

The crystal structure of $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ and its relationship to schröckingerite

YAPING LI, S. V. KRIVOVICHEV AND P. C. BURNS*

Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick, Notre Dame, Indiana 46556-0767, USA

ABSTRACT

Crystals of the compound $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ have been synthesized and the structure has been solved. It is trigonal with $a = 9.3417(6)$, $c = 12.824(1)$ Å, $V = 969.2(1)$ Å³, space group $P\bar{3}c1$ and $Z = 4$. The structure was refined on the basis of F^2 ($wR2 = 4.2\%$) for all unique data collected using Mo- $K\alpha$ X-radiation and a CCD-based detector. The final $R1$ was 2.0%, calculated for 534 unique observed ($F_o \geq 4\sigma_F$) reflections, and the goodness-of-fit (S) was 0.91. The structure contains a uranyl tricarbonate cluster composed of a uranyl hexagonal bipyramid that shares three equatorial edges with CO_3 triangles. The uranyl tricarbonate clusters are connected through NaO_6 and NaO_5 polyhedra, forming a heteropolyhedral framework structure. This compound may be related to a uranyl carbonate phase with the same composition which has been reported as an alteration phase on the surface of Chernobyl 'lava', and as a mineral in the Jachymov ore district, Czech Republic.

KEYWORDS: uranyl carbonate, sodium uranyl carbonate, crystal structure, nuclear waste.

Introduction

MORE than 25 uranyl carbonate minerals are known (Mandarino, 1999), and actinide-carbonate complexes are important over a wide variety of environmental conditions (Clark *et al.*, 1995). The crystal structures of eight uranyl carbonate minerals have been reported. On the basis of the polymerization of cation polyhedra of higher bond valence, uranyl carbonates have been grouped into those containing infinite sheets and those with an isolated uranyl tricarbonate cluster (Burns, 1999). The structures have been solved for liebigite, $\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_{11}$ (Mereiter, 1982), schröckingerite, $\text{NaCa}_3[(\text{UO}_2)(\text{CO}_3)_3](\text{SO}_4)\text{F}(\text{H}_2\text{O})_{10}$ (Mereiter, 1986*a*), swartzite, $\text{CaMg}[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_{12}$ (Mereiter, 1986*b*), andersonite, $\text{Na}_2\text{Ca}[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_5$ (Mereiter, 1986*c*), bayleyite, $\text{Mg}_2[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})_{18}$ (Mayer and Mereiter, 1986), roubaultite,

$[\text{Cu}_2(\text{UO}_2)_3(\text{CO}_3)_2\text{O}_2(\text{OH})_2](\text{H}_2\text{O})_4$ (Ginderow and Cesbron, 1985), rutherfordine, $[(\text{UO}_2)(\text{CO}_3)]$ (Finch *et al.*, 1999), and bijvoetite, $[\text{M}_8(\text{UO}_2)_{16}\text{O}_8(\text{OH})_8(\text{H}_2\text{O})_{25}](\text{H}_2\text{O})_{14}$, $M = \text{REE}$, Y (Li *et al.*, 2000). Of these, roubaultite, rutherfordine and bijvoetite each contain sheets of polyhedra, whereas the others contain the uranyl tricarbonate cluster.

There are several reports of the compound $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ in the literature, although the structure has not been published. Douglass (1956) synthesized $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ and provided X-ray powder diffraction (XRD) data. An unnamed mineral with composition $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ was reported from the Jachymov ore district, where it occurs as part of the secondary uranyl mineral assemblage (Ondrus *et al.*, 1997). A compound of the same composition was also reported as an alteration phase on Chernobyl 'lava' (Burakov *et al.*, 1999). Recently, a mineral with the composition $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ was approved by the Commission on New Minerals and New Mineral Names of the International Mineralogical Association (Grice and Ferraris, 2000), but detailed information is still unavailable. Table 1

* E-mail: pburns@nd.edu

TABLE 1. Crystallographic information reported for $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$.

Sources	Unit cell	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Refs
Douglass	trigonal	9.32(1)		12.80(1)				[1]
Unnamed mineral from Czech	triclinic	16.468(2)	27.578(3)	5.222(2)	94.155(2)	100.58(1)	121.25(1)	[2]
	hexagonal	18.621(3)		12.801(4)				[2]
Unnamed mineral	triclinic	9.280	9.295	12.864	90.293	91.124	119.548	[3]
Current work	trigonal	9.3417(6)		12.824(1)				

[1] Douglass (1956), [2] Ondrus *et al.* (1997), [3] Grice and Ferraris (2000)

presents a summary of crystallographic information reported for compounds with the composition Na₄(UO₂)(CO₃)₃. We have grown a single crystal of Na₄(UO₂)(CO₃)₃ using hydrothermal techniques, and report the structure here.

Experimental

Crystal synthesis

Crystals of Na₄(UO₂)(CO₃)₃ were synthesized by hydrothermal reaction of 4 ml of a 0.2 M solution of uranyl acetate with 0.17 g of sodium carbonate. The solution was heated to 220°C in a Teflon-lined Parr bomb for 2 weeks. Yellowish anhydrous crystals were recovered by filtration, washed with de-ionized water, and dried in air.

Single-crystal XRD

A single crystal of Na₄(UO₂)(CO₃)₃ with dimensions 0.10 × 0.10 × 0.10 mm was selected and mounted on a glass fibre, and diffraction data were collected using a Bruker Iκ SMART CCD diffractometer by using Mo-Kα X-radiation and a crystal-to-detector distance of 5.0 cm. More than a hemisphere of 3-dimensional data was collected using frame widths of 0.3° in ω, with 10 s spent counting per frame. The unit-cell parameters (Table 2) were refined from 2210 reflections using least-squares techniques. The data were integrated and corrected for Lorentz, polarization and background effects using the Bruker program SAINT. A semi-empirical absorption correction was applied on the basis of equivalent reflections by modelling the crystal as an ellipsoid; the correction reduced R_{int} of 1646 intense reflections from 4.9 to 4.1%. A total of 5555 reflections were

measured, of which 804 reflections were unique, with 534 classed as observed ($F_o \geq 4\sigma_F$).

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. The structure was solved by direct methods in space group $P\bar{3}c1$ and was refined on the basis of F^2 for all unique data. The final model included all atomic-positional parameters, anisotropic-displacement parameters for all atoms, and a refinable weighting scheme of the structure factors. The refinement converged to a $wR2$ of 4.2% for all data, an $R1$ of 2.0%, calculated for the 534 unique observed ($F_o \geq 4\sigma_F$) reflections, and a goodness-of-fit (S) of 0.91 for all data. The final atomic coordinates and anisotropic-displacement parameters are given in Table 3, with selected interatomic distances given in Table 4, and a bond-valence analysis given in Table 5. Observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available upon request.

Discussion

Cation coordination

The structure of Na₄(UO₂)(CO₃)₃ contains a single symmetrically unique U⁶⁺ cation, which is part of an approximately linear (UO₂)²⁺ uranyl ion (designated U_r) with an average U–O _{U_r} bond length of 1.81 Å (Table 1). The uranyl ion is further coordinated by six O atoms that are arranged at the equatorial (designated eq)

TABLE 2. Crystallographic information for Na₄(UO₂)(CO₃)₃.

a (Å)	9.3417(6)	Crystal size (mm)	0.10 × 0.10 × 0.10
c (Å)	12.824(1)	Total ref.	5555
V (Å ³)	969.2(1)	Unique ref.	804
Space group	$P\bar{3}c1$	R_{int} (%)	5.35
$F(000)$	968	Unique $F_o \geq 4\sigma_F$	534
μ (mm ⁻¹)	16.986	Final $wR2$ (%)	4.2
D_{calc} (g/cm ³)	3.715	Final $R1$ (%)	2.0
		S	0.91
Unit-cell contents: 4[Na ₄ (UO ₂)(CO ₃) ₃]			

$$R1 = \frac{\sum(|F_o| - |F_c|)}{\sum |F_o|}$$

$$S = [\sum w(|F_o - F_c|^2 / (m-n))]^{1/2}, \text{ for } m = 804 \text{ observations and } n = 60 \text{ parameters}$$

$$w = 1/[\sigma^2(F_o^2) + (0.0217 \times P)^2], P = (\max(F_o^2, 0) + 2 \times F_c^2) / 3$$

TABLE 3. Atomic coordinates ($\times 10^4$) and displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> *(eq)	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
U1	6667	3333	1303(1)	11(1)	10(1)	10(1)	13(1)	0	0	5(1)
Na1	0	0	2500	23(1)	22(1)	22(1)	24(2)	0	0	11(1)
Na2	0	0	0	22(1)	23(1)	23(1)	20(2)	0	0	11(1)
Na3	8769(3)	3076(3)	3764(2)	27(1)	13(1)	16(1)	49(1)	5(1)	1(1)	6(1)
O1	6667	3333	2718(4)	20(1)	22(2)	22(2)	17(3)	0	0	11(1)
O2	6667	3333	-106(4)	23(1)	30(2)	30(2)	9(3)	0	0	15(1)
O3	9651(4)	7833(4)	3784(3)	21(1)	15(2)	19(2)	33(2)	-3(2)	-2(2)	12(2)
O4	460(4)	5959(5)	3817(3)	23(1)	10(2)	10(2)	49(3)	6(2)	6(2)	5(2)
O5	1471(4)	3765(5)	3563(3)	26(1)	12(2)	15(2)	55(3)	-2(2)	0(2)	10(2)
C1	733(7)	7444(7)	3723(4)	17(1)	11(3)	13(3)	22(3)	-1(2)	-4(2)	2(2)

* *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor

positions of a hexagonal bipyramid. The average $\text{U}^{6+}\text{-O}_{\text{eq}}$ bond length is 2.41 Å (Table 4), which compares well with the average $^{18}\text{U}\text{-O}_{\text{eq}}$ bond length of 2.47(12) Å derived from numerous well-refined structures (Burns *et al.*, 1997). The structure contains one symmetrically unique C^{4+} cation in the usual triangular coordination, with an average C–O bond length of 1.28 Å (Table 4).

There are three symmetrically distinct Na cations in the structure. Na1 and Na2 are octahedrally coordinated by O atoms, with an average Na1–O bond length of 2.501(3) Å and an

average Na2–O bond length of 2.444(3) Å. The Na3 cation is coordinated by five anions with an average Na3–O bond length of 2.398 Å.

Structural connectivity

As is the case with other known uranyl carbonates with U:C ratios of 1:3, the structure of $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ contains the uranyl tricarbonate cluster shown in Fig. 1a. The cluster contains one UrO_6 hexagonal bipyramid that shares three of its equatorial edges with CO_3 triangles. As for all

TABLE 4. Bond lengths (Å) and angles (°) for $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$.

U1–O2	1.807(5)	Na1–O3a,d,e,f,g,h	2.501(3) × 6
U1–O1	1.814(5)		
U1–O5a,b,c	2.385(4) × 3	Na2–O3h,k,a,e,l,m	2.444(3) × 6
U1–O4a,b,c	2.427(3) × 3		
U1–O _{eq} >	2.41	Na3–O5n	2.286(4)
O2–U1–O1	180	Na3–O3i	2.323(4)
		Na3–O4n	2.345(4)
C1–O3j	1.236(7)	Na3–O1	2.488(3)
C1–O5f	1.310(7)	Na3–O2o	2.547(4)
C1–O4	1.284(6)	<Na3–O>	2.398
<C1–O>	1.28		
O3j–C1–O4	124.2(5)		
O3j–C1–O5f	122.6(5)		
O4–C1–O5f	113.2(5)		
<O–C1–O>	120		

$a = -x + 1, -x + y, -z + 1/2, b = y, x, -z + 1/2, c = x - y + 1, -y + 1, -z + 1/2; d = -y + 1, x - y, z; e = y - 1, x - 1, -z + 1/2; f = -x + y, -x + 1, z; g = x - 1, y - 1, z; h = x - y, -y + 1, -z + 1/2; i = -x + y + 1, -x + 1, z; j = x - 1, y, z; k = -x + y, y - 1, z - 1/2; l = x - 1, x - y, z - 1/2; m = -y + 1, -x + 1, z - 1/2; n = x + 1, y, z; o = -y + 1, -x + 1, z + 1/2$

CRYSTAL STRUCTURE OF $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ TABLE 5. Bond valence analysis* for $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$.

	O1	O2	O3	O4	O5	Σ
U1	1.57	1.59		$0.47 \times 3 \rightarrow$	$0.51 \times 3 \rightarrow$	6.10
Na1			$0.15 \times 6 \rightarrow$			0.90
Na2			$0.18 \times 6 \rightarrow$			1.08
Na3	$0.16 \times 3 \downarrow$	$0.13 \times 3 \downarrow$	0.24	0.23	0.27	1.03
C1			1.54	1.35	1.27	4.16
Σ	2.05	1.98	2.11	2.05	2.05	

* bond-valence parameters for U^{6+} from Burns *et al.* (1997) and for other cations from Brese and O'Keefe (1991)

known structures that contain the uranyl tricarbonate cluster, these clusters are not directly linked but are connected through bonds to lower-valence cations. Burns *et al.* (1996) and Burns (1999) therefore grouped these structures with those that contain isolated clusters of polyhedra of higher bond-valence.

Three symmetrically related Na_3O_5 polyhedra share a common edge, resulting in a trimer of composition Na_3O_{11} (Fig. 1b). Each trimer is linked to three uranyl tricarbonate clusters by sharing equatorial edges of UrO_6 hexagonal bipyramids with Na_3O_5 polyhedra, resulting in a heteropolyhedral sheet that is parallel to (001) (Fig. 1c). Additional linkages within the sheet are provided by the sharing of a vertex of the Na_3O_5 polyhedron with a CO_3 triangle. Adjacent sheets are connected along [001]; vertices common to all three Na_3O_5 polyhedra in the Na_3O_{11} trimer of one layer correspond to uranyl ion O atoms of adjacent offset sheets (Fig. 1d). The NaIO_6 and Na_2O_6 octahedra share faces, resulting in chains of octahedra that extend along [001] (Fig. 1e). Each octahedral vertex is shared with a CO_3 triangle and a Na_3O_5 polyhedron (Fig. 1f,g).

Related structures with U:C = 1:3

The structures of uranyl carbonate minerals are reviewed and illustrated in Burns (1999). Of these, the structure of $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ is most closely related to that of schröckingerite, $\text{NaCa}_3[(\text{UO}_2)(\text{CO}_3)_3](\text{SO}_4)\text{F}(\text{H}_2\text{O})_{10}$, which contains a heteropolyhedral layer that is similar to the layer in $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ (Mereiter, 1986a).

In schröckingerite, three symmetrically unique $\text{Ca}\phi_7$ polyhedra (ϕ : unspecified ligand) link by sharing three vertices to form a trimer of

composition $\text{Ca}_3\phi_{18}$. This trimer differs from the Na_3O_{11} trimer in $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ in the coordination of the cations and in the mode of connection of the polyhedra: shared vertices in $\text{Ca}_3\phi_{18}$, in contrast to a shared edge in Na_3O_{11} . However, the way that these trimers are linked with uranyl tricarbonate clusters to form heteropolyhedral sheets is similar in the two structures (Figs 1c, 2a). In schröckingerite, the sheets are linked to SO_4 tetrahedra on one side, and adjacent sheets are connected through hydrogen bonds to H_2O groups in the interlayers (Fig. 2b). Note that the structure of schröckingerite is triclinic, but has a pseudo-trigonal unit cell with parameters $a = 9.634$, $b = 9.635$, $c = 14.391$ Å, $\alpha = 91.41$, $\beta = 92.33$, $\gamma = 120.26$ (°).

The XRD patterns were reported for two polymorphs of $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ in the Powder Diffraction File (International Center for Diffraction Data). The calculated XRD pattern for $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ agrees well with PDF 11-0081, drawn from the work of Douglass (1956), but is significantly different from 13-0038, suggesting that the compound we studied is identical to that prepared by Douglass (1956).

$\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ from the Czech Republic and Chernobyl

A sodium uranyl carbonate mineral with the composition $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ was found at the Jachymov ore district, Czech Public (Ondrus *et al.*, 1997), but the structure has not been reported and a complete description of the mineral has not yet appeared. Based on powder diffraction data, both triclinic and trigonal unit cells (Table 1) were given for the mineral (Ondrus *et al.*, 1997); it was not possible to index all reflections using the cell of Douglass (1956). The material studied

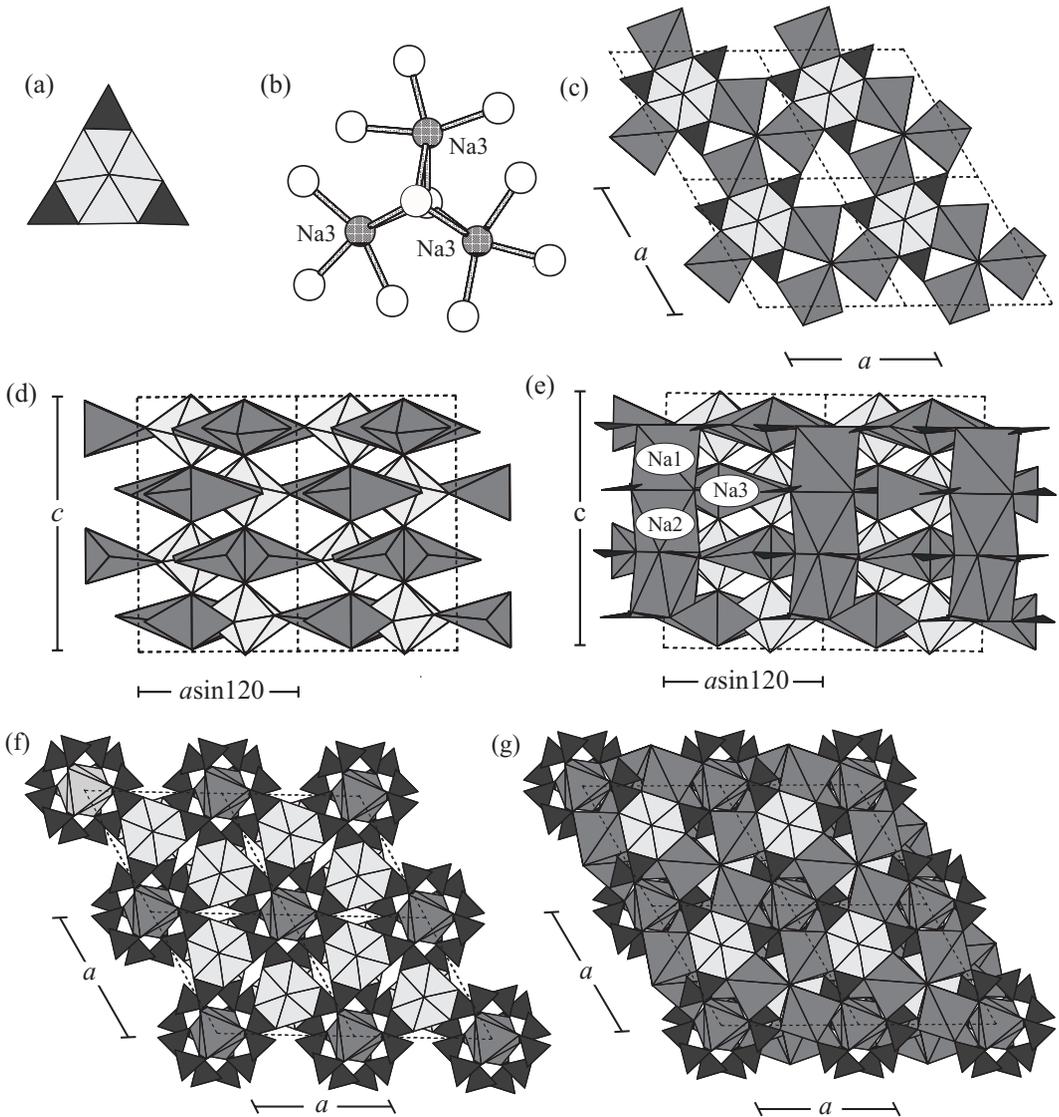


FIG. 1. The structure of $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$. (a) Uranyl tricarbonate cluster; (b) Na_3O_{11} trimer; (c) heteropolyhedral sheet formed by sharing corners and edges among uranyl tricarbonate clusters and Na_3O_{11} trimers, projected onto (001); (d) the structure projected onto (010), Na1, Na2 and C are omitted; (e) the structure projected onto (010); (f) the structure projected onto (001), with Na(3) polyhedra omitted; (g) the structure projected onto (001). The CO_3 groups are shown as black triangles, the UO_6 polyhedra are light grey, and the NaO_n polyhedra are dark grey.

by Ondrus *et al.* (1997) was fine grained. It is possible that some peaks in the diffraction pattern are due to impurities. The results of our work may provide the structure of the unnamed mineral.

Uranyl carbonate phases have been identified on radioactive materials that resulted from the

nuclear accident in the Chernobyl No. 4 reactor. Alteration products collected from the Chernobyl 'lava' were identified by XRD and energy dispersive spectroscopy (EDS) as $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$, along with $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{UO}_4 \cdot 4\text{H}_2\text{O}$, and

CRYSTAL STRUCTURE OF $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$

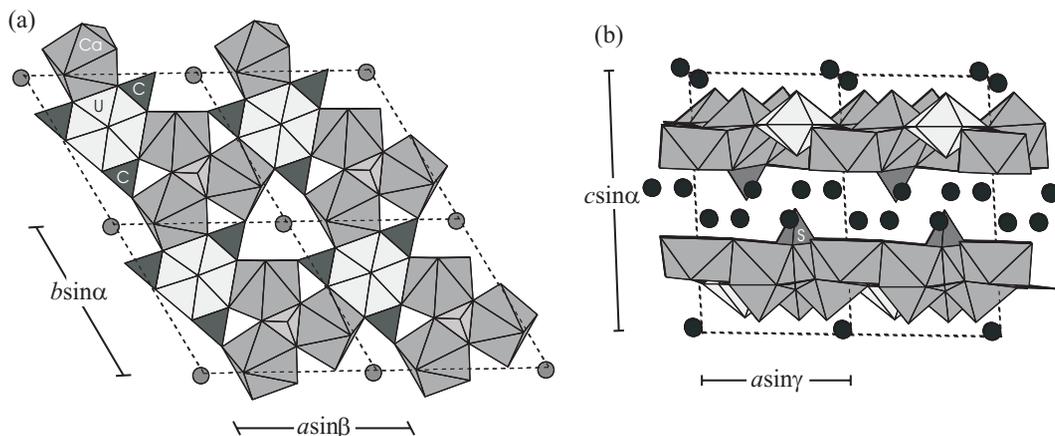


FIG. 2. The structure of schroëckingerite. (a) Structure projected along [001]; grey circles represent Na cations; (b) structure projected along [010]; black circles represent H_2O groups.

$\text{UO}_2(\text{CO}_3)$ (Burakov *et al.*, 1999). The phase we have studied may be the same as one of the Na uranyl carbonates forming at Chernobyl.

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