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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; up to 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.

Keywords PGE · Platinum group elements · Hydrothermal palladium · Subsolidus enrichment · Selenium · Tellurium · Sulphur isotopes · Archean · Superior Province

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. 1). It belongs to a suite of late Archean mafic-ultramafic plutons in the southern Wabigoon Province

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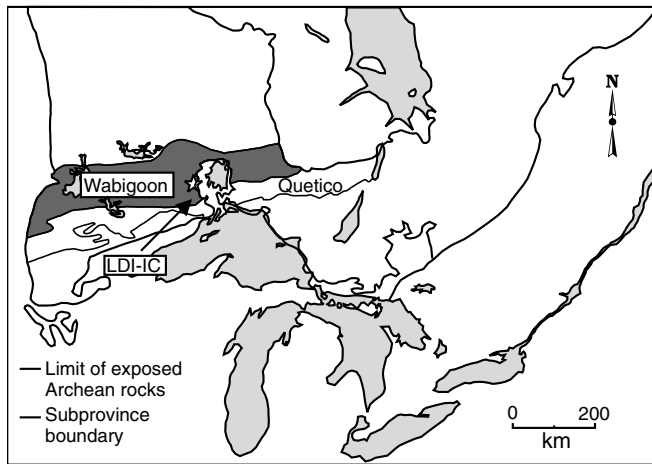


Fig. 1 Simplified map of the Superior Province illustrating the locations of Wabigoon Subprovince and the Lac des Iles Intrusive Complex (modified after Card and Ciesielski 1986)

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

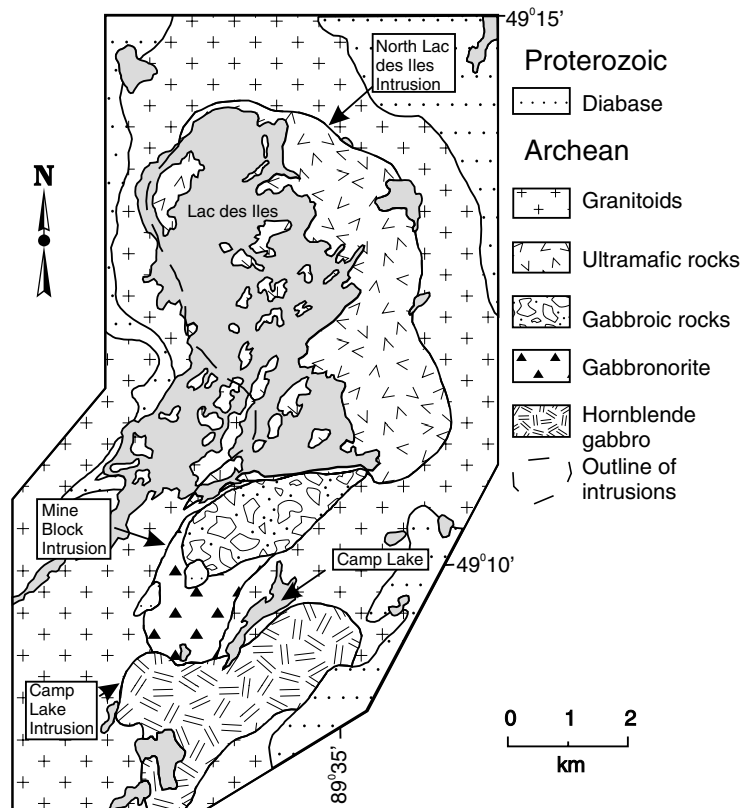
by secondary minerals. In addition, it has high Pd/Pt ratios compared to other zones.

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. 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.

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). 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

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



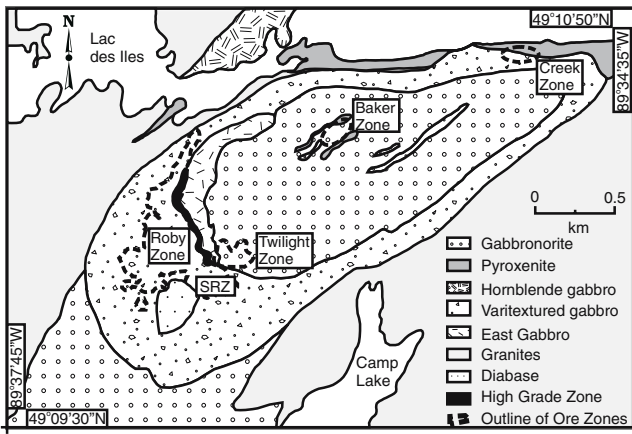


Fig. 3 Simplified geological map of the Mine Block Intrusion of the Lac des Iles Intrusive Complex illustrating the locations of the southern Roby, Twilight, and High Grade Zones. Also shown are the East Gabbro and other mineralized zones in the Mine Block Intrusion (modified after Suttle and Sweeney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

rocks of the Mine Block Intrusion (Figs. 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. 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.

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 s 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 chalcocopyrite 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

Table 1 Representative chemical composition of mineralized rock types at the southern Roby Zone (SRZ), Twilight Zone (TZ) and High Grade Zone (HGZ)

Rock type	Melanogabbro	Clinopyroxenite	Dark gabbro	Melanonorite	Altered melanogabbro/clinopyroxenite										
Sample no.	JH02-037	JH02-140	JH02-138	JH02-089	JH02-146	JH02-148	JH02-173	JH02-181	JH02-173	JH02-173	JH02-173	JH02-173	JH02-173	JH02-173	JH02-173
Location	SRZ	SRZ	SRZ	SRZ	SRZ	SRZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ	TZ
S ^a (w%)	0.60	0.67	1.35	0.82	0.77	0.77	0.86	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57
Ni ^b (ppm)	974	1,530	2,080	1,840	2,208	2,208	7,950	1,738	1,738	1,738	1,738	1,738	1,738	1,738	1,738
Cu ^c	1,360	2,390	3,430	2,290	2,426	2,426	3,500	2,270	2,270	2,270	2,270	2,270	2,270	2,270	2,270
Se ^e	2.9	5.6	9	4.6	6.7	9.3	16.2	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
Te ^e	0.5	1.5	2	1.4	2.2	2.7	7.1	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Au ^d (ppb)	174	868	855	416	917	1,280	1,925	411	411	411	411	411	411	411	411
Pt ^d	190	752	1,020	382	998	1,370	355	587	587	587	587	587	587	587	587
Pd ^d	1,460	6,940	8,790	3,280	9,160	11,720	1,100	4,570	4,570	4,570	4,570	4,570	4,570	4,570	4,570

^a Elemental analyzer

^b XRF

^c Aqua regia digestion with ICP-MS

^d Fire assay ICP-MS

Table 2 $\delta^{34}\text{S}$ for mineral separates of the Southern Roby Zone (SRZ), Twilight Zone (TZ), and High Grade Zone (HGZ)

Sample No.	Ore zone	Mineral separate	$\delta^{34}\text{S}$ (‰)
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/Chalcopyrite	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

raw X-ray data were converted to weight percentage 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 $\pm 5.4\%$ and $\pm 1.4\%$ respectively. Blank contribution of S to the total 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 $\pm 9.2\%$ and $\pm 4\%$, 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 ppb and 0.5 ppb, respectively. Precision and accuracy of Pt and Pd, as determined through duplicate analyses of a reference material are $\pm 0.61\%$ and $\pm 2.03\%$ for Pt, and $\pm 0.49\%$ and $\pm 4.68\%$ 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 $1,800^\circ\text{C}$ 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 $\pm 0.24\%$. Results are given in Table 2.

Results and discussion

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 (names 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.

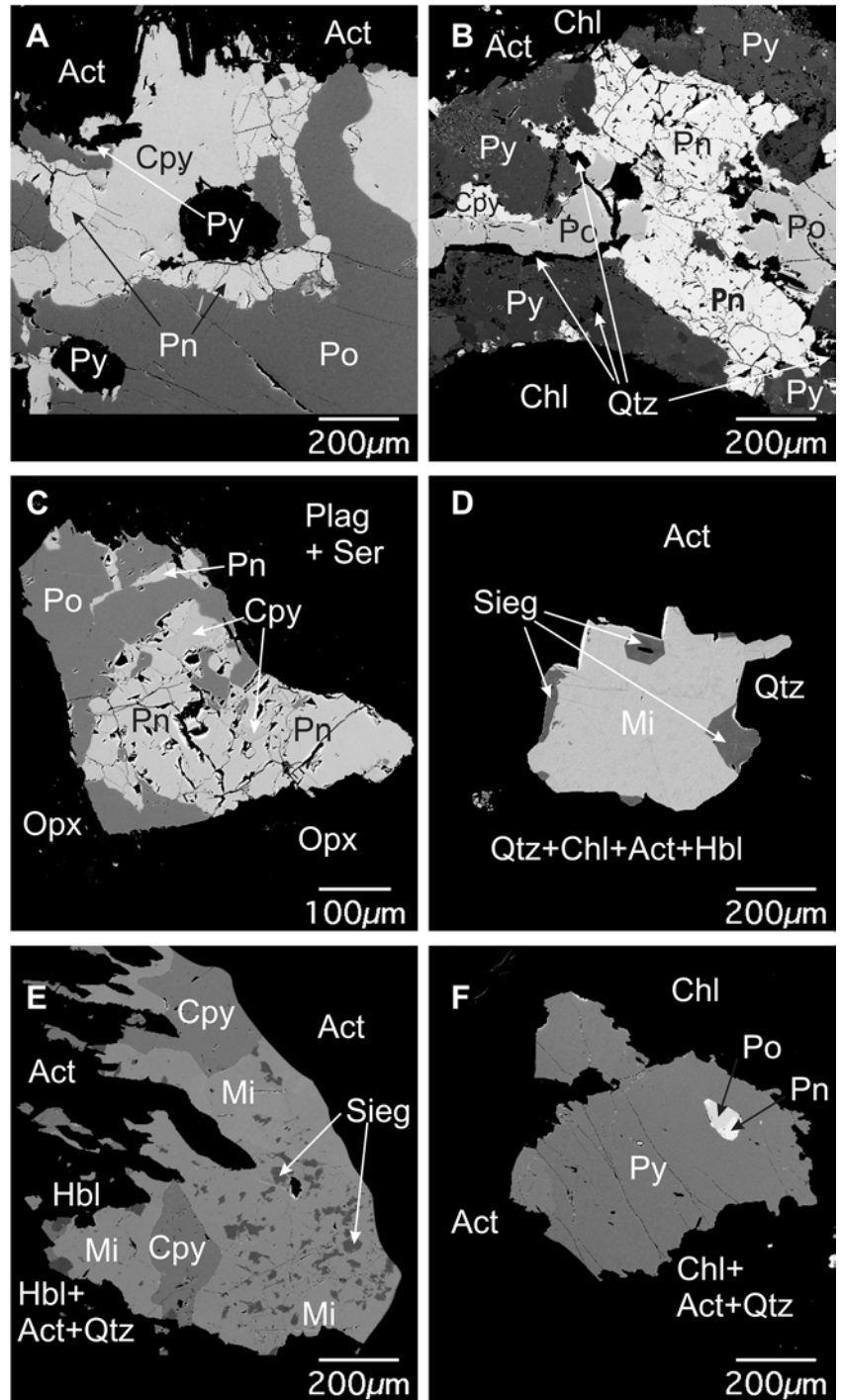
The mineralized rocks at Twilight Zone are similar to those in the southern Roby Zone. They also show orthocumulate texture with subhedral to euhedral cumulus orthopyroxene (3–10 mm; 70–95 vol%), and intercumulus minerals consisting of plagioclase (5–30 vol%), clinopyroxene (< 10 vol%), minor biotite, 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.

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. 4a, 4b, 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. 4a).

Fig. 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 *Po*. 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* + hornblende (*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 *Mi*) along cleavages and grain boundaries of *Act* 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 *Py* with small inclusions of blebby *Po* and *Pn*. Silicate alteration is intense and is dominated by chloritization of clinopyroxene. (Sample JH-02-SZ2)



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. 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. 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

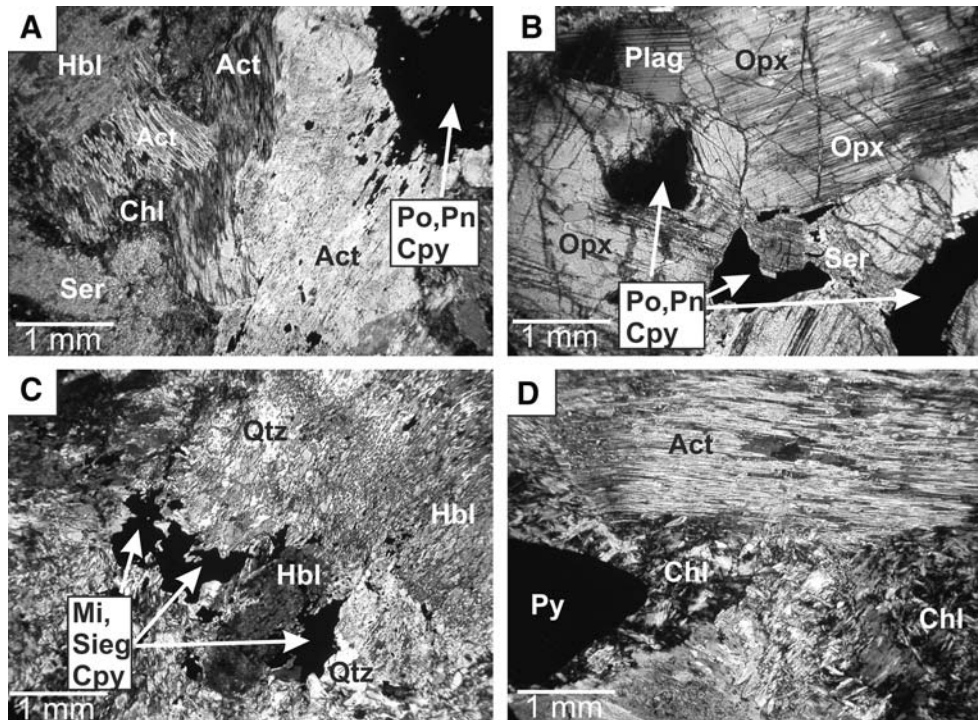


Fig. 5 Representative photomicrographs of mineralized zones: **a** intense silicate alteration of dark gabbro at the southern Roby Zone with Act + Hbl + Chl replacing clinopyroxene and Ser replacing plag. The opaque minerals consist of Po with exsolved blebs of Pn and Cpy. Note the presence of Cpy along cleavage planes of Act. (Sample JH-02-146). **b** Mineralized melanonorite at the Twilight Zone showing minor Ser in plag. Note the Opx crystal enclosing magmatic sulphides that consist of Pn and Cpy exsolved from 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 Py (Sample JH-02-SZ2)

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. 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 Cu was limited.

High Grade Zone

The High Grade Zone represents the most intensely altered rocks in the deposit where magmatic minerals are rarely present (Figs. 5c, 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. 4d, e) $\pm$ 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. 4d, 4e). Chalcopyrite occurs as anhedral blebs and is commonly associated with millerite and siegenite (Fig. 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 (Fig. 5c).

Assemblage B predominantly consists of anhedral to subhedral pyrite grains with variable chalcopyrite. Small inclusions of pyrrhotite and pentlandite (Fig. 4f) are common in pyrite. This is associated with the assemblage of chlorite + actinolite (Fig. 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 $\sim 300\text{--}400^\circ\text{C}$. 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

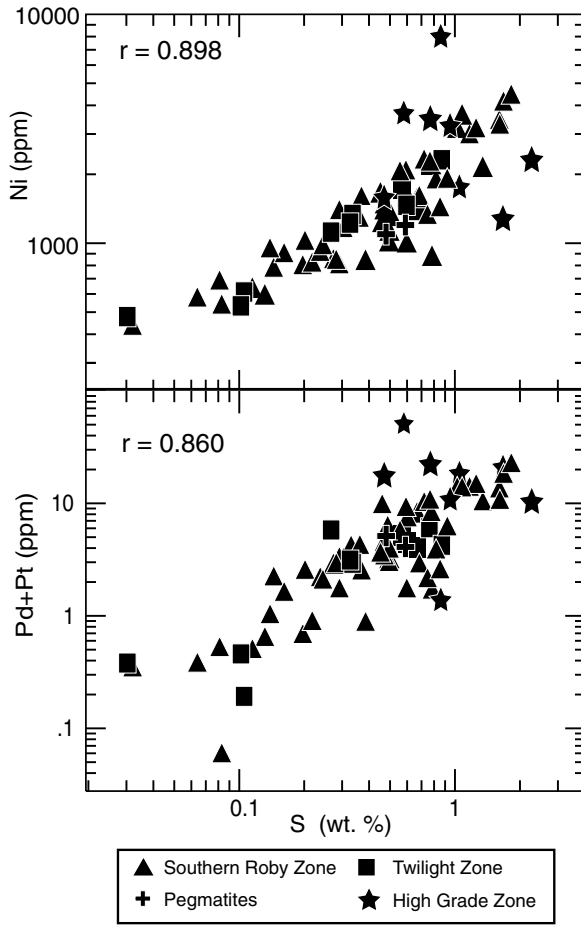


Fig. 6 Bivariate plots of S (wt.%) versus Ni (ppm) and Pd + Pt (ppm). Note the good positive correlations between Ni and S ($r = 0.898$) and (Pd + Pt) and S ($r = 0.86$) for samples from southern Roby Zone and Twilight Zone and the scatter for samples from High Grade Zone. Note that the symbol legend is identical to that for Figs. 6, 7, 8, 9, and 10

that the mineralized hydrothermal activity took place over a wide range of temperatures.

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 $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ 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

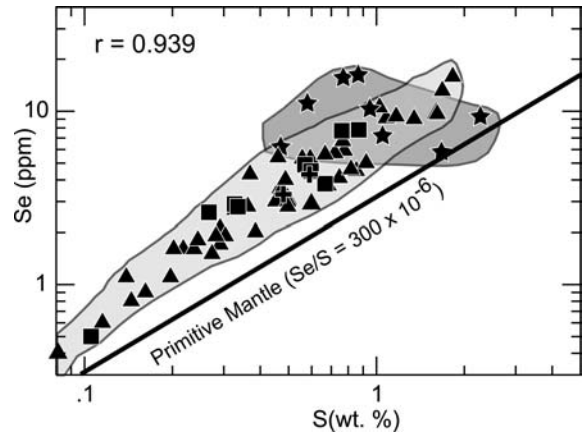


Fig. 7 Bivariate plot of S (wt.%) versus Se (ppm). Note the well-defined correlation for southern Roby Zone and Twilight Zone ($r = 0.989$) and the scatter for the High Grade Zone samples. All samples plot above the ratio of the primitive mantle value (McDonough and Sun 1995)

stages. This is consistent with their formation at a wide range of temperatures.

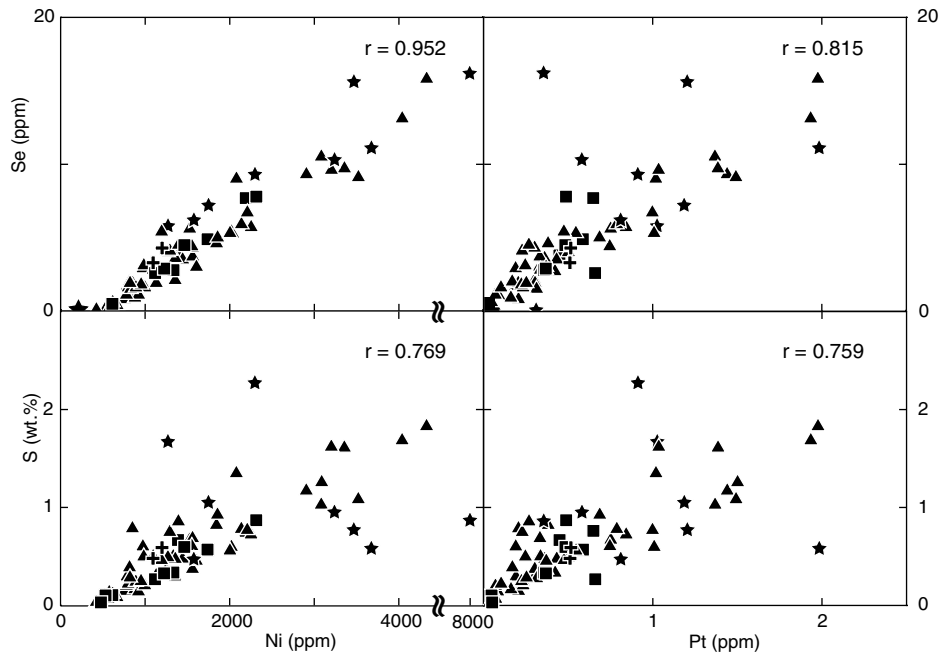
Metal, sulphur, tellurium, and selenium concentrations in the southern Roby and Twilight Zones

Sulphur contents from the southern Roby Zone and Twilight Zone show positive correlations with the contents of Ni, Pt, and Pd + Pt, (Figs. 6, 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. 7) and Te/S ratio of $192 \pm 104 (1\sigma) \times 10^{-6}$ (Fig. 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. 7, 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 solubilities 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 2002). This is supported by the presence of

Fig. 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



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 SRZ and TZ. 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

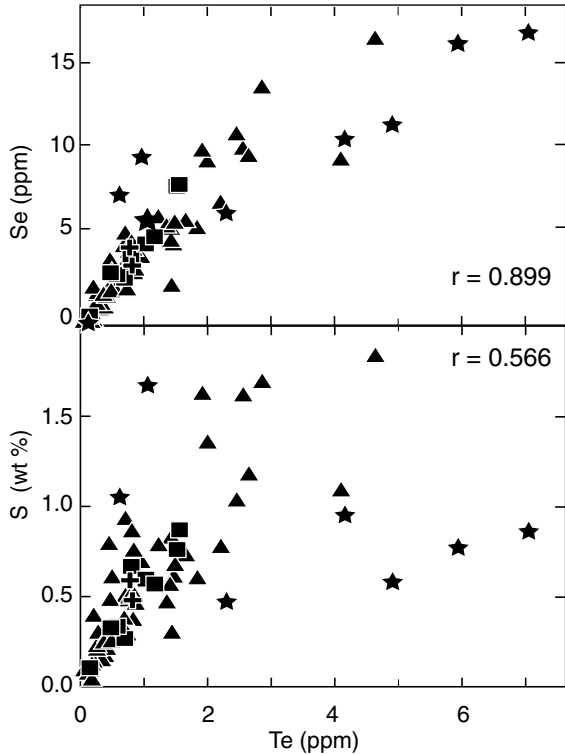


Fig. 9 Bivariate plot of Te (ppm) versus S (wt%) and Se (ppm). Note the good correlation between Se and Te compared to the correlation between Te and S

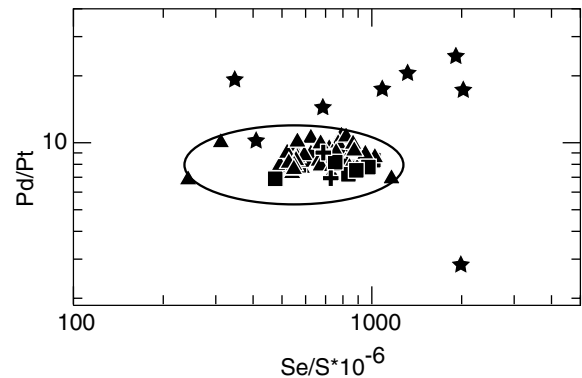


Fig. 10 Se/S versus Pd/Pt. Note the narrow spread of values from the southern Roby Zone and Twilight Zone compared to the scatter from the High Grade Zone

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).

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 within the range for magmatic deposits in the world (Fig. 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. 9). The data are consistent with the magmatic mineralization, but the High Grade Zone samples show scatters on the diagrams of S versus Se and S versus Te (Figs. 7, 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. 10). In addition, the High Grade Zone samples show scatter on the diagrams of Pd versus Se and Pt versus 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,

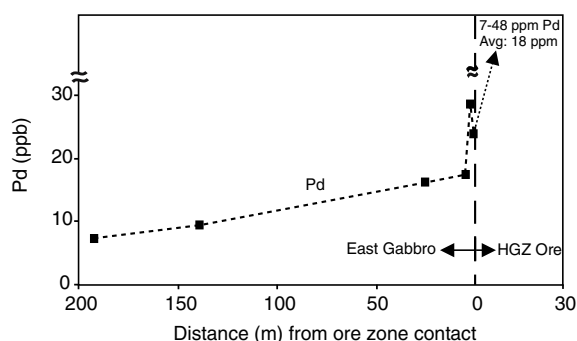


Fig. 11 Palladium concentrations of rocks in the East Gabbro near the contact with the High Grade Zone

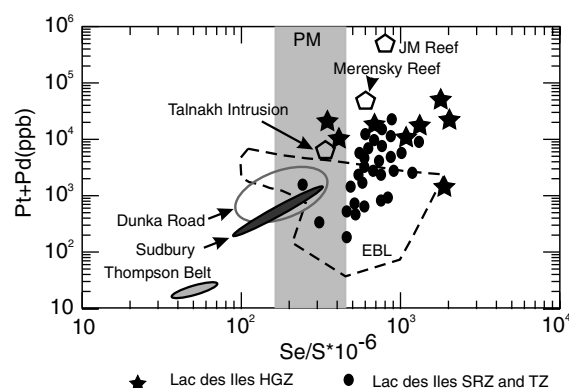


Fig. 12 Plot of $\text{Se/S} \times 10^{-6}$ versus $\text{Pt} + \text{Pd}$ (ppb) comparing the Lac des Iles ore to various other deposits. Note that the Lac des Iles data fall on the general trend defined by other large deposits. The shaded vertical box represents the range of $\text{Se/S} \times 10^{-6}$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

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. 3). The zone is bound by relatively Pd-rich (2.5–5 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. 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. 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).

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.

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