The crystal structure of metanatroautunite, Na[(UO₂)(PO₄)](H₂O)₃, from the Lake Boga Granite, Victoria, Australia

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ABSTRACT

Metanatroautunite, Na[(UO₂)(PO₄)](H₂O)₃, from the Lake Boga granite, Victoria, Australia, has tetragonal symmetry, space group P4/ncc, with the unit-cell parameters: a = 6.9935(7), c = 17.5101(12) Å, V = 856.40(13) Å³, and Z = 4. The crystal structure has been solved and refined to $R_1 = 0.0398$ for 368 unique reflections [$F > 4\sigma(F)$] and 0.0456 for all 496 unique reflections. Metanatroautunite has an almost identical corrugated polyhedral sheet to meta-autunite-group minerals, consisting of corner-sharing uranyl square pyramids and phosphate tetrahedra. Hydrogen bonds (and cation-oxygen bonds) link the water molecules in the interlayer into square-planar sets, which are connected together creating 8-membered arrays. Metanatroautunite is identical to synthetic Na[(UO₂)(PO₄)](H₂O)₃.

Keywords: Meta-autunite, metanatroautunite, uranium, phosphate, Lake Boga, crystal structure

INTRODUCTION

Minerals of the autunite and meta-autunite groups, as well as synthetic variants, have been well studied (e.g., Smith 1984; Finch and Murakami 1999; Burns 1999; Locock and Burns 2003; Locock et al. 2004). These minerals are fairly common in various environments and may control U concentration in many groundwater systems (Finch and Murakami 1999). Granitic rocks commonly release small amounts of uranium during the weathering process (e.g., Dill et al. 2010; Korzeb et al. 1997), and in combination with the weathering of other minerals, particularly fluorapatite, can create diverse assemblages of uranium phosphate secondary minerals. An example of this process and occurrence is the Devonian Lake Boga Granite, which is a highly fractionated, S-type intrusion, and one of the largest in the southern part of the Palaeozoic Lachlan Fold Belt of eastern Australia (Mills 2003; Mills et al. 2008a; Birch et al. 2011). Uranium contents in the granite range from 3 to 64 ppm (mean ~ 20 ppm) in samples from the only accessible outcrop. Assuming that these are representative of the entire intrusion, the Lake Boga Granite, at least in part, can be interpreted as a disseminated, low-grade uranium reservoir containing accessory magmatic uraninite and monazite-cheralite series phases (with up to 7.9 wt% UO₂), as well as hydrothermal fluorapatite crystals exhibiting U-enriched zones (up to 400 ppm) (Mills et al. 2008a). Weathering of these primary phases (especially uraninite and fluorapatite) has given rise to a suite of secondary uranium phosphates, two of which (ulrichite and lakebogaite) are new species (Birch et al. 1988; Mills 2004; Mills et al. 2008b; Mills and Birch 2010). Other uranyl phosphate species present at Lake Boga include saléeite, torbernite, and metanatroautunite, the subject of this manuscript.

Metanatroautunite was first described from Lake Boga by Mills (2004) and its complicated history, nomenclature, and naming were discussed therein. Originally described as "sodium

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meta-autunite" by Chernikov et al. (1957) and Chernikov and Organova (1994) from the Kuruk U deposit, Tajikistan, metanatroautunite formed there by rapid dehydration of natroautunite upon exposure to air (Chernikov 1981). Metanatroautunite was thought to be tetragonal, with the space group *P4/nmm* (by analogy with meta-autunite—Frondel 1958); however, crystal-structure analysis was not performed by Chernikov and Organova (1994).

An exceptional cluster (Fig. 1) of transparent lemon yellow metanatroautunite crystals up to 0.7 mm across, were discovered in a small miarolitic cavity within vuggy granite (registered specimen M51559, Museum Victoria). One of these crystals was selected for single-crystal analysis and herein we report the results.

EXPERIMENTAL METHODS

Single-crystal X-ray data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized MoK α radiation. The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical absorption correction. As described by Locock et al. (2004), careful examination of the data for all meta-autunitegroup minerals needs to be undertaken. Initially, a good fit to the diffraction data was found by using the unit cell: a = 6.9916(4) and c = 8.7529(6) Å; in fact, the data can be refined, with an R_{merg} of 0.0539, to $R_1 = 0.0475$. However, further examination of the data showed that the correct unit cell for metanatroautunite is, in fact, a = 6.9935(7) and c = 17.5101(12) Å. Reflections corresponding to the doubled *c* axis are weak and can easily be overlooked. The doubled *c* dimension is corroborated by examining the effect of halving *c* in the full data set by using the matrix [100/010/00½]. The result is that about half of the reflections intensity greater than 3σ .

The structure was solved by direct methods using SHELXS-97 (Sheldrick 2008) and the location of the U and O atoms in the polyhedral sheet was straightforward. The Na/O atom was located upon inspection of the difference-Fourier map and its occupancy was fixed during refinement to a ratio of 0.75O:0.25Na, consistent with the chemistry. SHELXL-97 software (Sheldrick 2008) was used, with neutral atom scattering factors, for the refinement of the structure. During the refinement, the structure of synthetic Na[(UO₂)(PO₄)](H₂O)₃, denoted as NaUP by Locock et al. (2004), was used as a guide to determine the correct atom placements in the structure. Refining the atoms of the polyhedral sheet with anisotropic displacement parameters except for the Na/O site, yielded R_1 =

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0.0398 for 368 unique reflections [$F > 4\sigma(F)$] and 0.0456 for all 496 reflections. The details of the data collection and structure refinement are provided in Table 1. The final fractional coordinates, atom displacement parameters, and occupancies are listed in Table 2. Selected interatomic distances are given in Table 3. A bond-valence analysis is provided in Table 4.



FIGURE 1. Transparent lemon yellow crystals of metanatroautunite lining a small miarolitic cavity. The largest crystal is 0.7 mm across (Museum Victoria specimen M51559). (Color online.)

 TABLE 1. Data collection and structure refinement details for metanatroautunite

Cry	rstal data						
Cell parameters	<i>a</i> = 6.9935(7) Å						
	c = 17.5101(12) Å						
	V = 427.86(5) Å ³						
	Z = 4						
Space group	P4/ncc						
Data	collection						
Temperature (K)	293(2)						
λ (Μο <i>Κ</i> α)	0.71075						
Crystal shape, size	triangular, 520 × 380 × 100 μm						
2θmax (°)	54.86						
Reflection range	-8 ≤ h ≤ 9; -8 ≤ k ≤ 9; -22 ≤ l ≤ 22						
Total no. reflections	5330						
No. unique reflections	496						
No. reflections, $F > 4\sigma(F)$	368						
Absorption correction	$\mu = 4.801 \text{ mm}^{-1}$						
R _{merg} on F ²	0.0558						
Refinement							
No. parameters refined	27						
$R_1, F > 4\sigma(F)$	0.0398						
R1, all data	0.0456						
$wR_2(F^2)^*$, all data	0.0944						
GOF	1.172						
$\Delta \sigma_{\min}, \Delta \sigma_{\max} (e/Å^3)$	-0.95, 2.67						
$\frac{* w = 1/[\sigma^2(F_o^2) + (0.0399P^2 + 11.1617)]}{100}$	$P], P = [2F_c^2 + Max(F_o^2, 0)]/3.$						

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Due to the reported difference in unit cell and space group between metanatroautunite and meta-autunite (P4/nmm with a = 6.96 and c = 8.40 Å), metanatroautunite cannot be considered isostructural with meta-autunite; however, there are some problems with the structure of meta-autunite reported by Makarov and Ivanoc (1960). The corrugated polyhedral sheet of the metanatroautunite structure is almost identical to that described



FIGURE 2. The corrugated autunite-type sheet found in metanatroautunite. θ is the acute angle of the parallelogram formed between the PO₄ tetrahedra and uranyl square bipyramids. (Color online.)

TABLE 3. Selected bond distances (Å) for metanatroautunite

U1	01	1.773(15)	
U1	02	1.799(13)	
U1	O3	2.291(7)	x4
<u-o<sub>apical></u-o<sub>		1.786	
<u-0></u-0>		2.123	
P1	O3	1.537(7)	x4
Na4	04	2.66(3)	x2
Na4	02	3.053(19)	x4
Na4	O3	2.878(19)	
<na-o></na-o>		2.916	

TABLE 4. Bond-valence summations for metanatroautunite							
	U1		P1		Na4		Σ
01	0.96	↓x4	1.24	↓x4	0.10	↓x2	2.30
02	1.05	x2→			0.05		2.16
03	1.06	x2→					2.11
04					0.03	↓x4	
Σ	5.93		4.97		0.39		

Notes: Multiplicity is indicated by $\times \rightarrow \downarrow$; U⁶⁺–O bond strengths from Burns et al. (1997); other parameters from Brown and Altermatt (1985). Overall sums include rounding errors.

TABLE 2. Fractional coordinates and atom displacement parameters $(Å^2)$ for metanatroautunite

					()					
Atom	x/a	y/b	z/c	$U_{\rm eq}$	U_{11}	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
U1	0.25	0.25	0.40959(3)	0.0197(3)	0.0145(3)	0.0145(3)	0.0300(4)	0.0	0.0	0.0
P1	0.75	0.25	0.0	0.0187(7)	0.0092(10)	0.0092(10)	0.0377(19)	0.0	0.0	0.0
01	0.25	0.25	0.1508(8)	0.034(3)	0.031(4)	0.031(4)	0.040(7)	0.0	0.0	0.0
02	0.25	0.25	0.9468(7)	0.033(3)	0.030(5)	0.030(5)	0.037(7)	0.0	0.0	0.0
03	0.7191(11)	0.0760(10)	0.4478(4)	0.0344(16)	0.043(4)	0.012(3)	0.047(4)	-0.000(2)	-0.003(3)	-0.003(3)
Na4/04*	0.173(3)	0.988(3)	0.3110(9)	0.143(5)						
* Site occu	pancy set at Na	4:04 0.25:0.75.								



FIGURE 3. The interlayer contents of metanatroautunite and NaUP projected along [001]. (Color online.)

for the meta-autunite structure type (e.g., Locock et al. 2004), in which uranyl square bipyramids and phosphate tetrahedra share vertices (Fig. 2). In various structures with these sheets, the acute angle θ of the parallelogram formed between the tetrahedra and square bipyramids differs to varying extents from a regular rectilinear pattern. In meta-autunite, there is no deviation from 90°, which is incorrect; however, as reported by Locock et al. (2004), members that crystallize with a halved c are merohedrally twinned, which changes the acute angle, θ , from ~90 to ~80°. Makarov and Ivanov (1960) did not take twinning into account in their structure refinement, which also indicates that their atomic positions are not likely to be correct. Additionally, Makarov and Ivanov (1960) reported the Ca atom in 10-fold coordination, bonding to two O atoms and eight H₂O molecules. However, their model gives an impossibly one-sided coordination; including short O...O distances (~1.69 Å). Based on these facts, redetermination of the crystal structure of meta-autunite is clearly warranted. Considering the difficulties in determining the correct c length in meta-autunite-group minerals, it is also possible that meta-autunite actually is isostructural with metanatroautunite and other members (both natural and synthetic), and that all have a unit cell with $a \sim 6.96$ and $c \sim 17.50$ Å and space group P4/ncc.

On the other hand, metanatroautunite is isostructural and equivalent to synthetic Na[(UO₂)(PO₄)](H₂O)₃ (NaUP) described by Locock et al. (2004). The two structures are virtually identical, with only minor differences in average bond lengths and θ . These minor differences are almost certainly only due to the differing quality of the crystals. The <P–O> for metanatroautunite and NaUP are identical, 1.537 Å, and match the ideal average P–O given by Huminicki and Hawthorne (2002). Average <U–O> distances are also almost identical within experimental errors (2.123 vs. 2.112 Å). The slightly longer U–O bond also accounts for the small difference in θ (79.4 vs. 78.4°).

In metanatroautunite and NaUP, the Na atom is situated in

the interlayer and shares a partly occupied site with a water molecule. The Na atom is in sevenfold coordination, with an <Na–O> of 2.916 Å in metanatroautunite and 2.96 in NaUP. In Figure 3, the interlayer arrangements in metanatroautunite and NaUP are shown, along with the O…O links consistent with hydrogen bonds. Hydrogen bonds (and cation-oxygen bonds) link the water molecules in both metanatroautunite and NaUP into square-planar sets, which are connected together creating 8-membered arrays.

THE REAL FORMULA OF METANATROAUTUNITE

The formula of metanatroautunite reported by various workers has been inconsistent, mostly because of the changes in chemistry (and porosity) due to dehydration of the original material (e.g., Chernikov et al. 1957; Chernikov and Organova 1994) and, more recently, because of the difficulty in analyzing samples due to rapid reaction under vacuum (Mills 2004). Metanatroautunite is commonly written as either Na₂(UO₂)₂(PO₄)₂·8H₂O or Na₂(UO₂)₂(PO₄)₂·10–16H₂O; however, there is no need to double each of the components in the simplified formula. Nevertheless, the "old" formulas overestimated the water content of the mineral. Based on these crystal-structure analyses, we recommend using Na[(UO₂)(PO₄)](H₂O)₃ as the simplified formula for metanatroautunite.

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