FRANKHAWTHORNEITE, Cu₂Te⁶⁺O₄(OH)₂, A NEW MINERAL SPECIES FROM THE CENTENNIAL EUREKA MINE, TINTIC DISTRICT, JUAB COUNTY, UTAH¹

ANDREW C. ROBERTS

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

JOEL D. GRICE

Research Division, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

ALAN J. CRIDDLE

Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

MARTIN C. JENSEN²

Mackay School of Mines, MS168, University of Nevada, Reno, Nevada 89557-0047, U.S.A.

DONALD C. HARRIS

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

ELIZABETH A. MOFFATT

Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario K1A 0C8

Abstract

Frankhawthorneite, ideally $Cu_2Te^{6+}O_4(OH)_2$, is monoclinic, $P2_1/n$ (14), with unit-cell parameters refined from powder data: a 9.095(3), b 5.206(2), c 4.604(1)Å, $\beta 98.69(2)^{\circ}, V 215.5(1)$ Å³, *a:b:c* 1.7470:1:0.8844, $\overline{Z} = 2$. The strongest eight lines of the X-ray powder-diffraction pattern [d in Å(l)(hkl)] are: 4.506(40)(110, 200), 4.337(60)(101), 3.838(50)(101), 2.891(70)(211),2.598(100)(020,310,211), 1.834(40)(312), 1.713(40)(022) and 1.500(40)(330,231,600). The mineral is found on the dumps of the Centennial Eureka mine, Juab County, Utah, where it occurs as isolated crystals 0.1 mm in size or as groupings of crystals on drusy white quartz. Associated minerals include mcalpineite, pyrite, hematite, acanthite, chrysocolla, connellite, enargite, hinsdalite, svanbergite and an undefined Cu-Zn-Te-bearing pale green botryoidal crust. Individual crystals of frankhawthorneite are prismatic to stubby bladed, are subhedral to euhedral, and have slightly curved faces. They are elongate [001], with a length-to-width ratio of approximately 3:1. Forms are {010} major, and possible {100} and {011} minor. The mineral is transparent, medium leaf green, with a less intense streak of the same color and an uneven fracture. Frankhawthorneite is vitreous, brittle and nonfluorescent; H(Mohs) 3-4; D(calc.) 5.43 for the idealized formula, 5.44 g/cm³ for the empirical formula. In polished section, frankhawthorneite is weakly bireflectant and nonpleochroic. In reflected plane-polarized light in air it is pale grey, in oil it is purple-grey, with ubiquitous viridian green internal reflections. The anisotropy is weak with brown rotation tints. Measured reflectance values, in air and in oil, are tabulated. Electron-microprobe analyses yielded CuO 45.20, TeO3 48.77, H2O (calc.) [5.05], total [99.02] wt. %. The empirical formula, derived from crystal-structure analysis and electronmicroprobe analyses, is $Cu_{2.03}Te_{0.99}^{6+9}O_{4.00}(OH)_{2.00}$, based on O = 6 and with (OH) = 2.00. The mineral name honors Professor Frank C. Hawthorne, University of Manitoba, for his many important contributions to the fields of mineralogy and crystallography, and especially for his ongoing studies of the crystal chemistry of Cu²⁺ oxysalt minerals.

Keywords: frankhawthorneite, new mineral species, copper hydroxide-tellurate, X-ray data, electron-microprobe data, reflectance data, Centennial Eureka mine, Juab County, Utah.

¹ Geological Survey of Canada contribution number 34294.

² Present address: 121-2855 Idlewild Drive, Reno, Nevada 89509, U.S.A.

THE CANADIAN MINERALOGIST

SOMMAIRE

La frankhawthorneïte, de composition idéale $Cu_2Te^{6+}O_4(OH)_2$, est monoclinique, $P2_1/n$ (14); ses paramètres réticulaires, affinés à partir du spectre de diffraction X obtenu sur poudre, sont: a 9.095(3), b 5.206(2), c 4.604(1) Å, β 98.69(2)°, V 215.5(1) Å³, a:b:c 1.7470:1:0.8844, Z = 2. Les huit raies les plus intenses du spectre [d en Å(I)(hkl)] sont: 4.506(40)(110, 200), $4.337(60)(\overline{101}), \ 3.838(50)(101), \ 2.891(70)(\overline{2}11), \ 2.598(100)(020,310,211), \ 1.834(40)(\overline{3}12), \ 1.713(40)(022) \ et \ 1.500(40)$ (330,231,600). Il s'agit d'un minéral découvert dans les rejets extérieurs à la mine Centennial Eureka, dans le comté de Juab, au Utah, en cristaux isolés 0.1 mm de largeur ou regroupés, sur les cristaux de quartz des parois de cavités. Lui sont associés mcalpineïte, pyrite, hématite, acanthite, chrysocolle, connellite, énargite, hinsdalite, svanbergite et une croûte méconnue vert pâle et botryoïdale contenant Cu, Zn et Te. Les cristaux individuels de frankhawthorneïte sont prismatiques, en lames trappues, idiomorphes à sub-idiomorphes, et ont des faces légèrement courbes. Ils sont allongés sur [001], environ trois fois plus longs que larges. La forme majeure est {010}, tandis que les formes {001} (possible) et {011} sont mineures. Les cristaux sont transparents, vert feuille moyen, ayant une rayure de la même couleur mais moins intense, et une cassure inégale. La frankhawthorneïte a un aspect vitreux, et est cassante et non fluorescente. La dureté de Mohs est entre 3 et 4. La densité calculée pour la formule idéale est 5.43, tandis qu'elle est 5.44 pour la formule empirique. En lames polies, la frankhawthorneïte est faiblement biréflectante et non pléochroïque. En lumière réfléchie polarisée, dans l'air, elle est gris pâle, et dans l'huile, elle est gris violacé montrant des réflexions internes vert viridien ubiquistes. L'anisotropie est faible, avec des teintes de rotation brunâtres. Nous présentons les valeurs de réflectance, mesurées dans l'air et dans l'huile. Les analyses à la microsonde électronique ont donné CuO 45.20, TeO₃ 48.77, H₂O (calculé) [5.05], pour un total de 99.02% (en poids). La formule empirique, dérivée des résultats de l'ébauche de la structure cristalline et des analyses à la microsonde électronique, serait Cu_{2.03}Te⁶⁺_{0.99}O_{4.00}(OH)_{2.00}, sur une base de six atomes d'oxygène et deux groupes d'hydroxyle. Le nom veut honorer Frank C. Hawthorne, professeur à l'université de Manitoba, pour ses nombreuses contributions aux domaines de la minéralogie et de la cristallographie, et signale surtout ses études courantes de la chimie cristalline des oxysels de Cu2+.

(Traduit par la Rédaction)

Mots-clés: frankhawthorneïte, nouvelle espèce minérale, hydroxyde-tellurate de cuivre, données de diffraction X, données de microsonde électronique, données de réflectance, mine de Centennial Eureka, comté de Juab, Utah.

INTRODUCTION

Frankhawthorneite, ideally $Cu_2Te^{6+}O_4(OH)_2$, is a newly recognized mineral species. It was first encountered during megascopic examination, scanning electron energy-dispersion study and routine X-ray powder-diffraction characterization of a suite of secondary Cu- and Te-bearing minerals. These were originally collected by one of us (MCJ) in July 1992 from the mineralized dumps adjacent to the Centennial Eureka mine, Tintic district, Juab County, Utah. This mineral is the second of at least five new secondary Cu- and Te-bearing phases that will eventually be characterized; it was given the designation "unknown no. 8" in Marty *et al.* (1993), who described the primary and secondary minerals found at the Centennial Eureka mine.

The mineral is named *frankhawthorneite* in honor of Professor Frank C. Hawthorne, Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba. Professor Hawthorne has made many significant contributions to the science of structural and experimental mineralogy and crystallography, more specifically on the topic of Cu^{2+} oxysalt minerals. Frankhawthorneite has an infinite framework structure with edge-sharing octahedra (M=M) within the classification scheme proposed by Eby & Hawthorne (1993). The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA. Holotype material is housed in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario, under catalogue number NMC 67263.

OCCURRENCE AND ASSOCIATED MINERALS

Frankhawthorneite has been identified on six specimens collected from the dumps of the Centennial Eureka mine, Tintic district, Juab County, Utah (lat. 39°56'38"N, long. 112°7'18"W). This property, worked primarily from 1876 to 1927, was formerly the most productive and profitable deposit in the district. The immense dumps of the mine were largely removed and processed for their low-grade concentrations of gold in late 1991. At this time, a wide variety of mineralized samples were exposed, including several boulders that contain the new Cu- and Te-bearing assemblages. Frankhawthorneite was observed in two of these boulders, and must be considered very rare; only about 2 mg of the mineral is presently known. On the holotype specimen, the mineral is found in two interconnected vugs, approximately 2 mm in length, where it occurs as isolated crystals or crystal groups that are perched on drusy white to colorless quartz. The quartz, in turn, has been coated by a thin veneer of olive green cryptocrystalline mcalpineite Cu₃TeO₆·H₂O (Roberts et al. 1994). Associated minerals include pyrite grains partially replaced by hematite, acanthite, chrysocolla, connellite, enargite, hinsdalite, svanbergite and an undefined Cu-, Zn-, and Te-bearing pale green botryoidal crust. Additional Cuand Te-bearing secondary minerals that have been identified by X-ray powder-diffraction methods on similar specimens include cesbronite, xocomecatlite, dugganite, quetzalcoatlite and five additional crystalline unnamed Cu- and Te-bearing phases that are currently under investigation. Additional information regarding the geology and mineralogy of the Centennial Eureka mine can be found in Marty et al. (1993). Frankhawthorneite is a secondary mineral that formed from the breakdown of primary Cu- and Tebearing sulfides.

PHYSICAL PROPERTIES

Frankhawthorneite occurs on drusy quartz as isolated single crystals or as groupings of several crystals. An SEM photomicrograph of several individual crystals scattered on quartz is presented in Figure 1. Individual prismatic to stubby bladed crystals are subhedral to euhedral, with slightly curved faces. They are up to 0.1 mm in length, elongate [001], with a length-to-width ratio of approximately 3:1. These crystals are too small to determine crystal forms by optical goniometric study; single-crystal precession studies indicate that the dominant form is {010}, and other possible minor forms are {100} and {011}. Twinning was not observed megascopically, nor was it

found in X-ray single-crystal studies. Frankhawthorneite crystals are medium leaf green and transparent; the streak is the same color but less intense relative to the uncrushed material. The mineral is brittle, possesses an uneven fracture and a vitreous luster, and is nonfluorescent under both long- and short-wave ultraviolet radiation. The density could not be measured owing to the size of available specimens and dearth of material. The calculated density based on the empirical formula is 5.44 g/cm³; that based on the idealized formula derived from an investigation of its crystal structure is 5.43 g/cm³. The Mohs hardness is estimated to be 3-4.

X-RAY CRYSTALLOGRAPHY

Two crystals of frankhawthorneite were examined by single-crystal precession methods employing Zrfiltered Mo radiation. One was mounted such that b^* , and the other such that c^* , is parallel to the dial axis. The following levels were collected: hk0, hkl, $0kl \rightarrow$ $3kl, h0l \rightarrow h2l, 110^* \Lambda c^*, 101^* \Lambda b^* \text{ and } \overline{1}01^* \Lambda b^*.$ Precession films indicate monoclinic symmetry, with measured and calculated unit-cell parameters a 9.050. b 5.184, c 4.640 Å, β 98.58°. Systematic absences (h0l with $h + l \neq 2n$ and 0k0 with $k \neq 2n$) dictate that the space group is uniquely determined as $P2_1/n$ (14). Crystal-structure analysis (Grice & Roberts 1995) has confirmed that this is the correct space-group. The refined unit-cell parameters, a 9.095(3), b 5.206(2), c 4.604(1) Å, β 98.69(2)°, V 215.5(1) Å³, a:b:c 1.7470:1:0.8844, and Z = 2, are based on the d values of 20 X-ray powder lines between 2.891 and 1.313 Å



FIG. 1. SEM photomicrograph of four subhedral to euhedral crystals of frankhawthorneite (at end of arrows) protruding from a quartz matrix. Scale bar: 100 μm.

I,	I.	dÅmeas.	dÅcalc.	hkl	Io	I.	dÅmeas.	dÅcalc.	hkl
	36	4.506	4.505	110	*10	10	1.766	1.766	501
40	10	4.506	4.495	200	3	2	1.739	1.736	4 02
60	100	4.337	4.333	ī01	*40	36	1.713	1.713	022
50	70	3.838	3.834	101	* 5	3	1.665	1.665	222
3	2	3.333	3.330	ī11	*30	26	1.610	1.610	312
3	2	3.084	3.087	111	*10	9	1.591	1.592	501
*70	85	2.891	2.888	$\bar{2}11$	*15	11	1.552	1.552	<u>2</u> 31
3	2	2.694	2.697	301	* 5	4	1.533	1.534	1 03
	24		2.603	020		21		1.502	330
100	64	2.598	2.597	310	40	10	1.500	1.500	231
	53		2.587	211		11		1 .498	600
3	2	2.510	2.500	120	1.5	10	1 461	1.461	521
*10	6	2.397	2.395	3 11	15	3	1.401	1.460	103
*15	12	2.274	2.276	002	*10	9	1.448	1.449	213
•	5	0.054	2.259	021	*10	8	1.358	1.358	521
3	3	2.254	2.248	400	10	5	1 249	1.350	431
*30	34	2.231	2.231	Ī21	10	3	1.540	1.348	602
*20	21	2.152	2.153	121	*10	8	1.331	1.330	213
5	6	2.135	2.138	311	3	5	1.322	1.322	<u>1</u> 23
* 5	4	2.096	2.096	Ī12	* 5	5	1.313	1.312	413
*15	12	1.987	1.986	4 11		3		1.301	040
*40	39	1.834	1.835	312	20	4	1.299	1.299	332
*15	13	1.787	1.788	411		6		1.299	620

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR FRANKHAWTHORNEITE

114.6 mm Debye-Scherrer powder camera

Cu radiation, Ni filter (λ CuK α 1.54178 Å)

I_a visually estimated intensities

 $I_{\rm s}$ calculated intensities from crystal structure

not corrected for shrinkage and no internal standard

* = reflections used for unit-cell refinement

indexed with a 9.095, b 5.206, c 4.604 Å, B 98.69°

for which unambiguous indexing was possible, based on visual inspection of precession single-crystal films. All reflections down to 1.27 Å were visually examined on the precession films. A full indexed powder pattern is presented in Table 1. The powder data are unique and bear no resemblance to any other inorganic phase listed in the Powder Diffraction File. As far as the authors can tell, this phase does not have an inorganic chemical synthetic equivalent.

CHEMISTRY

Frankhawthorneite crystals were analyzed with a Cameca SX-50 electron microprobe, utilizing an operating voltage of 20 kV, a beam current of 20 nA, a beam 5 μ m in diameter and a 10-second count time. The following standards and wavelengths were employed: Cu metal (CuK α) and Te metal (TeL α). A wavelength-dispersion scan indicated the absence of any other elements with atomic number greater than 9 except those reported here. The valence states for both copper and tellurium, as well as the number of oxygen atoms, were determined by crystal-structure analysis (Grice & Roberts 1995) prior to interpretation of the

electron-microprobe results. The paucity of pure material prevented the quantitative determination of water. However, its presence as hydroxyl was confirmed by both crystal-structure analysis and powder infraredabsorption study; the formula was therefore calculated to give 2(OH). The average result of five analyses gave CuO 45.20 (range 44.54-46.15), TeO₃ 48.77 (range 47.95-49.31), H₂O [5.05], total [99.02] wt.%. With O = 6, the empirical formula for this copper tellurate hydroxide is $Cu_{2.03}Te_{0.99}^{6+}O_{4.00}(OH)_{2.00}$. The ideal formula, Cu₂Te⁶⁺O₄(OH)₂, requires CuO 45.10, TeO₃ 49.79, H₂O 5.11, total 100.00 wt.%. This is yet another example of the use of crystal-structure analysis in order to determine the precise chemical formula of a complex mineral species (cf. Hawthorne & Grice 1990). Frankhawthorneite is the second reported simple copper tellurate hydroxide [after xocomecatlite, $Cu_{2}TeO_{4}(OH)_{4}].$

The Gladstone–Dale constants of Mandarino (1981) and the oxide proportions determined from the electron-microprobe data and from the crystal structure lead to K_C values of 0.180 and 0.180, respectively. K_P , calculated using the average index of refraction, 2.00, and the calculated density derived from the empirical formula, is 0.184; for the same average index of refraction, and the calculated density derived from the idealized formula, K_P is 0.184. The compatibility index is -0.023 for the empirical formula, and -0.025 for the idealized formula, indicating excellent compatibility (Mandarino 1981) among the physical and chemical data.

INFRARED SPECTROSCOPY

The infrared spectrum of frankhawthorneite was obtained using a Spectra-Tech IR-Plan infrared microscope interfaced to a Bomem Michelson MB-120 Fourier-transform infrared spectrometer, which utilizes a 0.25 mm liquid-nitrogen-cooled mercury cadmium telluride detector. A small amount of the pure mineral was mounted in a diamond-anvil microsample cell, then pressure was applied to crush the mineral and cause it to spread as a randomly oriented powder; after crushing, the pressure was released. The diamond cell was then positioned in the microscope accessory, and the powdered sample masked, so as to isolate a circular area measuring 100 μ m in diameter and between 1 and 5 μ m in uniform thickness. Two hundred scans were

collected and added together, at 4 cm^{-1} resolution, from 700 to 4000 cm⁻¹. The transmittance spectrum (Fig. 2) was produced by taking the ratio of the singlebeam spectrum of the specimen in the diamond-anvil cell against a single-beam spectrum of the empty diamond-anvil cell collected with the same parameters. The spectrum shows a shallow broad band, centered on 3370 cm⁻¹, which is due to O–H stretching in the hydroxyl groups.

OPTICAL PROPERTIES

In plane-polarized reflected light, frankhawthorneite is pale grey, weakly bireflectant but not pleochroic; immersed in oil, N_D 1.515, it is a dark, rather purple-grey. It is weakly anisotropic, with somber brown rotation tints that are generally masked by abundant viridian green internal reflections. Reflectance measurements were made using the equipment and some of the procedures described by Criddle *et al.* (1983); however, because of the very small grainsize of the mineral, and because nearly all of the grains possess internal reflections, only one area 4 μ m in diameter proved suitable for measurement.



FIG. 2. Infrared-absorption spectrum for frankhawthorneite.



FIG. 3. Reflectance spectra of frankhawthorneite measured in air and in oil (N_D 1.515).

Measurements were made relative to a Zeiss silicon carbide standard, SiC no. 472. Inevitably, the flux of reflected light (from a mineral with a reflectance as low as that of frankhawthorneite) was insufficient to provide reliable measurements at the extremes of the visible spectrum for the immersed specimen. This is evident from Figure 3, where the mean and range of five measurements for each vibration direction in both media are plotted. The measured values for ${}^{im}R_1$ and ${}^{im}R_2$ from 400 nm to 430 nm were rejected and replaced with values extrapolated into the blue from the rest of the measured reflectance spectra in oil (and taking into account the dispersion of the R_1 and R_2 values). These data, and color values relative to CIE illuminant C, are shown in Table 2. It is interesting to note the similarities between these data and those for mcalpineite, another new copper tellurate recently described from the Centennial Eureka mine (and from its type locality, the McAlpine mine, California) (Roberts et al. 1994). The more so, since the two minerals were measured under identical optical conditions by the same operator; the only observable difference between the minerals is that frankhawthorneite is bireflectant, whereas mcalpineite, as is to be expected for a cubic mineral, is sensibly isotropic. Analysis of the optical constants calculated from the reflectance data in Table 2, using the two-media method (Embrey & Criddle 1978), proves that the measurements for the first vibrationdirection in air or, more probably, in oil are erroneous, i.e., the calculated absorption-coefficients are imaginary. Comparison of the indices of refraction, computed separately from the reflectances in air and in oil and assuming zero absorption (a reasonable assumption for most of the visible spectrum, given the green internal reflections), shows, however, that errors in the reflectance values in both media are smaller than are measurable. In other words, the errors are in the second place after the decimal point for all measurements, and one or less in the second place after the decimal point for oil measurements. At 590 nm, the mean index of refraction calculated from these reflectances (using the Fresnel equation) is 2.00, and the dispersion is normal.

lambda	R _I	R ₂	$m_{R_{j}}$	^{im} R ₂	
nm					
400	12.6	14.2	2.41	3.23	
420	12.3	13.7	2.21	3.02	
440	12.0	13.3	2.08	2.81	
460	11.7	12.9	2.02	2.70	
470	11.5	12.8	1.98	2.66	
480	11.4	12.6	1.96	2.63	
500	11.2	12.4	1.88	2.55	
520	11.0	12.2	1.81	2.45	
540	10.9	12.0	1.74	2.37	
546	10.85	11.95	1.73	2.35	
560	10.7	11.9	1.69	2.29	
580	10.6	11.7	1.64	2.22	
589	10.5	11.6	1.61	2.18	
600	10.5	11.6	1.59	2.13	
620	10.4	11.4	1.53	2.06	
640	10.3	11.3	1.49	2.01	
650	10.2	11.3	1.46	1.99	
660	10.2	11.2	1.45	1.97	
680	10.1	11.2	1.43	1.96	
700	10.1	11.2	1.41	1.96	

TABLE 2. REFLECTANCE DATA AND COLOR VALUES FOR FRANKHAWTHORNEITE

ACKNOWLEDGEMENTS

.300

.305

11.9

476

5.0

.288

.295

1.7

478

10.5

.288

.296

2.3

479

10.5

.300

.305

10.8

476

4.9

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