

## CRYSTAL STRUCTURES AND SYNTHESIS OF THE COPPER-DOMINANT MEMBERS OF THE AUTUNITE AND META-AUTUNITE GROUPS: TORBERNITE, ZEUNERITE, METATORBERNITE AND METAZEUNERITE

ANDREW J. LOCOCK<sup>§</sup> AND PETER C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame,  
156 Fitzpatrick Hall, Notre Dame, Indiana, 46556, U.S.A.

### ABSTRACT

Torbernite,  $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{12}$ , zeunerite,  $\text{Cu}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$ , metatorbernite,  $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$  and metazeunerite,  $\text{Cu}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$  were synthesized directly by diffusion in gels or by hydrothermal methods. Single-crystal X-ray-diffraction intensity data were collected at room temperature using  $\text{MoK}\alpha$  radiation and a CCD-based area detector. The crystal structures of the four compounds were solved by direct methods and refined by full-matrix least-squares techniques on the basis of  $F^2$  for all unique reflections to agreement indices  $wR_2$  (torbernite, zeunerite, metatorbernite and metazeunerite) of 5.6, 3.5, 4.8 and 5.1% for all data, and  $R1$  of 2.4, 1.6, 2.0 and 2.3%, calculated for 764, 468, 794 and 1447 unique observed reflections ( $|F_o| \geq 4\sigma_F$ ), respectively. Torbernite is tetragonal, space group  $P4/nmc$ ,  $a$  7.0267(4),  $c$  20.807(2) Å,  $V$  1027.3(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.264(1) g/cm<sup>3</sup>. Zeunerite is isostructural with torbernite,  $a$  7.1797(3),  $c$  20.857(1) Å,  $V$  1075.1(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.391(1) g/cm<sup>3</sup>. The structure of metatorbernite was determined from a merohedrally twinned crystal. It is tetragonal, space group  $P4/n$ ,  $a$  6.9756(5),  $c$  17.349(2) Å,  $V$  844.2(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.689(1) g/cm<sup>3</sup>. Metazeunerite is isostructural with metatorbernite,  $a$  7.1094(1),  $c$  17.416(1) Å,  $V$  880.3(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.869(1) g/cm<sup>3</sup>; the crystal studied also is twinned. These minerals contain the autunite-type sheet, of composition  $[(\text{UO}_2)(\text{PO}_4)]^-$ , which involves the sharing of equatorial vertices of uranyl square bipyramids with phosphate tetrahedra. In each of these structures,  $\text{Cu}^{2+}$  cations are located between the sheets in Jahn–Teller-distorted (4 + 2) octahedra, with short bonds to four  $\text{H}_2\text{O}$  groups in a square-planar arrangement and two longer distances to oxygen atoms of uranyl ions. A symmetrically independent  $\text{H}_2\text{O}$  group is held in each structure only by H-bonding, and in torbernite (and in zeunerite) forms square-planar sets of interstitial  $\text{H}_2\text{O}$  groups both above and below the planes of the  $\text{Cu}^{2+}$  cations. In metatorbernite (and in metazeunerite), the square-planar sets of interstitial  $\text{H}_2\text{O}$  groups are either above or below the planes of the  $\text{Cu}^{2+}$  cations. Bond-length-constrained refinement provided crystal-chemically reasonable descriptions of the H-bonding in the four structures.

**Keywords:** torbernite, zeunerite, metatorbernite, metazeunerite, uranyl phosphate, uranyl arsenate, crystal structure.

### SOMMAIRE

Nous avons synthétisé la torbernite,  $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{12}$ , la zeunérite,  $\text{Cu}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_{12}$ , la métatorbernite,  $\text{Cu}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_8$ , et la métazeunérite,  $\text{Cu}[(\text{UO}_2)(\text{AsO}_4)]_2(\text{H}_2\text{O})_8$ , par diffusion dans des gels ou bien par voie hydrothermale. Les intensités des raies en diffraction X sur monocristal ont été mesurées à température ambiante en utilisant un rayonnement  $\text{MoK}\alpha$  et un détecteur de type CCD. Nous avons résolu la structure des quatre composés par méthodes directes, avec affinement sur matrice entière par techniques de moindres carrés en utilisant les facteurs  $F^2$  pour toutes les réflexions uniques jusqu'à un résidu  $wR_2$  (torbernite, zeunérite, métatorbernite et métazeunérite) de 5.6, 3.5, 4.8 et 5.1% pour toutes les données, et  $R1$  de 2.4, 1.6, 2.0 et 2.3%, calculé pour 764, 468, 794 et 1447 réflexions uniques observées ( $|F_o| \geq 4\sigma_F$ ), respectivement. La torbernite est tétragonale, groupe spatial  $P4/nmc$ ,  $a$  7.0267(4),  $c$  20.807(2) Å,  $V$  1027.3(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.264(1) g/cm<sup>3</sup>. La zeunérite est isostructurale avec la torbernite,  $a$  7.1797(3),  $c$  20.857(1) Å,  $V$  1075.1(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.391(1) g/cm<sup>3</sup>. La structure de la métatorbernite a été déterminée à partir d'un cristal maclé par méroédrisme. Elle est tétragonale, groupe spatial  $P4/n$ ,  $a$  6.9756(5),  $c$  17.349(2) Å,  $V$  844.2(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.689(1) g/cm<sup>3</sup>. La métazeunérite est isostructurale avec la métatorbernite,  $a$  7.1094(1),  $c$  17.416(1) Å,  $V$  880.3(1) Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}}$  3.869(1) g/cm<sup>3</sup>; le cristal qui a servi à l'ébauche aussi est maclé. Ces minéraux contiennent un feuillet de type autunite, de composition  $[(\text{UO}_2)(\text{PO}_4)]^-$ , dans lequel il y a un partage des coins équatoriaux des bipyramides carrées à uranyle avec des tétraèdres de phosphate. Dans chacune des structures, les cations  $\text{Cu}^{2+}$  sont situés entre les feuillets dans des octaèdres rendus difformes (4 + 2) à cause de l'effet de Jahn–Teller, avec des liaisons courtes à quatre groupes  $\text{H}_2\text{O}$  dans un agencement carré planaire, et deux liaisons plus longues aux atomes d'oxygène des ions uranyle. Un groupe

<sup>§</sup> E-mail address: alocock@nd.edu

H<sub>2</sub>O symétriquement indépendant est présent dans chaque structure, lié seulement par liaisons hydrogène, et dans la torbernite (et la zeunerite) forme des agencements planaires carrés de groupes interstitiels de H<sub>2</sub>O par-dessus et par-dessous les plans contenant les cations Cu<sup>2+</sup>. L'affinement des quatre structures avec certaines contraintes à propos des longueurs des liaisons impliquant l'hydrogène a mené à des descriptions cristallographiquement raisonnables des liaisons hydrogène.

(Traduit par la Rédaction)

*Mots-clés:* torbernite, zeunerite, métatorbernite, métazeunerite, phosphate d'uranyle, arsenate d'uranyle, structure cristalline.

## INTRODUCTION

Torbernite and zeunerite, as well as metatorbernite and metazeunerite, belong to the autunite and meta-autunite groups, respectively, which together consist of approximately forty mineral species of hydrated uranyl phosphates and arsenates (Smith 1984, Finch & Murakami 1999). The structures, compositions and stabilities of minerals of the autunite and meta-autunite groups are of interest because of their environmental significance. They are widespread and abundant, and exert an impact on the mobility of uranium in phosphate-bearing systems (Sowder *et al.* 1996) such as uranium deposits (Murakami *et al.* 1997), and soils contaminated by actinides (Buck *et al.* 1996, Roh *et al.* 2000). Minerals of these groups precipitate at reactive barriers that use phosphate to limit the transport of uranium in groundwater (Fuller *et al.* 2002), and their stabilities under conditions of the vadose and saturated zones may determine the long-term effectiveness of such remediation strategies.

## PREVIOUS STUDIES

Minerals of the autunite and meta-autunite groups were first mentioned by von Born, who referred to them as *mica viridis*, or green mica (von Born 1772, cited in Chester 1896, Clark 1993). These groups include some of the earliest described uranium minerals; they were found by Klaproth to contain uranium only eight years after the discovery of that element (Klaproth 1797, 1801). Early research on these minerals is reviewed in Frondel (1958), and the descriptions and localities are summarized in Anthony *et al.* (2000) and Gaines *et al.* (1997). Although the crystal structure of torbernite has not been reported previously, space group *I4/mmm* has been proposed (Goldsztub 1932). Space groups *P4/nnc* and *I4/mmm* have been suggested for zeunerite (Garavelli & Mazzi 1958, Walenta 1964), and Hennig *et al.* (2003) have recently presented a structure refinement for zeunerite in *I4/mmm* involving partially occupied Cu and O positions. The four previous structure refinements for metatorbernite are not in agreement. Models in space groups *P4/nmm* and *P4/n* have both been presented, and the magnitude of the *c* cell dimension of metatorbernite is a matter of dispute: Makarov & Tobelko (1960) *a* 6.95(2) Å, *c* 17.26(2) Å, *P4/nmm*,

*R1* 25%; Ross *et al.* (1964) *a* 6.969(1) Å, *c* 17.306(5) Å, *P4/n*, *R1* 9.7%; Stergiou *et al.* (1993) *a* 6.972(1) Å, *c* 17.277(8) Å, *P4/n*, *R1* 5.6%; Calos & Kennard (1996) *a* 6.950(1) Å, *c* 8.638(4) Å, *P4/n*, *R1* 9.2%. The structure of metazeunerite was reported by Hanic (1960) in space group *P4<sub>2</sub>/nmc*. However, the resulting interatomic distances are in poor agreement with bond lengths experimentally determined by U *L*<sub>III</sub>-edge EXAFS for metazeunerite (Hennig *et al.* 2001, 2003), and with expected U–O distances for well-refined uranyl compounds (Burns *et al.* 1996, 1997, Burns 1999). Hennig *et al.* (2003) recently presented structure refinements for metazeunerite in space groups *P4/ncc*, *c* 17.420(1) Å, and *P4/nmm*, *c* 8.710(1) Å, that involve partially occupied Cu positions in both models, and disordered O positions in the case of *P4/nmm*.

As part of our ongoing research into the structures of uranyl phosphates and arsenates (Locock & Burns 2002a, b, 2003), we have developed methods of synthesis that yield excellent single crystals of torbernite, zeunerite, metatorbernite and metazeunerite. We report their crystal structures herein.

## EXPERIMENTAL

### Crystal synthesis

Crystals of metatorbernite and zeunerite were grown at room temperature over three weeks by slow diffusion of 0.5 M H<sub>3</sub>PO<sub>4(aq)</sub> (metatorbernite) or 0.167 M H<sub>5</sub>As<sub>3</sub>O<sub>10(aq)</sub> (zeunerite), and 0.5 M UO<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>6(aq)</sub> into Cu-bearing silica gels. The gels were formed by the hydrolysis of a mixture (1:10) of (CH<sub>3</sub>O)<sub>4</sub>Si<sub>(liq)</sub> and 0.26 M Cu(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3(aq)</sub> (method modified after: Arend & Connelly 1982, Manghi & Polla 1983, Zolensky 1983, Perrino & LeMaster 1984, Robert & LeFauchoux 1988, Henisch 1988). Crystals of torbernite were grown at ~5°C (Berman 1957) in a similar fashion over two months by slow diffusion of 0.1 M H<sub>3</sub>PO<sub>4(aq)</sub> and 0.1 M UO<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>6(aq)</sub> into a Cu-bearing silica gel formed by the hydrolysis of a mixture (1:10) of (CH<sub>3</sub>O)<sub>4</sub>Si<sub>(liq)</sub> and 0.1 M Cu(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3(aq)</sub>. Crystals of metazeunerite were obtained by hydrothermal reaction of 0.1980 g UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub> (Alfa), 0.0574 g CuCl<sub>2</sub> (Alfa), 0.0546 g H<sub>5</sub>As<sub>3</sub>O<sub>10</sub> (prepared by the method of Walton 1948), and 5.52 g of ultrapure H<sub>2</sub>O<sub>(l)</sub>. The reactants were weighed into a

Teflon-lined Parr acid digestion vessel and heated in a Fisher Isotemp oven from 50(1)°C at a rate of six degrees per hour to 220(1)°C, held at temperature for 24 hours, and cooled back to 50(1)°C at a rate of six degrees per hour. The Parr autoclave was then removed and allowed to cool in air to room temperature. The hydrothermal products consisted of tabular crystals of metazeunerite.

### Single-crystal X-ray diffraction

For each of the four compounds, a suitable crystal (coated in epoxy to forestall dehydration) was mounted on a Bruker PLATFORM three-circle X-ray diffractometer operated at 50 keV and 40 mA, and equipped with either a 4K APEX CCD detector (torbernite and metazeunerite), or an 1K SMART CCD detector (zeunerite and metatorbernite), and a crystal-to-detector distance of ~4.7 cm. A sphere of three-dimensional data was collected at room temperature for each crystal using graphite-monochromatized MoK $\alpha$  X-radiation and frame widths of 0.3° in  $\omega$ , with count-times per frame of 20 seconds for torbernite, and 10 seconds for zeunerite, metatorbernite and metazeunerite. Data for torbernite and metazeunerite were collected for 3.9° ≤

20 ≤ 69.0° in 15 and 8 hours, respectively. Data for zeunerite and metatorbernite were collected for 3.9° ≤ 20 ≤ 56.6°, each over 8 hours. Comparison of the intensities of equivalent reflections measured at different times during data collection showed no significant decay for any of the four compounds. The unit cells (Table 1) were refined using least-squares techniques and 7761 reflections for torbernite, 3993 reflections for zeunerite, 4166 reflections for metatorbernite and 6483 reflections for metazeunerite.

The intensity data were reduced and corrected for Lorentz, polarization, and background effects using the program SAINT (Bruker 1998a). For torbernite and metazeunerite, empirical corrections for absorption were applied using the program SADABS (G. Sheldrick, unpubl.) on the basis of the intensities of equivalent reflections. For zeunerite and metatorbernite, face-indexed analytical corrections for absorption were applied using the program XPREP (Bruker 1998b).

Systematic absences of reflections for torbernite and zeunerite were found to be consistent with space group *P4/nnc* only. For torbernite, 21,082 intensities were collected, of which 2724 were discarded as being inconsistent with the space group. Seven of these discarded intensities were classified as observed, corresponding

TABLE 1. CRYSTALLOGRAPHIC DATA AND DETAILS OF THE STRUCTURE REFINEMENTS

Compound	torbernite	zeunerite	metatorbernite	metazeunerite
<i>a</i> (Å)	7.0267(4)	7.1797(3)	6.9756(5)	7.1094(1)
<i>c</i> (Å)	20.807(2)	20.857(1)	17.349(2)	17.416(1)
<i>V</i> (Å <sup>3</sup> )	1027.3(1)	1075.1(1)	844.2(1)	880.3(1)
Space group	<i>P4/nnc</i>	<i>P4/nnc</i>	<i>P4/n</i>	<i>P4/n</i>
<i>Z</i>	2	2	2	2
Formula*	Cu[(UO <sub>2</sub> (PO <sub>4</sub> )) <sub>2</sub> (H <sub>2</sub> O)] <sub>12</sub>	Cu[(UO <sub>2</sub> (AsO <sub>4</sub> )) <sub>2</sub> (H <sub>2</sub> O)] <sub>12</sub>	Cu[(UO <sub>2</sub> (PO <sub>4</sub> )) <sub>2</sub> (H <sub>2</sub> O)] <sub>8</sub>	Cu[(UO <sub>2</sub> (AsO <sub>4</sub> )) <sub>2</sub> (H <sub>2</sub> O)] <sub>8</sub>
Formula weight (g/mol)*	1009.73	1097.62	937.66	1025.56
$\lambda$ (Å) - MoK $\alpha$	0.71073	0.71073	0.71073	0.71073
<i>F</i> (000)*	918	990	838	910
$\mu$ (mm <sup>-1</sup> )*	17.01	19.16	20.67	23.38
<i>D</i> <sub>calc</sub> (g/mL)*	3.264(1)	3.391(1)	3.689(1)	3.869(1)
Crystal size (mm)	0.06 x 0.06 x 0.06	0.106 x 0.106 x 0.022	0.114 x 0.114 x 0.04	0.2 x 0.1 x 0.04
Crystal morphology	tetragonal dipyramid	square plate	square plate	rectangular plate
Colour	grass green	emerald green	grass green	emerald green
2 $\theta$ range of data collection	3.9 – 69.0°	3.9 – 56.6°	3.9 – 56.6°	3.9 – 69.0°
Data collected	h ± 10, k ± 10, l ± 32	h ± 9, k ± 9, l ± 27	h ± 9, k ± 9, l ± 22	h ± 11, k ± 11, l ± 27
Total reflections	18358	11053	10044	18087
Unique reflections, <i>R</i> <sub>int</sub>	1087, 0.069	685, 0.085	1063, 0.084	1877, 0.055
Unique   <i>F</i> <sub>o</sub>   ≥ 4 $\sigma$ <sub><i>F</i></sub>	764	468	794	1447
Extinction	---	0.00087(12)	0.00125(17)	0.00776(24)
Parameters varied	46	47	77	77
<i>R</i> 1 † for   <i>F</i> <sub>o</sub>   ≥ 4 $\sigma$ <sub><i>F</i></sub>	2.4	1.6	2.0	2.3
<i>R</i> 1 † all data, <i>wR</i> <sub>2</sub> ‡ all data	3.7, 5.6	3.6, 3.5	3.4, 4.8	3.1, 5.1
Goodness of fit all data	1.043	0.961	1.007	0.961
Max. min. peaks (e/Å <sup>3</sup> )	5.6, -1.5	1.4, -0.6	2.1, -1.9	2.8, -3.8

\* Calculated with ideal occupancy of all atomic positions †  $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100$  ‡  $wR2 = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}}{\sum [w(F_o^2)^2]} \times 100$ ,  $w = 1/(\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P)$ , and  $P = 1/3 \max(0, F_o^2) + 2/3 F_c^2$ .

to four unique reflections, all of which are within  $5\sigma$  of the background. Of the 18,358 remaining intensities, 1087 were unique ( $R_{\text{INT}} = 0.069$ ), of which 764 were classified as observed reflections ( $|F_o| \geq 4\sigma_F$ ). For zeunerite, 13,023 intensities were collected, of which 1970 were discarded as being inconsistent with the space group; none of these intensities were classified as observed. Of the 11,053 remaining intensities, 685 were unique ( $R_{\text{INT}} = 0.085$ ), of which 468 were classified as observed reflections ( $|F_o| \geq 4\sigma_F$ ).

Systematic absences of reflections for metatorbernite and metazeunerite were found to be consistent with space groups  $P4/nmm$  and  $P4/n$ ; reasonable displacement parameters were obtained only for solutions in  $P4/n$ . For metatorbernite, 10,044 intensities were collected, of which 1063 were unique ( $R_{\text{INT}} = 0.084$ ), and 794 were classified as observed reflections ( $|F_o| \geq 4\sigma_F$ ). For metazeunerite, 18,087 intensities were collected, of which 1877 were unique ( $R_{\text{INT}} = 0.055$ ), and 1447 were classified as observed reflections ( $|F_o| \geq 4\sigma_F$ ).

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-ray Crystallography, Volume IV* (Ibers & Hamilton 1974). The SHELXTL Version 5 (Bruker 1998c) series of programs was used for the solution and refinement of the crystal structures.

#### Structure solution and refinement

All four structures were solved by direct methods and were refined on the basis of  $F^2$  for all unique data. In the final cycle of each refinement, the mean parameter shift/esd was 0.000. In every structure, possible H atom positions were located in difference-Fourier maps, calculated following refinement of the model. Their positions were refined with the constraint that O–H bond-lengths be  $\sim 0.96 \text{ \AA}$  and with fixed isotropic displacement parameters. The refinements provided a crystallochemically reasonable network of H-bonds in each case.

A structure model for torbernite in space group  $P4/nnc$  including anisotropic displacement parameters for all non-H atoms converged, and gave an agreement index ( $R1$ ) of 2.4%, calculated for the 764 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The final value of  $wR_2$  was 5.6% (Table 1) for all data using the structure-factor weights assigned during least-squares refinement:  $a = 0.0285$  and  $b = 0$ .

A structure model for zeunerite in space group  $P4/nnc$  including anisotropic displacement parameters for all non-H atoms converged, and gave an agreement index ( $R1$ ) of 1.6%, calculated for the 468 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The final value of  $wR_2$  was 3.5% for all data using the structure-factor weights assigned during least-squares refinement:  $a = 0.0147$  and  $b = 0$ .

The initial structure-model for metatorbernite in space group  $P4/n$  gave unusually large uncertainties in interatomic distances, and several significant electron-density peaks were present in the difference-Fourier maps at locations incompatible with additional atomic sites. Inspection of the observed and calculated structure-factors showed that the most disagreeable reflections all had  $F_{\text{obs}}$  greater than  $F_{\text{calc}}$ , consistent with the presence of twinning. Re-examination of the raw intensity data showed that the twinning involved essentially complete overlap of the diffraction patterns that corresponded to each twin component. The twin law  $[010/100/001]$  was applied, and the structure was refined according to published methods (Jameson 1982, Herbst-Irmer & Sheldrick 1998), and resulted in a significant improvement of the agreement index (from 4.9 to 2.0%). The twin-component scale factor refined to 0.508(4). The site occupancy (Hawthorne *et al.* 1995) of the Cu(1) site refined to 88.3(6)% occupied. The final structure-model including anisotropic displacement parameters for all non-H atoms converged, and gave an agreement index ( $R1$ ) of 2.0%, calculated for the 794 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The final value of  $wR_2$  was 4.8% for all data using the structure-factor weights assigned during least-squares refinement:  $a = 0.0182$  and  $b = 1.06$ .

Initial refinement results for the structure of metazeunerite in space group  $P4/n$  were consistent with the presence of twinning, similar to the case for metatorbernite. The twin law  $[010/100/001]$  was applied, and the structure was refined according to published methods (Jameson 1982, Herbst-Irmer & Sheldrick 1998), resulting in a significant improvement of the agreement index (from 5.0 to 2.3%). The twin-component scale factor refined to 0.475(3). The final structure-model including anisotropic displacement parameters for all non-H atoms converged, and gave an agreement index ( $R1$ ) of 2.3%, calculated for the 1447 observed unique reflections ( $|F_o| \geq 4\sigma_F$ ). The final value of  $wR_2$  was 5.1% for all data using the structure-factor weights assigned during least-squares refinement:  $a = 0.0273$  and  $b = 0$ .

The atomic positional parameters and displacement parameters of torbernite, zeunerite, metatorbernite and metazeunerite are given in Tables 2–5 respectively, and selected interatomic distances and angles are in Tables 6–9. Observed and calculated structure-factors for these four compounds are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. Bond-valence sums at the cation and anion sites for the four compounds are in Tables 10–13, and were calculated using the parameters of Burns *et al.* (1997) for  $\text{U}^{6+}$ , Brown & Altermatt (1985) for  $\text{P}^{5+}$ ,  $\text{As}^{5+}$  and  $\text{Cu}^{2+}$ , and Ferraris & Ivaldi (1988) for H (calculated from the donor-to-acceptor distances).

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS ( $\text{\AA}^3$ ) FOR TORBERNITE

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
U(1)	¼	¼	0.4584(1)	0.010(1)	0.009(1)	0.009(1)	0.013(1)	0	0	0
P(1)	¼	-¼	½	0.011(1)	0.008(1)	0.008(1)	0.016(1)	0	0	0
Cu(1)	¼	¼	¼	0.022(1)	0.018(1)	0.018(1)	0.028(1)	0	0	0
O(1)	¼	¼	0.3728(2)	0.017(1)	0.019(1)	0.019(1)	0.012(2)	0	0	0
O(2)	¼	¼	0.5429(2)	0.021(1)	0.024(2)	0.024(2)	0.017(2)	0	0	0
OW(3)	¼	-0.0222(6)	¼	0.036(1)	0.049(3)	0.020(2)	0.040(2)	0	0.021(2)	0
O(4)	0.2194(3)	-0.0762(3)	0.4565(1)	0.016(1)	0.016(1)	0.009(1)	0.022(1)	0.002(1)	-0.003(1)	0.001(1)
OW(5)	0.0205(4)	-0.1667(4)	0.3391(1)	0.025(1)	0.027(1)	0.026(2)	0.023(1)	0.003(1)	0.002(1)	-0.002(1)
H(1)	-0.067(6)	-0.103(7)	0.313(2)	0.050*						
H(2)	0.054(6)	-0.143(7)	0.381(1)	0.050*						
H(3)	0.185(7)	-0.107(6)	0.278(2)	0.050*						

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The anisotropic displacement parameter exponent takes the form:  $-2\pi^2 [h^2a^*U_{11} + \dots + 2hka^*b^*U_{12}]$ .

\* Value constrained during refinement.

TABLE 3. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR ZEUNERITE

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
U(1)	¼	¼	0.4551(1)	0.010(1)	0.009(1)	0.009(1)	0.013(1)	0	0	0
As(1)	¼	-¼	½	0.011(1)	0.009(1)	0.009(1)	0.016(1)	0	0	0
Cu(1)	¼	¼	¼	0.019(1)	0.016(1)	0.016(1)	0.025(1)	0	0	0
O(1)	¼	¼	0.3690(2)	0.019(1)	0.020(2)	0.020(2)	0.017(2)	0	0	0
O(2)	¼	¼	0.5401(2)	0.024(1)	0.028(2)	0.028(2)	0.016(3)	0	0	0
OW(3)	¼	-0.0187(5)	¼	0.036(1)	0.040(2)	0.020(2)	0.047(3)	0	0.021(3)	0
O(4)	0.2091(3)	-0.0669(4)	0.4517(1)	0.018(1)	0.021(2)	0.011(1)	0.023(2)	0.003(1)	-0.004(1)	0.001(1)
OW(5)	0.0162(4)	-0.1649(5)	0.3363(1)	0.026(1)	0.026(2)	0.029(2)	0.025(2)	0.002(1)	0.001(1)	-0.001(1)
H(1)	-0.100(4)	-0.107(7)	0.332(3)	0.050*						
H(2)	0.091(7)	-0.149(8)	0.372(2)	0.050*						
H(3)	0.181(7)	-0.098(6)	0.277(2)	0.050*						

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The anisotropic displacement parameter exponent takes the form:  $-2\pi^2 [h^2a^*U_{11} + \dots + 2hka^*b^*U_{12}]$ .

\* Value constrained during refinement.

## DESCRIPTION OF THE STRUCTURES

Of the four compounds investigated, only torbernite and metatorbernite are described here, as they are isostructural with the corresponding arsenates, zeunerite and metazeunerite, respectively.

Torbernite contains a single symmetrically independent  $U^{6+}$  cation that is part of a linear  $(UO_2)^{2+}$  cation (Table 6, Table 7 for zeunerite). The uranyl ion is coordinated by four additional O atoms arranged at the equatorial positions of a square bipyramid, with the uranyl

ion O atoms at the apices of the bipyramid. Phosphate tetrahedra share the equatorial vertices of uranyl square bipyramids to form the corrugated autunite-type sheet, of composition  $[(UO_2)(PO_4)]^-$  (Fig. 1a), which was originally described by Beintema (1938). Metatorbernite also contains the autunite-type sheet (Fig. 1b), but because of its lower symmetry, there are two similar but symmetrically independent  $U^{6+}$  cations in its structure (Table 8, Table 9 for metazeunerite). Although the topologies of the uranyl phosphate sheets in torbernite and metatorbernite are identical, the stacking of the sheets

TABLE 4. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR METATORBERNITE

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
U(1)	¼	¼	0.0517(1)	0.011(1)	0.010(1)	0.010(1)	0.013(1)	0	0	0
U(2)	¼	¼	0.5513(1)	0.009(1)	0.009(1)	0.009(1)	0.011(1)	0	0	0
Cu(1)*	¼	¼	0.3112(1)	0.016(1)	0.017(1)	0.017(1)	0.015(1)	0	0	0
P(1)	¼	¾	0	0.010(1)	0.009(1)	0.009(1)	0.013(1)	0	0	0
P(2)	¼	¾	½	0.010(1)	0.009(1)	0.009(1)	0.013(1)	0	0	0
O(1)	¼	¼	0.4490(4)	0.019(2)	0.020(3)	0.020(3)	0.018(4)	0	0	0
O(2)	¼	¼	-0.0503(4)	0.021(2)	0.028(3)	0.028(3)	0.008(4)	0	0	0
O(3)	¼	¼	0.6539(5)	0.024(2)	0.025(2)	0.025(2)	0.021(4)	0	0	0
O(4)	¼	¼	0.1564(4)	0.023(2)	0.029(3)	0.029(3)	0.012(4)	0	0	0
O(5)	0.2873(10)	0.9233(6)	0.0522(2)	0.016(2)	0.015(5)	0.011(2)	0.024(3)	-0.002(2)	-0.003(2)	-0.003(2)
O(6)	0.2055(9)	0.9221(6)	0.5519(2)	0.018(2)	0.024(5)	0.011(2)	0.019(3)	-0.003(2)	0.003(2)	0.002(2)
OW(7)	0.5266(6)	0.2834(10)	0.3104(4)	0.030(2)	0.022(2)	0.045(5)	0.023(2)	0.003(3)	0.001(2)	-0.006(3)
OW(8)	0.3456(8)	0.5153(7)	-0.1917(4)	0.031(1)	0.037(3)	0.032(3)	0.025(3)	-0.008(2)	0.005(3)	-0.012(2)
H(1)	0.363(11)	0.591(11)	-0.147(3)	0.050†						
H(2)	0.581(10)	0.384(8)	0.340(4)	0.050†						
H(3)	0.568(11)	0.374(10)	-0.273(4)	0.050†						
H(4)	0.224(6)	0.453(10)	-0.186(5)	0.050†						

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The anisotropic displacement parameter exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 hka^* b^* U_{12}]$ .

\* Cu(1) refined occupancy: 88.3(6)%.

† Value constrained during refinement.

TABLE 5. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR METAZEUNERITE

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
U(1)	¼	¼	0.0561(1)	0.010(1)	0.009(1)	0.009(1)	0.011(1)	0	0	0
U(2)	¼	¼	0.5545(1)	0.009(1)	0.008(1)	0.008(1)	0.009(1)	0	0	0
Cu(1)	¼	¼	0.3111(1)	0.017(1)	0.017(1)	0.017(1)	0.017(1)	0	0	0
As(1)	¼	¾	0	0.010(1)	0.009(1)	0.009(1)	0.012(1)	0	0	0
As(2)	¼	¾	½	0.009(1)	0.008(1)	0.008(1)	0.011(1)	0	0	0
O(1)	¼	¼	0.4515(3)	0.019(1)	0.022(2)	0.022(2)	0.011(2)	0	0	0
O(2)	¼	¼	-0.0452(3)	0.024(1)	0.029(2)	0.029(2)	0.014(2)	0	0	0
O(3)	¼	¼	0.6562(2)	0.017(1)	0.023(1)	0.023(1)	0.007(2)	0	0	0
O(4)	¼	¼	0.1592(3)	0.017(1)	0.021(1)	0.021(1)	0.011(2)	0	0	0
O(5)	0.2938(4)	0.9329(4)	0.0580(1)	0.018(1)	0.025(2)	0.010(1)	0.019(2)	-0.003(1)	-0.004(1)	-0.002(1)
O(6)	0.1949(4)	0.9327(4)	0.5572(1)	0.016(1)	0.022(2)	0.010(1)	0.015(1)	-0.001(1)	0.005(1)	-0.001(1)
OW(7)	0.5223(5)	0.2856(5)	0.3096(2)	0.023(1)	0.018(1)	0.029(3)	0.021(1)	0.000(2)	-0.001(1)	-0.003(1)
OW(8)	0.3534(5)	0.5075(5)	-0.1940(2)	0.029(1)	0.033(2)	0.032(2)	0.021(2)	-0.004(1)	-0.001(2)	-0.007(2)
H(1)	0.378(8)	0.570(7)	-0.147(2)	0.050*						
H(2)	0.577(7)	0.349(7)	0.351(2)	0.050*						
H(3)	0.575(7)	0.348(7)	0.266(2)	0.050*						
H(4)	0.218(3)	0.507(9)	-0.199(3)	0.050*						

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The anisotropic displacement parameter exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 hka^* b^* U_{12}]$ .

\* Value constrained during refinement.

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å)  
FOR TORBERNITE

U(1)-O(2)	1.759(4)	Cu(1)-OW(3)	1.913(4) x 4
U(1)-O(1)	1.779(5)	Cu(1)-O(1)	2.556(5) x 2
U(1)-O(4)	2.303(2) x 4		
<U(1)-O <sub>ap</sub> >	1.77	P(1)-O(4)	1.535(2) x 4
OW(3)-H(3)	0.96(2) x 2	H(1)···OW(5)	2.13(2)
OW(5)-H(1)	0.93(2)	H(2)···O(4)	2.01(2)
OW(5)-H(2)	0.92(2)	H(3)···OW(5)	1.76(2)
OW(5)-H(1)···OW(5)	129°		
OW(5)-H(2)···O(4)	159°		
OW(3)-H(3)···OW(5)	155°		

O-H···O angles are rounded to the nearest degree

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å)  
FOR ZEUNERITE

U(1)-O(2)	1.774(5)	Cu(1)-OW(3)	1.929(4) x 4
U(1)-O(1)	1.795(5)	Cu(1)-O(1)	2.482(5) x 2
U(1)-O(4)	2.295(3) x 4		
<U(1)-O <sub>ap</sub> >	1.79	As(1)-O(4)	1.683(3) x 4
OW(3)-H(3)	0.94(2) x 2	H(1)···OW(5)	1.91(2)
OW(5)-H(1)	0.93(2)	H(2)···O(4)	1.96(2)
OW(5)-H(2)	0.92(2)	H(3)···OW(5)	1.78(2)
OW(5)-H(1)···OW(5)	172°		
OW(5)-H(2)···O(4)	166°		
OW(3)-H(3)···OW(5)	158°		

O-H···O angles are rounded to the nearest degree

TABLE 8. SELECTED INTERATOMIC DISTANCES (Å)  
FOR METATORBERNITE

U(1)-O(2)	1.769(7)	P(1)-O(5)	1.533(4) x 4
U(1)-O(4)	1.815(7)		
U(1)-O(5)	2.293(4) x 4	P(2)-O(6)	1.533(4) x 4
<U(1)-O <sub>ap</sub> >	1.79		
		Cu(1)-OW(7)	1.944(5) x 4
U(2)-O(1)	1.775(7)	Cu(1)-O(1)	2.391(7)
U(2)-O(3)	1.780(8)	Cu(1)-O(4)	2.685(8)
U(2)-O(6)	2.308(4) x 4	<Cu(1)-O <sub>ap</sub> >	2.54
<U(2)-O <sub>ap</sub> >	1.78		
OW(7)-H(2)	0.95(2)	H(1)···O(5)	1.89(2)
OW(7)-H(3)	0.95(2)	H(2)···O(6)	2.09(2)
OW(8)-H(1)	0.95(2)	H(3)···OW(8)	1.72(2)
OW(8)-H(4)	0.96(2)	H(4)···OW(8)	1.83(2)
OW(8)-H(1)···O(5)	171°		
OW(7)-H(2)···O(6)	138°		
OW(7)-H(3)···OW(8)	165°		
OW(8)-H(4)···OW(8)	171°		

O-H···O angles are rounded to the nearest degree

TABLE 9. SELECTED INTERATOMIC DISTANCES (Å)  
FOR METAZEUNERITE

U(1)-O(2)	1.764(5)	As(1)-O(5)	1.676(3)
U(1)-O(4)	1.796(4)		
U(1)-O(5)	2.276(3) x 4	As(2)-O(6)	1.683(3) x 4
<U(1)-O <sub>ap</sub> >	1.78		
		Cu(1)-OW(7)	1.953(3) x 4
U(2)-O(3)	1.772(4)	Cu(1)-O(1)	2.445(5)
U(2)-O(1)	1.794(5)	Cu(1)-O(4)	2.645(4)
U(2)-O(6)	2.290(3) x 4	<Cu(1)-O <sub>ap</sub> >	2.55
<U(2)-O <sub>ap</sub> >	1.78		
OW(7)-H(2)	0.93(2)	H(1)···O(5)	1.86(2)
OW(7)-H(3)	0.95(2)	H(2)···O(6)	1.90(2)
OW(8)-H(1)	0.95(2)	H(3)···OW(8)	1.70(2)
OW(8)-H(4)	0.97(2)	H(4)···OW(8)	1.94(2)
OW(8)-H(1)···O(5)	171°		
OW(7)-H(2)···O(6)	169°		
OW(7)-H(3)···OW(8)	170°		
OW(8)-H(4)···OW(8)	145°		

O-H···O angles are rounded to the nearest degree

is quite different (Fig. 2). Considering only the uranyl phosphate sheets, from a geometrical point of view, the transition from torbernite to metatorbernite involves the relative displacement of every second uranyl phosphate sheet by half the  $a$  unit-cell dimension along both [100] and [010].

In both torbernite and metatorbernite, there is a symmetrically independent  $\text{Cu}^{2+}$  cation in the interlayer between the uranyl phosphate sheets (Fig. 2). The  $\text{Cu}^{2+}$  cation occurs in typical Jahn–Teller distorted (4 + 2) octahedra (Burns & Hawthorne 1996, Eby & Hawthorne 1993), with short bonds to four  $\text{H}_2\text{O}$  groups in a square-planar arrangement and two longer distances to oxygen atoms of uranyl ions that serve to link the uranyl phosphate sheets (Tables 6 and 8, Tables 7 and 9 for zeunerite and metazeunerite, respectively). The  $\text{Cu}^{2+}$  cation in metatorbernite has a refined occupancy of

88%, similar to that found in natural metatorbernite by Stergiou *et al.* (1993); charge balance may be achieved by the protonation of interlayer  $\text{H}_2\text{O}$  groups to form oxonium, in analogy with chemikovite (Atencio 1988, Morosin 1978).

The interlayer regions of both torbernite and metatorbernite contain a symmetrically independent  $\text{H}_2\text{O}$  group (OW5 and OW8, respectively) that is held in each structure only by H-bonding (Tables 6 and 8, Tables 7 and 9 for zeunerite and metazeunerite, respectively). The proposed H-bond network in torbernite is illustrated in Figure 3; H bonds link the interstitial  $\text{H}_2\text{O}$  groups into square-planar sets, extend from these sets to acceptors within the uranyl phosphate sheets, and connect the  $\text{H}_2\text{O}$  groups that coordinate  $\text{Cu}^{2+}$  to the interstitial  $\text{H}_2\text{O}$  groups. The proposed H-bond acceptors in the uranyl phosphate sheets are the anions at the equa-

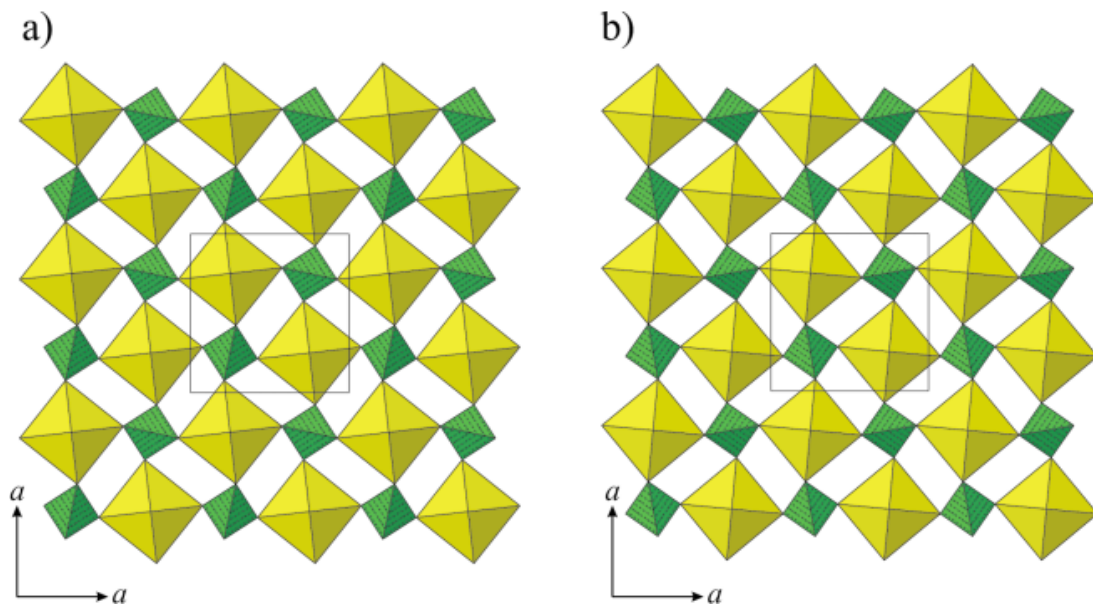


FIG. 1. Polyhedral representation of the uranyl phosphate sheet a) in torbernite, projected along [001], and b) in metatorbernite, projected along [001]. The uranyl polyhedra are yellow, and the phosphate tetrahedra are green and stippled.

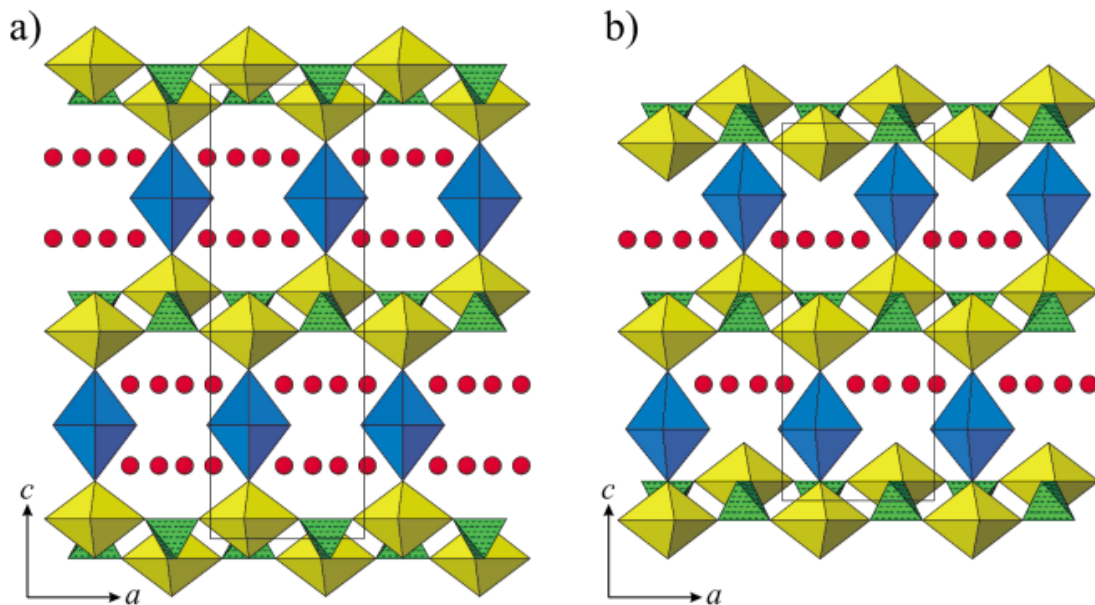


FIG. 2. Polyhedral representation of a) torbernite, projected along [100], and b) metatorbernite, projected along [100]. Uranyl polyhedra are yellow, phosphate tetrahedra are green and stippled, copper bipyramids are blue, and H<sub>2</sub>O groups are shown as red spheres.



torial vertices of uranyl square bipyramids that are also shared with phosphate tetrahedra. The square-planar sets of interstitial H<sub>2</sub>O groups occur both above and below the plane of the Cu<sup>2+</sup> cations in torbernite.

In contrast to the structure of torbernite, the square-planar sets of interstitial H<sub>2</sub>O groups in metatorbernite occur either above or below the plane of the Cu<sup>2+</sup> cations. The proposed H-bond network in metatorbernite is illustrated in Figure 4. Hydrogen bonds link the free H<sub>2</sub>O groups into square-planar sets, and extend from these interstitial H<sub>2</sub>O groups to acceptors within the uranyl phosphate sheets. However, the H<sub>2</sub>O groups that coordinate Cu<sup>2+</sup> cations not only have H bonds that connect with the interstitial H<sub>2</sub>O groups, but also have H bonds that extend to acceptors within the uranyl phosphate sheets.

TABLE 10. BOND-VALENCE ANALYSIS FOR TORBERNITE (*vu*)

	U(1)	P(1)	Cu(1)	H(1)	H(2)	H(3)	Total
O(1)	1.703		0.093 <sup>x21</sup>				1.80
O(2)	1.766						1.77
OW(3)			0.531 <sup>x41</sup>			0.75 <sup>x2→</sup>	2.03
O(4)	0.661 <sup>x41</sup>	1.248 <sup>x41</sup>			0.16		2.07
OW(5)				0.18, 0.82	0.84	0.25	2.09
Total	6.11	4.99	2.31	1.0	1.0	1.0	

The symbols  $\downarrow$  and  $\rightarrow$  indicate that summation is carried out multiple times only in the given direction, and once in the other direction.

## DISCUSSION

*Equivalence with natural material*

The unit-cell dimensions of the synthetic torbernite, zeunerite, metatorbernite and metazeunerite investigated (Table 1) are in good agreement with data for natural specimens: torbernite  $a$  7.04 Å,  $c$  20.80 Å (Walenta 1962), zeunerite 7.17–7.20 Å,  $c$  20.7–20.8 Å (Henmi 1957, Garavelli & Mazzi 1958, Hennig *et al.* 2003), metatorbernite  $a$  6.97–6.98 Å,  $c$  17.28–17.41 Å (Donnay & Donnay 1955, Ross *et al.* 1964, Stergiou *et al.* 1993), metazeunerite 7.10–7.11 Å,  $c$  17.38–17.70 Å (Donnay & Donnay 1955, Hanic 1960, Hennig *et al.* 2003). Therefore, the synthetic material examined in this study is presumed to be equivalent to these four mineral species.

TABLE 11. BOND-VALENCE ANALYSIS FOR ZEUNERITE (*vu*)

	U(1)	As(1)	Cu(1)	H(1)	H(2)	H(3)	Total
O(1)	1.719		0.114 <sup>x21</sup>				1.83
O(2)	1.655						1.66
OW(3)			0.509 <sup>x41</sup>			0.76 <sup>x2→</sup>	2.03
O(4)	0.671 <sup>x41</sup>	1.255 <sup>x41</sup>			0.16		2.09
OW(5)				0.17, 0.83	0.84	0.24	2.08
Total	6.06	5.02	2.26	1.0	1.0	1.0	

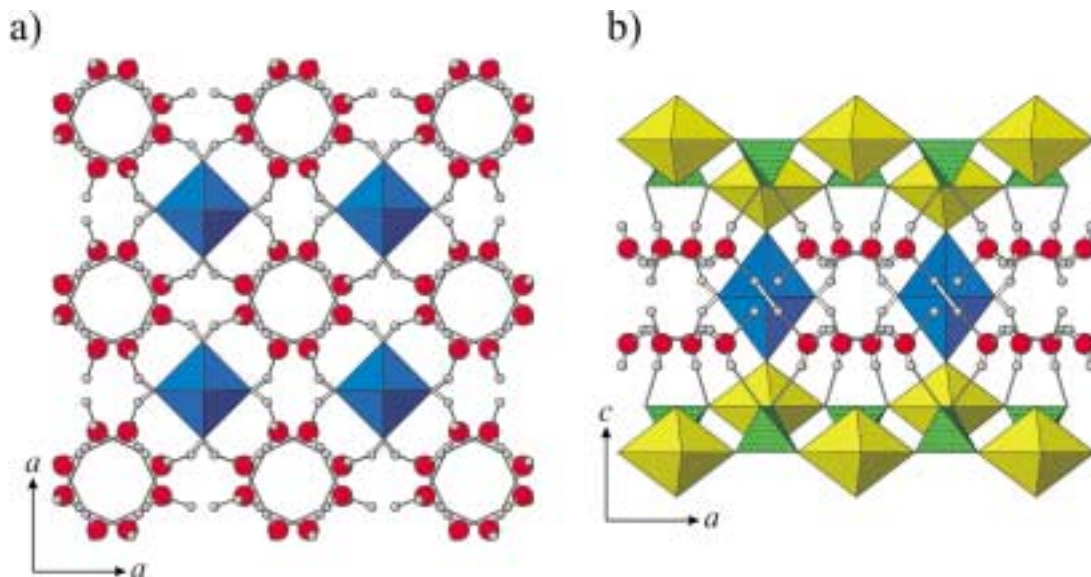


FIG. 3. Proposed scheme of hydrogen bonding in a portion of the torbernite structure a) projected along [001], and b) projected along [100]. Hydrogen atoms are shown as gray spheres, O–H bonds as thick rods, and H...O bonds as thin rods.

TABLE 12. BOND-VALENCE ANALYSIS FOR METATORBERNITE (*vu*)

	U(1)	U(2)	P(1)	P(2)	Cu(1)*	H(1)	H(2)	H(3)	H(4)	Total
O(1)		1.716			0.146					1.86
O(2)	1.734									1.73
O(3)		1.700								1.70
O(4)	1.596				0.066					1.66
O(5)	0.673 <sup>x41</sup>		1.255 <sup>x41</sup>			0.17				2.10
O(6)		0.655 <sup>x41</sup>		1.255 <sup>x41</sup>			0.16			2.07
OW(7)					0.489 <sup>x41</sup>		0.84	0.74		2.07
OW(8)						0.83		0.26	0.19, 0.81	2.09
Total	6.02	6.04	5.02	5.02	2.17	1.0	1.0	1.0	1.0	

\* Cu(1) refined occupancy: 88.3(6)%. Bond valence parameters were calculated assuming full occupancy.

TABLE 13. BOND-VALENCE ANALYSIS FOR METAZEUNERITE (*vu*)

	U(1)	U(2)	As(1)	As(2)	Cu(1)	H(1)	H(2)	H(3)	H(4)	Total
O(1)		1.658			0.126					1.78
O(2)	1.750									1.75
O(3)		1.725								1.73
O(4)	1.652				0.073					1.73
O(5)	0.694 <sup>x41</sup>		1.279 <sup>x41</sup>			0.18				2.15
O(6)		0.677 <sup>x41</sup>		1.255 <sup>x41</sup>			0.17			2.11
OW(7)					0.477 <sup>x41</sup>		0.83	0.74		2.04
OW(8)						0.82		0.26	0.19, 0.81	2.08
Total	6.18	6.09	5.12	5.02	2.11	1.0	1.0	1.0	1.0	

### Symmetry and twinning

Both torbernite and zeunerite are pseudo-*I*-centered; for torbernite, *P*-centering is required by 396 observed (mean  $I = 4.3\sigma$ ) reflections of the 10,588 reflections in the sphere of data, whereas for zeunerite *P*-centering is required by 226 observed (mean  $I = 6.6\sigma$ ) reflections of the 6,531 reflections in the sphere of data. This strong pseudosymmetry presumably resulted in the previous assignments of *I4/mmm* for torbernite (Goldsztub 1932) and zeunerite (Garavelli & Mazzi 1958, Hennig *et al.* 2003).

The current study confirms the identical models of Ross *et al.* (1964) and Stergiou *et al.* (1993) for the structure of metatorbernite in *P4/n*, with  $c \approx 17.3$  Å. For comparison to the earlier work of Makarov & Tobelko (1960), the structure of metatorbernite was solved for the current dataset with  $c \approx 17.3$  Å in *P4/nmm*; this model yielded unreasonable anisotropic displacement parameters for the O atoms, and an agreement index (*R1*) of 4.1%, double that of the *P4/n* model. Most recently, Calos & Kennard (1996) refined the structure of metatorbernite in *P4/nmm* with a *c* cell dimension half that of previous refinements and the current work. They justified the higher-symmetry structure

by the *absence* of the phosphate-deformation absorption at  $\sim 405$  cm<sup>-1</sup> in the infrared (IR) spectrum. In principle, the presence of this feature would denote  $S_4$  ( $\bar{4}$ ) local symmetry for the phosphate group, and therefore space group *P4/n* for the structure, whereas its absence would indicate  $D_{2d}$  ( $\bar{4}2m$ ) local symmetry and be consistent with *P4/nmm* for the structure. However, the  $\nu_2$  band of PO<sub>4</sub><sup>3-</sup> is of practically insignificant intensity in the IR spectra of uranyl phosphates (Čejka *et al.* 1985), and its *absence* is therefore not indicative of the symmetry of the phosphate group and the metatorbernite structure. For comparative purposes, a solution was undertaken in space group *P4/nmm* with  $c \approx 8.7$  Å. This model yielded an excellent agreement index (*R1*) of 2.1%, but gave unreasonable anisotropic displacement parameters for some of the O atoms. More importantly, the larger 17.3 Å unit cell for metatorbernite is required by 1346 observed ( $I > 3\sigma$ ) reflections of the 10,044 intensities in the sphere of data, and therefore the smaller 8.7 Å cell is warranted.

Hanic (1960) reported the structure of metazeunerite in space group *P4<sub>2</sub>/nmc*. For comparison, the current dataset for metazeunerite was also refined in this space group, but there were 208 intense ( $I > 5\sigma$ ) violations of systematic absences, inappropriate interatomic distances

and coordinations, large uncertainties in the interatomic distances, and an agreement index ( $R1$ ) of 14.8%. In contrast, the bond lengths experimentally determined by U  $L_{III}$ -edge and As  $K$ -edge EXAFS for metazeunerite at room temperature: U–O<sub>ap</sub> 1.77, U–O<sub>eq</sub> 2.29, As–O<sub>eq</sub> 1.68, (Hennig *et al.* 2001, 2003), are in excellent agreement with those reported in Table 7 for the  $P4/n$  structure model. In addition to the EXAFS data, Hennig *et al.* (2003) presented structure refinements for metazeunerite in space groups  $P4/ncc$ ,  $c$  17.420(1) Å, and  $P4/nmm$ ,  $c$  8.710(1) Å. Using our dataset, a structure model in space group  $P4/ncc$  gave several problems: there are 616 systematic absence violations, corresponding to violations of the  $c$ -glides, the Cu position is half-occupied, and the agreement index ( $R1$ ) is 5.8%. As in the case of metatorbernite, refinement of the structure of metazeunerite in space group  $P4/nmm$  with  $c \approx 8.7$  Å is inappropriate, as the larger 17.4 Å unit cell is required by 2372 observed ( $I > 3\sigma$ ) reflections of the 18,087 intensities in the sphere of data.

The presence of merohedral twinning in metatorbernite and metazeunerite does not appear to have been recognized previously. The twin operator [010/100/001] does not belong to the Laue group ( $4/m$ ) of the crystal. According to Herbst-Irmer & Sheldrick (1998), because “the different twin domains have similar contributions, the reflection intensities appear to possess a higher symmetry than the true structure”; this effect may have led to previous assignments of higher-symmetry space groups for metatorbernite and metazeunerite.

#### Hydration states and dehydration behavior

We have found that torbernite and zeunerite have 12 H<sub>2</sub>O groups per formula unit (pfu), and metatorbernite and metazeunerite have 8 H<sub>2</sub>O pfu, in accord with Walenta (1964, 1965), Čejka *et al.* (1985), Vochten *et al.* (1979, 1981) and Vochten & Goeminne (1984). Some previous studies have described a range of hydration states, with zeunerite ranging from 10 to 16 H<sub>2</sub>O pfu (Frondel 1951, Garavelli & Mazzi 1958). However, the unit-cell volumes of three zeunerite specimens with “different” hydration states (10, 13, 16 H<sub>2</sub>O pfu) determined by Garavelli & Mazzi (1958) vary by less than 0.5%, and the intermediate 13-hydrate has the smallest volume, suggesting that their reported states of hydration may be in error. Note that the exceedingly high H<sub>2</sub>O content for zeunerite listed in Smith (1984), Cu(UO<sub>2</sub>)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>•40H<sub>2</sub>O, is probably a typographical error. The presence of hydroxyl in the interlayer region of metatorbernite is not supported by the crystal-structure refinement presented here, despite the interpretation of IR spectral evidence put forward by Suzuki *et al.* (1998).

In addition to crystallizing directly from solution, minerals of the meta-autunite group can generally be related to their chemical analogues in the autunite group by partial dehydration, although consensus is lacking in

the literature concerning the nature of the dehydration process. Buchholz (1903) demonstrated that torbernite readily loses one-third of its water of hydration in a desiccator, and Hallimond (1916, 1920) showed that the dehydration of torbernite to metatorbernite is sharply defined, although the transition conditions depend on H<sub>2</sub>O vapor pressure and temperature.

In contrast to earlier studies, Frondel (1951) suggested that the dehydration of torbernite to lower hydrates is similar to behavior exhibited by zeolite-group compounds. In zeolites (Smith 2000, Bish & Carey 2001), extra thermal energy causes H<sub>2</sub>O molecules to escape from holes in the coherent three-dimensional framework *via* channels and windows. Upon cooling, H<sub>2</sub>O molecules can refill the holes. During partial dehydration, the aluminosilicate framework of a zeolite retains its connectivity, but the positions of occluded atoms, molecules and cations change to minimize the thermochemical energy (Smith 2000). The variable hydration-states of some zeolite minerals (Bish & Carey 2001) are not consistent with the dehydration behavior and structure of torbernite. In contrast to the zeolites, the H<sub>2</sub>O groups in torbernite are required to maintain the integrity of the structure (Fig. 3). The removal of some of these groups entails a ~16% decrease in the  $c$  cell dimension as well as changes in the stacking geometry of the uranyl phosphate sheets, and reconfiguration of the hydrogen-bonding network (Fig. 4).

Walenta (1965) investigated the dehydration behavior of autunite and meta-autunite group compounds and concluded that the H<sub>2</sub>O content of the existing phases is constant and does not vary in a manner similar to zeolites, but that dehydration proceeds in a stepwise fashion, in agreement with the structural arguments presented herein.

#### Other Cu<sup>2+</sup> uranyl phosphates

The only other Cu<sup>2+</sup> uranyl phosphates with known structures are the mineral ulrichite, Cu[Ca(H<sub>2</sub>O)<sub>2</sub>(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub> (Kolitsch & Giester 2001) and the synthetic compound Cu<sub>2</sub>(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub> (Guesdon *et al.* 2002). No other copper uranyl arsenates have yet been reported.

The structure of ulrichite, like those of torbernite and metatorbernite, involves uranyl phosphate layers connected by Jahn–Teller-distorted Cu<sup>2+</sup> octahedra, but its sheets of composition [Ca(H<sub>2</sub>O)<sub>2</sub>(UO<sub>2</sub>)(PO<sub>4</sub>)<sub>2</sub>]<sup>2-</sup> have the uranophane anion-topology (Burns 1999, Burns *et al.* 1996, Stohl & Smith 1981) rather than the autunite-type sheet. In ulrichite, the uranyl pentagonal bipyramid shares an equatorial edge with the CaO<sub>8</sub> polyhedron, giving a chain of alternating UO<sub>7</sub> and CaO<sub>8</sub> polyhedra that is one polyhedron wide. Phosphate tetrahedra are attached to either side of the chains by sharing edges with the UO<sub>7</sub> and CaO<sub>8</sub> polyhedra. Translationally equivalent calcium uranyl phosphate chains are joined by the sharing of equatorial vertices of UO<sub>7</sub> and CaO<sub>8</sub>

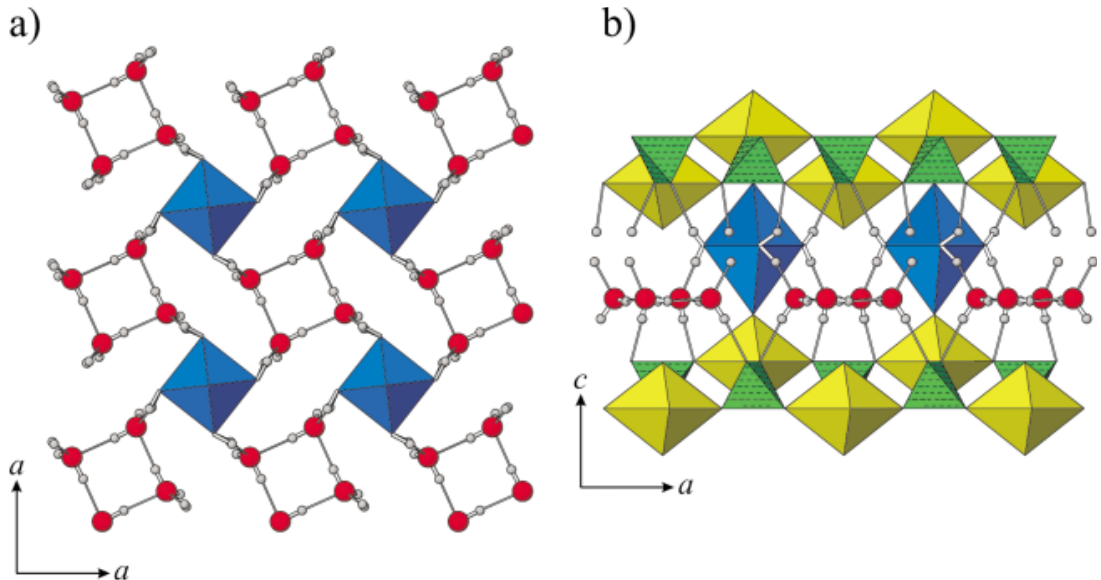


FIG. 4. Proposed scheme of hydrogen bonding in a portion of the metatorbernite structure a) projected along [001], and b) projected along [100]. Hydrogen atoms are shown as gray spheres, O–H bonds as thick rods, and H...O bonds as thin rods.

polyhedra with phosphate tetrahedra from adjacent chains, resulting in sheets.

The compound  $\text{Cu}_2(\text{UO}_2)(\text{PO}_4)_2$  consists of uranyl phosphate chains that are similar to the uranyl arsenate chains in walpurgite (Mereiter 1982): uranyl square bipyramids share equatorial vertices with phosphate tetrahedra, resulting in chains. The opposing vertices of the phosphate tetrahedra share the equatorial vertices of Jahn–Teller distorted  $(4 + 2)$   $\text{Cu}^{2+}$  octahedra. The apical vertices of the  $\text{Cu}^{2+}$  octahedra are shared with the apical vertices of the uranyl square bipyramids, such that the  $\text{Cu}^{2+}$  octahedra form infinite face-sharing chains.

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#### REFERENCES

- ANTHONY, J.W., BIDEAUX, R.A., BLADH, K.W. & NICHOLS, M.C. (2000): *Handbook of Mineralogy. IV. Arsenates, Phosphates, Vanadates*. Mineral Data Publishing, Tucson, Arizona.
- AREND, H. & CONNELLY, J.J. (1982): Tetramethoxysilane as gel forming agent in crystal growth. *J. Cryst. Growth* **56**, 642-644.
- ATENCIO, D. (1988): Chernikovite, a new mineral name for  $(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$  superseding “hydrogen autunite”. *Mineral. Rec.* **19**, 249-252.
- BEINTEMA, J. (1938): On the composition and crystallography of autunite and the meta-autunites. *Recl. Trav. Chim. Pays-Bas* **57**, 155-175.
- BERMAN, R. (1957): Studies of uranium minerals. XXIII. Torbernite, zeunerite and uranospherite. *Am. Mineral.* **42**, 905-908.
- BISH, D.L. & CAREY, J.W. (2001): Thermal behavior of natural zeolites. In *Natural Zeolites: Occurrence, Properties, Applications* (D.L. Bish & D.W. Ming, eds.). *Rev. Mineral. Geochem.* **45**, 403-452.
- BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.
- BRUKER-AXS (1998a): *SAINT, V 5.01 Program for Reduction of Data Collected on Bruker AXS Ccd Area Detector Systems*. Bruker Analytical X-ray Systems, Madison, Wisconsin.
- \_\_\_\_\_ (1998b): *XPREP, V5.0 Program for Data Preparation & Reciprocal Space Exploration*. Bruker Analytical X-ray Systems, Madison, Wisconsin.

- \_\_\_\_\_ (1998c): *SHELXTL NT, V5.1 Program Suite for Solution and Refinement of Crystal Structures*. Bruker Analytical X-ray Systems, Madison, Wisconsin.
- BUCHHOLZ, Y. (1903): Das Wassergehalt des Kupferuranits. *Zentralbl. Mineral. Geol. Palaeontol.*, 362.
- BUCK, E.C., BROWN, N.R. & DIETZ, N.L. (1996): Contaminant uranium phases and leaching at the Fernald site in Ohio. *Environ. Sci. Technol.* **30**, 81-88.
- BURNS, P.C. (1999): The crystal chemistry of uranium. In *Uranium: Mineralogy, Geochemistry and the Environment* (P.C. Burns & R. Finch, eds.). *Rev. Mineral.* **38**, 23-90.
- \_\_\_\_\_, EWING, R.C. & HAWTHORNE, F.C. (1997): The crystal chemistry of hexavalent uranium: polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *Can. Mineral.* **35**, 1551-1570.
- \_\_\_\_\_, & HAWTHORNE, F.C. (1996): Static and dynamic Jahn-Teller effects in  $\text{Cu}^{2+}$  oxysalt minerals. *Can. Mineral.* **34**, 1089-1105.
- \_\_\_\_\_, MILLER, M.L. & EWING, R.C. (1996):  $\text{U}^{6+}$  minerals and inorganic phases: a comparison and hierarchy of structures. *Can. Mineral.* **34**, 845-880.
- CALOS, N.J. & KENNARD, C.H.L. (1996): Crystal structure of copper bis(uranyl phosphate) octahydrate (metatorbernite),  $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$ . *Z. Kristallogr.* **211**, 701-702.
- ČEJKA, J., JR., MUCK, A. & ČEJKA, J. (1985): Infrared spectra and thermal analysis of synthetic uranium micas and their deuteroanalogues. *Neues Jahrb. Mineral., Monatsh.*, 115-116.
- CHESTER, A.H. (1896): *A Dictionary of the Names of Minerals* (annotated facsimile reprint). *Rochester Mineral. Symp., Spec. Publ.* **6** (1989).
- CLARK, A.M. (1993): *Hey's Mineral Index*. Chapman and Hall, London, U.K.
- DONNAY, G. & DONNAY, J.D.H. (1955): Contribution to the crystallography of uranium minerals. *U.S. Geol. Surv., Trace Elements Invest. Rep.* **507**.
- EBY, R.K. & HAWTHORNE, F.C. (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.
- FERRARIS, G. & IVALDI, G. (1988): Bond valence vs. bond length in O...O hydrogen bonds. *Acta Crystallogr.* **B44**, 341-344.
- FINCH, R.J. & MURAKAMI, T. (1999) Systematics and paragenesis of uranium minerals. In *Uranium: Mineralogy, Geochemistry and the Environment* (P.C. Burns & R.J. Finch, eds.). *Rev. Mineral.* **38**, 91-179.
- FRONDEL, C. (1958): Systematic mineralogy of uranium and thorium. *U.S. Geol. Surv., Bull.* **1064**.
- FRONDEL, J.W. (1951): Studies of uranium minerals. VII. Zeunerite. *Am. Mineral.* **36**, 249-255.
- FULLER, C.C., BARGAR, J.R., DAVIS, J.A. & PIANA, M.J. (2002): Mechanisms of uranium interactions with hydroxyapatite: implications for groundwater remediation. *Environ. Sci. Technol.* **36**, 158-165.
- GAINES, R.V., SKINNER, H.C.W., FOORD, E.E., MASON, B., ROSENZWEIG, A. & KING, V.T. (1997): *Dana's New Mineralogy* (eighth ed.). John Wiley & Sons, New York, N.Y.
- GARAVELLI, C.L. & MAZZI, F. (1958): Prima segnalazione in natura della zeunerite fra i minerali secondari di uranio del Val Rendana. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat. Rend.* **25**, 75-80.
- GOLDSZTAUB, S. (1932): Communication sur la chalcocite. *Bull. Minéral.* **55**, 7.
- GUESDON, A., CHARDON, J., PROVOST, J. & RAVEAU, B. (2002): A copper uranyl monophosphate built up from  $[\text{CuO}_2]_8$  chains:  $\text{Cu}_2\text{UO}_2(\text{PO}_4)_2$ . *J. Solid State Chem.* **165**, 89-93.
- HALLIMOND, A. F. (1916): The crystallography and dehydration of torbernite. *Mineral. Mag.* **17**, 326-339.
- \_\_\_\_\_ (1920): Meta-torbernite I. Its physical properties and relation to torbernite. *Mineral. Mag.* **19**, 43-47.
- HANIC, F. (1960): The crystal structure of meta-zeunerite  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8(\text{H}_2\text{O})$ . *Czech. J. Phys.* **B10**, 169-181.
- HAWTHORNE, F.C., UNGARETTI, L. & OBERTI, R. (1995): Site populations in minerals: terminology and presentation of results of crystal structure refinement. *Can. Mineral.* **33**, 907-911.
- HENISCH, H.K. (1988): *Crystals in Gels and Liesegang Rings*. Cambridge University Press, New York, N.Y.
- HENMI, K. (1957): Natural occurrences of zeunerite. *Mineral. J.* **2**, 134-137.
- HENNIG, C., RECK, G., REICH, T., ROSSBERG, A., KRAUS, W. & SIELER, J. (2003): EXAFS and XRD investigations of zeunerite and meta-zeunerite. *Z. Kristallogr.* **218**, 37-45.
- \_\_\_\_\_, REICH, T., FUNKE, H., ROSSBERG, A., RUTSCH, M. & BERNHARD, G. (2001): EXAFS as a tool for bond-length determination in the environment of heavy atoms. *J. Synchrotron Rad.* **8**, 695-697.
- HERBST-IRMER R. & SHELDRIK, G.M. (1998): Refinement of twinned structures with *SHELXL97*. *Acta Crystallogr.* **B54**, 443-449.
- IBERS, J.A. & HAMILTON, W.C., eds. (1974): *International Tables for X-ray Crystallography IV*. The Kynoch Press, Birmingham, U.K.
- JAMESON, G.B. (1982): On structure refinement using data from a twinned crystal. *Acta Crystallogr.* **A38**, 817-820.

- KLAPROTH, M.H. (1797): *Beiträge zur chemischen Kenntniss der Mineralkörper* 2. Heinrich August Rottmann, Berlin, Germany (217-218).
- \_\_\_\_\_ (1801): *Analytical Essays Towards Promoting the Chemical Knowledge of Mineral Substances* 1. T. Cadell and W. Davies, London, U.K. (492-493).
- KOLITSCH, U. & GIESTER, G. (2001): Revision of the crystal structure of ulrichite,  $\text{CaCu}^{2+}(\text{UO}_2)(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . *Mineral. Mag.* **65**, 717-724.
- LOCOCK, A.J. & BURNS, P.C. (2002a): The crystal structure of triuranyl diphosphate tetrahydrate. *J. Solid State Chem.* **163**, 275-280.
- \_\_\_\_\_ & \_\_\_\_\_ (2002b): Crystal structures of three framework alkali metal uranyl phosphate hydrates. *J. Solid State Chem.* **167**, 226-236.
- \_\_\_\_\_ & \_\_\_\_\_ (2003): The crystal structure of synthetic autunite,  $\text{Ca}[(\text{UO}_2)(\text{PO}_4)]_2(\text{H}_2\text{O})_{11}$ . *Am. Mineral.* **88**, 240-244.
- MAKAROV, E.S. & TOBELKO, K.I. (1960): Crystal structure of metatorbernite. *Dokl. Akad. Nauk SSSR* **131**, 87-89.
- MANGHI, E. & POLLA, G. (1983): Hydrogen uranyl arsenate hydrate single crystals:  $\text{H}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ; gel growth and characterization. *J. Crystal Growth* **61**, 606-614.
- MEREITER, K. (1982): The crystal structure of walpurgite,  $(\text{UO}_2)\text{Bi}_4\text{O}_4(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ . *Tschermaks Mineral. Petrogr. Mitt.* **30**, 129-139.
- MOROSIN, B. (1978): Hydrogen uranyl phosphate tetrahydrate, a hydrogen ion solid electrolyte. *Acta Crystallogr.* **B34**, 3732-3734.
- MURAKAMI, T., OHNUKI, T., ISOBE, H. & TSUTOMU, T. (1997): Mobility of uranium during weathering. *Am. Mineral.* **82**, 888-899.
- PERRINO, C.T. & LEMASTER, C.B. (1984): Preparation of  $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$  single crystals from gel. *J. Crystal Growth* **69**, 639-640.
- ROBERT, M.C. & LEFAUCHEUX, F. (1988): Crystal growth in gels: principle and applications. *J. Crystal Growth* **90**, 358-367.
- ROH, Y., LEE, S.R., CHOI, S.K., ELLESS, M.P. & LEE, S.Y. (2000): Physicochemical and mineralogical characterization of uranium contaminated soils. *Soil and Sediment Contamination* **9**, 463-486.
- ROSS, M., EVANS, H.T., JR. & APPLEMAN, D.E. (1964): Studies of the torbernite minerals. II. The crystal structure of metatorbernite. *Am. Mineral.* **49**, 1603-1621.
- SMITH, D.K. (1984): Uranium mineralogy. In *Uranium Geochemistry, Mineralogy, Geology, Exploration and Resources* (B. DeVivo, F. Ippolito, G. Capaldi & P.R. Simpson, eds.). Institute of Mining and Metallurgy, London, U.K. (43-88).
- SMITH, J.V. (2000): Microporous and other framework materials with zeolite-type structures. A. Tetrahedral frameworks of zeolites, clathrates and related materials. In Landolt-Börnstein Group IV: Physical Chemistry **14** (W.H. Baur & R.X. Fischer, eds.). Springer, New York, N.Y.
- SOWDER, A.G., CLARK, S.B. & FJELD, R.A. (1996): The effect of silica and phosphate on the transformation of schoepite to becquerelite and other uranyl phases. *Radiochim. Acta* **74**, 45-49.
- STERGIOU, A.C., RENTZEPERIS, P.J. & SKLAVOUNOS, S. (1993): Refinement of the crystal structure of metatorbernite. *Z. Kristallogr.* **205**, 1-7.
- STOHL, F.V. & SMITH, D.K. (1981): The crystal chemistry of the uranyl silicate minerals. *Am. Mineral.* **66**, 610-625.
- SUZUKI, Y., MURAKAMI, T., KOGURE, T., ISOBE, H. & SATO, T. (1998): Crystal chemistry and microstructures of uranyl phosphates. *Mater. Res. Soc., Symp. Proc.* **506**, 839-846.
- VOCHTEN, R. & GOEMINNE, A. (1984): Synthesis, crystallographic data, solubility and electrokinetic properties of meta-zeunerite, meta-kirchheimerite and nickel-uranyl-arsenate. *Phys. Chem. Minerals* **11**, 95-100.
- \_\_\_\_\_, HUYBRECHTS, W., REMAUT, G. & DELIENS, M. (1979): Formation of meta-torbernite starting from curite: crystallographic data and electrokinetic properties. *Phys. Chem. Minerals* **4**, 281-290.
- \_\_\_\_\_, PIRET, P. & GOEMINNE, A. (1981): Synthesis, crystallographic data, solubility and electrokinetic properties of copper-, nickel- and cobalt-uranylphosphate. *Bull. Minéral.* **104**, 457-467.
- VON BORN, I. (1772): *Lithophylacium Bornianum* 1. Prague, Czech Republic [p. 42, cited in Chester (1896)].
- WALENTA, K. (1962): Torbernit aus der Grube Clara bei Oberwolfach (Schwarzwald). In Hermann Aldinger Festschrift, Stuttgart, Germany (185-190).
- \_\_\_\_\_ (1964): Beiträge zur Kenntnis seltener Arsenatminerale unter besonderer Berücksichtigung von Vorkommen des Schwarzwaldes. *Tschermaks Mineral. Petrogr. Mitt.* **9**, 111-174.
- \_\_\_\_\_ (1965): Die Uranglimmergruppe. *Chem. Erde* **24**, 254-278.
- WALTON, H.F. (1948): *Inorganic Preparations, A Laboratory Manual*. Prentice-Hall Inc., Englewood Cliffs, N.J. (143-144).
- ZOLENSKY, M.E. (1983): *The Structures and Crystal Chemistry of the Autunite and Meta-autunite Mineral Groups*. Ph.D. thesis, Pennsylvania State Univ., University Park, Pennsylvania.