LANGISITE, A NEW MINERAL, AND THE RARE MINERALS COBALT PENTLANDITE, SIEGENITE, PARKERITE AND BRAVOITE FROM THE LANGIS MINE, COBALT-GOWGANDA AREA, ONTARIO

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ABSTRACT

An unusual assemblage of arsenides, sulphides and native bismuth has been found in an ore-bearing fault vein in the Langis mine, Casey township in the Cobalt-Gowganda area of Ontario. The arsenides are safflorite, a cobalt monoarsenide and maucherite. The cobalt monoarsenide, for which the name langisite is proposed, is a new mineral that corresponds to the cobalt-rich end-member of the NiAs isostructural series. Its composition corresponds to $Co_{0.84}Ni_{0.16}As_{1.04}$. The sulphides consist of two distinct sub-assemblages, one of pyrite and marcasite intimately intergrown, and the other of bismuthinite, parkerite, cobalt pentlandite, siegenite, bravoite and a late pyrite. The parkerite is the bismuth-rich end-member of the $Ni_3Bi_2S_2$–Ni_3BiPbS_2 isostructural series. The cobalt pentlandite has a composition corresponding to $Co_{6.8}Ni_{1.4}S_{8.0}$, and the siegenite has the composition equivalent to $Co_{1.83}Ni_{1.17}S_{4.0}$. The bravoite has a variable composition but most of it is cobalt-rich. Interpretations of the textural relationships of the minerals in this assemblage show that the sequence of deposition was arsenides, pyrite-marcasite, native bismuth, other sulphides.

INTRODUCTION

During the course of a mineralogical investigation of the ores in the Cobalt-Gowganda area in Ontario, a vein that has several unique characteristics was studied. This vein, Vein 30 in the Langis Mine, Casey township, has an abundance of mineralized fault gouge and breccia, and contains an unusual assemblage of minerals. This assemblage includes the cobalt-rich analogue of niccolite, which is a new mineral, and four relatively rare minerals that have not been previously reported from the Cobalt-Gowganda area. These four minerals are cobalt pentlandite, siegenite, parkerite and bravoite. W. Petruk conducted this study, D. C. Harris analysed the minerals by means of the electron probe microanalyser, and J. M. Stewart performed the *x*-ray diffraction analyses. The geology of the Langis mine has been described by Thomson (1965).

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EXPERIMENTAL PROCEDURE

A Materials Analysis Company (MAC) model 400 electron-probe microanalyzer was used to determine the compositions of the minerals given in this paper. Both synthetic and naturally-occurring sulphides and arsenides were used as standards, except for the mineral parkerite for which pure metals were used since suitable standards were not available. For analysis of the arsenide minerals synthetic compounds having the compositions CoAs, $CoAs_2$, $(Co_{0.5}Fe_{0.5})As$, and FeAs, and the natural minerals niccolite (NiAs) and rammelsbergite ($NiAs_2$) were used as standards. The sulphide analyses were determined by use of synthetic standards of the compositions FeS_2, NiS, NiS_2 and CoS_2. With these standards inter- and extrapolations were made. For the parkerite analysis it was necessary to apply the absorption correction procedures using the tables published by Adler & Goldstein (1965) and mass absorption coefficients published by Heinrich (1964), and atomic-number corrections using the method outlined by Thomas (1964). Fluorescence corrections were not applied.

The apparatus used for measuring the reflectivities was a Leitz Ortholux-Pol microscope, a Leitz MPE microscope photometer equipped with a Dumont 6467 photomultiplier tube, two six-volt storage batteries connected in parallel and maintained under constant charge during operation by a 6V battery charger, and a Veril B200 continuous-band interference filter. A 50:1 objective with a numerical aperture of 0.65 was used except where specified otherwise in the text.

Silicon was used as a standard for all measurements and was supplied by the Commission on Ore Microscopy of the International Mineralogical Association and had been calibrated by the National Physical Laboratory in Great Britain. The reflectivity values for silicon were taken from the NPL report, reference N2538, dated August 22, 1966.

The samples were mounted in Araldite and polished on lead laps with graded diamond abrasives down to 0–2 microns in diameter. Final buffing was done on a cloth lap with a slurry of magnesium oxide in water for a period of two minutes.

The microhardnesses of the minerals were determined with the aid of a Leitz Durimet hardness tester equipped with polarizing filters and rotating stage. The values are given in terms of Vickers Hardness Number (VHN). The polishing procedure is the same as that for reflectivity measurements.

The x-ray diffraction data and unit-cell dimensions were obtained by the film method using 114.6-mm-diameter Debye–Scherrer powder cameras, and Fe filtered Co radiation. Film-shrinkage corrections were applied and the intensities were estimated visually.

GENERAL DESCRIPTION OF THE DEPOSIT

Vein 30 is a fault vein that contains silver ore and fault material in Cobalt Group sedimentary rocks and underlying Keewatin volcanic rocks. It is about 1,000 feet long, and pinches and swells from hairline thickness to about 6 inches. The silver ore, now largely mined out, formed an ore body about 400 feet long which was localized near the contact between the sedimentary rocks and underlying Keewatin rocks at a point where Vein 30 intersects another vein. Samples from the edge of the orebody contain zoned glaucodot and other Co-Fe-As minerals, whereas those from a pillar in the other vein contain high-grade silver in an assemblage of Ni-Co-As minerals. These characteristics of the orebody are similar to those of ore bodies in the Silverfields mine in the Cobalt area which have been described elsewhere (Petruk, 1968).

The fault material consists of gouge and breccia cemented with calcite and quartz, and contains pockets of ore minerals. The ore minerals in some pockets are largely marcasite, in others arsenides, in still others silver sulphides, and in some an unusual assemblage of arsenides and sulphides. This unusual assemblage will be referred to as the "Langis arsenide-sulphide assemblage" in this paper.

The ore minerals in the marcasite pockets are largely marcasite, but some sphalerite, chalcopyrite and pyrite are also present. The marcasite occurs as irregular grains, veinlets and cementing material in the fault gouge, and contains inclusions of pyrite, chalcopyrite and sphalerite. The sphalerite occurs largely as veinlets, up to 1/2 inch wide, interlayered with marcasite. The cell parameter of the sphalerite is 5.4064 Å which is lower than the theoretical value 5.4093 for pure ZnS (Barton & Toulmin, 1966). The reason for this low value is not apparent.

The ore minerals in the arsenide pockets are safflorite and minor amounts of cobaltite and arsenopyrite. Some are present as irregular grains and rosettes, and some as a powder in calcite which gives the calcite a black appearance.

The silver sulphide pockets occur near the orebody. The main ore minerals in them are acanthite (Ag_2S), stephanite (Ag_5SbS_4), pyrargyrite (Ag_3SbS_3) and freibergite $(Cu,Ag,Fe)_{12}Sb_4S_{13}$, and associated minerals are chalcopyrite, marcasite, sphalerite, galena, arsenopyrite, cobaltite, and chalcocite. The minerals are present as irregular grains up to several millimeters in size, and are disseminated in fault gouge, calcite and red feldspar. Some grains are composed of one mineral and others of several minerals intimately intergrown.

Pockets containing the "Langis arsenide-sulphide assemblage" were found in several places in the ore vein below the orebody, and up to 300 feet from it. The ore minerals in these pockets occur as irregular grains, up to 1/2 inch in size, disseminated in calcite and fault gouge. The grains are composed of arsenides, sulphides and native bismuth. In most grains the native bismuth forms the core and is surrounded by sulphides. The sulphides are in turn surrounded by arsenides (Fig. 1), and the arsenides are bordered and veined by pyrite intergrown with marcasite. Some sulphides also occur as veinlets and irregular grains in the arsenides and the pyrite-marcasite intergrowths. The arsenides are safflorite, a cobalt monoarsenide, and maucherite; the sulphides are pyrite and marcasite intimately intergrown, bismuthinite, parkerite, cobalt pentlandite, siegenite, bravoite, late pyrite, chalcopyrite and sphalerite.

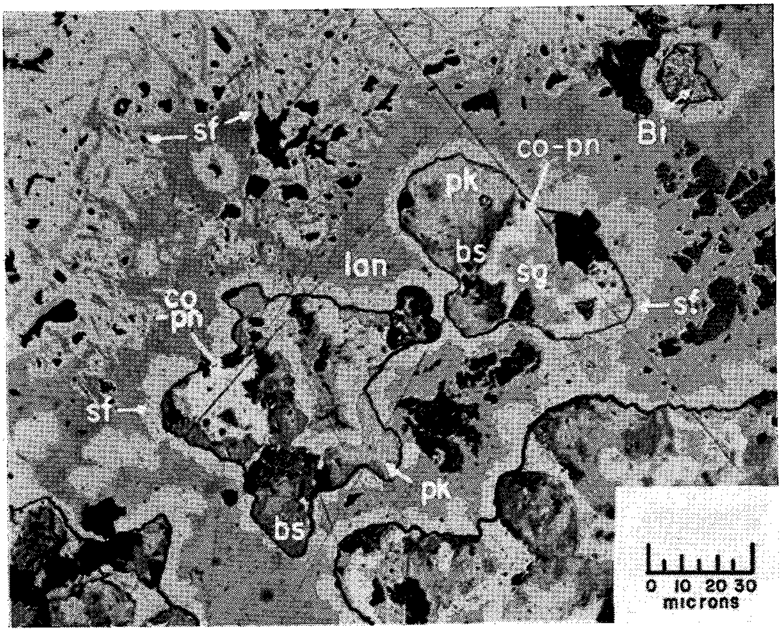

FIG. 1. Part of a grain containing the "Langis arsenide-sulphide assemblage." It consists of the main safflorite (sf, in upper left hand corner), safflorite (sf) borders around the sulphide grains, cobalt monoarsenide (langisite-lan), and the sulphide grains. The sulphide grains consist of parkerite (pk), cobalt pentlandite (co-pn) siegenite (sg) bismuthinite (bs) and native bismuth (Bi). The sulphide grains are outlined to enhance contrast.

ARSENIDES IN THE "LANGIS ARSENIDE-SULPHIDE ASSEMBLAGE"

The arsenides in the "Langis arsenide-sulphide assemblage" are safflorite, a cobalt monoarsenide and maucherite. The safflorite and maucherite are common to the Cobalt-Gowganda area but the cobalt monoarsenide is a new mineral.

Common Minerals

Safflorite $(Co,Ni,Fe)As_2$

The safflorite is present as irregular grains and narrow borders, up to 20 microns wide, around the sulphides (Fig. 1). The *irregular grain* safflorite contains feather-shaped inclusions of chlorite and the cobalt monoarsenide. Its composition is equivalent to $Co_{0.96}Ni_{0.04}As_{2.11}$. The *border* safflorite contains a few minute inclusions of niccolite and is surrounded by the cobalt monoarsenide. Its composition is variable, with the cobalt content decreasing, and the nickel content increasing towards the sulphide grains (Fig. 2). The average composition of several areas in this layer is equivalent to $Co_{0.46}Ni_{0.54}As_{1.82}$.

Maucherite $(Ni_{11}As_8)$

The maucherite was found only as small irregular grains in calcite, and it contains inclusions of siegenite.

New Mineral: Langisite $(Co_{0.8}Ni_{0.2}As)$

No naturally occurring cobalt monoarsenides have been previously reported; thus the one in this sample is considered to be a new mineral. Studies of synthetic CoAs by Heyding & Calvert (1957) have shown that at 700°C, CoAs has the orthorhombic FeAs structure, and that alloys whose compositions vary between $Co_{0.8}Ni_{0.2}As_{1.0}$ and NiAs have the hexagonal NiAs structure. The chemical composition of the monoarsenide in Vein 30 is equivalent to $Co_{0.84}Ni_{0.16}As_{1.04}$ (Table 1). Its *x*-ray powder diffraction pattern is similar to that of niccolite (NiAs) (Table 2), and its cell parameters, computed from the powder pattern, are $a = 3.538$ Å and $c = 5.127$ Å. This mineral, therefore, corresponds closely to the cobalt end-member of the solid-solution series NiAs-$Co_{0.8}Ni_{0.2}As_{1.0}$. Hence it is the cobalt analogue of niccolite. The name langisite is proposed for this mineral because it was found in the Langis mine. This name was approved by the Commission on New Minerals and Mineral Names, IMA on October 8, 1968. The type specimen has been deposited with the National Mineral Collection, Ottawa.

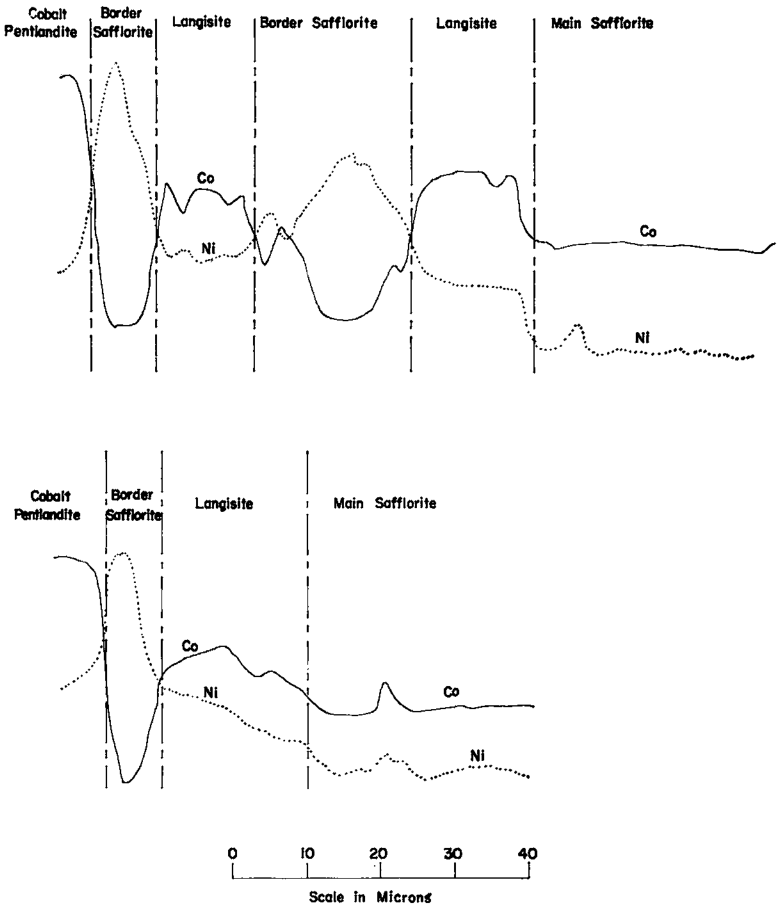

FIG. 2. Two electron-probe scans across the *border* safflorite and cobalt monoarsenide (langisite) for cobalt and nickel. The scans extend from cobalt pentlandite on one side to *irregular* (main) safflorite on the other side. (In the top scan the cobalt monoarsenide had an inclusion of border safflorite).

The langisite was found only as irregular grains and lamellae in safflorite. (Fig. 3). It is generally present near the sulphides, but most of it is separated from the sulphides by safflorite as discussed earlier (Figs. 1 and 2).

Langisite is pinkish-buff in reflected light, very weakly bireflecting and is moderately anisotropic with the polarization colours ranging from bluish-grey to light brown. The microhardness and reflectivity are given in Table 3, where they are compared to those of niccolite from the Silver

TABLE 1. ELECTRON-PROBE MICROANALYSIS OF LANGISITE AND NICCOLITE

Element	Langisite		Niccolite (Silver Bar Mine) ROM M12218	
	Wt. %	At. Prop.	Wt. %	At. Prop.
Co	35.5	0.835	0.2	0.005
Ni	7.0	0.165	45.1	0.993
Fe	—	—	0.1	0.002
As	56.0	1.036	57.1	0.985
Total	98.5		102.5	

TABLE 2. *X*-RAY DIFFRACTION DATA FOR LANGISITE AND NICCOLITE

Langisite Hexagonal $a = 3.538$, $c = 5.127$Å				Niccolite (Silver Bar Mine) ROM M12218 Hexagonal $a = 3.619$, $c = 5.027$Å			
I	*d*(meas)Å	*hkl*	*d*(calc)Å	*I*	*d*(meas)Å	*hkl*	*d*(calc)Å
2	3.065	100	3.064	4	3.135	100	3.134
10	2.631	101	2.632	10	2.656	101	2.659
9	1.966	102	1.966	7	1.956	102	1.960
8	1.770	110	1.770	6	1.809	110	1.810
4	1.493	103	1.493	3	1.495	201	1.496
3	1.470	201	1.468	3	1.477	103	1.477
3	1.315	202	1.315	5	1.328	202	1.329
2	1.282	004	1.282	2	1.254	004	1.256
3	1.141	203	1.141	4	1.151	211	1.153
2	1.129	211	1.130	2	1.144	203	1.144
2	1.055	212	1.055	5	1.071	212	1.072
1	1.038	114	1.038	2	1.045	300	1.044
3	1.022	300	1.022	4	1.033	114	1.032
1	0.959	213	0.959	3	0.969	213	0.967

Bar mine in the Cobalt area (Sample ROM M12218). A 16.5:1 objective with a numerical aperture of 0.40 was used for the reflectivity measurements. Attention is drawn to the rather pronounced differences in reflectivity dispersion and microhardness between the two minerals.

SULPHIDES IN THE "LANGIS ARSENIDE-SULPHIDE ASSEMBLAGE"

The sulphides in the "Langis arsenide-sulphide assemblage" consist of two sub-assemblages, one of pyrite and marcasite intimately intergrown and containing associated chalcopyrite and sphalerite, and the other of bismuthinite, cobalt pentlandite, siegenite, parkerite, bravoite, and late pyrite. The cobalt pentlandite, siegenite, parkerite and bravoite are rare

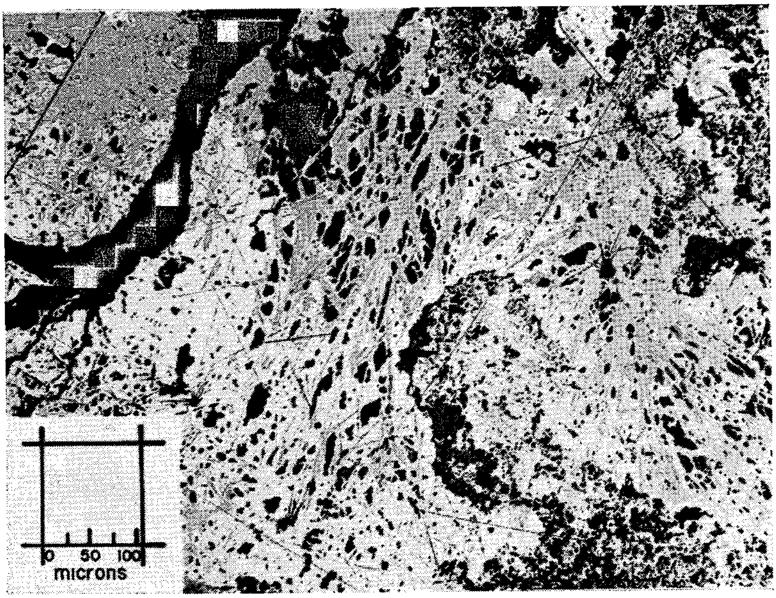

FIG. 3. Lamellae and irregular grains of langisite (grey) in safflorite (white).

TABLE 3. REFLECTIVITY AND MICROHARDNESS OF LANGISITE AND NICCOLITE

	Micro-hardness* VHN (in Kg/mm²)	Wave-length mμ	Reflectivity			
			Min. Refl. (%)		Max. Refl. (%)	
			Range	Av	Range	Av
		470	44.9–46.0	45.4	46.0–46.8	46.4
Langisite	780–857	546	46.1–46.8	46.4	46.7–47.4	47.1
(Two	825 (av)	589	47.1–47.7	47.5	47.9–48.7	48.2
crystals)		650	49.4–50.3	49.9	50.3–51.3	51.0
Niccolite Silver Bar Mine,		470	38.5–39.2	38.8	46.2–46.8	46.5
Cobalt, Ont.	362–376	546	48.9–49.1	49.0	52.6–52.9	52.7
Sample ROM	371 (av)	589	54.4–54.8	54.6	56.6–56.9	56.8
M12218 (Three crystals)		650	59.6–61.6	60.7	60.3–62.4	61.5

*50-gram load.

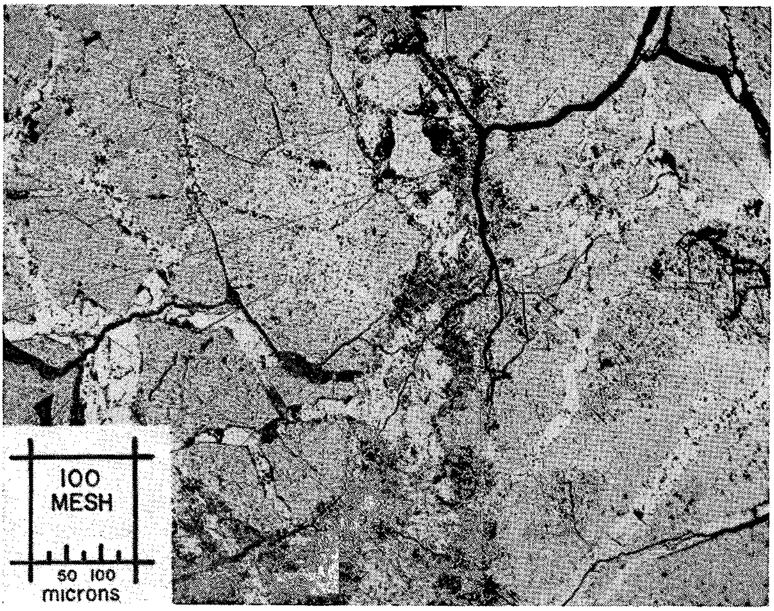

FIG. 4. Pyrite veinlets in pyrite-marcasite intergrowth.

minerals that have not been previously reported from the Cobalt-Gowganda area.

Common Minerals

Pyrite and Marcasite

Pyrites of two different ages were found and these will be referred to as early and late pyrite. The early pyrite is a constituent of the pyrite-marcasite sub-assemblage where it occurs as minute grains intimately intergrown with marcasite. The intergrowth occurs only as borders on arsenides and as veinlets in arsenides. Its composition is Fe 43.8%, Co 1.6%, S 48.5% and As 3.0%. This analysis suggests that the intergrowth may contain minute inclusions of an arsenide mineral, but no arsenide could be detected by *x*-ray diffraction.

The late pyrite is present as veinlets in the pyrite-marcasite intergrowth (Fig. 4), and narrow borders on bravoite.

Bismuthinite (Bi_2S_3)

Bismuthinite occurs near the cores of the grains referred to in Fig. 1 where it surrounds native bismuth, and is generally intergrown with parkerite.

Chalcopyrite and Sphalerite

The chalcopyrite and sphalerite are associated with the pyrite-marcasite intergrowth. They are present as minute grains and veinlets in the arsenides, pyrite-marcasite intergrowths and calcite.

Rare Minerals

Cobalt pentlandite (Co_9S_8)

Natural occurrences of cobalt pentlandite, the cobalt analogue of pentlandite, have been reported from several localities in Finland (Kouvo *et al.*, 1959), and from the Vauze mine in Quebec, Canada (Stumpfl & Clark, 1964). The discovery of this mineral in the Langis mine provides another locality for its occurrence. The cobalt pentlandites reported by Kouvo *et al.* (1959) have compositions that vary between the equivalents of $(Ni_{4.1}Co_{0.3}Fe_{4.3})S_8$ and $(Ni_{1.3}Co_{6.8}Fe_{1.5})S_8$; the one reported by Stumpfl & Clark has a composition corresponding to $(Co_{9.1}Fe_{0.2})S_8$; and the one in the Langis mine has the composition:

Element	Weight %	Atomic Prop.
Co	54.1	6.88
Ni	10.4	1.33
S	34.2	8.00
Total	98.7	

This composition is equivalent to $(Co_{6.9}Ni_{1.3})S_8$. The metal : sulphur ratio of 8.2:8 is considerably lower than any cobalt pentlandite previously reported.

Cobalt pentlandite is isostructural with normal pentlandite (Geller, 1962), and there is a complete solid solution between them. The cell parameters of the members in the solid-solution series decrease with increasing cobalt content (Knop & Ibrahim, 1961), although Knop *et al.* (1965) found that the cell parameters of synthetic pentlandites are larger than those of natural ones with equivalent compositions, and that the lattices of natural ones expand irreversibly upon heating. Consequently, the cell parameters of natural and synthetic samples cannot be related directly. The relationship between the cell parameters and cobalt contents of naturally occurring cobalt pentlandites, established from cell parameters reported by Kouvo *et al.* (1959) and from the cell parameter of the Langis cobalt pentlandite (9.937 Å) is given in Fig. 5.

The cobalt pentlandite is present in the arsenides and the pyrite-marcasite intergrowth. That in the arsenides occurs as veinlets and irregular grains either adjacent to or surrounding bismuth minerals, and

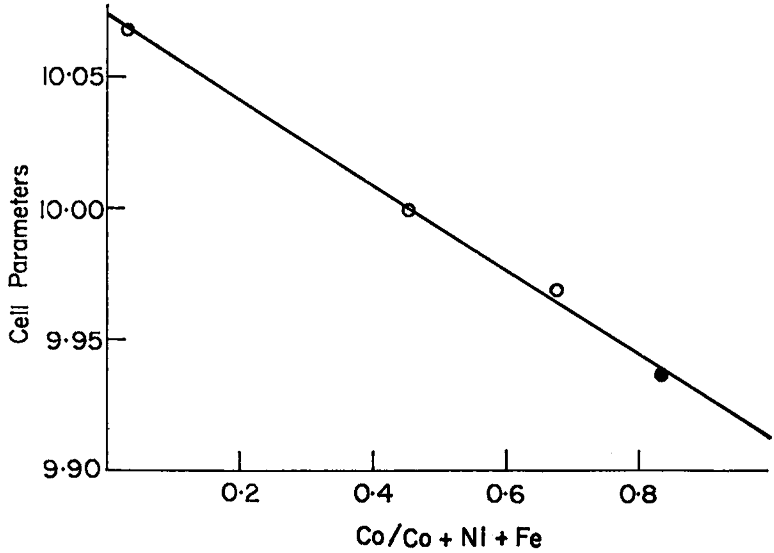

FIG. 5. Relationship between cell parameters and cobalt contents in natural cobalt pentlandites. ○ = from Kouvo *et al.*, 1959, ● = present study.

is intergrown with siegenite (Fig. 6). That in the pyrite-marcasite intergrowth is present as veinlets and as a constituent of cobalt pentlandite-siegenite grains (Fig. 7). Some textural relationships suggest that the cobalt pentlandite is replaced by siegenite, and others suggest that it replaces siegenite.

The reflectivity and microhardness of the Langis cobalt pentlandite are given in Table 4. Only one grain suitable for reflectivity measurements was found in the sample studied. Kouvo *et al.* have shown that the microhardness of cobalt pentlandite increases with increase in cobalt content, and this trend was confirmed by measurements on the cobalt pentlandite from the Langis mine (Fig. 8).

TABLE 4. REFLECTIVITY AND MICROHARDNESS OF COBALT PENTLANDITE

Microhardness† VHN (in Kg/mm²)	Reflectivity*	
	Wavelength mμ	%
	470	49.5
327–363	546	53.7
345 (av)	589	55.2
	650	57.2

*Only one crystal measured.
†25-gram load.

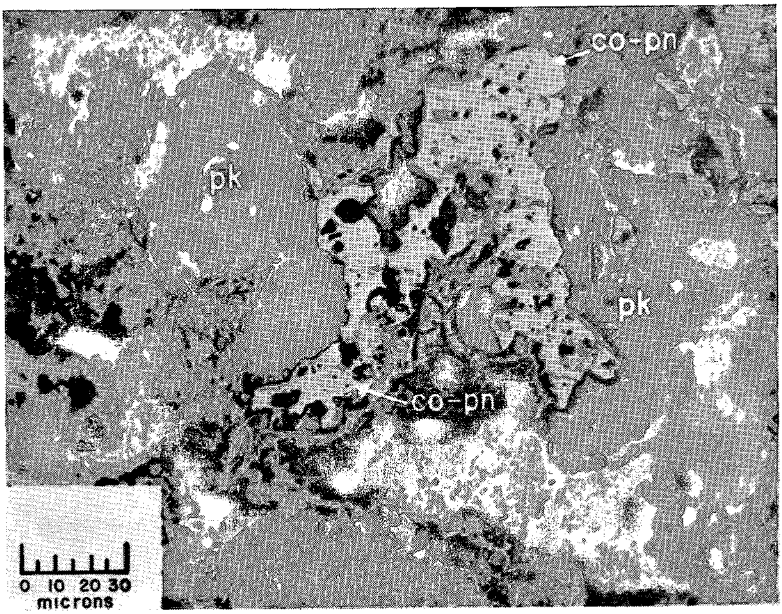

FIG. 6. A sulphide grain in arsenides. The sulphide grain consists largely of parkerite (pk) and cobalt pentlandite (co-pn).

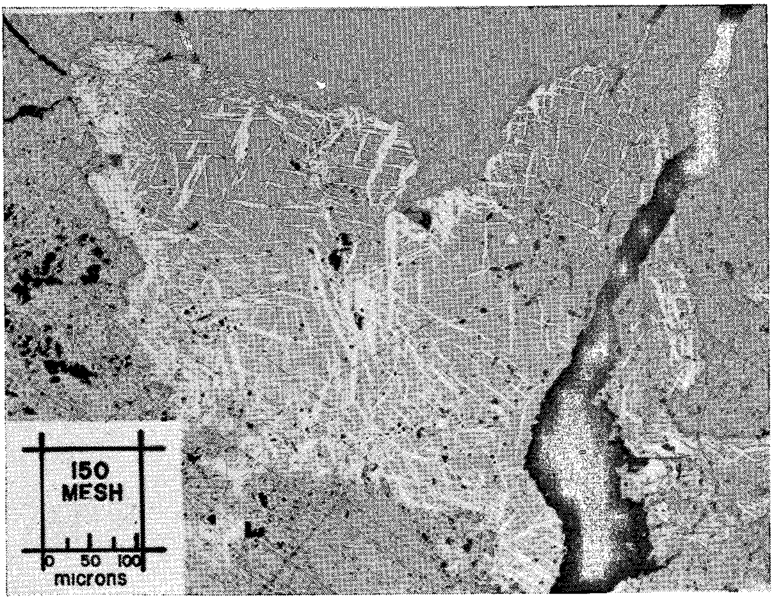

FIG. 7. A siegenite-cobalt pentlandite grain in pyrite-marcasite. The cobalt pentlandite is present as lamellae (white) in siegenite (light grey). The siegenite-cobalt pentlandite grain is partly rimmed by bravoite (dark grey).

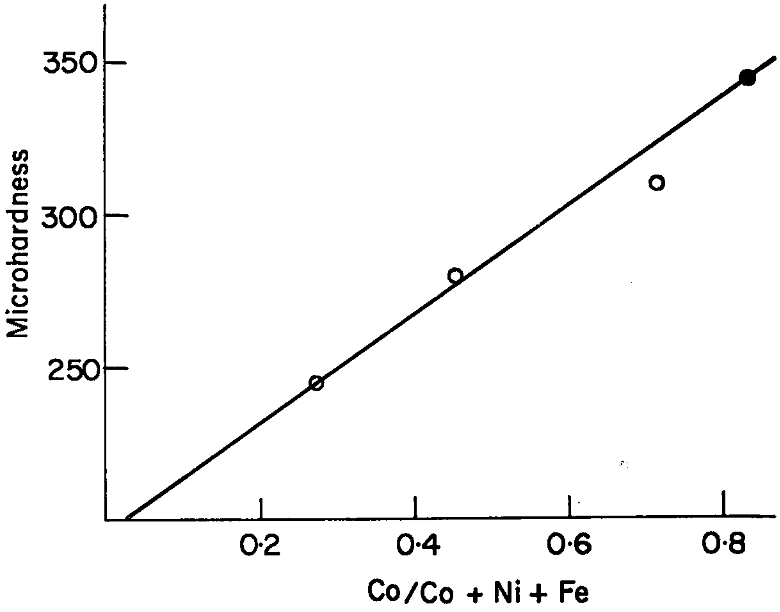

FIG. 8. Relationship between Vickers microhardness and cobalt content in natural cobalt pentlandites. ○ = from Kouvo *et al.* 1959, ● = present study.

Siegenite $(Co,Ni)_3S_4$

Minerals of the linnaeite series, $(Ni,Co,Fe)_3S_4$, are present in many veins in the Cobalt-Gowganda area. The siegenite, $(Co,Ni)_3S_4$, in Vein 30 in the Langis mine, however, is a cobalt-rich variety and no such siegenite has been previously reported (Vokes, 1967). In addition, cobalt pentlandites in all reported occurrences are associated with a mineral of the linnaeite series; thus the presence of siegenite in this occurrence is significant. Most of the siegenite in this occurrence is intimately intergrown with cobalt pentlandite (Fig. 1), although some is also present as separate grains. The chemical composition of that associated with cobalt pentlandite, is:

Element	Weight %	Atomic Prop.
Co	33.0	1.63
Ni	23.5	1.17
S	44.0	4.00
Total	100.5	

This composition corresponds to $Co_{1.63}Ni_{1.17}S_4$. The cell parameter of the siegenite is 9.428 Å. The microhardness and reflectivity values are given in Table 5. Only two grains were found to be suitable for measurement.

TABLE 5. REFLECTIVITY AND MICROHARDNESS OF SIEGENITE

Microhardness† VHN (in Kg/mm^2)	Reflectivity (%)*		
	Wavelength mμ	Range	Av.
437–514 464 (av.)	470	42.5–43.1	42.8
	546	44.9–45.4	45.3
	589	46.3–46.9	46.7
	650	47.6–49.0	48.5

*Two crystals measured.
†25-gram load.

Parkerite ($Ni_3Bi_2S_2$)

Parkerite is another rare mineral that was found in Vein 30 in the Langis mine. Only three other occurrences of this mineral have been reported: Insizwa, South Africa, (Scholtz, 1936); Sudbury, Ontario, Canada (Mitchener & Peacock, 1943); and Great Slave Lake, Northwest Territories, Canada (Thompson, 1951). The parkerite at Insizwa occurs in nickeliferous deposits and is associated with galena, native bismuth, niccolite, maucherite, pentlandite, chalcopyrite and sperrylite. The one at Sudbury occurs at the extremity of an orebody where it is associated with galena, native bismuth, niccolite, maucherite, pentlandite, chalcopyrite, sperrylite, bismuthinite, pyrrhotite, tetradymite, hessite, cubanite and gold. The parkerite in the Great Slave Lake area occurs as small inclusions in niccolite and is associated with native bismuth.

The parkerite from the Langis mine occurs as a component of sulphide grains within arsenides. The sulphide grains consist of bismuthinite, parkerite, native bismuth, cobalt pentlandite, siegenite and bravoite. The parkerite generally surrounds native bismuth, and is either intergrown with, or adjacent to, bismuthinite. In some places it is surrounded by cobalt pentlandite and siegenite, and in other places it is adjacent to these minerals (Figs. 1 and 6). The parkerite grains are up to 0.5 mm size.

Parkerite has an ideal composition corresponding to $Ni_3Bi_2S_2$, and it forms a complete solid solution with Ni_3BiPbS_2 (Peacock & McAndrew, 1950). The Langis parkerite does not contain any lead, thus its composition corresponds closely to that of the $Ni_3Bi_2S_2$ end member. The Sudbury parkerite was reported to contain a small amount of lead (Peacock & McAndrew) and the one from Insizwa, South Africa to contain a significant amount of lead (Du Preez, 1945, Cormack, 1948) (Table 6). The composition of the Insizwa parkerite, however, has been questioned by

TABLE 6. COMPOSITION AND CELL PARAMETER OF PARKERITE

	Langis		Sudbury		Insizwa			
			Reported		Reported		Cabri Sample	
	Wt. %	At. Prop.	Wt. %	At. Prop.	Wt. %	At. Prop.	Wt. %	At. Prop.
Ni	30.3	3.2	26.8*	3		3.0‡	29.7	3.2
Bi	60.1	1.8	63.6*	1.95		1.2‡	50.8	1.5
Pb	—	—	1.5†	0.05		0.8‡	9.5	0.3
S	9.1	1.9	9.2*	2.0		2.0‡	9.6	1.9
Total	99.5		101.1				99.6	
a	4.009 Å		4.03 Å*				4.031 Å	
b	5.541 Å		5.53 Å*				5.513 Å	
c	5.749 Å		5.73 Å*				5.712 Å	

*From Mitchener & Peacock 1943.
†From Peacock & McAndrew 1950.
‡From du Preez 1945.

Peacock & McAndrew (1950) because it was inferred from a spectrographic analysis of small samples that may have been contaminated with galena. A sample of the Insizwa parkerite from massive pyrrhotite ore at Insizwa, provided by Dr. L. J. Cabri of the Mines Branch who had obtained the sample from Prof. Scholtz, University of Stellenbosch, was analysed by means of the electron-probe microanalyzer. It was found to contain some lead but less than had been reported. The compositions, atomic proportions, and cell parameters for the parkerites reported to date are given in Table 6.

Parkerite is an orthorhombic mineral that is strongly bireflecting under the reflecting microscope, and is strongly anisotropic between crossed nicols. The microhardness and reflectivity of the material from the Langis mine and Insizwa are given in Table 7.

TABLE 7. REFLECTIVITY AND MICROHARDNESS OF PARKERITE

	Micro-hardness* VHN (in Kg/mm^2)	Wave-length mμ	Reflectivity			
			Min. Refl. (%)		Max. Refl. (%)	
			Range	Av.	Range	Av.
Parkerite		470	43.4–44.0	43.6	46.7–47.7	46.8
Cobalt	111–142	546	43.5–43.9	43.7	47.3–47.7	47.6
Ont.	125 (av.)	589	44.0–44.2	44.1	47.6–48.5	48.1
(4 grains)		650	45.2–46.2	45.7	48.0–50.1	49.7
		470	42.0–44.7	43.3	44.4–46.3	45.4
Parkerite		546	44.0–46.1	45.0	46.2–48.0	47.1
Insizwa		589	46.2–46.5	46.3	48.4–48.6	48.5
(2 grains)		650	47.5–47.6	47.5	49.5–49.6	49.5

*15-gram load.

Bravoite $(Co,Ni,Fe)S_2$

The mineral bravoite as generally understood refers to iron-nickel disulphides, but Kerr (1945) designated it as the intermediate member in the $(Fe,Ni,Co)S_2$ system. The Langis bravoite is generally cobalt-rich, but it has a variable composition and small amounts of nickel- and iron-rich varieties are present. Analyses of the cobalt-rich variety in two areas give compositions equivalent to $Co_{0.76}Ni_{0.22}Fe_{0.02}S_{1.86}$ and $Co_{0.76}Ni_{0.13}Fe_{0.11}S_{1.81}$ (Table 8). The nickel-rich variety was detected by means of an electron-probe microanalyser and approximate cell-parameter measurements, but the grains were too small for quantitative analysis. The iron-rich variety occurs as zoned bravoite (Fig. 9). A scan by means of an electron probe microanalyser, shows that the zoned bravoite is successively enriched in iron towards the outer layer with the outer layer being pyrite (Fig. 10). It is to be noted that the cobalt-rich bravoite has an appreciably lower sulphur content than the theoretical two atoms

Table 8. Electron-Probe Microanalysis of Bravoite

	Area I		Area II	
Element	Weight %	At. Prop.	Weight %	At. Prop.
Co	37.3	0.76	37.3	0.76
Ni	10.7	0.22	6.4	0.13
Fe	1.0	0.02	5.4	0.11
S	49.8	1.86	48.6	1.81
Total	98.8		97.7	

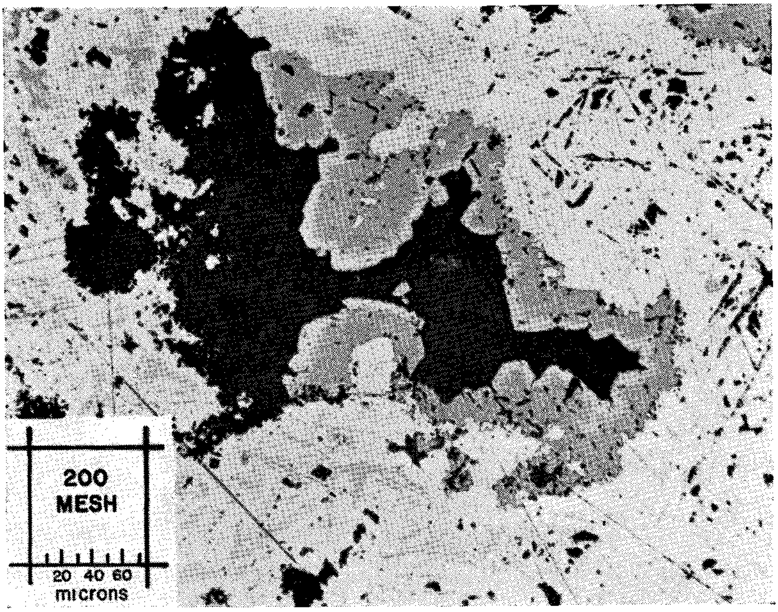

Fig. 9. A coating of layered bravoite on arsenides (white). A cobalt-rich layer (dark grey) is next to the arsenides, and an iron-rich one (lighter grey) borders it. The black area represents calcite.

per formula. However, the sulphur content was determined by using pyrite as a standard and is, therefore, considered to be reliable.

The bravoite in the Langis mine is present as veinlets and irregular grains in the pyrite-marcasite intergrowths, arsenides and cobalt pentlandite, and as zoned coatings on the pyrite-marcasite intergrowths and arsenides (Fig. 9). In contrast to pyrite it is grey in reflected light and has a lower reflectivity. Its reflectivity spectrum and microhardness could not be determined because homogeneous grains were too small to be measured. The cell parameter of a grain assumed to be the $Co_{0.76}Ni_{0.13}Fe_{0.11}S_{1.81}$ bravoite is 5.524 Å.

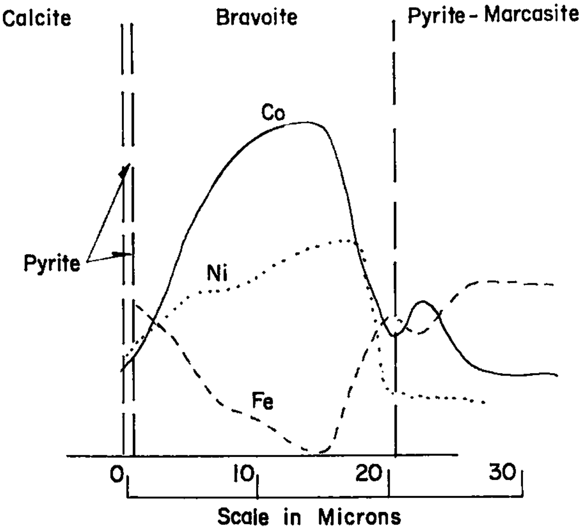

FIG. 10. Electron-probe scan across a layered bravoite for cobalt, nickel and iron. The scan extends from pyrite-marcasite to calcite.

DISCUSSION AND CONCLUSIONS

There are both differences and similarities in Vein 30 in the Langis mine with respect to those of other veins in the Cobalt-Gowganda area. The mineralogical features of the orebody and associated silver sulphides are similar to those in most ore veins, and the pockets of marcasite and arsenides in fault gouge and calcite are common features in most fault veins. The "Langis arsenide-sulphide assemblage," on the other hand, has not been found in any other vein. This suggests that the conditions that existed for ore deposition in the main part of the vein were similar to those that existed in other ore-bearing fault veins in the Cobalt-Gowganda area (report in preparation), whereas the conditions that produced the minerals in the "Langis arsenides-sulphide assemblage" appear to have been different.

The "Langis arsenide-sulphide assemblage" consists of sub-assemblages of arsenides, pyrite-marcasite, and sulphides with associated native bismuth. Interpretations of textural relationships show that the sub-assemblages were deposited in the order given above, and analyses show that most of the minerals in the sub-assemblages are enriched in cobalt. The arsenide sub-assemblage, the first to be deposited, consists of safflorite, langisite, and maucherite. Langisite is a new mineral corresponding to the cobalt analogue of niccolite. Textures suggest that it has a similar relationship to safflorite as late niccolite has to arsenides in other veins. This indicates that the conditions for deposition of langisite were similar to those for deposition of late niccolite in other veins but the amount of available nickel was lower.

Interpretations of textural relationships show that the sub-assemblage of pyrite intergrown with marcasite was the second one to be deposited, and that some chalcopyrite and sphalerite were also deposited at this time.

The sub-assemblage of sulphides and associated native bismuth was deposited during a final period of mineralization at the cores of grains and as veinlets in arsenide and pyrite-marcasite. This sub-assemblage consists of a variety of minerals including the rare minerals, parkerite, cobalt pentlandite, siegenite and bravoite. The parkerite corresponds to the bismuth end-member of the $Ni_3Bi_2S_2$-Ni_3BiPbS_2 isostructural series. The cobalt pentlandite and siegenite are cobalt-rich varieties, and the bravoite is generally cobalt-rich, but some is enriched in iron and is zoned. Interpretations of textural relationships show that the minerals of this sub-assemblage were deposited in the following sequence; native bismuth, bismuthinite, parkerite, cobalt pentlandite, siegenite, homogeneous bravoite, zoned bravoite and late pyrite. This gives the elemental sequence of deposition as bismuth, nickel, cobalt, iron. The sequence cobalt pentlandite, siegenite, bravoite and the presence of zoned bravoite corresponds to experimental observations made by Springer *et al.* (1964). They showed that deposition from ore solutions followed the sequence NiS, Ni_3S_4, NiS_2 and CoS, Co_3S_4, CoS_2, and that slight changes in the concentrations of the ore solutions surrounding bravoite gave rise to zoned bravoite (p. 485). It is to be noted that the sulphur:metal ratios in cobalt pentlandite, siegenite and bravoite are different from the theoretical. In cobalt pentlandite and siegenite it is higher than theoretical and in bravoite it is lower. This suggests that the fugacity of sulphur changed as the minerals were being deposited.

The presence of native bismuth and bravoite in the sub-assemblage of sulphides and associated native bismuth suggests that the native bismuth, bravoite and associated sulphides were deposited at low temperatures. Native bismuth melts at 271°C. Iron and nickel bravoites are metastable phases that break into the end members upon heating (Kullerud, 1962), and it is inferred that the cobalt-rich bravoite found in this deposit is a similar metastable phase.

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