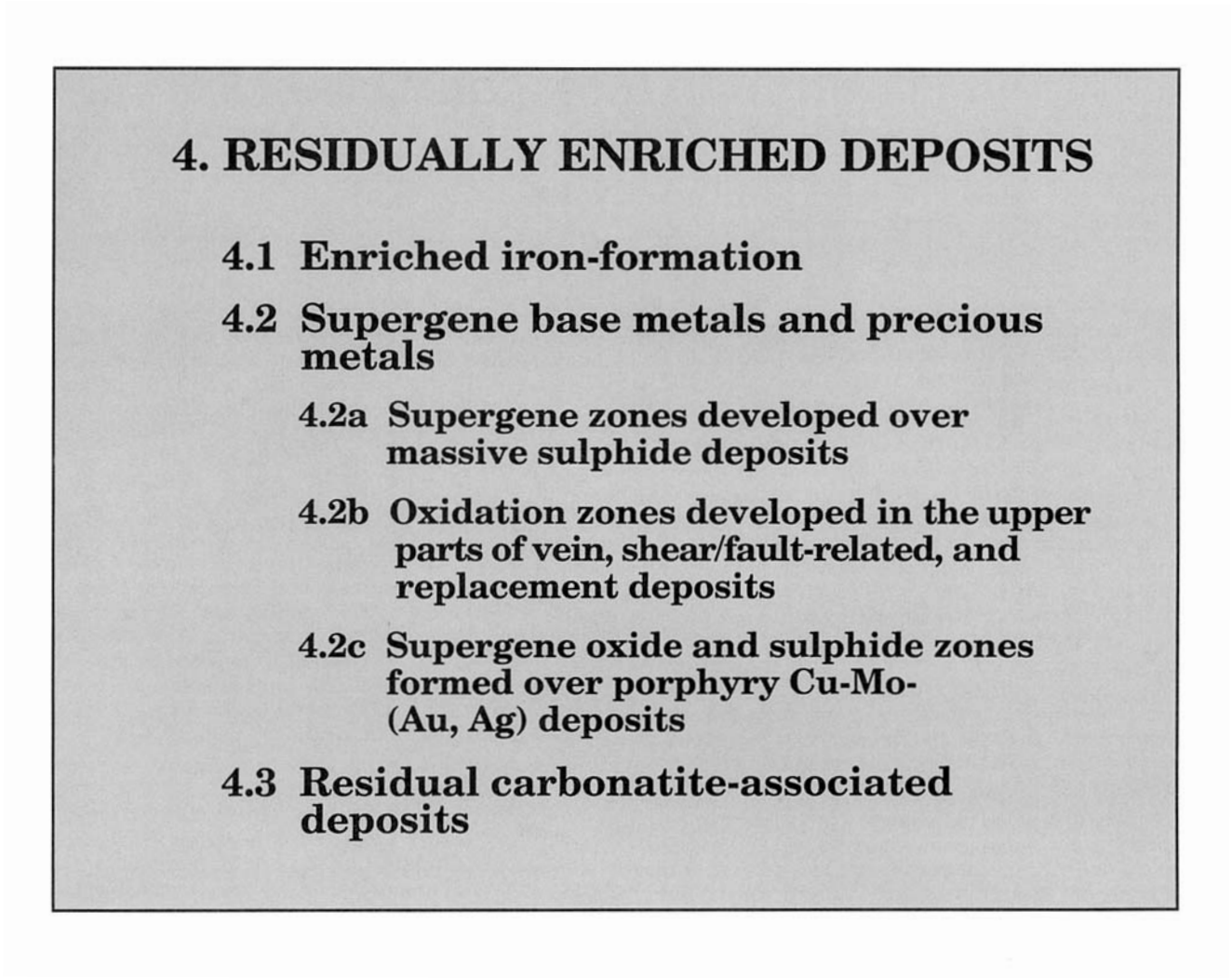

4. RESIDUALLY ENRICHED DEPOSITS

INTRODUCTION

Residually enriched deposits are sedimentary concentrations of commodities achieved by in situ weathering of a suitable precursor rock. By the mechanism of uplift, surficial exposure, and weathering of the precursor rock, the original low concentrations of the commodities of interest become enriched to economic or improved economic grades in residual deposits that overlie, or are adjacent to, the parent rocks. The enrichment is achieved by two separate processes, depending on the solution characteristics of the protore minerals. If the protore minerals are resistant to chemical weathering, these minerals become concentrated through dissolution and removal of the surrounding matrix; this can be termed "concentration of resistates". If the protore minerals are relatively soluble in oxygenated surficial waters, but insoluble in reduced solutions, the enrichment proceeds by dissolution of the protore minerals in the oxidizing zone and reprecipitation, generally as new ore minerals, in the lowest part of the oxidizing zone and/or in the underlying reduced environment; this process is commonly referred to as "supergene enrichment".

Three principal types of residually enriched deposits, reflecting different types of precursor rocks and processes of enrichment, are distinguishable in Canada. Residually enriched ore deposits of iron (subtype 4.1, "Enriched iron-formation") have resulted from the actions of both concentration of resistates and supergene enrichment operating on Lake Superior-type and Algoma-types of iron-formation (subtypes 3.1, 3.2) as protore. Secondary deposits of base metals and precious metals (subtype 4.2, "Supergene base metals and precious metals") are the product mainly of supergene enrichment acting on several sulphidic protore types including massive sulphides (subtype 6.4), various vein and fault related deposits, and porphyry Cu-Mo-Au-Ag deposits (Type 19). Deposits of niobium, phosphate, and rare-earth elements (subtype 4.3, "Residual carbonatite-associated deposits") are the result of weathering of carbonatite, and enrichment of the ore elements by both concentration of resistates and supergene enrichment.

4.1 ENRICHED IRON-FORMATION

G.A. Gross

INTRODUCTION

Main geological characteristics and commodities

Residually enriched iron deposits are large, tabular and irregular in situ masses of high grade direct-shipping iron and manganese ore hosted in iron-formation protore. The iron ore consists of hard lumpy fragments and earthy masses of friable and porous, fine grained, granular to dusty iron oxide minerals. The ore consists mainly of residual and secondary fine grained mineral aggregates of hematite and goethite which were derived from iron-formation protore and iron-rich rocks by oxidation, leaching, and deep weathering processes. They are associated with ancient regoliths and were formed by the action of circulating groundwater that penetrated along fractures, faults, and porous permeable zones in the iron-formation. Silica, carbonate, and gangue minerals were removed leaving residual masses and rich concentrations of ferric iron oxides.

Zones of disseminated manganese oxide in the residual iron deposits provide manganiferous iron ore, and pockets of rich manganese ore occur within, or in association with, the residually enriched iron deposits. Most of the deposits of high grade manganese ore throughout the world are hosted in manganese-bearing lithofacies of iron-formation and formed by secondary enrichment processes.

Some of the common characteristic features of residually enriched iron deposits that have been derived from Lake Superior-type iron-formation protore in the Knob Lake iron ranges of Quebec and Labrador are described in this paper.

Examples

The most important residual iron deposits in Canada occur in Lake Superior-type iron-formation in the Knob Lake iron ranges in the Labrador-Quebec fold belt near Schefferville, Quebec (Fig. 4.1-1). Other large well known deposits of this type occur in the Mesabi Range of Minnesota, in the Marquette Range in Michigan, in the Belo Horizonte area of Brazil, at Mount Whaleback in northwest Australia, in India, near Krivoy Rog in the Ukraine and Kursk in Russia, and in South Africa.

Gross, G.A.
1996: Enriched iron-formation; in Geology of Canadian Mineral Deposit Types, (ed.) O.R. Eckstrand, W.D. Sinclair, and R.I. Thorpe; Geological Survey of Canada, Geology of Canada, no. 8, p. 82-92 (also Geological Society of America, The Geology of North America, v. P-1).

Other world-class examples derived from oxide lithofacies of Algoma-type iron-formation include Cerro Bolivar in Venezuela (Ruckmick, 1962), Carajas in northern Brazil, Nimba in Liberia, and large deposits in Swaziland. The Steep Rock Lake deposits in Canada appear to have formed by leaching and enrichment of a carbonate-sulphide lithofacies of Algoma-type iron-formation (Table 4.1-1).

IMPORTANCE

Large high-grade residually enriched iron ore deposits are the principal resource base for modern iron and steel industries in North and South America, Eastern Europe, Japan, India, and Africa, and have become an important source of ore in recent years for Western Europe and China. Approximately half of the world iron ore production in recent years, including lump ore and sinter fines, have come from residually enriched iron-formation.

Mine development in the Knob Lake-Schefferville area in the Labrador-Quebec fold belt of Canada was based on residually enriched deposits. The maximum annual production during the operation of the mines in this area from 1954 to 1984 was achieved in 1959 when more than 12 million tonnes of direct shipping ore was produced.

SIZE AND GRADE OF DEPOSITS

Individual deposits in the Knob Lake iron range of Labrador and Quebec are relatively small and the largest contain about 50 Mt (million tonnes) of ore. Deposits of this type in Australia and Brazil range from 100 Mt to more than 1000 Mt. Residually enriched deposits contain from 45 to 69% iron, overall grades average from 50 to 60% iron, and many deposits have large mineable sections that contain from 65 to 69% iron (Table 4.1-1.)

GEOLOGICAL FEATURES

Geological setting

Residually enriched iron ore deposits occur in lithofacies of Lake Superior- and Algoma-type iron-formation in most of the major iron ranges of the world (see Lake Superior- and Algoma-type iron-formation, deposit subtypes 3.1 and 3.2). Prominent geological features of residually enriched deposits in Lake Superior-type iron-formation are illustrated in the Labrador-Quebec fold belt (Fig. 4.1-1), and have been described in detail by Gross (1968) and Gross et al. (1972).

Stratigraphy of protore iron-formation

More than 50 residually enriched deposits of iron ore are hosted in the Sokoman Formation which has a maximum thickness of about 150 m in the Knob Lake basin in the

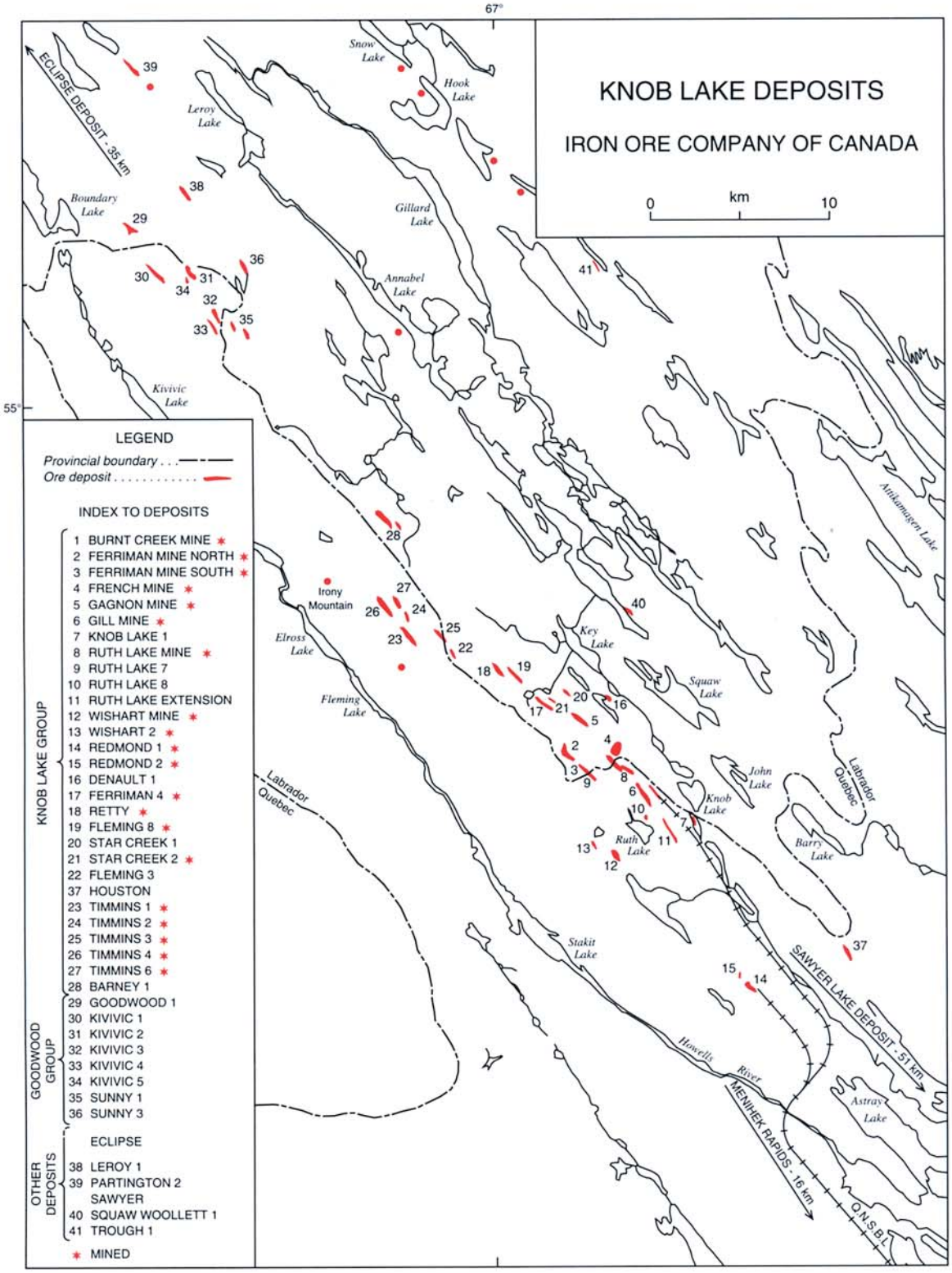

Figure 4.1-1. Distribution of residually enriched iron deposits in the Knob Lake iron range, Quebec and Labrador (after Gross et al., 1972).

central part of the belt (Fig. 4.1-1). It is part of an Early Proterozoic sequence of continental shelf sediments outlined in Table 4.1-2.

Typical lithofacies of protore iron-formation near the French mine, which hosts residual ore, are described in Table 4.1-3, and their composition is given in Table 4.1-4. Typical oolitic textures in protore oxide lithofacies of iron-formation from the northwestern part of the Knob Lake Basin are shown in Figure 3.1-6 (see subtype 3.1, Lake Superior-type iron-formation).

Table 4.1-1. Iron content in iron ore resources in major deposits of enriched iron-formation (Bolis and Bekkala, 1986).

COUNTRY/DEPOSIT	% IRON	RESOURCES IN SITU (Mt)
AUSTRALIA		
Mount Tom Price	61.9	650
Mount Whaleback	61.4	1676
Paraburdoo	63.4	450
Robe River	57.0	140
Rhodes Ridge	61.8	1000
Wittenoom	54.9	1000
Yandicoogina	58.5	1243
BRAZIL		
Aguas Claras	62.2	260
Carajas	66.1	1340
Caue	56.1	620
Conceicao-Dos Corregos	66.6	1050
Timbopeba	66.6	170
GABON		
Belinga	63.9	514
INDIA		
Bailadila #5	64.4	209
Bolani	58.9	480
LIBERIA		
Nimba	59.1	62
Western area	52.2	411
SENEGAL		
Faleme area	63.6	340
SOUTH AFRICA		
Sishen	64.0	1314
VENEZUELA		
Altamira	63.1	130
Cerro Bolivar	63.1	187
San Isidro	64.1	391

Structure in main ore zone, Knob Lake Basin

The central part of the Knob Lake Basin area has been highly deformed by doubly plunging isoclinal folds, with axes trending northwest, that are cut by steep easterly dipping thrust faults which give rise to a complex imbricate regional structure. Cross faults strike east to northeast and have vertical displacements of 20 m or less. Many faults of both sets were reactivated during Cretaceous or later time, resulting in further thrusting from the northeast and causing brecciation in some pockets of ore and overlapping of Cretaceous clay and gravel or rubble ore by unaltered strata (Fig. 4.1-2).

Form and relationship of residual ore and host iron-formation

Deep residual enrichment of the iron-formation took place along the height of land that now forms the watershed between streams flowing to the Atlantic coast and northward or westward to Ungava and Hudson Bay. Unlike the surrounding area, this highland area probably was not covered by Paleozoic rocks and may have been exposed to deep chemical weathering and erosion from middle Proterozoic to relatively recent times.

Residually enriched ore was developed in lenticular, tabular, or irregular masses in the cherty iron-formation protore under stratigraphic and structural control, where ground water could circulate in permeable fold, fault, and fracture zones. The distribution of ore bodies along the height of land in the Knob Lake area is shown in Figure 4.1-1. Typical relationships of ore to stratigraphy and to the folded and faulted structures are shown in a cross-section of the Ferriman mine in Figure 4.1-3.

Ore types, mineralogy, and textures

Residually enriched ore in the Knob Lake deposits consists of red to blue, fine grained hematite, yellow to brown or black goethite, and mixtures of these main mineral aggregates. Porosity, density, and the relative proportions of dense lumpy material and dusty granular fine grained ore of clay-like consistency may vary greatly in the different types of ore. The physical and chemical properties of the prominent types of ore in the Knob Lake Range are shown in Table 4.1-5. The mineralogy and physical properties of the main types of residual ore reflect the lithofacies of iron-formation from which they were derived. Relict bedding and evidence of primary sedimentary features are preserved in some of the ore zones (Gross, 1964a, b, 1968).

Blue ore was derived from cherty oxide lithofacies of iron-formation and is composed of fine grained, blue to dark grey-black hematite with lesser amounts of red hematite, martite, and brown goethite. It has a distinctly porous granular texture and contains primary ovoid granules or oolites of iron oxide replaced by later hematite or goethite, or enlarged by overgrowths of iron oxide. Blue ore may be friable to crumbly or nodular, or hard coherent and lumpy where a high proportion of secondary iron oxide cements relict fragments. Silica remaining in the ore after leaching and oxidation is mostly very fine grained, less than 100 mesh in size, with a sugary to equigranular texture.

Table 4.1-2. Stratigraphy of the Knob Lake Group, Schefferville area, Labrador and Quebec.

Menihek Formation	carbonaceous slate, shale, quartzite, greywacke, mafic volcanic rocks; minor dolomite and chert.
Purdy Formation	dolomite, developed locally.
Sokoman Formation	oxide, silicate, and carbonate lithofacies iron-formation, minor sulphide lithofacies iron-formation, interbedded mafic volcanic rocks, ferruginous slate, slaty iron-formation, black and brown slate, and carbonaceous shale.
Wishart Formation	feldspathic quartz arenite, arkose, minor chert, greywacke, slate and intercalated mafic volcanic rocks.
Fleming Formation	chert breccia, thin-bedded chert, limestone; minor lenses of shale and slate.
Denault Formation	dolomite and minor chert.
Attikamagen Formation	green, red, grey, and black shale, and argillite, interbedded with mafic volcanic rocks.

Table 4.1-3. Iron-formation lithofacies, French mine, Knob Lake range.

Lithofacies	**Description of lithofacies**	
Thickness of section sampled	**Megascopic**	**Microscopic**
B523 --- 15 m Silicate-carbonate	Olive-green to brown with orange-red to brown weathered surface, fine grained magnetite, iron-silicates and chert, beds 1-5 cm thick with laminae <5 mm thick.	Microbanding <1 mm thick, dense felty mass of minnesotaite with ovoid granules, granules are sheared or distorted in some microbeds, minor quartz and carbonate.
B524 --- 12 m Lower red chert	Bright red jasper and grey-blue hematite chert in bands, stubby lenses, laminae, nodules, 5 to 20 mm thick, granules and oolites of chert and hematite in chert matrix, dense blue-black hematite beds and fine grained specular hematite.	Hematite and chert in ovoid granular to oolitic texture, chert granules rimmed by coarser hematite, coarser quartz patches in matrix and cores of granules and oolites.
B525 --- 8 m Pink chert	Thin (5-10 mm) banded pink chert and hematite interbedded with blue-grey hematite-rich beds, 5-20 mm thick, some wavy laminated beds with coarse granules, some brown chert beds.	Coarse granular, oolitic and nodular chert with patches of coarse grained quartz and hematite, minor brown iron-oxide.
B526 --- 15 m Grey chert	Mainly pink to grey or brown thin banded <5 mm, to crudely laminated or lenticular beds, some massive beds 5-15 cm thick. Chert beds and iron-rich beds are well differentiated.	Medium grained quartz with fine 0.5 mm granules, granular to oolitic textures in some beds, hematite in discrete grains.
B527 --- 6 m Brown chert	Brownish grey to pink jasper facies in lenticular beds 5 to 10 cm thick, blue to brown iron-rich beds, coarse granular texture, nodes and lenses of pink or brown jasper 10 mm thick.	Pure hematite, goethite and chert, oxide facies, jasper nodules, coarse hematite and secondary goethite.
B528 --- 20 m Upper red chert	Thick massive beds <30 cm thick with patches of blue to grey-pink, iron-rich beds interbedded with banded, lenticular, and nodular jasper, 1 to 2 cm thick, magnetite- and hematite-rich lenses in granular jasper.	Granular textured hematite, magnetite, and chert, minor goethite and minnesotaite, coarse patches of quartz in matrix and cores of granules.
B529 --- 25 m Grey upper chert	Grey-green magnetite-carbonate-chert with blue to brown hematite-goethite-rich beds, spotty carbonate nodes in grey chert and iron oxide beds, granular texture in jasper beds, metallic lustre on hematite beds.	Hematite, magnetite, and goethite in coarse chert, fine chert in cores of granules, and coarse grained chert in matrix, hematite grains on rims of granules, brown iron oxide replaces hematite, siderite, and iron-silicate in green chert.

Table 4.1-4. Chemical analyses of samples of iron-formation lithofacies, French mine, Knob Lake range, Labrador and Quebec (from Gross, 1968).

B523 - Silicate-carbonate facies
B524 - Lower red cherty facies
B525 - Pink cherty facies
B526 - Grey cherty facies
B527 - Brown cherty facies
B528 - Upper red cherty facies
B529 - Grey upper cherty facies

Sample	B523	B524	B525	B526	B527	B528	B529
SiO_2	49.41	41.42	48.16	51.24	43.77	49.01	56.49
Al_2O_3	0.68	0.79	0.53	0.42	0.42	0.37	0.37
Fe_2O_3	16.34	54.49	46.96	41.97	49.85	44.50	38.10
FeO	24.19	1.35	1.50	3.25	2.27	3.65	1.99
CaO	0.02	0.00	0.01	0.00	0.00	0.00	0.00
MgO	2.95	0.37	0.31	0.62	0.37	0.19	0.00
Na_2O	0.03	0.08	0.03	0.02	0.02	0.03	0.02
K_2O	0.07	0.01	0.01	0.01	0.01	0.01	0.01
H_2O+	5.20	0.98	2.04	2.10	2.54	1.94	2.42
H_2O-	0.38	0.06	0.04	0.05	0.05	0.02	0.03
TiO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.08	0.04	0.04	0.03	0.04	0.05	0.04
MnO	0.65	0.02	0.02	0.02	0.03	0.03	0.03
CO_2	0.22	0.02	0.02	0.06	0.02	0.04	0.04
S	0.05	0.05	0.03	0.00	0.00	0.00	0.00
C	0.15	0.12	0.10	0.08	0.13	0.04	0.03
Total	100.42	99.80	99.80	99.87	99.52	99.88	99.57

Analysts: G.A. Bender and W.F. White, Geological Survey of Canada;
Spectrographic analyses, composition of samples within these ranges: Co- 0.1-1.0%, Ni- <0.01%, Ti- <0.01%, Cr-0.01-0.1%, Cu- <0.01%, Ba- <0.01%, B- not detected

Beds originally rich in iron oxide minerals usually remain hard and relatively unaltered and have a distinct blue metallic lustre. Ore derived from oxide lithofacies commonly has a red to pink or grey cast, depending on the predominant colour of the cherty protore beds. Much of the blue hematite, martite, and goethite form vermicular to irregular microscopic intergrowths, and some are euhedral and fine grained. Partial leaching of the equigranular blue ore usually results in a sandy friable mass of well segregated silica and iron-oxide grains, and many lean or partially leached lithofacies of iron-formation can be beneficiated by simple washing and gravity processes.

Yellow to brown ore, referred to as "SCIF" ore, was derived from silicate-carbonate iron-formation lithofacies and is composed mainly of goethite or hydrous iron oxide minerals and dark brown martite. It is earthy to ochreous and has a high proportion of clay-size particles. Textures vary from fine colloform intergrowths of brown or yellow goethite, to crudely banded fragments with patchy needle-like or radial intergrowths of pseudomorphous iron oxide developed over the textural features of the protore iron-silicate and carbonate-chert lithofacies. Silica from the chert or iron-silicate minerals is intimately mixed with iron oxide in yellow ore and has a spongy clay-like cohesion when squeezed in the hand. Porosity is high in this ore and it has a high moisture content due to adsorption of water on the earthy clay particles. Silica is readily removed from minnesotaite-carbonate-chert lithofacies of iron-formation by weathering processes, and felty textured iron-silicate and siderite mineral aggregates are the first to show signs of oxidation and leaching. The yellow ore is much more difficult to beneficiate than the blue.

Red ore is composed of earthy red hematite, goethite, soft aluminous silicates, and very fine grained chert or quartz. It is derived from the upper iron-rich part of the Ruth slate at the base of the iron-formation and from black slaty facies within it. Individual layers consist of dense earthy hematite or nodular to colloform hematite intergrowths, and most of the red ore is soft, spongy, and clay-like and has high porosity and moisture content. Red, blue, and blood-red laminae give the ore a distinct banded appearance. When silica, calcium, magnesium, and iron are leached from fine grained black shale and slate, the primary beds and banding stand out in the red ore as punky, soft saprolitic alumina-rich clay layers that contain no appreciable amount of iron. These leached slaty beds vary

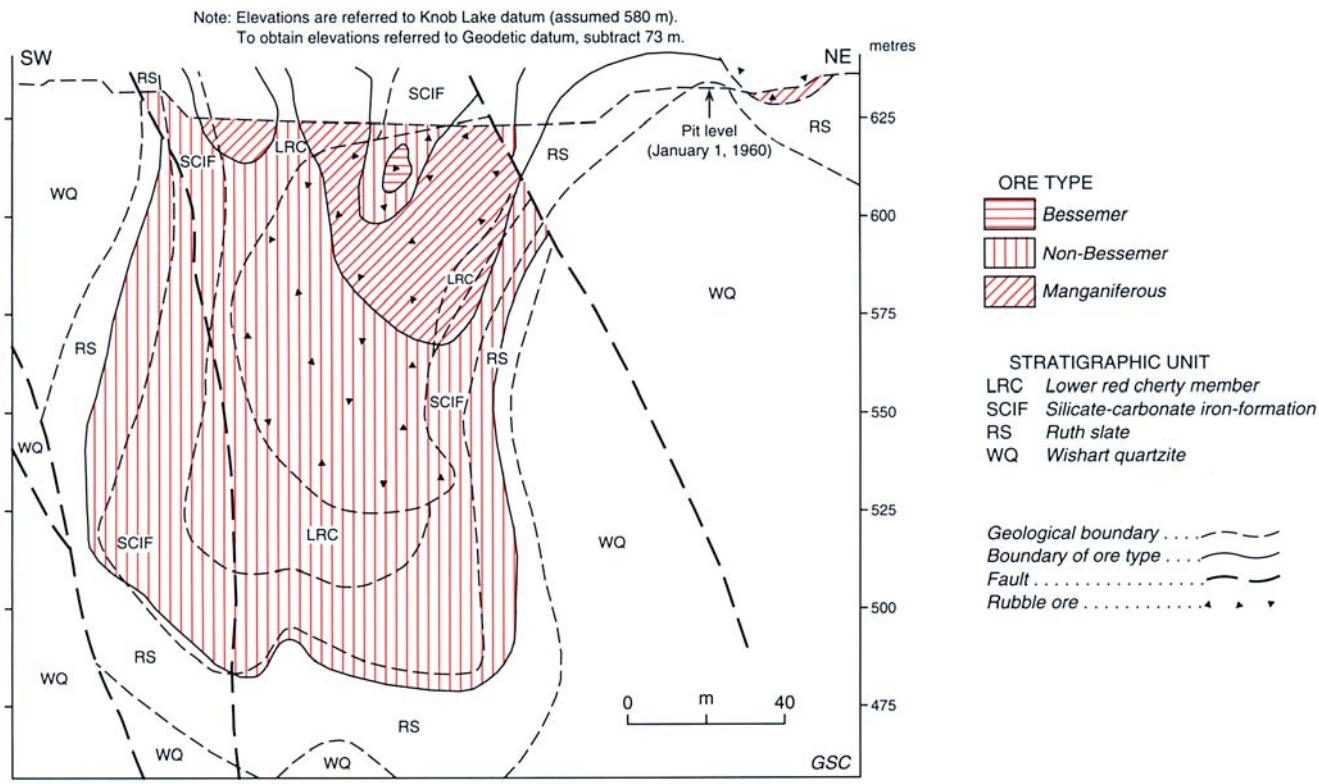

Figure 4.1-2. Typical cross-section of Ruth Lake 3N deposit, Burnt Creek mine, showing distribution of ore (from Iron Ore Company of Canada).

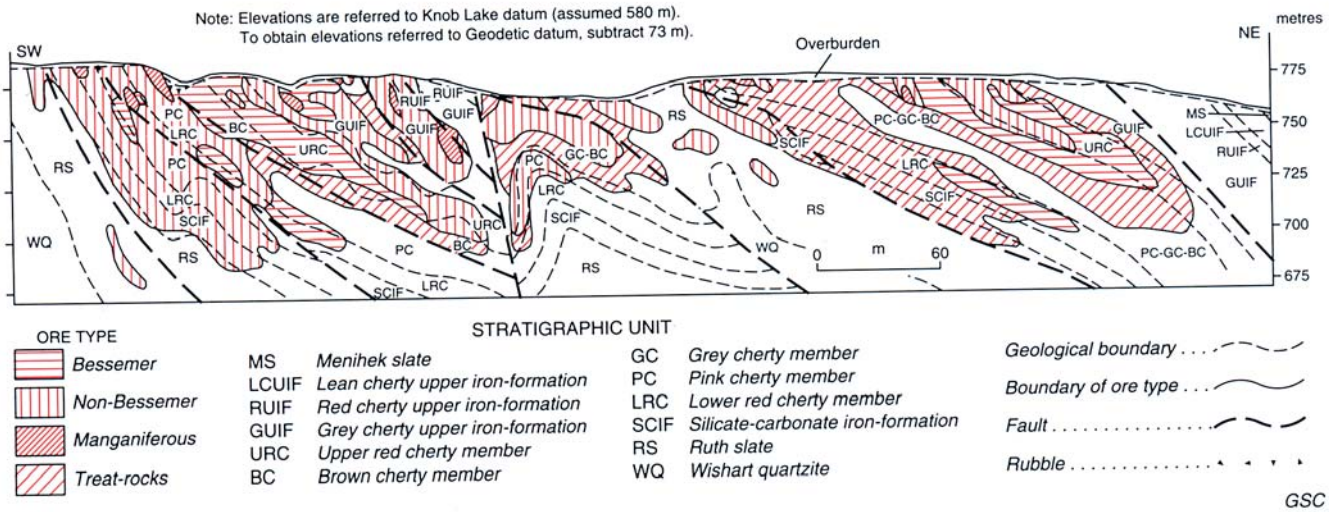

Figure 4.1-3. Typical cross-section of Ferriman mine, showing distribution of ore (from Iron Ore Company of Canada; Gross, 1968).

Table 4.1-5. Physical and chemical properties of typical iron ores, Knob Lake range (data from Stubbins et al., 1961).

Type of ore Relative abundance in mines	Blue 66%	Yellow 20%	Red 14%
Average composition of natural material (analyses in %)			
Fe	54.5	50.0	48.0
P	0.038	0.103	0.123
Mn	0.56	1.13	2.41
SiO_2	8.2	5.6	6.2
Al_2O_3	0.72	1.0	2.1
Moisture	8.9	14.2	13.7
Critical moisture	9-11	15-16	15-18
Porosity in % of volume	10-44	19-49	7-47
Average porosity	31	36	30
Permeability	Medium	Low	Low
Specific gravity	3.2	2.6	2.8
Tonnage factor, m^3/t	0.096	0.120	0.108
Typical sieve analyses, dry screening (%)			
+1 inch	19	22	20
+6 mesh	26	35	14
+35 mesh	20	25	26
+100 mesh	15	9	9
-100 mesh	20	9	11
Ore minerals	Blue hematite goethite magnetite	Geothite limonite	Earthy red hematite goethite limonite
Amenability to concentration by washing			
	Medium to high	Very low	Very low

Table 4.1-6. Iron Ore Company of Canada, mine production, 1959, Knob Lake Iron Range (from Elver, 1960; Gross, 1968).

	Analyses of unprocessed ore from 5 mines					
Kind of ore Long tons	Fe Iron	P_2O_5	Mn	Silica	Al_2O_3 Alum	Moisture
Bessemer 1 991 104	55.7	0.026	0.319	6.64	0.84	8.73
Non-Bessemer 9 179 134	51.4	0.083	1.104	6.55	1.46	11.8
Manganiferous 1 451 019	47.1	0.108	4.69	6.44	1.5	11.5
Total all mines 12 621 256	51.6	0.077	1.39	6.56	1.36	11.29

from white to pink or deep red and are known as "paint rock". The intimate intergrowths of iron oxide minerals and aluminous clay or silica make the red ore difficult to beneficiate.

Rubble ores (solid triangle pattern in Fig. 4.1-2), the fourth main type in the Knob Lake iron range, are similar to the canga and talus deposits developed in tropical areas. They overlie some of the banded residual ore deposits and consist of irregular masses and pockets of clastic ore fragments, bedded clay, and rock clasts and gravel, and in some deposits contain an abundance of fossil wood and plant debris.

Three main kinds of rubble ore, which consist of sand and gravel, talus, and breccia ores, were contemporaneous in their development and grade from one type to another in some of the mine pits. They represent reworked parts of ore bodies that formed at an earlier stage and contain fossil wood, leaves, and insects considered to be early Late Cretaceous (Dorf, 1959). Rubble ore is usually uniform, high grade material mostly of non-Bessemer quality (0.045 to 0.18% P).

Sand and gravel ores are mainly well sorted, unconsolidated sediments that occur in the upper parts of ore deposits. They are composed of subangular ore fragments, mostly 5 cm to 20 cm in size, which are distributed in a matrix of sandy ore, chert, and quartz grains. Layers and crossbeds dip toward the centre of the rubble pockets and rubble ore deposits may be more than 100 m thick and have no topographic expression.

Sand and gravel rubble ores grade downward to talus ores, which are poorly sorted and consist of angular to subangular blocks of bedded ore from all parts of the iron-formation sequence that have slumped into fissures and crevices along fault scarps. Breccia ores are developed along fault zones and are composed of broken layered ore fragments less than a centimetre to several metres in size cemented by sandy material. Breccia ore contains vugs filled with colloform secondary iron and manganese oxide minerals or quartz.

The margins of enriched ore bodies are usually irregular, defined by cut-off grades, composition, and textural criteria, and extend transitionally into altered iron-formation from which only part of the silica has been leached. Some beds and laminae are more extensively oxidized and leached than others and broad marginal zones around enriched ore bodies are composed of friable, sugary-textured iron-formation, silica, and iron oxide sand. The marginal, partially leached oxide facies of the iron-formation are usually amenable to beneficiation by removal of the silica grains by washing, and concentration of the iron oxide mineral grains and oolites by flotation and gravity processes.

This partly leached iron-formation has been termed "treat rock" or "wash ore" and provides an important fifth type of ore derived from residually enriched iron-formation. Several million tonnes of iron ore concentrate were produced annually during the later years of mining on the Knob Lake range from treat rock containing 46 to 56% iron.

The various types of deposits reflect the different lithofacies of iron-formation from which they were derived by oxidation, leaching of silica, and enrichment of iron and manganese by the accumulation of residual and secondary oxide minerals.

Table 4.1-7. Compositions of typical residually enriched iron ore mined in Canada and the United States.

Composition in per cent	1	2	3
Fe=metal equivalent	54.0	57.45	54.0
P	0.064	0.02	0.02
SiO_2	7.94	5.13	8.45
Mn	0.17	0.17	0.52
Al_2O_3	1.01	1.01	1.5
H_2O	3.17	3.17	8.5

1/ Average for 3 Mt of direct shipping non-Bessemer quality ore mined in the Schefferville area in the Knob Lake range in 1981.
2/ Residually enriched ore, including both coarse and fine material, probably derived from carbonate-sulphide lithofacies protore, from the Caland mine in the Steep Rock iron range in Ontario.
3/ Average for 35 Mt of typical residually enriched iron ore mined in 1962 in the Lake Superior area of United States, mostly from the Mesabi range.

Residually enriched ore deposits are related to present and paleotopographic features. They were developed in permeable zones in the iron-formation protore in fold, fault, and fracture zones where circulating groundwater caused oxidation, leaching, and enrichment of the host rocks in iron and manganese. The compositions of typical residually enriched iron ore mined in Canada in the past are given in Table 4.1-7. Table 4.1-6 shows the average composition and proportions of Bessemer (<0.045% P), non-Bessemer (0.045 to 0.18% P), and manganiferous ore produced from the Gagnon, French, Ferriman, Ruth Lake, and Burnt Creek mines in the Knob Lake range in 1959, prior to the processing of treat rock ore.

Definitive characteristics of residually enriched iron ore in iron-formation

Residually enriched iron ore deposits hosted in iron-formation protore are irregular, lenticular or tabular masses of hematite and goethite. The compositions and proportions of hard lump and fine grained dusty ore vary from deposit to deposit and are directly related to the kind and quality of protore lithofacies from which they have been derived (Gross, 1968; Gross et al., 1972) (Table 4.1-2, 4.1-3, 4.1-4).

Blue ores are lumpy to granular aggregates of blue to dark grey and red hematite, martite, and brown goethite that have been derived mainly from oxide lithofacies of the protore iron-formation. In some cases, they retain relict oolitic textures pseudomorphous after the textures of the protore. Yellow to brown ores are earthy to ochreous to clay-like goethite and hydrous iron oxide minerals, that were derived from silicate-carbonate lithofacies of protore. Red ore consists of earthy red hematite, goethite, soft aluminous silicate minerals, clay minerals, and fine grained quartz derived from iron-rich slate.

Rubble ores are accumulations of alluvial and residual fragments and fine clastic material composed of enriched and weathered iron-formation, fossil carbon and plant debris, sand, silt, and gravel. They may represent brecciated, reworked, or residual accumulations of the various types of residually enriched iron ore and commonly have a higher content of manganese than the iron-formation hosting them.

The compositions of typical residually enriched iron ores mined in North America in the past are shown in Table 4.1-7. Most of the iron ore resources of this type in countries outside of North America contain significantly higher amounts of iron with less silica and other constituents as shown in Table 4.1-1.

GENESIS OF RESIDUALLY ENRICHED IRON ORE IN IRON-FORMATION

The soft "direct-shipping" type of hematite-goethite residually enriched iron ore was derived from iron-formation as a result of two principal processes: 1) leaching of silica, carbonate, and gangue minerals, and 2) enrichment of iron by oxidation, residual accumulation, and deposition of goethite, hematite, and other iron oxide minerals. Leaching and enrichment processes were carried out by groundwater circulating in deep porous zones along faults, fractures, and folds, and by weathering processes under tropical climatic conditions. As a result of these processes the protore iron-formation lithofacies were reconstituted. The structures, primary textures, and sedimentary features of the host iron-formation were almost completely destroyed and secondary iron and manganese oxides were deposited with the residual iron oxide minerals in the weathered and leached protore.

Consistent relationships between the blue, yellow, and red types of ore and protore lithofacies from which they were derived were clearly defined in the Knob Lake range by geological mapping of the mine areas and zones of oxidation and enrichment in the protore iron-formation. Removal of silica by leaching took place in advance of secondary iron enrichment, as shown by a lateral transition along beds from protore through zones of partially leached friable protore to dense, hard, enriched masses of iron oxide minerals and iron ore. Goethite forms a matrix around hematite, chert, and iron-oxide granules in the hard, lumpy, dense ore, and is present in veins and discordant masses. Selective alteration of carbonate and iron-silicate minerals to goethite, and oxidation of magnetite to martite, are usually the first changes detected in the conversion of protore iron-formation to ore and indicate that leaching took place in strongly oxidizing environments.

Controversy in the past has centred on whether the residually enriched iron ores were formed by the action of descending groundwater, hydrothermal solutions, or meteoric waters mixed with ascending emanations from deep seated, probably magmatic sources. Several different lines of evidence lead to the conclusion that the residual iron deposits on the Knob Lake range formed near a surface of considerable topographic relief by the action of descending groundwater, and the environmental conditions at the time of their genesis appear to have been similar to those observed in deposits forming today in temperate, warm, or tropical climates.

The solubility of silica increases directly with increasing temperatures and with an increase in pH above 8.9, but ferric iron is relatively insoluble and is particularly stable under conditions of high pH and Eh. Weathering processes in most tropical environments remove silica and leave residual iron. When humic acids are present in the groundwater, the ratio of iron to silica in the solutions increases at temperatures below 20°C and decreases above this temperature. Higher temperatures and an increase in the activity of bacteria cause the decomposition of humic acids. The organic constituents formed by the decomposition of the humic acids are effective in leaching silica from soils, but ferric iron is not affected significantly. Evidently, temperature fluctuations have been a major factor in controlling the content of humic acids and the leaching and transportation of silica and iron.

Humic acids appear to have been an important media for solution and deposition of the secondary goethite and enrichment of iron in this type of ore deposit. Ferric oxides and hydroxides are relatively soluble in humic acids and in many other organic compounds, and with increasing pH or saturation in these acids they coagulate and are precipitated as amorphous hydrous iron oxide.

Interpretation of climatic conditions in the Knob Lake area from fossil plants (Dorf, 1959) indicate a warm, humid environment with abundant vegetation in the Late Cretaceous. These conditions would have been suitable for both organic and inorganic solution and transportation of iron and silica and may have existed throughout the Mesozoic. Ruckmick (1962) suggested that the Cerro Bolivar deposit in Venezuela formed in about 26 million years, or since the Oligocene, if climatic conditions were similar to those at present and had prevailed during that period in the past. Springs emerging from the lower flanks of the ore bodies have a pH of 6.1 and contain an average of 7 ppm silica and 0.05 ppm iron, indicating that the rate of removal of silica is about 80 times greater than that for ferric iron.

Study of the rubble ore pockets in the Knob Lake range show that much of the enrichment and leaching in the development of the ore may have taken place prior to Cretaceous time but relatively little definitive work has been done on the timing of formation of the ore in the Knob Lake iron range. It is highly possible that major enrichment of the iron-formation was related to deep weathering and regolith development at the close of the Precambrian as observed in many other parts of Canada.

Morris (1980) referred to work on several major deposits which indicated that deep weathering and/or enrichment processes may have started in the Precambrian, probably as early as 1800 Ma for the Tom Price and Whaleback deposits in Australia, that the hematite ores of Nimba Range, Liberia, formed in the Precambrian, and that deposits at Sishen and in the Manganore iron-formation in the Postmasburg Group in South Africa probably were formed in the early to middle Proterozoic. Ore zones in the Krivoy Rog iron range related to Precambrian paleotopography extend to depths greater than 2000 m (Belevtsev, 1973) and evidence from microspores show that deep weathering processes were active in the late Precambrian.

The sequence of events leading to the development of the residually enriched iron ore deposits on the Knob Lake range in Labrador and Quebec are summarized as follows:

1. Deposition of the Sokoman Formation in the Knob Lake Basin on a continental shelf along the margin of the Ungava Craton coincided with deep faulting and deformation in the offshore tectonic belt, and probably took place during the initial stages of subduction of the craton under the eastern crustal block.
2. Folding and faulting of the Labrador-Quebec fold belt, probably associated with subduction and orogenic processes between 1400 and 1900 Ma, produced permeable structures in the iron-formation.
3. Erosion of the fold belt, accompanied by deep weathering and ore forming processes, was followed by submergence and possibly deposition of Paleozoic marine sediments.
4. Rugged highland topography was developed during the Permian and Mesozoic when further uplift and sufficient erosion exposed the Knob Lake range and most of the shelf strata of the fold belt to weathering in a warm and arid climate.
5. Deep chemical weathering developed in this highland belt, probably before and during the Mesozoic. Evidently groundwater penetrated from surface along permeable structures and produced extensive oxidized zones that were associated with leaching of silica and carbonate minerals, hydration and martitization of iron oxides, deposition of secondary goethite, and redistribution of iron oxide in residual zones near the surface.
6. During the Late Cretaceous an abundance of vegetation developed in a warm, humid, tropical climate; about the same time, recurrence of reverse movement on easterly dipping thrust faults, reactivation of cross-faults, and downfaulting of some fault blocks resulted in brecciation of residual iron ore along fault zones.
7. Rubble ore derived by sloughing and erosion from the rising blocks and along the reactivated fault scarps accumulated in the downfaulted blocks, and extensive secondary enrichment and redistribution of goethite and manganese oxide minerals took place in the rubble ore and upper permeable parts of the ore deposits.
8. Further enrichment of manganese oxides has taken place in porous and permeable zones in the residual iron deposits since the Cretaceous.
9. Glacial erosion during the Pleistocene, the last major event identified, appears to have removed most of the weathered rock, plucked off most of the hard surface cappings and canga from the orebodies, and scoured the ridges to expose fresh, unaltered rock around the ore deposits. The ore bodies remain as parts of the deeply leached and altered zones that were protected by topographic and structural features and subsequently covered by glacial till and soil.

RELATED TYPES OF DEPOSITS

Residually enriched iron deposits are associated with unaltered iron-formation and taconite deposits, with partially leached and enriched iron-formation which provides wash ore and treat rock, and with manganiferous iron ore and manganese deposits of various grades and quality.

The friable and sandy, partially leached and enriched iron-formation on the margins of ore zones has provided wash ore or treat rock for concentration of the iron oxide mineral aggregates and removal of silica and clay constituents through processing by washing, jigging, gravity spirals and cones, and by flotation. Extensive amounts of treat rock were processed from the mines in the Lake Superior and Knob Lake ranges by utilizing crude ore containing less than 45% iron and upgrading it to 55 to 65% iron with 5 to 8% silica for blending as sinter fines or in pellets.

Manganiferous iron ore was recovered from many of the deposits in the Lake Superior and Knob Lake ranges. At the beginning of mining operations in the Knob Lake range in 1954, estimates of proven ore reserves in 44 deposits included 12 to 13% manganiferous ore in the total 42.4 Mt of reserves. Of the 55.8 Mt of ore shipped in the first five years of production from the Knob Lake range, about 12% was manganiferous grade and contained Fe – 46.9%, Mn – 5.26%, P – 0.118%, SiO_2 – 6.15%, Al_2O_3 – 1.52%, CaO – 0.12%, MgO – 0.02%, S – 0.005%, Moisture – 10.44%, and Loss on ignition – 5.97%. The manganese was derived mainly from carbonate facies iron-formation. Possibly some manganese-bearing oxide facies was oxidized and mobilized by enrichment processes, and redistributed within the ore zones. Highly aluminous or shaly protore facies provided a favoured site for manganese deposition. Most of the high grade manganese deposits throughout the world have developed by enrichment of manganese-bearing lithofacies associated directly with iron-formation or stratafer lithofacies. Iron and manganese are strongly differentiated under highly oxidizing conditions in the depositional basins, and manganese-rich lithofacies are usually distal from the cherty iron-rich lithofacies and have been deposited near the margins of the sedimentary basins. Iron and manganese are separated further by oxidation and enrichment processes and secondary manganese-rich lithofacies of ore may be deposited some distance from their protore facies.

Important examples of enriched manganese deposits developed in iron-formation are Moanda in Gabon; Serra do Navio in Amapa, Brazil; deposits in the Dharwar, Iron Ore, and Aravalli supergroups of India; and in the Khondalite, Sausar, and Gangpur Groups of India; in the Transvaal and Damara supergroups of southern Africa and Namibia; and in Ghana.

The distribution of gold in residually enriched iron ore deposits is being investigated in different parts of the world.

EXPLORATION GUIDELINES

1. Areas should be selected in which:
   a) iron-formations are 30 to 100 m thick, and contain 30% or more iron;
   b) silica in the iron-formation has cherty fine grained textures in preference to coarse granular textures, enabling a maximum exposure of grain surfaces to the leaching solutions;
   c) lithofacies consist of a high proportion of minerals that are readily amenable to leaching and oxidation, such as siderite, iron silicates, and fine grained cherty iron oxide, and a minimum of sulphide lithofacies;
   d) iron-formation has relatively thin banding and primary sedimentary features that enhance permeability;
   e) structural deformation through faulting, fracturing, and shearing has developed high permeability in the iron-formation, and has repeated stratigraphic units to provide large structural blocks of protore lithofacies of the iron-formation; and
   f) there is evidence of paleoenvironments suitable for deep penetration and circulation of groundwater to promote oxidation, leaching, and enrichment of the iron-formations over extended periods of geological time.
2. The stratigraphy, structure, and distribution of the iron-formation protore should be clearly defined through geological mapping and drilling to provide a basis for defining deposit settings and characteristics, and to enable assessment of resource potential. Drilling and test pitting are usually required to define the borders and distribution of the iron-formation units.
3. Aeromagnetic surveys are used effectively for tracing the regional distribution of iron-formations. Combinations of gravity and magnetic surveys have been used successfully for locating residually enriched zones within units of iron-formation.
4. Residually enriched ore deposits within the protore iron-formation may be detected directly through observation and study of topographic and related features such as:
   a) the presence of gossans, red and brown stained soil, the presence of enriched fragments of iron oxide and iron-formation in the soil (a number of ore deposits were found in the Knob Lake range by examining the frost boils and searching for enriched fragments of iron-formation); rock fragments in the soil are commonly used in deeply weathered terrain to trace the distribution of iron-formation; iron-formation fragments serve as important lithological markers for tracing the direction of transport and source areas for till, eskers, and moraines, and the glacial deposits may be followed to the iron-formation source areas;
   b) outcrops and cores of iron-formation may show evidence of leaching of silica and enrichment of iron, and secondary manganese distributed in fractures, veins, pods, or stain, may indicate significant mobilization of highly oxidized iron and manganese in the vicinity of enriched zones;
   c) synclinal fold structures and traces of fault zones, in iron-formation; and
   d) ridges of iron-formation broken by areas of low relief, which may mark areas of leaching, enrichment, and ore development.

5. Reconstruction of paleotopography to trace regoliths and deeply weathered zones which may be capped by hard rock overthrust by late faults, as in the case of the deep pockets of rubble ore in the Ruth Lake deposits of the Knob Lake range (Fig. 4.1-2).

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4.2 SUPERGENE BASE METALS AND PRECIOUS METALS

D.R. Boyle

INTRODUCTION

Prior to glaciation, the Canadian geological landscape was subjected to a long period of physico-chemical weathering during Cambrian to late Tertiary with considerable variations in regional climates. Sulphide-bearing deposits at or near the land surface at this time, especially during the Tertiary, underwent extensive oxidation leading to formation of supergene precious metal and base metal deposits. Many of these deposits experienced considerable enrichments in these metals. The various supergene mineral deposits associated with primary sulphide-bearing deposits in Canada (Fig. 4.2-1) can be divided into three subtypes 4.2a: supergene zones developed over massive sulphide deposits; 4.2b: oxidation zones developed in the upper parts of vein, shear/fault-related, and replacement deposits; and 4.2c: supergene oxide and sulphide zones formed over porphyry Cu-Mo-(Au-Ag) deposits.

Boyle, D.R.
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The term oxidation as used here does not simply denote formation of oxide, carbonate, or sulphate minerals *sensu stricto*, but rather a state in which primary sulphide

minerals are progressively oxidized, or precipitated from oxidizing solutions, through attainment of higher oxidation states represented by formation of both sulphide (e.g., chalcocite-covellite-digenite) and oxide-carbonate-sulphate-silicate-phosphate secondary minerals. In this context, four processes are important in the formation of supergene mineral deposits: 1) alteration of an existing primary mineral to form a secondary mineral of similar composition but higher oxidation state (e.g., chalcocite after chalcopyrite), 2) coating of primary grains (reduction sites) by secondary sulphides (e.g., sooty chalcocite on chalcopyrite and pyrite), 3) replacement of primary sulphides by secondary minerals of different composition (e.g., chalcocite and covellite replacement of sphalerite and galena), and 4) precipitation of secondary minerals in primary and dissolution voids of the host or country rocks (e.g., precipitation of most oxides, sulphates, and native gold, silver, and copper).

The economic commodities associated with the three types of supergene deposits mentioned above are: subtype 4.2a – Au, Ag, Cu, Ni, and Hg; subtype 4.2b – Cu, Au, Ag, Zn, Pb, and Mn; and subtype 4.2c – Cu, Mo, Au, and Ag.

In Canada, the best examples of subtype 4.2a deposits are found in the Bathurst mining camp of New Brunswick (e.g., Murray Brook, Caribou, Heath Steele deposits) and at the Windy Craggy deposit in British Columbia. For subtype 4.2b deposits the best examples are the Copper Rand, Henderson II, Selbaie (Detour) deposits in Quebec, the Ross and Keeley mines in Ontario, the Bayonne mine in southern British Columbia, and the Keno Hill, Mount Nansen, Ketza River, Brewery Creek, and Williams Creek deposits in Yukon Territory. For subtype 4.2c deposits the best examples are the Casino deposit in Yukon Territory and the Afton, South Kemess, Gibraltar, Mount Polley, Bell, Berg, and Krain deposits in British Columbia (see Fig. 4.2-1 and Table 4.2-1).

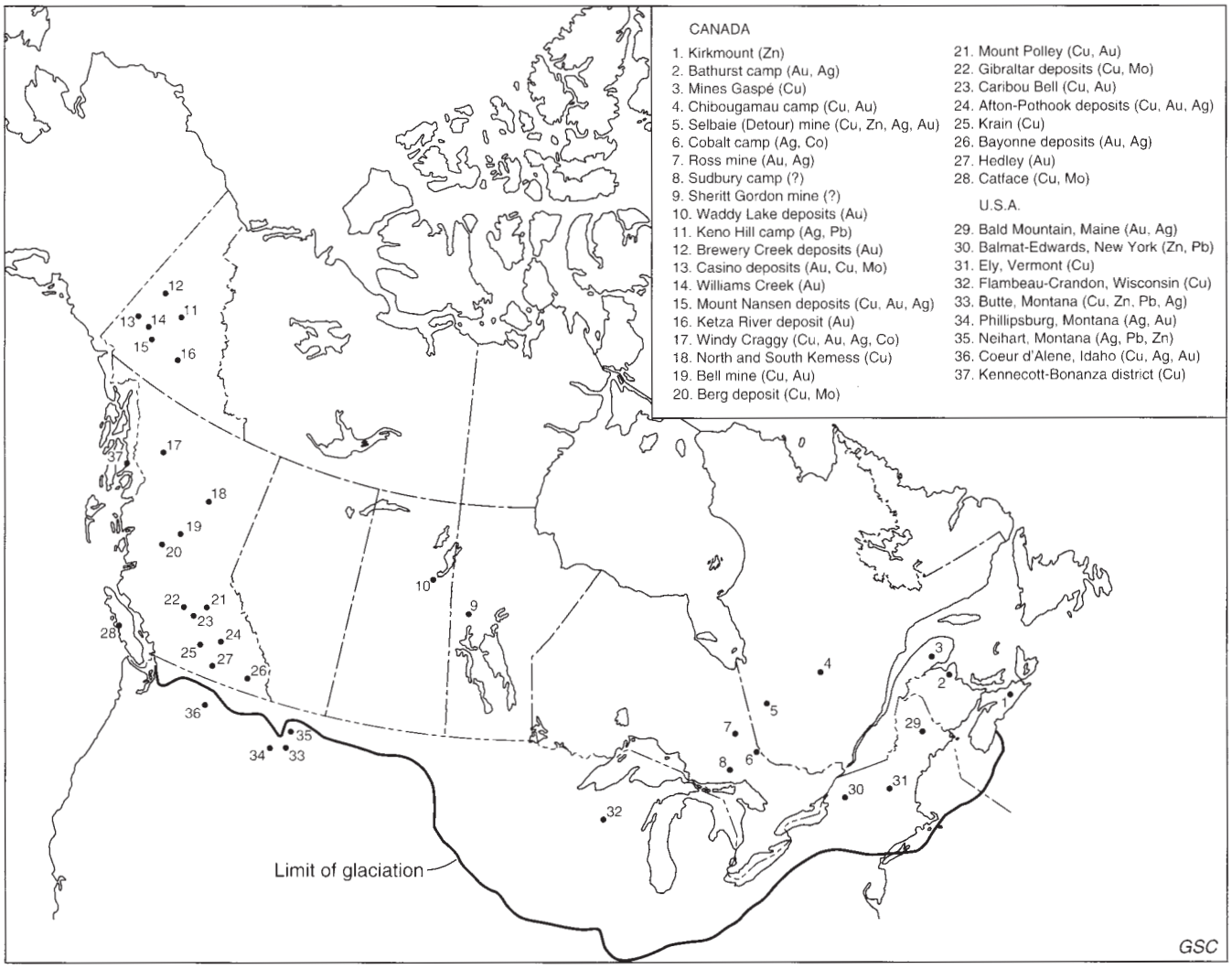

Figure 4.2-1. Location of supergene precious and base metal mineral deposits in Canada. Major supergene mineral camps in northern U.S.A. are also shown.

Table 4.2-1. Tonnages, grades, and supergene characteristics of Canadian precious metal and base metal supergene mineral deposits. For large mining camps in which supergene mineral deposits occur, only representative deposits are given. See Figure 4.2-1 for deposit locations.

Deposit		Tonnage (Mt)	Grades*	% of Deposit ‡ Supergene	Depth of Oxidation (m)	Ref.
Massive sulphide deposits (subtype 4.2a)						
Bathurst camp						
- Murray Brook	- gossan	1.02	Au(1.52), Ag(65.9)	15	60	1
	- primary	21.50	Cu(0.20), Zn(4.23), Pb(1.62) Au(0.6), Ag(54.3)	---	---	1,2
- Caribou	- gossan	0.06	Au(6.02), Ag(242.3)	2	20	2
	- secondary S_2	0.83	Cu(3.40), Zn(2.60), Pb(1.10)	20	20	2
	- primary	5.40+	Cu(<0.4), Zn(8.30) Pb(3.7), Au(1.5), Ag(102)	---	---	2
- Heath Steele B	- gossan	0.18	Au(5.03), Ag(171.6)	2	30	2
	- primary	15.80	Cu(1.0), Zn(4.48), Pb(2.88) Au(1.5), Ag(69.7)	---	---	2
Windy Craggy	- gossan	4.0+	Au(1.69), Ag(13.0), Cu(0.28)	0.2	5	3
	- secondary S_2	1.6+	Au(0.41), Ag(11.0), Cu(4.21)	0.1	2	3
	- primary	200+	Au(0.20), Ag(3.83), Cu(1.44) Co(0.07)	---	---	3
Vein, shear/fault-related, and replacement deposits (subtype 4.2b)						
Chibougamau camp						
- Copper Rand		9.5	Cu(1.81), Au(2.05)	20-30	350	4
- Henderson II		N/A	N/A	15-20	300	5
Selbaie (Detour)						
	- A1 zone	32.1	Cu(0.39), Zn(2.30), Au(0.31) Ag(36)	<20	150	6,7
	- B zone	0.9	Cu(3.51), Au(0.96), Ag(30.8)	50-60	200	6,7
Mount Nansen	- Webber lode	N/A	Au(12.0), Ag(836)	50	70	8
Bayonne mine	- oxide zone	N/A	Au(35 to 70)	>80	150	9
	- primary	N/A	Au(<13)	---	---	9
Ross mine		N/A	oxide ore considerably enriched in Au and Ag compared to primary ore	?	120	10
Cobalt Camp - Keeley mine		N/A	Ag(3300; up to 102 000) Au(19.9)	?	170	11
Keno Hill	- oxide ore	1.0	Ag(2300-16 600), Pb(25-60)	>80	200	12
	- primary ore	2.0	Ag(340-3400), Pb(4-22)	---	---	12
Ketza River	- oxide ore	0.5	Au(18.0)	100	150	13
Brewery Creek	- oxide zone	10.0	Au(1.99)	100	30	14
Williams Creek	- No. 1 zone	13.6	Cu(1.07), Au(0.5)	90	250	15
Porphyry Cu-Mo (Au, Ag) deposits (subtype 4.2c)						
Casino	- leached capping	31.0	Cu(0.11), Mo(0.024), Au(0.8)	5	60	16
	- secondary	95.0	Cu(0.43), Mo(0.031), Au(0.4)	15	130	16
	- primary	489.0	Cu(0.23), Mo(0.024), Au(0.3)	---	---	16
South Kemess	- all zones	200.4	Cu(0.22), Au(0.63)	20	70	17
Mount Polley	- all zones	155.0	Cu(0.29), Au(0.39)	25	250	18
Gibraltar	- four deposits	360.0	Cu(0.371), Mo(0.016)	30	100	19
Krain	- secondary	4.9	Cu(0.64)	50	100	20
	- primary	9.1	Cu(0.53)	---	---	20
Bell - all zones		116.0	Cu(0.48), Au(0.35)	25	70	21
Berg - all zones		400.0	Cu(0.4), Mo(0.05)	60	130	22
Afton - all zones		30.8	Cu(1.0), Au(0.58), Ag(4.19)	>80	500	23
Gaspe mines						
Mines Gaspé- Copper Mountain						
	-secondary	30.4	Cu(0.45)	15	100	24
	- primary	208.6	Cu(0.40)	---	---	24

N/A - not available * Au, Ag grades in g/t; base metals in % S_2 - sulphides ? - unknown ‡ - by volume

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In other parts of the world the best examples of subtype 4.2a deposits can be found in the famous Rio Tinto massive sulphide belt of Spain (Williams, 1934; Palermo et al., 1986), and the Mt. Lyell, Mt. Morgan, and Elura deposits of Australia (Solomon, 1967; Hughes, 1990). Supergene deposits associated with subtype 4.2b deposits are numerous throughout all base metal metallogenic regions in the world. Good examples of this group can be found in the U.S.A. in such mining camps as Butte and Granite-Bimetallic, Montana; Creede and Cripple Creek, Colorado; Tonopah, Nevada; and Tintic, Utah (Lindgren, 1923), and in practically all of the base and precious metal mining camps of Australia (Hughes, 1990). Much of the silver production from the famous Potosi tin-silver veins of Bolivia came from supergene ore zones. Good examples of subtype 4.2c deposits outside Canada can be found in Chile (e.g., Chuquicamata, El Salvador, La Escondida), U.S.A. (e.g., Bingham, Utah; Butte, Montana; Ray, Morenci, Santa Rita, Twin Buttes, and Sierrita, Arizona), Iran (Sar Cheshmeh), and many other porphyry copper metallogenic provinces.

For the descriptions of supergene mineral deposits that follow, it is assumed that the reader is familiar with the various primary mineralization features of the main deposit groups mentioned above (see subtypes 6.3, 6.4 and Types 16, 17, 19).

IMPORTANCE

Supergene weathering processes are economically important since they often lead to the enrichment of precious and base metals to the point that even very low grade primary sulphide or precious metal-bearing mineralized zones can evolve into economic mineral deposits. This can be accomplished by two main processes: secondary sulphide or precious metal enrichment contained within a smaller volume of rock than the primary ore, and conversion of original, less extractable, forms of primary sulphides or refractory precious metals into mineral forms which are more economical to extract, the primary and supergene grades largely remaining the same.

In unglaciated regions of the world, supergene precious and base metal deposits have made a major contribution to the mineral economy. Thus, if it were not for supergene enrichment processes many of the well known porphyry Cu deposits in the southwestern U.S.A., Chile, Middle East, and elsewhere would not be economic (Sillitoe and Clark, 1969; Titley, 1975). For many deposits in these regions, all of the ore is supergene (with enrichment). In Australia about 70% of Au reserves today are in supergene ores (calculated from Hughes, 1990). Indirectly, precious metal supergene ores were the source for the large bonanza Au, Pt placer deposits in Yukon Territory; Ballarat, Australia; Urals, Russia; and smaller placer regions such as those at Barkerville, British Columbia, and the Eastern Townships of Quebec.

In Canada, in situ supergene precious and base metal deposits have made only a modest contribution to overall mineral production due to the scouring effects of glaciation and the difficulties in detecting such ores under glacial cover. However, in some individual metallogenic provinces contributions have been quite significant. Thus, in the Bathurst base metal camp of New Brunswick, practically all of the Au production has come from supergene gossans, and in the western Cordillera porphyry Cu-Mo province, supergene ores have contributed significantly to the metal endowment. According to Ney et al. (1976), the widespread belief by explorationists that glaciation had removed the important supergene zones that make porphyry deposits such important sources of Cu was largely responsible for the late (mid-1950s) recognition and exploration of the porphyry Cu-Mo province of the Canadian Cordillera.

SIZE AND GRADE OF DEPOSITS

Tonnages for supergene ore deposits associated with massive sulphide deposits (subtype 4.2a) are typically in the 0.5 to 10 Mt range with grades for Au and Ag ranging from 1.0 to 10.0 g/t and 50 to 300 g/t, respectively. Typically Au is enriched in these gossans by factors of 2 to 4 (Table 4.2-1).

Tonnages for supergene ores associated with vein, shear/fault-related, and replacement deposits (subtype 4.2b) range from 2 to 15 Mt with grades for Au, Ag, Cu, and Pb typically ranging from 0.5-20.0 g/t, 30-1000 g/t, 1-5%, and 20-60%, respectively. Zinc is enriched only in willemite and smithsonite deposits such as those at Balmat-Edwards, New York (Brown, 1936) and Kirkmount, Nova Scotia (Sangster, 1986; Fig. 4.2-1), otherwise this element is severely depleted from these zones. Occasionally these deposits represent bonanza 'free Au' and 'native Ag' deposits (e.g., Keno Hill, Yukon Territory; Cobalt silver deposits, Ontario, and Bayonne and other mines in the Nelson area of British Columbia). Gold and silver grades in these deposits in many cases reach levels of 20-100 g/t and 3000-100 000 g/t, respectively. These represent considerable enrichments over protore grades.

Tonnages for supergene ore zones developed over porphyry Cu-Mo deposits (subtype 4.2c) can be as small as 30 Mt (e.g., Afton mine, British Columbia) to as large as the super giant porphyries, which are primarily supergene enriched deposits (e.g., Chuquicamata; 1 Bt). Grades for supergene Cu-Au-Ag porphyries are typically 0.2-3.0% Cu, 0.2-1.0 g/t Au, and 1-10 g/t Ag. Supergene enrichment factors for Cu over primary mineralization are in the order of 1.25 to 5.0 (Ney et al., 1976; Titley, 1982). Some deposits have been considered not to be enriched, but simply to represent a conversion of Cu-sulphides to a secondary form such as native Cu (e.g., Afton, South Kemess). True enrichment must be calculated on a mass balance basis, not on the basis of ore reserve calculations. From this viewpoint, practically all supergene zones associated with porphyry systems represent some overall metal enrichment.

Tonnages and grades for Canadian supergene precious and base metal deposits for which data are available are given in Table 4.2-1. For some deposits a comparison of supergene and primary ore grades and tonnages are also given together with the approximate percentage of the ore deposit that is supergene.

A number of supergene precious and base metal mineral deposits have failed at the mining stage due to improper ore reserve calculations. Unlike primary deposits, supergene ores are highly porous and simple use of "specific gravity x volume" methods are not applicable. Also, the use of the water balance method for calculating specific gravity is ineffective because the total porosity factor is not included in this measurement. Calculations may be further hampered by the fact that porosities will vary considerably

between supergene zones within a given deposit. Statistically representative analyses of porosity and use of powder pycnometry for specific gravity should be used for the calculation of supergene ore reserves.

GEOLOGICAL FEATURES

General zonation and mineralogy

Irrespective of the type of sulphide-bearing or precious metal deposit over which supergene ores form, there is a general zonation scheme that is common to all. Specific deviations from this scheme and descriptions of the behaviour of elements within each of the main supergene zones developed over the three primary deposit types mentioned above are given in detailed descriptions below and in Table 4.2-1. Generally, supergene precious metal and base-metal ore deposits can be divided into three main zones (see Fig. 4.2-2 to 4.2-6). The uppermost zone has been commonly termed "leached capping". It can vary in composition from highly siliceous-kaolinized and slightly ferruginized material to massive goethite-hematite-jarosite gossan. Below the leached capping an "oxide zone" generally forms which is characterized by the formation of base metal oxide, carbonate, sulphate, phosphate, silicate, halide, and native minerals formed after secondary sulphides as precipitates in rock voids. A "supergene sulphide zone", varying considerably in thickness, forms between the oxide zone and the primary ore. This zone is characterized by dissolution of carbonate minerals to create secondary voids, the coating of primary sulphides with 'sooty' secondary sulphides, and the replacement of primary sulphides by secondary sulphides. Depending on conditions of formation, this zone may or may not be characterized by strong enrichments of Cu and Ni. Zinc and lead are generally depleted in this zone.

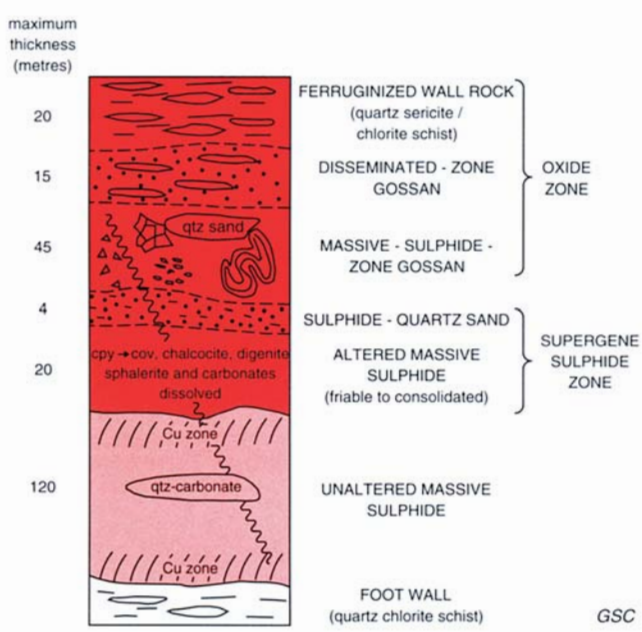

Figure 4.2-2. Representative stratigraphic profile of the supergene zones developed over massive sulphide deposits in the Bathurst camp, New Brunswick (after Boyle, 1993). Abbreviations: qtz = quartz; cpy = chalcopyrite; cov = covellite.

The principal minerals found in each of these three zones are presented in Table 4.2-2. It should be noted that adjacent zones, and thus their mineral assemblages, overlap.

The behaviour and disposition of Au during formation of the above zones is important to the economic viability of some of these deposits. Generally Au accumulates only in the leached capping and oxide zones in which it has two main forms of occurrence; as in situ freed grains initially occluded in primary sulphides, and as precipitated micrometre-size native Au and electrum grains formed in rock voids during descent of oxidizing solutions. Generally, only the latter process will lead to enrichment of Au in the upper supergene zones. This enrichment is generally in the order of 2 to 5 times primary Au concentrations. Both of the above mentioned processes lead to Au reserves that can be recovered using methods that are generally cheaper than those used in primary sulphide ore extraction.

Depth of oxidation

The depths to which supergene mineral deposits extend will be dependent largely on the position of the water table during the predominant time of formation. Emmons (1917) and Lindgren (1923) have described the formation of significant supergene sulphide and oxide zones down to depths of 500-700 m in some of the mining camps in the U.S.A. In Canada the various recorded depths of supergene ore development are presented in Table 4.2-1. For massive sulphide deposits the depths of oxidation are relatively shallow (7-60 m), but greater depths have been recorded elsewhere (Palermo et al., 1986; Hughes, 1990). For vein, shear/fault-related, and replacement deposits, the depth of oxidation in Canada varies from 30-350 m; depths which are similar to those recorded in unglaciated terranes. For porphyry Cu deposits in the Canadian Cordillera the depths of oxidation vary from 60 to 500 m, which makes them comparable in supergene development to the porphyry Cu provinces of the southwestern U.S.A. and the Andes Mountains of South America.

Although oxidation above the water table is the most dominant supergene process in these deposits, numerous examples have been given where significant oxidation has continued for considerable depths below the water table (Emmons, 1917; Lindgren, 1923; Guilbert and Park, 1986). This process is considered to be driven by differential electrochemical oxidation potentials involving anode-cathode cells (Sato and Mooney, 1960; Blain and Brotherton, 1975) and/or lateral influx into ore zones of groundwaters still containing considerable amounts of dissolved O_2.

Age of mineralization

All of the deposits outlined in Figure 4.2-1 and Table 4.2-1 are preglacial, but exact ages are very difficult to determine due to the lack of good geochronological dating methods for supergene deposits and the general absence of datable stratigraphic marker horizons. Some deposits, such

as Afton (late Paleocene-middle Paleocene), Krain (early Tertiary), and Bell Copper (post-Eocene to pre-Pleistocene), can be dated reasonably well due to the presence of overlying Tertiary volcanic and sedimentary rocks. Most of the supergene zones associated with porphyry Cu deposits in the Canadian Cordillera can be bracketed in age between late Cretaceous and late Tertiary since the host rocks for primary ore span this period. For the Selbaie (Detour) mine in Quebec (Sinclair and Gasparini, 1980) and the Flambeau deposit in Wisconsin (May, 1977) it has been suggested that oxidation took place in late Precambrian to Cambrian times, but in the opinion of the author evidence for this conclusion is weak. Recent paleomagnetic research on the supergene deposits overlying the massive sulphide deposits of the Bathurst camp places the period of weathering at 1-3 million years ago, just before onset of Pleistocene glaciation (Symons and Boyle, unpub. data, 1994).

It is the opinion of the author that most of the supergene deposits in Canada and the northern United States (see Fig. 4.2-1 and Table 4.2-1) were formed during late Cretaceous to late Tertiary times under regional climates that varied from tropical through semiarid to arid.

Subtype 4.2a

Supergene zones developed over massive sulphide deposits

Importance of structure and stratigraphy

Compared to other types of primary sulphide deposits, structure plays a minimal role in the formation of supergene zones over massive sulphide deposits. Where significant postmineralization faulting has occurred, these faults may act as channelways for localized oxidation within the deposit. Stratigraphy, however, does play a major role in sulphide oxidation processes. Massive sulphide deposits generally exhibit cyclical sulphide-gangue layering. Sphalerite-, pyrrhotite-, and carbonate-rich layers oxidize at a much faster rate than galena-, chalcopyrite-, pyrite-, and magnetite-rich layers. Deposits with a high proportion of the former mineral assemblages will oxidize faster, more completely, and to greater depths over a given time period than those with a predominance of the latter mineral sequence. Oxidation of sphalerite-pyrrhotite-carbonate zones will lead to significant secondary porosities since

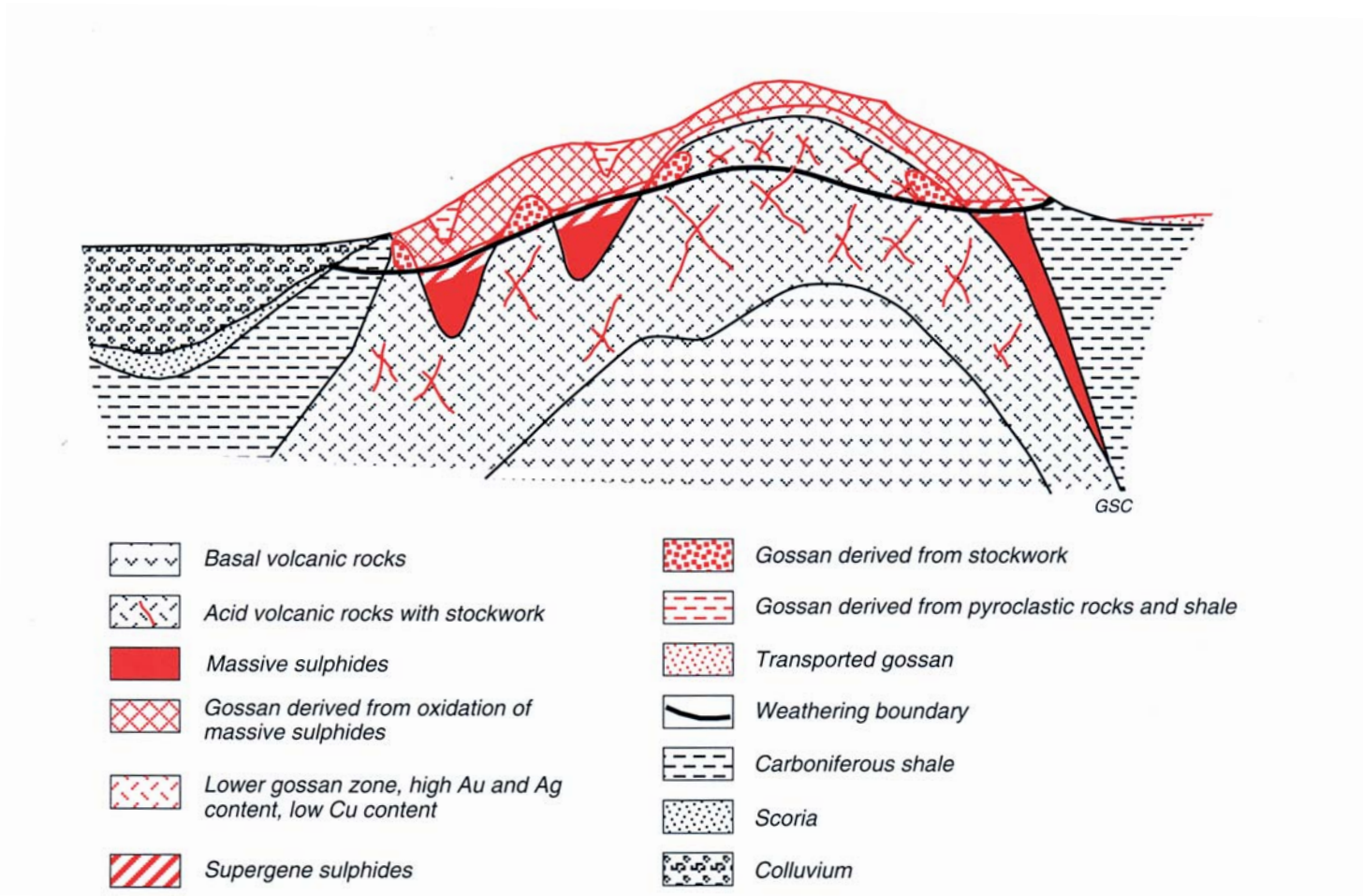

Figure 4.2-3. Schematic cross-section of the Rio Tinto Cerro Colorado massive sulphide district of Spain showing secondary and primary zones (after Palermo et al., 1986).

TYPE 4

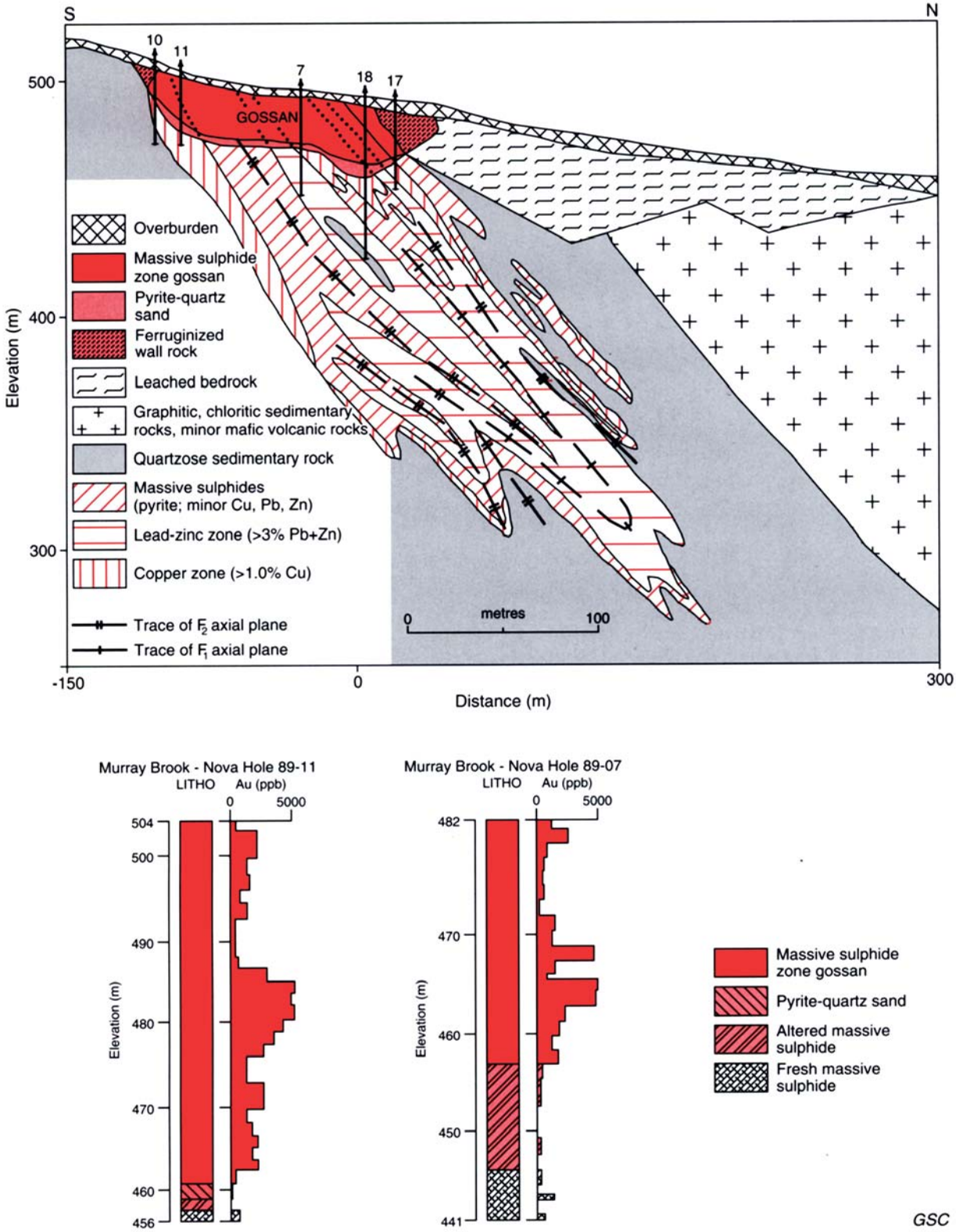

Figure 4.2-4. Cross-section and representative Au profiles of the Murray Brook gossan deposit, Bathurst mining camp, New Brunswick (modified after Boyle, 1993).

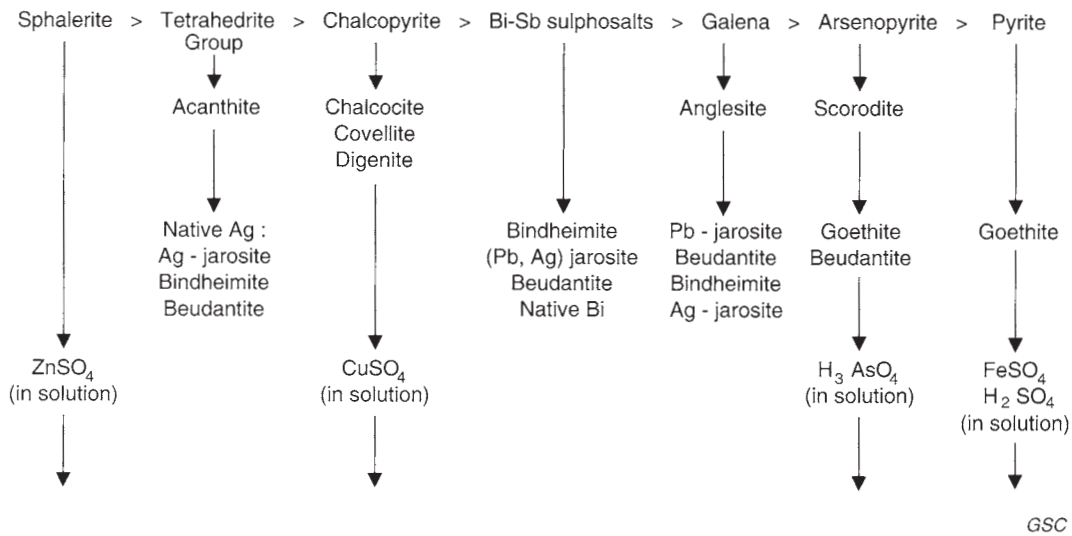

Figure 4.2-5. Typical alteration sequence for the oxidation of low-pyrrhotite massive sulphide deposits (after Boyle, 1993).

their weathering products are largely leached out of the sulphide zone. Greater porosity leads to accelerated oxidation and the formation of a larger reservoir for the precipitation of secondary phases that remain within the zone.

Alteration and texture

A typical stratigraphic section through an oxidized massive sulphide deposit is shown in Figure 4.2-2. The surrounding host rocks to these deposits are generally strongly ferruginized and argillized. If exposed, the stringer zone will be altered to a "disseminated-zone gossan" formed predominantly of goethite which can be very rich in Au.

When altered, the main body of the massive sulphide deposit forms a "massive-sulphide-zone gossan" consisting mainly of massive goethite and hematite showing highly vesicular, cellular-boxwork and pseudomorphic-replacement textural features of completely oxidized massive sulphide. Principal minerals in this zone are goethite, hematite, silica (anhedral and amorphous), hydroxy-sulphates and oxides (beudantite, plumbojarosite, jarosite, binheimite, scorodite), and traces of cinnabar, primary cassiterite, and native Au, Ag, and Bi. Primary carbonates (siderite, ankerite, dolomite, calcite) are completely dissolved by acid solutions, often leaving small lenticular cavities in the gossan.

Beneath the massive-sulphide-zone gossan, oxidation is dominated by almost total dissolution of carbonate-gangue phases, dissolution of sphalerite, alteration of chalcopyrite to supergene Cu sulphides (chalcocite, covellite, digenite), and partial oxidation of galena and arsenopyrite to anglesite and scorodite, respectively.

A unique feature of Canadian supergene deposits overlying massive sulphides is the presence between the gossan and supergene sulphide zones of a thin, 1-3 m, layer of pyrite-quartz sandy-mud which is almost totally devoid of base metals and precious metals. It has been suggested that this is a postglacial feature (Boyle, 1993).

The relational aspects of the various zones mentioned above are exemplified by the schematic cross-section in Figure 4.2-3 for the famous Rio Tinto massive sulphide belt of Spain and by the cross-section of the Murray Brook deposit in the Bathurst mining camp of New Brunswick shown in Figure 4.2-4.

Figure 4.2-5 shows the typical alteration sequence for low grade pyrrhotite-bearing massive sulphide deposits. When pyrrhotite is present in concentrations generally above 10-15%, this sequence is greatly disrupted, and pyrrhotite accelerates the oxidation of sphalerite and galena, and especially of pyrite.

Enrichment processes and metal zoning

For gossan deposits overlying massive sulphides, Cu and Zn are almost totally leached from the oxide zone. Zinc leaves the system as a whole, whereas Cu may be strongly enriched or follow a history similar to Zn. For example, in the Bathurst mining camp, both the Murray Brook and Caribou deposits have similar primary ore compositions, yet Cu is strongly enriched in the supergene sulphide zone at Caribou whereas at Murray Brook the element simply takes part in a 'constant grade' conversion of chalcopyrite to chalcocite-covellite-digenite. These two deposits are only 10 km apart and occur at the same elevation. The reasons for this disparity for Cu are not clearly understood, but it would appear that the difference between the enrichment and constant Cu grade scenarios is exemplified by strong replacement of sphalerite and galena by chalcocite within the enriched zones in addition to the conversion of chalcopyrite to secondary sulphides.

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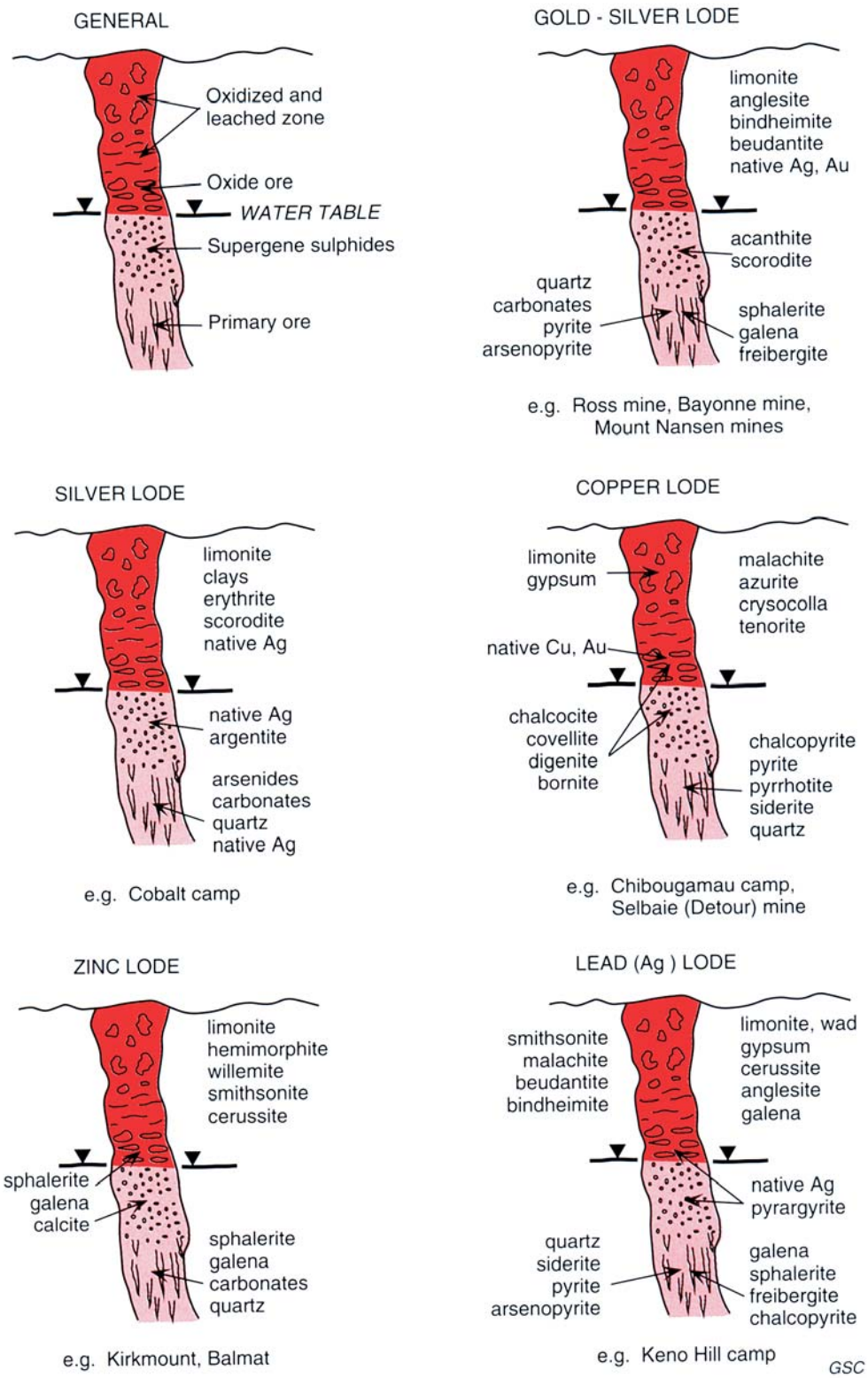

Figure 4.2-6. Generalized cross-section and specific mineralogical cross-sections for precious metal and base metal lode deposits.

Table 4.2-2. Principal minerals in supergene zones associated with sulphide-bearing ore deposits. Main zones are presented in descending lithostratographic order. In some deposits transition zones may occur between these main zones and thus contain minerals of each zone. To the author's knowledge all of the minerals listed below have been found in Canadian supergene mineral deposits.

Leached cappings	
Goethite - $FeO(OH)$	Antlerite - $Cu_3(SO_4)(OH)_4$
Hematite - Fe_2O_3	Brochantite - $Cu_4(SO_4)(OH)_6$
Jarosite - $KFe_3(SO_4)_2(OH)_6$	Chrysocolla - $(Cu,Al)_2H_2Si_2O_5(OH)_4 \bullet nH_2O$
Pitch limonite - $H(Fe,Cu)O_2$	Cuprite - Cu_2O
Native - Au, Cu	Tenorite - CuO
Kaolinite - $Al_2Si_2O_5(OH)_4$	Turquoise - $CuAl_6(PO_4)_4(OH)_8 \bullet 4H_2O$
Chlorite - $(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	Neotocite - $(Mn,Fe)SiO_3 \bullet H_2O$
Smectites	Ferrimolybdite - $Fe_2(MoO_4)_3 \bullet 7H_2O$
Oxide zones	
Goethite - $FeO(OH)$	Native - Au, Ag, Cu, Bi, Zn, S
Silica - SiO_2	Anglesite - $PbSO_4$
Hematite - Fe_2O_3	Cerussite - $PbCO_3$
Alunite - $KAl_3(SO_4)_2(OH)$	Scorodite - $FeAsO_4 \bullet 2H_2O$
Jarosite - $KFe_3(SO_4)_2(OH)_6$	Beudantite - $PbFe_3(AsO_4)(SO_4)(OH)_6$
Plumbojarosite - $PbFe_6(SO_4)_4(OH)_{12}$	Bindheimite - $Pb_2Sb_2O_6(O,OH)$
Argentojarosite - $AgFe_3(SO_4)_2(OH)_6$	Minium - Pb_3O_4
Cuprite - Cu_2O	Litharge/Massicot - PbO
Tenorite - CuO	Ferrimolybdite - $Fe_2(MoO_4)_3 \bullet 8H_2O$
Malachite - $Cu_2(CO_3)(OH)_2$	Wulfenite - $PbMoO_4$
Azurite - $Cu_3(CO_3)_2(OH)_2$	Cinnabar - HgS
Chrysocolla - $(Cu,Al)_2H_2Si_2O_5(OH)_4 \bullet nH_2O$	Valentinite - Sb_2O_3
Brochantite - $Cu_4(SO_4)(OH)_6$	Stibiconite - $Sb_3O_6(OH)$
Chalcanthite - $CuSO_4 \bullet 5H_2O$	Pyrolusite MnO_2
Antlerite - $Cu_3(SO_4)(OH)_4$	Manganite - $MnO(OH)$
Turquoise - $CuAl_6(PO_4)_4(OH)_8 \bullet 4H_2O$	Rhodochrosite - $MnCO_3$
Hemimorphite - $Zn_4Si_2O_7(OH)_2 \bullet H_2O$	Rhodonite - $(Mn,Fe,Mg,Ca)SiO_3$
Smithsonite -$ZnCO_3$	Neotocite - $(Mn, Fe)SiO_3 \bullet H_2O$
Hydrozincite - $Zn_5(CO_3)_2(OH)_6$	Chlorargyrite - $AgCl$
Goslarite - $ZnSO_4 \bullet 7H_2O$	Iodargyrite - AgI
Willemite - Zn_2SiO_4	Marshite - CuI
Gypsum - $CaSO_4 \bullet 2H_2O$	Miersite - $(Ag,Cu)I$
Calcite - $CaCO_3$	Bromargyrite - $AgBr$
Dolomite - $CaMg(CO_3)_2$	Atacamite - $Cu_2Cl(OH)_3$
Kaolinite - $Al_2Si_2O_5(OH)_4$	Mimetite - $Pb_5(AsO_4)_3Cl$
Chlorite - $(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	Pyromorphite - $Pb_5(PO_4)_3Cl$
Smectites	Vanadinite - $Pb_5(VO_4)_3Cl$
Supergene sulphide zones*	
Chalcocite - Cu_2S	Pyrite - FeS_2
Covellite - CuS	Marcasite - FeS_2
Digenite - Cu_9S_5	Violarite - $FeNi_2S_4$
Bornite - Cu_5FeS_4	Bravoite - $(Ni,Fe)S_2$
Djurleite - $Cu_{31}S_{16}$	Krennerite - $AuTe_2$
Acanthite - Ag_2S	Pyrargyrite - Ag_3SbS_3
Native - Au, Ag, Cu, Bi, S	Sylvanite - $(Au,Ag)_2Te_4$
Sphalerite - $(Zn,Fe)S$ (rare)	Stromeyerite - $AuCuS$
Kaolinite - $Al_2Si_2O_5(OH)_4$	Galena - PbS (rare)
Chlorite - $(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	

* secondary sulphides only

Gold is greatly enriched within the gossan portion of these deposits. For the Murray Brook, Caribou, Heath Steele, and Windy Craggy deposits the Au enrichment factors (on a weight/weight basis) are 2.5, 4.0, 3.5, and 8.5, respectively. Practically all of the Au occurs as fine submicrometre grain precipitates in voids within the gossan. For the same deposits mentioned above, Ag enrichment factors are 1.2, 2.4, 2.5, and 3.4, respectively. The Ag is partitioned between three main phases: 1) native Ag in voids, 2) argentojarosite, and 3) sequestration in Fe-oxyhydroxide and hydrated-sulphate minerals. As shown in the Au profiles for the Murray Brook deposit (Fig. 4.2-4), this element (and Ag, not shown) is distinctly zoned within the gossan. Zonation appears to be strongly controlled by the pyrite concentration in primary ore. During oxidation of massive sulphides, Pb and As are immobile and thus become concentrated in the gossan (see minerals, Table 4.2-2).

Subtype 4.2b

Oxidation zones developed in the upper parts of vein, shear/fault-related, and replacement deposits

Importance of structure

Structural elements play an important role in the development and localization of vein, shear/fault-related, and replacement precious metal and base metal deposits. These same structures also play a strong role in the development of supergene ore zones in the upper parts of these deposits. Primary structures become the channelways for descending oxidizing solutions which first attack the carbonate, sphalerite, and chalcopyrite phases. Because these deposits in many cases contain high concentrations of carbonates, a significant secondary porosity for precipitation of enriched supergene base metal and precious metal minerals can develop and oxidation zones can extend for considerable depths (see Table 4.2-1).

One of the most interesting features of these deposits is that in a given mining camp containing a number of vein or shear zone-related deposits, only a few will show extensive oxidation, and in some cases (e.g., Chibougamau and Cobalt camps) down to the deepest depths recorded from throughout the world. In the opinion of the author, this selective oxidation may be due to the relative locations of the deposits to groundwater discharge and recharge zones. Deposits in recharge zones would be more susceptible to deeper oxidation.

Alteration and texture

A general oxidation profile for this deposit type and specific mineralogical profiles for Au-Ag, Ag, Cu, Zn, and Pb-Ag lodes are presented in Figure 4.2-6. The general oxidation scheme is very similar to that described above for massive sulphide deposits, but the gossan zone may not be as developed in lode deposits. These deposits are known for their spectacular development of botryoidal, reniform, vermiform, and massive crystal aggregates of secondary base metals and precious metals. Many of these deposits have generated considerable income as sources of rare or exceptional quality minerals for the mineral collection industry.

Enrichment process and metal zoning

For the precious metal-bearing deposits, Au is generally enriched in the upper oxide zones (e.g., Ross and Bayonne mines) wheras Ag is generally enriched in the lower oxide and supergene sulphide zones (e.g., Cobalt and Keno Hill camps). For some deposits, enrichments of Au and Ag can reach spectacular levels. Thus in the Keeley mine in the Cobalt camp, metres of almost solid native Ag and pyrargyrite were mined from the lower oxidized levels, whereas at the Bayonne and Ross gold mines, Au in the 30-100 g/t range was mined from the upper oxide zones.

The mobilization and enrichment processes for lode supergene deposits are very similar to those of the massive sulphide deposits, except that a much larger proportion of the enriched Au comes simply from concentration of primary free gold grains by volume wastage. Silver migrates down the lode structure to become concentrated in both the lower oxide and upper supergene sulphide zones as native silver, pyrargyrite, and acanthite. Lead in lodes such as the rich Pb-Ag Keno Hill veins of Yukon Territory is generally shielded by anglesite or cerussite coatings and thus becomes concentrated by volume wastage. Zinc rarely accumulates in lode deposits in which it is a minor constituent, although in Zn lode deposits, especially those with high carbonate contents, this element may become enriched through the formation of secondary willemite-sphalerite-galena deposits or secondary smithsonite oxide deposits (Fig. 4.2-6).

Subtype 4.2c

Supergene oxide and sulphide zones formed over porphyry Cu-Mo-(Au, Ag) deposits

Importance of structure and stratigraphy

Porphyry Cu-Mo systems are generally concentrically zoned, and have a potassic low grade, pyrite-poor core surrounded by a quartz-sericite-pyritic (1-3%) ore shell (Cu, Mo), which in turn is surrounded by a strongly pyritized (10-30%) low grade propylitic zone (Fig. 4.2-7). The types of supergene alteration associated with porphyry Cu-Mo deposits are therefore controlled largely by the styles of primary mineralization and alteration, the compositions of rocks hosting the porphyry system, and fracture densities of the various zones. Highly siliceous and kaolinized cappings containing Cu-silicates and -oxides form over the potassic core of these deposits. These cappings generally contain low concentrations of Au. Supergene alteration developed over the ore shell and outer propylitic zone consists of a goethite-hematite-jarosite-clay caprock underlain by well developed oxide-supergene sulphide zones. Fracture densities are usually greatest over these two zones (Titley, 1982)

Porphyry Cu-Mo systems may be hosted in rocks varying from highly felsic intrusive-volcanic to intermediate-mafic intrusive-volcanic as well as volcanic-sedimentary stratigraphies. Occasionally skarn zones develop in calcareous host rocks. The types of supergene ores that develop are therefore strongly affected by host rock lithologies. Mineralogically, the main controlling parameters are pyrite, magnetite, hornblende, biotite, and carbonate contents. Strongly pyritized rocks favour formation of rich

chalcocite blankets, whereas rocks rich in magnetite, biotite-hornblende, and carbonates favour formation of secondary native Cu deposits after chalcocite.

Alteration and texture

The supergene zones developed over potassic core zones consist of vesicular, highly siliceous and kaolinized, and slightly limonitized caprocks that contain crustations of Cu-oxides, Cu-carbonates, and Cu-silicates lining voids. These zones are generally not very thick due to minimal fracturing. For some porphyry Cu provinces this is an important source of ore, but in Canada this type of mineralization is not well developed.

Leached cappings developed over phyllic and propylitic zones consist of highly vesicular, spongy, and often pulverulent rocks composed of Fe-Mn oxyhydroxides and sulphates in a clay-rich matrix. Replacement boxwork textures are generally evident and the proportions of goethite, hematite, jarosite, and alunite are controlled by the original composition of the mineralized host rock (Anderson, 1982).

The alteration and textures in the supergene sulphide zone are dominated by sooty coatings of chalcocite-covellite-digenite on primary sulphides, pseudomorphic replacement textures of primary sulphides by these minerals, kaolinization and chloritization of silicates, and dissolution of calcite and gypsum, if present. In some deposits, the upper portion, and occasionally all, of the chalcocite blanket has been further oxidized leading to void fillings of Cu-oxides and native Cu (e.g., Afton and South Kemess).

Enrichment process and zonation

During formation of supergene mineralization over porphyry Cu-Mo deposits, Cu is strongly leached from the capping zone and transported down to the water table to form an enriched supergene sulphide blanket. If sometime during the formation of this enrichment blanket the water table is lowered, either through epeirogenic uplift or a climatic shift to more arid conditions, the chalcocite blanket will be oxidized to form Cu oxide-sulphate-carbonate, native Cu, hematite mineralization. For some deposits in the Canadian Cordillera, native Cu ore predominates in the

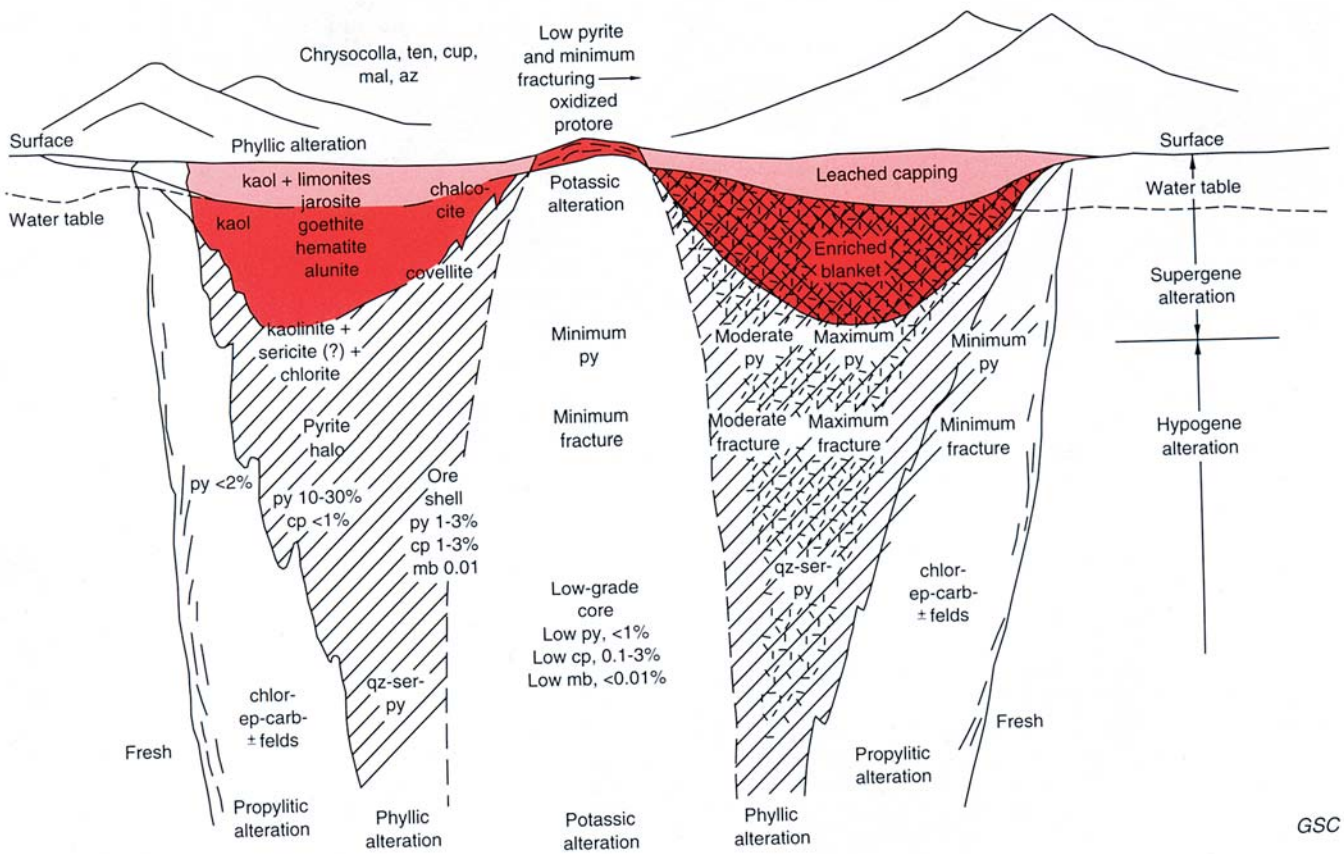

Figure 4.2-7. Schematic cross-section of a porphyry copper system showing the development of various types of supergene ore associated with underlying stratigraphy, ore and gangue tenor, and structure (after Guilbert and Park, 1986). Abbreviations: py = pyrite; ten = tenorite; cup = cuprite; mal = malachite; az = azurite; kaol = kaolinite; cp = chalcopyrite; chlor = chlorite; ep = epidote; carb = carbonates; qz = quartz; ser = sericite; felds = feldspars; mb = molybdenite.

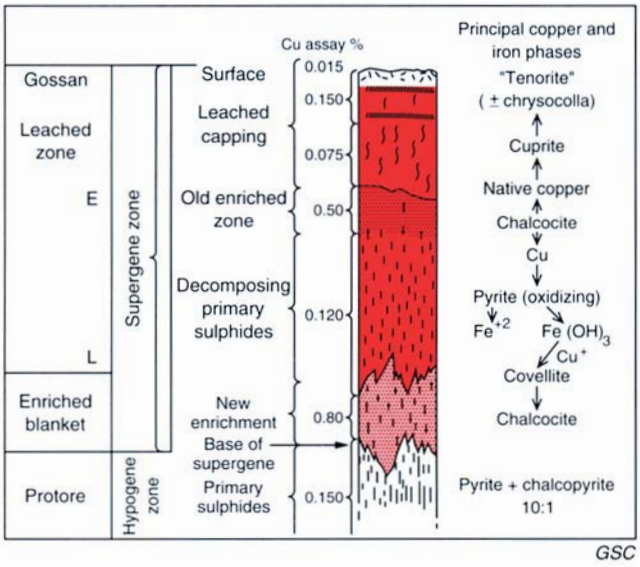

Figure 4.2-8. Profile of supergene zones developed over Plesyumi porphyry copper deposit, Papua New Guinea showing effects of multicycle weathering due to lowering of water table (modified from Guilbert and Park, 1986; after Titley, 1978).

supergene zone (e.g., Afton, South Kemess, Mt. Polley), whereas others show a more typical oxide-sulphate-carbonate and supergene sulphide zonation. Multicycle oxidation is a characteristic feature of most porphyry Cu-Mo provinces (Titley, 1982; Fig. 4.2-8). The formation of native Cu in these deposits is still not clearly understood. The deposits in which this metal predominates are generally characterized by low pyrite concentrations and high magnetite, carbonate, and biotite or hornblende contents. These minerals may have a controlling influence on the redox conditions under which chalcopyrite-chalcocite mineralization is oxidized and native Cu precipitated (Carr and Reed, 1976; Kwong et al., 1982). Afton, South Kemess, and Mt. Polley, which contain significant concentrations of native Cu, are hosted by alkaline suite intrusions and/or volcanic rocks, as opposed to the more dominant calc-alkaline intrusive hosts which are typified by oxide-carbonate-sulphate and chalcocite zones.

Molybdenum is relatively immobile during the oxidation of porphyry Cu-Mo deposits and therefore generally shows little or no enrichment. In the leached capping and oxide zones it may be partially converted to ferrimolybdite.

During the oxidation process, Au may be enriched in the leached capping of some deposits (e.g., Casino), but generally this metal is merely freed from its occluded habit in sulphides with little remobilization. Silver is generally leached from the upper zones and may occasionally be concentrated in the supergene sulphide zone.

Deposits that are rich in anhydrite-gypsum and carbonates may produce a gypsum layer below the chalcocite blanket that effectively seals the primary ore from further oxidation (e.g., Berg deposit).

GLACIATION

The perception in the early part of this century that glaciation in Canada destroyed preglacial weathered landscapes created serious doubts in the minds of explorationists that viable supergene ore deposits could be discovered in Canada. However, in the Canadian Cordillera the continual discovery of preserved, well developed supergene zones over porphyry Cu-Mo deposits demonstrates the often minimal effects glaciation has had. Today, most porphyry systems in the Canadian Cordillera, unless very large, would not be economic without rich supergene Cu and Au zones.

In the Appalachians, the discovery over the years of numerous economic gossan deposits in the massive sulphide camps of New Brunswick and Maine, and the important supergene enrichments over the Gaspésie Cu deposits (Fig. 4.2-1), indicate that glaciation has not been as destructive towards supergene ore deposits as earlier believed.

With respect to the Canadian Shield the above-mentioned perception still remains the norm for most explorationists, but compilation of existing data by the author indicates that important supergene mineral deposits (e.g., Au-Ag, base metals, iron, phosphate, rare-earth elements, kaolin, silica) have been discovered throughout the present century at an average rate of one every five years. No doubt more are to be discovered under thick glacial cover.

DEFINITIVE CHARACTERISTICS

The definitive characteristics for supergene precious metal and base metal deposits relate entirely to the recognition of the effects of secondary chemical weathering on primary metal-bearing zones. Thus these deposits are characterized by three main zonational features: 1) a leached capping composed of variable concentrations of Fe-Mn oxyhydroxides and sulphates (goethite, hematite, wad, jarosite), clays (kaolinite, chlorite, smectites), and occasionally Cu-silicates; this zone may contain important reserves of Au and Cu (rarely Ag and Mo), 2) an oxide zone which is characterized by a large array of Cu, Pb, Zn, Ag, and Sb oxides, sulphates, carbonates, phosphates, and halides, native Au, Ag, Cu, Bi, Zn, and S, as well as the same mineralogy for the capping zone; these zones constitute important reserves of Cu, Au, Ag, Zn, and Pb; and 3) a supergene sulphide zone typified largely by the formation, through precipitation or replacement of secondary Cu, Ni, and Ag sulphides (see Table 4.2-2). This zone often displays supergene enrichments of base metals and precious metals.

Transitional zones may occur between these three main zones. The host rocks surrounding these zones are in many cases strongly ferruginized and/or altered to clay-silica rock. At surface, the most definitive feature of these deposits is the presence of various types of gossanous-siliceous-argillized rocks.

GENETIC MODEL

The sizes, grades, mineralogical compositions, and preservation of supergene mineral deposits will be controlled to a large extent by the following physicochemical factors and

processes: 1) climatic history, 2) tectonic history, 3) geomorphological development, 4) position of the sulphide body in the hydrological regime, 5) size, geometry, and structure of the sulphide body, 6) primary sulphide composition of the ore body, 7) nature and distribution of acid-neutralizing gangue minerals, 8) primary permeability (porosity) and degree to which secondary permeability can be developed during oxidation, 9) strength and sustainability of electrochemical oxidation cells within the sulphide body, 10) diversity and strength of microbiological activity within the ore zone, and 11) diffusion rate of atmospheric O_2 into the sulphide body.

If there has not been a sufficient period of tectonic quiescence, or if the tectonic history after formation has been largely destructive, these deposits will either not form or not be preserved, regardless of whether all other factors mentioned above were optimal. For this reason a detailed understanding of recent tectonic history, largely early Cenozoic to present, is paramount to the recognition of supergene base metal and precious metal metallogenic provinces. In Canada these provinces are most apparent in the northern Appalachian regions of New Brunswick (Bathurst camp) and Quebec (Gaspé copper camp), in a large central region of the Canadian Shield stretching from the Labrador Trough to the Flin Flon base metal camp in Manitoba, and throughout the entire Intermontane region of the Yukon Territory-British Columbia Cordillera (see Fig. 4.2-1).

Climatic conditions will control the rate of oxidation and ultimate composition of secondary phases. Temperature controls the rate of chemical reaction, whereas precipitation controls the rate of leaching and depth of oxidation. Under humid conditions shallow oxidation prevails. Under semiarid conditions deep oxidation, leaching, and enrichment will occur, and under arid conditions deep oxidation may occur, but there will be little leaching and enrichment. It is therefore important to know the historical characteristics of climate during ore formation and the durations of each climatic period.

High primary sulphide contents will produce low pH capillary water conditions and thus greater mobility of some elements out of the oxidation zone. Some elements (e.g., Zn) will not be concentrated in sulphide-rich environments, whereas others (e.g., Cu, Ag) move freely downward to become concentrated under more reducing conditions in the supergene sulphide zone.

High silica and carbonate contents in primary ore, together with moderate to low pyrite contents, will lead to the formation of metal-oxide-silicate-carbonate-sulphate deposits.

It is not difficult to see from the diversity of factors mentioned above that a given mineralized province can produce supergene deposits with widely different tonnages, grades, and mineral assemblages.

RELATED DEPOSIT TYPES

Base metal and precious metal supergene deposits represent just two groups of a large variety of weathered regolith deposits which have been preserved from the effects of glaciation in various regions throughout Canada. The entire class of preglacial regolith deposits includes residually enriched iron ore deposits (see "Enriched iron-formation", subtype 4.1), residual enrichments over REE- and phosphate-bearing carbonatites (e.g., Cargill and Martinson, Ontario; Lac Shortt, Quebec; see subtype 4.3), kaolin deposits (e.g., Moose River basin, Ontario), silica sand deposits (e.g., Sussex, New Brunswick; north shore of St. Lawrence River, Quebec), gold and platinum placers remobilized from Cenozoic residual profiles (e.g., central Yukon Territory; Similkameen area, British Columbia; Lower St. Lawrence, Quebec), and various saprolitic and lateritic profiles located throughout all of the Canadian geological provinces. To date no lateritic Au, Ni, or Al deposits have been discovered beneath glacial cover or in unglaciated regions of the country, although evidence of lateritization does exist.

EXPLORATION GUIDES

Gossan, ironstone, and leached capping evaluation

The occurrence of gossan zones and gossanous/siliceous cappings at surface is not always indicative of underlying supergene or primary ore. Ironstone formations (false gossans) may occur in many different forms (fault, drainage, stratigraphic, leakage, chemically transported, and lateritic ironstones) and many intrusive bodies, especially those rich in magnetite and/or biotite can have associated leached cappings that are very similar to those overlying porphyry Cu-Mo-Au systems. For this reason a number of mineralogical (Emmons, 1917; Blanchard, 1939; Anderson, 1982), textural (Locke, 1926; Blanchard, 1939), colour (Blanchard, 1939; Anderson, 1982), and lithogeochemical (Clema and Stevens-Hoare, 1973; Bull and Mazzucchelli, 1975, Gulson and Mizon, 1979; Andrew, 1984) techniques have been proposed for differentiating fertile from barren gossans and leached cappings. Today, the most promising lithogeochemical exploration methods involve multi-element geochemical evaluations in concert with sound mineralogical and textural analyses. The creation of a database on known fertile and barren gossans and leached cappings is important. Lithogeochemical interpretations may be further complicated by the fact that chemically transported gossans may form from emergent groundwaters passing through primary ore extant from the gossan, and ferruginized wall rock gossans may be the only exposed portion of an economic supergene zone. Both are, in their own right, indicative of nearby mineralization and their identification requires a good geochemical database of known indicative and false occurrences.

Hydrogeochemistry

Because many indicator elements in gossans and leached cappings are strongly depleted and other elements are converted to stable secondary mineral forms, surficial hydrogeochemical methods are often ineffective in outlining this type of mineralization. For supergene deposits that are still undergoing development or alteration by a lowering water table, groundwater geochemical surveys may be effective in outlining hydrogeochemical haloes around deposits.

Pedogeochemistry

Although many supergene deposits have been well preserved in the Canadian landscape (Fig. 4.2-1), most have been at least partially affected by glacial scouring. Some deposits have been affected by glacial erosion to the point that only their supergene roots remain. The use of till geochemistry for the detection of this type of mineralization requires the application of different indicator element associations than might be traditionally expected from primary sulphide occurrences. For example, in the Bathurst massive sulphide camp, the gossans overlying mineralization have had more than 95% of their Cu and Zn leached out and Pb and As concentrations are greatly enhanced (Boyle, 1993). Analysis of tills dispersed from these zones would generally give strong anomalies for Pb and As, and occasionally Hg and Bi, but these anomalies would not be supported by coincident anomalies for Cu and Zn. Anomalies unsupported by Cu and Zn in overburden and stream sediments have traditionally been given low exploration priority. Further caution is required when using Au as a tracer of gossan or leached cappings, since this metal is generally present in grain sizes <10 μm and specialized concentration methods must therefore be used. If glaciation has scoured the metal oxide or supergene sulphide zones, special attention must be paid to the fact that the sulphide minerals are generally much finer grained (e.g., sooty chalcocite) or of different composition (e.g., native Cu, Cu-oxides, carbonates) than primary sulphides. This is especially important if the heavy mineral fraction of till is to be used as a sampling medium.

Biogeochemistry

Supergene base metal and precious metal deposits may in some climatic zones be characterized by certain base metal indicator plants, thus permitting the use of geobotanical surveys. Occasionally sulphide oxidation zones may also be outlined as biological 'kill zones' where the overlying soils are incapable of supporting the vegetation typical of that climate. In this respect remote sensing methods can be useful in detecting potential mineralization. Biogeochemical methods, where a specific genus of plant is analyzed for specific indicator elements, can be used in areas of residual and shallow glacial overburden.

Geophysics

Most oxidation zones developed over sulphide mineralization will display strong negative self potentials in the order of -100 to -500 mV (Blain and Brotherton, 1975) and surface self potential surveys are therefore not only useful in detecting supergene zones, but are also helpful in differentiating between fertile and barren (ironstone) gossan zones. The self potential method is not effective where the depth of oxidation is deep (>200 m). Because of differences in acoustic characteristics between oxidized and primary mineral zones, ground penetrating radar can be useful in mapping the thicknesses and topology of supergene zones.

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4.3 RESIDUAL CARBONATITE-ASSOCIATED DEPOSITS

D.G. Richardson and T.C. Birkett

INTRODUCTION

Weathering and erosion of carbonatites can produce both mechanical accumulations of inert minerals, such as apatite, and secondary, chemically-enriched deposits of relatively immobile elements such as niobium, titanium, yttrium, and rare-earth oxides (REOs). In some cases, vermiculite deposits have also formed during weathering of carbonatite.

IMPORTANCE

Weathered carbonatites are major sources of phosphates in Brazil (Araxá and Catalão) and Finland (Sokli). They dominate the world niobium supply (Araxá and Catalão 1) and contain enormous exploitable titanium reserves in the form of anatase in Brazilian carbonatites (e.g., Minas Gerais State – Salitre I and II, Serra Negra, Tapira; Goiás State – Catalão I; Pará State – Serra de Maicuru). In Canada, residual accumulations of apatite have been formed on carbonatites within Cargill Township and at Martison Lake, Ontario (Fig. 4.3-1) that are potential sources of phosphate. Although no tonnage or grade figures have been published, residuum developed on the carbonatites of the Tomtor alkaline-carbonatite complex, northern Russia (latitude 71°N and longitude 117°E), contains significant concentrations of rare-earth elements, including scandium and yttrium (predominantly monazite, REE-carbonates). According to Epstein et al. (1994), the residuum at Tomtor has potentially economic reserves comparable to those of Araxá (i.e., several hundred million tonnes), covers an area of 8 km by 6 km, ranges in thickness from 20 to 350 m, and has average grades of 3.9% $(REE)_2O_3$, 12% P_2O_5, and 0.74% Nb_2O_5.

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SIZE AND GRADE OF DEPOSITS

Significant production of phosphate (apatite, francolite $[Ca_5(PO_4,CO_3)_3(F,OH)]$), niobium (pyrochlore/bariopyrochlore), and titanium (anatase) is derived from very large

(>150 Mt of ore), high grade (>8% P_2O_5; >1.2 % Nb_2O_5; >15% TiO_2), enriched carbonatite-associated residual deposits in Brazil and elsewhere. Residual carbonatite-associated phosphate/niobium/titanium deposits range in size from 4 to 1000 Mt grading 7% to >30% P_2O_5; 0.4% to >2.5% Nb_2O_5; and 13% to >27% TiO_2. Published grades and tonnages of Canadian and world deposits are presented in Tables 4.3-1 and 4.3-2, respectively. The grade-tonnage relationships of these deposits are shown in Figure 4.3-2.

GEOLOGICAL FEATURES

Geological setting

Carbonatite deposits, and associated residual enriched deposits, are typically located in relatively stable, anorogenic settings, but some are found near plate margins and may be linked with orogenic activity or rifting. Carbonatites tend to form clusters or provinces (e.g., Brazil, East African rift system), and are commonly located either on

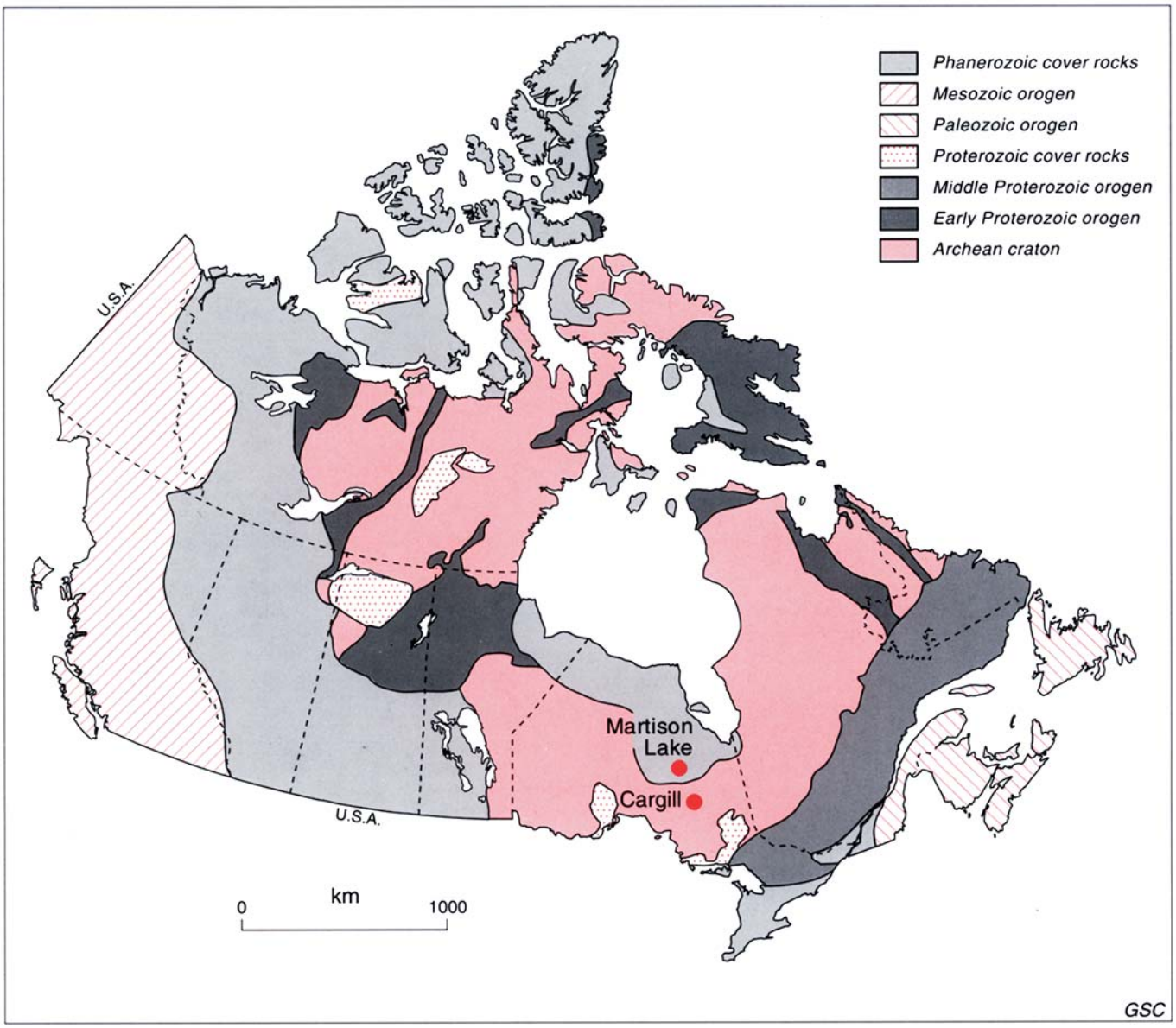

Figure 4.3-1. Location of Canadian residual carbonatite-associated phosphate-niobium deposits and occurrences.

Table 4.3-1. Production/reserves of selected Canadian residual carbonatite-associated deposits and occurrences.

DEPOSIT	PRODUCTION/RESERVES/GRADE	COMMENTS/REFERENCES
Cargill, Ontario Lat. - 49°19'N Long. - 82°49'W	South subcomplex carbonatite (to a depth of ~170 m) diamond drill indicated reserves: 62.5 Mt grading 19.5% P_2O_5. Crandallite-rich zone between residuum and periglacial sediments contains 1 Mt grading 0.015% U_3O_8, 0.07-0.4% Nb_2O_5, and 1.0-4.0% REO (Sage, 1988)	Undeveloped preglacial residual-type phosphate deposit developed over Precambrian (1906 ± 30 Ma) carbonatite-alkalic complex. Of the three subcomplexes present at Cargill, only the southern one has been drilled in detail; the north subcomplex has been explored in a superficial manner; and the small west subcomplex has not been drilled to date. Karstic weathering of the carbonatite in Cretaceous time produced an apatite-rich residuum that has variable thickness. In the preglacial troughs, thickness locally exceeds 170 m and thins to a few metres or disappears altogether on ridges. The Cargill carbonatite complex has undergone post-emplacement deformation and recrystallization as evident by the presence of cataclastic rock textures (Sandvik and Erdosh, 1977; Vos, 1981; Sage, 1988, 1991a; Erdosh, 1989).
Martison Lake, Ontario Lat. - 50°20'N Long. - 83°25'W	Carbonatite A (to a depth of ~150 m) proven + probable + possible diamond drill indicated reserves: 145 Mt grading 20.1% P_2O_5, 0.35% Nb_2O_5. Within a portion of the unconsolidated residuum, a zone of 57 Mt grading 0.4% REO has been delineated (Potapoff, 1989; Mariano, 1989b; Sage, 1991b).	Undeveloped preglacial residual-type phosphate-niobium deposit, covered by 30 to 90 m of glacial till. Economic mineralization is contained in both cemented and unconsolidated residuum. The residuum averages 11 m in thickness, but reaches 50 to 100 m in several locations. The cemented residuum appears to be composed of the same minerals and grain sizes as the unconsolidated residuum. (Woolley, 1987; Potapoff, 1989).

major lithospheric domes or along major lineaments (Woolley, 1989). The Cargill deposit appears to be associated with the Lepage fault, which is contained in the larger regional northeast-trending Kapuskasing magnetic-gravity high/tectonic zone (Percival and West, 1994).

Age of deposits

Because the development of residual enriched carbonatite deposits is dependent on the formation of residuum in response to prolonged periods of weathering of carbonatitic protore, the ages of these deposits are limited by the ages of the associated carbonatites. The Mt. Weld carbonatite in Australia has been dated at 2064 Ma (Middlemost, 1990), and the overlying residual deposit, which formed during the Mesozoic, represents a laterite that has developed over one of the oldest known carbonatites (Mariano, 1989a). The known carbonatites of the Amazon Basin, including Morro do Seis Lagos, in the State of Amazonas, and Serra de Maicuru, in the state of Pará, are thought to be Precambrian. In contrast, the carbonatites that rim the periphery of the Paraná basalt flow basin (i.e., Catalão I and II, Serra Negra, Salitre I and II, Araxá and Tapira) were emplaced during the Cretaceous (Eby and Mariano, 1992). Development of extensive residuum over Brazilian carbonatites began at the start of the Cenozoic, and, in the case of carbonatites in the Amazon Basin, is ongoing (CBMM, 1984). The Cargill and Martison Lake residual carbonatites are thought to have formed during Cretaceous time (Sage, 1988).

Form of deposit

The differential leaching of carbonatitic material, notably along joints, related fractures, and particularly faults, resulted in the development in many carbonatite complexes of a highly irregular, karstic topography characterized by pinnacles of unweathered carbonatite bedrock separating pits and depressions filled with residual weathered material. The faults not only determine the sites of deeper weathering, but also control the development of internal drainage and sinkholes. Therefore, depending on the nature of the topography on the underlying primary carbonatite, enriched carbonatite-associated deposits commonly have blanket-like to highly irregular forms that overlie carbonatite protore, and phosphate-rich residuum produced in this manner usually contains both primary apatite derived from the carbonatite and supergene crandallite-group minerals (Notholt, 1980). The well-developed, high relief, buried preglacial topography of the Cargill deposit is a good example of the development of a karstic system. The south subcomplex is dominated by the development of three subparallel northeast-trending troughs in the carbonatite (Fig. 4.3-3A, B). Two major troughs, both filled with residuum greater than 170 m thick, wrap around the outer edge of the carbonatite and converge in a large buried topographic low of undetermined depth, which has been interpreted by Sandvik and Erdosh (1977, 1984) and Erdosh (1989) to be a large 'master sinkhole' solution collapse structure. It is through this structure that leached carbonate solution products were removed, leaving behind the highest concentration of apatite-rich residuum. The troughs are commonly steep-sided, and at several locations, depth exceeds width. The Martison Lake residual carbonatite deposits (Fig. 4.3-4, 4.3-5) lack such karstic features, and instead consist of nearly horizontal layers that range from 1 to 55 m thick and have flat tops and irregular keels.

Mineralogy and ore zonation

The mineralogy of residual carbonatite-associated deposits is highly variable. Chemical weathering of carbonatites and the dissolution of Ca and Mg contained in carbonate

minerals (calcite, dolomite, and siderite) results in concentration of resistant primary minerals (e.g., apatite, magnetite, pyrochlore, ilmentite, rutile, zircon, and quartz), as well as formation of supergene phosphates, carbonates, and sulphates containing less mobile elements released during carbonate dissolution. Potentially economic supergene mineralization associated with enriched residual carbonatites includes the following:

1) In situ lateritic decalcification of perovskite ($CaTiO_3$) in pyroxenites of the carbonatite complexes of Goiás, Minas Gerais, and Pará states of Brazil produces polycrystalline aggregates of micrometre-size anatase (TiO_2) platelets (Mariano, 1989a; Kurtanjek and Tandy, 1989; Mariano and Mitchell, 1990).
2) The most common supergene REE mineral formed is monazite [$(REE)PO_4$]. Other REE minerals commonly found in carbonatite laterites include bastnaesite [$(Ce,La)(CO_3)F$], parisite [$(Ce,La)_2Ca(CO_3)_3F$], synchysite [$(Ce,La)Ca(CO_3)_2F$], cerianite [$(Ce^{+4},Th)O_2$], and the crandallite-group minerals florencite [$(REE)Al_3(PO_4)_2(OH)_6$], gorceixite [$(Ba,REE)Al_3(PO_4)_2(OH_5{\cdot}H_2O)$], and goyazite [$(Sr,REE)Al_3(PO_4)_2(OH)_5{\cdot}H_2O)$]. Rhabdophane [$(REE)PO_4{\cdot}H_2O$] is less common. Light REE-bearing supergene minerals generally predominate over heavy REE minerals. At Mt. Weld, supergene light REE-bearing monazite and rhabdophane are contained in the upper part of the residuum, whereas heavy REEs and Y are selectively concentrated at depth as xenotime [YPO_4] and churchite [$YPO_4{\cdot}2H_2O$].

Vertical mineralogical zonation displayed by carbonatites that have undergone extreme lateritic weathering has been summarized by Mariano (1989a, b). In the upper parts, lateritic residuum consists primarily of insoluble ferric iron oxides, aluminum oxides, clays, supergene monazite, crandallite-group minerals rich in Ba, Nb, light REEs and Sr, and cerianite. In this zone all primary minerals have disappeared with the exception of zircon and

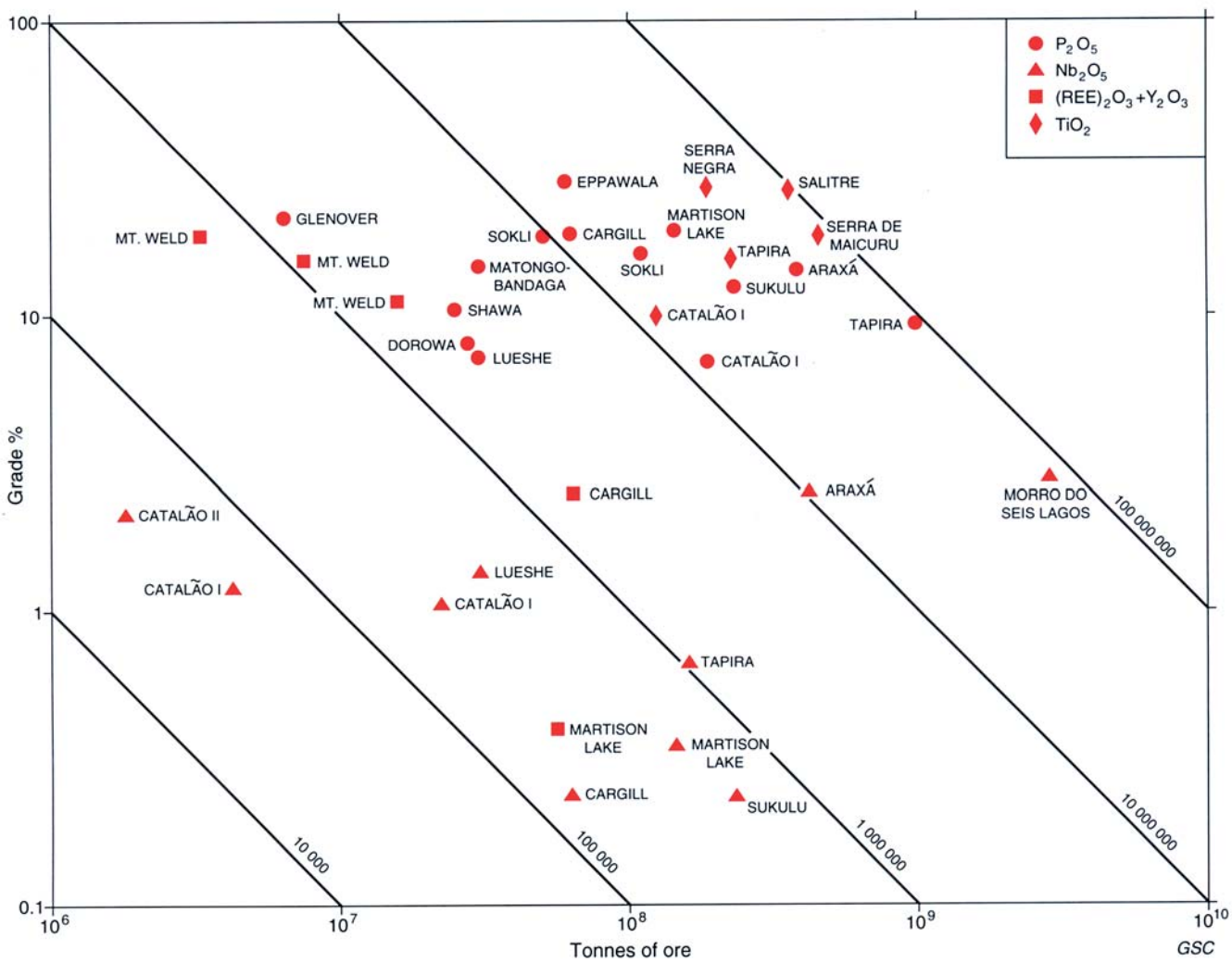

Figure 4.3-2. Grade-tonnage relationships for residual carbonatite-associated deposits and occurrences. P_2O_5, Nb_2O_5, $(REE)_2O_3 + Y_2O_3$, and TiO_2 are expressed in weight per cent. The diagonal lines indicate the quantity, in tonnes, of the contained commodity in the deposits.

Table 4.3-2. Production/reserves of selected foreign residual carbonatite-associated deposits and occurences.

DEPOSIT	PRODUCTION/RESERVES/GRADE	COMMENTS/REFERENCES
Mt. Weld, Western Australia	Indicated reserves: 15.4 Mt; 11.2% (REO + Y_2O_3), or 7.43 Mt; 15.7% (REO +Y_2O_3), or 3.47 Mt; 19.6% (REO + Y_2O_3)	Proterozoic (2021 ± 13 Ma) circular carbonatite structure having a diameter of about 4 km. A residuum rich in primary igneous apatite overlies the carbonatite and in turn is overlain by a supergene zone that contains abundant secondary phosphates and aluminophosphates with elevated concentrations of REEs, U, Th, Nb, Ta, Zr, Ti, Ba, Sr, and Fe. Supergene monazite is the principal REE hostmineral;lesser quantities are in apatite, crandallite group minerals, cerianite, churchite [$YPO_4 \cdot 2H_2O$] and rhabdophane [$(Nd,Ce,La)PO_4 \cdot H_2O$] (Duncan and Willett, 1989; Mariano, 1989a; Lottermoser, 1990).
Sokli, Finland	Proven reserves: 50 Mt; 19% P_2O_5 Indicated reserves: 110 Mt; 16.5% P_2O_5	The circular Sokli residual carbonatite has an aerial extent of 18 km^2 and is part of the Kola Peninsula igneous alkaline province. Carbonatite-apatite-francolite regolith forms the phosphate deposit at Sokli. The thickness of the regolith averages 25 m but locally attains a maximum thickness of 72 m. Residual primary minerals derived from carbonatite include apatite, magnetite, amphiboles, micas, dolomite, ilmenite, pyrochlore, zircon, baddeleyite, and rutile; secondary minerals of supergene origin include francolite, goethite, siderite, Mn-oxides, hematite, and rhabdophane (Notholt, 1979; Vartiainen, 1989; Harben and Bates, 1990b).
Eppawala, Anuradhapura, Sri Lanka	Proven & inferred reserves (Block A to F): 60 Mt; 20-38% P_2O_5, 0.24% Nb_2O_5	Residuum/lateritic soil developed to a depth of 75 m over a Proterozoic (?) apatite-magnetite-bearing carbonatite. Phosphate deposit is composed of chlor-apatite, francolite, martite, and goethite. Six deposits (Block A to F) have been delineated by drilling (Notholt, 1980; Jayawardena, 1989).
African deposits		
Sukulu, Uganda	Reserves in North, South, and West valleys: 230.7 Mt; 12.8% P_2O_5, 0.24% Nb_2O_5	Apatite-rich residuum, ranging in thickness from 15 m to a maximum of 67 m, developed on a circular carbonatite body having a diameter of approximately 4 km. The apatite-rich soil consists of 20-25% apatite, 20-25% crandallite, 15-20% quartz, 20% magnetite, and 10% hematite (Kabagambe-Kaliisa, 1989).
Glenover, western Transvaal, Republic of South Africa	Drill indicated reserves: 6.3 Mt; 21.8% P_2O_5	Ferruginous carbonate apatite residuum formed by karstic weathering of carbonatite. Economic deposit is restricted to a central pear-shaped high grade zone (maximum of 32% P_2O_5 and 10% Fe_2O_3) (Deans, 1978).
Dorowa and Shawa, Zimbabwe	Indicated reserves - Dorowa south orebody to a depth of 120 m: 27 Mt; 8% P_2O_5 Indicated reserves at Shawa to a depth of 23 m: 25 Mt; 10.8% P_2O_5	Residuum developed over late Paleozoic to Mesozoic decalcified Dorowa and Shawa ijolite-syenite-carbonatite pipe-like bodies that have intruded Archean granite gneiss (Deans, 1978; Fernandes, 1989).
Lueshe, Zaire	Estimated reserves: 30 Mt; 1.34% Nb_2O_5, 4.2-10% P_2O_5	Mantle of niobium-rich ferruginous residuum developed over an elliptical (3.0 km x 1.9 km) plug of pyrochlore-aegirine-carbonatite. Moderate degree of weathering has resulted in pyrochlore becoming friable (Gittins, 1966; Mariano, 1989b).
Matongo-Bandaga, Burundi	Drill indicated reserves: 30 Mt; 11% P_2O_5 (high grade zone = 13.2 Mt; 13% P_2O_5)	Phosphate deposits lie in subhorizontal lateritic masses directly overlying fresh carbonatite. Thicknesses of individual apatite-rich bands are highly variable, and the maximum thickness observed to date is 55 m. Troughs formed in the irregular subcrop of the carbonatite are the sites of deepest weathering and are marked by thickening of phosphate-rich zones. Karstic weathering is evident and residuum minerals are apatite, niobian rutile, ilmenite, quartz, K-feldspar, and goethite. Fluorapatite, cacoxenite [$Fe_4(PO_4)_3(OH)_3 \cdot 12H_2O$], goyazite [$SrAl_3(PO_4)_2(OH)_5 \cdot H_2O$] and crandallite/pseudo-wavellite [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$] may also be present in the phosphate-rich zones (Kurtanjek and Tandy, 1989; Mariano, pers. comm., 1994).

Table 4.3-2. (cont.)

DEPOSIT	PRODUCTION/RESERVES/GRADE	COMMENTS/REFERENCES
Brazilian deposits		
Barreiro, Araxá, Minas Gerais	Proven and indicated reserves: 375 Mt; 14.5% P_2O_5 418 Mt; 2.5% Nb_2O_5 495 000 t; 10-11% REO	Deposit is in Late Cretaceous circular, 16 km^2, carbonatite (minor pyroxenite and glimmerite). Main carbonatite complex is capped by 150 to 230 m thick, deeply weathered residuum. Three distinct zones of the residuum have been delineated: 1) niobium as bariopyrochlore [$(Ba,Sr)_2(Nb,Ti)_2(O,OH)_7$] in a 1 km^2 area, in the centre of the complex with associated REEs; 2) secondary carbonate apatite in the northwest and southeast part of the complex; and 3) REEs contained in earthy monazite and goyazite in the northeast quadrant of the complex (800 000 tonnes grading 13% REO). Only niobium and phosphate are presently being mined (Woolley, 1987; Mariano, 1989b; Gomes et al., 1990)
Catalão I & II, Goias	Proven + inferred reserves, Catalão I: 188 Mt; 7.04% P_2O_5 4.2 Mt; 1.20% Nb_2O_5 22 Mt; 1.07% Nb_2O_5 125 Mt; 10% TiO_2	Catalão I is hosted in an approximately 27 km^2 circular stock of pyroxenite-serpentinized peridotite-glimmerite-carbonatite. The lateritic residuum developed on the central core carbonatite has an average thickness of 30 m. The residuum contains supergene monazite, rhapdophane, florencite, and gorceixite/goyazite. Anatase, derived from the weathering of perovskite, overlies the phosphate-rich ore (CBMM, 1984; Woolley, 1987; Mariano, 1989a, b; Gomes et al., 1990).
	Estimated reserves, Catalão II: 1.8 Mt; 2.19% Nb_2O_5	Catalão II, located 15 km north of the Catalão I deposit, is hosted in a 14 km^2 circular calcitic carbonatite-phoscorite-pyroxenite intrusive dome. Bariopyrochlore is contained in lateritic soil that is 3 to 10 m thick (CBMM, 1984; Woolley, 1987; Gomes et al., 1990).
Tapira, Minas Gerais	976 Mt; 8.11% P_2O_5 162 Mt; 0.67% Nb_2O_5 229 Mt; 15.98% TiO_2	Late Cretaceous, oval-shaped, 35 km^2 intrusion of different generations of carbonatite emplaced in Precambrian quartzites. The complex is deeply weathered and the average thickness of the residuum is 30 m, but locally attains 250 m. The residual deposit consists of 1) apatite ores; 2) titanium (anatase) ore, which overlies the phosphate ores; and 3) niobium (bariopyrochlore and pyrochlore) mineralization (CBMM, 1984; Woolley, 1987; Harben and Bates, 1990c; Gomes et al., 1990).
Patrocinio area (Bananeira deposit), Minas Gerais	Salitre: 353 Mt; 27.50% TiO_2	The Bananeira deposit is actually composed of the Salitre and Serra Negra deposits. The 500 m^2 Salitre Late Cretaceous carbonatite plug is associated with a larger 35 km^2 syenite-nepheline syenite intrusive complex. The residuum is generally 37 m to 60 m thick, but locally exceeds 100 m. Residuum contains anatase, francolite, perovskite, and magnetite with high values of U, Th, and REEs (CBMM, 1984; Woolley, 1987; Gomes et al., 1990).
	Serra Negra: 181 Mt; 27.68% TiO_2	Circular carbonatite-pyroxenite stock, having a diameter of 9 km, contained in 65 km^2 oval complex of nepheline syenites and major peripheral bebedourite pyroxenites containing significant perovskite and magnetite. The residuum overlying the carbonatite averages 150 m in thickness and contains a significant concentration of anatase (Woolley, 1987; Gomes et al., 1990).
Morro do Seis Lagos, Amazonas	Indicated resources: 2800 Mt; 2.81% Nb_2O_5	Reported to be the world's largest niobium deposit; consists of three north-south aligned circular structures with approximate diameters of 5.5, 0.75, and 0.5 km. Laterite covered hills developed over ferrocarbonatite, carbonatite breccias, and syenite which intrude Precambrian gneisses and migmatites. Laterites have an average thickness of 230 m, are radioactive and consist of siderite, ankerite, dolomite, barite, goethite, pyrite, and niobium rutile (Woolley, 1987; Verwoerd, 1989; Gomes et al., 1990).
Serra de Maicuru, Pará	Potential reserves: 450 Mt; 19% TiO_2	Deeply weathered laterite developed over circular topographic high consisting of pyroxenites, alkali syenites, and carbonatites that are intrusive into rocks of the Guyana Shield. Economic mineralization consists primarily of anatase derived from decalcification of perovskite (Woolley, 1987; Mariano, 1989b; Gomes et al.,1990).

rutile. Vadose water or low-temperature hydrothermal solutions can introduce quartz and supergene apatite (francolite) into the laterite. As lateritic weathering diminishes with depth, magnetite is encountered, followed by partly decomposed pyrochlore rimmed by crandallite-type minerals rich in Nb. At deeper levels, fresh pyrochlore is present, and primary apatite is prominent. With increasing depth, partly decomposed calcite/dolomite or siderite is encountered, below which is fresh unweathered carbonatite.

The mineralogy of the residuum of the Cargill south subcomplex has been described by Sandvik and Erdosh (1977, 1984), Vos (1981), and Erdosh (1989). The unconsolidated sand-sized residuum consists of primary white or colourless apatite, with minor goethite, siderite, magnetite, and crandallite [$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$]. Calcite and dolomite are absent. In many places, the apatite residuum is diluted by other weathering products, such as clay, vermiculite, iron oxide, quartz, and chlorite. A thin supergene REE-bearing crandallite-rich blanket, which has not been investigated in detail, is present in many places at the top of the apatite residuum. Secondary pyrite occurs locally near the top of the residuum (Vos, 1981; Sandvik and Erdosh, 1984).

At Martison Lake, the cemented residuum constitutes about 10% of the total mass of residuum, except in those areas where the thickness exceeds 20 m, where it comprises 25% of the total residuum (Fig. 4.3-5). The cemented residuum appears to be composed of the same minerals and grain sizes (i.e., predominantly silt size – 0.002-0.06 mm; with subordinate amounts of clay size – <0.002 mm, and sand size – 0.06-1.1 mm) as the unconsolidated residuum, but contains greater amounts of secondary phosphate minerals and lesser amounts of lanthanide (light REEs), clay, and iron minerals (Potapoff, 1989). The main primary minerals of the residuum are apatite, magnetite, phlogopite, biotite, and pyrochlore; the dominant secondary minerals are francolite, florencite [$(La,Ce)Al_3(PO_4)_2(OH)_6$], goethite, limonite, hematite, and clay minerals. Primary and secondary accessory minerals, which occur in minor quantities and only in restricted areas of the residuum, include: columbite, chlorite, alkali feldspar, perovskite [$CaTiO_3$], zirkelite [$(Ca,Th,Ce)Zr(Ti,Nb)_2O_7$], monazite [$(La,Ce,Nd)PO_4$], bastnaesite [$(La,Ce)(CO_3)F$], siderite, crandallite,

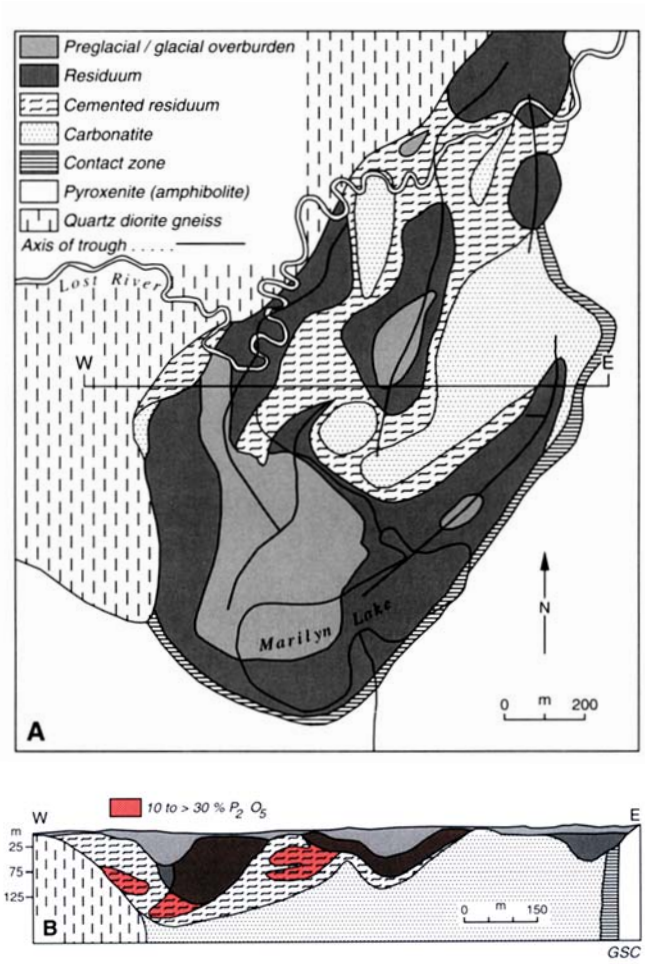

Figure 4.3-3. A) Geology of the South Cargill Subcomplex - 50 m level (after Erdosh, 1989), **B)** Typical west-east section across the central part of the South Subcomplex; areas in red denote zones of high grade (10% to >30%) P_2O_5 mineralization (after Sandvik and Erdosh, 1977).

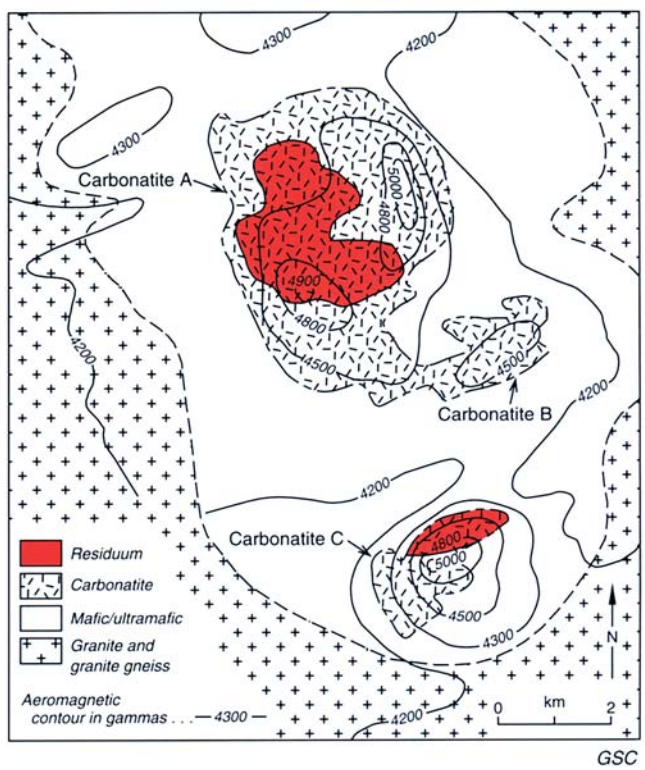

Figure 4.3-4. Aeromagnetic expression of the Martison Lake area, showing location of carbonatite bodies (after Potapoff, 1989).

woodhousite [$CaAl_3(PO_4)(SO_4)(OH)_6$], waylandite [$(Bi,Ca)Al_3(PO_4,SiO_4)_2(OH)_6$], barite, pyrite, ilmentite, rutile, cerianite [$(Ce^{+4},Th)O_2$], zircon, quartz, and sphene (Potapoff, 1989; Sage, 1991b). As shown in Figures 4.3-5B and C, the cemented, and to a lesser extent, the unconsolidated residuum contain the most significant mineralized zones (P_2O_5>30%; Nb_2O_5>2%). Potapoff (1989) noted that anomalous (>0.12% rare-earth oxides) lanthanide concentrations only occur in unconsolidated residuum that is also enriched in niobium (>0.5% Nb_2O_5). This correlation is likely attributed to the substitution of REEs in residual apatite and pyrochlore, rather than the presence of independent REE-bearing minerals in the residuum.

DEFINITIVE CHARACTERISTICS

Residual enriched carbonatite deposits form irregular to blanket-like layers draped over eroded weathered carbonatitic intrusions (Dawson and Currie, 1984). Although the geometry and mineralogy of these deposits can be highly variable, these deposits all formed by supergene processes and/or the residual concentration of primary materials during prolonged periods of weathering. Weathering develops residuum that can contain concentrations of economically important elements (P, Nb, Ti, REEs) that are as much as ten times greater than those found in the underlying unweathered carbonatite (Sage, 1991a).

GENETIC MODEL

Carbonatites weather relatively easily under a variety of climatic conditions and in some cases contain mineral deposits formed by surficial processes. The climate during weathering determines which rock is most resistant to chemical erosion, and consequently which particular types of deposits are developed. According to Mariano (1989b), the best conditions for the development of abundant supergene REE mineralization in carbonatites exist in humid tropical climates with moderate to high rainfall conditions (e.g., Amazon basin of Brazil), and in complexes in which a karst system is absent and interior drainage and a basin-type topography allows for the entrapment of both eluvial and supergene residuum from decalcified carbonatites. Sandvik and Erdosh (1977) and Erdosh (1979) noted that in dry, hot climates (e.g., South Africa and east Africa) carbonatites in general tend to form topographic highs; under more temperate cool, moist climates (e.g., Cargill and Martison Lake), a greater degree of leaching results in the development of karstic features. The development of topographic lows associated with karstic terrane enhances the potential for larger eluvial accumulations of primary apatite and/or pyrochlore, but not for the development of extensive accumulations of secondary REE minerals. This is because karst weathering effectively removes and flushes the elements dissolved from carbonates and apatite (i.e., REEs, Ca, Mg, Sr, and Ba) out of the carbonatite. As noted by Mariano (1989b), in carbonatites in which karstic weathering has occurred to an advanced level (e.g., Matongo-Bandaga, Burundi, and Cargill, Canada), the accumulation of significant concentrations of secondary REE minerals is negligible.

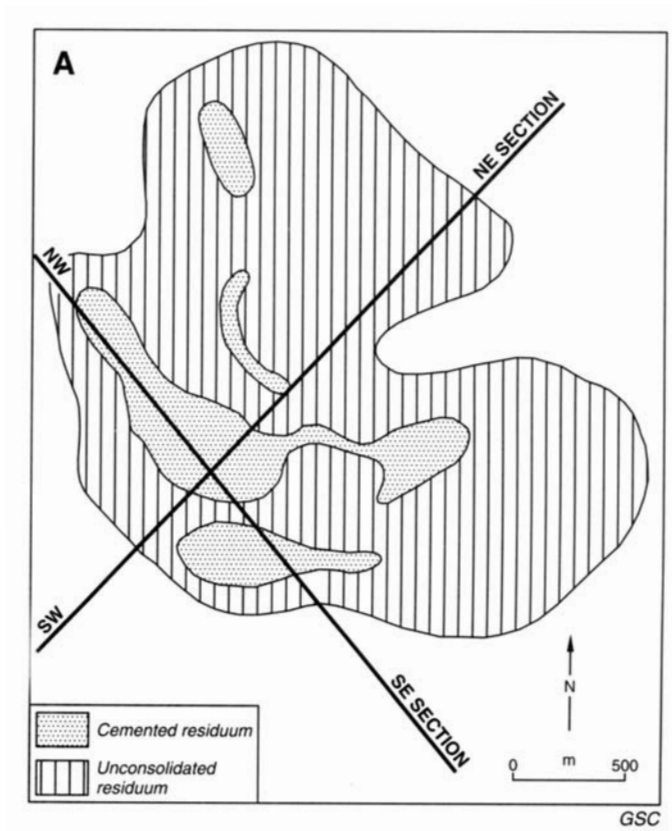

Figure 4.3-5A. Geology of the Martison Lake 'A' carbonatite, showing location of unconsolidated and cemented residuum and traces of NW-SE and SW-NE sections (after Potapoff, 1989),

The preservation of resistant phases is probably linked to a number of factors which, according to Mariano (1989b), include:

1. the concentration of H_2CO_3 in meteoric waters;
2. the development of H_2SO_4 from accessory sulphides; and
3. the development of internal drainage systems within carbonatites in response to carbonatite lithology.

Alternatively, supergene phosphate, carbonate, and sulphate minerals can form subsequent to the release of less mobile elements during chemical dissolution of calcite, dolomite, and siderite (e.g., REE mineralization at Mt. Weld, and crandallite-rich portions of the Cargill deposit of Ontario). Mariano (1989a, b) and Möller (1989a) have suggested that REEs derived from the decalcification of primary carbonates, apatites, and perovskite in the presence of oxygen, PO_4^{3-}, and F^-, commonly form residual supergene REE minerals that remain stable under conditions of lateritic weathering.

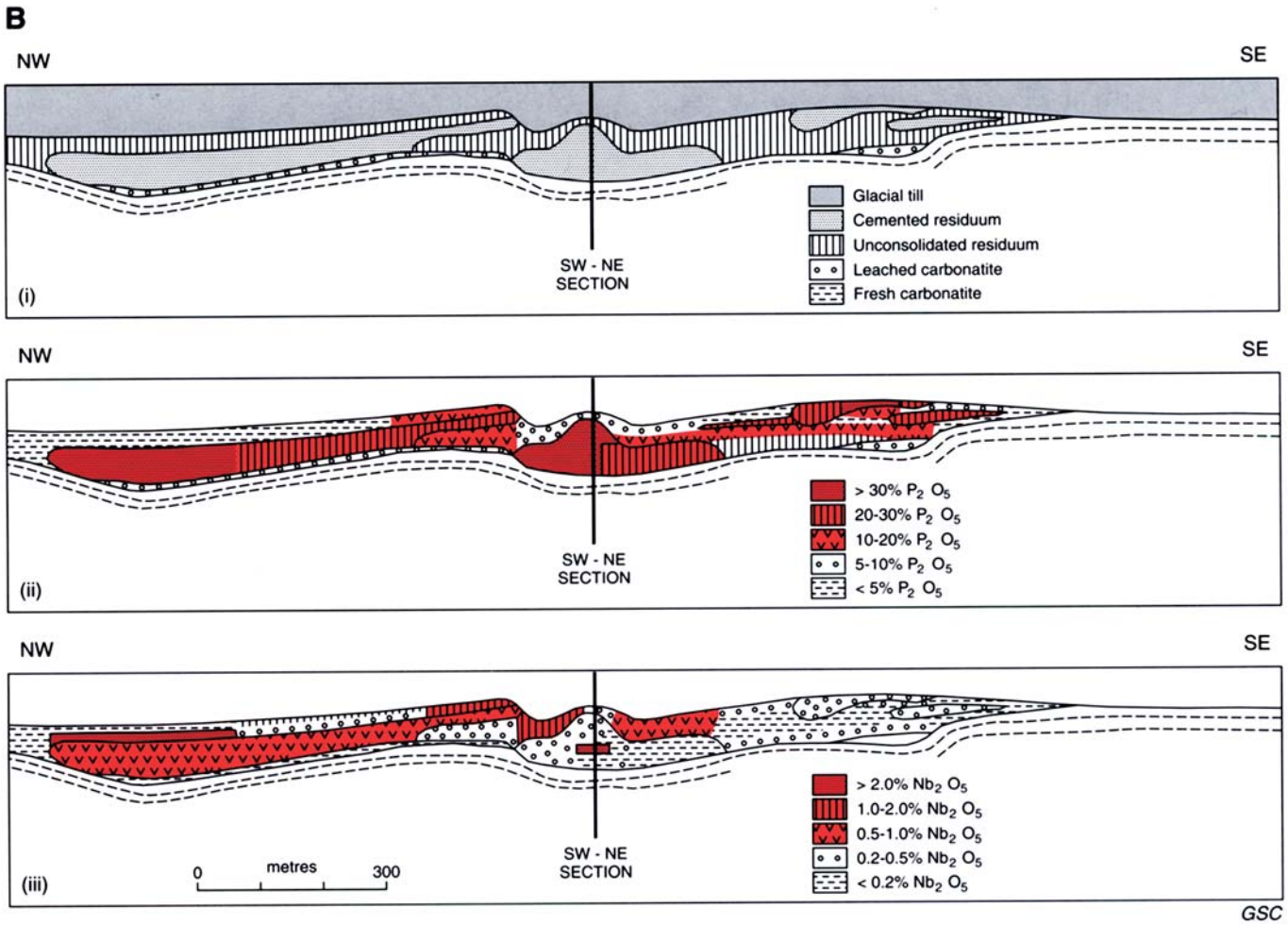

Figure 4.3-5B. NW-SE section of the Martison Lake A carbonatite including: i) geology, ii) P_2O_5 grade, and iii) Nb_2O_5 grade (after Potapoff, 1989). Areas in red denote potential ore zones,

RELATED DEPOSIT TYPES

Deep chemical weathering of other types of mineral deposits and lithologies can result in the formation of enriched residual deposits of other types. Significant examples include:

1. Oxidized and chemically enriched zones of porous, friable iron-formation and earthy hydrated iron oxide developed on Lake Superior-type and Algoma-type iron-formation protore (see subtype 4.1 – "Enriched iron-formation").
2. Physico-chemical oxidation processes which led to the formation of supergene precious and base metal zones that overlie massive sulphide deposits; the upper portion of sulphide vein, shear/fault related, and replacement deposits; and porphyry Cu-Mo-Au-Ag deposits (see subtype 4.2 - "Supergene base metals and precious metals").
3. Lateritic or silicate aluminum bauxites associated with, and derived from, the weathering of rocks rich in aluminum silicates (e.g., nepheline syenites, kaolinitic sandstones and arkoses and clays) (Harben and Bates, 1990a).
4. Lateritic nickeliferous ores (garnierite [$(Ni,Mg)_3Si_2O_5(OH)_4$]) that have resulted from the weathering of ultramafic rocks, peridotites, and serpentinites in tropical to subtropical climates (e.g., New Caledonia, Indonesia). In São Paulo state, Brazil, which contains numerous residual carbonatite-associated deposits, part of the residuum overlying the peridotites-pyroxenites of the Jacupiranga alkaline-carbonatite complex contains in excess of 2.7 Mt of garnierite-rich ore with an average grade of 1.39% Ni (Woolley, 1987; Gomes et al., 1990).
5. Residual manganese oxide (pyrolusite) deposits that usually overlie manganiferous carbonaceous black shale or manganese-bearing carbonate rocks (e.g., Moanda mine, Gabon; Nsuta mine, Ghana; Serra do Navio deposit, Brazil) (DeYoung et al., 1984; Machamer, 1987).

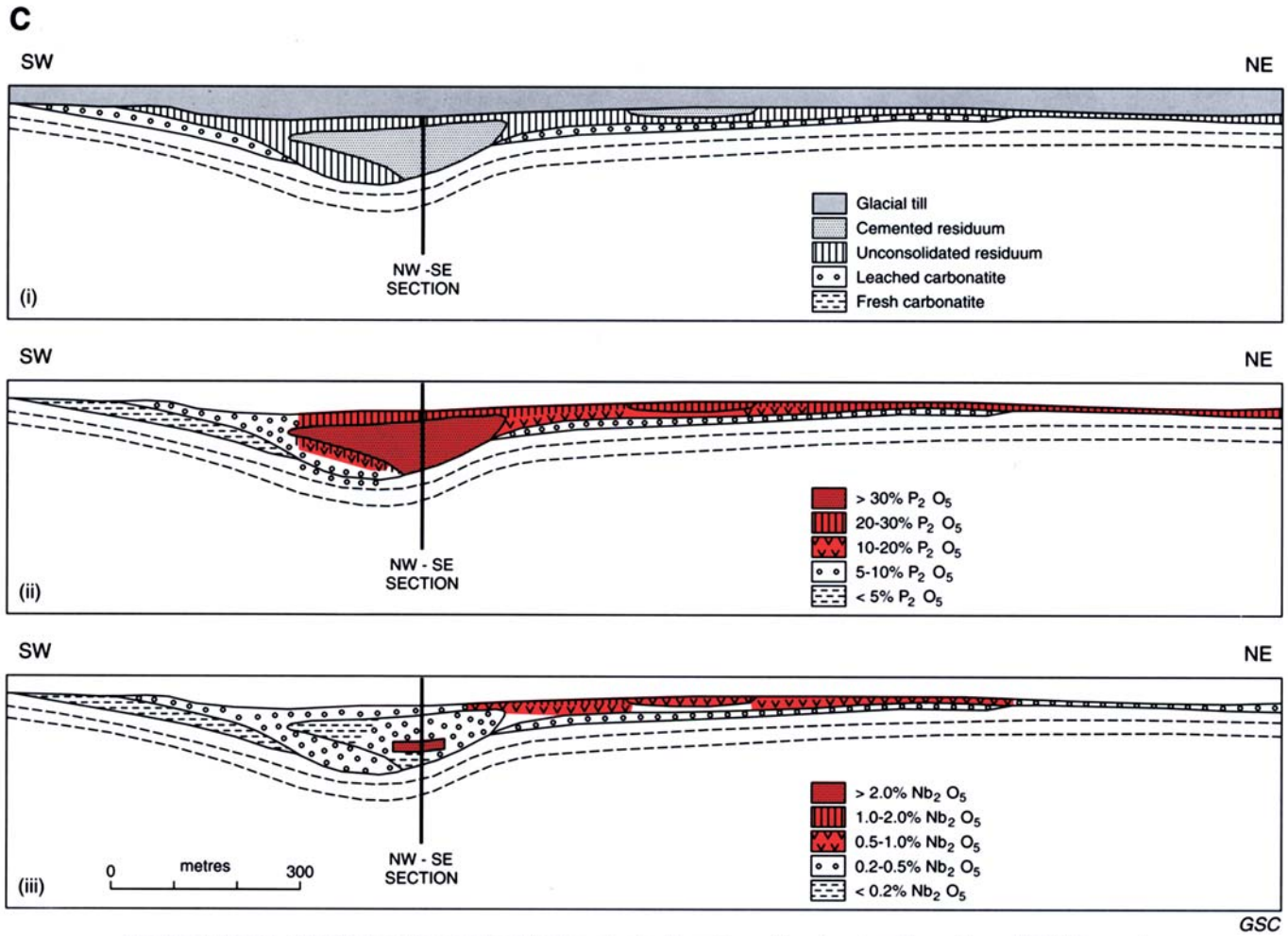

Figure 4.3-5C. SW-NE section of the Martison Lake A carbonatite showing: i) geology, ii) P_2O_5 grade, and iii) Nb_2O_5 grade (after Potapoff, 1989). Areas in red denote potential ore zones.

6. Vermiculite deposits produced by the supergene alteration of mafic/ultramafic minerals (biotite, phlogopite, diopside, hornblende, serpentine) by the combined effects of weathering and circulating meteoric water.

EXPLORATION GUIDES

Exploration guidelines for residual enriched carbonatite deposits include the following:

1. Broad scale features: when the carbonatites are exposed, topography is usually the best exploration guide. Because the protoliths of these deposits usually consist of nepheline syenite-carbonatite bodies that form rounded plugs and curved bodies centrally located within relatively small (generally <50 km^2), steep-sided alkaline complexes, recognition of discrete annular features can be particularly useful in identifying sites that may contain mineralized carbonatites (Notholt, 1980). Potentially economic minerals can be found in thin surface crustifications in cool temperate climates and to depths exceeding 300 m in tropical regions (Mariano, 1989b). Usually, fresh rock in outcrop is absent or extremely rare. In the Brazilian residual deposits, concentric/radial faults and fractures have resulted in the development of distinctive ring-like, and radial drainage which can control the distribution of the deposits (Gomes et al., 1990).
2. Geochemical approaches: stream sediment and soil sampling, and panning of heavy mineral concentrates (anatase, pyrochlore, monazite) from the residuum developed over certain ultramafic-carbonatite complexes in Brazil has been successful in delineating zones of both primary and secondary mineralization (Costa et al., 1991). However, in areas where the background levels of crucial indicative trace elements (REEs, Nb, Ti, P, etc.) are high (i.e., small carbonatite(s) that have intruded areally extensive alkaline plutons), geochemical sampling may be inadequate to localize potential mineralized zones (Möller, 1989b). According to Mariano (pers. comm., 1994) in Minas Gerais and Goiás

states, Brazil, once a carbonatite has been discovered, the standard exploration procedure includes detailed soil sampling and analysis for Nb_2O_5, REOs, PO_4, and TiO_2.

3. Geophysical approaches: most residual enriched carbonatite deposits, including Cargill and Martison Lake, are characterized by pronounced, closed, positive magnetic anomalies and coincident elevated radiometric responses (Fig. 4.3-4) (Notholt, 1979; Sage, 1979; CBMM, 1984; Mariano, 1989a; Potapoff, 1989). However, because strongly alkali conditions typically associated with late-stage carbonatites and fenite aureoles can, in many cases, stabilize iron in the ferric state and prevent the development of magnetite, deposits may also have a negative magnetic response. Depending on U and Th contents in the residuum, airborne gamma ray spectrometry results can be as much as 10 to 20 times regional background. Large amounts of magnetite (martite) are typically found in residual enriched carbonatites and result in well-defined circular aeromagnetic anomalies. If the host rocks contrast sufficiently in density from surrounding phases of the complexes, a marked gravity response in conjunction with a positive magnetic anomaly may reflect the presence of residual-carbonatite deposits in alkaline-carbonatite complexes (Erdosh, 1979).
4. Specific geochemical and geophysical exploration approaches are required for each carbonatite. The techniques applied should be appropriate to the characterisitics displayed by the deposit (i.e., petrology, mineralogy, and geochemistry of both protolith and laterite).

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