GEOCHEMISTRY OF THE ORES

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ABSTRACT

The geochemistry of the ores from the Cobalt-Gowganda region was determined by chemical and mineralogical analysis of 150 examples. The principal mineralogical categories represented in all the samples are arsenides and carbonates. The carbonates are calcite and dolomite, and they contain small quantities of manganese and iron. The arsenides are present as assemblages of nickel, cobalt and iron arsenides, and these assemblages can be correlated with the bulk compositions of the ore samples. The highest concentrations of antimony occur in the nickel-rich arsenide assemblages, and silver is most abundant in those of nickel-cobalt arsenide. In samples with a low nickel content, the silver occurs as veinlets; in those with moderate nickel contents, it occurs predominantly as cores of arsenide rosettes; and in those with high nickel only trace amounts of disseminated silver are present. Only small quantities of sulphides, silicates and oxides are present in samples from the ore zones. Larger quantities of sulphides, however, are present in some of the samples from beyond the ore zones, and from mineralized Keewatin interflow rocks.

INTRODUCTION

The geochemistry of the ores from the Cobalt-Gowganda region was determined by analysing 150 samples that had been studied mineralogically and classified according to ore types. These samples were selected from a suite of 1000 samples taken from various mines and are considered to be representative of the Cobalt-Gowganda ores. Furthermore they consisted of a cross-section across the full width of the vein. The analyses were performed in the Spectrochemistry and Analytical Chemistry Sections, Mineral Sciences Division, Mines Branch by a variety of techniques. Four samples were analysed completely by wet chemical methods, 116 by emission-spectographic methods, and 30 by x-ray fluorescence. In addition, 33 of the samples were analysed for silver by the fire assay method, and 5 were analysed for gold by neutron-activation analysis. The samples that were analysed chemically were used as standards for the spectro-chemical analyses.

INVESTIGATORS

The analyses in the Spectrochemistry Section were performed, under the supervision of A. H. Gillieson, as follows : emission spectrographic

analyses by G. L. Mason and D. P. Palombo, x-ray fluorescence by Mrs. D. J. Reed, and neutron-activation analyses by C. Mahon. The analyses in the Analytical Chemistry Section were performed under the supervision of R. C. McAdam using classical and instrumental techniques including spectrophotometry, atomic-absorption spectrophotometry and polarography. The analysts were R. R. Craig, H. R. Lauder, R. W. Buckmaster and D. Bjerstedt. The fine assays for silver were performed by L. Lutes, C. A. Derry and D. M. Cumming. W. Petruk performed the mineralogical study and prepared this report.

RESULTS

The compositions of the samples analysed by wet chemical methods are given in Table 13.

TABLE 13. COMPOSITIONS OF SAMPLES (in weight per cent)
ANALYSED BY WET CHEMICAL METHODS.

Element and Oxide	Ni-Co-As Assemblage		Co-As Assemblage	Fe-As Assemblage
	Sample 17	Sample 157	Sample 109	Sample 688
C.O	5.82	11.20	7.98	21.60
MgO	4.41	3.50	0.36	2.02
MnO	0.25	0.39	0.05	0.06
Fe	1.61	4.04	8.55	11.60
Co	10.56	10.00	14.35	9.18
Ni	12.19	4.41	1.82	0.54
Cu	tr	0.07	0.10	0.01
Zn	0.04	0.13	0.01	0.01
Pb	0.04	0.05	0.03	nd
As	44.53	41.11	57.00	35.57
Sb	2.00	0.82	0.09	0.10
S	1.51	0.64	3.27	4.86
CO_2	7.61	10.60	6.44	16.50
Ag	7.85	10.78	0.01	0.04
Hg	0.37	0.87	0.01	0.03
Insol.	0.48	0.87	0.31	0.31
Total	99.27	99.48	100.38	102.43

nd = not detected
Sample 17 : in Huronian sediments, 91-foot level, Cadesky vein, Hi-Ho mine.
Sample 157 : in Huronian sediments, 24 feet above 4th level — Vein No. 1, Silver-fields mine.
Sample 109 : in Keewatin rocks above diabase, Vein 407, Christopher mine.
Sample 688 : in Keewatin rocks below diabase, Giroux Lake vein, Hi-Ho mine.

The samples analysed by spectrochemical and *x*-ray fluorescence methods were classified according to arsenide assemblages and the mean quantities of the elements in each were determined from these analyses (Table 14). The analysed values for the elements in individual samples of specific assemblages significantly overlapped the values in individual samples from other assemblages. Nevertheless, the mean is considered to have some significance.

Partial compositions of the ore from the Gowganda area, reported by Todd (1926) are given in Table 15 for comparison. The values reported

TABLE 14. QUANTITIES OF ELEMENTS IN ORE TYPES FROM THE COBALT-COWGANDA REGION (DETERMINED BY ANALYSING SAMPLES SPECTROCHEMICALLY AND BY X-RAY FLUORESCENCE : ALL VALUES IN WT. %).

Element	ORE VEINS							Mineralized Keewatin interflow (mean of 3)
	Mineral assemblages in ore zone					Mineralization beyond ore zone		
	Ni-As (mean of 2)	Ni-Co-As (mean of 27)	Co-As (mean of 49)	Co-Fe-As (mean of 19)	Fe-As (mean of 9)	arsenides + sulphides (mean of 8)	sulphides (mean of 5)	
CaO	NA	11.08	13.91	12.05	17.01	10.38	19.02	tr
MgO	NA	4.64	2.88	4.11	3.85	1.58	4.48	2.85
MnO	NA	0.26	0.18	0.15	0.19	0.09	0.14	0.11
Fe	1.60	3.03	5.88	9.96	8.83	5.08	8.20	13.20
Co	1.60	8.52	7.25	5.49	2.04	3.82	0.90	2.60
Ni	24.60	7.74	2.24	0.71	0.39	1.04	tr	tr
Cu	0.03	0.06	0.15	0.07	0.07	0.21	0.14	0.19
Zn	nd	tr	NA	NA	NA	0.60	0.40	0.43
Pb	nd	0.09	tr	tr	0.14	0.11	0.40	1.20
Mo	0.04	0.02	0.02	0.04	0.01	0.02	tr	0.01
Sb	5.50	1.15	0.10	nd	nd	1.62	NA	nd
Bi	0.19	0.13	0.07	0.10	0.05	0.08	tr	nd
Cr	0.04	0.06	0.03	0.01	0.07	NA	NA	NA
In	nd'	0.02	0.02	0.02	0.01	NA	NA	NA
Ti	nd	0.03	0.04	0.04	0.04	0.05	0.06	0.07
V	NA	0.03	0.03	0.03	NA	NA	NA	NA
Si	0.53	0.47	0.46	0.44	0.41	NA	NA	PC
Al	0.14	0.15	0.17	0.15	0.23	NA	NA	PC

nd = not detected   NA = not analysed for   PC = principal constituent   tr = trace

in Tables 13, 14, and 15 show that the compositions of the ores from the Cobalt and Gowganda areas are exceedingly variable.

It may be noteworthy that the deposits in the Cobalt and Gowganda areas are referred to repeatedly in the literature as members of six element veins, Co-Ni-As-Ag-Bi-U. They are, however, low in bismuth (Table 14), particularly low in uranium (less than 0.3 ppm, Boyle *et al.* 1969), and contain significant iron (Table 16).

TABLE 15. PARTIAL COMPOSITION OF ORE FROM THE GOWGANDA AREA (from Todd 1926).

Element	Crushed Rock	Ore					Dendritic Ore	
CaO	27.48	NA	NA	NA	NA	18.30	NA	NA
MgO	tr	NA	NA	NA	NA	tr	NA	NA
Fe	7.19	4.28	6.69	7.43	12.42	10.40	4.81	6.05
Co	5.04	21.10	13.97	12.10	9.27	6.25	16.02	9.56
Ni	0.74	tr	0.53	2.24	tr	0.47	1.10	0.78
Cu	nd	0.19	0.40	tr	nd	nd	tr	0.26
As	31.86	64.45	50.70	62.56	52.93	47.65	64.79	38.90
Sb	NA	tr	1.05	tr	NA	NA	tr	0.27
S	0.66	4.77	1.71	0.67	1.32	tr	1.26	0.72
Ag	2.68	NA	0.17	0.12	0.03	2.81	9.48	0.39
SiO$_2$	1.50	NA	NA	NA	NA	0.13	NA	NA

nd = not detected   NA = not analysed   tr = trace

TABLE 16. MINERALOGICAL COMPOSITIONS OF ORE SAMPLES.

Mineral	Ni-Co-As Assemblage		Co-As assemblage Sample 109 (modal comp.)	Fe-As assemblage Sample 688 (modal comp.)
	Sample 17 (modal comp.)	Sample 157 (modal comp.)		
Carbonates				
calcite	3.46	15.88	13.83	37.52
dolomite	12.76	7.58	0.76	—
Arsenides	71.58	60.00	84.88	61.82
Silicates and oxides	2.35	3.10	0.55	2.97
Native silver plus				
allargentum	9.00	12.47	0.02	0.07
Sulphides				
chalcopyrite	0.01	0.20	0.29	0.03
sphalerite	0.06	0.10	0.02	0.02
galena	0.05	0.06	0.03	—
Total	99.27	99.48	100.38	102.43

Mineralogical compositions of samples

Mineralogical studies show that the samples analysed consist of carbonates, arsenides, sulphides, sulphantimonides, native elements, silicates and oxides. The approximate mineralogical compositions of Sample Nos. 17, 157, 109 and 688 were calculated from the data in Table 13 as follows:

(1) CO_2 was combined with CaO, MgO, MnO and as much iron as necessary to convert all CO_2 to carbonates. From the molecular proportions the dolomite content was then determined by combining the molecular weight % of ($MgCO_3$ + $MnCO_3$ + $FeCO_3$) with an equal molecular weight per cent of $CaCO_3$, and the remaining $CaCO_3$ was taken to be calcite.

(2) The excess (MgO + MnO), if any, over that required to utilize all the CO_2 was added to insol. and referred to as "silicates plus oxides".

(3) The Cu, Zn, and Pb were combined with appropriate amounts of S and Fe to form $CuFeS_2$ (chalcopyrite), PbS (galena) and ZnS (sphalerite).

(4) The Ag was combined with Hg and appropriate amounts of Sb to form native silver plus allargentum. (The appropriate amount of Sb was considered as either 10% of the amount of Ag, or all of Sb, whichever is lower).

(5) The remaining Fe, S, Sb, and all of Ni, Co and As were combined as arsenides.

TABLE 17. SPECTROCHEMICAL ANALYSES OF DOLOMITE SAMPLES.

Element	Sample 3	Sample 13	Sample 15	Sample 28	Average
Ca	PC	PC	PC	PC	PC
Mg	PC	PC	PC	PC	PC
Mn	1.0	1.0	0.6	0.1	0.67
Fe	0.75	0.74	0.74	0.38	0.66
Cu	0.05	0.03	0.04	0.06	0.04
Pb	0.04	0.03	nd	nd	tr
Si	0.39	0.02	0.02	0.03	tr
Al	0.04	tr	tr	tr	tr

Sample　3: in Huronian sediments, east end Patricia vein, Hi-Ho mine, Cobalt area.
Sample 13: in Huronian sediments, middle Patricia vein, Hi-Ho mine, Cobalt area.
Sample 15: in Keewatin volcanics below diabase, Vein No. 21, Hi-Ho mine, Cobalt area.
Sample 28: in Keewatin tuff about 100 feet below diabase, Vein No. 6, Deer Horn mine, Cobalt area.

The results of the calculations, given in Table 16, show that the main constituents in the samples are carbonates and arsenides, and the minor ones are native silver, silicates, oxides, and sulphides. These results also show that the quantities of the constituents are variable from sample to sample.

Carbonates

Mineralogical studies show that the carbonates in the ore are calcite and dolomite, and the analytical data for CaO, MgO and MnO indicate that calcite is the only carbonate in some samples (Table 15 and Sample 688 Table 16), and that variable amounts of dolomite and calcite are present in other samples (Tables 13 and 16). Spectrochemical analyses show that the dolomite contains minor amounts of manganese and iron (Table 17), and Scott (1964) reported that the calcite from the Gowganda area contains up to 6.2 mole per cent $MgCO_3$, and small amounts of manganese and iron. There is no aparent correlation between the varieties of carbonates and occurrence of ore.

Arsenides

Mineralogical studies show that the arsenides are present in assemblages that can be classified as Ni-As, Ni-Co-As, Co-As, Co-Fe-As and Fe-As. The proportion of nickel, cobalt and iron to Ni + Co + Fe in samples from the ore zones were calculated and the values were plotted on a ternary Ni-Co-Fe diagram (Fig. 97). The results show that there is a correlation between the proportions of nickel, cobalt and iron and the mineralogical assemblages in the samples. The boundaries between the Co-As and Co-Fe-As assemblages and the Co-Fe-As assemblages, however, are poorly defined reflecting the gradation in mineralogy between these assemblages.

In order to show how the relationship between elemental distribution and mineralogical classification applies to a mineralogically zoned vein, the proportions of nickel, cobalt and iron were determined for samples of arsenides taken from within the east-west trending Vein No. 2, 3rd level, Silverfields mine in the Cobalt area. The results show that the nickel content decreases and the iron content increases for a distance of 140 feet from the east end of the vein (Fig. 98), and that the proportions of these elements are relatively constant for the remaining 215 feet of the vein. This elemental distribution corresponds to the distribution of mineral assemblages in these veins (Petruk 1968).

The arsenic : metal ratios, calculated from the data in Tables 13 and 15, vary from 1.57 to 2.31 and from 2.38 to 2.95 respectively. This indicates that the samples analysed contain mixtures of mono- and higher arsenides.
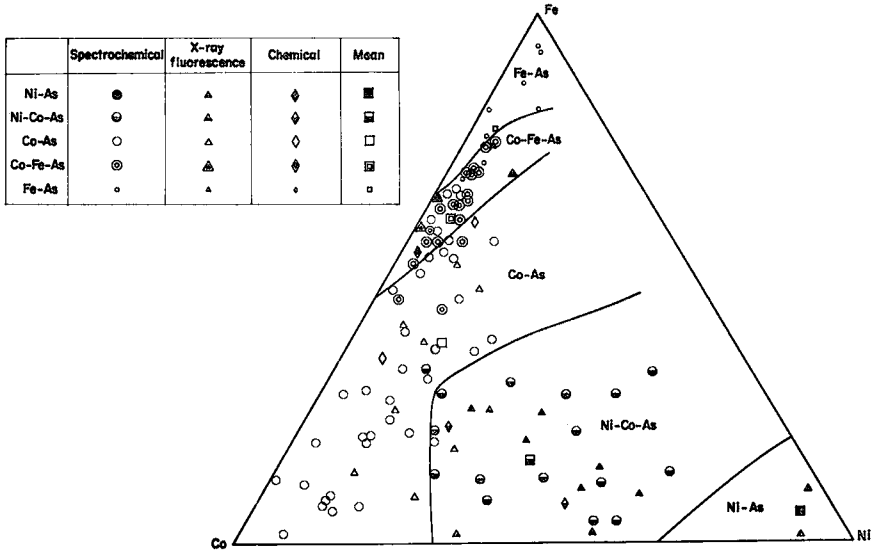
FIG. 97. Ternary diagram showing the proportions of nickel, cobalt and iron in samples from various mineralogical assemblages.
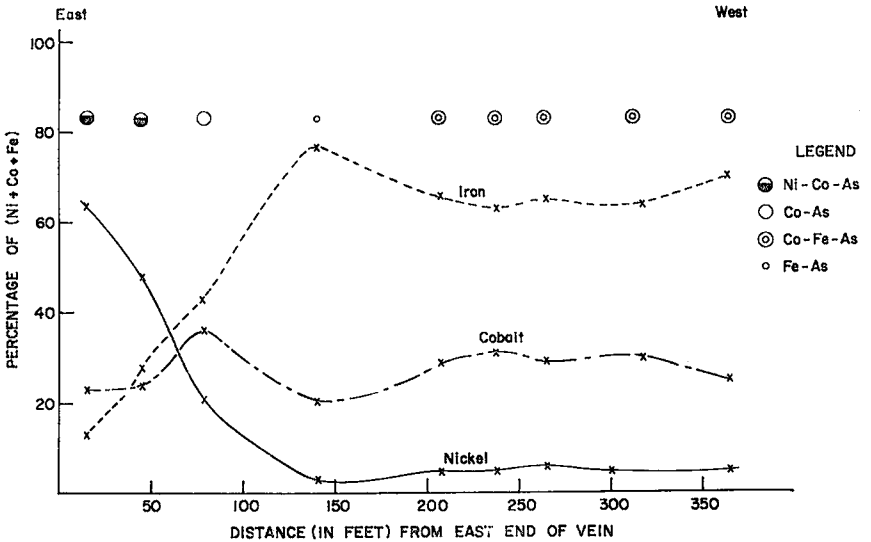

FIG. 98. Variations of nickel, cobalt and iron contents in samples from the 3rd level of Vein 2 in the Silverfields mine.

Sulphur was determined in too few samples to allow an interpretation. Mineralogical investigations of the ores, however, indicate that the arseno-pyrite and cobaltite contents increase in the proximity of the Fe-As assemblage ; thus the sulphur content may also increase towards the Fe-As assemblage.

Significant quantities of antimony are present in samples from the Ni-As assemblages, but only small amounts are present in the other assemblage (Table 13 and 14).

Native metals

The native metals in the ore are silver, bismuth, gold and arsenic, but only silver is present in significant quantities. Most of the silver is associated with the arsenide assemblages, and it occurs as cores in arsenide rosettes, as dendritic silver, and as veinlets and disseminated grains in arsenides and carbonates. A correlation between the silver contents in the ore, mode of occurrence of the silver, and types of arsenide assemblages, was made from samples that were studied microscopically, assayed for silver, and analysed for nickel, cobalt and iron by x-ray fluorescence. The results, plotted on a full logarithmic scale as weight per cent silver versus Ni + Co/Fe + Co (Fig. 99), show that silver occurs as cores of rosettes in samples that have a Ni + Co/Fe + Co value of 0.8 to 3.0, and as veinlets in arsenides and carbonates in samples where this value varies from 0.2 to 0.8. They also show that although there is no specific corre-lation of silver content with other parameters, most samples containing large amounts of silver belong to the Ni-Co-As assemblage. These results agree with the mineralogical observations that silver at the cores of rosettes occurs largely in the Ni-Co-As assemblages (Ni + Co/Fe + Co = 1.40), and that most of the high-grade silver ore is in the Ni-Co-As assemblage (page 127).

Variable amounts of native bismuth are present in the ore, and the samples analysed contain from trace amounts to 0.19% Bi (Table 14).

No native gold was found in the ore, but the mine operators have reported that trace amounts are present locally (Thomson 1960). The gold contents in three samples of mineralized Keewatin interflow rocks, one sample of ore from the Ni-Co-As assemblage, and one from the Fe-As assemblage, were determined by neutron-activation analyses. The results are given in Table 18.

Sulphides

The copper, zinc, lead, molybdenum, and some of the sulphur, iron, antimony, silver and bismuth are present as constituents of sulphides.

The results of the spectrochemical analyses (Table 14) show that only small quantities of these elements, and hence of sulphides, are present in the ore zones, and that somewhat larger amounts are present in parts of the veins beyond the ore zones, and in mineralized Keewatin interflow rocks. The quantities of practically all the sulphides are variable from sample to sample and no specific trends are apparent.

Silicates and oxides

Microscopical studies show that the samples contain small quantities of chlorite, quartz, actinolite, feldspar, epidote, sphene, ilmenite, rutile,
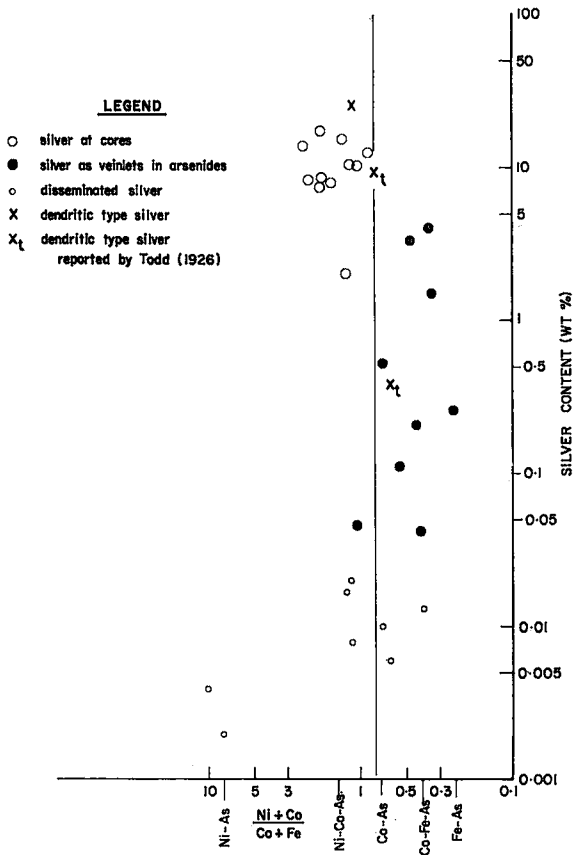

FIG. 99. Relationship between the silver content in ore, mode of occurrence of the silver, and types of arsenide assemblages in the samples.

TABLE 18. GOLD CONTENTS OF SAMPLES (determined by neutron-activation analyses)

Sample	Type of Sample	Mine	Vein	Gold Content (in parts per billion)
370	Mineralized Keewatin interflow	Silverfields		440
451	Mineralized Keewatin interflow	Deer Horn		47
433	Mineralized Keewatin interflow	Deer Horn		31
17	Ni-Co-As assemblage	Hi-Ho	Cadesky	53
688	Fe-As assemblage	Hi-Ho	Giroux Lake	133

anatase, chromite, and magnetite. The constituents of these minerals are reported in Tables 13 and 14 as insol., Si, Al, Cr, MgO, MnO, CaO, and Fe. The approximate quantities of silicates plus oxides present in sample Nos. 17, 157, 109 and 688 are reported in Table 16.

CONCLUSIONS

This investigation shows that there is a correlation between the mineralogical classification of the arsenide assemblage as determined in polished sections for small pieces of vein material and the composition of the ore vein at each point. The trace elements generally do not exhibit any systematic bulk distribution, except for antimony, which is associated with nickel. Most of the high-grade silver ore is associated with the Ni-Co-As assemblage, the silver occurs at the cores of arsenide rosettes in the samples with a moderate Ni content, and as veinlets in arsenides where the nickel content is lower. These observations suggest that there was some relationship between silver and arsenides during the formation of the rosettes.