BUCKHORNITE, AuPb$_2$BiTe$_2$S$_3$, A NEW MINERAL SPECIES FROM BOULDER COUNTY, COLORADO, AND NEW DATA FOR AIKINITE, TETRADYMITE AND CALAVERITE

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ABSTRACT

Buckhornite, ideally AuPb$_2$BiTe$_2$S$_3$, is a new mineral from the long abandoned Buckhorn mine (40°8′N, 105°24′W), near Jamestown, Boulder County, Colorado. Occurring in vugs in pyrite as splendent black blades up to 1.5 × 0.2 × 0.01 mm, it is associated with aikinite, tetradymite, calaverite, gold and minor chalcopyrite and covellite. It is sectile and flexible, has a perfect cleavage, a gray streak and a VHN$_{10}$ of 54. D_{calc} 8.43 (for the empirical formula) or 8.34 g/cm^3 (for the idealized formula). Electron-microprobe analyses give Cu 0.1, Au 17.0, Pb 34.5, Bi 18.4, Te 22.3, S 7.8, sum 100.1 wt%. The empirical formula of buckhornite, calculated on the basis of 9 atoms in the formula unit, is Cu$_{0.02}$Au$_{1.02}$Pb$_{1.97}$Bi$_{1.04}$Te$_{2.06}$S$_{2.89}$. In reflected light, buckhornite is opaque, bireflectant, pleochroic (brownish gray – pale bluish gray) and distinctly anisotropic (blue to mauve rotation tints). Color values relative to CIE illuminant C, for R_1 and R_2, respectively, are: x 0.311, y 0.318, Y% 40.95, λ_d 571, P_e% 0.7, and x 0.300, y 0.308, Y% 47.4, λ_d 480, P_e% 4.4. The symmetry is orthorhombic, space group *Pmmm* or *P222*, with a 4.092(2), b 12.245(4), c 9.322(4) Å, V 467.1 Å^3. The selection of a nonstandard orientation for the cell emphasizes the observed relationship to a tetragonal subcell. The strongest seven reflections of the X-ray powder-diffraction pattern [d in Å (I) (*hkl*)] are: 3.739(s)(101,131), 3.108(vs)(003), 2.763(vvs)(131), 2.456(vs)(132,140), 2.390(vvs)(141), 2.044(s)(200,060), 1.7084(s)(203,063). Compositional data, reflectance spectra and color values are also supplied for aikinite, tetradymite and calaverite.

Keywords: buckhornite, new mineral species, X-ray data, chemical composition, reflectance data, gold lead bismuth sulfotelluride, Buckhorn mine, Jamestown, Boulder County, Colorado.

SOMMAIRE

La buckhornite, de composition idéale AuPb$_2$BiTe$_2$S$_3$, est une nouvelle espèce minérale découverte à la mine Buckhorn (40°8′N, 105°24′W), abandonnée depuis longtemps, située près de Jamestown, comté de Boulder, au Colorado. Elle se trouve dans des cavités dans la pyrite, en lames noires resplendissantes atteignant 1.5 × 0.2 × 0.01 mm, associée à aikinite, tétradymite, calavérite, or, et chalcopyrite et covelline accessoires. Elle est sectile et flexible, possède un clivage parfait, une rayure grise et une dureté VHN$_{10}$ de 54. La densité calculée est 8.43 pour la formule empirique et 8.34 pour la formule idéale. Les analyses à la microsonde ont donné Cu 0.1, Au 17.0, Pb 34.5, Bi 18.4, Te 22.3, S 7.8, total 100.1% (par poids). La formule empirique de la buckhornite, calculée sur une base de neuf atomes, est Cu$_{0.02}$Au$_{1.02}$Pb$_{1.97}$Bi$_{1.04}$Te$_{2.06}$S$_{2.89}$. En lumière réfléchie, il s'agit d'un minéral opaque, biréflectant, pléochroïque (gris brunâtre à gris bleuâtre pâle) et anisotrope (teintes de rotation du bleu au mauve). Les valeurs de couleur, en relation avec l'illuminant C de CIE, pour R_1 et R_2 respectivement, sont: x 0.311, y 0.318, Y% 40.95, λ_d 571, P_e% 0.7, et x 0.300, y 0.308, Y% 47.4, λ_d 480, $_e$% 4.4. La symétrie est orthorhombique, groupe spatial *Pmmm* ou *P222*, avec a 4.092(2), b 12.245(4), c 9.322(4) Å, V 467.1 Å^3. Le choix d'une maille en orientation non standard souligne la relation observée avec une sous-maille tétragonale. Les sept raies les plus intenses du cliché de poudre [d en Å (I) (*hkl*)] sont: 3.739(s)(101,131), 3.108(vs)(003), 2.763(vvs)(131), 2.456(vs)(132,140), 2.390(vvs)(141), 2.044(s)(200,060), 1.7084(s)(203,063). Nous présentons, de plus, des données sur la composition, la réflectance et les couleurs de l'aikinite, la tétradymite et la calavérite.

(Traduit par la Rédaction)

Mots-clés: buckhornite, nouvelle espèce minérale, données de diffraction X, composition chimique, données de réflectance, sulfo-tellurure d'or, de plomb et de bismuth, mine Buckhorn, Jamestown, comté de Boulder, Colorado.

INTRODUCTION

In October, 1940, Cornelius S Hurlbut, Jr., Professor at Harvard, was sent the samples described in this paper by Mr. Eugene Staritzky, then Associate Director of the Colorado School of Mines Experimental Plant. Partial chemical analysis of some of the crystals revealed the presence of gold, lead, bismuth, tellurium and sulfur. The sulfur was attributed to admixture with pyrite, and the mineral, believed to be new, was considered to be a telluride of Au, Pb and Bi. Completion of its characterization had to wait for more than fifty years, however, until the current investigation, in which it was discovered that sulfur is an essential component, *i.e.*, the mineral is a sulfotelluride of the three elements, and superficially similar to nagyagite.

The provenance of the mineral was somewhat enigmatic: Staritzky (in the letter accompanying the sample sent to Hurlbut) wrote "I have traced the source of this material and visited the locality last Sunday. I found the mine has been condemned as unsafe because of runny ground and was shut down several years ago. The dump has been reworked and milled and apparently no more material is available for study of the telluride mineral." What he failed to note was where the mine was. As it happened, Professor Clifford Frondel, of Harvard, had earlier obtained a few isolated crystals of the new mineral. These crystals (together with some crumbs of pyrite) had been stored at Harvard, in a glass vial labeled as "Buckhorn, Jamestown, Col.". From their identity with the crystals of Staritzky, we infer that his samples also came from the Buckhorn mine in the Jamestown mining district, Boulder County, Colorado. Hence, our choice of name for the mineral.

The bulk of the holotype material is preserved at the Harvard Mineralogical Museum, where it is catalogued as H126786. That part of the holotype on which most of the characterization was conducted is a polished mount E.1102, registered as BM 1991,51 (with some fragments from the Harvard sample, registered as BM 1991,52), at The Natural History Museum (London). Cotype material is deposited at the U.S. National Museum in Washington. The total amount of buckhornite present in these samples is estimated at 50 mg. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (CNMMN–IMA).

OCCURRENCE

The Jamestown district is in Boulder County in the Front Range, 14.5 km northwest of Boulder, at the northeastern end of the Colorado mineral belt. The telluride ores of Boulder County (but excluding those of the Buckhorn mine) are described in considerable detail by Kelly & Goddard (1969). In 1865, a mineral prospecting party, including a gentleman called James (after whom the mining district and town were named),

prompted a minor gold rush in the area. One of the first claims, the Buckhorn, was not, however, for gold, but for lead and silver, and the Buckhorn mine, patented in 1873, was mined chiefly for these metals (Lovering & Goddard 1950). The mine, situated 1.6 km northwest of Jamestown (40°8′N, 105°24′W), was sunk in the Precambrian Silver Plume granite near its contact with the Porphyry Mountain stock (a sodic granite – quartz monzonite porphyry), of Tertiary age. The ore, described by Lovering & Goddard (1950) as consisting of "pyrite, chalcopyrite, and galena, some gray copper and sphalerite", included gold (associated with the pyrite and chalcopyrite) and silver (associated with the galena and "gray copper"). It was found in a near-vertical vein, up to 1.6 meters wide, striking N15–20°W, associated with quartz, silicified granite and fluorite. The Pb–Ag ore was concentrated in pockets, 3–5 meters long, at the intersection of the main vein with subsidiary veinlets.

In hand specimen, buckhornite occurs as bladed, free-standing crystals and clusters within cavities and vugs in pyrite. The buckhornite crystals are black, have a splendent metallic luster, and vary considerably in size, the larger crystals being up to $1.5 \times 0.2 \times 0.01$ mm. SEM photomicrographs of a typical buckhornite cluster (uncoated and rather dusty) in a pyrite vug (Fig. 1a) reveal how thin and foil-like are the individual crystals, and also how some are warped and bowed. Figure 1b, taken at higher magnification, shows crystal-growth features and illustrates the perfection of individual crystals. The pyritic host is coarsely to finely granular, with individual grains varying from 0.2 to 10 mm in size. In and adjacent to the vugs, the pyrite is euhedral to subhedral: the cubes are modified by stepped octahedral faces, and many of the faces are striated and pitted, and the edges rounded. Aikinite crystals, shorter and stouter than buckhornite, and heavily striated along their length, are intergrown with buckhornite in some of the vugs. Sericite "dusts" the vug contents (*cf.* the "dust" in Fig. 1b) and completely fills others. Native gold also was observed by Staritzky on blades of buckhornite.

ORE MICROSCOPY

A polished section (E. 1102) was prepared for microscopy and electron-microprobe analysis following the procedure described by Criddle *et al.* (1983), except that MgO proved to be unsuitable as a buffing agent and was replaced by 0.25 μm diamond.

Textural features

Several cavities, or vugs, containing buckhornite, were exposed in the polished section. In these, it is associated and intergrown with aikinite, tetradymite, gold, and with minor amounts of chalcopyrite and covellite. In the plane section of the polished mount, buckhornite appears as euhedral to subhedral blades
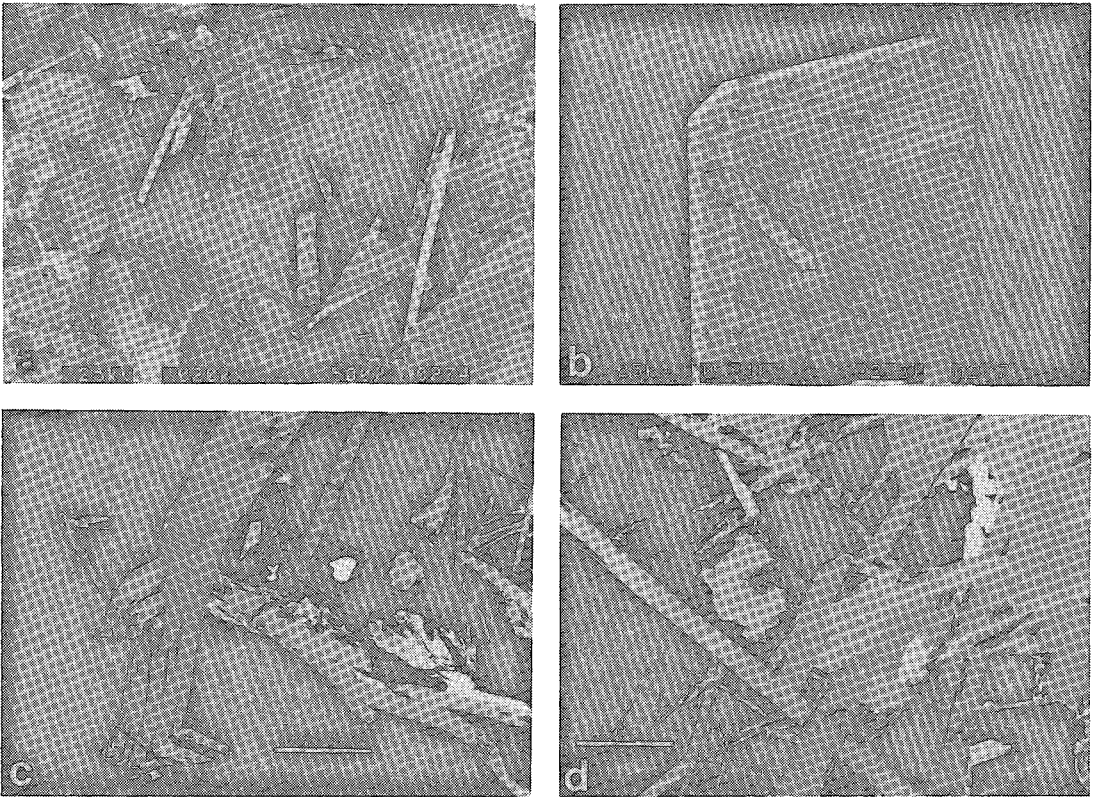
FIG. 1. a. An SEM photograph of a cavity in pyrite partially lined with buckhornite crystals. Note the bladed habit of the buckhornite, its variable grain-size, and the bent nature of some crystals. b. Part of one of the crystals in a, at much higher magnification, showing stepped growth-related features, a fragmentary small blade, or cleavage fragment, of buckhornite stuck to the larger crystal, and dust (which may be sericite). c. In plane-polarized light, an optical photomicrograph (oil immersion) showing deformed and cleaved (or fractured) blades of buckhornite (gray) with tetradymite (light gray-white) and irregular blebs of gold (white). The scale bar equals 300 μm. d. The same photographic conditions as c; here, buckhornite is intergrown with aikinite, tetradymite and gold. The scale bar equals 300 μm.

(ratio of width to length varying from 1:4 to 1:40), some of which are distorted, bent and cleaved (Fig. 1c), and as subhedral to anhedral intergrowths with more coarsely crystalline aikinite and granular tetradymite (Fig. 1d). The three minerals replace and overgrow each other. Some rounded grains of gold (up to 70 μm) are apparently replaced by these minerals, but gold also occurs as angular masses occupying the interstices between buckhornite and aikinite grains and between grains of pyrite. We suggest that the four minerals are near-contemporaneous. Chalcopyrite is generally interstitial to these minerals. It also coats some grains of gold; in both cases, it is partially replaced by covellite.

The contact between the "vug" minerals and the pyrite "host" is usually sharp, with little evidence of replacement. Within the pyrite, inclusions are abundant, ranging from unidentifiable submicrometric blebs to euhedral, 45 μm × 680 μm crystals of tetradymite. Many of the inclusions are monophase, including anhedral grains of aikinite, buckhornite, bornite, chalcopyrite, chalcocite, calaverite, galena, sphalerite, tetradymite, and euhedral crystals of hematite and tetradymite. Two- and three-phase inclusions of groups of these minerals are, however, more abundant. Their morphology is extremely variable, from anhedral to euhedral, roundish to angular. Many are square, rectangular, triangular or hexagonal, which suggests that some filled pre-existing cavities in the pyrite, whereas others replaced it.

Optical properties

In plane-polarized light (at a color temperature of about 3,100 K), buckhornite is moderately reflecting, bireflectant and pleochroic. R_I is a slightly brownish

gray, and R_2 is much lighter and gray with a bluish tint. If observed next to aikinite, R_2 of buckhornite is a clear light blue-gray, and the higher reflecting vibration direction of aikinite, R_2, appears a light greenish gray. If aligned with their R_1 vibration directions, both minerals are very similar in brightness and in their brownish to pinkish gray hue. Some grains of buckhornite are nearly isotropic; their reflectance corresponds to R_2. Immersed in oil ($N_D = 1.515$), buckhornite is moderately to strongly bireflectant and distinctly pleochroic; R_1 is gray with a slight purplish tint, and R_2 is a clear pale blue.

Between crossed polars, the mineral has straight extinction, and is distinctly anisotropic, with rotation tints ranging from blue to mauve. The sequence (for the most anisotropic grains) is, from extinction: dark blue (ultramarine), lighter clear blue, extinction, dark lilac to mauve to purplish brown. The only change, when immersed in oil, is that the tints are intensified. In air, with the polars uncrossed, *i.e.*, with the analyzer rotated by 3°, the rotation sequence is: khaki, bright silvery blue, greenish light gray, khaki, brown, reddish brown, strong purple-brown to khaki. In oil, the reds and browns in this sequence are replaced by mauve and purple. None of the many grains examined show evidence of twinning (*cf.* nagyagite: Picot & Johan 1982, p. 276).

Reflectance and quantitative color data

Reflectance measurements were made on four grains of buckhornite and, for comparison (and to identify the minerals in the early stages of the investigation), on aikinite, tetradymite and calaverite. The equipment and procedures used were those described by Criddle *et al.* (1983), except that the Illuminator Aperture Diaphragm was adjusted to provide effective numerical apertures of 0.26 for both objectives. The reflectance standard used for all measurements was a Zeiss calibrated WTiC (no. 314); oil measurements were made with Zeiss immersion oil, $N_D = 1.515$, DIN 58 884, at an ambient temperature of 20°C. The measurements on buckhornite were made on two of the most strongly bireflectant grains and on two weakly bireflecting, nearly isotropic, grains. For the latter, because extinction positions could not be established by eye, measurements were made at positions of maximum and minimum reflectance, determined photometrically, at 550 nm. These positions were found not to be orthogonal. The data (Table 1), shown graphically in Figure 2, are consistent with the visual impression of a blue-gray-pleochroic, distinctly bireflectant mineral. R_2 and $^{im}R_2$ for the more bireflectant grains are demonstrably the spectra of a blue mineral,

TABLE 1. REFLECTANCE DATA AND COLOR VALUES FOR BUCKHORNITE

		1		2		3		4		1		2		3	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	R_1	R_2	$^{im}R_1$	$^{im}R_2$	$^{im}R_1$	$^{im}R_2$	$^{im}R_1$	$^{im}R_2$
400	40.5	51.15	41.3	50.3	50.7	52.35	52.3	51.7	26.1	37.5	26.7	36.2	35.6	38.0
420	40.6	51.6	41.4	50.65	50.8	53.1	52.6	51.5	25.8	37.25	26.5	36.35	36.0	39.3
440	40.6	51.55	41.4	50.6	50.7	53.3	52.35	51.2	25.5	36.7	26.4	35.25	35.95	39.6
460	40.5	51.0	41.3	50.1	50.2	53.0	51.6	50.9	25.4	36.0	26.3	35.7	35.3	39.1
470	40.5	50.6	41.4	49.8	49.8	52.7	51.1	50.7	25.4	35.6	26.3	35.3	34.8	38.6
480	40.5	50.25	41.4	49.5	49.3	52.3	50.6	50.5	25.4	35.2	26.3	34.9	34.2	38.1
500	40.7	49.5	41.4	48.9	48.4	51.45	49.65	50.0	25.5	34.3	26.3	34.2	33.1	36.95
520	40.8	48.8	41.4	48.2	47.3	50.4	48.6	49.25	25.7	33.5	26.3	33.3	31.9	35.7
540	41.0	48.0	41.4	47.5	46.0	49.2	47.5	48.4	25.8	32.7	26.2	32.6	30.6	34.4
546	41.0	47.8	41.4	47.3	45.7	48.9	47.25	48.2	25.8	32.5	26.15	32.4	30.3	34.1
560	41.1	47.3	41.3	46.8	44.9	48.0	46.5	47.5	25.9	31.9	26.1	31.8	29.5	33.2
580	41.1	46.5	41.2	46.1	43.9	46.9	45.6	46.7	25.9	31.1	26.0	31.0	28.5	32.1
589	41.2	46.2	41.2	45.7	43.45	46.3	45.2	46.3	25.85	30.8	25.9	30.7	28.1	31.6
600	41.0	45.9	41.1	45.4	43.1	46.0	44.9	45.9	25.8	30.5	25.8	30.4	27.7	31.2
620	40.9	45.3	41.0	44.8	42.5	45.3	44.35	45.3	25.7	29.9	25.7	29.8	27.1	30.55
640	40.8	44.9	40.85	44.3	42.05	44.7	43.9	44.8	25.5	29.4	25.5	29.3	26.75	29.95
650	40.7	44.7	40.7	44.0	41.8	44.5	43.7	44.5	25.4	29.2	25.4	29.0	26.6	29.7
660	40.4	44.5	40.6	43.8	41.65	44.2	43.5	44.3	25.2	29.0	25.25	28.7	26.3	29.4
680	40.2	44.1	40.3	43.3	41.3	43.7	43.2	43.9	24.9	28.6	24.9	28.3	25.9	28.9
700	40.0	43.8	40.1	42.9	40.9	43.3	43.0	43.6	24.6	28.3	24.7	27.8	25.6	28.45

COLOR VALUES (Illuminant C, 6774K):

x	.311	.300	.309	.301	.296	.297	.298	.300	.311	.295	.308	.295	.289	.290
y	.318	.308	.316	.309	.305	.307	.305	.309	.318	.303	.316	.304	.297	.300
Y%	40.95	47.4	41.3	46.9	45.3	48.3	46.8	47.7	25.75	32.1	26.1	32.0	29.9	33.6
$λ_d$	571	480	492	481	480	481	479	482	568	479	487	480	479	480
P_e%	0.7	4.4	0.3	4.2	6.3	5.7	5.8	4.3	0.6	7.0	0.9	6.8	9.9	9.1

COLOR VALUES (Illuminant A, 2856K):

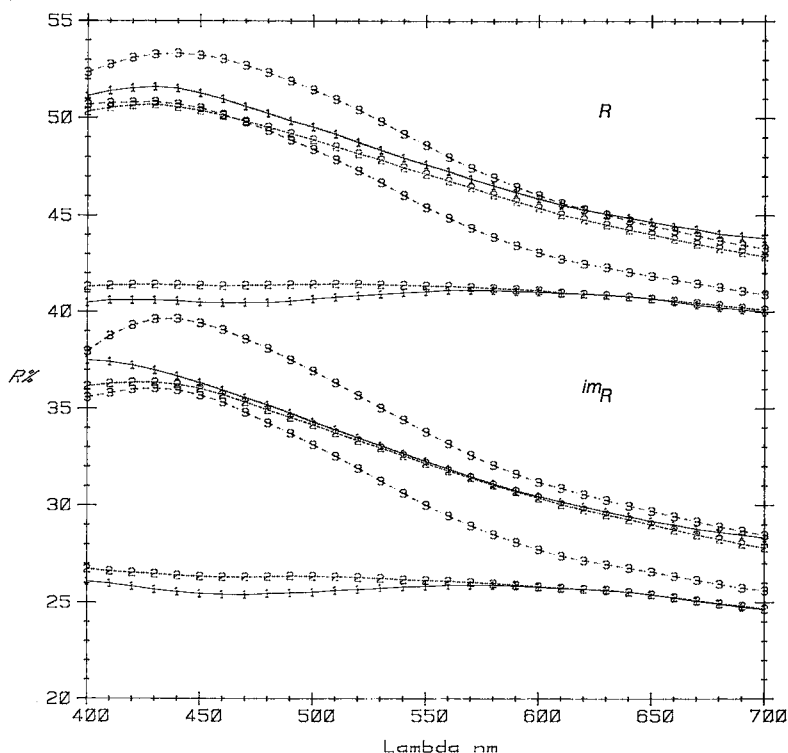|														
x	.448	.438	.446	.438	.434	.435	.435	.437	.447	.432	.445	.433	.427	.428
y	.409	.406	.408	.406	.405	.406	.405	.407	.409	.404	.408	.405	.402	.403
Y%	41.0	46.9	41.2	46.4	44.6	47.6	46.2	47.1	25.75	31.5	26.0	31.4	29.2	32.8
$λ_d$	571	492	504	493	492	493	491	494	564	491	499	492	491	491
P_e%	0.8	2.4	0.4	2.3	3.3	3.1	3.0	2.4	0.7	3.7	0.7	3.6	5.2	4.9

FIG. 2. R and ^{im}R spectra for three grains of buckhornite: the numbers on the spectral curves correspond to those used in Table 1.

whereas the corresponding spectra for R_1 and $^{im}R_1$ are those of a nondescript gray mineral. The color values, listed for both Illuminant A and C in Table 1, but hereafter discussed in terms of the Illuminant A, which most closely corresponds to the color temperature of the light source used for qualitative description, summarize this point: the saturation (quantitatively, the excitation purity, $P_e\%$) of the color, or hue (dominant wavelength), for R_1 is less than 1%, i.e., over 99% of the perceived color is due to the color attributes of the light source. The fact that visually an impression is created, in air, of a brownish gray and, in oil, of a purplish gray, owes more to visual confusion that results from the juxtaposition of variously oriented (and colored) grains of buckhornite, aikinite, tetradymite, etc. Similarly, the paleness of the blue hue for R_2 is explained by the relatively low levels of excitation purity, 2–3% in air, and 3–5% in oil.

The reflectance spectra for buckhornite are, nevertheless, distinctive, and match nothing in the Quantitative Data File (QDF2, Criddle & Stanley 1986). Both the tabulated and graphical data illustrate a point that is sometimes overlooked by those who use reflectance-based identification schemes, such as that of Gerlitz *et al.* (1989): the paired spectra for grains 1 and 2 (Table 1) are closely similar, as are those for grains 3 and 4, but the two sets differ. The point is that the crystallographic

orientation of different grains of the same mineral in a polished section may vary, in which case the reflectance, bireflectance *etc.*, will also vary, and this is particularly true for minerals of low optical symmetry, such as buckhornite. Common sense suggests that one searches for the most bireflectant grain to measure, but in some instances, preferred orientation limits the choice. For these reasons, in the characterization of a new mineral, it is useful to provide data for the most *and least* bireflectant grains. An added advantage of this procedure (as applied to opaque minerals) is that it will usually indicate whether the mineral is optically uniaxial or "biaxial".

Comparison of the reflectance data for buckhornite (Table 1) and aikinite (Grain 5, Table 2) shows that their R_1 spectra are indistinguishable; the color values also show that their "summary" bireflectances, *i.e.*, the differences between luminance values ($Y\%$), are similar. In fact, the only significant differences are between the dominant wavelengths computed from their R_2 spectra. Those for buckhornite (relative to Illuminant A), at 492 nm, are in the blue sector of the color diagram, whereas those for aikinite are in the greenish yellow sector, at 564 nm. The reflectance spectra for the Buckhorn aikinite (A) also are plotted for direct comparison with those of buckhornite (B) in Figure 3. The similarities between the

TABLE 2. REFLECTANCE DATA AND COLOR VALUES FOR AIKINITE, TETRADYMITE AND CALAVERITE

	5		6		7		5		6		7	
λnm	R_1	R_2	R_1	R_2	R_1	R_2	$^{im}R_1$	$^{im}R_2$	$^{im}R_1$	$^{im}R_2$	$^{im}R_1$	$^{im}R_2$
400	39.7	45.75	51.9	54.9	46.2	54.5	24.5	31.1	38.6	43.0	33.9	44.0
420	40.0	45.9	51.95	55.5	48.0	56.3	24.8	31.1	38.5	43.1	36.7	45.5
440	40.3	46.1	52.2	56.1	50.6	58.4	25.1	31.3*	38.6	43.5	39.6	47.8
460	40.7	46.7	52.4	56.8	53.6	60.8	25.4	31.8	38.65	43.9	42.6	50.35
470	40.8	47.0	52.5	57.1	54.9	61.9	25.6	32.2	38.7	44.2	44.1	51.6
480	41.0	47.4	52.7	57.5	56.2	62.9	25.7	32.6	38.9	44.6	45.4	52.6
500	41.2	48.2	53.3	58.5	58.5	64.7	25.8	33.3	39.5	45.7	47.8	54.55
520	41.3	48.6	54.1	59.1	60.3	66.15	25.85	33.7	40.3	46.1	49.8	56.3
540	41.3	48.8	54.7	59.5	61.7	67.2	25.8	33.8	40.9	46.5	51.3	57.6
546	41.3	48.8	54.8	59.5	62.0	67.4	25.8	33.75	40.95	46.5	51.5	57.75
560	41.3	48.7	55.1	59.55	62.7	68.0	25.8	33.6	41.1	46.4	52.0	58.0
580	41.25	48.4	55.1	59.4	63.4	68.4	25.7	33.2	41.1	46.2	52.65	58.5
589	41.2	48.2	55.1	59.3	63.6	68.6	25.7	33.05	41.0	46.0	52.9	58.7
600	41.1	48.0	55.1	59.2	63.8	68.6	25.5	32.75	40.95	45.9	53.1	58.8
620	40.8	47.5	55.0	59.0	64.1	68.7	25.2	32.2	40.75	45.65	53.35	58.8
640	40.5	46.9	54.7	58.75	64.3	68.8	24.9	31.6	40.5	45.35	53.3	58.7
650	40.3	46.7	54.6	58.7	64.3	68.75	24.7	31.25	40.3	45.2	53.4	58.7
660	40.1	46.4	54.4	58.55	64.4	68.75	24.5	30.95	40.1	45.0	53.4	58.6
680	39.7	45.8	54.2	58.3	64.5	68.65	24.1	30.3	39.75	44.8	53.25	58.3
700	39.3	45.2	54.0	58.2	64.6	68.5	23.8	29.7	39.5	44.6	53.2	58.2
COLOR VALUES (Illuminant C, 6774K):												
x	.310	.311	.314	.313	.326	.321	.310	.311	.314	.313	.329	.323
y	.319	.322	.322	.322	.336	.331	.319	.323	.323	.323	.342	.335
$Y\%$	41.2	48.3	54.6	59.1	61.9	67.3	25.7	33.1	40.6	46.0	51.3	57.4
λ_d	557	561	574	569	574	574	539	555	573	567	574	573
$P_e\%$	0.8	1.9	2.5	2.4	9.5	6.7	0.6	2.1	2.8	2.7	12.0	8.6
COLOR VALUES (Illuminant A, 2856K):												
x	.447	.447	.450	.449	.459	.455	.446	.445	.450	.448	.461	.457
y	.410	.411	.410	.411	.415	.413	.410	.413	.411	.412	.417	.415
$Y\%$	41.1	48.2	54.8	59.2	62.6	67.8	25.6	33.1	40.8	46.0	51.95	57.9
λ_d	551	564	581	576	583	582	520	554	579	574	583	582
$P_e\%$	0.7	2.0	3.5	3.2	12.9	9.2	0.6	2.1	4.0	3.3	16.1	11.5

R_1 curves are evident, as are the differences in the R_2 curves. For completeness, the measured data for tetradymite (T) and calaverite (C) from Buckhorn are included. These provide a graphic expression of the distinctive nature of the spectral reflectances of the ore minerals (cf. Criddle et al. 1991, on the gold tellurides). Data taken from QDF2 (Criddle & Stanley 1986) for nagyagite (N), from its type locality, also are plotted. This has been done, in part, because of the concern, expressed by some members of the CNMMN, that buckhornite and nagyagite are similar, if not the same mineral. Optically, they are not. Nagyagite is weakly bireflectant compared with buckhornite and, though the dispersion of the R_2 spectrum of buckhornite is similar to the dispersion (for both vibration directions) of nagyagite, its overall reflectance is 5–7% higher, a significant amount in terms of reflectance, and one that certainly indicates a substantial difference in chemical composition.

Given the sensitivity of reflectance spectra to a mineral's composition and structure, it is worth noting that the reflectance spectra quoted in Anthony et al. (1990) for nagyagite (attributed to a "compilation prepared within the Department of Geology and Geophysics of the University of Missouri at Rolla") are identical (except for extrapolation to 400 nm) with those of Picot & Johan (1982). Compositional data were not provided

by Picot & Johan, so that it is doubly unfortunate that none of the compositions of nagyagite from three different localities, quoted by Anthony et al. (1990), correspond to their quoted (but inadequately attributed) reflectance data.

OTHER PHYSICAL PROPERTIES

Buckhornite has a gray streak; it is flexible (Figs. 1a, c) and sectile. Vickers Hardness Numbers were obtained (using a Leitz Miniload 2 hardness tester) at a loading of 10 g; this was the maximum possible because of the small grain-size, and because, even at this load, every indentation fractured. Only twelve indentations were possible, seven of which were measurable. These gave a range of 46–60 and an average of 54. Fracturing was particularly intense parallel to the elongation of the buckhornite blades, and consistent with a well-developed cleavage. It is unfortunate that a direct comparison with the VHN of nagyagite is not possible. Published data for this mineral (Criddle & Stanley 1986) give a range of 60–94, but for a loading of 100 g. The sectility and deformable nature of buckhornite were highlighted by the difficulty with which satisfactory mounts were made for X-ray powder photography. Indexable patterns were obtained only when thin foils of the mineral were finely "chopped" with a scalpel before the resultant
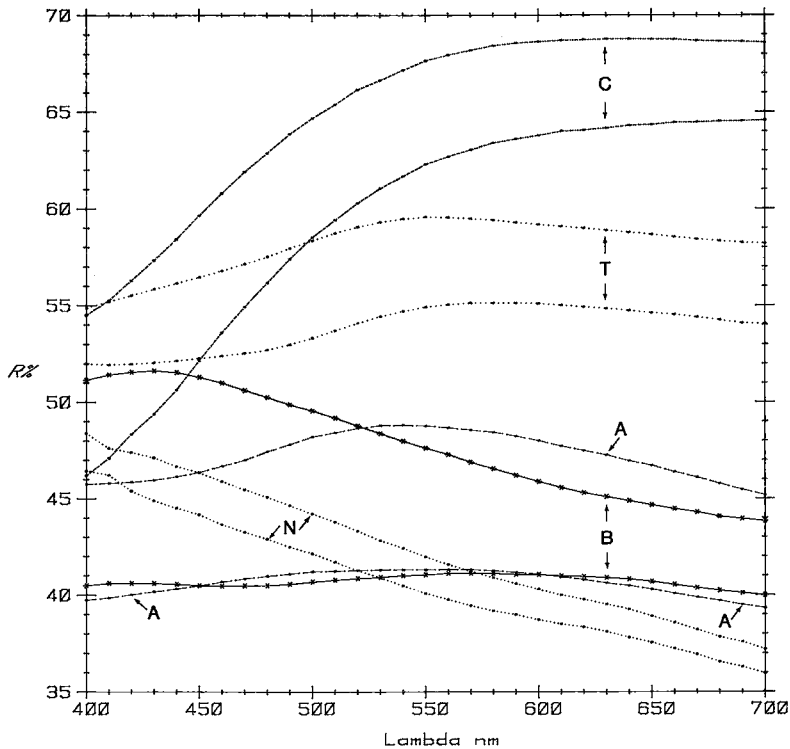
FIG. 3. Reflectance spectra for buckhornite (B), aikinite (A), calaverite (C), nagyagite (N) and tetradymite (T). Note the marked similarities and differences in dispersion between aikinite and buckhornite, and the substantial difference between the R spectra of buckhornite and those of nagyagite.

fragments were randomly oriented in the X-ray mount. There was too little material to measure the density of buckhornite.

CHEMISTRY

Chemical analyses were first performed on buckhornite, around 1940, by W. P. Schroder, at the Colorado School of Mines Experimental Plant. The results of these analyses (anal. 2, Table 3), though partial, suggested that buckhornite was a new mineral species. At that time, the presence of sulfur was attributed to contamination by pyrite. In the present investigation, electron-microprobe analyses were performed on different samples at Harvard and in London.

The analyses at Harvard (by D.E.L.) were made with a Cameca MBX electron microprobe, with pure element standards, and galena for Pb and S. Initially, analyses were attempted at 25 kV, using the $L\alpha$ lines for Au, Pb and Bi, but many of the buckhornite crystals proved too thin. The analyses (anal. 3, Table 3) were made, instead, at 15 kV and 23 nA, using the $M\alpha$ lines for Au, Pb and Bi. The Bi values were corrected for overlap from the

$M\tau$ peak, and the Sb values were corrected for overlap from the Te $L\eta$ peak. Antimony, which was reported by Schroder, was not found above the detection limit of 0.04 wt%. The copper content of buckhornite varies from crystal to crystal; none was detected in three crystals (detection limit, 0.04 wt%), and the other two gave 0.07 ± 0.03 (average of 5 analyses) and 0.19 ± 0.02 wt% (average of 4 analyses).

Analyses (by C.J.S.) of the samples used for the optical characterization (the identifying numbers used in Tables 1 and 2 are cross-referred in Table 3) were made with a Cambridge Instruments Microscan IX electron microprobe operated at 20 kV with a beam current of 25 nA on the Faraday cage. PbTe, FeS, PbS and the pure elements were used as standards.

The empirical formula, calculated from the averaged compositions (anal. 4, Table 3), and based on 9 atoms in the formula unit, is: $Cu_{0.02}Au_{1.02}Pb_{1.97}Bi_{1.04}Te_{2.06}S_{2.89}$, corresponding to a simplified formula of $AuPb_2BiTe_2S_3$. Table 3 also provides our analytical data for those minerals (aikinite, tetradymite, calaverite and gold) with which buckhornite is intimately associated. In addition, we have included data for nagyagite to demonstrate the

TABLE 3. COMPOSITIONAL DATA FOR BUCKHORNITE AND OTHER SPECIES

wt%	Cu	Ag	Au	Pb	Bi	Sb	Te	S	Total
1.	--	--	16.8	35.4	17.8		21.8	8.2	--
2.	1.5	--	9	28	18	4	18	7	85.5
3.	0.04	--	16.5	34.8	17.7	0.04	21.5	8.4	98.9
(range:	0.00-	--	16.1-	34.1-	17.1-		21.1-	8.3-	)
	0.19		16.7	35.6	18.2		21.7	8.6	)
4.	0.1	--	17.0	34.5	18.4	--	22.3	7.8	100.1
(range:	0.0-	--	16.5-	34.4-	17.8-	--	21.4-	7.7-	)
	0.1		17.3	35.0	18.9		22.4	7.9	)
5.	--	--	16.8	34.6	18.6	--	22.4	7.8	100.2
6.	0.1	--	17.1	34.6	18.2	--	22.1	7.9	99.9
7.	0.1	--	17.0	34.5	18.7	--	22.3	7.9	100.5
8.	2.7	--	17.0	38.1	11.4	1.2	21.1	8.3	99.8
9.	--	--	16.8	36.6	16.5	--	22.3	8.2	100.4
10.	10.2	--	--	32.6	41.5	--	--	16.2	100.5
11.	0.2	--	--	--	60.1	--	35.1	4.3	99.7
12.	0.2	0.8	42.0	--	--	--	56.2	--	99.2
13.	0.1	5.2	94.3	--	--	--	--	--	99.6
14.	0.1	0.1	7.5	56.9	--	7.8	16.3	10.4	99.1

1. Ideal formula $AuPb_2BiTe_2S_3$ - buckhornite
2. W.P. Schoder analysis
3. Buckhornite, D.E.L. average of 14 analyses on 5 grains, EPMA
4. .. .. C.J.S. average of 7 analyses, EPMA
5. .. .. .. corresponds to grain 1 of R data, EPMA
6. .. .. .. corresponds to grain 2 of R data, EPMA
7. .. .. .. corresponds to grain 3 of R data, EPMA
8. Unnamed phase of Pašava et al. (1986), EPMA (contains As and Se)
9. Unnamed phase of Kovalenker et al. (1990), EPMA
10. Alkinite, C.J.S., corresponds to grain 5 of R data, EPMA
11. Tetradymite, C.J.S., corresponds to grain 6 of R data, EPMA
12. Calaverite, C.J.S., corresponds to grain 7 of R data, EPMA
13. Gold, C.J.S., EPMA
14. Nagyagite, Nagyag, Romania, Criddle & Stanley (1986, QDF2.250)

TABLE 4. X-RAY POWDER DATA FOR BUCKHORNITE

I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl
w	9.25	9.32	001	ms	1.8158	1.8141	134
w	6.11	6.12	020	ms	1.7900 (	1.7923	161
mw	5.129	5.118	021			1.7915	222
mw	4.649	4.661	002	w	1.7478	1.7493	070
vvw	4.042	4.082	030	s	1.7084 (	1.7088	203
vs	3.739 (	3.747	101			1.7058	063
		3.739	131	vvw	1.6461	1.6459	232
vvw	3.580	3.583	111	ms	1.5655	1.5666	135
w	3.424	3.402	120	vvw	1.5199	1.5205	172
vw	3.224	3.196	121	vvw	1.4864	1.4880	252
vs	3.108	3.107	003	vvw	1.4618	1.4543	082
vvw	2.971	2.982	112	ms	1.4460	1.4449	260
mw	2.894	2.890	130			1.3781	205
vvs	2.763	2.760	131	vvw	1.3779 (	1.3765	065
vs	2.456 (	2.456	132			1.3463	091
		2.451	140	w	1.3467 (	1.3123	146
vvs	2.390	2.370	141			1.3119	056
vw	2.292 (	2.294	123	ms	1.3121 (	1.3102	263
		2.289	014			1.2814	331
vvw	2.178 (	2.181	043	m	1.2807 (	1.2802	322
		2.178	024	ms	1.2428	1.2425	313
mw	2.115	2.116	133			1.2141	0.10.1
s	2.044 (	2.046	200	w	1.2136 (	1.2128	266
		2.041	060	w	1.1888	1.1917	350
vvw	1.9908	1.9937	061	vvw	1.1715	1.1718	314
vw	1.9308	1.9245	143	vvw	1.1473	1.1472	246
vw	1.8655	1.8644	005	m	1.1300	1.1294	194

differences between its composition and that of buckhornite.

X-RAY DATA

Single crystals studied by the precession method using Zr-filtered MoKα radiation show buckhornite to be orthorhombic. An apparent systematic absence $0kl$ with $k+l = 2n$ was observed in a-axis films, but weak powder lines violate this rule. Thus, the possible space-groups are $Pmmm$ or $P222$. Unit-cell parameters refined from the powder data (collected and indexed by JGF) in Table 4 are: a 4.092(2), b 12.245(4), c 9.322(4) Å, and V 467.1 Å^3. The non-standard orientation of the cell was chosen to emphasize its relationship to a tetragonal subcell in which a_T is equal to a_o and $1/3b_o$, and c_T is equal to c_o, which is evident from the precession photographs. Most of the strong lines in the powder pattern correspond to subcell reflections. The density calculated for the empirical formula (anal. 4, Table 3) is 8.43 g/cm^3, and that for the ideal formula (anal. 1, Table 3) is 8.34 g/cm^3.

This is not the place to address the uncertainty concerning the symmetry of nagyagite. There is an obvious need for further investigation of the mineral; unfortunately, however, a holotype specimen does not exist, and it will be a laborious process to establish satisfactory neotypes. Suffice it to say that X-ray data for buckhornite are distinctive and different from those of the inadequately characterized nagyagite.

POSSIBLE RELATIONSHIPS

After nagyagite, buckhornite is the second known sulfotelluride of gold and lead. Their simplified formulae, $AuPb_2BiTe_2S_3$ for buckhornite and $Pb_5Au(Te,Sb)_4S_{5-8}$ (Anthony et al. 1990) for nagyagite, were sufficient for some members of the CNMMN to suggest that the two minerals are part of a homologous series. It is an easy matter to construct such a hypothetical series (and this we have done). However, it is our view that too little is known of what may well be a very complex system, certainly one that is poorly understood, to publish such speculation. In addition, the lack of simple charge-balance points to metal-metal bonding in nagyagite.

Two unnamed minerals have recently been described that are similar, at least compositionally, to buckhornite, but neither description included X-ray data. We have included the compositional data for these minerals in Table 3. The mineral described by Pašava et al. (1986) (anal. 8, Table 3) is from the Pepr mine, Jílové u Prahy, Czechoslovakia. The second mineral, from the Megradzor orefield, Armenia (Kovalenker et al. 1990) is compositionally (anal. 9, Table 3) virtually identical with buckhornite. As described, it is also physically similar, sharing the platy habit of buckhornite, and it occurs in a similar mineral association.

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