

## THE CRYSTAL STRUCTURE OF BURGESSITE, $\text{Co}_2 (\text{H}_2\text{O})_4 [\text{AsO}_3(\text{OH})]_2 (\text{H}_2\text{O})$ , AND ITS RELATION TO ERYTHRITE

MARK A. COOPER AND FRANK C. HAWTHORNE<sup>§</sup>

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

### ABSTRACT

The crystal structure of burgessite, ideally  $\text{Co}_2 (\text{H}_2\text{O})_4 [\text{AsO}_3(\text{OH})]_2 (\text{H}_2\text{O})$ , a newly recognized supergene mineral from the Keeley mine, South Lorrain Township, Timiskaming District, Ontario, Canada, has been solved by direct methods and refined to an *R* index of 4.3% based on 494 observed reflections collected on a four-circle diffractometer with  $\text{MoK}\alpha$  X-radiation. Burgessite is monoclinic, space group  $P2_1/n$ , *a* 4.7058(12), *b* 9.299(3), *c* 12.738(4) Å,  $\beta$  98.933(8)°, *V* 550.6(5) Å<sup>3</sup>, *Z* = 2, *D*<sub>meas</sub> = 2.93 g/cm<sup>3</sup>. The structure consists of one unique *As* site that is [4]-coordinated by O atoms and occupied by  $\text{As}^{5+}$  with a  $\langle \text{As}-\text{O} \rangle$  distance of 1.694 Å. There is one *Co* site occupied by Co and [6]-coordinated, with a  $\langle \text{Co}-\text{O} \rangle$  distance of 2.096 Å. Bond-valence analysis of the final structure indicates three O atoms ( $\text{O}^{2-}$ ), one (OH) group and three ( $\text{H}_2\text{O}$ ) groups in the asymmetric unit; note that the (OH) group is bonded to the  $\text{As}^{5+}$  cation, forming an acid arsenate group:  $\text{AsO}_3(\text{OH})$ . The resulting ideal formula is  $\text{Co}_2 (\text{H}_2\text{O})_4 [\text{As}^{5+}\text{O}_3(\text{OH})]_2 (\text{H}_2\text{O})$ , where the ( $\text{H}_2\text{O}$ ) groups before the arsenate group are bonded to Co, and the ( $\text{H}_2\text{O}$ ) group following the arsenate group is held in the structure solely by hydrogen bonds. A prominent motif in the burgessite structure is the  $[\text{Co}_2(\text{H}_2\text{O})_4[\text{As}^{5+}\text{O}_3(\text{OH})]_2]$  chain, which extends in the [100] direction and occurs at the vertices of an orthorhombic net. These chains are linked into a three-dimensional structure by hydrogen bonds that involve (OH) bonded to  $\text{As}^{5+}$ , ( $\text{H}_2\text{O}$ ) bonded to Co, and ( $\text{H}_2\text{O}$ ) held in the structure solely by hydrogen bonds. The crystal structure of erythrite is based on  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}^{5+}\text{O}_4)_2]$  chains of the same bond-topology as that found in burgessite.

*Keywords:* burgessite, crystal structure, arsenate, erythrite.

### SOMMAIRE

Nous avons résolu par méthodes directes la structure cristalline de la burgessite, de composition idéale  $\text{Co}_2 (\text{H}_2\text{O})_4 [\text{AsO}_3(\text{OH})]_2 (\text{H}_2\text{O})$ , espèce minérale d'origine secondaire provenant de la mine Keeley, canton de South Lorrain, district de Timiskaming, Ontario, Canada, et nous l'avons affiné jusqu'à un résidu *R* de 4.3% en utilisant 494 réflexions observées et prélevées avec un diffractomètre à quatre cercles et avec rayonnement  $\text{MoK}\alpha$ . La burgessite est monoclinique, groupe spatial  $P2_1/n$ , *a* 4.7058(12), *b* 9.299(3), *c* 12.738(4) Å,  $\beta$  98.933(8)°, *V* 550.6(5) Å<sup>3</sup>, *Z* = 2, *D*<sub>mes</sub> = 2.93 g/cm<sup>3</sup>. La structure contient un seul site *As* où loge  $\text{As}^{5+}$ , entouré de quatre atomes d'oxygène à une distance  $\langle \text{As}-\text{O} \rangle$  de 1.694 Å. Il y a un site *Co* où loge le Co à coordinence [6], avec une distance  $\langle \text{Co}-\text{O} \rangle$  de 2.096 Å. D'après une analyse des valences de liaison de la structure finale, il y a trois atomes d'oxygène ( $\text{O}^{2-}$ ), un groupe (OH) et trois groupes ( $\text{H}_2\text{O}$ ) dans l'unité asymétrique, agencés autour du cation  $\text{As}^{5+}$  et formant ainsi un groupe arsenate acide:  $\text{AsO}_3(\text{OH})$ . Il en résulte la formule idéale  $\text{Co}_2 (\text{H}_2\text{O})_4 [\text{As}^{5+}\text{O}_3(\text{OH})]_2 (\text{H}_2\text{O})$ , dans laquelle les groupes ( $\text{H}_2\text{O}$ ) inscrits devant le groupe arsenate sont liés au Co, et le groupe ( $\text{H}_2\text{O}$ ) suivant le groupe arsenate n'est retenu dans la structure que par des liaisons hydrogène. Un motif proéminent dans la structure de la burgessite est la chaîne  $[\text{Co}_2(\text{H}_2\text{O})_4[\text{As}^{5+}\text{O}_3(\text{OH})]_2]$  allongée dans la direction [100], située aux sommets d'un réseau orthorhombique. Ces chaînes sont rattachées à la structure tridimensionnelle par des liaisons hydrogène qui impliquent (OH) lié à  $\text{As}^{5+}$ , ( $\text{H}_2\text{O}$ ) lié au Co, et ( $\text{H}_2\text{O}$ ) retenu dans la structure seulement par des liaisons hydrogène. La structure cristalline de l'erythrite est fondée sur des chaînes  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}^{5+}\text{O}_4)_2]$  faisant preuve de la même topologie des liaisons que dans la burgessite.

(Traduit par la Rédaction)

*Mots-clés:* burgessite, structure cristalline, arsenate, erythrite.

<sup>§</sup> E-mail address: frank\_hawthorne@umanitoba.ca

## INTRODUCTION

Burgessite,  $\text{Co}_2(\text{H}_2\text{O})_4[\text{AsO}_3(\text{OH})]_2(\text{H}_2\text{O})$ , was recently approved as a new mineral species (IMA 2007–055) by Sejkora *et al.* (2009). It occurs as a supergene phase at the Keeley mine, South Lorrain Township, Timiskaming District, Ontario, Canada. The Keeley mine was a significant producer of silver and cobalt from 1908 to 1942 and from 1963 to 1965. Mineralization is associated with the Nipissing diabase and calcite veins containing native silver, “smaltite”, nickeline, proustite and many other sulfide and sulfosalts minerals. Moreover, the primary mineralization has been affected by subsequent supergene alteration (Boyle & Dass 1971) leading to secondary oxysalts, including burgessite. Here, we report the structure of burgessite, and explore the relation of burgessite to erythrite.

## EXPERIMENTAL DETAILS

A crystal was attached to a glass fiber and mounted on a Bruker *P4* diffractometer equipped with an Apex CCD detector and a  $\text{MoK}\alpha$  X-radiation. In excess of a

hemisphere of data (4012 reflections) was measured out to  $45^\circ 2\theta$  [the crystal was quite small (Table 1), and no data were observed beyond a  $2\theta$  value of  $45^\circ$ ] using a frame width of  $0.1^\circ$  and a frame time of 120 s. Unit-cell dimensions were determined from 682 reflections [with  $|I| > 7\sigma|I|$ ], and are given in Table 1, together with other information pertaining to data collection and structure refinement. Of the 711 unique reflections, 494 reflections were considered as observed [ $|F_o| > 5\sigma|F|$ ]. Absorption corrections were done using the program SADABS (Sheldrick 1998). The data were then corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors.

All calculations were done with the SHELXTL PC (Plus) system of programs using neutral scattering factors; *R* indices are of the form given in Table 1 and are expressed as percentages. Systematic absences in the single-crystal X-ray-diffraction data are consistent with space group  $P2_1/n$ , and the structure was solved with this symmetry. The structure was solved by direct methods and refined by full-matrix least-squares on  $|F|$  to an *R* index of 4.3%. At the final stages of refinement, four H (hydrogen) sites were identified in difference-Fourier maps and were inserted into the refinement. The O (donor) – H distances were softly constrained to be close to 0.98 Å, *e.g.*, Cooper & Hawthorne (1995), and the H–H distances were softly constrained to be close to 1.59 Å during refinement. The refined coordinates and displacement parameters of the atoms are listed in Table 2, selected interatomic distances and angles are given in Table 3, and bond valences (Brown & Altermatt 1985) are given in Table 4. A table of structure factors is available from the Depository of Unpublished Data on the MAC website [document Burgessite CM47\_165].

TABLE 1. MISCELLANEOUS INFORMATION ABOUT BURGESSITE AND THE REFINEMENT OF ITS STRUCTURE

<i>a</i> (Å)	4.7058(12)	size of crystal (µm)	7 × 14 × 40
<i>b</i>	9.299(3)	radiation, monochromator	MoK $\alpha$ , graphite
<i>c</i>	12.738(4)	No. of reflections	4012
$\beta$ (°)	98.933(8)	No. in Ewald sphere	2353
<i>V</i> (Å <sup>3</sup> )	550.6(5)	No. unique reflections	711
<i>Z</i>	2	No. $ F_o  > 5\sigma F $	494
Space group	$P2_1/n$	$R_{\text{neg}}$ %	7.1
		$R_{\text{obs}}$ %	4.3
		$wR_{\text{obs}}$ %	4.8
Cell content	2 $[\text{Co}_2(\text{H}_2\text{O})_4[\text{AsO}_3(\text{OH})]_2(\text{H}_2\text{O})]$		
$R = \Sigma( F_o  -  F_c ) / \Sigma F_o $	$wR = [\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o^2]^{1/2}$ , $w = 1$		
Goof	2.97		

TABLE 2. COORDINATES AND DISPLACEMENT PARAMETERS (Å<sup>2</sup>) OF ATOMS IN BURGESSITE

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{0q}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
As	0.4837(3)	0.18791(16)	0.03248(12)	0.0148(5)	0.0124(8)	0.0150(8)	0.0178(9)	0.0008(8)	0.0043(6)	0.0007(8)
Co	0.4498(4)	0.4601(2)	0.37868(16)	0.0170(7)	0.0138(11)	0.0195(12)	0.0183(11)	−0.0019(11)	0.0043(9)	0.0004(9)
O(1)	0.148(2)	0.6329(11)	0.3589(7)	0.019(3)	0.017(6)	0.025(6)	0.015(5)	−0.006(5)	0.004(4)	0.005(5)
O(2)	0.2812(19)	0.4083(10)	0.5168(7)	0.014(3)	0.016(6)	0.010(6)	0.017(5)	−0.006(4)	0.002(4)	0.007(4)
O(3)	0.7590(19)	0.2968(11)	0.4195(7)	0.019(3)	0.012(5)	0.027(7)	0.017(5)	−0.006(5)	0.003(4)	0.007(5)
O(4)(OH)	0.600(3)	0.3615(11)	0.0676(9)	0.031(4)	0.048(7)	0.015(6)	0.033(6)	−0.005(5)	0.011(5)	−0.006(5)
O(5)(H <sub>2</sub> O)	0.627(2)	0.5311(12)	0.2488(8)	0.019(3)	0.017(5)	0.025(6)	0.016(6)	−0.004(5)	0.007(5)	−0.000(5)
O(6)(H <sub>2</sub> O)	0.170(2)	0.3317(12)	0.2767(8)	0.023(4)	0.018(6)	0.023(6)	0.027(6)	−0.004(6)	0.006(5)	−0.006(5)
O(7)(H <sub>2</sub> O)	0.444(5)	0.052(2)	0.4278(17)	0.031(6)						
H(1)	0.64(2)	0.470(14)	0.186(7)	0.03(2)*						
H(2)	0.818(13)	0.573(15)	0.271(10)	0.03(2)*						
H(3)	0.04(3)	0.270(10)	0.312(10)	0.03(2)*						
H(4)	0.26(3)	0.272(11)	0.228(9)	0.03(2)*						

\* constrained to be equal during the refinement.

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

Co–O(1)	2.132(10)	As–O(1)b	1.682(10)		
Co–O(2)	2.095(10)	As–O(2)c	1.699(10)		
Co–O(2)a	2.086(9)	As–O(3)d	1.655(9)		
Co–O(3)	2.112(10)	As–O(4)	1.740(10)		
Co–O(5)	2.074(11)	<As–O>	1.694		
Co–O(6)	2.078(10)				
<Co–O>	2.096				
O(5)–H(1)	0.98(11)	H(1)...O(4)	1.81(10)	O(5)...O(4)	2.781(15)
O(5)–H(2)	0.98(7)	H(2)...O(1)e	1.85(9)	O(5)...O(1)e	2.795(13)
H(1)–O(5)–H(2)	108(10)	O(5)–H(1)–O(4)	173(7)	O(5)–H(2)–O(1)e	160(10)
O(6)–H(3)	0.98(12)	H(3)...O(3)f	2.08(13)	O(6)...O(3)f	2.869(15)
O(6)–H(4)	0.98(12)	H(4)...O(1)b	1.80(11)	O(6)...O(1)b	2.756(15)
H(3)–O(6)–H(4)	108(9)	O(6)–H(3)–O(3)f	137(8)	O(6)–H(4)–O(1)b	165(9)
O(7)...O(5)b	3.23(2)	O(5)b–O(7)–O(3)	114.9(8)		
O(7)...O(6)b	3.29(2)	O(6)b–O(7)–O(3)	120.7(8)		
O(7)...O(3)	2.73(3)				
O(4)...O(7)g	2.71(3)				
O(4)...O(7)h	2.78(3)				

a:  $\bar{x} + 1, \bar{y} + 1, \bar{z} + 1$ ; b:  $\bar{x} + \frac{1}{2}, \bar{y} - \frac{1}{2}, \bar{z} + \frac{1}{2}$ ; c:  $\bar{x} + 1, \bar{y} + \frac{1}{2}, \bar{z} - \frac{1}{2}$ ; d:  $\bar{x} - \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} - \frac{1}{2}$ ; e:  $\bar{x} + 1, \bar{y}, \bar{z}$ ; f:  $\bar{x} - 1, \bar{y}, \bar{z}$ ; g:  $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} - \frac{1}{2}$ ; h:  $\bar{x} + 1\frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$ .

TABLE 4. BOND-VALENCE\* ( $\nu u$ ) TABLE FOR BURGESSITE

	Co	As	$\Sigma$	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	$\Sigma$
O(1)	0.30	1.26	1.56		0.20		0.20				1.96
O(2)	0.34	1.20	1.88								1.88
	0.34										
O(3)	0.32	1.35	1.67			0.10			0.20 <sup>1/2</sup> –		1.87
O(4)	1.08	1.08	1.08	0.20	0.80					0.80	2.08
O(5)	0.36	0.36	0.80	0.80				0.05 <sup>1/2</sup> –			1.99
O(6)	0.35	0.35				0.90	0.80	0.05 <sup>1/2</sup> –			2.08
O(7)		0.00						0.90	0.80	0.20 <sup>2</sup> –	2.10
	2.01	4.89		1.00	1.00	1.00	1.00	1.00	1.00	1.00	

\* parameters from Brown & Altermatt (1985).

## CRYSTAL STRUCTURE

### Coordination of cations

There is one As site completely occupied by As and coordinated by a tetrahedral arrangement of anions with a <As– $\Phi$ > distance ( $\Phi$  represents O, OH) of 1.694 Å, typical for tetrahedrally coordinated As<sup>5+</sup>. There is one Co site occupied dominantly by Co and coordinated by an octahedral arrangement of four O atoms and two (H<sub>2</sub>O) groups. The chemical composition determined by electron-microprobe analysis (Sejkora *et al.* 2009) indicates a mean Co-site composition of Co<sub>0.875</sub>Ni<sub>0.125</sub>. Summing the constituent cation and

anion radii (Shannon 1976) gives a prediction for the <Co–O> distance of 2.095 Å, in close agreement with the observed value of 2.096 Å (Table 3).

### Anion identities and hydrogen bonding

There are seven crystallographically distinct anions, O(1)–O(7). Inspection of the bond-valence table (Table 4) shows that O(4) is an (OH) group and that O(5), O(6) and O(7) are (H<sub>2</sub>O) groups, in accord with the stereochemistry of the H atoms located at the final stages of refinement. In addition to being an (OH) group, O(4) also bonds to As<sup>5+</sup>, forming an acid arsenate group: (AsO<sub>3</sub>OH). The O(7) site is disordered off the center

of symmetry at  $(\frac{1}{2} 0 \frac{1}{2})$  and is half-occupied, with an O(7)–O(7) distance of 2.07(4) Å. Details of the hydrogen bonds are given in Table 3 and are described below. The H(1) atom forms a hydrogen bond to O(4), the acid anion of the arsenate group (Table 4), H(4) forms a hydrogen bond to O(1), which also accepts a hydrogen bond from H(2), and H(3) forms a hydrogen bond to O(3). Three additional H sites could not be found, but the bond valence incident at O(4) and O(7) indicates that these anions must be (OH) and (H<sub>2</sub>O), respectively; these H atoms are labeled H(5), H(6) and H(7) in Table 4. From the local stereochemistry and the bond valence incident at adjacent anions, it is apparent that the H atom attached to O(4) forms a hydrogen bond with O(7), and the H atoms of the (H<sub>2</sub>O) group at O(7) form a hydrogen bond to O(3) and a bifurcated hydrogen bond to O(5) and O(6).

### Bond topology

Pairs of adjacent CoΦ<sub>6</sub> octahedra (Φ represents an unspecified anion) share an edge to form a [Co<sub>2</sub>Φ<sub>10</sub>] dimer, and AsΦ<sub>4</sub> tetrahedra link pairs of vertices in the adjacent octahedra to form a compact [Co<sub>2</sub>(AsΦ<sub>4</sub>)<sub>2</sub>Φ<sub>6</sub>] cluster (Fig. 1a). This cluster is one of four predicted by Hawthorne (1983) to be the most stable of the (twenty-eight completely connected) graphical and geometrical isomers of the form [L<sup>6</sup>M<sub>2</sub>(L<sup>4</sup>TΦ<sub>4</sub>)Φ<sub>n</sub>]. In burgessite, these clusters polymerize in the *a* direction through linkage of tetrahedron vertices to the shared edge of two octahedra of each adjacent cluster to form

a chain of the form [Co<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>[As<sup>5+</sup>O<sub>3</sub>(OH)]<sub>2</sub>] (Figs. 1b, c). These chains extend in the [100] direction and occur at the vertices of an orthorhombic net (Fig. 2). They are linked into a three-dimensional structure by hydrogen bonds that involve (OH) bonded to As<sup>5+</sup>, (H<sub>2</sub>O) bonded to Co, and (H<sub>2</sub>O) held in the structure solely by hydrogen bonds.

### Related structures

Burgessite is not isostructural with any other mineral or inorganic compound; however, it is chemically similar to erythrite Co<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>8</sub> (Wildner *et al.* 1996, Capitelli *et al.* 2007). Both erythrite and burgessite contain chains of the form [Co<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(AsΦ<sub>4</sub>)<sub>2</sub>]; these differ only in the composition of the oxyanion of the (AsΦ<sub>4</sub>) group that does not share a vertex with a Co octahedron of the [Co<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(AsΦ<sub>4</sub>)<sub>2</sub>] chain: O in erythrite (Fig. 3a), and (OH) in burgessite (Fig. 3b). The [Co<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(AsΦ<sub>4</sub>)<sub>2</sub>] chains are parallel to [001] in erythrite and [100] in burgessite, and the corresponding unit-cell translations in these directions are 4.76 and 4.71 Å, respectively (Wildner *et al.* 1996, Table 1). In erythrite, the [Co<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(AsO<sub>4</sub>)<sub>2</sub>] chains are connected at the outward-projecting vertices of the (AsO<sub>4</sub>) groups, which share corners with the Co(H<sub>2</sub>O)<sub>4</sub>O<sub>2</sub> octahedra (Fig. 4a), forming a (010) sheet of composition [Co<sub>3</sub>(H<sub>2</sub>O)<sub>8</sub>(AsO<sub>4</sub>)<sub>2</sub>]. These sheets are linked into a three-dimensional structure by hydrogen bonding in the [010] direction.

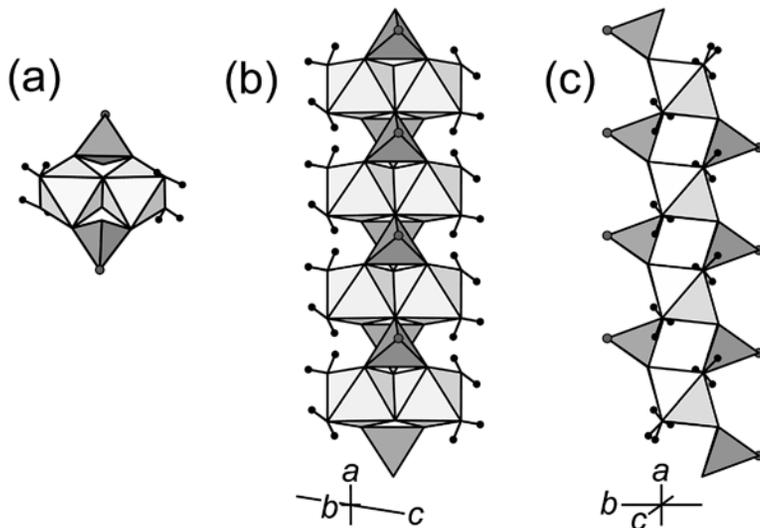


FIG. 1. Polyhedron linkages in the crystal structure of burgessite. (a) The [Co<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>O<sub>2</sub>(AsΦ<sub>4</sub>)<sub>2</sub>] cluster. Shown in (b), (c) are oblique views of the [Co<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(As<sup>5+</sup>O<sub>3</sub>(OH))<sub>2</sub>] chain. Convention: (AsΦ<sub>4</sub>) tetrahedra: dark grey, (CoΦ<sub>6</sub>) octahedra: pale grey, (OH) group: dark grey circle, and H atoms: black circles. The O<sub>donor</sub>–H bonds are shown as solid black lines.

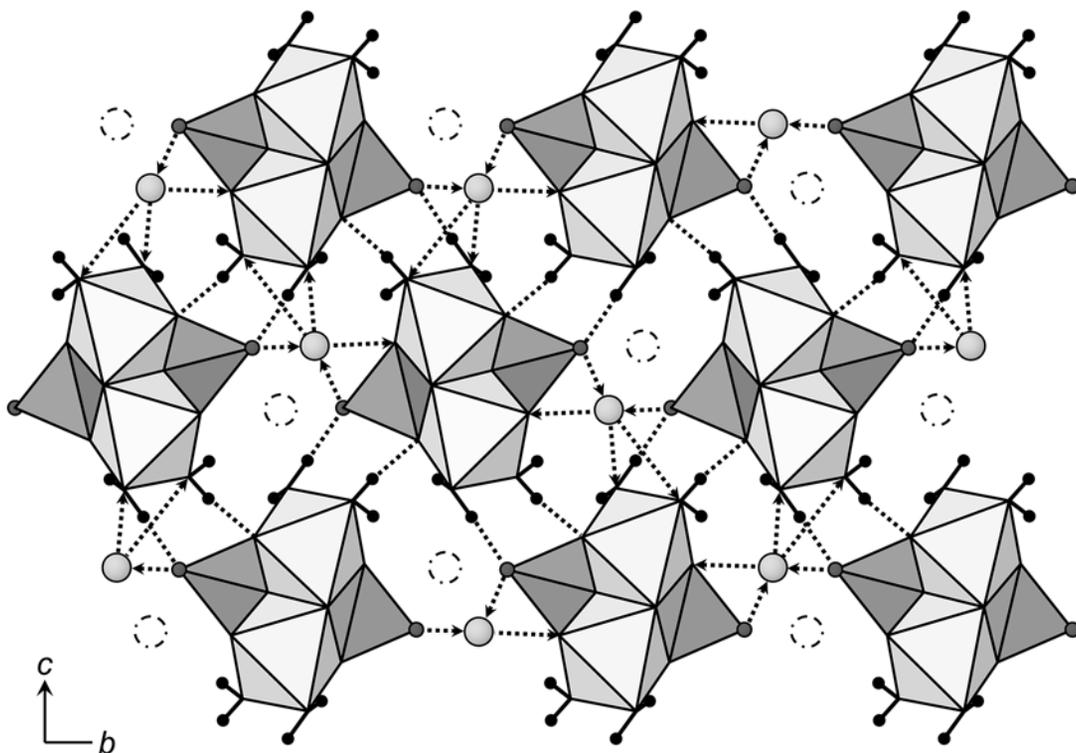


FIG. 2. The crystal structure of burgessite projected down [100]; legend as in Figure 1, plus interstitial ( $\text{H}_2\text{O}$ ) groups: large light grey circle; occupied, large dashed circle: vacancy. Hydrogen bonds are shown as dotted lines. Note: only the interchain H-bonds are shown, and the pattern of local ( $\text{H}_2\text{O}$ ) occupation is arbitrary.

A conceptual transformation of erythrite to burgessite is shown in Figures 4 and 5. Hydroxylation of the ( $\text{AsO}_4$ ) group in erythrite is accompanied by loss of interchain  $\text{Co}(\text{H}_2\text{O})_3$  components (Figs. 4b, 5b). The transformation begins with an “attack” on the Co–O–As link between the  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{AsO}_4)_2]$  chains and the intervening  $[\text{Co}(\text{H}_2\text{O})_4\text{O}_2]$  octahedra (Figs. 4a, 5a), giving rise to  $[\text{AsO}_3(\text{OH})]$  groups, and a net loss of interchain  $\text{Co}(\text{H}_2\text{O})_3$ , with retention of one ( $\text{H}_2\text{O}$ ) group (Figs. 4b, 5b). The net chemical reaction is: erythrite + 2  $\text{H}^+$   $\rightarrow$  burgessite +  $\text{Co}(\text{H}_2\text{O})_3$ . This exchange is accompanied by coupled rotation and lateral offset of neighboring  $[\text{Co}_2(\text{H}_2\text{O})_4[\text{AsO}_3(\text{OH})_2]]$  chains (Figs. 4b, 5b). In addition to the lateral shift in chains shown in Figure 5b (*i.e.*, relative to [001] in erythrite), there is an additional offset between neighboring chains that is perpendicular to the first shift, *cf.* the  $\beta$  angles in erythrite (Fig. 5a) and burgessite (Fig. 5c). Finally, the interstitial ( $\text{H}_2\text{O}$ ) group in burgessite assumes one of two equally likely positions equidistant from the neighboring (OH) groups that are involved in mutual hydrogen-bonding (Figs. 4c, 5c). The net geometrical change associated with the erythrite  $\rightarrow$  burgessite trans-

formation is a 13% reduction in cell volume, resulting from contraction of the interchain region.

#### *Connectivity details in erythrite and burgessite*

A comparison of the erythrite and burgessite structures reveals key differences in the linkage between the  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chains, in particular the anion of the ( $\text{As}\Phi_4$ ) group that projects outward from the  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chain. In erythrite, bond-valence requirements of this O(1) anion are satisfied by (1) a strong bond (0.40 *vu*) from the interchain Co(1) atom, and (2) two hydrogen bonds (0.20 *vu* each) from the H(1) atoms of two ( $\text{H}_2\text{O}$ ) groups [O(4)] from an adjacent interchain Co(1) octahedron (Table 5, Figs. 4a, 5a). In burgessite, the bond-valence requirements of the O(4) anion are satisfied by (1) an attached H(7) atom (0.80 *vu*), and (2) a hydrogen bond (0.20 *vu*) from the H(1) atom of an ( $\text{H}_2\text{O}$ ) group [O(5)] from an adjacent chain (Table 4, Fig. 4c). In both structures, ( $\text{H}_2\text{O}$ ) groups along the outer margins of the chain hydrogen-bond to shared octahedron–tetrahedron vertices within the chain (Fig. 3, Tables 4, 5). The O(2) anions near the

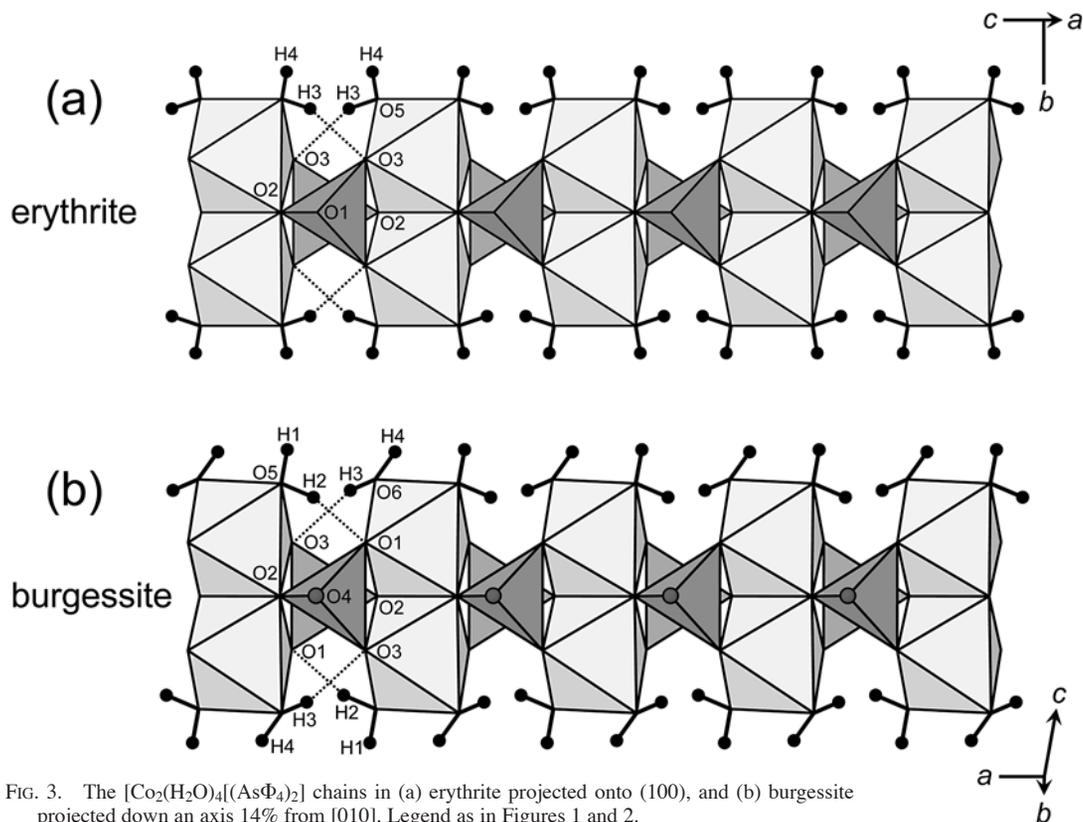


FIG. 3. The  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chains in (a) erythrite projected onto (100), and (b) burgessite projected down an axis 14% from [010]. Legend as in Figures 1 and 2.

TABLE 5. BOND-VALENCE ( $\nu v$ ) TABLE FOR ERYTHRITE\*

	Co(1)	Co(2)	As	$\Sigma$	H(1)	H(2)	H(3)	H(4)	$\Sigma$
O(1)	0.40 <sup>+2</sup>		1.15	1.55	0.20 <sup>+2</sup>				1.95
O(2)		0.33 <sup>+2-1</sup>	1.25	1.91					1.91
O(3)		0.33 <sup>+2</sup>	1.23 <sup>+2</sup>	1.56		0.20	0.20		1.96
O(4)	0.28 <sup>+4</sup>			0.28	0.80	0.80		0.10	1.98
O(5)		0.32 <sup>+2</sup>		0.32			0.80	0.90	2.02
	1.92	1.96	4.86		1.00	1.00	1.00	1.00	

Note: Relabeling of sites: O(4) = OW(1), O(5) = OW(2), H(1) = H(11), H(2) = H(12), H(3) = H(21), H(4) = H(22). \* from the structure-refinement results of Wildner *et al.* (1996).

central axis of the chains bond to one As and two Co cations, and their bond-valence requirements are satisfied in the same way in both structures (Fig. 3, Tables 4, 5). In erythrite, the O(3) anion receives an intrachain hydrogen bond from H(3) (Fig. 3a), and a hydrogen bond from the H(2) atom belonging to an (H<sub>2</sub>O) group of the linking Co(1) octahedron (Fig. 5a). In burgessite, the analogous anions are O(1) and O(3). In addition to the intrachain hydrogen bond from H(2) (Fig. 3b), O(1)

also receives a hydrogen bond from H(4) belonging to an (H<sub>2</sub>O) group from a neighboring chain (Fig. 4c). In addition to the intrachain hydrogen bond from H(3) (Fig. 3b), O(3) also receives a hydrogen bond from the half-occupied H(6) that belongs to the interstitial (H<sub>2</sub>O) group at O(7) (Fig. 4c).

The As–O(3) bond in burgessite is somewhat shorter than the As–O(3) bond in erythrite; this shortening occurs in response to a local bond-valence deficiency at O(3), where the neighboring interstitial (H<sub>2</sub>O) group is absent (Fig. 4c). The (H<sub>2</sub>O) group at O(5) belongs to the  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chain in erythrite and does not receive any hydrogen bonds (Table 5), whereas its counterpart [O(5),O(6)] in burgessite receives a weak bifurcated hydrogen-bond from H(5) of the interstitial O(7) (H<sub>2</sub>O) group (50% of the time) (Fig. 4c).

Hydrogen bonds are directed outward from the  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chains from the flanking (H<sub>2</sub>O) groups in a different manner in erythrite and burgessite. In erythrite, H(4) forms a hydrogen bond to the O(4) (H<sub>2</sub>O) group of the interchain Co(1) octahedron (Fig. 4a). In burgessite, the analogous H atoms, H(1) and H(4), form hydrogen bonds with O(1) and O(4) in adjacent chains (Fig. 4c). In burgessite, there is an

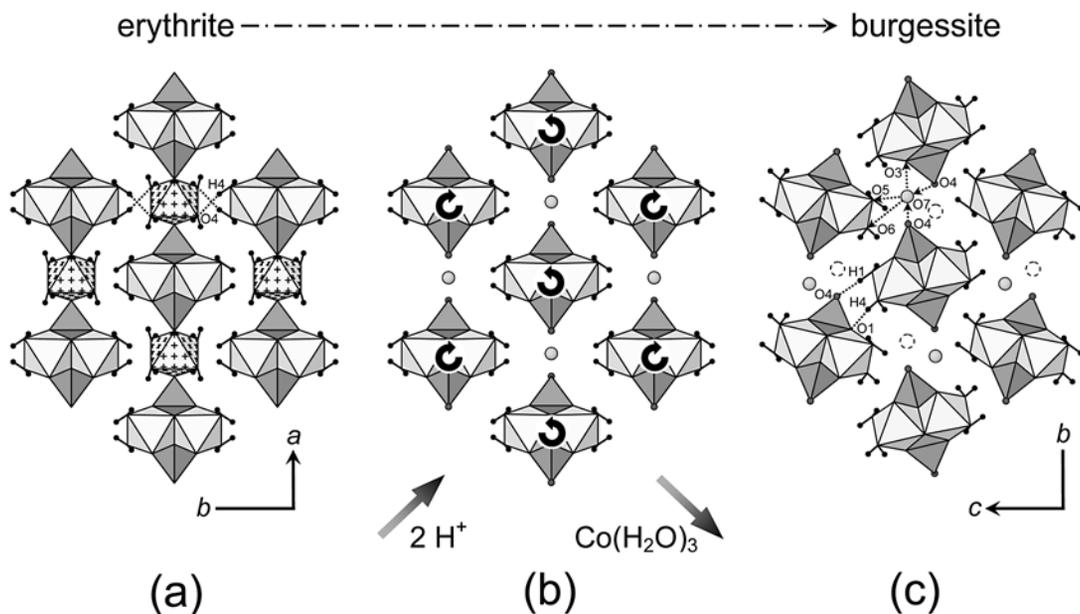


FIG. 4. Graphical transformation from (a) erythrite projected down  $[001]$ , to (c) burgessite projected down  $[100]$ , looking down the  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chains. Legend as in Figures 1 and 2; grey shaded octahedron with crosses:  $\text{Co}(1)$  octahedron in erythrite. Grey to black shaded straight arrows show movement of chemical constituents. Black curved arrows show relative rotation of  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chains.

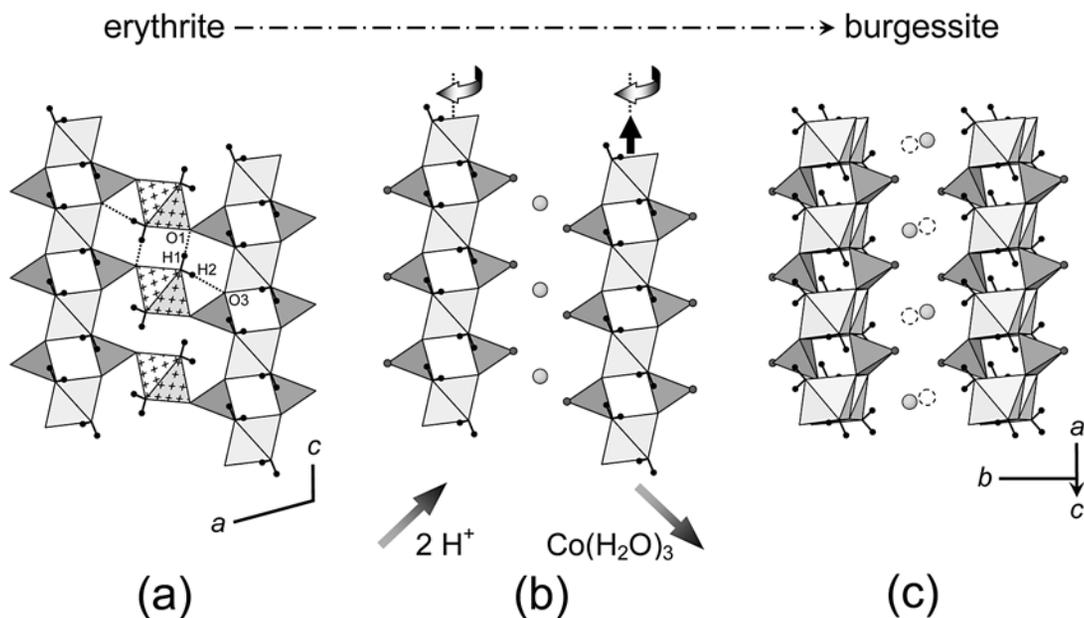


FIG. 5. Graphical transformation of (a) erythrite projected down  $[010]$ , to (c) burgessite projected onto  $(010)$ , looking onto two neighboring  $[\text{Co}_2(\text{H}_2\text{O})_4(\text{As}\Phi_4)_2]$  chains positioned to show the interchain region in the vicinity of the  $(\text{As}\Phi_4)$  vertex that projects outward from the chain. Legend as in Figures 1, 2, and 4, with black straight arrow showing chain translation, and the grey to black shaded curved arrow showing the relative rotation of the chains.

additional hydrogen-bond from the H(7) proton of the (OH) group at O(4) to the (H<sub>2</sub>O) group occupying one (of two possible) adjacent O(7) sites (Fig. 4c). We noted above that the H atoms associated with the (OH) group and the interstitial (H<sub>2</sub>O) group could not be located in the difference-Fourier map; this can be attributed to the positional disorder that must occur at these H positions in relation to the disorder present at the O(7) position.

Burgessite and erythrite occur together at the Keeley mine and are very similar in appearance, but are easily distinguished by their powder-diffraction patterns. Their close paragenetic and structural association leads us to suggest that careful inspection of "erythrite" samples from this and other localities will likely lead to further discoveries of burgessite.

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