# KIDDCREEKITE, A NEW MINERAL SPECIES FROM THE KIDD CREEK MINE, TIMMINS, ONTARIO AND FROM THE CAMPBELL OREBODY, BISBEE, ARIZONA

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#### ABSTRACT

Kiddcreekite, a copper-tin-tungsten sulfide, is a new mineral species that occurs as irregular grains, as much as 100  $\mu$ m across, in a bornite-rich ore zone on the 1200 level of the Kidd Creek mine, Timmins, Ontario and in the Campbell orebody, Bisbee, Arizona. Intimately associated minerals in the Kidd Creek samples are scheelite, clausthalite, tennantite and tungstenite. In the Bisbee material, associated minerals are pyrite, colusite, stuetzite and altaite. The mineral has the ideal formula Cu<sub>6</sub>SnWS<sub>8</sub> and is thus the tungsten analogue of hemusite Cu<sub>6</sub>SnMoS<sub>8</sub>. Kiddcreekite is opaque and optically isotropic in reflected light. In reflected plane-polarized light, the Kidd Creek grains are pale grey-brown, and the Bisbee grains are pale grey. Some grains in each locality display a purplish tint. The refined unit-cell parameter is a 10.856(2) Å,  $V = 1279.4 \text{ Å}^3$ . With Z = 4, the calculated density for stoichiometric  $Cu_6SnWS_8$  is 4.88 g/cm<sup>3</sup>. The strongest five lines in the X-ray-powder pattern  $[d \text{ in } \hat{A} (I) (hkl)]$  are: 6.29(100)(111), 1.919(60)(440). 3.138(50)(222), 5.41(30)(200), 3.270(30)(311). Indexing indicates a cubic F-lattice with aspect F\*\*\*. The Vickers microhardness of a Bisbee grain gave  $VHN_{100} = 183$ .

Keywords: kiddcreekite, new mineral species, Kidd Creek mine, Timmins, Ontario, Campbell orebody, Bisbee, Arizona, microprobe, reflectance, X-ray diffraction.

#### SOMMAIRE

La kiddcreekite, sulfure de cuivre, d'étain et de tungstène et nouvelle espèce minérale, provient d'une zone minéralisée en bornite du niveau 1200 de la mine Kidd Creek à Timmins (Ontario) et du gîte Campbell à Bisbee (Arizona). Elle se présente en grains xénomorphes atteignant jusqu'à 100  $\mu m$  de diamètre. Dans les échantillons de Kidd Creek, elle est intimement associée à scheelite, clausthalite, tennantite et tungstenite; dans ceux de Bisbee, elle est accompagnée de pyrite, colusite, stuetzite et altaïte. Sa formule idéalisée, Cu<sub>6</sub>SnWS<sub>8</sub>, montre son analogie à l'hémusite Cu<sub>6</sub>SnMoS<sub>8</sub>, avec remplacement de Mo par W. Elle est opaque, optiquement isotrope. En lumière polarisée réfléchie, les cristaux de Kidd Creek sont gris-brun pâle et ceux de Bisbee, gris pâle; dans chaque cas, certains grains montrent une teinte violacée. L'arête de la maille, après affinement, a 10.856(2) Å, donne V = 1279.4 Å<sup>3</sup>. La densité calculée pour le composé stoechiométrique (Z = 4) est de 4.88. Les cinq raies les plus intenses du cliché de poudre  $[d \text{ en } \text{\AA} (I) (hkl)]$  sont:

6.29(100)(111), 1.919(60)(440), 3.138(50)(222), 5.41(30)(200)et 3.270(30)(311). L'indexation est celle d'un réseau cubique *F* d'aspect *F*\*\*\*. La microdureté Vickers *VHN*<sub>100</sub> d'un grain de Bisbee est de 183.

(Traduit par la Rédaction)

*Mots-clés:* kiddcreekite, nouvelle espèce minérale, mine Kidd Creek, Timmins (Ontario), gîte Campbell, Bisbee (Arizona), microsonde, réflectance, diffraction X.

# INTRODUCTION

Kiddcreekite  $Cu_6SnWS_8$  is a new mineral species from the massive sulfide Kidd Creek mine, Timmins, Ontario. The mineral was first reported as an unidentified Cu-W-Sn-S-Se phase by Thorpe *et al.* (1976), who found a single grain in a polished section. It was considered too small for reliable quantitative analysis. More favorable material became available when four polished sections prepared in 1981 were found to contain several grains, the largest 100  $\mu$ m in diameter. A second occurrence was discovered in 1982 by A.J. Criddle and C.J. Stanley, who encountered the mineral in polished sections cut from drill core from the Campbell orebody, Bisbee, Arizona, U.S.A.

Kiddcreekite is named after the Kidd Creek mine, where the mineral was first recognized. Type material is preserved at the British Museum (Natural History) in polished mounts: the Bisbee material in polished mount E.760 (BM 1982,2) and the Kidd Creek material in polished mount E.805 (BM 1982, 3). Other Kidd Creek polished sections are preserved in the National Mineral Reference Collection housed in the Geological Survey of Canada, Ottawa as GSC 64076, GSC 64077, GSC 64078 and the Royal Ontario Museum, Toronto as M 39791.

The mineral and the name *kiddcreekite* have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

### MINERALOGY

Kiddcreekite occurs in a bornite-rich ore zone on the 1200 level of the Kidd Creek mine. Ore from the



FIG. 1. (a) Photomicrograph (reflected light) of kiddcreekite (dark grey) with a scheelite core (black) and a rim of tungstenite. The surrounding light grey mineral is clausthalite. Oil immersion. Kidd Creek mine. (b) Back-scattered image of kiddcreekite grain in 1 (a), obtained by scanning-electron microscopy. The kiddcreekite grain in approximately 60  $\mu$ m wide.



FIG. 2. (a) Photomicrograph (reflected light) of kiddcreekite (dark grey) enclosing two grains of scheelite with associated clausthalite (light grey), tennantite (medium grey) and silicate gangue (black). Oil immersion. Kidd Creek mine. (b) Back-scattered image of kiddcreekite grain in 2 (a), obtained by scanning-electron microscopy. The silicate gangue consists of quartz (black) and an unidentified Gd, Dy phosphate (dark grey). The largest grain of scheelite is 10 μm wide.

bornite zone formed a very small part of the total ore mined from this level. The bornite-rich ore, which is particularly complex in its mineralogy, is characterized by the presence of macroscopic amounts of tennantite, carrollite and, in places, clausthalite. Preliminary descriptions of the diverse assemblage were reported by Thorpe *et al.* (1976) and Pringle & Thorpe (1980). Kiddcreekite has been found in four polished sections cut from a hand specimen collected and provided to us by D.H. Watkinson, Carleton University, Ottawa. The mineral commonly rims scheelite in a matrix of clausthalite or tennantite or both (Figs. 1a, 1b, 2a, 2b). In turn, tungstenite forms nearly complete rims around kiddcreekite. Other associated minerals are mawsonite, chalcopyrite and pyrite. The minerals identified in the original kiddcreekite specimen of Thorpe *et al.* (1976) and Pringle & Thorpe (1980) include bornite, chalcopyrite, tennantite, pyrite, carrollite, naumannite, mawsonite, chalcocite, colusite, bohdanowiczite, eucairite, electrum, sphalerite, fischesserite, roquesite and tungstenite. The grain of kiddcreekite occurs in contact with sphalerite, chalcopyrite, bornite and tennantite.

Grains of kiddcreekite were also found in five polished sections cut from drill core from the Campbell orebody at Bisbee, Arizona. All of them occur in pyrite as discrete anhedral grains, usually less than  $50 \,\mu\text{m}$  across, as irregular cores to zoned subhedral grains of colusite (<50  $\mu$ m) (Fig. 3), and as compound intergrowths with colusite, tungsten-bearing colusite, stuetzite and altaite (<120  $\mu$ m) (Fig. 4).

# CHEMICAL COMPOSITION

Electron-microprobe analyses were carried out at the Geological Survey of Canada (GSC) and the British Museum (Nat. Hist.) (BM). At the GSC, the instrument is a Material Analysis Company electron probe operated with an accelerating voltage of 20 kV at a specimen current of approximately  $0.02 \times 10^{-6}$  A. The following standards were used: synthetic Cu<sub>2</sub>FeSnS<sub>4</sub>, ZnWO<sub>4</sub> and CuSe; the X-ray



FIG. 3. Photomicrograph (reflected light) of a subhedral grain of colusite (light grey) and tungsten-bearing colusite (medium grey) with irregular 'cores' of kiddcreekite (dark grey) in pyrite (white). Note the presence of zoning in colusite and tungsten-bearing colusite. Campbell orebody, Bisbee.



FIG. 4. Photomicrograph (reflected light) of an irregular, angular, compound grain consisting of kiddcreekite (dark grey), zoned colusite and tungsten-bearing colusite (medium grey) with stuetzite (light grey) and altaite (white) in pyrite (also white). Campbell orebody, Bisbee.

lines CuK $\alpha$ , FeK $\alpha$ , SnL $\alpha$ , WL $\alpha$ , SK $\alpha$  and SeK $\alpha$  were examined. At the BM, a Cambridge Instruments Microscan 9 electron probe was operated with an accelerating voltage of 20 kV at a specimen current of approximately 2.5 × 10<sup>-8</sup> A on the Faraday cage. Pure Cu, V, W, Sb, Mo and Te and the compounds FeS (natural), SnO<sub>2</sub> (synthetic) and PbSe (synthetic) were used as standards, and the X-ray lines CuK $\alpha$ , VK $\alpha$ , WL $\alpha$ , MoL $\alpha$ , SbL $\alpha$ , TeL $\alpha$ , FeK $\alpha$ , SK $\alpha$ , SnL $\alpha$ and SeK $\alpha$  were examined.

Results of the analyses are listed in Table 1. The most notable difference in the composition of kiddcreekite from the Timmins and Bisbee localities lies in the selenium content. On the basis of 64 atoms in the unit cell, selenium accounts for close to one atom in the Kidd Creek material. The composition of kiddcreekite is close to the ideal formula  $Cu_6SnWS_8$ , the tungsten analogue of hemusite  $Cu_6SnMOS_8$ .

# X-RAY STUDIES

Grains of kiddcreekite are too small for singlecrystal studies. Consequently, the Gandolfi powder pattern (Table 2) was indexed initially by reference to hemusite (PDF 25-300) and then by analogy with a doubled sphalerite structural cell. The indexing strongly suggests a cubic *F*-lattice with aspect *F*\*\*\*. The refined unit-cell parameter, based on 8 lines between 3.270 and 1.451 Å for which unambiguous indexing was possible, is *a* 10.856(2) Å, V = 1279.4Å<sup>3</sup>. With Z = 4, the calculated density for

TABLE 1. CHEMICAL COMPOSITION OF KIDDCREEKITE FROM KIDD CREEK AND BISBEE

		Bisbee						
	GSC Gr.1	BM Gr.3A	BM Gr.3B	BM Gr.3C	<u>Gr.1</u>	Gr.2		
Cu	39.6	39.6	39.7	38.3	40.6	40.1		
Fe	-	-	0.1		0.7	1.5		
V.	-		Ξ.		0.1	0.3		
Mo		0.2	0.4	0.5				
W	20.4	18.6	19.0	21.4	19.0	18.3		
Sn	12.3	12.5	12.4	12.4	11.9	11.0		
SD	<b>.</b>	2.		2.2	0.5	0.7		
Se	2.1	3.1	2.5	2.3	-	-		
ie S	24 7	25 6	25.2	25 1	26.0	26.9		
2	24.7	20.0	20.2	23.1	20.0	20.0		
Total	99.1	99.8	100.5	100.1	99.6	99.3		
Atom proportions based on 64 atoms in the unit cell								
Cu	24.40	23.87	23.67	23.50	24.10	23.73		
Fe	-	-	0.07	-	0.47	1.00		
V	-	-	-	-	0.07	0.22		
Мо	-	0.08	0.16	0.20	-	-		
W	4.35	3.88	3.91	4.54	3.90	3.74		
Sn	4.06	4.03	3.96	4.07	3.78	3.67		
Sb	-	-	-	-	0.15	0.21		
Se	1.04	1.51	1.20	1.13	-	-		
Te		0.06	0.06	0.03				
S	30,16	30.58	30,96	30.52	31.52	31.42		
Total	64.01	64.01	63.99	63.99	63,99	63.99		
Calc. S.G.	5.04	4.96	4.94	5.06	4.87	4.84		

Theoretical Formula Cu2+Sn+W+S32. - not detected

TABLE 2. X-RAY POWDER DATA FOR KIDDCREEKITE

	<sup>I</sup> obs.	aA <sub>meas</sub> .	Acalc.	hki
	100	6.29	6.27	111
	30	5.41	5.43	200
	5	3.82	3.84	220
	งกั	3,270	3,273	311
	50	3 139	3 134	222
	20	2 712	2 714	100
	20	2 401	2 401	221
	20	2.431	2.431	130
	10	2.429	2.428	420
	10	2.220	2.216	422
	20	2.095	2.089	511,333
	60	1.919	1.919	440
*	30	1.839	1.835	531
	5	1.807	1.809	600,442
	20	1.636	1,637	622
*	10	1.522	1.520	711.551
	20	1 451	1 451	642
*	10	1 400	1 413	721 552
	20	1 265	1 257	/01,000
•	20	1.305	1.337	200
			1.254	/51
*	20	1.250	1.254	555
			1.245	662

114.6 mm Gandolfi camera; Cu radiation, Ni filter,  $\lambda Cu\kappa_{\Lambda 1} = 1.5405$  Å. Pattern run and measured at CANMET (Canada Centre for Mineral and Energy Technology) by E.J. Murray, film #1008. The indexation is based on a 10.856 Å. \* Enhancement of intensity and displacement of line due to clausthalite overlap.

stoichiometric  $Cu_6SnWS_8$  is 4.880 g/cm<sup>3</sup>. Calculated density for stoichiometric  $Cu_{24}Sn_4W_4S_{31}Se_1$  is 4.941 g/cm<sup>3</sup>.

### PHYSICAL PROPERTIES

Because of the small grain-size, only one measurement of the Vickers hardness was possible in a grain from Bisbee; this grain was fractured at the corners of the indentation. The value obtained for this grain,  $VHN_{100} = 183$ , can only be regarded as a general indication of the hardness, and will require confirmation when more, and larger, grains become available. Specific gravity could not be measured.

### QUALITATIVE OPTICAL PROPERTIES

Kiddcreekite grains from Kidd Creek and Bisbee are pale grey-brown and pale grey, respectively, in reflected plane-polarized light (unfiltered quartzhalogen at  $\sim 3200$  K) and when isolated in the microscope field by means of a field stop. Under these conditions, some grains from each locality display a purplish tint. With the field stop removed, the observer's eye is influenced by the color and brightness of the minerals enclosing and adjacent to kiddcreekite. At Kidd Creek some of the grains are enclosed in clausthalite, a bright bluish white mineral, and associated with tungstenite, which is strongly bireflectant and bluish white to grey. In this association, kiddcreekite appears distinctly brown, commonly with a slight purplish tint. At Bisbee, kiddcreekite associated with colusite and tungstenbearing colusite (Fig. 3) appears grey in comparison to the lighter brown-grey of colusite, but when enclosed in pyrite it appears purplish grey.

### QUANTITATIVE OPTICAL PROPERTIES

All measurements were made against a WTiC standard (Zeiss no. 314). Immersion measurements were made with Zeiss oil,  $N_D$  1.515 at a room temperature of 20°C. The equipment used, a Zeiss MPM 03 microscope-photometer, is equipped with a motor-driven line-interference filter (wavelength range 400–700 nm, band-width  $\sim 12$  nm); this is interfaced, as is the digital voltmeter, to a Hewlett Packard 9830 calculator that controls the stepscanning measurement procedure and computes the reflectance and reflectance-derived values. Specimens and standard were leveled and brought into the same focal plane on a modified Lanham leveling superstage. Air and oil objectives of high potential numerical aperture and magnification were used (N.A. 0.85,  $\times$  40), but the illuminator aperturediaphragm was adjusted to give an effective N.A. of 0.22. A plane-glass reflector was used, as was a side-window (Hamamatsu, type R928, S20) photomultiplier.

Measurements were made by step-scanning at an interval of 10 nm from 400 to 700 nm, first on the specimen, then on the standard. The results were plotted with an HP9872A graphical plotter; because of the introduction of 'white' light *via* a 'pin-hole' in the interference filter at 410 nm, they were smoothed by hand, and digitized. The digitized values were used to compute the color values (relative to the CIE illuminants A, C and  $D_{65}$ ) and to check errors in the air and oil reflectances (as recommended by Embrey & Criddle 1978).



FIG. 5. R and imR spectra between 400 and 700 nm for kiddcreekite from each locality.

The values tabulated in this paper have been rounded to the first place of decimals and, to save space, are reported at an interval of 20 nm. For the same reason, color values are reported only for the COM-IMA-recommended illuminants C and A. All the computer programs used (unpublished) were written by G.S. Bearne.

The reflectance measurements reported here were made by A.J.C.; however, measurements were also made on the same grains by C.J.S. to check the reproducibility of the measured reflectances. The results obtained in all instances differ by no more than  $\pm$  0.3–0.4 percentage units, well within the generally accepted limits of individual measurement accuracy of  $\pm$  1% absolute.

The reflectance spectra of kiddcreekite from each locality are distinctive between 400 and 700 nm (Fig. 5), all of them displaying three minima, at 400 nm, between 500 and 550 nm, and at 700 nm. The spectra of the two grains from Bisbee are smooth and remarkably similar, differing from each other by no more than 0.7 percentage units at any wavelength (Table 3). The Kidd Creek spectra share a broadly similar trend to those from Bisbee, except that all three display an upward 'kink' at the red end of the

spectrum, above 640 nm. This kink is much less pronounced for grain 3 than for grains 1 and 2. It is also interesting that, whereas the reflectances for grains 1 and 2 differ from those of the Bisbee grains by 1% or less (except above 640 nm), those of grain 3 are 1-2% higher. These differences may be attributable to compositional differences between the grains from the two localities; it is difficult to avoid the conclusion that the kink in the Kidd Creek curves is related to the presence of selenium, which is absent from the Bisbee grains. We are unable, however, to find an explanation for the discrepancy in overall magnitude between grains 1 and 2, and grain 3, from Kidd Creek. The compositional differences seem too small to account for a 1% difference in reflectance; also, neither specimen preparation nor artifacts of measurement procedure should be responsible, since these procedures were the same for all three grains.

Color values calculated relative to the CIE illuminants A and C (Table 3) are in agreement with the observed colors. In quantitative terms the hues, usually expressed as dominant wavelengths  $(\lambda_d)$ , are here all complementary  $(\lambda_c)$ , that is, they all lie in the purple sector of the color diagram, and their complements, for illuminant A, lie between 510 and

TABLE 3. KIDDCREEKITE: REFLECTANCE DATA

	Kidd Creek specimens						Bisbee specimens			
	1		2	2		3		1		
	R	<sup>†m</sup> R	R	<sup>im</sup> R	R	<sup>im</sup> R	R	im <sub>R</sub>	R	<sup>tm</sup> R
λnm										
400 420 440 460 500 520 540 550 580 600 620 640	23.3 24.0 24.5 24.8 23.5 23.5 22.8 23.9 24.5 24.5 24.5 24.3 24.0	9.2 9.6 10.0 10.4 9.8 9.2 9.3 10.1 10.5 10.5 10.3 10.2	23.2 23.9 24.5 24.7 24.4 23.6 22.9 22.8 23.8 24.5 24.5 24.6 24.3 24.2	9.8 10.2 10.6 10.7 10.5 9.9 9.4 9.4 10.1 10.6 10.6 10.4 10.4	24.2 24.9 25.6 25.6 25.2 24.3 25.6 25.2 24.3 25.9 25.9 25.9 25.9 25.8 25.8	10.8 11.2 11.5 11.6 11.6 11.3 10.8 10.6 11.0 11.5 11.8 11.8 11.8 11.7	22.7 23.2 23.6 23.7 23.3 22.6 22.1 22.5 23.3 23.9 24.1 24.0 23.7	9.8 10.1 10.3 10.2 9.7 9.1 8.9 9.2 9.8 10.2 10.4 10.2 9.9 5	22.6 23.3 23.8 23.9 23.6 22.8 22.2 22.4 23.3 24.0 24.2 24.4 24.4 24.4	9.1 9.7 10.1 10.2 9.9 9.3 8.9 9.1 9.8 10.2 10.4 10.5 10.5
660 680	25.3 24.5	11.0	25.3	10.6	25.9	11.8	23.2	9.5 9.1	23.9	9.5
700	23.5	9.7	23.6	9.9	25.2	11.2	22.2	8.8	22.6	9.0
Color	values re	elative to	the CIE	illumin	ant C					
x y Y%	0.311 0.311 23.8	0.315 0.312 10.0	0.312 0.311 23.8	0.313 0.308 10.1	0.312 0.313 25.1	0.313 0.311 11.2	0.313 0.313 23.2	0.314 0.308 9.7	0.314 0.312 23.3	0.316 0.309 9.7
λd Pe%	c538 2.4	c504 2.7	c532 2.2	c529 3.8	c510 1.5	c519 2.8	c506 1.9	c520 3.9	c507 2.3	c506 3.9
Color	values r	elative to	o the CIE	E illumin	ant A					
x y Y% <sup>Ad</sup> % <sup>P</sup> e%	0.450 0.404 23.9 c545 1.7	0.453 0.403 10.1 c511 2.6	0.450 0.404 23.9 c534 1.8	0.452 0.401 10.2 c529 3.1	0.451 0.405 25.2 c515 1.6	0.452 0.402 11.3 c520 2.8	0.451 0.405 23.4 c510 1.6	0.453 0.402 9.8 c519 2.8	0.452 0.404 23.5 c511 2.2	0.456 0.401 9.9 c511 3.7

The dominant wavelengths for all these grains are complementary, hence the use of the prefix c.

545 nm. Although the five grains are, therefore, 'purple', the saturation of their hues, or their excitation purities, expressed as percentages  $(P_e\%)$ , are all very low (below 2.2% in air and 3.7% in oil), which means that the observed colors will be very weakly saturated. The close proximity of the color coordinates x and y, for all five grains, to those of the illuminant also means that an interpretation of their complementary wavelengths in terms of the observed colors cannot be made with confidence. At most, there is a tendency for the Kidd Creek grains, particularly 1 and 2, to display higher complementary wavelengths than the Bisbee grains; this is due to the upward kink of the reflectance curve at the red end of the spectrum which, in turn, may be the reason why the Kidd Creek grains appear browner than those from Bisbee.

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#### REFERENCES

- EMBREY, P.G. & CRIDDLE, A.J. (1978): Error problems in the two-media method of deriving the optical constants n and k from measured reflectances. *Amer. Mineral.* 63, 853-862.
- PRINGLE, G.J. & THORPE, R.I. (1980): Bohdanowiczite, junoite and laitakarite from the Kidd Creek mine, Timmins, Ontario. *Can. Mineral.* 18, 353-360.
- THORPE, R.I., PRINGLE, G.J. & PLANT, A.G. (1976): Occurrence of selenide and sulphide minerals in bornite ore of the Kidd Creek massive sulphide deposit, Timmins, Ontario. Geol. Surv. Can. Pap. 76-1A, 311-317.
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