

FRANKHAWTHORNEITE, A UNIQUE HCP FRAMEWORK STRUCTURE OF A CUPRIC TELLURATE¹

JOEL D. GRICE

Research Division, Canadian Museum of Nature, P.O. Box 3443, Station "D", Ottawa, Ontario K1P 6P4

ANDREW C. ROBERTS

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8

ABSTRACT

The crystal structure of frankhawthorneite, $\text{Cu}_2^{2+}\text{Te}^{6+}\text{O}_4(\text{OH})_2$, has been determined and refined to indices $R = 5.4$ and $R_w = 4.6\%$. The structure is monoclinic $P2_1/n$ (14), with cell parameters a 9.107(4), b 5.213(1), c 4.605(2) Å, β 98.74(3)°, V 216.1(1) Å³, and with $Z = 2$. The structure analysis was essential in determining the valence state of Cu^{2+} and Te^{6+} and the number of O^{2-} and $(\text{OH})^-$ anions in the formula. The crystal structure consists of a framework of edge-sharing octahedra. In the hexagonal closest packed (HCP) array of anions, one-half of the octahedrally coordinated sites are filled. The unique topology of the filled cation sites gives rise to a ribbon of alternating single $[\text{TeO}_4(\text{OH})_2]^{2-}$ and double $[\text{CuO}_4(\text{OH})_2]^{8-}$ octahedra.

Keywords: frankhawthorneite, crystal structure, tellurate, cupric, hexagonal closest packing.

SOMMAIRE

Nous avons résolu la structure cristalline de la frankhawthorneïte, $\text{Cu}_2^{2+}\text{Te}^{6+}\text{O}_4(\text{OH})_2$, jusqu'à un résidu R de 5.4% ($R_w = 4.6\%$). Il s'agit d'une structure monoclinique, $P2_1/n$ (14), ayant comme paramètres réticulaires a 9.107(4), b 5.213(1), c 4.605(2) Å, β 98.74(3)°, V 216.1(1) Å³, avec $Z = 2$. L'ébauche de la structure cristalline a été nécessaire pour établir la présence du Cu et du Te à l'état 2+ et 6+, respectivement, et le nombre de O^{2-} et de $(\text{OH})^-$ dans la formule chimique. La structure est constituée d'une trame d'octaèdres dont les arêtes sont partagées. Dans l'assemblage hexagonal compact des anions, la moitié des sites à coordinence octaédrique est occupée. La topologie unique des sites occupés par les cations définit un ruban le long duquel il y a alternance d'un seul octaèdre $[\text{TeO}_4(\text{OH})_2]^{2-}$ et de deux octaèdres $[\text{CuO}_4(\text{OH})_2]^{8-}$.

(Traduit par la Rédaction)

Mots-clés: frankhawthorneïte, structure cristalline, tellurate, cuprique, assemblage hexagonal compact.

INTRODUCTION

Frankhawthorneite, described by Roberts *et al.* (1995) from the Centennial Eureka mine, Juab County, Utah, is one of several Cu-bearing tellurates that occur in this deposit (Marty *et al.* 1993). The small amount of material available precluded standard chemical analytical techniques capable of differentiating the valence states of Cu and Te and the determination of H_2O ; the structure-analysis method (Hawthorne & Grice 1990) established these quantities; the formula is $\text{Cu}_2^{2+}\text{Te}^{6+}\text{O}_4(\text{OH})_2$.

EXPERIMENTAL

The single crystal of frankhawthorneite used for the collection of intensity data (cotype material with National Mineral Collection of Canada Systematic Reference Series, catalogue number NMC 67263) is a roughly equant fragment that measures $0.03 \times 0.04 \times 0.06$ mm. Single-crystal precession photographs yielded a unique space-group, $P2_1/n$ (14) (monoclinic), based on systematic absences of reflections. The cell orientation is consistent with $c < a$ (Roberts *et al.* 1995), which leads to the less conventional space-group for this set of systematic absences. Intensity data were collected on a fully automated Nicolet R3m four-circle diffractometer operated at 50 kV, 40 mA, with graphite-monochromated $\text{MoK}\alpha$ radiation. A set of

¹ Geological Survey of Canada contribution number 30294.

TABLE 1. DATA COLLECTION SUMMARY FOR FRANKHAWTHORNEITE

Space Group	F_2/m (14)	Unique reflections	631
<i>a</i> (Å)	9.107(4)	Observed reflections [$>5\sigma(F)$]	485
<i>b</i> (Å)	5.213(1)	Minimum transmission	0.321
<i>c</i> (Å)	4.805(2)	Maximum transmission	0.452
β (°)	98.74(3)	<i>R</i> (%)	5.4
<i>V</i> (Å ³)	216.1(1)	<i>R_w</i> (%)	4.6
<i>Z</i>	2	<i>S</i>	2.14
μ (mm ⁻¹)	16.5	$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	$w = [(\sigma^2(F_o))]^{-1}$

20 reflections was used to orient the crystal and subsequently to refine the cell dimensions. One asymmetric set of intensity data was collected up to $2\theta = 60^\circ$ using a $\theta:2\theta$ scanning mode, with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. Data pertinent to the intensity-data collection are given in Table 1.

Reduction of the intensity data, structure determination and structure refinement were accomplished by means of the SHELXTL (Sheldrick 1990) package of computer programs. Data reduction included correction for background, scaling, Lorentz and polarization and linear absorption. For the absorption correction, 11 intense diffraction-maxima in the range 7 to 54° 2θ were chosen for ψ diffraction-vector scans after the method of North *et al.* (1968). An absorption correction, when applied to the ψ -scan data set, decreased the merging *R* from 6.1% to 3.3%.

CRYSTAL-STRUCTURE ANALYSIS

Assignment of phases to a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.922, indicative of a centrosymmetric space-group. The *E*-map coordinates were assigned to appropriate scattering curves, one Cu, one Te and three O atoms. This structure model refined to *R* = 8.3%.

In the final least-squares refinement, the sites of all atoms were refined with anisotropic displacement-factors to final residuals of *R* = 5.4% and *R_w* = 4.6%. The weighting scheme is inversely proportional to

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR FRANKHAWTHORNEITE

Cu octahedron			
Cu - O1	2.522(10)	O1 - O2	170.8(3)
Cu - O2A	2.463(9)	O1' - O3	172.6(5)
Cu - O1A	1.940(9)	O2' - O3'	166.2(4)
Cu - O2E	2.056(9)	O1 - O1'	87.0(4)
Cu - O3	1.944(9)	O1 - O2'	72.3(3)
Cu - O3B	1.970(9)	O1 - O3	86.1(4)
		O1 - O3'	96.8(4)
Te octahedron			
Te - O1	1.916(9) x 2	O1 - O2	86.8(4)
Te - O2	1.988(9) x 2	O1 - O3	96.9(4)
Te - O3	1.912(10) x 2	O2' - O3'	89.5(4)
		O1 - O1'	180
O - O distances			
O2 - O1	2.82(1)	O2 - O3	3.16(1)
O2 - O3'	3.21(1)		

O2 is an OH anion

$\sigma^2(F)$. The addition of an isotropic extinction-correction did not improve the refinement. The final positional and displacement parameters are given in Table 2, and selected bond-lengths and angles, in Table 3. A table listing the observed and calculated structure-factors has been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The analysis of the structure of frankhawthorneite permitted the calculation of bond-valence sums for the various atomic sites based on the constants of Brese & O'Keeffe (1991). The sums are: Cu atom 2.02, Te atom 5.68, O1 atom 1.62, O2 atom 1.31 and O3 atom 1.96 *v.u.* These calculations allow the assignment of the correct valence to the cations Cu²⁺ and Te⁶⁺ and to the recognition of O2 as an OH anion. The resultant

TABLE 2. POSITIONAL AND THERMAL PARAMETERS (X100, Å²) FOR FRANKHAWTHORNEITE

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{eq}
Cu	0.1780(2)	0.5352(3)	-0.002(3)	1.15(9)	0.50(7)	1.01(8)	-0.08(6)	-0.20(6)	0.18(7)	0.83(6)
Te	0	0	0	0.89(9)	0.48(8)	0.42(8)	-0.08(6)	0.01(4)	0.08(6)	0.81(3)
O1	-0.012(1)	0.297(2)	0.241(2)	0.8(4)	0.9(4)	0.7(4)	0.2(3)	-0.1(4)	-0.1(4)	0.8(3)
O2*	0.828(1)	0.299(2)	0.289(2)	0.7(4)	0.9(4)	0.5(4)	0.2(3)	0.1(4)	0.1(3)	0.7(2)
O3	0.328(1)	0.356(2)	0.275(2)	1.3(5)	0.5(4)	0.7(4)	0.3(3)	-0.2(4)	0.2(4)	0.9(3)

*O2 is an OH anion

Temperature factors are of the form: $\exp [-2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + \dots + 2U_{12}hka^2b^2)]$

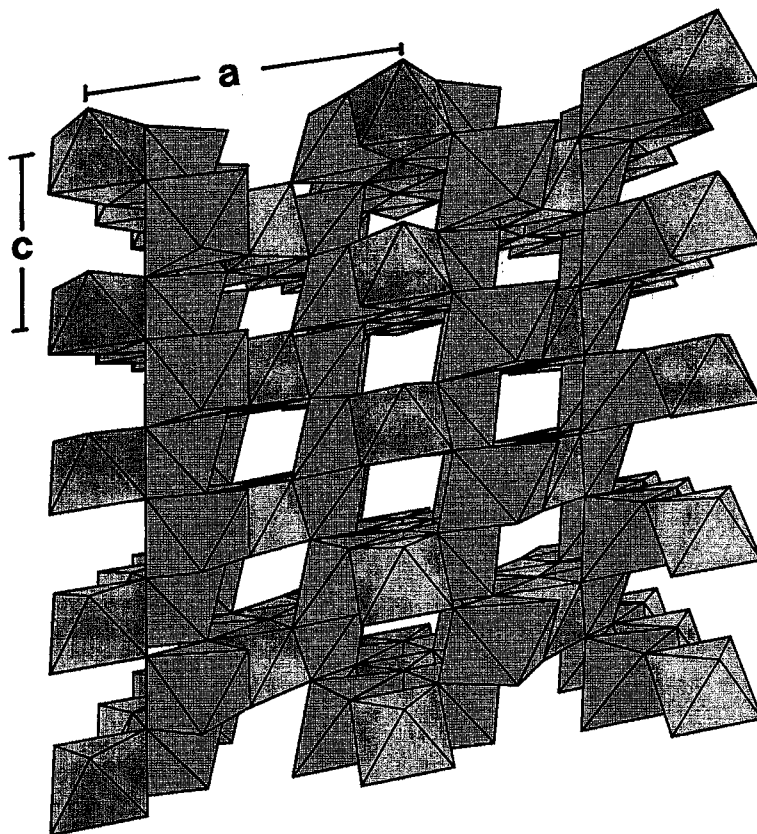


FIG. 1. A y -axis perspective view of the frankhawthorneite structure showing the infinite framework of edge-sharing $[\text{Cu}\phi_6]$ octahedra (light shading) and $[\text{Te}\phi_6]$ octahedra (dark shading).

simplest formula for frankhawthorneite is $\text{Cu}_2^{2+}\text{Te}^{6+}\text{O}_4(\text{OH})_2$, with $Z = 2$. The low bond-valence sum of O1 is due to H-bonding to O2, with an intrapolyhedral O1 – O2 bond-distance of 2.62(1) Å. In the structure, there is only one unique $[\text{CuO}_4(\text{OH})_2]$ octahedron, subsequently designated $[\text{Cu}\phi_6]$, and one unique $[\text{TeO}_4(\text{OH})_2]$ octahedron, subsequently designated $[\text{Te}\phi_6]$. From Table 3 and Figures 1 and 2, it can be seen that both of these polyhedra are distorted from regular octahedral symmetry. The Jahn–Teller effect on the Cu^{2+} cation is evident, with the elongate axis having bond lengths Cu–O1 of 2.52 Å and Cu–O2 of 2.46 Å, in comparison to the average of 1.98 Å for the other four Cu– ϕ bonds. The $[\text{Te}\phi_6]$ octahedron also has one elongate axis (Table 3), with the two Te–O2 [O2 is an $(\text{OH})^-$ anion] bond lengths of 1.99 Å in comparison to the average Te–O of 1.91 Å for the other four bond-lengths. The relevance of these distorted octahedra to the unique topology will be discussed later.

The crystal structure of frankhawthorneite may be described as a three-dimensional framework of stacked $[\text{Cu}\phi_6]$ and $[\text{Te}\phi_6]$ octahedra with square, open channels parallel to the y axis (Fig. 1). Each layer within the sequence parallel to $\{001\}$ consists of ribbons of edge-sharing octahedra, with a $[\text{Te}\phi_6]$ octahedron alternating with a doublet of $[\text{Cu}\phi_6]$ octahedra (Fig. 2). This type of ribbon is that observed in the crystal structures of the kotoite group of minerals and lindgrenite (Hawthorne 1986), in which adjacent ribbons are cross-linked by (BO_3) triangles and (MoO_4) tetrahedra, respectively. In contrast, the ribbons, which parallel the y axis in frankhawthorneite, are not cross-linked within the same plane but are alternately stacked *via* corner-sharing of octahedra in adjacent layers ...*ABAB*... This layering scheme of O atoms (Fig. 2) is that of hexagonal closest packing (HCP), although it is somewhat distorted by Jahn–Teller effects and by H-bonding. Although the

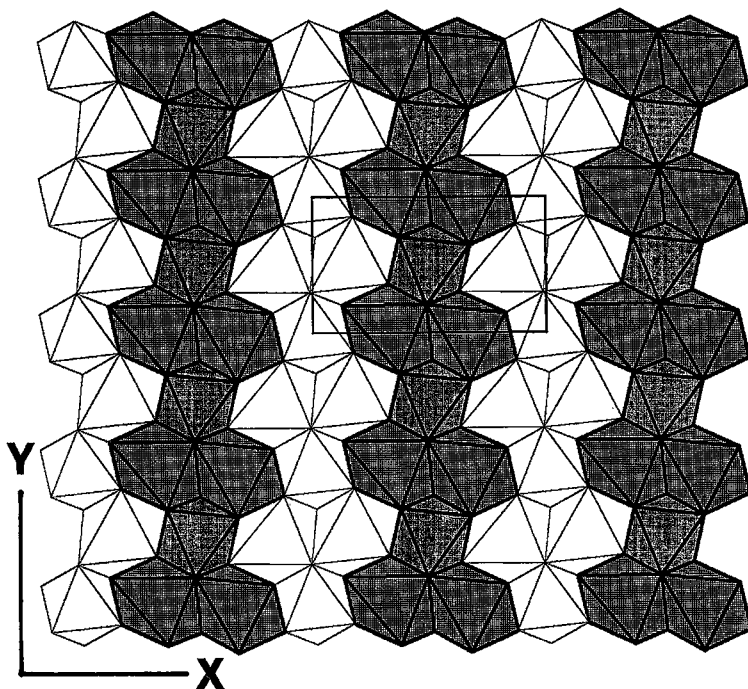


Fig. 2. The {001} HCP layering in the frankhawthorneite structure, with upper and lower layers differentiated by light and heavy ruling of polyhedra. In the upper layer, the ribbons of $[\text{Cu}\phi_6]$ octahedra (light shading) and $[\text{Te}\phi_6]$ octahedra (dark shading) are seen. The unit cell is outlined.

O atoms are in HCP, one-half of the octahedrally coordinated cation sites are vacant. These regions of the structure with cation vacancies become the loci for the H atoms. Even though the structure refinement did not yield the sites of the H atoms, they are inferred to occupy the tetrahedrally coordinated site of the HCP layer.

Eby & Hawthorne (1993) classified this type of copper oxysalt mineral structure as an infinite framework $M = M$, where M denotes octahedrally coordinated cations, and the double hyphen denotes edge sharing. One of the most interesting features of the structure is the apparent uniqueness of the topology of the ribbons of octahedrally coordinated cations.

Frankhawthorneite, $\text{Cu}_2\text{TeO}_4(\text{OH})_2$, is a mineral with a formula of the type AB_2X_6 or, in terms of octahedrally coordinated cations and ions, it is of the type MX_2 . Wells (1975) listed six structure-types for MX_2 compounds having an HCP arrangement and one-half the octahedral sites occupied. Within these six types, four are topologically unique, whereas the other two are derivative structures.

The brucite structure-type has alternating (0001) layers entirely filled or entirely empty of cations in the octahedrally coordinated sites. In the "vacant site"

layers, H occupies the tetrahedral sites and bonds the layers together. The rutile structure-type (Fig. 3a) is a framework structure with alternate rows of cation sites occupied in each layer; this gives a characteristic linear edge-sharing ribbon. The third structure-type common in inorganic materials is that of $\alpha\text{-PbO}_2$ (Fig. 3b), which has cations in octahedral coordination occupying alternate rows in a zigzag ribbon. The fourth structure-type, diaspore, $\alpha\text{-AlO}(\text{OH})$, has straight, edge-sharing octahedra in ribbons of double width (Fig. 3c). A comparison of the three framework structures in Figure 3 with that of frankhawthorneite (Fig. 2) shows that the cation-filling arrangement of frankhawthorneite is distinct. The shift in topology is brought about by the elongate distortions of the octahedra. There is not sufficient space to accommodate all octahedra on one plane; as a result, the axes of elongation adopt a herring-bone pattern in order to accommodate the HCP array.

It is informative to observe how a simple chemical composition with a fundamental HCP array of anions must generate a novel distribution of cations during crystallization in order to accommodate the polyhedral distortion imposed by Jahn-Teller effects and H-bonding.

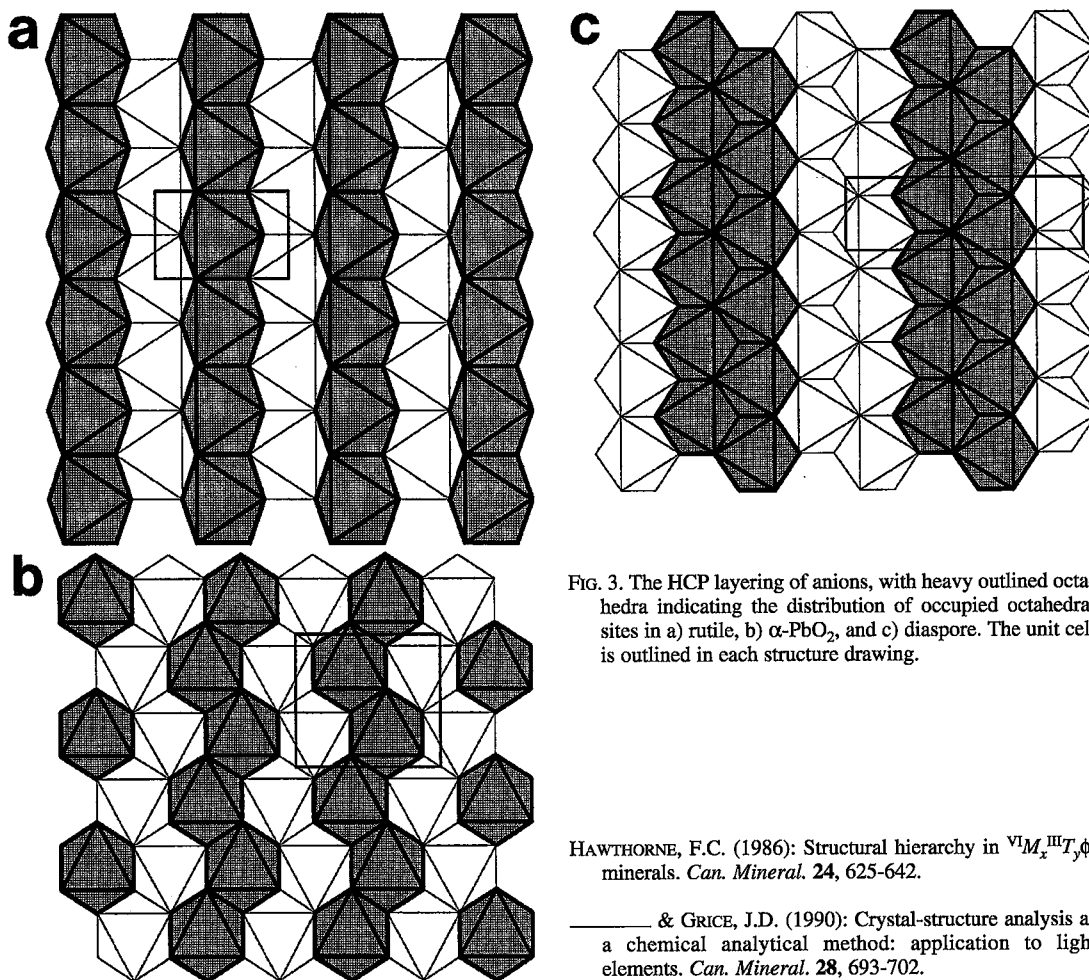


FIG. 3. The HCP layering of anions, with heavy outlined octahedra indicating the distribution of occupied octahedral sites in a) rutile, b) α -PbO₂, and c) diaspore. The unit cell is outlined in each structure drawing.

ACKNOWLEDGEMENTS

The financial support of a Research Advisory Committee Grant from the Canadian Museum of Nature to JDG is gratefully acknowledged. The authors thank Dr. Frank Hawthorne for the use of the single-crystal diffractometer at the Department of Geological Sciences, University of Manitoba. The authors appreciate the improvements brought about by the helpful suggestions of Josef Zemann, an anonymous referee, Associate Editor Carl Francis and Editor R.F. Martin.

REFERENCES

- BRESE, N.E. & O'KEEFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.
- EBY, R.K. & HAWTHORNE, F.C. (1993): Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallogr.* **B49**, 28-56.
- HAWTHORNE, F.C. (1986): Structural hierarchy in $^{VI}M_x^{III}T_y\phi_z$ minerals. *Can. Mineral.* **24**, 625-642.
- _____ & GRICE, J.D. (1990): Crystal-structure analysis as a chemical analytical method: application to light elements. *Can. Mineral.* **28**, 693-702.
- MARTY, J., JENSEN, M.C. & ROBERTS, A.C. (1993): Minerals of the Centennial Eureka mine, Tintic district, Eureka, Utah. *Rocks and Minerals* **68**, 406-416.
- NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.
- ROBERTS, A.C., GRICE, J.D., CRIDDLE, A.J., JENSEN, M.C., HARRIS, D.C. & MOFFATT, E.A. (1995): Frankhawthorneite, Cu₂Te⁶⁺O₄(OH)₂, a new mineral species from the Centennial Eureka mine, Tintic District, Juab County, Utah. *Can. Mineral.* **33**, 641-647.
- SHELDRIK, G.M. (1990): *SHELXTL, a Crystallographic Computing Package* (revision 4.1). Siemens Analytical Instruments, Inc., Madison, Wisconsin.
- WELLS, A.F. (1975): *Structural Inorganic Chemistry* (4th ed.). Clarendon Press, Oxford, U.K.

Received July 27, 1994, revised manuscript accepted November 9, 1994.