

**THE CRYSTAL STRUCTURE OF GOLDQUARRYITE,  
(Cu<sup>2+</sup>,□)(Cd,Ca)<sub>2</sub>Al<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>F<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>{(H<sub>2</sub>O),F}<sub>2</sub>, A SECONDARY PHOSPHATE  
FROM THE GOLD QUARRY MINE, EUREKA COUNTY, NEVADA, U.S.A.**

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ABSTRACT

The crystal structure of goldquarryite, (Cu<sub>0.70</sub>□<sub>0.30</sub>)(Cd<sub>1.67</sub>Ca<sub>0.33</sub>)Al<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>F<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>{(H<sub>2</sub>O),F}<sub>2</sub>, triclinic,  $P\bar{1}$ ,  $a$  6.787(1),  $b$  9.082(2),  $c$  10.113(2) Å,  $\alpha$  101.40(1),  $\beta$  104.27(1),  $\gamma$  102.51(1)°,  $V$  568.7(3) Å<sup>3</sup>,  $Z = 1$ , was solved by direct methods and refined to an  $R$  index of 5.2% based on 1630 observed reflections collected on a four-circle diffractometer equipped with a 1K CCD detector and MoK $\alpha$  X-radiation. The structure contains two crystallographically distinct (PO<sub>4</sub>) groups, three distinct {Al(1)O<sub>4</sub>F<sub>2</sub>}, {Al(2)O<sub>4</sub>F<sub>2</sub>} and {Al(3)O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>} octahedra, one {CdO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} octahedron and one {CuO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>} octahedron where Cu = (Cu<sup>2+</sup><sub>0.70</sub> + □<sub>0.30</sub>). The {Al(1)O<sub>4</sub>F<sub>2</sub>} and {Al(2)O<sub>4</sub>F<sub>2</sub>} octahedra share corners through common F vertices to form an [Al $\phi$ <sub>5</sub>] chain ( $\phi$ : unspecified anion) that extends along the  $a$  direction. This chain is decorated by (PO<sub>4</sub>) tetrahedra that link to the four O atoms of each (Al $\phi$ <sub>6</sub>) octahedron, linking the [Al $\phi$ <sub>5</sub>] chain along its length to form an [Al(PO<sub>4</sub>)<sub>2</sub>F] chain. {CdO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} octahedra share edges to form a [CdO<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] chain that also extends along  $a$ . These two types of chains link through the (PO<sub>4</sub>) tetrahedra to form a sheet of composition [AlCd(PO<sub>4</sub>)<sub>2</sub>F(H<sub>2</sub>O)<sub>2</sub>], which we designate as the  $A$  layer, in the (001) plane. The Al(3) and Cu sites are intercalated between the  $A$  layers, forming {CuO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>} and {Al(3)O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>} octahedra that are isolated from each other. These two octahedra form an open layer, the  $B$  layer, in which both octahedra form linear arrays extending in the  $a$  direction. The  $B$  layer links to the  $A$  layer by sharing octahedron corners with (PO<sub>4</sub>) tetrahedra. The  $A$  and  $B$  layers alternate along the  $c$  axis to form a heteropolyhedral framework. There are interstitial channels within this framework, also extending along  $a$ , and these are filled with the H atoms of the (H<sub>2</sub>O) groups that coordinate the cations of the  $B$  layer.

**Keywords:** goldquarryite, phosphate, crystal structure, Gold Quarry mine, Eureka County, Nevada.

SOMMAIRE

Nous avons résolu la structure cristalline de la goldquarryite, (Cu<sub>0.70</sub>□<sub>0.30</sub>)(Cd<sub>1.67</sub>Ca<sub>0.33</sub>)Al<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>F<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>{(H<sub>2</sub>O),F}<sub>2</sub>, triclinique,  $P\bar{1}$ ,  $a$  6.787(1),  $b$  9.082(2),  $c$  10.113(2) Å,  $\alpha$  101.40(1),  $\beta$  104.27(1),  $\gamma$  102.51(1)°,  $V$  568.7(3) Å<sup>3</sup>,  $Z = 1$ , par méthodes directes, et nous l'avons affinée jusqu'à un résidu  $R$  de 5.2% en utilisant 1630 réflexions observées avec un diffractomètre à quatre cercles muni d'un détecteur 1K de type CCD (rayonnement MoK $\alpha$ ). La structure contient deux groupes (PO<sub>4</sub>) cristallographiquement distincts, trois octaèdres distincts, {Al(1)O<sub>4</sub>F<sub>2</sub>}, {Al(2)O<sub>4</sub>F<sub>2</sub>} et {Al(3)O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>}, un octaèdre {CdO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} et un octaèdre {CuO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>} dans lequel le Cu est en fait (Cu<sup>2+</sup><sub>0.70</sub> + □<sub>0.30</sub>). Les octaèdres {Al(1)O<sub>4</sub>F<sub>2</sub>} et {Al(2)O<sub>4</sub>F<sub>2</sub>} partagent des coins où est situé l'anion F pour former une chaîne [Al $\phi$ <sub>5</sub>] ( $\phi$ : anion non spécifié) dans la direction  $a$ . Cette chaîne est décorée par des tétraèdres (PO<sub>4</sub>) en liaison avec les quatre atomes d'oxygène de chaque octaèdre (Al $\phi$ <sub>6</sub>), et les chaînes [Al $\phi$ <sub>5</sub>] sont connectées pour former une chaîne [Al(PO<sub>4</sub>)<sub>2</sub>F]. Les octaèdres {CdO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} partagent des arêtes pour former une chaîne [CdO<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], elle aussi parallèle à  $a$ . Ces deux sortes de chaînes sont liées par les tétraèdres (PO<sub>4</sub>) pour former un feuillet de composition [AlCd(PO<sub>4</sub>)<sub>2</sub>F(H<sub>2</sub>O)<sub>2</sub>] dans le plan (001), que nous désignons la couche  $A$ . Les sites Al(3) et Cu sont intercalés entre les couches  $A$  pour former des octaèdres {CuO<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>} et {Al(3)O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>}, isolés l'un de l'autre. Ces deux octaèdres constituent une couche ouverte désignée  $B$ , dans laquelle les deux octaèdres sont agencés en ligne le long de  $a$ . La couche  $B$  est liée à la couche  $A$  par partage de coins d'octaèdres avec les tétraèdres (PO<sub>4</sub>). Les couches  $A$  et  $B$  alternent le long de l'axe  $c$  pour former une trame hétéropolyédrique. Il y a de plus des canaux interstitiels dans cette trame, aussi orientés le long de  $a$ , et ils contiennent les atomes d'hydrogène des groupes (H<sub>2</sub>O) en coordinence avec les cations de la couche  $B$ .

(Traduit par la Rédaction)

**Mots-clés:** goldquarryite, phosphate, structure cristalline, mine Gold Quarry, comté d'Eureka, Nevada.

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## INTRODUCTION

Jensen *et al.* (1995) reported the occurrence of two unknown minerals at the Gold Quarry mine, Carlin Trend, Eureka County, Nevada, U.S.A., and subsequent work has led to the characterization of these two mineral species. Nevadaite,  $(\text{Cu}^{2+}, \square, \text{Al}, \text{V}^{3+})_6\text{Al}_8(\text{PO}_4)_8\text{F}_8(\text{H}_2\text{O})_{22}$ , was recently described by Cooper *et al.* (2004). It occurs as radiating clusters of pale green to turquoise-blue prismatic crystals associated with fluellite, wavellite, strengite–variscite, hewettite, and rare anatase, kazakhstanite, tinctite, torbernite and tyuyamunit. Goldquarryite,  $(\text{Cu}^{2+}, \square)(\text{Cd}, \text{Ca})_2\text{Al}_3(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_{10}\{(\text{H}_2\text{O}), \text{F}\}_2$ , was reported as a new species by Roberts *et al.* (2003). It occurs as clusters of radiating sprays and parallel aggregates of pale blue to blue-grey crystals associated with opal, carbonate-fluorapatite and hewettite in a late-stage supergene assemblage. Here, we report on the crystal structure of goldquarryite, the fourteenth mineral found to contain essential Cd.

## EXPERIMENTAL

## Single-crystal X-ray diffraction

Intensity data were collected on a slender prism ( $14 \times 14 \times 230 \mu\text{m}$ ) using a BRUKER single-crystal diffractometer equipped with a 1K CCD detector. A three-minute frame-time and  $0.2^\circ$  frame width were used. A total of 6505 reflections was collected to  $60^\circ 2\theta$  (5270 individual reflections belong to the Ewald sphere); of the 3226 unique reflections in triclinic symmetry ( $P\bar{1}$ ), 1630 were classed as observed ( $F_o > 5\sigma F$ ). Cell dimensions were refined by least squares from 1457 reflections with  $I > 10 \sigma I$ , and the refined values are given in Table 1. A Gaussian absorption correction was done. All calculations were done with the SHELXTL PC (Plus) system of programs;  $R$  indices are of the form given in Table 1 and are expressed as percentages. The crystal structure was solved by direct methods and difference-Fourier synthesis in the space group  $P\bar{1}$  and refined to an  $R$  index of 5.2% for 1630 observed reflections with anisotropic-displacement factors on all atoms except the positionally split OW(6) and OW(7) sites. Hydrogen atoms could not be located directly from the diffraction data. Final atom parameters are given in Table 2, selected interatomic distances are given in Table 3 and a bond-valence analysis is shown in Table 4. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

## Electron-microprobe analysis

Crystals were analyzed with a Cameca SX-50 electron microprobe operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a speci-

men current of 10 nA, and a beam diameter of  $10 \mu\text{m}$ . The following standards were used:  $\text{VP}_2\text{O}_7$  (V), maricite (P), brazilianite (Al), Cd metal (Cd), cuprite (Cu), fluorite (Ca, F), gahnite (Zn) and pentlandite (Ni). The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1984, 1985). The presence and quantity of  $(\text{H}_2\text{O})$  groups were established from the refined crystal-structure, and their presence is in accord with the infrared spectrum presented by Roberts *et al.* (2003). Table 5 gives the chemical composition and unit formula for a representative crystal based on 30 anions, including 11.86  $(\text{H}_2\text{O})$  groups *pfu* (per formula unit). The crystals were very unstable under the electron beam, and the oxide sums are very high (104–109 wt.%), suggesting that  $\text{H}_2\text{O}$  is being driven off (possibly with other constituents) very rapidly. We did not chemically analyze the single crystal used for structure refinement as we wished to preserve the crystal, and hence we place more weight on the results of the site-scattering refinement to give accurate (Cd,Ca) and Cu contents.

## DESCRIPTION OF THE CRYSTAL STRUCTURE

## Cation sites

The structure of goldquarryite contains two  $P$  sites completely occupied by P and coordinated by four O atoms, with  $\langle P-O \rangle$  distances of 1.536 and 1.537 Å, respectively; these values are in accord with the grand  $\langle P-O \rangle$  distance of 1.537 Å given by Huminicki & Hawthorne (2002) for well-refined phosphate minerals. There are three Al sites, each fully occupied by Al and coordinated by six anions; Al(1) and Al(2) are each coordinated by four O atoms and two F atoms with  $\langle Al-(O,F) \rangle$  distances of 1.876 and 1.878 Å, respectively, and Al(3) is coordinated by two O atoms and four  $(\text{H}_2\text{O})$  groups with a  $\langle Al-O, (\text{H}_2\text{O}) \rangle$  distance of 1.867 Å. There is one Cd site occupied by Cd with minor Ca, and surrounded by four O atoms and two *cis*  $(\text{H}_2\text{O})$  groups in a

TABLE 1. MISCELLANEOUS INFORMATION FOR GOLDQUARRYITE

$a$ (Å)	6.787(1)	crystal size (mm)	$0.014 \times 0.014 \times 0.23$
$b$	9.082(2)	radiation	MoK $\alpha$
$c$	10.113(2)	No. of reflections	6505
$\alpha$ ( $^\circ$ )	101.40(1)	No. in Ewald sphere	5270
$\beta$	104.27(1)	No. unique reflections	3226
$\gamma$	102.51(1)	No. $ F_o  > 5\sigma( F_c )$	1630
$V$ (Å <sup>3</sup> )	568.7(3)	$R_{\text{merge}}$ (%)	3.1
Sp. Gr.	$P\bar{1}$	$R_{\text{obs}}$ (%)	5.2
$Z$	1	$wR_{\text{obs}}$ (%)	4.9
$D_{\text{meas}}^*$ (g/cm <sup>3</sup> )	2.78(1)		
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	2.80		
$R = \Sigma( F_o  -  F_c ) / \Sigma F_o $			
$wR = [\Sigma w( F_o  -  F_c )^2 / \Sigma F_o^2]^{1/2}$ , $w = (1 / \sigma^2(F) + 0.0005 F^2)$			

\* Jensen *et al.* (1995)

TABLE 2. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR GOLDQUARRYITE

	x	y	z	$U_{eq}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Cu	0	0	0	0.0189(10)	0.0342(16)	0.0096(14)	0.0075(15)	0.0013(10)	0.0024(12)	0.0006(11)
Cd	0.27682(11)	0.51849(9)	0.55938(9)	0.0108(3)	0.0079(4)	0.0127(5)	0.0131(5)	0.0039(4)	0.0045(3)	0.0036(3)
P(1)	0.2389(4)	0.1857(3)	0.3288(3)	0.0098(9)	0.0091(12)	0.0082(12)	0.0130(14)	0.0031(11)	0.0048(10)	0.0024(10)
P(2)	0.1077(4)	0.7124(3)	0.3264(3)	0.0099(9)	0.0094(12)	0.0088(12)	0.0116(14)	0.0028(11)	0.0040(11)	0.0020(10)
Al(1)	1/2	0	1/2	0.0087(14)	0.0063(18)	0.009(2)	0.011(2)	0.0022(17)	0.0026(17)	0.0020(15)
Al(2)	0	0	1/2	0.0097(15)	0.0094(19)	0.009(2)	0.010(2)	0.0030(17)	0.0034(17)	0.0021(16)
Al(3)	0	1/2	0	0.0133(15)	0.016(2)	0.014(2)	0.011(2)	0.0015(18)	0.0057(18)	0.0065(17)
F(1)	0.2842(8)	0.0232(7)	0.5781(6)	0.019(2)	0.016(3)	0.021(3)	0.018(3)	-0.001(3)	0.007(2)	0.004(2)
O(1)	0.3678(9)	0.3563(7)	0.3982(7)	0.013(2)	0.010(3)	0.007(3)	0.017(4)	-0.001(2)	0.005(3)	-0.004(3)
O(2)	0.3792(9)	0.0736(7)	0.3467(7)	0.013(3)	0.009(3)	0.015(4)	0.021(4)	0.008(3)	0.007(3)	0.009(3)
O(3)	0.1427(10)	0.1677(7)	0.1703(7)	0.017(3)	0.020(3)	0.018(4)	0.010(4)	0.007(3)	0.000(3)	-0.002(3)
O(4)	0.0610(9)	0.1459(7)	0.3956(7)	0.012(2)	0.012(3)	0.015(4)	0.017(4)	0.011(3)	0.010(3)	0.008(3)
O(5)	-0.0178(9)	0.8332(7)	0.3468(6)	0.012(2)	0.008(3)	0.015(3)	0.015(4)	0.006(3)	0.004(3)	0.004(3)
O(6)	0.3473(9)	0.7923(7)	0.3968(7)	0.013(2)	0.007(3)	0.011(4)	0.018(4)	0.002(3)	-0.001(3)	0.001(3)
O(7)	0.0393(9)	0.5815(7)	0.3952(7)	0.016(3)	0.014(3)	0.016(4)	0.023(4)	0.013(3)	0.009(3)	0.005(3)
O(8)	0.0647(10)	0.6484(8)	0.1678(7)	0.020(3)	0.020(4)	0.023(4)	0.017(4)	0.002(3)	0.008(3)	0.006(3)
OW(1)	0.4187(9)	0.3769(8)	0.7146(7)	0.018(3)	0.011(3)	0.017(4)	0.022(4)	0.006(3)	0.002(3)	-0.002(3)
OW(2)	0.1833(10)	0.6375(7)	-0.0544(7)	0.016(3)	0.021(3)	0.017(4)	0.015(4)	0.004(3)	0.010(3)	0.008(3)
OW(3)	0.2319(10)	0.4193(8)	0.0784(7)	0.017(3)	0.020(3)	0.019(4)	0.011(4)	0.003(3)	0.003(3)	0.009(3)
OW(4)	0.2734(10)	0.7378(8)	0.7235(8)	0.024(3)	0.018(4)	0.015(4)	0.036(5)	0.000(3)	0.015(3)	-0.001(3)
OW(5)	0.1786(12)	0.1097(10)	-0.0962(8)	0.039(4)	0.047(5)	0.042(5)	0.023(5)	0.003(4)	0.009(4)	0.007(4)
OW(6)*	0.409(3)	-0.0751(15)	0.0905(13)	0.048(5)						
OW(7)*	0.263(5)	-0.082(3)	0.066(3)	0.036(11)						

\* partly occupied sites, see text. Occupancies: Cd:  $\text{Cd}_{0.835}\text{Ca}_{0.165}$ ; Cu:  $\text{Cu}_{0.7}\square_{0.3}$ ; OW(2):  $(\text{H}_2\text{O})_{0.8}\text{F}_{0.2}$ ; OW(6):  $(\text{H}_2\text{O})_{0.7}\square_{0.3}$ ; OW(7):  $(\text{H}_2\text{O})_{0.3}\square_{0.7}$ .

distorted octahedral arrangement (Table 3, Fig. 1) with  $\langle \text{Cd}-\text{O}(\text{H}_2\text{O}) \rangle = 2.317 \text{ \AA}$ .

There is one Cu site with a refined site-scattering value of 20.5(2) *epfu* (electrons per formula unit), and the unit formula indicates that this site should be occupied by 0.70  $\text{Cu}^{2+}$  + 0.30  $\square$  (vacancy), in accord with the refined site-scattering. This site occurs at a center of symmetry; the cation is coordinated by two O atoms and two ( $\text{H}_2\text{O}$ ) groups in a square-planar arrangement, and two ( $\text{H}_2\text{O}$ ) groups that form long (2.97  $\text{Å}$ ) apical bonds to the central cation. This Jahn–Teller-distorted [4 + 2]-coordination is typical for  $\text{Cu}^{2+}$  (Eby & Hawthorne 1993, Burns & Hawthorne 1996). The apical ( $\text{H}_2\text{O}$ ) group shows strong positional disorder: refinement of the structure gave two distinct sites, OW(6) and OW(7) at 2.97 and 2.09  $\text{Å}$ , respectively, from the Cu site. The relative site-populations are as follows: OW(6) = 1.4 ( $\text{H}_2\text{O}$ ); OW(7) = 0.6 ( $\text{H}_2\text{O}$ ) *pfu*, and the separation of these two sites (0.94  $\text{Å}$ ) indicates that they cannot both be locally occupied simultaneously. These occupancies (given above), together with the arrangement of the OW(6) and OW(7) sites, the refined occupancy at the Cu site, and local bond-valence requirements, suggest two simple configurations (Fig. 2). Configuration A involves occupancy of the Cu site by  $\text{Cu}^{2+}$ , OW(6) by ( $\text{H}_2\text{O}$ ), and OW(7) by  $\square$  (Fig. 2a). Configuration B involves a vacancy at the Cu site, occupancy of OW(6) by  $\square$  and OW(7) by ( $\text{H}_2\text{O}$ ) (Fig. 2b). The incident bond-valence sum at the Cu site for configuration A is 2.02 *vu* (Table 4), in good agreement with the valence-sum

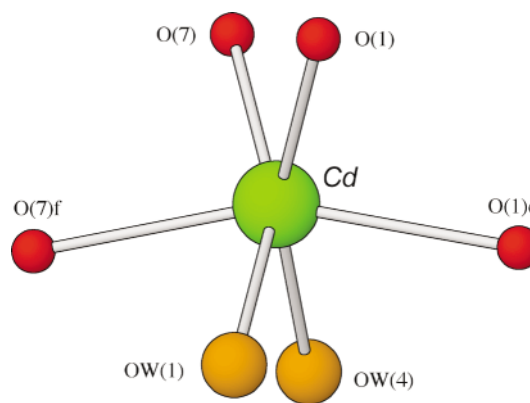


FIG. 1. Coordination of the Cd site in goldquarryite.

rule (Brown 1981). If configuration B were to involve occupancy of the Cu site by  $\text{Cu}^{2+}$  rather than  $\square$ , the bond-valence sum incident at the Cu site would be too large (2.62 *vu*).

#### Anion sites

There are eight anion sites occupied by O atoms, each of which is bonded to one P atom and receives >1.70 *vu* from the cations in the structure (omitting con-

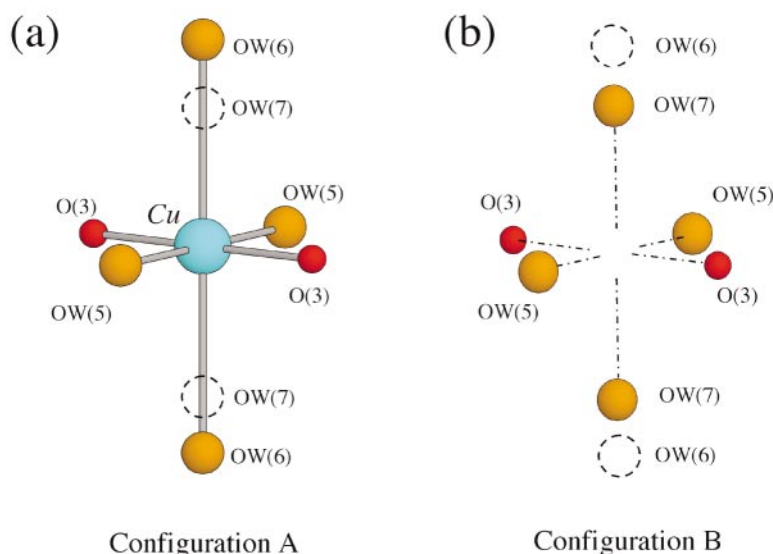


FIG. 2. Local configurations around the *Cu* site: (a) the *Cu* site is occupied by  $\text{Cu}^{2+}$ , the OW(6) site is occupied by  $(\text{H}_2\text{O})$ , and the OW(7) site is not occupied; (b) the *Cu* and OW(6) sites are not occupied, and the OW(7) site is occupied.

tributions from hydrogen bonds) (Table 4). There is one anion site, which links only to the Al atoms at the Al(1) and Al(2) sites. When this atom was assigned as O, the equivalent-isotropic displacement parameter refined to near-zero, indicative of more scattering at this site; replacement of O by F led to reasonable displacement parameters (Table 2), and the resulting bond-lengths (Table 3) and bond-valences (Table 4) are in accord with this assignment. There are seven anion sites at which the sums of the incident bond-valences are less than 0.65 *vu*, and these were assigned as  $(\text{H}_2\text{O})$ . As noted above, the OW(6) and OW(7) sites are very close, 0.94 Å, and cannot both be locally occupied simultaneously. On the basis of bond-valence and electroneutrality arguments (see below), the OW(2) site was assigned as 1.6  $(\text{H}_2\text{O})$  and 0.4 F (*apfu*).

#### Structure topology

The  $\{\text{Al}(1)\text{O}_4\text{F}_2\}$  and  $\{\text{Al}(2)\text{O}_4\text{F}_2\}$  octahedra share corners through common F vertices to form an  $[\text{Al}\phi_5]$  chain ( $\phi$ : unspecified anion) that extends along the *a* direction (Fig. 3a). This chain is decorated by  $(\text{PO}_4)$  tetrahedra that link to four O atoms of each  $(\text{Al}\phi_6)$  octahedron, linking the  $[\text{Al}\phi_5]$  chain along its length to form an  $[\text{Al}(\text{PO}_4)_2\text{F}]$  chain. The  $\{\text{CdO}_4(\text{H}_2\text{O})_2\}$  octahedra share edges to form a  $[\text{CdO}_2(\text{H}_2\text{O})_2]$  chain that also extends along *a*. These two types of chains link through the  $(\text{PO}_4)$  tetrahedra to form a sheet of composition  $[\text{AlCd}(\text{PO}_4)_2\text{F}(\text{H}_2\text{O})_2]$ , which we designate as the A layer, in the (001) plane (Fig. 3a). The Al(3) and *Cu* sites

are intercalated between the A layers, forming  $\{\text{CuO}_2(\text{H}_2\text{O})_4\}$  and  $\{\text{Al}(3)\text{O}_2(\text{H}_2\text{O})_4\}$  octahedra (Fig. 3b) that are isolated from each other. These octahedra form an open layer, the B layer, in which the  $\{\text{CuO}_2(\text{H}_2\text{O})_4\}$  and  $\{\text{Al}(3)\text{O}_2(\text{H}_2\text{O})_4\}$  octahedra each form linear arrays extending in the *a* direction (Fig. 3b); note that in Figure 3b, both occupied and vacant  $\{\text{CuO}_2(\text{H}_2\text{O})_4\}$  octahedra are shown. The B layer links to the A layer by sharing octahedron corners with  $(\text{PO}_4)$  tetrahedra. The A and B layers alternate along the *c* axis to form a heteropolyhedral framework (Fig. 4). There are interstitial channels within this framework, also extending along *a* (Fig. 4), and these are filled with the H atoms of the  $(\text{H}_2\text{O})$  groups that coordinate the cations of the B layer.

#### Hydrogen bonding

Extensive disorder in the structure of goldquarryite makes complete understanding of the hydrogen-bond arrangement impossible. However, some donor-acceptor pairs were identified; these are listed in Table 6. It is apparent from the bond-valence table (Table 4) that significant re-arrangement of hydrogen bonds must couple to the  $\text{Cu}^{2+} \leftrightarrow \square$  substitution at the *Cu* site. Approximately 0.5 *vu* are associated with the *Cu*-O(3) and *Cu*-OW(5) bonds, suggesting incidence of at least two hydrogen-bonds at these anion sites where the *Cu* site is vacant. Conceivable hydrogen-bonding configurations are shown for an occupied (Fig. 5a) and vacant (Fig. 5b) *Cu*-site.

## RELATED STRUCTURES

The  $[\text{Al}(\text{PO}_4)_2\text{F}]$  chain in goldquarryite may be written in a more general form as  $[M(\text{TO}_4)_2\phi]$ , where  $M$  represents octahedrally coordinated divalent and trivalent cations,  $T$  represents tetrahedrally coordinated cations, and  $\phi$  stands for (OH), F,  $(\text{H}_2\text{O})$ , O. This  $[M(\text{TO}_4)_2\phi]$  chain (Hawthorne 1985) occurs in the structures of tancoite,  $\text{Na}_2\text{LiH}[\text{Al}(\text{PO}_4)_2(\text{OH})]$  (Hawthorne 1983), sideronatrite,  $\text{Na}_2[\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})](\text{H}_2\text{O})_3$  (Scordari 1981), the minerals of the jahnsite,  $\text{CaMn}^{2+}\text{Mg}_2[\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})_2](\text{H}_2\text{O})_8$  (Moore & Araki 1974) and segelerite,  $\text{CaMg}[\text{Fe}^{3+}(\text{PO}_4)_2(\text{OH})](\text{H}_2\text{O})_4$  (Moore & Araki 1977) groups, guildite,  $\text{Cu}^{2+}[\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})](\text{H}_2\text{O})_4$  (Wan *et al.* 1978), yftisite,  $\text{Y}_4[\text{Ti}(\text{SiO}_4)_2\text{O}](\text{F},\text{OH})_6$  (Balko & Bakakin 1975), and sinkankasite,

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN GOLDQUARRYITE

$\text{Cd}-\text{O}(1)$	2.270(7)	$\text{P}(1)-\text{O}(1)$	1.529(6)
$\text{Cd}-\text{O}(1)\text{c}$	2.324(6)	$\text{P}(1)-\text{O}(2)$	1.544(7)
$\text{Cd}-\text{O}(7)$	2.267(7)	$\text{P}(1)-\text{O}(3)$	1.536(7)
$\text{Cd}-\text{O}(7)\text{f}$	2.334(7)	$\text{P}(1)-\text{O}(4)$	<u>1.534(7)</u>
$\text{Cd}-\text{OW}(1)$	2.373(8)	$\langle\text{P}(1)-\text{O}\rangle$	1.536
$\text{Cd}-\text{OW}(4)$	<u>2.336(7)</u>		
$\langle\text{Cd}-\text{O}\rangle$	2.317		
<i>Cu-site (occupied)</i>			
$\text{Cu}-\text{O}(3)\text{,d}$ x2	1.930(5)	$\text{P}(2)-\text{O}(5)$	1.540(7)
$\text{Cu}-\text{OW}(5)\text{,d}$ x2	1.962(9)	$\text{P}(2)-\text{O}(6)$	1.546(5)
$\text{Cu}-\text{OW}(6)\text{,d}$ x2	<u>2.969(17)</u>	$\text{P}(2)-\text{O}(7)$	1.536(8)
$\langle\text{Cu}-\text{O}\rangle$	2.287	$\text{P}(2)-\text{O}(8)$	<u>1.524(7)</u>
		$\langle\text{P}(2)-\text{O}\rangle$	1.537
<i>Cu-site (vacant)</i>			
$\square-\text{O}(3)\text{,d}$ x2	1.930(5)	$\text{Al}(1)-\text{F},\text{a}$ x2	1.858(6)
$\square-\text{OW}(5)\text{,d}$ x2	1.962(9)	$\text{Al}(1)-\text{O}(2)\text{,a}$ x2	1.883(7)
$\square-\text{OW}(7)\text{,d}$ x2	<u>2.09(3)</u>	$\text{Al}(1)-\text{O}(6)\text{c,e}$ x2	<u>1.888(5)</u>
$\langle\square-\text{O}\rangle$	1.994		1.876
$\text{Al}(2)-\text{F},\text{b}$ x2	1.843(5)	$\text{Al}(3)-\text{O}(8)\text{,g}$ x2	1.834(6)
$\text{Al}(2)-\text{O}(4)\text{,b}$ x2	1.890(7)	$\text{Al}(3)-\text{OW}(2)\text{,g}$ x2	1.830(7)
$\text{Al}(2)-\text{O}(5)\text{e,f}$ x2	<u>1.901(6)</u>	$\text{Al}(3)-\text{OW}(3)\text{,g}$ x2	<u>1.938(7)</u>
	1.878		1.867
$\text{O}(1)\text{c}-\text{Cd}-\text{O}(1)$	77.7(2)		
$\text{O}(1)\text{c}-\text{Cd}-\text{O}(7)$	116.7(2)		
$\text{O}(1)\text{c}-\text{Cd}-\text{OW}(4)$	86.2(2)		
$\text{O}(1)\text{c}-\text{Cd}-\text{OW}(1)$	82.8(2)		
$\text{O}(7)\text{f}-\text{Cd}-\text{O}(1)$	116.8(2)		
$\text{O}(7)\text{f}-\text{Cd}-\text{O}(7)$	78.2(3)		
$\text{O}(7)\text{f}-\text{Cd}-\text{OW}(4)$	80.3(2)		
$\text{O}(7)\text{f}-\text{Cd}-\text{OW}(1)$	84.5(2)		
$\text{O}(1)-\text{Cd}-\text{O}(7)$	94.6(2)		
$\text{O}(7)-\text{Cd}-\text{OW}(4)$	87.5(2)		
$\text{OW}(4)-\text{Cd}-\text{OW}(1)$	100.2(2)		
$\text{OW}(1)-\text{Cd}-\text{O}(1)$	<u>83.6(2)</u>		
	90.8		

a:  $\bar{x}+1, \bar{y}, \bar{z}+1$ ; b:  $\bar{x}, \bar{y}, \bar{z}+1$ ; c:  $\bar{x}+1, \bar{y}+1, \bar{z}+1$ ; d:  $\bar{x}, \bar{y}, \bar{z}$ ;  
e:  $x, y-1, z$ ; f:  $\bar{x}, \bar{y}+1, \bar{z}+1$ ; g:  $\bar{x}, \bar{y}+1, \bar{z}$

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

	Cu	Cd	Al(1)	Al(2)	Al(3)	P(1)	P(2)	$\Sigma$
F			0.43 <sup>x2</sup>	0.45 <sup>x2</sup>				0.88
O(1)		0.38 0.33				1.27		1.98
O(2)			0.53 <sup>x2</sup>			1.22		1.75
O(3)	0.51 <sup>x2</sup>					1.24		1.75
O(4)				0.52 <sup>x2</sup>		1.25		1.77
O(5)				0.51 <sup>x2</sup>			1.23	1.74
O(6)			0.53 <sup>x2</sup>				1.21	1.74
O(7)	0.38 0.32						1.24	1.94
O(8)					0.61 <sup>x2</sup>		1.29	1.90
OW(1)	0.29							0.29
OW(2)				0.62 <sup>x2</sup>				0.62
OW(3)				0.46 <sup>x2</sup>				0.46
OW(4)	0.32							0.32
OW(5)	0.47 <sup>x2</sup>							0.47
OW(6)	0.03 <sup>x2</sup>							0.03
OW(7)								0.00
$\Sigma$	2.02	2.02	2.98	2.96	3.38	4.98	4.97	

\* curves from Brown & Altermatt (1985)

TABLE 5. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (apfu) FOR GOLDQUARRYITE

$\text{P}_2\text{O}_5$	29.60	P	3.87
$\text{Al}_2\text{O}_3$	16.95		
$\text{V}_2\text{O}_5$	0.13	Al	3.08
CuO	4.90	$\text{V}^{3+}$	0.02
NiO	0.19		
ZnO	0.07	Cu	0.57
CdO	26.15	Zn	0.01
CaO	1.49	Ni	0.02
F	4.42		
$(\text{H}_2\text{O})^*$	23.03	Cd	1.89
$\text{O}=\text{F}$	<u>-1.86</u>	Ca	0.25
Sum	105.07		
		F	2.16
		$(\text{H}_2\text{O})$	11.86

\* calculated from the crystal structure

TABLE 6. PROPOSED HYDROGEN BONDS (Å) IN GOLDQUARRYITE

$\text{OW}(2)\dots\text{OW}(4)\text{h}$	2.737(11)	$\text{OW}(4)\text{h}-\text{OW}(2)\dots\text{OW}(6)\text{i}$	82.9(4)
$\text{OW}(2)\dots\text{OW}(6)\text{j}$	2.637(13)	$\text{OW}(4)-\text{OW}(2)\dots\text{OW}(7)\text{i}$	85.6(8)
$\text{OW}(2)\dots\text{OW}(7)\text{j}$	2.47(3)		
$\text{OW}(3)\dots\text{O}(3)$	2.640(10)		
$\text{OW}(5)\dots\text{O}(3)$	2.724(11)	$\text{O}(3)-\text{OW}(5)\dots\text{O}(3)\text{d}$	89.1(3)
$\text{OW}(5)\dots\text{O}(3)\text{d}$	2.781(9)		
$\text{OW}(7)\dots\text{OW}(5)$	2.67(3)	$\text{OW}(5)-\text{OW}(7)\dots\text{OW}(5)\text{d}$	86(1)
$\text{OW}(7)\dots\text{OW}(5)\text{d}$	3.05(4)		

a:  $\bar{x}+1, \bar{y}, \bar{z}+1$ ; b:  $\bar{x}, \bar{y}, \bar{z}+1$ ; c:  $\bar{x}+1, \bar{y}+1, \bar{z}+1$ ; d:  $\bar{x}, \bar{y}, \bar{z}$ ;  
e:  $x, y-1, z$ ; f:  $\bar{x}, \bar{y}+1, \bar{z}+1$ ; g:  $\bar{x}, \bar{y}+1, \bar{z}$ ; h:  $x, y, z-1$ ; i:  $x, y+1, z$

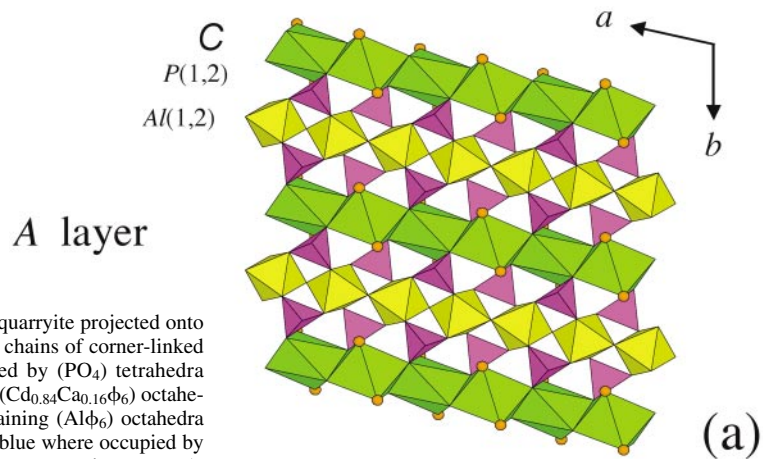


FIG. 3. The crystal structure of goldquarryite projected onto (001): (a) The A layer, containing chains of corner-linked ( $Al\Phi_6$ ) octahedra (yellow) flanked by ( $PO_4$ ) tetrahedra (pink) and chains of edge-sharing ( $Cd_{0.84}Ca_{0.16}\Phi_6$ ) octahedra (green); (b) the B layer, containing ( $Al\Phi_6$ ) octahedra and  $\{(Cu_{0.70}\square_{0.30})\Phi_6\}$  octahedra (blue where occupied by Cu, uncolored with a blue  $\square$  at the center where vacant); ( $H_2O$ ) groups are shown as large orange circles, O atoms are shown by small red circles.

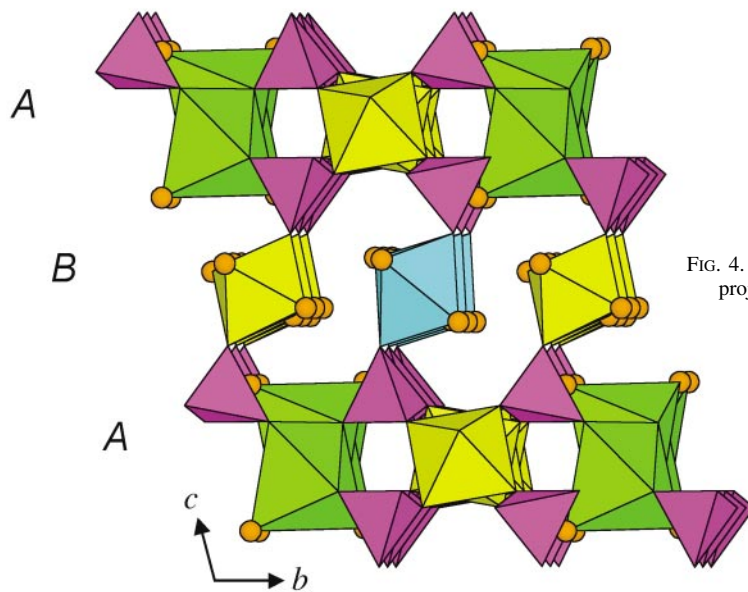
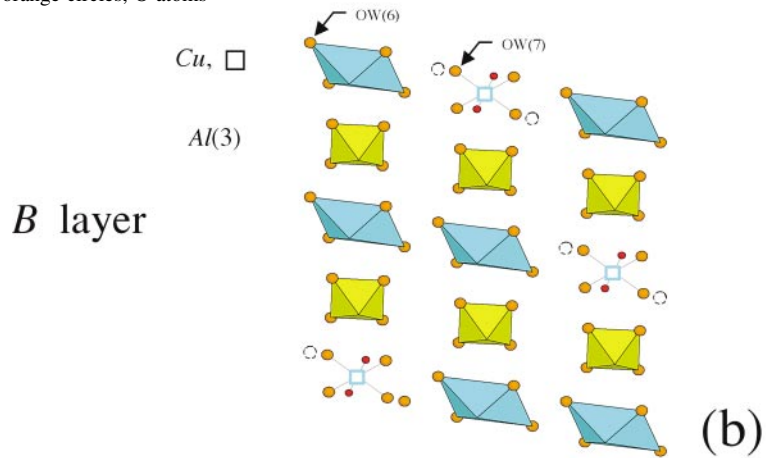


FIG. 4. The crystal structure of goldquarryite projected onto (100); legend as in Figure 3.

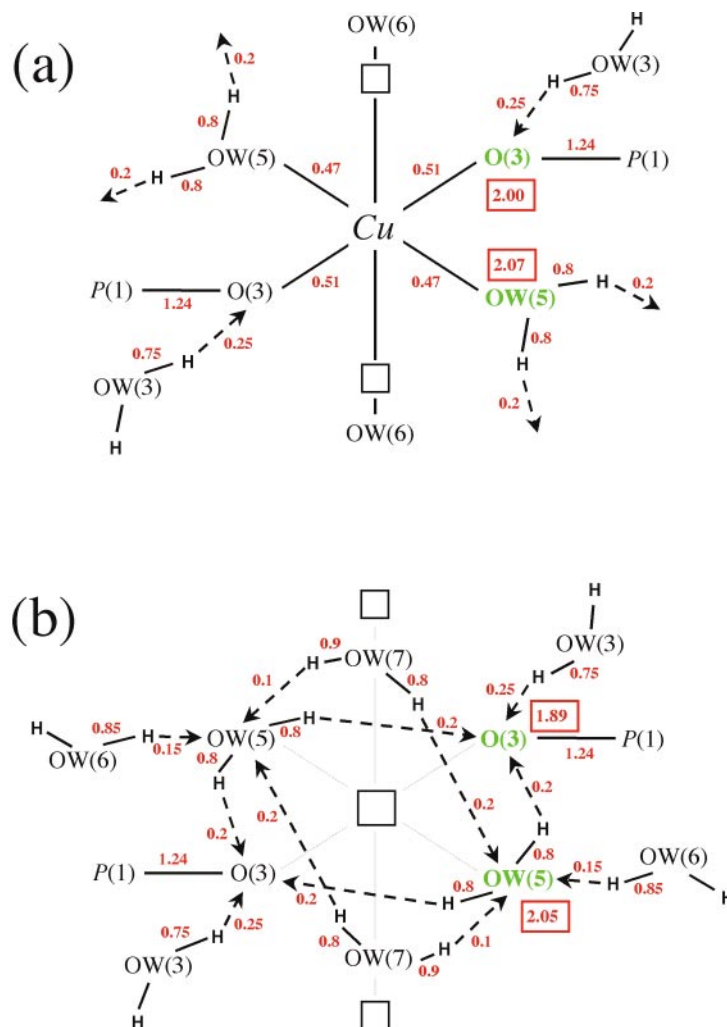


FIG. 5. Sketch of the local hydrogen-bonds around the *Cu* site (a) where *Cu* is occupied by  $\text{Cu}^{2+}$ , and (b) where *Cu* is occupied by  $\square$ . Legend as in Figures 2, 5. Bond valences from donor-H and H-acceptor atoms are the average values recommended by Brown (1981), except where local stereochemistry suggests different values (see also Fig. 6).

$\text{Mn}^{2+}(\text{H}_2\text{O})_4[\text{Al}(\text{PO}_3\text{OH})_2(\text{OH})](\text{H}_2\text{O})_2$  (Burns & Hawthorne 1995).

Moore (1970) first noted the importance of  $[\text{M}\phi_5]$  chains in the structures of hydroxy-hydrated oxysalt minerals, and examined aspects of the stereochemical and topological isomerisms of the chains where decorated by  $(\text{SiO}_4)$  tetrahedra. Both goldquarryite and nevadaite contain decorated  $[\text{M}\phi_5]$  chains as essential components of their crystal structures. The  $[\text{M}(\text{TO}_4)\phi_3]$  chain in nevadaite has several different geometrical isomers (Cooper *et al.* 2004), and there are many structures based on this general type of chain. On the other hand, the  $[\text{M}(\text{TO}_4)_2\phi]$  chain in goldquarryite and the

other structures noted above does not have any geometrical isomers that are stereochemically reasonable.

#### CHEMICAL FORMULA

The cation part of the formula as derived from the crystal structure is  $\{(\text{Cu}^{2+}_{0.7}\square_{0.3})(\text{Cd}_{1.67}\text{Ca}_{0.33})\text{Al}_3\}$  and has a net charge of  $14.4^+$ . The anion part of the formula is  $[(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_{12}]$  and has a net charge of  $14^-$ . Electroneutrality results from an additional 0.4 negative charges from substitution of F or OH for  $\text{H}_2\text{O}$  at one of the OW sites. We can rule out  $\text{O}^{2-} \leftrightarrow (\text{H}_2\text{O})$  substitution, as the structure cannot provide enough incident

bond-valence at the O atom in the absence of two H atoms. The most likely candidate is the OW(2) site, which receives 0.62 *vu* from the Al(3) site (Table 4). If the OW(2) site were occupied by F, acceptance of two additional hydrogen bonds would satisfy the bonding requirements of F. These two possible anion-configurations for the OW(2) site are shown in Figure 6. Where the OW(2) site is occupied by an H<sub>2</sub>O group (Fig. 6a), the OW(4) and OW(6)–OW(7) sites act as hydrogen-bond acceptors; where the OW(2) site is occupied by F (Fig. 6b), the F atom receives two hydrogen bonds from the same (H<sub>2</sub>O) groups. Additional support for F at OW(2) is provided by the F in excess of 2 *apfu* from electron-microprobe analysis (Table 5). We propose that the OW(2) site is occupied by 1.6 (H<sub>2</sub>O) and 0.4 F, giving a total anion composition of (PO<sub>4</sub>)<sub>4</sub>F<sub>2</sub>(H<sub>2</sub>O)<sub>11.6</sub>F<sub>0.4</sub>, which provides the necessary 14.4<sup>-</sup> to balance the cation component of the formula. We note that minor (OH) ⇌ (H<sub>2</sub>O) substitution cannot be ruled out; however, there is no clear evidence of an (OH) group in the infrared spectrum (Roberts *et al.* 2003). In addition, substitution of (OH) for (H<sub>2</sub>O) at the OW(2) site seems unlikely, as two or three hydrogen bonds would be required at OW(2), and there is only one feasible donor-atom available. The unit formula resulting from crystal-structure refinement, (Cu<sub>0.70</sub> □<sub>0.30</sub>) (Cd<sub>1.67</sub> Ca<sub>0.33</sub>) Al<sub>3</sub> (PO<sub>4</sub>)<sub>4</sub>F<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>(H<sub>2</sub>O,F)<sub>2</sub>, is in reasonable

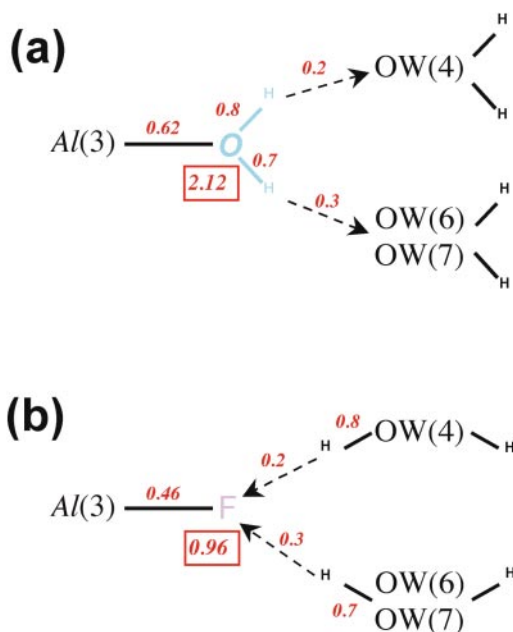


FIG. 6. Sketch of the local hydrogen-bonds around the OW(2) site (a) when OW(2) is occupied by (H<sub>2</sub>O), and (b) when OW(2) is occupied by F. Bond valences are given in red.

accord with that calculated from the electron-microprobe analysis (Table 5).

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