H_2O. The peaks observed between 960 and 1140 cm^{-1} are probably those of the stretching vibrations of PO_4 tetrahedra. The band at 885 cm^{-1} is due to UO_2.

Phurcalite is insoluble or very slowly soluble in water but soluble in cold 1:1 acids: HCl (readily, with effervescence), HNO_3 (readily), and H_2SO_4 (slowly, with a grey coating).

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

X-ray powder-diffraction data for phurcalite from Perus were obtained utilizing graphite-monochromatized Cu$K\alpha$ radiation. The results are compared with those for phurcalite from other occurrences in Table 3.

A single crystal of dimensions 0.03 × 0.10 × 0.45 mm was selected for intensity measurements on a CAD–4 Enraf–Nonius diffractometer using graphite-monochromatized Mo$K\alpha$ radiation. Room-temperature cell parameters (Table 4) were determined by a least-squares procedure applied to the setting angles of 25 strong reflections in the range $9.45° < \theta < 20.53°$. The unit cell is orthorhombic, space group *Pbca*, $Z = 8$. The a:b:c relation for the unit-cell parameters is 1.086:1:0.848 for the Perus sample.

Calculations using the Gladstone–Dale relationship were performed using the chemical data, the measured density and the recorded indices of refraction of the Perus phurcalite. Most constants used are those reported by Mandarino (1981); the constant for UO_3, 0.134, is that given by Larsen (1921), allowing a better agreement for the uranyl phosphates (Piret & Deliens 1989). These calculations yielded $K_P = 0.172$ and $K_C = 0.175$. Hence $1-(K_P/K_C)$ is 0.017 indicating, according to Mandarino (1979), superior compatibility.

The diffraction intensities were measured by the ω–2θ scan technique up to $\theta = 25°$ in the range $0 \leq h \leq 16$, $0 \leq k \leq 19$ and $-2 \leq l \leq 20$, using an intensity-dependent variable rate of scanning between 2.88°θ.min^{-1} and 10.00°.min^{-1}. A total of 3298 unique reflections were measured; of these, 2065 had an intensity greater than $3\sigma(I)$. Two periodically monitored reflections showed no significant changes in intensity. Intensity data were corrected for Lorentz, polarization and absorption (Enraf–Nonius Structure Determination Package), owing to

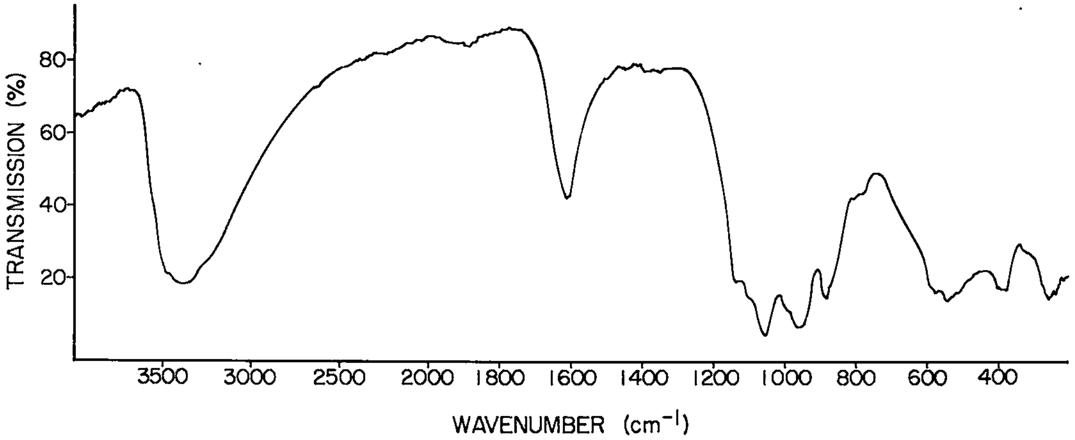

FIG. 5. Infrared-absorption spectrum of phurcalite from Perus.

the elongate shape of the crystal and high coefficient of linear absorption (251.91 cm^{-1}) . After the correction for absorption, R_{int} fell from 10.2 to 5.8%.

Scattering factors for neutral atoms and coefficients of anomalous dispersion were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The position of uranium atom U(1) was determined by the Patterson method, and those of U(2) and U(3), by difference-Fourier techniques. After least-squares refinement of the coordinates and the anisotropic temperature-factors of the U atoms, the position of atoms other than uranium was obtained by the difference-Fourier technique. Isotropic refinement of all 30 atoms [U(1), U(2) and U(3) anisotropic] converged to an R index of 4.2% and R_w of 4.4%, where $R = \Sigma|F_o|-k|F_c|)/\Sigma|F_o$. The function minimized in the refinement was $\Sigma w(|F_o|-k|F_c|)^2$, where $w = [\sigma^2(F_o) + 0.001F_o{}^2]^{-1}$, and k is the scale factor. Refinement with all anisotropic temperature-factors presented some problems regarding O(10) and O(19) (nonpositive definite). For this reason, they were included in the model with isotropic temperature-factors. A few more cycles of full-matrix (261 parameters) least-squares refinement yielded a final R index of 3.8% and R_w of 4.0%.

Final atomic positions are given in Table 5. The coordinates are not those originally determined, but we performed translations in order to easily compare them with those from the paper of Piret & Declercq (1978). Anisotropic temperature-factors are listed in Table 6, and selected interatomic distances and angles, in Table 7. The several footnotes in Table 7 are pertinent to the translations made in Table 5.

Empirical bond-valences (Table 8) were calculated using parameters from Brown & Wu (1976) for $U^{6+}-O^{2-}$ bonds and from Brown & Altermatt (1985) for $Ca^{2+}-O^{2-}$ and $P^{5+}-O^{2-}$ bonds. Originally, this table was obtained using all the constants from Brown & Altermatt (1985), but the bond valences involving uranium seemed less accurate than those involving other cation–oxygen bonds. Brown & Shannon (1973) reported a root mean square deviation of 5% for the bond-valence method. However, the values for all U atoms in phurcalite were found to deviate from ideality (6 v.u.) by a much greater extent (up to 10% using the constants from Brown & Altermatt (1985) (R_o = 2.075 and B = 0.37). Using the older constants for $U^{6+}-O^{2-}$ bonds from Brown & Wu (1976) (R_o = 2.059 and N = 4.3), we found an improved result not only for U^{6+}, but also for all oxygen ions bonded to U^{6+}. It must be noted that the values for R_o quoted by both Brown & Wu (1976) and Brown & Altermatt (1985) represent the average of values for reported structures and may differ owing to physical variations in the cation environment. Brown & Altermatt (1985) recorded a standard deviation of 0.046 for R_o = 2.075. The value for R = 2.059 from Brown & Wu (1976) fits in the interval determined by this standard deviation.

Observed and calculated structure-factors (Table 9) may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A OS2.

Most of the calculations were performed on a VAX 11/780 computer. Both Patterson and Fourier-difference methods and refinement of the structure were performed using the SHELX–76 program (Sheldrick 1976). Bond lengths and angles were calculated using program NRC-12 (Pippy & Ahmed 1968). The structure projections were drawn with program ORTEP (Johnson 1965), which is incorporated in the Enraf–Nonius Structure Determination Package.

DISCUSSION

The structure of phurcalite consists of $[(UO_2)_3O_2(PO_4)_2]_n^{4n-}$ layers, similar to those in

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR PHURCALITE

1				2		3		4		5		6		7		8			h	k	l
d_{obs}	I_{obs}	d_{calc}	I_{calc}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{calc}			
		8.915	2													8.883	3	8.911	1	1	1
		8.713	3	8.67	<5			8.75	30	8.69	10	8.68	20	8.70	5			8.707	2	0	0
8.05	100	8.031	100	8.02	100	7.97	100	8.00	100	7.94	100	7.96	100	7.92	100	8.014	100	8.017	0	2	0
		7.659	17	7.63	10			7.60	50	7.50	30	7.50	20	7.57	10	7.648	3	7.652	2	1	0
6.85	5	6.914	6	6.89	10			6.95	30	6.86	15b	6.88	20	6.88	10	6.910	1	6.906	0	2	1
		6.672	3	6.63	<5											6.667	<1	6.689	2	1	1
				6.30	<5											6.380	<1	6.333	1	0	2
		5.905	3	5.88	10			5.86	50	5.83	10			5.79	5	5.898	<1	5.898	2	2	0
				5.37	<5													5.411	2	2	1
		5.068	3	5.00	5									5.06	5	5.065	<1	5.065	3	1	1
		4.972	2					4.97	30	4.97	15b			4.84	10	4.969	<1	4.970	1	2	2
4.53	10	4.562	6	4.54	10			4.55	70	4.51	25	4.52	20	4.53	10	4.554	2	4.555	2	3	0
																4.437	<1	4.444	3	2	1
		4.325	4													4.320	1	4.319	2	3	1
4.24	30	4.258	17	4.24	30	4.28	30	4.25	70	4.22	50	4.24	35	4.26	10	4.254	2	4.256	3	1	2
		4.205	2													4.204	<1	4.202	4	1	0
4.00	30	4.015	11	3.99	20			4.00	80	3.978	35	3.967	25	3.97	30	4.008	15	4.009	0	4	0
		3.946	3													3.946	1	3.946	0	2	3
3.83	25	3.861	8	3.83	20	3.85	50	3.82	70	3.810	35	3.816	20	3.81	30	3.844	4	3.845	0	4	1
		3.781	2	3.76	<5									3.68	5	3.781	<1	3.777	3	3	1
		3.647	2	3.61	<5			3.64	40	3.622	10	3.608	15	3.64	5	3.642	1	3.641	2	4	0
										3.496	<10	3.505	15					3.487	3	1	3
3.39	50	3.398	17	3.39	30	3.39	50	3.39	70	3.379	45	3.378	35	3.36	60	3.396	2	3.399	0	0	4
		3.336	2	3.32	<5											3.347	<1	3.337	1	0	4
																3.248	<1	3.263	3	2	3
				3.20	5											3.193	<1	3.213	2	3	3
3.10	80	3.129	17											3.16	10	3.128	3	3.130	0	2	4
				3.10	40	3.10	60	3.09	80	3.097	90	3.104	60								
3.09	80	3.101	24											3.07	60	3.100	3	3.100	5	0	2
		3.045	2															3.043	5	1	2
		3.006	4	2.99	<5			3.00	10	2.991	25	2.982	20			3.000	1	3.003	0	4	3
		2.971	2															2.968	3	4	2
		2.961	2															2.959	1	4	3
		2.943	3	2.94	<5			2.95	10					2.91	20	2.940	<1	2.938	2	5	1
2.878	70	2.893	24	2.878	30	2.88	60	2.88	80	2.873	75	2.888	40	2.86	50	2.891	3	2.891	5	2	2
				2.805	<5							2.808	10					2.830	1	3	4
				2.737	<5			2.74	40	2.735	15	2.737	15	2.71	5	2.748	<1	2.749	3	5	1
		2.677	2	2.660	<5			2.67	40	2.660	15	2.646	20	2.66	5	2.671	2	2.672	0	6	0
		2.627	4													2.621	2	2.622	0	6	1
2.608	10			2.611	5			2.62	50			2.603	15	2.60	10						
		2.594	5							2.594	30					2.592	1	2.593	0	4	4
2.572	10	2.584	5	2.574	10	2.58	15	2.58	60	2.571	30	2.573	20	2.57	20	2.584	1	2.581	5	4	1
																2.558	<1	2.555	2	6	0
				2.498	<5											2.508	<1	2.507	2	5	3
2.439	10	2.454	6	2.442	10	2.44	10	2.45	70	2.440	20	2.448	15	2.44	30	2.453	1	2.452	5	4	2
				2.404	<5							2.386	15	2.37	5			2.405	5	1	4
				2.331	<5			2.35	10	2.324	10			2.32	5			2.338	7	0	2
				2.294	<5													2.302	0	6	3
				2.226	5	2.21	8	2.25	10	2.223	15	2.237	15	2.25	5			2.237	3	3	5
				2.176	<5											2.184	<1	2.187	2	7	1
		2.158	4					2.16	70			2.156	10			2.158	1	2.157	8	1	0
2.148	10			2.150	10	2.15	15			2.151	20			2.14	5	2.153	<1	2.152	6	5	0
		2.108	2															2.105	3	7	1
		2.103	3													2.102	1	2.101	0	6	4
								2.10	70												
		2.098	4													2.096	1	2.095	5	6	1
2.090	15b	2.093	5	2.088	10	2.08	15			2.088	30	2.087	10	2.09	5	2.092	1	2.093	3	1	6
				2.064	<5									2.05	5			2.071	5	2	5
		2.026	2													2.026	<1	2.024	5	6	2
		2.018	3	2.012	5			2.02	60	2.015	20	2.021	10			2.018	<1	2.016	8	3	0
		1.9928	2															1.990	2	7	3
		1.9862	2	1.981	5			1.98	50							1.981	1	1.983	0	8	1
		1.9635	2															1.964	3	3	6
		1.9565	2															1.953	2	8	0
		1.9542	2															1.953	3	5	5
		1.9497	2	1.949	5			1.94	10							1.949	<1	1.950	4	2	6
		1.9224	3					1.92	10							1.921	<1	1.921	5	6	3
		1.9138	2	1.914	<5											1.913	<1	1.911	1	8	2
		1.9074	2													1.908	<1	1.906	0	6	5
																1.899	<1	1.900	5	0	6
				1.885	5			1.88	10									1.886	5	1	6
																1.848	<1	1.848	5	2	6
1.841	25			1.841	10	1.84	20	1.84	60							1.842	<1	1.842	8	3	3
																1.834	<1	1.833	0	8	3
																1.830	<1	1.830	3	1	7
								1.82	60							1.821	<1	1.821	8	1	4
				1.814	5			1.80	10							1.816	<1	1.818	1	3	7
				1.781	<5			1.78	50							1.786	<1	1.786	8	5	1
				1.756	<5			1.76	10							1.760	<1	1.758	9	3	2
								1.74	50							1.742	<1	1.742	10	0	0
				1.733	5											1.733	<1	1.734	8	3	4
				1.715	5			1.72	50							1.722	<1	1.723	5	8	1
																1.703	<1	1.702	10	2	0
								1.70	40												
				1.695	<5											1.697	<1	1.700	0	0	8
								1.69	20							1.689	<1	1.689	10	2	1
				1.671	<5			1.67	20							1.672	<1	1.672	5	6	5
																1.661	<1	1.660	5	2	7
				1.653	5											1.656	<1	1.656	1	2	8
								1.65	20							1.648	<1	1.649	6	8	0
								1.62	10							1.619	<1	1.620	8	3	5
																1.593	<1	1.594	3	9	3
								1.59	60							1.591	<1	1.592	0	10	1
								1.56	10									1.559	1	4	8
								1.55	40							1.550	<1	1.550	10	0	4
								1.52	40							1.522	<1	1.522	10	2	4
								1.50	30							1.506	<1	1.508	10	4	3
								1.45	50							1.446	1				
								1.42	10												
								1.40	10												
								1.38	50												
								1.309	50												
								1.275	40												

d in Å, b: broad line

1. Bergen an der Trieb, Vogtland, Saxony, West Germany, d_{obs} and I_{obs} from Deliens & Piret (1978)*, d_{calc} and I_{calc} from PDF 30-284
2. Streuberg, Vogtland, Saxony, West Germany (PDF 30-285)*
3. Riverside County, California, USA (Chew 1982)
4. Nisa, Alto Alentejo, Portugal (Lencastre & Vairinho 1970); lines at 10 and 6.85 Å are probably due to admixtures
5. Nisa, Alto Alentejo, Portugal (Braithwaite *et al.* 1989)*
6. Merrivale quarry, Dartmoor, Southwest England (Braithwaite *et al.* 1989)*
7. Perus, São Paulo, Brazil (Camargo 1985)*
8. Perus, São Paulo, Brazil (this paper)

*some minor errors in indexing corrected here

TABLE 4. CELL PARAMETERS OF PHURCALITE

	1	2	3	4	5
a (Å)	17.426(3)	17.366	17.33(4)	17.44(2)	17.415(2)
b (Å)	16.062(3)	15.957	15.94(2)	15.87(2)	16.035(3)
c (Å)	13.592(3)	13.548	13.56(6)	13.56(3)	13.598(3)
V (Å^3)	3803	3754	3746	3753	3797(2)

1. Bergen an der Trieb, Vogtland, Saxony, West Germany (Deliens & Piret 1978)
2. Streuberg, Vogtland, Saxony, West Germany (PDF 30-285), *a* interchanged with *b* (*)
3. Nisa, Alto Alentejo, Portugal (Braithwaite *et al.* 1989) (*)
4. Merrivale quarry, Dartmoor, Southwest England (Braithwaite *et al.* 1989) (*)
5. Perus, São Paulo, Brazil (this paper)

(*)volume here calculated

TABLE 5. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS $(B_{eq})^{*}$ FOR PHURCALITE

Atom	X	Y	Z	B_{eq}(Å^2)
U(1)	0.3433(1)	0.2137(1)	0.6123(1)	0.91(2)
U(2)	0.4515(1)	0.2171(1)	0.8688(1)	0.91(3)
U(3)	0.2374(0)	0.2348(1)	0.8661(1)	0.87(2)
Ca(4)	0.1456(2)	0.0453(3)	0.0313(3)	1.4(1)
Ca(5)	0.0898(3)	0.1098(3)	0.2884(3)	2.2(2)
P(6)	0.1576(3)	0.2466(4)	0.6205(4)	1.2(2)
P(7)	0.0316(3)	0.1928(4)	0.8877(4)	0.9(2)
O(8)	0.3418(8)	0.3978(9)	0.094(1)	1.5(5)
O(9)	0.3416(7)	0.1744(9)	0.131(1)	1.7(5)
O(10)	0.4394(8)	0.1143(9)	0.916(1)	1.6(5)
O(11)	0.4721(8)	0.3182(9)	0.818(1)	1.4(5)
O(12)	0.2293(7)	0.3727(9)	0.405(1)	1.7(5)
O(13)	0.2328(8)	0.3438(9)	0.828(1)	1.7(5)
O(14)	0.3443(7)	0.302(1)	0.275(1)	1.4(5)
O(15)	0.2063(8)	0.2044(8)	0.702(1)	1.1(4)
O(16)	0.2110(8)	0.267(1)	0.031(1)	1.7(5)
O(17)	0.3458(7)	0.2669(9)	0.947(1)	1.2(4)
O(18)	0.4747(8)	0.241(1)	0.546(1)	2.1(5)
O(19)	0.4834(8)	0.168(1)	0.704(1)	2.3(6)
O(20)	0.0984(7)	0.2488(9)	0.358(1)	1.2(5)
O(21)	0.0846(8)	0.1973(9)	0.6058(9)	1.5(5)
O(22)	0.1417(7)	0.1604(9)	0.141(1)	1.2(4)
O(23)	0.0605(8)	0.115(1)	0.937(1)	2.5(6)
O(24)	0.4712(9)	0.066(1)	0.139(1)	3.3(7)
O(25)	0.0346(9)	0.480(1)	0.647(1)	2.7(6)
O(26)	0.363(1)	0.045(1)	0.393(1)	3.4(7)
O(27)	0.2807(8)	0.472(1)	0.564(1)	3.0(6)
O(28)	0.3263(9)	0.008(1)	0.775(1)	3.0(6)
O(29)	0.140(1)	0.462(1)	0.218(1)	4.1(8)
O(30)	0.608(1)	0.427(1)	0.537(1)	2.8(6)

* $B_{eq} = 4/3\ \Sigma\ B_{ij}(\underset{\sim}{a}_i . \underset{\sim}{a}_j)$

TABLE 6. THERMAL-VIBRATION PARAMETERS FOR PHURCALITE

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
U(1)	0.0132(4)	0.0147(5)	0.0068(4)	-0.0002(3)	-0.0002(3)	-0.0010(3)
U(2)	0.0083(4)	0.0169(5)	0.0094(4)	0.0014(4)	-0.0004(3)	-0.0007(3)
U(3)	0.0093(4)	0.0181(4)	0.0057(4)	-0.0005(4)	-0.0003(3)	0.0009(3)
Ca(4)	0.015(2)	0.017(3)	0.020(2)	-0.001(2)	0.000(2)	0.003(2)
Ca(5)	0.041(3)	0.026(3)	0.016(2)	-0.004(2)	0.004(2)	-0.008(3)
P(6)	0.008(2)	0.026(3)	0.010(3)	-0.002(2)	-0.002(3)	0.004(3)
P(7)	0.003(2)	0.019(3)	0.015(3)	0.000(2)	-0.001(2)	0.001(2)
O(8)	0.022(8)	0.009(8)	0.024(8)	-0.004(6)	0.000(7)	-0.002(7)
O(9)	0.021(8)	0.008(8)	0.034(9)	-0.010(8)	0.004(8)	-0.005(6)
O(10)	0.021(4)					
O(11)	0.018(7)	0.011(8)	0.026(9)	0.005(7)	-0.005(7)	0.004(7)
O(12)	0.012(7)	0.019(9)	0.03(1)	-0.003(7)	-0.004(7)	0.001(7)
O(13)	0.037(9)	0.016(8)	0.009(7)	-0.006(6)	-0.008(7)	0.001(8)
O(14)	0.007(6)	0.03(1)	0.017(7)	-0.008(7)	0.002(6)	0.000(7)
O(15)	0.025(8)	0.002(7)	0.015(8)	0.000(6)	0.009(6)	-0.005(6)
O(16)	0.018(8)	0.04(1)	0.011(7)	-0.004(7)	0.010(6)	0.005(7)
O(17)	0.016(7)	0.016(8)	0.014(7)	-0.005(7)	-0.009(6)	0.002(7)
O(18)	0.020(8)	0.04(1)	0.019(9)	0.001(8)	-0.008(7)	-0.007(8)
O(19)	0.027(4)					
O(20)	0.007(7)	0.015(8)	0.022(9)	-0.007(7)	-0.005(6)	-0.006(6)
O(21)	0.030(9)	0.013(9)	0.013(8)	-0.010(7)	-0.001(7)	0.005(7)
O(22)	0.008(7)	0.016(8)	0.023(8)	-0.001(7)	0.002(6)	0.006(6)
O(23)	0.025(8)	0.05(1)	0.023(9)	0.003(9)	0.008(7)	0.001(9)
O(24)	0.04(1)	0.04(1)	0.04(1)	0.00(1)	-0.02(1)	0.000(9)
O(25)	0.05(1)	0.04(1)	0.01(1)	-0.023(9)	0.008(8)	-0.006(9)
O(26)	0.06(1)	0.02(1)	0.05(1)	0.009(9)	0.02(1)	0.008(9)
O(27)	0.028(9)	0.04(1)	0.05(1)	-0.01(1)	0.016(9)	-0.003(8)
O(28)	0.05(1)	0.02(1)	0.05(1)	-0.012(9)	-0.008(9)	-0.007(9)
O(29)	0.09(2)	0.03(1)	0.03(1)	-0.005(9)	-0.02(1)	0.00(1)
O(30)	0.05(1)	0.04(1)	0.03(1)	-0.005(9)	-0.002(8)	0.013(9)

TABLE 7. SELECTED BOND-LENGTHS (ÅNGSTRÖMS) AND ANGLES (DEGREES) IN PHURCALITE

U(1)-O(8)A	1.81(1)	P(6)-O(15)	1.55(1)	O(15)-P(6)-O(16)A	99.9(8)
-O(9)A	1.81(1)	-O(16)A	1.55(1)	O(15)-P(6)-O(21)	109.1(8)
MEAN	1.81	-O(21)	1.51(1)	O(15)-P(6)-O(22)A	113.0(8)
		-O(22)A	1.54(2)	O(16)A-P(6)-O(21)	109.2(8)
U(1)-O(14)A	2.23(1)	MEAN	1.54	O(16)A-P(6)-O(22)A	112.7(8)
-O(15)	2.68(1)			O(21)A-P(6)-O(22)	112.3(8)
-O(16)A	2.57(1)			MEAN	109.3
-O(17)A	2.27(1)				
-O(18)	2.50(1)	P(7)-O(18)B	1.55(2)	O(18)B-P(7)-O(19)B	104.4(9)
-O(19)	2.84(2)	-O(19)B	1.55(1)	O(18)B-P(7)-O(20)A	109.4(8)
MEAN	2.51	-O(20)A	1.54(1)	O(18)B-P(7)-O(23)	111.7(9)
		-O(23)	1.50(2)	O(19)B-P(7)-O(20)A	110.6(8)
U(2)-O(10)	1.78(1)	MEAN	1.53	O(19)B-P(7)-O(23)	109.0(9)
-O(11)	1.80(1)			O(20)A-P(7)-O(23)	111.5(9)
MEAN	1.79			MEAN	109.4
U(2)-O(14)A	2.28(1)	O(24)-O(9)	2.85(2)	O(9)-O(24)-O(29)C	80.1(6)
-O(17)	2.27(1)	-O(11)A	3.06(2)	O(9)-O(24)-O(30)A	129.8(8)
-O(18)A	2.53(1)	-O(29)C	2.77(3)	O(11)A-O(24)-O(29)C	93.5(7)
-O(19)	2.44(1)	-O(30)A	2.76(2)	O(11)A-O(24)-O(30)A	111.8(7)
-O(21)B	2.36(1)				
MEAN	2.38	O(25)-O(11)B	2.85(2)	O(11)B-O(25)-O(28)C	110.2(7)
		-O(22)A	2.92(2)	O(22)A-O(25)-O(28)C	67.6(5)
U(3)-O(12)A	1.81(2)	-O(23)F	2.85(2)	O(23)F-O(25)-O(28)C	124.3(7)
-O(13)	1.82(1)	-O(28)C	3.02(2)		
MEAN	1.81				
		O(26)-O(8)A	2.81(2)	O(8)A-O(26)-O(25)D	109.4(7)
U(3)-O(14)A	2.31(1)	-O(23)E	2.85(3)	O(8)A-O(26)-O(29)C	168.4(9)
-O(15)	2.35(1)	-O(25)D	3.06(2)	O(23)E-O(26)-O(25)D	58.8(5)
-O(16)	2.35(1)	-O(29)C	2.73(2)	O(23)E-O(26)-O(29)C	76.2(7)
-O(17)	2.24(1)				
-O(20)A	2.44(1)	O(27)-O(9)A	2.73(2)	O(9)A-O(27)-O(29)E	83.1(7)
MEAN	2.34	-O(12)	2.83(2)	O(9)A-O(27)-O(30)G	112.4(7)
		-O(29)E	2.72(2)	O(12)-O(27)-O(29)E	165.2(8)
Ca(4)-O(8)C	2.52(2)	-O(30)G	2.88(2)	O(12)-O(27)-O(30)G	99.5(7)
-O(12)A	2.61(1)				
-O(22)	2.37(1)	O(28)-O(8)A	2.90(2)	O(8)A-O(28)-O(25)C	60.9(5)
-O(23)	2.26(2)	-O(13)C	2.92(2)	O(13)C-O(28)-O(25)C	106.9(7)
-O(25)A	2.53(2)	-O(25)C	3.02(2)		
-O(26)B	2.38(2)				
-O(27)A	2.41(2)	O(29)-O(15)A	2.82(2)	O(15)A-O(29)-O(24)C	143.0(8)
MEAN	2.44	-O(24)C	2.77(3)	O(15)A-O(29)-O(26)C	121.3(8)
		-O(26)C	2.73(2)	O(15)A-O(29)-O(27)E	95.6(7)
Ca(5)-O(11)D	2.76(1)	-O(27)E	2.72(2)	O(24)C-O(29)-O(26)C	91.8(8)
-O(13)A	2.65(2)			O(24)C-O(29)-O(27)E	79.8(7)
-O(20)	2.43(1)			O(26)C-O(29)-O(27)E	119.4(8)
-O(22)	2.34(1)				
-O(24)B	2.39(2)	O(30)-O(21)D	2.81(2)	O(21)D-O(30)-O(24)A	104.5(7)
-O(25)A	2.59(2)	-O(24)A	2.76(2)	O(21)D-O(30)-O(27)G	99.6(7)
-O(28)E	2.40(2)	-O(27)G	2.88(2)		
-O(30)D	2.47(2)				
MEAN	2.50				

A: X, 1/2-Y, Z-1/2; B: 1/2+X, Y, 1/2-Z; C: 1/2-X, Y-1/2, Z; D: 1/2+X, 1/2-Y, -Z;
E: 1/2-X, -Y, 1/2+Z; F: -X, 1/2+Y, 1/2-Z; G: -X, -Y, -Z.

dumontite (Piret & Piret-Meunier 1988). The coordination polyhedra are: for U(1) a hexagonal bipyramid, for U(2) and U(3) pentagonal bipyramids, and for P(6) and P(7) tetrahedra (Fig. 6). The layers are parallel to (010) and connected by two Ca and seven H_2O. The coordination polyhedra for Ca(4) and Ca(5), shown in Figure 7, are capped trigonal prism (seven vertices) and triangulated dodecahedron (eight vertices), respectively. The methods of Porai-Koshits & Aslanov (1972) and Muetterties & Guggenberger (1974) were used for determining the polyhedron around Ca(5). The angles δ between pairs of faces intersecting along the type-*b* edges [the ones that link O(20), O(22), O(28) and O(24)] are, in phurcalite, 15.3, 27.9, 28.1 and 28.7°. The angles φ between two planes (the first plane contains the short base of the body-diagonal

TABLE 8. BOND-VALENCE* TABLE FOR PHURCALITE

	U(1)	U(2)	U(3)	Ca(4)	Ca(5)	P(6)	P(7)	Σ	Chem. Group
O(8)	1.78			0.22				2.00	UO_2^{2+}
O(9)	1.74							1.74	UO_2^{2+}
O(10)		1.87						1.87	UO_2^{2+}
O(11)		1.83			0.12			1.95	UO_2^{2+}
O(12)			1.78	0.18				1.96	UO_2^{2+}
O(13)			1.70		0.16			1.86	UO_2^{2+}
O(14)	0.72	0.65	0.61					1.98	O^{2-}
O(15)	0.32		0.58			1.20		2.10	PO_4^{3-}
O(16)	0.39		0.58			1.21		2.18	PO_4^{3-}
O(17)	0.66	0.66	0.70					2.02	O^{2-}
O(18)	0.44	0.41					1.21	2.06	PO_4^{3-}
O(19)	0.25	0.48					1.18	1.92	PO_4^{3-}
O(20)			0.49		0.29		1.21	1.99	PO_4^{3-}
O(21)		0.56				1.34		1.90	PO_4^{3-}
O(22)				0.33	0.36	1.22		1.91	PO_4^{3-}
O(23)				0.46			1.36	1.82	PO_4^{3-}
O(24)					0.31			0.31	H_2O
O(25)				0.22	0.19			0.41	H_2O
O(26)				0.33				0.33	H_2O
O(27)				0.30				0.30	H_2O
O(28)					0.31			0.31	H_2O
O(29)								0.00	H_2O
O(30)					0.26			0.26	H_2O
Σ	6.30	6.47	6.44	2.04	2.00	4.97	4.96		

*Calculated from Brown & Wu (1976) and Brown & Altermatt (1985); bond-valences are in v.u. (valence units).

trapezoid and passes through the midpoint of the long base, whereas the second contains the long base of the trapezoid and passes through the midpoint of the short base) are, in phurcalite, 0.3 and 5.4°. In the ideal dodecahedron, all four δ angle are equal to 29.5°, and $\varphi_1 = \varphi_2 = 0°$; in the ideal bicapped trigonal prism, $\delta_1 = 0°$, $\delta_2 = 21.8°$, $\delta_3 = \delta_4 = 48.2°$ and $\varphi_1 = \varphi_2 = 16.1°$; and in the ideal square antiprism, $\delta_1 = \delta_2 = 0°$, $\delta_3 = \delta_4 = 52.4°$ and $\varphi_1 = \varphi_2 = 24.5°$. Consequently, the polyhedron around Ca(5) in phurcalite is very close to an ideal dodecahedron. The projections of the phurcalite structure parallel to (010), (100) and (001) are shown in Figure 8.

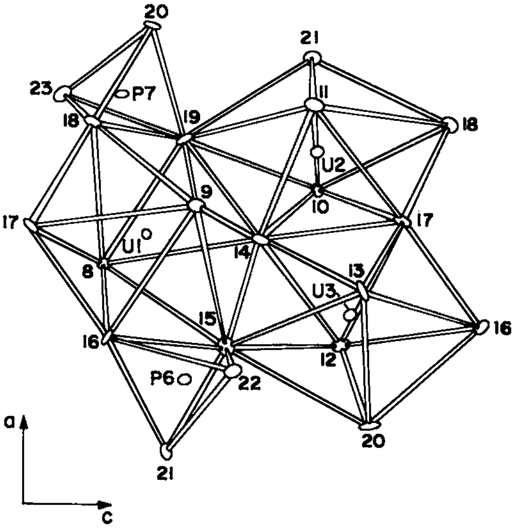

FIG. 6. Hexagonal and pentagonal bipyramids around uranium and tetrahedra around phosphorus.

Final atomic positions (Table 5) are practically identical to those from Piret & Declercq (1978), except for the additional atom O(30), not found by them. Although the hydrogen atoms were not located directly from the X-ray data, a sensible hydrogen-bond arrangement could be derived from local bond-valence requirements (Donnay & Allmann 1970). The variation in bond length (Table 7) correlates well with the bond-valence analysis (Table 8). Intersheet linkage is increased through hydrogen bonding from the H_2O groups to oxygen anions of the sheets.

The suspected possible errors in the crystal-structure determination by Piret & Declercq (1978) were confirmed by this new study. The present result suggests the formula $Ca_2(UO_2)_3O_2(PO_4)_2 \cdot 7H_2O$ for phurcalite.

Relationship to other hydrous calcium uranium phosphates

Several hydrous calcium uranium phosphates have been described in addition to phurcalite, including autunite, meta-autunite, pseudo-autunite, phosphuranylite, ningyoite, tristramite, lermontovite, and Blinkoff's compound I, quoted by Ross (1956). No structural data are available for pseudo-autunite, lermontovite and Blinkoff's compound I. Tristramite is probably isostructural with rhabdophane-(Ce), rhabdophane-(La) and brockite: the overall arrangement may be described as columns built up of alternate Ca^{2+} (or U^{4+}) and (PO_4^{3-}) ions, extending along the *c* axis, each column linked to four neighboring columns; ningyoite has a similar structure (Atkin *et al.* 1983). Neither the microprobe analysis nor the bond-valence sums of phurcalite support the U–Ca replacement that seems to occur in tristramite and ningyoite.

Autunite and meta-autunite possess sheets of the type $(UO_2PO_4)_n^{n-}$; between the sheets lie water molecules and calcium atoms (Beitema 1938). Phosphuranylite is quite similar to phurcalite. Unit-cell parameters are the same for both minerals. The X-ray-diffraction patterns differ only by different systematic absences. The crystal structure of phosphuranylite (Shashkin & Sidorenko 1975) has little value because the studied mineral has 3.0% Pb and 0.5% Ca and is really a probable case of calcian renardite. Besides, the final *R* value found was 15.7%, and no H_2O oxygen ion was located. A crystal-structure study of phosphuranylite is in

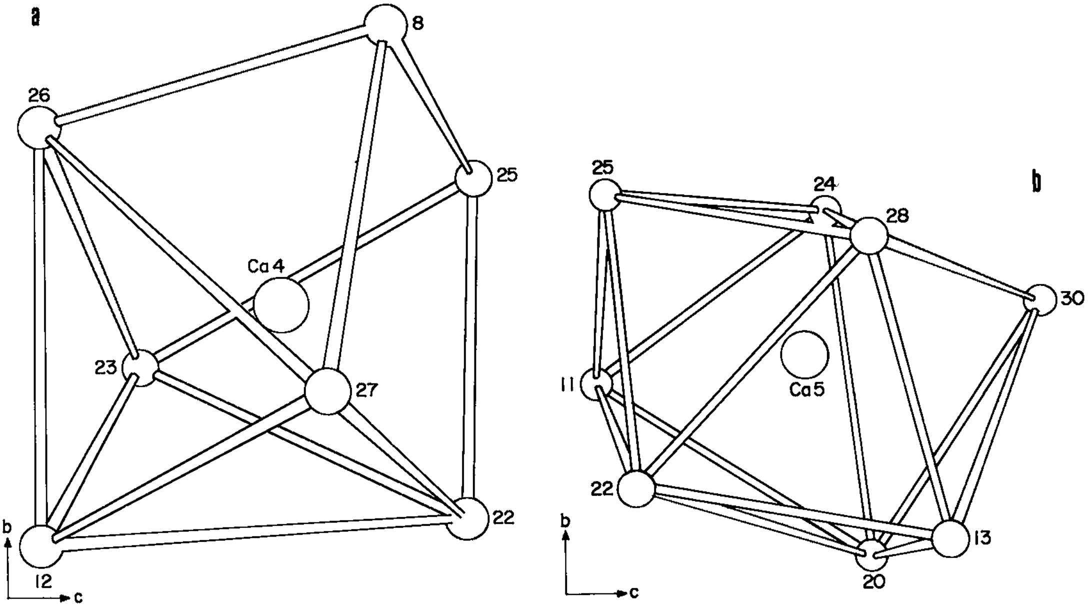

FIG. 7. Coordination polyhedra around Ca: a) capped trigonal prism around Ca(4); b) triangulated dodecahedron around Ca(5).

progress in order to test whether phosphuranylite and phurcalite are polymorphs.

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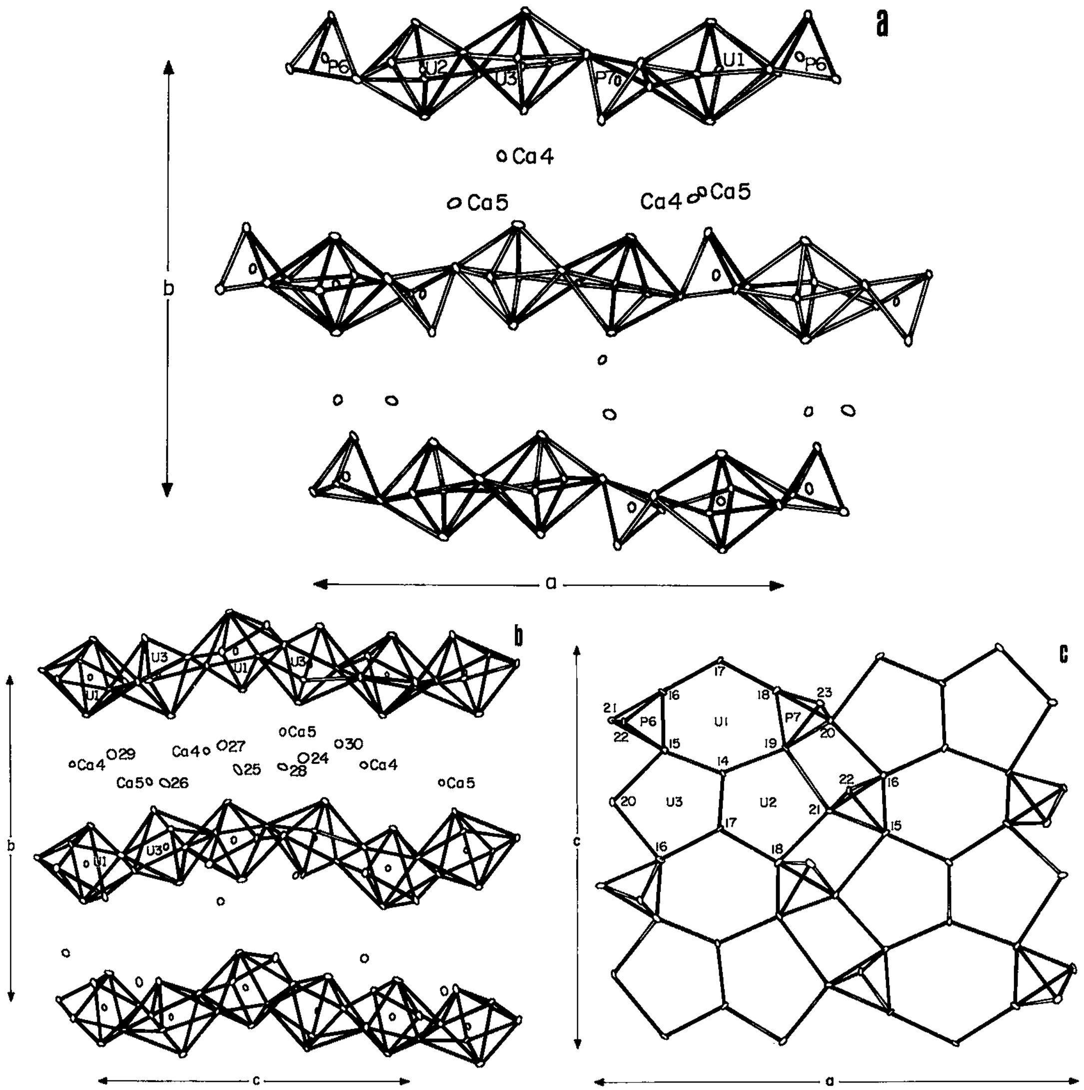

FIG. 8. Phurcalite structure: a) parallel to (001), water molecules not drawn; b) parallel to (100), PO_4^{3-} tetrahedra and pentagonal bipyramids around U(2) not shown, and only one water assemblage drawn; c) projection of the $[(UO_2)_3O_2(PO_4)_2]_n^{4n-}$ layers on (010).

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