IGOR ROJKOVIČ*

COBALT-NICKEL ARSENIDES AND SULFARSENIDES OF SOME U-Co-Ni-Bi-Ag VEINS AT GREAT BEAR LAKE, CANADA

(Figs. 1—17)

Abstract: Cobalt-nickel arsenides and sulfarsenides are widespread minerals of U-Co-Ni-Bi-Ag veins at Great Bear Lake area. Ore microscopy, X-ray powder diffraction and electron microprobe study have proved the following minerals of this group: niccolite, maucherite, rammelsbergite, safflorite, skutterudite, gersdorffite and cobaltite. They occur in the close association with the native silver. They followed pitchblende and preceeded sulfides in the sequence of the ore mineralization.

Резюме: Арсениды и сульфоарсениды кобальта и никеля являются широко распространенными минералами U-Co-Ni-Bi-Ag жил в области Большого Медвежьего озера (Канада). Микроскопически, рентгенографически, а также методом электронового микрозондирования были исследованы следующие минералы этой группы: никелин, маухерит, раммельсбергит, саффлорит, скуттерудит, герсдорфит и кобальтин. Они выходят в узком парагенезисе со самородным серебром. Их образование произошло после осаждения урановой смолки и предшествовало минерализации сульфидов.

This paper presents the part of the results achieved during a mineralogical study of ores from McTavish Arm area, Great Bear Lake. The most complex suite of cobalt-nickel arsenides and sulfarsenides was observed at Echo Bay Mines property, less at the Eldorado Mine on LaBine Point and properties on Contact Lake and on Camsell River, 10 miles southeast and 35 miles south of LaBine Point, respectively.

Mineralogical study of U-Co-Ni-Bi-Ag veins permits subdivision into at least five distinct stages of mineralization:

1. Hematite with quartz.
2. Pitchblende.
3. Cobalt-nickel arsenides and sulfarsenides with native silver I.
4. Base metal sulfides, silver minerals and bismuth minerals.
5. Supergene minerals.

The above mentioned assemblages and depositional sequence of ore minerals are in general agreement with those of D. F. Kidd and M. H. Haycock (1935) and D. D. Campbell (1955, 1957), except for the position of the silver minerals. Differences in the depositional sequence are the subject of the separate paper.

Cobalt-nickel arsenides and sulfarsenides are widespread and abundant in the deposits studied. They occur mainly as zonal rims or multilayered sequence of several phases, usually around cores of silver or niccolite, less around wall-rock fragments.

The patterns displayed by the rims mentioned above closely correspond to typical native silver dendrites. This feature was explained by D. F. Kidd and M. H. Haycock (1935) as follows: „Native silver has been introduced into the central portions of skeletal dendrites of safflorite-rammelsbergite.“ However, observations to

* RNDr. I. Rojkovič, CSc., Geological Institute of Slovak Academy of Sciences, Bratislava, Štefánikova ul. 41.

be presented later indicate that at least part of native silver preceeded deposition of arsenides. Accordingly the rims are regarded as having been formed on dendritic silver. This succession is very similar to those described at Cobalt, Canada (W. P e t r u k 1968) and at Jáchymov, Czechoslovakia (F. M r ň a and D. P a v l ů 1967).

Several mineralogical types of rims were noted in the samples examined (in each case the core mineral is listed the first):

a) native silver-rammelsbergite-safflorite
b) native silver-skutterudite-niccolite-rammelsbergite-safflorite
c) native silver-niccolite-rammelsbergite-safflorite
d) native silver-niccolite-gersdorffite
e) niccolite-rammelsbergite-safflorite
f) niccolite-gersdorffite.

The detailed characteristic of these types is as follows:

a) Rammelsbergite-safflorite rims around native silver were encountered mostly in the samples from Eldorado and Echo Bay Mines. Dendrites and cubic crystals of native silver, or silver minerals auch as acanthite or polybasite, which have replaced pseudomorphously native silver, are rimmed by rammelsbergite. This is succeeded by a safflorite zone, or by several alternating thin bands of safflorite and rammelsbergite (Fig. 1). Usually the outermost part of the rim is safflorite. In general, the proportion of safflorite increases towards the outer part of the aggregate.

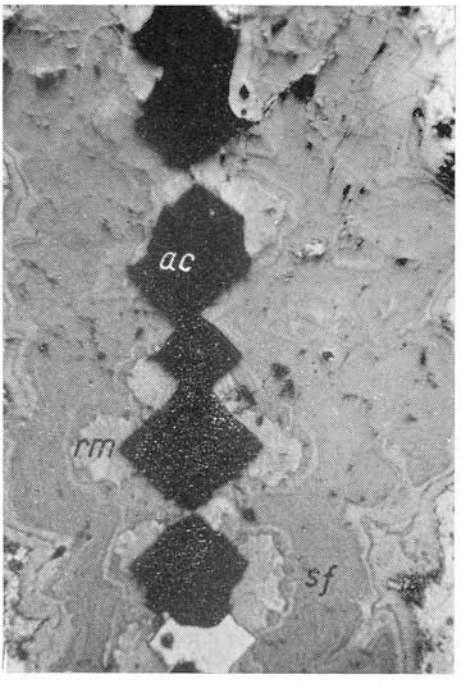

Fig. 1. Acanthite (ac) pseudomorphs after native silver with rammelsbergite (rm) and safflorite (sf) rims. Carbon coated, one nicol, 200 ×. Photo I. R o j k o v i č.

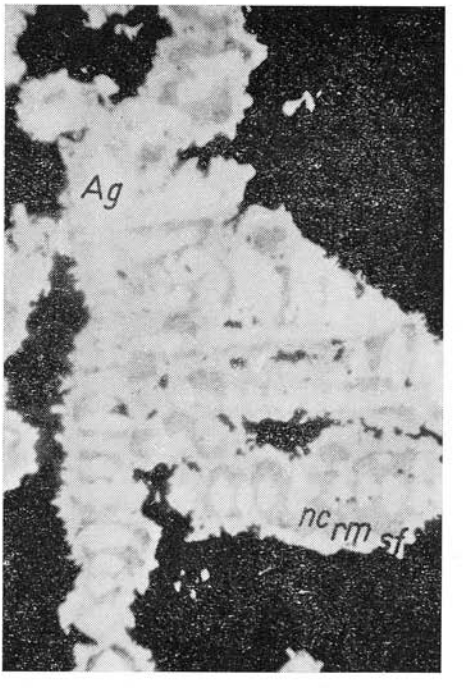

Fig. 2. Native silver dendrites (Ag) with niccolite (nc), rammelsbergite (rm) and safflorite (sf) rims. One nicol, 200 ×. Photo I. R o j k o v i č.

b) Skutterudite-niccolite-rammelsbergite-safflorite rims have the same general textural character as the last described type, but here niccolite is sparsely included with rammelsbergite, while skutterudite is intergrown, partly as conformal layers within the sequence, with rammelsbergite and safflorite.

c) Niccolite-rammelsbergite-safflorite rims are the most abundant in the samples from Camsell River and Echo Bay Mines properties. Silver in cubic crystals, long dendrites and cruciforms is rimmed successionaly by niccolite and by relatively thin layers of rammelsbergite and safflorite (Fig. 2). Again safflorite is concentrated in the outermost parts.

d) Niccolite-gersdorffite rims similarly comprise alternate zones of these minerals (Fig. 3). Gersdorffite predominates as thinner bands towards the outsides of the rims less against silver.

e) Rammelsbergite-safflorite form zonal rims around concentric niccolite. Safflorite represents the outermost zone or in the case of thin alternating bands of rammelsbergite and safflorite, the proportion of safflorite increases towards the outer part of the aggregate.

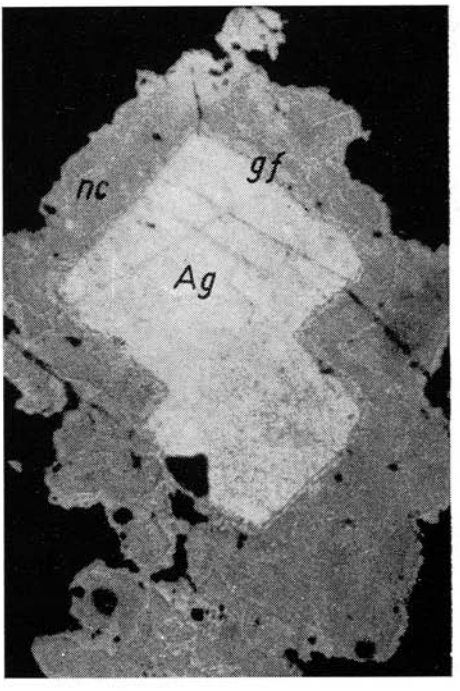

Fig. 3. Crystals of native silver (Ag) with niccolite (nc) and gersdorffite (gf) rims. One nicol, 400 ×. Photo I. R o j k o v i č.

f) Gersdorffite forms thin rims around niccolite cores. The alternating bands of niccolite and gersdorffite around niccolite cores are less widespread.

As was mentioned before, arsenides and sulfarsenides form also multilayered sequence of several phases around the niccolite cores. The main mineral of the multilayered aggregates is niccolite, but maucherite is quite abundant in several samples from Echo Bay Mines property (Fig. 4). The two minerals are commonly separated by relatively

thin zones of rammelsbergite and safflorite and the outermost zone is made up of gersdorffite (Fig. 5).

The zonal aggregates of cobalt-nickel arsenides and sulfarsenides also occur around fragments of siliceous wall-rock in carbonate gangue. Such rims consist of niccolite zones alternating with rammelsbergite and safflorite, and the outermost part is a thin rim of gersdorffite. Niccolite contains also intergrown maucherite.

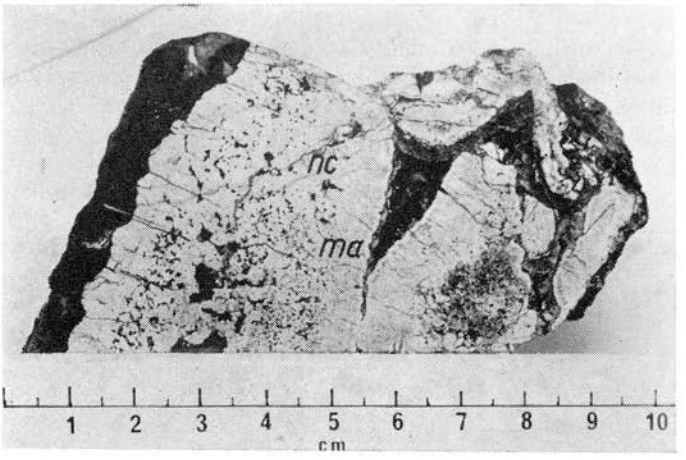

Fig. 4. Zonal aggregate of arsenides mainly niccolite (nc) and maucherite (ma). Polished sample. Photo I. R o j k o v i č.

In a few cases evidence for cataclasis was found. Fragments of zonal arsenides occur in a carbonate gangue with chalcopyrite and silver sulfosalts, suggesting local brecciation of arsenides before deposition of sulfides. All cobalt-nickel arsenides and sulfarsenides in the samples studied are veined and enclosed by numerous sulfides and other minerals. This places them in an earlier stage of mineralization than sulfides. However, they are distinctly younger than pitchblende which they cut and replace.

Niccolite $Ni_{1\pm x}As$ forms small (approximately 100 microns) more or less concentric aggregates with internal radiated texture. These are often rimmed by rammelsbergite and safflorite. Niccolite occur also as bands in multilayered aggregates of cobalt-nickel arsenides and sulfarsenides. Size of these aggregates goes to several centimeters. The radiated texture is typical for rims around silver, especially in the case of thinner zones and also in thicker bands alternating with other arsenides (Fig. 6). In some cases niccolite does not form thin rims around native silver, but rather large radiated or leaf-like aggregates with centres on silver.

The compositional departure of niccolite from stoichiometric NiAs was delimited for synthetic specimens by R. A. Y u n d (1961), who proposed the formula given above. Similar non-stoichiometry for natural niccolites was confirmed by C. H a l l s and E. F. S t u m p f l (1969) in ores from Cobalt, Ontario.

In the Great Bear Lake ores three distinct compositional groups were observed. Niccolite in alternating bands show an antimony content up to 4 weight percent. However, in the inner parts of zonal aggregates more or less concentric aggregates of niccolite about 1 milimetre across with a radiated internal texture are found which

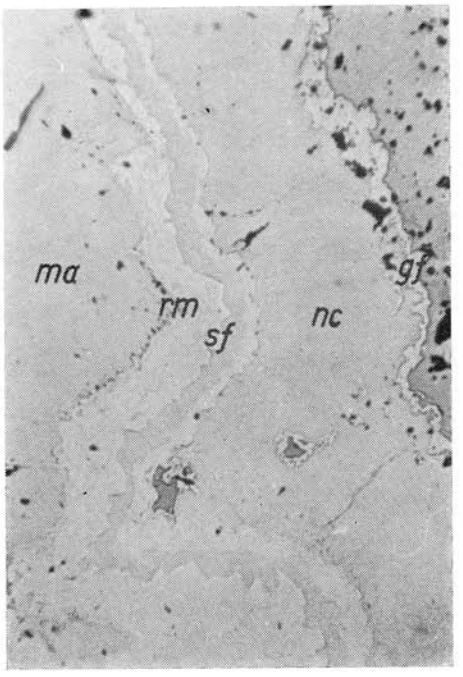

Fig. 5. Alternating zones of maucherite (ma), rammelsbergite (rm), safflorite (sf), niccolite (nc) and gersdorffite (gf). One nicol, 200 ×. Photo I. Rojkovič.

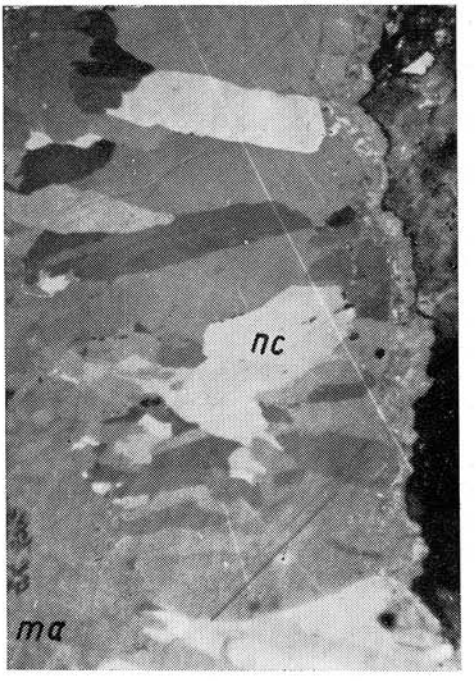

Fig. 6. Radiated texture of niccolite within niccolite zone (nc). Niccolite is in direct contact with maucherite (ma). Crossed nicols, 200 ×. Photo I. Rojkovič.

have a higher content of antimony (about 7 percent), than the surrounding niccolite. These aggregates are separated from the enclosing niccolite by thin safflorite rims. An increase of cobalt content outwards within such polymineralic aggregates is shown not only by presence of safflorite rims but also by a cobalt-rich zone at the boundary with safflorite. This relatively thin zone (approximately 50—100 microns in thickness) can not be distinguished in untreated polished sections. However carbon coating and electron beam scanning show clearly the compositional differences (Fig. 7, 8). A further mode of occurence for niccolite is as tiny veinlets in niccolite and maucherite (Fig. 9). This is the purest niccolite found in the samples studied and its composition is sensibly stoichiometric (Table 1). The relatively low contents of minor elements do not produce any marked change in the X-ray powder diffraction patterns (Table 2).

Corrections for electron microprobe data were calculated for atomic number factor (P. Duncomb and S. J. Reed 1968), fluorescence (S. J. Reed 1965) and absorbtion (J. A. Philibert 1963) emplying a Fortran computer program written by Dr. M. I. Corlett.

Maucherite $Ni_{11}As_8$ was found only in samples from the Echo Bay Mines property. It is less widespread than niccolite, but is locally abundant, mostly az zones alternating with other arsenides, or irregularly intergrown with niccolite. Zones of maucherite with

internal radiated texture alternate either with niccolite or are separated from niccolite by thin zones of rammelsbergite and safflorite (Fig. 6, 10).

Experiments performed by R. A. Y u n d (1961) indicated only very slight departures from stoichiometric $Ni_{11}As_8$, contrary to the earlier reported $Ni_{12-x}As_8$ (M. A. P e a c o c k 1941). The Great Bear Lake samples all lie close to this formula (Table 3) and their X-ray powder diffraction patterns also correspond to data from literature (Table 4).

Rammelsbergite $NiAs_2$ is the nost intimately associated with safflorite in zonal aggregates or rims around native silver and niccolite. In both cases it forms towards the inner part of the rammelsbergite-safflorite zones (Fig. 1, 5, 11). Here rammelsbergite is composed of interlocking grains, commonly sharing radiated textures and twinnings. In some cases two different textural types may be differentiated. Rammelsbergite in the outer part of such zones comprises radiated intergrowths of bladed, and in part skeletal crystals, whereas the inner portions are formed of fine-grained aggregates of irregularly formed grains.

The composition of rammelsbergite, according to R. A. Y u n d (1961) and E. H. R o s e b o o m (1963) is very near $NiAs_2$. Analyses of samples from Great Bear Lake show them to be close to stoichiometric $NiAs_2$, within the limit of analytical error (Table 5). The analyses show less variability than those of safflorite. The content of minor elements rarely exceeds one percent, except for a few values for cobalt (Fig. 12).

Safflorite (Co, Fe, Ni)As_2 occurs in the Great Bear Lake samples mainly in zonal

Fig. 7. Antimony-rich niccolite (Sb-nc) and cobalt-rich niccolite (Co-nc) rimmed by safflorite (sf). Carbon coated, one nicol, 200 ×. Photo I. R o j k o v i č.

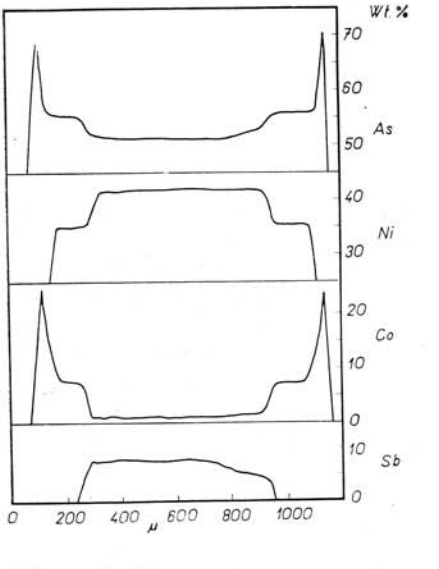

Fig. 8. Microprobe K^{α} intensity profile adjusted to weigh percent. Cobalt-rich and antimony-rich zones in niccolite, rimmed by safflorite (see Fig. 7).

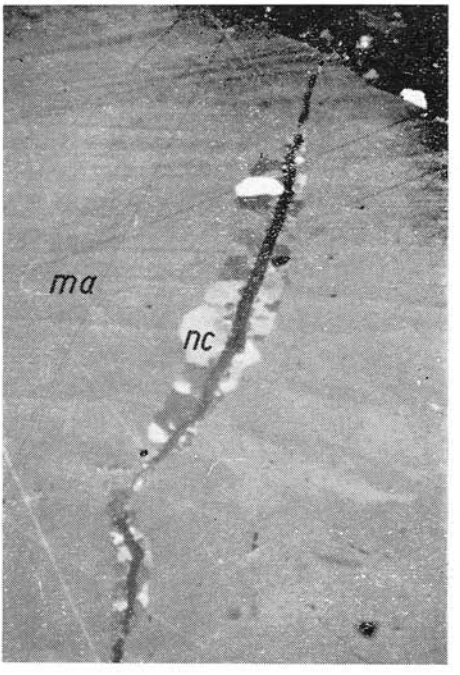

Fig. 9. Niccolite (nc) replacing maucherite (ma) along thin carbonate veinlet. Crossed nicols, 200 ×. Photo I. Rojkovič.

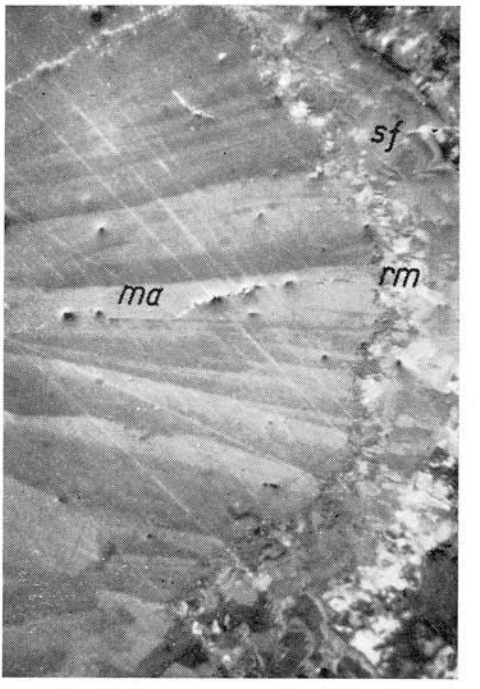

Fig. 10. Radiated texture of maucherite (ma) succeded by rammelsbergite (rm) and safflorite (sf) zones. Crossed nicols 200 ×. Photo I. Rojkovič.

aggregates and in rims around native silver along with other cobalt-nickel arsenides particularly rammelsbergite (Fig. 1, 5, 11). Star-shaped twins (W. Uytenbogaardt 1968, „Saffloritsternchen" after P. Ramdohr 1960) occur sporadicaly in gangue. Safflorite grains are commonly enclosed in skutterudite and, in some cases, together with rammelsbergite, replace skutterudite completely, forming pseudomorphs, retaining the imprint of the zonal skutterudite and cleavage of that mineral.

Homogeneous cobalt safflorite (term used by E. H. Roseboom 1963) was synthetized by E. H. Roseboom (1963) with the composition range $CoAs_{1\text{-}98\ 1\text{-}99}$. However, analyses of natural diarsenides by E. H. Roseboom (1963) as well as those by D. Radcliffe and L. G. Berry (1968), indicate rather variations in metallic elements. E. H. Roseboom (1963) established complete miscibility between $CoAs_2$ and $NiAs_2$ and between $CoAs_2$ and $FeAs_2$ at 800 °C. The miscibility between $NiAs_2$ and $FeAs_2$ was broken by a solvus lying closer to $NiAs_2$. In natural assemblages, there is an apparent complete absence of members along the $FeAs_2$-$NiAs_2$ join (D. Radcliffe and L. G. Berry 1968).

The $FeAs_2$ content in the analysed safflorites does not exceed either the 50 mole percent limit proposed by E. H. Roseboom (1963) for safflorite, or the 70 mole percent of R. J. Holmes (1947). Thus they may be termed safflorite, sensus stricto. The analyses show extended solid solution between $CoAs_2$ and $NiAs_2$ as well as between

Table 1. Electron microprobe results on niccolite

No.	Weight percent Ni	Co	As	S	Sb	Total
NiAS	43,9		56,1			100,0
1	44,1	0,6	50,1	0,5	4,0	99,3
2	44,0	0,6	50,5	0,5	4,0	99,6
3	44,0	0,4	56,5	0,1	0,0	101,0
4	43,9	0,4	56,8	0,1	0,0	101,2
5	41,5	1,4	51,1	0,2	6,8	101,0
6	35,4	7,1	56,1	0,9	0,4	99,9
7	42,4	1,2	54,5	0,2	1,8	100,1
8	42,4	1,4	53,2	0,2	1,8	99,0
9	42,9	1,2	53,4	0,2	1,8	99,5
No.	Atomic percent Ni	Co	As	S	Sb	Total
1	50,8	0,7	45,2	1,1	2,2	100,0
2	50,6	0,7	45,5	1,1	2,2	100,1
3	49,5	0,4	49,8	0,2	0,0	99,9
4	49,3	0,4	50,0	0,2	0,0	99,9
5	48,0	1,6	46,3	0,4	3,8	100,1
6	40,0	8,0	49,8	1,9	0,2	99,9
7	48,4	1,4	48,8	0,4	1,0	100,0
8	48,9	1,6	48,0	0,4	1,0	99,9
9	49,2	1,4	48,0	0,4	1,0	100,0

No.	Atomic percent Ni + Co	As + Sb + S	Atomic proportion Ni	As
1	51,5	48,5	1,06	1,00
2	51,3	48,8	1,05	1,00
3	49,9	50,0	1,00	1,00
4	49,7	50,2	0,99	1,00
5	49,6	50,5	0,98	1,00
6	48,0	51,9	0,92	1,00
7	49,8	50,2	0,99	1,00
8	50,5	49,4	1,02	1,00
9	50,6	49,4	1,02	1,00

No.	Sample	Close association	Remarks
1	**EB-2-09-5	ma*, sf, rm	More external zone
2	EB-2-09-5	ma, sf, rm	More internal zone
3	EB-3-05-5	ma	Veinlet
4	EB-3-05-5	ma	Veinlet
5	EB-3-05-5	Co-nc, sf	Radial aggregate
6	EB-3-05-5	Sb-nc, sf	Rim around Sb niccolite
7	EB-3-05-5	ma, sf, rm	Zonal aggregate
8	EB-2-18-1	Ag, rm, sf	Radial aggregate around Ag-dendrite
9	EB-2-18-2	Ag, rm, sf	Radial aggregate around Ag-dendrite

* Abbreviations of more common minerals after F. M. Chace (1956), ma = maucherite
** EB = Echo Bay Mines, EL = Eldorado Mine, CR = Camsell River, CL = Contact Lake

Table 2. X-ray powder differection on niccolite

1		2		3			
I	d	I	d	1	d	hkl	d(calc.)
1	3,13	1	3,14	1	3,14	$10\bar{1}0$	3,125
10	2,66	10	2,66	10	2,66	$10\bar{1}1$	2,653
9	1,961	9	1,961	9	1,961	$10\bar{1}2$	1,957
7	1,813	8	1,811	8	1,811	$11\bar{2}0$	1,805
2	1,494	2	1,498	2	1,497	$20\bar{2}1$	1,493
3	1,480	3	1,480	2	1,475	$10\bar{1}3$	1,475
2	1,329	3	1,330	3	1,328	$20\bar{2}0$	1,327
1	1,258	1	1,258	1	1,256	$00\bar{0}4$	1,255
1	1,151	2	1,153	2	1,152	$21\bar{3}1$	1,150
1	1,146	1	1,146	1	1,142	$20\bar{2}3$	1,142
2	1,071	3	1,072	4	1,071	$21\bar{3}2$	1,069
—	—	1	1,045	2	1,043	$30\bar{3}0$	1,042
2	1,034	2	1,034	3	1,033	$11\bar{2}4$	1,030

1 Sample: EB-3-05-5 Sb and Co-rich niccolite aggregates
2 EB-2-09-5 Niccolite zone in zonal aggregate of arsenides
3 L. G. Berry and R. M. Thompson (1962)

Table 3. Electron microprobe results on maucherite

	Weight percent				
No.	Ni	Co	As	S	Total
$Ni_{11}As_3$	51,85		48,15		100,00
1	51,2	1,1	48,4	0,2	100,9
2	51,4	0,5	48,1	0,2	100,2
	Atomic percent				
No.	Ni	Co	As	S	Total
1	56,5	1,2	41,9	0,4	100,0
2	57,1	0,6	41,9	0,4	100,0

	Atomic percent		Atomic proportion	
No.	Ni + Co	As + S	Ni	As
1	57,7	42,3	10,91	8,00
2	57,7	42,3	10,91	8,00

No.	Sample	Close association
1	EB-2-09-5	nc, rm, sf
2	EB-3-05-5	nc, rm, sf

Table 4. X-ray powder diffrection on maucherite

1		2		3			
I	d	I	d	I		hkl	d(calc.)
1	3,05	1	3,05	1	3,04	120	3,06
10	2,69	9	2,69	9	2,69	008	2,72
4	2,37	2	2,37	2	2,37	222	2,36
9	2,01	10	2,02	10	2,01	226	2,01
2	1,970	2	1,970	2	1,977	029	1,975
3	1,899	3	1,899	3	1,899	230	1,901
2	1,814	2	1,817	2	1,814	0.0.12	1,813
10	1,714	10	1,714	10	1,713	040	1.713
3	1,621	3	1,621	3	1,621	2.2.10	1,619
1	1,503	2	1,506	2	1,503	0.2.13	1,504
5	1,449	5	1,449	5	1,449	048	1,450
1	1,363	1	1,363	1	1,361	0.0.16	1,360
—	—	—	—	0,5	1,299	$24\bar{9}$	1,295
—	—	—	—	1	1,247	0.4.12	1,245
						440	1,211
5	1,212	5	1,212	6	1,212	2.4.11	1,211
—	—	—	—	0,5	1,202	0.2.17	1,198
3	1,132	3	1,133	4	1,133	2.4.13	1,130
4	1,108	4	1,109	5	1,108	448	1,106
4	1,081	4	1,083	5	1,083	0.0.20	1,088
						2.2.18	1,081
2	1,068	2	1,068	4	1,068	0.4.16	1,065
2	1,039	2	1,039	3	1,039	266	1,038

1 Sample: EB-3-05-5
2 EB-2-09-5
3 L. G. Berry and R. M. Thompson (1962)

$CoAs_2$ and $FeAs_2$ end-members (Table 5, Fig. 12), but very limited solid solution between $NiAs_2$ and $FeAs_2$.

Skutterudite (Co, Ni, Fe) As_{3-x} forms coarse, subhedral aggregates with a zonal texture emphasised by cleavage. This mineral also occurs in the inner parts of rims around native silver or silver sulfides pseudomorphous after silver (Fig. 13, 14). Skutterudite is mostly replaced by safflorite and rammelsbergite, which retain the form of the original zoned grains.

R. J. Holmes (1947) criticized the formula accordingly C. Palache et al. (1944) for skutterudite (Co, Ni) As_{3-x} with x ranging from zero to 0.5 for nickel skutterudite and from 0.5 to 1 for cobalt skutterudite. R. J. Holmes (1947) suggested arsenic-defficiency for formula $As_{2.95-3.00}$. Lower arsenic ratio in previous analyses R. J. Holmes regards as contamination. This is also supported by E. H. Roseboom's (1962) experimental studies. However, as the latter author pointed out, the detection of additional phases in natural specimens is difficult, even with the aid of X-ray powder diffraction. D. D. Klemm's (1965) 140 electron microprobe analyses of natural skutterudites show a variation in the metal-arsenic ratio between 1 : 1.9 to 1 : 3.3. According to D. Radcliffe (1967), who criticized these results, this large variation was probably caused by the presence of safflorite, which remained undetected.

In the samples studied skutterudite nearly always contains safflorite and rammelsbergite. For electron microprobe analysis, only grains of opticaly homogeneous skutterudite

were used. Most of the analyses fall below a range (Co, Ni, Fe) $As_{2\cdot95-3\cdot00}$, with arsenic defficiency in formula down to 0.3 (Table 6). The analysed skutterudites show interesting relations between cobalt, nickel and iron. Zoned skutterudite rims around native silver show trends similar to those found in safflorite and rammelsbergite, with the proportion of cobalt increasing away from the silver core. Generally, most skutterudites analysed have Ni : Co ratios close to 1 : 1. The Co : Ni ratio shows a distinct increase towards the outer part of arsenide rims, together with a less significant nonetheless dictinct increase in iron in the same direction (Fig. 15). These relationships suggest similar conditions prevailed the deposition of both diarsenides and triarsenides.

Gersdorffite NiAsS. The samples studied showed several different modes of occurence for gersdorffite accompanied by slight variations in the composition of the mineral. Gersdorffite was formed in the zonal aggregates or rims around native silver and niccolite, largely in their outermost part (Fig. 3,5). This gersdorffite most closely approaches the composition NiAsS, except for small contents of cobalt and iron (Table 7). In addition, gersdorffite occurs as rims around cobaltite crystals disseminated in carbonate gangue (Fig. 16). Such gersdorffite shows higher content of antimony and part of it compositionaly corresponds to corynite (Fig. 17). Gersdorffite occurs also replacing skutterudite. In this case analyses show a small but obvious excess of arsenic, equivalent to $NiAs_{1\cdot10}S_{0\cdot90}$.

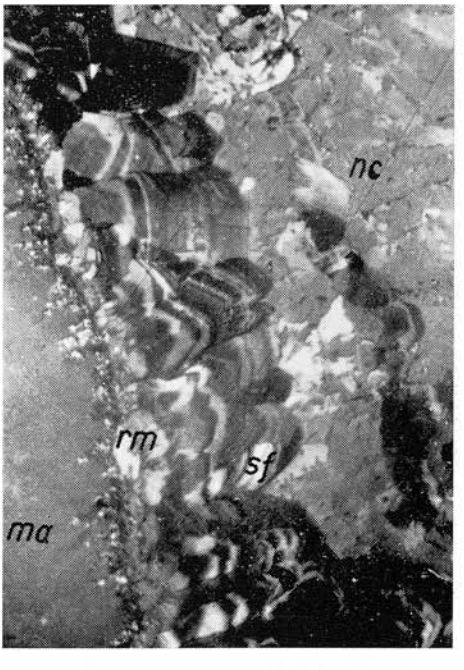

Fig. 11. Rammelsbergite (rm) and safflorite (sf) zones between maucherite (ma) and niccolite (nc). Crossed nicols, 625 ×, oil immersion. Photo I. R o j k o v i č.

The system nickel-arsenic-sulfur was studied by R. A. Y u n d (1962). He found that synthetic gersdorffite has a wide compositional range from $NiAs_{1\cdot77}S_{0\cdot23}$ to $NiAs_{0\cdot77}S_{1\cdot23}$ at 700 °C. Gersdorfite in equilibrium with $NiAs_2$ (rammelsbergite or pararammelsbergite) has the composition $NiAs_{1\cdot80}S_{0\cdot20}$ at 660 °C, and $NiAs_{1\cdot72}S_{0\cdot28}$ at 450 °C, both more arsenic-rich than the natural material under discussion. This suggests the latter,

Table 5. Electron microprobe results on rammelsbergite and safflorite

No.	Weight percent Co	Ni	Fe	As	S	Total
$NiAs_2$		28,15		71,85		100,00
1rm[2]	5,7	22,1	0,2	69,8	1,0	98,8
2rm	5,9	21,7	0,2	69,7	1,0	98,5
3rm	6,1	21,0	0,2	69,6	0,4	97,3
4rm	0,4	27,9	0,0	71,3	0,5	100,1
5rm	0,4	27,9	0,0	71,5	0,5	100,3
6rm	4,0	24,0	0,4	71,3	0,9	100,6
7rm	4,3	23,9	0,3	70,4	0,9	99,8
8rm	1,7	26,3	0,0	70,3	0,3	98,6
9rm	1,1	27,1	0,0	70,5	0,4	99,1
10rm	0,8	27,0	0,0	70,4	0,6	98,8
11rm	1,1	27,0	0,1	70,6	0,3	99,1
$CoAs_2$	28,23			71,77		100,00
12sf	18,4	2,8	7,1	69,0	2,1	99,4
13sf	18,8	1,6	7,5	69,8	1,5	99,2
14sf	19,8	4,2	5,1	70,1	1,5	100,7
15sf	23,5	2,2	3,0	68,7	2,4	99,8
16sf	25,0	2,5	1,9	69,0	2,0	100,4
17sf	23,6	2,5	3,1	69,1	2,0	100,3
18sf	21,7	2,6	2,9	69,6	2,3	99,1
19sf	21,5	1,7	4,2	69,9	1,9	99,2

No.	Mole percent Co	Ni	Fe	Atomic percent Co + Ni + Fe	As + S	Atomic proportion (Co, Ni, Fe)	As
1rm	20,3	79,0	0,8	33,1	66,9	1,00	2,02
2rm	21,1	78,1	0,8	33,0	67,0	1,00	2,03
3rm	22,3	77,0	0,8	33,0	67,0	1,00	2,03
4rm	1,4	98,6	0,0	33,3	66,7	1,00	2,00
5rm	1,4	98,6	0,0	33,2	66,8	1,00	2,01
6rm	14,0	84,5	1,5	33,1	66,9	1,00	2,02
7rm	15,0	83,9	1,1	33,4	66,6	1,00	1,99
8rm	6,0	94,0	0,0	33,5	66,5	1,00	1,99
9rm	3,9	96,1	0,0	33,5	66,5	1,00	1,99
10rm	2,9	97,1	0,0	33,1	66,9	1,00	2,02
11rm	3,9	95,7	0,4	33,5	66,5	1,00	1,99
12sf	64,1	9,8	26,1	33,0	67,0	1,00	2,03
13sf	66,4	5,7	27,9	33,0	67,1	1,00	2,03
14fs	67,3	14,3	18,3	33,7	66,3	1,00	1,97
15sf	81,4	7,6	11,0	33,1	66,9	1,00	2,02
16sf	84,7	8,5	6,8	33,7	66,3	1,00	1,97
17sf	80,3	8,5	11,1	33,6	66,4	1,00	1,98
18sf	79,3	9,5	11,2	33,2	66,8	1,00	2,01
19sf	77,8	6,2	16,0	33,3	66,7	1,00	2,00

No.	Sample	Close association	Remarks
1— 3	EB-2-09-5	sf, nc, ma	Internal part of sf-rm zone between ma-nc
4— 5	EB-2-09-9	sk, sf	In rim around ac pseudomorph after Ag
6	CL-2668-1	sf	Safflorite-rammelsbergite zonal aggregate
7	EB-3-05-5	sf, nc, ma	Thin zone between ma-nc
8— 9	EB-2-18-1	sf, nc, Ag	Rim around native silver
10—11	EB-2-18-2	sf, nc, Ag	Rim around native silver
12—13	EB-2-09-5	rm, ma, nc	External part of sf-rm zone between ma-nc

14	EB-3-05-5	nc
15	EB-2-09-9	rm, sk
16—17	EB-2-09-9	rm, ac
18	EL-548-2	rm, nc
19	EL-2752-2	rm, nc

Rim around Sb and Co-rich niccolite
In rim around ac pseudomorph after Ag
In rim around ac pseudomorph after Ag
sf-rm rim around niccolite
sf-rm rims around niccolite

Fig. 12. Microprobe analyses (mole percent) of safflorite and rammelsbergite. (Dash-lines represent solvus for natural phases after E. H. Roseboom 1963.)

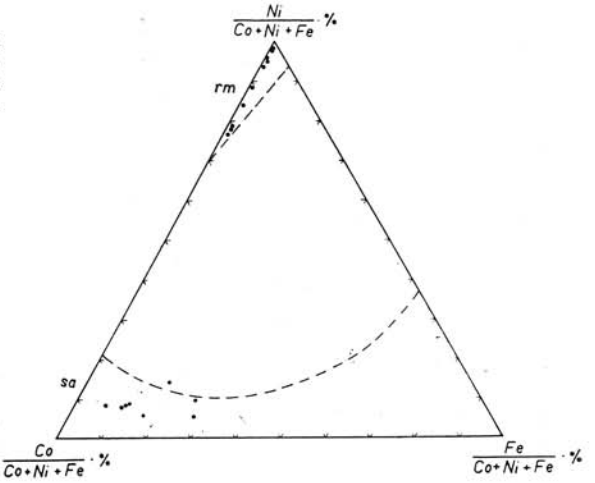

Fig. 13. Skutterudite (sk), safflorite (sf) and rammelsbergite (rm) in rims around silver dendrites. One nicol, 200 ×. Photo I. Rojković.

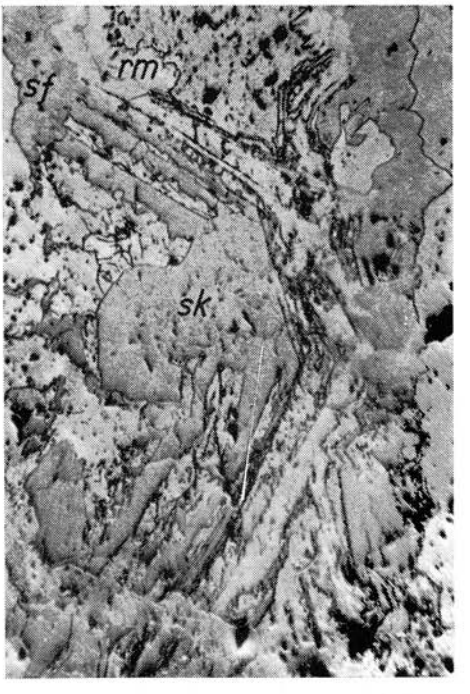

Fig. 14. Skutterudite (sk), safflorite (sf) and rammelsbergite (rm) as Fig. 13. Carbon coated, one nicol, 200 ×. Photo I. Rojković.

Table 6. Electron microprobe results on skutterudite

No.	Weight percent Co	Ni	Fe	As	S	Total
$CoAs_3$	20,8			79,2		100,0
A 1	9,1	10,7	2,1	76,4	0,8	99,1
B 2	8,6	11,4	2,2	76,6	0,6	99,4
C 3	10,0	10,1	2,3	76,1	0,8	99,3
D 4	9,0	10,0	1,8	76,2	1,2	98,2
E 5	10,3	9,4	2,1	76,5	0,7	99,0
E 6	9,8	10,7	2,1	76,1	0,7	99,4
E 7	9,7	10,9	2,2	76,4	0,8	100,0
E 8	10,2	9,9	2,6	76,5	0,9	100,1
E 9	11,2	7,8	2,6	76,1	0,7	98,4
E 10	11,4	6,6	3,1	76,2	1,0	98,3

No.	Mole percent Co	Ni	Fe	Atomic percent Co + Ni + Fe	As + S	Atomic proportion (Co, Ni, Fe)	As
A 1	41,3	48,7	10,0	26,4	73,6	1,00	2,79
B 2	38,5	51,2	10,4	26,7	73,3	1,00	2,75
C 3	44,3	44,9	10,8	26,9	73,1	1,00	2,72
D 4	43,0	47,9	9,1	25,2	74,8	1,00	2,96
E 5	46,9	43,0	10,1	26,3	73,7	1,00	2,80
E 6	43,1	47,2	9,7	27,1	72,9	1,00	2,69
E 7	42,2	47,7	10,1	27,2	72,8	1,00	2,67
E 8	44,6	43,4	12,0	27,0	73,0	1,00	2,70
E 9	51,4	36,0	12,6	26,3	73,7	1,00	2,80
E 10	53,5	31,1	15,4	25,6	73,4	1,00	2,91

Sample EB-2-09-9. A, B, C, D, E are different zonal crystals. The succession of analyses within one crystal (E) corresponds the direction towards the most external zone.

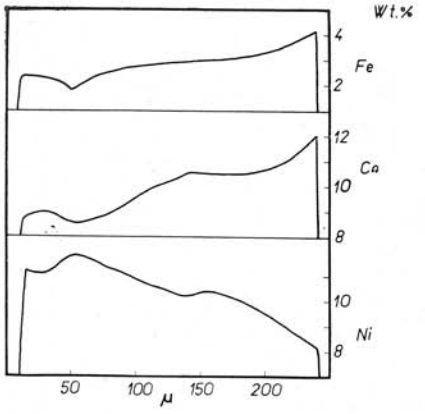

Fig. 15. Microprobe K_α intensity profile of skutterudite (adjusted to weigh percent) showing decrease of nickel towards the outermost zone.

although crystallizing in an arsenic-rich environment, has not attained a composition comparative to that in equilibrium with diarsenides. This may be in agreement with the replacing character of the latter gersdorffite.

Cobaltite CoAsS was not found as widespread as gersdorffite in the Great Bear Lake samples. Mostly occurs as rims around gersdorffite. In the samples from Echo Bay

Table 7. Electron microprobe results on gersdorffite

No.	Weight percent						
	Ni	Co	Fe	As	S	Sb	Total
NiAsS	35,4			45,2	19,4		100,0
1	30,7	3,6	1,0	44,7	18,8	0,0	98,8
2	34,6	1,1	0,3	45,0	19,1	0,0	100,1
3	34,3	1,5	0,7	45,7	18,5	0,0	100,7
4	29,0	3,1	2,0	49,0	16,5	0,0	99,6
5	29,4	2,3	2,2	48,5	16,5	0,0	98,9
6	29,3	2,4	2,0	47,5	16,6	0,0	97,8
7	29,1	3,0	2,2	47,1	16,6	0,0	98,0
8	29,0	3,5	2,3	48,3	16,6	0,0	99,7
9	29,1	3,1	1,7	47,5	16,9	0,0	98,3
10	30,9	3,2	1,6	43,7	17,9	2,9	100,2
11	31,0	2,5	2,5	38,9	17,7	8,2	100,8
12	30,8	3,5	2,0	40,2	17,8	7,0	101,3
13	31,5	3,3	0,6	42,9	17,8	4,3	100,4
14	34,1	0,5	0,0	45,3	20,4	0,0	100,3
15	29,0	7,1	2,1	43,5	20,2	0,0	101,9
16	34,4	0,5	0,0	43,9	20,1	0,0	98,9
17	26,3	2,8	2,1	48,2	20,5	0,0	99,9

No.	Atomic percent			Atomic proportion		
	Ni + Co + Fe	As + Sb	S	Ni	As	S
1	33,7	33,4	32,8	1,01	1,00	0,98
2	33,9	33,2	32,9	1,02	1,00	0,99
3	34,4	33,7	31,9	1,03	1,01	0,96
4	33,2	37,4	29,4	1,00	1,12	0,88
5	33,3	37,2	29,6	1,00	1,12	0,89
6	33,4	36,7	30,0	1,00	1,10	0,90
7	33,8	36,3	29,9	1,01	1,09	0,90
8	33,8	36,7	29,5	1,01	1,10	0,89
9	33,2	36,4	30,3	1,00	1,09	0,91
10	34,4	34,2	31,5	1,03	1,03	0,95
11	35,1	33,4	31,5	1,05	1,00	0,95
12	35,1	33,5	31,4	1,05	1,01	0,94
13	34,2	34,4	31,4	1,03	1,03	0,94
14	32,2	33,0	34,8	0,97	0,99	1,04
15	35,0	31,2	33,8	1,05	0,94	1,01
16	32,9	32,4	34,7	0,99	0,97	1,04
17	29,4	35,4	35,2	0,88	1,06	1,06

No.	Sample	Close association	Remarks
1	EB-2-09-5	nc	The outermost zone of zonal arsenides
2	EB-3-05-5	nc	The outermost zone of zonal arsenides
3	EB-1-11-60-4	nc, Ag	In nc-gf rim around native silver
4— 9	EB-2-09-9	sk	Replacing skutterudite
10—13	EB-2-06-3	cob	Thin rim around cobaltite
14—17	CR-2710	cob	Aggregate rimmed by cobaltite

Mines property, cobaltite forms euhedral crystals rimmed by antimony-rich gersdorffite (Fig. 16, 17). Both minerals are associated with carbonate, which veins fragments of siliceous wall-rock with arsenide rims. All analyses of cobaltite show relatively high

contents of nickel, up to 12 weight percent (Table 8). The cobaltite rims around gersdorffite from Camsell River samples show a distinct increase of nickel towards gersdorffite.

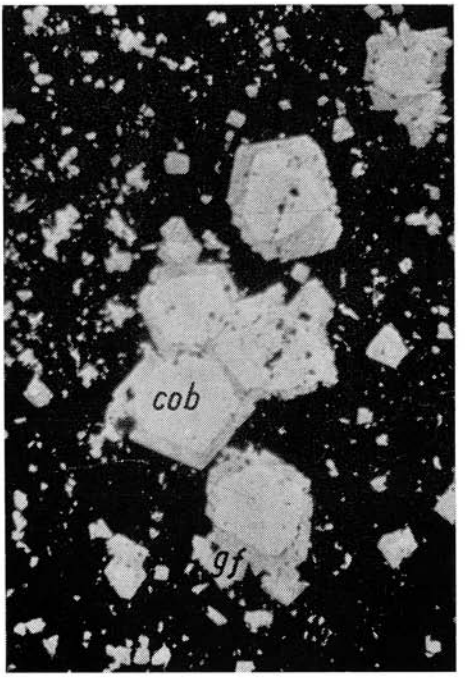

Fig. 16. Cobaltite crystals (cob) rimmed by antimony-rich gersdorffite (gf). One nicol, 625 ×, oil immersion. Photo I. Rojkovič.

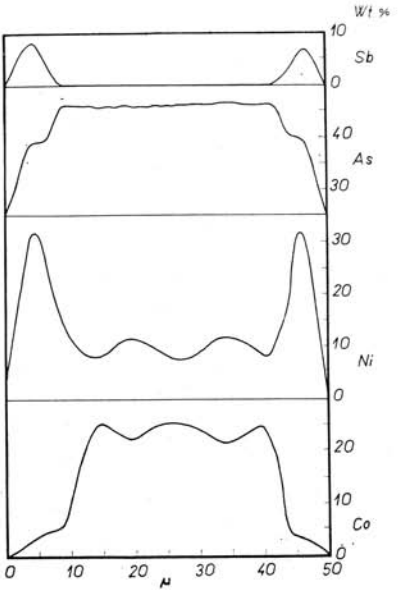

Fig. 17. Microprobe K_α intensity profile of antimony-rich gersdorffite (outer parts) and cobaltite (central part). Adjusted to weight percent.

Banding and zoning of nickel-cobalt arsenides and sulfarsenides as well as some zonal variations in composition within individual minerals (niccolite, skutterudite) presumably reflect changes in the composition of ore-forming fluids. The principal trend noted is a relative decrease of nickel and increase of cobalt (and to a less degree, iron) during the deposition of this assemblage.

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due to N. S. Edgar, President and H. E. Lake, Vice-President of Echo Bay Mines, Limited, who supplied a suite of ore samples from that property.

Table 8. Electron microprobe results on cobaltite

No.	Weight percent						
	Co	Ni	Fe	As	Sb	S	Total
CoAsS	35,5			45,2		19,3	100,0
1	25,0	8,2	0,9	45,6	0,3	19,0	99,0
2	25,7	7,2	1,3	45,3	0,4	18,9	98,8
3	21,4	13,0	0,9	45,7	0,3	19,1	100,4
4	20,3	13,5	1,3	45,9	0,4	19,0	100,4
5	23,4	8,3	0,9	46,2	0,0	22,4	101,2
6	24,2	7,1	1,1	46,0	0,0	22,3	100,7

No.	Atomic percent			Atomic proportion		
	Co+Ni+Fe	As+Sb	S	Co	As	S
1	32,5	34,2	33,2	0,98	1,03	1,00
2	32,7	34,2	33,1	0,98	1,03	0,99
3	33,2	33,8	32,9	1,00	1,01	0,99
4	33,1	34,1	32,8	0,99	1,02	0,98
5	29,7	33,0	37,4	0,89	0,99	1,12
6	29,7	33,0	37,4	0,89	0,99	1,12

No.	Sample	Close association	Remarks
1—4	EB-2-06-3	gf	Euhedral crystals rimmed by gf
5—6	CR-2710	gf	Rim around gf aggregate

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Review by B. Cambel.