

CHARACTERISTICS OF THE ARSENIDES, SULPHARSENIDES, AND ANTIMONIDES

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ABSTRACT

Arsenides, sulpharsenides and antimonides are the main ore minerals in the Cobalt-Gowganda ores. The varieties present are nickeline, langisite, maucherite, safflorite, loellingite, rammelsbergite, pararammelsbergite, skutterudite, cobaltite, gersdorffite, arsenopyrite, glaucodot, alloclasite, breithauptite and ullmannite. Some of these minerals have large compositional variations, some have moderate, and others have small variations. The minerals with large compositional variations are safflorite cobaltite, nickeline, and gersdorffite. The variations correlate with the varieties of associated minerals and/or modes of occurrence as follows: 1) Safflorite and cobaltite, associated with nickel arsenides particularly at the cores of arsenide rosettes, are enriched in nickel, 2) Safflorite associated with iron arsenides, particularly in the outer parts of arsenide rosettes, is enriched in iron, 3) Nickeline associated with breithauptite contains up to 6.5% antimony, 4) A gersdorffite associated with rammelsbergite contains up to 61.5% arsenic. Minerals having moderate compositional variations are rammelsbergite, skutterudite, glaucodot, and alloclasite. These variations do not appear to correlate with any characteristics of the ore deposits. Pararammelsbergite and arsenopyrite have small compositional variations. The pararammelsbergite is recrystallized and therefore its composition has probably been homogenized. Arsenopyrite is the last arsenide to have been deposited in these ores, probably under conditions where it has a very narrow stability field.

INTRODUCTION

Arsenides, sulpharsenides and antimonides of cobalt, nickel and iron are the most abundant minerals in the Cobalt-Gowganda ores. The minerals present are grouped as monoarsenides, a metal-rich arsenide, diarsenides, triarsenides, sulpharsenides and antimonides. The characteristics of these minerals, which were determined by studying polished sections of approximately 1,000 samples, are described in this paper. The methods of study included ore microscopy, x-ray diffraction, electron microprobe analyses, reflectance measurements, and microhardness determinations. W. Petruk conducted the study and did the ore microscopy, D. C. Harris conducted the microprobe analyses, and J. M. Stewart provided the x-ray diffraction data.

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MONOARSENIDES

Nickeline (NiAs)

Nickeline is a common mineral in the Ni-As and Ni-Co-As assemblages (pages 111 and 113), and trace amounts are also present in the Co-As assemblage and wall rock. In the Ni-As assemblage, nickeline occurs in massive arsenides, in botryoidal arsenide bodies, in arsenide rosettes, in layered arsenides, and in arsenide veinlets. Nickeline in the massive arsenides is present as masses with small amounts of cobaltite and breithauptite, and as irregular grains intergrown with other nickel and cobalt arsenides. The nickeline masses vary from a few inches to several feet in size and generally occur at the ends of ore veins. Nickeline, in the botryoidal arsenide bodies, is present in concentric nickeline and nickeline-rammelsbergite layers (Fig. 49). That is arsenide rosettes occurs as irregular grains at the cores and is surrounded by rammelsbergite (Fig. 50), whereas that in layered arsenides occurs in layers that are parallel and adjacent to the wall rock (Fig. 52). The nickeline in veinlets emanates from irregular grains of nickeline, and is interpreted as representing a remobilized phase.

The nickeline in the Ni-Co-As assemblage occurs as irregular grains at the cores of rosettes (Fig. 54) and as veinlets emanating from the irregular grains (Fig. 115) * It contains inclusions of cobaltite and is intergrown with breithauptite, silver, parammelsbergite, and other arsenides.

The nickeline in the Co-As assemblage and wall rock is present as veinlets and disseminated grains. Some veinlets are monomineralic and others consist of nickeline, cobaltite, parammelsbergite, and gersdorffite.

Chemical compositions of nickeline, in 16 samples determined by means of the electron microprobe by using analysed nickeline as a standard, are given in Table 19. The results show that the nickeline contains up to 6.5 wt.% antimony, 3.9 wt.% cobalt, and 0.7 wt.% iron. These values are in general agreement with those reported by Halls & Stumpfl (1969). Antimony in nickeline is highest in samples where breithauptite is present, and low to absent where breithauptite is absent. Yund (1961) correlated the d_{103} spacing with the arsenic content in synthetic nickeline in the Ni-As system, and this relationship was studied for the nickeline in Samples Nos. 686, 828, and M-12218 which do not contain antimony. The results suggest that the arsenic contents determined from d_{103} do not agree with analysed values (Table 19), but in fact they do agree within the limits of experimental accuracy. The d_{103} values for the nickeline in the other

* Page 183.

samples studied are also given in Table 19. The values were measured from 114.6 mm x -ray powder diffraction films corrected for shrinkage.

The x -ray powder diffraction pattern, reflectance spectrum, and microhardness data for the nickeline in Sample No. M-12218 were reported earlier by Petruk *et al.* (1969).

An application of the nickeline data to Yund's (1961) phase equilibrium diagram may provide some idea of the depositional temperature of the mineral. The nickeline in the massive arsenides and the botryoidal arsenide bodies in the Ni-As assemblage coexists with rammelsbergite and, to a small extent, with parammelsbergite. This indicates that it was deposited at temperatures at or above the rammelsbergite-parammelsbergite inversion temperature of approximately 590° C. The nickeline in

TABLE 19. COMPOSITIONS AND d_{103} VALUES FOR NICKELINE FROM THE COBALT-GOWGANDA ORES

Sample	Arsenide assemblage	Associated Ni arsenides	Chemical Compositions					Total	d_{103} Å	As Wt.% from d_{103}
			Ni	Co	Fe	As	Sb			
836	Ni-As	ramm.	45.5	0.7	nd	55.8	0.3	102.3	1.4782	
M11594	Ni-As	paramamm.	44.6	0.6	—	54.4	—		1.4782	
355	Ni-As	ramm. + paramamm.	42.3	0.6	nd	54.4	2.0	99.3	1.4788	
470	Ni-As	breith.	43.0	0.4	0.7	52.0	5.3	101.4	1.4789	
828	Ni-As	gersdor.	43.8	0.6	nd	55.9	nd	100.3	1.4772	56.8
686	Ni-As	paramamm.	44.0	0.4	—	56.0	nd	100.4	1.4770	56.8
M11764	Co-As	—	43.5	nd	—	53.5	—			
M11636	Ni-As	paramamm.	44.0	0.6	—	55.5	—		1.468	
M12218	Ni-As	paramamm.	45.1	0.2	0.1	57.1	nd	102.5	1.4770	56.8
9573	Ni-As	ramm.	44.7	nd	—	55.4	nd		1.4777	
9503	Ni-As	—	44.0	nd	—	56.0	—			
157	Ni-Co-As	paramamm.	43.5	nd	—	55.4	1.4	100.3	1.4788	
633	Ni-Co-As	—	43.1	nd	0.1	55.1	1.5	99.8		
687	Ni-Co-As	breith.	41.1	0.9	—	50.6	6.5	99.1	1.4819	
M 8922	Ni-Co-As	mauch. + breith.	40.6	3.2	—	54.1	4.3	102.2		
M 8700	Ni-Co-As	mauch. + breith.	39.2	3.9	—	53.3	3.2	99.6	1.4845	

nd = not detected ; — not analysed

the Ni-Co-As assemblage, the next assemblage in the depositional sequence of the Cobalt-Gowganda ores, and the nickeline in veinlets in the Co-As assemblage and wall rock, coexist with pararammelsbergite. This indicates that the nickeline in these parts of the veins was deposited at temperatures below the inversion temperature. The Ni-As phase equilibrium diagram given by Yund (1961) also shows that, at higher temperatures, nickeline exhibits at slight compositional range, depending upon its depositional temperature and whether it coexists with maucherite or nickel diarsenides. This variation, however, is less than the limits of accuracy of the electron microprobe, and therefore cannot be used as a geothermometer in this study.

Langisite ($\text{Co}_{0.8}\text{Ni}_{0.2}\text{As}$)

Langisite, first described by Petruk *et al.* (1969), is the cobalt end-member of the solid-solution series $\text{NiAs-Co}_{0.8}\text{Ni}_{0.2}\text{As}$ (Heyding & Calvert 1957). It was found in mineralized pockets up to several inches in size in Vein No. 30, a fault vein in the Langis mine, at about 200 to 300 feet beyond a high-grade orebody. The mineral occurs as veinlets, as irregular grains, and as lamellae in safflorite, and is associated with a variety of bismuth and cobalt sulphides (Fig. 116*). The composition of the langisite in the samples studied is equivalent to $\text{Co}_{0.81}\text{Ni}_{0.15}\text{As}_{1.00}$. Its x-ray powder diffraction pattern is similar to that of nickeline (NiAs), and its cell parameters, computed from the powder pattern, are $a = 3.538 \text{ \AA}$ and $c = 5.127 \text{ \AA}$. Its x-ray powder diffraction pattern, reflectivity spectrum, and microhardness data were reported by Petruk *et al.* (1969).

METAL-RICH ARSENIDES

Maucherite ($\text{Ni}_{11}\text{As}_8$)

Maucherite was found in a few samples from the Cobalt area and the Langis mine in Casey township. In addition, it was reported as temiskamite in samples from the Moose Horn mine in the Elk Lake area (Walker 1914) and the Coleroy mine in the Gowganda area (Todd 1926). Maucherite in the Cobalt area occurs in samples that contain large amounts of nickeline, breithauptite, and silver in the Ni-Co-As assemblage and coexists with these minerals. The maucherite in the Langis mine is present in the mineralized pockets that contain langisite, and occurs as disseminated grains in calcite, and in complex grains where it is surrounded by cobaltite

* Page 183.

and safflorite. The maucherite from the Moose Horn mine is reported to occur as radiating fibres covered with nickeline, and that in the Coleroy mine is reported to contain nickeline veinlets. The composition of maucherite in Sample No. M-8922 from the Seneca Superior mine in the Cobalt area, determined by means of the electron microprobe (Table 20), is equivalent to $\text{Ni}_{9.72}\text{Co}_{0.81}\text{As}_{7.97}\text{Sb}_{0.03}$, and the composition reported by Walker (1914) for material from the Moose Horn mine is equivalent to $\text{Ni}_{10.27}\text{Co}_{0.36}\text{As}_{7.60}\text{S}_{0.40}$. The cell parameters of the maucherite in Sample No. M-8922, computed from powder diffraction data, are $a = 6.857 \pm .005 \text{ \AA}$ and $c = 21.67 \pm .01 \text{ \AA}$. The maucherite in Sample No. M-8922 coexists with the nickeline and breithauptite reported in Table 36.

DIARSENIDES

The diarsenides in the Cobalt-Gowganda ores are safflorite, loellingite, rammelsbergite, and pararammelsbergite. The term safflorite, as used in this paper, refers largely to the CoAs_2 - FeAs_2 solid-solution series but it also includes some of the NiAs_2 component. The term loellingite refers to FeAs_2 with small amounts of $(\text{Co},\text{Ni})\text{As}_2$ in solid solution. Pararammelsbergite is the low-temperature form of rammelsbergite (Yund 1961). This terminology is largely in keeping with previous usage (Berry & Thompson 1962, Holmes 1947, and Radcliffe & Berry 1968).

Safflorite $(\text{Co},\text{Fe},\text{Ni})\text{As}_2$

Safflorite is orthorhombic and isostructural with loellingite and rammelsbergite, iron and nickel readily substitute for cobalt (Roseboom 1963). These substitutions cause changes in the unit-cell parameters and shifting

TABLE 20. CHEMICAL COMPOSITION OF MAUCHERITE

Element	Sample M8922 Seneca Superior Mine, Cobalt, Wt. %	Reported by Walker (1914) Moose Horn Mine, Elk Lake, Wt. %	$\text{Ni}_{11}\text{As}_8$ (theor.)
Ni	46.9	49.07	51.86
Co	3.9	1.73	—
As	49.0	46.34	48.14
Sb	0.3	—	—
S	—	1.03	—
Total	100.1	98.17	100.00

of the diffraction lines, thereby producing a series of different x-ray diffraction patterns. Berry & Thompson (1962) classified safflorite into 5 types on the basis of these apparently different x-ray diffraction patterns, and Radcliffe & Berry (1968) gave the compositional ranges for each type (Fig. 100). This subdivision will not be used in this study, although it is referred to in a few places to indicate approximate compositions.

Safflorite is the most common arsenide in the Cobalt-Gowganda ores, but most of it contains small inclusions of cobaltite, skutterudite, and arsenopyrite. The safflorite occurs as a constituent of arsenide rosettes, masses, and botryoidal bodies, and as irregular, euhedral, and stellate grains in carbonate (Fig. 69). That in rosettes generally occurs as prismatic crystals oriented radially around cores and cruciform grains, and as large euhedral and small irregular grains at the cores (Figs. 63, 66, and 70). The safflorite in the arsenide masses and botryoidal bodies is present as irregular grains.

Complete and partial compositions of the safflorites in the Cobalt-Gowganda ores were obtained by means of the electron microprobe, using synthetic and natural minerals as standards. Complete analyses and recalculated atomic proportions for 9 safflorites and 1 loellingite are given in Table 21. These analyses show that the Cobalt area safflorites have the following properties :

- (1) The metal : non-metal varies from 1.05 : 2 to 1.12 : 2.

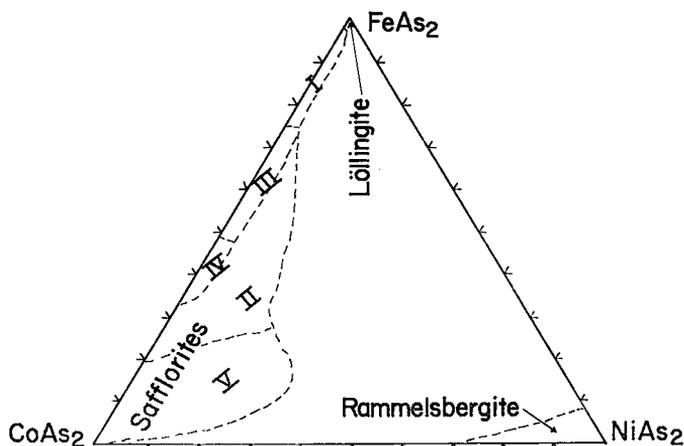


FIG. 100. CoAs_2 - FeAs_2 - NiAs_2 ternary diagram showing known compositional fields of safflorites I-V and rammelsbergite (adapted from Radcliffe & Berry 1968).

(2) They contain up to 3.0 weight per cent sulphur, apparently substituting for arsenic in the anion lattice sites.

(3) They contain variable amounts of cobalt, iron and nickel.

(4) Some analyses, not included in Table 21, reported up to 3% antimony.

Details of the variations of cobalt, iron and nickel were determined by spot analyses for these elements. Analyses where the sum of Co + Fe + Ni varied between 28 and 32 weight per cent were considered as reliable analyses for safflorite, whereas those with higher and lower sums were

TABLE 21. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF SAFFLORITE-LOELLINGITES FROM THE COBALT-GOWGANDA REGION

Sample	Compositions in weight per cent					Total
	Fe	Co	Ni	As	S	
2603	28.0	0.0	0.8	72.0	0.0	100.8
2603	20.7	7.9	0.8	68.5	1.8	99.7
145	15.7	3.2	10.8	70.1	0.4	100.2
9570	11.0	17.5	1.5	68.0	1.3	99.3
145	10.8	7.3	10.8	70.1	0.4	99.4
511	6.7	22.5	1.0	68.8	2.0	101.0
145	5.5	15.3	8.7	69.6	1.2	100.3
145	5.5	21.5	2.9	69.6	1.2	100.7
9573	5.0	23.1	3.6	66.0	3.0	100.7
468	3.9	23.6	1.5	66.5	1.4	96.9

ATOMIC PROPORTIONS *

Sample	Fe	Co	Ni	Fe + Co + Ni	As	S	As + S
2603	1.04	0.00	0.03	1.07	2.00	0.00	2.00
2603	0.77	0.28	0.03	1.08	1.88	0.12	2.00
145	0.59	0.11	0.39	1.09	1.97	0.03	2.00
9570	0.42	0.63	0.05	1.10	1.91	0.09	2.00
145	0.41	0.26	0.39	1.06	1.97	0.03	2.00
511	0.25	0.78	0.03	1.06	1.87	0.13	2.00
145	0.20	0.54	0.31	1.05	1.92	0.08	2.00
145	0.20	0.76	0.10	1.06	1.92	0.08	2.00
9573	0.18	0.81	0.13	1.12	1.81	0.19	2.00
468	0.15	0.86	0.05	1.06	1.91	0.09	2.00

* Calculated on the basis of As + S = 2.00

considered to be mixtures with cobaltite and skutterudite, respectively. This was confirmed in a few instances by *x*-ray diffraction. A total of 910 spot analyses were made on safflorite in 34 samples of the Cobalt-Gowganda ores. The 34 samples used were selected from about 1,000 samples taken from 59 mines in the Cobalt, Gowganda, South Lorrain township, and Langis Mine areas, and are considered to be representative of the Cobalt-Gowganda ores as a whole. The results, recalculated to mole per cent $\text{CoAs}_2 : \text{FeAs}_2 : \text{NiAs}_2$, were plotted on a CoAs_2 - FeAs_2 - NiAs_2 ternary diagram and contoured on the basis of percentage of analysed safflorites (Fig. 101). Figure 101 shows that the compositions of the safflorites in the Cobalt-Gowganda ores include the safflorites I to V of Berry & Thompson (1962), but that the compositional field extends beyond the limits given by Radcliffe & Berry (1968). Figure 101 also includes data obtained from 80 spots analyses for loellingite and 12 analyses for rammelsbergite.

The composition of safflorite in specific samples bears some relation to the arsenide assemblage from which the sample was taken. Thus safflorite becomes progressively richer in iron, and lower in nickel and cobalt through the sequence of assemblages NiCoAs — CoFeAs (Fig. 102).

Safflorite compositions in specific grains are variable from spot to spot, but this variation falls within specific limits for each grain. Furthermore,

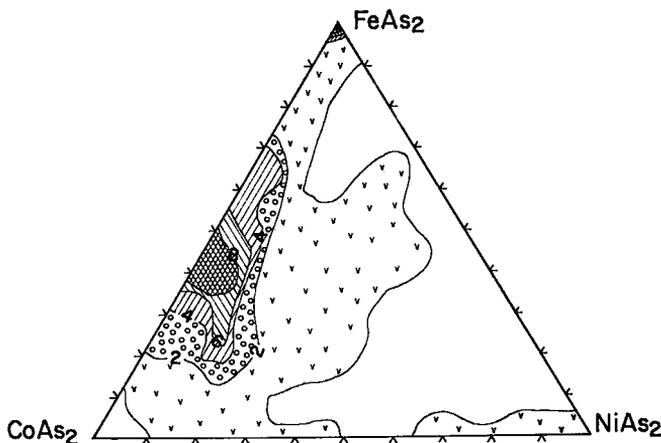


FIG. 101. Compositional ranges of the diarsenides in the Cobalt-Gowganda ores as determined from 1,002 spot analyses for Co, Ni and Fe. The analyses were plotted as points, and the numbers of points per equal area, expressed as a percentage of the total number of analyses, were contoured. The equal area was a triangle 1/100 the area of the ternary diagram. Every equal-area triangle within the field enclosed by the 8-level contour contained at least 80 points.

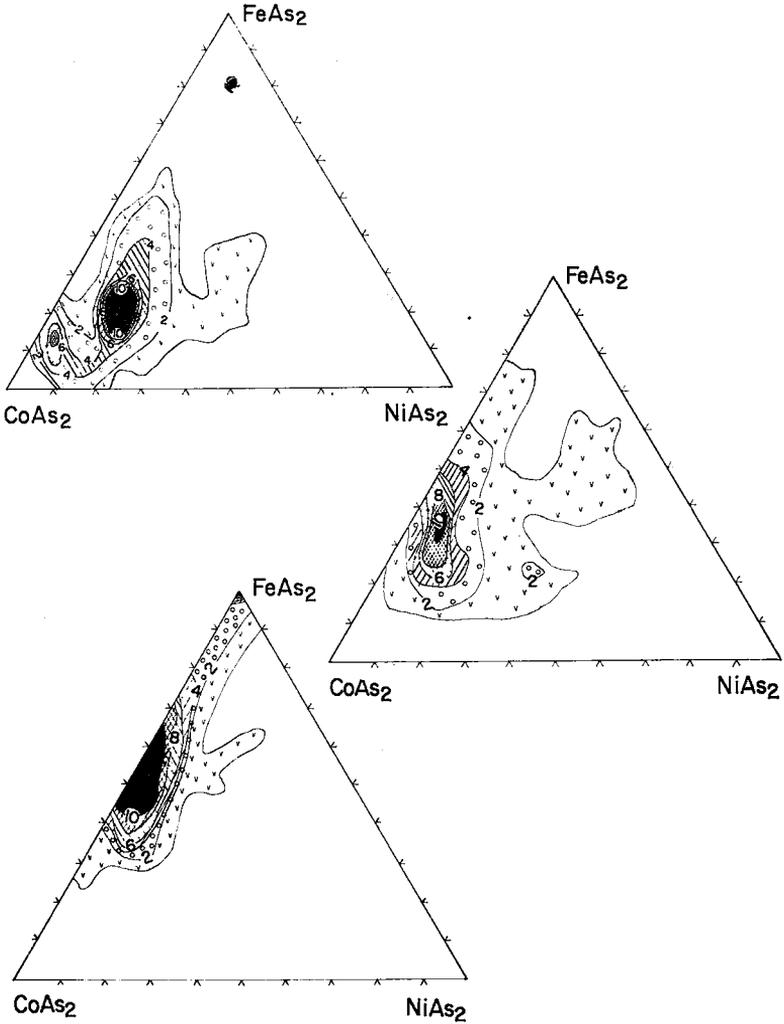


FIG. 102. Compositional ranges of safflorite in the Ni-Co-As assemblage (top), in the Co-As assemblage (middle), and in the Co-Fe-As assemblage (bottom), as determined from spot analyses for Co, Ni and Fe. The analyses were plotted as points, and the numbers of points per equal area, expressed as a percentage of the total number of analyses, were contoured. The equal area was a triangle 1/100 of the area of the ternary diagram.

this variation is generally the same for all grains in the same sample. Examples of such variations in safflorite from the core to the rim of rosettes for two samples from the Ni-Co-As assemblage are given in Figure 103; for four samples from the Co-As assemblage in Figure 104; and a representative sample from the Co-Fe-As assemblage in Figure 105. It is noted that safflorite in the inner parts of the rosettes is generally enriched in nickel. Safflorite at the outer edges of rosettes in the Ni-Co-As assemblage is generally enriched in iron and nickel, whereas in the Co-Fe-As assemblages it is enriched only in iron. The results on safflorite at the outer edges of rosettes in the Co-As assemblage show some characteristics similar to those from the other assemblages, and are in general agreement with those reported by Radcliffe & Berry (1968). In a few samples the safflorite at the cores and outermost parts of the rosettes has a composition that falls outside the limits reported by Radcliffe & Berry (1968).

Safflorites with two different compositions are associated with langisite in the Langis mine (Petruk *et al.* 1969). The main one, occurring in the outer parts of rosettes, is orthorhombic and has a composition of $\text{Co}_{0.91}\text{Ni}_{0.04}\text{As}_{2.00}$. The second one is separated from the main safflorite by langisite and occurs at the cores in association with an assemblage of late sulphides (Fig. 116). It has a variable composition with nickel increasing and cobalt decreasing towards the sulphides at the cores. Its mean composition is $\text{Co}_{0.51}\text{Ni}_{0.59}\text{As}_{2.00}$.

The safflorites in massive arsenides and botryoidal bodies also have variable compositions. The compositions vary randomly from spot to spot, but the variations stay within specific limits depending upon the assemblage from which the sample was taken.

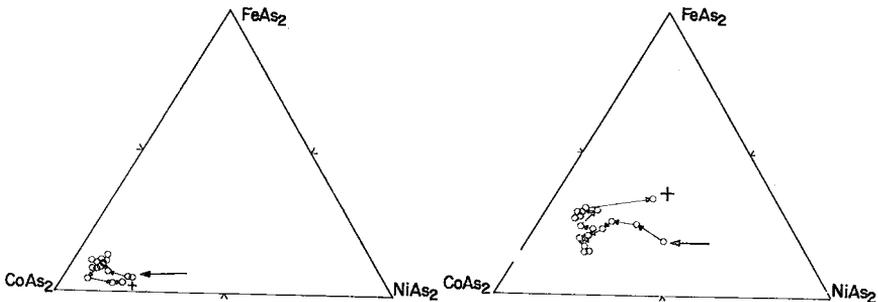


FIG. 103. Compositional variations of safflorite in rosettes in the Ni-Co-As assemblage, determined by step scan analyses at 10-micron intervals from the cores (large arrow) of arsenide rosettes to the outer layers (+). The variation in the diagram on the right is typical for this assemblage, and the left one is an example of another variation observed.

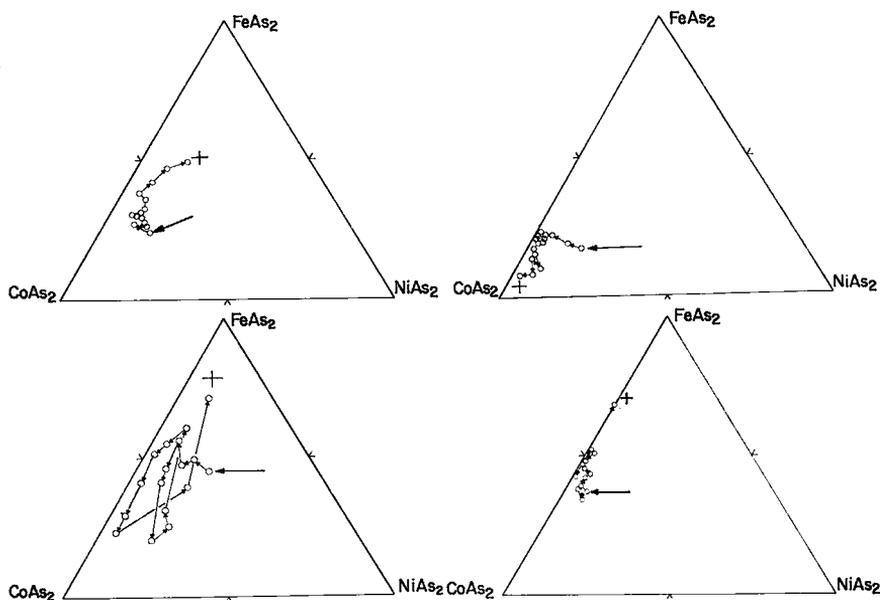


FIG. 104. Compositional variations of safflorites in rosettes in the Co-As assemblage determined by step scan analyses from the cores (large arrow) to the outer layers (+). The variation in the top left diagram is typical for this assemblage, the one in the right was obtained from safflorite surrounding dendritic silver, the one in the bottom left represents rhythmic deposition, and bottom right is for safflorite near the Co-Fe-As assemblage.

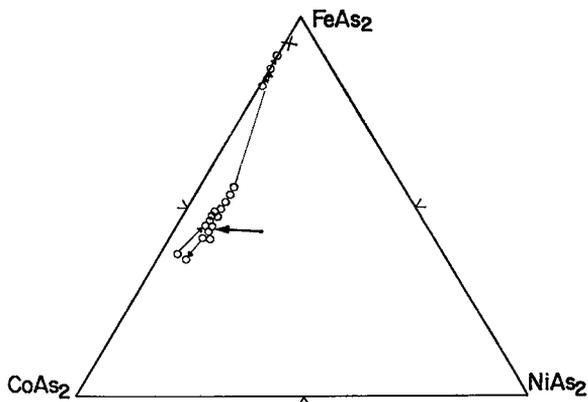


FIG. 105. Compositional variations of safflorite in arsenide rosettes in the Co-Fe-As assemblage determined by step scan analyses from the cores (large arrow) to the outer layers (+).

X-ray diffraction patterns were obtained for 7 samples of analysed diarsenides, and the d values of the lines corresponding to hkl values of 101, 120, 111 and 210 are given in Table 22. Roseboom (1963) correlated the d spacings of safflorite with compositions of the synthetic binary solid solutions. The writer combined Roseboom's data to a simple function by

means of the formula $f(d) = \frac{d_{101} + d_{111} - 4.000}{d_{120} + d_{210} - 4.000}$ and plotted the resulting

values as a series of lines on a CoAs_2 - FeAs_2 - NiAs_2 ternary diagram (Fig. 106). The diarsenides reported in Table 22 are plotted as points on this ternary diagram on the basis of atomic per cent $\text{CoAs}_2 : \text{FeAs}_2 : \text{NiAs}_2$, and the values for $f(d)$ are given beside each point (Fig. 106). The results show that there is a general correlation between the $\text{CoAs}_2 : \text{FeAs}_2 : \text{NiAs}_2$ ratios of naturally occurring safflorites and measured d spacings.

Reflectances were determined for some analysed safflorites, a loellingite from the Gowganda area (Sample 544), a rammelsbergite from Thuringia, East Germany (Royal Ontario Museum sample M-19708), and a para-

TABLE 22. CHEMICAL COMPOSITIONS, $\text{FeAs}_2 : \text{CoAs}_2 : \text{NiAs}_2$ RATIOS AND SPACINGS IN LOELLINGITE, SAFFLORITES AND RAMMELSBERGITE

Sample	Chemical compositions (Wt.%)			Arsenide ratios		
	Fe	Co	Ni	FeAs_2	CoAs_2	NiAs_2
2603	20.7-28.0	0.0-7.9	0.8	70-97	0-27	3
9570	11.0	17.5	1.5	37	58	5
1	6.0	21.0	3.0	20	70	10
4	4.0	26.0	2.0	12	82	6
9573	5.0	23.1	3.6	16	73	11
9573	0.9	6.6	24.5	3	20	77
355	0.0-2.2	2.0-7.8	22.1-29.0	0-8	7-24	68-93

Sample	d Spacings in Å				$f(d)$
	d_{101}	d_{120}	d_{111}	d_{210}	
2603	2.548	2.596	2.342	2.411	0.88
9570	2.610	2.554	2.354	2.389	1.03
1	2.626	2.554	2.393	2.360	1.11
4	2.665	2.543	2.429	2.326	1.26
9573	2.671	2.530	2.430	2.315	1.30
9573	2.803	2.474	2.519	2.209	1.94
355	2.790	2.480	2.510	2.230	1.83

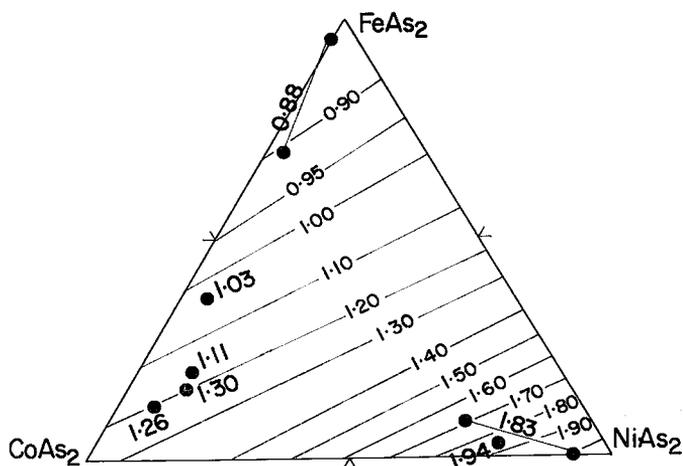


FIG. 106. Relationship between the function $f(d)$ and the compositions of diarsenides, as established from data reported by Roseboom (1963). The composition of analysed diarsenides are plotted as points with lines joining points representing variable compositions. The values for $f(d)$ of the analysed diarsenides are indicated beside each point.

rammelsbergite from the Silverfields mine. The values were determined for grains showing maximum bireflectance and the results are given in Table 23 as values from curves of best fit. The curves were obtained from readings taken at intervals of 20 nm from 440 to 660 nm inclusive. Exam-

TABLE 23. REFLECTANCES OF DIARSENIDES

Sample	Mineral	Cation proportions			Reflectivities in per cent *			
		Fe	Co	Ni	470 nm	546 nm	589 nm	650 nm
544	loellingite	100	0	0	min. 52.3	52.3	50.8	50.2
					max. 56.2	53.4	53.9	54.0
2603	safflorite	70	27	3	min. 54.0	54.9	53.5	52.8
					max. 58.5	54.9	55.1	55.8
9570	safflorite	37	58	5	min. 53.0	52.2	51.5	50.2
					max. 56.0	53.7	54.0	53.8
157	safflorite	8	80	12	min. 55.5	53.7	53.2	52.5
					max. 57.3	54.8	54.6	54.8
M19708	rammelsbergite	0	0	100	min. 56.3	55.7	56.0	57.0
					max. 60.3	60.0	60.0	60.0
157	pararammelsbergite	0	0	100	60.0	59.6	59.6	60.0

* The reflectivity represents points on a curve of best fit as obtained from readings taken at intervals of 20 nm from 440 to 660 nm inclusive. All values are within 1.5% of actual readings.

ples of spectra for loellingite, safflorite and rammelsbergite are given in Figure 107. It is noted that the spectra obtained from different orientations of grains of safflorite and loellingite cross, whereas those for rammelsbergite do not. Figure 107 suggests that there may be a greater difference between the maximum and minimum reflectivities for loellingite than for safflorite. This is only because the safflorite grains measured apparently were not in the ideal orientation to obtain maximum and minimum reflectivities, and studies on other samples indicate that the spectrum of safflorite is similar to that of loellingite. Hence randomly oriented grains of safflorite and loellingite cannot be differentiated on the basis of reflectance.

Clinosafflorite (CoAs_2)

Clinosafflorite is the monoclinic polymorph (Darmon & Wintenberger 1966). This mineral was first found by Radcliffe & Berry (1971) in three

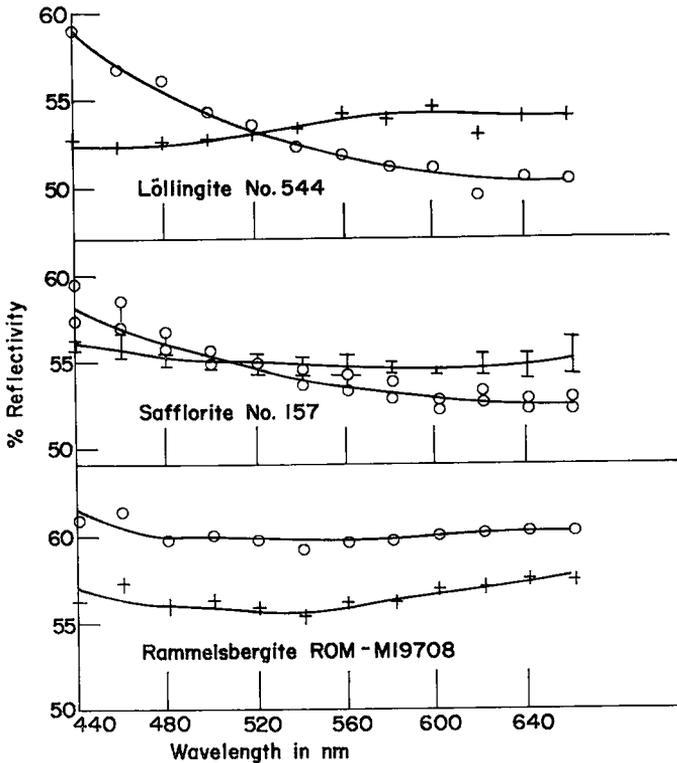


FIG. 107. Reflectivity spectra for loellingite (löllingite), safflorite and rammelsbergite.

specimens from the Cobalt area but was not found in this study. They report that the clinosafflorite is finely intergrown with skutterudite and that its composition varies from $\text{Co}_{0.70}\text{Fe}_{0.21}\text{Ni}_{0.09}\text{As}_2$ to $\text{Co}_{0.76}\text{Fe}_{0.14}\text{Ni}_{0.10}\text{As}_2$ which is equivalent to that of safflorite.

Loellingite (FeAs₂)

Loellingite is a common mineral in the Gowganda ores, but it occurs only in a few places in the Cobalt area. The local mine operators at Cobalt reported that one vein in the Lawson mine contained large amounts of loellingite, but the writer was unable to obtain a sample of this material. Loellingite at both Gowganda and Cobalt was found only in the Fe-As and Fe-Co-As assemblages where it occurs as outer layers on arsenide rosettes and safflorite grains, and as separate and stellate grains disseminated in carbonate. The stellate loellingite grains generally radiate outward from a core of safflorite.

Eighty-five spot analyses were made on loellingite in 4 samples. The results show that most of the loellingite has a composition near FeAs_2 , but that some contains variable amounts of cobalt and nickel in solid solution.

The x-ray diffraction properties and reflectivities of loellingite are included in the section under safflorite so that they can be readily compared to orthorhombic safflorite and rammelsbergite.

Rammelsbergite (NiAs₂)

Rammelsbergite was found only in the Ni-As assemblage where it occurs in arsenide rosettes and masses, and in botryoidal arsenide bodies. In the arsenide rosettes it occurs as prismatic crystals radially oriented around nickeline cores (Fig. 50), and as plumose-textured rammelsbergite at the cores (Fig. 51). The rammelsbergite in the arsenide masses is present as irregular grains intergrown with other arsenides, and in the botryoidal-arsenide bodies it is present as layers of rammelsbergite, rammelsbergite-nickeline and rammelsbergite-paramrammelsbergite (Fig. 49).

The compositions and atomic proportions for some rammelsbergites in different occurrences are given in Table 24. These analyses are in general agreement with those reported by Walker & Parsons (1921).

Table 24 shows that rammelsbergite contains variable amounts of sulphur, antimony, and cobalt. The plumose-textured rammelsbergite in Sample 511 appears to consist of an intergrowth of very minute grains having two compositions. One has low sulphur and cobalt, and the other has high sulphur and cobalt.

Pararammelsbergite ($NiAs_2$)

Pararammelsbergite was first found in samples from Cobalt and Elk Lake, Ontario, (Peacock & Mitchener 1939, and Peacock & Dadson 1940), and its textural relations were described in detail by Ramdohr (1948). The senior author confirmed Ramdohr's observations, thus only a summary is given here. Pararammelsbergite in the Cobalt-Gowganda ores occurs in the Ni-Co-As and Ni-As assemblages. In the Ni-Co-As assemblage it occurs at the cores of rosettes (Fig. 60), where it generally surrounds irregular grains of skutterudite and is intergrown with silver, and in a few places with nickeline. In the Ni-As assemblage, the pararammelsbergite occurs as large prismatic crystals (Fig. 117*), as veinlets, as masses, and as irregular grains intergrown with nickeline, safflorite, cobaltite, gersdorffite, skutterudite, and rammelsbergite. The prismatic crystals cut across all arsenides, hence they represent late crystallization or recrystallization. The veinlets cut other arsenides, and the masses contain small irregular grains

TABLE 24. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF SOME RAMMELSBERGITES IN THE COBALT-GOWGANDA ORES

Sample	Location	Type of occurrence	Chemical composition in wt. %						
			Fe	Co	Ni	As	Sb	S	Total
511	Siscoe mine	plumose texture	0.1	3.1	25.8	69.8	0.0	0.6	99.4
511	Siscoe mine	plumose texture	0.2	7.6	20.8	66.9	0.0	2.8	98.3
9573	Silverfields mine	prismatic crystals in rosettes	0.8	6.6	20.9	68.6	1.2	0.7	98.8
836	Langis mine	irregular grains in arsenide masses	0.0	2.6	29.5	69.0	—	1.0	102.1
355	Hi-Ho mine	irregular grains in arsenide masses	0.0	2.0	29.0	69.0	—	2.0	102.0

Sample	Atomic proportions *							
	Fe	Co	Ni	Co + Fe + Ni	As	Sb	S	As + S
511	0.00	0.11	0.93	1.04	1.96	0.00	0.04	2.00
511	0.01	0.26	0.72	0.99	1.82	0.00	0.18	2.00
9573	0.03	0.24	0.75	1.02	1.94	0.02	0.04	2.00
836	0.00	0.09	1.05	1.14	1.93	—	0.07	2.00
355	0.00	0.07	1.00	1.07	1.97	—	0.13	2.00

* Calculated on basis of $(As + Sb + S) = 2.00$

of safflorite, cobaltite, and gersdorffite. The intergrowths of parammelsbergite with other arsenides are variable and complex: intergrowths with nickeline generally occur in late nickeline-parammelsbergite veinlets: intergrowths with skutterudite form graphic intergrowths by replacement of skutterudite: and intergrowths with cobaltite generally contain gersdorffite at the parammelsbergite-cobaltite boundary, apparently as a reaction product. Intergrowths of parammelsbergite with rammelsbergite were indicated by x-ray diffraction studies of individual grains, but they were not observed in polished sections because the reflectivities of these minerals are so similar that the authors could not distinguish the individual minerals. The textures described above indicate that the parammelsbergite in the Ni-As assemblage is a late mineral, and that it was probably deposited after the Ni-As assemblage was formed. The parammelsbergite in the Ni-Co-As assemblage, on the other hand, is intergrown with

TABLE 25. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF SOME PARAMMELSBERGITES IN THE COBALT-GOWGANDA ORES

Sample	Mineral assemblage	Type of occurrence	Chemical compositions in wt. %						
			Fe	Co	Ni	As	Sb	S	Total
465	Ni-Co-As	core of rosettes	0.2	2.7	28.5	68.0	0.0	1.3	100.7
157	Ni-Co-As	core of rosettes	0.0	0.0	28.7	70.5	0.8	0.3	100.3
145	Ni-Co-As	core of rosettes	0.0	1.8	27.4	69.6	0.0	1.2	100.0
9503	Ni-As	euhedral crystal	0.0	0.7	29.0	70.0	0.4	1.1	101.2
p-1	Ni-As	massive	0.0	5.5	26.0	69.0	0.0	1.5	102.0
429	Ni-As	massive	0.7	1.7	28.0	71.0	0.0	0.6	102.0
M11636	Ni-As	massive with skutterudite	0.0	2.2	29.1	69.0	0.0	0.5	100.9

Sample	Atomic proportions *							
	Fe	Co	Ni	Fe + Co + Ni	As	Sb	S	As + Sb + S
465	0.01	0.10	1.02	1.13	1.91	0.00	0.09	2.00
157	0.00	0.00	1.02	1.02	1.97	0.01	0.02	2.00
145	0.00	0.06	0.97	1.03	1.92	0.00	0.08	2.00
9503	0.00	0.02	1.02	1.04	1.92	0.01	0.07	2.00
p-1	0.00	0.19	0.92	1.11	1.90	0.00	0.10	2.00
429	0.03	0.06	0.99	1.08	1.96	0.00	0.04	2.00
M11636	0.00	0.08	1.06	1.14	1.97	0.00	0.03	2.00

* Calculated on basis of As + Sb + S = 2.00

the other minerals and may have been deposited contemporaneously with this assemblage. This suggests that the Ni-As assemblage was deposited at a temperature above the rammelsbergite-pararammelsbergite inversion temperature, and that the Ni-Co-As assemblage was deposited below the inversion temperature.

The compositions of some pararammelsbergites, determined by means of the electron microprobe are given in Table 25, together with their atomic proportions. The results show that there is no systematic relationship between composition and mode of occurrence. Pararammelsbergite is weakly to non-birefracting, and its reflectivities at the 4 standard wave lengths (470, 546, 589 and 650 nm) are $60 \pm 0.5\%$ (see Table 23).

TRIARSENIDES

Skutterudite $((Co,Fe,Ni)As_{3-x})$

Skutterudite is a common mineral in the Cobalt-Gowganda ores and is present in all arsenide assemblages. It occurs at the cores and outer parts of arsenide rosettes, as separate crystals in the ore veins, and as cubes in the wall rock. The skutterudite at the cores of arsenide rosettes is present as euhedral crystals, and as minute grains embedded in calcite and sometimes grouped in the form of dendritic bodies (Figs. 63 and 65). In these cases the skutterudite is partly corroded and surrounded by radially oriented safflorite crystals, and partly replaced by native silver, sulphides, calcite, and parammelsbergite. Some replacements are haphazard, some are along crystallographic directions, some are in the form of dendritic bodies (Fig. 64), and some in the form of graphic intergrowths (Figs. 118, 119, and 120). The skutterudite in the other parts of the arsenide rosettes is present as minute grains intimately intergrown with safflorite, cobaltite, and arsenopyrite. The euhedral crystals in the ore veins were found only in the Ni-As and Co-As assemblages (Fig. 119*). These crystals are up to 2 cm in size and are partly replaced by pararammelsbergite, nickeline, rammelsbergite, and cobaltite along crystallographic directions (Fig. 120*). The skutterudite cubes in the wall rock are present near the Co-Fe-As and Co-As assemblages and contain irregular grains of arsenopyrite.

The compositions and atomic proportions for 10 skutterudites analysed by means of the electron microprobe are given in Table 26. The results show that most of the skutterudites are cobalt-rich, and that there is no apparent compositional variation from assemblage to assemblage. The results also show that the metal:arsenic ratio varies from 1:2.66 to

* Page 184.

TABLE 26. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF COBALT-GOWGANDA SKUTTERUDITES

Sample	Arsenide assemblage	Chemical composition (wt.%)					Atomic proportions *			
		Co	Fe	Ni	As	Total	Co	Fe	Ni	As
465	Ni-Co-As	17.7	2.6	3.0	79.0	102.3	0.76	0.11	0.13	2.66
M11636	Ni-As	18.3	1.0	1.5	78.5	99.3	0.82	0.08	0.10	2.73
M11594	Ni-As	19.1	1.5	2.0	79.0	101.6	0.84	0.07	0.09	2.74
62	Co-Fe-As	18.6	1.6	2.3	79.0	101.5	0.83	0.07	0.10	2.75
145	Ni-Co-As	17.3	2.9	2.2	79.3	101.7	0.77	0.13	0.10	2.76
157	Ni-Co-As	17.6	1.7	3.1	79.2	101.6	0.78	0.08	0.14	2.77
M11764	Co-As	17.3	1.8	2.1	77.6	98.8	0.81	0.09	0.10	2.85
429	Ni-As	17.7	2.0	2.0	81.0	102.7	0.81	0.10	0.09	2.92
836	Ni-As	18.2	1.0	1.5	78.5	99.2	0.88	0.05	0.07	2.92
355	Ni-As	17.9	1.3	1.5	77.4	98.1	0.86	0.07	0.07	2.93

* Calculated on basis of $\text{Co} + \text{Fe} + \text{Ni} = 1.00$

1 : 2.93, with the mean being 1 : 2.80. Roseboom (1962) has shown that synthetic skutterudites have small but real arsenic deficiencies, and Klemm (1956b) reported variable metal : arsenic ratios for naturally occurring skutterudites. The relative proportions of Fe : Ni, as determined by spot analyses of grains in 17 samples, are relatively constant (Fig. 108), although

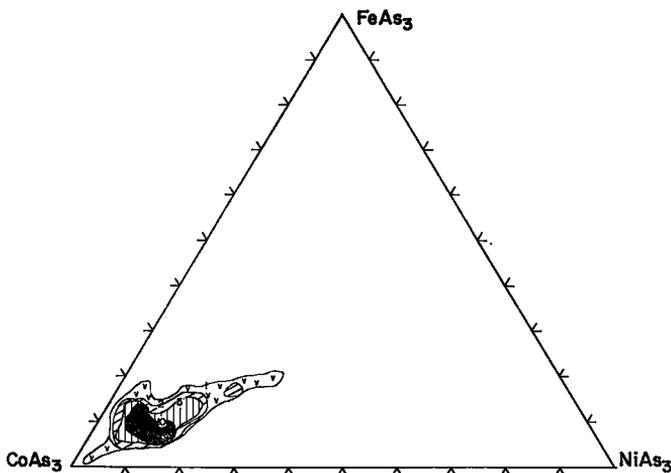


FIG. 108. Compositional variation of skutterudites in the Cobalt-Gowganda ores. Determined from 121 spot analyses of skutterudite in 17 samples.

there is a substantial amount of variation in the cobalt content from ($\text{Co}_{0.52}\text{Fe}_{0.21}\text{Ni}_{0.28}$) to ($\text{Co}_{0.97}\text{Fe}_{0.01}\text{Ni}_{0.02}$) with the most common composition ($\text{Co}_{0.80}\text{Fe}_{0.08}\text{Ni}_{0.12}$). This variation stays within the skutterudite solid-solution field which goes from the cobalt corner to the iron-nickel mid-point.

The cell parameters of 3 randomly selected non-analysed skutterudites from the Cobalt-Gowganda ores are 8.2066, 8.2069, and 8.2137 Å respectively. These values are in agreement with Roseboom's data (1962) for cobaltian skutterudites containing small amounts of iron and nickel.

SULPHARSENIDES

Sulpharsenides include some of the cobaltite and arsenopyrite group minerals. The cobaltite group sulpharsenides are cobaltite and gersdorffite, and the arsenopyrite group are arsenopyrite, glaucodot and alloclasite. The Co : Ni : Fe ratios for the cobaltite and arsenopyrite group sulpharsenides in the Cobalt-Gowganda ores, determined by electron microprobe spot analysis using analysed arsenopyrite and synthetic mono-, di- and triarsenides as standards, are plotted on a ternary Co-Ni-Fe diagram (Fig. 109). Other properties of these minerals are given below.

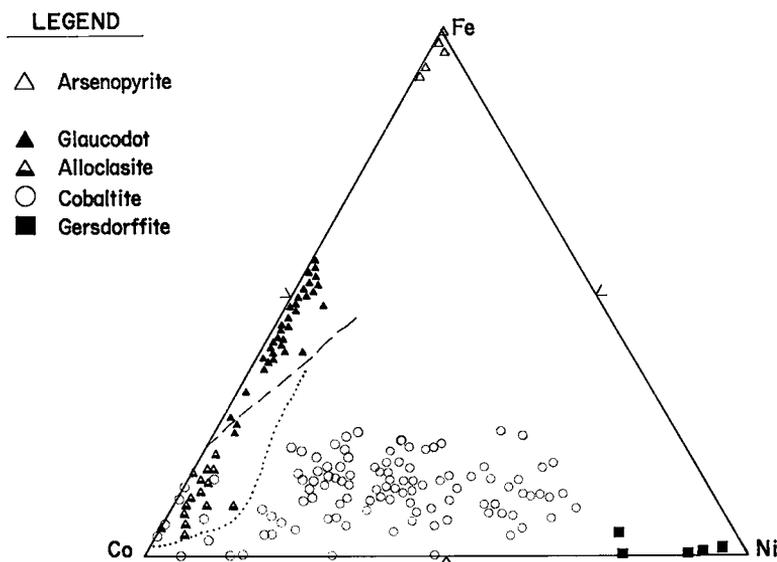


FIG. 109. Compositions of sulpharsenides from the Cobalt-Gowganda ores, plotted in terms of their metal ratios.

Cobaltite ((Co,Fe,Ni)AsS)

Cobaltite has the ideal composition CoAsS, but significant amounts of nickel and iron may substitute for the cobalt, and sulphur and arsenic may substitute for each other (Bayliss 1969a, and Klemm 1965a). Substitution of cobalt by nickel causes the cell size of cobaltite to increase, and substitution of arsenic by sulphur causes the cell size to decrease (Bayliss 1969b). Cobaltite can occur in two structural forms, isometric with disordered space group *Pa3*, and orthorhombic with ordered non-metal, space group *Pca2* (Giese & Kerr 1965). The *Pa3* cobaltite is isotropic in reflected light, and the *Pca2* variety is anisotropic. The *Pa3* structure can be distinguished from the *Pca2* structure in x-ray powder diffraction patterns by the absence of 001 and 011 reflections. The 001 and 011 reflection intensities and the strength of the optical anisotropism are related to the degree of distortion, of the crystal structure from cubic symmetry, caused by movement of the metal atoms away from the threefold crystal axis (Bayliss 1969a).

The cobaltite in the Cobalt-Gowganda ores gives an x-ray diffraction pattern that has weak 001 and 011 reflections. It is very weakly anisotropic in reflected light, and its polarization figure is a black cross which shows no separation of isogyres when the stage is rotated. The presence of 001 and 011 reflections in the x-ray powder diffraction pattern, and the weak anisotropism indicate that there is some distortion from the isometric *Pa3* structure to the orthorhombic *Pca2* structure, but the polarization figure indicates that the distortion is very small. Peacock & Henry (1948) and Gammon (1966) reported x-ray diffraction patterns for cobaltites from Cobalt that did not have the 001 and 011 reflections. To check this apparent anomaly, a study was made of euhedral crystal in samples E-1397, E-1398, M-13147 and M-20219 from the Royal Ontario Museum, Toronto, sample 1247 from the Ebbutt collection, National Museum, Ottawa, and sample M-14469 from the Royal Ontario Museum, which is believed to be the sample that Peacock & Henry (1948) studied and reported as sample M-14499 (J. A. Mandarino, personal comm.). Well-exposed x-ray powder diffraction patterns from Debye-Scherrer and Guinier cameras for all the above samples contained both the 001 and 011 reflections. It is thus concluded that the cobaltite in the Cobalt-Gowganda ores has a transitional structure that gives weak 001 and 011 reflections, and that these reflections can be found only with a Guinier powder camera or with a Debye-Scherrer camera using cobalt radiation, and making long exposures.

The composition of the cobaltite in the Cobalt-Gowganda ores covers a wide range, and varies from near the CoAsS end-member to $\text{Co}_{0.24}\text{Ni}_{0.67}$ -

$\text{Fe}_{0.09}\text{AsS}$, which represents a cobaltian gersdorffite composition (Fig. 109). The cobaltian gersdorffite is optically indistinguishable from the CoAsS end-member and is isostructural with it. Furthermore, intermediate cobaltite ($(\text{Co}_{0.80}\text{Ni}_{0.20})\text{AsS}$) is indistinguishable from the cobaltian gersdorffite and CoAsS by x-ray diffraction using a 114.6-mm-diameter Debye-Scherrer powder camera. Hence, for purposes of this paper the mineral name cobaltite will be used for material that is isostructural with the CoAsS end-member in these ores and has a compositional range between CoAsS and $(\text{Co}_{0.24}\text{Ni}_{0.67}\text{Fe}_{0.09})\text{AsS}$.

Cobaltite is a common mineral in the Cobalt-Gowganda ores, but it is present only as minute grains. It occurs in all assemblages in a variety of ways, as shown in Table 27.

The compositions of cobaltites in 14 samples were determined by electron microprobe and the atomic proportions of the elements were calculated (Table 28). The results show that the proportions of Co to Ni to Fe, and of arsenic to sulphur, are variable. The percentages of Co, Ni, and Fe in individual grains were determined by step scan analyses at 50-micron intervals across two euhedral crystals in sample 1247 from the

TABLE 27. MODES OF OCCURRENCE OF COBALTITE

Type of occurrence	Assemblage	Illustration
Intergrown with other arsenide minerals in massive arsenides.	Ni-As	
As irregular grains in wall rock adjacent to ore veins.	Ni-As	Fig. 52
Partly replaced by gersdorffite in ore veins.	Ni-As	Fig. 53
As euhedral crystals in nickeline, rammelsbergite and silver, at cores of rosettes.	Ni-As and Ni-Co-As	Fig. 121
Layers in rosettes surrounding rammelsbergite.	Ni-As	Fig. 50
Layers in rosettes surrounding safflorite.	Ni-Co-As and Co-As	Fig. 57
Intergrown with safflorite and skutterudite.	Ni-Co-As Co-As and Co-Fe-As and Fe-As	Fig. 60
Layers surrounded by skutterudite.	Co-Fe-As	Fig. 96
Grains surrounded by arsenopyrite.	Fe-As	Fig. 73
Euhedral crystals in vugs.	—	—

Ebbutt collection (Fig. 110), and at 5-micron intervals across a cobaltite layer in sample 64 (Fig. 111). The results show that one grain has a fairly uniform composition, but that the other grain and the cobaltite layer show variations. The quantities of Co, Ni and Fe in cobaltites from different occurrences were determined by microprobe analysis of different grains in a number of samples. The results, plotted in Figure 112, show variable cobaltite compositions from grain to grain and from sample to sample. These variations, however, stay within certain limits, depending both upon the mode of occurrence of the cobaltite and upon the arsenide assemblage. Thus cobaltites at the cores of rosettes have higher nickel contents than those in the outer layers (diagrams in upper right and lower left corners of Fig. 112), and cobaltite in the Ni-As assemblages generally has a higher nickel content than that in the other assemblages.

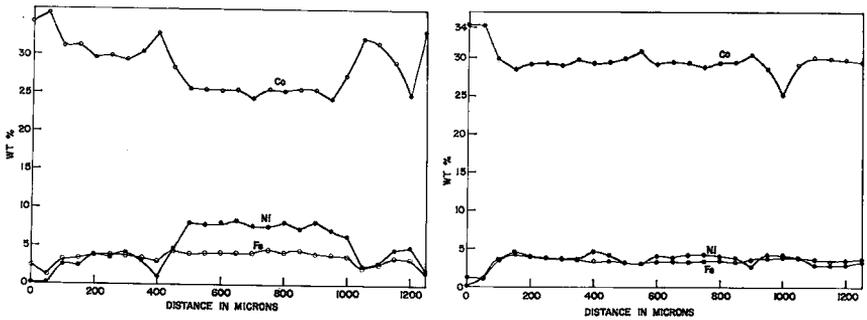


FIG. 110. Step scan analyses for cobalt, nickel and iron across two cobaltite grains in sample 1247, Ebbutt Collection, National Museum, Ottawa.

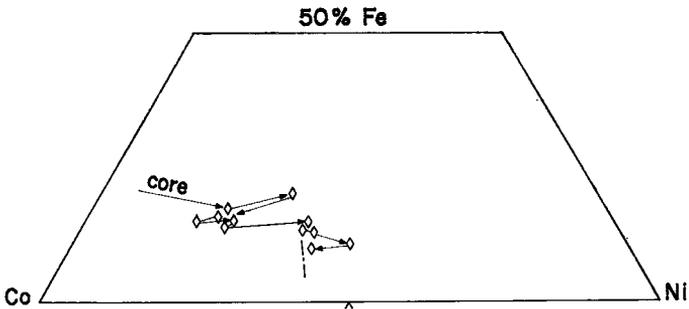


FIG. 111. Step scan analysis at 5-micron intervals across a cobaltite layer in sample 64. A photomicrograph of this layer is shown in figure 96.

Table 28 shows that the As : S ratios in the cobaltites from the Cobalt-Gowganda ores vary from 1 : 1 to 1.17 : 0.83. Klemm (1965a) reported that this values varies from 0.90 : 1.10 to 1.05 : 0.95 for natural cobaltites from other areas, and Bayliss (1969b) has shown by synthetic studies that sulphur can replace up to 50% of the arsenic to form a cobaltite with the composition $\text{CoAs}_{0.42}\text{S}_{1.5}$.

Table 28 also shows that the metal : non-metal ratio for the cobaltites in the Cobalt-Gowganda ores varies from 0.46 to 0.53. This ratio was reported as varying from 0.49 to 0.60 for cobaltites from other areas (Klemm 1965).

The cell parameters of some non-analysed cobaltites were calculated from indexed powder diffraction patterns, on the basis of a cubic cell, and are shown in Table 29. It is noted that three different cell parameters could be measured for the cobaltite in some samples. This undoubtedly reflects the variation of cobaltite composition in individual grains. It is also noted that, in general, cobaltites in the Ni-As assemblage have large cells and those associated with the Co-As and Fe-As assemblages have small cells. Furthermore cobaltite at the cores of arsenide rosettes in sample 461 has a larger cell than cobaltite in the outer layers. These variations of cell

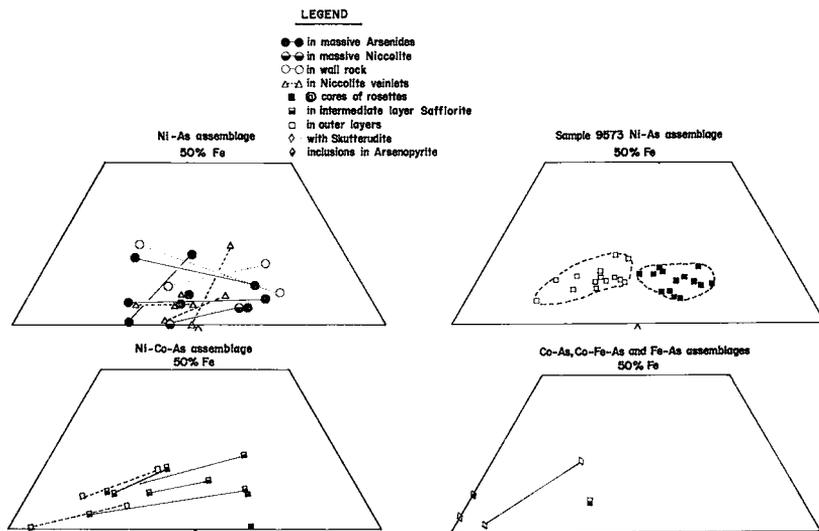


Fig. 112. Compositional variations of cobaltite in different occurrences. The bottom left corner of each diagram represents CoAsS , the bottom right corner represents NiAsS , and the top is 50% FeAsS . The lines joining individual points represent the compositional extremes of cobaltite in one sample.

TABLE 28. COMPOSITIONS AND ATOMIC PROPORTIONS OF COBALTITE IN THE COBALT-GOWGANDA ORES

Sample	Composition (weight per cent)						Atomic proportions					Metal/	
	Co	Ni	Fe	As	S	Total	Co	Ni	Fe	As	S	As + S	
M16675	31.2	0.2	1.5	47.5	18.8	99.2	0.87	tr	0.04	1.04	0.96	0.46	
7	30.0	2.0	1.0	49.0	17.5	99.5	0.85	0.06	0.03	1.09	0.91	0.47	
Ebbutt 1247	28.2	3.1	3.7	47.1	19.0	101.0	0.78	0.09	0.11	1.03	0.97	0.47	
465	26.9	6.5	1.5	50.5	15.3	100.7	0.79	0.19	0.04	1.17	0.83	0.51	
145	25.9	5.1	2.9	51.3	16.5	101.7	0.73	0.14	0.09	1.14	0.86	0.48	
145	25.0	7.5	4.2	50.8	16.2	100.7	0.72	0.21	0.13	1.15	0.85	0.53	
62	20.7	8.5	4.8	46.0	19.6	99.6	0.57	0.24	0.14	1.00	1.00	0.48	
157	20.5	11.4	3.7	47.9	17.2	100.7	0.59	0.33	0.11	1.09	0.91	0.52	
M11764	19.2	10.5	3.3	50.5	15.5	99.0	0.56	0.31	0.10	1.17	0.83	0.49	
686	18.2	16.5	0.0	47.0	17.5	99.2	0.53	0.48	—	1.09	0.93	0.51	
828	18.0	14.0	2.0	52.0	15.5	101.5	0.50	0.41	0.06	1.18	0.82	0.49	
74	17.7	7.0	7.5	48.0	18.6	98.8	0.49	0.20	0.22	1.05	0.95	0.46	
828	17.3	14.0	2.8	50.0	16.3	100.4	0.50	0.41	0.09	1.14	0.86	0.50	
157	14.0	16.7	5.6	47.9	17.2	101.4	0.40	0.48	0.17	1.09	0.91	0.53	

TABLE 29. CELL PARAMETERS OF SOME COBALTITES FROM THE COBALT-GOWGANDA ORES

Sample	Cubic cell * parameter (Å)	Assemblage	Remarks
749	5.584	Fe-As	Inclusion in arsenopyrite
357	5.593	Co-As	In massive arsenides in Co-As assemblage
354	5.599	Co-As	In massive arsenides in Co-As assemblage
894	5.6049, 5.6059, 5.6053	Co-As adjacent to Ni-As	In massive arsenides in Co-As assemblage
461	5.604	Ni-Co-As	Outer layer of rosette
461	5.618	Ni-Co-As	Core of rosette
Rusty Lake-A	5.612, 5.616, 5.625	Co-As	Outer layer of rosette
685	5.619	Ni-Co-As	
Rusty Lake-F	5.625		
9573	5.623	Ni-As	Outer layer around rammelsbergite
632	5.632	Ni-As	Adjacent to wall rock
135	5.632	Ni-As	Adjacent to wall rock
135	5.631	Ni-As	Intergrown with gersdorffite
155, 475	5.632	Ni-Co-As	Intergrown with gersdorffite
134	5.632	Ni-As	Intergrown with gersdorffite
Rusty Lake	5.639	Ni-As	Intergrown with rammelsbergite
Rusty Lake	5.663	Ni-As	Replacement of skutterudite

* Estimated accuracy 0.01%

parameter with respect to occurrences of cobaltite correspond to the observed compositional variations of cobalt, nickel, and iron.

The above observations show that cobaltites in the Cobalt-Gowganda ores contain variable amounts of cobalt and nickel, and that these compositional variations can be correlated to certain features of the ore. Nickel-rich varieties occur at the cores of arsenide rosettes and in the Ni-As assemblage, and cobalt-rich ones in the outer layers of the arsenide rosettes and in the Co-As and Fe-As assemblages. These compositional variations appear to reflect compositional variations of ore solutions that deposited the various assemblages. Such variations are to be expected by deposition from circulating solutions.

Gersdorffite

The ideal gersdorffite composition is NiAsS , but substitutions are common. Cobalt and iron readily substitute for nickel (Klemm 1965a), and arsenic and sulphur can be mutually substituted to the limits of $\text{NiAs}_{1.77}\text{S}_{0.23}$ and $\text{NiAs}_{0.77}\text{S}_{1.23}$ (Yund 1962). These substitutions cause the size of the cubic gersdorffite cell to change as follows :

(1) Co and Fe substituting for Ni cause the cubic-cell parameter to decrease from 5.6939 Å, which is the parameter for pure NiAsS .

(2) Substitution of S by As causes the cell to increase up to 5.7318 Å, and substitution of As by S a decrease to 5.6864 Å.

Gersdorffite is an isometric mineral but it can have 3 different structures : disordered isometric with space group $Pa\bar{3}$ (Bayliss 1968), partly ordered isometric with space group $P2_13$ (Bayliss & Stephenson 1967), and pseudo-isometric with triclinic symmetry and space group $P1$ (Bayliss & Stephenson 1968). These structures can be differentiated by x-ray powder diffraction patterns, as follows : $Pa\bar{3} = 001$ and 011 absent, $P2_13 = 001$ absent and 011 present, and $P1 = 001$ and 011 both present.

Gersdorffite in the Cobalt-Gowganda ores has the $P2_13$ structure. It is a relatively rare mineral, and was found only in the Ni-As assemblage. Kulkarni (1968), and Halls & Stumpfl (1969) reported gersdorffite as being a common mineral in the cobalt ores. They obviously referred to the material that is referred to as cobaltite in this paper.

Two varieties of gersdorffite are present in the Cobalt-Gowganda ores. One is present as rather diffuse material between cobaltite and nickel arsenides (Fig. 53), and will be referred to here as arsenian gersdorffite ; the other variety referred to here as gersdorffite (Fig. 122*), is present as partial replacements of cobaltite and as massive gersdorffite. The arsenian

* Page 184.

gersdorffite is isotropic and its reflectivity is higher than that of cobaltite and gersdorffite, it contains so many remnants of gersdorffite and nickel arsenides that mono-mineralic mounts could not be obtained for x -ray powder diffraction analysis. However, it was possible to obtain enough line separation on a film taken with a 114.6-mm camera to identify the phases and measure the cell parameters. The information, obtained from several x -ray diffraction mounts (Table 30), shows that arsenian gersdorffite has a larger cell than the co-existing gersdorffite. Only the 011 line was present in the x -ray powder diffraction patterns for Samples 134, 135 and 686, and its d spacing corresponds to that of arsenian gersdorffite. Hence arsenian gersdorffite is a partly ordered isometric mineral, space group $P2_13$.

Electron microprobe analyses show that the arsenian gersdorffite contains large amounts of arsenic apparently substituting for sulphur (Table 31). The possibility of contamination of this gersdorffite by very finely divided rammelsbergite has not been completely eliminated, but the large cell size is consistent for gersdorffite with a high arsenic content (Yund 1962), and the high reflectivity supports the view that the arsenian gersdorffite is, in fact, a separate arsenic-rich phase.

Gersdorffite has a lower reflectivity and smaller cell (Table 30) than arsenic gersdorffite, and contains approximately equal molecular proportions of arsenic and sulphur (Table 31). It is a partly ordered isometric mineral, with space group $P2_13$. Massive gersdorffite was found in one veinlet about $\frac{1}{2}$ inch wide on the No. 6 level in the Glen Lake mine about 150 feet south of Vein No. 6, in Keewatin rocks below Huronian

TABLE 30. CELL PARAMETERS OF GERSDORFFITE AND COBALTITE FROM THE COBALT-GOWGANDA ORES

Sample	d (Å) * Arsenian gersdorffite	d (Å) * Gersdorffite	d (Å) * Cobaltite	Other minerals in sample
134	5.70 (major constituent)	5.688	5.630	
135	5.712 (major constituent)	5.680	5.631	rammelsbergite
155	—	5.686	5.632 (Major)	
475	—	5.680	5.630 (Major)	
686	5.712 (major constituent)	5.680	5.655	pararammelsbergite
708		5.680		nickeline

* Estimated error = 0.01%.

sediments (sample 708). It contains minute exsolutions of nickeline, its cell parameter is 5.680 Å, and its composition is equivalent to $(\text{Ni}_{0.79-0.97}\text{Co}_{0.04-0.19}\text{Fe}_{0.01-0.06})\text{As}_{1.08}\text{S}_{0.92}$.

Arsenopyrite

The ideal arsenopyrite composition is FeAsS, but some cobalt can substitute for iron, and sulphur and arsenic can substitute for each other (Clark 1960). Substitution of sulphur by arsenic and iron by cobalt both cause the cell size and the value of d_{131} to increase (Morimoto & Clark 1961; and Gammon 1966). According to Morimoto & Clark (1961) arsenopyrite has a triclinic unit cell, space group $P1$, but this symmetry tends to become monoclinic, space group $P2_1/c$, as the arsenic content increases.

Arsenopyrite in the Cobalt-Gowganda ores is the main mineral in the Fe-As assemblage, is common in the Co-Fe-As and Co-As assemblages, and is rare in the Ni-As and Ni-Co-As assemblages. It occurs in veins as part of the arsenide assemblages, and, in the wall rock near the ore veins, as disseminated euhedral crystals. In the veins, the arsenopyrite is present as euhedral crystals (Figs. 63 and 72), as masses, as botryoidal bodies

TABLE 31. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF GERSDORFFITE IN THE COBALT-GOWGANDA ORES

Sample	Chemical composition in weight per cent							Remarks
	Co	Fe	Ni	As	Sb	S	Total	
686	2.7	0.0	33.0	47.0		17.5	100.2	gersdorffite
686	0.0	2.5	32.0	58.5	0.2	8.0	101.2	arsenian gersdorffite
686	6.7	1.8	27.0	58.8	0.2	8.0	102.2	arsenian gersdorffite
130	1.8	0.5	31.0	61.5		6.7	101.5	arsenian gersdorffite
	Atomic proportions *							
	Co	Fe	Ni	$\frac{A}{x+y}$	As	S		
686	0.08	0.00	0.96	0.52	1.07	0.93	gersdorffite	
686	0.00	0.09	1.06	0.59	1.52	0.48	arsenian gersdorffite	
686	0.22	0.06	0.89	0.58	1.52	0.48	arsenian gersdorffite	
130	0.06	0.01	1.03	0.55	1.60	0.40	arsenian gersdorffite	

* Calculated on basis of As + S = 2.00

$$** \frac{A}{x+y} = \frac{\text{As} + \text{S}}{\text{Co} + \text{Fe} + \text{Ni}}$$

(Fig. 71), and as veinlets in the other arsenides. The euhedral crystals occur outside arsenide rosettes and as borders on arsenide rosettes. They contain inclusions of cobaltite, skutterudite, safflorite and fine-grained arsenopyrite, and some are zoned with the central zone being arsenopyrite and the outer zone, glaucodot (Fig. 113). The euhedral crystals outside arsenide rosettes are interpreted as evidence for late deposition. The massive and botryoidal arsenopyrite occurs only in the Fe-As assemblage. It is generally fine-grained and some is intergrown with skutterudite, cobaltite, and trace amounts of iron-rich safflorite. Some fine-grained arsenopyrite is also present as diffuse veinlets in other arsenides.

The compositions, atomic proportions, and the measured and calculated d_{131} values of arsenopyrite in some samples are given in Table 32. The calculated d_{131} values were calculated from the composition according to the formula $d_{131} = 1.6006 + 0.00098x$ (Morimoto & Clark 1961) where x is the arsenic content in atomic per cent. It is apparent that there is a large discrepancy between the measured and calculated d_{131} values. The reason for this is not obvious since both the analysed and measured values are considered to be reliable. The analyses were made with an electron microprobe using analysed arsenopyrite as a standard, and the d_{131} spacings were measured from a 114.6-mm film using Fe-filtered Co radiation corrected for film shrinkage. The discrepancy appears to indicate that the relationship determined from the synthetic products are not entirely valid for the natural samples.

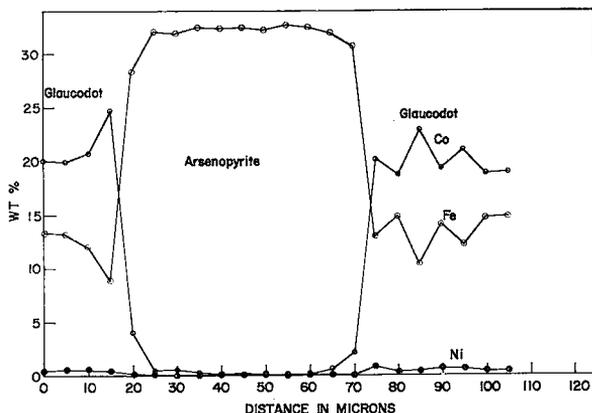


Fig. 113. Electron microprobe step scan analysis, at 5-micron intervals, across a zoned arsenopyrite crystal in Sample No. 383 (near east end Vein 1, 5th level, Silverfields mine).

Glaucodot

Glaucodot is closely related to arsenopyrite in composition, crystal form, and x-ray diffraction pattern, but it contains nearly equal amounts of iron and cobalt, and its crystal structure is different from that of arsenopyrite. It has orthorhombic symmetry with space group *Cmmm* (Ferguson 1946). Glaucodot in the Cobalt-Gowganda ores was found alternating with alloclasite in Sample 180 (Fig. 114), and as outerlayers on arsenopyrite

TABLE 32. CHEMICAL COMPOSITIONS, ATOMIC PROPORTIONS, AND d_{131} VALUES FOR ARSENOPIRYTE FROM THE COBALT-GOWGANDA ORES

Sample	Chemical composition (wt.%)				Atomic proportions			Measured d_{131}	Calculated
	Fe	As	S	Total	Fe	As	S		
51 ²								1.627	
O'Brien ¹	34.53	44.34	20.22	99.09	1.02	0.97	1.03		1.631
749 ³	33.8	46.2	20.1	100.1	0.97	0.99	1.01	1.626	1.633
74 ³	32.74	48.64	19.78	101.16	0.93	1.03	0.97	1.631	1.635
767 ⁴	32.37	45.15	21.28	98.80	0.90	0.95	1.05		1.631
381 ³								1.633	

¹ Taken from Ellsworth (1916)

² Border on an arsenide rosette

³ Euhedral crystals outside arsenide rosettes

⁴ Fine-grained arsenopyrite at cores of arsenide rosettes.

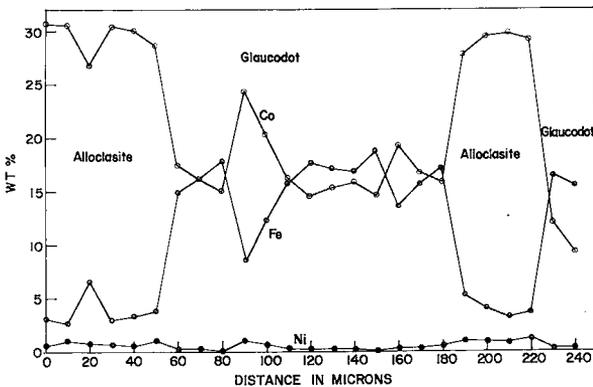


FIG. 114. Step scan analysis at 10-micron intervals from the core to the outside of an arsenide grain in sample 180. It shows that this grain is composed of alternate layers of glaucodot and alloclasite. The cobalt-rich spot in the glaucodot field may be a small alloclasite inclusion (near west end Vein 4, 4th level, Silverfields mine).

in a number of samples, including Sample No. 383 (Fig. 113). The quantities of cobalt, iron and nickel in the glaucodot in Sample No. 180, as determined by step scan analysis, are given in Table 33.

The x -ray powder diffraction data of glaucodot, arsenopyrite, and alloclasite are given in Table 34 for comparison. The data for glaucodot has extra reflections as compared to data reported by Ferguson (1946). The reason for these lines is not apparent.

Alloclasite

The mineral name alloclasite was given to a mineral whose physical and optical properties and x -ray diffraction patterns are similar to those of arsenopyrite and glaucodot, but which contains larger amounts of cobalt. Some workers (Gammon 1966 and Shishkin 1962) referred to this type of material as a cobalt-rich glaucodot, Borishanskaya, *et al.* (1965) referred to it as a separate mineral, and Kingston (1969, 1971) described it as a separate mineral species with orthorhombic symmetry, space group $P22_12_1$. The material that occurs in the Cobalt ores and has the alloclasite composition is crystallographically different from glaucodot and arsenopyrite. It has orthorhombic symmetry space group $P22_1$.

Alloclasite in the Cobalt-Gowganda ores was found only in the Fe-As and Co-Fe-As assemblages. It occurs as euhedral crystals around an iron-rich safflorite in Sample 9570 (Table 21 and Fig. 70), as alternating layers with glaucodot in Sample No. 180 (Fig. 114), as separate euhedral crystals embedded in calcite at the cores of rosettes, and as masses in samples from the Langis mine and the Maple Mountain area. The alloclasite in the samples from Maple Mountain is bordered and cut by veinlets of safflorite.

Textural relations indicate that deposition of some alloclasite preceded the deposition of safflorite, while some was later. The reason for this contradictory order of deposition is not apparent, nor is it evident why alloclasite was deposited rather than cobaltite, which has the same composition and is the common mineral in the Cobalt-Gowganda ores. It is

TABLE 33. COMPOSITIONS OF GLAUCODOT IN SAMPLE NO. 180

Location	No. of analyses	Remarks	Co wt. %	Fe wt. %	Ni wt. %
Inner layer	25	range	14.7-20.6	12.3-18.8	0-2.3
		mean	16.8	16.0	0.5
Outer layer	11	range	18.6-24.7	8.8-14.9	0.3-0.8
		mean	20.4	12.9	0.5

TABLE 34. X-RAY POWDER DATA FOR ARSENOPYRITE, GLAUCODOT AND ALLOCLASITE

Arsenopyrite Sample 749			Glaucodot Sample 180 (inner layer)			Alloclasite Sample 9570		
<i>hkl</i>	<i>d</i> Å	<i>I</i> (est)	<i>hkl</i>	<i>d</i> Å	<i>I</i> (est)	<i>hkl</i>	<i>d</i> Å	<i>I</i> (est)
$\bar{1}11$	3.636	0.5	061	3.625	1.5	110	3.584	5
			080	3.570	3			
			*	3.278	5			
			240	3.015	3			
						011	2.904	2
020	2.842	3	0.10.0	2.803	1	020	2.811	2
111	2.791	1						
			260	2.742	8	101	2.744	10
			*	2.701	2			
002 } 200 }	2.664	9						
$\bar{1}12$	2.549	2						
			261	2.461	7	111	2.461	10
$\bar{1}21$	2.433	10	280	2.428	6			
012 } 210 }	2.409	3	062	2.405	6	120	2.410	9
			0.12.0	2.364	1			
						200	2.329	1
$\bar{2}12$	2.195	3				210	2.155	3
			222	2.146	0.5			
$\bar{1}02$	2.090	3						
$\bar{1}22$ } $\bar{2}21$ }	2.003	1						
$\bar{1}12$ } 211 }	1.961	0.5	262	1.961	3	121	1.965	4
022 } 220 }	1.941							
			*	1.865	1			
$\bar{3}11$	1.814	7	2.12.1	1.817	10	211	1.818	8
031	1.784	1	*	1.784	0.5	220	1.797	1
$\bar{1}31$	1.754	3	063	1.759	0.5			
	1.738	0.5	*	1.733	0.5	130	1.739	2
			*	1.705	0.5	002	1.696	2
	1.678	0.5	083	1.684	0.5			
131	1.626	6	0.14.2	1.637	4	031	1.639	4
202	1.605	3						
$\bar{3}21$	1.587	4	242	1.584	2	221	1.587	3
$\bar{3}13$	1.540	4	0.18.1	1.547	2	131	1.548	1

NOTE: The *hkl* indices for glaucodot are those given by Ferguson (1946), and lines marked with an asterisk are extra lines in the powder pattern of glaucodot from Cobalt. The extra lines were also present in other powder patterns for glaucodot from the Cobalt area.

to be noted, however, that alloclasite was found only where silver is absent.

Chemical compositions and atomic proportions for alloclasite, as determined by means of the electron microprobe, are given in Table 35. X-ray powder diffraction data for the alloclasite in Sample No. 9570 are included in Table 34. Other data for the alloclasite in Sample No. 9570 are: measured density 6.02; S.G. (calc) 6.20, cell volume 89.00 Å³, Z = 2, measured cell parameters $a = 4.658$ Å, $b = 5.621$ Å and $c = 3.399$ Å. The mineral was heated to 600° C and held there for three weeks by L. J. Cabri in the Mines Branch Laboratories at Ottawa. It broke down to skutterudite and pyrrhotite.

ANTIMONIDES

Breithauptite (NiSb)

Breithauptite in the Cobalt-Gowganda ores was described in detail by Ellsworth (1916), thus only its major characteristics are mentioned here. It is present in the Ni-As and Ni-Co-As assemblages. In the Ni-As assemblage the breithauptite occurs in massive arsenides, whereas in the Ni-Co-As assemblage it occurs at the cores of arsenide rosettes. It is intimately inter-

TABLE 35. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF ALLOCLASITE FROM THE COBALT-GOWGANDA ORES

Sample	Chemical composition wt. %						Atomic proportions				
	Co	Fe	Ni	As	S	Total	Co	Fe	Ni	As	S
9570	26.5	6.0	tr	49.0	17.0	98.5	0.76	0.18	—	1.10	0.90
62	28.5	1.9	2.9	47.0	19.3	99.6	0.79	0.05	0.08	1.02	0.98
74	23.9	4.9	7.4	47.5	19.5	103.2	0.65	0.14	0.20	1.02	0.98
74	32.3	0.5	2.8	47.4	19.4	102.4	0.89	0.01	0.08	1.02	0.98
M.M.-1 *	29.7	4.0	0.5	48.2	18.9	101.3	0.82	0.12	0.01	1.04	0.96
180	29.1	4.1	0.9								
838	28.4	5.1	0.6	46.3	19.4	99.8	0.79	0.09	0.02	1.01	0.99
(spot 1) **											
838	27.0	3.4	4.1	46.5	19.5	101.0	0.75	0.10	0.11	1.01	0.99
(spot 2) **											
838	31.3	2.5	0.6	46.4	19.5	100.3	0.87	0.07	0.02	1.01	0.99
(spot 3) **											
838	31.1	1.7	1.3	46.3	19.5	99.9	0.86	0.05	0.04	1.01	0.99
(spot 4) **											

* Sample from Maple Mountain.

** Sample 838 from Vein No. 425-86 in Langis mine at end of orebody.

grown with nickeline in all occurrences, but in some places the intergrowth is surrounded by a narrow nickeline layer. The breithauptite-nickeline intergrowth in the Ni-Co-As assemblage is also associated with silver and, in some places, with maucherite. The association of breithauptite, nickeline, and silver in the Ni-Co-As assemblage is so consistent that local mine

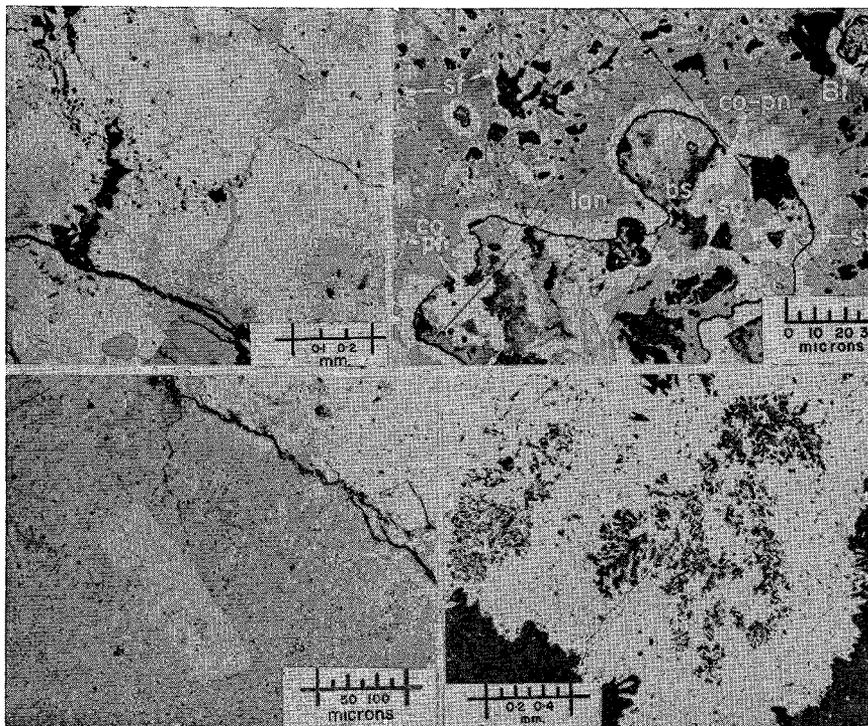


FIG. 115. (Top, left) Photomicrograph of a polished section showing nickeline veinlets (grey) in safflorite (white). The nickeline veinlets emanate from irregular nickeline grains.

FIG. 116. Photomicrograph of a polished section of part of a grain containing langisite (grey, labelled lan) in safflorite (sf). The grain also contains the associated sulphides parkerite (pk), cobalt pentlandite (co-pn), siegenite (sg), bismuthinite (bs) and native bismuth (Bi). The sulphide grains are outlined to enhance contrast.

FIG. 117. (Bottom, left) Photomicrograph of a polished section showing a large prismatic crystal of pararammelsbergite in a matrix of nickeline intergrown with rammelsbergite.

FIG. 118. Skutterudite at the cores of arsenide rosettes partly replaced by calcite (black) in the form of graphic intergrowths. The skutterudite in this photograph cannot be differentiated from the other arsenides in the rosettes, which are all white.

operators consider the presence of breithauptite in the rosette-type ores as being indicative of high-grade silver ore.

The compositions of breithauptite and associated nickeline in Sample M-8922 were determined by means of the electron microprobe. The results, given in Table 36, show that the breithauptite in this sample contains 4.8

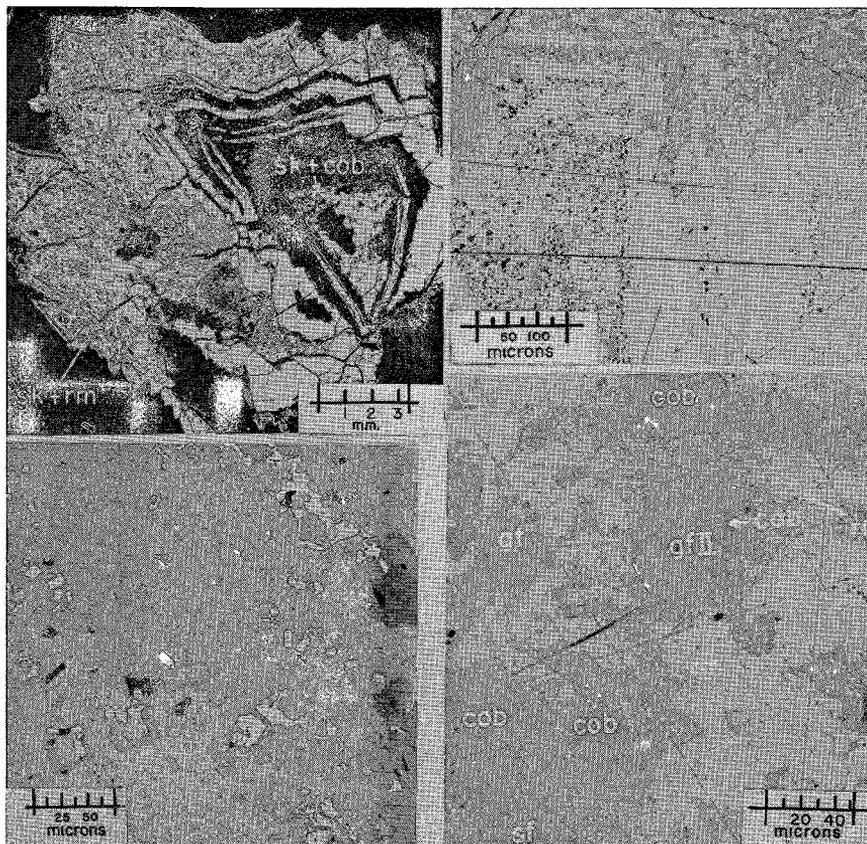


FIG. 119. (Top, left) Separate skutterudite crystal in the ore veins, partly replaced by rammelsbergite (rm) and cobaltite (cob).

FIG. 120. Part of a skutterudite grain (grey) intergrown with paramrammelsbergite in the form of a graphic intergrowth.

FIG. 121. (Bottom, left) Euhedral cubic cobaltite crystals (grey) in nickeline (grey) and rammelsbergite (light grey). Some of the cobaltite crystals are partly replaced by silver (white) and rammelsbergite.

FIG. 122. Cobaltite (cob) partly replaced by gersdorffite (gf II). Some arsenian gersdorffite (gf), rammelsbergite (rm) and safflorite (sf) are also present,

atom per cent arsenic in the Sb site, and the associated nickeline contains 4.6 atom per cent antimony in the As site. These results are in general agreement with those reported by Halls & Stumpfl (1969) and by Ellsworth (1916).

Ullmannite (NiSbS)

Ullmannite, identified by x-ray diffraction studies combined with ore microscopy, was found as separate grains in calcite in Vein No. 6 in the Deer Horn mine, and in a vein in the Silverfields mine. That in the Deer Horn mine was found in an ore zone that contained large amounts of tetrahedrite, pyrrargyrite, cobaltite, silver, and allargentum. That in the Silverfields mine occurred in carbonate beyond an ore zone representing the Ni-Co-As assemblage, and was associated with tetrahedrite, pyrrargyrite, and proustite. The ullmannite in both occurrences is in an antimony-rich section of the ore near a Ni-Co-As assemblage.

CONCLUSIONS

Most of the arsenides in the Cobalt-Gowganda ores have variable compositions, hence they have not been homogenized and therefore provide a partial record of the nature of the ore forming solution. The compositions of some minerals vary from point to point along veins, and from cores to the outer parts of arsenide rosettes. These compositional variations follow the same trend for all arsenides, progressing from nickel to cobalt to iron varieties, and correlate with varieties of associated arsenides and antimonides. This suggests that the arsenides were deposited from an ore solution whose composition was changing systematically from one end

TABLE 36. CHEMICAL COMPOSITIONS AND ATOMIC PROPORTIONS OF BREITHAUPTITE AND NICKELINE IN SAMPLE M8922

Element	Breithauptite		Nickeline	
	weight	atomic prop.	weight	atomic prop.
Ni	32.9	1.016	40.6	0.912
Co	0.1	0.003	3.2	0.076
Fe	nd	—	nd	—
As	2.0	0.048	54.1	0.954
Sb	65.0	0.952	4.3	0.046
Total	100.0		102.2	

of the vein to another, and from the wall rock to the centre of the vein. Such a compositional change likely occurred by precipitation of certain elements as minerals at a specific point, thereby depleting the ore solution of these elements and concentrating others. The other elements would then have been deposited elsewhere as the ore solution moved along the vein in either an open or closed vein system.

It is also noteworthy that some minerals, pararammelsbergite and arsenopyrite, have relatively uniform compositions. The pararammelsbergite is recrystallized and hence its composition has been homogenized. Arsenopyrite is the latest arsenide mineral to have been deposited in these ores, probably at low temperatures and under conditions where it has a very narrow stability field.

ACKNOWLEDGEMENTS

The authors wish to thank D. Radcliffe, University of Georgia who read the section on diarsenides and made many constructive suggestions, most of which were incorporated into this paper. Any interpretations, however, are the sole responsibility of the senior author.

Acknowledgements are also extended to J. A. Mandarino, Curator of Mineralogy, Royal Ontario Museum, Toronto, L. Moyd, Curator of Mineralogy, National Museum, Ottawa, and N. Carmichael, President, Argentinum Mines Limited, Toronto, for providing some of the samples studied.

We also thank L. J. Cabri of the Mines Branch, Ottawa, for conducting the heating experiments.