THE GEOCHEMISTRY OF THE SUPERGENE PROCESSES IN THE NATIVE SILVER VEINS OF THE COBALT - SOUTH LORRAIN AREA, ONTARIO

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Abstract

Oxidation of the native silver veins is limited at Cobalt, but one vein, "Wood's vein", at South Lorrain is deeply oxidized providing an excellent example for the study of supergene processes. The supergene minerals formed as a result of oxidation are mainly erythrite, annabergite, scorodite, limonite, and wad. The supergene migration, concentration, and dispersion of the various ore and gangue elements in the soils, glacial materials, meteoric waters, and oxidized zones are discussed in terms of Eh, pH, and solubilities.

Introduction

This paper summarizes the geochemistry of the supergene processes in the native silver deposits of the Cobalt–South Lorrain area, Ontario. The work is based on extensive analytical data which cannot be recorded here. For details the interested reader is referred to the paper by Boyle *et al.* (1969). Most of the analytical work was done in field laboratories, and some laboratory investigations have been done on the oxidation of the various arsenides.

General Geology, Mineral Deposits, Topography, Climate, Glacial Deposits and Soils of the Cobalt–South Lorrain Area

The general geology of the Cobalt–South Lorrain area is discussed in previous papers. For the purposes of the present paper we need only recall briefly that the basement rocks are mainly steeply dipping Archean Keewatin intermediate to basic volcanic flows with a number of sedimentary interflow bands containing variable amounts of Fe, Cu, Zn and Pb sulphides. These rocks in turn are overlain in places by steeply dipping greywacke, quartzite, and conglomerate of the Timiskaming Series. Intruding both the Keewatin and Timiskaming rocks are granites (Lorrain granite) and hornblende syenite. Lying over the above Archean rocks with

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profound unconformity is the Proterozoic Cobalt Group consisting of conglomerate, greywacke, and quartzite which contain in places scattered and variable amounts of Cu, Pb, Zn and Fe sulphides near the base of the Group. Both the Archean and Proterozoic rocks are intruded by a gently dipping diabase sill (Nipissing diabase) and locally by olivine and quartz diabase dykes. All of these rocks in places are overlain by limestone, dolomite, and shale of Ordovician and Silurian age.

Three types of deposits characterize the Cobalt area, namely base metal sulphides in Keewatin interflow sediments ; disseminated sulphides in the arkose, greywacke, and conglomerate at or near the base of the Coleman Member ; and veins, composed essentially of carbonates, arsenides, sulpharsenides, sulphides, sulphosalts, and native silver in the Keewatin rocks, Cobalt Group sediments, and Nipissing diabase. These deposits are discussed in detail in previous papers. For purposes of comparison Table 95 indicates the range in the content of elements in the native silver veins.

The topography of the Cobalt–South Lorrain area is typical of the Precambrian Shield. Viewed from the highest elevations, which rarely exceed 1,250 feet, the country is an eroded peneplain carved into numerous valleys and flat-topped rocky hills, many of which follow north, northeast, and northwest trends, determined in part by pre-glacial and glacial erosion. The drainage systems generally follow the northeast slope of the peneplain towards Lake Timiskaming or the southwest one towards Montreal River.

TABLE 95. COMPOSITIONAL RANGES — VEINS IN THE COBALT AREA, ONTARIO

Element	*Content in percent* (range)	*Element*	*Content in percent* (range)
Pb	0.01 - 0.5	Fe	1.6 - 11.6
Zn	0.01 - 0.2	Bi	0.003 - 0.19
Cu	0.02 - 0.7	Hg	0.0002 - 0.8
As	2 - 57	Au	<0.000001 - 0.00001
Sb	0.03 - 3		(<10 - 100 ppb)
S	0.5 - 5	U	<0.00003 (<0.3 ppm)
Mo	0.001 - 0.04	CaO	6 - 21
W	<0.0005	MgO	0.4 - 4.6
Ag	0.003 - 10	MnO	0.1 - 0.4
Ni	0.05 - 24	CO_2	6.4 - 16.5
Co	0.10 - 15	SiO_2	0.5 - 1.5

Locally, however, the streams are diverted by linear valleys overlying faults and by glacial deposits which dam many of the old pre-glacial valleys.

The climate of the area is temperate. The winters are cold with a mean temperature of about 10°F. and the summers are warm with a mean temperature of about 65°F. The mean annual temperature is about 38°F. The average annual precipitation is 31.58 inches.

The region was severely glaciated during the Pleistocene Epoch by an ice sheet that spread over the whole area during Wisconsin time and moved generally in a southerly direction. On its retreat this sheet gave rise first to boulder till and later to the vast meltwater lake, Lake Barlow-Ojibway, in which thick varved clays were laid down in the deeper parts and poorly sorted gravel and sand along its bars and beaches.

The glacial deposits vary in thickness from a few inches up to 300 feet or more, and rock outcrops make up less than 10 per cent of the surface area in the vicinity of Cobalt. The deposits include boulder till, glacial clay, and glacio-fluvial deposits consisting of poorly sorted sand and gravel. These assorted materials lie in recessional moraines and outwash deposits, in varved clay deposits in some of the valleys, in poorly sorted stratified beach, spit, and bar deposits, in outwash plains, and a few eskers. Further details concerning the glaciation of the area are given by Thomson (1965) and Boyle *et al.* (1969).

The soils of the area developed under a variety of differences in parent materials, relief, vegetation, and climate. On the higher elevations in the silver belts at Cobalt and South Lorrain the parent materials are mainly boulder tills of various types with local occurrences of sand and gravel. In the vicinity of Sharp Lake and Gillies Lake the soils are developed on sand and gravel. North of New Liskeard in the "Little Clay Belt", in the Harrison-Hibbert valley near Cobalt, and locally elsewhere the soils overlie varved clay. Only locally, and then only sparsely, is there any soil developed from weathered bedrock.

The soils include those classified in the Great Soil Groups as Brown Forest, Grey Wooded, Podzol, and Dark Grey Gleisolic. In addition there are occurrences of highly organic soils including muck, peat, and half-bog soils in numerous places. With the exception of the organic soils, all of the soil types exhibit good profiles and are well- to moderately-well drained. Most of the organic soils are poorly drained or water saturated throughout the year. The organic soils yield a slightly acid reaction (pH 5-6) ; the other soils are variable giving neutral and slighly acid or alkaline reactions depending on the amount of calcareous materials in their parent tills and clays. More details on the soils of the Cobalt area are given by Hoffman, Wicklund & Richards (1952) and Boyle *et al.* (1969).

GEOCHEMISTRY OF THE SUPERGENE PROCESSES

Because of glaciation and a persistent cover of till and clay most of the veins in the Cobalt–South Lorrain area exhibit remarkably little oxidation beyond thin surficial effects manifested mainly by the presence of cobalt and nickel blooms (erythrite and annabergite). Most veins present fresh arsenides, carbonates, and native silver in their sub-outcrops below the till and clay. Some, however, exhibit shallow oxidation zones, a few inches in thickness, and one vein in particular — Wood's vein in the Keeley mine at South Lorrain — was deeply oxidized to a depth of 500 feet

TABLE 96. WATER ANALYSIS OF TYPICAL WATER LEACHING SILVER VEINS AT COBALT.[1]

Constituents, etc.	Content in ppm	Constituents, etc.	Content in ppm
Temp. at sampling– °C	6.0	Calcium (Ca)	64.7
Temp. at testing– °C	23.7	Magnesium (Mg)	7.9
CO_2 calculated	10	Iron (Fe), Total	0.43
pH	7.5	Dissolved	—
Colour (Hazen units)	5	Aluminum (Al), Total	0.00
Alkalinity as (— Phenolphthalein)	0.0	Manganese (Mn), Total	0.07
$CaCO_3$ (— Total)	160	(Dissolved)	—
		Sodium (Na)	4.1
Sp. conductance, micromhos at 25°C	384	Potassium (K)	1.4
Hardness as (Total)	194	Ammonia (NH_3)	—
$CaCO_3$ (Non-carbonate)	34	Carbonate (CO_3)	0.0
		Bicarbonate (HCO_3)	195
		Sulphate (SO_4)	35.2
		Chloride (Cl)	5.0
		Nitrate (NO_3)	0.5
		Silica (SiO_2)	8.0
		Sum of constituents	223
		% Sodium	4.4
		Saturation index at test temperature	+0.1
		Stability index at test temperature	7.3
		Sodium Absorption Ratio (SAR)	0.1

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[1] Analysis by Inland Waters Branch, Water Quality Division, Department of Energy, Mines & Resources, Ottawa. For location see Table 4, Spring No. 1, Boyle *et al.* 1969.

or more. This vein provides an example of the oxidation phenomena that probably prevailed in all veins before glaciation took place.

Circulating ground waters are the principal agents responsible for the oxidation of the veins at South Lorrain and Cobalt. These waters enter the veins at the surface and effect numerous changes discussed briefly below. In addition they contribute elements derived from the veins to the tills and other unconsolidated materials where the water table is high and/or where the waters flow down gradient through the unconsolidated materials.

In the following sections analyses of the circulating waters and their precipitates, the glacial materials and soils, and the oxidized parts of veins are given and briefly commented on. These form the data for a discussion of the migration, dispersion, or concentration of the principal elements during the oxidation of the native silver veins. The reader interested in

Table 97. Maximum, Minimum, and Average Values of pH, HCO_3, and Other Constituents in Water from Wells, Springs, and Diamond Drill-Holes in Areas of Precambrian Rocks Cobalt Area, Ontario

(Eh in millivolts; cations and anions in ppm; CO_2 calculated).

	No. of samples	Maximum	Minimum	Mean	Std. dev.		No. of samples	Maximum	Minimum	Mean	Std. dev.
pH	210	8.8	4.0	7.3	0.79	Al	8	0.26	0.02	0.11	0.34
Eh	210	+665.	+30.	+412.	96.9	Na	33	74.0	0.6	9.15	0.57
HCO_3	33	553.	2.6	183.	0.48	K	33	21.3	0.3	1.86	0.45
CO_2	33	13.	0.00	6.3	0.36	Pb	19	0.06	0.005	0.008	0.35
SO_4	33	288.	3.9	26.0	0.48	Zn	37	0.32	0.005	0.03	0.57
Cl	33	145.	0.4	5.0	0.72	Cd	20	0.002	0.0002	0.0004	0.30
NO_3	25	1840.	0.05	0.66	1.03	Cu	52	0.35	0.001	0.006	0.68
SiO_2	33	29.	0.6	10.5	0.27	As	42	9.10	0.002	0.04	1.02
Ca	33	230.	5.2	53.1	0.35	Sb	53	0.48	0.0001	0.0009	0.78
Mg	33	70.3	0.09	11.5	0.57	Ag	56	0.004	0.0002	0.0007	0.22
Fe	60	40.	0.02	0.21	0.59	Co	28	0.70	0.001	0.007	0.85
Mn	62	0.88	0.01	0.02	1.05	Ni	39	0.60	0.001	0.004	0.77
Mn/Fe	58	7.0	0.01	0.15	0.59	Ni/Co	21	0.009	0.0002	0.001	0.45

Footnotes: For pH and Eh the mean and the standard deviation are arithmetic. For the other constituents the mean is the geometric mean, and the standard deviation is in log-units.

Analyses of highly acid groundwaters, etc. such as those shown in Table 100 have not been included in the compilation of this table.

the details of the analyses of waters, soils, etc., should consult the paper by Boyle *et al.* (1969).

Natural waters and their precipitates

A representative sample of a groundwater leaching veins and old workings is given in Table 96, and the maximum, minimum, and average values of pH, Eh, and metal content of all waters analyzed from the Precambrian and Palaeozoic areas at Cobalt are given in Tables 97 and 98. Analyses of the precipitates from some of the natural waters are included in Table 99. The following conclusions can be drawn from the data.

1. The natural waters leaching the veins at Cobalt are mainly bicarbonate-sulphate waters with small amounts of chloride, nitrate, and silica.

2. The pH of the waters in areas underlain by Paleozoic rocks is generally higher than the pH of waters in areas underlain by Precambrian rocks. This is evidently due to the presence in the former areas of abundant calcareous rocks, a feature that is further reflected by the relatively large amounts of HCO_3 in the waters.

Table 98. Maximum, Minimum, and Average Values of pH, Eh, HCO_3, and Other Constituents in Water from Wells, Springs, and Diamond Drill-Holes in Areas of Palaeozoic Rocks, Cobalt Area, Ontario
(Eh in millivolts; cations and anions in ppm; CO_2 calculated).

	No. of samples	Maximum	Minimum	Mean	Std. dev.		No. of samples	Maximum	Minimum	Mean	Std. dev.
pH	66	9.6	6.9	7.98	0.60	Al	11	<0.02	—	—	—
Eh	66	+480.	+60.0	+341.	89.	Na	11	139.	14.4	37.2	0.25
HCO_3	11	690.	127.0	249.	0.22	K	11	26.	2.0	6.45	0.37
CO_2	11	35.	4.0	10.1	0.27	Pb	3	0.02	0.01	0.015	0.16
SO_4	11	1362.	1.30	58.0	0.77	Zn	16	7.70	0.009	0.062	0.78
Cl	11	96.	0.90	8.32	0.58	Cd	5	0.002	0.0002	0.0005	0.37
NO_3	10	65.	<0.05	0.65	1.15	Cu	12	0.016	0.001	0.003	0.46
SiO_2	11	20.	9.6	11.8	0.8	As	12	0.029	0.002	0.0076	0.42
Ca	11	526.	16.3	54.9	0.47	Sb	15	0.0005	0.0002	0.0003	0.14
Mg	11	43.1	7.8	23.2	0.21	Ag	17	0.002	0.0003	0.0006	0.20
Fe	20	2.74	0.06	0.34	0.56	Co	12	<0.001	—	—	—
Mn	20	2.1	0.01	0.01	1.19	Ni	12	0.006	0.001	0.0016	0.29
Mn/Fe	20	1.05	0.01	0.10	0.48	Ni/Co	12	>6	—	—	—

Footnote: For pH and Eh the mean and the standard deviation are arithmetic. For the other constituents the mean is the geometric mean, and the standard deviation is in log-units.

TABLE 99. TRACE ELEMENT CONTENT (PPM) OF SPRING AND DRILL-HOLE PRECIPITATES, COBALT AREA, ONTARIO

Location	Pb	Zn	Cu	As	Sb	Ag	Ni	Co	Bi	Mn	Cd	Hg
1. North Cobalt, DDH*	120	180	60	56	2	<0.5	70	50	<10	1,500	<2	1.5
2. Hwy. 11 (Bypass) at Sharp L.; spring	5	50	8	66	<2	<0.5	15	100	<10	>10,000	<2	1.25
3. Sharp Lake; spring	<5	50	20	44	<2	<0.5	15	10	25	1,000	<2	1.12
4. Hwy. 11 (Bypass) at Sharp L.; spring	5	130	8	40	<2	<0.5	7	15	25	1,500	<2	0.9
5. Silverfields mine; DDH 231	10,000	>800	7,000	>2,000	130	0.5	50	30	25	300	16	4.4
6. Silverfields mine; fault zone	10,000	>800	2,000	>2,000	80	100	200	100	135	1,500	25	2.8
7. Silverfields mine; DDH	5,000	>800	1,500	No sample	nd	70	150	300	70	2,000	nd	nd
8. Langis mine; DDH 355–24	15	100	80	>2,000	15	1	20	15	<10	700	6	2.4
9. Langis mine; DDH 355–B–793	5	90	88	>2,000	20	<0.5	10	15	<10	200	5	nd
10. Langis; fault zone	15	110	144	>2,000	20	50	300	1,000	40	500	<2	7.0
11. Langis; DDH L–7	1,500	110	1,500	>2,000	50	7	150	200	<10	1,500	<2	nd
12. Langis; DDH L–4	1,000	140	3,000	>2,000	15	10	200	500	25	5,000	2	3.8
13. Langis; DDH L–4	7,000	720	640	>2,000	20	10	500	10,000	<10	>10,000	2	3.2
14. Langis; fracture zone near DDH L–4	5,000	>800	2,000	>2,000	30	30	700	>10,000	<10	>10,000	4	2.6
15. Agaunico property; DDH	80	>800	560	>10,000	20	0.5	2,000	5,000	35	2,000	5	nd
16. Nipissing diabase, cliff on Hwy. 11 (Bypass)	20	30	28	42	<2	<0.5	15	10	<10	300	<2	0.35
17. Cobalt area, spring in fracture	170	2,000	290	200	10	7	70	150	<10	200	11	nd
18. Beaver mine, 200 foot level	230	2,800	4,200	1,700	15	15	2,000	m	<10	M	nd	nd
19. La Rose vein, Cobalt	tr	nf	tr	M	tr	tr	m	M	1,150	m	3	12
20. Several localities, Cobalt area	nf	nf	tr	M	tr	tr	M	m	200	tr	2	4.7

* DDH = diamond drill-hole; nd = not determined; nf = not found; tr = trace; m = minor constituent (1–10%); M = major constituent (>10%) — by spectrographic methods.

1–10: limonitic (hydrous iron oxide) red-brown precipitates.
11–12: pink and yellowish flocculant, slimy precipitates.
13–14: black (hydrous manganese oxide) flocculant, slimy (wad).
15: yellow-brown, slimy (flocculant) with some white carbonate precipitate.
16: white, crystalline calcite and gypsum precipitate.
17: white or greyish, nodular, crystalline aragonite precipitate. Mo = 5 ppm; W = <4 ppm.
18: sooty black (manganiferous) precipitate, up to 1/4 inch thick, beside water course along vein. Presently being deposited. Sample provided by Dr. R. Thomson. Mo = 380 ppm.
19: erythrite on walls. Alteration product of Co arsenides. Mo = tr; W = nf.
20: annabergite and minor scorodite alteration of Ni arsenides. Mo, W = nf.

3. The Eh of the waters ranges widely in the two areas of rocks. The range is greatest in waters of Precambrian areas, from greater than + 665 millivolts to + 30 millivolts. Most of the underground waters have, however, readings from + 430 to + 30 mv indicating a reducing tendency. The same feature is evident for the well and spring waters in Paleozoic rocks where the Eh values range from + 480 to + 60 mv.

4. The SO_4 content of the waters is greatest in the Paleozoic rocks, which is surprising considering the amount of sulphides in the Precambrian rocks. It should be noted, however, that some acid waters in the Precambrian rocks are highly charged with sulphate (Table 100). The reason for the greater average content of sulphate in the Paleozoic rocks compared with the Precambrian rocks may be due to slightly soluble sulphates such as gypsum and anhydrite in the former rocks.

5. The chloride and silica contents of waters in both Precambrian and Paleozoic rocks show little difference and are about normal for most groundwaters. Nitrates are generally low in both types of waters, but a few springs and wells contain relatively high amounts of nitrate that are generally balanced by high contents of ammonium (ammonia). The source of the NH_4NO_3 is unknown. It may derive from contaminating agencies.

6. The precipitates in the vicinity of the silver deposits carry much higher contents of the ore and gangue elements than those outside the silver-bearing areas. This information may be useful for locating general areas containing silver deposits.

7. The trace element content of the natural waters and precipitates depends on many factors, including the availability of the elements in deposits or rocks, the degree of oxidation necessary to release the metals

TABLE 100. PARTIAL ANALYSES OF ACID GROUNDWATERS, CHRISTOPHER MINE, COBALT, ONTARIO (Elements in ppm)

Description	T°C	pH	Pb	Zn	Cd	Cu	As
407 drift N; fault 1	7	3.0	1.36	29	1.14	0.84	5.91
fault 2	7	6.4	0.84	885	0.02	178	0.05

Description	Ag	Ni	Co	Mn	Fe	SO_4	Cl
407 drift N; fault 1	0.05	75.0	445	100	780	9,370	2.9
fault 2	0.02	1.5	8.0	6.45	39.0	790	<0.4

from the deposits, and the pH and Eh. It is evident in some cases that the metals are not released from the silver veins by oxidation, or that the groundwaters are not in contact with the minerals long enough to dissolve sufficient metal for detection by analysis. During field investigations a number of cases of this type were found in the Silverfields mine where the water from certain drill-holes intersecting the rich silver veins, contained only infinitesimal amounts of nickel, cobalt, and other metals even though the Eh and pH conditions were favourable for the mobility of these metals. The influence of the pH on the mobility of the various elements is obvious, the more acid the waters the greater the metal content (Table 100). Many of the metals, however, retain considerable mobility even in waters with pH as high as 8 or more. The influence of the Eh is more difficult to interpret, and further work is necessary before any concrete statements can be made. It was found, however, that the trace metals tend to be in the highest concentrations in waters with Eh between +490 and +190 mv. All of the data on cobalt and nickel in the waters in Precambrian rocks show that cobalt is more mobile than nickel. This is confirmed by the fact that, compared with nickel, cobalt is generally present in higher amounts in the limonitic and manganiferous precipitates. In the Palaeozoic rocks on the other hand the evidence suggests that nickel is more mobile than cobalt, although both elements are present in very low amounts (Table 98).

Soils and glacial materials

The average trace element content of normal soils, till, and clay in the cobalt area is given in Table 101, and the distribution of a suite of trace elements in the vicinity of the O'Brien vein 6 is shown in Figure 226. From these data and numerous other analyses obtained on the soil and glacial materials at Cobalt (Boyle *et al.* 1969) the following conclusions can be drawn :

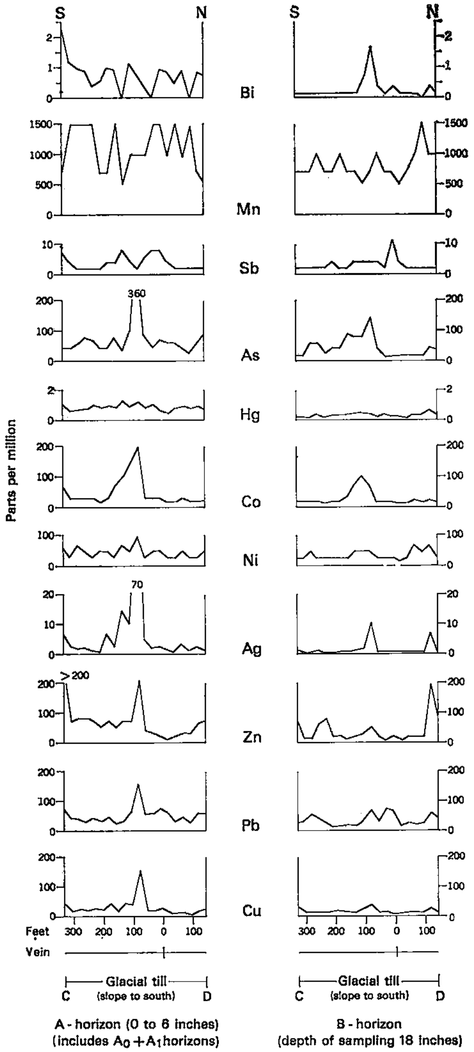
1. Tills and their overlying soils show the greatest increase in metal content in the vicinity of the veins, nearly all of the elements in the veins being enriched in these unconsolidated materials. On the other hand clay and derived soils exhibit little if any enrichment in the ore and gangue elements near veins.

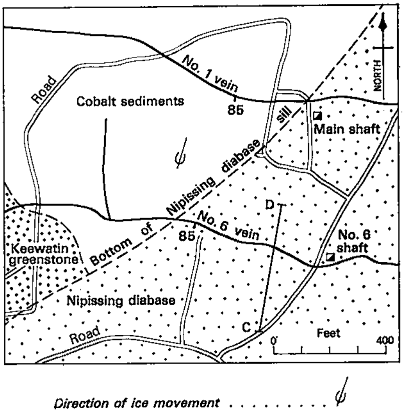
2. The A horizons are generally enriched in the ore and gangue elements compared with the B horizons (Boyle & Dass 1967). The C horizons near bed-rock may be greatly enriched in the vein elements in places.

3. The degree of enrichment of the vein elements in the tills and derived soils in the vicinity of the silver deposits is variable but is always

greater than 2, mostly greater than 10, and for some elements greater than 100 times that recorded as the background trace element content in these unconsolidated materials (Table 101).

4. In the vicinity of the silver veins most of the vein elements are taken up by vegetation, their ash containing equivalent or greater amounts of





Geological plan, Nipissing-O'Brien mine, Agnico Mines Ltd.

FIG. 226. Trace element distribution in soil and glacial till, O'Brien vein 6, Agnico Mines Ltd., Cobalt, Ontario (after Boyle *et al.* 1969).

elements, such as Ag, Ni, Co, Cu, and Zn, to that present in the soils (Hornbrook 1971).

Oxidized zones in silver veins

As mentioned above most silver veins exhibit little oxidation except for surficial developments of erythrite and annabergite. Some, however, have shallow oxidation zones, and one, Wood's vein in the Keeley mine at South Lorrain, was deeply oxidized to a depth of 560 feet or more (Bell 1923 ; Bell & Thomson 1924 ; and Walker 1924). The oxidized zone of this

TABLE 101. AVERAGE TRACE ELEMENT COMPOSITION (PPM) OF SOILS, TILL, AND CLAY, COBALT AREA, ONTARIO.[1]

Soil type	Pb	Zn	Cu	As	Sb	Mo	Ag	Ni	Co	Mn	Hg
Soil on till A_1 horizon	10	33	16	2	3	<1	0.5	30	11	572	0.20
Soil on till B horizon	12	30	15	<2	<2	<1	<0.5	35	13	505	0.11
Till C horizon	10	30	16	2	<2	<1	<0.5	35	10	500	0.20
Soil on sand & gravel A_1 horizon	25	60	7	<5	2	1	<0.5	25	10	500	0.50
Soil on sand & gravel A_2 horizon	5	7	4	<2	<2	<1	<0.5	11	3	400	0.20
Soil on sand & gravel B horizon	5	27	5	<2	<2	<1	<0.5	20	10	600	0.30
Sand & gravel C horizon	5	18	9	<2	<2	<1	<0.5	27	15	500	0.10
Soil on clay * A_1 horizon	14	131	41	5	2	<1	<0.5	46	15	490	0.20
Soil on clay * B or G (gley horizon)	12	106	33	2	1	<1	<0.5	46	17	590	0.14
Clay * C horizon	13	90	34	2	1	<1	<0.5	54	19	880	0.11

[1] Average values have been computed from composite and single analyses of soils, etc. well removed from sites of known mineralization. In all samples W = <4 ppm, Bi = <0.5 ppm.

* Cobalt area and Casey and Harris townships.

vein was sampled and the results of major and trace element analyses of the limonite-clay material are given in Tables 102 and 103.

The unoxidized parts of Wood's vein contain a mineral assemblage similar to that in the typical Cobalt veins, the principal minerals being carbonates, arsenides, native silver, native bismuth, etc. Thorough oxidation of these minerals and the immediately adjacent wall rock alteration zones has left a brownish puggy limonitic clay consisting essentially of

TABLE 102. CHEMICAL ANALYSES OF LIMONITE — CLAY COMPLEX, WOOD'S VEIN, KEELEY MINE, SOUTH LORRAIN[1]

Constituent	Percentage in limonite — clay complex (average of three composite samples)
SiO_2	49.7
Al_2O_3	19.2
Fe_2O_3	16.1
CaO	1.6
MgO	5.4
Na_2O	0.7
K_2O	0.8
H_2O (total)	9.2
TiO_2	0.9
MnO	0.3
CO_2	0.1
S	0.6
SO_3	0.7

[1] Analyses, Analytical Section, Geological Survey of Canada.

TABLE 103. TRACE ELEMENT ANALYSES OF OXIDIZED VEIN MATERIAL (LIMONITE — CLAY COMPLEX) WOOD'S VEIN, KEELEY MINE, SOUTH LORRAIN

Element	Content (ppm)	Element	Content (ppm)
Ba	175	Sb	50
Sr	40	Bi	540
Zr	250	V	180
B	<10	Mo	6
Ni	1,000	W	<2
Co	3,185	Sn	<10
Ag	350	Cd	0.7
Cu	750	Zn	500
Pb	450	Hg	1.7
As	4,135	U	<0.3

limonite, clay minerals, and minor amounts of carbonate, native silver, wad, and locally traces of malachite, azurite, erythrite, annabergite, and scorodite. This assemblage is referred to as "ferric" material by Bell (1923) and Walker (1924). At depth and locally along strike in Wood's vein, material referred to as "ferrous" occurred. This phase was a bluish puggy clay rich in wire, platy, spongy, and stalactitic silver, chlorite, argentite, disintegrated arsenides, etc. This material has been nearly completely removed from the vein and was not seen in any quantity by the writers. Analyses from Walker (1924) of the "ferrous" and "ferric" phases are given in Table 104.

Wood's vein is a good example of thorough oxidation of the native silver Ni-Co-arsenide veins in the Cobalt–South Lorrain area and will be used

TABLE 104. ANALYSES OF "FERROUS" AND "FERRIC" PHASES IN THE OXIDIZED ZONE OF WOOD'S VEIN, KEELEY MINE, SOUTH LORRAIN (AFTER WALKER 1924)

Constituent	*Ferrous type* %	*Ferric type* %
SiO_2	34.22	41.32
Al_2O_3	12.45	12.35
FeO	12.46	0.43
Fe_2O_3	—	22.56
MgO	10.26	6.45
CaO	1.37	1.84
Na_2O	0.27	0.30
K_2O	0.54	0.51
H_2O	7.46	11.57
CO_2	0.30	0.24
TiO_2	0.44	0.48
Fe	4.20	0.23
Co	1.27	0.20
Ni	0.17	0.16
Cu	0.12	0.06
Ag	0.25	—
As	11.90	1.16
Sb	0.48	0.18
S	1.30	0.26
P_2O_5	0.39	0.32
Total	99.85	100.62

to explain the migration of the elements in the discussion that follows. Other veins seen by the writers exhibit only superficial effects. Supergene minerals occurring in these veins include the following : limonite, wad, clay minerals, erythrite, annabergite, scorodite, melanterite, malachite, and azurite. Of the arsenates, erythrite is the most abundant followed by scorodite and annabergite. Supergene quartz, calcite, and rutile occur in minor amounts in some oxidized zones. Symplesite, the iron arsenate chemically analogous to erythrite and annabergite, was identified many years ago by Ellsworth (1916) but was not seen by the writers. Chapmanite, Sb (OH) Fe_2 $(SiO_4)_2$, was identified by Walker (1924) in the oxidized zones of the Keeley Mine. "Silver leach" the silvery blue lustrous matertal that commonly appears in and near some of the high grade silver ore shoots in the Cobalt area and also at South Lorrain and Gowganda is acanthite mixed with calcite and wad.

A study of the mineralogy of the oxidized zones and of the analyses given in Tables 95, 102, 103 and 104 indicates the following gains and losses in the oxidized (ferric) zones as compared with the primary zones from which they were derived : The constituents of the carbonates, Ca, Mg, and CO_2 are strongly depleted as are also the various constituents of the arsenides, sulphosalts, and sulphides, including As, Sb, S, Ni, Co, Cu, and Zn. The alkalies may exhibit a depletion in places. The main enrichments are Fe, Mn, SiO_2, and Al_2O_3. Silver is lost in substantial quantities where oxidation is pervasive and thorough. In the zone of reduction (ferrous zone) there is a general enrichment of Al_2O_3, SiO_2 and MgO, the latter constituent being present mainly in chlorite. The above observations as well as those based on the analyses of the waters and their precipitates (Tables 96, 97, 98, 99, and 100) and limited experimental work on the oxidation of the arsenides in the laboratory, permit a relatively accurate synthesis of the fate of the principle elements during supergene processes.

GEOCHEMISTRY OF THE ORE AND GANGUE ELEMENTS DURING SUPERGENE PROCESSES

The supergene processes in the veins are due to the action of meteoric waters containing dissolved oxygen and carbon dioxide of atmospheric origin. During these processes the mobility of the various elements is a function of the solubility of their salts, generally their sulphates, arsenates, antimonates, or hydrogen carbonates, the pH of the migrating solutions, and the Eh of the environment, manifested principally by the presence of free oxygen.

The supergene waters near the surface effect an oxidation of the hypogene lode minerals and remove various soluble components. As the waters pass downward from oxidizing to reducing conditions some of the dissolved components are precipitated as new minerals. The remainder of the dissolved components are dispersed into the groundwater system and finally through springs into the lakes and stream systems.

The meteoric solutions in the veins are multicomponent systems that do not readily admit of simple interpretation because their phase relationships are complex, and they undergo constant change due to reaction with gangue or ore minerals. Because of these complexities it seems best to discuss the various minerals and their constituents individually and attempt an integration of the chemical factors from the analyses of the waters and the final mineral products, as observed in the field.

Iron, manganese, calcium, and magnesium

In the hypogene parts of the veins iron is concentrated principally in pyrite, arsenopyrite, various arsenides, sphalerite, and chalcopyrite. Manganese, calcium, and magnesium occur mainly in dolomite and calcite. In the zones of oxidation iron is bound mainly in limonite and scorodite, manganese in wad, and calcium and magnesium in secondary carbonates. The zones of reduction are minor but where present contain some iron in micaceous minerals, chlorite, marcasite, and supergene pyrite.

Dolomite, calcite, iron arsenides, arsenopyrite, pyrite, and chalcopyrite, being abundant in the veins, influence many of the reactions in the zones of oxidation and reduction. The dissolved oxygen and carbon dioxide in the meteoric waters attack these minerals and release the iron, manganese, calcium, and magnesium mainly as soluble hydrogen carbonates and sulphates. Thereafter, the Eh of the environment, as manifested principally by the presence of free oxygen, and the pH modify the course of the chemical reactions and result in some cases in a differential separation of the four elements. Thus, much of the iron and manganese may be fixed as insoluble hydrous oxides in the oxidized zones, whereas the calcium and magnesium may migrate downward in the solutions. The various reactions, though complex in detail, can be discussed simply as follows :

Dolomite and calcite, when attacked by water containing CO_2 yield soluble hydrogen carbonates thus :

$$MgCO_3 \text{ (magnesium component) } + H_2O + CO_2 = Mg(HCO_3)_2$$

$$CaCO_3 \text{ (calcium component) } + H_2O + CO_2 = Ca(HCO_3)_2$$

$$FeCO_3 \text{ (iron component) } + H_2O + CO_2 = Fe(HCO_3)_2$$

$$MnCO_3 \text{ (manganese component) } + H_2O + CO_2 = Mn(HCO_3)_2$$

Arsenopyrite and pyrite when oxidized yield soluble ferrous sulphate, ferric arsenate, and sulphuric acid as final products :

$$2FeAsS + 7O_2 + 2H_2O = 2FeAsO_4 + 2H_2SO_4$$
$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

The FeS and MnS components of sphalerite (Zn,Fe,Mn)S oxidize to give soluble ferrous and manganous sulphates

$$FeS + 2O_2 = FeSO_4$$
$$MnS + 2O_2 = MnSO_4$$

and chalcopyrite yields copper sulphate and ferrous sulphate

$$CuFeS_2 + 4O_2 = CuSO_4 + FeSO_4$$

The sulphuric acid derived from the oxidation of arsenopyrite and pyrite would react immediately with any available dolomite or calcite, thus reducing the acidity and producing soluble iron, manganese, calcium, and magnesium sulphates. The reaction for the iron and magnesium components of the dolomite may be written :

$$FeCO_3 + H_2SO_4 = FeSO_4 + H_2CO_3$$
$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2CO_3$$

In solution the Fe and Mn are markedly affected by the oxidation-reduction potential (Eh) and pH of the environment because these elements have two possible oxidation states. Calcium and magnesium are not markedly affected by the Eh because of their single oxidation state in nature (oxidation state 2). Their mobility is essentially dependent on the pH of the solution (H^+ concentration), the concentration of H_2CO_3, CO_3^{2-}, and HCO_3^- or the concentration of SO_4^{2-}.

A study of the redox potentials of the half reactions for iron and manganese indicates that ferrous iron will be oxidized to the ferric state by atmospheric oxygen in both an acid and alkaline environment; the reaction will, however, proceed with greatest facility in alkaline solutions. As regards manganese, however, the potential developed by the oxygen couple is not sufficiently powerful to oxidize Mn^{++} to MnO_2 in acid solutions but is adequate in an alkaline environment.

In the oxidized zones a separation of manganese and iron may take place in some veins because of the difference in the oxidation potentials of the two elements. Thus in some parts of Wood's and other veins limonite derived from sphalerite, dolomite, and manganiferous silicates is not accompanied by wad, the reason being that at the lower pH's (*circa* 4.5) the manganese is more mobile because it remains largely in the soluble Mn^{2+} state whereas the ferrous iron is nearly all oxidized and precipitated as ferric iron (limonite).

During the oxidation of the lodes, the iron, once it is released as ferrous salts from the various hypogene minerals, may follow several courses, as follows :

1. In relatively dry parts of the oxidized zones where pyrite is abundant small amounts of iron are precipitated as melanterite and other hydrated sulphates. These probably result largely from evaporation and supersaturation, and most are temporal, redissolving during the influx of further increments of meteoric water. They are rare.

2. Most of the iron is bound in limonite. The reactions to produce this mineral aggregate are complex but simplified probably run as follows : — As released initially at a relatively high acidity the iron in solution would be in the ferrous state. As the acidic solutions are neutralized by reaction with dolomite, calcite, and other gangue minerals, much of the ferrous iron is oxidized to ferric iron which undergoes extensive hydrolysis with the precipitation of hydrous ferric oxide. Water may then be split out from the colloidal hydrous ferric oxide with the consequent formation of limonite.

Beginning with ferrous sulphate, the most abundant iron salt in the initial oxidizing solutions, the reaction may be described as follows : At a pH of about 2.5, ferrous sulphate in the presence of abundant oxygen begins to oxidize to ferric sulphate and some insoluble hydrous ferric oxide.

$$12FeSO_4 + 3O_2 + xH_2O = 4Fe(SO_4)_3 + 2Fe_2O_3 . xH_2O$$

Hydrolysis of the ferric sulphate will then take place with the formation of basic salts under certain conditions and finally insoluble hydrous ferric oxide and sulphuric acid thus —

$$Fe_2(SO_4)_3 + xH_2O = Fe_2O_3 . xH_2O + 3H_2SO_4$$

Splitting out of water from the colloidal-like hydrous ferric oxides yields limonite (FeOOH).

The reactions with respect to soluble iron hydrogen carbonate are, likewise, those of oxidation and hydrolysis followed by precipitation of hydrous ferric oxides which ultimately yield limonite.

Some of the limonite in the veins and precipitates from the waters contain hydrous manganese oxides (wad). This is probably because at the pH of the oxidizing waters (4-8) part of the manganous ion in solution is oxidized to MnO_2 and coprecipitated with the hydrous ferric oxides. Colloidal phenomena may also play a part. The colloidal hydrous manganese oxides carry a negative charge whereas the colloidal hydrous iron oxides are positively or negatively charged depending on the conditions of precipitation. When positively charged the hydrous iron oxides tend to coprecipitate the negatively charged manganese sols; when negatively charged the manganese sols are repelled and dispersed to precipitate in other sites.

3. Where arsenides are abundant in the lodes some of the iron is bound in scorodite, $(Fe,Al)(AsO_4) \cdot 2H_2O$. With prolonged leaching by meteoric water the arsenate component may be removed to lower levels probably as soluble alkali arsenates leaving the iron bound mainly as limonite.

4. Traces of iron are coprecipitated with several secondary minerals such as calcite, malachite, erythrite, annabergite, etc.

5. The remainder of the iron (~0.2 ppm) migrates in the groundwater and is dispersed through springs into the streams and lakes of the area. There the waters again absorb oxygen, and some of the iron is thrown down as hydrous ferric oxides, ultimately to accumulate as limonite.

The chemistry of manganese in the oxidized zones is similar in many respects to that of iron and many of the details can be omitted. Once the element is released from dolomite and other minerals as either manganous sulphate or hydrogen carbonate, it may follow the following courses.

1. Some of the manganese is bound in wad, an indefinite mineral aggregate composed of various manganese oxides. This aggregate is the final product of the oxidation and hydrolysis of manganous sulphate and manganous hydrogen carbonate. The simplified reactions giving pyrolusite (MnO_2) can be stated as follows:

$$2MnSO_4 + 2H_2O + O_2 = 2MnO_2 + 2H_2SO_4$$

$$2Mn(HCO_3)_2 + 2H_2O + O_2 = 2MnO_2 + 4H_2CO_3$$

Unlike iron, the oxidation and hydrolysis of manganous salts is suppressed at low pH, and the two elements may be separated — limonite precipitating in one part of the oxidized zone and wad in another. More generally, however, both are found in close proximity to or intergrown with each other. This is probably because the initial acidic solutions are quickly neutralized by calcite and dolomite, causing nearly simultaneous precipitation of both iron and manganese. The negatively charged colloidal manganese oxides also tend to precipitate the positively charged hydrous oxides as already discussed under the formation of limonite. In addition they also tend to carry down relatively large amounts of cations, especially cobalt, nickel, arsenic, and lead (Table 99).

2. Small amounts of manganese are captured in the lattices of various secondary minerals, particularly erythrite. The supergene carbonates may also contain small amounts of the element.

3. Manganese is dispersed into the tills and soils in the vicinity of veins, mainly through the agency of ground waters, aided by vegetation (Figure 226).

4. The remainder of the manganese (~0.02 ppm) migrates in the groundwater and is ultimately dispersed through springs into the streams and lakes of the area where some is precipitated as wad in the sediments of these bodies of water.

Calcium and magnesium are not particularly affected by the Eh of the environment and are in general relatively mobile under oxidizing conditions, especially in solutions containing dissolved CO_2. The contents in the spring and mine waters average about 55 ppm for calcium and 17 ppm for magnesium, an order of magnitude greater than those for iron and manganese (Tables 97 and 98).

In the oxidized zones, the calcium and magnesium are released from dolomite and calcite and other carbonates in the form of sulphates and hydrogen carbonates; they may follow one or more of the following courses:

1. Small amounts of calcium and magnesium are precipitated in the oxidized zones as supergene calcite.

2. In oxidized zones such as those at the Keeley Mine much of the magnesium is retained and precipitated as a greenish clay mineral (chlorite?) in the ferrous type of material. Some is also retained in the clay complex in the ferric material (Tables 102 and 104).

3. Relatively large amounts of both calcium and magnesium migrate in the groundwaters (Tables 97 and 98).

Alkalies, silica, and alumina

The chemistry of sodium and potassium is not affected by the Eh of the environment, nor to any marked degree by the pH. Consequently each is highly mobile under both oxidizing and reducing conditions. According to the most recent data the equilibrium solubility of silica is essentially independent of the pH between the range 2 to 8. Above pH 8 the solubility increases rapidly with alkalinity because of the formation of soluble silicate anions. Aluminum, an amphoteric element, however, shows a marked pH dependence. Below pH 4 and above pH 10, Al_2O_3 is readily soluble, between pH 6 to 8, Al_2O_3 is relatively insoluble.

In the veins the alkalies and alumina are mainly in the wall-rock minerals, but small amounts occur in the carbonates and various other gangue minerals. Silica is bound in the wall-rock silicates and in the quartz in the veins. During oxidation of the lodes the carbonated meteoric water and H_2SO_4 released during oxidation of pyrite and other sulphides attack the silicates and quartz releasing the alkalies as soluble carbonates, hydrogen carbonates, sulphates, and arsenates. Silica may be released either as soluble alkali silicates or as dissolved silica probably in the form of monosilicic acid, $Si(OH)_4$. Aluminum probably enters solution mainly as the soluble sulphate or as the complex alkali sulphates. Sodium and potassium follow two main courses :

1. Some sodium and potassium are precipitated in the clay minerals. The amounts are not great, averaging about one per cent combined Na_2O and K_2O (Tables 102 and 104).

2. Small amounts of sodium and potassium (~10 ppm combined) are dispersed into the ground waters and ultimately into the streams and lakes of the area.

Alumina follows three main courses during oxidation processes :

1. Large amounts of alumina are bound in the secondary clay minerals and chlorite that occur in parts of the oxidized zones. These minerals probably result mainly by hydrolysis of aluminum salts due to changes in acidity, followed by interactions with K, Na, Mg, Fe, SiO_2, etc.

2. Some alumina is bound in limonite, wad, and scorodite. This alumina is coprecipitated with hydrous ferric oxide between pH 5-7.5 largely as $Al(OH)_3$ as a result of the hydrolysis of aluminum sulphate either by dilution or by neutralization of the acidic solutions :

$$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3H_2SO_4$$

Colloidal aluminum hydroxide carries a positive charge and may also be coprecipitated by the negatively charged manganese hydrosols.

3. Small amounts of alumina (<0.1 ppm) are dispersed into the groundwater and finally through springs into the stream systems and lakes of the area.

There is a general enrichment of alumina in the oxidized zones compared with the primary veins.

Silica probably enters solution as soluble alkali silicates, complex aluminosilicates, or as monosilicic acid, $Si(OH)_4$. The reaction representing the solubility of the last molecule may be represented thus :

$$(SiO_2)_n + 2n(H_2O) = nSi(OH)_4$$

This is a hydration and depolymerization reaction (Iler 1955).

The precipitation of silica is actually a most complicated process, not readily treated in detail here. For the purposes of discussion it is sufficient to say that the precipitation is a polymerization process represented by the reverse equilibrium given above.

$$nSi(OH)_4 = (SiO_2)_n + 2n(H_2O)$$

The precipitate is often of a colloidal nature, the colloid carrying a negative charge in alkaline, neutral, and weakly acid solutions and a positive charge in strongly acid solutions.

The solubility of silica is lowered by the presence of $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, Na_2SO_4, and other similar compounds in solution. Positively charged cations tend to precipitate colloidal silica at slightly acid or near neutral pH by neutralizing the negative charge on the colloids. Al^{3+} precipitates silica from a sol with the formation of insoluble aluminum silicates, and other cations capable of forming insoluble silicates probably behave in a similar manner. Hydrous ferric oxides cause rapid coagulation of excess silica from supersaturated solutions.

During the oxidation of the silver veins silica follows one or all of the following courses :

1. Much silica is bound in microcrystalline quartz in the limonitic and manganiferous debris of the oxidized zones. This quartz probably resulted by super saturation of the solutions with respect to silica as a result of changes in acidity and the presence of abundant hydrous ferric oxides, $Ca(HCO_3)_2$, and other components.

2. Large amounts of silica are bound in the clay minerals that are intimately mixed with limonite and other secondary minerals.

3. Some silica is bound in limonite, wad, and other products of oxidation. The precise nature of much of this silica is unknown. Some is probably present as microcrystalline quartz ; the remainder may be present as hydrated silica, $SiO_2 . nH_2O$. Much of this silica was probably coprecipitated as a colloid with hydrous oxides and hydrous manganese oxides as a result of neutralization of the negative charges of the silica sols, mainly by $Fe_2O_3 . xH_2O$.

4. A little silica (~10 ppm) is dispersed into the groundwater and ultimately through springs into the stream systems and lakes of the area.

There is a general enrichment in silica in the highly oxidized parts of the native silver veins over that present in the primary ore. Probably all of this silica was in solution at one time and was precipitated before migrating far by the processes discussed above.

Sulphur

In the primary veins sulphur is bound in the various sulphides and sulphosalts, with small amounts in the various arsenides.

During the oxidation of the various sulphides, sulphosalts, and arsenides the bulk of the sulphur is oxidized directly to SO_4^{2-}.

During oxidation of the veins sulphur behaves as follows :

1. Some of the sulphur oxidized to sulphate is precipitated as melanterite and amorphous sulphates as a result of supersaturation, most probably due to evaporation. These minerals form in dry environments and are temporal, dissolving again in fresh increments of meteoric waters.

2. A little sulphate is bound in anglesite where galena is abundant in the veins. Other sulphates are also present in the deeply oxidized zones as at the Keeley mine as witnessed by the presence of relatively large amounts of SO_3 in the analyses of the limonite-clay (Table 102). The nature of these sulphates is unknown since they cannot be physically separated from the limonite-clay matrix.

3. A little sulphur is bound in secondary sulphides, such as pyrite, marcasite, and acanthite, in the zones of reduction and in local sites where reducing conditions prevailed. Silver leach (acanthite) is an example of the latter.

4. Relatively large quantities of sulphur are dispersed as sulphate into the groundwater (26 ppm) in Precambrian rocks and are ultimately delivered through springs into the stream systems and lakes of the area.

During intense oxidation of the veins sulphur as sulphate is strongly leached. In the Keeley veins we estimate that more than half the sulphur of the hypogene ores was lost as a result of oxidation.

Arsenic

The principal primary arsenic minerals in the veins are various nickel, cobalt, and iron arsenides and arsenopyrite. Small amounts of arsenic are also bound in tetrahedrite and pyrite. The secondary arsenic minerals are annabergite, erythrite, and scorodite.

The reactions involved in the oxidation of the various arsenides are complex to say the least and not entirely understood. From our field studies supplemented by some laboratory experiments we think we can make out the various steps involved, although we would point out that the processes are in general continuous and concomitant in nature and do not take place in any recognized steps or stages. Taking arsenopyrite first the steps appear to be as follows :

Initial oxidation yields ferrous sulphate and arsenious oxide, an intermediate product which does not appear in the Cobalt deposits because the arsenic is oxidized on to the pentavalent state (As_2O_5) and dissolved as arsenic acid. A simplified equation expressing the oxidation of arsenopyrite can be written as :

$$4FeAsS + 13O_2 + 6H_2O = 4FeSO_4 + 4H_3AsO_4$$

Similar equations for the oxidation of cobaltite and gersdorffite can be written :

$$4CoAsS + 13O_2 + 6H_2O = 4CoSO_4 + 4H_3AsO_4$$

$$4NiAsS + 13O_2 + 6H_2O = 4NiSO_4 + 4H_3AsO_4$$

From this point onward the reactions are controlled largely by the pH and Eh. Where highly acid conditions prevail and where the solutions encounter little carbonate the iron, cobalt, nickel and arsenic are relatively mobile and may be completely removed from the oxidized zones. This condition prevails in some places as witnessed by the water analyses given in Table 100. Where neutralization of the solution prevails, especially where they come into contact with carbonates the dissolved iron is oxidized to the ferric state, undergoes hydrolysis, and may be precipitated as limonite. Alternatively, reactions of the ferric iron with the arsenic acid (or dissolved arsenates) yields scorodite. Dissolved cobalt and nickel on reacting with soluble arsenates yield erythrite and annabergite respectively. The simplified equations for these reactions can be written as follows :

$$Fe_2(SO_4)_3 + 2H_3AsO_4 + 4H_2O$$
$$= 2Fe(AsO_4) \cdot 2H_2O \text{ [scorodite] } + 3H_2SO_4$$

$$3CoSO_4 + 2H_3AsO_4 + 8H_2O$$
$$= Co_3(AsO_4)_2 \cdot 8H_2O \text{ [erythrite] } + 3H_2SO_4$$

$$3NiSO_4 + 2H_3AsO_4 + 8H_2O$$
$$= Ni_3(AsO_4)_2 \cdot 8H_2O \text{ [annabergite] } + 3H_2SO_4$$

Colloidal reactions also seem to be involved in the precipitation of scorodite, erythrite, and annabergite since we have found many greenish and pinkish gel-like substances precipitating from the ground waters (Table 99). These give no *x*-ray patterns but are composed essentially of hydrous iron and manganese oxides, cobalt and nickel hydroxides, and arsenates of undetermined constitution. On aging *in situ* they yield scorodite, erythrite, or annabergite often mixed with limonite or wad. The colloidal reactions[1] to produce scorodite can be written schematically as

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[1] In these reactions the iron species is characterized as the hydroxide to facilitate writing the colloidal equations. Actually the iron species is usually hydrous ferric oxide, $Fe_2O_3 \cdot xH_2O$.

follows :

$$\mathrm{Fe(OH)_3 + H_3AsO_4 = Fe(OH)_3 \,.\, \underbrace{AsO_4}_{\text{fixed}} + 3H^+}$$

$$\mathrm{Fe(OH)_3 \,.\, \underbrace{AsO_4}_{\text{fixed}} + 3H^+ = FeAsO_4 \,.\, 2H_2O\ [\text{scorodite}] + H_2O}$$

Similarly, the colloidal reactions to produce erythrite and annabergite can be written schematically as :

$$\mathrm{Co(OH)_2} + x\mathrm{H_3AsO_4} = \mathrm{Co(OH)_2} \,.\, \underbrace{x\mathrm{AsO_4}}_{\text{fixed}} + x\mathrm{H^+}$$

$$3\mathrm{Co(OH)_2} \,.\, \underbrace{x\mathrm{AsO_4}}_{\text{fixed}} + x\mathrm{H^+} + x\mathrm{H_2O} = \mathrm{Co_3(AsO_4)_2 \,.\, 8H_2O}\ [\text{erythrite}]$$

$$\mathrm{Ni(OH)_2} + x\mathrm{H_3AsO_4} = \mathrm{Ni(OH)_2} \,.\, \underbrace{x\mathrm{AsO_4}}_{\text{fixed}} + x\mathrm{H^+}$$

$$3\mathrm{Ni(OH)_2} \,.\, \underbrace{x\mathrm{AsO_4}}_{\text{fixed}} + x\mathrm{H^+} + x\mathrm{H_2O} = \mathrm{Ni_3(AsO_4)_2 \,.\, 8H_2O}\ [\text{annabergite}]$$

Minerals such as rammelsbergite and safflorite oxidize in a complex number of steps similar to those above, finally yielding annabergite and ~~erythrite.~~

Nearly all of the arsenates are unstable under conditions of intense weathering and leaching by meteoric waters. Scorodite gradually alters to limonite setting free the bulk of its arsenic component mainly as arsenic acid and/or soluble arsenates.

$$\mathrm{FeAsO_4 \,.\, 2H_2O} + x\mathrm{H_2O} = \mathrm{FeO(OH)} \,.\, x\mathrm{H_2O}\ [\text{limonite}] + \mathrm{H_3AsO_4}$$

Erythrite and annabergite are gradually removed if sufficient quantities of water are available, especially if the water has an acid reaction.

Under conditions of deep and prolonged oxidation, therefore, much arsenic (as well as nickel and cobalt) may be removed from the oxidized parts of the deposits and ultimately dispersed through the ground water system of the area. This condition has prevailed at the Keeley mine ; it is not marked in other deposits.

During the oxidation of the silver veins the behaviour of arsenic can be summarized as follows :

1. In veins carrying abundant cobalt arsenides much arsenic is bound in erythrite ; in those with abundant nickel arsenides the arsenic is bound largely in annabergite. Veins containing abundant arsenopyrite tend to yield much scorodite in which the bulk of the arsenic is contained.

2. Some arsenic is adsorbed and/or coprecipitated by $Fe_2O_3 . xH_2O$ and $MnO_2 . xH_2O$ and is bound in limonite and other secondary iron and manganese minerals. The amount of arsenic adsorbed and/or coprecipitated by hydrous iron oxides is generally higher than that found in the manganese hydrosols (Tables 99 and 103). The reason for this is probably due to the fact that colloidal hydrous iron oxides generally carry a positive charge which tends to neutralize and precipitate the arsenate ion, $(AsO_4)^{3-}$. The manganese sols, on the other hand carry a negative charge and hence repel the arsenate ions.

3. In local zones of reduction some arsenic is precipitated in proustite and/or xanthoconite. Such zones are rare. "Silver leach" may contain proustite in places.

4. Considerable amounts of arsenic are dispersed into the tills and soils in the vicinity of veins, mainly through the agency of ground waters aided in part by vegetation (Figure 226).

5. Small amounts of arsenic (up to 9 ppm in the Precambrian rocks) are dispersed into the groundwater system and through springs into the streams of the area. This arsenic may be in the form of soluble alkali or alkaline earth arsenates.

During extensive oxidation of the silver veins there is considerable migration of arsenic as indicated by comparing the composite analyses in Tables 95 and 103. In the oxidized (ferric) parts of Wood's vein we estimate that more than 80 per cent of the arsenic has been removed.

Antimony

In the primary ores most of the antimony is present in native silver and allargentum. Small amounts are bound in minerals such as tetrahedrite and the various arsenides. We have found no secondary (supergene) antimony minerals either at Cobalt or South Lorrain.

During the oxidation of the veins antimony follows one or all of the following courses :

1. Small amounts of antimony are adsorbed and/or coprecipitated by hydrous iron and manganese oxides (Table 99) and are retained by the limonite, wad, clays, and other minerals in the oxidized parts of the veins (Tables 103 and 104). The amounts precipitated in this manner are variable, but do not generally exceed 100 ppm.

2. Very small amounts of antimony are captured in the lattices of the supergene arsenates, erythrite and annabergite. In places small amounts of antimony are precipitated in chapmanite, $Sb(OH)Fe_2(SiO_4)_2$, according to Walker (1924). In local zones of reduction small amounts of antimony

may be bound in proustite, acanthite, and other sulphides (the "ferrous" zones mentioned by Bell & Thomson 1924).

3. Small amounts of antimony are dispersed into the tills and overlying soils, mainly through the agency of ground waters, aided in part by vegetation (Figure 226).

4. Small amounts of antimony (<0.001 ppm) are dispersed into the ground water system and ultimately through springs into the streams and lakes of the area.

During intensive oxidation of the veins, such as occurred at the Keeley mine, considerable amounts of antimony are removed — we estimate at least 75 per cent or more.

Bismuth

In the primary ores most of the bismuth is present in the native form; only small amounts of bismuthinite occur in the veins. We have found no secondary (supergene) bismuth minerals either at Cobalt or South Lorrain.

Our studies of the geochemistry of bismuth indicate that native bismuth oxidizes slowly in water carrying free oxygen, forming a hydrated oxide from which water is split out to give the yellow oxide, Bi_2O_3, bismite. The reaction, while complex, probably runs in two steps as follows :

$$4Bi + 3O_2 + n\,.\,H_2O = 2Bi_2O_3\,.\,nH_2O$$

$$Bi_2O_3\,.\,nH_2O = Bi_2O_3 \text{ [bismite] } + nH_2O$$

Bismite, Bi_2O_3, is a basic oxide and is practically insoluble in water. It does dissolve, however, in acidic solutions yielding hydrolyzed bismuth ion which can be characterized as BiO^+, $BiOH^{++}$, or $Bi(OH)_2^+$. It is probably in this form that some of the bismuth migrates in the ground waters at Cobalt. Native bismuth, when acted upon by water containing CO_2, as is the normal case in nature, alters to bismutite, $(BiO)_2CO_3$. This mineral can also be precipitated from slightly acid, neutral, or slightly alkaline solutions during the hydrolysis of bismuth ion.

The alteration of bismuth to bismutite in solutions containing CO_2 and O_2 appears to take place in a number of complex stages which are not well understood. It is apparent that the bismuth is first hydrated with the consequent formation of the oxy ion, BiO^+, in slightly acid solutions. On neutralization of the solutions this ion undergoes rapid hydrolysis with the formation of bismuthyl carbonate. The reaction can be expressed as follows :

$$4(BiO)^+ + O_2 + 2CO_2 = 2(BiO)_2CO_3 \text{ [bismutite]}$$

A similar situation prevails where the gangue or wall rocks carry carbonate. The simple reactions in this case involve the formation of the hydrogen carbonate ion which fixes the bismuthyl ion as the carbonate :

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2(HCO_3)^-$$

$$2(BiO)^+ + HCO_3^- = (BiO)_2CO_3 \text{ [bismutite] } + H^+$$

Other reactions may yield bismutite during the oxidation of native bismuth. One of these probably involves the formation of bismuth hydroxide or hydrated bismuth oxides during the hydrolysis of bismuth ion, followed by the formation of bismutite through the absorption of CO_2 or carbonate ion by the hydroxide or hydrated oxides. The reactions while complex in detail probably run as follows :

$$4Bi + 6H_2O + 3O_2 = 4Bi(OH)_3$$

$$2Bi(OH)_3 + CO_2 = (BiO)_2CO_3 \text{ [bismutite] } + 3H_2O$$

During the oxidation of the silver veins at Cobalt and South Lorrain bismuth follows one or all of the following courses.

1. Small amounts of bismuth are adsorbed and/or coprecipitated by hydrous iron and manganese oxides (Table 99) and are retained by the limonite, wad, clays, and other minerals in the oxidized parts of the veins (Table 103). The amounts precipitated in this manner are variable, but do not generally exceed 500 ppm. The nature of the bismuth in the limonite, wad, and limonite-clay complexes is unknown despite considerable work to isolate the mineral phases. It may be present solely in an adsorbed state; alternatively some bismuth may be present as bismite, Bi_2O_3, or bismutite, $(BiO)_2(CO_3)$.

2. Minor amounts of bismuth are captured in the lattices of the supergene arsenates, erythrite and annabergite (Table 99).

3. Small amounts of bismuth are dispersed into the tills and overlying soils, mainly through the agency of ground waters probably aided in part by vegetation (Fig. 226).

4. Very small amounts of bismuth (<0.0001 ppm) are dispersed into the ground water system and ultimately through springs into the streams and lakes of the area.

During intensive oxidation of the veins, such as occurred at the Keeley mine, most of the bismuth appears to be retained by the limonite-clay complex (Table 103).

Nickel and cobalt

In the primary ores nickel and cobalt are fixed mainly as arsenides. During oxidation these yield the secondary arsenates, annabergite and erythrite. The chemistry involved in these transformations is discussed in the section on arsenic and will not be repeated.

During the oxidation of the silver veins nickel and cobalt follow one or all of the following courses :

1. Under near neutral and mildly alkaline pH conditions considerable amounts of nickel are fixed as the hydrated nickel arsenate, annabergite. Cobalt, likewise, is fixed as erythrite. Under conditions of prolonged oxidation these two minerals are unstable, their components being dissolved and carried downward in the ground waters.
2. Much nickel and cobalt are adsorbed and/or coprecipitated by limonite and wad. The latter mineral aggregate is particularly enriched in cobalt in some occurrences (Table 99).
3. Considerable amounts of nickel and cobalt are dispersed into the ground water system and ultimately through springs into the streams and lakes of the area. The mobility of both nickel and cobalt are markedly affected by the pH of the ground waters. Under acid conditions the mobility is high (Table 100), whereas under near neutral to slightly alkaline conditions only relatively small amounts of both elements are mobile (Tables 97 and 98). In general, cobalt has a higher mobility than nickel in waters leaching Precambrian rocks ; the reverse appears to be true in Paleozoic rocks.
4. Both nickel and cobalt are dispersed into the tills and soils in the vicinity of the veins, mainly through the agency of ground waters, aided by vegetation (Fig. 226).

During intensive oxidation of the veins such as occurred at the Keeley mine large amounts of both nickel and cobalt are removed. We estimate that up to 80 per cent of both elements are lost during oxidation of the veins.

Mercury

Most of the mercury in the veins is bound in native silver and allargentum, with small amounts in the various sulphides, arsenides, and sulphosalts. During oxidation of these minerals mercury is liberated and probably goes into solution as mercurous sulphate which is slightly soluble in water, or mercuric sulphate which exhibits a moderate solubility in solutions containing sulphuric acid. From this point onward much of the mercury appears to be adsorbed and/or precipitated by limonite, wad, erythrite, and annabergite in the oxidized zones (Tables 99 and 103). Small amounts of the element may migrate in the natural waters, although we have no data on this feature of the geochemistry of mercury at Cobalt. Small amounts of mercury are dispersed into the tills and soils (Fig. 226) near the silver veins mainly by the ground waters, aided in part probably by vegetation.

Silver

In the veins at Cobalt and South Lorrain silver is present in the primary ores mainly in the native form or combined with antimony as allargentum and dyscrasite. Small amounts are also present in a variety of sulphides and sulphosalts, including acanthite (argentite), tetrahedrite, stephanite, pyrargyrite, proustite, and stromeyerite. These minerals are generally rare and are not considered in any detail in the discussion that follows. Supergene silver minerals are rare at Cobalt except for minor amounts of wire silver, xanthoconite, proustite, and the "silver leach" which comprises acanthite mainly. At the Keeley mine secondary silver minerals were common in the lower parts of the oxidized zones referred to as "ferrous ore" by Bell (1923) and others. There, the secondary silver minerals were acanthite (argentite) and native silver in the form of wires, spongy accumulations of tiny scaly crystals resembling miniature stalactites, and thin plates.

Under oxidizing conditions at Cobalt and South Lorrain silver probably enters solution as the soluble sulphate, Ag_2SO_4, or the slightly soluble carbonate, Ag_2CO_3, which in solutions saturated with CO_2 exhibits an increased solubility. The reactions to producte the sulphate from native silver by the action of sulphuric acid and ferric sulphate can be written as follows :

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2$$
$$2Ag + Fe_2(SO_4)_3 = Ag_2SO_4 + 2FeSO_4$$

Ferrous sulphate readily precipitates metallic silver from solutions containing Ag_2SO_4 and Ag_2CO_3, but due to the formation of ferric sulphate during the reactions the precipitation is not complete. The reactions may be expressed as follows :

$$Ag_2SO_4 + 2FeSO_4 \rightleftarrows 2Ag + Fe_2(SO_4)_3$$
$$Ag_2CO_3 + 3FeSO_4 \rightleftarrows 2Ag + FeCO_3 + Fe_2(SO_4)_3$$

It should be particularly noted that the presence of large amounts of ferric sulphate will reverse the equilibrium and inhibit the precipitation of silver. This point should be kept in mind in the discussion that follows :

Other factors that may lead to the precipitation of supergene native silver are a decrease in acidity, a decrease in the oxidation-reduction potential, and the presence of various reactive sulphides and gangue minerals. Tetrahedrite, chalcopyrite, arsenopyrite, and Ni-Co arsenides cause nearly complete precipitation of either metallic silver or argentite from solutions of silver carbonate or sulphate. Galena will also precipitate some silver, but pyrite and sphalerite have little effect. Other effective precipitants are carbonaceous matter, kaolin, and other silicates.

Hydrogen sulphide and alkali sulphides precipitate silver as sulphide from solutions of the sulphate and carbonate :

$$Ag_2SO_4 + H_2S = Ag_2S + H_2SO_4$$
$$Ag_2CO_3 + H_2S = Ag_2S + H_2CO_3$$

Solutions carrying soluble arsenates, antimony sulphate, and hydrogen sulphide react with tetrahedrite to form pyrargyrite or proustite. Alternatively these solutions on mingling with those carrying silver sulphate or carbonate will precipitate the silver as pyrargyrite or proustite in a neutral or alkaline environment. The minor local occurrences of proustite and xanthoconite may be formed as the result of the reaction of silver-bearing solutions on various arsenides.

Oxidation of the silver-rich veins at Cobalt generally yields a thin rubble of limonite, wad, and disintegrated arsenides and sulphides in which nodules, plates, and flakes of native silver are present. Some supergene wire and other forms of native silver may occur, but these are rare. With increasing intensity of oxidation such as occurred at the Keeley mine, South Lorrain, much of the native silver, as well as that in other minerals, is dissolved and migrates downward in the meteoric waters.

Once released from its primary minerals in a soluble form the silver may follow one or all of the following courses :

1. Some silver is bound in the vein limonites and wads (Table 103), and a little occurs in the natural iron and manganese precipitates from the circulating waters (Table 99). In the latter the high manganese material tends to concentrate more of the element than the hydrous iron oxides. Most of the silver in limonite and wad results from adsorption and/or coprecipitation processes involving the Ag^+ ion. Since hydrous manganese oxides generally carry a negative charge their precipitating effect on silver ion is greater than hydrous iron oxides which usually carry a positive charge on their colloids.

2. Small amounts of silver are captured in various secondary minerals, particularly in erythrite, annabergite, scorodite, malachite, and azurite.

3. Some silver is reprecipitated as the native metal in the so-called "ferrous zones" near the lower part of the oxidized zones (Table 104). This silver is probably precipitated as a result of reduction by ferrous and manganous ions as follows :

$$Ag^+ + Fe^{2+} = Ag + Fe^{3+}$$

$$2Ag^+ + Mn^{2+} + 4OH^- = 2Ag + MnO_2 + 2H_2O.$$

Alternatively, the reactions between nickel and cobalt arsenides and silver sulphate may precipitate native silver. The schematic equation for niccolite can be written as follows :

$$5Ag_2SO_4 + 2NiAs + 3H_2O = 10Ag + 2NiSO_4 + As_2O_3 + 3H_2SO_4$$

4. Small amounts of silver are reprecipitated as acanthite (argentite) in the "ferrous zones" as at the Keeley mine. This mineral appears to have formed in local sites where a high H_2S potential developed, precipitating the sulphide :

$$Ag_2SO_4 + H_2S = Ag_2S + H_2SO_4$$

A similar reaction probably gives rise to the acanthite formed in the so-called "silver leach" on exposed faces of silver ore and occasionally at the orifices of water seeps along faults.

5. Some silver is dispersed into the ground water system and ultimately through springs into the streams and lakes of the area. The silver content of the natural waters (Table 98) in the Paleozoic rocks is low (0.0003-0.002 ppm). In Precambrian rocks (Table 97) the incidence of higher values is notable, but in general the content of the element in the waters is low (0.0002-0.004 ppm). The acid waters (Table 100), however, are generally high, with silver contents up to 0.05 ppm. There is a suggestion that high amounts of silver tend to occur in waters rich in bicarbonate, a trend which may indicate that the metal is dissolved as the carbonate. In the highly acid waters the element probably migrates as the sulphate.

6. Small amounts of silver are dispersed into the tills and soils in the vicinity of the veins, mainly through the agency of ground waters, aided by vegetation (Fig. 226).

During extensive oxidation of the veins such as occurred at the Keeley mine relatively large amounts of silver are removed from the oxidized parts of the veins and reprecipitated at a lower level in the zones of reduction. Some silver is ultimately lost in this process ; we estimate about 10 per cent of the amount present in the primary veins.

Copper, lead, zinc and cadmium

These elements occur in small quantities but are not generally considered as ore elements in the native silver veins. On this account less emphasis was placed on the supergene dispersion of these four elements during our studies.

Copper occurs mainly in chalcopyrite and tetrahedrite, and lead and zinc in galena and sphalerite respectively in the primary parts of the veins. Cadmium is present mainly in sphalerite with trace amounts in galena. The supergene minerals of copper are malachite and azurite, and anglesite is the common oxidation product of galena. We have observed no supergene zinc and cadmium minerals.

Copper enters the supergene solutions mainly as the sulphate. Its mobility is high in an acidic medium and relatively low in neutral and alkaline solutions. Lead is relatively immobile because of the general insolubility of its sulphate. As the carbonate, lead exhibits an increased solubility if the solutions are charged with hydrogen carbonates. Zinc and cadmium are highly soluble as the sulphate. Zinc is relatively mobile under both acid and alkaline conditions. At or near a pH of 7 its mobility is reduced because of the precipitation of the hydroxide. Cadmium is relatively mobile under acid conditions but has a restricted mobility in alkaline solutions.

The elements follow the following courses during oxidation of the veins :

1. Some copper is retained as malachite and azurite in the oxidized parts of the veins. Lead is retained as anglesite, but zinc and cadmium are largely removed and do not form supergene minerals.

2. All four metals are strongly adsorbed and/or coprecipitated by the limonitic and wad precipitates at spring orifices and by the limonite and wad of the oxidized zones of the veins (Tables 99 and 103).

3. In the zones of reduction in Wood's vein of the Keeley mine, some copper appears to have been precipitated with the supergene sulphides (Table 104). The fate of lead, zinc, and cadmium is unknown in these zones.

4. Small amounts of copper, lead, and zinc are dispersed into the tills and soils in the vicinity of the veins, mainly through the agency of ground waters aided in part by vegetation (Fig. 226). We have not investigated the dispersion of cadmium in the overburden.

5. Some copper, lead, zinc and cadmium are dispersed into the ground water system and ultimately through springs into the streams and lakes of the area. The acidic waters are enriched in the elements (Table 100) ;

those with pHs in the near neutral and alkaline range tend to carry much lower contents of all of the four elements (Tables 97 and 98).

During intense oxidation of the veins all elements are lost. In the Keeley veins we estimate that at least 50 percent of these elements was lost from the veins as a result of oxidation.

Summary and Conclusions

Oxidation of the native silver veins is limited at Cobalt, but one vein "Wood's vein", at South Lorrain is deeply oxidized providing an excellent example for the study of supergene processes. The supergene minerals formed as a result of oxidation are mainly erythrite, annabergite, scorodite, limonite, and wad. The migration, concentration, and dispersion of the various ore and gangue elements in the soils, glacial materials, meteoric waters, and oxidized zones is controlled largely by the presence of abundant carbonates in the ores and by the Eh and pH of the environment. Most of the ore elements including Ag, Ni, Co, As, and Sb exhibit relatively high mobilites under acidic conditions, and restricted mobilities under neutral and alkaline conditions.

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