IGOR ROJKOVIČ:

SILVER MINERALIZATION AT GREAT BEAR LAKE, CANADA

(Fig. 1-10)

A b s t r a c t: The mineralogy of U-Ni-Co-Bi-Ag deposits mostly at Eldorado Mine. Echo Bay Mines, less at Camsell River and Contact Lake in the Great Bear Lake area in Canada was studied. Besides before determined native silver, acanthite and stromeyerite the following silver minerals have been determined: polybasite, pearceite, pyrargyrite, freibergite and mckinstryite. These silver minerals do not form one association in the last stage of primary mineralization, as was regarded before, but were deposited during three stages of mineralization. Their position is compared with known thermodynamical studies.

Резюме: Была изучена минералогия U-Ni-Co-Bi-Ag месторождений главным образом Эльдорадо Майн, Эхо Бей, в меньшей мере Камзел Ривер и Контакт Лейк в области Грейт Бэр Лейк в Канаде. Кроме ранее определенного самородного серебра, акантита и стромейерита были определены следующие минералы: полибазит, пеарцеит, пираргирит, фрайбергит, мекинстриит. Эти минералы не кристаллизировали вместе во время последней стадии первичной минерализации, как презполагалось ранее, но осаждались из растворов во время трех стадий минерализации. Последовательность их осаждения сравнивается с известными экспериментальными исследованиями.

U-Ni-Co-Bi-Ag deposits at Eldorado Mine, Echo Bay, Camsell River and Contact Lake lie on the eastern shore of Great Bear Lake within the Bear Province of the Canadian Shield (A. W. Jelliffe 1948). The area contains volcanic and sedimentary rocks of the Echo Bay Group 1.800 m. y. old (B. W. Robinson 1971 in J. P. N. Badham et al. 1972). These rocks are intruded by granitoid rocks and diabases. All rocks except diabases are cut by system of ore-bearing fractures, most members of which trend northeasterly. The vein mineralization occured after the last of the granitic and porphyry intrusions (1.700 m. y.) and before (1.400 m. y.) the main diabase intrusive activity (J. P. N. Badham et al. 1972). The source of metals in ore were by J. P. N. Badham et al. (1972) originally enriched rocks of the Echo Bay Group.

The first detail mineralogical examination of the Great Bear Lake ores is that one of D. F. Kidd and M. H. Haycock (1935). These authors distinguished four characteristic types of ore mineralization:

- 1. Pitchblende with Co-Ni minerals
- 2. Co-Ni minerals
- 3. Pb. Zn and Cu sulfides
- 4. Native silver, Cu and Ag sulfides.
- D. D. Campbell (1955) distinguished five principal stages of mineralization as follows:
- 1. Hematite-quartz
- 2. Pitchblende
- 3. Quartz, cobalt-nickel arsenides and sulfides
- 4. Copper sulfides
- 5. Silver, bismuth and chalcopyrite.

The observed assemblages and paragenetic sequence of ore minerals are in general

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agreement with above mentioned authors. Five stages of mineralization were observed in this study:

- 1. Quartz veins with hematite
- 2. Pitchblende
- 3. Ni-Co arsenides and sulfarsenides with native silver I.
- 4. Sulfides, sulfosalts and native elements with dolomite and calcite.
 - a) Native silver II and sulfides
 - b) Native bismuth and Bi-minerals
 - c) Acanthite with Ag-sulfosalts
 - d) Native silver III with stromeyerite and Cu sulfides
- 5. Supergene minerals

D. D. Campbell (1955) lists brecciaton after deposition of hematite with quartz and after arsenides. Fragmentation of pitchblende was observed by D. F. Kidd and M. H. Haycock (1935) as well as by D. D. Campbell (1955). Fragmentation of pitchblende and its veining by arsenides and sulfides and similar relation of arsenides and sulfides were observed also in this study. Differences with the previous authors shows post-arsenide mineralization. Silver minerals were not deposited during the last stage of ore mineralization, but during the last three stages of ore mineralization. In the recent paper of J. P. N. Badham et al. (1972) is mineralization of silver explained similarly during last three phases: Ag-arsenide, intermediate sulfide and sulfosalt phase.

Paragenetic sequence was described more detaily in other papers (I. Rojkovič 1970, 1972). Here will be described the last three stages related to silver mineralization. In the third stage native silver I occurs with the Ni-Co arsenides and sulfarsenides

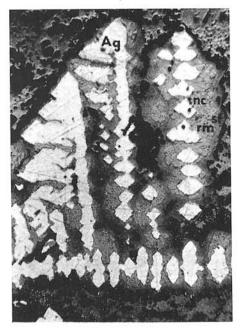


Fig. 1. Native silver dendrites (Ag) with niccolite (nc), rammelsbergite (rm-lighter) and safflorite (sf-darker) rims, Carbon coated; one nicol, 80 ×. Photo 1. Rojkovič.

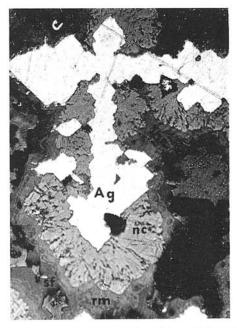


Fig. 2. Cross-shaped native silver (Ag) with niccolite (nc), rammelsbergite (rm) and safflorite (sf) rims. Carbon coated, one nicol, 160 X. Photo 1. Rojkovič.

(I. Rojkovič 1971). In the fourth stage occurs native silver II with tennantite, galena and sphalerite, in the association with chalcopyrite occur acantite, polybasite, pearceite, pyrargyrite and freibergite and together with bornite, chalcopyrite, tetrahedrite, chalcocite and wittichenite occur native silver III and stromeyerite. There is only one silver mineral associated with the supergene minerals — mckinstryite.

Silver minerals are widespread and important at the deposits studied especially at Echo Bay Mines and Camsell River Mine. Besides before determined native silver, acanthite and stromeyerite the following silver minerals have been determined: polybasite, pearceite, pyrargyrite, freibergite and mckinstryite.

Native silver Ag. The earliest native silver I was deposited with Co-Ni arsenides, Occurs as cubic crystals, as cruciform and dendritic aggregates or as irregular grains enclosed and rimmed by rammelsbergite, safflorite, skutterudite, niccolite and gersdorffite (fig. 1, 2). Arsenide and sulfarsenide rims suggest that this portion of native silver crystallized mainly before arsenides. However the occurence of native silver within various arsenide rims, and as small irregular inclusions in niccolite, suggest crystallization of some silver within at least the earliest part of the arsenide deposition stage. Native silver has undergone some deformation and remobilization. Thin veinlets of remobilized silver cut the surrounding arsenide and sulfarsenide rims (fig. 3). Later native silver I was replaced by acanthite and silver sulfosalts, commonly as pseudomorphs retaining the shapes of silver crystals and dendrites (fig. 4). Locally silver was completely removed, leaving dendroform negatives which are now occupied by quartz (fig. 5). This is in disagreement with the succession proposed by D. F. Kidd

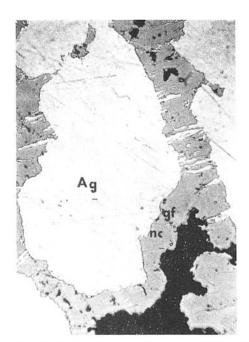


Fig. 3. Deformed crystals and veinlets of native silver (Ag) with niccolite (nc) and gersdorffite (gf) rims. One nicol, 160 X. Photo I. Rojkovič.



Fig. 4. Acantite (ac) and polybasite (plb) forming pseudomorphs after silver dendrites with rims of arsenides mainly niccolite (nc). One nicol, 80 X. Photo I. Rojkovič.

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and M. H. Haycock (1935) which places native silver as the latest ore mineral (accompanied by carbonate gangue), with quartz as an earlier gangue mineral.

A later generation of native silver (II) was deposited in association with chalcopyrite, sphalerite, galena and tennantite. The main portion occurs in veins as shapeless irregular masses intergrown with chalcopyrite, sphalerite, tennantite and galena. In vugs it forms wires or plates, but these can not be regarded as supergene, so far as the samples studied are concerned, since they also contain intergrown chalcopyrite, galena and are replaced by acanthite. This silver often veins other sulfides of this assemblage, mainly chalcopyrite as well as earlier formed arsenides and sulfarsenides.

The youngest native silver III occurs as small irregular inclusions in bornite in the assemblage; bornite, chalcocite, stromeyerite and wittichenite.

Antimony and mercury-rich phases within the ternary system Ag-Sb-Hg, such as have been described from Cobalt (C. Halls et al, 1967), have not been found in the samples studied, where native silver shows only very low contents of antimony and mercury (with Sb up to 0.3 and Hg up to 0.4 weight percent). This relatively low content of antimony, as compared with that in silver in the Cobalt ores, is parallel to the different mineral assemblages. Breithauptite associated with silver ore at Cobalt, has not been found among the arsenides associated with native silver I at Great Bear Lake, and the later silver II is associated with tennantite rather than with tetrahedrite.

A c a n thite Ag₂S is associated with such silver sulfosalts as polybasite, pearceite, pyrargyrite and freibergite, as well as with chalcopyrite. It is the most abundant silver mineral in this assemblage, It occurs mainly as large aggregates of grains, commonly intergrown with silver sulfosalts (fig. 6), as veinlets and as pseudomorphs after native silver. Perfectly developed euhedral crystals of "argentite" occur in vugs (fig. 7), but under the microscope, distinct twinning lamellae can be seen in them (fig. 8), and the X-ray powder diffraction are those of acanthite (tab. 1). It replaces native silver I to form cubic, cruciform or dentritic pseudomorphs (fig. 4). Irregular grains and veinlets of native silver II are enclosed and replaced. Acanthite is also very closely associated and intergrown with chalcopyrite. Some chalcopyrite grains within acanthite show freibergite along the grain contact. Acanthite replaces galena and along with silver sulfosalts and chalcopyrite, veins both arsenides and the earlier sulfides such as pyrite and sphalerite.

Microprobe analyses of acanthite show slight departures from stoichiometry. These seem to be due to loss of sulfur during analysis. For this reason, the lowest possible beam current 15 KV, and the longest possible counting time 20 seconds were used. Even so, slight deficiences in sulfur content were obtained (tab. 2).

Polybasite (Ag. Cu)₁₆Sb₂S₁₁ is much less abundant than acanthite, but it is the most widespread mineral among the silver sulfosalts. Its occurence parallels that of acanthite, and these minerals are often intergrown, both in veinlets and in pseudomorphs after silver dendrites (fig. 4, 6).

Studies of synthetic as well as natural polybasite and pearceite have established that these two minerals are end-members of two distinct series; polybasite-arsenpolybasite and pearceite-antimonpearceite, which are characterized by a different unit cell (M. A. Peacock—L., G. Berry 1947, C. Frondel 1963, H. T. Hall 1967). The upper limit for arsenic members of the both series was proposed by C. Frondel (1963) at 50 atomic percent of antimony of the total As+Sb content. H. T. Hall's (1967) experimental study has proved that copper is an essential component of these phases and has delimited contents. These minerals are homogeneous at 200 °C over a compositional interval which extends for copper as follows (in weight percent):

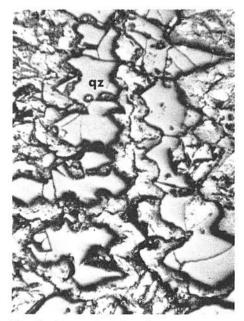


Fig. 5. Quartz (qz) forming pseudomorphs after silver dendrites, One nicol, 80 × . Photo I. Rojkovič.

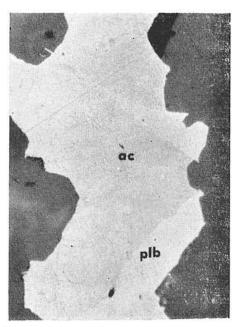


Fig. 6. Laths of polybasite (plb) intergrown with acanthite (ac). One nicol, 160 X. Photo L. Rojkovič.



Fig. 7. Isometric crystals of Ag₂S. Scale in cm. Photo I. Rojkovič.



Fig. 8. Twinning lamellae in acanthite, Crossed nicols, 160 X. Photo I. Rojkovič.

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Table 1, X-ray powder diffraction on acauthite

	L		2		3
1	al.	1	d	I	ď
1	3,44	1	3,44	1	3,45
1	3,39	1	3,39 3,09 2,84	0,5	3,38
3	3,08	3	3,09	3	3,09
5	2,85	5	2.84	3 4	2,85
2	2.67	2	2,66	2	2.67
10	2.60	10	2.59	10	2,60
7	2.44	8	2.44	8	2,45
3 5 2 10 7 6 2 2	2,44 2,38 2,21 2,09	3 5 2 10 8 5 2 2 2	2.44 2.38 2.21	2 10 8 5 3 4	2,45 2,38 2,22 2,09
2	2.21	2	2,21	3	2.22
2	2,09	2	2.08		2,09
	2.04	1	2.04	0,5	2,04
0.5	2.00	0.5	1.996	0.5	2.00
1	1,961	1	1,960	1	1,961
1	1,906	1	1,910	1	1,910
2	1.869	$\frac{2}{3}$	1.867	1	1.870
2 3 0.5	1.718	3	1.716	3	1,719
0.5	1.690	-	_	0.5	1,689
1	1,580	1	1.580	2 0,5	1,580
0.5	1,555 1,539	-	-	0,5	1,556
1	1,539	1	1.540	1	1,542
1	1.512	1	1.510	T.	1,512
0.5	1.483	0.5	1.481	0,5	1,484
0.5	1.477	0.5	1,476	0.5	1,475
1	1,454	1	1.454	$\frac{2}{0.5}$	1,455
	-	0.5	1.411	0.5	1,412
_		-		1	1.336

¹ Sample: 3-02-W-1 2 Sample: 1-11-60-5

arsenpolybasite from 3.0 to 5.2; polybasite from 3.0 to 7.6; pearceite from 5.5 to 19.7 and antimonpearceite from 7.9 to 19.2. On the contrary to the above mentioned results D. C. Harris et al. (1965) suggest to return to the original classification in which pearceite and polybasite are the As and Sb end-members of one series.

Table 2. Electron microprobe results on acanthite

Y.		Weight of	Neight ⁰ / ₀		ic 0′0	Atomic proportion		
No	$\Lambda \mathbf{g}$	S	Total	Λg	S	Λg	S	
Ag ₂ S 1 2 3	87.1 87.2 86,7 87.6	12,9 12,5 12,3 12,3	100,00 99,7 99,0 99,9	67,5 67,7 67,9	32,5 32,3 32,1	$\frac{2}{2}$	0,96 0,95 0,95	

³ L. G. Berry — R. M. Thompson (1962).

Table 3. E	lectron mi	croprobe res	sults on p	oolybasite, 4	pearceite and	pyrargyrite
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	ν.						Weig	tht %		
	No			Ag	Cu		Sb	Λs	s	Total
$\begin{array}{c} {\rm Ag_{16}Sb_{2}S} \\ {\rm 1~plb} \\ {\rm 2~plb} \\ {\rm 3~plb} \\ {\rm 4~plb} \\ {\rm 4~plb} \\ {\rm 4~pg} \\ {\rm 4~pc} \\ {\rm 2~pc} \\ {\rm 2~pc} \\ {\rm Ag_{3}SbS_{3}} \\ {\rm 1~pr} \end{array}$				74,32		2,7 3,7 3,5 - 6,72 7,0 6,7 - 0,3	15,19 14,3 14,9 14,6 14,7 15,82 15,2 15,5 17,76 15,6	100,00 99,0 100,4 98,5 99,1 100,00 100,4 99,6 100,00 98,4		
			Ato	omic %				Ato	mic propor	tion
No	Λg	Cu	Sb	Λs	s	Ag+ Cu	As+ Sb	(Ag, Cu)	(As, Sb)	S
1 plb 2 plb 3 plb 4 plb 1 pc 2 pc 1 pr	54,2 53,6 53,7 48,8 48,0 47,8 45,3	3,6 3,7 3,5 7,2 9,8 9,6	3,8 2,8 3,0 7.8 — — 14,9	2,9 3,8 3,7 - 6,9 6,7 0,3	35,6 36,1 36,1 36,2 35,2 36,0 39,5	57,8 57,3 57,2 56,0 57,8 57,4 45,3	6,7 6,6 6,7 7,8 6,9 6,7 15,2	16,00 16,00 16,00 16,00 16,00 16,00 3,00	1,85 1,84 1,87 2,23 1,91 1,87 1,01	9,85 10,08 10,10 10,34 9,74 10,03 2,62

Analyses of the Great Bear Lake polybasite show substitution of antimony by arsenic, but antimony prevails over arsenic. Copper contents range from 2,8 to 5.8 weight percent (tab. 3), which correspond to the compositional limit of copper in polybasite according to H. T. Hall (1967). As with acanthite, the silver sulfosalts yield microprobe values for sulfur slightly below stoichiometric requirements, due to loss of sulfur during analysis. However, the analyses serve to distinguish between pearceite and pyrargyrite from polybasite (tab. 3). The identification of polybasite, was also confirmed by X-ray powder diffraction (tab. 4).

Pearceite (Ag. Cu)₁₆As₂S₁₁ occurs only rarely, and is not as intimately intergrown with acanthite as polybasite. However, like polybasite, it is closely associated with chalcopyrite. No antimony was detected in the pearceite analyzed (tab. 3). The content of copper varies from 8.1 to 8.4 weight percent, which corresponds more to pearceite than arsenpolybasite, according to H. T. Hall (1967). The small size of the pearceite grains did not permit X-ray powder diffraction study.

Pyrargyrite Ag₃SbS₃ occurs only rarely at Echo Bay Mines property. It occurs intergrown with polybasite and was determined by the microprobe analysis (tab. 3).

Freibergite (Cu, Ag. Zn, Fe)₁₂(Sb, As)₄S₁₃ is one member of the complex

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Table 4. N	-ray powdo	r diffraction	011	polybasite
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	1	2				
I	d	Ţ	d			
1	3,62		3,62			
1 0,5	3,49	0.5	3.48			
0,0		0,5 0,5	3.28			
3,5	3,16	9	3.19			
.),.)	3.00	10	3.00			
10 3	200	10	2.88			
	2.00	0.5	9.77			
2 3 2 1 2 0,5	2.88 2.69 2.53 2.42 2.34 2.21 2.15 2,12	8 0.5 5 6 4 2 2 0.5	2.70			
2	2,09	.3	2.70			
.;	2.5.3	9	2.7.7			
2	2,42	1	2.72			
1	2.34	- 2	2,07			
2	2.21	2	2,21			
0,5	2.15	0.5	2.15			
1	2.12	2	2.11			
_		1	2.07			
1	2,03	3	2.02			
-		0.5	1,977			
1	1.938	1	1,933			
1 3	1,938 1,890	6	1.892			
	10 mm	0.5	1.859			
	-	1	1,791			
		ì	1.743			
1	1,708	3	1.707			
8	1.0	9	1.658			
		ī	1 621			
_	- (E)	5	1.595			
-		ī	1.554			
ī	1.518	4	3,48 3,28 3,19 3,00 2,88 2,77 2,70 2,53 2,42 2,34 2,21 2,15 2,11 2,02 1,977 1,933 1,892 1,859 1,791 1,743 1,743 1,743 1,595 1,595 1,595 1,595			

I Sample: I-11-60-5

2 L. G. Berry — B. M. Thompson (1962)

tetrahedrite series described at deposits studied (I. Rojkovič 1972). Freibergite occurs intergrown with the above mentioned silver sulfosalts and chalcopyrite. Where chalcopyrite is enclosed in acanthite, freibergite forms a thin rim along the contact.

Analysed freibergite contains up to 21.8 weight percent of silver (tab. 5). This is substantially higher than the maximum of 18 percent silver reported by C. Palache et al. (1944). However R. S. Boorman (1968) reports freibergite associated with silver sulfosalts as containing up to 22 percent of silver.

Stromeyerite Cu_{1+x}Ag_{1-x}S occurs in a different assemblage from that just described. It occurs in the last stage of hypogene mineralization, which is represented by the assemblage; bornite, chalcopyrite, chalcocite and tetrahedrite. Stromeyerite is the mineral most closely associated with chalcocite, It forms aggregates with grains up to 50 microns across with typical bireflection and strong anisotropy (fig. 9). In the Contact Lake deposits stromeyerite occurs mostly as irregular or tongue-like clongated aggregates in chalcocite, associated with bornite, native silver III and wittichenite.

N. Suhr (1955) and S. Djurle (1958) have found that stromeyerite is more

							We	ight 0	0		
	.\0				No Cu Fe Zn Ag Sb			As S		Total	
(iu ₁₂ Sb ₄ S ₁₃ 1 2 3	3	4: 2: 2: 2:	2.9 1 2.7 1	.3	5.8 5.2 5.2	21,0 21,8 21,4	29,2 27,2 27,3 27,6	- 1,2 0,4 0,5	25,0 21,8 21,5 21,1	100,0 101,2 101,2 100,5
No						Aton	nie °,):			
. 10	Cu	Fe	Zn	Лg	Sb	As		5 (iu+Fe+	-Zn+Ag	Sb+As
$\frac{1}{2}$	22,7 22,6 22,6	1,5 1,5 1,5	5,6 6,0 6,1	12,3 12,8 12,7	14.1 14.2 14.5	1,0 0,3 0,4	4: 4:	2,9 2,5 2,2	42 42 42	.9	15,1 14,5 14,9
No					Λı	mic p	ropoi	tion			
	(C	(Cu, Fe, Zu, Ag)				(Sb.	$\Lambda s)$			s	
1 2		12,0 12,0					(i0 06			12,23 11,89	

Table 5. Electron microprobe results on freibergite

copper-rich than CuAgS, and the formula proposed by J. B. Skinner (1966) is $\text{Cu}_{1+x}\text{Ag}_{1-x}S$, where x ranges from zero to 0.1. The analyses of the samples studied are in good agreement with this formula and all show a higher ratio Cu : Ag than 1 : 1 (tab. 6). The association acanthite with stromeyerite, reported from the Great Bear Lake ores by D. F. Kidd and M. H. Haycock (1935), has been criticized by J. B. Skinner (1966) due to its desiquilibrium. As was mentioned, in this paper, these two minerals occur in different assemblages, which is in agreement with J. B. Skinner's (1966) experimental study,

4.17

11,80

12.00

Mckinstryite Cu_{0.8+x}Ag_{1.2-x}S (formula proposed by J. B. Skinner et al. 1966). As was described before bornite occurs in assemblage with chalkopyrite, tetrahedrite, chalcocite and stromeyerite. During local oxidation processes chalcopyrite was partially altered to covellite and goethite, and bornite was locally almost completely replaced by covellite, idaite and goethite. Instead of stromeyerite, mckinstryite and covellite are present (fig. 10, tab. 7), suggesting the possible inversion of stromeyerite during supergene processes to mckinstryite and covellite (I. Rojkovič 1970), Accord-

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ing to B. W. Robinson — R. D. Morton (1971) mckinstryite replaces chalcopyrite and dolomite in late sulfide phase together with sphalerite, galena (?), acanthite, native bismuth (?), native silver before deposition of chalcocite.

Table 6. Electron microprobe results on stromeyerite

200		We	ight 00		Atomic 0 0				
No	Cu	$\Lambda \mathbf{g}$	S	Total	Cu	Ag	S		
CuAgS 1 2 3	31,2 32,0 32,1 32,8	53,0 52,2 52,2 52,8	15,8 15,4 15,2 15,3	100,0 99,7 99,5 100,9	34.3 34.5 34.8	33,0 33,1 33,0	32,7 32,4 32,2		
			.\10	omic proport	ion				
No		Cu		$\Lambda \mathbf{g}$		S			
1 2 3	1	1,02 1,02 1,03		0,98 0,98 0,97	0,97 0,96 0,95				

Table 7. Electron microprobe results on mckinstryite

		Weight 0 0				Atomic %				
No	Cu	$\Lambda \mathbf{g}$	S	Total	Cu	Λg	S	Total		
$\begin{array}{c} \mathrm{Cu_{0,8}Ag_{1,2}S} \\ \mathrm{1~mck} \\ \mathrm{2~mck} \end{array}$	23,94 24,60 24,59	60,96 60,34 59,56	15,10 14,97 14,76	100,0 99,91 98,91	27,39 27,65	39,57 39,45	33,03 32,89	99,99 99,99		
				Atomic	proporti	on*				
No		Cu		2	/it			S		
1 mck 2 mck		0,82 0,82			,18 .18			,00 ,00,		

^{*} Cu and Ag calculated as Cu + Ag = 2, due to small leak of S, presuming S = 1

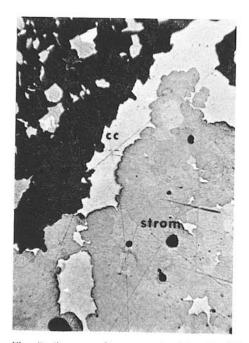


Fig. 9. Stromeyerite aggregate (strom) with distinct pleochroism is rimmed by and partly enclosing chalcocite (cc). One nicol, 80 X. Photo I. Rojkovič.

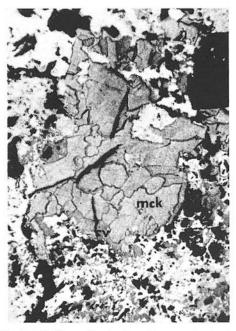


Fig. 10. Mckinstryite (mck) with covellite (cv) along grain boundaries and around aggregates of mckinstryite. One nicol, 125 ×, oil immersion. Photo L. Rojkovič.

Paragenesis of ore minerals

Stage 3. Cobalt-nickel arsenides and sulfarsenides.

Previous investigators (D. F. Kidd-M. H. Haycock 1935; D. D. Campbell 1955) regarded deposition of native silver as the final stage of primary mineralization. However, the present study suggests that the earliest native silver (I) was deposited with cobalt-nickel arsenides and sulfarsenides. With this change the Great Bear Lake ores become strikingly similar in sequence of deposition to deposits such those at Cobalt. Canada (W. Petruk 1968) or Jachymov. Czechoslovakia (F. Mrña-D. Pavlů 1967). According to W. Petruk (1968) deposition of native silver, at Silverfields in the Cobalt area, may have been promoted by a catalytic action of the arsenide minerals.

Stage 4. Sulfides, sulfosalts and native elements.

The earliest minerals of this assemblage are represented by pyrite and arsenopyrite or with marcasite and sphalerite with the higher content of iron. These are followed by chalcopyrite, galena and iron-poor sphalerite. The last three minerals also occur with tennantite and native silver II.

Experimental data concerning the minerals described are listed below:

Minerals Temperature of stability Author arsenopyrite-pyrite < 491 ± 42 °C L. A. C1 a r k (1960) yrite-marcasite < 432 ± 3 °C G. Kullerud (1967) 336 ROJKOVIĆ

Accordingly the upper limit of this sulfide stage can be placed probably at 491 \pm 12 °C or 432 \pm 3 °C.

The replacement of galena by acanthite and the veining of earlier sulfides by silver sulfosalts, acanthite and chalcopyrite suggest their later deposition. Silver sulfosalts are very intimately associated with acanthite and chalcopyrite. Native silver is mostly replaced by acanthite but some portion enclosed in acanthite may be contemporaneous. Experimental data concerning these minerals are listed below:

		Kracek Kracek		
		IX I di C S IX	(1940)	
< 197 ± 5 °C	C. W.	. Keighi	(1969) n — R.	М.
> 197 ± 5 °C	C. W	. Keighi		
	152 °C < 197 ± 5 °C > 197 ± 5 °C	152 °C	152 °C L. A. Taylor C. W. Keighi Honea (1969)	152 °C L. A. Taylor (1969) C 197 ± 5 °C C. W. Keighin – B. Honea (1969) > 197 ± 5 °C C. W. Keighin – B.

The system Ag-S was studied by F. C. K r a c e k (1946) and A. J. F r u e h (1957). Both investigators describe acanthite as a low-temperature monoclinic polymorph of Ag₂S, which inverts at above listed temperatures to the body-centered cubic polymorph, argentite. The Great Bear Lake acanthite, since it shows cubic morphology, as well as twinning lamellae is considered to have formed, at least in part, through the inversion of cubic argentite during cooling. It should be noted that the twinning previously regarded as proof of this inversion and of original deposition above 177 °C. is of itself a doubtful criterion. The development of twinning below this temperature was reported by R. S a d a n a g a + S. S u e n o (1967), while L. A. T a y l o r (1969) reports that "premonitory" polysynthetic twinning occurs as low as 152 °C. Some portion of Great Bear Lake acanthite does not show twinning and may represent Ag₂S deposited as acanthite, implying formation below 177 °C. But most of acanthite is twinned and is associated with polybasite. Pyrargyrite is rare but is closely associated with the last two minerals. The association pyrargyrite with acanthite (inverted from argentite) suggest deposition above 197 °C.

Bornite and chalcocite with accompanied minerals vein and replace pitchblende, nickel-cobalt arsenides and sulfarsenides and some earlier sulfides. The assemblage is more complex at Echo Bay Mines where is represented by bornite, chalcopyrite, tetrahedrite, chalcocite and stromeyerite. At Contact Lake the last assemblage is accompanied by digenite, wittichenite and native silver III.

Experimental data relating to this assemblage are listed below:

Temperature of stability		Author
< 103.5 °C	E. 1	H. Roseboom (1966)
< 76 ± 2 °C	E. 1	H. Boseboom (1966)
	E.	H. Roseboom (1966)
	1. 1	B. Skinner (1966)
	.1. 1	B. Skinner (1966)
	< 103.5 °C < 76 ± 2 °C < 83 ± 2 °C < 93.3 ± 0.7 °C	$< 76 \pm 2 ^{\circ}\text{C}$ E. $< 83 \pm 2 ^{\circ}\text{C}$ E. $< 93.3 \pm 0.7 ^{\circ}\text{C}$ J. $< 67 \pm 2 ^{\circ}\text{C}$ J.

Most minerals in this assemblage suggest equilibrium temperatures below 100 °C.

Stage 5, Supergene minerals

The effect of supergene processes in the Great Bear Lake area are very scarce and local (A. W. Jolliffe — personal communications). Observations on the samples studied support this view. The supergene minerals probably represent only the initial stage of oxidation.

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