Low-Sulfide PGE-Cu-Ni Mineralization From Five Prospects Within The Footwall Of The Sudbury Igneous Complex, Ontario, Canada

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Geology
University of Toronto

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Abstract

North Range low-sulfide mineralization is dominantly hosted by Sudbury breccia, with amphibole-plagioclase equilibrium metamorphic temperatures of 440 to 533 ± 75°C, produced by the SICs thermal aureole. Mineralization led to increases in the bulk halogen content of the host Sudbury breccia and the formation of Ni-enriched ferromagnesian silicates. South Range low-sulfide mineralization is typically hosted by metabasalts of the Huronian Supergroup. Garnet-biotite-plagioclase-quartz geothermobarometry produced equilibrium metamorphic conditions of 513 to 645 ± 50°C and 2.0 to 7.7 ± 1.0 kbar, probably corresponding to a late-Penokean overprint of peak Blezardian/Penokean metamorphism. Silicates associated with South Range mineralization are compositionally similar to the host rock equivalents and no alteration selvage is commonly observed due to subsequent recrystallization.

Platinum-group minerals (PGM) from the North Range comprise platinum and palladium tellurides and bismuth-tellurides, with Sb-bearing palladium bismuth-tellurides and sperrylite from the South Range. Kotulskite-sobolevskite from the North Range shows a previously unreported Ag-Pd substitution, with michenerite from irregular veinlet style mineralization
showing the substitution of Se and Sb for Bi. Two unknown PGMs were identified from the South Range, along with kotulskite-sobolevskite-sudburyite crystals displaying extensive Te-Bi-Sb solid-solution not noted before at Sudbury. A new Se-bearing variant of pilsenite was identified at McKim. Polyphase aggregates from both Ranges indicate that Bi-Te melts may have been widespread at some stage postdating the emplacement of the main magmatic sulfides.

Normalized plots for low-sulfide mineralization show enrichments in the precious and semimetals relative to contact and sharp-walled vein mineralization. This enrichment has resulted in elevated concentrations of Ag and Se in chalcopryite and Pd+Ag and Se in pentlandite from the North Range. The mass balance for North Range samples found that a significant fraction of Ag and Se occurs in sulfides with all other elements preferring discrete phases. A substantial fraction of Pd is hosted by pentlandite on the South Range, with gersdorffite also a major host despite its low abundance. The enrichments observed reflect the formation of low-sulfide mineralization from a fractionated sulfide liquid and hydrothermal fluids that have interacted with a fractionated sulfide source, and suggest that the precious and semimetals behave incompatibly with crystallizing sulfide.
Acknowledgements

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>SIC</td>
<td>Sudbury Igneous Complex</td>
</tr>
<tr>
<td>Ma</td>
<td>Mega-annum before present ($10^6$ years)</td>
</tr>
<tr>
<td>Ga</td>
<td>Giga-annum before present ($10^9$ years)</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometre (1 mm = 1000 micrometres)</td>
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<td>avg.</td>
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<td>Wave dispersive spectrometry</td>
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<td>LA-ICP-MS</td>
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<td>IPGE</td>
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<tr>
<td><em>mss</em></td>
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</tr>
<tr>
<td><em>hzss</em></td>
<td>Heazlewoodite solid solution</td>
</tr>
<tr>
<td><em>R</em></td>
<td>Pearson correlation coefficient</td>
</tr>
<tr>
<td><em>D</em></td>
<td>Partition coefficient</td>
</tr>
<tr>
<td><em>IRV</em></td>
<td>Irregular Veinlet (mineralization)</td>
</tr>
<tr>
<td><em>QCS</em></td>
<td>Quartz–carbonate–sulfide (mineralization)</td>
</tr>
</tbody>
</table>
List of Mineral Abbreviations

Mineral abbreviations are based on those outlined by The Canadian Mineralogist. Abbreviations for minerals not contained within the Canadian Mineralogist list were produced by the author.

Ccp Chalcopyrite
Mi Millerite
Pn Pentlandite
Py Pyrite
Po Pyrrhotite
Mrc Marcasite
Sp Sphalerite
Gn Galena
Gdf Gersdorffite
Nc Nickeline
Vio Violarite
Pyd Polydymite
Qtz Quartz
Act Actinolite
Mhb Magnesiohornblende
Amp Amphibole
Ep Epidote
Chl Chlorite
Pl Plagioclase
Ab Albite
An Anorthite
Olg Oligoclase
Kfs Potassium feldspar
Ttn Titanite
Grt Garnet
Ms Muscovite
Bio Biotite
Crb Carbonate
Czo Clinozoisite
Mgt Magnetite
Mch Michenerite (PdBiTe)
Mon Moncheite (PtTe2)
Sbv Sobolevskite (PdBi)
Kot Kotulskite (PdTe)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Mineral Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sud</td>
<td>Sudburyite</td>
<td>(PdSb)</td>
</tr>
<tr>
<td>Fdt</td>
<td>Froodite</td>
<td>(PdBi₂)</td>
</tr>
<tr>
<td>Spy</td>
<td>Sperrylite</td>
<td>(PtAs₂)</td>
</tr>
<tr>
<td>Hss</td>
<td>Hessite</td>
<td>(Ag₂Te)</td>
</tr>
<tr>
<td>Vln</td>
<td>Volynskite</td>
<td>(AgBiTe₂)</td>
</tr>
<tr>
<td>Mkv</td>
<td>Makovickyite</td>
<td>(Ag₁₅Bi₅₅S₉)</td>
</tr>
<tr>
<td>AuAg</td>
<td>AuAg alloy</td>
<td>(AuAg)</td>
</tr>
<tr>
<td>Tet</td>
<td>Tetradymite</td>
<td>(Bi₂Te₂S)</td>
</tr>
<tr>
<td>Prk</td>
<td>Parkerite</td>
<td>(Ni₃[Bi, Pb]₂S₂)</td>
</tr>
<tr>
<td>Tsu</td>
<td>Tsumoite</td>
<td>(BiTe)</td>
</tr>
<tr>
<td>Tbs</td>
<td>Tellurobismuthite</td>
<td>(Bi₂Te₃)</td>
</tr>
<tr>
<td>Bs</td>
<td>Bismuthinite</td>
<td>(Bi₂S₃)</td>
</tr>
<tr>
<td>Bhc</td>
<td>Bismutohauchecornite</td>
<td>(Ni₀Bi₂S₈)</td>
</tr>
<tr>
<td>Js-B</td>
<td>Joséite-B</td>
<td>(Bi₄[S, Te]₃)</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction: The Sudbury Igneous Complex and its Mineralization

1.1 The Geology and Origin of the Sudbury Igneous Complex

The Sudbury Igneous Complex (SIC); Canada, represents the end result of a 1850 ± 1Ma (Krogh et al., 1984; Davis, 2008) astrobleme event (Dietz, 1964) with subsequent late Penokean, Mazatzal-Larbradorian and Grenvillian deformation (Rousell, 1984a; Rousell et al., 1997; Bailey et al., 2004).

The impact occurred into a shallow marine basin, underlain by Archaean crystalline basement and the Paleoproterozoic submarine volcanic rocks and metasediments of the Huronian Supergroup, along the continental margin of the proposed supercontinent Nuna (Ames et al., 2008). The 30 km deep transient cavity (Mungall et al., 2004), settled to produce a multi-ring basin some 150 to 280 km in diameter (Grieve, 1994; Deutsch et al., 1995), filled with a melt sheet of lower crustal andesitic or mantle contaminated upper crustal origins (Mungall et al., 2004; Lightfoot et al., 1997). Remnants of the associated ejecta blanket have been identified in the Animikie Group; Ontario/Minnesota and Baraga Group, Marquette Range Supergroup; Michigan (Addison et al., 2005; Pufahl et al., 2007), with the latter displaying anomalous Ir concentrations similar to those identified within the proximal ejecta of the Onaping fallback breccias (Mungall et al., 2004; Ames and Farrow, 2007) and is believed consistent with an impact event.

The topographic low created by the impact was rapidly covered by the sediments of the Whitewater group, comprising the Onaping, Onwatin and Chelmsford Formations. The lower units of the basal Onaping formation are presently interpreted as representing fallback and tsunami material (Peredery, 1972; Avermann, 1994), composed as it is from a heterolithic assemblage of igneous, metamorphic and sedimentary clasts, dominantly recrystallized quartz arenite (Muir and Peredery, 1984). The clasts are enclosed within a fine grained recrystallized matrix, likely the result of quenching of the upper melt sheet during a post impact flow of
seawater into the depression. This lower layer displays abundant normal fault bound horst and graben structures, the probable result of subsidence of the layer into the underlying melt sheet, which helped to localize later fluid and melt migration. The Onaping formation grades conformably into the overlying argillaceous sediments of the Onwatin formation, which is dominated by carbonaceous and pyritic schists with localized regions of calcitization related to Zn-Pb-Cu mineralization. The upper portion of these regions is defined by increasing chert, moving into a chert breccia, the result of the aforementioned fluid venting onto the paleo-seafloor. The deposition of the formation corresponds to relatively inactive period, during which the crater depression formed a restricted anoxic basin (Rousell, 1984b). The overlying Chelmsford formation constitutes a turbidite sequence with a paleocurrent direct to the southwest (Rousell, 1984b). The sediments were sourced during the erosion of a ‘tonalitic’ terrain, most likely the crystalline Archaean basement of the North Range. The erosion of this material probably relates to post impact deformation and uplift during the late Penokean Orogeny, which also deformed the multi-ring impact crater (Riller and Schwerdtner, 1997; Riller et al., 2010). Post impact deformation was particularly strong along the South Range, with the development of a thrust duplex termed the South Range shear zone in some instances leading to over-steepening the SICs southern limb, with dips typically around 75° and locally overturned, contrasting with the 35 to 40° on the northern limb (Peredery and Morrison, 1984; Milkereit and Green, 1992).

The heat imparted into the surround country rock and the overlying fill (i.e. the Whitewater Group), from a crystallizing melt sheet has been observed to drive hydrothermal fluid circulation associated with a number of impact structures (Hagerty and Newsom, 2003; Hode et al., 2003 Pirajno et al., 2003; Zürcher and Kring, 2004; Osinski, 2005; Sandford, 2005), with Sudbury being no exception. Observations from the Onaping formation have identified consistent variations in alteration and associated Zn-Pb-Cu mineralization, coincident with 1848 +3.8/-1.8 Ma titanite associated with hydrothermal circulation, which penetrates some 2 km of the crater-filling Onaping Formation (Ames et al., 1998, 2006). The footwall lithologies are also observed to display alteration that extends 1 km into the footwall, commonly associated with bodies of Sudbury breccia and Cu-Ni-PGE mineralization. Fluid inclusion analysis has revealed a range of fluids from pre-impact, SIC, Cu-Ni-PGE and post impact sources (Farrow and Watkinson, 1992, 1996, 1997; Marshall et al., 1999; Molnar et al., 1997, 1999, 2001a, 2001b, Pentek et al., 2008).
The longevity of the circulation established is uncertain with models ranging from < 10,000 to 800,000 years (Cathles et al., 1997).

1.2 The Metamorphic History of the Sudbury Igneous Complex

The footwall of the SIC is broadly separated into two provinces, the Archean crystalline basement of the Superior Province to the north and the Paleoproterozoic Southern Province to the south.

The footwall lithologies of the North Range are dominated by the felsic crystalline rocks of the Levack Gneiss Complex and the Cartier Batholith. Formation of the Levack Gneiss occurred between 2711 and 2647 Ma (Ames et al., 2008), with peak granulite facies metamorphism producing a plagioclase + quartz + clinopyroxene + hornblende + orthopyroxene + biotite assemblage between 2647 and 2642 Ma (Ames et al., 2008), at a depth of 21 to 28 km (6 to 8 kbar) and temperatures of 750 to 800 °C (James et al., 1992). Cartier batholith formation is timed to 2642 ± 1 Ma and resulted from significant partial melting of the gneiss complex (Meldrum et al., 1997). Emplacement of the Cartier Batholith was coeval with the uplift of the Levack Gneiss Complex, which was complete before the intrusion of 2473 ± 16 Ma Matachewan diabase dykes (Ames et al., 2008). Meldrum et al. (1997) postulated that North Range diorites and monzogranites containing ≥ 30 % mafic phases may represent the restite portion of the migmatite complex. Where in contact with the Cartier Granite, the Levack Gneiss metamorphic assemblage displays a regression to a 2 to 3 kbar and 500 to 550 °C amphibolite assemblage (Meldrum et al., 1997). The effects of regional metamorphism upon the North Range of the Sudbury structure have on the whole received little study. The Levack Gneiss Complex and Cartier Granite have undergone pervasive retrograde metamorphism, to a chlorite + actinolite + epidote + quartz + albite assemblage (i.e. greenschist facies), often attributed to the Penokean Orogeny (Rousell, 1975; Card, 1978; Fleet et al., 1987; James et al., 1992). There is however no strong evidence to constrain timing, and as such it must be considered the combined result of the Blezardian, Penokean, Yavapai–Mazatzal (Killarnean) orogenies.
Although dominated by the felsic Archean basement, the northwest portion of the North Range contains a region of Huronian outliers situated within a band between the northern portion of the Foy offset to the east and the Ministic offset to the west, mirroring the basal contact of the SIC. These outliers were initially interpreted as having resulted from the preservation of the overlying Huronian sediments as part of a downthrown fault block during crater collapse (Dressler, 1984; Peredery and Morrison, 1984). A growth fault controlled component was also proposed by Rousell and Long, (1998), with the outliers considered the result of syn-depositional faulting during basin development, which was subsequently tectonically modified. Alternatively the outliers are the result of syncline formation along the margins of doming, concurrent with emplacement of the Creighton granite (Riller and Schwerdtner, 1997). The Huronian outliers were extensively studied by Mungall and Hanley (2004) who noted no systematic facies change from northwest to southeast, inconsistent with models proposing formation within half-grabens. The northwest margins of the larger outliers were observed to have acted as detachment surfaces, which in places truncate bedding and fold axes, along regional faults concentric to the SIC. This is consistent with preservation along ring faults during crater collapse, however it is inconsistent with the syncline and homocline forms of the outliers. It is therefore clear that deformation of the footwall must have occurred before the impact event, with a substantial Blezardian component (Riller and Schwerdtner, 1997; Mungall and Hanley, 2004).

The limitations of Penokean tectonism are also apparent within the unfoliated carbonaceous argillite clasts of the Onaping Formation fallback breccia (Bunch et al., 1999; Mungall and Hanley, 2004, references therein). These clasts are part of argillaceous sequence continuing into the overlying Onwatin Formation. Both clasts and overlying carbonaceous argillites are interpreted as correlating with the Virginia Formation; Minnesota, which was dated by Ripley et al. (2001) to approximately 1850 Ma. The lack of deformation is also reflected in the 1873 ± 1.3 Ma (Fralick et al., 2002) Gunflint Formation; Michigan and clasts within the overlying < 1879 Ma to > 1836 Ma (Addison et al., 2005) ejecta and tsunami sediments in the same area resulting from the Sudbury impact. The lack of deformation would imply that Penokean tectonics were not advanced during deposition and lithification, suggesting that the folding displayed across the Sudbury footwall pre-dates the Penokean Orogeny.
The Southern Province is dominantly composed of a Huronian metavolcanic–metasedimentary sequence interpreted as a complete Wilson Cycle (Young et al., 2001), with lesser Paleoproterozoic felsic plutonic intrusions and several generations of diabase dykes. The Southern Province is bounded by the Grenville Front Tectonic Zone (GFTZ) along its southern margin and the Superior Province to its north. The Huronian Supergroup represents a sequence of rift related metavolcanic rocks grading into a passive marginal sequence deposited along the southern flank of proposed supercontinent Nuna (Ames et al., 2008). The contact between the two subprovinces is on the whole tectonically inactive but tightly folded unconformity, although it has been activated by the South Range Shear Zone (SRSZ) within the SIC’s western footwall. Metamorphic grade across the Southern Province increases to the south and is typically higher south of the Murray Fault (Card, 1978). The South Range footwall falls within the amphibolite-facies staurolite zone and the SW footwall within the middle–to upper greenschist facies garnet-chloritoid zone (Card, 1978). Peak metamorphism was considered by Riller and Schwerdtner (1997) to have been achieved during the 2.4 to 2.2 Ga Blezardian tectonic pulse, with foliations within the Creighton and Murray plutons and the host Huronian package consistent with overturning of the metavolcanic–metasedimentary sequence. Analysis of ~ 2.2 Ga Nipissing gabbro (Fairbairn et al., 1969) using "Thermobarometry With Estimation of Equilibrium State" (TWEEQU) software, indicated P–T conditions of 3.1 ± 2.5 kbar and 417 ± 60 °C for rocks north of the Murray Fault and 4.3 ± 0.8 kbar and 580 ± 60 °C for those to the south of it, safely within greenschist and amphibolite facies respectively (Easton, 2000; reference therein). These values are consistent with burial depth and temperature estimates of Zolnai et al. (1984) and Piercey (2006).

Observations of retrograde greenschist assemblages (albite + actinolite + chlorite + epidote/clinozoisite) after hornblende have been interpreted as Penokean overprinting of the earlier Blezardian metamorphism and are consistent with ductile strain fabrics of the SRSZ developed under greenschist facies (Riller and Schwerdtner, 1997). \(^{40}\text{Ar}^{39}\text{Ar}\) analysis of Huronian material by Piercey (2006) failed to display any significant resetting associated with 1.88 to 1.83 Ga Penokean metamorphism. This seems counterintuitive given the Penokean related deformation of the SIC, South Range, SRSZ development and reactivation of the Murray fault (Riller et al., 1999). The lack of geochronologically definable retrograde alteration suggests that either the regional effects of the Penokean Orogeny were not as strong within the eastern portion
of the orogen as they were to its west, that Penokean metamorphism was heterogeneously distributed, or that the effects of the Penokean Orogeny within the Southern Province have themselves been overprinted. The latter suggestion is backed by biotite data from the McKim and Ramsey Lake Formations located north of the Murray fault, which indicates crystallization between $1677 \pm 2$ Ma and $1714 \pm 5$ Ma respectively, consistent with mid Yavapai–Mazatzal Orogeny greenschist facies metamorphism (Piercey, 2006) and consistent with $1658 \pm 68$ Ma $^{207}$Pb/$^{206}$Pb dating for titanite margins from the Thayer Lindsley mine (Bailey et al., 2004). The biotite dates are also coeval with recrystallization associated with Paleoproterozoic felsic intrusions, of which the Cutler batholith is the largest. Monazites proximal to these intrusions yielded a range of ages between $1775 \pm 8$ Ma and $1714 \pm 11$ Ma concordant with the associated plutonics, although Cannon (1970) interpreted any intrusion-related metamorphism as not wholly related to static heating (Piercey, 2006; references therein). The offset of Sudbury diabase dykes dating to 1235 Ma (Fueten and Redmond, 1997, references therein) by the Murray Fault, indicate that dextral movement occurred post emplacement. Reactivation of the fault likely resulted from Grenvillian tectonics, however $^{40}$Ar/$^{39}$Ar analysis of South Range lithologies failed to identify any resetting/recrystallization of minerals c.a. 1000 Ma (Piercey, 2006).

The emplacement of the SIC led to the formation of a ~2 km wide metamorphic aureole, which is best preserved along the North Range. The initial classification was made by Dressler (1984) who identified a 1.4 km wide aureole comprising pyroxene hornfels, hornblende hornfels and plagioclase recrystallization (albite–epidote hornfels) zones. The aureole was redefined by Boast and Spray (2006) who outlined zones (with increasing distance from the basal contact) of partial melting (25 m), pyroxene hornfels (200 m), hornblende hornfels (900 m) and albite–epidote hornfels (1000 m). Temperatures for the aureoles (using Dressler, 1984) are defined according to Winkler (1967) with albite–epidote hornfels facies metamorphism beginning at temperatures < 400 °C, hornblende hornfels at 520 to 540 ± 20 °C and pyroxene hornfels at 580 to 630 ± 20 °C. The contact metamorphic aureole along the SIC’s South Range has been lost due to subsequent metamorphism, although Thomson et al. (1985) claimed that relict green–brown hornblende cores within crystals from the Elsie Mountain formation, near the Kirkwood Mine, represented the remnants of the hornblende hornfels zone.
1.3 Pseudotachylite Genesis

Pseudotachylite breccias are the most important hosts of sharp-walled vein and low-sulfide PGE mineralization at Sudbury, with the exception of the Podolsky property where a significant portion of the 'hybrid' mineralization is also hosted by grey gabbro. The formation of pseudotachylite breccias within the footwall of the SIC is believed to have resulted from either cataclasis caused by the milling of soft minerals during fault movement, frictional melting along faults during the transient crater collapse or shockwave related heating (Reimold, 1995; Dressler and Reimold, 2001; Melosh, 2005; Reimold and Gibson, 2005).

Classification of pseudotachylite within the Sudbury footwall has produced several varying systems. Initial categorization was based on wall rock clasts within the pseudotachylite with Speers (1957) separating Sudbury breccias into in situ varieties, containing clasts composed primarily of proximal wall rock and injection which contains fragments foreign to the host rock. The study of Dressler (1984) and review by Peredery and Morrison (1984) identified three distinct Sudbury breccia types, 1) massive breccias resulting from shock wave induced ‘milling’ of footwall rocks, 2) igneous looking matrix breccia, interpreted as the result of partial to complete melting due to heating during ‘milling’ and 3) flow banded breccia, now classified as ductile margin Sudbury breccia, which displays flow lines and contains foreign clasts suggesting that it was generated in response to fault movement during transient crater collapse. Sudbury breccia was again reclassified by Spray (1998), who defined two distinct Sudbury breccia types 1) early S-type breccias within the inner shock zone of the impact, occurring as randomly distributed pseudotachylite veins of < 2 mm generated during the contact and compression stage of the impact event, and 2) E-type pseudotachylites comprising > 1 cm to 1 km belts formed during extreme comminution along fault walls during collapse of the transient cavity. The more recent classification of Rousell et al. (2003) identified three Sudbury breccia types: 1) Clastic Sudbury breccia is predominant in the South Range and is characterised by flow-surface structures i.e. weak compositional banding parallel to the breccia margins, with pseudotachylite hosting rounded wall-rock clasts, 2) pseudotachylite Sudbury breccia, which mainly occurs within the crystalline basement of the North Range and is characterised by wall-rock clasts within a black, aphanitic matrix formed by comminution and frictional melting, and 3)
microcrystalline Sudbury breccia, located within a 1.2 km zone along the basal contact of the SIC in which the Sudbury breccia matrix has recrystallized or locally melted.

Major element and REE studies of pseudotachylite indicate that it contains a significant host rock component (Randall, 2004). Lafrance et al. (2005) proposed that approximately 20% plagioclase and 10% would have had to be removed in order to produce the observed intermediate pseudotachylite composition from an average tonalitic footwall gneiss precursor. Thompson and Spray (1996) hypothesized that these minerals may have been retained within resistant mono or polycrystalline clasts, commonly observed within pseudotachylite (Dressler, 1985; McCormick et al., 2002; Lafrance et al., 2008), which were removed from the breccia due to their diameter, as the pseudotachylite progressed from broad to narrow conduits. This model is not in agreement with the generally homogeneous composition of the Sudbury pseudotachylites, suggesting that the mafic component must have been sourced from an alternative footwall lithology. Initial predictions by Thompson and Spray (1996) proposed addition from diabasic material, however the dissociation of P_2O_5 values compared to those of pseudotachylite indicate that this cannot be the case (Lafrance et al., 2008). Major element vs. SiO_2 plots from Lafrance et al. (2008) indicate a linear compositional trend between tonalitic and dioritic gneiss, with pseudotachylite situated between these end-members.

The cataclasis model proposes fracture, comminution and possible melting of lower temperature phases (chlorite, actinolite, hornblende and biotite) along fault planes, with resistant minerals (quartz, plagioclase feldspar and potassium feldspar) preferentially retained in clasts, thus producing a more mafic breccia matrix (Spray, 1988; 1992; 1995; Magloughlin and Spray, 1992). Initial predictions of cataclasis proposed comminution of phases without melting, although it has become clear that heating during the ‘milling’ process would likely result in partial to complete melting (Spray, 1995; Thompson and Spray, 1996; Rousell et al., 2003). Frictional heating was proposed by Thompson and Spray (1996) to have exceeded the melting point of the lower temperature phases, with the melt crystallizing a quartz + phlogopite + sanidine + labradorite assemblage, which recrystallized to the pseudotachylite assemblage and textures commonly observed (Dressler, 1984). The effects of melt formation and the associated reduction in the shear forces imparted into the wall rocks and mineral grains due to its lubricating effect remain
unconstrained and may well be contrary to the formation of substantial thickness of pseudotachylite.

Genesis of shock induced melts is possible if the energy released during the compression and decompression stages of crater formation is in excess of the melting point of the target material (Reimold, 1995; 1998; Kenkmann et al., 2000). Complete anatexis of the footwall is avoided due to heterogeneous distribution of shock pressure (Gibson and Reimold, 2005). The genesis of such melts is commonly accompanied by the formation of high pressure minerals, specifically coesite and stishovite (Martini, 1978; 1991) within terrestrial material, along with ringwoodite and majorite within chondrites (Langenhorst and Poirier, 2000; Chen et al., 1996; 2003), however the high pressure SiO\textsubscript{2} polymorphs are not observed at Sudbury. Furthermore pseudotachylite analysis by Lafrance et al. (2008) identified shear fabrics along the margins of ductile margin breccia, a probable indicator of fault related formation. Analysis of shock veins from the Catherwood and Tenham meteorites and the Vredefort impact structure by Spray (1999) and references therein, identified a slip component associated with shock induced melt veins, suggesting that the two are not mutually exclusive. The formation of pseudotachylite within the Sudbury footwall is at present best explained by cataclasism and frictional melting along major fault zones related to impact processes, with a possible minor shock melt constituent. Breccia bodies appear to exploit pre-existing weaknesses, chiefly faults, dykes, lithological contacts and metamorphic fabrics along which slip could occur.

1.4 Mineralization of the Sudbury Igneous Complex

The Sudbury Igneous Complex hosts the world’s third largest collection of deposits of the platinum group elements (PGE), exceeded only by the Bushveld Complex of South Africa and the Noril’sk Talaekh intrusions in Russia. Total production and reserves are around 1500 Mt, grading 1% Ni, 1% Cu and 1g/t Pt + Pd (Farrow and Lightfoot, 2002) distributed across massive sulfide bodies at the contact (Ni-Co-IPGE), within the footwall (Cu-Ni-PPGE-Au) and the quartz-diorite offset dykes (Ni-Cu-PGE) (Coats and Snajdr, 1984; Morrison et al., 1994).

The contact and offset sulfide ores of the Sudbury Igneous Complex are nearly universally agreed to be of magmatic origin. The cause of sulfur saturation of the silicate melt sheet remains
uncertain, although mass balance calculations by Lightfoot et al. (2001) indicate that the melt sheet possessed enough Cu and Ni to satisfy the formation of the known mineral deposits without the need for external sources. Such a hypothesis is consistent with δ³⁴S data from Thode et al. (1962), which indicated no sulfur input from footwall lithologies. Sulfur saturation is believed to have occurred early (Lightfoot et al., 2001), with the majority of sulfides rapidly settling out under gravity into fault controlled topographic lows in the crater floor termed embayments and secondary terraces (Morrison, 1984). Separation of a sulfide liquid continued throughout the crystallization of the Main Mass. Mungall and Su (2005) and Chung and Mungall (2009) have argued that some sulfide can migrate through a cumulate layer, down to near solidus conditions, providing certain conditions are met.

The contact deposits, commonly hosted within sublayer norite and footwall breccia close to the crater floor are interpreted to have formed as a Fe-Ni monosulfide solid solution (\textit{mss}) crystallized from the parent sulfide melt around 1191 °C (Craig and Kullerud, 1969), with pentlandite crystallizing through exsolution from \textit{mss} and the reaction \textit{mss} + (Ni, Fe)$_{3-x}$S$_2$ (\textit{hzss}) at 610 °C (Craig and Kullerud, 1969). The extensive experimental data available (Keays and Crocket, 1970; Naldrett et al., 1982; Barnes and Naldrett, 1986; Naldrett and Barnes, 1986; Li and Naldrett, 1994; Li et al., 1996; Mungall et al., 2005) consistently display the preference of Co, Ir, Os, Ru, Rh and at reduced temperatures Ni (≤ 950 °C, approaching the sulfide liquid solidus) for the \textit{mss} fraction, with some \textit{fS}$_2$ control (Barnes et al., 1997; Mungall et al., 2005). This pattern is matched by the contact ores, which have a pyrrhotite >> pentlandite > chalcopyrite assemblage (Naldrett, 1984), with Cu/Ni ratios of ~ 0.7 and total precious metal (TPM) of < 1 g/t (Naldrett and Pessaran, 1992; Farrow and Lightfoot, 2002).

The quartz-diorite hosted offset dikes represent an early sample of the silicate melt (Tuchscherer and Spray, 2002), with the sulfide-free chilled margins indicating that initial emplacement occurred before sulfur saturation (Lightfoot et al., 2001). Separation of dyke lithologies into inclusion-free and inclusion-bearing quartz-diorite, the latter containing quartz-diorite clasts, indicates two phases of emplacement, although the similarities in bulk chemistry indicate that these pulses were temporally closely spaced (Tuchscherer and Spray, 2002). Mineralization occurs up to 7 km from the basal contact of the SIC and is typically limited to inclusion-bearing quartz diorite. The limited ability of the residual sulfide liquid that formed during \textit{mss}...
crystallization to migrate produced ores with a higher Cu and total precious metal content than contact ores (Cu/Ni ratios = 1.5 to 2, TPM > 2.5 g/t), although Naldrett and Duke (1980) noted an increase in Cu, Ni, Pt, Pd, Au and Ag and associated decreases in Ir, Ru and Rh with increasing distance from the SIC, suggesting some migration of residual sulfide liquid into distal portions of the offset dykes.

The origin of the sharp-walled chalcopyrite + pentlandite + pyrrhotite ± cubanite ± bornite ± millerite deposits of the footwall is contentious. Deposits comprise massive sulfide veins < 1 cm to > 10 m thick, presenting sharp contacts with the host lithology and commonly occurring as stacked sets oriented sub-parallel to the basal contact of the SIC (Farrow and Lightfoot, 2002). Veins display a Cu/Ni ratio of > 6.5 and a TPM content of > 7 g/t. The elevations in elements that are incompatible with mss, i.e., Cu, Pt, Pd and Au (Craig and Kullerud, 1969; Distler, 1977; Fleet and Pan, 1994; Ballhaus et al., 2001; Mungall et al., 2005) has led to the hypothesis that they represent iss-mss-hzss cumulates crystallized from a residual sulfide liquid sourced from the contact (Mungall, 2007). Such a migration was likely aided by the development of porous zones due to fault movement within the footwall, typified by the presence of Sudbury breccia and the high Cu content of the residual sulfide liquid which may have enhanced its wetting properties (Ebel and Naldrett, 1996). The permeability of such zones would have been increased by the development of fractures in response to crater settling and the opening up of space along Sudbury breccia clast-matrix contacts due to contraction during cooling. A purely magmatic origin has been questioned by several works that note the presence of a precious-metal mineral-bearing hydrous alteration selvage and halo surrounding veins, and the occurrence of saline fluid inclusions that homogenize between 300 to 500 °C with a broad range of salinities of ~ 45 wt % NaCl equivalent (Farrow and Watkinson, 1992, 1996; Molnár et al., 1997, 1999, 2001; Marshall et al., 1999; Watkinson, 1999; Molnár and Watkinson, 2001). Such models propose that base- and precious metals were scavenged from contact mineralization by aqueous fluids, with Cu, PPGEs and Au preferentially entering solution. The need for a non-magmatic, saline fluid is contradicted by experimental and fluid inclusions studies which suggest that the residual sulfide liquid could contain sufficient volatiles, including H2O and halogens, to form a late stage base and precious metal bearing highly saline fluid during fractionation (Mungall and Brenan, 2003). Such a fluid would enter the surrounding rock inducing the formation of hydrous ferromagnesian silicates and the precipitation of disseminated sulfide and precious metal minerals (Mungall and
Brenan, 2003; Wykes and Mayrogenes, 2005; Hanley at al., 2005b). The source of the alkali metals, the presence of which is inferred through the formation of Na, Ca, K and Mg halides in fluid inclusions associated with mineralization remains uncertain. Hanley at al., (2005b) proposed that these metals were also sourced from the sulfide liquid, with initially low levels being enriched through fractional crystallization until saturation is achieved. These metals may also have been provided by a non-magmatic hydrothermal fluid within the footwall, whose circulation was driven by heat from crystalling sulfide veins and/or the SIC. It is therefore unsurprising that at present a model combining both magmatic and non-magmatic hydrothermal processes offers the simplest explanation for the observed geochemical and mineralogical signatures associated with sharp-walled vein mineralization.

South Range mineralization (contact, footwall and offset ores) commonly displays a degree of tectonic redistribution, recrystallization and hydrothermal alteration, enhanced by post-mineralization orogenic events (Ames and Farrow, 2007; Bailey et al., 2006; Molnar and Watkinson, 2001; Carter et al., 2001, Hecht et al., 2010). The South Range also contains an additional deposit type termed breccia belt deposits which is typified by the Frood-Stobie mine. (Farrow and Lightfoot, 2002). The deposit was initially classified as an offset dyke (Grant and Bite, 1984), however, reclassification of the belt followed the realization the inclusion-bearing quartz-diorite comprises only 10% of the belt's lithologies, with Sudbury breccia constituting the bulk of the downward tapering body. At lower levels these lithologies are overprinted by a quartz-dominated assemblage, termed the siliceous zone, at the termination (Farrow and Lightfoot, 2002). The breccia hosted mineralization displays systematic variations in Cu/Ni and PGE tenor, both increasing with depth.

1.5 Low-Sulfide Mineralization – Our Current Knowledge

A strict classification of material as definitively low-sulfide or ‘hybrid’ is at present impossible due to the limited published dataset available. Farrow et al. (2005) established the notion of a ‘threshold interval’ to help define these mineralizing styles. Low-sulfide mineralization is defined for suites within which greater than 50% of samples (separated based on their S content) possess economic concentrations of Pt and Pd (set at > 5 g/t). When applied to the low-sulfide
PM Zone mineralization the threshold interval occurred within samples displaying an S content of ≥ 1 to < 2 wt %. This is significantly different from the sharp-walled vein mineralization of the 700 Zone where the threshold interval occurred within samples bearing ≥ 20 wt % S. The hybrid mineralization of the Podolsky North and 2000 Zone fell within the interval separating low-sulfide from sharp-walled styles, with threshold values from material containing ≥ 5 to < 10 wt % S and ≥ 10 to < 20 wt % S respectively. The use of a threshold value thereby allows us to define low-sulfide mineralization as zones in which greater than 50 % of economic material (samples containing > 5 g/t Pt+Pd) is associated with samples containing < 2 wt % S. If this threshold value is associated with samples containing ≥ 20 wt % S the mineralization is sharp-walled in nature, with thresholds associated with material containing between > 2 and < 20 wt % S classified as hybrid. It must be remembered however that this classification is based on data from a single deposit and may not be representative.

The first identified economic occurrence of low-sulfide mineralization was made at the PM Zone, McCreedy West mine, with indicated resources of 2.25 Mt, at 1.11 % Cu, 0.26 % Ni, 2.12 g/t Pt, 2.68 g/t Pd and 0.78 g/t Au (Farrow et al., 2005). The host Sudbury breccia was already known to contain mineralization of the sharp-walled vein type in the 700 Zone, up dip from the PM Zone. The low-sulfide mineralization of the PM Zone is contained within a region some 40 m thick, dipping at approximately 35° to the SE (i.e. roughly parallel to the lower contact of the SIC), with mineralization that is superficially similar to sharp-walled vein systems, containing sulfide veins, typically < 30 cm wide, dipping at 40 to 50° to the SE (Farrow et al., 2005). The PM Zone is different, however, in having considerably lower sulfide abundances (< 5 modal %) and an increased range of economic mineralizing styles, with PGEs not only associated with chalcopyrite dominated veins and stringers, but also with disseminations. Cu/Ni ratios between styles and across the mineralized intersection are inconsistent, however Pt:Pd ratios decrease from near 1:1 for material with < 1 modal % sulfide, through to 2:3 within sulfide veins (Farrow et al., 2005). The relationship between the PM Zone and the contact and sharp-walled vein systems of the McCreedy West mine remains uncertain, however the spatial proximity and location within the same Sudbury breccia body would suggest that the low-sulfide mineralization is part of a larger scale deposit system including both types.
Advanced prospects for low-sulfide and hybrid mineralization remain limited to the North Range, where PGE-Cu-Ni mineralisation has been identified at the South Zone and Broken Hammer Zone, in Wisner Township (Wallbridge Mining Xstrata joint venture) and the 2000 and Podolsky North Zones, on the Whistle-Parkin offset dyke (QuadraFNX Mining; Murphy and Spray, 2002).

Economic mineralization in the Whistle-Parkin area was formerly limited to the Ni-Cu Whistle mine, hosted within the sublayer of the 250 m wide Whistle embayment. Mineralization in both the 2000 zone and the Podolsky North zones comprises ‘breccia’ veins, stringers and disseminations as well as typical sharp-walled veins at the 2000 Zone. A significant portion of the mineralization is hosted within inclusion-bearing quartz diorite and metabreccia both containing clasts of footwall lithologies between 1 cm and tens of metres in size, with lesser fractions in 'grey gabbro' and recrystallized gneiss (Farrow et al., 2005). Both zones contain volumes of rock in which PGE concentrations are not dependant on sulfide abundance, but there are also sulfide veins akin to ‘sharp-walled’ systems, so both zones are therefore classified as ‘hybrid’ in character (Farrow et al., 2005).

Mineralization at the Broken Hammer and South Zones, Wisner Township, is again dominantly hosted within footwall-hosted Sudbury breccia. The zones display some variation of mineralizing styles. The Broken Hammer Zone contains sulfide veins ranging from several centimetres up to the 1m wide ‘Big Boy’ vein, whereas the South Zone presents sparse sulfide veins with widths not exceeding 3 cm. (Péntek et al., 2008). Proportionally the South Zone mineralization appears dominated by disseminated-replacement sulfides hosted within Sudbury breccia and footwall rocks. Mineralisation is dominated by disseminated chalcopyrite and associated alteration aligned due to the exploitation of pre-existing conduits i.e. fracture sets. Outcrop maps of the Broken Hammer property suggest that mineralization is dominated by disseminations proximal to sulfide veins. Sulfide bearing quartz + epidote + chlorite ± carbonate silicate veins 0.5 to 3 cm in width were observed at both zones (Péntek et al., 2008).

Alteration assemblages from the Broken Hammer and South Zones varied between mineralizing styles and were described in detail by Péntek et al. (2008). Sulfide veins are bounded by alteration zones several cm in diameter comprising an assemblage of epidote + greenalite +
actinolite + biotite + chlorite. Disseminated-replacement mineralization occurring both proximal to and independently of sulfide veins is associated with epidote and minor greenalite and actinolite alteration. Biotite is typically absent from the alteration assemblage, however biotite increases in abundance with proximity to sulfide veins, in response to the heat that they impart into the wall-rock. Silicate-quartz dominated veins are associated with alteration of variable intensities, ranging from unmodified host rocks, through to marginal epidote development grading locally into selvages of chlorite + epidote up to 5 cm wide.

Platinum group minerals (PGM) described from the PM Zone and advanced prospects (Farrow et al., 2005; Pénét et al., 2008) were consistent with the results of previous studies of the North Range (Cabri and Laflamme, 1976; Farrow and Watkinson, 1997), including moncheite (PtTe₂)–merenskyite (PdTe₂)–melonite (NiTe₂) solid solutions, maslovite (PtBiTe)–michenerite (PdBiTe) solid solutions and sperrylite (PtAs₂), with lesser froodite (PdBi₂) plumbopalladinite (Pd₃Pb₂), kotulskite (PdTe), sopcheite (Ag₄Pd₃Te₄) and an unknown CuPdBiS₃ phase from Broken Hammer only.

The alteration assemblage associated with low-sulfide mineralization from the Wisner and Frost Lake properties (Wallbridge Mining Company) was investigated by Tuba et al. (2010). Their study noted that both mineralization and alteration displays a strong structural control, with the consistent northwest-southeast orientation taken as clear evidence that the extensional veins (unmineralized amphibole, quartz-epidote and quartz veins) and mineralization (sulfide veins and disseminated zones) observed were 1) syntectonic, and 2) both formed by hydrothermal circulation driven by the SIC. The study also attributed the presence of highly saline, polyphase fluid inclusions within unmineralized epidote-quartz veins to the same mechanism. Analysis of amphibole from both barren and mineralized samples identified a consistent trend from Mg and K enriched cores with a reduced Fe²⁺/Fe³⁺ ratio, through to Fe and Ni enriched margins, interpreted as having resulted from two distinct hydrothermal fluids. Observations identified S-shaped sulfide veins within Sudbury breccia and deformed footwall granophyre within low-sulfide zones, with the irregular nature proposed to be the result of deposition within a ductile environment. This is to be contrasted with the deposition of extensional veins and disseminated zones that could only have occurred within a brittle regime. It was therefore concluded that an initial plastic phase was followed by the opening of brittle fractures during crater settling, with
additional vein orientations and reactivation of existing veins occurring during the latter stages of crater settling and subsequent regional metamorphism.

To date three studies of low-sulfide mineralization (Farrow et al., 2005; Péntek et al., 2008; Tuba et al., 2010) have been published with all presenting hydrothermal genesis models. Farrow et al. (2005) interpreted the high Pt/Pd ratio displayed by mineralization with a low sulfide content to be the result of a cooling and evolving hydrothermal fluid preferentially depositing Pt due to its lower solubility in saline fluids when compared to Pd. The remaining fluid, now with a reduced Pt/Pd ratio went on to form sharp-walled vein mineralization, which represent the 'freezing' of the system due to the decompression of the footwall during tectonic readjustment causing the formation of dilatational features. Portions of the footwall where circulation of these fluids overlapped produced hybrid mineralization. The remaining studies (Péntek et al., 2008; Tuba et al., 2010) favour this model, with Péntek et al. (2008) concluding that the similarities in the sulfides, gangue silicates and fluid inclusion populations between massive sulfide veins and disseminated mineralization indicates that all low-sulfide mineralization is hydrothermal in origin.
Chapter 2
Properties and Mineralizing Styles

Drill core was sampled from all five low-sulfide prospects, two from the North Range (Levack North and Wisner), one from the East Range (Capre) and two from the South Range (Denison and McKim). Drill core samples were selected in order to define: 1) mineralizing styles, 2) footwall lithologies, 3) barren hydrothermal veins, 4) alteration assemblages, 5) metamorphic conditions and 6) precious metal mineral minerals. Core was logged by the author using assay data to identify PGE-bearing material. A running tally of different mineralizing styles and the number of times they were observed was maintained for each borehole. Mapping was only undertaken at the Wisner property as it was the only stripped area available at the time. The Denison and Capre properties were visited by the author to view the surface exposure available. Descriptions of the property geology were taken from Vale-Lonmin reports and published sources. All petrographic observations were made by the author.

2.1 North Range Properties

The Sudbury Igneous Complex is typically separated into three distinct portions termed the North, South and East Ranges, given their positions along the margins of the SIC. The Capre property falls along the SIC’s East Range, however here it has been grouped with the North Range (Levack North and Wisner) properties due to similarities in mineralizing styles and footwall lithologies (Figure 2.1).

2.1.1 Levack North

The Levack North property sits within the footwall of the Onaping-Levak embayment, a trough 8 km long striking northeast and dipping southeast at between 40 to 45° (Figure 2.1). The mineralized belt hosts a number of present and past-producing contact and footwall deposits, particularly the hanging wall hosted Craig–Onaping contact deposit and the contact–footwall systems of the McCreedy West, Strathcona mines and Levack Mines.
The footwall is dominated by 2647 ± 2 Ma (Krogh et al., 1984) undifferentiated plagioclase dominated ‘granodioritic–tonalitic’ gneiss of the Levack Complex (Figure 2.2). This lithology displays a weak to well-defined gneissosity, with leucosomes containing 0.25 to 2 cm wide quartz mosaics, displaying 50 to 400 μm elongate, sutured crystals with isolated planar deformation features, constituting 10 to 40 % of the quartzo-feldspathic bands. The remaining fraction is dominated by abundant granoblastic (50 to 100 μm) plagioclase and a lesser potassium feldspar component making up around 20 % of these zones. The feldspar rich portions have undergone moderate to strong pervasive sericitization combined with abundant microcrystalline Fe-oxides producing a weak to strong pink hue in hand specimen.

Figure 2.1. Schematic map of the Sudbury Igneous Complex (SIC) and bedrock geology, with property locations and selected structural features (modified from Ames et al., 2005).
Melanosomes are typically discontinuous and no wider that 5 mm, with bands dominated by 100 to 750 μm actinolite aggregates, likely resulting from the retrograde uralitic alteration of pyroxene (Legault et al., 2003). Alteration occurred at some time after peak granulite facies metamorphism, which occurred between 2647 and 2645 +7/-4 Ma, at depths of 21 to 28 km (Ames et al., 2008). Uralite bodies commonly display a chlorite + epidote + magnetite dominated rind, resulting from further retrograde action. The uralite domains are generally limited to the mafic bands, although 5 to 10% of aggregates are hosted within quartzo-feldspathic portions. The majority of uralite free mafic bands are dominated by 80% chlorite, with 15% epidote, 5% magnetite with accessory titanite and apatite. Biotite is commonly not observed and where present is nearly totally chloritized with associated fine grained titanomagnetite located along relict cleavage planes.

Mafic dominated domains within the larger gneiss package typically are no more than 2 m in thickness and are termed mafic gneiss. Where unaltered this material contains abundant biotite, constituting 60 to 80% of the sample, separating domains composed of mosaic quartz and granoblastic feldspar, comparable with the felsic gneiss hosted equivalents. The origin of these mafic zones remains unclear, with possible mechanisms ranging from formation due to retention of restite mafic phases during the formation of the Cartier granite through to pelitic sediments within the protolith sequence. The gneissosity was observed to be weak and commonly only defined by the orientation and fabric of felsic units bounding its upper and lower contacts. Alteration is dominated by chloritization of biotite and the development of sporadic uralite after pyroxene, the former typically present due to retrograde alteration, although the intensity of chlorite alteration increased in response to proximity to sulfide and barren quartz + epidote veins.

The majority of unfoliated quartzo-feldspathic material was classified as ‘granite’. These samples are typified by the presence of coarser potassium feldspar crystals, within a groundmass dominated by equigranular quartz and plagioclase. The granitic material was further distinguished from gneissic samples due to the development of granophyric bodies not exceeding 750 μm in size. These can be distinguished from the abundant granophyric/micrographic veinlets that are observed to cross cut footwall lithologies by their isolated occurrence and the finer-grained nature of their texture, with quartz typically no greater than 5 to 75 μm. Granite samples typically have less that 10% mafic phases, which are dominated by chlorite and lesser uralite,
with accessory titanite and hornblende. The granitic lithology is likely part of the 2642 ± 1 Ma monzonitic-granodioritic Cartier Granite suite, resulting from partial melting of the gneiss complex during uplift (Meldrum et al., 1997).

The crystalline basement is crosscut by numerous granophyric to pegmatitic veins ranging in width from 0.5 to 50 cm in width, the latter being dominated 0.5 to 3 cm subhedral to euhedral microcline, with interstitial quartz and lesser albite. Both veins and veinlets display a coarse granophyric texture better classified as graphic, with cuneiform quartz between 100 μm to 2 mm, clearly distinguishable from the granite hosted counterparts. These bodies are not observed to cross-cut diabase or Sudbury breccia, an indication of their genesis from the residuum of the Cartier Batholith. Diabase dykes are rare within the Levack North footwall and where observed range from 50 cm to 1 m, displaying a diabasic groundmass with 5 to 100 μm euhedral plagioclase laths displaying moderate to strong sericitization, with interstitial pyroxene altered to fine grained chlorite (< 1 to 50 μm) and cryptocrystalline phases, likely clays, exhibiting a red brown hue, as a probable result of ferric straining. The passage of later fluids, mineralizing or otherwise, has induced intense sericitization and epidotization, the latter occurring as fine crystals of ≤ 20 μm.

The Sudbury breccia within the Levack North footwall displays an actinolite-epidote-chlorite-plagioclase-quartz–biotite ± hornblende ± titanite pseudotachylite assemblage (Figure 3.3A), consistent with equilibration at a position in P-T space straddling the hornblende hornfels to albite-epidote hornfels contact facies (Dressler, 1984). Wall rock clasts range from 0.5 to 10 cm and are 90 % quartzofeldspathic, of which 50 % are ‘granite’, 10 % are felsic gneiss, 35 % are wholly recrystallized and 5 % are mafic (diabase or mafic gneiss). The high granite content results from the small size limiting the observation of metamorphic fabrics and the full recrystallization of clasts producing granoblastic quartz with interstitial potassium feldspar. At surface the breccia body crops out over an area of 3 km by 500 m (Figure 2.2), with its elongate dimension sub-parallel to the basal contact of the SIC, an orientation that is continued to depth. It is within the eastern portion of the Sudbury breccia belt that the mineralized 148 Zone is located, within a fault bounded block.
The footwall of the property was subsequently brittlely deformed with the Pumphouse Creek deformation zone, a NE striking zone and normal faulting developing. The zone is truncated and offset to the north along the property’s eastern margin by the NNW-SSE trending Fecunis and Bob’s Lake faults, the latter likely a splay from its large partner. The zone between these faults is termed the Eastern Block hosts the 148 zone, from which the sample material was collected.

2.1.2 Wisner

The 10 km by 1.5 km Wisner property sits along the NE portion of the North Range, within the footwall of a 12 km long embayment, bounded by the Foy offset to the west and the eastern margin of the Joe Lake gabbro to the east (Figure 2.1). Unlike the other properties the Wisner area has no history of metal production, although the property is proximal to the advanced...
Broken Hammer and South Zone (Wallbridge) and Podolsky (QuadraFNX) properties. The property footwall is dominated by the Joe Lake Gabbro, an elongate intrusion parallel to the basal contact, bounded by the SIC to its south and the Levack Gneiss Complex to the north (Figure 2.3). The gabbro body covers the central and eastern portion of the property, with the exploration to date focused upon the brecciated western ‘Rapid River’ area.

The western portion is dominated by quartzo-feldspathic and mafic Levack gneiss displaying a moderate to strong foliation dipping 70 to 80° NNW-NNE (dominantly 000 to 010°), defined by bands of between 0.25 and 1 cm. Observed felsic gneiss displays a ‘granodioritic’ composition with leucosomes presenting a crystal range between 25 and 200 μm, separating quartz dominated domains (0.25 to 4 mm), composed of coarse (50 to 250 μm) crystals ranging from weak to moderately strained, with sutured contacts, through to unstrained anhedral - polygonal crystals, consistent with the groundmass quartz. Melanosomes displayed a range of phases including biotite, chlorite (both primary and secondary), actinolite and uralite. The foliation is typically defined by biotite crystals between 75 and 700 μm, with pervasive weak to moderate alteration to chlorite, low-Ti green biotite and associated fine Ti-magnetite throughout all samples. Where present uralite occurs as rounded aggregates between 150 to 400 μm, either as isolated bundles or ‘chains’ of 3 to 15 aggregates, presenting ubiquitous fine grained chlorite rinds up to 75 μm wide. Primary chlorite (50 to 400 μm) is rare and commonly occurs with actinolite (50 to 150 μm).

The timing of the unfoliated to weakly foliated ‘granite’ package intruding into the footwall gneiss is unknown, although it is likely part of the 2642 ± 1 Ma Cartier Batholith. The intersected granites are petrographically similar to those of the Levack North property with a 50 to 700 μm groundmass composed of 20 % plagioclase, 60 % potassium feldspar and 40 % quartz, along with accessory biotite, chlorite, apatite and zircon, all < 35 μm. Phenocrysts are dominated by 0.5 to 5 mm wide microcline crystals, displaying perthitic texture. A lesser generation of plagioclase phenocrysts are also observed, up to 1.2 mm in size, with a single example fully enclosed by porphyritic microcline. In outcrop the granite displays a moderate to strong pink hue resulting from the pervasive moderate to intense sericitization of feldspars and the deposition of associated microcrystalline Fe-oxides. Patches of granophyric texture were observed in domains of between 500 to 2000 μm, with irregular quartz bodies between 10 and 100 μm, enclosed within potassium
feldspar between 250 and 1000 μm. As with the Levack North properties these patches are distinct from granophyric veinlet and pegmatite veins which display a coarser ‘micrographic’ texture presenting larger crystals of quartz (25 to 200 μm) within potassium feldspar crystals of 500 to 2200 μm. The dominant syenogranite displays gradational contacts with a potassium feldspar porphyritic biotite quartz monzogranite, displaying between 10 to 25 % biotite and 15 % quartz. The relative timing of these felsic plutonics is uncertain, but inclusions of mafic gneiss within both plutonics indicate that they both intruded the gneiss package, with both cross-cut by pegmatite veins, a likely late residue from the crystallizing granite, between 2657 ± 5 Ma and 2644 ± 3 Ma (Ames et al., 2008, references therein).

The footwall package is intruded by plagioclase porphyritic diabase dykes, of probable 2.47 Ga Matachewan origin (Siddorn and Halls, 2002), trending just off N-S. Dyke rocks have a fine grained groundmass with moderate to intense pervasive sericitization and epidotization of plagioclase, the latter primarily associated with barren hydrothermal veinlets. The groundmass comprises randomly orientated plagioclase laths with interstitial material containing discernible actinolite and chlorite, the former occurring as both discrete crystals (25 to 50 μm) and as bodies of uralite (50 to 200 μm). The majority of interstitial material is too fine grained for accurate identification with patchy ferric staining due to oxidation of magnetite by later fluids further complicating the issue. Plagioclase phenocrysts range between 2 and 12 mm and display no preferential orientation. Phenocrysts are not as heavily altered as the groundmass equivalents displaying moderate sericitization along margins, typically within a zone of around 100 μm. Epidotization of these crystals is only observed when they are crosscut by barren quartz ± carbonate veins resulting in the formation of fine grained (< 10 μm) epidote along the veinlet margin.

Sudbury breccia is limited to the property’s western portion with the single largest body some 750 m by 2 km, oriented SW-NE. This orientation differs from the more commonly observed North Range breccia bodies that tend to be oriented sub-parallel to the SIC’s basal contact. The western breccia body observed therefore likely follows a pre-existing heterogeneity, although whether this is the margin of the Levack gneiss, a fault or a dyke remains uncertain. The breccia contains clasts of all footwall lithologies ranging from 0.5 cm to 5 m (Figures 2.4 and 2.5),
within a fine grained (10 to 100 μm) chlorite + epidote + actinolite + quartz + plagioclase ± biotite groundmass (Figures 4 and 12B).

Figure 2.3. Geological map of the Wisner property (modified from Vale, 2009).

Only 10 % of quartzo-feldspathic clasts observed displayed recrystallization, producing rounded to polygonal quartz crystals between 25 and 200 μm with interstitial potassium feldspar. The majority of felsic clasts (80 %) were classified as granite, due to the small size typically inhibiting observations of metamorphic fabrics. In contrast microscopic examination reveals that 60 % of felsic clasts are from felsic gneiss, distinguishable through the presence of coarse polygonal quartz and its finer 25 to 150 μm quartz + plagioclase + potassium feldspar groundmass. Mafic (diabase and mafic gneiss) clasts comprise around 15 % of those intersected. Clasts are apparently unaffected by inclusion within Sudbury breccia, with the exception of chloritization of biotite, likely of retrograde origin.

The footwall displays abundant indications of hydrothermal alteration, primarily associated with barren quartz + epidote and lesser carbonate veinlets. The presence of these veins produces a range of outcrop scale color variation, ranging from a bleached appearance associated with sericitization, a pink hue associated with deposition of fine grained Fe-oxides, commonly associated with sericitization, especially related to carbonate veinlets, and a greenish hue associated with epidotization, typically associated with the quartz + epidote veins. Although it is
not visible in hand specimen, hydrothermal veins are also associated with chloritization of biotite and replacement of feldspars by calcite, the latter only associated with carbonate veining.

Tectonically the Wisner property is relatively unaffected by faulting, with the exception of the western portion which displays several parallel NW-SE trending faults cutting both the footwall and SIC. The sense of displacement of these faults and their effect upon the west breccia body in particular is uncertain.

2.1.3 Capre

The Capre property is located within the East Range of the SIC and covers an area of some 1.5 by 2 km, oriented parallel to the basal contact of the SIC (Figure 2.6). The property sits to the north of the contact and footwall mineralization of the Victor, Nickel Rim and Nickel Rim South mines and directly in the footwall of the Capre Lake Ni-Cu occurrence.

The footwall of the property is dominated by felsic gneiss of the Levack Gneiss Complex, defined by 0.25 to 2 cm compositional banding. Leucosomes display a granodioritic composition with quartz + plagioclase feldspar and potassium feldspar between 25 and 300 μm separating monomineralic quartz domains of between 0.25 and 6 mm, composed of 25 to 150 μm crystals ranging from sutured and moderately strained, through to recrystallized polygonal with uniform extinction. Melanosomes are biotite dominated with crystals between 25 and 300 μm displaying weak to strong pervasive chloritization. Uralite domains between 100 and 750 μm occurs both individually and as ‘chains’ of three to ten aggregates. Uralite aggregates have 25 to 100 μm chlorite + epidote rinds, with proximal biotite typically fully chloritized. Mafic gneiss was observed to occur more frequently than at the Levack North and Wisner properties with mapping indicating a distinct bands some 50 to 250 m thick cropping out at surface, with mafic minerals making up between 40 and 60 modal % of samples. Mafic rocks are dominated by hornblende
and biotite with crystals varying between 100 and 500 μm. Mafic minerals display pervasive moderate to strong alteration with hornblende altered to 10 to 100 μm chlorite + actinolite + epidote and biotite partially to fully replaced by chlorite. The felsic portion constitutes between 30 and 45 % of samples and displays a tonalitic composition with plagioclase, quartz and rare potassium feldspar crystals between 25 and 125 μm.

Samples typically show weak to moderate pervasive sericitization of plagioclase, however Fe-oxide staining is not as strong as that displayed by felsic units, possibly as a result of Fe sequestering by ferromagnesian alteration phases. As with felsic gneiss the mafic samples contain monomineralic quartz domains between 200 and 500 μm wide and composed of 50 to 400 μm crystals displaying weak undulose extinction.
Figure 2.5. Geological map of the upper stripped outcrop, Rapid River breccia body, Wisner property, produced by the author. See Appendix M for a larger scale version.
Isolated bodies of gabbro are observed within mafic gneiss. These bodies are composed of coarse 250 μm to 1 cm plagioclase with weak pervasive sericitization and uralite aggregates, likely after clinopyroxene. These minor intrusions were classified as Nipissing (Muir et al., 1980), with emplacement ages between 2218 to 2209 Ma (Buchan et al., 1994).

Granitic material was commonly observed in drill core; however a significant portion of this is likely better classified as weakly foliated gneiss. Potassium feldspar-porphyritic granite displays a 25 to 600 μm groundmass composed of an average of 20 % plagioclase, 60 % potassium feldspar and 40 % quartz, consistent with material from Levack North and Wisner. Phenocrysts
comprise 0.5 to 7 mm potassium feldspar, with all samples displaying moderate to intense sericitization and associated Fe-oxide staining. Granites displayed gradational contacts with coarse 0.25 to 3 cm alkali feldspar granite domains between 10 cm and 5 m in size, composed of 60% potassium feldspar and 40% quartz. This material is distinct from granophyric veins, which crosscut the Archaean footwall and display micrographic 50 to 500 μm cuneiform quartz and 100 to 600 μm albitic plagioclase within 0.5 to 10 mm potassium feldspar. As with all felsic lithologies sericitization is pervasive, varying between moderate and intense. Diabase dykes varied between 0.5 and 19.5 m dipping near vertically and trending north–south. The groundmass displays 50 to 400 μm randomly oriented plagioclase laths with 25 to 75 μm interstitial chlorite and actinolite. Ten to 14 mm plagioclase phenocrysts display no preferential orientation and moderate sericitization similar to groundmass crystals.

Sudbury breccia crops out in three discrete exposures within the main and South blocks of the property (Figure 2.6). The main 2 km by 250 m belt outcrops NE of Capre and trends NW–SE subparallel to the basal contact of the SIC. The belt dips at ~ 70° east, parallel to the basal contact of the East Range, and hosts three mineralized zones; the 3000, 2700 and 3001, of which the former and latter were sampled and for ease of identification will be termed the upper and lower zones respectively.

Sampled Sudbury breccia shows an actinolite + chlorite + epidote + biotite + plagioclase + quartz ± hornblende assemblage in the pseudotachylite matrix (Figure 3.3A), similar to that of the Levack North property. Mafic minerals range from 10 to 75 μm, with granoblastic quartz and plagioclase (5 to 50 μm) making up the bulk of the material. Biotite occurs in higher quantities than the other properties with groundmass crystals between 10 and 100 μm, and poikiloblastic crystals between 75 and 250 μm, primarily enclosing quartz. The development of such large crystals was not as commonly observed in samples from Levack North or Wisner and where present gives the breccia a ‘spotted’ appearance. Hornblende typically occurs as sparse porphyroblasts between 50 and 200 μm, with rare irregular, 10 to 25 μm crystals observed within pseudotachylite. The porphyroblasts are magnesiohornblende, with no visible zonation or alteration observed.
Quartzo-feldspathic clasts constitute 80 % of observed breccia clasts, of which 75 % are fully recrystallized, with rounded to polygonal quartz (40 to 150 μm) and interstices dominated by potassium feldspar. Clast margins display recrystallized rinds between 50 and 100 μm thick, composed of interlocking quartz and potassium feldspar reminiscent of micrographic texture, and patches (50 to 100 μm) of granophyric texture.

The property sits astride the axial trace of the SIC’s syncline, and displays significant north–south trending faults within the property’s western block, with NE–SW trending faulting within the main and south blocks. Faults crosscut and offset both the hanging wall SIC lithologies and the footwall lithologies and Sudbury breccia bodies.

2.2 South Range Properties
2.2.1 Denison

The 4 km x 3 km Denison property is situated within the SW footwall of the SIC, containing within its limits the past producing Crean Hill contact deposit and Vermilion offset deposit (Szentpeteri et al., 2003), the former being part of a 14 km long embayment that also contains the Ellen and Lockerby deposits (Figure 2.7). Low-sulfide mineralization has primarily been identified mantling the Main, Intermediate and West orebodies of the Crean Hill deposit and within fault controlled panels emanating from these zones (Figure 2.8).

The property’s footwall is segmented by the WSW-ESE trending Creighton Fault, a plane of unknown dip and sense of movement, juxtaposing metabasalts of the Elsie Mt formation with metabasalts, metarhyolites and metasediments of the Stobie, Copper Cliff and Matinenda Formations (Figure 2.7), which form part of a sequence of rift-related volcanic rocks grading into basin fill sediments deposited between 2500 and 2150 Ma (Dressler, 1984). The NW portion of the footwall includes a ~ 0.4 km² metagabbro intrusion, likely part of the Nipissing suite and emplaced into the Elsie Mountain Formation. The deposit and its footwall are cut by olivine diabase and other mafic dykes locally referred to as trap dykes.

The property’s footwall has undergone extensive ductile and brittle deformation related to the Penokean and Grenville orogenies. The basal contact of the SIC displays a general ENE strike,
with a steep to vertical northerly dip, overturning to the south at depth. The contact is further complicated by the development of a 10 to 40 m thick shear zone typified by the development of strong schistose fabrics, containing boudins of proximal footwall lithologies. The Beeper Zone, which crops out along the eastern margin of the adjoining Xstrata property, is the only surface expression of this zone. The shear zone displays a near vertical fabric trending between 65 and 90°, with lenticular boudins orientation parallel to shear fabrics. Drill data suggests that the zone extends through to the main embayment (host of the Main Orebody) where shear is accommodated by the development of splay faults extending some 100 m into the footwall (Vale, 2007). The pervasive shear fabric of the northern block (Elsie Mountain Formation) displays trends of 30 to 60°, with dips between −90° to 60° (SE). This differs substantially from the 70 to 90° strike of the 9400 zone, situated in the footwall of the West Orebody, suggesting that the contact shear zone has provided a conduit for the low-sulfide mineralization. The southern block (Stobie Formation) presents a near vertical fabric trending 70 to 80°. The property is cut by a generation of late thrust faulting trending 90 to 100°, discordant to shear fabric. The presence of veins displaying large, euhedral and colloform carbonate suggest low temperature precipitation within fault voids at shallow crustal levels, an indicator of prolonged fault movement.

The sampled lithologies are exclusively located within the Northern block and consist of a greenschist dominated assemblage with intercalated metarhyolites and metasediments and isolated bodies of biotite schist and amphibolite. The footwall assemblage is crosscut by plagioclase porphyritic diabase dykes, formally referred to as trap dykes and olivine diabase dykes, with cross cutting relationships identifying the latter as the youngest (Figure 2.8). The greenschists sampled consisted of an amphibole dominated groundmass, with crystals between 50 and 700 μm grading from magnesiohornblende cores to actinolitic margins, displaying a subparallel orientation. The abundance of chlorite varies between samples with modal abundances between 0 and 40 % of the groundmass, typically occurring as porphyroblastic books between 10 and 100 μm although isolated crystals do reach 500 μm. The chlorite does not appear to have pseudomorphed earlier minerals. The interstices between mafic phases comprise a granoblastic quartz + plagioclase + potassium feldspar assemblage with a 50 to 100 μm grain size. Feldspar crystals display a pervasive weak to moderate mottling, resulting from sericitization, with quartz displaying no to weak undulose extinction, the probable result of late recrystallization during the waning stages of regional deformation.
This hypothesis is further supported by the development of unstrained 50 to 100 μm polygonal quartz along the margins of coarse moderately to strongly undulose; sutured anhedral vein quartz. Samples are typically uniform in hand specimen, although the presence of 0.25 to 3 mm magnesiohornblende porphyroblasts results in a ‘spotted’ appearance.

Metarhyolitic or metasedimentary units have a granoblastic groundmass dominated by quartz (25 to 100 μm) with interstitial muscovite (25 to 100 μm). Groundmass quartz varies from polygonal and unstrained, to irregular and sutured with moderate to strong undulose extinction, the result of varying degrees of recrystallization. Plagioclase feldspar is typically rare. Potassium feldspar
abundances increase to 30 % of groundmass material with decreasing muscovite. The groundmass separates quartz domains some 0.25 to 2 mm in diameter displaying sutured crystals between 100 and 750 μm with weak to moderate undulose extinction. The distinction between metarhyolite and arkosic metasedimentary units is complicated by their mineralogical similarities. Classification would have been primarily based on mica content, making differentiation subjective, so instead all occurrences of metarhyolite or arkosic metasediments were classified as granoblastic granofels.

Bodies of amphibolite were observed within sheared metabasalts and varied between 10 and 50 cm. Samples display randomly oriented 1 to 8 mm actinolite crystals, with interstices containing coarse 500 μm to 3 mm clinozoisite crystals. Samples are bi-mineralic with only trace magnetite, titanite and biotite. The coarse nature of the crystals observed would suggest that either the amphibolite equilibrated under a different P and T regime from the bulk of the Elsie Mountain metavolcanics and were sheared into the footwall, or that the coarse crystals reflect the protolith, probably gabbro.

![Composite schematic geological map of the 300 Level, Crean Hill Mine, with low-sulfide mineralization overlain. (modified from Vale, 2009)](image-url)
Biotite schist layers are interpreted as having resulted from the metamorphism of pseudotachylite and display a strong lepidoblastic fabric, reflecting the parallel orientation of 50 to 500 μm groundmass biotite and lesser muscovite. Non-mica phases are dominated by quartz, plagioclase and accessory potassium feldspar forming granoblastic polygonal crystals between 50 and 150 μm. Quartz crystals show uniform extinction, with plagioclase displaying little to no mottling. Biotite typically displays little chloritization unless proximal to barren hydrothermal veins or mineralization where it shows moderate patchy alteration to chlorite + epidote + Ti-magnetite. Radiation halos are ubiquitous within biotite.

The property is transected by two generations of mafic dykes, an early generation of NE (~ 65°) trending plagioclase porphyritic quartz diabase trap dikes, and later crosscutting NW (~ 330°) trending olivine diabase dykes. Underground observations show that both generations cross-cut the SIC and footwall lithologies. The early trap dykes comprise a plagioclase dominated groundmass composed of randomly oriented plagioclase laths between 10 and 200 μm in length, with interstices containing aggregates of weakly transparent cryptocrystalline minerals. Sparse olivine was observed within all analyzed samples, occurring as isolated anhedral 50 to 200 μm crystals, rarely partially enclosed by porphyritic plagioclase, occurring as crystals between 300 μm and 1 mm and clearly distinguishable from groundmass plagioclase crystals.

Olivine diabase dykes also displayed a plagioclase dominated groundmass (60 modal %) composed of 250 μm to 1.5 mm laths partially enclosed within 400 μm to 1 mm sub-ophitic clinopyroxene, constituting ~ 35 % of the groundmass. The remaining 5 % is anhedral olivine between 50 and 250 μm, partially enclosed by groundmass plagioclase and in one instance fully enclosed by a single 8 mm plagioclase phenocryst. The timing of dyke emplacement is uncertain, however, trap and olivine diabase dykes can be tentatively dated to 1415 ± 40 Ma and 1239 ± 4 Ma respectively (Krogh et al., 1987; Rousell et al., 1997).

2.2.2 McKim

The McKim property covers an area some 5 km by ~3 km, including the past producing Little Stobie mine and a substantial portion of the active Frood-Stobie deposit (Figure 2.9). The low-sulfide mineralization identified to date sits within zones proximal to the No.1 and No.2
orebodies of the Little Stobie Mine, the former sitting within a trough filled with sublayer norite, bounded to its west by the Murray Pluton and to the south and east by greenschists of the Elsie Mountain formation. The No.1 orebody dips at around 55° and strikes 315°, averages 30 m in thickness and extends to a vertical depth from surface of ~ 610 m (Hoffman et al., 1979). The No.2 orebody trends WNW-ESE around 50° off the SIC’s basal contact for ~ 273 m. The orebody averages 52 m in thickness and lies between 91 and 366 m below surface. The No.2 orebody sits wholly within the footwall and is hosted by greenschist and Sudbury breccia located along the western margin of a granite plug, which is not visible at surface. Both the breccia and mineralization mantle this western margin. Detailed descriptions of the mineralizing styles and their base and precious metal contents were published by Hoffman et al. (1979), Davis (1984) and Molnár et al. (1999), the former noting that the No.2 orebody is twice as enriched in PGEs, with no substantial variation in the Ni/Cu ratio, when compared to the No.1 orebody. Furthermore both orebodies displayed chalcopyrite + PGE enriched stringers emanating from them and hosted within the footwall rocks. When compared to the No.1 and No.2 orebodies these stringers were IPGE depleted and PPGE enriched, with the low abundance of these veins when compared to North Range footwall systems (e.g., McCreedy West) being attributed to a higher lithostatic pressures during emplacement (Hoffman et al., 1979).

The footwall rocks of the McKim property are dominated by the greenschists of the Elsie Mountain Formation (Krogh et al., 1984). A weak to moderate steeply dipping foliation is defined by a parallel alignment of actinolite and rare ferrotschermakite (20 to 150 μm) with lesser chlorite, epidote, titanite and biotite, within a 20 to 50 μm granoblastic quartz + plagioclase groundmass. Samples contain rare porphyroblastic magnesiohornblende grading into actinolite dominated margins, along with poikiloblastic biotite between 250 μm and 2 mm enclosing groundmass quartz and plagioclase. The porphyroblastic texture produces a ‘spotted’ appearance in hand specimen. The greenschists mark the lowest formation of the Huronian Supergroup and were likely erupted during Paleoproterozoic rifting between 2500 and 2150 Ma (Dressler, 1984). The metavolcanic package was intruded by the 2477 ± 9 Ma Murray Pluton (Krogh et al., 1996), which is an equigranular medium grained biotite quartz monzonite, presenting an anhedral microcline–plagioclase (oligoclase–andesine)–quartz assemblage with isolated biotite bundles composed of randomly oriented plates.
The metavolcanic package and pluton were deformed in two phases, a first \( (D_1) \) Blezardian event imparting a steeply dipping (70 to 85°) approximately east to west striking foliation, overprinted by the later \( (D_2) \) ca. 1.85 Ga –Penokean related deformation which imparted a 75 to 88° dipping,
NE-SW striking foliation (Riller et al., 1996). Both phases of deformation are visible within the Murray Pluton, with the metavolcanic–metasedimentary footwall preferentially displaying D₂ fabric. The strength of the D₂ foliation was noted by Riller et al. (1996) to increase with proximity to the basal contact of the SIC and was interpreted as resulting from strain localization within the heated and more malleable SIC proximal footwall rocks. In hand specimen the intersected granitic material displays at most an extremely weak foliation, with pervasive epidote–clinozoisite and sericite–Fe–Oxide alteration of plagioclase of potassium feldspar. The groundmass is quartz dominated and comprises anhedral, undulose crystals with sutured contacts, the result of recrystallization and regional deformation, whilst potassium feldspar, typically only moderately sericitized, displays rare corrosion of the crystal margins and replacement by quartz. Biotite plates ranging from 25 to 250 μm form randomly oriented bundles (up to 2 mm in diameter) interstitial to feldspar and less commonly quartz. Samples display a weak to moderate pervasive chloritization of biotite along margins and cleavage, with alteration increasing proximal to mineralization.

The main mineralized zone sits astride the 1400 Level of the Little Stobie mine extending ~200 m up dip and ~100 m down dip following the contact of the No.1 orebody (Figure 2.10). Mineralization is dominantly hosted within the Elsie Mountain greenschists, with additional minor fabric-discordant sulfide veinlets hosted by granite. Sudbury breccia occurrences are sporadic and similar in appearance to the metabasalts, with a homogenous dark green appearance resulting from pervasive strong chloritization of the pseudotachylite. A field distinction is typically only possible due to the presence in pseudotachylite of irregular 0.5 to 5 cm quartzofeldspathic bodies which were probably granite clasts. Mineralization with ore grade is typically dominated by inclusion-bearing sulfide veins, containing 0.25 to 10 cm wall rock clasts, the probable result of movement of sulfide along terrace controlling faults. The position of mineralization along the margin of the Little Stobie orebodies would at least superficially suggest a connection.
2.3 Mineralization: Textures and Mineralogy

Four distinct mineralizing styles (sulfide vein, irregular veinlets, quartz–carbonate sulfide veins and disseminations) were recognized from the North Range properties, in good agreement with observations by Farrow et al. (2005) and Péntek et al. (2008). All North Range mineralization was chalcopyrite dominated, with the exception of Ni-sulfide veins from the Capre property. Millerite was the primary Ni phase, although pentlandite was also present in sulfide veins from Levack North and Capre. Accessory sphalerite, galena and cassiterite were noted from all mineralizing styles, with accessory magnetite, pyrrhotite and polydymite, and bornite also observed in sulfide veins and irregular veinlets respectively. A total of five mineralizing styles were identified from the South Range (sulfide veins, veinlets, quartz–carbonate sulfide veins, disseminations and stockwork mineralization). All South Range mineralizing styles contained pyrrhotite, pentlandite and chalcopyrite, with gersdorffite also occasionally observed in veinlet and stockwork mineralization. The description of disseminated mineralization below is consistent with observation from both the North and South Ranges. The characteristics of each type of mineralization are discussed below with reference to examples as shown in Figures 2.11 and 2.12. The reported percentages for mineralizing styles reflected the number of observed occurrences divided by the total number of observations from sampled boreholes. This simple approach was used due to the variable abundance in precious and base-metal concentrations in the lower sulfide mineralizing styles (irregular veinlets, veinlets, disseminations and stockwork). This variation means that the amount of base or precious metals contained within a certain mineralizing style as a portion of the total available is not an accurate guide as not all occurrences will be represented.
2.3.1 North Range Low-Sulfide Mineralization

2.3.1.1 Sulfide Veins

Sulfide veins are dominated by base-metal sulfide minerals and constitute between 4 and 14% of mineralization observed by the author. These veins range from 0.5 to 50 cm in thickness, typically < 25 cm, and display sharp to moderately defined margins. At the Levack North and Wisner properties 66 to 85% of the sulfide veins are hosted by pseudotachylite, but at Capre,
which is dominated by megabreccia with little pseudotachylite, only 30 to 56% of the sulfide veins occur between clasts. Most veins hosted by basement lithologies are either proximal to bodies and veins of pseudotachylite or are situated within large clasts in the breccia. Veins display an assemblage of chalcopyrite + millerite + magnetite ± pentlandite ± pyrite with chalcopyrite comprising 60 to 100% of vein sulfide. These crystals display anhedral to subhedral habits, measuring 0.1 to 5 mm and presenting abundant lamellar twinning (Figure 2.12A). Millerite constitutes the bulk of Ni sulfides present, with rarer pentlandite observed only at Levack North and Capre. Millerite and pentlandite are most commonly observed as bands parallel to the vein margins, up to 4 cm in thickness, however isolated millerite ± pentlandite aggregates up to 1 cm in diameter are also observed within the veins.

Two distinct varieties of millerite were observed in marginal Ni sulfide bands from the Capre property. The majority of millerite displays a uniform appearance, lamellar twinning, and little or no patchy violarite alteration (Figure 2.12B). It was not uncommon for this uniform millerite to display abundant 10 to 150 μm lamellar twinning and 10 to 250 μm globular bodies of chalcopyrite located along cleavage planes, within which skeletal and idioblastic pyrite has commonly nucleated (Figure 2.12C). The second type of millerite crystals display abundant exsolved chalcopyrite lamellae, resulting in partial replacement of crystal cores, with moderate to intense pervasive violarite and lesser pyrite alteration focused along crystal margins, cleavage and exsolution planes (Figure 2.12D). Exsolved chalcopyrite lamellae were not observed within millerite crystals from the Levack North or Wisner properties.

Magnetite is the dominant accessory phase, occurring as anhedral crystals within all common sulfides. Crystals are primarily inclusion free, although sporadic examples are observed to display cores rich in 10 to 25 μm chalcopyrite inclusions and inclusion-free rims. Galena, sphalerite and cassiterite are generally present as minor accessory phases, the latter two occurring as anhedral interstitial grains, although skeletal sphalerite is rarely observed.

A distinctive population of micro-veinlets was identified at all three North Range properties. Micro-veinlets are 10 to 300 μm wide elongate aggregates of sulfide that occur along grain boundaries surrounding chalcopyrite crystals. The mineral assemblages in the micro-veinlets are
unique to each property, with millerite from Levack North, polydymite and pyrrhotite from Wisner and millerite, pyrrhotite and violarite, after millerite, from Capre (Figure 2.12E).

At the Capre property another subset of veins was observed to have high Ni sulfide abundances (80 to 100 %) unlike the chalcopyrite-dominated sulfide veins described above. These millerite + chalcopyrite ± pentlandite veins range from 1 to 15 cm in width and are located exclusively within pseudotachylite. Examples from the Lower Zone contain some pentlandite, whereas in the Upper Zone specimens were millerite-dominated. Millerite crystals from both the Upper and Lower Zones are typically homogeneous and host idioblastic pyrite. Crystals displaying chalcopyrite exsolution occur along vein margins, but commonly only constitute 5 to 10 % of Ni-sulfides within samples. Ni sulfide veins were observed to crosscut the chalcopyrite dominated equivalents on two occasions.

All sulfide veins, regardless of the host lithology, are mantled by a 0.5 to 5 mm wide alteration selvage dominated by anhedral epidote, with lesser actinolite and minor chlorite. The origin of the alteration selvage mantling sulfide veins in uncertain with three possible causes: 1) ferromagnesian silicates crystallized in response to heating of the wall-rock by a saline fluid at tempertures in excess of 400 °C, 2) ferromagnesian silicates crystallized in response to heating from a sulfide melt and any volatile-rich liquids that exsolved from it, or 3) the alteration selvage was produced by pre-mineralization fluid circulation, with the same conduit exploited by the mineralizing liquid later. The possible origin(s) of the alteration assemblage are discussed in greater detail in Chapters 4 and 6. Epidote and chlorite crystals range between 25 and 150 μm in size, with actinolite between 50 and 400 μm. Quartzo-feldspathic hosts display an epidote dominated selvage commonly including accessory chlorite bundles between 25 and 200 μm replacing biotite and feldspar. Actinolite-tremolite is rare within quartzo-feldspathic host rocks, with modal abundances significantly higher within pseudotachylite. Crystals typically occur along vein margins and are commonly partially enclosed within sulfide. Orientations range from random through to uniformly perpendicular to vein margins. Mafic gneiss clasts composed mainly of biotite and hornblende are commonly altered to 25 to 150 μm chlorite. Disseminated sulfide mineralization is ubiquitous in the alteration halos. Textural relations between this disseminated sulfide and the associated silicate alteration phases are complex. In all instances the disseminated crystals and aggregates of sulfide within the broader alteration halo were seen to be
surrounded by 50 to 200 μm wide epidote + chlorite haloes after mafic phases and feldspar. In pseudotachylite-hosted selvages the disseminated sulfide may also be associated with 25 to 200 μm actinolite. The hydrous ferromagnesian minerals of the alteration assemblage typically appear to be in textural equilibrium with the associated sulfide. Epidote, actinolite and chlorite are commonly partially or fully enclosed by sulfide and vice versa, suggesting the syngenetic crystallization of silicates and sulfides, however replacement of sulfide by silicates was observed by Li et al. (2004) within the margins of sulfide veins from the Strathcona mine. In the present study examples of actinolite replacing chalcopyrite, millerite and pentlandite within alteration selvages were observed in samples from the Levack North and Capre properties. These properties further displayed partial replacement of fully enclosed epidote by chalcopyrite. In summation, these observations indicate that although the alteration assemblage contains both sulfide minerals and silicate phases, the conditions attending the alteration process were quite variable and produced contradictory paragenetic sequences from place to place and perhaps also from time to time.

2.3.1.2 Irregular Veinlets (IRV)

These highly uneven concentrations of sulfide comprise a collection of chalcopyrite ± millerite ± pyrite disseminations and blebs (50 μm to 2 mm) aligned on planar trends (Figure 2.11B and 2.11C). Irregular veinlets typically follow Sudbury breccia clast–pseudotachylite boundaries, pre-existing joints, granophytic and pegmatite veins and rarely metamorphic fabric, occurring as individual veinlets and stockworks of up to 10 veinlets. Sulfides are chalcopyrite dominated with minor (< 1 to 10 modal %) uniform millerite forming 25 to 300 μm aggregates along chalcopyrite margins. Pseudotachylite-hosted veinlets have associated epidote + chlorite ± actinolite alteration selvages extending 0.25 to 10 mm from sulfide margins. Alteration in quartzo-feldspathic hosts contains abundant 25 to 250 μm anhedral epidote and lesser 25 to 100 μm chlorite after mafic minerals and feldspar. Actinolite grains between 50 and 300 μm in size are typically fully enclosed within sulfide aggregates. Sericitization and associated Fe-oxide staining of quartzo-feldspathic lithologies within the alteration halo of IRV varies between weak to intense, perhaps indicating that this alteration predates mineralization, with IRV merely following the same pathways. Pseudotachylite-hosted examples display epidote + actinolite dominated margins with
minor 25 to 100 μm chlorite interstitial to randomly orientated actinolite. Substantial sulfide aggregates (200 to 750 μm) locally replace the host silicates, but finer 25 to < 200 μm sulfide aggregates occur along silicate grain boundaries, with mineralization initially exploiting these contacts, followed by replacement of the surrounding minerals.

2.3.1.3 Quartz ± Carbonate + Sulfide (QCS) Veins

These uncommon veins comprise 1 to 3 % of mineralization intersected. Veins range from 1 mm to 8 cm in width and are dominated by gangue minerals consisting of coarse euhedral-subhedral quartz (300 μm to 5 mm) and patchy subhedral carbonate (100 μm to 2 mm), occurring within isolated domains of up to 5 mm or sporadically along the vein margin. Sulfides typically occur as chalcopyrite + sphalerite + galena ± millerite aggregates 1 to 20 mm thick along vein margins. Aggregates are dominated by chalcopyrite with abundant galena inclusions (1 to 500 μm), although rare sphalerite-dominated aggregates do occur (Figure 2.12F). QCS veins were seen to crosscut both IRV and barren quartz + epidote veins (Figure 2.11B and 2.11D) and are also crosscut by epigenetic chalcedony veinlets which are associated with alteration of chalcopyrite to secondary covellite or pyrite. Vein margins commonly display abundant coarse euhedral to subhedral epidote crystals (5 to 40 mm) oriented approximately perpendicular to the edge. The selvage assemblage comprises epidote + chlorite, the former being limited to a band no wider than 100 μm. The host rocks display strong pervasive chloritization of ferromagnesian and feldspar crystals within haloes of up to 40 mm. QCS veins show no clear association with pre-existing veining, lithological contacts or fabrics. Care must be taken when classifying veins as QCS because some barren quartz + epidote veins have been reactivated by the deposition of later sulfides, likely related to sulfide vein emplacement. The presence of marginal sulfide and sulfide inclusions within quartz are considered key diagnostic features of the QCS vein type.

2.3.2 South Range Low-Sulfide Mineralization

2.3.2.1 Sulfide Veins

Veins range from 1 cm to 3.6 m wide with a pyrrhotite + chalcopyrite ± pentlandite assemblage, with a highly variable po:ccp ratio. Primary sulfides have undergone weak to intense replacement
by fine grained to idioblastic pyrite and laminar marcasite (i.e. elongate ‘flames’, comprising 10 to 100 μm crystals after pyrrhotite) (Figure 2.12G). Sulfide veins constitute only 3 to 7 % of intersected mineralization, but host a substantial fraction of total base-metals within analyzed boreholes. Sulfide crystals display an anhedral habit and chalcopyrite twins commonly are deformed to display a weakly sinusoidal appearance (Figure 2.12H). Veins commonly contain rounded clasts of host rock 0.5 to 10 cm wide with diffuse margins likely resulting from recrystallization (Figure 2.11E). Clasts comprise 5 to 25 % of vein volume and are fully enclosed within sulfide, with samples reminiscent of brecciated ‘durchbewegung’ texture (Figure 2.11E). Vein margins display a coarsening and recrystallization of the host assemblage to the assemblage actinolite + biotite + quartz ± epidote ± chlorite with subhedral-euhedral crystals from 100 μm to 10 mm in size. This vein selvage extends up to 3 cm from the margin, but outside this zone the host rocks display no alteration halo.

2.3.2.2 Quartz ± Carbonate + Sulfide (QCS) Veins

These veins comprise 3 to 15 % of intersected mineralization with vein widths ranging from 1 mm to 10 cm (Figure 2.11G). Gangue is dominated by coarse milky quartz (100 μm to 1 cm) and lesser carbonate (100 μm to 2 mm), the latter typically occurring along the vein margin or as isolated domains 0.5 to 3 mm across within the vein. The opaque assemblage comprises pyrrhotite + chalcopyrite ± pentlandite ± magnetite, with variable modal abundances and moderate to intense patchy replacement of pyrrhotite and pentlandite by pyrite and marcasite. Several fine granofels-hosted examples contain minor gersdorffite occurring as anhedral to subhedral crystals 10 to 100 μm in size, with larger examples containing nickeline inclusions. Veins display a slight coarsening of the host rock assemblage with a selvage of amphibole + chlorite + plagioclase + quartz ± epidote commonly observed within metabasalts (the dominant host). No preferential orientation of phases was noted in the selvage, which extends up to 5 mm into the host rock. Beyond the selvage no indications of alteration are present.
2.3.2.3 Sulfide Veinlets

These range from < 1 to 10 mm wide and comprise 5% of observed mineralization at the McKim property but only 1% at Denison. Samples typically present a chalcopyrite ± pyrrhotite ± pentlandite ± gersdorffite assemblage with veinlets occurring individually or as stockworks, running parallel to the margins of sulfide veins. Isolated examples hosted within greenschists and granite (McKim only) are observed, with attitudes typically discordant to metamorphic fabrics, with their emplacement apparently guided by fractures and pre-existing barren quartz + carbonate veins. Alteration selvages are typically difficult to distinguish from those of any associated sulfide vein, with isolated examples hosted by greenstones displaying no obvious selvage, whilst biotite in granitic host rocks is chloritized up to 1 mm from the margin.

2.3.2.4 Stockwork

A structural style exclusive to the Denison property, stockwork mineralization is located within strongly sheared greenschists, within fabric concordant bands of ≤ 5 cm width, displaying an anastomosing stockwork of abundant < 1 mm carbonate ± quartz veinlets, along with 500 μm to 7 mm magnesiohornblende porphyroblasts and disseminated pyrrhotite + chalcopyrite ± pentlandite ± gersdorffite (Figure 2.11H). Within these vein systems sulfide comprises ≤ 1 modal % of samples, with 50 to 200 μm crystals located interstitial to silicates. Pyrrhotite and pentlandite crystals typically display limited alteration to pyrite and marcasite, although chalcopyrite is always unaffected. Although this style of mineralizing occurs very sparsely, representing just 10% of intersected material from Denison, it’s extremely high TPM grades make it an important host, with some samples exceeding 200 g/ton TPM. Stockwork mineralization occurs within fault controlled panels in the footwall of the Crean Hill mine. The zones containing stockwork mineralization display abundant sub-mm scale carbonate ± quartz veinlets which likely result from fluids being channeled along the fault plane. The apparent association of stockwork mineralization with hydrothermal veinlets and its occurrence within a fault plane makes predictions about its genesis difficult as it could be the result of shearing of sulfide from the contact, deposition from a hydrothermal fluid, or crystallization from a
fractionated sulfide liquid. Discussions on the origin of stockwork mineralization can be found in Chapter 4 and 5.

2.3.2.5 Disseminations (North and South Ranges)

Disseminated sulfide and accessory PGM are hosted by all lithologies, constituting a volumetrically important style which comprises 26 to 89 % of intersected mineralization. Disseminations range from single crystals (10 to 200 μm) to chalcopyrite ± millerite (North Range) and pyrrhotite + chalcopyrite ± pentlandite aggregates up to 5 mm in size, occurring interstitial to silicates within chlorite clots and epidote + chlorite selvages (< 50 μm thick) replacing ferromagnesian phases and rarely feldspar on the North Range. Disseminated sulfides from the South Range were rarely rimmed by epidote, although the vast majority of crystals displayed no alteration halo.

2.3.3 Low-Sulfide: A Distinct Mineralizing Style?

Observations from low-sulfide material from the both ranges of the SIC clearly indicate that it does not resemble footwall mineralization as classically defined (e.g. Abel et al., 1979; Morrison et al., 1994; Farrow and Lightfoot, 2002; Farrow et al., 2005), containing not only elevated precious metal concentrations and an increased number of mineralizing styles, but also a distinctive sulfide assemblage on the North Range. Sharp-walled veins observed from North Range footwall deposits (e.g. McCreedy West and Strathcona), commonly contain a sulfide assemblage of chalcopyrite + pyrrhotite + pentlandite ± cubanite, consistent with formation from mixtures of mss, intermediate sulfide solid solution (iss) and heazlewoodite solid solution (hZss) (Abel et al., 1979; Farrow et al., 2005; Mungall, 2007). Vein widths commonly exceed one meter and precious metal mineralization is limited to the vein and a narrow alteration selvage (Farrow et al., 2005). Formerly recognized economic material was typically limited to massive sharp-walled sulfide veins of sufficient width to warrant mining, with any sulfide-poor material treated as dilution. In sharp contrast, the low-sulfide mineralization described here incorporates an increased number of economic mineralizing styles, with mineralization varying between cm to
meter scale massive sulfide veins through to disseminated material with < 1 modal % sulfide. It
is notable moreover that the mineral assemblage in the North Range low-sulfide mineralization
(chalcopyrite + millerite ± pentlandite ± pyrite) was previously recognized only at the
terminations of sharp-walled veins. The presence of sulfide veins suggests that a continuum with
sharp-walled vein systems may be present on the North Range with the thinner, more PGE-rich
veins of the low sulfide zone possibly representing the distal portion of a sharp-walled vein
system encroaching into zones of truly low-sulfide mineralization. It must be noted however, that
even with the presence of these veins the modal abundance of sulfide across the mineralized
intersection remains low when compared to sharp-walled vein systems. It is this increased
diversity of mineralizing styles and the decoupling of precious metal grades from modal sulfide
abundance that defines low-sulfide mineralization as a mineralizing style distinct from classically
described footwall mineralization, with all the properties studied displaying some of these tell-
tale traits.
Figure 2.11. A: Sudbury breccia hosted sulfide vein exploiting pre-existing barren quartz vein, visible along the right-hand margin. B: Diorite hosted IRV mineralization displaying ‘apple’ green epidote selvage, cross-cut by chalcopyrite bearing QCS vein. C: Sudbury breccia hosted IRV exploiting clast-pseudotachylite contact. D: QCS vein displaying strongly chloritized halo, note strongly altered clast within right-hand portion, cross cutting a mm scale barren quartz + epidote veinlet, on left-hand margin. E: Greenschist hosted chalcopyrite dominated sulfide vein displaying pyrrhotite + pentlandite eyes and host rock clasts displaying partial assimilation along margins and fractures. F: Strongly pyritized sulfide vein exploiting a pre-existing barren quartz vein in greenschist. G: QCS stockwork within biotite schist. H: Greenschist hosted stockwork mineralization displaying white carbonate dominated veinlets, magnesiohornblende porphyroblasts and disseminated sulfide.
Figure 2.12. A: Acid etched sulfide vein chalcopyrite (Ccp) displaying lamellar twinning. B: Sulfide vein type-1 millerite (Mi) with chalcopyrite inclusions acting as nucleation sites for pyrite (Py). C: Millerite in XPL displaying lamellar twinning, same as B. D: Sulfide vein type-2 millerite displaying abundant chalcopyrite exsolution, with millerite altering to purple violarite (Vio). E: BSE image of sulfide vein hosted polydymite (Pyd) micro-veinlet along chalcopyrite crystals margins. F: QCS hosted marginal sulfide dominated by sphalerite (Sp) with lesser chalcopyrite and pyrite, within a quartz (Qtz) dominated vein. G: Sulfide vein (South Range) sample displaying replacement of pyrrhotite (Po), chalcopyrite and minor pentlandite (not resolvable) by laminar marcasite and sub-euhedral pyrite. The sample displays a chlorite (Chl) bearing selvage with several resistant quartz clasts within sulfide. H: Sulfide vein chalcopyrite displaying deformed lamellae. Note that the principle stress must have been oriented perpendicular to the NW-SE trending twins for them to avoid deformation.
Chapter 3
Low-Sulfide Mineralization: Metamorphic Grade, Alteration Assemblage and Fluid Inclusions

3.1 Abstract

The presence of low-sulfide mineralization within the footwall of the SIC is marked by the development of halogen-bearing hydrous ferromagnesian alteration selvages and haloes. North Range mineralization of magmatic origin within Sudbury breccia is associated with an epidote + actinolite + chlorite ± biotite alteration, whereas hydrothermal veins (both barren and PGE-bearing) show a chlorite + epidote assemblage, with epidote abundance increasing when hosted within Archaean gneiss and granite. South Range mineralization is marked only by a coarsening of the host rock assemblage suggesting that any alteration related to magmatic processes has re-equilibrated, whilst any fluids producing hydrothermal mineralization were of probable metamorphic origin and therefore in equilibrium with the metamorphic assemblages present. Alteration phases within Sudbury breccia show few notable compositional traits when compared to crystals from unmineralized material, although on the North Range elevated levels of NiO were identified within amphibole (up to 1.18 wt %), biotite (up to 1.06 wt %) and chlorite (up to 1.95 wt %) and as such could be used to identify prospective areas. These enrichments are not observed on the South Range. Halogen concentrations within the alteration assemblage from two North Range properties show an increase in average bulk Cl concentrations with proximity to mineralization, with Cl levels doubling around irregular veinlets and increasing between five- and ten-fold near sulfide veins. This increase is not reflected in the compositions of alteration phases, which have Cl and F concentrations typically consistent with unmineralized material. The observed increase is therefore thought to be the result of either the presence of discrete halides interstitial to silicates or an increase in the modal abundance of the halogen bearing hydrous ferromagnesian phases within the halo of mineralization. Hydrothermal mineralization from the North Range was associated with two saline fluids occurring as isolated inclusions termed Type 1A, homogenizing between 223.8 °C and 377.5 °C (33.1 to 45.1 wt % NaCl, or 15 to 18 wt % MgCl₂ equiv.) and type 1B between 391.6 °C and 413.3 °C (46.5 to 48.9 wt % NaCl equiv.).
former inclusion type is considerably more common and is interpreted as possibly representing hydrothermal fluid responsible for quartz ± carbonate + sulfide veins within the low-sulfide zones. Type 1B inclusions are rarely observed and likely represent late stage magmatic fluids emanating from proximal sulfide veins and irregular veinlets. Circulation of barren hydrothermal fluids likely occurred both pre-, syn- and post-mineralization. Three generations of fluids between 87.1 °C and 299.6 °C with salinities of 16.8 to 26.7 wt % CaCl$_2$ and 31.7 to 38.1 wt % NaCl have been identified in secondary inclusion trails.

Calculated equilibrium temperatures from amphibole-plagioclase geothermometry indicate that the low-sulfide mineralization from the North Range was deposited in Sudbury breccia which equilibrated between 440 °C and 533 °C, consistent with the albite-epidote to hornblende hornfels contact metamorphic assemblage observed in unmineralized pseudotachylite. The host rocks for low-sulfide mineralization from the South Range Denison property record equilibrium temperatures and pressures between 513 to 645 ± 50 °C and 2.0 to 7.7 ± 1.0 kbar. These temperatures and pressures are consistent with the pre-impact Blezardian or post-impact Penokean amphibolite to greenschist facies assemblage observed within metabasalts. The broad pressure range might result from partial re-equilibration of Blezardian assemblages in the contact metamorphic aureole of the SIC.

### 3.2 Introduction

The majority of mineralization within the Sudbury footwall shows a close spatial relation to Sudbury breccia. These Sudbury breccia bodies represent a window into footwall conditions post impact, since they were likely formed during crater collapse and thus escaped the complicating features imposed on their host rocks by previous metamorphic events. Sudbury Breccia along the North Range commonly retains assemblages consistent with its position in the metamorphic aureole of the SIC, and these conditions likely persisted during the mineralizing event.

The presence of both sharp-walled vein and low-sulfide mineralization within Sudbury breccia and the crystalline basement typically result in the formation of alteration assemblages dominated by actinolite + epidote and epidote + chlorite, respectively. Although controversy
persists regarding the magmatic or hydrothermal origins of the alteration halo, the trace element chemistry has proven useful in the delineation of mineralized zones and as a vectoring tool. Analyses of ferromagnesian minerals compositions, particularly amphibole, have identified halogen-rich compositions and phases proximal to sulfide bodies (Springer, 1989; Li and Naldrett, 1993a; McCormick and McDonald, 1999), and the high modal abundance of such phases has been interpreted to be the cause for elevations in the whole rock halogen content (Jago et al., 1994; Hanley and Mungall 2003; McCormick et al., 2002). The variation in halogen content, specifically the Cl:Br ratio, was noted by Hanley et al. (2004) to increase with proximity to mineralization, although unlike previous investigators they attribute the increase not to the presence of unusually halogen-rich ferromagnesian minerals, but rather to an increase in the modal abundance of hydrous ferromagnesian minerals bearing unremarkable halogen concentrations (Hanley and Mungall, 2003, Hanley et al., 2004). More recently analysis of amphibole has revealed an increase in Ni content within low-sulfide mineralized zones (Tuba et al., 2010) and with proximity to sharp-walled veins (Hanley and Bray, 2009).

The presence of saline hydrothermal fluids associated with footwall mineralization from both the North and South ranges is well established (Farrow and Watkinson, 1992; Li and Naldrett, 1993; Farrow and Jones, 1994; Molnár et al., 1997, 1999; 2001; Marshall et al., 1999; Molnár and Watkinson, 2001; Hanley et al., 2005b; Péntek et al., 2008), with the majority of models proposing a major role for these fluids in the generation of sharp-walled veins and low-sulfide mineralization. The importance of these fluids remains debatable; however, the gangue-dominated PGE-rich quartz ± carbonate + sulfide (QCS) veins of both the North and South Ranges would appear to be firm evidence that hydrothermal fluids made some contribution to low-sulfide mineralization.

### 3.3 Analytical Methods

Electron microprobe analysis was undertaken to identify major and selected trace element concentrations of sulfides and silicates. Furthermore these data were applied to geothermometric and geobarometric equations in order to estimate temperatures and pressures of equilibration of key mineral assemblages.
Quantitative silicate mineral microanalyses were carried out using a JEOL SX-50 electron microprobe (EMP), housed within the Department of Geology, University of Toronto. The silicate analysis routine employed a beam diameter of 1 to 8 μm, typically the latter, at 20 kV, 10 nA. The beam diameter was decided upon in advance based on the size of phases to be analyzed, which were determined by optical methods. Possible sulfide contributions to the signal were monitored by measuring Cu and Ni, with the assumption that significant counts of either might indicate a contribution of X-rays from a sulfide phase outside the silicate mineral of interest. Corrections for contamination were made assuming stoichiometry where required. The routine employed the following X-ray lines for analysis and calibration: Fe Kα, Ca Kα, Al Kα and Mg Kα (hornblende, 20 s), Mn Kα (bustamite, 40 s), Ni Kα (pentlandite, 40 s), Cu Kα (chalcopyrite, 40 s), K Kα (sanidine, 30 s), Cl Kα (turgutroe, 40 s), Cr Kα (chromite, 40 s), Ti Kα (hornblende, 40 s), F Kα (fluorite, 40 s) and Na Kα (albite, 40 s). Initial epidote analyses also included the La Lα, Ce Lα and Y Lα lines (60 s count-time), however they were removed after all analyses displayed concentrations below detection. Sulfides were analyzed using an extended routine calibrated to Fe Kα (pentlandite, 40 s), Ni Kα (millerite, 80 s), Cu Kα (chalcopyrite, 20 s), S Kα (millerite, 80 s), Sn Lα (stannite, 20 s), Sb Lα (stibnite, 20 s), Zn Kα (sphalerite, 40 s), Pb Mα (galena, 40 s), Mn Kα (bustamite, 40 s), Bi Mα (matildite, 40 s), Ag Lα (matildite, 80 s), Co Kα (cobaltite, 80 s), As Kα (cobaltite, 80 s) and Se Kα (stilleite, 200 s). Interference corrections were made using Probe for EMPA © (J. Donovan Advanced Microbeam Inc.), with mineral formulae calculated by MinPet © or Excel spreadsheet, assuming stoichiometry.

Qualitative analyses were undertaken for micro-veinlet and alteration phases too fine-grained for quantitative analysis. A JEOL JSM-840 scanning electron microscope with a PGT/AAT energy dispersive spectrometry (EDS) detector, IXRF 500 digital pulse processor and EDS2008 software was used for all analyses. Point analyses were run at 20 kV, with a 60 second count time. Silicates were analyzed using the following X-ray lines: Fe Kα, Ni Kα, Si Kα, Al Kα, Mg Kα, Ca Kα, Na Kα, Mn Kα and Ti Kα, and Fe Kα, Ni Kα, S Kα, Cu Kα, Zn Kα and Pb Lα for sulfides.

X-Ray florescence spectroscopy for Cl and Br was undertaken at the Department of Geology, University of Toronto, using a Phillips 2404 spectrometer, with a Cu X-ray source. Representative samples were first crushed by jaw-crusher before being pulverized to a fine
powder within a tungsten-carbide puck mill. A fraction of the resulting powder was lightly compressed into a 1 to 2 mm (visual estimation) disc before addition of a borax substrate and final compression to form a solid 2.8 cm pressed powder pellet. The apparatus was brushed down and cleaned with ethyl alcohol between pellets. The XRF was calibrated to the international reference standard MAG-1 (marine mud) and a range of in-house synthetic standards containing KCl, NaCl and KBr of known concentration within a silica powder matrix. The halogens were measured sequentially with minimum detection limits (3σ) of 5 ppm for Cl and 0.45 ppm for Br.

Fluid inclusion analysis was focused on quartz-hosted, isolated inclusions and secondary trails. Samples were taken from irregular veinlet (IRV) and quartz ± carbonate + sulfide (QCS) mineralization, and sulfide + PGM free barren quartz + epidote veins. Resolvable inclusions could not be obtained from IRV. Doubly-polished quartz wafers were analyzed using a Leitz microscope-mounted Linkam THMS600 heating-cooling stage. Temperature measurements have a conservative accuracy of ± 1 °C, for the 5 to 10 μm inclusions analyzed. The stage temperature was calibrated using synthetic fluid inclusions from Bubble Inc. The calibration curve employed was generated from three reference points, 1) the homogenization temperature of H₂O inclusions (critical density), expected at 374.1 °C, 2) the ice melting temperature of H₂O inclusions (critical density), expected at 0.0 °C and 3) the melting temperature of H₂O-CO₂ (25 mole % CO₂) inclusions, expected at -56.6 °C. The equation of the resulting curve was used to obtain the true temperatures.

3.4 Major Silicates of Interest

3.4.1 Amphibole

Actinolite is common within all major footwall lithologies, i.e. felsic gneiss, pseudotachylite, mafic gneiss and diabase. Three discrete actinolite types were identified from petrographic observations. Type 1 (T1) is the dominant amphibole within pseudotachylite, with crystals occurring individually or as aggregates, located within the pseudotachylite groundmass which is dominated by granoblastic quartz and lesser plagioclase and potassium feldspar, along with
chlorite, epidote, biotite and accessory titanite and apatite. These acicular actinolite (25 to 200 μm) crystals were commonly observed to form aggregates with epidote ± chlorite. Type 2 (T2) actinolite comprises short, stubby crystals principally located along the margins of, and oriented into, quartzo-feldspathic clasts. Crystals range from 50 to 200 μm, displaying a subhedral habit, often with minor epidote and lesser chlorite located within actinolite interstices. Clasts with T2 actinolite typically display monomineralic quartz cores with 50 to 300 μm rinds composed of quartz, potassium feldspar and plagioclase feldspar. These rinds have commonly been affected by loss of feldspar, which has been replaced by T2 actinolite and lesser chlorite. Type 3 (T3) actinolite is limited to uralite bodies some 100 to 600 μm in size, composed of parallel masses of fine acicular actinolite, with margins of fine grained epidote + chlorite ≤ 30 μm thick apparently replacing earlier ferromagnesian porphyroblasts or phenocrysts. Uralite was also commonly observed within samples of felsic gneiss from the North Range properties, displaying similar marginal assemblages. The precursor phase remains uncertain in most rock types although in examples hosted by pseudotachylite hornblende is favoured over pyroxene, given the distances from the sampled localities to the pyroxene hornfels zone around the base of the SIC (Dressler, 1984). A second generation of actinolite in felsic gneiss was also observed with large (50 to 450 μm) optically continuous crystals replacing an unknown brown phase, displaying a single cleavage, parallel to the elongation direction, where visible, likely a ferro- or magnesiohornblende.

Type-1, type-2 and uralite actinolite display compositional ranges covering most of the actinolite field (Figure 3.1A). The actinolite consistently contains trace concentrations of Na and K averaging 0.50 % Na₂O and 0.21 % K₂O, respectively. Correlations between elements are dominantly controlled by stoichiometry as expected, e.g. Fe²⁺ ↔ Mg²⁺. The presence of IRV mineralization can be seen to coincide with a decrease in the Mg# and Si atoms per formula unit (apfu) in associated actinolite. A similar trend is not noted for amphibole associated with sulfide veins, which ranges from ferroactinolite-tremolite. Amphibole from mineralized material has lower Na₂O and K₂O concentrations, with sulfide vein and IRV material averaging 0.14 % Na₂O and 0.05 % K₂O and 0.25 % Na₂O and 0.08 % K₂O, respectively (Table 3.1). As noted by Hanley and Bray (2009), there is an increase in Ni content in actinolite proximal to mineralization at the three North Range properties. Actinolite associated with alteration selvage
(ferroactinolite-actinolite) has Ni contents above 0.02 apfu, whereas unmineralized material remains below this value (Figure 3.2A). This distinction is not as strong for crystals straddling the actinolite-tremolite compositional divide (Mg # of ≥ 0.9), in which Ni contents vary between < 0.01 to 0.05 apfu.

Groundmass amphiboles from the metavolcanic Elsie Mountain and Stobie formations on the South Range define a broad compositional field (Figure 3.1B), with crystals typically having magnesiohornblende cores that grade into actinolite or ferrotschermakite margins (Figure 3.3E) along with abundant magnesiohornblende porphyroblasts (50 to 5000 μm). Groundmass amphibole covers a broad range of Ni concentrations from below detection limits (B.D.) (avg. < 0.08 %) to 1.12 % NiO, with cores averaging 0.45 % and rims 0.32 %. Mineralized material shares this broad NiO range, ranging from 0.08 to 0.43 % NiO (Figure 3.2B and Table 3.1). Magnesiohornblende porphyroblasts have NiO concentrations consistently below detection (avg. < 0.08 %).

The halogen content of North Range amphibole is highly variable, with analyses of Cl and F commonly below detection limits. Unmineralized footwall material set a background level ranging from below detection to 0.50 wt % (avg. 0.07 wt %) F and below detection to 0.33 wt % (avg. 0.04 wt %) Cl. Samples close to irregular veinlets samples display no average Cl enrichment with values ranging from below detection to 1.176 wt % (avg. 0.04 wt %), with slightly reduced F concentrations ranging from below detection to 0.49 wt % (avg. 0.06 wt %). Amphibole associated with sulfide veins presented crystals displaying reduced Cl concentrations from below detection to 0.10 wt % (avg. 0.01 wt %) and F enrichment to values as high as 0.74 wt % (avg. 0.13 wt %). Crystals from mineralized zones displayed no Mg-Cl, Fe-F correlations indicating that halogen avoidance played little part in controlling halogen concentrations (Ramberg, 1952). The presence of strongly positive K-Cl and A-site Na-Cl correlations (IRV only) indicate that filling of the amphibole A-site has to some degree controlled Cl distribution (Morrison, 1991). This association is in keeping with mineralizing fluid analysis that indicated the presence of abundant alkali-metals in solution (Hanley at al., 2005b), with K-Cl correlations ascribed to crystallization in Cl-rich environments (Morrison, 1991).
Examples of South Range amphibole associated with mineralization contain Cl and F concentrations similar to the groundmass hosted equivalents. Groundmass crystals display a broad Cl/(Cl + F) ratio range, between 0.08 and 1.00, averaging 0.42 (core) and 0.55 (rim), reflecting a doubling of average Cl concentrations form the centre to the margin of crystals (see Table 3.1). Halogen levels within silicates associated with mineralization show increases in average F from QCS and stockwork mineralization and Cl from sulfide veins relative to unmineralized groundmass crystals. These data are however somewhat variable, with the Cl and F showing considerable overlap for both mineralized and unmineralized material.
Figure 3.1. Classification of calcic amphibole analyses following Leake, (1997), (Na+K)A-SITE < 0.5; Ti < 0.5. A: Average points for all North Range properties, light grey field denotes data range of pseudotachylite. B: Average points for all South Range properties, colorless field denotes the data range of groundmass amphibole cores, with the dark grey field denoting the data range for groundmass amphibole rims.
Figure 3.2. Ni (apfu) vs. Mg# [Mg/(Mg+Fe)] plots for (A) North Range amphibole: Grey triangles: Footwall lithologies, open circles: Sulfide vein and black circles: IRV and (B) South Range amphibole: Dark grey pentagons: Footwall lithologies, black diamonds: Sulfide vein, and open diamonds: QCS. Note the separation of mineralized and mineralized material on the North Range (A), but not on the South Range (B).
Figure. 3.3 A: Representative pseudotachylite consistent with that of the Levack North and Capre properties composed of granoblastic quartz (Qtz) and plagioclase (Pl), fully and partially enclosed by poikilitic biotite (Bio), with coarse amphibole (Amp) and lesser epidote (Ep) and chlorite (Chl). B: Representative pseudotachylite from the Wisner property displaying granoblastic quartz and plagioclase, along with abundant chlorite and lesser poikiloblastic biotite, titanite (Ttn) and magnetite (Mgt), enclosing a single potassium feldspar (Kfs) dominated clast. C: Recrystallized granoblastic quartz dominated clast, with interstitial potassium feldspar and chlorite, Levack North property. D: Sudbury breccia clast under XPL displaying granophyric margin, well developed in the top left of the clast. Clast margins assemblage comprised of irregular quartz and irregular-angular potassium feldspar, enclosing granoblastic quartz with marginal chlorite and epidote, Capre property. E: Greenschist groundmass displaying abundant aligned amphibole grading from brown magnesiohornblende cores grading to green-yellow-brown actinolitic-ferrotschermakitic margins. Interstices are quartz dominated with accessory titanite, magnetite and muscovite (Ms), Denison property. F: Garnet (Grt) porphyroblast within a biotite + quartz dominated groundmass with magnetite dominated domains and accessory plagioclase, Denison property.
3.4.2 Biotite

Fresh examples of biotite from the North Range properties are almost exclusively limited to pseudotachylite, as biotite hosted within the Archaean basement is typically moderately to completely chloritized. Unmineralized Sudbury breccia typically displays poikiloblastic biotite crystals enclosing quartz and lesser plagioclase, ranging from 100 μm to 1.5 mm, which are visible in core as black specks (Figure 3.3A and 3.3B). Biotite constitutes up to 5 modal % of pseudotachylite, although it is commonly < 1 modal %. A generation of subhedral, inclusion-free biotite porphyroblasts ranging from 200 to 500 μm was also noted. This latter generation is universally moderately to completely chloritized, with the development of fine epidote along crystal margins and the growth of titanomagnetite along cleavage planes. Poikilitic biotite generally remains fresh, showing only weak, patchy alteration to chlorite and titanomagnetite along crystal margins.

Pre-existing biotite did not survive the introduction of any of the mineralization types, with modal abundances rapidly dropping to near zero approaching the veins; however proximal to sulfide vein and IRV mineralization new growth of biotite is observed, displaying no to moderate chloritization. Microprobe analyses were obtained on biotite proximal to sulfide vein and IRV mineralization as well as from unmineralized Sudbury breccia (Table 3.2). Biotite from footwall lithologies in the North Range displays a broad range in AlIV which overlaps completely with both biotite proximal to both IRV and sulfide vein (Figure 3.4).

Biotite associated with mineralized material displayed comparative enrichments in Fe, with IRV and sulfide vein proximal material displaying slightly elevated FeO contents of 16.74 to 29.02 % (avg. 20.59 %) and 16.87 to 29.18 % (avg. 22.94 %), respectively, compared with 14.93 to 24.30 % (avg. 19.80 %) in unmineralized material. NiO is also enriched close to IRV and sulfide vein occurrences, with concentrations ranging from B.D. to 0.61 % (avg. 0.29 %) and B.D. to 1.06 % (avg. 0.27 %) respectively, compared with background values of B.D. to 0.11 % (avg. 0.03 %) in unmineralized material. Similar variation of Fe content, associated with increasing proximity to mineralization, was noted by Hanley and Mungall (2003), however the present results do not display the same strong trend towards the annite-siderophyllite join (Figure 3.4).
Figure 3.4. Compositional classification of averaged biotite analyses (after Bailey, 1984) based on Mg# [Mg/(Mg+Fe)] vs. AlIV (apfu). Light Grey Field: Compositional range of pseudotachylite biotite, from this study. Dark grey field: Compositional range of South Range groundmass biotite, from this study.
Figure 3.5. Cl/(Cl+F) vs. Mg# (atomic proportions), all biotite data from North Range pseudotachylite associated with unmineralized and mineralized (sulfide vein and IRV) material, after Hanley and Mungall, (2003). Hydrothermal and magmatic fields defined by Farrow and Watkinson (1999), the former being defined by biotite analyses from the McCreedy West, Fraser Cu Zone and Thayer Lindsley mines, marking a trend of decreasing Mg# and increase in Cl/(Cl+F) ratio approaching mineralization footwall mineralization (Hanley and Mungall, 2003). The magmatic field was defined by analyses of biotite from primary magmatic Ni-Cu-PGE mineralization bearing intrusions.
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Footwall

North Range
Footwall Sulf. Vein
IRV
Hbl Porp.
Average Average Average
10
37
135

Footwall
Core
Average
98

Footwall
Rim
Average
90

South Range
Sulf. Vein

QCS

Stockwork

Average
33

Average
28

Average
28

n=

Average
144

SiO 2

52.91

47.59

54.90

52.57

46.53

50.11

48.76

48.24

46.82

TiO 2

0.15

0.88

0.03

0.06

1.50

0.14

0.17

0.17

1.45

Al2 O3
FeO
Cr2 O3
NiO
MnO
MgO
CaO
Na2 O

2.93
14.27
0.02
0.03
0.34
14.13
11.99
0.50

5.82
15.61
0.04
0.00
0.23
13.49
11.64
1.38

0.92
12.34
0.00
0.51
0.24
15.85
12.81
0.14

1.70
17.00
0.01
0.42
0.31
12.14
12.14
0.25

8.11
17.24
0.04
0.45
0.27
11.09
11.41
0.81

6.10
16.55
0.02
0.32
0.23
11.85
12.34
0.57

7.96
14.41
0.21
0.22
0.26
13.01
12.01
0.94

8.53
16.40
0.11
0.11
0.37
11.27
11.94
0.88

8.47
16.33
0.05
0.04
0.32
11.50
11.35
0.93

K2O
F
Cl
Subtotal
O = Cl, F
Total

0.21
0.07
0.04
97.53
0.04
97.49

0.73
0.42
0.20
98.00
0.22
97.78

0.05
0.13
0.01
97.41
0.06
97.35

0.08
0.06
0.04
96.37
0.03
96.34

0.35
0.02
0.03
97.36
0.02
97.34

0.14
0.03
0.07
98.13
0.03
98.10

0.23
0.02
0.27
98.04
0.07
97.97

0.22
0.08
0.09
98.20
0.05
98.15

0.34
0.08
0.01
97.61
0.04
97.57

Si
Al

7.70
0.30

7.03
0.97

7.92
0.08

7.85
0.15

6.89
1.11

7.33
0.67

7.07
0.93

7.05
0.95

6.89
1.11

Fe3+
Ti
T Sites

0.00
0.00
8.00

0.00
0.00
8.00

0.00
0.00
8.00

0.00
0.00
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0.00
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8.00

0.00
0.00
8.00

Al
Cr

0.20
0.00

0.04
0.01

0.08
0.00

0.15
0.00

0.30
0.00

0.38
0.00

0.43
0.03

0.52
0.01

0.36
0.01

Fe3+
Ti
Mg

0.12
0.02
3.07

0.36
0.10
2.97

0.00
0.00
3.41

0.02
0.01
2.70

0.38
0.17
2.45

0.15
0.02
2.58

0.28
0.02
2.81

0.23
0.02
2.46

0.33
0.16
2.52

Fe2+
Ni
Mn
Ca
C Sites

1.57
0.00
0.02
0.00
5.00

1.51
0.00
0.01
0.00
5.00

1.43
0.06
0.02
0.00
5.00

2.05
0.05
0.02
0.00
5.00

1.63
0.05
0.02
0.00
5.00

1.83
0.04
0.01
0.00
5.00

1.40
0.03
0.02
0.00
5.00

1.73
0.01
0.02
0.00
5.00

1.59
0.01
0.02
0.00
5.00

Mg

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

0.00

Fe2+
Mn
Ca
Na
B Sites

0.04
0.02
1.87
0.07
2.00

0.06
0.01
1.84
0.08
2.00

0.06
0.01
1.93
0.00
2.00

0.06
0.02
1.93
0.00
2.00

0.13
0.02
1.81
0.05
2.00

0.05
0.01
1.93
0.00
2.00

0.07
0.02
1.87
0.05
2.00

0.05
0.02
1.87
0.06
2.00

0.08
0.02
1.79
0.11
2.00

Ca
Na
K
A Sites

0.00
0.08
0.04
0.11

0.00
0.31
0.14
0.45

0.05
0.04
0.01
0.10

0.02
0.07
0.02
0.11

0.00
0.18
0.07
0.25

0.00
0.16
0.03
0.19

0.00
0.22
0.04
0.26

0.00
0.19
0.04
0.24

0.00
0.16
0.06
0.22

Cation Σ

15.11

15.45

15.10

15.11

15.25

15.19

15.26

15.24

15.22

Cl
F
Oxygen Σ

0.01
0.03
23.05

0.05
0.20
23.00

0.00
0.06
23.02

0.01
0.03
23.04

0.01
0.01
23.00

0.02
0.01
23.00

0.07
0.01
23.00

0.02
0.04
23.00

0.00
0.04
23.01

Mg#
Cl/(Cl + F)

0.66
0.25

0.66
0.20

0.70
0.05

0.57
0.26

0.60
0.42

0.59
0.55

0.67
0.88

0.59
0.37

0.61
0.08


The metabasalts and “metarhyolite” of the lower Elliot Lake Group typically have biotite abundances of < 1 modal %, with 25 to 100 μm anhedral crystals located interstitial to groundmass amphibole and granoblastic quartz. This contrasts with the sporadic biotite schist horizons, which typically show groundmass biotite abundances exceeding 65 modal %. Biotite analyses dominantly plot in the siderophyllite quarter of the phlogopite–annite– eastonite–siderophyllite system (Figure 3.4). The most Fe rich mica is hosted by fine granoblastic granofels. The presence of sulfide vein and QCS mineralization is associated with a coarsening of groundmass phases and a minor increase in biotite abundance (up to 2 modal %). Mineralization in contact with granofels has a biotite-dominated selvage, likely after chlorite and potassium feldspar.

Analyses of biotite from South Range footwall lithologies indicate two distinct populations; those with an Mg# of > 0.3 and those with an Fe# of < 0.2. The separation is purely lithological. Biotite hosted within greenstones, greenschists and biotite schists has Fe# values of > 0.3, whilst crystals from granofels samples have values of < 0.2. The comparatively elevated Fe content in the granofels is attributed to the initial compositions of the protolith mica and the lack of other major Fe bearing phases i.e. amphibole and primary chlorite. Mineralization is primarily hosted within the volumetrically dominant metabasalts and therefore crystals with an Fe# of > 0.3 are considered more suitable for general compositional comparisons between biotite from mineralized and unmineralized metabasalt. Mineralized materials (sulfide vein, QCS and stockwork samples) display little compositional difference when compared to unmineralized samples, with minor reductions in average Fe# and AlIV content the only discernible variation (Table 3.2). Comparisons of the Fe content of South Range biotites from mineralized and unmineralized samples reveal little compositional difference. The observed reduction in Fe# is mirrored by increased Mg concentrations, with levels increasing from an average of 9.08 % MgO in unmineralized material to an average of between 11.07 and 12.99 % MgO for mineralized material. Correlations between AlIV and Fe + Mg were strongly negative, with values for
mineralized and unmineralized biotite between $R = -0.47$ and -0.77, consistent with the substitution of Mg and Fe for Al within the Y-Site, balanced by Al replacing Si within the tetrahedral sites, a Tschermak substitution (Waters and Charnley, 2002). Interestingly Fe and Mg display no consistent correlation to Al$^{VI}$. In contrast tetravalent and trivalent ions (Ti and Cr) within the Y site did show some correlation, with Cr producing strong negative ($R = -0.55$) and moderately positive ($R = 0.45$) correlations with Fe and Mg, respectively, and Ti the reverse ($R_{Ti:Fe} = 0.41$ and $R_{Ti:Mg} = -0.53$). The lack of correlation would suggest that substitutions of Ti, Cr and Al have a substantial control on Mg and Fe concentrations, whilst requiring balancing through Al $\rightarrow$ Si substitution in the tetrahedral site. Associations between Si, Al$^{IV}$ and Al$^{VI}$ and Cr and Ti failed to show strong correlations. The lack of consistent correlations indicates that Tschermak substitutions must occur in conjunction with an additional process. Walters and Charnley (2002) noted that the substitutions into the Y-Site were also accommodated by vacancy formation, reducing the need for Al $\rightarrow$ Si substitution. A combination of these processes will be sufficient to reduce their respective signatures.

Granofels Fe-rich biotite failed to display any correlation between Al$^{IV}$ and Fe + Mg, consistent with Fleet’s (1993) observation that excess Al within Fe-rich biotite could not be exclusively explained by Tschermak substitution, with excess Al instead explained by increased concentrations of dioctahedral components, in this instance Ti. The proposed Ti enrichment is consistent with analyses of granofels hosted biotite having Mg# < 0.2 which contained an average TiO$_2$ concentration 0.4 wt % greater than those of biotite with an Mg# of > 0.3.

North Range biotite crystals contain consistently detectable concentrations of F and Cl, with Cl/(Cl+F) ratios for crystals from unmineralized samples between 0.02 and 0.56 (avg. 0.17). Analyses from sulfide vein and IRV mineralization displayed significant overlap with unmineralized material. The Cl/(Cl+F) ratio ranged from 0.04 to 0.72 (avg. 0.32) and 0.02 to 0.80 (avg. 0.18) respectively, displaying a weak trend of increasing Cl/(Cl+F) proximal to mineralization (Figure 3.5). A similar but considerably stronger trend was noted by Hanley and Mungall (2003) approaching sharp-walled vein mineralization.

South Range footwall biotite contains consistently detectable concentrations of Cl, however F concentrations vary. Biotite from unmineralized footwall rocks (Fe# < 0.7) contain detectable F
in 81 % of analyses, with Cl/(Cl+F) ratios between 0.08 and 0.30 (avg. 13). Mineralized material produced measureable F in 10 to 34 % of points, whilst crystals from stockwork mineralization produced levels consistently below detection. Sulfide vein and QCS mineralization did yield increases in F concentrations, with Cl/(Cl+F) ratios ranging from 0.24 to 0.67 (avg. 0.36) and 0.12 to 0.36 (avg. 0.25), with averages calculated only from points with detectable F. Halogens from both ranges displayed no correlations to major or trace elements suggesting that halogen avoidance is not a major control on F and Cl concentrations (Ramsberg, 1952; Rosenberg and Foit, 1977).

### 3.4.3 Chlorite

Chlorite was observed within all footwall lithologies and mineralizing styles. Chlorite associated with unmineralized Sudbury breccia occurs as clots of crystals located along the faces and junctions of granoblastic groundmass quartz and intergrown with it. Plates range from 10 to 50 μm in size and display an anomalous green-grey birefringence. In contrast chlorite that replaces older, non-poikiloblastic, biotite shows anomalous blue birefringence. Chlorite is rarely a major constituent of sulfide vein and IRV selvages, however where present it typically occurs as radiating aggregates (50 to 250 μm) interstitial to amphibole, presenting anomalous purple-blue birefringence. The alteration haloes of all North Range mineralization display abundant chlorite, commonly exceeding its modal abundance in unmineralized material, likely due to replacement of ferromagnesian minerals and feldspar. Secondary growth of chlorite is particularly well developed in alteration haloes surrounding QCS veins, where chlorite replaces all phases except quartz and, rarely, albite. On the South Range chlorite occurs as bundles of aligned plates typically situated with quartz between groundmass amphibole. Bundles typically measure 20 to 50 μm in size with some examples displaying radiation damage expressed as pleochroic haloes, resulting from abundant accessory zircon and lesser monazite within the groundmass. Biotite shows moderate patchy alteration to chlorite and fine grained titanomagnetite. Chlorite displays no significant morphological difference or modal increase within the alteration haloes of mineralization, when compared to unmineralized material. Chlorite within the alteration selvage of sulfide and QCS veins varies from radiating bundles interstitial to amphibole and biotite, to aligned bundles orientated parallel to the vein margin.
Chlorite crystals from footwall and mineralized samples on the North Range display broad and overlapping compositional ranges with respect to Fe# and Si/Al ratio, with crystals from unmineralized samples displaying compositions around the ripidolite–brunsvigite–pycnochlorite intersection; with chlorite from mineralized samples clustering dominantly within the ripidolite field, in the Hey (1954) classification. The estimation of Fe$^{3+}$ concentrations was achieved using the method of Droop (1987), with the majority of analyses (90 %) displaying no cation excess, calculated using a 28 oxygen stoichiometry. Because the ferric component did not exceed 0.178 apfu, with Fe$^{3+}$/Fe$^{2+}$ ratios between 0.0006 and 0.436 (avg. 0.0164), the bulk of chlorites were classified as “fresh”. Trace elements are remarkably uniform, with Ti, Cr, Ca, Na and K below or just above detection limits. Only Ni displays any significant variation and strictly within North Range chlorite (Figure 3.6 and Table 3.3). Chlorite in mineralized material contains zero to 1.95 % NiO, averaging 0.85 % around sulfide veins, 0.89 % around IRV and 0.58 % around QCS mineralization, with detectable levels in 91 to 100 % of points. In contrast unmineralized footwall lithologies and barren hydrothermal chlorite displayed concentrations from below detection to 0.796 % NiO, averaging 0.07 % in the footwall and 0.08 % in alteration associated with barren hydrothermal veins (Figure 3.3). Detectable concentrations of NiO occurred in only 54 and 59 % of points respectively.

Chlorite is rare on the South Range properties. No ferric component was calculated in 96 % of analyses and the majority of chlorite fell within the ripidolite field, with three crystals associated with sulfide veins classified as brunsvigite. The Fe# of footwall chlorite is skewed by 5 analyses, which straddle the ripidolite–daphnite divide (Fe# 0.83 to 0.89), whereas the remaining analyses lie within the range of mineralized material, with an Fe# of 0.30 to 0.56. Chromium concentrations are slightly elevated in chlorite close to sulfide veins and QCS veins, ranging from zero to 0.93 % (avg. 0.39 %) and zero to 0.23 % (avg. 0.10 %), respectively. These differ from background footwall values which remain below 0.10 % (avg. 0.02 %) (Table 3.3). Chlorite within zones of stockwork mineralization has Cr concentrations consistently below detection limits. The nickel content of South Range footwall chlorite ranges between zero and 0.30 % (avg. 0.13 %), with QCS and stockwork mineralization yielding similar values of 0.05 to 0.22 % (avg. 0.13 %) and zero and 0.29 % (avg. 0.13 %) respectively. Chlorite associated with sulfide mineralization displayed a minor enrichment, with between zero and 0.36 % NiO, averaging 0.23 % (Table 3.3).
Figure 3.6. Mg# vs. Ni (apfu) plot of chlorite analyses from the North Range. Light grey triangles (Ftwl, Bar. Hy.) denote points where data from unmineralized footwall lithologies and barren hydrothermal (quartz + epidote) veins overlap. Note: A significant number of footwall (42 %) and barren hydrothermal (34 %) analyses possessed Ni apfu values of 0, not presented on the figure above.

Halogen concentrations within chlorite were typically extremely low, with F concentrations near universally below detection. Crystals from both ranges contain measureable Cl in only 26 to 59 % of points, with average concentrations between 0.10 and 0.30 wt %.

3.4.4 Epidote

Epidote is a ubiquitous phase in both mineralized and unmineralized material from the North Range, commonly occurring with actinolite and/or chlorite within pseudotachylite and quartzofeldspathic lithologies. Epidote in granite and felsic gneiss is typically located within mafic aggregates interstitial to quartz, plagioclase and potassium feldspar, likely replacing hornblende, pyroxene or biotite. Epidote is rarely observed to replace plagioclase within the selvage and alteration halo of barren quartz + epidote veins. Identification of precursor phases within pseudotachylite is complicated by the fine crystal size (10 to 50 μm). Where epidote is associated with sulfide mineralization, it is typically located along the sulfide-silicate interface,
Table 3.2. Averaged biotite analyses for barren footwall lithologies, PGE-Cu-Ni free quartz veins and varies mineralizing styles from the North and South Range.

<table>
<thead>
<tr>
<th>North Range</th>
<th>South Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulf. Vein</td>
<td>IRV</td>
</tr>
<tr>
<td>n =</td>
<td>25</td>
</tr>
<tr>
<td>SiO₂</td>
<td>37.61</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.87</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.27</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02</td>
</tr>
<tr>
<td>FeO</td>
<td>22.94</td>
</tr>
<tr>
<td>NiO</td>
<td>0.27</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
</tr>
<tr>
<td>MgO</td>
<td>10.12</td>
</tr>
<tr>
<td>CaO</td>
<td>0.10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>F</td>
<td>0.27</td>
</tr>
<tr>
<td>Cl</td>
<td>0.24</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.94</td>
</tr>
<tr>
<td>Subtotal</td>
<td>100.00</td>
</tr>
<tr>
<td>O = Cl, F</td>
<td>0.17</td>
</tr>
<tr>
<td>Total</td>
<td>99.83</td>
</tr>
<tr>
<td>Si</td>
<td>5.64</td>
</tr>
<tr>
<td>Al⁴⁺</td>
<td>2.28</td>
</tr>
<tr>
<td>Al⁶⁺</td>
<td>0.07</td>
</tr>
<tr>
<td>Ti</td>
<td>0.32</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>2.88</td>
</tr>
<tr>
<td>Cr</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03</td>
</tr>
<tr>
<td>Mn</td>
<td>0.02</td>
</tr>
<tr>
<td>Mg</td>
<td>2.25</td>
</tr>
<tr>
<td>Ca</td>
<td>0.02</td>
</tr>
<tr>
<td>Na</td>
<td>0.02</td>
</tr>
<tr>
<td>K</td>
<td>1.75</td>
</tr>
<tr>
<td>Cation</td>
<td>15.29</td>
</tr>
<tr>
<td>F</td>
<td>0.25</td>
</tr>
<tr>
<td>Cl</td>
<td>0.12</td>
</tr>
<tr>
<td>OH</td>
<td>2.90</td>
</tr>
</tbody>
</table>

| Fe# | 0.56 | 0.50 | 0.50 | 0.43 | 0.50 | 0.52 | 0.57 | 0.89 |
| Cl/(Cl+F) | 0.33 | 0.17 | 0.14 | 0.82 | 0.53 | N/A | 0.19 | 0.71 |
occurring as anhedral crystals both fully and partially enclosed in sulfide and vice versa. Unmineralized pseudotachylite typically contains epidote abundances of 1 to 3 modal %, which increases (5 to 25 modal %) approaching both mineralization and barren quartz + epidote veins.

<table>
<thead>
<tr>
<th></th>
<th>North Range</th>
<th>South Range</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Footwall 153</td>
<td>Barren 61</td>
<td>Sulf. 29</td>
<td>IRV 56</td>
<td>QCS 55</td>
<td>Footwall 20</td>
<td>Sulf. 16</td>
<td>QCS 15</td>
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<tr>
<td>TiO₂</td>
<td>0.07</td>
<td>0.01</td>
<td>0.08</td>
<td>0.04</td>
<td>0.01</td>
<td>0.06</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.39</td>
<td>0.10</td>
</tr>
<tr>
<td>FeO</td>
<td>26.70</td>
<td>26.27</td>
<td>29.28</td>
<td>25.46</td>
<td>28.29</td>
<td>29.12</td>
<td>23.24</td>
<td>20.87</td>
</tr>
<tr>
<td>MnO</td>
<td>0.35</td>
<td>0.33</td>
<td>0.34</td>
<td>0.33</td>
<td>0.35</td>
<td>0.30</td>
<td>0.24</td>
<td>0.18</td>
</tr>
<tr>
<td>NiO</td>
<td>0.07</td>
<td>0.08</td>
<td>0.85</td>
<td>0.89</td>
<td>0.58</td>
<td>0.13</td>
<td>0.23</td>
<td>0.13</td>
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<tr>
<td>MgO</td>
<td>14.47</td>
<td>14.79</td>
<td>11.86</td>
<td>14.67</td>
<td>12.97</td>
<td>12.21</td>
<td>16.61</td>
<td>18.09</td>
</tr>
<tr>
<td>CaO</td>
<td>0.15</td>
<td>0.05</td>
<td>0.07</td>
<td>0.06</td>
<td>0.02</td>
<td>0.03</td>
<td>0.10</td>
<td>0.03</td>
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<tr>
<td>Na₂O</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
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</tr>
<tr>
<td>K₂O</td>
<td>0.08</td>
<td>0.02</td>
<td>0.14</td>
<td>0.02</td>
<td>0.01</td>
<td>0.00</td>
<td>0.22</td>
<td>0.01</td>
</tr>
<tr>
<td>F</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
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<td>0.01</td>
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<td>0.00</td>
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<tr>
<td>Cl</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>H₂O</td>
<td>11.34</td>
<td>11.13</td>
<td>10.81</td>
<td>11.74</td>
<td>10.57</td>
<td>10.93</td>
<td>10.79</td>
<td>11.78</td>
</tr>
<tr>
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<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>O = Cl, F</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 3.3. Averaged chlorite analyses for barren footwall lithologies, PGE-Cu-Ni free quartz veins and varies mineralizing styles from the North and South Range.
Increasing modal abundance of epidote produces a lightening in colour of pseudotachylite and the development of an apple-green colouration within quartzo-feldspathic rocks.

Few systematic variations in major or trace element compositions of epidote were discerned between mineralization types, all of which show extensive compositional overlap with epidote from unmineralized rocks (Table 3.4). Crystals associated with unmineralized footwall lithologies, barren hydrothermal veins, IRV and QCS mineralization all contain mole fractions of epidote \( (X_{\text{epi}}) \) of 59 to 96 %, clinozoisite \( (X_{\text{czo}}) \) 3 to 40 % and piemonte \( (X_{\text{pie}}) \) of 0 to 2 %, calculated following Franz and Liebscher (2004). However, epidote crystals associated with sulfide veins display a comparatively tight range of composition with \( X_{\text{epi}} \) between 79 and 95 %, \( X_{\text{czo}} \) between 4 and 21 %, and \( X_{\text{pie}} \) below 1 %, averaging \( X_{\text{epi}}= 88, X_{\text{czo}}= 12 \) and \( X_{\text{pie}}= 1 \) (Table 3.4). Analyses of common trace elements, especially REE by EMPA and a pilot LA ICP-MS study identified only sporadic low REE concentrations, with no variation between crystals from mineralized and unmineralized samples.

On the South Range epidote crystals were sparse and extremely irregular, in many cases containing inclusions of groundmass quartz. Epidote occurs interstitial to groundmass amphiboles, displaying a first order yellow-orange to anomalous blue birefringence consistent with compositions at the epidote-clinozoisite transition \( X_{\text{epi}} 50 \) to 51, \( X_{\text{czo}} 49 \) to 50. Epidote comprises \(< 1 \) modal % of greenschist and granofels groundmass. Its abundance increases near to barren hydrothermal and sulfide veins and veinlets, the latter displaying epidote only within the selvage.

### 3.4.5 Garnet

Although its low modal abundance and limited distribution preclude garnet as a possible vectoring tool its presence within samples from the Denison property is of interest with respect to metamorphic equilibrium. To date the presence of garnet associated with mineralization has been limited to the alteration haloes of mineralization hosted within quartz-diorite offset type deposits (Fleet et al., 1987; Carter et al., 2001; Magyarosi et al., 2002; Szentpeteri et al., 2003). The study of Fleet et al. (1987) noted that garnet typically occurred within the more fractionated (Fe-rich) quartz-diorite compositions. Fleet et al. (1987) presented average garnet compositions from
quartz-diorite within the Frood-Stobie breccia belt and Kirkwood Mine area of approximately almandine$_{74}$ grossular$_{12}$ pyrope$_{4}$ spessartine$_{10}$ and almandine$_{70}$ grossular$_{8}$ pyrope$_{13}$ spessartine$_{9}$ respectively. Data from the Copper Cliff South Mine produced more Mn-rich compositions with an average of almandine$_{58}$ grossular$_{14}$ pyrope$_{1}$ spessartine$_{26}$ (Carter et al., 2001). These values are slightly elevated with respect to Mn when compared to those of Magyarosi et al. (2002) from the Copper Cliff South 800 and 810 orebodies.

The garnet crystals analyzed within this study presented two morphologies. Garnet contained within granofels material (DN-196-004 and DN-196-011) displays subhedral to euhedral crystals between 40 and 150 μm occurring both individually and within domains containing up to 43 crystals, with the majority of examples occurring without associated ferromagnesian minerals (e.g. biotite, chlorite). In contrast the single garnet bearing biotite schist (DN-194-014) contained irregular garnet porphyroblasts of between 150 μm and 2.5 mm, presenting subhedral to euhedral faces (Figure 3.3F). In all cases the garnet appeared fresh, with only minor fracturing and no alteration. Cartier et al. (2001) and references therein noted the presence of weak zonation within garnet from the Copper Cliff South mine. In contrast all the crystals analyzed within this study display only patchy and typically minor variation. Spessartine (Sps) and pyrope (Prp) components are usually stable around Sps$_{20}$ and Prp$_{2}$ respectively. The almandine (Alm) component typically varies between 50 and 65, although more Fe-rich examples from the granofels samples contain a maximum component of Alm$_{75}$. The greatest variation occurs with respect to the grossular (Grs) component, which ranges between 3 and 25 %. The broad range for Ca is commonly accommodated by decreases in the Fe component, with a correlation of $R = -0.96$. Sample DN-194-014 yielded an average garnet composition of Alm$_{55}$Sps$_{21}$Grs$_{19}$Prp$_{05}$, with DN-196-011 producing an average of Alm$_{74}$Sps$_{22}$Grs$_{03}$Prp$_{01}$, from which the individual analyses displayed very little deviation. The greatest compositional play is associated with sample DN-196-004 which averaged Alm$_{63}$Sps$_{20}$Grs$_{09}$Prp$_{02}$, with a range of grossular components between 4 and 20 (Table 3.5).
Table 3.4. Averaged epidote analyses for barren footwall lithologies, PGE-Cu-Ni free quartz veins and varies mineralizing styles from the North and South Range.

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3.4.6 Ferromagnesian Silicate Summary

Although the diffuse nature of low-sulfide mineralization makes a clear boundary of mineralization difficult to define, the host lithologies do display some consistent changes in the composition of major silicate phases. Unlike previous studies (Li and Naldrett, 1993; McCormick et al., 2002; Hanley and Mungall, 2003) the halogen content of ferromagnesian minerals within the studied intersections failed to yield any clear distinction between PGE-Cu-Ni bearing and barren material from both ranges. Furthermore it is clear that for low-sulfide mineralization at least, epidote does not present a viable tool for compositional vectoring. The presence of mineralization within the North Range footwall is marked by a clear enrichment in the Ni content of amphibole, chlorite and biotite likely after Fe$^{2+}$, a substitution hinted at by the low levels of Ni associated with tremolite-actinolite from sulfide vein margins. This enrichment is weakly mirrored by the FeO content of amphibole and biotite, with crystals within the mineralized zone trending towards more Fe-rich compositions. In contrast South Range biotite within mineralized intersections display a decrease in Fe#, resulting from increases in MgO, whilst FeO contents remain comparable to unmineralized material. Analyses of amphibole, biotite and chlorite failed to yield any major variation in NiO content between mineralized and unmineralized samples, with only a minor enrichment in Cr observed from chlorite associated with the sulfide-rich mineralizing styles i.e. sulfide veins and QCS veins. Silicates from the South Range footwall lithologies display substantial compositional overlap making clear distinctions difficult.

3.5 Bulk Cl:Br Analysis

Increases in bulk Cl:Br ratios approaching mineralization have been noted for North Range footwall mineralization from the Fraser Mine (Hanley et al., 2004). The bulk Cl and Br concentrations within pseudotachylite represent the sum of halogens bound within silicates as well as halide salts hosted by fluid inclusions or interstitial to silicates. In this study analysis of samples was focused on unmineralized pseudotachylite matrix both near to and far from mineralization from the Levack North and Wisner properties, with samples selected to minimize
the sulfide content, which was typically << 1 modal %. The abundance of different and overlapping mineralizing styles associated with PGE-bearing intersections made it extremely difficult to separate pseudotachylite proximal to different mineralizing styles. Furthermore, very little unmineralized pseudotachylite material was present in the crystalline footwall at either side of the mineralized intersections available for sampling, so sampling opportunities in the majority of cases were limited. In light of these limitations, samples from within the mineralized intersections, (sulfide vein and IRV mineralization) are broadly distinguished from those collected in unmineralized pseudotachylite, but no attempt has been made to establish spatial trends in the data. Samples from the Capre property were deemed unsuitable given the high degree of hydrothermal alteration suffered by the footwall lithologies and the lack of significant pseudotachylite within brecciated zones.

Elevations in the whole rock halogen content associated with sulfide vein mineralization were noted, with Cl, Br and Cl:Br ratios significantly higher than background within sulfide vein hosting pseudotachylite from both the Levack North and Wisner properties (Figure 3.7 and Table 3.6). In contrast the halogen signal of IRV mineralization is not as strong, with moderate increases in Cl concentration, whilst Br levels are comparable to unmineralized pseudotachylite.

Mineralized and unmineralized material from the Denison property has overlapping Cl and Br concentrations. All samples, both mineralized and unmineralized, fell within a Cl range of 71.5 to 1306.4 ppm and Br range of 0.5 to 2.4 ppm, making any distinctions based on bulk rock halogen contents impossible. Unlike the Levack North and Wisner properties the Denison property has experienced considerably greater post-emplacement metamorphic effects, including circulation of hydrothermal fluids. The broad Cl and Br concentrations and the homogenization of the values are therefore unsurprising.
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Table 3.5. Selected and average garnet analyses from the Denison property. See text for sample information. Compositions based on 24 oxygen, with Fe³⁺ calculated following Droop (1987).
Table 3.6. XRF halogen data for mineralized and unmineralized pseudotachylite from the Levack North and Wisner properties.

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<td>1176</td>
</tr>
<tr>
<td>Average</td>
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<td>523</td>
<td>393</td>
</tr>
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</table>

The data collected from the Levack North and Wisner properties presents an increase in Cl within mineralized zones. Concentrations proximal to sulfide vein mineralization display substantial enrichments, with Cl concentrations approximately 11 and 5 times higher than barren pseudotachylite from the Levack North and Wisner properties respectively. Concentrations proximal to IRV mineralization display ranges overlapping with those of barren pseudotachylite, however average proximal values do display a near doubling of levels. Br levels associated with mineralization do not display any substantial variation. In contrast to the North Range samples the scatter of both Cl and Br concentrations from the Denison property was so great as to make comparisons impossible.
Figure 3.7. Log-log plot of bulk Cl vs. Br XRF analyses of pseudotachylite from distal unmineralized and samples proximal to mineralization. Dashed diagonal lines denote trends of constant Cl:Br ratio. LN = Levack North and WN = Wisner.

### 3.6 Fluid Inclusions

A pilot fluid inclusion study was undertaken on quartz ± carbonate + sulfide vein gangue from the Wisner and Capre properties. Definitively primary inclusions were sought, however no growth zones were clear within the analyzed crystals. Two types of isolated inclusions were identified, however their origin is uncertain, with the majority of recent works viewing inclusions of this type as secondary. The following data represents only a limited number of thin sections and analyses and should not be considered as a complete catalogue of the fluid inclusion populations present within North Range low-sulfide zones. Doubly-polished thin sections containing fluid inclusions suitable for microthermometry were prepared from quartz associated with QCS mineralization from the Wisner and Capre properties. Quartz associated with IRV mineralization yielded no usable inclusions. Coarse quartz associated with sulfide veins and capable of hosting inclusions was deemed on textural grounds to pre-date mineralization and therefore was not examined. Veins were discounted if the sulfide clearly post-dated the gangue
assemblage, with the migration of sulfide along crystal faces and fracture, the recrystallization of the chlorite dominated alteration selvage and the presence of abundant angular fragments of quartz within sulfide being taken as indicators of a magmatic origin.

As no growth zones displaying definitively primary inclusions were observed within the QCS vein quartz isolated inclusions i.e. single inclusions with no visible association with a secondary trail, were sought. Such isolated inclusions have previously been interpreted as primary i.e. the inclusion was trapped during the growth of the crystal, however recent work has suggested that they may simply represent secondary inclusions with the section orientated at 90° to the inclusion trail. All samples examined displayed abundant trails of secondary inclusions, occurring as randomly orientated chains of inclusions crosscutting quartz crystals and crystal margins.

Isolated inclusions were identified by their larger size (5 to 15 μm) and sub-rounded morphology. These inclusions were noted to contain 1 to 4 daughter phases and a vapor bubble volume fraction (at 25 °C) of 10 to 20 vol %. In this instance the term daughter phase (S₁) was used to describe a solid phase(s) within the inclusion that are soluble within the liquid portion. The predominant daughter phase typically occupies 25 to 40 vol % of the host inclusion and occurs as colourless isotropic crystals, with a cubic habit and high refractive index (RI) and is likely halite. Where additional phases are present they are small (≤ 1 μm), colorless, cubic or lath-shaped crystals with a high RI, making up around 1 vol % of the inclusion. Isolated inclusions occur in groups of no more than three, with the majority of examples (Type 1A) displaying a liquid (L) + vapor (V) + 1 to 2 daughter phase (S₁) assemblage (Figure 3.8). Type 1B (L + V + S₂ or S₄) inclusions (Figure 3.9) were also identified within the same samples and so it must be considered that the L + V + S₂ inclusion may have been misidentified, with a third or fourth daughter phase not optically visible due to its small size or masking by larger halide crystals or the vapor bubble.

Secondary trails are typically dominated by extremely abundant angular inclusions around 5μm in size within all QCS samples, in many cases totally masking any isolated inclusions that might have been present. Two discrete groupings of secondary inclusions were identified, Type 1SA (L + S₁ ± V) inclusions (Figure 3.10) and Type 2SA and 2SB, which are both L + V inclusions (Figure 3.11 and 3.12). Type 1SA inclusions display a sub-angular equant habit, with inclusions dominated by a single daughter phase, totalling 30 to 60 vol % of the inclusion. The presence of
small vapor bubbles within larger examples suggests that the inclusion is vapor saturated, however in smaller inclusions such a vapor bubble could not be observed, likely due to its small scale.

Type 2SA inclusions typically display a sub-angular morphology with a vapor bubble of 2 to 10 vol %. In contrast 2SB inclusions display irregular inclusions with sub-angular to angular margins and vapor bubble of 20 to 60 vol %; their irregular form would likely indicate entrapment along crystal margins and fractures, with subsequent 'necking', caused by the dissolution and precipitation of host quartz along the vein wall producing a range of complex intermediate forms and chains of equant secondary inclusions.

3.6.1 Microthermometry

The following temperature data represents values calculated using a calibration curve produced from fluid inclusion standards (see Section 3.3). The correction allowed for the effects of instrumental drift to be removed from the measured values.

Type 1A (L + V + S₁ to S₂) showed vapour bubble disappearance over a temperature range from 128.8 to 278.2 °C (Figure 3.13), consistently below the temperature of final daughter phase dissolution at 223.8 to 377.53 °C. Inclusions froze to a crystalline aggregate only after a double cycle of cooling and reheating. First melting temperatures were obtained from -26.9 to -36.9 °C with complete melting observed at -17.7 to -22.9 °C (Figure 3.14). The first melting values sit within a field of hydrated Mg, Na and K chlorides, with estimated salinities of between 33.1 and 45.1 wt % NaCl equivalent and 15 to 18 wt % MaCl₂ (Goldstein and Reynolds, 1994; Sterner et al., 1998). Temperatures of first melting between -30 and -40 °C were considered by Goldstein and Reynolds (1994) to be difficult to interpret as the exact concentrations of dissolved salts is unknown. As such the temperatures of first melting for type 1A inclusions might reflect a complex fluid, rather than a MgCl₂ dominated solution.

Type 1B (L + V + S₂ to S₄) inclusions homogenized by vapor disappearance at temperatures of 108.9 to 269.8 °C, with the low volume fraction daughter phases (S₁ to S₃) dissolving between 155.7 and 346.8 °C. Complete homogenization was achieved through halite dissolution between
391.6 and 413.3°C. Freezing of inclusions failed to yield resolvable ice crystals, even after repeated heating-freezing cycles. The failure of “ice” crystal nucleation was interpreted by Shepard et al. (1985) as an indication of trapped fluids of a highly saline and complex nature. An estimation of salinity was made following Sterner et al. (1988), producing a salinity range of 46.54 to 48.92 wt % NaCl equiv., however this value is inaccurate given the presence of additional phases that will interfere with halite dissolution.

Type 1SA inclusions commonly display no visible vapor bubble, although 35 % of them contain a bubble of < 0.1 vol %, suggesting that the fluid was near vapor saturation. The vapour bubble was observed to disappear between 101.6 and 131.6 °C with complete homogenization achieved by halite dissolution at temperatures of 223.7 to 276.8 °C (Figure 3.13). Temperatures of first ice melting could not be measured reliably, due to the daughter phase typically inhibiting observation. Final ice melting occurred at -30.2 to -38.4 °C, below published values for NaCl-H₂O melting point depression, although calculations following Steiner et al. (1988) produced NaCl equiv. of 33.5 to 36.5 wt %, with data from Oakes et al. (1990) indicating approximate salinities of 25.4 to 26.8 wt % NaCl + CaCl₂ = 0.169 equivalent, for inclusions displaying vapor saturation.

Type 2SA inclusions homogenized to the liquid phase through vapour dissolution between 87.1 and 149.7 °C, with final ice melting at -15.2 to -20.6 °C. Only two inclusions yielded temperatures of first melting, at -21.7 and -23.8 °C, placing them within a NaCl + H₂O system, possibly with additional dissolved KCl or Na₂SO₄. The final melting range equates to 31.7 to 38.1 wt % NaCl equivalent (Sterner et al., 1988).

In contrast to Type 2SA inclusions Type 2SB inclusions homogenized at significantly higher temperatures (197.4 to 299.6 °C). Frozen inclusions underwent first ice melting at -47.3 to -53.7 °C, with the final ice melting between -13.7 and -35.7 °C. The first melting temperatures suggest a CaCl₂ bearing system with additional Mg and K chloride components. Salinities were estimated from the experimental data of Oakes et al., 1990) at between 16.8 and 26.7 wt % CaCl₂, although these values do not take the KCl and MgCl₂ components into account.

Examination of QCS samples from the South Range properties produced few useable inclusions. Quartz crystals display abundant secondary trails of inclusions (consistently < 5 μm in size),
whereas isolated inclusions are rare. Associated vein carbonates were considered unsuitable for microthermometry because carbonate crystals display strong deformation features and cracked fluid inclusions. Three isolated 5 to 10 μm liquid + vapour + 1 daughter phase inclusions were identified within QCS vein quartz from the Denison property. The colourless daughter phase observe displayed a cubic habit, with no birefringence and is likely halite. The inclusions homogenized through daughter phase dissolution at 341.8 to 379.2 °C. Attempts to ascertain both the salinity and the dissolved salts failed as temperatures of both first and last melting could not be obtained, primarily due to the small inclusion size, with estimated salinities using Sterner et al. (1988) of between 41.7 to 45.3 wt % NaCl equivalent.

Figure 3.8. Isolated 7.5 μm Type 1A (L + V + 1 to 2 S) fluid inclusion within QCS vein quartz, Wisner property.
Figure 3.9. Isolated 7.5 μm Type 1B (L + V + 2 to 4 S) fluid inclusion in QCS vein quartz from the Wisner property. Note the of secondary Type 2SA inclusions in the bottom right of the image.

Figure 3.10. 5 μm Type 1SA (L + S ± V) fluid inclusion in QCS vein quartz, Wisner property. (A) Type 1SA inclusion with a 0.1 vol. % vapour bubble, (B) Type 1SA inclusion without a visible vapour bubble.
Figure 3.11. 5 μm Type 2SA (L + V) fluid inclusions in QCS vein quartz, Wisner property.

Figure 3.12. 7.5 μm Type 2SB (L + V) fluid inclusion trail in QCS vein quartz, Wisner property. Note: Inclusions display 'necking-down' due to the dissolution of the hosted quartz.
Table. 3.7. Summary of fluid inclusion data gathered during this study. Actual T = The corrected temperature calculated using the calibration curve. Homogenization was achieved through either total dissolution the vapour phase or the total dissolution of all daughter phases (S_i).

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Please note that the separation of Type 1A and 1B inclusions by number of daughter phases is the likely result of the authors inability to identify small daughers phases, or their masking by larger crystals.
Figure 3.13. Homogenization temperature of fluid inclusions from the Wisner and Capre properties. The final phase to dissolve is listed in brackets. See text for more information.

Figure 3.14. Temperature of final ice melting for fluid inclusions from the Wisner and Capre properties. See text for more information.
3.7 Discussion

3.7.1 Metamorphic Grade

In any effort to relate alteration processes to mineralization, it is first necessary to unravel the effects of pre-impact metamorphism, as well as later metamorphic effects, from the processes that accompanied the deposition of ore. It is furthermore necessary to distinguish thermal metamorphism related to cooling of the Sudbury Igneous Complex from possible more local effects related to emplacement of sulfide magmas and aqueous fluids into the footwall. These latter effects might have been felt prior to, during, or after the time of the peak temperature in the thermal aureole.

3.7.1.1 North Range

The footwall lithologies of the North Range underwent extensive metamorphism prior to the emplacement of the SIC. Burial of the Levack gneiss to between 21 and 28 km led to peak granulite grade metamorphism between $2661 \pm 2$ Ma to $2645 \pm 7/-4$ Ma. Consequent partial melting, along with contemporaneous uplift and unroofing contributed to the formation of the granitic Cartier batholith (Meldrum et al., 1997; Ames et al., 2008, references therein). The region was peneplained and buried under Paleoproterozoic sediments of the Huronian Supergroup (Young et al., 2001; Hanley and Mungall, 2004). Subsequent deformation and metamorphism during the poorly defined Blezardian orogeny led to the development of greenschist metamorphic mineral assemblages within isoclinally folded metasediments of the Cobalt Group (Riller and Schwerdtner, 1997; Mungall & Hanley 2004) and attendant retrogression of amphibolite or granulite facies assemblages in the basement gneiss.

The pseudotachylite matrix to bodies of the Sudbury breccia was formed at the time of the impact event and consequently is the only footwall lithology to have been affected exclusively by the thermal aureole of SIC and any subsequent metamorphic processes associated with the emplacement of mineralization. Pseudotachylite from all three properties contains an assemblage of actinolite + epidote + chlorite + plagioclase ($\text{An}_{17-46}$, avg. $\text{An}_{31}$) + quartz + biotite + titanite ± hornblende (Figures 3.3A and 3.3B). At the Levack North and Capre properties hornblende
occurs as porphyroblasts within a pseudotachylite assemblage dominated by actinolite \(\gg\) epidote \(>\) chlorite, whereas a hornblende porphyroblast free, chlorite \(\gg\) epidote \(>\) actinolite assemblage is present at Wisner. The reduced modal chlorite abundance shown by pseudotachylite from the Levack North and Capre properties is consistent with temperature in the region of 550 to 575 °C (Liou et al., 1974). This range denotes the upper stability limit for chamositic chlorite, which is coincident with the range of experimental conditions over which actinolite is replaced by hornblende.

Granoblastic quartz with feldspar along crystal margins and junctions is common in clasts within the sampled breccia. Felsic clasts typically display a well annealed granoblastic texture, displaying little undulose extinction and an equant form (Figure 3.3C). This contrasts sharply with the unbrecciated felsic gneiss and granite starting material, which displays irregular anhedral quartz, with sutured boundaries and moderate to strong undulose extinction. Several clasts from the Levack North and Capre properties displayed what appear to be coarse granophyric margins (Figure 3.3D). Experimental data indicates quartz recrystallization to a granoblastic texture between 675 to 775 °C, at 5 to 6 kbar (Releigh, 1965). The onset of granite anatexis in the presence of water has been established at temperatures at or above 625 °C (Luth et al., 1964). Similar observations were made by Hanley and Mungall (2003), who noted similar recrystallization and eventual development of granophyric patches within Sudbury breccia from the Fraser mine and environs. Granophyric patches along clast margins are common throughout the Sudbury breccia at the Levack North and Capre in both mineralized and unmineralized material. This is contradictory to the assertion of Morrison et al. (1994) that the development of granophyric patches, associated ‘flood’ quartz, biotite and actinolite are indicative of strongly metamorphosed breccia within zones of fluid flow associated with footwall ore zones.

Estimates of the equilibrium conditions for coexisting actinolite and plagioclase pairs were made using the amphibole-plagioclase geothermometer (Blundy and Holland, 1990), which was calibrated for temperatures of 500 to 1000 ± 75 °C, with plagioclase crystals of < An\(_{92}\) and amphibole containing less than 7.8 Si atoms per formula unit (apfu). A constant pressure of 1.3 kbar was assumed, consistent with published data (Molnár et al., 2001), equivalent to ~ 5 km depth of burial, and consistent with the inferred position of the footwall rocks under the combined thickness of the SIC and its cover sequence at the time of formation of the thermal
aureole. Calculations yielded temperatures of equilibration from averaged data (Table 3.8) of 440 to 491 °C for Levack North, 442 to 514 °C for Wisner, and 472 to 533 °C for Capre (Figure 3.16). The upper values calculated fall well within limits of the calibration, whereas the lower values are within the ±75 °C margin of error and hence can be considered equivalent to approximately 500 °C.

In summary, the limits of stability of ferromagnesian phases indicate that temperatures approached and likely exceeded 550 °C on the North Range properties; whereas temperatures recorded by amphibole-plagioclase pairs are all below 533 °C, both estimates being broadly consistent with the development of mineral assemblages characteristic of the albite-epidote hornfels to hornblende hornfels transition, with the lower calculated equilibrium temperatures likely reflecting retrogression of the peak assemblage. The spatially restricted local presence of granophyric and granoblastic textures in some quartzo-feldspathic clasts might indicate that temperatures were locally perturbed to higher ranges, possibly as high as 625 °C, although the texture may also reflect the higher temperatures experienced during the early stages of Sudbury breccia formation, before re-equilibrating to albite-epidote to hornblende hornfels facies. The general absence of textures indicative of the wider onset of melting is consistent with much higher experimental determinations of dehydration melting of andesite at 850 to 900 °C, 3 kbar and biotite gneiss at 850 to 930 °C, 3 to 15 kbar (Beard and Lofgren, 1991; Douce and Beard, 1995) both of which are broadly representative of the bulk composition of the pseudotachylite.

Estimations of mineralizing temperatures using the alteration assemblage have been limited to garnet-bearing selvages within offset hosted deposits (Magyarosi et al., 2002). The use of chlorite as a geothermometer is on the whole considered risky, with reviews (Caritat et al., 1993) indicating the myriad variables that affect composition; strong similarities to the calibrated system are therefore deemed essential. This complexity disqualifies all footwall and mineralizing styles from the use of chlorite geothermometry with the exception of North Range QCS material. In QCS samples, the chlorite composition, alteration (chlorite + epidote + albite + quartz), sulfide and oxides assemblages and host lithology are similar to the calibration of Kranidiotis and MacLean (1987) thermometer. Estimated temperature were calculated using the Kranidiotis and MacLean (1987) geothermometer, with the AlIV correction from Zang and Fyfe (1995). Chlorite compositions from the three North Range properties produced a temperature range of 296.55 to
Table 3.8. Average groundmass actinolite analyses from unmineralized pseudotachylite employed in actinolite—plagioclase geothermometry. Cations based on 23 (O, Cl, F) and average ferric Fe. Values were calculated from an average of 15Enk and 13eCNK. n = number of analyzed pairs per sample.
Table 3.8 cont. Average groundmass plagioclase analyses from unmineralized pseudotachylite employed in amphibole—plagioclase geothermometry. Cations based on 32 oxygen. Temperatures are calculated using Blundy and Holland (1990) and represent equilibrium formation of plagioclase and amphibole at 1.30 kbar (Molnar et al., 2001). n = number of analyzed pairs per sample.

### 3.7.1.2 South Range

Estimates of metamorphic grade within the lower units of the Huronian Supergroup (e.g. the Elsie Mountain and Stobie formations) have proven difficult due to the lack of peraluminous phases. The typical metabasalt assemblage of actinolite + magnesiohornblende + quartz + epidote + plagioclase + potassium feldspar + chlorite + titanite (Figure 3.3E) allows conditions to be bracketed at 475 to 550 °C if the pressure was approximately 2 kbar (Liou et al., 1974), although...
the lack of an accurate pressure gauge makes inferences about the dominance of regional or contact metamorphic process difficult to achieve.

Three garnet-biotite-plagioclase-muscovite bearing samples were identified from two boreholes. Both holes dipped at between 50 and 55°, with one (DN-194) oriented approximately parallel to the basal contact of the SIC and the second (DN-196) perpendicular to it. They were situated within the footwall of the Intermediate orebody of the Crean Hill Mine and intersected the low-sulfide mineralization of the 101 Zone. The boreholes were dominated by greenstones and greenschists of the Elsie Mountain formation, with intercalated centimeter to meter scale bands of metasediments or metarhyolites and biotite schist; it is these latter units that contain garnet.

Borehole DN-196 intersected two garnet bearing granofels layers comprising a granoblastic quartz + potassium feldspar + plagioclase groundmass, with biotite and muscovite and subhedral to euhedral garnet, represented by samples DN-196-004 and DN-196-011. The samples display a pervasive but weak sericitization of feldspar. Biotite has been affected by patchy weak chloritization along crystal margins. The lithologies proximal to the sampled granofels comprise moderately sheared granofels, a single 6 m wide garnet-free biotite schist horizon and a 6.5 m trap dyke. The granofels and biotite schists display several quartz ± carbonate veins between < 1 mm and 10 cm, proximity to which results in increases in hematitic straining, epidotization of feldspar and chloritization of biotite. The garnet bearing samples collected display no hydrothermal veining and little visible alteration. The relationship between the garnet bearing granofels samples remains uncertain. The trap dyke situated between the two samples displays intense brecciation along its lower margin, with fragments cemented by subhedral to euhedral carbonate and anhedral pyrite. This 0.5 m wide zone is interpreted as fault breccia, although no sense of movement or displacement can be obtained.

A single 1.5 m wide garnet-bearing unit was intersected by DN-194, comprising a medium grained biotite + quartz + plagioclase + muscovite + potassium feldspar schist. The sample displays extremely weak sericitization of feldspar and patchy weak chloritization of biotite. Unlike the granofels samples that were well outside the mineralized intersection, this sample (DN-194-014) is situated along the western margin of the 101 Zone. Samples immediately above the biotite schist layer comprise strongly sheared granofels hosting QCS and veinlet mineralization with a chalcopyrite + pyrrhotite ± gersdorffite ± pentlandite assemblage. The host
granofels displays strong to intense Fe-oxide staining, consistent with strong sericitization of feldspar, whilst biotite is pervasively altered to chlorite. The sampled biotite schist contains trace disseminated sulfide, with a single 5 mm chalcopyrite + pyrrhotite bleb at the start of the sample. Garnet displays no preference for the sulfide. The lack of a relationship differs from previous observations of garnet within mineralized zones (Fleet et al., 1987; Carter et al., 2001; Magyarosi et al., 2002; Szentpeteri et al., 2003), where it was reported to be present in the associated alteration assemblage.

Biotite within each of the three garnet-bearing samples displays restricted compositions indicative of complete equilibration with the surrounding silicates, however biotite compositions show significant variation between samples. The granofels hosted crystals (25 to 100 μm) were typified by Fe # above 0.8, with Al$_{IV}$ concentrations between 2.7 and 3.0 $apfu$, compositions approaching siderophyllite. Biotite from the single biotite schist sample (DN-194-014) has a consistent Fe # between 0.63 and 0.66, with Al$_{IV}$ contents remaining high at an average of 3.0 $apfu$, along the eastonite—siderophyllite join. The Fe # of biotite in the two samples of granofels
is higher than in most unmineralized footwall biotite. The micas from the biotite schist are more representative of the footwall population, with FeO falling within the footwall range of 18.7 to 24.0 %. All footwall biotite contains substantial Al₂O₃ with concentrations between 16.3 to 19.1 %, producing compositions dominantly along the eastonite—siderophyllite join. Whether these data are representative of South Range biotite is uncertain, because other published analyses are exclusively associated with sulfide mineralization, typically within quartz diorite (Magyarosi et al., 2002).

Equilibrium temperatures from the composition of coexisting biotite and garnet were calculated using methods of Holdaway (2000) and Kaneko and Miyano (2004); the latter being applied due to inclusion of the mole fraction of Mn (X\text{Mn}^{\text{Grt}}) within the equilibrium equation, which is applicable at values of X\text{Mn}^{\text{Grt}} of up to 0.28. These two geothermometers provide values within an absolute error of ± 50°C and ± 30 °C respectively, with calibration ranges dominantly between 500 and 750 °C. Pressure estimation was undertaken using the Wu et al. (2004) garnet-biotite-plagioclase-quartz (GBPQ) geobarometer. The barometer was calibrated for X\text{Grs} > 3 %, X\text{An} > 17 % and X\text{Al}^{\text{Bio}}> 3 %, within a range of 515 to 878 °C and 1 to 11.4 kbar.

Estimated pressures range from 2.0 to 7.7 ±1.0 kbar, with sample DN-194-014 (biotite schist) indicating pressures of 2.5 to 7.7 kbar and DN-196-011 (granofels) from 2.0 to 3.4 kbar. Sample DN-196-004 (granofels) produced only 2 successful pairs with pressures of 3.1 and 6.1 kbar. Geothermometers produced equilibrium temperatures of 513 to 645 °C (avg. 559 to 570 °C), with the pressure for garnet-biotite pairs without additional plagioclase and quartz, set for an averaged value per host sample (Figure 3.15 and Table 3.9).

### 3.7.2 Fluid pathways and crosscutting relations

Structural features like brittle closed or dilatant fractures and ductile shear zones commonly appear to have guided the emplacement of ore-forming melts or fluids in the footwall of the SIC. These structures were to an important extent controlled by host rock characteristics. A significant secondary control is the composition of the host rock, particularly in cases where important mineralization occurs in disseminations surrounding fractures.
Table 3.9. Selected garnet-biotite-plagioclase-(quartz) pairs from the Denison property

On the North Range mineralization at the Levack North and Wisner properties is predominantly hosted within pseudotachylite or the wall-rock clasts that it enclosed. At Capre the identity of rocks hosting mineralization is somewhat more difficult to constrain, because the Sudbury breccia clasts ranged from centimeters to meters in scale, but are typically constrained by narrow
pseudotachylite veins of less than 10 cm, which when exploited by sulfide veins or strong to intense alteration are difficult to recognize.

Sulfide vein and IRV mineralization commonly occurs along clast-pseudotachylite contacts, which suggests that migration of the mineralizing fluid(s) was aided by detachment along these interfaces. Development of such weaknesses could have been tectonic in origin, driven by either crater settling or post impact tectonism, or may have resulted from differential thermal contraction of pseudotachylite and clasts during initial cooling immediately after pseudotachylite formation. In either case, the opening of fractures between clasts and the pseudotachylite host rock has resulted from differences in elastic properties of the contrasting rock types, and therefore clearly dates the mineralizing event to a time after complete solidification of the pseudotachylite matrix. The settling of the crater and its deformation by the Penokean orogeny likely aided the development of fractures within the North Range footwall, once again indicating that the emplacement of mineralization must have post-dated solidification of the Sudbury breccia. The continued settling of the footwall and the regional deformation will have caused veins to dilate, thus improving the flow of the dense sulfide melt and hydrothermal fluids into the footwall. On the South Range terrace controlling faults formed during crater settling have acted as conduits for sulfide melts to migrate e.g. McKim or as planes along which crystalline sulfide from the contact has been sheared e.g. Denison and McKim. The timing of sulfide shearing in unknown and could have occurred due to fault movement caused by crater settling or an subsequent orogenic event.

The North Range footwall has undergone extensive metamorphism which was locally accompanied by hydrothermal alteration due to circulating fluids. The timing of both mineralizing and barren fluid circulation remains only weakly constrained. A key constraint is given by the presence of felsic clasts displaying weak to intense sericitization and epidotization within unaltered pseudotachylite. Such a discrepancy indicates that some fluid circulation and associated alteration must have taken place before the Sudbury impact at 1.85 Ga and was likely driven by the Blezardian orogeny. Mineralized quartzo-feldspathic footwall lithologies commonly show the same alteration style as is seen in these demonstrably older assemblages, however there is no correlation between the intensity of sericite-epidote alteration and the quality or extent of sulfide and PGE mineralization. This dissociation implies that a substantial portion
of alteration suffered by footwall lithologies predates mineralization, although some of the same fluid conduits were later exploited by base and precious metal bearing liquids.

In other similar examples mineralization within the North and South Range exploited pre-existing quartz or quartz + epidote veins. The presence of sulfides along the margins of the barren veins, along gangue crystal interfaces and within fractures in the vein suggests that mineralizing fluids exploited pre-existing veins. The ability of base-metal and PGE bearing liquids to follow the same pathway was likely aided by the opening up of dilatant fractures during crater settling. These fractures would have opened up along the vein margin, along interfaces of the coarse gangue crystals or simply crosscutting optically continuous crystals. The presence of pre-existing quartz dominated veins would suggest that substantial hydrothermal circulation and alteration must have already taken place prior to impact.

The circulation of barren fluids certainly continued during the deposition of mineralization. Rare observations of QCS mineralization that is both cross-cut by and cross-cutting barren quartz + epidote veins suggest that barren and ore forming hydrothermal fluids were coeval. Two chalcopyrite dominated sulfide veins from the Capre footwall were observed to be cross-cut by pyrite-bearing carbonate veins, which were not associated with observable alteration of the vein sulfides. In general cross-cutting relationships between mineralizing styles are also rare, although irregular veinlets (IRV) from the Wisner and Capre properties were observed to be cross-cut by QCS mineralization.

No cross-cutting relations involving sulfide veins, except the two low temperature carbonate veins described above, were observed, although IRV are locally observed to emanate from some sulfide veins at the Levack North and Capre properties. This association may however be coincidental in light of the common occurrence of well-developed IRV showing no association to sulfide veins. This is especially clear at to the Wisner property where IRV mineralization contributes significantly to the metal budget, yet only one substantial sulfide vein was intersected, the remainder being ill-defined and less than 5 cm in diameter. Sulfide veins are therefore interpreted as having locally exploited the same conduits as IRV. Farrow et al. (2005) suggested that sulfide veins may have been deposited after IRV mineralization, which they called ‘stringers’.
The relative timing of South Range mineralization remains even more poorly constrained. Sulfide vein mineralization from both properties typically displays abundant cm scale wall-rock clasts, within a sulfide matrix displaying some degree of deformation, i.e., fabric parallel “smearing”, elongation of crystals and textural deformation. This combination of textures is called durchbewegung texture and is interpreted as indications of tectonic redistribution of sulfide in the solid state along embayment and terrace controlling faults and their subsidiaries that were re-activated during subsequent orogenic events (Misra, 1999).

A strong fault control offers a simple explanation to the panel-like morphology of low-sulfide mineralization within the Denison footwall. The ubiquitous replacement of pyrrhotite, pentlandite and to a lesser degree chalcopyrite by pyrite and marcasite indicates that post-mineralization fluid flow occurred within the footwall of the Denison property, producing alteration sulfides and textures similar to those observed in hydrothermally altered ore from the Thayer-Lindsley mine by Bailey et al. (2004). The presence of a post-mineralization fluid remobilizing both base and precious metals within the footwall of the Denison property is therefore inferred. The passage of these fluids was likely aided by the fault zones that traverse and re-shape the mineralized embayment structures, with sheared contact sulfide deposits providing a metal source. The timing of fault controlled sulfide redistribution and hydrothermal scavenging remains uncertain, however the presence of mineralization along major post-impact fault structures with metamorphic overprints strongly suggests that at least some mineralization on the South Range occurred as a result of fluid flow during later orogenies.

At the McKim property only one observation of pyrite replacing sulfide occurred within pyrrhotite and consisted of a single isolated 100 µm pyrite idioblast. The relatively unaltered sulfides of the McKim footwall would imply that the base and precious metals contained within QCS mineralization were either scavenged from an alternative source or that the remobilizing fluid had a lower $f_{S2}$ than that present within the Denison footwall. Molnar et al. (1999) identified isolated fluid inclusions, interpreted as primary, within base and precious metal rich veins from the Little Stobie mine that contained extremely saline fluids with homogenization temperatures of 180 to 270 °C (No. 1 orebody) and 280 to 350 °C (No. 2 orebody). It is possible that fluids such as these were instrumental in carrying base and precious metals out of contact orebodies and into shear zones in the South Range footwall, forming sulfide vein, veinlet and
QCS mineralization. On the other hand the presence of increased chalcopyrite/pyrrhotite ratios within sulfide vein material \((\text{Cu}/[\text{Cu+Ni}] = 0.60)\) from McKim, when compared to the Little Stobie orebodies \((\text{Cu}/[\text{Cu+Ni}] = 0.46)\) and the position of the mineralized zone along the flanks of the Little Stobie orebodies, might indicate that the veins formed as residua from fractionated sulfide liquid, as suggested by Hoffman et al. (1979). It is likely that primary magmatic sulfide veins equivalent to the sulfide veins of the North Range have undergone varying degrees of metamorphic and tectonic remobilization on the South Range.

### 3.7.3 Metamorphic Assemblages and Their Alteration

The effect of post-mineralization metamorphism on North Range mineralization has received scant attention. In contrast the deformation and redistribution of sulfide along the South Range due to faulting and metamorphic fluid circulation are well established (Bailey et al., 2004; 2006).

A limit on plausible post-mineralization heating can be imposed by the presence of linnaeite group minerals on the North Range. Polydymite is a rare phase within the Sudbury footwall, although occurrences have been reported from the Vermillion Mine and the Broken Hammer prospect (Coleman, 1905; Kjarsgaard and Ames, 2010). The micro-veinlets observed within sulfide veins from Wisner are interpreted by the author as having resulted from late stage Ni exsolution from cooling \(\text{iiss}\) and/or chalcopyrite. This contrasts with observations from the Broken Hammer prospect (Kjarsgaard and Ames, 2010) where polydymite replaces millerite, however, such alteration was lacking from the Wisner samples where only violarite was observed after NiS within the margins of sulfide veins. Experimental data indicates that end-member polydymite will melt incongruently to millerite + vaesite + liquid at temperatures > 356 ± 3 °C (Kullerud and Yund, 1962; Craig, 1971). Its continued existence within the sulfide vein assemblage indicates that post mineralization temperatures could not have exceeded this lower greenschist limit. The possibility of polydymite formation after peak regional or contact metamorphism cannot be discounted; however there is no indication that low-temperature fluid flow affected sulfide veins after their solidification. The presence of violarite after pentlandite and millerite also sets an upper limit for temperature estimates, however, it can only be applied to those assemblages whose places in the paragenetic sequence can be established. Analyses of
violarite from all three North Range properties cover Fe/Ni (atomic percent) ratios between 0.41 and 0.50, equating to an upper stability of 490 to 500 °C (Chamberlain and Dunn, 1998). The timing of violarite alteration remains uncertain. The extensive fluid circulation within the footwall of the Wisner and Capre properties may have been driven by the latent heat from the SIC or any of the major orogenic events, so the relative timing of violarite alteration cannot be established. In contrast the violarite alteration of Ni-sulfides along the margins of sulfide veins from the Levack North property can be better constrained. The sulfide veins display no signs of post-mineralization remobilization, with veins commonly displaying no proximal barren hydrothermal veins or cross-cutting relationships. The violarite alteration is therefore interpreted as having occurred late in the mineralizing event, possibly as the result of fluids emanating from the vein or due to an external, but concurrent hydrothermal fluid. The presence of violarite would therefore suggest that the Levack North property did not experience regional metamorphic temperatures and associated fluids exceeding 450 °C.

Unmineralized pseudotachylite from the North Range properties contains an actinolite—epidote—chlorite—plagioclase (An$_{17-46}$)—quartz—titanite ± biotite ± hornblende assemblage suggesting that the host rocks of the mineralization were last equilibrated to assemblages straddling the albite epidote to hornblende hornfels facies contact metamorphic aureoles. This is consistent with average actinolite—plagioclase equilibrium temperatures of 440 to 533 ± 75 °C from this study. The proximity of samples to the basal contact of the SIC means that the temperatures presented are very likely the result of contact metamorphism, although as there has been such little examination of North Range metamorphism post-SIC that a firm assertion about the cause of metamorphism is impossible. Estimated equilibration temperatures for pseudotachylite from the Capre property are higher than on the North Range, perhaps because the Main Block Sudbury breccia belt of the Capre property is only 250 to 300 m from the near-vertical lower contact of the SIC, placing the pseudotachylite within the hornblende hornfels aureole (Boast and Spray, 2006), whereas the Levack North and Wisner pseudotachylite were some 750 m into the footwall, below a contact presently dipping at 40°, dominantly within the albite-epidote hornfels zone.

Distal alteration haloes associated with all North Range mineralizing styles are typically defined by the retrograde development of chlorite and epidote after biotite, actinolite and groundmass
plagioclase and a reduction in the Si \textit{apfu} of amphibole. Proximity to sulfide vein and IRV mineralization is marked by the return of actinolite and lesser biotite, within host the pseudotachylite, indicative of increased temperatures along their margins, analogous to upper albite-epidote hornfels facies. In contrast the presence of QCS and disseminated mineralization is associated with a moderate to intense chloritization of pseudotachylite and development of lesser epidote, which becomes more common approaching the vein margins, whilst biotite or actinolite are absent. The mineral assemblages imply formation at temperatures lower than those associated with IRV or sulfide veins, with chlorite geothermometry producing temperatures of 296.55 to 338.90 °C (av. 321.05 °C), comparable with albite-epidote facies metamorphism and consistent with the ferromagnesian assemblage of the QCS vein alteration selvage. These relations can be used to infer that the alteration associated with emplacement of sulfide vein and IRV mineralization occurred after the passage of the main thermal metamorphic pulse from the SIC, producing distal retrogression from peak contact metamorphic conditions, simultaneous with a return to near-peak conditions proximal to high temperature mineralization. The QCS veins were associated with widespread retrogression, both distally and proximally, consistent with lower emplacement temperatures than those of the magmatic sulfide veins.

The groundmass mineral assemblages in metabasalts from the two South Range properties straddle the greenschist-amphibolite divide, with groundmass amphibole transitioning from magnesiohornblende cores out to actinolite and ferrotschermakite margins, consistent with greenschist facies retrogression of peak Blezardian or Penokean amphibolite facies metamorphic assemblages. The continuous variation of Mg\# and Si \textit{apfu} across the whole amphibole dataset and the absence of sharp compositional boundaries within grains are consistent with retrograde alteration of hornblende. It is unlikely that the zonation is related to hydrothermal alteration because rims are not associated with epidote or chlorite. Rim formation due to a calcic amphibole miscibility gap is discounted due to the compositional range displayed and lack of sharp contacts (Grapes and Graham, 1978; Robinson et al., 1982; Yamaguchi et al., 1983; Shinjoe et al., 1993).

Geothermometry from the Denison property produced a temperature range (513 to 645 ± 50°C) in good agreement with petrographic observations and established metamorphic assemblages, falling as they do within the upper greenschist to amphibolite fields (Figure 3.16). The equilibrium pressure calculated covers a wide range from 2.0 to 7.7 ±1.0 kbar, with data from
each of the three samples forming a discrete cluster of points. It is of somewhat debatable merit to apply geothermometers and geobarometers calibrated on pelitic assemblages to quartzofeldspathic rocks. The application of the garnet-biotite-plagioclase-muscovite-quartz (Hoisch, 1990) would be advisable, however, the analyzed $X_{\text{Mg}}^\text{Bio}$ and $X_{\text{Fe}}^\text{Bio}$ values fall well outside the calibration range, whilst those equations whose calibrations span an appropriate range of intensive parameters are hampered by the assumption of ideal mixing of mica components. The 2.5 to 7.7 kbar range of DN-194-014 and DN-196-004 equates to ~8.5 to 25.7 km of overburden (Yardley, 1989), well in excess of the 1.8 to 2.0 kbar proposed from fluid inclusion trapping conditions (Molnár et al., 1997; 1999) and predicted depths (8 to 12 km) of South Range deposit formation (Hoffman et al., 1979; n.b. Hoffman's estimated conditions may themselves have been post-emplacement metamorphic overprints rather than original conditions of formation). These higher pressures must therefore be attributed to regional metamorphism, perhaps Blezardian pre-dating SIC emplacement, or post-SIC Penokean. The overburden thickness for the latter during crustal-scale folding of the SIC, modeled by Shanks and Schwerdtner (1991), would produce pressures covering a substantial portion of those calculated by this study. Despite their fresh appearance, and the complete lack of evidence for a hydrothermal overprint, the compositions of minerals in sample DN-196-011 indicate that it equilibrated at a comparatively lower T and P between 519 and 569 ± 30 °C and 2.0 to 3.4 kbar, straddling the hornblende hornfels—amphibolite transition. The two garnet bearing granofels samples (DN-196-004 and DN-196-011) display comparatively low pressures of equilibrium suggesting that they represent either the waning stages of Penokean regional metamorphism or the contact aureole of the SIC (Figure 3.11). Interestingly sample DN-196-004 provided only two usable pairs, one of which falls within the aforementioned range of DN-196-011, whilst the other is comparable to results from sample DN-194-014 (garnet biotite schist). These data suggest that regional metamorphic grades of 519 to 669 ± 30 °C and 4.6 to 7.7 ± 1.0 kbar, likely of Blezardian or peak Penokean origin, have been overprinted by a lower grade assemblage. Although the cause of this metamorphism cannot be established with certainty, it is noteworthy that sample DN-196-011 is 50 m closer to the SIC and hence may have been completely overprinted by the thermal aureole, whereas the slightly more distant DN-196-004 suffered somewhat less heating by the SIC thereby allowing indicators of previous metamorphic grade to persist. Although the 50 meter spacing between samples DN-196-004 and DN-196-011 might be too short to account for the difference, it is also
possible that retrogression in the thermal aureole of the SIC was aided or suppressed by local variations in the availability of fluids, whilst the "true" distance between the samples may have been increased or decreased by the aforementioned fault transecting the footwall between the samples. Although the peak metamorphic temperatures calculated likely pre-date the emplacement of mineralization the lower temperatures may reflect conditions during mineralization. If the low temperature assemblage is interpreted as reflecting the hornblende hornfels aureole of the SIC then these temperatures mark the conditions present during the movement of sulfide liquids into the footwall i.e. veinlet style mineralization. However if the equilibrium conditions reflect a lower temperature regional overprint, be it from a later orogenic event e.g. the Mazatzal-Labradorian orogeny, or the waning of the Penokean orogeny it seems likely that such conditions (519 and 569 ± 30 °C and 2.0 to 3.4 kbar) would have been sufficient to induce hydrothermal fluid circulation. Therefore, although no definitive link can be made to a specific orogenic event it seems likely that at least a portion of the QCS mineralization observed at the Denison property were formed within a footwall experiencing hornblende hornfels—amphibolite facies metamorphism.

The alteration assemblage of South Range mineralization typically differs little from that of the host lithology, particularly for samples hosted by greenstones and greenschists. Although the inclusion-bearing and sheared nature of sulfide veins from the Denison and McKim properties suggests that sulfide has been redistributed by fault movement or exploited fault planes, the abundant pyrite and marcasite alteration displayed by material from Denison indicates that tectonic transport was not the only mineralizing process. The margins of sulfide veins, QCS veins, veinlets, disseminations and stockwork mineralization from the South Range properties are typically marked by little to no alteration, with some coarsening of groundmass phases. This would imply that any mineralizing hydrothermal fluid was in equilibrium with the footwall lithologies and as such is likely of a metamorphic origin, with alteration associated with magmatic sulfides likely continuously recrystallizing until achieving equilibrium with the host environment. The timing of such a fluid remains unknown, with any of four orogenies the possible source. Unlike the Denison property the base and precious metals associated with QCS mineralization from McKim were likely scavenged from the Little Stobie ore bodies. If the QCS veins are syn-SIC, the proximity to the crystallizing melt sheet may well have offered an
additional heat source helping to further increase fluid circulation, consistent with Molnar et al. (1999). It should however be noted that fluid flow could also have been driven by post-SIC regional metamorphism, although Marshall et al. (1999) proposed a mixed magmatic-metamorphic origin for fluids associated with footwall mineralization.

In summary, the mineralization on the South Range has been overprinted by amphibolite-facies assemblages which themselves have been variably retrogressed. Primary mineral assemblages may have been re-equilibrated and it is difficult to establish relative timing of formation of the assemblages currently observed. This complex history has undoubtedly included a significant
The amount of tectonic and associated hydrothermal emplacement of mineralization during orogenic activity long after the meteorite impact.

3.7.4 Identification of Mineralized Zones

Major element compositions of common mafic phases (actinolite, chlorite, biotite and epidote) show little variation between unmineralized and mineralized footwall lithologies. Concentrations of most trace elements in both mineralized and unmineralized material are typically below detection and therefore inconclusive. Concentrations of NiO within chlorite and amphibole allow for separation of mineralized and unmineralized material from the North Range. The substitution of Ni into the amphibole C-site and into the chlorite cation\(^{2+}\) site is likely achieved at the expense of Fe\(^{2+}\) or Mg\(^{2+}\), however the Ni correlation coefficients for both major and trace elements are all well below 0.5 in chlorite. In contrast, NiO contents of mineralized amphibole displayed two strong associations, with SiO\(_2\) and Al\(_2\)O\(_3\) yielding correlations of -0.53 and 0.56 respectively, whilst FeO and MgO display correlations with NiO of 0.47 and -0.47, suggesting that Ni may well be substituting for Mg, with the resulting strain on the lattice allowing increased substitution of Al for Si in the amphibole T-site. Biotite crystals associated with mineralization have elevated NiO concentrations, averaging eight times those of biotite from unmineralized material. Substitution of Ni into biotite likely occurs through substitution of Fe\(^{2+}\) or Mg\(^{2+}\) in the octahedral site. Crystals proximal to sulfide veins display a strong Ni:Fe anticorrelation (R = -0.94), with Mg also producing a negative correlation against Ni (R = -0.68). These are not matched by biotite proximal to IRV mineralization, where Ni displays only a weak correlation with Fe (R = 0.36) and Mg (R = -0.17), the probable result of the relatively consistent Fe\# of biotite within individual IRV samples, despite variations in Ni content.

The use of actinolite-hosted Ni as an exploration tool was outlined by Hanley and Bray (2009), however the data within this study do not indicate systematic variations with distance from recognized mineralization, perhaps because of the abundant and widely distributed low modal sulfide mineralizing styles. As obtaining samples of unmineralized Sudbury a significant distance i.e. > 15 m from the edge of the mineralized zone was difficult, as drilling normally didn't proceed too far past the target, it cannot be definitively said that the analyzed silicates from the
unmineralized Sudbury breccia sampled in this study are wholly representative. As such, it is difficult to truly define the zone in which the ferromagnesian silicates display a noticeable increase in their NiO content and therefore the extent to which they can be used as a vectoring tool. Analyses in this study do clearly show a NiO enrichment proximal to sulfide veins, or zones with several irregular veinlets, however given that this strong signal only occurs some 2 to 3 m from the mineralization it is likely that in the majority of cases the upcoming mineralization will be apparent in hand specimen due to the appearance of sulfides.

Although the ability of Ni to substitute into the crystal structure of chlorite and biotite has been established, most analyses of these phases typically ignore Ni. The few previously published analyses for the Sudbury camp available have extremely low Ni concentrations in both chlorite and biotite (Carter et al., 2001). The increase in Ni content displayed by all three ferromagnesian phases documented here offers potential to develop a method to identify and outline mineralized zones, or zones through which a mineralizing fluid as passed, within the North Range footwall, however the lack of a consistent compositional variation with proximity to mineralization means that it cannot be used as a directional vector.

The presence of increased concentrations of halogens within alteration phases proximal to footwall mineralization has been known for some time (Springer, 1989; Farrow and Watkinson, 1992; Li and Naldrett, 1993a; Jago et al., 1994; McCormick and McDonald, 1999). A halogen-enriched halo 50 to 150 m wide has been documented surrounding both contact and footwall mineralization (Jago et al., 1994; Hanley, 2002; McCormick et al., 2002). The variation of halogen concentrations with increasing proximity to footwall mineralization was established by Hanley and Mungall (2003), whilst Hanley et al., (2004) demonstrated the use of bulk Cl and Br concentrations within Sudbury breccia as a viable exploration tool.

In the present study, analysis of actinolite hosted within pseudotachylite produced Cl concentrations ranging from below the detection limit to 0.33 wt % (avg. 0.04 wt %), with 50.7 % of crystals yielding detectable concentrations, consistent with published data (McCormick and McDonald, 1999; Hanley and Mungall, 2003). Actinolite hosted by sulfide veins has Cl concentrations ranging from below detection limit to 0.10 wt % (avg. 0.01 wt %), with Cl detected in 29.5 % of crystals, comparable with unmineralized material. Irregular veinlets show a
minor increase in the maximum Cl concentrations, with levels from below detection limit to 0.25 wt % (avg. 0.04 wt %), with 40.7 % of crystals displaying concentrations above detection.

The plot of Mg# vs. Cl/(Cl+F) (Figure 3.5) indicates that the composition of biotite from both mineralized and unmineralized samples is similar to samples from the peripheral and distal portions of the Fraser Mine. Hanley and Mungall (2003) noted a decrease in Mg# and an increase in Cl/(Cl+F) ratio approaching mineralization. Hanley and Mungall (2003) determined that biotite proximal to sharp walled sulfide veins display compositions typical of hydrothermal origin, but this was not observed in the present study. Biotite is consistently the dominant halogen bearing phase analyzed, with Cl and F concentrations sporadically exceeding 1.0 wt %.

A minor two fold increase in average Cl concentrations was also noted for crystals associated with sulfide vein and IRV mineralization, although the range of concentrations measured were comparable with unmineralized samples. The lack of an enrichment in Cl and/or F relative to biotite from the matrix of unmineralized Sudbury breccia is difficult to explain if it is assumed that the crystals proximal to mineralization formed in response to a volatile-rich (H₂O and halogen-rich) liquid exsolving from the sulfide melt. If such a liquid had ben present biotite proximal to mineralization would be expected to show a significant enrichment in their halogen content, a trend noted by Hanley and Mungall (2003). Three possible scenarios may explain this discrepancy: 1) Alteration caused an increase in the modal abundance of halogen-bearing phases, thus reducing the amount of Cl and F available to each crystal, 2) the sulfide melt could have already exsolved a halogen-rich liquid closer to the contact, thus reducing the halogen content of the melt by the time it entered the low-sulfide zone, or 3) the emplacement of mineralization did not impart any halogens into the wall-rock, with the biotite crystals having formed earlier in response to the circulation of an unmineralized hydrothermal fluid in equilibrium with the wall-rocks. The increase in the whole-rock Cl and Br concentrations of mineralized Sudbury breccia and the Cl/(Cl+F) content of biotite proximal to mineralization strongly suggests that the ferromagnesian silicate dominated alteration selvage along the margins of sharp-walled veins at the Fraser mine are the result of a volatile-rich fluid exsolving from the cooling sulfide melt (Hanley and Mungall 2003, 2004). This was given further backing with the identification of halide melts associated with sharp-walled vein mineralization (Hanley et al., 2005b). It is likely that the sulfide melt from which sulfide vein and IRV mineralization formed is an extension of the system that formed sharp-walled vein mineralization and it is therefore possible that the
sulfide melt had already exsolved a halogen-bearing fluid earlier in its history i.e. during the formation of sharp-walled veins. The formation of such a volatile-rich fraction would likely strip the sulfide liquid of the majority of dissolved halogens thereby reducing the amounts that can be imparted into the wall-rock surrounding magmatic low-sulfide mineralization. Any volatile-rich fluid exsolving from the highly fractionated sulfide liquid would therefore be likely to form a weak whole-rock halogen enriched halo (see below), however this would not be reflected within the EMP analyses as it would be dispersed throughout an increased modal abundance of ferromagnesian silicates. A combination of scenarios 1 and 2 may therefore be sufficient to explain the halogen data collected. In contrast, the biotite crystals analyzed may not have formed in response to mineralization. It is likely that crater settling caused fractures to develop within the SIC footwall, including the solidified Sudbury breccia. Such fracture networks would allow barren hydrothermal fluids to circulate through the Sudbury breccia producing ferromagnesian alteration assemblages (Tuba et al., 2010). The presence of barren hydrothermal veins being both truncated or exploited by mineralization (see Chapter 2) suggests that barren fluid circulation was occurring in Sudbury breccia before the low-sulfide mineralization was deposited. It is, therefore, not inconceivable that these fluids, which were in equilibrium with the wall-rock, could have caused the development of the ferromagnesian silicates observed. These fractures were later exploited by sulfide vein and IRV mineralization producing a superficial link between the sulfides and the alteration assemblage, although some re-equilibration with the mineralization would be required to produce the Ni-enrichments observed in the silicates, whilst the weak halogen enriched whole-rock halo observed proximal to mineralization merely reflects the saline nature to the pre-mineralization hydrothermal fluids and the increase in the modal abundance of halogen-bearing silicates that it caused. It is extremely difficult to come to a decision about the mechanism that limited the halogen content of ferromagnesian silicates associated with mineralization, with the scenarios suggested above both valid.

The whole-rock halogen data from the Levack North and Wisner properties indicate that both sulfide vein and IRV mineralization are distinguished by an increase in Cl when compared to unmineralized pseudotachylite, whilst Br concentrations remain variable. This elevation in Cl at first appears contradictory to mineral analyses which indicate that chlorite, actinolite and biotite associated with mineralization display no substantial halogen enrichment when compared to crystals from footwall lithologies. The XRF data might therefore imply that Cl and Br are not
bound within silicates, but may occur as halides interstitial to silicates and within fluid
inclusions. However, as noted by Hanley and Mungall (2004), much of the bulk increase in Cl
and Br might be accounted for by the increased modal abundance of hydrous silicates in the
altered rocks, even if the mineral compositions are no more halogen-rich than in their
unmineralized equivalents. The comparatively elevated NiO content of ferromagnesian silicates
proximal to mineralization clearly indicates that they are inextricably linked with or have been
affected by the mineralizing process. Analysis of fluid inclusions associated with North Range
footwall mineralization has established the connection at least in part between mineralization and
saline fluids (Li and Naldrett, 1993; Farrow et al., 1994; Molnár et al., 1997; 2001; Molnár and
Watkinson, 2001; Hanley et al., 2005b). It therefore seems likely that during the emplacement of
low-sulfide mineralization halogens may have been imparted into the surrounding wall-rocks,
either bound within ferromagnesian silicates or as discrete phases. The source of the increase in
bulk Cl concentrations proximal to mineralization remains uncertain, with precipitation of
silicates due to interactions with a late stage highly fractionated magmatic fluid residue (Mungall
and Brenan, 2003; Hanley et al., 2005b) or the passage of pre-, syn- or post-mineralization saline
fluids sourced from the basement and SIC both being plausible explanations (Frape and Fritz,
1982; Marshall et al., 1999; Molnar et al., 2001). The inability of this study to identify the
presence of discrete halides, with the exception of a single bismoclite crystal and the of lack of
significant increases in the halogen contact of ferromagnesian silicates would suggest that the
proposal of Hanley and Mungall (2004) is correct and that halogen enriched zones surrounding
mineralization are the result of increases in the modal abundance of halogen bearing
ferromagnesian phases rather than their enrichment or the precipitation of halides.

There is substantial overlap in major and trace element concentrations between mineralized and
unmineralized material in ferromagnesian phases from the South Range properties. Groundmass
amphibole has the highest NiO concentrations with magnesiohornblende cores and actinolitic
rims displaying averages of 0.45 wt % and 0.32 wt % respectively. These levels are not much
higher than concentrations from mineralized material, where average levels are between 0.04 and
0.22 wt %. Halogen levels typically remain low with only ≤ 10 % of amphibole crystals
containing measureable F, and average Cl concentrations typically < 0.1 wt %, although crystals
proximal to sulfide veins displayed an average of 0.27 wt %. Chlorite compositions varied little,
with NiO and halogen concentrations near indistinguishable between mineralized and
unmineralized samples. Footwall biotite compositions cover a broad compositional range from near end-member siderophyllite to compositions near intermediate to the four end-members. The majority of analyses proximal to sulfide veins yielded a reduced Fe#, with crystals averaging around 3.5 and 4.0 (Figure 3.4), a reduction compared to the 0.5 to 0.9 range displayed by unmineralized samples. Biotite crystals proximal to QCS mineralization have compositions extremely similar to those in unmineralized material, with analyses from all three settings (unmineralized, sulfide vein and QCS) displaying comparable Ni, Cl and F concentrations. There is no evident systematic variation in bulk halogen concentrations proximal to mineralization. Analyses of unmineralized and mineralized metabasalts from the Denison footwall show highly variable whole rock halogen concentrations with Cl between 71.5 to 1306.4 ppm and Br ranging from 0.5 to 2.4 ppm. The remarkable similarity of the major trace element content of silicates and bulk halogen compositions displayed by mineralized and unmineralized material from the South Range suggest that recrystallization/re-equilibration of the footwall has occurred syn- or post-mineralization. Any primary halogen enrichment might therefore have suffered dispersal during subsequent regional metamorphism. As previously stated the alteration selvage assemblage displayed by mineralization differs little from that of the host metabasalts. The re-equilibration of groundmass crystals with mineralizing or metal bearing fluids must have been an extended process, with amphibole cores and rims displaying measureable Ni concentrations in ≥ 90 % of analyses, with development of actinolitic rims a possible result of this circulation. The relative timing of fluid circulation and mineralization remains uncertain, although the consistent presence of Ni would suggest that fluids have come into contact with sulfide mineralization, a view consistent with the pyritization of sulfides from the Denison property. The driving force of fluid circulation is likely a combination of Penokean or Yavapai–Mazatzal tectonics and/or heating from the SIC, with metamorphic basement fluids producing re-equilibration or recrystallization of footwall assemblages, at amphibolite facies temperatures and pressures.

3.7.5 Fluid Inclusions

The fluid inclusion homogenization temperatures and salinities determined in this study fall within the range of published Sudbury values (Farrow and Watkinson, 1997; Molnar et al., 1997; 1999; 2001 Molnar and Watkinson, 2001). Two distinct fluids associated with isolated inclusions
in quartz from QCS veins have been identified, with Type 1A and Type 1B inclusions homogenizing at 223.8 to 377.5 ºC and 391.6 to 413.3 ºC, respectively. The fluids display distinct compositions, evidenced by differences in the number of daughter phases present and estimated salinities of 33.1 to 45.1 wt % NaCl or 15 to 18 wt % MgCl₂ (T1A) and 46.5 to 48.9 wt % NaCl equivalent (T1B). The association of these fluids with QCS mineralization would indicate that two discrete fluids, possibly containing dissolved base and precious metals, were circulating within the footwall, either simultaneously or at different times. These were followed by three distinctly defined non-mineralizing fluids between 87.1 to 299.6 ºC, one of which (T2SB) was CaCl₂ bearing, and of likely basement origin; the remaining Type 1SA and 2SA inclusions are from an unknown source, although highly saline. Fluid inclusion data from the Denison property was extremely limited with only three isolated inclusions identified, homogenizing at through daughter phase dissolution at 341.8 to 379.2 ºC. Although these data are sparse, the homogenization temperatures are consistent with data from a mineralized PGE-bearing quartz + chalcopyrite vein at the Vermilion Mine, where primary inclusions homogenized at temperatures of ≥ 350 ºC (Szentpeteri et al., 2003). The presence of such a fluid implies that the circulation and associated remobilization of base and semimetals by a hydrothermal fluid is a feasible mechanism for distributing PGEs into the footwall, although it is uncertain if the circulation occurred in response to heating from the SIC, orogenic processes or both, and as such its timing cannot be constrained.

3.7.6 The Possible Origins of Base and Precious Metals

The origin of the base and precious metals in fluids associated with North Range low-sulfide mineralization is uncertain. The only significant proximal sources available for mineralization are the sulfide veins, which do display some violarite alteration of pentlandite and millerite and rare covellite/chalcocite after chalcopyrite indicating that veins have been affected by later fluids. This alteration is however extremely limited in its extent with alteration haloes typically no greater than 50 μm in width. It therefore seems unrealistic to suggest that they are the sole source of metals in the aqueous fluids that were associated with some low-sulfide mineralizing styles. With the exception of QCS mineralization, which is clearly hydrothermal in origin, there are no firm indicators of whether the transport medium was a saline fluid or a sulfide melt, although the
broad (up to 5 cm) hydrous silicate dominated selvage and halo of IRV mineralization, would hint at the passage of a large amount of aqueous liquid, be it magmatic or hydrothermal, relative to the volume of sulfide, with a moderate $fO_2$ (magnetite remained stable within the alteration halo). Péntek et al. (2009) interpreted the consistent sulfide assemblage displayed by the mineralization of the Broken Hammer property and the perceived difficulty of sulfide melt migration into the deep footwall as clear indicators that the transport medium was a hydrothermal fluid. However in the case of all North Range properties the sulfide vein, IRV + disseminations and QCS mineralization each display a unique sulfide mineral assemblage, silicate trace element distribution, bulk Cl:Br ratios (sulfide vein and IRV) and PGM assemblage (see Chapter. 4) indicating that the formation of each mineralizing style could be the result of distinct processes.

The same fracture network assumed by Péntek et al (2009) and Tuba et al. (2010) to have served as conduits for aqueous fluids could just as easily have served as conduits for dense sulfide liquids, representing the extreme fractionated residue of crystallizing contact type ore magmas (Mungall and Su, 2005; Mungall, 2007; Chung and Mungall, 2009). When combined with the prolonged tectonic settling of the footwall and the impermeable nature of its rocks the movement of such liquids some 1 km into the footwall is not inconceivable (Hooper, 1991).

South Range mineralization differs substantially from the North Range. Mineralization at the Denison property probably records tectonic redistribution of magmatic base-metal sulfides along embayment-controlling fault zones, followed by or synchronous with remobilization by metamorphic fluid redistributing base and precious metals proximal to the fault zone. The passage of this metamorphic fluid likely led to wholesale re-equilibration of the wall-rocks proximal to fluid conduits, producing consistent major and trace element concentrations for major ferromagnesian phases over long distances and largely erasing the local effects of syn-mineralization alteration in the vein selvages. Mineralization from the McKim property in contrast likely represents a mixture of solid state redistribution of sulfides from the contact and the fractionated residuum of the Little Stobie contact orebodies, with metals for QCS mineralization likely scavenged by hydrothermal fluids interacting with the contact ores.
Chapter 4
Precious Metal Minerals From Five Low-Sulfide PGE-Cu-Ni Prospects in the Footwall of the Sudbury Igneous Complex, Canada

4.1 Abstract

The discovery of low-sulfide mineralization in the footwall of the Sudbury Igneous Complex represents a new locality for the study of precious metal minerals and associated bismuth chalcogenides, including some phases that have not previously been described.

Analysis of platinum group minerals within magmatic mineralization from the North Range properties reveals a sequence of Pt and Pd minerals that formed under conditions ranging from high to low temperatures. As noted in previous studies, Pt on the North Range is dominantly hosted by moncheite, whereas Pd is hosted within a kotulskite-merenskyite-sobolevskite-michenerite assemblage indicating changes in both temperature and Bi–Te concentrations. Such compositional variation is reflected by the Pd mineral assemblage, with sulfide veins from the Wisner and Capre properties dominated by merenskyite and michenerite, whereas kotulskite and michenerite are prevalent within veins from Levack North. The preference for mono- or bi-telluride phases is interpreted to reflect the composition of the residual sulfide melt and thereby implies that sulfide liquids within the North Range footwall should not be considered to have been compositionally homogeneous. The additional presence of sperrylite and froodite within irregular veinlets, along with elevated concentrations of Se within michenerite and merenskyite, are taken to reflect the formation of irregular veinlet (IRV) mineralization from a highly fractionated sulfide liquid, representing the final distillate from larger sulfide bodies. Platinum group minerals associated with quartz ± carbonate + sulfide veins from the North Range are dominated by michenerite and merenskyite, with lesser kotulskite and sobolevskite. Both michenerite and merenskyite show a reduction in Pt concentrations when compared to sulfide vein–hosted equivalents. Discrete Pt phases (sperrylite) were only observed from the Capre
property. However based on the bulk precious metal grades it is likely that additional but unrecognized Pt phases are present within QCS veins from the two other properties. Platinum group minerals from the Denison property in the South Range are dominated by sperrylite and michenerite, in keeping with previous studies. In contrast to previous works, however, significant numbers of sobolevskite–kotulskite–sudburyite crystals were identified, primarily hosted within stockwork mineralization. These phases show significant Bi–Te–Sb exchange, with similar compositions having previously been reported from deposits with a hydrothermal component. Platinum from the McKim property is hosted by sperrylite with Pd in froodite. The lack of higher temperature Pd phases is likely the result of an incomplete cataloguing of PGMs by the author. Identification of PGMs was hindered by abundant hessite and Bi-chalcogenides masking precious metal minerals during BSE analysis and the small PGM crystal size.

The identification of polyphase precious metal mineral aggregates from both the North and South Range properties and Bi-chalcogenide micro-veinlets from McKim suggest that fractionation of residual sulfide liquids is capable of producing Ag–Te ± Bi ± Pd melts along the North Range, Pd–Ag–Te–Bi–Sb melts (Denison) and Bi–Te–S–Se melts (McKim), although a metamorphic origin can also not be discounted on the South Range. Although the majority of precious metal minerals are interpreted as having crystallized directly from a either a sulfide melt or hydrothermal fluid, the presence of Pd-phases along cleavages and fractures within gersdorffite from the Denison property suggests that the exsolution of precious metal minerals from certain phases contributes to the PGM budget. Analysis of PGMs within gersdorffite from the Denison property identified two unknown Pd phases: (Pd, Ag, Ni, Pt)$_3$(Sb, Bi, Te, As)$_2$ and (Pd,Ag)$_3$(Bi, As, Te)$_4$. Two previously unseen substitutions were also observed, with kotulskite from the Levack North and Capre properties showing substitution of Pd by Ag, and Se replacing Te in pilsenite from the McKim property. Both instances are the first occurrences of such substitutions in the literature.
4.2 Introduction

Because low-sulfide PGE mineralization was comparatively recently discovered, information about its precious metal mineral assemblage is extremely limited. To date only two studies provide details of the platinum group mineral (PGM) assemblage, associated bismuth chalcogenides and Au and Ag phases, all of which are consistent with previous studies of footwall mineralization (Cabri and Laflamme, 1976; Li and Naldrett, 1993; Farrow and Watkinson, 1997; Everest, 1999). The two studies focusing on low-sulfide mineralization (Farrow et al., 2005; Péntek et al., 2009) identified merenskyite (PdTe$_2$), moncheite (PtTe$_2$), michenerite (PdBiTe), maslovite (PtBiTe), sperrylite (PtAs$_2$), kotulskite (PdTe), froodite (PdBi$_2$), plumbopalladinite (Pd$_3$Pb$_2$) and sopcheite (Ag$_4$Pd$_3$Te$_4$), although the former study provided no compositional information.

An understanding of the compositions and relative abundances of precious metal minerals within low-sulfide mineralization not only offers the opportunity to compare data with that of contact and sharp-walled vein mineralization, but also offers a window into the movement of precious metals within low-sulfide systems and low temperature processes.

4.3 Analytical Methods

Attempts to separate PGM using crushing of rocks samples followed by hydrosedeparation were unsuccessful, so all PGM were observed and analyzed in situ in polished thin sections.

The quantitative microanalysis of platinum-group minerals and Bi-chalcogenides was carried out using a JEOL SX-50 electron microprobe (EMP), housed within the Department of Geology, University of Toronto. The PGM/Bi-chalcogenide routine employed a 1 μm beam with an accelerating voltage of 20 kV and a beam current of 50 nA, The following X-ray lines, standards and count-times were used, calibrated to synthetic and natural standards: Fe Ka (chalcopyrite; 20 s), Ni Ka (pentlandite; 30 s), S Ka (matildite; 20 s), Sn La (stannite, 40 s) PbMa (galena, 60 s), Pt Ma (Pt metal, 30 s), Pd La (Pd$_5$[As, Sb]$_2$, 30 s), Au Ma, (electrum; Au$_{80}$, 40 s), Ag La (matildite, 40 s), Te La (kotulskite, 60 s), Bi Ma (sobolevskite, 20 s), Sb La (sudburyite, 60 s),
As $K\alpha$ ($\text{GaAs}, 40\ s$) and Se $K\alpha$ ($\text{Bi}_2\text{Se}_3, 60\ s$). Initial analyses also contained Co, Ru, Rh, Os and Ir; however they were removed once it became clear that their levels were below detection. The inclusion of Ni, Fe and S was not only due to their occasional presence in trace levels within PGMs and Bi-chalcogenides, but also to allow recognition of and corrections for data influenced by X-ray emissions from nearby phases, particularly sulfides. Data were deemed acceptable if analytical totals fell within a range of $100 \pm 3.0 \text{ wt } \%$. All totals associated with clean analyses fell within this range, although totals for AuAg alloy were often in excess of it and were discarded.

Due to the small scale of some crystals, heterogeneities and the presence of PGM aggregates it was necessary to image and analyze phases by scanning electron microscope. Semi-quantitative analysis of PGMs and Bi-chalcogenides was carried out using a JEOL JSM-840 SEM with a PGT/AAT energy dispersive spectrometry (EDS) detector, IXRF 500 digital pulse processor and EDS2008 software, which was used to process all analyses. Point analyses were run at 20 kV, over a 60 second count time. When the composition of the phase to be analyzed was unknown it was given an initial 10 to 20 second scan to allow the selection of the appropriate elements. Analyses used some or all of the following X-ray lines: Fe $K\alpha$, Ni $K\alpha$, S $K\alpha$, Sb $L\alpha$, Pt $L\alpha$, Pd $L\alpha$, Au $L\alpha$, Ag $L\alpha$, Te $L\alpha$, Bi $L\alpha$, As $L\alpha$ and Se $L\alpha$. Elements were calibrated to pure metal standards and natural and synthetic minerals with known compositions where available.

4.4 Platinum Group Minerals

4.4.1 Merenskyite ($\text{PdTe}_2$)

Observations from all North Range properties revealed merenskyite to be present as a major (Capre; Wisner) or minor (Levack North) PGM across a range of mineralizing styles. All merenskyite crystals analyzed displayed some solid solution toward the Pt end member, moncheite. The control(s) on Pd-Pt substitution remain unclear, although a temperature control has been suggested, with increased Pt concentrations reflecting higher temperatures of crystallization (Helmy et al., 2007, references therein), although at lower temperatures it is likely
that composition the of the parent liquid is the primary control. Merenskyite was not observed on the South Range.

**Sulfide veins**

Most of the merenskyite observed at the Wisner and Capre properties is hosted by sulfide veins. Six and 83 merenskyite crystals were observed in sulfide vein material from the Wisner and Capre properties, respectively, comprising 18 and 52 % of all Pd phases and 100 and 57 % of all Pt phases present, the latter values having been calculated based on the total number of PGMs containing more than 1 wt % Pt, not weighted for grain size. These sulfide-hosted grains accounted for almost all of the merenskyite crystals observed at these two properties. Crystals ranged from 3 to 8 μm and 3 to 120 μm at the Wisner and Capre properties, with analyses producing average compositions of \((\text{Pd}_{0.83}\text{Pt}_{0.14}\text{Fe}_{0.04}\text{Ni}_{0.03}\text{Ag}_{0.01})_{1.05}(\text{Te}_{1.57}\text{Bi}_{0.37}\text{S}_{0.01})_{1.95}\) and \((\text{Pd}_{0.57}\text{Pt}_{0.29}\text{Ni}_{0.15}\text{Fe}_{0.02})_{1.03}(\text{Te}_{1.59}\text{Bi}_{0.37})_{1.97}\) respectively. Only three sulfide vein hosted merenskyite crystals were identified from the Levack North property. These crystals range between 4 and 11 μm and are enclosed within sulfide. They make only a minor contribution to the total Levack North PGMs, comprising 2 and 5 % of the Pd and Pt phases present. The average composition of the analyzed grains is \((\text{Pd}_{0.68}\text{Pt}_{0.31}\text{Fe}_{0.03}\text{Ag}_{0.01})_{1.03}(\text{Te}_{1.50}\text{Bi}_{0.47})_{1.97}\).

All sulfide vein-hosted merenskyite crystals show extensive Pd–Pt(–Ni) and Te–Bi solid solution (Figure 4.1 & Table 4.1), with Pt and Bi contents of 0.8 to 19.0 wt % and 11.4 to 25.4 wt %. Merenskyite crystals from the Capre property display a substantial Ni component of between 0.06 and 2.73 wt %, with the majority of analyses clustering around the average of 2.15 wt %. These increased Ni concentrations occur at the expense of Pd, with the elements displaying a strong anticorrelation (R = -0.82). Trace concentrations of Ag are noted from all North Range properties, with one fifth of analyses producing concentrations between 0.19 and 0.76 wt %.

**IRV**

Eight merenskyite crystals were observed in IRV material from the Wisner property, occurring within sulfide, and along sulfide-silicate and silicate-silicate grain boundaries. Crystals were observed to range from 5 to 12 μm, with two examples forming aggregates with hessite.
Merenskyite is the dominant Pt bearing phase within IRV samples from Wisner, with Pt concentrations up to 11.3 wt %. Crystals produce an average composition of

![Diagram showing compositional variation in the merenskyite (PdTe$_2$)–moncheite (PtTe$_2$)–Melonite (NiTe$_2$) solid-solution series. 175 analyses plotted on the Pd-Pt-Ni ternary in atomic percent.](image)

Figure 4.1. Compositional variation in the merenskyite (PdTe$_2$)–moncheite (PtTe$_2$)–Melonite (NiTe$_2$) solid-solution series. 175 analyses plotted on the Pd-Pt-Ni ternary in atomic percent.
Table 4.1. Representative merenskyte analyses (wt %) from sulfide vein (1 and 2 Levack North, 3 and 4 Wisner and 5 and 6 Capre), IRV (7 and 8 Wisner, 9 Capre) and QCS (10 and 11 Capre) mineralization. Compositions are calculated based on apfu.

(Pd_{0.73}Pt_{0.17}Fe_{0.02}Ni_{0.01}Au_{0.01})_{0.94} (Te_{1.53}Bi_{0.049}Sb_{0.01}Se_{0.03})_{2.06}, with trace Sb and Se concentrations of up to 0.34 wt % and 0.99 wt % respectively.

A single merenskyte crystal was also recovered within IRV samples from Capre, located along a sulfide-silicate boundary and measuring 7 μm. The crystal provided a composition of (Pd_{0.87}Pt_{0.09}Fe_{0.04}Ag_{0.02})_{1.02}(Te_{1.57}Bi_{0.41})_{1.98}.

QCS

Thirteen merenskyte grains were observed within QCS veins from the Capre property. All were located within sulfide and display a wide variation in Pt concentrations, ranging from below...
detection limit to 8.93 wt %, a decrease when compared analyses from sulfide veins (Figure 4.1). Average Ni concentrations were around half those of sulfide vein crystals, with a mean value of 1.11 wt %. QCS merenskyite crystals yielded an average composition of $(\text{Pd}_{0.91}\text{Pt}_{0.05}\text{Ni}_{0.07}\text{Fe}_{0.02})_{1.06}(\text{Te}_{1.62}\text{Bi}_{0.32})_{1.94}$.

All analyses fell within the range of previously published values (Cabri and Laflamme, 1976; Farrow and Watkinson, 1997; Péntek et al., 2008). It remains uncertain whether the sporadic trace Ag detected was the result of unidentified hessite inclusions or its substitution for Pd.

### 4.4.2 Moncheite (PtTe$_2$)

Moncheite, like merenskyite, was observed within sulfide veins from all three north range properties and comprised the only discrete Pt phase, although extensive Pt-Pd solid-solution was observed (Figures 4.1 and 4.2A and Table 4.2). Its occurrence within other mineralizing styles is limited to IRV material from Levack North, where sperrylite is also present. Its presence was not noted on the South Range.

Forty grains with sizes ranging from 2 to 120 μm were observed in vein material from the Levack North property, almost all hosted by sulfide. Moncheite does not form aggregates with other PGM, although it was observed in proximity of kotulskite. Crystals comprised 49% and 18% of Pt and Pd bearing phases respectively, averaging 27.0 wt % and 8.4 wt %.

#### Sulfide veins

Moncheite within sulfide veins from the Levack North property ranged between 2 and 120μm and made up 49% and 18% of Pt and Pd bearing phases respectively. Crystals display extensive Te–Bi substitution, with Bi contents of 18.9 to 25.5 wt %. The crystals produced an average composition of $(\text{Pt}_{0.63}\text{Pd}_{0.35}\text{Fe}_{0.01}\text{Ni}_{0.01})_{1.00}(\text{Te}_{1.53}\text{Bi}_{0.47})_{2.00}$, with the average Pd content towards the upper limit of published values (Cabri and Laflamme, 1976, Farrow and Watkinson, 1997), whilst the minimum Pt content (22.4 wt %) approaches the moncheite-merenskyte compositional divide (Figure 4.1). The single 25 μm moncheite crystal was identified within the alteration.
selvage of a sulfide vein from the Wisner property and formed an aggregate with merenskyite. The calculated composition of \((\text{Pt}_{0.67}\text{Pd}_{0.35}\text{Fe}_{0.03}\text{Ag}_{0.05})_{1.10}(\text{Te}_{1.38}\text{Bi}_{0.47}\text{S}_{0.03}\text{Se}_{0.01}\text{As}_{0.01})_{1.90}\) shows a slight excess precious metal content, possibly the result of the inadvertent analysis of an unobserved Ag phase intergrown with the moncheite.

Seven moncheite crystals were observed at the Capre property, five within chalcopyrite and two within pentlandite. They had Ni contents of 0.2 to 1.5 wt %, which displays a strong anticorrelation with Pt \((R = -0.58)\), and a moderate correlation with Pd \((R = 0.48)\). The observed moncheite crystals range from 8 to 55 μm and display an average composition of \((\text{Pt}_{0.58}\text{Pd}_{0.35}\text{Ni}_{0.06}\text{Fe}_{0.05})_{1.04}(\text{Te}_{1.48}\text{Bi}_{0.45}\text{S}_{0.03})_{1.96}\).

**IRV**

The seven moncheite crystals identified in IRV samples from the Levack North property displayed an average composition of \((\text{Pt}_{0.83}\text{Pd}_{0.15}\text{Fe}_{0.02}\text{Ni}_{0.01})_{1.01}(\text{Te}_{1.44}\text{Bi}_{0.54}\text{Sb}_{0.01})_{1.99}\), a significant reduction in Pt-Pd substitution and a minor enrichment in Bi, when compared to sulfide vein analyses. Moncheite was observed within sulfide, within silicates and along sulfide–silicate boundaries (see Figure 3.7A), displaying a homogeneous appearance and ranging between 2 and 30 μm. Two aggregates were observed, one with hessite and a second with kotulskite, both showing sharp linear grain boundaries.

A single sample of IRV mineralization from the Capre property yielded four moncheite crystals all located along sulfide-silicate boundaries, which present lower Bi:Te ratios than moncheite in Capre sulfide veins. The IRV-hosted moncheite has up to 1.91 wt % Ni and 0.35 wt % Sb, an increase over their sulfide vein hosted counterparts. The crystals gave an average composition of \((\text{Pt}_{0.48}\text{Pd}_{0.41}\text{Ni}_{0.11}\text{Fe}_{0.02})_{1.02}(\text{Te}_{1.56}\text{Bi}_{0.41}\text{Sb}_{0.01})_{1.98}\).
Figure 4.2. Sulfide vein hosted hessite (Hss) and moncheite (Mon), within pentlandite (Pn) with associated chalcopyrite (Ccp) and quartz (Qtz), pyrite (Py) porphyroblast after pentlandite (A). Sulfide vein hosted michenerite (Mch) and tetradymite (Tet) aggregate within chalcopyrite (Ccp) enclosing millerite (Mi). Note: In order to emphasize PGM and Bi-chalcogenide colors the image has been artificially enhanced (B). Sobolevskite (Sbv) crystals enclosed within chalcopyrite (Ccp) (C). AuAg alloy (AuAg) enclosed within chalcopyrite (Ccp) with associated millerite (Mi) enclosing sphalerite (Sp). Note: Chalcopyrite tarnish is the result of HNO3 etching (D). Bi-chalcogenide veinlet within the
margin of sulfide vein from the McKim prospect. Vein halo displays abundant chalcopyrite (Ccp) and bismuthohauchecornite (Bhc), crosscut by creamy-white bismuthinite (Bs), white-grey joséite-B (Js-B) and deeper white-grey parkerite (Prk), within an quartz (Qtz) and actinolite (Act) groundmass (E).

4.4.3 Sobolevskite (PdBi)–Kotulskite (PdTe)–Sudburyite (PdSb)

Mineralization from four of the prospects studied contain PGM with compositions in the sobolevskite–kotulskite–sudburyite series. Kotulskite forms a significant fraction of Pd phases within sulfide veins from the Levack North and is a minor phase at Capre. Sobolevskite was also observed within sulfide veins from Levack North where it is a minor phase. Kotulskite is present within IRV mineralization from the Levack North and Capre properties, with sobolevskite also occurring within QCS veins from the Levack North and Wisner properties. Substitution of Pd for Ag was identified within kotulskite and sobolevskite from the North Range, a previously unknown substitution. Sobolevskite–kotulskite–sudburyite crystals were identified within mineralization from the Denison property, primarily with stockwork material, although sobolevskite and sudburyite crystals were identified within a QCS sample. These crystals present extensive Bi–Te–Sb substitution and constitute a more significant fraction of Pd phases within mineralization than has previously been noted on the South Range.

Sulfide veins

Kotulskite represents the primary Pd phase within sulfide veins from the Levack North property, accounting for 59 % of vein hosted Pd-PGM, with eighty-five percent of the 132 crystals analyzed hosted within chalcopyrite. Analyses document extensive Te–Bi, Te–Sb and Pd–Ag substitutions (see Table 4.3 & Figure 4.3), the latter of which has not previously been published (Figure 4.4). The Ag concentration ranges from below detection limit to 2.8 wt %, producing an average formula of \((\text{Pd}_{0.98}\text{Fe}_{0.01}\text{Ag}_{0.01})_{1.00} (\text{Te}_{0.58}\text{Bi}_{0.41}\text{Sb}_{0.01})_{1.00}\). Overall Ag distribution in kotulskite from the Levack North property shows a strong negative correlation with Pd \((R = -0.84)\), however no associated variations in semimetal (i.e. Te or Bi) content or significant deviations from stoichiometry (based on a standard formula unit) were observed.
Tellurium shows a nearly perfect anticorrelation with Bi as expected ($R = -0.97$), but in contrast there is no correlation between either Te or Bi and Sb ($R = -0.17$ and 0.09, respectively).

Unlike at Levack North kotulskite is a minor phase within sulfide veins from the Capre property with only one crystal identified. The crystal displays Bi and Te concentrations consistent with those from Levack North, with a minor Sb component. The crystal has the composition of $\text{Pd}_{0.98} (\text{Te}_{0.55}\text{Bi}_{0.46}\text{Sb}_{0.01})_{1.02}$.

Sobolevskite is a minor constituent of the Pd-bearing phase assemblage in sulfide vein mineralization from the Levack North property, with nine grains hosted within chalcopyrite (Figure 4.2C) and one within epidote, all ranging between 3 and 50 μm in diameter. Some substitution of Ag for Pd was noted, with two crystals displaying concentrations of 1.0 and 1.4 wt % Ag, producing an average composition of $(\text{Pd}_{0.99}\text{Fe}_{0.02}\text{Ag}_{0.01})_{1.02} (\text{Bi}_{0.51}\text{Te}_{0.48}\text{Sb}_{0.01})_{1.00}$.
**IRV**

Only five grains of kotulskite were observed in IRV hosted mineralization from Levack North, three along sulfide-silicate boundaries and two in silicates, four of which were within the same sample. These four crystals have a uniform composition with Ag concentrations of 3.1 to 3.3 wt %, whereas the remaining crystal has undetectable Ag. Both Sb and Bi concentrations are slightly higher than in sulfide vein-hosted kotulskite, with an average composition of \((\text{Pd}_{0.90}\text{Ag}_{0.07})_{0.97}(\text{Te}_{0.55}\text{Bi}_{0.45}\text{Sb}_{0.02})_{1.02}\). These values must be considered carefully due to the limited dataset and skewing effect of one sample. Two kotulskite crystals were identified within IRV mineralization from the Capre property. The presence of Ag was noted in the analyses of both crystals with 0.9 and 1.3 wt % detected, producing an average composition of \((\text{Pd}_{0.91}\text{Ag}_{0.03}\text{Fe}_{0.01})_{0.95}(\text{Te}_{0.69}\text{Bi}_{0.34}\text{Sb}_{0.02})_{1.05}\). Antimony is present as a minor constituent with levels within one crystal reaching 1.31 wt %.

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Table 4.3. Representative kotulskite analyses (wt %) from sulfide vein (1 and 2 Levack North and 3 Capre), IRV (4 and 5 Levack North, 6 Capre) and stockwork (7 and 8, Denison) mineralization. Compositions are calculated based on 2 apfu.
Thirteen QCS hosted sobolevskite crystals were analyzed from the Levack North property. They range from 2 to 15 μm, all within chalcopyrite, and comprise 62% of Pd phases seen in the QCS mineralization. They contain less Te than sulfide vein-hosted sobolevskite, with an average of 11.2 wt %. Nine analyses revealed substitution of Pd by Ag (R = -0.80), with concentrations of up to 1.07 wt % Ag measured however, as with kotulskite, no associated variation in Bi, Te or Sb was observed. The crystals yielded an average composition of (Pd$_{1.02}$Fe$_{0.01}$Ag$_{0.01}$)$_{1.04}$ (Bi$_{0.70}$Te$_{0.25}$Sb$_{0.01}$)$_{0.96}$. Semimetal correlations reveal the replacement of Bi by Te (R = -0.99), however as with kotulskite the presence of Sb results in no related change in either Bi (R = -0.12) or Te (R = 0.12).

A single 5 μm silicate-hosted sobolevskite crystal was identified within the alteration selvage of a QCS vein from the Wisner property. The crystal contains traces of Ag, Sb and Se (Table 4.4), and has an average composition of (Pd$_{0.94}$Ag$_{0.06}$Fe$_{0.03}$)$_{1.03}$ (Bi$_{0.64}$Te$_{0.33}$Se$_{0.01}$)$_{0.98}$.

South Range

Kotulskite–sobolevskite–sudburyite crystals account for 27 % of Pd minerals observed in this study from the Denison property, where sobolevskite (n = 30), kotulskite (n = 2) and sudburyite (n = 3) show extensive PdBi, PdTe and PdSb solid solution (Figure 4.3) differing substantially from North Range compositions reported here or in the published literature (Cabri and Laflamme, 1974, 1976; Li and Naldrett, 1993; Farrow and Watkinson, 1997; Molnár et al., 2001; Penték et al., 2008). No kotulskite–sobolevskite–sudburyite crystals were observed in sample from McKim.

Apart from one sudburyite and two sobolevskite crystals hosted with QCS veins, all Pd(Bi–Te–Sb) crystals observed are hosted by stockwork style mineralization, all but one being located interstitial to silicates or along sulfide-silicate contacts. Crystals range from 1 to 75 μm in size, most occurring individually, with the exception of four examples occurring in polyphase aggregates with michenerite, froodite, sperrylite, AuAg alloy, hessite and Bi-chalcogenides.
Figure 4.3. Compositional variation in the sobolevskite (PdBi)–kotulskite (PdTe)–Sudburyite (PdSb) solid-solution series. 198 analyses plotted on onto the Bi-Te-Sb ternary in atomic percent.
Table 4.4. Representative sobolevskite analyses (wt %) from sulfide vein (1 and 2 Levack North), QCS (3 and 4 Levack North, 5 and 6 Denison) and stockwork (7 and 8 Denison) mineralization. Compositions are calculated based on 2 apfu.

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Sobolevskite from both stockwork and QCS mineralization from the Denison property display similar compositions averaging \( (\text{Pd}_{0.99}\text{Fe}_{0.01})_{1.00}(\text{Bi}_{0.50}\text{Te}_{0.25}\text{Sb}_{0.25})_{1.00} \) and \( (\text{Pd}_{1.00}\text{Fe}_{0.01})_{1.01}(\text{Bi}_{0.49}\text{Te}_{0.21}\text{Sb}_{0.29})_{0.99} \) respectively, although the latter is only based on two analyses. Moderate Te:Bi, and Sb:Bi, and Te:Sb anticorrelations of -0.50, -0.55 and -0.43 respectively were calculated, probably resulting from the three-way competition for the semimetal sites. The two kotulskite crystals analyzed from stockwork samples yield an average composition of \( (\text{Pd}_{0.97}\text{Fe}_{0.01})_{0.98}(\text{Te}_{0.48}\text{Bi}_{0.38}\text{Sb}_{0.16})_{1.02} \), however both crystals display significant differences in semimetal concentrations (Table 4.4). Sudburyite analyses from stockwork samples display elevated Te concentrations of 1.97 and 7.66 wt % when compared to published values from Sudbury mines (Cabri and Laflamme, 1974; 1976) (Table 4.5). In contrast the QCS hosted crystal was in keeping with previous studies, sitting as it does along the sobolevskite-sudburyite join (Figure 4.3). Crystals from stockwork samples averaged \( (\text{Pd}_{0.96}\text{Pt}_{0.01}\text{Fe}_{0.01})_{0.98}(\text{Sb}_{0.57}\text{Bi}_{0.36}\text{Te}_{0.10})_{1.03} \) with the single QCS hosted crystal at \( (\text{Pd}_{1.01}\text{Pt}_{0.01})_{1.02}(\text{Sb}_{0.72}\text{Bi}_{0.26}\text{Te}_{0.01})_{0.99} \).
Table 4.5. Representative sudburyite analyses (wt %) from QCS (1 Denson) and stockwork (2 and 3 Denison) mineralization. Compositions are calculated based on 2 apfu.

4.4.4 Michenerite (PdBiTe)

Michenerite occurs within all mineralizing styles examined from all properties, except McKim. Michenerite from the North Range shows variable degrees of Pd–Pt substitution, whereas on the South Range it is Pt free (c.f., Cabri and Laflamme, 1976), however minor Sb substitution is nearly universal.

**Sulfide vein**

Sulfide vein hosted michenerite is abundant at the three North Range properties, where it is dominantly hosted within sulfide. Thirty eight michenerite crystals were identified from Levack North and ranged between 1 and 175 μm. Consistent detectable Pt concentrations of up to 8.80 wt %, and sporadic Ni and Ag up to 0.72 wt % and 0.52 wt % respectively were detected. As with Pt, Ag displays a strong anticorrelation with Pd (R = -0.59), whilst Ni shows no correlation. Observed antimony concentrations reach a maximum of 0.66 wt % and display no correlation with Bi or Te, unlike data reported by Barkov et al. (2002), however Sb concentration is moderately correlated with Pt (R = 0.48). Michenerite analyzed from Levack North has an average composition of (Pd

$$\text{Pd}_{0.97}\text{Pt}_{0.04}\text{Ni}_{0.02}\text{Fe}_{0.01})_\text{Te}_{0.04}(\text{Te}_{0.03}\text{Bi}_{0.91}\text{Sb}_{0.01})_\text{As}_{0.00}$$

The 32 analyzed michenerite crystals within sulfide veins from the Wisner property range from 1 to 50 μm and display sporadic Pt enrichments of up to 6.33 wt % and minor Ag (up to 0.76 wt %). Antimony concentrations are consistently below detection limits on the EMP. Michenerite
crystals from Wisner yield an average composition of $(\text{Pd}_{0.97}\text{Fe}_{0.04}\text{Pt}_{0.01}\text{Ag}_{0.01})_{1.02} (\text{Te}_{1.04}\text{Bi}_{0.93}\text{Sb}_{0.01})_{1.98}$.

The 63 michenerite crystals observed within sulfide veins from the Capre property range between 2 and 150 μm, with Pt levels of up to 3.86 wt %, comparable to those from Levack North. Crystals display consistent trace Ni and Sb of up to 0.96 wt % and 0.76 wt % respectively. Analyses averaged $(\text{Pd}_{0.98}\text{Pt}_{0.05}\text{Ni}_{0.01}\text{Fe}_{0.01})_{1.05} (\text{Te}_{1.07}\text{Bi}_{0.88}\text{Sb}_{0.01}\text{S}_{0.01})_{1.97}$.

Figure 4.4. Scatter plot of the Pd and Ag content of kotulskite and sobolevskite from the North Range. Note the negative correlation between the elements.

IRV

Michenerite was identified in IRV mineralization from all North Range properties and accounted for about half of the Pd and Pt bearing phases identified within IRV at Levack North and Wisner and over 90% of Pd minerals observed in IRV material from Capre. Michenerite crystals from all
properties are hosted in near equal proportions by chalcopyrite and along sulfide-silicate grain boundaries, range in diameter between 2 and 55 μm and although generally isolated were rarely observed in contact with hessite and tetradyosite (Figure 4.2B).

Michenerite from IRV mineralization at the Levack North property displays Pt concentrations of up to 6.31 wt %, with trace concentrations of up to 0.49 wt % Sb and 1.03 wt % Se commonly observed. Analyses produced an average composition of \((\text{Pd}_{0.92}\text{Pt}_{0.08})_{1.00} (\text{Te}_{1.03}\text{Bi}_{0.93}\text{Sb}_{0.01}\text{Se}_{0.04})_{1.99}\). The trace semimetal levels are matched by crystals from the Wisner property, although Pt concentrations display a greater variation, with levels of up to 2.57 wt %, yielding an average composition of \((\text{Pd}_{0.97}\text{Pt}_{0.02})_{0.99}(\text{Te}_{1.05}\text{Bi}_{0.93}\text{Sb}_{0.01}\text{Se}_{0.02})_{2.01}\). The presence of Sb within michenerite from both the Levack North and Wisner produces a strong anticorrelation with Bi (\(R = -0.50\) and \(-0.60\) respectively), with Se also displaying a strong negative correlation to Bi (\(R = -0.94\)) at the Levack North property, both likely resulting from simple Sb–Bi and Se–Bi substitution reactions.

Michenerite within IRV samples from the Capre property only rarely contains measurable Pt, whilst Se is consistently below detection limits. Concentrations of Ag were consistently detected, with levels of up to 0.91 wt %, which do not correlate with any other element. Antimony was detected sporadically, with concentrations up to 0.22 wt %, producing an average composition of \((\text{Pd}_{0.98}\text{Ni}_{0.01}\text{Ag}_{0.03})_{1.02}(\text{Te}_{1.11}\text{Bi}_{0.87})_{1.98}\).

**QCS**

Michenerite hosted within QCS material from the Levack North and Capre properties range between 3 and 23 μm, with crystals enclosed within chalcopyrite and pyrite. Crystals display a Pt range between 1.41 and 1.64 wt % at Levack North and below detection to 3.08 wt % at Capre. Trace concentrations of Sb and Se were noted in crystals from the Levack North property, with levels reaching up to 0.35 wt % and 0.55 wt % respectively. Analyses yielded an average composition of \((\text{Pd}_{0.90}\text{Pt}_{0.04})_{0.94}(\text{Te}_{1.10}\text{Bi}_{0.92}\text{Sb}_{0.01}\text{Se}_{0.03})_{2.06}\). Consistent Sb concentrations are also present in crystals from Capre, with levels of up to 0.77 wt %, noticeably above the levels from
sulfide vein and IRV samples. Crystals from Capre produced an average composition of 
$$(\text{Pd}_{1.04}\text{Pt}_{0.01})_{1.05}(\text{Te}_{1.10}\text{Bi}_{0.83}\text{Sb}_{0.02})_{1.95}.$$ 

**South Range**

Michenerite crystals were identified from sulfide vein, QCS and stockwork mineralization from the Denison property, where it represents about two thirds of observed Pd phases. As with previously published South Range data (Cabri et al., 1973; Cabri and Laflamme, 1976), only trace concentrations of Pt, Ni and Sb are present in michenerite from Denison (Table 4.6).

Sulfide vein hosted crystals range from 2 to 25 μm and are dominantly enclosed within sulfide. Michenerite crystals display Sb concentrations of up to 3.41 wt % and minor Ni up to 1.04 wt %, both slightly elevated when compared to stockwork and QCS mineralization. Analyses produced an average composition of 
$$(\text{Pd}_{0.99}\text{Ni}_{0.03})_{1.01}(\text{Te}_{1.05}\text{Bi}_{0.85}\text{Sb}_{0.09})_{1.99}.$$ Three of the four analyzed crystals display consistent Au concentrations ranging between 0.18 and 0.52 wt % (avg. 0.25 wt %). Although based on a very small data Au displays a very strong anticorrelation with Pd ($R = -0.97$) and moderate correlations with Te and Bi ($R = -0.46$ and 0.40 respectively).

Michenerite crystals observed from QCS mineralization range between 1 and 40 μm in diameter and are distributed equally between silicates and sulfide-silicate boundaries. Crystals display sporadic Ni concentrations of up to 0.93 wt %, whilst Sb was constantly detected, reaching up to 2.09 wt %. All but one QCS hosted crystal display Au concentration above detection (0.078 wt %), with concentrations ranging from 0.09 to 0.27 wt % and displaying a strong correlation with Bi ($R = 0.52$) and anticorrelation with Te ($R = -0.65$), suggestive a coupled substitution of Au-Bi for Te. The correlation between Au and Pd shows a moderate anticorrelation ($R = -0.43$) and when combined with strong negative correlation displayed by sulfide vein hosted crystals would suggest the substitution of Au for Pd, with Bi replacing Te to maintain the charge balance. Analyses produced an average composition of 
$$(\text{Pd}_{0.99}\text{Ni}_{0.03})_{1.01}(\text{Te}_{1.05}\text{Bi}_{0.85}\text{Sb}_{0.09})_{1.99}.$$ 

Examination of stockwork mineralization revealed 71 michenerite crystals (Figure 4.7F), almost all located along silicate and sulfide-silicate grain boundaries. Grain size ranges from 5 to 500 μm, with 8 examples occurring in aggregates with froodite, PdBi–PdTe–PdSb, sperrylite, AuAg
alloy and Bi-chalcogenides. Michenerite displayed trace amounts of Ni, reaching up to 0.42 wt %, with consistent levels of Sb up to 2.21 wt %. Analyses yielded an average composition of $(\text{Pd}_{1.02}\text{Ni}_{0.01})_{1.03}(\text{Te}_{0.98}\text{Bi}_{0.94}\text{Sb}_{0.04})_{1.96}$.

Across the South Range michenerite dataset Ni display no correlation with major or trace elements. As previously noted, (Barkov et al., 2002), Sb shows a strong negative correlation with Bi ($R = -0.62$), however given the high Sb concentrations displayed by Denison michenerite a higher correlation may well have been expected.

### 4.4.5 Froodite (PdBi$_2$)

Froodite is a rare phase within North Range samples, with only one crystal having been identified. The 40 μm crystal identified was hosted within IRV mineralization from the Levack North property and occurred along a sulfide-silicate interface (Figure 4.7B). The froodite crystal was located within an area containing michenerite, hessite and AuAg alloy, although it was not in contact with these phases. Its composition is Pd$_{1.08}$Bi$_{1.92}$.

Examination of material from the Denison identified froodite as a minor phase, located within polyphase PGM aggregates and along the margins of gersdorffite hosted michenerite and Bi-Sudburyite. Analysis was hampered by contamination of the fluorescence signal from the associated PGMs and sulfarsenides; this was especially true of gersdorffite-hosted crystals where froodite was typically small (< 1 μm), poorly defined and highly irregular in form. A total of six successful analyses were obtained using SEM-EDS, using only X-Ray peaks from Pd and Bi. These analyses produced an average semi-quantitative value of 19.76 wt % Pd and 80.24 wt % Bi, consistent with near stoichiometric PdBi$_2$.

Froodite is the only Pd phase identified from the McKim property; five crystals were analyzed. The crystals are all hosted by pentlandite or chalcopyrite from two sulfide vein samples. Froodite crystals from both samples occur individually, although one sample displays a region about 250 μm in diameter containing around twenty-five 0.25 to 3 μm crystals. In both cases froodite typically occurs proximal to abundant Bi-chalcogenides, particularly bismuthinite and Se-pilsenite. Analyzed crystals range from 1 to 3 μm in size and yielded an average composition
displaying elevated Pd and reduced Bi (Table 4.7) when compared to published data (Cabri, 2002), but somewhat in keeping with the early analyses of Chernyaev and Yushko-Zakharova (Cabri et al., 1973 reference therein). The crystals show recalculated trace Fe and Ni concentrations of up to 1.12 wt % and 0.81 wt % respectively, with the original data modified assuming that all S detected resulted from the host phase and that the host sulfide compositions were stoichiometric. The presence of up to 0.81 wt % Te is consistent with published values for the Sudbury area (Cabri and Laflamme, 1976; Li and Naldrett, 1993; Molnár et al., 2001). An average composition of \((\text{Pd}_{1.06}\text{Ni}_{0.05})_{1.11}(\text{Bi}_{1.88}\text{Te}_{0.01})_{1.89}\) was calculated, with the deviation from stoichiometry likely reflecting the difficulty in obtaining "clean" analyses.

### 4.4.6 Sperrylite (PtAs\(_2\))

Sperrylite provides only a minor contribution to the Pt levels at the three North Range properties studied. Observations of sperrylite occurrences were typically rare and were limited to IRV and QCS mineralization, but it is the dominant Pt phase within IRV samples from the Capre property. The presence of sperrylite within the PGM assemblage of IRV and QCS material contrasts with the sulfide vein mineralization which is lacking in the arsenide and is dominated instead by bismuthtellurides. Sperrylite crystals from the North Range properties are between 3 and 25 μm and are dominantly located along sulfide-silicate interfaces (85 %), with a minority of crystals enclosed within chalcopyrite (15 %). Crystals typically occur individually, although they are commonly proximal to michenerite and hessite.

**IRV**

Microanalyses of sperrylite within IRV samples from the North Range properties were hampered by the small crystal sizes and evident contamination of the signal with fluorescence from associated mineral phases. Sperrylite comprises only a fraction of Pt-phases within IRV mineralization from the Levack North and Wisner properties, at 13% and 4% respectively, although at Wisner it as the only discrete Pt phase observed. Sperrylite comprises 64 % of Pt minerals within IRV mineralization from the Capre property. All analyses are close to
stoichiometric PtAs$_2$, although the data do display a consistent but small excess of Pt, possibly accounted for by observations of minor quantities of Te and S which may be substituting for As (Table 4.8).

**QCS**

The two 7 and 10 μm sperrylite crystals located within QCS material from the Capre property were seen hosted by chalcopyrite, although one was fully enclosed within michenerite. Analyses remained near stoichiometric, although both crystals displayed minor Sb (0.22 and 0.34 wt %), inconsistent with the surrounding minerals.

**South Range**

As was noted in previous studies of South Range mineralization (Cabri and Laflamme, 1976) Pt from the Denison and McKim properties is nearly exclusively hosted within sperrylite. Stockwork mineralization from the Denison property yielded 61 crystals, of which 95 % were hosted along silicate–silicate interfaces. Crystals range from 1 to 3500 μm in size; with larger sperrylite crystals partially enclosing the surrounding silicate minerals (Figure 4.6). More than half of sperrylite crystals analyzed display measureable concentrations of Fe (up to 0.89 wt %) and Sb (up to 1.11 wt %). Fe concentration does not correlate with that of other elements, whereas Sb concentration is strongly anticorrelated with As (R = -0.56), in keeping with published data (Barkov et al., 2002; Augé et al., 2002). The average sperrylite composition is Pt$_{1.01}$(As$_{1.98}$Sb$_{0.01}$)$_{1.99}$.

In quartz–carbonate–sulfide veins from the Denison deposit eight crystals of sperrylite were observed, between 3 and 20 μm in size and located along silicate–silicate (75 %) and silicate–sulfide (25 %) interfaces. Sperrylite crystals occur individually, although proximal hessite and lesser AuAg alloy were observed. Analyses produced inconsistent trace concentrations of Sb and S, with only Fe occurring consistently up to concentrations of 0.49 wt %. The sperrylite analyses gave an average composition of Pt$_{1.02}$As$_{1.98}$. 
Figure 4.5. (A) Michenerite compositional ternary. Grey shaded area (B)–219 analyses from North Range prospects. Checkered area (C)–84 analyses from Denison prospect. All values in atomic percent.
Table 4.6. Representative Michenerite analyses (wt %) from sulfide veins (1 and 2 Levack North, 3 and 4 Wisner, 5 and 6 Capre and 17 and 18 Denison), IRV (7 and 8 Levack North, 9 and 10 Wisner and 11 and 12 Capre), QCS (13 and 14 Levack North, 15 and 16 Capre and 19 and 20 Denison) and stockwork (21 and 22 Denison) mineralization. Compositions are calculated based on apfu.
In contrast to sperrylite crystals from stockwork and QCS mineralization, the three 1 to 3 μm crystals seen within sulfide vein samples at Denison are all hosted within pyrrhotite. Average Fe, Te and Sb concentrations fell below 0.5 wt %, with one crystal displaying 1.77 wt % S, with no substantial corresponding increase in Fe. The average composition of sperrylite in sulfide veins at Denison is \( \text{Pt}_{1.00} \left( \text{As}_{1.98} \text{Sb}_{0.01} \text{Te}_{0.01} \right)_{2.00} \).

A single 2 μm sperrylite crystal from the McKim property was identified within sulfide vein pyrrhotite and proximal to abundant 1 to 20 μm crystals of hessite and bismuthinite. Analysis of this grain identified minor concentrations of Fe (0.50 wt %) and Sb (0.20 wt %). Although it is uncertain if these are representative, the crystal yielded a composition of \( \text{Pt}_{1.00} \left( \text{As}_{1.99} \text{Sb}_{0.01} \right)_{2.00} \).

### 4.4.7 Previously Undescribed PGMs

Two previously undescribed PGMs were analyzed in gersdorffite-bearing stockwork samples from the Denison property. WDS analysis produced two distinct formulae approaching \((\text{Pd}, \text{Ag}, \text{Ni, Pt})_3(\text{Sb, Bi, Te, As})_2\), termed UNK1, and \((\text{Pd,Ag})_3(\text{Bi, As, Te})_4\), termed UNK2. Analyses can be seen in Table 4.9.

Four crystals of UNK1 were identified, three hosted within gersdorffite and one along a gersdorffite–actinolite contact. UNK1 has a Pd concentration of 40.53 to 44.02 wt % (avg. 42.60 wt %), in keeping with the upper limits of kotulskite and sudburyite (Cabri, 2002), however the
50:50 Pd + Ni + Pt + Ag : Bi + Te + Sb + As ratio displayed by the PdBi–PdTe–PdSb series is not reflected by the 60:40 ratio of UNK1 (based on atomic percent). The 3 gersdorffite-hosted crystals of UNK1 occur independently, as crystals from 4 to 10 μm in size, one of which appears along a gersdorffite–silicate contact. Assuming five atoms per formula unit, UNK1 has an average composition of \((Pd_{2.53}Ag_{0.44}Fe_{0.02}Pt_{0.01})_{3.00}(Sb_{0.93}Bi_{0.79}Te_{0.22}As_{0.06}Sn_{0.01})_{2.00}\), with measured As concentrations within the gersdorffite–silicate hosted crystal nearly sixty times lower than the gersdorffite hosted crystals.

Figure 4.6. Sperrylite partially enclosing groundmass silicates and disseminated sulfide. Spy = sperrylite, Po = pyrrhotite, Pn = pentlandite, Ccp = chalcopyrite, Py = pyrite, Amp = amphibole, Chl = Chlorite, Crb = Carbonate, Czo = Clinozoisite and Qtz = quartz.

The two crystals of UNK2 hosted individually within gersdorffite measure 3 and 5 μm. They are associated with no other PGM phases and have a Pd + Ni + Pt + Ag : Bi + Te + Sb + As ratio of 43:57 (based on atomic percent). Assuming 7 atoms per formula unit, the analyses can be recast to an average composition of \((Pd_{2.56}Ag_{0.42}Fe_{0.01})_{3.00}(Bi_{3.81}As_{0.13}Te_{0.06})_{4.00}\).
Around one third of the detected As within the gersdorffite hosted crystals can be accounted for through X-ray contamination from the host phase assuming a 1:1 ratio of Ni and As, in keeping with stoichiometry, with the required amount of As removed before the composition is calculated.

4.5 Polyphase Aggregates and Ag-Micro-veinlets

Observations from both the North and South Ranges revealed the presence of some aggregates containing three or more discrete precious metal and/or Bi-chalcogenide phases. These aggregates differ from those PGMs more commonly observed within low-sulfide mineralization, which typically occur individual crystals or aggregates of no more than two phases, often with sharp contacts (Figure 4.2B).

Polyphase aggregates range from 15 to 80 μm and were observed within sulfide veins from the Levack North property, IRV mineralization from the Wisner property (see Figures. 4.8 and 4.9) and stockwork mineralization from the Denison property (Figures 4.12 and 4.13). Examples within sulfide veins from the Capre property comprise Ag-bearing micro-veinlets (Figure 4.10) and crystals at triple junctions (Figure 4.11), with compositions approaching hessite, although contamination from surrounding phases made a definitive classification impossible. Aggregates from both North Range properties were located within sulfide, whilst those from Denison were located along silicate contacts. All examples displayed a cuspatte form reminiscent of trapped sulfide melt pockets commonly observed in silicate rocks. Examples from the North Range are dominated by Ag minerals with lesser michenerite and bismuth–telluride phases. The assemblage is repeated on the South Range, although there the observed aggregates are dominated by Pd minerals, particularly michenerite, Sb-sobolevskite and lesser froodite along with tsumoite and bismuthinite, whereas Ag minerals were a minor component. The Ag-micro-veinlets from the Capre property are located along sulfide–sulfide and sulfide–silicate contacts and are ≤ 1 μm in width, with the longest example extending over 250 μm.
Table 4.8. Representative sperrylite analyses (wt %) from IRV (1 and 2 Levack North, 3 Wisner, 4 and 5 Capre), QCS (6 and 7 Capre, 11 and 12 Denison), sulfide vein (8 and 9 Denison, 10 McKim) and stockwork (13 and 14 Denison). Compositions calculated based on 3 apfu.

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Table 4.9. Analyses of unknown PGMs (wt %) from the Denison hosted by gersdorffite (excluding #4, hosted interstitial to silicates). Compositions are calculated based on 5 \( \text{apfu} \) (1 to 4) and 7 \( \text{apfu} \) (5 and 6). Ni, Fe and As concentrations are not considered to have resulted from gersdorffite contamination as S concentrations are not consistent with such an assumption.

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Figure 4.7. IRV selvage composed of actinolite (Act) and epidote (Ep) with interstitial chalcopyrite (Ccp). Actinolite and epidote crystals host abundant michenerite and a single crystal of moncheite (Mon) (A). IRV margin displaying a single froodite (Fdt) crystal, located at the sulfide-silicate boundary. Note: heterogeneities displayed by the froodite crystal are the result of surface topography (B). IRV alteration halo comprising an albite (Ab) + oligoclase (Olg) + epidote (ep) assemblage with interstitial millerite (Mi) and AuAg alloy (AuAg 1: 62.05wt % Au; AuAg 2: 84.92wt % Au, both analyses by EDS) (C). Michenerite (Mch) and froodite (Fdt) bearing vein crosscutting gersdorffite (Gdf) crystal, Denison (D). Froodite (Fdt) + michenerite (Mch) aggregate and Sb-Sobolevskite hosted within gersdorffite (Gdf), Denison (E). Actinolite (Act) dominated groundmass with disseminated pentlandite (Pn), with hessite (Hss) and michenerite (Mch), partially enclosing a single pentlandite crystal (F).
Figure 4.8. Hessite (Hss), volynskite (Vln) and michenerite (Mch) polyphase aggregate hosted within sulfide vein chalcopyrite (Ccp), Levack North property.

Figure 4.9. Hessite (Hss), volynskite (Vln) and michenerite (Mch) polyphase aggregate hosted within irregular veinlet chalcopyrite (Ccp), Wisner property.
Figure 4.10. Ag-micro-veinlet within sulfide vein chalcopyrite, Capre property.

Figure 4.11. Hessite (Hss) rimming disseminated chalcopyrite (Ccp) within the actinolite (Act) and epidote (Ep) alteration selvage of a sulfide vein halo, Capre property.
Figure 4.12. Polyphase aggregate composed of bismuthinite (Bs), michenerite (Mch), froodite (Fdt), Sb-Sobolevskite (Sb-Sbv), and an Unknown Ag, Bi, S, Se phase, with proximal tellurobismuthite (Tbs), Denison property.

Figure 4.13. Polyphase aggregate composed of Sb-sobolevskite (Sb-Sbv), michenerite (Mch), froodite (Fdt) and possible Makovickyite (Mkv), hosted interstitial to actinolite and quartz and proximal to disseminated chalcopyrite (Ccp) with froodite.
Table 4.10. Average PGM analyses by property and mineralizing style. Sulf = PGM enclosed within sulfide, Sulf:Sil = PGM located along sulfide-silicate contact and Sil = PGM enclosed or interstitial to silicates. SV = sulfide vein, IRV = irregular veinlet, QCS = Quartz + carbonate + sulfide vein and STK = stockwork mineralization. MON = moncheite, MER = merenskyite, KOT = kotulskite, SBV = sobolevskite, SUD = sudburyite, MCH = mchenerite, FDT = froodite and SP = sperrylite.

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<th>Size Range (μm)</th>
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*Contains one or more analysis recalculated due to questionable contamination.

All sizes are in μm and are based on an approximate 10 μm scale bar

Pd and PGM bearing phases are those containing ≥ 0.5 wt%, percentages are calculated for mineralizing styles, by property.
4.6 Accessory Phases

4.6.1 Argentopentlandite (Ag[Fe,Ni]₈S₈)

Sixteen isolated argentopentlandite crystals were identified within three samples of stockwork mineralization from the Denison property. They range from 10 to 5000 μm, occurring interstitial to silicates (n = 7) or as aggregates with pyrrhotite, chalcopyrite and pentlandite (n = 9). Argentopentlandite crystals were not observed to contain any PGMs, although in three cases hessite occurred nearby. Crystals are mostly fresh, although three examples are partially replaced by fine grained pyrite and elongate marcasite. The Ag content of the argentopentlandite crystals varies between 9.78 and 14.32 wt %, with Ni from 22.36 to 25.76 wt %, and Fe is between 31.06 and 34.68 wt %, producing an average argentopentlandite composition of Ag₁₀.₈₁(Ni₃.₃₃Fe₄.₇₈)₈.₁₁S₈.₀₈ (assuming 17 apfu). The lower range of Ag contents reported here is below that of some published data for natural occurrences, (Vuorelainen et al., 1972; Cabri and Laflamme, 1976; Kontny et al., 1994) but falls within the range of experimental values (Mandzuik and Scott, 1977). Mandzuik and Scott (1977) also described high Ag argentopentlandite from the Kamaishi mine, Japan, resulting from Ag-Ni substitution. Correlation coefficients for Ag within argentopentlandite from Denison indicate that it does not correlate to any other elements, with the strongest relationship being a moderate anticorrelation to Ni (R = -0.32).

4.6.2 Tetradymite (Bi₂Te₂S)

Eight tetradymite crystals were identified within samples from the Wisner property, with a further seven from Capre. Most tetradymite at Wisner and Capre occurs in sulfide veins, although two crystals were identified within IRV and QCS mineralization from the Wisner and Capre properties respectively. The tetradymite observed in sulfide veins and irregular veinlets from Wisner are between 5 and 20 μm and are enclosed in chalcopyrite. Examples from sulfide veins and QCS mineralization bear a close spatial relationship with merenskyite, michenerite and hessite, and both IRV hosted crystals occur as aggregates with the latter two precious metal minerals. Sulfide vein and IRV-hosted tetradymite from the Wisner property contains up to 1.95 wt % Fe, 1.5 wt % Ag and 1.73 wt % Se (Table 4.11). Increased concentrations of Fe and Ag appear to result from substitution with Bi, with correlations of R = -0.84 and R = -0.62 respectively in the sulfide vein hosted samples. Selenium displays no
significant correlation with S, but is positively correlated to Bi ($R = 0.62$) and is anticorrelated with Fe ($R = -0.63$) and Te ($R = -0.53$). Sulfide vein crystals yielded an average composition of $(\text{Bi}_{1.82}\text{Fe}_{0.17}\text{Ag}_{0.07})_{2.06}\text{Te}_{1.98}(\text{S}_{0.89}\text{Se}_{0.07})_{0.96}$ from Wisner and $(\text{Bi}_{1.97}\text{Te}_{1.92})_{1.11}$ from Capre, assuming $5 \text{ apfu}$. The two IRV hosted crystals lack the high Ag contents of the tetradymite hosted by sulfide veins, with an average composition of $(\text{Bi}_{1.98}\text{Fe}_{0.03})_{2.01}\text{Te}_{1.89}(\text{S}_{1.03}\text{Se}_{0.08})_{1.11}$. The two $5 \mu m$ crystals of tetradymite identified within QCS mineralization from Capre are located within millerite. They display no minor constituents except $1.36 \text{ wt }% \text{ Ni}$ in one of the analyses, with no corresponding increase in S content noted. The average measured composition of QCS-hosted tetradymite is $(\text{Bi}_{1.91}\text{Te}_{2.04})_{1.11}$.

The S rich nature of the analyses accords with previously published data (Cook et al., 2007 references and data therein); the compositions determined in this study are more in keeping with a stoichiometry of Bi$_2$Te$_2$S (Bayliss, 1991) than the proposed Bi$_{14}$Te$_{13}$S$_8$ of Pauling (1975).

### 4.6.3 Tellurobismuthite (Bi$_2$Te$_3$)

Two crystals of tellurobismuthite were identified within sulfide vein chalcopyrite from the Wisner property. The crystals measure 3 to 5 $\mu m$, one occurring individually and the second occurring within a hessite–tellurobismuthite–bismuthinite aggregate. Microprobe analysis indicated trace concentrations of Se from below detection limit to $0.70 \text{ wt }%$, Ag from $0.21$ to $0.69 \text{ wt }%$ and Pb from $0.38$ to $0.68 \text{ wt }%$, all consistent with published data (Cook et al., 2007, data therein; Ciobanu et al., 2009; Voicu et al., 1999). The average composition is $(\text{Bi}_{1.97}\text{Ag}_{0.03}\text{Pb}_{0.02})_{2.02}(\text{Te}_{2.94}\text{Se}_{0.04})_{2.98}$.

### 4.6.4 Hessite (Ag$_2$Te)

Hessite was observed to occur within all mineralizing styles across all properties and is particularly abundant at the Wisner and Denison properties. Hessite on the North Range ranges from 2 to $50 \mu m$ in size, occurring discretely and as aggregates with tetradymite, merenskyite, moncheite and lesser bohdanowiczite and volynskite (both of the latter identified by EDS). Eighty-six percent of North Range hessite grains are hosted within sulfide, regardless of mineralizing style. In contrast, the distribution of hessite on the South Range is
primarily controlled by mineralizing style. At Denison 94 % of hessite grains observed are located interstitial to silicates, a result of the dominance of disseminated and stockwork mineralization, whereas at McKim 91 % of hessite crystals are located within sulfide veins. Occurrences of hessite on the South Range range from 1 to 125 μm, both as individual crystals and in aggregates with other Ag-bearing phases including bohdanowiczite, volynskite and possible makovickyite (all identified by EDS). Where enclosed by sulfide, hessite from the Denison property is commonly located within gersdorffite.

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Table 4.11. Representative tetradymite analyses (wt %) from sulfide vein (1 and 2 Wisner, 3 and 4 Capre, IRV (5 and 6 Wisner) and QCS (7 and 8 Capre) mineralization. Compositions are calculated based on 5 apfu.

Microanalyses of hessite from the North Range properties and Denison are free of minor elements, with average compositions from $\text{Ag}_{1.97-2.00}\text{Te}_{1.00-1.03}$. Slight apparent deviations from stoichiometry probably result from minor contamination of the X-ray signal by activation of the host phase surrounding small hessite crystals. All analyses from the McKim property failed to produce suitable totals.
4.6.5 Au-Ag Alloy

Crystals of Au-Ag alloy were observed in samples from all North Range properties as well as the Denison property. Analysis by WDS typically failed to produce analytical totals within the 100 ± 3 % range, however crystals were consistently observed both optically and using BSE-SEM imaging (Figures 4.2D and 4.7C). Crystals were observed within sulfide veins, IRV, QCS and stockwork mineralization. A total of four valid analyses were produced, two from the Capre property and two from the Denison property. Both alloy grains from Capre are about 5 µm in size, occurring along sulfide–silicate boundaries, within IRV style mineralization. They both contain 0.88 wt % Bi, giving an average composition of \((\text{Au}_{0.84}\text{Bi}_{0.01})_{0.85}\text{Ag}_{0.15}\). The two QCS-hosted alloy grains found at Denison have similar Bi contents, with one crystal also containing 1.41 wt % Se (c.f., Farrow and Watkinson, 1997). The average composition of alloy grains analyzed at Denison is \((\text{Au}_{0.71}\text{Bi}_{0.01})_{0.72}(\text{Ag}_{0.27}\text{Se}_{0.02})_{0.29}\).

4.6.6 Selenian Pilsenite (\(\text{Bi}_4[\text{Te}, \text{S}, \text{Se}]_3\))

Three crystals of Se-pilsenite were identified within two sulfide veins from the McKim property, hosted along pyrrhotite, pentlandite and chalcopyrite-silicate boundaries and ranging from 3 to 5 µm in size. All analyses indicated concentrations of up to 0.16 wt % Sb, 0.48 wt % As and 0.09 wt % S (Table 4.12). The distinction between Se-pilsenite and Se-joséite was made on the S concentration, which ranges from 0.43 to 3.02 wt % in joséite (Gu et al., 2001; Cook et al., 2007) (Figure 4.14). The extremely limited present dataset provides contradictory correlations; with both As and Se showing negative correlations with Bi and Te. Although these apparent substitutions are questionable, it is clear that As-Se substitution is coupled (R = 0.57). Analyses yielded an average composition of \(\text{Bi}_{3.98}(\text{Te}_{2.45}\text{Se}_{0.48}\text{As}_{0.05}\text{S}_{0.03}\text{Sb}_{0.01})_{3.02}\).
Figure 4.14. Compositional variation in the Bi$_4$S$_3$–Bi$_4$Te$_3$–Bi$_4$Se$_3$ system. 7 joséite-B analyses from the McKim prospect overlain of Joséite-B compositional field (Cook et al., 2007). Values in atomic percent. Grey Circles–Joséite-B analyses, Bi-chalcogenide veinlets; McKim (n = 7). White Circles – Selenian pilsenite analysis, within sulfide veins; McKim (n = 3). Black squares – Published selenian joséite-B analyses (Gu et al., 2001; Cook et al., 2007).
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Table 4.12. Representative analyses (wt %) of tellurobismuthite (1 to 3) and selenian pilsenite (4 to 6) from Wisner (1 and 2) and McKim (3 to 6), with bismuthinite (7 to 9), parkerite (10 to 12), josèite-B (13 to 15), tsumoite (16) and sulphotsumoite (17) from Bi-chalcogenide veinlets, McKim.
4.7 Sulfarsenides and Arsenides

In the present study, sulfarsenides and arsenides were only observed within low-sulfide mineralization from the Denison property, within samples from the 9400 and 101 Zone. The presence of sulfarsenides and arsenides (i.e. gersdorffite–cobaltite and nickeline) within South Range ores is in contrast to the typically As-mineral free assemblages of North Range mineralization (Ames and Farrow, 2007). The source of the As remains uncertain. It may have been scavenged from As-bearing metasedimentary units which are common on the South Range, either through direct assimilation or via interactions with hydrothermal fluids, or through the early sequestering of As into the sulfide liquid leading to its accumulation within embayments at depth. This stratigraphic compositional control has been suggested to reflect a deeper erosional level along the steeply dipping South Range (Carter et al., 2001), however the similar distance from mineralization to the lower contact of the SIC on both North and South Ranges makes this interpretation rather questionable.

At Denison gersdorffite and lesser nickeline were observed within veinlet and stockwork mineralization, the former displaying particularly high modal abundances when hosted by metasedimentary or metavolcanic granofels (Figure 4.15A). In all instances gersdorffite dominates the As-bearing phases present and displays extensive Ni–Co–Fe solid solution (Figure 4.15B), with compositions from \((\text{Ni}_{0.95}\text{Co}_{0.00}\text{Fe}_{0.04})\text{As}_{0.95}\text{S}_{1.05}\) to \((\text{Ni}_{0.42}\text{Co}_{0.33}\text{Fe}_{0.25})\text{As}_{0.93}\text{S}_{1.07}\). The substitution of Fe and Co into the gersdorffite structure is likely coupled, Co and Fe both displaying a strong correlation \((R = 0.86)\). The substitution occurs at the expense of Ni, which shows strong negative correlations to both Co and Fe \((R = \geq 0.89)\). Whereas previous studies identified concentric sulfarsenide zonation within sulfide hosted crystals, the gersdorffite crystals analyzed in the present work display extremely irregular marginal bands and heterogeneous zonation. Marginal regions typically display an increase in the Co content and comparatively Ni rich cores (Figure 4.15B), in keeping with observations from the Copper Cliff North mine (Rickard and Watkinson, 2001; Szentpéteri et al., 2002), whereas heterogeneous crystals display interconnecting high Co-gersdorffite domains separating "islands" of low Co-gersdorffite (Figure 4.15C).

Gersdorffite is the only sulfide or sulfarsenide commonly observed to host PGM within typically sulfide poor stockwork mineralization. It commonly displays inclusions of Sb-sobolevskite, Sb-michenerite and froodite, with two unknown PGMs, typically occurring
within fractures and cleavage planes hosted by both high and low Co-gersdorffite (Figure 4.7D and 4.7E). A similar preference of gersdorffite for hosting antimonide phases was noted by Cabri and Laflamme (1976). It must however be noted that assay data shows no correlation between precious metals and As in the whole rock, suggesting that any correlation, if present, is masked by other PGM-bearing As free samples. The presence of gersdorffite is however thought to be a positive indicator for possibly elevated precious metal contents.

Nickeline displays a strong association with gersdorffite, with crystals occurring as subangular to rounded inclusions within gersdorffite or as discrete crystals 25 to 500 μm in size. The discrete grains of nickeline commonly display rims and isolated inclusions of gersdorffite, perhaps a result of alteration. Similar textures were noted by Fanlo et al. (2006) and attributed to alteration of gersdorffite by a late high \( f_2S_2 \) fluid. The presence of irregular elongate and globular inclusions of chalcopyrite within several nickeline crystals was noted, and are reminiscent of quenching or symplectite textures (Figure 4.15D).

Figure 4.15. A: Gersdorffite (Gdf) bearing pyrrhotite (Po) + chalcopyrite (Ccp) veinlet hosted by fine granoblastic granofels, displaying a well-developed chlorite selvage. B: BSE image of heterogeneous gersdorffite crystal, with EDS determined Ni concentrations. The crystal encloses minor tsumoite (Tsu) with galena (Gn) hosted within the enclosing silicates. C: Gersdorffite after nickeline (Nc); note the darker gersdorffite associated with decreasing Ni content. D: Nickeline crystal with an incomplete gersdorffite rim. Nickeline encloses irregular chalcopyrite inclusions reminiscent of quench textures or symplectites.
Accessory gersdorffite was also identified within a single sulfide vein from the Wisner property, located proximal to the alteration selvage. These 5 to 50 μm crystals present a euhedral habit and are all hosted by chalcopyrite. Analysis by EMP produced consistent Cu concentrations of up to 4.21 wt %, likely due to the excitation of the host chalcopyrite. The presence of Ag was also detected in 38 % of points with concentrations of up to 0.06 wt %. Larger crystals (> 10 μm) produced an average composition of (Ni₉₀₉₀Co₀₆₆Fe₀₄₄)₁₄₀₈₅As₀₉₈S₁₄₅, with margins displaying an increase in Co and Fe content, yielding an average composition of (Ni₇₉₇₉Co₀₉₉Fe₀₉₉)₀₉₉₉₉As₀₉₉₉₉S₁₄₅. This contrasts with the average core compositions of (Ni₉₄₈₄Co₀₆₄Fe₀₄₄)₁₄₀₈₅As₁₄₀₈₅S₁₄₅. Crystals of ≤ 10 μm displayed no compositional heterogeneities, with an intermediate composition of (Ni₈₈₈₈Co₀₈₈Fe₀₄₄)₁₄₀₈₅As₀₉₈S₁₄₅.

4.8 Bi-Chalcogenide Veinlets

Observations of chalcopyrite-rich sulfide veins from the McKim property revealed the presence of abundant sub-mm scale Bi-chalcogenide veinlets crosscutting sulfide veins and their alteration selvages within host greenschist and metabreccia. The veinlets comprise abundant anhedral crystals, ranging from 5 to 50 μm in size, displaying white, white-blue, white-grey and white-yellow colors in plane polarized light (Figure 4.2E). WDS analysis distinguished the presence of bismuthinite, parkerite, joséite-B, tsumoite and sulphotsumoite within the veinlets, with the sulfide veins proximal to the Bi-chalcogenide veinlets containing abundant bismuthinite, hessite and lesser Se-parkerite. Numerous crystals of bismutohauchecornite were also noted within the disseminated sulfides along the vein margin, however they displayed no preference for sulfides of Bi-chalcogenide veinlets (Figure 4.2E). No PGMs were identified within these veinlets. The compositions of several grains of bismuthinite, parkerite, and joséite are shown in Table 4.12, along with single analyses of tsumoite and sulphotsumoite. The ten grains of white-yellow tarnished bismuthinite analyzed gave an average composition of (Bi₁₀₋₂Fe₀₄₋₅Ni₀₁₋₀S₃₋₁Sₑ₀₅₋₁)₁₋₀₋₉₋₀₃, assuming 5 apfu. Trace element concentrations range from below detection to up to 1.16 wt % Fe, 0.76 wt % Ni and 0.20 wt % Se, with Fe displaying a strong negative correlation with Bi (R = -0.53). The composition is in keeping with Lin et al. (1996), who found near stoichiometric Bi₂S₃ to be the only stable Bi-phase within the Bi-S system.
Five cream-bronze colored parkerite grains were analyzed to give an average composition of Ni$_{3.03}$Bi$_{1.92}$(S$_{2.04}$Se$_{0.01}$)$_{2.05}$. Selenium is the only trace element present, with concentrations up to 0.14 wt %. Selenium displays a strong correlation with S ($R = 0.61$), however unlike Michener and Peacock (1943) who analyzed a parkerite concentrate by the dithizone method, calibrated to Ni and Bi from a synthetic sample, no trace Pb and associated Bi-Pb substitution was observed, suggesting that its occurrence within that study may have reflected contamination from or re-equilibration with galena, with the former issue arising due to its similar specific gravity to parkerite.

Five white grains of joséite-B were analyzed. Cook et al. (2007) and references therein, illustrated the extensive compositional variation of joséite-B, with veinlet hosted crystals showing a wide variation in Bi and Te concentrations (Figure 4.14). Here the composition of joséite-B was found to contain traces of up to 0.16 wt % As and 0.75 wt % Se, which are both positively correlated with S and negatively correlated with Te. The average composition of joséite-B is Bi$_{3.87}$(Te$_{1.77}$Se$_{0.08}$As$_{0.02}$)$_{1.87}$S$_{1.21}$.

Both tsumoite and sulphotsumoite contain traces of Pb, Sb, As and Se (Table 4.12), providing compositions of (Bi$_{1.00}$Pb$_{0.02}$Sb$_{0.01}$)$_{1.03}$(Te$_{0.93}$As$_{0.02}$Se$_{0.02}$)$_{0.97}$ and (Bi$_{3.05}$Pb$_{0.02}$Sb$_{0.01}$)$_{3.08}$(Te$_{1.98}$Se$_{0.06}$As$_{0.03}$)$_{2.07}$S$_{0.85}$ respectively. Similar Bi-Se-Te assemblages were noted in footwall samples from the Creighton mine, with Bi-chalcogenides exploiting parting along a biotite cleavage in one instance (Dare et al., 2010a).

4.9 Discussion

The presence of platinum group minerals within the analyzed low-sulfide material offers an opportunity to study the mineralizing process and sheds light on subsequent thermal events. The compositions of PGMs across a range of different mineralizing process i.e. magmatic, hydrothermal and metamorphic remobilization, in some instances display a large compositional range e.g., the kotulskite–sobolevskite–sudburyite system, or compositions that vary little from stoichiometry e.g. sperrylite. It is for this reason that a separation of PGMs based on compositions from different mineralizing processes is impossible, and as such a classification must be based on associated textural observations and phase associations.
4.9.1 Indications of the Mineralizing Process

4.9.1.1 Sulfide Veins, IRV mineralization and Veinlets

The majority of magmatic PGM deposits typically occur within igneous bodies which present silicate assemblages in keeping with the temperature of the parental melt which existed at equilibrium with sulfide liquid. Such deposits are typically associated with ultramafic to mafic igneous rocks, within which Fe–Ni–Cu–S melts could have remained liquid, i.e. above the pyrrhotite-rich mss solidus at 1192 °C (Craig and Kullerud, 1969). Such assemblages are often host to a range of PGM phases, including a number of higher temperature minerals, specifically IPGE alloys and sulfides e.g. laurite, many of which are stable at temperatures in excess of 1000 °C (Makovicky and Karup-Møller, 1999; Karup-Møller and Makovicky, 1999; 2002; Brenan and Andrews, 2001), although Rh-S phase relations are unknown above 900°C (Makovicky et al., 2002). It should however be noted that the phase relations of the most common IPGE sulfarsenide phases i.e. irarsite, hollingworthite and ruarsite (all of which have been identified within SIC contact deposits) remain uncertain, although their occurrence partially and fully enclosed within chromite from ophiolites and ultramafic complexes would suggest crystallization at elevated temperatures (Talkington and Lipin, 1986; Tarkian and Prichard, 1987; Merkle, 1992; Prichard et al., 2001). In the case of systems comprising abundant sulfide melt such as Sudbury, IPGE phases are associated with the mss cumulate contact deposits, with IPGE sulfarsenides occasionally acting as nucleation points for gersdorffite-colbaltite (e.g., Dare et al., 2010a). Such PGMs are typically enclosed or along the margins of sulfide crystals, where the compositions of sulfide accumulations in the enclosing mafic sublayer and overlying norite are consistent with mss crystallization. In the case of footwall mineralization the sharp-walled vein assemblage appears consistent with crystallization from combinations of mss, iss and heazlewoodite solid-solution (Mungall, 2007), suggesting a sulfide liquid of around 850 °C (Craig and Kullerud, 1969). These temperatures are inconsistent with derivation in situ at the upper albite-epidote to lower hornblende hornfels facies of the host Sudbury breccia and indicate that any sulfide liquid was sourced from the SIC. A PPGE enriched Cu–Ni residual sulfide liquid that forms sulfide vein and IRV mineralization would therefore be expected to crystallize a PGM assemblage with upper limits beyond that of alternative mineralizing processes such as anatexis in the thermal aureole of the SIC or deposition from fluids in that aureole. Such high temperature phases are observed, with Pt from North Range sulfide veins commonly hosted by moncheite, stable
below 920 °C (Helmy et al., 2007), whilst sperrylite, stable below 1369 °C (Skinner et al., 1976; Makovicky et al., 1992, Okamoto, 1990), dominates on the South Range.

The hydrous selvage displayed by sulfide veins and IRV mineralization appears contradictory to a purely magmatic origin, with fluid inclusion data indicating formation in the presence of saline hydrothermal liquids between 300 and 500 °C and with a broad range of salinities of up to ~ 45 % NaCl equivalent. It is clear that hydrothermal circulation must have been occurring within the footwall, both pre-, syn- and post-SIC emplacement. The remobilization of base and precious metals by hydrothermal fluids has been proposed as a possible mechanism of sharp-walled vein genesis (Farrow and Watkinson, 1992; Farrow et al., 1994; Watkinson, 1999; Molnár et al., 2001). However the majority of veins and IRV samples contain little to no soluble gangue minerals (i.e. quartz and carbonate), although a substantial quantity might be expected, given that a large volume of base-metal bearing hydrothermal fluids would have been required to produce the meter scale sharp-walled veins observed in footwall deposits such as Strathcona and McCreedy West. On the other hand, the presence of a hydrous alteration selvage does indicate that alteration by hydrothermal fluids accompanied the emplacement of the sharp-walled veins, or that such mineralization exploited conduits that had undergone earlier hydrous alteration. Experimental work has indicated the capacity of sulfide liquids to transport volatile phases i.e. H₂O and halogens (Mungall and Brenan, 2003; Wykes and Mavrogenes, 2005), which could form discrete saline liquids and halide melts (Hanley et al., 2005b) during late-stage fractionation of a sulfide liquid. The release of such liquids from cooling magmatic sulfide bodies may be sufficient to account for the formation of the narrow hydrous alteration selvages observed and perhaps also for any halogen-enriched haloes associated with footwall mineralization. In contrast, very narrow sulfide veinlets, i.e. IRV mineralization, display alteration selvages on a par with, and generally wider than those of sharp-walled sulfide veins. This observation can be accounted for either by proposing that IRV mineralization represents the last stages of sulfide liquid fractionation, with a high volatile content reflecting its more evolved melt composition, or that the hydrous selvages are not connected to mineralization. The former model is consistent with geochemical observations of IRV mineralization which displays tenors of incompatible elements (Pt, Pd, Au, Ag, As, Sb, Te, Pb and Bi) above those of any other North Range mineralizing style (see Chapter 5). It is also not inconceivable that the host lithologies, particularly Sudbury breccia underwent some degree of pre-mineralization alteration before the movement of Cu–Ni–PPGE-rich sulfide liquids into the footwall environment along the same conduits. The
identification of sulfide-free carbonate–actinolite–epidote–chlorite veins (Molnár et al., 2001) and amphibole dominated veins (Tuba et al., 2010) indicates that such a process is at least feasible. Exploitation of such veins by the later injection sulfide melt into the same fractures may have masked the existence of pre-existing gangue phases within the veins, which may also simply not have been present in significant quantities. The Ni-enriched compositions of ferromagnesian minerals (Hanley and Bray, 2010; see Chapter 3) within the alteration selvage would therefore have to be explained through either the re-equilibration of the silicates with the sulfide liquid or through the presence of Ni within the hydrothermal fluid, possible sourced from proximal pre-existing footwall sulfides likely pyrite or interactions with massive sulfides related to the SIC. The disparity between the alteration selvage thickness displayed by sulfide vein and IRV mineralization is of interest if it is assumed that any pre-mineralization saline fluid passing through the footwall would produce a uniform alteration selvage thickness. Three possible explanations may explain this difference, 1) the thickness of pre-mineralization alteration was not uniform, 2) the passage of a sulfide melt may have stripped the vein margins of some alteration silicates and 3) that alteration silicates were replaced by sulfide. 1) Variation in the thickness of the alteration selvage may well result from differences in the permeability of the fracture, or the duration of the fluid flow. Conduits with a high permeability will encourage high rates of fluid flow over a longer period than those which a lower permeability. Such 'paths of least resistance' will likely be surrounded by a thicker alteration selvage and will act as preferential conduits for low-volume strongly fractionated sulfide liquids like those that deposited IRV mineralization. In contrast the conduits with a lower permeability will have a lower rate of fluid flow resulting in a thinner alteration selvage. Mineralization moving along such conduits would require a significant fluid pressure to ensure that conduit remained open. The low-volume sulfide melt from which IRV mineralization was deposited would likely not possess sufficient fluid pressure to move along less permeable conduits, however the greater volumes of sulfide liquid associated with sulfide vein formation may well have been sufficient to open the vein further allowing liquids to migrate along it with ease. 2) It is not uncommon for North Range sulfide veins to contain numerous minor wall-rock inclusions typically displaying a ferromagnesian silicate assemblage (epidote + chlorite + actinolite) similar to the alteration selvage, along with uniform polygonal quartz. Such inclusions may well simply represent wall-rock material that has recrystallized due to heating from the vein, but they may also represent fragments of the alteration selvage pulled from the vein margin during passage of the sulfide liquid. The erosion of the vein margin by this process may have stripped off sufficient material to
noticeably reduce the size of the alteration selvage. Such losses would not have occurred during the deposition of IRV mineralization as it formed from a much lower volume sulfide melt with insufficient energy to detach material from the margin. 3) The alteration of sulfide by silicates is well established (Li et al., 2004, 2007), however little evidence of this process was observed during this study. In contrast observations of optically homogeneous epidote being replaced by chalcopyrite along the margins of sulfide veins were observed from the Levack North and Capre properties. The loss of epidote, which constitutes the largest portion of sulfide vein and IRV alteration selvages may have not only reduced the size of the alteration selvage present but also weakened the margin thereby allow fragments to fall into the sulfide liquid further reducing the selvage size.

Figure 4.16. Reflected light image (ppl) of epidote (ep) being replaced by chalcopyrite (ccp) along the margin of a sulfide vein from the Capre property. Qtz = quartz.

In the case of South Range veinlets the alteration selvage displays an assemblage consistent with the metamorphic grade of the host rock, although a coarsening of crystals is observed. The lack of a well-defined alteration assemblage is interpreted as having been caused by metamorphic processes, with the selvage recrystallizing until an assemblage in equilibrium with the host rock and the metamorphic conditions was achieved and the primary signature of local metal or halogen enrichment was erased.
4.9.1.2 Inclusion-bearing Sulfide Veins

Evidence for movement of sulfide along shear zones within the South Range footwall is not uncommon, with examples noted from the Garson and Thayer-Lindsley Mines (Lefort et al., 2011; Binney et al., 1994; Bailey et al., 2006). All South Range deposits have been affected by varying degrees of deformation, often with associated indicators of fluid migration (Bailey et al., 2006). Such ores are typically limited to a defined and elongate zone, oriented along major structural features, and the mineralization commonly displays highly deformed wall rock clasts. Clast bearing sulfide from the South Range is typically split into inclusion-bearing or contorted schist–inclusion sulfide. The latter was defined by Hoffman et al. (1979) as containing twisted fragments of schist within massive sulfide, whereas the former was simply defined as bearing occasional rock fragments. The material sampled from the Denison and McKim properties for the present study does not contain deformed schistose clasts, with inclusions typically appearing homogeneous, in contrast to the often moderately to strongly foliated host metabasalts. The lack of fabric is interpreted as having resulted from recrystallization of the clasts during metamorphism and the resulting interaction between the sulfide and silicates, a process similar to that occurring along the margins of the sulfide vein. As such, wall rock clast–bearing sulfide from the two South Range properties was classified here as 'inclusion-bearing'.

The mineralized sheet-like "panels" bearing low-sulfide mineralization situated behind the three contact orebodies of the Crean Hill mine are likely shear-zones. These zones are hosted within metabasalts which display a moderate to strong pervasive fabric and likely represent tectonically reactivated terrace forming fault sets, within whose depressions the contact orebodies sit. The inclusion-bearing sulfide veins of the Denison property are modally similar to contact ores, being dominated by pyrrhotite with lesser pentlandite and chalcopyrite. These veins display irregular edges with marginal veinlets typically oriented parallel to the vein margin. Where present wall rock clasts are rounded and display sharp contacts with the surrounding sulfide. Textural indications of sulfide shearing i.e. elongated crystals are not readily observed, likely due to metamorphic recrystallization. The alteration selvage of these veins is typically weak suggesting that either it has recrystallized, that the sulfide vein had a limited thermal effect, or that the sulfides were emplaced tectonically during regional metamorphism and hence were not associated with the kind of fluid motions considered to have created the alteration selvages observed on the North Range.
Inclusion-bearing sulfide veins from the McKim property are similar although clasts do display more poorly defined margins. This results from the development of a coarse actinolite–biotite–chlorite–epidote assemblage, consistent with that of the host metabasalt. The diffuse margins may be the result of metamorphic growth of these coarse silicate crystals, reflecting a greater degree of re-equilibration and recrystallization between sulfides and silicates than at the Denison property.

The inclusion-bearing veins of the Denison property and the majority from the McKim property are, therefore, interpreted as having been formed through the shearing of solid sulfides sourced from the margins of proximal contact orebodies. Where present, inclusion-free and inclusion-bearing chalcopyrite-dominated veins are interpreted as having formed by the same mechanism as their North Range counterparts, with residual sulfide liquids exploiting fault planes.

4.9.1.3 Quartz–Carbonate–Sulfide Veins

Unlike the aforementioned sulfide veins, sulfides and associated PGMs of unequivocal hydrothermal origin are typically allied with soluble gangue phases, specifically quartz and to a lesser degree carbonate. The majority of hydrothermal PGM-bearing deposits display a relationship to syngenetic or pre-existing mineralization, typically magmatic, which is often considered the source of the PGEs (Prichard and Lord, 1990; Watkinson and Ohnenstetter, 1992; Augé et al., 2002; Barkov and Fleet, 2004; Wang et al., 2008). The solubility of Pt, Pd and Au metals and PGMs i.e. PtS and PdS in hydrothermal fluids has typically focused on the transport of precious metals as Cl⁻ complexes at temperatures of < 500 °C. These studies have concluded that significant quantities of Au can be transported in such solutions, however the transport of noteworthy concentrations of Pt and Pd requires highly oxidizing, acidic and saline conditions (Gammons et al., 1992; Gammons, 1996). The presence of a precious-metal bearing fluid with such a composition under geological conditions is considered uncommon, with the lack of a high fO₂, low pH alteration assemblages in systems where the precious metals have been redistributed by hydrothermal fluids i.e. the Bushveld Complex, the Stillwater Complex and the Lac-des-Iles Complex, making it unlikely that Cl⁻ complexes make a substantial input to the hydrothermal transport of Pt and Pd in saline fluids at temperatures of less than 500 °C. Above 500 °C there is little experimental data, although
Hanley et al. (2005c) undertook solubility experiments at salinities of 20, 50 and 70 wt % NaCl equivalent, with pH between 4.5 and 6.1, $f_{O_2}$ buffered by Ni-NiO (NNO) and temperatures between 600 and 800 °C. Analysis of the saline fluids identified between 1 and 1000 ppm Pt and Au to be present in solution. Such data indicates that at higher temperatures (> 500 °C) extremes of pH and $f_{O_2}$ have a reduced effect on the solubility of Pt and Pd in saline fluids. Such information is however of limited use at Sudbury where primary fluid inclusions associated with Cu-Ni-PGE mineralization homogenize between > 250 and 480 °C (Farrow et al., 1994; Molnár et al., 1999, 2001b; Molnár and Watkinson, 2001) and as such it seems unlikely that Cl− was a major ligand in the transport of Pt, Pd and Au. The ability of bisulfide complexes to transport substantial concentrations of Au in solution has long been known. (Seward, 1973). Under near neutral conditions the Au(HS)$_2$− complex dominates, with dissolved Au concentrations between 2 and 300 ppm (Wood et al., 1992), thus its ability to transport Pt and Pd must also be considered. Experimental studies of the solubility of PtS, PdS and Au in aqueous bisulfide solutions have consistently found that the solubility of Au is two or three orders of magnitude higher than that of Pt and Pd (Pan and Wood, 1994; Wood et al., 1994). The experimental work was buffered using coexisting H$_2$S, HS− and SO$_4^{2−}$, equating to a pH range of 5.91 to 9.43, and at temperatures between 200 and 350 °C. Dissolved concentrations of Au ranged between 2 and 300 ppm, with Pt between 4 and 800 ppb and palladium between 1 to 400 ppb. Interestingly, during higher temperature runs ≥ 300 °C the solubility of the precious-metals decreased. This reduction of Pt, Pd and Au solubility is the result of the expansion of the H$_2$S field at the expense of HS− (Wood et al., 1992) and suggests that as temperature increases Cl− may eventually overtake HS− as the dominant ligand. The preference for Au to enter solution has been interpreted as the reason for the formation of abundant Au-deposits i.e. epithermal and mesothermal systems and the rarity of hydrothermal PGE-deposits, with formation of the latter requiring a PGE-rich source (Pan and Wood, 1994). The transport of precious-metals as hydroxide complexes in hydrothermal fluids is considered of only minor importance (Wood et al., 1992). Experimental data run under the same conditions used for the bisulfide experiments (Pan and Wood, 1994), identified a correlation between the concentration of dissolved precious-metals and the OH− concentration. Hydroxide molalities between 0.01 and 1.3 m led to < 1 to < 100 ppb of Pt, < 1 to < 10 ppb Pd and 0.2 ppm Au entering solution, however concentrations may be higher in more oxidised surficial waters (Wood et al., 1992). Due to the < 500 °C homogenization temperatures and the near neutral pH of hydrothermal mineralizing fluids in the SICs footwall it is likely that the primary ligand is HS− and as such hydrothermal PGMs should display a strong association
with sulfide. Given the availability of HS- for hydrothermal fluids circulating in the Sudbury footwall it likely that fluids remobilized significant quantities of precious- and base-metals, however in the case of North Range low-sulfide mineralization it would appear that the input from such fluids was low, when compared to the TPM contributed by magmatic sulfide liquid(s). In contrast on the South Range QCS mineralization constitutes a significant fraction of low-sulfide mineralization, with the pervasive pyrite-marcasite alteration of footwall sulfides testifying to the ability of this fluid(s) to remobilized metals.

The presence of hydrothermal mineralization is typically accompanied by an alteration halo in keeping with temperature of the mineralizing fluid. These alteration assemblages would typically equilibrate at lower temperatures than the host igneous assemblage but commonly at higher temperatures than ambient conditions at the time of fluid transport and ore deposition. In contrast the presence of hydrothermal fluids associated with metamorphism should display an alteration assemblage in keeping with the hosts metamorphic facies, assuming simultaneous metamorphism and fluid flow (Masters and Ague, 2005; Bucholz and Ague, 2010). Quartz ± carbonate + sulfide mineralization from the North Range was accompanied by the development of chlorite + epidote selvages grading into a chlorite halo within which all but quartz and rare albite are replaced. Chlorite geothermometry was applied to QCS veins from the Levack North, Wisner and Capre properties and produced equilibrium temperatures of 296.55 to 338.90 °C (avg. 321.05 °C). The range is consistent with isolated saline fluid inclusion within QCS vein quartz that yielded homogenization temperatures 229.5 to 386.8 °C. The mechanism driving this fluid flow remains uncertain, but the most likely heat source is the SIC. Experimental data indicates that the solubility of Pd in saline H2O-dominated fluids ranges from levels slightly greater than, to equal to those of Pt (Gammons et al., 1992; Gammons and Bloom, 1993; Wood et al., 1994; Wood, 2002). The solubility of the IPGEs and their minerals in similar saline H2O-dominated fluids remains unknown. The hydrothermal model for sharp-walled formation (Molnár and Watkinson, 2001; Molnár et al., 2001) suggests that metals were scavenged from contact mineralization, with Cu and the PPGE's being preferentially remobilized relative to the IPGEs. Such a model is consistent with the fluid inclusion data of Hanley at al., (2005a, b) whose LA-ICP-MS studies of fluid inclusions below the J-M Reef, Stillwater Complex, and the Fraser Mine, Sudbury, identified ppm concentrations of Cu, Pt and Pd in solution, although IPGE concentrations were not measured. The data does however demonstrate the ability of saline fluids to transport precious metals. Such a model for the formation of QCS veins in low-sulfide zones assumes that the
metals must have come from contact ores, however, if sharp-walled vein systems had already solidified before the formation of low-sulfide QCS veins then they may present a more suitable metal source, thereby removing the need for the fluid to interact with contact mineralization. The IPGE depleted, PPGE enriched precious metal profile for North Range QCS veins (see Chapter 5) are similar to those of sharp-walled vein mineralization. This may reflect the preference of the PPGEs to enter solution in a saline fluid, relative to the IPGEs, producing the enrichment in low-sulfide QCS PPGE levels observed in normalized precious metal plots, relative to sharp-walled veins. As with the hydrothermal model for sharp-walled vein formation the assumption must be made that the PPGEs are more soluble in saline H₂O-dominated fluids than the IPGEs, although no strong evidence for this difference in solubility is present in the published literature. The origin of the hydrothermal fluid is also uncertain. LA-ICP-MS analysis of fluid inclusions by Hanley et al. (2005b) produced Ca/Na rations of 0.03 to 3.9. Such ratios are consistent with those obtained in Shield brines from the Victor and Strathcona mines, Sudbury (Bottomley et al., 2003), however given that the composition of any magmatic saline fluid exsolving from the SIC melt sheet, or mineralization remains unknown it is impossible to distinguish the fluid source. Furthermore ratios would also have been effected by wall-rock interactions which would have had an unknown effect on the fluid chemistry. It is clear that at present that the simplest source for the metals within QCS North Range are sharp-walled vein systems, as the PPGE concentrating process would have to be less extreme when compared to a contact ore source. Quartz ± carbonate + sulfide veins from the South Range display actinolite + quartz + chlorite + biotite + epidote + plagioclase alteration selvages consistent with the host greenschist assemblage. Unlike their North Range equivalents the QCS veins on the South Range produced only a minor coarsening of the host assemblage, with no discernible alteration halo, suggesting a fluid in equilibrium with the host environment or complete recrystallization of the silicates. Observations of sulfide veins from the Denison property consistently showed replacement of pyrrhotite, pentlandite and to a lesser degree chalcopyrite by pyrite and marcasite. The alteration is consistent with the interaction of the sulfides with a metamorphic hydrothermal fluid with a comparatively elevated $f_{S_2}$ and thereby provides a suitable metal source for QCS mineralization. Footwall mineralization from the McKim property displayed no pyrite/marcasite alteration suggesting that the metals were scavenged from the Little Stobie contact orebodies.

The presence of pre-mineralization fluid flow offered pre-existing conduits along which later sulfide liquids could migrate. Such exploitation occasionally results in veins within which
sulfide has clearly migrated along quartz and carbonate crystal margins, with sulfide containing numerous angular quartz fragments, whilst the vein quartz contains no base-metal mineral inclusions. Such veins also display a higher temperature PGMs i.e. moncheite and the patchy development of increased modal abundances of epidote and lesser actinolite where the sulfide is in contact with the barren veins chlorite + epidote alteration selvage. These changes in the ferromagnesian silicate assemblage reflect the entrance of the higher temperature sulfide melt and the recrystallization of the selvage assemblage that it causes. Such veins were noted in samples from all North Range properties and the McKim property. It is therefore essential to make textural observations before classifying material.

4.9.1.4 Disseminations and Stockwork Mineralization

The origins of both of these mineralizing styles remain uncertain. Disseminations on the North Range are accompanied by the development of epidote + chlorite alteration selvages, with actinolite only rarely observed, whereas the South Range equivalents occur along crystal interfaces with little obvious alteration. This observation is contradictory to another study of the Denison property that identified the development of dissolution features along the margins of PGM bearing veinlets, caused by the alteration of oligoclase to albite, with void spaces produced by the volume change (D.J. Kontak, personal communication, March 30, 2012), however no similar textures were observed in the thin sections analyzed for this study. North Range disseminations typically occur within broader regions of alteration dominantly comprising the alteration of ferromagnesian phases to chlorite. Such selvages and the general alteration appear consistent with a hydrothermal origin for North Range disseminated mineralization and a metamorphic–hydrothermal origin for South Range samples, however no association with soluble gangue phases is observed in either case. Experimental work has indicated the ability of a sulfide liquid to migrate through a packed substrate via crystal margins (Rose and Brenan, 2001; Brenan and Rose 2002), whilst Mungall (2002) postulated the migration of sulfide liquids within the SICs main mass. Furthermore Godel et al. (2006) identified 3D interconnecting sulfide networks in samples of apparently disseminated ore. As with a hydrothermal model a purely magmatic source is questionable, because sulfide migration typically results in regions of net-textured mineralization indicative of melt migration. These were not observed at the North Range properties, although rare net-textured sulfide was observed at the Denison property. At present the wetting properties of extremely
differentiated sulfide melts rich in volatile components and semimetals against solid silicates are not known. It is therefore impossible to judge whether traces of highly evolved sulfide melt could have migrated through silicate host rocks at the temperatures recorded by silicate phase equilibria in the alteration halos of the low-sulfide mineralization. At present a firm mechanism for formation of disseminated mineralization is therefore unknown.

The stockwork ores of the Denison property occur within strongly sheared metabasalts displaying abundant sub-millimetre carbonate ± quartz veinlets. As with previously described South Range mineralizing styles, the rock displays no associated alteration, although a coarsening of the mineral assemblage is observed. Such observations would suggest formation from a metamorphic fluid, however sulfide and PGMs occur disseminated throughout the sample with no obvious connection to gangue filled veinlets. Both macroscopic and microscopic patches of net-texture are observed, however these are relatively rare. A magmatic origin is seems questionable due to the lack of proximal sulfide veins, although drilling may not have intersected them. As with disseminations the formation mechanism remains uncertain.

4.9.2 Low temperature assemblages: Fractional crystallization, hydrothermal or metamorphic?

The PGM and Bi-chalcogenide assemblages noted for the North Range properties are in keeping with previous observations of footwall mineralization. However this study of low-sulfide mineralization has also yielded an additional three distinct assemblages and textures that have not previously been investigated in detail at Sudbury. The three textures observed were 1) polyphase PGM aggregates, 2) Michenerite + froodite + Sb-sobolevskite veins in gersdorffite from the Denison property, and 3) Bi-chalcogenide veinlets from the McKim property. These three assemblages are of interest as they contain low-temperature phases that could not have been stable at peak metamorphic conditions either in the thermal aureole of the SIC or, on the South Range, during subsequent tectonic events, suggesting that they may represent very late-stage mineralizing processes. Observations of natural systems indicate that the formation of such melts be it by magmatic or metamorphic processes can lead to the formation of distinct microtextures i.e. 'myrmekitic' intergrowths (Tomkins et al., 2007). Such textures have been reported for PGM aggregates from the Broken Hammer property, Wisner
Township (Kjarsgaard and Ames, 2010), although due to the low quality of the images presented it is difficult to be certain of the claim. All PGM and Bi-chalcogenide analyses in this study failed to identify any obvious textural evidence of melting, likely due to the host environment not being conducive to rapid cooling (Sparks and Mavrogenes, 2005), or subsequent recrystallization.

The difference in the envisaged compositions of late-stage Bi-Te melts from the North and South Ranges, which formed the observed polyphase aggregates, likely reflects both the initial composition of the parental sulfide melt and the PGMs that crystallized from it. Certain elements i.e. As and Sb display strong differences in concentration when North and South Range mineralization are compared. The clear enrichment of these elements within South Range mineralization, when compared to North Range deposits, is the result of As and Sb being remobilized from the Paleoproterozoic footwall rocks, a process that was not possible with the comparatively As and Sb-poor Archaean crystalline basement of the North Range (Ames and Farrow, 2007). It is therefore unsurprising that any Bi-Te melts that form on the South Range will be Sb-enriched when compared to their North Range equivalents, although As was likely removed well before Bi-Te melt formation, through the crystallization of sperrylite and sulfarsenides. The preference for Ag-Bi-Te melts in North Range magmatic mineralization and Pd-Bi-Te melts at the Denison property reflects the sulfide melt compositions. It is clear North Range magmatic low-sulfide mineralization is the result of a strongly fractionated sulfide liquid, which likely contained concentrations of Pd, Ag, Bi and Te in excess of the less fractionated sulfide melt that crystallized the South Range sulfide veins and veinlets. Such an enriched melt would likely begin crystallizing Pd-phases earlier and at higher temperatures leading to the formation of merenskyite and kotulskite-sobolevskite, not often observed in South Range magmatic mineralization (Cabri and Laflamme, 1976). On the South Range the sulfide liquid did not begin crystallizing Pd-phases until later when it had fractionated further and become enriched in Pd, Te and Bi. This would mean that a late stage Bi-Te liquid forming on the South Range would be in contact with a sulfide liquid containing a higher concentration of Pd than a North Range sulfide melt which had crystallized significant amounts of Pd minerals. The dominance of Ag-phases in North Range polyphase aggregates likely reflects the Ag-rich nature of the North Range sulfide melt, resulting in the common occurrence of hessite and the high levels of dissolved Ag in chalcopyrite (see Chapter 5) when compared to the Denison property.
4.9.2.1 Polyphase Aggregates and Ag-Micro-veinlets

On their own the polyphase PGM aggregates observed are not uncommon, with multi-PGM aggregates having been described from non-Sudbury deposits (Genkin and Evstigneeva, 1986) and also rarely from Sudbury (Li and Naldrett, 1993; Ames et al., 2010). They are however of interest within the Sudbury system where PGMs typically occur individually or as aggregates of two phases, typically separated by sharp linear contacts. For Sudbury at least the presence of polyphase aggregates appears anomalous.

The presence of polyphase aggregates within sulfide veins and IRV mineralization form the Levack North and Wisner properties, respectively, suggests that the formation of precious metal bearing Bi-Te liquids may have occurred within the North Range Sudbury system. Formation through anatexis is deemed unlikely as sufficient temperatures were probably not reached during post-mineralization greenschist facies metamorphism. Instead, it appears more likely that such domains formed at the end stage of fractionation of the sulfide magma. The lowest temperature phases within these aggregates indicate that they could have remained liquid to temperatures between 540 and 489 °C. The cuspatc form of these inclusions suggests that they became trapped within pore spaces at the junctions of sulfide crystals, and also indicate that no subsequent recrystallization has occurred. Whether such a Bi-Te melt was formed late through fractionation or earlier, as proposed by Dare et al. (2010a, b), is uncertain, although Fleet et al. (1993) identified the development of a late-stage semimetal melt during the quenching of Bi-Te-As doped sulfide liquids. Any such liquid formed clearly persisted to temperatures below the solidus of the base-metal sulfides.

The Ag-bearing micro-veinlets of the Capre property occur within fractures crosscutting sulfide vein chalcopyrite. Although these chalcopyrite crystals contain significant trace concentrations of Ag (see Chapter 5), the lack of fine exsolution lamellae or exsolution of Ag phase along crystal margins are taken as indications that the Ag was not sourced from cooling sulfides and is likely the product of a late-stage Ag–Te liquid, produced during the latter stages of fractionation and cooling. EDS analysis failed to clearly distinguish any Ag phases although the presence of peaks for Ag and Te would suggest that a Ag-telluride, likely hessite, is present. A clear distinction between phases within the micro-veinlets could not be achieved.
due to their small size, whilst slight contrast variations in backscattered electron images were interpreted as resulting from surface topography.

The observations of polyphase aggregates from the Denison property were made within samples of stockwork mineralization, which are, as previously discussed, of an uncertain origin. The polyphase aggregates display one or more phases with a melting point below 550 °C, chiefly froodite (485 °C), michenerite (489 to 501 °C) and tsumoite (540 °C), and are hosted within metabasalts with grades spanning the upper greenschist–lower amphibolite transition, with equilibrium temperatures and pressures of 513 to 645 ± 50 °C and 2.0 to 7.7 ± 1.0 kbar (see Chapter 3). This would indicate that metamorphic grades were sufficient to induce PGM or Bi-chalcogenide anatexis, with the resulting melt suppressing the liquidus of proximal, higher temperature PGMs. Although these occurrences are not common, the importance of the remobilization of precious metals, due to the formation of low temperature sulfide, arsenide and chalcogenide dominated melts, has in recent years been recognized as a viable deposit forming or concentrating process (e.g. Tomkins et al., 2007 references therein). The bulk of these redistributions documented in the literature have been driven by sulfide anatexis during amphibolite-granulite facies metamorphism, although formation by fractional crystallization has also been inferred (Gervilla et al., 1996; Hanley, 2007). On the South Range, formation of such anatectic melts through metamorphic remobilization is deemed possible with metamorphic grades from both the metabasalts and alteration selvages associated with mineralization consistent with temperatures of at least 550 to 575 °C (Liou et al., 1974; James et al., 1976; Spear, 1981), although the equilibrium temperatures and pressures calculated may not reflect metamorphic conditions during mineralization, being of possible Blezardian (i.e., pre-impact) or Penokean (i.e., post-impact) origin. A metamorphic model must also explain the ubiquitous occurrence of michenerite. Michenerite will be lost through incongruent melting between 489 and 501 °C, during which it forms kotulskite and a Bi-Te phase (Hoffman and MacLean, 1976). Although it is likely that the majority of such pairs would be lost through re-equilibration during subsequent cooling or the melting of the associated Bi-Te phase, indicators should also be present i.e. rare kotulskite + Bi-Te intergrowth or multi-phase Pd-Bi-Te aggregates resulting from the melting of kotulskite in the presence of a Bi-Te melt. It is possible that some of the observed polyphase aggregates represent the result of the latter process, although given the occurrence of Ag-phases, Sb-bearing minerals and rare Pt-phases within the aggregates such an assumption requires additional Ag, Sb and Pt possibly from proximal PGMs.
As with the polyphase aggregates observed from the North Range, a purely magmatic origin cannot be discounted. The possibility of forming a late low-temperature precious metal bearing assemblage through the fractionation of a sulfide liquid is not inconceivable and offers a simple explanation for the complex bulk compositions of these aggregates. This model does present three issues: 1) the source of such a liquid, bearing in mind that the majority of sulfide veins present on the South Range resulted from the shearing of solidified sulfide, 2) whether these extremely low-volume melts would be capable of migrating from the source, something the North Range equivalents appear to have been unable to achieve, and 3) if they could migrate why were no polyphase micro-veinlets observed. The only proximal source would therefore appear to be the contact ores of the Crean Hill mine, which is between 10 and 100 m from the sampled low-sulfide zones. The migration of a melt over such distances was suggested by Mungall (2002), who noted the migration of sulfide liquids through the near solidified norite in the sublayer and Main Mass over distances of hundreds of metres, although whether such low-volume melts would be capable of permeating that far into the footwall is highly questionable. This is further backed by the lack of elongate aggregates located along silicate grain boundaries from which the movement of a melt could be inferred.

### 4.9.2.2 Gersdorffite Hosted Micro-veinlets

Gersdorffite crystals within veinlet and stockwork mineralization, the latter of indeterminate origin, are cut by < 1 to 20 μm wide michenerite + froodite + Sb-sobolevskite micro-veinlets. The > 1 μm micro-veinlets are observed to follow fractures within gersdorffite, but do not extend past the margins of the host crystals, whereas < 1 μm micro-veinlets appear to follow cleavage planes in the host gersdorffite (Figure 4.7D). Based on these observations it is likely that these features represent a process limited to the gersdorffite crystal and not a broader mechanism. Observations by Cabri and Laflamme (1976) and Dare et al. (2010a) have indicated the ability of sulfarsenides to contain substantial PGE concentrations, leading to the conclusion that the PGMs observed in micro-veinlets within gersdorffite are likely the result of late stage exsolution during cooling (Barnes et al., 2006; Barnes et al., 2008).
4.9.2.3 Bi-Chalcogenide Micro-veinlets

Veins containing abundant Bi-chalcogenides are noted from several magmatic, hydrothermal and metamorphic deposits (Lowry et al., 1994; Wagner and Jonsson, 2001; Cook et al., 2007, Dare et al., 2010a), although they are typically associated with precious metals. The Bi-chalcogenide micro-veinlets at McKim clearly post-date the host lithology, mineralization and its associated alteration. The mineral assemblage presents four phases with known melting points, joséite-B; 478 °C (Verryn et al., 1991, reference therein), tsumoite; 540 °C (Hoffman & MacLean, 1976), tellurobismuthite; ~ 582 °C (Dumas et al., 1987) and bismuthinite; 775 °C (Lin et al., 1996). The remaining phases, parkerite and sulphotsumoite, as yet have no experimentally defined stability limits. The lower temperature phases are within the metamorphic conditions of the actinolite-magnesiohornblende-chlorite-quartz-plagioclase-biotite-epidote-titanite assemblage of the host metabasalts and the actinolite-biotite-chlorite-epidote alteration selvages of the proximal sulfide veins, both representative of temperatures at least as high as 550 to 575 °C (Liou et al., 1974; James et al., 1976; Spray, 1981). These veins could therefore represent a Bi–Te–S–Se melt produced through metamorphic anatexis of low temperature Bi-chalcogenides, although several problems persist. The sulfide veins proximal to the Bi-chalcogenide micro-veinlets contain a significant amount of bismuthinite, tellurobismuthite and Se-parkerite, the melting point of at least one of which falls near the lower limit of the metamorphic assemblage. Despite the possibility of anatexis no morphological indicators of melt migration associated with Bi-chalcogenides within sulfide veins is present; that is, cuspat e crystals or aggregates located at sulfide crystal junctions, or elongate crystals along crystal margins are not observed in the sulfide veins. Furthermore the absence of precious metal minerals within these micro-veinlets would seem to require that any Bi-Te-S-Se liquid that existed somehow avoided crystals of both hessite and froodite during its migration, the former of which are extremely common, whilst the latter could also have been liquid and thereby easily soluble within such a melt. The lack of such morphologies may result from a recrystallization of the sulfides and associated phases, whereas the lack of lack of Pd and Ag minerals within the micro-veinlets may result from the authors inability to discern precious metal phases during BSE analysis, due to the high molecular mass of the surrounding Bi-chalcogenides and the small grain sizes in the veinlets.

The formation of a Bi–Te–S–Se liquid due to late stage fractionation is also viewed as a possible source. The formation of such a liquid does present some issues, chiefly again related to the lack of Ag and Pd in this hypothetical melt. The lack of Pd may result from the
sequestering of Pd within sulfides, particularly pentlandite, or through the crystallization of unobserved higher temperature PGMs. This does not however explain the lack of Ag, which would likely have been readily available in the form of hessite. The 478 °C upper temperature limit set by the presence of joséite-B suggests that the liquid persisted to temperatures below froodite solidification. This may have allowed sufficient time for hessite and froodite to crystallize thereby allowing a precious metal free Bi-Te melt to form. The position of the micro-veinlets along vein margins suggests that any Bi-Te melts likely formed within this region. This may have allowed the melt to exit the vein without significant contact with the vein sulfides and the PGMs within them and to enter the PGM free alteration selvage and wall-rock.

At present it is uncertain whether the veins are the result of fractionation or metamorphic processes, with the former currently presenting a slightly simpler scenario. The extremely low temperature phases within these micro-veinlets would make melting through metamorphism very likely, especially along the SICs tectonically active South Range. It must therefore be concluded that any magmatic Bi-Te micro-veinlets have been fully or partially melted and as such the minerals observed may well reflect this event rather than the initial mineral assemblage. Alternatively, the veinlets could have formed from aqueous metamorphic fluids at even lower temperatures well below their solidus temperatures, although the lack of soluble gangue phases (i.e. quartz and carbonate) and base and precious metal minerals which would likely have been scavenged along with Bi, Te and S, make this option less probable.

4.9.2.4 "Quench" Textured Arsenide Aggregates

The complex intergrowth textures shown rarely by nickeline from the Denison property are extremely problematic. However, similar nickeline–maucherite–gersdorffite assemblages have been noted from the Garson, Falconbridge, Worthington, Frood and Creighton deposits, with nickeline enclosing chalcopyrite observed from the Copper Cliff South mine (Hawley, 1962; Hawley and Staton, 1962; Cabri and Laflamme, 1976).

The texture superficially appears to be the result of the quenching of an arsenide melt. The formation of such liquids from a Fe–Ni–Cu–S melt was demonstrated by Fleet et al. (1993), and Wood (2003) presented evidence of their ability to sequester precious metals. The origin of the Cu phase is uncertain, with Cu solubility within an arsenic melt unknown. The
existence of such a liquid is, however, questioned by Hanley (2007), who considered Cu to be incompatible with As melts, whereas Moore (1971) found a negligible Cu solubility in nickeline at 510 ± 5 °C. The crystallization temperature of such a liquid is uncertain, although the Pd–Ni–As system indicates complete crystallization by 450 °C (Gervilla et al., 1994), consistent with the Ni–As–S system of Yund (1962) who proposed the existence of As–S liquids down to that value. Nickeline would likely crystallize early from any such melt, being stable at ≤ 962 ± 3°C (Yund, 1961). The presence of a Ni–Cu–Fe–Co–As–S liquid is conceivable, but at present deemed unlikely, especially when one considers that the formation of quench textures from sulfide liquids requires extremely fast cooling rates which are not consistent with the regional metamorphic history of the host rocks.

The intergrowth texture could also be considered to have resulted from a symplectic breakdown of one or more precursor phases, or through breakdown of a primary phase due to the presence of a metasomatic fluid e.g. myrmekitic texture. Although the author can find no publications showing the symplectic breakdown of arsenides and sulfarsenides, experimental systems have indicated that no stable phase exists within the Cu-Fe-As-S system (McKinstry, 1963; Raghavan, 2004b), with any minerals present representing solid solutions of ternary and binary phases from the Cu–As–S, Fe–As–S, Fe–Cu–As and Cu–Fe–S ternary systems. High temperature solid solutions were also identified between nickeline and α-NiS, becoming incomplete below 595 ± 5 °C (Yund, 1962). The breakdown of such intermediate phases and the development of the observed texture would require addition of Ni, Cu or Fe depending on the initial phase, all of which would have been in plentiful supply within metamorphic fluids. The interaction of a primary phase with a metasomatic fluid (Ashworth, 1986; Collins, 1988), likely derived from a crystallizing sulfide melt or a metamorphic fluid interacting with mineralization, could also have produced the observed texture. The breakdown of the precursor phase typically occurs along crystal margins and fractures along which the metasomatic fluid can move. The myrmekitic texture replaces the primary phase; however, alteration is often incomplete. If the observed nickeline–chalcopyrite intergrowths are considered to represent the secondary phases then the gersdorffite was likely the primary phase. The formation of the intergrowths would therefore require an interaction with a fluid containing Cu and additional S. At present the symplectic breakdown of an unknown phase is favored, as interactions of gersdorffite with a Cu-S bearing metasomatic fluid would likely have resulted in the texture being far more common.
4.9.3 PGM Assemblage

4.9.3.1 North Range Sulfide Veins

The sulfide vein assemblages of the Capre and Wisner properties represent a complete sequence of PGM crystallization from high to low temperatures (Figure 4.18). Platinum group minerals will typically not precipitate from sulfide melts until the PGE have reached very high concentrations in the melt, typically in the range of several wt % (Andrews and Brenan, 2002). Absolute upper temperature limits at which this process can occur are defined by the melting points of the pure PGM phases. Assuming sufficient PGE concentrations crystallization likely began with moncheite between 1150 and 920 °C, with merenskyite appearing below 740 ± 3 °C (Hoffman and MacLean, 1976; Ipser and Schuster, 1986; Kim and Chao, 1990a,b; Kim et al., 1990; Okamoto, 1992; Kim, 1996; Helmy et al., 2007). The exact temperatures remain uncertain with the effects of Pd, Pt and Ni substitution into the precious metal site and Bi for Te exchange untested, although plotting of merenskyite compositional data over a polythermal section (500 to 720 °C) indicates formation between ~ 650 and 500 °C (Figure 4.17). It seems likely that both moncheite and merenskyite represent the first crystallizing Pt and Pd phases, thereby explaining their places as major reservoirs for both Pt and Pd at the Wisner and Capre properties. Merenskyte and to a lesser extent michenerite crystallizing in the Pd-Bi-Te system of Hoffman and MacLean, (1976) coexisted with a Bi-Te-Pd liquid (Figure. 4.17), which became more Bi-rich with decreasing temperature. Estimated compositions for polyphase aggregates observed in merenskyite-michenerite bearing sulfide vein and IRV mineralization are plotted in Figure. 4.17. The aggregates present two distinct groups, consisting of hessite dominated assemblages, with accessory michenerite and volynskite, and michenerite and volynskite dominated aggregates, with accessory hessite and froodite. The latter (Pd, Ag)BiTe dominated aggregates plot along the Bi-Te-Pd liquid isotherms and suggest that they could represent samples of the Bi-Te-(Pd,Ag) liquid that was present during merenskyte and/or michenerite crystallization. In contrast the hessite dominated aggregates likely represent crystals that have engulfed smaller PGMs and Bi-chalcogenides.

In contrast, the Levack North property displays a marked difference in PGM assemblage. As with the other North Range properties moncheite likely represents the first PGM crystallized and as such dominates the Pt budget. However instead of merenskyite, the mono-telluride kotulskite is dominant. Helmy et al. (2007) indicated the requirement of a (Pd+Pt)/Te ratio ≥
0.65 to achieve a moncheite + merenskyite bearing assemblage, with kotulskite preferred at or below a ratio of 0.5. The observations from sulfide veins of the Levack North property would therefore suggest that crystallization of moncheite was sufficient to drive the (Pt + Pd + Ni):Te ratio below 0.5 before substantial merenskyite crystallization could occur. This hypothesis also indicates that the composition of any sulfide liquid entering the footwall cannot be considered homogenous across the entire North Range.

Kotulskite would have begun crystallization at or below 746 °C (Hoffman and MacLean, 1976; Kim and Chao, 1990a; Okamoto, 1992), although experimental data at present has failed to constrain the effects of Te–Bi substitution. The Te–Bi exchange was present within the data of Hoffman and MacLean (1976) and indicated that Bi concentrations in kotulskite was related to the Bi content of their Pd–Bi–Te melt, irrespective of temperature and associated PGMs. It must also be noted that the presence of a PdTe–PdTe₂ solid solution was noted between 575 ± 10 and 710 ± 10 °C. This field was partially backed by Kim and Chao (1990a), between 600 and 670 °C, with runs above this range failing to yield conclusive telluride phases. Hoffman and Maclean (1976) noted that the composition of the PdTe–PdTe₂ solid solution was approximate to that of fine kotulskite–merenskyite intergrowths from the Stillwater Complex (Cabri and Pickwick, 1974), with coarser intergrowths from the Merensky Reef interpreted as having formed below 575 ± 10 °C. The lack of such intergrowths or indeed recrystallized kotulskite–merenskyite pairs may suggest that crystallization of PdTe did not occur from a solid solution and therefore may have transpired below 575 ± 10 °C. Crystallization of sobolevskite would begin below 618 °C (Okamoto, 1994), although it is only rarely observed. The lack of sobolevskite may result from the Te–Bi exchange of moncheite–merenskyite and possibly kotulskite at higher temperatures and therefore limited Bi availability. It should also be noted that its liquidus coincides with pentlandite formation through the reaction of mss and Ni₃±xS₂ at 610 °C (Craig and Kullerud, 1969), with Pd sequestering by pentlandite possibly driving down Pd availability.

The significant exchange of Pd for Ag within kotulskite and sobolevskite from all North Range properties is, to the best of the author's knowledge, the first reported example anywhere in the literature. Whether this exchange is limited to possible low-sulfide mineralization within the footwall of the SIC, or a reflection of exclusion of Ag from PGM analytical routines remains uncertain, with further work required.
In all cases michenerite represents the lowest temperature PGM observed, becoming stable below 489 to 501 ± 3 °C (Hoffman & MacLean, 1976). A substantial number of michenerite crystals have been noted from all three North Range properties despite the presence of other, higher temperature, Pd-bearing phases. This observation seems to support a late increase in Pd, Te and Bi concentrations, either through the formation of a low-volume Pd–Bi–Te melt or through the release of these elements via exsolution from cooling sulfides, directly forming discrete PGMs or enriching any residual liquids present. Either mechanism allows Pd levels to increase sufficiently for michenerite to form, with any remaining Pt substituting for Pd.

4.9.3.2 South Range Sulfide Veins

The sulfide veins of the Denison and McKim properties display remarkably simple PGM assemblages comprising a single Pt phase and a single Pd phase. (Figure 4.19) The presence of sperrylite across the South Range is well established and likely results from the comparatively As rich natures of the South Range sulfide liquid. Given the 1360 °C liquidus of sperrylite (Okamoto, 1990) it is conceivable that it crystallized early and therefore could have precipitated directly from the sulfide melt at the contact and was then sheared in with the sulfide. However, in light of the known incompatibility of Pt in mss and the low initial concentration of Pt in the sulfide melt from which the mss-dominated contact ores formed, it is more likely that sperrylite did not form until temperatures had fallen to a point approaching the sulfide solidus. In the case of the chalcopyrite-dominated inclusion-bearing and inclusion-free sulfide veins of the McKim property the proposal above may be correct, with crystals precipitating directly from the residual sulfide melt.

The presence of low temperature Pd phases (michenerite and froodite) presents a point of interest since no higher temperature Pd minerals have been observed in South Range sulfide veins during this study. Observations from Cabri and Laflamme (1976) indicate the additional existence of merenskyite at the Crean Hill mine, although it was a minor phase. The inability to form higher temperature phases, specifically the moncheite-merenskyite and kotulskite-sobolevskite-sudburyite solid solutions can be explained through either a lack of available precious or semimetals or the sequestration of Pd by other crystallizing phases.
Table 4.13. Summary table of platinum-group minerals and Bi-Chalcogenides observed during this study. Temperatures represent the maximum thermal stability of each phase, please see text for accurate values.

<table>
<thead>
<tr>
<th>Levack North</th>
<th>Wisner</th>
<th>Capre</th>
<th>Denison</th>
<th>McKim</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide Vein</td>
<td>Irregular Veinlet</td>
<td>Qtz ± carb + sulf.</td>
<td>Sulfide Vein</td>
<td>Irregular Veinlet</td>
</tr>
<tr>
<td>&gt;1100</td>
<td>Sperrylite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;900</td>
<td>Moncheite</td>
<td>Moncheite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;800</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;700</td>
<td>Kotulskite</td>
<td>Merenskyte</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;600</td>
<td>Sobolevskite</td>
<td>Sobolevskite</td>
<td>Sobolevskite</td>
<td></td>
</tr>
<tr>
<td>&gt;500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt;400</td>
<td>Michenerite</td>
<td>Michenerite</td>
<td>Froodite</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>Unknown</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Temperatures represent the maximum thermal stability of each phase, please see text for accurate values.
In the case of Denison, the presence of michenerite may reflect the presence of a late stage Pd–Bi–Te liquid, with metal concentrations only becoming high enough after substantial fractionation of the residual sulfide liquid in the footwall or the parental sulfide liquid at the contact. Such a model is consistent with experimental work by Helmy et al. (2010) that clearly indicates the incompatibility of Sb, Te and Bi with crystallizing mss and as such elevated concentrations would be expected within the residuum at temperatures approaching the sulfide liquid solidus. It therefore seems likely that Pd, Bi and Te availability was the primary control, with levels kept low through the sequestration of low concentrations of Pd within chalcopyrite, iss, hzss and pentlandite, Bi in all sulfides and Te within pentlandite (see Chapter 5). The release of these metals upon the cooling and breakdown (in the case of iss and hzss) of sulfide phases would have released significant quantities back into the environment, perhaps driving the formation of a discrete Pd–Bi–Te liquid or the direct precipitation of Pd phases.

At McKim the absence of high temperature Pd phases presents a unique problem. The lack of such minerals, i.e. merenskyite, kotulskite–sobolevskite–sudburyite and michenerite would suggest that either Pd, Te and/or Bi concentrations were so low as to not allow Pd mineral precipitation until temperatures at or below 485°C (Okamoto, 1994), or that sufficient metals were unavailable due to sequestration by sulfides, and/or through the crystallization of substantial quantities of hessite and bismuthinite, stable below 960 °C and 775 °C (Cabri, 1965; Karakaya and Thompson, 1991; Lin et al., 1996). Given the presence of such large quantities of hessite and Bi chalcogenides it is clear that Bi and Te were freely available and as such PGM precipitation should have proceeded. It also seems highly unlikely that the crystallization of hessite and Bi-chalcogenides, combined with the sequestration of metals, especially Pd, within sulfide could have been so efficient as to inhibit the formation of Pd phases. The loss of higher temperature Pd PGMs through recrystallization or dissolution cannot be discounted. Such an event could have been sufficient to produce froodite, although the excess of Te which would be expected from the precursor phases e.g. merenskyite, kotulskite–sobolevskite–sudburyite and michenerite cannot be accounted for, with froodite crystals presenting no observed partner Bi chalcogenides. The breakdown of higher temperature phases, particularly michenerite, is possible within the likely range of regional metamorphic temperatures experienced by the McKim footwall. If Te within the resulting melt could be sequestered within an alternative phases e.g. hessite, a Pd–Bi melt could be
maintained to froodite solidus. At present the author feels that human error is the most reasonable explanation for the lack of alternative Pd phases observed, with higher temperature Pd minerals likely present, but masked from observation due to the prevalence of hessite and Bi sulfides.

4.9.3.3 North Range Quartz-Carbonate-Sulfide Veins

Analyzed QCS vein PGMs from all three North Range properties present an assemblage in keeping with formation at temperatures below that of sulfide veins. Veins from the Levack North and Capre properties contain abundant michenerite, stable below 489 to 501 ± 3 °C (Hoffman & MacLean, 1976) with each property displaying additional sobolevskite and merenskyite respectively, stable below 618 °C and 740 ± 3 °C (Hoffman and MacLean, 1976; Kim and Chao, 1990a Okamoto, 1994). A single sobolevskite crystal was also identified from the Wisner property. Both sobolevskite and merenskyite crystals display compositional shifts towards the end-members, with reductions in Bi–Te and Pd–Pt exchange when compared to sulfide vein–hosted equivalents, which may also indicate precipitation at temperatures lower than in the sulfide veins. Platinum is primarily present in solid solution within michenerite from Levack North and merenskyite from Capre, although sperrylite was observed on two occasions from the latter. The low concentrations of Pt in solid solution are inconsistent with bulk assays that show a Pt:Pd ratio of around 1:1, itself consistent with the similar experimental solubilities of Pt and Pd in aqueous fluids (Gammons et al., 1992; Gammons and Bloom, 1993; Wood, 2002). The lack of Pt minerals would therefore imply that an as yet unidentified Pt phase exists within QCS veins from the Levack North and Wisner properties. The presence of sperrylite would also indicate that the hydrothermal fluid has come into contact with an As-bearing medium, be it a late stage residuum from crystallizing sulfide veins or contact or sharp-walled vein sulfides containing sulfarsenides and arsenides in low abundances.

\[ \text{Pd} = \text{Pd} + \text{Pt} + \text{Fe} + \text{Ni} + \text{Ag}, \text{Te} = \text{Te} + \text{S}, \text{all values in atomic percent.} \]

4.9.3.4 South Range Quartz–Carbonate–Sulfide Veins

Platinum-group minerals within South Range QCS mineralization were only observed from the Denison property. The QCS veins, like the sulfide veins, host a simple PGM assemblage with near end-member sperrylite and michenerite hosting all Pt in the former and nearly all Pd in the latter. A single sudburyite and two sobolevskite crystals displaying significant Sb–Bi–(Te) substitution were also identified. Ratios of both Pt:Pd phases and bulk Pt:Pd concentrations sit near 1:1 and are consistent with observations from sulfide veins. The
presence of pyrite and marcasite replacing pyrrhotite, pentlandite and lesser chalcopyrite within sulfide veins indicate that metamorphic-hydrothermal replacement of these base-metal sulfides presented a plausible source for the scavenging of base and precious metals that were re-deposited in QCS mineralization.

4.9.3.5 Irregular Veinlets (IRV)

Irregular veinlet mineralization from the three North Range properties displayed PGM assemblages that could have crystallized from a high temperature sulfide liquid, yet these PGMs have compositional traits and distributions differentiating them from sulfide veins (Figure 4.18). At all three North Range properties, IRV veinlets contain sperrylite, a phase not observed within sulfide veins. These crystals are near stoichiometric, although sperrylite only makes a significant input into the Pt budget in IRV samples from Capre. The majority of Pt from the Levack North property is hosted within moncheite, several crystals of which are also noted from Capre. The moncheite crystals display a distinct compositional variation by property, with examples from the Levack North property displaying an increase in Pt content compared to sulfide vein hosted crystals, whereas examples from Capre show a minor increase in Pd. Differences in the degree of semimetal substitution are negligible, with Te and Bi concentrations typically differing by an average of 1.5 wt % from sulfide vein values. Platinum within IRV mineralization at the Wisner property is almost exclusively hosted by merenskyite, which is compositionally similar to that from sulfide veins, although it does display enrichments in Sb and Se. A single merenskyite crystal was also identified from the Capre property and displays comparatively low Pt. In all instances the majority of Pd was hosted within michenerite. The major element chemistry of these crystals is consistent with examples from sulfide veins, although michenerite from the Levack North and Wisner property does display elevated Se, with crystals from the latter also displaying elevated Sb, whilst crystals from Capre displayed Ag concentrations above for michenerite from sulfide veins. A single crystal of froodite was identified from the Levack North property and represents the lowest temperature phase in the assemblage, suggesting that a liquid melt may have been sustained down to ≤ 485 °C (Okamoto 1994), given that the crystal’s 40 μm size makes it unlikely to have formed by exsolution.
The PGM assemblages display a continuous series of PGM crystallization akin to that displayed by sulfide veins. It is likely that the melt had a maximum temperature of around 850 °C, suggesting that the presence of sperrylite reflects a compositional rather than temperature control. It must however be noted that the presence of sperrylite and compositional differences displayed by michenerite from all three properties and merenskyite from Wisner indicate that the sources were similar to but not identical to sulfide veins. The presence of As phases, increases in Sb and Se content and variation in Pd:Pt ratios of IRV hosted PGMs are taken by the author to represent formation from an extremely fractionated sulfide liquid. Observations in Chapter 3 noted cross-cutting relationships between QCS and IRV mineralization suggesting their presence within the footwall at the same time. In contrast sulfide veins from all three properties displayed no cross-cutting relationships with the exception of a single low temperature carbonate vein from Capre. This would suggest that sulfide veins postdate both IRV and QCS mineralization. This difficulty in relating IRV mineralization to sulfide veins is further illustrated at the Wisner property, where IRV mineralization makes a substantial contribution to the property's metal budget, yet only a single sulfide vein was intersected. All other examples had widths of less than 5 cm and were highly irregular. The source of any IRV forming melt is therefore uncertain, but was possibly sourced from proximal contact or sharp-walled vein systems, or from sulfide veins within the low-sulfide intersection, which in the case of Wisner were not intersected by drilling.

4.9.3.6 Stockwork

Interpreting the PGM assemblage of stockwork mineralization is complicated by the poorly understood nature of the mineralizing process. As with all South Range mineralization, Pt is hosted within stoichiometric sperrylite, and the majority of Pd resides within michenerite (Figure 4.19). The mineralizing style is distinct, however, in that 28 % of the Pd phases were sobolevskite and minor kotulskite and sudburyite, all displaying substantial Te–Bi–Sb substitution. The extensive solid solution displayed by crystals of the PdBi–PdSb–PdTTe series from the Denison prospect, represents a significant deviation from the bulk of previous Sudbury data. Analyses by Cabri and Laflamme (1973, 1974b, 1976), identified three crystals displaying a similar composition, with a Pd : (Bi, Te, Sb) ratio of 1:1, although it is unknown whether they were homogeneous phases. Observations from this study revealed a light pink-orange to pink-cream PGM with an appearance in keeping with the dominantly sobolevskite
composition. The strong anisotropy expected was not present, with crystals appearing isotropic in crossed polarized light. The lack of anisotropy differs from that of the PdBi-PdTe-PdSb end-members, suggesting that either increased solid-solution results in a decrease in bireflectance or that this intermediate composition may represent a discrete phase in its own right, as hypothesized by Cabri and Laflamme, 1976. The degree of solid solution also places Denison in a group with a limited group of deposits and prospects, including the Wellgreen deposit, Yukon, the Mesamax Northwest deposit, Quebec, the Baula Complex, India, and the Keivitsansarvi deposit and Lukkulaisvaara pluton, Finland, (Grokhovskaya et al., 1992; Barkov et al., 2002, McDonald et al., 2005; Augé et al., 2002; Gervilla and Kojonen, 2002). All of these deposits, excluding the Lukkulaisvaara pluton, display a certain hydrothermal component related to mineralization (Marcantonio et al., 1994; McDonald et al., 2005; Augé et al., 2002; Gervilla and Kojonen, 2002), providing the possibility that the majority of PGMs within the stockwork style of mineralization are of hydrothermal origin. Evidence for such a hypothesis is scant, with base-metal sulfides and PGMs displaying no relationship to the carbonate ± quartz veins present. However if a low-volume hydrothermal fluid was involved, the gangue phases associated with PGMs and polyphase aggregates may have recrystallized to the point of being indistinguishable from the groundmass silicates. Such a fluid is envisaged to be of magmatic origin, as a metamorphic-hydrothermal fluid interacting with massive sulfide at the contact or in the footwall would likely struggle to achieve the high levels of Pt and Pd observed without also scavenging significant quantities of base-metals, which would be expected to have precipitated with the PGMs. The preference for the fluid to exploit the strongly sheared metabasalts is likely a reflection of the higher level of permeability offered by these zones when compared to the massive weakly sheared metabasalts that dominate the Denison footwall.

Formation through a late stage magmatic Pd–Bi–Te–Sb melt cannot be discounted. Experimental data (Fleet et al., 1993) indicates that Bi–Te–As liquids can separate from a sulfide liquid in the latter stages of sulfide crystallization. Such melts display a preference for scavenging Pt over Pd (Fleet et al., 1993), with Pt/(Pt+Pd) ratios for stockwork mineralization peaking between 0.5 and 0.6 (see Chapter 5), which may weakly reflect this fractionation. As the sulfide veins within the Denison footwall formed from sulfide sheared from the contact, it is probable that any residual liquids were sourced from the Crean Hill orebodies. The passage of a low-volume Pt and Pd–bearing Bi–Te–Sb liquid into the footwall may have been aided by the simultaneous presence of a low-volume, highly fractionated sulfide liquid, with sulfide
associated with stockwork mineralization displaying levels of dissolved precious and semimetals in excess of other South Range mineralizing styles (see Chapter 5). The increased volume of melt produce by the sulfide liquid – Bi–Te–Sb liquid emulsion may have allowed for movement further into the footwall. As previously discussed, it has been suggested that sulfide liquids could move through a fully solidified silicate substrate (Mungall and Su, 2005; Chung and Mungall, 2009), although the properties of a Bi–Te–Sb liquid remain unconstrained. The passage of such a liquid would allow for the lack of correlation between hydrothermal carbonate ± quartz veins and disseminated sulfide and explain the single net-textured sample observed.

4.9.3.7 Previously Undescribed PGMs

The presence of UNK1 (Pd,Ag,Pt)$_3$(Sb,Bi,Te,As)$_2$ and UNK2 (Pd,Ag)$_3$(Bi,As,Te)$_4$ hosted as they are within gersdorffite containing froodite, michenerite and Sb-sobolevskite could be considered the result of erroneous counting of X-rays produced by activation and fluorescence of surrounding phases. This hypothesis is rejected by the author due to the consistency of the data and the inability to balance the Ag content of both phases with contamination by hessite (the most likely Ag phase). Experimental analysis of the Pd–Bi (Brasier & Hume-Rothery, 1959; Okamoto, 1994) and Pd–Sb–Te (Kim & Chao, 1991) systems failed to yield any phases displaying even an approximate match to the stoichiometry of the unknowns. Charge balancing of the calculated composition is possible in the simplest scenarios, UNK1; Pd$_{3+}$(Sb,Bi)$_{3+}$ and Pd$_{4+}$(Bi,As)$_{3+}$, however, this is complicated by the imbalances resulting from substantial concentrations of Ag and Te. At present it seems that these phases may represent the exsolution product from cooling gersdorffite, with subsequent recrystallization possibly leading to the formation of more common PGMs.

4.9.3.8 Accessory Phases

The majority of the semimetal accessory phases associated with PGE mineralization from the five properties fall within the tetradymite group, specifically tetradymite, joséite, tsumoite, sulphotsumoite, tellurobismuthite, volynskite and bohdanowiczite (Bayliss, 1991).
The tetradymanite observed in North Range samples shows slight sulfur enrichment. The Ag and Fe enrichment (vs. stoichiometry) displayed by sulfide vein hosted crystals from the Wisner prospect may result from interference caused by the host chalcopyrite or an unknown silver phase. Corrections for these interferences could not be made as Cu was not part of the EMP routine and Te from hessite would be masked by the tetradymanite composition. A similar effect was not noted for vein crystals from Capre, probably due the larger crystal size. The upper limit of tetradymanite stability ranges from 609 ± 3 °C to 638 °C (Cook et al., 2007, references therein); its occurrence in aggregates with michenerite suggests that crystallization occurred below 489 to 501 ± 3 °C. Although analysis of tellurobismuthite was limited to only two crystals from Wisner and one from McKim, it was also observed in BSE and EDS analysis of sulfide vein samples from Wisner and Capre, the bulk of analyses having failed due to small crystal sizes and contamination from associated phases. The tellurobismuthite liquidus occurs at 585°C, increasing with rising Se substitution (Dumas et al., 1987). The effect of Se on the liquidus can be substantial, however, at the low concentrations observed from the Wisner and McKim properties (Se:Bi ratios of 0.04 and 0.06, using at %) it will actually reduce the melting point to ~ 582 °C (Dumas et al., 1987).

By far the most common accessory minerals within all mineralizing styles are Ag phases, chiefly hessite, with lesser volynskite and bohdanowiczite observed within BSE-EDS analyses from Levack North, Wisner, Capre and Denison, the latter property also possessing possible makovickyite. The presence of near end-member hessite was expected given its abundance within footwall mineralization. Its stability, up to 960 °C (Cabri, 1965; Karakaya and Thompson, 1991), makes it a stable phase with all other observed minerals. The presence of volynskite could only have occurred within a range of 443 to 555 °C (Babanly et al., 2007), below which it decomposes to hessite + tellurobismuthite, a possible explanation for several complex Ag₂Te–Bi₂Te₃ aggregates observed and the often sporadic, small, irregular crystals of AgBiTe₂ observed in the majority of examples. The persistence of volynskite within the Sudbury precious metal mineral assemblage would imply that the limits of Babanly et al. (2007) may be inaccurate or that it may reappear as a stable phase at lower temperatures given the correction conditions. Bohdanowiczite was noted within sulfide vein and IRV mineralization from Capre. Where present, crystals are extremely heterogeneous, with Bi concentrations especially variable. Shykhyev et al. (2003) noted that the polymorphic transition of AgBiSe₂ at 316 °C, marks a non-stoichiometric to stoichiometric transition. The
heterogeneities displayed by bohdanowiczite may therefore be explained as the result of cooling through this transition, with incomplete recrystallization.

Samples of stockwork mineralization from Denison yield several argentopentlandite crystals. Crystals displayed two Ag ranges, 9.78 to 10.10 wt % and 14.30 to 14.32 wt %, with former producing an Ag value of < 1 atom per formula unit (apfu), the latter > 1. Analyses display an Fe/Ni ratio of 1.27 to 1.57, thereby making Ag concentration the primary control of melting, with crystals with > 1 apfu melting at 455 °C and those with 0.7 apfu around 452 °C (Mandziuk & Scott, 1977). Although the sulfides of the Denison property will have undergone some degree of re-equilibration, pentlandite crystals in contact with argentopentlandite display Ag concentrations below detection, suggesting no significant Ag loss.

4.9.3.9 Selenian Pilsenite

Cook et al. (2007, reference therein) reported the presence of selenian pilsenite from the Lega Dembi deposit, Ethiopia. This was subsequently reclassified as selenian joséite-B, a reflection of the S component. In contrast the McKim analyses, from sulfide veins, display < 0.1 wt % S and a Bi:(Te + Se + S + As + Sb) ratio of 3.98 : 3.02, near stoichiometric and considerably tighter than the broader Bi:(Te + Se + S) ratio of joséite-B. Although the crystals analyzed displayed a near consistent composition, caution must be exercised, as the crystals could not be relocated once their unique composition was established. The possibility of a mixed analysis due to heterogeneities or multiple phases cannot therefore be discounted. The composition produced does not achieve the end-member Bi₄Te₂Se composition envisaged with the complete replacement of 1 apfu of Te for Se, however the data does indicate the possible presence of a solid-solution not previously indicated by published pilsenite analyses (Cook et al., 2007, data and references therein). The cause of the Se-enrichment displayed by these crystals is uncertain, however their association with sulfide veins implies a magmatic source. In both instances the host veins were chalcopyrite dominated, a composition interpreted to have formed from a residual sulfide liquid, likely from the Little Stobie orebodies. The presence of such high quantities of Se likely replacing Te were not observed within Bi chalcogenide micro-veinlets, despite the ability of phases such as joséite-B to contain significant levels of Se (Gu et al., 2001). The selenian pilsenite is therefore interpreted to be the result of a late stage extremely fractionated Bi–Te–Se melt (later than that which
formed the Bi-chalcogenide micro-veinlets) occurring as isolated pockets. The lack of sulfur within the selenian pilsenite suggests that the Bi-Te liquid that it crystallized from is not related to the Bi-Te-S liquid that formed the Bi-chalcogenide micro-veinlets. The lack of significant quantities of Se within micro-veinlet Bi-chalcogenides suggests that when the Bi-Te-S melt formed Se levels were not highly enriched, suggesting that the formation of a Bi-Te-Se melt directly from the sulfide melt is questionable. Although the melting point of parkerite has yet to be determined it is not unrealistic to suppose that it's melting temperature could be reached during regional metamorphism. Such a process may well have caused some of the Bi-Te mineral(s) within the sulfide veins to melt, producing a liquid that re-equilibrated with the surrounding sulfides and scavenged Se from them. This now Bi-Te-Se liquid went on to crystallize the Se-pilsenite analyzed.
Figure 4.18. Proposed paragenetic sequence for precious metal minerals and Bi-chalcogenides in magmatic low-sulfide mineralization from the North Range. Common precious metal minerals are emboldened, with sulfide phases and Bi-Te melts in red. Sulfide temperatures from Craig and Kullerud (1969), precious-metal and Bi-chalcogenide position based on their maximum thermal stability, see text for references.
Figure 4.19. Proposed paragenetic sequence for precious metal minerals and Bi-chalcogenides in magmatic low-sulfide mineralization from the North Range. Common precious metal minerals are emboldened, with sulfide phases and Bi-Te melts in red. Sulfide temperatures from Craig and Kullerud (1969), precious-metal and Bi-chalcogenide position based on their maximum thermal stability, see text for references. Note: The origin of the polyphase aggregate forming Bi-Te-Pd-Ag-Sb melt from stockwork mineralization is uncertain and may have been sourced from a fractionated sulfide liquid in the footwall, or from the fractionation of contact sulfides.
Chapter 5

The Distribution of Chalcophile Elements in Samples from the Levack North, Wisner, Capre, Denison and McKim PGE-Cu-Ni Low-Sulfide Prospects within the Footwall of the Sudbury Igneous Complex; Canada

5.1 Abstract

Low-sulfide mineralization contains chalcophile element concentrations suggesting that it represents a combination of late magmatic sulfide liquid and hydrothermal mineralization. Samples of probable magmatic sulfide mineralization from the North Range present Cu and Ni concentrations, normalized to 100 % sulfide, show that they are composed of cumulus intermediate solid solution (iss) and heazlewoodite solid solution (hzss) in varying combinations. Furthermore, some samples have normalized compositions with Cu and Ni above the iss–hzss join, which are interpreted to result from the additional presence of solidified Cu–Ni sulfide liquid. South Range magmatic mineralization has compositions along the join between monosulfide solid solution (mss) and iss trend. Precious metals (Pt, Pd, Ag and Au) and semimetals (As, Se, Sb, Te, Bi and Pb) are enriched in magmatic sulfides from the North Range low-sulfide properties relative to contact and sharp-walled mineralization, trends mirrored at the McKim property. These increases suggest that the metals of interest behaved incompatibly with mss, iss and hzss. Quartz–carbonate–sulfide veins from the North Range and McKim properties are considered to be hydrothermal in origin and have precious metal and semimetal contents and inter-element ratios similar to the magmatic footwall mineralization. Interaction between magmatic sulfides and hydrothermal fluids was likely buffered by the mineral assemblage of the ore, resulting in hydrothermal deposits with a similar chemical signature, although some selective scavenging is clearly in operation with PPGE, Ag, Au and semimetals having been preferentially remobilized from contact mineralization. The latter point is borne out by data from the Denison property where inclusion-bearing sulfide veins show strong pervasive alteration to pyrite and marcasite, likely due to an interaction with a metamorphic hydrothermal fluid. In contrast to the flat
precious metal profile of magmatic sulfide veins from the Denison property and contact ores from the Crean Hill mine, mineralization of probable (QCS) and possible (stockworks and disseminations) metamorphic hydrothermal origin shows depletions in IPGEs and enrichments in PPGEs, Au and Ag, suggesting selective remobilization.

Increases in the dissolved precious metal content of base-metal sulfides when compared to their equivalents from contact and sharp-walled vein systems indicate the enriched nature of the residual sulfide liquid and the ability of hydrothermal fluids to scavenge metals. Levels of Ag within chalcopyrite, Pd within pentlandite, and Se within Ni sulfides from North Range low-sulfide mineralization fall well above those of contact and sharp-walled vein samples. Mass balance for North Range mineralization indicates that significant quantities of Ag and Se are hosted by sulfide. However, the low modal abundance of pentlandite limits its effects on the Pd budget. In contrast the bulk of the remaining elements of interest (As, Sb, Te, Pt, Au, Pb and Bi) occur in discrete phases. Levels of dissolved metals in sulfide vein base-metal sulfides from the Denison property are similar to those shown by material from the Crean Hill mine. In contrast, QCS, veinlet and stockwork mineralization concentrations show enrichments in dissolved elements ranging from minor to significant. Samples from the McKim property show noticeable enrichments in Se and Pb in all major sulfides, Pd and Bi in pentlandite and Ag in chalcopyrite and pentlandite, when compared to sulfides from the Little Stobie mine. Such enrichments match those from the North Range deposits and as such are interpreted as reflecting the presence of fractionated sulfide liquids producing sulfide veins, veinlets and disseminations, with hydrothermal fluids interacting with and scavenging metals from both contact and footwall sulfides to produce QCS veins. The mass balance for South Range mineralization produces levels which are dominantly in keeping with those from comparable North Range mineralizing styles and the published literature. The proportion of Ag dissolved in sulfides are lower than in North Range mineralization and reflect the lower modal abundance of chalcopyrite, with Ag also hosted by pentlandite. In contrast a greater fraction of Pd is dissolved in pentlandite, despite measurements showing that dissolved concentrations are lower than those from North Range sulfide veins. The mass balance identified an average of 9.52 to 70.45 % of Pd in solid solution, likely resulting from the higher modal abundance of pentlandite compared to North Range mineralization.
Where present, gersdorffite from the South Range hosts significant quantities of Pd, Sb, Bi, Pt and Au in solid solution compared to the base-metal sulfides. However its low modal abundance reduces its effects upon the distribution of these elements.

5.2 Introduction

The distribution of chalcophile elements in magmatic sulfide deposits depends on their grain-scale distribution both at the liquidus and below the solidus during subsequent cooling or metamorphism. During cooling and crystallization the chalcophile elements are distributed among coexisting solids and melt according to their equilibrium partitioning behavior. If residual liquid is physically removed from the early-formed cumulus phases, a large-scale spatial fractionation will be imparted onto the chalcophile element distribution. Superimposed on this fractionation will be the grain-scale fractionation imposed by liquidus and subsolidus redistribution of chalcophile elements among coexisting phases during cooling.

Extensive experimental work on the Ni–Cu–Fe–S–O system and the subsidiary systems has been undertaken over the past sixty years in attempts to understand the sulfide assemblages observed within magmatic sulfide systems and the partitioning of chalcophile elements between these phases (Kullerud and Yund, 1962; Craig and Kullerud, 1969; Distler et al., 1977; Fleet and Stone, 1991; Fleet et al., 1993; Fleet and Pan, 1994; Ebel and Naldrett, 1996; Li et al., 1996; Fleet et al., 1999; Ballhaus et al., 2001; Barnes et al., 2001; Mungal et al., 2005; Helmy et al., 2010).

High temperature phase relations within the Ni–Cu–Fe–S–O system are dominated by monosulfide solid solution (mss), which begins to crystallize below a maximum of 1192 °C (Craig and Kullerud, 1969), with complete solid solution between the Fe_{1-x}S and Ni_{1-x}S end-members achieved at or below 992 °C (Kullerud and Yund, 1962; Craig and Kullerud, 1969). The lower temperature phase relations of mss are not well documented, although it is clear that below 254 °C monoclinic pyrrhotite becomes stable, with hexagonal pyrrhotite (stable below 1190 °C) becoming unstable below 100 °C (Vaughan et al., 1971; Raghavan, 2004c). Monosulfide solid solution compositions towards the Ni_{1-x}S end member persist to around 379 °C, at which time a phase transformation to millerite occurs (Kullerud and Yund, 1962).
Although mss (in the form of pyrrhotite) dominates in sulfide ores, magnetite is commonly observed to be present in significant quantities. Its presence within the sulfide assemblage was interpreted by Naldrett (1969) to reflect the crystallization of sulfide liquids along the mss-magnetite cotectic. Although not commonly thought of as a major constituent of sulfide liquids, experimental data indicates that within sulfide liquid compositions with low concentrations of Cu and Ni, oxygen concentrations can exceed those of sulfur (Doyle and Naldrett, 1987; Mungall et al., 2005). The inability of sulfide liquids to crystallize abundances of magnetite in excess of mss was interpreted by Doyle and Naldrett (1987) and Naldrett (1989) to be the result of higher levels of Ni and Cu within natural sulfide liquid systems expanding the mss stability field, a supposition that was borne out by Mungall et al. (2005).

Between 862 and 865 °C the reaction of mss and Ni-rich sulfide liquid results in the formation of heazlewoodite solid solution (hZSS), referred to as (Ni, Fe)₃₋ₓ S₂ in earlier works (Craig and Kullerud 1969; Sugaki and Kitakaze, 1998). At 610 °C hZSS is lost as a stable phase due to its reaction with mss and a Ni-bearing residual sulfide liquid, which produces pentlandite + bornite solid solution + mss (Craig and Kullerud, 1969; Sugaki and Kitakaze, 1998). Crystallization of Cu-phases begins with intermediate solid solution (iss) between 960 and 850 °C (Craig and Kullerud, 1969; Raghavan, 2004a), which breaks down to chalcopyrite + Fe-iss at below 590 °C to ~550 °C, or chalcopyrite and cubanite at 590 °C (Craig and Kullerud, 1969; Barton, 1973; Cabri, 1973).

The partitioning of precious metals between silicate melts (typically basaltic) and sulfide liquids, and sulfide liquids and mss have been extensively studied, with the majority of data presenting a consistent pattern. The partitioning of Cu, Ni and the noble metals indicate their strong affinity with sulfide liquid, with experimental partition coefficients (Dᵢ) of 274 ± 34 and 245 ± 33 to 1303 for Ni and Cu (Rajamani and Naldrett, 1978; Ripley et al., 2002). The noble metals display a significant range of D values, reflecting the various methods, silicate and sulfide compositions and buffering regimes used during experimental runs. The D_{sulfide melt/silicate liquid} for Os, Ir, Ru, Rh Pt, Pd and Au are all >> 10000, indicating their compatibility in sulfide melts and thereby providing a process for concentrating them within magmatic sulfides sourced from mafic silicate liquids (Stone et al., 1990; Fleet et al., 1991; Crocket et al., 1992; Peach et al., 1994; Fleet et al., 1996, 1999). The partitioning of Cu, Ni and the noble metals between mss and sulfide melt has been experimentally established for Fe–Ni–S and Fe–Ni–Cu–S liquids (Distler et al., 1977; Fleet and Stone, 1991; Fleet et al., 1993, 1999;
Fleet and Pan, 1994; Ebel and Naldrett, 1996; Li et al., 1996; Ballhaus et al., 2001; Barnes et al., 2001; Mungall et al., 2005). Copper behaves incompatibly, with $D_{\text{mss/sulfide liquid}}$ of between 0.15 and 0.27 (Li et al., 1996; Ballhaus et al., 2001; Mungall et al., 2005), with the partitioning of Ni seemingly dependent upon both temperature and S content (Ebel and Naldrett, 1996; Li et al., 1996, Mungall et al., 2005, 2007). The $D_{\text{Ni mss/sulfide liquid}}$ varies between 0.19 to 1.17, becoming more compatible with mss as temperature decreases or within S saturated or oversaturated systems. The partitioning behaviour of the noble metals displays a split between the IPGEs (Ir, Os, Ru and Rh) and, the PPGEs (Pt and Pd) and Au. The IPGEs display compatible behavior with mss with $D_{\text{mss/sulfide liquid}}$ values of between 0.061 and 14.32 for Ir, 3.7 and 10 for Os, 1.80 and 17.43 for Ru and, 0.25 and 10.93 for Rh (Fleet et al., 1993; Ballhaus et al., 2001; Barnes et al., 2001; Mungall et al., 2005). In contrast the PPGEs and Au behave incompatibly with mss, with $D_{\text{mss/sulfide liquid}}$ values of between 0.004 and 0.26 for Pt, 0.012 and 0.43 for Pd and 0.006 and 0.09 for Au (Fleet et al., 1993; Ballhaus et al., 2001; Barnes et al., 2001; Mungall et al., 2005). Barnes et al. (2001) noted that the mss/sulfide liquid partition coefficients for Rh, Ir, Pt and Pd are sensitive to S content, with the D's increasing from S undersaturated to S oversaturated runs. The partitioning of the above elements is reflected within magmatic sulfide mineralization. Cumulates comprising significant quantities of mss (recrystallized to pyrrhotite and pentlandite) display normalized enrichments in Ni and the IPGEs with mineralization resulting from the residual sulfide liquid enriched in Cu, Pt, Pd and Au. This pattern is particularly clear within deposits where the residual sulfide liquid has migrated away from the mss cumulates, with Sudbury the primary example. The Sudbury camp is marked by strong compositional differences between the Ni-IPGE bearing mss-iss contact ores and the Cu-PPGE-Au enriched mss-iss and iss-hzss sharp-walled veins situated in the footwall, which reflect the partition coefficients outlined above.

To date partitioning data for the semimetals between sulfide liquids and phases crystallizing from them is extremely scarce, with partition coefficients for Se, As, Sb, Te and Bi established by Helmy et al. (2010). Antimony, Te and Bi produced $D_{\text{mss/sulfide liquid}}$ values of $< 0.03$, with Se and As somewhat less incompatible in mss with values between 0.65 and 0.66, and 0.01 and 0.39 respectively. Partitioning behavior for base and precious metals between the residual sulfide liquid and iss remain nearly unknown, a reflection of the more complex phase relations experienced at lower temperatures where mss, hzss and iss can all be present in varying abundances. To date iss/sulfide liquid partitioning has only tentatively been
established for Pt and Pd, which are simply referred to as incompatible with iss (Peregoedova, 1998; Peregoedova and Ohnenstetter, 2002).

Given the difficulties in experimentally determining the evolution of sulfide liquids crystallizing mss, iss and hzss, analysis of natural magmatic sulfides offers the possibility of establishing the broader trends that can be expected. Through the analysis of contact, sharp-walled vein and low-sulfide mineralization, the evolution of a sulfide liquid(s) at Sudbury can be studied, with LA-ICP-MS analysis offering a window into the partitioning of precious and semimetals between sulfide phases within these three distinct mineralizing styles.

The ability of sulfide minerals in Ni–Cu–PGE deposits to sequester ppb to wt % concentrations of platinum group elements (PGE) has been established for about 30 years (Cabri and Laflamme, 1981). Pyrrhotite, pentlandite and to a lesser degree chalcopyrite are common hosts for PGE and semimetals (Cabri et al., 1984, 1985; Rucklidge et al., 1992; Chai et al., 1993; Li et al., 1993; Ballhaus and Sylvester, 2000; Barnes et al., 2006, 2008). In situ analyses of base-metal sulfides from the Sudbury Igneous Complex (SIC) are limited. Published values indicate a range of PGE concentrations from 0.3 ppb to 4 ppm (sulfarsenide not included), whilst semimetals (e.g., Se) are present in concentrations up to 238 ppm (Cabri et al., 1984; Rucklidge et al., 1992; Huminicki et al., 2005). These concentrations contribute only a minor proportion of the PGE budget, the remainder of which occurs within discrete phases, chiefly Pt and Pd tellurides and bismuth-tellurides on the North Range and Pt arsenides and Pd bismuth-tellurides on the South Range (Cabri and Laflamme, 1976).

The timing of separation of discrete PGM from the volumetrically dominant base-metal sulfide phases, including melt and crystals, is not well known. Some PGM may form by direct precipitation from PGE-rich residual sulfide melts, whereas others might form by subsolidus breakdown of PGE-rich solid phases. The formation of platinum group minerals (PGM) through the exsolution of PGEs from initially PGE-rich base-metal sulfides during subsequent recrystallization was proposed by Barnes et al. (2008). This proposal was partially backed by Hutchinson and McDonald (2008), who suggested that some early crystallization of PGMs driven by semimetal contamination of sulfide liquids from country rocks was followed by later growth of PGMs through the exsolution process. To date the bulk of in situ analyses of PGE contents of base-metal sulfides from Sudbury have focused either on samples of unspecified origin (Cabri et al., 1984; Rucklidge et al., 1992), the Creighton and McCreedy East contact deposits (Dare et al., 2010b, 2011), or from relatively unFractionated
material from Offset dykes (Huminicki et al., 2005); only Li et al. (1993) analyzed samples from a footwall sharp-walled sulfide vein system. Much remains unknown about the distribution of chalcophile elements at the grain scale in Sudbury ores and the implications this holds for large-scale fractionation of sulfide liquids during magmatic or hydrothermal processes.

5.3 Analytical Methods

Whole rock data was provided by Vale-Lonmin Joint Venture and comprised the results of two distinct analytical routines: 1) A 36 element low-grade assay, termed the MG-package, containing amongst others Ni, Cu, S, As, Pt, Pd, Rh, Au, Ag, Zn, Pb, Bi and Sb, and 2) A 12 element high-grade assay, termed the MX-package, which contained Ni, Cu, S, As, Co, Fe, Pt, Pd, Au, Pb, Zn and occasionally Mg. In some instances both packages were applied to the same sample.

Samples submitted for assay by the Vale-Lonmin joint venture were analyzed by ALS Chemex labs, Sudbury. Precious metal analysis for the MG-package was done using the PGM-ICP23 low-grade PGM assay. A 30 g sample was combined with fire assay fluxes (lead oxide, sodium carbonate, borax and silica) and 8 mg of inquarted Au-free silver. The mixture is heated between 850 and 1060 °C in increasing increments, over a 60 minute period. Upon cooling the Ag + Pt, Pd and Au bead is recovered and heated within a microwave oven on high power for 2 minutes with 0.5 mL of dilute nitric acid. The solution is cooled, 0.5 mL of concentrated HCl is added, and it is returned to the microwave for a further 2 minutes at half power. The solution produced is diluted to 4 mL with 2 % HCl and measured for Pt, Pd and Au by ICP-AES. The PGM-ICP27 ore grade assay used in the MX-package follows the same steps, with the precious metal bearing solution being diluted to 10 mL with 2 % HCl before analysis by ICP-AES. Additional elements for the MG-package were analyzed using the 33 element ME-ICP61 assay, excluding tungsten. 0.25 g of powdered sample was digested by four acid leach (HNO₃-HClO₄-HF-HCl), with the residue topped up with dilute HCl. The solution produced was analyzed by ICP-AES. Base-metal assays for the MX-package were undertaken using the ME-ICP81 routine for ore and high grade materials. A 0.2 g powdered sample was heated with 2.6 g of sodium peroxide flux at 670 °C, until fully molten. Upon cooling the sample was dissolved in 30 % HCl, with the resulting solution analyzed by ICP-
AES. The application of the MG and MX-packages was based on a visual estimation of S content with sample containing > 10 % sulfide analyzed using the MX-package. Although the MX-package was rarely applied to samples containing around 1 to 2 % sulfide in the majority of cases it was used for the analysis of sulfide veins, with all other mineralizing styles dominantly analyzed using the MG-package.

Neither the MG or MX-package provided values for Se or Te, with Ag values somewhat sporadic due to its exclusion from the MX-package. A total of 100 samples (26 contact and sharp-walled vein ores, 72 low-sulfide samples and 2 standard materials) were analyzed by Actlabs Canada using the Ultratrace 2 routine to gain concentrations of Se, Te and where appropriate Ag. The Ultratrace 2 package comprises the digestion of a powdered 0.5 g sample by aqua regia, for 2 hours at 90 °C. Fifty-nine elements were analyzed by ICP-MS (Perkin Elmer SCIEX ELAN 6000, 6100 or 9000) with an additional three (Ti, P and S) analyzed by ICP-OES. Two standard materials JSd-3 (marine sediment) and WMS-1 (massive sulfide, Wellgreen Complex, Yukon) were included within the sample run to monitor accuracy. Where concentrations of Cu, Ni and/or Ag exceeded the upper analytical limit of the Ultratrace 2 routine they were measured using the 8-AR package. For these samples an additional 0.5 g of powdered material was digested by aqua regia with the resulting solution diluted by 250 ml of 18 megaohm (ultra-pure) water. Samples were analyzed on a Varian Vista 735 ICP-OES.

Concentrations of Ir, Rh and Ru were also not analyzed by the routine Vale-Lonmin exploration assay so 30 15 g samples were submitted for NiS-fire assay with an ICP-MS finish following Richardson and Burnham (2002), at the Geolabs of the Ontario Geological Survey in Sudbury. Detection limits for the assay methods listed above can be found in Appendix A.

The recalculation of whole-rock data to 100% sulfide (i.e., the calculation of a sulfide norm) was dependent upon the observed sulfide assemblage. The majority of North Range material contained chalcopyrite and millerite and as such samples were initially calculated assuming all Cu in chalcopyrite and all Ni in millerite, with the required amount of S used to satisfy stoichiometry. Any excess S was attributed to pyrite, in keeping with observations. Where insufficient S was present two separate approaches were taken: (1) Assemblages containing pentlandite and millerite were assumed to contain all Cu as chalcopyrite with the corresponding S removed. The Ni concentration required to produce all millerite or all
pentlandite based on the remaining S was calculated, with those values incrementally iterated until a satisfactory solution was achieved, with the result used to calculate the $\alpha$ factor by which all whole rock concentrations were multiplied to give their nominal concentrations in 100% sulfide. Due to the coarse nature of the increments applied (1% steps) this method typically produced a percent sulfide value within $\pm 0.1\%$ of test compositions. This method was only applied to sulfide veins from the Levack North and Capre properties where pentlandite was commonly observed. (2) If no pentlandite had been observed i.e. sulfide veins from Wisner and IRV, QCS and disseminated mineralization from all North Range properties, negative calculated sulfur values were attributed to the presence of bornite. Calculation assumed that all Ni occurred as millerite with stoichiometric concentrations of S removed. The remaining S was used to calculate the amount of Cu required to produce only chalcopyrite or only bornite, with these values incrementally iterated until a satisfactory solution was achieved.

South Range samples were primarily composed of pyrrhotite + pentlandite + chalcopyrite and were recalculated assuming all Cu in chalcopyrite and all Ni in pentlandite, with any remaining S attributed to pyrrhotite. Where relevant, arsenic was attributed to gersdorffite-cobaltite with a stoichiometric 1:1 As:S ratio used to remove sufficient sulfur before recalculation to chalcopyrite, pentlandite and pyrrhotite. The spreadsheets employed and the resulting data can be seen in Appendix C.

LA-ICP-MS analysis was undertaken at the Department of Geology, University of Toronto using a VG PlasmaQuad ExCell ICP-MS, attached to a New Wave UP-213 Nd-YAG laser. Ablated material was transported to the ICP-MS by He carrier gas, at a rate of 1 l/min. Sample points were given a pre-analysis traverse to minimize surface contamination, with analyses lasting 100 seconds following an initial 20 second laser ‘warm-up’ before each point, during which the laser shutter was closed. Isotopes of S, Ni, Cu, As, Se, Ru, Rh, Pd, Ag, Sb, Te, Re, Os, Ir, Pt, Au, Pb and Bi were measured synchronously, with dwell times of 10 ms. The elements analyzed reflect those within the MSS5 standard used during runs and cover the majority of the precious metals and semimetals of interest. Other elements of interest i.e. Zn and Sn were not included as this would have required additional standards to be added to the run, thereby increasing the run time, decreasing the number of points that could be analyzed during a run, and increasing the chances of technical issues and variations in counts per second that could be caused by having to open the sample holder multiple
times. Isotopes were selected based on their abundance and to exclude the possibility of argide interferences, i.e. $^{63}\text{Cu} + ^{40}\text{Ar} = ^{105}\text{Pd}$. When possible, additional isotopes of the same element were analyzed to ensure the accuracy of the collected data. Analyses were undertaken at 65% op, 10 Hz, with a 30 μm beam diameter, over a linescan length of 50 to 250 μm, with the laser typically producing around 0.075 mJ/10.5 J/cm$^3$. A 2 minute ‘wash-out’ was incorporated between points, during which only the carrier gas entered the ICP-MS. The laser was tuned for maximum counts using the NIST610 standard glass on $^{115}\text{In}$, with oxide production rates of less than 1.5 percent. Analytical runs of up to 14 points were bracketed by two analyses of the in-house standard MSS5, a homogeneous Fe-Ni-Cu-S sulfide PGE and semimetal doped material. Table 5.1 shows the average concentrations of metals within MSS5, as determined by LA-ICP-MS at the University of Toronto and Université du Québec à Chicoutimi and by ICP-MS at the Université du Québec à Chicoutimi. An additional in-house PGE free (CW-1) or low-PGE (CW-2) doped Fe-Ni-Cu-S standard was inserted into the routine during short runs to monitor accuracy. Interference corrections for $^{100}\text{Rh} (^{60}\text{Ni})$, $^{101}\text{Rh} (^{61}\text{Ni})$ and $^{103}\text{Rh} (^{63}\text{Cu})$ were made using pure Ni and Cu metals, with correction factors calculated for each run. Data reduction and error estimation was done with Glitter© software. Internal standardization was achieved using S. The S concentration of each major sulfide phase was established by EMP, with this value being entered into Glitter© for the relevant phase; e.g., 34.94 wt % S for chalcopyrite. Sulfur values are therefore known for the standard material (MSS5) and for the sulfide being analyzed, with isotopes of interest e.g. $^{105}\text{Pd}$, being compared to $^{32}\text{S}$ to produce an intensity ratio from which a concentration can be derived.

Time resolved spectra for the elements of interest were consistently monitored during analysis and data processing in an attempt to limit erroneous data caused by micro-inclusions of precious or semimetal-rich phases. Spectra were considered to be suitable if a near constant rate of counts were maintained for an element during the analysis. Sudden increases in the counts per second, producing steep-sided peaks within the spectra were interpreted to be the result of micro-inclusions and the data for that element was either discarded or the peak was selectively removed if a region of consistent counts during the analysis existed. Phases that presented polishing pits, e.g. pentlandite, polydymite and violarite, and polishing scratches, e.g. pyrite often presented a slightly more uneven signal. Where possible transects were selected to avoid pitted areas, although this was not always possible. Although the count
rate for these uneven areas did not remain constant, spikes due to micro-inclusions were still resolvable.

Internal standardization of sulfides and sulfarsenides employed S values gathered on a Cameca SX-50 electron microprobe (EMP), using a simplified sulfide routine. The following X-ray lines, standards and count-times were employed: Fe Kα (pentlandite, 40 s), Ni Kα (pentlandite, 80 s), Cu Kα (chalcopyrite, 20 s), Co Kα (cobaltite, 80 s), Se Kα (ZnSe, 200 s) and S Kα (pentlandite, 80 s), under beam conditions of 30 kV, 50 nA.

Table 5.1. Analysis of internal standard material MSS5, all values in ppm. MSS5 Average = calibrated to S content of MSS5 (n = 400). U of T = Internal analysis Department of Geology, University of Toronto, PGE + Re from internal sulfide standard, values calibrated to Ni, all remaining metals calibrated to Cu in NIST 610 reference material (n = 5). UQAC laser = LA-ICP-MS analysis Université du Québec à Chicoutimi. UQCS Sol. = ICP-MS analysis Université du Québec à Chicoutimi, note that Os and Ir concentrations are not from the isotopes employed in this study and that Os, Ir and Pt concentrations are likely reduced due to the difficulties in keeping these elements in solution. * = 188Os, ** = 191Ir

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<th>Rh</th>
<th>Pd</th>
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<th>Ag</th>
<th>Sb</th>
<th>Te</th>
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</tbody>
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5.4 Whole rock compositions

The comparison of 100 % sulfide normalized precious metal concentrations between distinct mineralizing styles and ore zones is commonly achieved through the normalization of these values to published concentrations within CI chondrites or pyrolite. Such a comparison is suitable for deposits formed from mantle derived melts, e.g. the Bushveld Complex, South Africa and Noril'sk, Russia; however, the Sudbury melt sheet represents a magma of lower crustal origin, with a minor input from the impactor (Mungall et al., 2004). Whole-rock data within this study have therefore been normalized to an average composition for the initial sulfide liquid (Pt, Pd, Au, Ir, Ru and Rh) (Mungall et al., 2005) and average values for the lower crust (Ag, As, Se, Sb, Te, Bi, Pb) (Wedepohl, 1995; Gao et al., 1998).

Normalization of contact and sharp-walled vein ores to CI chondrite and pyrolite by previous workers have yielded two distinct trends, 1) levels of Ni and the IPGEs are enriched within contact ores and comparatively depleted in sharp-walled veins and 2) the PPGEs, Au and Cu
are strongly enriched within sharp-walled veins, with contact mineralization also enriched, although not as strongly. Such observations are consistent with the formation of the contact ores through mss crystallization which sequestered significant concentrations of Ni and the IPGEs, with the residual sulfide liquid, containing the mss incompatible Cu, PPGEs and Au, entering the footwall to produce the sharp-walled vein systems (Naldrett, 1984; Naldrett and Barnes, 1986; Li et al., 1992; Mungall et al., 2005; Mungall, 2007). These trends are also visible within the initial sulfide liquid – normalized plots used here, with IPGE levels within contact ores remaining around 1, suggesting that mss crystallization removed the majority of Ir, Ru and Rh present in the original sulfide melt, whilst sharp-walled veins display significant enrichments in the PPGEs, Au and Ag relative to contact material.

A comparison of averaged low-sulfide mineralization from all properties to contact and sharp-walled vein ores reveals that they are enriched with respect to Pt, Pd, Au, Ag and the semimetals (As, Se, Sb, Te, Bi and Pb) and depleted in the IPGEs (Figures 5.1A and 5.3A).

The normalized concentrations of Pt, Pd and Au from sharp-walled vein samples display a relatively flat profile, reflecting approximately equal average enrichment of each of these elements compared to the primary sulfide melt. This trend is not maintained within sulfide vein samples from the North Range properties which display a noticeable increase in Pd relative to Pt and Au (excluding Wisner). In contrast, IRV mineralization displays levels of Pt equal to or greater than Pd. The variation between these mineralizing styles is consistent with observations from Farrow et al. (2005) who noted that Pt/Pd ratios increased within the lower modal sulfide mineralizing styles, i.e. IRV, when compared to more sulfide rich material i.e. sulfide veins.

The precious metal patterns for QCS mineralization from the North Range properties must be treated tentatively due to the limited dataset available (Figure 5.1C). Trends from the Wisner and Capre properties clearly indicate that QCS mineralization is enriched in the PPGEs, Au and Ag when compared to an average sharp-walled vein composition. The lack of a consistent pattern for Pt, Pd and Au from the two properties may reflect the distinct hydrothermal fluids(s) remobilizing precious metals within the Wisner and Capre footwalls, or it may reflect the limited number of analyses and therefore the skewing effects of outlying data points. The Levack North trend is taken to be unrepresentative as it reflects only a single analysis. Disseminated mineralization from the Levack North property displays a different trend, showing elevated levels of Pd relative to Pt and Au, a pattern mirroring that of sulfide
vein mineralization (Figure 5.1D). Disseminations from the Wisner and Capre properties display comparable or slightly enriched levels of Pt relative to Pd. In both instances Au levels are below those for Pt and Pd. This trend is similar to that IRV mineralization and suggests that the disseminated mineralization from the three North Range properties may not be the result of the same process.

Normalized precious metal trends from the Denison property define a relatively flat profile for sulfide vein material, similar to that of the nearby Crean Hill contact mineralization (Figure 5.2A). The remaining mineralizing styles (QCS, veinlet, stockwork and disseminations) show pronounced IPGE profile depletions (excluding stockwork mineralization) and clear enrichments in the PPGEs, Au and Ag relative to average contact and sulfide vein values (Figures 5.2 B to E). Concentrations of the PGEs within sulfide vein mineralization from Denison are similar to those from the Crean Hill contact orebodies. Based on the observations of PPGE and Au enrichment and IPGE depletions between contact and sharp-walled veins from the North Range it would be expected that the sulfide veins of the Denison property would follow a similar pattern. The lack of a clear separation therefore implies that massive sulfides from the contact have been sheared into the footwall.

Stockwork mineralization displays a unique trend of extreme enrichments in PPGEs, Au and Ag, with levels two orders of magnitude greater than the Crean Hill contact ores. This contrasts with the levels of the PPGEs, Au and Ag within QCS, veinlet and disseminated mineralization which are typically less than one order of magnitude higher than Crean Hill ores. It is uncertain whether the Ir and Ru values for stockwork mineralization are representative of the mineralizing style as a whole, or are simply the effect of the extremely limited number of Ni-sulfide fire assay analyses \( n = 2 \). All mineralizing styles from the McKim property display levels of PPGEs, Au and Ag in excess of the proximal Little Stobie orebodies, with the IPGEs relatively depleted. The similarity of these patterns to those of North Range sharp-walled vein and low-sulfide mineralization imply that a comparable process has occurred within the McKim footwall (Figure 5.2A). Because most of the sulfide vein analyses from the McKim property were produced using the MX-package,j7 the number of Ag data points is well below that of the other precious metals (Table 5.2 and 5.3). Although the elevated levels of Ag relative to the Little Stobie orebodies displayed in Figure 5.2A is consistent with the high abundance of hessite within the observed sulfide vein thin sections it should be regarded with caution.
Normalized semimetal trends for low-sulfide mineralization from North Range properties display profiles morphologically consistent with analyzed sharp-walled vein material. Levels of all semimetals associated with sulfide vein mineralization from the North Range are observed to be in excess of those from contact and sharp-walled vein mineralization, although not significantly above the latter. Levels of As, Te, Pb and Bi from IRV and disseminated mineralization displayed levels significantly above contact and sharp-walled vein mineralization.

Average concentrations of Se from IRV samples were comparable with sharp-walled vein mineralization, whilst Sb from Levack North and Capre were enriched compared to sharp-walled vein material, with IRV mineralization from Wisner comparatively depleted (see Figures 5.3 A to C). Antimony levels from disseminated mineralization were significantly above average sharp-walled vein concentrations. Semimetal levels from QCS mineralization from the Levack North and Wisner properties were comparable to the average sharp-walled veins, with the exception of Bi from Levack North which was significantly enriched. In contrast normalized levels of As, Se, Te, Pb and Bi in QCS mineralization from Capre were enriched compared to average sharp-walled veins.

Semimetal profiles for mineralization from the Denison property display a similar morphology to that produced by samples from the Crean Hill contact orebodies. Semimetal levels from veinlet, QCS and stockwork mineralization are enriched when compared to the average Crean Hill profile (Figure 5.4A). The substantial As enrichment when normalized to lower crustal values reflects the presences of gersdorffite–cobaltite and accessory nickeline, with the similar trend displayed by veinlet, QCS and stockwork mineralization also likely the result of sulfarsenides (Figures 5.4 B to E). Semimetal levels from Denison sulfide vein samples are also well above those from Crean Hill. The comparatively depleted As and Sb levels reflect the presence of the aforementioned sulfarsenides within the Crean Hill samples.

The Little Stobie semimetal profile presents a morphology and levels of enrichment relative to the lower crust that are consistent with contact material from the North Range. Normalized levels of the semimetals from all footwall mineralizing styles at McKim are consistently above those of the Little Stobie contact orebodies. Veinlet, QCS and disseminated mineralization display a significant enrichment in normalized semimetals values relative to the Little Stobie ores, with sulfide veins the least enriched, with levels of As and Pb akin to the Little Stobie samples.
The application of 100 % sulfide normalized plots to the origin of sulfide ores and the fractionation of chalcophile elements has been applied over recent decades (e.g., Hoffman et al., 1979; Naldrett et al., 1982; Mungall, 2007; Mungall et al., 2010). Interpretation of compositions of contact and sulfide ores by Mungall (2007) indicated that they are best envisaged as cumulates comprised of mixtures of monosulfide solid solution (mss) at the contact and either mss and iss or iss and hzss in the footwall. Plots of low-sulfide material of probable magmatic origin from the three North Range properties indicate that the majority of material falls along the iss–hzss mixing line (Figure 5.5), with a slight deflection to the right due to the high modal abundance of millerite. The presence of pyrite within these samples is marked by a shift towards diminished Cu and Ni, however this trend is not consistent with the mss–iss mixing line, suggesting that the Fe-mss input into these mineralizing styles is low and consistent with the lack of pyrrhotite. Mungall (2007) suggested that the sulfide liquid from which the sulfides crystallized would possess a composition to the right of the iss–hzss mixing line, with those points falling within this region considered to include some residual sulfide liquid. Several points from this study fall not only within the range of Cu-rich compositions suggested by Mungall (2007) but are also more Ni-rich, producing a separate near vertical trend. The plotting of South Range material (Figure 5.6) produced compositions dominantly falling along the mss–iss mixing line, consistent with the pyrrhotite + pentlandite + chalcopyrite assemblage commonly observed. A number of points displaying a shift above the mss–iss trend resulting from the addition of iss and hzss from a fractionated residual sulfide liquid, although this input is only discernible in the minority of cases.
Table 5.2 Average whole rock analyses for the chalcopyrite elements of interest from the Levack North, Wiser and Capre properties with corresponding α factors.
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<th>Pd (ppm)</th>
<th>Au (ppm)</th>
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<th>Ir (ppm)</th>
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<th>en (%)</th>
<th>en (%)</th>
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Table 5.3. Average whole rock analyses of the Denison and McKim properties, with corresponding α factors.
The fractionation of precious metals during the crystallization of sulfides from a sulfide melt is reflected by the composition of the ore produced. Plots of 100% sulfide normalized Cu vs. Pt, Pd or Au failed to identify any clear distinction between the magmatic low-sulfide mineralizing styles, however, when put in the context of the larger Sudbury system a pattern is visible. Plots of the Pt, Pd and Au contents of North Range material (Figures 5.7, 5.8 and 5.9) indicate an increase in precious metals resulting from their concentration along with Cu, in the residual sulfide liquid during mss crystallization (Mungall et al., 2005). The sulfide ore crystallizing from this enriched residual liquid, i.e. sharp-walled veins, generally contain levels of Pt, Pd and Au comparable with, or above the upper limit of contact compositions. The compositions of low-sulfide material are comparable to sharp-walled vein compositions with respect to Cu, however Pt, Pd and Au are all noticeably enriched, suggesting that the magmatic portions of low-sulfide mineralization have crystallized from, or contain a larger proportion of a more fractionated sulfide liquid and therefore that Pt, Pd and Au are behaving incompatibly with iss and hzss, consistent with the very limited experimental data for the PGEs (Peregoedova and Ohnenstetter, 2002). This trend is matched by low-sulfide samples from the South Range properties (Figures 5.10, 5.11 and 5.12), although compositions do not become as rich in Cu and the precious metals when compared to North Range footwall ores, suggesting a lesser degree of fractionation.
Figure 5.1. Average North Range 100% sulfide precious metal values by mineralizing style normalized to the composition of the initial Sudbury sulfide melt. (A) North Range sulfide vein, (B) North Range IRV, (C) North Range QCS and (D) North Range disseminations. Maximum and Minimum denotes the range of values from low-sulfide mineralization. Contact (N.R. Contact) and sharp-walled vein (N.R. Footwall) data from Naldrett et al. (1999), initial sulfide liquid composition from Mungall et al. (2005), Ag from Geo et al. (1998).
Figure 5.2. Average South Range 100 % sulfide precious metal values by mineralizing style normalized to the composition of the initial Sudbury sulfide melt. (A) South Range sulfide vein, (B) South Range veinlet, (C) South Range QCS, (D) South Range stockwork and (E) South Range disseminated. Maximum and Minimum denotes the range of values from low-sulfide mineralization. Crean Hill contact ore from Naldrett et al. (1999), Little Stobie contact ore from Hoffman et al. (1979), initial sulfide liquid composition from Mungall et al. (2005), Ag from Geo et al. (1998).
Figure 5.3. Average North Range 100% sulfide semi-metal values by mineralizing style normalized to lower crustal values. (A) North Range sulfide vein, (B) North Range IRV, (C) North Range QCS and (D) North Range disseminations. Maximum and Minimum denotes the range of values from low-sulfide mineralization. Contact (N.R. Contact) and sharp-walled vein (N.R. Footwall) data this study, lower crust composition from Gao et al. (1998), Te from Wedepohl (1995).
Figure 5.4. Average South Range 100% sulfide semi-metal values by mineralizing style normalized to lower crustal values. (A) South Range sulfide vein, (B) South Range veinlet, (C) South Range QCS and (D) South Range stockwork (E) South Range disseminations. Maximum and Minimum denotes the range of values from low-sulfide mineralization. Crean Hill and Little Stobie data this study, lower crust composition from Gao et al. (1998), Te from Wedepohl (1995).
Figure 5.5. Variations of 100 % sulfide normalized Cu (wt %) vs. Ni (wt %) for mineralized material from the North Range low-sulfide prospects. Modelled compositions for coexisting mss-cumulates (pink) and sulfide liquid (yellow) compositions from Mungall et al. (2005). Tick marks indicate the fractionation of liquid remaining or cumulates solidified.

Figure 5.6. Variations of 100 % sulfide normalized Cu (wt %) vs. Ni (wt %) for mineralized material from the South Range low-sulfide prospects. Modelled compositions for coexisting mss-cumulates (pink) and sulfide liquid (yellow) compositions from Mungall et al. (2005). Tick marks indicate the fractionation of liquid remaining or cumulates solidified.
Figure 5.7. Variation of 100 % sulfide normalized Cu (wt %) vs. Pt (ppm) for mineralized material from the North Range. Contact and sharp-walled vein data from Naldrett et al. (1999). Modelled compositions for coexisting mss-cumulates (pink) and sulfide liquid (yellow) compositions from Mungall et al. (2005). Tick marks indicate the fractionation of liquid remaining or cumulates solidified.

Figure 5.8. Variation of 100 % sulfide normalized Cu (wt %) vs. Pd (ppm) for mineralized material from the North Range. Contact and sharp-walled vein data from Naldrett et al. (1999).
Figure 5.9. Variation of 100 % sulfide normalized Cu (wt %) vs. Au (ppm) for mineralized material from the North Range. Contact and sharp-walled vein data from Naldrett et al. (1999).

Figure 5.10. Variation of 100 % sulfide normalized Cu (wt %) vs. Pt (ppm) for mineralized material from the South Range. Contact deposit data from Naldrett et al. (1999). Modelled compositions for coexisting mss-cumulates (pink) and sulfide liquid (yellow) compositions from Mungall et al. (2005). Tick marks indicate the fractionation of liquid remaining or cumulates solidified.
Figure 5.11. Variation of 100 % sulfide normalized Cu (wt %) vs. Pd (ppm) for mineralized material from the South Range. Contact deposit data from Naldrett et al. (1999).

Figure 5.12. Variation of 100 % sulfide normalized Cu (wt %) vs. Au (ppm) for mineralized material from the South Range. Contact deposit data from Naldrett et al. (1999).
5.5 LA-ICP-MS Analyses

Previous studies focusing primarily on sulfide blebs in mafic silicate rocks indicated substantial concentrations of precious metals can be hosted by common base-metal sulfides (BMS). In some occurrences, concentrations of PGE, Re, Au, and Ag within mss, pyrrhotite and pentlandite (Barnes et al., 2006, 2008) are much higher than published sulfide liquid/mss partition coefficients would seem to suggest. The presence of Pt and Pd in high ppb to ppm concentrations within Fe-sulfides would indicate that either rapid cooling of these droplets prevented equilibrium from being achieved between the mss and residual sulfide liquid, or that an unknown post crystallization redistribution of elements has occurred. As such the relevance of these studies to the fractionation of the PGEs within natural systems is questionable. The ore samples within this study represent the result of fractionation of substantial sulfide melt bodies and as such may be considered more representative of the fractionation experienced within large Ni-Cu-PGE camps. However, due to the limited number of contact and sharp-walled vein samples available for study any interpretations made here must be treated with caution.

Samples of contact and footwall mineralization used within this study were gathered from the collections of the Royal Ontario Museum (Main Orebody Crean Hill, Main Zone and 700 Zone McCreedy West and, Main Zone and Deep Cu Zone Strathcona deposits) and the Department of Geology, University of Toronto (Craig, Deep Cu Zone Strathcona and No. 1 orebody Little Stobie). Samples from the Craig mine have previously been analyzed by Searcy (1995). A full table of LA-ICP-MS data for contact, sharp-walled vein, and low-sulfide mineralization can be seen in Tables 5.4, 5.5 and 5.6.

5.5.1 Pyrrhotite

Pyrrhotite represents the dominant base-metal sulfide within contact ore from both the North and South Ranges, and it is also very common in North Range sharp-walled veins. Low-sulfide mineralization from the Denison and McKim prospects normally also contains pyrrhotite as the major sulfide. At North Range low-sulfide prospects pyrrhotite only occurs as small isolated un-analyzable crystals and micro-veinlets along chalcopyrite crystal margins, which constitute << 1 modal % of the visible sulfides. Pyrrhotite displays no consistent trace levels of the PGEs or Au, with Ag only occurring within sharp-walled vein
samples from the Deep Cu Zone, Strathcona mine. These samples display concentrations from below detection limit to 55.91 ppm, with Ag correlating strongly to Se (R = 0.53). Consistent concentrations of Ni, Se, Pb and Bi were detected in Po from all properties. Analyzed Ni concentrations range from below detection to 1.12 wt %, with the majority of analyses between 0.5 and 1 wt % Ni. Nickel displays no consistent variation in concentration between North Range contact and sharp-walled vein samples, although low-sulfide mineralization from the Denison and McKim properties does contain higher Ni concentrations than pyrrhotite from the Crean Hill and Little Stobie mines (Figure 5.13). Selenium is the most consistent trace element, with measureable concentrations detected in all pyrrhotite analyses. Selenium concentrations in pyrrhotite from contact mineralization are typically below 100 ppm, whereas in low-sulfide mineralization a significant number of Se analyses are greater than 100 ppm. The range of Se values from contact, sharp-walled vein and low-sulfide mineralization are, however, so broad as to make a clear separation of the mineralizing styles based on the dissolved Se content impossible. Concentrations of Pb and Bi are consistently in the ppb range with Pb concentrations from below detection to 11.08 ppm (avg. 0.97 ppm). Bismuth concentrations range from below detection to 6.13 ppm (avg. 0.56 ppm). Neither Pb nor Bi display any consistent variation in concentration between different types of mineralization, or correlations with any other trace elements.

5.5.2 Millerite

Millerite represents the dominant Ni-sulfide in low-sulfide mineralization from the North Range. Millerite is not usually a major sulfide phase within sharp-walled veins, although its modal abundance is noted to increase approaching vein terminations and within sub-economic stockworks mantling sharp-walled vein zones (Abel et al., 1979; Li et al., 1992). Due to its low abundance, only two sharp-walled vein samples in this study contained millerite, one from the McCreed West mine 700 Zone and one from the Deep Cu Zone, Strathcona mine. Concentrations of the PGEs, Au and Ag in millerite are typically below detection, although Pd and Ag were sporadically detected. Consistent Ag concentrations were only identified within QCS mineralization from the Capre property, with 66 % of points containing detectable Ag. Detected concentrations for the QCS samples ranged between 1.24 and 26.95 ppm and averaged 6.57 ppm (including points with Ag concentrations below detection). Only Se was consistently detected within the analyzed millerite with
concentrations between 109.20 and 2279.17 ppm (avg. 427.66 ppm), considerably higher than those from the other major sulfides. As with pyrrhotite, Pb and Bi are typically detected within millerite at concentrations dominantly above 1 ppm. Detectable Pb was only identified in 59% of points, with concentrations from below detection to 9.10 ppm (avg. 0.83 ppm). Concentrations of Bi were detected in 89% of points with concentrations from below detection to 25.14 ppm (avg. 2.27 ppm). The Bi data is somewhat skewed due to the high Bi contents of QCS millerite (n = 9) from the Capre property, with the average dropping to 1.55 ppm if these data are excluded. Analyses from the McCreedy West and Capre properties commonly yielded dissolved Te concentrations of > 2 ppm. Tellurium concentrations were also detected in millerite crystals from the Strathcona Deep Cu zone and the Levack North property, with concentrations where present of > 2 ppm, however they were extremely sporadic. Tellurium within millerite from the McCreedy West and Capre samples failed to correlate with any other trace element, suggesting that it is substituting for a major component, likely S.

Figure. 5.13. Ni (wt %) vs. Se (ppm) scatter plot for all LA-ICP-MS pyrrhotite analyses
5.5.3 Chalcopyrite

Chalcopyrite is the only ubiquitous phase across all mineralizing styles and properties. Crystals consistently display trace concentrations of Se, Ag, Pb and Bi, with detectable Pd also sporadically identified.

Detectable Pd was identified in 31 % of chalcopyrite analyses for North Range samples (contact, sharp-walled vein and low-sulfide) and 27 % of South Range samples (contact and low-sulfide). Palladium concentrations ranged from below detection to 9.53 ppm, with an average of 0.33 ppm across the whole chalcopyrite dataset. The low average level is consistent with previously published data for the SIC (Li et al., 1993; Huminicki et al., 2005; Dare et al., 2010b) with the majority of analyses below 1 ppm, although the higher (ppm) levels detected are also consistent with reported values from the Strathcona mine (Chyi and Crocket, 1976).

Chalcopyrite from the North Range displays a consistent variation in Ag content between contact and footwall (sharp-walled vein and low-sulfide) mineralization. Analysis of contact material from the Craig, McCreedy West and Strathcona mines consistently produced Ag concentrations of < 3 ppm, although a single sample from the McCreedy West mine yielded concentrations of 6.11 and 19.72 ppm. Footwall mineralization from the McCreedy West mine, Levack and Capre properties, and IRV mineralization from Wisner produced Ag concentrations typically exceeding 10 ppm and reaching a maximum of 276.51 ppm. Silver concentrations in chalcopyrite from the Strathcona mine cover a broad range from 0.78 to 103.90 ppm, with these low concentrations also present in sulfide vein and QCS mineralization from the Wisner property (Table 5.4). The low dissolved Ag displayed by chalcopyrite from these two properties is contradictory to the elevated whole rock Ag concentrations discussed earlier in this chapter, suggesting that Ag from these properties has been more efficiently sequestered by an alternative base-metal phase, with levels in pentlandite typically higher than the other sampled North Range properties or that Ag has been removed to form discrete minerals, chiefly hessite.

Mineralization from the South Range does not display the systematic variation in Ag contents observed in North Range material. Mineralization yielded a broad range of Ag concentrations within chalcopyrite, with levels from below detection to 691.90 ppm, although if data from stockwork mineralization are excluded the maximum value decreases to 102.45 ppm. Silver
from the South Range analyses correlates strongly with Se (R = 0.69), suggesting a coupled substitution, although not into the same site, with Ag likely substituting for Cu and Se for S.

The substitution of Ag for Cu in copper sulfide minerals has been previously noted for phases where Ag occurs in wt % levels (Miller and Craig, 1983; Barkov et al., 2004), however the exchange with respect to chalcopyrite is not commonly noted within peer reviewed sources. To date Cu–Ag exchange in chalcopyrite has been noted from surficial Ag deposits (Barkov et al., 2004 and references therein), and Ag has also been detected in chalcopyrite by LA-ICP-MS (Barnes et al., 2008; Dare et al., 2010b), although it is typically viewed as a minor impurity and not investigated further. In order to accurately measure the exchange it is clear that LA-ICP-MS runs using extended count times will be required to offer better resolution of Cu and Ag concentrations in order to allow any associations between the two to be better established. At present this remains difficult due to the high counts per second for Cu that chalcopyrite produces.

Selenium levels in North Range chalcopyrite, like Ag, display a strong compositional divide between contact and footwall (sharp-walled and low-sulfide) mineralization. Analysis identified Se concentrations within contact ore samples (Craig, McCreedy West and Strathcona mines) which consistently fell at or below 60 ppm, with an average of 45.63 ppm, including just three outlying points from a McCreedy West sample which exceeded 100 ppm (122.98 to 149.76 ppm) (Figure 5.14). In contrast Se levels from North Range footwall mineralization exceeded 60 ppm in 94 % of analyses (n = 382), with 79 % of these points containing greater than 100 ppm (n = 300). This compositional divide is not seen on the South Range where Se concentrations range between 25.1 to 367.41 ppm (avg. 103.08 ppm). Stockwork mineralization displays the highest dissolved Se concentrations with between 101.72 and 367.41 ppm (avg. 234.99 ppm) well above those of the other low-sulfide mineralizing styles from Denison (Figure 5.15), whilst chalcopyrite from Denison sulfide veins produced Ag and Se concentrations within the ranges of contact mineralization from the Crean Hill mine. Selenium concentrations in chalcopyrite within the different mineralizing styles from the North Range properties are relatively tight, with the majority of points falling over a 50 ppm range. In contrast the dissolved Se content of chalcopyrite from Levack North sulfide veins displays a substantial variation in concentration, with values falling across a range of > 250 ppm. Although this range is large the the concentrations of dissolved Se in chalcopyrite were typically tight across individual veins.
Dissolved Pb levels for chalcopyrite from both ranges display a significant range, with values from below detection to 143.57 ppm (avg. 6.94 ppm), excluding QCS mineralization from Capre. The majority (84 %) of points, excluding QCS mineralization from Capre, are below 10 ppm. Chalcopyrite from QCS mineralization from the Capre property is noticeably Pb enriched with dissolved concentrations between 1.59 and 1865.51 ppm (avg. 217.50 ppm). The Pb signals for the analyses exceeding 100 ppm were more uneven than other points suggesting that micro-inclusions of a Pb-phase, likely galena, may have been ablated during the laser transects. These high values are therefore treated as suspect.

Bismuth concentrations within chalcopyrite from both Ranges were generally low, with concentrations from below detection to 130.28 ppm (avg. 3.35 ppm). The majority of points (74 %) yielded Bi concentrations of < 2 ppm, with levels above 10 ppm only encountered in 6 % of points. Although significantly elevated relative to the dataset as a whole those points with > 10 ppm Bi were not so enriched relative to other points from the same sample as to be considered outliers, they were therefore retained. Lead and bismuth values for chalcopyrite from the North Range displayed a strong correlation (R = 0.54, excluding data from Capre QCS veins) (Figure 5.16). This positive correlation was not shared by the South Range dataset as a whole; however analyses from individual mineralizing styles did display a strong correlation. It would there seem that Pb and Bi are entering the crystal structure in a coupled substitution, although which element they are replacing is uncertain.

5.5.4 Pentlandite

Pentlandite constitutes the dominant nickel sulfide from contact and sharp-walled vein mineralization, and low-sulfide mineralization from the South Range. Crystals from North Range low-sulfide mineralization were limited to sulfide veins from the Levack North and Capre properties, where it is typically subordinate to millerite.

Previous LA-ICP-MS analysis of pentlandite has indicated its ability to contain both Pd and Ag and, on occasion, the IPGEs in trace amounts (Barnes et al., 2006, 2008, Huminicki et al., 2005; Dare et al., 2010b). Analysis of pentlandite from the North and South Ranges has identified a distinct compositional variation, with North Range crystals commonly containing Pd as the dominant dissolved precious metal, whilst Ag is the principle dissolved precious metal in South Range crystals. Furthermore the Pd and Ag present a consistent variation in concentration between samples from the contact and the footwall (sharp-walled vein and low-
sulfide), with Pd and Ag levels increasing in footwall sulfides relative to contact ores on both the North (Pd and Ag) and South Ranges (Ag) (Figure 5.17 and 5.18)

Figure 5.14. Se (ppm) vs. Ag (ppm) scatter plot for all LA-ICP-MS chalcopyrite analyses from the North Range.

Analysis of North Range pentlandite yielded Pd concentrations ranging from below detection to 198.47 ppm (avg. 13.82 ppm). Dissolved Ag ranges in concentration from below detection to 198.92 ppm (avg. 4.51 ppm). Levels are typically in the ppb range for North Range samples, with the majority (62 %) of points containing < 1 ppm Ag, of which 69 % were below detection. Palladium is the dominant dissolved precious metal in pentlandite from all the North Range properties, with the exception of samples from the Deep Cu Zone, Strathcona mine, where Ag was more common. Silver concentrations in these sharp-walled vein samples ranged from below detection to 198.92 ppm (avg. 13.41 ppm), with Pd from below detection to 34.26 ppm (avg. 1.74 ppm). Silver was also seen to exceed Pd in two samples from McCreedy West, one of contact ore and one from a sharp-walled vein.
Due to this variation in the dominant dissolved precious metal displayed by some North Range samples the difference in the precious metal content of pentlandite from contact and footwall samples is discussed here in terms of a combined precious metal total (Pd + Ag), rather than one element alone. Palladium + silver concentrations for contact material ranged from below detection to 6.81 ppm (avg. 2.68 ppm), with a single point yielding 20.03 ppm Ag. These Pd + Ag concentrations contrast sharply with pentlandite from footwall mineralization which produced concentrations from below detection to 198.99 ppm (26.94 ppm), with the increase clearly visible in Figure 5.17. From Figure 5.17 it is clear that dissolved concentration of Se and Pd + Ag within pentlandite show a steady increase as samples go from contact ore, through sharp-walled vein material and into low-sulfide mineralization. Correlation coefficients for North Range pentlandite indicate that Ni: Se (R = 0.61), Ni: Pd (R = 0.64) and Se: Pd (R = 0.69) correlate strongly, suggesting a coupled substitution based on the exchange of Ni for Pd, and the probable substitution of S for Se due to increases in the Ni:Fe ratio and the resulting changes in the crystal lattice. Correlations for Ag from the North Range samples in which it is dominant were all weak.
Measurable Pd concentrations in South Range pentlandite are uncommon in contact material (Crean Hill and Little Stobie mines), with only 24% (n = 8) of points yielding detectable concentrations. This should be compared to low-sulfide mineralization in which 69% (n = 64) of points contained measurable Pd. South Range pentlandite crystals yield Pd concentrations from below detection to 74.81 ppm (avg. 3.59 ppm). Silver concentrations ranged from below detection to 432.17 ppm (avg. 22.67 ppm), with contact samples not exceeding 5 ppm (avg. 1.31 ppm) Ag, with the exception of one point which contained 16.41 ppm. These concentrations from the contact ores are noticeably below the majority of South Range low-sulfide pentlandite crystals with Ag concentrations ranging from below detection to 432.17 ppm (avg. 30.10 ppm), with 65% of crystals containing over 5 ppm Ag. Silver correlates strongly to Bi (R = 0.75) across the South Range dataset, with Ag known to replace Ni and Fe in the pentlandite octahedral site (Mandziuk and Scott, 1977). The correlation of Ni to Ag varies between R = -0.25 and -0.90 for the South Range low-sulfide mineralization. All of the South Range mineralizing styles excluding stockwork and QCS mineralization from Denison (the latter consisting of data from a single sample), display Ni:Ag correlation coefficients of < -0.5. The lack of a strong negative correlation is consistent with Mandziuk and Scott (1977) who predicted that the substitution of Ag into the octahedral site must be charge balanced through the addition of Fe into the tetrahedral site. It would therefore seem likely the moderately negative correlation coefficients for Ni:Ag reflect the substitution of Fe into the tetrahedral site rather than the straight exchange of Ni for Ag. Correlation coefficients for Ni:Bi from South Range pentlandite are between 0.09 to -0.78, with sulfide veins from the Denison and McKim properties (the two largest datasets) both producing correlations of -0.47. It is therefore uncertain whether Bi is substituting for Ni or whether increases in the Fe-Ni ratio allow increased levels of Bi either through exchange with Fe or due adjustments in the crystal lattice.

Selenium concentrations within North Range pentlandite range from below detection to 1542.08 ppm (avg. 166.17 ppm). Crystals from the contact samples contained Se levels from below detection to 126.20 ppm (avg. 42.13 ppm), with crystals typically displaying levels of < 60 ppm, with the exception of one sample from Main Zone, McCreedy West mine that contains concentrations between 76.64 and 126.2 ppm. In contrast pentlandite from sharp-walled vein and low-sulfide mineralization displays considerably higher Se concentrations, with between 23.52 and 1542.08 ppm (avg. 237.93 ppm) measured. The observed enrichment relative to contact material is consistent with the elevated Se concentrations from
chalcopyrite from the same low-sulfide zones. Selenium concentrations from South Range pentlandite display no compositional variation between contact and low-sulfide material with levels ranging from 24.91 to 623.76 ppm (avg. 111.80 ppm).

As with the other major base-metal sulfides analyzed, Pb and Bi were commonly detected in pentlandite. Lead concentrations from both the North and South Range display no significant differences with levels from below detection to 261.77 ppm (avg. 11.22 ppm). Bismuth is similar in that concentrations showed little variation between the Ranges with levels from below detection to 53.13 ppm (avg. 1.44 ppm). Both elements failed to correlate with other trace elements within North Range samples, although Bi from the South Range correlated strongly with Ag. Tellurium concentrations in pentlandite from the North and South Range are typically sporadic and display a wide variation in concentration. Consistently detectable concentrations were identified from sharp-walled vein samples (McCready West and Strathcona) sulfide veins from the Capre property, and QCS and stockwork mineralization from Denison. Concentrations ranged from below detection to 143.77 (avg. 26.41 ppm), with Te levels correlating strongly with Ni (R = 0.64) across Te bearing groups listed above. Correlations for Te with Se were strong in both the North and South Range samples with R = 0.64 and 0.78 respectively. North Range pentlandite also display a strong correlation between Te and Pd (R = 0.61), although this is not evident in the South Range samples.

Comparison of pentlandite data from the North and South Ranges indicates that the Ni content varies from above 40 wt % in the chalcopyrite + millerite + pentlandite sulfide veins of the Levack property, through to 15 to 25 wt % Ni in pentlandite from the contact and South Range low-sulfide zones. The range described is consistent with experimental work on the composition of pentlandite by Misra and Fleet (1973). The initial concentration of Ni within a pentlandite is a reflection of the initial composition of the system, with pentlandite compositions ranging from 18 at % Ni for crystals formed from a liquid crystallizing troilite + pentlandite and up to 34 at % in the assemblage millerite + heazlewoodite + pentlandite, with experimental runs at 600 °C reaching a maximum Ni content of 41.3 at %. These values are in broad agreement with sulfide data from this study with Ni contents measured by EMPA of between 27 to 29 at % Ni associated with pentlandite from the pyrrhotite + pentlandite + chalcopyrite contact ores (North and South Range), through to 31 to 33 at % for pentlandite from the chalcopyrite + millerite + pentlandite sulfide veins of the Levack North and Capre properties. Misra and Fleet (1973) also noted that the Ni content of associated
Pyrrhotite and the Fe content of millerite in natural assemblages were lower than the synthetic equivalents at 230 °C, which was interpreted being the result of re-equilibration of natural compositions down to lower temperatures. This systematic change was also noted for synthetic pentlandite with the Fe content increasing from 33 at % at 600 °C, to 40 at % at 285 °C and finally to 30 at % at 230 °C, a reflection of the constant re-equilibration taking place during cooling. The ability of pentlandite to re-equilibrate down to temperatures below 230 °C brings into question the relevance of the dissolved element concentrations to conditions of formation; the low levels of certain elements, e.g. Pd within contact and South Range pentlandite, may reflect the slower rate of cooling due to the proximity of the melt sheet and repeated orogenic events along the South Range, with the higher Ni and Pd levels of North Range sharp-walled and sulfide veins the result of quicker cooling within the comparatively cooler footwall. However, the entire region eventually underwent slow cooling after each orogenic event, so all compositions may in fact represent to some extent the closure temperatures of re-equilibration in the microscopic environment surrounding each crystal.

5.5.5 Accessory Sulfide Phases

Although their effect on the distribution of precious and semimetals within low-sulfide mineralization is limited due to their low modal abundances, pyrite, violarite, polydymite and gersdorffite display trace element levels considerably different from the major base-metal sulfides.

Violearite analyses were limited to sulfide veins from the Capre property as it was the only occurrence where crystals reached suitable dimensions as replacements of millerite crystals. Comparison of LA-ICP-MS analysis of violarite and the precursor phase indicates that they displayed similar concentrations of As, Se and Te (Table 5.5). However, average levels of Ag and Bi were 10 times higher in violarite and 100 times higher for Sb and Pb. It should also be noted that Au was detected in four out of the five violarite points, a significant increase when compared to the Au content of the precursor millerite which only produced detectable Au in one out of thirty three analyses (Table 5.5).

Two polydymite analyses were collected from a single sulfide vein from the Wisner property. The crystals were located interstitial to chalcopyrite and presented a pitted surface leading to an uneven LA-ICP-MS signal. The analyses display Se concentrations similar to the surrounding chalcopyrite, however As, Ag, Pb and Bi values are considerably higher. Silver
values show significant variation with 397.49 ppm in one point and 6322.93 ppm in the other. Due to the uneven nature of the polydymite signal it is difficult to determine whether the upper value is the result of a Ag-mineral inclusion, and as such the data must be treated with care. Lead concentrations are 174.83 and 832.89 ppm with Bi levels of 78.77 and 114.90 ppm. These concentrations are substantially above those for any other base-metal sulfide from the Wisner property, although the presence of < 1 μm galena inclusions within polydymite does make it possible that the Pb levels listed are too high (Figure 5.19 A and B). No Bi-bearing phases were identified within polydymite.

![Figure 5.16. Pb (ppm) vs. Bi (ppm) scatter plot for all LA-ICP-MS chalcopyrite analyses from the North Range](image)

Pyrite occurs in mineralization from all three North Range properties, commonly associated with globular chalcopyrite inclusions within millerite. Pyrite crystals within sulfide veins from the three North Range properties are typically subhedral to euhedral and of uncertain origin with no clear evidence of sulfide replacement observed. It is therefore difficult to compare the pyrite to any precursor phase as it is unknown what or how many phases are being replaced. Crystals from IRV mineralization were limited to the margins of larger chalcopyrite aggregates, likely after millerite.
Figure 5.17. Se (ppm) vs. Pd + Ag (ppm) scatter plot for all LA-ICP-MS pentlandite analyses from the North Range. Dashed grey line represents the upper limit of the majority of contact points.

Figure 5.18. Ag (ppm) vs. Bi (ppm) scatter plot for all LA-ICP-MS pentlandite analyses from the South Range.
Pyrite crystals displayed elevated concentrations of As, Au, Pb and Bi when compared to the major base-metal sulfides from the three North Range properties. Platinum was detected in 44% (*n* = 12) of North Range pyrite analyses, making it the only base-metal sulfide to display such consistently measureable levels. Concentrations range from below detection to 2.03 ppm and average 0.14 ppm. The average level of Pt within pyrite is consistent with data from the McCreedy East deposit (Dare et al., 2011). Those crystals were interpreted to have exsolved directly from *mss*, with concentrations of the IPGEs, Pt and semimetals above those of the host sulfide.

South Range pyrite occurred as crystals after pyrrhotite, pentlandite and rarely chalcopyrite. Pyrite analyses have Se concentrations slightly in excess of precursor pyrrhotite and pentlandite, falling between 246.26 and 959.45 ppm. Average concentrations of Pb and Bi were also enriched when compared to base-metal sulfides from sulfide vein and stockwork mineralization, with pyrite crystals from the former also enriched in As, Ag and Te. Concentrations of the PPGEs were comparable to the host sulfide, although Ag was enriched. Unlike North Range crystals no Pt was detected, although the two stockwork hosted crystals analyzed did yield detectable Au with 0.13 to 0.22 ppm measured.

Gersdorffite analyses were limited to veinlet and stockwork samples from the Denison property. Previous analyses by SEM and EMP have identified several PGMs within gersdorffite, with textural evidence suggesting at least partial formation of these phases through exsolution from the sulfarsenide. It is therefore unsurprising that gersdorffite
contains Pd levels of between 27.27 and 48.65 ppm (avg. 33.36 ppm) and 278.07 and 1338.86 ppm (avg. 882.76 ppm) in veinlet and stockwork crystals respectively, with levels considerably higher and more consistent than the associated base-metal sulfides. Semimetal concentrations are dominated by Sb, with the majority of points around or exceeding 1000 ppm (Table 5.6). Tellurium was detected in all but one analysis with concentrations between 3.07 and 282.60 ppm (avg. 125.72 ppm), again considerably higher than the other South Range sulfides. Lead levels are high, averaging 7.76 ppm; however they fall within the range of other sulfide phases. This was not the case for Bi, with concentrations between 8.41 and 995.15 ppm (avg. 154.87 ppm), well in excess of any other base-metal sulfide analyzed.

The presence of measureable Pt in > 50 % of gersdorffite analyses is consistent with observations of sulfarsenides from the Copper Cliff, Parkin and Worthington offsets (Huminicki et al., 2005; Hecht et al., 2010). Concentrations range from below detection to 246.9 ppm (avg. 19.52 ppm), however values from stockwork hosted gersdorffite (4.56 to 237.91 ppm) must be treated carefully due to the possibility of the uneven signal masking the ablation of micro-inclusions. Gold was detected at levels from below detection to 7.32 ppm (avg. 0.77 ppm). Whether this Au is truly dissolved within gersdorffite is questionable; Sung et al. (2009) described the presence of ‘invisible’ gold within arsenopyrite, which they considered to be present either as nanoparticles or lattice-bound Au.

The trace element compositions of the major base-metal sulfide minerals analyzed in this study do show some noticeable differences from proton microprobe, atomic mass spectrometry and other LA-ICP-MS studies of Sudbury sulfides (Cabri et al., 1984; Li et al., 1993, Huminicki et al., 2005; Dare et al., 2010b, 2011). Pyrrhotite analyses from all settings differ little from the published data for Sudbury. Pentlandite and chalcopyrite compositions from the contact ore samples are also comparable to previous results. The Se content of footwall sulfides (sharp-walled vein and low-sulfide) is considerably higher than previous measurements, with Pd and Ag in pentlandite and Ag in chalcopyrite also considerably enriched when compared to published data. Concentrations of As, Sb, Pt, Au, Re and the IPGEs across the major base-metal sulfides were typically sporadic in their occurrence, suggesting that they are distributed as discrete phases.
<table>
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<th>Craig (Contact)</th>
<th>Pyrrhotite</th>
<th>Pentlandite</th>
<th>Chalcopyrite</th>
<th>Strathcona</th>
<th>McCreedy West</th>
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Table 5.4. LA-ICP-MS results for contact and sharp-walled vein sulfides of relevance to low-sulfide material. The presence of an * denotes ranges from which outliers have been removed, n = number of data points.
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Table 5.5. LA-ICP-MS results for low-sulfide material from the three North Range prospects. The presence of an * denotes ranges from which outliers have been removed, n = number of data points.
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Table 5.5. Continued.
Table 5.6. LA-ICP-MS results for low-sulfide material from the two South Range prospects. The presence of an * denotes ranges from which outliers have been removed, n = number of data points.
<p>|                | SV     | QCS    | VNLT   | STOCK  | SV     | QCS    | VNLT   | STOCK  | SV     | QCS    | VNLT   | STOCK  | SV     | QCS    | VNLT   | STOCK  | SV     | QCS    | VNLT   | STOCK  | SV     | QCS    | VNLT   | STOCK  | SV     | QCS    | VNLT   | STOCK  |
|----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| <strong>Chalcopyrite</strong> |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
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| <strong>Pyrrhotite</strong>  |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
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| <strong>Pentlandite</strong> |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
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| <strong>Pyrite</strong>     |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| <strong>Gersdorffite</strong>|        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| <strong>McKee</strong>      |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |        |</p>
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<td><strong>McKim</strong></td>
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<tr>
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<td>1 (11)</td>
<td>4 (14)</td>
</tr>
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Table 5.6. Continued.
Table 5.7. Pearson correlation coefficients for dissolved metal within major BMS. Chalcopyrite (ccp), millerite (mi), pentlandite (pn), pyrrotite (po), pyrite (py) and gersdorffite (gdf).
5.6 Mass Balance

In order to gauge the proportion of each element within the major sulfides (chalcopyrite, pentlandite, pyrrhotite and millerite) and accessory phases (pyrite and gersdorffite) a mass balance was calculated using the method of Barnes et al. (2008). The mass balance requires that each element in the whole rock is recalculated to 100 % sulfide, with all elements of interest dissolved within sulfides analyzed by LA-ICP-MS. The weight percent of pyrrhotite, pentlandite and chalcopyrite from South Range samples was calculated assuming all Cu as chalcopyrite and all Ni as pentlandite, with any remaining S attributed to pyrrhotite, with the calculated abundances typically in keeping with observations from hand specimens and thin sections. Due to the chalcopyrite + millerite ± pentlandite assemblage of North Range low-sulfide material, sulfur loss during acid digestion caused some problems. Such sulfur loss is less noticeable in samples containing pyrrhotite, however, in the Cu-sulfide dominated North Range mineralization the addition of bornite was required to accurately recalculate to 100 % sulfide. Bornite was only very rarely observed within IRV mineralization from the Levack North and Capre properties where it occurs as small irregular crystals along the margins of chalcopyrite, it is not however observed in either sulfide vein or QCS mineralization. An accurate mass balance requires all of the major phases to be analyzed, however, with the addition of theoretical bornite this could not be achieved and as such an accurate mass balance is in most cases impossible. In samples with excess S, which contained both millerite and pentlandite, Ni was split between the phases based on a visual estimation of their relative abundances, following the method outlined by Li and Naldrett, (1993). All remaining S after the requirements of chalcopyrite, millerite and pentlandite were satisfied was attributed to pyrite. Mass balance data for all five low-sulfide properties and values from previous studies are presented in Tables 5.8, 5.9 and 5.10.

5.6.1 North Range

The mass balance for North Range low-sulfide mineralization indicates the preference for Pt, Au, As, Bi, Pb, Sb and Te to not enter solid-solution within base-metal sulfides, which typically contribute < 10 % of the total. Levels of the IPGEs in solid solution are particularly variable and
reflect the extremely limited dataset employed and should at best be considered as a guide to possible host phases. The highest concentrations of dissolved Pd from the North Range properties were hosted by pentlandite (Tables 5.8 and 5.9), with between 0.54 and 7.68 % of total Pd dissolved within it. Where present in significant quantities pentlandite has a major effect on Pd distribution, however as its modal abundance is typically low (1 to 16 % of sulfide present) its effects on the total Pd budget are relatively small. The exception to this is a single Ni-sulfide rich sample which contains 78.13 % pentlandite, which contains 63 % of the Pd present. These levels for samples bearing a high modal abundance of pentlandite are in good agreement with data from Dare et al. (2010b), who determined that between 40.4 and 56.1 % of total Pd was hosted in base-metal sulfide, with pentlandite containing the highest fraction.

Although dissolved Pd concentrations within chalcopyrite in this study are typically sporadic, with the majority of points below detection limits, a few rare occurrences do somewhat skew the averages for individual samples and thereby the mass balance. Chalcopyrite-hosted palladium constitutes between 0.15 and 7.46 % of total Pd from the North Range properties. Consistent concentrations were only detected in sulfide veins from the Wisner property where concentrations of ≤ 1 ppm Pd were detected, with the two analyzed veins averaging 0.21 and 0.26 ppm. The mass balance for these veins yielded 1.89 and 1.17 % of total Pd dissolved within chalcopyrite. These low levels are consistent with published data for Sudbury (Li et al., 1993; Dare et al., 2010b) and indicate that chalcopyrite must be considered as a Pd host when present in significant modal abundances.

Chalcopyrite from the Wisner property displays lower concentrations of dissolved Ag than it does at the Levack North and Capre properties. These low levels are reflected in the mass balance with ≤ 5.5 % of total Ag dissolved in chalcopyrite. In contrast the comparatively Ag-rich analyses of chalcopyrite of the Levack North and Capre properties led to the estimation of significant quantities of the total Ag being retained in solid solution, with between 3.26 and 100 % in chalcopyrite, with averages from the two properties of 29.40 % and 69.87 % respectively. These levels are considerably greater than average values from the Creighton and McCreedy East contact ores (Dare et al., 2010b, 2011) and reflect the higher modal abundance of chalcopyrite and concentrations of dissolved Ag. Future studies must therefore ensure that Ag levels within the base-metal sulfides are analyzed in order to better understand its distribution in contact, sharp-walled vein, offset and low-sulfide mineralization.
Dissolved semimetals within North Range base-metal sulfides are dominated by selenium, with between 11.09 and 100 % of total Se in solid solution, with an average across all North Range usually samples exceeding 50 % (Tables 5.8 and 5.9). The concentrations of the other semimetals analyzed within this study (As, Sb, Te, Pb and Bi) are noticeably lower than those from the Creighton and McCreedy East contact orebodies (Dare et al., 2010b, 2011). In the case of As and Sb these low levels are likely due to their removal though the development of sulfarsenide phases and rare sperrylite. The mass balance results from the Levack North and Wisner properties indicate that Te and Bi are overwhelmingly located within discrete phases, chiefly as PGMs and Bi-chalcogenides. This is not the case at the Capre property where dissolved Te levels within pentlandite bearing samples averaged between 19.83 and 100 % of the total Te, in contrast to pentlandite free samples which typically contain < 5 % of total Te in solid solution. Bismuth levels are extremely variable, but dominated by chalcopyrite as a host phase, likely due to its high modal abundance and the skewing effect of rare Bi-rich analyses.

Despite being the major Ni sulfide in the majority of samples, millerite contributed little to the dissolved precious metal budget. Precious metal concentrations for all but Pd were consistently below detection limits, with the fraction of Pd hosted by millerite typically well below that of the other major sulfides. Its contribution to the semimetal distribution is also minimal with its comparatively low modal abundance (typically < 10 %) restricting the fraction of total Se contained within it. Analyzed accessory phases included within the mass balance were limited to pyrite. Its presence did not result in any significant change in the proportion of dissolved elements, in keeping with data from McCreedy East (Dare et al., 2011).

5.6.2 South Range

The mass balance for precious metals within South Range mineralization deviates somewhat from North Range samples. The higher modal abundance of pentlandite within the South Range material has resulted in an increased proportion of total Pd residing in base-metal sulfides, with levels typically around or in excess of 10 %. The IPGE budget cannot be accurately assessed within Denison samples due to the small dataset available, however four out of the five analyzed sulfide vein samples from McKim have IPGE data, and therefore a greater degree of confidence
can be placed in the distribution. Iridium concentrations within the base-metal sulfides are usually low and extremely sporadic, with the mass balance finding no dissolved Ir. The mass balances for Ru and Rh found the former to be distributed within pyrrhotite and chalcopyrite and the latter within pentlandite, with 25% of Ru and 33% of Rh in solid solution. Platinum again displays a preference for discrete phases. Dissolved Au levels are also typically low, although the mass balance identified up to 11.93% of total Au to be hosted by the major sulfides. Unlike the North Range samples, in which dissolved Ag was nearly universally hosted by chalcopyrite, the South Range material has dissolved Ag split between pentlandite and chalcopyrite, with the former being the dominant host phase, except in cases where the modal abundance of chalcopyrite is higher, e.g., QCS veins from McKim. The total dissolved Ag for the South Range mineralization is consistent with data from Dare et al. (2010b).

The mass balance for As, Te, Pb and Bi in South Range samples shows that their concentrations within base-metal sulfides are typically low. However, unlike North Range material, where whole-rock Sb concentrations are low, the comparatively Sb-rich South Range mineralization (Ames and Farrow, 2007) offers a window into its distribution in base-metal sulfides. Pentlandite is the dominant host, with lesser concentrations in pyrrhotite and chalcopyrite. The fraction within pyrrhotite is typically low, whilst the fraction within chalcopyrite unsurprisingly increases with rising modal abundances. The fraction of total Se within base-metal sulfides ranges from 22.40 to 72.21%, with values below this range likely to result from an incomplete analysis of the sulfide assemblage present. The fraction of dissolved Se is near equally split between the major base-metal sulfides, with the highest total levels associated with sulfide veins (Table 5.10). Total dissolved Se percentages are lower than those reported for the Creighton mine and likely reflect a movement into discrete phases, likely bismuth chalcogenides in levels not seen with contact ores.

Accessory phases included within South Range mass balances were limited to gersdorffite in veinlet and stockwork mineralization from the Denison property. The mass balance for gersdorffite reflects its ability to contain significant quantities of precious metals (Rh, Pd, Pt and Au) and semimetals (Sb and Bi) in solid solution. The capacity of the PGEs both to form discrete phases and to dissolve within sulfarsenides from Sudbury is well established (Cabri and Laflamme, 1976; Huminicki et al., 2005; Dare et al., 2010a). The presence of Au within
gersdorffite appears to represent a first occurrence. Both microscopic and SEM analysis failed to identify any Au-phases within gersdorffite, although the presence of nanoparticles cannot be excluded (Sung et al., 2009). Further study would be required to ascertain whether Au is a common component in Sudbury sulfarsenides or whether the data within this study are erroneous. The substitution of Sb into gersdorffite, is consistent with published data that indicates a negative correlation with S (Béziat et al., 1996), with Bi likely substituting in a similar fashion.

Comparison of North and South Range low-sulfide samples is broadly consistent with respect to Ir, Ru, Rh, Pt, Pd, Au, Re, As, Bi, Pb, Sb, Se and Te, with the mass balance indicating the preference of these elements to form discrete phases. The distribution of Ag in mineralization from the Wisner and South Range is also consistent with published values, however the fraction of total Ag dissolved within base-metal sulfides from the Levack North and Capre properties represents a movement of Ag into solid solution not seen before at Sudbury.
Table 5.8. Proportion (%) of each element hosted in chalcopyrite, millerite, pentlandite and pyrite from the Levack North and Wisner properties. n = number of samples.

| Levack North |  | Element | Ir | Ru | Rh | Pt | Pd | Au | Re | Ag | As | Bi | Pb | Sb | Se | Te |
|--------------|  | Isotope | 193 | 101 | 103 | 195 | 105/108 | 197 | 185 | 107 | 75 | 208 | 209 | 121 | 77 | 125 |
| **Sulfide Vein (Pb bearing)** |  | Ccp | 0.77 | 5 | 0.000 | 0.000 | 0.000 | 0.064 | 1.833 | 0.000 | 81.385 | 0.000 | 2.693 | 4.809 | 7.020 | 65.076 | 0.135 |
|  |  | Mi | 0.09 | 4 | 0.000 | 0.000 | 50.000 | 0.000 | 0.295 | 0.000 | 0.000 | 0.002 | 3.933 | 0.458 | 0.106 | 0.000 | 49.534 | 0.041 |
|  |  | Pn | 0.11 | 4 | 0.000 | 0.000 | 50.000 | 0.008 | 3.563 | 0.058 | 0.000 | 0.004 | 1.802 | 2.083 | 0.229 | 0.342 | 31.121 | 8.334 |
|  |  | Total | 0.000 | 100.000 | 0.014 | 3.923 | 1.891 | 0.000 | 81.392 | 5.734 | 5.233 | 5.145 | 7.362 | 145.731 | 8.510 |
| **Sulfide Vein (Cu-Sulfide dominated >96% ccp+bn)** |  | Ccp | 0.91 | 4 | 0.000 | 0.000 | 0.000 | 0.271 | 0.151 | 0.799 | 0.000 | 42.905 | 0.000 | 0.409 | 1.240 | 0.000 | 49.842 | 0.000 |
|  |  | Mi | 0.01 | 1 | 0.003 | 0.024 | 0.297 | 0.089 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
|  |  | Bn | 0.08 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Total | 0.000 | 0.000 | 0.000 | 0.274 | 0.175 | 1.095 | 0.000 | 42.993 | 0.000 | 0.409 | 1.240 | 0.000 | 49.842 | 0.000 |
| **Wisner** |  | Ccp | 0.90 | 1 | 0.000 | 0.000 | 0.000 | 1.174 | 0.271 | 4.435 | 0.000 | 2.765 | 2.330 | 13.133 | 55.651 | 0.431 |
|  |  | Mi | 0.01 | 1 | 0.000 | 0.000 | 0.000 | 0.514 | 0.051 | 0.028 | 0.357 | 10.765 | 7.969 | 0.000 | 5.337 | 1.240 |
|  |  | Py | 0.09 | 1 | 48.334 | 0.000 | 0.514 | 0.051 | 0.028 | 0.357 | 10.765 | 7.969 | 0.000 | 5.337 | 1.240 |
|  |  | Total | 0.000 | 0.000 | 0.000 | 0.042 | 0.073 | 0.077 | 6.801 | 18.064 | 0.000 | 0.117 | 0.659 | 0.067 | 28.502 | 0.000 |
| **Sulfide Vein (Ccp + Mn + Py)** |  | Ccp | 0.99 | 1 | 0.000 | 0.000 | 0.000 | 1.889 | 13.941 | 0.000 | 4.725 | 2.653 | 0.000 | 10.968 | 0.193 |
|  |  | Mi | 0.00 |  | Not Analyzed |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Bn | 0.01 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Total | 0.000 | 0.000 | 0.000 | 1.889 | 13.941 | 0.000 | 4.725 | 2.653 | 0.000 | 10.968 | 0.193 |
| **Sulfide Vein (Ccp > 98.5%)** |  | Ccp | 0.99 | 1 | 0.000 | 0.000 | 0.000 | 1.889 | 13.941 | 0.000 | 4.725 | 2.653 | 0.000 | 10.968 | 0.193 |
|  |  | Mi | 0.00 |  | Not Analyzed |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Bn | 0.01 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Total | 0.000 | 0.000 | 0.000 | 1.889 | 13.941 | 0.000 | 4.725 | 2.653 | 0.000 | 10.968 | 0.193 |
| **IRV** |  | Ccp | 0.83 | 6 | 0.000 | 0.000 | 0.000 | 0.424 | 0.073 | 0.077 | 6.801 | 18.064 | 0.000 | 0.117 | 0.659 | 0.067 | 28.502 | 0.000 |
|  |  | Mi | 0.05 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Bn | 0.12 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Total | 0.000 | 0.000 | 0.000 | 0.424 | 0.073 | 0.077 | 6.801 | 18.064 | 0.000 | 0.117 | 0.659 | 0.067 | 28.502 | 0.000 |
| **QCS** |  | Ccp | 0.72 | 3 | 50.000 | 0.000 | 0.000 | 0.000 | 0.026 | 5.797 | 33.333 | 4.837 | 0.157 | 4.784 | 2.040 | 0.000 | 20.897 | 2.356 |
|  |  | Mi | 0.07 |  | Not Analyzed |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Bn | 0.22 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Total | 50.000 | 0.000 | 0.000 | 0.000 | 0.026 | 5.797 | 33.333 | 4.837 | 0.157 | 4.784 | 2.040 | 0.000 | 20.897 | 2.356 |

Table 5.8. Proportion (%) of each element hosted in chalcopyrite, millerite, pentlandite and pyrite from the Levack North and Wisner properties. n = number of samples.
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Table 5.9. Proportion (%) of each element hosted in chalcopyrite, millerite, pentlandite and pyrite from the Capre property. n = number of samples.
Table 5.10. Proportion (%) of each element hosted in pyrrhotite, pentlandite, chalcopyrite and gersdorffite from the Denison and McKim properties. n = number of samples.
5.7 Discussion

5.7.1 Sulfide Phase Relations

5.7.5.1 North Range

Consideration of contact and sharp-walled vein mineralization by Mungall (2007) indicated that the common view of contact mineralization as having resulted from the crystallization of mss and its re-equilibration with a residual sulfide liquid may not be correct. Analysis of contact ores produced a strong compositional trend between Fe-rich mss compositions and iss, which was interpreted as being the result of formation from mss + iss cumulates which recrystallized to pyrrhotite + pentlandite + chalcopyrite, rather than the interaction of mss with any significant volumes of residual liquids. The migration of a late stage Cu-Ni enriched residual sulfide liquid from the contact ores is inferred to have formed sharp-walled veins within the footwall. This residual liquid crystallized cumulates comprising first mss and iss, and later iss and hzss, the latter (or a similar (Ni, Fe)$_{3.5}$S$_2$) being envisaged to have formed through the reaction of mss and a Ni-rich liquid at 862 to 865 °C (Sugaki and Kitakaze, 1998; Craig and Kullerud, 1969).

The sulfide phase relations for low-sulfide mineralization remain uncertain and must explain the lack of pyrrhotite and the development of significant modal abundances of millerite, both of which are inconsistent with the phase relations commonly applied to typical Sudbury sulfide ores. The presence of Ni-sulfides along the margins of sulfide veins (Figure 5.20A) from the Levack North and Capre properties would suggest that mss and (Ni, Fe)$_{3.5}$S$_2$ were crystallizing from the residual liquid before significant iss, which occurs between 960 and 850 °C (Craig and Kullerud, 1969; Raghavan, 2004a). As hzss is not stable above 862 to 865 °C (Craig and Kullerud, 1969; Sugaki and Kitakaze, 1998), it is likely that the margins were initially dominated by mss which becoming more Ni rich with complete Fe$_{1-x}$S to Ni$_{1-x}$S solid solution at and below 992 °C (Kullerud and Yund, 1962; Craig and Kullerud, 1969), or that the sulfide veins formed at temperatures well below 862 °C. The more Fe-rich mss precursor is envisaged to have broken down to hzss at 865 °C through the reaction of mss and the Ni-bearing residual sulfide liquid. The heazlewoodite solid solution breaks down at and below 610 °C producing pentlandite + bornite solid solution + mss (Craig and Kullerud, 1969; Sugaki and Kitakaze, 1998). The presence of millerite within these Ni-sulfide bearing margins could be the result of either high or
low temperature processes. The high temperature form of millerite ($\text{Ni}_{1-x}\text{S}$) is stable at temperatures at and below 992 °C and forms the Ni end-member of the $mss$ solid solution series. The phase relations of these extremely Ni-rich $mss$ compositions is uncertain, although the Ni-S system of Kullerud and Yund (1962) identified no phase changes before the $\text{Ni}_{1-x}\text{S} \rightarrow \text{NiS}$ transition at or below 379 °C (Kullerud and Yund, 1962); experimental analyses of the Cu-Fe-Ni-S system also failed to note any changes (Craig and Kullerud, 1969; Ballhaus et al., 2001). Although formation at high temperature is favored the possibility of crystallization of millerite at low temperatures cannot be ignored. Low temperature relations require the breakdown of Ni-bearing $mss$ at 300 °C, with millerite produced through the reaction $mss = mss + \text{millerite} + \text{violarite}$ at the former temperature, with any remaining Ni-bearing $mss$ breaking down to violarite + pentlandite at 200 °C (Craig, 1973). Whether this low temperature reaction would be sufficient to produce the high modal abundances of millerite observed is debatable and as such an early formation as Ni-rich $mss$ is preferred. The existence of Ni-$mss$ would suggest that either the mineralizing fluid was enriched with in Ni or that the $mss$/sulfide liquid partition coefficient rises above 1 at temperatures below 950 °C (Mungall et al., 2005; Mungall 2007). The lack of pyrrhotite may reflect an increase in $f_{S_2}$ relative to contact and sharp-walled vein sulfide liquids, stabilizing pyrite. The formation of pyrite (Figure 5.20C) could be either the result of S being released from base-metal sulfides during phase transitions, thus causing pyrrhotite to become unstable, or pyritization resulting from the interaction of sulfides with hydrothermal fluids. Pyrite is nearly ubiquitous and commonly occurs as an accessory phase within millerite where it typically nucleates on rounded chalcopyrite inclusions. Experimental data from the Ni-S system indicates that the high temperature form ($\alpha\text{Ni}_{1-x}\text{S}$) has a S content of between 35.3 and 39 wt % S (Kullerud and Yund, 1962), whilst millerite has a tight S range around the stoichiometric value of 35.33 wt % S. It is clear that upon cooling Ni-$mss$ would likely alter to millerite + Cu-sulfide solid solution + $mss$, a reaction akin to the breakdown of more Fe-rich $mss$ compositions that produce $h_zss$. The expelled phases likely formed the precursors to the rounded inclusions observed (Figure 5.20C), with S loss during the transition from $\alpha\text{Ni}_{1-x}\text{S}$ to NiS destabilizing any pyrrhotite or bornite solid solution present, thus producing the observed chalcopyrite + pyrite assemblage. The release of excess S and its subsequent reaction with any remain $mss$ may also have been sufficient to drive the formation of violarite after pentlandite and millerite, an alteration commonly observed along the margins of sulfide veins. The occurrence of millerite
Figure 5.20. Textural relationships of major and accessory sulfide from the North Range. (A) Lower margin of sulfide vein from the Levack North property. Note Ni-sulfide dominated margin composed of millerite (Mi) and pentlandite (Pn), the latter displaying a purple tint due to violarite alteration. Scale in mm. (B) Magnetite (Mgt) bearing chalcopyrite (Ccp) dominated sulfide vein from the Capre property displaying pyrrhotite micro-veinlets along the margins of chalcopyrite containing galena (Gn) inclusions. (C) Millerite from Ni-sulfide dominated vein from the Capre property, note the presence of pyrite (Py) along cleavage planes and the development of irregular to skeletal pyrite in chalcopyrite inclusion. (D) Chalcopyrite dominated sulfide vein from the Wisner property displaying a polydymite micro-veinlet along the margins of chalcopyrite. Sample has been acid etched.

and pyrrhotite interstitial to chalcopyrite from the Levack North and Capre properties (Figure 5.20B), along with polydymite and rare pyrrhotite micro-veinlets from Wisner are consistent with Ni–(Fe) exsolution along the rims. Experimental data indicates that complete solid solution between \( \text{iss} \) and Fe–Ni–S is present at temperatures of 760°C (Peregoedova and Ohnenstetter, 2002; Raghavan, 2004a, references therein). A mechanism is envisaged by which Ni is expelled upon the cooling and breakdown of Ni-bearing \( \text{iss} \), producing a ‘rim’ exsolution texture.
Exsolution lamellae were redistributed to the rim aggregates or incorporated into rounded inclusions within chalcopyrite during recrystallization (Figure 5.20D).

5.7.5.2 South Range

The pyrrhotite + pentlandite + chalcopyrite assemblage of the South Range properties is consistent with the majority of Sudbury sulfide ores. The sulfide phase relations for this assemblage are comparable with previous Sudbury models (Naldrett, 1981; 1984; Li et al., 1992). The pyrrhotite + pentlandite + chalcopyrite assemblage from Denison and McKim represents the crystallization of mss and iss from a sulfide liquid, with some variation in the degree of fractionation. Monosulfide solid solution crystallized below 1050 °C (Jensen, 1942; Craig and Kullerud; 1969; Ballhaus et al., 2001), followed by iss and hzss below 960 and 850 °C and 862 to 865 °C, respectively (Craig and Kullerud, 1969; Sugaki and Kitakaze, 1998; Raghavan, 2004a). Pentlandite formed through the reaction of mss and (Ni, Fe)$_{3-x}$S$_2$ at 610 °C, with chalcopyrite forming below 590 °C to ~550 °C, through the breakdown of iss to give chalcopyrite + Fe-iss, the latter recrystallizing as pyrrhotite (Barton, 1973; Cabri, 1973).

5.7.2 Partitioning of Chalcophile Elements

The distribution of precious metals during sulfide crystallization has been extensively studied within the Fe–Ni–S (Distler et al., 1977; Fleet and Stone, 1991; Fleet et al., 1999) and Fe–Ni–Cu–S systems (Fleet et al., 1993; Fleet and Pan, 1994; Ebel and Naldrett, 1996; Li et al., 1996; Ballhaus et al., 2001; Barnes et al., 2001; Mungall et al., 2005, Helmy et al., 2010). Inferences from these studies are backed by observations from the Sudbury and Noril’sk mining camps, the Jinchuan deposit and sulfide droplets (Hoffman et al., 1979; Naldrett et al., 1982; Chai et al., 1993; Zeintek et al., 1994; Pritchard et al., 2004; Barnes et al., 2006), and indicate that IPGEs (Os, Ir, Ru and Rh), Re and Co are compatible within crystallizing monosulfide solid solution (mss), whereas the PPGEs (Pt and Pd), Au, Ag, As, Se, Bi, Cu, Sb, Te and Pb are concentrated within the residual liquid. The mss/sulfide liquid partition coefficient for Ni displays a temperature dependency, become more compatible with decreasing temperature (Li et al., 1996;
Mungall et al., 2005; Mungall, 2007). The partitioning behavior of the majority of chalcophile elements with \textit{iss} and \textit{hzss} is unknown. Experimental studies in the S-poor Fe–Ni–Cu–S system indicate that Pt will behave incompatibly with \textit{mss}, \textit{iss} and \textit{hzss}, with high temperature Pt–Fe–Ni alloys readily forming at very low sulfur fugacities (Peregoedova and Ohnenstetter, 2002). The behavior of palladium is affected by the Ni content of the crystallizing sulfides, with Pd concentrations increasing in \textit{mss} and \textit{hzss} as their Ni content increases; it does however behave incompatibly with Fe-\textit{mss} and Cu-rich \textit{iss} (Peregoedova and Ohnenstetter, 2002). Rhodium behaves compatibly with \textit{mss}, although its behavior varies in low and high $f_{S_2}$ regimes (Peregoedova and Ohnenstetter, 2002; Mungall et al., 2005).

5.7.3 100 % Sulfide Normalized Copper and Nickel

The normalization of mineralization to 100 % sulfide allows for a comparison of metal concentrations between the mineralizing styles. The majority of elements of interest are either contained within (e.g. Cu, Se), or associated with (e.g. Pt, Pd, Au) sulfides and normalization is wholly valid. Normalization does however become problematic for samples with $< 1$ wt % S, which contain minerals that can also host the elements of interest i.e. silicates, oxides or arsenides, with disseminations and to a lesser degree IRV mineralization falling within these categories. The presence of Ni within ferromagnesians minerals (see Chapter. 3) brings into question the accuracy of Ni 100 concentrations within the lowest S samples, especially from the North Range. The effect of Ni contained within silicates cannot be accurately estimated as both the Ni content and the modal abundance of ferromagnesian minerals will vary between samples and as such the concentration of Ni within the lowest modal sulfide material must be treated as a maximum for Ni occurring in sulfides.

5.7.3.1 North Range

The plots of Cu and Ni normalized to 100 percent sulfide indicate that the sulfide veins of the North Range prospects fall upon the \textit{iss–hzss} trend, in keeping with the majority of footwall ores (Mungall, 2007), and well to the right of the modelled residual sulfide liquid composition of Mungall et al. (2005), suggesting formation from a highly fractionated sulfide liquid. A slight
deviation to the right of the $iss$-$hzss$ trend is noted and likely results from the presence of millerite in the common North Range low-sulfide assemblage. The majority of IRV and disseminations also plot towards the Cu-rich end of the $iss$-$hzss$ trend, although additional deviations are noted. The presence of analyses within the bottom left of the diagram would suggest an $mss$ input, however the positive trend between $mss$ and $iss$ displayed by the North Range low-sulfide plot are not consistent with the negative slope of the $mss$-$iss$ mixing line produced by Mungall (2007). The shift towards diminished Cu and Ni in the current samples likely reflects an increased modal abundance of pyrite. This may be the result of pyritization related to interactions with a hydrothermal fluid or it could mark a shift to increased $fS_2$ within the mineralizing process, leading to pyrrhotite becoming unstable. The positive slope observed likely reflects the reduction in excess S as Cu and Ni concentrations increase. Mungall (2007) postulated that the sulfide liquid from which any $iss$ or $hzss$ crystallized would sit to the right of the $iss$-$hzss$ trend, upon which sharp-walled veins and a significant number of low-sulfide samples sit. The Cu 100 vs. Ni 100 plot displays an additional trend at approximately 33 % Cu and becomes distinct from that of sulfide veins above 20 % Ni. These compositions denote a chalcopyrite + bornite + millerite assemblage with a ccp:bn ratio approaching 1:1, well above that shown by the majority of bornite bearing samples, where it constitutes only a minor phase. This trend may indicate the presence of significant proportions of a Cu enriched residual liquid which pulls compositions to the right of the $iss$-$hzss$ trend.

5.7.3.2 South Range

The Cu 100 vs. Ni 100 plot of mineralization from the Denison and McKim properties indicates that the majority of analyses fall along the $mss$-$iss$ mixing line, a trend along which contact and proximal footwall mineralization sits, with $mss$ dominated compositions plotting around the modelled $mss$-cumulate compositions of Mungall et al. (2005). Inclusion-bearing sulfide veins from both the Denison and McKim properties fall along the $mss$-$iss$ mixing line, with the majority of points falling towards the $mss$ i.e. Fe-rich range. Such compositions are consistent with the hypothesis that the majority of these inclusion-bearing sulfide veins represent $mss$ cumulates from contact orebodies that have been sheared into the footwall. Mungall (2007) predicted that the sulfide liquid would initially crystallize $mss$ (contact ores), followed by $mss$ +
**iss** (footwall mineralization proximal to the contact) and finally **iss + hzss** (sharp-walled vein systems). The distribution of points along the **mss–iss** mixing line is indicative of this process, with sulfide vein compositions ranging from **mss** dominated through to compositions falling between cubanite (23.41 wt % Cu) and chalcopyrite (34.63 wt % Cu), representing **iss** crystallized from a residual sulfide liquid that has entered the footwall from the contact.

The Cu 100 vs. Ni 100 values for the South Range properties displays a scatter of points extending above the **mss–iss** mixing line, but not extending past the **hzss–iss** mixing line. This scatter was not noted by Mungall (2007), who instead identified two discrete mixing lines, without intermediate compositions. The presence of these points represents **mss + iss + hzss** compositions, which were likely produced when some of the residual liquid was incapable of migrating away from the **mss–iss** that it had crystallized. The residual liquid would crystallize **iss + hzss** thus producing the intermediate compositions observed. The presence of such intermediate and **iss** rich compositions indicates that inclusion-bearing sulfide veins, veinlets and disseminations are not only the result of contact material sheared into the footwall, but also of sulfide liquids crystallizing **mss + iss** and their residual liquids.

### 5.7.4 Precious Metals

#### 5.7.4.1 Lower Crust Normalized Patterns and Chalcophile Partitioning

Normalized precious metal plots when combined with experimental partitioning data have proven a valuable tool in identifying fractionation processes within magmatic sulfide systems. Previous work on the ores of the SIC have identified a trend from relatively flat mantle normalized PGE plots for contact deposits, through to IPGE depleted, PPGE enriched compositions associated with sharp-walled vein mineralization. This trend is consistent with experimental data that shows Cu, Au and the PPGEs to be incompatible with crystallizing **mss**. The most common interpretation of this fractionation when applied to the Sudbury ores envisages that the contact ore represents **mss-cumulates** enriched in Ni and the IPGEs whose complementary PPGE + Au-rich residual sulfide liquid migrated into the footwall.
Mineralization of probable magmatic origin i.e. North Range sulfide vein, irregular veinlets, South Range veinlets and inclusion-bearing sulfide veins from McKim all display lower crustal normalized PPGE, Au and Ag concentrations higher than seen in contact and sharp-walled vein mineralization from the North Range and contact samples from the South Range. These comparative enrichments, when combined with the lower normalized concentrations of the IPGEs compared to contact and sharp-walled vein mineralization would indicate that the mineralization has originated from, or equilibrated with an evolved sulfide liquid from which mss has been removed. Furthermore the higher levels of these elements within low-sulfide mineralization relative to sharp-walled vein data would imply that they continue to behave incompatibly with iss and hss. This incompatible behaviour would retain the PPGEs, Au and Ag within a residual liquid of constantly decreasing volume and assuming constant partition coefficients would explain the increases in dissolved metals within North Range sharp-walled vein and low-sulfide mineralization. This is particularly true for dissolved concentrations of Pd + Ag ad Se in pentlandite which display a steady increase as samples progress from contact ore, through sharp-walled vein sample and into low-sulfide mineralization. Such an increase reflects the composition of the sulfide melt, from which pentlandite is crystallizing, or equilibrating with. This strongly suggests that Pd, Ag and Se behave incompatibly with crystallizing sulfide and were retained in the sulfide melt that moved into the footwall. Such enrichments are also reflected in the distinct difference between the dissolved Ag concentration of chalcopyrite, with crystals from footwall mineralization (sharp-walled vein and low sulfide) noticeably enriched when compared to chalcopyrite from contact ores. The large range in concentrations of dissolved Se in chalcopyrite in sulfide veins from the Levack North property suggests that either the sulfide veins formed from a number of distinct sulfide melts, or that each vein represents a portion of the fractionation process, with high levels of Se in chalcopyrite due to crystallization or re-equilibration of chalcopyrite with a late stage fractionated sulfide liquid. Conversely veins that formed earlier from a less fractionated sulfide liquid will have lower concentrations of dissolved Se in chalcopyrite. As such it is proposed that IRV mineralization and veinlet mineralization represent the later stages of this process with normalized precious metal concentration in excess even of sulfide vein mineralization. The relatively flat IPGE profile displayed by sulfide vein analyses from the Denison property would imply an input from contact mineralization. This is consistent with the previously discussed hypothesis that these veins
represent sheared contact ores, with the slight enrichment in Pd, Au and Ag suggesting that either the mineralization has been sheared from the more fractionated margins of the Crean Hill orebodies or that during shearing a minor residual sulfide liquid input was also transported into the footwall along with the mss cumulates.

Quartz ± carbonate + sulfide mineralization from both Ranges has PPGE, Au and Ag concentrations in excess of contact and sharp-walled vein data. Samples from the South Range display a slight decrease in normalized IPGE concentrations when compared to mineralization from the Crean Hill and Little Stobie orebodies. This is interpreted as reflecting the preferential scavenging of PPGE, Au and Ag relative to the IPGEs from contact mineralization. The lack of a substantial decrease in IPGE levels in QCS mineralization from McKim relative to the Little Stobie orebodies, suggests that the metals were not scavenged from the footwall low-sulfide mineralization as the IPGE depletion would likely be even more pronounced than that displayed by sulfide vein and veinlet mineralization. Quartz ± carbonate + sulfide veins from the North Range (excluding Levack North) display normalized levels of the PPGEs, Au and Ag slightly above those of sulfide veins. IPGE concentrations are consistent with both sharp-walled vein and magmatic low-sulfide mineralization, with either considered a suitable source for precious and base-metals.

The semimetal profiles of these magmatic mineralizing styles display levels of Se, Sb, Te, Pb and Bi higher than in either contact or sharp-walled vein material. Arsenic concentrations for sulfide veins from the North Range properties and McKim are equal to, or below those of contact mineralization, with North Range IRV mineralization enriched compared to contact and sulfide vein samples. The enrichments are consistent with partitioning data from Helmy et al. (2010) who found mss/sulfide liquid partition coefficients for all of the semimetals of interest, excluding Pb, which was not present within experimental runs, to be less than one. The increase in normalized concentrations of semimetals between sharp-walled vein and low-sulfide mineralization indicate that the iss/sulfide liquid and hzss/sulfide liquid partition coefficients for these elements were likely less than one. Despite the incompatible behaviour of As with mss the normalized concentrations for North Range and McKim sulfide veins are lower than those for contact mineralization from the North Range and Little Stobie deposit respectively. This discrepancy likely results from the retention of As as discrete phases within contact
mineralization, with magmatic gersdorffite–cobaltite and IPGE sulfarsenides the most probable hosts (Cabri and Laflamme, 1976; Dare et al., 2010). The crystallization of these minerals would likely have removed significant amounts of As thus reducing levels entering the footwall within the residual sulfide liquid. The increase in As levels between sharp-walled vein and low-sulfide material suggest that a significant fraction of the available As in the parental sulfide liquid had been removed at the contact, with levels within the residual sulfide liquid below those required for sulfarsenide crystallization, and that once in the footwall that As behaved incompatibly with iss and hzss.

Semimetal profiles for North Range sulfide vein and IRV mineralization are extremely similar, with the exception of As and Sb. Lower crust normalized values for As in IRV mineralization are nearly an order of magnitude above those from sulfide veins. The enrichment is interpreted as being representative of the high levels of As within the late stage extremely fractionated sulfide liquid from which IRV mineralization is derived. As the mass balance for IRV mineralization did not identify any As in solid solution it must be present as discrete phases, likely gersdorffite–cobaltite. This hypothesis is consistent with the near equal levels of As and Sb in IRV mineralization from the Levack North property suggesting significant substitution of Sb for As in gersdorffite. In contrast Sb levels in IRV mineralization from Wisner and Capre are respectively depleted and enriched when compared to sulfide veins from the same properties. The increase in Capre samples may reflect the presence of an additional Sb phase. The lower levels of Sb within IRV mineralization from the Wisner property suggest that it has been removed from the residual sulfide liquid. This could be achieved through the crystallization of stibnite, previously observed within sharp-walled veins from the Strathcona mine (Ames and Farrow, 2007; references therein). The crystallization of stibnite would allow Sb levels within the sulfide liquid to be reduced, whilst not lowering the amount of As, which would also decrease if sulfarsenides were crystallizing. The lack of a substantial Sb enrichment in sulfide veins from the Wisner property relative to contact and sharp-walled vein mineralization probably reflects a nugget effect due to the rare occurrence of stibnite, with analyzed material not sampling any crystals.

The presence of gersdorffite within contact ore samples from the Crean Hill mine has resulted in a semimetal profile with a distinct As "bump". Although dissimilar from the consistent pattern displayed by the other semimetals the "bump" is shared by South Range veinlet, QCS, stockwork
and disseminated mineralization from both South Range properties and should be considered a clear indicator of sulfarsenides within the sulfide assemblage. The enrichments in Se, Te, Pb and Bi displayed by sulfide veins from the Denison property relative to Crean Hill sulfides is consistent with the requirement for an input from a fractionated source as previous outlined. The precious metal profile for stockwork mineralization is distinct with PPGE, Au and Ag levels in excess of all other mineralizing styles. The IPGE enrichment relative to Crean Hill material is the probable result of a (Ir, Ru, Rh)AsS nugget effect and as such it is uncertain whether this portion of the profile is correct. The semimetal profile for stockwork mineralization is broadly consistent with the other South Range mineralizing styles, with the exception of slight enrichments in Se and Bi. A hydrothermal origin would require a saline fluid that is extremely enriched in precious metals, whilst not having semimetal concentrations significantly above the other mineralizing styles, which must be considered unlikely. At present the simplest scenario requires the addition of a low-volume Pt–Pd–Bi–Se–S liquid or a late stage magmatic fluid. Wood (2003) demonstrated the ability of semimetal melts to transport significant quantities of the PGEs. Such a liquid is conceivable in light of textural evidence of low temperature, precious metal bearing and precious metal free semimetal melts seen in samples from the Denison and McKim properties (see Chapter. 4), although whether such a melt was formed in response to fractional crystallization or a metamorphic remobilization is unknown.

South Range semimetal profiles display a pattern consistent with North Range mineralization suggesting a uniform fractionation process with regards to the semimetals across both Ranges. Although modally inferior the accessory phases analyzed within this study give some indication to lower temperature processes not reflected within the major base-metal sulfides. Polydymite from the Wisner property contains more Ag, Pb and Bi than the surrounding chalcopyrite. These three elements, along with Se, were the only ones consistently identified within chalcopyrite analyses from the Wisner property. Their elevated concentrations would suggest that the $D_{\text{polydymite/chalcopyrite}}$ is $> 1$, whilst the $D$ for Se must be around 1 with near equal dissolved concentrations in both phases. The partitioning of these elements into polydymite is further evidence that of the common sulfide phases present the (Ni, Fe) sulfides constitute the preferred hosts for the dissolved metals. Violarite after pentlandite and millerite is typically associated with the interaction of these Ni-sulfides with a hydrothermal fluid, be it of magmatic or basement origin. The violarite analyses within this study show either that this fluid was enriched in Ag,
Au, Sb, Pb and Bi, or that these elements partition strongly into violarite. The latter possibility is consistent with the relative absence of Pt and Pd which would be expected to be present within both late stage magmatic and basement hydrothermal fluids that have interacted with sulfides.

Pyrite within North Range low-sulfide mineralization is of indeterminate origin and may result from alteration of pre-existing pyrrhotite due to increases in $fS_2$. At present given the lack of violarite alteration displayed by the host millerite it seems more likely that the enriched levels of As, Pt, Au, Pb and Bi within pyrite is the result of their movement from the parental Ni-$mss$ (millerite) during the exsolution of Fe-$mss$ + iss. The subsequent alteration of the Fe-$mss$ to pyrite likely redistributed these elements into the growing crystal as the surrounding millerite and chalcopyrite were replaced. The presence of pyrite within low-sulfide mineralization from the Denison property has been interpreted by the author as having been caused by the interaction of sulfides with a metamorphic hydrothermal fluid. Analyses from sulfide veins indicates that pyrite is enriched in As, Ag, Te, Pb and Bi when compared to the dominant base-metal sulfides and likely reflects the composition of the metamorphic hydrothermal fluid. The lack of palladium in crystals that were replacing Pd-bearing pentlandite would suggest that the hydrothermal fluid was stripping the crystals of Pd, but not re-depositing it during pyrite growth. This is surprising given that the loss of bisulfide ligands to form pyrite should lead to a reduced solubility for Pd. The lack of Pd would suggest that it is being retained in solution, either due to their being an excess of bisulfide or due to the presence of another ligand within the fluid not effected by sulfide deposition, e.g. chloride.

Analyses normalized to 100 % sulfide have identified no distinct differences between different mineralizing styles within the low-sulfide mineralization group. When samples of low-sulfide material from the North Range prospects are put into a larger context through comparisons with contact and sharp-walled vein style mineralization a trend is apparent. Plots of Pt 100, Pd 100 and Au 100 vs. Cu 100 display the expected trend with respect to established mineralizing styles, with sharp-walled vein material containing elevated levels of Cu, PPGEs and Au when compared to contact mineralization. This trend is continued within the low-sulfide material however concentrations of Pt, Pd and Au are comparable with and above those of sharp-walled vein mineralization. The elevated concentrations between contact and footwall mineralization reflect established partitioning values (c.f. Mungall et al., 2005 and reference therein) with Cu, PPGEs
and Au concentrating within the residual sulfide liquid at the contact before entering the footwall, consistent with the modelled sulfide liquid compositions of Mungall et al. (2005) (Figure. 5.7). The comparative increase in precious metals between sharp-walled vein and low-sulfide mineralization would suggest that this incompatible behaviour continues between iss and hzss, and the residual sulfide liquid. This observation would imply that low-sulfide mineralization is at least in part the result of crystallization from an extremely fractioned, late stage sulfide liquid. The proposed incompatibility of precious metals with mss, iss and hzss would further suggest that the formation of precious metal phases is dominated by direct precipitation from the sulfide liquid, rather than through exsolution from sulfides containing substantial quantities within solid-solution.

Comparison of Pt 100, Pd 100 and Au 100 vs. Cu 100 for South Range mineralization identified significant overlap between Pt and Pd levels within low-sulfide and contact mineralization. Concentrations of 100% sulfide normalized Pt and Pd typically range between 0.01 and 10 g/t, with the majority of low-sulfide material typically containing > 1 g/t, a slight enrichment relative to contact ores. The overlap is contradictory to the comparison of low-sulfide mineralization from the Denison and McKim properties to contact mineralization from the Crean Hill and Little Stobie mines. Initial sulfide melt normalized values clearly indicate an enrichment of Pt and Pd in low-sulfide mineralization relative to their proximal contact orebodies. The overlap displayed by Pt 100 and Pd 100 vs. Cu 100 plots can therefore be explained due to the inclusion of additional data points from unconnected embayments, especially the Creighton mine, which displays a significant range of precious metal concentrations (Naldrett et al., 1999). Such comparisons show that the sampled South Range low-sulfide zones although enriched when compared to their proximal contact orebodies, are not significantly enriched when compared to the South Range as a whole, although the low-modal sulfide that they contain and the broad range of Cu 100 values clearly marks them out a distinct mineralizing style. Comparison of the Pt 100 concentrations of South Range low-sulfide material to modelled mss-cumulate and residual sulfide liquid compositions from Mungall et al. (2005) show that the majority of Pt 100 concentrations are above those of the modelled mss-cumulates. This difference may be the result of discrete Pt-phases within the analyzed samples, or due to the initial sulfide liquid having a Pt concentration slightly higher than that used in the modelling. In either case it appears that a significant proportion of South Range low-sulfide mineralization represent mss cumulates, with
the more scattered, but Cu-rich points likely reflecting sulfide cumulates crystallized from the low-volume residual sulfide liquid. In contrast to Pt and Pd the Au 100 content of low-sulfide mineralization shows a clear enrichment when compared to contact mineralization. Low-sulfide samples dominantly contain Au 100 concentrations in excess of 1 g/t, with the majority of these points from disseminated and veinlet mineralization. Contact ores and a large fraction of inclusion-bearing sulfide vein samples provided Au 100 values of less than 1 g/t. The comparative enrichment of Au is difficult to explain given the lack of elevated Pt and Pd concentrations. Estimations of the composition of the initial sulfide liquid by Mungall et al. (2005) set Au concentrations at approximately half those of Pt and Pd. Even though Au has the lowest mss/sulfide liquid partition coefficients of any of the precious metals, at between D = 0.006 and 0.025 it is probable that the PPGE concentrations became enriched to the levels required for the crystallization of Pt and Pd phases before Au. This would allow the deposition of discrete PPGE minerals within the contact assemblage before the residual liquid became saturated with Au. The crystallization of Au phases, chiefly AuAg alloy (electrum), may also have been partially inhibited by the movement of Ag into tellurides minerals, particularly hessite. The activity of Au did not rise to sufficient levels to induce crystallization in its native form, with crystals only rarely observed within the South Range footwall (Cabri et al., 1973; Molnár et al., 1997), so the availability of Ag must be considered as a limiting factor to Au-mineral formation. The movement of small packets of residual sulfide liquid into the footwall due to fault movement and localized variations in fluid pressure will allowed the development of comparatively Au enriched low-sulfide mineralization, with precious metal concentrations becoming particularly enriched within mineralization containing an input from trapped sulfide liquid. Due to the typically minor nature of South Range footwall mineralization it seems likely that a significant portion of the residual sulfide liquid was retained at the contact and should therefore provide Au 100 concentrations similar to low-sulfide material. The lack of these data points suggests to the author these Au enriched ores have not been sampled, as they are likely part of the zones along the margins of South Range contact orebodies that have not been the focus of substantial investigation, as their lower modal sulfide content would make them visually appear uneconomic when compared to massive contact sulfides. The higher heat flow experienced by contact deposits relative to their footwall systems could also have played a part with the elevated temperatures allowing a prolong fractionation of Au into the residual portion, whilst Pt and Pd
were removed through the formation of discrete PGMs. Such an Au enriched liquid could then have entered the footwall either in the form of a residual sulfide liquid or a saline hydrous fluid, with these liquid(s) forming or adding to the Au budget of low-sulfide mineralization. A metamorphic redistribution of Au is considered unlikely as Au would be remobilized from both contact and low-sulfide zones and would therefore be incapable of producing the difference in Au content which is observed.

5.7.4.2 Pt/(Pt + Pd) Ratios

Figure 5.10 shows histograms of the distribution of various metal ratios in low-sulfide mineralization. Mineralized samples normalized to 100 % sulfide typically display 28 to 38 wt % Cu, reflecting the dominance of chalcopyrite in the sulfide assemblage. Material from all North Range properties yielded Cu/(Cu + Ni) ratios between 0.75 and 0.97, similar to values of ≥ 0.85 reported for sharp-walled vein mineralization by Farrow and Lightfoot (2002). The separation of mineralizing styles with respect to Pt/(Pt + Pd) ratios was noted by Farrow et al. (2005), with Pt/(Pt + Pd) values increasing from ratios of 0.40 to 0.50, as modal sulfide decreases from ≥ 20 to ≤ 1 %. A similar pattern was noted here for all North Range properties. Pt/(Pt + Pd) ratios in sulfide veins display average values of 0.30 to 0.41, consistently remaining lower than IRV, QCS and disseminated mineralization (Figures 5.21A, 5.21B and 5.21C). Samples from the McKim prospect displayed a similar Pt/(Pt + Pd) distribution to North Range material, with styles averaging between 0.40 and 0.49, although no distinction between mineralizing styles is apparent (Figure 5.21E). Pt/(Pt + Pd) values for mineralization from the Denison property, excluding disseminations show a weak normal distribution, peaking around 0.5 to 0.6. Pt/(Pt + Pd). Ratios of 1 are extremely common in material from the Denison property and reflect “nugget” effects, particularly amongst low modal sulfide material where the PGE grade is controlled by single sparsely distributed PGMs (Figure 5.21D). The effect would not be so great were it not for the preference of South Range mineralization to host sperrylite and Pd phases displaying no Pt solid solution. Mineralizing styles from Denison produced an average Pt/(Pt + Pd) range of 0.47 to 0.59. The reduced Pt/(Pt+Pd) ratio displayed by North Range sulfide veins when compared to the other mineralizing styles reflects the retention of Pd over Pt. As the PGMs analyzed from the North Range properties often display Pt–Pd substitution it is probable that the elevated Pd
content of the sulfide veins has at least in part been caused by an alternative process. The partition coefficients for Pt and Pd between hzss or iss and sulfide liquid are at present unknown, although Peregoedova and Ohnenstetter, (2002) did identify an approximate $D_{\text{mss/hz-iss}}$ for Pd of between 0.016 and 1.5, with the majority of runs yielding D's of less than 1. The same study also noted that Pd became more compatible with heazlewoodite–intermediate solid solution (hzss–iss) and mss as their Ni content increases. The compatibility of Pd was also controlled by variations in $f_{S_2}$ with dissolved levels of Pd increasing with $f_{S_2}$. In contrast to Pd, platinum consistently behaves incompatibly (Peregoedova and Ohnenstetter, 2002). Such partitioning behavior may explain the observed decrease in Pt/(Pt+Pd) values between sulfide veins where hzss and Ni-rich mss cumulates have made an input into the sulfide assemblage and IRV and disseminated mineralization which are dominated by chalcopyrite and pyrite likely after iss. The crystallization of hzss and Ni-rich mss would therefore allow for a more efficient removal of Pd from the sulfide liquid than the crystallization of PGMs alone. This would thereby allow Pt levels within the residual sulfide liquid to exceed those of Pd, with mineralization likely formed from these late stage sulfide melts i.e. IRV and disseminations reflecting this increase in their Pt/(Pt+Pd) ratio.

Due to the limited North Range QCS dataset it is difficult to conclude whether the Pt/(Pt+Pd) ratios displayed are representative. The two largest datasets, from the Wisner and Capre properties when normalized to the initial Sudbury sulfide liquid, display increased levels of Pt relative to Pd within QCS veins from Wisner, with the opposite occurring at Capre (Figures 5.20B and 5.20C). Given the broadly similar solubilities of Pt and Pd in hydrothermal solutions (Gammons and Bloom, 1993; Pan and Wood, 1994; Wood et al., 1994) it seems unlikely that these differences can be attributed to variations in the hydrothermal fluid from each property. Instead they may reflect the interaction of the QCS vein forming saline fluid(s) with differing mineralizing styles. The dominance of IRV and disseminated mineralization at the Wisner property may be reflected in the comparative enrichment of Pt relative to Pd, within its QCS samples, with the common occurrence of sulfide veins within the Capre footwall resulting in the slight enrichment in Pd relative to Pt in QCS there.

Farrow et al. (2005) used a threshold interval (see Chapter 1) to classify mineralized intersections as low-sulfide on the PM Zone at McCreedy West. Samples were classified as
economic if they contained ≥ 5 g/t Pt + Pd. Subdivision of sample sets based on S content allowed the definition of a threshold S concentration within which more than 50 % of samples possess economic concentrations. The threshold interval for the PM Zone fell between ≥ 1 to < 2 wt % S. In contrast, the intersected zones from the Levack North and Wisner properties display threshold intervals of < 2 wt % S, with 56.6 and 56.3 % of economic mineralization occurring within samples with < 2 wt %. This threshold value is matched by mineralization from the Denison property where 61 % of economic mineralization is contained within samples with < 1 wt % S. This low S content is the result of the presence of stockwork mineralization, whereas grades from disseminated mineralization are typically < 1 to 2 g/t. These low threshold values should be compared to the Capre property where the no clear threshold value can be identified, although the majority of economic samples (52 %) contain ≥ 5 wt % S. Although mineralization from the McKim property is dominated by disseminated sulfides typically containing < 1 to 2 g/t Pt + Pd, economic mineralization as defined by Farrow et al. (2005) is dominated (57 %) by samples containing ≥ 20 wt % S i.e. sulfide veins. The data from the Capre and McKim prospects therefore brings their classification as low-sulfide zones into question; according the Farrow’s (2005) classification the Capre property should be considered hybrid, and the McKim prospect is classified as sharp-walled mineralization.

5.7.5 Chalcophile Element Correlation Coefficients

Bulk metal correlations have been applied in an attempt to identify possible pathfinder elements and to identify mineralogical variation. Comparisons of base (Ni, Cu and Zn), precious (Pt, Pd, Au and Ag) and semimetals (Bi, Te, Sb, As, Se, Pb) against lithophile elements failed to identify a consistent bulk compositional variation with changes in grade. This lack of correlation is considered to result from several factors: the footwall rocks have undergone alteration; mineralization is not limited only to Sudbury breccia; and mineralizing processes did not induce the re-equilibration of large volumes of rock. The situation is further complicated on the South Range by regional metamorphism which overprinted primary assemblages. Variations between siderophile and chalcophile elements commonly associated with the presence of mineralization are summarized in Tables 5.1A to 5.1E.
Pearson correlation coefficients (R) for the North Range properties display strong indications of the PGM assemblage, with Pt and Pd correlating strongly with Te, Bi and Se, a reflection of the dominance of tellurides and bismuth tellurides as precious metal hosts. Platinum group elements from both the Wisner and Capre properties are not correlated with base-metals and S (Tables 5.1B and 5.1C), taken by Farrow et al. (2005) as an indicator of low-sulfide mineralization. In contrast at Levack North the PPGES are strongly correlated with Cu and S (Table 5.1A).

Precious metals from the Levack North and Wisner properties show strong correlations between Ag and both Pt and Pd, suggesting that they were all present simultaneously from the same mineralizing fluid(s) or melts. Gold from the Wisner property also displays a strong association with Ag, Pt and Pd. This association is not observed within mineralization from the Levack North and Capre properties and may reflect a nugget effect, with samples from the Wisner property containing Au-minerals associated with the PPGEs and Ag that were not sampled at the other two North Range properties. A similar correlation was noted for the McKim property where Au correlated strongly with Pt and Pd. The reason for these extremely strong correlations is unknown and may simply reflect the levels of Au within South Range mineralization, which are comparable to the PPGEs, thus reducing nugget effects (Table 5.20A, B and E). The lack of correlation between Ag and Au from McKim is a reflection of the ubiquitous nature of hessite within the sampled low-sulfide mineralization, thus masking silver's association with all other elements apart from Te and Se. The former correlation is due to the presence of Te along with Ag in hessite, whilst the latter reflects the presence of numerous of Bi-chalcogenide phases containing Se occurring with hessite.

The South Range properties are marked by few correlations between the base and precious metals, with the exception of Cu:Ag from the Denison property (Table 5.20D). The presence of gersdorffite–cobaltite within South Range material, particularly that from the Denison property, allows for correlations unseen in the North Range material i.e. Co:Pd (R = 0.58), As:Sb (R = 0.53) and Co:As (R = 0.56). Unlike the other four properties Pt and Pd at Denison do not correlate strongly. This likely results from nugget effects with low modal sulfide mineralization especially commonly only containing single sparsely distributed PGMs. Platinum from the Denison property failed to correlate within any other elements probably because the presence of gersdorffite–cobaltite masking any Pt:As correlation (sperrylite is the only Pt mineral observed),
with the aforementioned nuggets effect reducing correlations with Te and Bi, elements common within Pd phases which would be expected to partner sperrylite. Platinum from the McKim property displays strong correlations with Bi, Te and Se, a clear reflection of the presence of sperrylite within mineralization bearing abundant Bi-chalcogenides. Palladium from the Denison property correlates strongly with Bi, Te and Se because Pd is predominantly hosted by bismuth telluride phases, i.e. michenerite and sobolevskite–kotulskite–sudburyite, which are in turn associated with Bi-chalcogenides bearing trace Se. Palladium mineral and Bi-chalcogenide bearing samples also commonly contained associated AuAg alloy, a relationship reflected in the strong correlation of Au to Pd, Bi, Ti and Se from both the Denison and McKim properties. Although the Pd:Bi correlation displayed by samples from the McKim property is strong (R = 0.55) it is surprising that it is not stronger, given that froodite is the only observed Pd phase in the McKim samples. This weakened correlation is likely caused by the presence of Bi-chalcogenide phases within samples containing low Pd grades.

The absence of an association of precious metals and S was noted for low-sulfide mineralization from the PM Zone, McCreedy West mine by Farrow et al. (2005). A similar lack of correlations between the precious metals and S, Cu and Ni is noted from the Wisner, Capre, Denison and McKim properties. The strong correlations between the precious metals and Cu and S from the Levack North property suggest that it may be better classified as hybrid mineralization. The strong correlations of Pt and Pd with Bi and Te across all five properties indicate the dominance of discrete PGMs as hosts for the PGEs. These correlations may well have been stronger had the clouding effects of Bi-chalcogenides not been present.
The threshold intervals and base-metal – precious metal correlations from the five low-sulfide properties reveal the difficulty in definitively classifying the mineralization as low-sulfide. Based on the classification of Farrow et al. (2005) only the Wisner and Denison properties can be classified as low-sulfide. The threshold intervals for the Levack North, Capre and McKim properties are strongly affected by the requirement for 'economic' mineralization to contain ≥ 5 g/t. Such a cut-off is unrepresentative of mineralized zones in which Pt + Pd grades typically lie between < 1 and 2 g/t with sporadic high grade samples bring up the grade over the entire intersection to economic levels. It therefore seems highly questionable whether ignoring these lower Pt + Pd samples is justified. As such it seems that only the use of Pt and Pd correlations offers a fair method of identifying low-sulfide mineralization, by making use of the whole dataset. Based on this criterion alone all of the deposits studied should be considered low-sulfide,
except for the Levack North property which should be considered as an example of hybrid mineralization.

<table>
<thead>
<tr>
<th>S wt %</th>
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<th>Wisner</th>
<th>Capre</th>
<th>Denison</th>
<th>McKim</th>
</tr>
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<tr>
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<td>43.8</td>
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<td>60.7</td>
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<td>18.8</td>
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<td>17.9</td>
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<tr>
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<td>6.3</td>
<td>25.9</td>
<td>7.1</td>
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</table>

* Based on single analysis

Table 5.11. S (wt %) content intervals for economic mineralization (Pt + Pd ≥ 5 g/t) from five low-sulfide prospects. (A) Percentage of total economic mineralization by property (B) Average Pt + Pd grade (g/t).

5.7.6 The Distribution of the Chalcophile elements in Low-Sulfide Mineralization

Although it is by no means certain that the levels of chalcophile elements within the analyzed samples are representative of their initial distributions, given the extensive metamorphic reworking of the Sudbury area, the material sampled represents the only route to investigating the evolution of the SIC with respect to its sulfide mineralization and chalcophile element budget.

The distribution of the chalcophile elements offers a window into the processes controlling PGM crystallization. Analysis of PGM bearing samples by SEM combined with LA-ICP-MS analysis of associated sulfides has led to models suggesting that a significant proportion of PGE-bearing phases form through exsolution from base-metal sulfides rather than direct precipitation (Barnes
Evidence for exsolution is primarily textural with lath shaped crystals occurring within base-metal sulfides considered reminiscent of exsolution textures produced during experimental runs. No textural indicators of exsolution were observed within major sulfides in the present study. Such a hypothesis requires elements to enter solid solution readily within the major base-metal sulfides. This is feasible for elements that partition strongly into sulfide e.g. Ir, Os, Ru and Rh into mss (Fleet et al., 1993; Li et al., 1996; Barnes et al., 2001; Mungall et al., 2005), but with the steady increase in whole rock precious (Pt, Pd, Au and Ag) and semimetal concentrations from contact to sharp-walled vein to low-sulfide mineralization it seems reasonable to suggest that they are behaving incompatibly with mss, iss and hzss, a view which is consistent with experimental data for Pt and Pd (Peregoedova and Ohnenstetter, 2002).

Experimental runs displaying the presence of exsolved PGMs commonly present PGE-bearing alloys and sulfides. In order to produce the Bi–Te–Sb bearing PGMs commonly observed within magmatic sulfide deposits the semimetals would be required to be present in similar dissolved concentrations. Experimental data from Helmy et al. (2010) indicates that Se, As, Sb, Te and Bi all behave incompatibly with mss, with Sb, Te and Bi presenting D values well below those for Pt and Pd. Furthermore the presence of semimetals along within Pt and Pd bearing experimental runs (Helmy et al., 2007, 2010) failed to produce any PGMs through exsolution from mss, with discrete phases or precious metal – bearing liquids formed instead. Helmy et al. (2010) suggested that PGE participate in the formation of semimetal molecules and polyatomic clusters within the sulfide liquid, helping to stabilize discrete PGMs and PGE-bearing liquids. This data would suggest that the ability of precious metals to enter solid solution is not only controlled by their partitioning behavior but is also further reduced due to the formation of discrete PGMs.
Table 5.12. Bulk rock Pearson correlation coefficients from the Levack North and Wisner properties, the Capre property and the Denison and McKim properties. Correlations with R values ≥ 0.5 are shown in bold face and highlighted in dark grey.

Primary crystallization of PGMs within sulfide veins is dependent on the longevity of the proposed Cu–Ni–Fe–S sulfide liquid. Cabri (1973) and Barton (1973) showed that a Cu–Fe–S melt continued to react with iss down to 600 °C; with the Cu–Fe–Ni–S system maintaining a similar liquid until 574 ± 3 °C (Craig and Kellerud, 1969). The possibility that a sulfide liquid could persist to such low temperatures allows for the sulfide melt to be present during the
crystallization of the majority of PGMs commonly observed, particularly moncheite–merenskyite and kotulskite–sobolevskite solid solutions, although the latter remains poorly constrained. The crystallization of low temperature PGM, i.e. those that form below the sulfide solidus like michenerite, requires either 1) subsolidus precipitation from sulfide minerals i.e. exsolution, 2) the formation of a separate Pd–Pt–Bi–Te melt or 3) a depression of the sulfide liquid solidus by the presence of fluxing components. Analysis of pentlandite bearing samples from the North and South Range did identify significant amounts of Pd in solid solution, primarily in pentlandite. Its presence is consistent with experimental data which indicates the preference for Pd to enter solid solution within hzss over mss (Peregoedova and Ohnenstetter, 2002), whilst the ability of Te and Bi to enter solid solution in pentlandite has been also established (Dare et al., 2010b), so the formation of michenerite through exsolution is theoretically possible. Exsolution of Pd–Bi–Te phases is, however, deemed unlikely, in light of the following considerations: 1) given that the vast majority of exsolved PGMs in the literature are between < 1 and 5 μm in size it is difficult to account for the existence of natural michenerite crystals of up to 175 μm; 2) if low temperature Pd phases are exsolved from pentlandite, then michenerite should not be expected to appear as inclusions in chalcopyrite; 3) low temperature Pd minerals appear in mineral assemblages entirely lacking pentlandite, such as chalcopyrite-dominated veins from the Wisner property; and 4) given the apparently incompatible nature of Pt with hzss and iss, the occurrence Pt-michenerite crystals is problematic. Such issues make the hypothesis that low temperature PGMs are forming through exsolution within the studied low-sulfide zones highly unlikely. The formation of discrete Bi–Te melts of late magmatic or metamorphic origin has been inferred from observations of polyphase precious metal mineral aggregates from the North Range and Denison property and Bi-chalcogenide veinlets from the McKim property (see Chapter. 4). The ability of such Pd–Bi–Te–Pt–Sb melts to crystallize single crystals is feasible for phases such as moncheite–merenskyite and kotulskite–sobolevskite–sudburyite which present significant Pd–Pt and Bi–Te–Sb substitution, however more phases like michenerite with simple stoichiometry would likely be accompanied by accessory Bi-chalcogenides, or multiple PGMs, if they were crystallized from multi-component Pd–Bi–Te–Pt–Sb liquids, neither of which is typically observed. Although it is a rare phase within North Range mineralization, froodite is typically observed to occur within precious metal mineral aggregates (Li and Naldrett, 1993; Farrow and Watkinson, 1997). Such associations
suggest that it may have crystallized from a Pd–Bi–Te–Ag melt. Although the single crystal of froodite observed within North Range low-sulfide mineralization occurs alone, the crystal’s large size (~ 40 μm) and its surface topography may have obscured the presence of associated PGMs and Bi-chalcogenides. It is therefore likely that froodite has been deposited from a Pd-Bi-Te melt, with crystals from the Denison property likely forming by the same process. Due to the small size of froodite from the McKim property it is at present uncertain whether they are occurring alone, or with associated phases.

At present, the crystallization of PGMs from the sulfide liquid offers the most succinct explanation for the majority of precious metal minerals observed within the low-sulfide mineralizing styles of magmatic origin. Direct crystallization allows the PGMs to sequester the required elements, occur individually and to grow to a range of sizes. Reductions in the solidus of sulfide magmas of up to 85 °C have been observed within a magnetite bearing Fe–Ni–Cu–S–O system (Skinner and Peck, 1966), whilst H₂O can induce a minor depression of up to 20 to 35 °C (Craig and Kullerud, 1969, reference therein; Wykes and Mavrogenes, 2005). Fe–Ni–Cu–S liquids can also dissolve several wt % Cl, which causes several tens of degrees of lowering of the liquidus surface (Mungall and Brenan, 2002). Such experimental observations indicate the possibility of solidus depression, although the Cu–Fe–S–O system failed to display any magnetite related reduction (McKinstry, 1959). The suppression of the sulfide melt solidus would allow a prolonged window for PGM crystallization and may have allowed small volumes sulfide liquid to persist down to temperatures at which michenerite crystallization became possible. It is probable that the low-volume sulfide liquid would have been approaching the point of Bi–Te saturation, but that a separate Bi–Te liquid did not exist. The presence of such a Bi-Te melt would likely have stripped the sulfide liquid of precious metals and semimetals, thereby inhibiting michenerite crystallization. Once formed, the Bi–Te melt would have persisted to temperatures of ≤ 485 °C (Okamoto, 1994), the crystallization point of froodite.

The high levels of Se observed within major base-metal sulfide presents another problem, because they seem to contradict the incompatible behavior inferred from the steady increase in its abundance from sharp-walled vein to low-sulfide mineralization. The discrepancy may be an analytical artifact resulting from Se loss during the acid digestion prior to solution ICP-MS and ICP-AES analysis of the samples, thereby producing low Se concentrations, which when placed
into the mass balance equation results in an increased fraction of total Se in solid solution. The high levels of Se dissolved within base-metal sulfides may primarily reflect the elevated concentrations of Se within the residual sulfide liquid which produced the magmatic footwall (sharp-walled vein and low-sulfide) mineralization, with the low levels within contact mineralization reflecting the lower Se concentration within the sulfide melt from which they crystallized. Assuming constant $mss$, $iss$, $hzss$/sulfide liquid partition coefficients for Se, this hypothesis is consistent with LA-ICP-MS data that shows increasing concentrations of dissolved Se within chalcopyrite, pentlandite and pyrrhotite between samples from contact and footwall (sharp-walled vein and low-sulfide) mineralization. The same mechanism is envisaged for the elevated dissolved concentrations of Ag in chalcopyrite and Pd in pentlandite as you progress.
Chapter 6
Summary and Conclusions

6.1 Introduction

In recent years industrial use of platinum-group elements has increased dramatically, particularly within the automotive industry due to their catalytic properties. Although the advent of electric automobiles may effect demand in the long term, in the short to medium terms the demand for these metals can only increase, as the populations of developing nations like China and India, become more prosperous. It is for this reason that the development of new PGM resources is extremely attractive.

The goal of this study was to identify geochemical and mineralogical indicators to the presence of low-sulfide PGE mineralization and through them to produce methods for the delineation of low-sulfide zones, grade estimation and to formulate a genetic model. The identification of low-sulfide mineralization is complicated by the low average modal abundance of sulfide in rocks containing significant quantities of precious metals, such as IRV mineralization from the North Range and disseminated and stockwork mineralization from the South Range.

6.2 Genesis

6.2.1 North Range

Low-sulfide mineralization in the three North Range properties was emplaced in footwall rocks heated to equilibrium temperatures (calculated using amphibole-plagioclase pairs) of between 440 °C to 533 ± 75 °C. Four distinct mineralizing styles are recognized, of which only QCS mineralization has a clear origin, with sulfides, PGMs and vein gangue precipitated from a hydrothermal fluid. Based on the data collected in this study the sulfide veins and irregular veinlets (IRV) observed are interpreted as having formed from a highly fractionated Fe–Cu–Ni sulfide liquid. The liquid represents a sulfide melt that was residual to nearly complete
crystallization of contact mineralization and then migrated into the footwall primarily along permeable zones typified by Sudbury breccia. Permeability in the Sudbury breccia bodies was increased through the development of fracture sets in response to creater settling and syntectonic Penokean deformation, and the parting of clast-matrix contacts caused by thermal contraction during cooling. The chalcopyrite + millerite ± pentlandite ± pyrite sulfide assemblage of these veins is interpreted as having formed through the magmatic crystallization of an extremely Ni-rich monosulfide solid solution (αNi$_{1-x}$S), along with heazlewoodite and intermediate solid solutions. These primary solids then broke down to pentlandite and chalcopyrite as temperatures decreased. As temperatures dropped, Cu and Fe would have exsolved from the Ni-rich mss, in which they were present in low concentrations (Peregoedova and Ohnenstetter, 2002), likely as iss and mss respectively. At 379 °C the breakdown of the Ni-rich mss led to the formation of millerite, with excess S destabilizing enclosed Fe and Cu sulfides to produce pyrite and chalcopyrite respectively. Micro-veinlets composed of millerite, polydymite and rarely pyrrhotite along the margins of sulfide vein chalcopyrite are interpreted as having formed by exsolution from iss during cooling and its breakdown to chalcopyrite. Subsequent alteration of the major sulfide minerals was limited to sulfide vein margins where violarite and lesser pyrite replaced pentlandite and millerite. The cause of this alteration is uncertain, but it may have come about due to the release of excess S during the breakdown of the Ni-rich mss, or through interactions with hydrothermal fluids. Any such hydrothermal fluid is believed to have been magmatic in origin and derived from the fractionating sulfide liquid. Analysis of violarite replacing millerite from Capre identified levels of Sb, Pb and Bi significantly above those in the major base-metal sulfides, with Ag and Te higher than the precursor millerite. These increased concentrations are interpreted as reflecting the interaction of millerite with a late stage strongly fractionated enriched saline fluid sourced from the sulfide liquid which transported these elements into the surrounding footwall. The substantial hydrous alteration selvages shown by irregular veinlets may indicate that the highly fractionated sulfide liquid was extremely enriched in volatiles. It is uncertain whether the fluid(s) responsible for alteration surrounding the veinlets were sourced from the sulfide liquid, distal contact and/or sharp-walled vein mineralization or the crystalline basement. In the latter two scenarios, the thick alteration selvages may well have formed around open fluid-filled fractures before the emplacement of the magmatic sulfide veins along the same openings, thus bringing into question whether the alteration selvages and haloes are truly the
result of the immediate mineralizing process. Given the uncertainties about the development of the alteration selvages a firm ascertain about their origin is difficult. It is questionable whether a late-stage low volume volatile-rich sulfide melt, like the one envisaged to form IRV mineralization, could carry enough H$_2$O to produce the thicknesses of alteration minerals observed. At present the author favours the development of the alteration selvage before the emplacement of mineralization, with the passage of higher volume sulfide melts i.e. those that formed sulfide veins, stripping and replacing silicates from the fracture margin, thus reducing the thickness of the alteration selvage. A similar process did not take place during the deposition of IRV mineralization due the low volume of sulfide melt passing along the fracture and the rapidity with which it would have crystallized out, when compared to sulfide veins. Subsequent re-equilibration between the sulfides and the alteration silicates produced the Ni-enriched actinolite, chlorite and biotite observed in this study.

Enrichments of the PPGEs, Au, Ag, As, Se, Sb, Te, Pb and Bi in low-sulfide mineralization, compared to sharp-walled veins and the contact deposits indicates that all of these elements behaved incompatibly with the mss, iss and hzs cumulates that had crystallized from the sulfide liquid to form contact deposits and sharp-walled massive sulfide veins. These enrichments are shown by the high levels of Pd, Ag and Se in base-metal sulfide minerals, particularly chalcopyrite and pentlandite, attesting to the extraordinarily high concentrations of these elements within the sulfide liquid that formed sulfide veins, irregular veinlets and possibly disseminations. Consideration of the mass balance for these elements indicates that significant proportions of the whole-rock budget of Ag and Se occur within sulfide mineral phases. Such high levels would suggest that these elements, which had behaved incompatibly throughout the evolution of the sulfide melt, either become more compatible at the closing stages of solidification, possibly as a result of increases in fS$_2$ or decreases in temperature, or that the sulfides re-equilibrated with an unknown Ag and Se rich fluid. The incompatibility of PGM forming elements, i.e., Pd, Pt, Te, Bi, Sb and As with sulfide minerals, coupled with the absence of obvious subsolidus exsolution textures, suggest that platinum group minerals formed as a result of direct precipitation from the highly enriched residual sulfide melt, which persisted due to the suppression of its solidus down to temperatures of 489 to 501 °C, allowing the crystallization of michenerite. It also seems plausible that Te, Bi, Ag and Pd concentrations within the sulfide liquid became high enough to form a discrete immiscible liquid which, upon
cooling below the solidus of the sulfide magma, formed the polyphase precious metal mineral aggregates and Ag-micro-veinlets observed within sulfide veins and IRV mineralization from the North Range.

Quartz ± carbonate + sulfide veins are abundant in the low-sulfide mineralization and locally carry significant precious metal grades. They are inferred to have acquired their precious metals by scavenging them from pre-existing magmatic sulfide mineralization. The unaltered appearance of the sulfides within the intersected low-sulfide zones suggests that the base and precious metals within quartz ± carbonate + sulfide veins were not locally derived from their immediate surroundings in the footwall. Furthermore, the PPGE, Au, Ag and semimetal enriched normalized profile suggests that either the hydrothermal fluids selectively removed these elements from contact mineralization, or that they were scavenged from sharp-walled veins. This suggests that the quartz ± carbonate + sulfide veins formed independently of the low-sulfide magmatic veins, which might partly account for the occasional observation of magmatic irregular veinlets being crosscut by quartz ± carbonate + sulfide veins. Fluid inclusions are common in quartz in the QCS veins. The majority of isolated fluid inclusions homogenized between 223.8 to 377.5 °C, with salinities between 33.1 and 45.1 wt % NaCl equivalent. This temperature range and salinities are consistent with published values from the Broken Hammer prospect, with Penték et al. (2008) interpreting them as being of late magmatic-hydrothermal origin. The origin of this fluid is uncertain and may represent either a complex basement fluid or a mixture between magmatic and basement fluids. Disseminated sulfides are distributed throughout the mineralized intersections associated with all low-sulfide mineralizing styles and are of uncertain origin. The chlorite + epidote ± actinolite alteration selvage that surrounds the disseminated sulfide crystals is reminiscent of the alteration assemblage associated with both sulfide vein and IRV mineralization, however a significant number of crystals are hosted in chlorite 'clots', similar to alteration associated with QCS veins. The disseminations are therefore thought to be of both magmatic and hydrothermal origin, but whether one process was dominant is unknown.

In summary, the sequence of events is likely to have involved the early crystallization of mss cumulates at the contact of the SIC, followed by invasion of the footwall by sharp-walled veins containing cumulus mss and iss. Continued crystallization of sulfide melt in the sharp-walled
veins, fluxed by minor constituents including volatiles, semimetals, and precious metals, was followed by infiltration of widely dispersed fine fracture networks by extremely fractionated sulfide melt which formed the low-sulfide irregular veinlets and associated disseminations accompanied by the development of increasingly wide alteration selvages. The movement of this highly fractionated sulfide melt into the footwall was coincident with the circulation of saline hydrothermal fluids which equilibrated with sharp-walled veins or contact mineralization and gave rise to quartz ± carbonate + sulfide veins and disseminations at relatively low temperatures. This was followed by the introduction of additional fractionated sulfide melt(s) into the low-sulfide zones forming sulfide veins. The formation of these sulfide veins towards the end of the mineralizing process is consistent with the lack of crosscutting quartz ± carbonate veins suggesting that fluid circulation within the footwall was waning. The low-sulfide mineralization invaded volumes of rock that had previously been altered by hydrothermal fluids depositing barren quartz + epidote veins. This led to the superposition hydrous phases associated with mineralization in an already altered footwall. The departure of the highly fractionated residual sulfide melt from the cooling sharp-walled veins left them with essentially entirely cumulate mss + iss compositions unlike the veins in the low-sulfide zone, which show evidence for the retention of the final sulfide liquids themselves. The suggest late-stage emplacement of sulfide vein style mineralization is consistent with the observations of Farrow et al. (2005), and would suggest that the North Range low-sulfide prospects analyzed straddle the divide between true low-sulfide mineralization and the outer limits of sharp-walled vein systems.

6.2.2 South Range

Elucidation of the petrogenesis of mineralization on the South Range is greatly hindered by the overprinting effects of multiple post-emplacement orogenies. The origin of the sulfide veins sampled from the two South Range properties differs between the properties. The pyrrhotite + pentlandite + chalcopyrite assemblage and flat, mantle-normalized precious metal profiles indicate that the veins observed from the Denison property represent contact ore sheared into the footwall. This hypothesis is consistent with LA-ICP-MS data for pyrrhotite and chalcopyrite which show that the majority of sulfide vein hosted crystals are consistent with the compositional range from Crean Hill samples. In contrast to Denison sulfide veins, the enrichments in Cu,
PPGEs, Au and Ag shown by sulfide veins from the McKim property suggest formation from a fractionated sulfide liquid; however, the inclusion-bearing nature of the veins suggests subsequent movement along fault zones. They are, therefore interpreted to represent either sulfides sheared into the footwall from the margins of the Little Stobie orebodies, or that the sulfide liquid exploited fault planes which were susceptible to later reactivation. Sulfide veinlets from both South Range properties present elevations in Cu, Au and Ag when compared to contact mineralization, with samples from McKim also enriched in Pt and Pd. These elevations suggest formation from a fractionated sulfide liquid at McKim, whereas the absence of such elevations in Pd and Pt at Denison points to inputs from contact material similar to the sulfide veins.

Pyrrhotite, pentlandite and, to a lesser degree, chalcopyrite show pervasive alteration to pyrite and marcasite at the Denison property. Such alteration is interpreted as having resulted from interactions with a metamorphic hydrothermal fluid. Metals removed from the sulfide veins during this process are inferred to have been re-deposited in the form of metamorphic QCS mineralization. Analyses of pyrite from sulfide veins have elevated concentrations of As, Se, Ag, Te, Pb and Bi when compared to the primary sulfide minerals, indicating that these elements were concentrated in the metamorphic fluids. In contrast, little alteration of sulfides was noted in samples from McKim, suggesting either that the metals were scavenged from footwall mineralization which was not intercepted by drilling or that the metals were remobilized from the Little Stobie contact orebodies.

As on the North Range, the origin of sulfide disseminations, along with the stockwork mineralization which is unique to the South Range, remains uncertain. Clear indications of significant hydrothermal circulation suggest that the majority of disseminated mineralization was deposited through hydrothermal processes. Such a hypothesis could also be applied to stockwork mineralization which is associated with sets of carbonate ± quartz veinlets oriented along metamorphic fabrics. Sulfides within stockwork samples are distributed evenly throughout samples, suggesting that these strongly sheared areas may have represented porous zones that were preferentially exploited by late stage highly fractionated sulfide liquids and possible Pd–Ag–Bi–Te–Sb melts. Such liquids would be consistent with the extremely PPGE, Au and Ag enriched profile displayed in mantle normalized plots. At present a magmatic origin for
stockwork mineralization is favored, although it is by no means certain. This hypothesis is also consistent with the high Ag and Se concentrations in chalcopyrite from stockwork samples, suggesting formation from a fractionate sulfide liquid, although given that the high Ag and Se content of pyrite after pyrrhotite it is not impossible that the concentrations of these elements in chalcopyrite is the result of re-equilibration with a hydrothermal fluid. There is, however, only limited evidence e.g. pyritization of pyrrhotite and pentlandite for such an interaction having occurred. The relative timing of the putative magmatic mineralization and the deformation that produced the obvious metamorphic fabrics surrounding the stockworks is difficult to define.

6.3 Vectoring and Indicator Minerals

A major goal of this study was the identification of compositional parameters ("vectors") that show predictably consistent spatial variations approaching mineralization, with the element or elements of interest preferably distributed throughout a significant volume of rock. Although enrichments of certain elements within silicate phases associated with mineralization were noted, chiefly elevations of Ni in biotite, chlorite and amphibole from the North Range properties, these were not identified throughout the larger volume of rock and were found to be present only proximal to mineralization. These Ni elevations do however offer a tool to identify Sudbury breccia through which mineralizing fluids have passed. An increase in bulk chlorine concentrations proximal to mineralization was identified in Sudbury breccia from the Levack North and Wisner properties, with increases observed within three metres of sulfide veins along with minor enrichments associated with IRV mineralization. Such variations in the halogen content were not observed from the Capre property, likely due to the redistribution of halogens by hydrothermal fluids. At present no viable vector for low-sulfide mineralization has been identified. Visual identification of Cu and Ni sulfides remains the only significant and cheaply measurable indicator that mineralization is present. Recognition of base-metal sulfides, combined with textural observations of commonly observed mineralizing styles and alteration assemblages associated with the sampled North Range low-sulfide zones, especially irregular veinlets, will permit the inference that a given intersection may contain PGMs by the core logger prior to the acquisition of precious metal assays.
The principal benefit of the present study to exploration geologists is therefore the establishment of a rigorous definition and description of the ore deposit footprint that can be used by field geologists to recognize and categorize low-sulfide mineralization based on mineralogical and textural criteria in the absence of assays or complicated geochemical techniques. When attempting to identify possible low-sulfide zones on the North Range it is important to:

1) Identify all mineralizing styles present, with special attention given to the identification of low modal sulfide mineralization e.g. irregular veinlets

2) Identify possible proximal sources for sulfide melts and metals for hydrothermal fluids. The highest grade low-sulfide mineralization (sulfide veins and IRV) formed from magmatic sulfide liquids, with the presence of a nearby contact deposit or sharp-walled system is considered preferable

3) Identify zones of increased permeability in the footwall. Analysis to identify pre-existing conduits e.g. actinolite dominated veins and barren quartz + epidote veins and areas of hydrothermal alteration by barren hydrothermal fluids allow the areas most likely to have channeled to the flow of the mineralizing fluid(s) to be recognized

4) Do not ignore sulfide, even though the correlation between the precious metal and the S content of samples does not show the same strong correlation observed in contact or sharp-walled vein systems it is still useful to identify zones through which a mineralizing fluid(s) has passed

4) Identify the sulfide assemblage. Analysis of mineralization from the three properties shows the mineralization to be dominated by chalcopyrite and millerite, a reflection of the Cu-Ni rich sulfide liquids from which most of the mineralization formed. Unlike other sharp-walled vein mineralization pyrrhotite and pentlandite will typically be absent

On the South Range the homogenizing effects of regional metamorphism and the circulation of metamorphic hydrothermal fluids have largely removed geochemical indicators of mineralization while greatly complicating the textural indicators that are so useful on the North Range. The
presence of pyritized sulfides can be used as a visual indicator that metals have been remobilized and may therefore have been re-deposited in the footwall, likely within fault controlled zones. The presence of sulfarsenides within mineralization from the Denison property is considered a positive indicator, with dissolved metal concentrations and PGMs within gersdorffite indicating its association with PGEs. Due to the wide distribution of disseminated sulfides with no PGE grades on the South Range, the effectiveness of using Cu and Ni sulfides as an indicator for mineralized intersections is limited. This variation in grade also limits the use of stockwork mineralization as an indicator of high grades, although the majority of samples collected were PGM bearing. Thus far no solid geochemical or mineralogical indicator of low-sulfide mineralization within the South Range footwall has been identified.
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