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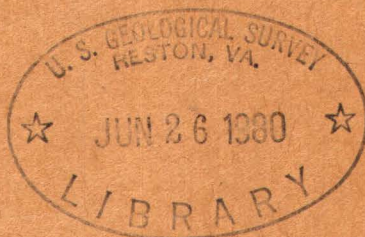
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No. 584

SOME OBSERVATIONS ON RUTHERFORDINE

By Joan R. Clark and C. L. Christ

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Trace Elements Investigations Report 584

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

Geology and Mineralogy

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By

Joan R. Clark and C. L. Christ

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## SOME OBSERVATIONS ON RUTHERFORDINE

By Joan R. Clark and C. L. Christ

## ABSTRACT

The optical properties of rutherfordine,  $\text{UO}_2\text{CO}_3$ , previously determined on microscopic crystals, have been redetermined on considerably larger crystals; and the relations among the indices of refraction, the morphology, and the crystal structure have been examined. Rutherfordine is orthorhombic, biaxial positive, with  $\alpha = 1.715$ ,  $\beta = 1.730$ ,  $\gamma = 1.795$ ,  $2V = 53^\circ$  (calc.);  $X = b$ ,  $Y = c$  (elongation),  $Z = a$ . The crystal structure of  $\text{UO}_2\text{CO}_3$  consists of layers of carbonate groups parallel to (010) with linear  $(\text{O-U-O})^{+2}$  ions normal to the layers. The indices  $\beta$  and  $\gamma$  correspond to vibration directions parallel to layers; the unexpectedly large difference in value between  $\beta$  and  $\gamma$  is ascribed to the optical anisotropy of the uranium-oxygen bonding in the layer. Indexed X-ray powder data are given.

## INTRODUCTION

Rutherfordine,  $\text{UO}_2\text{CO}_3$ , was originally described by Marckwald (1906) and recently has been restudied by Frondel and Meyrowitz (1956), who have confirmed the validity of the species including the chemical formula and established the identity of rutherfordine with diderichite (Vaes, 1947). The crystal structure of the naturally occurring mineral was reported by Christ, Clark, and Evans (1955). Subsequently, Cromer and Harper (1955a, b), working with synthetic crystals, verified the structure and also gave an accurate determination of the U-O bond length in the uranyl ion.

Previous mineralogical work on rutherfordine was carried out on microscopic crystals. For this study a mineral specimen containing sizable single crystals was available; thus it was possible to redetermine the optical properties on oriented crystals and to relate the optics with the morphology and the structure. The results of this study are given in the present paper, which also includes indexed X-ray powder data for rutherfordine.

#### DESCRIPTION AND OPTICAL PROPERTIES

The crystals of rutherfordine used were found by us on the type specimen of masuyite from Shinkolobwe, Katanga, Belgian Congo,<sup>1/</sup> which was loaned to Harvard University by Dr. J. F. Vaes, Union Minière du Haut Katanga, who described masuyite in 1947. The specimen was placed at our disposal through the kindness of Professor Clifford Frondel. Rutherfordine occurs on this specimen not only as the usual white to pale-yellow microscopic fibrous aggregates but also profusely as thin lath-like single crystals as long as 2 or 3 mm. Maintaining the orientation defined by the X-ray cell, the crystals are elongated along [001], with large (100) and somewhat less dominant (010). Cleavage parallel to (010) is perfect and a secondary less perfect cleavage parallel to (001) was noted. The crystals are frequently striated on (100) parallel to [001] and often form radiating clusters resembling bundles of straws. Color of the crystals varied, the majority being pale yellow, while some appeared amber orange in clusters and brownish when separated. A few examples were found which showed a brown core surrounded by a pale-yellow envelope. Within the limitations of observations, neither the optical properties nor the X-ray powder data varied with the color of the

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<sup>1/</sup> The crystals used in the structure study of Christ et al. (1955) came from the same specimen. The locality was not stated in the 1955 paper.

crystals. All of the crystals appeared to be growing on a uraninite substrate and were intimately associated with lemon-yellow becquerelite and orange masuyite crystals.

Rutherfordine is orthorhombic, biaxial positive, with low dispersion, slight pleochroism, strong birefringence (0.080) and moderate  $2V$  ( $53^\circ$ , calculated). The indices of refraction and optical orientation determined in the present study are listed in table 1, together with the other values reported in the literature. Agreement for the two lower indices is satisfactory. Accurate measurement of the maximum index requires that the crystals lie flat on (010); any deviation will result in observation of a lower index. It would, therefore, be expected that the larger value found by us, which is in good agreement with that found by Larsen and Berman (1934), would be more nearly the correct one.

#### REFRACTIVE INDICES AND CRYSTAL STRUCTURE

Since the initial investigations of Born (1915) and Bragg (1924a, b) on the relations between indices of refraction and crystal structure, many examples of layer structures have been studied (Bunn, 1946, p. 282). In general it is found for biaxial crystals that two higher indices, close in value, correspond to vibration directions parallel to the layers, while a lower index occurs for the vibration direction normal to the layers. Such crystals consequently are biaxial negative with moderate to large birefringence. Examples are aragonite with  $\alpha = 1.530$ ,  $\beta = 1.681$ ,  $\gamma = 1.686$ , and  $\text{KNO}_3$  with  $\alpha = 1.335$ ,  $\beta = 1.506$ , and  $\gamma = 1.506$  (Bunn, 1946, p. 282).

Rutherfordine, although having a layer structure, is biaxial positive, with  $\alpha = 1.715$ ,  $\beta = 1.730$ , and  $\gamma = 1.795$  (table 1). The crystal structure of rutherfordine consists of layers of carbonate groups parallel to (010) with linear uranyl,  $(\text{O}-\text{U}-\text{O})^{+2}$ , ions normal to (010), as shown in figure 1.

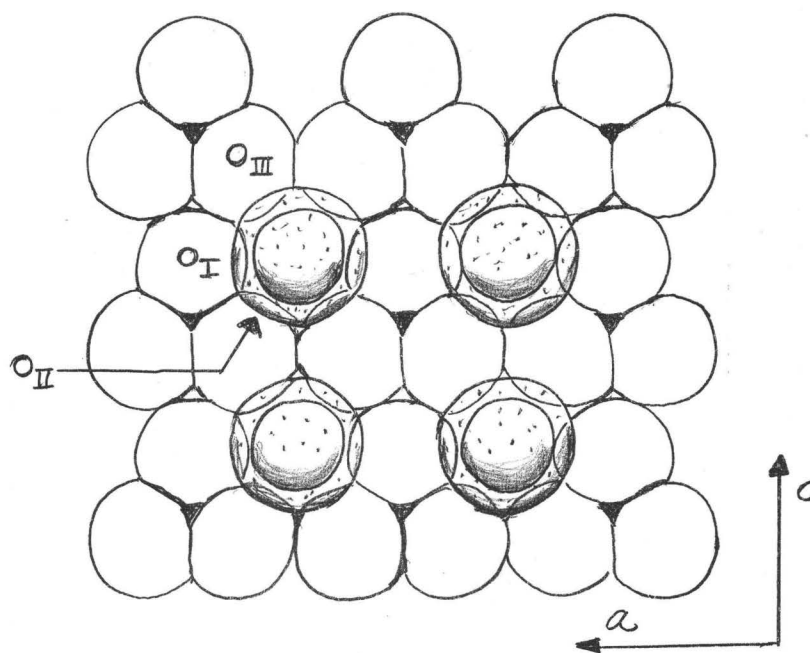
Table 1.--Optical data for rutherfordine.

Orthorhombic, biaxial (+)

Reference	$\alpha$	$\beta$	$\gamma$	Orientation	2V
This study	1.715	1.730	1.795	X = b Y = c (elongation) Z = a (normal to (100))	53° (calc.)
Fron del and Meyrowitz (1956)	1.723	1.730	1.760	Y along elongation Z normal to flat-tening	not given
Vaes (1947) (on diderichite)	1.722 to 1.728	1.728	1.728 to 1.74	Y along elongation Z normal to flat-tening	large
Larsen and Berman (1934)	1.72	1.75 $\pm$	1.80	none given	not given

Each uranium atom lies in a layer surrounded by six oxygen atoms and is bonded to two additional oxygen atoms at 1.67 Å above and below the plane. The lowest index of refraction occurs for the vibration direction normal to the layers, i.e., X = b. This is in agreement with the results found for other layer structures. However, the two remaining indices for vibration directions parallel to layers differ considerably. It seems likely that this difference must be ascribed to the optical anisotropy of the uranium-oxygen bonding in the layer. The six U-O bonds formed within the layer are not all equivalent in length or in directional effect on the electric vector in the two principal optical polarization directions. Two of the bonds lie very nearly parallel to [100] with length 2.43 Å, while the other four lie at approximately 45° to both [100] and [001] with length 2.52 Å. Light vibrating parallel to the two short bonds would be expected to induce greater mutual polarization and hence





Rutherfordine

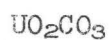


Figure 1.--Structure of a layer in  $\text{UO}_2\text{CO}_3$ , parallel to (010) (after Christ et al., 1955). The  $\text{UO}_2^{+2}$  groups lie normal to the plane with the uranium atoms lying in the hexagonal holes formed by the carbonate groups. Each uranium atom has six bonds in the plane, with distances  $\text{U}-\text{O}_{\text{III}}$  (4) = 2.52 Å,  $\text{U}-\text{O}_{\text{I}}$  (2) = 2.43 Å, and two bonds normal to the plane with  $\text{U}-\text{O}_{\text{II}}$  = 1.67 Å (Cromer and Harper, 1955b).

greater retardation than light vibrating normal to these bonds. The other four bonds would be expected to contribute equally to the [001] and [100] vibration directions. Qualitatively, then, a satisfactory explanation of the difference in indices of refraction and positive birefringence can be based on the known bond lengths and directions. The coupling in the linear uranyl ion,  $(O-U-O)^{+2}$ , undoubtedly exerts some influence on the value of  $\alpha$ , but the nature of this influence is not clear at present.

The values of the six U-O bond lengths were not determined directly (Christ et al., 1955) but were based on the assumption of an equilateral triangular carbonate ion with C-O bond lengths of 1.25 Å (Brown, Peiser, and Turner-Jones, 1949). Confirmation of the validity of this assumption follows from the work of Cromer and Harper (1955b). Using the values of the U-O bond lengths given and following the method of Zachariasen (1954), they calculated the length of the U-O bond in the uranyl ion to be 1.68 Å; their measured value is  $1.67 \pm 0.09$  Å.

#### POWDER DIFFRACTION DATA

An X-ray powder pattern was made using hand-picked pale-yellow crystals. The data obtained from the pattern are given in table 2, together with the d-spacings and Miller indices calculated from the results obtained in the previous single crystal study (Christ et al., 1955). The powder data given by Frondel and Meyrowitz (1956) are also included in the table, and are in excellent agreement with ours. Powder data on synthetic  $UO_2CO_3$  have previously been given by Miller, Pray, and Munger (1949). Examination of their results indicates that the powder was a mixture, one component of which was  $UO_2CO_3$ . In the present study only a cursory attempt, which was unsuccessful, was made

to account for all the lines listed. It was also obvious that there was a systematic error in their d-spacings for  $\text{UO}_2\text{CO}_3$  which were all too large.

#### ACKNOWLEDGMENTS

We are greatly indebted to Professor Clifford Frondel of Harvard University for the mineral specimen used. We are also grateful to several colleagues in the U. S. Geological Survey who lent help; Daphne D. Riska and Mary E. Mrose prepared powder patterns, and the latter also assisted in the optical determinations. This work was completed as part of a program undertaken by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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Table 2.--X-ray powder data: Rutherfordine,  $\text{UO}_2\text{CO}_3$ .

Orthorhombic  $\text{Pmmn}$  ( $\text{D}_{2h}^{13}$ );  $a = 4.845 \pm 0.010$ ,  
 $b = 9.205 \pm 0.008$ ,  $c = 4.296 \pm 0.006$  Å

Fron del and Meyrowitz (1956)		Present study			
Measured		Measured*		Calculated**	
Cu/Ni	$\underline{d}$ (Å)	Cu/Ni	$\lambda = 1.51418$ Å		
I	$\underline{d}_{hkl}$	I	$\underline{d}_{hkl}$	$\underline{d}_{hkl}$	$\underline{hkl}$
10	4.60	100	4.61	4.603	020
8	4.29	70	4.30	4.287	110
6	3.90	30	3.92	3.893	011
9	3.21	40	3.23	3.214	101
4	2.64	25	2.64	2.635	121
		6	2.60	2.592	130
1	2.51	9	2.512	2.497	031
2	2.41	15	2.420	2.423	200
3	2.32	20	2.309	2.301	040
4	2.15	9	2.156	{ 2.148	002
				{ 2.144	220
5	2.05	20	2.062	2.057	211
1	1.95	4	1.953	1.947	022
2	1.914	15	1.926	1.921	112
2	1.874	9	1.879	1.871	141
3	1.734	6	1.746	1.739	231
		4	1.723	1.721	150
		3	1.701	1.692	051
		3	1.670	1.668	240
1	1.658	3	1.660	1.654	132
1	1.603	3	1.606	1.607	202
1	1.588	3	1.593	1.591	310
		2	1.572	1.570	042
		6	1.537	1.534	060
2	1.510	3	1.514	{ 1.517	222
				{ 1.512	301
2	1.435	3	1.435	1.436	321
3	1.388	6	1.388	{ 1.387	251
				{ 1.385	161
1	1.373	2	1.376	1.373	103
1	1.346	2	1.346	1.343	152
1	1.318	4	1.320	{ 1.318	242
				{ 1.316	123

Table 2.--X-ray powder data: Rutherfordine,  $\text{UO}_2\text{CO}_3$ --Continued.

Orthorhombic  $\text{Pmmn}$  ( $D_{2h}^{13}$ );  $a = 4.845 \pm 0.010$ ,  
 $b = 9.205 \pm 0.008$ ,  $c = 4.298 \pm 0.006$  Å

Fron del and Meyrowitz (1956)		Present study			
Measured		Measured*		Calculated**	
Cu/Ni	$\underline{d}$ (Å)	Cu/Ni	$\lambda = 1.51418$ Å		
I	$\underline{d}_{hkl}$	I	$\underline{d}_{hkl}$	$\underline{d}_{hkl}$	$hkl$
1	1.275	2	1.298	{ 1.298	260
		3	1.280	{ 1.296	033
		3	1.224	{ 1.278	312
		< 2	1.212	{ 1.222	213
		< 2	1.158	{ 1.214	350
		< 2	1.116	{ 1.211	400
		< 2	1.071	{ 1.157	411
		< 2	1.057	{ 1.116	271
		< 2	1.043	{ 1.074	004
		< 2	1.029	{ 1.072	440
				{ 1.057	352
				{ 1.055	402
				{ 1.046	024
				{ 1.044	323
				{ 1.042	114
				{ 1.028	422

\*Not corrected for shrinkage. Lower limit of 2 $\theta$  measurable: approximately 7° (13 Å for CuK).

\*\* $\underline{d}_{hkl}$  calculated for all planes for which  $h+k+l = 2n$  down to 1.028 Å, the smallest observed value. Of these, only (420) with  $\underline{d} = 1.171$  Å does not appear on powder film. Lines for which  $h+k+l \neq 2n$  are too weak to appear on film. (See Christ et al., 1955.)