

## CRYSTAL CHEMISTRY OF URANYL MOLYBDATES. I. THE STRUCTURE AND FORMULA OF UMOHOITE

SERGEY V. KRIVOVICHEV\* AND PETER C. BURNS§

Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, Indiana, 46556-0767, U.S.A.

### ABSTRACT

The structure of umohoite,  $[(\text{UO}_2)\text{MoO}_4(\text{H}_2\text{O})](\text{H}_2\text{O})$ , triclinic, space group  $P\bar{1}$ ,  $a$  6.3748(4),  $b$  7.5287(5),  $c$  14.628(1) Å,  $\alpha$  82.64(1),  $\beta$  85.95(1),  $\gamma$  89.91(1)°,  $V$  694.52(8) Å<sup>3</sup>, has been solved by direct methods and refined by full-matrix least-squares to an agreement index ( $R$ ) of 4.6% and a goodness-of-fit of 1.02 for 2456 unique observed reflections collected using  $\text{MoK}\alpha$  X-radiation and a CCD-based detector. The structure differs substantially from models previously proposed in both the coordination of the cations and the connectivity of the structure. The structure contains two non-equivalent U sites that are occupied by  $\text{U}^{6+}$  cations. Each is part of a nearly linear  $(\text{UO}_2)^{2+}$  uranyl ion ( $Ur$ ) that is further coordinated by five O atoms arranged at the equatorial corners of pentagonal bipyramids capped by the  $\text{O}_{Ur}$  atoms. Two non-equivalent  $\text{Mo}^{6+}$  cations are each coordinated by five O atoms and one  $\text{H}_2\text{O}$  group; the O atoms are arranged at the apices of a square bipyramid, with  $\text{Mo}^{6+}\text{-O}$  bond-lengths in the range 1.69 to 1.96 Å. The  $\text{H}_2\text{O}$  groups are located at the apical positions of highly distorted octahedra, with  $\text{Mo}^{6+}\text{-H}_2\text{O}$  bond-lengths in the range 2.44 to 2.46 Å. The cation polyhedra link by sharing edges, forming sheets with the uranophane anion-topology, in which the pentagons are populated by uranyl ions and the squares are populated by  $\text{Mo}^{6+}$ . This is the first mineral structure known that is based upon the uranophane anion-topology with the squares populated by octahedra. The interlayer at  $z = 0$  contains  $\text{H}_2\text{O}$  groups, whereas the interlayer at  $z = 0.5$  is not occupied. Sheets are linked together by hydrogen bonding, with bonds bridging between sheets where  $\text{H}_2\text{O}$  is absent in the interlayer, and to  $\text{H}_2\text{O}$  groups in the interlayer where they are present.

*Keywords:* umohoite, uranium, uranyl mineral, uranophane anion-topology, crystal structure.

### SOMMAIRE

La structure de l'umohoïte,  $[(\text{UO}_2)\text{MoO}_4(\text{H}_2\text{O})](\text{H}_2\text{O})$ , triclinique, groupe spatial  $P\bar{1}$ ,  $a$  6.3748(4),  $b$  7.5287(5),  $c$  14.628(1) Å,  $\alpha$  82.64(1),  $\beta$  85.95(1),  $\gamma$  89.91(1)°,  $V$  694.52(8) Å<sup>3</sup>, a été résolue par méthodes directes et affinée par moindres carrés sur matrice entière jusqu'à un résidu  $R(I)$  de 4.6% et un indice de concordance de 1.02 en utilisant 2456 réflexions uniques observées avec rayonnement  $\text{MoK}\alpha$  et mesurées avec un détecteur à aire avec couplage de charges. La structure diffère sensiblement des ébauches antérieures, tant dans la coordination des cations que dans la connectivité de la structure. Celle-ci contient deux sites U non équivalents, occupés par des ions  $\text{U}^{6+}$ . Chacun fait partie d'un ion uranyle,  $(\text{UO}_2)^{2+}$ , presque linéaire ( $Ur$ ), qui est en plus coordonné à cinq atomes d'oxygène disposés aux coins équatoriaux de bipyramides pentagonales avec terminaisons par les atomes  $\text{O}_{Ur}$ . Deux cations  $\text{Mo}^{6+}$  non équivalents sont coordonnés par cinq atomes d'oxygène et un groupe  $\text{H}_2\text{O}$ ; les atomes d'oxygène sont disposés aux sommets d'une bipyramide carrée, la longueur des liaisons  $\text{Mo}^{6+}\text{-O}$  étant entre 1.69 et 1.96 Å. Les groupes  $\text{H}_2\text{O}$  sont situés aux sommets d'octaèdres fortement difformes, avec les liaisons  $\text{Mo}^{6+}\text{-H}_2\text{O}$  entre 2.44 et 2.46 Å. Les polyèdres sont liés par partage d'arêtes, pour former des feuillets ayant la topologie anionique de l'uranophane, les pentagones contenant les ions uranyle, et les carrés,  $\text{Mo}^{6+}$ . Il s'agit de la première structure fondée sur la topologie anionique de l'uranophane dans laquelle les carrés représentent des octaèdres. L'interfeuillelet à une élévation  $z = 0$  contient des groupes  $\text{H}_2\text{O}$ , tandis que l'interfeuillelet à  $z = 0.5$  est vide. Les feuillets sont interliés par des liaisons hydrogène, directement entre feuillets sans groupes  $\text{H}_2\text{O}$  dans l'interfeuillelet, et impliquant des groupes  $\text{H}_2\text{O}$  dans les interfeuillelets où ils sont présents.

(Traduit par la Rédaction)

*Mots-clés:* umohoïte, uranium, minéral à uranyle, topologie anionique de l'uranophane, structure cristalline.

\* *Permanent address:* Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia.

§ *E-mail address:* pburns@nd.edu

## INTRODUCTION

Uranyl molybdates are common constituents of the oxidized zones of U–Mo deposits at several localities in the U.S. and in the Russian Federation. Knowledge of the structures and fields of stability of uranyl molybdates is essential for understanding the alteration and weathering of uranium deposits, as well as the mine and mill tailings that result from resource utilization (Burns 1999a, Finch & Murakami 1999). The possible importance of uranyl molybdates for nuclear waste disposal was demonstrated by the recent discovery of the phase  $(\text{Cs}_{2x}\text{Ba}_{1-x})[(\text{UO}_2)_5(\text{MoO}_6)(\text{OH})_6] \cdot n\text{H}_2\text{O}$  ( $x \approx 0.4$ ,  $n \approx 6$ ) (Buck *et al.* 1997, Finch & Buck 1998) that formed as a result of the alteration of spent nuclear fuel at 90°C in tests designed to simulate conditions in the proposed nuclear waste repository at Yucca Mountain, Nevada. Several recent studies have shown that uranyl phases forming by the alteration of nuclear waste, such as spent nuclear fuel rods, borosilicate waste glasses, or the components of the Chernobyl Nuclear Power Plant fourth block, may incorporate various radionuclides into their structures, thus controlling to a large extent the release of these radionuclides into the biosphere (Buck *et al.* 1997, Burns 1999b, Burns *et al.* 1997a, b, 2000, Burns & Hill 2000, Chen *et al.* 1999, 2000, Hill & Burns 1999, Wronkiewicz & Buck 1999, Pazukhin 1994, Teterin *et al.* 1997).

Seven uranyl molybdate minerals are known (Finch & Murakami 1999), but the structures have only been reported for three of these: deloryite (Pushcharovsky *et al.* 1996), iriginite (Serezhkin *et al.* 1973) and umohoite (Makarov & Anikina 1963). The lack of structural information is likely due to the scarcity of crystals of suitable size and quality for structure determination. We have redetermined the structure of umohoite, and found it to be substantially different from that reported by Makarov & Anikina (1963); the results are reported herein.

## PREVIOUS STUDIES

Umohoite was described by Brophy & Kerr (1953) from the Freedom No. 2 mine in Marysvale, Utah, with the formula  $\text{UO}_2\text{MoO}_4 \cdot 4\text{H}_2\text{O}$ , and a hexagonal unit-cell with  $a$  8.60,  $c$  14.45 Å. Coleman & Appleman (1957) examined samples from the Lucky Mc mine, Wyoming, and reported a monoclinic unit-cell with  $a$  14.30,  $b$  7.50,  $c$  6.38 Å,  $\beta$  99.08° and possible space-groups  $P2_1$  and  $P2_1/m$ . On the basis of X-ray powder-diffraction studies, Kamhi (1959) proposed an orthorhombic unit-cell with  $a$  6.32,  $b$  7.48,  $c$  12.4 or 14.5–17.0 Å, depending on the degree of hydration. Hamilton & Kerr (1959) examined umohoite from several localities in the U.S. and what was then the U.S.S.R., noted instability of crystals under X-ray irradiation, and found evidence for three modifications, which differ in the  $c$  unit-cell parameter (16.83, 18.99 and 21.53 Å).

Skvortsova *et al.* (1961) reported umohoite from an unspecified locality in the former U.S.S.R. and determined the formula to be  $\text{UO}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . They provided unit-cell dimensions  $a$  14.17,  $b$  7.33,  $c$  6.41 Å,  $\beta$  98.7°.

The structure of umohoite was reported by Anikina & Makarov (1961) and Makarov & Akinina (1963) using specimens from an unspecified locality in the former U.S.S.R. The structure was given in space group  $P2_1/c$  with the unit cell  $a$  6.32,  $b$  7.50,  $c$  57.8 Å,  $\beta$  94°, with the long  $c$  dimension defined by the presence of weak spots on rotation photographs. The structure reportedly contained electrostatically neutral uranyl molybdate sheets linked through H bonds to interlayer  $\text{H}_2\text{O}$  groups, with the formula  $[\text{UMoO}_6(\text{H}_2\text{O}_2)](\text{H}_2\text{O})_2$ . The sheets were said to contain uranyl and molybdate hexagonal bipyramids. According to Burns *et al.* (1996), the sheets reported by Makarov & Akinina (1963) are based upon the  $\alpha$ - $\text{UO}_3$  anion-topology. Serezhkin *et al.* (1977) re-examined the single crystals of umohoite studied by Makarov & Anikina (1963). They determined the mineral to have triclinic symmetry, and reported the unit-cell parameters  $a$  6.402(6),  $b$  7.489(7),  $c$  14.60(2) Å,  $\alpha$  85.3(2)°,  $\beta$  96.3(2)°,  $\gamma$  90.5(2)°, which are similar to the parameters determined in the current study. However, Serezhkin *et al.* (1977) did not redetermine the crystal structure.

Fedorov (1967) examined umohoite from an unspecified locality in the former U.S.S.R. and proposed the formula  $\text{U}^{4+}(\text{UO}_2)_2(\text{MoO}_3)_3(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , which is notable by the presence of  $\text{U}^{4+}$  along with  $\text{U}^{6+}$ . Fedorov (1967) indicated that umohoite crystals are replaced by transparent greenish yellow crystals of iriginite. Zhigach (1974) and later Deliens (1975), Piret & Deliens (1977) and Belova *et al.* (1985) described green, orange-red and yellow varieties of umohoite, although most are black. The unusual colors of these samples may be due to admixtures of compounds of Mg, Fe and Ni, respectively. Belova *et al.* (1985) reported that a specimen of black umohoite contains 2.51 wt. % CaO.

## EXPERIMENTAL

Umohoite from an unspecified locality in the former U.S.S.R. was obtained from the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow (sample Kz-601). Although the locality is not recorded, the specimen is most likely from the Kazakhstan U–Mo deposits described by Skvortsova *et al.* (1961) and Fedorov (1967). The sample contains tabular black crystals of umohoite that are partially replaced by greenish yellow and yellow crystals of iriginite, and is similar to those shown in photographs given by Skvortsova *et al.* (1961) and Fedorov (1967). An opaque black tabular crystal with dimensions 0.10 × 0.08 × 0.01 mm was selected for data collection with a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD detector and a crystal-to-detector distance of 5 cm

(Burns 1998a). A sphere of data was collected using monochromatic  $\text{MoK}\alpha$  X-radiation and frame widths of  $0.3^\circ$  in  $\omega$ , with 30 s counting time per frame. Several hundred frames of data were analyzed to locate reflections for the determination of unit-cell parameters (Table 1), which were refined using 528 reflections and least-squares techniques. Although the unit-cell lengths are similar to those reported by Coleman & Appleman (1957) and Skvortsova *et al.* (1961), it is clear from the unit-cell angles that the crystal is triclinic, as was reported by Serezhkin *et al.* (1977) (Table 1). Data were collected for  $3^\circ \leq 2\theta \leq 56.7^\circ$  in approximately 24 hours. The three-dimensional data were integrated using the Bruker program SAINT, and corrected for Lorentz, polarization, and background effects. An empirical absorption-correction was based upon 2404 intense reflections with the crystal modeled as a (001) plate; reflections with a plate-glancing angle less than  $0.3^\circ$  were discarded, lowering  $R_{\text{azimuthal}}$  from 23.4 to 8.6%. A total of 8261 intensities remained after correction for absorption, of which 3281 were unique ( $R_{\text{INT}} = 9.4\%$ ), with 2456 classed as observed ( $|F_o| \geq 4\sigma_F$ ).

### 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 system of programs was used for the determination and refinement of the structure. Reflection statistics indicated space group  $P\bar{1}$ , which was verified by successful solution of the structure by direct methods. The initial solution provided the positions of the U and Mo cations, with anions located in difference-Fourier maps following refinement of the model. Refinement of all atom-position parameters and allowance for isotropic displacement gave an agreement index ( $R_I$ ) of 8.0%. Conversion of the displacement parameters for all atoms to anisotropic form, and inclusion of a weighting scheme of the structure factors, resulted in a final  $R(I)$  of 4.6%

TABLE 1. CRYSTALLOGRAPHIC DATA FOR UMOHOITE

$a$ (Å)	6.3748(4)	Crystal size (mm)	$0.08 \times 0.10 \times 0.01$
$b$ (Å)	7.5287(5)	Radiation	$\text{MoK}\alpha$
$c$ (Å)	14.628(1)	Total Reflections	8261
$\alpha$ (°)	82.64(1)	Unique Reflections	3281
$\beta$ (°)	85.95(1)	Unique $F_o \geq 4\sigma_F$	2456
$\gamma$ (°)	89.91(1)		
$V$ (Å <sup>3</sup> )	694.52(8)	$R(1)$	4.6%
Space group	$P\bar{1}$	$S$	1.02
$F_{000}$	808		
$\mu$ (cm <sup>-1</sup> )	250.9		
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	4.457		
Unit-cell contents:	4{[(UO <sub>2</sub> )MoO <sub>4</sub> (H <sub>2</sub> O)](H <sub>2</sub> O)}		
$R(1) = \sum  F_o - F_c  / \sum F_o$			
$S = \{ \sum [w(F_o^2 - F_c^2)] / (n - p) \}^{1/2}$ , where $n$ is the number of reflections and $p$ is the number of refined parameters.			

for the 2456 observed reflections, and a goodness-of-fit ( $S$ ) of 1.02. The final atomic parameters are presented in Table 2, and selected interatomic distances are in Table 3. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

### RESULTS

#### Cation polyhedra

The structure contains two non-equivalent U cations. Consideration of the bond-valence sums incident upon each site (Table 4) and the polyhedron geometries (Table 3) clearly indicates that all U is present as  $\text{U}^{6+}$ . Each  $\text{U}^{6+}$  cation is strongly bonded to two O atoms, resulting in nearly linear  $(\text{UO}_2)^{2+}$  uranyl ions ( $U_r$ ) with  $\text{U}-\text{O}_{U_r}$  bond-lengths  $\sim 1.8$  Å, as is typical for  $\text{U}^{6+}$  in inorganic compounds (Evans 1963, Burns *et al.* 1997c). Each uranyl ion is coordinated by five additional O atoms arranged at the equatorial vertices of pentagonal bipyramids capped by  $\text{O}_{U_r}$  atoms. The structure determination does not support the presence of  $\text{U}^{4+}$  in the crystal of umohoite studied.

TABLE 2. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS ( $\times 10^4 \text{ \AA}^2$ ) FOR UMOHOITE

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
U(1)	0.25592(7)	0.80029(6)	0.29699(4)	115(2)	88(2)	62(3)	198(3)	-24(2)	3(2)
U(2)	0.15158(7)	0.29981(6)	0.29871(4)	123(2)	86(2)	66(3)	219(3)	-26(2)	3(2)
Mo(1)	0.7073(2)	0.0575(2)	0.2721(1)	161(3)	65(5)	121(6)	303(8)	-36(5)	6(4)
Mo(2)	0.7073(2)	0.5558(2)	0.2724(1)	173(3)	60(5)	130(6)	335(8)	-47(5)	3(4)
O(1)	0.640(2)	0.804(1)	0.2893(8)	190(20)	150(50)	70(50)	360(70)	-90(40)	0(40)
O(2)	0.232(2)	0.768(1)	0.4200(8)	240(20)	280(60)	130(50)	310(70)	-10(50)	-20(40)
O(3)	0.993(1)	0.590(1)	0.2957(8)	170(20)	50(40)	70(50)	370(70)	0(40)	20(30)
O(4)	0.769(1)	0.300(1)	0.2970(8)	200(20)	100(50)	60(50)	450(80)	-40(50)	-10(40)
O(5)	0.117(2)	0.268(1)	0.4233(8)	240(20)	310(60)	180(60)	240(70)	-30(50)	-60(50)
O(6)	0.993(2)	0.011(1)	0.2961(8)	190(20)	110(50)	70(50)	370(70)	10(40)	0(40)
O(7)	0.412(1)	0.090(1)	0.2984(8)	160(20)	20(40)	70(40)	410(70)	-70(40)	30(30)
O(8)	0.178(2)	0.331(2)	0.1758(8)	260(30)	280(60)	200(60)	310(70)	-60(50)	-20(50)
O(9)	0.413(1)	0.509(1)	0.2993(8)	200(20)	30(40)	130(50)	430(70)	-40(50)	-50(40)
O(10)	0.280(2)	0.828(2)	0.1744(8)	240(20)	290(60)	250(60)	180(60)	-70(50)	-10(50)
O(11)	0.724(2)	0.093(2)	0.1546(9)	300(30)	220(60)	350(70)	320(70)	-10(60)	20(50)
O(12)	0.724(2)	0.577(2)	0.1556(8)	310(30)	230(60)	460(80)	240(70)	-50(60)	0(50)
H <sub>2</sub> O(13)	0.687(2)	0.527(2)	0.4407(8)	290(30)	300(60)	360(70)	200(60)	0(50)	50(50)
H <sub>2</sub> O(14)	0.686(2)	0.996(2)	0.4421(9)	350(30)	320(70)	400(80)	310(80)	0(60)	40(50)
H <sub>2</sub> O(15)	0.743(3)	0.126(2)	-0.002(1)	770(60)	560(110)	720(140)	1080(170)	-290(120)	230(100)
H <sub>2</sub> O(16)	0.753(2)	0.624(2)	0.003(2)	800(70)	450(100)	500(110)	1500(200)	-400(120)	0(110)

\* $U_{\text{eq}} = (1/3) \sum U_{ij}^2 a_i^2 a_j^2$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN THE STRUCTURE OF UMOHOITE

U(1)-O(10)	1.77(1)	U(2)-O(8)	1.78(1)
U(1)-O(2)	1.78(1)	U(2)-O(5)	1.80(1)
U(1)-O(6)a	2.302(9)	U(2)-O(7)	2.290(9)
U(1)-O(3)b	2.31(1)	U(2)-O(9)	2.303(9)
U(1)-O(7)c	2.40(1)	U(2)-O(3)b	2.398(9)
U(1)-O(9)	2.41(1)	U(2)-O(6)b	2.41(1)
U(1)-O(1)	<u>2.45(1)</u>	U(2)-O(4)b	<u>2.442(9)</u>
<U(1)-O <sub>U<sub>1</sub></sub> >	1.78	<U(2)-O <sub>U<sub>2</sub></sub> >	1.79
<U(1)-φ <sub>U<sub>1</sub></sub> >	2.37	<U(2)-φ <sub>U<sub>2</sub></sub> >	2.37
O <sub>U<sub>1</sub></sub> -U1-O <sub>U<sub>1</sub></sub>	178.9(5)	O <sub>U<sub>2</sub></sub> -U2-O <sub>U<sub>2</sub></sub>	178.5(5)
Mo(1)-O(11)	1.70(1)	Mo(2)-O(12)	1.69(1)
Mo(1)-O(6)	1.91(1)	Mo(2)-O(3)	1.902(9)
Mo(1)-O(7)	1.914(8)	Mo(2)-O(9)	1.903(9)
Mo(1)-O(1)d	1.937(9)	Mo(2)-O(1)	1.959(9)
Mo(1)-O(4)	1.95(1)	Mo(2)-O(4)	1.960(9)
Mo(1)-H <sub>2</sub> O(14)d	2.46(1)	Mo(2)-H <sub>2</sub> O(13)	2.44(1)
<Mo(1)-O>	1.88	<Mo(2)-O>	1.88
<Mo(1)-φ>	1.98	<Mo(2)-φ>	1.98

a = x - 1, y + 1, z; b = x - 1, y, z; c = x, y + 1, z; d = x, y - 1, z.

There are two non-equivalent Mo cations in the structure. Bond-valence sums are 5.73 and 5.81 *vu* (valence units) for the Mo(1) and Mo(2) sites, respectively, indicating that each is occupied by Mo<sup>6+</sup>. It is impossible to rule out small amounts of Mo<sup>5+</sup> at these sites, which could account for the crystals being black, as suggested by Coleman & Appleman (1957). Each Mo<sup>6+</sup> cation is bonded to five atoms of O with bond-lengths in the range 1.69 to 1.96 Å, and to one H<sub>2</sub>O group with a bond-length of 2.44–2.46 Å. Taken together, the coordinating ligands define a highly distorted octahedron. Considering only the bonds with lengths less than 2 Å, the O atoms are arranged at the vertices of square bipyramids. The apical O atoms are 1.69–1.70 Å from the Mo<sup>6+</sup> cation, whereas the equatorial Mo<sup>6+</sup>–O bond-lengths are in the range 1.90 to 1.96 Å. The O<sub>apical</sub>–Mo–O<sub>equatorial</sub> bond-angles range from 98.6 to 101.2°, indicating that the cation is located above the plane defined by the equatorial O atoms. The H<sub>2</sub>O groups are the sixth ligands of the distorted octahedra, and although the bond lengths are considerably longer than for the other ligands (2.44 to 2.46 Å), they are appropriately located to be considered as part of the coordination polyhedra about the Mo<sup>6+</sup> cations. The bond-valence calculations (Table 4) indicate that each of these bonds has ~0.2 *vu* associated with it.

### Structural connectivity

Projection of the structure along [100] reveals sheets of edge-sharing uranyl and molybdate polyhedra, with H<sub>2</sub>O groups occurring in the interlayer (Fig. 1).

*Sheets of polyhedra:* The Urφ<sub>5</sub> pentagonal bipyramids share equatorial edges, resulting in chains one polyhedron wide that extend along [010] (Fig. 2a). The chains of uranyl polyhedra are cross-linked by sharing

TABLE 4. BOND-VALENCE\* (*vu*) ANALYSIS FOR UMOHOITE

	U(1)	U(2)	Mo(1)	Mo(2)	Σ
O(1)	0.46		0.92	0.87	2.25
O(2)	1.68				1.68
O(3)	0.59	0.50		1.02	2.11
O(4)		0.46	0.84	0.87	2.17
O(5)		1.62			1.62
O(6)	0.61	0.49	1.02		2.12
O(7)	0.50	0.61	0.98		2.09
O(8)		1.68			1.68
O(9)	0.49	0.60		1.01	2.10
O(10)	1.71				1.71
O(11)			1.75		1.75
O(12)				1.80	1.80
H <sub>2</sub> O(13)				0.24	0.24
H <sub>2</sub> O(14)			0.22		0.22
H <sub>2</sub> O(15)					0.00
H <sub>2</sub> O(16)					0.00
Σ	6.04	5.96	5.73	5.81	

\*Values calculated using the parameters for U<sup>6+</sup> from Burns *et al.* (1997c) and Mo<sup>6+</sup> from Brese & O'Keeffe (1991). Contributions from H atoms are not included.

equatorial edges of uranyl polyhedra with Mo<sup>6+</sup>φ<sub>6</sub> octahedra (φ: unspecified anion), resulting in sheets parallel to (001) (Figs. 1, 2a). The corresponding sheet anion-topology, derived using the method of Burns *et al.* (1996), is shown in Figure 2b. This anion topology, referred to as the uranophane anion-topology by Burns *et al.* (1996), is the basis for sheets found in eight mineral structures. Of these, seven involve population of the pentagons with uranyl ions, and the triangles are the faces of tetrahedra. In schmitterite, the pentagons are populated with uranyl ions and the squares in the anion topology are occupied by highly distorted TeO<sub>4</sub> tetrahedra. Umohoite is the first mineral shown to contain sheets based upon the uranophane anion-topology with the squares populated. Sheets based upon the uranophane anion-topology that involve both populated pentagons and squares are known in several inorganic compounds (Burns *et al.* 1996). The squares in the anion topology correspond to the equatorial ligands of UrO<sub>4</sub> square bipyramids in K<sub>2</sub>[(UO<sub>2</sub>)<sub>2</sub>O<sub>3</sub>] (Saine 1989), and to the equatorial ligands of Urφ<sub>4</sub> square bipyramids and distorted Cu<sup>2+</sup>O<sub>6</sub> octahedra in [(UO<sub>2</sub>)(CuO<sub>4</sub>)] (Dickens *et al.* 1993). The phase UMoO<sub>5</sub> (D'yachenko *et al.* 1996) contains sheets that are topologically similar to those in umohoite.

*Interlayer of the structure:* There are two symmetrically distinct interlayers in the structure of umohoite: the interlayer at *z* ≈ 0 contains H<sub>2</sub>O groups, whereas the interlayer at *z* ≈ 0.5 is unoccupied. Sheets are linked *via* H bonds. Where H<sub>2</sub>O groups are present in the interlayer, linkage involves H bonds between the sheets and the interlayer H<sub>2</sub>O groups; where H<sub>2</sub>O groups are absent, H bonds bridge directly between sheets. The latter is an unusual configuration for uranyl minerals, in which it is most common for the interlayer to be occupied by H<sub>2</sub>O groups or by low-valence cations. In ura-

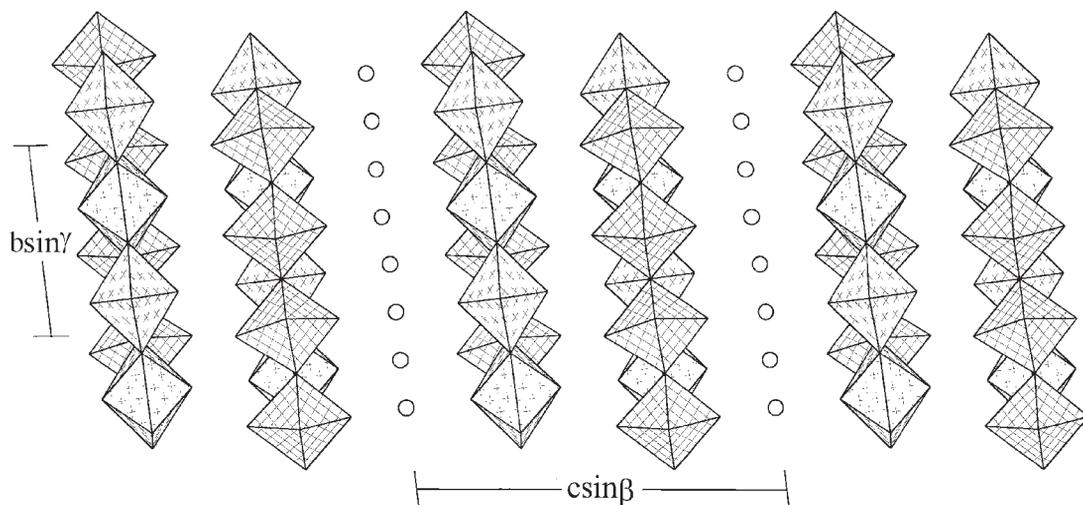


FIG. 1. The structure of umohoite projected along [100].  $U_7O_{15}$  and  $Mo_6O_{18}$  polyhedra are shown shaded with crosses and cross-hatching, respectively.

nyl minerals in which the interlayer is empty, sheets tend to be linked through van der Waals bonds only. Recently, a similar structural connectivity was described by Duribreux *et al.* (1999) for  $CsUV_3O_{11}$ . In that compound, two sheets of composition  $[UV_3O_{11}]$  are linked by  $Cs^+$  cations, forming electrostatically neutral double  $\{Cs_2[UV_3O_{11}]_2\}$  layers, with adjacent double layers linked through van der Waals bonding only.

As is typical for uranyl compounds, it was not possible to determine the positions of  $H^+$  cations in the structure with only X-ray-diffraction data. However, using arguments given by Finch *et al.* (1996) for schoepite and Burns (1997) for vandendriesscheite, involving the bond-valence model for  $(OH)^-$  and  $H_2O$  in oxysalt minerals (Brown 1976, Hawthorne 1992), an H bonding scheme is proposed. The details of H bond-

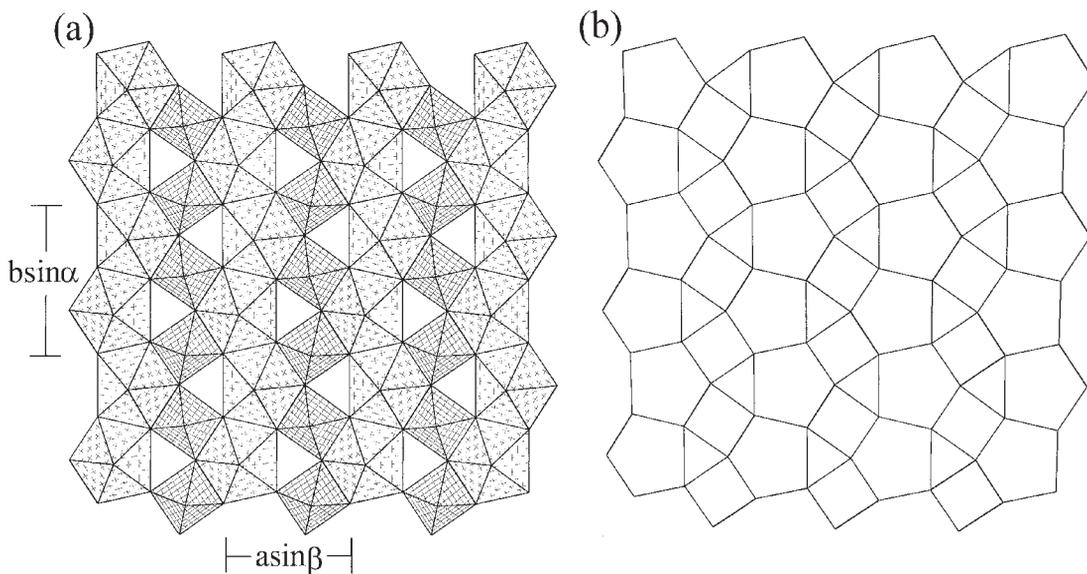


FIG. 2. The sheet of uranyl and molybdate polyhedra in the structure of umohoite projected along [001]; (a) polyhedral representation, (b) anion topology derived using the methods of Burns *et al.* (1996). Legend as in Figure 1.

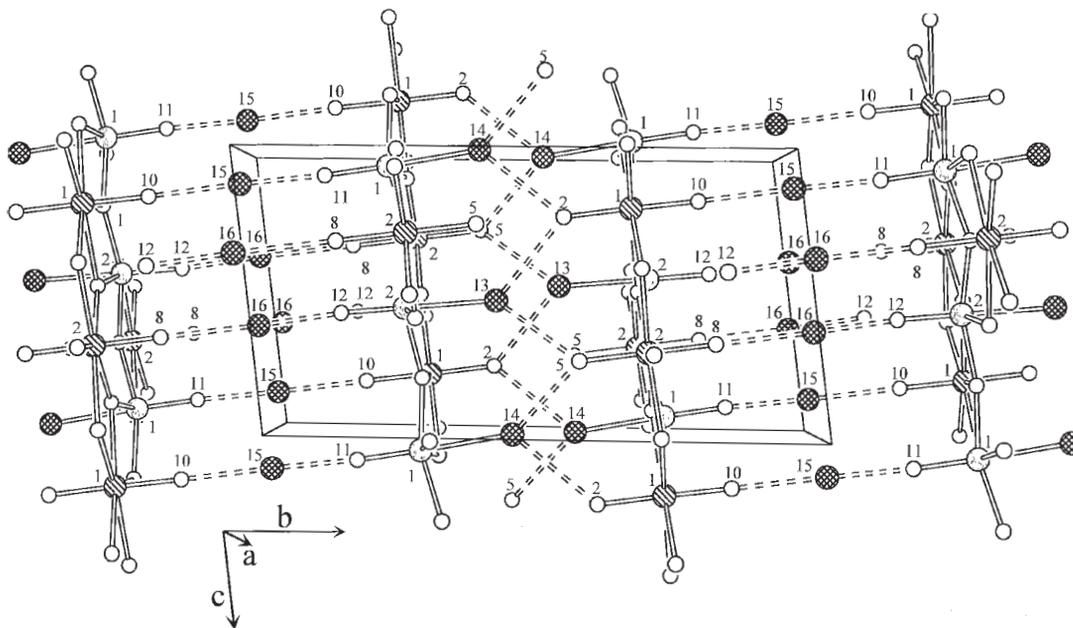


FIG. 3. Hydrogen bonding in the structure of umohoite. Anion-anion separations corresponding to hydrogen bonds are shown as broken lines. Legend:  $U^{6+}$ : circles shaded with parallel lines,  $Mo^{6+}$ : large circles with shading in the lower-left sides,  $O^{2-}$ : smaller unshaded circles,  $H_2O$ : cross-hatched circles.

ing between the sheets of polyhedra depend on whether or not  $H_2O$  groups are located in the interlayer. There are two general types of H bonds in the structure: those that bridge between sheets of uranyl and molybdate polyhedra, and those that bridge between the sheets of polyhedra and interlayer  $H_2O$  groups.

The structure contains four symmetrically independent  $H_2O$  groups:  $H_2O(13)$  and  $H_2O(14)$  are weakly bonded to  $Mo^{6+}$  cations, whereas  $H_2O(15)$  and  $H_2O(16)$  occur within the interlayers and are not bonded to cations, other than  $H^+$ . The proposed H-bonding scheme is shown in Figure 3.

*Hydrogen bonds that bridge directly between sheets:* The  $H_2O(13)$  and  $H_2O(14)$  groups at  $z \approx 0.5$  are weakly bonded to the  $Mo^{6+}$  cations within the sheets, and each donates H bonds that extend to the adjacent sheet (Fig. 3). The  $H_2O(13)$  group donates H bonds that are accepted by the O(2) and O(5) anions of the adjacent sheet, with anion-anion separations of 2.89(2) and 3.01(2) Å, respectively. Both acceptor anions are  $O_{Ur}$  of uranyl polyhedra. The H bonds donated by the  $H_2O(14)$  group are also accepted by the O(2) and O(5) anions, with anion-anion separations of 2.92(2) and 2.96(2) Å, respectively. The O(2)– $H_2O(13)$ –O(5) and O(2)– $H_2O(14)$ –O(5) angles are 81.0 and 81.4°, respectively. Each of these H bonds is weak, on the basis of the length of the anion-anion separations.

*Hydrogen bonds that bridge between sheets and interlayer  $H_2O$  groups:* The  $H_2O(15)$  and  $H_2O(16)$

groups are located in the interlayer at  $z \approx 0$ , and each donates H bonds that are accepted by the adjacent sheets of polyhedra (Fig. 3). The  $H_2O(15)$  group donates H bonds that are accepted by the O(10) and O(11) anions, with anion-anion separations of 2.51(2) and 2.28(2) Å, respectively. The O(10) anion is an  $O_{Ur}$  of the  $U(1)\phi_7$  polyhedron, whereas the O(12) anion is bonded to  $Mo(2)$ , with a bond-length of 1.69(1) Å. The O(10)– $H_2O(15)$ –O(11) bond-angle is 173.5°. The O(8) and O(12) anions accept the H bonds donated by the  $H_2O(16)$  group, with corresponding anion-anion separations of 2.60(3) and 2.20(3) Å, respectively. The O(8) anion is an  $O_{Ur}$  bonded to U(2), and O(12) is bonded to  $Mo(2)$ , with a bond-length of 1.69(1) Å. The O(8)– $H_2O(16)$ –O(12) angle is 174.7°. Note that all of the H bonds extending from the interlayer  $H_2O$  groups to the sheets of polyhedra are strong, as indicated by the anion-anion separations.

#### *Crystal-chemical formula of umohoite*

All atoms are in general positions in the space group  $P\bar{1}$ , and polyhedron geometries (Table 4), as well as bond-valence sums (Table 5), indicate that the structure contains  $U^{6+}$  and  $Mo^{6+}$ . The formula of our crystal of umohoite is  $[(UO_2)MoO_4(H_2O)](H_2O)$ , which may be written as  $UMoO_6 \cdot 2H_2O$ , in agreement with the formula proposed by Skvortsova *et al.* (1961).

There have been reports of substantial variability of the  $c$  dimension of umohoite (see above). This may be in part due to variation of the  $\text{H}_2\text{O}$  content. In the event that  $\text{H}_2\text{O}$  enters the interlayer a  $z = 0.5$  that is unoccupied in the crystal we studied, expansion of the structure by 2–3 Å along  $z$  could be expected. It is also possible that polytypism accounts for the variation in the unit-cell parameters. Several authors have reported  $c \approx 14.1\text{--}14.5$  Å (Brophy & Kerr 1953, Coleman & Appleman 1957, Kamhi 1959, Hamilton & Kerr 1959, Skvortsova *et al.* 1961, Serezhkin *et al.* 1977), indicating that the crystal we studied corresponds to the common state of umohoite.

*Umohoite – iriginite transformation and stability of anion-topologies*

Umohoite is commonly partially replaced by iriginite,  $[(\text{UO}_2)(\text{MoO}_3\text{OH})_2(\text{H}_2\text{O})](\text{H}_2\text{O})$  (Serezhkin *et al.* 1973, Krivovichev & Burns 2000), which also has sheets of polyhedra based upon an anion-topology with pentagons, triangles and squares. However, the iriginite anion-topology is distinct from the uranophane anion-topology (Fig. 4); it contains chains of pentagons and squares that share edges, and zigzag chains of edge-sharing squares and triangles. In the structure of iriginite, each pentagon of the anion topology is populated by a  $\text{UrO}_5$  polyhedron, two-thirds of the squares are populated with  $\text{Mo}^{6+}\text{O}_6$  octahedra that occur as edge-sharing dimers; the triangles, as well as one-third of the squares, are empty.

The sheets of uranyl and molybdate polyhedra in iriginite and umohoite have features in common. Figure

5 shows the local relationships between pentagons and squares in the anion topology, as well as the connectivity diagrams for polygons of the anion topologies drawn following the methods proposed in Krivovichev *et al.* (1997) and Krivovichev (1997). Double and heavy lines represent polygon edges shared between the equivalent and non-equivalent polygons, respectively. The circles at the vertices of the polygons indicate that the vertex is shared between itself and another polygon, without regard to the polygon with which it shares an edge adjacent to the vertex. The unfilled and filled circles are used to indicate that the vertex is shared with the same or a distinct polygon, respectively. Only populated polygons should be taken into account. The connectivity diagrams show similar topological structures for the umohoite and iriginite sheets. However, whereas in umohoite  $\text{UrO}_5$  pentagonal bipyramids share four of their five equatorial edges, in iriginite they share only two. Therefore, the umohoite  $\rightarrow$  iriginite transformation during alteration of U–Mo deposits, corresponding to a change of the U:Mo ratio from 1:1 to 1:2, involves a change of anion topology to one with a smaller number of edges shared between coordination polyhedra.

The expansion of sheet anion-topologies as sequences of stacked chains was introduced by Miller *et al.* (1996) and expanded by Burns (1999a). The uranophane anion-topology that is the basis of the umohoite sheet is shown expanded in Figure 6a. Construction of the anion topology requires the **U** and **D** arrowhead chains as well as the **R** chain, with the chain-stacking sequence **URDRURDR...** The iriginite anion-topology is expanded as chains in Figure 6b. It contains the same chains as the umohoite (uranophane) anion-topology,

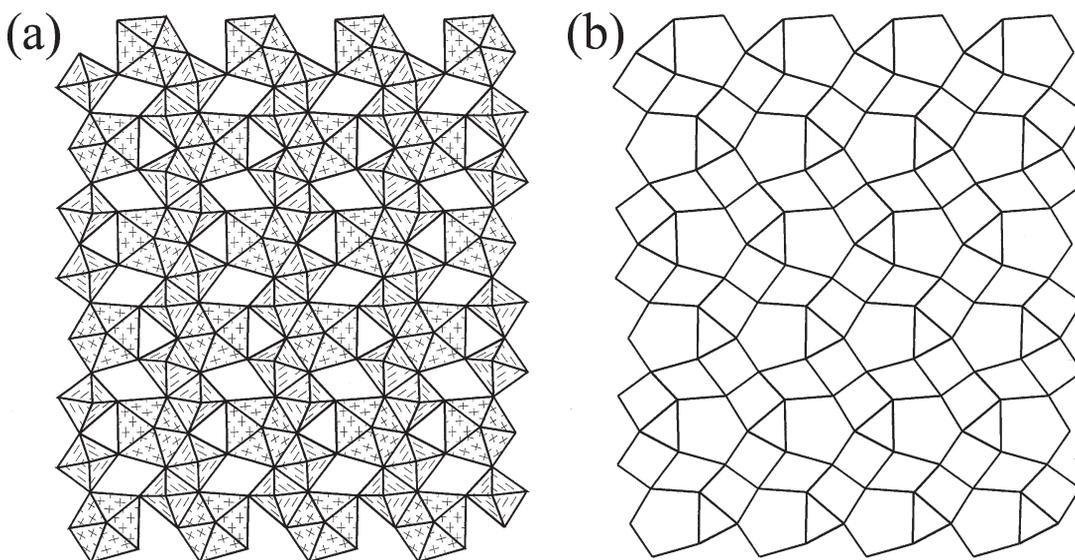


FIG. 4. Uranyl-molybdate sheet in iriginite (a) and iriginite anion-topology (b).

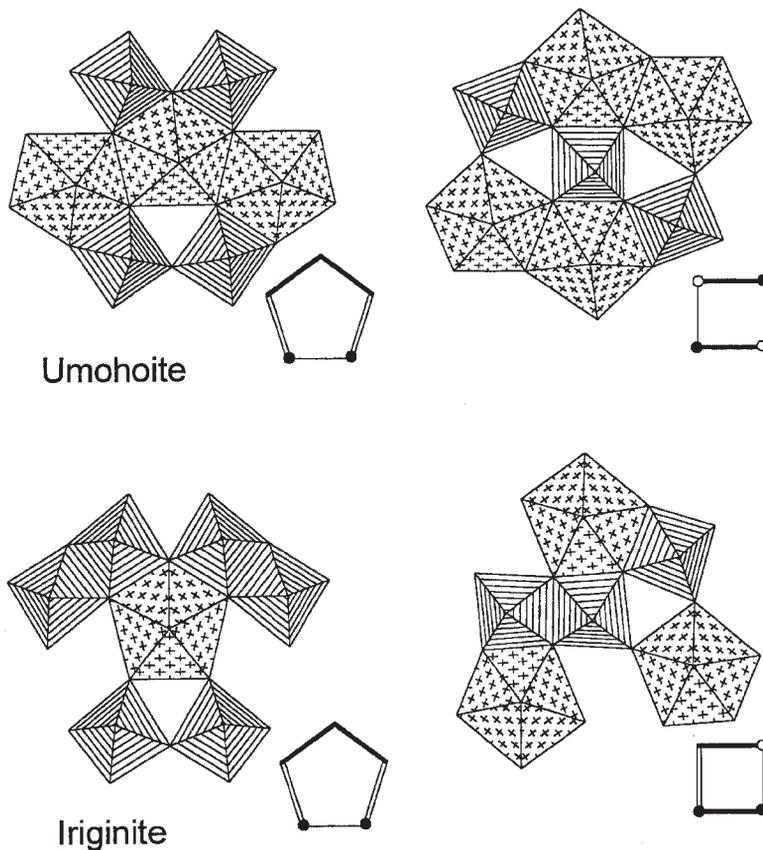


Fig. 5. Relationships between pentagon and squares in U-Mo sheets in umohoite and iriginite and connectivity diagrams for  $(U\phi_7)$  pentagonal bipyramids and  $(Mo\phi_6)$  octahedra in both sheets (see text for details).

but the chain-stacking sequence is **URRRDRRR URRRDRRR...** The ratio of arrowhead (**U** and **D**) chains to **R** chains in the umohoite and iriginite anion-topologies is 1:1 and 1:3, respectively. In the umohoite sheet, all rhombs of the **R** chains are populated with  $Mo^{6+}$  cations, whereas in the iriginite sheet, only two-thirds of the rhombs contain  $Mo^{6+}$ , with the remaining third empty. The result is U:Mo ratios of 1:1 and 1:2 in the umohoite and iriginite sheets, respectively.

Iriginite is commonly observed to have partially replaced umohoite. The iriginite anion-topology may be derived from that of umohoite by expansion of the umohoite anion-topology along a vector within the sheet that is perpendicular to the arrowhead chain, together with the insertion of two additional **R** chains between adjacent arrowhead chains. This transformation mechanism requires addition of  $Mo^{6+}$  to populate the rhombs of the **R** chains. Another mechanism for obtaining the iriginite anion-topology from that of umohoite is the replacement of every second **DRU** sequence in the

umohoite anion-topology with an **R** chain. This mechanism requires the removal of the  $U^{6+}$  that populated the **D** and **U** arrowhead chains. Given the relatively high mobility of  $U^{6+}$  in groundwater, this appears to be the most likely mechanism of the umohoite-to-iriginite transformation.

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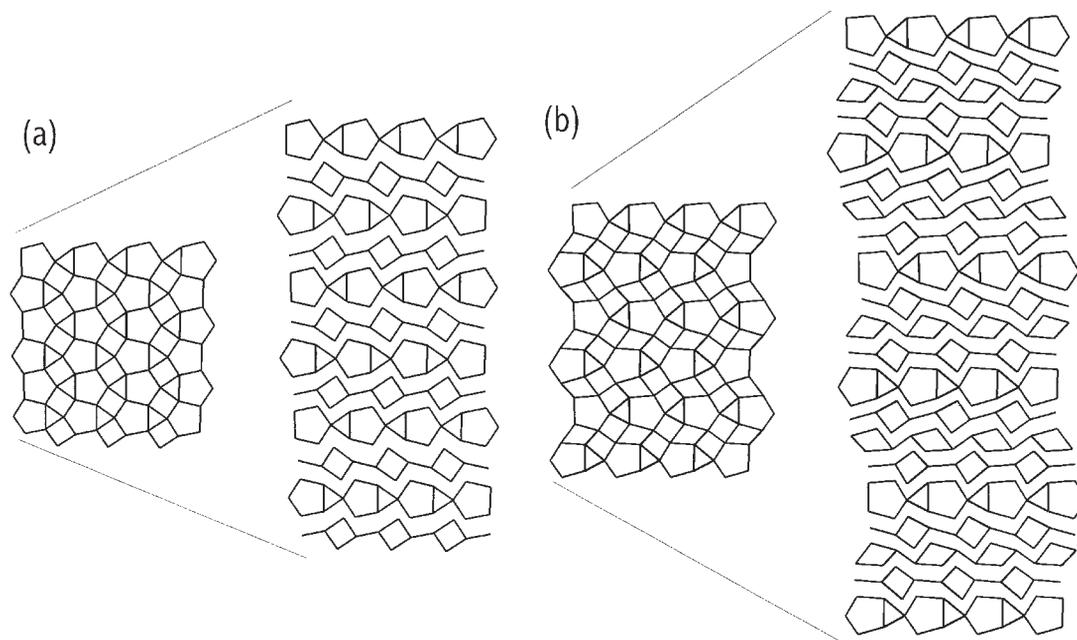


FIG. 6. Expansion of the umohoite (a) and iriginite (b) anion-topologies as chain-stacking sequences.

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