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The Geology and Palladium Mineralization of the Southern Roby, Twilight, and High Grade Zones of
the Lac des Iles Mine, Western Superior Province of Canada

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**THE GEOLOGY AND PALLADIUM MINERALIZATION OF THE
SOUTHERN ROBY, TWILIGHT, AND HIGH GRADE ZONES OF
THE LAC DES ILES MINE, WESTERN SUPERIOR PROVINCE OF
CANADA.**

by

John Glenn Hinchey , B.Sc.H., M.Sc.

A thesis submitted to the
Faculty of Graduate & Postdoctoral Studies
in partial fulfillment of the requirements for the
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Abstract

The Lac des Iles Pd mine is hosted by 2.69 Ga. gabbroic rocks of the Lac des Iles Intrusive Complex in the southern Wabigoon subprovince, Superior province of Canada. Economic mineralization, ~ 159 Mt at 1.55 g/t Pd before major mining in 2001, occurs in the Roby zone of the Mine Block Intrusion. The southern Roby and Twilight zones contain gabbroic/gabbronoritic intrusions with complicated textures, such as brecciation and magma mingling. Ore has low concentrations of sulphide (~ 1-3 vol. %) and high Pd/Pt of ~8-10. Detailed mapping and geochemical analysis of the southern Roby and Twilight Zones indicate that early leucocratic rocks are barren and that the bulk of the platinum group elements (PGE) were introduced by late melanocratic magmas. Sulphur correlates positively with base and precious metals. In addition to exsolution of pentlandite and chalcopyrite from pyrrhotite, the data suggests a magmatic origin of the PGE where immiscible sulphide melt concentrated PGE.

Fractionation of olivine, chromite, and high temperature platinum group minerals likely resulted in high concentrations of Pt-group PGE/Ir-group PGE in the parental magmas. Extreme enrichment of Pd and high Pd/Pt ratios in the late melanocratic magmas is interpreted to be due to incorporation of earlier formed sulphide melt. The interpretation is supported by high Cu/Pd in the early leucocratic rocks and low Cu/Pd in the late melanocratic rocks. Highly radiogenic Pb isotope compositions of sulphides compared to plagioclase in the same samples also suggest that sulphide segregated during the intrusion. Aqueous fluids driven from country rocks during the intrusion liberated soluble radiogenic Pb and imparted a radiogenic isotopic signature to the sulphide at the base of the chamber.

The High Grade Zone, on the eastern margin of the Roby Zone, contains only ~7

vol. % of the Roby Zone but hosts ~ 35% of the Pd at the mine. The zone is intensely altered and contains two mineral assemblages: a) millerite + siegenite ± chalcopyrite ± pyrite co-existing with hornblende + plagioclase ± quartz ± carbonate, and b) pyrite ± chalcopyrite with chlorite + actinolite ± albite ± quartz ± carbonate. The ore is high in Pd and Pd/Pt (mean of 16.5; max. 25) compared to the southern Roby and Twilight zones. Although plots of S versus Se and base and precious metals show scatters, positive correlations are observed for Se versus Te and less mobile elements, such as Pt, Ni and Co. The data suggest that magmatic mineralization was followed by hydrothermal transport of mobile elements. Hydrothermal activity enriched the zone by up to 40 ppm Pd. The lack of fluid pathways and the distribution of the zone adjacent to mineralized breccia are consistent with magmatic-hydrothermal activity by aqueous fluids exsolved from the parental magmas of the Roby zone.

Geochemical and Pb, Sr, and Nd isotope compositions from the Mine Block Intrusion suggest that the parental magmas were derived through high degrees of partial melting of a previously metasomatized depleted mantle source. The Lac des Iles Intrusion, as well as the surrounding mafic/ultramafic and sanukitoid suite of intrusions, display subduction influenced geochemical signatures, such as negative HFSE and enriched LILE. Calculated parental magmas for the Mine Block Intrusion have an average $(\text{Ce}/\text{Yb})_{\text{CN}}$ of 2.3, whereas the surrounding mafic/ultramafic intrusions have average ratios of ~ 9-10, with the sanukitoid suite of intrusions averaging ~ 50-80. The low concentrations and unfractionated nature of the REE at Lac des Iles suggest high degrees of partial melting. The heat required for such high degrees of partial melting for Lac des Iles is interpreted to be from upwelling of hot asthenospheric mantle associated with either in a slab window, mantle plume or delamination/slab break-off processes. The fractionated REE patterns of the surrounding intrusions are interpreted to be associated with relatively low degrees of partial melting and/or crustal assimilation. Both of these processes can be detrimental to the formation of an economic PGE deposit as they

may allow for PGE retention in the mantle and/or early sulphur saturation at depth, respectively. It is suggested that further exploration for PGE deposits in the central Wabigoon subprovince should focus on the identification of primitive mafic/ultramafic intrusions with unfractionated REE patterns.

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Introduction

The Lac des Iles Pd mine in northwestern Ontario, containing 159 Mt at 1.55 g/t Pd before major mining in 2001, represents the only primarily Pd-producing mine in Canada. The mine is hosted by the Lac des Iles Intrusive Complex in the southern Wabigoon subprovince of the Superior Province, and is characterized by low proportions of sulphide, variable alteration, and complex igneous textures.

Over the last number of years PGE exploration has been heightened due to the recent increase in metal prices. Similar textures and rock types as those of the Lac des Iles deposit are considered favorable characteristics for the identification of potential PGE-bearing intrusions.

Since the discovery of the Lac des Iles deposit there has been substantial controversy regarding the origin of the PGE mineralization. In particular, the extremely high Pd concentrations, Pd/Pt ratios (~ 10 compared to $\sim 1-3$ for typical deposits associated with mafic/ultramafic rocks), and high Pd/Ir ratios ($\sim 10,000$) of the ore contributed to much debate over whether magmatic or hydrothermal processes were the dominant control on the mineralization. Variable degrees of alteration throughout the ore body, as well as complex textures such as brecciation, magma mingling, and pegmatite development have fueled the discussions.

Previous researchers have proposed numerous possible models for the deposit invoking either magmatic or hydrothermal, or a combination of both processes. Hydrothermal models for ore formation suggest that base and precious metals were enriched by the separation of an immiscible Pd-bearing aqueous fluid (Watkinson and Dunning, 1979) and use the occurrence of PGM containing Te, As, and Bi, and the spatial association of PGM with hydrous minerals and pyrite as evidence for a hydrothermal

control on the mineralization (Talkington and Watkinson, 1984; Macdonald, 1988). Brügmann et al. (1989) proposed that the ore deposit was formed through constitutional zone refining which involves formation of volatile-rich magmas through fractional crystallization which subsequently partially melt earlier formed cumulates and liberate the PGE from sulphides into a leucocratic partial melt. Lavigne and Michaud (2001) proposed that the mineralization was derived through the forceful intrusion of a PGE-, Ni-, and Cu-rich immiscible sulphide melt into the partially crystallized chamber which was followed by the exsolution of an aqueous phase resulting in redistribution of the metals. All these models try to explain the high Pd, Pd/Pt, and Pd/Ir characteristics of the deposit. However, as additional outcrop was exposed through mining processes and more information became available, none of the above models adequately explained the method of ore formation at Lac des Iles.

This thesis addresses the origin of the mineralization. The study involved detailed and thorough examinations of the southern Roby, Twilight, and High Grade Ore zones of the Lac des Iles Pd deposit. These zones contain all rock types and lithological relationships representative of the ore. The study involved a total of 6 months of field mapping and drill core examination. Subsequent mineralogical, petrological, geochemical, and Pb and Sr isotopic studies were carried out to address the above mentioned questions.

The thesis also examines the petrogenesis of the Lac des Iles Intrusion and compares the intrusion with the surrounding mafic/ultramafic and sanukitoid suite intrusions through the use of extended trace element geochemistry and radiogenic isotope chemistry (Pb and Sr). The data are used to discuss the tectonic setting of the mineralized Lac des Iles Intrusive Complex.

As many other PGE showings associated with mafic/ultramafic intrusions have been the focus of exploration in the central Wabigoon subprovince, the results of this thesis are relevant to exploration for this type of mineralization.

Outline

This thesis has been presented as four papers (Chapters 1, 2, 3, and 4), each written to address different themes of the research. Chapters 1 and 2 have been published in refereed journals. The method of presentation introduces some unavoidable redundancies, especially with respect to geological descriptions. Chapter 1 presents detailed descriptions of lithological units in the southern Roby and Twilight zones of the Lac des Iles deposit. Detailed geochemical investigations are utilized to characterize the ore deposit, defining which units introduced the bulk of the PGE, and to present a genetic model to explain the unusually high Pt-group PGE/Ir-group PGE ratios associated with the ore. Our model for ore formation involves sulphide segregation from early leucocratic magmas with subsequent incorporation of the sulphide by later melanocratic magmas.

Chapter 2 focuses on a comparison of the High Grade ore zone with the southern Roby and Twilight zones. Although the High Grade zone only comprises ~ 7 vol. % of the deposit, it contains ~ 35 % of the Pd. Petrographical data, in addition to plots of base and precious metals versus S and Se, are used to characterize the High Grade zone as being hydrothermally enriched in mobile elements, such as Pd.

Chapter 3 focuses on Pb isotopic compositions of plagioclase and sulphide separates from the southern Roby and Twilight zones and sulphide separates from the High Grade zone. The data reveals that the sulphides from all zones characteristically contain much higher radiogenic isotopes (e.g. ^{206}Pb , ^{207}Pb , and ^{208}Pb) than plagioclase from the same samples; interpreted to result from the incorporation of radiogenic lead from the country rock during intrusion. The data are used to put genetic constraints on the origin and history of the sulphides and PGE mineralization and supports the genetic model proposed in Chapter 1.

Chapter 4 includes a petrogenetic study of the Mine Block Intrusion of the Lac des Iles Intrusive Complex and compares the geochemical characteristics with

surrounding mafic/ultramafic and sanukitoid suite intrusions. Through the use of extended trace element chemistry in addition to radiogenic isotopes (Pb and Sr), it is suggested that the Mine Block Intrusion was derived from a high Mg-magma with unfractionated REE compared to the surrounding intrusions.

Chapter 5 is a brief summary of the conclusions.

Statement of Original Contribution

All mapping, geochemical data, and interpretations used throughout this thesis result from my original work. The following represents the major original findings of the research.

This research focuses on the further understanding of the Lac des Iles deposit through an investigation of the geology, petrology, and geochemistry of the southern Roby, Twilight, and High Grade zones at Lac des Iles. Research involved six months of fieldwork in the summers of 2002 and 2003, during which time I carried out surface lithological mapping and sampling of the southern Roby and Twilight zones at scales of 1:60 and 1:120, respectively. They are published in Hinchey et al., 2005 and presented in the back pocket of the thesis. The High Grade zone was studied and sampled from diamond drill core. Samples were collected for major and trace element geochemistry, PGE analysis, isotopic (Pb and Sr) geochemistry and petrographic studies.

The research represents the first PhD thesis on the ore deposit. Petrographical studies were carried out to characterize the various lithologies identified during the field mapping, followed by geochemical investigations into the base and precious metal characteristics, as well as petrogenetic aspects, of each unit. These studies were the first to present a detailed characterization of which units introduced the PGE as well as the relationships between the various units. A new model of ore formation to explain the extremely enriched Pd/Pt and PPGE/IPGE characteristics of the ore was proposed. This study provided new insights into the origin of the deposit as we introduced new data

regarding the relative influences of magmatic and/or hydrothermal processes during ore formation. In addition, we determined that the High Grade zone was enriched in Pd by hydrothermal processes which altered and overprinted original mineralization in the zone. This study provided important new data on the characteristics of the High Grade Ore Zone which is currently the focus of a planned underground mining operation at Lac des Iles.

This thesis presents the first recorded Pb isotope data for the Lac des Iles deposit. These new data is important as it provides constraints on the history of the sulphides which control and host the PGE mineralization. The data supports our proposed model for ore formation whereby early sulphides were exsolved from initial leucocratic magmas and ponded at the base of the intrusion. Subsequent melanocratic magmas intruded and incorporated the sulphides and brought them to surface. This new model explains both the different Pb isotopic characteristics of plagioclase versus sulphides from individual samples, as well as the extremely enriched Pd characteristics of the ore. This model has important implications for further exploration, both at Lac des Iles and elsewhere.

Through the use of extended trace element chemistry and radiogenic isotopes (Pb and Sr), this thesis has built upon and modified petrogenetic interpretations from earlier studies (e.g. Sutcliffe et al., 1989, Brüggmann et al., 1997). We determined that the Lac des Iles Intrusion was derived from high degrees of partial melting of a depleted mantle source and was intruded into mid-crustal levels without any significant crustal assimilation.

The data produced in this study provide a new interpretation of ore genesis of the Lac des Iles deposit and supplied important information on the petrogenesis of the intrusion.

Contributions of collaborators

I conducted my own field mapping and interpretations during the summers of

2002 and 2003, and I collected much of the geochemical and isotopic data presented in the thesis. Drafting of figures as well as the geochemical investigations and interpretations were my own work. Staff of North American Palladium Ltd. helped with the initial introduction to the geology of the mine.

CHAPTER 1
Geology, Petrology and Controls on PGE Mineralization of the
Southern Roby and Twilight Zones, Lac des Iles Mine, Canada

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Abstract

The Lac des Iles Pd mine, with reserves of 88 Mt containing 1.51 g/t Pd, is hosted by the 2.69 Ga Lac des Iles intrusive complex in the southern Wabigoon subprovince of the Superior province of Canada. The known economic concentration of Pd occurs in the Mine Block intrusion, the central body of the intrusive complex, where gabbroic rocks range from leucogabbro to pyroxenite and show complicated textures, such as breccias, magma mingling, and pods and veins of pegmatite. The ore is characterized by low concentrations of sulfide (typically less than 3 vol. %) and exceptionally high Pd contents (Pd/Pt ~ 10, Pd/Au ~ 13). Detailed mapping of the southern Roby and Twilight Zones shows that early leucocratic rocks are barren and that the bulk of Pd was introduced by late melanocratic magmas. The average concentration of Pd in the melanocratic rocks, excluding the High Grade Zone, is estimated to be ~ 4 ppm. The concentrations of sulfur correlate positively with those of base metals, PGE, and Au. Furthermore, sulfide grains commonly show exsolution textures. The evidence suggests a magmatic origin of the PGE mineralization where the PGE were concentrated in an immiscible sulfide melt in the parental magma.

Bulk chemical compositions suggest that all mafic igneous rocks in the mineralized zones, except for late clinopyroxenite, are cogenetic. The hypothetical parental magmas have high MgO and low (~15x chondrite), unfractionated rare earth elements (REE) with $(\text{Ce}/\text{Yb})_{\text{chondrite}} < 3$, suggesting that the magmas formed through high degrees of partial melting in a moderately depleted mantle. Fractional crystallization of olivine, chromite and high-temperature platinum group minerals resulted in high concentrations of Pt, Pd and Rh relative to Ir, Os and Ru in the parental magmas. Extreme enrichment of Pd in the late melanocratic magmas is interpreted to have been attained through the incorporation of earlier formed sulfide melt. This proposed interpretation is supported by high Cu/Pd in early barren leucocratic rocks and low Cu/Pd in fertile

melanocratic rocks. Rocks in the volumetrically minor but economically important High Grade Zone (> 35 % of Pd in the deposit) on the eastern margin of the Roby Zone have much higher concentrations of Pd than any other rocks, and do not show correlations between sulfur and precious and base metals. Furthermore, the rocks are intensely and pervasively altered to actinolite, talc, anthophyllite, hornblende, chlorite, sericite, calcite and quartz. These observations suggest subsolidus enrichment of Pd and mobility of S. The lack of apparent fluid pathways within the High Grade Zone and the distribution of the zone are consistent with the enrichment of Pd at high temperatures by fluids that originated from the mafic magmas.

The textures of the Lac des Iles deposit are similar to those of contact-type PGE deposits, but there are fundamental differences between the two. The Lac des Iles deposit is not localized near the contact between the host intrusion and the country rocks and evidence of the assimilation of the host rocks is lacking. Instead, the mineralization at Lac des Iles has many features in common with layered intrusion-hosted deposits, in which pulses of primitive magma introduced the PGE. Unlike the quiescent magma chambers of most layered deposits, the magmas at Lac des Iles were intruded energetically, forming breccias and magma-mingling textures.

1.1 Introduction

The Lac des Iles mine is the only primary Pd-producer in Canada. The deposit is hosted by the Neoproterozoic Lac des Iles mafic-ultramafic intrusive complex in the southern Wabigoon subprovince of the Superior province (Fig. 1-1). In contrast to many platinum group element (PGE) deposits, which are hosted by Ni-sulfides at the base of large mafic intrusions (e.g., Sudbury and Noril'sk), or as stratiform layers within large layered intrusions (e.g., Bushveld Intrusion), the Lac des Iles deposit is characterized by low contents of sulfides, common alteration of silicate minerals, and complex igneous textures, such as breccias and pegmatites (Lavigne and Michaud, 2001). The

mineralization is extremely enriched in Pd compared to other PGE, with Pd/Pt ratios of ~ 10 and Pd/Ir ratios of ~ 10,000. These features are not easily explained by genetic models for other PGE deposits. Previously proposed origins for the deposit include hydrothermal/deuteric mineralization based on the occurrence of Bi-bearing platinum group minerals (PGM) (Watkinson and Dunning, 1979) and the close association of secondary hydrous silicate minerals with PGM (Talkington and Watkinson, 1984), and a constitutional zone refining process (Brügmann et al., 1989) based on high Pd contents and coexisting melanocratic and leucocratic rocks in the mineralized zones. The latter process, as originally proposed by McBirney (1987), involves partial melting of gabbro cumulates.

We conducted detailed mapping of the southern Roby Zone and Twilight Zone at scales of 1:60 and 1:120, respectively, in the summers of 2002 and 2003. Field observations by Hinchey et al. (2003) show a clear relationship between mineralization and rock types. This paper documents new data on the geochemistry of different rock types and discusses the origin of the mineralization.

1.1.2 Previous work and exploration history

Geological investigations in the area began with reconnaissance mapping by Jolliffe (1934), followed by more detailed mapping of the area by Pye (1968). Economic interest in the area was sparked by the discovery of aeromagnetic anomalies in the late 1950s. Significant Pd mineralization was first discovered in the Roby Zone in 1963 by prospectors and was subsequently investigated by Gunnex Ltd and Anaconda Ltd. The Ontario Geological Survey conducted several mapping projects in the area (Sutcliffe and Sweeny, 1986; Macdonald, 1988; Sutcliffe et al., 1989), and M.Sc. thesis projects on the deposit were completed by Dunning (1979), Sweeny (1989), and Michaud (1998).

Madeleine Mines Ltd. commenced mining in 1990, but this lasted only several months. Lac des Iles Mines Ltd. began production in 1993 at a rate of 2,000 metric tonnes per day. Today the Lac des Iles Mine is an open pit operation conducted by North

American Palladium Ltd. Current proven and probable reserves consist of 88 million metric tonnes grading 1.51 g/t Pd, 0.17 g/t Pt, 0.12 g/t Au, 0.06% Cu, and 0.05% Ni, with additional measured and indicated resources of 65 million metric tonnes grading 1.58 g/t Pd, 0.17 g/t Pt, 0.11 g/t Au, 0.05% Cu, and 0.05% Ni (North American Palladium Ltd. Annual Report, 2002).

1.2 Geology

1.2.1 Regional geological setting

The Lac des Iles intrusive complex is located in the granite-greenstone terrane of the Wabigoon subprovince of the Archean Superior province of the Canadian Shield (Blackburn et al., 1992; Fig. 1-1). The intrusive complex is one of a suite of late Archean mafic-ultramafic plutons in the southern Wabigoon subprovince close to the Quetico subprovince (Pye, 1968; Sutcliffe, 1986). It is part of a 30 km-diameter circular array of mineralized mafic and ultramafic intrusions, including Legris Lake, Tib Lake, and Buck Lake, of which the Lac des Iles intrusive complex is the largest (Gupta and Sutcliffe, 1990; Fig. 1-2).

Regional metamorphic grades in the area are low, up to greenschist facies (Blackburn et al., 1992; Pettigrew and Hattori, 2002), which contrasts with the granulite and migmatite in the adjacent Quetico subprovince (Williams, 1992; Fig. 1-2). The low grade of regional metamorphism in the study area is supported by the presence of pristine clinopyroxene and orthopyroxene in the northern part of the complex and in the gabbroite of the Mine Block intrusion.

1.2.2 Geology of the Lac des Iles Complex

The Lac des Iles intrusive complex (2692 ± 4/-2 Ma; Blackburn et al., 1992) is subdivided into three main intrusive bodies (Lavigne and Michaud, 2001; Fig. 1-3): (1) the North Lac des Iles ultramafic intrusions, centered on the lake, (2) the Mine Block intrusion, consisting of lithologically and texturally complex gabbroic rocks, and (3)

the Camp Lake intrusion, which is a homogeneous hornblende gabbro southwest of Camp Lake. The three intrusions are separated by tonalitic country rocks (Lavigne and Michaud, 2001). All rocks in the area have been intruded by diabase dikes and sills, which range from ~2120 Ma to ~ 1140 Ma (Buchan and Ernst, 2004).

The North Lac des Iles intrusion (Fig. 1-3) ranges from clinopyroxenite/websterite in the northern part to minor gabbro/gabbro-norite in the southern part. Igneous layering is common and pristine igneous minerals are well preserved. The ultramafic rocks are in direct contact with the tonalitic country rocks but are also locally separated by thin gabbroic layers (Lavigne and Michaud, 2001). The gabbro/gabbro-noritic rocks of Mine Block intrusion (Figs. 1-3 and 1-4) range from anorthosite to clinopyroxenite. They have complicated textures, including breccias and magma-mingling structures, which vary at scales of less than 5 m.

1.3 Mineralized Zones

Anomalous concentrations of PGE occur locally throughout the Lac des Iles intrusive complex, but known economic mineralization occurs only in the Mine Block intrusion. The mineralized zones include the Roby, Twilight and Baker Zones (Fig. 1-4). The Roby Zone has dimensions of 950 m north-south, 700 m east-west, and greater than 1000 m vertically, and contains the narrow High Grade Zone on its eastern margin (Fig. 1-4). The High Grade Zone is 15 to 25 m wide and 400 m long and is bounded by the barren East Gabbro to the east. This ore zone consists of pervasively altered melanocratic rocks and dips nearly vertically to a depth of 250 m, at which depth it shallows out to the east. The High Grade Zone comprises only 7.6 volume percent of the current reserves (Lavigne and Michaud, 2001), but contains approximately 35 % of the Pd in the Roby Zone.

Most of the Roby Zone, including the High Grade Zone, is being mined in the Phase 3 open pit, but the southwest part of the Roby Zone was still exposed on the surface in

2003 and was mapped in detail in this study (approximately 65 to 70 m north-south and 35 to 40 m east-west: Fig. 1-5). The Twilight Zone, with a surface exposure of 175 to 200 m north-south and 200 to 225 m east-west, lies southeast of the Roby Zone (Fig. 1-4), with 50 to 70 m of East Gabbro between the two zones. The Baker Zone is located approximately 1 km northeast from the Roby and Twilight Zones (Fig. 1-4) and contains rocks and textures similar to those in the Roby and Twilight Zones.

1.4 Petrology of the Southern Roby Zone

The detailed mapping by Hinchey et al. (2003) classified rocks into three groups; (1) early leucocratic rocks, (2) sulfide-bearing melanocratic gabbroic rocks, and (3) late, sulfide-free melanocratic gabbroic rocks. The area also contains young felsic dikes and diabase dikes that cut all rocks of the Lac des Iles intrusive complex (Fig. 1-5).

Most rocks of the southern Roby Zone show cumulate textures, consisting of subhedral to euhedral cumulus crystals of clinopyroxene, plagioclase and minor orthopyroxene with intercumulus material consisting of the same assemblage plus minor biotite, magnetite, ilmenite, and sulfides. Breccias are common and are named on the basis of matrix composition. For example, a breccia with melanogabbro matrix is referred to as a melanogabbro breccia (Fig. 1-6a). Gabbroic rocks with varying grain size from fine to coarse and local pods and veins of pegmatite are termed “varitextured” gabbro.

1.4.1 Early leucocratic rocks (group 1)

The early leucocratic rocks consist of (1a) medium-grained anorthosite/leucogabbro, (1b) medium-grained gabbro, which is commonly varitextured close to pegmatite, (1c) medium-grained, light-gray gabbro with local layering that strikes N64-68°E, defined by alternating layers of plagioclase and clinopyroxene, and (1d) medium-grained, locally foliated gabbro. The relationships between these rocks are not certain due to the lack of exposed contacts. All leucocratic rocks have similar mineral abundances,

with 45-65 volume percent plagioclase, 35-55 volume percent clinopyroxene, and less than 10 volume percent of combined orthopyroxene, biotite, and epidote. They contain less than 1 volume percent of finely disseminated pyrite, chalcopyrite, and oxides. The plagioclase in the rocks commonly displays cumulus texture, with crystals 1-7 mm in length. Intercumulus material is dominated by clinopyroxene (grain sizes of 1-3 mm), with lesser amounts of orthopyroxene, biotite, sulfides, and oxides. The rocks are unaltered to moderately altered, with variably sericitized plagioclase. Clinopyroxene is commonly replaced by actinolite, hornblende, epidote, and chlorite.

1.4.2 Mineralized melanocratic rocks (group 2)

The mineralized melanocratic rocks range from gabbro to clinopyroxenite, contain sulfide, and have irregularly shaped pods and veins of pegmatite. Brecciation and magma-mingling structures with the earlier leucocratic rocks of group 1 are common. From north to south, the melanocratic rocks are (2a) medium-grained meso- to melanogabbro breccia, (2b) medium- to relatively coarse-grained clinopyroxenite, and (2c) medium-grained, dark gabbro (Fig. 1-5). Pegmatite (2d) is common within and in contact with these melanocratic rocks. Most rocks are altered with very rare relict pyroxenes and plagioclase. Clinopyroxene is commonly replaced by a mixture of hornblende, actinolite, and chlorite, whereas interstitial clinopyroxene is replaced by chlorite. Plagioclase is mostly sericitized.

1.4.2.1 Medium-grained mesogabbro to melanogabbro breccia (2a): This breccia contains fragments of leucocratic rocks of group 1 (Fig. 1-6a). The matrix of the breccia is dominated by subhedral, equigranular clinopyroxene (1-6 mm, 50-80 vol.%) that commonly forms aggregates, with lesser amounts of plagioclase (1-4 mm, 30-50 vol.%) and minor (< 5 vol.%) orthopyroxene and biotite. Interstitial minerals are plagioclase (1-4 mm with minor aggregates of small ~0.5 mm crystals), minor clinopyroxene and biotite, and sulfide and oxide minerals. A mixture of sulfide and oxide minerals occur as blebs (1-6 mm in diameter) and fine-grained disseminations (1-3 vol.% of the matrix). The sulfide

minerals are mostly pyrrhotite with exsolved chalcopyrite and pentlandite. Minor pyrite and magnetite are present, and minor amounts of calcite occur in the blebs of sulfide minerals. Chalcopyrite also commonly occurs along cleavage planes of actinolite.

1.4.2.2 Medium- to coarse-grained clinopyroxenite (2b): These rocks range from massive, medium-grained clinopyroxene-rich melanogabbro to clinopyroxenite, and consist of equigranular clinopyroxene (1-7 mm, 85-100 vol.%) with interstitial clinopyroxene, plagioclase, orthopyroxene, biotite, sulfides and oxides, and rare gahnite. The rocks have an orthocumulate texture, with minor adcumulate texture. Sulfides (1-5 vol.%) are disseminated, blebby (0.5-2 mm), and net-textured, consisting of pyrrhotite with intergrown chalcopyrite and pentlandite. The texture suggests that the sulfides were once monosulfide solid solution. The clinopyroxenite also contains minor chalcopyrite along cleavage planes of secondary actinolite (Fig. 1-7a).

1.4.2.3 Medium-grained dark gabbro (2c): This rock type occurs in the southern portion of the mapped area (Figs. 1-5 and 1-6b) and due to its dark color, including dark plagioclase in hand specimens, has been described in the field as melanocratic. However, it contains less than 60 volume percent of ferromagnesian minerals (40-60 vol.% clinopyroxene, < 5 vol.% orthopyroxene). Disseminated, blebby sulfides (1-5 vol.%), 1 to 5 mm in size, consist of intergrown pyrrhotite, chalcopyrite, pentlandite, and pyrite (Fig. 1-7b). Chalcopyrite is commonly observed along cleavage planes of secondary actinolite. The gabbro has an equigranular to orthocumulate texture with local adcumulus clinopyroxene. Cumulus phases are dominated by subhedral clinopyroxene (1-5 mm) and minor plagioclase, and the intercumulus material consists of plagioclase with minor clinopyroxene and orthopyroxene.

1.4.2.4 Pegmatite (2d): Pegmatite occurs as dikes and pods and is composed of coarse-grained plagioclase and clinopyroxene. Isolated pods of pegmatite on the surface are commonly connected to large pods of pegmatite through veinlets. The cores of the pods are commonly quartz-rich and contain minor biotite, magnetite, ilmenite, pyrite, and

traces of chalcopyrite. The sulfide aggregates commonly enclose fine-grained (< 0.5 mm) calcite.

1.4.3 Late stage intrusions (group 3)

Post-mineralization intrusions include (3a) medium-grained, sulfide-free clinopyroxenite, and (3b) medium-grained, salt-and-pepper-textured gabbro. The clinopyroxenite cuts earlier leucocratic rocks (group 1), and commonly displays magma-mingling with the earlier clinopyroxenite (2b). The clinopyroxenite (3a) and gabbro (3b) display cumulate texture, and are altered, with uralization of clinopyroxene and sericitization of plagioclase.

1.4.4 Intrusions unrelated to the Lac des Iles Complex

Late intrusions that cut rocks of the southern Roby Zone are felsic dikes and diabase dikes. The felsic dikes are several centimeters to 1 m in width with random orientations and range in composition from tonalite to granodiorite. The dikes are commonly accompanied by narrow (< 5 cm) symmetrical alteration haloes with reddish K-feldspar. Very fine-grained diabase dikes, ranging from a few centimeters to 1.5 m in width, cut all rock types.

1.4.5 Contact relationships between different rock types

The contacts between the early leucocratic rocks of group 1 and the melanocratic rocks of group 2 are well exposed on the outcrop. The latter contains fragments of leucocratic gabbro of group 1 (Fig. 1-6a) and also intruded the partially solidified leucocratic rocks, developing magma-mingling structures (Fig. 1-6b). This suggests that mafic magmas intruded prior to the solidification of the earlier magmas that produced the leucocratic rocks. Varitextured and pegmatitic phases (rock type 2d) are commonly developed near the contact between group 1 and group 2, suggesting the release of aqueous fluids from the magmas that produced the melanocratic rocks.

1.4.6 Hydrothermal alteration

All rocks show some degree of alteration, especially melanocratic rocks which are pervasively altered, but rocks adjacent to the Roby Zone, including those of the Twilight Zone and East Gabbro, are not altered. Although minor faults occur in the southern Roby Zone, as observed by Michaud (1998), alteration is not controlled by these faults. The alteration likely took place at high temperatures and was possibly related to aqueous fluids released from the magmas for the melanocratic rocks. This interpretation is supported by abundant pods and veins of pegmatite associated with the melanocratic rocks.

The High Grade Zone within the Roby Zone is composed of intensely altered medium-grained melanogabbro and pyroxenite, similar to the melanocratic rocks of group 2 in the southern Roby Zone. Primary minerals are entirely replaced by secondary amphiboles, talc, anthophyllite, chlorite, sericite, and calcite. The occurrence of blue quartz is also common. Sulfide minerals are dominated by pyrite (up to 10 vol. %), with lesser amounts of pyrrhotite, chalcopyrite, and pentlandite.

1.5 Petrology of the Twilight Zone

The Twilight Zone (Fig. 1-8) is dominated by noritic/gabbronoritic intrusions, which are divided into three types following from the rock types recognized in the southern Roby Zone: (4) leuconorite/gabbronorite, (5) medium-brown norite/gabbronorite, and (6) sulfide-bearing melanonorite/gabbronorite. Minor phases include (7) anorthosite, (8) gabbro, (9) melanogabbro/clinopyroxenite and, (10) fine-grained gabbro. Late felsic and diabase dikes, similar to those in the Roby Zone, are also present in the Twilight Zone. They cut all other rock types and are not related to the Lac des Iles intrusive complex. This zone also has complex structures, but alteration is not as intense and pervasive as in the Roby Zone. Orthopyroxene has been variably replaced by talc and magnetite, clinopyroxene by actinolite, and plagioclase by sericite.

All noritic/gabbronoritic intrusions (rock types 4, 5, 6) are medium-grained with granular, orthocumulate textures, and are relatively unaltered. The early leuconorite (4) and the medium-brown norite (5) are very similar in texture and mineralogy. The leuconorite/gabbronorite (4) consists of subhedral to euhedral cumulus orthopyroxene (2-4 mm, 20-30 vol.%), equigranular plagioclase (60-70 vol.%), and intercumulus clinopyroxene (< 10 vol.%). The medium-brown norite/gabbronorite (5) contains equal amounts of cumulus orthopyroxene and intercumulus plagioclase. Other minor intercumulus phases (< 10 vol.%) are clinopyroxene and biotite. Disseminated aggregates of sulfide and oxide (< 1-2 vol.%) occur in both rock types where they are in contact with melanonorite/gabbronorite (6), including intergrown pyrrhotite, chalcopyrite, and pentlandite, and rounded magnetite. Orthopyroxene crystals in both the early leuconorite (4) and the medium-brown norite (5) are locally poikilitic, containing smaller crystals of pyroxene and plagioclase. Some of the orthopyroxene crystals contain exsolution lamellae of clinopyroxene (inverted pigeonite).

The mineralized melanocratic norite/gabbronorite (6) has a texture similar to other norite/gabbronorite although it is rich in sulfides. This rock consists of subhedral to euhedral cumulus orthopyroxene (3-10 mm, 70-95 vol.%), intercumulus plagioclase (5-30 vol.%), intercumulus clinopyroxene (<10 vol.%), minor biotite, and interstitial blebby sulfides and oxides (2-8 vol.%). The sulfides consist of intergrown pyrrhotite, chalcopyrite, and pentlandite, and oxides are magnetite and ilmenite. As in the other noritic/gabbronoritic rocks, clinopyroxene occurs as an exsolved phase in orthopyroxene (inverted pigeonite). Minor amounts of chalcopyrite and magnetite occur along the cleavage of secondary amphiboles.

1.5.1 Contact relationships of different rocks

The three noritic/gabbronoritic rocks display breccias and magma-mingling structures (Fig. 1-6c). Matrix and clast relationships indicate that the leucocratic norite/gabbronorite (4) is the earliest and that the melanocratic norite/gabbronorite

orthopyroxene (6) is the youngest. The magma-mingling structures suggest that successive intrusions occurred while earlier intrusions were not completely solidified.

Anorthosite (7), gabbro (8), and melanogabbro/clinopyroxenite (9) were contemporaneous with the norite/gabbronorite (5). These rocks commonly occur as fragments in a matrix of norite/gabbronorite. Fragments of gabbro and anorthosite are especially common in the northern part of the Twilight Zone. These rocks are medium-grained, moderately to intensely altered, and free of sulfide.

The south-central portion of the Twilight Zone is dominated by late, medium-grained melanogabbro/clinopyroxenite (9), which produces breccias containing fragments of norite, gabbronorite, and gabbro. The breccias and intrusions contain irregularly shaped pods and veins of pegmatite, which consist of plagioclase, pyroxene, quartz, magnetite, and sulfide dominated by pyrite. The rocks are more intensely altered than the volumetrically dominant norite/gabbronorite. Alteration has produced actinolite after clinopyroxene, and chlorite and sericite after intercumulus clinopyroxene and plagioclase. These rocks commonly contain blebs (up to 5 vol.%) that consist of pyrrhotite, chalcopyrite, pentlandite, and minor magnetite. The textures and alteration are very similar to those of the melanogabbro and clinopyroxenite of the southern Roby Zone.

1.6 Geochemistry of Mineralized Zones

1.6.1 Sampling and analytical methods

Samples representing various rock types were collected from the southern Roby and Twilight Zones following detailed mapping. Samples of the High Grade Zone were collected from the pit. Major and minor elements were determined on fused disks using a Philips PW 2400 X-ray fluorescence spectrometer at the University of Ottawa. For samples with high Cu content, LiBr was added to prevent the fused glass from sticking to the Pt crucible. Precision based on eleven replicate runs was 0.35 % for Al_2O_3 , 0.48 % MgO, 3.7 % for Sr, 1.3 % for Cr, 9.2 % for Ni. The accuracy, which was monitored

using international references MRG-1 and Sy-2, was within 0.039 % for Al_2O_3 , 0.28 % for MgO, 3.5 % for Sr, 3.4 % for Cr, 4.0 % for Ni, and better than 1 % and 10 % for other major and minor elements, respectively. Loss of ignition was determined after heating samples at 1050 °C for over 1 hr. Sulfur contents were determined using an elemental analyzer (Carlo Erba 1110) at the University of Ottawa. Precision based on 9 runs of one sample was 5.4 %; and the accuracy based on a set of references was 1.4 %. Blank samples yielded less than the detection limit of sulfur (0.001 wt.%).

The concentrations of Ir, Os and Ru were determined at the University of Ottawa by an isotope dilution technique using a solution enriched in ^{191}Ir , ^{190}Os , and ^{99}Ru . The analytical procedure was essentially identical to that described in Guillot et al. (2000). Precious metals in 3 g samples mixed with 6 g of $\text{Na}_2\text{B}_4\text{O}_7$ were concentrated into a Ni sulfide bead at 1050 °C. The bead was dissolved in HCl, and the insoluble residue was dissolved in HNO_3 before isotope ratio measurements using an inductively-coupled plasma mass spectrometry (ICP-MS; model HP-4500). Blank contributions of Ir, Ru, and Os, mostly from the Ni powder, were 0.005, 0.011, and 0.008 ng/g of flux, respectively, and less than 1% of the concentrations of the metals in the samples. Gold, Pt, Pd, and Rh were determined by a Pb-collection fire assay followed by an ICP-MS analysis on 30-g sample splits at Acme Analytical Laboratories Ltd. in Vancouver, with detection limits of 1, 0.1, 0.5, and 0.05 ppb, respectively. Precision and accuracy of the analysis based on 9 replicate analyses of a reference were 4.50 and 9.2 % for Au, 0.61 and 2.03 % for Pt, 0.49 and 4.68 % for Pd; and 16.4 % and an undetermined accuracy for Rh. The concentrations of REE and other trace elements were determined at Acme Analytical Laboratories Ltd. using ICP-MS after digesting samples with HNO_3 - HClO_4 -HF-HCl. Acid digestion technique was selected because of lower detection limits for many elements than fusion technique and because of the lack of refractory minerals in the samples. The precision of the REE analyses based on four replicates was mostly better than 10 %, but the analyses of samples with concentrations close to the detection limits had precisions

of only 28%. The precision and accuracy of REE analyses of reference materials with high concentrations of REE were better than 10 %. Concentrations of Cu and other chalcophile elements were determined at Acme Analytical Laboratories Ltd. after *aqua regia* digestion followed by an ICP-MS analysis. The precision and accuracy of the Cu determinations based on replicate analyses was 0.85 % and 0.87 %, respectively.

1.6.2 Compositional variation

In all of the studied rocks $\text{FeO}_{(T)}$ (total Fe expressed as FeO) and MnO concentrations increase with MgO (Fig.1-9) whereas Al_2O_3 , Na_2O , K_2O , and Sr decrease. The higher concentrations of Al_2O_3 , Na_2O , and Sr correspond to greater abundances of plagioclase in the rocks, whereas higher $\text{FeO}_{(T)}$ and MgO correspond to greater abundances of pyroxene and oxides in the rocks.

A positive correlation between Zr and Hf confirms a cogenetic origin for most rocks (Fig. 1-10) (Pearce and Norry, 1979; Leshner et al., 1991; Jenner, 1996). The late clinopyroxenite (3a) has distinctly higher concentrations of incompatible elements than other rocks (not plotted in Figs. 1-10 to 1-20 for clarity), suggesting that this rock type is not related to other igneous rocks in the study area.

Almost all rock types, except the late clinopyroxenite (3a), show relatively unfractionated REE (Fig. 1-11). The average values of $(\text{Ce}/\text{Yb})_{\text{chondrite}}$ for the melanocratic and leucocratic rocks from the southern Roby Zone are 1.3 and 1.9, respectively, and the values for the melanonorite and the norite/leuconorite of the Twilight Zone are 1.0 and 1.5. The late clinopyroxenite (3a) shows a fractionated REE pattern with overall higher concentrations of REE compared to the other rocks.

The concentrations of Pd, Pt and Au vary widely within each rock type, but the melanocratic rocks (2a to 2c, with > 14 wt% MgO) generally have higher metal concentrations than the leucocratic rocks (1a to 1d, with < 10 wt.% MgO; Fig. 1-12), suggesting that the bulk of PGE was introduced by the more Mg-rich magmas. Within the melanocratic rocks, dark gabbro (2c) has the highest average concentrations of Pd, Pt and

Au, and the clinopyroxenite (2b) has higher concentrations than the melanocratic breccia matrix (2a) (Table 2).

All rocks, except in the High Grade Zone, show positive correlations between sulfur and Pd (correlation coefficient $r = 0.891$), Pt ($r = 0.907$), and Ni ($r = 0.901$) (Fig. 1-13). Although the rocks from the Roby Zone have higher concentrations of metals than those of the Twilight Zone, the two sets of data show the same positive correlations (Fig. 1-13), suggesting that the bulk of the PGE in these zones are associated with sulfide. This is further supported by a positive correlation between precious metals and Cu (Pd versus Cu, $r = 0.89$; not plotted). The minor scatter between sulfur and Ni is likely related to the Ni present in silicate minerals, such as pyroxene, as shown by the elevated Ni concentrations in sulfur-free rocks (Fig. 1-13). The scatters of Pt and Pd in Figure 1-13 may be explained by the sub-solidus mobility of PGE, or by nugget effects of PGM. Although we do not discount mobility of PGE by hydrothermal fluids, the variation of PGE concentrations in Figure 1-13 is most likely due to the presence of discrete PGM. Mineralogical studies carried out by Watkinson and Dunning (1979) and Edgar and Sweeny (1991) show that the bulk of the PGE in the ore form discrete PGM.

Primitive mantle-normalized plots of Ni, Cu, and PGE in mineralized rocks show low Ni, Os, Ir, and Ru compared to Cu, Rh, Pt, Pd, and Au (Fig. 1-14). The High Grade Zone samples have slightly higher ratios of platinum-group PGE (PPGE) to iridium-group PGE (IPGE) than other samples (Fig. 1-14). The PPGE include Pt, Pd and Rh, and the IPGE include refractory Ir, Os and Ru. This is also illustrated by the low Ir/Pd, with an average value of 1.5×10^{-4} (Fig. 1-15a).

1.6.3 Element mobility during alteration and metamorphism

The total concentrations of REE and Zr show a positive correlation (Fig. 1-16a), suggesting that REE acted as immobile elements during alteration. In contrast, considerable scatter is evident in the plot of Rb versus Zr (Fig. 1-16b), as expected for a mobile alkali element. The immobile behavior of the REE is further supported by the

similar, relatively flat patterns of chondrite-normalized REE for all rocks, regardless of the intensity of alteration (Fig. 1-11). As light REE are more soluble in fluids than heavy REE, this pattern would have been modified during alteration.

1.7 DISCUSSION

1.7.1 Parental magma composition

Most rocks of the study area are cumulates and the bulk chemical compositions do not represent those of their parental magmas. Therefore, we calculated the compositions of parental melt following the method described by Bédard (1994). This method requires the primary mineralogy of rocks. Due to the variable degree of alteration in the rocks, we used CIPW normative minerals of plagioclase, clinopyroxene, orthopyroxene, and olivine in the calculation. The remaining fraction is assigned as a trapped melt, which ranged up to 12 wt.%, with an average of 9.5 wt.%.

The REE in the calculated parental melt for each rock type show relatively flat normalized patterns, about 10-15 times chondrite values (Fig. 1-11). The primary melt would have contained less than the calculated values because the magmas were enriched in REE through fractional crystallization of chromite and olivine that do not incorporate REE. The average $(Ce/Yb)_{\text{chondrite}}$ for the parent magmas of the melanocratic and leucocratic rocks in the southern Roby Zone are 2.4 and 2.5, respectively, whereas the average values for the melanonorite and the norite/leuconorite of the Twilight Zone are 1.7 and 2.6.

Light REE are preferentially incorporated into a melt during partial melting. The relatively unfractionated REE patterns of our samples suggest that the source was a moderately refractory mantle where previous partial melting resulted in lower LREE than HREE. This interpretation is further supported by the similarity between the calculated concentrations and patterns of REE in the parental melts and enriched mid-oceanic ridge basalts. The melt for typical oceanic ridge basalts forms through relatively high degrees

of partial melting in the moderately depleted mantle (e.g., Saunders, 1984).

The MgO content of the parental melt of the melanocratic rocks is calculated to be 8.9 wt% using the partition coefficient for MgO between clinopyroxene and melt of Hart and Dunn (1993) and a MgO content of 15.7 wt% for clinopyroxene in group 2 rocks. The primary melt probably had much higher concentrations of MgO due to fractional crystallization of olivine. For example, 20 % fractional crystallization of olivine (Fo_{92}) from the melt yields 17.3 wt% MgO in the original parental melt. Fo_{92} is the composition of olivine in equilibrium with mantle peridotites (e.g., Arai, 1992), but the choice of olivine composition does not significantly affect the result. Therefore, the MgO content of the primary melt was similar to that of picritic or komatiitic basalts which form through high degrees of partial melting in the mantle. We suggest that the primary magmas for the Lac des Iles intrusive complex were most likely products of relatively high degrees of partial melting of a moderately depleted, refractory mantle source. This interpretation is further supported by Nd isotopic compositions of the mineralized rocks. Recalculation of ϵNd values at 2690 Ma from data obtained by Brüggmann et al. (1997) yields values ranging from +1.0 to +1.5 for most rocks in Mine Block intrusion. The values are similar to the ϵNd value of +2 for late Archean igneous rocks derived from a depleted mantle (e.g., Stern et al., 1989; Hattori et al., 1996).

1.7.2 Sulfur saturation in the parental magma

The ratio of Cu/Pd changes in a magma during sulfide separation because Pd has a higher partition coefficient between sulfide and silicate melt than Cu at a given temperature and fO_2 (i.e., ~34,000 versus 1,400: Peach and Mathez, 1996, Crocket, 2002). Therefore, the ratio of Cu/Pd reflects the timing of sulfur saturation in the silicate magmas (e.g., Barnes et al., 1993). A lower Cu/Pd ratio than that of the primitive mantle implies that there was no early removal of sulfide from the magma. Higher ratios of Cu/Pd imply early removal of sulfide from the magma, and the retention of sulfide at the

source. Samples from the Lac des Iles complex have a large range of Cu/Pd ratios (Fig. 1-17). The majority of the melanocratic rocks have lower Cu/Pd than the primitive mantle (Fig. 1-17), suggesting that there was no early separation of sulfide melt. In contrast, the leucocratic phases have high Cu/Pd, suggesting early removal of sulfide from the magma, or that residual sulfide remained in the mantle source.

1.7.3 High PPGE/IPGE in the ore

Mineralized rocks from the southern Roby and Twilight Zones have similar primitive mantle-normalized PGE patterns (Fig. 1-14), suggesting a common origin for the mineralization in these zones. Palladium has a high solubility in aqueous fluids compared to other PGE (e.g., Wood, 2002), but the pattern and ratios of PPGE/IPGE are similar, regardless of the H₂O contents of the rocks, which vary from 0.1 to 5.5 wt%. There is no correlation between Pd and H₂O (Fig. 1-16 c; high H₂O values not shown), suggesting that aqueous fluids had a limited role in concentrating Pd. In contrast, the samples from the High Grade Zone show extreme enrichment of Pd as indicated by low Ir/Pd and Pt/Pd ratios (Fig. 1-15). In addition, there is no correlation between Pd and S. This is consistent with the hydrothermal enrichment of Pd, as suggested by previous workers (Talkington and Watkinson, 1984).

There are two possible processes for mafic magmas to acquire fractionated PGE with high PPGE: low degrees of partial melting and fractional crystallization. IPGE are preferentially incorporated into olivine, chromite, and high-temperature PGM, such as laurite and iridosmine (Puchtel and Humayun, 2001; Andrews and Brenan, 2002; Sattari et al., 2002; Righter et al., 2004). Retention of these minerals in the mantle during low degrees of partial melting results in low IPGE in the melt. This is consistent with low Ir/Pd in gabbro-hosted deposits compared to komatiite-hosted deposits (Fig. 1-15). Evolved magmas also have fractionated PGE because olivine, chromite and high-temperature PGE are removed during the early stages of fractional crystallization. We discount low

degrees of partial melting of the parental magmas as the cause of high PPGE because this is not consistent with the flat normalized REE patterns and the high MgO contents of the calculated parental magmas. Therefore, high PPGE in our samples is best explained by the removal of IPGE during early crystallization of the magmas.

1.7.4 High palladium in the Southern Roby and Twilight Zones

The average concentration of Pd in the melanocratic rocks, excluding the High Grade Zone, is estimated to be ~4 ppm, on the basis of average grade, tonnage, and abundance (~ 20 vol.%) of mineralized melanocratic rocks in the Roby Zone. This is very high compared to average Pd concentrations of basalts (0.46 ppb) and komatiites (~11 ppb; Crocket, 2002). Various processes were suggested for such enrichment of Pd. Watkinson and Dunning (1979) proposed that sulfur, Ni, Cu, and PGE were enriched during evolution of the parental magmas, followed by immiscible separation of Pd-bearing aqueous fluid from the magmas. Talkington and Watkinson (1984) argued for an important role of hydrothermal activity in the mineralization, based on the occurrence of PGM containing Te, As, and Bi, and the spatial association of PGM with secondary hydrous minerals and pyrite. Macdonald (1988) also suggested hydrothermal enrichment of PGE by fluids that originated from the parental magmas, also based on the abundant hydrothermal minerals in the mineralized zones. Brügmann et al. (1989) proposed “constitutional zone refining” for the enrichment of Pd and other PPGE relative to IPGE. Constitutional zone refining (McBirney, 1987) involves the formation of volatile-rich magmas through fractional crystallization and partial melting of earlier formed cumulates. Brügmann et al. (1989) suggested that a volatile-rich silicate magma re-melted gabbro cumulates and selectively incorporated the PPGE from sulfides in the cumulates, and that the melanocratic and leucocratic rocks in the Roby Zone represent the residue and partial melt, respectively. In another model, Lavigne and Michaud (2001) suggested that the mineralization involved the forceful intrusion of a PGE-, Ni- and Cu-

rich immiscible sulfide liquid into the partially crystallized overlying magma chamber. Exsolution of aqueous fluids from magmas resulted in the redistribution of precious metals.

Our data, showing positive correlations between sulfur and base and precious metals, are not consistent with hydrothermal concentration of Pd in the southern Roby and Twilight Zones. Furthermore, our detailed mapping shows that the bulk of PGE are in late melanocratic rocks. Hydrothermal processes cannot explain the preferential enrichment of Pd in the mafic rocks. Therefore, we discount any significant contributions of hydrothermal fluids to the Pd mineralization in the southern Roby and Twilight Zones. However, aqueous fluids may have been responsible for mineralization in the High Grade Ore samples as indicated by the scatter in the plots of sulfur and base and precious metals (see below).

The zone-refining process is also not consistent with our data. First, the zone-refining process produces leucocratic melt and melanocratic and ultramafic rocks as the residue (Brügman et al., 1989). Our detailed mapping shows that melanocratic rocks carry most of the Pd, and leucocratic rocks are essentially barren (Fig. 1-12, Table 2). Second, the zone-refining process involves partial melting of a cumulate (Brügmann et al., 1989) containing clinopyroxene, orthopyroxene, and a solidified, trapped melt. Partial melting would dissolve the solidified melt first, then clinopyroxene. The solidified melt contains high concentrations of incompatible elements, such as REE, compared to any other phases. Clinopyroxene also contains high concentrations of incompatible elements compared to olivine and orthopyroxene. Therefore, any partial melt should contain elevated incompatible elements compared to earlier rocks. The late clinopyroxenites (3a) are the only rock type with high REE, but these rocks are free of sulfides and barren of Pd. Similar concentrations of REE in all rocks in the southern Roby and Twilight Zones (Fig. 1-11) argue against the zone-refining process. Dissolution of significant amounts of clinopyroxene would have increased the Sc content of the melt, as Sc is preferentially

included in clinopyroxene, but this is inconsistent with the similar Sc/Y ratios of all rocks (Fig. 1-18).

We suggest that Pd in the late melanocratic magmas was enriched by incorporating pre-existing sulfide melt formed by earlier magmas. This is consistent with all data, including low Cu/Pd ratios in the ore and high Cu/Pd in earlier leucocratic rocks (Fig. 1-17). Earlier magmas lost sulfide melt with low Cu/Pd at depth, and later melanocratic magmas incorporated the sulfide melt.

1.7.5 Enrichment of palladium in the High Grade Zone of the Roby Zone

Although the High Grade Zone was not the focus of this investigation, it is important because it contains high Pd, ~ 8 ppm in most samples, and hosts approximately 35 % of the Pd in the mine. The samples from the High Grade Zone do not plot on the correlation trends of sulfur versus base metals and sulfur versus precious metals (Fig. 1-13). The data suggest that Pd enrichment in this zone may have been caused by aqueous fluids. This interpretation is supported by abundant quartz aggregates, the lack of exsolution textures in sulfides, and the common occurrence of pyrite.

The High Grade Zone is located on the eastern margin of the Roby Zone, adjacent to East Gabbro, which is older than the rest of Mine Block intrusions. The High Grade Zone is adjacent to high grade breccia ore in the Roby Zone (Lavigne and Michaud, 2001), suggesting a genetic link between the two. We propose that aqueous fluid exsolved from late, fertile, melanocratic magmas migrated into the area of the High Grade Zone. The barren East Gabbro would have acted as a physical barrier for such an aqueous fluid, resulting in precipitation of Pd along the boundary with the East Gabbro. The mineralized zone is subvertical at present, but this steepening probably occurred during the docking of the Quetico accretionary prism and Wawa arc to the Wabigoon subprovince to the north (Percival, 1989).

1.7.6 A model of igneous activity and PGE mineralization at Lac des Iles

This section summarizes the evolution of the southern Roby and Twilight Zones, which is illustrated schematically in 1-19. First, relatively high degrees of partial melting in a moderately depleted mantle formed the parental magmas of early gabbroic rocks. These magmas became enriched in Cu and PPGE during the fractional crystallization of olivine, chromite, and high-temperature PGM. The magmas eventually reached sulfur saturation, forming an immiscible sulfide melt with low Cu/Pd in the conduit, which resulted in high Cu/Pd ratios in the evolving magma. The magmas reached the site of the deposit and partly solidified as leucocratic gabbros. A new batch of magmas, also formed by relatively high degrees of partial melting of a similar source, passed through the same conduit as the earlier, leucocratic magmas and incorporated the pre-existing sulfide melt formed by the earlier magmas. The melanocratic magmas reached sulfur saturation, forming a second sulfide melt and inheriting the low Cu/Pd ratios of the earlier sulfide melt. In this model the late mafic magmas became rich in water and other volatiles, which caused the brecciation and pegmatite formation observed in the surface outcrops. The hydrothermal fluids released from melanocratic magmas migrated upward along the boundary between the East Gabbro and mineralized gabbroic rocks resulting in intense hydrothermal alteration at the margin of the Roby Zone, and forming the High Grade Zone.

1.7.7 Comparison with other types of PGE mineralization

Major PGE deposits occur as stratiform layers in large layered intrusions or are hosted by Ni-sulfides at the base of large mafic igneous intrusions. The former type includes the Merensky Reef in the Bushveld (Von Gruenewaldt et al., 1985; Schoenberg et al., 1999), the Main Sulfide Zone in the Great Dyke (Wilson and Prendergast, 2001) and the J-M Reef of the Stillwater Complex, Montana (Todd et al., 1982). PGE ore in layered intrusions are interpreted to result from additions of significant volumes of

magma, or pulses of relatively primitive magmas into quiescent magma chambers (Todd et al., 1982; Von Gruenewaldt et al., 1985; Maier et al., 1998; Schoenberg et al., 1999). The Ni sulfide-hosted deposits include the Noril'sk and Sudbury ore deposits (Lightfoot and Naldrett, 1994). Contact-type deposits are represented by the River Valley-East Bull Lake suite of intrusions in Ontario (Peck et al., 2001), the Coldwell Complex, Ontario (Barrie et al., 2002), the Federov Pansky intrusion in Russia (Schissel et al., 2002), and the Portimo intrusion, Finland (Alapieti et al., 1989). Typical contact-type deposits occur near the basal "inclusion-rich" zones of the intrusions that contain abundant xenoliths of country rocks and felsic intrusive rocks. The partial digestion of these fragments is thought to have resulted in increased H₂O and SiO₂ contents in the magmas, forming breccias and pegmatites, and leading to sulfide saturation (Barrie et al., 2002).

1.7.8 Comparison with contact-type PGE mineralization

The southern Roby and Twilight Zones of the Lac des Iles intrusive complex share many characteristics with contact-type deposits. They include low sulfide abundance in the mineralized rocks, high Pd compared to other PGE, and the common occurrence of breccias and pegmatites. However, the PGE mineralization at the southern Roby and Twilight Zones is not localized near the contacts with country rocks. Instead, the mineralization is in the center of the Mine Block Intrusion. In addition, there is no evidence that enrichment of SiO₂ resulted in sulfur saturation in the ore deposit. In contrast, the most primitive, melanocratic rocks are the most PGE- and sulfide-rich. Thirdly, there is no evidence suggesting the interaction between mineralized mafic magmas and felsic magmas/rocks. Sutcliffe (1989) and Sutcliffe et al., (1989) described contemporaneous emplacement of granitoid magmas with gabbroic rocks, but later studies (e.g., Michaud, 1998; Lavigne and Michaud, 2001), including our study, failed to identify any xenoliths of granitic rocks in the area of mineralization. Minor inclusions of tonalitic rocks are present, but they are restricted to the barren margin of the Mine Block Intrusion adjacent to the surrounding tonalite. These observations suggest that the origin

of Pd mineralization at Lac des Iles is fundamentally different from that of the contact-type deposits.

1.7.9 Comparison with stratiform-type mineralization in large layered intrusions

We propose that the bulk of Pd mineralization was brought by pulses of primitive magmas, as illustrated by the sequence of intrusions with various compositions (Fig. 1-20). The proposed mode of the mineralization is analogous to that suggested for typical stratiform deposits. However, the mode of emplacement of magmas is different. Unlike the quiescent magma chambers necessary for the formation of large, continuous ore horizons in stratiform deposits, the intrusive environment at Lac des Iles was apparently dynamic, forming breccias and magma mingling instead of layering. In addition, the Lac des Iles intrusive complex shows highly fractionated PGE with high Pd compared to the ore in layered intrusions, although the Lac des Iles ore lies on the general trend of Ir/Pd versus Pd defined by many deposits (Fig. 1-15).

1.8 Conclusions

Our detailed mapping of the southern Roby and Twilight Zones shows multiple intrusions of gabbroic rocks, which are divided into a group of early barren leucocratic gabbros and late mineralized melanocratic rocks. All rocks, except for late clinopyroxenite are co-genetic, formed from magmas generated by high degrees of partial melting in a moderately depleted mantle. Positive correlations between sulfur and precious and base metals and exsolution textures in sulfide grains suggest that the mineralization is of primary magmatic origin where PGE were concentrated in an immiscible sulfide melt in the parental magmas. Very high ratios of PPGE/IPGE and the extreme enrichment of Pd, which characterize the mineralization at Lac des Iles, are attributed to fractional crystallization of parental magmas and two stages of PGE enrichment. Earlier magmas, which evolved to the parental magmas of leucocratic gabbro, separated immiscible sulfide melt at depth. Later magmas, which formed the

melanocratic gabbros, incorporated the early-formed magmatic sulfide melt.

The mineralization at Lac des Iles is commonly compared to contact-type PGE ore because of similar textures in both types of deposits, but the Lac des Iles ore shows no evidence for host-rock assimilation. In addition, the ore is not localized near contacts with the country rocks. The Lac des Iles mineralization also shows similarities with PGE deposits in large layered intrusions, with the bulk of the PGE in both types being introduced by pulses of fertile primitive magmas. However, the intrusion of this fertile magma was much more energetic and dynamic at Lac des Iles than that associated with the quiescent magma chambers in large layered deposits.

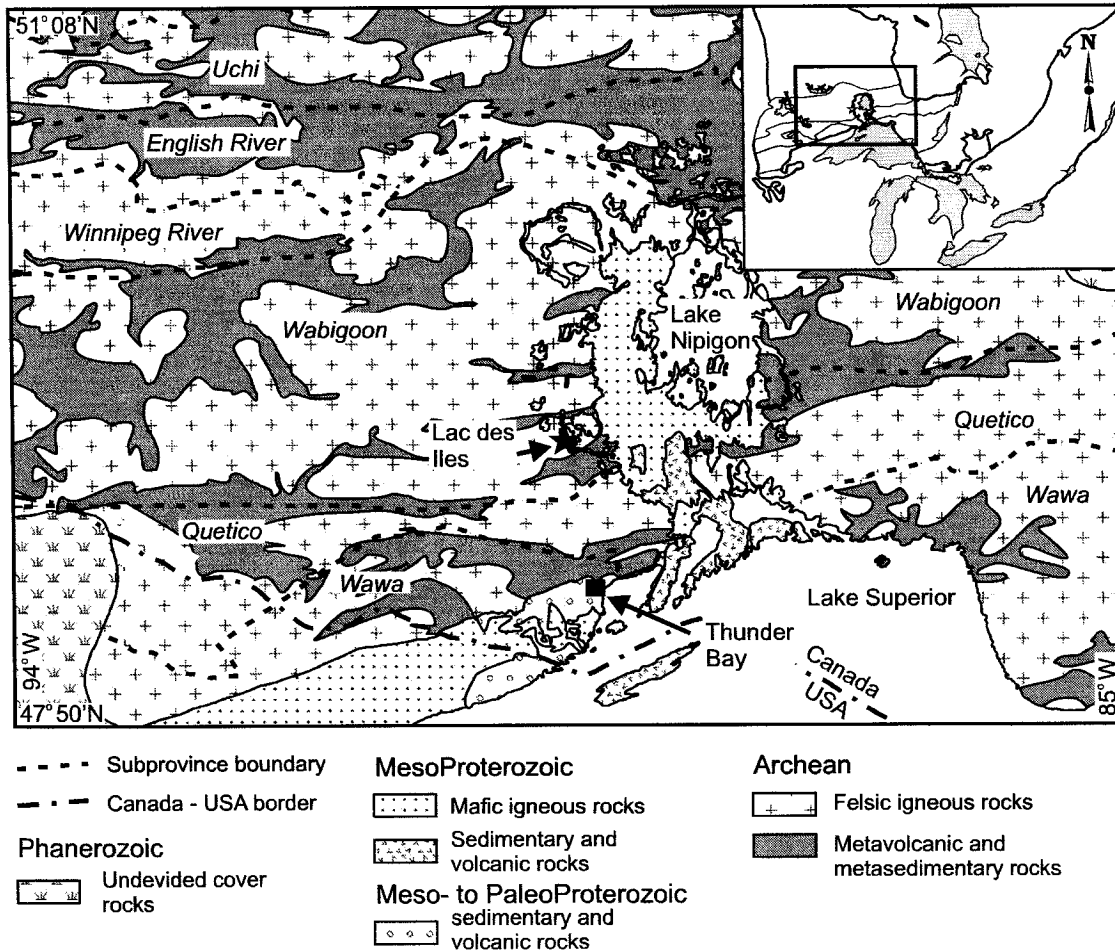


Figure 1-1. Regional geology of the western Superior Province illustrating the boundaries of subprovinces, the locations of the Nipigon Plate and the Lac des Iles mine (modified from Ontario Geological Survey, 1991). The subprovince names are shown in italics. The Nipigon Plate is the northern extension of the igneous province related to the Mid-continental Rift. The inset displays a simplified map of the Superior Province. The square outlines the area shown in the Figure 1-1.

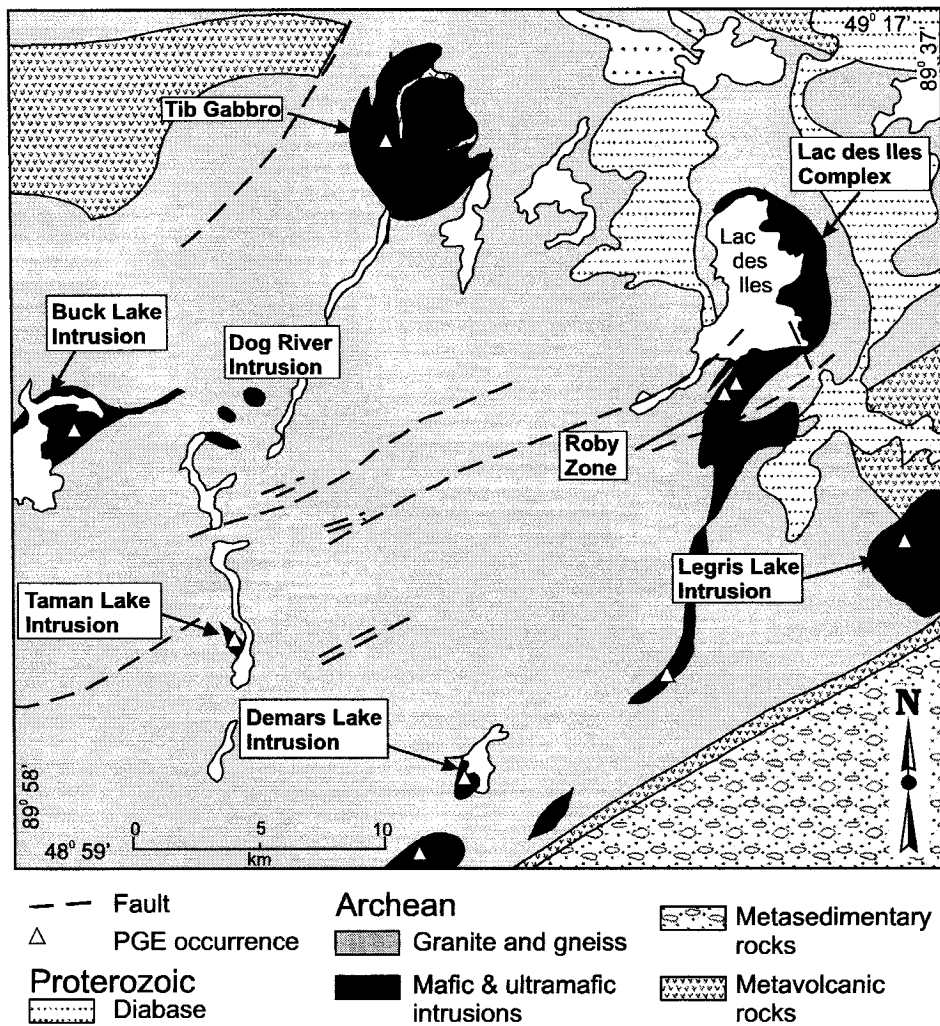


Figure 1-2. Simplified regional geological map of the study area showing the occurrence of mafic/ultramafic intrusions with PGE mineralization (modified after Sutcliffe and Smith, 1988). Note the circular distribution of mafic-ultramafic intrusions. The diabase sills belong to the igneous rocks of the Nipigon Plate.

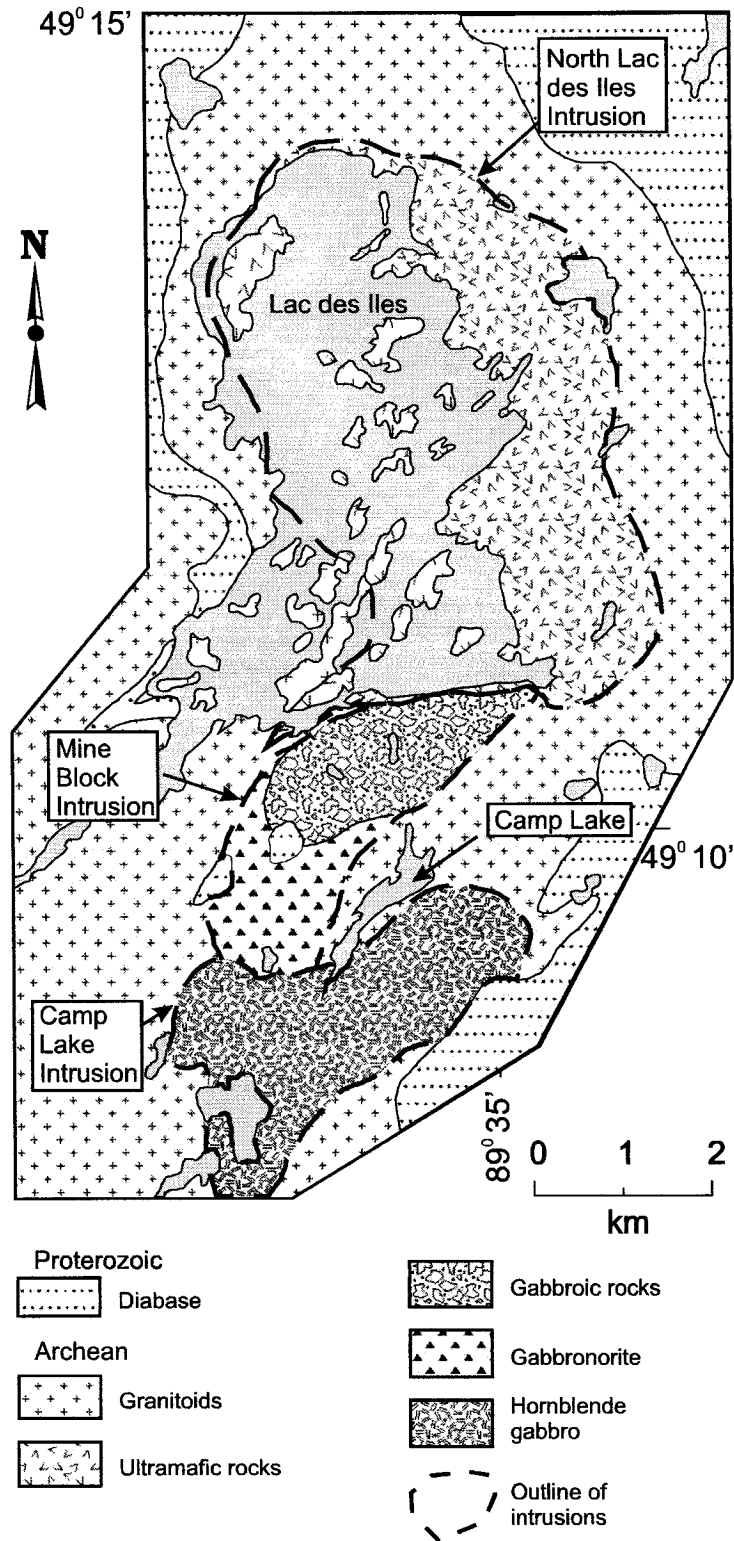


Figure 1-3. Simplified geological map of the Lac des Iles intrusive complex illustrating the distribution of the North Lac des Iles, Mine Block, and Camp Lake intrusions (modified after Sutcliffe et al., 1989).

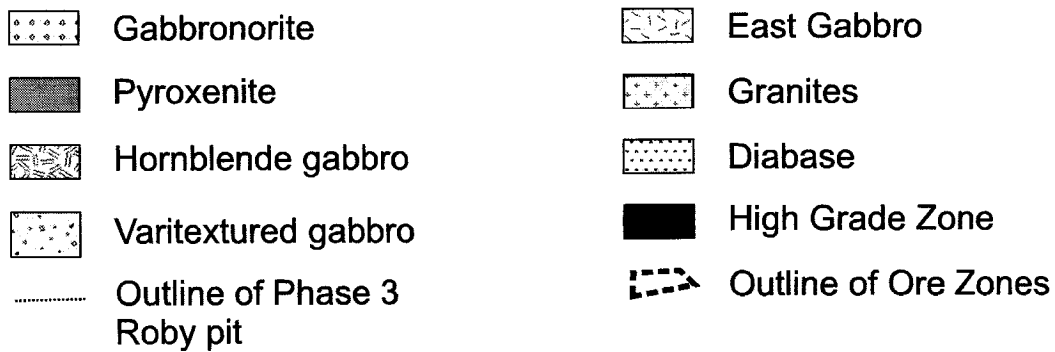
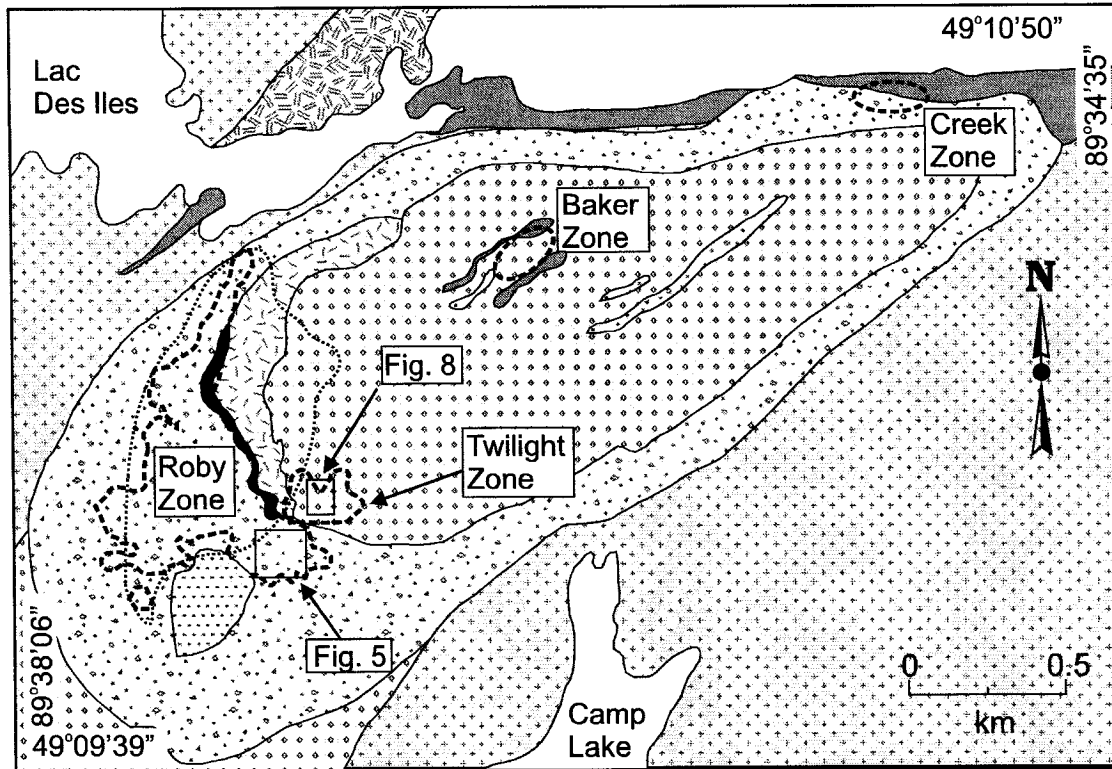


Figure 1-4. Simplified geological map of the Mine Block Intrusion of the Lac des Iles intrusive complex (modified after Sutcliffe and Sweeney, 1986). It shows the distribution of East Gabbro, the locations of the Roby, Twilight, and High Grade Zones, and the outline of the Phase 3 open pit.

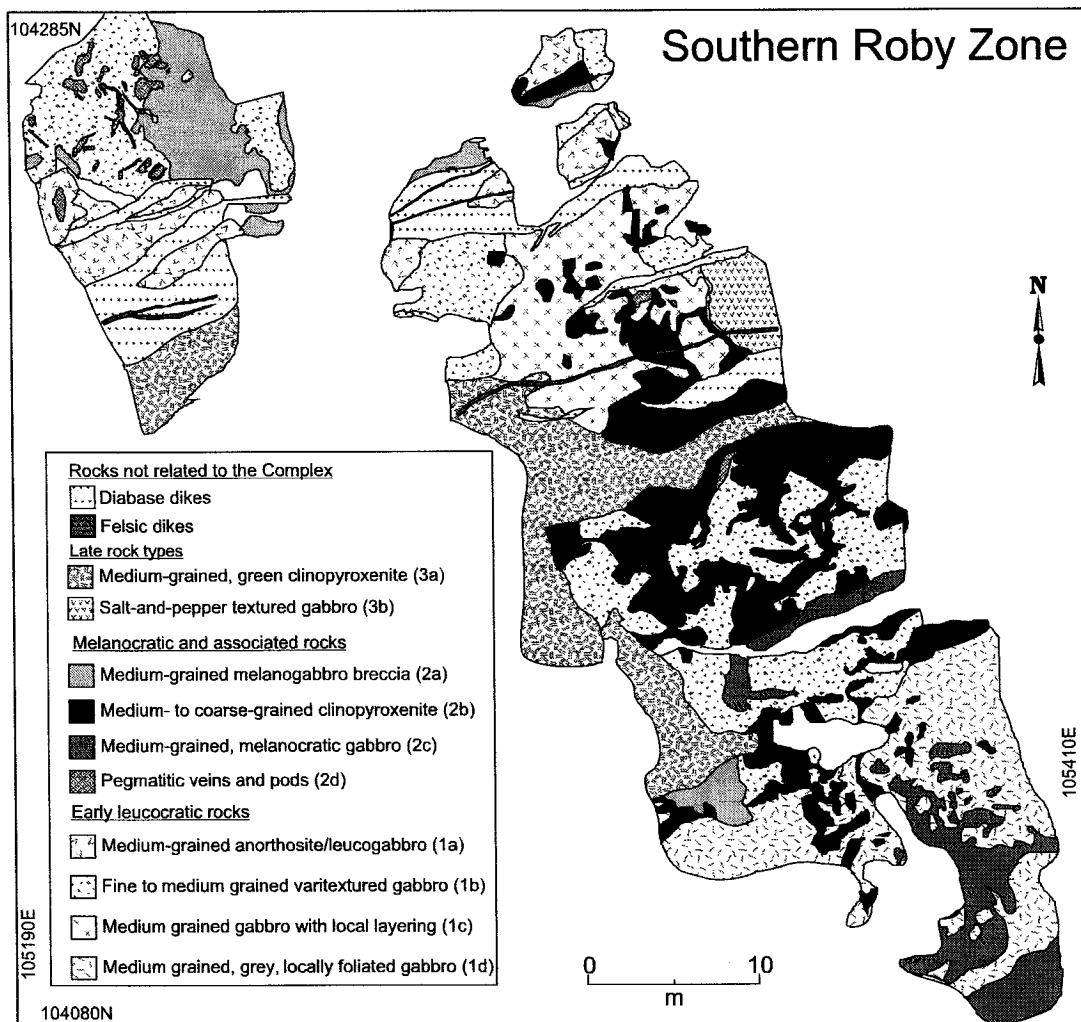


Figure 1-5. Illustration of the complicated distribution of various rock types in the southern Roby Zone in the Mine Block intrusion after 1:60 scale mapping by Hinchey et al. (2003). Rocks are divided into early leucocratic, mineralized melanocratic and late barren melanocratic rocks. The mineralized melanocratic rocks are commonly accompanied by pegmatitic veins and pods of various sizes from several centimeters to 50 cm. Only large pegmatites are shown in the map. Felsic and diabase dikes cut all rock types of the Lac des Iles intrusive complex. Numbers on the sides correspond to the mine grid.

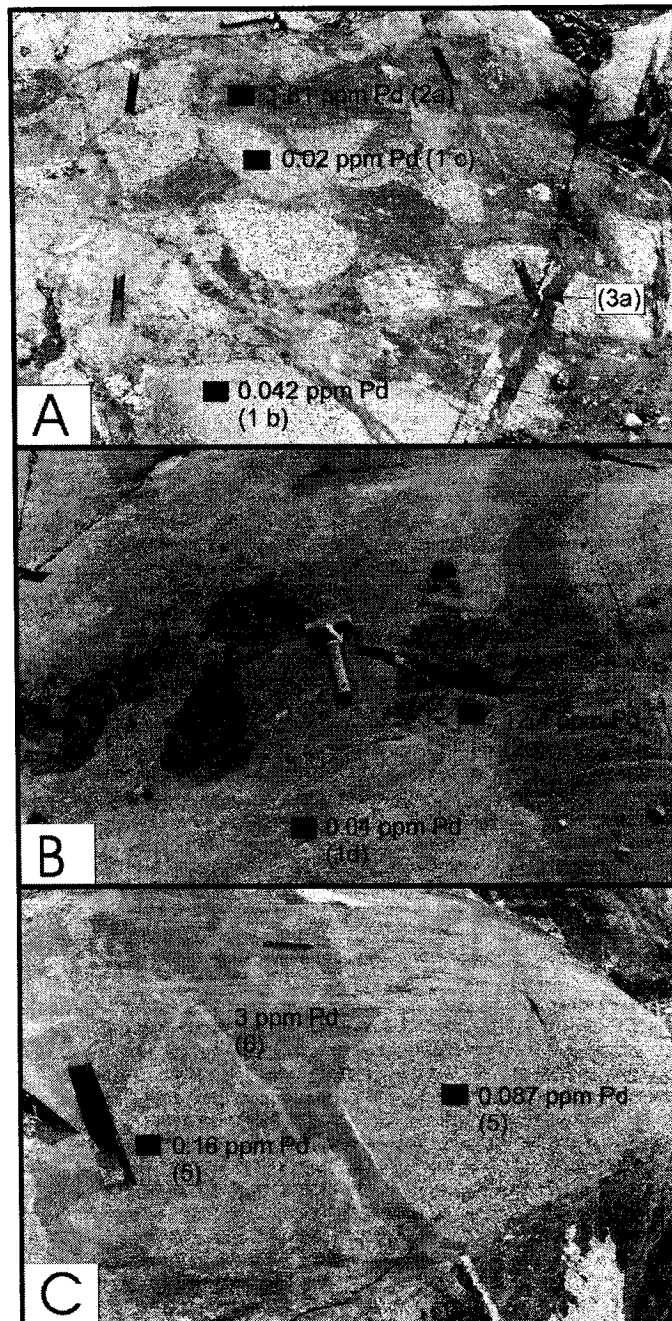


Figure 1- 6. Representative photographs of the ore zone and the concentrations of Pd in different rock types. Solid squares show the locations of samples used for Pd analysis after the photographs were taken. The Pd value of the melanonorite in the centre of Fig. 1-6c is for a sample outside the field of view. The numbers in parentheses correspond to the rock types described in the text. Rock hammer for scale. A) Medium-grained melanogabbro breccia (2a) containing fragments of earlier leucocratic rocks (1b and 1c) in the northern section of the southern Roby Zone. Note low concentrations of Pd in leucocratic rocks and a dike of late barren clinopyroxenite (3a) cutting the melanogabbro breccia (2a). B) Magma mingling between early leucogabbro (1d) and late melanogabbro (2c) from the southern portion of the southern Roby Zone. C) Magmatic brecciation of late melanonorite (6) and earlier norite (5) in the Twilight Zone.

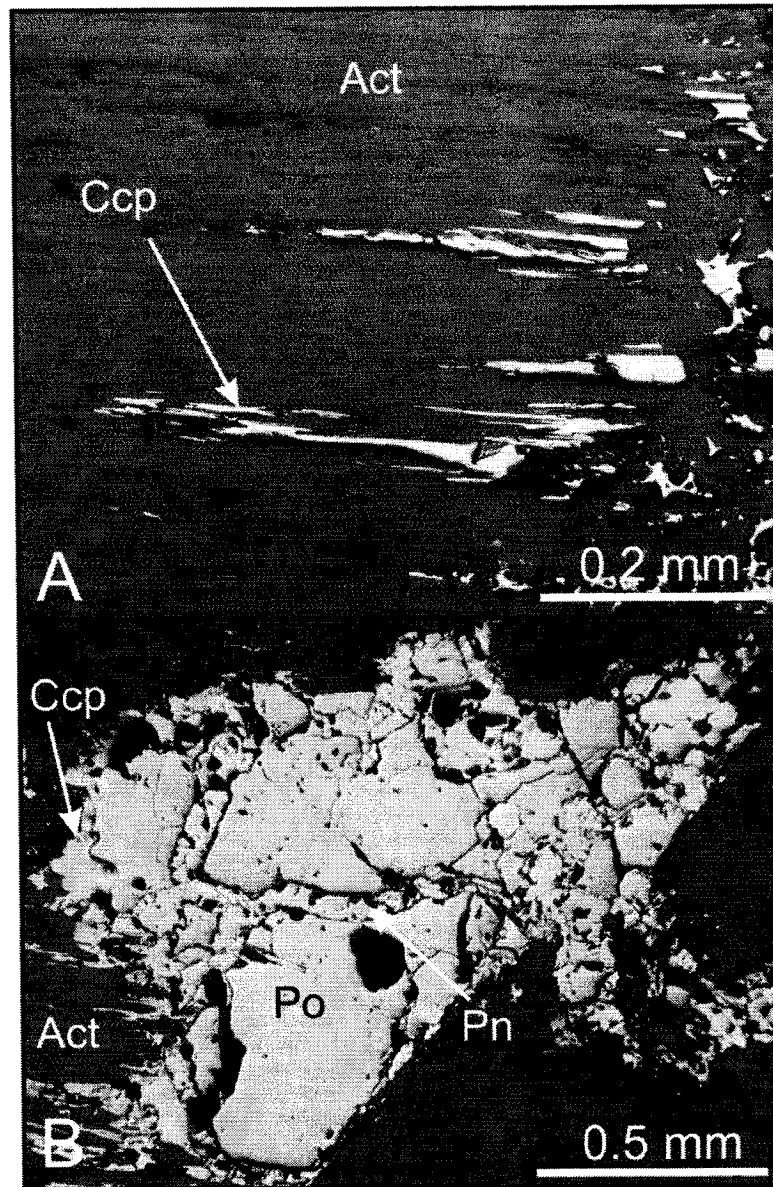


Figure 1-7. Photomicrographs showing the textures of sulfide minerals. A) Chalcopyrite (Ccp) along cleavage planes of actinolite (Act). The sample is from the medium-grained clinopyroxenite (2b) of the southern Roby Zone. B) Primary magmatic sulfide bleb with apparent exsolution of chalcopyrite (Ccp) and pentlandite (Pn) in late fractures within pyrrhotite (Po). The sample is from the medium-grained melanocratic gabbro (2c) of the southern Roby Zone. Note the thin lamellae of chalcopyrite along cleavage planes of actinolite (lower left).

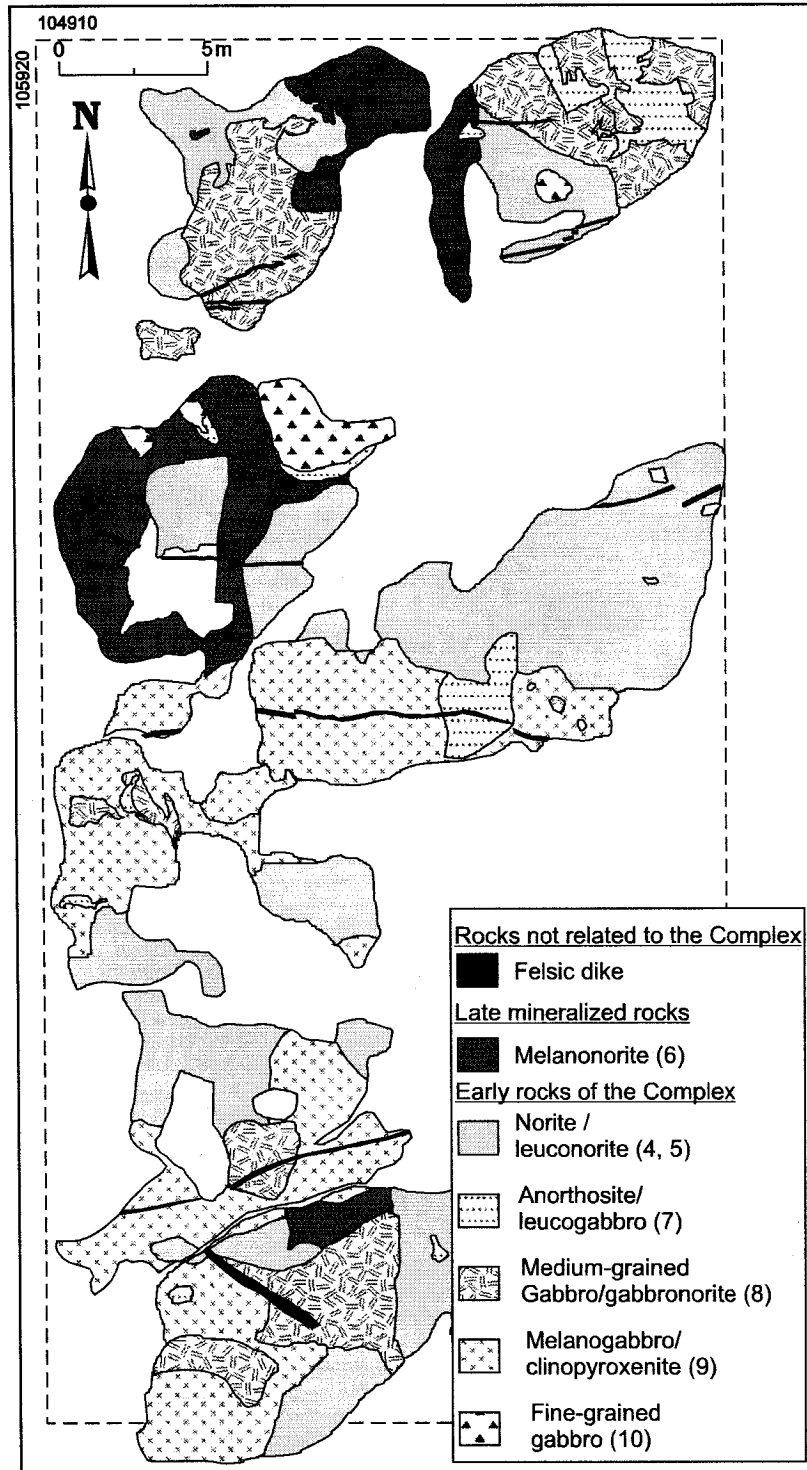


Figure 1-8. Illustration of the complicated distribution of different rock types in the Twilight Zone based on the 1:120 scale mapping by Hinchey et al. (2003). Dashed lines show the mine grid. The numbers in parentheses after rock names correspond to the rock types in the text. The mineralized melanonorite (6) is the latest rock type of the Lac des Iles intrusive complex in the outcrop. It shows the intrusive contacts with fine-grained gabbro (10), leuconorite (4), norite (5), and medium-grained gabbro (8).

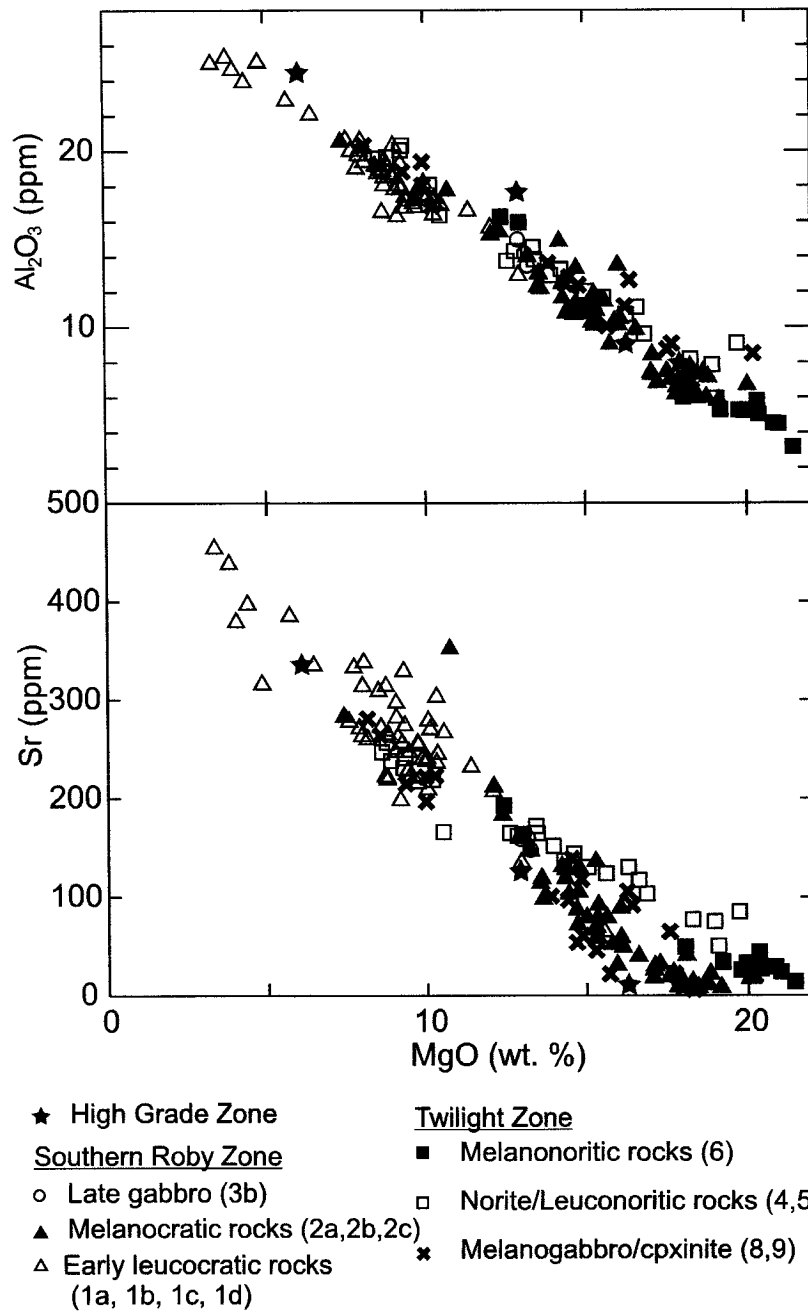


Figure 1-9. MgO (wt %) versus Al₂O₃ (wt %) and Sr (ppm) for whole rocks from the southern Roby, Twilight, and High Grade Zones. Note the well displayed correlations suggesting a common parental origin of all rock types. Numbers in parentheses are rock types in the text.

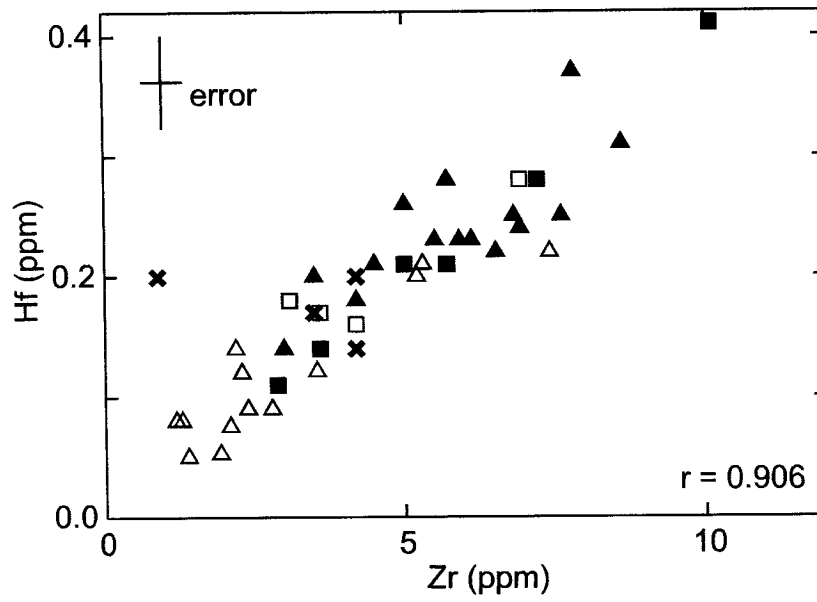
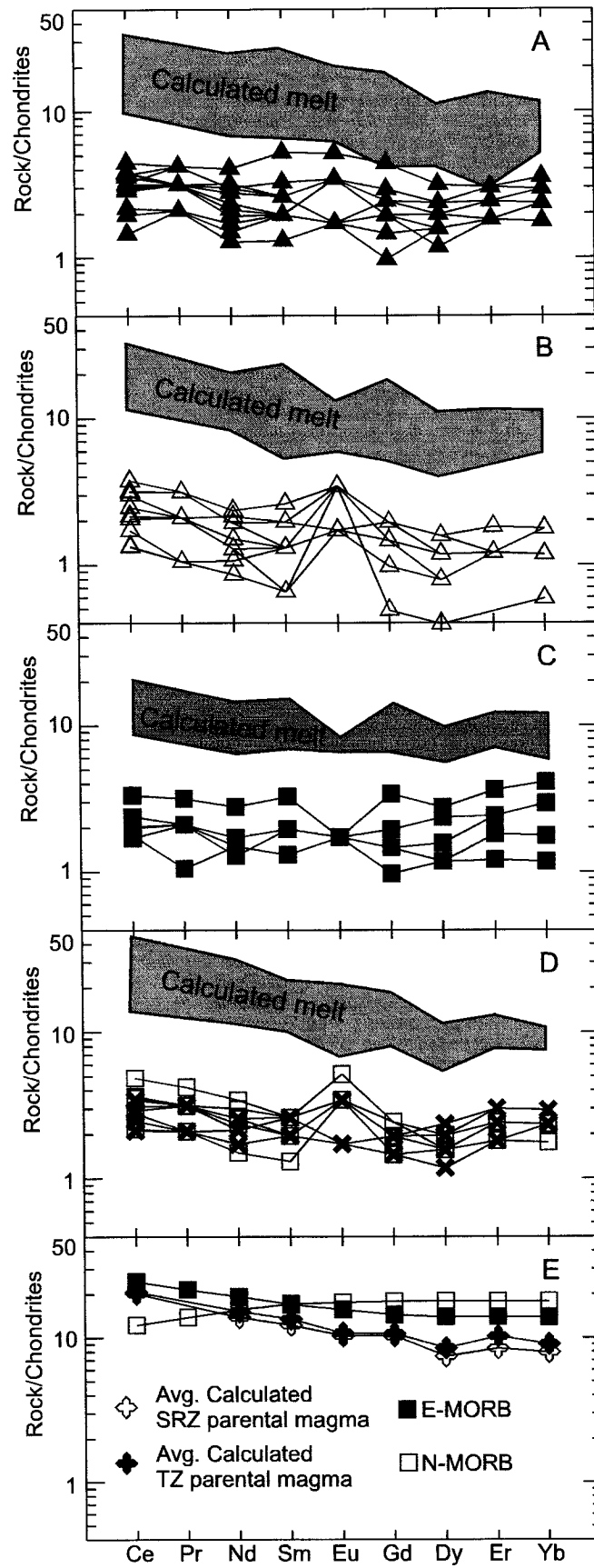


Figure 1-10. Hf versus Zr concentrations for the rocks from the southern Roby, Twilight and High Grade Zones. Note the well displayed correlation suggesting a co-genetic origin of all rock types. See legend in Fig. 1-9. Correlation coefficient (r) is shown in the lower right and error bars in 2 sigma are given in the upper left of the diagram.

Figure 1-11. Chondrite normalized rare earth elements (REE) plots for a variety of rocks; (A) the melanocratic rocks and (B) leucocratic rocks from the southern Roby Zone, (C) the melanonorite and (D) norite/leuconorite rocks from the Twilight Zone, and (E) normal- and enriched-mid oceanic ridge basalts (N- and E-MORB, respectively) compared to the hypothetical parental melt (shaded) for the rocks in southern Roby and Twilight Zones. The composition of the hypothetical melt was calculated following the method of Bédard (1994). Note the low degrees of REE fractionation for both the bulk rocks and calculated melt. The calculation of the composition of the hypothetical melt used CIPW normative minerals of plagioclase, clinopyroxene, orthopyroxene, and olivine. The remaining is attributed to a trapped melt fraction. Using the REE concentrations of bulk rocks and the modal abundance of minerals, and partition coefficients of the minerals and melt, the concentrations of REE in different phases were calculated using mass balance. We used the concentration of REE in clinopyroxene and the partition coefficients between clinopyroxene and melt listed in Bédard (1994) to calculate the REE concentrations of the parental liquid. Chondrite and MORB values are from McDonough and Sun (1995), and Sun and McDonough (1989), respectively.



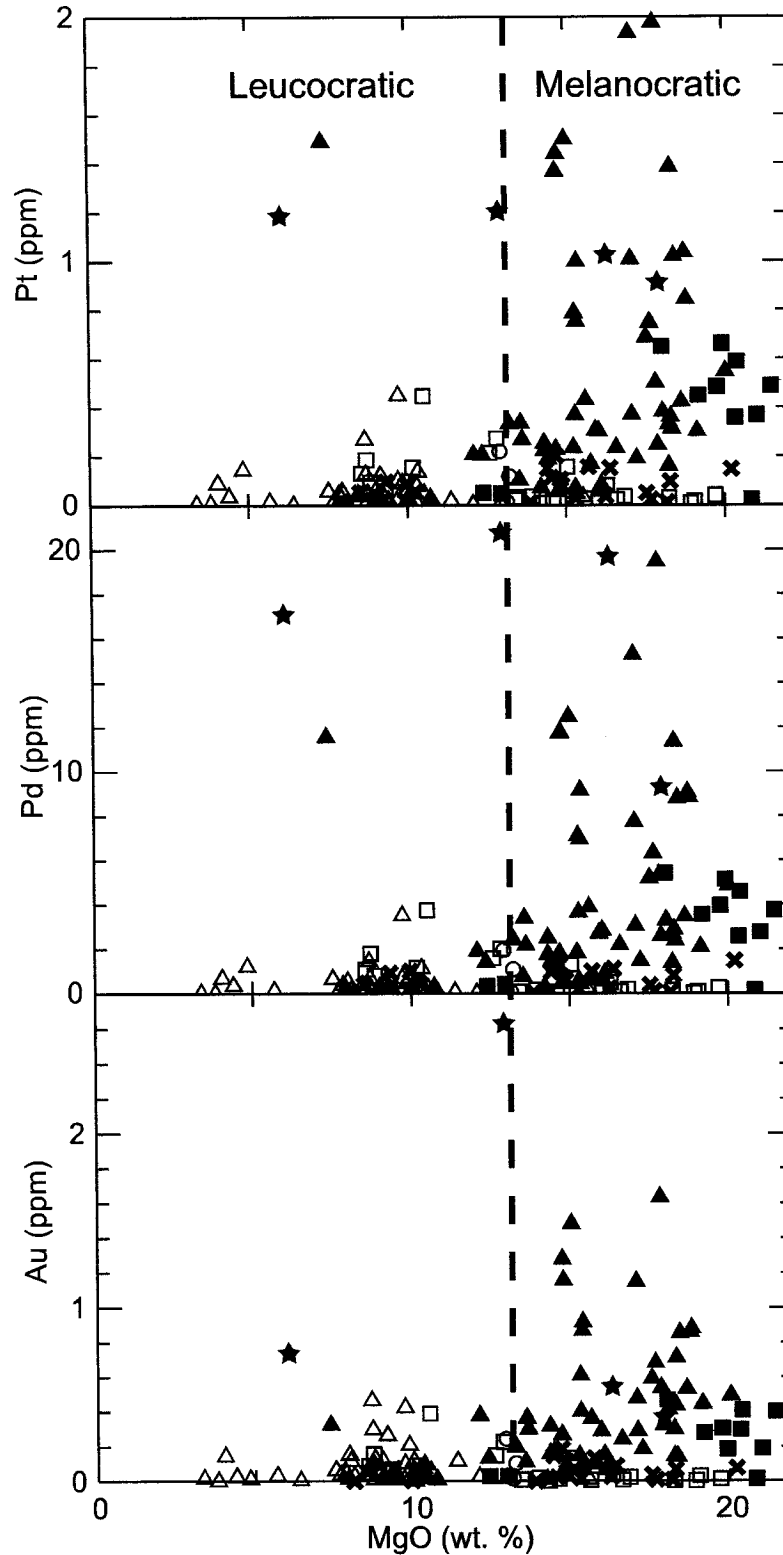


Figure 1-12. Bivariate plots of MgO (wt.%) versus Au, Pd, and Pt (ppm). Note the high concentrations of precious metals in the melanocratic rocks in the southern Roby and Twilight Zones. The dashed line broadly separates the melanocratic rocks from the leucocratic rocks.

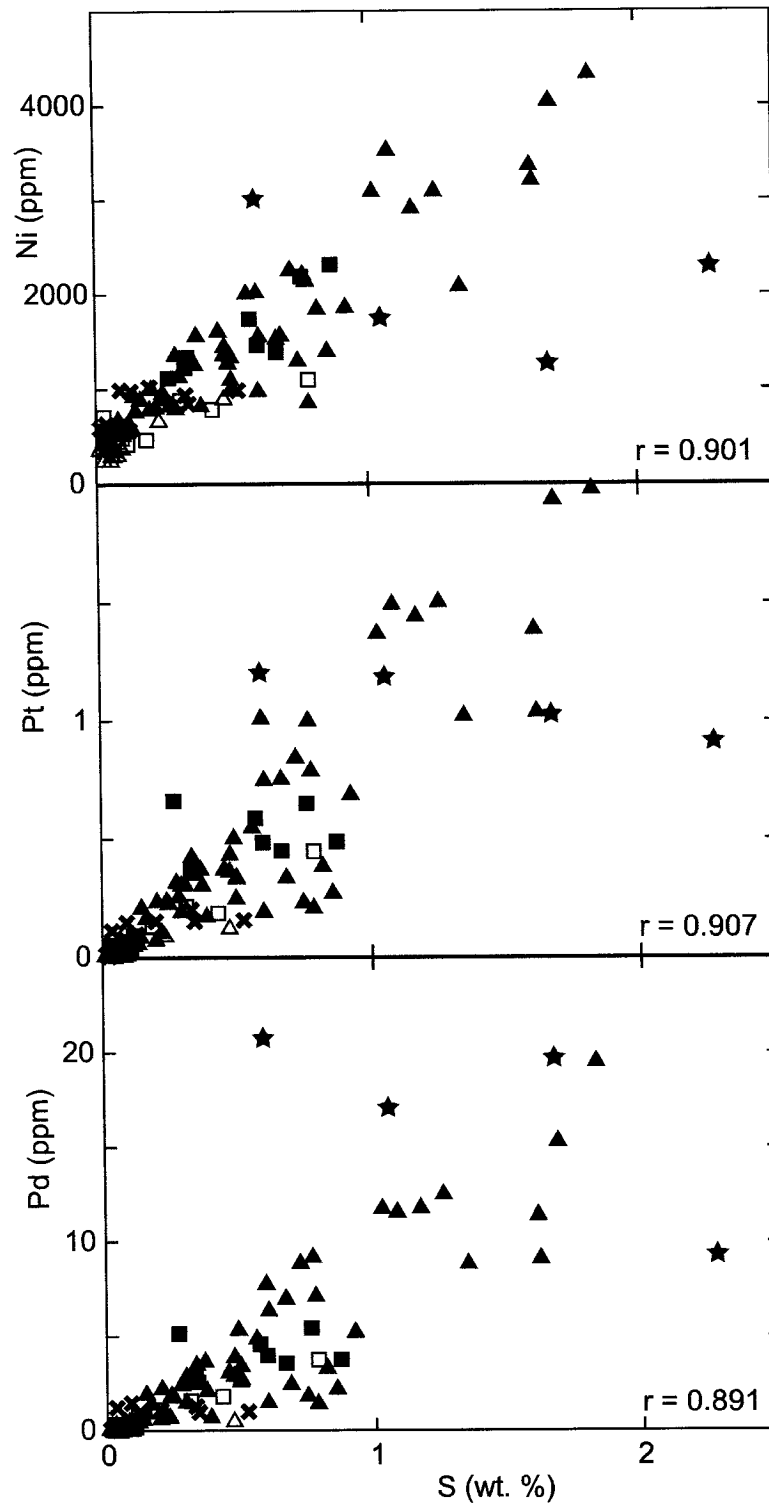


Figure 1-13. Bivariate plots of sulfur (wt.%) versus Ni, Pt, and Pd (ppm). Note the positive correlations suggesting a sulfide control on mineralization. Elevated Ni concentrations in samples without sulfides suggest the presence of minor Ni in silicate minerals. Preliminary electron microprobe data confirm that clinopyroxene contains significant Ni. Correlation coefficients (r) are calculated for samples, excluding the High-Grade zone.

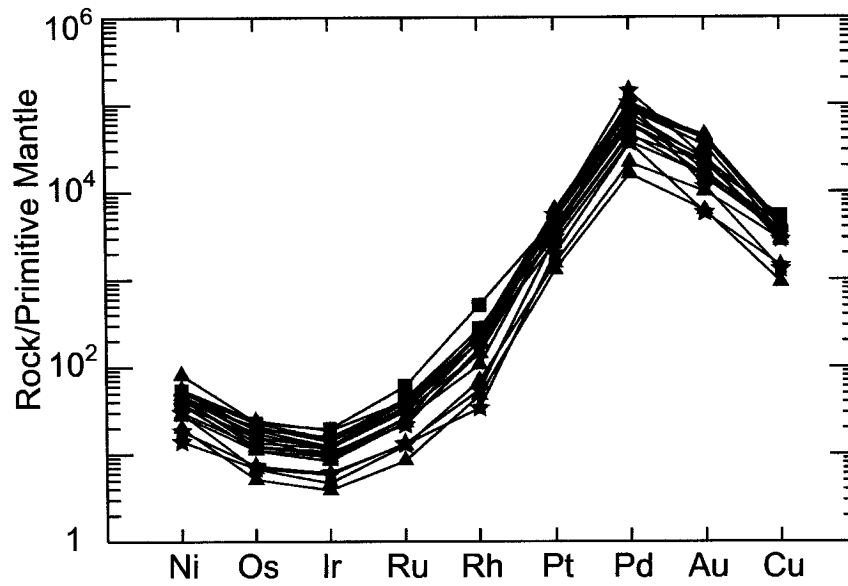


Figure 1-14. Primitive mantle-normalized plot for Ni, Cu, and PGE of the southern Roby, Twilight, and High Grade Zones. The data have been recalculated to 100% sulfide following Naldrett (1981). Note similar patterns for all rocks with low concentrations of Ni, Ir, Os, and Ru and high concentrations of Cu, Rh, Pt and Pd. Primitive mantle values for Ni and Cu are from McDonough and Sun (1995) and PGE values from Guillot et al. (2000).

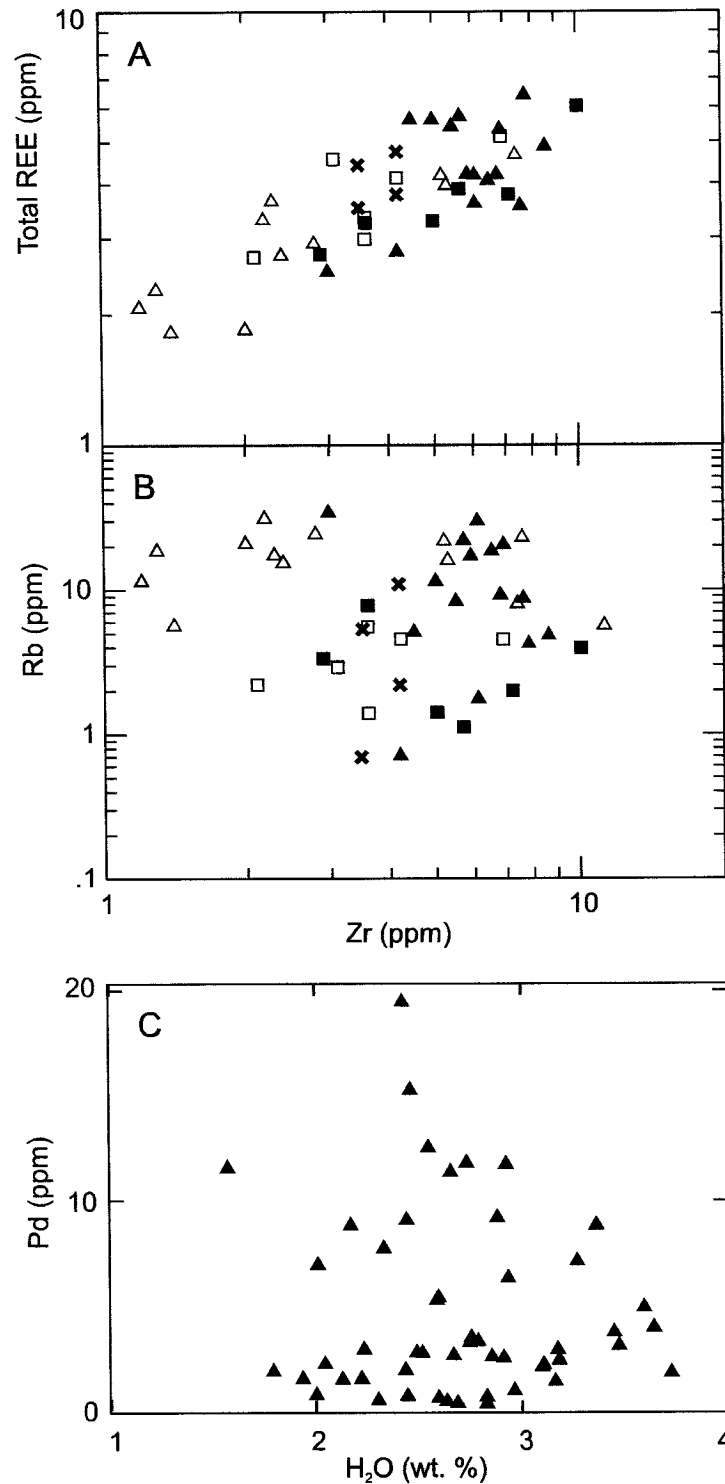


Figure 1-16. A) Plot of total REE versus Zr for all rock types. Zirconium is an incompatible and immobile element. The positive correlation suggests that the REE were also immobile. B) Plot of Rb versus Zr illustrating that Rb acted as a mobile element during alteration, and C) Plot of H₂O (wt.%) versus Pd (ppm) for variably altered melanocratic rocks of the southern Roby Zone. The lack of any positive correlation suggests that aqueous fluid likely was not important in the concentration of Pd.

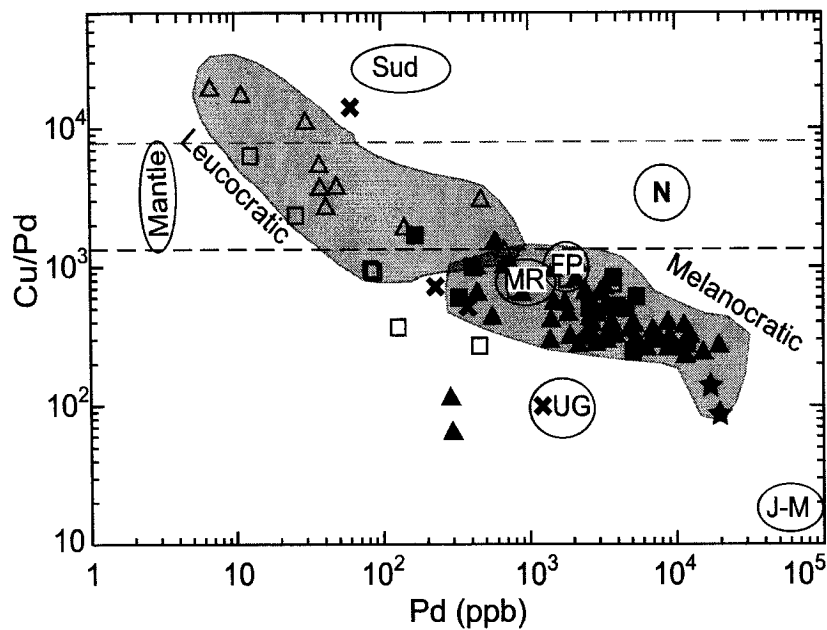


Figure 1-17. Pd versus Cu/Pd plot for samples from the southern Roby and Twilight Zones compared to other PGE deposits. Note that the rocks from Lac des Iles show a wide variation in Cu/Pd ratios. The mineralized melanocratic rocks show low Cu/Pd ratios, similar to those for other primary PGE deposits, whereas the barren leucocratic rocks display high Cu/Pd ratios. Sud = Sudbury, Canada (Naldrett, 1981), N = Noril'sk (Smirnov, 1966), FP = Federov Pansky (Schissel et al., 2002), Russia; MR = Merensky Reef, Bushveld (Maier et al., 1996) and UG = UG2 Reef, Bushveld (Maier et al., 1996), South Africa; and JM = JM Reef, Stillwater, USA (Barnes and Naldrett, 1985).

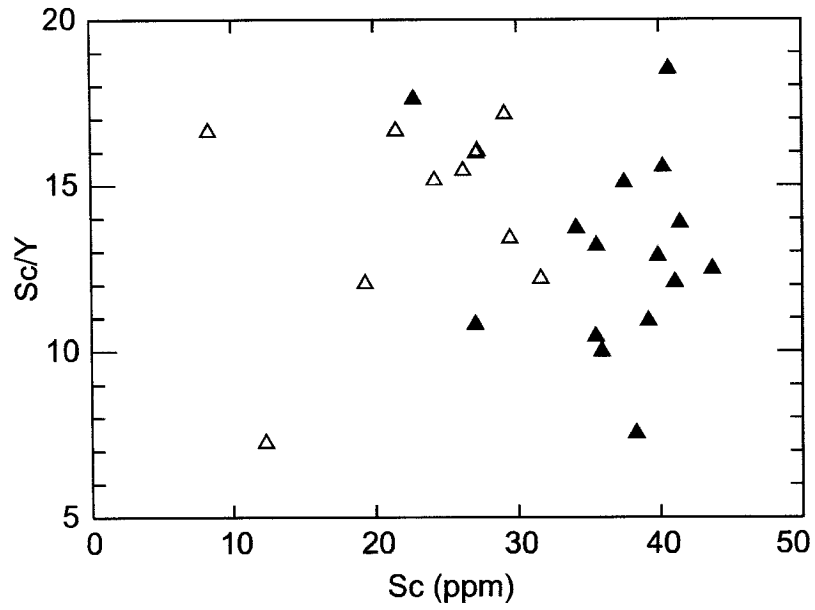
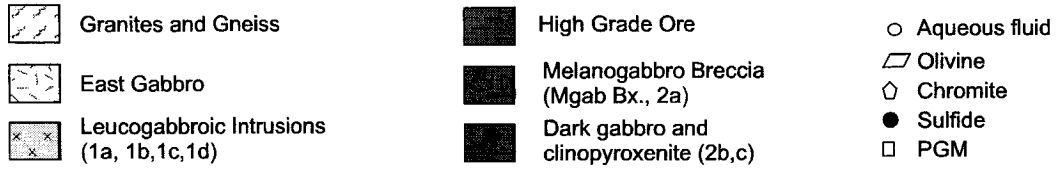
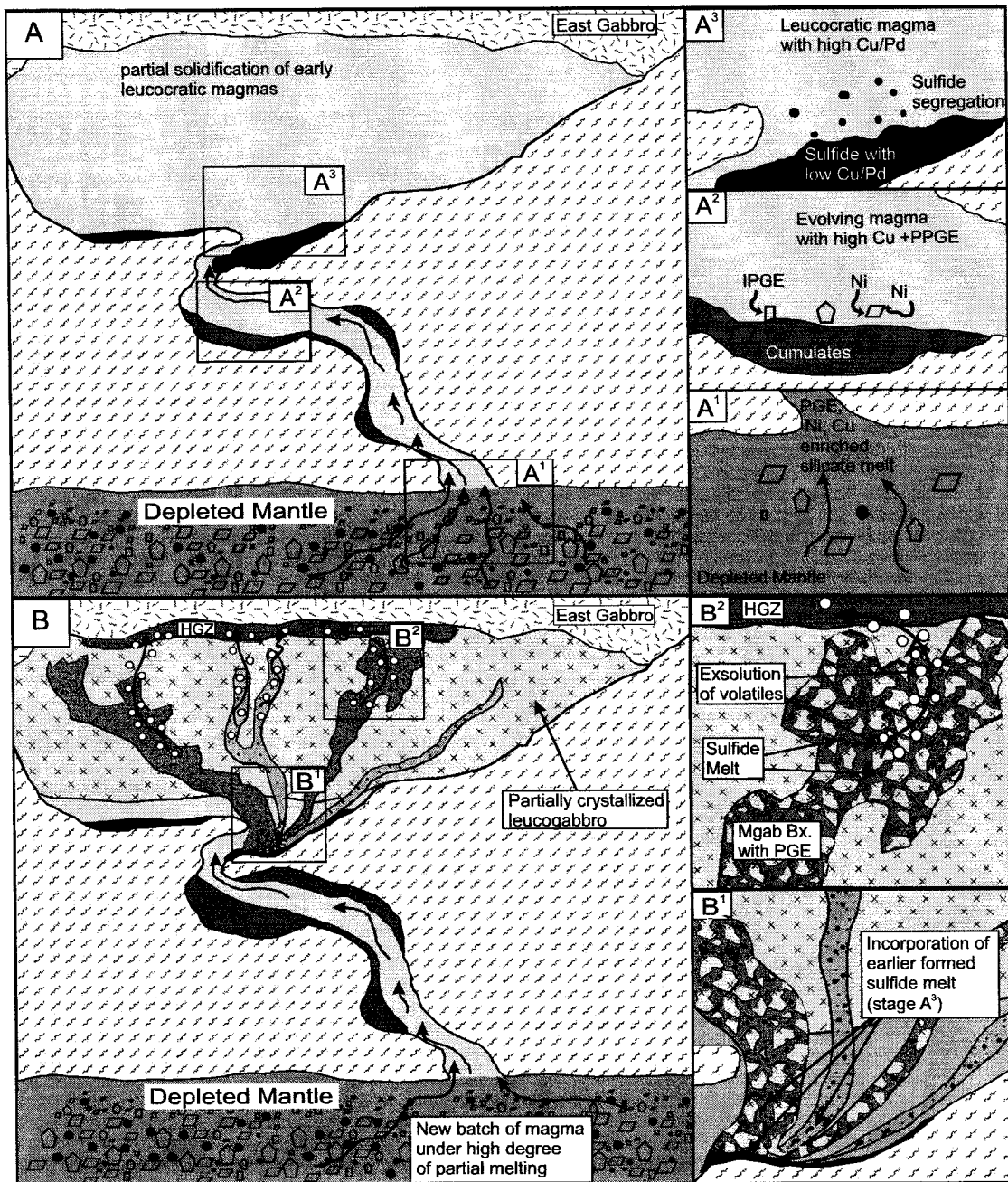


Figure 1-18. Sc versus Sc/Y for samples from the southern Roby Zone. Note that the Sc/Y ratios of the melanocratic rocks are similar to or lower than those of the leucocratic rocks.

Figure 1-19: Schematic model showing the history of mineralization at the southern Roby Zone. Magmas formed by a high degree of partial melting in a depleted mantle source (A1) became enriched in Cu, Pt and Pd through fractional crystallization of olivine, chromite and high-temperature PGM (A2), segregated sulfide melt that had low Cu/Pd ratios along the conduit and the base of the magma chamber (A3), and solidified as the early leucocratic gabbros. A second episode of partial melting in the mantle source produced another batch of fertile magma. As with the early magma, this magma was enriched in Cu, Pt and Pd through fractional crystallization (analogous to Fig. A2). This magma incorporated the earlier sulfide melt and intruded forcefully into the partially crystallized leucocratic rocks (B1), causing brecciation and magma mingling, and solidified as fertile melanocratic gabbro. Aqueous fluids that separated from the melanocratic magma percolated through the cumulates, partially dissolving Pd and concentrating it in the High Grade Ore Zone adjacent to barren East Gabbro (B2).



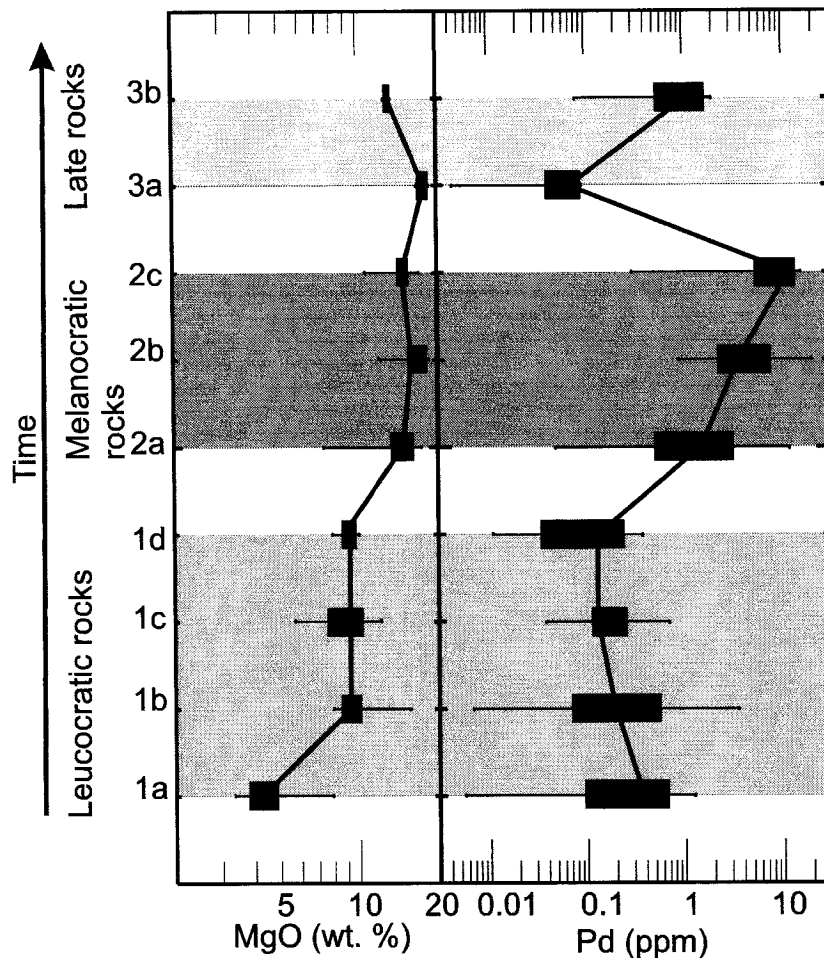


Figure 1-20. Temporal evolution of palladium mineralization at the southern Roby and Twilight Zones, Lac des Iles mine. The concentrations of MgO (wt%) and Pd (ppb) are shown by box-whisker plots where a box is defined by the 1st-quartile and 3rd-quartile values. The total ranges of values are shown as lines and median values of rock types are connected by the thick line. Note the increased MgO and Pd concentrations associated with the sulfide-bearing melanocratic rocks. The numbers on the left side of the diagram correspond to the rock types: 1a = leucogabbro/anorthosite, 1b = varitextured gabbro, 1c = medium-grained light gray gabbro, 1d = medium-grained gabbro, 2a = matrix of melanogabbro breccia, 2b = clinopyroxenite, 2c = dark gabbro, 3a = late clinopyroxenite, and 3b = late gabbro.

Table 1-2. Palladium, platinum, and gold concentrations in various rock types in the southern Roby Zone and Twilight Zone, reported as median, first quartile and third quartile values in ppb.

Rock type	Zone	# of Samples	Palladium			Platinum			Gold		
			median	1st Q'til	3rd Q'til	median	1st Q'til	3rd Q'til	median	1st Q'til	3rd Q'til
Leucocratic rocks	SRZ	55	150	45.9	382	28.6	7.2	55.9	37.5	17.0	103
Melanogabbro (2a)	SRZ	16	1460	554	2830	190	69.7	302	153	70.0	292
Clinopyroxenite(2b)	SRZ	25	3560	2460	6900	402	303	777	441	307	606
Dark Gabbro (2c)	SRZ	6	11700	9800	12300	1400	1090	1490	1150	975	1250
Norite/Leuconorite	TZ	31	184	84.8	1120	36.2	21.8	142	24.0	8.5	92.5
Melanogabbro	TZ	17	8900	267	1270	109	40.6	155	74.0	24.3	142
Melanonorite	TZ	10	3560	1490	4260	449	204	537	282	110	355

CHAPTER 2

Magmatic mineralization and hydrothermal enrichment of the High Grade Zone at the Lac des Iles palladium mine, northern Ontario, Canada.

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Abstract

The economic mineralization of Pd at the Lac des Iles mine occurs in the gabbroic rocks of the Mine Block Intrusion in the 2.69 Ga Lac des Iles Intrusive Complex. The Complex intruded the tonalitic rocks of the Lac des Iles greenstone belt in the Wabigoon Subprovince of the Superior Province of Canada.

We conducted a detailed study on the Pd mineralization in the southern Roby Zone and the Twilight Zone. Sulphide minerals commonly display exsolution textures where pentlandite and chalcopyrite are exsolved from pyrrhotite. Sulphur contents from these zones display positive correlations with the contents of platinum group elements (PGE), Se, and Te, suggesting a magmatic origin of the mineralization where PGE were concentrated in immiscible sulphide melt in the parental magmas. The average ratios of Se/S ($703 \pm 192 \times 10^{-6}$) and Te/S ($192 \pm 104 \times 10^{-6}$) in the two zones are higher than the primitive mantle values of $\sim 300 \times 10^{-6}$ and $\sim 48 \times 10^{-6}$, respectively. The high ratios are consistent with the derivation of their parental magmas from a depleted mantle source.

The High Grade Zone forms a narrow northwest-trending zone in the margin of the Roby Zone, and is hosted by an intensely altered clinopyroxenite/ melanogabbroic unit. It contains two mineral assemblages; millerite + siegenite \pm chalcopyrite \pm pyrite co-existing with hornblende + plagioclase \pm quartz \pm carbonate, and pyrite \pm chalcopyrite with chlorite + actinolite \pm albite \pm quartz \pm carbonate. The ore is high in Pd (mean Pd/Pt ratio of 16.5; max. 25) compared to the southern Roby Zone and Twilight Zone where the Pd/Pt ratios are ~ 8 . It shows positive correlations between Se and Te and between Se and immobile metals, such as Ni and Co. The data suggest a primary magmatic origin of mineralization of the High Grade Zone, but there is substantial scatter on diagrams involving S, such as the plot between S and Se. The evidence suggests that the primary magmatic mineralization was followed by hydrothermal transport of mobile elements. Using the relationships between Se and metals, the ore most likely had 0.8 – 2 ppm Pt

and 8 – 21 ppm Pd during the primary mineralization. The subsequent hydrothermal activity resulted in the enrichment of Pd by up to 40 ppm. The lack of fluid pathways in the High Grade Zone, and the distribution of the zone are consistent with magmatic-hydrothermal activity by aqueous fluids exsolved from the parental magmas of the Roby Zone and High Grade Zone.

Sulphide minerals from the southern Roby Zone, Twilight Zone, and High Grade Zone have similar $\delta^{34}\text{S}$ values, ranging from 0.0 to + 1.5 ‰. The data are consistent with the derivation of S from the mantle. In individual samples from the southern Roby Zone and High Grade Zone, pyrite shows lower $\delta^{34}\text{S}$ than chalcopyrite, suggesting isotopic disequilibrium of S. This likely reflects the crystallization and re-crystallization of sulphide minerals over a wide range of temperatures.

2.1 Introduction

The Lac des Iles mine in northwestern Ontario represents the only primary Pd-producing mine in Canada. The ore is hosted by the Lac des Iles Intrusive Complex in the Lac des Iles greenstone belt in the southern Wabigoon Subprovince of the Superior Province of Canada (Blackburn et al. 1992; Stone et al. 2003);(Fig. 2-1). It belongs to a suite of late Archean mafic-ultramafic plutons in the southern Wabigoon Province close to the Quetico Subprovince (Pye 1968; Sutcliffe 1986).

The Roby Zone, the main ore body at the Lac des Iles mine, displays complicated igneous textures, such as breccias and pegmatites. The High Grade Zone in the Roby Zone is volumetrically small (< 7 vol. %), but of economic importance as it contains approximately 35 % of the Pd in the mine. The rocks in the High Grade Zone are intensely altered with all primary minerals replaced by secondary minerals. In addition, it has high Pd/Pt ratios compared to other zones.

We conducted detailed mapping of the southern Roby Zone and Twilight Zone at scales of 1:60 and 1:120, respectively, and detailed logging of core samples of the High

Grade Zone in the summer of 2002 and 2003 (Hinchey et al. 2003). The southern Roby Zone was the only remaining portion of the main Roby Zone exposed on the surface in 2003 (Fig. 2-3). This field work, combined with chemical analyses, demonstrates a clear relationship between the mineralization and rock types (Hinchey et al. 2003). This paper focuses on the sulphide petrology and S, Se, and Te contents of the mineralization and discusses the origin of mineralization, especially the High Grade Zone.

2.2 The Lac des Iles Intrusive Complex

The Lac des Iles Intrusive Complex intruded tonalitic rocks in the Wabigoon Subprovince at 2692 \pm 4/-2 Ma (Blackburn et al. 1992). It is divided into three main bodies (Lavigne and Michaud 2001) consisting of (1) the North Lac des Iles ultramafic intrusions, centered on the lake, (2) the Mine Block intrusion, consisting of lithologically and texturally complicated gabbroic rocks, and (3) the massive hornblende gabbro of the Camp Lake intrusion (Fig. 2-2). The rocks were intruded by diabase dikes and sills, ranging from 2120 to 1140 Ma (Blackburn et al. 1992; Buchan and Ernst 2004). The gabbroic rocks of the Mine Block intrusion (Figs. 2-2 and 2-3) range from anorthosite to clinopyroxenite, and they contain all the economic PGE mineralization discovered to date including the Roby, Twilight, and Baker Zones.

The Twilight Zone occurs east of the main Roby Zone and is separated by ~ 50 m of the barren East Gabbro. The High Grade Zone, 15-25 m wide and 400 m long, is hosted by a highly altered pyroxenitic/ melanogabbro unit on the eastern margin of the main Roby Zone (Fig. 2-3). The high Pd tenors are restricted to the High Grade Zone, but not all rocks in the zone are evenly mineralized (Lavigne and Michaud 2001). The pale green pyroxenitic/melanogabbro unit is lithologically distinct and bound by the barren East Gabbro to the east and the melanogabbro breccia of the main Roby Zone to the west.

2.3 Sampling and Analytical Methods

Samples representing various rock types were collected following detailed mapping in the southern Roby and Twilight Zones. Samples of the High Grade Zone were

collected from the Phase III open pit and from diamond drill-core. Mineral compositions were determined using a Camebax MBX electron microprobe by wavelength dispersive X-ray analysis at Carleton University. Operating conditions were 20 kV accelerating potential with a beam current of 35 nA for sulphide minerals and 15 kV and 20 nA for silicate minerals. Counting times were 15-40 sec or 40,000 accumulated counts for each element. Standards for the calibration of sulphide analysis were a synthetic troilite for Fe and S, cobalt metal for Co, natural millerite for Ni, synthetic MnS for Mn, natural chalcopyrite for Cu, silver metal for Ag, and natural niccolite for As. A suite of well characterized natural and synthetic minerals and compounds were used as calibration standards for silicate analysis. The raw X-ray data were converted to weight % by the Cameca PAP matrix correction program. Analyses were accurate to 1-2% relative for major elements, and 3-5 % for minor elements (i.e. < 1 wt. %).

Sulphur contents were determined using an elemental analyzer (Carlo Erba 1110) at the University of Ottawa. Precision and accuracy, as determined through duplicate analyses and the analysis of reference materials, are ± 5.4 % and ± 1.4 % respectively. Blank contribution to S was less than the detection limit (~ 0.001 wt. %); therefore the contribution was safely ignored. Nickel contents were determined from fused disks using a Philips PW 2400 X-ray fluorescence spectrometer at the University of Ottawa. Precision and accuracy were ± 9.2 % and ± 4 % respectively. Platinum and Pd were determined by fire assay followed by the use of an inductively-coupled plasma mass spectrometer (ICP-MS) on 30-g sample splits at Acme Analytical Laboratories Ltd. in Vancouver, with detection limits of 0.1 and 0.5 ppb, respectively. Precision and accuracy of Pt and Pd, as determined through duplicate analyses of a reference material are ± 0.61 % and ± 2.03 % for Pt, and ± 0.49 % and ± 4.68 % for Pd, respectively. Concentrations of Se, Te, and Cu were determined after aqua regia digestion followed by ICP-MS at Acme Analytical Laboratories Ltd. in Vancouver. Precision and accuracy of Se and Te, based upon duplicate analysis of an internal reference material, are 0.00% and 0.00% for Se,

and 1.31 % and 3.13 % for Te, respectively. Representative chemical compositions are given in Table 1.

Sulphur isotope analyses were conducted at the University of Ottawa on hand-picked sulphide separates. The purity of > 99 % was checked under a binocular microscope before isotope analysis. The sample mixed with WO_3 was placed in a tin capsule and combusted at 1800°C to release SO_2 gas. The gas was purified with the VarioEL III elemental analyzer for the isotopic ratio measurements using a FinniganMat Delta^{Plus} mass spectrometer. A total of 12 reference materials were run during the analysis. Duplicate analysis of five samples show the precision is ± 0.24 ‰. Results are given in Table 2.

2.4 Results and Discussion

2.4.1 Petrography and mineralogy of ore zones

The mineralized rocks in the southern Roby Zone contain subhedral to euhedral, cumulus crystals of clinopyroxene, plagioclase and minor orthopyroxene with intercumulus material consisting of the same minerals plus minor biotite, magnetite, ilmenite, quartz, and 1-5 vol. % of sulphides. The rocks consist of: (1) medium-grained meso- to melano-gabbro breccia (named based upon the matrix composition), (2) medium to relatively coarse-grained clinopyroxenite, and (3) medium-grained, dark gabbro. All rocks are variably altered with rare relict pyroxenes and plagioclase. Pyroxene is commonly replaced by a mixture of hornblende + actinolite + chlorite, whereas plagioclase is mostly sericitized.

The mineralized rocks at Twilight Zone are similar to those in the southern Roby Zone. They also show orthocumulate texture with subhedral to euhedral cumulus orthopyroxene (3-10 mm; 70-95 vol. %), and intercumulus minerals consisting of plagioclase (5 – 30 vol. %), clinopyroxene (< 10 vol. %), minor biotite, blebby sulphides and oxides (2-8 vol. %). The sequence of intrusions in the Twilight Zone is similar to that in the southern Roby Zone and the early leucocratic rocks are essentially barren.

Alteration is not as intense and pervasive as that of the Roby Zone. It includes the variable replacement of orthopyroxene by tremolite + talc + magnetite, replacement of clinopyroxene by actinolite, and plagioclase by sericite.

The High Grade Zone consists of intensely altered medium- to coarse-grained melanogabbro and pyroxenite. Primary minerals are entirely replaced by actinolite + hornblende + chlorite + sericite \pm talc, and \pm calcite. Blue quartz, < 1 cm in size, is common. Sulphide minerals, up to 10 vol. %, are dominated by pyrite, millerite, siegenite, and chalcopyrite, with lesser amounts of pyrrhotite and pentlandite.

2.4.2 Sulphide and silicate mineral assemblages

The sulphide minerals in the southern Roby Zone and Twilight Zone most likely formed as monosulphide solid solution, which upon cooling crystallized to pyrrhotite, pentlandite and chalcopyrite. Granular and flame-like pentlandite and blebby chalcopyrite are common in pyrrhotite (Figs. 2-4A, 2-4B, and 2-4C) and such textures are interpreted as the exsolution products (Craig and Vaughan 1994). Minor pyrite associated with these minerals may have been formed upon cooling (Fig. 2-4A). These minerals define an early sulphide assemblage of pyrrhotite + pentlandite + chalcopyrite \pm pyrite. In the southern Roby Zone this assemblage is associated with an assemblage of clinopyroxene + plagioclase \pm orthopyroxene. In the Twilight Zone, the same assemblage without pyrite is associated with orthopyroxene + plagioclase \pm clinopyroxene. These sulphide and silicate minerals represent the high temperature assemblages in the deposit.

The Twilight Zone does not show significant alteration (Fig. 2-5B), and the rocks contain partially sericitized plagioclase and a mixture of amphiboles + talc + magnetite partially replacing orthopyroxene. Rare quartz is associated with sulphides.

In contrast, the southern Roby Zone is variably altered. Relatively high-temperature alteration, which most likely took place shortly after the solidification, produced an assemblage of hornblende + sericite \pm epidote (Fig. 2-5A). Some rocks do not contain hornblende and are dominated by actinolite and chlorite, and the assemblage

suggests that they most likely formed at temperatures comparable to those for greenschist facies conditions. Minor quartz and carbonate are common in highly altered rocks. Alteration mineral assemblages suggest that the rocks have undergone alteration at varying temperatures. Pyrite occurs as anhedral blebs and overgrowths on pyrrhotite and the abundance of pyrite (Fig. 2-4B) increases with increasing degrees of silicate alteration. The evidence suggests that pyrite mostly formed during the hydrothermal alteration of silicate minerals either by sulphidation of earlier formed pyrrhotite or precipitation from hydrothermal fluids. Chalcopyrite occurs along the cleavage planes of actinolite, suggesting the mobility of Cu even at relatively low temperatures. However, Cu versus Ni, S, and Se display well-defined positive correlations, suggesting that the mobility of copper was limited.

2.4.3 High Grade Zone

The High Grade Zone represents the most intensely altered rocks in the deposit where magmatic minerals are rarely present (Figs. 2-5C and 2-5D). As in the southern Roby Zone, the High Grade Zone has undergone continuous alteration at varying temperatures whereby earlier alteration minerals are overprinted by later low-temperature alteration products. Sulphide minerals define two assemblages and are associated with two different silicate alteration assemblages. Assemblage A is dominated by millerite + siegenite \pm chalcopyrite (Figs. 2-4D and 2-4E) \pm pyrite. Minor pentlandite and galena are also rarely observed. Siegenite is a linnaeite group mineral with an ideal formula of $\text{Ni}_{2.25}\text{Co}_{0.75}\text{S}_4$. Siegenite in our samples contains Fe, with an average formula of $\text{Ni}_{2.25}(\text{Fe}_{0.11}\text{Co}_{0.64})\text{S}_4$ and forms euhedral crystals and anhedral blebs in millerite (Figs. 2-4d and 2-4e). Chalcopyrite occurs as anhedral blebs and is commonly associated with millerite and siegenite (Fig. 2-4E). Chalcopyrite also forms cross-hatches with pentlandite and millerite, indicating that chalcopyrite filled the fractures of the latter minerals. The evidence suggests that chalcopyrite formed at high and low temperatures.

The sulphide assemblage A is associated with the silicate assemblage of hornblende + sericite \pm albite \pm quartz. The quartz has distinct blue luminescence and is commonly in direct contact with sulphide minerals (Figs. 2-5C).

Assemblage B predominantly consists of anhedral to subhedral pyrite grains with variable chalcopyrite. Small inclusions of pyrrhotite and pentlandite (Fig. 2-4F) are common in pyrite. This is associated with the assemblage of chlorite + actinolite (Fig. 2-5D) + sericite \pm albite \pm quartz \pm epidote. The occurrence of chlorite + actinolite \pm epidote + albite (An_2) suggests that the alteration took place at \sim 300-400°C. The anorthite component of plagioclase varies from 2 to 55 in the High Grade Zone and from 55 to 67 for melanocratic rocks at the southern Roby Zone and Twilight Zone, suggesting that the mineralized hydrothermal activity took place over a wide range of temperatures.

2.4.4 Sulphur isotope compositions

Sulphur isotopic compositions for sixteen separates (pyrite, pyrrhotite, chalcopyrite, and siegenite) from the southern Roby Zone, Twilight Zone, and High Grade Zone are given in Table 2. All samples have $\delta^{34}S$ ranging from 0.0 to + 1.5, similar to the meteoritic value of 0 ‰ (Faure 1986), suggesting the negligible contribution of S from the country rocks. This is consistent with the magmatic origin of the parental magmas and S.

Under equilibrium conditions, pyrite is enriched in ^{34}S compared to other sulphides (Faure 1986). However, pyrite shows comparable or lower $\delta^{34}S$ than co-existing chalcopyrite, suggesting that sulphide minerals are not in isotopic equilibrium (Table 2). The isotopic disequilibrium suggests that the minerals formed at different stages. This is consistent with their formation at a wide range of temperatures.

2.4.5 Metal, sulphur, tellurium, and selenium concentrations in the southern Roby and Twilight Zones

Sulphur contents from the southern Roby Zone and Twilight Zone show positive correlations with the contents of Ni, Pt, and Pd+Pt, (Figs. 2-6 and 2-8) and Cu (not shown). In conjunction with the observed magmatic sulphides in the mineralized gabbro/gabbro-noritic rocks, the data suggest that magmatic mineralization with immiscible separation of a sulphide liquid from a silicate melt concentrated metals in these zones.

Sulphur, Se and Te have similar chemical properties and are mainly hosted by sulphide minerals. The samples from the southern Roby Zone and Twilight Zone show well-defined positive correlations between S and Se, and between S and Te with an average Se/S ratio of $703 \pm 192 (1\sigma) \times 10^{-6}$ (Fig. 2-7) and Te/S ratio of $192 \pm 104 (1\sigma) \times 10^{-6}$ (Fig. 2-9). These positive correlations are consistent with the primary magmatic mineralization in cogenetic parental magmas.

The ratios of Se/S and Te/S are, however, slightly higher than the primitive mantle values of 300×10^{-6} and 48×10^{-6} , respectively (McDonough and Sun 1995) (Figs. 2-7 and 2-9). The high ratios may be explained by the nature of the source mantle or post-depositional processes, such as metamorphism and hydrothermal alteration. We discount the latter possibilities because of good correlations between S, Se, and Te. The solubility's of these elements in aqueous fluids are different and it is too fortuitous to yield good correlations during alteration and metamorphism. Furthermore, the regional metamorphic grades in the area are relatively low, up to greenschist facies (Blackburn et al. 1992; Pettigrew and Hattori 2003). This is supported by the presence of pristine clinopyroxene and orthopyroxene in the Lac des Iles Intrusive Complex, especially in the northern part of the complex and in the gabbro-norites of the Mine Block intrusion.

We therefore consider that the ratios of Se/S and Te/S reflect those of the parental magmas and most likely the source mantle. Assimilation of sedimentary rocks could

modify the ratios of the parental magmas because Se/S ratios of sedimentary rocks are commonly different from those of igneous rocks (Stanton 1972; Eckstrand et al. 1989; Hulbert 1997). This possibility is discounted because there is no evidence for assimilation of country rocks. In addition, there is no difference in Se/S and Te/S ratios among melanocratic and less melanocratic rocks in the southern Roby and Twilight Zones. We suggest that these ratios reflect those of the source mantle.

The ratios of Se/S and Te/S of the mantle vary during the melt extraction because S is preferentially incorporated into partial melt (Garuti et al. 1984; Peach et al. 1990; Hattori et al. 2002). Therefore, high Se/S, Te/S and Te/Se ratios of the mineralized rocks compared to the primitive mantle values are consistent with the parental magmas being derived from a depleted mantle source. This is similar to the process proposal by Hamlyn et al. (1985) that fertile magmas formed by second partial melting in the mantle.

Lorand et al. (2003) suggested 23-33 ppb Se and 70-120 ppm S in the primitive mantle, which are much lower than the estimates of 75 ppb Se and 250 ppm S by McDonough and Sun (1995). Their values yield a range in Se/S from 191×10^{-6} to 471×10^{-6} for the primitive mantle. However, the Se/S ratios of the southern Roby Zone and Twilight Zone are still higher than the primitive mantle values by Lorand et al. (2003).

2.4.6 Origin of the High Grade Zone

The ratios of Se/S from the High Grade Zone samples show a relatively large variation compared to those from the southern Roby Zone and Twilight Zone, although all values are still in the range for magmatic deposits in the world (Fig. 2-12). The range in values is much narrower than that for hydrothermal deposits, such as volcanic massive sulphide deposits (Yamamoto et al. 1968, 1984; Fouquet et al. 1996) and metamorphosed magmatic deposits (Maire and Barnes 1999).

The High Grade Zone samples show a good correlation between Se and Te ($r = 0.89$), and the correlation line overlaps with that for the samples from the southern

Roby Zone and Twilight Zone ($r=0.899$, calculated using all data) (Fig. 2-9). The data are consistent with the magmatic mineralization, but the High Grade Zone samples show scatters on the diagrams of S vs Se and S vs Te (Figs. 2-7 and 2-9). Selenium and Te are less mobile during hydrothermal alteration than S (Howard 1977). Therefore, the data are explained by primary magmatic mineralization followed by the transport of fluid-soluble elements.

The samples from the High Grade Zone commonly display high, but variable Pd/Pt ratios (mean 16.5, up to 25) compared to the southern Roby Zone and Twilight Zone (~ 8) (Fig. 2-10). In addition, the High Grade Zone samples show scatter on the diagrams of Pd vs Se and Pt vs Se, suggesting that Pd and Pt were also mobile. Using the linear relationship between Se and metals in the southern Roby Zone and Twilight Zone, the primary concentrations in the High Grade Zone are estimated to be 0.8 - 2 ppm Pt and 8 - 21 ppm Pd. The comparison between the observed and the estimated values suggests that Pd tenor increased up to 40 ppm during the hydrothermal activity. Platinum was less mobile with no significant upgrade.

The High Grade Zone is confined to a lenticular, highly altered portion of a pyroxenitic/melanogabbroic unit (Fig. 2-3). The Zone is bound by relatively Pd-rich (2.5 to 5 ppm Pd) breccia ore of the main Roby Zone (Fig. 12 of Lavigne and Michaud 2001) and barren East Gabbro. The pyroxenitic/melanogabbroic unit extends along the strike of the High Grade Zone, and the rocks of the unit outside the High Grade Zone do not carry high Pd (Fig. 12 of Lavigne and Michaud 2001; Fig. 2-6). The distribution of the High Grade Zone and the intensity of hydrothermal alteration in the Zone suggest the localized hydrothermal activity. The East Gabbro appears to have acted as a barrier to the mineralized hydrothermal activity. This hydrothermal activity resulted in minor enrichment of Pd in the margins of East Gabbro (Fig. 2-11; also see Fig. 12 of Lavigne and Michaud 2001). Furthermore, the East Gabbro typically does not show pervasive alteration, but the rocks adjacent to the High Grade Zone are intensely altered and

bleached.

Our proposed interpretation is supported by the mineralogy of the High Grade Zone. Unlike the southern Roby and Twilight Zones, the dominant sulphide minerals are pyrite, millerite, siegenite, and chalcopyrite, and they locally occur along cleavages and grain boundaries of actinolite. Siegenite and millerite are common in hydrothermal deposits (Ramdor 1980; Craig and Vaughan 1994). Well-known occurrences of siegenite are associated with the Mississippi Valley-type mineralization in the Viburnum Trend in southeastern Missouri (Le Font 1984), and millerite is common in Ni deposits that have undergone low-temperature alteration (e.g. Barnes and Hill 2000). Furthermore, blue quartz is common in close spatial association with sulphides.

This is in accord with the earlier workers who suggested a hydrothermal component of the mineralization based on the intense silicate alteration (Watkinson and Dunning 1979; Macdonald 1988; Lavigne and Michaud 2001), the occurrence of platinum group minerals with As, Bi and Te, and the spatial association of platinum group minerals with secondary silicates and pyrite (Talkington and Watkinson 1984).

Breccias and pegmatites, that contain minor quartz and carbonate, are ubiquitous in the southern Roby Zone and they are associated with the melanocratic units that intruded after leucocratic units (Hinchey et al. 2003). The evidence suggests that the parental magmas of late melanocratic units were volatile-rich and that aqueous fluids were likely released during the solidification of melanocratic units. It is likely that the parental magmas for the clinopyroxenitic rocks hosting the High Grade Zone were also fluid-rich and released aqueous fluids during the solidification. The aqueous fluids from these mafic magmas percolated through the rocks, resulting in the alteration of primary minerals and transportation of mobile metals. The fluids stewed near the impermeable East Gabbro, depositing the metals carried from within and elsewhere in the mineralizing system.

During the hydrothermal activity, silicate and sulphide minerals formed at high

temperatures were no longer stable and were replaced by low-temperature minerals. Fluid-soluble elements were locally depleted and enriched. Rocks with low and high Pd compared to base metals suggest Pd was mobile. High mobility of Pd compared to Pt is consistent with experimental work indicating that Pd is the most mobile PGE (Sassani and Shock 1998; Wood 2002).

2.5 Conclusion

1) Mineralized rocks in the southern Roby and Twilight Zones show well-defined positive correlations between Se, S, Te, and metals. The positive correlations suggest that the mineralization is magmatic whereby immiscible sulphide melts concentrated precious metals in the parental magmas.

2) The values of Se/S and Te/Se for the Lac des Iles ore are higher than the values of the primitive mantle and they are consistent with the origin of parental magmas from a depleted mantle.

3) The High Grade Zone on the margin of the Roby Zone shows intense alteration of silicate and sulphide minerals and high Pd/Pt ratios. Sulphide minerals in the High Grade Zone are dominated by low-temperature minerals, such as pyrite, siegenite, and millerite. The ore shows good positive correlations between less mobile elements, such as Ni, Se and Te, and the correlations overlap with those for the southern Roby Zone and Twilight Zone, but it shows wide scatters on the plots for mobile elements, including Pd. Our data suggest that primary magmatic mineralization was followed by hydrothermal activity, which resulted in the enrichment of Pd. The correlations of metals suggest that the rocks had 0.8-2 ppm Pt and 8-21 ppm Pd during the primary mineralization and upgraded to a maximum of 48 ppm Pd during the hydrothermal activity. We propose that the mineralized aqueous fluids likely originated from fertile, mafic magmas in the Roby Zone and High Grade Zone.

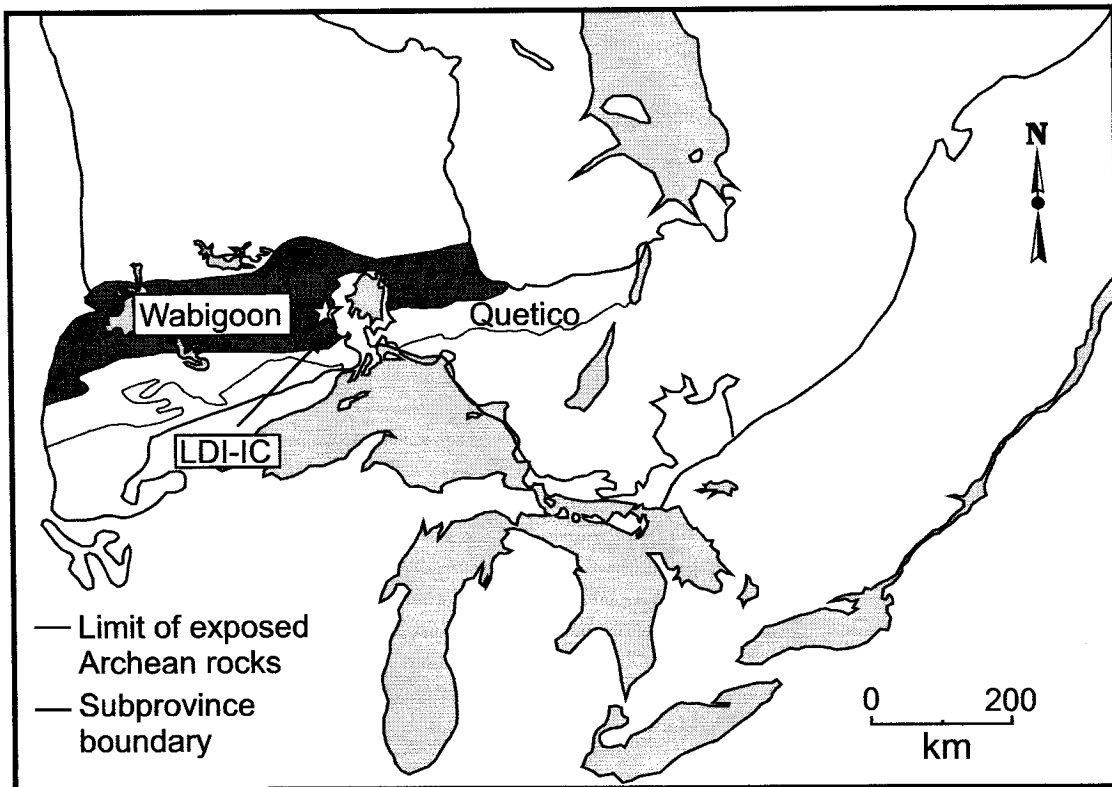


Figure 2-1. Simplified map of the Superior Province illustrating the locations of Wabigoon Subprovince and the Lac des Iles Intrusive Complex (modified after Card and Ciesielski 1986).

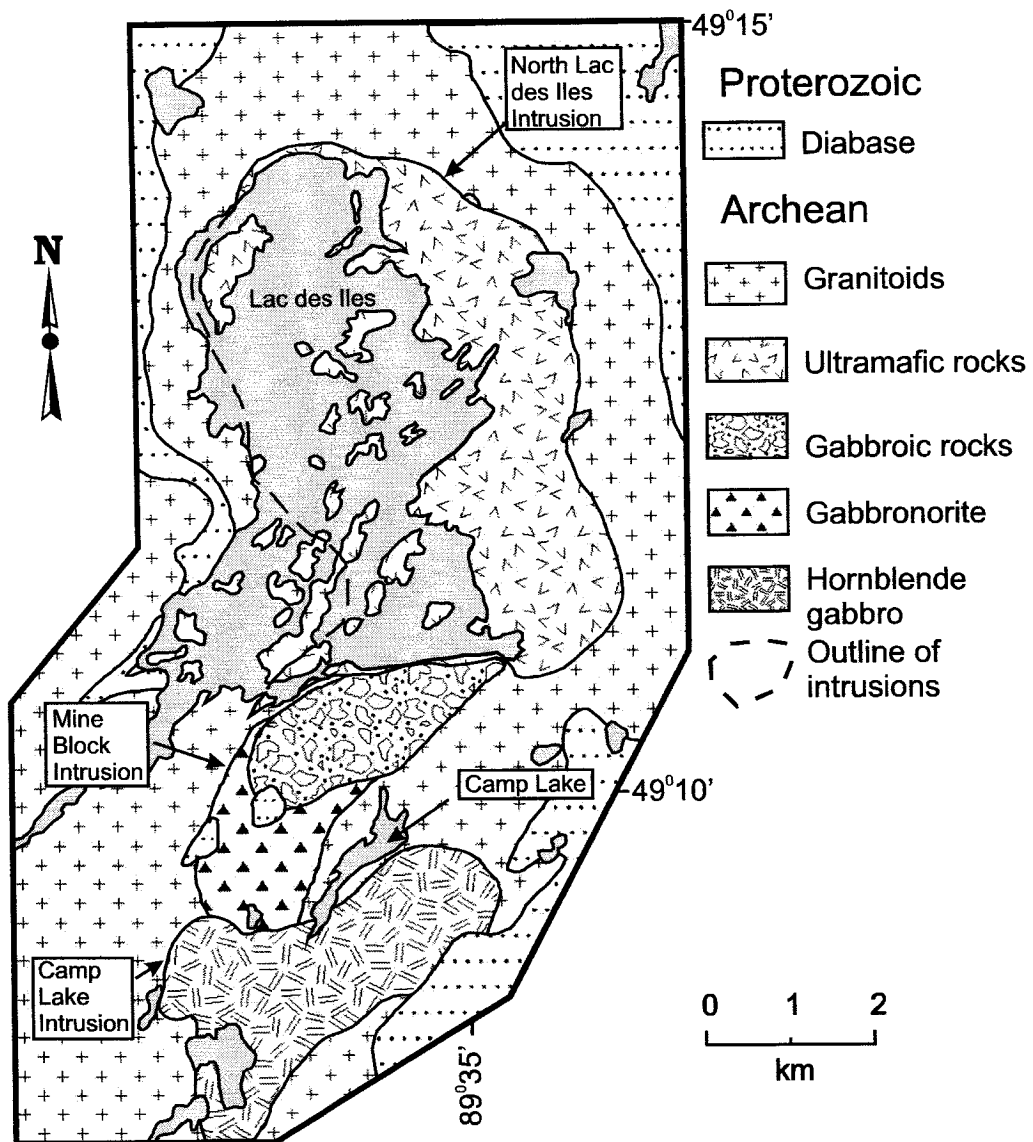


Figure 2-2. Simplified geological map of the Lac des Iles Intrusive Complex (modified after Sutcliffe et al. 1989).

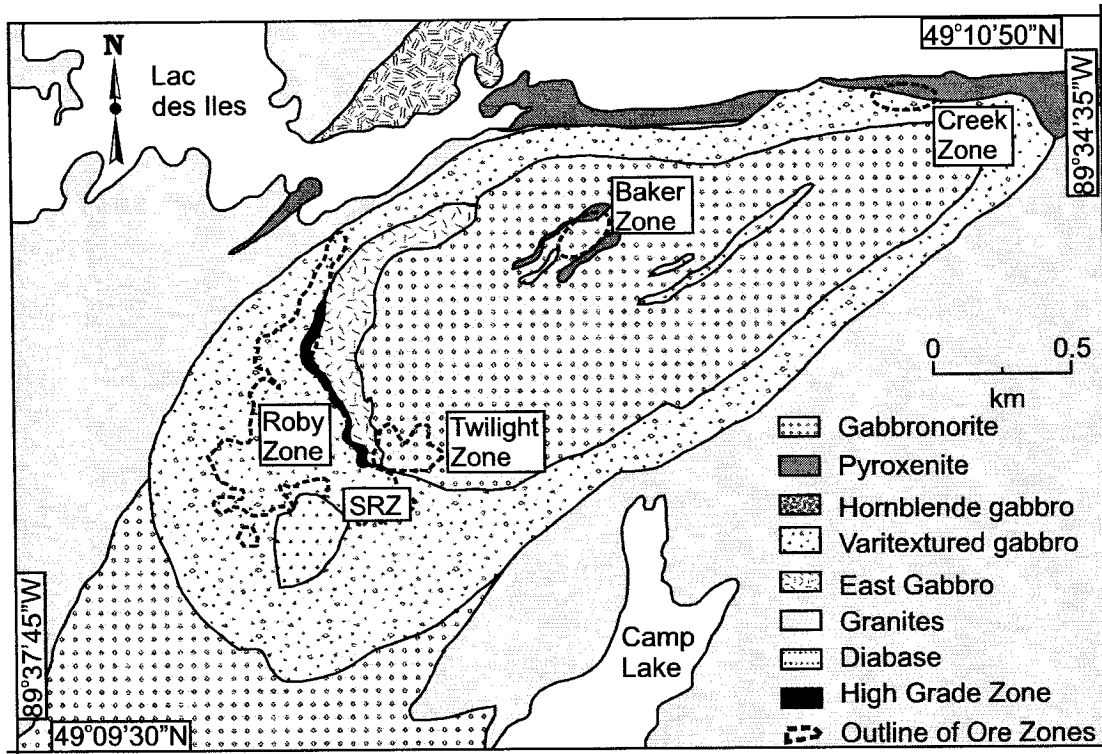
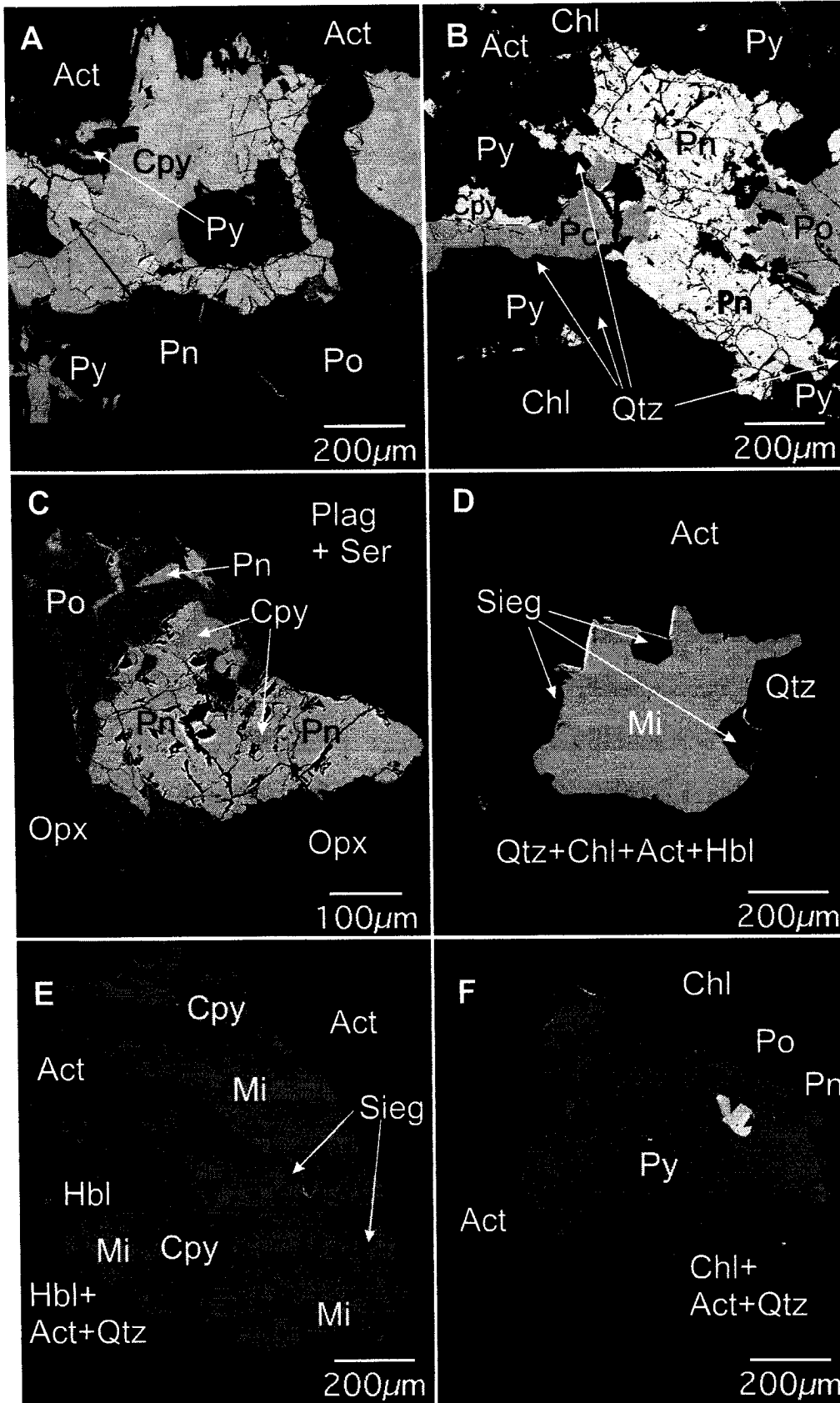


Figure 2-3. Simplified geological map of the Mine Block Intrusion of the Lac des Iles Intrusive Complex illustrating the locations of the southern Roby, Twilight, and High Grade Zones. Also shown are the East Gabbro and other mineralized zones in the Mine Block Intrusion (modified after Sutcliffe and Sweeney 1986).

Figure 2-4. Back-scattered electron images showing representative textures of sulphide minerals: (A) primary magmatic sulphide bleb consisting of pentlandite (Pn) and chalcopyrite (Cpy) exsolved from pyrrhotite (Po). Note small grains of pyrite (Py) in pyrrhotite. The sulphide bleb is surrounded by aggregates of actinolite (Act) replacing clinopyroxene (Sample JH-02-143, southern Roby Zone); (B) magmatic sulphide, consisting of a mixture of Po, Pn, and Cpy, rimmed by Py. The sulphide minerals are hosted by a mixture of chlorite (Chl)+ Act that replace clinopyroxene. Note the small grains of quartz (Qtz) in the sulphide aggregate (Sample JH-02-138); (C) Magmatic sulphide bleb from the Twilight Zone consisting of coarse granular Pn and Cpy exsolved from Po. Note that orthopyroxene (Opx) is unaltered whereas plagioclase (Plag) is altered to contain sericite (Ser). (Sample JH-02-173); (D) sulphide assemblage A in the High Grade Zone with euhedral crystals of siegenite (Sieg) in the rim of millerite (Mi). The sulphide minerals are surrounded by Act + Hbl + Chl+ Qtz (Sample JHC-03-070); (E) sulphide assemblage A in the High Grade Zone. Mi contains inclusions of blebby Sieg and Cpy. Note sulphides (dominantly millerite) along cleavages and grain boundaries of actinolite in the upper left. Alteration is characterized by Act + Hbl after clinopyroxene. Note the occurrence of Qtz adjacent to sulphide. (Sample JHC-03-070); (F) sulphide assemblage B from the High Grade Zone consisting of a large sub-anhedral pyrite (Py) with small inclusions of blebby pyrrhotite (Po) and pentlandite (Pn). Silicate alteration is intense and is dominated by chloritization of clinopyroxene. (Sample JH-02-SZ2).



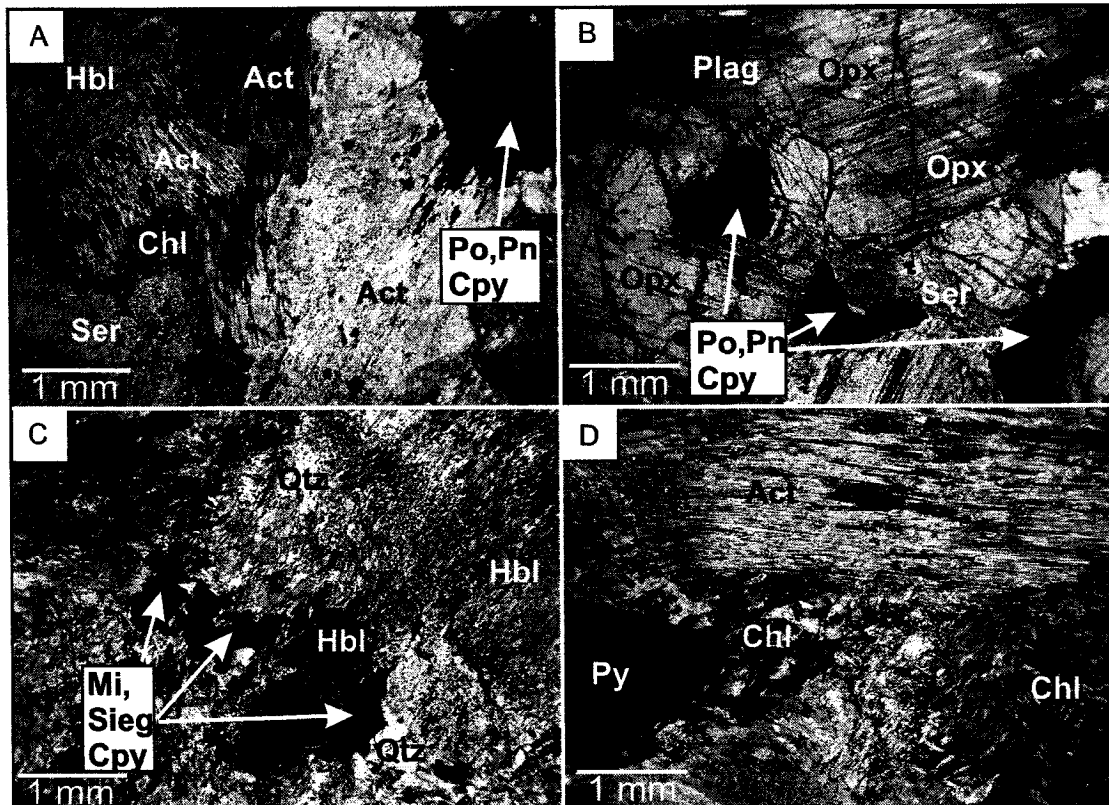


Figure 2-5: Representative photomicrographs of mineralized zones: (A) intense silicate alteration of dark gabbro at the southern Roby Zone with Act + hornblende (Hbl) + Chl replacing clinopyroxene and sericite (Ser) replacing plagioclase. The opaque minerals consist of pyrrhotite (Po) with exsolved blebs of Pn and Cpy. Note the presence of chalcopyrite along cleavage planes of actinolite. (Sample JH-02-146). (B) Mineralized melanonorite at the Twilight Zone showing minor Ser in plagioclase. Note the orthopyroxene crystal enclosing magmatic sulphides that consist of Pn and Cpy exsolved from pyrrhotite (Po) (Sample JH-02-170). (C) Intense alteration associated with the High Grade Zone. Note the abundant secondary Hbl and Qtz. The opaque blebs are Mi + Sieg + Cpy (Sample JHC-03-070). (D) Intense alteration associated with the High Grade Zone. Note the abundant Chl and minor Act replacing clinopyroxene. Opaque mineral is pyrite (Sample JH-02-SZ2).

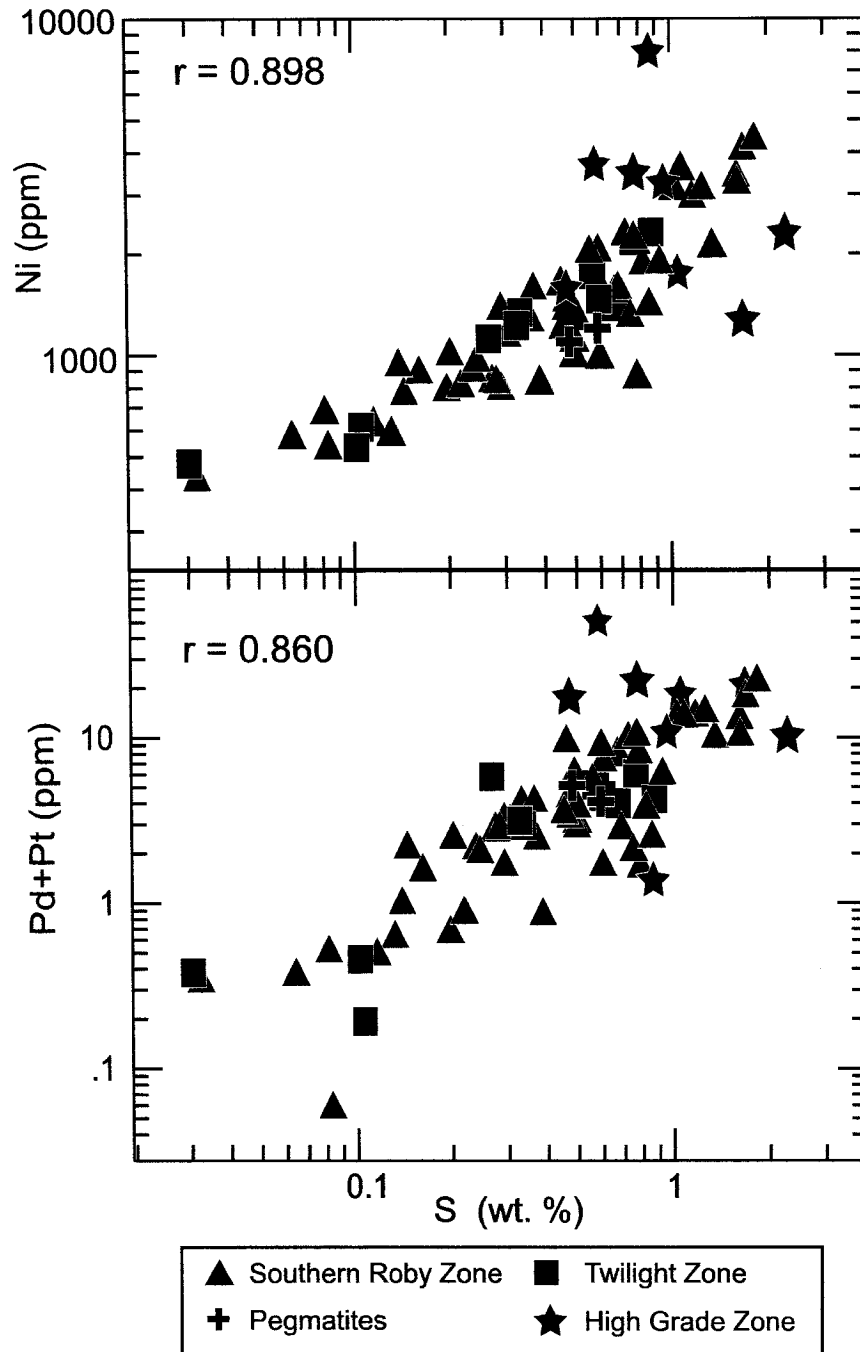


Figure 2-6. Bivariate plots of S (wt.%) versus Ni (ppm) and Pd+Pt (ppm). Note the good positive correlations between Ni and S ($r = 0.898$) and (Pd+Pt) and S ($r = 0.86$) for samples from southern Roby Zone and Twilight Zone and the scatter for samples from High Grade Zone. Note that the symbol legend is identical to that for Figures 2-6 to 2-10.

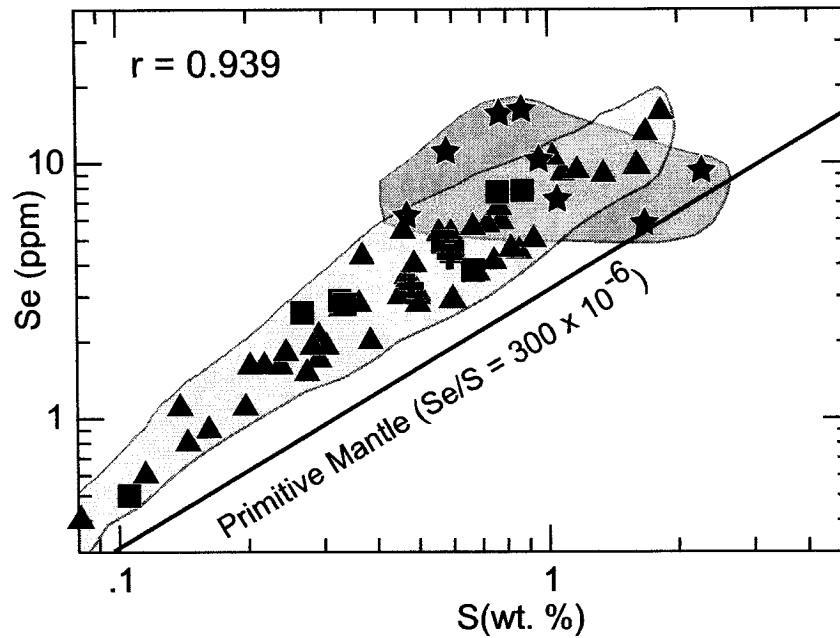


Figure 2-7. Bivariate plot of S (wt.%) versus Se (ppm). Note the well-defined correlation for southern Roby Zone and Twilight Zone ($r = 0.989$) and the scatter for the High Grade Zone samples. All samples plot above the ratio of the primitive mantle value (McDonough and Sun 1995).

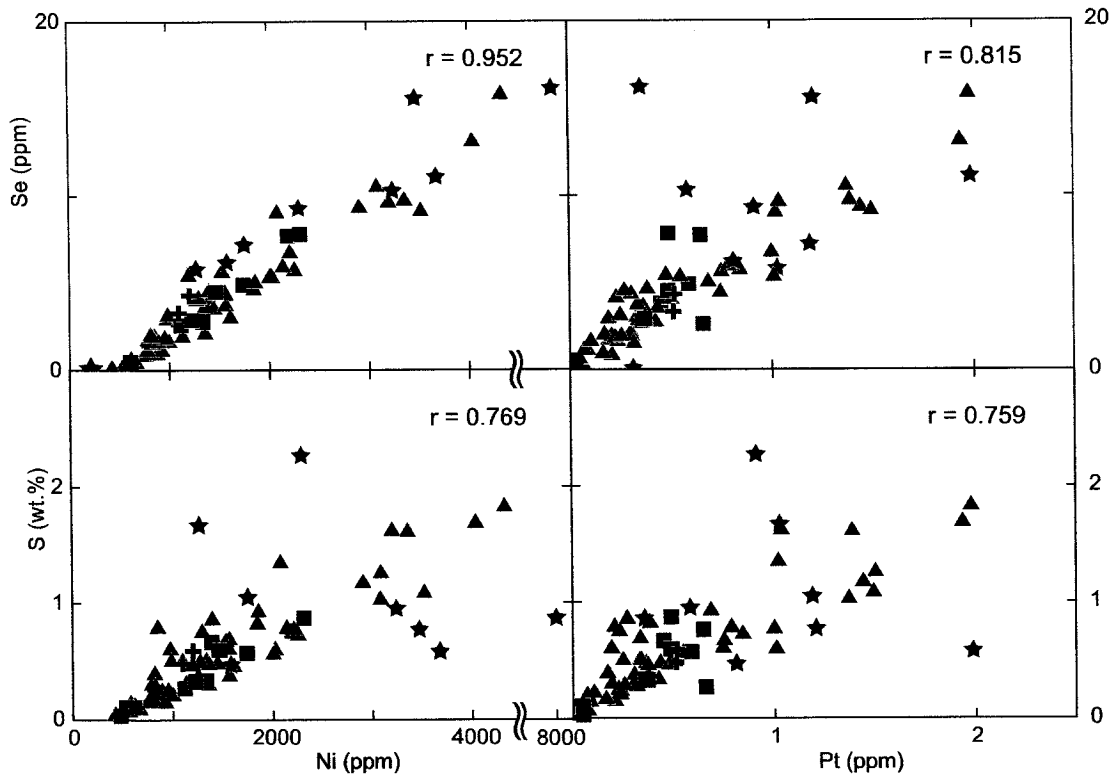


Figure 2-8. Bivariate plots of Ni (ppm) and Pt (ppm) versus S (wt.%) and Se (ppm). Note good correlations between metals and Se compared with the correlations between metals and S. The correlation coefficients (r) are calculated for all samples.

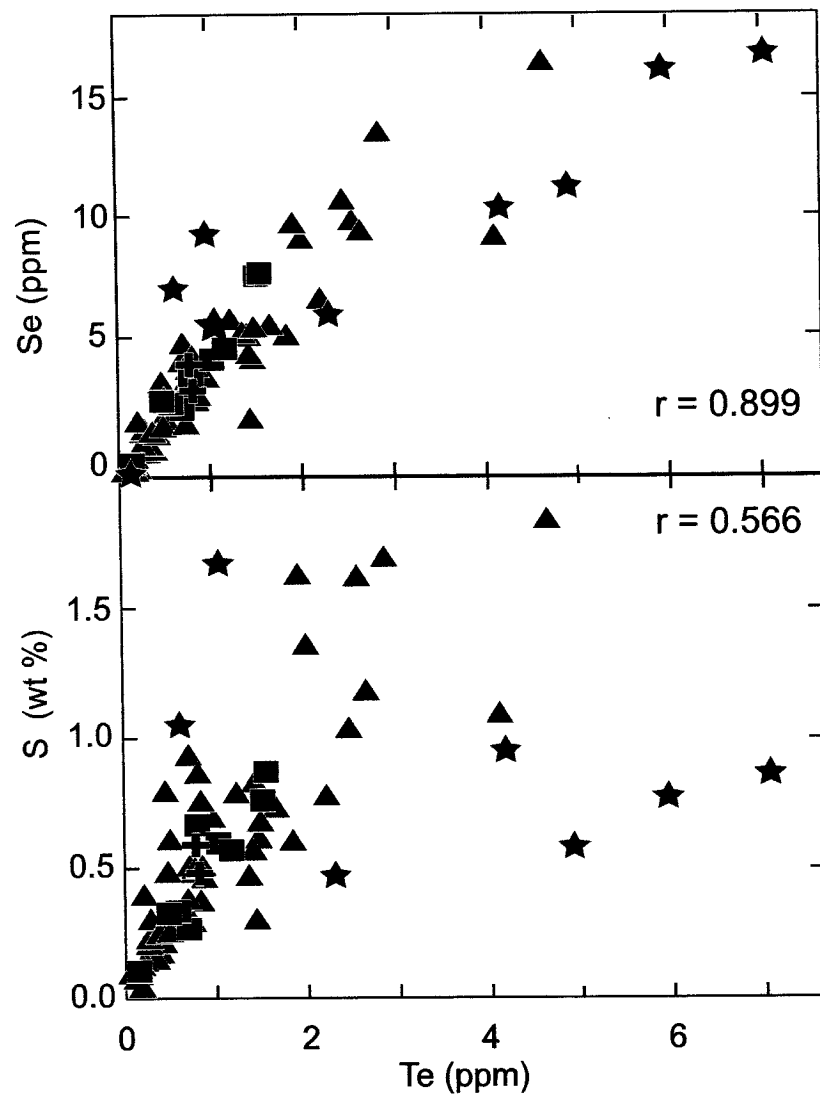


Figure 2-9. Bivariate plot of Te (ppm) versus S (wt.%) and Se (ppm). Note the good correlation between Se and Te compared to the correlation between Te and S.

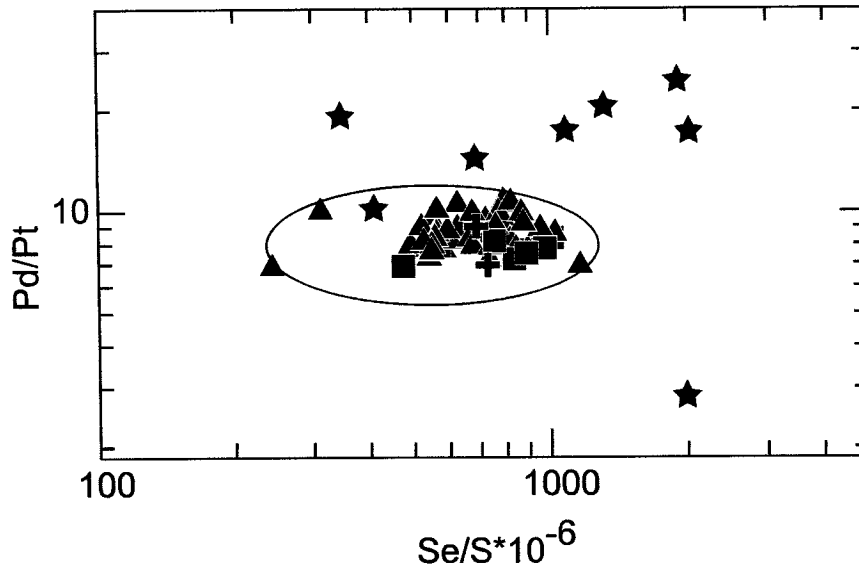


Figure 2-10. Se/S versus Pd/Pt. Note the narrow spread of values from the southern Roby Zone and Twilight Zone compared to the scatter from the High Grade Zone.

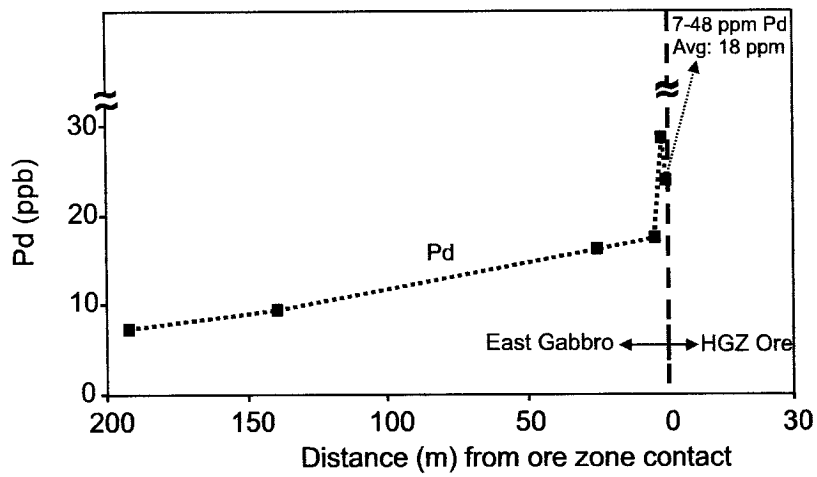


Figure 2-11. Palladium concentrations of rocks in the East Gabbro near the contact with the High Grade Zone.

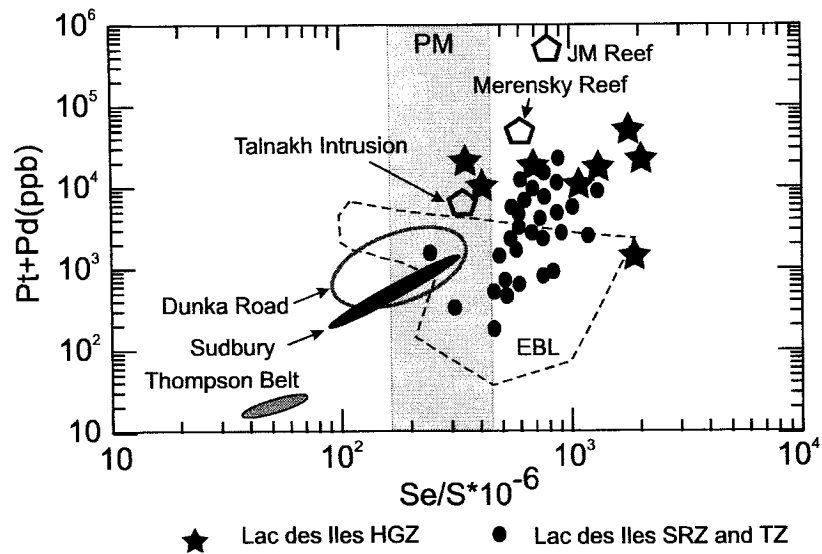


Figure 2-12. Plot of $\text{Se/S} \times 10^{-6}$ versus Pt + Pd (ppb) comparing the Lac des Iles ore to various other deposits. Note that the Lac des Iles data falls on the general trend defined by other large deposits. The shaded vertical box represents the range of $\text{Se/S} \times 10^{-6}$ for the primitive mantle. Data sources: Lac des Iles Intrusive Complex- This Study, East Bull Lake, Ontario (EBL-shown by dashed line)- Peck et al. (2001) all other deposits- Unpublished data of Eckstrand in Thériault et al. (1997).

Table 2-1: Representative chemical composition of mineralized rock types at the southern Roby Zone, Twilight Zone and High Grade Zone.

Rock type	melanogabbro		clinopyroxenite		dark gabbro		melanonorite	
Sample no.	JH02-037	JH02-140	JH02-138	JH02-089	JH02-148	JH02-146	JH-02-181	JH02-173
Location*	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	TZ	TZ
wt. %								
S ¹	0.60	0.67	1.35	0.82	0.77	1.02	0.67	0.57
(ppm)								
Ni ²	974	1530	2080	1840	2208	3080	1389	1738
Cu ³	1360	2390	3430	2290	2426	3440	1810	2270
Se ³	2.9	5.6	9	4.6	6.7	9.3	3.8	4.9
Te ³	0.5	1.5	2	1.4	2.2	2.7	0.8	1.2
(ppb)								
Au ⁴	174	868	855	416	917	1280	282	411
Pt ⁴	190	752	1020	382	998	1370	449	587
Pd ⁴	1460	6940	8790	3280	9157	11720	3560	4570
Rock type	altered melanogabbro/clinopyroxenite							
Sample no.	JH-02-SZ3	JH-02-SZ1	JH-02-SZ2	JH-02-SZ4	JHC-02-035	JHC-03-050	JHC-03-063	JHC-03-070
Location*	HGZ	HGZ	HGZ	HGZ	HGZ	HGZ	HGZ	HGZ
wt. %								
S ¹	0.86	2.27	1.67	1.05	0.77	0.95	0.47	0.58
(ppm)								
Ni ²	7950	2298	1270	1749	3468	3240	1576	3675
Cu ³	3500	2540	1703	2369	2877	2702	1507	3094
Se ³	16.2	9.3	5.8	7.2	15.6	10.3	6.2	11.1
Te ³	7.1	1	1.1	0.6	5.9	4.2	2.3	4.9
(ppb)								
Au ⁴	1925	372	545	737	2632	1105	294	1415
Pt ⁴	355	912	1026	1186	1204	582	811	1984
Pd ⁴	1010	9300	19695	17072	20766	10125	16645	48565

1= elemental analyzer, 2= XRF, 3= Aqua Regia digestion with ICP-MS, 4= Fire Assay ICP-MS.

*: SRZ=Southern Roby Zone, TZ=Twilight Zone, HGZ=High Grade Zone.

Table 2-2: $\delta^{34}\text{S}$ from mineral separates of the SRZ, TZ, and HGZ.

Sample #	Ore Zone	Mineral Separate	δ^{34}
JH-02-146	SRZ	Pyrite	0.31
JH-02-146	SRZ	Chalcopyrite	0.83
JH-02-146a	SRZ	Pyrrhotite	0.53
JH-02-146b	SRZ	Pyrrhotite	0.10
JH-02-143	SRZ	Pyrrhotite	0.00
JH-02-062	SRZ	Pyrite	0.85
JH-02-095	SRZ	Pyrite	0.30
JH-02-173	TZ	Pyrrhotite/Chalco.	0.30
JH-02-SZ2	HGZ	Pyrite	0.99
JH-02-SZ2	HGZ	Chalcopyrite	1.52
JHC-03-070	HGZ	Siegenite	0.80
JHC-03-070	HGZ	Chalcopyrite	0.85
JHC-03-063	HGZ	Pyrite	0.30
JHC-03-063	HGZ	Chalcopyrite	0.30
JH-02-SZ3	HGZ	Pyrite	0.60
JH-02-SZ1	HGZ	Pyrite	0.95

SRZ=South Roby Zone, TZ=Twilight Zone, HGZ=High Grade Zone.

Abstract

Lead isotopic compositions were determined for mineral separates from the southern Roby, Twilight, and High Grade zones of the Lac des Iles Pd deposit and country rock tonalite in the western Superior Province. Sulphides have high ratios of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ compared to plagioclase, even within single hand specimens. High ratios for sulphide minerals are explained by leaching of radiogenic Pb isotopes (e.g. ^{206}Pb , ^{207}Pb , and ^{208}Pb) from older rocks by fluids and transfer into sulphide melts close to the base of the chamber during the solidification of the igneous complex. The proposed interpretation is consistent with the earlier formation of sulphide melt which was incorporated by later mafic magma.

3.1 Introduction

Large differences in concentrations of U, Th, and Pb in mantle versus crustal rocks make Pb isotopes a sensitive indicator to detect contributions of crustal rocks to parental magmas and mineralization. The purpose of this study was to investigate the Pd mineralization in the southern Roby, Twilight, and High Grade zones of the Mine Block Intrusion of the Lac des Iles Intrusive Complex in order to evaluate the origin of the magmas and the mineralization. For this study, we obtained pure separates of plagioclase and sulphide minerals. These minerals likely retain the primary Pb isotopic compositions at the time of their crystallization because of their low concentrations of U and Th compared to Pb.

3.2 Geological Setting and Mineralization

The study area is located in the southern Wabigoon Subprovince of the Superior Province, Canada (Fig. 3-1).

3.2.1 Country rocks

The area is underlain by a series of biotite-tonalitic gneisses and massive biotite-hornblende tonalites. U-Pb zircon ages of these rocks are 2775 ± 8 Ma to 2722 ± 3 Ma for the gneiss and 2727.8 ± 1.5 Ma for the massive tonalite, respectively (D. Davis cited in Stone et al., 2003). The wide range in ages of the tonalite gneisses likely reflects both their crystallization ages as well as subsequent metamorphic events.

The biotite-tonalite gneiss are considered to be the oldest plutonic rocks in the area. They are medium grained and contain between 20-25 vol. % mafic minerals, predominantly biotite, with approximately equal proportions of quartz and feldspar in the remainder of the rock.

The massive to slightly foliated biotite-hornblende tonalite is the most common country rock of the Lac des Iles Intrusive Complex. It is medium-coarse grained and contains up to 30 vol. % mafic minerals dominated by biotite. Alteration is weak and limited to minor sericite after plagioclase feldspar.

3.2.2 Lac des Iles Intrusive Complex

The Lac des Iles Intrusive Complex is divided into three portions: a) the North Lac des Iles Intrusion, centered on the lake, b) the Mine Block Intrusion, consisting of a series of contemporaneous gabbroic intrusions immediately south of the lake, and c) the Camp Lake Intrusion, consisting of hornblende gabbro (Lavigne and Michaud, 2001). The Mine Block Intrusion contains all economic mineralization discovered to date and samples for this study were collected after detailed mapping and core logging of the southern Roby, Twilight, and High Grade zones in the summers of 2002 and 2003 (Hinchey et al., 2003, 2005; Fig. 3-2).

The southern Roby zone represented the only remaining surface exposure of the main Roby zone deposit during our mapping. The rocks in the southern Roby zone are mostly moderately to intensely altered mafic gabbros and they show complex textures and contact relationships (Hinchey et al., 2003, 2005). The Twilight zone outcrops ~ 50

m to the east of the main Roby zone and is dominated by gabbroic rocks with similar textures and relationships as those observed in the Roby zone. The Twilight zone is only weakly to moderately altered. In both zones, early leucocratic intrusions (leucogabbro and leuconorite) with low PGE are intruded by later PGE-rich melanocratic gabbroic rocks (gabbro, melanogabbro, melanonorite, pyroxenite) (Hinchey et al., 2005). The High Grade zone is hosted within a 400m long, 15-20 m wide pyroxenitic unit at the eastern margin of the main Roby zone and is bound to the east by the barren East Gabbro. It is intensely altered with all primary silicates altered to assemblages of sericite, chlorite, albite, quartz, and amphibole.

PGE mineralization within the southern Roby and Twilight zones is controlled and hosted by magmatic sulphides whereby PGE were concentrated in an immiscible sulphide melt in parental magmas (Hinchey et al., 2005). Sulphides dominantly consist of blebby sulphide with exsolution of pentlandite and chalcopyrite from pyrrhotite (Hinchey and Hattori, 2005). Variable amounts of pyrite are common in the southern Roby zone, with amounts increasing with increasing degrees of silicate alteration, and are interpreted as either a sulphidation product of earlier pyrrhotite or hydrothermal precipitates. Sulphides within the High Grade zone include pyrite, millerite, siegenite, and chalcopyrite, with minor amounts of pentlandite and pyrrhotite.

A detailed description of the geology, mineralogy, and geological setting of the Lac des Iles Intrusive Complex and the Pd mineralization is given by Sutcliffe (1989), Sutcliffe et al. (1989), Edgar and Sweeny (1991), Lavigne and Michaud (2001), Hinchey et al. (2003, 2005), Hinchey and Hattori (2005), and others.

3.3 Analytical Techniques

Samples were gently crushed and sieved between 60 – 80 mesh. Separates with > 99% purity of plagioclase and sulphide grains were obtained using a magnetic separator, followed by hand picking under a binocular microscope. Plagioclase grains with cloudy interiors, inclusions and signs of alteration were not selected.

Plagioclase separates of ~ 100 mg were rinsed with Milli-Q water in an ultrasonic bath for ~10 min. prior to a series of overnight leachings at ~50°C, consisting of 2N HCl (Leach 1), 6N HCl (Leach 2), 16N HNO₃ (Leach 3), and 16N HNO₃ with 1 drop of 48% HF (Leach 4) following the method by Cumming and Krstic (1987). An additional leach (Leach 5) using a 8:1 mixture of 5% HF and 8N HNO₃ at ~ 50°C for 20 min. was applied to two samples. But, as this leaching dissolved most grains, Pb collected during the leach 5 was reported as residue. After the four leach steps, the residues were dissolved in a sealed Teflon vial overnight in a 4:1 mixture of 48% HF and 16N HNO₃ at ~100°C. The resulting solution was dried and re-dissolved in 6N HCl at ~90°C. The samples were re-dried and re-dissolved in 3N HBr, and finally dissolved in 0.5N HBr after evaporation. Lead was eluted in 2 ml 6N HCl in Bio-Rad AG 1-X8 anion resin (200-400 mesh). The resin separation was repeated using a reduced volume of resin and the final Pb separate was eluted in 0.5 ml 6N HCl.

For Pb isotope analysis of sulphides, samples of ~ 40-100 mg were rinsed with Milli-Q water in an ultrasonic bath for ~ 10 min. The pyrite and millerite/siegenite samples were then subjected to leaching in 6N HCl for 1 hr at 60-80°C. Pyrrhotite samples were leached in 2.5N HCl for 1 hr at 40-60°C. Similar isotopic compositions for residues of sulphide grains from the same hand specimens suggest that the leaching process effectively removed Pb that was not held in the structure of the sulphides (e.g. JH-02-146 and JH-02-SZ3, Table 3-1). The leachates were therefore discarded. All samples were dissolved in closed Teflon vials in a 3:1 mixture of 16N HNO₃: 9N HBr at ~60-80°C for ~ 2 days. After evaporation, the solution was re-dissolved in 0.5 N HBr and the evaporation-dissolution process was repeated prior to the separation of Pb with anion resin. Lead was eluted in 1.0 ml of Milli-Q water following the method described in Kuritani and Nakamura (2002). The resin separation was repeated using reduced volume of resin with the elution of Pb in 0.3 ml Milli-Q water. Total procedural blanks ranged from 0.05 to 0.3 ng and were negligible compared to the total Pb in samples that ranged

from 12-170 ng for plagioclase leachates and residues and 20 to 6020 ng for sulphide separates. As both the plagioclase and sulphide samples have similar Pb concentrations, we suggest that the higher Pb isotopic ratios of the sulphides are not related to laboratory contamination.

Isotopic measurements were made on a ThermoFinnigan Triton thermal ionization mass spectrometer after loading samples on Re filaments with silica gel. The isotopic compositions were obtained in dynamic mode with smaller samples measured in static mode using an electron multiplier. Measured ratios were corrected against the value of NBS981 recommended by Todt et al. (1996) with an average fractionation correction of 0.145 ‰/amu. The average measured ratios of four runs are $^{206}\text{Pb}/^{204}\text{Pb}=16.902 \pm 0.001$, $^{207}\text{Pb}/^{204}\text{Pb}=15.444 \pm 0.001$, $^{208}\text{Pb}/^{204}\text{Pb}=36.551 \pm 0.003$ (1σ).

The concentrations of Pb were determined on 10% aliquots of the final Pb solutions. Analyses were run on a HP 4500 inductively coupled plasma mass spectrometer at the University of Ottawa. The counts of ^{208}Pb from sample solutions were compared to a curve calibrated with 4 solutions with known Pb concentrations.

3.4 Results

Acid leaching effectively removed radiogenic Pb as the residues yielded lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than the corresponding leachates (Table 3-1). “Radiogenic Pb isotopes” refers to Pb formed by radioactive decay of U and Th in rocks and minerals after their formation. The isotopic ratios of the residues should be taken as the maximum values because of the uncertainty that the leaching procedures removed 100% of the radiogenic Pb component, but the values likely reflect those of their parental magmas.

Sulphide samples were obtained from the same zones, and where possible from the same samples as the plagioclase separates. All Pb isotopic data from the plagioclase residues, leachates, and sulphide separates plot on a single line with a slope of 0.2469 ($r^2=0.9985$) on the diagram of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ (Fig. 3-3). Plagioclase

residues display the lowest Pb isotope ratios and plot very close to both the 2.69 Ga isochron and the value estimated for a depleted mantle in late Archean time (e.g., Dupre et al., 1984; Tilton and Kwon, 1990; Carignan et al., 1995), suggesting that the measured values likely represent the initial Pb isotopic composition of the parental magmas for the Lac des Iles complex. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratios of the sulphides are much higher than those for plagioclase.

Lead concentrations of the plagioclase separates range from 0.05 – 1.2 ppm and those for most sulphide separates from 0.7 – 2.0 ppm, with one sulphide sample (JH-02-SZ3, fraction A) containing 65 ppm. Fraction B from the same hand specimen contains 0.07 ppm Pb. Examination of the sample with a scanning electron microscope shows the presence of Se-rich galena as inclusions in other sulphide minerals. The concentrations of Pb in fractions A and B are very different but the Pb isotopic ratios are similar (Table 3-1). The data suggests that there is no correlation between lead concentrations of the sulphides and isotopic compositions.

There is no apparent correlation between sulphide mineralogy and isotopic compositions. For example, hydrothermal sulphides from the High Grade zone show high and low values. Pyrite in the sample JH-02-SZ3 shows the highest $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratios, and millerite/siegenite from sample JHC-03-070 shows the lowest among sulphide samples. In the southern Roby zone, pyrrhotite, magmatic sulphide, in samples JH-02-151 and JH-02-146 show high ratios compared to pyrite in sample JH-02-089.

3.5 Discussion

3.5.1 Lead Isotopic Compositions of Plagioclase

Plagioclase residues from the southern Roby and Twilight zones plot very close to 2.69 Ga isochron (Fig. 3-3). The values are also similar to those for the late Archean depleted mantle that is estimated from compositions of mafic and ultramafic rocks and

associated sulphides in the Abitibi and Wabigoon Subprovinces (Carignan et al., 1995 and references therein). The values for the residues are likely to be close to the initial Pb isotopic compositions of the Lac des Iles Intrusive Complex, although we cannot rule out the possible presence of radiogenic Pb that was not removed during the leach. Although the plagioclase leachates are consistently more radiogenic than the residues, they are not as radiogenic as the sulphide separates from the same samples (Table 3-1, see below). The Pb isotopes values are slightly higher for the inferred parental magmas than for the Archean mantle and this may reflect the nature of the source mantle. The parental magmas for the Lac des Iles Complex are considered to have originated from a depleted mantle that had undergone subduction-related metasomatism (Hinchey et al., 2005). Fluid-mobile elements, such as Pb, are commonly transferred from slabs to the mantle wedge during subduction (e.g., Taylor and Nesbitt, 1998; Hattori and Guillot, 2003).

3.5.2 Lead Isotope Compositions of Sulphides

High concentrations of radiogenic Pb isotopes may be attributed to (1) radiogenic Pb isotope signature of the parental magmas for sulphides, (2) incorporation of radiogenic Pb through bulk assimilation of old crustal rocks, or (3) incorporation of ^{206}Pb , ^{207}Pb , and ^{208}Pb isotopes leached from the country rocks by hydrothermal fluids. The hydrothermal input of radiogenic Pb is further divided into two scenarios; (3a) incorporation of radiogenic Pb during regional metamorphism, or (3b) during the intrusion of the Lac des Iles Complex. Lead is soluble in aqueous fluids, and radiogenic Pb isotopes in particular can be easily liberated from minerals and rocks to fluids (Faure and Mensing, 2005).

Option 1 implies that parental magmas for sulphides and plagioclase originated from sources with different $^{238}\text{U}/^{204}\text{Pb}$ (= μ -values) at 2689 Ma. Furthermore, isotope compositions of sulphides and plagioclase should fit Pb isotope evolution curves with different μ -values. However, the highest observed Pb isotopic values cannot be explained by any μ -value (calculated for 2689 Ma.) in either a single stage or two stage Pb growth model of Stacey and Kramers (1975). For these reasons, this possibility is discarded.

Option 2, the assimilation of crustal rocks, is commonly invoked to explain high $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of igneous rocks and ore deposits (e.g., Faure and Mensing, 2005). For example, Henry et al. (1998) suggested such a process to explain the relatively radiogenic isotopic ratios of Pb in sanukitoids in the western Superior Province. However, this is not consistent with our detailed study of trace element geochemistry, which concluded that parental magmas for the Mine Block Intrusion were derived from a depleted mantle source with very little crustal assimilation (Hinchey et al., 2005). More importantly, crustal assimilation would affect the bulk Pb isotopic signature of the rocks and it can not explain the different Pb isotopic compositions of plagioclase and sulphide separates.

Option 3a involves incorporation of radiogenic Pb isotopes into solidified intrusions from external fluids during hydrothermal activity related to regional metamorphism or late orogenic events. Anomalously high Pb isotopic ratios from some volcanogenic massive sulphide deposits and base metal sulphide deposits of the Abitibi and Wawa Subprovinces of the Superior Province have been explained by these later processes (Thorpe, 1999 and references therein). Examples include the Lorraine Cu-Ni deposit and the Patry Cu prospect in Québec (Carignan et al., 1993), the Noranda and Matagami volcanic massive sulphide deposits (Vervoort et al., 1993), and the Kam Kotia deposit in the Timmins district (Franklin et al., 1983). The majority of the anomalous Pb data associated with these deposits, summarized in Thorpe (1999), are associated with secondary galena in veins and/or major faults, with some anomalous values also associated with low lead sulphides such as pyrite and sphalerite (e.g. the Temagami Mine; Franklin et al., 1983). However, numerous examples of non-radiogenic low-Pb sulphides are also present within komatiites of the Abitibi belt (e.g. Alexo and Newton; Dupré and Arndt, 1990) which appear to preserve the original mantle Pb isotopic composition, suggesting that the Pb isotope compositions of low-Pb sulphides are not necessarily reset by later orogenic events.

Based upon a number of reasons, this process of the incorporation of radiogenic Pb during regional orogenic events is discounted for the Lac des Iles sulphides. First, the Lac des Iles deposit contains primary magmatic mineralogy and sulphides are not associated with faults or fractures (Hinchey et al., 2005). Secondly, the regional metamorphic grade in the area of Lac des Iles is relatively low greenschist facies (e.g. Blackburn et al., 1991; Pettigrew and Hattori, 2002). This is consistent with the pristine augite/diopside and plagioclase feldspar in the Northern part of the Lac des Iles Complex as well as in gabbro-norites of the Mine Block Intrusion. Thirdly, and more importantly, a regional alteration event cannot explain different Pb isotope compositions for plagioclase residues, plagioclase leachates, and magmatic sulphides from single hand samples (samples JH-02-151 and JH-02-185). Although the plagioclase leachates consistently display more radiogenic Pb isotopic signatures compared to the plagioclase residues, they are always less radiogenic than associated sulphides. As the leaching process successfully removed the majority of the radiogenic isotope component of the plagioclase samples, one can safely assume that the radiogenic Pb was held in cracks/imperfections in the plagioclase crystal structure and that the radiogenic component was derived from an external source. If the deposit had been influenced by a regional metamorphic/orogenic event, the radiogenic Pb liberated from the plagioclase during leaching would be expected to have been dominantly derived from the regional alteration event, and as such it should represent the most radiogenic Pb (or at least equally radiogenic as the sulphides) in the deposit. As our samples do not concur with such data, we suggest that the radiogenic Pb in the sulphides is not related to regional alteration/metamorphic processes. The data suggest that the high $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the sulphides were acquired before the solidification of the parental magmas of the intrusion. This argument is further supported by the blebby shape and exsolution textures of sulphides in the southern Roby and Twilight zones, documented by Hinchey et al., 2005. The evidence suggests that the sulphides have not undergone recrystallization

during hydrothermal activity.

Option 3b involves the introduction of radiogenic Pb derived from country rocks by hydrothermal fluids during intrusive activity. As magmas crystallize and cool, fluids commonly exsolve. The emplacement of the intrusion also generates fluid from the dehydration of the country rocks. These hydrothermal fluids leach radiogenic isotopes from the country rocks. This process could possibly explain the more radiogenic signature of the plagioclase leachates compared to the residues, and the high Pb isotopic signatures of the sulphides.

Single samples contain sulphides with more radiogenic compositions compared to plagioclase. Furthermore, pyrrhotite, magmatic sulphide, from sample JH-02-185 of the non-altered Twilight zone, also shows a high radiogenic composition. The decoupling of isotopic compositions of two minerals in one hand specimen requires different positions for the two during the evolution of the parental magmas. As is common in many magmatic sulphide ore deposits, sulphide melt was immiscible in parental magmas, and the immiscible separation took place early during the evolution of the Lac des Iles Intrusive Complex as evidenced by high Cu/Pd ratios in early leucocratic rocks (Hinchey et al., 2005). As sulphide melt is significantly denser than the silicate magmas, the sulphide melt probably settled at the base of the Lac des Iles magma chamber, close to the contact with the host rocks. As the temperature of the intrusive complex decreased, the silicate magmas would solidify, but sulphide melt would remain liquid for a longer time. The complete solidification of the sulphide melt would occur at lower temperatures ($\sim 300^{\circ}\text{C}$, Kelly and Vaughan, 1983). Therefore, the sulphide melt is susceptible to contamination by hydrothermal fluids. Dehydration of country rocks would have liberated radiogenic Pb from U-Th rich minerals and rocks. The sulphides, sitting close to the contact with the country rock, would preferentially incorporate the radiogenic Pb isotopes.

Sulphides in the Lac des Iles deposit contain relatively low concentrations of Pb (0.81

ppm in average excluding one anomalous sample with 25 ppm), and small amounts of radiogenic Pb from country rocks could easily raise the Pb isotope ratios of sulphide melt.

Hinchey et al. (2005) proposed the sequence of intrusions and mineralization based on metal ratios and concentrations. Earlier leucocratic magmas formed sulphide melt and later mafic magmas incorporated the earlier formed sulphides. The proposed process is consistent with the observed high Pb isotopic ratios for sulphides compared to plagioclase separates.

Figure 3-4 shows $^{206}\text{Pb}/^{208}\text{Pb}$ versus $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of plagioclase residues, leachates, and sulphides, and calculated $^{206}\text{Pb}/^{208}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for rocks of variable ages. The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios for Pb derived from rocks are calculated using the average Th/U ratio of 3.87 for the bulk continental crust (Taylor and McLennan, 1995) (Fig. 3-4). Continental crust with an age of ~2750 Ma plot on the extrapolation of the trend defined by the Lac des Iles data (Fig. 3-4). There are large uncertainties in the estimate because Th/U ratios vary among rocks (e.g. Paul et al., 2003), which result in different calculated $^{206}\text{Pb}/^{208}\text{Pb}$ ratios in possible contaminants. The incorporation of ^{206}Pb , ^{207}Pb , and ^{208}Pb derived from such rocks into the immiscible sulphide melt could explain the observed trends in the data.

3.6 Conclusions

Higher Pb isotopic ratios for sulphides than those for plagioclase from the same samples of the southern Roby and Twilight zones suggest that the sulphide melt acquired radiogenic Pb isotopes. Immiscible sulphide melt ponded in the conduit or at the base of magma chamber likely incorporated radiogenic ^{206}Pb , ^{207}Pb , and ^{208}Pb from older (~2750 Ma) country rock. The sulphides with radiogenic Pb isotope signatures were subsequently incorporated and brought to the upper crustal level by late melanocratic magmas. Thus, Pb isotopic compositions support our model based on metal ratios of sulphides (Hinchey et al., 2005) where earlier formed immiscible sulphide melt was incorporated by later mafic magmas, providing a mechanism to explain the high Pd in the deposit.

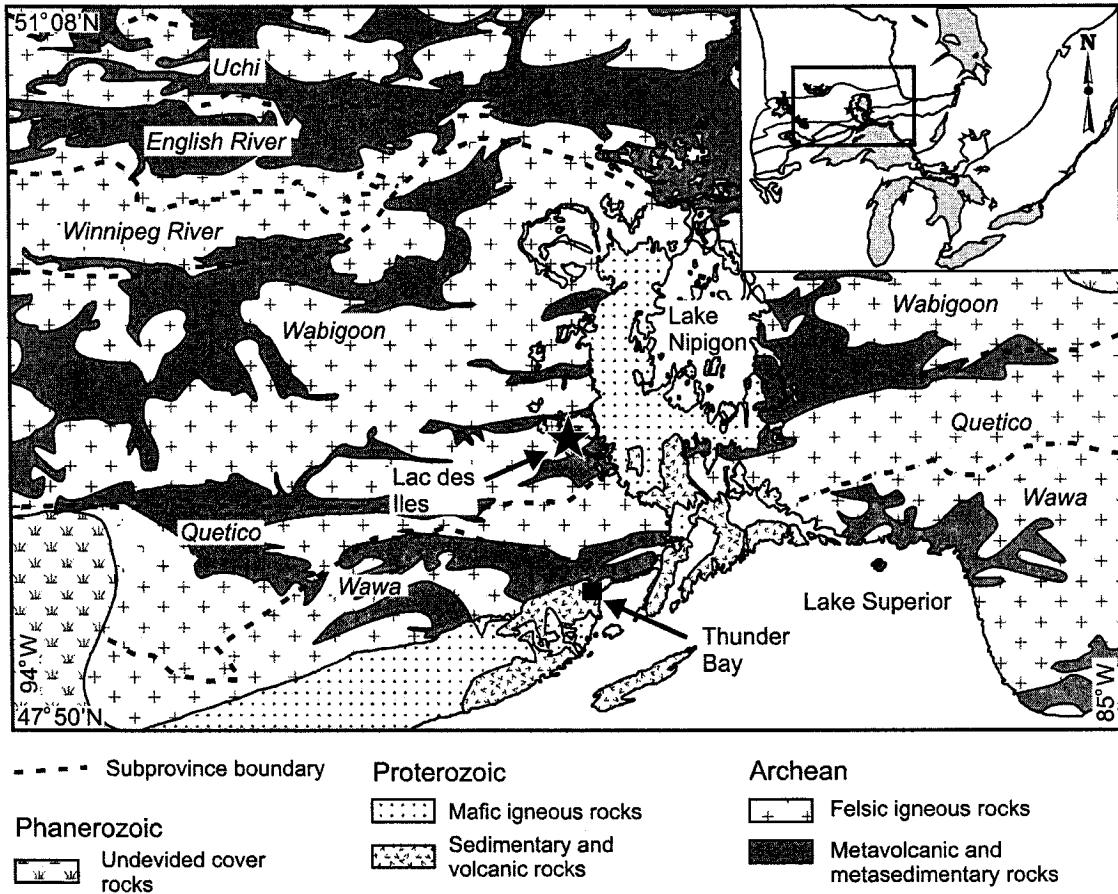


Figure 3-1. Regional geology of the western Superior province illustrating subprovince boundaries and the location of the Lac des Iles Intrusive Complex (modified from Ontario Geological Survey, 1991; Stern et al., 1989). Subprovince names are given in italics. Inset shows a simplified map of the Superior province with the figure area outlined by the square.

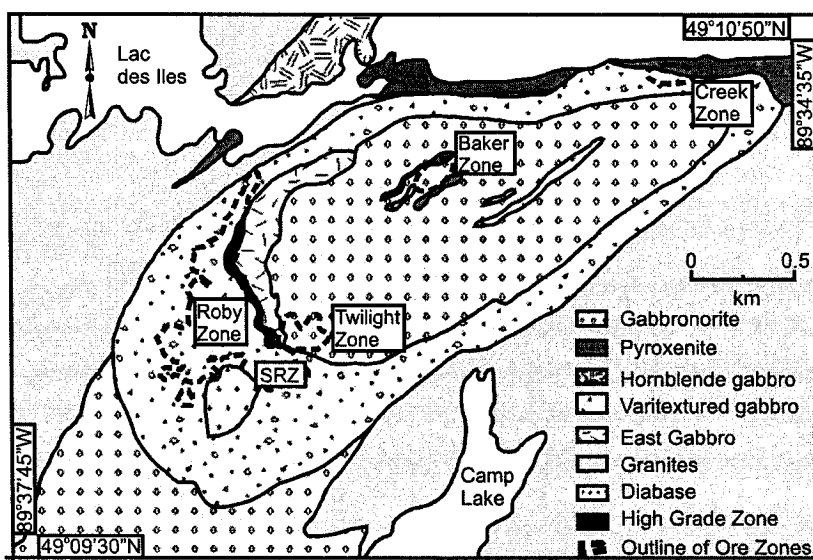
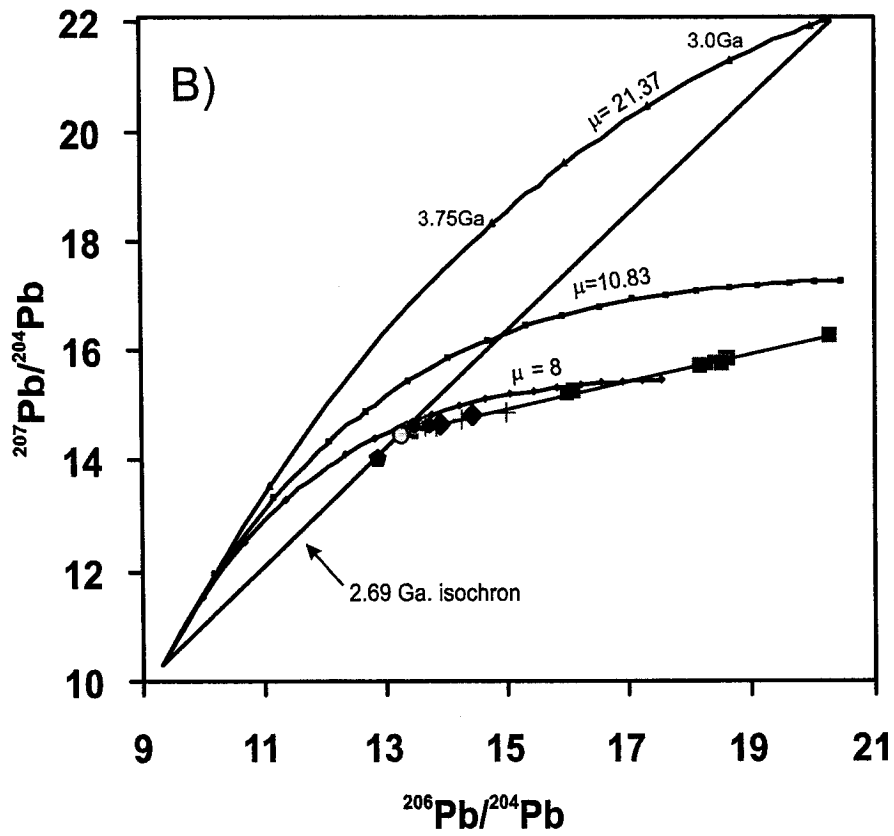
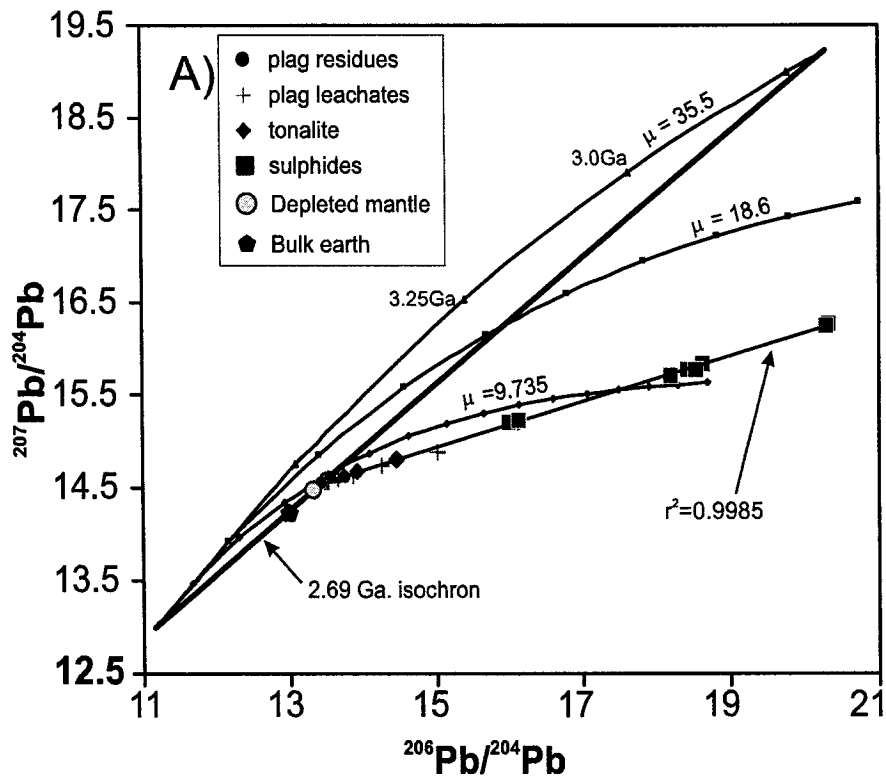


Figure 3-2. Simplified geological map of the Mine Block Intrusion of the Lac des Iles Intrusive Complex (modified after Sutcliffe and Sweeny, 1986), displaying the locations of the Roby, Twilight, and High Grade zones.

Figure 3-3. A) Lead isotope compositions for residues and leachates of plagioclase and sulphides from the Mine Block Intrusion, and the host tonalite. Shown is the field of the late Archean depleted mantle (Carignan et al; 1995 and references therein), the bulk earth value, and a 2.69Ga isochron. Also plotted are two-stage Stacey and Kramer (1975) Pb evolution curves for various μ values. B) Lead isotopic compositions of samples compared to single stage Pb evolution curves. Note that the sulphides do not correspond with any single Pb evolution curve. Small symbols along the growth curves in both figures A and B represent 0.25Ga. Analytical errors (1σ) for $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ were better than $\pm 10^{-4}$ of the reported values in dynamic mode and $\pm 10^{-3}$ in static mode and as such error bars were not plotted. The ticks along the evolution curves represent 0.25 Ga.



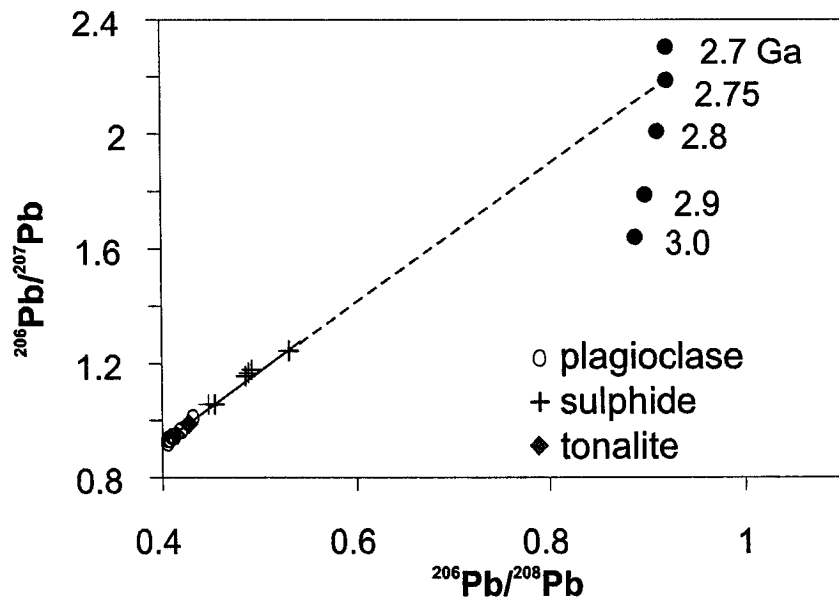


Table 3-1. Lead isotope compositions of plagioclase feldspar and sulphide separates from the Mine Block Intrusion, Lac des Iles Intrusive Complex, and feldspar from the country rock tonalite.

Sample No.	Zone	Mineral	Fraction		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
JH-02-151	SRZ	Plagioclase	A	L1	14.261	14.741	34.046
				L2	13.527	14.559	33.330
				L3	13.651	14.595	33.465
				L4	13.858	14.628	33.631
				R	13.687	14.618	33.516
			B	R* after L4	15.001	14.877	34.715
			C	R after L4	13.742	14.610	33.518
JH-02-185	TZ	Plagioclase	A	L1	13.661	14.641	33.536
				L4	13.466	14.554	33.258
				R	13.433	14.539	33.218
			B	R* after L4	13.502	14.564	33.299
JH-02-214	TZ	Plagioclase	A	R after L4	13.489	14.598	33.330
JHC-03-91	Tonalite	Plagioclase	A	R after L4	13.925	14.668	33.563
JHC-03-92	Tonalite	Plagioclase	A	R after L4	14.43	14.810	33.641
JH-02-146	SRZ	Pyrrhotite	A	R**	18.610	15.819	37.785
		Pyrrhotite	B	R**	18.534	15.769	37.619
JH-03-151	SRZ	Pyrrhotite	A	R**	18.428	15.772	37.600
JH-02-185	TZ	Pyrrhotite	A	R**	16.115	15.227	35.568
JH-02-037	SRZ	Pyrite	A	R**	18.634	15.835	37.724
JH-02-089	SRZ	Pyrite	A	R**	18.192	15.706	37.401
JH-02-SZ3	HGZ	Pyrite	A	R**	20.315	16.259	38.232
	HGZ	Pyrite	B	R**	20.292	16.264	38.263
JHC-03-070	HGZ	Millerite/Siegenite	A	R**	16.001	15.222	35.789

Fractions represent different grains from a single hand specimen.

L1 = leach 1, L2 = leach 2, L3 = leach 3, L4 = leach 4, L5 = leach 5, R = residue,

R* Extracted with 8:1 mixture of 5%HF and 8N HNO₃ at 50 °C.

R** Extracted after leaching with 6N HCl for pyrite and millerite/siegenite, 2.5N HCl leach for pyrrhotite. Leachates from sulphide samples were not collected for isotopic analysis.

SRZ = southern Roby zone, TZ = Twilight zone, HGZ = High Grade zone.

Detailed descriptions and locations of samples are given in Appendix A.

Appendix A: Sample Descriptions

Southern Roby zone

JH-02-037: Moderately to intensely altered, medium-grained, melanogabbro/clinopyroxenite consisting of ~ 85 vol.% clinopyroxene and 15 vol.% plagioclase feldspar with approximately 2-3 vol. % disseminated sulphides. Most primary silicates have been altered to assemblages of secondary amphiboles (actinolite/tremolite) and chlorite after clinopyroxene and sericite after plagioclase. Blebby sulphides consist of relict pyrrhotite with exsolved pentlandite and chalcopyrite, and abundant secondary pyrite. (105242.5 E and 104262N on North American Palladium's mine imperial grid).

JH-02-089: Moderately to intensely altered, medium-grained, melanogabbro/clinopyroxenite consisting of ~ 90-95 vol.% clinopyroxene and 5-10 vol.% plagioclase feldspar with approximately 2-3 vol. % disseminated sulphides. Primary clinopyroxene is altered to secondary amphiboles (actinolite/tremolite) and chlorite with plagioclase variably altered to sericite. Sulphides consist of pyrrhotite with lesser amounts of exsolved pentlandite and chalcopyrite, and abundant secondary pyrite replacing the magmatic sulphides. (105242.5 E and 104262N on North American Palladium's imperial mine grid).

JH-02-151: Moderately altered, medium-grained, dark gabbro consisting of ~ 45-55 vol.% clinopyroxene and 45-55 vol.% plagioclase feldspar with approximately 2-3 vol. % disseminated sulphides dominated by pyrrhotite with lesser amounts of exsolved pentlandite and chalcopyrite. Pyrite is observed to variably replace the magmatic sulphides. (105320 E, 104199N on North American Palladium's mine imperial grid).

JH-02-146: Moderately altered, medium-grained, dark gabbro consisting of ~ 55-60 vol.% clinopyroxene and 40-45 vol.% plagioclase feldspar with approximately 4-5 vol. % disseminated sulphides consisting of pyrrhotite with exsolved pentlandite and chalcopyrite. Minor pyrite is observed overprinting the primary magmatic sulphide assemblages. (105375 E, 104120N on North American Palladium's imperial mine grid).

Twilight zone

JH-02-185: Weakly altered, medium grained, melanonorite consisting of ~ 80-85 vol.% orthopyroxene and 15-20 vol.% plagioclase feldspar with ~ 4 vol.% blebby sulphides consisting of pyrrhotite with exsolved pentlandite and chalcopyrite. Primary

orthopyroxene is weakly altered to secondary amphiboles (tremolite) whereas plagioclase feldspar is weakly altered to sericite. (105935E, 104780N North American Palladium's imperial mine grid).

JH-02-214: Weakly altered, medium grained, melanonorite consisting of ~ 75-80 vol.% orthopyroxene and 20-25 vol.% plagioclase feldspar with ~ 2 vol.% blebby sulphides consisting of pyrrhotite with exsolved pentlandite and chalcopyrite. Primary orthopyroxene is weakly altered to secondary amphiboles (tremolite) whereas plagioclase feldspar is weakly altered to sericite. (105978E, 104637N North American Palladium's imperial mine grid).

High Grade zone

JH-02-SZ3: Intensely altered, melanogabbro/clinopyroxenite. All primary silicates have been altered to an assemblage of chlorite + actinolite + sericite ± albite ± quartz ± epidote. Sulphides, ranging up to 8-10 vol.%, are dominated by pyrite with variable chalcopyrite and minor pyrrhotite and pentlandite. (Collected from the High Grade zone at the bottom of the phase 3 open pit).

JHC-03-070: Very intensely altered, clinopyroxenite. All primary silicates have been altered to an assemblage of hornblende + sericite ± albite ± quartz. Sulphide, ~ 4-5 vol.%, is dominated by millerite + siegenite ± chalcopyrite. (Depth of 685.2-685.5 m in DDH 02-017).

Tonalite

JHC-03-091: Slightly foliated biotite-hornblende tonalite. Medium-coarse grained with ~ 30 vol.% mafic minerals dominated by biotite. (Depth of 28.8 m in DDH NL-03-003).

JHC-03-092: Biotite-tonalite gneiss with ~ 25 vol. % mafic minerals dominated by biotite. (Depth of 188.0 m in DDH NL-03-003).

Abstract

The Lac des Iles Intrusive Complex in northwestern Ontario comprises one of many ~ 2680-2690 Ma mafic/ultramafic and sanukitoid suite intrusions in the western Wabigoon subprovince of the Superior Province, Canada. These intrusions formed after the major greenstone/TTG magmatism.

Geochemical and Pb isotopic data from the Mine Block Intrusion of the Lac des Iles Intrusive Complex, as well as the surrounding 2680-2690 Ma intrusions, suggest that they were derived through partial melting of a previously metasomatized depleted mantle source. All intrusions display typical arc-like, subduction influenced geochemical attributes such as negative HFSE and enriched LILE patterns. However, compared to the surrounding intrusions, the Mine Block Intrusion displays relatively unfractionated REE patterns. The average calculated parental magma $(Ce/Yb)_{CN}$ ratio for all melanocratic and leucocratic lithologies of the southern Roby and Twilight zones of the Mine Block Intrusion of the Lac des Iles Intrusive Complex is 2.3, compared to average values of 10 and 9.3 for the Tib Lake and Legris Lake mafic/ultramafic intrusions and 51 and 82 for the Roaring River and Norway Lake sanukitoid suites respectively.

The 2680-2690 Ma mafic/ultramafic and sanukitoid suite intrusions represent late intrusions after greenstone formation. If the intrusions occurred during active subduction, they could be explained through partial melting of a metasomatized, mantle wedge in a slab-window environment. If the magmas were generated after the cessation of subduction, potential tectonic environments include delamination or slab break-off of the subducted slab beneath the Wabigoon subprovince, or a mantle plume environment. All cases would result in adiabatic melting of previously metasomatized depleted lithospheric mantle by upwelling of hot asthenospheric mantle. The unfractionated REE patterns of the Mine Block Intrusion, compared to the fractionated patterns of the surrounding mafic/ultramafic and sanukitoid suite rocks could be related to different degrees of

partial melting and/or crustal assimilation processes. The average Mg# (= atomic ratio of $(\text{Mg})/(\text{Mg}+\text{Fe}_T)$) of the leucocratic and melanocratic lithologies at Lac des Iles are 0.68 and 0.67 respectively, compared to 0.65, 0.49, and ~ 0.50 for the mafic/ultramafic Tib Lake and Legris Lake intrusions and the sanukitoid suite of intrusions; suggesting increased fractionation in the latter. The Lac des Iles Intrusive Complex is interpreted to have intruded along a pre-existing fault system (the Shelby Lake fault) allowing for rapid intrusion without substantial crustal assimilation/fractional crystallization.

The Lac des Iles Roby zone deposit represents the only primarily PGE deposit in Canada. Although many of the other mafic/ultramafic intrusions in the area of Lac des Iles share some textural and lithological similarities with the ore zone (e.g. common occurrence of varitextured gabbro and brecciation), the Lac des Iles Intrusive Complex is geochemically more primitive. Lower degrees of partial melting and/or substantial crustal assimilation processes interpreted to have been associated with the other intrusions can be detrimental to the formation of an economic PGE deposit as they allow for PGE retention in the mantle, and/or sulphur saturation before reaching shallow crustal levels of the parental magmas causing early stripping out of PGE, respectively. Exploration for PGE deposits similar to the Lac des Iles deposit should focus on the identification of primitive mafic/ultramafic intrusions with non-fractionated REE patterns.

4.1 Introduction

The Wabigoon Subprovince represents one of a series of east-west trending granite-greenstone belts, bordered by metasedimentary belts, in the western Archean Superior Province. Prior to ca. 2700 Ma., the area experienced major widespread granite-greenstone forming magmatic activity (Blackburn et al., 1991) (Fig. 4-1). Substantial intrusive activity took place from 2698 to 2680 Ma (Stern et al., 1989; King et al., 1998 and references therein; Stevenson et al., 1999; Percival et al., 2004) (Fig. 4-1). The intrusions varied in composition from mafic/ultramafic through to the sanukitoid series of

intrusions (e.g. Henry et al., 1998; Stevenson et al., 1999; Percival et al., 2004; Whalen et al., 2004). The Lac des Iles Intrusive Complex, ~ 30 Km² in outcrop area, represents a large example of these mafic/ultramafic intrusions and is the focus of this manuscript. It is located approximately 80 km north of Thunder Bay, Ontario, and is the largest of a circular outcropping group of middle NeoArchean mafic/ultramafic intrusions in the immediate area (Fig. 4-2). Other major intrusions in the surrounding area comprise the Legris Lake, Buck Lake, and the Tib Lake Intrusions (Sutcliffe and Smith, 1988). A recent U-Pb zircon age of a gabbroic pegmatite from the Roby zone suggest the intrusion age of 2689 ± 1.0 Ma (D. Davis unpublished data in Stone et al., 2003). Available age data from the Tib Lake mafic/ultramafic Intrusion to the north (2685.9 ± 1.6 Ma U-Pb zircon date from a gabbro pegmatite, D. Davis unpublished data in Stone et al., 2003) suggest that they were contemporaneous. The intrusions are predominantly hosted by tonalite intrusions and gneiss of the Lac des Iles greenstone belt (Stone et al., 2003).

This paper presents whole rock trace elements and radiogenic isotope data for mineral separates from the southern Roby and Twilight zones of the Mine Block Intrusion of the Lac des Iles Intrusive Complex. Hypothetical parental magma compositions for the Mine Block Intrusion and the surrounding intrusions are also presented. Data suggests that the Lac des Iles Intrusive Complex formed through high degrees of partial melting in a depleted mantle, and displays unfractionated REE compared to the surrounding intrusions. The data are used to discuss the origin and tectonic setting of the mineralized Lac des Iles Intrusive Complex.

4.2 Geology of the Lac des Iles Intrusive Complex

4.2.1. Geological Setting

The Lac des Iles Intrusive Complex is situated in the southern Wabigoon Subprovince of the Superior Province (Fig.4-1); an area represented by a volcano-plutonic terrain bound by the Quetico metasedimentary Subprovince to the south and the

English River metasedimentary Subprovince to the north (Card and Ciesielski, 1986). The Wabigoon Subprovince is commonly divided into three; the western, central, and eastern portions (Blackburn et al., 1991) (Fig. 4-1). The western and eastern portions are characterized by abundant mafic volcanic rocks and tonalitic plutons, whereas the 200 km wide central Wabigoon Subprovince is dominated by middle Neoproterozoic plutonic and gneissic rocks with lesser amounts of greenstone belts (Blackburn et al., 1991).

The Lac des Iles Intrusive Complex represents one of a series of middle Neoproterozoic (~2698-2678 Ma) granitic to gabbroic/ultramafic intrusions in the central Wabigoon Subprovince. In the immediate vicinity of Lac des Iles, the mafic/ultramafic intrusions form part of a 30 km circular array of mafic/ultramafic intrusions close to the boundary with the metasedimentary Quetico Subprovince to the south (Gupta and Sutcliffe, 1990) (Fig. 4-2). These intrusions include the Legris Lake, Tib Lake, Buck Lake, and Lac des Iles Intrusions, of which the Lac des Iles Intrusive Complex is the largest.

The contemporaneous sanukitoid rocks (2698-2685 Ma; Percival et al., 2004) are typically monzodioritic in composition and are characterized by high Mg numbers (atomic ratio of $Mg/(Mg+Fe_T)$; 0.43-0.59) and elevated concentrations of Cr, Sr, Ba and P_2O_5 , with low Rb/Sr ratios and fractionated REE (Shirey and Hanson, 1984; Stern et al., 1989). Stern et al. (1989) defined the sanukitoid suite of intrusions in the Archean Superior Province as being comprised of high Mg-andesitic compositions and their fractionated equivalents. The chemical characteristics of the sanukitoid suite suggests that they are derived from a metasomatized mantle wedge (e.g. Stern et al., 1989).

Detailed geology of the Wabigoon Subprovince have been given by Blackburn et al. (1991) and others.

4.2.2. The Lac des Iles Intrusive Complex

The Lac des Iles Intrusive Complex is commonly divided into three main intrusive bodies: 1) the North Lac des Iles ultramafic Intrusion, centered on Lac des

Iles, 2) the Mine Block Intrusion which contains all economic PGE mineralization in association with lithologically and texturally complex gabbroic rocks, and 3) the homogeneous hornblende gabbro Camp Lake Intrusion to the south (Fig.4-3) (Lavigne and Michaud, 2001).

The North Lac des Iles Intrusion varies in lithology from clinopyroxenite/websterite in the northern portion to gabbronorite in the southern portion. The Mine Block Intrusion, which forms the focus of this manuscript, is dominated by a series of brecciated and intermingled lithologies ranging from anorthositic/gabbroic/gabbronoritic to pyroxenitic lithologies (Hinchey et al., 2003, 2005).

The southern Roby zone represented the only portion of the main Roby zone exposed on surface during our mapping in the summers of 2002 and 2003. It serves as an excellent area to study the rocks in the main Roby zone deposit. The Twilight zone outcrops approximately 50 meters to the east of the main Roby zone and consists dominantly of noritic/gabbronoritic rocks.

Descriptions of the geology of the Lac des Iles Intrusive Complex and the surrounding geology are given by Pye (1968), Sutcliffe (1986, 1989), Brüggmann et al., (1989, 1997), Sutcliffe et al. (1989), Edgar and Sweeny (1991), and Lavigne and Michaud (2001). The geology and PGE mineralization of the southern Roby and Twilight zones of the Mine Block Intrusion have been presented by Hinchey et al. (2003, 2005) and Hinchey and Hattori (2005).

4.2.3. Mineralogy

Pristine igneous minerals are well retained in the Northern Lac des Iles Intrusion and some gabbronorites of the Mine Block Intrusion. However, the southern Roby zone, and to a lesser extent the Twilight zone, of the Mine Block Intrusion show moderate degrees of alteration. In all rock types plagioclase appears to be the least altered silicate phase; varying from being weakly to moderately replaced by sericite in the southern Roby and Twilight zones. The primary mafic minerals of clinopyroxene and orthopyroxene have

been variably replaced by secondary amphiboles. Clinopyroxene in the southern Roby zone is extensively altered and replaced by an assemblage of actinolite, hornblende, and chlorite. Orthopyroxene in the Twilight zone is only weakly altered and replaced by assemblages of tremolite/actinolite. The predominance of orthopyroxene at the Twilight zone may suggest that the parental magmas were slightly more siliceous than those of the southern Roby zone. Minor secondary magnetite, biotite, quartz, and carbonate are also locally observed.

Petrographical and textural relationships suggest the early crystallization of plagioclase + clinopyroxene \pm orthopyroxene in the southern Roby and Twilight zones. Some norite/melanonorite in the Twilight zone show earlier crystallization of plagioclase and orthopyroxene before clinopyroxene. In all cases in the Mine Block Intrusion plagioclase is an early crystallization product.

Mineral analysis from the Mine Block Intrusion show plagioclase compositions ranging from bytownite to labradorite (An_{52-82}); orthopyroxene compositions (dominantly enstatite) from $En_{61-74}Wo_{1-9}Fs_{15}$, and clinopyroxene (diopside and augite) compositions from $En_{38-47}Wo_{36-51}Fs_{3-19}$ (Watkinson and Dunning (1979), Sutcliffe et al. (1989), Edgar and Sweeny (1991), Michaud (1998), and Hinchey and Hattori, (2005).

4.3. Geochemistry

4.3.1. Sampling and analytical techniques

Samples of representative rock types were collected from the southern Roby and Twilight zones. Major and selected minor elements were analyzed from fused disks using a Phillips PW 2400 X-ray fluorescence spectrometer. Accuracy and precision are better than 0.5% for all major elements and better than 10% for all trace elements. The concentration of the rare earth elements (REE) as well as other trace elements were determined at Acme Analytical Laboratories Ltd., using inductively coupled plasma mass spectrometry (ICP-MS) after digesting the samples with $HNO_3 - HClO_4 - HF - HCl$.

Precision and accuracy of the REE and other trace elements are typically better than 10%, except for samples which had concentrations close to the detection limits which had precisions of only 28%.

Samples for Pb and Sr isotopic analysis were gently crushed and sieved between 60 – 80 mesh. Separates of plagioclase were obtained using a magnetic separator, followed by hand picking under a binocular microscope. Plagioclase grains with cloudy interiors, inclusions and signs of alteration were removed during the hand picking. The purity is greater than 99.9%.

Plagioclase separates of ~ 100 mg for Pb isotope measurements were rinsed with Milli-Q water in an ultrasonic bath for ~10 min. prior to a series of overnight leachings at ~50°C, consisting of 2N HCl (Leach 1), 6N HCl (Leach 2), 16N HNO₃ (Leach 3), and 16N HNO₃ with 1 drop of 48% HF (Leach 4) following the method by Cumming and Krstic (1987). An additional leach (Leach 5) using 8:1 mixture of 5% HF and 8N HNO₃ at ~ 50°C for 20 min. was applied to two samples. But, as this leaching dissolved most grains, Pb collected during the leach 5 was reported as residue. After leaching the residues were dissolved in a sealed Teflon vials overnight in a mixture of 4:1 mixture of 48% HF and 16N HNO₃ at ~100°C. The resulting solution was dried and re-dissolved in 6N HCl at ~90°C. The samples were re-dried and re-dissolved in 3N HBr, and finally dissolved in 0.5N HBr after evaporation. Lead was eluted in 2 ml 6N HCl in Bio-Rad AG 1-X8 anion resin (200-400 mesh). The anion resin separation was repeated using a reduced volume of resin and the final Pb separate was eluted in 0.5 ml 6N HCl. Pb isotopic measurements of samples on Re filaments were made with a ThermoFinnigan Triton thermal ionization mass spectrometer. The majority of analyses were measured in the Faraday dynamic mode with smaller samples measured in static mode using an electron multiplier. Measured ratios were corrected against the value of NBS 981 recommended by Todt et al. (1996) with an average fractionation correction of 0.145 ‰/amu. The average ratios for NBS 981 are $^{206}\text{Pb}/^{204}\text{Pb}=16.902 \pm 0.001$, $^{207}\text{Pb}/^{204}\text{Pb}=15.444$

± 0.001 , $^{208}\text{Pb}/^{204}\text{Pb}=36.551 \pm 0.003$ (1σ), based on four runs during our analysis.

Plagioclase separates of ~ 30-70 mg for Sr isotopic measurements were initially rinsed with Milli-Q water in an ultrasonic bath for ~10 min. Samples were leached in 0.2N HCl in an ultrasonic bath for 10 min., before digestion in 48% HF at room temperature for 1 hour, followed by digestion in ~ 0.3 ml of 4:1 48%HF:16NHNO₃ in a sealed Teflon vial heated at ~ 150°C overnight. Rubidium and Sr were eluted following the standard column chemistry using Bio-Rad cation resin. Rubidium samples were run with a Finnigan MAT 261 and Sr samples on single Ta filaments were measured with a ThermoFinnigan Triton thermal ionization mass spectrometer. The average ratio for NBS 987 is $^{87}\text{Sr}/^{86}\text{Sr} = 0.71024 \pm 0.000004$ based on two runs during our analysis.

4.3.2. Trace element and REE Characteristics

Representative whole rock major, trace, and REE data from various lithologies of the southern Roby and Twilight zones are given in Table 4-1. Primitive mantle normalized bulk rock, as well as calculated parental magma compositions, multi-element spider diagrams are illustrated for representative lithological units within the southern Roby and Twilight zones in Figure 4-6. The parental magma compositions were calculated following the method of Bedard (1994) and will be discussed in more detail in a following section.

The well defined positive correlations between HFSE suggest that all lithologies in the southern Roby and Twilight zones, with the exception of a late clinopyroxenite unit at southern Roby zone, are cogenetic. All cogenetic lithologies display low concentrations of REE with flat, relatively non-fractionated patterns (Fig.4-6). Bulk rock $(\text{Ce}/\text{Yb})_{\text{CN}}$ for the melanocratic and leucocratic lithologies of the southern Roby and Twilight zones are 1.26 (n=15), 1.85 (n=10), 0.91 (n=6), and 1.77 (n=6) respectively. Fine grained gabbro from the Twilight zone has $(\text{Ce}/\text{Yb})_{\text{CN}}$ of 0.36 (n=2); whereas the late, non-cogenetic clinopyroxenite of the southern Roby zone has a ratio of 2.00 (n=2). Representative $(\text{Ce}/\text{Yb})_{\text{CN}}$ for various lithologies from the southern Roby and Twilight

zones are given in Table 4-1. The REE pattern of the late clinopyroxenite also differs from the other lithologies in that it forms a concave up pattern with relatively enriched MREE (not shown for clarity). As indicated by Hinchey et al., 2005 and discussed below, the relatively flat, low concentration patterns of the REE suggest high degrees of partial melting of a depleted mantle source.

All lithologies display similar multi-element trace element patterns with enrichment of LILE (e.g. Cs, Rb, Ba, Th, U) and varied degrees of negative HFSE anomalies (e.g. Nb, Zr) (Figs. 4-6, 4-7). Tantalum also displays negative anomalies but was not plotted on the diagram because its concentrations are close to, or below, the detection limit of 0.1 ppm. The pattern with negative HFSE is commonly called an arc geochemical signature and interpreted to represent a metasomatized source influenced by subduction (e.g. McCulloch and Gamble, 1991; Hawkesworth et al., 1993; Pearce and Peate, 1995). Low $^{87}\text{Sr}/^{86}\text{Sr}$ (2.689 Ga) (see below) suggests that the metasomatism took place shortly before the partial melting. Fluid-soluble elements, such as LILE, are enriched in the source and parental magmas.

4.3.3. Radiogenic isotopes: Pb and Sr

For the purposes of this manuscript the terminology “radiogenic lead” refers to lead formed as a result of radioactive decay of uranium or thorium (e.g. ^{206}Pb , ^{207}Pb , and ^{208}Pb). All four of the plagioclase residues analyzed yielded lower $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratios than the leach fractions; therefore the isotopic ratios of the residues in Table 4-2 should be taken as maximum values for initial compositions.

As observed in Table 4-2 and Figure 4-8, representing $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ evolution with Stacey-Kramers (1975) two stage Pb evolution model, all Pb isotopic data from the plagioclase residues and leachates plot along a single line with a slope of 0.2073 with $r^2=0.9629$, yielding an isochron age of 2921 ± 250 Ma; within error of the U-Pb zircon age for the intrusion (calculated using Isoplot, version 3, Ludwig, 2003). The plagioclase residues from the Twilight zone display the least radiogenic ratios and

plot very close to both the 2.69 Ga isochron and the depleted mantle field (e.g. Dupre et al., 1984; Tilton and Kwon, 1990; Carignan et al., 1995), suggesting that they serve as reasonable estimates for the initial Pb isotopic composition of Lac des Iles.

Strontium isotopic compositions were determined on a set of plagioclase separates (Table 4-3, Fig. 4-9). The data consist of two samples from the host tonalite, two samples from the Mine Block Intrusion, and one sample from the southern portion of the Northern Ultramafic Intrusion. The host tonalite and Lac des Iles Intrusive Complex samples provide average values for $^{87}\text{Sr}/^{86}\text{Sr}$ (2.689 Ga) of 0.70142 and 0.70098, respectively, which support the derivation of the Lac des Iles Intrusive Complex from a depleted mantle source because the bulk earth value at 2.689 Ma is 0.70223; calculated using values of 0.70455 for present day and 0.69897 at 4.6Ga (Rollinson, 1993; Faure and Mensing, 2005; Fig.4-9). Some data from the southern Roby and Twilight zones resulted in unrealistically low initial ratios. The anomalously values are interpreted to be related to the enrichment of Rb during the alteration.

4.4. Discussion

4.4.1.1. Element Mobility

The high field strength elements (HFSE), such as Zr, are interpreted to behave as immobile elements during low grade alteration/metamorphism (e.g. Lesher et al., 1991; Jenner, 1996; Polat and Hofmann, 2003). Positive correlations between Zr and HFSE, (Fig. 4-5a and Fig.4-10 of Hinchey et al., 2005), as well as total REE, suggest that the REE and the HFSE have not been subjected to post-solidus modification. In contrast, large ion lithophile elements (LILE) display scatter on plots against Zr (Fig. 4-5b and Fig. 4-16b of Hinchey et al., 2005) suggesting that they were mobile. The differences in mobility can be observed on the primitive mantle normalized multi-element diagrams (Fig.4-6) where the HFSE and REE have much tighter patterns compared to the LILE. Although the LILE show scatter, similar patterns for samples with different degrees of

alteration (Fig. 4-6) suggests that the observed pattern of LILE likely reflects the primary characteristics of the magmas.

4.4.1.2. Parental magma composition of the Mine Block Intrusion

Based upon the presence of early plagioclase as a cumulate phase in the Mine Block Intrusion, the parental magmas were likely to be Al_2O_3 rich. In addition, the PGE mineralization implies that the parental magmas were sulphur undersaturated at the time of intrusion (Hinchey et al., 2005). Due to the cumulate nature of the Mine Block Intrusion at Lac des Iles, coupled with the lack of chilled margins, parental magma compositions were calculated following the method of Bedard (1994) using the modal mineralogy and partition coefficients between minerals and melt by Bedard (1994) and Rollinson (1993). We used normative minerals of plagioclase, clinopyroxene, orthopyroxene, olivine, magnetite, and ilmenite for the calculation with the remaining proportion being attributed to a trapped melt fraction. Trapped melt fractions vary from 6.3 to 15.4 vol %.

As the major mineral phases observed in the Mine Block Intrusion do not significantly fractionate elements, the calculated parental trace element patterns approximately parallel the bulk rock compositions (Fig. 4-6). All parental magma compositions display so-called arc geochemical signatures (e.g. McCulloch and Gamble, 1991; Hawkesworth et al., 1993; Pearce and Peate, 1995) with the enrichment of LILE (e.g. Cs, Rb, Ba, Th, U) and negative anomalies of HFSE (Figs. 4-6, 4-7). Parental magma $(\text{Ce}/\text{Yb})_{\text{CN}}$ ratios for the melanocratic and leucocratic lithologies of the southern Roby and Twilight zones are 2.4 (n=15), 2.4 (n=10), 1.6 (n=6), and 3.0 (n=6) respectively. Fine grained gabbro from the Twilight zone has $(\text{Ce}/\text{Yb})_{\text{CN}}$ of 1.00 (n=2); whereas the late, apparently non-cogenetic clinopyroxenite of the southern Roby zone has a ratio of 4.5 (n=2). The majority of the samples display slightly negative Eu anomalies (average Eu/Eu^* for all samples = 0.92). The positive Sr anomalies may either be attributed to mantle metasomatism via fluids and/or melt from the subducting slab,

or they may be an artifact as the partition coefficient of Sr between plagioclase and melt varies depending on the composition of plagioclase. For the purposes of this manuscript we used the mineral/melt partition coefficient for plagioclase in a basaltic/basaltic andesitic liquid given in Rollinson (1993). However, as Sr substitutes into the Ca site of the plagioclase structure, not the Na or K sites, the composition of the plagioclase influences the partition coefficients. Accurate partition coefficients require precise An contents of the samples and the temperature. The proposed interpretation is supported by approximate depleted mantle isotopic compositions for Pb (this study) and Sr (this study and Brüggmann et al., 1997) from plagioclase residues, as well as depleted mantle recalculated ϵ_{Nd} values at 2689 Ma ($\sim +1$ to $+1.5$) from Brüggmann et al., (1997).

4.4.2. The Tectonic setting of the Lac des Iles Complex.

The Superior province, dominated by east-west verging subprovinces, formed through the accretion of volcano-plutonic and metasedimentary belts onto the North Cariboo terrain in the north (Card and Ciesielski, 1986; Williams et al., 1992; White et al., 2003; Percival et al., 2004). Prior to ~ 2700 Ma, the Wabigoon Subprovince represented the southern margin of the Superior province (e.g. Percival et al., 2004) where the subducting oceanic slab formed an Andean-type continental arc (e.g. White et al., 2003, Percival et al., 2004). Based on structural and geochronological relationships and interpretations by Percival et al., (2004), Whalen et al., (2004), Stevenson et al., (1999), Henry et al., (1998), and others, deformation in the Wabigoon Subprovince peaked at ~ 2710 - 2700 Ma, when the Wawa subprovince collided with the Wabigoon subprovince to the north. At ~ 2690 Ma, the Lac des Iles Intrusive Complex, as well as the surrounding mafic/ultramafic intrusions (e.g. Tib Lake Intrusion) and sanukitoid intrusions were emplaced, representing late magmatism. Prior to these intrusions, magmatism was dominated by granitic/tonalite-trondhjemite-granodiorite (TTG) plutons as well as greenstone volcanic magmatism, the former interpreted to have formed either through direct melting of down-going slabs (e.g. Martin, 1986, 1999) or partial melting of

thickened, amphibole-rich lower crust (e.g. Whalen et al., 2002).

The parental magmas for the Mine Block Intrusion were derived through high degrees of partial melting. Supporting attributes include: a) relatively unfractionated REE patterns, and b) high MgO contents for calculated parental magmas (see Hinchey et al., 2005).

The level of crustal emplacement of the Lac des Iles Intrusive Complex is inferred by Watkinson and Dunning (1979) and Sutcliffe et al. (1989) who suggested crystallization temperatures for the complex ranging from 726 to 1100°C using the two pyroxene geothermometry by Wells (1977). Sutcliffe (1989) suggested that hornblende in the country rock tonalite for the Lac Des Iles Intrusive Complex formed at pressures between 3-5 kbar, which is equivalent to the depth of ~ 25 km. One hornblende from a hornblendite outside the Lac des Iles Intrusive Complex in Sutcliffe (1989) gives a pressure of ~7.2 kbar. The latter sample is devoid of quartz. According to the geobarometer of Hammarstrom and Zen (1986), the lack of equilibrium with quartz may yield anomalously high pressure estimates; therefore this sample was not incorporated in the discussion by Sutcliffe (1989). All other data from the study of Sutcliffe (1989) give pressure estimates of equal or less than 5 kbar, which agree well with the low degrees of greenschist facies metamorphism in the country rocks (e.g. Blackburn et al., 1991; Pettigrew and Hattori, 2002). The pressures reported in Brüggmann et al. (1997) are also from the analysis of Sutcliffe (1989) but appear to be misquoted as 5-8kbar. The high pressure estimates were used to infer that the crystallization of magmas occurred at the roots of volcanic arc complex at a depth of approximately 40 km.

We consider three possible tectonic settings for the partial melting of metasomatized mantle for the Lac des Iles Complex: a) the oceanic slab was broken off or delaminated following the collision of the Wawa and Wabigoon Subprovinces, allowing for hot asthenospheric mantle to upwell, b) a slab window was developed during subduction which would allow hot asthenospheric mantle to invade, or, c) a mantle plume

caused increased temperature gradients.

Delamination processes have been proposed for the production of the sanukitoid suite in the central Wabigoon Subprovince (Stevenson et al., 1999). Delamination is based on the idea that dense lower lithosphere founders into underlying less dense asthenosphere (e.g. Kay and Mahlburg-Kay, 1993). A caveat of the process is lithospheric mantle shortening, which aids in increasing density, which drives the delamination process. The delamination of oceanic lithosphere would allow hotter asthenospheric mantle to upwell into the vicinity of previously metasomatized Archean mantle wedge, causing adiabatic melting of the depleted mantle source. Similar processes would occur during slab-breakoff, a process involving detachment of oceanic lithosphere from continental lithosphere during continental collision (e.g. Davies and von Blanckenburg, 1995).

Slab windows are typically associated with the upflow of hot asthenospheric mantle into a gap in subducting plates (Dickinson and Snyder, 1979). This process could also potentially explain the geochemical characteristics observed at the Lac des Iles Intrusive Complex. If interpretations from earlier structural and geochronological studies in the central Wabigoon subprovince by Percival et al., (2004), Whalen et al., (2004), and others, are correct, and active subduction waned at ~ 2700 Ma, this process may be ruled out as a major contributor to the genesis of the abundant magmatism at 2680-2690 Ma. However, uncertainty in the exact timing of cessation of subduction leaves this mechanism open as a possibility. Additionally, subduction of a ridge is commonly accompanied by generation of adakitic-type magmas before the subduction of the ridge. The generation of such slab derived melts may suggest a slab-window environment for voluminous (~ 2718 Ma, Sanborn-Barrie and Skulski, 1999; e.g. during active subduction) niobium-enriched basalts in the Central Sturgeon Lake assemblage of the Wabigoon subprovince north of Lac des Iles (e.g. Wyman et al., 2000 and references therein).

The last proposed idea involves partial melting caused by heat from a mantle plume. The emplacement of a plume beneath the Wabigoon subprovince could explain the voluminous mafic magmas, potentially associated with rifting processes. However, the chemical signature observed at Lac des Iles with negative HFSE, high LILE, and S-undersaturated parental magmas suggest that the plume would only provide a thermal heat source for melting. In addition, the regional area surrounding Lac des Iles is devoid of any radiating dyke swarms commonly associated with mantle plume environments (Buchan and Ernst, 2004), questioning the possibility that such an environment existed.

Although the regional area lacks radiating dyke swarms typically associated with plume environments, there were some pre-existing fault zones prior to the intrusion of the Lac des Iles Intrusive Complex and surrounding intrusions. As pointed out by Stone et al. (2003), many of the mafic/ultramafic intrusions in the Lac des Iles area are spatially associated with northeast trending fault systems. Some intrusions were cut by the faults (e.g. Tib Lake), but at least the Mine Block Intrusion of the Lac des Iles Intrusive Complex appears to have intruded along the pre-existing Shelby Lake fault. Assuming that such a fault may have acted as a conduit for the emplacement of the Lac des Iles Intrusion, thereby acting as a mechanism for emplacement without substantial assimilation and fractional crystallization, either the delamination or slab break-off model may explain high degrees of partial melting and the observed chemistry. If subduction was ongoing during intrusion the slab-window model also remains a possibility.

4.4.3. Comparison to other ~2.69 Ga Intrusions and implications for PGE mineralization.

The Lac des Iles Intrusive Complex is commonly compared to other ~2690 Ma intrusions in the Wabigoon Subprovince, especially since the dramatic increase in PGE prices and associated increased exploration in recent years. Characteristics of the Lac des Iles mine are commonly focused on as exploration tools in the surrounding mafic/ultramafic intrusions. Although many of the surrounding intrusions share broad textural

and mineralogical characteristics with the Lac des Iles Intrusive Complex, significant differences are present. The immediate area surrounding the Lac des Iles Intrusive Complex is host to numerous mafic/ultramafic intrusions, commonly referred to during the PGE exploration boom as “the ring of fire” (Fig. 4-2). The larger intrusions, in addition to Lac des Iles, include Legris Lake, Tib Lake, and Buck Lake. Tib Lake most resembles Lac des Iles as both intrusions have been shown to be similar in age and both are dominated by mafic/ultramafic lithologies with similar textural relationships (e.g. presence of varitextured gabbro and heterogenous gabbro) (Smith and Sutcliffe, 1986; Smith, 1991; Lavigne and Michaud, 2001; Hinchey et al., 2005). However, although the Tib Lake Intrusion has been shown to contain sporadic PGE-Ni-Cu mineralization, no economic finds have yet been recorded. Although the margins of the Legris Lake Intrusion appear texturally similar to the Mine Block Intrusion (e.g. abundant brecciation; Pettigrew and Hattori, 2001, 2002), it appears to be much more evolved/fractionated than either the Lac des Iles Intrusion or the Tib Lake Intrusion (Fig.4-10). PGE mineralization is associated with leucogabbro in the Legris Lake Intrusion compared to melanocratic units at Lac des Iles and Tib Lake Intrusions.

Based upon high MgO, Ni, and Cr values, both the Lac des Iles Intrusive Complex and the contemporaneous sanukitoid suites of rocks were derived from high degrees of partial melting of a depleted mantle source. However, the sanukitoid bodies appear to represent much more fractionated magmas compared to Lac des Iles. Based on Pb and Nd isotopic studies, Henry et al. (1998) suggested that crustal assimilation was an important factor attributing to the chemical characteristics of the sanukitoid suites of rocks; suggesting that assimilation-fractional crystallization processes explain the major differences observed between the mafic/ultramafic intrusions and the sanukitoid suite of rocks. Higher average Mg numbers for Lac des Iles of 0.68 and 0.67 for the leucocratic and melanocratic lithologies respectively, compared to 0.65, 0.49, and ~ 0.50 for the mafic/ultramafic Tib Lake and Legris Lake intrusions and the sanukitoid suite of

intrusions, suggest increased fractionation in the latter intrusions.

Figure 4-10 displays $(\text{Ce/Yb})_{\text{CN}}$ versus $(\text{Nd})_{\text{CN}}$ of calculated parental magma compositions for the Mine Block Intrusion of Lac des Iles, Tib Lake Intrusion, Legris Lake Complex, and the sanukitoid suite of rocks (Roaring River and Norway lake). As observed, the Mine Block Intrusion displays a much more primitive, non-fractionated signature compared to the other intrusions. Interestingly, the late clinopyroxenite which was interpreted not to be co-genetic with the other lithologies in the Mine Block Intrusion plots very close to the Tib and Legris Lake Intrusions. As all the above mentioned intrusions are interpreted to have been intruded approximately contemporaneously in a relatively small area ($\sim 100\text{km}^2$), and as that they all display arc-like signatures suggesting that they were derived from a mantle that has been metasomatized by subduction processes, it can be assumed that they sampled a similar source material, with possible minor variations as discussed below. As such, the cause of the observed discrepancy in Figure 4-10 must be related to the conditions of degree of partial melting of the mantle source and/or assimilation-fractional crystallization processes. In terms of the Tib Lake Intrusion, due to its mafic/ultramafic nature, we suggest that its fractionated REE patterns are most likely related to either minor crustal assimilation processes which would increase the LREE in the parental magmas, or higher degrees of mantle metasomatism for its parental source through subduction processes. Other explanations for the fractionated REE patterns associated with the Tib Lake Intrusion include that the intrusion was located farther from the main heat pump than the Lac des Iles Intrusion or that the Tib Lake Gabbro was intruded during the waning stages of the high geothermal gradient associated with the delamination or plume influenced processes discussed above. However, the mafic/ultramafic nature of the rocks, as well as the relatively high MgO and high Mg-numbers for the Tib Gabbro argue against the latter possibilities as they would involve relatively low degrees of partial melting. In contrast, the fractionated characteristics of the Legris Lake and sanukitoid suite intrusions, including the fractionated REE (e.g.

Pettigrew 2004, Stevenson et al., 1999), relatively low Mg-numbers, and Nd and Pb isotopic studies on the sanukitoid suites (Henry et al., 1998), imply that their parental magmas been modified by fractional crystallization and crustal assimilation processes. These intrusions represent evolved fractions of the original parental magmas. In addition to crustal assimilation and fractional crystallization processes, lower degrees of partial melting may have also helped produce the observed fractionated REE patterns.

In order for potential PGE deposits to form from mafic/ultramafic intrusions, a number of requirements must be met, including: a) high degrees of partial melting of a mantle source (generally a depleted source) are required in order to liberate the PGE into the parental magmas , and b) the parental magmas must be intruded in a sulphur under-saturated state; suggesting that they intrude to the potential mineral deposit site without undergoing substantial assimilation at depth which could prompt sulphur saturation and lead to the stripping out of PGE (e.g. Hamlyn and Keays, 1986). Hamlyn and Keays (1986) emphasized the importance of second-stage magmas in the development of PGE deposits. They suggested that second-stage melting produces fertile magmas through melting of a previously depleted mantle source. The initial extraction of partial melts from a previously undepleted mantle source would remove the majority of mantle sulphide, but leave behind some sulphides enriched in PGE (e.g. Keays, 1995). Subsequent high degrees of partial melting of such a depleted mantle residue would effectively liberate the remaining PGE-rich sulphides and concentrate the PGE in the second stage parental magmas. Providing that the parental magmas do not experience substantial crustal assimilation or become sulphur saturated at depth, the potential for a PGE deposit exists. Based upon the above comparison between the Mine Block Intrusion of the Lac des Iles Intrusive Complex and surrounding intrusions, it appears as though only the Mine Block Intrusion has met these conditions, an observation reflected in the fact that it represents the only intrusion discovered to date in the southern Wabigoon that hosts economically mineable PGE mineralization.

4.5. Summary

Our detailed geochemical investigation of the southern Roby and Twilight zones of the Mine Block Intrusion of the Lac des Iles Intrusive Complex has highlighted several important aspects on the petrogenesis of the intrusion as well as highlighting some major differences between Lac des Iles and the surrounding ~2690 Ma intrusions. Within the Mine Block Intrusion, all lithologies with the exception of a late clinopyroxenite are cogenetic and were derived through high degrees of partial melting of a metasomatized depleted mantle source. As with all other surrounding intrusions, the Lac des Iles Intrusive Complex represents a late intrusion after greenstone formation.

The Lac des Iles Intrusive Complex, as well as the other surrounding mafic/ultramafic intrusions and the sanukitoid suite of intrusions, require a metasomatized mantle source to explain their geochemical attributes. Metasomatized mantle under an Archean subduction zone, such as that present below the Wabigoon subprovince at ~2690Ma, could provide such a source. However, the source of the heat required to produce the abundant magmatism at 2680-2690 Ma is problematical. We suggest that the depleted mantle may have been induced to undergo partial melting due to either delamination (or slab break off) processes or the influence of a mantle plume; both of which would lead to adiabatic melting of the sub-Wabigoon depleted mantle source via upwelling of hot asthenospheric mantle. If subduction was still ongoing at the time of intrusions, a slab-window environment could also explain the observations.

Although there are a number of mafic/ultramafic intrusions in the area surrounding Lac des Iles with apparently similar lithologies and textures as observed within the main Roby zone of Lac des Iles, they are interpreted to be derived from lower degrees of partial melting and/or were influenced by crustal assimilation processes compared to Lac des Iles. As such, Lac des Iles is interpreted to have been derived from a source close to a major heat source, and most likely intruded along a pre-existing zone of weakness allowing rapid ascent without substantial amounts of assimilation. We

suggest that further PGE exploration in the southern Wabigoon Subprovince should be directed towards finding primitive mafic/ultramafic intrusions with un-fractionated REE geochemical signatures.

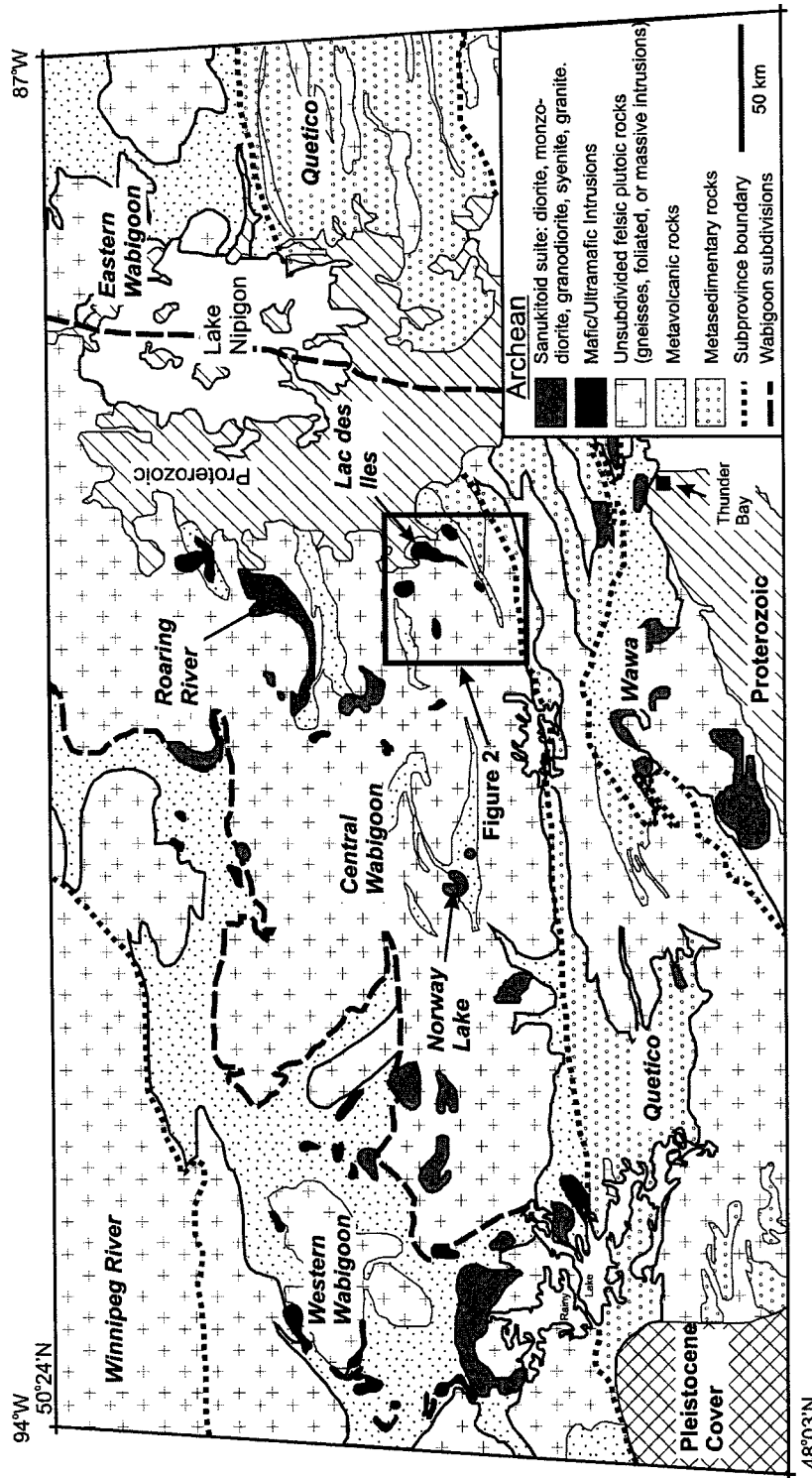


Figure 4-1. Regional geology of the western Superior province illustrating subprovince boundaries, subdivisions of the Wabigoon subprovince, and the locations of the abundant mafic/ultramafic intrusions and sanukitoid suites of rocks in the central Wabigoon subprovince. (Modified from Ontario Geological Survey, 1991, and Stern et al., 1989). Subprovince names are given in italics.

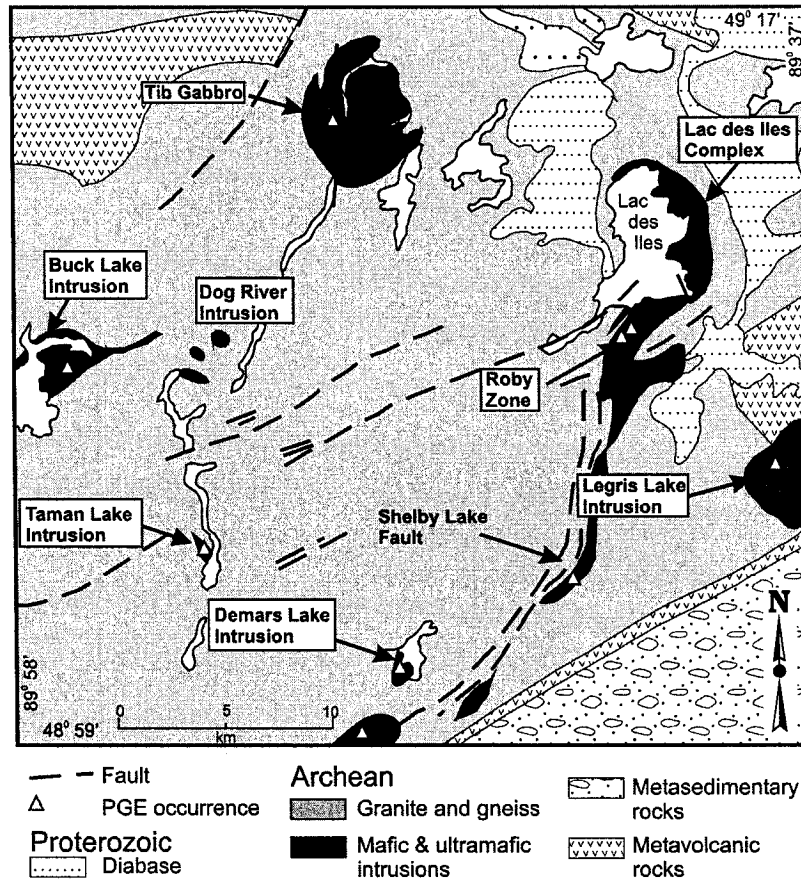


Figure 4-2. Regional geological map of the study area showing the positioning of mafic/ultramafic intrusions with PGE mineralization (modified after Sutcliffe and Smith, 1988). Note the positioning of the Tib Lake and Legris Lake intrusions with respect to the Lac des Iles Intrusive Complex.

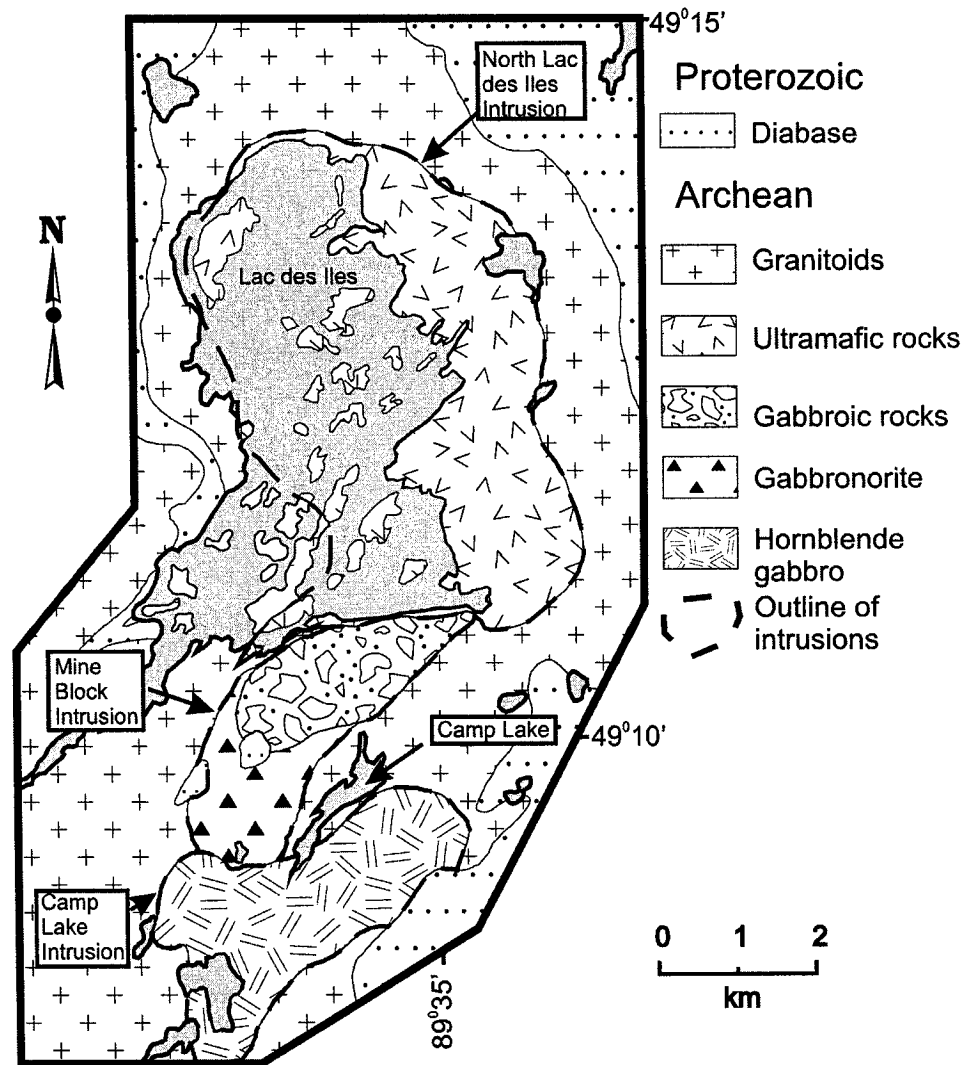


Figure 4-3. Geological map of the Lac des Iles Intrusive Complex displaying the locations of the North Lac des Iles, Mine Block, and Camp Lake Intrusions (modified after Sutcliffe et al., 1989). Note that the current study focuses on the Mine Block Intrusion, displayed in Figure 4.

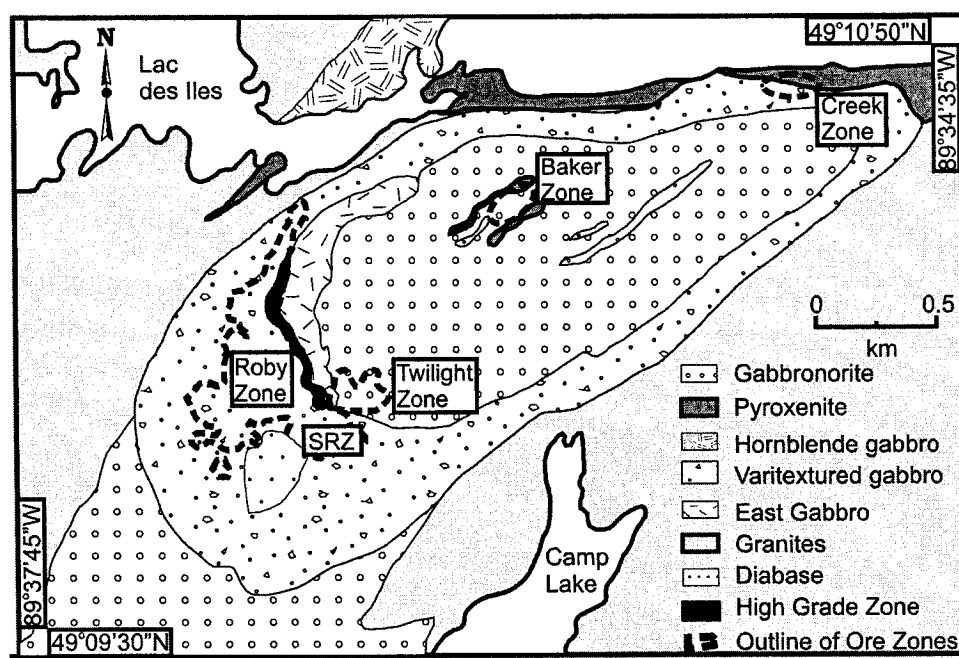


Figure 4-4. Simplified geological map of the Mine Block Intrusion of the Lac des Iles Intrusive Complex (modified after Sutcliffe and Sweeny, 1986), displaying the locations of the Roby, Twilight, and High Grade zones.

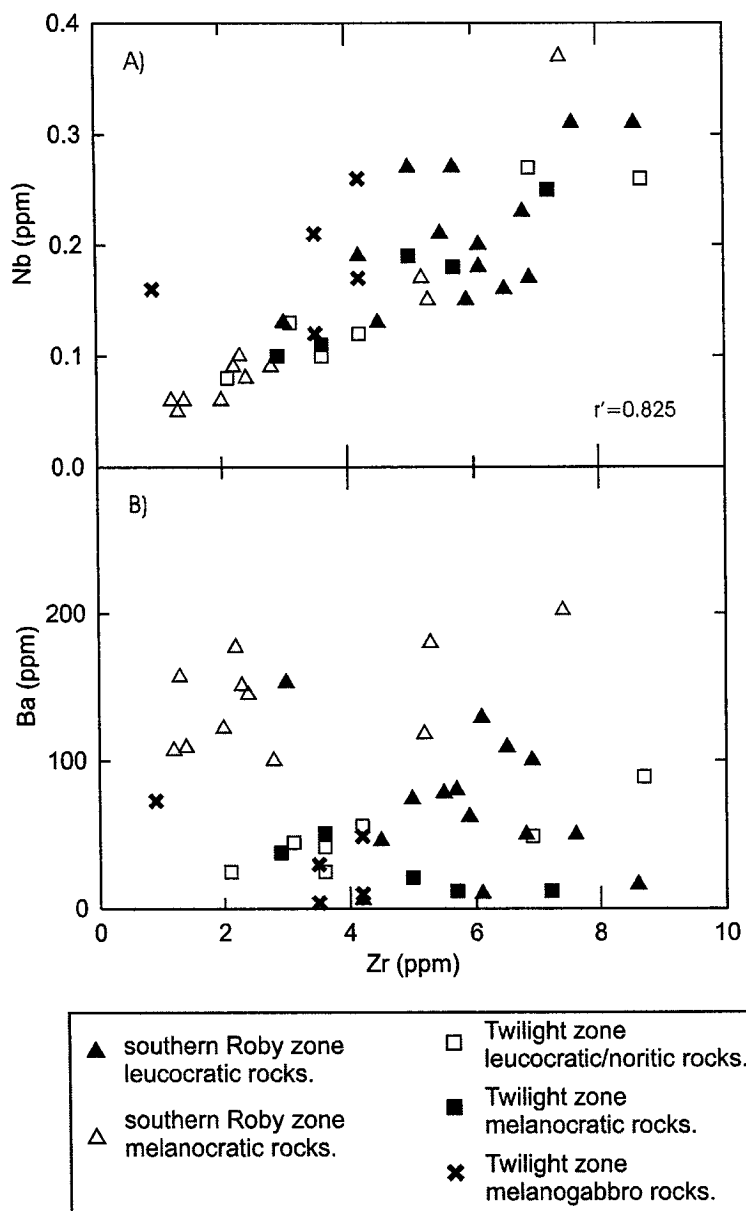


Figure 4-5. A) Plot of Zr vs. Nb for the rocks of the southern Roby and Twilight zones, excluding the late clinopyroxenite. Note the well defined positive correlation suggesting a cogenetic origin for all rocks. Spearman rank correlation coefficient (r') shown in the bottom right hand corner. B) Zr vs. Ba illustrating that Ba acted as a mobile element during alteration.

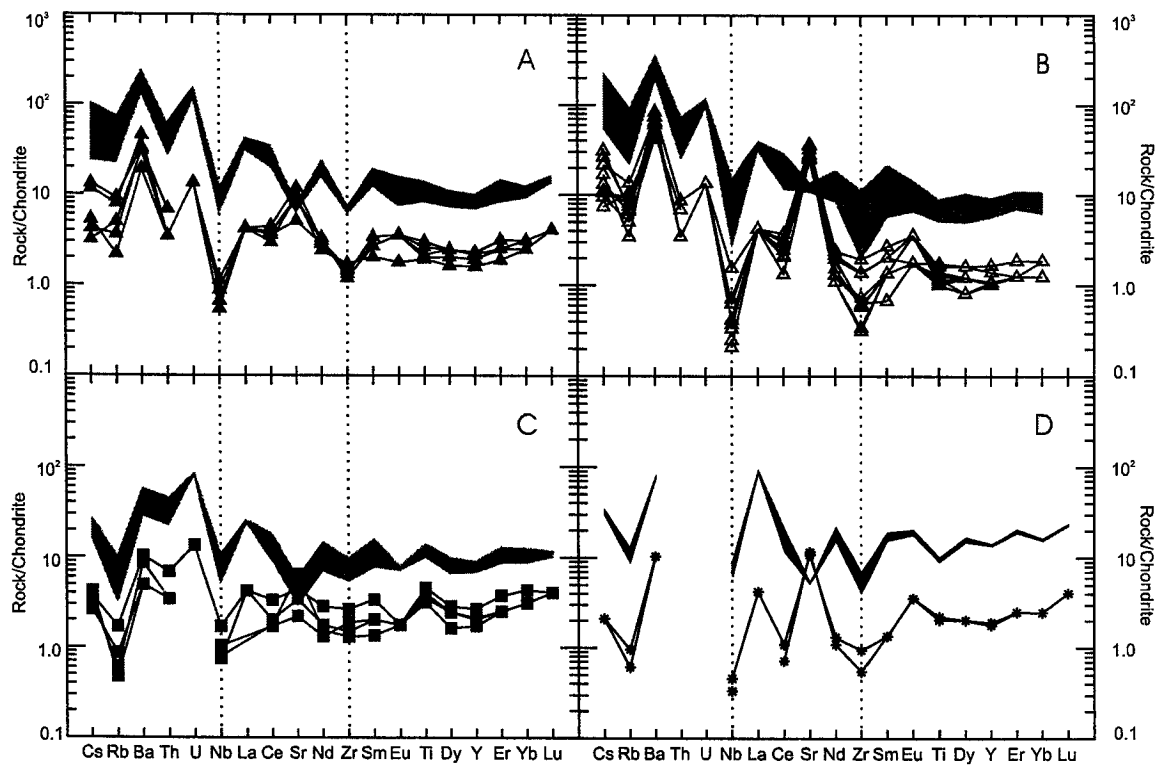


Figure 4-6. Chondrite-normalized multi-element diagrams for representative rock types from the southern Roby and Twilight zones. A) mineralized melanogabbro breccia from the southern Roby zone, B) leucocratic rocks from the southern Roby zone, C) mineralized melanonorite from the Twilight zone, and D) fine-grained gabbro from the Twilight zone. Note the low degrees of REE fractionation as well as the consistent increased LILE and negative HFSE anomalies in all rock types. Shaded areas represent parental magma compositions calculated following the method of Bédard (1994). The calculation used the CIPW normative minerals of plagioclase, clinopyroxene, orthopyroxene, olivine, magnetite, and ilmenite with the remaining being attributed to a trapped melt fraction. Concentrations of trace elements were calculated in various mineral phases through mass balance using bulk rock element concentrations, modal abundance of minerals, and partition coefficients of Bédard (1994) and Rollinson (1993). Chondrite values are from McDonough and Sun (1995). Some elements (e.g. Ta) are left out of plots as the concentrations approach the limits of detection.

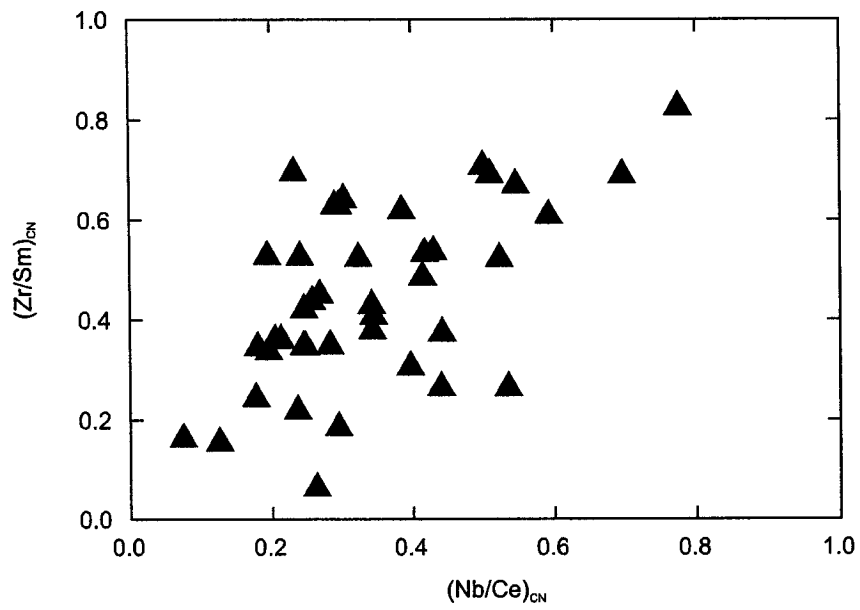


Figure 4-7. Plot of $(Nb/Ce)_{CN}$ vs. $(Zr/Sm)_{CN}$ for calculated parental magmas of all rock types in the southern Roby and Twilight zones. Note that all ratios plotted are <1 indicating negative HFSE patterns for all rock types.

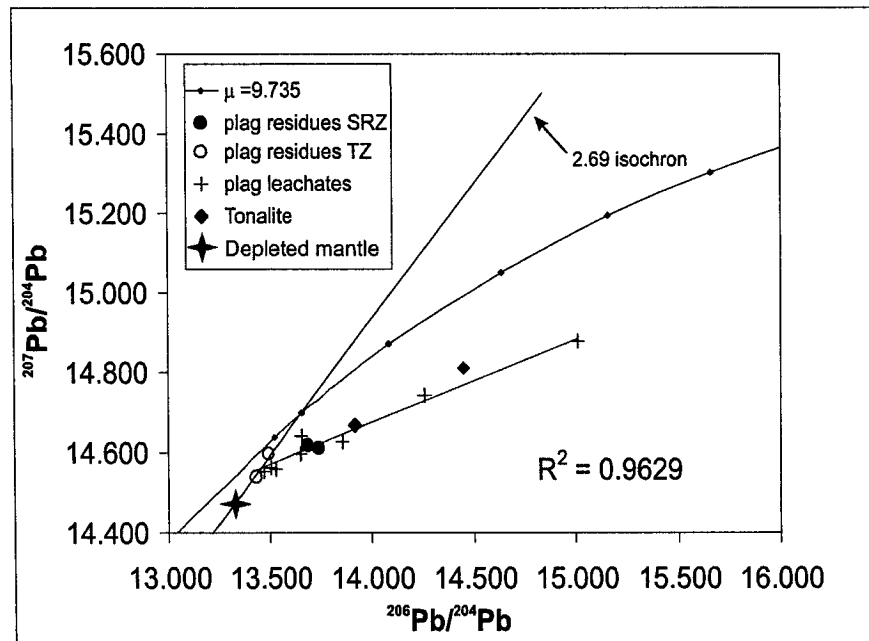


Figure 4-8. Plot of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ showing the distribution of lead isotopes from plagioclase residues and leachates from the Mine Block Intrusion, as well as the host tonalite. Also shown is the field of the depleted mantle (Dupre et al., 1984; Tilton and Kwon, 1990; and Carignan et al., 1995), and a 2.69Ga isochron. The two-stage Stacey and Kramer (1975) lead evolution curve ($\mu = 9.735$) is shown for reference. Note that the plagioclase residues from the Twilight zone plot on the 2.69Ga reference isochron and just above the depleted mantle values whereas the southern Roby zone residues as well as all leachates plot with more radiogenic values.

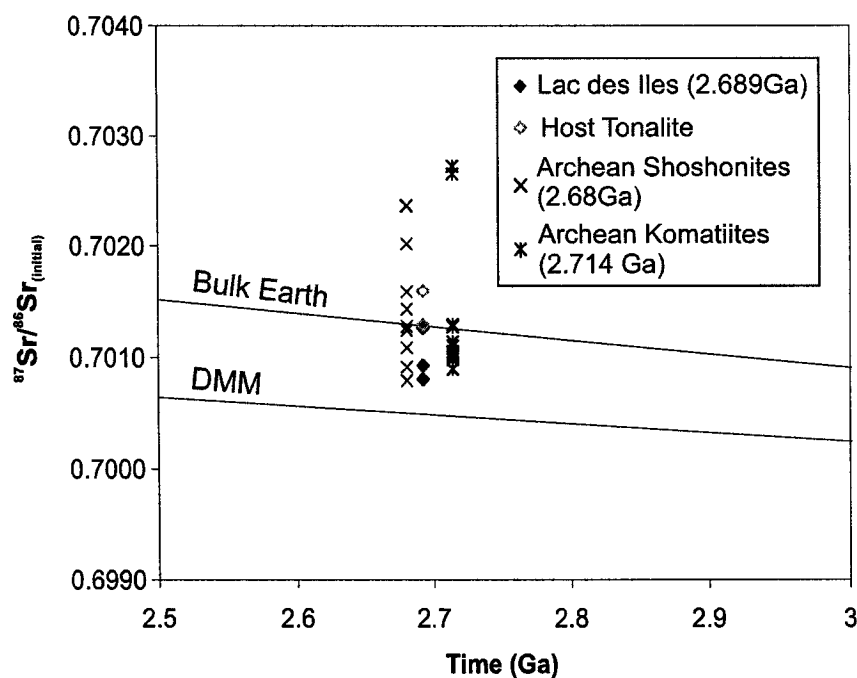


Figure 4-9. Plot of $^{87}\text{Sr}/^{86}\text{Sr}_{(\text{initial})}$ vs. time (Ga.). Data from this study are from plagioclase separates whereas data from Brüggmann et al., 1997 are from both bulk rock and mineral separates. The bulk earth evolution line (0.70455 of present day, 0.69897 at 4.6Ga) is from Rollinson 1993 and Faure and Mensing, 2005, and the depleted MORB mantle (DMM) evolution line (0.70263 at present day) is from Workman and Hart, 2005. Values of depleted mantle derived Archean shoshonites (2.68Ga) and Archean komatiites (recalculated to 2.714Ga. based on Jackson and Fyon, 1991) are from Hattori et al., 1996 and Machado et al., 1986 respectively.

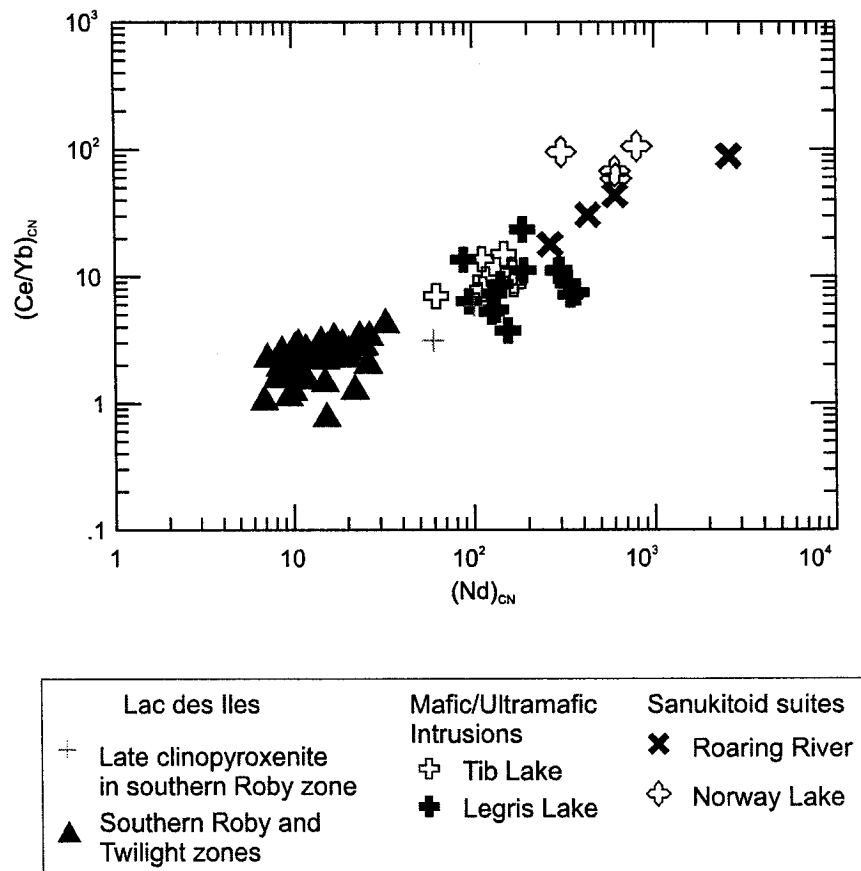


Figure 4-10. Plot of $(\text{Ce}/\text{Yb})_{\text{CN}}$ vs. $(\text{Nd})_{\text{CN}}$ for rocks from Lac des Iles as well as surrounding mafic/ultramafic intrusions (Tib Lake and Legris Lake Intrusions) and sanukitoid suites (Roaring River and Norway Lake Intrusions). Data for Tib and Legris Lake from McDougall (1990) and Pettigrew (2004) respectively, with data for Roaring River and Norway lake Intrusions from Stern et al. (1989) and Stevenson et al. (1999) respectively. Note that Lac des Iles is less fractionated than the other intrusions; interpreted to result from a combination of higher degrees of partial melting of a depleted mantle source for Lac des Iles and significant crustal assimilation and fractional crystallization processes associated with some of the other intrusions.

Table 4-1. Representative Whole-rock major and trace element compositions for Late des lites intrusion rocks.

Rock type Sample	Clinopyroxenite		Dark gabbro		Late Clinopyroxenite		Leucogabbro		Light Gabbro		Medium-grained Gabbro									
	JH02-061	JH02-081	JH02-089	JH02-138	JH02-008	JH02-023	JH02-037	JH02-140	JH02-144	JH02-146	JH02-151	JH02-091	JH02-114	JH02-012	JH02-051	JH02-136	JH02-141	JH02-145	JH02-079	JH02-121
Location	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ
Major (Wt.%)	50.03	48.20	50.43	47.84	49.04	49.62	48.54	47.58	49.70	48.43	50.79	51.23	51.97	52.08	49.27	51.58	51.42	51.26	50.58	49.53
SiO ₂	0.20	0.19	0.25	0.19	0.16	0.19	0.22	0.14	0.18	0.17	0.21	0.37	0.32	0.05	0.08	0.09	0.12	0.10	0.10	0.08
TiO ₂	5.83	7.30	7.11	5.97	8.98	10.11	10.80	10.43	10.81	10.76	11.64	6.71	9.55	24.62	25.04	18.02	17.39	17.47	19.99	19.95
Al ₂ O ₃	12.98	12.60	10.92	13.26	10.43	11.09	10.36	10.75	12.52	11.55	11.44	8.41	8.31	3.66	4.08	6.62	6.95	6.21	5.18	5.87
FeO _(total)	0.23	0.23	0.22	0.24	0.22	0.22	0.20	0.19	0.23	0.22	0.22	0.16	0.18	0.06	0.08	0.13	0.15	0.15	0.10	0.11
MnO	19.15	17.08	18.07	18.44	15.79	15.33	14.44	15.34	15.00	14.71	14.32	19.26	16.76	4.03	4.83	9.22	9.43	9.98	7.70	8.12
MgO	9.61	7.62	9.59	7.24	7.91	7.56	7.91	6.57	7.48	7.48	7.49	9.81	8.94	10.01	11.07	10.01	9.85	8.33	10.11	9.53
CaO	0.14	0.37	0.79	0.23	0.16	0.98	1.57	0.93	0.82	0.93	1.03	0.50	0.94	4.24	3.03	2.52	2.55	2.98	2.97	3.16
Na ₂ O	0.07	0.31	0.22	0.05	0.12	0.02	0.02	0.02	0.02	0.02	0.02	0.21	0.85	0.77	1.18	0.80	0.74	1.17	0.76	0.76
K ₂ O	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02
P ₂ O ₅	0.37	0.59	0.62	1.35	0.39	0.12	0.60	0.67	1.25	1.02	0.28	0.31	0.04	0.23	-1.00	0.08	0.01	0.06	0.05	0.07
S	3.47	2.93	3.60	3.52	2.83	2.42	2.73	2.68	3.81	3.95	3.14	3.42	3.15	1.28	1.58	2.14	2.10	1.81	1.17	1.58
LOI																				
Trace (ppm)																				
Sc	40.7	40.2	38.3	39.8	35.9	35.5	43.6	27	35.5	34.2	39.2	19.9	20.7	8.3	12.3	27.2	29.5	26.2	19.3	24.2
V	176	174	180	170	136	158	159	135	151	142	159	101	110	35	44	100	101	101	80	84
Cr	323	291	880	516	263	383	310	370	313	310	286	1360	1297	63	173	129	157	156	119	140
Co	132	118	128	151	97	82	98	114	139	128	89	77	60	41	32	49	46	42	39	48
Ni	1560	2020	1840	2080	816	616	974	1530	3090	3080	821	1160	762	668	482	294	352	285	398	336
Cu	1680	2250	2290	3430	660	420	1360	2390	3900	3440	820	880	180	860	80	190	200	140	390	280
Zn	61	70	475	166	55	52	109	56	89	48	70	352	77	87	33	47	45	53	43	32
Ga	8	12	11	11	11	12	11	11	15	11	15	15	15	22	11	17	15	17	18	18
As	0.4	1	1.5	0.2	1.5	0.4	0.5	0.4	1.3	0.2	0.8	1.5	1.7	1.7	2.1	2.4	1.4	1.9	1.9	2.2
Sb	0.7	8.7	4.2	1.7	5	11.4	8.3	18.2	17	29.4	20.2	5.6	22.8	5.6	7.9	24.3	21.7	31.1	15.2	17.3
Rb	6	23	38	7	62	66	37	69	68	64	111	100	187	303	256	202	204	203	264	231
Sr	2.2	2.6	5.1	3.1	3.6	3.4	3.5	2.5	2.7	2.5	3.6	6.9	5.6	0.5	1.7	1.7	2.2	1.7	1.6	1.6
Y	4.2	7.6	7.8	6.1	4.5	5	5.5	6.5	5.9	6.1	6.9	11.3	7.6	1.4	7.4	2.8	5.2	2.2	2.4	2.3
Zr	0.19	0.91	0.13	0.2	0.13	0.27	0.21	0.16	0.15	0.18	0.17	0.11	0.13	0.06	0.09	0.17	0.09	0.09	0.08	0.1
Nb	0.18	0.25	0.37	0.23	0.21	0.26	0.23	0.23	0.23	0.23	0.24	0.72	0.54	0.05	0.22	0.09	0.2	0.14	0.09	0.12
Pb	0.7	3.4	92.48	31.83	1.32	1.35	3.54	1.38	1.94	1.9	1.25	121.55	1.24	3.68	1.73	1.46	1.03	3.05	1.2	1.24
Th	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	0.25	<0.1	<0.1	<0.1	0.1	0.1
U	<0.1	0.1	0.1	<0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	0.1
Cs	0.2	0.9	0.8	1.2	1	0.6	0.8	2.2	2.1	3	1.9	0.8	1.4	2.4	3.2	1.4	2	4.1	2.5	5
Ba	6	50	57	10	46	74	78	109	62	129	100	74	165	109	202	100	118	177	145	151
Se	4.3	5.3	4.6	9	2	0.6	2.9	5.6	5.6	2	10.5	1.9	-	-	-	-	-	-	-	-
Te	0.69	1.84	1.43	2	0.21	0.18	0.5	1.49	-	2.46	0.74	-	-	-	-	-	-	-	-	-
Bi	0.29	1.25	0.42	0.35	0.12	0.07	0.11	0.38	0.43	0.4	0.13	0.26	<0.04	0.07	0.21	<0.04	<0.04	<0.04	0.06	<0.04
REE (ppm)																				
La	<1	1	1	<1	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	1
Ce	0.89	1.34	1.98	1.2	2.36	2.33	2.19	1.82	1.76	1.9	2.27	5.57	3.56	1.05	2.3	1.32	1.82	1.51	1.26	1.95
Pr	0.2	0.4	0.4	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.4	1.3	0.8	0.1	0.3	0.2	0.3	0.2	0.2	0.3
Nd	0.6	0.8	1.9	0.7	1.5	1.4	1.3	1.1	1	0.9	1.4	7.2	4.8	0.4	1.1	0.6	0.9	0.7	0.6	0.9
Sm	0.2	0.3	0.8	0.3	0.3	0.4	0.3	0.3	0.3	0.3	0.4	2.4	1.6	0.1	0.4	0.2	0.3	0.2	0.1	0.2
Eu	0.1	0.1	0.3	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.2	0.6	0.6	0.2	0.2	0.1	0.2	0.2	0.1	0.2
Gd	0.2	0.4	0.9	0.4	0.6	0.5	0.5	0.3	0.4	0.4	0.5	2	1.7	0.1	0.4	0.3	0.4	0.3	0.3	0.3
Tb	<1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.4	0.2	<1	0.1	0.1	0.1	<1	<1	0.1
Dy	0.4	0.3	0.8	0.5	0.6	0.6	0.6	0.4	0.5	0.4	0.6	1.5	1.2	0.1	0.3	0.3	0.4	0.3	0.3	0.2
Ho	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.2	<1	0.1	0.1	0.1	0.1	<1	<1
Er	0.3	0.3	0.5	0.3	0.5	0.4	0.5	0.3	0.3	0.4	0.4	0.7	0.5	<1	0.2	0.2	0.2	0.2	0.2	0.2
Tm	<1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<1	0.1	0.1	<1	<1	<1	<1	<1	<1	<1	<1
Yb	0.3	0.3	0.6	0.4	0.5	0.5	0.5	0.4	0.4	0.3	0.4	0.6	0.6	0.1	0.2	0.2	0.3	0.3	0.2	0.2
Lu	0.1	<1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<1	<1	<1	<1	<1	<1	<1
CeYb _{tot}	0.78	1.17	0.87	0.79	1.24	1.22	1.15	1.20	1.16	1.66	1.49	2.44	1.58	2.76	3.02	1.73	1.68	1.32	1.65	2.56

Notes: Major elements, Ni, Zn, Co, Cr, Ga, and V data by X-ray fluorescence; S data by elemental analyzer; LOI data determined after heating samples to 1,000°C for over 1 hr; Cu, Pb, As, Bi, Se, and Te data by aqua regia digestion with inductively plasma mass spectrometry; all other trace element data by four acid inductively coupled mass spectrometry.
SRZ = southern Roby zone, TZ = Twilight zone, LOI = loss on ignition, - = not analyzed, FeO(total) = total Fe expressed as FeO; normalizing values from McDonough and Sun (1995).

Table 4-1 continued.

Rock type	Varifexured Gabbro			Leuconite			Melanogabbro			Melanonorite			Norite			Fine-grained Gabbro			
	JH02-006	JH02-016	JH02-130	JH02-172	JH02-177	JH02-183	JH02-157	JH02-186	JH02-195	JH02-202	JH02-173	JH02-181	JH02-184	JH02-185	JH02-214	JH02-159	JH02-165	JH02-167	
Location	SRZ	SRZ	SRZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	
Major (Wt.%)																			
SiO ₂	50.12	51.45	50.64	45.30	50.40	49.83	50.70	50.16	49.08	51.03	51.25	50.94	50.73	46.57	50.35	49.47	51.68	50.44	51.10
TiO ₂	0.07	0.07	0.13	0.20	0.21	0.15	0.21	0.21	0.26	0.28	0.26	0.26	0.34	0.23	0.29	0.19	0.25	0.16	0.15
Al ₂ O ₃	17.00	17.15	16.27	16.34	19.57	19.85	13.50	12.83	6.07	7.44	5.04	5.30	15.92	6.02	3.19	13.27	11.89	15.90	16.71
FeO (total)	6.22	5.61	6.95	9.49	8.21	7.73	10.23	10.23	14.74	14.05	16.53	16.65	9.57	15.34	17.71	10.61	12.53	8.52	7.71
MnO	0.13	0.12	0.12	0.14	0.13	0.12	0.17	0.26	0.26	0.25	0.24	0.26	0.15	0.23	0.28	0.18	0.21	0.16	0.16
MgO	9.68	9.45	9.16	10.51	8.58	8.86	17.55	14.54	18.36	18.20	20.39	19.20	12.97	18.04	21.45	14.28	14.60	12.32	10.73
CaO	10.52	11.66	11.07	8.37	10.29	10.35	5.09	7.48	5.61	5.05	3.81	4.95	8.43	4.22	2.93	7.09	7.07	9.91	11.40
Na ₂ O	2.37	2.29	2.71	1.60	2.01	1.91	0.63	1.28	0.13	0.21	0.33	0.38	1.36	0.47	1.24	1.20	1.52	1.72	1.72
K ₂ O	0.49	0.71	0.69	0.12	0.19	0.24	0.18	0.67	0.03	0.05	0.06	0.11	0.11	0.06	0.06	0.19	0.18	0.09	0.11
P ₂ O ₅	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02
S	0.07	0.06	0.47	0.79	0.18	0.12	0.09	0.04	0.27	0.01	0.57	0.67	0.10	0.76	0.87	0.03	0.10	0.06	0.08
LOI	0.85	1.05	1.74	-0.18	0.25	0.77	2.98	3.23	3.46	3.54	1.80	1.41	0.35	0.60	0.42	0.07	0.65	1.27	1.09
Trace (ppm)																			
Sc	27.3	29.1	31.6	20.1	10.7	21.1	35.9	29.5	24.7	44.5	44.1	45.9	24.1	40	44	27.7	30	26	26.8
V	97	108	130	141	135	118	194	180	213	216	235	251	138	219	247	157	168	240	229
Cr	215	154	147	350	318	297	623	485	574	515	683	598	453	586	607	519	435	471	471
Co	54	45	65	81	54	50	100	78	119	108	143	136	74	143	166	78	86	56	43
Ni	333	340	889	1100	464	417	529	538	827	589	1740	1390	532	2190	2310	467	481	216	223
Cu	110	130	1390	2840	130	540	200	120	720	870	2270	1810	410	3280	3120	60	80	2500	100
Zn	37	35	48	64	62	60	88	71	89	89	105	105	61	100	118	77	92	57	51
Ga	15	14	15	16	18	19	14	16	12	14	11	12	14	12	13	16	15	16	16
As	1.6	2.1	1.3	1.6	2.4	2.3	2.3	2.4	<1	1.6	0.6	0.4	1.4	<1	<1	1	2.4	1.6	2.1
Rb	11.5	18.6	15.8	2.9	4.4	4.6	5.3	19.4	0.7	2.2	1.1	3.9	3.3	1.4	2	5.5	4.6	1.4	2.2
Sr	194	182	187	183	240	216	69	126	7	13	25	32	142	2.7	16	136	126	79	84
Y	1.7	1.7	2.6	2.5	2.4	2	2.5	2.8	3.5	4.2	3.3	4.2	2.1	2.7	2.2	2.2	2.9	3.6	3
Zr	1.2	1.3	5.3	3.1	50.2	4.2	3.5	0.9	3.5	4.2	5.7	10.1	2.9	5	7.2	3.6	6.9	2.8	2.1
Nb	0.06	0.05	0.15	0.13	0.21	0.16	0.17	0.16	0.21	0.26	0.18	0.41	0.11	0.19	0.25	0.17	0.27	0.11	0.08
Hf	0.08	0.08	0.21	0.18	0.19	0.16	0.17	0.2	0.2	0.2	0.21	0.41	0.11	0.21	0.28	0.17	0.28	0.12	0.08
Pb	0.51	0.41	2.48	2.88	36.44	2.03	0.88	1.56	0.43	0.59	0.87	0.69	0.67	1.9	0.91	0.61	0.63	3.58	0.93
Th	<0.1	<0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
U	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.4	0.4
Cs	1.8	2.1	5.9	0.5	0.7	0.6	1.2	1	0.5	0.9	0.8	0.7	0.8	0.6	0.5	0.9	1.2	0.4	0.4
Ba	107	157	180	45	68	56	30	73	4	10	12	25	38	21	12	42	49	25	25
Se	0.3	0.3	3.3	6	-	-	-	-	1.5	-	4.9	3.8	-	7.7	7.8	<1	-	-	-
Te	0.13	0.02	0.23	1.22	-	-	-	-	0.42	-	1.17	0.8	-	1.52	<0.2	<1	-	-	-
Bi	0.03	0.04	0.06	0.23	4.39	0.06	<0.04	0.07	0.41	0.51	0.2	0.28	<0.04	0.2	0.2	<0.2	<0.04	0.21	0.08
REE (ppm)																			
La	<1	1	1	1	28	2	1	<1	1	1	1	1	1	<1	<1	1	1	1	<1
Ce	0.81	0.82	1.83	2.23	2.98	1.91	1.3	2.11	1.52	1.79	1.23	2.04	1.25	1.09	1.04	1.33	2.17	0.67	0.44
Pr	0.1	0.1	0.2	0.3	0.4	0.3	0.2	0.3	0.2	0.3	0.2	0.3	0.2	0.1	0.2	0.2	0.3	0.1	0.1
Nd	0.5	0.5	1	1.2	1.6	1.1	0.8	1.2	1	1	0.8	1.3	0.7	0.7	0.6	0.7	1.4	0.6	0.5
Sm	0.2	0.2	0.3	0.3	0.4	0.3	0.3	0.4	0.4	0.4	0.3	0.5	0.2	0.2	0.3	0.2	0.4	0.2	0.2
Eu	0.1	0.1	0.1	0.2	0.3	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
Gd	0.2	0.3	0.4	0.4	0.5	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.7	0.2	0.3	0.4	0.5	0.4	0.4
Tb	0.1	<1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<1	0.1	0.1	0.1	0.1	0.1	0.1
Dy	0.2	0.3	0.4	0.4	0.4	0.4	0.4	0.5	0.6	0.5	0.6	0.7	0.3	0.4	0.6	0.4	0.5	0.5	0.5
Ho	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Er	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.4	0.6	0.2	0.4	0.4	0.3	0.4	0.4	0.4
Tm	0.2	<1	0.1	<1	<1	<1	<1	<1	<1	0.1	0.1	0.1	<1	0.1	<1	<1	0.1	0.1	0.1
Yb	0.2	0.2	0.3	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.7	0.2	0.5	0.5	0.3	0.4	0.4	0.4
Lu	<1	<1	<1	<1	<1	<1	0.1	0.1	0.1	0.1	0.1	0.1	<1	<1	0.1	0.1	0.1	0.1	0.1
Ce/Yb Cn	1.06	1.08	1.60	1.95	2.51	1.57	0.85	1.39	0.80	0.94	0.65	0.77	1.64	0.57	0.55	1.16	1.42	0.44	0.29

Table 4-2. Lead isotope compositions of plagioclase feldspar from the southern Roby and Twilight zones, Mine Block Intrusion, Lac des Iles Intrusive Complex, and feldspar from the country rock tonalite.

Sample No.	Zone	Mineral	Fraction	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	
JH-02-151	SRZ	Plagioclase	A	L1	14.261	14.741	34.046
			L2	13.527	14.559	33.33	
			L3	13.651	14.595	33.465	
			L4	13.858	14.628	33.631	
SRZ	Plagioclase	B	R	13.687	14.618	33.516	
		C	R* after L4	15.001	14.877	34.715	
		A	R after L4	13.742	14.61	33.518	
JH-02-185	TZ	Plagioclase	A	L1	13.661	14.641	33.536
			L4	13.466	14.554	33.258	
JH-02-214	TZ	Plagioclase	B	R	13.433	14.539	33.218
			A	R* after L4	13.502	14.564	33.299
JHC-03-91	Tonalite	Plagioclase	A	R after L4	13.489	14.598	33.33
JHC-03-92	Tonalite	Plagioclase	A	R after L4	13.925	14.668	33.563
			A	R after L4	14.43	14.81	33.641

Fractions represent different grains from a single batch of crushed rock.

L1 = leach 1, L2 = leach 2, L3 = leach 3, L4 = leach 4, L5 = leach 5, R = residue,

R* extracted with 8:1 mixture of 5% HF and 8N HNO₃ at 50°C

The leaching steps are described in Analytical Method.

SRZ = southern Roby zone, TZ = Twilight zone

Table 4-3: Rb-Sr data from the Lac des Iles Intusive Complex and country rock tonalite.

Sample No.	Type	Sample area	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}(i)$ 2689 Ma
JH-02-185	Plagioclase	MBI	4.6	539.9	0.025	0.701876	0.700920
LDI-08	Gabbro	MBI	8.2	355	0.067	0.706919	0.701258
LDI-73	Diorite	NUM	18.7	965	0.056	0.702973	0.700789
JHC-03-091	Tonalite	Country rk.	3.8	562	0.019	0.702320	0.701562
JHC-03-092	Tonalite	Country rk.	3.2	464.2	0.02	0.702052	0.701280

Note: data for samples LDI-08 and LDI-73 from Brüggmann et al.(1997).

MBI = Mine Block Intrusion; NUM = Northern Ultramafic Intrusion; Country rk. = Country tonalite.

Chapter 5

Conclusions

The Lac des Iles Intrusive Complex hosts the Pd-producing Lac des Iles mine in Canada. The intrusive complex represents one of many ~2680-2690 Ma. mafic/ultramafic intrusions in the central Wabigoon subprovince. Palladium mineralization in the main Roby zone of the Lac des Iles deposit was introduced by late melanocratic magmas. High Pd concentrations and high Pd/Pt ratios are explained by segregation of sulphides from early leucocratic rocks and the incorporation of this sulphide by later melanocratic magmas. Palladium is controlled by magmatic sulphides whereby PGE were concentrated in an immiscible sulphide melt. The High Grade zone is intensely altered and displays evidence suggesting enrichment of Pd by hydrothermal fluids during the intrusion.

All of the ~2680-2690 Ma. mafic/ultramafic intrusions in the central Wabigoon subprovince display so-called arc geochemical signatures with negative HFSE anomalies and enrichment of LILE. However, compared to the other intrusions, the Lac des Iles Intrusive Complex displays relatively non-fractionated REE. The data suggests that the other intrusions either experienced lower degrees of partial melting or were substantially influenced by crustal assimilation during intrusion. We suggest the former based on high Mg-numbers for many of the intrusions.

Chapter 1:

Detailed mapping within the southern Roby and Twilight zones at Lac des Iles identified multiple intrusions of gabbroic rocks. In both zones early intrusions were dominated by barren leucocratic rocks with late PGE-bearing melanocratic rocks. All rocks, with the exception of a very late clinopyroxenite at the southern Roby zone appear co-magmatic and were derived through high degrees of partial melting of a depleted

mantle. Positive correlations between sulphur versus base and precious metals, as well as common exsolution textures associated with sulphides, suggest that the PGE were concentrated in immiscible sulphide melt in the parental magmas.

The origin of the Lac des Iles deposit has always been considered problematical due to the extremely high Pd and Pd/Pt ratios (~8-10) of the deposit. Detailed geochemical investigations revealed that the early leucocratic rocks had undergone a previous episode of sulphide segregation as identified by high Cu/Pd ratios. The segregated sulphide melt most likely ponded either at the base of the chamber or in a conduit. Subsequent intrusion of melanocratic magmas were sulphur-undersaturated, and incorporated the sulphide melt and raised the Pd tenor of the ore.

The Lac des Iles deposit has commonly been compared to contact-type PGE deposits. However, lack of evidence for crustal assimilation at the Lac des Iles deposit argues against such a comparison. In addition, unlike contact-type deposits which are located near the contacts with country rocks, the Lac des Iles deposit is situated in the center of the Mine Block Intrusion. Based upon the good correlation of the Pd mineralization with the late melanocratic rock types, it is suggested that the deposit formed in a manner analogous to large layered intrusions where the bulk of the mineralization is introduced by pulses of fertile, primitive magmas. The intrusion at Lac des Iles was energetic and dynamic causing brecciation and magma mingling, whereas the environment for large deposits associated with layered intrusions is more quiescent.

Chapter 2:

Compared to the southern Roby and Twilight zones, the High Grade zone is intensely altered throughout with all primary silicates and sulphides replaced by secondary minerals. Two mineral assemblages are identified consisting of a) pyrite ± chalcopyrite associated with chlorite + actinolite ± albite ± quartz ± carbonate, and b) millerite + siegenite ± pyrite ± chalcopyrite associated with an assemblage of hornblende

+ plagioclase \pm quartz \pm carbonate.

The High Grade zone shows increased Pd tenors and Pd/Pt ratios compared to the southern Roby and Twilight zones. The High Grade zone sulphides of pyrite, millerite, and siegenite are generally considered to be of low-temperature origin. The High Grade zone displays positive correlations between relatively non-mobile elements such as Se, Ni and Te. The correlations overlap with the trends for the southern Roby and Twilight zones. The High Grade zone also shows large scatters on plots involving more mobile elements, such as Pd. Data suggest that primary magmatic mineralization was upgraded by hydrothermal processes where fluids were derived from the fertile mafic parental magmas of the Roby zone. Ore tenors were upgraded to a maximum of 48 ppm Pd during the hydrothermal activity.

Chapter 3:

Different Pb isotope signatures of plagioclase and sulphide from individual samples from the southern Roby and Twilight zones, as well as higher radiogenic Pb isotope signatures for sulphide in all zones, suggest that the sulphide melt acquired radiogenic isotopes. The data suggest that the sulphide melt acquired a high radiogenic isotopic component prior to being incorporated into the same magmas as the plagioclase.

The results agree with the model of ore formation proposed in Chapter one whereby early leucocratic intrusions segregated a sulphide melt in the base of the Lac des Iles chamber. Modeling suggests that hydrothermal fluids derived by the heat of the intruding igneous complex may have leached radiogenic ^{206}Pb , ^{207}Pb , and ^{208}Pb from older (~ 2750 Ma) country rock. As the sulphide melt was sitting close to the contact with the country rock, they were preferentially influenced and enriched in a radiogenic isotopic component. The model serves to explain the Pb isotopic compositions as well as the high Pd tenor and Pd/Pt ratios of the ore at Lac des Iles.

Chapter 4:

Within the Mine Block Intrusion of the Lac des Iles Complex, all lithologies except a late clinopyroxenite are cogenetic and were derived from high degrees of partial melting of a depleted mantle source. The Lac des Iles Intrusive Complex, as well as the surrounding mafic/ultramafic and sanukitoid suite intrusions, display geochemical characteristics (e.g. negative HFSE and enriched LILE) suggesting that they were all derived from a mantle source that had been metasomatized by subduction.

There are several possible tectonic settings to explain the required high degrees of partial melting. If the intrusions are post-subduction, high degrees of partial melting may have been attained during delamination/slab breakoff of the subducted oceanic crust, or rise of a mantle plume. Both possibilities would allow the upwelling of hot asthenospheric mantle. Alternatively, if the intrusions occurred during subduction, a slab window environment could explain the high degrees of partial melting.

The Lac des Iles Intrusive Complex differs from the surrounding intrusions in that it displays relatively non-fractionated REE. The data suggest that the other intrusions either experienced lower degrees of partial melting than Lac des Iles, or that they underwent crustal assimilation processes during intrusion; both of which could be detrimental to the formation of a PGE deposit. Regional mapping by Stone et al.,(2003) suggests that unlike the other intrusions which are cut by faults, the Mine Block Intrusion of the Lac des Iles Intrusive Complex appears to have intruded along the pre-existing Shelby Lake fault; providing a mechanism for ascent without substantial crustal assimilation. Due to the differences highlighted in this study, we suggest that further PGE exploration in the southern Wabigoon subprovince should be directed towards finding primitive mafic/ultramafic intrusions with un-fractionated REE signatures.

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APPENDIX I

Sample Locations

Sample #	Zone	Rock Type	Easting*	Northing*	DDH/open pit
JH-02-006	SRZ	Varitextured Gabbro	105205	104265	
JH-02-008	SRZ	Melanogabbro	105209	104269	
JH-02-012	SRZ	Leucogabbro	105200	104245	
JH-02-016	SRZ	Varitextured Gabbro	105215	104270	
JH-02-023	SRZ	Melanogabbro	105223	104274	
JH-02-037	SRZ	Melanogabbro	105242.5	104262	
JH-02-051	SRZ	Leucogabbro	105300	104275	
JH-02-061	SRZ	Clinopyroxenite	105318	104243.5	
JH-02-062	SRZ	Clinopyroxenite	105313	104257.5	
JH-02-079	SRZ	Medium Grained Gabbro	105312.5	104215.5	
JH-02-081	SRZ	Clinopyroxenite	105307	104222	
JH-02-089	SRZ	Clinopyroxenite	105320	104199	
JH-02-091	SRZ	Late Clinopyroxenite	105335	104200	
JH-02-095	SRZ	Pegmatite	105336.5	104192	
JH-02-114	SRZ	Late Clinopyroxenite	105300	104185	
JH-02-121	SRZ	Medium Grained Gabbro	105335.5	104117	
JH-02-130	SRZ	Varitextured Gabbro	105367	104158	
JH-02-136	SRZ	Light Gabbro	105375.5	104135.5	
JH-02-138	SRZ	Clinopyroxenite	105356.5	104116	
JH-02-140	SRZ	Melanogabbro	105367	104127.5	
JH-02-141	SRZ	Light Gabbro	105370	104130	
JH-02-144	SRZ	Dark Gabbro	105380	104125	
JH-02-145	SRZ	Light Gabbro	105370	104117.5	
JH-02-146	SRZ	Dark Gabbro	105375	104120	
JH-02-148	SRZ	Dark Gabbro	105385	104120	
JH-02-151	SRZ	Dark Gabbro	105385	104100	
JH-02-157	TZ	Melanogabbro	105982	104865	
JH-02-159	TZ	Norite	105985	104895	
JH-02-165	TZ	Norite	106055	104870	
JH-02-166	TZ	Fine Grained Gabbro	105980	104820	
JH-02-167	TZ	Fine Grained Gabbro	105975	104820	
JH-02-172	TZ	Leuconorite	105941	104800	
JH-02-173	TZ	Melanonorite	105944	104800	
JH-02-174	TZ	Melanonorite	105946	104800	
JH-02-177	TZ	Leuconorite	105967	104800	
JH-02-181	TZ	Melanonorite	105965	104790	
JH-02-183	TZ	Leuconorite	105957	104782	
JH-02-184	TZ	Melanonorite	105940	104780	
JH-02-185	TZ	Melanonorite	105935	104780	
JH-02-186	TZ	Melanogabbro	105940	104770	
JH-02-195	TZ	Melanogabbro	105990	104755	
JH-02-202	TZ	Melanogabbro	105930	104715	
JH-02-214	TZ	Melanonorite	105978	104637	
JH-02-SZ1	HGZ	pyroxenite/melanogabbro			phase 3 open pit
JH-02-SZ2	HGZ	pyroxenite/melanogabbro			phase 3 open pit
JH-02-SZ3	HGZ	pyroxenite/melanogabbro			phase 3 open pit
JH-02-SZ4	HGZ	pyroxenite/melanogabbro			phase 3 open pit
JHC-02-035	HGZ	pyroxenite/melanogabbro			DDH-02-086, 420.95 m.
JHC-03-050	HGZ	pyroxenite/melanogabbro			DDH-02-085, 448.5 m.
JHC-03-063	HGZ	pyroxenite/melanogabbro			DDH-02-008, 532.2 m.
JHC-03-070	HGZ	pyroxenite/melanogabbro			DDH-02-017, 685.2 m.
JHC-03-091	Tonalite	Tonalite			DDH NL-03-003, 28.8 m.
JHC-03-092	Tonalite	Tonalite			DDH NL-03-003, 188.0 m.

SRZ = southern Roby zone, TZ = Twilight zone, HGZ = High Grade zone

DDH = diamond drill hole

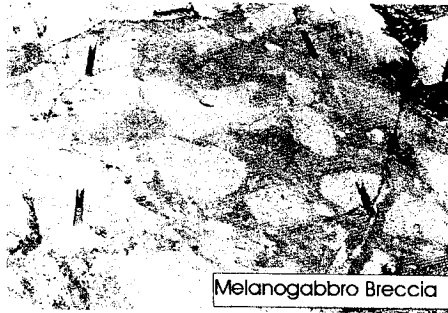
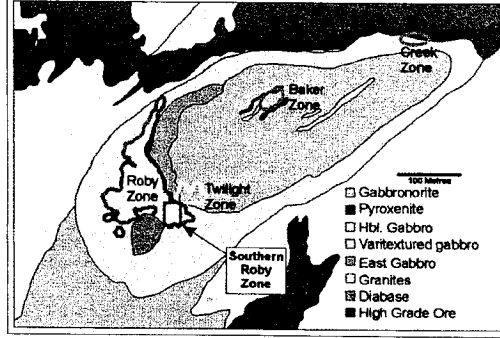
Easting and Northing refer to North American Palladium Ltd. Imperial Grid.

**Map 1.
Geology map of the southern
Roby Zone, Lac des Iles
Intrusive Complex,
northwestern Ontario.**

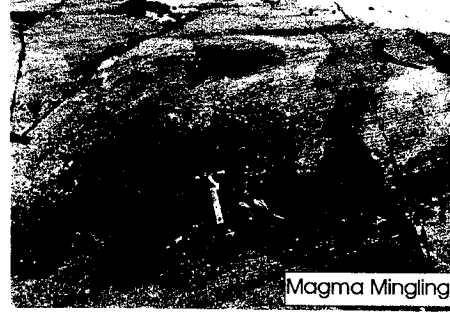
Mapping by J.G. Hinchey, 2002, 2003
Scale 1:60

Mine Block Intrusion map modified
after Sutcliffe and Sweeney, 1986.
Coordinates refer to North American
Palladium Imperial Mine Grid.

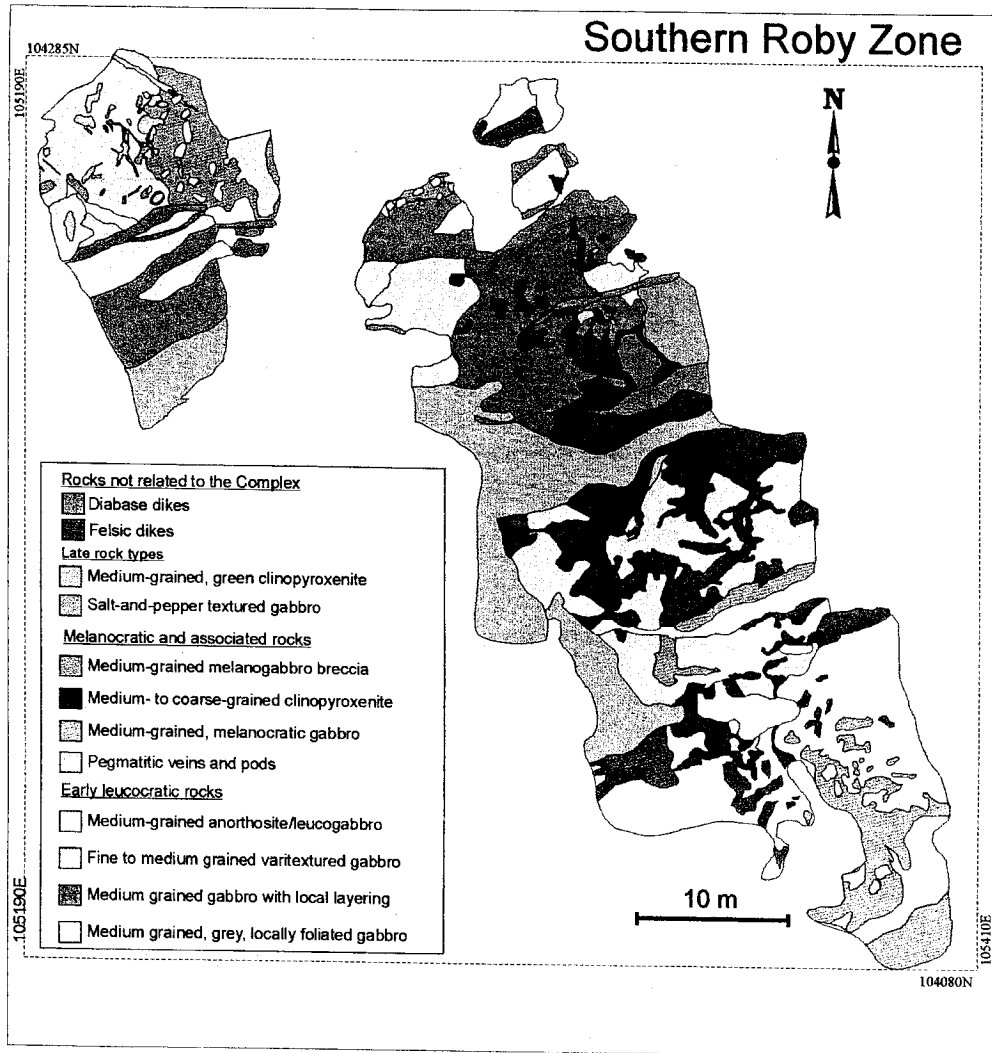
Mine Block Intrusion, Lac des Iles Intrusive Complex.



Melanogabbro Breccia



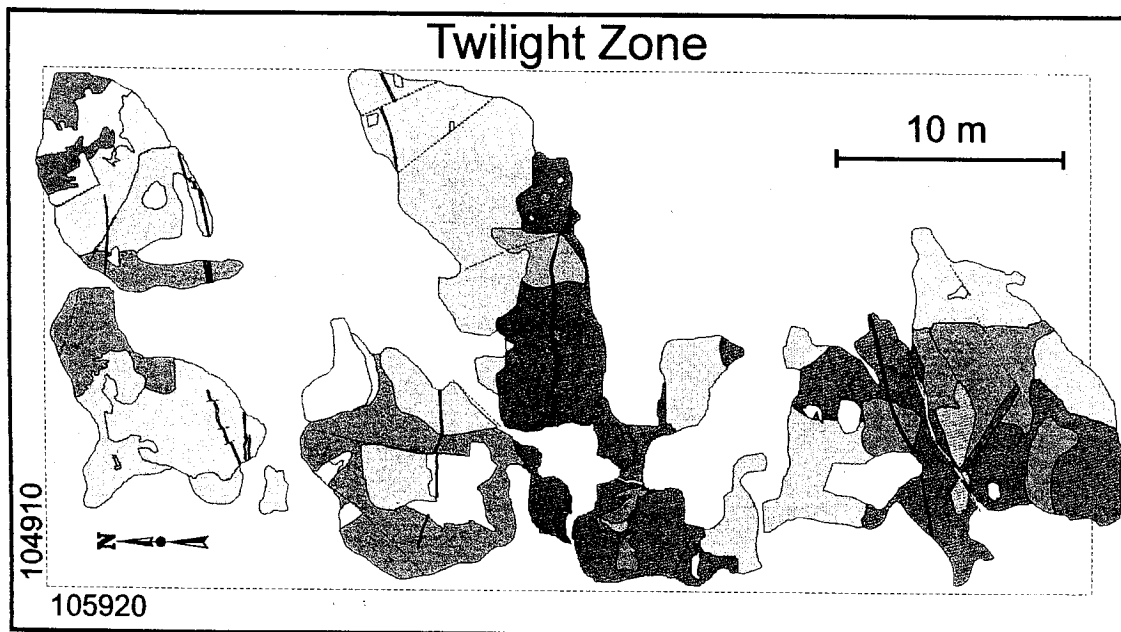
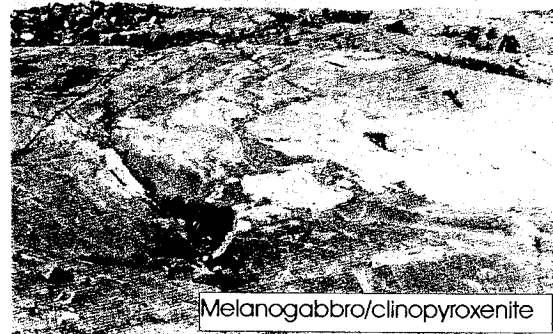
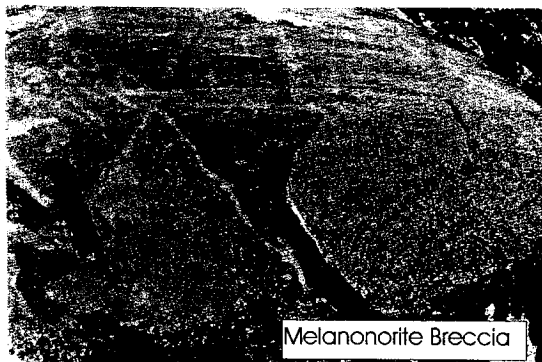
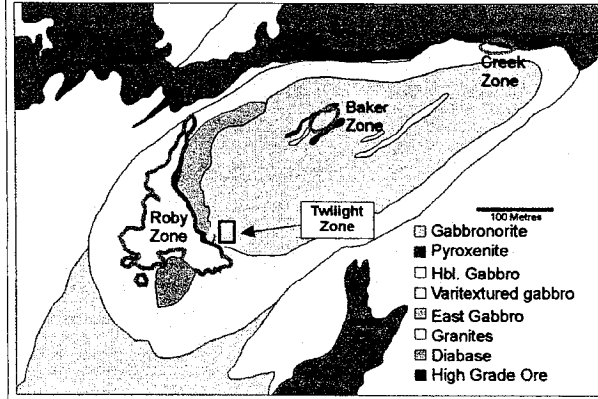
Magma Mingling



Map 2.
Geology map of the Twilight Zone, Lac des Iles Intrusive Complex, northwestern Ontario.

Mapping by J.G. Hinchey, 2002, 2003
 Scale 1:120
 Mine Block Intrusion map modified after Sutcliffe and Sweeney, 1986.
 Coordinates refer to North American Palladium Imperial Mine Grid.

Mine Block Intrusion, Lac des Iles Intrusive Complex.



Rocks not related to the Complex	Early rocks of the Complex	Medium-grained Gabbro/gabbronorite
■ Felsic dike	□ Norite / leuconorite	■ Melanogabbro/clinopyroxenite
Late mineralized rocks	□ Anorthosite/leucogabbro	□ Fine-grained gabbro
■ Melanonorite		