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THE OD (ORDER–DISORDER) STRUCTURE OF HOLFERTITE, A HYDRATED URANYL TITANATE MINERAL FROM SEARLE CANYON, THOMAS RANGE, UTAH, USA

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ABSTRACT

The crystal structure of holfertite, hexagonal, *a* 10.824(2), *b* 10.824(2), *c* 7.549(2) Å, *V* 766.0(9) Å^3, *P*3, *Z* = 3, *D* (calc.) = 4.311 g.cm^{-3}, was solved by direct methods and refined to an R_1 factor of 21.1%, a GoF of 1.02, on the basis of 1127 observed ($F_o > 4\sigma|F|$) unique reflections (Mo*K*α radiation, Bruker CCD Smart diffractometer). Single-crystal diffraction patterns show streaking parallel to the *a* direction, suggesting strong one-dimensional disorder in the structure; the high value of R_1 is due to this OD (Order–Disorder) character, which complicates the refinement of the structure. There are two *U* sites in the crystal structure of holfertite. The *U*(1) site is split into three subsites, *U*(1A), *U*(1B), and *U*(1C), with 75, 15 and 10% occupancy, respectively, and a mean distance of 1.11 Å separating them. Because of splitting of the *U*(1) site, it was not possible to find all O-atoms of the uranyl groups for *U*(1B) and *U*(1C); hence the coordination polyhedra around *U*(1B) and *U*(1C) are not complete. The *U*(1) is [6]-coordinated, with <*U*(1A)–O> = 2.30 Å and average U–O_{ur} (uranyl oxygen) distance of 1.92 Å. The *U*(2) site is 77% occupied, with <*U*(2)–O> = 2.23 Å and average U–O_{ur} distance of 1.77 Å. Taking into account the *U*(1A) and *U*(2) sites with 75 and 77% occupancy, U^{6+} polyhedra share common edges to form a $[UO_4]^{2-}$ chain extending along [001]. There are four [5]-coordinated *Ti* sites. The *Ti*(1) and *Ti*(2) sites are fully occupied, with <*Ti*(1,2)–O> = 1.76 Å, and the *Ti*(3) and *Ti*(4) sites are half-occupied with <*Ti*(3,4)–O> = 1.92 Å. The *Ti*(1) and *Ti*(2) trigonal bipyramids share common vertices to form $[TiO_4]^{4-}$ chains along [001]. The *Ti*(3) and *Ti*(4) trigonal bipyramids also share common vertices along [001], but from the structure refinement, we cannot determine what type of chain they form because of partial occupancy of the cation sites. In the generalized model of the structure, U chains and Ti chains link through common vertices to form a framework with channels along [001]. The channels have a diameter of ~8 Å and occlude eight sites that are partly occupied by Ca atoms and (H_2O) groups, giving the total channel constituents as {$Ca_{0.25}$ $(H_2O)_{3.00}$} *apfu*. In the crystal structure of holfertite, only five of the twenty-eight sites are fully occupied. The OD nature of the structure and the uncertainty concerning the nature of the *Ti*(3)–*Ti*(4) chain result in some ambiguity regarding the chemical composition of holfertite. There are two possibilities for the chemical formula of the crystal of holfertite examined here: (1) $U^{6+}_{1.75}$ Ti $O_{7.5}$ $Ca_{0.25}$ $(H_2O)_3$, and (2) $U^{6+}_{1.75}$ Ti $O_{7.17}$ $(OH)_{0.67}$ $Ca_{0.25}$ $(H_2O)_3$, both with *Z* = 3. As the infrared spectrum is not definitive concerning the presence or absence of (OH) in the structure, we have no evidence to distinguish between these two possible formulae. The short-range coupling of the partial occupancies of many of the sites in holfertite is almost certainly the cause of the OD nature of the structure.

Keywords: holfertite, crystal structure, Searle Canyon, Thomas Range, Utah, USA.

SOMMAIRE

Nous avons résolu la structure cristalline de la holfertite, hexagonale, *a* 10.824(2), *b* 10.824(2), *c* 7.549(2) Å, *V* 766.0(9) Å^3, *P*3, *Z* = 3, *D* (calculée) = 4.311 g.cm^{-3}, par méthodes directes, et nous l'avons affinée jusqu'à un résidu R_1 de 21.1% et un facteur de concordance de 1.02, en utilisant 1127 réflexions uniques observées ($F_o > 4\sigma|F|$; rayonnement Mo*K*α, diffractomètre Bruker CCD Smart). Les spectres de diffraction obtenus sur monocristaux font preuve d'étirement des taches parallèle à la direction *a*, ce qui indique un fort désordre le long d'une direction. La valeur élevée du résidu R_1 est attribuable à ce caractère OD (Ordre–Désordre), qui complique l'affinement de la structure. La structure contient deux sites *U*. Le site *U*(1) est décomposé en trois sous-sites, *U*(1A), *U*(1B), and *U*(1C), avec un taux d'occupation de 75, 15 et 10%, respectivement, et une distance moyenne de 1.11 Å entre elles. A cause de cette présence de sous-sites de *U*(1), nous n'avons pas pu trouver tous les atomes d'oxygène associés aux groupes d'uranyle à *U*(1B) et *U*(1C); c'est donc dire que les polyèdres de coordinence autour de *U*(1B) et *U*(1C) ne sont pas complets. Le site *U*(1) possède une coordinence [6], avec <*U*(1A)–O> = 2.30 Å et, en moyenne, une liaison U–O_{ur}

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(oxygène de l'uranyle) de 1.92 Å. Le site *U*(2) est rempli à 77%, avec <*U*(2)–O> = 2.23 Å et, en moyenne, une distance U–O_{ur} de 1.77 Å. Vus les taux d'occupation de 75 et 77% des sites *U*(1A) et *U*(2), respectivement, les polyèdres de U^{6+} partagent leurs arêtes communes pour former une chaîne $[UO_4]^{2-}$ le long de [001]. Il y a quatre sites *Ti* à coordinence [5]. Les sites *Ti*(1) et *Ti*(2) sont remplis, avec <*Ti*(1,2)–O> = 1.76 Å, et les sites *Ti*(3) et *Ti*(4) sont à moitié remplis, avec <*Ti*(3,4)–O> = 1.92 Å. Les pyramides trigonales *Ti*(1) et *Ti*(2) partagent leurs coins communs pour former des chaînes $[TiO_4]^{4-}$ le long de [001]. Les pyramides trigonales *Ti*(3) et *Ti*(4) partagent aussi leurs coins communs le long de [001], mais à partir des résultats de l'affinement, nous ne pouvons pas déterminer de quelle sorte de chaîne il s'agit à cause de l'occupation partielle des sites des cations. D'après le modèle généralisé de la structure, les chaînes U et les chaînes Ti sont liées grâce à leurs coins communs pour former une trame ayant des canaux le long de [001]. Les canaux ont un diamètre d'environ 8 Å et renferment huit sites à occupation partielle, où logent les atomes de Ca et les groupes (H_2O), ce qui donne en tout $\{Ca_{0.25}(H_2O)_{3.00}\}$. Dans la structure de la holfertite, seulement cinq des 28 sites sont remplis. La nature OD de la structure et l'incertitude concernant la nature de la chaîne *Ti*(3)–*Ti*(4) mènent à une certaine ambiguïté à propos de la composition chimique de cette espèce. Il y a deux possibilités pour le cristal que nous avons examiné: (1) $U^{6+}_{1.75}$ Ti $O_{7.5}$ $Ca_{0.25}$ $(H_2O)_3$, et (2) $U^{6+}_{1.75}$ Ti $O_{7.17}$ $(OH)_{0.67}$ $Ca_{0.25}$ $(H_2O)_3$, les deux ayant $Z = 3$. Le spectre d'aborption infrarouge n'offrant aucune indication définitive à propos de la présence ou l'absence de (OH) dans la structure, nous ne pouvons choisir entre ces deux possibilités. Le couplage des occupations partielles à courte échelle impliquant plusieurs sites est presque certainement la cause de la nature OD de la structure.

(Traduit par la Rédaction)

Mots-clés: holfertite, structure cristalline, Searle Canyon, Thomas Range, Utah, USA.

Introduction

Holfertite was described as a new mineral species found on hematite and topaz crystals in cavities and fractures in rhyolite from Searle Canyon, Thomas Range, Utah, USA (Belakovskiy *et al*. 2006). Previously, its occurrence was discussed by Foord *et al*. (1995), Holfert *et al*. (1996) and Belakovskiy & Pautov (2002). It is of pneumatolitic origin and occurs in association with hematite, pseudobrookite, bixbyite, niobian rutile, topaz, beryl, cerianite, thorianite, quartz, orthoclase, zircon and fluorite. Holfertite forms elongate (usually hollow) prismatic crystals up to 3 × 0.3 × 0.3 mm (Fig. 1). Here, we report a general model for its crystal structure.

Chemical Composition

A chemical analysis of holfertite (Table 1) was done with a JEOL JCXA–50A electron microprobe with an energy-dispersion spectrometer and three wavelength-dispersion spectrometers operating at 20 kV and 20 nA. The following standards and crystals were used: Ca: diopside USNM 117733; U: synthetic UO_2; Ti, Fe: ilmenite USNM 96189; K: microcline USNM 143966. Data were reduced using the $\phi(\rho Z)$ procedure of Pouchou & Pichoir (1985). Infrared spectra show the presence of uranyl groups and evidence of (H_2O) (Belakovskiy *et al*. 2006). The chemical composition and unit formulae (Table 1) for the two compositions were calculated on the basis of (1) 10.5 O-atoms with (OH) = 0 and (H_2O) = 3 *pfu*, and (2) 10.84 O-atoms with (OH) = 0.67 and (H_2O) = 3 *pfu*. The first calculation corresponds to the formula $U^{6+}_{1.75}$ Ti $O_{7.5}$ $Ca_{0.25}$ $(H_2O)_3$, and the second calculation corresponds to the formula $U^{6+}_{1.75}$ Ti $O_{7.17}$ $(OH)_{0.67}$ $Ca_{0.25}$ $(H_2O)_3$ (see text below for further details).

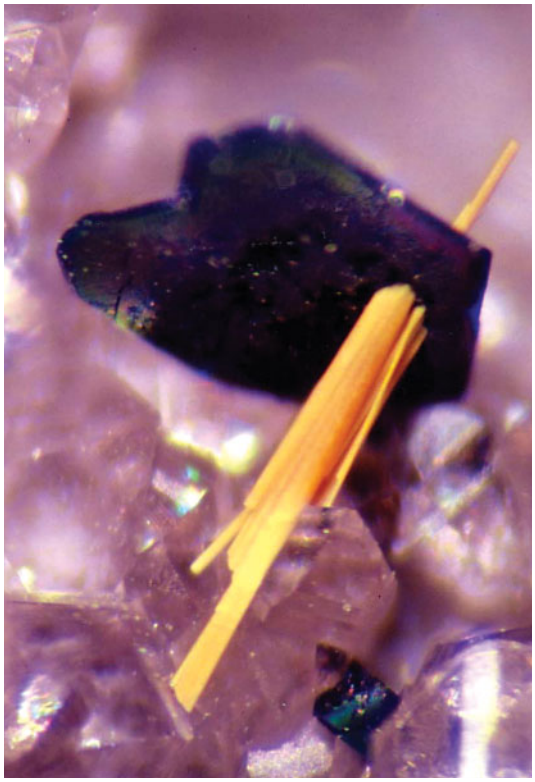

FIG. 1. A bundle of yellow crystals of holfertite piercing a crystal of hematite (photograph by Patrick Haynes).

Single-Crystal X-Ray Diffraction

Holfertite is a very difficult material to work with. The best crystal chosen from available samples and used for single-crystal X-ray data collection is characterized by a very specific type of anomalous diffraction. Figure 2 shows diffraction photographs for the single crystal before data collection. A precession photograph taken down the *a** axis (Fig. 2a) shows a strong pseudotranslation $c' = c/2$; lines of reasonably sharp spots (l even) alternate with streaks (l odd). A Laue photograph (Fig. 2b) also shows sharp spots and diffuse streaks, which indicates that holfertite is an OD (Order–Disorder) structure (Merlino 1997).

Crystals of holfertite are generally hollow, and consist of hexagonal "tubes". The crystal used for intensity-data collection was cut from one sector of the hollow crystal. This fragment was mounted on a Bruker *P*4 automated four-circle diffractometer equipped with graphite-filtered Mo*K*α X-radiation and a Bruker 1K CCD detector. The intensities of 7895 reflections with $-15 < h < 15$, $-15 < k < 15$, $-8 < l < 8$ were collected to 59.92°2θ using 60 s per 0.3° frame, and an empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters (Table 2) were obtained from 1183 reflections with $I > 10\sigma I$.

Structure solution and refinement

On the basis of 1127 unique observed reflections, the crystal structure of holfertite was solved by direct methods and refined with the Bruker SHELXTL Version 5.1 system of programs (Sheldrick 1997) to $R_1 = 21.1\%$ and a GoF of 1.024, space group *P*3. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). *R* indices are of the form given in Table 2, and are expressed as percentages. Site occupancies for the *U*(1A–C), *U*(2) and *Ti*(1–4) sites were refined with the scattering curves of U and Ti. The metal sites are not fully occupied, and we have no information on the short-range occupancy of these sites. Because of splitting of the *U*(1) site into three subsites, *U*(1A), *U*(1B) and *U*(1C), it was not possible to find all O-atoms of the uranyl groups for *U*(1B) and *U*(1C). However, it was possible to find oxygen atoms coordinating the *Ti*(1), *Ti*(2), *Ti*(3) and *Ti*(4) sites. Coordinates of the O-atoms were taken from difference-Fourier maps and refined with fixed displacement-parameters. After completing the cation–anion framework, the channel atoms, mainly O atoms of (H_2O), were found in the difference-Fourier maps, and included in the refinement with fixed positional and displacement parameters. Possible twinned models were investigated, but none led to an improvement in the refined model. As discussed below, various modifications to the structure model were made during interpretation of the local stereochemistry and the chemical formula. In particular, the occupancies of the uranyl anions were constrained to be the same as the occupancies of the U sites with

TABLE 1. CHEMICAL COMPOSITION* (wt.%) AND UNIT FORMULA (*apfu*) OF HOLFERTITE

	1**	2**		1	2
CaO	3.01	2.29	Ca	0.34	0.27
UO_3	75.97	76.03	U^{6+}	1.68	1.74
TiO_2	13.02	11.89	Ti	1.03	0.97
Fe_2O_3	0.47	0.44	Fe^{3+}	0.04	0.04
K_2O	0.31	0.30	K	0.04	0.04
$H_2O(1)^{+}$	8.56	8.27	(OH)1	–	–
			$(H_2O)1$	3	3
Total	101.34	99.22	O1	7.5	7.5
$H_2O(2)^{++}$	9.51	9.19	(OH)2	0.67	0.67
			$(H_2O)2$	3	3
Total	102.29	100.14	O2	7.17	7.17

* Na_2O, MgO, BaO, Y_2O_3, Ce_2O_3, Nd_2O_3, Eu_2O_3, Tb_2O_3, Ho_2O_3, Tm_2O_3, Lu_2O_3, La_2O_3, Pr_2O_3, Sm_2O_3, Gd_2O_3, Dy_2O_3, Er_2o_3, Yb_2O_3, Ta_2O_5 not detected.
** Mean of 14 and 10 points, respectively.
\+ Calculated for (OH) = 0 and (H_2O) = 3 *pfu*.
\++ Calculated for (OH) = 0.67 and (H_2O) = 3 *pfu*.

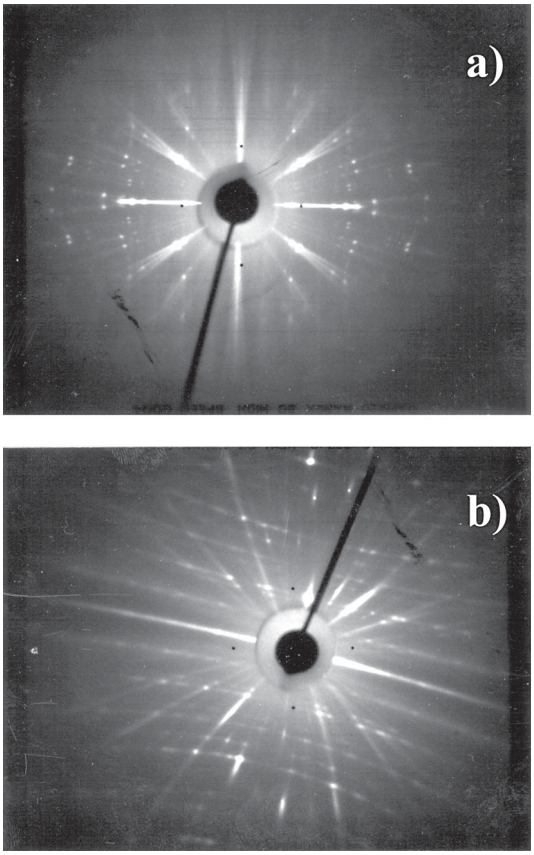

FIG. 2. X-ray photographs of the single crystal of holfertite used for data collection: (a) precession photograph down the *a* axis, 40-minute exposure, (b) Laue photograph, one-hour exposure.

which they are associated. The fact that U^{6+} and Ca sum to 2 atoms per formula unit (*apfu*) *suggests* that Ca is replacing U^{6+} [or rather $\{U^{6+}O_2\}^{2+}$]. However, attempts to put Ca at the *U*(2) site were (slightly) less favorable than assigning Ca to a channel site in terms of the refined model. Thus we assign Ca to a channel site, while recognizing that the diffraction data support this assignment only weakly over an assignment with Ca at the *U*(2) site.

At the final stages of the refinement, it was not possible to refine all positional and displacement parameters of the framework (as the refinement diverged). In order to obtain (minimum) estimates of the standard deviations on bond lengths, the displacement parameters of all framework atoms except Ti were fixed, and all positional parameters were allowed to vary to convergence. We emphasize that such high *R* indices as were obtained are typical of OD structures, as not all of the diffracted intensity can be accounted for by a long-range-ordered model. Atom positions, displacement parameters and site occupancies for holfertite are given in Table 3, and selected interatomic distances are given in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Description of the Structure

Cation sites

In the crystal structure of holfertite, there are 28 sites. Of these, 20 sites constitute the U–Ti–O framework, but only five of them are fully occupied. There are eight channel sites, all partly occupied.

There are two *U* sites in the crystal structure of holfertite. The *U*(1) site is split into three subsites, *U*(1A), *U*(1B), and *U*(1C), with 75, 15 and 10% occu-

TABLE 2. MISCELLANEOUS INFORMATION FOR HOLFERTITE

a (Å)	10.824(2)	Crystal size (mm)	0.05 × 0.05 × 0.32
c	7.549(2)	Radiation	Mo*Kα*
V (Å^3)	766.0(9)	Maximum 2θ (°)	59.92
Space group	*P*3	*R*(int) (%)	28.4
Z	3	Total no. of reflections	7895
D_{calc} (g.cm^{-3})	4.288	Unique reflections	2842
Absorption coefficient (mm^{-1})	28.9	$F_o > 4\sigma F$	1127
F(000)	849.4		
Method of refinement		Full-matrix least-squares on F^2, fixed weights proportional to 1/σ (F^2)	
Goodness of fit on F^2	0.996	Final *R*, index (%) [$F_o > 4\sigma F$]	21.0
		R, index (%) (all data)	35.5
		wR_2 (%)	56

TABLE 3. ATOM POSITIONS AND ANISOTROPIC-DISPLACEMENT FACTORS FOR HOLFERTITE

	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
U(1A)	0.75	0.4559(5)	0.4504(3)	0.0724(6)	0.141(4)	0.058(2)	0.0000(8)	0.0038(11)	0.0029(12)	–0.033(2)	0.1033(19)
U(1B)	0.15	0.536(3)	0.595(3)	0.072(2)	0.167(16)	0.22(2)	0.02702	–0.028(10)	–0.047(9)	0.141(16)	0.117(9)
U(1C)	0.10	0.559(2)	0.512(2)	0.079(4)	0.005(7)	0.017(10)	0.13(2)	0.019(11)	0.013(11)	–0.035(7)	0.068(9)
U(2)	0.77	0.4869(7)	0.4936(5)	0.5703(6)	0.162(5)	0.128(5)	0.0000(11)	–0.006(2)	–0.0006(17)	0.003(4)	0.127(3)
Ti(1)	1.0	2/3	1/3	–0.1810(17)	0.098(9)	0.098(9)	0.000(5)	0	0	0.049(5)	0.066(6)
Ti(2)	1.0	2/3	1/3	0.3233(16)	0.081(8)	0.081(8)	0.000(5)	0	0	0.040(4)	0.054(5)
Ti(3)	0.5	1/3	2/3	0.320(2)	0.022(8)	0.022(8)	0.000(8)	0	0	0.011(4)	0.015(5)
Ti(4)	0.5	1/3	2/3	0.826(3)	0.035(9)	0.035(9)	0.000(8)	0	0	0.017(5)	0.023(6)
O(1)	1.0	0.829(5)	0.461(5)	0.341(7)	0.09						
O(2)	1.0	0.526(5)	0.361(5)	0.798(7)	0.09						
O(3)	0.5	0.353(6)	0.507(6)	0.815(8)	0.03						
O(4)	0.5	0.153(4)	0.652(4)	0.299(5)	0.01						
O(5)(OH)	0.33	0.263(8)	0.631(12)	0.580(15)	0.05						
O(6)	0.75	0.629(5)	0.5615(4)	0.574(5)	0.04						
O(7)	0.33	0.648(12)	0.373(11)	0.066(14)	0.05						
O(8)	0.75	0.300(7)	0.268(8)	0.582(13)	0.11						
O(9)(OH)	0.33	0.270(10)	0.571(11)	0.081(15)	0.05						
O(10)	1.0	0.331(10)	0.230(8)	0.062(14)	0.18						
O(11)	1.0	2/3	1/3	0.572(13)	0.10						
O(12)	1.0	0.615(16)	0.615(18)	0.069(2)	0.02						
Ca	0.25	0.073	0.127	0.560							
O(13)(H_2O)	0.5	0.151	0.874	0.786							
O(14)(H_2O)	0.5	0	0	0.478							
O(15)(H_2O)	0.5	0.737	0.879	0.067							
O(16)(H_2O)	0.5	0.996	0.061	0.062							
O(17)(H_2O)	0.5	0.080	0.845	0.169							
O(18)(H_2O)	0.5	0.127	0.084	0.558							
O(19)(H_2O)	0.33	0.115	0.129	0.067							

pancy and a mean distance of 1.11 Å between them (Tables 3, 4). Because of splitting of the *U*(1) site, it was not possible to find all O-atoms of the uranyl groups for *U*(1B) and *U*(1C); hence the coordination polyhedra around *U*(1B) and *U*(1C) are not complete. Thus we leave the occupancies of the uranyl O-atoms O(10) and O(12) at 1.0 in order to "count" the uranyl O-atoms for the *U*(1B) and *U*(1C) sites. The *U*(1*A*) atom is [6]-coordinated, with <*U*(1A)–O> = 2.30 Å and an average U–O distance for the uranyl group [O(10) and O(12)] of 1.92 Å. The *U*(2) site is 77% occupied, with <*U*(2)–O> = 2.23 Å and an average U–O distance for the uranyl group [O(6) and O(8)] of 1.77 Å. For both the *U*(1a) and *U*(2) sites, two O-sites, O(3) and O(4), are 50% occupied. In total, the *U*(1A–C) and *U*(2) sites give 1.77 *apfu*.

There are four [5]-coordinated *Ti* sites. Each site is of the form (⅓ ⅔ *z*), has point symmetry 3, and is coordinated by five anions arranged at the corners of a trigonal bipyramid. The *Ti*(1) and *Ti*(2) sites are fully occupied, with <*Ti*(1,2)–O> = 1.76 Å, and one of the five coordinating anions, O(7), in each polyhedron is positionally disordered into three equally occupied sites. All coordinating anions are O-atoms. In particular, the O(7) and O(11) anions that bridge along the *Ti*(1)–*Ti*(2) chain have bond-valence sums of 1.93 and 1.70 *vu* (plus possible contributions from hydrogen bonds), and hence O(7) and O(11) are O-atoms. The *Ti*(3) and *Ti*(4) sites are half occupied with <*Ti*(3,4)–O,OH> = 1.92 Å, and two of five O-atoms, O(5) and O(9), are statistically disordered. The O(5) and O(9) anions bridge along the *Ti*(3)–*Ti*(4) chains. The distribution of occupied and vacant sites along this chain affects the identity of the bridging anions: O atoms or (OH) groups; this issue will be examined in more detail below.

There are eight partly occupied sites (occupancies in the range 0.25–0.50) that do not belong to the U–Ti–O framework. These sites are occupied by Ca and (H_2O) groups, with short distances between them: 0.86–1.47 Å (Table 3). The O(14–18) sites are O atoms of (H_2O) groups. Only one O-atom site, O(14), is in a special position, (0 0 *z*); the other O sites are at general positions. For the channels, site-occupancy refinement gave a total of {$Ca_{0.25}$ (H_2O)$_{3.00}$} *apfu*.

TABLE 4. INTERATOMIC DISTANCES (Å) IN HOLFERTITE

U(1A)–*U*(1B)	1.36(3)		
U(1A)–*U*(1C)	0.97(2)		
U(1B)–*U*(1C)	1.04(2)		
U(1A)–O(1)	2.55(5)	*U*(2)–O(1)	2.43(5)
U(1A)–O(2)	2.55(5)	*U*(2)–O(2)	2.41(5)
U(1A)–O(3)	2.46(6)	*U*(2)–O(3)	2.40(6)
U(1A)–O(4)	2.28(4)	*U*(2)–O(4)	2.57(4)
U(1A)–O(10)	2.07(8)	*U*(2)–O(6)	1.33(4)
U(1A)–O(12)	1.75(17)	*U*(2)–O(8)	2.26(7)
<*U*(1A)–O>	2.28	<*U*(2)–O>	2.23
Ti(1)–O(2) × 3	1.70(5)	*Ti*(2)–O(1) × 3	1.61(4)
Ti(1)–O(7)* × 3	1.94(11)	*Ti*(2)–O(7)* × 3	2.02(11)
Ti(1)–O(11)	1.86(11)	*Ti*(2)–O(11)	1.88(11)
<*Ti*(1)–O>	1.78	<*Ti*(2)–O>	1.75
Ti(3)–O(4) × 3	1.89(4)	*Ti*(4)–O(3) × 3	1.85(7)
Ti(3)–O(5)* × 3	2.07(11)	*Ti*(4)–O(5)* × 3	1.97(11)
Ti(3)–O(9)* × 3	2.02(11)	*Ti*(4)–O(9)* × 3	2.13(11)
<*Ti*(3)–O>	1.95	<*Ti*(4)–O>	1.93
O(5)–O(5)c	1.14(14)		
O(7)–O(7)a	0.96(18)		
O(9)–O(9)c	1.58(17)		

a: –*y* + 1, *x*–*y*, *z*; b: –*x* + *y* + 1, –*x* + 1, *z*; c: –*x* + *y*, –*x* + 1, *z*; d: –*y* + 1, *x*–*y* + 1, *z*.
* as O(5), O(7), O(9) sites are party occupied by O atoms, only one atom out of three contributes to the coordination of Ti.

Structure topology

Taking into account the *U*(1A) and *U*(2) sites with 75 and 77% occupancy, respectively, U^{6+} polyhedra share common edges [O(1)–O(2) and O(3)–O(4)] to form a $[UO_4]^{2-}$ chain along [001], and the O atoms of the uranyl groups are exposed on the outside of the chain (Figs. 3a, b). The *Ti*(1) and *Ti*(2) trigonal bipyramids share common vertices to form [Ti_2O_8] chains along [001]. The *Ti*(3) and *Ti*(4) trigonal bipyramids also share common vertices along [001], but as the *Ti*(3) and *Ti*(4) sites are only half-occupied, there are various possibilities as to the constitution of this chain: (1) adjacent *Ti*(3) and *Ti*(4) sites are occupied to form continuous chains that have an occupancy of the chain arrangement of 0.50; (2) adjacent *Ti*(3) and *Ti*(4) sites only have one site occupied to produce a Ti–□–Ti– arrangement that has an occupancy of the chain arrangement of 1.00. For possibility (1), the linking anions O(5) and O(9) have incident bond-valence sums of 1.65 and 1.39 *vu*, and must be O(5) = O^{2-} and O(9) = O^{2-} or $(OH)^-$, and the chains have the form [Ti_2O_8] or [Ti_2O_7(OH)]. For possibility (2), the anions O(5) and O(9) have incident bond-valence sums of 1.11 and 1.03, and 1.00 and 0.86 *vu* for the *Ti*(3) and *Ti*(4) polyhedra, respectively, and hence O(5) and O(9) are (OH) anions. The corresponding chain is thus of the form [Ti O_3(OH)$_2$].

Each [U–O] chain links through common vertices with two adjacent [Ti–O,OH] chains (Fig. 3a). Each [Ti–O,OH] chain links through common vertices to three adjacent [U–O] chains (Fig. 3b). These three types of chain form a mixed [U–Ti–O] framework with channels along [001] (Fig. 4). The channels have a diameter of ~8 Å and occlude eight sites that are partly occupied by Ca atoms and (H_2O) groups.

Chemical Formula

A derivation of the chemical formula of holfertite is complicated by the OD nature of the structure, particularly because the extensive disorder makes it difficult to refine the structure without any crystal-chemical constraints on site occupancies. First, we will set the total amount of U in the unit formula to 1.75 *apfu* (not significantly different from the refined value of 1.77 *apfu*).

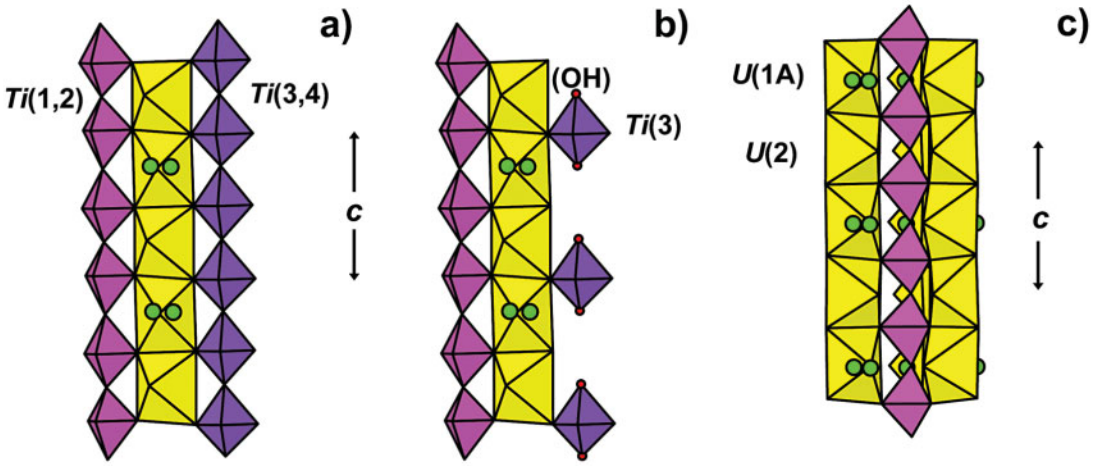

FIG. 3. Fragments of the crystal structure showing linkage of U and Ti chains: (a) linkage of a U chain to two adjacent chains of [5]-coordinated Ti polyhedra; (b) linkage of a U chain to an adjacent chain of *Ti*(1,2) polyhedra and isolated *Ti*(3) polyhedra; (c) linkage of a chain of *Ti*(1,2) polyhedra to three adjacent U-bearing chains. U octahedra are yellow, [5]-coordinated *Ti*(1,2) and *Ti*(3,4) polyhedra are pink and purple, *U*(1B) and *U*(1C) sites are shown as green circles.

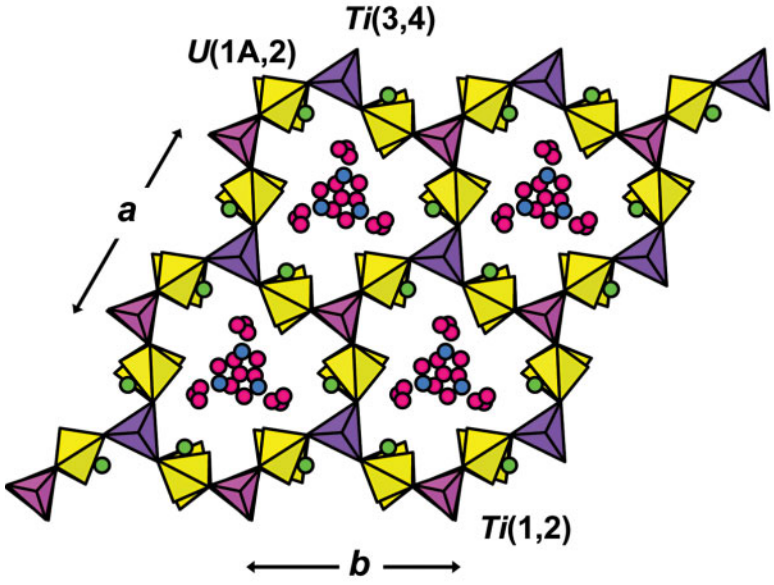

FIG. 4. The crystal structure of holfertite projected onto the (001) plane. Legend as in Figure 3. Ca and H_2O sites in the channels of the structure are shown as blue and red circles, respectively.

Let us now consider the formula by summing the different structural motifs that have been identified in the crystal structure: (1) the uranyl ion: $(U^{6+}O_2)_{1.75}$, (2) the continuous chain of *Ti*(1) and *Ti*(2) polyhedra, $[Ti_2O_8]$, plus the chain of half-occupied *Ti*(3) and *Ti*(4) sites, and (3) the interstitial $Ca_{0.25}(H_2O)_3$ species. Inspection of Figure 4 shows that the proportion of U chains to Ti chains to interstitial species is 3 : 2 : 3; summing the units (1) to (3) in the proportions indicated above should thus give the unit formula. This process is complicated by the fact that we do not know the detailed bond-topology of the *Ti*(3)–*Ti*(4) chain. However, we do have three possible stoichiometries for this chain (see above): (i) $[Ti_2O_8]$, (ii) $[Ti_2O_7(OH)]$, and (iii) $[Ti\ O_3(OH)_2]$. Arrangements (i) and (ii) have chain occupancies of 0.5, and arrangement (iii) has a chain occupancy of 1.0 (*i.e.*, the total amount of Ti in the chain has to be one atom per two polyhedra). Thus we may sum our motifs (1), (2) and (3) in the relevant proportions using the three possibilities (i), (ii) and (iii) for the *Ti*(3)–*Ti*(4) component of motif (2). In possibility [1], *Ti*(3)–*Ti*(4) corresponds to $[Ti_2O_8]$: summing the motifs in the proportion 3 : 2 : 3 gives $\{(U^{6+}O_2)_{1.75}\}_3\ \{[Ti_2O_8]\ [Ti_2O_8]_{0.5}\}\ \{Ca_{0.25}(H_2O)_3\}_3$, which reduces to $U^{6+}_{1.75}\ Ti\ O_{7.5}\ Ca_{0.25}\ (H_2O)_3$ with $Z = 3$, a formula that is electronically neutral. In possibility [2], *Ti*(3)–*Ti*(4) corresponds to $[Ti_2O_7(OH)]$: summing the motifs in the proportion 3 : 2 : 3 gives $\{(U^{6+}O_2)_{1.75}\}_3\ \{[Ti_2O_8]\ [Ti_2O_7(OH)]_{0.5}\}\ \{Ca_{0.25}(H_2O)_3\}_3$, which reduces to $U^{6+}_{1.75}\ Ti\ O_{7.33}\ (OH)_{0.17}\ Ca_{0.25}\ (H_2O)_3$ with $Z = 3$, a formula that is not electronically neutral and hence cannot occur. Thus we may discard this model, and with it the possibility that O(5) = O^{2-} and O(9) = (OH). In possibility [3], *Ti*(3)–*Ti*(4) corresponds to $[Ti\square O_3(OH)_2]$: summing the motifs in the proportion 3 : 2 : 3 gives $\{(U^{6+}O_2)_{1.75}\}_3\ \{[Ti_2O_8]\ [Ti\ O_3(OH)_2]\}\ \{Ca_{0.25}(H_2O)_3\}_3$, which reduces to $U^{6+}_{1.75}\ Ti\ O_{7.17}\ (OH)_{0.67}\ Ca_{0.25}\ (H_2O)_3$ with $Z = 3$, a formula that is electronically neutral. Thus we have two possibilities for the chemical formula of the crystal of holfertite examined here: (1) $U^{6+}_{1.75}\ Ti\ O_{7.5}\ Ca_{0.25}\ (H_2O)_3$, and (2) $U^{6+}_{1.75}\ Ti\ O_{7.17}\ (OH)_{0.67}\ Ca_{0.25}\ (H_2O)_3$, both with $Z = 3$. The key issue here is whether or not holfertite contains significant (OH). The infrared spectrum (Belakovsky *et al*. 2006) is rather ambiguous in this regard. There is a very strong broad band centered on 3390 cm^{-1} and a strong sharper band at 1621 cm^{-1}, both attributable to (H_2O). The broad band centered on 3390 cm^{-1} has a broad subsidiary band at 3240 cm^{-1}. It is not clear if this band is due to disordered (OH), the disorder accounting for the unusual breadth of a band attributed to (OH), or another (H_2O) band. Thus we have no evidence to distinguish between these two possible formulae for holfertite.

Writing the formula as $(U^{6+}O_2)_{1.75}\ Ti^{4+}\ O_4\ Ca_{0.25}\ (H_2O)_3$ or $(U^{6+}O_2)_{1.75}\ Ti^{4+}\ O_{3.67}\ (OH)_{0.67}\ Ca_{0.25}\ (H_2O)_3$ suggests that Ca may be substituting for $(U^{6+}O_2)$, although not necessarily at the same site in the structure. In turn, this suggests end-member formulae of $(U^{6+}O_2)_2\ Ti^{4+}\ O_4\ (H_2O)_3$ for $Z = 3$, or $(U^{6+}O_2)_2\ Ti^{4+}\ O_{3.67}\ (OH)_{0.67}\ (H_2O)_3$ for $Z = 3$ and $(U^{6+}O_2)_6\ Ti^{4+}{}_3\ O_{11}\ (OH)_2\ (H_2O)_3$ for $Z = 1$. As end members, these formulae are not compatible with the observed cell of holfertite, as they involve partly occupied sites, suggesting in turn that the observed OD structure involves a compromise involving the chemical composition, symmetry and unit-cell characteristics of the material.

The OD Nature of the Structure

The streaking parallel to the *a* axis that is present in precession and Laue photographs of holfertite (Fig. 2) strongly indicates that there is one-dimensional disorder parallel to the chain direction in this structure. Such one-dimensional OD nature is not common in structures, but has been observed in sideronatrite, $Na_2\ [Fe^{3+}\ (OH)\ (SO_4)_2]\ (H_2O)_3$ (Scordari 1981), and metasideronatrite, $Na_4\ [Fe^{3+}{}_2\ (OH)_2\ (SO_4)_4]\ (H_2O)_3$ (Scordari *et al*. 1982). What is the origin of this disorder? One very unusual characteristic of holfertite is its chemical composition. The *Ti*(3)–*Ti*(4) chain is either (1) only half occupied by a continuous Ti–Ti–Ti–Ti chain, or (2) is completely occupied by a Ti–□–Ti–□ chain. In the first case, Ti–Ti–Ti–Ti chains, chain fragments and strings of vacancies will be disordered, and in the second case, Ti–□–Ti–□ chains may show disorder through the occurrence of adjacent Ti atoms or adjacent vacancies. Thus the chemical composition of holfertite seems disposed to allow such chain disorder as is observed.

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