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REFINEMENT OF THE CRYSTAL STRUCTURE OF RUTHERFORDINE

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ABSTRACT

Rutherfordine, UO_2CO_3, is orthorhombic, a 4.840(1), b 9.273(2), c 4.298(1) Å, V 192.90(7) Å^3, space group *Imm*2, $Z = 2$. The structure was refined to an R index of 2.2% on the basis of 306 unique data [$|F_o|/\sigma(|F_o|) > 5$] measured with Mo$K\alpha$ X-radiation on a single-crystal diffractometer. The structure consists of neutral sheets of edge- and corner-sharing (UO_8) hexagonal bipyramids and (CO_3) triangles, as originally proposed by Christ *et al.* (1955); our refinement, however, shows that (CO_3) groups in alternate layers have the same orientation, not opposite orientations as originally reported. The refined value of the U–O(uranyl) distance is strongly affected by the details of the absorption correction, ranging from 1.71 to 1.80 Å as a function of the plate-glancing angle used in an empirical psi-scan absorption correction and as a function of the type of weighting scheme used in the refinement. The Gaussian-quadrature method of integration also shows similar problems, but they are less extreme. The preferred value for the U–O(uranyl) distance in rutherfordine is ~1.745 Å; as rutherfordine contains no H atoms, the O(uranyl) atom is [1]-coordinated, and should have the shortest U–O(uranyl) distance stereochemically possible. The current work suggests that U–O(uranyl) values less than 1.745 Å reported in other studies are adversely affected by less-than-optimum absorption corrections.

Keywords: rutherfordine, crystal structure, uranyl carbonate, uranium mineral.

SOMMAIRE

La rutherfordine, UO_2CO_3, est orthorhombique, a 4.840(1), b 9.273(2), c 4.298(1) Å, V 192.90(7) Å^3, groupe spatial *Imm*2, $Z = 2$. Nous en avons affiné la structure jusqu'à un résidu R de 2.2% en utilisant 306 données uniques [$|F_o|/\sigma(|F_o|) > 5$] mesurées avec un rayonnement Mo$K\alpha$ et un diffractomètre à cristal unique. La structure est faite de feuillets neutres contenant des bipyramides hexagonales (UO_8) à arêtes et à coins partagés et des triangles (CO_3), comme l'avaient préconisé Christ *et al.* (1955). Notre affinement montre toutefois que les groupes (CO_3) possèdent une orientation constante d'un feuillet à l'autre, contrairement à ce qui avait été conclu antérieurement. La valeur affinée de la distance U–O (uranyle) dépend fortement des détails de la correction pour l'absorption; cette distance varie de 1.71 à 1.80 Å selon l'angle de transmission au travers du cristal, qui a la forme d'une plaquette, dans le protocole de correction empirique par balayage psi, et selon le choix de pondération au cours de l'affinement. La méthode d'intégration par quadrature gaussienne montre aussi des problèmes semblables, quoique moins extrêmes. Notre valeur préférée de la distance U–O (uranyle) dans la rutherfordine est ~1.745 Å. Dans ce minéral, qui ne contient aucun atome de H, la coordinence de l'atome d'oxygène associé à l'uranyle est donc [1], et la distance U–O (uranyle) devrait être la plus courte qui soit stéréochimiquement possible. D'après nos mesures, il semble clair que les valeurs U–O (uranyle) de moins de 1.745 Å dans la littérature soient dues à des corrections non optimales de l'absorption des raies diffractées par le minéral.

(Traduit par la Rédaction)

Mots-clés: rutherfordine, structure cristalline, carbonate d'uranyle, minéral d'uranium.

INTRODUCTION

There is considerable interest in the paragenesis and structures of U^{6+} minerals, in part because of their role as products of alteration of uraninite under oxidizing conditions (Frondel 1958, Garrels & Christ 1959, Finch & Ewing 1992). Phases containing U^{6+} also are important products of corrosion of UO_2 in spent nuclear fuel (Finch & Ewing 1991, Forsyth & Werme 1992, Wronkiewicz *et al.* 1992, 1996, Johnson & Werme

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1994, Buck *et al.* 1998, Finn *et al.* 1998), and they may control groundwater concentrations of uranium in U-contaminated soils (Buck *et al.* 1994, Morris *et al.* 1996). Studies of the natural occurrences of uranyl minerals can be used to test the extrapolation of results of short-term experiments to periods relevant to the disposal of high-level nuclear waste (Ewing 1993) and to assess models that predict the long-term behavior of spent nuclear fuel (Bruno *et al.* 1995). Understanding the structural and thermodynamic stabilities of U carbonates is particularly germane to nuclear-waste disposal (Clark *et al.* 1995, Finch 1997a, Neu *et al.* 1997) because of the high mobility of U in carbonate-bearing groundwaters (Hostetler & Garrels 1962, Langmuir 1978, Grenthe *et al.* 1994). Uranium carbonates may precipitate where evaporation is significant or where the fugacity of CO_2 is greater than atmospheric (Garrels & Christ 1959, Hostetler & Garrels 1962, Ippolito *et al.* 1984, Finch & Ewing 1992, Finch 1997a). Carbonate minerals may therefore be important in actinide-contaminated soils and certain repository settings (*e.g.*, Yucca Mountain) because they may be sinks for ^{14}C (Murphy 1995), transuranic actinides (Burns *et al.* 1997a, b, Wolf *et al.* 1997) and possibly certain fission-products (Finch & Ewing 1991, Wronkiewicz *et al.* 1996). From a historical perspective, 1898 was the year that Sir Ernest Rutherford began his pioneering investigations into the properties of the nucleus. Now, one hundred years later, his namesake mineral is assuming importance in the long-term handling of spent nuclear materials.

PREVIOUS WORK

The crystal structure of rutherfordine, UO_2CO_3, was first proposed by Christ *et al.* (1955) on the basis of X-ray data measured with photographic film. However, they did not collect quantitative intensities, and based their structure on assumed C–O and U–O distances. The short U–O(uranyl) bond-length suggested by Christ *et al.* (1955) was 1.93 Å, based on analogy with U–O(uranyl) distances reported for anhydrous uranates. Cromer & Harper (1955) did a one-dimensional refinement of synthetic $UO_2(CO_3)$ and reported a U–O(uranyl) distance of 1.67 Å; however, this is the shortest U–O distance reported for any well-refined uranyl compound (Burns *et al.* 1997c). Christ *et al.* (1955) noted that the diffraction pattern of rutherfordine shows the structure to be very strongly pseudo-*I*-centered; only a small number of reflections weakly violate the extinction criterion for *I*- centering. They also noted that these weak violating reflections show diffuse streaking along *b**. Christ *et al.* (1955) presented two structures: (1) structure *A* is consistent with *Pmmn* symmetry, and adjacent layers have the (CO_3) groups pointing in opposite directions; (2) structure *B* is consistent with *Imm*2 symmetry, and adjacent layers have the (CO_3) groups pointing in the same direction. They suggested that structures *A* and *B* are energetically equivalent, and that crystals can contain domains of each structure, separated by stacking faults.

EXPERIMENTAL

An amber-brown crystal of rutherfordine (with forms {100}, {010} and {001}) was removed from a sample from the Shinkolobwe mine, Shaba, Democratic Republic of Congo. Precession photographs confirmed orthorhombic symmetry and indicated an *I*-centered lattice. A thin bladed cleavage fragment, approximately 0.026 × 0.14 × 0.18 mm, was glued to a glass fiber (with the blade inclined ~15° to the axis of the fiber) and mounted on a Siemens *P*4 automated four-circle diffractometer with a graphite monochromator and a Mo*K*α X-ray tube. Thirty-seven intensities were centered, thirty-two of which were between 25° and 45° 2θ, and the unit-cell dimensions were derived and refined by least squares (Table 1). Following the data collection, the reflections were recentered, and the unit-cell parameters redetermined. Differences from the previously determined values were within the reported standard deviations, indicating that the crystal had not undergone significant change during data collection.

Intensity data were collected in θ:2θ scan-mode with a variable scan-rate scaled to the peak intensity (minimum and maximum scan-speeds were 0.75° 2θ min^{-1} and 29.30° 2θ min^{-1}, respectively). A full sphere of data was collected ($-6 \le h \le 6$, $-13 \le k \le 13$, $-6 \le l \le 6$) on the unconstrained unit-cell [*a* 4.8398(4), *b* 9.2726(9) *c* 4.2976(4) Å, α 89.977(8)°, β 90.002(7)°, γ 89.957(8)°] with no lattice restrictions. A total of 2233 intensities were measured over the range $9.5° \le 2\theta \le 60.0°$ Three standard intensities were measured after every fifty intensities. Standard intensities varied by approximately ±2% during the 11-day collection of the data. An empirical absorption-correction was applied, based on 71 psi-scans of each of 20 intensities at psi-values at least every 5° 2θ from 9.5° to 59.4°. The crystal was modeled as a {010} plate, and 347 intensities with a plate-glancing angle less than 7° were discarded (see Appendix). The absorption correction reduced *R*(azimuthal) from 30.0% to 3.5%. The remaining 1886 data were corrected for drift, Lorentz, polarization and background effects, and reduced to structure factors.

STRUCTURE REFINEMENT

All calculations were done with the SHELXTL PC Plus system of programs. We collected a full sphere of data on a primitive cell as Christ *et al.* (1955) reported diffraction symmetry consistent with a primitive cell. However, we did not observe any reflections violating *I*-centered symmetry, and the space group *Imm*2 was adopted. We used the atomic parameters of Christ *et al.* (1955) as a starting model, but shifted the origin by (¼, ¼, ¼) to be consistent with space group *Imm*2, with the

TABLE 1. CRYSTAL DATA AND STRUCTURE-REFINEMENT INFORMATION FOR RUTHERFORDINE

Empirical formula	UO_2CO_3	Crystal size (mm)	0.18 x 0.14 x 0.026
Formula weight	330.04	2θ range for data collection	9.5° to 60.00°
Wavelength	0.71073 Å	Index ranges	$-6 \le h \le 6$
Crystal system	Orthorhombic		$-13 \le k \le 13$
Space group	*Imm*2		$-6 \le l \le 6$
Unit-cell dimensions	a = 4.840(1) Å	Total No. of I	2233
	b = 9.273(2) Å	No. of I remaining after 7° glancing angle	1886
	c = 4.298(1) Å		
Volume	192.90(7) A^3	No. of I allowed by I-centering	946
Z	2	No. of $\|F\|$	306
Density (calculated)	5.682 g/cm^{-3}	No. of $\|F_o\| > 5\sigma$	306
Density (measured)	5.7 g/cm^{-3} *	R(merge) %	2.6
Absorption coefficient	42.0 mm^{-1}	R(obs) %	2.2
F(000)	276	wR(obs) %	3.0

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2]^{½}$, $w = 0.002766$

* Frondel (1958)

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR RUTHERFORDINE

	x	y	z	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	0	0	0.0	148(1)	55(2)	312(3)	76(2)	0	0	0
C	1/2	0	0.3864(47)	168(42)	120(79)	285(74)	97(63)	0	0	0
O(1)	0	−0.1880(9)	−0.0049(92)	284(23)	309(44)	279(34)	263(43)	27(109)	0	0
O(2)	0.2638(18)	0	0.5066(76)	232(20)	83(30)	448(38)	166(36)	0	39(91)	0
O(3)	1/2	0	0.0795(38)	391(66)	104(69)	979(169)	90(77)	0	0	0

* $U = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})] \times 10^4$ Å^2

U_{eq} is one-third of the trace of the orthogonalized U_{ij} tensor

U site at the origin, as there were no reflections of significant intensity that violated the extinction conditions for *I*-centering. Convergence was rapid, and difference-Fourier maps through the plane of the structural sheet (at $y = 0$) showed no significant residual electron-density. Anisotropic-displacement factors for all atoms were refined. The structure was refined until the maximum shift /esd for all parameters was 0.000; the absolute configuration could not be determined reliably. The final R_1 index is 2.2% for 306 unique data ($|F_o|/\sigma(|F_o|) > 5$). The final parameters are given in Table 2, and selected interatomic distances and angles, in Table 3. A table of structure factors is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

TABLE 3. SELECTED INTERATOMIC DISTANCES [Å] AND ANGLES [°] IN RUTHERFORDINE

U–O(1),a	1.744(8)	O(1)a–*U*–O(1)		179(3)
U–O(3),c	2.444(2)	O(1)–*U*–O(2)	x4	91(1)
U–O(2)b,d	2.48(3)	O(1)–*U*–O(2)b	x4	89(1)
U–O(2),c	2.52(3)	O(1)–*U*–O(3)	x4	90.1(2)
		O(2)–*U*–O(2)c		60.8(8)
U–*C*	2.94(1)	O(2)b–*U*–O(2)d		62.1(8)
		O(3)–*U*–O(2)b	x2	67.0(6)
C–O(2),e	1.26(2)	O(3)–*U*–O(2)	x2	51.6(6)
C–O(3)	1.32(3)			
<*C*–O>	1.28	O(2)–*C*–O(2)e		131(3)
		O(2)–*C*–O(3)	x2	114(2)
C–O(1)f	2.93(1)	<O–*C*–O>		120

Symmetry transformations used to generate equivalent atoms: a: $x, \bar{y}, z$; b: $x, y, z-1$; c: $\bar{x}, y, z$; d: $\bar{x}, y, z-1$; e: $\bar{x}+1, y, z$; f: $x+1/2, y+1/2, z+1/2$

DESCRIPTION OF THE STRUCTURE

Cation coordination

The C atom is coordinated by three O atoms in a triangular arrangement (Fig. 1). The resulting (CO_3) group is unusually distorted for such a tightly bonded entity (Table 3). However, this distortion may be rationalized *via* the local connectivity of the principal polyhedra in the structure. The (CO_3) group shares two edges with adjacent (UO_8) polyhedra (Fig. 2), and these edges

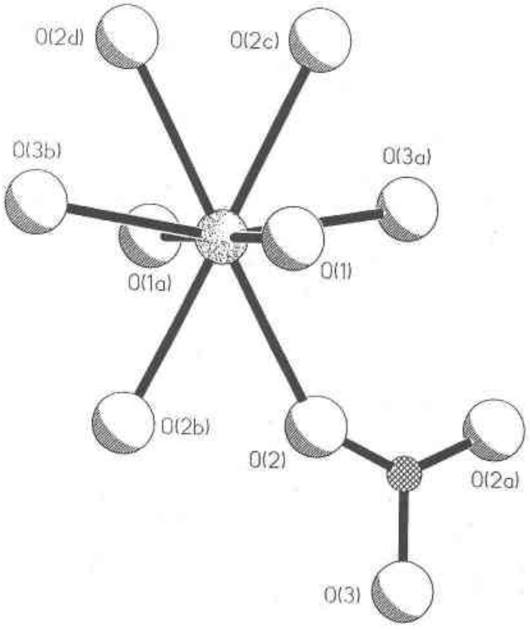

FIG. 1. An oblique view of the (UO_8) and (CO_3) groups in rutherfordine; C: cross-hatched circle, U: random dot-shaded circle, O: highlighted circle.

are significantly shortened [note the O(2)–C–O(3) angle of 114°, Table 3]. This distortion is consistent with the infrared data reported for rutherfordine by Urbanec & Čejka (1979) and Čejka & Urbanec (1988). The U atom is surrounded by eight O atoms in a hexagonal bipyramidal arrangement. The two apical O atoms of the hexagonal biypyramid are 1.744(8) Å from the central U atom, forming a (UO_2) group. The six meridional O atoms are ~2.48 Å from the central U atom, and the O(2)d–O(3)b edge shared with the (CO_3) group subtends the smallest O–U–O angle of the (UO_8) polyhedron.

Topology of the structure

The (UO_8) hexagonal bipyramids link by sharing pairs of *trans* edges to form chains extending along [001]. These chains link in the [100] direction by sharing *trans* vertices to form a sheet of hexagonal bipyramids (Fig. 2). The C atoms occupy triangular interstices within the polyhedral sheet, and the resulting (CO_3) group shares two edges with adjacent (UO_8) polyhedra. All (CO_3) groups within the sheet point in the same direction, and each structural sheet has the same chemical formula as the complete structure: $UO_2(CO_3)$. Thus rutherfordine is a "miscellaneous structure containing sheets based on anion topologies containing hexagons" in the structural hierarchy of Burns *et al.* (1996).

The heteropolyhedral sheets stack along [010] (Fig. 3) such that adjacent sheets intermesh. There is no direct linkage between adjacent sheets, which are held together only by van der Waals forces, and the carbonate groups in adjacent sheets all point in the same direction.

OH in rutherfordine

Does rutherfordine contain OH groups in the structure? How might these substitute for (CO_3) groups? Infrared spectra commonly indicate OH in both natural and synthetic samples of uranyl carbonates isostructural with rutherfordine (Urbanec & Čejka 1979, Čejka & Urbanec 1988, 1990). Čejka & Urbanec (1988) noted that the infrared (IR) spectrum of (natural) rutherfordine is most similar to synthetic UO_2CO_3 prepared hydrothermally (200° to 220°C) at elevated $P(CO_2)$ (4.2–42 MPa). The IR spectra of synthetic uranyl carbonates commonly differ from that of rutherfordine, and typically indicate higher amounts of H (as OH or H_2O groups, or both). Čejka & Urbanec (1988) proposed a substitutional solid-solution in uranyl carbonates, $UO_2(CO_3)_{1-x}(OH)_{2x}$. This type of substitution could occur in the structure if U^{6+} coordination polyhedra adjacent to a missing (CO_3) group distorted from hexagonal dipyramids to pentagonal dipyramids (Čejka & Urbanec 1988). Such a distortion would probably shift the U atoms only slightly, as for the topologically similar mineral schmitterite (Meunier & Galy 1973, Loopstra & Brandenburg 1978).

Frondel (1958) noted that the appearance of rutherfordine is variable, and that the composition of crystals may differ: some samples of rutherfordine contain measurable amounts of H_2O. Whether OH groups incorporated in rutherfordine affect U–O(uranyl) distances is unknown; however, U–O(uranyl) distances are strongly affected by H bonds in other structures (Finch 1997b). Finch *et al.* (1996) found that U–O(uranyl) distances in schoepite, $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$, vary from 1.82 Å, where the uranyl O-atom receives a strong H-bond contribution, to 1.74 Å, where uranyl O-atoms do not act as H-bond acceptors. A U–O(uranyl) distance of 1.745 Å is therefore consistent with the lack of significant H-bonding in rutherfordine. Burns *et al.* (1997c) have recently provided coordination-specific bond-valence parameters for U^{6+}–O bonds. The resulting distribution of bond valences (Table 4) is in reasonable accord with the valence-sum rule. The sum of the bond valences incident at U^{6+} is 6.12 *vu* (valence units), and the U–O(uranyl) bond-valence is 1.80 *vu*. The latter value is somewhat low, but is in accord with the results for schoepite (Finch *et al.* 1996). The U–O(uranyl) distance determined by us for rutherfordine, 1.744 Å, is shorter than the 1.77 Å determined recently by X-ray absorption spectroscopy (Thompson *et al.* 1997); it is

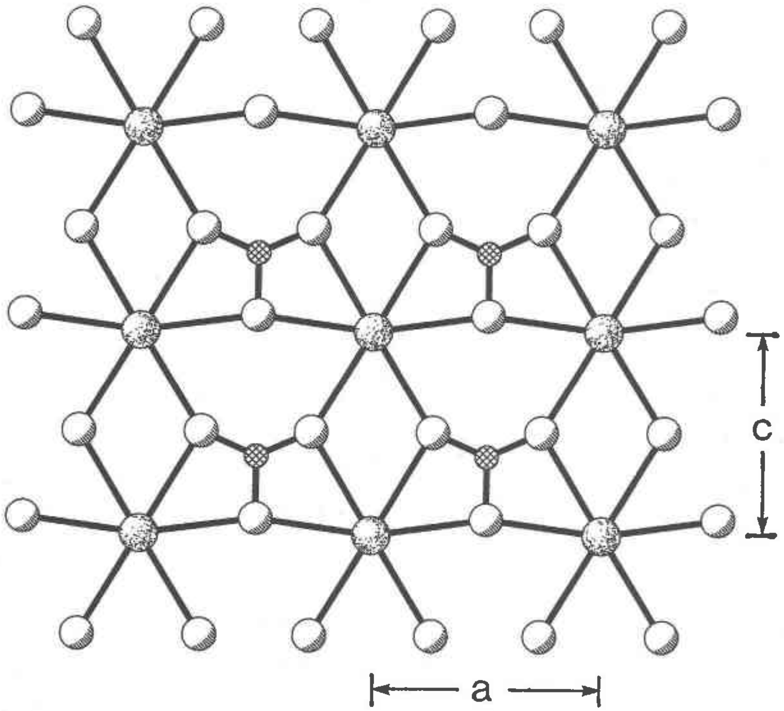

FIG. 2. The crystal structure of rutherfordine projected down [010]; legend as in Figure 1, and apical O atoms omitted for clarity.

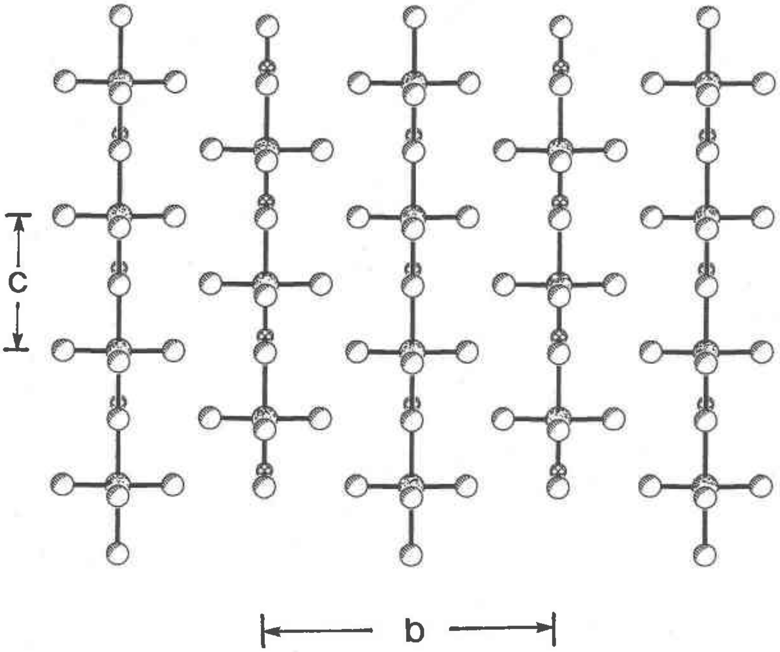

FIG. 3. The crystal structure of rutherfordine projected down [100]; legend as in Figure 1.

TABLE 4. BOND-VALENCE TABLE FOR RUTHERFORDINE

	U	*C*	Σ
O(1)	$1.80^{\times2}\downarrow$		1.80
O(2)	$0.42^{\times2}\downarrow$ $0.39^{\times2}\downarrow$	$1.44^{\times2}\downarrow$	2.25
O(3)	$0.45^{\times2}\downarrow\rightarrow$	1.19	2.09
Σ	6.12	4.07	

* bond-valence relations for C–O and U^{6+}–O from Brown (1981) and Burns *et al.* (1997c)

possible that their sample of rutherfordine contained significant (OH) substituting for (CO_3).

COMPARISON WITH RELATED STRUCTURES

There are two other uranyl carbonate minerals: blatonite, $UO_2(CO_3)(H_2O)$ (Vochten & Deliens 1998) and joliotite, $UO_2CO_3(H_2O)_2$ (Walenta 1976); the structures of both of these minerals are unknown. UO_2SeO_3 is a monoclinic uranyl selenite (nearly) isostructural with rutherfordine. The SeO_3 triangles within the sheets alternate in UO_2SeO_3 (Loopstra & Brandenburg 1978), whereas in *Imm*2 rutherfordine, all CO_3 triangles point the same way.

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APPENDIX. THE EFFECT OF ABSORPTION ON *U*–O(URANYL) DISTANCE

The uranyl minerals have structural arrangements that tend to be dominated by sheets of $(U\phi_n)$ polyhedra (ϕ: unspecified anion) in which the *U*–O(uranyl) bonds are arranged approximately orthogonal to the plane of the sheet. These sheets are usually linked *via* interstitial cations and (H_2O) groups. The structure of rutherfordine is of particular interest as the sheets are held together only by van der Waals interactions. This means that the *U*–O(uranyl) distance *must* correspond ideally to a bond valence of 2.0 *vu*, as unlike all other U-minerals, the O(uranyl) atom is [1]-coordinated and receives no incident bond-valence contributions from interstitial cations or H bonds.

One of the problems associated with highly absorbing materials such as rutherfordine is that part of the data is lost (or rather discarded) because of excessively long path-length (and the possibility of total attenuation of parts of the beam) through the crystal. In a thin-plate absorption correction, this problem is handled by discarding data for which the X-ray beam subtends an angle of less than a certain value (the glancing angle) at the plate. In a crystal-shape correction (Gaussian quadrature integration), this issue is not addressed; all path lengths through the crystal are calculated. However, at very small values of transmission, the equation used is not accurate, as the degree of transmission asymptotically approaches zero, whereas the actual transmission *is* zero above a certain path-length. Thus in the Gaussian-type correction, very-low-transmission data should also perhaps be discarded.

Two questions relevant to rutherfordine arise from the above discussion: (1) What proportion of the data should be discarded? (2) What effect does the discarded data have on the observed *U*–O(uranyl) bond-length? Here, we examine these two issues in regard to the refinement of the structure of rutherfordine.

TABLE A1. RESULTS OF REFINEMENTS OF THE CRYSTAL STRUCTURE OF RUTHERFORDINE FOR DIFFERENT PLATE-GLANCING ANGLES, DIFFFERENT WEIGHTING SCHEMES, AND FOR GAUSSIAN-ABSORPTION CORRECTIONS

Glancing angle (°)	Total No. of *I*	*I* unique	*R* (merge) %	Unit weights			$w = 1/\sigma^2(F)$			Refining weight			
				R %	*wR* %	*U*–O(1) Å	*R* %	*wR* %	*U*–O(1) Å	*R* %	*wR* %	*U*–O(1) Å	*w*
2	1062	323	4.1	3.9	5.4	1.795(21)*	3.9	4.1	1.770(12)*	3.9	4.8	1.775(12)*	0.003548
3	1038	319	3.5	3.2	4.9	1.799(19)*	3.0	3.1	1.763(11)*	3.0	4.0	1.779(12)*	0.004876
4	1004	315	3.1	3.1	4.9	1.789(19)	2.8	2.9	1.759(10)*	2.9	3.9	1.761(11)*	0.002378
5	982	309	2.9	2.4	3.5	1.754(15)	2.4	2.6	1.755(9)	2.4	3.2	1.747(9)	0.004072
6	958	306	2.6	2.3	3.3	1.751(12)	2.2	2.5	1.751(8)	2.2	3.0	1.746(8)	0.004257
7	946	306	2.6	2.3	3.3	1.746(12)	2.2	2.5	1.749(8)	2.2	3.0	1.744(8)	0.002766
8	932	305	2.4	2.3	3.3	1.748(12)	2.2	2.6	1.753(8)	2.2	3.0	1.746(8)	0.001596
9	902	298	2.3	2.0	2.7	1.783(12)	2.0	2.5	1.752(8)	2.0	2.7	1.745(7)	0.000854
10	866	289	2.1	2.0	2.6	1.782(13)	2.0	2.4	1.755(9)	1.9	2.7	1.749(9)*	0.000745
11	836	277	2.0	1.8	2.5	1.778(14)	1.9	2.3	1.744(9)	1.8	2.5	1.738(10)	0.002002
12	808	270	1.9	1.8	2.4	1.764(13)	1.7	2.1	1.730(9)	1.7	2.3	1.725(9)	0.001089
13	798	270	1.7	1.8	2.4	1.763(13)	1.7	2.1	1.729(9)	1.7	2.2	1.722(9)	0.003263
14	790	267	1.6	1.6	2.2	1.746(12)	1.6	1.9	1.721(8)	1.6	2.1	1.715(8)	0.000515
15	770	261	1.5	1.6	2.2	1.744(12)	1.6	1.9	1.718(7)	1.6	2.0	1.709(7)	0.000648
16	742	254	1.5	1.6	2.2	1.747(11)	1.6	2.0	1.725(8)	1.6	2.0	1.718(7)	0.001322
17	716	245	1.5	1.6	2.2	1.768(14)	1.6	1.9	1.736(9)	1.5	2.0	1.732(10)	0.000972
18	700	240	1.5	1.4	2.0	1.780(15)	1.4	1.6	1.758(11)	1.4	1.7	1.760(11)	0.000770
19	686	236	1.5	1.4	2.0	1.780(15)	1.4	1.6	1.757(11)	1.3	1.7	1.759(11)	0.000494
20	676	234	1.5	1.4	2.0	1.780(15)	1.4	1.7	1.760(13)	1.4	1.7	1.759(12)	0.000616
Gaussian (all data)	1108	325	2.3	2.1	2.9	1.762(10)	2.1	2.4	1.749(8)	2.1	2.5	1.743(7)	0.000220
Gaussian ($\mu m \times t < 2.4$)	1058	322	2.2	2.0	2.7	1.764(10)	2.1	2.3	1.7581(7)	2.1	2.4	1.747(7)	0.000204

* didn't completely converge

First, plate corrections were done for a series of glancing angles from 2 to 20°, and the crystal structure of rutherfordine was refined for each data-set using three different weighting schemes: unit weights, statistical [$1/\sigma^2(F)$] weights, and refinable weights. The results of these refinements are given in Table A1. The *R* index decreases from 3.9 to 1.4% as the glancing angle increases, but the amount of unique data also decreases from 323 to 234 reflections. Moreover, the reflections "lost" during this process are not random, but occur in specific localized regions of reciprocal space, and hence may systematically affect the results of the refinements. Inspection of the refinement results shows that no parameters in the plane of the sheet are significantly affected. However, the U–O(uranyl) distance shows significant and systematic variation (Fig. A1) over a total range of 0.09 Å (1.71–1.80 Å). The form of the variation of each set of bond lengths (*i.e.*, for the three different weighting schemes) is more-or-less the same: troughs around 7 and 15%, and high values around 3, 10 and 19%. This variation must be related to the specific reflections discarded and included by the specific glancing-angle used.

So which is the *correct* (*i.e.*, true) value of the U–O(uranyl) distance? In order to make this decision, we also did a Gaussian-type absorption correction (maximum- and minimum-transmission values of 0.422 and 0.081, respectively). Figure A2 shows values of $\mu m \times t$ (where μ is the maximum value of the path length for the data used in the structure refinement) ordered against the number of intensities. The concern is that there is total attenuation of (at least part of) the beam for very high values of (μm × t). The trend in Figure A2 shows a discontinuity at some value above (μm × t) ≈ 2.4. We refined the structure with all of the Gaussian-corrected data and with the Gaussian-corrected data with (μm × t) < 2.4. The results are given in Table A1; note that although we have discarded ~25 reflections from the total data set owing to very high attenuation, we have only lost three unique reflections. The observed U–O(uranyl) distances for the optimum (7°) plate-glancing-angle refinement and the Gaussian refinement are (statistically) the same: 1.744(8) and 1.747(7) Å, suggesting that the best value is ~1.745 Å. As a consequence of this (somewhat woolly) argument, we present the results for the 7° glancing-angle refinement in the main body of the paper.

All crystallographers are aware of the general problem of low-precision results for highly absorbing materials. The current results also show, in a quantitative matter, how the accuracy of the results is affected by the details of a plate-absorption correction. Specifically, the refined *U*–O(uranyl) distance in rutherfordine varies in an oscillatory manner over the range 1.71–1.80 Å (Fig. A1) as a result of differences in the minimum plate-glancing angle for data accepted in the refinement. This

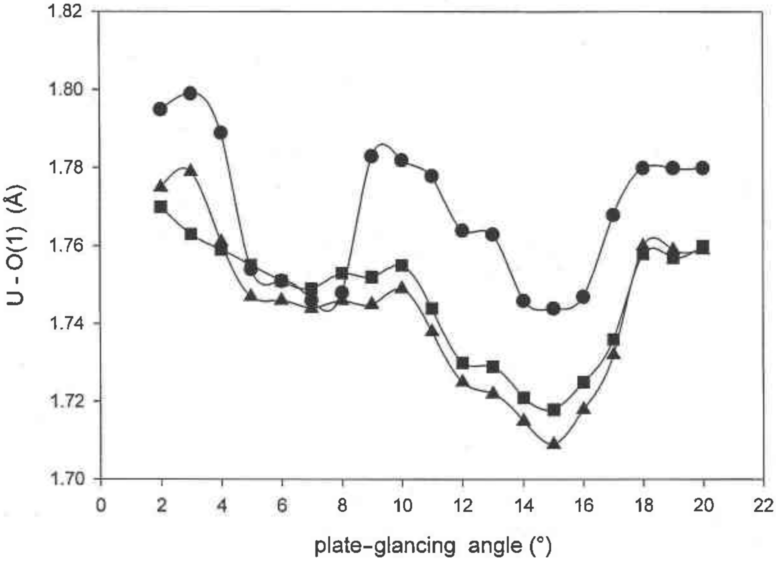

FIG. A1. Variation in *U*–O(1) distance in rutherfordine as a function of plate-glancing angle. Symbols: black circles: structures refined with unit weights, black squares: structures refined with $1/\sigma^2(F)$ weights, black triangles: structures refined with refinable weights.

finding suggests that data on the *U*–O(uranyl) bond in the literature may contain a random inaccuracy of the order of (at least) ±0.05 Å, depending on whether the investigators have used a thin-plate absorption correction and on the value of the minimum plate-glancing angle used in the correction. Of course, this problem may be ameliorated by collecting data with a CCD detector.

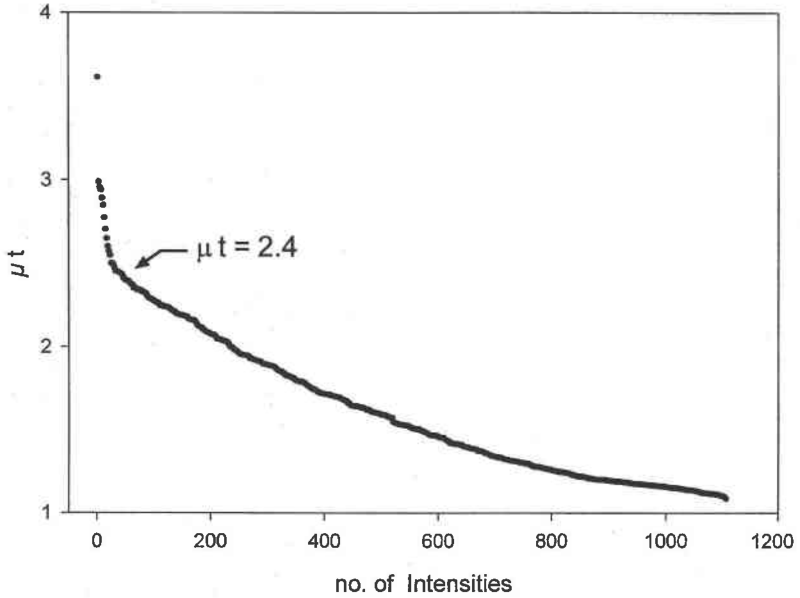

FIG. A2. Ordered variation in path length × absorption coefficient for Gaussian-corrected data for rutherfordine. The discontinuity at (μm × t) = 2.4 corresponds to a plate-glancing angle of 7°.