THE CRYSTAL STRUCTURE OF DEHYDRATED WYARTITE,
Ca (CO₃) [U⁵⁺ (U⁶⁺O₂)₂ O₄ (OH)] (H₂O)₃

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ABSTRACT

Dehydrated wyartite from the Shinkolobwe mine, Shaba, Democratic Republic of Congo, ideally Ca (CO₃) [U⁵⁺ (U⁶⁺O₂)₂ O₄ (OH)] (H₂O)₃, is orthorhombic, \( a = 11.2610(6), b = 7.0870(4), c = 16.8359(10) \) Å, \( V = 1343.6(2) \) Å³, 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 MoKα X-radiation on a four-circle single-crystal diffractometer equipped with a CCD detector. The structure consists of neutral sheets of the form \([U⁵⁺ (U⁶⁺O₂)₂ O₄ (OH)]\) that contains edge- and corner-sharing \((U⁶⁺O₂)_7\) polyhedra (\(\phi: O²–, OH–, H₂O\)), two of which are pentagonal bipyramids with five equatorial \(O²–\) and \(OH–\) groups bonded to a central uranyl ion, \((U⁶⁺O₂)_7^2⁺\). The third \(U\) atom is part of a unique \(U⁵⁺O₇\) polyhedron, in which two \(O²–\) anions are part of an interlayer \((CO₃)_2⁻\) group and another is the \(O\) atom of an \(H₂O\) group. The plane of the \((CO₃)\) groups lies perpendicular to the structural sheets, and each \((CO₃)\) group is coordinated to \(U⁵⁺\) in the structural sheet and to \(Ca\) in the interlayer. The sheet is topologically similar to that found in \(β-U₃O₈\), and the sheets are bonded to each other through interlayer \(Ca\) atoms and interlayer \((H₂O)\) 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.

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INTRODUCTION

Dehydrated wyartite is a product of alteration of wyartite, ideally Ca UO$_2$ (UO$_2$O$_2$) (CO$_3$) O$_4$ (OH) (H$_2$O)$_7$ (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 et al. 1995). Wyartite (Burns & Finch 1999) and dehydrated wyartite are of particular interest in this regard as they contain UO$_2^+$, 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 P4 automated four-circle diffractometer equipped with a graphite monochromator, MoKα 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 $I > 10I_{obs}$. A Gaussian absorption-correction was applied to the data, followed by an empirical absorption-correction using the program SADABS (Sheldrick 1998).

<table>
<thead>
<tr>
<th>TABLE 1. MISCELLANEOUS INFORMATION FOR DEHYDRATED WYARTITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>$b$</td>
</tr>
<tr>
<td>$c$</td>
</tr>
<tr>
<td>$V$ ($Å^3$)</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>$Z$</td>
</tr>
<tr>
<td>$D_m$ (g cm$^{-3}$)</td>
</tr>
<tr>
<td>$μ$ (mm$^{-1}$)</td>
</tr>
<tr>
<td>crystal size (µm)</td>
</tr>
<tr>
<td>radiation/filter</td>
</tr>
<tr>
<td>Total no. of f</td>
</tr>
<tr>
<td>Unique reflections</td>
</tr>
<tr>
<td>$R$(merge) (%)</td>
</tr>
<tr>
<td>$R_f$</td>
</tr>
<tr>
<td>$wR_f$ (%)</td>
</tr>
<tr>
<td>Max/min in final $DF$ map (e/Å$^3$)</td>
</tr>
</tbody>
</table>

Note: $R_f = \sum |F_o| - |F_c| |F_o|$, $w = \langle \sigma^2|F_o|^2 + |F_c|^2 \rangle^{-1} - 3$, and $P = \langle \max(|F_o|, |F_c|) \rangle^{2} |F_o|^{-3}$.

* close to U(2).
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 (H2O) 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 $P_{2_1}cn$. The final $R$ index for this space group is 2.52%, but several soft constraints were necessary in order to obtain sensible $U_{ij}$–$O_{ij}$ 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 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 \( \text{vu} \), in accord with the presence of U\(^{5+} \), as found for wyartite. In local configurations where the \((\text{CO}_3)\) group is absent, the U\(^{5+}\) cation at the \( U(2) \) site links to an (OH) group, which is not present where the \((\text{CO}_3)\) group does occur. This is the O(8) anion, which where bonded to \( \text{Ca}(1) \), is a ligand of the \((\text{CO}_3)\) group, and where bonded to \( \text{Ca}(2) \), 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 \( \text{vu} \).

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\(^\circ\); the occupancy of the central C\(^{4+}\) and coordinating anions is 0.70(1).

There are two symmetrically distinct \( \text{Ca} \) sites, each partly occupied by Ca\(^{2+}\), such that the sum of the joint occupancies is 1.0: \( \text{Ca}(1) = 0.70(2) \), \( \text{Ca}(2) = 0.30(2) \), the former value similar to the occupancy of the \((\text{CO}_3)\) group. Where the \( \text{Ca}(1) \) site is occupied, the central Ca atom is coordinated by seven anions, as shown in Figure 1; Ca bonds to two uranyl O-atoms \([O(1) \times 2]\) of the \( U(1) \) polyhedron, one \((\text{H}_2\text{O})\) group linked to the U\(^{5+}\) cation at the \( U(2) \) site \([\text{OW}(1)]\), two anions belonging to the group \([O(7) \text{ and } O(8)]\) and two \((\text{H}_2\text{O})\) groups \([\text{OW} \times 2] \) that do not bond to any other cations. The bond valence incident at the \( \text{Ca}(1) \) site (Table 4) is somewhat low at 1.78 \( \text{vu} \); this may be the result of the extensive disorder in this structure, but we note that the \( \text{Ca} \) site in wyartite (Burns & Finch 1999) also has a low incident bond-valence sum (1.85 \( \text{vu} \)). Where the \( \text{Ca}(2) \) site is occupied, the \((\text{CO}_3)\) is not present locally, and O(7) and O(8) become (OH) groups. The \( \text{Ca}(2) \) site (Fig. 1b) is only \([5]\)-coordinated (Table 4) with an incident bond-valence of ~1.0 \( \text{vu} \). However, there is smeared electron-density around the \( \text{Ca}(2) \) site, which suggests that there are additional \((\text{H}_2\text{O})\) 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).

### Structural unit

The \( U(1)\text{dp} \) 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 \( U(2)\text{dp}_{6} \) polyhedron that shares edges and corners with adjacent \( U(1)\text{dp}_{7} \) pentagonal bipyramids (Fig. 2). Moreover, the \( U(2)\text{dp}_{7} \) polyhedron shares an edge with the \((\text{CO}_3)\) group where

![Fig. 1. Linkage of \{U(2)O\}_5 polyhedra (red) and (CO\(_3\)) triangles (black), and the coordination details of the \( \text{Ca}(1) \) site in dehydrated wyartite; yellow polyhedra: \{U(1)O\}_7\) groups, OW sites \([(\text{H}_2\text{O}) \text{ groups}]\) are shown as red circles, the \( \text{Ca}(1) \) site is shown as a green circle.](image)

### Table 4: Bond-valence (\( \text{vu} \)) Table* for dehydrated Wyartite

<table>
<thead>
<tr>
<th></th>
<th>( U(1) )</th>
<th>( U(2) )</th>
<th>( \text{Ca}(1) )</th>
<th>( \Sigma )</th>
<th>Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>1.60</td>
<td>0.29(^{\text{a}})</td>
<td>1.88</td>
<td>( \text{O} )</td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>1.58</td>
<td>1.58</td>
<td></td>
<td>( \text{O} )</td>
<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>0.55</td>
<td>0.61(^{\text{a}})</td>
<td>2.07</td>
<td>( \text{O} )</td>
<td></td>
</tr>
<tr>
<td>O(4)</td>
<td>0.59</td>
<td>0.59(^{\text{a}})</td>
<td>2.06</td>
<td>( \text{O} )</td>
<td></td>
</tr>
<tr>
<td>O(5)</td>
<td>0.61(^{\text{a}})</td>
<td></td>
<td></td>
<td>( \text{O} )</td>
<td></td>
</tr>
<tr>
<td>OW(1)</td>
<td>0.44</td>
<td>0.10</td>
<td>0.54</td>
<td>( \text{OH} )</td>
<td></td>
</tr>
<tr>
<td>OW(2)</td>
<td>0.30(^{\text{a}})</td>
<td>0.30(^{\text{a}})</td>
<td>0.30(^{\text{a}})</td>
<td>( \text{H}_2\text{O} )</td>
<td></td>
</tr>
</tbody>
</table>

\* Calculated with the parameters of Burns et al. (1997a) for \( \text{U(O)} \), Brown & Altamatt (1985) for \( \text{Ca(O)} \), and with Pauling bond-strengths for \( C=O \) bonds.

### Table 5: Unit-cell Parameters for Three Orthorhombic Ca-Uranyl Carbonates

<table>
<thead>
<tr>
<th></th>
<th>wyartite</th>
<th>dehydrated wyartite</th>
<th>uranacarite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) (Å)</td>
<td>11.2706(8)</td>
<td>11.2610(6)</td>
<td>15.42(3)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>7.1055(5)</td>
<td>7.0370(4)</td>
<td>16.08(4)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>20.9371(1)</td>
<td>16.8359(1)</td>
<td>6.970(6)</td>
</tr>
<tr>
<td>( V ) (Å(^3))</td>
<td>1666.3(3)</td>
<td>1343.6(2)</td>
<td>1728(6)</td>
</tr>
<tr>
<td>Space group</td>
<td>( P2_12_12 )</td>
<td>( Pmn )</td>
<td>( Pmnn )</td>
</tr>
</tbody>
</table>

References: (1) Burns & Finch (1999), (2) this study, (3) Deliers & Piret (1984).
the latter is present. This sheet is topologically identical to the analogous sheet in wyartite (Burns & Finch 1999) and $\beta$-$\text{U}_3\text{O}_8$ (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($1$) polyhedra (Fig. 3), the (CO$_3$) groups linking the U($2$) and Ca($1$) 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$^{\text{U}^{5+}}$($\text{U}^{6+}$O$_2$)$_{2+2}$ (CO$_3$) O$_4$ (OH) (H$_2$O)$_3$, 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 ($\text{U}^{6+}$O$_2$)$_{2+2}$. 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 v.u. 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$^{\text{U}^{4+}}$($\text{U}^{5+}$O$_2$)$_{2+2}$ (CO$_3$)$_{0.7}$ O$_4$ (OH)$_{1.3}$ (H$_2$O)$_{1.6}$
2. Ca U$^{5+}$ ($\text{U}^{6+}$O$_2$)$_{2+2}$ (CO$_3$)$_{0.7}$ O$_4$ (OH)$_{1.6}$ (H$_2$O)$_{1.6}$

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
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 U⁴⁺ to U⁵⁺. However, Burns & Finch (1999) showed that wyartite contains U⁵⁺ and U⁶⁺, and not U⁴⁺ and U⁶⁺ as suggested by Clark (1960). The results presented here indicate that dehydrated wyartite also contains U⁵⁺ and U⁶⁺, but that it has less (H₂O) [and (CO₃)] than wyartite. The formulae are compared below:

**Wyartite:** Ca U⁵⁺ (U⁶⁺O₂)²⁺₂ (CO₃) O₄ (OH) (H₂O)₇

**Dehydrated wyartite (obs.):** Ca U⁵⁺ (U⁶⁺O₂)²⁺₂ (CO₃)₀.₇ O₄ (OH)₁.₆ (H₂O)₁.₆ + n

**Dehydrated wyartite (ideal):** Ca U⁵⁺ (U⁶⁺O₂)²⁺₂ (CO₃) O₄ (OH) (H₂O)₇

The composition of dehydrated wyartite in the sample from which we extracted the single crystal for examination showed yellow mottling, suggesting partial oxidation. The optic angle, 2V, 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 (CO₃) would result in a composition similar to that of urancalcarite, Ca(UO₂)₃(CO₃)(OH)₆ (H₂O)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, [U⁴⁺₂(UO₂)₄ O₆(OH)₄(H₂O)₄] (H₂O)₅, but with the a dimension doubled in ianthinite (Burns et al. 1997b). Ianthinite oxidizes to schoepite (Finch et al. 1996a) or meta-schoepite (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 (CO₃) groups in urancalcarite must occupy interlayer sites between the structural sheets.

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