INVESTIGATIONS OF CRYSTAL-CHEMICAL VARIABILITY
IN LEAD URANYL OXIDE HYDRATES. I. CURITE

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ABSTRACT

Structures have been refined for 14 single crystals of curite from various localities in the Democratic Republic of Congo, and for one synthetic crystal grown at 220 °C using hydrothermal techniques. Single-crystal diffraction data were collected using Mo Kα X-radiation and a CCD-based detector mounted on a Bruker three-circle diffractometer. The crystals have orthorhombic symmetry, space group Pnam, and have similar unit-cell parameters: \( a = 12.53 - 12.58 \), \( b = 13.01 - 13.03 \), \( c = 8.39 - 8.40 \) Å. The structures were refined to agreement indices (R) in the range 3.7 to 7.9%. The structures obtained are in good general agreement with earlier studies; they contain uranyl square bipyramids and uranyl pentagonal bipyramids that share edges and corners to form sheets oriented parallel to (100). There are two symmetrically distinct Pb\(^{2+}\) cations and one H\(_2\)O group located in the interlayer. On the basis of the structure refinements, the site occupancy of Pb(1) is slightly deficient, ranging from 89 to 100%, whereas the Pb(2) site occupancy ranges from 57 to 63%. Earlier investigators suggested that hydroxyl occurs in the interlayer of the structure and provides the charge-balance mechanism that permits variation of the Pb content. However, the current study indicates that Pb variability in curite is limited, and supports minor variation in the hydroxyl content of the sheet of uranyl polyhedra as the charge-balancing mechanism. On the basis of the structure refinements, the structural formula for curite may be written as \( \text{Pb}_{3+x}(\text{H}_2\text{O})_2[(\text{UO}_2)_4\text{O}_{4+x}(\text{OH})_{3-x}]_2, Z = 2\), with the constituents of the sheets of uranyl polyhedra enclosed in square braces.

Keywords: curite, uranyl mineral, structure determination, crystal chemistry, uranium, lead.

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INTRODUCTION

Uranyl minerals have recently been the subject of numerous studies owing to their significance in environmental issues: they form in soils contaminated with actinides (Buck et al. 1996), are present in uranium mine and mill tailings (Abdelouas et al. 1999), and are likely to be common products of the alteration of spent nuclear fuel in a geological repository, such as the proposed Yucca Mountain repository in Nevada (Finn et al. 1996, Wronkiewicz et al. 1996). Seven Pb uranyl oxide hydrates have been described as minerals (Table 1). They are commonly associated with the oxidation of geologically old uraninite, owing to the presence of radiogenic
Pb in substantial amounts (Frondel 1958, Finch & Ewing 1992). Recent studies of the crystal chemistry of Pb uranyl oxide hydrates have demonstrated the extraordinary complexity of these minerals (Burns 1997, 1999, Burns & Hanchar 1999).

Study of the crystal structures of Pb uranyl oxide hydrates, and uranyl minerals in general, is difficult because of the common lack of single crystals of suitable size for conventional techniques, as well as the extreme absorption of X-rays by the crystals. The recent introduction of CCD-based detectors of X-rays to mineralogy (Burns 1998b) has permitted the determination of more than a dozen new uranyl structures (Burns 1997, 1998a, c, d, 1999, Burns & Finch 1999, Burns & Hill 2000a, b, Burns & Hanchar 1999, Hill & Burns 1999). This approach has been particularly successful in the case of Pb uranyl oxide hydrates, with the solutions of the structures of masuyite (Burns & Hanchar 1999), vandendriesscheite (Burns 1997), richetite (Burns 1998a), and wölsendorfite (Burns 1999). Previously, the structures were reported for fourmarierite (Piret 1985), sayrite (Piret et al. 1983) and curite (Taylor et al. 1981).

The structure of each Pb uranyl oxide hydrate mineral is now known, but many details of these fascinating structures remain unresolved. Only a single structure analysis has been reported for each mineral, with the exception of curite, for which Mereiter (1979) reported the structure for a synthetic crystal. All involve sheets of uranyl polyhedra, some of which exhibit extraordinary complexity, such as the wölsendorfite and vandendriesscheite sheets, with primitive lattice repeats of 56 and 41 Å, respectively (Burns 1999, 1997). Many involve partial occupancy of Pb sites in the interlayer, suggesting that considerable chemical variation may occur within each structure type. As the basis for developing an understanding of the relationships between the structures of these minerals and their paragenesis, we have undertaken a systematic study of Pb uranyl oxide hydrates from multiple specimens and localities, in order to ascertain the nature of chemical variation within the structures. This contribution is the first in a series that examines the crystal-chemical variations in these minerals, and presents data for 15 crystals of curite (Table 2).

### Previous Studies

The structure of curite was reported for a synthetic crystal (Mereiter 1979), and later for a natural crystal (Taylor et al. 1981). Partial occupancies of Pb sites in the interlayers were observed in both studies (Table 3). The structural formula

$$[\text{Pb}_{8-x}(\text{OH})_{4-2x}(\text{H}_{2}\text{O})_{2x}]\text{[(UO}_{2}\text{)}_{8}\text{O}_{8}(\text{OH})_{6}]$$

was suggested for curite (Mereiter 1979). In this formula, the composition of the sheet is fixed, and charge balance is attained by assuming that (OH$^-$) occurs in the interlayer and is bonded to Pb$^{2+}$.

### Table 1. Crystallographic and Compositional Data for the Seven Pb Uranyl Oxide Hydrate Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>S.G.</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Pb/U</th>
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<tr>
<td>wölsendorfite</td>
<td>Ccmn</td>
<td>14.131</td>
<td>13.885</td>
<td>55.969</td>
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<td></td>
<td></td>
<td>1.25</td>
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<tr>
<td>sayrite</td>
<td>P2_1/c</td>
<td>10.704</td>
<td>6.960</td>
<td>14.533</td>
<td>116.81</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>curite</td>
<td>Pbau</td>
<td>12.551</td>
<td>13.003</td>
<td>8.390</td>
<td></td>
<td></td>
<td></td>
<td>1.267</td>
</tr>
<tr>
<td>massyite</td>
<td>Pn</td>
<td>12.241</td>
<td>7.008</td>
<td>6.983</td>
<td>96.402</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fourmarierite</td>
<td>R32</td>
<td>13.896</td>
<td>6.400</td>
<td>14.293</td>
<td></td>
<td></td>
<td></td>
<td>1.49</td>
</tr>
<tr>
<td>richetite</td>
<td>Fd3m</td>
<td>20.839</td>
<td>12.109</td>
<td>16.3450</td>
<td>103.87</td>
<td>115.37</td>
<td>90.27</td>
<td>1.445</td>
</tr>
<tr>
<td>vandendriesscheite</td>
<td>Piba</td>
<td>14.116</td>
<td>41.478</td>
<td>14.5347</td>
<td></td>
<td></td>
<td></td>
<td>1.36</td>
</tr>
</tbody>
</table>


### Table 2. Information Pertaining to Crystals for Structure Determination

<table>
<thead>
<tr>
<th>Specimen*</th>
<th>Locality</th>
<th>Crystal size (mm)</th>
<th>Frame width (° in n)</th>
<th>Exposure time (s/frame)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JVS4338</td>
<td>Shinkolobwe</td>
<td>0.27±0.01×0.01</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>JVS4331</td>
<td>Swaziland</td>
<td>0.3±0.02×0.02</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>JVS901</td>
<td>Shinkolobwe</td>
<td>0.36±0.06×0.05</td>
<td>0.15</td>
<td>60</td>
</tr>
<tr>
<td>JVS4331(b)</td>
<td>Swaziland</td>
<td>0.14±0.03×0.04</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>JVS6132</td>
<td>Shinkolobwe</td>
<td>0.40±0.02×0.02</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>CMNMC303997</td>
<td>Shinkolobwe</td>
<td>0.26±0.05×0.05</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>CMNMC301992</td>
<td>Shinkolobwe</td>
<td>0.18±0.30×0.30</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>CMNMC301993</td>
<td>Shinkolobwe</td>
<td>0.15±0.03×0.03</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>CMNMC302099</td>
<td>Shinkolobwe</td>
<td>0.10±0.04×0.04</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>FC8</td>
<td>Shinkolobwe</td>
<td>0.28±0.04×0.04</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>M41067</td>
<td>Shinkolobwe</td>
<td>0.30±0.06×0.04</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>FC5</td>
<td>Shinkolobwe</td>
<td>0.26±0.04×0.04</td>
<td>0.3</td>
<td>30</td>
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<tr>
<td>FC11</td>
<td>Shinkolobwe</td>
<td>0.22±0.04×0.04</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>M14266</td>
<td>Shinkolobwe</td>
<td>0.09±0.02×0.02</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>SYN</td>
<td>Synthetic</td>
<td>0.18±0.03×0.03</td>
<td>0.3</td>
<td>60</td>
</tr>
</tbody>
</table>

* Sources of samples: JVS: Prof. Joseph V. Smith; CMNMC: Canadian Museum of Nature; FC: Mr. Forrest Curaten; M: Royal Ontario Museum.
CRYSTAL—CHEMICAL VARIABILITY OF CURITE

This formula does not recognize Pb variability, but it also involves (OH)\(^{-}\) variations within the interlayer. Significantly, (OH)\(^{-}\) ↔ O\(^{2-}\) substitution within the sheet of uranyl polyhedra also is suggested by the formula.

EXPERIMENTAL METHODS

Specimens of curite were provided by the Canadian Museum of Nature, the Royal Ontario Museum, Prof. Joseph V. Smith, and Mr. Forrest Cureton. Crystals of synthetic curite also were obtained by hydrothermal techniques developed by Mereiter (1979). Starting materials were uranyl nitrate, lead oxide and ultrapure water, which were combined and heated at 220°C for two weeks in a Teflon-lined Parr bomb.

X-ray diffraction

Well-formed acicular crystals of curite were chosen for X-ray-diffraction experiments. Single-crystal diffraction data were collected for each using MoKα X-radiation and a CCD-based detector mounted on a Bruker three-circle diffractometer (Burns 1998b). Localities and details of the data collection are listed in Table 2. The raw data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. Each dataset was corrected for absorption; where well-developed faces bounded the crystals, Gaussian interpolation was used, whereas semi-empirical corrections based upon the intensities of equivalent reflections were used for crystals with less-well-defined faces. The structures were refined in space group \(Pnam\) using the Bruker SHELXTL software package. Refinement began with isotropic displacement parameters for all atoms, followed by conversion to anisotropic displacement parameters for the U and Pb atoms. The final cycles of refinement included the Pb occupancies, and gave agreement indices \(R\) ranging from 3.7% to 7.9% (Table 3). Unit-cell parameters and Pb occupancies for each crystal are listed in Table 3, together with the corresponding final \(R\) value, and final atomic parameters are provided in Table 4. Observed and calculated structure-factors for each crystal are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Electron-microprobe analysis

The synthetic crystal for which X-ray-diffraction data were obtained was mounted in the center of an aluminum tube with epoxy. The crystal was hand-polished and coated with carbon. The elemental analysis was done using an electron microprobe (JEOL Superprobe 733) equipped with four wavelength-dispersion spectrometers and operated at 15 kV at the Canadian Museum of Nature. A beam current of 20 nA and beam diameter of 20 \(\mu\)m was used. Synthetic UO\(_2\) and crocoite were used as standards for U and Pb, respectively. The data were collected for 25 seconds for each element and processed using the Tracor Northern Program 5500 and 5600 software, and ZAF correction using the PAP correction program (C. Davidson, CSIRO, pers. commun.). The results of the chemical analysis are given in Table 5, with H\(_2\)O determined on the basis of stoichiometry.

RESULTS

The results of the current refinements confirm the structures given by Mereiter (1979) and Taylor et al. (1981), although our study has provided insight into Pb variability in curite, and details of the charge-balancing mechanism.
Cation polyhedra

The structure of curite contains three symmetrically unique U atoms, each of which is strongly bonded to two atoms of oxygen, forming approximately linear uranyl ions (UO$_2$)$_{2+}$ (designated $\text{Ur}^{2+}$) with $<\text{U–O}_{\text{Ur}}>$ $\approx$ 1.8 Å (Table 6). This uranyl geometry is typically observed in the structures of U$^{6+}$-bearing phases (Burns et al. 1997). The U$^{6+}$ cations are coordinated by additional anions, forming $\text{Ur}(1)_{\text{O}}$, $\text{Ur}(2)_{\text{O}}$, and $\text{Ur}(3)_{\text{O}}$ polyhedra, respectively [$\phi$: O$_2^-$ or (OH)$^-$]. The U(1) cation is coordinated by three atoms of oxygen and one (OH)$^-$ group arranged at the equatorial positions of a uranyl square bipyramid with $<\text{U–O}_{\text{eq}}>$ (eq: equatorial) bond lengths ranging from 2.25 to 2.27 Å. The U(2) and U(3) cations are both coordinated by three atoms of oxygen and two (OH)$^-$ groups, giving uranyl pentagonal bipyramids. Bond lengths $<\text{U–O}_{\text{eq}}>$ and $<\text{U–(OH)}>$ range from 2.32 to 2.34 Å and 2.34 to 2.35 Å, respectively, except for crystal M14266, in which an unusually short mean bond-length of 2.28 Å was observed for U(2) (Table 6).

There are two distinct Pb sites, and one symmetrically distinct H$_2$O site in the curite structure. Both of the Pb(1) and Pb(2) sites are coordinated by six O$_\text{Ur}$ atoms, one equatorial oxygen atom of uranyl polyhedra, and two H$_2$O groups, with $<\text{Pb–O}_{\text{eq}}>$ and $<\text{Pb–(OH)}>$ ranging from 2.77 to 2.79 and from 2.75 to 2.77 Å, respectively (Table 6). The geometries of the Pb polyhedra are distorted owing to the electron lone-pair stereoelectronicity of Pb$^{2+}$ (Fig. 1).
Structural connectivity

The $Ur_{9}$ polyhedra share edges and corners to form symmetrically equivalent sheets that are oriented parallel to (100) (Fig. 2) at $x \approx 0.25$ and $x \approx 0.75$ (Fig. 3). The Pb$^{2+}$ cations and the H$_2$O group are located in the interlayer and link adjacent sheets (Fig. 3). Each Pb(1)$f_{9}$ polyhedron shares two faces (each contains two O$_{Ur(3)}$ atoms and one H$_2$O group) with Pb(2)$f_{9}$ polyhedra, forming a chain of alternating Pb(1)$f_{9}$ and Pb(2)$f_{9}$ polyhedra that is parallel to [001].

Variation of unit-cell parameters

The volume of the unit cell decreases with increasing Pb in the interlayer, although the trend is weak (Fig. 4). This decrease presumably occurs because of the increased bonding between the sheets of uranyl polyhedra as Pb enters the interlayer, which tends to pull the sheets closer together.
Site-occupancy refinement for the Pb sites indicates that both are only partially occupied in all of the crystals studied (Table 3). The total Pb content ranges from 5.78 to 6.66 atoms per unit cell, with the highest value obtained for the synthetic crystal. These results are consistent with earlier findings. Mereiter (1979) reported 6.56 Pb per unit cell in synthetic curite. Taylor et al. (1981) reported that a crystal from Jabiru, Northern Territory, Australia contains 6.04 Pb per unit cell.

Mereiter (1979) presented the ideal formula of the sheet of uranyl polyhedra in curite as [(UO$_2$)$_8$O$_8$(OH)$_6$]$^{12-}$. The sheet formula is confirmed by the current work; bond-valence analyses readily distinguish among O, (OH)$^-$ and H$_2$O (Table 7), and indicate that there are 48 O$^{2-}$ and 12 (OH)$^-$ in the unit cell, all of which are contained within the sheets of uranyl.
We examined the variation of bond-valence sums at the anion sites, but no substantial supporting trends of the substitution $O^{2-} \rightarrow (OH)^-$ resulted, presumably because of the limited Pb variability. Our study of the crystal chemistry of fourmarierite, which exhibits substantially more variation in Pb content, provided significant evidence of $O^{2-} \rightarrow (OH)^-$ substitution in the sheets of uranyl polyhedra (Li & Burns 2000). It seems likely that $O^{2-} \rightarrow (OH)^-$ substitution within the sheets of uranyl polyhedra is the charge-balancing mechanism that permits limited variation of the Pb content of curite.

### Structural formula

The structure formula calculated for the synthetic crystal on the basis of the electron-microprobe results is $Pb_{3.08} (H_2O)_2 [(UO_2)_4 O_4 (OH)_3]_2$, $Z = 2$. The Pb:U ratio is 0.38, which is close to the value of 0.42 obtained from the X-ray structure refinement for the same crystal, and within the cluster of Pb:U ratios of 0.36 to 0.42 for all curite crystals in the current study.

On the basis of the results for the fifteen crystals of curite, the structural formula may be written as $Pb_{3x} (H_2O)_2 [(UO_2)_4 O_{4x} (OH)_{3x-1}]$. This formula is consistent with the proposed charge-balancing mechanism.

### Acknowledgements

This research was supported by the National Science Foundation (EAR98-04723). We are grateful to the Canadian Museum of Nature, the Royal Ontario Museum, Prof. Joseph V. Smith, and Mr. Forrest Cureton for providing the specimens used in this study. Mr. Robert Gault, Canadian Museum of Nature, provided electron-microprobe access and expertise. We thank Drs. D.J. Wronkiewicz and J.M. Hughes for their reviews, and R.F. Martin for editing the manuscript.

### References


### TABLE 7: BOND VALENCE* (x) ANALYSIS FOR SYNTHETIC CURITE

|        | U(1) | U(2) | Zr(1) | Pb(1) | Pb(2) | $\Sigma$
|--------|------|------|-------|-------|-------|--------
| U(1)   | 0.87±0.04 | 0.85±0.04 | 0.65±0.04 | 2.07±0.04 |
| U(2)   | 1.48±0.04 | 1.79±0.04 | 0.66±0.04 | 1.79±0.04 |
| Zr(1)  | 1.50±0.04 | 1.77±0.04 | 0.23±0.04 | 1.77±0.04 |
| Pb(1)  | 1.56±0.04 | 1.71±0.04 | 0.16±0.04 | 1.71±0.04 |
| Pb(2)  | 0.57±0.04 | 1.99±0.04 | 0.26±0.04 | 1.99±0.04 |

*Bond-valence parameters for $U^{4+}$ from Burns et al. (1997) and for $Pb^{2+}$ from Brown & Alternatt (1985). Bond-valence contributions to the anion sums from Pb-O bonds have been scaled by the corresponding occupancy of each Pb site.

polycrystals. If the interlayer contains only Pb and H$_2$O, then the ideal formula of the sheet requires 6.0 Pb per unit cell for electroneutrality. The observed variability in the amount of Pb must therefore involve additional substitutions.

Charge balance may be achieved either by the addition of a charged species to the interlayer or by modification of the charge of the sheet polyhedra by the substitutions $O^{2-} \rightarrow (OH)^-$ or $(OH)^- \rightarrow O^{2-}$ (or both). First consider the possibility of substitution of a charged species into the interlayer. Difference-Fourier maps did not reveal additional sites in the interlayer, indicating that the most feasible substitution is $(OH)^- \rightarrow H_2O$ at the H$_2$O(3) site. Note that this substitution may only provide charge balance for those crystals containing more than 6 Pb per unit cell. Assuming that all Pb sites are locally occupied, the H$_2$O(3) oxygen atom is bonded to two Pb(1) cations at ~3.14 Å, and two Pb(2) cations at ~2.64 Å. Using the parameters provided by Brown & Alternatt (1985), these bonds result in 0.60 $vu$ incident upon the H$_2$O(3) oxygen atom. This is the maximum bond-valence that can be incident upon the H$_2$O(3) site; typically at least one of the Pb sites will be vacant locally, reducing the valence sum. On the basis of the bond-valence analysis, the H$_2$O(3) site is not consistent with (OH)$^-$ substitution because of the substantial underbonding that would occur. The charge-balancing mechanism involving $(OH)^- \rightarrow H_2O$ substitution in the interlayer is not supported by the data for the fifteen crystals.

The substitutions $O^{2-} \rightarrow (OH)^-$ and $(OH)^- \rightarrow O^{2-}$ within the sheets of uranyl polyhedra potentially provide charge balance for the entire range of Pb concentration in the curite crystals studied. Where there are less than 6 Pb per unit cell, the substitution $(OH)^- \rightarrow O^{2-}$ could occur at any of the O sites in the equatorial positions of uranyl polyhedra [O(1), O(6) and O(9)]. For those crystals with more than 6 Pb per unit cell, the substitution $O^{2-} \rightarrow (OH)^-$ could occur at any of the hydroxyl sites [O(10), O(12)].

Acknowledgements

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References


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