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THE CRYSTAL STRUCTURE OF DEHYDRATED WYARTITE, $Ca\ (CO_3)\ [U^{5+}\ (U^{6+}O_2)_2\ O_4\ (OH)]\ (H_2O)_3$

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ABSTRACT

Dehydrated wyartite from the Shinkolobwe mine, Shaba, Democratic Republic of Congo, ideally $Ca\ (CO_3)\ [U^{5+}\ (U^{6+}O_2)_2\ O_4\ (OH)]\ (H_2O)_3$, is orthorhombic, *a* 11.2610(6), *b* 7.0870(4), *c* 16.8359(10) Å, *V* 1343.6(2) Å^3, space group *Pmcn*, *Z* = 4. The structure was solved by direct methods and refined to an R_1 index of 2.9% based on 2045 observed reflections measured with Mo$K\alpha$ X-radiation on a four-circle single-crystal diffractometer equipped with a CCD detector. The structure consists of neutral sheets of the form $[U^{5+}\ (U^{6+}O_2)_2\ O_4\ (OH)]$ that contains edge- and corner-sharing $(U^{6+}\phi_7)$ polyhedra (ϕ: O^{2-}, OH^-, H_2O), two of which are pentagonal bipyramids with five equatorial O^{2-} and OH^- groups bonded to a central uranyl ion, $(U^{6+}O_2)^{2+}$. The third U atom is part of a unique $U^{5+}\phi_7$ polyhedron, in which two O^{2-} anions are part of an interlayer $(CO_3)^{2-}$ group and another is the O atom of an H_2O group. The plane of the (CO_3) groups lies perpendicular to the structural sheets, and each (CO_3) group is coordinated to U^{5+} in the structural sheet and to Ca in the interlayer. The sheet is topologically similar to that found in β-U_3O_8, and the sheets are bonded to each other through interlayer Ca atoms and interlayer (H_2O) groups. The principal difference between the structures of wyartite and dehydrated wyartite is that the sheets in the former are linked only through interstitial hydrogen-bonding, whereas the sheets in the latter are linked directly by Ca–O bonds (plus interstitial hydrogen-bonds).

Keywords: dehydrated wyartite, wyartite, crystal structure, carbonate, uranyl, pentavalent uranium, dehydration, spent nuclear fuel.

SOMMAIRE

La wyartite déshydratée provenant de la mine Shinkolobwe, au Shaba, République Démocratique de Congo, de composition idéale $Ca\ (CO_3)\ [U^{5+}\ (U^{6+}O_2)_2\ O_4\ (OH)]\ (H_2O)_3$, est orthorhombique, *a* 11.2610(6), *b* 7.0870(4), *c* 16.8359(10) Å, *V* 1343.6(2) Å^3, groupe d'espace *Pmcn*, *Z* = 4. Nous avons résolu la structure par méthodes directes et nous l'avons affiné jusqu'à un résidu R_1 de 2.9% en utilisant 2045 réflexions observées, mesurées sur monocristal avec rayonnement Mo$K\alpha$ et un diffractomètre à quatre cercles muni d'un détecteur de type CCD. La structure est faite de feuillets neutres $[U^{5+}\ (U^{6+}O_2)_2\ O_4\ (OH)]$ contenant des polyèdres $(U^{6+}\phi_7)$ à arêtes et à coins partagés (ϕ: O^{2-}, OH^-, H_2O), dont deux sont pentagonaux, avec cinq groupes O^{2-} et OH^- équatoriaux liés à un ion uranyle central, $(U^{6+}O_2)^{2+}$. Le troisième atome d'uranium fait partie d'un polyèdre unique $U^{5+}\phi_7$, dans lequel deux anions O^{2-} font partie d'un groupe $(CO_3)^{2-}$ et un autre atome d'oxygène fait partie d'un groupe H_2O. Le plan des groupes (CO_3) est perpendiculaire aux feuillets, et chaque groupe (CO_3) est coordonné à U^{5+} du feuillet et à Ca dans l'interfeuillet. Les feuillets sont topologiquement semblable à ceux de β-U_3O_8, et ils sont liés l'un à l'autre grâce aux atomes de calcium et les groupes (H_2O) entre les feuillets. La différence principale entre les structures de la wyartite et de la wyartite déshydratée réside dans les liaisons interfeuillets: elles impliquent seules les liaisons hydrogène dans la wyartite, et des liaisons directes Ca–O avec les liaisons hydrogène dans la wyartite déshydratée.

(Traduit par la Rédaction)

Mots-clés: wyartite déshydratée, wyartite, structure cristalline, carbonate, uranyle, uranium pentavalent, déshydratation, déchets nucléaires.

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Introduction

Dehydrated wyartite is a product of alteration of wyartite, ideally Ca U^{5+} $(U^{6+}O_2)^{2+}{}_2$ (CO_3) O_4 (OH) $(H_2O)_7$ (Burns & Finch 1999), as shown by Clark (1960). For many years, wyartite was confused with ianthinite (Bignand 1955), and it was described as a separate mineral species by Guillemin & Protas (1959). A single-crystal X-ray study of type material (Clark 1960) showed that wyartite crystals contain intergrowths of two phases, which she designated as wyartite I, with properties corresponding to those of the original description of the mineral, and wyartite II, a previously unknown phase. The alteration of wyartite to dehydrated wyartite is characterized by a change in the *c* dimension, from 20.81 Å in wyartite to ~17.00 Å in dehydrated wyartite; however, there is no measurable change in the *a* and *b* dimensions (Clark 1960).

Interest in the paragenesis and structures of uranium minerals arises not only because of their role as products of secondary alteration of uraninite under oxidizing conditions (Finch & Ewing 1992, Frondel 1958), but also because of their potential importance as products of the alteration of UO_2 in nuclear fuel (Finch & Ewing 1991, Finch *et al.* 1992, Johnson & Werme 1994, Forsyth & Werme 1992, Wronkiewicz *et al.* 1992, Wronkiewicz & Buck 1999). Studies of the paragenesis of uranyl-oxide hydrate minerals can be used to test the extrapolation of results of short-term experiments to periods relevant to nuclear-waste disposal (Ewing 1993) and to assess models used to predict the long-term behavior of spent nuclear fuel (Bruno *et al.* 1995). Wyartite (Burns & Finch 1999) and dehydrated wyartite are of particular interest in this regard as they contain U^{5+}, an ion with a charge and radius similar to some actinides occurring in spent nuclear fuel. Wyartite and dehydrated wyartite thus could be potentially important actinide and fission-product host-phases in oxidizing carbonate-rich groundwaters associated with a breached spent-fuel repository. Furthermore, Schindler *et al.* (2004) showed that wyartite forms on the surface of calcite during interaction with acidic and basic uranyl-bearing solutions.

Experimental

The crystal of dehydrated wyartite used in this work was taken from a museum specimen (Pinch Collection, National Museum of Canada) containing rutherfordine, masuyite and uraninite; the original sample is from the Shinkolobwe mine in Shaba, Democratic Republic of Congo. The crystal is dark purple and strongly pleochroic (pale lavender to dark purple).

Precession photographs confirm its orthorhombic symmetry. An approximately rectangular plate (Table 1) showing uniform extinction in cross-polarized light and cut from a larger crystal was attached to a glass fiber and mounted on a Siemens *P*4 automated four-circle diffractometer equipped with a graphite monochromator, Mo*K*α X-radiation and a CCD detector. Intensity data were collected according to the procedure described by Cooper & Hawthorne (2001). Intensities of 13,000 reflections were collected to 60° 2θ using 60 s per 0.125° frame; the resulting number of unique reflections is 2045 with an *R*(merge) of 2.0%. The refined unit-cell parameters (Table 1) were obtained from 8192 reflections with $I > 10\sigma I$. A Gaussian absorption-correction was applied to the data, followed by an empirical absorption-correction using the program SADABS (Sheldrick 1998).

Structure Solution and Refinement

The *U* sites and some other sites were located by direct methods in the space group *Pmcn*, and other sites were located by successive cycles of least-squares refinement and difference-Fourier synthesis; scattering species were assigned according to local stereochemistry arguments. Two *U* sites, two *Ca* sites, one *C* site and ten anion sites were located. However, the displacement factors indicated that several of the sites are only partly occupied or are positionally disordered, and many steps in the refinement were necessary to untangle the details:

(1) The two *Ca* sites are only partly occupied and are only 0.75(1) Å apart; hence both these sites cannot be occupied in any one local configuration, suggesting some sort of positional disorder involving Ca. Site-population refinement at both sites converged to a joint occupancy of 0.97(3) Ca; this value is not significantly different from complete joint occupancy of the *Ca*(1) and *Ca*(2) sites; in subsequent stages of refinement, the occupancies of these two sites were refined with the constraint that the sum of the occupancies is 1.0. This constraint allowed independent refinement of the anisotropic-displacement factors at the *Ca*(1) and *Ca*(2) sites. We also tried models with the *Ca*(2) site occupied by (H_2O), but refinement led to significantly higher *R* indices (3.1%), and the equivalent isotropic-displacement factor for (H_2O) was 0.00.

(2) The C atoms and one of the coordinating O atoms showed indications of partial occupancy (large displace-

TABLE 1. MISCELLANEOUS INFORMATION FOR DEHYDRATED WYARTITE

a (Å)	11.2610(6)	crystal size (μm)	150 × 96 × 14
b	7.0870(4)	radiation/filter	Mo*K*α / Graphite
c	16.8359(10)	Total no. of I_o	13000
V (Å^3)	1343.6(2)	Unique reflections	2045
Space group	*Pmcn*	*R*(merge) (%)	2.0
Z	4	R_1 ($\vert F_o\vert > 4\sigma_F$) (%)	2.9
D_{calc} (g.cm^{-3})	5.01	wR_2 (F_o^2) (%)	10.2
μ (mm^{-1})	36.5	Max/min in final ΔF map* (*e*/Å^3)	3.0/–2.6

$R_1 = \Sigma(|F_o|-|F_c|) / \Sigma|F_o|$ $\quad wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$

$w = [\sigma^2(F_o^2) + (0.0837\ YP^2)]^{-1}$ $\quad P = [\{\max(0,F_o^2)\} + 2F_c^2] / 3$

* close to *U*(2).

TABLE 2. ATOM POSITIONS AND DISPLACEMENT FACTORS FOR DEHYDRATED WYARTITE

Site	*x*	*y*	*z*	U_{11}	U_{12}	U_{33}	U_{23}	U_{13}	U_{12}	$U_{eq/iso}$	*E**	*SP***
U(1)	–0.06061(2)	0.88930(3)	0.26385(2)	0.0077(2)	0.0072(2)	0.0190(2)	–0.0008(1)	0.0013(1)	–0.0001(8)	0.0113(1)	1	1
U(2)	1/4	0.89101(5)	0.20930(3)	0.0064(2)	0.0075(2)	0.0198(2)	–0.0011(1)	0	0	0.0112(1)	1/2	1
Ca(1)	1/4	0.2881(11)	0.4443(3)	0.0312(22)	0.051(4)	0.020(2)	0.004(2)	0	0	0.0343(14)	1/2	0.70(1)
Ca(2)	1/4	0.3941(16)	0.4537(5)	0.029(4)	0.022(5)	0.006(3)	0.003(4)	0	0	0.019(2)	1/2	0.30(1)
O(1)	0.1166(6)	0.3712(8)	0.3367(4)	0.014(3)	0.032(3)	0.026(4)	0.007(3)	0.000(2)	–0.005(2)	0.024(1)	1	1
O(2)	–0.0055(6)	0.9067(8)	0.3647(4)	0.027(3)	0.026(3)	0.020(3)	–0.003(2)	0.004(2)	–0.006(2)	0.0242(13)	1	1
O(3)	0.1087(5)	0.7068(8)	0.2326(4)	0.009(2)	0.014(3)	0.041(4)	–0.001(2)	0.001(2)	0.002(2)	0.0213(14)	1	1
O(4)	0.1032(5)	0.0698(8)	0.2212(4)	0.014(3)	0.009(2)	0.026(4)	0.003(2)	0.003(2)	0.000(2)	0.0165(12)	1	1
O(5)	–1/4	0.8874(10)	0.3158(6)	0.005(2)	0.027(4)	0.025(5)	0.004(4)	0	0	0.0190(18)	1/2	1
OW(1)	1/4	0.9314(16)	0.3555(6)	0.057(7)	0.057(6)	0.012(5)	–0.000(5)	0	0	0.042(3)	1/2	1
C	1/4	0.6211(19)	0.5337(9)	0.031(9)	0.014(7)	0.076(13)	0.017(8)	0	0	0.040(5)	1/2	0.70(1)
O(7)	1/4	0.626(2)	0.4588(9)	0.081(12)	0.089(9)	0.044(8)	–0.004(8)	0	0	0.072(4)	1/2	1
O(8)	1/4	0.468(2)	0.5723(9)	0.109(12)	0.105(9)	0.077(9)	0.050(8)	0	0	0.097(4)	1/2	1
O(9A)	1/4	0.745(3)	0.5852(14)	–	–	–	–	–	–	0.083(6)	1/2	0.70(1)
O(9B)	1/4	1.074(6)	0.511(3)	–	–	–	–	–	–	0.083(6)	1/2	0.30(1)
OW(2)	0.0530(17)	0.222(3)	0.4848(14)	–	–	–	–	–	–	0.030(7)	1	0.33(2)

* *E* = equipoint fraction; ** Site occupancy: values given are in accord with formula (2), see text.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN DEHYDRATED WYARTITE

U(1)–O(1)a	1.811(7)		*Ca*(1)–O(1)	2.425(8)	×2
U(1)–O(2)	1.811(7)		*Ca*(1)–OW(1)	2.926(13)	
U(1)–O(3)	2.363(6)		*Ca*(1)–O(7)	2.403(15)	
U(1)–O(3)a	2.314(6)		*Ca*(1)–O(8)	2.50(2)	
U(1)–O(4)a	2.327(6)		*Ca*(1)–OW(2)	2.37(2)	×2
U(1)–O(4)b	2.356(6)				
U(1)–O(5)	2.305(4)		<*Ca*(1)–O>	2.49	
U(2)–O(3)	2.095(6)	×2	*Ca*(2)–O(1)	2.482(10)	×2
U(2)–O(4)b	2.092(6)	×2	*Ca*(2)–O(8)	2.07(2)	
U(2)–OW(1)	2.476(11)		*Ca*(2)–O(9B)	2.47(9)	
U(2)–O(8)c	2.512(19)				
U(2)–O(9A)c	2.301(23)				
O(7)–*C*–O(8)	125(2)		*C*–O(7)	1.262(17)	
O(7)–*C*–O(9A)	131(2)		*C*–O(8)	1.262(15)	
O(8)–*C*–O(9A)	104(2)		*C*–O(9A)	1.236(17)	
<O–*C*–O>	120		<*C*–O>	1.253	

ment-factors), and site-scattering refinement resulted in site occupancy significantly less than 1.0 (Table 2). Thus we constrained the occupancies of C and O(9A) to be equal during site-occupancy refinement.

(3) Two anions, O(9A) and O(9B), are only 2.13 Å apart, and therefore they cannot be occupied simultaneously. Site-population refinement indicated that the site occupancies of these two sites sum (approximately) to 1.0, and hence the sum of the occupancies of O(9A) and O(9B) were constrained to 1.0 during refinement.

(4) One anion, subsequently identified as (H_2O) on bond-valence criteria, is only partly occupied, and the site population was unconstrained in the refinement.

Full-matrix least-squares refinement of all variables (including all the site-population parameters discussed above) converged to an R_1 index of 2.82%. As discussed below, the bond-valence sums around the *Ca*(1) and *Ca*(2) sites are significantly less than the ideal values of 2.0 valence units (*vu*), and hence we refined the structure also in space group $P2_1cn$. The final *R* index for this space group is 2.52%, but several soft constraints were necessary in order to obtain sensible U–O_{ur} distances, and the sums of the bond valences incident at *Ca*(1) and *Ca*(2) were only marginally improved. Thus we give the results for the space group *Pmcn*. Final atom coordinates are given in Table 2, anisotropic-displacement parameters for the cations in Table 3, selected interatomic distances and angles in Table 4, and bond valences in Table 5. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Description of the Structure

Cation sites

There are two symmetrically distinct *U* sites, each occupied by U. The *U*(1) site is surrounded by seven anions in a pentagonal-bipyramidal arrangement. The apical U–O bonds are ~1.81 Å long, forming a nearly linear $(U^{6+}O_2)^{2+}$ uranyl group that is linked to five meridional anions between 2.306 and 2.365 Å. This arrangement is typical for U^{6+} (Burns *et al*. 1997a), and the resultant incident bond-valence sum at the *U*(1) site is 6.09 *vu* (Table 4), in accord with the presence of hexavalent U at this site. The *U*(2) site is coordinated by seven or six anions, depending on the local (short-range) arrangement of coordinating anions and adjacent interstitial Ca^{2+} cations. Where [7]-coordinated, *U*(2) is involved in four short (2.093–2.098 Å) and three long (2.337–2.497 Å) bonds, and the sum of the incident bond-valence is 5.10 *vu*, in accord with the presence of U^{5+}, as found for wyartite. In local configurations where the (CO_3) group is absent, the U^{5+} cation at the *U*(2) site links to an (OH) group, which is not present where the (CO_3) group does occur. This is the O(8) anion, which where bonded to *Ca*(1), is a ligand of the (CO_3) group, and where bonded to *Ca*(2), is an (OH) group. In the latter situation, the coordination of *U*(2) is reduced to [6]. Inspection of Table 4 indicates that removal of O(9) as a ligand for U^{5+} results in a reduction of the bond valence incident at *U*(2) to 4.52 *vu*. However, most of the other anions coordinating *U*(2) show large anisotropic components in their displacement parameters, suggesting that *U*(2)–O bonds shorten where U^{5+} at *U*(2) becomes [6]-coordinated. There is one *C* site that is occupied by C^{4+} and surrounded by three O-atoms arranged at the vertices of a triangle with a <*C*–O> distance of 1.225 Å and a <O–C–O> angle of 120°; the occupancy of the central C^{4+} and coordinating anions is 0.70(1).

There are two symmetrically distinct *Ca* sites, each partly occupied by Ca^{2+}, such that the sum of the joint occupancies is 1.0: *Ca*(1) = 0.70(2), *Ca*(2) = 0.30(2), the former value similar to the occupancy of the (CO_3) group. Where the *Ca*(1) site is occupied, the central Ca atom is coordinated by seven anions, as shown in Figure 1; Ca bonds to two uranyl O-atoms [O(1) × 2] of the *U*(1) polyhedron, one (H_2O) group linked to the U^{5+} cation at the *U*(2) site [OW(1)], two anions belonging to the group [O(7) and O(8)] and two (H_2O) groups [OW × 2] that do not bond to any other cations. The bond valence incident at the *Ca*(1) site (Table 4) is somewhat low at 1.78 *vu*; this may be the result of the extensive disorder in this structure, but we note that the *Ca* site in wyartite (Burns & Finch 1999) also has a low incident bond-valence sum (1.85 *vu*). Where the *Ca*(2) site is occupied, the (CO_3) is not present locally, and O(7) and O(8) become (OH) groups. The *Ca*(2) site (Fig. 1b) is only [5]-coordinated (Table 4) with an incident bond-valence of ~1.0 *vu*. However, there is smeared electron-density around the *Ca*(2) site, which suggests that there are additional (H_2O) groups disordered around this site (because even ordered sites would have occupancies of only ~0.3; our inability to resolve these disordered groups is not surprising).

TABLE 4. BOND-VALENCE (*vu*) TABLE* FOR DEHYDRATED WYARTITE

	U(1)	*U*(2)	*Ca*(1)	*C*	Σ	Anion
O(1)	1.60		0.28$^{\times2}$↓		1.88	O
O(2)	1.58				1.58	O
O(3)	0.55					
	0.61	0.91$^{\times2}$↓			2.07	O
O(4)	0.59					
	0.55	0.92$^{\times2}$↓			2.06	O
O(5)	0.61$^{\times2}$→				1.22	(OH)
OW(1)		0.44	0.10		0.54	(H_2O)
O(7)			0.30	1.33	1.63	O
O(8)		0.42	0.22	1.33	1.97	O
O(9A)		0.58		1.33	1.91	O
O(9B)						(H_2O)
OW(2)			0.30$^{\times2}$↓		0.30	(H_2O)
Σ	6.09	5.10	1.78	3.99		

* Calculated with the parameters of Burns *et al.* (1997a) for U--O, Brown & Altermatt (1985) for Ca–O, and with Pauling bond-strengths for C–O bonds.

Structural unit

The *U*(1)ϕ_7 pentagonal bipyramid shares two edges with other pentagonal bipyramids to form a chain extending in the *b* direction with a repeat distance of 7.087 Å (= *b*). Chains adjacent in the *a* direction link by sharing corners to form a continuous sheet of pentagonal bipyramids, and additional linkage in the plane of the sheet is provided by the *U*(2)ϕ_{6-7} polyhedron that shares edges and corners with adjacent *U*(1)ϕ_7 pentagonal bipyramids (Fig. 2). Moreover, the *U*(2)ϕ_{6-7} polyhedron shares an edge with the (CO_3) group where

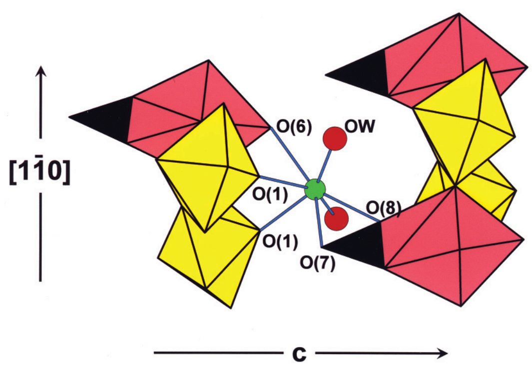

FIG. 1. Linkage of {*U*(2)O_6} polyhedra (red) and (CO_3) triangles (black), and the coordination details of the *Ca*(1) site in dehydrated wyartite; yellow polyhedra: {*U*(1)O_7} groups, OW sites [(H_2O) groups] are shown as red circles, the *Ca*(1) site is shown as a green circle.

TABLE 5. UNIT-CELL PARAMETERS FOR THREE ORTHORHOMBIC Ca-URANYL CARBONATES

	wyartite	dehydrated wyartite	urancalcarite
a (Å)	11.2706(8)	11.2610(6)	15.42(3)
b	7.1055(5)	7.0870(4)	16.08(4)
c	20.807(1)	16.8359(10)	6.970(6)
V (Å^3)	1666.3(3)	1343.6(2)	1728(6)
Space group	$P2_12_12_1$	*Pmcn*	$Pbn2_1$
Reference	1	2	3

References: (1) Burns & Finch (1999), (2) this study, (3) Deliens & Piret (1984).

the latter is present. This sheet is topologically identical to the analogous sheet in wyartite (Burns & Finch 1999) and β-U_3O_8 (Burns 1999).

Interstitial linkage

The structural units stack in the *c* direction. As structural units are repeated by a *c*-glide operation, they repeat by simple translation every other sheet, with a consequent *c*-repeat of 16.8 Å. Adjacent sheets are linked directly by *Ca*(1)ϕ_7 polyhedra (Fig. 3), the (CO_3) groups linking the *U*(2)ϕ_7 and *Ca*(1)ϕ_7 polyhedra (Fig. 1).

The Chemical Composition of Dehydrated Wyartite

Ignoring the partial occupancy of the carbonate group [and assuming that the occurrence of vacancies at the *Ca*(1) site and the occurrence of the partly occupied *Ca*(2) site are related to the partial occupancy of the (CO_3) group], we may write the ideal formula of dehydrated wyartite as Ca U^{5+} $(U^{6+}O_2)^{2+}{}_2$ (CO_3) O_4 (OH) $(H_2O)_3$, assuming full occupancy for the *W*(1) and *W*(2) sites. The considerable disorder and partial occupancies of sites in dehydrated wyartite make determination of the exact formula somewhat more complicated. Absence of the (CO_3) group means less negative charge in the formula, and electroneutrality requires compensation. There are two possibilities for such compensation: (1) the presence of lower valence-states for U (*i.e.*, less positive charge), or (2) retention of simple anions that were part of the (CO_3) group (*i.e.*, more negative charge).

First, let us consider the possible occurrence of lower valence-states for U. The *U*(1) site is well ordered, and its coordination is not directly affected by loss of the (CO_3) group, and this remains as part of the uranyl ion $(U^{6+}O_2)^{2+}$. The *U*(2) site is coordinated by the O(8) and O(9A) anions; these anions are part of the (CO_3) group and may not be present in the absence of the (CO_3) group. Inspection of Table 4 shows that removal of O(8) and O(9A) from the coordination of *U*(2) will result in a decrease in the bond valence incident at that site to 4.10 *vu*. This will compensate for one of the two negative charges removed by loss of the (CO_3) group, but is not sufficient to maintain electroneutrality by itself. Next, let us consider the possibility that one or more of the O(7), O(8) and O(9A) anions remain on loss of the (CO_3) group. The O(9A) anion is too close to the O(9B) anion for full occupancy of O(9A), leaving us with O(7) and O(8). If these sites were occupied by (OH) where the (CO_3) group is absent, this would introduce $0.3 \times 2 = 0.6$ negative charge [compensating for the loss of 0.3 (CO_3) group]. Alternatively, if only one of the O(7) and O(8) anions were retained as (OH), and coupled with the occurrence of U^{4+} at *U*(2), electroneutrality also would occur, and if the O(8) anion were retained, the U^{4+} would have octahedral coordination.

To summarize, we have two possible candidates for the formula of dehydrated wyartite:

(1) Ca $(U^{4+}{}_{0.3}U^{5+}{}_{0.7})$ $(U^{6+}O_2)^{2+}{}_2$ $(CO_3)_{0.7}$ O_4 $(OH)_{1.3}$ $(H_2O)_{1.6}$

(2) Ca U^{5+} $(U^{6+}O_2)^{2+}{}_2$ $(CO_3)_{0.7}$ O_4 $(OH)_{1.6}$ $(H_2O)_{1.6}$

These formulae have slightly different implications with regard to the refinement of the structure, as the occupancies of the O(7) and O(8) anions are different. Refinement of the structure with the O(7) and O(8) occupancies fixed for the above two formulae led to *R* indices of 2.84 and 2.83%, and equivalent isotropic-displacement factors of O(7) = 0.053(5), O(8) = 0.098(6) and O(7) = 0.072(5), O(8) = 0.097(6) for

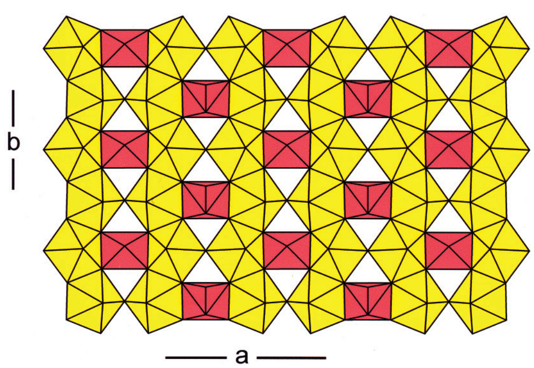

FIG. 2. The arrangement of polyhedra in the structural unit of dehydrated wyartite viewed down the *c* axis. The legend is as in Figure 1; red polyhedra: {*U*(2)O_6} groups.

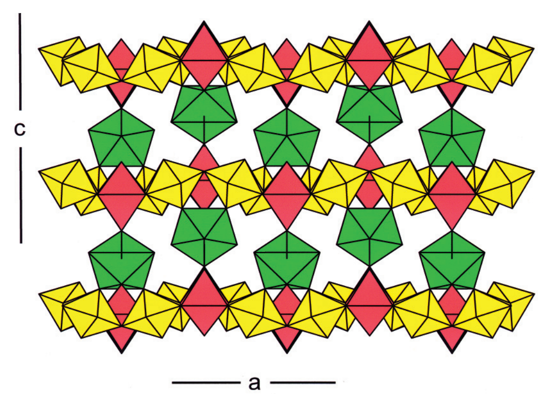

FIG. 3. Linkage of structural units by {*Ca*(1)ϕ_7} polyhedra (green) in the structure of dehydrated wyartite viewed down the *b* axis. The legend is as in Figures 1 and 2.

formulae (1) and (2), respectively. Thus refinement does not distinguish between these two possibilities.

Both of these models have bond-valence implications at the *U*(2), O(7) and O(8) sites. Examination of Table 4 suggests that full occupancy of O(7) is unlikely, as this anion already has a low incident bond-valence sum where bonded to C. The O(8) anion is bonded to cations at *U*(2) and *Ca*(1), with a long-range sum of 0.64 *vu* excluding C (Table 4). Some relaxation, coupled with possible hydrogen bonding from OW (see Fig. 1), may lead to a more reasonable incident bond-valence sum for (OH) occupying this site and acting as a ligand for U^{4+} at the *U*(2) site. The *U*(2)–OW(1) distance would need to increase significantly to maintain a suitable incident bond-valence at *U*(2) [together with other relaxation in around the *U*(2) site].

Clark (1960) noted that wyartite had changed to wyartite II (dehydrated wyartite) after two-and-a-half years in the laboratory, an observation that constrains the possible chemical formula for dehydrated wyartite. The formula for wyartite is Ca U^{5+} $(U^{6+}O_2)^{2+}{}_2$ (CO_3) O_4 (OH) $(H_2O)_7$, and as wyartite alters spontaneously to dehydrated wyartite, it can lose only gaseous constituents (H_2O, CO_2). Removing 0.3 (CO_2) from the formula of wyartite leaves one anion still present, *i.e.*, $(CO_3) \rightarrow (CO_3)_{0.7} + (CO_2)_{0.3} + O_{0.3}$. This mechanism is consistent with loss of O(7) and O(9), and retention of O(8) [as (OH)] as indicated above. Calcium must remain as 1 *apfu* because there is no mechanism for removal of Ca from the structure, and electroneutrality is maintained by reduction of U^{5+} to U^{4+}. This mechanism gives rise to formula (1) above:

$$\text{Ca } U^{5+} (U^{6+}O_2)^{2+}{}_2 (CO_3) O_4 (OH) (H_2O)_7 + 0.15 H_2 \rightarrow \text{Ca } (U^{4+}{}_{0.3}U^{5+}{}_{0.7}) (U^{6+}O_2)^{2+}{}_2 (CO_3)_{0.7} O_4 (OH)_{1.3} (H_2O)_{1.6} + (CO_2)_{0.3} + (H_2O)_{5.4}$$

Alternatively, alteration may occur as follows:

$$\text{Ca } U^{5+} (U^{6+}O_2)^{2+}{}_2 (CO_3) O_4 (OH) (H_2O)_7 \rightarrow \text{Ca } U^{5+} (U^{6+}O_2)^{2+}{}_2 (CO_3)_{0.7} O_4 (OH)_{1.6} (H_2O)_{1.6} + (CO_2)_{0.3} + (H_2O)_{5.1}$$

The second process seems more simple and more probable, but a definitive decision as to the formula cannot be made, although the arguments given here do provide significant constraints on the possible formulae.

Wyartite, Dehydrated Wyartite, Urancalcarite and Ianthinite

Detailed work by Clark (1960) showed that wyartite dehydrates in the laboratory over a period of two and one-half years, and that this alteration preserves the structural orientation of both phases. Clark (1960) suggested that the dehydration of wyartite involves oxidation of U^{4+} to U^{6+}. However, Burns & Finch (1999) showed that wyartite contains U^{5+} and U^{6+}, and not U^{4+} and U^{6+} as suggested by Clark (1960). The results presented here indicate that dehydrated wyartite also contains U^{5+} and U^{6+}, but that it has less (H_2O) [and (CO_3)] than wyartite. The formulae are compared below:

Wyartite: Ca U^{5+} $(U^{6+}O_2)^{2+}{}_2$ (CO_3) O_4 (OH) $(H_2O)_7$

Dehydrated wyartite (*obs.*): Ca U^{5+} $(U^{6+}O_2)^{2+}{}_2$ $(CO_3)_{0.7}$ O_4 $(OH)_{1.6}$ $(H_2O)_{(1.63 + n)}$

Dehydrated wyartite (*ideal*): Ca U^{5+} $(U^{6+}O_2)^{2+}{}_2$ (CO_3) O_4 (OH) $(H_2O)_3$

The composition of dehydrated wyartite (labeled *obs.* above) is deficient in (CO_3) relative to that of wyartite. The end-member composition of dehydrated wyartite (labeled *ideal* above) is written with stoichiometric (CO_3). As some (H_2O) in dehydrated wyartite was found to be strongly disordered and is represented as smeared electron density about the *Ca* sites, the value of (H_2O) in the formula is written as 1.63+n, where n represents this disordered (H_2O). In ideal dehydrated wyartite, we have assumed that the OW(1) and OW(2) sites are completely occupied [to give sufficient coordination to the *Ca*(1) site].

Crystals of dehydrated wyartite in the sample from which we extracted the single crystal for examination show yellow mottling, suggesting partial oxidation. The optic angle, 2*V*, is approximately 40° in homogeneous purple crystals of dehydrated wyartite, increasing to 50 or 60° in crystals with yellow mottling. Complete oxidation of wyartite with no accompanying loss of (CO_3) would result in a composition similar to that of urancalcarite, $Ca(UO_2)_3(CO_3)(OH)_6 (H_2O)_3$ (Deliens & Piret 1984). The unit-cell dimensions within the plane of the structural sheets in wyartite and dehydrated wyartite are similar to the analogous dimensions in the mixed-valence U mineral, ianthinite, $[U^{4+}{}_2(UO_2)_4 O_6(OH)_4(H_2O)_4](H_2O)_5$, but with the *a* dimension doubled in ianthinite (Burns *et al.* 1997b). Ianthinite oxidizes to schoepite (Finch *et al.* 1996a) or metaschoepite (Finch *et al.* 1996b), both of which have cell dimensions (parallel to the structural sheets) similar to those of urancalcarite, but with the *a* cell edge doubled (Table 5). It seems likely that urancalcarite forms as an oxidation product of wyartite (Finch *et al.* 1992). If this is true, the (CO_3) groups in urancalcarite must occupy interlayer sites between the structural sheets.

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