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Lead isotope study of the late Archean Lac des Iles palladium deposit, Canada: enrichment of platinum group elements by ponded sulfide melt

John G. Hinchey · Kéiko H. Hattori

Abstract Lead isotopic compositions of mineral separates are presented from the mineralized zones (Roby, Twilight, and High Grade zones) of the Lac des Iles palladium deposit (approximately 2.69 Ga) and tonalitic country rocks (approximately 2.727 to 2.775 Ga) in the Wabigoon subprovince of the western Superior Province of Canada. Plagioclase separates show Pb isotope ratios similar to those of the late Archean depleted mantle. Sulfide minerals coexisting with plagioclase have a more radiogenic Pb isotope composition, but very low concentrations of U (<0.2 ppb U) and Th (<0.01 ppb) compared to Pb (≫50 ppb). The isotope data are consistent with a model involving the incorporation of radiogenic Pb from country rocks to sulfide melt near the base of the magma chamber or along the conduit of the parental magmas. The proposed interpretation is also supported by decreasing Cu/Pd ratios from earlier barren to late fertile gabbro intrusions in the complex. The ponding sulfide melt became enriched in platinum group elements, as it was interacting with a large magma volume during the evolution of the Lac des Iles igneous complex.

Keywords Lead isotopes · Platinum group elements · PGE mineralization · Lac des Iles · Canada

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Introduction

The Lac des Iles mine is hosted by the Neo-Archean Lac des Iles mafic–ultramafic igneous complex (Fig. 1) and represents the only primary Pd mine in Canada. It had proven and probable reserves of 88 million metric ton grading 1.51 g/t Pd, 0.17 g/t Pt, and 0.12 g/t Au before the major expansion of mining in 2002. As of December 2005, proven and probable reserves were 13.5 and 3.5 million metric ton grading 2.13 and 6.62 g/t Pd in the open pit and underground operations, respectively, (North American Palladium Annual Report, 2006). Unlike many other platinum group element (PGE) deposits that are hosted by Ni sulfides at the base of mafic intrusions (e.g., Sudbury and Noril'sk), the mineralization at Lac des Iles is characterized by low contents (<2 vol.%) of sulfides disseminated in altered gabbroic rocks. The host rocks formed by successive intrusions of comagmatic mafic magmas and show a variety of breccias containing earlier intrusions as fragments (Fig. 3). Later, fertile mafic intrusions are accompanied by abundant veins and pods of pegmatites, suggesting that they were volatile rich. In addition, the ore at Lac des Iles is highly enriched in Pd compared to other PGE (i.e., Pd/Pt ratios ~10, Pd/Ir ratios ~10,000; Hinchey et al. 2005). These characteristics had lead to various models for the mineralization, including hydrothermal/deuteric mineralization (Watkinson and Dunning 1979) and zone-refining processes (Brügmann et al. 1989). Based on recent detailed mapping, Hinchey et al. (2005) proposed that the mineralization is essentially magmatic and that PGE were enriched by reworking of earlier formed sulfide melt by later magmas.

Crustal rocks contain high concentrations of U and Th compared to mantle rocks, which makes Pb isotope compositions a sensitive indicator in detecting the contributions of crustal components to mantle-derived magmas

(Faure and Mensing 2005). Lead isotope data are particularly useful in the study of sulfide mineralization because sulfide minerals retain their isotopic compositions due to low U/Pb and Th/Pb (e.g., Tosdal et al. 1999; Marschik et al. 2003). This paper presents Pb isotope compositions for mineral separates from the Lac des Iles Pd deposit and discusses the origin of the parental magmas for the Lac des Iles intrusive complex and the Pd mineralization.

Geological setting of the Lac des Iles complex

The 2.69-Ga Lac des Iles complex intruded the tonalitic rocks in the granite–greenstone belt of the southern Wabigoon subprovince of the Superior Province, Canada (Fig. 1). The country rock tonalites have U–Pb zircon ages ranging from 2,775±8 to 2,722±3 Ma for the gneissic phase and 2,727.8±1.5 Ma for the massive phase (D. Davis cited in Stone et al. 2003). The tonalite gneiss is considered to be the oldest plutonic rock in the area and is medium grained and contains between 20–25 vol.% ferromagnesium minerals, predominantly biotite, with approximately equal proportions of quartz and feldspar. The massive to slightly foliated tonalite is the main country rock of the Lac des Iles intrusive complex. It is medium to coarse grained and contains up to 30 vol.% of biotite and hornblende. Alteration is weak and limited to minor sericite replacing plagioclase

feldspar. Regional metamorphic grades in the area are low, up to greenschist facies (Blackburn et al. 1992), and this is consistent with the presence of pristine clinopyroxene and orthopyroxene in the northern part of the Lac des Iles 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 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.

Mineralization

The economic mineralization at Lac des Iles occurs in the Roby, Twilight, and Baker zones in the Mine Block Intrusion (Fig. 2). The following sections describe the Roby and Twilight zones because our detailed mapping and sampling were focused on these two areas. The southern Roby zone is the southern portion of the Roby zone that was the only remaining surface exposure of the main Roby zone during the mapping in 2002 and 2003.

The rocks in the southern Roby zone are predominantly mafic to intermediate gabbros with minor clinopyroxenites, and they show breccia and magma mingling textures (Hinchey et al. 2005, Fig. 3). The Twilight zone outcrops ~50 m to the east of

Fig. 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*
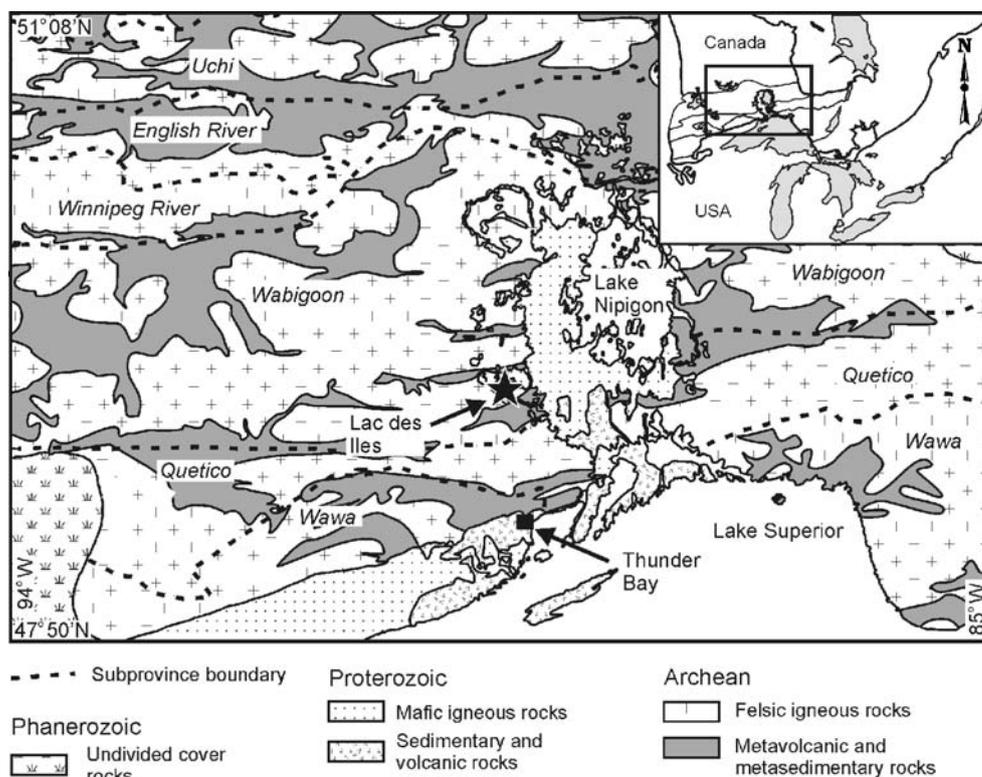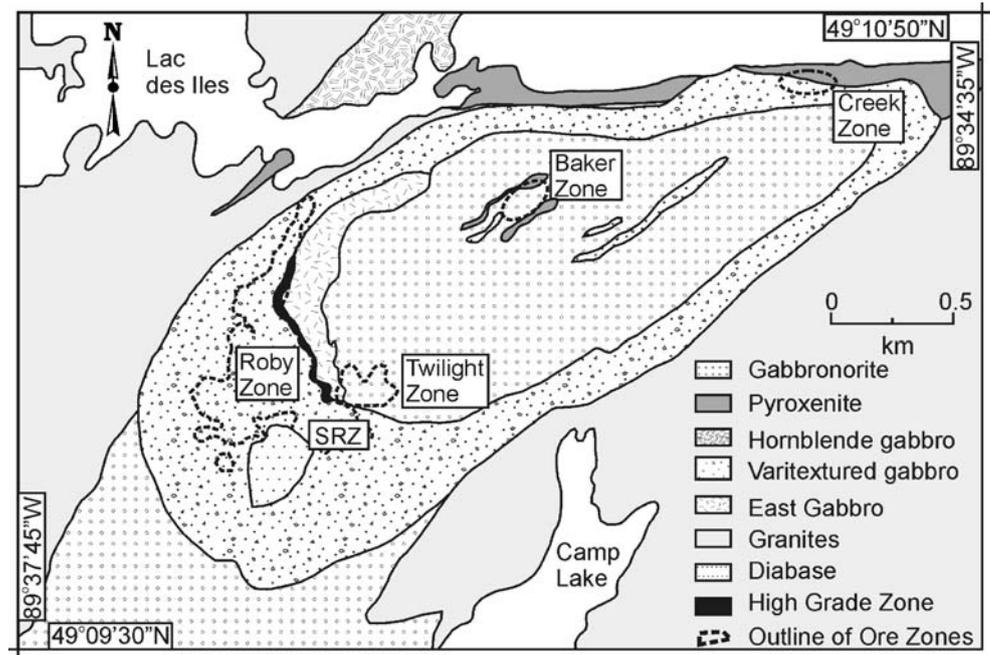
the main Roby zone and is dominated by gabbronoritic rocks with similar textures and relationships as those observed in the Roby zone. The Twilight zone is only weakly to moderately altered, and primary magmatic minerals, such as orthopyroxene and plagioclase, are well preserved. In both zones, all gabbroic units are comagmatic with similar geochemical properties (Hinchey et al. 2005). The mineralized rocks show cumulate textures, consisting of subhedral to euhedral, variably altered crystals of clinopyroxene, plagioclase, and orthopyroxene with interstitial sulfides and oxides (Fig. 4). Alteration at the southern Roby zone is pervasive, particularly in the mineralized mafic rocks, with primary minerals variably replaced by secondary amphiboles, talc, chlorite, sericite, and calcite (Fig. 4). Brecciation and magma mingling textures are common, with earlier leucocratic rocks forming fragments of later breccia units (Fig. 3). Detailed examinations of gabbroic rocks show that early leucocratic gabbros (leucogabbro and leuconorite) are low in PGE and that PGE are high in later melanocratic rocks (gabbro, melanogabbro, melanonorite, pyroxenite; Hinchey et al. 2005). The High Grade zone is hosted by a 400-m long, 15- to 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 (Fig. 2). The rocks in the High Grade zone are intensely altered to sericite, chlorite, albite, quartz, amphibole, and talc. The zone has experienced pervasive alteration at different temperatures, as earlier alteration minerals are overprinted by later low temperature alteration minerals.

Hinchey et al. (2005) documented that the PGE mineralization in the southern Roby and Twilight zones is
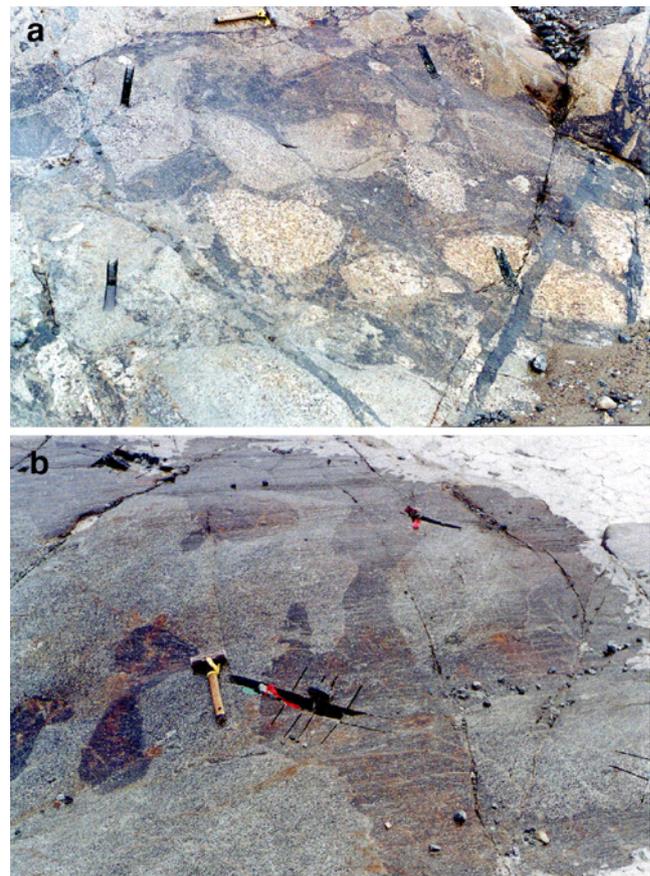

Fig. 3 Representative photographs of the ore zone at Lac des Iles. a Medium-grained melanogabbro breccia containing angular fragments of earlier barren leucocratic rocks. b Magma mingling between early barren leucogabbro and late PGE-rich melanogabbro. Earlier and later gabbroic rocks are all comagmatic based on trace element patterns (Hinchey et al. 2005)
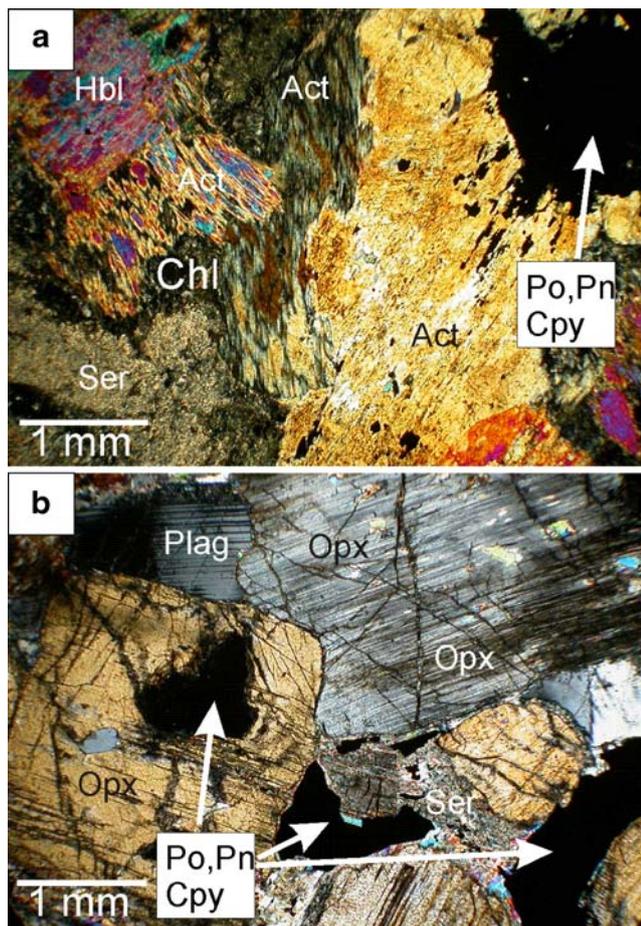
Fig. 4 Representative photomicrographs of ore zones. **a** Intense silicate alteration of dark gabbro from the southern Roby zone with actinolite, hornblende, and chlorite replacing clinopyroxene and sericite replacing plagioclase. **b** Relatively unaltered melanonorite from the Twilight zone. Opaque material is exsolved sulfide blebs

alteration, platinum group minerals, where observed, are spatially associated with sulfide minerals.

Detailed descriptions of the geology, mineralogy, and geological setting of the Lac des Iles intrusive complex and the Pd mineralization are given by Sutcliffe (1989), Sutcliffe et al. (1989), Edgar and Sweeny (1991), Lavigne and Michaud (2001), Hinchey et al. (2005), and Hinchey and Hattori (2005).

Samples and analytical methods

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. 2005; Fig. 2). Samples were crushed and sieved between 60 to 80 mesh. Separates with >99% purity of plagioclase, and sulfide grains were obtained using a
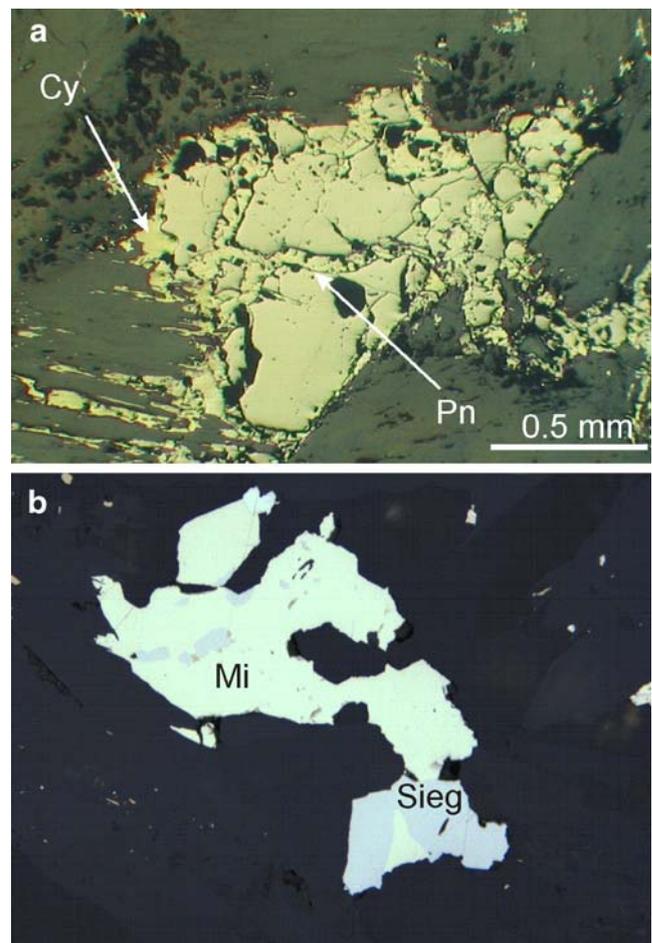

Fig. 5 Representative photomicrographs of sulfide mineralogy. **a** Primary magmatic sulfide bleb with exsolution of chalcopyrite (*Cy*) and pentlandite (*Pn*) in fractures in pyrrhotite. Note the overprinting pyrite in the upper right portion of the sulfide bleb. Southern Roby zone **b** low-temperature millerite (*Mi*) and siegenite (*Sieg*) from the High Grade zone

controlled and hosted by magmatic sulfides based on positive correlations between S and PGE and concluded that PGE were concentrated in an immiscible sulfide melt in parental magmas. The proposed interpretation is consistent with the texture of magmatic sulfides and unaltered silicate minerals in contact with sulfides in some samples. Sulfides are blebby with exsolution of pentlandite and chalcopyrite from pyrrhotite (Fig. 5). Pyrite is common in the southern Roby zone with amounts increasing with higher degrees of alteration and is interpreted as either a sulfidation product of earlier pyrrhotite or a hydrothermal product. In contrast, the High Grade zone is intensely altered with only rare magmatic sulfides or silicates present. The sulfides in the High Grade zone include pyrite, millerite, siegenite [$Ni_{2.25}(Fe_{0.11}Co_{0.64})S_4$], and chalcopyrite, with minor amounts of pentlandite and pyrrhotite (Hinchey and Hattori 2005). The sulfide assemblages are interpreted as the products of relatively low temperature hydrothermal mineralization. Regardless of the degree of

magnetic separator, followed by hand picking under a binocular microscope. Plagioclase grains with cloudy interiors, inclusions and signs of alteration were discarded. Plagioclase grains totaling ~100 mg were used for analysis without grinding them to powder. They were rinsed first with Milli-Q water in an ultrasonic bath for ~10 min before a series of overnight leachings at ~50°C, consisting of 2 N HCl (Leach 1), 6 N HCl (Leach 2), 16 N HNO_3 (Leach 3), and 16 N HNO_3 with one drop of 48% HF (Leach 4) following the method by Cumming and Krstic (1987). An additional leach (Leach 5) applied to two samples using a 8:1 mixture of 5% HF and 8 N HNO_3 at ~50°C for 20 min dissolved plagioclase, and the Pb extracted during Leach 5 was reported as residue. The leaching treatments were carried out to remove, inasmuch as possible, labile radiogenic Pb held in crystal defects, crystal fractures, or in nonsilicate impurities. For the remaining samples, the residual plagioclase after four successive leaches was dissolved in sealed Teflon vials overnight in a 4:1 mixture of 48% HF and 16 N HNO_3 at ~100°C. The samples were dried and redissolved in 6 N HCl at ~90°C, followed by evaporation and dissolution in 3 N HBr. Lead was loaded to Bio-Rad AG1-X8 anion resin (200–400 mesh) in 0.5 N HBr and eluted in 2 ml 6 N HCl. Lead was further purified using a second column containing a reduced volume of resin, and the final Pb separate was eluted in 0.5 ml 6 N HCl.

For Pb isotope analysis of sulfide minerals, sample grains totaling ~40–100 mg were rinsed with Milli-Q water in an ultrasonic bath for ~10 min. Sample grains of 60–80 mesh were used for leaching and digestion without powdering samples. The samples of pyrite and millerite/siegenite were subjected to leaching in 6 N HCl for 1 h at 60–80°C. Pyrrhotite samples were leached in 2.5 N HCl for 1 h at 40–60°C. All samples were digested in sealed Teflon vials in a 3:1 mixture of 16 N HNO_3/9 N HBr at ~60–80°C for ~2 days. Considering that different fractions of sulfide minerals from individual hand specimens had similar isotopic compositions (e.g., JH-02-146 and JH-02-SZ3, Table 1), leaching effectively removed loosely held Pb in the samples. The sample solution was subjected to repeated evaporation and redissolution in 0.5 N HBr before loading to an anion–resin column. Lead was eluted in 1.0 ml of Milli-Q water following the method described in Kuritani and Nakamura (2002). Lead purification was repeated using a reduced volume of resin with the final 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 6,020 ng for sulfide separates. The data show that plagioclase and sulfide samples have comparable Pb concentrations, and as such, the consistently high Pb isotopic ratios of sulfide samples compared to plagioclase separates are not related to blank contributions.

Isotopic measurements were made on a ThermoFinnigan Triton thermal ionization mass spectrometer after loading samples on single Re filaments with silica gel. The isotopic compositions were measured with Farady cups in dynamic mode, whereas those with low quantities of Pb (i.e., leachates) were measured with an electron multiplier. Measured ratios were corrected using the mass fractionation factor of 0.145%/amu, which was obtained from the measured values compared to the recommended values of NBS 981 by Todt et al. (1996). Four runs of NBS 981 yielded $^{206}Pb/^{204}Pb=16.902\pm0.001$, $^{207}Pb/^{204}Pb=15.444\pm0.001$, and $^{208}Pb/^{204}Pb=36.551\pm0.003$ (1σ).

The concentrations of Pb were determined on 10% aliquots of the final Pb solutions. The concentrations of U and Th in selected samples were determined using an Agilent HP-4500 inductively coupled plasma mass spectrometer.

Results

The concentrations of Pb in the residues of plagioclase separates range from 0.05–1.2 ppm. The residues characteristically yielded lower $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ than the corresponding leachates, suggesting that radiogenic Pb was removed during leaching (Table 1) and that the isotopic ratios of the residues should be taken as the maximum values. The values are likely to be very close to those of their parental magmas residues as some samples show higher leachate ratios than the final residue (e.g., JH-02-151). In addition, Pb isotope compositions of residues are very similar to those estimated for depleted mantle underlying the Canadian Shield in late Archean time (e.g., Dupré et al. 1984; Tilton and Kwon 1990; Carignan et al. 1995).

Most sulfide samples were obtained from the same samples as the plagioclase separates. Sulfide samples show higher $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ than plagioclase in individual samples. Lead isotopic compositions of different aliquots of sulfide separates show similar isotopic compositions (Table 1). Different aliquots represent different grains of sulfide with different Pb concentrations. Lead concentrations for most sulfide separates range from 0.7–2.0 ppm, with one sulfide sample (JH-02-SZ3, fraction A) recording 65 ppm. A different fraction, fraction B, of sulfide separate from the same hand specimen yielded a much lower concentration 0.07 ppm Pb, suggesting a nugget effect for the high concentration of Pb in the fraction A. A scanning electron microscopy examination of the sample showed the presence of Se-rich galena enclosed in sulfide minerals. Although the concentrations of the two fractions, A and B, are very different, the two fractions yielded similar Pb isotopic compositions (Table 1). There is no correlation between Pb concentrations of the sulfides and isotopic

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

Sample no.	Zone	Mineral	Fraction		$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
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
		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 rock sample. Leachates from sulfide samples were not collected. Detailed descriptions and locations of samples are given in Appendix A

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 8 N HNO$_3$ at 50°C, *R*** extracted after leaching with 6 N HCl for pyrite and millerite/siegenite, 2.5 N HCl leach for pyrrhotite, *SRZ* southern Roby zone, *TZ* Twilight zone, *HGZ* High Grade zone

compositions, and the data suggest that the observed Pb isotope data likely reflect the primary values at the time of crystallization. Furthermore, similar Pb isotopic compositions for the two fractions with different Pb concentrations argue against any significant growth in radiogenic Pb from U and Th in sulfides. To confirm this, we determined U, Th, and Pb concentrations of a representative sample in JH-02-089. The concentrations of Pb, Th, and U are 50.6, 0.01, and 0.13 ppb, respectively. As such, the contribution from radiogenic Pb is insignificant for the observed Pb isotope compositions.

Isotopic compositions are independent of sulfide mineralogy, their textures, and the timing of their formation. For example, hydrothermal sulfides from the High Grade zone show high and low values. Pyrite in the sample JH-02-SZ3 shows the highest $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ values, and millerite/siegenite, low temperature hydrothermal minerals, from sample JHC-03-070 shows the lowest Pb isotope values among sulfide samples (Table 1). In the southern Roby zone, magmatic pyrrhotite in samples JH-02-151 and JH-02-146 shows high ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ compared to hydrothermal pyrite in sample JH-02-089 (Table 1).

Lead isotopic data from the plagioclase residues, leachates, and sulfide separates form a single line with a slope of 0.2469 (r^2=0.9985) on the diagram of $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$ (Fig. 6).

Discussion

Lead isotopic compositions of plagioclase

Plagioclase residues from the southern Roby and Twilight zones plot very close to the 2.69-Ga isochron (Fig. 6). The values are also similar, but slightly higher than those for the values of depleted mantle underlying the Canadian Shield in the late Archean that are estimated from mafic and ultramafic rocks and associated sulfides in the Abitibi and Wabigoon subprovinces (Carignan et al. 1995 and references therein). The origin of their parental magmas from a depleted mantle is consistent with positive εNd values (Brügmann et al. 1997), and low concentrations of rare earth elements (Hinchey et al. 2005). Furthermore, this is supported by high Se/S, Te/S, and Te/Se ratios of sulfides presented in Hinchey et al. (2005) because Se and Te tend
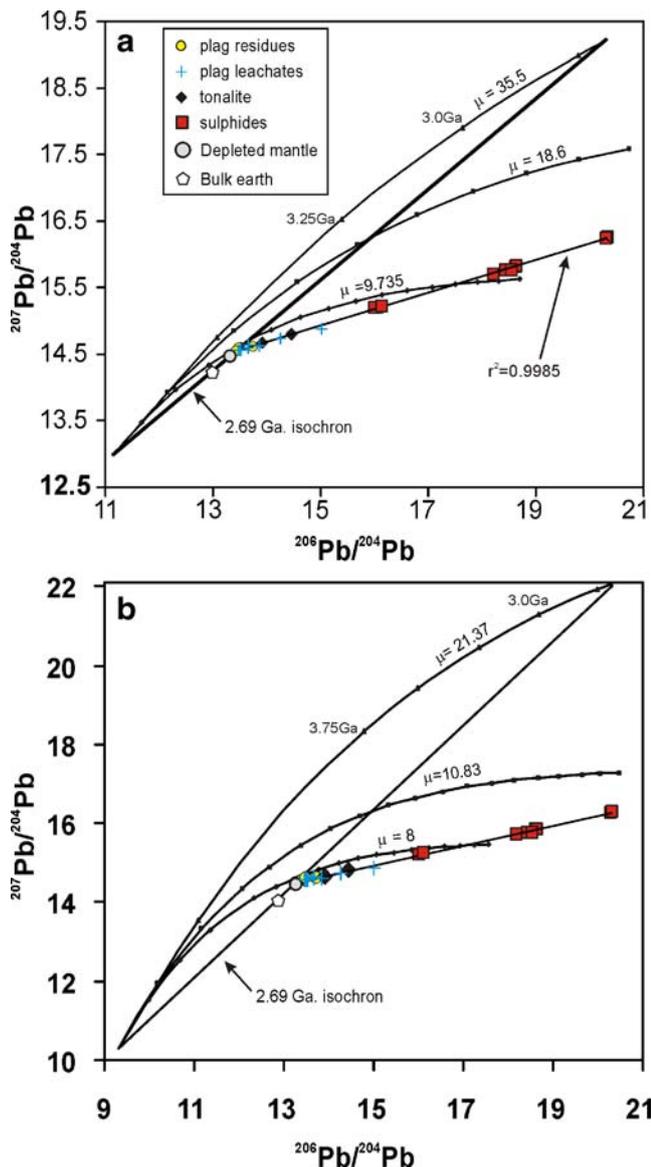
Fig. 6 a Lead isotope compositions for residues and leachates of plagioclase and sulfides from the Mine Block Intrusion and the country rock tonalite. Shown is the field of the late Archean depleted mantle (Carignan et al. 1995 and references therein), the bulk earth value, and a 2.69-Ga isochron. Also plotted are two-stage Stacey and Kramers (1975) Pb evolution curves for various μ values. **b** Lead isotopic compositions of samples compared to single-stage Pb evolution curves. Note that the sulfides do not correspond with any single Pb evolution curve. Uncertainties on measured values (1σ) for $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ 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 tick intervals along the evolution curves represent 0.25 Ga

to remain in a refractory mantle residue (Hattori et al. 2002). Peridotites in depleted mantle wedges are commonly metasomatized by fluids released from slabs and gain radiogenic Pb isotope values (e.g., Taylor and Nesbitt 1998) because Pb is easily transferred by aqueous fluids from the slab to overlying mantle (e.g., Hattori and Guillot 2003).

Lead isotope compositions of sulfides

High concentrations of radiogenic Pb isotopes in sulfides may be attributed to (1) radiogenic Pb isotope signature of the parental magmas, (2) incorporation of radiogenic Pb through bulk assimilation of old crustal rocks, or (3) incorporation of radiogenic Pb (^{206}Pb, ^{207}Pb, and ^{208}Pb) leached from the country rocks by hydrothermal fluids. The hydrothermal input of radiogenic Pb isotopes is further divided into two possible processes: (a) incorporation of radiogenic Pb during regional metamorphism or (b) 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 as demonstrated by resetting of U–Pb zircon ages during high-temperature regional metamorphism (Faure and Mensing 2005).

Option 1 implies that parental magmas for sulfides and plagioclase originated from sources with different $^{238}U/^{204}Pb$ ratios (=μ values). Furthermore, isotope compositions of sulfides and plagioclase should fit Pb isotope evolution curves with different μ values at 2,689 Ma. However, this cannot explain the highest observed Pb isotopic values using any μ value at 2,689 Ma in either the single-stage or two-stage Pb growth model of Stacey and Kramers (1975). For these reasons, this possibility is discarded as the main cause for the radiogenic Pb isotope signature of the sulfides.

Option 2, the assimilation of old crustal rocks, is commonly invoked to explain high $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios of igneous rocks and metallic mineral deposits (e.g., Faure and Mensing 2005). For example, Henry et al. (1998) attributed relatively radiogenic isotopic ratios of Pb in late Archean sanukitoids in the Wabigoon subprovince to the assimilation of old crustal rocks. This possibility is not applicable to our samples because our detailed study of trace element geochemistry concluded that parental magmas were derived from a depleted mantle with little crustal assimilation (Hinchey et al. 2005). More importantly, crustal assimilation would affect the Pb isotopic signature of the bulk rocks, and it does not explain the observed disparity between plagioclase and sulfides in individual samples.

Option 3a involves an incorporation of radiogenic Pb isotopes by aqueous fluids during regional metamorphism or late orogenic events. Anomalously high Pb isotopic ratios for sulfides from a few volcanogenic massive sulfide deposits and other base metal sulfide deposits in the Abitibi and Wawa greenstone belts of the Superior Province have been explained by these later processes (Thorpe 1999 and references therein). Examples include sulfide minerals from the Lorraine Cu–Ni deposit and the Patry Cu prospect in Québec (Carignan et al. 1993), the volcanogenic massive sulfide deposits in Noranda and Matagami districts (Vervoort et al. 1993), and the Kam

Kotia volcanogenic massive sulfide deposit in Timmins (Franklin et al. 1983). Thorpe (1999) suggested that Pb isotope compositions of low Pb sulfide minerals, such as pyrite and pyrrhotite, are susceptible to later orogenic events. We discount this possibility for our sulfide samples. First, not all low-Pb sulfides in Archean terrain are affected by late orogenic processes. Instead, many retain the primary Pb isotope signatures similar to the contemporaneous mantle values. Examples include pyrrhotite and pentlandite in komatiites, such as the Alexo and Newton deposits (Dupré and Arndt 1990), indicating that the Pb isotope compositions of low-Pb sulfides are not necessarily modified by later orogenic events. Secondly, the majority of the anomalous Pb data reported by Thorpe (1999) are from deposits containing secondary galena in veins and along major faults in areas that underwent upper greenschist to amphibolite facies metamorphism. The Lac des Iles deposit has primary magmatic mineralogy and textures. Sulfide minerals do not form veins and are not associated with faults or fractures. Thirdly, the regional metamorphic grade in the area of Lac des Iles is relatively low greenschist facies (e.g., Blackburn et al. 1992; 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 gabbronorites of the Mine Block Intrusion. Furthermore, a regional alteration event cannot explain different isotopic compositions among plagioclase and magmatic sulfides in single hand samples (samples JH-02-151 and JH-02-185). Although the plagioclase leachates are consistently more radiogenic than the residues, they are not as radiogenic as the sulfide separates from the same samples (Table 1, see below). If a regional metamorphic/orogenic event had influenced Pb isotopic compositions of sulfides, leachates from plagioclase may be expected to show radiogenic Pb isotope signatures comparable to the sulfides. As our samples do not concur with such data, we suggest that the radiogenic Pb isotope values for sulfides are intrinsic and not related to post-mineralization events. The observed high $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios of the sulfides were acquired before the solidification of the parental magmas of the intrusion.

Option 3b involves the introduction of radiogenic Pb from country rocks by hydrothermal fluids during intrusive activity. Aqueous fluids commonly exsolve in silicate magmas during their crystallization. Furthermore, intrusions also generate aqueous fluids in the country rocks during their dehydration reactions. These hydrothermal fluids may dissolve radiogenic isotopes from the country rocks.
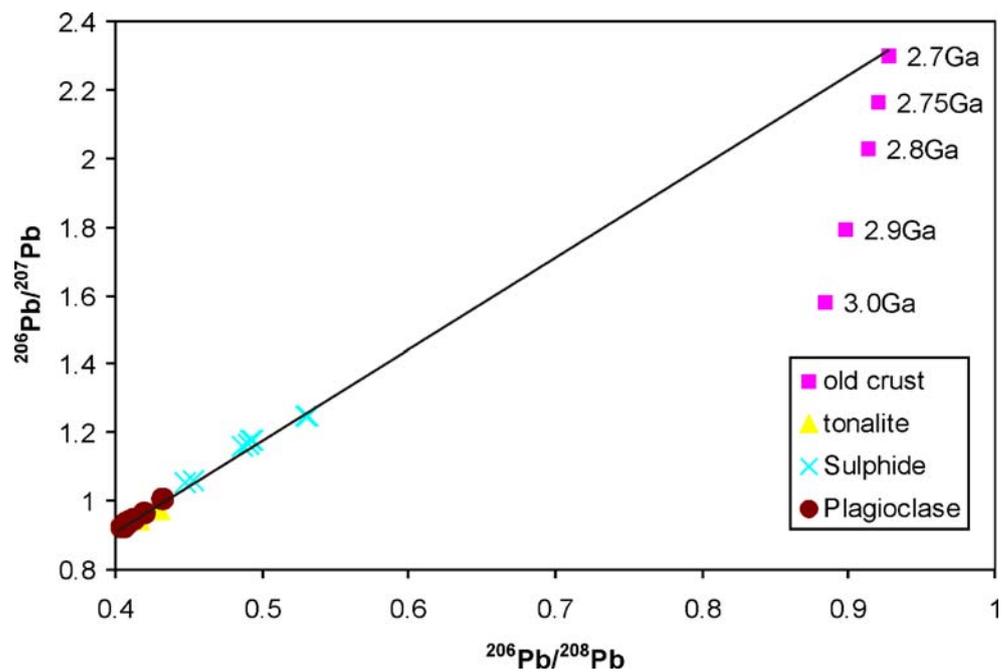
Pyrrhotite of magmatic origin with exsolved pentlandite in sample JH-02-185 also shows a highly radiogenic Pb isotope signature. The sample is an unaltered gabbronorite containing pristine orthopyroxene and plagioclase. The decoupling of isotopic compositions of sulfides and silicates in one hand specimen requires that the two formed at different locations during the evolution of the parental magma. At Lac des Iles, the immiscible separation of sulfide melt took place early during the evolution of the intrusive complex as evidenced by high Cu/Pd ratios in early leucocratic rocks (Hinchey et al. 2005). Parental magmas for early leucocratic intrusions lost sulfide at depth. The dense sulfide melt likely settled at the base of the magma chamber or along the conduit of their magmas. Later, volatile-rich magmas became fertile by picking up the PGE-enriched sulfide melt and show low Cu/Pd (Hinchey et al. 2005). The variation of Cu/Pd ratios and the intrusive history of the Lac des Iles complex suggest that sulfide melt was present for a long time during the entire evolution of the Lac des Iles complex because earlier leucocratic phases were already solidified to form angular fragments in later mafic phases (Fig. 3a). Furthermore, mafic magmas would solidify at temperatures above 800°C, but the complete solidification of sulfide melt would occur at much low temperatures, ~300°C (e.g., Kelly and Vaughan 1983). Sulfide melt, ponding at the base or along the conduit of magmas, was close to the contact with the country rock and could easily incorporate the radiogenic Pb isotopes leached from country rocks.

Hinchey et al. (2005) proposed that the Lac des Iles intrusive complex formed through a series of intrusions of comagmatic parental magmas and that the mineralization is primarily magmatic in which sulfide melt was enriched in PGE. Earlier leucocratic magmas formed sulfide melt and later mafic magmas incorporated the earlier formed sulfide melt at the base or along the magma conduit. This implies that the earlier formed sulfide melt was exposed to large volumes of magma during the evolution of the Lac des Iles complex to become enriched in PGE. The fertile sulfides with radiogenic Pb isotope signatures were subsequently incorporated and brought to the upper crustal level by late melanocratic magmas. The proposed process is consistent with the observed high Pb isotopic ratios for sulfides compared to plagioclase separates.

Although the Wabigoon subprovince contains rocks as old as 3.0 Ga (Blackburn et al. 1992), the immediate country rocks of the Lac des Iles intrusive complex range from 2.78 to 2.72 Ga (D. Davis cited in Stone et al. 2003). To evaluate the source of Pb for the radiogenic signatures of sulfides, we plotted $^{206}Pb/^{208}Pb$ vs $^{206}Pb/^{207}Pb$ ratios of our samples and possible country rocks in the area in Fig. 7. The $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ 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). It should be noted that this is not meant to give a unique explanation of the data considering variable concentrations and ratios of Th/U in actual rocks, but it provides an estimate of possible source rocks for the radiogenic Pb.

Continental crust with an age of ~2,700 Ma plots on the extrapolation of the trend defined by the samples from the Lac des Iles deposit (Fig. 7). Although there are large uncertainties in the estimated $^{206}Pb/^{208}Pb$ ratios due to different Th/U ratios among rocks (e.g., Paul et al. 2003), the model calculation shows that hydrothermal leaching of radiogenic ^{206}Pb, ^{207}Pb, and ^{208}Pb could explain the observed values for sulfide minerals. Radiogenic ^{206}Pb, ^{207}Pb, and ^{208}Pb produced by the decay of U and Th would be loosely held in minerals and easily released during hydrothermal activity (e.g., Faure and Mensing 2005). An additional calculation was made to estimate the increase in Pb isotope compositions of sulfide melt by incorporating radiogenic Pb from such country rocks. The calculation shows that radiogenic Pb released from even 2.70–2.75 Ga rocks may explain the observed values. Sulfides 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 the ore has low sulfide content (<1–2 wt% in most cases). The entire ore of 88 million metric ton contains ~1 ton Pb. Assuming that the Pb isotope composition of sulfide changed from the values similar to plagioclase ($^{206}Pb/^{204}Pb=13.5$, $^{207}Pb/^{204}Pb=14.55$) to the observed values ($^{206}Pb/^{204}Pb=18.5$, $^{207}Pb/^{204}Pb=15.77$) and that the decay products of U were leached from country rocks (1 ppm U), only 8 million tonnes or 68 million tonnes of 2.75 Ga rocks are required to explain the observed increase in ^{206}Pb and ^{207}Pb, respectively. Considering the size of the Lac des Iles intrusion, ~30 km^2 in outcrop area, the required amount of country rocks is very reasonable.

Sulfide minerals in many other PGE deposits are considered to be of magmatic origin, but they commonly contain too high of concentrations of PGE to be explained by a single magmatic process (e.g., Hamlyn and Keays 1986). The finding at the Lac des Iles deposit based on Pb isotopes sheds light on the PGE enrichment process for these sulfide minerals. Ponding of sulfide melt at the base of a magma chamber or along the conduits provides an opportunity for sulfide melt to be exposed to and interact with large quantities of magma and to become enriched in PGE. It is likely that sulfide ponding was an important process in the enrichment of PGE in other PGE deposits. Indeed, other PGE deposits also show decoupling of Pb isotopes between sulfide and coexisting silicate minerals (e.g., Harmer et al. 1995; Mathez and Waight 2003). Unlike large layered intrusions, the Lac des Iles intrusive complex provided Pb isotope data retaining primary values because it formed by injections of a series of small intrusions that cooled quickly without extensive recrystallization.

Conclusions

Radiogenic Pb isotopic signatures for sulfides compared to plagioclase from the same samples of the southern Roby and Twilight zones suggest that the sulfide melt acquired radiogenic Pb leached from country rocks. The ponded sulfide melt was exposed to large quantities of magma during the evolution of the Lac des Iles intrusive complex. Thus, Pb isotopic compositions support our model based on Cu/Pd ratios of sulfides (Hinchey et al. 2005) where earlier formed immiscible sulfide melt was incorporated by later mafic magmas. The proposed interpretation explains the high PGE concentration in late mafic intrusions at the Lac des Iles deposit and may also apply to other PGE deposits.

Appendix

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 sulfides. Most primary silicates have been altered to assemblages of secondary amphiboles (actinolite/tremolite) and chlorite after clinopyroxene and sericite after plagioclase. Blebby sulfides consist of relict pyrrhotite with exsolved pentlandite and chalcopyrite, and abundant secondary pyrite (10°52″ 42.5′E and 10°42″62′N 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 sulfides. Primary clinopyroxene is altered to secondary amphiboles (actinolite/tremolite) and chlorite with plagioclase variably altered to sericite. Sulfides consist of pyrrhotite with lesser amounts of exsolved pentlandite and chalcopyrite, and abundant secondary pyrite replacing the magmatic sulfides (10°52″42.5′E and 10°42″62′N 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 sulfides dominated by pyrrhotite with lesser amounts of exsolved pentlandite and chalcopyrite. Pyrite is observed to variably replace the magmatic sulfides (10°53″20′E, 10°41″99′N 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 sulfides consisting of pyrrhotite with exsolved pentlandite and chalcopyrite. Minor pyrite is observed overprinting the primary magmatic sulfide assemblages (10° 53″75′E, 10°41″20′N 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 sulfides 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 (10°59″35′E, 10°47″80′N 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 sulfides 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 (10°59″78′E, 10°46″37′N 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. Sulfides, 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. Sulfide, ~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).

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