

Using the High Mobility of Palladium in Surface Media in Exploration for Platinum Group Element Deposits: Evidence from the Lac des Iles Region, Northwestern Ontario

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Abstract

Platinum group element (PGE) mineralization is commonly accompanied by large amounts of Ni-Fe sulfides, which are explored for using a variety of geophysical and geochemical methods. Appreciation of a new type of PGE mineralization is emerging, hosted by gabbroic rocks with low concentrations (<5 vol %) of disseminated sulfides. The host rocks commonly display textural complexity, such as brecciation, pods and veins of pegmatite, and magma mingling of different lithological units. Examples include the Lac des Iles deposit in northwestern Ontario, the East Bull Lake suite in eastern Ontario, and several intrusions in the Kola Peninsula, and northern Finland. Such mineralization does not result in prominent geophysical and geochemical anomalies, thus posing a challenge for exploration. We initiated a project to develop new geochemical exploration approaches for such PGE deposits with low sulfides and selected the Lac des Iles district, northern Ontario, Canada, which contains one producing mine and many Pd showings. Mineralization is hosted by gabbroic rocks with low concentrations (<5 vol %) of sulfides. Enriched elements include Pd, Pt, Au, Ni, Cu, and Co. In separate sulfide-rich mineralization, base metals can be abundant, up to 1 wt percent, but Pd is insignificant (<200 ppb). This reduces the relevance of Ni, Cu, and Co as possible pathfinders for sulfide-poor PGE mineralization, leaving Pd, Pt, and Au.

A detailed study in the Baker zone at the Lac des Iles mine and the Legris Lake property indicates the essentially immobile nature of Pt in these surface environments. By contrast, Pd is depleted in B horizon soil, suggesting its removal during the conversion of C to B horizon soils. The loss of Pd in B horizon soil reflects the transport of Pd as neutral and anionic complexes, probably with OH⁻ and possibly with organic ligands, which are not adsorbed by Fe oxyhydroxides in the soils. Instead, Pd migrates in solution to accumulate in humus in swamps and organic-rich lake sediments downslope from mineralization. The distribution of Pd in humus, therefore, provides a distal indicator of nearby mineralization.

Total digestion of humus using fire assay or aqua regia yielded up to 160 ppb Pd, whereas a variety of commercially available leaching methods extracted few ppb Pd. The results indicate that Pd is tightly held in organic matter. This behavior of Pd contrasts with many metallic elements, such as Cu and Ni, that are enriched in B horizon soil and may be extracted by a variety of leaching techniques.

Palladium arsenides, tellurides, antimonides, and sulfides are unstable in weathering environments and their dissolution releases Pd to surface waters. Therefore, Pd can be used to indicate other PGE mineralization as it is always abundant among PGE. Where PGE mineralization is associated with high concentrations of Fe sulfides, their oxidation produces acidic waters, which further promotes Pd dispersion. Thus, the findings of this study are applicable to exploration for both sulfide-rich and -poor PGE mineralization.

Introduction

SIGNIFICANT platinum group element (PGE) mineralization is accompanied by large quantities of Ni-Fe sulfides. A variety of geophysical and geochemical techniques are effective in exploring for this type of ore. For example, pyrrhotite, the predominant mineral in the ore, is magnetic, conductive, and dense, producing geophysical anomalies around the deposits that are useful for exploration. Furthermore, pyrrhotite promotes weathering of rocks because its oxidation produces acidic waters. Metals, such as Cu, Ni, and Co, are readily released to surface media and the dispersion of these metals can be used as pathfinders.

A new type of PGE deposit has recently been recognized, distinct from those associated with massive sulfides. PGE are

disseminated in sulfide-poor (<5 vol %) gabbroic rocks that show textural complexity, i.e., brecciation, magma mingling, veining of pegmatite, and mixing of lithological units with different grain size (varitextured gabbro). Examples include deposits in the Lac des Iles district in northwestern Ontario (Sutcliffe, 1986; Sutcliffe et al., 1989; Lavigne and Michaud, 2001; Pettigrew and Hattori, 2002; Hinchey et al., 2003), the Coldwell Complex on the north shore of Lake Superior (Barrie et al., 2002), East Bull Lake intrusive suites in eastern Ontario (Peck et al., 2001; James et al., 2002), and several intrusions in the Baltic Shield (Schissel et al., 2002). The current exploration method for this type of mineralization relies on assays of exposed rocks and drill core samples. This may be useful in the immediate vicinity of known deposits, but it is not practical during regional exploration and in targeting new areas. Conventional geophysical exploration techniques also

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are not readily applicable to these sulfide-poor PGE deposits. Indeed, cursory examination of mineralized rocks gives the initial appearance of ordinary gabbros. In order to find a suitable geochemical exploration technique for this type of deposit, we initiated a project in the summer of 2002 in the Lac des Iles-Legris Lake district.

Previous work has shown significant mobility of Pd in surface and near-surface environments. Palladium concentrations, up to 96 ppb, were found in organic fractions of soil near the Stillwater Complex (Fuchs and Rose, 1974). High Pd values, up to 2.3 ppm, in tree ash from the Ferguson Lake, Northwest Territories, and Rottenstone Lake, Saskatchewan, confirm transport of Pd by surface waters (Coker et al., 1991). The evidence suggests that Pd has the potential to be used as a pathfinder element for PGE mineralization. However, the results of previous studies are puzzling. The data by Fortescue et al. (1987) and Coker et al. (1991) show that high Pd values were found also in soils overlying barren rocks away from the mineralized zones. Such results have cast doubt on whether Pd is a reliable pathfinder for exploration because it is assumed that greater concentrations should be found close to mineralization. In order to use Pd as a reliable indicator for exploration, we need to know how and where Pd is enriched in the surface media. The low sulfide contents of mineralized rocks pose an additional question: in the absence of sulfide oxidation are metals from such mineralization still mobile?

This paper presents data on the Pd contents of soil in the Lac des Iles-Legris Lake district and evaluates the mode of

dispersion of Pd in the surface environment. This information is applicable to exploration for a variety of PGE deposits elsewhere because Pd is abundant in nearly all PGE-bearing deposits (e.g., Naldrett et al., 1994; James et al., 2002).

Geologic Settings

The study area is located in the southern Wabigoon subprovince of the Archean Superior Province of Canada. A suite of Late Archean mafic-ultramafic rocks intruded the southern Wabigoon subprovince over a distance of 230 km, from Atikokan to Lake Nipigon along the border with the Quetico metasedimentary belt (Pye, 1968; Sutcliffe, 1986). Among the intrusions, Pd mineralization is hosted by a group of mafic-ultramafic igneous rocks that form a circular aeromagnetic anomaly approximately 30 km in diameter (Fig. 1; Gupta and Sutcliffe, 1990). The largest is the Lac des Iles Complex, which intruded tonalitic rocks and volcano-sedimentary rocks of the Lac des Iles greenstone belt. The Lac des Iles Complex hosts the Lac des Iles palladium mine, which has been in operation since 1993. The current reserve is 159 million metric tons (Mt), grading 1.55 g/t Pd, 0.17 g/t Pt, 0.12 g/t Au, 0.06 percent Cu, and 0.05 percent Ni at a Pd cutoff grade of 0.7 g/t (Lavigne and Michaud, 2001).

Other intrusions that host mineralization with greater than 2 ppm Pd include the Legris Lake, Tib Lake, and Wakinoo Lake Complexes (Fig. 1). Palladium mineralization is restricted to gabbroic rocks that show textural complexity, such as pegmatite veining and brecciation (Sutcliffe et al., 1989;

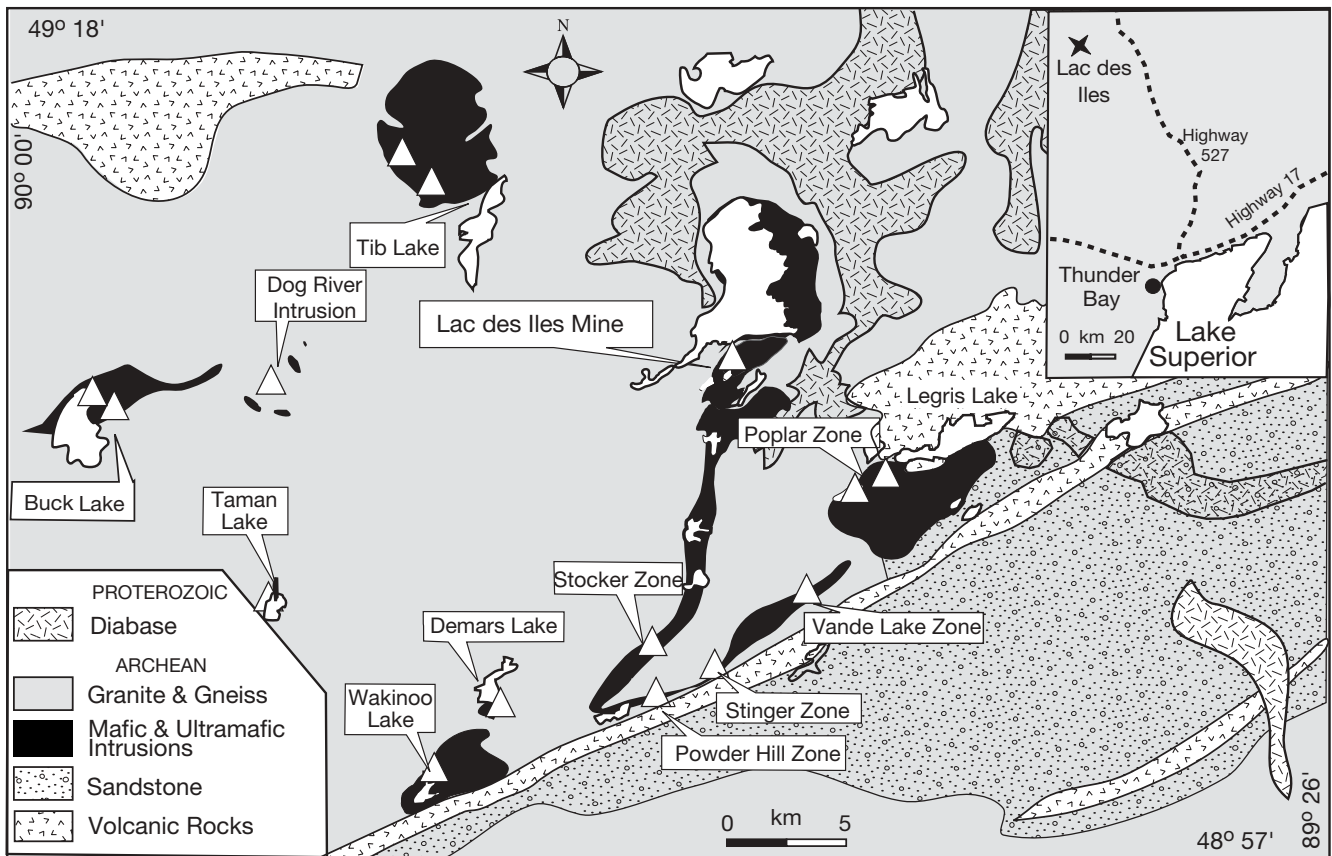


FIG. 1. Mineralized gabbroic rocks in the Lac des Iles-Legris Lake district, north of Thunder Bay, Ontario.

Lavigne and Michaud, 2001; Hinchey et al., 2003). Homogeneous gabbros and ultramafic rocks, such as voluminous ultramafic rocks in the northern part of the Lac des Iles Complex and hornblende gabbro in the southern part of the Complex (Fig. 2), are essentially barren. In the Legris Lake Complex, massive leucogabbro in the center of the complex is barren and all known mineralization is restricted to the north-western part where the host rocks are extensively brecciated (Fig. 3; Pettigrew and Hattori, 2001, 2002).

In all cases, mineralization is characterized by low contents of disseminated sulfide minerals (less than 3 vol % in most rocks), although there is a broad positive correlation between Pd and sulfide contents (Pettigrew and Hattori, 2002; Hinchey et al., 2003). Sulfide minerals are predominantly pyrrhotite and chalcopyrite with minor pentlandite. Pyrite is not common in most mineralized zones but is locally abundant in rocks that have been affected by late hydrothermal activity. Accordingly, surface exposure of mineralized rocks does not produce gossans, although minor stains of Fe oxides and hydroxides are observed locally on the surface and along fractures.

Quaternary glacial sediments and surficial deposits

The exposure of bedrock in the study region is poor. More than 80 percent of the surface is covered by lakes and Quaternary glacial sediment. The last ice direction was mainly to the southwest (200°–240°), and large eskers are present north of Lac des Iles and south of the Legris Lake property (Mollard, 1979). In the region, glacial till is the predominant Quaternary deposit and occurs as thin (<5-m-thick) discontinuous veneers overlying bedrock, with thicker accumulation in valleys (Pye, 1968; Mollard, 1979). Till consists of cobbles and pebbles in a matrix of silt-sized sands with rare local clays;

they are porous and permeable and mildly oxidized to brown colors, caused by percolating rainwater.

Humus is commonly developed over bedrock and till, but the underlying B horizon soil is poorly developed. There are several modes of occurrence of humus: (1) in upland forested areas, a relatively thick humus, >10 cm, underlies leaf fall and sphagnum and overlies a thin B horizon soil, less than several centimeters in thickness; (2) near lakes, thick sphagnum and organic-rich soil directly cover cobbles and boulders without B and C horizon soils; (3) in wetlands along the drainages, sedges are abundant and thick organic-rich soil (>20 cm) and partially decayed sedges directly cover wet cobbles and boulders. We refer to the latter two occurrences as “swamp humus,” where the predecessor plants are in close contact with water that has run off adjacent ground. We refer to humus from the forested areas as “forest humus.”

Sampling, Sample Preparation, and Analytical Methods

Preliminary sampling in May 2001 at several properties showed high Pd values in humus along drainage paths and swamps, whereas underlying soil samples are not highly anomalous. Therefore, we collected mostly swamp humus during subsequent sampling between June and October 2002. A hand-held auger was used to collect different horizons of soil samples, but humus was mostly collected by hand. Approximately 2 liters of humus or soil was taken at each site. Samples were air-dried at temperatures less than 60°C and sieved to minus 80 mesh (<117 μm). A 15-g subsample was digested by aqua regia (1:3 mixture of concentrated nitric acid and HCl) and analyzed by inductively coupled plasma-emission spectrometer (ICP-ES) and inductively coupled plasma-mass spectrometer (ICP-MS) for Pd, Pt, Au, Cu, and

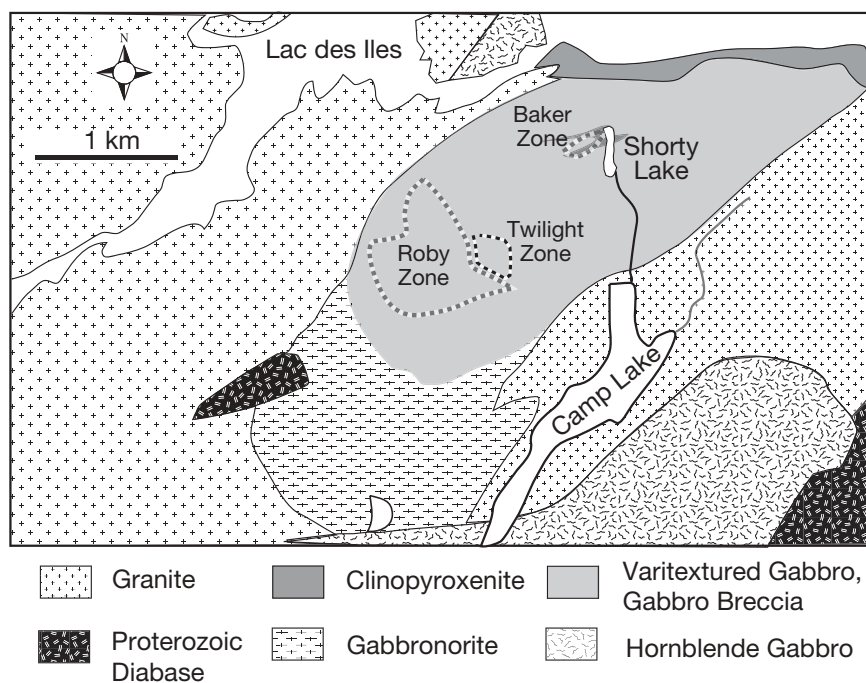


FIG. 2. Geology of the central part (Mine Block intrusion) of the Lac des Iles mafic-ultramafic complex and the locations of major ore zones (Roby, Twilight, and Baker) and Shorty Lake. Thick dashed line outlines the ore zones.

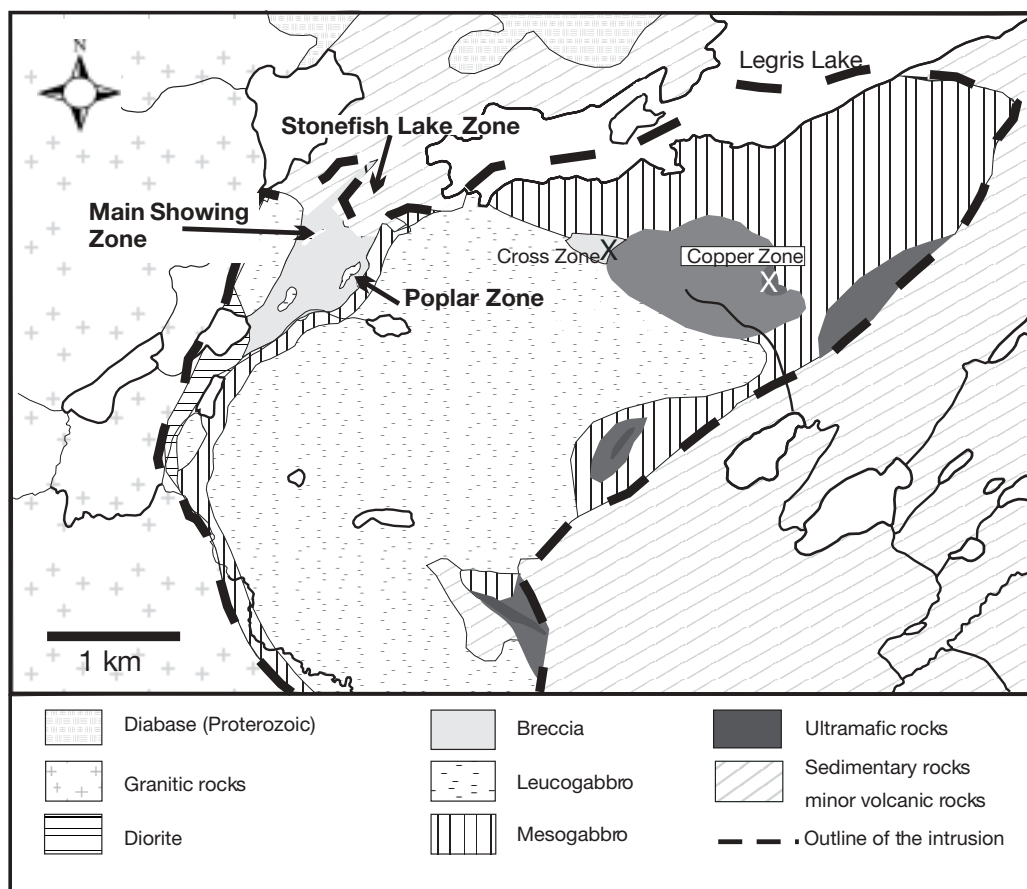


FIG. 3. Geology of the Legris Lake Complex and the location of the Pd mineralization (Poplar zone, Main Showing zone, Stonefish Lake zone). The Cross Lake and Copper zones in the center of the property contain significant sulfides but do not contain significant Pd (<500 ppb). Modified after Pettigrew and Hattori (2001).

Ni (reported here) and for other elements. For approximately half of the samples a further 15-g aliquot was fire-assayed to preconcentrate precious metals to the Pb collector, followed by nitric acid digestion for ICP-MS measurements of Pt, Pd, and Au. The values of Pd, Pt, and Au obtained by the two methods are comparable, but the fire assay method gave better detection limits for Pd (2 ppb, compared to 10 ppb by aqua regia). Base metal contents were determined by ICP-ES and ICP-MS after aqua regia digestion.

Lake sediments were collected using a gravity corer (80 cm in length) from the float of a helicopter by R. Dyer of the Ontario Geological Survey. These were taken at two depth intervals: surface samples at <15 cm and deep samples from ~20 to ~55 cm. Sediment at the depths between 15 and 20 cm was discarded. They were analyzed by similar methods to those used for the soils, including aqua regia digestion and fire assay for the precious metals. A split of the lake sediment samples was also analyzed at the Ontario Geological Survey and tabulated in Dyer and Russell (2002). These data are similar to our results.

Water samples from streams running over the mineralized rocks, from lakes, water discharging from drill holes, and along the boundary between glacial sediments and rocks were collected and the conductivity and pH were measured at the time of collection. The water samples were collected

in 125- or 500-ml Nalgene high-density polyethylene bottles, and the compositions of the waters were determined directly by ICP-ES and ICP-MS.

Representative mineralized rock samples from drill core and surface exposures were collected between 2000 and 2002. They were examined using a petrographic microscope and a scanning electron microscope equipped with an energy-dispersive spectrometer to identify Pd-bearing minerals. The bulk-rock samples were also analyzed by X-ray fluorescence spectrometer (XRF) after fusion with Li metaborate and Li tetraborate. Minor and trace chalcophile elements were determined after aqua regia digestion using ICP-ES and ICP-MS, similar to the methods applied to humus samples. Platinum, Pd, and Au were preconcentrated into a Pb button by fire assay, before dissolving into nitric acid for ICP-MS analysis. For quality control, one mineralized rock sample from Legris Lake and one humus sample from Shorty Lake were analyzed every 10 samples. Palladium and Pt contents of five humus samples were also determined by the NiS fire assay technique, using a mixed spike containing ^{105}Pd and ^{194}Pt , as described in Guillot et al. (2000).

Representative samples (16 B horizon soils and 16 humus samples) were analyzed by commercially available partial extraction methods. Elements were extracted by cyanide

solution (a mixture of 0.3% NaCN and 0.1% NaOH) at Acme Laboratory and by the proprietary Enzyme Leach™ and TerraSol Leach™ of Activation Laboratories Ltd. The Enzyme Leach™ is a weak leach containing gluconic acid, which extracts metals adsorbed on Mn oxides (Clark, 1993). TerraSol Leach™ dissolves both Mn and Fe oxides. The cyanide leach (0.3% NaCN and 0.1% NaOH) dissolves elements bound to clay, organic matter, and Fe and Mn oxides.

Results

Palladium-bearing minerals and enriched elements in the mineralization

Palladium forms arsenides, tellurides, antimonides, and bismuthinides in the mineralized rocks. Precious metal-bearing minerals so far identified include moncheite (PdTe_2), merenskyite (PdTe_2), sperrylite (PtAs_2), palladoarsenide (Pd_2As), stillwaterite (Pd_8As_3), vysotskite (PdS), braggite (PdS), stibiopalladinite ($\text{Pd}_{5+x}\text{Sb}_{2-x}$), sopcheite ($\text{Ag}_4\text{Pd}_3\text{Te}_4$), and native gold (Au, Ag; see also Edgar and Sweeny, 1991; Lavigne and Michaud, 2001; Cabri, 2002; Pettigrew and Hattori, 2002; Watkinson et al., 2002). Among them, kotulskite (PdTe) is the most common phase in the district (Fig. 4). Braggite, (Pt, Pd, Ni)S, the only PGE-bearing sulfide, is not as common as other minerals, probably reflecting low sulfide contents in the mineralization.

Although platinum group minerals commonly contain Te, As, Sb, and Bi, their concentrations are not significantly elevated in the bulk rocks. Tellurium and Bi concentrations are commonly below 0.5 ppm with sporadically high values. Metals enriched in the mineralized rocks are Pd, Pt, Au, Ni, Cu, and Co (Figs. 5, 6). Any one of these metals may be used as a pathfinder element for Pd mineralization, but Ni, Cu, and Co are also enriched in separate sulfide-rich rocks in the study area, which are not associated with Pd. High contents of Au are erratically distributed along late faults (Pettigrew and Hattori, 2002). Therefore, base metals and Au are not necessarily reliable indicators of Pd mineralization. Silver is enriched in Pd mineralization and correlates broadly with Pd (not shown in this study) in some showings, such as the Legris Lake, Buck Lake, and Wakinoo Lake showings. In addition, sopcheite ($\text{Ag}_4\text{Pd}_3\text{Te}_4$) is identified in the showings of Legris Lake property (Pettigrew and Hattori, 2002). However, the concentration of Ag at the Lac des Iles mine is very low (Fig. 5). Therefore Ag is also not a consistently good indicator of Pd mineralization, which leaves only Pd and Pt as potential pathfinders during exploration for PGE mineralization.

Shorty Lake area, Lac des Iles mine

The small, north-trending Shorty Lake (Figs. 2, 7) is located immediately east and downslope from the Baker zone, which contains high-grade ore ($> 3\text{g/t Pd} + \text{Pt}$) in its west central part (unpub. data, North American Palladium Ltd.). The company has thoroughly explored the land to the east of the lake, sampling rocks along the trenches shown in Figure 7. However, there are only a few occurrences of Pd with assay results over 0.2 g/t Pd (Fig. 7).

Searcy (2001) recently tabulated high-quality data on Pd, Pt, Au, and base metals for B and C horizon soils across and peripheral to the Baker zone on traverses parallel to the

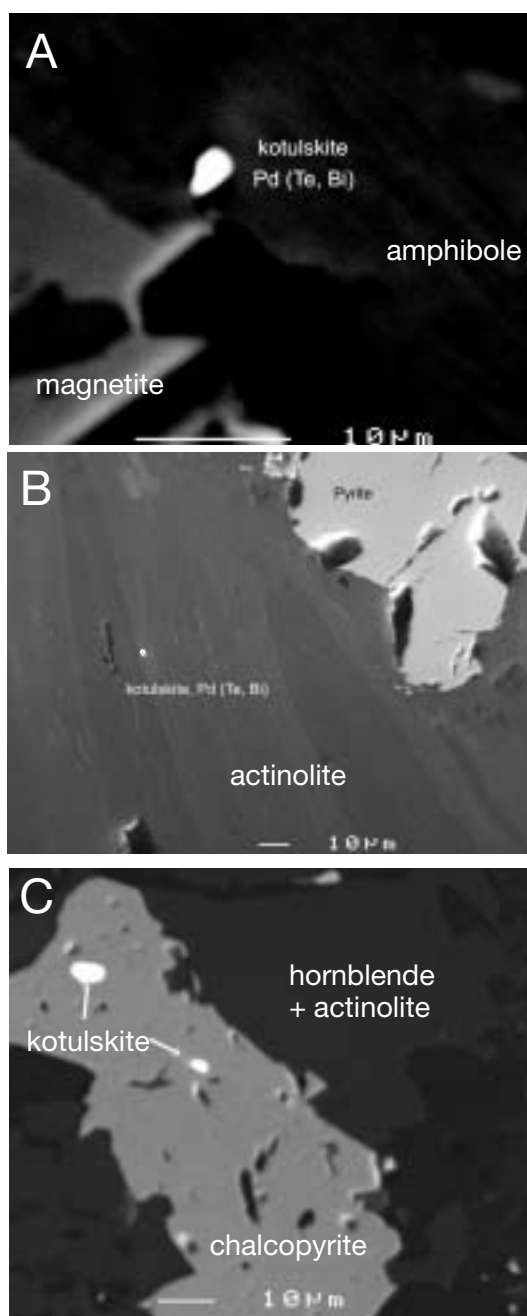


FIG. 4. Backscattered electron images of representative platinum group minerals at the Lac des Iles mine and Legris Lake. A. Kotulskite (Pd(Te, Bi) , white in the image) in amphibole in the Poplar zone, Legris Lake property. B. Kotulskite (white in the center) in actinolite blades, in the Main Showing zone, Legris Lake property. C. Kotulskite enclosed in chalcopyrite, which is surrounded by a mixture of hornblende and actinolite, in the Baker zone.

direction of ice movement in order to define the glacial dispersion of metals (Fig. 7). These mostly represent soil profiles from topographically high areas (Fig. 7). The C horizon soil samples have a wide range of Pd and Pt concentrations (Fig. 8), reflecting the presence of fragments of mineralized rock. The median values (lower and upper quartiles in parentheses) of 42 samples are 4.1 ppb Pd (2.9, 6.1) and 2.8 ppb Pt (2.4,

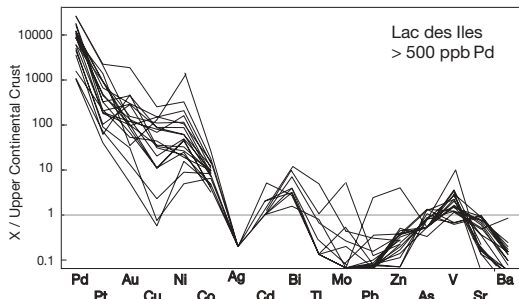


FIG. 5. Elemental abundance of ore zones at the Lac des Iles mine. The values are normalized to the concentration in upper continental crust from McLennan and Taylor (1999). Antimony, Te, and Se are not shown because their concentrations in selected samples are highly variable, probably due to nugget effects, with most samples below the detection limit of 0.02 ppm.

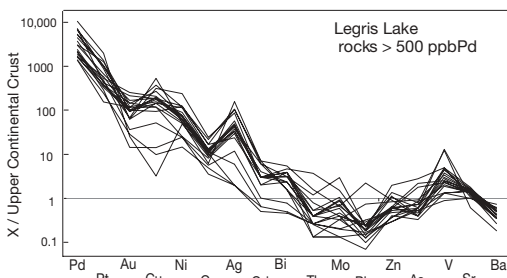


FIG. 6. Elemental abundance of mineralized rocks (>500 ppb Pd) in the Legris Lake property. The values are normalized to the concentration in upper continental crust from McLennan and Taylor (1999). Antimony, Te, and Se are not shown because their concentrations in most samples are below the detection limit of 0.02 ppm.

3.3). The B horizon soils do not contain as much Pd as observed in the C horizon samples (Fig. 8). The median values (lower and upper quartiles in parentheses) are 2.5 ppb Pd (1.7, 3.9) and 2.2 ppb Pt (1.7, 3.0). The low values of Pd in B horizon soil suggest the removal of Pd during the conversion of C into B horizon soil.

We collected swamp humus along drainage and in swamps in topographically low areas surrounding the lake (Fig. 9). These sample sites were commonly moist to partially wet in May 2002 and directly overlie wet cobbles and boulders, without B or C horizon soil. The swamp humus samples are notably enriched in Pd up to 160 ppb Pd. The values are high compared to forest humus samples and B and C horizon soil samples (Fig. 8), suggesting that the Pd removed from soil enters the drainage system in solution and is fixed in the humus. High values of Pd in the swamp humus along the west side of the lake are considered to reflect PGE mineralization in the Baker zone, whereas low values are found on the eastern shore of the lake.

Platinum concentrations in all samples are generally low, with a few significant values from swamp humus samples on the west side of the lake (Fig. 9). Similar comparisons for Ni and Cu (Fig. 8) indicate that there is no enrichment in these elements in the humus samples relative to the B and C horizon samples. Gold is mobile and behaves in a manner similar to Pd, but the concentrations of Au in the mineralized rocks and soil samples are generally much lower than Pd.

There is a difference in the Pd content of humus taken from a well-drained area (forest humus) and down-drainage from the Baker zone (swamp humus), as shown by the analyses of humus samples along two lines from Shorty Lake

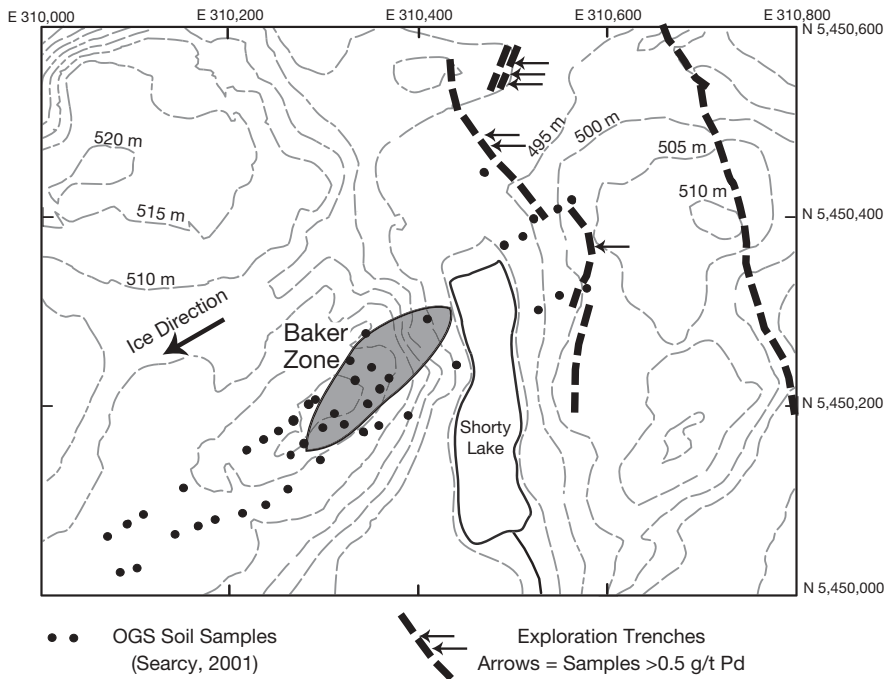


FIG. 7. Topographic map of the area around Shorty Lake, showing the outline of the high-grade zone (>3 g/t PGE) of the Baker zone, the location of exploration trenches east of the lake, and the location of the B and C horizon soil samples taken by Searcy (2001). Water from Shorty Lake drains south through a wide swamp. The swamp is covered by tall (>1 m) sedges with small dry islands that are covered by thick (>20 cm) moss. Water is not visible from the surface, but is apparently flowing slowly through boulders and cobbles underlying humus and sedge south of the lake.

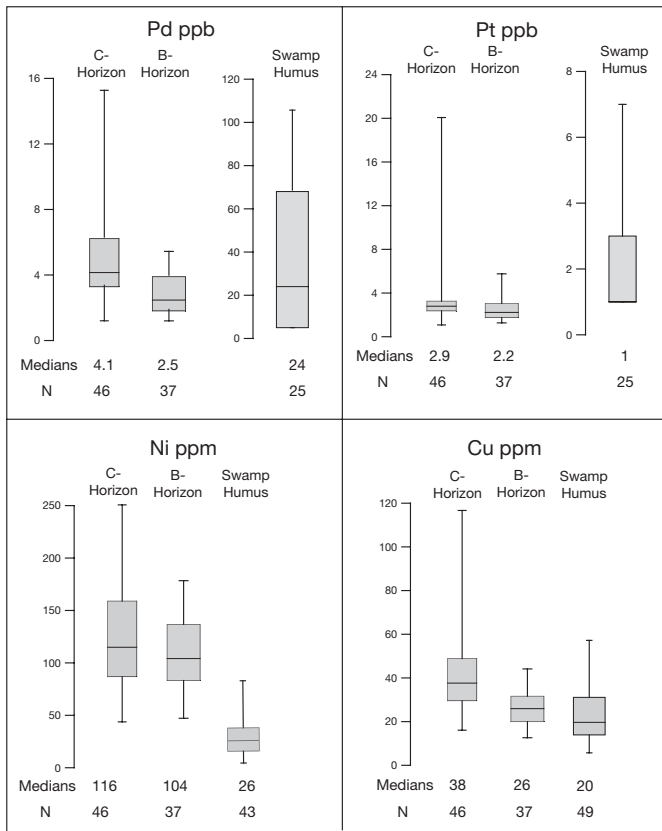


FIG. 8. Box-whisker plots for Pd and Pt (ppb) and Ni and Cu (ppm) in samples from around Shorty Lake. B and C horizon soil data are from Searcy (2001); humus samples from the swamp are from this study. N = number of samples.

upslope to the Baker zone (Fig. 9). The C horizon soil samples underlying the humus east of the Baker zone contain little Pd

because the southwestward ice movement carried away the scoured mineralized rock fragments to the southwest. Palladium contents of the upslope forest humus samples are less than 10 ppb, whereas the humus from swamps around the lake is strongly anomalous in this element (Fig.9).

Organic-rich lake sediments at two sites in Shorty Lake (LS1 and LS2, Fig. 9) are enriched in Pd compared to the median for a large number of lake sediments from the region (Table 1). Platinum is less mobile and has not reached the lake sediments, hence Pt concentrations are not greater than the regional median (Table 1). Sulfur is not anomalously enriched in the lake sediments, consistent with the sulfide-poor nature of the PGE mineralization. The Cu, Ni, and Cr contents in the Shorty Lake sediments listed in Table 1 are substantially greater than the regional median values for lake sediments but within the range of values for C horizon soils around the lake (Fig. 8). Samples at the surface (shallower than 15 cm) and from depth (greater than 20 cm) at the two sites have similar compositions, including major elements and Pd concentrations.

The Legris Lake Complex

Searcy (2001) conducted sampling along a southwest-trending traverse, down-ice direction from the Poplar zone (Fig. 3). Plots of results for Pd, Pt, Ni, and Cu in these samples are shown in Figure 10. The C horizon soils have a large range of metal concentrations, reflecting the presence of mineralized fragments. The B horizon soils contain low concentrations of all four elements, with median values of 1.6 ppb Pd, 1.7 ppb Pt, 30 ppm Cu, and 43 ppm Ni. The evidence in these samples is consistent with the removal of Pd during the transformation of C to B horizon soil. Forest humus samples from the Legris Lake Complex have median values of 3.8 ppb Pd, 2.3 ppb Pt, 14 ppm Cu, and 11 ppm Ni (Fig. 10). The values are slightly higher than those of B horizon soil, but the values overall are low. Swamp humus from the same area is

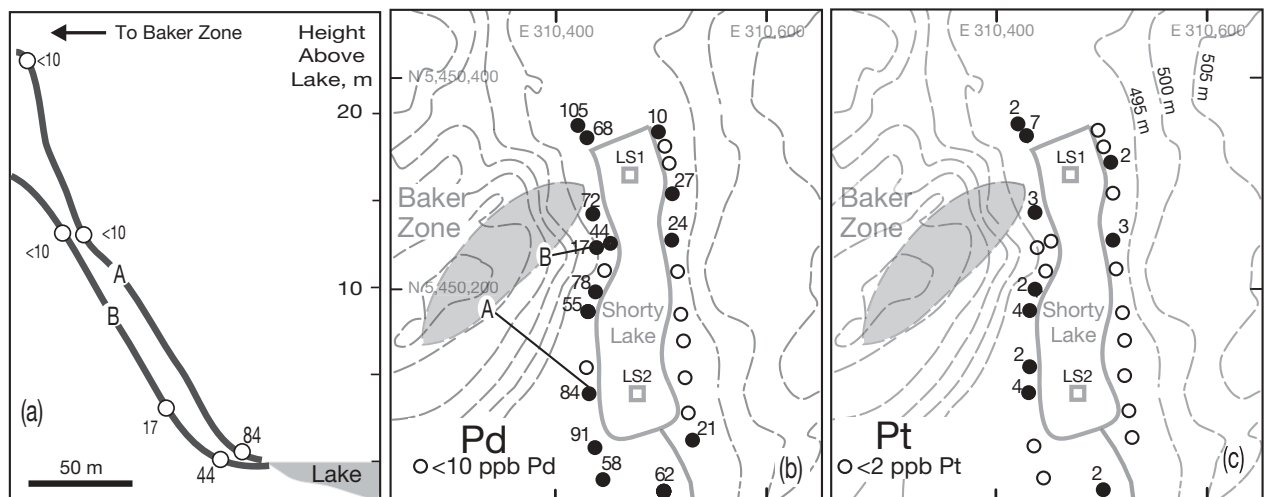


FIG. 9. Distributions of Pd and Pt (ppb) in samples of humus in the Shorty Lake area. A. Distribution of Pd in humus (ppb) along two sampling lines west from the shore of Shorty Lake. The samples on higher ground (forest humus) toward the mineralized Baker zone contain less Pd than humus from swamp around the lakeshore. Location of lines (A, B) shown in the adjacent diagram. B. and C. Distributions of Pd and Pt (ppb) in swamp humus around the shore of Shorty Lake. Analysis by aqua regia-ICP-MS. Contour interval is 5 m (see Fig. 7). Lake sediment sites shown as LS1 and LS2 and the results are in Table 1.

TABLE 1. Lake Sediment Data for Samples from Shorty Lake

Site	Depth, (cm)	Pd ¹ (ppb)	Pt ¹ (ppb)	Au ¹ ppb	S (wt %)	Se (ppm)	Cu (ppm)	Ni (ppm)	Cr (ppm)	Fe (wt %)	Mn (ppm)
LS1, <15 cm	0–15	10.3	1.9	3.7	0.28	2.0	105	141	195	1.36	188
LS1, 20–50 cm	>20	15.1	2.1	3.8	0.21	2.5	142	156	220	1.50	175
LS2, <15 cm	0–15	13.7	2.1	3.2	0.36	2.3	105	127	167	1.49	180
LS2 20–50 cm	>20	10.1	1.4	1.4	0.22	2.1	121	148	199	1.83	234
Regional ²											
Median		3.9	1.3	<1.0	0.26	n.d.	45	23	21	1.19	163
95 percentile		12.8	3.2	3.2	0.65		102	48	53	4.46	700
5 percentile		1.3	<0.3	<1.0	0.13		17	12	8	0.34	48

Notes: Sampling locations are shown in Figure 10; n.d. = not determined

¹ Determined by fire-assay

² Regional median, 95th and 5th percentile values are for 675 lake sediment samples taken from the data of Dyer and Russell (2002) from a district surrounding Lac des Iles between the coordinates 48° 45' N, 49° 30' N, and 89° 30' W, 90° 00' W

substantially enriched in Pd compared to the values from forest humus, with up to 12 ppb Pd (Fig. 11, Table 2) over the

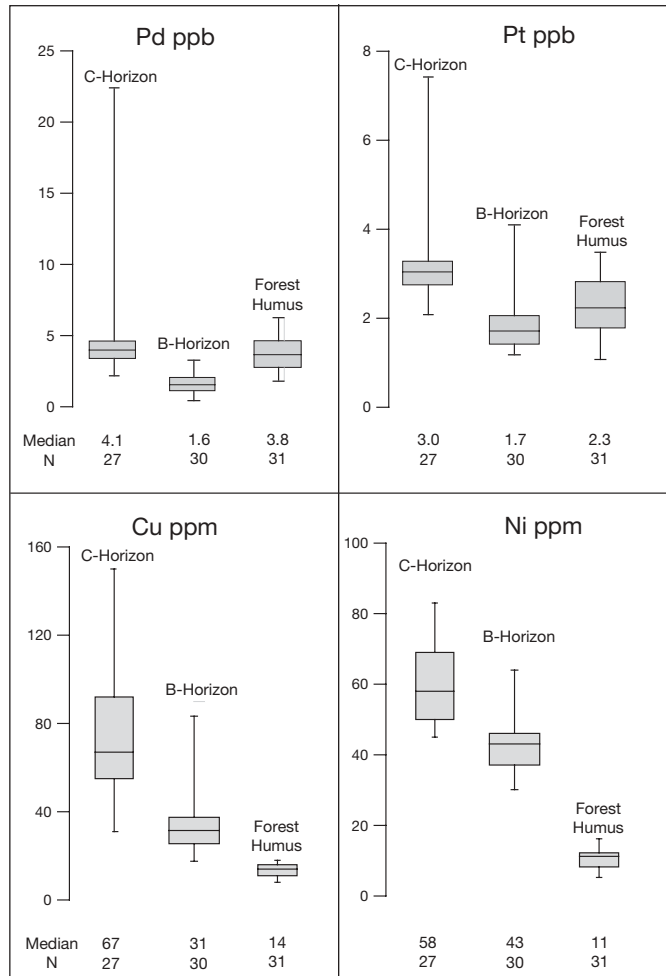


FIG. 10. Box-whisker plots for Pd and Pt (ppb) and Ni and Cu (ppm) for B and C horizon soils and humus from the mineralized northwestern part of the Legris Lake Complex shown in Figure 3 (Searcy, 2001). The sampling was conducted southwestward from the Poplar zone along the glacial path. The humus samples are labeled "forest humus" to distinguish them from humus samples collected along drainage and swamps in the entire intrusion. The Pd and Pt analyses are by fire assay-ICP-MS, and the Cu and Ni analyses are by aqua regia-ICP-MS. N = number of samples.

mineralized Poplar zone to the northwest (Fig. 3). The data confirm that Pd is accumulated in swamp humus, but the values are much lower than those observed in the Lac des Iles property. Only those samples in the vicinity of known mineralization in the northwestern part of the intrusion were anomalous (Fig. 11).

Leaching experiments

Soil and humus samples were subjected to selective leaching and the results were compared to those from the total extraction by fire assay. Comparison of the data shows that negligible amounts of Pd were extracted by the Enzyme Leach™ and TerraSol Leach™ (Fig. 12). Somewhat higher amounts were extracted by the cyanide leach but much less than the total amount of Pd as determined by fire assay (Fig.12). The results indicate that Pd is not loosely adhered to the surface of samples. Instead, the bulk of Pd is tightly bound in organic matter.

Surface waters

Surface waters in the study district are close to neutral and mostly clear and dilute (Table 3), reflecting high precipitation (711 mm/yr) and low evaporation under a cool climate. Subsurface waters along the contacts between the rocks and

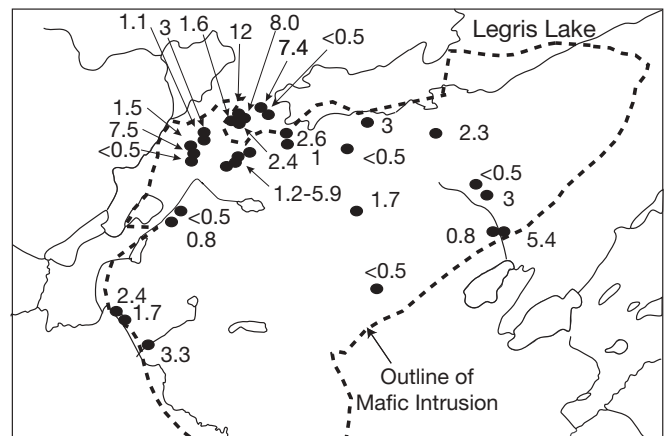


FIG. 11. Palladium contents (ppb) of swamp humus from the Legris Lake intrusion, determined by fire assay-ICP-MS. All of the high values are in the northwestern part of the intrusion, where all known Pd mineralization occurs (Poplar zone, Main Showings zone, and Stonefish Lake zone: Fig. 3).

TABLE 2. Comparison of Precious Metal Contents in Humus and Underlying Soil Horizons (UTM coordinates, NAD 27 Canada, Zone 16)

Sample no.	Soil horizon (depth)	Pd (ppb)	Pt (ppb)	Au (ppb)	Cu (ppm)	Ni (ppm)	Cr (ppm)
Pump House, Lac des Iles (307550E, 5449295N)							
020502-2	Forest humus	2.0	2.1	6	8.4	17	23
020502-3	B (<5 cm)	1.3	1.7	3	11	24	28
020502-4	B (5–10 cm)	1.3	1.5	3	16	36	34
020502-5	B (10–15 cm)	1.8	1.9	3	22	42	38
Shorty Lake, Lac des Iles (310432E, 5450072N)							
SLDI-22	Swamp humus	72.0 ¹	3 ¹	2.6 ¹	43	42	36
SLDI-23	C (25–35 cm)	7.6	2.7	<1	54	116	117
Shorty Lake, Lac des Iles (310435E, 5449984N)							
SLDI-25	Swamp humus	55.0	4	4.2	40	53	58
SLDI-26	B (>20 cm)	10 ¹	3.4 ¹	2 ¹	39	120	152
Shorty Lake, Lac des Iles (310425E, 5450006N)							
H2808-10A	Swamp humus	68.0	5	3	29	55	57
S2808-10C	C	10 ¹	<2 ¹	1.9 ¹	84	50	44
Vande Lake zone (310273E, 5436327N)							
H2705-3	Swamp humus	3.2	0.4	2	63	170	9
S2810-1C	C (20–30 cm)	<2 ¹	<2 ¹	<2 ¹	23	115	141
Poplar East, Legris Lake (315722E, 5444084N)							
SLL-02-0	Swamp humus	12 ¹	<2 ¹	1.9 ¹	17	15	18
SLL-02-01	B (6–10 cm)	1.8	2.3	2	14	21	29
SLL-02-02	B (10–20 cm)	2.1	2.7	2	13	21	30
SLL-02-03	B (20–25 cm)	1.4	1.9	3	12	21	29
Poplar West, Legris Lake (315575E, 5444149N)							
SLL-03	Swamp humus	10	<2	0.3	29	19	25
SLL-04	B (5–15 cm)	5.3	2.5	3	63	35	29
SLL-05	C (15–25 cm)	5	3.7	3	74	41	30
Poplar West, Legris Lake(315578E, 5443983N)							
SLL-06	Swamp humus	10	<2	0.4	21	15	19
SLL-07	B (5–20 cm)	7	3.4	4	45	41	47
Poplar West (315591E, 5444158N)							
SLL-10	Swamp humus	2.1	0.9	<1	18	20	27
SLL-11	B (20 cm)	2	1.9	1	34	37	49

Notes: Vande Lake zone is shown in Figure 1; Poplar zone in the Legris Lake intrusion is shown in Figure 3

¹ Concentrations were determined after fire-assay extraction or aqua regia digestion

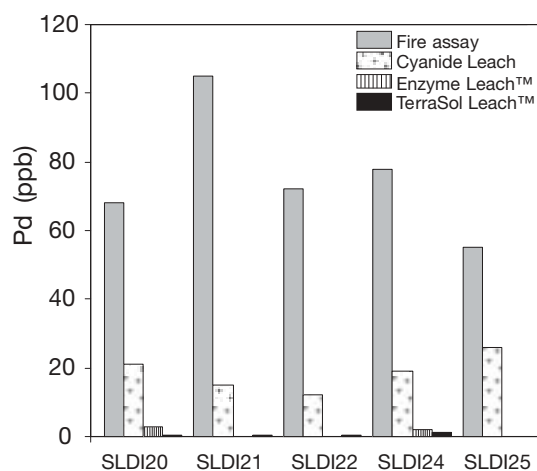


FIG. 12. Comparison of Pd extracted from swamp humus from the Shorty Lake area by fire assay technique, NaCN-NaOH solution (Cyanide Leach™), Enzyme Leach™, and TerraSol Leach™. Samples with UTM coordinates in NAD 27 Canada, zone 16: SLDI 21 (310422, 5450144), SLDI 22 (310415, 5450152), SLDI 23 (310432, 5450072), SLDI 24 (310448, 5449998), and SLDI 25 (310435, 5449984).

tills are well aerated because of the porous nature of the tills, and they are again clear and dilute. Subsurface waters collected from drill holes and springs are slightly alkaline, pH approximately 8, due to dissolution of carbonates in rocks (Table 3).

Discussion

Release of palladium from mineralized rocks and till

High concentrations of Pd in humus suggest that Pd is released from Pd-bearing minerals by surface waters, despite the very limited oxidation of rocks and the near-neutral to mildly alkaline (up to pH 8.3) conditions in surface waters in the area (Table 3). Low concentrations of Fe sulfide minerals mean that acidic waters were not produced.

There are no experimental studies on the weathering of Pd-bearing minerals. However, there is a striking difference in the platinum group minerals between hard rock ore and placers that provides a clue to the behavior of these minerals during weathering. Common platinum group minerals in rocks are arsenides, sulfides, and tellurides (Cabri, 2002), whereas the dominant minerals of placers are Pt-bearing metal alloys

TABLE 3. Composition of Waters

Site ¹	UTM Easting	UTM Northing	pH	Conductivity (μ S/cm)	Na (ppm)	Ca (ppm)	K (ppm)	Al (ppm)	Mn (ppb)	Cl (ppm)	S (ppm)	TDOC (ppm)
W009	310297	5450176	7.3	105	0.9	5.1	2	0.10	2	< 1	< 1	
LDI-08	310554	5450406	6.6	30	0.6	1.7	1	0.20	2	< 1	1	
LDI-27	310438	5450113	7.4	109	1.0	5.4	1	0.22	8	< 1	1	30.1
W21007-3	310528	5449867	7.5	110	1.3	6.9	1	0.09	3	1	< 1	
LDI-01	307550	5449295	7.1	42	0.8	3.6	0	0.07	2	< 1	< 1	
LDI-30	310752	5450536	7.4	75	1.1	4.4	1	0.16	2	< 1	1	
WLL-18	315544	5444164	8.1	350	12	44	1	0.01	55	< 1	7	4.6
WLL-20A	315749	5444015	6.8	82	1.2	11	2	0.21	28	< 1	2	
WLL-22	315322	5444394	6.9	60	1.2	8.4	2	0.21	16	< 1	1	
WDR-14	309393	5391319	7.5	133	1.5	15	1	0.03	1	1	2	

Notes: Reported values are for water without filtration except for the values of total dissolved organic carbon (TDOC); samples were also analyzed after filtration through a 0.45-mm membrane filter, but the results did not show any significant differences compared to the unfiltered samples

¹ UTM coordinates: NAD 27 Canada, Zone 16: W009 = small stream running down the Baker zone ore at the Lac des Iles mine; LDI-08 = small pond at the bottom of the Baker zone ore at the Lac des Iles mine; LDI-27 = Shorty Lake, collected in May, 2002; W21007-3 = Shorty Lake, collected in October, 2002; LDI-01 = Lac des Iles; LDI-30 = Lac des Iles; WLL-18 = water flowing out from the drill hole 16 at the west of the Poplar zone in the Legris Lake property; WLL-20A = small stream running over the swamp, east of the Poplar zone in the Legris Lake property; WLL-22 = swamp surrounding the discovery site in the Legris Lake; WDR-14 = Dog River

(Weiser, 2002). There are few reported occurrences of sulfides and tellurides in placer deposits except for inclusions in other minerals (e.g., Hattori and Cabri, 1992), suggesting that these minerals are not stable in the weathering environment. This is consistent with a detailed mineralogical study of drill core samples and weathered rocks of the Great Dyke in Zimbabwe by Evans et al. (1994). They found sulfides, arsenides, and tellurides in the deeper parts and Pt-Fe alloys in the upper parts of the core where rocks are weathered. The dissolution of Pd by surface waters is further supported by low Pd/Pt in weathered ore in the Bacuri Complex in northeastern Brazil (Prichard et al., 2001).

In the Lac des Iles-Legris Lake district, Pd occurs in Pd sulfides, arsenides, and tellurides, which appear to break down and release Pd to surface waters when they are exposed at the surface. In addition, fine-grained Pd-bearing minerals in porous, permeable tills readily release Pd to percolating rainwater.

Dissolution of palladium in surface waters

Palladium is considered to be the most mobile platinum group element in aqueous solution and is thought to form soluble complexes with a variety of ligands, such as chloride, bisulfide, ammonia, thiosulfate, and hydroxide (see reviews by Sassani and Shock, 1998; Byrne and Yao, 2000; Wood, 2002). Palladium also may form soluble organic complexes with humic acid, fulvic acid, amino acid, acetate, and oxalate (Li and Byrne, 1990; Wood, 2002).

Complexes with chloride and sulfur are unlikely to be important in the waters in the study area because most water samples contain less than 1 ppm Cl and less than 1 ppm S. The amount of PdCl⁺ is slightly less than that of Pd²⁺ in such dilute water, based on the formation constants for these complexes listed in Table 4. The Pd sulfate complex is unlikely to be significant because of the small stability constant for Pd(SO₄)₂²⁻ (Table 4). This leaves hydroxide complexes as the most likely important inorganic species in the waters. There are considerable discrepancies in the estimates of stability constants (see reviews and discussions by Byrne and Kump, 1993; Sassani and Shock, 1998; Wood, 2002; Table 4). For

example, the estimated stability constant for Pd(OH)⁺ varies by five logarithmic units among different researchers (Table 4). Nevertheless, a high value, >7, suggests far greater abundance of Pd(OH)⁺ than Pd²⁺ in dilute neutral to alkaline waters. Pd(OH)₂ and Pd(OH)₃⁻ are most likely significant in slightly alkaline solutions (pH > 8). Earlier work by Mountain and Wood (1988) suggested Pd(OH)₄²⁻ as the predominant species over a wide range of pH in dilute solutions at 25°C. Thus, the predominant species are likely to be neutral Pd(OH)₂⁰, negatively charged Pd(OH)₃⁻ or possibly Pd(OH)₄²⁻ in near-neutral pH waters.

The transport of Pd as neutral and anionic complexes is consistent with a lack of enrichment of Pd in B horizon soils, since Fe oxides in B horizon soils attract and coprecipitate positively charged ions. The concentration of Pd(OH)₄²⁻ may reach 10 ppb even in mildly oxidizing, alkaline conditions (Mountain and Wood, 1988). The high solubility of Pd suggests that Pd can be transported by surface water once it is dissolved and that the amounts of Pd in surface waters are likely limited by the dissolution of Pd minerals during weathering.

Palladium organic complexes may be significant even in solutions containing very low concentrations of organic matter. For example, Li and Byrne (1990) documented that Pd complexing with amino acids and glycine would be significant even in a solution containing nanomolar concentrations of the acids, comparable to that of natural seawater. Wood et al. (1994) suggested that oxalate complexes may be significant for the solubility of Pd in solutions containing as low as 10⁻⁸ to 10⁻⁹ M oxalic acid. Dissolved organic carbon contents of selected samples are relatively high, up to 30 ppm (Table 3). The environment of the Canadian Shield, with forested uplands and abundant swamp-covered lowlands, may provide ample dissolved organic matter (Millot et al., 2003) and thus may be contributing to Pd complexing.

Composition of humus

Factor analysis of element concentrations in the humus samples (Table 5, Fig. 13) identified three factors with eigenvalues >1. Factor 1 includes Fe, Al, Mg, Cr, La, Ni, and Co.

TABLE 4. Logarithmic Values of Cumulative Formation Constants of Pd Complexes at 25°C

Complex	Cumulative Formation Constants								
PdCl ⁺				4.2	5.5				4.5
PdCl ₂				7.5	9.8				7.8
PdCl ₃ ⁻				9.9	12.				10.2
PdCl ₄ ²⁻				11.3	13.5				11.5
Pd(OH) ⁺	11.7	12.4		8.1	13	11.95	13		
Pd(OH) ₂	23.6	25.2	18.9	15.3		23.8	25.8		
Pd(OH) ₃ ⁻	25.4		20.9	21.4		26.2	38.4		
Pd(OH) ₄ ²⁻	26.4			26.5			50.8		
Pd(SO ₄) ₂ ²⁻							3.16		
References	1	2	3	4	5	6	7	8	

Notes: Pd chloride complex: Pd²⁺ + m Cl⁻ = Pd(Cl)_m^{2-m} (m = 1, 2); Pd hydroxide complexes: Pd²⁺ + n OH⁻ = Pd(OH)_n²⁻ⁿ (n = 1-4); Pd sulfate complex: Pd²⁺ + p SO₄²⁻ = Pd(SO₄)_p^{2-2p} (p = 1, 2)

References: 1 = values from Nabivanets and Kalabina, (1970), cited by Van Middlesworth and Wood (1999) and Wood (2002); 2 = values from Izatt et al. (1967), cited in Van Middlesworth and Wood (1999) and Wood (2002); 3 = Wood (1991); 4 = Byrne and Kump (1993); 5 = Sassani and Shock (1998); 6 = Van Middlesworth and Wood (1999); 7 = Mountain and Wood (1988); the value for Pd(SO₄)₂²⁻ obtained by Högfeldt (1982), cited in Mountain and Wood (1988); 8 = values obtained by Elding (1972), cited in Byrne and Kump (1993) and Van Middlesworth and Wood (1999)

For these elements, the median values (lower and upper quartiles in parentheses) are 0.56 wt percent Fe (0.34, 0.85), 0.38 wt percent Al (0.27, 0.56), 0.26 wt percent Mg (0.19, 0.36), 14 ppm Cr (9.2, 32), 3.6 ppm La (2.7, 4.8), 25 ppm Ni (16, 35), and 3.5 ppm Co (2.2, 6.9). Cursory examination of this element association suggests the possible contribution of detrital particles because Cr, Al, and La are generally considered to be immobile. However, chromite has not been identified in gabbroic rocks in the region. Instead, Cr is mostly present in pyroxenes, which would be easily decomposed during weathering. In addition, the association of Cr with soluble Ni and Co suggests that Cr may have been transported by hydromorphic processes. Therefore, the elements in factor 1 most likely represent those transported by hydromorphic processes and incorporated through adsorption on Fe oxyhydroxides.

Factor 2 includes Pd and Au. Gold, like Pd, readily migrates in surface water as anion complexes (Benedetti and Boulegue, 1990). Although the amount of Au in humus samples is small

(median value of 3 ppb with lower and upper quartiles 2 and 5.5 ppb, respectively), the concentrations of Au in humus correlate well with Pd (Fig. 14). They are concentrated in the organic matter in humus samples. Factor 3 includes Ca and Mg, representing carbonates present in the humus.

Incorporation of palladium in humus

Hydromorphic transport of Pd and its incorporation in organic-rich sediments are consistent with previous work. Fortescue et al. (1987) collected 23 humus samples along a traverse of 200-m length across the Roby zone at the Lac des Iles deposit and found a high Pd value (330 ppb) from a single sample directly above the mineralization. The Pd-rich sample also contained high Al and had low loss on ignition,

TABLE 5. Factor Analysis of 49 Humus Samples from Shorty Lake-Baker Zone Area

Element	Factor 1	Factor 2	Factor 3
Pd	-0.13	<i>0.88</i>	-0.03
Pt	0.31	0.51	-0.23
Au	-0.21	<i>0.81</i>	-0.25
Ag	0.10	<i>0.63</i>	0.14
Cu	0.34	<i>0.80</i>	0.15
Cr	<i>0.95</i>	0.03	0.09
Fe	<i>0.94</i>	0.10	0.06
Co	<i>0.91</i>	0.18	0.19
Al	<i>0.91</i>	0.06	-0.12
La	<i>0.87</i>	-0.17	-0.17
Ni	<i>0.84</i>	0.38	0.23
Mg	<i>0.66</i>	0.11	<i>0.61</i>
Mn	<i>0.64</i>	0.52	0.05
Ca	0.33	0.53	0.44

Notes: Logarithmic data and varimax rotation of three factors with eigenvalues >1; loadings >0.6, which represent 36% of the total variance of the element, are shown in italics; see Figure 13 for the plot of factor 1 vs. factor 2

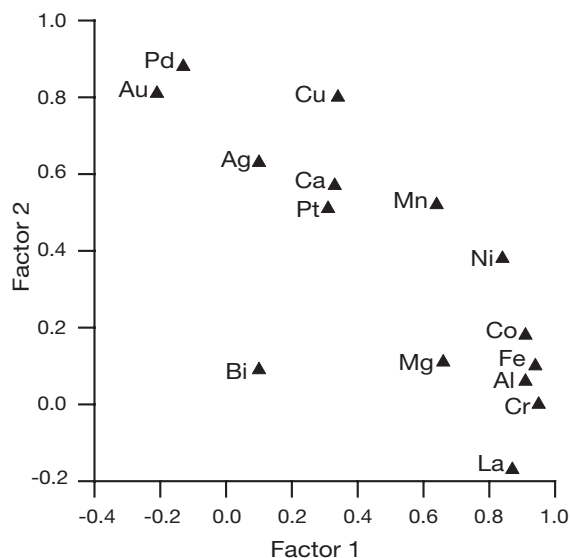


FIG. 13. Plot of factor loadings for factors 1 and 2 from the factor analysis of humus samples from the Baker-Shorty Lake area in the Lac des Iles property. The factor loadings are listed in Table 5. The factor analysis was conducted using the Systat 10.2 computer program.

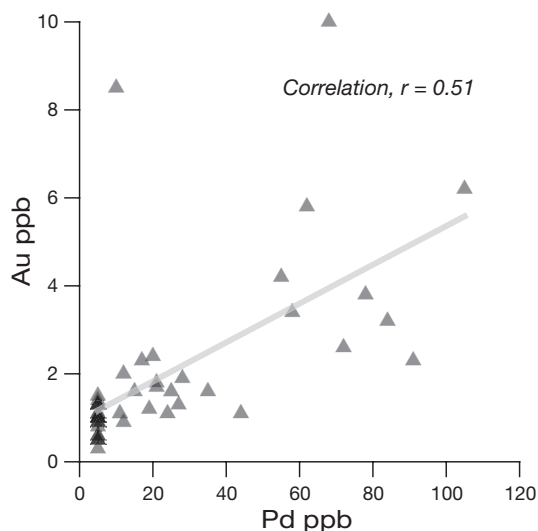


FIG. 14. Plot of Pd vs. Au for 49 samples of humus from the Shorty Lake-Baker zone area. A light gray triangle represents each sample. Darker symbols indicate where sample points overlap.

suggesting that the high Pd value may be attributed to the presence of rock fragments. More importantly, Fortescue et al. (1987) found high Pd values from three humus samples downslope from the mineralization. They are more than 100 m from the mineralization and underlain by barren rocks, and humus samples closer to the mineralization are not enriched in Pd. Our study provides the explanation for these puzzling data: low concentrations of Pd close to the mineralization and high values in the topographic low. Palladium leached from the mineralization was most likely transported downward along the slope and concentrated in organic matter where the surface waters were stagnant.

The high concentrations of Pd in humus are explained either by an uptake of Pd by plants or adsorption of Pd by organic matter. The leaching experiments (Fig. 12) suggest that Pd is tightly bound. Our interpretation is consistent with other studies that show incorporation of Pd into the structure of organic matter (Jedwab et al., 1999; Mizutani et al., 1999) and vegetation (Dunn, 1992). For example, ashed twigs containing greater than 3 ppm Pd have been reported from the Fergusson Lake Ni deposit in the Northwest Territories, Canada (Coker et al., 1991). Sphagnum and sedges in the study region may have accumulated Pd from surface waters during their growth. Decayed plants may be further enriched in Pd by absorption of Pd from waters. High Pd values, greater than 500 ppb, are also reported from many organic-rich shales, such as the Proterozoic shales in the Bohemian massif (Pašava et al., 1996), Devonian shales in Yukon, Canada (Hulbert et al., 1992), and Paleozoic shales in southern China (Coveney and Nansheng, 1991).

Sources of palladium in humus

High Pd concentrations, over 30 ppb, are found in swamp humus in the Shorty Lake area, whereas the highest concentration of Pd in swamp humus in the Legris Lake area was 12 ppb adjacent to the Poplar zone. This difference most likely reflects different Pd concentrations in the source rocks.

Shorty Lake collects waters from the western part of the Baker zone, which contains more than 3 ppm Pd in ore over a large area.

An alternative possibility is an anthropogenic contribution of mine dusts in the Shorty Lake area, which is 1.2 km east of the open-pit mine. This possibility is discounted because swamp humus samples on the eastern shore of Shorty Lake contain much lower concentrations of Pd than from the western shore adjacent to the Baker zone. If dust contributed significant Pd to these samples, values of Pd should be comparable on both sides of the lake, considering the narrow width of the lake.

Our proposed interpretation is further supported by the nearly uniform concentrations of Pd and similar bulk compositions of lake sediment samples at surface (<15 cm) and deep (20–55 cm) levels. Deposition rates for organic-rich lake sediments vary between and within lakes but are low, on the order of several cm/100 yr. For a typical lake in the southern Canadian Shield, Shilts and Farrell (1982) found up to 5 m of organic-rich sediment. Given that lake sedimentation commenced after the retreat of the glaciers at ca. 10,000 yr (Barnett, 1992), this translates into an average deposition rate of 5 cm/100 yr. For a typical northern Shield lake, Cameron et al. (1998) estimated an average deposition rate of 1 cm/100 yr. Therefore, similar contents of Pd in samples from the two depths suggest either homogenization of Pd in lake sediments or a near-steady flux of Pd into the lake. We discount the former possibility because Pd is tightly held in organic matter, as evidenced by the results of leaching experiments using Enzyme Leach™ and cyanide solution (Fig. 12). Therefore, similar Pd contents and bulk compositions from different depths suggest a near-steady flux of Pd into the lake at least for the last several 100 to 1,000 yr. There was essentially no change in the flux to the lake after the start of mining in the Roby zone in 1993; the Baker zone has not yet been mined.

High concentrations of Pd in humus in other districts with smelters have been attributed to anthropogenic sources because underlying soils and rocks are not necessarily enriched in Pd (Boyd et al., 1997; Bajc and Hall, 2000). There are no smelters near the study district and our data are consistent with those of Coker et al. (1991), who also found high Pd concentrations in humus in the Ferguson Lake, Rottenstone Lake, and Sudbury areas. Since the Ferguson Lake area does not have any mining activities, Coker et al. (1991) concluded that enrichment of Pd in humus, tree leaves, twigs, and barks in the three study areas was by natural processes. Our study, combined with the results by Coker et al. (1991), suggests that high Pd contents in the top soil (humus) in the mining districts do not necessarily indicate anthropogenic contribution of metals.

Comparison to results from Western Australia

Our findings of the behavior of Pd, depletion of Pd in B horizon soils, and enrichment in organic-rich soils and sediments are similar to those in northern Canada reported by Coker et al. (1991). Similar depletion of Pd relative to Pt and Au has been found in weathered ore in the Great Dyke (Evans et al., 1994) and the Bacuri Complex, Brazil (Prichard et al., 2001).

Our results, however, contrast with the enrichment of Pd in gossans overlying PGE-bearing Ni-Fe sulfide deposits in Western Australia. At the Perseverance deposit, approximately 330 km north of Kalgoorlie, Pd is depleted in the uppermost part of the lateritic layer but enriched in the lowermost layer directly overlying the Ni sulfide deposits (McGoldrick and Keays, 1981). A similar depth profile of Pd concentrations is reported from Gilgarna Rocks, approximately 90 km north of Kalgoorlie (Travis et al., 1976). In the Ora Banda sill deposit, Pd is enriched in saprolitic residual soils adjacent to Fe-rich soils (Gray et al., 1996). The depth profiles of Pd concentrations from Western Australia indicate mobility of Pd over short distances and retention of part of the Pd in the residual soils.

The different behavior of Pd in Western Australia and Canada is attributed to the different climates, different soil development, and different mineralogy of the ore. Deposits in Western Australia are subjected to weathering under hot, dry conditions, forming thick Fe oxides in which metals are less mobile in surface media. The gossans even retain As and Sb (McGoldrick and Keays, 1981), which are readily leached from gossans in temperate conditions. In Canada, glacial ice flows scoured the mineralized rocks, exposing fresh surfaces, and milled the mineralized rocks into tills. Precipitation is high and water runs over mineralization and percolates through tills into streams, wetlands, and lakes. The cool, damp climate is conducive to the development of thick layers of organic-rich soils and/or sediments and there are less Fe oxides at the surface. Palladium remains in solution until the waters reach wetlands where the Pd is taken up by abundant organic matter.

Use of humus Pd for PGE exploration

Our study suggests that the geochemical exploration technique for Pd mineralization is significantly different from conventional approaches. For most metallic deposits, such as volcanogenic massive sulfide deposits, Mississippi Valley-type deposits, and Au deposits, sampling of B horizon soil is recommended. Many metals are enriched in the B horizon soil as they are adsorbed on the surface of Mn and Fe (hydr)oxides in this horizon (e.g., Rose et al., 1979). Our study suggests that B horizon soil is not useful for Pd exploration because Pd is released during the conversion of soil from C to B horizon soil. Instead, soil with high organic matter is better suited for Pd exploration.

Geochemical exploration, especially regional exploration, commonly involves systematic sampling along grids with equal spacing to cover large areas. Anomalous values are assumed to be proximal to the mineralization, but previous studies show perplexing results with high Pd values of humus overlying barren rocks remote from the mineralization (Fortescue et al., 1987; Coker et al., 1991). Our study shows that Pd-rich humus does not necessarily occur above Pd-rich tills and rocks because humus incorporates Pd from running waters and stagnant waters. Therefore, the conventional approach, higher values closer to mineralization, is not applicable in the case of Pd in organic material. Instead, samples should be collected along the drainage and data interpretation needs to take topography and hydrology into consideration.

These findings are applicable to exploration for PGE mineralization elsewhere, as long as the amount of precipitation is adequate. Where PGE mineralization is accompanied by Ni-Fe sulfide, such as at Noril'sk and Sudbury, surface exposure of Fe sulfides forms acidic surface waters, which promote further dissolution of sulfides and disintegration of sulfide ore. In this case, Pd is more readily leached from its primary minerals.

Humus is abundant under most climate conditions and easily collected by hand. In addition, samples are ready for digestion after drying at room temperatures. Thus, collection of humus along drainage and in swamps can be employed during the reconnaissance stage of PGE exploration. In targeted areas, the distribution of Pd values in humus may provide a vector toward mineralization.

Summary

Palladium is mobile in surface environments under temperate climatic conditions. Common Pd minerals, such as arsenides, tellurides, antimonides, and sulfides, are not stable during weathering and Pd is readily released from these minerals, even from sulfide-poor rocks. Palladium is likely transported as neutral and/or anionic complexes in dilute, near-neutral surface waters and incorporated into humus and organic-rich sediments along drainages and swamps.

Our study has implications for the exploration of PGE deposits. For Pd, sampling of humus provides an inexpensive reconnaissance tool in regional exploration. In this case, sampling of humus and organic-rich soil is more appropriate than sampling of B horizon soils, which is recommended in geochemical exploration for base metal and gold deposits. Partial extraction of metals by leaching is not effective for Pd that is bound in organic matter, although this is considered to be useful for many metallic elements that are loosely adsorbed on Mn and Fe oxides. Furthermore, it is generally assumed that greater concentrations of pathfinder and indicator elements should be found closer to mineralization. Palladium transported by hydromorphic processes may not show such a concentration gradient with distance from mineralization. Careful examination of Pd values together with the relief of bedrocks and movement of water is required to vector toward mineralization.

The results have relevance to the interpretation of Pd anomalies in the top soil (humus). High Pd values of humus overlying barren rocks have been attributed to fallout from smelters (Boyd et al., 1997; Bajc and Hall, 2000). However, in some cases these high values may represent transport of Pd from nearby mineralized sources in bedrock.

Sediments in lakes surrounded by organic-rich wetland may not show high Pd values because the wetland intercepts much of the mobile Pd. Lake sediment anomalies should, on average, be lower in lakes surrounded by wetlands than lakes with a rocky shore.

Mineralization in the study areas is low in sulfides, but the results are also applicable to the exploration for sulfide-rich PGE deposits. Acidic surface waters formed by oxidation of sulfide promote the dispersion of Pd. Since Pd is an abundant PGE in most PGE deposits, the findings of this study are applicable to exploration for all styles of PGE mineralization.

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