

PARACOSTIBITE (CoSbS) AND NISBITE (NiSb₂), NEW MINERALS FROM THE RED LAKE AREA, ONTARIO, CANADA

L. J. CABRI, D. C. HARRIS AND J. M. STEWART

*Mines Branch, Department of Energy, Mines and Resources,
Ottawa, Canada*

ABSTRACT

Paracostibite (CoSbS) and nisbite (NiSb₂) are new minerals found in drill-core from the Red Lake area, Ontario. Paracostibite is orthorhombic with $a = 5.764$, $b = 5.952$, $c = 11.635$ Å; $Z = 8$, space group $Pbca$, calc. $D = 7.1$ g/cc. The strongest lines of the x -ray powder pattern are 5.81(8)(002), 2.83(7)(113), 2.65(7)(022), 2.555(10)(211, 121), 2.409(7)(122), and 2.035(8)(221). It is weakly birefracting and weakly anisotropic, showing faint polarization colours from pinkish to pale buff in oil. In air and in oil it is white in colour with faint greyish tinge. Its microhardness is 1009 kg/mm² for a 15 g weight.

Nisbite is also orthorhombic with $a = 5.16$, $b = 6.30$, $c = 3.84$ Å; $Z = 2$, probable space group $Pnmm$, calc. $D = 8.0$ g/cc. The strongest lines are 2.76(s)(111), 2.70(m)(120), 2.03(m)(211), and 1.84(ms)(031). In reflected light nisbite is very weakly birefracting and appears white in oil and in air. It is also weakly anisotropic. Microhardness value is 479 kg/mm² for a 5 g weight.

INTRODUCTION

Paracostibite and nisbite are two new minerals that were found during the course of mineralogical examination of drill-core from claims held by Cochenour Willans Gold Mines Ltd. in Mulcahy Township, District of Kenora, Red Lake Mining Division, Ontario (Fig. 1).

The Red Lake area is well known for its gold mines, but Mulcahy township has received only sporadic attention prior to 1956. Since then, there has been an interest in copper-nickel mineralization, culminating in 1967 in the discovery of a small, high grade base-metal deposit in the northeast part of the township by geologists of the Cochenour Willans company engaged in a systematic and detailed exploration program. The geology of the area is given by Riley (1968). The deposit occurs on the northeast limb of an arcuate structure, about 20 miles west of Red Lake, which consists of sequences of metavolcanic and metasedimentary rocks that have been intruded by several gabbroic sills. The deposit is located about 4000 feet south-southwest of the south end of Trout Bay. The mineralized host rock appears to be an altered mafic rock that could be classified as a carbonatized-chlorite-anthophyllite schist.

*Sulphide Research Contribution No. 14, Mineral Sciences Division.

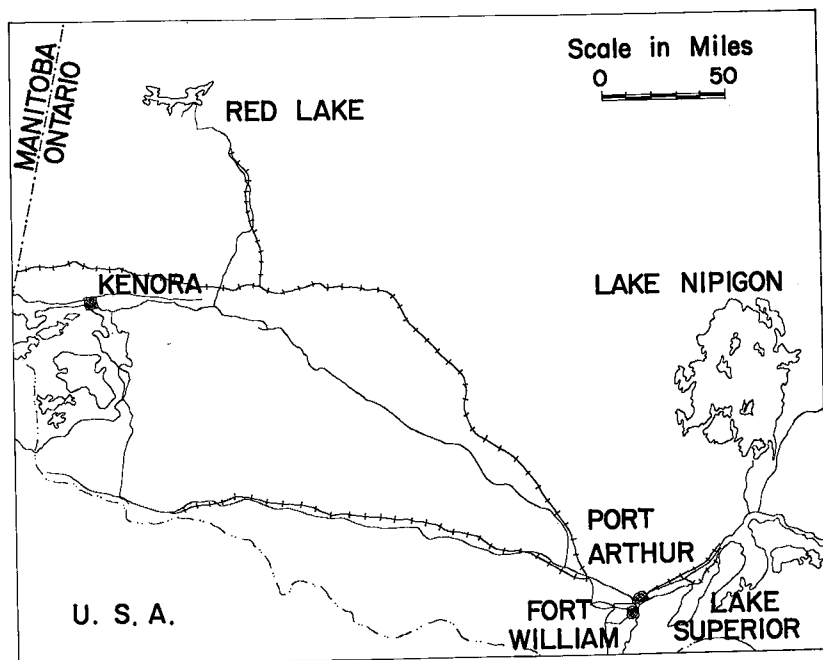


FIG. 1. Location sketch map.

PROCEDURES

The minerals in the drill core were studied by means of ore microscopy, x -ray diffraction and electron-probe microanalysis. The x -ray data and unit-cell dimensions for the new minerals 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 visually estimated. Unit-cell parameters were refined by a least-squares computational method. A Guinier-de Wolfe forward-reflection, focussing, multiple-exposure powder camera was also used for the synthetic equivalents because of its greater resolution at low Bragg angles and a precession camera was used for crystals of synthetic CoSbS.

The compositions of the minerals were determined by using a Materials Analysis Company (MAC) model 400 electron-probe microanalyser. Synthetic CoSbS, NiSb₂ and NiSb were used as standards for paracostibite and nisbite. Antimonial silver, allargentum, chemically analysed tetrahedrites and some pure metals were used as standards for the other minerals.

The synthetic standards were prepared from high-purity elements. The procedure employed for the Ag-Sb standards is described in Petruk

et al. (1969). The CoSbS, NiSb₂, and NiSb were synthesized in evacuated silica-glass tubes. The CoSbS was first heated for two hours at 300°C, then for an hour at 540°C, and then left for six days at 800°C. It was quenched, ground, pelletized and then re-heated at 800°C for six days, then annealed at 600°C for one day, and finally quenched. The NiSb₂ and NiSb were slowly heated up to 800°C and then left to anneal for six days at 540°C. After quenching, grinding, and pelletizing, they were re-heated at 600° and 800°C, respectively, for seven days.

The specific gravity of the synthetic CoSbS was determined on a 178-mg sample by a hydrostatic method using the hexachloro-1, 3 butadiene reported by Cabri (1969).

The ore microscopy, including reflectivity measurements and microhardness determinations, were performed on samples mounted in cold-setting Araldite resin and polished on lead laps with graded diamond abrasives down to 0-2 microns in diameter. Final buffing was done for 1½ minutes by hand on a cloth lap with a slurry of "Linde B" 0.05 micron MgO in water.

The apparatus and techniques used for reflectivity measurements and microhardness determinations are those described by Cabri & Traill (1966), except that a 45:1 objective with a numerical aperture of 0.65 was used for most reflectivity measurements. The reflectivities of the two smallest nisbite grains were measured with a 50:1 objective having a numerical aperture of 0.65.

GENERAL MINERALOGY

The new minerals were found in a massive base-metal sulphide ore in which the principal opaque minerals consist of coarse grains and inclusions of pyrrhotite, sphalerite and chalcopyrite. There are lesser amounts of galena, marcasite, arsenopyrite, cobaltite, pyrargyrite, paracostibite, gudmundite, stannite, argentian tetrahedrite, antimonial silver, allargentum, ilmenite, breithauptite, cassiterite and nisbite.

Some of the silver minerals, all of which contain antimony, are of special interest. The assemblage includes allargentum as redefined by Petruk *et al.* (1970). This is only the second authenticated occurrence of allargentum in Canada, and probably in the world, since in the only other reported occurrence (Markham & Lawrence 1962), only qualitative microscopic identifications were employed. The allargentum was found in a few grains associated with antimonial silver in only one section and was distinguishable by its better polish compared to that of antimonial silver. It was determined by microanalysis to have 83.3 wt. % Ag and 16.7 wt. % Sb, which is equivalent to Ag_{0.849}Sb_{0.151}. The co-existing

antimonial silver had 97.3% Ag, 2.6% Sb, and 0.1% Hg which is equivalent to $\text{Ag}_{0.976}\text{Sb}_{0.028}\text{Hg}_{0.0005}$.

The argentian tetrahedrite (var. freibergite), has one of the highest reported silver contents for tetrahedrite (see Table 1), comparable to a reported tetrahedrite from Beaverdell, B.C. with 26.4% Ag (Staples & Warren 1946). The formula for the Red Lake tetrahedrite comes to $(\text{Cu,Ag})_{2.5}(\text{Zn,Fe})_{0.46}(\text{Sb,As})_{0.96}\text{S}_{3.36}$, which is not too different from the general one obtained by Springer (1969) of $(\text{Cu,Ag})_{2.5}(\text{Zn,Fe})_{0.50}(\text{Sb,As})_{1.0}\text{S}_{3.25}$. The Red Lake tetrahedrite has a unit-cell edge of $10.6308 \pm 0.002 \text{ \AA}$.

Table 1 also includes analyses of some of the other minerals in the ore.

TABLE 1. ELECTRON-PROBE MICROANALYSES, IN WEIGHT PER CENT

Sample No	CW1	CW12A	CW12A	CW1-B
Mineral	tetrahedrite*	arsenopyrite	cobaltite	gudmundite†
Cu	18.7	—	—	—
Zn	1.4	—	—	—
Ag	26.8	—	—	—
Fe	4.4	29.6	1.7	29.0
Co	—	3.7	29.9	—
Ni	—	-0.0	0.5	—
Sb	24.5	—	—	58.5
As	0.6	47.5	45.6	—
S	23.4	19.2	20.6	15.4
Totals	99.8	100.0	98.3	102.9

*Pb, Bi, Hg not detected.

†Fe is probably too high; a metal standard was used.

PARACOSTIBITE

Paracostibite was found in several sections as irregular and subhedral grains up to about 130 microns in size. In reflected light the mineral is weakly birefracting, appearing white in colour with a faint greyish tinge, both in air and in oil immersion. It is weakly anisotropic and, in oil immersion, it shows faint polarization colours from pinkish to pale buff. Paracostibite was found in two types of assemblage, one of which is shown in Figs. 2 and 3. The second type of assemblage consisted of paracostibite, pyrargyrite, pyrrhotite, antimonial silver, galena and chalcopyrite. It was never found in close proximity to arsenopyrite or cobaltite but did occur in one section where these two sulpharsenides also occurred. Its optical appearance is such that it can easily be mistaken for cobaltite, but it does not show the same faint pinkish tinge usually seen in cobaltite.

The reflectivity spectrum of paracostibite for seven grains which showed maximum birefractance, using a calibrated silicon standard, was

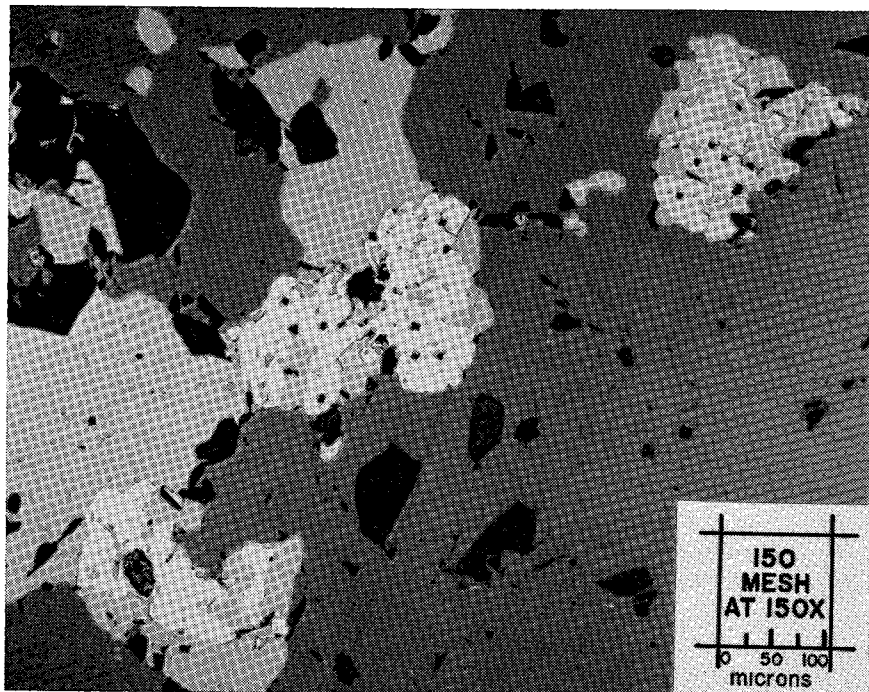


FIG. 2. Photomicrograph showing four groups of paracostibite grains (white) associated with sphalerite (grey), and chalcopyrite (light grey). Dark areas are pits.

measured from 440 to 650 nm but was found to be rather featureless. The values at four wavelengths are given in Table 2.

TABLE 2. REFLECTIVITY OF PARACOSTIBITE, IN PER CENT

Wavelength nm	Max. Reflectivity		Min. Reflectivity	
	Range	Average	Range	Average
470	45.3-49.4	47.8	45.3-48.0	46.9
546	46.6-49.8	48.1	46.1-48.5	47.5
589	47.3-50.2	48.4	46.0-49.2	47.7
650	46.6-50.7	48.8	46.6-49.1	48.0

Reflectivity values for synthetic CoSbS are: 48.4-48.0% (470 nm), 49.2-48.2% (546 nm), 48.8-48.6% (589 nm), and 50.1-49.6% (650 nm).

The VHN microhardness gave an average value of 1009 kg/mm² (range 936-1091 for ten indentations) with a 15 g weight. Both diagonals were measured for each indentation. The synthetic CoSbS gave a value of 1028 kg/mm² (range 972-1113 for 10 indentations).

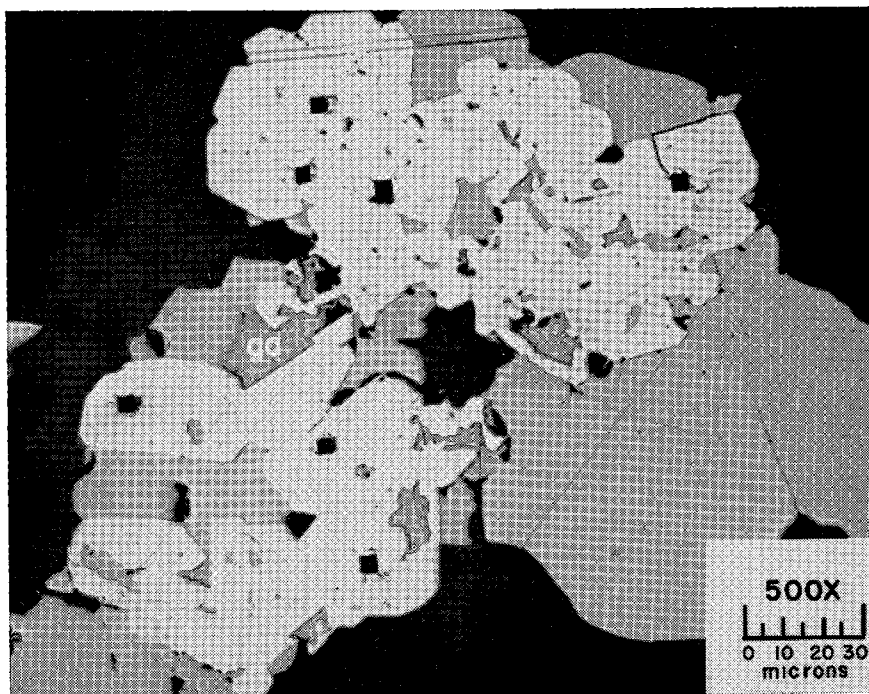


FIG. 3. Photomicrograph of the upper-right group of paracostibite grains (white) shown in Fig. 2 but with greater magnification. Also shown are galena (ga) and chalcopyrite (grey) as well as some microhardness indentations.

Electron-probe microanalyses of five grains from three polished sections gave $(\text{Co,Fe,Ni})_{1.004}\text{Sb}_{1.000}\text{S}_{0.996}$; therefore equivalent to CbSbS . The analyses are shown in detail in Table 3, below.

TABLE 3. ELECTRON-PROBE MICROANALYSES OF PARACOSTIBITE, IN WEIGHT PER CENT

Sample No.	Co	Fe	Ni	Sb	S	Totals
CW-7C	27.0	—	0.6	57.6	15.4	100.6
CW-1-B	25.1	0.6	1.6	56.9	14.7	98.9
CW-14A	26.4	0.5	0.7	56.1	14.8	98.5
CW-14A	26.6	0.5	0.7	56.1	14.9	98.8
CW-14A	26.7	0.5	0.6	57.5	14.9	100.2
Averages	26.4	0.4	0.8	56.8	14.9	99.3

The x -ray powder diffraction patterns of paracostibite and synthetic CoSbS are identical, although patterns of the mineral invariably contained lines corresponding to the other minerals associated with it in the

TABLE 4. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC CoSbS AND PARACOSTIBITE

Fe filter, Co radiation						
Synthetic CoSbS				Paracostibite		
$a = 5.768 \pm 0.009$,				$a = 5.764 \pm 0.001$,		
$b = 5.949 \pm 0.002$,				$b = 5.952 \pm 0.003$,		
$c = 11.666 \pm 0.002 \text{ \AA}$				$c = 11.635 \pm 0.005 \text{ \AA}$		
$I(\text{est})$	$d(\text{meas.})\text{\AA}$	$d(\text{calc.})\text{\AA}$	hkl	$I(\text{est})$	$d(\text{meas.})\text{\AA}$	$d(\text{calc.})\text{\AA}$
6	5.826	5.833	002	8	5.813	5.817
4	4.093	4.101	102			4.095
	3.927*	3.902	111			3.901
	3.389*	3.377	112	4	3.441†	
				<1	3.372	3.373
				<1	3.181 \square	
				7	3.037 $\triangle\square$	
1	2.971	2.974	002	4	2.978†	2.976
6	2.915	2.916	004	4	2.905	2.906
7	2.877	2.882	021	4	2.876	2.883
6	2.831	2.835	113	7	2.826	2.831
6	2.647	2.650	022	7	2.654	2.649
6	2.600	2.600	104	4	2.596	2.597
10	2.555†	2.579	121	10	2.555	2.578
		2.533	211			2.532
5	2.407	2.408	122	7	2.409	2.407
2	2.383	2.384	114			2.380
				1	2.279 \square	
2	2.1866	2.1862	123	2	2.1856	2.1848
				4	2.0941†	
<1	2.0647	2.0704	220	<1	2.0651	2.0704
9	2.0332	2.0386	221	8	2.0354	2.0384
2	1.9574	1.9587	124	1	1.9579	1.9567
1	1.9361	1.9387	214	<1	1.9357	1.9360
5	1.8500	1.8514	131	8	1.8525 \triangle	1.8520
4	1.8327	1.8358	025	2	1.8355	1.8332
				3	1.7875	1.7854
2	1.7847	1.7852	132	4	1.7638	1.7562
7	1.7619	1.7600	116	1	1.7324	1.7322
2	1.7340	1.7350	215	3	1.6890	1.6888
3	1.6875	1.6891	133	2	1.6630	1.6539
4	1.6653	1.6553	313	3	1.6390	1.6342
3	1.6385	1.6339	230	4	1.6238	1.6247
3	1.6244	1.6275	026			1.6183
2	1.6149	1.6181	231	3	1.5782	1.5765
3	1.5758	1.5773	134	2	1.5638	1.5638
2	1.5640	1.5663	126	1	1.5038	1.5060
1	1.5096	1.5064	233			1.4903
<1	1.5027	1.4912	323	<1	1.4758	1.4760
3	1.4741	1.4753	041	1	1.4551	1.4544
2	1.4567	1.4582	008			1.4248
1	1.4242	1.4255	234	<1	1.4162	1.4102
1	1.4143	1.4138	108	2	1.4054	1.4073
4	1.4057	1.4098	127	<1	1.3727	1.3722
1	1.3743	1.3755	118	1	1.3432	1.3430
4	1.3402	1.3432	332	<1	1.3251	1.3247
1	1.3237	1.3249	044	<1	1.3081	1.3067
3	1.3080	1.3094	028	<1	1.2763	1.2744
2	1.2762	1.2769	128	1	1.2552	1.2536
3	1.2524	1.2541	045			

TABLE 4 (concluded)

Fe filter, Co radiation						
Synthetic CoSbS			Paracostibite			
$a = 5.768 \pm 0.009,$			$a = 5.764 \pm 0.001,$			
$b = 5.949 \pm 0.002,$			$b = 5.952 \pm 0.003,$			
$c = 11.666 \pm 0.002 \text{ \AA}$			$c = 11.635 \pm 0.005 \text{ \AA}$			
$I(\text{est})$	$d(\text{meas.})\text{\AA}$	$d(\text{calc.})\text{\AA}$	hkl	$I(\text{est})$	$d(\text{meas.})\text{\AA}$	$d(\text{calc.})\text{\AA}$
1	1.2368	1.2370	119	<1	1.2375	1.2341
1	1.2249	1.2255	145			1.2250
1	1.1909	1.1922	228	<1	1.1904	1.1901
1	1.1662	1.1662	430	1b	1.1677	1.1660
2	1.1580	1.1595	151	1b	1.1601	1.1600
3	1.1440	1.1436	432	2	1.1439	1.1432
2	1.1313	1.1316	502	1	1.1315	1.1309
1	1.1241	1.1255	336	<1	1.1238	1.1245
1	1.1099	1.1096	047	1	1.1101	1.1086
<1	1.1028	1.0998	250	<1	1.1029	1.1002
1	1.0988	1.0987	229			1.0966
1	1.0909	1.0909	344	1b	1.0918	1.0906
1	1.0867	1.0873	513			1.0865
3	1.0838	1.0828	434	<1	1.0830	1.0823
1	1.0668	1.0663	139	1	1.0679	1.0645
1	1.0540	1.0556	514			1.0548
<1	1.0422	1.0425	155			1.0423
3	1.0355	1.0356	247	2	1.0348	1.0347
1	1.0321	1.0352	440			1.0352
1	1.0302	1.0312	441	2	1.0317	1.0311
1	1.0291	1.0291	254			1.0291
1	1.0143	1.0155	239			1.0139
1	1.0062	1.0065	346			1.0058
<1	1.0009	1.0004	443			1.0002
2	0.9920	0.9921	506			0.9910
2	0.9889	0.9879	061			0.9884
2	0.9775	0.9774	062			0.9779
3	0.9751	0.9756	444			0.9753
<1	0.9641	0.9637	162			0.9641
8	0.9593	0.9586	1, 0, 12			0.9562
7	0.9581	0.9573	256			0.9569
4	0.9502	0.9494	2, 3, 10			0.9478
5	0.9484	0.9485	602	2b	0.9477	0.9479
3	0.9243	0.9241	0, 2, 12			0.9219
3	0.9198	0.9212	2, 0, 12			0.9190
3	0.9130	0.9130	604			0.9123
2	0.9023	0.9024	614			0.9017
3	0.9007	0.9006	542			0.9004

*Measured only on Guinier film, very weak reflections.

†This was resolved into two reflections at 2.586 (121) and 2.558 (211) on Guinier film, the (211) being the strongest reflection of the whole pattern, and the (121) was quite weak.

+, O, Δ, □ represent reflections of the following minerals, either alone or coinciding with paracostibite: galena, sphalerite, chalcopyrite, calcite, respectively.

Intensities estimated visually, b signifies broad.

ore. The two patterns are compared in Table 4, and were indexed satisfactorily on an orthorhombic cell. The patterns also exhibit a close

similarity to that of pararammelsbergite (Fig. 4), which has a similar unit cell. The measured density of the synthetic CoSbS was 6.9 g/cc, (calculated = 7.069 g/cc), which would give a density of 7.1 g/cc for the natural paracostibite using the cell parameters and 8 formula weights per cell.

PARARAMMELSBERGITE

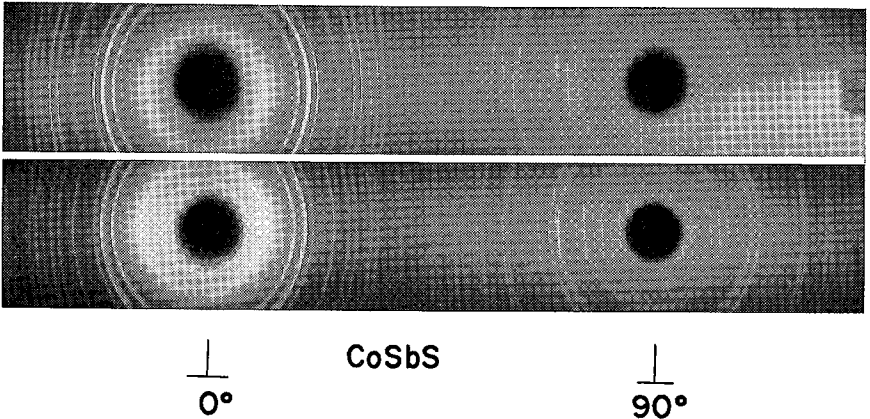


FIG. 4. X-ray powder diffraction patterns of pararammelsbergite (from Deer Horn Mine, Cobalt, Ontario #34A) compared to synthetic CoSbS (#153). Fe-filtered Co radiation.

The name paracostibite (PARA-K \bar{O} -ST \bar{I} B-AIT), is for the composition and its probable structural relation to pararammelsbergite. It has been approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material is preserved at the National Mineral Collection, Ottawa, and the Royal Ontario Museum, Toronto.

NISBITE

Nisbite was found in only two polished sections, and therefore appears to be much rarer than paracostibite. It is easily mistaken for fine-grained gudmundite, and could only be distinguished grain by grain, with the electron-probe. It was found as irregular grains up to 20 microns in size together with chalcopyrite, breithauptite, pyrargyrite, galena, pyrrhotite and tetrahedrite.

In reflected light nisbite is very weakly bireflecting and appears white in oil and in air. It is also weakly anisotropic. Reflectivity values for three grains, using calibrated silicon as a standard, averaged 58.8% (470 nm), 59.4% (546 nm), 60.2% (589 nm), and 59.6% (650 nm).

These compare to the following values for synthetic NiSb_2 : 60.9% (470 nm), 60.5% (546 nm), 61.3% (589 nm), and 62.0% (650 nm).

The microhardness value for 10 indentations with a 5 g weight was 479, with a range from 420–513 kg/mm². Synthetic NiSb_2 gave 555, with a range from 302–758 kg/mm² for 13 indentations.

Electron-probe microanalyses of four grains, using synthetic NiSb_2 as a standard, gave Ni 19.15%, Sb 80.43%, total 99.58% giving $\text{Ni}_{1.0}\text{Sb}_{2.15}$; therefore equivalent to NiSb_2 .

Because of the small grain size and rarity of the mineral, only mixed x -ray powder diffraction patterns of natural NiSb_2 and chalcopyrite, with lesser amounts of galena, breithauptite, and pyrargyrite could be obtained; one such pattern is shown in Table 5. Synthetic NiSb_2 , also

TABLE 5. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC NiSb_2 AND NISBITE

Fe filter, Co radiation						
Synthetic NiSb_2 $a = 5.178$, $b = 6.319$ $c = 3.832$, all $\pm 0.003 \text{ \AA}$			Nisbite $a = 5.162 \pm 0.008$, $b = 6.303 \pm 0.001$, $c = 3.839 \pm 0.009 \text{ \AA}$			
$I(\text{est})$	$d(\text{meas.})\text{\AA}$	$d(\text{calc.})\text{\AA}$	hkl	$I(\text{est})$	$d(\text{meas.})\text{\AA}$	$d(\text{calc.})\text{\AA}$
				4	3.427 ⁺	
4	3.270	3.277	011	1	3.203 [†]	3.279
5	3.078	3.080	101	10	3.041 Δ	3.080
				7	2.953 [*]	
				2	2.837 \square	
10	2.761	2.769	111	7	2.764	2.767
9	2.689	2.697	120	6	2.699	2.690
3	2.587	2.589	200	2	2.587	2.581
1	2.388	2.396	210	<1	2.373	2.388
<1	2.198	2.205	121	<1	2.275 [†]	2.203
				5	2.098 ⁺	
				<1	2.051 \square	
8	2.0301	2.0314	211	6	2.0273	2.0280
1	1.9982	2.0025	220	<1	1.9902	1.9968
				<1	1.9580 \square	
1	1.9492	1.9511	130			1.9460
3	1.9153	1.9160	002	1	1.9111	1.9195
				<1	1.8592 Δ	
7	1.8427	1.8458	031	7	1.8445	1.8430
				3	1.8090 ⁺	
1	1.7735	1.7748	221	1	1.7831	1.7715
2	1.7374	1.7387	131			1.7357
				1	1.7151 ⁺	
2	1.6632	1.6650	310			1.6599
<1	1.6288	1.6339	230			1.6294
				2	1.6127 [†]	

TABLE 5. (concluded)

Synthetic NiSb ₂ <i>a</i> = 5.178, <i>b</i> = 6.139, <i>c</i> = 3.832, all ± 0.003 Å				Nisbite <i>a</i> = 5.162 ± 0.008, <i>b</i> = 6.303 ± 0.001, <i>c</i> = 3.839 ± 0.009 Å		
<i>I</i> (est)	<i>d</i> (meas.)Å	<i>d</i> (calc.)Å	<i>hkl</i>	<i>I</i> (est)	<i>d</i> (meas.)Å	<i>d</i> (calc.)Å
1	1.5739	1.5737	301	2	1.5838 ^Δ	1.5702
6	1.5611	1.5620	122	2	1.5668	1.5660
1	1.5410	1.5401	202			1.5402
2	1.5252	1.5271	311	1	1.5287	1.5236
1	1.5116	1.5147	320			1.5102
1	1.4992	{ 1.5030 1.4963	231 121			1.4999 1.4962
1	1.4062	1.4056	141	<1	1.4859 ⁺	1.4029
1	1.3829	1.3844	222			1.3838
1	1.3627	1.3670	132	1	1.3603	1.3666
5	1.3453	1.3485	240			1.3449
<1	1.3336	1.3350	330			1.3312
1	1.2936	1.2945	400	1	1.3211 ⁺	1.2905
<1	1.2684	1.2682	410			1.2643
2	1.2558	1.2568	312			1.2556
1	1.2400	1.2402	103	2	1.2421	1.2421
5	1.2178	1.2189	113	3	1.2090 ⁺	
4	1.1986	1.1979	051			1.1995
4	1.1885	1.1882	322			1.1869
6	1.1683	1.1692	151		1.1658 [*]	1.1667
4	1.1570	1.1544	123			1.1556
2	1.1439	1.1433	421	1	1.1450	1.1437
3	1.1296	1.1271	213			1.1280
3	1.1144	1.1149	341			1.1122
6	1.1024	1.1028	242		1.1021 [*]	1.1015
2	1.0929	1.0922	033			1.0929
<1	1.0779	1.0769	223			1.0774
2	1.0735	1.0726	402	2	1.0742	1.0710
<1	1.0701	1.0687	133			1.0692
5	1.0593	1.0598	431			1.0571
<1	1.0518	1.0531	060			1.0505
2	1.0310	1.0320	160			1.0294
2	1.0137	1.0135	313			1.0135
1	1.0066	1.0068	233			1.0064
<1	1.0002	0.9997	501	<1	0.9982	0.9984
5	0.9850	0.9854	351	1	0.9804	0.9830
1	0.9772	0.9770	252			0.9755
1	0.9595	0.9580	004			0.9597
1	0.9455	0.9454	261			0.9432
3	0.9295	0.9293	530	<1	0.9286	0.9266
6	0.9090	0.9086	162			0.9072
7	0.9045	0.9043	450			0.9018
3	0.9003	0.9001	352			0.8986

⁺, †, ^Δ, □ represent reflections, either alone or coinciding with nisbite, of the following minerals: galena, pyrrargyrite, chalcopyrite, and breithauptite, respectively.

* Measured on 57.3 mm film only.

Intensities estimated visually.

shown in Table 5, gave a good x -ray diffraction pattern; the cell parameters, based on an orthorhombic cell, compare closely to those reported by Rosenqvist (1953a). The calculated density is 8.0 g/cc with $Z = 2$.

The name nisbite (NĪ-ZBAIT) is for the composition and has been approved by the Commission for New Minerals and Mineral Names, I.M.A. Type material is preserved at the National Mineral Collection, Ottawa.

PHASE AND CRYSTAL CHEMISTRY

Allargentum and antimonial silver

The latest work on the Ag-Sb system (Somanchi 1966) suggests that the solid-solution field of the ϵ -phase (allargentum) extends to about 9.5 wt % Sb on the Ag-rich solvus at 300°C. Somanchi, however, was unable to determine the exact location of the Ag-rich solvus and it is uncertain if the very steep slope of this solvus represents equilibrium conditions at lower temperatures. The apparent slope of the solvus of the Sb-rich antimonial silver could conceivably change below 300°C to cross 2.6 wt % Sb at about 100°C. It is much more difficult, however, to postulate that the Ag-rich solvus of allargentum shrinks abruptly from a composition of about 9.5 wt % Sb at 300°C to about 16.7 wt % Sb at 100°C, which would be required to accommodate the Red Lake allargentum. Therefore, either the slope of the Ag-rich solvus of allargentum is grossly misrepresented or the assemblage we have examined is not representative of equilibrium conditions. The numerous analyses of allargentum given by Petruk *et al.* (1970) suggest that the Ag-rich solvus of allargentum is in error, but the existence of several different compositions for antimonial silver associated with allargentum at Cobalt suggests, on the other hand, that non-equilibrium conditions may be common with these minerals. Further work is obviously needed on the low-temperature phase relations of the Ag-Sb and Ag-Sb-Hg systems.

Nisbite

The incongruent melting temperature of NiSb₂ to form Sb-rich NiSb and liquid has been given by Sibata (1941) as 626°C, from D.T.A. and microscopic work. We have obtained a value of $621 \pm 5^\circ\text{C}$ by polished-section examination of quenched charges from $617\frac{1}{2}^\circ\text{C}$ to 624°C, using a calibrated Pt-PtRh 10% thermocouple. Electron-probe microanalyses of the melted charge indicated two components: NiSb with 71% Sb (compared to 67.46% for stoichiometric NiSb), and antimony containing 5.5% Ni.

There is considerable disagreement in the literature on the composition of NiSb₂. Sibata (1941) gave Ni₂Sb₅ as the composition of this phase,

based on the appearance of phases at 600°C. He reported difficulty in synthesizing homogeneous NiSb₂ (Ni₂Sb₅) and annealed for 16 days at 600°C. Rosenqvist (1953*b*), on the basis of *x*-ray powder diffraction and a density determination of a run annealed at 600°C, concluded that the true formula is close to NiSb₂ but that the structure has nickel vacancies to the extent of Ni_{0.9}Sb₂.

Though we had no trouble obtaining homogeneous NiSb₂ by grinding and pelletizing, as described in "Procedures", we carried out longer-term experiments on closely-spaced compositions. After melting, the charges were quenched, ground and pelletized; then annealed for 19 days. They were then quenched, ground and pelletized a second time and annealed for a further period of 37 days. The annealing temperature was 600°C in all cases. The results obtained by microscopic examination, compared to those of Sibata and Rosenqvist, are shown in Table 6, and we therefore

TABLE 6

Reference	Formula	Wt % Ni	Phases reported
Theoretical	NiSb _{2.000}	19.427	
This paper	NiSb _{2.000}	19.423	Homogeneous NiSb ₂
This paper	NiSb _{2.001}	19.415	Homogeneous NiSb ₂
This paper	NiSb _{2.057}	18.988	NiSb ₂ + trace Sb
Rosenqvist (1953 <i>b</i>)	NiSb ₂	19.427	Ni _{0.9} Sb ₂ (= 17.82% Ni) + trace NiSb
Sibata (1941)	Ni ₂ Sb ₅	16.17	Homogeneous Ni ₂ Sb ₅

propose that the NiSb₂ phase is essentially stoichiometric. The conclusions arrived at by the previous workers can be explained by experimental difficulties since we suspect that at least one grinding and pelletizing operation is needed to make all the Ni and Sb react to give NiSb₂.

NiSb₂ likely has 6 non-bonding *d*-electrons in order to produce the marcasite structure which was suggested by Rosenqvist (1953*a,b*). This is consistent with the tendency of transition metal disulphides, diarsenides, and sulpharsenides to form structures in which maximum electron spin-pairing takes place (Nickel 1968). NiSb₂ is visualized as consisting of metal octahedra that share edges parallel to *c*. This produces a metal-metal interaction, which, in the case of nisbite, actually is one of repulsion since the *c* value is 3.83 Å rather than the ideal 3.62 Å for undeformed edge-sharing octahedra. (This 3.62 Å was obtained by using Rosenqvist's value of 2.56 for Ni-Sb distances.) The space group for NiSb₂ reported by Rosenqvist (1953*a*) is *Pnmm* and the reflections we have observed are consistent with the systematic absences for that space group.

Paracostibite

There are only sparse literature references to CoSbS. Lange & Schlegel (1951) reported that CoSbS melts incongruently to form two liquids near Sb_2S_3 in composition, plus CoS. No temperature or other data are provided for this reaction, but it can be supposed that their conclusions were based on D.T.A. and microscopic observations. Both these authors, as well as Bayliss (1969), report having synthesized CoSbS, but the only observation offered in both cases was that CoSbS was non-cubic. Hulliger (1959, p. 633) lists CoSbS as being diamagnetic and having the pyrite-type structure. He has corrected this in a personal communication (17 June 1969) in which he gives $a = 5.840$, $b = 5.958$, and $c = 11.673$ Å. This is close to our data.

Figure 4 shows the similarity of the powder patterns of parammelsbergite and synthetic paracostibite. This suggests that the structures of the two are probably related. Parammelsbergite has space group $Pbca$ (Stassen & Heyding 1968), and therefore obeys the extinction rules where, for $0kl$, $k = 2n$; for $h0l$, $l = 2n$, and for $hk0$, $h = 2n$. None of the 82 measured reflections for synthetic CoSbS violate these extinction rules, and this was confirmed by the precession method on crystals of synthetic CoSbS; therefore paracostibite belongs to the space group $Pbca$.

Synthetic paracostibite was annealed at temperatures varying from 800° to 100°C for three days, and the x -ray films after quenching, were essentially the same. X -ray patterns of CoSbS quenched from just below and just above its melting point also did not show any differences.

D.T.A. experiments in sealed silica glass tubes gave a very strong endothermic peak on heating at 888°C, but gave two exothermic peaks on cooling—at 904° and 840°C. The peak at 904°C was much smaller, and probably represents a reaction between two immiscible liquids, or a solid and a liquid, which is masked by the strong endothermic reaction at the incongruent melting point. The incongruent melting point was determined to be $876 \pm 5^\circ\text{C}$ by polished section examination of quenched charges from 874°C and 878°C using a calibrated Pt-PtRh 10% thermocouple. Examination of the melted charge showed rounded areas of Sb-bearing CoS with a ground-mass of Sb containing lamellae of CoSbS. Very rapidly quenched charges did not show well defined phases in polished section.

The nearest mineral in the literature to paracostibite is willyamite (Pittman, 1893), a pseudo-cubic mineral that has recently been redefined (Cabri *et al.* 1970a). Another orthorhombic CoSbS mineral, but with a distinctly different x -ray diffraction pattern has also been identified from New South Wales (Cabri *et al.* 1970b). The polymorphic relations between these three minerals is currently under investigation.

ACKNOWLEDGEMENTS

We would like to thank Mr. D. A. Hutton, Chief Geologist, and the management of Cochenour Willans Gold Mines Ltd. for permission to publish our findings. Our thanks, also, to Dr. E. J. Gabe for helpful discussions regarding the space group and indexing of paracostibite, to R. H. Lake for the D.T.A. measurements, to R. G. Pinard for the density measurement, and to D. R. Owens for the photographs.

REFERENCES

- BAYLISS, P. (1969): Isomorphous substitution in synthetic cobaltite and ullmannite. *Amer. Mineral.*, **54**, 426-430.
- CABRI, L. J. (1969): Density determinations: accuracy and application to sphalerite stoichiometry. *Amer. Mineral.*, **54**, 539-548.
- CABRI, L. J. & TRAILL, R. J. (1966): New palladium minerals from Noril'sk, Western Siberia. *Can. Mineral.*, **8**, 541-550.
- CABRI, L. J., HARRIS, D. C., STEWART, J. M. & ROWLAND, J. F. (1970a): Willyamite redefined. *Aust. Inst. Min. Met., Proc.* No. 233, March (in press).
- CABRI, L. J., HARRIS, D. C. & STEWART, J. M. (1970b): Submitted to *Amer. Mineral.*
- HULLIGER, F. (1959): Über den Zusammenhang zwischen Magnetismus und elektrischer Leitfähigkeit von Verbindungen mit Übergangselementen. *Helv. Phys. Acta*, **32**, 615-653.
- LANGE, W. & SCHLEGEL, H. (1951): Die Zustandsbilder der Systeme Eisen-Antimon-Schwefel und Kobalt-Antimon-Schwefel. *Zeit. F. Metallk.*, **B. 42**, 257-268.
- MARKHAM, N. L. & LAWRENCE, L. J. (1962): Primary ore minerals of the Consols lode, Broken Hill, New South Wales, *Australasian Inst. Min. Met. Proc.* No. 201, 43-80.
- NICKEL, E.H. (1968) Structural stability of minerals with the pyrite marcasite, arsenopyrite and löllingite structures. *Can. Mineral.* **9**, 311-321.
- PETRUK, W., CABRI, L. J., HARRIS, D. C., STEWART, J. M. & CLARK, L. A. (1970): Allargentum redefined. *Can. Mineral.*, **10**, 163-172
- PITTMAN, E. F. (1893): Note on the occurrence of a new mineral at Broken Hill. *Royal Soc. N.S.W., Proc.* **27**, 366-375.
- RILEY, R. A. (1968): Mulcahy Township (North half), District of Kenora (Patricia Portion) in Summary of Field work, 1968, (Ed. E. G. Pye), *Ontario Dept. Mines*, Misc. Paper **22**, 10-22.
- ROSENQVIST, T. (1953a): Magnetic and crystallographic studies on the higher antimonides of iron, cobalt, and nickel. *Acta Metal.*, **1**, 761-763.
- ROSENQVIST, T. (1953b): Magnetic and crystallographic studies on the higher antimonides of iron, cobalt, and nickel. *NTH-TR YKK, Trondheim*, 61 pages.
- SIBATA, N. (1941): The equilibrium diagram of the nickel-antimony system. *Sci. Rept. Tohoku Univ.*, **29**, 697-727.
- SOMANCHI, S. (1966): Subsolidus phase relations in the system Ag-Sb. *Can. J. Earth Sci.*, **3**, 211-222.
- SPRINGER, G. (1969): Electronprobe analyses of tetrahedrite. *N. Jb. Miner. Mh.*, 24-32.
- STAPLES, A. B. & WARREN, H. V. (1946): Minerals from the Highland-Bell Silver Mine, Beaverdell, British Columbia, *Univ. Toronto Studies Geo. Ser.*, **50**, 27-33.
- STASSEN, W. N. & HEYDING, R. D. (1968): Crystal structures of RuSe₂, OsSe₂, PtAs₂, and α -NiAs₂. *Can. J. Chem.*, **46**, 2159-2163.

Manuscript received July 9, 1969