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THE CRYSTAL STRUCTURES OF SYNTHETIC ANHYDROUS CARNOTITE, $K_2(UO_2)_2V_2O_8$, AND ITS CESIUM ANALOGUE, $Cs_2(UO_2)_2V_2O_8$ *

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ABSTRACT

The crystal structures of synthetic anhydrous carnotite, $K_2(UO_2)_2V_2O_8$ and its cesium analogue, $Cs_2(UO_2)_2V_2O_8$ have been determined, and the latter has been refined by Fourier and least-squares techniques to a final *R*-factor of 0.096 for the 837 observed non-zero reflections. The structures contain tightly bonded sheets made up of uranium and vanadium coordination polyhedra sharing edges. The sheets, which extend parallel to (001), are held together by bonds from oxygen atoms to the interlayer K^+ or Cs^+ cations. In the cesium compound the linear, symmetrical uranyl ion, with a U-O distance of 1.77 ± 0.06 Å, is coordinated by five oxygen atoms in the form of a plane pentagon, at an average U-O distance of 2.32 Å. The vanadium atom is coordinated by five oxygen atoms in the form of a square pyramid, with V-O distances ranging from 1.71 to 1.97 Å. Two such pyramids share an edge of the base, their apices pointing in opposite directions, to form divanadate groups, V_2O_8 . The interlayer bonding consists of eleven Cs-O bonds, with an average length of 3.32 Å, five to one layer and six to the adjacent layer.

INTRODUCTION

Carnotite, $K_2(UO_2)_2V_2O_8 \cdot nH_2O$, and the analogous calcium compound tyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot nH_2O$, were formerly the principal ore minerals mined in the uranium-vanadium ore deposits of the Colorado Plateau region in the western United States. In the early workings of these deposits, the predominance of the "carnotite ores" and their obvious dependence on sedimentary structures led to the widely held belief that the uranyl vanadate minerals were of primary origin. However, in recent years, more extensive and deeper mining has uncovered large amounts of relatively unoxidized "black ores." Detailed field and laboratory investigation has shown that the "black ores," which contain mostly 4-valent uranium and 3- and 4-valent vanadium, are the primary minerals of these deposits. The "carnotite ores," which contain 6-valent uranium and 5-valent vanadium, are the products of secondary oxidation of the "black ores" during the weathering process (Garrels and Larsen, 1959).

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In their highest oxidation states both U(+6) and V(+5) are rather soluble in dilute aqueous solutions. The greater part of these elements, therefore, would be lost into circulating ground waters, were the elements not fixed by the formation of very insoluble uranyl vanadate complexes of the carnotite type. Consequently, carnotite plays a crucial role in the geochemistry of oxidized uranium-vanadium ore deposits, and knowledge of its crystal chemistry and mode of formation is essential to an understanding of the origin of these deposits (Evans and Garrels, 1958).

Although previous studies of secondary uranium and vanadium minerals revealed many new and unexpected structure types, the results of these studies did not seem to account for the unique behavior of the minerals of the carnotite group. The detailed structural analysis reported in this paper was undertaken with the hope of filling this gap in our knowledge of the crystal chemistry of uranium and vanadium.

PREVIOUS X-RAY DIFFRACTION STUDIES

The only previous crystal-structure investigation of carnotite is that of Sundberg and Sillén (1949). Working with very crude x -ray diffraction intensity data obtained from synthetic anhydrous carnotite, $K_2(UO_2)_2V_2O_8$, these authors were able to locate only the uranium atoms with certainty. Approximate positions were obtained for the potassium and vanadium atoms. The oxygen atoms were then placed by consideration of the packing of spheres, assuming vanadium to be in tetrahedral coordination. The resulting structure was said to consist of $(UO_2VO_4)^{-2}$ sheets, in which a linear uranyl ion was coordinated by four oxygen atoms from three different VO_4 tetrahedra, in a highly asymmetrical configuration.

This structure seemed unsatisfactory to us for several reasons, chiefly because of anomalously short V-U distances and the extreme irregularity of the coordination around the uranyl ion. In addition, Barton (1958) showed that carnotite precipitates most rapidly from solutions with a pH between 7 and 9.5, in which the concentration of the tetrahedral orthovanadate group is only about 10^{-9} moles/l (Evans and Garrels, 1958). In work published since the appearance of Sundberg and Sillén's paper, Byström *et al.* (1950) and many other authors have found pentavalent vanadium in non-tetrahedral coordination. Therefore, it could no longer be assumed that the carnotite structure contained tetrahedral VO_4 groups.

Donnay and Donnay (1955) studied natural and synthetic carnotites, in various stages of hydration, by single-crystal and powder-diffraction x -ray techniques. They confirmed Sundberg and Sillén's determination

of the space group and unit-cell parameters and also described the twin laws and the effects of hydration on the cell dimensions.

Barton (1958) carried out a detailed investigation of the synthesis and properties of carnotite and its alkali analogues. He determined the cell parameters of this isomorphous series of compounds by the Buerger precession method. Those of Barton's results that are pertinent to our investigation are summarized in the following section of this paper.

A preliminary report on the crystal structure of carnotite appeared in an abstract by Appleman and Evans (1957), and a brief discussion of the crystal chemistry was published by Barton and Appleman (1957).

EXPERIMENTAL PROCEDURE

The crystals used in this study were prepared by Paul B. Barton of the U. S. Geological Survey (Barton, 1958). Large single crystals of compounds with the formula type $M_2(\text{UO}_2)_2\text{V}_2\text{O}_8$, with $M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ or Tl , were synthesized by crystallization from fused MVO_3 fluxes containing added uranyl nitrate, uranyl acetate, or uranium trioxide hydrate. Unit-cell, x -ray powder-diffraction and optical data are given by Barton for all of the above compounds, as well as for a number of related natural and artificial crystals. X -ray diffraction and optical examination showed that the potassium and cesium compounds formed the best crystals; these two substances were therefore selected for structure analysis.

The two crystals which were selected for x -ray diffraction intensity measurements are yellow diamond-shaped plates approximately 0.2 mm thick, bounded by the micaceous (001) cleavage and the well-developed $\{110\}$ form. The longest dimension, parallel to [010], is 0.7 mm for $\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ and 1 mm for $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$. The cesium compound also shows fairly well-developed $\{010\}$ and $\{100\}$ forms. Crystallographic data for these compounds, taken from Barton (1958), are reproduced for convenience in Table 1. Optical goniometric measurements confirm the axial ratios and β -angles derived from the x -ray data.

The main experimental difficulty encountered in the crystal-structure analysis of carnotite-like compounds lies in the large errors introduced by absorption into the measurement of the x -ray diffraction intensities. This difficulty is largely eliminated by the use of Buerger precession photographs of the reciprocal-lattice nets perpendicular to [001]. Donnay and Donnay (1955) demonstrate that when a crystal approximating a uniform sheet, larger than the cross-section of the incident x -ray beam, is photographed by the Buerger precession method, the amount of absorption is constant for all reflections in a given reciprocal-lattice net parallel to the sheet. Because of the monoclinic symmetry, the reciprocal-

TABLE 1. CRYSTALLOGRAPHIC DATA FOR SYNTHETIC CARNOTITE ANALOGUES
(AFTER BARTON, 1958)

Compound Space Group	$K_2(UO_2)_2V_2O_8$ monoclinic, $P2_1/a$	$Cs_2(UO_2)_2V_2O_8$ monoclinic, $P2_1/a$
a (Å)	10.47 ± 0.02	10.51 ± 0.02
b (Å)	8.41 ± 0.01	8.45 ± 0.01
c (Å)	6.59 ± 0.01	7.32 ± 0.01
β	$103^\circ 50' \pm 05'$	$106^\circ 05' \pm 05'$
Cell contents	$2[K_2(UO_2)_2V_2O_8]$	$2[Cs_2(UO_2)_2V_2O_8]$
Specific gravity (calc)	4.99	5.52
Specific gravity (obs)	4.95 ± 0.05	5.48 ± 0.05
Optics:		
α (calc)	1.77 ± 0.04	< 1.83
β	2.010 ± 0.005	2.49 ± 0.01
γ	2.090 ± 0.005	> 2.70
$2V$ (Na light)	$53^\circ 30' \pm 1^\circ$	$45^\circ 30' \pm 1^\circ$

lattice nets perpendicular to [001] in carnotites make an angle of 14° – 16° with the perfect (001) cleavage; however, there is still considerable compensation for absorption. Therefore, most of our intensity measurements were made on precession photographs of these nets.

Intensity data were collected on the precession camera with $MoK\alpha$ radiation for the $hk0$ net of $K_2(UO_2)_2V_2O_8$, and for the $hk0$, $hk1$, $hk2$ and $hk3$ nets of $Cs_2(UO_2)_2V_2O_8$, which give sharper diffraction patterns. In addition, the $0kl$ net of $K_2(UO_2)_2V_2O_8$ and the $h0l$ net of $Cs_2(UO_2)_2V_2O_8$ were recorded, although these nets are strongly affected by absorption. All nets were recorded on several exposures of varying duration in order to cover the greatest possible range of reflection intensities. The intensities were measured by visual comparison with a calibrated strip of spots made in the precession camera from one of the reflections (Appelman and Ross, in preparation). Lorentz and polarization corrections were calculated on a digital computer. No corrections were made for absorption, which was assumed to be minimal for the reasons given above. Initial temperature and scale factors for the $hk0$ data, which were used for the preliminary structure analysis, were obtained by Wilson's method. In the structure-factor calculations, the following atomic scattering-factor curves were used: U° from the Internationale Tabellen (1935), reduced uniformly by 5.6 electrons to correct for anomalous dispersion (Zachariasen, 1954 b); Cs^+ from Thomas and Umeda (1957), V° from Viervoll and Ögrim (1949), and K^+ and O° from Berghuis *et al.* (1955).

DETERMINATION OF THE STRUCTURE

Analysis and comparison of the Patterson projections along [001] for the isostructural potassium and cesium compounds readily yielded the x and y coordinates of the U, V, and K or Cs atoms. After further refinement by electron-density syntheses, the reliability factor R was 0.192 for the 106 non-zero F_{obs} of the potassium compound and 0.169 for the 110 non-zero F_{obs} of the cesium compound, based entirely on the heavy-atom contributions. These contributions were then subtracted from the scaled observed structure amplitudes, with the assumption that the heavy atoms determined virtually all of the phases. The residues were used as the coefficients in Fourier syntheses. In the resulting maps (Figs. 1A, B) all of the oxygen atoms are resolved, although their images are badly distorted and there are many spurious background peaks, probably due to the remaining effects of absorption. However, since the distortion and background "noise" are different for the two isostructural compounds, a comparison between Figs. 1A and 1B makes it a simple matter to locate the oxygen atoms. When the oxygen contributions were included, the R -factors for these projections dropped to 0.161 for the potassium compound and 0.124 for the cesium compound.

At this stage we were able to derive the main features of the carnotite structure from a reasonable interpretation of Figs. 1A, B combined with a knowledge of the interatomic distances to be expected around uranium and vanadium, and of the markedly layered nature of the material. Each vanadium atom is surrounded by 5 oxygen atoms in the form of a tetragonal pyramid, with two such coordination polyhedra sharing an edge to form double $\text{V}_2\text{O}_8^{6-}$ "divanadate" groups. For this reason we have adopted the dimeric formulae $\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ and $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$. The linear uranyl ion is also surrounded by five oxygen atoms, in the form of a plane pentagon, which shares edges with adjacent divanadate groups and uranyl coordination groups to form infinite sheets parallel to (001). The cesium or potassium ions lie between the sheets in irregular coordination.

Approximate z -coordinates for the U, V, Cs and K atoms were obtained from Patterson and electron-density projections along [100] for $\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ and along [010] for $\text{Cs}(\text{UO}_2)_2\text{V}_2\text{O}_8$. In conjunction with spatial considerations, these badly distorted electron-density projections also yielded an initial set of z -coordinates for the oxygen atoms. These coordinates confirmed the structure derived above, which is completely different from that postulated by Sundberg and Sillén (1949).

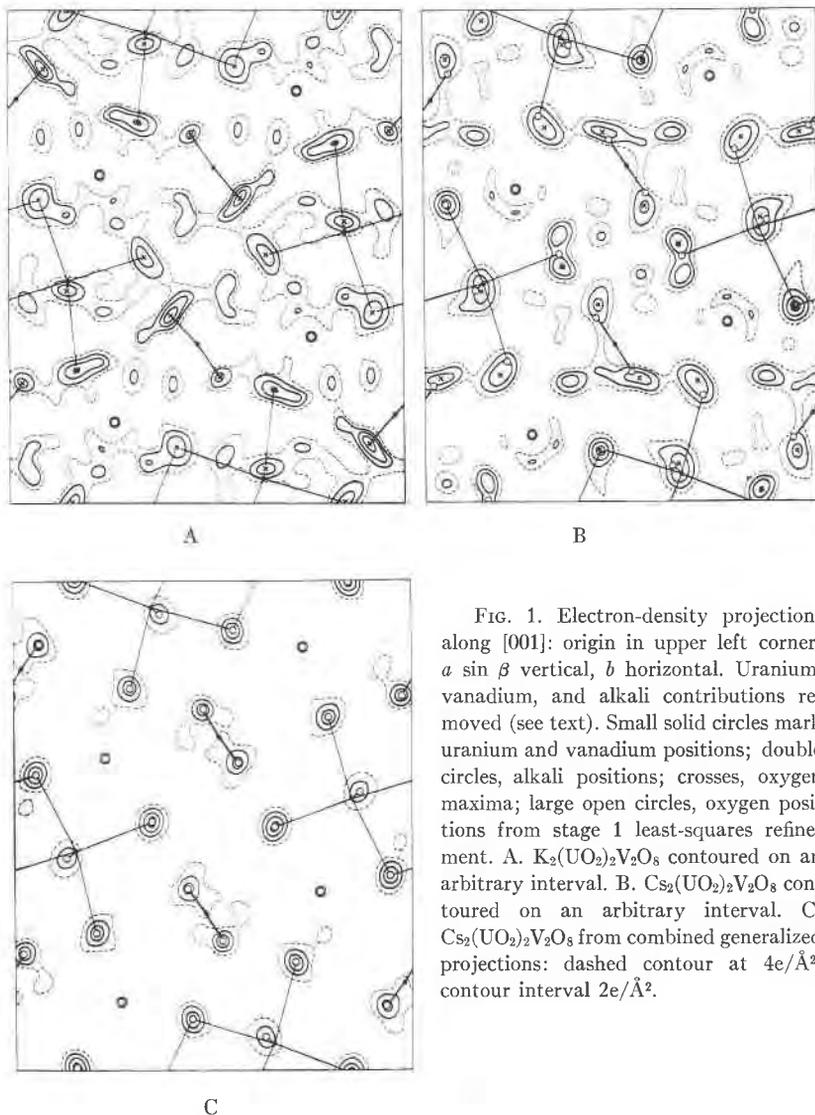


FIG. 1. Electron-density projections along [001]: origin in upper left corner; $a \sin \beta$ vertical, b horizontal. Uranium, vanadium, and alkali contributions removed (see text). Small solid circles mark uranium and vanadium positions; double circles, alkali positions; crosses, oxygen maxima; large open circles, oxygen positions from stage 1 least-squares refinement. A. $\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ contoured on an arbitrary interval. B. $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ contoured on an arbitrary interval. C. $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ from combined generalized projections: dashed contour at $4e/\text{\AA}^2$, contour interval $2e/\text{\AA}^2$.

REFINEMENT OF THE $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ STRUCTURE

Further refinement of the carnotite structure was carried out on the cesium analogue alone, since this compound gave sharper diffraction patterns. The refinement proceeded in three stages. In the first stage, coordinates and individual isotropic temperature parameters for all atoms were refined with a diagonal-approximation least-squares program

written by D. Appleman and E. Monasterski and described in Clark and Christ (1959). The data for the $hk0$, $hk1$, $hk2$, and $hk3$ nets were treated separately, as required by the program, since it was impossible to pre-scale the data satisfactorily because of the absorption problem on the cross-levels. The values obtained from the refinement of each level were then averaged to yield a set of refined atomic parameters.

In the second stage, further refinement of the x - and y -parameters of the oxygen atoms was carried out by means of generalized electron-density projections (Clews and Cochran, 1949; Cochran and Dyer, 1952). Following the procedure of Fridrichsons and Mathieson (1955) the modulus of the generalized projection, $|\rho_n(x, y)| = [C_n^2 + S_n^2]^{\frac{1}{2}}$ was calculated for $n=1, 2$, and 3. These three projections were summed point-by-point together with the standard electron-density projection $\rho_0(x, y)$ to give the combined projection $\rho_{\Sigma}(x, y) = \frac{1}{2}\rho_0 + |\rho_1| + |\rho_2| + |\rho_3|$. The coefficients used in these syntheses were formed from residuals which were obtained by subtracting the contributions of U, V, and Cs, calculated in the first-stage least-squares refinement, from the scaled observed structure amplitudes. Therefore, the combined projection, shown in Fig. 1C, includes only the oxygen contributions and is directly comparable with the projection of Fig. 1B which is based on the $hk0$ data alone. The spectacular improvement in resolution enabled us to obtain improved x and y coordinates of the oxygen atoms by least-squares fitting of a two-dimensional Gaussian function to each peak in Fig. 1C (Frasson, 1955).

The final stage of structure refinement was undertaken after large-scale computing facilities became available. Full-matrix least-squares refinement of positional parameters and individual isotropic temperature parameters for all atoms was carried out employing the combined $hk0$, $hk1$, $hk2$ and $hk3$ data. A separate scale factor was refined for each level. The program and weighting scheme are described in Clark *et al.* (1964).

The final set of refined atomic parameters obtained in this study is listed in Table 2. The standard errors were obtained from the full-matrix least-squares refinement in the usual way (Busing and Levy, 1959a). The errors in the z parameters are 3 to 4 times as large as the errors in x and y because of the limited range of l in the observed data. The anomalously low temperature factor found for vanadium, as well as the large variations in the temperature factors for oxygen atoms in similar environments, are probably due to the remaining effects of absorption on the intensity measurements.

The structure factors calculated from the parameters of Table 2 are listed along with the scaled observed structure factors in Table 7.¹ The

¹ Table 7, listing the observed and calculated structure factors, has been deposited as Document No. 8450 with the American Documentation Institute, Auxiliary Publica-

TABLE 2. ATOMIC PARAMETERS AND STANDARD ERRORS FROM FINAL LEAST-SQUARES REFINEMENT

Atom	Designation on Fig. 2	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
O ₁	A	.6238	.0031	.4382	.0039	.7415	.0097	1.28	.51
O ₂	B	.7406	.0028	.5226	.0034	1.2330	.0090	0.91	.45
O ₃	G	.5098	.0023	.6525	.0028	.9667	.0077	0.22	.36
O ₄	K	.9347	.0033	.6342	.0039	.6603	.0110	1.42	.55
O ₅	E	.8953	.0026	.4424	.0031	.9820	.0084	0.63	.41
O ₆	F	.7786	.0027	.7077	.0032	.9418	.0082	0.75	.43
V		.9440	.0005	.6495	.0007	.8959	.0021	0.02	.09
Cs		.6358	.0003	.7681	.0003	.4576	.0009	1.46	.05
U		.6813	.0001	.4795	.0001	.9873	.0004	0.20	.03

final R -factor is 0.096 for the 847 reflections with $F_{\text{obs}} > 0$. The weighted average standard error in F for these non-zero reflections is 8.1.

DESCRIPTION OF THE $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ STRUCTURE

The uranium coordination polyhedron. In carnotite, as in almost all compounds of hexavalent uranium, the uranium atom occurs coordinated with oxygen as the linear uranyl ion, UO_2^{2+} . The uranyl ion, in turn, is coordinated in $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$ by five oxygen atoms lying approximately in a plane passing through the uranium atom and perpendicular to the uranyl axis. The resulting pentagonal dipyrmaid is described fully in Table 3 and is illustrated in Fig. 3. The bond lengths and angles and their associated standard errors, given in Tables 3, 4 and 5 were computed by a method similar to the one used by Busing and Levy (1959b).

The equation of the plane which gives the best least-squares fit to the five oxygen atoms surrounding the uranyl ion has been determined by the method of Hebert (1960). For the pentagon associated with the uranium atom at $x=0.3187$, $y=0.5205$, $z=1.0127$, the equation, expressed in perpendicular form in terms of a Cartesian coordinate system with X, Y, Z , in Å is: $0.043X + 0.180Y + 0.983Z = 7.798$. The deviations from this plane of the five oxygen atoms and of the uranium atom are not significant. Examination of Table 3 shows that within the limits of error of this study the uranyl ion is linear and symmetrical and is perpendicular to the plane of the five coordinating oxygen atoms.

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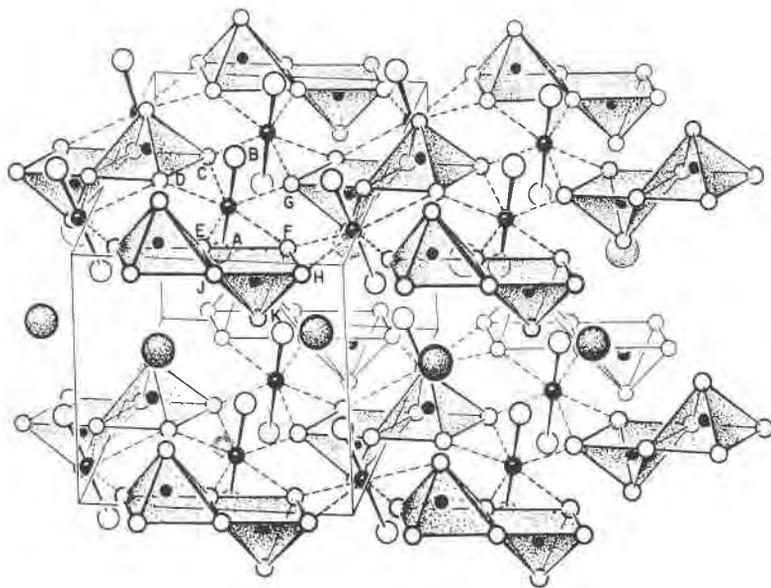


FIG. 2. Crystal structure of $\text{Cs}_2(\text{UO}_2)_2\text{V}_2\text{O}_8$; origin at lower left rear corner; b horizontal, c vertical. Small solid circles are vanadium atoms; solid circles with highlights, uranium atoms; open circles, oxygen atoms; and large stippled circles, cesium atoms. Letters identify atoms on Tables 2, 3, 4, and Figs. 3 and 4.

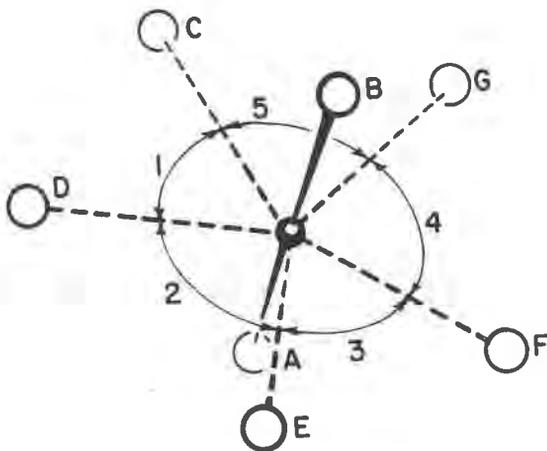


FIG. 3. Uranium coordination polyhedron. Letters identify atoms in Table 3.

TABLE 3. INTERATOMIC DISTANCES AND BOND ANGLES IN THE URANIUM COORDINATION POLYHEDRON

(a) Bond lengths to uranium atom at $x=0.6813$, $y=0.4795$, $z=0.9873$					
Atom bonded to uranium	Coordinates of atom bonded to uranium			Designation on Figs. 2, 3	Bond length and standard error (Å)
	x	y	z		
O ₁	.6238	.4382	.7415	A	1.77 ± .06
O ₂	.7406	.5226	1.2330	B	1.77 ± .06
O ₃	.4902	.3475	1.0333	C	2.40 ± .03
O ₆	.7214	.2077	1.0582	D	2.37 ± .03
O ₅	.8953	.4424	.9820	E	2.28 ± .03
O ₆	.7786	.7077	.9418	F	2.25 ± .03
O ₃	.5098	.6525	.9667	G	2.29 ± .02

(b) Bond angles at uranium atom at $x=0.6813$, $y=0.4795$, $z=0.9873$					
Atoms	Designation on Fig. 3	Bond angle and standard error	Atoms	Designation on Fig. 3	Bond angle and standard error
O ₁ -U-O ₂	A-U-B	179°13' ± 2°38'	O ₂ -U-O ₅	B-U-E	88°32' ± 1°40'
O ₁ -U-O ₃	A-U-C	89°18' ± 1°39'	O ₂ -U-O ₆	B-U-F	85°51' ± 1°41'
O ₁ -U-O ₆	A-U-D	91°14' ± 1°46'	O ₂ -U-O ₃	B-U-G	89°08' ± 1°54'
O ₁ -U-O ₅	A-U-E	90°56' ± 2°27'	O ₃ -U-O ₆	1	67°53' ± 0°56'
O ₁ -U-O ₆	A-U-F	93°26' ± 2°23'	O ₆ -U-O ₅	2	75°45' ± 1°05'
O ₁ -U-O ₃	A-U-G	91°02' ± 1°42'	O ₅ -U-O ₆	3	67°58' ± 1°00'
O ₂ -U-O ₃	B-U-C	91°29' ± 2°21'	O ₆ -U-O ₃	4	79°56' ± 1°06'
O ₂ -U-O ₆	B-U-D	89°11' ± 2°00'	O ₃ -U-O ₃	5	68°27' ± 1°00'

(c) Oxygen-oxygen distances in uranium coordination polyhedron					
Atoms	Designation on Figs. 2, 3	Interatomic distance and standard error (Å)	Atoms	Designation on Figs. 2, 3	Interatomic distance and standard error (Å)
O ₁ -O ₂	AB	3.54 —	O ₂ -O ₅	BE	2.85 ± .07
O ₁ -O ₃	AC	2.96 ± .08	O ₂ -O ₆	BF	2.76 ± .08
O ₁ -O ₆	AD	2.98 ± .07	O ₂ -O ₃	BG	2.88 ± .05
O ₁ -O ₅	AE	2.91 ± .05	O ₃ -O ₆	CD	2.66 ± .04
O ₁ -O ₆	AF	2.94 ± .05	O ₆ -O ₅	DE	2.85 ± .05
O ₁ -O ₃	AG	2.92 ± .07	O ₅ -O ₆	EF	2.53 ± .04
O ₂ -O ₃	BC	3.02 ± .04	O ₆ -O ₃	FG	2.92 ± .04
O ₂ -O ₆	BD	2.94 ± .05	O ₃ -O ₃	GC	2.64 ± .05

The plane pentagon which coordinates the uranyl ion shares two edges, CD and EF (Fig. 2), with two separate vanadium coordination polyhedra; and one edge, CG, with the adjacent uranium coordination polyhedron. These shared edges are considerably shorter than the un-

TABLE 4. INTERATOMIC DISTANCES AND BOND ANGLES IN THE VANADIUM COORDINATION POLYHEDRON

(a) Bond lengths to vanadium atom at $x=0.9440$, $y=0.6495$, $z=0.8959$					
Atom bonded to vanadium	Coordinates of atom bonded to vanadium			Designation on Figs. 2, 4	Bond length and standard error (Å)
	x	y	z		
O ₅	.8953	.4424	.9820	E	1.97 ± .03
O ₆	.7786	.7077	.9418	F	1.92 ± .04
O ₃	1.0098	.8475	.9667	H	1.83 ± .03
O ₅	1.1047	.5576	1.0180	J	1.85 ± .03
O ₄	.9347	.6342	.6603	K	1.71 ± .07

(b) Bond angles at vanadium atom at $x=0.9440$, $y=0.6495$, $z=0.8959$					
Atoms	Designation on Fig. 4	Bond angle and standard error	Atoms	Designation on Fig. 4	Bond angle and standard error
O ₄ -V-O ₅	1	107°57' ± 2°12'	O ₃ -V-O ₅	6	91°23' ± 1°36'
O ₄ -V-O ₆	2	113°15' ± 2°19'	O ₆ -V-O ₅	7	81°02' ± 1°46'
O ₄ -V-O ₃	3	105°30' ± 2°02'	O ₆ -V-O ₃	F-V-J	145°18' ± 2°—
O ₄ -V-O ₅	4	104°14' ± 2°25'	O ₅ -V-O ₃	8	75°54' ± 1°18'
O ₃ -V-O ₆	5	90°20' ± 1°20'			
O ₃ -V-O ₅	H-V-E	146°07' ± 2°—	V-O ₅ -V	V-E-V	104°06' ± 1°18'

(c) Oxygen-oxygen and other interatomic distances in vanadium coordination polyhedron		
Atoms	Designation on Figs. 2, 4	Interatomic distance and standard error (Å)
O ₄ -O ₅	KE	2.98 ± .09
O ₄ -O ₆	KF	3.03 ± .09
O ₄ -O ₃	KH	2.81 ± .07
O ₄ -O ₅	KJ	2.81 ± .08
O ₃ -O ₆	HF	2.66 ± .04
O ₃ -O ₅	HE	3.64 ± .04
O ₃ -O ₅	HJ	2.63 ± .03
O ₆ -O ₅	FE	2.53 ± .04
O ₆ -O ₅	FJ	3.55 ± .04
O ₅ -O ₆	EJ	2.35 ± .05
V-V	V-V ₁	3.016 ± .006
V-O ₄	V ₁ -K	3.95 ± .07

shared edges DE and FG (Table 3C), so that the plane pentagon deviates significantly from a regular pentagon. The U-U distance across the shared edge CG is 3.882 ± 0.008 Å; the next shortest U-U distance in the structure is 4.452 ± 0.005 Å between the closest uranium atoms related by the screw axis. The U-V distances across the shared edges CD

and EF are 3.297 Å and 3.340 Å, respectively. Standard errors were not computed for these distances.

Plane-pentagon coordination of the uranyl ion has been discussed in detail by Evans (1963), who has pointed out that this configuration is as common as four- or six-fold coordination in uranyl compounds. In the crystal structures of uranophane, $\text{Ca}(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Smith *et al.* 1957), johannite, $\text{Cu}(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ (Appelman, 1957), and $\text{Cs}_2(\text{UO}_2)_2(\text{SO}_4)_3$ (Ross and Evans, 1960), the coordinating pentagon consists entirely of oxygen atoms as it does in carnotite. Of these three structures, only that of $\text{Cs}_2(\text{UO}_2)_2(\text{SO}_4)_3$ has been refined to the point where bond distances can be reasonably estimated; the uranyl U-O bond distance is 1.74 ± 0.10 Å and the average U-O bond distance in the pentagon is 2.43 ± 0.10 Å. These values are in reasonable agreement with the corresponding distances of 1.77 ± 0.06 Å and 2.32 ± 0.03 Å determined in the present study. In the structures of $\text{K}_3\text{UO}_2\text{F}_5$ (Zachariasen, 1954a) and $\text{Cs}_x\text{UO}_2\text{OCl}_x$ ($x \approx 0.9$) (Allpress and Wadsley, 1964), which have been refined to a stage comparable to that of the present study, the coordinating pentagon includes atoms other than oxygen. The uranyl U-O bond distance in $\text{K}_3\text{UO}_2\text{F}_5$ is 1.76 ± 0.03 Å, and the average distance from the uranium atoms to the five coordinating fluorine atoms is 2.24 ± 0.03 Å. In $\text{Cs}_x\text{UO}_2\text{OCl}_x$, the uranyl U-O distances are 1.82 ± 0.06 Å and 1.85 ± 0.07 Å; the average of the three U-O distances in the pentagon is 2.26 ± 0.07 Å and the two U-Cl distances in the pentagon are 2.98 ± 0.07 Å. These comparisons indicate that the U-O distance in the uranyl ion probably does not vary more than a few hundredths of an Ångstrom from a mean value of about 1.77 Å in 5-coordinated uranyl compounds, regardless of the chemical bonding in the rest of the structure.

The vanadium coordination polyhedron. The vanadium atom in carnotite is coordinated by five oxygen atoms which form a slightly distorted square pyramid. Two such pyramids share one edge of the approximately square base, with their apices pointing in opposite directions. The resulting divanadate coordination polyhedron is described fully in Table 4 and is pictured in Fig. 4.

A plane was fitted by least-squares techniques to the six oxygen atoms forming the base of the two square pyramids in the divanadate group shown in Fig. 4. The equation for this plane, expressed in the same coordinates as the equation given in the previous section for the uranium coordination polyhedron, is: $-0.125X - 0.081Y + 0.989Z = 6.551$. None of the six atoms deviates significantly from this plane, within the limits of error of the determination. The two vanadium atoms are 0.57 Å above and below this plane, respectively. The apical oxygen atoms are 2.27 Å above and below the basal plane.

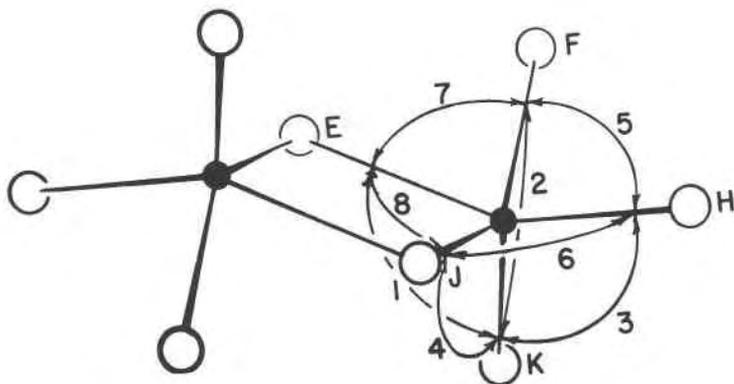


FIG. 4. Vanadium coordination polyhedron. Letters identify atoms in Table 4.

The square-pyramid coordination polyhedron about 5-coordinated vanadium, first described by Byström and Evans (1959) in the structure of $K_3V_5O_{14}$, has since been found in a number of other compounds (Evans, 1960a,b; Bachmann and Barnes, 1961). Moreover, as pointed out by the latter authors, in several structures which have been described as containing 5-valent vanadium in trigonal bipyramidal coordination, the trigonal bipyramids are so distorted that they actually approach the form of square pyramids. For example, the compounds V_2O_5 (Bachmann, *et al.*, 1961) $Na_{2-x}V_6O_{15}$ (Wadsley, 1955), $Li_{1+x}V_3O_8$ (Wadsley, 1957), and rossite, $Ca(VO_3)_2 \cdot 4H_2O$ (Ahmed and Barnes, 1963) contain 5-coordinated vanadium surrounded by a polyhedron which in most cases resembles a square pyramid at least as closely as it does a trigonal bipyramid. In all of these structures, each square pyramid shares *two* edges with adjacent pyramids to form infinite chains, with the apices of the pyramids alternately pointing up and down. The divanadate group described in the present paper may be considered as two links of such a chain.

The vanadium coordination in the carnotite structure is unusual in several respects. First, the square pyramids have one shared edge, as compared with the corner-linked pyramids in $K_3V_5O_{14}$ or those which share two edges to form infinite chains, described in the previous paragraph. Second, in most of the other structures containing square pyramids, a sixth quasi-coordinating oxygen occurs opposite the apex at distances ranging approximately 2.2 to 3.5 Å from the vanadium atom (Evans, 1960b), so that in many cases the coordination polyhedron may be considered as a very distorted octahedron with one vertex at a much greater distance than the other five. However, in the carnotite structure the vanadium coordination is strictly 5-fold; no other atom even remotely

approaches the vanadium on the side opposite the apex of the square pyramid, and the next-nearest oxygen outside of the same divanadate group is at 3.59 Å (D, Fig. 2).

The dimensions of the square-pyramid coordination polyhedron are quite comparable with those found in the infinite-chain structures mentioned above, except for the distance from the vanadium to the apical oxygen (K in Fig. 4) which is anomalously long. In the other structures this distance has an average value of 1.60 Å with a maximum deviation of about 0.05 Å, whereas in carnotite the value is 1.71 ± 0.07 Å. We believe that this discrepancy is due to the large error in the determination of the z -coordinate of O₄, and that the true value of the V-O₄ distance in carnotite is probably closer to 1.65 Å. In general, the errors in the lengths of bonds nearly parallel to c are large in the present determination owing to the limited range of l represented in the data.

It should be noted that while the edge shared between the two square pyramids in the divanadate group is considerably shorter than the other edges, there are no significant differences between the lengths of the edges EF and FH (Fig. 4), which are shared with the uranyl coordination pentagon, and that of the edge HJ, which is not shared at all. This suggests that these distances are entirely controlled by the strongly bonded vanadium coordination polyhedron and that the more weakly bonded uranyl coordination pentagon must adjust itself accordingly.

Interlayer bonding. The uranium and vanadium coordination polyhedra in the carnotite structure are linked, as described in the previous sections, into extremely strongly bonded sheets extending parallel to (001). There are no bonds from the oxygen atoms of one layer to the uranium and vanadium cations of another layer. Therefore, adjacent layers are held together only by bonds from the oxygen atoms to the interlayer cations. In Fig. 5 this bonding scheme is illustrated for the Cs⁺ ion in the structure of the synthetic anhydrous Cs₂(UO₂)₂V₂O₈ which was refined in the present study. Presumably, this scheme will be somewhat different for carnotites with different degrees of hydration and different interlayer cations. The cesium-oxygen bond distances are given in Table 5.

There are 11 cesium-oxygen bonds. Five, designated A, B, C, K, and L on Figure 5, extend upward to one layer; six, designated D, E, F, G, H, and J, extend downward to the adjacent layer. The six short Cs⁺-O bonds, C, D, E, J, K, and L, have an average length of 3.16 Å; the five long bonds, A, B, F, G, and H, have an average length of 3.52 Å. The arrangement of bonds around the Cs⁺ ion is highly irregular, and there would appear to be no reason why the structure should not be capable of accommodating a whole host of different interlayer cations in varying

TABLE 5. BOND LENGTHS TO CESIUM ATOM AT $x=0.6358$, $y=0.7681$, $z=0.4576$

Atom bonded to cesium	Coordinates of atom bonded to cesium			Designation on Fig. 5	Bond length and standard error (\AA)
	x	y	z		
O ₆	.7786	.7077	.9418	A	$3.48 \pm .05$
O ₁	.6238	.4382	.7415	B	$3.50 \pm .05$
O ₄	.9347	.6342	.6603	C	$3.28 \pm .04$
O ₁	.3762	.5618	.2585	D	$3.23 \pm .03$
O ₂	.7406	.5226	.2330	E	$3.04 \pm .05$
O ₃	.5098	.6525	-.0333	F	$3.60 \pm .05$
O ₁	.8762	.9382	.2585	G	$3.55 \pm .05$
O ₅	.6047	.9424	.0180	H	$3.47 \pm .05$
O ₄	.5653	1.1342	.3397	J	$3.24 \pm .03$
O ₂	.7594	1.0226	.7670	K	$3.13 \pm .04$
O ₄	.4347	.8658	.6603	L	$3.01 \pm .06$

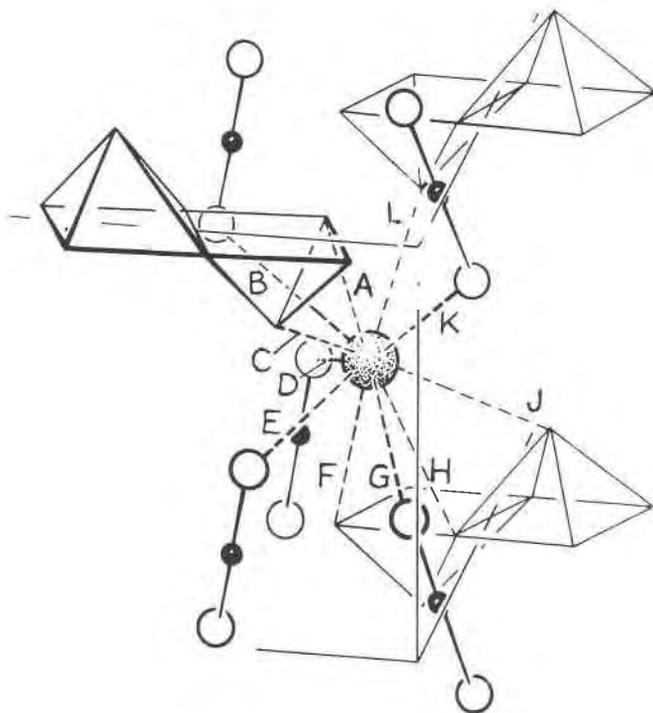


FIG. 5. Cesium coordination, representing the right front edge of Fig. 2. Letters identify Cs-O bonds in Table 5.

TABLE 6. CHARGE-BALANCE CALCULATIONS

A. Assumptions

1. The two U-O bonds in the uranyl ion have equal strength.
2. The five U-O bonds coordinating the uranyl ion have equal strength.
3. The six short Cs-O bonds have equal strength.
4. The five long Cs-O bonds have equal strength.

B. Environment of the oxygen atoms

Atom	Coordination
O ₁	1 U (uranyl bond), 3 Cs (1 short, 2 long)
O ₂	1 U (uranyl bond), 2 Cs (short)
O ₃	2 U (UO ₂ -O bond), 1 V, 1 Cs (long)
O ₄	1 V, 3 Cs (short)
O ₅	1 U (UO ₂ -O bond), 2V, 1 Cs (long)
O ₆	2 U (UO ₂ -O bond), 1 V, 1 Cs (long)

C. Calculations of bond strengths

1. From assumptions (1), (3), (4):

$$1 \text{ U-O (uranyl)} + 1 \text{ Cs-O (short)} + 2 \text{ Cs-O (long)} = 1 \text{ U-O (uranyl)} + 2 \text{ Cs-O (short)}$$

$$2 \text{ Cs-O (long)} = 1 \text{ Cs-O (short)}$$

$$6 \text{ Cs-O (short)} + 5 \text{ Cs-O (long)} = 1.0 \quad (\Sigma \text{ Cs-O} = 1.0)$$

$$\text{Cs-O (short)} = 0.12; \text{Cs-O (long)} = 0.06$$

at uranyl oxygens O₁ and O₂:

$$\text{U-O (uranyl)} + 0.24 = 2.0; \text{U-O (uranyl)} = 1.76$$

2. From assumption (2):

$$2(1.76) + 5 \text{ UO}_2\text{-O} = 6.0 \quad (\Sigma \text{ U-O} = 6.0)$$

$$\text{UO}_2\text{-O} = 0.50$$

3. From the results of C.1 and C.2:

$$\text{V-O}_3 = \text{V-O}_6 = 0.94$$

$$\text{V-O}_5 (2) = 0.72$$

$$\text{V-O}_4 = 1.64$$

as a check on the above results:

$$\Sigma \text{ V-O} = 2(0.94) + 2(0.72) + 1.64 = 4.96$$

degrees of hydration, without appreciably changing the geometry of the $[(\text{UO}_2)_2\text{V}_2\text{O}_8]_n^{-2n}$ sheets. This offers an explanation for the small variations in a and b relative to those in c and β found for various natural and synthetic carnotites (Barton, 1958, p. 812).

The extremely low solubility of carnotite in dilute aqueous solutions can be readily explained in terms of the stable sheet structure found in the present study. The formation of tightly bonded infinite uranyl vanadate sheets prevents ordinarily soluble 6-valent uranium and 5-valent vanadium species from being dissolved in circulating ground waters, and is thus an efficient mechanism for fixing these elements in nature in their highest oxidation states.

Charge-balance and bond strengths. In Table 6 an attempt has been made to assign bond strengths, starting with certain assumptions which appear reasonable in view of the experimentally determined interatomic distances. The scheme as worked out results in a final evaluation of the charge on the vanadium atom of 4.96, which is in good agreement with the theoretical value of 5.0.

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REFERENCES

- AHMED, F. R. AND W. H. BARNES (1963) The crystal structure of rossite. *Can. Mineral.* **12**, 713-726.
- ALLPRESS, J. G. AND A. D. WADSLEY (1964) The crystal structure of caesium uranyl oxychloride $Cs_x(UO_2)OCl_x$ (x approximately 0.9). *Acta Cryst.* **17**, 41-46.
- APPLEMAN, D. E. (1957) Crystal-chemical study of johannite (abs.). *Bull. Geol. Soc. Am.* **68**, 1696.
- AND HOWARD T. EVANS, JR. (1957) The crystal structure of carnotite (abs.). *Acta Cryst.* **10**, 765.
- AND M. R. ROSS Calibrated intensity strips for the Buerger precession camera (in prep.).
- BACHMANN, H. G., F. R. AHMED AND W. H. BARNES (1961) The crystal structure of vanadium pentoxide. *Zeit. Krist.* **115**, 110-131.
- AND W. H. BARNES (1961) Bonding in the trigonal bipyramidal coordination polyhedra of V_2O_5 and of certain other structures containing pentavalent vanadium. *Zeit. Krist.* **115**, 215-230.
- BARTON, PAUL B., JR. (1958) Synthesis and properties of carnotite and its alkali analogues. *Am. Mineral.* **43**, 799-817.
- AND D. E. APPLEMAN (1957) Crystal chemistry of carnotite. In *Advances in Nuclear Engineering*, J. R. Dunning and B. R. Prentice, ed. (Vol. II). Pergamon Press, London.
- BERGHUIS, J., IJ. M. HAANAPPEL, M. POTTERS, B. O. LOOPSTRA, C. H. MACGILLAVRY AND A. L. VEENENDAAL (1955) New calculations of atomic scattering factors. *Acta Cryst.* **8**, 478-483.
- BUSING, W. R. AND H. A. LEVY (1959a) A crystallographic least squares refinement program for the IBM 704. *Oak Ridge Nat. Lab., ORNL* **59-4-37**.
- (1959b) A crystallographic function and error program for the IBM 704. *Oak Ridge Nat. Lab., ORNL* **59-12-3**.
- BYSTRÖM, A., K. A. WILHELMI AND O. BROTZEN (1950) Vanadium pentoxide—a compound with five-coordinated vanadium atoms. *Acta Chem. Scand.* **4**, 1119-1130.
- BYSTRÖM, ANN MARIE AND HOWARD T. EVANS, JR. (1959) The crystal structure of $K_3V_5O_{14}$. *Acta Chem. Scand.* **13**, 377-378.

- CLARK, JOAN R., D. E. APPLEMAN AND C. L. CHRIST (1964) Crystal chemistry and structure refinement of five hydrated calcium borates. *Jour. Inorg. Nucl. Chem.* **26**, 73-95.
- AND C. L. CHRIST (1959) Studies of borate minerals (VIII): the crystal structure of $\text{CaB}_3\text{O}_3(\text{OH})_3 \cdot 2\text{H}_2\text{O}$. *Zeit. Krist.* **112**, 213-233.
- CLEWS, C. J. B. AND W. COCHRAN (1949) The structures of pyrimidines and purines. III. An x-ray investigation of hydrogen bonding in aminopyrimidines. *Acta Cryst.* **2**, 46-57.
- COCHRAN, W. AND H. B. DYER (1952) Some practical applications of generalized crystal-structure projections. *Acta Cryst.* **5**, 634-636.
- DONNAY, GABRIELLE AND J. D. H. DONNAY (1955) Contribution to the crystallography of uranium minerals. *U. S. Geol. Survey Trace Elements In. Rept.* **507**.
- EVANS, HOWARD T., JR. (1960a) Crystal structure refinement and vanadium bonding in the metavanadates KVO_3 , NH_4VO_3 and $\text{KVO}_3 \cdot \text{H}_2\text{O}$. *Zeit. Krist.* **114**, 257-277.
- (1960b) Square pyramid coordination in polyvanadate complexes (abs.). *Acta Cryst.* **13**, 1019.
- (1963) Uranyl ion coordination. *Science* **141**, 154-158.
- AND R. M. GARRELS (1958) Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits. *Geochim. Cosmochim. Acta* **15**, 131-149.
- FRASSON, E. (1955) Localizzazione rapida ed esatta dei massimi nelle proiezioni Fourier. *Ric. Scient.* **25**, 3028-3091.
- FRIDRICHSONS, J. AND A. McL. MATHIESON (1955) A direct determination of molecular structure, DL-isoCryptopleurine methiodide. *Acta Cryst.* **8**, 761-772.
- GARRELS, R. M. AND E. S. LARSEN, 3d. (ed) (1959) Geochemistry and mineralogy of the Colorado Plateau uranium ores. *U.S. Geol. Survey Prof. Paper* **320**.
- HEBERT, K. J. (1960) A Burroughs 220 computer program for a least squares plane or line through a set of points. *Burroughs Corp. Tech. Bull.* **97**.
- Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935). Borntraeger, Berlin.
- ROSS, M. AND HOWARD T. EVANS, JR. (1960) The crystal structure of cesium biuranyl trisulphate, $\text{Cs}_2(\text{UO}_2)_2(\text{SO}_4)_3$. *Jour. Inorg. Nucl. Chem.* **15**, 338-351.
- SMITH, D. K., JR. J. W. GRUNER AND W. N. LIPSCOMB (1957) The crystal structure of uranophane $(\text{Ca}(\text{H}_3\text{O})_2)(\text{UO}_2)_2(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}$. *Am. Mineral.* **42**, 594-618.
- SUNDBERG, INGRID AND L. G. SILLÉN (1949) On the crystal structure of KUO_2VO_4 (synthetic anhydrous carnotite). *Arkiv Kemi* **1**, 337-351.
- THOMAS, L. H. AND K. UMEDA (1957) Atomic scattering factors calculated from the TFD atomic model. *Jour. Chem. Phys.* **26**, 293-301.
- VIERVOLL, H. AND O. ÖGRIM (1949) An extended table of atomic scattering factors. *Acta Cryst.* **2**, 277-279.
- WADSLEY, A. D. (1955) The crystal structure of $\text{Na}_{2-2x}\text{V}_6\text{O}_{15}$. *Acta Cryst.* **8**, 695-701.
- (1957) The crystal chemistry of non-stoichiometric pentavalent vanadium oxides: crystal structure of $\text{Li}_{1+x}\text{V}_3\text{O}_8$. *Acta Cryst.* **10**, 261-267.
- ZACHARIASEN, W. H. (1954a) Crystal chemical studies of the 5f-series of elements. XX. The crystal structure of tri-potassium uranyl fluoride. *Acta Cryst.* **7**, 783-787.
- (1954b) Crystal chemical studies of the 5f-series of elements. XXI. The crystal structure of magnesium orthouranate. *Acta Cryst.* **7**, 788-791.

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