CHARACTERISTICS OF THE SULPHIDES

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Abstract

A wide variety of sulphide minerals are present in the Cobalt-Gowganda ores, but in too small concentrations to be of economic value. The minerals present are chalcopyrite, tetrahedrite, galena, marcasite, pyrite, sphalerite, stephanite, pyrargyrite, acanthite, bornite, chalcocite, stromeyerite, mckinstryite, wittichenite, proustite, polybasite, xanthoconite, freieslebenite, bismuthinite, galenobismutite, pavonite, matildite, parkerite, bravoite, pyrrhotite, smythite, siegenite, cobalt pentlandite, covellite, molybdenite, samsonite, and larosite. These minerals occur in carbonate veins, in silver-arsenide veins, in the wall rock, and in mineralized Keewatin interflow rocks. The characteristics of the minerals were determined in this study and compared with data on synthetic materials to provide an understanding of the mineral assemblages. This comparison shows that the sulphides in veins and wall rock were deposited from a complex hydrous ore solution at progressively lower temperatures. Geothermometric indicators are: chalcocite-galena exsolutions from a solid solution that is stable between 486°C and 523°C; galena–matildite exsolutions from a solid solution that is stable above 215°C; silver–argentite–pyrargyrite assemblage — co-existing between 200°C and about 400°C; isometric Ag_2S crystals that can be deposited only above 176°C; stephanite — stable below 197°C; smythite — stable below 100°C; mckinstryite — stable below 94.4°C; stromeyerite — stable below 93.3°C; and a stromeyerite–chalcocite pair — co-existing only below 67°C.

The sulphides in the mineralized Keewatin interflow rocks consist of the characteristic minerals typical of base-metal stratiform deposits.

Introduction

Many sulphide minerals are present in the Cobalt-Gowganda ores, but in concentrations too small to be of economic value. A study of the characteristics of these minerals was undertaken as part of a larger study to provide information on the minerals and to establish a sound basis for interpreting depositional conditions of the ore. The characteristics were determined by studying a large suite of samples by ore microscopy, *x*-ray diffraction, and electron microprobe analyses. These characteristics were then correlated with known data on synthetic materials from appropriate systems. This paper gives the characteristics of the minerals and an interpretation of the depositional conditions of the ore. This study was conducted by W. Petruk and assisted by the staff in the Mineral Sciences Division. The electron microprobe analyses were performed by D. C. Harris and D. R. Owens; the *x*-ray diffraction work by J. M. Stewart and E. J. Murray, and other related work by other members of the Division.

Of the sulphide minerals present in the Cobalt-Gowganda ores, the more abundant ones are chalcopyrite, tetrahedrite, galena, marcasite, sphalerite, pyrite, acanthite (argentite), pyrargyrite, and stephanite. Less abundant are bornite, chalcocite, stromeyerite, mckinstryite, wittichenite, proustite, polybasite, xanthoconite, freieslebenite, bismuthinite, galenobismutite, pavonite, matildite, parkerite, bravoite, pyrrhotite, smythite, minerals of the linnaeite series, cobalt pentlandite, covellite, molybdenite, samsonite, and larosite. Detailed characteristics of these minerals are given in this paper.

ELECTRON MICROPROBE ANALYSES

The compositions of most of the sulphides were determined by means of a Materials Analysis Company (MAC) model 400 electron microprobe. The chalcopyrite, pyrrhotite and smythite in the ore were analysed by using synthetic $CuFeS_2$ and FeS as standards and computing the data by direct comparison. The $CuFeS_2$ composition is Cu 35.88%, Fe 31.52% and S 32.59%, and the FeS compositions are :

Fe	S	Co	Ni	Cu
62.86	37.14			
61.75	38.25			
60.60	39.40			
57.47	38.45	1.35	1.35	1.38

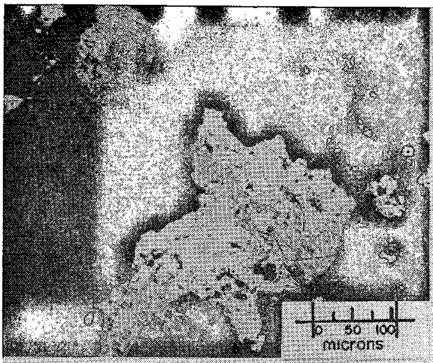
The other minerals in the ore were analysed by using a number of standards and processing the data with a computer program of Rucklidge (1967). The standards used are (1) natural pyrite, enargite, bismuthinite, stibnite, galena, and cadmium-bearing sphalerite, (2) synthetic CuS, FeS_2, ZnS, HgS, $FeAs_2$ and $AgBiS_2$, and (3) the metals Ag, Cu, Mn, Cd, Bi, Ni, and Co.

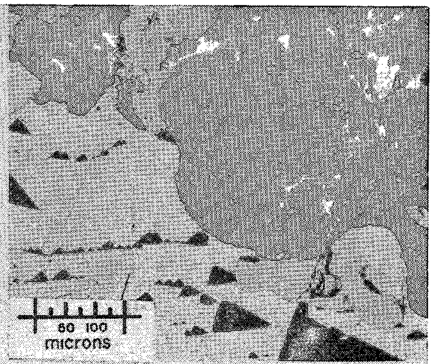
The statistical accuracy of analysis was not determined because it could not be established whether any variations from spot to spot are due to minor compositional variations of the mineral or to analytical variations. Some idea of the compositional variations for the minerals in this ore is provided by analyses for the same mineral from different locations within the deposit. It is judged that analyses obtained by computing the results directly from synthetic equivalents are within 1% of the amount present. On the other hand, analyses obtained by processing data with a computer program are judged to be within 2% of the amounts present in most minerals except the silver-rich minerals and bornite. These latter minerals appear to decompose during electron bombardment resulting in a change in constitution. To achieve an analysis for these minerals, the electron beam was expanded to a 40-micron diameter, and the specimen current reduced to about 0.025 microamp. The accuracies of analyses thus obtained are not known, but the results are judged to be within 5% of the amount present.

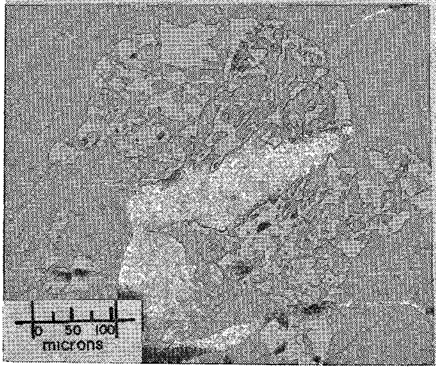
CHARACTERISTICS OF THE MINERALS

Chalcopyrite ($CuFeS_2$)

Chalcopyrite is the most common sulphide mineral in the Cobalt-Gowganda ores. It occurs in veins, and in the wall and country rock.







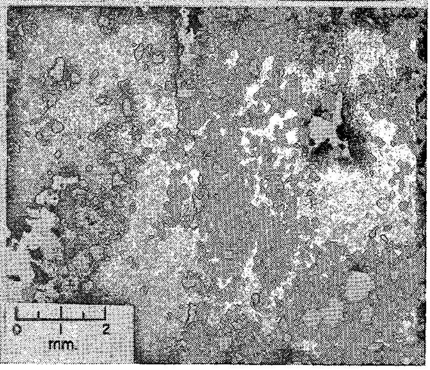


FIG. 129. (Top, left) Sulphide grain in calcite, showing chalcopyrite (dark grey) intergrown with marcasite (white). (Langis mine, sample 80).

FIG. 130. Irregular grains of chalcopyrite (light grey) in galena (white) and sphalerite (dark grey), and exsolution globules of chalcopyrite in sphalerite. (Deer Horn mine, sample 449).

FIG. 131. (Bottom, left) Chalcopyrite inclusions (white) in stromeyerite (grey). The chalcopyrite has a myrmeketic texture as a result of the partial replament of chalcopyrite by stromeyerite (sample M-16326).

FIG. 132. Massive tetrahedrite (grey) from Vein 470 in the Agnico Christopher mine. The black area represents calcite and the white, arsenopyrite (sample 111).

The chalcopyrite in veins is present in zones of arsenide-silver mineralization, hereafter referred to as ore zones, and in almost barren carbonate. The chalcopyrite in ore zones tends to be associated with tetrahedrite and is present as irregular grains and veinlets in carbonates and arsenides. Chalcopyrite in almost barren carbonate is most abundant at short distances beyond the ore zones. It occurs as irregular grains, as isolated masses and botryoidal bodies up to several inches in size, as intergrowths with other sulphides (Figs. 129 and 130), as exsolution globules in sphalerite and tetrahedrite (Fig. 130), and as inclusions in galena and stromeyerite. Usually, the inclusions are rounded, but some of those in stromeyerite are partly replaced by stromeyerite, resulting in a myrmekitic texture (Fig. 131). Chalcopyrite contains inclusions of tetrahedrite, sphalerite, marcasite, pyrite, pyrrhotite, rutile, cobaltite, arsenopyrite, and chlorite.

The chalcopyrite in the wall rock is present as disseminated grains and veinlets, as cores of chlorite segregations, and as a constituent of sulphide pebbles in conglomerate. The quantity of disseminated chalcopyrite appears to increase towards the ore veins which suggests that at least some of the wall rock chalcopyrite is genetically related to the ore vein chalcopyrite.

Chalcopyrite is also in mineralized Keewatin interflow rocks and occurs as disseminated grains associated with sphalerite, galena, and pyrrhotite (Figs. 92 and 93).

Microprobe analyses of chalcopyrite in six samples (Table 41) show that the chalcopyrite does not contain significant amounts of impurities and that its composition is vcry close to that of stoichiometric chalcopyrite.

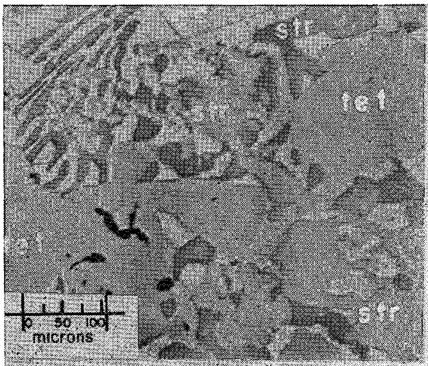
TABLE 41. COMPOSITIONS OF CHALCOPYRITE

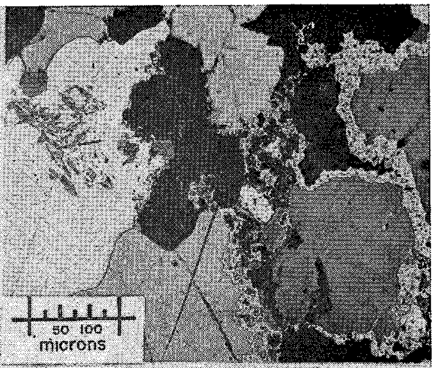
Sample	Sample location		Compositions in wt. % *			
	Mine	Zone	Cu	Fe	S	Total
3	Hi-Ho	Main Ore Zone	34.8	29.9	35.2	99.9
237	Silverfields	Beyond Ore Zone	34.9	30.5	35.2	100.6
309	Langis	Beyond Ore Zone	34.7	30.1	35.1	99.9
781	Silverfields	Pebble in Conglomerate	35.4	30.4	35.3	101.1
1140	Deer Horn	Interflow	35.1	30.5	35.4	101.0
765	Silverfields	Interflow	35.1	30.4	34.5	100.0
Theoretical $CuFeS_2$	—	—	34.6	30.4	35.0	100.0

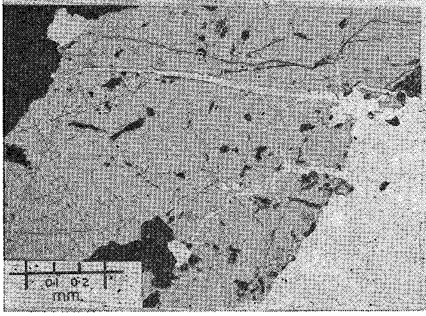
* Co, Ni and As were looked for but not detected.

Tetrahedrite $(Cu,Ag,Fe,Zn)_{12}(Sb,As,Bi)_4S_{13}$

Tetrahedrite is a common mineral in the Cobalt-Gowganda ores, but it is not as widespread as chalcopyrite. It occurs in the ore and carbonate veins and in adjacent wall rock. The tetrahedrite in veins is present as irregular grains, as veinlets, as masses (Fig. 132), and as remnants in late sulphides such as chalcocite and stromeyerite (Fig. 133). Some of the irregular grains occur at the cores of arsenide rosettes (Fig. 134), some as minute grains replacing arsenides, particularly skutterudite (Fig. 64) and some as intergrowths with chalcopyrite and pyrargyrite. The masses are up to several inches in size and locally form silver ore. The tetrahedrite grains and masses contain remnants of arsenides and silver,







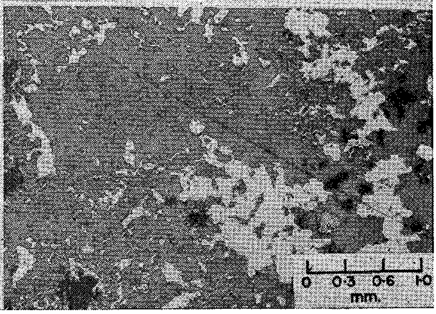


FIG. 133. (Top, left) Tetrahedrite (*tet*) remnants in a chalcocite (*cc*) - stromeyerite (*str*) intergrowth. (Foster mine).

FIG. 134. Photomicrograph of a tetrahedrite-rich high-grade silver ore showing tetrahedrite at the cores of two arsenide grains (right half of photograph), silver with allargentum lamellae (left half of photograph), and a late stephanite partly bordering the silver and arsenide grains. (Vein 6, Deer Horn mine, sample 27).

FIG. 135. (Bottom, left) Tetrahedrite (grey) cut by veinlets of silver (white). (Silverfields mine, sample 590).

FIG. 136. Bornite (grey) intergrown with silver (white). (Foster mine).

veinlets of silver (Fig. 135), acanthite and stephanite, and exsolution globules of chalcopyrite and bornite. Some tetrahedrite is found on plates, wires, and horns of native silver. The tetrahedrite in the wall rock occurs only near ore veins as minute disseminated grains commonly associated with chalcopyrite.

Electron microprobe analyses were made on tetrahedrites in nine samples, and cell-parameter measurements on tetrahedrites in six samples. The results of the electron microprobe analyses show that the tetrahedrites contain variable amounts of copper, silver, iron and zinc, small amounts of arsenic, and one sample contains bismuth (Table 42). Mercury was not detected with the electron microprobe. The cell parameters of the tetrahedrites appear to increase as the silver content increases up to about 20% silver, but for tetrahedrites containing more than 20% silver there is no correlation between the cell parameter and the silver content.

The atomic proportions were calculated by making the total of Cu + Ag + Fe + Zn equal 12, and obtaining relative atomic proportions for the other elements (Table 42). The calculations were conducted in this manner because it is considered that much better analyses were obtained for Cu, Ag, Fe, and Zn than for S and Sb. These calculated atomic proportions show larger deviations from the stoichiometric composition of $(Cu,Ag,Fe,Zn)_{12}(Sb,As,Bi)_4S_{13}$ than was reported by Springer (1969) for tetrahedrite from other areas. To determine whether the lack of stoichiometry is real or apparent, three samples were re-analysed and checked for homogeneity, and some tetrahedrites from other areas were analysed under the same conditions. The tetrahedrites from the Cobalt area were found to be more or less homogeneous, but poor reproducibilities were obtained for Ag, Sb, and S. On the other hand, stoichiometric compositions were obtained for the tetrahedrites from the other areas. The poor reproducibilities of compositions for the tetrahedrites, particularly the silver-rich varieties from the Cobalt area, may be due to compositional changes resulting from electron bombardment.

Bornite (Cu_5FeS_4)

Bornite is rare in the Cobalt-Gowganda ores and is present mainly at the ends of ore zones. It occurs as disseminated grains and veinlets in carbonates, arsenides, and wall rock; as minute exsolution globules in tetrahedrite; and as a constituent of larger sulphide grains and masses. The bornite is generally associated and intergrown with chalcopyrite, silver, and tetrahedrite. A sample from the Foster mine contains bornite intergrown with silver and chalcopyrite at the edges of the vein (Fig. 136)

Table 42. Chemical Compositions, Atomic Proportions and Unit-Cell Parameters of Tetrahedrites

Element (wt. %)	Chemical compositions in wt. %								
	a	b	c	d	e	f	g	h	i
Cu	40.6	35.2	32.3	26.8	26.4	25.9	16.0	15.2	13.4
Ag	0.5	5.1	7.4	18.2	18.7	17.3	30.4	32.9	35.6
Fe	2.5	6.6	2.9	3.5	3.7	3.9	4.7	5.5	6.5
Zn	2.6	1.0	4.8	3.3	2.7	3.0	1.3	1.4	0.1
Sb	24.5	24.5	25.0	26.4	24.7	26.8	26.0	25.4	23.1
As	3.8	0.8	3.2	tr	1.3	0.1	0.1	0.1	0.2
Bi	tr	3.1	—	—	tr	—	—	—	—
S	24.2	25.6	24.1	23.2	22.1	22.4	21.1	20.4	20.1
Total	98.7	101.9	99.7	101.4	99.6	99.4	99.6	100.9	99.0
Element (wt. %)	Atomic proportions (Cu + Ag + Fe + Zn = 12.00)								
	a	b	c	d	e	f	g	h	i
Cu	10.56	9.04	8.72	7.20	7.20	7.16	4.72	4.32	3.84
Ag	0.08	0.80	1.16	2.88	2.96	2.84	5.32	5.52	6.00
Fe	0.72	1.92	0.88	1.08	1.16	1.20	1.56	1.76	2.12
Zn	0.64	0.24	1.24	0.84	0.68	0.80	0.40	0.40	0.04
Sb	3.32	3.28	3.52	3.76	3.48	3.88	4.00	3.76	3.44
As	0.84	0.16	0.72	tr	0.28	tr	tr	tr	0.08
Bi	tr	0.24	—	—	tr	—	—	—	—
S	12.40	13.00	13.08	12.76	11.96	12.28	12.44	11.52	11.44
Unit cell parameters in Å	10.33	10.43	—	10.49	—	10.48	10.50	10.48	—

a) Sample from Foster mine, tetrahedrite in sulphides.
b) Sample 485, from Hi-Ho mine, in arsenides in ore zone.
c) Sample 141, from Silverfields mine, in arsenides at edge of an ore zone.
d) Sample 111, from Christopher mine, massive tetrahedrite at the edge of an ore zone.
e) Sample 728, from Agnico 407 mine, in wall rock.
f) Sample 125, from Christopher mine, coating on plate silver.
g) Sample 457, from Deer Horn mine, in a carbonate vein, associated with chalcopyrite and stephanite.
h) Sample 27, from Deer Horn mine, in massive tetrahedrite in an ore zone.
i) Sample 5, from Hi-Ho mine, in massive pyrargyrite.

and some is partly replaced by late chalcocite. R. I. Thorpe of the Geological Survey of Canada reported (personal communication) that bornite in Sample Co-C-16 at Queen's University at Kingston, Ontario contains exsolution lamellae of chalcopyrite and rounded inclusions of silver.

The composition of bornite in the sample from the Foster mine is Cu 64.3%, Fe 10.9%, S 26.0% (Total 101.2%) which is equivalent to $Cu_{5.03}Fe_{0.97}S_{4.02}$, and bornite intergrown with chalcopyrite from the Siscoe mine at Gowganda contains Cu 63.6%, Fe 11.6%, and S 26.5%, (Total 101.2%) which is equivalent to $Cu_{4.96}Fe_{1.04}S_{4.15}$. The *x*-ray diffraction pattern of the bornite from both samples corresponds to that of normal bornite.

Chalcocite (Cu_2S)

Chalcocite from the Cobalt-Gowganda region was found only in a sample from the Foster mine at Cobalt (G.S.C. collection) and in Sample No. 526 from the Siscoe mine at Gowganda. The chalcocite in the sample from the Foster mine occurs at the centre and intermediate parts of a zoned vein (Fig. 137). That at the centre occurs as intergrowths with

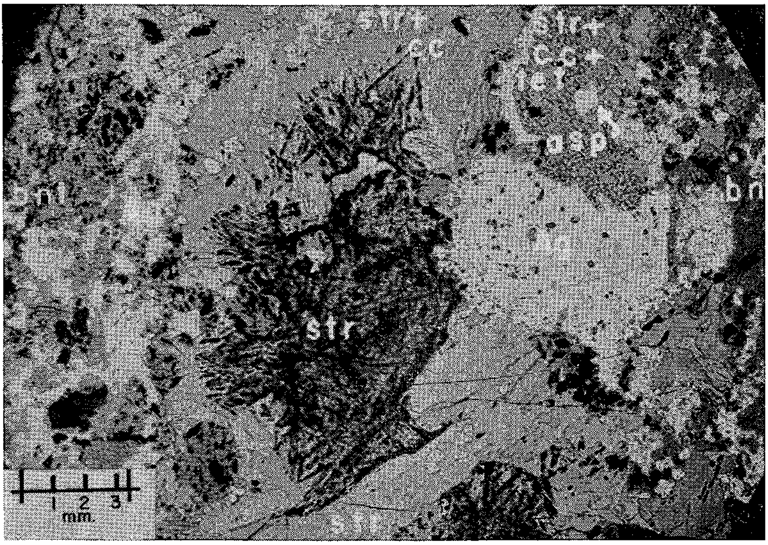


Fig. 137. Photomicrograph showing the full width of sulphide vein. It is composed of bornite (*bnt*) intergrown with silver (*Ag*) at the edges (see Fig. 136) ; chalcocite intergrown with stromeyerite at the centres (*str* + *cc*), and tetrahedrite (*tet*) partly replaced by chalcocite and stromeyerite (see Fig. 133). (Foster mine).

stromeyerite and larosite (Fig. 138). An analysis of this chalcocite gave Cu 79.7%, Ag 0.8%, and S 20.0% (Total 100.5%), which is equivalent to $Cu_{1.99}Ag_{0.01}S_{0.99}$. The binary section of the Cu_2S-Ag_2S phase equilibrium diagram shows that chalcocite can co-exist with stromeyerite only below the chalcocite–stromeyerite eutectic temperature of 67°C (Fig. 140) (Skinner 1966). The chalcocite in the intermediate zone occurs as grains with exsolved galena (Fig. 139). Data on the Cu-Pb-S system (Fig. 141) (Craig & Kullerud 1968) indicates that chalcocite cannot contain enough lead in solid solution to exsolve significant amounts of galena on cooling, but a phase with the composition Cu 55.5%, Pb 26.5%, S 18.0%, reported as phase A, exists between 486°C and 523°C (Fig. 141). The bulk composition of the chalcocite with exsolved galena, determined by means of the electron microprobe by using a normal operating specimen current and an expanded beam of 130-micron diameter, is Cu 53.1%, Pb 28.6%, and S 18.1%. Phase A can be quenched, but it probably breaks down to galena and chalcocite on cooling presumably giving exsolution textures. Hence, the chalcocite with exsolved galena probably represents the decomposed naturally occurring equivalent of phase A. An interpretation of these two occurrences of chalcocite in the same vein is given in the section "Discussion".

The chalcocite in Sample 526 occurs as veinlets in chalcopyrite and as intergrowths with bornite in a carbonate vein.

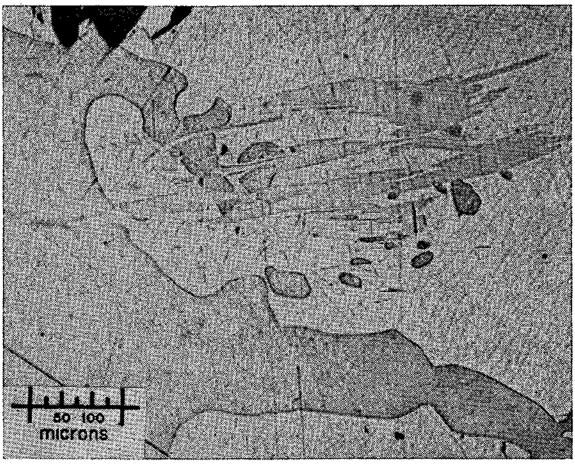


FIG. 138. Chalcocite (light grey) intergrown with stromeyerite (grey) and cut by feather-like grains of larosite. (Foster mine).

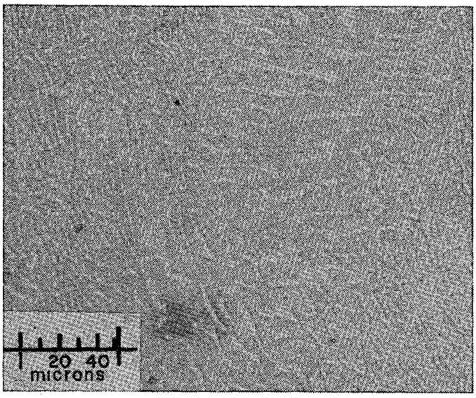


FIG. 139. Chalcocite (grey) with exsolved galena (white). (Foster mine).

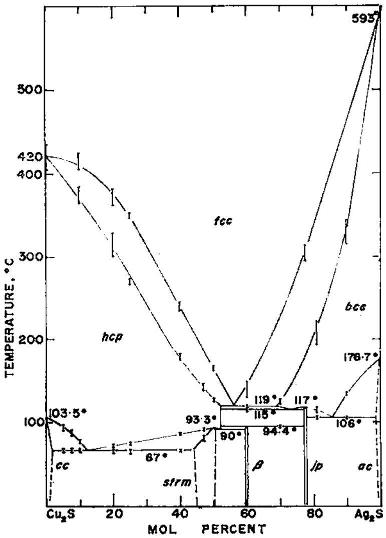


FIG. 140. Binary section of the Cu_2S-Ag_2S system (from Skinner 1966). *ac* = acanthite, *bcc* = body centered cubic, *cc* = chalcocite, *fcc* = face centered cubic, *hcp* = hexagonal close packed, *jp* = jalpaite, *strm* = stromeyerite, β = mckinstryite ($Cu_{0.8}Ag_{1.2}S$). All phases co-exist with vapour.

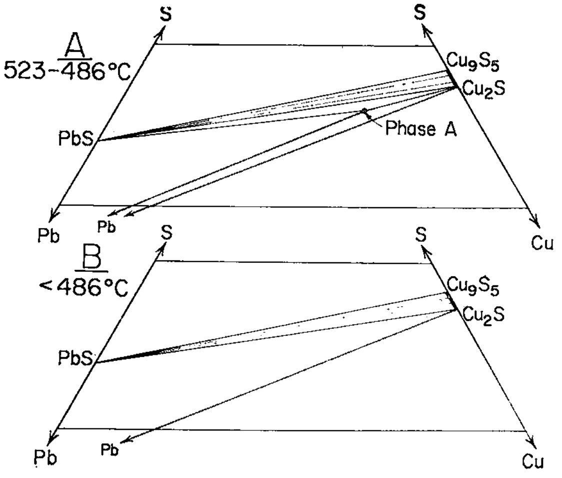
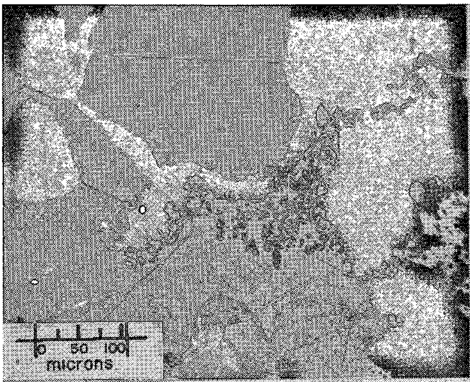
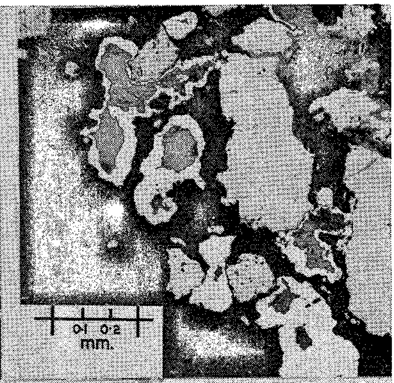


FIG. 141. Portions of the Cu-Pb-S ternary system below 486°C and at 486-523°C (from Craig & Kullerud 1968). Phase A is shown in the top illustration but not in the lower one.

Stromeyerite (*CuAgS*)

Stromeyerite was found in samples from the O'Brien mine in the Cobalt area (ROM, M-15826), the Morrison mine in the Gowganda area (ROM, M-16326), and the Foster mine in the Cobalt area (G.S.C. collection, and ROM, M-20792). The stromeyerite from the O'Brien mine is present as





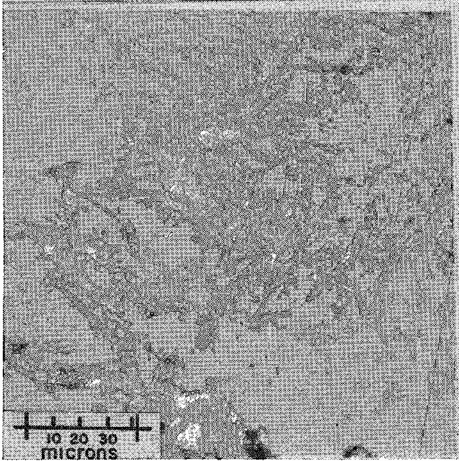


FIG. 142. (Top, left) Irregular grain of stromeyerite (grey) with pearceite (111) (lighter grey at centre of photograph). A grain of chalcopyrite (white) is present in calcite (black) at extreme right of photograph. (Morrison mine, sample M-16326).

FIG. 143. Rounded acanthite grains (grey) bordered by a late silver (white). The large dull-white grains at right side of photograph are safflorite. (Silerfields mine, sample 242).

FIG. 144. (Bottom, left) Pyrargyrite lamellae (dark grey) replacing allargentum lamellae (light grey) in silver (white). (Deer Horn mine, sample 27).

FIG. 145. Stephanite veinlets (grey) near the edge of the ore vein in carbonates (black) and arsenides (white). (Hi-Ho mine, sample 6).

large grains intergrown with small grains of wittichenite. That from the Morrison mine is present as a mosaic of crystals intergrown with small grains of pearceite (111) (see page 208) and acanthite, and contains a few small inclusions of chalcopyrite and galena (Fig. 142). The chalcopyrite inclusions are partly replaced by stromeyerite, and some chalcopyrite remnants have a myrmeketic texture (Fig. 131). The stromeyerite from the Foster mine (G.S.C. collection) occurs at the centre of a zoned vein (Fig. 137) and is intergrown with chalcocite, a copper-rich polybasite (111) see (page 208), and larosite (Fig. 138). Some of the stromeyerite in this sample is present as grains composed of large crystals and some as a mosaic of very small crystals. Some of the finely crystalline variety occurs as either veinlets or remnants in the coarsely crystalline variety. Stromeyerite from the Foster mine was also reported by Skinner *et al.* (1966) as an intergrowth with mckinstryite. Data on the Cu-Ag-S system (Fig. 140) shows that stromeyerite is stable only below 93.3°C.

The compositions and equivalent atomic proportions for the stromeyerite from the Morrison and Foster mines are :

	Chemical Compositions				Atomic Proportions		
	Cu	Ag	S	Total	Cu	Ag	S
Morrison mine	31.2	52.3	15.8	99.3	1.01	0.99	1.01
Foster mine	31.5	52.5	15.4	99.4	1.01	0.99	1.00

Bi, Sb, Pb, Fe, Co, and Ni were looked for, but not detected.

Mckinstryite ($Cu_{0.8}Ag_{1.2}S$)

Mckinstryite was found as a new mineral in a sample from the Foster mine at Cobalt by Skinner *et al.* (1966). It was not observed by the present authors ; hence the reader is referred to the original paper for details of its properties. The mineral was reported to occur as a coarse-grained aggregate of intergrown crystals in association with chalcopyrite, stromeyerite, silver, and arsenopyrite. Mckinstryite is stable only below 94.4°C (Fig. 140).

Wittichenite (Cu_3BiS_2)

Wittichenite was found and identified by *x*-ray diffraction in Sample ROM, M-20792 from the O'Brien mine at Cobalt. It is present as small rounded grains in stromeyerite.

Covellite (CuS)

Covellite in the Cobalt-Gowganda ores was found in a fault zone in the Christopher mine and was identified only by ore microscopy. It is associated with other sulphides and forms a coating as an alteration product on chalcopyrite and tetrahedrite.

Polybasite ($(Ag,Cu)_{16}Sb_2S_{11}$) *and Pearceite* ($(Ag,Cu)_{16}As_2S_{11}$)

Polybasite and pearceite are antimony- and arsenic-bearing end members of two parallel series (Frondel 1963). Both series have the same crystal structure (space group *C*2/*m*) (Peacock & Berry 1947) but the minerals in one series have large unit cells that are multiples of the other. Frondel (1963) proposed that the names polybasite and arsenopolybasite be used for the large-cell antimony- and arsenic-rich end members respectively and that the names pearceite and antimonpearceite be used for the small-cell arsenic- and antimony-rich end members. Harris *et al.* (1965) suggested that the names polybasite and pearceite be used as compositional names indicating antimony- and arsenic-rich varieties respectively, and that the suffixes (222) and (111) be used to designate large and small unit-cell sizes respectively. They also found a polybasite with an intermediate cell for which they proposed the suffix (221). The large and small cells can be differentiated by means of *x*-ray powder diffraction patterns. The terminology proposed by Harris *et al.* will be used in this paper and, in addition, the term polybasite- pearceite, followed by the appropriate suffix, will be used when the compositions is unknown.

Polybasite-pearceite (222) was found in samples from the O'Brien mine (ROM, M-15826) and the Siscoe mine (Dr. H. Frohberg's private collection, Toronto). The polybasite-pearceite (222) in these samples is present as euhedral crystals in vugs associated with proustite, xanthoconite, acanthite, stephanite, and pyrargyrite.

Polybasite (111) was found in a sample from the Foster mine (G.S.C. collection) and pearceite (111) was found in a sample from the Morrison mine (ROM, M-16326). The polybasite (111) from the Foster mine occurs as irregular grains associated with chalcocite, stromeyerite, and

TABLE 43. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF POLYBASITE (111) AND PEARCEITE (111)

Sample	Chemical compositions (weight per cent)						
	Ag	Cu	As	Sb	Bi	S	Total
M16326	58.1	11.9	4.4	2.0	7.0	15.7	99.1
Foster	54.6	17.6	2.5	7.8	1.8	18.3	102.6
	Atomic proportions						
M16326	11.88	4.12	1.27	0.35	0.74	10.80	
Foster	10.37	5.63	0.68	1.33	0.18	11.60	

tetrahedrite; and the pearceite (111) from the Morrison mine is intergrown with stromeyerite. The polybasite (111) and pearceite (111) in these two samples contain a significant amount of bismuth and more copper than has been reported previously for these minerals (Table 43). A study on synthetic materials has shown that copper-rich polybasites and pearceites exist only as small-cell varieties (Hall 1967), which explains the small-cell size of the copper-rich varieties found in the Foster and Morrison mines. The *x*-ray powder diffraction pattern of the polybasite (111) from the Foster mine was indexed on a hexagonal cell, which gave pseudohexagonal cell parameters of $a = 7.33$ Å and $c = 11.77$ Å. Conversion to a monoclinic cell gives cell parameters of $a = 12.73$ Å, $b = 7.33$ Å, $c = 11.77$ Å, and $\beta = 90°$.

Larosite $(Cu,Ag)_{21}(Pb,Bi)_2S_{14}$

Larosite is a new mineral found in a sample from the Foster mine (Petruk *et al.* in press). The mineral is present as acicular crystals cutting across stromeyerite, chalcocite, and polybasite (G.S.C. collection) (Fig. 138). Two electron microprobe spot analyses on this mineral gave the compositions Cu 48.3%, Ag 15.6%, Pb 8.5%, Bi 9.6%, and S 19.8% (Total 101.8%); and Cu 49.7%, Ag 15.6%, Pb 9.0%, Bi 8.9%, and S 18.5% (Total 101.7%). These compositions are equivalent to $(Cu_{17.6}Ag_{3.4})(Pb_{0.9}Bi_{1.1})S_{14.3}$ and $(Cu_{17.7}Ag_{3.3})(Pb_{1.0}Bi_{1.0})S_{13.1}$ respectively. The compositions are similar to those of betekhtinite $(Cu,Ag,Fe)_{21}Pb_2S_{14}$, but the mineral has a different *x*-ray diffraction pattern. The optical and *x*-ray diffraction properties of this mineral are described elsewhere. The mineral and mineral name were approved by the Commission on New Minerals and Mineral Names in April, 1971.

Freieslebenite $(Pb_3Ag_5Sb_5S_{12})$

A minute veinlet of freieslebenite was found in one sample in a large skutterudite grain (ROM, M-21270). This mineral is so rare that all the material found in the sample was used for the *x*-ray diffraction mount, and none remained for analysis or photomicrography.

Acanthite and argentite (Ag_2S)

Acanthite is the low-temperature form of Ag_2S and argentite the high-temperature form (Kracek 1946). Argentite, however, inverts to acanthite upon cooling below the inversion temperature of 176.7°C, hence at room temperature all Ag_2S is in the form of acanthite. Wherever crystals are developed, the cubic morphology of argentite may be preserved, indicating that the Ag_2S was originally deposited as argentite.

The acanthite in the Cobalt-Gowganda ores occurs in zones containing silver and is present in ore veins, in late veins and veinlets, and on drift faces. The acanthite in the ore veins occurs as irregular grains and veinlets in carbonates and arsenides, as masses, and as isometric crystals. Some of the irregular grains occur at the cores of dendritic arsenides, some are surrounded by a later silver (Fig. 143), and some have a typical replacement texture with acanthite replacing silver. This replacement texture forms a matte of acanthite and silver and is associated with pyrargyrite. Data on synthetic materials from the Ag-Sb-S system shows that the assemblage argentite-pyrargyrite-silver can co-exist above 200°C (Keighin & Honea 1969) but is forbidden at 400°C (Barstad 1959). Some of the acanthite in the ore veins is in the form of cubic and octahedral crystals up to 1 inch in size and some of the massive variety contains nearly submicroscopic globules of silver. The acanthite in late calcite veinlets is present as irregular grains, some of which are cut by veinlets of late silver.

Drift faces in zones of silver ore commonly become coated with grease-like spots within several weeks after the drifts are opened. X-ray studies combined with ore microscopy show that these spots are acanthite and that they are formed on minute grains of silver in the drift faces. This occurrence shows that acanthite can form at about 15°C in the presence of mine gases in a short time.

Pyrargyrite (Ag_3SbS_3)

Pyrargyrite is a common silver sulphantimonide in the Cobalt-Gowganda ores and it generally occurs near zones containing silver ore. The

TABLE 44. CHEMICAL COMPOSITIONS OF PYRARGYRITE

Sample	Mode of occurrence	Chemical compositions wt. %				
		Ag	Sb	As	S	Total
5	pyrargyrite veinlet	59.6	24.2	nd	18.1	101.9
606	pyrargyrite veinlet	60.6	24.2	nd	18.3	103.1
168	late fault vein	58.4	22.3	—	17.5	98.2
12	in ore zone in arsenides	59.2	20.0	1.4	16.7	97.3
Ag_3SbS_3	theoretical	59.8	22.5	—	17.7	100.0

NOTE: The analyses on the pyrargyrite sample Nos. 5, 606 and 168 were made with a wide beam and low voltage to minimize decomposition. Sample No. 12 contains only small pyrargyrite grains, hence it was analysed with a narrow beam which could have resulted in poor analyses. The As value could be due to stray radiations from the host mineral.

nd = not detected

mineral is present in ore veins, in late fault veins, in late mineralized calcite veins, and in separate pyrargyrite veinlets. The pyrargyrite in the ore veins occurs as veinlets and disseminated grains in arsenides and carbonates, as coronas around silver grains, as intergrowths with silver, as intergrowths with allargentum, (Fig. 144), and as a constituent of galena-sphalerite-stephanite-pyrargyrite masses. The intergrowth with silver has a typical replacement texture with pyrargyrite replacing silver and is commonly associated with acanthite. This intergrowth forms an acanthite-pyrargyrite-silver assemblage as described in the section on acanthite. The pyrargyrite associated with allargentum is present as a replacement of allargentum in silver (Fig. 144).

The pyrargyrite in late calcite veinlets and late fault veins is present as masses and disseminated grains in carbonate. It is intergrown with stephanite and contains veinlets of silver and irregular grains of tetrahedrite and chalcopyrite.

The pyrargyrite veinlets are up to ½ inch wide, and they occur in the wall rock generally near the parts of ore veins containing silver ore. The pyrargyrite in one veinlet (sample 5) is associated with tetrahedrite and silver.

Some of the pyrargyrite contains a few minute rounded grains whose optical properties are similar to those of Sb-billingsleyite (Keighin & Honea 1969) but the grains are too small for *x*-ray diffraction or electron microprobe analyses.

Electron microprobe analyses for four samples are given in Table 44. The results show that a sample from the arsenide zone contains a small amount of arsenic. Copper, cobalt, and nickel were looked for but not detected.

Stephanite (Ag_5SbS_4)

Stephanite is the most common silver sulphantimonide in the Cobalt-Gowganda ores. It generally occurs in zones enriched in silver and is present in the ore veins, in late fault veins, and in late mineralized calcite veins. The stephanite in the ore veins is present as irregular grains and veinlets in carbonates, arsenides and sulphides, particularly near the edges of the veins (Fig. 145). It is associated with galena, sphalerite, and pyrargyrite in some places, with silver and pyrargyrite in other places, and with acanthite elsewhere. It cuts all other sulphides and contains inclusions of chalcopyrite, tetrahedrite, sphalerite, galena, pyrargyrite and silver. Hence it appears to be a late mineral in the ore veins.

The stephanite in late fault veins and late mineralized calcite veins is present as irregular grains and veinlets in calcite and sulphides and as

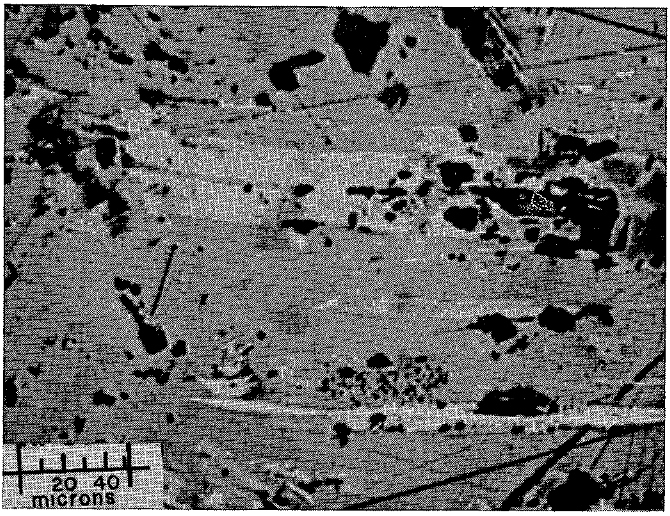


FIG. 146. Prismatic pyrrhotite crystals (light grey) in a matrix of stephanite and pyrargyrite (unresolved in photograph). Some of the pyrrhotite is partly replaced by marcasite (white lath at bottom of photograph). (O'Brien mine, sample M-9661).

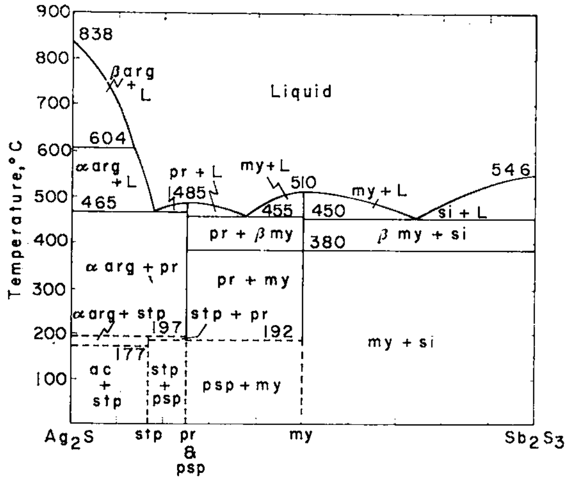


FIG. 147. Pseudobinary system Ag_2S-Sb_2S (from Keighen & Honea 1969). All assemblages are in equilibrium with vapour. *arg* = argenite, *pr* = pyrargyrite, *stp* = stephanite, *ac* = acanthite, *psp* = pyrostilpnite, *my* = miargyrite, *si* = stibnite. The dotted lines indicate the uncertainty of low temperature relations. Both stephanite and pyrostilpnite have never been synthesized, and the pyrargyrite-pyrostilpnite reaction has not been established.

masses. The late mineralized calcite veins containing stephanite generally occur at the boundary between the ore veins and wall rock and contain layers of ore minerals. The stephanite is intergrown with all the minerals in the later veins, hence, it is part of the later vein mineral assemblage.

Stephanite in one sample from the O'Brien mine at Cobalt, obtained from the Royal Ontario Museum (Sample M-9661) is intergrown with pyrargyrite and contains inclusions of prismatic pyrrhotite crystals (Fig. 146) and minute rounded galena grains.

The pseudobinary phase-equilibrium diagram for the Ag_2S-Sb_2S_3 system (Fig. 147) indicates that stephanite is stable only below 197°C and that it may co-exist with any of pyrargyrite, argentite, acanthite, or pyrostilpnite.

Electron microprobe analyses of stephanite from a late fault vein (Sample 168), from an ore vein (Sample 12), and from a sample obtained from the Royal Ontario Museum (Sample M-15826), are given in Table 45.

Xanthoconite (Ag_3AsS_3)

Xanthoconite was found in two samples from the Christopher mine, and was reported by Parsons (1924) from the La Rose mine. The samples from the Christopher mine were taken from a fault zone where most of the carbonate had been leached away, and some redeposited as botryoidal siderite. The xanthoconite in one sample occurs in complex sphalerite-xanthoconite veinlets associated with arsenopyrite and cobaltite, and in the other sample as intergrowths with botryoidal siderite in the form concentric rings and irregular grains (Fig. 148). Prismatic proustite crystals extend outward from the xanthoconite into open spaces. A similar occur-

TABLE 45. CHEMICAL COMPOSITIONS OF STEPHANITE

Sample	Chemical compositions wt. %				
	As	Sb	As	S	Total
168	68.2	14.6	nd	16.0	98.8
M15826	69.4	15.1	—	15.9	100.4
12	68.1	13.8	1.5	15.4	98.8
Ag_5SbS_4	68.3	15.4	—	16.3	100.0

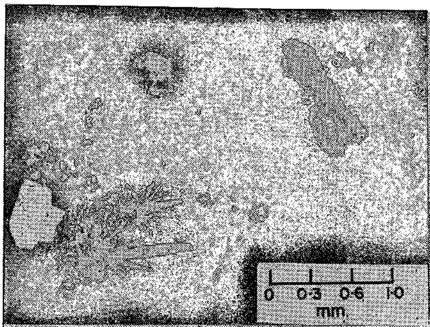
NOTE : The analyses on stephanite in Samples 168 and M15826 were made with a wide beam and low voltage to minimize decomposition. Sample 12 contains only small stephanite grains, hence it was analysed with a narrow beam which could have resulted in poor analyses. The As value could be due to stray radiations from the host.

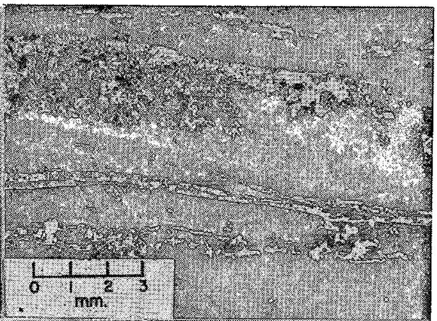
nd = not detected

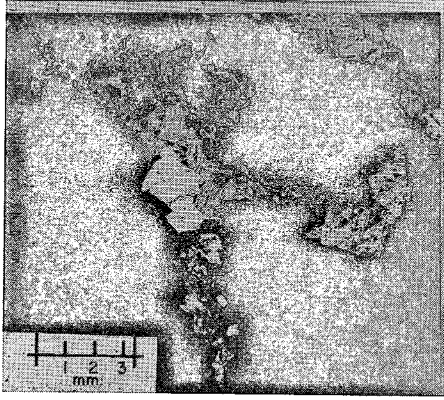
rence was reported for the xanthoconite from the La Rose mine (Parsons 1924). These modes of occurrence suggest that the xanthoconite may be a secondary mineral deposited from circulating ground waters in a fault zone.

Proustite (Ag_3AsS_3)

Proustite was found and identified by *x*-ray diffraction in only four samples (129, ROM, M15826, ROM, M20792 and 647), although it was







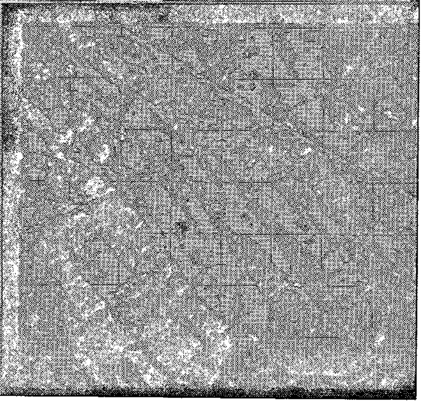


FIG. 148. (Top, left) Irregular grains of xanthoconite bordered by a few prismatic crystals of proustite (xanthoconite and proustite are both grey). The rounded dark grey grains are siderite, and the white one at left side of photograph is arsenopyrite. (Christopher mine, sample 129).

FIG. 149. Irregular grains and veinlets of proustite (white) in a late calcite vein at the boundary between a dolomite vein (bottom part of photograph) and wall rock (top of photograph). (Silverfields mine, sample 647).

FIG. 150. (Bottom, left) Galena (grey) and arsenopyrite (white), in calcite (black). (Glen Lake mine, sample 102).

FIG. 151. Electron microprobe backscatter pattern showing matildite (grey) in galena (white). (O'Brien mine, sample M-16084).

looked for in all the samples studied. The proustite in samples 129, M-15826, and M-20792 occurs as prismatic grains extending into open spaces from irregular grains of xanthoconite, acanthite, stephanite, and stomeyerite. The proustite in sample 647 is present as a late veinlet at the boundary between a carbonate vein and wall rock and as irregular grains adjacent to the veinlet (Fig. 149). The mineral contains inclusions of tetrahedrite, stephanite, pyrrhotite, and ullmannite. Sample 647 was taken from an ore vein about 50 feet west of the ore zone in Vein No. 11 on the third level in the Silverfields mine. The above mentioned occurrences show that proustite is a very late mineral in the ore and that it was probably formed where arsenic was released from the arsenides by circulating solutions. In this respect it can be considered as a secondary mineral.

The composition of the proustite in sample ROM, M15826 is Ag 64.7%, As 16.3% and S 19.3% (Total 100.3%), which is equivalent to $Ag_{2.94}$-$As_{1.06}S_{2.95}$.

Galena (PbS)

Galena is a common sulphide in the Cobalt-Gowganda ores. It occurs in the ore veins, in faults, in calcite veins, and in the wall and country rock. Galena in the ore veins was found in the Fe-As and Ni-As arsenide assemblages (for a definition of arsenide assemblages see pages 111 to 122), and in almost barren carbonate (Fig. 150). That in the Fe-As assemblage is present in interstices between arsenopyrite grains, and some contains lamellae and irregular grains of matildite (Fig. 151). Galena in the Ni-As assemblage, found only in sample 828 from the Bonsall mine, Miller Lake area occurs in interstices between nickeline and cobaltite grains. The galena in almost barren carbonate veins is present as irregular grains and as intergrowths with sphalerite, stephanite, pyrargyrite, tetrahedrite, chalcopyrite, and pyrrhotite. Some contains inclusions of other sulphides including pyrite, pyrrhotite, chalcopyrite, and tetrahedrite.

The galena in faults is present as masses and as intergrowths with sphalerite, marcasite, and stephanite. Galena masses, up to 4 inches in size and extending several feet along a vein, were reported from several faults and from some silver ore veins (Knight 1924), for example, in the Galena vein in the Buffalo mine. Massive galena from the Christopher mine was analysed chemically and found to contain 0.34% Bi and 0.26% Ag.

Some of the galena occurs in low-angle calcite veins that offset the ore veins several feet and in calcite veins that are at the boundary between the ore veins and wall rock. The galena in these veins is present as parallel veinlets commonly interlayered with sphalerite and marcasite. Some of this galena contains inclusions of sphalerite, pyrite, and marcasite, and some is intergrown with stephanite.

Galena is also present as minute grains in stephanite, apparently as remnants, and in a graphic intergrowth with chalcocite (Fig. 139). The graphic intergrowth of galena with chalcocite is discussed in the section on chalcocite and in the "Discussion".

Galena in the wall and country rock is present in Keewatin interflow rocks and as disseminated grains in Huronian sediments. That in the interflow rocks is present as galena masses up to several inches in size, and as intergrowths with sphalerite, chalcopyrite, and pyrrhotite. Galena in Huronian sediments was found as disseminated grains near the tops of slate beds (Fig. 152).

Electron microprobe analyses of galena in samples from the Cobalt-Gowganda ores, given in Table 46, show nearly stoichiometric compositions. Trace amounts of silver and bismuth were indicated but not with certainty; hence any silver and bismuth in the galena is likely below the limit of detection by the electron microprobe. Other elements, looked for but not detected, were Fe, As, Cu, Sb and Zn.

Matildite ($AgBiS_2$)

Matildite was found in two samples obtained from the Royal Ontario Museum (M16084 and M9667), and in samples from the Silverfields and

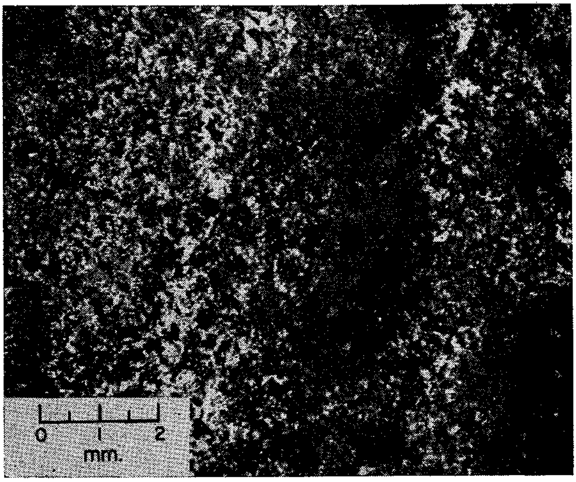


FIG. 152. Disseminated galena (white) and sphalerite (grey) at tops of slate beds in Huronian sediments. The tops of two beds are shown. (Silverfields mine, sample 763).

Canadian Keeley mines (samples 9561 and 424 respectively). The matildite is present as lamellae and irregular grains in galena, apparently as exsolutions (Fig. 151), and as an intergrowth with pavonite in sample 424. Data on the Ag-Bi-Pb-S system shows that, at low temperatures, matildite can co-exist with either galena or pavonite, but not with both minerals in the same assemblage. Craig (1967) has also shown that, in the presence of vapour, the $AgBiS_2$-PbS solvus is intersected at 215 ± 15°C and that galena-matildite exsolutions form by a breakdown of an $AgBiS_2$-PbS solid solution at this temperature.

Electron microprobe analyses for the matildite co-existing with pavonite gives Ag 26.4%, Bi 55.7% and S 16.7% (Total 98.8%) which is equivalent to $Ag_{0.95}Bi_{1.05}S_{2.03}$.

Pavonite ($AgBi_3S_5$)

Pavonite was found in a sample taken from an ore chute in the Canadian Keeley mine in South Lorrain township (sample 424). The pavonite occurs as veinlets in calcite near a large irregular chalcopyrite grain. It is intergrown with bismuthinite, matildite, and native bismuth, and it contains minute inclusions of chalcopyrite, sphalerite and pyrite. Data on the Ag_2S-Bi_2S_3 system show that pavonite is stable below 732°C and can co-exist with $AgBiS_2$ and bismuthinite over a wide temperature range. The low-temperature form of $AgBiS_2$ is matildite. Electron microprobe analysis for the pavonite in this sample gives Cu 3.1%, Ag 10.4%, Bi 65.7%, S 17.9% (Total 97.1%) which is equivalent to $Cu_{0.43}Ag_{0.83}Bi_{2.74}$-$S_{4.85}$; Fe, Sb and As were looked for but not detected. These data show that pavonite can contain an appreciable amount of Cu.

TABLE 46. CHEMICAL COMPOSITIONS OF GALENA FROM THE COBALT-GOWGANDA ORES

Sample	Mode of occurrence	Wt %		
		Pb	S	Total
580	late vein	85.9	13.2	99.1
900	ore vein	86.1	13.3	99.4
141	late vein	86.8	13.5	100.3
433	interflow	86.4	13.3	99.7
372	interflow	87.9	13.3	101.2
PbS	—	86.6	13.4	100.0

Galenobismutite ($PbBi_2S_4$)

Galenobismutite was found in Vein 93, 650 level of the Siscoe mine in the Gowganda area (sample 545). The galenobismutite in this sample occurs as a veinlet and as crystals up to 1 cm in size. It contains remnants of arsenopyrite. The binary section of the PbS-Bi_2S_3 phase-equilibrium diagram shows that galenobismutite is stable below 750°C and that it can co-exist with bismuthinite below 680°C. Electron microprobe analyses for the galenobismutite in the sample studied gave Pb 26.4%, Bi 55.5%, and S 17.0% (Total 98.4%), which is equivalent to $Pb_{0.97}Bi_{2.03}S_{4.04}$. Fe, Cu, Sb and Ag were looked for but not detected.

Bismuthinite (Bi_2S_3)

Bismuthinite is present in many places in the Cobalt-Gowganda ores but only in small quantities. It occurs in the ore veins and in late calcite veins that are at the boundary between the ore veins and wall rock. The mineral is most abundant near the ends of ore veins and is commonly associated with native bismuth, arsenopyrite, and galena. The bismuthinite occurs as irregular grains and veinlets, in carbonates and arsenides, and is intergrown with native bismuth, arsenopyrite, galena, pavonite, and chalcopyrite.

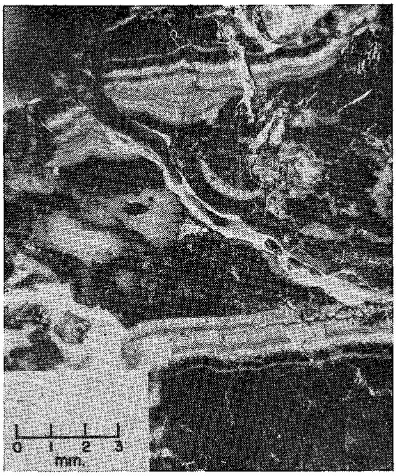


FIG. 153. Colloform sphalerite bands in a late vein. (Silverfields mine, sample 141). Photomicrograph taken by oblique illumination.

Sphalerite (ZnS)

Sphalerite is a common mineral in the Cobalt-Gowganda ores. It occurs in the ore veins, in late calcite veins, in fault veins, and in the wall and country rock. The sphalerite in the ore veins is present in the ore zones and beyond them. It occurs as irregular grains up to 1 inch in size, and as a constituent of massive sulphides composed of sphalerite, galena, pyrargyrite, and stephanite. Some of the irregular sphalerite grains contain inclusions of marcasite, some are intergrown with chalcopyrite, galena, and tetrahedrite, and some are present as inclusions in chalcopyrite. Some of the irregular grains in the ore veins and faults have more or less uniform compositions containing about 1.5% Fe and 65.5% Zn. Other grains have variable compositions from spot to spot, containing 0.3 to 7.8% Fe, and 58.2 to 67.5% Zn, but the variations are not systematic. This sphalerite also contains up to 0.41% Cd, but no detectable Mn, In, Cu or Pb (Table 47).

The sphalerite in late calcite veins and in fault veins occurs as parallel veinlets commonly interlayered with marcasite and galena veinlets (Fig. 88). Some of the sphalerite in these veinlets has a colloform banding (Fig. 153) with the lightest-coloured band being at the centre of the

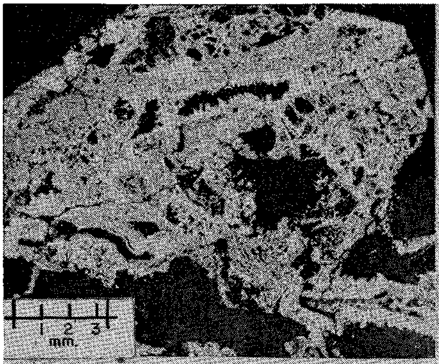
TABLE 47. CHEMICAL COMPOSITIONS OF SPHALERITE

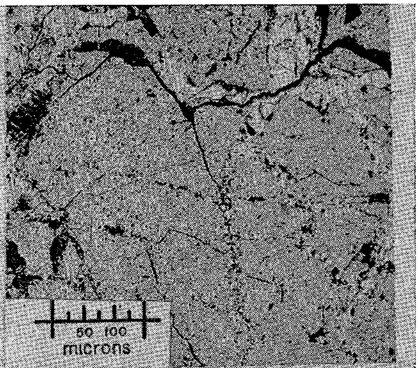
Sample	Mode of occurrence		Wt. %					
			Zn	Fe	Mn	Cd	S	Total
183	end of ore vein (massive sphalerite)		65.54	1.61	nd	0.08	33.53	100.76
900	massive sulphide in ore vein	low Zn	58.42–	7.18	nd	0.03	35.08–	100.71
		high Zn	67.46	0.32	nd	0.19	35.03	103.00
580	fault vein		65.61	1.45	nd	0.41	32.56	100.03
1140	interflow		60.06	6.25	0.04	0.13	33.53	100.01
372	interflow		61.87	5.52	0.07	0.14	33.40	101.00
433	interflow		62.99	5.64	0.04	0.14	33.11	101.92
13	parallel veinlet	low Zn	58.18–	7.79–	nd	0.18	33.74–	99.89
		high Zn	66.48	1.38	nd	0.18	32.62	100.66
365*	in carbonate vein*	low Zn	61.59–	3.04–	nd	0.17	31.07–	96.87
		high Zn	63.44	0.67			32.09	—
ZnS (theor.)			67.10	—	—	—	32.90	100.00

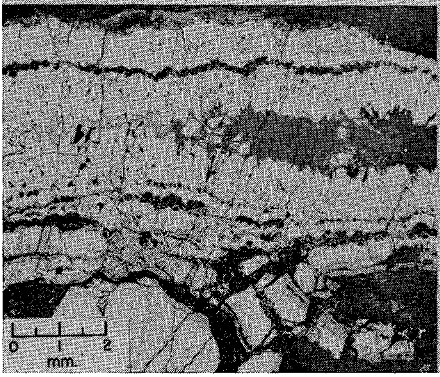
* Sphalerite from middle layer of cross vein as described in the section on bravoite, and shown in Fig. 90.

vein and the dark brown one being nearest the wall rock. The sphalerite in these bands contains variable amounts of iron but the variation is not systematic.

The sphalerite in the wall and country rock is present as a constituent of mineralized Keewatin interflow rocks and of sulphide pebbles in Huronian conglomerate. That in Keewatin interflow rocks occurs as small sphalerite masses and as intergrowths with galena, chalcopyrite, and pyr-







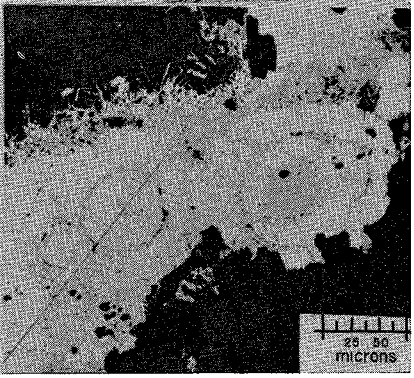


FIG. 154. (Top, left) Intergrowth of sooty-textured cryptocrystalline pyrite and marcasite (light grey area), partly bordered by marcasite crystals (white). (Langis mine, sample 89).

FIG. 155. Late pyrite veinlets in a cryptocrystalline intergrowth of pyrite and marcasite. (Langis mine, sample 329).

FIG. 156. (Bottom, left) Marcasite (white) with interstitial sphalerite (dark grey) and galena (light grey). (Silverfields mine, sample 587).

FIG. 157. Bravoite (grey) at cores of concentrically-zoned pyrite (white). Prismatic marcasite crystals border the concentrically-zoned bravoite. (Silverfields mine, sample 365).

rhotite (Fig. 93). Most of it contains exsolution globules of chalcopyrite. This interflow sphalerite has a relatively uniform composition containing 60-63% Zn, 5.5-6.3% Fe, 0.05% Mn, and 0.14% Cd (Table 47). The sphalerite in sulphide pebbles in conglomerate is present as minute inclusions in chalcopyrite.

Pyrite (FeS_2)

Pyrite is widespread in the Cobalt-Gowganda ores. It occurs in the ore and carbonate veins and in the wall and country rock. The pyrite in veins is weakly to moderately anisotropic and is present as a constituent of marcasite-pyrite intergrowths (Fig. 154), as late veinlets cutting the marcasite-pyrite intergrowths (Fig. 155), and as euhedral crystals and irregular grains in vugs, carbonates, and sulphides. The pyrite in the pyrite-marcasite intergrowth is present as euhedral crystals, irregular grains, and sooty-textured cryptocrystalline pyrite.

Pyrite in the wall and country rock is present as disseminated grains and as a constituent of the mineralized Keewatin interflow rocks. The pyrite in the mineralized interflow rocks is present as masses, nodules, and as intergrowths with chalcopyrite and pyrrhotite. The pyrite nodules were found in massive pyrrhotite in a large mineralized interflow band in the Deer Horn mine. The nodules are up to ¾ inches in size and are enveloped by a narrow layer composed of quartz, carbonate, and clay minerals (Fig. 94). The pyrite in the nodules is weakly to moderately

TABLE 48. CHEMICAL COMPOSITIONS OF SOME PYRITE IN THE COBALT-GOWGANDA ORES

Sample	Mode of occurrence	Chemical composition (wt %)						
		Fe	S	Cu	Co	As	Zn	Total
65	in vug	46.8	53.5	nd	0–0.3	0–0.2	—	100.8
309	remnants in chalcopyrite	46.6	53.6	0.6–1.1	0.1	nd	—	101.4
89	intergrown with marcasite	46.1	53.1	0–0.7	nd	nd	—	99.9
372	Keewatin interflow	46.6	53.9	nd	nd	nd	0.07–0.2	100.7
365*	concentrically zoned pyrite*	45.5	52.4	nd	nd	0.2	nd	98.1
FeS_2 (theor.)		46.6	53.5	—	—	—	—	100.0

* Pyrite in intermediate layer of a cross vein as described in the section on "bravoite" and shown in Fig. 157.

nd = not detected.

anisotropic and contains a few inclusions of pyrrhotite, marcasite, and chalcopyrite. The results of electron microprobe analyses on some pyrites are given in Table 48; Ni, Sb, and Ag were also looked for but not detected.

Taylor (1970) reported that he found bladed pyrite inclusions in smythite from the Silverfields mine and that this pyrite contains 5.4 wt % Ni.

Marcasite (FeS_2)

Marcasite is a common mineral in the Cobalt-Gowganda ores. It occurs in faults, in late calcite veins, in the ore veins, and in mineralized Keewatin interflow rocks. The marcasite in faults and veins is present as parallel veinlets interlayered with sphalerite and galena (Figs. 88, 89, and 156), as interstitial material between other minerals and rock fragments, as disseminated grains, as feather-like stringers along carbonate grain boundaries, and as remnants in galena, chalcopyrite, tetrahedrite, stephanite, and acanthite. The parallel veinlets are 1/16 to 1/2 inches wide, and commonly have a colloform texture. The marcasite in these occurrences is in the form of prismatic crystals, minute grains, and sooty textured material intimately intergrown with pyrite.

Marcasite in mineralized Keewatin interflow rocks is rare but it is present as minute grains in massive pyrite, in pyrite nodules, and in massive chalcopyrite and pyrrhotite.

The results of electron microprobe analyses on marcasite from a few occurrences are given in Table 49; Ni, Cu, Zn, Sb, and Ag were looked for but not detected.

TABLE 49. CHEMICAL COMPOSITIONS OF SOME MARCASITES

Sample	Mode of occurrence	Chemical composition wt %				
		Fe	Co	As	S	Total
89	intergrown with pyrite	46.50	nd	nd	53.52	100.04
132	in veinlets	46.51	0–0.3	0–0.29	53.57	100.08
141	in veinlets	45.97	nd	nd	52.57	98.54
580	in veinlets	46.98	0–0.07	nd	53.92	100.90
580	inclusions in galena	47.08	0–0.03	nd	54.56	101.64
329	sooty textured (Pyrite-marcasite intergrowth)	43.8	1.6	3.0	48.5	96.9
FeS_2 (theor.)		46.5	—	—	53.5	100.0

nd = not detected.

Bravoite $[(Co,Ni,Fe)S_2]$

The mineral name bravoite, as used in this paper, follows the usage proposed by Kerr (1945) and adopted by Springer *et al.* (1964). According to this usage, bravoite is the intermediate member in the FeS_2-NiS_2-CoS_2 system. Bravoite in the Cobalt-Gowganda ores was found in a cross vein in the Silverfields mine on the third level about 50 feet east of ore vein No. 2, and in the Langis mine, in a pocket of sulphides several hundred feet from silver ore in vein No. 30.

The cross vein in the Silverfields mine consists of layers that can be classified as outside, intermediate, and central. The outside layer (adjacent to the wall rock) contains disseminated pyrite in calcite, the intermediate one contains large grains of concentrically zoned pyrite surrounded by marcasite, and the central layer contains an unusual dendritic pattern composed of sphalerite in calcite (Fig. 90). Bravoite occurs in the intermediate layers as cores of the concentrically zoned pyrite (Fig. 157). These cores are up to 200 microns in size and the bravoite generally contains minute grains of chalcopyrite and sphalerite. A microprobe scan across the concentrically zoned grain shows that the core bravoite and the pyrite layer surrounding the bravoite contain some arsenic (Fig. 158). The composition of this bravoite, given in Table 50, is equivalent to $Co_{0.62}Ni_{0.19}$-$Fe_{0.20}As_{0.15}S_{1.84}$.

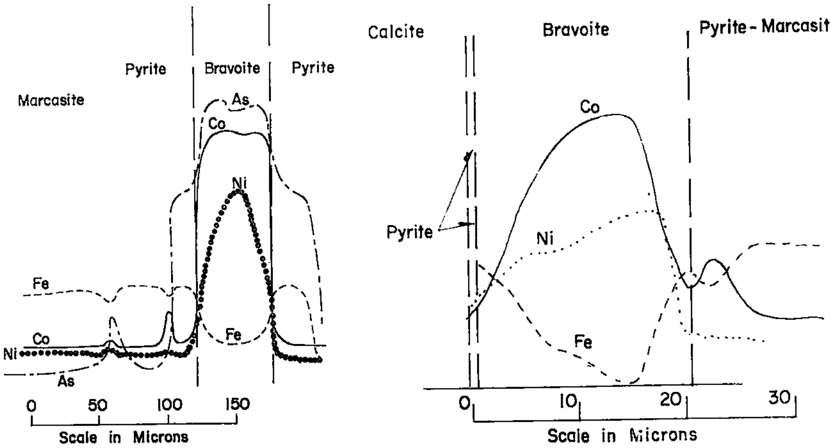


FIG. 158. Electron microprobe scans (left) for cobalt (Co), nickel (Ni), iron (Fe), and arsenic (As) across the bravoite in the concentrically-zoned grains (sample 365) (Fig. 157) ; and (right) bravoite in layers outside the pyrite-marcasite intergrowth (sample 329) (Fig. 159).

The bravoite in the Langis mine is present as zoned coatings on pyrite-marcasite and arsenide grains (Fig. 159) and as veinlets in these grains. A scan by means of the electron microprobe across a zoned coating from the marcasite-pyrite intergrowth towards the outer edge shows that the zoned bravoite is a cobalt-rich variety, but is it successively enriched in iron towards the outer layer, with the outer layer being pyrite (Fig. 158). Analyses of the cobalt-rich bravoite in two areas give compositions equivalent to $Co_{0.76}Ni_{0.22}Fe_{0.02}S_{1.86}$ and $Co_{0.76}Ni_{0.13}Fe_{0.11}S_{1.81}$.

Pyrrhotite ($Fe_{1-x}S$)

Pyrrhotite was found in the mineralized Keewatin interflow rocks, in the wall rock, and in carbonate veins beyond zones of arsenide mineralization. That in the mineralized Keewatin interflow rocks is present as masses and as intergrowths with chalcopyrite, sphalerite, and galena, and smythite. The pyrrhotite in the wall rock is present as disseminated grains and as a constituent of sulphide pebbles in Huronian sediments. That in pebbles in conglomerate is intergrown with chalcopyrite and sphalerite.

TABLE 50. CHEMICAL COMPOSITIONS OF BRAVOITE

Sample	Chemical composition (wt %)					
	Co	Ni	Fe	S	As	Total
Silverfields Mine Sample #365	27.9	8.4	8.5	44.9	8.5	98.2
Langis Mine Sample #329						
Area I	37.3	10.7	1.0	49.8	—	98.0
Area II	37.3	6.4	5.4	48.6	—	97.7

TABLE 51. CHEMICAL COMPOSITIONS OF SOME PYRRHOTITES

Sample	Mode of occurrence	Chemical compositions (wt %)				Atomic proportions	
		Fe	Ni	S	Total	Fe	S
433	Keewatin interflow	59.4	nd	40.2	99.6	0.85	1.0
M9661	Pyrrhotite lath	60.1	nd	40.1	100.2	0.86	1.0
372	Keewatin interflow	60.5	0.1	39.9	100.5	0.87	1.0

nd = not detected.

The pyrrhotite in veins is present as irregular grains intergrown with chalcopyrite, sphalerite, galena, tetrahedrite, stephanite, silver, and marcasite and as prismatic crystals in stephanite, pyrargyrite, and chalcopyrite. The prismatic crystals have been partly replaced by marcasite (Fig. 146).

Pyrrhotite from various occurrences was etched with HI and studied by *x*-ray diffraction to determine whether it is hexagonal or monoclinic. The results show that pyrrhotite occurring in massive sulphides is hexagonal and that present as small separate grains is monoclinic. The chemical compositions and atomic proportions of the pyrrhotite in two samples is given in Table 51.

Smythite (Fe_3S_4)

Smythite was found in the Silverfields mine, by the author in Keewatin interflow rocks on the fifth level at the west end of vein No. 1 (drift 501), and by Taylor (1968b) in a horizontal cross vein. The smythite in Keewatin interflow rocks occurs as disseminated grains associated with pyrrhotite, sphalerite, chalcopyrite, and galena. Some of the grains contain irregular and flame-like pyrrhotite (Fig. 160), and some are intergrown with pyrrhotite. Electron microprobe analyses on this smythite give compositions of Fe 58.6%, S 41.5%, and Ni 0.1% (Total 100.2%), which is equivalent to $Fe_{3.25}S_{4.00}$.

Taylor reported that the smythite in horizontal cross veins occurs in two distinct mineral assemblages. In one assemblage, it is associated with pyrite, marcasite and sphalerite and, in the other, it is associated with

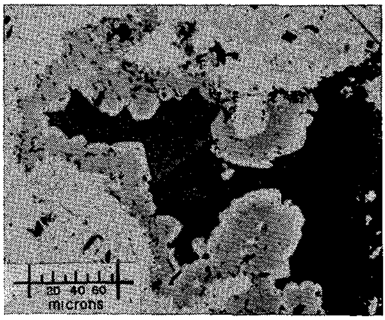


FIG. 159. A coating of layered bravoite (grey) on arsenides (white). A cobalt-rich bravoite (dark grey) is next to the arsenides, and an iron-rich one (light grey) borders it. (Langis mine, sample 329).

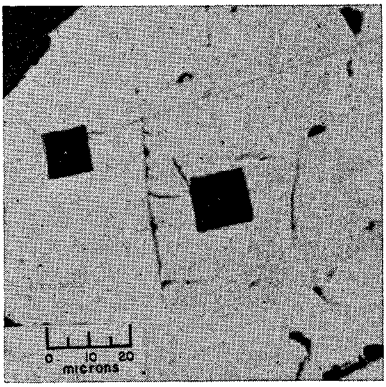


FIG. 160. A smythite grain (light grey) with pyrrhotite at the core (Silverfields mine, sample 372).

galena, chalcopyrite, monoclinic pyrrhotite, and sphalerite. Detailed characteristics on the smythite in these assemblages were reported by Taylor (1970). It is to be noted that the horizontal veins in the Silverfields mine offset the ore veins and hence are late veins. They may, therefore, contain remobilized sulphides. Taylor (1970) reports that smythite is stable only below 75°C.

Molybdenite (MoS_2)

Trace amounts of molybdenite were found in minor subsidiary veins, in late calcite veins, and in the wall rock up to several inches from ore veins. The molybdenite is present as separate crystals and small bundles of crystals, transecting other ore minerals.

Parkerite ($Ni_3Bi_2S_2$)

Parkerite was found in Vein 30, several hundred feet beyond an ore zone in the Langis mine, as reported by Petruk *et al.* (1969). It occurs as a component of sulphide grains with arsenides. The parkerite in the sulphide grains is associated with bismuthinite, native bismuth, cobalt pentlandite, and siegenite. It generally surrounds native bismuth and is intergrown with bismuthinite (Fig. 116). Electron microprobe analyses show that the parkerite composition is equivalent to $Ni_{3.2}Bi_{1.8}S_{1.9}$ which indicates that it is the bismuth end-member of the $Ni_3Bi_2S_2$-$Ni_3(Bi,Pb)_2S$

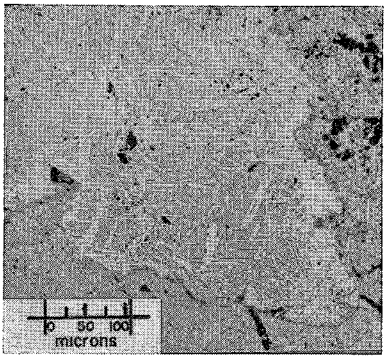


Fig. 161. A cobalt pentlandite-siegenite grain in cryptocrystalline pyrite-marcasite. The cobalt pentlandite (white) is present as lamellae in siegenite (light grey). The cobalt pentlandite-siegenite is partly bordered by a thin rim of bravoite (dark grey). (Langis mine, sample 329).

series. Parkerite is an orthorhombic mineral; and x-ray diffraction studies show that the unit cell parameters of the parkerite in the Langis mine are $a = 4.01$ Å, $b = 5.41$ Å, and $c = 5.75$ Å.

Cobalt pentlandite (Co_9S_8)

Cobalt pentlandite, the cobalt analogue of pentlandite, was found in the Langis mine in Vein 30 and reported by Petruk *et al.* (1969). The mineral occurs in arsenides, sulphides, and the pyrite-marcasite intergrowth. That in the arsenides and sulphides is present as veinlets and irregular grains either adjacent to or surrounding parkerite, bismuthinite, and native bismuth and it is intergrown with siegenite (Fig. 116). That in the pyrite-marcasite intergrowths is present as veinlets and as irregular grains composed of cobalt pentlandite-siegenite intergrowths (Fig. 161).

Electron microprobe analyses show that the composition of this cobalt pentlandite is equivalent to $Co_{6.9}Ni_{1.3}S_{8.0}$. X-ray diffraction studies show that its cell size is 9.94 Å.

Linnaeite series [$(Co,Ni)_3S_4$]

Minerals of the linnaeite series are present in late veins in the Cobalt-Gowganda ores and most of those studied have the x-ray diffraction pattern of violarite. That in one sample, however, has a slightly different x-ray diffraction pattern. Its composition, determined with the electron microprobe, is equivalent to $Co_{1.63}Ni_{1.17}S_4$, which corresponds to that of siegenite according to the classification given by Vokes (1967). This siegenite occurs in Vein 30 in the Langis mine and is associated with cobalt pentlandite. The composition of violarite was not determined.

Samsonite ($Ag_4MnSb_2S_6$)

Samsonite was found in samples from a mine in the New Lake basin in the Cobalt area by P. Ramdohr (personal communication), but was not found in this study. Manganese is a common constituent of the carbonates, hence it is reasonable to expect manganese-bearing sulphides in the ore.

DISCUSSION

The information obtained on mineral characteristics, distributions, textural relations, and assemblages provides a basis for interpreting and determining the paragenetic sequence, the nature of the ore carrier, and the depositional conditions of the minerals. The generalized paragenetic sequence for the sulphide minerals in veins is given in Fig. 162. This sequence is divided into stages because different modes of occurrence and mineral associations can be recognized and correlated with the depositional sequence. Minerals of the first and second stages occur largely in the ore and carbonate veins as separate grains, veinlets, and as replacements of carbonate minerals, arsenides, silver, and rock-forming minerals (Figs. 129, 134, 145, 150, 64, 86, and 87). The most abundant first-stage minerals are copper-bearing varieties, whereas the most abundant second-stage ones are silver-bearing. Minerals of the third stage occur in late veins that offset ore veins, in narrow calcite veins that occur at the boundary between the ore veins and wall rock (Fig. 48), and, to a small extent as replacement in ore veins. Those minerals are present as parellel veinlets in calcite and as massive sulphides (Fig. 88, 89, and 156). The fourth-stage minerals were found only in small samples from museum collections. Most of them are copper- and/or silver-bearing varieties that are stable only at low temperatures.

The nature of the ore carrier can be interpreted from the mineral varieties in the ore. The elements contained in the sulphide minerals in the Cobalt-Gowganda ores are S, Fe, Cu, Ag, Zn, Pb, Sb, Bi, Ni, Co, As, and Mo, hence it is assumed that these elements were present in the ore

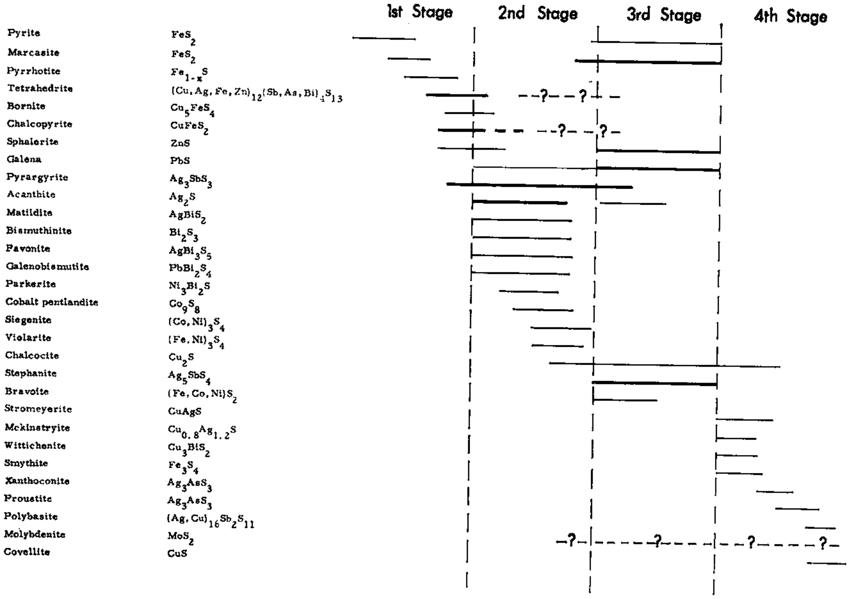


FIG. 162. Generalized paragenetic sequence for the sulphides in veins in the Cobalt-Gowganda ores. The most abundant minerals are indicated with heavy lines.

carrier. These elements could have been deposited as minerals from a multi-component ore carrier or they could have become localized at different places and deposited as minerals from localized ore carriers containing fewer components. The mineral assemblages in these ores are too complicated to permit a reliable interpretation of the nature of the ore carrier, but a few can provide some information. One of these is tetrahedrite, a mineral that can contain from three to ten elements in its structure. The tetrahedrite in these ores contains most of the elements (Table 42) assumed to have been present in the ore carrier, which indicates that, during the period of tetrahedrite deposition, the ore carrier behaved as a multi-component system.

Depositional conditions for the ore minerals from this multi-component solution can be interpreted by correlating mineral data with data on synthetic material and by making the assumption that deposition of minerals from multi-component systems is similar to growing synthetic materials from simple systems. The only mineral occurrence from the first stage that can be correlated with experimental data is a sample from the Foster mine consisting of chalcocite with exsolved galena (Fig. 142). Data on the Cu-Pb-S system (Fig. 141 and Craig & Kullerud 1968) suggest that this occurrence could represent phase A of Craig & Kullerud (1968), which is stable between 486° and 523°C.

Depositional temperatures for minerals interpreted as second stage can be inferred from the following observations : firstly, Ag_2S crystallizes as isometric argentite crystals above 176.7°C, but below this temperature it inverts to monoclinic acanthite, although its crystal form may be preserved. The presence of isometric acanthite crystals in the ore veins indicates that the Ag_2S was deposited at some temperature above 176.7°C ; secondly, the silver pyrargyrite-acanthite assemblage suggests a temperature of formation between 200°C and 400°C, since studies of the synthetic system (Keighin & Honea 1969) show that the assemblage silver–argentite–pyrargyrite can exist between these temperatures ; thirdly, the occurrence of galena–matildite exsolutions can be correlated with information on the Ag-Pb-Bi-S system (Craig 1967) which shows that galena and matildite exsolve from a PbS-$AgBiS_2$ solid solution below 215°C. These three occurrences indicate that the second-stage minerals were deposited at some temperature above 215°C and probably below 400°C.

Stephanite-pyrargyrite is the only stage-three mineral pair that provides information on depositional conditions. Stephanite is stable below 197°C and can be deposited with pyrargyrite at this temperature. At lower temperatures, it would probably be deposited with pyrostilpnite (Fig. 147). This suggests that the mineral pair stephanite-pyrargyrite was deposited at some temperature near 197°C. The stephanite generally occurs in late veins in association with stage-three minerals, therefore it is inferred that the rest of the stage-three minerals were also deposited under the same conditions. Because no pre-existing phases were recognized in these veins, it is interpreted that the stage-three minerals were deposited directly from an ore solution rather than by replacement of earlier minerals. It is noted that in some places stephanite extends from the late veins into the ore veins and surrounds early minerals, as in Figure 134. In other places stephanite is present in the main ore veins as a constituent of sulphide masses composed of sphalerite, galena, pyrargyrite, and stephanite. This shows that locally the main ore veins may contain some stage-three minerals, probably introduced from late-stage veins.

Four occurrences that can be correlated with data on synthetic materials were either found or reported for the fourth-stage minerals. These occurrences include the minerals smythite, mckinstryite, stromeyerite, and stromeyerite intergrown with chalcocite. Smythite is stable below about 75°C (Taylor 1970), mckinstryite below 94.4°C (Skinner *et al.* 1966), stromeyerite below 93.3°C (Skinner 1966), and stromeyerite-chalcocite intergrowths below 67°C (Fig. 140). The textures formed by the chalcocite and stromeyerite in the chalcocite-stromeyerite intergrowth (Figs. 133, 137, and 138) are similar to exsolution textures described by Brett (1964), and the stromeyerite in this intergrowth has two distinct grain sizes. This suggests that the chalcocite-stromeyerite intergrowth was formed by a breakdown of a higher temperature phase; this could imply that fourth-stage minerals are final phases of mineral assemblages formed at higher temperatures. Any such high-temperature mineral assemblages would have re-equilibrated during cooling to form the low temperature minerals. It is possible, however, that the fourth-stage minerals were deposited directly at some temperature below 100°C.

It is interpreted that the minerals xanthoconite, proustite, and polybasite-pearceite (222) were deposited as a result of late circulating ground waters and in this respect are secondary. In addition, some minerals are present in the zone of oxidation; these include acanthite, erythrite, and annabergite and others (page 370). The acanthite is presently being deposited in ores exposed to mine gases, and is locally referred to as silver leach. The erythrite and annabergite occur in open faults and old mine workings where cobalt and nickel arsenides are exposed. Most of the sulphide minerals in the wall rock have the characteristic properties of those in the ore veins and appear to be disseminated outward from the ore veins. This suggests that at least some of them are genetically related to the ore sulphides. Disseminated pyrite in Keewatin volcanic rocks, however, appears to be related to the host rock, and stratified galena and sphalerite in a bedded Huronian sediment found in the Silverfields mine (Fig. 152) appear to be unrelated to the ore vein sulphides.

The minerals in the mineralized Keewatin interflow rocks, including chalcopyrite, sphalerite, galena, pyrrhotite, and pyrite have similar characteristics to those of stratiform base-metal deposits in volcanic rocks. Smythite was also found in the Keewatin interflow rocks, as intergrowths with pyrrhotite, but its relationship to the host rock and nearby ore veins is not apparent.