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New Structural Arrangements in Three Ca Uranyl Carbonate Compounds with Multiple Anionic Species

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Three new Ca uranyl carbonates containing nitrate or chlorine have been synthesized by room temperature evaporation of solutions. The structures of each were determined and refined on the basis of F^2 for all unique data collected using an APEX CCD-based detector and Mo$K\alpha$ radiation. The structures of each contain uranyl tricarbonate clusters of composition $[UO_2(CO_3)_3]^{4-}$ that involve a uranyl hexagonal bipyramid that shares three equatorial edges with CO_3 groups. The structure of $Ca_5[(UO_2)(CO_3)_3]_2(NO_3)_2(H_2O)_{10}$ (UND-1) consists of a sheet of uranyl tricarbonate clusters that share edges and vertices with $Ca\phi_n$ polyhedra (Ca:U = 5:2 in the sheet). An $(NO_3)^-$ group is attached to the sheet by sharing an edge with a $Ca\phi_n$ polyhedron. Adjacent sheets are linked by H bonding only. The structure of $Ca_6[(UO_2)(CO_3)_3]_2Cl_4(H_2O)_{19}$ (UND-2) has a sheet of uranyl tricarbonate clusters and $Ca\phi_n$ polyhedra that is similar to that found in UND-1, but adjacent sheets are linked by bonds to Ca cations and Cl anions located between the sheets. The structure of $Ca_{12}[(UO_2)(CO_3)_3]_4Cl_8(H_2O)_{47}$ (UND-3) involves uranyl tricarbonate clusters that share vertices and edges with clusters containing six-member rings of $Ca\phi_8$ polyhedra, resulting in a heteropolyhedral framework, with Cl anions and H_2O groups located in channels through the framework. Crystallographic data: UND-1, $R1 = 0.0467$, w$R2 = 0.1022$, monoclinic, space group $P2_1/n$, $a = 6.5729(9)$, $b = 16.517(2)$, $c = 15.195(2)$ Å, $\beta = 90.494(3)^\circ$, $Z = 2$; UND-2, $R1 = 0.0362$, w$R2 = 0.1115$, tetragonal, space group $P4/mbm$, $a = 16.744(2)$, $c = 8.136(1)$ Å, Z = 2; UND-3, $R1 = 0.0367$, w$R2 = 0.1110$, cubic, space group $Fd\bar{3}$, $a = 27.489(3)$ Å, $Z = 8$.

Key Words: calcium uranyl carbonate.

INTRODUCTION

Uranyl minerals are significant constituents of the oxidized portions of U deposits (1), they impact upon the release rates of U and Pb from radioactive mine and mill tailings, are common in soils contaminated by actinides (2), and are likely to be important alteration phases of nuclear waste in a geological repository (3–8). Uranyl carbonates are common in oxidized U-bearing rocks containing carbonate, and more than 25 mineral species have been described (9). Actinide–carbonate complexes are important over a wide range of environmental conditions (10), thus understanding the structures of uranyl carbonates is important for understanding the mobility of actinides in the environment.

Uranyl compounds are structurally diverse, although their hierarchy of structures is dominated by sheets of polyhedra that contain cations of high valence (11). Uranyl carbonates are an interesting exception to this generality; of the 14 known structures of uranyl carbonates, only the minerals rutherfordine, bijvoetite, roubaultite and wyartite contain sheets of polyhedra that contain a cation of high valence (12–15). The others contain the uranyl tricarbonate cluster of composition $[(UO_2)(CO_3)_3]^{4-}$, which occurs as an isolated cluster of polyhedra in each of the structures. As such, uranyl carbonates are a fruitful means of probing the structural connectivity of uranyl compounds containing finite clusters. As part of our continuing studies of various uranyl compounds, we have synthesized three complex uranyl carbonates by evaporation of solutions at room temperature. These compounds are unusual in the diversity of their anionic species; one is a mixed carbonate–nitrate, and two contain carbonate and Cl.

EXPERIMENTAL

Crystals of $Ca_5[(UO_2)(CO_3)_3]_2(NO_3)_2(H_2O)_{10}$ (designated UND-1) were grown at room temperature from a solution containing 0.25 g $UO_2(NO_3)_2(H_2O)_6$ (Alfa), 0.30 g $NaHCO_3$ (Fisher), 0.655 g $Ca(NO_3)_2$ (Fisher) and 10 mL ultrapure H_2O. After mixing the components in a test tube, the solution was transferred to a 50 mL beaker and stirred for ~2 min. The beaker was covered by perforated film and left standing. After 10 days, the solution was transferred to

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an open dish and tabular greenish-yellow crystals were recovered.

Crystals of $Ca_6[(UO_2)(CO_3)_3]_2Cl_4(H_2O)_{19}$ and $Ca_{12}[(UO_2)(CO_3)_3]_4Cl_8(H_2O)_{47}$ (designated UND-2 and UND-3, respectively), were grown at room temperature from a solution containing 0.25 g $UO_2(NO_3)_2(H_2O)_6$ (Alfa), 0.30 g $NaHCO_3$ (Fisher), 0.60 g $CaCl_2$ (Fisher) and 10 mL ultrapure H_2O. The components were mixed in a test tube and the solution was transferred to a 50 mL beaker. The beaker was stirred for ~2 min, covered with a perforated film, and left standing. After 10 days, the solution was transferred to an open dish; tabular greenish-yellow crystals of UND-2 were recovered after two additional days of evaporation. After about a week, the tabular crystals in contact with the solution began to dissolve, and blocky crystals of UND-3 formed.

Single-Crystal X-Ray Diffraction

A single crystal of UND-1 was selected for data collection and was mounted on a Bruker PLATFORM three-circle goniometer with an SMART CCD (charge-coupled device) APEX detector; the crystal-to-detector distance was 4.5 cm. A sphere of data was collected using monochromatic Mo$K\alpha$ X-radiation and frame widths of 0.3° in ω, with 10 s used to acquire each frame. The unit-cell dimensions of UND-1 (Table 1) were refined from 843 reflections using least-squares techniques. The data were corrected for Lorentz, polarization and background effects. A semi-empirical absorption correction was applied based on equivalent reflections by modeling the crystal as an ellipsoid, and lowered the R_{int} of 1699 intense reflections from 11.3 to 4.5%. Information pertinent to the data collection is given in Table 1.

X-ray data collections and reductions for crystals of UND-2 and UND-3 were done in a similar fashion to UND-1. The unit-cell dimensions of UND-2 and UND-3 (Table 1) were refined from 1016 and 931 reflections, respectively. Semi-empirical absorption corrections were applied based on equivalent reflections by modeling the crystals as a plate and ellipsoid for UND-2 and UND-3, respectively, and lowered the R_{int} of 4794 and 976 intense reflections from 9.0 to 6.1%, and 7.4 to 5.7%, respectively. Information pertinent to the data collections is given in Table 1.

Structures were solved with SHELXS (16) and refined with SHELXL (17) within the SHELXTL (18) suite of programs. Systematic absences indicated space group $P2_1/n$ for UND-1. The structure contains four cations that are each coordinated by three O atoms in triangular arrangements, of which three share an equatorial edge of the uranyl hexagonal bipyramid, giving the well-known uranyl

TABLE 1
Crystallographic Data and Refinement Results for UND-1, UND-2, and UND-3

	UND-1	UND-2	UND-3
Structural formula	$Ca_5[(UO_2)(CO_3)_3]_2(NO_3)_2(H_2O)_{10}$	$Ca_6[(UO_2)(CO_3)_3]_2Cl_4(H_2O)_{19}$	$Ca_{12}[(UO_2)(CO_3)_3]_4Cl_8(H_2O)_{47}$
Formula weight	1404.7	1624.7	3411.55
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Space group	$P2_1/n$	$P4/mbm$	$Fd\bar{3}$
a (Å)	6.5729(9)	16.744(2)	27.489(3)
b (Å)	16.517(2)		
c (Å)	15.195(2)	8.136(1)	
β (°)	90.494(3)		
V (Å^3)	1649.6(4)	2281.0(4)	20772(4)
Z	2	2	8
ρ_{calc} (g/cm^3)	2.83	2.37	2.18
μ (mm^{-1})	10.72	8.11	7.14
$F(000)$	1316	1548	13104
Crystal size (mm^3)	0.14 × 0.08 × 0.06	0.12 × 0.12 × 0.08	0.16 × 0.160.16
Reflections collected	32,861	45,597	25,088
Independent reflections	6846 [R(int) = 0.10]	2658 [R(int) = 0.08]	1277 [R(int) = 0.13]
Observed reflections ($\lvert F_o \rvert \geq 4\sigma_F$)	3768	2061	919
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6846/0/148	2658/0/106	1277/0/102
Goodness-of-fit on F^2	0.882	1.096	1.043
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0467$, w$R2 = 0.1022$	$R1 = 0.0362$, w$R2 = 0.1115$	$R1 = 0.0367$, w$R2 = 0.1110$
R indices (all data)	$R1 = 0.1053$, w$R2 = 0.1214$	$R1 = 0.0492$, w$R2 = 0.1181$	$R1 = 0.0594$, w$R2 = 0.1176$
Extinction coefficient	0.00021(9)	0.00012(9)	0.000007(5)
Largest diff. Peak and hole	2.273 and −1.206e Å^{-3}	3.698 and −1.199e Å^{-3}	1.655 and −0.503e Å^{-3}

tricarbonate cluster (see below). The other, which shares an edge with a Ca polyhedron, is designated as containing N. This is supported by charge-balance considerations and infrared spectra (see below). The final structure model included refined atomic coordinates, anisotropic displacement parameters for the cations, and a weighting scheme of the structure factors. It was refined on the basis of F^2 for all unique reflections, and gave a final $R1$ of 4.7%, calculated for the 3768 unique observed reflections.

Systematic absences of reflections for UND-2 are consistent with space groups $P4/mbm$, $P\bar{4}b2$ and $P4bm$. The structure was solved and refined in space group $P4/mbm$. In addition to the U, Ca and O positions, the difference-Fourier map revealed a fully occupied Cl site. The Ca(3) site is partially occupied, with a refined occupancy of 0.453(3). In the final cycle of refinement, the occupancy of the Ca(3) site was constrained to 0.5, as required for electroneutrality. The refined model involves some atomic positions that are split off their corresponding special positions (see below); lowering the symmetry to $P4bm$ did not remove these features. The final refinement, done on the basis of all unique F^2, included atomic positional parameters and anisotropic displacement parameters for all atoms, and a weighting scheme for the structure factors. The refinement converged to an $R1$ of 3.6%, calculated for the 2061 unique observed reflections.

Systematic absences indicated space group $Fd\bar{3}$ or $Fd\bar{3}m$ for UND-3. The structure was successfully solved and refined in space group $Fd\bar{3}$. In addition to the U, Ca, C and O atoms, the structure contains a single Cl site, with a refined occupancy of ~60%. In the final cycle of refinement, the occupancy of the Cl site was constrained to $\frac{2}{3}$, as is required to achieve electroneutrality. During refinement of the model it was noted that the displacement parameter for OW(12) was unusually large; the occupancy of the site was subsequently refined to $\sim\frac{1}{3}$. The final structure model included refined atomic coordinates, anisotropic displacement parameters for all atoms except OW(12), and a weighting scheme of the structure factors. The structure was refined on the basis of F^2 for all unique reflections, and gave a final $R1$ of 3.7%, calculated for the 919 unique observed reflections.

A complete listing of atomic coordinates and selected interatomic distances and angles for UND-1, UND-2 and UND-3 is given in Tables 2–7.

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for UND-1

	x	y	z	U(eq)
U(1)	0.8316(1)	0.1747(1)	0.1787(1)	21(1)
Ca(1)	0.6741(2)	−0.0532(1)	0.2242(1)	23(1)
Ca(2)	$\frac{1}{2}$	0	$\frac{1}{2}$	27(1)
Ca(3)	0.0608(3)	0.2304(1)	−0.0552(1)	30(1)
C(1)	0.4133(12)	0.1595(4)	0.6341(5)	26(2)
C(2)	0.8247(13)	0.0571(5)	0.0418(5)	29(2)
C(3)	0.6855(13)	0.1268(5)	0.3475(5)	29(2)
N(1)	0.9373(13)	0.01287(6)	−0.2507(6)	58(2)
O(1)	0.6384(8)	−0.1828(3)	0.2876(4)	30(1)
O(2)	0.9262(8)	0.2841(4)	0.0774(4)	33(1)
O(3)	0.4381(8)	0.0852(3)	0.6186(3)	27(1)
O(4)	0.7213(8)	0.0747(3)	0.2887(4)	27(1)
O(5)	0.2336(8)	0.2990(4)	−0.1709(4)	30(1)
O(6)	0.7682(9)	0.0090(4)	−0.0173(4)	38(1)
O(7)	0.8089(8)	0.0394(3)	0.1243(4)	31(1)
O(8)	0.5732(9)	0.1903(4)	0.1483(4)	36(1)
O(9)	0.0185(9)	0.1331(4)	−0.1771(4)	39(2)
O(10)	0.0876(9)	0.1585(4)	0.2099(4)	36(1)
O(11)	0.5978(10)	0.1120(4)	0.4206(4)	45(2)
O(12)	0.8892(9)	0.1305(4)	0.0265(4)	35(1)
O(13)	0.9993(11)	0.0770(5)	−0.3093(5)	55(2)
O(14)	0.7853(15)	0.1723(6)	−0.2693(7)	88(3)
OW(15)	0.6417(9)	−0.1228(4)	0.0711(4)	45(2)
OW(16)	0.3483(9)	−0.0009(4)	0.1879(4)	48(2)
OW(17)	0.3696(11)	0.2822(5)	0.0245(5)	60(2)
OW(18)	0.7246(12)	0.2711(5)	−0.1087(5)	70(2)
OW(19)	0.1747(16)	0.0170(7)	0.04313(7)	114(4)

Infrared Spectroscopy

The infrared spectrum in the 400–4000 cm^{-1} range was obtained for a single crystal of UND-1 using a Bomem Michelson MB-100 spectrometer. A major absorption band centered at 3437 cm^{-1} is indicative of H_2O or OH, in agreement with the presence of H_2O groups in the refined structure. Absorptions at 1546, 1397, 740 and 690 cm^{-1} may be attributed primarily to carbonate groups, and a peak shoulder at 1356 cm^{-1} is attributed to a nitrate group (19, 20). Multiple vibrational modes for $(UO_2)^{2+}$ occur due to the low site symmetry of the uranyl ion. A strong and sharp band at 900 cm^{-1} is attributed to the uranyl asymmetric stretching band (ν_3), and one of the weaker bands at 840, 825 and 816 cm^{-1} may result from the symmetric uranyl stretch (ν_1) (21–23). Cejka (24) discussed features of infrared spectra observed in uranyl carbonates including minerals and synthetic phases, and concluded that the ν_3 of uranyl ions in tricarbonate environments are in the range of 882–926 cm^{-1} for liebigite, andersonite, schröckingerite, bayleyite, grimselite, voglite, widenmannite and znucalite, and the assignment of ν_1 of uranyl carbonates is difficult due to weak peaks and potential overlapping with modes from CO_3 groups.

Elemental Analysis

Single crystals (10–20 μm diameter) of UND-1, UND-2 and UND-3 were analyzed for Ca, Cl and U by wavelength dispersive spectrometry using a Cameca SX-50 electron microprobe operated at an accelerating voltage of 15 kV and a probe current of 15 nA, with a fixed but defocused

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for UND-1

U(1)–O(10)a	1.765(6)	C(1)–O(3)	1.260(8)	C(2)–O(6)	1.254(9)
U(1)–O(8)	1.775(6)	C(1)–O(2)g	1.272(9)	C(2)–O(7)	1.291(9)
U(1)–O(7)	2.388(6)	C(1)–O(1)f	1.299(9)	C(2)–O(12)	1.305(9)
U(1)–O(1)b	2.416(6)	⟨C(1)–O⟩	1.277	⟨C(2)–O⟩	1.283
U(1)–O(5)c	2.418(5)	O(3)–C(1)–O(2)g	125.3(7)	O(6)–C(2)–O(7)	121.7(7)
U(1)–O(2)	2.457(6)	O(3)–C(1)–O(1)f	119.7(7)	O(6)–C(2)–O(12)	123.7(7)
U(1)–O(12)	2.459(6)	O(2)g–C(1)–O(1)f	115.0(7)	O(7)–C(2)–O(12)	114.4(7)
U(1)–O(4)	2.464(5)	⟨O–C(1)–O⟩	120.0	⟨O–C(2)–O>	119.9
⟨U(1)–O$_{Ur}$⟩	1.770				
O(10)a–U(1)–O(8)	179.3(3)	N(1)–O(9)a	1.24(1)	Ca(1)–O(7)	2.335(6)
⟨U(1)–O$_{eq}$⟩	2.434	N(1)–O(14)	1.26(1)	Ca(1)–O(4)	2.350(6)
		N(1)–O(13)	1.30(1)	Ca(1)–O(1)	2.360(6)
C(3)–O(4)	1.264(9)	⟨N(1)–O⟩	1.27	Ca(1)–OW(16)	2.370(7)
C(3)–O(11)	1.279(9)	O(9)a–N(1)–O(14)	120.3(10)	Ca(1)–O(9)d	2.522(6)
C(3)–O(5)c	1.296(9)	O(9)a–N(1)–O(13)	121.5(8)	Ca(1)–O(13)e	2.527(7)
⟨C(3)–O⟩	1.280	O(14)–N(1)–O(13)	118.2(9)	Ca(1)–O(3)f	2.562(5)
O(4)–C(3)–O(11)	124.8(7)	⟨O–N(1)–O⟩	120.0	Ca(1)–OW(15)	2.601(7)
O(4)–C(3)–O(5)c	116.3(7)			⟨Ca(1)–ϕ⟩	2.453
O(11)–C(3)–O(5)c	118.8(7)	Ca(3)–O(12)h	2.358(6)		
⟨O–C(3)–O⟩	120.0	Ca(3)–O(2)h	2.380(6)		
		Ca(3)–O(5)	2.388(6)		
Ca(2)–O(11), f	2.303(7) ×2	Ca(3)–OW(18)h	2.443(8)		
Ca(2)–O(3), f	2.324(5) ×2	Ca(3)–O(9)	2.465(6)		
Ca(2)–OW(19), f	2.39(1) ×2	Ca(3)–OW(17)	2.506(8)		
⟨Ca(2)–ϕ⟩	2.34	Ca(3)–O(11)i	2.642(7)		
		Ca(3)–OW(15)d	2.654(7)		
		⟨Ca(3)–ϕ⟩	2.479		

Note. Symmetry transformations used to generate equivalent atoms: (a) $x+1, y, z$; (b) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (c) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (d) $-x+1, -y, -z$; (e) $-x+2, -y, -z$; (f) $-x+1, -y, -z+1$; (g) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (h) $x-1, y, z$; (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

beam 20 μm in diameter. The crystals were unstable under the electron beam; the resulting elemental abundances are therefore semi-quantitative, but are in fair agreement with those expected from the single-crystal structure refinement. Mean analyses of 3–4 points in wt% element are: UND-1: Ca 14.9(0.3), U 36.9(0.2), expected: Ca 14.27, U 33.89; UND-2: Ca 16.2(0.8), U 34.4(2.9), Cl 8.3(0.3), expected: Ca 14.80, U 29.30, Cl 8.73; UND-3: Ca 16.9(1.0), U 24.6(7.4), Cl 9.9(2.5), expected: Ca 14.10, U 27.91, Cl 8.31. Each crystal was analyzed for Na, which was below the detection limit in all the cases.

RESULTS

UND-1

The structure of UND-1 contains a single symmetrically distinct U^{6+} cation, which is part of an approximately linear $(UO_2)^{2+}$ uranyl ion (designated *Ur*), with U^{6+}-O_{Ur} bond lengths of ~1.8 Å, as typically observed in U^{6+} compounds (25). The uranyl ion is coordinated by six anions, arranged at the equatorial vertices of hexagonal bipyramids, with a ⟨U(1)–O$_{eq}$⟩ (O$_{eq}$: equatorial O atoms) bond length of 2.434 Å , which is consistent with the

TABLE 4
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for UND-2

	x	*y*	*z*	*U*(eq)
U(1)	0.3216(1)	0.1784(1)	0	20(1)
Ca(1)	0.2660(1)	−0.0545(1)	0	22(1)
Ca(2)	0	0	0	20(1)
Ca(3)^a	0.3110(3)	0.1890(3)	$\frac{1}{2}$	42(1)
Cl(1)	0.1515(2)	0.1110(2)	$\frac{1}{2}$	69(1)
C(1)	0.1576(3)	0.1281(3)	0	23(1)
C(2)^a	0.4381(5)	0.0619(5)	0.1050(30)	46(5)
O(1)	0.3221(3)	0.1779(3)	0.2186(10)	58(2)
O(2)	0.1798(3)	0.2031(3)	0	35(1)
O(3)^a	0.4838(4)	0.0162(4)	0.1864(19)	55(4)
O(4)^a	0.3661(3)	0.0420(3)	0.0532(11)	41(3)
O(5)	0.2160(3)	0.0778(2)	0	29(1)
O(6)	0.0850(3)	0.1094(3)	0	33(1)
OW(7)	0.3773(3)	−0.1227(3)	−0.1717(9)	53(2)
OW(8)	0.2242(3)	−0.0364(3)	−0.2843(5)	45(1)
OW(9)	0	0	0.2931(14)	77(3)
OW(10)	0.1871(4)	0.3129(4)	$\frac{1}{2}$	38(2)
OW(11)	$\frac{1}{2}$	0	$\frac{1}{2}$	12(1)
OW(12)^a	0.3477(9)	0.0299(12)	$\frac{1}{2}$	66(5)

^{a}Occupancy = 0.5

TABLE 5
Selected Interatomic Distances (Å) and Angles (°) for UND-2

U(1)–O(1)a	1.778(8) × 2	C(1)–O(6)	1.254(7)
U(1)–O(2)b	2.410(4) × 2	C(1)–O(5)	1.291(7)
U(1)–O(4)a, b, c	2.441(6) × 4	C(1)–O(2)	1.308(7)
U(1)–O(5)b	2.442(5) × 2	⟨C(1)–O⟩	1.284
⟨U(1)–O$_{\mathrm{Ur}}$⟩	1.778	O(6)–C(1)–O(5)	124.8(6)
O(1)a–U(1)–O(1)	179.2(5)	O(6)–C(1)–O(2)	120.9(5)
<U(1)–O$_{\mathrm{eq}}$⟩	2.431	O(5)–C(1)–O(2)	114.2(5)
		⟨O–C(1)–O⟩	118.6
C(2)–O(3)	1.27(2)	Ca(1)–O(2)d	2.348(5)
C(2)–O(4)	1.32(1)	Ca(1)–C(4)	2.368(6)
C(2)–O(4)b	1.32(1)	Ca(1)–O(5)	2.368(4)
⟨C(2)–O⟩	1.30	Ca(1)–OW(8), a	2.436(4)2
O(3)–C(2)–O(4)	124.5(6)	Ca(1)–OW(7)a	2.593(4) × 2
O(3)–C(2)–O(4)b	124.5(6)	Ca(1)–O(6)d	2.671(5)
O(4)–C(2)–O(4)b	110.8(13)	⟨Ca(1)–ϕ ⟩	2.477
⟨O–C(2)–O⟩	119.9		
Ca(2)–O(6)d, e, f	2.321(5) × 4	Ca(3)–O(1)h	2.305(8) × 2
Ca(2)–OW(9)f	2.384(11) × 2	Ca(3)–OW(12)b	2.74(2) × 2
⟨Ca(2)–ϕ ⟩	2.34	Ca(3)–OW(10)	2.934(11)
		Ca(3)–Cl(1)b	2.972(4) × 2
		⟨Ca(3)–ϕ ⟩	2.71
Cl(1)–OW(8)g, j	3.222(5) × 2	Cl(1)–OW(12)	3.55(2)
Cl(1)–OW(8)a, i	3.264(5) × 2	Cl(1)–OW(9)k	3.567(6) × 2
Cl(1)–OW(10)	3.433(6)		

Note. Symmetry transformations used to generate equivalent atoms: (a) $x, y, -z$; (b) $-y+\frac{1}{2}, -x+\frac{1}{2}, z$; (c) $-y+\frac{1}{2}, -x+\frac{1}{2}, -z$; (d) $y, -x, -z$; (e) $-y, x, z$; (f) $-x, -y, -z$; (g) $-y, x, -z$; (h) $x, y, -z+1$; (i) $x, y, z+1$; (j) $-y, x, z+1$; (k) $-x, -y, -z+1$.

⟨$^{[8]}$U^{6+}–O$_{\mathrm{eq}}$⟩ bond length of 2.47(12) Å derived from many well-refined structures (25). The structure contains three symmetrically unique C atoms, each of which is coordinated by three atoms of O arranged at the vertices of triangles, with ⟨C–O⟩ bond lengths of 1.277, 1.283, and 1.280 Å. There is a single distinct N atom that is triangularly coordinated by O atoms, with an ⟨N–O⟩ bond length of 1.27 Å. The structure contains three symmetrically distinct Ca atoms that are coordinated by six to eight ligands, with ⟨Ca–ϕ⟩ (ϕ: unspecific ligand) bond lengths ranging from 2.34 to 2.48 Å. There are five H_2O groups, each of which is bonded to Ca.

TABLE 6
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for UND-3

	x	*y*	*z*	*U*(eq)
U	0.0204(1)	0.2296(1)	0.0204(1)	25(1)
Ca	−0.0707(1)	0.2735(1)	0.1264(1)	31(1)
C	0.0803(4)	0.2033(4)	−0.0606(4)	27(3)
Cl^a	0.0969(3)	0.4801(3)	0.0336(3)	104(3)
O(1)	−0.0167(3)	0.2667(3)	−0.0167(3)	37(3)
O(2)	0.0590(3)	0.1910(3)	0.0590(3)	36(3)
O(3)	0.0411(3)	0.1806(3)	−0.0484(3)	33(2)
O(4)	0.0087(3)	0.2835(3)	0.0902(3)	32(2)
O(5)	0.1066(3)	0.1899(3)	−0.0949(3)	32(2)
OW(6)	−0.0496(3)	0.3632(3)	0.1199(3)	37(2)
OW(7)	−0.0298(4)	0.2081(3)	0.1885(3)	64(3)
OW(8)	−0.1125(4)	0.2940(4)	0.0514(3)	60(3)
OW(9)	0	$\frac{1}{2}$	0	38(5)
OW(10)	$\frac{1}{8}$	$\frac{5}{8}$	$\frac{1}{8}$	35(7)
OW(11)	$\frac{1}{8}$	$\frac{1}{8}$	0.0085(6)	88(5)
OW(12)^b	$\frac{1}{8}$	0.7060(30)	$\frac{1}{8}$	150(30)

^{a}Occupancy of Cl = 2/3.

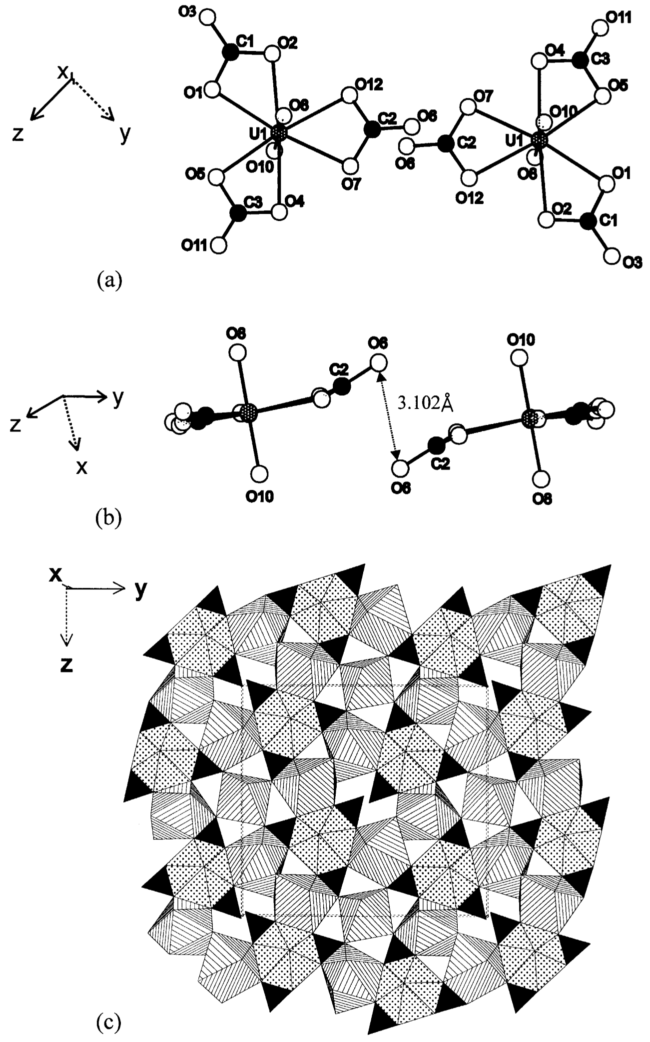
^{b}Occupancy of OW(12) ∼ 1/3.

The structure of UND-1 contains the well-known uranyl tricarbonate cluster of composition $[(UO_2)(CO_3)_3]^{4-}$, which consists of a uranyl hexagonal bipyramid that shares three equatorial edges with CO_3 triangles (Fig. 1a). Each uranyl tricarbonate cluster is attached to two Caϕ_8 polyhedra by the sharing of equatorial edges of the uranyl hexagonal bipyramid, to two other Caϕ_8 polyhedra by sharing the edges of two of the CO_3 triangles, and two Caϕ_6 octahedra by sharing vertices of two CO_3 groups. Linkage of the uranyl tricarbonate clusters and Caϕ_n polyhedra results in a Ca uranyl carbonate sheet with a Ca:U ratio of 5:2 (Fig. 1c). The sheet contains three CO_3 groups that play two unique structural roles. The C(1)O_3 and C(3)O_3 groups each share an edge with a Caϕ_8 polyhedron and a vertex with a Caϕ_6 octahedron, as well as an equatorial edge of the uranyl hexagonal bipyramid. In contrast, the C(2)O_3 group shares an equatorial edge with the uranyl hexagonal bipyramid, and the two vertices of the shared edge are also linked to Caϕ_8 polyhedra. The third vertex [O(6)] of the C(2)O_3 group is unshared within the sheet, and the O(6) atoms of adjacent C(2)O_3 groups are directed towards each other. As a result, the C(2)O_3

TABLE 7
Selected Interatomic Distances (Å) and Angles (°) for UND-3

U–O(1)	1.77(1)	C–O(5)	1.24(1)
U–O(2)	1.84(1)	C–O(3)	1.29(1)
U–O(3)a, b	2.391(7)	C–O(4)b	1.31(1)
U–O(4)a, b	2.446(7)	⟨C–O>	1.28
⟨U–O$_{\mathrm{Ur}}$⟩	1.81	O(5)–C–O(3)	122.6(10)
O(1)–U–O(2)	180.0(8)	O(5)–C–O(4)b	123.1(10)
⟨U–O$_{\mathrm{eq}}$⟩	2.419	O(3)–C–O(4)b	114.3(10)
		⟨O–C–O⟩	120
Ca–O(5)c	2.373(8)	Cl–OW(9)	2.871(9)
Ca–O(4)	2.413(7)	Cl–OW(6)f	2.993(11)
Ca–OW(8)	2.425(10)	Cl–OW(8)g	3.129(11)
Ca–O(3)b	2.447(7)	Cl–OW(12)h	3.16(4)
Ca–OW(6)	2.538(8)	Cl–OW(8)e	3.320(12)
Ca–OW(6)d	2.604(8)		
Ca–OW(7)	2.723(10)		
Ca–OW(7)e	2.893(10)		
⟨Ca–ϕ⟩	2.55		

Note. Symmetry transformations used to generate equivalent atoms: (a) $-y+\frac{1}{4}, -z+\frac{1}{4}, x$; (b) $z, -x+\frac{1}{4}, -y+\frac{1}{4}$; (c) $x-\frac{1}{4}, -y+\frac{1}{2}, z+\frac{1}{4}$; (d) $z-\frac{1}{4}, x+\frac{1}{4}, -y+\frac{1}{2}$; (e) $y-\frac{1}{4}, -z+\frac{1}{2}, x+\frac{1}{4}$; (f) $-y+\frac{1}{2}, -z+\frac{1}{2}, -x$; (g) $x+\frac{1}{4}, y+\frac{1}{4}, -z$; (h) $-x+\frac{1}{4}, -y+\frac{5}{4}, z$.



(a)

(b)

(c)

FIG. 1. The structure of UND-1. (a, b) Ball-and-stick representation of two adjacent uranyl tricarbonate clusters; (c) polyhedral representation of the sheet of uranyl tricarbonate clusters and Caϕ_n polyhedra. *Ur*O$_6$ and Caϕ_n polyhedra are shaded by dots and parallel lines, respectively, and carbonate groups are shown as black triangles.

groups are tilted, relative to the plane defined by the equatorial ligands of the uranyl hexagonal bipyramid, to increase the distance between adjacent O(6) atoms to 3.1 Å (Fig. 1b).

The NO$_3$ group is attached to the layer by sharing an edge with the Ca(1)ϕ_8 polyhedron and a vertex with the Ca(3)ϕ_8 polyhedron (Fig. 2). The heteropolyhedral layers are connected only by hydrogen bonds (Fig. 2).

UND-2

The structure of UND-2 contains a single unique U^{6+} cation that is part of an approximately linear (UO$_2$)$^{2+}$ uranyl ion, which is coordinated by six O atoms arranged at the equatorial vertices of a hexagonal bipyramid. The O(4) position is split off its corresponding special position of Wyckoff symbol *i*, giving an O(4)–O(4) separation of 0.87 Å; only one of these two sites is occupied locally. The structure of UND-2 contains two symmetrically distinct C atoms that are each coordinated by three O atoms. C(1) is in a triangular coordination with a $\langle$C(1)–O$\rangle$ of 1.284 Å. C(2) is split off its corresponding special position with Wyckoff symbol 4*g*. Symmetrically equivalent C(2) atoms are separated by 1.71 Å, but only one site of each pair is occupied locally. The O(3) site is also split, and the C(2)O$_3$ group is disordered, such that it is located either above or below the plane defined by the equatorial ligands of the adjacent uranyl hexagonal bipyramid (Fig. 3). Either of the configurations shown in Figs. 3c and d occur locally, resulting in the long-range average structure depicted in Figs. 3a and 3b.

The structure of UND-2 contains three symmetrically unique Ca atoms. Ca(1), Ca(2) and Ca(3) are coordinated by eight, six and seven ligands, respectively, with $\langle$Ca(1)-$\phi\rangle = 2.477$, $\langle$Ca(2)–$\phi\rangle = 2.34$, and $\langle$Ca(3)–$\phi\rangle = 2.71$ Å. The structure contains a single Cl site that is weakly bonded to Ca(3), and that is also held to the structure by hydrogen bonding. The structure contains six symmetrically unique H$_2$O groups that are either bonded to Ca or held to the structure by hydrogen bonding only.

The structure of UND-2 contains the same sheet of uranyl tricarbonate clusters and Caϕ_n polyhedra that occurs in UND-1 (Fig. 3e), but no NO$_3$ groups are present in UND-2. The partially occupied Ca(3) group is located between the sheets, and provides linkages, together with hydrogen bonds, that hold the sheets together (Fig. 4). The C(2)O$_3$ groups are tilted away from the plane defined by the equatorial ligands of the uranyl hexagonal bipyramid, resulting in a separation of 3.1 Å between the O(3) positions of adjacent uranyl tricarbonate clusters (Fig. 3c).

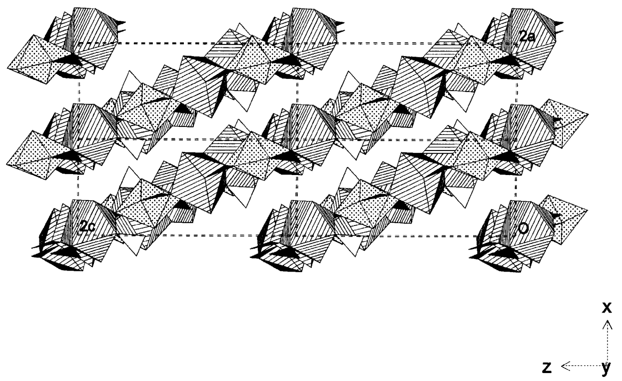


FIG. 2. The structure of UND-1 projected along [010]; nitrate groups are shown as unfilled triangles, otherwise legend as in Fig. 1c.

UND-3

The structure of UND-3 contains a single unique U^{6+} cation that is present in a uranyl hexagonal bipyramidal coordination analogous to that found in UND-1 and UND-2. The structure contains one CO_3 group with a $\langle$C–O$\rangle$ bond length of 1.28 Å. There is a unique Ca atom that is bonded to eight ligands with bond lengths ranging from 2.373(8) to 2.89(1) Å. The structure contains a single symmetrically unique Cl atom that is partially occupied. There are six H_2O groups, of which three [OW(6), OW(7) and OW(8)] are bonded to Ca, and three [(OW(9), OW(10) and OW(11)] are held to the structure by hydrogen bonding only.

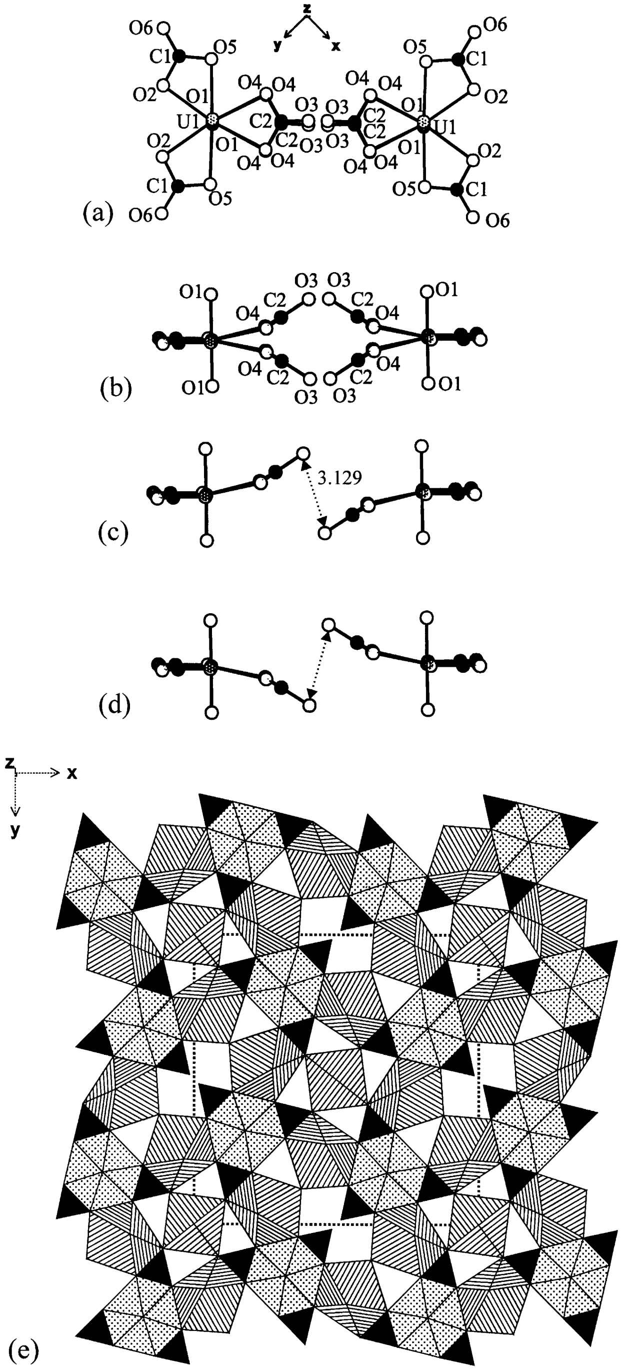


FIG. 3. The structure of UND-2. (a–d) Ball-and-stick representation of two adjacent uranyl tricarbonate clusters; (e) polyhedral representation of the sheet of uranyl tricarbonate clusters and $Ca\phi_n$ polyhedra, projected along [001]. Legend as in Fig. 1c.

The structure of UND-3 contains the uranyl tricarbonate cluster observed in UND-1 and UND-2 (Fig. 5a). The $\mathit{Ur}O_6$ polyhedra share three of their equatorial edges with $Ca\phi_8$ polyhedra, and the CO_3 groups are attached to additional $Ca\phi_8$ polyhedra by vertex sharing (Fig. 5a). The $Ca\phi_8$ polyhedra share faces, resulting in a ring containing six $Ca\phi_n$ polyhedra, and the rings share edges of the $Ca\phi_8$ polyhedra with six $\mathit{Ur}O_6$ polyhedra, three on one side of the ring, and three on the opposite side (Fig. 5b), resulting in a Ca uranyl carbonate framework structure (Fig. 6a). The framework can be expressed by a fragment of a three-dimensional net shown in Fig. 6b, in which each uranyl tricarbonate cluster links three Ca polyhedra on three different six-member Ca polyhedral rings, and each member of the Ca polyhedral ring in turn links one uranyl tricarbonate cluster that is alternatively arranged relative to the plane of the Ca polyhedral ring, as well as two adjacent Ca polyhedra of the same ring. Hydrogen-bonded H_2O groups and Cl are located in channels through the framework (Fig. 6a).

DISCUSSION

The structures of the Ca uranyl carbonates reported herein involve interesting features. The Ca uranyl carbonate sheet observed in UND-1 and UND-2 is novel, although the local polyhedral connectivity is generally consistent with other structures. In both cases, the uranyl hexagonal bipyramids share two equatorial edges with $Ca\phi_8$ polyhedra, and linkages between CO_3 groups and $Ca\phi_8$ polyhedra by sharing edges, and $Ca\phi_6$ polyhedra and CO_3 triangles by vertex sharing, results in the Ca uranyl carbonate sheets. In the case of UND-3, the uranyl tricarbonate cluster shares all three of its available equatorial edges with $Ca\phi_8$ polyhedra. Similar modes of connection occur in other Ca uranyl carbonates that contain the uranyl tricarbonate cluster. In the structure of swartzite, $CaMg[(UO_2)(CO_3)_3](H_2O)_5$ (26), each uranyl hexagonal bipyramid shares one of its equatorial edges with a $Ca\phi_8$ polyhedron, resulting in heteropolyhedral clusters that are connected through H bonding to $Mg(H_2O)_6$ octahedra. In schröckingerite, $NaCa_3[(UO_2)(CO_3)_3](SO_4)F(H_2O)_{10}$ (27), each uranyl hexagonal bipyramid shares all three of its available equatorial edges with $Ca\phi_8$ polyhedra, resulting in a sheet that also contains

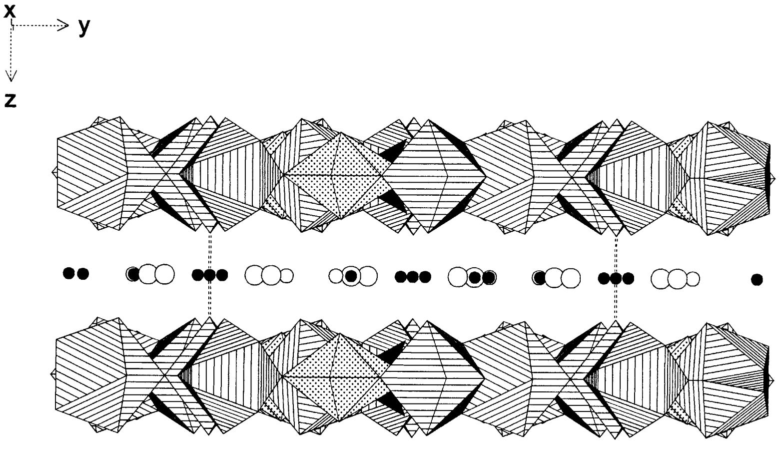


FIG. 4. The structure of UND-2 projected along [100]. Cl, Ca and H_2O groups are shown as larger open circles, smaller open circles, and black circles, respectively. Legend as in Fig. 1c.

$Na\phi_6$ polyhedra and that is decorated by the attachment of SO_4 tetrahedra. The structure of liebigite, $Ca_2[(UO_2)(CO_3)_3](H_2O)_{11}$ (28), involves uranyl hexagonal bipyramids that share two of their equatorial edges with $Ca\phi_8$ polyhedra, resulting in an open-modulated sheet.

The uranyl tricarbonate clusters in UND-1 and UND-2 both involve one CO_3 group that is significantly inclined to the plane defined by the equatorial ligands of the uranyl hexagonal bipyramid. Meinrath (29) reviewed the geometries of uranyl tricarbonate clusters in several solids, and noted that the carbonate groups tend to be slightly twisted relative to the equatorial planes of the uranyl hexagonal bipyramids, but this is a relatively minor structural feature. In the case of UND-1 and UND-2, the substantial twisting of the $C(2)O_3$ groups is due to steric constraints, as it is necessary to avoid short interatomic distances between O atoms.

Spent nuclear fuel is unstable under the moist oxidizing conditions expected in the proposed repository at Yucca Mountain, Nevada (3, 4, 7, 8), and alteration rates are likely to be appreciable. It is possible that groundwater will contact spent fuel in the repository, leading to the formation of a variety of uranyl compounds (7, 8). An understanding of the chemistry and structures of uranyl alteration phases is important for predicting the long-term behavior of the repository, as some of the alteration products are likely to incorporate radionuclides into their structures (30–32). Wherein this is the case, the alteration phases become the near-field source terms for the radionuclides, and their stabilities will impact radionuclide release rates. Groundwater from well J13, taken from the unsaturated zone near the proposed emplacement area at Yucca Mountain, contains 0.29 mM Ca, 0.18 mM Cl^-, 0.16 mM NO_3^- and 2.81 mM total carbonate, amongst other constituents (33). Given that all the necessary

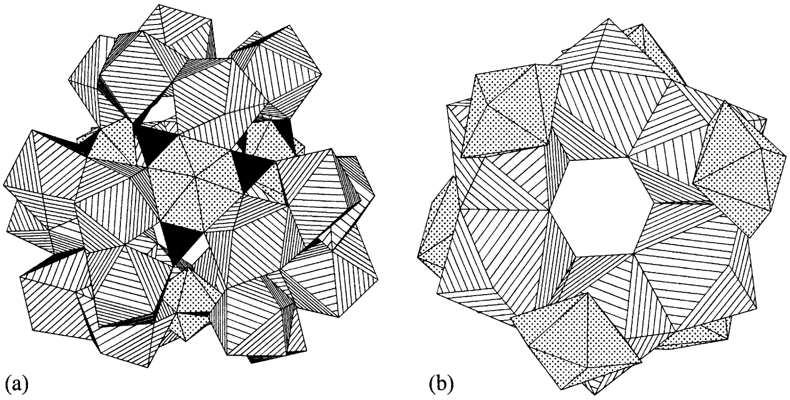


FIG. 5. Fragments of the structure of UND-3. (a) A sphere-like cage composed of four rings of $Ca\phi_n$ polyhedra and four uranyl tricarbonate clusters; (b) edge sharing of the Ca polyhedral ring with six UrO_6 polyhedra. Legend as in Fig. 1c.

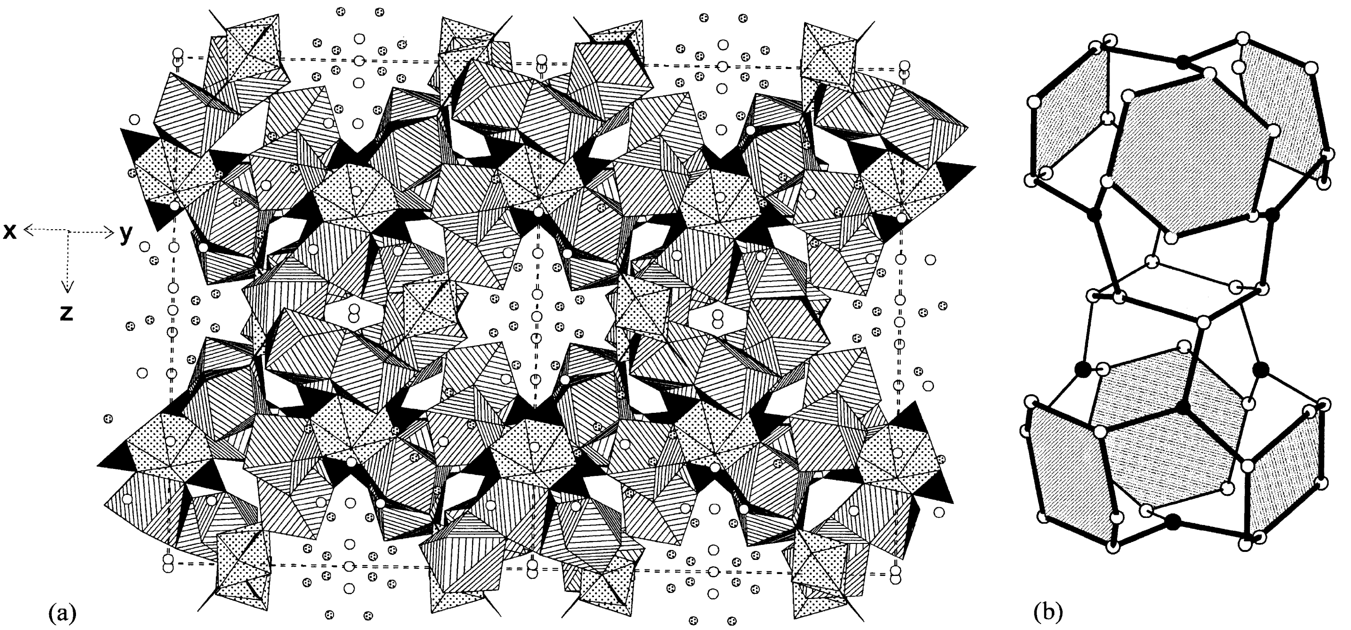


FIG. 6. (a) Structure of UND-3 projected along [110]. Cl- and H-bonded H_2O groups are shown as filled and open circles, respectively. Legend as in Fig. 1c; (b) a fragment of the three-dimensional net corresponding to the structure of UND-3. The black and open circles represent uranyl tricarbonate clusters and Ca cations, respectively, and Ca rings are shaded.

constituents are present where Yucca Mountain water interacts with spent nuclear fuel, it is possible that UND-1, UND-2 or UND-3 will form due to the alteration of spent fuel in the repository. The higher concentrations of Na and Si in the groundwater are also expected to result in Na uranyl oxide hydrates and silicates (34). Significant effort is needed to further delineate the structures and chemistries of uranyl phases that may form due to alteration of nuclear waste under repository conditions, and to determine the thermodynamic stability of these compounds.

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