

## ELECTRON MICROPROBE INVESTIGATION OF COPPER SULPHIDES IN THE PRECAMBRIAN LEWIS SERIES OF S.W. ALBERTA, CANADA

R. J. GOBLE

*Kintla Exploration Limited, 7 — 8540 — 109 Street  
Edmonton, Alberta, Canada*

D. G. W. SMITH \*

*Department of Geology and Mineralogy, University of Adelaide  
Adelaide, S.A. 5000, Australia*

### ABSTRACT

The compositions of Cu and Cu,Fe-sulphides from a stratabound deposit in southwestern Alberta have been investigated by means of the electron microprobe. Although the compositions of the bornites closely approach  $\text{Cu}_5\text{FeS}_4$ , the associated Cu-sulphides — blaubleibender covellite and anilite — show a wide range of compositions, with, however, certain Cu:S ratios ( $1.12 \pm 0.01$ ,  $1.32 \pm 0.04$  and  $1.76 \pm 0.06$ ) numerically dominant. Simple statistical treatments are used to assess and interpret the data from a total of more than 350 analytical points. Optical observations suggest that preferred values correspond to compositions of phases exsolved from pre-existing solid solutions in the region covellite-chalcocite.

### INTRODUCTION

Stratabound and associated Cu mineralization found within the Precambrian Upper Appekunny, Grinnell, and Lower Siyeh Formations (Price 1962) of the Lewis Series in southwestern Alberta has been studied. The deposits are located within a sequence of continental margin, shallow water, red-bed sediments and are confined almost entirely to horizons of white or green quartzite and green or black argillite. The most significant showings are restricted to the Upper Grinnell Formation, richer zones in some instances occurring adjacent to faults and the contact zones of highly metasomatized, Precambrian diabases. Bornite + covellite  $\pm$  digenite is the dominant Cu-bearing assemblage but minor amounts of wittichenite, chalcopyrite, enargite and/or galena have been observed. Mineragraphic studies revealed two distinct varieties of covellite. One is pale to medium blue in colour, weakly anisotropic and commonly associated with bornite. The other is dark blue, strongly anisotropic and occurs principally filling fractures and replacing the paler blue covellite, the bornite or the chal-

cocite. Both varieties of covellite remain blue when viewed in oil of refractive index 1.55, whereas 'normal' covellite appears reddish-violet (Cameron 1961). This is a characteristic of *blaubleibender* covellite (Sillitoe & Clark 1969). A microprobe study was undertaken to determine the relationships between the two different coloured varieties of covellite and to investigate the composition and stoichiometry of these and other Cu-sulphides and Cu,Fe-sulphides present.

The analytical data obtained from the covellites indicate a considerable compositional scatter. The treatment which follows shows how such microprobe data may be evaluated by simple statistical means to eliminate unreliable data and to allow a more detailed interpretation than one which simply accepts the probable presence of a range of compositions.

### ANALYTICAL PROCEDURE

The six samples studied were selected from quartzites occurring within the Upper Grinnell Formation at the Yarrow Creek — Spionkop Creek copper deposit, southwestern Alberta. One sample (number 1) was taken from a sulphide-bearing carbonate vein cutting a quartzite adjacent to a diabase dike; the other five samples are from sulphide-bearing quartzites.

Samples were mounted in epoxy, polished and carbon-coated. Analyses were performed on an A.R.L. EMX microprobe. A 15 kv operating voltage and a focussed beam were used throughout the analyses. Standards have the following compositions:

Standard 1: 35.2% Cu, 32.5% S, 32.5% Fe,  
(Synthetic)

Standard 2: 34.29% Fe, 46.01% As, 19.69% S,  
(Arsenopyrite)

Cu and S were determined against Standard 1 and Fe against Standard 2 except where, as noted in the tables, Cu and Fe were determined simultaneously, in which case Fe was determined

\* Permanent address: Department of Geology, University of Alberta, Edmonton, Alberta, Canada, T6G 2E1.

against Standard 1. Arsenic was determined against Standard 2 and Se against pure metal. Ten 20 sec. counts were taken on every grain analysed in each sample; five 50 sec. counts were made at standards peaks before and after the specimen readings. Background corrections were based on measurements either side of the analytical lines used. Counting rates for Cu, Fe and S present as major components were approximately 600-1000 cps (on bornite, covellite and chalcocite), 300 cps (on bornite), 500-750 cps (on chalcocite, bornite and covellite) respectively. A beam current intergrating system was used to eliminate errors from short-term instrumental drift.

Full ZAF corrections to the average background-corrected intensities for each grain were made using the APL computer program of Smith & Tomlinson (1970). Low counting rates allowed the dead-time correction to be neglected. Not all elements present were determined in some specimens; in such cases the presence of unanalysed elements was confirmed by a wavelength scan and the concentrations calculated by difference, using a subroutine of Smith & Tomlinson (1970). When this procedure was used it is indicated in the tables. Structural formulae were determined by another subroutine.

### RESULTS

The initial results for individual grains (after the ZAF correction procedure but unevaluated as to reliability), together with the calculated mineral formulae (based on a multiple of one sulphur) are given in Table 1. Letters appended to specimen numbers refer to the colour of the mineral in reflected light and are keyed in the table. Calculated average Cu:S ratios for the various Cu-sulphide grains analysed are plotted in the form of a histogram in Figure 1. The term Cu-sulphide will be used henceforth in this paper to refer to the minerals covellite, digenite and chalcocite and does not include Cu, Fe-sulphides such as bornite and chalcopyrite.

Within individual Cu-sulphide grains there is a wide range of compositions, with individual points (*i.e.* individual 20 second counts) showing considerable variance from the mean for the ten points comprising the analysis of the grain. This is apparent in Figure 2 where Cu:S ratios for individual points are plotted as a histogram (only those points for which Cu and S were determined simultaneously are included). The compositional spread is particularly great for individual grains in specimens 1, 3, 5 although this is not strikingly apparent in Figure 2 because the compositions for several grains are plotted

together. In contrast, the Cu:S ratios of bornite points plot as tight groups (Fig. 3).

Compositions and Cu:S ratios for individual points were based upon the approximate formula: % element at individual point =

$$\frac{\text{Counts for element at individual point}}{\text{Average counts for elements for 10 points}} \times \text{\% element for average of 10 points}$$

This relationship holds true if compositions of individual points approximate the average com-

TABLE 1. RESULTS OF ELECTRON PROBE ANALYSES - AVERAGE COMPOSITIONS OF EACH GRAIN

SPE- CIMEN	%Cu	%S	%Fe	ND	Total %	Formula	
1	tb	77.83	22.06*	0.11†	Se	100.00	Cu <sub>1.79</sub> S
	lb	65.56	23.71		As	89.27	Cu <sub>1.40</sub> S
	w	78.70	21.10		As	99.80	Cu <sub>1.88</sub> S
	p	64.23	26.08	11.16	As, Bi	101.47	Cu <sub>4.97</sub> Fe <sub>0.98</sub> S <sub>4</sub>
	o	35.0	33.9	26.2	As, Bi, Se	95.1	Cu <sub>1.04</sub> Fe <sub>0.89</sub> S <sub>2</sub>
2	db	69.69	30.23*	0.08†	Se	100.00	Cu <sub>1.16</sub> S
	lb	71.06	28.86*	0.08†	Se	100.00	Cu <sub>1.24</sub> S
	db	71.31	29.59		As	100.90	Cu <sub>1.22</sub> S
	db	72.13	27.93		As	100.06	Cu <sub>1.36</sub> S
	db	66.52	31.61		As	98.13	Cu <sub>1.06</sub> S
	lb	74.83	25.00*	0.17†	Se	100.00	Cu <sub>1.51</sub> S
	lb	72.82	25.68		As	98.50	Cu <sub>1.43</sub> S
	lb	72.80	27.33		As	100.13	Cu <sub>1.34</sub> S
	w	77.69	22.36		As	100.05	Cu <sub>1.75</sub> S
	w	76.97	22.30		As	99.27	Cu <sub>1.74</sub> S
	p	63.14	25.80	11.27	As, Bi, Se	100.21	Cu <sub>4.94</sub> Fe <sub>1.00</sub> S <sub>4</sub>
	c	40.7	20.3	0.2	As, Se	100.0 <sup>a</sup>	Cu <sub>3.04</sub> Bi <sub>0.88</sub> S <sub>3</sub>
3	db	71.54	28.44*	0.02†	Se	100.00	Cu <sub>1.27</sub> S
	db	69.60	31.75		As	101.35	Cu <sub>1.11</sub> S
	db	70.00	31.56		As	101.56	Cu <sub>1.12</sub> S
	lb	75.47	25.58		As	101.05	Cu <sub>1.49</sub> S
	p	61.53	27.71*	10.76†	Se	100.01	Cu <sub>4.48</sub> Fe <sub>0.89</sub> S <sub>4</sub>
	p	56.15	31.70	11.69	As, Bi	99.54	Cu <sub>3.58</sub> Fe <sub>0.85</sub> S <sub>4</sub>
4	db	68.95	30.85*	0.20†	Se	100.00	Cu <sub>1.13</sub> S
	db	68.91	30.54		As	99.45	Cu <sub>1.14</sub> S
	lb	77.19	22.67*	0.14†	Se	100.00	Cu <sub>1.72</sub> S
	lb	69.35	30.88		As	100.23	Cu <sub>1.13</sub> S
	lb	72.93	27.80		As	100.73	Cu <sub>1.32</sub> S
	w	77.77	22.36		As	100.13	Cu <sub>1.76</sub> S
	w	77.46	22.67		As	100.13	Cu <sub>1.72</sub> S
	p	62.91	25.62	11.21	As, Bi	99.73	Cu <sub>4.85</sub> Fe <sub>1.00</sub> S <sub>4</sub>
	y	50.6	28.2	2.0	Bi, Se	96.8 <sup>b</sup>	Cu <sub>3.8</sub> Fe <sub>2.2</sub> As <sub>0.5</sub> S <sub>2</sub>
5	db	72.19	27.55*	0.26†	Se	100.00	Cu <sub>1.32</sub> S
	db	69.97	29.63*	0.40†	Se	100.00	Cu <sub>1.19</sub> S
	lb	67.97	26.56		As	94.53	Cu <sub>1.29</sub> S
	w	77.84	22.12		As	99.96	Cu <sub>1.78</sub> S
	p	63.94	25.73	10.50	As, Bi	100.17	Cu <sub>5.02</sub> Fe <sub>0.94</sub> S <sub>4</sub>
6	db	68.26	31.72*	0.02†	Se	100.00	Cu <sub>1.09</sub> S
	db	68.56	31.44*	ND	Se	100.00	Cu <sub>1.10</sub> S
	db	68.76	32.68		As	101.44	Cu <sub>1.06</sub> S
	db	68.71	32.11		As	100.82	Cu <sub>1.08</sub> S
	db	67.99	31.91		As	99.90	Cu <sub>1.08</sub> S
	lb	78.21	21.76*	0.03†	Se	100.00	Cu <sub>1.81</sub> S
	lb	78.39	22.50		As	100.89	Cu <sub>1.76</sub> S
	lb	75.14	22.17		As	97.31	Cu <sub>1.71</sub> S
	w	78.15	22.04		As	100.19	Cu <sub>1.79</sub> S
	w	77.60	22.03		As	99.63	Cu <sub>1.78</sub> S
	p	63.70	25.69	10.81	As, Bi	100.20	Cu <sub>5.00</sub> Fe <sub>0.97</sub> S <sub>4</sub>

ND=sought but not detected

\* calculated as 100% - elements analysed

† determined against standard 1

<sup>a</sup> includes 38.8% Bi. The apparent (uncorrected) concentration of Bi was determined on an M-line as 36.4%.

<sup>b</sup> includes 16.0% As

Colour in reflected light: db-dark blue; lb-light blue; w-white; p-purple; o-orange; c-cream; y-yellow

NOTE: Sb, Pb, Ag sought but not detected in representative db, lb, w, p grains

All concentrations determined by the electron probe have been corrected for background, atomic number, absorption, and fluorescence effects.

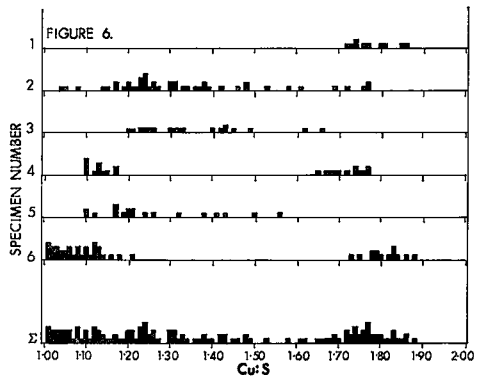
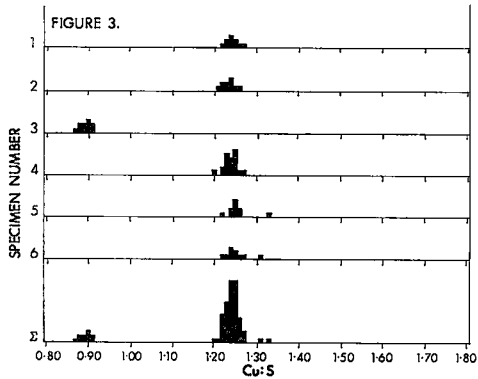
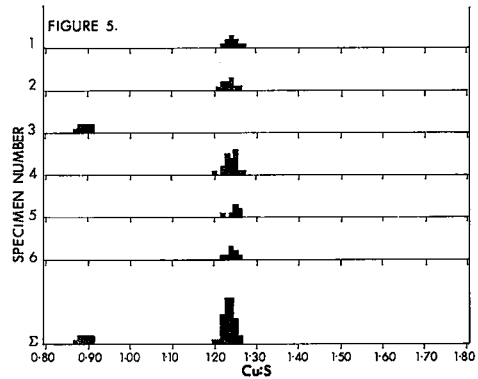
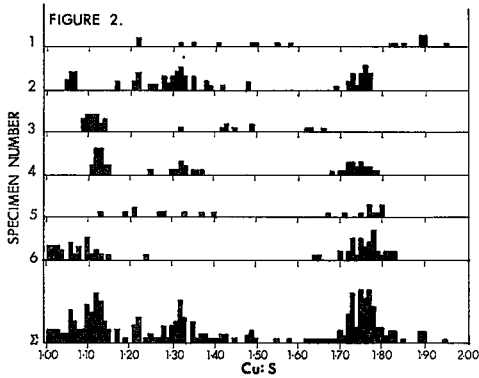
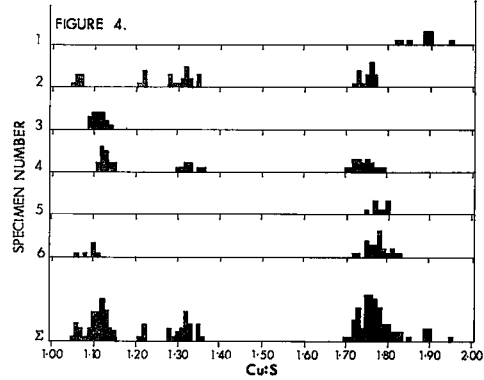
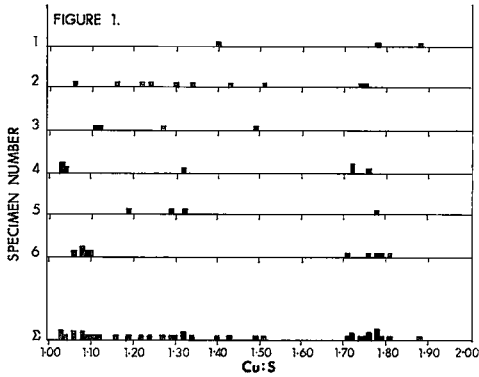


FIG. 1. Mean compositions of Cu-sulphide grains.

FIG. 2. Compositions of Cu-sulphide points at which Cu and S were determined simultaneously.

FIG. 3. Compositions of 'bornite' points at which Cu and S were determined simultaneously.

FIG. 4. Compositions of Cu-sulphide points at which Cu and S were determined simultaneously and with all anomalous points excluded.

FIG. 5. Compositions of 'bornite' points at which Cu and S were determined simultaneously and with all anomalous points excluded.

FIG. 6. Compositions of anomalous Cu-sulphide points at which Cu and S were determined simultaneously and compositions of Cu-sulphide points for which Cu was analysed and S was determined by difference.

position of the ten points. For widely varying compositions small errors may be introduced by the fact that the size of ZAF corrections depends upon the Cu and S contents. The error is negligible for compositional ranges encountered within individual grains in this work.

The compositional spread demonstrated by Figure 2 may arise from several sources other than sample inhomogeneity and therefore an attempt has been made to distinguish the more reliable data. Possible sources of data spread other than true compositional variation include instrumental factors, surface irregularities and effects of the third dimension being unknown. Instrumental drift was effectively eliminated by using a beam current integrating system which controls counting times, and by the measurement of standard intensities before and after specimen intensities. Whilst every attempt was made to eliminate surface effects by careful sample preparation, some scatter from this source may still remain. However, the major source of variation not related to changes in mineral composition is likely to stem from the selection of analytical points: it is not possible to determine what lies beneath the surface in a polished mount of opaque minerals. Thus the excited volume may include material other than that selected for analysis (e.g. quartz gangue, other sulphides etc.) A simple statistical approach was adopted in attempting to evaluate the data. Surface irregularities and inclusions of 'foreign' material in the excited volume would tend to give totals for the analysed elements that deviate appreciably from 100%. Consideration of count rates and concentrations for Cu and S in the Cu-sulphides and the standards showed that the combined statistical counting error should give totals of  $100 \pm$  approximately 2.1%. Analyses with totals lying outside this range were considered unreliable and discarded. In a case where the foreign material inadvertently included in the excited volume was another Cu-sulphide the analysis would not be rejected on this statistical criterion and indeed at least some of the 'intermediate' compositions retained by this screen may reflect such situations. In an attempt to evaluate the remaining data, a statistical approach was again adopted. For a truly homogeneous grain the total counts ( $N$ ) at any individual point should not deviate by more than  $2.58\sqrt{N}$  from the mean total counts ( $N_m$ ) obtained from the ten points analysed (assuming that the 99% confidence level is being aimed at and other sources of error have been eliminated). This test was applied to counts obtained at every analysed point for both of the principal elements (Cu and S). Points that lay outside these limits are hereafter termed 'anomalous'

(but not discarded). Note that where S was obtained by difference, the analyses were set aside for the time being and were not included in this statistical treatment.

Of the 70 bornite points evaluated by these methods, 4 are anomalous with respect to Cu counts, and 5 anomalous with respect to S counts. Three points are anomalous for both Cu and S (and give unreliable totals). Hence only 6 points out of a total of 70 are anomalous. In contrast, of the 259 Cu-sulphide points, 40 are anomalous in their Cu counts and 61 anomalous in S counts. Of these, 21 points are anomalous for both Cu and S, leaving a total of 80 anomalous points out of 259. Fifty-six of these points were discarded as unreliable, having totals outside the range  $100 \pm 2.1$ . Of these 56 points, 27 occurred in just 3 grains. As the conditions for the bornite and Cu-sulphide analyses were the same, it is probable that the majority of *anomalous* Cu-sulphide readings reflect true sample inhomogeneity.

Data for the Cu-sulphides and bornites that are not classified as anomalous are plotted as histograms in Figures 4 and 5. For Figure 4, if more than half of any set of 10 readings from an individual grain was anomalous none of the readings was plotted, since it is essentially meaningless to compare individual readings with an average in such a situation. It is evident from a comparison of Figures 2 and 4 that, as might be expected, it is mainly the scattered intermediate data that are anomalous.

Of the 26 Cu-sulphide grains analysed, 3 grains gave totally unreliable analyses (the majority of points giving totals of much less than 100%), 19 grains gave analyses that were reliable but had some anomalous points that were apparently of different compositions and were consequently not included in Figure 4, and 4 grains gave analyses with numerous anomalous points (7 or more out of 10) and appear to be composed of more than one type of Cu-sulphide (i.e. showed two or more different Cu:S values). These latter cases were examined to see if they could be divided into groups of points each having values within the statistical counting error for that group. A sample calculation (tabulated in Table 2) shows the original and evaluated data for a dark blue Cu-sulphide grain in sample 6. The evaluation of the data indicates that this particular set of points may represent sulphide compositions with Cu:S ratios of approximately 1.02 and 1.10, or possibly 1.02, 1.08 and 1.13.

Figure 6 is a histogram of anomalous Cu-sulphide points combined with those points for which Cu was analysed directly and S calculated. As might be anticipated there is a greater scatter of points, although comparison indicates that

preferred compositions in Figure 4 are also slightly preferred in Figure 6. It may be noted that the preferred composition at  $Cu_{1.28}S$  is enhanced and an additional preferred composition is suggested in the range  $Cu_{1.01-1.06}S$ .

## INTERPRETATION

*Cu-sulphides*

Application of the methods outlined above to the Cu-sulphide data indicates that certain Cu:S ratios appear to be numerically more significant. Column 1 of Table 3 indicates only points that were not classified as anomalous and for which both Cu and S were determined. Column 2

shows data for all the anomalous points. Column 3 gives the data for points at which S was not analysed directly but calculated by difference. No data for which  $Cu\% + S\%$  lies outside the range  $100 \pm 2.1\%$  are tabulated.

Examination of the results suggests that there are three dominant varieties of Cu-sulphides present, with compositions  $Cu_{1.12 \pm 0.08}S$ ,  $Cu_{1.32 \pm 0.04}S$  and  $Cu_{1.76 \pm 0.06}S$ . Various compositions intermediate to these and between these and covellite (CuS) on the one hand and chalcocite ( $Cu_2S$ ) on the other, also exist;  $Cu_{1.06 \pm 0.02}S$  and  $Cu_{1.22 \pm 0.02}S$  are most prevalent. Figure 4 suggests that variation within the ranges given may be real; for example, in specimen 2, grains with compositions near to  $Cu_{1.76 \pm 0.06}S$  actually have a bimodal distribution, indicating possible compositions of  $Cu_{1.73 \pm 0.01}S$  and  $Cu_{1.76 \pm 0.01}S$ .

*Cu-Fe-sulphides*

Bornites in specimens 1, 2, 4, 5 and 6 closely approach stoichiometric  $Cu_5FeS_4$  although slightly deficient in Cu and Fe. Since the Fe content of the standard was assumed from stoichiometry, little significance can be attached to the small deficiency in this element. Compositions of these bornites vary within the range  $Cu_{4.95 \pm 0.12}Fe_{0.98 \pm 0.08}S_4$  (see Fig. 3). Sample 3 contains a bornite-like mineral tentatively identified as idaite but with a composition  $Cu_{3.57 \pm 0.07}Fe_{0.85 \pm 0.08}S_4$ . This is somewhat enriched in Cu and depleted in Fe compared to the mineral that Sillitoe & Clark (1969) consider stoichiometric idaite ( $Cu_3FeS_4$ ). Sample 3 also contains an 'anomalous' bornite which is very depleted in Cu compared to the 'normal' bornites of other samples. It has a composition approximating  $Cu_{4.48}Fe_{0.89}S_4$ , although individual points vary from about  $Cu_4Fe_{0.9}S_4$  to  $Cu_5Fe_{0.9}S_4$  (as S was

TABLE 2. STATISTICAL ANALYSIS OF DATA FOR TEN POINTS COMPRISING ONE DARK BLUE GRAIN IN SPECIMEN 6

Specimen	Total Counts Cu Peak	% Cu	Total Counts S Peak	% S	Total %	Cu:S
6db	16452	67.56	14108**	32.98	100.54	1.03
	16409	67.39	14284**	33.62	101.01	1.01
	16454	67.57	14298	33.42	100.99	1.02
	16321	67.02	14278	33.37	100.39	1.01
	17106*	70.25	13462	31.47	101.72	1.13
	16416	67.41	14045**	32.83	100.24	1.04
	16471	67.64	12704**	29.69	97.33†	1.15
	16793	68.96	12008**	28.07	97.03†	1.24
	16678	68.49	13715	32.06	100.55	1.08
	16466	67.62	13534	31.63	99.25	1.08
Average	16557	67.99	13654	31.97	99.97	1.03

## POSSIBLE GROUPING OF POINTS OF SIMILAR COMPOSITIONS IN SPECIMEN 6db

6db	16471	67.64	12704	29.69	97.33	1.15†
	16793	68.96	12008	28.07	97.33	1.24†
	16321	67.02	14278	33.37	100.39	1.01
	16409	67.39	14384	33.62	101.01	1.01
	16454	67.57	14298	33.42	100.99	1.02
	16452	67.56	14108	32.98	100.54	1.03
	16416	67.41	14045	32.83	100.24	1.04
Av. for 5 similar points	16410	67.39	14223	33.24	100.63	1.02
	Statistical counting error for Cu=330; statistical counting error for S=307 (99% confidence limits-no anomalous readings)					

	16466	67.62	13534	31.63	99.25	1.08
	16678	68.49	13715	32.25	100.55	1.08
	17106	70.25	13462	31.47	101.72	1.13
Av. for above 3 points	16760	68.79	13570	31.78	100.57	1.10
	Statistical counting error for Cu=334; statistical counting error for S=301 (99% confidence level)					

\* anomalous- Statistical counting error for Cu=2.58√16557=±332 (99% confidence each) anomalous if <16225, >16889.

\*\* anomalous- Statistical counting error for S=2.58√13654=±301 (99% confidence level) anomalous if <13353, >13955.

† unreliable- Lie outside range  $100 \pm 2.1\%$  defined by using maximum positive and negative counting errors for Cu and S.

Under "Total Counts S Peak" read 14298\*\*, average = 13654.

TABLE 3. COMPOSITIONAL RANGES OF ANALYSED Cu-SULPHIDES

'corrected' Cu-sulphides	Cu:S 'anomalous' Cu-sulphides	Cu:S of Cu-sulphides for which S not analysed	Total No. of Points
1.06±0.02(9)	1.02±0.02(8)	1.02±0.02(2)	10
1.12±0.03(39)	1.06±0.02(6)	1.06±0.02(8)	23
	1.12±0.03(4)	1.12±0.03(23)	66
	1.16±0.01(3)	1.16±0.01(6)	9
1.22±0.02(6)	1.22±0.02(1)	1.22±0.02(21)	28
1.32±0.04(25)	1.32±0.04(7)	1.32±0.04(6)	38
	1.43±0.05(10)	1.43±0.05(5)	15
	1.65±0.04(4)	1.65±0.04(4)	8
1.76±0.06(71)	1.76±0.06(7)	1.76±0.06(24)	102
1.88±0.02(6)		1.88±0.02(3)	9
other (2)	other (5)	other (16)	23

'corrected' Cu-sulphides are those points composing a grain for which more than five points are not 'anomalous' (for further details, see text)

Note: The no. of points lying in a range is indicated in brackets.

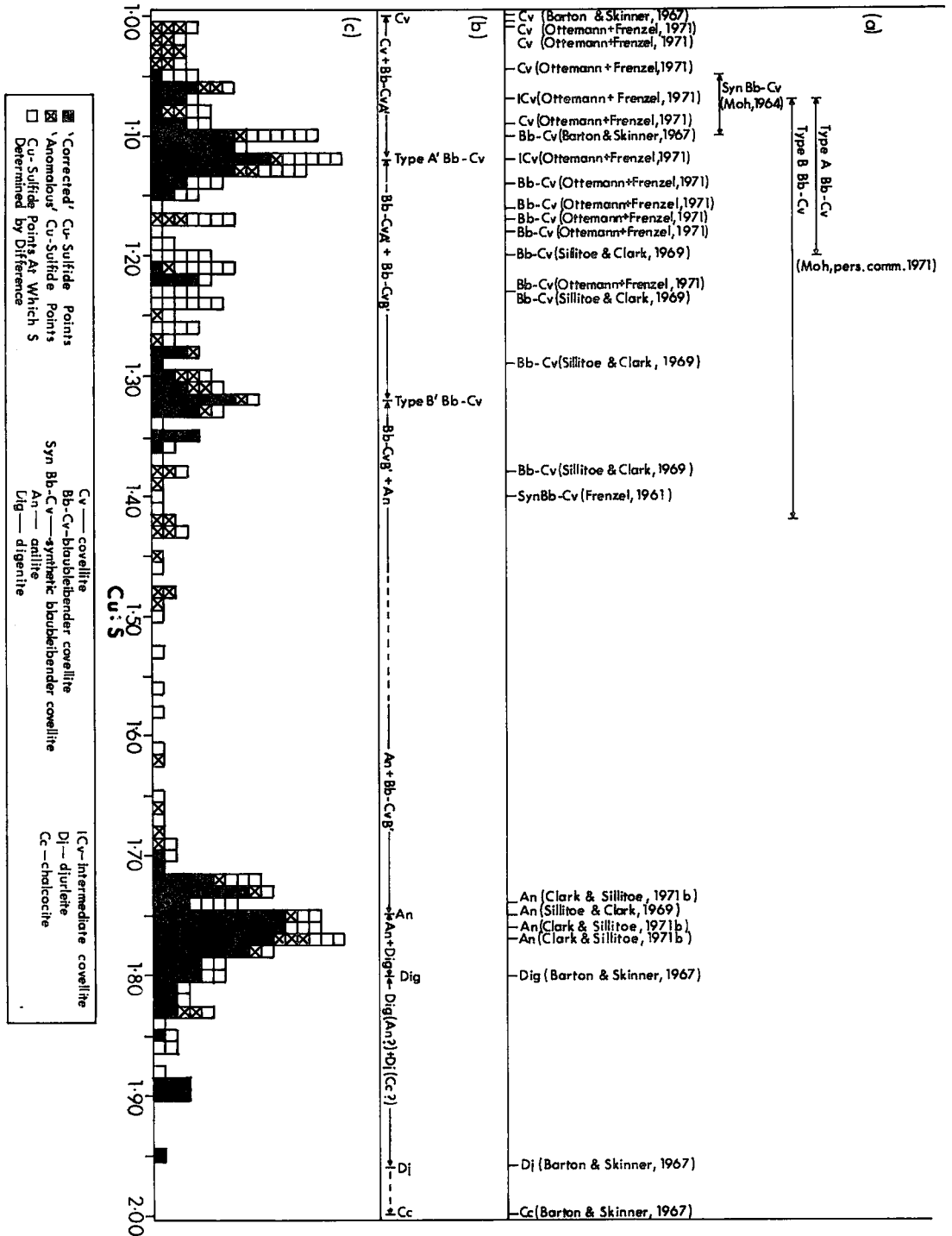


Fig. 7. Compositions of Cu-sulphide points determined in this paper (c) compared with compositions of Cu-sulphides determined by other authors (a) and 'idealised' compositions (b).

determined by difference this grain is not included in Figures 3 or 5).

The remaining Cu,Fe-sulphides were analysed merely to check optical identifications. The orange ('o') and yellow ('y') grains of specimens 1 and 4 occur as irregular blebs associated with Cu-sulphides. The cream ('c') grain of sample 2 occurs as an irregular mass within a bornite grain. The orange grain of specimen 1 is probably chalcopyrite although it shows a slight Fe deficiency. The yellow grain of specimen 4 is possibly tennantite but if so shows a marked deficiency in As and contains a minor amount of Fe. Both of these analyses total well below 100%, and they are therefore somewhat suspect. The cream-coloured grain of specimen 2 is tentatively identified as wittichenite although its composition ( $\text{Cu}_{3.04}\text{Bi}_{0.88}\text{S}_3$ ) is depleted in Bi relative to the formula  $\text{Cu}_3\text{BiS}_3$ , quoted by Dietrich (1969). A spectrometer scan on this grain revealed no other constituents, so it is unlikely that the assumed Bi content is greatly in error (see also footnote to Table 1).

#### DISCUSSION

Sillitoe & Clark (1969) found that anilite ( $\text{Cu}_{1.75}\text{S}$ ) was converted to a digenite-type solid solution even by gentle grinding at room temperature and thus, presumably, by polishing. It

therefore seems likely that much of the Cu-sulphide reported here with a composition of  $\text{Cu}_{1.76\pm 0.06}\text{S}$  was originally anilite. Analyses in the upper part of this range may perhaps represent original digenite.

Cu-sulphides with compositions of  $\text{Cu}_{1.12\pm 0.08}\text{S}$  and  $\text{Cu}_{1.32\pm 0.04}\text{S}$  are probably two distinct structural varieties of blaubleibender covellite. Moh (personal communication, 1971) has found two such varieties each giving distinct X-ray powder patterns and having compositional ranges of approximately  $\text{Cu}_{1.07-1.20}\text{S}$  and  $\text{Cu}_{1.07-1.42}\text{S}$ . The  $\text{Cu}_{1.12\pm 0.08}\text{S}$  and  $\text{Cu}_{1.32\pm 0.04}\text{S}$  reported in this paper may be preferred compositions of these two varieties of blaubleibender covellite. If this is the case the compositions reported here may be represented in the manner shown in Figure 7 where data of other workers are summarized in part (a), the compositions reported here in part



FIG. 8. Grain of blaubleibender covellite showing pale blue (white) and dark blue (grey) exsolved phases. The latter shows lighter and darker blue, incompletely resolved lamellae. Reflected light,  $100\times$  oil immersion objective; magnification:  $\times 1360$ .

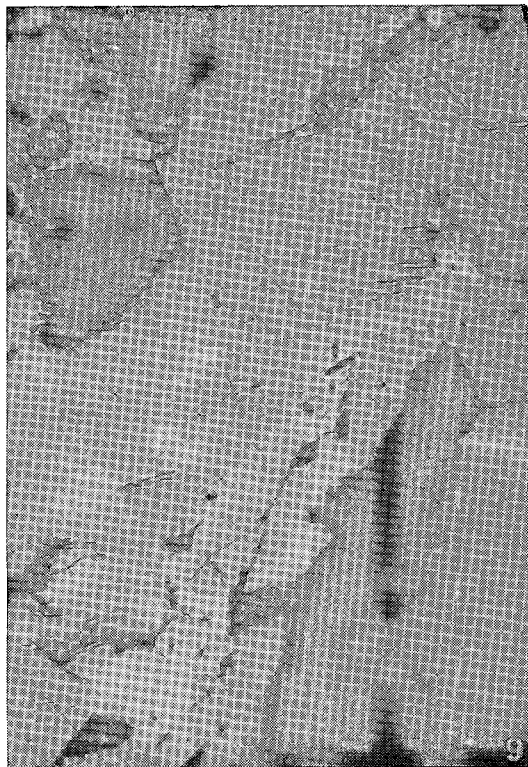


FIG. 9. Grain of blaubleibender covellite showing darker blue phase (grey) with patches of a lighter blue (white) phase intergrown. The former shows extremely fine and poorly resolved, paler blue, somewhat sinuous lamellae. The NW-SE grain running across the photograph is due to the polishing compound used to buff the sample before photographing. Reflected light,  $100\times$  oil immersion objective; magnification:  $\times 1360$ .

(c), and inferred 'ideal' compositions and mixtures of ideal compositions suggested by this work, in part (b).

Whether intermediate compositions represent solid solution of end members or whether they represent intergrowths of the various phases was not apparent from the microprobe data. However, an optical re-examination of the specimens using a 100 $\times$  oil immersion objective revealed the presence of intergrowths of dark blue and lighter blue phases on an extremely fine scale, ranging down to a fraction of a micron in size. Typical textures are illustrated in Figures 8 and 9. Re-investigation of one sample (number 2) with the electron microprobe showed that it was not possible to resolve areas of different composition within a grain by means of  $x$ -ray scanning pictures. However, on positioning the beam as closely as possible on carefully selected points, in the great majority of cases the following compositions were obtained: lighter blue areas apparently free of lamellae —  $\text{Cu}_{1.29-1.32}\text{S}$ ; darker blue areas with very fine regularly oriented and spaced lighter blue lamellae —  $\text{Cu}_{1.18-1.22}\text{S}$ ; darkest blue areas either free of lamellae or containing very few lamellae —  $\text{Cu}_{1.08-1.12}\text{S}$ . In the last case it was possible to find only a few areas in which the beam could be placed with sufficient precision. It is therefore suggested that original compositions lying between chalcocite and covellite have exsolved to give compositions close to the 'preferred' Cu:S ratios of 1.12, 1.32 and 1.76. The ratios of 1.18-1.22, found principally

in sample number 2, could possibly represent an intermediate composition stable at some higher temperature. There is no evidence concerning the temperature at which the exsolution took place. However, in view of the previously mentioned observation of Sillitoe & Clark (1969) that anilite is converted to digenite by even gentle grinding at room temperatures, the possibility should be borne in mind that the exsolution features reported here could have been promoted by sample preparation techniques. The lowest Cu:S ratios observed in the exsolution products correspond closely to those recorded for the dark blue covellite, described earlier as filling fractures and replacing other Cu-sulphides.

In Figure 10 the compositions of bornite, 'anomalous' bornite, and idaite grains reported in this paper are plotted together with data on these minerals given by previous investigators. The 'normal' bornites of this paper are similar to those of Sillitoe & Clark (1969), but contain slightly more Cu (and perhaps less Fe). The one 'anomalous' bornite encountered also apparently contains less Fe than those of Sillitoe & Clark (1969). The idaite (?) grain analysed is intermediate in composition between 'anomalous' bornite and  $\text{Cu}_3\text{FeS}_4$  (idaite) but once again appears to contain less Fe than those idaite determined by either Sillitoe & Clark (1969) or Ottemann & Frenzel (1971). On the other hand, compositions in the region between bornite and anilite (or digenite) such as those reported by

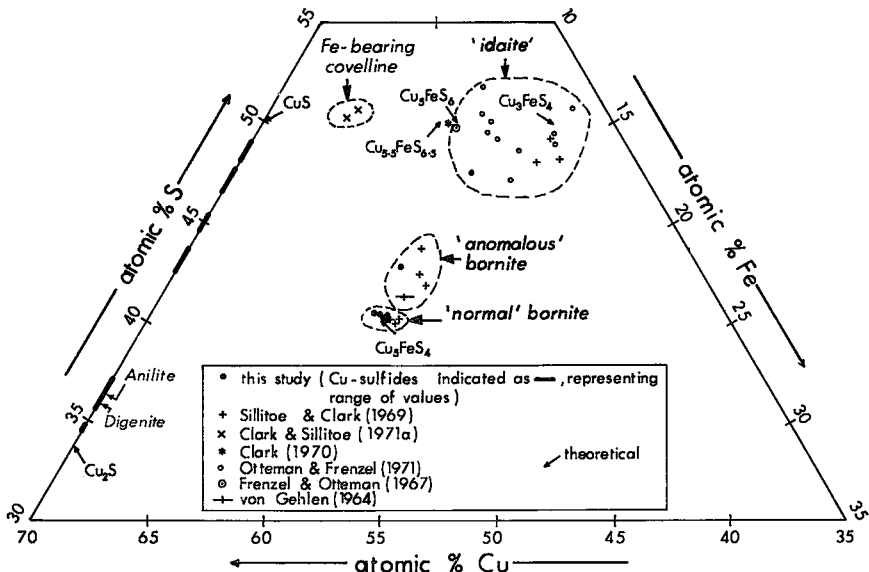


FIG. 10. Triangular plot of compositions of Cu- and  $\text{Cu}_3\text{Fe}$ -sulphides determined in this paper compared with compositions determined by other workers.



Morimoto & Gyobu (1971) have not been observed in the course of this study.

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