

COPPER SULFIDES FROM ALBERTA: YARROWITE Cu_9S_8 AND SPIONKOPITE $\text{Cu}_{39}\text{S}_{28}$

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ABSTRACT

Yarrowite, Cu_9S_8 , and spionkopite, $\text{Cu}_{39}\text{S}_{28}$, are new minerals that have been identified in the red-bed copper deposits in the Yarrow Creek and Spionkop Creek areas of southwestern Alberta. Previous reports on these deposits describe these minerals under the name *blaubleibend covelline*. Yarrowite and spionkopite occur in replacement of other copper sulfides by selective removal of copper. Yarrowite also replaces spionkopite and copper-iron sulfides. The overall structures, as evidenced by cleavage traces and optical properties, are crystallographically related throughout the replacement process. Yarrowite has a hexagonal lattice with $a = 3.800$ (1), $c = 67.26$ (4) Å, $Z = 3$ and $D(\text{calc.}) = 4.89$ g/cm³. Spionkopite also is hexagonal with $a = 22.962$ (3), $c = 41.429$ (11) Å, $Z = 18$ and $D(\text{calc.}) = 5.13$ g/cm³. Space groups for both minerals are $P3m1$, $P\bar{3}m1$ or $P321$. Yarrowite and spionkopite have well-developed subcells that strongly resemble the unit cell of covelline. These subcells have formed the basis of previous attempts to index the X-ray powder patterns of the minerals.

Keywords: yarrowite, spionkopite, red-bed copper, blaubleibend covelline, copper sulfide, Yarrow Creek – Spionkop Creek copper deposit, Alberta.

SOMMAIRE

La yarrowite Cu_9S_8 et la spionkopite $\text{Cu}_{39}\text{S}_{28}$, deux nouvelles espèces minérales, ont été découvertes dans le Sud-ouest de l'Alberta dans les gîtes de cuivre de type red-bed des régions de Yarrow Creek et Spionkop Creek, respectivement. Jusqu'à présent, on les avait considérées comme variétés de "covelline blaubleibend". Elles résultent du remplacement d'autres sulfures de cuivre par élimination sélective du Cu; la yarrowite remplace aussi la spionkopite et les sulfures de cuivre-fer. D'après les traces de clivage et les propriétés optiques, les deux nouveaux minéraux ont des structures qui restent en relation cristallographique au cours du remplacement. La yarrowite est hexagonale, a 3.800(1), c 67.26(4) Å, $Z = 3$, $D(\text{calc.}) = 4.89$, groupe spatial $P3m1$, $P\bar{3}m1$ ou $P321$; la spionkopite est hexagonale aussi, a 22.962(3), c 41.429(11) Å, $Z = 18$, $D(\text{calc.}) = 5.13$, groupe spatial $P\bar{3}m1$, $P3m1$ ou $P321$. Dans chaque cas,

on observe une maille sous-multiple qui ressemble fortement à la maille de la covelline; c'est celle qui a servi aux tentatives antérieures de dépouillement du cliché de poudre.

(Traduit par la Rédaction)

Mots-clés: yarrowite, spionkopite, gîte de cuivre de type red-bed, covelline blaubleibend, sulfure de cuivre, gîte Yarrow Creek – Spionkop Creek, Alberta.

INTRODUCTION

Microprobe studies by Goble & Smith (1973) led to the identification of two and possibly three varieties of blaubleibend covelline within the stratabound red-bed copper deposits of southwestern Alberta, Canada. X-ray data indicate that these blaubleibend covellines consist of two distinct minerals, yarrowite ($\bar{y}\bar{a}'\bar{r}\bar{o}\bar{i}\bar{t}$) and spionkopite ($\text{spi}'\bar{u}\bar{n}\bar{k}\bar{o}\bar{p}\bar{i}\bar{t}$). The minerals are named for the type localities, the Yarrow Creek and Spionkop Creek valleys. The minerals and names have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

THE YARROW CREEK – SPIONKOP CREEK COPPER DEPOSIT

Copper sulfides in the Yarrow Creek – Spionkop Creek deposit occur by the selective replacement of small (~0.5 mm diameter) spheroidal quartz aggregates, feldspar grains, fractured quartz grains and carbonate cement within the sandstones and quartzites of the Precambrian Grinnell Formation, a redbed, marginal continental, shallow water sequence. Copper minerals are also found in diorite sills and dykes that intruded the Grinnell Formation. Details of the deposit are summarized by Goble (1970, 1977) and Morton *et al.* (1973, 1974).

Copper-bearing sulfides identified by Morton *et al.* (1974) include chalcopyrite, bornite, blaubleibend covelline, digenite, djurleite, idaite, wittichenite and tennantite. Goble & Smith (1973) showed the blaubleibend covelline to have preferred compositions of $\text{Cu}_{1.12\pm 0.03}\text{S}$, $\text{Cu}_{1.32\pm 0.04}\text{S}$ and possibly $\text{Cu}_{1.22\pm 0.02}\text{S}$. They also

found that the "digenite" has a composition of $\text{Cu}_{1.76\pm 0.06}\text{S}$, which is more characteristic of anilite than of digenite. All the above phases, with the exception of $\text{Cu}_{1.22}\text{S}$, idaite and digenite, have been re-identified in this study. When analyzed, "digenite" was found to be anilite; idaite was not encountered, and $\text{Cu}_{1.22}\text{S}$ will be discussed below. Tennantite is abundant in samples from sedimentary rocks but absent in the diorites that intruded these rocks. Blaubleibend covellines of approximate compositions $\text{Cu}_{1.12}\text{S}$ and $\text{Cu}_{1.32}\text{S}$ have been shown to be the new minerals yarrowite and spionkopite, respectively. All blaubleibend covellines of the approximate composition $\text{Cu}_{1.22}\text{S}$ noted by Goble & Smith (1973) were found to be mixtures of yarrowite and spionkopite. Near-surface leaching of copper from the natural specimens produced the following mineralogical changes: djurleite \rightarrow anilite + $\text{Cu}(\text{aq}) \rightarrow$ spionkopite + $\text{Cu}(\text{aq}) \rightarrow$ yarrowite + $\text{Cu}(\text{aq}) \rightarrow$ covellite (minor) + $\text{Cu}(\text{aq})$. In this sequence, faint djurleite cleavage traces parallel the anilite (101) cleavage traces and the traces of the spionkopite, yarrowite and covellite basal cleavages, suggesting progressive structural changes with loss of copper from specific crystallographic sites. Spionkopite occurs only as the lamellar replacements of anilite and djurleite; yarrowite also occurs as stellate aggregates replacing copper sulfides and within fractures in copper-iron sulfides.

PROCEDURES

Slices cut from hand samples were mounted in cold-setting plastic, polished and examined with the ore microscope. Reflectivity and micro-indentation-hardness measurements were made where grain size permitted. A small single crystal of covellite from Summitville, Colorado, supplied by G.W. Robinson*, was used for comparison in the X-ray studies. Its optical and X-ray properties and composition corresponded to "optically normal" covellite.

With the exception of the covellite mentioned above, samples for X-ray analysis were selected from polished sections on the basis of size, optical homogeneity, constancy in orientation and degree of segregation from associated sulfides. The grains selected were plucked from the polished surface, cleaned of other sulfides using a needle set in a pin vise, washed

in acetone and mounted on glass fibres using a nail polish - cyanoacrylate adhesive mixture.

For the X-ray powder data, standard films of covellite, yarrowite and spionkopite were prepared using fragments mounted in a 114.6 mm diameter Gandolfi camera. The blaubleibend covellines were first analyzed using an Applied Research Laboratories-AMX electron microprobe equipped with a Tracor Northern NS-880 energy-dispersive spectrometer. Operating conditions were: accelerating voltage 15 kV, sample current about 1.5 nA, beam diameter about $2\mu\text{m}$. Standards used were CuS and $\text{Cu}_{1.8}\text{S}$ for Cu and S, and pyrrhotite (60.4% Fe, 39.6% S) for Fe. Apparent concentrations were corrected for absorption, secondary fluorescence and atomic number effects using a general ZAF program, TAPEEMX2 (Department of Geological Sciences, Queen's University). Samples with compositions close to the values of $\text{Cu}_{1.12}\text{S}$, $\text{Cu}_{1.22}\text{S}$ and $\text{Cu}_{1.32}\text{S}$ determined by Goble & Smith (1973) were plucked from polished sections and X-rayed on the 114.6-mm Gandolfi camera. Standard films of associated sulfides, silicates and carbonates were similarly prepared from material plucked from polished surfaces. X-ray patterns were checked against JCPDS diffraction data, where possible.

The unit-cell parameters of the blaubleibend covellines were determined from precession and Weissenberg photographs prepared using cleavage fragments of these phases. These parameters were then refined using Gandolfi simulated powder-data (corrected for film shrinkage) and a least-squares refinement program (Appleman & Evans 1973). For the selection of fragments suitable for use in single crystal work, the grain to be examined was X-rayed on the Gandolfi camera, and the resulting film was compared to the standard films mentioned above. If this comparison showed the grain to be composed of either of the observed blaubleibend covellines, it was transferred to a goniometer head and X-rayed on the precession camera to check its suitability for single-crystal work. On this basis one sample of each of yarrowite and spionkopite was selected as suitable for further study (Goble, in prep.).

Intensities were estimated by visual comparison with the {110} covellite reflection on standard-scale films prepared from multiple exposures. Filtered Cu radiation was used for all Gandolfi and Weissenberg films, and Mo radiation for all precession films.

OPTICAL AND PHYSICAL PROPERTIES

Yarrowite and spionkopite are opaque. In

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reflected light in air these minerals are bireflectant in blue and bluish-white for the *O* and *E* rays, respectively. The blue of the *O* ray is darker for yarrowite than for spionkopite. In oil yarrowite is dark blue with a violet tint (*O* ray) and bluish-white (*E* ray); spionkopite has colors only slightly darker than those observed in air.

Yarrowite is strongly anisotropic in orange-red, with no internal reflections. Reflectances in air for light of 546 nm are: R_o 12.1%, R_e 20.6%. Vickers microhardness is 93–98 kg/mm² (15 g load). Spionkopite is anisotropic in orange, with no internal reflections. Reflectances in air for light of 546 nm are: R_o 15.5%, R_e 20.6%. Vickers microhardness is 63–93 kg/mm² (15 g load).

In most cases yarrowite can be distinguished from spionkopite because the former is a darker shade of blue and is more strongly bireflectant and anisotropic. In immersion oils yarrowite has a faint violet tint that spionkopite lacks. Both yarrowite and spionkopite are blaubleibend (blue-remaining) covellines; that is, both lack the characteristic red-violet color of "optically normal" covellite when viewed through immersion oils.

COMPOSITION AND UNIT CELL

Extensive electron-microprobe analyses by Goble & Smith (1973) indicated compositions of $Cu_{1.12 \pm 0.03}S$ for yarrowite and $Cu_{1.32 \pm 0.04}S$ for spionkopite. Traces of Fe were detected. The fourteen energy-dispersive analyses shown in Table 1, performed to check composition prior to X-ray analysis, gave values of $Cu_{1.12 \pm 0.05}S$ for yarrowite and $Cu_{1.32 \pm 0.01}S$ for spionkopite. Traces of Fe were detected in two samples of yarrowite. Because of the poor totals, these analyses are not regarded as being as reliable as those of Goble & Smith (1973) but they serve to confirm the original data. Relationships between the crystal structure of the copper sulfides and mineral composition (Goble, in prep.) indicate "ideal" structural compositions of $Cu_{1.12}S$ and $Cu_{1.40}S$ for yarrowite and spionkopite, respectively.

The yarrowite X-ray powder pattern (Gandolfi) was indexed as hexagonal with $a = 3.800 \text{ \AA}$, $c = 67.26 \text{ \AA}$ (Table 2). The space group is determined as $P3m1$, $P\bar{3}m1$ or $P321$ (Goble, in prep.). With the composition of $Cu_{1.12}S$ in this hexagonal cell, the most reasonable formula is Cu_9S_8 with $Z = 3$. $D(\text{calc.})$ is 4.89 g/cm³.

Representative (*h0l*) precession photographs of

TABLE 1. ELECTRON MICROPROBE ANALYSES OF YARROWITE, SPIONKOPITE AND COVELLINE

MINERAL	% Cu	% S	% Fe	Total %	Cu:S ratio
yarrowite	65.3	30.6	nd	95.9	1.08
yarrowite	68.5	30.4	nd	98.9	1.14
yarrowite ?	70.1	30.8	nd	100.9	1.15
yarrowite ?	70.3	30.2	0.5	101.0	1.17
yarrowite ?	71.7	30.8	0.3	102.7	1.17
yarrowite	69.7	33.1	nd	102.8	1.06
yarrowite	70.1	32.8	nd	102.9	1.08
yarrowite	70.8	32.8	nd	103.5	1.09
spionkopite	67.1	25.8	nd	92.9	1.31
spionkopite	67.8	25.9	nd	93.7	1.32
spionkopite	68.8	26.4	nd	95.2	1.32
spionkopite	69.0	26.5	nd	95.5	1.31
spionkopite	69.8	26.7	nd	96.5	1.32
spionkopite	70.8	27.2	nd	98.0	1.32
covellite	66.9	33.8	nd	100.7	1.00
covellite	67.1	34.1	nd	101.2	0.99

Standards used are Cu_9S_8 , Cu_3S_2 , Fe (pyrrhotite: $Fe = 60.4\%$, $S = 39.6\%$); ZAF corrections applied; mineral identification based upon optical data; covellite sample from Summitville, Colorado; nd designates an element analyzed for but not detected.

yarrowite and covellite are shown schematically in Figure 1. The strong resemblance of the yarrowite to the covellite reciprocal lattice is apparent, reflecting a well-developed yarrowite subcell with $a' = a = 3.800 \text{ \AA}$, $c' = c/4 = 16.815 \text{ \AA}$, corresponding approximately to the covellite unit cell with $a = 3.796 \text{ \AA}$, $c = 16.36 \text{ \AA}$ (Berry 1954). However, double reflections near (105), (108) and (208) (covellite indexing used) clearly illustrate the deviation of the yarrowite from the covellite unit cell. This is also reflected in changes of spacing of major reflections. The X-ray powder pattern of covellite is similar to that of yarrowite but includes a reflection at $d = 2.724 \text{ \AA}$ (55%) indexed as (006). There is also an overall weakening of the yarrowite lines (based upon $I_{110} = 100\%$) relative to covellite.

The spionkopite X-ray powder pattern (Gandolfi) was indexed as hexagonal with $a = 22.962 \text{ \AA}$ (i.e., $6 \times 3.827 \text{ \AA}$), $c = 41.429 \text{ \AA}$ (Table 3). The space group is determined as $P\bar{3}m1$, $P3m1$ or $P321$ (Goble, in prep.). With the "ideal" composition of $Cu_{1.40}S$ in this cell, the most reasonable formula is $Cu_{36}S_{28}$ with $Z = 18$. $D(\text{calc.})$ is 5.13 g/cm³. The natural material would have an analyzed composition of $Cu_{37}S_{28}$.

Representative (*h0l*) precession photographs of spionkopite and covellite are shown schematically in Figure 2. The strong resemblance of spionkopite and covellite reciprocal lattices is again apparent, reflecting a well-developed spionkopite subcell with $a' = a/6 = 3.827 \text{ \AA}$, $c' = 3c/7 = 17.736 \text{ \AA}$, corresponding approximately to the covellite unit cell with $a = 3.796 \text{ \AA}$, $c = 16.36 \text{ \AA}$ (Berry 1954). However, double reflections near (105), (205), (108) and (208) (covellite indices used) clearly il-

TABLE 2. X-RAY SIMULATED POWDER DATA (GANDOLFI CAMERA) FOR YARROWITE

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	hkl	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	hkl
20	5.955		mal	12	1.613	1.615	208
5	5.332			12	1.586	(1.589)	(20.15)
30	5.032		mal	15	1.572	1.573	11.24
5	4.828	(4.804)	(00.14)	5	1.534	1.532	20.16
5	4.296			5	1.504	(1.506)	(20.18)
8	3.896			8	1.472	1.470	11.29
25	3.678		mal	5	1.441	(1.440)	(10.42)
5	3.537	(3.540)	(00.19)	5	1.421	(1.419)	(20.24)
8	3.215	3.230	104	5	1.385	(1.386)	(10.44)
55	3.061	3.065	108	8	1.360	1.361	10.45
25	2.949		mal	5	1.314	(1.314)	(11.37)
35	2.767	2.777	10.13	5	1.279	1.280	20.33
12	2.513		mal	8	1.232	1.230	218
12	2.292	2.295	10.21	5	1.210	1.209	21.13
8	2.180	(2.186)	(10.23)	5	1.163	1.160	00.58
8	2.120			12	1.097	1.097	300
8	2.075	2.083	10.25	5	1.073	(1.073)	(30.13)
5	1.961			5	1.063	1.062	21.33
100	1.899	1.900	110	5	1.028	(1.028)	(11.55)
5	1.827	(1.829)	(11.10)	5	1.022	1.022	30.24
8	1.783	(1.784)	(11.13)	5	0.9907	0.9899	11.58
15	1.731	1.733	10.33	8	0.9505	0.9501	220
8	1.687	(1.682)	(00.40)	5	0.9001	0.8998	22.24
8	1.670	(1.674)	(11.19)	5	0.8188	0.8188	408
5	1.639	1.638	204				

"mal" refers to d-spacings identified as belonging to admixed malachite; bracketed d_{calc} and hkl values were assigned by the refinement program but were not observed on single-crystal patterns. 2.796 Å (00.24) with $I_{obs} = 20$ is obscured by a malachite line.

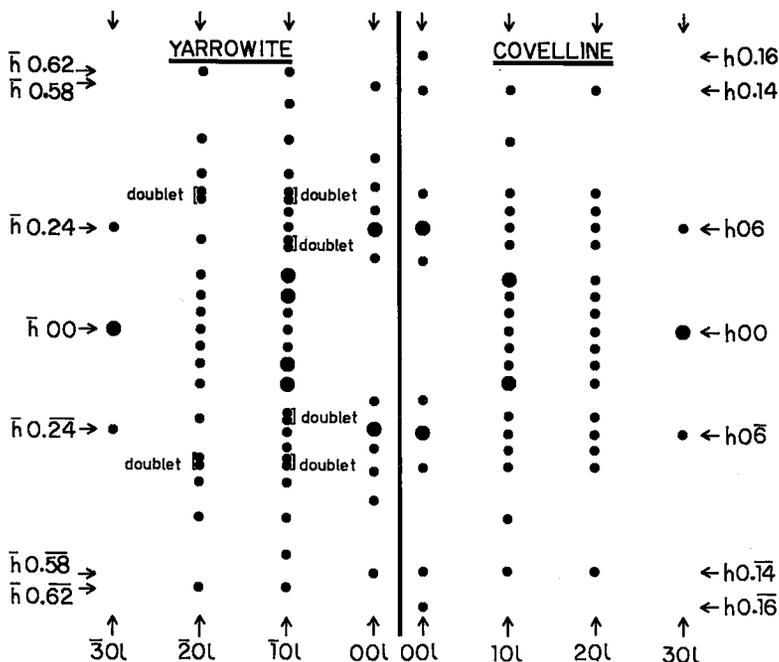


FIG. 1. Comparison of observed (h0l) precession data for yarrowite (left) and covellite (right); doublet reflections in yarrowite are indicated.

illustrate the deviation of the spionkopite from the covellite unit cell. This is also demonstrated by changes of spacing of major re-

flections. The X-ray powder pattern of spionkopite is readily distinguished from those of covellite and yarrowite by the presence of the rela-

TABLE 3. X-RAY SIMULATED POWDER DATA (GANDOLFI CAMERA) FOR SPIONKOPITE

I_{obs}	d_{obs} (Å)	d_{calc} (Å)	hkℓ	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	hkℓ
8	5.955		mal	30	1.820	1.822	6.0.19
5	5.324			12	1.738	(1.737)	(6.6.10)
15	5.032		mal	8	1.684		
5	4.653			20	1.622	1.625	12.0.5
20	3.681		mal	12	1.573	1.578	12.0.8
5	3.530			15	1.473	1.470	12.0.13
8	3.408			8	1.424	1.421	12.0.15
15	3.278	(3.273)	(6.0.2)	8	1.406	1.406	6.6.20
5	3.223	3.223	6.0.3	8	1.386	(1.381)	(0.0.30)
85	3.076	3.078	6.0.5	8	1.361	1.374	6.6.21
8	2.964	2.964	0.0.14	12	1.321	1.319	12.0.19
5	2.926			12	1.241	1.239	6.0.31
20	2.849		mal	5	1.151	1.151	0.0.36
30	2.777	2.792	6.0.8	12	1.104	1.105	18.0.0
5	2.592	2.588	6.0.10	12	1.089	(1.090)	(0.0.38)
20	2.517		mal	8	1.065		
5	2.483	(2.488)	(6.0.11)	8	1.032	1.035	18.0.14
20	2.386	2.391	6.0.12	12	0.9880	0.9862	6.6.36
25	2.297	2.297	6.0.13	12	0.9568	0.9569	12.12.0
8	2.185	(2.180)	(0.0.19)	8	0.9124	(0.9113)	(18.6.6)
8	2.123	2.122	6.0.15	8	0.8823		
8	2.060			5	0.8156	(0.8156)	(24.0.9)
12	1.965	1.963	6.0.17	5	0.7982	(0.7983)	(12.6.40)
100	1.910	1.910	6.6.0				

mal refers to d-spacings identified as belonging to intergrown malachite; bracketed d_{calc} and $hk\ell$ values were assigned by the refinement program but were not observed on single crystal photographs.

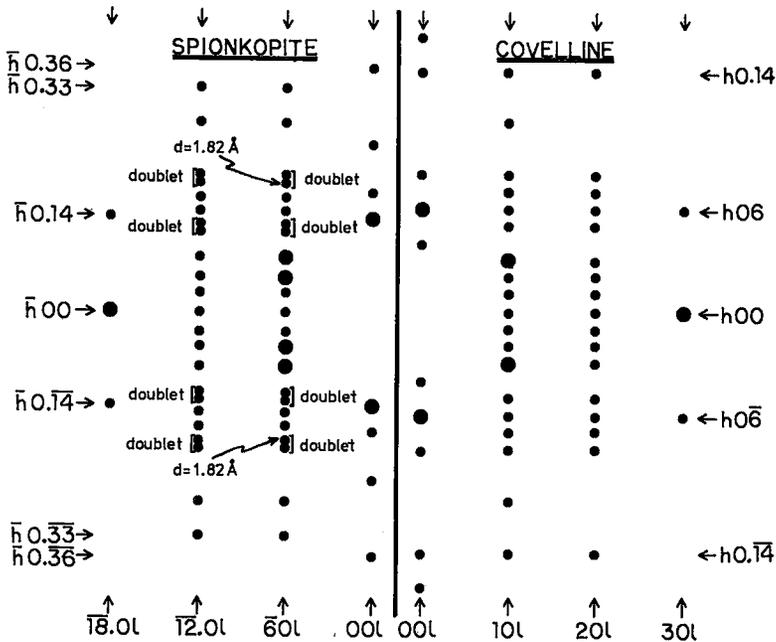


FIG. 2. Comparison of observed ($h0l$) precession data for spionkopite (left) and covellite (right); doublet reflections in spionkopite are indicated. In spionkopite only very weak reflections are observed with $|h| \neq 6n$; these have not been included.

tively strong line at $d = 1.820 \text{ \AA}$ (Table 3, Fig. 2).

DISCUSSION

Natural blaubleibend (or blue-remaining)

covellines have been reported in nature for some time (e.g., Ramdohr 1943, 1969) and attributed to a small excess of Cu in the covellite structure. Frenzel (1959) synthesized blaubleibend covellite with a composition approxi-

TABLE 4. COMPARISON OF PUBLISHED BLAUBLEIBEND COVELLINE POWDER PATTERNS WITH THE POWDER PATTERN OF YARROWITE

I _{obs}	FRENZEL (1959) CORNWALL			RICKARD (1972)			MOH (1971) TYPE A			YARROWITE		
	d _{obs} (Å)	hkl	I _{obs}	d _{obs} (Å)	hkl	I _{obs}	d _{obs} (Å)	hkl	I _{obs}	d _{obs} (Å)	hkl	
VW	3.34	100				5	3.28	100		-	3.293	100
VW	3.19	101	VW	3.24		20	3.22	101		8	3.215	104
S	3.06	102	S	3.07		70	3.05	102	3.035	55	3.061	108
S	2.80	103	m/s	2.85		40	2.81	103	2.797	**	2.796	00.24
		006	m	2.73		30	2.75	006	2.718	35	2.767	10.13
m/w	2.51	104										
VW	2.27	105				5	2.09	106		8	(2.075)	(10.25)
VW	2.09	106				5	2.06	008				
VS	1.895	107	VS	1.896		100	1.896	107	1.899*	100	1.899	110
VW	1.813	112	VW	1.800								
m/w	1.736	108	VW	1.728		5	1.741	108	1.732	15	1.731	10.33
VW	1.617	202	VW	1.620					1.632	5	1.639	204
S	1.570	116	m	1.567		5	1.558	116	1.558	15	1.572	11.24
VW	1.458	10.10										
VW	1.360	10.11	VW	1.358						8	1.360	10.45
VW	1.283	208								5	1.279	20.33
VW	1.233	11.10								8	(1.232)	(218)
		212	VW	1.220		5	1.226	212				
VW	1.213	209								5	(1.210)	(21.13)
m/w	1.094	20.11	VW	1.100						12	1.097	300
W	1.022	00.16								5	1.022	30.24
W	0.9883	20.13								5	0.9907	11.58
W	0.9490	20.14								8	0.9505	220
W	0.9033	30.10								5	0.9001	22.24

*The pattern labelled MOH (1971) is as measured from a photograph and scaled to produce d_{110} equal to d_{110} for yarrowite.

**The plane (00.24) at a spacing of 2.796 Å is obscured on powder patterns by a malachite line.

mating yarrowite by treating digenite and chalcocite with strong inorganic acids. Subsequent research and synthesis (Frenzel 1961) led to the production of blaubleibend covelline with a composition approximating spionkopite.

Moh (1971) also synthesized two varieties of blaubleibend covelline with compositions approximating yarrowite and spionkopite, which he designated as Type A and Type B. Table 4 includes a listing of powder data obtained by measuring a powder photograph (reproduced in his paper) and scaling these data so that d_{110} is equal to d_{110} for yarrowite. As such, the data represent only an approximation and are used simply to make a general comparison with the yarrowite data shown in Table 4. Nevertheless, the close correspondence of the powder data for Moh's Type A blaubleibend covelline and for yarrowite, together with the similarity of composition ($\text{Cu}_{1.2}\text{S}$ for Type A blaubleibend covelline, $\text{Cu}_{1.12}\text{S}$ for yarrowite) indicates that Moh's Type A blaubleibend covelline is a synthetic analogue of yarrowite. His Type B blaubleibend covelline, with composition $\text{Cu}_{1.3}\text{S}$, has a reflection in that position corresponding to $d = 1.82 \text{ \AA}$ (relative to d_{110} adjusted to 1.91 Å), identifying the phase as a synthetic anal-

ogue of spionkopite. More recently, Potter (1977) used the technique of Moh (1971) to synthesize phases with compositions of $\text{Cu}_{1.1\pm 0.1}\text{S}$ and $\text{Cu}_{1.4\pm 0.1}\text{S}$, corresponding to the "ideal" yarrowite and spionkopite compositions; he showed that these phases are metastable in the system copper-sulfur.

Both Frenzel (1959) and Rickard (1972) have reported X-ray powder data for synthetic blaubleibend covelline. These data are reproduced in Table 4 and are compared with the data for yarrowite. The similarity of these powder patterns to that of yarrowite again indicates that the materials studied were synthetic analogues of yarrowite. Direct comparison of X-ray films produced by synthesizing blaubleibend covelline (using Rickard's method) with standard yarrowite films confirms this correspondence.

The observed presence of (1) natural phases (yarrowite and spionkopite) having compositions of $\text{Cu}_{1.12}\text{S}$ and $\text{Cu}_{1.32-1.40}\text{S}$ produced by natural leaching of more copper-rich sulfides and of (2) corresponding metastable synthetic phases of approximately the same compositions produced by synthetic leaching of more copper-rich sulfides (the natural and synthetic phases

having similar powder patterns) suggest that yarrowite and spionkopite are naturally occurring but metastable phases in the system copper-sulfur. However, as will be shown in a subsequent paper (Goble, in prep.), synthetic blaubleibend covellines may exist in a metastable pseudocubic structure that is different from the hexagonal structure of spionkopite, even though the powder patterns are similar. Therefore, while it is clear that synthetic analogues of yarrowite and spionkopite have been produced, it has not been shown conclusively that these synthetic analogues are structurally identical to yarrowite and spionkopite. Because these correspondences based upon compositional and powder data are of doubtful validity, the work of Potter (1977) should be applied to natural yarrowite and spionkopite with caution. Whereas Potter has shown that the synthetic blaubleibend covellines with which he was working are metastable, his use of optical and X-ray powder data did not prove that these phases were in fact yarrowite and spionkopite. Until the ambiguity is resolved by the use of single-crystal X-ray data, the stability of yarrowite and spionkopite must remain in doubt.

Previous attempts to index the blaubleibend covelline X-ray powder data have led to indices based on a covelline-like unit cell, because of similarities in powder data (see, for example, Frenzel 1959, Rickard 1972). This cell would approximate the subcells present in yarrowite and spionkopite. For example, in both yarrowite

and spionkopite such an indexing scheme would almost certainly result in those reflections on the powder pattern equivalent to covelline (103) and (006) [covelline spacings are 2.829 and 2.720 Å, yarrowite spacings 2.787 and 2.796 Å, spionkopite spacings 2.801 and 2.972 Å; because of the interference of malachite reflections, all spacings are as determined on precession films] being assigned indices of (006) and (103), respectively, owing to the increased spacing of the (\sim 006) planes relative to the (\sim 103) planes of yarrowite and spionkopite in comparison with covelline. Such misindexing would result in approximate unit cells with $a = 3.80$ Å, $c \simeq 16.7$ Å for yarrowite and with $a = 3.80$ Å $c \simeq 16.85$ Å for spionkopite. Both of these unit cells correspond closely to that of covelline, although $a:c$ ratios are different from that of covelline. This is possibly what has been done for those previously published powder data for blaubleibend covellines that are indexed on a covelline unit cell.

One consequence of the revised indexing for yarrowite is shown in Figure 3. Rickard (1972) determined the relationship between formation pH and cell volume for covelline, indicated by the solid line through the solid circles of Figure 3. His data for synthetic blaubleibend covelline are shown in Figure 3 by solid triangles, with the cell volume calculated on the basis of powder data indexed for a covelline-type cell. If we make the change to a yarrowite-type subcell ($c' = c/4$), the data for Rickard's

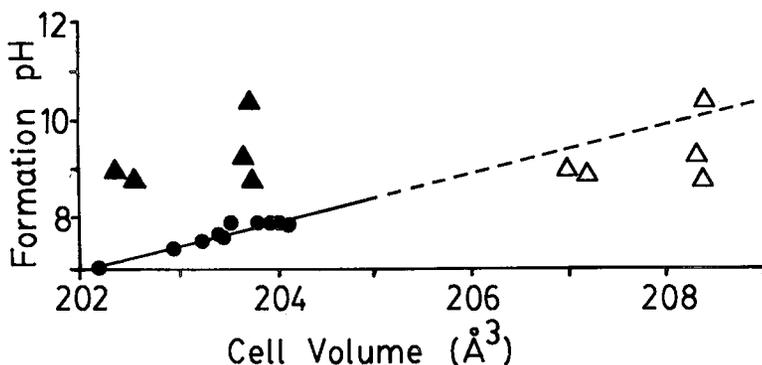


FIG. 3. Adaptation of the data of Rickard (1972) linking cell volume of covelline (●) and blaubleibend covelline (▲) with formation pH to allow for change from a covelline-type subcell for the blaubleibend covelline (▲) to a yarrowite-type subcell for the blaubleibend covelline (△). The solid line correlating formation pH with cell volume for covelline is from Rickard (1972); the dashed line is an extension based upon the approximate positioning of the re-indexed blaubleibend covelline data.

blaubleibend covelline will be shifted to the right into the approximate positions indicated by the open triangles. The data now show a direct relationship between formation pH and cell volume that holds for synthetic blaubleibend covellines of yarrowite composition as well as for covelline.

The structures of yarrowite and spionkopite have been partly determined using single-crystal data by Goble (1977).

PRESERVATION OF TYPE MATERIAL

Polished sections and a typical hand specimen containing yarrowite and spionkopite are preserved in the collection of Queen's University, Kingston, Ontario. The type specimen is preserved in the National Mineral Collection of the Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8. The cleavage fragments used in the X-ray examinations are preserved, mounted on glass fibres, by the author.

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