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A NEW RARE-EARTH-ELEMENT URANYL CARBONATE SHEET IN THE STRUCTURE OF BIJVOETITE-(Y)

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ABSTRACT

The crystal structure of bijvoetite-(Y), $[M_8^{3+}(H_2O)_{25}(UO_2)_{16}O_8(OH)_8(CO_3)_{16}](H_2O)_{14}$, M = (Y, *REE*), pseudo-orthorhombic, monoclinic, *a* 21.234(3), *b* 12.958(2), *c* 44.911(6) Å, β 90.00(2)°, *V* 12,357(6) Å^3, space group $B12_11$, $Z = 4$, was solved by direct methods and refined by least-squares techniques to an agreement index (*R*) of 8.4% and a goodness of fit (S) of 0.81 for 6622 unique observed ($|F_o| > 4\sigma_F$) reflections collected for a twinned crystal using graphite-monochromatic Mo*K*α X-radiation and a CCD area detector. There are 16 symmetrically independent U^{6+} positions, each of which is part of near-linear $(U^{6+}O_2)^{2+}$ uranyl ion. Eight uranyl ions are coordinated by three O^{2-} and two $(OH)^-$ anions each, resulting in uranyl pentagonal bipyramids, and eight uranyl ions are coordinated by six O^{2-} anions each, forming uranyl hexagonal bipyramids. The structure contains 16 unique carbonate groups and eight unique M^{3+} sites that are occupied by variable amounts of Y, Dy and other *REE*s. The structure of bijvoetite-(Y) is based on a novel uranyl carbonate chain that is parallel to [100], involving edge-sharing dimers of uranyl pentagonal bipyramids, edge-sharing dimers of uranyl hexagonal bipyramids, and carbonate groups. The chains are cross-linked by irregular $M^{3+}\phi_n$ (ϕ: unspecified ligand) polyhedra, forming (Y,*REE*)-bearing uranyl carbonate sheets that are parallel to (010). The sheet in bijvoetite-(Y) is based upon a new sheet anion-topology. There are 39 symmetrically unique H_2O groups in the structure, 25 of which are bonded to M^{3+} and 14 of which are located in the interlayer, where they are held in place by H bonds. The interlayer of the structure contains only H_2O groups, and adjacent sheets are connected by H bonds only. The discovery of the structure may have implications for nuclear waste disposal because uranyl carbonates may be abundant in a geological repository due to the corrosion of uranium oxide nuclear fuel. It is proposed that the structure may incorporate transuranium elements.

Keywords: bijvoetite-(Y), uranyl carbonate, uranyl mineral, structure determination, nuclear waste disposal.

SOMMAIRE

Nous avons résolu la structure cristalline de la bijvoetite-(Y), $[M_8^{3+}(H_2O)_{25}(UO_2)_{16}O_8(OH)_8(CO_3)_{16}](H_2O)_{14}$, M = (Y, terres rares), pseudo-orthorhombique, monoclinique, *a* 21.234(3), *b* 12.958(2), *c* 44.911(6) Å, β 90.00(2)°, *V* 12,357(6) Å^3, groupe spatial $B12_11$, $Z = 4$, par méthodes directes et nous l'avons affiné par moindres carrés jusqu'à un résidu *R* de 8.4% et un indice de concordance S de 0.81 en utilisant 6622 réflexions uniques observées ($|F_o| > 4\sigma_F$). Le prélèvement s'est fait sur un cristal maclé en utilisant un rayonnement MoKα monochromatisé au graphite et un détecteur à aire CCD. La structure contient seize atomes U^{6+} symétriquement indépendants, chacun faisant partie d'un groupe uranyle $(U^{6+}O_2)^{2+}$ presque linéaire. Huit de ces ions uranyle sont en coordinence avec trois anions O^{2-} et deux groupes $(OH)^-$, en bipyramides pentagonales, et huit autres sont en coordinence avec six anions O^{2-} chacun, en bipyramides hexagonales. La structure contient 16 groupes carbonate uniques et huit sites M^{3+} uniques où logent des proportions variables de Y, Dy et autres terres rares. La structure de la bijvoetite-(Y) est fondée sur une chaîne à uranyle et carbonate inconnue auparavant; elle est parallèle à [100], et contient des dimères à arêtes partagées de bipyramides pentagonales et hexagonales d'uranyle, et de groupes carbonate. Ces chaînes sont rattachées transversalement par des polyèdres irréguliers $M^{3+}\phi_n$ (ϕ: ligand non spécifié), pour former des feuillets de carbonate d'uranyle, d'yttrium et de terres rares paralèlles à (010). Ce feuillet de la bijvoetite-(Y) constitue une nouvelle topologie anionique. Il s'y trouve 39 groupes H_2O symétriquement disposés dans la structure, dont 25 sont liés à M^{3+}, et 14 sont situés dans l'interfeuillet, maintenus par des liaisons hydrogène. L'interfeuillet ne contient que des groupes H_2O, et les feuillets adjacents ne sont liés que par des liaisons hydrogène. La découverte de cette structure pourrait bien avoir des répercussions pour l'enfouissement des déchets nucléaires; les carbonates

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d'uranyle pourraient se former abondamment dans un site d'enfouissement où il y a corrosion des tiges d'oxyde d'uranium ayant servi comme source d'énergie. Nous croyons que cette structure pourrait incorporer des éléments trans-uraniques.

(Traduit par la Rédaction)

Mots-clés: bijvoetite-(Y), carbonate d'uranyle, minéral uranylé, détermination de la structure, enfouissement des déchets nucléaires.

INTRODUCTION

Compared to other mineral groups, uranyl minerals are generally poorly characterized despite their significance to mineral sciences and environmental issues (Burns 1999a). This situation reflects experimental difficulties associated with their commonly large unit-cells, strong X-ray absorption by the crystals, twinning, and pseudosymmetry. The recent introduction of the CCD-based (charge-coupled device) X-ray diffractometer to mineralogy has permitted the solution of the structure of several uranyl minerals: wyartite (Burns & Finch 1999), wölsendorfite (Burns 1999b), richetite (Burns 1998a), compreignacite (Burns 1998b), vandendriesscheite (Burns 1997), masuyite (Burns & Hanchar 1999), haiweeite (Burns 2000b), boltwoodite (Burns 1998c), parsonsite (Burns 2000a) and agrinierite (Cahill & Burns 2000). We have used a CCD-based diffractometer to determine the structure of bijvoetite-(Y), a (Y,*REE*) uranyl carbonate that possesses a large unit-cell and exhibits twinning, and report the results herein.

BACKGROUND

Uranyl carbonates are common minerals precipitated from carbonate-bearing waters in the oxidized zones of uranium deposits, and several uranyl carbonate minerals contain Y and the rare-earth elements (*REE*), which are common, but generally minor, constituents of uraninite, UO_{2+X} (Finch & Ewing 1992, Janeczek & Ewing 1992). As such, uranyl carbonates are important products in the dissolution of uraninite and formation of secondary uranium minerals. In addition, these minerals may be important for the disposal of nuclear waste. A knowledge of the structures and parageneses of uranyl carbonates is essential to properly understand migration of radionuclides in soils and groundwater (Titayeva 1994, Langmuir 1978). In addition, uranyl carbonates may form owing to alteration of spent nuclear fuel in a geological repository.

Of the ~25 uranyl carbonate minerals, the structures are known for only seven. The most common structural theme found in uranyl carbonate minerals is the uranyl tricarbonate ion, $[(UO_2)(CO_3)_3]^{4-}$, which occurs as an isolated finite cluster. Liebigite, $Ca_2[(UO_2)(CO_3)_3](H_2O)_{11}$ (Mereiter 1982), schröckingerite, $NaCa_3[(UO_2)(CO_3)_3](SO_4)F(H_2O)_{10}$ (Mereiter 1986a), swartzite, $CaMg[(UO_2)(CO_3)_3](H_2O)_5$ (Mereiter 1986b), andersonite, $Na_2Ca[(UO_2)(CO_3)_3](H_2O)_6$ (Mereiter 1986c), and bayleyite, $Mg_2[(UO_2)(CO_3)_3](H_2O)_{18}$ (Mayer & Mereiter 1986) all contain this finite cluster. In each structure, the uranyl tricarbonate clusters are interconnected by low-valence cations or H bonds (or both). The structures of roubaultite, $[Cu_2(UO_2)_3(CO_3)_2O_2(OH)_2](H_2O)_4$ (Ginderow & Cesbron 1985), and rutherfordine, $[(UO_2)(CO_3)]$ (Christ *et al.* 1955, Finch *et al.* 1999), contain uranyl carbonate sheets, and as such are more highly connected than structures containing isolated uranyl tricarbonate clusters.

Several studies have shown that U^{6+} can occur in solution as uranyl carbonate complexes of the general form $[(UO_2)_x(CO_3)_y(OH)_z(H_2O)_q]$ (Kim *et al.* 1994, Titayeva 1994). Minerals with a U:C ratio of 1:3 tend to grow in fluids with relatively high pH, and have structures that are based upon isolated uranyl tricarbonate clusters. Minerals with a U:C ratio other than 1:3 may form in waters of lower pH and higher pCO_2, and may involve other structural themes, such as uranyl carbonate sheets. The coexistence of these two groups of uranyl carbonate minerals has not been reported. Thus, uranyl carbonates constitute a sensible mineral group to investigate the relationship between crystal structures and mineral paragenesis.

Bijvoetite-(Y) was described from the Shinkolobwe uranium mine, Likasi, in Shaba, Democratic Republic of Congo, by Deliens & Piret (1982). It is associated with lepersonnite, sklodowskite, curite, uranophane, becquerelite, rutherfordine, studtite, and oursinite. Deliens & Piret (1982) reported that bijvoetite-(Y) is orthorhombic, space groups $C2ma$, $Cm2b$, or $Cmma$, a 21.223(3), b 45.30(7), c 13.38(2) Å, $Z = 16$. On the basis of an analysis done with an electron microprobe, the empirical formula was given as $(Y_{1.26}Dy_{0.57}Gd_{0.29}Tb_{0.10})_{\Sigma 2.20}U_{4.01}C_{3.82}O_{23}\bullet 14.26H_2O$ or, ideally, $(Y,REE)(UO_2)_2(CO_3)_2(OH)_3\bullet\sim 5.5H_2O$. Kamotoite-(Y), $Y_2(UO_2)_4(CO_3)_3(OH)_8\bullet 10\text{–}11H_2O$, which also contains *REE* cations, may be structurally closely related to bijvoetite-(Y), and crystallizes in space group $P2_1/n$ with cell dimensions a 21.22, b 12.93, c 12.39 Å, β 115.3° (Deliens & Piret 1986).

EXPERIMENTAL

X-ray diffraction

Data were collected for two crystals from different specimens, both of which were provided by Dr. Mark Feinglos of Duke University. The first crystal provided

TABLE 1. MISCELLANEOUS INFORMATION PERTAINING TO THE STRUCTURE OF BIJVOETITE-(Y)

a (Å)	21.234(3)	Crystal size(mm)	0.14 × 0.06 × 0.01
b (Å)	12.958(2)	Radiation	Mo*K*α
c (Å)	44.911(7)	$2\theta_{max}$(°)	57.2
β (°)	90.00(2)	Total reflections	72,834
V ($Å^3$)	12,357(3)	Unique reflections	29,357
Space group	$B12_11$	Unique $\vert Fo\vert > 4\sigma\vert Fo\vert$	6622
D (g/cm^3)	3.87	*R* (%)	8.37
μ (cm^{-1})	24.8	*S*	0.814

Unit-cell contents $4\{[M_8(H_2O)_{25}(UO_2)_{16}O_8(OH)_8(CO_3)_{16}](H_2O)_{14}\}$ *M* = Y,REE

$R = \Sigma(|F_o| - |F_c|)/ \Sigma |F_o|$

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

superior data, as shown by the final refinement, and results are reported for that crystal only. A sphere of three-dimensional data to 2θ = 57.2° was collected using a Bruker CCD-based detector mounted on a three-circle diffractometer equipped with Mo*K*α X-radiation (Burns 1998d). Frame widths of 0.6° in ω were used, with 120 seconds spent counting per frame. The unit-cell dimensions (Table 1) were refined using least-square techniques and 6238 reflections. The data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. An empirical absorption-correction was done based on equivalent reflections by modeling the crystal as an ellipsoid. A total of 72,834 reflections was collected, and merging of equivalent reflections gave 29,357 unique reflections, of which 6622 were classed as observed ($|F_o| \geq 4\sigma_F$).

TABLE 2. CHEMICAL COMPOSITIONS* (Wt %) OF BIJVOETITE BY EMPA

	Point1	Point2	Point3	Average
	Oxides (wt. %)			
Y_2O_3	5.95	5.72	5.76	5.81
Ce_2O_3	0.33	0.32	0.34	0.33
Nd_2O_3	1.79	2.39	2.22	2.13
Sm_2O_3	1.67	1.83	1.69	1.73
Eu_2O_3	0.41	0.47	0.51	0.46
Gd_2O_3	1.84	1.81	1.69	1.78
Tb_2O_3	0.39	0.38	0.00	0.26
Dy_2O_3	1.90	2.32	2.24	2.15
Er_2O_3	0.55	0.52	0.78	0.62
CaO	0.18	0.23	0.16	0.19
UO_3	67.08	67.35	67.48	67.30
CO_2**	9.31	9.80	9.43	9.51
H_2O**	9.29	9.78	9.41	9.49
Total	100.70	102.91	101.71	101.76
	Cations on the basis of *M* = 2			
Y	1.00	0.91	0.95	0.95
Ce	0.04	0.04	0.04	0.04
Nd	0.20	0.26	0.25	0.23
Sm	0.18	0.19	0.18	0.18
Eu	0.04	0.05	0.05	0.05
Gd	0.19	0.18	0.17	0.18
Tb	0.04	0.04	0.00	0.03
Dy	0.19	0.22	0.22	0.21
Er	0.05	0.05	0.08	0.06
Ca	0.06	0.07	0.05	0.06
U	4.43	4.23	4.40	4.35

*Na, K, Sr, Ba, Pb, Al, La, Pr, Ho, Tm, Yb, Lu, Th, F, and Cl were analyzed but were not detected.

** calculated on the basis of stoichiometry with Σ of *M* = 2.

Electron-microprobe analysis

A crystal of bijvoetite-(Y) from the specimen used for the X-ray experiment was mounted on the center of a hollow aluminum tube using epoxy. The specimen was hand-polished and coated with carbon. The elemental analysis was done using an electron microprobe (JEOL Superprobe 733 and Tracor Northern 5500 and 5600 automation) equipped with four wavelength-dispersion spectrometers and operated at 15 kV at the Canadian Museum of Nature. A beam current of 20 nA and a beam diameter of 10 μm were used. The following standards were employed: YIG (Y*L*α), a set of synthetic *REE* phosphates (Ce*L*α, Nd*L*α, Sm*L*α, Eu*L*α, Gd*L*α, Tb*L*α, Dy*L*β, Er*L*α), diopside (Ca*K*α) and synthetic UO_2 (U*M*β). Concentrations of the *REE*s were corrected for overlaps. Data for all elements were collected for 25 seconds or 0.50% precision, whichever was attained first. Data reduction was done using a PAP routine in XMAQNT (C. Davidson, CSIRO, pers. commun.). The results of the chemical analysis are given in Table 2, with the proportion of CO_2 and H_2O calculated from the crystal-structure analysis.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography*, Vol IV (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the refinement of the crystal structure.

Initially, we assumed that the structure is orthorhombic, but were unable to solve the structure in any of the possible space-groups. In subsequent attempts to solve the structure, we used the primitive monoclinic unit-cell *a* 21.234(3), *b* 12.958(2), *c* 24.839(3) Å, β 115.30(2)°. Systematic absences and reflection statistics were found to be consistent with space group $P2_1$, and a structure model was obtained using direct methods. However, the model only refined to an agreement index (*R*) of ~20%, with numerous significant features in the difference-Fourier maps at locations that were incompatible with additional atomic sites. Examination of the observed and calculated structure-factors revealed that the most significant deviations corresponded to $F_{obs} >> F_{calc}$, suggesting that the crystal was twinned, and that the diffraction pattern corresponded to the superposition of two or more reciprocal lattices.

The transformation matrix $[001/010/\bar{2}0\bar{1}]$ was applied to obtain the unconventional *B*-centered pseudo-orthorhombic unit cell with *a* 21.234(3), *b* 12.958(2), *c* 44.911(6) Å, β 90.00(2)° in order to facilitate a model that included the effects of twinning. The structure was solved in space group $B12_11$ using direct methods. The

TABLE 3. ATOMIC POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR THE STRUCTURE OF BIJVOETITE-(Y)

	x	y	z	*U_{eq}
U(1)	0.3938(1)	0.3646(2)	0.4320(1)	176(8)
U(2)	0.0549(1)	0.4264(2)	0.4726(1)	207(8)
U(3)	0.5551(2)	0.3387(3)	0.4728(1)	228(11)
U(4)	0.0540(1)	0.4134(2)	0.3899(1)	193(8)
U(5)	0.2158(1)	0.4179(2)	0.4306(1)	178(8)
U(6)	0.7162(1)	0.3480(2)	0.4310(1)	171(10)
U(7)	0.3045(2)	0.4134(3)	0.6398(1)	233(11)
U(8)	0.1432(1)	0.4022(2)	0.6821(1)	211(11)
U(9)	-0.1050(2)	0.4018(3)	0.4318(1)	165(11)
U(10)	0.4666(2)	0.4179(3)	0.6809(1)	185(12)
U(11)	0.5541(2)	0.3508(3)	0.3897(1)	179(11)
U(12)	-0.0338(2)	0.3493(3)	0.6814(1)	232(14)
U(13)	0.3047(2)	0.4271(3)	0.7226(1)	212(12)
U(14)	-0.1960(2)	0.3520(3)	0.6400(1)	227(14)
U(15)	0.6445(2)	0.3651(3)	0.6822(1)	180(13)
U(16)	-0.1948(2)	0.3384(3)	0.7228(1)	228(13)
M(1)	0.5587(2)	0.3224(4)	0.5647(1)	104(14)
M(2)	0.0592(2)	0.4357(4)	0.5644(1)	220(17)
M(3)	0.3097(3)	0.4255(4)	0.8141(1)	152(16)
M(4)	0.5520(2)	0.4535(3)	0.3013(1)	186(15)
M(5)	0.3087(3)	0.3198(4)	0.3147(1)	134(17)
M(6)	-0.1977(3)	0.4401(4)	0.5509(1)	172(17)
M(7)	0.0529(3)	0.3322(4)	0.3005(1)	181(17)
M(8)	0.3020(3)	0.3204(5)	0.5510(1)	147(20)
O(1)	0.450(1)	0.282(1)	0.6829(8)	97(4)
O(2)	0.2172)	0.280(1)	0.4354(8)	97(4)
O(3)	0.713(2)	0.486(1)	0.4272(8)	97(4)
O(4)	-0.046(2)	0.486(1)	0.680(1)	97(4)
O(5)	0.675(1)	0.4921)	0.6761(7)	97(4)
O(6)	0.411(1)	0.500(1)	0.4316(9)	97(4)
O(7)	-0.1012)	0.264(1)	0.4322(9)	97(4)
O(8)	0.167(1)	0.271(1)	0.6877(8)	97(4)
O(9)	0.053(2)	0.289(1)	0.4650(7)	97(4)
O(10)	0.323(1)	0.290(1)	0.7207(8)	97(4)
O(11)	-0.124(1)	0.539(1)	0.4305(9)	97(4)
O(12)	0.123(2)	0.539(1)	0.681(1)	97(4)
O(13)	-0.196(2)	0.478(1)	0.7254(8)	97(4)
O(14)	0.553(2)	0.478(1)	0.4686(9)	97(4)
O(15)	0.570(1)	0.484(1)	0.4003(7)	97(4)
O(16)	0.619(1)	0.233(1)	0.6873(8)	97(4)
O(17)	-0.198(2)	0.490(1)	0.6472(9)	97(4)
O(18)	0.300(2)	0.278(1)	0.6500(9)	97(4)
O(19)	0.355(1)	0.241(1)	0.4278(8)	97(4)
O(20)	0.053(2)	0.275(1)	0.395(1)	97(4)
O(21)	-0.015(1)	0.214(1)	0.6869(8)	97(4)
O(22)	0.726(2)	0.210(1)	0.4286(9)	97(4)
O(23)	0.482(2)	0.556(1)	0.682(1)	97(4)
O(24)	0.234(2)	0.552(1)	0.4242(9)	97(4)
O(25)	-0.198(2)	0.218(1)	0.6284(7)	97(4)
O(26)	0.564(2)	0.217(1)	0.3783(8)	97(4)
O(27)	0.067(1)	0.522(1)	0.5013(4)	97(4)
O(28)	0.308(2)	0.566(1)	0.7296(8)	97(4)
O(29)	0.049(2)	0.548(1)	0.3794(8)	97(4)
O(30)	0.300(2)	0.546(1)	0.6266(8)	97(4)
O(31)	0.550(2)	0.199(1)	0.4751(9)	97(4)
O(32)	-0.193(2)	0.199(1)	0.728(1)	97(4)
O(33)	-0.079(2)	0.422(3)	0.2311(3)	97(4)
O(34)	0.174(2)	0.440(3)	0.4793(4)	97(4)
O(35)	-0.328(2)	0.366(2)	0.4811(4)	97(4)
O(36)	0.429(2)	0.334(2)	0.2312(4)	97(4)
O(37)	0.187(2)	0.408(3)	0.7332(3)	97(4)
O(38)	-0.058(2)	0.431(2)	0.4812(4)	97(4)
O(39)	-0.1344(8)	0.402(3)	0.2714(6)	97(4)
O(40)	0.1143(8)	0.423(3)	0.5187(6)	97(4)
O(41)	-0.3824(8)	0.376(3)	0.5209(7)	97(4)
O(42)	0.3676(8)	0.379(3)	0.2693(8)	97(4)
O(43)	0.189(2)	0.421(2)	0.6310(4)	97(4)
O(44)	0.188(2)	0.347(3)	0.2319(3)	97(4)
O(45)	0.428(1)	0.373(3)	0.4836(4)	97(4)
O(46)	0.1318(8)	0.372(2)	0.5932(7)	97(4)
O(47)	-0.1067(9)	0.348(2)	0.3382(6)	97(4)
O(48)	0.175(2)	0.436(2)	0.3789(4)	97(4)
O(49)	-0.000(1)	0.428(3)	0.4295(8)	97(4)
O(50)	0.3914(9)	0.429(3)	0.3372(6)	97(4)
O(51)	0.242(2)	0.456(3)	0.682(1)	97(4)
O(52)	0.668(2)	0.365(2)	0.3820(4)	97(4)
O(53)	0.469(1)	0.412(2)	0.2722(6)	97(4)
O(54)	-0.2810(8)	0.387(3)	0.5254(6)	97(4)
O(55)	0.1392(9)	0.386(2)	0.7769(6)	97(4)
O(56)	-0.1127(8)	0.413(3)	0.5205(6)	97(4)
O(57)	-0.0044(8)	0.411(3)	0.5225(6)	97(4)
O(58)	0.2435(7)	0.418(4)	0.7724(7)	97(4)
O(59)	0.367(2)	0.432(3)	0.6827(8)	97(4)
O(60)	-0.0044(7)	0.379(3)	0.3457(8)	97(4)
O(61)	-0.256(2)	0.315(3)	0.680(1)	97(4)
O(62)	0.495(2)	0.336(3)	0.433(1)	97(4)
O(63)	0.613(2)	0.324(3)	0.433(1)	97(4)
O(64)	-0.134(2)	0.325(4)	0.680(1)	97(4)
O(65)	0.7166(9)	0.423(3)	0.3382(6)	97(4)
O(66)	0.4990(8)	0.348(3)	0.5213(8)	97(4)
O(67)	0.2433(8)	0.388(2)	0.2734(6)	97(4)
O(68)	0.3716(8)	0.359(3)	0.5909(6)	97(4)
O(69)	0.3936(9)	0.368(3)	0.5277(6)	97(4)
O(70)	0.2170(9)	0.412(3)	0.5245(5)	97(4)
O(71)	0.1476(8)	0.353(3)	0.2795(5)	97(4)
O(72)	0.2441(8)	0.377(3)	0.5939(8)	97(4)
O(73)	-0.0284(8)	0.393(3)	0.2737(7)	97(4)
O(74)	0.1127(8)	0.361(3)	0.3464(7)	97(4)
O(75)	0.6154(8)	0.401(3)	0.3436(8)	97(4)
O(76)	0.2158(9)	0.354(3)	0.3383(6)	97(4)
O(77)	0.439(2)	0.388(2)	0.3819(4)	97(4)
O(78)	0.4957(7)	0.421(3)	0.3438(7)	97(4)
O(79)	0.117(2)	0.475(2)	0.4292(9)	97(4)
O(80)	-0.071(2)	0.405(3)	0.3825(4)	97(4)
O(81)	0.4713(9)	0.391(2)	0.5916(6)	97(4)
O(82)	0.423(2)	0.409(2)	0.6320(4)	97(4)
O(83)	0.689(2)	0.353(3)	0.6311(4)	97(4)
O(84)	-0.080(2)	0.338(2)	0.6298(4)	97(4)
O(85)	0.7442(8)	0.394(4)	0.5945(9)	97(4)
O(86)	-0.1354(8)	0.381(3)	0.5932(8)	97(4)
O(87)	0.6381(9)	0.407(3)	0.5879(6)	97(4)
O(88)	-0.0271(8)	0.414(3)	0.5927(7)	97(4)
OH(1)	0.557(2)	0.408(3)	0.6506(8)	97(4)
OH(2)	0.310(2)	0.410(3)	0.4003(9)	97(4)
OH(3)	0.046(2)	0.370(3)	0.652(1)	97(4)
OH(4)	0.802(2)	0.369(3)	0.4633(8)	97(4)
OH(5)	0.061(2)	0.343(3)	0.7122(8)	97(4)
OH(6)	0.806(2)	0.386(3)	0.400(1)	97(4)
OH(7)	0.552(2)	0.384(3)	0.713(1)	97(4)
OH(8)	0.303(3)	0.395(4)	0.463(1)	97(4)
H_2O(1)	0.313(2)	0.230(2)	0.3611(7)	11(9)
H_2O(2)	0.545(1)	0.520(3)	0.5612(7)	11(9)
H_2O(3)	0.289(2)	0.243(3)	0.8138(9)	11(9)
H_2O(4)	0.043(2)	0.261(3)	0.5648(9)	11(9)
H_2O(5)	0.307(2)	0.501(3)	0.5511(8)	11(9)
H_2O(6)	0.643(1)	0.196(2)	0.5547(7)	11(9)
H_2O(7)	0.133(1)	0.587(2)	0.5633(7)	11(9)
H_2O(8)	0.392(2)	0.545(2)	0.8109(7)	11(9)
H_2O(9)	0.410(1)	0.200(2)	0.3176(8)	11(9)
H_2O(10)	-0.204(2)	0.530(2)	0.5014(7)	11(9)
H_2O(11)	0.548(2)	0.566(2)	0.2540(8)	11(9)
H_2O(12)	0.299(2)	0.213(3)	0.5056(8)	11(9)
H_2O(13)	0.230(1)	0.189(2)	0.5648(7)	11(9)
H_2O(14)	-0.269(2)	0.589(3)	0.5580(7)	11(9)
H_2O(15)	0.466(1)	0.562(2)	0.3065(7)	11(9)
H_2O(16)	0.620(1)	0.605(2)	0.3118(7)	11(9)
H_2O(17)	0.118(2)	0.184(3)	0.3123(8)	11(9)
H_2O(18)	0.357(2)	0.171(3)	0.5672(8)	11(9)
H_2O(19)	0.057(2)	0.515(3)	0.3029(9)	11(9)
H_2O(20)	0.254(1)	0.602(3)	0.8001(7)	11(9)
H_2O(21)	-0.009(1)	0.609(2)	0.5608(7)	11(9)
H_2O(22)	0.266(1)	0.157(3)	0.2990(8)	11(9)
H_2O(23)	0.507(2)	0.180(2)	0.5600(7)	11(9)
H_2O(24)	0.436(2)	0.757(3)	0.6979(9)	11(9)
H_2O(25)	0.563(2)	0.231(3)	0.6114(1)	11(9)
H_2O(26)	0.076(1)	0.145(2)	0.6263(7)	11(9)
H_2O(27)	0.833(1)	0.174(2)	0.3682(7)	11(9)
H_2O(28)	0.574(1)	0.064(2)	0.4349(7)	11(9)
H_2O(29)	-0.310(1)	0.095(3)	0.6299(7)	11(9)
H_2O(30)	-0.175(1)	0.095(2)	0.6783(7)	11(9)
H_2O(31)	0.577(2)	0.595(3)	0.6279(8)	11(9)
H_2O(32)	-0.081(2)	0.184(3)	0.5811(7)	11(9)
H_2O(33)	0.151(1)	0.193(2)	0.8242(7)	11(9)
H_2O(34)	0.458(1)	0.682(2)	0.7488(7)	11(9)
H_2O(35)	0.178(1)	0.657(2)	0.5089(7)	11(9)
H_2O(36)	0.695(2)	0.107(3)	0.5111(7)	11(9)
H_2O(37)	0.567(2)	0.567(2)	0.7404(7)	11(9)
H_2O(38)	0.351(1)	0.150(2)	0.7635(7)	11(9)
H_2O(39)	0.085(1)	0.137(2)	0.5086(7)	11(9)
C(1)	0.1696(8)	0.416(4)	0.5070(4)	143(1)
C(2)	0.1912(9)	0.366(4)	0.2600(4)	143(1)
C(3)	0.4431(8)	0.366(4)	0.5113(4)	143(1)
C(4)	0.1874(7)	0.389(3)	0.6038(4)	143(1)
C(5)	0.1868(8)	0.417(4)	0.7618(3)	143(1)
C(6)	-0.0794(8)	0.414(4)	0.2598(4)	143(1)
C(7)	0.6713(8)	0.387(3)	0.3541(4)	143(1)
C(8)	0.1695(8)	0.383(2)	0.3545(5)	143(1)
C(9)	0.4395(8)	0.421(3)	0.3546(4)	143(1)
C(10)	0.4235(8)	0.371(3)	0.2580(5)	143(1)
C(11)	-0.3291(8)	0.396(3)	0.5085(4)	143(1)
C(12)	-0.0623(8)	0.385(3)	0.3546(4)	143(1)
C(13)	-0.0577(8)	0.404(4)	0.5089(4)	143(1)
C(14)	0.4228(8)	0.363(3)	0.6065(4)	143(1)
C(15)	0.6868(8)	0.386(3)	0.6039(4)	143(1)
C(16)	-0.0792(8)	0.382(3)	0.6040(5)	143(1)

*$U_{eq} = U_{eq} \times 10^4$

twin law [100/00$\bar{1}$/00$\bar{1}$] was applied, and the structure was refined according to the method of Jameson (1982) and Herbst-Irmer & Sheldrick (1998). It was then possible to resolve the entire structure by inspection of difference-Fourier maps.

Because of the presence of twinning and the fairly poor parameter-to-observation ratio caused by fairly weak data from the superstructure, some uranyl ion U–O and carbonate group C–O bond lengths refined beyond reasonable values. The structure was subsequently refined with the "soft" constraints that uranyl ion U–O and carbonate group C–O bond lengths are ~1.80 and ~1.29 Å, respectively. Occupancy refinements were done for the M^{3+} sites using the scattering factors of Y and Dy, with the total occupancy of each site constrained to be unity. This resulted in reasonable displacement-parameters for the M^{3+} sites. Refinement of the entire model, including anisotropic- displacement parameters for U and three overall isotropic-displacement factors, for O^{2-} and $(OH)^-$, for H_2O, and for C, converged to an agreement index (R) of 8.37% for the 6622 unique observed reflections ($|F_o| > 4\sigma_F$). The maximum electron-density peaks in the difference-Fourier maps were 5.35 e/Å^3 and –4.82 e/Å^3, and were located close to the uranium atoms. Final positional parameters and equivalent isotropic-displacement parameters are given in Table 3, anisotropic-displacement parameters for the U atoms are in Table 4, mean bond-lengths of the cation polyhedra are in Table 5, the refined occupancies of the M^{3+} sites are in Table 6, and bond-valence sums at the cation and anion sites are in Table 7. Additional selected interatomic distances and observed and calculated structure-factors are available from the Depositary of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS FOR BIJVOETITE-(Y)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(1)	61(1)	306(16)	162(13)	-68(12)	28(13)	20(14)
U(2)	211(13)	281(16)	129(13)	-49(16)	-66(12)	44(14)
U(3)	84(14)	467(24)	132(18)	-15(20)	-7(15)	-21(18)
U(4)	151(13)	262(16)	165(14)	-51(16)	-47(13)	55(15)
U(5)	124(12)	251(16)	160(15)	-36(13)	-27(12)	35(16)
U(6)	140(16)	207(18)	164(19)	-23(15)	-36(15)	34(19)
U(7)	141(17)	427(24)	123(18)	9(21)	-34(17)	-28(20)
U(8)	149(16)	353(23)	129(18)	-22(17)	-43(17)	-31(19)
U(9)	107(18)	240(23)	148(21)	-50(18)	-5(19)	-27(20)
U(10)	118(19)	313(23)	124(22)	19(20)	35(17)	-16(22)
U(11)	82(19)	331(24)	124(21)	-21(21)	57(18)	-4(21)
U(12)	100(21)	469(29)	128(25)	7(23)	10(20)	41(25)
U(13)	99(19)	450(27)	87(20)	-10(22)	17(18)	-82(20)
U(14)	93(22)	479(30)	111(24)	-27(26)	40(21)	17(24)
U(15)	91(20)	337(27)	112(23)	20(20)	13(20)	-33(22)
U(16)	64(20)	537(31)	82(23)	-11(25)	59(19)	-6(23)

$U_{ij} = U_{ij}$ Å^2 × 10^4

TABLE 5. AVERAGE BOND-LENGTHS (Å) IN BIJVOETITE-(Y)

<U(1)-O_{ur}>	1.80	<U(2)-O_{ur}>	1.81	<M(1)-8ϕ>	2.20	<M(2)-7ϕ>	2.39
<U(1)-5ϕ_{eq}>	2.37	<U(2)-6ϕ_{eq}>	2.44	<M(3)-7ϕ>	2.36	<M(4)-8ϕ>	2.70
<U(3)-O_{ur}>	1.82	<U(4)-O_{ur}>	1.82	<M(5)-7ϕ>	2.46	<M(6)-6ϕ>	2.39
<U(3)-6ϕ_{eq}>	2.45	<U(4)-6ϕ_{eq}>	2.43	<M(7)-6ϕ>	2.37	<M(8)-8ϕ>	2.39
<U(5)-O_{ur}>	1.81	<U(6)-O_{ur}>	1.81				
<U(5)-5ϕ_{eq}>	2.38	<U(6)-5ϕ_{eq}>	2.38	<C(1)-O>	1.29	<C(2)-O>	1.29
<U(7)-O_{ur}>	1.81	<U(8)-O_{ur}>	1.81	<C(3)-O>	1.29	<C(4)-O>	1.29
<U(7)-6ϕ_{eq}>	2.50	<U(8)-5ϕ_{eq}>	2.41	<C(5)-O	1.29	<C(6)-O>	1.29
<U(9)-O_{ur}>	1.81	<U(10-O_{ur}>	1.81	<C(7)-O>	1.29	<C(8)-O>	1.29
<U(9)-5ϕ_{eq}>	2.37	<U(10)-5ϕ_{eq}>	2.34	<C(9)-O>	1.29	<C(10)-O>	1.29
<U(11)-O_{ur}>	1.82	<U(12)-O_{ur}>	1.81	<C(11)-O>	1.29	<C(12)-O>	1.29
<U(11)-6ϕ_{eq}>	2.46	<U(12)-5ϕ_{eq}>	2.32	<C(13)-O>	1.29	<C(14)-O>	1.29
<U(13)-O_{ur}>	1.83	<U(14)-O_{ur}>	1.82	<C(15)-O>	1.29	<C(16)-O>	1.29
<U(13)-6ϕ_{eq}>	2.45	<U(14)-6ϕ_{eq}>	2.40				
<U(15)-O_{ur}>	1.80	<U(16)-O_{ur}>	1.82				
<U(15)-5ϕ_{eq}>	2.38	<U(16)-6ϕ_{eq}>	2.54				

DESCRIPTION OF THE STRUCTURE

Cation polyhedra

The structure contains 16 U sites in the asymmetric unit. The polyhedron geometries (Table 5) and bond-valence sums (Table 7) associated with the U sites demonstrate that all are occupied by U^{6+}. Each U^{6+} cation involves an approximately linear $(UO_2)^{2+}$ uranyl ion (designated *Ur*) with <U–O_{Ur}> bond lengths of ~1.80 Å. Of the 16 uranyl ions, half are coordinated by 3 O^{2-} and 2 $(OH)^-$ anions, arranged at the equatorial corners of pentagonal bipyramids, and eight are coordinated by 6 O^{2-} anions, giving hexagonal bipyramids. In each case the bipyramids are capped by the O atoms of the uranyl ions (O_{Ur}). The <U–5ϕ_{eq}> and <U–6ϕ_{eq}> (ϕ: O^{2-}, OH^- or H_2O; eq: equatorial) bond lengths range from 2.32 to 2.41 Å and 2.40 to 2.54 Å, respectively, which are consistent with the values reported for well-refined structures of U^{6+} phases (Burns *et al.* 1997).

The structure contains 16 C atoms that are triangularly coordinated, with <C–O> bond lengths of 1.29 Å, as imposed by the soft constraints during refinement of the structure. The eight M^{3+} sites are occupied by different proportions of Y and *REE* cations (Table 5) and are coordinated by four O^{2-} equatorial anions of uranyl polyhedra in the sheets and various numbers of H_2O groups with <M^{3+}–ϕ> ranging from 2.20 to 2.70 Å. The distribution of Y and *REE* atoms over the eight *M* sites is fairly uniform; according to the results of site-scattering refinement, the Y content of the sites ranges from 40 to 66% (Table 6).

TABLE 6. REFINED OCCUPANCIES OF M^{3+} SITES IN BIJVOETITE

	M(1)	M(2)	M(3)	M(4)	M(5)	M(6)	M(7)	M(8)
Y	0.66(1)	0.40(2)	0.60(2)	0.50(1)	0.55(2)	0.51(2)	0.45(2)	0.55(2)
REE	0.34(1)	0.60(2)	0.40(2)	0.50(1)	0.45(2)	0.49(2)	0.55(2)	0.44(2)

TABLE 7. BOND VALENCE* (vu) ANALYSIS FOR THE STRUCTURE OF BIJVOETITE-(Y)

U(1)	5.90	O(5)	1.65	O(49)	2.15	OH(5)	1.01
U(2)	5.92	O(6)	1.63	O(50)	1.59	OH(6)	1.01
U(3)	5.98	O(7)	1.64	O(51)	1.82	OH(7)	1.05
U(4)	6.07	O(8)	1.64	O(52)	2.22	OH(8)	1.04
U(5)	5.86	O(9)	1.57	O(53)	1.88	$H_2O(1)$	0.36
U(6)	5.87	O(10)	1.54	O(54)	1.95	$H_2O(2)$	0.22
U(7)	5.65	O(11)	1.55	O(55)	1.83	$H_2O(3)$	0.38
U(8)	5.69	O(12)	1.55	O(56)	1.80	$H_2O(4)$	0.44
U(9)	5.83	O(13)	1.55	O(57)	2.09	$H_2O(5)$	0.42
U(10)	6.02	O(14)	1.57	O(58)	2.02	$H_2O(6)$	0.31
U(11)	5.80	O(15)	1.53	O(59)	2.08	$H_2O(7)$	0.27
U(12)	6.17	O(16)	1.60	O(60)	2.15	$H_2O(8)$	0.40
U(13)	5.82	O(17)	1.55	O(61)	1.95	$H_2O(9)$	0.18
U(14)	6.15	O(18)	1.58	O(62)	2.08	$H_2O(10)$	0.27
U(15)	5.87	O(19)	1.61	O(63)	2.04	$H_2O(11)$	0.22
U(16)	5.49	O(20)	1.56	O(64)	2.04	$H_2O(12)$	0.31
M(1)	3.29	O(21)	1.57	O(65)	1.88	$H_2O(13)$	0.39
M(2)	2.88	O(22)	1.58	O(66)	2.14	$H_2O(14)$	0.31
M(3)	2.87	O(23)	1.56	O(67)	1.87	$H_2O(15)$	0.44
M(4)	3.04	O(24)	1.60	O(68)	1.96	$H_2O(16)$	0.29
M(5)	2.30	O(25)	1.57	O(69)	1.81	$H_2O(17)$	0.33
M(6)	2.47	O(26)	1.55	O(70)	1.65	$H_2O(18)$	0.39
M(7)	2.47	O(27)	1.57	O(71)	1.86	$H_2O(19)$	0.41
M(8)	3.01	O(28)	1.52	O(72)	2.10	$H_2O(20)$	0.18
C(1)	3.97	O(29)	1.57	O(73)	1.89	$H_2O(21)$	0.17
C(2)	3.93	O(30)	1.56	O(74)	2.04	$H_2O(22)$	0.36
C(3)	3.97	O(31)	1.55	O(75)	2.03	$H_2O(23)$	0.61
C(4)	3.93	O(32)	1.54	O(76)	1.84	$H_2O(24)$	0.23
C(5)	3.93	O(33)	2.15	O(77)	2.09	$H_2O(25)$	0.33
C(6)	3.97	O(34)	2.20	O(78)	2.11	$H_2O(26)$	0
C(7)	3.97	O(35)	2.13	O(79)	1.71	$H_2O(27)$	0
C(8)	3.97	O(36)	2.13	O(80)	2.17	$H_2O(28)$	0
C(9)	3.93	O(37)	2.08	O(81)	1.71	$H_2O(29)$	0
C(10)	3.97	O(38)	2.20	O(82)	2.20	$H_2O(30)$	0
C(11)	3.97	O(39)	2.11	O(83)	2.15	$H_2O(31)$	0
C(12)	3.92	O(40)	2.17	O(84)	2.09	$H_2O(32)$	0
C(13)	3.93	O(41)	2.00	O(85)	2.10	$H_2O(33)$	0
C(14)	3.97	O(42)	1.96	O(86)	2.05	$H_2O(34)$	0
C(15)	3.93	O(43)	2.13	O(87)	1.84	$H_2O(35)$	0
C(16)	3.97	O(44)	2.18	O(88)	1.91	$H_2O(36)$	0
O(1)	1.61	O(45)	2.01	OH(1)	1.03	$H_2O(37)$	0
O(2)	1.60	O(46)	1.95	OH(2)	1.01	$H_2O(38)$	0
O(3)	1.63	O(47)	1.76	OH(3)	1.17	$H_2O(39)$	0
O(4)	1.63	O(48)	2.03	OH(4)	0.99		

* bond valence parameters for U^{6+} from Burns *et al.* (1997) and for Y^{3+}, Dy^{3+} and C^{4+} from Brese & O'Keeffe (1991)

Structural connectivity

Projection of the structure along [100] reveals that bijvoetite-(Y) contains sheets of cation polyhedra that are parallel to (010), with H_2O groups located in interlayer sites (Fig. 1). The structure contains chains of uranyl and carbonate polyhedra (Fig. 2) that are cross-linked by $M^{3+}\phi_n$ polyhedra to form a sheet (Fig. 3). There are two symmetrically distinct uranyl carbonate chains, although they are topologically identical (Fig. 2). Each chain contains uranyl pentagonal and hexagonal bipyramids, as well as triangular carbonate groups. Two pentagonal bipyramids share an equatorial edge, forming a dimer (designated *D*1) with its long axis parallel to the chain length (Fig. 2). Two hexagonal bipyramids also share edges to form a dimer (designated *D*2), but these dimers are oriented with their long axes perpendicular to the chain length (Fig. 2). The *D*1 and *D*2 dimers alternate along the chain length in the [100] direction, such that each *D*1 dimer is linked to a *D*2 dimer on either side (Fig. 2). The $(CO_3)^{2-}$ carbonate groups are attached to the chain by sharing one edge with a uranyl hexagonal bipyramid in *D*2, resulting in uranyl carbonate chains with a U:C ratio of 1:1 (Fig. 2).

The uranyl carbonate chains are cross-linked through M^{3+} cations, forming (Y,*REE*)-bearing uranyl carbonate sheets (Fig. 3). Each $M^{3+}\phi_n$ polyhedron shares one edge with dimer *D*2 of one chain, as well as two vertices with carbonate triangles of the same chain, and two vertices with carbonate triangle groups in the other adjacent chain.

There are 39 symmetrically independent H_2O groups in the structure, of which 25 are bonded to M^{3+} cations in the sheets, whereas 14 are held in the interlayer of the structure only by H bonds. The interlayer of the structure contains only H_2O groups, and the sheets are connected by H bonds only.

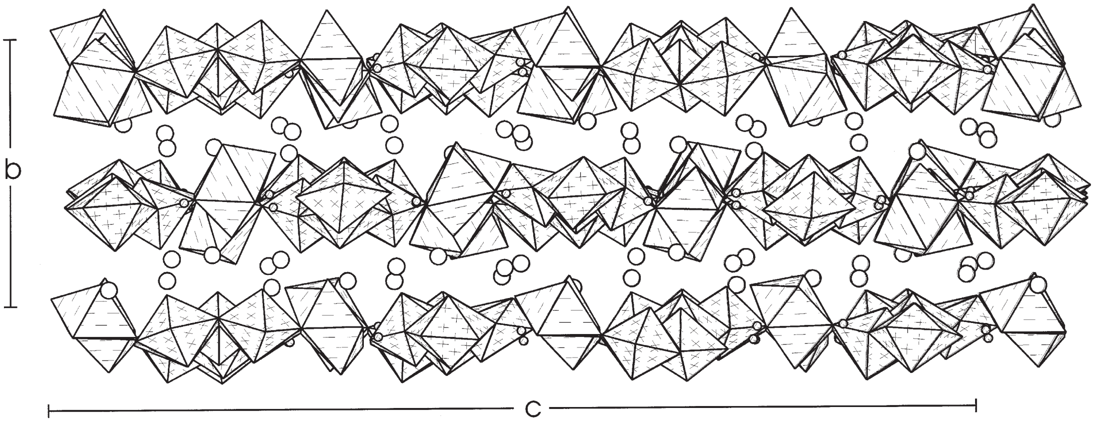

FIG. 1. Polyhedral representation of the structure of bijvoetite-(Y) projected along [100]. The $Ur\phi_n$ and $M\phi_n$ polyhedra are shown shaded with crosses and broken parallel lines, respectively. Interlayer H_2O groups that are held in the structure by H bonds only are shown as larger unshaded circles. C atoms are illustrated with smaller circles. The C–O bonds are omitted.

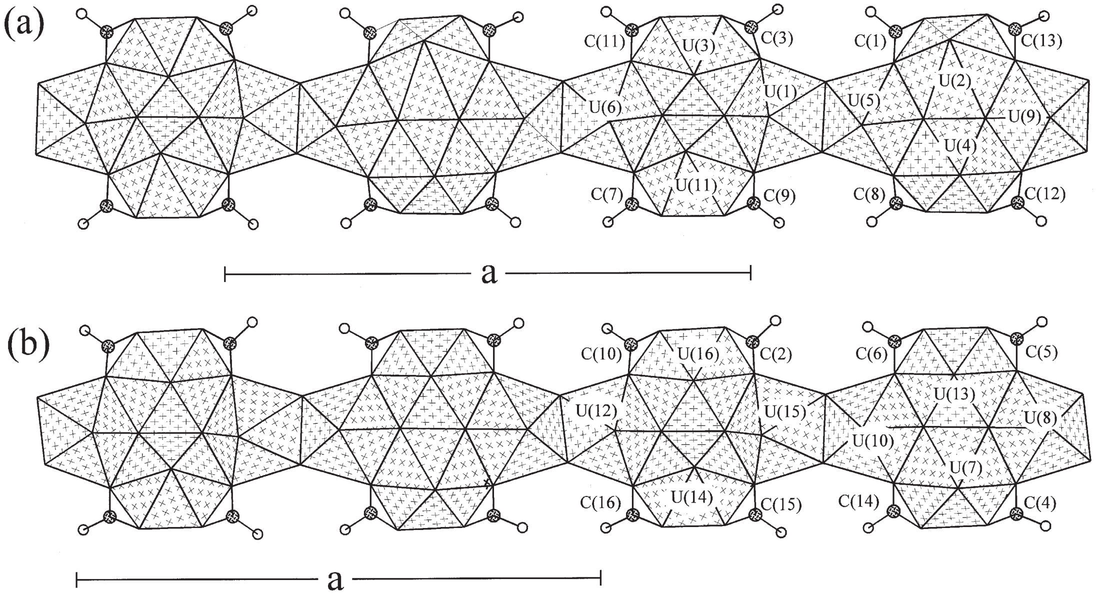

FIG. 2. The uranyl carbonate chains in the structure of bijvoetite-(Y) projected along [010]. The chains shown in (a) and (b) are symmetrically independent.

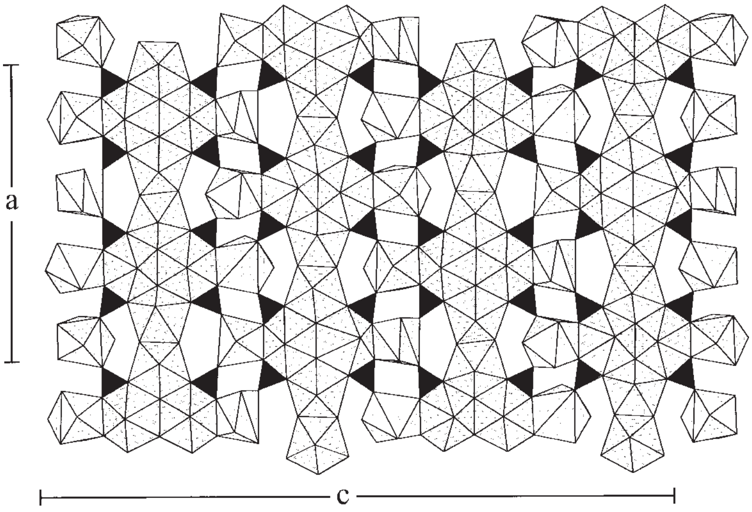

FIG. 3. The sheets of polyhedra in the bijvoetite-(Y) structure projected along [010]. Legend as in Figure 1 except the CO_3 triangles are shown in black.

Bijvoetite-(Y) anion-topology

The sheet anion-topology for bijvoetite-(Y), generated using the procedure of Burns *et al.* (1996), is shown in Figure 4. This novel anion-topology contains a chain of edge-sharing pentagons and hexagons that are separated by two chains: a chain of edge-sharing triangles, and a chain of alternating, edge-sharing squares and trapezoids. The *REE*-bearing uranyl carbonate sheet in bijvoetite-(Y) may be derived from the sheet anion-topology by populating each pentagon and hexagon with a uranyl ion, each trapezoid with a M^{3+} cation, and each

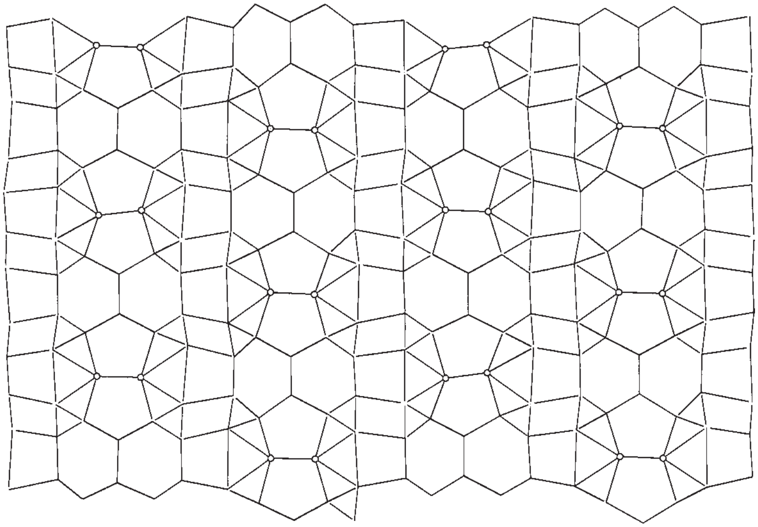

FIG. 4. The bijvoetite sheet anion-topology. The positions of $(OH)^-$ groups are indicated by circles.

triangle that shares an edge with a hexagon, with a $(CO_3)^{2-}$ group.

Interlayer of the structure

Of the ~65 known structures of uranyl minerals, 50 are based upon sheets of polyhedra of higher bond-valence (Burns 1999a), in which low-valence cations or H_2O (or both) are usually located in the interlayers of the structure, connecting the sheets and, in some cases, providing charge balance. The sheet in bijvoetite-(Y) is neutral, thus the net charge of the interlayer must be zero. Adjacent sheets are connected through H bonds to H_2O groups. $H_2O(1)$ through $H_2O(25)$ are bonded to M^{3+} cations in the sheet, whereas $H_2O(26)$ through $H_2O(39)$ are held in the structure by H bonds only (Fig. 1).

Formula for bijvoetite-(Y)

The structure determination indicates that all atoms are on general positions of space group $B12_11$. There are 16 U^{6+}, 16 C^{4+} and 8 M^{3+} symmetrically independent sites. There are 135 symmetrically unique anions in the structure, and bond-valence sums (Table 6) indicate that these correspond to 88 O^{2-}, 8 $(OH)^-$ and 39 H_2O. The structural formula for the crystal studied is therefore $[M_8(H_2O)_{25}(UO_2)_{16}O_8(OH)_8(CO_3)_{16}](H_2O)_{14}$, with $Z = 4$. This formula is similar to that given by Deliens & Piret (1982), except for the number of H_2O groups. The results of the electron-microprobe analysis show that the M^{3+} sites are dominated by Y, with substantial Nd, Sm, Gd, and Dy, and lesser Ce, Eu, Tb, and Er (Table 2). The chemical analysis gives U : C : M^{3+} proportions of 2 : 1.97 : 0.92, which are consistent with results obtained from the structure determination. The calculated density of bijvoetite-(Y) is 3.87 g/cm^3.

DISCUSSION

Several aspects of the structure of bijvoetite-(Y) are unique. The structural sheet has not been observed previously in a mineral or synthetic compound, nor has the uranyl carbonate chain that occurs within the sheet. The bijvoetite-(Y) sheet is the only uranyl-bearing sheet known in a mineral that contains Y and *REE* cations, and as such may be of considerable significance to nuclear waste disposal (see below). Bijvoetite-(Y) is only the second uranyl carbonate (after roubaultite) known to contain both uranyl pentagonal and hexagonal bipyramids; all others contain only uranyl hexagonal bipyramids. Bijvoetite-(Y) is only the third uranyl carbonate known to possess a structure based upon sheets; all others contain isolated uranyl tricarbonate clusters.

Potential transuranium actinide-host phase

Spent uranium oxide nuclear fuel contains UO_2 as well as transuranium actinides and fission products. Under moist oxidizing conditions, such as exist at the proposed geological repository at Yucca Mountain, Nevada, UO_2 fuel is unstable, and radionuclides may be released from the spent fuel as it is altered (Finn *et al.* 1996). Uranyl carbonates may be important phases that form where spent nuclear fuel is altered under moist oxidizing conditions in a carbonate-bearing environment. The crystal chemistries of the trivalent actinide elements (Pu^{3+}, Am^{3+}, Cm^{3+}) are similar to those of the *REE*s. We therefore suggest that trivalent actinides released from spent fuel in a geological repository may be incorporated in a phase such as bijvoetite-(Y), with these actinides located in M^{3+} sites. Such a phase may serve to retard the migration of actinides from the repository; as such, it may be desirable to "manipulate" the chemical environment locally to enhance the formation of such a phase.

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