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***GENESIS OF POLYMETALLIC MINERALIZATION AND THE METALLOGENY OF
THE PALEOPROTEROZOIC COBALT EMBAYMENT, NORTHERN ONTARIO***

By

Eric Gordon Potter

*A thesis submitted in partial fulfillment of
the requirements for the degree of
Doctorate of Philosophy in Earth Sciences*

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Genesis of Polymetallic Mineralization and the Metallogeny of the Paleoproterozoic Cobalt Embayment, Northern Ontario

The recent discoveries of gold-rich and uranium-bearing, polymetallic mineralization in a geological setting akin to that of the historical Cobalt Ag-Co veins has: (i) clearly demonstrated the potential of the Cobalt Embayment to host hydrothermal mineral deposits enriched in economic metals other than silver; and (ii) prompted a re-evaluation of the metallogeny of this important Paleoproterozoic basin, which covers an area of 60,000 km² in northern Ontario. This re-evaluation has integrated field mapping, ore mineralogy, petrography, and stable and radiogenic isotope studies in order to assess the petrogenetic similarities of the regionally distributed hydrothermal mineralization whose main characteristics are its:

- 1) Occurrence in steeply-dipping, discordant calcite-quartz vein systems;
- 2) Location in Early Proterozoic host rocks, most importantly the Nipissing Diabase and the upper Huronian sedimentary rocks;
- 3) Spatial association with periodically reactivated, regional fault systems; and
- 4) Polymetallic (Cu, Co, Ni, Fe, As, Au, Ag, ±U) ore assemblage.

Radiogenic and stable isotope results confirm the occurrence of at least two basin-wide mineralizing events that occurred in the Early Proterozoic (*ca.* 2220 and *ca.* 1700 Ma). In addition, the integrated field and geochemical data suggest a petrogenetic model for vein mineralization in which oxidized basin fluids reacted with localized reductants along major regional fault systems that were reactivated both during and post-intrusion of the Nipissing Diabase. Such features are suggestive of a hydrothermal system in which the polymetallic veins may represent a peripheral element of a previously unrecognized unconformity-associated mineralization at depth. This model represents the development of a new mineral exploration model for the Proterozoic rocks of the Cobalt Embayment.

Keywords: Cobalt Embayment, gold, uranium, polymetallic, ore deposits, unconformity-associated, Proterozoic, carbon, oxygen, lead, strontium, stable isotopes, radiogenic isotopes, Merico-Ethel, Elk Lake, Brett property.

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Chapter One: Introduction

1.1 The Cobalt Embayment

The Cobalt Embayment (figure 1.1) is a large (~60,000 km²), irregular domain of relatively thin (<6000m) Huronian-age siliciclastic sedimentary rocks that unconformably overlie steeply-dipping Archean basement rocks. The embayment is bounded in most directions by Archean rocks, except to the south where it is truncated by the Grenville Front. Throughout the embayment, both the Huronian and Archean rocks are intruded by an extensive system of Early Proterozoic sheets (sills) and dykes of Nipissing Diabase (Andrews *et al.*, 1986a). Also, regional-scale fault systems cross-cut both the Archean and Huronian rocks with displacements as great as 305 metres noted along the Lake Timiskaming fault (Andrews *et al.*, 1986a; Jambor, 1971a). In the northeastern corner of the embayment, outliers of Paleozoic sedimentary rocks comprised of limestone, dolostone, and sandstone unconformably overly the Huronian sedimentary rocks. To the north and northeast, the Archean basement rocks are primarily comprised of massive to pillowed basalts of the Abitibi volcanic-sedimentary (greenstone) belt, whilst felsic intrusive and metamorphic lithologies predominate along the western margin. Interflow, tuffaceous, and sedimentary rocks of the Abitibi Greenstone Belt consist of green-grey chert intercalated with graphitic argillite, siltstone, lithic wacke, and coarse feldspar-quartz sandstone (Goodz *et al.*, 1986). The ubiquitous Nipissing Diabase sills have an overall composition of olivine tholeiite and are interpreted as the intrusive portion of an eroded continental flood basalt sequence (Lightfoot *et al.*, 1986). A representative stratigraphic column of the embayment and the associated country rocks is presented below (table 1.1).

Figure 1.1. Location of the Cobalt Embayment, highlighting the distribution of the Huronian-aged sedimentary fill and the cross-cutting Nipissing Diabase sills. The surrounding rocks are Archean-aged, greenstone-belt lithologies of the Abitibi Subprovince, with the exception of the southern margin of the embayment, which is bounded by the Grenville Orogenic Front. A large outlier of Paleozoic sedimentary rocks unconformably overlies the Huronian sedimentary rocks in the northeastern corner of the embayment.

Table 1.1. Representative stratigraphic column of the northern Cobalt Embayment and the associated country rocks (modified from Smyk, 1987).

	<i>Era (Period)</i>	<i>Group</i>	<i>Formation</i>	<i>Member</i>	<i>Lithology</i>
P	Cenozoic - Recent				Fluvial & lacustrine deposits
II					Glacial sand, gravel & varved clays
A					<i>Unconformity</i>
N	Paleozoic - Silurian	Liskeard	Lockport		Dolomite, limestone, sandstone
E					Limestone, shale
R			Farr		Limestone
O					Shale
Z					Sandstone
O	(Ordovician)		Guiges		<i>Unconformity</i>
I					
C					
P	(Keweenaw)		Sudbury Dikes (olivine- and quartz-diabase)		<i>Penokean Orogeny</i>
R					
O	(Huronian)	Cobalt	Lomain	Firstbrook	Arkose, quartzite
T					Argillite
E					
R					
O					
Z	(Huronian)		Gowganda	Coleman	Conglomerate, diamictite greywacke, quartzite, Arkose
O					
I					
C	(Matachewan)		Diabase dykes, minor lamprophyre		<i>Kenoran Orogeny</i>
A					
R					
C					
II					
E	(Timiskaming)		Lithic and feldspathic arenites & conglomerate		<i>Unconformity</i>
A					
N					
A	(Keewatin)		Mafic-intermediate mafic flows & tuffs;		
N					Felsic flows and pyroclastics; minor interflow black shales & cherts; iron formation

The underlying Archean rocks of the Abitibi Subprovince have experienced two episodes of metamorphism. The first episode resulted in the development of prehnite-pumpellyite assemblages, typical of those produced by sea-floor metamorphism (<500°C and <3.4kbar of pressure), which have been dated at 2700-2690 Ma (Easton, 2000a). This metamorphic event is also characterized by the presence of localized zones of hydrothermal alteration. The Kenoran Orogeny generated regional metamorphism from 2670-2660 Ma, producing the second widely recognized metamorphic assemblage: the metamorphic grade of the latter is subgreenschist in the core of the Abitibi Greenstone Belt, and grades into greenschist facies along the margins of the belt (*op. cit.*). Near Matachewan, which is located along the northern margin of the Cobalt Embayment, Powell *et al.* (1993) reported evidence of peak metamorphic temperatures of 250-270°C and pressures of 2-2.5kbar. Evidence for amphibolite-facies metamorphism has also been noted within the rocks of the subprovince, but only in the form of contact aureoles around late alkaline intrusions and near most of the large tonalite-granodiorite bodies (batholiths) intruded into the metasedimentary and metavolcanic rocks (Easton, 2000a). The composition of these batholiths varies amongst tonalite, granite, syentite, quartz diorite, and granodiorite (Jambor, 1971a). The large granitic mass near Elk Lake is considered to be the southern exposed edge of the Round Lake Batholith, which has been dated at 2698 ± 1 Ma by Mortensen (1993). In the Cobalt region, Jambor (1971a) reported that deformation during the Kenoran Orogeny produced folding along a northwest to west-trending axis, with the formation of at least one major anticline and several isoclinal folds oriented along west- to northwest-trending axes.

The basal Huronian sedimentary rocks were likely deposited in a rift setting, whereas the upper formations (*i.e.* Serpent Formation and above) represent a passive margin succession dominated by siliciclastic sediments (Zolnai *et al.*, 1984; Young *et al.*,

2001). The basal Huronian member typically rests unconformably on basement rocks with locally preserved paleosol (Prasad and Roscoe, 1996). As noted by Bekker *et al.* (2005), the basal sedimentary rocks above the reduced paleosols sometimes contain conglomerates with detrital pyrite and uraninite, suggesting low atmospheric pO_2 at the time of deposition. Interlayered mafic volcanic and intrusive contacts with the Murray and Creighton granites (Sudbury district) constrain the age of the basal Huronian to 2.49–2.45 Ga (Krogh *et al.*, 1984, 1996; Smith and Heaman, 1999).

The Huronian sedimentary rocks of the Cobalt Embayment were subjected to subgreenschist-facies metamorphism producing chlorite and muscovite porphyroblasts in the eastern region of the embayment and pyrophyllite plus the latter assemblage in the central part of the embayment (Easton, 2000b). Although the precise timing of the subgreenschist-facies metamorphism is unresolved, it has been broadly constrained between the ages of 2219 ± 3.6 Ma (*i.e.* post-intrusion of the Nipissing Diabase) and ~ 1747 Ma (*i.e.* pre-intrusion of the Cutler batholith, Andrews *et al.*, 1986b; Easton, 2000b). Part of the ambiguity in precisely dating this latter event arises from the difficulty in accurately determining the age of the transition from diagenesis to metamorphism in the host sedimentary rocks. As Frey (1987) first noted, the transition is not clear, especially in clastic rocks found in low-pressure environments where key diagnostic minerals such as zeolite may not develop. Furthermore, the boundary (between diagenesis and metamorphism) is complicated by the occurrence of post-burial fluid flow, intense post-depositional chemical alteration, and regional hydrothermal events (Easton, 2000b). An earlier phase of deformation (*ca.* 2.4–2.2 Ga; Blezardian

Orogeny) has long been suggested to have occurred (Church, 1968; Riller *et al.*, 1999), but there is no firm consensus on the exact nature or timing of this event, or indeed, if it even exists (Long *et al.*, 1999).

In contrast, the metamorphic mineral assemblage from the Sault Ste. Marie–Elliot Lake area (*i.e.* the southwestern margin of the embayment) consists of diaspore, kaolinite, illite–montmorillonite, stilpnomelane, chlorite, muscovite, and pyrophyllite, with localized andalusite (Chandler *et al.*, 1969; Wood, 1973). As noted by Easton (2000*b*), the presence of diaspore in this assemblage (Chandler *et al.*, 1969; Card, 1978) is especially problematic. The most plausible explanation of the presence of diaspore in the Huronian Supergroup in this region is either that of an origin by weathering or hydrothermal alteration. This interpretation also suggests that the mineral assemblages reported by Card (1978) from the Sault Ste. Marie–Elliot Lake are likely in disequilibrium, with phases such as diaspore, kaolinite, and illite–montmorillonite reflecting the weathering–alteration assemblage, and phases such as chlorite, muscovite, and pyrophyllite reflecting subgreenschist-facies regional metamorphism (Easton, 2000*b*).

As Easton (2000*b*) has indicated, the timing of the alteration that produced the diaspore remains unclear. On the basis of Rb–Sr ages of Huronian paleosols, Fedo *et al.* (1997) suggested that regional K-metasomatism occurred at 1728–1688 Ma. This event was followed closely by regional Na-metasomatism at 1700 ± 2 Ma (U–Pb methods on monazite grains; Schandl *et al.*, 1994). Complete replacement of detrital plagioclase grains in the Serpent Formation (the upper formation of the Quirke Lake Group in the

Elliot Lake area) by secondary albite was also noted by Fedo *et al.* (1997), who suggested fluid expulsion of brines due to uplift in the core of the Penokean orogen as a possible cause of this regional sodic alteration. Such brines would have required temperatures $>110^{\circ}\text{C}$ to produce the albitization of plagioclase and $>65^{\circ}\text{C}$ for the reaction of K-feldspar (Boles, 1982; Aagaard *et al.*, 1990). Such temperatures are attained at depths of greater than 3,300m in Gulf Coast sedimentary rocks (Boles, 1982).

As summarized by Easton (2000b), this reconstruction leaves two possible scenarios for the generation of the mineral assemblages observed in the Sault Ste. Marie–Elliot Lake area:

1) After deposition, the Huronian sedimentary rocks were intensely weathered, forming diaspor and kaolinite. This assemblage was then subjected to subgreenschist-facies regional metamorphism, forming the assemblage of pyrophyllite, chlorite, and muscovite. Short-lived and patchy regional metamorphism allowed preservation of the minerals formed during weathering and localized zones of K- and Na-metasomatism occurred more recently; or

2) The present assemblage of minerals reflects a combination of both regional metamorphism and regional K- and Na-metasomatism: the Huronian sedimentary rocks were metamorphosed to subgreenschist or higher metamorphic facies prior to ~ 1750 Ma, followed by regional K and Na-metasomatism at ~ 1700 Ma. The metasomatic event may be linked to the intrusion of granitoid plutons in the Southern structural province and the Grenville Front Tectonic Zone at 1700-1750 Ma (Schandl *et al.*, 1994). Morey (1999)

suggested a similar process for regional alteration in the nearby Animikie basin at roughly the same time (1750-1700 Ma); while Medaris *et al.* (1999) reported similar mineral assemblages from argillites in the 1760-1630 Ma Baraboo, Barron, and Sioux quartzites of the Animikie basin.

As noted by Easton (2000b), the results presented by Fedo *et al.* (1997), when taken into consideration with the similar observations of Morey (1999) and Medaris *et al.* (1999), suggest that the second of the two interpretations is the more likely. The northern portions of the Huronian sedimentary rocks in the Cobalt Embayment were likely unaffected by this alteration by virtue of their distance, as the alteration event appears to have been centered along the western portion of the Huronian fold belt near lakes Superior and Huron.

1.2 Formation of the Cobalt Embayment

The Cobalt Embayment is one of several Proterozoic basins that are aligned along a zone of weakness that represents the boundary between late Archean greenstone-granite complexes of the Superior Province and an early Archean gneiss terrane to the south (Keeweenawan Midcontinent Rift system). Imperfectly welded together at the end of the Archean, this boundary was repeatedly reactivated during the Proterozoic and was the center for both regional extension and compression. It was a hinge during deposition of the Huronian supracrustal rocks and a tectonic front during the two main stages in the development of the early Proterozoic orogen. During extension, the sedimentary basins

evolved in an intracratonic setting, likely far away from a continental margin (Sims *et al.*, 1981). Local disconformities and unconformities at the base of the Serpent and Gowganda Formations of the Huronian Supergroup (Young and Church, 1966) as well as the presence of abundant clastic dykes, breccias, and syndepositional faults contemporaneous with the Espanola Formation provide further evidence for tectonic reactivation likely related to extension accompanying the rift-drift transition (Eisbacher, 1970; Young, 1972). Furthermore, the Huronian sedimentary sequences are characterized by abundant soft-sediment deformation features, diffuse boundaries between sedimentary units, chaotic folding, and the incorporation of large fragments of sedimentary rock into adjacent units. These features are all suggestive of rapid deposition of both fine- and coarse-grained sediments in an area prone to seismic shock (Benson *et al.*, 2006; Long *et al.*, 1999). A generalized stratigraphic column and inferred tectonic setting for the deposition of the Huronian Supergroup is presented below in figure 1.2.

The asymmetrical patterns of stratigraphy and structures in the Huronian Supergroup/Cobalt Embayment appear to be related to differences in the mobility of the two basement crustal segments (Sims *et al.*, 1980). Deposition ceased following a terminal, compressional event, when the supracrustal cover and gneissic basement rocks were deformed together, and metamorphosed under low-to-moderate pressure, as a result of widespread diapiric doming of the gneissic crust and lateral transport of this crustal segment against the more rigid greenstone-granite crust (Sims *et al.*, 1981).

Figure 1.2. Generalized stratigraphic section, and inferred tectonic setting, for the deposition of the major Huronian Formations (from Fedo *et al.*, 1997). The authors proposed that the transition from a rift setting to a passive margin occurred during deposition of the upper Quirke Lake Group.

1.3 The Nipissing Diabase

The 2219 ± 3.6 Ma Nipissing Diabase is a complex system of intrusions, consisting mainly of well-differentiated dykes and sills with an overall olivine-tholeiite composition (Andrews *et al.*, 1986a). In many places the sills reach a thickness of up to 300 metres. The trace-element signature of these intrusive rocks suggest a derivation from a compositionally uniform, MORB-type parental magma characteristic of oceanic crust, which may have been underplated beneath the southern Superior Province margin, possibly under the Labrador Trough (Lightfoot *et al.*, 1993; Buchan *et al.*, 1998; Ernst, 2007). This location is 1300 kilometres to the northeast, suggesting that the magmas were transported through a series of radiating dike swarms (see figure 1.3). Regionally, the sills are horizontal-to-gently dipping and form broad dome-and-basin structures. Locally, the diabase preserves intrusive features such as steeply-dipping dykes and plugs, whilst a lack of flow-textures along the margins suggest that the magma was largely liquid during intrusion (Jambor, 1971b; Andrews *et al.* 1986a). A metamorphic mineral assemblage consisting of prehnite–pumpellyite–albite–calcite±chlorite was reported by Thomson (1966) from the Henwood portion of the Nipissing Diabase, but on the basis of field relationships, the author attributed the presence of this assemblage to localized hydrothermal alteration. Interestingly, near most of the mineralized veins systems in the Cobalt Embayment, the Nipissing Diabase sills contain curved, concentric joints, which often splay off mineralized vein intersections (figure 1.4). While still debated, theories behind the generation of these interesting joints are centered on either cooling or tectonic origins (Eakins, 1961; Hester, 1967). Jambor (1971b) noted that the concentric joints

Figure 1.3. The Ungava magmatic event (*ca.* 2220 Ma) linking the origin of the Nipissing Diabase sills with a plume center (star) located underneath the Labrador Trough, some 1300 km to the northeast. From Ernst (2007). Abbreviations: CSB is the Cape Smith Belt; NQO is the New Quebec Orogen.

typically form perpendicular to diabase dyke walls, suggesting a cooling origin. Similar cooling-related features have been noted in volcanic rocks and diabase from Tasmania and northern Russia (Hill, 1965; Goryainov and Pesterev, 1969). The relationship with both the mineralized and barren quartz-calcite veins is likely related to zones of increased fluid permeability in the otherwise crystalline Nipissing Diabase.

As first documented by Jambor (1971*b*) in the Cobalt Embayment, the Nipissing Diabase has been differentiated into several internal zones, which are typically: (1) quartz diabase; (2) hypersthene diabase; and (3) varied-texture diabase. Thus, a typical cross-section of the Nipissing Diabase in the embayment is dominated by a thick, central zone of hypersthene diabase that grades upwards to varied-texture diabase (*op. cit.*). Narrow zones of fine-grained, quartz-diabase form at the lower and upper contacts.

In hand sample, the aphanitic quartz-diabase is greenish to dark grey. In thin section, the quartz-diabase contains abundant sericitized plagioclase and clinopyroxene phenocrysts, with approximately 5 modal percent of anhedral and intergranular aggregates of quartz. Along thin, chilled margins, the thin section view is dominated by microphenocrysts of augite, glomerporphyritic plagioclase, and altered olivine set in a groundmass of plagioclase laths ($\sim\text{An}_{55}$); the latter are often distributed in radial growths (Jambor, 1971*b*).

Figure 1.4. Photograph of concentric joints commonly associated with quartz-calcite veining; both barren and mineralized. Red-dotted line traces the strike of a barren quartz-calcite vein at the Capital Silver Mine, Gowganda. The origin of the joints, which form perpendicular to the host-rock contacts, is thought to be related to the cooling of the Nipissing Diabase (*cf.* Eakins, 1961; Hester, 1967; Jambor, 1971*b*).

The hypersthene-diabase is characterized by the presence of brown orthopyroxene grains, typically 3-5mm in length, but often reaching lengths of 8-10 mm. The orthopyroxene, which with plagioclase comprises a subophitic texture, is partially altered to vermicular antigorite and may contain Ca-rich clinopyroxene exsolution lamellae. The plagioclase (*var.* labradorite) is relatively pristine, and interstitial quartz is persistent throughout. In lower parts of the zone, the hypersthene-diabase can be olivine-bearing, as evidenced by the presence of sparingly small anhedral crystals (Jambor, 1971*b*).

Varied-texture diabase is so named because it contains domains of contrasting grain size: fine-, medium- and even coarse-grained varieties exist, all characterized by the presence of pervasive deuteric alteration – where plagioclase and pyroxene crystals are completely altered to uraltite and/or saussurite. Locally, the varied-texture diabase can be pegmatitic, granophyric, or aplitic in nature. The presence of mineral pseudomorphs, atoll grains, and skeletal grains also characterize this unit of the Nipissing Diabase. Accessory minerals in the varied-texture diabase include: quartz, myrmekite, biotite, epidote, stilpnomelane, leucoxene, and ilmenite-magnetite-amphibole intergrowths exhibiting symplectite textures. The pegmatitic variety of the diabase consists of coarse-grained pockets and small dykes located within finer-grained diabase. Orthopyroxene is absent from the pegmatitic diabase and the textures are more granitic than diabasic in character. The granophyric diabase contains abundant fine-grained intergrowths of quartz and alkali feldspar. Clinopyroxene may be present, but is often replaced by amphibole, biotite, or chlorite. Most granophyric diabase also contains some carbonate; either along grain boundaries or in miarolitic cavities. The aplitic zones are pink and

devoid of mafic minerals. Equigranular, hypidiomorphic quartz and albite are the principal components with minor actinolite also being present locally. In some places, these aplitic zones contain miarolitic cavities lined with dolomite, calcite, and Fe-Ni-Co arsenides (Jambor, 1971*b*).

Younger (1238 ± 4 Ma), olivine-diabase dykes of the regionally-developed, Sudbury dyke swarm are easily distinguished from the older Nipissing Diabase dykes by their coarse-grained nature and intergranular-to-subophitic textures (Easton and Ketchum, 2002). Olivine occurs in the Sudbury dykes as interstitial, anhedral-to-subhedral grains, less than 1 millimetre in length, and is typically encapsulated by pyroxene. Pyroxene consistently displays varying degrees of alteration to actinolite. Zoned plagioclase laths are often intergrown with titanite and titanomagnetite, whilst accessory biotite is typically intergranular to plagioclase. Other major accessory minerals include zircon and iron sulphides. The Sudbury dykes are also characterized by the occasional presence of pale-green cherty amygdules (Jambor, 1971*b*; Bennett, 1978). The dykes are typically 50-120 metres wide, orientated in a northwest-southeast direction, and may have formed in relation to rifting along the southern margin of North America (Easton and Ketchum, 2002).

1.4 Precious- and Base-Metal Vein Mineralization

Historically, the silver-sulpharsenide vein deposits of the Cobalt and Gowganda region were discovered along the north and northeast margins of the Cobalt embayment, where the Proterozoic vein systems typically occur in proximity to pre-Huronian faults that were reactivated during emplacement of the Nipissing Diabase, *circa* 2219 Ma (Corfu & Andrews, 1986). In fact, all of the known deposits in the Cobalt and Gowganda camps are hosted within, or adjacent to the diabase sills, in close proximity to the Huronian-Archean unconformity, where the sills and Archean volcanic sequences coincide (figure 1.5; Andrews *et al.*, 1986*b*). The mineralized veins are characterized by a complex ore mineralogy comprised of arsenides and sulpharsenides of Co, Ni, Fe, together with native silver and bismuth, with minor antimonides, and sulphides of Pb, Sn, and Cu (Petruck, 1971*a*, 1971*b*). The gangue mineralogy is dominated by carbonate minerals (mainly calcite±dolomite), with silicate minerals (quartz, chlorite, amphibole, epidote, K-feldspar, albite) limited in their occurrence to thin selvages attached and/or immediately adjacent to vein walls. Where present, the ore assemblage occurs at or near the interface between the silicate and carbonate minerals and is, as a result, often distributed along vein walls (Andrews *et al.*, 1986*a*). Estimated figures for the total silver production from the Cobalt area are in the neighborhood of 12.6 billion grams or 445 million ounces (Marshall and Watkinson, 2000). Due to a moratorium on mineral exploration during the past two decades (*i.e.* the Temagami Land Caution), very little modern exploration has occurred in many areas the Cobalt Embayment.

Figure 1.5. Traditional model for the location of Co-Ag $\pm$ Au veins and representative geological cross-section of the Cobalt and Gowganda vein systems (after Marshall and Watkinson, 2000). Geochronological data from: Krogh *et al.*, (1984); Andrews *et al.* (1986*b*); Mortensen (1993); Smith and Heaman (1999); Easton (2000*a*); Easton and Ketchum (2002).

Ore genetic models for the silver-sulpharsenide veins of the Cobalt and Gowganda camps were developed for the most part in the 1970s and early 1980s (Jambor, 1971; Boyle and Dass, 1971; Andrews *et al.*, 1986*a*). Traditionally, such models have focused on silver as the major ore metal and have been centered on four main schools of thought, with the vein formation ascribed to: *i*) late-stage differentiation of the diabase magma at depth (Tyrell, 1907; Jambor, 1971); *ii*) circulation of connate brines and precipitation in a mechanically favourable host (Kissin, 1988); *iii*) hydrothermal fluids originating from a deep-seated intrusion, unrelated to the diabase (Bastin, 1939); and *iv*) mixing of hyper-saline hydrothermal brines with meteoric water (Marshall *et al.*, 1993).

The recent discovery of high-grade gold mineralization (up to 6,222 g/t Au; Temex Resources, 2004) on the Brett property near Latchford, in a geological setting very similar to that of the Cobalt and Gowganda camps has, however, led to a renewed interest in the ore genesis of mineralized vein systems and the metallogeny of the Cobalt Embayment. Gold at the Brett Property is hosted in discordant calcite-quartz veins, and is intergrown with Co-Ni sulpharsenide minerals, notably cobaltite, and minor sulphides (Taylor, 2004*b*). This discovery led Taylor (2004*b*) and Taylor & Campbell (2004*a*, 2004*b*) to: *(i)* hypothesize that the Brett gold mineralization is an analogue of the classical silver-sulpharsenide veins present in the Cobalt and Gowganda camps; and *(ii)* suggest that most of the currently identified, precious- and base-metal rich calcite-quartz vein systems in the embayment are petrogenetically interrelated and formed as part of a large-scale, regional hydrothermal event during the Early Proterozoic.

1.5 Purpose of Study

The hypothesis put forward by Taylor (2004*b*) and Taylor & Campbell (2004*a*, 2004*b*), relating to the possibility that all of the base- and precious-metal vein deposits within the Cobalt Embayment have a common petrogenetic origin related to the action/s of a regional hydrothermal event in the Early Proterozoic, thus became the basis of this Ph.D. research study; a study whose major objectives were:

1. To describe the mineralogy and textures of the recently discovered, precious- and base-metal rich vein systems, both from the Brett Property and other recently explored occurrences (*e.g.* the Merico-Ethel Property) and compare them to known mineralized vein occurrences from throughout the Cobalt Embayment.
2. To attempt to accurately determine the age of vein mineralization and relate these geochronological data to regional geodynamic, magmatic, and hydrothermal events.
3. To characterize the geochemical attributes of the hydrothermal mineralizing fluids, using both stable and radiogenic isotope tracers, and thereby constrain fluid pathways and regional metal zoning within the Cobalt Embayment.
4. To compare the newly acquired data with the historical geoscience database that exists for the mineralized vein systems of the Cobalt-Gowganda silver camps.
5. To develop a comprehensive ore genetic model of the basin evolution and the associated mineralizing events that produced the precious- and base-metal vein systems to help focus future mineral exploration programs.

Chapter Two: Field, Petrographic, and Mineralogical Studies

2.1 Fieldwork, Sample Collection, and Archival Material

After the completion of two field seasons, approximately 130 field samples and numerous archival samples had been collected, identified, and catalogued from documented mineralized occurrences throughout the Cobalt Embayment. Sampling locations were prioritized based on the nature, location, and geological setting of the mineralized vein occurrences and their inherent relationship to the Proterozoic mineralization that is broadly characteristic of the Cobalt Embayment. Figure 2.1 shows the location of the major sampling areas within the Cobalt Embayment in relation to the regional geology. A listing of the samples collected and brief field descriptions is presented in Appendix A. The mineralized vein occurrences sampled during the current study were selected based on the following criteria:

- The occurrence of steeply dipping, discordant calcite + quartz veins with,
- Polymetallic mineralization (Co, Cu, Ni, Fe, Pb, Au, Ag, $\pm$ U),
- Hosted in Proterozoic-aged rocks, and
- Spatially associated with regional fault systems.

Figure 2.1. Location of the major mineralized vein occurrences (**bold font**) that were sampled within the Cobalt Embayment, which is generally outlined by the limits of the Proterozoic (Huronian) sedimentary rocks. Due to a moratorium on mineral exploration during the past two decades (*i.e.* the Temagami Land Caution), very little exploration has occurred in the central portion on the embayment. The Wanapitei occurrences are (from north to south): Dolmac, Gordon Mine, Burda Mine, McLean-Watt, Glade, Davis shaft, and St. Genevieve. Abbreviations: RLB = Round Lake Batholith; SIC = Sudbury Igneous Complex.

2.2 The Merico-Ethel Property

Introduction

The Merico-Ethel property is located in the northwest corner of the Cobalt Embayment, just a few kilometres northwest of the town of Elk Lake (figure 2.1). The Abitibi Greenstone Belt of the Superior Province is exposed immediately northeast of the property and also underlies the property. The greenstone belt is comprised primarily of orthogneisses and large granitic intrusions separated by ultramafic to felsic volcanic and sedimentary rocks. The Round Lake Batholith intrudes the metavolcanic sequences of the Abitibi Greenstone Belt just to the north-northeast of the property. All of these units are intruded by the Late Archean Matachewan diabase dyke swarm, dated at 2633 Ma (Gates and Hurley, 1973). Unconformably overlying the Archean basement are the clastic sedimentary rocks of the Early Proterozoic Gowganda Formation and slightly younger Lorrain Formation: the Gowganda Formation is composed of two parts, the underlying Coleman Member diamictite and the overlying fluvial-deltaic Firstbrook Member sandstone, whilst the Lorrain Formation comprises arkosic and quartz arenites of alluvial and/or fluvial origin (Young, 1973; Chandler, 1986). All of these rocks are intruded by Nipissing Diabase, which has been dated, using U-Pb methods, at 2219 ± 3.6 Ma (Andrews *et al.*, 1986b). The mafic intrusive rocks of the Nipissing Diabase are typically massive, unaltered, medium-grained, and strongly magnetic in character. Zones of both fine-grained, quartz-dabase and coarser grained granophyric diabase were noted in diamond drillcore and the diabase is highly jointed and fractured near the base- and precious-metal mineralized vein occurrences. The Nipissing Diabase forms a large sill, approximately 200 metres thick, over most of the property, except in the northeastern

corner at the Sauvé occurrence, where it reportedly occurs as a dyke (Kettles *et al.*, 2006). Previous workers have speculated that this dyke cuts the sill and has acted to focus the structures that host both the Merico and Ethel vein occurrences (*cf.* Pinkerton, 1996).

The intrusion of the Round Lake Batholith caused the development of a non-penetrative fabric and produced deformation, which resulted in the development of major east–northeast and northeast faults and shear zones. The northwest-trending Montreal River Fault is present immediately to the southwest of the property, where it is situated along Elk Lake and the Montreal River (Kettles *et al.*, 2006). Johns (1986) suggested that the Montreal River Fault is a deep-seated fault that: (i) formed as part of the Lake Timiskaming Rift valley and is one of many regional-scale faults that were reactivated during intrusion of the Nipissing Diabase; and (ii) may have acted as a major pathway for the movement of mineralizing fluids (see also Born and Hitch, 1990). A northeast-trending fault, the Truax fault, is present on the northwest part of the property, and is also potentially related to the intrusion of the Round Lake Batholith (Kettles *et al.*, 2006).

Nature and Distribution of the Vein Mineralization

The Merico-Ethel property has an extensive exploration and mining history, with numerous exploration shafts and trenches having been completed in the early to mid 1900's in the search for high-grade silver mineralization (figure 2.2). The property also hosts the historical Ethel copper mine, a short-lived venture fraught with production problems, and also the recently discovered Sauvé uranium showing (Kettles *et al.*, 2006).

Recent exploration also uncovered the presence of gold mineralization in an unusual ore-mineral assemblage set in calcite-quartz-chlorite gangue. The geology of the main Merico mineralized vein systems, uncovered by backhoe trenching and pressure washing, and mapped by the author, is presented in Appendix B. The vein and vein-breccia mineralization at the Merico-Ethel property is dominated by the development of chalcopyrite, specular hematite, pyrite, cobaltian pyrite, cobaltite, and linnaeite-group minerals (*viz.* linnaeite and carrollite). Gold mineralization occurs primarily in the form of electrum (herein defined as gold with a content of >20 atomic percent silver) in small anhedral grains (5-20 μm in size). All of the recorded occurrences of gold mineralization are polymetallic in nature, with the preliminary results suggesting that the chalcopyrite-rich veins generally have lesser gold and silver contents than the specular hematite-bearing veins, which tend to have higher gold values. Blocky-to-granular calcite is the dominant gangue mineral in both the chalcopyrite- and the hematite-rich veins, with lesser amounts of anhedral quartz also being present. However, both calcite- and quartz-rich sections can occur along strike in the same vein or vein system. Localized zones of 'aplitic' alteration (herein defined as zones enriched in granular, secondary albite, calcite, chlorite and titanite) are often associated with quartz-calcite veining within the diabase, but are generally narrow (≤ 5 cm), rare, and have limited strike lengths (≤ 1 m). More commonly, alteration of the diabase host consists of a narrow (≤ 5 cm) band enriched in quartz+chlorite+epidote $\pm$ calcite. Such alteration is typically accompanied by the breakdown of minor magnetite-ilmenite intergrowths found within most varieties of Nipissing Diabase.

Figure 2.2. Geological map of the Merico-Ethel property, illustrating the local geology, the location of numerous historical occurrences with a record of significant exploration activity such as the presence of adits, shafts, and/or trenches, and significant occurrences that were encountered during recent exploration and sampled as part of the present study.

The mineralized veins systems, all of which are steeply dipping, strike in three dominant directions: east-west, northeast-southwest, and southeast-northwest. The steeply, northerly dipping E-W-oriented veins are best characterized by the Merico main vein ($260^{\circ}/75^{\circ}\text{N}$), the Ethel Mine veins, and the Nipissing Diabase dyke that hosts the Sauv occurrence ($250^{\circ}/87^{\circ}\text{N}$) (figure 2.2), all of which are located within a very large east-west arcuate structure visible on a regional government airborne magnetic survey (figure 2.3). The E-W structural orientation also controls the distribution of the mineralized veins in the southern part of the property, including the veins located in trenches to the south of the Paramount Shaft and at the Beaver Pond occurrence. A NE-SW strike (022° to 054°) and subvertical (75°S to 80°N) orientation controls the dominant structure for veins at the Silver Jackpot occurrences and also for the mineralized veins located on the east side of the large beaver pond. The SE-NW striking (292°), subvertical (80°N to 80°S) vein orientation is best exemplified by the veins at the Paramount occurrence, and this orientation is also a secondary controlling structure at the Silver Jackpot mine and in veins located on the east side of the large beaver pond. A less well developed, N-S striking (340° to 20°), subvertical (80°S to 80°N) set of fractures also affects all of the mineralized calcite-quartz veins. The N-S-striking fracturing may have been caused by local warping of both the NE-SW and SE-NW structures and is therefore not considered as a fourth major orientation of the mineralized veins (Kettles *et al.*, 2006).

Figure 2.3. Regional airborne magnetic survey over the Merico-Ethel property illustrating the location of a potential SW-trending structure (black dotted line) that may have controlled the development of the mineralized veins in three of the main occurrences (*i.e.* Sauv, Merico, and Ethel); and also the relationship of other significant mineralized showings with local magnetic highs (shown by the hotter colours such as pink and red). The image is the first vertical derivative of the total magnetic intensity and was provided courtesy of Temex Resources Corporation (Karen Rees, *pers. comm.*, 2007).

Narrow stringers and vein-breccias dominated by specular hematite were found on the southeastern corner of the property, within immature arkosic arenites of the Gowganda Formation (figure 2.4). Whilst specular hematite veins were frequently noted in association with the mineralized calcite-quartz veins in the area, the southeastern occurrences represent the only examples of this vein assemblage not hosted in Nipissing Diabase. Unfortunately no contacts between the arkosic arenites and Nipissing Diabase were observed in the field, although a large diabase sill lies immediately to the north and northeast of these occurrences. The arkosic sandstone host consists of large rounded grains of quartz set within an alkali feldspar-rich groundmass, which has been moderately chloritized. Near the veinlet margins the arkosic arenite has been intensely silicified creating a bleached appearance in outcrop (figure 2.4).

In association with the chlorite alteration, several grains of epidote-allanite have developed along veinlet margins and microfractures. Whilst the veins and veinlets are anastomosing, the dominant trend of the stringers is 070° , dipping steeply $70-90^{\circ}$ to the south (in same general trend as the main Merico vein system). Although none of the sedimentary-hosted specular hematite veins contain appreciable amounts of calcite or quartz, small specular hematite veinlets identical to them in mineralogy were noted branching off the main Merico vein system in fractures perpendicular ($\sim 360^{\circ}$) to the main trend of the veins.

Figure 2.4. Field photographs of specular to botryoidal hematite stringers and vein-breccias noted from the southern portion of the Merico-Ethel property. The stringers trend 070° , dip $70-90^{\circ}$ to the southeast, and are hosted in a coarse-grained, arkosic sandstone of the Huronian Gowganda Formation. The arkosic sandstone has been intensely silicified near the stringer margins to produce a bleached appearance.

Main Merico Vein System

The main Merico vein system consists of a series of anastomosing, polymetallic (Cu-Au-Ag-Co-As), quartz-calcite veins hosted in medium-grained Nipissing Diabase (figures 2.2). The main vein varies from 0.1 to 1.0 metres wide, and displays a fairly consistent overall westerly strike ($\sim 260^\circ$) with a steep, northerly dip ($\sim 75^\circ$) over depths of greater than 200 metres (figure 2.5). Historical diamond drilling reportedly intersected the mineralized zone at 50 and 100 foot levels beneath the main vein system (Kettles *et al.*, 2006). Recent diamond drilling undertaken by Temex Resources Corporation indicates that the veins (and present erosional surface) are located approximately 300 metres above the regional unconformity (on granitic basement). As with most of the property showings, the main vein system at Merico is hosted within a substantial zone (up to 2.5 metres wide) of intensely fractured diabase. Chlorite+quartz+epidote $\pm$ calcite alteration of the host diabase is very minor in its extent and is often limited to a few centimetres of alteration around fractures. None of the ‘aplitic’ alteration that was observed in the smaller occurrences was noted in the main vein system. The western portion of the main Merico vein system is characterized by sheared textures with ribbon-shaped zones of chalcopyrite mineralization, whilst more massive, non-sheared textures dominate in the eastern portion of the main Merico vein system (figure 2.6). In a few locations along the main Merico vein, small euhedral crystals of quartz and bladed calcite line late-stage vugs.

Figure 2.5. Representative section of the main Merico vein system (complete map in Appendix B), illustrating the overall westerly strike, anastomosing nature and a narrow zone of brittle deformation and carbonate alteration associated with the veins.

Figure 2.6. (previous page) Photographs of the main Merico Vein system, illustrating the dominant vein morphologies:

A) Intensely-fractured Nipissing Diabase hosting a vein branching off the main system at the Merico shaft, with vein strike indicated by gossanous staining.

B) Close-up of the highly-sheared vein illustrating the ribbon-like chalcopyrite mineralization and vein fragments hosted in dark grey calcite and quartz gangue.

C) Undeformed, specular hematite-rich vein hosted in highly fractured Nipissing Diabase.

D) Vuggy, quartz-rich sample from the main vein system illustrating euhedral chalcopyrite and pyrite hosted predominantly in milky quartz and dark grey calcite. Zoning in the sample consists of (margin to core): *i*) chlorite+quartz, *ii*) hematite+chlorite+quartz±sulphide, and *iii*) quartz+chalcopyrite+pyrite+calcite.

E) Zoned calcite- and specular hematite-rich vein containing large rosettes of specular hematite and relatively barren calcite core. This type of vein is typical of the eastern portion of the main vein system.

F) Narrow zone of aplitic (alkali feldspar+calcite) alteration developed in calcite+chalcopyrite stringer that branches off the main vein system. The stringer is hosted in medium-grained Nipissing Diabase of the hypersthene type.

Calcite is the dominant gangue mineral, with lesser amounts of quartz, although their modal abundances vary considerably over the strike length of the main Merico vein system. For example, at the eastern extent of the vein system, calcite comprises approximately 95 modal percent of the gangue, whereas in the southern branch in the central portion of the vein system quartz comprises approximately 70 modal percent of the gangue. As illustrated in figure 2.6(D), the veins typically exhibit a zoning, consisting of the following mineral assemblages (margin to core): (i) quartz + chlorite $\pm$ alkali feldspar; (ii) quartz + chlorite $\pm$ sulphides; (iii) calcite $\pm$ sulphides $\pm$ hematite $\pm$ chlorite; and (iv) massive calcite. The modal abundance of sulphides varies considerably over the strike length of the vein and vein system, from barren to approximately 30 modal percent. Figures 2.6B and 2.6D illustrate some of the highest grades of sulphide mineralization present in the main vein system. All of the carbonate minerals analyzed from the main Merico vein system are essentially stoichiometric calcite with compositions fairly close to that of pure CaCO_3 (table 2.1; figure 2.7). Typically, the magnesium, iron, and manganese contents of the vein calcites from the main Merico vein system are low, with concentrations of MgO, FeO, and MnO of <0.25 wt.%, <0.50 wt.%, and <0.50 wt.% respectively. However, a few calcite grains within the mineralized sheared zone contained elevated iron and manganese concentrations (up to 0.63 wt.% FeO and 2.47 wt.% MnO) and appear to represent examples of an early-stage calcite that is hosted in later calcite, which contains lower concentrations of these elements. The hematite is predominantly specular in variety and often forms large, centimetre-scale rosettes in the vein system along the quartz-calcite boundary.

Table 2.1. Representative electron-microprobe analyses of calcite from the main Merico vein system, Merico-Ethel property.

Sample #	ME1A-5	ME5-8	ME8A-6	ME8A-7	ME19A-7	ME19A-9	ME19A-10	ME23B-4
MgO	0.21	0.14	0.30	0.04	0.00	0.03	0.15	0.22
CaO	55.10	55.04	55.19	56.54	56.41	56.90	54.34	53.88
MnO	0.45	0.54	0.37	0.25	0.44	0.14	1.60	2.47
FeO	0.18	0.32	0.50	0.06	0.04	-	0.63	0.50
SrO	-	-	-	-	-	-	0.01	0.02
BaO	0.01	0.04	0.02	-	0.01	0.08	-	0.04
CO ₂ *	44.05	43.92	43.62	43.11	43.10	42.85	43.27	42.87
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Cation Proportion based on C=1.00								
Mg	0.005	0.003	0.007	0.001	--	0.001	0.004	0.006
Ca	0.983	0.983	0.989	1.017	1.016	1.026	0.979	0.975
Mn	0.006	0.008	0.005	0.004	0.006	0.002	0.023	0.035
Fe	0.003	0.004	0.007	0.001	--	--	0.009	0.007
Sr	--	--	--	--	--	--	--	--
Ba	--	--	--	--	--	--	--	--
Total	0.998	0.999	1.008	1.023	1.022	1.029	1.014	1.023

Note. All oxide concentrations are reported in weight percent (wt.%). Analyses #ME19A-10 and ME23B-4 (in columns #7 and 8) are from a sheared portion of the mineralized vein system and appear to represent fragments of an early calcite. The later generation of calcite envelopes the earlier calcite and is relatively depleted in MnO and FeO (see analyses in columns #1-6). CO₂* = CO₂ concentration calculated by difference and confirmed by stoichiometry. [-] = below analytical limit of detection.

Figure 2.7. Composition of calcite from the Merico vein system plotted in terms of atomic percent Ca, Mg, and (Fe+Mn) (*cf.* Deer *et al.*, 1992) illustrating the slight variation in Fe+Mn content ($n=96$).

The dominant sulphide minerals present in the main Merico vein system include chalcopyrite, pyrite, cobaltian pyrite, cobaltite, and linnaeite-group minerals. The sulphide minerals, which are typically associated with chlorite, are generally hosted in both calcite and quartz, being preferentially located along boundaries between the two gangue minerals. Ore mineral zoning and textures in the veins and in polished thin sections (figure 2.8) indicate that the main phase of sulphide mineralization followed the crystallization of specular hematite. When not deformed, the chalcopyrite and pyrite are euhedral to subhedral in habit and are very coarse-grained (up to 1.5 cm in diameter).

As shown in figure 2.9, almost all of the chalcopyrite grains record some evidence of formation after pyrite, either forming rims around pyrite grains or hosting relict inclusions of pyrite. Chalcopyrite also contains inclusions of cobaltian pyrite, some of which are euhedral in habit, and anhedral inclusions of linnaeite-group minerals $[\text{CoCo}_2\text{S}_4 - \text{Cu}(\text{Co},\text{Ni})_2\text{S}_4]$. Pyrite compositions display varying levels of cobalt enrichment (0-21 atomic %), but only trace amounts of nickel (figure 2.10). The linnaeite-group minerals represent a solid solution comprised of 75% linnaeite and 25% carrollite end members, calculated by stoichiometry. Where not hosted within chalcopyrite, the linnaeite-group minerals occur as euhedral grains set in calcite gangue.

Table 2.2. Representative electron-microprobe analyses of ore minerals from the main Merico vein system, Merico-Ethel property.

Mineral	Pyrite	Pyrite	Pyrite	Pyrite	Pyrite	Cobaltite	Cobaltite
Sample #	ME1AA-11	ME1AA-7	ME8B-4	B-A-2	B-C-2	ME9A-8	ME4A-6
As	0.06	0.05	0.26	0.26	0.03	44.83	43.35
S	53.40	52.04	53.23	52.56	53.02	19.58	19.77
Fe	46.13	44.17	43.37	40.60	36.57	1.17	2.70
Co	0.25	1.13	3.24	5.90	10.64	33.99	26.34
Se	-	-	-	-	-	0.24	0.27
Pb	-	-	-	-	-	-	-
Cu	0.08	1.89	-	0.16	0.1	0.07	1.75
Ni	0.04	0.01	0.15	-	-	0.32	6.51
Ag	0.03	-	0.03	-	-	-	0.02
Mn	-	0.01	0.01	-	-	-	0.01
Zn	-	0.01	0.01	-	-	-	0.01
Bi	-	0.04	-	-	-	0.01	-
Total	99.99	99.35	100.30	99.48	100.36	100.21	100.73

Proportions calculated on $\Sigma\text{Atoms}=1$

As	-	-	0.001	0.001	-	0.329	0.316
S	0.666	0.658	0.664	0.663	0.664	0.336	0.336
Subtotal	0.666	0.658	0.665	0.664	0.664	0.665	0.652

Fe	0.331	0.321	0.311	0.294	0.263	0.012	0.026
Co	0.002	0.008	0.022	0.040	0.072	0.318	0.244
Se	--	--	--	--	--	0.002	0.002
Pb	--	--	--	--	--	--	--
Cu	--	0.012	-	0.001	0.001	0.001	0.015
Ni	--	--	0.001	--	--	0.003	0.060
Ag	--	--	--	--	--	--	--
Mn	--	--	--	--	--	--	--
Zn	--	--	--	--	--	--	--
Bi	--	--	--	--	--	--	--
Subtotal	0.333	0.341	0.334	0.335	0.336	0.336	0.348

(Table 2.2 is continued on the next page)

Table 2.2 (continued).

Mineral	Cobaltite	Linnaeite	Linnaeite	Covellite	Electrum	Wittichenite	Aikinite
Sample #	ME4A-11	ME4A-15	ME4A-22	ME1AA-19	ME13A-1	ME17A-7	ME9A-10
As	43.42	0.05	-	0.02	0.01	0.05	1.35
S	19.28	40.98	40.83	30.36	0.07	19.36	17.38
Fe	1.01	0.90	1.10	13.35	0.45	0.38	1.06
Co	26.34	45.12	45.07	-	-	1.08	2.70
Se	0.24	0.06	0.02	0.03	-	-	0.74
Pb	-	-	-	-	-	-	19.02
Cu	0.50	11.04	8.49	55.76	0.74	38.51	6.89
Ni	8.32	2.07	3.61	-	0.01	0.09	0.41
Ag	0.05	-	-	-	17.14	0.15	6.74
Mn	-	-	-	-	-	-	-
Zn	-	-	-	-	-	0.01	0.04
Bi	-	-	-	0.04	0.01	40.56	44.02
Au	-	-	-	-	82.91	0.08	-
Total	99.16	100.22	99.12	99.56	101.34	100.27	100.35

Proportions calculated on $\Sigma\text{Atoms}=1$

As	0.322	0.000	0.000	0.000	-	-	0.02
S	0.334	0.563	0.565	0.459	0.004	0.421	0.49
Subtotal	0.656	0.563	0.565	0.459	0.004	0.421	0.50
Fe	0.010	0.007	0.009	0.116	0.013	0.005	0.02
Co	0.248	0.337	0.339	--	--	0.013	0.04
Se	0.002	--	--	--	--	--	0.01
Pb	--	--	--	--	--	--	0.08
Cu	0.004	0.076	0.059	0.425	0.019	0.423	0.10
Ni	0.079	0.015	0.027	--	-	0.001	0.01
Ag	--	--	--	--	0.264	0.001	0.06
Mn	--	--	--	--	--	--	--
Zn	--	--	--	--	--	--	0.00
Bi	--	--	--	--	--	0.135	0.19
Au	--	--	--	--	0.699	-	-
Subtotal	0.343	0.437	0.435	0.541	0.995	0.578	0.50

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical limit of detection.

Figure 2.8. Back-Scattered Electron (BSE) image of flakes of specular hematite (hm) intergrown with chalcopyrite (cpy) along the boundary between calcite (cc) and quartz (qtz) gangue. Sample# ME-1AA, the main Merico vein system, Merico Ethel property.

Figure 2.9. BSE-image of remnants of early-formed pyrite (py) included within later chalcopyrite (cpy) that is partially replaced (along fractures) by cobaltite (co). Sample# ME-4A, the main Merico vein system, Merico Ethel property.

Figure 2.10. Compositional variation of pyrite ($n=55$) from the main Merico vein system, plotted in pyrite-vaesite-cattierite ($\text{FeS}_2\text{-NiS}_2\text{-CoS}_2$) space (*cf.* Deer *et al.*, 1992 illustrating the significant enrichment of the Merico pyrite in Co, with only trace amounts of Ni substitution).

Figure 2.11. BSE-image of inclusions of aikinite-bismuthinite (minute, very bright white grains; circled) located in fractures within chalcopyrite (cpy) that is partially replaced by cobaltite along fractures (co). Sample# ME-9A, the main Merico vein system.

Figure 2.12. BSE-image of rosettes of specular hematite (hm) with a core of calcite+chlorite. Such hematite rosettes preferentially occur along the boundary between calcite-rich and quartz-rich zones in the zoned, mineralized veins of the main Merico system. Sample# ME-12B, the main Merico vein system.

The crystallization of chalcopyrite was followed by that of cobaltite, with the latter mineral often rimming and occurring along fractures within chalcopyrite (figure 2.9). Also, trace amounts of gold (*var.* electrum), galena, wittichenite (CuBiS_3) and aikinite-bismuthinite solid solutions ($\text{PbCuBiS}_3 - \text{Bi}_2\text{S}_3$) are hosted in both quartz and calcite gangue and within chalcopyrite. Representative analyses of the dominant sulphide, sulpharsenide and sulphosalt minerals are presented in table 2.2. From the textures noted in polished thin section, the general sequence of ore mineral deposition in the mineralized veins was: pyrite $\rightarrow$ Co-pyrite $\rightarrow$ linnaeite $\rightarrow$ chalcopyrite $\rightarrow$ cobaltite $\rightarrow$ wittichenite+aikinite. Whilst only noted in a few polished thin sections of samples from the main Merico vein system, small ($\leq 10 \mu\text{m}$), anhedral grains of native gold (electrum) were found, hosted in quartz and calcite gangue; and also, minute inclusions of aikinite-bismuthinite ($\leq 5 \mu\text{m}$) occur in trace amounts in fractured and brecciated chalcopyrite grains that are rimmed by cobaltite (figure 2.11).

Unlike many of the other vein systems in the Cobalt Embayment, the main Merico veins contain only trace amounts of galena. Other gangue minerals that occur in the veins include: chlorite, epidote, allanite-Ce, andradite, diopside, apatite, rutile, xenotime-Y, and titanite. After calcite and quartz, chlorite is the next most abundant gangue mineral in the veins and is seen to have been preferentially concentrated in the early quartz-rich phase of vein formation. Chlorite (in addition to calcite and trace diopside) also occurs in the center of the majority of the rosettes of specular hematite that are typical of the Merico veins (figure 2.12), a relationship that indicates these minerals acted as a nucleation site for the growth of the iron oxide mineral. The composition of

the chlorite is relatively constant, with its Fe/(Fe+Mg) ratio ranging from 0.57 to 0.41 and an equal molecular proportion of the Al-, Fe-, and Mg-chlorite end-members being present in the mineral structure (figure 2.13). Due to the presence of calculated octahedral site vacancies in the chlorite analyses, chlorite geothermometry was not pursued as studies have shown that such site vacancies and variation in tetrahedral Al³⁺ reflect the presence of minute mineral inclusions (Jiang *et al.*, 1994). Andradite garnet occurs in trace amounts and is preferentially associated with chalcopyrite, where it occurs as discontinuous/broken rims (10-20µm thick) around a few of the sulphide grains. Table 2.3 lists representative chemical compositions of the gangue minerals other than calcite and quartz. The rare-earth-element (REE)-rich minerals, allanite-Ce and xenotime-Y occur in both calcite and quartz and appear to have formed during the earliest stage of mineralization. The allanite-Ce that is present in the Merico samples was examined in detail for its potential use in U-Pb geochronology by laser-ablation microprobe-inductively coupled plasma-mass spectrometry, using the method outlined by Cox *et al.* (2003). The individual allanite grains (table 2.4 and figures 2.14 and 2.15) appear to be ideally suited for the method having low uranium and thorium contents (thereby reducing the amount of metamictization and significance of Pb loss), moderate total rare-earth ($\Sigma\text{REE}_2\text{O}_3$) contents, and a hydrothermal/unmetamorphosed origin. Unfortunately, due to external circumstances, this avenue of research was not completed in time for publication in the present study.

From a compositional and textural standpoint, there are two types of allanite-Ce present in the main Merico vein system. Euhedral allanite grains (figure 2.13) contain greater Al₂O₃ contents relative to subhedral-to-anhedral grains that contain greater

concentrations of $\text{FeO}_{\text{TOTAL}}$. Stoichiometric calculations indicate that the Fe^{3+} is substituting for Al^{3+} in the tetrahedral Si-site in the allanite structure. In table 2.3, this is evident in the calculated Si-site vacancies and excess of cations in the Fe^{3+} -bearing, anhedral grains. All of the Al_2O_3 -depleted grains (figure 2.15) appear to have been partially altered and/or corroded and may represent the earliest stage of vein formation. Conversely, some of the anhedral grains preserve faint grain boundaries suggesting that they may be pseudomorphic after a primary phase. Additional grains of allanite-Ce were noted in the underlying arkosic sedimentary rocks of the Gowganda Formation (observed in diamond drill core). These grains of allanite-Ce were confined primarily to microfractures and were accompanied by calcite-chlorite-albite alteration of the arkosic host rocks. This avenue of research is one of many which remains open for further investigation.

Table 2.3. Representative electron-microprobe analyses of accessory minerals from the Merico-Ethel vein system, Merico-Ethel property.

Mineral	cpx	cpx	cpx	chl	chl	chl	chl	chl	chl
Sample #	ME7c-6	ME7c-3	ME7c-4	ME3a-6	ME4a-1	ME4a-2	ME4a-3	ME5-3	ME6d-3
SiO ₂	54.13	52.68	54.21	28.19	29.25	29.78	30.14	29.12	28.58
TiO ₂	0.00	0.01	-	-	0.06	-	-	0.01	0.00
Al ₂ O ₃	1.42	1.21	0.69	18.38	18.43	18.00	17.70	17.79	16.66
FeO ^T	19.49	23.84	21.03	28.35	26.24	24.47	23.76	27.38	28.77
MnO	0.51	0.35	0.49	0.31	0.16	0.10	0.15	0.26	0.27
NiO	0.00	-	0.04	0.09	0.05	0.03	0.15	-	-
MgO	11.12	8.77	10.59	14.08	16.12	17.91	18.83	15.66	15.17
CaO	12.37	12.24	12.31	0.03	0.05	0.03	0.02	0.06	0.01
Na ₂ O	0.37	0.22	0.31	0.03	0.03	0.04	0.02	0.03	0.01
Cl	-	-	-	0.04	0.03	0.04	0.02	0.03	0.03
F	-	-	-	0.05	0.02	-	-	-	-
Less O=F,Cl	-	-	-	-	-0.04	-0.02	-0.01	-0.01	-0.01
Total	99.41	99.32	99.67	89.51	90.42	90.38	90.78	90.33	89.49
Cation Proportions**									
Si	2.100	2.087	2.113	2.941	2.976	3.002	3.016	2.990	2.995
Ti	--	--	--	--	0.005	--	--	--	--
Al	0.065	0.056	0.032	2.260	2.210	2.140	2.088	2.152	2.058
Fe ²⁺	0.632	0.790	0.686	2.474	2.232	2.063	1.989	2.350	2.522
Mn	0.017	0.012	0.016	0.027	0.014	0.008	0.013	0.023	0.024
Ni	0.000	--	0.001	0.007	0.004	0.002	0.012	--	--
Mg	0.643	0.518	0.615	2.190	2.446	2.692	2.809	2.397	2.369
Ca	0.514	0.519	0.514	0.003	0.006	0.003	0.002	0.006	0.001
Na	0.028	0.017	0.023	0.006	0.007	0.008	0.004	0.005	0.002
Cl	--	--	--	0.007	0.005	0.007	0.004	0.004	0.004
F	--	--	--	0.017	0.007	--	--	--	--
Total	4.00	4.000	4.000	9.931	9.911	9.926	9.937	9.928	9.976
Fe/Fe+Mg (at.)				0.530	0.477	0.434	0.414	0.495	0.516
Fe/Fe+Mg+Mn (at.)				0.527	0.476	0.433	0.413	0.493	0.513

Note. All oxide concentrations are reported in weight percent (wt.%). **Cation proportions calculated on $\sum O=6$ for clinopyroxene (cpx) and $\sum O=12$ for chlorite (chl) analyses, respectively. [-] = below the analytical detection limit.

Figure 2.13. Electron-microprobe analyses of chlorite ($n=44$) from the Merico vein system plotted in terms of the three chlorite end-member compositions (*cf.* Deer *et al.*, 1992), illustrating the relatively uniform composition of the vein chlorite. The location of the clinochlore-chamosite tie line is also shown for reference.

Table 2.4. Representative electron-microprobe analyses of allanite-Ce from the main Merico vein system, Merico-Ethel property.

Sample #	ME9A-5	ME9A-7	ME9A-9	ME9A-10	ep2-4	ep1-4	ep4-1	ep4-2
SiO ₂	32.11	32.19	32.62	32.50	32.47	31.91	31.69	31.47
Al ₂ O ₃	17.77	16.17	17.54	17.86	13.94	13.37	12.07	11.81
FeO ^T	10.97	12.64	11.40	11.08	16.56	16.81	18.56	18.75
MnO	0.27	0.09	-	0.02	-	0.01	-	-
MgO	0.08	0.13	0.12	0.08	0.34	0.31	0.38	0.38
TiO ₂	0.25	0.48	0.19	0.23	0.41	0.07	0.08	0.14
CaO	10.05	10.02	9.91	10.14	11.48	10.47	10.21	10.24
La ₂ O ₃	5.35	6.40	6.09	5.84	5.59	5.37	6.11	6.24
Pr ₂ O ₃	1.35	1.21	1.31	1.28	1.02	1.25	1.26	1.21
SrO	0.03	0.08	0.01	0.03	0.05	-	-	-
Nd ₂ O ₃	3.84	4.11	3.82	3.85	3.94	4.68	3.86	4.29
ThO ₂	-	-	0.01	-	0.04	-	0.03	-
Ce ₂ O ₃	15.19	13.39	14.05	13.83	11.03	12.86	13.01	12.84
Sm ₂ O ₃	0.40	0.47	0.35	0.47	0.34	0.54	0.42	0.47
Y ₂ O ₃	0.06	0.17	0.08	0.22	0.28	0.19	0.11	0.28
Gd ₂ O ₃	0.07	0.20	0.15	0.29	0.22	0.25	0.06	0.14
F	0.26	0.21	0.27	0.26	0.18	0.17	0.19	0.11
Less O=F	-0.11	-0.09	-0.11	-0.11	-0.07	-0.07	-0.08	-0.05
H ₂ O*	1.45	1.46	1.45	1.46	1.47	1.45	1.42	1.45
Total	99.39	99.33	99.26	99.33	99.29	99.64	99.38	99.77

Cation Proportions $\Sigma O=24$

Si	6.103	6.180	6.182	6.147	6.253	6.252	6.282	6.264
Al	3.981	3.659	3.918	3.981	3.165	3.087	2.821	2.770
Subtotal	10.084	9.839	10.101	10.128	9.418	9.339	9.103	9.034
Fe	1.744	2.030	1.807	1.753	2.668	2.754	3.077	3.122
Mn	0.043	0.015	--	0.003	--	0.001	--	--
Mg	0.023	0.037	0.034	0.023	0.098	0.091	0.113	0.112
Ti	0.036	0.069	0.027	0.033	0.060	0.010	0.012	0.021
Ca	2.047	2.061	2.013	2.055	2.369	2.198	2.169	2.184
La	0.375	0.453	0.426	0.407	0.397	0.388	0.446	0.458
Pr	0.093	0.085	0.090	0.088	0.071	0.089	0.091	0.088
Sr	0.003	0.009	0.001	0.003	0.006	--	--	--
Nd	0.261	0.282	0.259	0.260	0.271	0.327	0.273	0.305
Ce	1.057	0.941	0.975	0.958	0.778	0.923	0.945	0.936
Sm	0.026	0.031	0.023	0.031	0.023	0.036	0.029	0.032
Y	0.006	0.017	0.008	0.022	0.029	0.019	0.012	0.030
Gd	0.004	0.013	0.009	0.018	0.014	0.016	0.004	0.009
Subtotal	5.719	6.043	5.672	5.654	6.783	6.853	7.172	7.296
F	0.156	0.128	0.162	0.156	0.108	0.102	0.117	0.072
OH	1.844	1.872	1.838	1.844	1.892	1.898	1.883	1.928

Note. All oxide concentrations are reported in weight percent (wt.%). Analyses ME9A-5, -7, -9, and -10 are of euhedral allanite, analyses ep2-4, ep1-4, ep4-1, and ep4-2 are of anhedral allanite. FeO^T = total Fe reported as FeO; H₂O* = H₂O concentration calculated assuming [OH,F,Cl]=2; [-] = not detected; thorium, uranium, and lead concentrations were below detection limits.

Figure 2.14. BSE-image of a euhedral, zoned, allanite-Ce grain from the main Merico vein system (sample# ME-9A). The allanite is hosted in quartz gangue.

Figure 2.15. BSE-image of anhedral allanite-Ce from the main Merico vein system, which appears to be pseudomorphic after a primary phase and/or is highly corroded. The allanite-Ce grain is hosted in calcite gangue. Sample# ME-9A.

Directly south of the main Merico vein system (at a distance of ~300 metres), an exploration trench (the “Southern trench”) uncovered additional calcite-quartz veining that is virtually identical in its characteristics to that of the main system, and which is reported to have produced a grab sample containing 22.53 ppm gold (Kettles *et al.*, 2005) and that is interpreted, based on geological relationships, to be a part of the same system. The Southern trench is hosted in massive, medium-grained Nipissing Diabase, and consists of numerous narrow veins (1 to 8cm wide) composed of varying amounts of calcite+specular hematite+chalcopryite+quartz+cobaltite. Ore textures observed amongst the sulphide and sulphurarsenide minerals are identical to those in the main Merico vein system: early pyrite is partially replaced by chalcopryite, which in turn has been partially replaced by cobaltite along fractures. Numerous, minute inclusions of aikinite-bismuthinite were also noted within the chalcopryite. There are two dominant orientations of steeply dipping veins in the Southern trench, 030° and 290°, both of which appear to be joint-controlled (Appendix B). The mineralized veins vary in composition from equal parts of granular, specular hematite and chalcopryite with very little quartz or calcite gangue, to those that are predominantly composed of calcite and chlorite, to the more typical quartz+calcite+hematite+chalcopryite (±cobaltite) veins of the main Merico system. Weathering of vein material in the Southern trench has produced abundant secondary malachite and erythrite (*i.e.* cobalt bloom). Minor fracturing and alteration extends into the diabase in the selvages of the veins.

The Silver Jackpot Mine

The Silver Jackpot mine was one of the first developments on the Merico-Ethel property, the first shaft having been sunk in 1909, on the intersection of a northeast-trending calcite vein and northwest-trending complex of aplite veinlets and calcite veins. The main calcite vein trends to the northeast for 485 metres and dips steeply to the south, whilst the northwest-trending vein system has been traced for a distance of 152 metres, along which it pinches and swells from 40 and 90 centimetres in width (Johns, 1986). Since its origin, the 'mine' has experienced several changes in ownership, development of a large adit along the northwest-trending vein system, and also of some minor underground workings. Despite some high-grade silver ore (assays as high as 1079 oz/ton (36,999 g/t) have been reported from the northwest-trending vein exposed in the shaft; Johns 1986; 1oz/t = 34.28 g/t), the property has never achieved any significant production. The mineralization consists of massive to sheared calcite-quartz veins with sporadic occurrences of chalcopyrite, hematite, pyrite, and native silver mineralization. The veins are hosted in fine-to-medium grained Nipissing Diabase and typically are enclosed by centimetre-scale halos of 'aplitic'-alteration (figure 2.16). In intensely 'aplitic'-altered wall rock samples, the primary diabase mineralogy has been replaced by an assemblage of 55 percent (modal) albite, 30-40 percent calcite, with minor quartz, titanite, and zircon (combined 5 percent). Furthermore, spotted chlorite+titanite alteration (*i.e.* alteration of feldspars), similar in character to the spotted chlorite alteration noted in rocks adjacent to Nipissing Diabase sills (Jambor, 1971c), was noted in a few of the 'aplitic' samples. Despite the extensive workings, examples of a few mineralized veins remain exposed in outcrop, and are observed to be steeply dipping,

with trends of 030° and 203°. Due to the destructive nature of the trenching, cross-cutting relationships between the two veins systems could not be determined. The veins contain anhedral grains of native silver hosted in calcite, some of which are visible in hand specimen. Examination of native silver using Energy Dispersive X-ray Spectra (EDS) did not reveal detectable concentrations of other metals. Vein samples obtained by the Ontario Geological Survey from the main southeast-trending veins yielded 0.24 oz/t (8.23 g/t) silver, 0.10 oz/t (3.43 g/t) gold, and 2.58 percent copper (Johns, 1986).

Much like the main Merico vein system, portions of the veins at the Silver Jackpot mine are deformed, a feature most easily noted in calcite-rich sections. At the Silver Jackpot, the late-stage, sheared calcite is rose in colour and does not appear to contain significant base- or precious-metal mineralization (figure 2.17). Electron microprobe analysis of the late-stage, rose-coloured calcite, from the Silver jackpot veins, revealed the presence of lower concentrations of both MnO (<0.69 wt.% MnO) and FeO (<0.01 wt.% FeO) relative to the dark grey, paragenetically earlier calcite that contains concentrations of MnO and FeO of as great as 1.40 and 0.40 weight percent, respectively; all of the carbonate minerals that were analyzed from the Silver Jackpot mine do, however, have compositions representative of calcite (table 2.5) Much like the paragenesis of the main Merico vein system, early pyrite grains in the Silver Jackpot veins tend to be rimmed and partially altered to chalcopyrite. Similarly, hematite deposition appears to have preceded sulphide mineralization in the Silver jackpot veins, once again indicating that the sulphides may have precipitated as a result of an iron-oxide redox reaction. Anhedral silver grains, present in the Silver Jackpot veins, are

predominantly included in calcite gangue (figure 2.18) and less frequently, in chalcopyrite. The deposition of the chalcopyrite mineralization was followed by cobaltite and galena mineralization, with both of the latter ore minerals being preferentially located within earlier, fractured, chalcopyrite and pyrite grains (figure 2.19). However, unlike those of the Merico vein system, analyses of pyrite from the Silver Jackpot mine did not yield significant concentrations of cobalt. Likewise, galena did not contain detectable levels of silver. Cobaltite, from the Silver jackpot, did however exhibit minor variation in nickel and iron contents, as illustrated in table 2.6.

Table 2.5. Representative electron-microprobe analyses of calcite from the Silver Jackpot Mine, which is located on the Merico-Ethel property.

Analysis	ME15A-1	ME15A-5	ME15A-6	ME15A-11	ME15A-12	ME15A-15	ME16A-10	ME16A-12
MgO	0.03	0.10	0.03	0.21	0.17	0.05	0.20	0.17
CaO	57.42	56.65	56.91	54.75	55.59	56.02	55.27	54.35
MnO	0.09	0.64	0.40	1.35	1.40	0.61	0.94	1.11
FeO ^T	-	0.01	-	0.59	0.40	0.02	0.22	0.17
SrO	-	-	-	-	-	-	-	-
BaO	-	0.02	-	-	-	-	-	0.04
SiO ₂	0.02	0.02	0.01	0.02	0.03	-	-	-
CO ₂ *	42.44	42.56	42.65	43.08	42.41	43.30	43.37	44.16
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Cation proportions based on C=1.00								
Mg	0.001	0.002	0.001	0.005	0.004	0.001	0.005	0.004
Ca	1.040	1.025	1.029	0.987	1.008	1.007	0.993	0.969
Mn	0.001	0.009	0.006	0.019	0.020	0.009	0.013	0.016
Fe	--	--	--	0.008	0.006	--	0.003	0.002
Sr	--	--	--	--	--	--	--	--
Ba	--	--	--	--	--	--	--	--
Si	--	--	--	--	0.001	--	--	--
Total	1.042	1.037	1.035	1.020	1.039	1.017	1.014	0.992

Note. All oxide concentrations are reported in weight percent (wt.%). Analyses ME15A-1, ME15A-5, and ME15A-6 (columns 1-3) are of sheared, rose-coloured calcite; the remainder of the analyses (columns 4-10) are of earlier, dark-grey calcite. [-] = below analytical limit of detection; FeO^T = total Fe reported as FeO; CO₂* = CO₂ concentration calculated by difference and confirmed by stoichiometry.

CENTIMETRES

Figure 2.16. A polished hand specimen of vein material from the Silver Jackpot mine (sample# ME-16b), which contains minor native silver and chalcopryite mineralization in a sheared calcite-quartz vein. The calcite-quartz vein is hosted in 'aplitic' altered Nipissing Diabase.

CENTIMETRES

Figure 2.17. A polished hand specimen (sample# ME-15) of a calcite-quartz vein from the Silver Jackpot mine illustrating the sheared nature of the rose-coloured calcite, the earlier growth of dark-grey calcite, and the presence of a hematite-altered clast of Nipissing Diabase.

Table 2.6. Representative electron-microprobe analyses of cobaltite from the Silver Jackpot Mine, which is located on the Merico-Ethel property.

Analysis	ME16A-4	ME16A-5	ME16A-3	ME16A-1	ME16A-2	ME15B-5
As	45.17	46.06	44.94	44.29	44.52	46.18
S	19.44	18.80	19.26	19.09	19.48	17.01
Fe	2.73	2.92	1.57	1.47	0.70	6.16
Ni	4.04	4.33	4.60	4.76	5.89	9.67
Zn	-	-	-	0.04	0.02	-
Ag	0.02	0.05	0.06	0.05	-	0.04
Cu	1.62	0.55	0.63	0.23	0.41	1.42
Co	27.88	27.81	28.52	29.30	28.88	18.86
Au	0.21	0.15	0.09	-	-	0.04
Bi	-	-	-	-	-	-
Total	101.11	100.67	99.67	99.23	99.90	99.38

Proportions calculated on $\Sigma\text{Atoms}=1$

As	0.330	0.340	0.333	0.329	0.328	0.349
S	0.332	0.324	0.333	0.332	0.335	0.301
Subtotal	0.662	0.664	0.666	0.661	0.663	0.650
Fe	0.027	0.029	0.016	0.015	0.007	0.063
Ni	0.038	0.041	0.043	0.045	0.055	0.093
Zn	--	--	--	--	--	--
Ag	--	--	--	--	--	--
Cu	0.014	0.005	0.006	0.002	0.004	0.013
Co	0.259	0.261	0.269	0.277	0.271	0.181
Au	0.001	--	--	--	--	--
Bi	--	--	--	--	--	--
Subtotal	0.339	0.336	0.334	0.339	0.337	0.350

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below analytical detection limit.

An Unnamed Occurrence on the Merico Ethel Property

Directly 800 metres east of the Silver Jackpot mine shaft, on the edge of a small beaver pond, is a significant mineral showing (figure 2.2) that was the locus of some advanced exploration work by Big Jackpot Mines and Northern Silver Fox Resources in 1968 and 1972 (Kettles *et al.*, 2005). Two mineralized zones, containing narrow quartz-calcite veins with minor amounts of chalcopyrite, pyrite, and specular hematite are hosted in massive, medium-grained Nipissing Diabase. The veins preserved in outcrop range from sub-centimetre to 15 centimetres in width, are steeply dipping ($>85^\circ$), and strike in two dominant directions: northeast and northwest. Despite their identical mineralogy, the earlier northeasterly-striking veins are cross-cut, and commonly offset, by the north-northwest striking veins. The northeasterly-striking veins of the “unnamed occurrence” are also associated with, and deformed (warped) by, concentric cooling joints present in the medium-grained diabase host rock. Both sets of veins have textures and a mineral paragenesis virtually identical to those of the quartz-rich portions of the main Merico vein system (compare figures 2.4 and 2.20). However, unlike the main Merico vein system, it is clearly evident that at least two episodes of sulphide mineralization are represented in the veins of the “unnamed occurrence”: namely, a pre-specular hematite generation of sulphides and a post-specular hematite generation of sulphides. As is illustrated in figure 2.20(B) an early phase of chalcopyrite+pyrite mineralization occurs along the vein margins within quartz+chlorite gangue. This marginal zone is followed by inner zones of: (i) quartz+chlorite, (ii) quartz+specular hematite, and (iii) a calcite±chalcopyrite±pyrite core. Whilst the earlier stage of chalcopyrite mineralization is intergrown with minor iron oxides, the iron oxides are not as abundant as they are in

the later, specular hematite-rich core. Furthermore, the earlier, anhedral chalcopyrite grains are frequently rimmed by andradite garnet. Andradite was also noted in a few samples from the main Merico vein system, but is relatively more abundant in the “unnamed occurrence”. Representative analyses of the garnet are presented in table 2.7. The garnet grains occur as: narrow rims (20-100 μm) on euhedral chalcopyrite grains, aggregations of euhedral grains hosted within calcite and quartz gangue, and euhedral grains associated with specular hematite (figure 2.21). The euhedral grains of garnet associated with specular hematite are interpreted to post-date the first phase of sulphide mineralization and typically appear (in addition with calcite, chlorite, and diopside) in the core of many rosettes of specular hematite (figure 2.22). Analyses of the major sulphide phases did not reveal any unusual mineralogical features; notably absent are the cobaltian pyrite and linnaeite-group minerals that occur in minor amounts throughout the main Merico vein system. Electron-microprobe analyses of the major ore minerals from the “unnamed occurrence” are presented in table 2.8. Gold mineralization at the “unnamed occurrence” is manifested by the presence of small (<20 μm), anhedral grains of electrum that are preferentially hosted as inclusions in chalcopyrite and calcite (figure 2.22). Trace amounts of iron and copper were detected in some of the grains of electrum, but most likely these represent contamination from the chalcopyrite host, due to the relatively large excitation volume of the electron beam. An assay of vein material from chalcopyrite- and specular hematite-rich vein material from the “unnamed occurrence”, by the Ontario Geological Survey, yielded values of 1.04 ounces silver per ton (29.33 g/t Ag), 0.04 oz/t (1.12 g/t) gold and 3.59 percent copper (Johns, 1986).

Figure 2.20. Polished samples (A = sample# ME-10 and B = sample# ME-12) of quartz-calcite veins from the “unnamed occurrence”, located just east of the Silver Jackpot mine on the Merico Ethel property. The mineralized veins contain significant amounts of chalcopryite, pyrite, and specular hematite. Note the similarities in vein mineralogy, zoning, and ore textures of these samples with those of the Merico vein system (*e.g.* figure 2.5D). White coloured, euhedral comb-textured quartz lines the interior of the vein and is followed by pockets of calcite.

Table 2.7. Representative electron-microprobe analyses of andradite garnet from the “unnamed occurrence”, located just east of the Silver Jackpot mine on the Merico-Ethel property.

Sample #	ME12B-4	ME12B-1	ME12B-5	ME12B-12	ME12B-13	ME12B-16	ME12B-17	ME12B-18
SiO ₂	37.81	37.40	37.60	37.60	37.69	37.55	37.69	37.47
TiO ₂	0.06	0.05	0.14	-	-	0.02	0.01	0.02
Al ₂ O ₃	0.36	0.54	0.50	0.31	0.25	0.15	0.18	0.46
Cr ₂ O ₃	-	-	-	-	-	-	-	-
Fe ₂ O ₃ *	27.61	28.17	27.86	28.35	28.38	28.50	28.39	28.74
FeO*	3.29	2.36	2.77	2.72	2.67	2.63	2.44	1.77
MnO	0.21	0.23	0.28	0.14	0.14	0.13	0.17	0.15
MgO	-	-	-	-	-	0.01	0.05	-
CaO	34.19	34.58	34.43	34.55	34.67	34.60	34.77	35.21
Total*	103.53	103.33	103.58	103.67	103.80	103.59	103.70	103.82

Cation proportions based on $\Sigma O=12$

Si	3.085	3.056	3.066	3.066	3.069	3.066	3.071	3.047
Ti	0.003	0.003	0.008	--	--	0.001	0.001	0.001
Al	0.035	0.052	0.048	0.030	0.024	0.014	0.018	0.044
Cr	--	--	--	--	--	--	--	--
Fe ³⁺	1.695	1.732	1.709	1.740	1.739	1.751	1.741	1.759
Fe ²⁺	0.225	0.161	0.189	0.185	0.182	0.180	0.166	0.120
Mn	0.014	0.016	0.019	0.009	0.010	0.009	0.012	0.010
Mg	--	--	--	--	--	0.001	0.006	--
Ca	2.989	3.028	3.008	3.019	3.025	3.028	3.036	3.068
Total	8.046	8.049	8.047	8.049	8.049	8.050	8.049	8.050

Note. All oxide concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit. *Weight percent oxide totals are >100 due to conversion of FeO_{TOTAL} to FeO and Fe₂O₃ after electron-microprobe analysis using the methods outlined by Droop (1987).

Figure 2.21. BSE-images of: (A) Andradite garnet (grnt) rimming early chalcopyrite mineralization associated with trace amounts of calcite (cc); and (B) aggregate of eu-subhedral andradite grains associated with specular hematite (hm) and calcite, all hosted in quartz (qtz) gangue (both images from sample# ME-12B, the “unnamed occurrence”).

Figure 2.22. Electron-microprobe BSE images of: (A) a rosette of specular hematite cored by calcite (cc), chlorite (chl), andradite (grnt), magnetite (mt), and diopside (di) from sample# ME-12B, the “unnamed occurrence”; and (B) an anhedral grain of electrum (Au) hosted in deformed chalcopyrite, which also contains grains of andradite garnet (sample# ME-13A, the “unnmaed occurrence”). Rosettes of specular hematite tend to occur along the boundary between quartz- and calcite-rich zones within the veins.

Table 2.8. Representative electron-microprobe analyses of the major ore minerals from the “unnamed occurrence”, located just east of the Silver Jackpot Mine on the Merico Ethel property.

Mineral	chalcopyrite	pyrite	galena	electrum	electrum	electrum
Sample #	ME10B-1	ME12A-1	ME12B-1	ME13A-1	ME13A-2	ME13A-3
S	34.38	53.36	13.68	0.07	0.01	0.02
Fe	30.72	48.19	0.07	0.45	0.68	0.43
Ni	-	0.03	-	0.01	0.03	0.03
Zn	0.03	-	0.03	-	-	-
Ag	0.01	-	-	17.14	13.74*	15.83*
Cu	35.03	0.50	-	0.74	1.09	0.70
Co	-	-	-	-	-	-
Pb	-	-	86.11	-	-	-
Au	0.12	0.07	0.09	82.91	84.22	82.99
Bi	0.03	-	-	0.01	0.23	-
Total	100.32	102.15	99.98	101.33	100.00	100.00

Proportions calculated on $\Sigma\text{Atoms} = 1$

S	0.493	0.656	0.504	0.004	0.001	0.001
Subtotal	0.493	0.656	0.504	0.004	0.001	0.001
Fe	0.253	0.340	0.001	0.013	0.021	0.013
Ni	--	--	--	--	0.001	0.001
Zn	--	--	0.001	--	--	--
Ag	--	--	-	0.264	0.217	0.250
Cu	0.253	0.003	--	0.019	0.029	0.019
Co	--	--	--	--	--	--
Pb	--	--	0.491	--	--	--
Au	--	--	0.001	0.699	0.729	0.717
Bi	--	--	--	--	0.002	-
Subtotal	0.506	0.343	0.494	0.995	1.000	1.000

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below analytical detection limit. *Silver concentrations calculated by stoichiometry due to technical problems with electron microprobe (presence of Ag confirmed in EDS).

The Paramount Occurrence

The Paramount occurrence on the Merico-Ethel property experienced significant exploration in the 1940's due to the presence of chalcopyrite-rich, quartz-calcite veins hosted in Nipissing Diabase (Moorhouse, 1944). The occurrence consists of two vein systems that are located approximately 260 metres apart. Little remains of the northern occurrence as a shaft was sunk on two northwest-trending veins and obliterated much of the exposure. The quartz-calcite veins were reported as being mineralized with an unidentified pyrite-like, cobalt-bearing mineral (possibly, cobaltian pyrite), chalcopyrite, and galena (*op. cit.*) Samples for the present study were collected from the waste pile of material removed from the old shaft, and also from a small trench located immediately to the south. The large hand sample collected from the waste pile consists of a narrow (≤ 4 cm) quartz-calcite vein that carries significant amounts of mineralization, comprising pseudomorphic chalcopyrite replacing euhedral pyrite and, trace amounts of bornite, cobaltite (from presence of erythrite), and hematite. The *in situ* specimen taken from the trench consists of a sample of a narrow quartz-calcite vein whose orientation is $292^{\circ}/80^{\circ}\text{N}$. The vein is rich in quartz and contains minor hematite, chalcopyrite, pyrite, and bornite. Both of the samples are hosted in medium-grained Nipissing Diabase; typically, with associated narrow (≤ 10 cm) 'aplitic' alteration halos (figure 2.23).

Figure 2.23. 'Aplitic' (*i.e.* albite+calcite+chlorite) alteration of Nipissing Diabase that is commonly associated with calcite-quartz veining at the Paramount occurrence. This hand specimen was observed in the waste pile of the northern showing of the Paramount occurrence.

Figure 2.24. BSE-image of atoll-textured chalcopyrite (cpy) replacing euhedral cobaltian pyrite (py); rimmed by cobaltite (cb). Sample# PARA-1a, the Paramount occurrence.

The southern occurrence was extensively stripped during mineral exploration, with a trench (approximately 100 metres in length) preserved on the site. Moorhouse (1944) reported that the trench exposed an easterly-striking, quartz-calcite vein that dipped steeply to the south. The vein itself ranged from 1 to 10 inches in width (2-25 cm) and mineralization was chiefly comprised of chalcopyrite with minor erythrite and malachite staining. Associated with the main vein were aplitic alteration halos and veinlets, up to 5 inches (~12 cm) in width (*op. cit.*). The author also reports that mineralization was occasionally noted in the aplitic alteration halos. Along the southern margin of the trench, concentric joints within the Nipissing Diabase exhibit some influence on the orientation of the mineralized veins system. However, most of the trench remains submerged under water and very little vein material remains intact, making field observations difficult. However, a secondary vein striking $354^{\circ}/80^{\circ}\text{E}$ which splay off the main vein system was sampled in the current study. The narrow vein (<5 cm) is calcite-rich and hosts minor chalcopyrite and cobaltite (erythrite) mineralization.

The ore and gangue mineral textures and mineralogy of the two mineralized vein occurrences at the Paramount occurrence are identical. Calcite is the dominant gangue mineral with lesser abundances of quartz and chlorite. Sulphide mineralization is dominated by chalcopyrite, which is typically pseudomorphic after cobalt-bearing pyrite (figure 2.24). The nature and extent of this replacement is visible in hand specimen and resembles zoning in the pyrite grains. Minor sulphide minerals include cobaltite, bornite, and galena. Representative analyses of the major sulphide minerals from the Paramount occurrence are listed in table 2.9. Cobaltite and galena occur as rims and fracture-

controlled replacements of chalcopyrite (figure 2.24). One small (~50 μ m) inclusion of native silver hosted in bornite was also noted. Much like the aplitic alteration that is present throughout the Merico property, the wallrock alteration at the Paramount occurrence consists of an assemblage of secondary albite, calcite, titanite, and zircon.

Table 2.9. Representative electron-microprobe analyses of the ore minerals present at the Paramount occurrence on the Merico-Ethel property.

	pyrite	pyrite	cobaltite	cobaltite	cobaltite	cobaltite	bornite	Nat. silver
Sample	par1a-3	par1a-1	para3-1	par1a-2	par1a-5	par1a-6	par2b-4	par2b-1
As	-	0.03	46.87	47.99	45.31	46.51	-	0.02
S	51.30	51.19	17.67	17.27	18.43	17.91	23.94	0.35
Fe	46.12	45.28	0.65	1.79	0.77	0.60	11.48	0.05
Co	1.78	2.45	23.11	24.04	29.53	30.25	-	0.02
Pb	-	-	-	-	-	-	-	0.04
Cu	-	-	0.35	0.58	0.61	0.02	64.15	0.56
Ni	0.02	0.04	10.95	9.59	5.35	3.90	-	0.04
Ag	-	-	0.08	-	0.02	-	0.08	97.28
Zn	-	-	0.01	-	-	0.01	0.01	-
Au	0.06	0.07	-	0.13	-	-	-	-
Bi	-	-	-	-	-	-	0.10	0.09
Total	99.28	99.06	99.69	101.39	100.02	99.20	99.76	98.45
Proportions calculated on $\Sigma\text{Atoms} = 1$								
As	0.000	0.000	0.353	0.357	0.337	0.351	0.000	0.000
S	0.650	0.651	0.311	0.300	0.320	0.316	0.380	0.012
Subtotal	0.650	0.651	0.664	0.658	0.657	0.666	0.380	0.012
Fe	0.336	0.331	0.007	0.018	0.008	0.006	0.105	0.001
Co	0.012	0.017	0.221	0.228	0.279	0.290	--	--
Pb	--	--	--	--	--	--	--	--
Cu	--	--	0.003	0.005	0.005	--	0.514	0.010
Ni	--	--	0.105	0.091	0.051	0.038	--	0.001
Ag	--	--	--	--	--	--	--	0.976
Zn	--	--	--	--	--	--	--	--
Au	--	--	--	--	--	--	--	--
Bi	--	--	--	--	--	--	--	--
Subtotal	0.350	0.348	0.336	0.342	0.343	0.334	0.620	0.988

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit.

The Beaver Pond Occurrence

The Beaver Pond occurrence on the Merico-Ethel property is located 600 metres southeast of the Paramount occurrence, on the eastern shore of a large beaver pond (figure 2.2). Some minor trenching and diamond drilling were completed in the late 1950's by Min-Ore Mines Limited, with one reported diamond drill core intersection of 7.5 feet (~2.3 m) of massive chalcopyrite (Johns, 1986). Since then, no development appears to have occurred on the site. During the property visit by the author, one 6 centimetre wide vein-breccia was observed hosted in the medium-grained, hypersthene-bearing variety of Nipissing Diabase; and a large waste pile containing material from trenching is also still present. The vein preserved in outcrop strikes to the east (080°), dips steeply to the south (84°), and consists of altered diabase clasts, sulphides, and hematite-rimmed quartz grains set in a matrix of calcite gangue (figure 2.25). Whilst the samples collected from the waste pile contain the same vein mineralogy and textures as those observed in the vein in outcrop, some of the waste pile samples are also hosted in small blocks of granophyric Nipissing Diabase. The latter typically occurs in the upper portions of the regionally-distributed mafic sills; it is characterized by the presence of pink alkali feldspar intergrown with quartz and amphibole laths that form at the expense of the pyroxene characteristic of the hypersthene variety of the Nipissing Diabase. In all the samples collected at the Beaver Pond occurrence, calcite is the dominant gangue mineral with lesser quantities of chlorite and brecciated quartz also being present. The vein mineralization is dominated by chalcopyrite, with lesser amounts of pyrite, hematite, and cobaltite also occurring (figure 2.26). Chalcopyrite is granular to glomeroporphyritic in texture within the veins, where it commonly forms aggregations that are several

Figure 2.25. Photographs of polished slabs of vein material from the Beaver Pond occurrence. Bright-red hematite typically rims early quartz grains, which appear to have been plucked from the vein margins. Chip sample# BV-01.

Figure 2.26. BSE images of: (A) Chalcopyrite partially replacing pyrite rimmed by a narrow band of cobaltite (co), therein creating an atoll-textured sulphide-sulpharsenide intergrowth (sample# BV-1a, Beaver Pond occurrence); (B) Chalcopyrite with an unnamed Cu-Sb-Sulphide (sb) inclusion rimmed by cobaltite (sample# BV-2a, Beaver Pond occurrence).

centimetres in diameter. Hematite occurs as bright-red, fine-grained rims along the vein margins and individual quartz fragments; and also as a specular variety that is typically associated with chalcopyrite. Textures in polished thin sections from the Beaver Pond occurrence samples mimic those observed in all of the other mineralized veins on the Merico property: with early pyrite being partially replaced by later chalcopyrite, which is in turn, is rimmed by late cobaltite (figure 2.26). When not pseudomorphic after pyrite, chalcopyrite is anhedral in habit and was noted in a few instances to contain inclusions of quartz and an unidentified Cu-Sb-sulphide (*possibly* chalcostibite: CuSbS_2). In contrast to most of the mineralized vein systems on the Merico property, pyrite in samples from the Beaver Pond occurrence does not contain significant amounts of cobalt, but rather displays minor enrichment in nickel (up to 1.38 wt.% Ni). Representative compositions of the major sulphide minerals observed in the Beaver Pond occurrence samples are presented in Table 2.10. From the ore and gangue mineral textures noted in the hand specimens, the Beaver Pond occurrence has experienced several episodes of vein formation and sulphide mineralization, with an early chlorite+quartz+calcite±sulphide mineral assemblage followed by a later stage of quartz+hematite+sulphide mineral+calcite deposition. Hematite crystallization appears to have followed quartz formation just before the second phase of sulphide precipitation.

Table 2.10. Representative electron-microprobe analyses of the main sulphide minerals that occur in samples from the Beaver Pond occurrence, which is located on the Merico-Ethel property.

Mineral	cobaltite	cobaltite	cobaltite	cobaltite	cobaltite	cobaltite	pyrite	pyrite
Sample #	BV2a-7	BV2a-3	BV2a-2	BV2a-8	BV2a-4	BV2a-9	BV1a-2	BV1a-3
As	42.10	42.87	42.36	44.55	43.27	43.57	-	0.02
S	20.06	20.07	20.33	18.40	18.50	19.42	52.35	52.29
Fe	3.65	2.96	2.58	4.07	3.71	2.36	46.47	46.88
Ni	0.81	0.89	0.94	1.18	3.76	4.62	0.47	1.38
Zn	0.02	0.01	0.01	0.01	-	0.01	0.03	-
Ag	0.04	-	-	-	-	-	-	-
Cu	0.87	0.36	0.49	0.11	0.11	1.42	-	0.08
Co	31.89	32.86	33.79	31.49	28.73	29.24	0.50	0.11
Au	0.02	0.05	0.05	0.07	-	-	-	0.14
Total	99.46	100.07	100.55	99.88	98.08	100.64	99.82	100.90

Proportions calculated on $\Sigma\text{Atoms} = 1$								
As	0.308	0.313	0.307	0.331	0.325	0.318	0.000	0.000
S	0.343	0.342	0.344	0.319	0.325	0.331	0.658	0.653
Subtotal	0.651	0.655	0.651	0.650	0.650	0.649	0.658	0.653

Fe	0.036	0.029	0.025	0.041	0.037	0.023	0.335	0.336
Ni	0.008	0.008	0.009	0.011	0.036	0.043	0.003	0.009
Zn	--	--	--	--	--	--	--	--
Ag	--	--	--	--	--	--	--	--
Cu	0.007	0.003	0.004	0.001	0.001	0.012	--	--
Co	0.297	0.305	0.311	0.297	0.275	0.272	0.003	0.001
Au	--	--	--	--	--	--	--	--
Subtotal	0.348	0.345	0.349	0.350	0.349	0.350	0.341	0.346

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical limit of detection.

The Sauvé Occurrence

Initially advanced as a copper prospect in the early 1900's, the Sauvé occurrence has a long history of mineral exploration. The occurrence is located in the northeast corner of the Merico-Ethel property (figure 2.2), along the contact between a dyke of Nipissing Diabase that has intruded into Gowganda Formation diamictite. Since the first mineral discovery in 1903, two diamond drill programs have intersected the Nipissing Diabase dyke, and several exploration trenches have been dug along its intrusive contact. One of the drill programs reported minor intersections of calcite veins containing chalcopryrite and specular hematite, yet no assay values were given and the claims were allowed to lapse. As noted by Johns (1986), the mineralization reportedly consists of chalcopryrite and bornite with abundant specular hematite, hosted in calcite veins and vein-breccias, along the contact of the diabase dyke with the Huronian sedimentary rocks and within the diabase dyke. Additional work in the 1950's exposed the southern contact of the diabase and revealed a 5-foot wide (~1.5 m) fracture zone containing pink calcite, chalcopryrite, bornite, pyrite, and abundant specular hematite. The chalcopryrite occurs in rounded and irregular shaped massive zones up to 10 centimetres wide. Interestingly, pitchblende was also found associated with chlorite in the some of the vein-breccias; with a sample of the radioactive material collected by the Ontario Geological Survey assaying 1.56 percent U_3O_8 equivalent (Johns, 1986). The samples collected during the current study consist of an intensely hematitized calcite vein-breccia with altered diabase fragments (figure 2.27) and a medium-grained Nipissing Diabase host. The hematitic sample is dominated by large calcite grains set in a mosaic of intergrown chlorite, calcite, and altered plagioclase laths.

Figure 2.27. Intensely hematitized sample of calcite vein-breccia with altered Nipissing Diabase fragments interspersed within boudinaged calcite veinlets from the Sauvé occurrence (sample# SV-002).

Figure 2.28. (A) Plane-polarized light photomicrograph of hematitic sample# SV-002 from the Sauvé occurrence, highlighting the presence of barren calcite-quartz veinlets cross-cutting an altered diabase host comprised of cloudy albite, green chlorite, and abundant interstitial rutile and hematite (opaques). (B) Cross-polarized light photomicrograph of the same section, illustrating the presence of radial feldspars in the centre of the image, above the calcite-quartz veinlet. The field of view in both images is 2.5 mm.

The plagioclase laths have abundant fine-grained sericite and chlorite alteration. Aside from the boudinaged and brecciated calcite veinlets, the sample is composed of approximately 50 modal % plagioclase, 25-30 modal % chlorite, 15 modal % calcite, 5 modal % accessory phases, and trace interstitial quartz (figure 2.28). The dominant accessory phases include: rutile, hematite, apatite, zircon, and pyrite. The fine-grained rutile occurs interstitial to the plagioclase laths throughout the sample and constitutes approximately 2 volume percent. In hand specimen (figure 2.27) the altered material preserves some igneous textures and is thought to represent highly altered Nipissing Diabase. In thin section, radial growths of feldspar are similar to those typically noted from the quartz-diorite zone of the Nipissing Diabase (Jambor, 1971*b*). The rutile likely formed in response to the breakdown of titanium-bearing augite and ilmenite that were originally present in Nipissing Diabase. Thorough petrographic examination did not reveal the presence of any copper or uranium-bearing minerals. Sampling of the diorite host revealed a mildly altered, medium-grained Nipissing Diabase of the hypersthene variety, with laths of orthopyroxene and clinopyroxene set in a highly sericitized and saussuritized feldspathic groundmass. The pyroxenes have been partially altered to uraltite, in some cases creating a corona texture. Whilst augite is the dominant clinopyroxene present, some grains of Ti-bearing augite were also noted. In the groundmass, secondary chlorite and abundant hematite, pyrite, ilmenite, and magnetite (1-2%) occur interstitial to the pyroxenes. The alteration that is present is characteristic of that resulting from deuteric, rather than hydrothermal processes, and is typical of that which is present in most phases of the Nipissing Diabase (Jambor, 1971*b*).

The Beaver Auxiliary Mine

Whilst not located within the confines of the Merico-Ethel property, the nearby Beaver Auxiliary Mine is strikingly similar, mineralogically and texturally, to the Merico vein systems. Located approximately 7.5 kilometres west of the main Merico vein system, the Beaver Auxiliary mine is hosted in medium-grained Nipissing Diabase, which has intruded Gowganda Formation (Huronian) sedimentary rocks. According to MacKean (1968), a diamond drill program confirmed the (true) thickness of the Nipissing Diabase sill, at the Beaver Auxiliary Mine, to be approximately 760 feet (~230 m) from the present day surface. The drill program was planned to continue through the Gowganda diamictite to the granitic basement, but the results were never published (*op. cit.*). The property experienced significant development beginning in 1912 and operated in intervals until 1928. During this period, three shafts, several trenches, and significant underground working were developed. Despite the extensive workings, the property is currently covered by thick alder growth, which has developed following more recent logging activities. As a result, no veins were encountered in outcrop, and only one waste pile (associated with the No.1 shaft) was sampled during the current study. During a site visit, MacKean (1968) was able to locate four significant veins in outcrop. Much like those on the Merico-Ethel property, the dominant vein orientations are: north-south (vein 1), northeast-southwest (vein 2), northwest-southeast (possibly vein 3) and east-west (vein 4). Mineralization reportedly consists of chalcopyrite, galena, bornite, niccolite, smaltite (?), and native silver in veins ranging from 1 to 8 inches in width (*op. cit.*). Reported silver grades reached 5,000 to 6,000 ounces silver per ton (>140,000 g/t Ag) over 3 inches in some of the underground workings (Canadian Mining Journal, 1913, p.

623). Samples collected in this study consist of calcite-quartz veins and vein-breccias (4 to 8 cm wide) with sporadic development of chalcopyrite, pyrite, galena, and cobaltite mineralization. Calcite has a predominantly rose colour, often due to the presence of minute inclusions of hematite. Quartz content is minor in the veins, where it is often limited to thin vein selvages and small chlorite-rich zones rimming sulphides. The veins are typically hosted in the hypersthene and granophyric varieties of the Nipissing Diabase, vein mineralization consists of chalcopyrite, galena, pyrite, cobaltite, and specular hematite. Although no grains of native silver or electrum were observed, one inclusion of an Ag-Fe-sulphide mineral [possibly argentopyrite (AgFe_2S_3) or lenaite (AgFeS_2)] was noted within chalcopyrite. Representative sulphide compositions of the ore minerals are presented in table 2.11. Petrography reveals that early euhedral pyrite is partially replaced by chalcopyrite and/or sphalerite (figure 2.29A). Following chalcopyrite crystallization, galena was deposited along fractures and growth zones in pyrite (figure 2.29B). This late-stage galena mineralization is visible in hand specimen (figure 2.30) and makes field identification of the earlier sulphide mineralogy difficult. The replacement textures are very similar to those observed from the Silver Jackpot mine (compare figures 2.19A and 2.29B), albeit with increased amounts of galena mineralization. Cobaltite forms discontinuous rims on pyrite and subhedral grains set in calcite. Where not disturbed by brecciation, the original zoning in the veins consists of a thin quartz+chlorite±sulphide selvage followed by hematite+calcite±sulphide core. As shown in figure 2.30, the vein-breccias consist of fragments of the early quartz-chlorite-sulphide units set in coarse-grained calcite gangue.

Table 2.11. Representative electron-microprobe analyses of the major ore minerals in vein samples from the Beaver Auxiliary mine site, Merico-Ethel property.

Mineral	pyrite	pyrite	pyrite	pyrite	lenaite?	cobaltite	cobaltite	sphalerite
Sample	MT1a-1	MT1A-4	MT1A-2	MT3-3	MT2a-1	MT2a-5	MT4-3	MT4-2
As	-	0.08	0.02	0.04	-	43.89	42.97	-
S	52.28	51.84	51.99	52.85	40.44	19.28	20.34	32.20
Fe	46.93	45.43	45.13	44.86	33.66	5.55	2.80	0.50
Ni	0.33	0.05	0.03	-	0.02	0.04	2.59	-
Zn	-	-	-	-	-	0.02	0.07	66.46
Ag	-	0.03	-	0.04	20.35	-	-	0.01
Cu	0.03	0.02	-	0.05	-	0.01	0.02	0.12
Co	0.21	1.88	2.15	3.46	0.34	30.26	31.69	0.16
Au	-	-	-	-	0.05	-	-	-
Bi	-	-	0.08	0.08	0.14	-	-	-
Total	99.78	99.33	99.40	101.38	95.00	99.05	100.48	99.45

Proportions calculated on $\sum \text{Atoms}=1$

As	--	--	--	--	--	0.325	0.311	--
S	0.657	0.656	0.657	0.656	0.612	0.334	0.345	0.494
Subtotal	0.657	0.656	0.657	0.656	0.612	0.659	0.656	0.494
Fe	0.339	0.330	0.328	0.320	0.293	0.055	0.027	0.004
Ni	0.002	--	--	--	--	--	0.024	-
Zn	--	--	--	--	--	--	0.001	0.500
Ag	--	--	--	--	0.092	--	--	--
Cu	--	--	--	--	--	--	--	0.001
Co	0.001	0.013	0.015	0.023	0.003	0.285	0.292	0.001
Au	--	--	--	--	--	--	--	--
Bi	--	--	--	--	--	--	--	--
Subtotal	0.342	0.343	0.343	0.343	0.388	0.340	0.344	0.506

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical limit of detection.

Figure 2.29. BSE-images of: (A) Chalcopyrite (cpy) and galena (gl) partially infilling fractured pyrite. Note that galena is preferentially associated with pyrite yet followed chalcopyrite precipitation (sample# MT-03, Beaver Auxiliary mine); (B) Near-complete replacement of pyrite by galena, chalcopyrite, and sphalerite (sp) (sample# MT-04, Beaver Auxiliary mine). Calcite is the gangue mineral host in both images.

Figure 2.30. Polished hand specimen (sample# MT-04) from the Beaver Auxiliary mine site highlighting the significant replacement of sub-euhedral to euhedral pyrite by galena; hosted in white calcite gangue. Dark grey areas are areas of quartz and chlorite-rich gangue.

2.3 The Gowganda and Cobalt Mining Camps

In order to accurately relate historical data from the Cobalt and Gowganda mining camps with those of the current study, numerous historical silver occurrences with reported gold mineralization were sampled. Historical mines from the Gowganda area sampled in the current study include: the Bishop, Capital, Mann, and Parcher Brothers mines (figure 2.31). In addition, a newly discovered vein occurrence on Duncan Lake (located immediately northwest of the town of Gowganda) was sampled. Historical occurrences from the Cobalt area that were sampled include: the Bay, Gosselin (north and south showings), and Temagami-Lorrain mines. Archival material catalogued at Carleton University incorporated in the current study included: samples from the Brady Lakes, Bruce, Beaver-Temiskaming, Pan Silver, Silverside, and Silverfields mines.

The silver deposits from the Gowganda and Cobalt camps occur in steeply to vertical dipping calcite-quartz veins systems in close proximity to the Archean-Huronian unconformity. The veins are hosted primarily in Nipissing Diabase and less frequently, in Archean volcanic basement rocks and Huronian sedimentary rocks (Andrews *et al.*, 1986a). The veins are characterized by a complex ore mineral assemblage comprised of native silver, arsenides, and sulphurarsenides of cobalt, nickel, iron, bismuth, and subordinate concentrations of antimonides and sulphides of lead, zinc, and copper (Petruk, 1971b). The ore veins are commonly zoned vertically with respect to the sills of Nipissing Diabase, with distinctive Ni-As, Ni-Co-As, Co-Fe-As, Fe-As, and Co-As assemblages. The highest grades of silver mineralization reportedly occur in the Ni-bearing assemblages (Marshall and Watkinson, 2000). Gangue mineralogy is dominated by calcite, with lesser abundances of dolomite, quartz, chlorite, actinolite, epidote,

potassium feldspar, and albite (Andrews *et al.*, 1986a). Jambor (1971d) also noted trace amounts of accessory titanite, allanite-Ce, apatite, anatase, axinite, stilpnomelane, prehnite, and garnet in the mineralized veins. The latter are typically characterized by three variations in morphology: *i*) simple dilatant (open-space filling), *ii*) sheared, and *iii*) replacement veins; all of which may be present in a single ore structure. The less common replacement veins occur as discrete, linear zones of intense carbonate alteration (Andrews *et al.*, 1986a). Hydrothermal wall-rock alteration is minor, often limited to several centimetres in width, with a general depletion in Si and enrichment in Ca, Na, and CO₂ (Marshall and Watkinson, 2000). Aplitic dykes and aplitic alteration zones are ubiquitous throughout the Gowganda and Cobalt silver camps, although as Jambor (1971e) notes, they are most abundant where silver mineralization is less prominent. In mineralized aplitic dykes, the paragenetic sequence indicates that the ore minerals are a late phase of the aplitic dykes. An idealized zoning within the calcite-quartz silver veins consists of: *i*) a thin silicate selvage comprised of quartz, chlorite $\pm$ actinolite $\pm$ potassium feldspar; *ii*) the main stage of ore deposition; and finally, *iii*) the carbonate minerals calcite $\pm$ dolomite (Andrews *et al.*, 1986a). The ore minerals typically form discrete bands and fine disseminations associated with the early silicates or as compact masses in the center of the vein (Andrews *et al.*, *op.cit.*). The petrographic studies of Petruk (1971b), Jambor (1971d), and Goodz *et al.*, (1986) indicated that the main phase of silver mineralization accompanied and slightly post-dated the arsenide and sulphurarsenide phase of mineral deposition. Sulphides followed the main phase of ore deposition, preceding the main stage of calcite deposition. A sampling of the ore minerals reported in the aforementioned studies include: pyrite, chalcopyrite, safflorite, cobaltite,

gersdorffite, arsenopyrite, native silver, native gold, native bismuth, wittichenite, galena, galenobismuthinite, bismuthinite, acanthite, argentite, sphalerite, bravoite $[(\text{Co},\text{Ni},\text{Fe})\text{S}_2]$ and linnaeite series minerals. Representative compositions of the dominant ore minerals (cobaltite, pyrite, arsenopyrite, galena, bismuthinite, galenobismuthinite, emplectite, wittichenite, sphalerite, safflorite and argentite) encountered during this study are presented below in tables 2.12, 2.13, 2.14, and 2.15. Textures observed in thin section suggest that some of the sulphides precipitated at the same time, or prior to, cobaltite (figure 2.32A). Lead and bismuth-bearing minerals typically formed during the final phase of sulphide mineralization, and are often found rimming late chalcopyrite and/or precipitating in fractures in sulphide minerals (figure 2.33). An interesting accessory mineral found in many of the mineralized vein systems in the Cobalt and Gowganda camps is allanite-Ce. As is illustrated in figure 2.32B, the allanite-Ce appears to have precipitated during the sulphide phase of mineralization. Much like the Merico-Ethel property, allanite-Ce has been indentified in host Coleman sediments in the vicinity of mineralized vein systems at Cobalt (Little Silver Vein; Venance, 1989).

Figure 2.31. The location of the historical silver mines and newly-discovered Duncan Lake occurrence within the Cobalt Embayment. Mines sampled from the Cobalt camp include: the Brady Lakes, Bruce, Beaver-Temiskaming, Pan Silver, Silverside, and Silverfields mines. Mines sampled from the Gowganda camp include (north to south): the Capital, Bishop, Mann, Parcher, and Reeve-Dobie mines.

Table 2.12. Representative electron-microprobe analyses of cobaltite from the historical vein occurrences of the Gowganda and Cobalt camps.

Sample #	pr2b-5	bay3-2	rv1c-2	bay3-6	tm1a-4	bp1b-2	mn4-6	gs6a-8
As	44.56	46.10	47.46	44.85	46.47	45.14	45.87	45.69
S	18.97	19.06	18.13	19.25	17.94	19.64	17.98	19.45
Fe	0.48	0.88	1.68	3.37	3.20	4.90	6.10	9.16
Co	28.55	33.78	27.75	28.94	24.30	30.04	19.16	14.07
Cu	-	-	0.01	-	0.02	0.05	-	-
Ni	7.61	-	4.92	4.03	8.09	0.51	9.83	10.73
Ag	-	-	0.02	-	0.04	-	-	0.10
Mn	-	-	-	-	-	-	-	-
Zn	0.05	0.01	-	-	-	0.06	0.01	-
Au	-	-	-	-	0.04	-	0.18	-
Total	100.22	99.83	99.97	100.44	100.10	100.34	99.13	99.20

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	0.329	0.342	0.355	0.329	0.347	0.331	0.345	0.338
S	0.327	0.331	0.317	0.330	0.313	0.336	0.316	0.336
Subtotal	0.656	0.673	0.672	0.659	0.660	0.667	0.661	0.674
Fe	0.005	0.009	0.017	0.033	0.032	0.048	0.062	0.091
Co	0.268	0.319	0.264	0.270	0.231	0.280	0.183	0.132
Cu	--	--	--	--	--	--	--	--
Ni	0.072	0.000	0.047	0.038	0.077	0.005	0.094	0.101
Ag	--	--	--	--	--	--	--	0.001
Mn	--	--	--	--	--	--	--	--
Zn	--	--	--	--	--	0.001	--	--
Au	--	--	--	--	--	--	0.001	--
Subtotal	0.345	0.328	0.328	0.341	0.340	0.334	0.340	0.325

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below analytical detection limit. Abbreviations: pr = Parcher Brothers Mine; bay = Bay Mine; rv = Reeve-Dobie Mine; tm = Temagami-Lorrain Mine; bp = Bishop Mine; mn = Mann Mine; and gs = Gosselin Mine.

Table 2.13. Representative electron-microprobe analyses of pyrite and arsenopyrite from historical vein occurrences of the Gowganda and Cobalt camps.

Mineral	aspy	aspy	aspy	pyrite	pyrite	pyrite	pyrite	pyrite
Sample #	bay4-5	tm2-6	tm2-13	gs2-1	mn3-3	mn3-5	mn4-14	rv2a-1
As	43.81	44.61	42.90	-	0.20	0.16	0.18	0.03
S	19.91	19.73	22.00	51.47	52.96	52.68	53.37	52.97
Fe	36.45	35.84	34.85	47.63	46.69	46.31	47.18	46.81
Co	0.02	0.26	1.47	0.11	0.17	0.13	0.50	0.12
Ni	-	0.03	0.06	-	0.45	0.18	0.20	0.01
Ag	-	0.03	0.06	0.03	-	0.00	0.01	0.03
Zn	0.03	0.07	-	0.15	-	-	-	0.01
Au	0.08	-	0.23	0.20	0.02	-	-	0.06
Total	100.30	100.57	101.57	99.59	100.49	99.46	101.44	100.04

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	0.314	0.320	0.299	--	0.001	0.001	0.001	--
S	0.334	0.331	0.359	0.652	0.660	0.663	0.660	0.662
Subtotal	0.648	0.651	0.658	0.652	0.661	0.664	0.661	0.662
Fe	0.351	0.345	0.326	0.346	0.334	0.334	0.335	0.336
Co	--	0.002	0.013	0.001	0.001	0.001	0.003	0.001
Ni	--	--	0.001	--	0.003	0.001	0.001	--
Ag	--	--	--	--	--	--	--	--
Zn	--	0.001	--	0.001	--	--	--	--
Au	--	--	0.001	--	--	--	--	--
Subtotal	0.351	0.348	0.343	0.348	0.338	0.336	0.339	0.337

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit. Abbreviations: aspy = arsenopyrite; bay = Bay Mine; rv = Reeve-Dobie Mine; tm = Temagami-Lorrain Mine; mn = Mann Mine; and gs = Gosselin Mine.

Table 2.14. Representative electron-microprobe analyses of bismuth-bearing minerals from historical vein occurrences of the Gowganda and Cobalt camps.

Mineral	BiS	BiS	glBi	glBi	glBi	empl	empl	empl	witt
Sample #	gs8-1	gs8-2	gs8-6	gs9a-7	gs9a-8	tm2-1	tm2-12	tm2-14	tm2-2
As	0.02	-	2.88	-	0.03	0.02	0.06	0.04	0.01
S	19.25	19.58	17.12	17.68	17.58	18.32	19.52	19.02	17.94
Fe	-	0.01	1.75	-	-	0.08	0.18	0.30	0.07
Co	-	0.01	2.06	-	-	0.13	0.64	0.23	0.21
Pb	0.25	-	16.83	27.47	27.41	-	-	-	-
Cu	0.30	0.32	1.10	0.03	0.05	18.04	18.87	19.00	35.28
Ni	0.02	0.02	1.48	0.03	-	0.01	0.07	0.03	0.02
Ag	-	0.12	8.80	0.04	-	0.03	-	0.09	0.11
Zn	0.03	0.04	-	-	-	0.01	-	-	-
Au	0.07	0.04	0.18	-	0.21	0.02	-	0.26	0.07
Bi	81.76	81.45	46.70	51.78	52.11	61.64	60.97	61.02	42.12
Te	-	-	-	-	-	-	-	-	-
Total	101.70	101.59	98.90	97.03	97.39	98.30	100.31	99.99	95.83

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	--	--	0.036	--	--	--	0.001	--	--
S	0.601	0.606	0.500	0.591	0.588	0.495	0.502	0.496	0.423
Subtotal	0.601	0.606	0.536	0.591	0.588	0.495	0.503	0.496	0.423
Fe	--	--	0.029	--	--	0.001	0.003	0.005	0.001
Co	--	--	0.033	--	--	0.002	0.009	0.003	0.003
Pb	0.001	--	0.076	0.142	0.142	--	--	--	--
Cu	0.005	0.005	0.016	0.001	0.001	0.246	0.245	0.250	0.420
Ni	--	--	0.024	0.001	--	--	0.001	--	--
Ag	--	0.001	0.076	--	--	--	--	0.001	0.001
Zn	--	0.001	--	--	--	--	--	--	--
Au	--	--	0.001	--	0.001	--	--	0.001	--
Bi	0.392	0.387	0.209	0.266	0.268	0.255	0.240	0.244	0.152
Te	--	--	--	--	--	--	--	--	--
Subtotal	0.398	0.394	0.464	0.410	0.412	0.504	0.498	0.504	0.577

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit. Abbreviations: BiS = bismuthinite; glBi = galenobismuthinite; Bi = native bismuth; empl = emplectite; witt = wittichenite; tm = Temagami-Lorrain Mine; gs = Gosselin Mine.

Table 2.15. Representative electron-microprobe analyses of sphalerite, galena, safflorite, and argentite from historical vein occurrences of the Gowganda and Cobalt camps.

Mineral	sphalerite	sphalerite	sphalerite	galena	safflorite	safflorite	safflorite	argentite
Sample #	gs6a-7	gs1-3	gs1-1	rv1c-5	mn5-1	CP2-1	CP2-6	gs5-4
As	0.02	-	0.02	0.01	71.15	70.03	70.50	-
S	32.75	31.08	31.98	13.81	0.50	1.08	1.02	13.61
Fe	5.19	6.36	4.64	-	13.06	10.70	11.71	0.58
Co	0.04	0.19	0.17	-	13.66	18.61	16.96	-
Pb	-	-	-	86.73	0.07	-	-	-
Cu	0.29	0.37	0.21	-	0.01	0.09	0.04	2.63
Ni	0.01	0.02	-	0.01	0.81	0.41	0.41	-
Ag	0.05	-	0.02	0.21	-	-	0.01	81.41
Zn	63.58	60.55	63.63	-	-	-	0.02	-
Au	-	-	-	-	-	0.03	-	0.05
Bi	-	-	-	-	-	-	-	-
Total	101.93	98.57	100.67	100.77	99.26	100.95	100.67	98.28

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	--	--	--	--	0.657	0.630	0.637	--
S	0.488	0.480	0.484	0.506	0.011	0.023	0.021	0.345
Subtotal	0.488	0.480	0.484	0.506	0.668	0.653	0.658	0.345
Fe	0.044	0.056	0.040	--	0.162	0.129	0.142	0.008
Co	--	0.002	0.001	--	0.160	0.213	0.195	--
Pb	--	--	--	0.492	--	--	--	--
Cu	0.002	0.003	0.002	--	--	0.001	--	0.034
Ni	--	--	--	--	0.009	0.005	0.005	--
Ag	--	--	--	0.002	--	--	--	0.613
Zn	0.465	0.459	0.472	--	--	--	--	--
Au	--	--	--	--	--	--	--	--
Bi	--	--	--	--	--	--	--	--
Subtotal	0.511	0.520	0.515	0.494	0.331	0.348	0.342	0.655

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit. Abbreviations: gs = Gosselin Mine; rv = Reeve-Dobie Mine; mn = Mann Mine; and CP = Capital Mine.

Figure 2.32. BSE-images of: (A) cobaltite (co) rimming nickel- and cobalt-bearing pyrite (py) (sample# mn-3, Mann mine); and (B) anhedrall allanite-Ce (al) rimming chalcopyrite (cpy) (sample# mn-4, Mann mine). The gangue in both BSE-images is calcite.

Figure 2.33. BSE-images of: (A) galenobismuthinite (glBi) partially replacing chalcopyrite which contains inclusions of cobaltite (sample# gs-9a, Gosselin mine); and (B) brecciated, granular cobaltite (co) and pyrite (py) included in later chalcopyrite (cpy) and emplectite (em) (sample# tm-2, Temagami-Lorrain mine).

Duncan Lake Occurrence

The Duncan Lake vein system lies immediately northwest of the town of Gowganda (figure 2.31), on the southeast shoreline of Duncan Lake. Recently discovered by local prospectors, the vein system contains visible galena, chalcopyrite, pyrite and cobaltite mineralization (and reportedly trace gold concentrations) in a calcite-quartz vein system that strikes 070°-080°, while dipping steeply to the south (80°). The main vein is up to 10 centimetres in width and splays into at least two smaller vein systems less than 5 centimetres in width. The calcite-quartz veins sharply cross-cut medium-grained Nipissing Diabase and display open-space filling and sheared textures. As illustrated by figure 2.34, zoning in the vein systems consists of: *i*) a quartz + chlorite-rich margin; *ii*) a band of the main ore minerals; and *iii*) coarse-grained calcite. Much like the historical silver deposits of Cobalt and Gowganda, the main stage of sulphur and sulpharsenide deposition occurs along the transition from silicate to calcite gangue. In thin section, the ore minerals are dominated by galena (with up to 0.75 wt.% Ag), cobaltite, chalcopyrite, pyrite, gersdorffite, sphalerite, and minerals of the aikinite-bismuthinite series. Representative electron microprobe analyses of the main ore minerals are presented in tables 2.16, 2.17, and 2.18. Accessory phases included in the quartz, chlorite, and calcite gangue consist of iron-oxides, allanite-Ce, rutile, titanite, andradite, and zircon. As illustrated in figure 2.35, pyrite was the first ore mineral to crystallize, followed by chalcopyrite, and late-stage galena + bismuth-bearing minerals. The unusual aikinite-bismuthinite series minerals occur associated with chalcopyrite and galena (figure 2.36), and less frequently, as inclusions (in fractures) in chalcopyrite.

Figure 2.34. Photograph of a polished sample of vein material from the Duncan Lake occurrence, highlighting the presence of zoning within the main vein: *i*) silicate vein selvage comprising quartz+chlorite; *ii*) a narrow band of ore minerals, principally galena; and *iii*) coarse-grained calcite (cc). Sample# DUNC-8. Abbreviations: qtz = quartz, chl = chlorite, gl = galena, cc = calcite.

Table 2.16. Representative electron-microprobe analyses of cobaltite from the Duncan Lake vein system.

Sample #	dnc2-3	dnc2-4	dnc2-7	dnc2-8	dnc3-4	dnc6-6	dnc6-7	dnc6-8
As	45.15	44.16	44.34	45.57	44.02	44.08	43.86	44.29
S	19.35	19.15	19.13	19.05	18.87	18.80	19.48	19.06
Fe	2.86	1.24	2.52	2.50	3.45	1.64	1.70	1.51
Co	31.80	32.22	33.79	32.33	25.49	32.48	32.74	32.42
Se	0.38	0.39	0.25	0.45	0.20	-	-	-
Pb	-	-	-	-	1.14	-	-	-
Cu	0.03	-	0.02	0.02	0.11	-	0.02	0.01
Ni	1.18	1.98	0.06	1.06	5.67	2.21	1.60	2.48
Ag	0.04	-	-	0.05	0.06	-	0.01	0.03
Mn	0.01	0.02	-	0.02	-	-	-	-
Zn	-	0.01	-	0.02	-	-	-	-
Total	100.79	99.18	100.12	101.06	98.99	99.21	99.39	99.81

Proportions calculated on $\Sigma \text{Atoms} = 1$

As	0.331	0.328	0.327	0.334	0.331	0.328	0.324	0.327
S	0.331	0.333	0.329	0.326	0.331	0.327	0.336	0.329
Subtotal	0.662	0.661	0.656	0.660	0.662	0.655	0.660	0.657
Fe	0.028	0.012	0.025	0.025	0.035	0.016	0.017	0.015
Co	0.296	0.305	0.316	0.301	0.243	0.307	0.307	0.305
Se	0.003	0.003	0.002	0.003	0.001	--	--	--
Pb	--	--	--	--	0.003	--	--	--
Cu	--	--	--	--	0.001	--	--	--
Ni	0.011	0.019	0.001	0.010	0.054	0.021	0.015	0.023
Ag	--	--	--	--	--	--	--	--
Mn	--	--	--	--	--	--	--	--
Zn	--	--	--	--	--	--	--	--
Subtotal	0.338	0.339	0.344	0.339	0.338	0.345	0.339	0.343

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit. Abbreviation: dnc = Duncan Lake.

Table 2.17. Representative electron-microprobe analyses of the major sulphide minerals from the Duncan Lake vein system.

Mineral	sphalerite	sphalerite	pyrite	pyrite	pyrite	pyrite	pyrite	pyrite
Sample #	dnc2-10	dnc2-11	dnc3-1	dnc6-9	dnc2-12	dnc6-1	dnc6-4	dnc6-5
As	-	-	-	0.02	0.38	0.12	0.04	0.05
S	32.19	32.09	52.94	52.89	52.59	53.33	52.89	52.87
Fe	0.95	0.86	46.39	47.50	43.83	47.56	48.24	47.40
Co	0.02	0.03	-	0.01	0.04	0.31	0.10	0.07
Pb	-	-	-	-	-	-	-	-
Cu	0.16	0.06	-	-	-	-	-	-
Ni	-	-	-	0.02	1.74	-	0.01	0.01
Ag	-	0.01	0.01	0.01	0.04	0.02	-	0.01
Mn	-	0.01	-	-	-	-	-	-
Zn	65.58	65.91	-	-	0.04	0.02	-	0.03
Bi	-	0.03	-	0.08	-	-	-	0.04
Total	98.89	99.00	99.33	100.53	98.64	101.35	101.28	100.48

Proportions calculated on $\Sigma \text{Atoms} = 1$

As	-	-	-	-	0.002	0.001	-	-
S	0.495	0.494	0.665	0.658	0.665	0.659	0.656	0.659
Subtotal	0.495	0.494	0.665	0.665	0.668	0.660	0.656	0.659
Fe	0.008	0.008	0.334	0.339	0.318	0.338	0.343	0.339
Co	--	--	--	--	--	0.002	0.001	0.001
Pb	--	--	--	--	--	--	--	--
Cu	0.001	--	--	--	--	--	--	--
Ni	--	--	--	--	0.012	--	--	--
Ag	--	--	--	--	--	--	--	--
Mn	--	--	--	--	--	--	--	--
Zn	0.495	0.498	--	--	--	--	--	--
Bi	--	--	--	--	--	--	--	--
Subtotal	0.504	0.505	0.334	0.339	0.331	0.340	0.344	0.340

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit. Abbreviation: dnc = Duncan Lake.

Table 2.18. Representative electron-microprobe analyses of galena, gersdorffite, and aikinite-bismuthinite from the Duncan Lake vein system.

Mineral	galena	galena	gs	gs	ai-BiS	ai-BiS	ai-BiS
Sample #	dnc2-5	dnc2-6	dnc3-2	dnc3-3	dnc5-6	dnc5-7	dnc5-8
As	0.02	0.01	48.66	46.20	0.01	0.01	0.01
S	13.40	13.40	16.19	17.86	17.60	18.13	16.95
Fe	0.24	0.24	6.71	2.84	1.67	2.95	0.91
Co	0.04	0.02	12.68	20.14	0.01	0.02	0.01
Se	0.02	-	0.25	0.25	0.29	0.23	0.41
Pb	83.81	84.78	-	-	17.32	17.22	33.54
Cu	0.03	-	0.55	0.82	11.43	11.66	10.99
Ni	0.02	-	13.99	12.15	-	-	0.01
Ag	0.44	0.54	0.02	0.04	1.36	1.62	0.02
Mn	0.01	0.01	0.01	0.03	-	0.01	0.01
Zn	0.04	-	-	0.01	0.05	-	-
Bi	-	-	-	0.07	48.71	46.10	34.57
Total	98.07	98.99	99.05	100.41	98.43	97.96	97.42

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	--	--	0.373	0.344	--	--	--
S	0.501	0.499	0.290	0.311	0.502	0.503	0.503
Subtotal	0.501	0.499	0.663	0.655	0.503	0.503	0.503
Fe	0.005	0.005	0.069	0.028	0.027	0.047	0.015
Co	0.001	--	0.124	0.191	--	--	--
Se	--	--	0.002	0.002	0.003	0.003	0.005
Pb	0.485	0.489	-	-	0.077	0.074	0.154
Cu	0.001	--	0.005	0.007	0.165	0.163	0.165
Ni	--	--	0.137	0.116	--	--	--
Ag	0.005	0.006	--	--	0.012	0.013	--
Mn	--	--	--	--	--	--	--
Zn	0.001	--	--	--	0.001	--	--
Bi	--	--	--	--	0.213	0.196	0.157
Subtotal	0.497	0.500	0.336	0.344	0.497	0.496	0.497

Note. All elemental concentrations are reported in weight percent (wr%). [-] = below the analytical detection limit. Abbreviations: gs = gersdorffite; ai-BiS = aikinite-bismuthinite series minerals; dnc = Duncan Lake.

Figure 2.35. BSE-images of: (A) chalcopyrite (cpy) and galena (gl) partially replacing earlier pyrite (py), hosted in calcite and quartz gangue (sample# DUNC-3, Duncan Lake occurrence); and (B) early pyrite (py) partially replaced by chalcopyrite (cpy) and galena (gl) (sample# DUNC-6, Duncan Lake occurrence).

Figure 2.36. BSE-images of: (A) aikinite-bismuthinite (ai) associated with chalcopyrite (cpy) containing tiny inclusions of galena, all set in quartz gangue (sample# DUNC-5, Duncan Lake occurrence); and (B) zoned, euhedral andradite garnet (andr) and sub-euhedral allanite-Ce (al) grains set in calcite gangue (cc) (sample# DUNC-6, Duncan Lake occurrence).

2.4 The Brett Occurrence

The newly-discovered Brett occurrence, situated on the Brett property, consists of a few boulders and one possible outcrop of high-grade gold mineralization set in a calcite-quartz vein system with mineralogical and textural features common to the Cobalt-Gowganda silver vein deposits. A chip sample of the vein material from the initial discovery boulder produced assay results of 6,222 g/t Au (Temex Resources, 2004). The initial discovery is located in Gilles Township, just south of the town of Latchford (figure 2.37), along the northeast margin of an outlier of Archean mafic volcanics. As shown in figure 2.38, the property lies along the western margin of the Lake Temiskaming Structural Zone (LTSZ), a proposed graben structure that was likely initiated during the Archean and has been reactivated several times including post-intrusion of the Nipissing Diabase (Wilson, 1949; Symons, 1970; Card *et al.*, 1973; Morris, 1981; Sage, 1996). Despite numerous attempts, discovery of additional *in situ* vein mineralization has proven to be unsuccessful. The Brett samples are characterized by a gangue mineral assemblage dominated by calcite, with lesser abundances of interstitial epidote, actinolite, and chlorite. The samples display relatively consistent ore mineralogy comprised of visible native gold (figure 2.39), cobaltite, pyrite, pyrrhotite, pentlandite, chalcopyrite, and some unusual Bi-Te-sulphides (Taylor 2004b; Potter, 2007).

Figure 2.37. Location of the Brett property, along the central-eastern margin of the Cobalt Embayment, just south of the town of Latchford. Abbreviations: RLB = Round Lake Batholith; SIC = Sudbury Igneous Complex.

Figure 2.38. Regional geology map of the Brett occurrence, highlighting the proximity of the mineralized vein system to the margin of the Lake Temiskaming Structural Zone (LTSZ) and the historic Cobalt mining camp.

Figure 2.39. Photographs of high-grade sample# BRT-02 from the discovery boulder at the Brett occurrence, illustrating the abundant native gold mineralization in calcite vein/s containing clasts of the fine-grained mafic host rocks.

In polished thin section, the gangue of the veins is comprised of calcite with trace amounts of epidote, chlorite, and actinolite. Compositionally, the calcite has low concentrations of magnesium, iron, and manganese (<0.75 wt.%; table 2.19). Epidote compositions are very uniform throughout the veins, with no significant manganese content (table 2.20). A few grains with an increased concentration of rare-earth elements (REE) were noted from petrographic studies, suggesting some enrichment of the epidote in the allanite-Ce end-member. The compositions of amphibole crystals present within the veins are dominated by those of intermediate actinolite, with minor variations in Fe and Mg content (table 2.21). Pyrite is the dominant ore mineral in the veins with lesser abundances of cobaltite, native gold, pentlandite, arsenopyrite, and unusual Bi-Te-sulphide minerals such as: aleksite $[(\text{Pb,Bi})\text{Bi}_2\text{Te}_2\text{S}_2]$, galenobismutite $[(\text{Pb,Bi})_3\text{S}_4]$, tellurobismuthite $[\text{Bi}_2\text{Te}_3]$ and native bismuth (tables 2.22 and 2.23). The pyrite from the Brett vein occurrence displays some enrichment in nickel, for example, as evidenced by analysis R3#3-1 (4.67 wt.% Ni; table 2.22). Native gold occurs primarily alone in the calcite gangue but also may be found intergrown with pyrite, pyrrhotite, actinolite, cobaltite, aleksite, galenobismutite, and/or tellurobismuthite (figures 2.40 and 2.41). An average of fourteen electron-microprobe analyses of the native gold reveal a relatively uniform composition with a modest silver content (averages of 81 atomic percent Au and 18 atomic percent Ag, respectively), with less than 1 atomic percent (combined) iron, copper, and sulphur contents. Pentlandite occurs in trace amounts, typically as anhedral inclusions in pyrrhotite. As is well illustrated in both the photographs (figure 2.39) and the BSE-images (figures 2.40 and 2.41), none of the ore or gangue minerals display any obvious textural evidence that is suggestive of post-crystallization deformation.

The host rock to the mineralized vein samples from the Brett occurrence is dominated by an assemblage comprised of epidote, chlorite, altered plagioclase, calcite, amphibole, titanite, and minor quartz, with minor amounts of disseminated pyrite, pyrrhotite, and chalcopyrite. The amphibole in the host mafic intrusive has an actinolitic composition, and texturally appears to be replacing primary pyroxene. The host rocks has been mapped by the Geological Survey of Ontario as comprising Archean mafic metavolcanic rocks of fine-grained amphibolite to fine-grained, massive basalt (Born *et al.*, 1990).

Table 2.19. Representative electron-microprobe analyses of calcite from samples of the Brett vein occurrence.

Sample #	R1#2	R1#	R1#9	R2#2	53-1	53-2	B-C1-1	B-C1-2
MgO	-	0.01	0.02	-	0.09	0.09	0.16	0.01
CaO	56.02	56.94	56.49	56.76	54.27	56	55.46	55.74
MnO	0.02	0.05	0.13	0.18	0.69	0.73	0.38	0.28
FeO	0.22	0.11	0.18	0.1	0.78	0.37	0.54	0.17
SrO	0.03	0.02	0.01	0.01	-	-	0.01	-
BaO	0.01	-	0.03	0.01	-	-	0.05	-
CO ₂ *	43.70	42.87	43.14	42.94	44.17	42.80	43.4	43.8
Total	100	100	100	100	100	100	100	100

Cation proportions based on C=1.00

Mg	-	-	0.001	-	0.002	0.002	0.004	-
Ca	1.003	1.027	1.016	1.023	0.969	1.012	0.996	0.997
Mn	-	0.001	0.002	0.003	0.010	0.010	0.005	0.004
Fe	0.003	0.002	0.003	0.001	0.011	0.005	0.008	0.002
Sr	--	--	--	--	--	--	--	--
Ba	--	--	--	--	--	--	--	--
C	0.996	0.985	0.989	0.986	1.003	0.984	0.993	0.998
Sum	2.002	2.015	2.010	2.014	1.995	2.013	2.006	2.002

Note. All oxide concentrations are in weight percent (wt.%). [-] = below the analytical detection limit. CO₂* = CO₂ concentration calculated by difference and confirmed by stoichiometry.

Table 2.20. Representative electron-microprobe analyses of epidote from the Brett vein occurrence.

Sample #	R1#5-1	R1#9-1	R1#9-2	R2#3-2	R2#3-3	R2#4-3	R2#4-4	A-A-1
SiO ₂	38.36	38.38	38.94	38.88	38.25	38.2	38.8	38.38
Al ₂ O ₃	24.56	23.82	26.13	27.84	25.49	24.68	26.97	23.2
TiO ₂	0.08	-	0.09	0.03	0.09	0.05	0.07	0.07
Cr ₂ O ₃	0.03	-	-	0.01	0.01	0.01	-	0.47
Fe ₂ O ₃	11.88	12.93	10.06	7.95	10.46	11.5	8.75	14.52
MnO	0.11	0.05	0.06	0.01	0.04	0.06	-	0.12
MgO	0.01	-	0.01	-	-	-	-	-
CaO	23.92	23.41	23.93	24.09	23.76	23.44	24.25	22.98
Na ₂ O	0.01	-	0.02	0.01	-	-	-	0.01
Cl	0.01	0.01	-	0.01	-	-	-	-
F	0.07	0.01	0.01	-	-	0.02	-	-
Less O=F	0.03	--	--	--	--	--	--	--
Total	99.01	98.61	99.25	98.83	98.1	97.96	98.84	99.75

Note. All oxide and elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit.

Table 2.21. Representative electron-microprobe analyses of amphibole from the Brett vein occurrence.

Sample #	B-B1	A-B-3	R1#2-1	R1#3-1	R1#6-1	R2#3-1	R2#4-2	R2#5-1
SiO ₂	52.57	57.43	54.59	55.83	52.61	50.06	55.46	55.55
Al ₂ O ₃	0.24	0.54	0.85	0.94	2.82	4.97	0.59	0.48
TiO ₂	0.02	0.16	-	0.01	0.07	0.07	-	-
Cr ₂ O ₃	-	0.04	-	0.03	0.01	-	-	-
FeO	20.96	5.68	13.85	12.23	14.87	17.98	13.82	12.83
MnO	1.12	0.04	0.14	0.33	0.28	0.34	0.09	0.13
MgO	9.41	20.87	14.56	15.46	13.4	11.15	14.99	15.69
K ₂ O	-	0.07	0.01	0.02	0.03	0.06	0.01	0.01
CaO	11.93	11.4	12.76	12.69	12.68	12.41	12.85	12.96
Na ₂ O	0.16	0.54	0.05	0.13	0.32	0.64	0.08	0.06
Cl	-	-	-	-	0.02	0.01	-	0.01
F	0.03	0.09	0.03	0.01	0.03	0.03	0.08	0.02
Less O=F	0.01	0.04	0.01	-	0.02	0.01	0.03	0.01
Total	96.43	96.82	96.83	97.68	97.12	97.71	97.94	97.73

Note. All oxide and elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit.

Table 2.22. Representative electron-microprobe analyses of the major sulpharsenide and sulphide minerals from the Brett vein occurrence.

Mineral	cobaltite	pentlandite	pyrrhotite	cobaltite	cobaltite	cobaltite	cobaltite	pyrite
Sample #	RBT-2B-2	BRT3A-1	BRT3A-4	R2#1-1	R2#3-1	R3#3-1	R3#3-2	R3#3-6
As	43.38	0.01	-	41.03	40.29	34.37	43.71	-
S	19.58	32.55	39.88	21.69	23.31	27.38	20.44	54.22
Fe	1.23	27.62	59.99	1.77	1.84	6.11	1.37	42.11
Co	33.34	4.01	-	25.71	29.89	32.44	31.2	0.08
Se	-	-	0.02	-	-	-	-	-
Cu	0.02	-	-	-	0.02	0.01	0.01	0.01
Ni	1.23	35.12	0.81	8.56	3.88	0.7	2.84	4.67
Zn	-	0.06	0.08	-	-	-	-	-
Ag	0.07	0.01	0.01	-	-	-	-	-
Au	-	0.05	0.08	-	-	-	-	-
Total	98.83	99.43	100.86	98.76	99.23	101.01	99.57	101.09
Proportions calculated on $\Sigma\text{Atoms} = 1$								
As	0.322	--	--	0.298	0.287	0.231	0.320	--
S	0.339	0.466	0.533	0.368	0.389	0.430	0.350	0.669
Subtotal	0.661	0.466	0.533	0.666	0.676	0.661	0.670	0.669
Fe	0.012	0.227	0.460	0.017	0.018	0.055	0.013	0.298
Co	0.314	0.031	--	0.237	0.271	0.277	0.290	0.001
Se	--	--	--	--	--	--	--	--
Cu	--	--	--	--	--	--	--	--
Ni	0.012	0.275	0.006	0.079	0.035	0.006	0.027	0.031
Zn	--	--	--	--	--	--	--	--
Ag	--	--	--	--	--	--	--	--
Au	--	--	--	--	--	--	--	--
Subtotal	0.338	0.533	0.466	0.334	0.324	0.338	0.330	0.331

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit.

Table 2.23. Representative electron-microprobe analyses of unusual Pb-Bi-Te-sulphide minerals from the Brett vein occurrence.

Mineral	aleksite	aleksite	aleksite	glBi	glBi	glBi	Bi	TeBi
Sample #	RBT-2B-7	RBT-2B-7	RBT-2B-11	RBT-2B-13	RBT-2B-1	RBT-2B-10	RBT-2B-5	RBT-2B-18
As	-	-	-	0.01	-	-	-	0.03
S	6.82	6.77	6.71	16.08	15.91	16.76	0.02	0.11
Fe	-	-	-	-	-	-	0.01	0.10
Co	-	-	-	0.02	-	0.03	-	1.95
Se	0.19	0.22	0.17	0.15	-	0.17	-	0.45
Pb	12.59	13.13	12.61	46.39	46.19	37.32	-	1.49
Cu	-	-	-	0.04	-	0.00	0.03	0.02
Ni	-	-	0.01	0.06	-	0.00	-	0.16
Ag	-	-	-	1.01	0.95	0.24	-	0.17
Mn	-	-	-	-	-	-	-	-
Zn	0.04	0.08	-	-	-	-	-	-
Au	0.03	-	0.47	0.05	0.16	0.68	-	-
Bi	57.75	58.22	58.93	35.40	36.56	44.96	99.09	49.89
Te	20.36	20.50	20.63	0.10	-	0.13	-	44.49
Total	97.76	98.93	99.53	99.30	99.78	100.30	99.15	98.86

Proportions calculated on $\Sigma \text{Atoms} = 1$

As	--	--	--	--	--	--	--	0.001
S	0.298	0.294	0.291	0.552	0.55	0.564	--	0.005
Fe	--	--	--	--	--	--	--	0.003
Co	--	--	--	--	--	0.001	--	0.051
Se	0.003	0.004	0.003	0.002	--	0.002	--	0.009
Pb	0.085	0.088	0.085	0.246	0.25	0.194	--	0.011
Cu	--	--	--	0.001	--	--	--	-
Ni	--	--	--	0.001	--	--	--	0.004
Ag	--	--	--	0.010	0.01	0.002	--	0.002
Mn	--	--	--	--	--	--	--	--
Zn	0.001	0.002	--	--	--	--	--	--
Au	--	--	0.003	--	--	0.004	--	--
Bi	0.388	0.388	0.392	0.186	0.19	0.232	1.00	0.371
Te	0.224	0.224	0.225	0.001	--	0.001	--	0.542
Total	1.000	1.000	1.000	1.000	1.00	1.000	1.00	1.000

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit. Abbreviations: glBi = galenobismutite, Bi = native bismuth, TeBi = tellurobismuthite.

Figure 2.40. BSE-images of: (A) native gold (au) rimming sub-euhedral cobaltite (co) set in a calcite (cc) + epidote (ep) gangue; and (B) native gold (au) associated with nickel-bearing pyrite (py), set in a calcite (cc) + epidote (ep) gangue. Both images are from sample# RPT-2b, the Brett occurrence.

Figure 2.41. BSE-images of: (A) native gold (au) intergrown with aleksite (ak) and galenobismutite (gb), set in calcite gangue (sample# RBT-2b, Brett occurrence); and (B) pentlandite (pn) inclusion within pyrrhotite (po) set in calcite (cc) + epidote (ep) gangue. Sample# BRT-3, the Brett occurrence.

Johnson Lake Occurrence

Approximately 5.5 kilometres northwest of the Brett occurrence, several mineralized quartz-calcite stringers and joints occur in Gowganda Formation diamictite (figure 2.42). The highly gossanous, fracture and joint-hosted stringers are typically less than 0.25 cm in width, and occur in a series of east-striking (085°), parallel joints up to 10 centimetres in width that dip steeply to the south (70°S) (figure 2.43). A grab sample of the stringers and altered host rocks yielded assay values with up to 11.9 g/t Au. Given the proximity to the Brett occurrence and the margin of the Lake Temiskaming Structural Zone, representative samples were collected from the Johnson Lake occurrence. In polished thin section, the mineralization is dominated by the occurrence of fracture-controlled pyrite. Some minor propagation (<2 cm) of quartz-calcite stringers into the host rock and the presence of euhedral pyrite grains in the diamictite was observed. Within the diamictite, the pyrite preferentially replaces rounded clasts and often forms rims around clasts (figure 2.42). No gold-bearing minerals were observed, although the assay results suggest the presence of trace amounts of native gold. A few hundred metres north, an outlier of Archean mafic basement contains a system of random quartz-calcite veins with gold concentrations as high as 32.00 g/t.

Figure 2.42. Photograph of polished samples from the Johnson Lake occurrence, highlighting the presence of secondary, euhedral pyrite mineralization along joint surfaces (A), along microfractures (C), and rimming clasts within the diamictite matrix (D). The bleached appearance (B) is related to the presence of quartz-calcite alteration of the clay-rich diamictite matrix along the joint surfaces.

Figure 2.43. Field photograph of the Johnson Lake occurrence, illustrating the highly gossanous nature of the joints and associated stringers.

2.5 The Delhi Township Occurrence

The Delhi Township occurrence is situated in the central portion of the Cobalt Embayment, approximately forty kilometres west of the town of Temagami (figure 2.44). Due to the former existence of the Temagami Land Caution, which prohibited mineral exploration in the area for over twenty years, access to the property is difficult and must be accomplished by canoe from Obabika Lake with a portage into Wakima Lake (a distance of approximately 25 kilometres). From the southwestern shore of Wakima Lake, the Delhi Township occurrence is located approximately one kilometre to the southwest.

The main mineralized vein system is located on the northern tip of a northeast-trending Nipissing Diabase dyke several kilometres in length (figure 2.45A). The diabase dyke has intruded into thin-bedded greywackes of the Gowganda Formation and typically has sharp contacts that dip to the north, with very minor chill zones and localized brecciation of the sedimentary host rocks (Card *et al.*, 1973). Approximately 300 metres south of the main occurrence, an olivine-diabase dike of the Sudbury dike swarm (285° trend, dipping steeply to north) cross-cuts the Nipissing Diabase dyke and Huronian sedimentary rocks. The Delhi Township mineralized vein system is associated with a near-vertical shear zone trending roughly 300° which cross-cuts both the Nipissing diabase dyke and its greywacke host rocks. Also, a large regional fault zone has been mapped by the Ontario Geological Survey along the southwestern shoreline of Wakima Lake, one kilometre to the east of the main Delhi showings (figure 2.45A).

Figure 2.44. Location of the Delhi Township vein occurrence in relation to regional geology within the Cobalt Embayment. The occurrence is situated on the northern tip of a large Nipissing Diabase dyke trending to the northeast.

The regional fault zone is nearly vertical and strikes 330° (Lawton, 1952). The mineralization on the Delhi property consists of massive-to-vuggy calcite-quartz veins hosted in Nipissing Diabase and occasionally extending into the host greywacke. The veins reportedly contain argentiferous galena, with lesser abundances of chalcopyrite, pyrite and native gold (*op. cit.*). The Delhi property has experienced several episodes of exploration and development, beginning in 1907 with the sinking of test pits and culminating in 1950 with the development of two adits, roughly 800 feet of drifting, and several hundred feet of diamond drilling (Lawton, *op. cit.*; Card *et al.*, 1973). During its history, the occurrence has been known as the Lhay showing, the Delhi-Pacific occurrence, the Bonnehomme occurrence, and the New Delhi occurrences (Card *et al.*, *op. cit.*). Currently, the Ontario Geological Survey's Mineral Deposit inventory lists the occurrence as a "developed prospect without reserves". A 21,692 pound (or 9839 kg) bulk sample taken from seven mineralized vein intersections along the main eastern adit returned the following assay results: 7.13% Pb, 5.58oz/t (173g/t) Ag, and 0.25 oz/t (7.7g/t) Au (Lawton, 1952).

Samples collected during this study were taken from the historically most prospective showing: the Lhay veins (see figure 2.45B). Numerous high-grade samples are present in the adit waste pile and the Lhay vein can be traced on surface at the adit entrance. A high-grade grab sample (figure 2.46) collected from the adit waste pile returned significant gold, lead, and copper values: 36.62 g/t gold, 28.95% Pb, 2.23% Cu (with also 258 g/t Ag, and 285 ppm Co). Gold mineralization is manifested by the presence of anhedral grains ($\leq 25 \mu\text{m}$) of electrum comprised of approximately 48%

(atomic) Au and 47% (atomic) Ag, with traces of Fe and S, which are hosted in cobaltian pyrite. Also, galena analyzed during this study did not yield significant contents of silver (≤ 0.33 wt.% Ag). From petrographic analysis, the dominant ore minerals are (in decreasing abundance): galena, pyrite, chalcopyrite, pyrrhotite, cobaltite, sphalerite, and electrum. Representative electron-microprobe analyses of the major ore minerals are presented in table 2.24. Three distinct pyrite compositions were noted based on textural relationships, habit, and chemical composition. Pyrite I is cobalt-bearing (1.49-3.30 wt. % Co), pyrite II contains appreciable nickel contents (1.40-3.58 wt. % Ni), and pyrite III contains very little cobalt or nickel (< 0.5 wt. %). The compositions of all the pyrite generations are plotted on the pyrite-vaesite-cattierite (FeS_2 - NiS_2 - CoS_2) ternary diagram in figure 2.47; given the geochemical similarities of the Fe^{2+} (0.61 Å for six-fold coordination), Co^{2+} (0.65 Å) and Ni^{2+} (0.69 Å) ions, both ions readily substitute for ferrous iron in the pyrite crystal structure.

Figure 2.45. (Previous page) (A) Regional geology of the Delhi Township, illustrating the presence of a northeast-trending Nipissing Diabase dyke, numerous olivine-diabase dykes of the Sudbury swarm, and regional faults in the vicinity of the vein mineralization. Map created from digital data provided by the Ontario Geological Survey.

(B) Geological map of the Delhi Township occurrence highlighting the extensive veining and mineral development (*circa* 1951). Samples collected during this study focused on the Lhay veins and the associated waste pile located on the western margin of the Nipissing Diabase dyke. The map was redrawn from Lawton (1955).

(C) Schematic cross-section through line A-B of the Delhi Township mineralized vein occurrence illustrating the extent of the diabase-hosted vein systems inferred from the results of diamond drilling and the mapping of underground workings. The mineralized veins have an approximate overall strike to the northwest, dip moderately to the north and reach a maximum of 1.5 metres in width. The map was redrawn from Lawton (1955).

Figure 2.46. Photograph of sample# DL-6, collected from the adit waste pile (*i.e.* Lhay vein material). The high-grade, quartz-calcite vein contains significant galena, pyrite and chalcopyrite mineralization interstitial to fractured, milky quartz. Assay results from this material included: 36.62g/t Au, 28.95% Pb, 2.23% Cu, 258g/t Ag, and 285 g/t Co.

Table 2.24. Representative electron-microprobe analyses of the major ore minerals from the Delhi Township vein occurrence.

Mineral	pyrite	pyrite	pyrite	pyrite	pyrite	pyrrhotite	pyrrhotite
Sample	DL4-4	DL4-5	DL1a-11	DL4-8	DL4-1	DL4"-2	DL4"-4
As	-	-	0.01	0.12	0.02	0.01	-
S	53.19	53.43	52.74	52.78	53.40	39.48	41.21
Fe	45.44	43.42	46.69	45.90	43.97	60.05	57.93
Ni	1.40	3.58	0.02	-	-	0.18	0.16
Zn	0.03	-	-	0.03	0.01	0.01	-
Ag	-	-	-	0.03	-	0.07	-
Co	0.05	0.10	0.49	1.49	3.30	0.05	0.04
Au	-	0.04	0.01	0.06	-	0.18	-
Bi	-	-	0.08	-	0.07	-	0.08
Total	100.11	100.59	100.04	100.41	100.77	100.03	99.42

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	--	--	--	0.001	--	--	--
S	0.664	0.663	0.66	0.659	0.664	0.532	0.552
Subtotal	0.664	0.663	0.66	0.660	0.664	0.532	0.552
Fe	0.326	0.310	0.336	0.329	0.314	0.465	0.445
Ni	0.010	0.024	--	--	--	0.001	0.001
Zn	--	--	--	--	--	--	--
Ag	--	--	--	--	--	--	--
Co	--	0.001	0.003	0.010	0.022	--	--
Au	--	--	--	--	--	--	--
Bi	--	--	--	--	--	--	--
Subtotal	0.336	0.335	0.339	0.339	0.336	0.466	0.446

(table 2.24 is continued on the next page)

Table 2.24. (continued)

Mineral	galena	galena	sphalerite	sphalerite	cobaltite	cobaltite	Native Au
Sample	DL1b-4	DL1a-2	DL1b-12	DL2B-10	DL2B-19	DL2B-18	DL4"-6
As	-	-	0.06	0.05	41.19	40.79	-
S	13.60	13.94	32.27	32.31	21.86	22.17	0.22
Fe	0.00	-	6.63	3.82	3.84	4.20	0.79
Ni	-	-	-	-	0.70	0.53	-
Zn	0.10	-	61.52	64.56	-	0.02	-
Ag	0.33	0.05	0.03	-	-	0.01	33.32
Cu	-	-	-	0.16	0.01	0.08	-
Co	0.03	0.02	0.04	0.01	32.31	32.31	0.03
Pb	85.74	87.42	-	-	-	-	-
Au	-	-	-	-	0.27	0.05	62.08
Bi	-	-	0.14	-	-	-	-
Total	99.81	101.43	100.70	100.91	100.18	100.16	96.44

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	--	--	--	--	0.295	0.291	--
S	0.503	0.507	0.486	0.487	0.366	0.370	0.011
Subtotal	0.503	0.507	0.486	0.487	0.661	0.661	0.011
Fe	--	--	0.057	0.033	0.037	0.040	0.022
Ni	--	--	-	-	0.006	0.005	--
Zn	0.002	--	0.455	0.478	--	--	--
Ag	0.004	0.001	--	--	--	--	0.478
Cu	--	--	--	0.001	-	0.001	--
Co	0.001	--	--	--	0.294	0.293	0.001
Pb	0.491	0.492	--	--	--	--	--
Au	--	--	--	--	0.001	--	0.488
Bi	--	--	--	--	--	--	--
Subtotal	0.498	0.493	0.512	0.512	0.338	0.339	0.989

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit.

Figure 2.47. Pyrite-vaesite-cattierite ternary diagram illustrating the compositional variation of pyrite from the Delhi Township occurrence ($n=43$).

Figure 2.48: BSE-image of cobalt-bearing pyrite (py1) and nickel-bearing pyrite (py2) grains set in quartz gangue. Chalcopryite is seen to partially replace nickel-bearing pyrite, which also contains inclusions of galena (gl). Minor iron-oxides (Fe) are associated with the chalcopryite. Sample# DL-2a, the Delhi Township occurrence.

Textural relationships indicate that crystallization of the cobalt-bearing pyrite (*i.e.* pyrite I) occurred first and was followed by nickel-bearing pyrite (*i.e.* pyrite II) and then finally stoichiometric pyrite (*i.e.* pyrite III). Furthermore, cobalt-bearing pyrite grains (pyrite I) are the least altered by chalcopyrite replacement – whilst most of the pyrite inclusions within chalcopyrite are relatively pure (pyrite III). The electron-microprobe analysis of chalcopyrite grains did not reveal any evidence of minor element substitution. The chalcopyrite grains are predominantly anhedral in habit and typically have partially replaced and enveloped earlier pyrite (figure 2.48). Sphalerite occurs as rounded anhedral grains hosted in both stoichiometric pyrite (pyrite III) and chalcopyrite. A few, rare grains of costibite (CoSbS) were found to be associated with sphalerite. Isolated, sub-euhedral grains of cobaltite occur within quartz gangue and are frequently rimmed by a narrow layer of galena (figure 2.49). As shown in figure 2.46, in hand specimen, galena occurs as anhedral masses up to 1 centimetre in diameter, which often are found rimming cobalt-bearing pyrite (figure 2.51), cobaltite (figure 2.50), and also as inclusions within stoichiometric pyrite and/or chalcopyrite. The modal abundances of the ore minerals within the veins are highly variable with values ranging from 0% to a maximum of 30-40% (figure 2.46). Textural relationships suggest the following sequence for crystallization: early pyrite±cobaltite→pyrite→sphalerite→chalcopyrite→galena. Early pyrite grains are typically enriched in either cobalt or nickel, whereas the later pyrites have nearly ideal compositions. The relative timing of the crystallization of the early pyrite and cobaltite is ambiguous: however, the early precipitation of cobaltite may have been limited by the relatively low arsenic concentration in the hydrothermal fluid, and

once arsenic had been depleted by the precipitation of cobaltite, the remaining cobalt in aqueous solution was subsequently incorporated into the early pyrite (*i.e.* pyrite I).

Quartz is the dominant gangue mineral in the Delhi mineralized veins, with only minor amounts of interstitial white calcite (<5 modal percent) and chlorite being present locally. Textures in the mineralized veins indicate brecciation of earlier milky quartz followed by the co-precipitation of interstitial calcite gangue and the sulphide and sulpharsenide ore minerals. With the exception of a few, early-formed, cobalt- and nickel-bearing pyrite grains, all the sulphide minerals are fine-grained, anhedral in habit, and have textures that evidence some degree of deformation. Occasional, rounded-to-subangular fragments of altered Nipissing Diabase were also noted within the mineralized veins.

Figure 2.49. BSE-image of pyrite III (py) and sphalerite (sp) inclusions, in anhedronal chalcopyrite (cpy), hosted in quartz gangue. Sample# DL-4, Delhi Township.

Figure 2.50: BSE-image of a rounded grain of cobaltite (co) rimmed by anhedronal galena (gl), set in quartz (qtz) gangue. Sample# DL-2B, Delhi Township. The dark spots in the cobaltite grain were created by the electron beam during the microprobe analysis.

Figure 2.51. BSE-image of anhedral galena (gl) and chalcopyrite (cpy) rimming early, sub-euhedral, cobalt-bearing pyrite I (py), set in quartz (qtz) gangue. Sample# DL-2a, Delhi Township.

Figure 2.52. BSE-image of very small grains of electrum (Au) hosted in cobalt-bearing pyrite, set in quartz (qtz) gangue. Sample# DL-04, Delhi Township.

2.6 Occurences from the Wanapitei Area

Nine occurrences of mineralized quartz-calcite vein systems from the Wanapitei area were sampled during this study (figure 2.53):

1. Davis occurrence
2. McLean-Watt mine
3. Burda occurrence
4. Gordon Mine
5. Crystal Mine
6. Dolmac property
7. Decade and Parkin Township occurrences
8. Fraleck Township occurrences
9. Laura Lake occurrence.

A complete description of all occurrences visited and samples collected is presented in Appendix A.

Figure 2.53. Location of the vein occurrences in the Wanapitei area that were sampled in this study. The Wanapitei area is located in the southwestern corner of the Cobalt Embayment, due east of the Sudbury Igneous Complex (SIC). The McLaren Lake Fault (MLF) is also indicated.

Wanapitei Area - The Davis Occurrence

All that remains of the Davis occurrence is a small exploration shaft and a waste pile of mineralized debris located near the southern shoreline of Ashagami Lake. The Davis occurrence is one of three known mineralized vein occurrences (*i.e.* Davis, Burda, and Fraleck Township) that are spatially associated with the regionally extensive, NNW-trending McLaren Lake Fault (figure 2.53). Samples of the mineralized quartz-calcite veins contain minor amounts of disseminated chalcopyrite, with lesser pyrite, and are typically hosted in fine-grained Gowganda Formation (Huronian) quartzite. The cherty quartzite is intensely silicified, carbonatized, and brecciated in some samples collected from the waste pile. Calcite-lined vugs and/or negative crystal shapes within the altered quartzite may represent weathered ankerite or dolomite. A high-grade grab sample collected from the Davis shaft by the Ontario Geological Survey yielded 4.09 wt.% Cu and 7.7g/t Au (Shklanka, 1969; Kindle, 1933). Kindle (*op. cit.*) reported that two carloads of ore were produced from the ten-metre deep shaft. An exploration trench with traces of *in situ* mineralized material was discovered a few hundred metres southeast of the shaft. While fragments of mineralized material remained in the trench, the orientation of the mineralized system could not be accurately measured. The trench presumably follows the trend of the vein mineralization, striking roughly north ($\sim 350^\circ$), and the veining is sub-vertical with irregular, sharp contacts. Mineralized vein material from the exploration trench, like that from the waste pile, comprises minor amounts of chalcopyrite and pyrite disseminated within brecciated Gowganda Formation quartzite. Samples collected during this study comprise disseminated pyrite, chalcopyrite and arsenopyrite, hosted in quartzite. Trace amounts of albite were also noted, often rimmed

(or cemented) by secondary pyrite (figure 2.54). Pyrite is typically euhedral to sub-euhedral in habit, and occurs associated with anhedral chalcopyrite. Arsenopyrite occurs in trace amounts, included in anhedral pyrite. Accessory phases within the quartzite include rounded zircon grains, rutile, apatite, and trace amounts of an unresolved LREE-phosphate (figure 2.54B). Electron-microprobe analysis of pyrite from the mineralized samples indicated the presence of minor concentrations (≤ 0.65 weight percent) of As, Ni, and Co (table 2.25), whereas the arsenopyrite and chalcopyrite are almost pure with very low concentrations of minor elements.

Table 2.25. Representative electron-microprobe analyses of pyrite from the Davis occurrence, Wanapitei area.

Sample #	WN3-3	WN3-4	WN3-5	WN5-1	WN5-2	WN5-5	WN5-6	WN5-7
As	0.32	0.57	0.32	0.01	0.02	-	42.82	0.04
S	54.92	54.30	54.60	52.23	54.12	53.14	22.38	53.65
Fe	47.52	47.56	47.88	45.42	47.65	46.30	35.45	47.25
Co	0.11	0.13	-	-	-	-	0.17	-
Ni	0.08	0.02	0.02	0.25	0.01	0.25	0.65	0.34
Ag	-	0.00	0.02	-	0.01	-	-	0.03
Zn	0.02	0.03	0.01	-	-	0.04	0.05	0.00
Au	-	0.11	0.07	0.06	-	-	0.05	0.04
Total	102.97	102.71	102.91	97.96	101.81	99.73	101.56	101.34

Proportions calculated on $\Sigma \text{Atoms} = 1$

As	0.002	0.003	0.002	-	-	-	0.298	-
S	0.666	0.662	0.664	0.665	0.664	0.665	0.364	0.662
Subtotal	0.668	0.665	0.665	0.665	0.664	0.665	0.661	0.662

Fe	0.331	0.333	0.334	0.332	0.336	0.333	0.331	0.335
Co	0.001	0.001	--	--	--	--	0.002	--
Ni	0.001	-	-	0.002	-	0.002	0.006	0.002
Ag	--	--	--	--	--	--	--	--
Zn	--	--	--	--	--	--	--	--
Au	--	--	--	--	--	--	--	--
Subtotal	0.332	0.334	0.334	0.334	0.336	0.334	0.338	0.337

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit.

Figure 2.54. BSE-images of mineralized samples from the Davis occurrence, Wanapitei area: (A) sub-anhedra pyrite with very small inclusion of arsenopyrite (as) surrounding albite (ab) and chalcopyrite (cpy) (sample# WN-5); and (B) sub-euhedral pyrite with iron-oxidation rims hosted in quartz gangue (sample# WN-3). Also present in (B) are a tiny, rounded zircon grain (zr) and tiny grains of an unresolved sub-euhedral LREE-phosphate mineral.

Wanapitei Area - The McLean-Watt Mine

The mineralization at the McLean-Watt mine was discovered in 1973 and currently represents the largest known gold deposit of Proterozoic age in the Cobalt Embayment. Subsequently, the property changed ownership several times, while significant underground ore reserves were delineated, and three open-pit zones were mined (Hall, 2003). During a change of property rights in 1983, Northgate Minerals listed a “drill-indicated mineable reserve” of 136,496 tons at a cut grade of 0.211 oz/t gold (7.23g/t Au)(Botsford, 1985). This was revised to “probable mine reserves” of 119,000 diluted tons at a grade of 0.225 oz/t Au (7.71g/t Au) following an internal review and proposal for underground mining by Canadian Mine Development Limited (Vooro *et al.*, 1987). Work on the property culminated under the ownership of Orofino Resources Limited, which completed extensive underground workings that yielded 15,769 ounces of recovered gold in 1987 (Hall, 2003). Development on the property led to the recognition of four mineralized zones, termed the “North”, “Central”, “South” and “East” zones. The latter are aligned along a NNW- striking trend (330-340°), likely related by the McLaren Lake Fault (figure 2.53), with dips of 70-85° to the northeast recorded in the Central zone of mineralization (*op. cit.*). The North, South and East zones were the locus for open-pit mining, whereas the Central zone was developed *via* underground workings. The mineralization is associated with extensive zones of fractured, veined, and brecciated Serpent Formation quartzite of the Quirke Lake Group (Huronian Supergroup). The gold mineralization is mainly contained in chlorite-rich shear zones and chlorite-breccias next to the shear zones. The intensity of the chlorite alteration of wall rocks is proportional to the density of quartz+ankerite+chlorite+sulphide veinlets and breccias-matrix material.

Minor quartz veining is also present, but gold mineralization is generally sparse in the quartz veins (*op. cit.*). The brecciated textures and chlorite-rich matrix of the mineralized rocks are immediately visible in hand specimen (figure 2.55). Enrichments in Ag, Cu, As, Co, and Ni accompany that of gold, while the four zones of hydrothermal mineralization are enriched in Na₂O, SiO₂, CO₂, Fe-oxides and REE (Martin *et al.*, 1979; Schandl *et al.*, 1994). The chlorite-rich brecciated wall rocks are characteristically coarse-grained and dark green in colour. They commonly contain 70 modal percent chlorite and greater than 5 modal percent sulphide minerals (relative modal abundances: pyrite>pyrrhotite>chalcopyrite>arsenopyrite). Rosettes of biotite and actinolite, which are locally associated with chlorite, albite and quartz in the matrix of the breccias, may be products of regional metamorphism (Martin *et al.*, 1979). Common accessory minerals include magnetite, ilmenite, galena, apatite, rutile, titanite, xenotime-Y, zircon, thorite, and a LREE-phosphate (figure 2.56). Schandl *et al.*, (1994) also reported the presence of hydrothermal, REE-bearing minerals (monazite, bastnasite, synchysite, gadolinite), either as inclusions in albite or in association with the chlorite alteration assemblage. Hall (2003) noted the presence of zoning within the hydrothermal alteration (proximal to distal): *i*) green chloritic breccia and psammite with quartz + ankerite + sulphide stringers; *ii*) pink albitic + hematitic breccia and psammite with coarse dolomite + quartz stringers; and *iii*) grey arenite with net-vein fabrics.

Specimens collected for this study were sampled from the East zone of gold mineralization, which is associated with a fault structure striking east and dipping 65° to the south. Gold occurs in the native state as anhedral grains, set in chlorite-altered rocks,

and associated with chalcopyrite and pyrite. Representative electron-microprobe analyses of the major sulphide mineral, pyrite, illustrate the generally low content of minor elements (table 2.26). Gravity concentrates of ore from the Central zone contained gold and silver in the ratio of 26:1, together with small concentrations of Cu (0.3 wt.%) and As (0.1 wt.%; Hall, 2003). Furthermore, Schandl *et al.* (1994) noted positive correlations between Au, Co, Ni, and sulphide mineral contents in the breccias, whilst the Na content was correlated to the concentration of LREE. These observations led Hall (*op. cit.*) and Schandl *et al.*, (*op. cit.*) to suggest that the albitized breccias probably acted as mechanical and chemical traps for later hydrothermal fluids, which were channeled through internal fault structures and/or younger, cross-cutting shear zones. The transition from green to pink coloured rocks is a reduction-oxidation boundary which envelopes volumes of higher sulphide and gold content. Schandl *et al.*, (*op. cit.*) dated the breccias at $1700 \pm 2\text{Ma}$ by U-Pb geochronology of hydrothermal monazite found in the albitic alteration. The breccias were sampled in the present study due to the high gold concentrations and to investigate the possibility the mineralization may represent remobilization of an earlier, mineralized, quartz-calcite vein system.

Figure 2.55. Chlorite-rich breccia from the East zone of gold mineralization at the McLean-Watt mine, Wanapitei area. Visible are the sodic-altered quartzite fragments and minor gossanous staining associated with pyrite.

Figure 2.56. BSE-image of pyrite (py), rutile (rt), quartz (qtz), and a LREE-phosphate mineral set in chlorite-rich matrix in an altered and mineralized sample from the McLean-Watt mine, Wanapitei area. (Sample# WN-8).

Table 2.26. Representative electron-microprobe analyses of pyrite from the mineralized zones of the McLean-Watt mine, Wanapitei area.

Sample #	wn8a-1	wn8a-2	wn8b-1	wn8b-1	wn8b-2	wn8b-3
As	-	-	-	0.07	0.07	0.38
S	53.21	52.76	52.25	52.20	52.57	52.29
Fe	46.56	46.73	46.55	45.80	46.42	46.49
Co	-	-	-	-	-	-
Pb	-	-	-	-	-	-
Ni	0.01	0.02	0.01	-	-	-
Ag	-	0.03	-	-	0.03	0.00
Zn	-	-	0.05	-	-	0.02
Au	-	-	-	0.01	-	-
Bi	0.01	0.04	0.08	-	-	-
Total	99.78	99.57	98.95	98.08	99.09	99.19

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical detection limit.

Located approximately one kilometre north of the McLean-Watt mine is the mineralized vein system of the “Glade occurrence”. Several exploration trenches have exposed the quartz-calcite veins, and some bulk samples appear to have been taken. In addition, several drill holes reportedly intersected the main vein system at depth (Gordon *et al.*, 1979). To the east of the main showing at the Glade occurrence, evidence of additional trenching and several diamond drill collars were noted. At the main trench, two sets of gossanous quartz-calcite veins (≤ 100 cm wide) cross-cut fine-grained Nipissing Diabase and altered conglomeratic sedimentary units of the (Huronian) Serpent Formation. The quartz-calcite veins are preferentially concentrated along the contact between the diabase and conglomerate units (figure 2.57), with both displaying evidence of local deformation and hydrothermal alteration. Two dominant trends were observed in the quartz-calcite vein system: southeast (145°) and east-west (080°). The southeast-trending veins dip approximately 70° to the west, whereas the east-west trending veins are sub-vertical. Minor sulphide mineralization and quartz veining also occurs in the conglomeratic units below the Nipissing Diabase. Assays of grab samples obtained by the Ontario Geological Survey produced values of as high as 1.22 oz/t Au (34.5g/t Au), 2.6 wt.% Cu, and 0.26 oz/t Ag (7.35g/t Ag); whilst the highest grade reported from diamond drilling was 1.2 oz/t Au (33.9g/t Au) over a width of 5.1 feet (Gordon *et al.*, 1979). Despite numerous attempts by the author, samples of *in situ* mineralized vein material were not located.

Figure 2.57. Field photographs of: (A) Southeast-trending, quartz-calcite vein (~1m wide) with gossanous staining from the main trenched area at the Glade property, located near the McLean-Watt mine, Wanapitei area. The red lines trace the vein contacts; (B) View of the entire main trenched area, illustrating the contact between Nipissing Diabase and the Huronian conglomeratic sedimentary units; and (C) Mildly deformed and altered conglomerate lying below the Nipissing Diabase.

Wanapitei Area - The Burda Property

The Burda occurrence was one of the first copper and gold prospects discovered in the Wanapitei area of the Cobalt Embayment, with advanced exploration work dating back to 1902. From 1902 to 1959, two shafts and several hundred feet of drifting were completed, together with extensive diamond drilling, under the ownership of Alwyn Porcupine Mines Limited. The highest grades reported by the property owners were 0.42% Cu and 0.022oz/t Au (0.62g/t Au) over a width of 15 feet and a strike length of 300 feet (Shklanka, 1969). The mineralization consists predominantly of pyrite and chalcopyrite in quartz-calcite veins hosted in sheared and fractured Gowganda Formation conglomerate. The conglomerate is cut by Nipissing Diabase dykes and is located along the western margin of the northwest-trending, McLaren Lake Fault (figure 2.53). The fault was reportedly encountered in drilling, where it is characterized by the occurrence of abundant quartz-calcite veining on both sides of the fault, together with disseminated chalcopyrite and pyrite, and red carbonate alteration (Thomson, 1961). A vertical shaft and at least one large exploration trench (>50 m long) are still visible. Abundant, small quartz-calcite veins and veinlets are visible throughout the large trenched area (figure 2.58) where they have an overall east-west strike (090°) and are steeply dipping (70°-90°) to the south. Abundant, boulders and cobbles of medium-grained Nipissing Diabase are present in the waste piles, suggesting that the contact between the Huronian sedimentary rocks and Nipissing Diabase dykes were encountered at depth during mining. Samples collected for this study are from examples of *in situ* veining in the exploration trench and from mineralized material in the shaft waste pile. All the samples consist of quartz-calcite veins and veinlets containing pyrite, chalcopyrite, native gold, and galena.

Chalcopyrite is primarily anhedral in habit and rims earlier pyrite or occurs interstitial to quartz crystals in the gangue. Pyrite is subhedral to anhedral in habit (figure 2.59) and electron-microprobe analyses indicate that it carries a minor content of (up to 1.75 wt.% Co) and also trace concentrations of nickel (table 2.27). Galena and native gold occur as tiny (<20µm) inclusions in pyrite (figure 2.59B). Native gold is comprised of 84 atomic % Au, 10 atomic % Ag, and 3 atomic % Fe, with traces of S and Cu (table 2.27). The proportion of quartz and calcite gangue varies considerably over the strike length of the mineralized vein systems, yet overall it appears to be dominated by quartz.

Figure 2.58. Field photographs from the Burda Property, Wanapitei area: (A) Vein sample# WN-25 from the waste pile located at the mine shaft, illustrating the dominant textural features of the waste pile samples. (B): *In situ* quartz-calcite veining with minor chalcopyrite and pyrite mineralization hosted in brecciated Gowganda Formation conglomerate (sample# WN-24).

Figure 2.59. BSE-images of mineralized veins from the Burda Property, Wanapitei area: (A) Sub-euhedral pyrite (py) rimmed by later, anhedral chalcopyrite (cpy), set in quartz (qtz) gangue (sample# WN-25); and (B) Rounded grain of pyrite with small inclusions of galena (gl) and native gold (au), set in quartz (qtz) gangue (sample# WN-25).

Table 2.27. Representative electron-microprobe analyses of pyrite and native gold from the mineralized vein samples of the Burda Property, Wanapitei area.

	pyrite	pyrite	pyrite	pyrite	pyrite	native Au	native Au
Sample #	wn24-4	wn24-8	wn25-2	wn24-2	wn24-1	wn24-6	wn24-7
As	0.14	0.02	0.01	0.29	0.36	-	0.02
S	53.69	53.35	53.44	53.33	53.28	0.18	0.19
Fe	47.43	47.02	47.15	46.58	45.06	1.03	1.33
Co	-	-	-	0.46	1.75	0.01	-
Pb	-	-	-	-	-	-	0.02
Cu	-	-	-	-	-	0.03	0.08
Ni	0.08	0.18	0.03	0.01	0.00	0.01	0.01
Ag	-	0.02	-	-	-	6.37	6.19
Zn	0.01	0.00	0.03	0.02	0.06	-	-
Au	0.12	0.02	-	-	0.05	93.09	93.81
Total	101.46	100.61	100.65	100.68	100.55	100.71	101.65

Proportions calculated on $\Sigma\text{Atoms} = 1$

As	0.001	--	--	0.002	0.002	--	--
S	0.662	0.663	0.664	0.663	0.663	0.010	0.011
Subtotal	0.663	0.663	0.664	0.664	0.665	0.010	0.011
Fe	0.336	0.335	0.336	0.332	0.322	0.033	0.042
Co	--	--	--	0.003	0.012	--	--
Pb	--	--	--	--	--	--	--
Cu	--	--	--	--	--	0.001	0.002
Ni	0.001	0.001	-	--	--	--	--
Ag	--	--	--	--	--	0.106	0.101
Zn	--	--	--	--	--	--	--
Au	--	--	--	--	--	0.849	0.843
Subtotal	0.337	0.337	0.336	0.336	0.335	0.990	0.989

Note. All elemental concentrations are reported in weight percent (wt.%). [-] = below the analytical limit of detection.

Wanapitei Area - The Gordon Mine

Very little information exists on the Gordon Mine, which represents one of the earliest mining developments in the Wanapitei area (figure 2.53), where a shaft was sunk on a gold-bearing quartz vein in 1896. The shaft reportedly intersected an auriferous quartz vein at 40 feet (12.2 m) of depth and traced the vein to a depth of 174 feet (53 m; Slaght, 1896). The same vein was located just east of the shaft and was traced to a similar depth by diamond drilling. During this study, several large (>10 cm wide) quartz veins were noted in outcrop, which sharply cross-cut Gowganda Formation quartz arenite. A large waste pile (containing very little vein material) occurs at the base of the shaft, which is partially buried. One mineralized vein sample was collected from the waste pile, while another sample was collected from the *in situ* vein system that occurs just southwest of the shaft. The mineralized vein that was sampled *in situ* occurred approximately 25 metres southwest of the shaft, has a strike of 090°, dips 70° to the south, and contains trace amounts of pyrite and chalcopyrite (figure 2.60). From the historical descriptions, this vein likely represents the vein system that was encountered in the shaft and further delineated by diamond drilling. Petrographic studies revealed the presence of pyrite and chalcopyrite as the most common ore minerals in the quartz-calcite veins. The euhedral to subhedral pyrite often contains tiny ($\leq 5 \mu\text{m}$) inclusions of an unnamed LREE-phosphate (figure 2.61) identified by electron-microprobe analysis. Trace amounts of galena and chalcopyrite also occur in the quartz-rich gangue, which is coarse-grained and relatively poor in accessory phases. The few accessory phases observed include muscovite, calcite, rounded zircon, and xenotime-Y.

Figure 2.60. Field photograph of the massive quartz-calcite vein adjacent to the Gordon Mine shaft, hosted in Gowganda Formation quartz arenite. The 10 cm-wide vein trends 090°/70°S and contains sporadic chalcopyrite and pyrite mineralization.

Figure 2.61. BSE-image of subhedral pyrite grain with small inclusions of an unnamed LREE-phosphate, hosted in massive quartz gangue; sample#WN-26, Gordon mine property, Wanapitei area.

Wanapitei Area - The Crystal Gold Mine

The Crystal Gold Mine property occurs along the northern shoreline of a small bay off Wanapitei Lake. Directly south, along the southern shoreline, the same vein system found on the Crystal Gold Mine property was developed into the Comstock Mine. According to Gordon *et al.* (1979), the area is underlain by flat-lying Gowganda Formation quartz arkoses and greywackes that have been intruded by sills and dykes of Nipissing Diabase. The vein systems occur along the contact between Gowganda Formation units and a Nipissing Diabase sill. In places the lithological contact is marked by brecciation of diabase and the host sedimentary rocks, as well as by a steepening in the dip of the metasedimentary rocks. Both the Nipissing Diabase intrusions and metasedimentary rocks are cut by numerous parallel quartz-calcite veins, most of which are less than 1 foot wide (<0.3m). The main vein system strikes to the southeast, dips 80° to the south, and was reportedly stripped along its strike for over 100 feet (30.5 m; Gordon *et al.*, *op.cit.*). Mineralization consists of pyrite with minor chalcopyrite and native gold. During the period 1892-1908 a shaft was sunk to a depth of 100 feet (30.5m) and an adit was driven for a distance of 106 feet (32.3m). Production during the years 1897-1898 and 1908 reportedly yielded 387, 730 tons of material at a grade of 0.53 oz/t Au (15.0 g/t) (*op.cit.*). The adjacent Comstock Property also consists of a quartz-calcite vein system that strikes southeast and dips 80° to the south. The latter was reportedly exposed for a distance of 100 feet and tested by a shaft to a depth of 102 feet (*op. cit.*). Visible gold was reported to occur in mineralized veins at a depth of 65 feet in the shaft and high-grade grab samples with as much as 12.9 oz/ton Au (364.9 g/t) were reported (*op.cit.*). During this study very little evidence of mineralization and/or veining was

found, although a small pit with fragments of narrow quartz-calcite veinlets containing disseminated pyrite and chalcopyrite, hosted in Huronian arkosic rocks, was located.

Wanapitei Area - The Dolmac Property

The Dolmac Property, located in the centre of the Wanapitei group of occurrences, represents an impressive showing of sulphide mineralization hosted in Nipissing Diabase (figure 2.53). Whilst not a representative example of a quartz-calcite vein deposit, it has yielded significant assay results in previous studies, and based on observations from this study it is suggested that the occurrence may represent a relatively pristine example of primary sulphide mineralization in the Nipissing Diabase. As such, the occurrence was sampled by the author in order to help determine the sulphur isotopic composition of the Nipissing Diabase. The mineralized occurrence lies along the southeastern shore of Rathbun Lake, near the western contact of a large Nipissing Diabase sill and Gowganda Formation sedimentary rocks. The main mineralized zone strikes perpendicular to the lithological contact and is approximately 12 metres long and up to 0.6 metres wide, striking 135° and dipping 60° - 70° to the north (Ogden, 1957; Dressler, 1982). Geological mapping of the shaft and drifts on the property highlighted the presence of a southwest-trending fault system that may have offset the mineralization at depth (Ogden, *op. cit.*). The main mineralized zone, comprising semi-massive sulphide mineralization is entirely hosted in the Nipissing diabase and gradually grades inwards into relatively unaltered and unmineralized hypersthene diabase. The dominant ore minerals include chalcopyrite, pyrite, pyrrhotite, magnetite, and traces of covellite. During this study, a small exploration shaft and trench were encountered, in addition to several broken trays of diamond drill core consisting of barren phases of the Nipissing Diabase. At the shaft, several samples of semi-massive sulphide dominated by pyrite and chalcopyrite were found in the waste pile. Along the shoreline of Rathbun Lake, a zone

of *in situ* banded quartz-epidote-carbonate alteration (figure 2.62) with minor pyrite and chalcopyrite mineralization was noted. Gangue in the main mineralized zone consists of plagioclase, quartz, epidote, chlorite, and minor biotite and carbonate. Notably absent in the mineralized zones (in comparison to unaltered Nipissing Diabase) are grains of pyroxene, which typically form up to 25 modal % of the hypersthene diabase (Dressler, *op.cit.*). A sample of the mineralized zone collected by the Ontario Geological Survey yielded 10.2 wt.% Cu, 2.22 oz/t Ag (62.8g/t Ag), 0.14 wt.% Ni, 0.056 oz/t Pt (1.58g/t Pt), 0.02 oz/t Au (0.56g/t Au) and 34.6 g/t Pd (Dressler, *op.cit.*). Ogden (1957) and Dressler (1982) noted that the mineralization is preferentially concentrated near folds and irregularities in the sedimentary-d diabase contact and that it likely it originally formed schlieren-like features within the diabase. The schlieren-like features were probably part of a larger sulphide body that was disrupted during the intrusion of the diabase or by post-intrusion faulting.

Figure 2.62. Chip sample of *in situ*, banded epidote-quartz-carbonate alteration in Nipissing Diabase hosting minor pyrite and pyrrhotite mineralization, Dolmac occurrence, Wanapitei area (sample #WN-21).

Wanapitei Area - The Decade and Parkin Occurrences

The Decade and Parkin property is situated approximately 4 kilometres west of the McLaren Lake Fault and is the most westerly of the mineralized vein occurrences from the Wanapitei area sampled in this study (figure 2.53). It consists of three separate showings of precious- and base-metal vein mineralization in a North-South trending zone located within Parkin Township. The most northerly occurrence on the property is termed the “Decade”, whereas the two southern occurrences are termed the “Parkin” and “Parkin South” respectively. Upon entry to the property from the east, evidence of recent diamond drilling and the location of one drill collar was noted. The sedimentary rocks at the drill-site display traces of disseminated pyrite mineralization hosted in Quirke Group (Huronian) quartz arenite and the drill collar plunges at 48° with an azimuth of 310° (*i.e.* towards the main showings).

At the Decade showing, no obvious signs of exploration activity were noted, and although a few outcrops were flagged, no visible mineralization (or evidence of previous sampling) was noted. One outcrop with a trace of disseminated pyrite within a quartz arenite unit was however found and sampled. Historical reports indicate a quartz vein system hosted in sheared Quirke Group limestone striking N40°W and dipping vertically. The main vein is 1.8 metres wide (with stringers extending more than 6 m to one side) and was exposed by stripping for a distance of more than 60 metres. Mineralization associated with the vein system includes galena, chalcopyrite, and sphalerite. Geochemical assays produced by Decade Explorations Limited yielded gold values as high as 25.5 g/t Au (Gordon *et al.*, 1979).

By contrast, the Parkin occurrence does have evidence of its recent exploration history, with a large trenched and pressure-washed area being noted. Unfortunately, only a few barren quartz veins (<5 cm wide) were located within the trenched/exposed area (figure 2.63). The exposed sub-vertical quartz veins are aligned along the foliation in the host limestone, striking 305° and dipping 85° to the north. In addition, just north of the main trench, a small exploration trench did uncover some minor quartz-calcite veinlets and stringers associated with trace pyrite mineralization. The fine-grained limestone has been deformed, with a well-developed foliation and minor isoclinal folding present. The quartz-calcite veining and mineralization also occurs parallel to the dominant foliation. Historical reports, however, indicate the presence of a zone, 60 by 70 feet (18 x 20m), containing a number of quartz veins and stringers striking N80°E, which host some galena, pyrite, breunnerite [(Mg,Fe,Mn)CO₃], and have anomalous values of copper, gold, and silver. The latter zone occurs is reported to occur in an isoclinally folded belt of southeast-trending, steeply-dipping, brecciated Serpent Formation limestone. An example of a quartz vein from this zone, sampled by the Ontario Geological Survey, returned an assay of 0.20 oz/t Au (5.65g/t) (Gordon *et al.*, 1979; Meyn, 1970).

No evidence of significant exploration activity was noted at the Parkin South occurrence. Much like the Decade showing, no signs of trenching or bulk sampling programs were noted. One flagged outcrop was found, but did not contain any visible mineralization or previous sampling. One outcrop and one large boulder were located with some trace pyrite and chalcopyrite mineralization disseminated in the matrix of brecciated quartz arenite (Huronian metasedimentary rocks). Both specimens were

sampled in the hope that they represent examples of mineralization peripheral to a larger system. Very little information exists aside from an entry in the Ontario Geological Survey Mineral Deposits Inventory, which notes the presence of sulphides in brecciated Serpent Formation metasedimentary rocks.

Figure 2.63. Field photograph of barren quartz veins running parallel to the foliation present in deformed limestone from the Parkin occurrence, Wanapitei area. The veins and foliation strike approximately 305° , while dipping steeply 85° to the north.

Wanapitei Area - The Fraleck Township Showings

Fraleck Township is host to two occurrences of mineralized veins located within a large Nipissing Diabase sill, which outcrops along the eastern margin of the regional McLaren Lake Fault (figure 2.53). The northern Fraleck occurrence occurs along the southwestern flank of a large Nipissing Diabase sill, whereas the eastern Fraleck occurrence occurs separately on the southeast flank of the same diabase sill. Despite reports of significant veining at the northern showing (exposed over a distance of 350 feet or 106 metres; Meyn, 1971), no evidence of veining could be located during the current study. On the upper flank of the sill, sporadic boulders of pyrite- and pyrrhotite-mineralized, medium-grained Nipissing Diabase were discovered in talus. While the bedrock source for the mineralized boulders could not be located, the size, angularity, textures, and composition suggest a local source. The boulders were sampled in order to help determine the sulphur isotopic character of the Nipissing Diabase. Historical notes indicate the presence of a 5 to 30 centimetre wide, quartz-calcite vein, which strikes N20°W, dipping 65° to the east (Meyn, *op.cit.*). The vein was reportedly traced on the surface for 106 metres: at the north the vein disappears under talus, while at its southern end it terminates in a series of flat stringers. At the north end of the vein there is a small zone enriched in galena. A grab sample of the galena-rich mineralization collected by the Ontario Geological Survey yielded assays of 12.93 wt.% Pb, 1.50 wt.% Cu, 1.49 oz/t Ag (42.1 g/t) and 0.91 oz/t Au (25.74 g/t) (Meyn, *op.cit.*). The author also notes that in 1949, a 95-pound sample of ore from this location was tested by the Mineral Dressing and Metallurgical Laboratories, Ottawa (Investigation #M.D. 2597). The ore was found to

contain galena, cerussite, anglesite, chalcopyrite, pyrite, arsenopyrite, covellite, and native gold.

The eastern Fraleck showing is located one kilometre to the southeast of the northern Fraleck showing. Meyn (1971) reported on the presence of a strongly sheared zone striking N20°W on the southeastern flank of a Nipissing Diabase sill. As Meyn (*op. cit.*) noted, the sheared zone was several feet wide and contained "... a cherty quartz-carbonate vein that was traced for approximately 200 feet by test-pits". A grab sample taken by the Ontario Geological Survey from the quartz-carbonate vein was assayed for 30 elements and the results indicated: trace concentrations of Au; less than 0.1 wt.% of: Cr, Co, Pb, Mn, Ni, Ti, and Zn; and less than 0.5 wt.% Cu. During this study, the main exploration trench was located, although the majority of the bedrock has been covered by overburden and vegetation. The trench is approximately 2 metres wide and trends at 320°, with the same orientation as that of the historical reports. Several boulders containing sheared quartz-calcite veins were uncovered in the trench by the author; the sharp-walled veins within the boulders are up to 20 centimetres wide and are hosted in fine-grained Nipissing Diabase that is textually identical to the bedrock exposed in the trench (figure 2.64B). The veins contained variable minor amounts of anhedral chalcopyrite and pyrite mineralization, with abundant malachite staining. Although significant veining was not observed in outcrop, the Nipissing Diabase peripheral to the trench did contain small (<1 cm) quartz-carbonate veinlets free of visible mineralization. Detailed examination of the vein material sampled from the trench revealed the presence of chalcopyrite, cobaltite, pyrite, native silver, argentite, and cerussite. Chalcopyrite and

pyrite are both anhedral in habit and are preferentially hosted in calcite. Subhedral cobaltite and anhedral cerussite, native silver and argentite occur associated with chalcopyrite (figure 2.65). Representative electron microprobe analyses of the major ore minerals are presented in table 2.28. Aside from a minor variation in nickel and cobalt concentrations in the cobaltite grains, the major ore phases did not contain any anomalous metal contents. The dominant gangue mineral is calcite, with lesser concentrations of quartz and chlorite. An interesting accessory phase identified within the vein material was allanite-Ce. Altered fragments of Nipissing Diabase are scattered throughout the vein and consist of chlorite-quartz-albite masses containing accessory titanite, ilmenite, zircon, and iron-oxides.

Table 2.28. Representative electron-microprobe analyses of the major ore minerals from the eastern Fraleck Township vein occurrence, Wanapitei area.

Mineral	cobaltite	cobaltite	cobaltite	cobaltite	sphalerite	pyrite	cerussite	native Ag
Sample #	wn16-4	wn15-3	wn15-1	wn15-4	wn16-5	wn16-6	wn16-3	wn15-5
As	41.76	42.43	43.15	43.95	0.01	0.14	-	-
S	21.27	20.92	20.63	19.69	32.83	53.27	-	0.02
Fe	3.56	3.29	3.50	3.65	7.53	46.73	0.62	0.59
Co	32.02	30.73	28.29	25.68	0.09	-	-	-
Pb	-	-	-	-	-	-	77.98	-
Cu	0.02	0.05	0.06	0.10	4.67	-	1.78	0.07
Ni	1.08	1.76	2.12	5.30	-	0.01	-	-
Ag	-	-	0.03	0.02	-	-	-	103.64
Zn	0.03	0.01	0.02	-	57.23	0.01	0.02	-
Au	0.21	0.08	-	-	-	-	-	-
Total	99.96	99.26	97.80	98.40	102.37	100.16	80.40	104.32
Proportions calculated on $\Sigma\text{Atoms} = 1$								
As	0.302	0.309	0.320	0.327	--	0.001	--	--
S	0.359	0.356	0.358	0.342	0.485	0.665	--	0.001
Subtotal	0.661	0.666	0.678	0.669	0.485	0.665	--	0.001
Fe	0.035	0.032	0.035	0.036	0.064	0.335	0.027	0.011
Co	0.294	0.285	0.267	0.243	0.001	--	--	--
Pb	--	--	--	--	--	--	0.904	--
Cu	--	--	0.001	0.001	0.035	--	0.067	0.001
Ni	0.010	0.016	0.020	0.050	--	--	--	--
Ag	--	--	--	--	--	--	--	0.987
Zn	--	--	--	--	0.415	--	0.001	--
Au	0.001	--	--	--	--	--	--	--
Subtotal	0.339	0.333	0.322	0.331	0.514	0.335	1.000	0.999

Note. All elemental concentrations are reported as weight percent (wt.%). [-] = below the analytical detection limit.

Figure 2.64. (A) BSE-image of sub-euhedral cobaltite (co) rimmed by anhedral chalcopyrite (cpy) with minor iron-oxides (fe) set in calcite gangue (sample# WN-15); and (B) photograph of a boulder of mineralized vein material, located in the exploration trench at the eastern Fraleck showing, Wanapitei area, illustrating the sheared textures and sharp contacts with the diabase host. The boulder was sampled to produce hand samples# WN-14 and WN-15.

Figure 2.65. BSE-images of: (A) Anhedral pyrite (py) with minor iron-oxidation set in calcite (cc) gangue from sample# WN-14; and (B) Tiny, subhedral cerussite grains (cs) associated with anhedral chalcopyrite (cpy) set in calcite gangue from sample# WN-16 (Fraleck east occurrence, Wanapitei area).

Wanapitei Area - The Laura Lake Occurrence

The Laura Lake occurrence represents the northernmost of the mineralized vein occurrences from the Wanapitei area (figure 2.53) visited by the author. Although very little information is available on the Laura Lake occurrence, several trenches and at least one exploration shaft occur along the eastern shoreline of Laura Lake. The only known report of the occurrence was filed by Inco in 1981 (AFRO 1981 MCCONNELL-0010 INCO MET) and notes the presence of four quartz veins, 8 to 25 cm in width, striking S44°E and dipping 40° towards the northwest. The highest grades reported in assay were 0.52 oz/ton Au (14.71 g/t), 0.29 wt.% Cu, and 0.90 wt.% Pb. During this study, one large quartz-dominated vein (~30 cm wide) that trends 280° and dips 70° to the north, was noted in a small exploration pit where the vein sharply cross-cuts Gowganda Formation quartz-arenites. At least three trenches were also located in the area, with significant vein material being present in the respective waste piles. Samples of the host material, *in situ* vein material, and vein material from the waste pile were collected. In the limited number of mineralized samples collected, the main ore phases are chalcopyrite and galena, with both sulphide minerals being preferentially concentrated along the vein margins, near a quartz+chlorite±muscovite border zone. Galena present along the vein margin is sub-euhedral in habit, forming fine-grained cubes 1 to 2 millimetres in diameter. Galena mineralization also occurs disseminated throughout the veins, being situated along fractures and/or grain boundaries of coarse-grained quartz and as small (<5 µm) inclusions in anhedral chalcopyrite. Electron microprobe analysis of the pyrite and chalcopyrite indicated no significant concentration of any trace metals.

Figure 2.66. Field photograph of a $280^{\circ}/70^{\circ}\text{N}$ trending quartz vein (30 cm wide) from the Laura Lake occurrence, Wanapitei area; trace amounts of chalcopyrite and galena mineralization are preferentially concentrated along the vein margins.

2.7 Summary of Mineralized Vein Occurrences

Summarized below in figure 2.67 and table 2.29 are the main morphological, petrographic, mineralogical, and geochemical features of the mineralized vein occurrences ($n=30$) examined and sampled in detail during this study. For all of the occurrences, the assay data that are listed are from this study unless otherwise cited. The occurrences are listed in a general north-to-south trend beginning with the Merico-Ethel property and ending with the Wanapitei occurrences.

All but one of the mineralized vein occurrences are hosted in Proterozoic-aged rocks (*i.e.* Nipissing Diabase and Huronian sedimentary units). The lone exception is the Brett occurrence, which occurs within Archean metavolcanic units of the Abitibi greenstone belt close to the regional unconformity with the Gowganda Formation. Twenty of the mineralized occurrences are hosted in the Nipissing Diabase while the remaining nine occurrences are hosted in the middle to upper formations of the Huronian Supergroup (*e.g.* Serpent and Gowganda Formations). In all of the occurrences the mineralized veins display sharp contacts with the host rocks, with narrow carbonate and ‘aplitic’ alteration halos typically restricted to less than 10 centimetres in width.

Detailed petrographic examination of all the polymetallic vein systems has revealed the multistage nature of the sulphide mineralization, which is well-developed in all but three of the occurrences:

- i) Early-stage sulphide mineralization with associated quartz gangue and accessory chlorite;

- ii) Main-stage polymetallic mineralization (Cu, Co, Ni $\pm$ Pb, Ag, Au, U) hosted in calcite gangue; and
- iii) Late-stage galena mineralization.

Also, in the majority of the mineralized vein occurrences, specular hematite is associated with the transition from the early-stage to main-stage mineralization and gangue mineral deposition.

The idealized, complete paragenetic sequence in a simple, dilatant vein consists of: *i*) quartz + chlorite $\pm$ K-feldspar; *ii*) bands of quartz + chlorite $\pm$ early sulphides; *iii*) zones of calcite $\pm$ hematite + the main-stage sulphides $\pm$ chlorite; and *iv*) a core of massive calcite $\pm$ late-stage galena (figure 2.68). The early-stage is hosted in a silicate gangue and is typically dominated by pyrite, some of which contains appreciable concentrations of Ni and Co. The main-stage of mineralization occurs at the transition from a silicate to calcite gangue, often following significant hematite crystallization. The main-stage is marked by additional pyrite mineralization overprinted, and/or partially replaced by: chalcopyrite, linnaeite-group minerals, cobaltite, galena and an unusual suite of Bi-Pb $\pm$ Cu-sulphide minerals. The main-stage also contains the precious-metal mineralization. In many of the occurrences, an additional late-stage galena displays textural evidence indicating that it was the final ore mineral to crystallize. This paragenetic sequence has much in common with the historical Cobalt-Gowganda vein systems, yet contains lower modal abundances of sulphurarsenide minerals.

Not all of vein occurrences display the entire paragenetic sequence; in some mineralized veins, the main-stage of polymetallic mineralization is poorly developed to absent, whereas in quartz-rich veins, the late calcite-rich stage has not developed. Petrographic and geochemical analyses have also confirmed that the mineralized vein occurrences are commonly precious metal-bearing with both native gold and electrum having been commonly identified. In certain instances (*i.e.* Sauv occurrence, Merico-Ethel property) the mineralized vein occurrences also contain significant concentrations of uranium (up to 1.56 wt.% U_3O_8 equivalent).

As illustrated in figure 2.67, the mineralized veins display a spectrum of vein morphology and style from simple dilatant (*i.e.* open-space filling), to sheared, and brecciated textures, although the vein margins remain sharp and discordant in all three styles. In brecciated veins, fragments of both the early-and main-stage mineralization, and silicate gangue occur as angular fragments set in a late calcite matrix. In most of the mineralized vein systems, the complete spectrum of vein morphologies exists, although the dominant morphology present in the majority of the occurrences is that of simple, dilatants veins.

Figure 2.67. The spectrum of vein morphologies and styles of mineralization from the polymetallic vein occurrences of the Cobalt Embayment. Vein textures range from simple dilatants, to sheared, to brecciated. The nature of the sulphide and sulpharsenide mineralization ranges from disseminated, sub-euhedral grains to semi-massive, granular aggregates. In the dilatant style, the early-stage mineralization is often associated with the early silicate selvages, whereas the main-stage mineralization is hosted in calcite gangue. Within brecciated vein systems, hematite is preferentially associated with the sulphide/sulpharsenide mineralization. The gangue in the sheared and brecciated veins typically consisted of fragments of the early silicate selvage hosted in deformed-to-massive calcite.

Figure 2.68. Idealized paragenetic scheme for polymetallic vein systems of the Cobalt Embayment, Northern Ontario. The vein mineralization is broken down into three stages: early sulphide (silicate gangue), main stage (carbonate gangue) and late stage (galena+calcite).

Table 2.29. Summary of relevant features of all the mineralized vein occurrences sampled during this study.

Mineralized Vein Occurrence	Host Lithology	Strike/Dip	Vein Gangue	Dominant Ore Mineralogy	Accessory Minerals	Assay Results	Other
<i>Merico-Ethel Property</i>							
Merico veins	Nipissing Diabase	260°/75°N	calcite-quartz	chalcopyrite, pyrite, specular hematite, cobaltite, limnaeite, wittichenite, aikinite	chlorite, epidote, allanite-Ce, andradite, xenotime-Y	up to: 12.34g/t Au, 1.01% Co, 23.68% Cu, 44 ppm U	trace aplitic veinlets and alteration
Sauvé	Nipissing Diabase + Gowganda Fm.	250°/87°N	calcite-quartz	chalcopyrite, bornite, hematite, cobaltite	chlorite, pitchblende, rutile, zircon, apatite	1.56% U ₃ O ₈ (Johns, 1986); 0.21 g/t Au, 2.6 g/t Ag, 3.54% Cu, 67.5 g/t Co, 99 ppm U	hematite and aplitic-altered Nipissing Diabase brecciated along Huronian contact
Silver Jackpot	Nipissing Diabase	022°-054° / 75°-80°S	calcite-quartz	chalcopyrite, pyrite, cobaltite, native silver, specular hematite	chlorite, epidote, allanite-Ce	6.79g/t Ag, 2.83g/t Au and 2.58% Cu (Johns, 1986)	well-developed aplitic wall-rock alteration
"Unnamed Occurrence"	Nipissing Diabase	230°/90° and 046°/82°S	calcite-quartz	chalcopyrite, pyrite, specular hematite, cobaltite	chlorite, andradite, diopside	29.4g/t Ag, 1.13 g/t Au and 3.59% Cu (Johns, 1986)	sporadic aplitic wall rock alteration and aplitic dykes
Beaver Pond	Nipissing Diabase	080°/84°S	calcite-quartz	chalcopyrite, pyrite, specular hematite, cobaltite	chlorite, epidote, allanite-Ce, zircon	0.79 g/t Au, 14 g/t Ag, 13.48% Cu, 3254 g/t Co, 15 ppm U	narrow aplitic veinlets
Paramount	Nipissing Diabase	292°/ 80°N-80°S	calcite-quartz	chalcopyrite, pyrite, specular hematite, cobaltite, bornite, galena	chlorite, epidote, allanite-Ce,	39g/t Ag, 2043 g/t Co, 7974 g/t Cu, 7672 g/t Pb	narrow aplitic alteration zones and dykelets parallel to veins
Beaver Auxiliary	Nipissing Diabase	NW, N, SE	calcite-quartz	chalcopyrite, pyrite, galena, cobaltite, hematite, sphalerite	chlorite, epidote, allanite-Ce, andradite		

Table 2.29 Continued

Mineralized Vein Occurrence	Host Lithology	Strike/Dip	Vein Gangue	Dominant Ore Mineralogy	Accessory Minerals	Assay Results	Other
<i>Gowganda Area</i>							
Capital	Nipissing Diabase		calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		Sporadic aplitic wall-rock alteration and dikes
Bishop	Nipissing Diabase	212°/86°N and 020°/86°E	calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		Sporadic aplitic wall-rock alteration and dikes
Mann	Nipissing Diabase	237°-255°/82°N	calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		Sporadic aplitic wall-rock alteration and dikes
Parcher	Nipissing Diabase		calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		Sporadic aplitic wall-rock alteration and dikes
Reeve-Dobie	Nipissing Diabase	198°/78°N	calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		Sporadic aplitic wall-rock alteration and dikes
Duncan Lake	Nipissing Diabase	070°-080°/80-85°S	quartz-calcite	galena, chalcocopyrite, pyrite, cobaltite, sphalerite, aikinite-bismuthinite	chlorite, iron-oxides, allanite-Ce, rutile, titanite, andradite, and zircon	up to: 0.09 g/t Au, 224 g/t Ag, 211 ppm Co, 535 g/t Cu, 2.81% Pb	

Table 2.29 Continued

Mineralized Vein Occurrence	Host Lithology	Strike/Dip	Vein Gangue	Dominant Ore Mineralogy	Accessory Minerals	Assay Results	Other
<u>Cobalt Area</u>							
Bay	Nipissing Diabase		calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		sporadic aplitic wall rock alteration and dikes
Temagami-Lorrain	Nipissing Diabase		calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		sporadic aplitic wall rock alteration and dikes
Gosselin	Nipissing Diabase	236°/74°N	calcite-quartz	cobaltite, pyrite, native silver, galena, bismuthinite, emplectite, wittichenite, sphalerite, safflorite	chlorite, epidote, titanite, allanite-Ce, apatite, garnet		sporadic aplitic wall rock alteration and dikes
Brett Property	Archean mafic volcanics (Abitibi)		calcite-quartz	native gold, chalcopryrite, pyrite, cobaltite, pyrrhotite, aleksite-bismuthinite	epidote, actinolite, chlorite, allanite-Ce	grab sample 6,222 g/ton Au (Temex Resources, 2004)	calcite-quartz veins and vein breccias
Johnson Lake	Gowganda Fm.	085°/72°S	calcite-quartz	pyrite, chalcopryrite	chlorite, epidote, allanite-Ce		joint-controlled stringers with minor Si and CO ₂ alteration of host rocks
Delhi Township	Nipissing Diabase	300°/70-90°N	quartz-calcite	galena, pyrite, chalcopryrite, pyrrhotite, cobaltite, sphalerite, native gold	chlorite, epidote, allanite-Ce, iron-oxides	7.13% Pb, 157.8g/t Ag, and 7.07g/t Au (Lawton, 1952); 36.62g/t Au, 28.95% Pb, 2.23% Cu, 258g/t Ag, 285ppm Co	

Table 2.29 Continued

Mineralized Vein Occurrence	Host Lithology	Strike/Dip	Vein Gangue	Dominant Ore Mineralogy	Accessory Minerals	Assay Results	Other
<i>Wanapitei Area</i>							
Laura Lake	Gowganda Fm.	280°/70°N	quartz-calcite	galena, chalcopyrite, pyrite	chlorite, muscovite, epidote-allanite-Ce	14.71 g/t Au, 0.29% Cu and 0.90% Pb (AFRO 1981 MCCONNELL-0010 INCO MET)	
Fraleck East	Nipissing Diabase	320°/NA	calcite-quartz	chalcopyrite, pyrite, cobaltite, native silver, cerussite, argentite	allanite-Ce, chlorite, titanite, ilmenite, zircon and iron-oxides		
Fraleck North*	Nipissing Diabase	340°/65°E	calcite-quartz	galena, cerussite, anglesite, chalcopyrite, pyrite, arsenopyrite, covellite, native gold		12.93 % Pb, 1.50 % Cu, 42.15 g/t Ag and 25.74 g/t Au (Meyn, 1971)	
Decade*	Serpent Formation	320°/90°	quartz	galena, chalcopyrite and sphalerite	calcite	25.5 g/ton Au (Gordon <i>et al.</i> , 1979)	
Parkin Township*	Serpent Formation	305°/85°N	quartz	galena, pyrite, undefined copper, gold and silver	calcite	0.20 oz/ton Au (Meyn, 1970)	
Crystal	Gowganda Fm. + Nipissing Diabase	SE/80°S	quartz-calcite	pyrite, chalcopyrite, native gold	chlorite, epidote-allanite-Ce	387,730 t at 15.0 g/ton Au; grab sample 364.9 g/t Au (Gordon <i>et al.</i> , 1979)	vein systems occur contact between Gowganda Formation and Nipissing Diabase
Gordon	Gowganda Fm.	090°/70°S	quartz ± calcite	pyrite, chalcopyrite, galena	muscovite, zircon, xenotime-Y, LREE-phosphate		
Burda	Gowganda Fm. + Nipissing Diabase	090°/70-90°S	calcite-quartz	pyrite, chalcopyrite, native gold and galena	chlorite, muscovite, epidote-allanite-Ce	0.42 % Cu and 0.62 g/t Au over 15 feet by 300 feet (Shklanka, 1969)	Mineralization splays off regional McLaren Lake fault system.

Table 2.29 Continued

Mineralized Vein Occurrence	Host Lithology	Strike/Dip	Vein Gangue	Dominant Ore Mineralogy	Accessory Minerals	Assay Results	Other
Glade	Nipissing Diabase + Serpent Formation	145°/70°S	quartz-calcite	chalcopyrite, pyrite, cobaltite	chlorite, epidote-allanite-Ce, muscovite	34.51 g/t Au, 2.6% Cu, 7.35 g/t Ag (Gordon <i>et al.</i> , 1979)	
McLean-Watt	Serpent Fm.	330-340°/70-85° NE	chlorite-quartz-calcite breccias	pyrite, chalcopyrite, native gold	biotite, actinolite, albite, quartz, magnetite, ilmenite, galena, apatite, rutile, titanite, xenotime-Y, zircon, thorite, LREE-phosphate		Mineralization occurs in brecciated zones of albitized Serpent Formation quartzite
Davis	Gowganda Fm.		quartz-calcite	chalcopyrite, pyrite, arsenopyrite, cobaltite	albite, zircon, rutile, apatite, LREE-phosphate	4.09% Cu, 7.7 g/ton Au (Shklanka, 1969; Kindie, 1933)	

Note. Unless otherwise noted and referenced, the assay results are from this study. Conversion of historical assay results: 1 oz/t = 34.2857 g/t; 1 ppm = 1 g/t

Chapter Three: Carbon and Oxygen Isotopic Compositions of Vein Calcite

3.1 Introduction

Oxygen has three stable isotopes (^{16}O , ^{17}O , and ^{18}O) with natural abundances of 99.762, 0.038 and 0.200 percent, respectively. Typically, the oxygen isotopic composition of a substance is reported in terms of the difference, expressed in parts per thousand or per mil (‰), of the $^{18}\text{O}/^{16}\text{O}$ ratio relative to an internationally accepted standard called VSMOW (Standard Mean Ocean Water), using the delta (δ) notation (Faure and Mensing, 2005):

$$\delta^{18}\text{O} = \frac{(R_{\text{sam}} - R_{\text{std}})}{R_{\text{std}}} * 10^3 \text{ ‰} \quad \text{where, } R_{\text{sam}} = ^{18}\text{O}/^{16}\text{O} \text{ of sample}$$

$$R_{\text{std}} = ^{18}\text{O}/^{16}\text{O} \text{ of standard (VSMOW)}$$

Fractionation or partitioning between the two most abundant isotopes of oxygen is primarily controlled by equilibrium and kinetic effects and vary systematically with each other in proportions that can be approximated by the mass difference between the isotopes (*op. cit.*). Due to their relative large mass difference (12.5%) and natural abundances, the $^{18}\text{O}/^{16}\text{O}$ ratio is one of the most effective isotope ratios for observing the effects of fractionation in geological processes.

Hydrogen has two stable isotopes, namely ^1H and ^2H or D (*i.e.* deuterium) and its natural isotopic variations are reported, in a manner similar to those of oxygen, using the D/H ratio or δD notation. In combination, the stable isotopes of hydrogen and oxygen result in nine different isotopic varieties of water (*e.g.* H_2O^{18} , D_2O^{16}), all with very slightly different masses. Changes in state of water, by processes such as evaporation

and condensation, under equilibrium conditions at a constant temperature, will therefore cause significant fractionations in the D/H and $^{18}\text{O}/^{16}\text{O}$ ratios to occur. Such mass-dependent isotopic fractionations are also temperature dependent, with the magnitude of the fractionation factor, in most cases, decreasing with increasing temperature, and approaching unity at high temperatures (Faure and Mensing, 2005.). In the case of water, the isotopically lightest $^1\text{H}_2^{16}\text{O}$ molecule evaporates preferentially relative to the isotopically heaviest molecule (D_2^{18}O), thereby causing an enrichment in the heavier isotopes of D and ^{18}O in the residual aqueous fluid. As air masses that form in the equatorial regions travel towards the poles, condensation and precipitation drive these temperature-sensitive fractionations towards lower $^{18}\text{O}/^{16}\text{O}$ and D/H ratios in meteoric water near the poles relative to equatorial ocean water (*op.cit.*). As hydrogen and oxygen are subjected to the same processes, a linear trend (defined as $\delta\text{D} = (7.96) \delta^{18}\text{O} + 8.86$; Rozanski *et al.*, 1993) forms (see figure 3.1) termed the Meteoric Water Line (MWL). Dansgaard (1964) was the first to illustrate the temperature dependence of $^{18}\text{O}/^{16}\text{O}$ values, expressed in the equation $\delta^{18}\text{O}_a = 0.695T_a - 13.6$, where the subscript “a” denotes the annual mean value. Therefore, if the average annual temperature of a locality is known, then an average $^{18}\text{O}/^{16}\text{O}$ value of meteoric precipitation can be derived. Incorporating these data with the linear relationship defined by the Meteoric Water Line allows for a calculation of the $^2\text{D}/^1\text{H}$ ratio. Therefore, the influx and mixing of meteoric water with ore-forming fluids (*i.e.* more saline, hydrothermal fluids) should be observed as a cluster of data trending towards the point defined by the above relationships on the Meteoric Water Line. Since H_2O is the dominant component of most mineralizing fluids,

Figure 3.1. Hydrogen and oxygen isotopic composition of different fluid reservoirs in relation to the Meteoric Water Line defined by Rozanski *et al.* (1993). The isotopic compositions of the geological reservoirs are those defined in Sheppard (1986) and reflect equilibrium isotopic values in relation to the respective host material. The author defines organic waters as those containing D/H ratios derived from the transformation of organic matter by dehydration, dehydrogenation, oxidation and/or exchange while the $\delta^{18}\text{O}$ values are probably controlled by the $\delta^{18}\text{O}$ values of the reservoir rocks. The field for magmatic water implies primary water that was transported within the magma from its source. The compositional field for Canadian Shield brines represents saline, Ca-Na-Cl brines with high total dissolved solids present in fault and shear zones at depths greater than 600 m throughout the Canadian shield (Frape *et al.*, 1984).

knowledge of its origin is a fundamental aspect to any theory of hydrothermal ore deposition (*cf.* Taylor, 1997).

Carbon has two stable isotopes (^{13}C and ^{12}C) with natural abundances of 98.90 and 1.10 percent, respectively (Faure and Mensing, 2005). In a similar way to that used for oxygen isotope compositions, the carbon isotopic composition of a substance is reported in terms of the parameter called delta (δ) which is defined:

$$\delta^{13}\text{C} = \frac{(R_{\text{sam}} - R_{\text{std}})}{R_{\text{std}}} * 10^3 \text{‰} \quad \text{where, } R_{\text{sam}} = ^{13}\text{C}/^{12}\text{C} \text{ of sample}$$

$$R_{\text{std}} = ^{13}\text{C}/^{12}\text{C} \text{ of standard (PDB)}$$

Being the fourth most abundant element of the solar system, carbon plays an important role in most geochemical and biological processes at or near the surface of the Earth. One of the major fractionations occurs during photosynthesis when plants absorb CO_2 and preferentially incorporate ^{12}C over ^{13}C , causing a shift in isotopic values for most organically-derived matter (Faure and Mensing, 2005). Experimental evidence suggests that in natural hydrothermal fluids, isotopic exchange between aqueous carbonate species (CO_2 , HCO_3^- , etc.) is very rapid and isotopic equilibrium is likely to be achieved, unless species of differing valences are present which require redox reactions to facilitate isotopic exchange (Ohmoto, 1986). Furthermore, the rates of isotopic exchange between fluids and calcite under hydrothermal conditions are rapid enough to consider that isotopic equilibrium has been established between fluids and/or fluids and the wall rocks (O'Neil *et al.*, 1969). Therefore, the carbon isotopic composition of the

mineralizing fluids should reflect the isotopic composition of source reservoirs. Hydrothermal calcite crystallization is typically controlled by four dominant processes: *i*) “boiling” (the generation of CO₂ and H₂O vapour); *ii*) changes in temperature; *iii*) fluid mixing; and *iv*) reaction with wall rocks (*i.e.* wallrock alteration). In particular, calcite precipitated by fluid-mixing processes should produce a covariation in the carbon and oxygen trend that is controlled by the mixing ratio, precipitation temperature and pH and isotopic composition of the mixing fluids (Schwinn *et al.*, 2006).

3.2 Methodology

One hundred and fourteen calcite samples, collected from mineralized vein occurrences located throughout the Cobalt Embayment (figure 3.2), were selected for carbon and oxygen isotopic analysis. The samples were carefully selected based upon: *i*) the nature, location, and geological setting of the mineralized vein occurrence and its inherent relationship to the Proterozoic mineralization that is broadly characteristic of the Cobalt Embayment as a whole; and *ii*) the ease with which a pure (*i.e.* lacking any discernible mineral inclusions), well characterized, 2-10 gm sample of vein calcite could be extracted from the vein material collected in the field.

The main sample locations are shown in figure 3.2, and serve to highlight the broad, basin-wide coverage of the field sampling program. After their physical separation from large mineralized vein samples, the calcite separates were prepared and analyzed within the G.G. Hatch Stable Isotope Laboratories of the Ottawa-Carleton Geoscience Centre (OCGC). The analytical procedure used is as follows: 0.3 mg of pure

calcite was weighed into a glass vial; 0.1 mL of H_3PO_4 was added to the side and Helium-flushed while horizontal. The vials were then placed vertically in a sample block and heated at 25°C for 24 hours, followed by extraction of the released gases in a continuous flow of ultra-pure helium gas. The measurements were generated by passing the gases through a Gas Bench II and Delta XP isotope-ratio mass spectrometer, both manufactured by Thermo Finnigan. Analytical precision (2σ) is determined to be $\pm 0.1\text{‰}$ (Wendy Abdi, *pers. comm.*). The carbon isotopic compositions are reported in reference to the Pee Dee belemnite (PDB), whereas the oxygen isotopic compositions are referenced to Vienna Standard Mean Ocean Water (VSMOW). The results of the carbon and oxygen isotope analyses of all of the mineralized vein samples from the Cobalt Embayment are presented in [Appendix C](#).

Figure 3.2. Major sampling locations (**bold typeface**) of mineralized quartz-calcite veins in the Cobalt Embayment that were selected for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements, highlighting the basin-wide coverage of the mineralized vein occurrences. The lack of sampling from the western and central portion of the Cobalt Embayment reflects the limited exploration and infrastructure in these regions.

3.3 Results

The results of the current study are summarized in figure 3.3. As illustrated by the plot of carbon *versus* oxygen isotopic compositions, with the exception of a few outliers, the data exhibit a relatively constrained range in oxygen isotope values while varying significantly in terms of their carbon isotopic composition. The majority of the data cluster within the range of: -10.00 to +2.69‰ $\delta^{13}\text{C}$ and +8.59 to +12.64‰ $\delta^{18}\text{O}$. Furthermore, occurrences from the same geographic region display some degree of consistency in terms of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. The data in figure 3.3 are organized based on proximity to each other and in a general north-to-south trend through the Cobalt Embayment. The data can be divided geographically and isotopically into: the Elk Lake area, the Gowganda area, the Cobalt area, and the Wanapitei area.

Individual occurrences from the central portion of the embayment, such as the Delhi Township and Brett, plot within the main cluster of values. The main exception comes from the main Merico-Ethel vein systems, which data are clearly differentiated from nearby occurrences by having a significant number of markedly negative $\delta^{13}\text{C}$ values; values that define a steeply inclined trend (red circles in figure 3.3), with significant variation in $\delta^{13}\text{C}$ (-22.43 to +0.96‰) but only a relatively narrow range in $\delta^{18}\text{O}$ values (+9.94 to +14.67‰). Petrographic and electron microprobe investigations of the Merico-Ethel vein calcites did not reveal any obvious systematic controls (*i.e.* textures, composition, etc.) on the $\delta^{13}\text{C}$ composition of the vein calcite.

Analysis of samples from the Cobalt mines produced the greatest variability of $\delta^{18}\text{O}$ values, ranging from +9.03 to +22.24 ‰. These results are supportive of the range of $\delta^{18}\text{O}$ values reported by Kerrich *et al.*, (1986) and provide further support for incursion of a low temperature (~50°C) fluid post-mineralization. The authors suggest meteoric-dominant waters where $\delta^{18}\text{O} = -8$ to -22 ‰ (*op.cit.*).

Figure 3.3. Carbon and oxygen isotopic composition of calcite sampled from mineralized vein occurrences throughout the Cobalt Embayment. The samples are grouped according to geographic position (north to south) and proximity to each other: the colour-filled circles (●) represent occurrences in the Elk Lake Area; the colour-filled squares (■) represent occurrences in the Gowganda area; the colour-filled triangles (▲) represent the Cobalt area; and the colour-filled stars (★) represent occurrences in the Wanapitei area (*i.e.* Fraleck and Burda occurrences).

3.4 Discussion

As illustrated by figure 3.4, the carbon and oxygen isotope analyses of the base- and precious-metal mineralized calcite-quartz veins are similar to the historical data from the Cobalt silver-dominated mineralization (*cf.* Kerrich *et al.*, 1986). Whilst broadly similar to the historical carbon and oxygen isotopic data for calcites reported by Kerrich *et al.* (1986), the newly-acquired isotopic data do, however, exhibit a more constrained set of $\delta^{18}\text{O}$ values and greater variability in $\delta^{13}\text{C}$ values. The greater variability in $\delta^{13}\text{C}$ values is perhaps not unexpected, given the broader geographical coverage and regional variation in source rocks. However, the reduced variability of oxygen isotopic data is quite distinctive and suggests that the vein occurrences may be linked by a common fluid composition (given that H_2O is the dominant oxygen source in mineralizing fluids)

Although a review of the literature has provided ranges of the isotopic values for the important fluid-rock reservoirs found within the Cobalt Embayment, it should be stressed that there is a scarcity of stable isotopic data for the major rock units present in the Northern Cobalt Embayment, as is evidenced by the fact that *only one* isotopic measurement has been reported for the Lower Gowganda Formation (*i.e.* Bekker *et al.*, 2006). Thus, the majority of the stable isotopic compositions that are available in the published literature have been obtained from upper Huronian sedimentary units sampled near the southern margin of the Cobalt Embayment and the southwestern tract that extends towards Sault Ste. Marie (*i.e.* Bekker *et al.*, 2005 and 2006). This is significant in that the lower Huronian sedimentary units sampled in the southern margin do not extend northwards over the entire extent of the Cobalt Embayment. Only the upper

Huronian units, beginning with the Lower Gowganda Formation, cover the majority of the embayment (see figure 1.2, a schematic cross-section of Cobalt Embayment).

As shown in figure 3.4, the majority of the carbon and oxygen isotopic compositions of the vein calcite from mineralized occurrences examined in this study fall within the ranges reported for calcite from the lower Huronian sedimentary units. These data thus indicate that whilst the majority of the mineralized calcite veins are hosted in Nipissing Diabase, the primary source of carbon and oxygen for the vein calcite may have been derived *via* fluid interaction with the Huronian sedimentary units. Also, the majority of the vein calcite isotopic compositions sampled from the Gowganda area (and one “unnamed” occurrence on the Merico-Ethel property) have elevated $\delta^{13}\text{C}$ values (> 0 ‰; *i.e.* Duncan Lake, Parcher, and Bishop Brothers) and plot above the majority of the sampled occurrences (figure 3.3). These elevated values indicate the potential derivation of a component of their carbon from either: (i) the Archean mafic metavolcanic rocks that underlie the majority of the Cobalt Embayment; or (ii) the influx of meteoric water.

Figure 3.4. Carbon and oxygen composition of vein calcite from mineralized occurrences throughout the Cobalt Embayment plotted in relation to the important fluid-rock reservoirs, and also pyrobitumen from the Elliot Lake region. It is important to note that only one analysis has been completed on the carbon and oxygen isotopic composition of the upper Huronian sedimentary rocks (from a sample of the Gowganda Formation).

The unusually depleted (negative) $\delta^{13}\text{C}$ values of vein calcite from the base- and precious-metal mineralized veins (figure 3.3) of the Merico-Ethel property (figures 3.2) likely reflect the late-stage interaction of hydrothermal fluids with organic matter in local lithological units in the footwall of the deposit. Organic matter can cause shifts in the carbon isotopic composition of its host rock/s by virtue of its degradation during diagenesis and/or a low-temperature hydrothermal processes. As noted by Ohmoto and Goldhaber (1997), the decomposition of organic matter during diagenesis is accomplished through a series of biological and abiotic steps by:

i) aerobic organisms ($\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$)

ii) iron- and manganese-reducing bacteria

($\text{CH}_2\text{O} + 4\text{FeOOH} + 8\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{CO}_2 + 7\text{H}_2\text{O}$)

and, finally

iii) sulphate-reducing bacteria ($2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$)

The resultant CO_2 (aq) and HCO_3^- become significantly lighter isotopically ($\delta^{13}\text{C} \approx -25\text{‰}$) and the addition of this lighter HCO_3^- to pore fluids can cause saturation in isotopically lighter calcite. At depths of greater than 2 m below the seafloor, methanogenic bacteria can cause further decomposition of organic matter producing methane and CO_2 with extremely negative $\delta^{13}\text{C}$ values (*i.e.* -60 to -110‰) (Schoel, 1984). Analyses of Proterozoic-aged kerogen illustrate that the lowest recorded $\delta^{13}\text{C}$ values are remarkably constant between -30 and -35‰. Only the lowest $\delta^{13}\text{C}$ values in kerogen are considered since diagenesis is known to cause enrichment in ^{13}C within the remaining organic matter, releasing fluids preferentially enriched in ^{12}C . Furthermore, Archean-aged kerogens are interpreted to have even more negative values of $\delta^{13}\text{C}$ ranging from -40 to -50‰ (Hayes *et al.*, 1983). For example, solid pyrobitumen (a black

to dark brown bitumen that is infusible and contains less than 2% carbon disulphide) present in the Matinenda Formation at Elliot Lake has $\delta^{13}\text{C}$ values of -33‰ (PDB) (Stevenson *et al.*, 1990). The pyrobitumen blebs are thought to be a product of the natural migration and maturation of Precambrian petroleum in the lower Huronian sediments due to interaction with water and increased temperatures brought on by regional metamorphism (*op. cit.*).

Oswiacki (1982) was the first geologist to note the presence of an extensive grey argillite (later termed black shale), which is enriched in Ag, Co, Ni, As, Pb, *etc.*, in the Huronian sedimentary rock sequence. In fact, Oswiacki also noted that many of the background values for metal contents are higher outside of the Cobalt camp, potentially illustrating the effects of localized hydrothermal cells that may have leached some of the vein metals from the Huronian sedimentary rocks. The basin-wide $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite are in general support of this observation, with $\delta^{13}\text{C}$ values suggesting fluid interaction with the lower units of the Huronian sedimentary rocks. The observed covariation of carbon and oxygen isotopes at Merico-Ethel appears to be anomalous in comparison to the C and O isotopic characteristics of the rest of the vein deposits. One potential cause of the anomalously low $\delta^{13}\text{C}$ values, in the Merico-Ethel vein calcites, may have been the interaction of organic matter with the mineralizing fluids in the underlying Huronian sedimentary rocks, which also may have facilitated sulphide mineral precipitation in the Merico-Ethel vein systems.

Where plotted individually (or as a group from a localized mineralized vein occurrence), only the vein calcites from the Merico-Ethel property display systematic carbon and oxygen isotope covariation (figure 3.5). In the literature, isotopic covariation in hydrothermal calcites has been ascribed to fluid mixing, wall rock alteration and CO₂ degassing (boiling). Estimates of the carbon isotope composition of the fluid in equilibrium with the Merico-Ethel vein calcites at the time of crystallization can be made by subtracting the temperature-dependent fractionation factors from the composition of the calcite. For most geologically reasonable pH and redox conditions, H₂CO₃ (aq) and HCO₃⁻ are the dominant aqueous species, with concentrations of CO₃²⁻ and CH₄ several orders of magnitude smaller (Schwinn *et al.*, 2006). However, since H₂CO₃ behaves like CO₂, the fractionation factor involving CO₂ is applied where H₂CO₃ is involved (Zheng & Hoefs, 1993). At temperatures above 100°C, the δ¹³C composition of CO₂ (aq) can be approximated by:

$$\delta^{13}\text{C}_{\text{CO}_2} = \frac{(\delta^{13}\text{C}_{\text{calcite}} + 10^3)}{\Delta_{\text{calcite-CO}_2}} - 10^3$$

where Δ_{calcite-CO₂} represents the fractionation factor between calcite and CO₂ at the specified temperature (Ohmoto and Goldhaber, 1987). Similarly, for the calculation the oxygen isotopic composition of the parental fluids, only the fractionation factor between calcite and H₂O at the temperature of precipitation has to be applied, as H₂O is the principal oxygen reservoir (Schwinn *et al.*, 2006). Therefore,

$$\delta^{18}\text{O}_{\text{fluid}} = \frac{(\delta^{18}\text{O}_{\text{calcite}} + 10^3)}{\Delta_{\text{calcite-H}_2\text{O}}} - 10^3$$

where Δ_{calcite-H₂O} represents the fractionation factor of calcite-H₂O at the specified temperature.

Calculations of the equilibrium fluid compositions were based on the carbon isotope fractionation factors $\alpha_{\text{calcite-CO}_2}$ modeled by Ohmoto and Rye (1979):

$$10^3 \ln \alpha = -0.891(10^9/T^3) + 8.557(10^6/T^2) - 18.11(10^3/T) + 8.27$$

The oxygen isotope compositions were calculated utilizing the fractionation factors $\alpha_{\text{calcite-H}_2\text{O}}$ derived by Zheng *et al.* (1999):

$$10^3 \ln \alpha = 4.010(10^6/T^2) - 4.66(10^3/T) + 1.71$$

Based on these determinations, the calculated isotopic fluid composition in equilibrium with the Merico-Ethel vein calcites during crystallization (at 300°C) displays very negative $\delta^{13}\text{C}$ (+3.5 to -14.8 ‰) values and $\delta^{18}\text{O}$ values that cluster near 5‰ (+4.2 to +8.8 ‰). Clearly, the vein calcites record precipitation from a hydrothermal fluid that was depleted in ^{12}C , most likely due to fluid interaction with organic matter in the adjacent Huronian sedimentary rocks or underlying Archean basement.

Figure 3.5. Carbon and oxygen isotopic compositions of vein calcites from base- and precious-metal calcite-quartz veins of the Merico-Ethel property (excluding the Silver Jackpot, Paramount, and Beaver Pond occurrences) illustrating the covariation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

The potential role of precipitational mechanisms in the creation of the correlated carbon and oxygen isotopic values of the Merico-Ethel vein calcites is more difficult to ascertain, because as mentioned above, the stable isotopic compositions of the source reservoirs are poorly constrained in the northern region of the Cobalt Embayment. Fluid mixing is considered to be a significant precipitational mechanism in the formation of hydrothermal ore deposits: one which commonly results in supersaturation of ore and gangue minerals under conditions far from equilibrium with the host rocks (Schwinn *et al.*, 2006; Bethke, 1996). In order to test whether or not fluid mixing was an important process in the formation of the Merico-Ethel vein calcites, suitable fluid-mixing models were developed involving probable fluid compositions: a) A highly saline basinal brine with negative $\delta^{13}\text{C}$ and positive $\delta^{18}\text{O}$ values interacting with meteoric-dominated fluids; and, b) Canadian shield brines with negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values interacting with meteoric-dominated fluids. Two different basement fluids were also modeled in order to reflect all of the potential isotopic reservoirs. Frape *et al.* (1984) reported oxygen isotopic values from deep Canadian Shield brines with negative $\delta^{18}\text{O}$ values that suggest fluid-rock interactions at depth can lead to depleted $\delta^{18}\text{O}$ values. This is in direct contrast to the isotopic composition of fluids interacting with igneous and sedimentary rocks near the surface (basinal brines), which display positive $\delta^{18}\text{O}$ values. Due to the presence of deep-seated regional faults (that were reactivated syn- and post-intrusion of the Nipissing Diabase; Andrews *et al.*, 1986b; Jambor, 1971a), mixing of deep-seated Canadian Shield brines could occur along the major fault systems. As illustrated in figure 3.6, the majority of the mineralized vein occurrences on the Merico-Ethel property are located near regional fault systems mapped by the Ontario Geological Survey. Several of the

faults display textures indicative of reactivation, post-intrusion of the Nipissing Diabase sills, with for example, as much as 305 m of displacement noted along the Lake Timiskaming fault (Jambor, 1971a). Given the temperature dependence of $\delta^{18}\text{O}$ in meteoric precipitation (Dansgaard, 1964; Wood, 1973; Chandler, 1984), the meteoric end-member compositions were estimated to be near 0‰ $\delta^{13}\text{C}$, with slightly negative $\delta^{18}\text{O}$ values (-3‰) and a fluid temperature of 50°C. The slightly negative $\delta^{18}\text{O}$ values of the meteoric water reflect the isotopic composition of meteoric precipitation of mid- to lower-latitudes near the equator (Faure and Mensing, 2005). While remnant magnetism studies have not unambiguously determined the paleolatitude of the Cobalt Embayment (Williams and Schmidt, 1997; Hilburn *et al.*, 2005), the presence of columnar stromatolites features in the lower Espanola carbonate and potential sabkha-type environments preserved in the upper Gordon Lake Formation (Chandler, 1988) suggest deposition in a near-equatorial climate. Furthermore, weathering of feldspars in the middle and upper part of the Lorrain Formation that produced pyrophyllite, sericite, kaolinite and diasporite is suggestive of deep weathering in a warm and humid environment, thereby providing some constraint on the paleolatitude.

In the first set of models, due to the presence of organic matter and interaction with predominantly siliciclastic sedimentary rocks, an estimated composition for the basinal brine was -25‰ $\delta^{13}\text{C}$ and +10‰ $\delta^{18}\text{O}$ at a temperature of 250°C. The oxygen isotopic composition was estimated based upon a meteoric-derived (~0 to -4‰ $\delta^{18}\text{O}$) fluid interacting with more positive (~+10 to +20‰ $\delta^{18}\text{O}$) sedimentary rocks. The $\delta^{18}\text{O}$ composition of the basement brines was estimated from the composition of Canadian

Shield brines sampled, in the Sudbury area, by Frape and Fritz (1987), whereas the $\delta^{13}\text{C}$ compositions likely represent Archean organic matter. Unfortunately, the Archean greenstone-hosted carbonate minerals also contain carbon and oxygen isotopic compositions enriched in the heavier isotopes, preventing an unequivocal distinction between the two potential isotopic source reservoirs to be made.

Regardless of the source of the isotopically heavier fluid, mixing models were created using the equations and models of Schwinn *et al.* (2006). Unlike the earlier models of Zheng and Hoefs (1993), the models of Schwinn *et al.* (2006) take into consideration the effect of salinity on the oxygen concentration in the two fluids. The latter authors note that in highly saline brines (*e.g.* Huronian brines) the oxygen concentration will be much lower than in meteoric waters, an important feature that must be accounted for in the isotopic mass-balance equations. Furthermore, while CO_2 and HCO_3^- are the dominant aqueous carbon species, the Zheng and Hoefs (1993) models fail to recognize the importance of the effects of temperature and pH on the CO_2 - HCO_3^- equilibria (Schwinn *et al.* 2006). Due to the similarity in the lithologies used in the calculations (*i.e.* siliciclastic basin with granitic basement), the fluid compositions and aqueous carbon speciation concentrations were taken from Schwinn *et al.* (2006), and are described in tables 3.1 and 3.2.

Figure 3.6. Location of major groups of polymetallic calcite-quartz vein occurrences within the Cobalt Embayment in reference to regional faults mapped by the Ontario Geological Survey (after Andrews *et al.*, 1986a). All of the major areas that contain base- and precious-metal calcite-quartz vein mineralization are locally cross-cut by regional faults, many of which have been periodically reactivated.

The total carbon concentrations utilized by the latter authors were estimated based on solubility calculations. The meteoric water saturated in carbon was estimated to contain 0.00068 mol/kg of carbon based on atmospheric CO₂ and O₂ fugacities and the temperature of the fluid. Calculated values of the total carbon content of the basinal brine were based on estimated pH values of the brine, which were likely controlled by water-rock reactions with the granitic basement. Model fluids were then evaluated by adding different CO₂ concentrations and adjusting the pH back to the granite-buffered values. Using these methods (*op. cit.*), the most likely basinal fluid composition would allow calcite dissolution or graphite oxidation without significantly changing the pH. Three separate fluid compositions were modeled for the Merico-Ethel vein calcites based upon different ratios of total carbon concentrations in the brine relative to the meteoric fluid ($R_c = m\text{Carbon}_{\text{BRINE}} / m\text{Carbon}_{\text{METEORIC}}$). An R_c value of 7 was estimated by Schwinn *et al.* (2006) to be most likely as this ratio allows calcite dissolution to occur without reaching aqueous fluid saturation. However, if calcite was the solubility-controlling phase in the sedimentary basin, it would be possible to produce greater values of R_c . As such, R_c values of 70 and 700 were also utilized in the mixing models. Utilizing these starting fluid compositions, speciation calculations were performed with the HCh software package, which models heterogeneous equilibria by minimization of the Gibbs free energy of the total system (Shvarov and Bastrakov, 1999; Shvarov, 1978).

The resultant fluid mixing models for the Merico-Ethel vein calcites are presented in figures 3.7 and 3.8. From the data presented in figure 3.7, it is apparent that the carbon and oxygen covariation of the Merico-Ethel vein calcites (+ symbols) can be modelled by

mixing of meteoric and basinal brines, but at significantly higher $\delta^{18}\text{O}$ values. Rather, the oxygen isotope compositions of the Merico-Ethel vein calcites suggest a fluid with $\delta^{18}\text{O}$ values significantly lighter ($\sim 8\text{‰}$) than those of the modelled fluid. In Figure 3.8, the second model incorporating compositions from Canadian Shield brines mixing with meteoric-dominated fluids does produce theoretical compositions closer to those of the Merico-Ethel vein calcites.

One potential explanation for the discrepancy in oxygen isotope values may be the temperature-dependent isotope fractionation factors. In both scenarios, the maximum fluid temperature modelled is 250°C , yet historical fluid inclusion data from the Cobalt-Gowganda camps and mineral parageneses from the current study suggest that temperatures of 350°C were reached during vein formation (Kerrick *et al.*, 1986, Marshall *et al.*, 1993). As the temperature-dependent fractionation factors decrease with increasing temperature, the higher temperatures would cause a shift towards lower $\delta^{18}\text{O}$ values in the modelled calcite. Unfortunately, calculation of the fluid compositions and aqueous carbon speciation concentrations of these higher temperature fluids was not possible during the current study.

Table 3.1. Chemical and isotopic composition of the aqueous fluids A, B, and C used in the fluid mixing models (from Schwinn *et al.*, 2006).

	<u>Fluid A ($Rc=7$)</u>		<u>Fluid B ($Rc=70$)</u>		<u>Fluid C ($Rc=700$)</u>	
	Meteoric	Brine	Meteoric	Brine	Meteoric	Brine
T°C	50	250	50	250	50	250
P (bar)	At.	1000	At.	1000	At.	1000
pH	8.3	4.9	8.3	4.9	8.3	4.9
H ₂ O (kg)	1.0	1.0	1.0	1.0	1.0	1.0
CO ₂ (mol)	0.00068	0.005	0.00068	0.05	0.00068	0.5
NaCl (mol)	0	7.6	0	7.6	0	7.6
KCl (mol)	0	0.62	0	0.62	0	0.62
CaCl ₂ (mol)	0	1.7	0	1.7	0	1.7
HCl (mol)	0	0.000095	0	0	0	0
NaOH (mol)	0	0	0	0.0012	0	0.0023
Ca(OH) ₂ (mol)	0.00015	0	0.00015	0	0.00015	0
$\delta^{13}\text{C}$ (PDB)	0	-25	0	-25	0	-25
$\delta^{18}\text{O}$ (SMOW)	-3	10	-3	10	-3	10

Note: $Rc = m\text{Carbon}_{\text{BRINE}} / m\text{Carbon}_{\text{METEORIC}}$.

Table 3.2. Aqueous carbon speciation of the mixed fluids utilizing the starting fluid compositions A, B, and C ($R_c = 7, 70$, and 700) and determined using the HCh software package (Shvarov and Bastrakov, 1999; Shvarov, 1978).

Temperature	Fluid A ($R_c=7$)			Fluid B ($R_c=70$)			Fluid C ($R_c=700$)		
(°C)	pH	HCO ₃	CO ₂ (aq)	pH	HCO ₃	CO ₂ (aq)	pH	HCO ₃	CO ₂ (aq)
250	4.6	0.0001	0.0049	4.4	0.0004	0.0495	4.2	0.0030	0.4976
240	4.6	0.0001	0.0047	4.3	0.0004	0.0471	4.2	0.0029	0.4727
230	4.6	0.0001	0.0045	4.3	0.0005	0.0446	4.1	0.0028	0.4478
220	4.6	0.0001	0.0042	4.3	0.0005	0.0421	4	0.0028	0.4229
210	4.7	0.0002	0.0040	4.2	0.0005	0.0396	4	0.0027	0.3980
200	4.7	0.0002	0.0038	4.2	0.0005	0.0371	3.9	0.0026	0.3731
190	4.7	0.0002	0.0035	4.2	0.0005	0.0347	3.9	0.0025	0.3482
180	4.8	0.0002	0.0033	4.2	0.0005	0.0322	3.8	0.0024	0.3233
170	4.8	0.0003	0.0030	4.1	0.0005	0.0297	3.8	0.0023	0.2984
160	4.9	0.0003	0.0028	4.1	0.0006	0.0272	3.7	0.0022	0.2735
150	4.9	0.0003	0.0025	4.2	0.0006	0.0248	3.7	0.0021	0.2486
140	5	0.0004	0.0023	4.2	0.0006	0.0223	3.7	0.0020	0.2237
130	5	0.0004	0.0020	4.2	0.0006	0.0198	3.7	0.0019	0.1988
120	5.1	0.0004	0.0018	4.2	0.0006	0.0173	3.7	0.0017	0.1739
110	5.2	0.0004	0.0015	4.3	0.0006	0.0148	3.7	0.0016	0.1491
100	5.3	0.0005	0.0013	4.4	0.0006	0.0124	3.8	0.0015	0.1242
90	5.4	0.0006	0.0010	4.5	0.0007	0.0099	3.8	0.0013	0.0993
80	5.6	0.0006	0.0007	4.7	0.0007	0.0074	3.9	0.0012	0.0745
70	5.8	0.0006	0.0005	4.9	0.0007	0.0049	4.1	0.0010	0.0496
60	6.2	0.0007	0.0002	5.2	0.0007	0.0025	4.3	0.0009	0.0248
50	8.1	0.0007	0.0000	8.1	0.0007	0.0000	8.1	0.0007	0.0000

Figure 3.7. Fluid-mixing model A was generated using the three different fluid compositions (models $R_c=7$, $R_c=70$, and $R_c=700$), which differ only in the ratio of carbon concentrations in the brine relative to the meteoric water ($R_c = m\text{Carbon}_{\text{BRINE}} / m\text{Carbon}_{\text{METEORIC}}$). The isotopic compositional ranges of calcites that would precipitate from the fluid mixing are also shown by the solid lines. The carbon and oxygen covariation of the Merico-Ethel vein calcites (+ symbols) can be modelled by mixing of meteoric (50°C) with basinal brines (250°C), but at significantly higher $\delta^{18}\text{O}$ values. In order to satisfy the mixing curves, the fluids would require geologically unreasonable $\delta^{18}\text{O}$ values (given the approximate paleolatitude and basement lithology).

Figure 3.8. Fluid-mixing model B generated using the three different fluid compositions (models $Rc=7$, $Rc=70$, and $Rc=700$), which differ only in the ratio of carbon concentrations in the brine relative to the meteoric water ($Rc = m\text{Carbon}_{\text{BRINE}} / m\text{Carbon}_{\text{METEORIC}}$). The mixing curves represent mixing of meteoric water (at 50°C) with Canadian Shield Brines (at 250°C). The isotopic compositional ranges of calcites that would precipitate from the fluid mixing are also shown by the solid lines. The Merico-Ethel vein calcites are represented by the plus (+) symbols.

As the solubility of calcite in hydrothermal systems increases with decreasing temperature and decreases with decreasing pressure, calcite precipitation cannot occur by the simple process of cooling in a closed system (Holland and Malinin, 1979; Zheng, 1990a). Isotopic covariation can be explained by CO₂ degassing (“boiling”); and one mineralized vein occurrence at the Merico-Ethel property does contain bladed calcite, which has been well documented as occurring in boiling zones in active epithermal systems and is considered diagnostic of boiling (Etoh *et al.*, 2002). However, boiling typically produces a variation in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, which is not recorded in the Merico-Ethel vein calcites. During CO₂ degassing or boiling, the $\delta^{18}\text{O}$ values in the calcite display greater variation than $\delta^{13}\text{C}$ since oxygen is lost in both degassed CO₂ and H₂O vapour. Such degassing would therefore cause a significant shift in isotopic compositions during calcite crystallization from the fluids. Interestingly, in epithermal systems, boiling is the process that is most effective in producing precipitation of bisulphide-complexed metals such as gold (Hedenquist *et al.*, 2000); and gold occurs in concentrations of as great as 22.53g/t in the Merico-Ethel veins. In order to quantitatively model potential CO₂ degassing from the hydrothermal fluids, the batch and Rayleigh distillation equations developed by Zheng (1990a) were applied to aqueous fluids that would simulate calcite compositions similar to those observed in the mineralized Merico-Ethel veins. Rayleigh fractionation accurately models an open system in which a fractional increment of a trace substance is removed from a larger reservoir. A fractionation factor is maintained between the reservoir and each increment at precipitation, and once formed each increment is isolated from the system (Criss, 1999). Batch fractionation also involves removal of increments from a larger reservoir,

although each increment is removed in clusters or batches (*i.e.* more than one calcite crystal). Assumptions applied to these calculations are that instantaneous isotopic equilibrium fractionation occurred amongst the various carbon species in the gas, dissolved fluids, and the precipitated calcite and that above 100°C, the carbon isotope fractionation between H₂CO₃ (apparent) and CO₂ are roughly equal (Ohmoto, 1972). As with the fluid-mixing models, the aqueous carbon species also becomes important in the quantitative models, as the carbon isotopic fractionation between calcite and HCO₃⁻ is significantly different than that between calcite and CO₂ (Ohmoto and Rye, 1979). Therefore, both batch and Rayleigh precipitation models were produced utilizing the carbon isotope fractionation factors between calcite, CO₂ and HCO₃⁻ (Ohmoto and Rye, 1979); calcite and HCO₃⁻ (Robinson, 1975); calcite and H₂O (Zheng, 1999c); and CO₂ and H₂O (Truesdell, 1974). Unfortunately, very little experimental data exists detailing the temperature effects on the fractionation factors between calcite and HCO₃⁻. Although Romanek *et al.* (1992) found no significant temperature effects on the fractionation factors of the latter from 10 to 40°C, the remainder of the studies have all been done at 25°C (*i.e.* Jimenez-Lopez *et al.*, 2001; Jimenez-Lopez *et al.*, 2006). In the original derivation of the quantitative models, Zheng (1990a) does not specify the values or source of the calcite-HCO₃⁻ fractionation factor used in his models, yet references a study by Robinson (1975) that evidences temperature dependence of carbon isotope fractionation of dissolved carbon species relative to calcite. In this study the enrichment factor (ε) of carbon between calcite and HCO₃⁻ defines an approximately linear equation from 300°C to 125°C: $y = -0.002857x - 2.6529$. This equation was generated from a graphical presentation of the enrichment factor relative to calcite, which was then

converted into the fractionation factor between calcite and HCO_3^- by the following relationship: $\epsilon = (\alpha - 1) \cdot 10^3$ (Miller *et al.*, 2001). Conversion of the enrichment factors presented by Robinson (1975) produced fractionation factors identical to the published experimental values ($\approx 1.0 \pm 0.2 \text{ ‰}$), and also confirms that the fractionation factor is not significantly affected by temperature. As noted by Zheng (1990a), quantitative modeling of the calcite precipitated from batch and Rayleigh distillation equations reveal identical results when the mole fraction of carbon in the degassed CO_2 is less than twenty percent. However, this author is careful to note that when the mole fraction of carbon in the degassed CO_2 is greater than twenty percent, larger variations in $\delta^{13}\text{C}$ values are observed using the Rayleigh distillation models. In the figure below, the batch and Rayleigh distillation models presented are those which most closely approximate the observed isotopic variation documented in the Merico-Ethel vein calcites.

From Valley (1986), the effect of batch degassing on the isotopic composition of a fluid can be expressed as:

$$\delta_{fluid}^f = \delta_{fluid}^i - (1 - F_1) \cdot 10^3 \ln \alpha_{\text{CO}_2\text{-fluid}}$$

where, F_1 is the mol fraction of the element of interest that remains in the fluid after degassing and the i and f superscripts represent the initial and final fluid isotopic compositions.

Likewise, the effect of batch crystallization of calcite on the isotopic composition of a fluid can be expressed as:

$$\delta_{fluid}^f = \delta_{fluid}^i - (1 - F_2) \cdot 10^3 \ln \alpha_{\text{calcite-fluid}}$$

where, F_2 is the mol fraction of the element of interest that remains in the fluid prior to calcite crystallization. If the mol fraction of carbon lost from the fluid through CO_2 degassing is identical to that through calcite crystallization, the following is applicable (Zheng, 1990a):

$$F_1 = 1 - X_{\text{CO}_2}$$

$$F_2 = F_1 - X_{\text{CO}_2} = 1 - 2X_{\text{CO}_2}$$

where X_{CO_2} represents the mole fraction of carbon in the degassed CO_2 .

Since the fractionation factors are different for the dominant aqueous species of oxidized carbon in hydrothermal fluids (H_2CO_3 and HCO_3^-), separate equations apply for each situation. Using batch fractionation models the composition of calcite precipitated from H_2CO_3 -dominated fluids can be modeled by (Zheng, 1990a):

$$\delta^{13}\text{C}_{\text{CAL}} = \delta^{13}\text{C}_{\text{fluid}}^i + (1 - 2X_{\text{CO}_2}) * 10^3 \ln \alpha_{\text{CAL-CO}_2}$$

$$\delta^{18}\text{O}_{\text{CAL}} = \delta^{18}\text{O}_{\text{fluid}}^i + (1 - 2X'_{\text{CO}_2}) * 10^3 \ln \alpha_{\text{CAL-H}_2\text{O}} - (X'_{\text{CO}_2}) * 10^3 \ln \alpha_{\text{CO}_2\text{-H}_2\text{O}}$$

Likewise, the composition of calcite precipitated from HCO_3^- dominated fluids using the batch distillation model is approximated by (*op. cit.*):

$$\delta^{13}\text{C}_{\text{CAL}} = \delta^{13}\text{C}_{\text{fluid}}^i + (1 - 2X_{\text{CO}_2}) * 10^3 \ln \alpha_{\text{CAL-HCO}_3^-} - (X_{\text{CO}_2}) * 10^3 \ln \alpha_{\text{CO}_2\text{-HCO}_3^-}$$

$$\delta^{18}\text{O}_{\text{CAL}} = \delta^{18}\text{O}_{\text{fluid}}^i + (1 - 2X'_{\text{CO}_2}) * 10^3 \ln \alpha_{\text{CAL-H}_2\text{O}} - (X'_{\text{CO}_2}) * 10^3 \ln \alpha_{\text{CO}_2\text{-H}_2\text{O}}$$

In Rayleigh degassing, the isotopic composition of a fluid can be modeled by the relationship (Rayleigh, 1902):

$$\underline{R}^f / R^i = F_1 (\alpha_{\text{CO}_2\text{-fluid}} - 1)$$

where R^f and R^i are the final and initial isotopic ratios of the element of interest. From Zheng (1990b), an approximation for the Rayleigh distillation equation becomes:

$$\delta_{fluid}^f = \delta_{fluid}^i + \ln F_1 * 10^3 \ln \alpha_{CO_2-fluid}$$

Similarly, the effect of Rayleigh distillation on the isotopic composition of calcite crystallized from the fluid can be described by (Zheng, 1990a):

$$\delta_{calcite} = \delta_{fluid}^i + \ln F_1 + 10^3 \ln \alpha_{CO_2-fluid} + (1 + \ln F_2) * 10^3 \ln \alpha_{calcite-fluid}$$

In the case of H_2CO_3 as the dominant dissolved carbon species, the carbon and oxygen isotopic composition of calcite precipitated via Rayleigh fractionation can be modeled by (Zheng, 1990a):

$$\delta^{13}C_{CAL} = \delta^{13}C_{fluid}^i + [1 + \ln(1 - 2X_{CO_2})] * 10^3 \ln \alpha_{CAL-CO_2}$$

$$\delta^{18}O_{CAL} = \delta^{18}O_{fluid}^i + [1 + \ln(1 - 2X'_{CO_2})] * 10^3 \ln \alpha_{CAL-H_2O} + \ln(1 - X'_{CO_2}) * 10^3 \ln \alpha_{CO_2-H_2O}$$

where X'_{CO_2} represents the mole fraction of oxygen in the degassed CO_2 .

In the case where HCO_3^- is the dominant dissolved carbon species, the carbon and oxygen isotopic composition of calcite precipitated by Rayleigh fractionation can be modeled by (*op. cit.*):

$$\delta^{13}C_{CAL} = \delta^{13}C_{fluid}^i + \ln(1 - X_{CO_2}) * 10^3 \ln \alpha_{CO_2-HCO_3^-} + [1 + \ln(1 - 2X_{CO_2})] * 10^3 \ln \alpha_{CAL-HCO_3^-}$$

$$\delta^{18}O_{CAL} = \delta^{18}O_{fluid}^i + \ln(1 - X'_{CO_2}) * 10^3 \ln \alpha_{CO_2-H_2O} + [1 + \ln(1 - 2X'_{CO_2})] * 10^3 \ln \alpha_{CAL-H_2O}$$

Figure 3.9. Calcite isotopic compositions produced by batch (dashed line) and Rayleigh (solid line) fractionation models (degassing/boiling models) from a decreasing temperature fluid using the methods outlined by Zheng (1990a) and the fractionation factors between calcite, H_2O and aqueous species of carbon of: Ohmoto and Rye (1979), Truesdell (1974), Robinson (1975), and Zheng (1999). A starting fluid was selected from the fluid-mixing models with an isotopic composition of $\delta^{13}\text{C} = -15 \text{ ‰}$ and $\delta^{18}\text{O} = 0 \text{ ‰}$ at a temperature of 300°C , with calcite precipitation and CO_2 degassing continuing until 100°C .

As illustrated on figure 3.9, both the batch and Rayleigh fractionation plots fail to accurately model the variation in $\delta^{13}\text{C}$ values observed in the Merico-Ethel vein calcites. Despite utilizing the models that generate the greatest variation in $\delta^{13}\text{C}$ values, the range of $\delta^{13}\text{C}$ values observed in the Merico-Ethel vein calcites could not be replicated within the narrow range of $\delta^{18}\text{O}$ values observed. Given the widespread occurrence of specular hematite in the surrounding sedimentary rocks and within the zoned calcite-quartz veins zoning, quantitative fluid-rock interactions were also calculated using relationships outlined by Zheng and Hoefs (1993) to model the effects of wall-rock alteration on calcite precipitation. The interaction between high-temperature fluids and relatively cool wall rocks can lead to cation exchange, redox reactions, or both. The loss of H^+ moves hydrothermal fluids toward saturation with respect to carbonate minerals such as calcite, while gains of Ca^{2+} , Mg^{2+} , Fe^{2+} to the aqueous fluid, from the wall rocks also reinforce this movement. If calcite precipitates due to a fluid-rock interaction, the isotopic compositions of carbon and oxygen in the calcite are controlled by the differences in isotopic compositions of the hydrothermal fluid and the wall rock (Zheng and Hoefs, 1993). Using the relationship defined by Taylor (1977), the isotopic compositions of the final fluid after fluid-rock interaction can be quantified by the mass balance equation:

$$W\delta_{fluid}^i + R\delta_{rock}^i = W\delta_{fluid}^f + R\delta_{rock}^f$$

where the superscripts *i* and *f* represent the initial and final compositions and W and R represent the atom percent of carbon and oxygen in the fluid and rock, respectively. Above 80°C, increasing rates of isotopic exchange between fluids and wall rock depend on the relative abundances of the element of interest, initial isotopic ratios, the fluid-rock isotopic fractionation factors, residence time, and surface contact (Gat, 1981; Zheng and

Hoefs, 1993). If the fluid and rocks are in equilibrium, then the isotopic composition of the fluid can be determined by (Zheng and Hoefs, 1993):

$$\delta_{fluid}^f = \delta_{fluid}^i + (R / W) * (\delta_{rock}^i - \delta_{rock}^f)$$

Taking into account the dominant aqueous carbon species and the temperature-dependant fractionation factors, the isotopic composition of calcite precipitated from the final fluids can be quantified by use of the following equations (Zheng and Hoefs, 1993):

$$\delta^{13}C_{calcite} = \delta^{13}C_{fluid}^i + 10^3 \ln \alpha_{calcite-fluid} + (R/W) * (\Delta^{13}C_f^i)$$

$$\delta^{18}O_{calcite} = \delta^{18}O_{fluid}^i + 10^3 \ln \alpha_{calcite-H_2O} + (R/W) * (\Delta^{18}O_f^i)$$

where $\Delta_f^i = \delta_{rock}^i - \delta_{rock}^f$. Where H_2CO_3 is the dominant carbon species, the fractionation factor between calcite and CO_2 is applied to represent the fractionation between calcite-fluid. Where HCO_3^- is the dominant aqueous species, the fractionation factor between HCO_3^- and H_2O is applied. This leads to two distinct curves in a $\delta^{13}C$ versus $\delta^{18}O$ plot. If HCO_3^- is the dominant dissolved carbon species, the calcite precipitated by fluid-rock interaction will have a very narrow range in $\delta^{13}C$ values, whilst exhibiting a large range in $\delta^{18}O$ values due to the temperature effect on the $CaCO_3$ - H_2O system. On the other hand, if H_2CO_3 is the dominant dissolved carbon species, a large variation in both $\delta^{13}C$ and $\delta^{18}O$ values can be observed in the precipitated calcite. This is illustrated in figure 3.10, a plot of the modeled calcite isotopic composition precipitated from fluid-rock interaction with decreasing temperature and increasing rock/fluid ratio (0 to 1.0). The trend was produced by modeling the interaction between the Merico-Ethel host rocks (Nipissing Diabase with $\delta^{13}C = -5.0$ ‰ and $\delta^{18}O = 6.8$ ‰), with a basinal brine produced by mixing of meteoric and basinal brines ($\delta^{13}C = -15$ ‰ and $\delta^{18}O = 0$ ‰). As shown in

figure 3.10, the calcites precipitated *via* fluid-rock interaction can produce significant variation in $\delta^{13}\text{C}$. Unfortunately, the $\delta^{13}\text{C}$ variation is accompanied by a similarly large variation in $\delta^{18}\text{O}$ values, which indicates that fluid-wall rock interaction was perhaps not the dominant precipitation mechanism for the Merico-Ethel vein calcites. As noted by Zheng and Hoefs (1993), increasing the concentration of CO_2 in solution could theoretically steepen the $\delta^{13}\text{C}$ *versus* $\delta^{18}\text{O}$ trends by decreasing the oxygen isotope fractionation between calcite and the bulk aqueous fluid. However, an increase in dissolved CO_2 requires an open-system type of behavior where carbonate is progressively taken up by the migrated fluid. Steepening of the $\delta^{13}\text{C}$ *versus* $\delta^{18}\text{O}$ trends could also be generated by an increase in fluid pH leading to the progressive enrichment of ^{13}C in the precipitated calcite relative to a closed-system behavior (Ohmoto, 1972).

Figure 3.10. Trend of carbon *versus* oxygen isotope compositions for calcite precipitated from wall-rock interaction with a H_2CO_3 -dominated fluid from 300°C to 100°C and decreasing ratio of rock / fluid (figures above the line). The isotopic composition of the fluid was $\delta^{13}\text{C} = -15\text{‰}$, $\delta^{18}\text{O} = 0\text{‰}$, interacting with Nipissing Diabase ($\delta^{13}\text{C} \approx -5\text{‰}$, $\delta^{18}\text{O} = 6.8\text{‰}$; Kerrich *et al.*, 1986).

3.5 Summary and Key Findings

Regional (Basin-wide):

- In general, the isotopic composition of vein calcites mirrors that of the Huronian sedimentary rocks and to a lesser degree, the carbonate-mineral component of the greenstone-belt lithologies of the Archean basement (see figure 3.4).
- The $\delta^{18}\text{O}$ values of the vein calcites are tightly grouped, with a mean value of $11.34 \pm 2.56\text{‰}$ ($n=120$), a feature that suggests a common source/origin for the ^{18}O in the hydrothermal fluid/s responsible for vein formation (see figure 3.4).
- The $\delta^{18}\text{O}$ values of the vein calcites fall within the field identified for 'metamorphic fluids' and straddles the field defined as 'sedimentary fluids' by Sheppard (1986) (see figure 3.1).
- The $\delta^{13}\text{C}$ values of the vein calcites are more scattered, with a *circa* 20‰ range of $\delta^{13}\text{C}$ values from 2.78‰ to -16.78‰, which likely reflects the availability of, and degree of hydrothermal fluid interaction with, organic matter in different regions of the Cobalt Embayment: the mean $\delta^{13}\text{C}$ value for the NW, NE, SE, and SW regions of the embayment are $0.33 \pm 1.89\text{‰}$ ($n=27$), $-7.24 \pm 5.27\text{‰}$ ($n=35$), $-4.01 \pm 2.68\text{‰}$ ($n=43$), and $-5.44 \pm 1.37\text{‰}$ ($n=9$) respectively.

Local (deposit-scale):

- A small group ($n=9$) of highly negative $\delta^{13}\text{C}$ values (-12 to -18‰) for vein calcites from the Merico-Ethel property likely reflect interaction of the hydrothermal fluids, locally, with organic matter (see figure 3.4).
- The isotopic covariation evident in the Merico-Ethel vein calcites may result from:
  - i)* The degradation of a limited-source, organic matter-rich unit in the wall rocks; and/or
  - ii)* Fluid mixing, with meteoric-derived basinal fluids from the Huronian sedimentary sequence mixing with reducing fluids from the basement (see figure 3.8).

Chapter Four: Lead Isotopic Compositions of Ore Minerals

4.1 Introduction

The element lead consists of four naturally occurring, stable isotopes (^{208}Pb , ^{207}Pb , ^{206}Pb , and ^{204}Pb); only one of which (^{204}Pb) is non-radiogenic. The other isotopes of lead form through the radioactive decay of ^{238}U , ^{235}U , and ^{232}Th and are members of a long series of daughter products. Because the half lives of the radioactive parents are much longer than their respective daughter products this allows the treatment of the decay as though it occurred directly to the isotopic varieties of lead: $^{238}\text{U} \rightarrow ^{206}\text{Pb}$, $^{235}\text{U} \rightarrow ^{207}\text{Pb}$, and $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$. Furthermore, since the half lives of all the isotopes have been accurately determined, the age of the mineral in question can be calculated based on the concentrations of daughter products in relation to the parent isotopes:

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}} = \frac{^{235}\text{U}(e^{\lambda' t}-1)}{^{238}\text{U}(e^{\lambda t}-1)}$$

where, ($^{207}\text{Pb}/^{206}\text{Pb}$) is the present-day isotopic ratio and λ and λ' are the respective U decay constants (^{235}U and ^{238}U). This relationship is the basis for the dating of uranium-bearing minerals that effectively retain the daughter products within their crystal structure while largely excluding lead during crystallization: zircon, baddeleyite, monazite, apatite, titanite, garnet, and perovskite (Faure and Mensing, 2005).

Unfortunately, none of these uranium-bearing minerals commonly occur in association with the precious- and base-metal vein mineralization that characterizes the Cobalt Embayment; and consequently their use is pre-empted. Galena and a variety of

base-metal sulphides (*e.g.* pyrite) are, however, commonly present in the mineralized veins, and therefore, the possibility exists, of applying a second geochronological method utilizing the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratios (*i.e.* the common Pb-Pb method; Dickin, 1995). These latter isotopic values of Pb are often plotted in reference to a Stacey and Kramers (1975) two-stage lead growth curve that models the isotopic evolution of lead in the continental crust throughout geologic time. In the Stacey and Kramers' lead isotope evolution model, the origin of the curve represents the primeval lead isotope ratios that existed when the Earth was molten and homogeneous. As the Earth solidified and differentiated, slight isotopic variations in the major lead reservoirs (U/Pb ratios) of the crust and lithospheric mantle were produced. Due to the greater abundance of uranium and thorium (causing enrichment in the daughter products ^{208}Pb , ^{207}Pb and ^{206}Pb), the lead isotopic composition of the crust follows the Stacey-Kramers growth curve. In the two-stage model, the $^{238}\text{U}/^{204}\text{Pb}$ (μ) ratio of the lead reservoir changed due to geochemical differentiation at approximately 3.7 Ga as a result of the emergence of significant continental crust. During an ore-forming process, lead is separated from its isotopic reservoir and precipitates in a U- and Th-poor phase such as galena, essentially 'freezing' its isotopic composition and in some instances, permitting calculation of a model age. In the absence of galena, the least radiogenic compositions of pyrite are commonly accepted as suitable alternatives for isotopic analysis, as Pb partitions into pyrite while U and Th are largely excluded (Ho *et al.*, 1994; Qui and McNaughton, 1999). Recently, Galarza *et al.* (2008) have also demonstrated that grains of native gold may yield geologically reasonable results using the common Pb-Pb method. Once the sulphide minerals, galena and/or pyrite, are isolated from further

sources of U and Th, the isotopic composition of the lead reflects the composition of its source reservoir within which it evolved for a period of time, ending with its removal and precipitation in the crust (Faure and Mensing, 2005). Since the isotopic composition of lead represents a mixture of crustal and primeval lead extracted from a volume of crust, when plotted on a Stacey-Kramers growth curve, a suite of samples may define a linear relationship reflecting this mixing. In minerals with non-zero U/Pb ratios, this relationship forms an isochron, the slope of which is related to the time at which the lead was extracted from the reservoir and crystallized:

$$m = {}^{235}\text{U}/{}^{238}\text{U} (e^{\lambda_2 t} - 1)/(e^{\lambda_1 t} - 1)$$

where, ${}^{235}\text{U}/{}^{238}\text{U}$ is a constant (1/137.88), λ_1 (${}^{238}\text{U}$ decay constant) = $1.55125 \times 10^{-10} \text{y}^{-1}$ and λ_2 (${}^{235}\text{U}$ decay constant) = $9.8485 \times 10^{-10} \text{y}^{-1}$ (Faure and Mensing, 2005).

Unfortunately, the isotopic composition of lead from mineralized occurrences often does not correspond well with the Stacey-Kramers growth curve because it contains excess radiogenic components that produce anomalously young ages. Russell and Farquhar (1960) and Kanasewich (1968) were the first to note that additional information could be obtained from these anomalous lead compositions if suites of samples yield linear relationships in a ${}^{207}\text{Pb}/{}^{204}\text{Pb}$ *versus* ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ plot. These anomalous lead lines form in response to mixing of initial lead with varying amounts of radiogenic lead and can yield information regarding the time at which the initial lead was separated from its reservoir (intersection of anomalous lead line with growth curve to produce a model age) and the point in the past when the radiogenic lead was added to the mineral in question (slope of anomalous lead line) (Faure and Mensing, 2005).

As summarized by Faure and Mensing (*op. cit.*), the slope (R) of the instantaneous anomalous lead line is the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of radiogenic lead:

$$R = {}^{235}\text{U}_t \lambda_2 / {}^{238}\text{U}_t \lambda_1$$

where λ_1 (^{238}U) = $1.55125 \times 10^{-10} \text{y}^{-1}$ and λ_2 (^{235}U) = $9.8485 \times 10^{-10} \text{y}^{-1}$ and $^{235}\text{U}_t$ and $^{238}\text{U}_t$ are the abundances of the uranium isotopes in the past, which are related by the law of radioactivity:

$${}^{238}\text{U}_t = {}^{238}\text{U}_p e^{\lambda_1 t} \text{ and } {}^{235}\text{U}_t = {}^{235}\text{U}_p e^{\lambda_2 t}$$

Substitution of the slope (R) into the above equation yields:

$$R = (\lambda_2/\lambda_1)({}^{235}\text{U}_p e^{\lambda_2 t}/{}^{238}\text{U}_p e^{\lambda_1 t})$$

which can be solved for t (to yield the maximum age in question)

$$t = (1/(\lambda_2 - \lambda_1)) \ln[(137.88 \cdot R \cdot \lambda_1)/\lambda_2]$$

If the age of the basement rocks are well constrained, the slope of the anomalous lead line can also be modeled after the continuous growth of radiogenic lead to yield secondary isochron lines or mixing lines. In this case, the isotopic evolution of radiogenic lead is expressed as:

$$(^{207}\text{Pb}/^{206}\text{Pb}) = ({}^{235}\text{U}/{}^{238}\text{U})_p [(e^{\lambda_2 t_r} - e^{\lambda_2 t})/(e^{\lambda_1 t_r} - e^{\lambda_1 t})]$$

where $({}^{235}\text{U}/{}^{238}\text{U})_p = (1/137.88)$, t_r is the present age of the basement rocks and t is the time when the radiogenic lead was removed from the basement rocks.

4.2 Methodology

All of the lead isotopic analyses were completed at the Carleton University Isotope Geochemistry and Geochronology Center using a ThermoFinnigan Triton TI thermal ionization mass spectrometer. Single grains of galena, pyrite, chalcopyrite (typically separated as small cleavage fragments of the respective sulphide minerals) and native gold were selected for lead isotopic analysis from several occurrences throughout the Cobalt Embayment (figure 4.1), using mineral concentrates prepared by hand under a binocular microscope. Individual grains of galena were dissolved in a mixture of nitric and hydrochloric acid. Small (0.5-3 mm) individual grains of native gold were extracted from hand samples of mineralized calcite veins *via* crushing and selective grain picking under a binocular microscope. Analysis of the native gold grains revealed lead concentrations in the order of 5 ppm, thus requiring approximately 20 mg of native gold for the achievement of suitable precision in the mass spectrometry. The gold separates were initially washed in dilute hydrochloric acid in order to dissolve any calcite adhering to the mineral surface and then rinsed thoroughly under distilled water. Once dried, the gold sample was then dissolved in aqua regia ($\text{HCl} + \text{HNO}_3$). After the aqua regia mixture was dried, bromic acid was added to the sample and the mixture was allowed to sit for a minimum of 24 hours before passing the solution through a conventional ion-exchange column under HCl. Individual grains of commonly occurring sulphide minerals (pyrite, chalcopyrite) were also separated under a binocular microscope after the hand samples of mineralized vein material had been crushed. Once isolated, the sulphides were ground in an agate mortar and pestle and an aliquot was separated for sulphur isotopic analysis. Between 20 to 30 mg of the sulphide mineral powder was then digested using 7N HNO_3 . After 24 hours, the nitric acid solution had dried and was then dissolved under 1N HBr.

The bromic acid solution was then passed through conventional ion-exchange columns under HCl and dried. After evaporation of all of the liquids, the remaining powders (native gold, galena and sulphides) were loaded on a rhenium filament using a mixture of H_3PO_4 and silica gel and then placed in the mass spectrometer under a high vacuum. The rhenium filament temperature was then raised in a step-wise fashion to 1300-1340°C in order to ionize the sample. Measured lead ratios for all samples included: $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$. Two sigma (2σ) errors (including fractionation corrections) for galena and sulphide minerals are estimated to be 0.10% and 0.13% for $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, respectively, based on the values of Todt *et al.* (1984). Two sigma (2σ) errors (~95% confidence) for the native gold analyses displayed more variation, with values ranging from 0.13% to 1.89% for both $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. The complete set of Pb isotopic data, comprising 11 galena, 8 native gold, 3 native silver and 26 sulphide analyses, are presented in table 4.1. All data were corrected for fractionation:—using averaged values of standard NBS981. Pre-correction average values for NBS981 are: $^{208}\text{Pb}/^{204}\text{Pb} = 36.502$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.429$ and $^{206}\text{Pb}/^{204}\text{Pb} = 16.890$. Isochron model ages were calculated using the ISOPLOT program written by K.R. Ludwig (Berkeley Geochronology Center) and procedures outlined in Faure and Mensing (2005). Robust regression lines were also generated using SigmaPlot® software. Grains of native silver from the Beaver-Temiskaming silver mine (Cobalt area) were prepared for lead isotopic analysis using the procedure outlined above for sulphide phases. Unfortunately, despite the several attempts the concentration of lead in the native silver was deemed too low for acceptable levels of accuracy and precision.

Figure 4.1. Location of samples selected for lead isotopic analysis. The sampling locations were based on the ease of extraction of monomineralic concentrates from representative vein occurrences throughout the Cobalt Embayment. SIC = Sudbury Igneous Complex.

Table 4.1: Lead isotopic composition of ore minerals from selected mineralized vein occurrences in the Cobalt Embayment.

Occurrence	Sample #	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
<i>Native Gold</i>						
Brett	75690a	34.873	15.221	15.470	2.254	0.984
Brett	75690b	35.127	15.322	15.514	2.264	0.987
Brett	BRT-01	35.250	15.293	15.508	2.273	0.986
Brett	BRT-1b	34.692	15.148	15.234	2.277	0.994
Brett	RPT-1-1	34.088	14.841	14.616	2.332	1.015
Brett	RPT-1-1_b	35.429	15.416	15.154	2.338	1.017
Brett	BRT-1a	34.603	15.125	15.164	2.282	0.997
McLeanWatt	WN-8 Au	47.374	18.214	35.969	1.317	0.506
<i>Native Silver</i>						
Beaver-Tem.	CB1	36.910	15.476	17.238	2.145	0.898
Beaver-Tem.	CU4382	35.805	17.401	39.624	0.904	0.439
Beaver-Tem.	CU5210	36.665	15.397	17.015	2.155	0.905
<i>Galena</i>						
Brady Lakes	BLM-16	34.353	15.129	14.727	2.333	1.027
Capital	CP-4A	34.345	15.126	14.755	2.328	1.025
Delhi twp.	DL-1A	35.027	15.362	15.706	2.230	0.978
Delhi twp.	DL-2	34.896	15.324	15.641	2.231	0.980
Delhi twp.	DL-3	34.918	15.331	15.647	2.232	0.980
Duncan Lk.	DUNC-4	34.526	15.202	15.029	2.297	1.011
Duncan Lk.	DUNC-7	34.680	15.249	15.260	2.273	0.999
Duncan Lk.	DUNC-8	34.633	15.233	15.186	2.281	1.003
Beaver-Tem.	N-17-14	34.336	15.126	14.737	2.330	1.026
Silverfields	SLV-1	34.283	15.112	14.720	2.329	1.027
Silverfields	SLV-2	38.753	15.700	18.836	2.057	0.833

Table 4.1. Continued.

Occurrence	Sample	Mineral	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
<i>Sulphides</i>							
Beaver Pd.	BV-1c	cpy	36.174	15.379	16.446	2.200	0.935
Beaver Pd.	BV-3a	brn	35.320	15.289	15.818	2.233	0.967
Beaver Pd.	BV-3b	cpy	34.778	15.240	15.666	2.220	0.973
Capital	CP-4a	cpy	34.698	15.243	14.840	2.338	1.027
Delhi Twp.	DL-1a	cpy	35.350	15.467	15.764	2.242	0.981
Delhi Twp.	DL-2a	cpy	35.040	15.368	15.701	2.232	0.979
Delhi Twp.	DL-4a	cpy	34.984	15.350	15.656	2.235	0.980
Delhi Twp.	DL-4b	py	35.080	15.382	15.692	2.236	0.980
Delhi Twp.	DL-5	py	35.658	15.610	15.939	2.237	0.979
Duncan Lk.	DUNC-5	cpy	36.625	15.767	17.465	2.097	0.903
Merico-Ethel	ME-3a	cpy	34.943	15.345	15.689	2.227	0.978
Merico-Ethel	ME-5	cpy	34.626	15.211	15.217	2.276	0.999
Merico-Ethel	ME-6c	cpy	34.940	15.319	15.922	2.195	0.962
Merico-Ethel	ME-6p	py	34.569	15.212	15.199	2.274	1.001
Merico-Ethel	ME-8c	cpy	34.593	15.192	14.992	2.308	1.013
Merico-Ethel	ME-8p	py	34.714	15.236	14.893	2.331	1.023
Merico-Ethel	ME-19	cpy	35.334	15.344	15.974	2.212	0.960
Merico-Ethel	ME-20p	py	34.829	15.268	15.557	2.239	0.981
McL-Watt	WN-8	py	44.396	16.786	26.535	1.673	0.633
Fraleck East	WN-14	cpy	42.227	16.377	22.534	1.874	0.727
Fraleck East	WN-15	cpy	42.969	16.880	25.539	1.683	0.661
Fraleck East	WN-16	cpy	39.853	16.022	21.038	1.894	0.762
Laura Lk.	WN-19	cpy	35.338	15.562	16.099	2.195	0.966
Laura Lk.	WN-20	py	34.755	15.256	15.550	2.235	0.981
Burda	WN-24c	cpy	38.966	15.966	20.464	1.904	0.780
Burda	WN-24p	py	41.354	16.385	23.985	1.724	0.683

Note. Abbreviations: McL-Watt = Mclean-Watt mine; brn = bornite; cpy = chalcopyrite; py = pyrite.

Figure 4.2. Lead isotopic composition of galena, base-metal sulphides, native gold and native silver extracted from the mineralized vein systems of the Cobalt Embayment sampled in this study. The three native silver samples were collected from the historical Cobalt silver camp. The majority of the sulphide minerals, and all of the native silver grains, analyzed in this study, contain excess radiogenic Pb, as illustrated by their anomalous lead compositions in reference to the Stacey-Kramers (1975) two-stage lead growth curve. With a few exceptions, the two sigma errors are smaller than the symbols illustrated (<0.02).

4.3 Results

Of the eight analyses of native gold, three analyses yielded ‘good’ results, two analyses produced ‘acceptable’ results, and three analyses yielded ‘poor’ data with analytical errors well above accepted norms. The poor precision present in these analyses likely represents decreasing quantities of lead within the grains of native gold. With the exception of WN-8 and RTP-1-1, the data produce Proterozoic model ages using the Stacey-Kramers (1975) two-stage lead evolution model and as such plot within error of the lead growth line. As illustrated in figure 4.3, the majority of the data are clearly differentiated from typical Abitibi-hosted Archean lode gold (quartz-Fe-carbonate veins) deposits, as presented by Olivo *et al.*, (2007).

The lead isotopic composition of galena from the mineralized occurrences produce model ages ranging from 1775 Ma to 2250 Ma, a range that is in good agreement with published Pb-Pb model ages for the Ag-Co vein mineralization of the Cobalt and Gowganda camps. However, unlike those analyzed by Kanasewich & Farquhar (1965), Thorpe (1974), and Thorpe *et al.* (1986), none of the galena samples in this study produce Archean model ages (*i.e.* plot on growth curve older than 2500 Ma). The “Archean-aged” galena in these previous studies were all sampled from mineralized veins hosted in Archean interflow sediments, and had apparently preserved the Archean lead isotopic composition of the host rocks. Interestingly, no other Archean-aged lead has been documented from the Cobalt mineralization, even silver-vein mineralization hosted within Archean rocks. One analysis (SLV-2) of galena from the Silverfields silver mine located in Cobalt, produced highly radiogenic values atypical from the current data set

and an additional sample from the same occurrences (SLV-1). Given that the sample was prepared from archival material, it is possible that the sample was mislabeled during storage and is not representative of the Silverfields mine. Given the suspicious nature of the sample and lead isotopic compositions, the lead isotopic values have been excluded in the discussion of the results.

As illustrated in figure 4.3, the base-metal sulphides are clearly enriched in radiogenic lead relative to galena and native gold from the majority of the occurrences. The lone exceptions to this trend are the sulphides analyzed from the Delhi Township occurrence, where analyses of chalcopyrite and pyrite fall within error of the values produced from galena. Interestingly, comparison of the values yielded from the mineralized vein occurrences closely follows the radiogenic trend of sulphides analyzed from the upper Huronian sedimentary rocks by McLennan *et al.* (2000).

Figure 4.3. Lead isotope composition of galena and native gold from mineralized vein occurrences sampled in this study, with reference to the major lead isotopic reservoirs in the Cobalt Embayment. Sources of comparative Pb isotopic data are: Kanasewich and Farquhar (1965), Thorpe (1974), Franklin *et al.* (1983), Thorpe *et al.* (1986), Carignan and Gariépy (1993), Thorpe (1999), McLennan *et al.* (2000), and Olivo *et al.* (2007).

Figure 4.4. Plot of ^{208}Pb versus ^{206}Pb (both normalized to ^{204}Pb). The data generally mirrors the trends noted in the ^{207}Pb versus ^{206}Pb plots, with a majority of the data points clustering along the Stacey-Kramers (1975) two-stage lead growth line from approximately 2450 to 1700 Ma. Much like the ^{207}Pb versus ^{206}Pb plot, eight of the sulphide, one native gold sample, and one of the native silver samples clearly show an anomalous enrichment in ^{208}Pb and ^{206}Pb . The comparative data for isotopic reservoirs comes from the same reference sources as are listed in the caption to figure 4.3.

4.4 Discussion

4.4a Native Gold

As illustrated by figures 4.5(A) and 4.5(B), the majority of the native gold samples from the Brett occurrence contain lead which clusters around an age of 2.0 Ga on the Stacey and Kramers (1975) two-stage growth curve. Unlike all of the other mineralized vein occurrences sampled in this study, the Brett mineralization is hosted within greenschist-facies, Archean metavolcanics. A Pb-Pb isochron-age of $4231 \pm 180/-4200$ Ma is clearly not geologically reasonable given that the host volcanic rocks of the Abitibi greenstone belt have been dated by various authors at 2730 to 2690 Ma (Vervoort *et al.*, 1994). Calculation of a Stacey-Kramers two-stage model isochron age yields a value of 1652 Ma, with very large errors due to a significant scatter in the data that produces large errors associated with the slope. Both isochrons (Pb-Pb and two-stage model) intersect the Stacey-Kramers growth curve at ~ 1850 Ma. When compared to the Pb isotopic compositions of pyrite sampled from gold-bearing, quartz-Fe-carbonate veins in the Abitibi Greenstone Belt, one of the native gold samples from the Brett mineralization plots within the error of the trend defining the 2566 ± 71 Ma isochron. Given the overlap, it is possible that the trend observed in the native gold samples represents a mixing line in which Archean lead from quartz-Fe-carbonate veins was mixed with more radiogenic lead at ~ 1850 Ma. Given the large analytical errors, it is also possible that the native gold grains contain lead which is concordant with the Stacey-Kramers two-stage growth curve ($u=9.735$), as illustrated on figure 4.5(B). In this case, the lead produces model ages ranging from 2250 to 1760 Ma.

Figure 4.5. (A) Lead isotopic composition of native gold samples from the Brett mineralization plotted with reference to the Stacey-Kramers (1975) two-stage lead growth line. (B) Native gold compositions (ellipses) and isochron age in contrast to lead compositions of pyrite (black hatches) from Archean quartz-Fe-carbonate veins from the Abitibi Greenstone Belt which define a $2566 \pm 71 \text{ Ma}$ isochron age (Olivo *et al.*, 2007). Ellipses represent analytical errors at $\sim 95\%$ confidence.

4.4b Galena

The lead isotopic composition of galena separates from mineralized occurrences located in the central to northern margins of the Cobalt Embayment are presented in figure 4.6. The data produce a linear trend with a R^2 value of 0.9968 that was initially thought to represent a Pb-Pb isochron. However, calculation of an age based on the slope of the isochron produces a geologically unrealistic age of 3017 Ma. This age is not realistic given the age of the host rocks (Nipissing Diabase) have been well constrained to 2219 ± 4 Ma (Andrews *et al.*, 1986b) and the underlying Archean basement rocks have been dated by various authors at 2730 to 2690 Ma (Vervoort *et al.*, 1994). Since the age of the host rocks have been well constrained, a secondary isochron age based on the slope of the linear trend was determined. Using the continuous growth model, calculation of a secondary isochron age yields 1675 Ma. Perhaps incidentally, the lead isotopic compositions plot along the Stacey-Kramers two-stage lead growth curve (with $u=10$) from 2250 Ma to 1775 Ma (figure 4.7). These data corroborate the interpretations of Thorpe *et al.*, (1986) who found evidence of significant lead remobilization at *circa* 1650 Ma from galena extracted from the Cobalt Ag-vein systems. This age approximately correlates with data from various authors which suggest that a significant, basin-wide potassic- and sodic metasomatic event occurred at approximately 1700 Ma. These ages correspond to the final stages of the Penokean orogeny which occurred at 1.9 to 1.7 Ga when an arc complex collided with the southeastern margin of the Superior Province and culminated with intrusion of several felsic plutons along the southern margin (Bennett *et al.*, 1991; Davidson *et al.*, 1992). In addition, along the southwestern tract of the Huronian Supergroup from Sudbury to Sault Ste. Marie, this collision caused extensive

folding of the Huronian sedimentary rocks (*i.e.* Huronian fold belt). During this time, whole-rock $^{40}\text{Ar}/^{39}\text{Ar}$ (Hu *et al.*, 1998), Rb-Sr (Fairbairn *et al.*, 1969; Roscoe *et al.*, 1992) and U-Pb (McLennan *et al.*, 2000) isotope systematics within the upper Huronian sedimentary rocks and paleosols along the unconformity were reset in an episode of related to potassium and sodium-metasomatism at 1690-1760 Ma (Rainbird *et al.*, 1990; Prasad, 1994). Furthermore, U-Pb isotope systematics of hydrothermal monazite in metasomatically albitized rocks from the McLean-Watt occurrence yields ages of 1700 ± 2 Ma (Schandl *et al.*, 1994). Unfortunately, evidence of the metasomatic event in the central to northern portions of the Cobalt Embayment is contradicting: whole rock Rb-Sr isotopic data from the Gowganda Formation in the Gowganda area yield ages within error of the Nipissing Diabase (Fairbairn *et al.*, 1969) while Pb isotopes from the Gowganda and Gordon Lake formations in the Gowganda area record resetting at approximately 1.7 Ga (McLennan *et al.*, 2000). One potential source of the discrepancies may lie in the sampling locations. Samples collected near the regional unconformity and/or structural features may record evidence of the isotopic disturbance, whereas specimens collected within the massive units may not.

Figure 4.6. Lead isotopic composition of galena from occurrences from the central to northern margin of the Cobalt Embayment. The data produces a geologically unrealistic Pb-Pb isochron age of 3017 Ma, given that the occurrences are hosted in $2219 \pm 3.6 \text{ Ma}$ Nipissing Diabase (Andrews *et al.*, 1986b). Using the continuous growth model to generate a secondary isochron ($t_r = 2219$) produces a slope that corresponds to $t = 1675 \text{ Ma}$. Two-sigma analytical errors are smaller than the symbols.

Figure 4.7. Lead isotopic composition of galena from occurrences located in the central to northern portions of the Cobalt Embayment, plotted in reference to the Stacey-Kramers two-stage lead growth curve ($u=10$). Two-sigma analytical errors are smaller than the symbols.

4.4c Base-Metal Sulphides

As illustrated by Figure 4.2 and 4.3, the lead isotopic compositions of the base-metal sulphides extracted from the mineralized occurrences are highly radiogenic in comparison to the isotopic composition of associated grains of galena. As illustrated in figure 4.8, the isotopic composition of the base-metal sulphides produces a linear trend (slope = 0.1401 ± 0.0112) with an R^2 value of 0.9635. Calculation of a Pb-Pb isochron age based on the slope of the trend produces an age of 2265 ± 140 Ma. This age is within error of the Nipissing Diabase intrusion (2219 ± 3.6 Ma; Andrews *et al.*, 1986) and is in direct contrast to the secondary isochron age of 1675 Ma produced from lead isotopic composition of galena. However, this contrast in ages is supported by ore petrography, which illustrates the late-stage replacement and/or alteration of early sulphides by galena. The data and textural observations therefore provide additional support to the multi-stage nature of the mineralized occurrences. Isolation of individual properties such as Merico-Ethel (figure 4.9) and all the Wanapitei occurrences (figure 4.10) reconfirms the association of the early-stage sulphide mineralization with the Nipissing Diabase intrusive event. As shown in figure 4.9, a Pb-Pb isochron of base-metal sulphides from the Merico-Ethel property produces a linear trend with a slope of 0.1351 ± 0.0562 ($R^2=0.7944$) which corresponds to an age of 2105 ± 930 Ma. Comparison of data from the current study with whole-rock sulphur isotopic compositions reported by McLennan *et al.* (2000) is highlighted in figure 4.11. As illustrated in the plot, the data of McLennan *et al.* (2000) produce a significantly younger Pb-Pb isochron

Figure 4.8. Lead isotopic composition of base-metal sulphides from mineralized occurrences throughout the Cobalt Embayment. The data produce a Pb-Pb isochron age of 2265 ± 140 Ma with an R^2 value of 0.9635. Two sigma errors are smaller than the symbols.

Figure 4.9. Lead isotopic composition of base-metal sulphides from the Merico-Ethel property. The data to produce an isochron age of $2105 \pm 930 \text{ Ma}$ ($R^2=0.7944$), which is within error of the Nipissing Diabase intrusive event ($2219 \pm 3.6 \text{ Ma}$).

Figure 4.10. Lead isotopic composition of base-metal sulphides from the Wanapitei area, southern Cobalt Embayment. The data produce a Pb-Pb isochron age of $2103 \pm 680 \text{ Ma}$ ($R^2=0.9852$). Two σ errors are smaller than the symbols.

Figure 4.11. Lead isotopic compositions of mineralized vein sulphides in reference to the whole rock isotopic compositions of the upper Huronian sedimentary rocks (Gowganda and Gordon Lake Formations) from McLennan *et al.* (2000).

age of 1667 ± 120 Ma (MSWD=1300). As noted in section 4.4b, these data are corroborated by additional isotopic data that links the isotopic resetting to the final stages of the Penokean orogeny.

The highly radiogenic nature of the base-metal sulphides may be a result of inclusion of U- or Pb-bearing phases during early-stage sulphide crystallization. As noted during ore petrography, the majority of the occurrences clearly record replacement textures and inclusions amongst the sulphides. This is clearly illustrated in examples from the Duncan Lake and Beaver Pond occurrences (figures 4.12 and 4.13). Inclusion of such phases likely disrupted the initial U/Pb ratio of the sulphides and led to the highly radiogenic compositions observed in the sulphides. Unlike the sulphides, the galena grains extracted for isotopic analysis were euhedral in habit and did not exhibit any intergrowths and/or replacements textures. The sole occurrence that yielded lead isotopic compositions from sulphides within error of the lead isotopic compositions of galena grains was the Delhi Township occurrence. Ore petrography did reveal ubiquitous replacement textures and inclusions amongst the sulphides, but unlike the other occurrences, the majority of the sulphides did not contain inclusions of Pb-bearing and/or Bi-Pb-Cu-Sb-bearing phases.

Figure 4.12. (A) BSE-image of porous chalcopyrite (cpy) replacing earlier pyrite (py) in a mineralized vein sample from the Beaver Pond occurrence. (B) BSE-image of small inclusions of an unidentified Cu-Sb-sulphide mineral (sb) within chalcopyrite that is rimmed by later cobaltite (co) in a vein sample from the Beaver Pond occurrence. Note the porous nature of chalcopyrite in both images, supporting a secondary (replacement) origin for the Cu-Fe-sulphide minerals.

Figure 4.13. BSE-images of: aikinite-bismuthinite (bi) inclusions within chalcopyrite (cpy). In both BSE-images, very fine-grained inclusions of galena are present in the chalcopyrite (the tiny white spots). The larger, more intense white spots (>5µm) are aikinite-bismuthinite intergrowths. In image (A), a fragment of altered diabase contains rutile (ti) rimmed by titanite, both of which are set in chlorite.

4.4d The Delhi Township Occurrence

Due to a greater abundance of historical data, additional interpretations can be drawn regarding the Delhi Township occurrence. The analysis of lead from galena and base-metal sulphides from the Delhi occurrence also produces geologically unrealistic ages using the Pb-Pb isochron method: a regression of eight points yields an isochron age of $5176 \pm 270/-680$ Ma. However, when plotted in reference to a Stacey-Kramers (1975) two-stage growth curve, the Delhi occurrence analyses reveal the presence of anomalous lead compositions which are enriched in radiogenic lead (figure 4.14A). These anomalous leads define a line with a slope of 0.9691 ± 0.0622 ($R^2=0.9759$) and which intersects the Stacey-Kramers growth curve at 1784 Ma (figure 4.14B). Calculation of a two-stage model age based on the intersection of the anomalous lead line with the Stacey-Kramers growth curve yields a value of 1784 ± 41 Ma, which likely reflects the time at which lead was separated from uranium and thorium-bearing sources and mixed with radiogenic lead to produce the anomalous compositions observed. This model age correlates well with two-stage model ages of galena from the Delhi occurrence (*viz.* 1803 Ma, 1808 Ma, and 1809 Ma). The analysis of the slope of the anomalous lead line should yield information regarding the point in time when lead formed having the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio equal to the anomalous line. Unfortunately, integration of the data yields an unrealistic age of 3.67 Ga suggesting that the anomalous compositions of the leads were produced by mixing of highly radiogenic lead. These results correlate well with the historical Pb isotopic data from the Delhi Township occurrence, reported by Kanasewich and Farquhar (1968) and Franklin *et al.*, (1983), which also demonstrated the presence of

anomalous lead compositions in galena and sulphide minerals. Incorporation of the historical data with the results obtained in this study produces an anomalous lead line that intersects the Stacey-Kramers growth curve at an age of 1787 Ma. Interpretation of the slope of the anomalous lead line yields present day $^{232}\text{Th}/^{238}\text{U}$ ratios in the order of 4.25–4.48.

Figure 4.14. (A) Interpolation of the anomalous lead line intersect the growth curve at $1784 \pm 41 \text{ Ma}$, reflecting the point in time when the lead was separated from U and Th sources and mixed with radiogenic lead. (B) Lead isotopic composition of galena and base-metal sulphides from the Delhi occurrence, incorporation historical data of Kanasewich and Farquhar (1968) and Franklin *et al.* (1983).

4.5 Summary and Key Findings

Regional (Basin-wide)

- The Pb isotopic compositions of pyrite and chalcopyrite grains extracted from nine, widely-separated, mineralized vein occurrences throughout the Cobalt Embayment yield a Pb-Pb isochron age of 2265 ± 140 Ma ($n=26$) (see figure 4.8), which is analytically indistinguishable from a single U-Pb age for the intrusion of the Nipissing Diabase in the northwestern quadrant of the embayment (2219 ± 3.6 Ma; Castle Mine in Gowganda camp; Andrews *et al.*, 1986).
- The Pb isotopic compositions of galena crystals ($n=11$) from six, widely-separated, mineralized vein occurrences yield a Pb-Pb secondary isochron age of *circa* 1675 Ma, indicating the occurrence of a major episode of hydrothermal remobilization at this time (see figures 4.6 and 4.7); a feature supported by the results ore mineralogy and textural study (see Chapter 2). The veracity of this 1675 Ma remobilization age for the vein galena mineralization is corroborated by the 1650 Ma age obtained for galena crystals from the Cobalt camp Ag-veins by Thorpe *et al.* (1986).
- The combination of the Pb isotopic data for both the base-metal sulphide minerals and galena crystals from the mineralized veins: *i*) Demonstrates the occurrence of at least two major episodes of hydrothermal fluid activity throughout the Cobalt Embayment at *circa* 2220 Ma and *circa* 1700 Ma; and *ii*) Provides further supporting evidence for the basin-wide extent of the regional Na- and K-

metasomatic event related to the final stages of the Penokean orogeny (1.9–1.7 Ga) (see figure 4.11).

- Unlike native gold and electrum, isotopic analysis of grains of native silver from the vein- occurrences indicated that Pb contents were too low for suitable levels of accuracy and precision.

Local (deposit-scale)

- The Pb isotopic composition of Fe- and Fe-Cu-sulphides from individual of the mineralized vein occurrences reinforces the *circa* 2.2 Ga, Pb-Pb isochron age determined for the regional data set; with the Merico-Ethel vein sulphides yielding a Pb-Pb age of 2105 ± 930 Ma ($n=8$) , and the sulphides from the Wanapitei-area deposits a Pb-Pb age of 2103 ± 680 Ma ($n=8$) (see figures 4.9 and 4.10).
- The galena ($n=3$) and base-metal sulphides ($n=5$) from Delhi Township mineralized vein occurrence produce an anomalous Pb line, which based on the Stacey-Kramers two-stage Pb evolution curve, indicates that radiogenic Pb was added to the system at *circa* 1784 Ma, which is consistent with the effects of the *circa* 1.7 Ga metasomatic event.
- The lead isotopic composition of native gold from the Brett occurrence is atypical of Archean, quartz-carbonate, lode-gold mineralization and may represent remobilization of Archean mineralization during the Proterozoic (figure 4.5B).

Chapter Five: Sulphur Isotopic Composition of Ore Minerals

5.1 Introduction

Sulphur has four stable isotopes (^{32}S , ^{33}S , ^{34}S , and ^{36}S) with natural abundances of 95.02, 0.75, 4.21, and 0.02 percent, respectively (Faure and Mensing, 2005). The most commonly utilized isotopic ratio measured in terrestrial systems is the $^{34}\text{S}/^{32}\text{S}$ ratio mainly due to the natural abundances and relative mass difference between the two isotopes. Fractionation or partitioning between the latter two sulphur isotopes is primarily controlled by equilibrium and kinetic effects: equilibrium processes include isotopic exchange reactions, which redistribute isotopes amongst molecules of different substances and are strongly influenced by temperature, chemical compositions, crystal structure, and pressure; and kinetic processes include irreversible chemical reactions, such as bacterially-mediated processes like sulphate reduction and physical processes such as evaporation and diffusion (O'Neil, 1986; Seal, 2006).

These physically and chemically controlled linear fractionation trends are known to be mass-dependent fractionations and are distinct from mass-independent fractionation. Mass-independent fractionation is reflected by non-linear variations in isotopic fractionation with mass and is primarily controlled by ultraviolet light-induced photochemical processes in the upper atmosphere in the sulphur and oxygen isotopic systems (Farquhar and Wing, 2003; Rumble, 2005; Seal, 2006). Due to the photochemical control on mass-independent fractionation (*i.e.* development of the ozone layer which blocks ultraviolet light), anomalies in sulphur isotopes driven by mass-independent fraction is one of the major pieces of evidence in the documentation of the

rise of atmospheric oxygen in the Paleoproterozoic (*e.g.* Papineau *et al.*, 2007), during which period the supracrustal rocks of the Cobalt Embayment were deposited.

As noted by Seal (2006), mass-dependent fractionations can profoundly fractionate sulphur isotopes away from bulk-Earth values in geological systems. The most dramatic effects are created by oxidation and reduction reactions. Oxidation processes produce mineral species that are enriched in ^{34}S relative to the starting material, whereas reduction produces mineral species that are depleted in ^{34}S . Furthermore, the effect of the oxidation state of sulphur is especially important in sulphur-bearing systems. The higher oxidation states of sulphur are enriched in the heavier isotopes relative to lower oxidation states such that ^{34}S enrichment follows the general trend $\text{SO}_4^{2-} > \text{SO}_3^{2-} > \text{S}_x^0 > \text{S}^{2-}$ (Sakai, 1968; Bachinski, 1969). In the geological record, this trend is reflected by the fact that sulphate minerals typically have higher $\delta^{34}\text{S}$ values than cogenetic sulphide minerals (Seal, 2006). In addition, the heavier sulphur isotope typically forms more stable bonds and are therefore less reactive than molecules which contain the lighter isotope (O'Neil, 1986; Faure and Mensing, 2005).

As noted by Ohmoto and Goldhaber (1997), precipitation mechanisms for sulphide minerals also have significant effects on the sulphur isotopic fractionation between minerals. For simple sulphide minerals such as sphalerite, galena, or pyrrhotite, the relative concentrations of metal, H_2S and SO_4^{2-} are important. Under conditions where the proportion of dissolved metals exceeds that of H_2S , disequilibrium fractionations are expected. Since sulphur needs to be obtained at the site of sulphide

deposition, the metal that reaches sulphur saturation first will consume a significant portion of the H₂S reservoir causing a shift, through Rayleigh processes, in the isotopic composition of the residual H₂S available for later mineral formation. These processes often give rise to the precipitation of monomineralic ores from oxidized fluids containing SO₄²⁻. In contrast, sulphide minerals from polymetallic ores generally show equilibrium fractionation between simple sulphides. In this instance, the concentration of H₂S in the fluid greatly exceeds those of the metals, resulting in the metals mutually reaching saturation rather than reaching saturation individually.

Ohmoto and Goldhaber (1997) also note that the precipitation of pyrite and chalcopyrite is more complex than that of simple sulphide minerals because their formation typically involves the process of oxidation in addition to other depositional mechanisms such as a change in pressure, temperature, or aqueous fluid pH. For example, pyrite contains disulphide (S₂²⁻) rather than sulphide (S²⁻) anions in its structure. Similarly, chalcopyrite precipitational mechanisms commonly involve oxidation-reduction reactions, as copper is typically transported as a Cu⁺-chloride species, but must be oxidized to Cu²⁺ in order to be accommodated in the chalcopyrite structure:

Chalcopyrite also often forms by replacement, causing its sulphur isotopic composition to be partially or completely inherited from the precursor mineral. Thus, because of the greater complexity of the precipitational mechanisms for pyrite and

chalcopyrite, equilibrium isotopic fractionations with other sulphide minerals are less likely to have occurred (Seal, 2006).

5.2 Methodology

Eighty-six (86) sulphide mineral concentrates were hand-picked for sulphur isotope analysis, from selected hand samples of mineralized vein occurrences located throughout the Cobalt Embayment (figure 5.1). The samples were carefully selected, based upon; (i) the nature, location, and geological setting of the mineralized vein occurrence and its inherent relationship to the Proterozoic mineralization that is broadly characteristic of the Cobalt Embayment as a whole; and (ii) the ease with which a pure (*i.e.* lacking any discernible mineral inclusions), well-characterized, 2-10 gm sample of sulphide mineral could be extracted from the vein material. The samples were prepared and analyzed to determine their sulphur isotopic composition in the G.G. Hatch Stable Isotope Laboratories of the Ottawa-Carleton Geoscience Centre (OCGC). Powdered, monomineralic aliquots of pure sulphide mineral were weighed into tin capsules with vanadium pentoxide. The sealed containers were then loaded into a VarioEL III elemental analyzer and flash combusted at 1800°C. The released gases were carried by ultra-pure helium gas through the Vario elemental analyzer to be cleaned and separated. Sulphur dioxide (SO₂) gas produced by the combustion was separated and transferred to a DeltaPlus isotope-ratio mass spectrometer (ThermoFinnigan) for analysis. The analytical precision (2σ) for the procedure is ± 0.2‰ (Paul Middlestead, *pers. comm.*). All of the sulphur isotopic compositions are reported in reference to the Canon Diablo troilite (CDT) meteorite reference standard. The Canyon Diablo troilite provides a convenient

reference because it is believed to approximate the bulk composition of the Earth and has an average sulphur isotope composition of $\delta^{34}\text{S} = 0.2 \pm 0.2\text{‰}$ (Kaplan and Hulston, 1966; Seal, 2006), which is indistinguishable from that of pristine mid-ocean ridge basalts ($\delta^{34}\text{S} = 0.3 \pm 0.5\text{‰}$; Sakai *et al.*, 1984).

The sulphur isotope compositions are, like those for carbon and oxygen, reported in terms of the delta (δ) notation, which, for sulphur isotopes, is defined as follows (Faure and Mensing, 2005):

$$\delta^{34}\text{S} = \frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} * 10^3 \text{‰}$$

where, $R_{\text{sample}} = {}^{34}\text{S}/{}^{32}\text{S}$ of sample

$R_{\text{standard}} = {}^{34}\text{S}/{}^{32}\text{S}$ of standard (CDT)

Figure 5.1. Locations of mineralized vein occurrences that were sampled for $\delta^{34}\text{S}$ research within the Cobalt Embayment. Occurrences within the Wanapitei area include (north to south): Dolmac, Gordon mine, Crystal Gold mine, Burda Mine, McLean-Watt mine, and Davis shaft. Samples from the historical Gowganda mines include: Mann and Capital. Abbreviation: SIC = Sudbury Igneous Complex.

5.3 Results

The locations of the mineralized veins from which the sulphide mineral samples were selected and analyzed are presented in figure 5.1 and serve to highlight the broad geographical coverage of the fieldwork. Due to the number of analyses, the sulphur isotope data produced in this study are presented in detail in Appendix B. As summarized in figure 5.2, the data exhibit significant variation throughout the embayment and within individual occurrences. The variation is highlighted by the sulphur isotopic composition of pyrites from the mineralized vein occurrences of the Merico-Ethel property which display a variation of 7.7‰. The broad variation in $\delta^{34}\text{S}$ values of the sulphide minerals is also illustrated by frequency plots (figures 5.3, 5.4 and 5.5) of the individual sulphide minerals sampled throughout the embayment. Only the pyrite population displays indications of a Gaussian distribution, centered on a $\delta^{34}\text{S}$ value of approximately +1.5‰.

Also illustrated in figure 5.2 is a decrease in sulphur isotopic values from occurrences in the Gowganda Lake area (*i.e.* Capital, Mann, and Duncan Lake occurrences), relative to the nearby Elk Lake occurrences (*i.e.* Merico and Beaver Auxiliary occurrences). Trending southwards from the Delhi Township occurrences (located in the central area of the Cobalt Embayment), the sulphur isotopic composition of the mineralized vein occurrences exhibits a trend towards more positive $\delta^{34}\text{S}$ values. The only exceptions to this trend are the pyrite and chalcopyrite samples from the Burda Mine. The Burda occurrence is the only property in which the mineralized veins are thought to occur in sedimentary rocks *overlying* a Nipissing Diabase sill at depth.

Several vein samples from the shaft waste pile are hosted in Nipissing Diabase, suggesting that the diabase was encountered at depth and the sedimentary rocks hosting the calcite-quartz veins are located above the sill. The diabase sill may have acted as an impermeable barrier for fluid migration and caused the Burda Mine occurrence to scavenge sulphur from a different isotopic reservoir than nearby occurrences which tend to occur near the lower margin of the Nipissing diabase sill (*i.e.* Huronian *versus* Archean).

Figure 5.2. Overview of the sulphur isotopic composition of chalcopyrite, pyrite, galena, bornite, pyrrhotite, and cobaltite sampled from mineralized vein occurrences throughout the Cobalt Embayment. The occurrences are plotted by proximity to one another and on a general north-to-south trend (*i.e.* from the bottom to the top of the diagram).

Figure 5.3. Frequency plot of chalcopyrite $\delta^{34}\text{S}$ compositions, from mineralized vein occurrences distributed throughout the Cobalt Embayment, illustrating the broad variation in values ($n=45$).

Figure 5.4. Frequency plot of pyrite $\delta^{34}\text{S}$ compositions, from mineralized vein occurrences distributed throughout the Cobalt Embayment, illustrating a wide range in isotopic compositions. A poorly defined normal distribution is centered at a $\delta^{34}\text{S}$ value of approximately +1.5‰ ($n=27$).

Figure 5.5. Frequency plot of galena $\delta^{34}\text{S}$ compositions, from mineralized vein occurrences distributed throughout the Cobalt Embayment, illustrating the variation in values. Aside from galena samples from the Duncan Lake occurrence (with $\delta^{34}\text{S}$ values of -5.0‰), the data clusters within the narrow range of $\delta^{34}\text{S}$ values from -1.5 to 0‰ ($n=11$).

5.4 Discussion

The isotopic compositions of the potential sulphur reservoirs, present in the Cobalt Embayment, are illustrated in figure 5.6 and were compiled from data in Hattori *et al.* (1985), Goodz *et al.* (1986), and Papineau *et al.* (2007). From these earlier studies, a wide range of $\delta^{34}\text{S}$ values have been documented for some of the key lithological units present in the embayment; a feature that is suggestive of the presence of potentially very different sources of sulphur in the environment into which the mineralized vein occurrences were emplaced.

The $\delta^{34}\text{S}$ values of sulphide minerals from the main Merico-Ethel veins range from +4.6 to +5.9‰, which are within the range of the sulphur isotope compositions of sulphide minerals from the Cobalt Ag-veins (-0.7 to +6.4‰) and examples of the underlying Archean base-metal mineralization (+1.7 to +7.5‰). In contrast, primary (magmatic) sulphide minerals from the Nipissing Diabase have $\delta^{34}\text{S}$ values that cluster around 0‰, and are virtually indistinguishable in their $\delta^{34}\text{S}$ values from pristine mid-oceanic basalts. These majority of the data indicate that, not only is the diabase an unlikely source of the sulphur in the base- and precious-metal vein mineralization, but that the sulphur within the Nipissing Diabase was probably not derived from assimilation of sulphur-rich Huronian sedimentary rocks into which the Nipissing Diabase was intruded. The Merico property also hosts numerous smaller vein occurrences that are represented on figure 5.7 as the “Merico Property”. It is interesting to note that the sulphide minerals from the smaller occurrences display a broader range in $\delta^{34}\text{S}$ values than those from the larger veins of the main Merico system, with an average sulphur

isotope composition for the smaller veins (mean $\delta^{34}\text{S}$ value of +1.29 ‰) that is significantly more depleted in ^{34}S than that of the sulphide minerals from the main Merico vein system (mean $\delta^{34}\text{S}$ value of +5.29 ‰).

The other large-scale sources of sulphur in the Cobalt Embayment include Archean basement mineralization and the Huronian sedimentary rocks. Sulphur isotope values for Archean base-metal mineralization underlying the Cobalt mining camp range from $\delta^{34}\text{S} = +1.7$ to $+7.5\text{‰}$, with a mean $\delta^{34}\text{S}$ value of $+4.3\text{‰}$. In contrast, the Huronian sedimentary rocks of the Lorrain Formation display a very large range in sulphur isotope compositions ($\delta^{34}\text{S}$ values of -20.4 to $+18.4\text{‰}$) and those of the Gowganda Formation cluster into two populations centered on $\delta^{34}\text{S}$ values of 0‰ and $+4.5\text{‰}$ respectively, but with a mean value of $\delta^{34}\text{S} = 0.4\text{‰}$. From these comparative data, one potential source of sulphur in the Merico-Ethel vein mineralization could be that of Archean basement mineralization, given that the mineralizing fluid in the Merico-Ethel veins must have been enriched in ^{34}S (*i.e.* $\delta^{34}\text{S} > 4.7\text{‰}$). As noted by Goodz *et al.* (1986) Archean mineralization underlying several of the Cobalt Ag-vein systems is dominated by a sulphide mineral assemblage in which pyrrhotite is found replacing pyrite; a relationship that led the authors (*op. cit.*) to propose that during reaction with Proterozoic-age formational brines, sulphur was released from pyrite in the Archean basement mineralization, to form pyrrhotite and a modified hydrothermal fluid with elevated $\delta^{34}\text{S}$ values (*i.e.* $\delta^{34}\text{S} +5.0$ to $+11.0\text{‰}$). Goodz *et al.* (*op. cit.*) provided support for this hypothesis by documenting a trend in the $\delta^{34}\text{S}$ values of the altered Archean sulphides that increases from the margin of the veins into the Archean basement.

Figure 5.6. The sulphur isotope compositions of sulphide minerals from mineralized vein occurrences throughout the Cobalt Embayment plotted in relation to the major sulphur isotopic reservoirs in the embayment. The comparative data for the major lithological units in the embayment are from: Hattori *et al.* (1985); Goodz *et al.* (1986); and Papineau *et al.* (2007).

The hypothesis of Goodz *et al.* (1986) is supported by observations made by Ohmoto and Goldhaber (1997), which predict that pyrite would decompose under reducing conditions, and that in the presence of carbon-rich sediments (*e.g.* graphitic schists), the reduction of pyrite to pyrrhotite would produce a fluid rich in H₂S and CO₂:

or

The wide range in $\delta^{34}\text{S}$ values noted in the Lorrain Formation is likely due to oxidation-reduction reactions involving sulphide and sulphate minerals in the Huronian sedimentary rocks. The wide natural variation in the $\delta^{34}\text{S}$ values, coupled with more recent work investigating mass-independent fraction ($\Delta^{33}\text{S} (\text{‰}) = 1000 \cdot [(1 + \delta^{33}\text{S}/1000) - (1 + \delta^{34}\text{S}/1000)^\lambda]$, where λ expresses the mass-dependent fractionation relationship between $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$), have indicated that these sedimentary rocks record the onset of an oxygenated atmosphere. The wide ranges in sulphur isotopic values are related to increased microbial sulphate reduction and blooms of oxygenic photosynthesis that led to the development of a protective oxygen-rich atmosphere that filtered out ultraviolet light (Papineau *et al.*, 2007).

Other base- and precious-metal mineralized vein occurrences, such as those at Duncan Lake, have sulphide minerals that display very low (-5.6‰) $\delta^{34}\text{S}$ values. Such low $\delta^{34}\text{S}$ values may be attributable to interaction with, and/or derivation of sulphur from the Upper Huronian sedimentary rocks, which record $\delta^{34}\text{S}$ values of as low as -20.4‰ in the Lorrain Formation (Hattori *et al.*, 1985).

Figure 5.7. Expanded view of the isotopic composition of sulphide minerals from the mineralized vein occurrences highlighting the variability in sulphur isotopic compositions throughout the embayment. Even within the group of mineralized vein occurrences from the Merico-Ethel property there is significant variation in the $\delta^{34}\text{S}$ values of the sulphide minerals. The occurrences are plotted based on geographic proximity to each other on a north-to-south trend through the embayment in relation to the major isotopic reservoirs in the embayment. The more negative $\delta^{34}\text{S}$ compositions of galena in relation to the other sulphides are likely a result of a larger fractionation factor between H_2S and PbS . At 150°C , the $\Delta_{\text{H}_2\text{S}-\text{PbS}}$ value is 4‰ (Ohmoto, 1986).

As mentioned above, sulphur isotopes display a temperature-dependent fractionation between two solid (mineral) phases, which forms the basis for sulphur isotope geothermometry (Ohmoto and Rye, 1979). The successful application of the geothermometric method is based on four requirements or assumptions: i) That the minerals must be in equilibrium at the time of crystallization; ii) That no post-depositional alteration has occurred; iii) That pure mineral concentrates must be used for the sulphur isotope analysis; and iv) That the temperature dependence of the fractionation factors must be accurately known. Fortunately, the fractionation factors of several common sulphide minerals have been determined, *i.e.* pyrite, pyrrhotite, chalcopyrite, galena, sphalerite, argentite, chalcocite, covellite, and bismuthinite (Seal, 2006). Uncertainties in sulphur isotope temperature estimates generally range between $\pm 10^{\circ}\text{C}$ to $\pm 40^{\circ}\text{C}$ if the above criteria are met (Ohmoto & Rye, 1979).

Based on the experimentally determined fractionation factors (F_A) the temperature estimate is derived as follows:

$$T^2 = \frac{(\Delta F_A * 10^6)}{\Delta \delta^{34}\text{S}} - 273.15$$

where, ΔF_A is the difference in fractionation factors, and $\Delta \delta^{34}\text{S}$ is the difference in $\delta^{34}\text{S}$ values for the coexisting mineral pair (*e.g.* sphalerite-galena)

Using these principles, possible depositional temperatures were calculated for cogenetic sulphide mineral pairs, from several of the mineralized vein occurrences in the Cobalt Embayment (figure 5.8).

Figure 5.8. Plot of the calculated temperatures of sulphide mineral deposition, based on equilibrium sulphur isotopic fractionation, for various mineralized vein occurrences throughout the Cobalt Embayment. Temperatures were calculated from the measured sulphur isotopic compositions of coexisting sulphide minerals. Geologically unrealistic temperatures record the effects of one or more of the following processes: disequilibrium between the sulphide mineral pairs, post-depositional alteration, or the occurrence of unrecognized mineral impurities in the monomineralic concentrates used for sulphur isotope analysis.

Table 5.1. Calculated depositional temperatures for sulphide-mineral pairs from different occurrences of vein mineralization in the Cobalt Embayment.

Occurrence	Sample	Mineral Pair	Calculated Temperature (°C)
Capital Mines	CP-4a	galena-chalcopryrite	1220
Capital Mines	CP-4b	galena-chalcopryrite	467
Delhi Township	DL-1	galena-chalcopryrite	267
Delhi Township	DL-2	galena-chalcopryrite	274
Delhi Township	DL-4a	galena-chalcopryrite	308
Delhi Township	DL-4b	galena-chalcopryrite	264
Delhi Township	DL-4c	galena-pyrite	416
Delhi Township	DL-4d	chalcopryrite-pyrite	1018
Delhi Township	DL-5	galena-pyrite	399
Gosselin	GS-5	chalcopryrite-pyrite	1191
Merico	ME-6	chalcopryrite-pyrite	608
Merico	ME-7	chalcopryrite-pyrite	486
Merico	ME-8a	chalcopryrite-pyrite	459
Merico	ME-8b	chalcopryrite-pyrite	640
Merico	ME-20	chalcopryrite-pyrite	1126
Beaver Auxiliary	MT-1	chalcopryrite-pyrite	119
Laura Lake	WN-19	galena-chalcopryrite	282
Burda Mine	WN-24b	chalcopryrite-pyrite	1520

Goodz *et al.* (1986) reported sulphur-isotope temperature estimates in the range of 130° to 250°C for the sulphide minerals (chalcopyrite, galena, sphalerite, and pyrrhotite) in the Cobalt silver veins, with the majority of the calculated temperatures suggesting that the sulphide mineral pairs formed under conditions of isotopic equilibrium; an interpretation supported by independent temperature estimates for mineral deposition in the same veins by fluid inclusion analysis (Kerrick *et al.*, 1986), and also geothermometry from arsenopyrite compositions (Scott, 1983; Goodz *et al.*, 1986). In contrast, for the many occurrences of vein mineralization in the Cobalt Embayment, outside of the immediate Cobalt mining camp, the results of the sulphur isotope geothermometry obtained in this study clearly record significant evidence of isotope disequilibrium as is evidenced by the preponderance of geologically unrealistic temperatures (the only exceptions from this study are for the sulphide-mineral pairs from the Delhi Township and Laura Lake occurrences; Table 5.1). The sulphur isotope data that evidence widespread disequilibrium during sulphide deposition in many of the mineralized vein occurrences examined in this study are supported by the widespread occurrence of well-established mineral replacement textures in several of the deposits (involving for example, chalcopyrite replacing pyrite, cobaltite intergrown with chalcopyrite). In some of the occurrences, the combined isotopic and petrographic evidence suggests that multiple episodes of hydrothermal mineralization (and possible mineral replacement) occurred. Therefore, it is suggested that each episode of hydrothermal deposition represents the growth of an essentially monomineralic ore assemblage, which in combination, form a vein containing polymetallic mineralization. The prevalence of specular hematite in the majority of the Merico vein occurrences and

surrounding Huronian sedimentary rocks also indicates that reduction-oxidation reactions were likely a mechanism for sulphide precipitation. Within the Merico veins, specular hematite occurs as radiating rosettes of sheet-like grains hosted in calcite along calcite-quartz boundaries, often associated with chlorite, chalcopyrite, pyrite, and andradite garnet. In the surrounding Huronian sedimentary rocks, trace amounts of hematite occur in interstitial spaces (*i.e.* rimming clasts within diamictite and interstitial to rounded detrital quartz grains in arenite).

As shown in figure 5.9, if hematite was a stable mineral coexisting with sulphide minerals, then the concentration of H_2S was likely less than the concentration of SO_4^{2-} in the hydrothermal fluid, thus indicating that the sulphur was transported in an oxidized aqueous fluid, and probably encountered a local reducing medium that caused precipitation of the metals as sulphide not sulphate minerals. This observation also suggests that the sulphide minerals did not precipitate *via* simple cooling or decompression, but more likely were deposited from the mixing of oxidized and reduced fluids. If we assume that the temperatures of the fluids were greater than 200°C (*cf.* Goodz *et al.*, 1986; Marshall and Watkinson, 2000), then all the sulphur species would be expected to be in equilibrium before deposition. For such fluids, where hematite is a stable phase, the sulphur isotopic composition of the fluid can be estimated by:

$$\delta^{34}\text{S}_{\Sigma\text{S}} = \delta^{34}\text{S}_{\text{H}_2\text{S}} + \Delta\text{SO}_4\text{-H}_2\text{S}$$

where $\Delta\text{SO}_4\text{-H}_2\text{S}$ is the temperature dependent fractionation factor between SO_4 and H_2S (figure 5.9) and $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ is the isotopic composition of the sulphide minerals in δ annotation (Ohmoto and Goldhaber, 1997).

Therefore, if we assume a fluid temperature of 250–350°C (*cf.* Cobalt-Gowganda veins; Marshall and Watkinson, 2000) then the $\delta^{34}\text{S}_{\text{bulk}}$ composition of the fluids at Merico-Ethel ($\delta^{34}\text{S}_{\text{AVG}} = +5.11\text{‰}$) would have been approximately +25 to +30‰. If these assumptions are correct, the only reasonable sources of the sulphur in the hydrothermal fluids of the Cobalt Embayment that could produce the mineralized vein occurrences are the upper Huronian sedimentary units that display a wide range in $\delta^{34}\text{S}$ values from -20 to +32‰ (Gordon Lake and Lorrain Formations; figure 5.6). While extremely positive $\delta^{34}\text{S}$ values have been recorded from the Quirke Lake Group, this horizon does not extend to the northern portions of the embayment (*cf.* Figure 2.2). The low-temperature oxidation of mineral sulphides or organic sulphide in the Huronian sedimentary rocks could have produced aqueous sulphate with $\delta^{34}\text{S}$ values nearly identical to the source sulphide given that negligible kinetic sulphur isotope fractionation has been observed in hot springs, ground water, and weathering environments (Ohmoto, 1986). Finally, as Ohmoto and Goldhaber (1997) note, reduction of aqueous sulphate by organic matter or Fe^{2+} -bearing minerals can cause the generation of hematite and H_2S in ore-forming fluids, leading to the precipitation of sulphide minerals:

Figure 5.9. Deviation of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ from $\delta^{34}\text{S}_{\text{FLUID}}$ as a function of temperature and $(\text{SO}_4^{2-} / \text{H}_2\text{S})$ ratio as illustrated by solid lines. Mineral boundaries are drawn with dashed lines for the fluid composition of pH = neutral, S = 0.01m, $\text{K}^+ = 0.05\text{m}$, $\text{Na}^+ = 0.05\text{m}$, $\text{Ca}^{2+} = 1.0\text{m}$ and $\text{Mg} = 0.25\text{m}$. Abbreviations: Bn = bornite; Py = pyrite; Cpy = chalcopyrite; Po = pyrrhotite; Mt = magnetite; Hm = hematite. After Ohmoto and Goldhaber (1997).

In summary, the sulphur isotopic data from the Merico-Ethel veins can be interpreted in two ways: i) Sulphur was derived from the conversion of pyrite (FeS_2) to form pyrrhotite (FeS) in mineralized zones of the Archean basement, releasing CO_2 and H_2S -rich fluids enriched in $\delta^{34}\text{S}$ that mixed with metal-bearing, oxidized basinal fluids from the overlying Huronian sedimentary sequence; or ii) The derivation of sulphur from sulphide and sulphate minerals in the Huronian sedimentary units and its transportation as a sulphate species, with precipitation initiated by a reducing medium such as Fe^{2+} -bearing minerals, organic matter, or pre-existing sulphide minerals. Both theories are supported by the presence of an extensive hematite-bearing halo within the Huronian sedimentary rocks surrounding the Merico-Ethel property suggesting that oxidized fluids were prevalent in the sedimentary horizons and that sulphide mineral precipitation involved a Fe^{2+} -bearing phase. Transportation in a relatively oxidized fluid also favours the formation of gold and silver chloride complexes with precipitation resulting from increased H_2S concentration (Barnes, 1979). Marshall *et al.* (1993) and Marshall and Watkinson (2000) also found evidence for the transportation of silver as a chloride complex from the geologically analogous Cobalt silver veins.

Applying the same school of thought to the remaining occurrences is more difficult due to the lack of abundant iron-oxide minerals. Outside the stability fields of the iron-oxides, the $\delta^{34}\text{S}$ deviation of the fluid ($\Delta_{\text{SO}_4\text{-H}_2\text{S}}$) displays a dependence on the ratio of ($\text{SO}_4^{2-} / \text{H}_2\text{S}$) rather than temperature (figure 5.9). As a result, without additional information on the geochemical nature of the fluids, no accurate estimates on the $\delta^{34}\text{S}$ composition of the source fluids could be derived by this method. However, the

remaining mineralized vein occurrences do record isotopic disequilibrium amongst sulphide minerals, which suggests that the concentration of metals in the mineralizing fluids exceeded the concentration of reduced sulphur species. The removal of sulphur from the fluid by the sequential crystallization of simple sulphide minerals would generate a Rayleigh fractionation trend in the remaining sulphur (aqueous) and produce sulphur isotopic disequilibrium amongst the sulphide minerals that were crystallizing. This may be interpreted to represent the same processes that generated the Merico-Ethel occurrences: sulphate-rich fluids derived from the Huronian sedimentary rocks encountering a localized reducing medium.

Only the Delhi Township and the Laura Lake occurrences appear to display any signs of isotopic equilibrium during sulphide mineral precipitation: for example, all but one of the seven sulphide mineral pairs from the mineralized veins of the Delhi Township occurrence yield geologically reasonable temperatures, of 264°-416°C (Table 5.1), with all four of the galena-chalcopyrite pairs clustering in the 264°-308°C temperature range, temperatures very close to those determined from fluid inclusion studies of the Cobalt silver veins (Marshall and Watkinson, 2000). However, textural and lead isotopic data indicate that galena is paragenetically later than chalcopyrite and may have precipitated in response to a much younger event. Therefore, any apparent sulphur isotopic equilibrium may have been produced by the inheritance of the sulphur isotopic composition of precursor minerals.

5.5 Summary and Key Findings

Regional (Basin-wide)

- The wide range in $\delta^{34}\text{S}$ values of sulphide minerals (from -5.24 to 5.95‰; $n=86$) indicates that the Nipissing Diabase was not a major source of sulphur in the hydrothermal fluids responsible for the genesis of the regionally-distributed mineralized veins.
- Significant, inter-deposit variation in the $\delta^{34}\text{S}$ values of sulphide minerals from individual vein occurrences (see figure 5.2) suggests that localized sulphur sources existed in the Huronian and/or basement rocks, and that these were possibly controlled by the lateral extent of aquifers and/or faulting (perhaps in relation to the presence of sub-basins within the Cobalt Embayment).
- The more positive $\delta^{34}\text{S}$ values (>2‰) of base-metal sulphides hosted in a number of the mineralized vein systems (see figures 5.2 and 5.6) likely reflect the introduction of sulphur, remobilized from the basement, as a result of the conversion of pyrite to pyrrhotite in the underlying Archean rocks (*cf.* Goodz *et al.*, 1986). The conversion of pyrite to pyrrhotite in the presence of organic matter could have released both reducing H_2S and CO_2 (the latter with negative $\delta^{13}\text{C}$ compositions) to the circulating hydrothermal fluids:

- The more negative $\delta^{34}\text{S}$ values ($<-3\text{‰}$) of base-metal sulphides in a number of the mineralized vein systems (*i.e.* Burda Mine, Wanapitei area) may reflect derivation of the sulphur in the hydrothermal fluids from the Upper Huronian sedimentary rocks (see figures 5.2 and 5.6).
- The wide range in sulphur isotopic compositions of the Lorrain and Gordon Lake Formations probably record the global onset of an oxygenated atmosphere (*cf.* Papineau *et al.*, 2007); and in a related way, the narrow range in sulphur isotopic compositions of the Gowganda Formation indicate that it was deposited prior to the onset of the oxygenation of the atmosphere. The presence of extensive hematite alteration in the rocks of the Gowganda Formation thus provides evidence of the circulation of oxidizing fluids.
- The sulphur isotopic composition of vein-hosted galena is significantly more negative than the isotopic composition of the base-metal sulphides, reflecting the larger fractionation factor between PbS and $\text{H}_2\text{S} (aq)$ as compared to the fractionation factors between other sulphides and $\text{H}_2\text{S} (aq)$.

Local (deposit-scale)

- The intra-deposit variation of the sulphur isotopic composition of base-metal sulphides in some of the mineralized vein occurrences (*e.g.* those of the Merico-Ethel property) suggests the possibility of multiple sources of sulphur being available to the hydrothermal fluids (*i.e.* Huronian and Archean), locally, and also that fluid mixing occurred.

- With the exception of the Delhi Township mineralized vein occurrence, the intra-deposit variation for all of the vein systems is greater than the variation modeled by Rayleigh-type fractionation, which suggests that the polymetallic mineral assemblages typical of the main-stage of vein formation may, in fact, represent several episodes of mono-metallic mineral deposition that have overprinted each other to create the main-stage polymetallic assemblage (concentration metals > concentration sulphur).
- If the widespread hematite alteration in certain of the mineralized vein occurrences was in equilibrium with the sulphide-mineral assemblage, hydrothermal fluid-sulphide fractionation factors indicate that the mineralizing fluids would have been enriched in isotopically heavy sulphur (*i.e.* with $\delta^{34}\text{S} > 20\text{‰}$). The only, regionally-extensive, isotopic reservoir with sulphide/sulphate values of this magnitude (*i.e.* $\delta^{34}\text{S} > 20\text{‰}$) are the upper Huronian sedimentary rocks of the Lorrain and Gordon Lake Formations. In the oxidized hydrothermal fluids, sulphur would have had to be transported in the form of sulphate anions, with precipitation triggered by localized reduction *via* interaction with organic matter, Fe^{3+} -bearing minerals, and/or pre-existing sulphides.

Chapter Six: Strontium Isotopic Composition of Calcite

6.1 Introduction

Strontium has four naturally occurring isotopes, all of which are stable: ^{88}Sr , ^{87}Sr , ^{86}Sr , and ^{84}Sr . Their natural relative isotopic abundances are approximately 82.53, 7.04, 9.87, and 0.56 percent respectively. The relative abundances are approximations since ^{87}Sr is formed by the beta decay of naturally occurring ^{87}Rb : $^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + \beta^- + \nu + Q$, where β^- is the beta particle, ν is an antineutrino, and Q is the decay energy (specifically, 0.275 MeV). Therefore, the precise strontium isotopic composition of a mineral depends on the age and Rb/Sr ratio of that mineral (Faure and Mensing, 2005). Thus, if a mineral isotopic system has remained closed to the transfer of rubidium and strontium since its formation, the time since formation can be calculated from the equation:

$$^{87}\text{Sr}/^{86}\text{Sr} = (^{87}\text{Sr}/^{86}\text{Sr})_i + (^{87}\text{Rb}/^{86}\text{Sr}) * (e^{\lambda t} - 1)$$

where $(^{87}\text{Sr}/^{86}\text{Sr})$ and $(^{87}\text{Rb}/^{86}\text{Sr})$ are the present-day isotopic compositions of the mineral, the subscript i refers to the initial isotopic ratio of the mineral at the time of formation, λ is the decay constant, and t is the time that the mineral has taken to acquire its present-day isotopic ratio (*op. cit.*). The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the isotopic system can be deduced by plotting the measured $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr values for a suite of mineral samples on an $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ diagram. If the isotopic system has remained closed, the samples will define a straight line (isochron) whose y-intercept value is the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

The distribution of strontium in rocks and minerals is controlled principally by the extent to which Sr^{2+} can substitute for Ca^{2+} . Both elements are members of the alkaline

earth group, with ionic radii in six-fold coordination of 1.32Å and 1.14Å, respectively. Despite having a slightly larger ionic radius, strontium can substitute for calcium in a number of common silicate (*e.g.* pyroxene) and non-silicate minerals (*e.g.* calcite). In addition to substituting for octahedrally coordinated Ca^{2+} cations in the calcite structure, Sr^{2+} can also be adsorbed to the crystal surface. Initial research indicated that strontium partitioning into calcite was directly proportional to the Sr/Ca ratio of the formational fluids and was independent of temperature in the range of 150-350°C (Jacobson and Usdowski, 1976). However, as summarized by Fujita *et al.* (2004), recent work has illustrated that increased rates of precipitation can result in an increased strontium content in calcite. One potential cause for the increased strontium content is related to sorption of the strontium on the calcite surface. When the rate of precipitation is high, strontium sorbs to the crystal surface and initially is only partially coordinated to oxygen in the carbonate mineral structure. However, if the rate of precipitation is reduced enough for equilibration, only fully-coordinated strontium atoms are maintained (Lorens, 1981). Pingitore and Eastman (1986) proposed another possible mechanism based on the assumption that strontium can occupy both the normal lattice position of Ca^{2+} and also non-lattice defect sites in calcite. At higher degrees of supersaturation (*e.g.* higher precipitation rates), the number of crystal defects increases because surface nucleation is the dominant growth mechanism and therefore there are more potential locations for strontium incorporation (Teng *et al.*, 2000). As a result, calcite that formed under higher rates of precipitation may be more susceptible to strontium loss than calcite that crystallized under lower rates of precipitation.

The distribution of rubidium in nature is generally controlled by the ability of the large alkali metal to substitute for K^+ in crystallographic sites in minerals such as mica and alkali feldspar (Faure and Powell, 1972). Given its large ionic radius in octahedral coordination (1.66Å) and valence of +1, rubidium is very unlikely to substitute for Ca^{2+} in the calcite structure: in those studies where the rubidium concentration of calcite has been determined using isotope dilution, values of <2 ppm are typical (*cf.* Reid *et al.*, 1990; Kinnaird *et al.*, 2004). Furthermore, rubidium has two naturally occurring isotopes: radioactive ^{87}Rb and stable ^{85}Rb , with natural abundances of 27.83 and 72.17 percent respectively (Faure and Mensing, 2005). Therefore, given that calcite typically has a very low Rb/Sr ratio (<0.01; *op. cit.*), and that the dominant rubidium isotope is the stable ^{85}Rb atom, the strontium isotope composition would not be expected to change significantly over time due to the addition of radiogenic ^{87}Sr . Consequently, an obvious application of strontium isotopic data is to the determination of the source of strontium in hydrothermal fluids and mineral deposits, mainly through comparison of their $^{87}Sr/^{86}Sr$ ratios with those of the potential source reservoirs, taking into account the possible influence of processes such as fluid mixing (Misra, 2000). Due to the lack of serious fractionation effects (because of the very small mass difference of the ^{87}Sr and ^{86}Sr isotopes), strontium isotope ratios have some distinct advantages over those of hydrogen and oxygen isotopic data (*op. cit.*). The strontium isotopic compositions of waters that interact with rocks are typically controlled by a few major rock-forming minerals that contain the bulk of strontium. These include plagioclase feldspar, alkali feldspar, hornblende, clinopyroxene, the micas, and clay-group minerals. Most other silicates only significantly alter the strontium isotopic composition when extensive alteration of the

primary minerals has occurred (*i.e.* epidote after plagioclase, chlorite after mica, *etc.*) (McNutt, 2000). As evidenced from the experimental work of Fritz *et al.* (1992), which replicated the interaction of a low-temperature, closed system with a low aqueous fluid/rock ratio in a granitic-meteoric water system, the dominant control on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the aqueous fluid is plagioclase. As illustrated in figure 6.1, early dissolution of mica and potassium feldspar causes an initial rise in the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the aqueous fluid due to the preferential removal of radiogenic ^{87}Sr from the potassium site in the micas and feldspars. However, the fluid system quickly becomes saturated with respect to quartz and potassium feldspar preventing any further dissolution and the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the aqueous fluid decreases - reflecting the influence of plagioclase. These experimental results are supported by research conducted on natural waters sampled from fracture zones at depth within the Lac du Bonnet granite-granodiorite batholith (Li *et al.*, 1989). When the $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of the rock-forming minerals are taken into consideration, the data clearly indicate that in terms of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, the groundwaters sampled reflect the isotopic composition of plagioclase and not that of the bulk rock (figure 6.2). The relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the rock-forming minerals and the bulk rock is: plagioclase < bulk rock < potassium feldspar < biotite. McLaughlin (1997) later analyzed intergranular pore fluids and intergranular salts from drill cores of the Lac du Bonnet batholith and noted that the $^{87}\text{Sr}/^{86}\text{Sr}$ compositions of these phases are much closer to the bulk-rock composition (see pore fluids in figure 6.2). The latter author proposed (*op. cit.*) that unlike the fracture-hosted waters, the pore fluids represent a closed system that has obtained isotopic equilibrium with the host rocks.

Although limited work has been done at higher temperatures, the published studies for water at 100-137°C interacting with granitic rocks suggests that biotite may play a larger role in influencing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at higher temperatures (Fritz *et al.*, 1992; Pauwels *et al.*, 1992; Richards *et al.*, 1992; Aquilina *et al.*, 1997). All of these studies indicate that at higher temperatures, biotite is more prone to dissolution than plagioclase and potassium feldspar, thereby producing a very large initial surge in ^{87}Sr in the aqueous fluid. This increased dissolution of biotite is supported by petrographic studies and also the presence of significant lithium and cesium concentrations for the aqueous fluid. However, McNutt (2000) notes that there is also a close agreement between the isotopic composition of potassium feldspar and that of the fluid. McNutt (*op.cit.*) further suggests that incongruent dissolution of potassium feldspar causing preferential loss of strontium could also explain the observed isotopic compositions of the higher temperature fluids.

Figure 6.1. Model of fluid evolution illustrating the change in composition of dilute meteoric water reacting with a granite comprised of quartz, microcline ($^{87}\text{Sr}/^{86}\text{Sr} = 0.876$), plagioclase ($^{87}\text{Sr}/^{86}\text{Sr} = 0.706$), and biotite ($^{87}\text{Sr}/^{86}\text{Sr} = 2.35$) at various temperatures. The starting $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the meteoric water is 0.710, at a pH of 4.5 to 5.5, in equilibrium with atmospheric CO_2 . As illustrated by the fluid curves, the initial dissolution of biotite causes an early spike in the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the aqueous fluid. Once biotite and potassium feldspar dissolution ceases, the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the fluid approaches that of plagioclase until calcite precipitates. The plot is from McNutt (2000) and was constructed using a combination of DISSOL and KINDIS thermodynamic and kinetic modeling software.

Figure 6.2. Histogram plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters sampled from fracture zones within the Lac du Bonnet batholith in relation to the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the rock-forming minerals. The data clearly indicate that the water reflects the range of plagioclase isotopic ratios and not the bulk-rock ratios. Pore fluids represent analyses of intergranular fluids and rock salts from McLaughlin (1997). Diagram from McNutt (2000), generated using the data of Li *et al.* (1992).

While the source of ^{87}Sr remains contentious, it is evident that at higher temperatures, it is possible to produce brines enriched in ^{87}Sr from fluid-granitic rock interactions. Furthermore, as illustrated in figure 6.1, the calcites that precipitate from the aqueous fluids reacting with aluminosilicate rocks at higher temperatures are clearly more enriched in radiogenic ^{87}Sr relative to the starting fluid and the host rocks.

In the Cobalt Embayment, the dominant basement lithologies are those typical of Archean greenstone belts: mafic to ultramafic volcanics interspersed with granitic batholiths. In the case of a granitic basement, the dominant control on the strontium isotopic composition of the whole rock will be the minerals plagioclase and clinopyroxene, both of which have low Rb/Sr ratios and which may have $^{87}\text{Sr}/^{86}\text{Sr}$ values lower than the bulk rock, as noted above (McNutt *et al.*, 1990). Despite lower modal concentrations of plagioclase, evidence presented by McNutt *et al.* (1987) from the East Bull Lake layered gabbroic body suggests that plagioclase and its alteration products (*i.e.* epidote) remain the dominant strontium isotopic reservoirs within the mafic intrusive body. As such, any fluid in equilibrium with the rocks would most likely reflect the strontium isotopic composition of plagioclase and its alteration products, which typically have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the whole-rock composition. Therefore, any calcite precipitating from aqueous fluids that have interacted with the basement lithologies in the Cobalt Embayment should have $^{87}\text{Sr}/^{86}\text{Sr}$ values that reflect those of plagioclase within the underlying Archean rocks. The analysis of the major mafic lithologies of the Archean Abitibi greenstone belt has yielded initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in the range of 0.7005 to 0.7013 (Hart and Brooks, 1974; Condie, 1976; O'Nions and Pankhurst, 1978;

Collerson and Fryer, 1978), with the minor associated metasedimentary rocks reaching values as high as 0.706 (Fairbairn *et al.*, 1967). Archean granitic plutons that intrude the greenstone belts also display very low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, as evidenced by the Round Lake batholith, which has initial strontium isotopic ratios of 0.7009–0.7021 (Bell and Blenkinsop, 1976; Purdy and York, 1968). According to Fairbairn *et al.* (1967) and Kerrich *et al.* (1986), these values would likely have increased to 0.710 – 0.721 at 2200 ± 100 Ma (the approximate time of Huronian sedimentation) due to the time-related addition of radiogenic ^{87}Sr .

6.2 Methodology

Twenty-two of the calcite concentrates prepared for carbon and oxygen isotope analysis were also selected for strontium isotopic analysis. Figure 6.3 illustrates the location of the samples within the Cobalt Embayment. Individual grains of macroscopically pure calcite were crushed in an agate mortar and pestle. Ten mg of the calcite concentrate was placed in a beaker, to which acetic acid (25 volume percent) was added. The samples were placed in an ultrasonic bath for one hour and then centrifuged for 10 minutes to remove any traces of non-carbonate minerals. Taking care not to disturb the samples, the solution was transferred by pipette from the centrifuge containers into beakers and dried down on a hot plate. Once dry, 1 mL of 2.5N HCl was added to the sample and it was dried down again. Another 1.5 ml of 2.5 N HCl was added to the sample and the sample was capped and stored for 12 hours. The solution was then drawn through ion-exchange columns under 2.5N HCl and dried. The sample was mounted on a single Ta filament with H_3PO_4 bedding and analyzed in a ThermoFinnigan Triton TI

thermal ionization mass spectrometer. The measured isotopic ratios were: $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{84}\text{Sr}/^{86}\text{Sr}$, and $^{85}\text{Rb}/^{86}\text{Sr}$. Two sigma errors (~95% confidence) for the ratios are less than $\pm 0.002\%$ and the ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.11940$ to correct for fractionation. The $^{85}\text{Rb}/^{86}\text{Sr}$ ratio was measured as a check against the presence of anomalous rubidium concentrations in the calcite. Given that ^{85}Rb is the dominant isotope, an internal correction factor was applied if the measured $^{85}\text{Rb}/^{86}\text{Sr}$ ratios were determined to be greater than 9.00×10^{-5} . Fifteen of the twenty-two calcite samples displayed $^{85}\text{Rb}/^{86}\text{Sr}$ ratios below 10^{-4} ; a correction factor was applied to the remaining seven samples. The correction factors applied to the seven calcite samples reduced the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios by a *maximum* of 0.00037 or 0.052 percent of the measured, uncorrected ratios. As such, the correction is insignificant when the range of values from the hydrothermal calcite grains is considered. Measured $^{87}\text{Rb}/^{86}\text{Sr}$ values are rarely reported in the literature for hydrothermal calcite. The few publications (*cf.* Hecht *et al.*, 1999), confirm the observations of Faure and Mensing (2005) that most calcite grains have very low $^{87}\text{Rb}/^{86}\text{Sr}$ values (0.001 to 0.024; Hecht *et al.*, 1999). Even if anomalously high $^{87}\text{Rb}/^{86}\text{Sr}$ values of 0.100 are modeled, the change in $^{87}\text{Sr}/^{86}\text{Sr}$ values due to the addition of radiogenic ^{87}Sr would be less than 0.003 over 2.2 Ga (approximate period of time that has elapsed since the genesis of the vein mineralization in the embayment). Changes of such magnitude, in the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values, would not alter the interpretation of the strontium isotopic data presented here, nor provide a cause for the significant variation noted amongst the various mineralized vein occurrences.

Figure 6.3. Location of mineralized vein occurrences selected for strontium isotopic analysis. Aliquots of the calcite concentrates prepared for carbon and oxygen isotopic analysis were used in the strontium isotopic analysis. Abbreviation: SIC = Sudbury Igneous Complex.

6.3 Results

As illustrated by table 6.1 and figure 6.4, on a basin-wide scale it is evident that the calcite samples collected from occurrences of vein mineralization throughout the Cobalt Embayment display quite a large variation in the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.702-0.727), despite the commonality of their geological setting and mineralogical characteristics (see Chapter Two). However, it is also clear from the strontium isotope data that vein calcites from neighbouring mineralized occurrences typically display similar values: a feature that is most evident in the vein calcites (with a limited range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from 0.708-0.710) from the Northern occurrences near the towns of Elk Lake and Gowganda (*e.g.* Merico-Ethel, Beaver Auxiliary, Paramount, Beaver Pond, Mann Mine, Duncan Lake). With one exception (*i.e.* Reeve-Dobie $^{87}\text{Sr}/^{86}\text{Sr} = 0.7279$) these occurrences yield a relatively narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios: 0.7079 to 0.7120. Despite containing varying carbon and oxygen isotopic compositions (see Chapter Three), the calcite grains from the Merico-Ethel property contain relatively uniform strontium isotopic compositions.

Table 6.1. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of selected calcites from mineralized vein occurrences throughout the Cobalt Embayment.

Occurrence	Sample ID	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\sigma$	Average*
Duncan Lake	DUNC-3	0.709143	0.000020	
Duncan Lake	DUNC-7	0.712017	0.000012	
<i>Duncan Lake (n=2)</i>				<i>0.710580</i>
Merico-Ethel	ME-1	0.709230	0.000015	
Merico-Ethel	ME-2	0.709452	0.000011	
Merico-Ethel	ME-5	0.710025	0.000012	
Merico-Ethel	ME-8	0.708333	0.000150	
Merico-Ethel	ME-10	0.710020	0.000012	
Merico-Ethel	ME-14	0.710065	0.000012	
Merico-Ethel	ME-16	0.707930	0.000014	
Merico-Ethel	ME-17	0.708191	0.000009	
<i>Merico-Ethel (n=8)</i>				<i>0.709156</i>
Paramount	PARA-1	0.709775	0.000029	
Beaver Pond	BV-3	0.708811	0.000017	
Beaver Auxiliary	MT-1	0.709771	0.000074	
Mann Mine	MN-6	0.710579	0.000008	
Reeve-Dobie	RV-2b	0.727905	0.000015	
Brett Occurrence	BRT-1	0.702067	0.000010	
Brett Occurrence	BRT-1b	0.701953	0.000011	
<i>Brett Occurrence (n=2)</i>				<i>0.702010</i>
Delhi Township	DL-2	0.717527	0.000011	
Delhi Township	DL-4	0.717846	0.000010	
Delhi Township	DL-5	0.716336	0.000026	
<i>Delhi Township (n=3)</i>				<i>0.717236</i>
Fraleck Twp.	WN-16	0.720849	0.000010	
Burda Mine	WN-25	0.709037	0.000011	

Note. * Average for specific vein occurrence. Merico-Ethel area includes: the Paramount, Beaver Auxiliary, and Beaver Pond occurrences. Gowganda area mines: Reeve-Dobie and Mann Mine. Wanapitei area: Fraleck Township and Burda Mine occurrences.

Figure 6.4. Strontium isotopic composition of calcite from mineralized veins in the Cobalt Embayment, in reference to the major isotopic reservoirs, formational brines, meteoric water, and historical data from the Cobalt silver mines. Historical and strontium isotopic reservoir data from: Kerrich *et al.*, 1986; Fairbairn *et al.*, 1969; Hart and Brooks, 1974; Condie, 1976; O'Nions and Pankhurst, 1978; Collerson and Fryer, 1978; Bell and Blenkinsop, 1976; McNutt *et al.*, 1984 and 1990; and Faure, 1977.

6.4 Discussion

From an inspection of the strontium isotope data (figure 6.4) it is evident that the calcite grains extracted from the Brett gold mineralization have an Archean signature; with an average $^{87}\text{Sr}/^{86}\text{Sr}$ value for the Brett occurrence of 0.70200 (table 6.1). These values fall within the range of strontium isotopic values of 0.7017–0.7021 calculated for the underlying rocks of the Abitibi greenstone belt in the Proterozoic (at 2200 Ma) (Kerrick *et al.*, 1986). Whilst the vein calcite from the Brett occurrence undoubtedly obtained its strontium isotopic signature from the Archean basement, the timing of vein calcite deposition is interpreted here to be Proterozoic in age. In a study of fracture-hosted calcite in mafic Archean basement rocks by McNutt *et al.* (1990), the authors found textural evidence of several generations of calcite filling fractures, each with differing strontium isotopic ratios reflecting multiple fluid sources and different ages of precipitation. In contrast, the preliminary petrographic and isotopic evidence from the Brett mineralization indicates the presence of only one generation of vein calcite despite the abundant evidence for extensive fault reactivation in the vicinity of the Brett occurrence (see figure 3.6).

The majority of the vein calcites (16 of 20 analyses) from the mineralized vein occurrences in the Cobalt Embayment (other than those of the Brett gold occurrence) display strontium isotope ratios that range from 0.7083 to 0.7178 (table 6.1 and figure 6.4), which fall within reported ranges of the strontium isotopic composition of the sedimentary rocks of the Gowganda Formation of the Huronian Supergroup (figure 6.4). The elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.7175 to 0.7279) of samples collected from the Reeve-

Dobie, Delhi township and Fraleck occurrences may reflect the mixing of basement brines (with $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.710 – 0.753; McNutt *et al.*, 2000) with the fluids that have interacted with the less radiogenic Gowganda Formation (initial $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7044 – 0.717; Fairbairn *et al.*, 1969). As shown on figure 6.4, meteoric-derived surface waters may also play a role in the source of strontium with the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of modern meteoric waters ranging from 0.712 – 0.726 (Faure, 1977). One obvious method of determining the influence of meteoric water in the occurrences of calcite vein mineralization would be the analysis of the deuterium content of hydrated minerals within the mineralized veins. Unfortunately, for the majority of the mineralized vein occurrences, no co-existing hydrated minerals are present in sufficient quantities for isotopic analysis. Furthermore, meteoric waters have very low strontium contents and therefore should not affect the strontium isotopic composition of brines until they become dominant in any mixing trend (*cf.* McNutt *et al.*, 1990). Another possible explanation for the strontium isotopic ratios of the vein calcites to plot slightly higher than that of the Gowganda Formation sedimentary rocks may be the result of interaction of aqueous fluids with the wallrocks at elevated temperatures. As shown in figure 6.1, interaction of hot fluids with granitic rocks can lead to calcite precipitation with elevated $^{87}\text{Sr}/^{86}\text{Sr}$ compositions.

Interestingly, the strontium isotopic compositions of vein calcites documented from the Reeve-Dobie mine and by Kerrich *et al.* (1986) from the Cobalt Ag-veins, are significantly more radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.727 to 0.771) than the majority of the population determined in this study. In addition to the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios for vein

calcite, Kerrich *et al.* (1986) reported strontium isotopic ratios from actinolite crystals associated with the Cobalt vein mineralization, with the hydrothermal amphiboles yielding somewhat lower $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.7169 to 0.7440) than the calcites. On the basis of oxygen isotopic data and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology (*op. cit.*), the vein actinolite crystals appear to have remained closed to isotopic disturbance, suggesting that the significantly more radiogenic values of the vein calcites may in fact reflect isotopic exchange with a low- O_2 fluid at a later time, rather than the strontium isotopic ratio of the mineralizing fluid. Research by McNutt *et al.* (1990) and McNutt (2000) has highlighted the presence of anomalously radiogenic brines in Precambrian shield areas. Notably, analyses of subsurface brines present in Proterozoic-aged, quartz-pebble conglomerates from the Elliot Lake uranium mines display strontium isotopic ratios that are highly radiogenic and clearly not in equilibrium with the host rocks ($^{87}\text{Sr}/^{86}\text{Sr} = 0.725\text{--}0.753$). While each mine displayed slight isotopic variations, brines leached from fractures hosted by different rocks yielded very similar strontium isotopic compositions. This suggests that while local variations do exist, the host lithology is not controlling the strontium isotopic ratios of the brines. As reported by Duane *et al.* (1997) and McNutt (2000), brines associated with Proterozoic gold and uranium mineralization in quartz-rich clastic units of the Witwatersrand basin are also anomalously radiogenic with $^{87}\text{Sr}/^{86}\text{Sr}$ values as great as 0.769. Duane *et al.* (1997) interpret these radiogenic strontium compositions to reflect the interaction of meteoric water with granitic basement rocks and overlying shales, siliciclastics, and dolomites. As noted by McNutt (2000), the experimental data of Fritz *et al.* (1992) and Pauwels *et al.* (1992), and the observations of Richards *et al.* (1992) and Aquilina *et al.* (1997) suggest that these radiogenic brines would have had to

reach elevated temperatures ($>100^{\circ}\text{C}$) in order to dissolve ^{87}Sr -enriched micas and potassium feldspars. An indication of the highly radiogenic nature of the brines is evident through comparison to modern surface waters draining from the Superior Province which have $^{87}\text{Sr}/^{86}\text{Sr}$ values within the range 0.71835–0.73844 (Wadleigh *et al.*, 1985). It is plausible therefore, that the more radiogenic strontium compositions observed in the calcite grains documented by Kerrich *et al.* (1986) reflect recent interaction with warm, highly radiogenic groundwater brines. Only three samples can be correlated with respect to strontium, carbon, and oxygen isotopes in the Kerrich *et al.* (1986) study: from these three analyses, the calcite containing the highest $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.74525) also yielded the lowest $\delta^{18}\text{O}$ value (+1.7‰); and the $\delta^{18}\text{O}$ value is significantly lighter than that of the majority of the analyses from vein occurrences. As proposed by Kerrich *et al.*, (1986), the lower $\delta^{18}\text{O}$ values may reflect increased from input of meteoric water with $\delta^{18}\text{O}$ values ranging from -8 to -22 ‰.

A comparison of the strontium isotopic composition of the vein calcites from the Cobalt Embayment, with carbon and oxygen isotope data from aliquots of the same mineral separates does not reveal any systematic relationships. Rather, it highlights the variability of the carbon isotopic composition of individual vein calcites, which maintain a relatively constant strontium isotopic composition (figure 6.5). This is especially evident in the occurrences of vein calcite mineralization from the northern margin of the embayment (*i.e.* the Elk Lake and Gowganda areas). This suggests that while the source of carbon in the mineralizing fluids may have varied quite markedly, the bulk composition of the strontium source remained relatively constant. This lends further

support for the presence of significant aqueous fluid flow in the Huronian sedimentary rocks during the Proterozoic, and also to the interpretation that the source of low $\delta^{13}\text{C}$ in Merico-Ethel calcites may reflect the presence of a localized reductant that facilitated vein-mineral precipitation.

Strontium isotope ratios are typically considered to reflect geochemical events that have affected dissolved constituents in aqueous fluids (or solutes), whereas oxygen and hydrogen isotopic compositions record changes in the composition of the aqueous fluid (or solvent) itself (Misra, 2000). Therefore, the relatively constant oxygen isotopic composition of the vein calcites (figure 6.6), together with their variable strontium isotopic ratios, may indicate the existence of a common aqueous fluid (solvent) with different sources (and different strontium ratios) of solutes such as strontium. This may reflect possible sub-basin development (as noted from the Proterozoic-aged Athabasca basin; *cf.* Kyser *et al.*, 2000) with differing strontium isotope ratios arising from changes in basement lithology and the lateral continuity of aquifers.

Figure 6.5. Carbon isotopic ratios *versus* strontium isotopic compositions of vein calcites from mineralized occurrences in the Cobalt Embayment, illustrating the variability of $\delta^{13}\text{C}$ values from mineralized occurrences from the northern portion of the Cobalt Embayment (*i.e.* Merico-Ethel, Paramount, Beaver Auxiliary, Beaver Pond, Duncan Lake, etc.), whilst demonstrating the relatively constant strontium isotopic compositions of the vein calcites.

Figure 6.6. Oxygen isotopic ratios *versus* strontium isotopic compositions of vein calcites from mineralized occurrences in the Cobalt Embayment. The data illustrate (with one exception, the Beaver Pond Occurrence) the relative consistency of the oxygen isotope values for the northern occurrences in contrast to the variability of their strontium isotope compositions.

6.5 Summary and Key Findings

Regional (Basin-wide):

- With the exception of the Brett occurrence, which has an Archean isotopic signature ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70201$), the majority (16 of 20 analyses) of the $^{87}\text{Sr}/^{86}\text{Sr}$ values of vein calcite fall within the range 0.7083 to 0.7163. These values correspond to the reported range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Gowganda Formation (0.7044 to 0.7171; Fairbairn *et al.*, 1969; see figure 6.4).
- The strontium isotopic ratios of calcite from the Delhi township and Fraleck occurrences ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7175$ and 0.7208, respectively) may either reflect: *i*) the interaction of hydrothermal fluids at elevated temperatures with the Gowganda Formation or *ii*) increased input of Canadian Shield basement (formational) brines.
- The highly radiogenic isotopic compositions of vein calcite from the Reeve-Dobie Mine ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7279$) and those from the Cobalt camp Ag-veins ($^{87}\text{Sr}/^{86}\text{Sr}$ of 0.727-0.771; Kerrich *et al.*, 1986) may reflect the very recent crystallization, or re-equilibration, of calcite from formational brines (*e.g.* the highly radiogenic composition of Canadian Shield brines sampled from Elliot Lake mines; McNutt, 2000), rather than the original isotopic composition of the hydrothermal mineral.
- The relatively narrow range of $\delta^{18}\text{O}$ values of the vein calcites, coupled with their fairly restricted range in strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.708$ to

0.721 for all of the of vein systems except that of the Brett occurrence) supports the presence of basin-wide, mineralizing, hydrothermal fluids.

Local (deposit-scale):

- The extreme variation in $\delta^{13}\text{C}$ values from the Merico-Ethel vein calcites does not correlate with any significant variation in the strontium isotopic composition of the same sample, indicating that the highly negative carbon in the hydrothermal fluid/s in the Merico-Ethel vein system was derived from a different source than that of the strontium.
- The only mineralized vein occurrence that exhibits a clear Archean signature, in one of its isotopic systems, is the Brett occurrence, where the vein calcites have an average measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70201.
- The strontium isotopic composition of the Brett vein calcites fall within the calculated range of the mafic Archean basement during the Proterozoic (*ca.* 2200 Ma; Kerrich *et al.*, 1986).

Chapter Seven: Fluid Inclusion Petrography

7.1 Introduction

In an attempt to derive information regarding hydrothermal fluid chemistry and temperatures of vein formation, numerous samples were collected and prepared for fluid inclusion analysis. The fluid inclusion samples were selected based on the results obtained from transmitted and reflected light, optical petrography, and comprised a suite of sixteen samples that were cut to a thickness of approximately 120 microns, doubly polished, and mounted with acetone-soluble epoxy on 40 x 30mm glass slides. These doubly-polished sections were then examined under a petrographic microscope for the presence of fluid inclusions suitable for microthermometric analysis. Despite the best efforts of the author, none of the doubly-polished sections yielded fluid inclusions large or abundant enough to warrant further work. In order to confirm these preliminary observations, the suite of samples was sent to Professor Dan Marshall of Simon Fraser University, who is an expert in terms of both fluid inclusion analysis and the fluid inclusion characteristics of the Cobalt Ag-vein mineralization (*cf.* Marshall, 1990; Marshall *et al.*, 1993; Marshall and Watkinson, 2000). Whilst Professor Marshall noted some close similarities with the fluid inclusions found in the Cobalt Ag-veins, he stressed that given the small size and difficulty in separation of primary *versus* secondary inclusions, not much reliable geochemical information was likely to be determined from detailed microthermometry. As per his suggestions (D. Marshall, *pers. comm.*), what follows is a brief description of the dominant fluid inclusion populations present in the mineralized vein samples studied here. Despite sampling ten separate mineralized vein occurrences in the Cobalt Embayment, only the main Merico veins and the Beaver Pond

occurrence, from the Merico-Ethel property, contain consistent populations and appreciable numbers of fluid inclusions. The remaining mineralized vein occurrences contain either: populations of fluid inclusions with very inconsistent phase ratios, or an abundance of secondary inclusions and/or inclusions deemed too small for petrography. The criteria used to describe the characteristics of the fluid inclusion populations, in samples from the Cobalt Embayment, follow those outlined in detail in Roedder (1984).

7.2 Results of the Fluid Inclusion Petrography

Five of the useable fluid inclusion samples were collected from the main Merico vein system, two are from the “unnamed showing” just east of the Silver Jackpot mine, and one is from the Beaver Pond occurrence (see Chapter Two).

At the Beaver Pond occurrence, euhedral quartz crystals contain fluid inclusion-rich growth zones dominated by small ($<10\ \mu\text{m}$), three-phase fluid inclusions (liquid+vapour+halite) with less abundant two-phase inclusions consisting of liquid+vapour (figure 7.1). The three-phase inclusions contain 5 – 25 volume percent vapour and 20 - 30 volume percent halite (as a cubic daughter mineral). The two-phase inclusions are more variable in their fluid-to-vapour ratio, with vapour percentages ranging from 10 - 60 volume percent of the inclusion. Many of the two-phase fluid inclusions also exhibit textures suggestive of a secondary origin (*e.g.* aligned along healed fractures perpendicular to growth zones or presence of smaller two-phase inclusions in a suite of three-phase inclusions).

Figure 7.1. Plane-polarized light photomicrograph of a three-phase fluid inclusion (liquid+vapour+solid; ~10µm long) hosted in zoned, euhedral quartz from the Beaver Pond occurrence within the Merico-Ethel property. Also illustrated are numerous examples of the smaller two-phase (liquid+vapour) inclusions and two small liquid-only inclusions. The field of view is approximately 45 µm. Abbreviations: l = liquid, v = vapour, h = halite.

Figure 7.2. Plane-polarized light photomicrograph of three-phase (liquid+vapour+halite) and two-phase (liquid+vapour) fluid inclusions hosted in zoned, euhedral quartz from the Beaver Pond occurrence within the Merico-Ethel property. The field of view is approximately 40 µm. Abbreviations: l = liquid, v = vapour, h = halite.

Despite the presence of zoned, euhedral quartz crystals in the main Merico vein system, the fluid inclusions noted from the quartz crystals were smaller than those from the Beaver Pond occurrence – making observations more difficult. As shown in figure 7.3, the fluid inclusion population in the Merico vein samples is also dominated by a three-phase type, with a lesser number of two-phase inclusions. Most of the three-phase inclusions (liquid+vapour+halite) that were noted in the Merico vein samples were less than 5 μm in diameter. The main Merico fluid inclusions typically are comprised of 10 - 40 volume percent halite and 20 - 30 volume percent vapour. Phase relations in the two-phase inclusions range from 10 - 50 volume percent vapour. In one of the Merico vein samples (ME-4), the primary inclusions were typically three-phase in nature whereas the secondary, two-phase inclusions are aligned along healed fractures. The secondary, two-phase inclusions contained a relatively consistent 20 - 40 volume percent vapour.

Similarly, the interstitial calcite within the main Merico veins is dominated by the presence of small ($<5\mu\text{m}$) two-phase (liquid+vapour) fluid inclusions containing 10 - 40 volume percent vapour. Unfortunately, many of the latter appear to be secondary in origin, with trains of inclusions aligned along healed fractures (*cf.* Roedder, 1984). A minor population of three-phase inclusions (liquid+vapour+halite) was also noted within the vein calcite, but the mode of their origin was ambiguous.

Figure 7.3. Photomicrograph, under plane-polarized light, of three-phase (liquid+fluid+halite) inclusions in euhedral quartz crystal from the main Merico vein system (ME-4). The field of view is approximately 60 μm , with the individual inclusions all having lengths of less than 5 μm .

Samples of mineralized vein collected from the “unnamed showing”, located 800 metres east of the Silver Jackpot mine on the Merico-Ethel property, also contain euhedral quartz crystals set in a drusy calcite gangue. The quartz crystals are zoned and host minor populations of small ($<10\text{ }\mu\text{m}$) fluid inclusions located along growth zones. The fluid inclusion populations are dominated by slightly smaller ($<5\text{ }\mu\text{m}$) two-phase (liquid+vapour) inclusions with variable phase ratios (20 - 70 volume percent vapour), with a lesser frequency of three-phase inclusions that are slightly larger in size (with an average length of $5 - 10\text{ }\mu\text{m}$). The three-phase inclusions are also more consistent in their phase ratios, being composed of approximately 10 volume percent halite and 40 volume percent vapour (figure 7.4).

Textural evidence indicates that interstitial calcite from the mineralized veins formed syn- to post-mineralization and contains tiny ($< 5\text{ }\mu\text{m}$) fluid inclusions in the drusy cores of the grains. As shown in figure 7.5, the fluid inclusions present in the calcite are predominantly two-phase (liquid+vapour) in nature and exhibit a wide range of phase ratios: with from 10 - 70 volume percent vapour. As is the case with the quartz-hosted fluid inclusions, less abundant three-phase inclusions also occur, but are slightly larger in diameter and contain relatively more consistent proportions of vapour (30 - 40 volume percent) and more variable halite contents (10 - 30 volume percent). No fluid inclusions were noted in the outer growth zones rimming the drusy cores of the calcite crystals.

Figure 7.4. Plane-polarized light photomicrograph of a quartz-hosted, three-phase fluid inclusion with roughly equal proportions of vapour and halite from the “unnamed occurrence” located 800m east of the Silver Jackpot mine (ME-12b). A small two-phase inclusion is just out of focus in the bottom left-hand corner of the photomicrograph. The field-of-view is approximately 30 μ m.

Figure 7.5. Plane-polarized light photomicrograph of two-phase fluid inclusions hosted in calcite from the “unnamed occurrence” located east of the Silver Jackpot mine (ME-12b). Note the variable volume of the vapour and liquid components of the inclusions and also the range in size. The field of view is approximately 40 μ m.

7.3 Discussion

There are two main attributes to the fluid inclusions documented in the quartz and calcite gangue from the mineralized vein samples from the Cobalt Embayment: (i) two populations of fluid inclusion are commonly present, with two-phase (liquid+vapour) inclusions being far more abundant than the three-phase (liquid+vapour+halite) inclusions; and (ii) the phase ratios in the less abundant, three-phase (liquid+vapour+halite) inclusions are generally more consistent than they are in the smaller, more abundant two-phase (liquid+vapour) inclusions. Overall, these characteristics are very similar to those of the type-III and type-IV fluid inclusion populations documented by Taylor (1970), Scott and O'Connor (1971), Kerrich *et al.*, (1986), and Marshall *et al.*, (1993) for mineralized vein samples from the Cobalt and Gowganda camps. These latter authors reported the presence of five types of fluid inclusion from barren and mineralized veins in the Cobalt and Gowganda regions, which are defined as: type I (liquid), type II (liquid+halite), type III (liquid+vapour), type IV (liquid+vapour+halite), and type V (vapour). Based on a detailed petrographic study, Marshall *et al.*, (1993) concluded that the fluid inclusion population from the Cobalt silver veins is dominated by a combination of type III (liquid+vapour) and type IV (liquid+vapour+halite) inclusions, and that the remaining populations of inclusions (*i.e.* types I, II, and V) were rare in occurrence and were very likely metastable in nature, based upon of textural and microthermometry evidence. In contrast, both the type III and type IV inclusions analyzed by Marshall *et al.* (*op. cit.*) were noted to occur in pre- syn- and post-ore assemblages. As summarized by Marshall *et al.*, (*op.cit.*) pre-, and post-ore type IV inclusions homogenize on the halite liquidus at temperatures of 230° to 250°C

and at pressures well above the liquid + vapour field. In addition, the syn-ore assemblages yield results indicative of vein and ore formation, at temperatures between 290 to 350°C and pressures of 480 to 1350 bars. The results published by Marshall *et al.*, (*op.cit.*) are in general agreement with those of the other fluid inclusion studies and indicate that silver mineralization in the Cobalt and Gowganda camps resulted from the mixing of silver-saturated brine with a less saline fluid at depths of approximately 2000 metres (hydrostatic) (Kerrick *et al.*, 1986; Marshall *et al.*, 1993).

Much like those from the Cobalt and Gowganda studies, the three-phase (or type IV) fluid inclusions present in quartz crystals from the mineralized vein occurrences on the Merico property are interpreted to be pre- to syn-ore deposition in age. They typically occur in quartz crystals that crystallized along the vein margins, immediately before the main phase of sulphide mineralization. The presence of a halite cube indicates that the individual inclusions are highly saline in character (with approximately 30-35 mass percent NaCl equivalent) and would likely homogenize on the halite liquidus at approximately 200-230°C (Marshall, *pers. comm.*). Syn-ore two phase (type III) inclusions were noted from calcite crystals in most of the occurrences and would likely produce very similar results to those reported from Marshall *et al.*, (1993). Despite the reported presence of a few bladed calcite crystals in the main Merico veins, the similarity in inclusion populations between the published studies on the Cobalt-Gowganda Ag-veins suggests that boiling was not the dominant mechanism for vein formation (*e.g.* inclusions homogenize at pressures well above the liquid + vapour field). This is also corroborated by carbon and oxygen isotopic studies of syn- and post-ore calcite (chapter Three).

Chapter Eight: Conclusions and Implications for Exploration

8.1 Conclusions

- The field, textural and mineralogical data collected during the current study clearly demonstrates that the majority of the mineralized vein systems share morphological, structural and paragenetic features consistent with their formation in response to a regional (basin-scale) hydrothermal event. The paragenetic sequence involves:
  - i) Narrow silicate selvages (chlorite + quartz $\pm$ K-feldspar)
  - ii) Early sulphide stage (dominated by Co- and Ni-bearing pyrite) set in a silicate gangue
  - iii) A transition to calcite gangue and the main sulphide stage mineralization $\pm$ hematite $\pm$ precious metals
  - iv) Late stage massive calcite $\pm$ late stage galena.
- Correlation of significant clusters of polymetallic vein mineralization with the regional structural data of the Cobalt Embayment (figure 8.1) illustrates the spatial association of the mineralized veins with regional fault systems that were likely initiated during the Archean and have been reactivated several times post-intrusion of the Nipissing Diabase (Wilson, 1949; Symons, 1970; Card *et al.*, 1973; Morris, 1981; Sage, 1996).

Figure 8.1. Locations of significant mineralized polymetallic vein systems, with reference to the major regional fault systems mapped by the Ontario Geological Survey (after Andrews *et al.*, 1986a). All of the major fault systems were likely initiated during the Archean and have been reactivated several times post-intrusion of the Nipissing Diabase (Wilson, 1949; Symons, 1970; Card *et al.*, 1973; Morris, 1981; Sage, 1996).

- Petrographic and geochemical analyses have also confirmed that the mineralized vein occurrences are commonly rich in precious metals (native gold and electrum). In certain instances (*i.e.* Sauv occurrence, Merico-Ethel property) the mineralized vein occurrences also contain significant concentrations of uranium (up to 1.56 wt.% U_3O_8 equivalent).
- The carbon and oxygen isotopic composition of vein calcite from mineralized occurrences mirrors the isotopic composition of the Huronian sedimentary rocks and to a lesser degree, the carbonate component of the Archean greenstone belt basement. Furthermore, the constrained $\delta^{18}O$ values ($+10 \pm 2\text{‰}$) from mineralized occurrence throughout the embayment suggest a commonality amongst hydrothermal fluids responsible for vein formation. These constrained $\delta^{18}O$ values of vein calcite fall in the field defined as ‘metamorphic fluids’ and straddle the field defined as ‘sedimentary fluids’ of Sheppard (1986).
- The highly negative $\delta^{13}C$ values of vein calcite from the Merico-Ethel property likely reflect degradation of organic matter by hydrothermal fluids. In addition to the input of organic matter, the isotopic covariation evident at Merico-Ethel may reflect: *i*) fluid mixing at elevated temperatures (meteoric-derived basinal fluids mixing with reducing basement fluids); and/or *iii*) a combination of fluid mixing and minor wallrock alteration.

- The lead isotopic composition of Fe- and Fe-Cu-sulphides from the mineralized vein occurrences yield a Pb-Pb isochron age of 2265 ± 140 Ma, which is within error of the Nipissing Diabase intrusive (2219 ± 3.6 Ma; Andrews *et al.*, 1986b). The regional Pb-Pb data are supported by Pb-Pb isochron ages of Fe- and Fe-Cu-sulphides from individual occurrences such as, Merico-Ethel (2105 ± 930 Ma) and the Wanapitei area (2103 ± 680 Ma).
- The lead isotopic composition of vein-hosted galena extracted from various occurrences produce a Pb-Pb secondary isochron age indicative of Pb remobilization *circa* 1675 Ma. The secondary isochron age of the vein galena are corroborated by previous studies (Thorpe *et al.*, 1986) of galena extracted from the Cobalt district Ag-veins (*circa* 1650 Ma). Furthermore, the lead isotopic composition of galena grains extracted from the Delhi Township occurrence produces an anomalous Pb line, which based on the Stacey-Kramers two-stage Pb evolution curve, suggests that radiogenic Pb was added to the system at *circa* 1784 Ma (within error of the *circa* 1.7 Ga metasomatic event).
- The combination of Fe-sulphide, Fe-Cu-sulphide and galena isotopic data indicate the presence of at least two stages of mineralization *circa* 2220 Ma and 1700 Ma. These data provide further evidence for a basin-wide influence of the regional Na- and K-metasomatic event related to the final stages of the Penokean orogeny (*ca.* 1.9 – 1.7 Ga).

- The occurrence of a basin-wide, Na- and K-metasomatic event at approximately 1700 Ma, is supported by whole-rock $^{40}\text{Ar}/^{39}\text{Ar}$ (Hu *et al.*, 1998), Rb-Sr (Fairbairn *et al.*, 1969; Roscoe *et al.*, 1992), and U-Pb (McLennan *et al.*, 2000) isotope systematics within the upper Huronian sedimentary rocks and paleosols along the regional unconformity. These isotopic systems were reset during a potassium and sodium-metasomatic event at 1690-1760 Ma (Rainbird *et al.*, 1990; Prasad, 1994) during the final stages of the Penokean orogeny (*ca.* 1.9 to 1.7 Ga). Furthermore, U-Pb isotope analysis of hydrothermal monazite, in metasomatically albitized rocks from the McLean-Watt mine, yields an age of 1700 ± 2 Ma (Schandl *et al.*, 1994).
- Petrographic examination of the highly radiogenic Fe- and Fe-Cu-sulphides revealed the presence of significant inclusions of Cu-Bi-Pb-sulphides (*i.e.* wittichenite, aikinite, aleksite, *etc.*) which likely disrupted the initial U/Pb isotopic ratio and produced the highly radiogenic Pb compositions. Ore textures also provide further support of the late-stage galena mineralization.
- The range in sulphur isotopic compositions of ore minerals indicate that the Nipissing Diabase intrusive event was not the dominant source of sulphur and that localized sources exist. The sources were possibly controlled by the lateral extent of aquifers, faulting and/or paleotopography.
- The positive $\delta^{34}\text{S}$ values of the base-metal sulphides hosted in the vein systems were likely derived from the Archean basement during desulphurization of pyrite

to pyrrhotite (*cf* Goodz *et al.*, 1986). The conversion of pyrite to pyrrhotite in presence of organic matter may have released reducing H_2S and CO_2 (with negative $\delta^{13}\text{C}$ compositions) to the fluids:

- As first noted by Cabri (1992), pyrite in gold- and base-metal deposits can often contain up to 1000 ppm gold incorporated in its crystal structure, where it is often associated with arsenic. Pyrrhotite, in contrast, hosts very little gold (or Co, Ni, As) and as a result, the desulphurization of pyrite to pyrrhotite could have released significant quantities of both sulphur and metals (Au, As, Co, Ni) to the circulating hydrothermal fluids. As silver is not readily incorporated in the pyrite structure (Cabri *et al.*, 1985), chalcopyrite, sphalerite, and/or galena would be a more probable source mineral for Ag in the basement rocks (*cf.* Taylor & Campbell, 2004b). Archean interflow sedimentary rocks commonly contain disseminated, stockwork, and 1-3 metre thick, massive lenses of pyrite, pyrrhotite, sphalerite, and chalcopyrite typically forming 5-30 volume percent of the unit (Goodz *et al.*, 1986; MacQueen, 1985). In a comprehensive examination of the metallogenetic relationships in the Cobalt area, Patterson (1979) noted that interflow sedimentary rocks are present in the Archean basement immediately below greater than 70% of the seventy-seven, known Ag-Co vein deposits. Furthermore, erosion of the Archean host rocks has dispersed base-metal sulphides into the lower strata of the Huronian sedimentary sequence, especially those adjacent to the regional unconformity (Jambor, 1971a).

- The negative $\delta^{34}\text{S}$ values of the base-metal sulphides hosted in the vein systems may reflect derivation of sulphur from the upper Huronian sedimentary rocks. As a result, the more negative sulphur isotopic compositions of vein-hosted galena may reflect a greater input of sulphur derived from the Huronian sedimentary rocks *circa* 1.7 Ga.
- The narrow range in sulphur isotopic compositions of sulphide minerals in the Gowganda Formation suggest that it was deposited before the onset of an oxygenated atmosphere. The presence of an extensive hematite alteration halo in the Gowganda Formation thereby provides evidence of circulation of oxidizing fluids.
- With the exception of the Delhi Township occurrence, the intra-deposit variation in sulphur isotopic composition of ore minerals is greater than the expected variation modeled by Rayleigh-type fractionation. This suggests that the polymetallic assemblages may represent several monometallic episodes overprinting each other to create a polymetallic assemblage, where the concentrations metals were greater than the concentrations of available sulphur.
- If the widespread hematite alteration halo is in equilibrium with the sulphide assemblage, fluid-sulphide fractionation factors indicate that the mineralizing fluids would be enriched in isotopically heavy $\delta^{34}\text{S}$ (*i.e.* $> 20\text{‰}$). The only isotopic reservoir with sulphide/sulphate values $\delta^{34}\text{S} > 20\text{‰}$ are the upper Huronian sedimentary rocks (Lorrain and Gordon Lake Formations). In the

oxidized fluid, sulphur would have been transported as sulphate species, with precipitation triggered by localized reduction via interaction of organic matter, Fe³⁺-bearing minerals and/or pre-existing sulphides:

- The strontium isotopic composition of vein-hosted calcite may reflect the interaction of hydrothermal fluids with the upper Huronian sedimentary rocks at elevated temperatures in an open-system behavior (with preferential dissolution of potassium feldspar and biotite and fluids not reaching isotopic equilibrium with the country rocks).
- The highly radiogenic strontium compositions of calcite from the Reeve-Dobie occurrence and the carbonate analyses of Kerrich *et al.*, (1986) may reflect recent crystallization of carbonate from basement brines in underground workings (*i.e.* highly radiogenic composition of groundwaters sampled from Elliot Lake mines; McNutt, 2000).
- The relatively narrow range of $\delta^{18}\text{O}$ values with mild variation in strontium isotopic composition of vein calcite suggests the presence of basin-wide brines with slight variations in strontium isotopic reservoirs (*i.e.* changes in basement lithology and/or composition of sedimentary rocks). The extreme variation in $\delta^{13}\text{C}$ values from the Merico-Ethel does not influence the strontium isotopic composition of vein calcite, indicating that highly negative carbon was derived

from a different source than strontium (and by extrapolation, the fluid solutes/metals).

- The sole occurrence to preserve an Archean strontium isotopic signature is the Brett occurrence. However, based on textures and the calculated strontium isotopic composition of the Archean basement at 2.2 Ga, the timing of calcite crystallization is interpreted to be Proterozoic in age
- A model which encompass all the observed isotopic, mineralogical, and textural features involves: (i) regional flow of oxidized, hydrothermal brines driven by sedimentary loading and the heat released by the Nipissing Diabase intrusive event, focused along the Huronian-Archean unconformity; and (ii) polymetallic mineralization related to interaction of the oxidized basinal brines with both the reducing fluid and solid components of the Archean basement, facilitated by fault reactivation and the localized displacement of the Huronian-Archean unconformity surface.
- These conditions support the generation of unconformity-associated mineralization (figure 8.2). This model is based on the potential of the regionally extensive sub-Huronian unconformity to: (a) focus massive volumes of fluid flow in a geological setting that juxtaposes two distinctly different lithogeochemical (sedimentary *versus* volcanic) and fluid source reservoirs (oxidized *versus* reduced); (b) host major faults and fault-controlled zones of enhanced permeability that were ideal sites for mixing of different fluids and consequently

ore deposition during periods of fault reactivation; and (c) create geological settings suitable for the genesis of very large zones of polymetallic (Fe, Cu, Co, Ni, As, $\pm$ Au $\pm$ Ag $\pm$ U) mineralization straddling the unconformity.

- In this conceptual model, vein mineralization hosted within the Nipissing Diabase likely represents the distal (upper) portions of the mineralizing system. The early-stage sulphide mineralization likely formed immediately post-crystallization of the Nipissing Diabase when brittle deformation of the diabase sheet allowed expulsion of hydrothermal fluids trapped below the diabase. The late-stage mineralization reflected in the lead isotopic composition of vein-hosted galena, likely formed in response to the basin-wide Na- and K-metasomatic event circa 1700 Ma that was confined to the regional unconformity.
- Unconformity-associated uranium deposits typically contain significant concentrations of Co, Cu, Ni, As, S, Pb, Fe, Au, and Ag in addition to high-grade uranium mineralization (Ruzicka, 1996; Jefferson *et al.*, 2007). As summarized by Jefferson *et al. (op.cit.)*, polymetallic unconformity-associated deposits in the Proterozoic Athabasca basin occur in pods, veins, and semi-massive concentrations straddling or located just above the regional unconformity between late Paleo- to Mesoproterozoic conglomeratic sandstones and metamorphosed basement rocks. The deposits are typically associated with faults or fracture systems in proximity to graphitic metapelite layers of the Wollaston Group (Ruzicka, 1996). As summarized by Jefferson *et al. (2007)*, the conventional ore genetic models invoke circulation of oxidizing, U-bearing, basin fluids, heated to

approximately 200°C, at the unconformity by geothermal gradients reacting with reducing fluids permeating out of reactivated basement shear zones. As uranium geochemistry is largely governed by oxidation state (Cuney *et al.*, 2009), uranium precipitation occurs in reactivated fault zones where the contrasting fluids mix. In the Athabasca Basin, zones of inferred fluid mixing are characterized by the presence of illite, kaolinite, dravite, chlorite, euhedral quartz, and locally, by concentrations of Ni-Co-As-Cu sulphide minerals (Hoeve and Quirt, 1984; Wallis *et al.*, 1985; Kotzer and Kyser, 1995; Jefferson *et al.*, 2007).

- As noted by Ruzicka (1996), unconformity-associated U deposits exhibit geological and mineralogical similarities with uranium-vein or arsenide-vein uranium-silver occurrences. In fact, several authors have suggested that the uranium-bearing vein systems of the Beaverlodge District (northern Saskatchewan) may represent exhumed representatives of the basement-hosted vein, monometallic, unconformity-associated deposits (Mazimhaka and Hendry, 1989; Jefferson *et al.*, 2007).

Figure 8.2. Idealized cross-section of the Cobalt Embayment, illustrating the key lithological, structural, and geochemical parameters in the generation of polymetallic vein and unconformity-associated mineralization. Oxidized basin fluid flow was focused along the regional unconformity during intrusion of the Nipissing Diabase sill *circa* 2.2 and again during the regional Na- and K-metasomatic event *circa* 1.7 Ga. These systems facilitated mixing of oxidized basin fluids with reduced fluids and/or reducing matter along the reactivated, regional fault systems. The mineralogy of the vein systems is primarily controlled by the basement lithology and the composition of the lower Huronian sedimentary rocks.

8.2 Implications for Exploration

The discovery of the high-grade polymetallic mineralization in association with evidence for potential unconformity-related mineralization requires changes in current exploration strategies employed in the Cobalt Embayment. As noted by Taylor and Campbell (2004*b*), throughout the Cobalt embayment there are several documented examples of polymetallic mineralization set in calcite gangue in discordant veins (*cf.* Born & Burbidge, 1987; Born & Hitch, 1990; Smyk *et al.*, 1997; Taylor 2004). When viewed together as part of a regional mineralizing event, they take on a previously unrecognized economic significance and suggest that additional, significant polymetallic mineralization may occur at depth near the regional unconformity. Prospecting vectors for regions of unconformity-associated mineralization should include:

- Proximity to regional, reactivated fault systems;
- Presence of conglomeratic, basal breccia and/or sandstone sedimentary units overlying the regional unconformity;
- Metal-rich basement lithology (mafic volcanic, interflow sediments, granitic, *etc.*);
- Evidence for hydrothermal alteration in the Huronian sedimentary rocks (chlorite, hematite and clay-alteration of feldspars, *etc.*); and
- Evidence of polymetallic and precious-metal rich vein mineralization.

References Cited

- Aagaard P., Egeberg P.K., Saigal G.C., Morad S., and Bjorlykke K. (1990): Diagenetic albitization of detrital K-feldspars in Jurassic, Lower Cretaceous, and Tertiary clastic reservoir rocks from offshore Norway, II. Formation water chemistry and kinetic considerations. *Journal of Sedimentary Petrology*, **60**, p. 575-581
- Andrews A.J., Masliwec A., Morris W.A., Owsiacki L, and York D. (1986b): The silver deposits at Cobalt and Gowganda, Ontario II: An experiment in age determination employing radiometric and paleomagnetic measurements. *Canadian Journal of Earth Sciences*, **23**, p. 1507-1518
- Andrews A.J., Owsiacki L., Kerrich R., and Strong D.F. (1986a): The silver deposits of Cobalt and Gowganda, Ontario. I: Geology, petrology and whole-rock chemistry. *Canadian Journal of Earth Sciences*, **23**, p. 140-1506
- Aquilina L., Pauwels H., Genter A., and Fouillac C. (1997): Water-rock interaction processes in the Triassic sandstone and the granite basement of the Rhine Graben: geochemical investigation of a geothermal reservoir. *Geochimica et Cosmochimica Acta* **61**, p. 4281-4296
- Bachinski D.J. (1969): Bond strength and sulfur isotopic fractionation in coexisting sulfides. *Economic Geology*, **64**, p. 56-65
- Barnes H.L. (1979): Solubilities of Ore Minerals. In: *Geochemistry of Hydrothermal Ore Deposits*, 2nd edition (H.L. Barnes, ed.), John Wiley & Sons, New York, p.404- 460
- Bastin E.S. (1939): The nickel-cobalt-native silver ore type. *Economic Geology*, **34**, p. 1-40
- Bekker A., Kaufman A.J., Karhu J.A., and Eriksson K.A. (2005): Evidence for Paleoproterozoic cap carbonates in North America. *Precambrian Research*, **137**, p.167-206
- Bekker A., Karhu J.A., and Kaufman A.J. (2006): Carbon isotope record for the onset of the Lombardi carbon isotope excursion in the Great Lakes area, North America. *Precambrian Research*, **148**, p. 145-180
- Bell K., and Blenkinsop J. (1976): A Rb-Sr whole-rock isochron from the Otto stock, Ontario. *Canadian Journal of Earth Sciences*, **13**, p. 998-1002
- Bennett G. (1978): Huronian volcanism, districts of Sault Ste. Marie and Sudbury. *Ontario Geological Survey, Miscellaneous Paper* **82**

- Bennett G., Dressler B.O. and Robertson J.A. (1991): The Huronian Supergroup and associated intrusive rocks. *In: Geology of Ontario* (P.C. Thurston, H.R. Williams, R.H. Sutcliffe, G.M. Stott eds), *Ontario Geological Survey*, Special Volume 4, Part 1, p. 549-591
- Benson A.A., Fletcher S.D.T., and Eyles C.H. (2006): Gowganda revisited: a Palaeoproterozoic rift-basin infill? Geological Association of Canada – Mineralogical Association of Canada Joint Meeting, Program with Abstracts, Vol. 31, p.14
- Bethke C.M. (1996): *Geochemical reaction Modeling*. Oxford University Press, New York.
- Boles J.R. (1982): Active albitization of plagioclase, Gulf Coast Tertiary. *American Journal of Science*, **282**, p. 165-180
- Born P., Hitch M.W. and Avlonitis A. (1990): Precambrian geology, Bay Lake area, eastern half. *Ontario Geological Survey*, Map 2551
- Born P. and Burbidge G.H. (1987): Geology of Brigstocke and Kittson townships. *Ontario Geological Survey Miscellaneous Paper 137*, p.198-204
- Born P. and Hitch M.W. (1990): Bay Lake area. *Ontario Geological Survey Report 276*, 81 p
- Botsford J.N. (1985): Evaluation of the Scadding Gold Mines Limited property, concentrator and equipment, Scadding Township, Sudbury District, Ontario; Unpublished technical report prepared for Orofino Resources Ltd
- Boyle R.W. and Dass A.S. (1971): Origin of the native silver veins at Cobalt, Ontario. *In: The Silver-Arsenide Deposits of the Cobalt-Gowganda region, Ontario* (L.G. Berry ed), *The Canadian Mineralogist*, **11**, p. 414-417
- Bryne N.W. (1969): Report on the Contact Lake Mine, Ulster Petroleums Limited, GreatBear lake area, Mackenzie Mining District, N.W.T. *Department of Indian and Northern Affairs, Assessment Report No.060371*, 33 p
- Buchan K.L., Mortensen J.K., Card K.D. and Percival J.A. (1998): Paleomagnetism and U-Pb geochronology of diabase dikes swarms of Minto block, Superior Province, Quebec. *Canadian Journal of Earth Sciences*, **35**, p. 1054-1069
- Cabri L. (1992): The distribution of trace precious metals in minerals and mineral products. *Mineralogical Magazine*, **56**, p. 289-308
- Cabri L., Campbell J.L., Laflamme J.H.G., Leigh R.G., Maxwell J.A. and Scott J.D. (1985): Proton-microprobe analysis of trace elements in sulfides from some massive-sulfide deposits. *The Canadian Mineralogist*, **23**, p. 133-148

- Card K.D., McIlwaine W.H. and Meyn H.D. (1973): Geology of the Maple Mountain area, Operation Maple Mountain, Districts of Timiskaming, Nipissing and Sudbury. *Ontario Geological Survey Geological Report 106*, 106 p.
- Card K.D. (1978): Metamorphic of the Middle Precambrian (Aphebian) rocks of the eastern Southern Province. *In* Metamorphism in the Canadian Shield. *Geological Survey of Canada, Paper 78-10*, 269-282
- Carignan J. and Gariépy C. (1993): Pb isotope geochemistry of the Silidor and Launay gold deposits: implications for the source of Archean Au in the Abitibi Subprovince. *Economic Geology*, **88**, p.1722-1730
- Chandler W.R. (1984): Sedimentary setting of an Early Proterozoic copper occurrence in the Cobalt Group, Ontario: a preliminary assessment, *Current Research, Part A. Geological Survey of Canada, Paper 84-1A*, p. 185-192
- Chandler W.R. (1986): Sedimentology and paleoclimatology of the Huronian (Early Aphebian) Lorrain and Gordon lake Formations and the bearing on models for sedimentary copper mineralization. *Geological Survey of Canada, Paper 86-1A*, p.121-132
- Chandler W.R. (1988): Diagenesis of sabkha-related, sulphate nodules in the Early Proterozoic Gordan Lake Formation, Ontario, Canada. *Carbonates and Evaporites*, **3**, p. 75-94
- Chandler W.R., Young G.M. and Wood J. (1969): Diaspore in Early Proterozoic quartzites (Lorrain Formation) of Ontario. *Canadian Journal of Earth Sciences*, **6**, p. 337-340
- Church W.R. (1968): The Penokean and Hudsonian orogenies in the Great Lakes region, and the age of the Grenville Front. Abstracts, 14th Annual Institute on Lake Superior Geology, Superior, Wisconsin, p. 16-18
- Collerson K.D. and Fryer, B.J. (1978): The role of fluids in the formation and subsequent development of early continental crust. *Contributions to Mineralogy and Petrology*, **67**, p. 151- 167
- Colvine A.C., Fyon, J.A., Heather, K.B., Marmont, S., Smith, P.M. and Troop, D.G. (1986): Archean lode gold deposits in Ontario. *Ontario Geological Survey Miscellaneous Paper 139*, 136 p
- Condie K.C., (1976): Trace-element geochemistry of Archean greenstone belts. *Earth Science Reviews*, **12**, p. 393-417
- Corfu F. and Andrews, A.J. (1986): A U-Pb age for mineralized Nipissing diabase, Gowganda, Ontario. *Canadian Journal of Earth Sciences*, **23**, p. 107-109

- Corriveau L. (2007): Iron oxide copper-gold deposits: a Canadian perspective. *In: Mineral Deposits of Canada: a Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces and Exploration Methods* (W.D. Goodfellow ed.) *Geological Association of Canada, Mineral Deposits Division, Special Publication*, **5**, p. 307-328
- Cox R.A., Wilton D.H.C. and Kosler J. (2003): Laser-ablation U-Th-Pb in situ dating of zircon and allanite: an example from the October Harbour granite, Central Coastal Labrador, Canada. *The Canadian Mineralogist*, **41**, p. 273-291
- Criss R.E. (1999): *Principles of Stable Isotope Distribution*. Oxford University Press, New York
- Cuney M. (2009): The extreme diversity of uranium deposits. *Mineralium Deposita*, **44**, p.3-9
- Dansgaard W. (1964): Stable isotopes in precipitation. *Tellus*, **16**, p.436-468
- Davidson A., van Breemen O., Sullivan R.W. (1992): Circa 1.75 Ga ages for plutonic rocks from the Southern Province and adjacent Grenville Province: what is the expression of the Penokean Orogeny. *Geological Survey of Canada, Paper 92-2*, p.107-118
- Deer W.A., Howie R.A. and Zussman J. (1992): *An Introduction to the Rock-Forming Minerals*, 2nd edition, Prentice Hall, New York, 696 p
- Dence M.R. and Popelar J. (1972): Evidence for an impact origin for Lake Wanapitei, Ontario. *In: New developments in Sudbury Geology*, J.V. Guy-Bray (ed). *Geological Association of Canada Special Paper*, **10**, p. 117-124
- Dickin A.P. (1995): *Radiogenic Isotope Geology*, Cambridge University Press, 490p
- Dressler B.O. (1982): Geology of the Wanapitei Lake area, District of Sudbury. *Ontario Geological Survey Report 213*, 131p
- Droop G.T.R. (1987): A general equation for estimating Fe³⁺ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. *Mineralogical Magazine*, **51**, p. 431-435
- Duane M.J., Pigozzi G. and Harris C. (1997): Geochemistry of some deeps gold mine waters from the Western portion of the Witwatersrand Basin, South Africa. *Journal of African Earth Sciences*, **24**, p. 105-123
- Eakins P.R. (1961): Cylindrical jointing in diabase at Gowganda Ontario, *Geological Association of Canada*, **13**, p.85-94

- Easton R.M. (2000a): Metamorphism of the Canadian shield, Ontario, Canada. I. The Superior Province, *The Canadian Mineralogist*, **38**, p.287-317
- Easton R.M. (2000b): Metamorphism of the Canadian shield, Ontario, Canada. II. Proterozoic metamorphic history, *The Canadian Mineralogist*, **38**, p.319-344
- Easton R.M. and Ketchum, J.W.F. (2002): Evidence for a major Mesoproterozoic magmatic province within the western Grenville Province near North Bay, Ontario. Abstracts with Programs, Geological Association of America **34**, p. 242
- Eisbacher G.H. (1970): Contemporaneous faulting and clastic intrusions in the Quirke Lake Group, Elliot Lake Ontario. *Canadian Journal of Earth Sciences*, **7**, p.215-225
- Ernst R.E. (2007): Large igneous provinces in Canada through time and their metallogenic potential. In: Mineral deposits of Canada: A Synthesis of Major Deposit Types, district Metallogeny, the Evolution of Geological Provinces and Exploration Methods, Goodfellow, W.D. (ed), Geological Association of Canada Special Publication No. 5, p. 929-937
- Etoh J., Izawa, E., Watanabe, K., Taguchi, S. and Sekine, R. (2002): Bladed quartz and its relationship to gold mineralization in the Hishikari low-sulfidation epithermal gold deposit, Japan. *Economic Geology* **97**, p. 1841-1851
- Fairbairn H.W., Hurley P.M., Card K.D. and Knight C.J. (1969): Correlation of radiometric ages of Nipissing diabase and Huronian metasediments with Proterozoic orogenic events in Ontario. *Canadian Journal of Earth Sciences* **6**, p. 498-497
- Fairbairn H.W., Hurley P.M. and Pinson W.H. (1967): Rb-Sr isochron ages of metasediments in the Canadian Shield. 15th Ann. Report. M.I.T. -1381-15, U.S. Atomic Energy Comm., p. 61-63
- Farquhar J. and Wing B. (2003): Multiple sulfur isotopes and the evolution of the atmosphere. *Earth and Planetary Science Letters* **213**, p. 1-13
- Faure G. (1977): Principles of Isotope Geology. John Wiley & Sons, Toronto, 464 p
- Faure G. and Hurley, (1963): the isotopic composition of strontium in oceanic and continental basalt: application to the origin of igneous rocks. *Journal of Petrology* **4**, p.31-50
- Faure G. and Mensing, T.M. (2005): Isotopes: principles and applications, 3rd Edition. J. Wiley & Sons, New Jersey, 897 p

- Faure G. and Powell J.L. (1972): Strontium Isotope Geology. Springer-Verlag, 188p
- Fedo C.M., Young G.M., Nesbitt H.W. and Hanchar J.M. (1997): Potassic and sodic metasomatism in the Southern Province of the Canadian Shield: evidence from the Paleoproterozoic Serpent Formation, Huronian Supergroup, Canada. *Precambrian Research* **84**, 17-36
- Franklin J.M., Roscoe S.M., Loveridge W.D. & Sangster D.F. (1983): Lead isotope studies in Superior and Southern provinces. Geological Survey of Canada, Bulletin **351**, 60 p
- Frape S.K. and Fritz P. (1987): Geochemical trends for groundwaters from the Canadian Shield. In: *Saline Water and Gases in Crystalline Rocks* (P. Fritz and S.K.Frape eds). Geological Association of Canada, Special Paper **33**, p. 19-38
- Frape S.K., Fritz P. and McNutt R.H. (1984): Water-rock interaction and chemistry of groundwaters from the Canadian Shield. *Geochimica et Cosmochimica Acta* **48**, p.1617-1627
- Frey M. (1987): Very low-grade metamorphism of clastic sedimentary rocks. In *Low Temperature Metamorphism* (M. Frey, ed.). Blackie & Son Limited, London, U.K., p.9-58
- Fritz P., Richard L., and McNutt R.H. (1992): Geochemical modeling of Sr isotopic signatures in the interaction between granitic rocks and natural solutions. In: Proc. 7th Int. Symp. Water-Rock Interaction (Y.K. Kharaka and A.S. Maest eds), A.A. Balkema, Rotterdam, p. 927-930
- Fujita Y., Redden G.D., Ingram J.C., Cortez M.M., Ferris F.G. and Smith R.W. (2004): Strontium incorporation into calcite generated by bacterial ureolysis. *Geochimica et Cosmochimica Acta* **68**, p. 3261-3270
- Galarza M.A., Macambira M.J.B. and Villas R.N. (2008): dating and isotopic characteristics (Pb and S) of the Fe oxide-Cu-Au-U-REE Igarape Bahia ore deposit, Carajas mineral province, Para state, Brazil. *Journal of South African Earth Sciences*, **25**, p.377-397
- Ghandi S.S. (1994): Geological setting and genetic aspects of mineral occurrences in the southern Great Bear magmatic zones, Northwest territories. In: Studies of Rare-Metal Deposits in the Northwest Territories (W.D. Sinclair and D.G. Richardson eds.), Geological survey of Canada, Bulletin **475**, p. 63-96
- Gat J.R. (1981): Groundwater. In: Stable Isotope Hydrology – Deuterium and Oxygen-18 in the Water Cycle (J.R. Gat and R. Gonfiantini eds), IAEA, Vienna, Technical report Series 210, p. 223-240

- Gates B.I. (1991): Sudbury mineral occurrence study. *Ontario Geological Survey, Open File Report 5771*
- Gates T.M. and Hurley P.M. (1973): Evaluation of Rb-Sr dating methods applied to the Matachewan, Abitibi, Mackenzie and Sudbury dike swarms in Canada. *Canadian Journal of Earth Sciences*, **10**, p. 900-919
- Gieré R. (1996): Formation of rare earth minerals in hydrothermal systems. *In: Rare Earth Minerals: Chemistry, Origin and Ore Deposits* (A.P. Jones F. Wall and C.T. Williams eds), Chapman & Hall
- Goad R.E., Mumin A.H., Duke N.A., Neale K.L., Mulligan D.L. and Camier W.J. (2000): The NICO and Sue-Dianne Proterozoic, iron oxide-hosted, polymetallic deposits, Northwest Territories: application of the Olympic Dam model in exploration. *Exploration and Mining Geology*, **9**, p. 123-140
- Goodz M.D., Watkinson D.H., Smejkal V. and Pertold Z. (1986): Sulphur-isotope geochemistry of silver – sulpharsenide vein mineralization, Cobalt, Ontario. *Canadian Journal of Earth Sciences*, **23**, p. 1551-1567
- Gordon J. B., Lovell H. L., de Grijs J. and Davie R. F (1979): Gold deposits of Ontario, Part Two: Part of District of Cochrane, Districts of Muskoka, Nipissing, Parry Sound, Sudbury, Timiskaming, and Counties of Southern Ontario. *Ontario Geological Survey, Mineral Deposits Circular*, **18**, 266p
- Goryainov P.M. and Pesterev F.V. (1969): Concentric spherical cleavage in basic rock dikes of the Oloenegorsk deposit. (Osn. Magmat. Sev.-Vost. Chastich Balt. Shchita, pp. 105-109), *Chemical Abstracts*, **73**, p.6021m
- Hall R.D. (2003): Scadding gold property at Sudbury, Ontario. Unpublished technical report prepared for Currie Rose Resources Inc. 94 p
- Harmon R.S. and Hoefs J. (1995): Oxygen isotope heterogeneity of the mantle deduced from global ^{18}O systematics of basalts from different geotectonic settings. *Contributions to Mineralogy and Petrology*, **120**, p. 95-114
- Hart S.R. and Brooks C. (1974): Clinopyroxene-matrix partitioning of K, Rb, Cs Sr and Ba. *Geochimica et Cosmochimica Acta* **38**, p. 1799
- Hattori K., Campbell F.A. & Krouse H.R. (1985): Sulphur isotope abundances in sedimentary rocks, relevance to the evolution of the Precambrian Atmosphere. *Geochemistry International*, **22**, p. 97-115
- Hayes J.M., Kaplan I.R. and Wedeking K.W. (1983): Precambrian organic geochemistry, preservation of the record. *In: Origin and Evolution of the Earth's Earliest*

- Biosphere* (J.W. Schopf *ed*). P.93-134. Princeton University Press, Princeton, New Jersey
- Hecht L., Freiburger R., Gilg A.H., Grundmann G. and Kostitsy Y.A. (1999): Rare earth element and isotope (C, O, Sr) characteristics of hydrothermal carbonates: genetic implications for dolomite hosted talc mineralization at Goepferrguen (Fichtelgebirge, Germany). *Chemical Geology*, **155**, p. 115-130
- Hedenquist J.W., Arribas A.J., and Gonzales-Urien E. (2000): Exploration for epithermal gold deposits. *Reviews in Economic Geology*, **13**, p. 245-277
- Hester B.W. (1967): Geology of the silver deposits near Miller Lake, Gowganda, *Canadian Institute of Mining, Metallurgy and Petroleum, Bulletin* **60**, p. 1277-1286
- Hill P.A. (1965): Curvilinear (radial, bow-tie, festoon) and concentric jointing in Jurassic dolerite, Mersey Bluff, Tasmania. *Journal of Geology*, **73**, p. 255-270
- Hilburn I.A., Kirschvink J.L., Tajika E., Tada R., Hamano Y. and Yamamoto S. (2007): A negative fold test on the Lorrain Formation of the Huronian Supergroup: Uncertainty on the paleolatitude of the Paleoproterozoic Gowganda glaciations and implications for the great oxygenation event. *Earth and Planetary Science Letters*, **232**, p. 315-332
- Ho S.E., McNaughton N.J. and Gorves D.I. (1994): Criteria for determining initial lead isotopic compositions of pyrite in Archean lode-gold deposits: a case study at Victory, Kambalda, Western Australia. *Chemical Geology*, **111**, p. 57-84
- Hoeve J. and Quirt D.H. (1984): Mineralization and host rock alteration in relation to clay mineral diagenesis and evolution of the Middle Proterozoic, Athabasca Basin, northern Saskatchewan, Canada. *Saskatchewan Research Council, SRC Technical Report* **187**, 187p
- Holland H.D. and Malinin S.D. (1979): The solubility and occurrence of ore minerals. *In: Geochemistry of Hydrothermal Ore Deposits*, 2nd ed (H.L. Barnes *ed*), John Wiley and Sons, New York. p. 461-508
- Hu Q., Evenson N.M., Norman P.E. and York D. (1998): A world in a grain of sand: regional metamorphic history from ⁴⁰Ar/³⁹Ar laser probe analyses of Proterozoic sediments from the Canadian Shield. *Precambrian Research*, **91**, p. 287-294
- Jacobson R.L. and Usdowski H.E. (1976): Partitioning of strontium between calcite, dolomite and liquids: an experimental study under higher temperature diagenetic conditions and a model for the prediction of mineral pairs for geothermometry. *Contributions to Mineralogy and Petrology*, **59**, p. 171-185

- Jambor J.L. (1971): Origin of the silver veins. *In: The Silver-Arsenide deposits of the Cobalt-Gowganda region, Ontario (L.G. Berry ed). The Canadian Mineralogist*, 11, p.402-41
- Jambor J.L. (1971a): General Geology, *In: The Silver-Arsenide deposits of the Cobalt-Gowganda region, Ontario (L.G. Berry ed). The Canadian Mineralogist*, 11, p.12-33
- Jambor J.L. (1971b): The Nipissing Diabase, *In: The Silver-Arsenide deposits of the Cobalt-Gowganda region, Ontario (L.G. Berry ed) The Canadian Mineralogist*, 11, p.34-75
- Jambor J.L. (1971c): Spotted chloritic alteration. *In: The Silver-Arsenide deposits of the Cobalt-Gowganda region, Ontario (L.G. Berry ed). The Canadian Mineralogist*, 11, p.305-319
- Jambor J.L. (1971d): Gangue mineralogy. *In: The Silver-Arsenide deposits of the Cobalt-Gowganda region, Ontario (L.G. Berry ed). The Canadian Mineralogist*, 11, p.232-262
- Jambor J.L. (1971e): General characteristics of the deposits. *In: The Silver-Arsenide deposits of the Cobalt-Gowganda region, Ontario (L.G. Berry ed). The Canadian Mineralogist*, 11, p.76-107
- Jefferson C.W., Thomas, D.J., Gandhi S.S., Ramaekers P., Delaney G., Brisbin D., Cutts C., Quirt D., Portella P. and Olson R.A. (2007): Unconformity-associated uranium deposits of the Athabasca Basin, Saskatchewan and Alberta. *In: Mineral Deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces and Exploratin Methods (W.D. Goodfellow ed). Geological Association of Canada, Mineral Deposits Division, Special Publication*, 5, p. 273-306
- Jiang W.T., Peacor D.R. and Busek P.R. (1994): Chlorite geothermometry? – contamination and apparent octahedral vacancies. *Clays and Clay Minerals*, 42, p. 593-605
- Jimenez-Lopez C., Caballero E., Huertas F.J. and Romanek C.S. (2001): Chemical, mineralogical and isotope behavior and phase transformation during the precipitation of calcium carbonate minerals from intermediate ionic solution at 25°C. *Geochimica et Cosmochimica Acta* 65, p. 3219-3231
- Jimenez-Lopez C., Romanek C.S. and Caballero E. (2006): carbon isotope fractionation in synthetic magnesian calcite. *Geochimica et Cosmochimica Acta* 70, p. 1163-1171

- Johns G.W. (1986): Geology of the Hill Lake Area, District of Timiskaming; *Ontario Geological Survey Report* **250**, 100p
- Kansewich E.R. and Farquhar R.M. (1965): Lead isotope ratios from the Cobalt-Noranda area, Canada. *Canadian Journal of Earth Sciences*, **2**, p.361-384
- Kanasewich E.R. (1968): The interpretation of lead isotopes and their geological significance. *In: Radiometric Dating for Geologists* (E.I. Hamilton and R.M. Farquhar eds.). Wiley-Interscience, New York, p. 147-223
- Kaplan I.R. and Hulston J.R. (1966): The isotopic abundance and content of sulfur in meteorites. *Geochimica et Cosmochimica Acta* **30**, p. 479-496
- Kerrich R., Strong D.F., Andrews A.J. and Owsiacki L. (1986): The silver deposits at cobalt and Gowganda, Ontario. III: Hydrothermal regimes and source reservoirs – evidence from H, O, C and Sr isotopes and fluid inclusions. *Canadian Journal of Earth Sciences*, **23**, p.1519-1550.
- Kettles K., Pettigrew N. and Potter E.G. (2005): Report on the Temex Resources Corporation 2004-2005 Exploration Programs at the Merico-Ethel Property, Elk Lake, Ontario. Ontario Assessment Report, Larder Lake Mining Division, Ontario, 49p
- Kindle L.F. (1933): Moose Mountain – Wanapitei area, *Ontario Department of Mines, Annual Report*, **41**, p.29-49
- Kinnaird D.L., Kruger F.J. and Cawthorne R.G. (2004): Rb-Sr and Nd-Sm isotopes in fluorite related to the granites of the Bushveld Complex. *South African Journal of Geology*, **107**, p. 413-430
- Kissin S.A. (1988): Five-element (Ni-Co-As-Ag-Bi) veins. *In: Ore Deposit Models Volume II* (P.A. Sheaham and M.E. Cherry eds), *Geological Association of Canada, Reprint Series* **6**, p. 87-98
- Kotzer T. and Kyser T.K. (1995): Fluid history of the Athabasca Basin and its relation to diagenesis, uranium mineralization and paleohydrology. *Chemical Geology*, **120**, p. 45-89
- Krogh T.E., Corfu F., Davis D.W., Dunning G.R., Heaman L.M., Kamo S.L., Machado N., Greenbough J.D. and Nakamura E. (1987): Precise U-Pb isotopic ages of diabase dykes and mafic to ultramafic rocks using trace amounts of baddeleyite and zircon. *In: Mafic Dyke Swarms* (H.C. Halls and W.F. Fahrig eds). Geological Association of Canada Special Paper, **34**, p. 147-152
- Krogh T.E., Davis D.W., Corfu F. (1984): Precise U-Pb zircon and baddeleyite ages for the Sudbury area. *In: The Geology and Ore Deposits of the Sudbury Structure*

- (Pye, E.G., Naldrett, A.J. and Giblin, P.E. eds), *Ontario Geological Survey Special*, 1, p. 431-446
- Krogh T.E., Kamo S.L. and Bohor B.F. (1996): Shock metamorphosed zircons with correlated U-Pb discordance and melt rocks with concordant protolith ages indicate an impact origin for the Sudbury structure. *Earth Processes: Reading the isotopic code. Geophysical Monograph* 95, Am. Geophys. Union, p. 343-353
- Lawton K.D. (1952): Preliminary report of the geology of Delhi Township, district of Sudbury. *Ontario Geological Survey Preliminary Report 1952-1*, 6 p
- Lawton K.D. (1955): Geology of Delhi Township. *Ontario Geological Survey Annual Report Volume* 63, p.15-19
- Leblanc M. (1986): Co-Ni arsenide deposits, with accessory gold, in ultramafic rocks from Morocco. *Canadian Journal of Earth Sciences*, 23, p. 1592-1602
- Leblanc M. (1991): Platinum-group elements and gold in ophiolite complexes: distribution and fractionation from mantle to ocean floor. *In: Ophiolite Genesis and Evolution of the Oceanic Lithosphere*, Kluwer Academic Publishers, Dordrecht, p. 231-260
- Leblanc M. and Billaud P. (1982): Cobalt arsenide orebodies related to an Upper Proterozoic ophiolite: Bou Azzer (Morocco). *Economic Geology*, 77, p. 162-175
- L'Heureux E., Ugalde H., Milkereit B., Boyce J., Morris W., Eyles N. and Artemieva N. (2005): Using vertical dykes as a new approach to constraining the size of buried craters: an example from Lake Wanapitei, Canada. *In: Large meteorite Impacts III* (T. Kenkmann, F. Horz and A. Deutsch eds.) Geological Society of America Special Paper v.384, p. 43-50
- Li W., Franklyn M.T., McNutt R.H., Schwarcz H.P., Gascoyne M., Kamenini D.C. and Frape S.K. (1989): A Sr isotopic study of the Eye-Dashwa pluton, Ontario and the Lac du Bonnet pluton, Manitoba: plagioclase/water reaction. *In: Proc. 6th Int. Symp. Water-Rock Interaction* (D.L.Miles ed), A.A. Belkema, Rotterdam, p. 441-444
- Lightfoot P.C., Conrod D. Naldrett A.J. and Evensen N.M. (1986): Petrologic, chemical, isotopic and economic potential studies of the Nipissing diabase, *Ontario Geological Survey Miscellaneous Paper* 130, p. 87-106
- Lightfoot P.C., De Souza H. and Doherty W. (1993): Differentiation and source of the Nipissing Diabase intrusions, Ontario, Canada. *Canadian Journal of Earth Sciences* 30, p. 1123– 1140

- Long D.G.F., Young G.M., Rainbird R. and Fedo C. (1999): Actualistic and nonactualistic Precambrian sedimentary styles: examples from the Proterozoic north of Lake Huron. Geological Association of Canada – Mineralogical Association of Canada Joint Meeting, Field Trip B5 Guidebook, 50 p
- Lorens R.B. (1981): Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochimica et Cosmochimica Acta* **45**, p. 553-561
- MacDonald A.J. (1986) (editor): *Gold '86: An International Symposium on the Geology of Gold Deposits*. Proceedings Volume, Toronto, 1986, 517 p
- MacKean B.E. (1968): Geology of the Elk Lake area, District of Temiskaming, *Ontario Geological Survey, Geological Report* **62**
- MacQueen J.K. (1985): Sulphide Mineralogy and Chemistry in Archean Rocks Near Silver Veins, Cobalt, Ontario. Unpublished B.S.c. Honours Thesis, Carleton University, 64 p
- Marshall D.D. (1990): Pressure, temperature, composition and state of the fluid during silver arsenide vein formation, Cobalt Ontario. Unpublished M.Sc. thesis, Carleton University, Ottawa, ON. 128 p
- Marshall D.D., Diamond, L.W. and Skippen G.B. (1993): Silver transport and deposition at Cobalt, Ontario, Canada: fluid inclusion evidence. *Economic Geology*, **88**, p. 837-854
- Marshall D. D. and Watkinson D.H. (2000): The Cobalt Mining District: silver sources, transport and deposition. *Exploration and Mining Geology*, **9**, p.81-90
- Martins, J.M., Horst R.E. and Giblin P.E. (1979): McLean-Watt Gold Property. *In: Annual Report of the Regional and Resident Geologists (C.R. Kustra ed), Ontario Geological Survey Miscellaneous Paper*, **91**, p.111-116
- Mazimhaka P. and Hendry H. (1989): Uranium deposits in the Beaverlodge area, northern Saskatchewan: their relationship to the Martin group (Proterozoic) and underlying basement. *In: Uranium Resources and Geology of North America*. IAEA Technical Document 500, Vienna, p.297-315
- McLaughlin R.M. (1997): Boron and strontium isotope study of fluids situated in fractured and unfractured rock of the Lac du Bonnet Batholith, eastern Manitoba. Unpublished PhD Thesis, McMaster University, 142 p
- McLennan S.M., Simonetti A. and Goldstein S.L. (2000): Nd and Pb isotope evidence for provenance and post-depositional alteration of the Paleoproterozoic Huronian Supergroup, Canada. *Precambrian Research*, **102**, p.263-278

- McNutt R.H. (2000): Strontium isotopes. *In: Environmental tracers in subsurface hydrology*. Kluwer Academic Press, p. 233-260
- McNutt R.H., Frappe S.K., Fritz P., Jones M.G. and MacDonald I.M. (1990): The $^{87}\text{Sr}/^{86}\text{Sr}$ values of Canadian Shield brines and fracture minerals with application to groundwater mixing, fracture history and geochronology. *Geochimica et Cosmochimica Acta* **54**, p. 205-215
- McNutt R.H., Gascoyne M. and Kamenini D.C. (1987): $^{87}\text{Sr}/^{86}\text{Sr}$ values in groundwater of the East Bull Lake pluton, Superior Province, Ontario, Canada. *Applied Geochemistry* **2**, p. 93-101
- Medaris L.G. R., Fournelle J.H., Boszhardt R.F., and Broihahn J.H., (1999): Chemical and mineralogical comparison of Baraboo, Barron and Sioux argillite, metapelite and pipestone. *Institute of Lake Superior Geology, Abstracts* **45**, 35-36
- Meyn H.D. (1970): Geology of Hutton and Parkin Townships, District of Sudbury. *Ontario Geological Survey, Geological Report*, **80**
- Meyn H.D. (1971): Geology of Roberts, Creelman, and Fraleck Townships, District of Sudbury. *Ontario Geological Survey, Geological Report*, **91**
- Miller L.G., Kalin R.M., McCauley S.E., Hamilton J.T.G., Harper D.B., Millet D.B., Oremland R.S. and Goldstein A.H. (2001): Large carbon isotope fractionation associated with oxidation of methyl halides by methylotrophic bacteria. *PNAS* **98**, p. 5833-5837
- Misra K.C. (2000): Understanding Mineral Deposits. Kluwer Academic Press, 845p
- Moorhouse W.W. (1944): Geology of the Bryce-Robillar area. *Ontario Department of Mines, Annual Report* **50**, part 4, 50 p
- Morey G.B. (1999): High-grade iron deposits of the Mesabi range, Minnesota – product of a continental-scale Proterozoic ground-water flow system. *Economic Geology* **94**, p.133-142
- Morris W.A. (1981): A positive fold test in Nipissing Diabase. *Canadian Journal of Earth Sciences* **18**, p. 591-599
- Mortensen J.K. (1993): U-Pb geochronology of the eastern Abitibi subprovince. 2. Noranda-Kirkland Lake area. *Canadian Journal of Earth Sciences*, **20**, p.29-41
- Ogden M. (1957): Report of Dolmac Mines Limited property, Rathbun Township, District of Sudbury. Ontario Geological Survey, Assessment File Research Office, Unpublished Assessment file #64-6035

- Ohmoto H. (1972): Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Economic Geology* **67**, p. 551-578
- Ohmoto H. (1986): Stable isotope geochemistry of ore deposits. *In: Stable Isotopes in High Temperature Processes* (J.W. Valley, H.P. Taylor, J.R.O. O'Neil eds). Mineralogical Society of America, *Reviews in Mineralogy* **16**, p. 491-559
- Ohmoto H. and Goldhaber M.B. (1997): Sulfur and carbon isotopes. *In: Geochemistry of hydrothermal Ore Deposits*. Barnes HL (ed) J. Wiley and Sons, p 517-611
- Ohmoto H. and Rye R.O. (1979): Isotopes of sulfur and carbon. *In: Geochemistry of Hydrothermal Ore Deposits*, Barnes H.L. (ed), p. 509-567
- Olivo G.R., Isnard H., Williams-Jones A.E. and Gariepy C. (2007): Pb isotope compositions of pyrite from the C-quartz tourmaline vein of the Siscoe gold deposits, Val d'Or, Quebec: constraints on the origin and age of the gold mineralization. *Economic Geology* **102**, p. 137-146
- O'Neil J.R. (1986): Theoretical and experimental aspects of isotopic fractionation. *Reviews in Mineralogy* **16**, p. 1-40
- O'Neil J.R., Clayton R.N. and Mayeda T.K. (1969): Oxygen isotope fractionation in divalent metal carbonates. *Journal of Chemical Physics* **51**, p. 5547-5558
- O'Nions R.K. and Pankhurst R.J. (1978): Early Archean rocks and geochemical evolution of the Earth's crust. *In: Trace elements in igneous petrology, developments in petrology*, v.5 (C.J. Allegre and S.R.Hart eds), Elsevier Scientific Publishing, p. 211-236
- Oswiacki L. (1982): Geology of Lundy Township (Northern half), district of Timiskaming. Ontario Geological Survey, Miscellaneous Paper **106**, p.201-206
- Panayiotou A. (1986): Sulphide and arsenide mineralization associated with the basic and ultrabasic plutonic rocks of the Troodos ophiolite, Cyprus. *In: Metallogeny of Basic and Ultrabasic Rocks*, Theophrastus Publications S.A., Athens, p. 417-447
- Papineau D., Mojzsis S.J. & Schmitt A.K. (2007): Multiple sulfur isotopes from Paleoproterozoic Huronian interglacial sediments and the rise of atmospheric oxygen. *Earth and Planetary Science Letters* **255**, p. 188-212
- Patterson G.C. (1979): Metallogenic relationships of base-metal occurrences in the Cobalt area. *In: Summary of Field Work, 1979, Ontario Geological Survey Miscellaneous Paper* **90**, p.222-229

- Pauwels H., Frouillac C. and Criaud A. (1992): Water-rock interactions during experiments within the geothermal Hot Dry Rock borehole GPK1, Soultz-sous-Forêts, France. *Applied Geochemistry* **7**, p. 243-255
- Petruk W. (1971): General characteristics of the deposits. *In: The Silver-Arsenide Deposits of the Cobalt-Gowganda region, Ontario* (L.G. Berry *ed*). *The Canadian Mineralogist*, **11**, p. 76-107
- Petruk W. (1971b): Mineralogical characteristics of the deposits and textures of the ore minerals. *In: The Silver-Arsenide Deposits of the Cobalt-Gowganda region, Ontario* (L.G. Berry *ed*). *The Canadian Mineralogist*, **11**, p. 108-139
- Pinkerton G. (1996): 1995 OPAP Report, File No. OP-95-126, Merico-Ethel Project, Tudhope Township, District of Timiskaming, Ontario; Assessment Work Report, Ontario Geological Survey, Regional Assessment Files
- Pingitore N.E. and Eastman M.P. (1986): The coprecipitation of Sr^{2+} with calcite at 25°C and 1 atm. *Geochimica et Cosmochimica Acta* **50**, p. 2195-2203.
- Potter E.G. (2007): Petrography of additional high-grade gold samples discovered from Gillies Township, Ontario. Internal technical report prepared for Temex Resources Corporation, April 2007, 8 p
- Powell W.G., Carmichael D.M. and Hodgson C.J. (1993): Thermobarometry in a subgreenschist to greenschist transition in metabasites of the Abitibi greenstone belt, Superior Province, *Canadian Journal of Metamorphic Geology*, **11**, p.165-178
- Prasad N. (1994): The concentration trends of alkalis and alkaline earths and timing of potash-enrichments in 2.45-2.2 Ga sub-Huronian paleosols. *International Sedimentological Congress*, **14**, p.S8.13, Recife, Brazil
- Prasad N. and Roscoe S.M. (1996): Evidence of anoxic to oxic atmospheric change during 2.45-2.22 Ga from lower and upper sub-Huronian paleosols, Canada. *Catena* **27**, p.105-121
- Purdy J.W. and York D. (1968): Rb-Sr whole rock and K-Ar minerals ages of rocks from the Superior Province near Kirkland Lake, northeastern Ontario. *Canadian Journal of Earth Sciences* **5**, p. 699-705
- Qiu Y. and McNaughton N.J. (1999): Source of Pb in orogenic lode-gold mineralization: Pb isotope constraints from deep crustal rocks from the southwestern Archean Yilgarn craton, Australia. *Mineralium Deposita* **34**, p. 366-381

- Rainbird, R.H., Nesbitt, H.W. and Donaldson, J.A. (1990): Formation and diagenesis of a sub-Huronian saprolith: comparison with a modern weathering profile. *Journal of Geology* **98**, p. 801-822
- Rayleigh L. (1902): On the distillation of binary mixtures. *Philosophy Magazine* **4**, p. 521-537
- Reardon N.C. (1990): Altered and mineralized rocks at Echo Bay, N.W.T. and their relationship to the Mystery island intrusive suite. *In: Current Research, Part C, Canadian Shield, Geological Survey of Canada, Paper 90-1C*, p.143-150
- Reid D.L., Cooper A.F., Rex D.C. and Harmer R.E. (1990): Timing of post-Karoo alkaline volcanism in Southern Namibia. *Geological Magazine*, **127**, p.427-433
- Richards H.G., Savage D. and Andrews J.N. (1992): Granite-water reactions in an experimental Hot Dry Rock geothermal reservoir, Rosemanowes test site, Cornwall, U.K. *Applied Geochemistry* **7**, p. 193-222
- Riller U., Schwerdtner W.M., Hall H.C. and Card K.D. (1999): Transpressive tectonism in the eastern Penokean orogen, Canada. Consequences for Proterozoic crustal kinematics and continental fragmentation. *Precambrian Research* **93**, p. 51–70.
- Robinson B.W. (1975): Carbon and oxygen isotopic equilibria in hydrothermal calcites. *Geochemistry Journal*, **9**, p.43-46
- Roedder, E. (1984): Fluid Inclusions. *Reviews in Mineralogy*, Volume 12, Mineralogical Society of America, 644 p
- Romanek C.S., Grossan E.L. and More J.W. (1992): Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. *Geochimica et Cosmochimica Acta* **56**, p. 419-430
- Roscoe S.M., Theriault R.J. and Prasad N. (1992): Circa 1.7Ga Rb-Sr re-setting of two Huronian paleosols, Elliot Lake, Ontario and Ville Marie, Quebec. *Geological Survey of Canada Paper* **92-2**, p.199-124
- Rozanski K., Araguas-Araguas L. and Conginadini R. (1993): Isotopic patterns in modern global precipitation. *In: Climate Change in Continental Isotopic Records*, American Geophysical Union, *Geophysical Monographs* **78**, p. 1-36
- Rumble D. (2005): A mineralogical and geochemical record of atmospheric photochemistry. *American Mineralogist* **90**, p. 918-930
- Russell R.D. and Farquhar R.M. (1960): *Lead isotopes in Geology*. Wiley-Interscience, New York

- Ruzicka V. (1996): Unconformity-associated uranium. *In: Geology of Canadian Mineral Deposit Types* (O.R. Eckstrand, W.D. Sinclair, R.I. Thorpe eds.), *Geological Survey of Canada, Special Publication No. 8*, p.197-210
- Sage R.P. (1996): Kimberlites of the Lake Temiskaming Structural Zone, *Ontario Geological Survey, Miscellaneous Release Data 20*
- Sakai H. (1968): Isotopic properties of sulfur compounds in hydrothermal processes. *Geochemistry Journal* **2**, p.29-49
- Sakai H., Des Marais D.J., Ueda A. and Moore J.G. (1984): Concentrations and isotope ratios of carbon, nitrogen, and sulfur in ocean-floor basalts. *Geochimica et Cosmochimica Acta* **48**, p. 2433-2442
- Seal R.S. (2006): Sulfur Isotope Geochemistry of Sulfide Minerals. *In: Sulfide Mineralogy and Geochemistry* D.J.Vaughan (ed), Mineralogical Society of America, *Reviews in Mineralogy and Geochemistry* **61**, p. 633-677
- Schandl E.S., Gorton M.P. and Davis D.W. (1994): Albitization at $1700 \pm 2\text{Ma}$ in the Sudbury-Wanapitei Lake are, Ontario: implications for deep-seated alkali magmatism in the Southern province. *Canadian Journal of Earth Sciences* **31**, p.597-607.
- Schoel M. (1984): Stable isotopes in petroleum research. *In: Advances in Petroleum Geochemistry*, Vol.1 (J. Brooks and D. Welte eds). Academic Press, London, p. 215-243
- Schwinn G., Wagner T., Baartartsogt B. and Markl G. (2006): Quantification of mixing processes in ore-forming hydrothermal systems of stable isotope and fluid inclusion studies. *Geochimica et Cosmochimica Acta*, **70**, p. 965-982
- Scott S.D. (1983): Chemical behavior of sphalerite and arsenopyrite in hydrothermal and metamorphic environments. *Mineralogical Magazine*, **47**, p. 427-435.
- Scott S.D. and O'Connor T.P. (1971): Fluid inclusions in vein quartz, Silverfields Mine. *In: The Silver-Arsenide deposits of the Cobalt-Gowganda region, Ontario* (L.G. Berry ed). *The Canadian Mineralogist*, **11**, p.263-271
- Shklanka R. (1969): Copper, nickel, lead and zinc deposits of Ontario, *Ontario Geological Survey, Mineral Resources Circular No. 12*
- Shvarov Y.V., (1978): Minimization of the thermodynamic potential of an open system. *Geochemistry International* **15**, p. 200-203

- Shvarov Y.V. and Bastrakov E. (1999): HCh: a software package for geochemical equilibrium modeling. User's guide. Australian geological Survey Organization, Department of Industry, Science and Resources
- Sheppard S.M.F. (1986): Characterization and isotopic variations in natural waters. *In: Stable Isotopes in High Temperature Geological Processes*, J.W. Valley, H.P. Taylor Jr., & J.R. O'Neil (eds), Mineralogical Society of America, *Reviews in Mineralogy* 16, p. 65-84
- Sims P.K., Card K.D. and Lumbers S.B. (1981): Evolution of early Proterozoic basins of the Great Lakes region, *In: Proterozoic Basins of Canada* (F.H.A. Campbell ed), Geological Survey of Canada, Paper 81-10, p. 379-397.
- Sims P.K., Card K.D., Morey G.B. and Peterman Z.E. (1980): The Great Lakes tectonic zone – a major a crustal structure in central North America. *Geological Society of America Bulletin*, Part I, 91, p. 690-698
- Slaght, A (1896): Fifth report of the Bureau of Mines, Ontario Bureau of Mines, 1895, p. 262-263
- Smith M.D. and Heaman L.M. (1999): Constraints on the timing of felsic magmatism associated with the Matachewan igneous events: preliminary results for the Creighton granite, Ontario. Geological Association of Canada – Mineralogical Association of Canada Joint Meeting, Program with Abstracts, 24, p.119.
- Smyk M.C. (1987): Geology of Archean interflow sedimentary rocks and their relationship to Ag-Bi- Co-Ni-As veins, Cobalt Area, Ontario. M.Sc. Thesis, Carleton University, 87 p
- Smyk M.C., Born P. and Owsjacki L. (1997): Banting Township and the western part of Best township. *Ontario Geological Survey Report* 285, 53 p
- Stacey J.S. and Kramers J.D. (1975): Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planetary Science Letters* 26, p. 207-221
- Stevenson J., Mancuso J, Frizado J., Truskoski P. and Kneller W. (1990): Solid pyrobitumen in veins, Panel Mine, Elliot lake District, Ontario. *The Canadian Mineralogist* 28, p. 161-169
- Symons D.T.A. (1970): Paleomagnetism of the Nipissing Diabase, Cobalt Area, Ontario. *Canadian Journal of Earth Sciences* 7, p.86-90
- Taylor H.P. Jr. (1977): Water/rock interactions and the origin of H₂O in granitic batholiths. *Journal of the Geological Society of London* 133, p. 509-558

- Taylor H.P. Jr. (1997): Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits. *In: Geochemistry of Hydrothermal Ore Deposits* 3rd edition (H.L. Barnes *ed*), John Wiley and Sons, New York
- Taylor L.A. (1970): Smythite, $\text{Fe}_{3+x}\text{S}_4$ and associated minerals from the Silverfields Mine, Cobalt Ontario. *American Mineralogist*, **55**, p. 1650-1658
- Taylor R.P. (2004): Mineralogy and Paragenesis of Rock Samples from the Merico-Ethel Property, Cobalt Embayment, Northern Ontario: Some Preliminary Observation of Both Local and Regional Significance. Internal technical report prepared for Temex Resources Corp., November 2004, 19 p
- Taylor R.P. (2004b): Mineralogy and paragenesis of a high-grade gold sample (#75690) from Gillies Township. Internal technical report prepared for Temex Resources Corporation, January 2004, 13 p
- Taylor R.P. and Campbell I. (2004a): A New Exploration Model for “Proterozoic Gold” in the Temagami (Latchford) Area of Northern Ontario. Internal technical report prepared for Temex Resources Corp., January 2004, 6 p
- Taylor R.P. and Campbell I. (2004b): A Unifying Exploration Model for the Genesis of Precious- and Base-Metal Mineralization in the Cobalt Embayment of Northern Ontario. Internal technical report prepared for Temex Resources Corp., November 2004, 17 p
- Temex Resources Corporation (2004): Temex acquires high grade gold properties, News release dated March 30, 2004, [www.temexcorp.com/s/NewsReleases.asp]
- Teng H.H., Dove P.M. and De Yoreo J.J. (2000): Kinetics of calcite growth: surface processes and relationships to macroscopic rate laws. *Geochimica et Cosmochimica Acta* **64**, p. 2255-2266
- Thomson J.E. (1961): MacLennan and Scadding Townships; *Ontario Department of Mines, Geological Report* **2**, 34p
- Thomson R. (1966): Geology of the Henwood township, district of Timiskaming. Ontario Department of Mines Miscellaneous Paper **5**
- Thorpe R.I. (1974): Lead isotope evidence on the genesis of the silver-arsenide deposits of the Cobalt and Great Bear Lake areas, Canada. *Economic Geology* **69**, p. 777-791
- Thorpe R.I. (1999): The Pb isotope linear array for volcanic massive sulfide deposits of the Abitibi and Wawa subprovinces, Canadian Shield. *Economic Geology Monograph* **10**

- Thorpe R.I., Goodz M.D., Jonasson I.R. & Blenkinsop J. (1986): Lead-isotope study of mineralization in the Cobalt district, Ontario. *Canadian Journal of Earth Sciences* **23**, p. 1568- 1575
- Todt W., Cliff R.A., Hanswer A. and Hofmann A.W. (1984): 202Pb – 205Pb spike for Pb isotopic analysis, *Terra Cognita* **4**, p. 209
- Truesdell A.H. (1974): Oxygen isotope activities and concentrations in aqueous salt solutions at elevated temperatures: consequences for isotope geochemistry. *Earth and Planetary Science Letters*, **23**, p. 387-396
- Tyrell J.B. (1907): Vein formation at Cobalt, Ontario, *Canadian Mining Journal*, **28**, p.301-303
- Venance K.E. (1989): Petrology of Coleman formation metasediments at the Little Silver Vein, near Cobalt Ontario. Unpublished HBSc. thesis, Carleton University
- Wadleigh M.A., Veizer J. and Brooks C. (1985): Strontium and its isotopes in Canadian rivers: fluxes and global implications. *Geochimica et Cosmochimica Acta* **49**, p. 1727-1736
- Wallis R.H., Sarcoglu N., Brummer J.J. and Golightly J.P. (1985): Geology of the McClean uranium deposits. In: *Geology of Uranium Deposits: Proceedings of the Canadian Institute of Mining –Society of Economic Geologists, Uranium Symposium, September 1981, Proceedings*, p. 101-113
- Williams G.E. and Schmidt P.W. (1997): Paleomagnetism of the Paleoproterozoic Gowganda and Lorrain Formations, Ontario: low paleolatitude for Huronian glaciation. *Earth and Planetary Science Letters*, **153**, p. 157-169
- Wilson J. (1949): Some major structures of the Canadian Shield. *Transactions of the Canadian Institute of Mining and Metallurgy*, **52**, p. 231-242
- Wood J. (1973): Stratigraphic and depositional environments of upper Huronian rocks of the Rawhide Lake-Flack Lake area, Ontario. In: *Huronian Stratigraphy and Sedimentation*, G.M. Young (ed). *Geol. Assoc. Can. Spec. Paper*, **12**, p.73-95
- Valley J.W. (1986): Stable isotope geochemistry of metamorphic rocks. In: *Stable Isotopes in High Temperature Processes* (J.W. Valley, H.P. Taylor, J.R.O. O'Neil eds). Mineralogical Society of America, *Reviews in Mineralogy* v.16, p. 445-489
- Veizer J., Clayton R.N. and Hinton R.W. (1992): Geochemistry of Precambrian carbonates: IV. Early Paleoproterozoic (2.25 ± 0.25) seawater. *Geochimica et Cosmochimica Acta* **56**, p. 875-885

- Veizer J., Hoefs J., Lowe D.R. and Thurstion P.C. (1989): Geochemistry of Precambrian carbonates: II. Archean greenstone belts and Archean sea water. *Geochimica et Cosmochimica Acta*, **53**, p. 859-871
- Vervoort J.D., White W.M. and Thorpe R.I. (1994): Nd and Pb isotope ratios of the Abitibi greenstone belt: new evidence for very early differentiation of the Earth. *Earth and Planetary Science Letters* **128**, p. 215-229
- Vooro G., Tatak J.I., Warren K.R., Jensen, T. and McGlade S. (1987): Orofino Resources Limited, Scadding Gold Mine, Proposal for Mining, Unpublished report prepared for Orofino Resources Limited. 16 pp
- Young G.M. (1972): Downward intrusive breccias in the Huronian Espanola Formation, Ontario. *Canadian Journal of Earth Sciences* **9**, p. 756-762
- Young G.M. (1973): Tillite and aluminous quartzites as possible time markers for middle Precambrian (Aphebian) rocks of North America. *In: Huronian Stratigraphy and Sedimentation* (G.M. Young ed.), *Geological Association of Canada*, Special Paper **12**, p. 97-127
- Young G.M. and Church W.R. (1966): The Huronian system in the Sudbury district and adjoining areas of Ontario: a review. *Geol. Assoc. Canada, Proc. Geol. Assoc. Canada*, **17**, p.65-82
- Young G.M., Long D.G.F., Fedo C.M. and Nesbitt H.W. (2001): Paleoproterozoic Huronian basin: product of a Wilson cycle punctuated by glaciations and a meteorite impact, *Sedimentary Geology*, **141**, p. 233-254
- York D. (1969): Least squares fitting of a straight line with correlated errors, *Earth and Planetary Science Letters*, **5**, p. 320-324
- Zheng Y.-F. (1990a): Carbon-oxygen isotopic covariation in hydrothermal calcite during degassing of CO₂. *Mineralium Deposita*, **25**, p. 246-250
- Zheng Y.-F. (1990b): The effect of Rayleigh degassing of magma on sulphur isotope composition: a quantitative evaluation. *Terra Nova*, **2**, p. 74-78
- Zheng Y.-F. (1999): Oxygen isotope fractionation in carbonate and sulfate minerals. *Geochemical Journal*, **33**, p. 109-126
- Zheng Y.-F. and Hoefs J. (1993): Carbon and oxygen isotopic covariations in hydrothermal calcites: theoretical modeling on mixing process and application to Pb-Zn deposits in the Harz Mountains, Germany. *Mineralium Deposita* **28**, p. 79-89

Zolnai A.I., Price R.A. and Helmstaedt H. (1984): Regional cross section of the Southern Province adjacent to Lake Huron, Ontario: implications for the tectonic significance of the Murray Fault Zone. *Canadian Journal of Earth Sciences* **21**, p.447-456

Appendix A. Descriptions of Samples Collected

Sample Id	Easting	Northing	Deposit Name	Strike/Dip	Field Description
Bay-01	587853	5244714	Bay Lk - Montreal River mine	032/28S	from trench in situ; on strike with shaft: vuggy Qtz vein (~2cm) in highly alt (Qtz+chlorite) Nip Diabase; cobaltite mineralz in diabase ¹ ; vugs lined with dog's tooth Qtz
Bay-02	587853	5244714	Bay Lk - Montreal River mine		from waste pile; coarse-grained carbonate vein & highly alt carbonate-diabase 'breccia'-chlorite; iron-staining and trace mineralization (cobaltite?) in diabase fragments
Bay-03	587853	5244714	Bay Lk - Montreal River mine		from waste pile; carbonate vein breccia with angular diabase fragments; coarse-grained calcite veins with some cobalt bloom visible, especially along host-vein contact
Bay-04	587853	5244714	Bay Lk - Montreal River mine		from waste pile; max. 3cm parallel carbonate veins (2-3) in fractured & heavily altered diabase; chlorite alt in vein and host; host is sheared with lineations; trace mineralization in diabase host
Bay-05	587853	5244714	Bay Lk - Montreal River mine		from waste pile at shaft; ~5 cm coarse-gr calcite+quartz vein with abundant chlorite alt; sheared host rock; pinkish carbonate with iron-staining vis.
BP-01	512543	5277743	Bishop Mine	212/86N	5cm cal-Qtz vein with cobalt bloom; stretched out alt diabase frags with cobaltite mineralz within frags only
BP-02	512562	5277739	Bishop Mine	020/86E	sample from waste pile of shaft; 10-15 cm coarse-gr blocky cal vein exposed beside the shaft; highly carb alt frags within vein?
BRT-01	595925	5229994	Brett Boulder		calcite veinlet with trace native Au & Co-Ni arsenides hosted in greenschist-facies metavolcanics; boulder at side of hwy#11.
BRT-02	595925	5229994	Brett Boulder		calcite veinlet with trace native Au & Co-Ni arsenides hosted in greenschist-facies metavolcanics; sub-crop (?) at same location as BRT-01
BRT-03	595925	5229994	Brett Boulders		calcite veinlet with trace native Au & Co-Ni arsenides hosted in greenschist-facies metavolcanics; boulder at side of hwy#11.
75690	595925	5229994	Brett Boulder		calcite veinlet with trace native Au & Co-Ni arsenides hosted in greenschist-facies metavolcanics; boulder at side of hwy#11.
BV-01	554588	5285694	Beaver Pond	080-84S	6cm cal-cpy-rich-hem-chlorite vein hosted in Nip diabase; very similar to merico veins; large aggregations of cpy grains (3-5cm)
BV-02	554639	5285721	Beaver Pond		from waste pile near shaft; ore pile? ~12 cm cal-Qtz vein with cpy mineralz and fine-gr hem bands; set in high alt granophyric diabase? Diabase frags in vein
BV-03	554639	5285721	Beaver Pond		from waste pile near shaft; ore pile? Qtz-cal-cpy-hem vein very similar to merico veins; sub cm cpy grains;
CP-01	520154	5279620	Capital Mine		from the waste pile at mine; 4-7cm Qtz-chlorite-cal vein in chloritized diabase host; trace opaques in vein and trace cpy? In alt diabase host; cal confined to vein margins
CP-02	520154	5279620	Capital Mine		from the waste pile at mine; one, barren, massive 10cm cal vein in chloritized & silicified diabase host; several other smaller Qtz and cal veins; cal vein have cobalt bloom prefer along margins
CP-03a	520154	5279620	Capital Mine		from the waste pile at mine; Qtz-chlorite vein; chloritized diabase frags?; gossanous surface; minor cpy + py visible;
CP-03b	520154	5279620	Capital Mine		from the waste pile at mine; ~3cm cal-Qtz-cpy in chloritized diabase host; Qtz present only on vein margins
CP-04a	520154	5279620	Capital Mine		from the waste pile at mine; 6.5 cm massive cal vein with some chloritized diabase frags; near inferred margin have <0.5cm galena>cpy band
CP-04b	520154	5279620	Capital Mine		from the waste pile at mine; series of stacked cal-rich and Qtz-rich veins; separated by chloritized/sheared diabase?; no vis mineralization
CP-05	520154	5279620	Capital Mine		from the waste pile at mine
DL-01	548637	5220942	Bonhomme Property; Delhi twp		Sample collected from shaft waste pile; milky Qtz-galena-cpy-rich vein material; abundant Fe-staining in Qtz;
DL-02	548637	5220942	Bonhomme Property; Delhi twp	240-255/32N	in situ sample collected from within adit; milky Qtz-galena-cpy-rich vein material with fine-gr chlorite masses assoc with minerlaz
DL-03	548637	5220942	Bonhomme Property; Delhi twp	240-255/32N	in situ sample collected from within adit; coarse-gr cal-rich vein sample; some galena+cpy mineralz; same sample as Neil's Delhi-2
DL-04	548637	5220942	Bonhomme Property; Delhi twp		in situ from within adit; cpy-rich+pyrrhotite vein material with fine-gr chloritic masses; same sample as Neil's Delhi-3
DL-05	548637	5220942	Bonhomme Property; Delhi twp		from shaft waste pile; milky Qtz-galena-cpy+pyrrhotite-rich vein material; some fine-gr chloritic masses with some mineralz within

Sample Id	Easting	Northing	Deposit Name	Strike/Dip	Field Description
DL-06	548637	5220942	Bonhomme Property; Delhi twp		from shaft waste pile; milky qtz-galena-rich + cpy+pyrrhotite vein material; same sample as Neil's Delhi-4; large sample
DL-07	548637	5220942	Bonhomme Property; Delhi twp		Nipissing Diabase host to Delhi occurrence; fine-gr; some cpy, py or cobaltite mineralz in 'bands' -pos fractures?
DUNC-01	501811	5287649	West Side of Duncan Lk; known	288/85N	qtz-vein with hematitized clasts cross-cutting Gowganda seds; large qtz-stockwork alteration zone
DUNC-02	503188	5288297	Duncan Lk occurrence	240/56	sample collected from main splay off main vein; in situ chip sample; cal-chlorite vein with some galena and cobaltite assoc with chlorite; bright red hematitized clasts in chlorite
DUNC-03	503188	5288297	Duncan Lk occurrence	240/56	same location as DUNC-02; taken from waste pile assoc with vein; qtz-cal-chlorite vein; mineralz in alt diabase along vein margin (cobaltite?); irregular vein width; chlorite 'bands'
DUNC-04	503188	5288297	Duncan Lk occurrence	086/80	chip sample of in situ vein; blows out to ~5 cm; cal-chlorite vein with galena cubes assoc with chlorite; some mineralz (cobaltite?) in diabase margin
DUNC-05	503188	5288297	Duncan Lk occurrence	070/84S	from in situ vein; 8-10 cm cal+ chlorite-rich vein; highly carb +chlorite alt of sheared diabase host; trace fine-gr cpy + hem?
DUNC-06	503188	5288297	Duncan Lk occurrence		from waste pile at base of trench; qtz-cal vein-breccia with carb+chlorite alt diabase; some mineralization in alt diabase; trace cpy in qtz+chlorite; qtz margin, cal center (vein)
DUNC-07	503188	5288297	Duncan Lk occurrence		from waste pile at base of trench; 8-10cm cal +chlorite vein; massive blocky cal in center of vein; minor galena in margins with chlorite? bands; mineralization in alt diabase margins
DUNC-08	503188	5288297	Duncan Lk occurrence		from waste pile at base of trench; Neil is sending other half for assaying; blocky cal vein (center) with chlorite-qtz margin; galena in cal near chlorite margin
EP-59	574544	5254483	Lady Evelyn River-mattagami property	235/50	qtz-carb vein with cpy & pyrite mineralz; upto 1m wide striking 235/50; site of old workings shaft?; sample taken in situ from surface; qtz-rich vein; many in area
GS-1	598929	5215817	Gosselin Lk	204/44N	in situ sample from shaft entrance; 4-5cm qtz-vein perpendicular to main vein/shear zone - see field image; qtz+chlorite with some highly alt diabase frags; trace cpy mineralz assoc with chlorite
GS-2	598929	5215817	Gosselin Lk	212/40N	in situ, but weathered vein sample from blow-out where vein reaches ~10cm; qtz+chlorite margin-cal+cpy center vein; cpy present along qtz-cal boundary with Fe- and Cu-staining in vugs
GS-3	598929	5215817	Gosselin Lk	212/40N	same vein as GS-2, taken more N; 2-4 cm qtz vein with abundant Fe-staining; trace py mineralz assoc with micas & vuggy textures; hosted in shear zone; pink K-spar developed along vein margin in some areas
GS-4	598926	5216310	N Gosselin Lk		from shaft waste pile; sulfide-rich grab samples; qtz-cal vein samples, but qtz-rich; pyrite + cpy mineralz with iron staining; some pieces contain coarse-gr diabase host
GS-5	598926	5216310	N Gosselin Lk		from shaft waste pile; qtz-cal vein breccia with large diabase frags & abundant anhedral cpy (upto ~1cm large); cpy assoc with diabase+chlorite frags
GS-6	598926	5216310	N Gosselin Lk	236/74N	~10cm calcite vein collected in situ at shaft entrance; coarse-gr cal with minor euhedral qtz grains; fine-gr chlorite 'blasts' with trace cpy mineralz and iron staining; some cobalt bloom vis in cal
GS-7	598926	5216310	N Gosselin Lk		from large angular boulder in waste pile; ~10 cm sugary cal+ minor cpy + diabase frags in vein/vein-breccia
GS-8	598926	5216310	N Gosselin Lk		from large angular boulder in waste pile; 8-9 cm sugary cal vein breccia with diabase frags; minor interstitial cpy + cobalt bloom
GS-9	598926	5216310	N Gosselin Lk		from large angular boulder in waste pile; sugary cal + interstitial cpy+py + cobalt bloom + diabase frags; hosted in mineralized diabase
J23_01	554347	5288326	Ethel mine		trench sample taken SE of Ethel mine shaft; 1-3 cm cal+cpy vein fracture-controlled in nip diabase; get info from Neil
JL-1	593867	5234322	Johnson Lk	344/88E	6 cm shear/alteration zone with malachite staining and abundant anderal pyrite; along pipeline, top of hill in Nip diabase
JM-1	593226	5234846	Johnson Lk Hwy occurrence	085/72S	<0.25 cm pyrite-rich vein hosted in parallel joints 10cm apart within Coleman seds; some pyrite in seds pseudomorphing granitic clasts
JM-2	593226	5234846	Johnson Lk Hwy occurrence	040/70S	similar in occurrence and style as JM-1; across the hwy-likely the same vein; unable to sample vein; sample is mineralized vein margin
ME-EP-01	555187	5288530	Merico Vein System	187/72W	channel sample of vein, 16cm wide cal (+-qtz)-cpy-specular hem vein at 8+56E/5+49S
ME-EP-02	555182	5288529	Merico Vein System	269/72N	channel sample of main vein, 36 cm wide cal-cpy-specular hem at 8+52E/5+54S
ME-EP-03	555183	5288529	Merico Vein System		cal-euhedral cpy-hem vein grab samples from just 0.5m East of ME-EP-02 at 8+53E/5+54S
ME-EP-04	554956	5288467	Merico Vein System	230/68N	channel sample just east of Merico Shaft; 32 cm qtz-rich-cal-cpy-hem vein at 6+25E/6+12S; anhedral sulphides; sheared texts

Sample Id	Easting	Northing	Deposit Name	Strike/Dip	Field Description
ME-EP-05	554956	5288467	Merico Vein System	230/68N	grab sample from same location as ME-EP-04; piece broken off by channel at 6+25E/6+12S
ME-EP-06	555034	5288474	Merico Vein System		channel sample of 11 cm qtz-rich +cpy+specular hem vein in southern branch of main vein at 7+04E/6+05S
ME-EP-07	555035	5288474	Merico Vein System	264/62N	channel sample of 8cm qtz-cpy-py-hem vein at 7+05E, 6+05S; very cpy-rich
ME-EP-08	555140	5288499	Merico Vein System	264/84N	8cm vuggy qtz-cal-cpy-py-specular hem vein at 8+10E/5+80S; vugs lined with dog's tooth qtz
ME-EP-09	554920	5288152	Merico Vein System, Hill Top Trench	360/86E	6cm cobalt-bloom-rich cpy-qtz-cal vein breccia at 5+89E/9+28S; fine-gr anhedral sulphides; alt diabase frags in vein?
ME-EP-10	556074	5287649	unnamed	230/88S	2 veins combining into 1; most of sample from 6cm qtz-rich-cpy-brn-specular hem vein; SV is the more southern Hem-rich vein; both offset by 356/82E veins that are accompanied by aplite veins
ME-EP-11	556074	5287649	unnamed	356/84E	max. 1.5cm aplitic veins which accompany the offsetting veins; some minor cpy mineralz assoc with aplitic alt
ME-EP-12	556074	5287649	unnamed	230/88S	same vein as ME-EP-10, 2.5m east, 5.5 cm wide cal-cpy-brn-specular hem vein
ME-EP-13	556054	5287657	unnamed	046/82S	3cm cal-cpy-rich vein joins 070/82S 5-15 cm vein; most of sample from blasting rubble (trench); some in situ 3cm vein
ME-EP-14	555418	5287798	Silver Jackpot	203/88NW	2.5cm cal-qtz-cpy-hem vein ~20m into adit; vein branching obliquely off main vein
ME-EP-15	555418	5287798	Silver Jackpot	032/72S	~3cm qtz-rose carb-chlorite vein oblique to main vein; at entrance to adit; shear textures esp rose carb; minor cpy + hem occurs along vein margins; host diabase;
ME-EP-16a	555439	5287785	Silver Jackpot		from shaft waste pile; aplitic alt of diabase asse with ~0.5cm hem-magnetite vein; cross cutting cal filled fractures; some chlorite spots in aplitic alt
ME-EP-16b	555439	5287785	Silver Jackpot		from shaft waste pile; ~2cm cal vein in alt diabase; margin of vein has aplitic + carb alt +hem band; trace cpy along vein margin and some mineralization in alt diabase
ME-EP-16c	555439	5287785	Silver Jackpot		from shaft waste pile; 1-2 cm cal vein in aplitic host; shear/flow texts: fine-gr cpy mineralz in vein + interstitial blebs in aplitic host; chlorite margin to vein?
ME-EP-17	555096	5287170	Unnamed		from waste pile of shaft; qtz-cal vein breccia with granophyric diabase frags with pink albite alt; small interstitial anhedral cpy <1cm+ minor Py & cobalt bloom in breccia (vein) matrix
ME-EP-18	555118	5287173	unnamed	045/83S	same unnamed occurrence as ME-EP-17; ~10cm cal-cpy-brn vein-vein breccia in substantial trenching to the East;
ME-EP-19	555034	5288495	Merico vein System	260/80-60N	in situ grab samples of 50 cm wide cal-hem-cpy-brn vein from Northern branch of main vein at 7+04E/5+84S; angular cpy +py set in massive hem
ME-EP-20	555034	5288495	Merico vein System	260/80-60N	in situ grab samples of 50 cm wide cal-hem-cpy-py-brn vein from Northern branch of main vein at 7+04E/5+84S; sheared cpy; euhedral py; massive hem
ME-EP-21	555034	5288495	Merico vein System	260/80-60N	in situ grab samples of 50 cm wide cal-hem-cpy-brn vein from Northern branch of main vein at 7+04E/5+84S
ME-EP-22	555147	5288498	Merico vein System		in situ grab sample of Merico main vein system at 8+17E/5+80S; junction of 2 veins into 1 5.5cm vein.
ME-EP-23	554949	5288467	Merico vein System		from the Merico Mine waste pile; cal-cpy-hem vein breccia with rounded alt diabase frags; anhedral to ~2 cm euhedral cpy grain in cal matrix; abundant sulphides
ME-EP-24	555217	5288556	Merico Vein System		unaltered host material for vein system; taken at 8+87E/5+23S; med-gr nip diabase; pos some chlorite spots; slightly magnetic -magnetite + pyrrhotite
MN-01a	513651	5274010	Mann Mine		from waste pile at shaft entrance; ~5cm cal + rose carb vein with parallel bands of chlorite within vein; trace cpy in vein;
MN-01b	513651	5274010	Mann Mine		from waste pile at shaft entrance; ~3 cm cal-qtz-chlorite vein; qtz band along vein margin; aplitic host with chlorite spots and qtz-cal filled fractures
MN-02	513651	5274010	Mann Mine		from waste pile at shaft entrance; ~5 cm cal-rose carb vein; hosted in diabase with some cobaltite present along margins; recrystallized diabase frags in vein
MN-03	513651	5274010	Mann Mine		from waste pile at shaft entrance; ~7 cm barren cal vein; hosted in diabase with minor cobaltite mineralization in diabase; sharp vein-host contact; vein has some flow texts
MN-04	513651	5274010	Mann Mine		from waste pile at shaft entrance; parallel 1-2cm cal veins pinch & swelling; hosted in coarse-gr -granophyric diabase; trace cobaltite & cpy along vein margins; cobaltite in alt diabase as well
MN-05	513651	5274010	Mann Mine	237/82N	~2cm cobaltite-rich (>90%) vein from trench 25 m South of MN-06; weathered cobalt bloom

Sample Id	Easting	Northing	Deposit Name	Strike/Dip	Field Description
MN-06	513805	5274182	Mann Mine	255/84N	2 - 0.25 cm cal vein in stope that broke the surface; vein margins are sheared, fine-gr chloritized diabase?; no vis mineralization
MT-01	547617	5287122	Beaver Auxiliary Shaft No.1		from small waste pile at shaft; 110m at 330 degrees from Beaver OGS location; 3-5 carb vein attached to granophyric diabase; vein cpy-rich (<1cm); coarse-grained diabase; bladed amphiboles~1cm
MT-02	547617	5287122	Beaver Auxiliary Shaft No.1		from small waste pile at shaft; massive blocky calcite + interstitial calcite with cpy +/- trace hematite & cobalt bloom; cpy 1-5 cm
MT-03	547617	5287122	Beaver Auxiliary Shaft No.1		from waste pile; pyrite+cpy intergrown -rich vein sample ~40% sulphides; massive blocky calcite + interstitial chlorite
MT-04	547617	5287122	Beaver Auxiliary Shaft No.1		from waste pile; massive calcite vein (pinkish) with interstitial, anhedral 1-5 cm cpy+pyrite+chlorite
MT-05	547617	5287122	Beaver Auxiliary Shaft No.1		host to mother lode; med-to-coarse grained (pos.granophyric) diabase; magnetic + trace dissem sulphides; from waste pile
NP-01	555439	5287785	Silver Jackpot		Fine-grained aplitic host with veins and veinlets of calcite with trace sulfide mineralization
NP-02	555439	5287785	Silver Jackpot		Fine-grained aplitic host with veins and veinlets of calcite with trace sulfide mineralization
NP-03	555439	5287785	Silver Jackpot		Narrow calcite veins (2cm) with possible native silver hosted in fine-grained, aplitic altered host
NP-04	555439	5287785	Silver Jackpot		Mafic-spotted (chlorite) aplitic altered host
PARA-01a	554413	5286138	Paramount Mine		from waste pile at mine shaft; image of pinching pink alteration; large (max 1cm) zoned cpy grains in 4-5cm cal vein; hosted in granophyric diabase; cpy grains pref assoc with chlorite
PARA-01b	554413	5286138	Paramount Mine		small fragment from waste pile; ~4cm qtz-cal-qty vein set in alt diabase; parallel band of aplitic alt? Two large feldspar grains in vein? Zoned cpy; vein= aplitic band, trace cpy, qtz+chlorite, cal+ cpy; end of sample
PARA-02a	554413	5286138	Paramount Mine		from waste pile at mine shaft; max 1.5 cm cal vein with pyrite or linnaeite grp minerals; set in carb + chlorite alt diabase; vis zone of carb alt; some cobaltite in diabase margin
PARA-02b	554413	5286138	Paramount Mine		small fragment of vein material from waste pile at mine shaft; qtz-qty-bornite; vein=cal margin, hem band, qtz+cpy+brn, qtz, hem, cal
PARA-03	554321	5285876	huge trench south of Paramount mine	354/80E	vein sample in situ; at near right angle to main vein exposed in trench; ~3 cm fine-gr cal-chlorite vein with abundant cpy mineralz; trace cobalt bloom in vein
PARA-03b	554321	5285876	huge trench south of Paramount mine		host to PARA-03; contact of vein with minor band of aplitic alt parallel to vein; silicified diabase?
PR-01	513924	5273861	Parcher Brothers Mine		from waste pile; blocky cal+qtz vein material with alt diabase frags; some rose cal & cobaltite mineralz in diabase frags
PR-02	513924	5273861	Parcher Brothers Mine		from waste pile; qtz-cal vein material with angular K-spar alt diabase frags; trace interstitial cobaltite mineralz in alt diabase?; rose cal
PR-03	513924	5273861	Parcher Brothers Mine		from waste pile; 1-3 cm qtz vein; interbanded wth cal veinlets; trace cpy developed along vein margin; cobaltite pos in highly alt, mafic diabase host
RPT-1-1	595925	5229994	Brett Boulder-Richard's sample		calcite veinlet with trace native Au & Co-Ni arsenides hosted in greenschist-facies metavolcanics; boulder at side of hwy#11.
RPT-1-1 b	595925	5229994	Brett Boulder-Richard's sample		calcite veinlet with trace native Au & Co-Ni arsenides hosted in greenschist-facies metavolcanics; boulder at side of hwy#11.
RV-1	513916	5271716	Reeve-Dobie Mine	198/78N	collected from the same vein along length of adit; ~3-5 cm sheared cal vein-breccia with cobalt bloom; no other vis sulphides; diabase host
RV-2	513929	5271903	Reeve-Dobie Mine		from the waste pile at mine; ~1cm cal vein hosted in nip diabase; vein sheared with chlorite? Bands
SV-001	556275	5288927	Sauve Occurrence		Host: medium-grained hypersthene variety of Nipissing diabase
SV-002	556275	5288927	Sauve Occurrence		boudinaged and brecciated calcite veins set in brecciated hematitic host (dark red colour)
TM-1	599745	5218024	Temagami-Lorrain shaft		from the waste pile; two parallel qtz veins (max 1cm) with relatively pristine diabase host; 1-2cm chloritic alteration halo with some trace mineralz
TM-2	599745	5218024	Temagami-Lorrain shaft		from the waste pile; max 4cm qtz-minor cal-chlorite vein; hosted in highly chloritized diabase host with cobaltite (& pos cpy) mineralz along vein margin and in diabase

Sample Id	Easting	Northing	Deposit Name	Strike/Dip	Field Description
TM-3	599745	5218024	Temagami-Lorrain shaft		from the waste pile; small fragments of vein material; small (1-2cm) qtz-cal veins in diabase host; some fairly dense with cobaltite mineralz;
WN-1	532515	5163411	St. Genevieve Occurrence	050/70S	in situ quartz vein that pinches & swells (<2cm -10cm wide) within foliated metasediments
WN-2	532494	5163410	St. Genevieve Occurrence	095/85S	from small waste pile in exploration trench; quartz-vein subparallel to foliated metasediments; vein pinches & swells from <2cm to 10cm in width
WN-3	534705	5165009	Davis Shaft		from waste pile next to exploration shaft; quartz-carbonate vein with minor cpy and pyrite mineralz in qtz-arenite
WN-4	534 677	5164935	Davis Shaft		quartz-arenite host to Davis mineralization; nearest outcrop to shaft
WN-5	534660	5164771	Davis Shaft		in situ samples from exploration trench in sedimentary rocks (Gowganda?); qtz-carb veining with minor cpy and pyrite mineralz; trench 1m wide by ~15m long
WN-6	529310	5165286	Glade Occurrence		in situ mineralized quartz arenite (Gowganda?) with minor to trace cobaltite (?) mineralization just below contact with Nipissing Diabase sill; some barren qtz-veining in overlying diabase
WN-7	529084	5165325	Glade Occurrence	145/70W	in situ gossanous qtz veins with some minor cpy & pyrite hosted in Nipissing diabase at contact b/w diabase and qtz-arenite seds; diabase at contact very convoluted with breccia developed
WN-8	529516	5166235	McLean-Watt Mine		highly gossanous sample with visible gold, pyrite & cpy mineralz; host is reported chloritized quartzite breccia -might be Archean-
WN-8b	529516	5166235	McLean-Watt Mine		host brecciated rocks to the McLean-Watt showing. Chloritized matrix with angular quartzo-feldspathic clasts and minor sulphide mineralization
WN-9	509765	5185695	Parking Twp South Occurrence		trace cpy & pyrite mineralized conglomeratic sedimentary units (Gowganda); rounded quartzo-feldspathic clasts set in a qtz-arenite matrix
WN-9b	509761	5185706	Parking Twp South Occurrence		in situ conglomeratic sedimentary rocks with trace cpy & pyrite mineralization; rounded quartzo-feldspathic clasts in a qtz-arenite matrix
WN-10	509731	5186080	Parking Twp Occurrence		in situ deformed (folded & sheared) fine-grained metasediments with some minor qtz-carbonated veining parallel to the foliation with trace pyrite mineralz; small exploration trench
WN-11	509260	5186273	Decade occurrence		in situ mineralized qtz-arenite outcrop with trace pyrite mineralization; no obvious development/exploration in area
WN-12	510260	5185754	Decade Occurrence Drill Collar		in situ pyrite mineralized qtz-arenite outcrop next to drill collar striking 310 with 48 West dip; Less than 10 yrs old drill site
WN-13	512356	5194192	Fraleck Showing		pyrite mineralized, medium-grained Nipissing Diabase 2/3 of the way up a sill; samples from "alus pile (large & angular) locally derived; but could not find outcrop of similarly mineralized samples
WN-14	512758	5193210	Fraleck East Showing		qtz-carbonate +cpy & pyrite vein material hosted in medium-grained Nipissing diabase; sample taken from boulders in exploration pit (2m by 20m long); adjacent diabase has minor (<1cm) carbonate veins
WN-15	512758	5193210	Fraleck East Showing		qtz-carbonate +cpy & pyrite vein material hosted in medium-grained Nipissing diabase; sample taken from boulders in exploration pit (2m by 20m long); adjacent diabase has minor (<1cm) carbonate veins
WN-16	512758	5193210	Fraleck East Showing		qtz-carbonate +cpy & pyrite vein material hosted in medium-grained Nipissing diabase; sample taken from boulders in exploration pit (2m by 20m long); adjacent diabase has minor (<1cm) carbonate veins
WN-17	531019	5197765	Laura Lake Showing		in situ qtz-arenite host rock to qtz-cpy-pyrite veining (trace cpy & pyrite in situ)
WN-18	531019	5197765	Laura Lake Showing	280/70N	in situ qtz vein ~30 cm wide with trace cpy mineralization; good vein exposure and several exploration trenches in area; host is qtz-arenite
WN-19	531019	5197765	Laura Lake Showing		samples collected from exploration trench waste pile; qtz veins with sporadic cpy-galena-pyrite mineralization; host rock are qtz-arenite
WN-20	526259	5178788	Dolmac Property		samples collected from waste pile in exploration shaft; medium-grained Nipissing diabase with minor pyrite-cpy mineralization & qtz-carbonate veining; trenching & drill core on site;
WN-21	526259	5178788	Dolmac Property		in situ qtz-carbonate veining with chlorite-epidote alteration halos around cpy-pyrite mineralized Nipissing Diabase
WN-22	528761	5177582	Crystal Gold Mine?		subcrop and waste pile samples from small exploration pit; qtz-pyr-cpy in subgreenschist quartz-arenite seds; OGS has mine mapped ~250m South across water; several old steam boilers on site; in situ veins not mineralized and too small to get trends
WN-23	528230	5171895	Burda Mine		in situ qtz-veined, fine-grained metaseds (mudstones?) with minor pyrite mineralization; mineralization is adjacent to ~10cm wide, barren qtz vein trending 158/60SW
WN-24	528243	5171894	Burda Mine		in situ gossanous qtz & mudstone vein breccia with minor pyrite & cpy mineralization in the mudstones; dominant qtz-vein trends 090/68S
WN-25	528315	5171851	Burda Mine		samples from waste pile at exploration shaft; mudstones & qtz+carb-vein breccias with minor cpy-pyrite mineralz; abundant Nipissing Diabase boulders in waste pile-suggestive that diabase-seds contact is close

Sample Id	Easting	Northing	Deposit Name	Strike/Dip	Field Description
WN-26	529095	5176769	Gordon Mine		samples from large waste pile at shaft entrance -most of shaft buried by waste pile; qtz-carb vein with trace cpy-pyrite in qtz-arenite host rock
WN-27	529081	5176755	Gordon Mine	090/70S	in situ qtz-vein with trace cpy-pyrite mineralized ~20m SW of shaft; vein ~25cm wide cross-cuts quartz arenite; good vein exposure
<i>University collection</i>					
BLM-16	599900	5247500	Brady Lakes Mine, Cobalt		qtz-rich +carbonate vein with abundant cpy + galena mineralz; coarse-gr, massive qtz crystals with interstitial carbs & cpy+galena; sulphide pref assoc with carb
BRC-1	599900	5247500	Bruce Mine, Cobalt		High-grade native silver interstitial to med-gr calcite
BT-2	599900	5247500	Beaver Temiskaming Mine, Cobalt		small <2cm carbonate-rich veins hosted in metasediments (subgreenschist qtz arenite?) carbs have lavender color; no sulphides vis
BT-6	599900	5247500	Beaver Temiskaming Mine, Cobalt		2-4 cm carb-vein hosted in fine-gr mafic metasediments; mafic (chlorite) banding along vein contact; minor cpy mineralz in metased adjacent to veining; trace malachite staining in vein
BT-13	599900	5247500	Beaver Temiskaming Mine, Cobalt		<2cm calcite vein with axinite(?) + trace cpy in vein; all hosted in fine-gr mafic metaseds; minor rounded qtz grains present in carb vein
BT-14	599900	5247500	Beaver Temiskaming Mine, Cobalt		coarse-gr carb vein with abundant native silver, cobaltite and/or pentlandite rimming country rock fragments(?) creating almost colliform texture; country rock frags are fine-gr highly chloritized (metaseds?)
BT-19	599900	5247500	Beaver Temiskaming Mine, Cobalt		high-grade massive sulphur-arsenides + native silver; trace interstitial carb and qtz; host is fine-gr metaseds (chloritized?); pos trace bormite?
BT-33	599900	5247500	Beaver Temiskaming Mine, Cobalt		granular calcite+qtz vein fragmentation (<3.5cm vein) hosted by highly alt diabase?; carb forms margins of vein, coarse-gr qtz in center of vein; no vis mineralz;
BT-34	599900	5247500	Beaver Temiskaming Mine, Cobalt		Small (~1cm) cal+qtz vein; coarse-gr qtz; margin of vein is massive, fine-gr cobaltite+sulphur-arsenides; hosted in pos sheared metaseds?
BT-36	599900	5247500	Beaver Temiskaming Mine, Cobalt		high-grade ore of massive native silver + cobaltite (+sulphur arsenides) with minor interstitial calcite; hosted in fine-gr mafic metaseds
BT-82-3	599900	5247500	Beaver Temiskaming Mine, Cobalt		fragment of high-grade ore of sheared carb vein with native silver + cobaltite; host is fine-gr, mafic highly chloritized;
BT-315	599900	5247500	Beaver Temiskaming Mine, Cobalt		fragment of high-grade ore of native silver + nickeline? + cobaltite rosettes in a blocky carbonate matrix; host is fine-gra mafic - alt diabase?
N-17-12	599900	5247500	Beaver Temiskaming Mine, Cobalt		fragment of high-grade ore; fine-gr cobaltite+silver+sulphur arsenides with minor calcite present;
N-17-14	599900	5247500	Beaver Temiskaming Mine, Cobalt		fragment of cal+ minor qtz vein with abundant galena, cobaltite and cpy mineralz in vein; small frags of fine-gr mafic host present
PS-1	599900	5247500	Pan Silver Mine, Cobalt		Coarse-gr qtz + interstitial, granular cal vein; abundant cpy mineralz along margin of vein and in adjacent host rocks: fine-gr mafic metaseds?; calcite is light pinkn in color;
SLS-1	599900	5247500	Silverside Mine, Cobalt		fragment of high-grade carb vein with native Ag + cobaltite and fine-gr, angular fragment of mafic host rock
SLV-1	599900	5247500	Silverfields Mine, Cobalt		fragment of carb vein with coarse-gr, euhedral galena crystals and minor cpy; minor fine-gr frags of mafic host rock?
SLV-2	599900	5247500	Silverfields Mine, Cobalt		fragment of high-grade native silver, carb vein breccia with angular host rock fragments; native Ag and frags cut by later galena mineraliz creating a second vein breccia

Appendix B: Merico-Ethel Trench Maps

Note: The larger main Merico trench map is folded in the insert, located at the end of the thesis. All coordinates are reported in UTM format, NAD27, zone 17.

The Eastern Merico-Ethel Trench

The Southern Merico-Ethel Trench Map

Appendix C: Carbon and Oxygen Isotopic Composition of Vein Calcite

Sample ID	Occurrence/Location	Vein Mineralogy	$\delta^{18}\text{O}$ (vsmow)	$\delta^{13}\text{C}$ (vpdb)
BAY-2	Bay Lake, Cobalt camp	coarse-grained, calcite-diabase vein breccia	10.84	-4.52
BAY3-1	South East	white calcite + diabase vein breccia	9.71	-4.21
Bay-4		parallel white calcite+quartz veins	10.3	-4.35
Bay-5		granular quartz+ rose calcite vein	9.21	-5.96
BP1-1	Bishop Brothers Mine	rose calcite + quartz vein	11.73	0.29
BP-2a	Gowganda camp	rose, coarse-grained calcite vein	11.34	0.01
BP-2a*	(North West)	rose, coarse-grained calcite vein	11.3	0.16
BP-2c		light grey, coarse-grained calcite vein	11.67	2.54
BRT-01	Brett	white calcite with trace native Au & Co-Ni arsenides	9.71	-3.86
BRT-01b	South East	white calcite with trace native Au & Co-Ni arsenides	9.65	-4.06
BRT-02		white calcite with trace native Au & Co-Ni arsenides	9.92	-2.56
BRT-3		white calcite with trace native Au & Co-Ni arsenides	9.54	-3.82
75690		white calcite with trace native Au & Co-Ni arsenides	9.34	-4.1
75690*		white calcite with trace native Au & Co-Ni arsenides	9.25	-4.13
75690b		white calcite with trace native Au & Co-Ni arsenides	9.09	-4.04
BV-2	Beaver Pond Elk Lake camp/North East	calcite-quartz vein with chalcopyrite & fine-gr hematite	11.9	-2.9
BV-3		calcite-quartz vein with chalcopyrite & fine-gr hematite	16.99	-3.08
CP-1	Capital Mine	quartz-chlorite-calcite vein in chloritized diabase host	11.11	-2.69
CP-2	Gowganda camp	white, coarse-grained calcite vein	11.44	-2.14
CP-3	North West	quartz-calcite-chalcopyrite vein	10.32	-4.18
CP-4		coarse-grained calcite vein with trace galena & chalcopyrite	10.94	-0.44
DL2-1	Delhi	milky quartz + white calcite vein w/galena+chalcopyrite	9	-5.15
DL-3	South-Central	white, coarse-grained calcite w/galena +chalcopyrite	8.85	-4.36
DL3-1		coarse-grained calcite vein w/trace galena+chalcopyrite	9.04	-4.17
DL-4		chalcopyrite+pyrrhotite+quartz vein w/fine-grained chlorite	8.93	-5.16
DL-5		milky quartz-galena-chalcopyrite+pyrrhotite-rich vein	8.97	-5.38
DUNC-2	Duncan Lake	calcite-chlorite vein w/trace galena & cobaltite	9.24	1.88
DUNC-3	North West	white quartz-calcite-chlorite vein	9.57	2.01
DUNC-4		rose calcite-chlorite vein w/euhedral galena	16.24	1.96
DUNC5-1		white calcite from quartz+calcite+ chlorite-rich vein	9.35	1.86
DUNC-6		white, quartz-calcite vein-breccia w/trace chalcopyrite calcite-quartz+chlorite vein; massive calcite center & quartz±galena margins	9.76	2.37
DUNC-7		calcite-quartz+chlorite vein; massive calcite center & quartz±galena margins	9.39	1.97
DUNC-7*		calcite-quartz+chlorite vein; massive calcite center & quartz±galena margins	9.45	1.97
DUNC-8		gossanous quartz±white calcite (interstitial) w/oxidized pyrite + chalcopyrite	9.72	2.45
EP-59	Lady Evelyn River Mattagami (East)		9.36	-15.2
GS2-1	Gosselin Lake	coarse-grained quartz margins & rose coloured calcite center	10.35	-5.46

Sample ID	Occurrence/Location	Vein Mineralogy	$\delta^{18}\text{O}$ (vs. mow)	$\delta^{13}\text{C}$ (vpdb)
GS-4	Cobalt camp	quartz-rich + calcite + pyrite + chalcopyrite vein	19.53	-5.55
GS-5	South East	quartz-calcite vein breccia w/anhydral chalcopyrite	9.32	-5.15
GS6-1		white, coarse-grained calcite with trace euhedral quartz	8.59	-3.23
GS-6b		white, coarse-grained calcite with trace euhedral quartz	8.82	-0.86
GS-7		granular calcite + chalcopyrite vein/vein-breccia	8.97	-0.46
GS-8		granular calcite vein breccia with diabase frags & minor chalcopyrite	8.9	-0.36
GS-9		granular calcite vein breccia with diabase frags & minor chalcopyrite	8.85	0.24
J23-1	Ethel mine	white calcite vein with subhedral chalcopyrite	12.6	-3.21
ME-1	Merico-Ethel Veins	chalky calcite ($\pm$ quartz) + chalcopyrite + specular hematite vein	12.26	-2.28
ME-2	Elk Lake/North East	chalky calcite ($\pm$ quartz) + chalcopyrite + specular hematite vein	11.23	-14.02
ME-2*		chalky calcite ($\pm$ quartz) + chalcopyrite + specular hematite vein	11.31	-13.45
ME3-1		white, chalky calcite with subhedral chalcopyrite + tiny hematite & quartz margin	12.14	-7.46
ME-4		deformed, dark grey calcite & interstitial white calcite vein w/chalcopyrite + hematite	10.41	-4.49
ME5-1		dark, coarse-grained calcite vein with anhedral chalcopyrite	10.25	-13.12
ME5-2		white, interstitial calcite from dark, coarse-grained calcite-rich vein	10	-6.46
ME8-1		white calcite from vuggy, quartz-rich vein with euhedral sulphides + specular hematite	10.8	-8.18
ME9-1		white calcite vein breccia with anhedral sulphides	12	-3.22
ME19-1		white calcite vein w/subhedral chalcopyrite & specular + red hematite	10.43	-16.28
ME-20a		white calcite-hematite+chalcopyrite+pyrite vein	11.1	-14.12
ME-20b		white calcite-hematite+chalcopyrite+pyrite vein	10.76	-14.73
ME-21		white calcite-hematite+chalcopyrite+pyrite vein	11.33	-3.05
ME-22		gossanous, quartz + chalcopyrite+pyrite vein	10.35	-8.4
ME23-1		calcite-rich vein breccia w/anhydral chalcopyrite & hematite	9.94	-16.78
ME-10	Unnamed (Merico)	quartz-rich, chalcopyrite+ bornite+specular hematite vein	11.4	-9.24
ME-12	Elk Lake/North East	white calcite-quartz +chalcopyrite+bornite+specular hematite vein	11.59	-5.36
ME-13		specular hematite-rich, white quartz+calcite vein w/chalcopyrite	11.3	-13.28
ME-17		quartz-calcite vein breccia w/granophyric diabase frags & chalcopyrite +pyrite	12.42	0.96
ME-17*		quartz-calcite vein breccia w/granophyric diabase frags & chalcopyrite +pyrite	12.49	0.99
ME18-1		white calcite vein breccia with subhedral chalcopyrite & bornite	12.11	1.46
ME-10	Unnamed (Merico)	quartz-rich, chalcopyrite+ bornite+specular hematite vein	11.4	-9.24
ME-12	Elk Lake/North East	white calcite-quartz +chalcopyrite+bornite+specular hematite vein	11.59	-5.36
ME-13		specular hematite-rich, white quartz+calcite vein w/chalcopyrite	11.3	-13.28
ME-17	Unnamed (Merico)	quartz-calcite vein breccia w/granophyric diabase frags & chalcopyrite +pyrite	12.42	0.96
ME-17*	Elk Lake/North East	quartz-calcite vein breccia w/granophyric diabase frags & chalcopyrite +pyrite	12.49	0.99
ME18-1		white calcite vein breccia with subhedral chalcopyrite & bornite	12.11	1.46
ME-14	Silver Jackpot	white calcite-quartz+chalcopyrite+hematite vein	11.5	-14.84
ME15-1	Elk Lake camp/North East	deformed rose calcite vein w/white calcite+quartz margin	14.67	-4.9
ME15-2		deformed rose calcite vein w/white calcite+quartz margin	11.1	-5.22

Sample ID	Occurrence/Location	Vein Mineralogy	$\delta^{18}\text{O}$ (vs mow)	$\delta^{13}\text{C}$ (vpdb)
ME-16b		calcite vein w/apilitic+carbonate+hematite band	11.85	-0.47
MN-1	Mann Mine	white calcite + rose calcite vein w/parallel bands of chlorite	11.31	-1.27
MN-2	Gowganda camp	milky quartz-rose calcite vein	11.74	-1.46
MN-3	North West	coarse-grained white calcite vein	10.99	-0.68
MN-3*		coarse-grained white calcite vein	11.16	-0.96
MN-4		parallel dark calcite w/trace cpy hosted in granophyric diabase	10.9	-0.99
MN6-1		small, white calcite-rich vein with no visible sulphides	11.61	-1.01
MT-1	Beaver Auxiliary Mine	white calcite+hematite+chalcopryrite	11.02	-9.17
MT2-1	Elk Lake/North East	coarse-grained, white calcite with subhedral chalcopryrite	10.24	-9.08
MT3-1		white calcite with abundant pyrite, chalcopryrite and chlorite	9.99	-9.86
MT-4		coarse-grained rose calcite +hematite+cpy+py & chlorite	11.26	-9.18
Para-1	Paramount Mine	white calcite+chlorite vein w/euhedral cpy replacing pyrite	11.19	-4.71
Para-3	Elk Lake/North East	quartz-chlorite vein w/chalcopryrite	11.16	-3.06
PARA3-1		white calcite vein with rounded, subhedral chalcopryrite	11.25	-3.02
PR-1	Parcher Brothers Mine	coarse-grained, white calcite+quartz vein	11.65	2.69
PR-1*	Gowganda camp	coarse-grained, white calcite+quartz vein	11.77	2.78
PR-2a	North West	rose-calcite+quartz vein +-chlorite	11.58	0.46
PR-2b		rose-calcite+quartz vein +-chlorite	16.92	0.84
PR-3		white quartz vein w/trace chalcopryrite along margin	12.02	-1.54
RV1-1	Reeve-Dobie Mine	deformed quartz+white calcite +-chlorite vein	10.56	-2.36
RV1-1b	Cobalt camp/South East	deformed quartz+white calcite +-chlorite vein	10.48	-1.73
RV-2b		deformed white calcite vein with chlorite bands	11.25	-2.63
TM-2	Temagami-Lorrain	parallel quartz+ white calcite veins	9.27	-9.12
TM-3	Cobalt camp/South East	quartz+ white calcite veins	9.03	-9.85
WN-14	Fracleck East		9.61	-4.9
WN-14 DUP	Wanapitei area/South West		9.8	-5.02
WN-16			10.25	-6.02
WN-25	Burda Mine Wanapitei area/South West		22.43	-8.81
BLM-16	Brady Lakes Mine Cobalt camp/South East	milky quartz-rich vein w/interstitial calcite+chalcopryrite & galena	11.76	-5.56
BRC-1	Bruce Mine Cobalt camp/South East	white, medium-grained calcite w/native silver	11.08	-1.33
BT-6	Beaver-Temiskaming	grey calcite vein w/malachite staining in fine-grained mafic	11.88	-3.2
BT-6b	Cobalt camp	grey calcite vein w/malachite staining in fine-grained mafic	12.03	-3.11
BT-8	South East	white + grey calcite vein w/rossettes of cobaltite & niccolite	11.25	-3.99
BT-13		white calcite vein w/ acicular amphibole + trace chalcopryrite	11.18	-3.64
BT-14		rose calcite+quartz vein w/rossettes of native Ag, cobaltite & niccolite	11.61	-2.66
BT-33		zoned, granular calcite vein w/quartz center	10.57	-3

Sample ID	Occurrence/Location	Vein Mineralogy	$\delta^{18}\text{O}$ (vsnow)	$\delta^{13}\text{C}$ (vpdb)
BT82-3		high-grade, deformed calcite vein with native silver + cobaltite	11.01	-3.47
BT-315		coarse-grained calcite w/native silver+nickeline/cobaltite rosettes	11.78	-2.06
BT-1307		semi-massive cobaltite + white calcite vein w/minor native Ag	10.9	-2.06
N-17-14		white calcite+quartz vein w/ chalcopyrite, galena & cobaltite	11.73	-3.96
III-1	III-Ho Mine Cobalt camp/South East)	high grade white calcite vein w/cobaltite native Ag & niccolite	12.64	-2.43
NCS-1	North Cobalt Shaft Cobalt camp/South East)	vuggy quartz+white calcite w/cobaltite native Ag & chalcopyrite	22.24	-4.88
PS-1	Pan Silver Cobalt camp/South East)	quartz+interstitial rose calcite vein w/chalcopyrite & pyrite	21.32	-6.31
PS-1*		quartz+interstitial rose calcite vein w/chalcopyrite & pyrite	21.42	-6.44
SLS-1	Silver Sides Mine Cobalt camp/South East)	white calcite+quartz vein-breccia w/native Ag + cobaltite	10.96	-4.43
SLS-2		white calcite+quartz vein-breccia w/native Ag + cobaltite	10.91	-2.51

Note: *=Quality control duplicate analysis

Appendix D: Sulphur Isotopic Composition of Ore Minerals

Occurrence	Sample	Mineral	Host	$\delta^{34}\text{S}$ (cdt)
Beaver Pd.	BV-1c	chalcopyrite	cal-cpy-hem vein hosted in Nipissing diabase	-2.00
	BV-1c	chalcopyrite	cal-cpy-hem vein hosted in Nipissing diabase	-1.98
	BV-3a	bornite	cal-cpy-hem vein hosted in Nipissing diabase	0.39
	BV-3b	chalcopyrite	cal-cpy-hem vein hosted in Nipissing diabase	3.09
Capital	CP-4a	galena	cal vein with chloritized mafic fragments	-0.77
	CP-4a-ch	chalcopyrite	cal vein with chloritized mafic fragments	-1.03
	CP-4cpy	chalcopyrite	cal vein with chloritized mafic fragments	-0.57
	CP-4gal	galena	cal vein with chloritized mafic fragments	-1.63
	CP-3a	chalcopyrite	qtz-chlorite vein in altered diabase	-1.20
Delhi Twp.	DL-1cpy	chalcopyrite	qtz-galena-cpy +-cal vein	1.07
	DL-1gal	galena	qtz-galena-cpy +-cal vein	-0.92
	DL-2a	chalcopyrite	qtz-galena-cpy +-cal vein	0.10
	DL-2b	galena	qtz-galena-cpy +-cal vein	-1.84
	DL-3	galena	qtz-cal-galena-cpy vein	-1.51
	DL-4a*	galena	qtz-galena-cpy +-po vein	-0.48
	DL-4a*	chalcopyrite	qtz-galena-cpy +-po vein	1.24
	DL-4cpy	chalcopyrite	qtz-galena-cpy +-po vein	0.50
	DL-4gal	galena	qtz-galena-cpy +-po vein	-1.61
	DL-4pyr	pyrite	qtz-galena-cpy +-po vein	0.56
	DL-4pyr*	pyrite	qtz-galena-cpy +-po vein	0.77
	DL-5gal	galena	qtz-galena-cpy +-po vein	-1.56
	DL-5pyr	pyrite	qtz-galena-cpy +-po vein	0.72
Duncan Lk.	DUNC-4	galena	cal-qtz-chlorite vein in Nipissing diabase	-5.13
	DUNC-5	chalcopyrite	cal-qtz-chlorite vein in Nipissing diabase	-1.16
	DUNC-5b	chalcopyrite	cal-qtz-chlorite vein in Nipissing diabase	-1.07
	DUNC-8	galena	cal-qtz-chlorite vein in Nipissing diabase	-5.24
Gosselin	GS-1cpy	chalcopyrite	qtz-chlorite vein in sheared Nipissing diabase	0.20
	GS-2	chalcopyrite	cal-qtz-cpy vein in Nipissing diabase	0.10
	GS-5cpy	chalcopyrite	qtz-cal vein breccia with diabase fragments	0.46
	GS-5pyr	pyrite	qtz-cal vein breccia with diabase fragments	0.25

Occurrence	Sample	Mineral	Host	$\delta^{34}\text{S}$ (cdt)
	GS-6	chalcopyrite+pyrite	cal-qtz-cpy vein	0.29
Ethel	J23	chalcopyrite	cal-cpy vein in Nipissing diabase	-1.09
Johnson Lk.	JL-1	pyrite+chalcopyrite	shear zone in Nipissing diabase	2.05
	JL-1*	pyrite+chalcopyrite	shear zone in Nipissing diabase	2.41
Johnson Lk.	JM-1pyr	pyrite	pyrite vein in conglomerate	-2.71
	JM-2apyr	pyrite	pyrite vein in conglomerate	-3.19
	JM-2bpyr	pyrite	pyrite vein in conglomerate	-4.88
Merico-Ethel	ME-3a	chalcopyrite	cal-cpy-hem vein in Nipissing diabase	4.70
	ME-5	chalcopyrite	qtz-cal-cpy-hem vein in Nipissing diabase	4.84
	ME-6cpy	chalcopyrite	qtz-hem-cpy vein in Nipissing diabase	5.95
	ME-6pyr	pyrite	qtz-hem-cpy vein in Nipissing diabase	5.37
	ME-7cpy	chalcopyrite	qtz-hem-cpy vein in Nipissing diabase	5.08
	ME-7pyr	pyrite	qtz-hem-cpy vein in Nipissing diabase	4.30
	ME-8	chalcopyrite	qtz-cal-cpy-hem vein in Nipissing diabase	5.60
	ME-8a	chalcopyrite	qtz-cal-cpy-hem vein in Nipissing diabase	4.70
	ME-8cpy	chalcopyrite	qtz-cal-cpy-hem vein in Nipissing diabase	5.00
	ME-8pyr	pyrite	qtz-cal-cpy-hem vein in Nipissing diabase	5.54
	ME-9a	chalcopyrite	qtz-cal-cpy-Co vein in Nipissing diabase	5.50
	ME-12cpy	chalcopyrite	cal-qtz-cpy-hem vein in Nipissing diabase	2.26
	ME-13cpy	chalcopyrite	cal-qtz-cpy-hem vein in Nipissing diabase	5.71
	ME-18	chalco+linnaeite	cal-cpy-brn vein breccia in diabase	2.70
	ME-18b	chalco+linnaeite	cal-cpy-brn vein breccia in diabase	2.57
	ME-19a	chalcopyrite	cal-hem-cpy vein in Nipissing diabase	5.56
	ME-20cpy	chalcopyrite	cal-hem-cpy vein in Nipissing diabase	5.08
	ME-20pyr	pyrite	cal-hem-cpy vein in Nipissing diabase	4.85
	ME-23	chalcopyrite	cal-qtz-cpy-hem vein breccia	4.62
Mann Mine	MN-5	cobaltite	cal-Co-chlorite vein in Nipissing Diabase	-2.35
Beaver-Aux.	MT-1cpy	chalcopyrite	qtz-cal-cpy vein breccias	1.14
	MT-1pyr	pyrite	qtz-cal-cpy vein breccia	4.06
	MT-2b	chalcopyrite	cal-qtz-cpy-hem vein in Nipissing diabase	0.60
	MT-3	pyrite	cal-qtz-cpy-hem vein in Nip Dia	0.12

Occurrence	Sample	Mineral	Host	$\delta^{34}\text{S}$ (cdt)
	MT-3b	chalcopryrite+pyrite	cal-qtz-cpy-hem vein in Nipissing diabase	-0.19
Paramount	Para-1cpy	chalcopryrite	cal-cpy vein with potassic alteration	4.38
	Para-1cpy*	chalcopryrite	cal-cpy vein with potassic alteration	5.15
	PARA-3	chalcopryrite	cal-qtz-cpy vein	1.50
Davis	WN-3	pyrite	qtz-cal vein in qtz arenite	2.56
McLeanWatt	WN-8	pyrite	chloritized quartzite breccia	3.57
Parkin Twp.	WN-9	pyrite	conglomerate matrix	1.13
Decade	WN-11	pyrite	qtz-arenite	1.03
Fraleck	WN-13	pyrrhotite	Nipissing diabase	1.65
Fraleck East	WN-14	chalcopryrite	qtz-cal vein in diabase	2.42
	WN-15	chalcopryrite	qtz-cal vein in diabase	0.80
	WN-16	chalcopryrite	qtz-cal vein in diabase	1.15
Laura Lk.	WN-18	chalcopryrite + bornite	qtz vein within qtz arenite	0.81
	WN-19cpy	chalcopryrite	qtz vein within qtz arenite	0.64
	WN-19gal	galena	qtz vein within qtz arenite	-1.24
Dolmac	WN-20a	pyrite	qtz-cal-epidote altered Nipissing diabase	-0.56
	WN-20b	pyrite	qtz-cal-epidote altered Nipissing diabase	-1.12
Crystal	WN-22qtz	pyrite	qtz veinlets hosted in subgreenschist qtz-arenite	2.91
	WN-22seds	pyrite	subgreenschist qtz arenite	1.47
Burda	WN-23	pyrite	qtz-veined mudstone	-1.89
	WN-24cpy	chalcopryrite	mudstone with qtz-vein breccia	-1.36
	WN-24pyr	pyrite	mudstone with qtz-vein breccia	-1.50
	WN-25	chalcopryrite	qtz-cal vein hosted in mudstone	-1.32
Gordon	WN-27	pyrite	qtz vein hosted in qtz-arenite	1.97
	WN-27*	pyrite	qtz vein hosted in qtz-arenite	2.03

Note: *=Quality Control Duplicate analysis.

Appendix D: Sulphur Isotope Geothermometry

Occurrence	Sample	Mineral	$\delta^{34}\text{S}$ cdt	$\Delta\delta^{34}\text{S}$	ΔF_A $\times 10^6$	calc T
Capital	CP-4a	galena	-0.77			
	CP-4a-ch	chalcopyrite	-1.03	0.26	580000	1220.43
	CP-4cpy	chalcopyrite	-0.57			
	CP-4gal	galena	-1.63	1.06	580000	466.559
Delhi twp.	DL-1cpy	chalcopyrite	1.07			
	DL-1gal	galena	-0.92	1.99	580000	266.718
	DL-2a	chalcopyrite	0.10			
	DL-2b	galena	-1.84	1.94	580000	273.631
	DL-4a QCD	galena	-0.48			
	DL-4a QCD	chalcopyrite	1.24	1.72	580000	307.547
	DL-4cpy	chalcopyrite	0.50			
	DL-4gal	galena	-1.61	2.01	580000	264.025
	DL-4pyr	pyrite	0.56	DL-4gal - DL4pyr 2.17	1030000	415.802
	DL-4pyrQCD #1	pyrite	0.77	DL-4cpy- DL4pyrqcd 0.27	450000	1017.84
	DL-5gal	galena	-1.56			
	DL-5pyr	pyrite	0.72	2.28	1030000	398.977
Gosselin	GS-5cpy	chalcopyrite	0.46			
	GS-5pyr	pyrite	0.25	0.21	450000	1190.7
Merico-Ethel	ME-6cpy	chalcopyrite	5.95			
	ME-6pyr	pyrite	5.37	0.58	450000	607.68
	ME-7cpy	chalcopyrite	5.08			
	ME-7pyr	pyrite	4.30	0.78	450000	486.405
	ME-8	chalcopyrite	5.60			
	ME-8a	chalcopyrite	4.70	me8pyr - me8a 0.84	450000	458.775
	ME-8cpy	chalcopyrite	5.00			
	ME-8pyr	pyrite	5.54	0.54	450000	639.721

Occurrence	Sample	Mineral	$\delta^{34}\text{S}$ cdt	$\Delta\delta^{34}\text{S}$	ΔF_A $\times 10^6$	calc T
	ME-20cpy	chalcopyrite	5.08			
	ME-20pyr	pyrite	4.85	0.23	450000	1125.61
Beaver-Aux.	MT-1cpy	chalcopyrite	1.14			
	MT-1pyr	pyrite	4.06	2.92	450000	119.418
Laura Lk.	WN-19cpy	chalcopyrite	0.64			
	WN-19gal	galena	-1.24	1.88	580000	282.287
Burda	WN-24cpy	chalcopyrite	-1.36			
	WN-24pyr	pyrite	-1.50	0.14	450000	1519.69

Note: $T^2 = [(\Delta F_A \times 10^6) / \Delta\delta^{34}\text{S}] - 273.15$, where ΔF_A is the difference in fractionation factors and $\Delta\delta^{34}\text{S}$ is the difference in $\delta^{34}\text{S}$ values for the coexisting mineral pair (i.e. sphalerite-galena)

Legend

- Overburden
- Mineralized Calcite-Quartz Vein
- Brittle Fracturing and Carbonate Alteration
- Jointing and Dip Direction
- Concentric Cooling Joints
- Nipissing Diabase