CHAPTER 13: PLATINUM GROUP ELEMENTS IN GEOCHEMICAL EXPLORATION

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INTRODUCTION

There are six platinum group elements (PGE): ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). The first three, the light PGE, have densities of ~12 g.cm^{-3}, whereas the others, with densities of ~22 g.cm^{-3}, are the heavy PGE. Osmium, Ir and Ru are refractory, with high fusion points, and tend to show compatible behavior in magmatic systems. The others, Rh, Pt and Pd, have lower fusion temperatures, and tend to show incompatible behavior in magmatic systems. In nature PGE exist as metal alloys and form compounds with S, As, Sb, Bi, Te, Sn and Hg.

Magmatic PGE deposits may be classified into several types based on a variety of criteria, but they are grouped into two in this review; sulfide-poor and sulfide-rich (Table 13-1). Important examples of sulfide-poor mineralization are at Bushveld, South Africa, and Stillwater, Montana. The second type contains sulfides, from which Ni, Cu and Co are extracted, in addition to PGE. Important deposits of this type are Noril'sk-Talnakh, Russia; Sudbury, Ontario; and Kambalda, Western Australia. Placer deposits were initially the principal source of PGE, but are of lesser importance today, and mainly produce Pt.

For geochemical exploration, the oxidation during weathering of the sulfide-rich deposits may enhance the dispersion of elements in the surface environment and the presence of Ni, Cu and Co supplement the PGE as potential indicator elements. Furthermore, sulfide-bearing ores can present a large mass with distinct physical characteristics, which are amenable to geophysical exploration.

Exploration for PGE is influenced by supply and demand for the different metals (Table 13-2). As of 2004, there is a supply deficit for Pt, with additional metal provided from pre-existing stocks. Over the years 1994–2003 the total deficit for Pt was 71 t (Kendall 2004), which has served to increase its price; this reached $950 per oz in April 2004. In contrast, there has been a supply surplus for Pd and Rh and declining prices. As of 2004, these factors have provided an incentive to search for Pt-rich PGE deposits. There are some industrial uses for Ir and Ru, but less than for Pt and Pd, and this is reflected in the low average prices of $93 for Ir and $35 for Ru in 2003.

Geochemical exploration is dependent on the availability of analytical methods that are rapid, low cost, sensitive and precise. Given the low crustal abundance of the PGE, methods must provide good precision to the part per billion levels. The development of methods has focussed on Pt and Pd, because they are the most abundant and economically significant elements of this group. Other PGE are rarely analyzed in routine surveys and data for them are scarce. PGE other than Pt and Pd are discussed only peripherally in this paper.

This paper deals with the dispersion of PGE in the surface environment and how this may be used in exploration. Another approach to exploration, lithogeochemistry, has also been used in the search for PGE and is discussed in another chapter in this volume (Maier & Barnes 2005).

BEHAVIOR OF PGE IN WEATHERING ENVIRONMENTS

In most weathering environments, there is a separation of Pt from Pd, a feature that is critical to the design of a geochemical exploration program sampling surficial materials. Platinum in minerals of magmatic origin dissolves in surface waters less

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TABLE 13-1. ABUNDANCES OF PGE, AU, NI, CU AND S IN PRINCIPAL TYPES OF PGE DEPOSIT AND IN PRIMITIVE MANTLE.

Locality	Os ppb	Ir ppb	Ru ppb	Rh ppb	Pt ppb	Pd ppb	Au ppb	Ni %	Cu %	S %
Primitive Mantle[1]										
	3.4	3.2	5.0	0.9	7.1	3.9	1.0	0.196	0.03	0.03
Sulfide-Poor Mineralization										
UG2[2]	98	123	629	363	2558	1850	174	0.146	0.173	0.45
Merensky[3]	63	74	430	240	3640	1530	310	0.170	0.090	0.42
Great Dyke[4]	75	110	360	38	128	1560	21	0.141	-	0.02
Stillwater[5]					1370	890	170	0.34	0.46	1.6
Lac des Iles[6]	1.4	0.95	3.9	2.4	542	4740	470	0.16	0.16	0.6
Sulfide-Rich Mineralization Normalized to 100% sulfide										
Sudbury[7]	5	8	9	19	590	511	79	3.6	2.8	
Talnakh[8]	280	200	200	520	2350	9980	260	4.74	3.57	31.3
Lennon Shoot[9]	357	197	365	212	1673	1899	7215	49.6	12.4	36.6
Suhanko[10]	20	50	44	357	1506	11030	100	2.0	0.72	25.8
Pechenga[11]	64	45	112	55	359	386	12	8.9	1.94	37.4
Placer Weighted mean of cumulative production 1936 to 1972										
Goodnews Bay[12]	Os %	Ir %	Ru %	Rh%	Pt %	Pd %	Au %			
	2.2	11.3	0.2	1.3	82.2	0.4	2.4			

[1]McDonough and Sun (1995) [2]UG2, Northern Limb, Bushveld Complex, von Gruenewaldt *et al.*. (1989); [3]Merensky, Western Limb, Bushveld Complex, Steele *et al.*. (1975); [4]Great Dyke, Zimbabwe, Sample SH2-402, Oberthür (2002); [5]Picket Pin, west side of Contact Mountain, Stillwater Complex, Williams (1981); [6]Average of 51 samples south Roby Zone, Lac des Iles, except for Os, Ir and Ru, average of 12, Hinchey *et al.*. (2005); [7]Weighted average of Sudbury ores, Naldrett *et al.*. (1984) [8]Talnakh massive pyrrhotite, Noril'sk, Russia, Distler (1994); [9]Lennon Shoot, Kambalda, Australia, Cowden *et al.*. (1986). [10]Ahmavaara massive sulfide deposit, Suhanko, Finland, Alapieti & Lahtinen (2002); [11]Pechenga, Kola, Russia, Barnes *et al.*. (2001); [12]Goodnews Bay, Alaska, Mertie (1976).

readily than Pd and thus tends to be retained in clastic particles. At the Freetown Layered Complex, Sierra Leone, Bowles *et al.* (1994) reported an average Pt/Pd ratio of 1.4 for mineralized rocks, which increased to 6.0 for lateritic soils and ferricrete and to 74 for stream sediments. This separation is most obviously shown by the composition of placer deposits (Weiser 2002). More than 90% of PGM in placers are alloys of Pt–Fe and Os–Ir–Ru–Pt, the grains of which range in size from tens of µm to a few mm, although rare nuggets range up to several kg in weight. PGM in placers are of high-temperature origin derived from the erosion and weathering of mafic and ultramafic rocks (Weiser 2002). Osmium and sulfur isotope ratios of PGM in placers derived from Alpine- and Alaskan-type mafic-ultramafic intrusions are similar to those found in the parent rocks and are homogeneous within grains, negating a supergene origin (Hattori 2002, Hattori *et al.* 2004). In 2003, the two principal placer mines of the world, Kondyor and Koryak, Russia, produced 6800 kg of Pt, but no Pd (Kendall 2004). For the Kondyor deposit, Doan and Bond (1994) estimated a grade of 1.6 $g.m^{-3}$ with 84.4% Pt, 2.1% Ir, 0.6% Rh and 0.4% Pd. Cumulative production of the Goodnews Bay placer, Alaska, over 36 years comprised 82% Pt to only 0.4% Pd (Table 13-1).

In addition to Sierra Leone, lateritic weathering elsewhere in Africa has been shown to cause the separation of Pt from Pd, the Pt retained in soils and stream sediments mainly as alloys and Pd dispersed in solution. For the Main Sulphide Zone (MSZ), Great Dyke, Zimbabwe, Evans *et al.*

TABLE 13-2. SUPPLY, DEMAND AND AVERAGE PRICE IN US$ FOR PT, PD AND RH IN 2003. FROM KENDALL (2004).

SUPPLY	Pt, kg	Pd, kg	Rh, kg
South Africa	145,257	71,851	16,952
Russia	32,659	91,757	4,355
North America	9,176	29,238	622
Others	9,998	7,776	467
Total Supply	***194,090***	***200,622***	***22,395***
DEMAND			
Auto Catalyst, Gross	99,222	107,621	20,684
Auto Catalyst, Recovery	(20,062)	(12,753)	(3,826)
Chemical	9,642	7,776	1,151
Dental	-	22,551	-
Electrical	10,575	27,838	187
Jewellery	75,894	7,776	-
Other	37,170	10,575	2,457
Total Demand	***202,799***	***163,608***	***19,502***
Average Price oz 2003	$692	$201	$530

(1994) found that Pt sulfides and Pt–Pd–Bi tellurides predominate in fresh rock, whereas in weathered rock Pt–Fe alloys are the principal phases. There are two types of alloy, a type that appears to be of igneous origin approximates to isoferroplatinum, whereas alloys that may have formed during weathering contain significant amounts of Cu, Pd, Bi, Te, and S. The authors showed a progressive depletion of Pd relative to Pt (and Au) from weathered rock to soils to stream sediments, similar to that reported by Bowles *et al.* (1994).

In another study of the Great Dyke, Zimbabwe, Oberthür (2002) traced the relative abundance of PGM from pristine MSZ through weathered MSZ to river sediments (Fig. 13-1). There is progressive loss of Pd-bearing phases and a relative increase in Pt–Fe alloys and sperrylite. Average Pt/Pd values increase from 1.3 in the pristine MSZ to 2.4 in the weathered MSZ. Grains of Pt–Fe alloy recovered from the weathered MSZ comprise both compact and porous types. Oberthür (2002) suggested that the latter are possibly replacements of precursor PGM. In the heavy mineral concentrate (HMC) of river sediments there is partial replacement of sperrylite by Pt alloy. Most Pt–Fe grains in the HMC are compact and chemically homogeneous, suggesting igneous origin. At the Hartley Pt mine, Oberthür *et al.* (2003) found that the Pt/Pd ratio of 1.3 for the MSZ increased to 2.0 to 2.4 in oxidized MSZ and to >10 in nearby fluvial sediments. In Madagascar soils, Salpeteur *et al.* (1995) also observed the replacement of Pt, Fe (Pd, Ni) sulfide by an alloy similar in composition to isoferroplatinum.

Although laterite environments in Africa show a strong separation of Pd from Pt, this is less marked or is absent in the laterite terrains of Australia. Examples are given in a later section showing that Pt and Pd are retained in the residual soils over mineralization and may even be enriched relative to the parent mineralized rocks. In most cases there is an increase in the Pt/Pd ratios in the weathered material but less than the African examples noted above. Laterites in Western Australia were first developed in a wet, warm to tropical climate from Cretaceous to mid-Miocene time, followed by drier climate to the present (Butt *et al.* 2001). The reason for this divergent behavior of Pt and Pd between different laterite environments is not known, although Hattori and Cameron (2004) have suggested that overall little precipitation during the development of lateritic soil likely led to little leaching of Pd in Australia.

The separation of Pd from Pt during weathering also applies to colder climates. During weathering of the PGE-enriched Cu sulfide ore at the New Rambler Mine, Wyoming, Pd has been largely removed from the oxide zone, whereas Pt and Rh have been enriched (McCallum *et al.* 1976). In ophiolite terrain in the Shetland Islands, Scotland, Gunn (1989) noted that Pt was consistently enriched

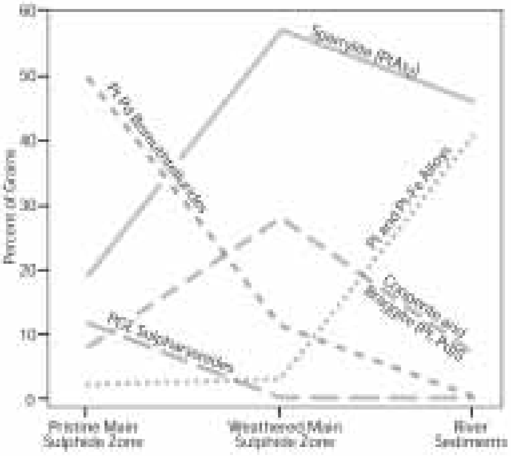

FIG. 13-1. Proportions of PGM in pristine Main Sulphide Zone, weathered Main Sulfide Zone and in river sediments, Great Dyke, Zimbabwe (Data from Oberthür 2002).

relative to Pd in stream sediment HMC, compared to bedrock. Over the same Shetland ophiolite complex, Prichard and Lord (1994) found that the Pd/Pt ratio decreases upwards in soil profiles from the mineralized bedrock interface to the surface. In soils over PGE mineralization at Ferguson Lake, NWT, Canada, Coker *et al.* (1991) found Pt more abundant in coarse fractions and HMC, whereas Pd was most abundant in fine fractions, which they attributed to clastic dispersion for Pt and hydromorphic dispersion for Pd. In soils derived from tills at the Stillwater Complex, Montana, Fuchs and Rose (1974) showed that Pt and Pd are depleted in the A-horizon relative to the B- and C-horizons and the Pd/Pt ratios are lower in the A than in the C, indicating leaching of Pd relative to Pt. Near the Lac des Iles mine, Ontario, there is loss of both Pt and Pd during conversion of C-horizon soils to B-horizon soils, but the loss of Pd is greater (Searcy 2001; Hattori and Cameron 2004).

In addition to Pt-bearing alloys, sperrylite ($PtAs_2$) is also found in streams in PGE-mineralized areas, including humid tropical zones, such as Madagascar (Salpeteur and Jezequel 1992). McCallum *et al.* (1976) found a greater frequency of grains of sperrylite in the oxide zone than in the underlying PGE-bearing Cu sulfide body of the New Rambler mine in Wyoming. Mountain and Wood (1988) found this mineral to be stable at the pH and fO_2 of typical surface waters.

MOBILITY OF PGE IN SURFACE ENVIRONMENTS

In this section emphasis is given to the dissolution of Pd in surface environments given the importance of this element in tracing PGE mineralization by hydromorphic dispersion.

In natural aqueous solutions the usual oxidation states are Pt(II) and Pd(II). Concentrations of hydrated, uncomplexed ions, Pt^{2+} and Pd^{2+}, are very small in equilibrium with the metals. Significant solubility requires ligands that can form stable complexes. Pt^{2+} and Pd^{2+} ions are soft and tend to form stable complexes with soft ligands, such as HS^- and CN^-, but harder ligands such as OH^- and carboxylic acids are also significant (Wood 2002). In saline waters, such as groundwaters in arid environments, both elements can dissolve as chloride complexes, with the solubility of Pt favored over Pd (Williams 2001). In zones of oxidizing sulfides, thio complexes can form, but only provided that the pH is neutral to alkaline, which requires carbonate to buffer acid formed by sulfide oxidation. Most weathering regimes are not suitable for dissolution by these ligands. Near the Lac des Iles, Pd deposit, Ontario, Hattori and Cameron (2004) found that Pd migrates in solution from mineralization. Surface waters in this typical Canadian Shield environment are clear and dilute, reflecting high precipitation and low evaporation in a cool climate. Hattori and Cameron reviewed the stability constants for various Pd(II) complexes. Complexes with chloride and sulfur are unlikely to be important because most water samples contain <1 ppm Cl and <1 ppm S. The amount of $PdCl^+$ is slightly less than that of Pd^{2+} considering the stability constant for complexes. Complexing with sulfate is unlikely because of low concentration of SO_4^{2-} in surface waters. This leaves hydroxide complexes as the most important inorganic species. Although there are considerable variations in the estimates of stability constants of hydroxides, the data suggest that the predominant speciation of Pd(II) in dilute surface waters is $Pd(OH)_2^o$, negatively charged $Pd(OH)_3^-$, or possibly $Pd(OH)_4^{2-}$. A stability diagram after Wood and Vlassopoulos (1990) showing $Pd(OH)_2^o$ as the stable phase in surface waters over a wide range of pH is shown in Figure 13-2. In contrast to the negative or neutral charge of the predominant hydroxide species of Pd(II), Azaroual *et al.* (2001) found that for waters with pH <9, and in the absence of other strong ligands, $Pt(OH)^+$, was the principal species.

Most metals, such as Cu, Ni, Zn, dissolve as simple cations in dilute surface waters. These tend to be adsorbed and fixed by negatively charged iron oxyhydroxides as are found in B-horizon soils and as coatings on grains in stream sediments. Given that Pd is transported as neutral or negatively charged complexes, it will not be fixed by iron oxyhydroxides and will not tend to accumulate in B-horizon soils (Hattori and Cameron 2004).

Wood (1990), Wood *et al.* (1994) and Bowles *et al.* (1995) have shown that Pt and Pd can dissolve in solutions containing fulvic, humic and other organic acids. For Pd, in addition to hydroxy complexes, there are soluble organic complexes with humic acid, fulvic acid, amino acid, acetate and oxalate (Li & Byrne 1990, Wood 2002).

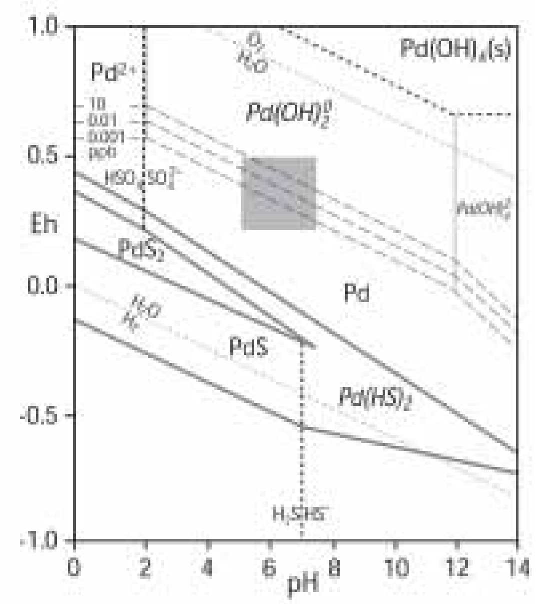

FIG. 13-2. Stability diagram for the system Pd–O–H–S–Cl at 25°C, ΣS 0.005 m and ΣCl 1 mg.L^{-1}. Modified from Wood and Vlassopoulos (1990). Heavy lines mark stability fields of solid Pd species and lighter lines of dissolved Pd species. Predominant dissolved S species are also shown. Solubility of Pd in ppb shown by dashed contours. Shaded area is typical Eh–pH values for surface lake

Palladium–organic complexes may be significant even in solutions containing very low concentrations of organic matter. For example, Li & Byrne (1990) documented that dissolved Pd complexes with amino acids and glycine would be significant even in a solution containing nanomolar concentrations of the acids, comparable to that of natural sea water. 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. It is difficult to evaluate the significance of organic complexes because of the lack of data on the nature and amounts of organic compounds in surface waters and limited experimental data on Pd-organic complexes. Nevertheless, the environment of many northern countries, with forested uplands and swamp-covered lowlands, may provide ample dissolved organic matter (Millot *et al.* 2003) for complexing with Pd.

GEOCHEMICAL EXPLORATION METHODS

Geochemical exploration for PGE-bearing deposits may be carried out by measuring either (a) clastic dispersion of Pt, (b) hydromorphic dispersion and precipitation of Pd, or its incorporation into vegetation or (c) residual concentrations of Pt or Pt and Pd in soils. Also, elements that are associated with PGE in mineralization may be determined as pathfinders to the mineralization.

Based on Clastic Dispersion

Stream Sediments

Stream sediment sampling has been the most important method for reconnaissance-scale geochemical exploration for PGE mineralization. The Merensky Reef of the Bushveld complex was discovered by mineralogical examination of HMC from stream sediments (Cawthorn 2001). Since Pd is essentially removed from the clastic component of stream sediments and placers, it is Pt that is the principal indicator element. In streams, hydraulic action deposits PGM together with coarse-grained silicates of lesser density. Removal of the coarser grained fraction by sieving magnifies PGM contents and enhances the anomaly/background contrast of Pt. Further concentration can be obtained by panning the sample (*e.g.*, Gunn 1989; Salpeteur and Jezequel 1992), or processing with heavy liquids (*e.g.*, Coker *et al.* 1991). In Madagascar, Salpeteur and Jezequel (1992) found that the maximum values for Pt were in the –125 +63 μm fraction, whereas most of the high Pd values were in the –63 μm fraction. The optimum grain size likely varies from area to area. Sieving through fine mesh sizes takes time; for this reason 80–mesh sieves are often used.

The abundance of the HMC in stream sediments is related to variation in hydraulic sorting along the stream or river. Thus the total amount of PGE in a sample may reflect local conditions of sedimentation. For this reason Salpeteur and Jezequel (1992) plotted PGE concentrations as a ratio to the total weight of the HMC. Alternatively, the ratio of a PGE to another element that is a constituent of the heavy mineral fraction, for example Cr in chromite, may be plotted.

Although concentration by sieving and/or panning will increase the number of grains of PGM in a sample, the number still remains small. Like gold, PGM are subject to the "nugget effect" and a sufficiently large sample should be taken to obtain reproducible data. Analyses of stream sediments from Zimbabwe by Evans *et al.* (1994) showed poor reproducibility for Pt, whereas the reproducibility of Pd was better, suggesting that it is not present as primary Pd-rich grains. Evans *et al.* collected 8 kg of sediment, which was sieved to –100 μm, then 10 g sub-samples were taken for analysis. To an even greater extent than other types of geochemical survey, the collection of replicate stream sediment samples is required, from which sampling and analytical precision are estimated (see discussion on quality control in a later section). Composite samples will also improve reproducibility, taking sediment at several locations along, *e.g.*, a 10 or 25 m length of stream.

Glacial Tills and Derived Soils

Cook and Fletcher (1993, 1994) carried out comprehensive studies of the distribution of Pt in soils of the Tulameen Alaskan-type ultramafic–mafic complex, southern British Columbia. The principal PGM in the rocks are alloys, Pt_2Fe_2 and Pt_3Fe, and tulameenite (Pt_2FeCu). Platinum has been produced from nearby placers. The area was glaciated and rocks have a thin cover of till on which immature soils have developed. Figure 13-3 shows Pt analyses for a soil profile in till over mineralized dunite. The results could suggest that Pt has been removed from the A- and B-horizons during their development from C-horizon parent material. However, Cook and Fletcher found that the soils comprising this profile are of mixed origins. The A- and B-horizons are composed of exotic, non-ultramafic material and it is only in the C-horizon that material from the underlying mineralized dunite was incorporated. In the C-horizon, the highest contents of Pt are in the coarsest fraction, –10 to +40 mesh, indicative of a local source. The highest concentration of Pt occurs in the magnetic heavy minerals, which contains chromite as well as magnetite. In other samples of dunitic till the differences between the Pt contents of the different size fractions are not as pronounced. Elsewhere in the area, where colluvial soils were derived from mineralized rock, the upper, colluvial soil horizons can have a higher content of Pt. This study shows the difficulty in interpreting data for PGE in soils where there are multiple sources for till and where high relief has caused colluvial movement of soil. For routine exploration Cook and Fletcher recommend separation and analysis of the magnetic HMC of C-horizon soils.

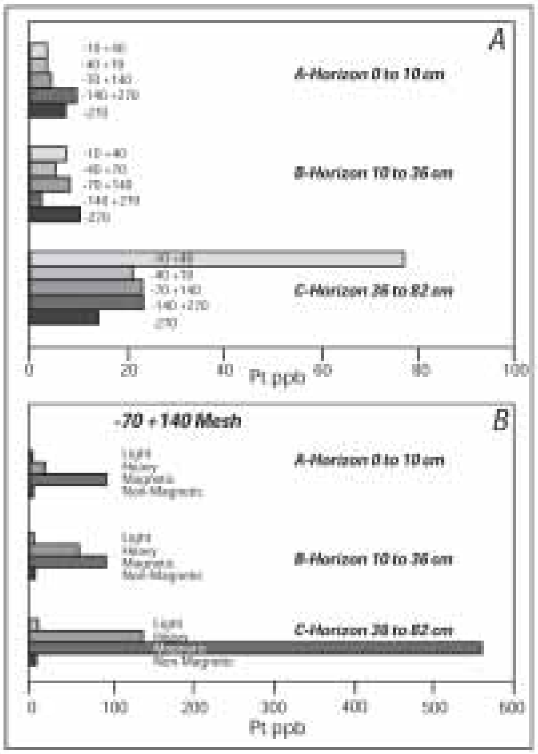

FIG. 13-3. Distribution of Pt in a profile of till soil at Tulameen complex, British Columbia. A shows distribution in different ASTM size fractions; B shows distribution in light, heavy, magnetic heavy and non-magnetic heavy components of -70 +40 mesh sieved soil. Modified from Cook and Fletcher (1994).

Coker *et al.* (1991) examined PGE distributions in soils at Ferguson Lake, Northwest Territories, Canada, and at Rottenstone, Saskatchewan. At Ferguson Lake PGE-bearing Cu–Ni sulfides are present in hornblendite. There is a thin till cover and spectacular gossans over the sulfide mineralization. The area is within the zone of continuous permafrost. Grab samples of gossanous rock contained up to 590 ppb Pt and 2500 ppb Pd. An earlier study of gossanous soils by DiLabio (1988) showed that Pd was present in the finer size fractions, whereas Pt was erratically distributed due to the nugget effect. Similar results were obtained by Coker *et al.* (1991) who found that Pt was most abundant in the HMC and coarser soil fractions, suggesting clastic dispersion, whereas Pd was most abundant in the fine fractions, suggesting hydromorphic dispersion. High contents of Pt were found in the gossanous soils, up to 1000 ppb Pt in the –180 and –63 μm soil fractions and close to 10 ppm Pt in the HMC. For Pd, several thousand ppb were found in the HMC and in all but the coarsest size fraction of soil, 2 to 6 mm. Despite these high values near source, the down-ice dispersion of anomalous values is limited to 100 to 200 m. This dispersion pattern was determined from bulk analysis of the –63 μm fraction, since it proved too difficult to extract sufficient HMC from non-gossanous tills.

The Rottenstone deposit is a small Ni–Cu deposit, but was a rich producer of PGE with 4.8 ppm Pt and 3.9 ppm Pd. On bedrock ridges there is a thin cover of till and in lower areas till interfingers with glaciofluvial and glaciolacustrine sediments. Anomalous concentrations of Pt, to 4500 ppb, along with up to 435 ppb Au were found in the HMC from tills and anomalous values for Pt extend to the limit of the survey, 1 km down-ice from the mineralization. This indicates clastic dispersion of Pt-rich grains by glacial action. The results for sieved fractions of the tills and soils were disappointing, the highest values for Pd being 6 to 31 ppb in samples from which the HMC gave results in the range 350 to 4500 ppb Pt.

The two studies by Coker and colleagues show that where there has been significant down-ice dispersion of mineralized material, as at Rottenstone, Pt in the HMC is an effective exploration tool. Where dispersion has been poor, as at Ferguson Lake, HMC are limited in amount and geochemical anomalies of any type only occur close to the mineralized body.

Based on Hydromorphic Dispersion

Organic Trapping of Pd along Drainage Courses

Palladium can be dispersed in solution along drainages as neutral or negatively charged hydroxide species or as organic complexes. These forms are not precipitated by negatively charged Fe oxyhydroxide colloids and coatings as are trace metal cations, but may be precipitated in organic traps. At the Tulameen complex, British Columbia, Cook and Fletcher (1993) found that the upper humic layer of soil mostly contained less Pt than the associated C-horizon. In seepage areas and downslope from Pt mineralization the humus gave higher Pt values. This suggests the hydromorphic transportation of Pt and fixing by organic material.

Hattori and Cameron (2004) focussed on organic trapping of Pd at the Baker Zone, an undeveloped body of PGE mineralization east of the main ore zone of the Lac des Isles Pd mine, Ontario. The Baker Zone lies on the slope above a small lake, Shorty Lake. Searcy (2001) collected C- and B-horizon soils over and peripheral to the Baker Zone. These were analyzed for Pt and Pd by fire assay–ICP–AES. The C-horizon soils represent minimally weathered rock fragments, which have been dispersed as till down-ice to the southwest of the mineralization. Soil-forming processes involved in the conversion of C-horizon to B-horizon soils have caused a decrease in both Pt and Pd (Fig. 13-4).

Hattori and Cameron (2004) collected black peaty humic material underlying moss in swamps that border the lake on all sides (Fig. 13-5). Water in the swamps is from runoff from the higher ground surrounding the lake and from the lake itself, particularly at the southern end, where the water drains out through a boulder field covered by humus and moss. Analyses of the humus for Pd and Pt were by fire assay–ICP–MS. Palladium is greatly enriched in the swamp humus, compared to the C- and B-horizon soils, whereas Pt is depleted (Fig. 13-4). Plots of Pd and Pt (Fig. 13-5) show that high Pd values in the swamp humus are mainly at the base of the slope beneath the Baker Zone and in the area south of the lake that is saturated by lake water. Lake sediments collected at locations LS1 and LS2 (Fig. 13-5) were taken from two depths: 0 to 15 cm and 20 to 50 cm. The shallow samples contain 10 ppb Pd and 2 ppb Pt (LS1) and 14 ppb Pd and 2 ppb Pt (LS2), and the deeper samples 15 ppb Pd and 2 ppb Pt (LS2) and 10 ppb Pd and 1.4 ppb Pt, (LS2). For Pd these values are well above the regional median for lake sediments of 4.8 ppb, whereas the Pt values are similar to the regional median of 1.6 ppb Pt. The data from both the swamp humus samples and the lake sediments are consistent with precipitation of dissolved Pd derived from the upslope mineralization. The Pd contents of the shallow and deep lake sediments are similar, indicating a long-term flux of Pd into the lake. As described later, the bark of spruce trees growing along the edge of the lake is strongly anomalous in Pd.

Fortescue *et al.* (1987) collected 23 humus samples along a traverse of 200 m length over the main (Roby) ore zone at the Lac des Iles deposit and found a single high Pd value (330 ppb) directly above the mineralization, which was undeveloped at the time. This type of humus, “forest humus” is derived from the decomposition of leaf litter, rather than the moss that is the parent of the swamp humus. Significantly, they found high Pd values from three humus samples overlying barren granite, but downslope from the mineralization.

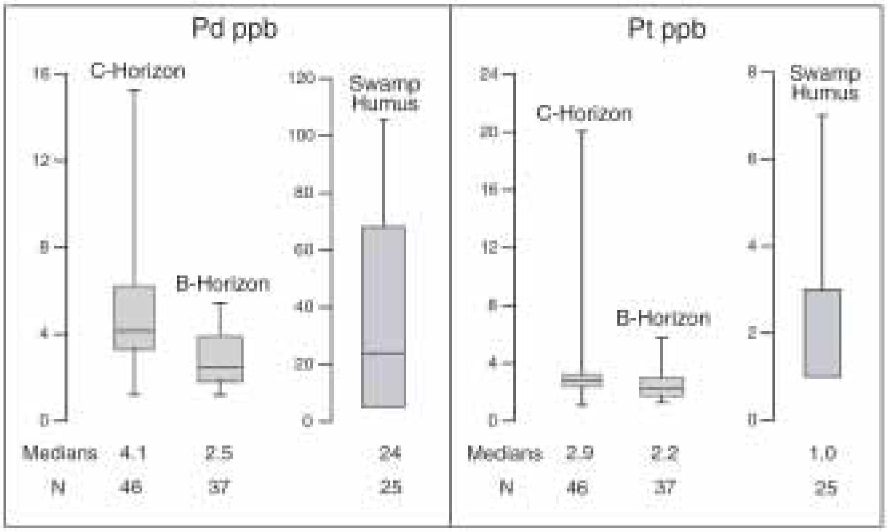

FIG. 13-4. For the Baker Zone - Shorty Lake area, box-whisker plots of B- and C-horizon soils from Searcy (2001) and swamp humus. From Hattori and Cameron (2004).

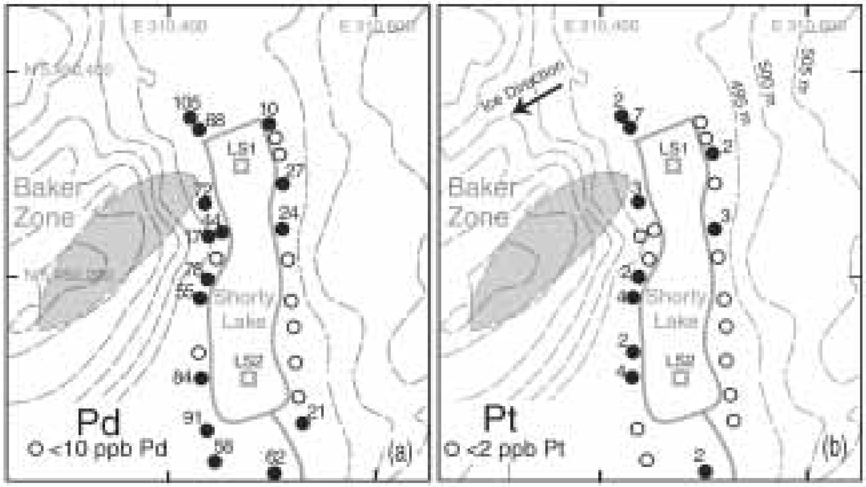

FIG. 13-5. Map of the Baker Zone and Shorty Lake showing the distribution of Pd and Pt in samples of "swamp humus" taken around the edge of the lake. Also shown are the lake sediment sampling sites LS1 and LS2. From Hattori and Cameron (2004).

Biogeochemistry

The practical application of biogeochemistry to PGE exploration was previously hindered by their low abundance. It was necessary to collect a large sample of vegetation to provide 10 g of ash for analysis (Dunn 1992). Hall *et al.* (1990) developed a method using a HF–aqua regia decomposition, followed by co-precipitation of noble metals on Te, then analysis by ICP–MS. This provides 1 to 2 ppb detection limits for Au, Pt and Pb on 1 g of ash, which requires the collection of *ca.* 50 g of dry twigs.

In an earlier section we described results obtained by Coker *et al.* (1991) on soils from Ferguson Lake, Northwest Territories. Biogeochemical studies were also carried out, collecting leaf and twig samples from dwarf birch and Labrador tea. Both species are common throughout the area and can bio-accumulate Pt and Pd (Table 13-3), with higher concentrations in the birch and in the twigs of both species. Anomalous values in these plants were found directly over the gossans and for a limited distance of a few hundred metres down-ice, corresponding to anomalies

TABLE 13-3. CONCENTRATION OF PT AND PD IN ASH OF DWARF BIRCH AND LABRADOR TEA, FERGUSON LAKE AREA, NORTHWEST TERRITORIES.

	Pt ppb in ash			Pd ppb in ash		
	Min	Med	Max	Min	Med	Max
Dwarf Birch						
Leaf, gossan (24)	2.6	188	226	30.8	471	509
Twig, gossan (26)	4.3	1011	1350	52.9	1980	3071
Leaf, background (10)	2.1	2.7	3.8	2.3	7.6	11.2
Twig, background (10)	0.4	2.8	4.1	4.3	10.9	14.8
Labrador Tea						
Leaf, gossan (22)	6.1	45.2	52.4	99.0	1001	1688
Twig, gossan (24)	4.9	47.1	59.0	68.4	1949	2322
Leaf, background (10)	2.4	4.2	7.0	11.0	17.2	21.7
Twig, background (10)	0.9	3.5	9.1	4.1	19.4	28.7

Min = minimum, Med = median, Max = maximum, numbers in brackets = number of samples.
From Coker *et al.*. (1991).

identified by analysis in the –63 μm fraction of the till. Rencz and Hall (1992) carried out further studies at Ferguson Lake, again using Labrador tea and dwarf birch. There were strong anomalies for Pt, Pd and Rh over the gossans, with Pd showing the greatest contrast in dwarf birch, a maximum of 4000 ppb over the gossans to background of 8.5 ppb. But anomaly dispersion down-ice was limited.

Following up on earlier work by Dunn (1986), Coker *et al.* (1991) carried out biogeochemical studies at the Rottenstone mine, Saskatchewan. A variety of vegetation was sampled and analyzed during an orientation survey (Table 13-4). The results show considerable variation between different types of plant tissues, with black spruce twigs and outer bark containing the most Pt and Pd. This prompted the selection of spruce twigs for a survey of the area. There is moderate to strong Pt and Pd enrichment for less than 200 m down-ice and weak enrichment in Pd farther away, but less than the 1 km dispersion for Pt in HMC. The authors noted that Pd is detectable in only some of the soils, is absent in the tills and HMC, yet is enriched in the spruce twigs. Their inference is that dissolved Pd is adsorbed to only a slight degree in the soil, but is being taken up by plant roots.

If dissolved Pd is dispersed away from mineralization, then analysis of vegetation may identify its distal presence. At the Shorty Lake

TABLE 13-4. CONCENTRATION OF PT AND PD IN ASH OF A VARIETY OF VEGETATION, FROM CLOSE TO THE OLD MINE SITE AT ROTTENSTONE LAKE, SASKATCHEWAN.

Sample Medium	Pt ppb in ash	Pd ppb in ash	Ash %
Black spruce twigs	800	1443	2.2
Black spruce outer bark	1187	1662	3.8
Black spruce inner bark	126	212	3.4
Black spruce needles	83	244	4.0
Black spruce trunk wood	89	70	0.4
Birch twigs	125	306	1.0
Birch leaves	87	326	4.0
Birch trunk wood	10	45	0.5
Alder twigs	62	170	1.1
Alder leaves	35	158	4.4
Willow twigs	16	74	1.4
Labrador tea twigs	166	368	2.0
Labrador tea leaves	279	499	3.9
Marsh grass	18	30	6.5
Background levels	<5	<2	

From Coker *et al.* (1991).

sampling site (Fig. 13-5) we have collected and analyzed bark from mature black spruce growing at the edge of the lake. For ash from samples of 8 trees the range and average concentration was 16 to 708 and 307 ppb Pd and 18 to 129 and 45 ppb Pt (Hattori and Cameron, unpublished results). Thus data from organic lake sediments, swamp humus and vegetation at Shorty Lake provide a consistent picture of the fixing of Pd dispersed in solution from mineralization by organic material.

Dunn (1992) provided a comprehensive review of biogeochemical methods for Au, Pt and Pd, including surveys for Pt and Pd over the Duluth Complex, Minnesota, the Stillwater Complex, Montana and the Tulameen Complex, British Columbia.

Palladium and Platinum in Waters

As might be expected from low crustal abundances, the amounts of these elements in surface waters are low, in the $ng.L^{-1}$ = parts per trillion range (ppt). Most analytical methods require a concentration stage, for example by evaporation or adsorption on activated carbon or resin, prior to measurement by ICP–MS. This increases the time and cost of the analyses, lessening the practical application of the methods. Because of the low concentration in waters, isobaric interference from other constituents in the waters is a serious issue. For example, $^{40}Ar^{65}Cu$ and $^{88}Sr^{16}OH$ are isobaric with ^{105}Pd. Evaporation alone does not resolve the issue, since the interfering species increase in concentration along with Pd and Pt. Thus separation of the PGE from interfering elements by adsorption on activated carbon (Hall and Pelchat 1993), Te-co-precipitation (Cook *et al.* 1992), or the use of ion exchange resins (Hattori and Cameron, unpublished work) have been used.

A further problem is the adsorption of Pd, Pt and Au onto the walls of the sample container (Chao *et al.* 1968, Samiullah 1985). Coker *et al.* (1991) reported that ~80% of metals is lost from dilute natural water samples within 20 days. Metals lost cannot be fully recovered from the walls by leaching with Br_2–HCl, which is effective in recovering Au (Hall *et al.* 1996). Cook *et al.* (1992) showed that only 12% Pd but 62% Pt was recovered when 50 ppt of each metal was kept in distilled water for 7–10 days and only an additional 10% Pd was recovered by extracting the container walls with 10% HCl and 5% HNO_3. The best recoveries of 75% Pd and 69% Pt were obtained when the metals were kept in a 20% HCl + HNO_3 solution.

Coker *et al.* (1991), who used activated charcoal for preconcentration of Pt and Pd, reported 2.8 ppt Pt and 2.0 ppt Pd in waters adjacent to gossanous zones at Ferguson Lake, Northwest Territories, but background levels of 0.2 ppt were measured just a few metres away. The Pt and Pd were separated using activated charcoal. A similar method was used by Cook *et al.* (1993) for water samples from the Tulameen Complex, British Columbia. Stream waters averaged 0.81 ppt Pt; water from seepage zones, 1.05 ppt Pt; and water from plateau bogs on dunitic till 2.45 ppt Pt. Hattori and Cameron (submitted) found up to 18 ppt Pd and 1 ppt Pt in waters draining from the Baker Zone of the Lac des Iles Pd mine. Background values in the area are ~1 ppt Pd and ~ 0.1 ppt Pt. Evaporation plus ion exchange resins were used to concentrate and separate the PGE.

Wood and Vlassopoulos (1990) and Cook *et al.* (1992) reported much higher values from Lac Sheen and Lac Long, Quebec, near PGE-bearing Ni sulfide mineralization. For filtered Lac Sheen waters the 1990 study reported an average of 158 ppt Pd and filtered Lac Long waters averaged 262 ppt Pd. For Pt, most lake waters were below the detection limit of 25 ppt. Analysis was by ICP–MS, preceded by evaporation of 1 L of water to 25 mL. There was no separation of PGE from the other dissolved constituents. Cook *et al.* (1992) evaporated 2 L samples and then separated the PGE and Au from the other constituents by a Te co-precipitation. They found that Pt contents in the Lac Sheen waters were generally below the detection limit of 10 ppt, but ranged up to 147 ppt in filtered waters. There were greater concentrations of Pd, but the results were inconsistent for different sampling periods, an average of 23 ppt in June, 26 ppt in August and 107 ppt in November. Possible analytical problems are suggested by higher values for filtered samples than unfiltered samples.

Based on both Clastic and Hydromorphic Dispersion

Lake Sediments

Lake sediments are used as sample media for exploration mainly in the glaciated Canadian and Fennoscandian Shield areas, where there is a high density of small lakes. Lake sediments consist of clastic particles from till and bedrock, precipitated Fe-, Al- and Mn-oxyhydroxides, and organic material. The concentrations of Pt, Pd and Au in lake sediments around a PGE-bearing Ni sulfide prospect at Lac Sheen, Quebec, were examined by

Wood and Vlassopoulos (1990) and Cook *et al.* (1992). This was combined with related studies of waters, soils and rocks. Values up to 38 ppb Pd and 122 ppb Pt were found in the lake sediments.

A reconnaissance survey of lake sediments over a large area west of Lake Nipigon, Ontario, in the Canadian Shield, was conducted by Dyer and Russell (2002) (Fig. 13-6). The eastern portion of their survey area is mainly overlain by Proterozoic Nipigon diabase sills that are emplaced during the Mid-Continental Rift and are known to contain exceptionally high concentrations of Pt and Pd as basaltic rocks, over 10 and 15 ppb, respectively (Cameron and Hattori 2003). Mafic intrusions associated with these dykes, such as the Duluth and Coldwell complexes, host significant PGE mineralization. The western part of the area is mainly Archean and includes the Lac des Iles Pd mine in an Archean mafic-ultramafic complex (Fig. 13-6). A total of 2258 centre lake sediment samples were collected and analyzed for a wide range of elements, including Pt and Pd by fire assay–ICP–MS. The median contents of the 2258 samples are 1.6 ppb Pt and 4.8 ppb Pd.

Cameron and Hattori (2003) examined the Pd lake sediment anomalies in a portion of the Dyer and Russell survey area that includes the Lac des Iles mine (Figs. 13-6 and 13-7). There are strong Pd anomalies throughout this area (Fig. 13-7A), but for most of the anomalies there is no known PGE mineralization in the vicinity. Moreover, the Pd anomaly associated with the Lac des Iles Pd deposit is not among the strongest. To explain this contradiction, data for ten elements most closely associated with PGE mineralization were treated by factor analysis. The three most important factors are shown in Table 13-5 and the scores for Factors 1 and 2 are plotted in Figure 13-7B and Figure 13-7C. Factor 1, comprising, Co, Cr, Ni, Pt and Pd, is interpreted to represent the dispersion of predominantly clastic material of mafic/ultramafic origin. The clastic material was initially dispersed as till by the ice sheet moving south-westwards, then washed into lakes to form sediment. The strongest Factor 1 anomaly lies directly down-ice from the Lac des Iles deposit. Another strong anomaly is near Dog Lake. Bedrock around Dog Lake is largely concealed beneath Quaternary cover and has been mapped as granitic. However, there are aeromagnetic anomalies and drilling has intersected pyroxenite, sheared serpentinite and minor sulfide with anomalous values for PGE.

Factor 2 is interpreted as hydromorphic dispersion and precipitation of Pd, S and As. This factor shows a close spatial correlation with glaciofluvial deposits, notably eskers that contain abundant boulders of Nipigon diabase and reddish sedimentary rocks of the Proterozoic Sibley Group,

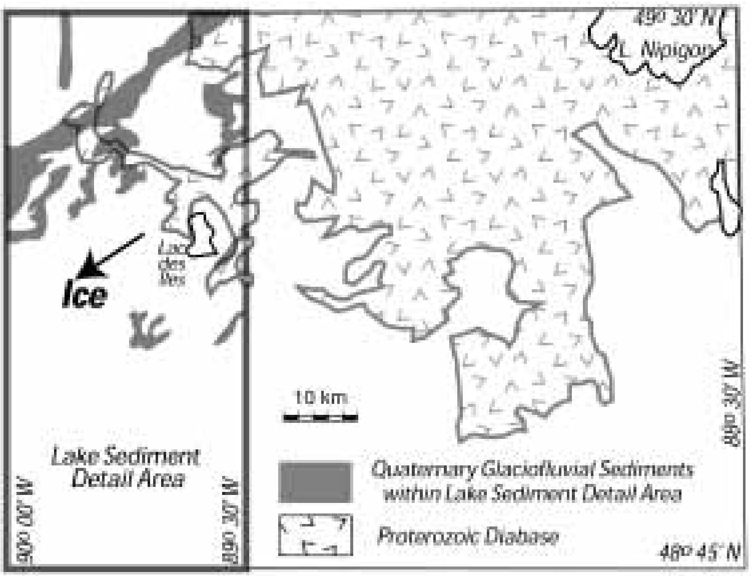

FIG. 13-6. Lake sediment survey area of Dyer and Russell (2002) lying east of 90°W. The detail area between 89°30' and 90°00' is described in text and shown in Figure 13-7.

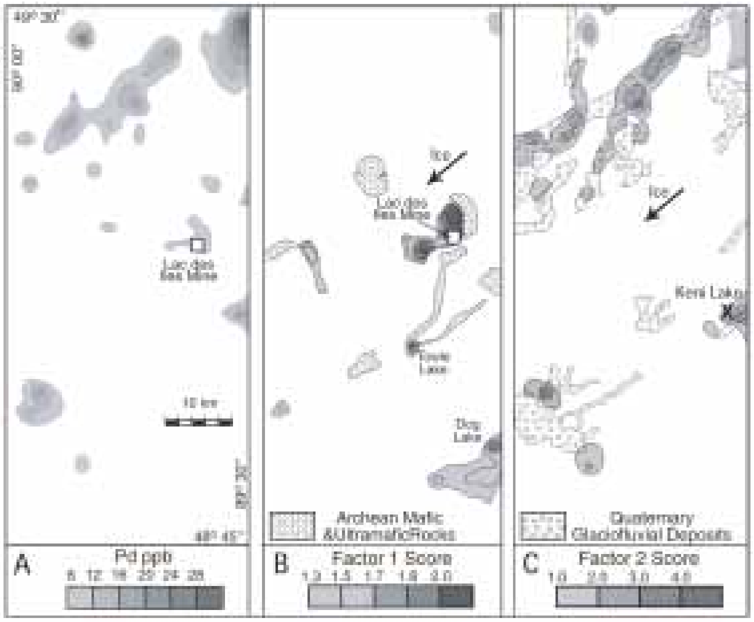

FIG. 13-7. Maps of the lake sediment survey area between 89° 30’ and 90° 00’. A: Contours of Pd in lake sediments. B: Contours of scores for Factor 1 and the distribution of mafic and ultramafic rocks; C: Contours of scores for Factor 2 and the distribution of Quaternary glaciofluvial deposits, from Mollard (1979a, 1979b). Arrows indicate predominant ice direction.

TABLE 13-5. FACTOR ANALYSIS OF 675 LAKE SEDIMENT SAMPLES FOR THE TEN ELEMENTS MOST CLOSELY ASSOCIATED WITH PGE MINERALIZATION.

Element	Factor 1	Factor 2	Factor 3
Co	**0.87**	0.06	0.08
Cr	**0.87**	-0.03	0.21
Ni	**0.82**	0.09	0.33
Pt	**0.78**	0.21	0.25
Pd	**0.51**	**0.64**	0.36
S	-0.27	**0.83**	0.22
As	0.36	**0.82**	-0.22
Cu	0.23	0.33	**0.86**
Ag	0.15	-0.08	**0.85**
Au	0.38	0.04	**0.50**

Shown is the Varimax rotated matrix for the 3 principal component factors with eigenvalues great than 1. Data logarithmically transformed prior to analysis. Shown in bold are loadings of 0.50 or greater, which represent 25 % or more of the total variance of the element.

which outcrop east and up-ice from the area shown in Figure 13-7. Many of the boulders are thoroughly weathered and disintegrated. Two of the least weathered boulders of Nipigon diabase were analyzed; they contain 15 and 20 ppb Pd and 12 and 12 ppb Pt, substantially higher than mantle peridotite. The Sibley Group contains abundant sulfate minerals of evaporitic origin and veins with high As. Thus the source of Pd is interpreted to be boulders and finer fragments of weathered Nipigon diabase, whereas As and S come from boulders and fragments of the Sibley Group. Groundwaters leach these elements from the disintegrating boulders in the permeable eskers. The Factor 2 Pd anomalies can be classed as “false anomalies” that derive from the ready mobility of Pd in the surface environment and a source of PGE within a highly permeable aquifer. Factor 3 anomalies, which directly overlie outcrops of Nipissing diabase, were not investigated.

Based on Residual Accumulations

Laterite Soils and Gossans

In parts of Australia, lateritic soils may extend to 100 m depth, presenting a formidable challenge to exploration. Western Australia’s first Ni deposit at Kambalda was discovered by identifying gossanous outcrops containing 1% Ni and 0.3% Cu. Repeating

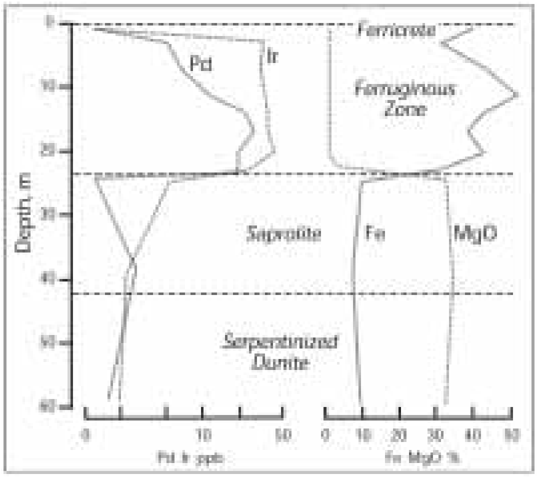

FIG. 13-8. Distribution of Ir, Pd, Fe and MgO in a lateritic profile over serpentinized dunite, Gilgarna Rocks, Western Australia. Modified from Travis *et al.* (1976).

this success proved difficult because other gossans of similar appearance and Ni and Cu contents were found to overlie barren sulfides. Travis *et al.* (1976) discovered that Pd and Ir present in Ni–Cu sulfide bodies were retained in the upper ferruginous zone of the laterite (Pt was not measured). A profile (Fig. 13-8) shows the distribution of Pd and Ir and the major constituents Fe and MgO through the laterite profile. Pd is more abundant than Ir in the primary sulfides of the area, but the Pd/Ir ratio is decreased in the ferruginous laterite implying that Ir is less easily lost during lateritization.

A later study by Moeskops (1977) showed the depletion of Pt and Pd in gossans, with median contents for both Pt and Pd of 1500 ppb, compared to median values for the Ni sulfide ores of 4500 ppb Pt and 7000 ppb Pd. Nevertheless, the contents of Pt and Pd in the gossans formed from PGE-rich rocks are distinctively different from barren gossans, the latter with values below the detection limits of 200 ppb. Taufen and Marchetto (1989) calculated the enrichment/depletion of elements in the gossan overlying Ni mineralization in Minas Gerais, Brazil; –84% for Cu, –70% for Co, –37% for Cu, –33% for Pd, –22% for Pt, –9% for Ru, +35% for Ir, and +37% for Rh.

Other studies in Western Australia have confirmed that PGE reach maximum values in the ferruginous zone at the top of the laterite profile. For soils developed on peridotite of the Ora Banda sill, Western Australia, Gray *et al.* (1996) showed maximum amounts of PGE in this ferruginous zone, rich in goethite and hematite (Fig 13-9). The enrichment factors of three to five times for PGE are comparable to those for insoluble Cr and Zr, indicating that the enrichment is due to the volume reduction of the rocks during the weathering and that the PGE were retained in the horizon during the weathering.

Near to Ora Banda is a similar PGE-mineralized ultramafic prospect, Mt. Carnage, on which laterites are developed. Butt *et al.* (2001) provided data on all of the PGE that enables comparisons to be made between the upper ferruginous zone and the underlying saprolite (Table 13-6). The results show that Pt is most enriched in the ferruginous zone relative to the saprolite.

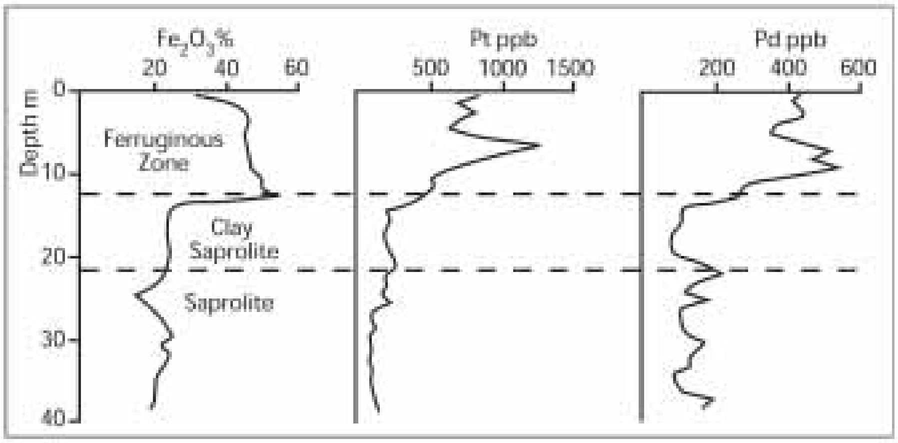

FIG. 13-9. Distribution of Fe, Pt and Pd in a lateritic profile over the Ora Banda ultramafic sill, Western Australia. Modified from Gray *et al.* (1996).

TABLE 13-6. ABUNDANCES OF ALL PGE IN THE UPPER FERRUGINOUS ZONE AND THE UNDERLYING SAPROLITE OF LATERITE OVERLYING MINERALIZED ULTRAMAFIC ROCKS, MT. CARNAGE, WESTERN AUSTRALIA.

Depth m	Pt ppb	Pd ppb	Ru ppb	Rh ppb	Os ppb	Ir ppb
Ferruginous Layer						
1	820	480	18	43	<2	12
3	780	450	22	54	<2	16
5	66	400	16	40	<2	12
7	1300	460	24	60	<2	<2
9	880	500	18	47	<2	16
11	490	440	14	33	<2	10
Average Ferruginous	723	455	19	46	1	11
Saprolite						
15	175	112	8	13	<2	6
19	195	88	8	12	8	4
23	180	215	16	26	<2	4
27	86	96	14	10	<2	4
31	94	160	14	16	8	4
35	96	94	14	12	<2	<2
39	140	170	12	10	8	4
Average Saprolite	138	134	12	14	4	4
Average Ferr./ Average Sap.	5.2	3.4	1.5	3.3	0.25	2.8

Data from Butt *et al.* (2001). Note that for some samples the Os and Ir abundances are at or below the detection limits of 2 ppb. For these samples a value of 1 ppb has been used to compute averages.

An alternative to laterite soil sampling was investigated at Ora Banda (Butt *et al.* 2001). This is to sample the surface lag, which is a cover of gravel derived from the underlying duricrust and laterite. Wind and water have removed the finer fraction. At Ora Banda the Pt and Pd contents of the lag clearly indicate the enrichment of these elements in the laterite overlying the mineralized pyroxenite.

An enrichment of Pt and Pd, along with Ni, Cu and Cr, is found in ferruginous saprolite at the top of a 80 m thick regolith over an ultramafic-hosted Ni sulfide deposit at Mt. Keith, Western Australia (Brand & Butt 2001). In this case the enriched saprolite is covered by 40 m of exotic sediment containing minimal PGE. Lateral dispersion of the PGE in this environment is limited, contrasting with the widespread dispersion of Au. Data for Pt, Pd, Cu and Ni in the profile below the exotic cover is given in Table 13-7. Relative to the sulfide-bearing primary zone, the ferruginous zone is enriched in all elements and particularly within a manganiferous sub-zone at the base of the ferruginous zone. The ratios indicate that Pt and Ni are enriched to approximately the same extent and there is minor loss of Pd and Cu.

These examples from Western Australia and Brazil show that Pt and Pd are mostly retained or even enriched in the upper ferruginous zones of lateritic soils and gossans and can effectively serve to identify underlying PGE-bearing mineralization. In some cases, *e.g.*, Mount Keith and Kambalda, Ni and Cu are also retained, but in other cases, Ora Banda and Minas Gerais, one or both of Ni and Cu are depleted in the ferruginous zone. Iridium and Rh may be retained or enriched to a greater extent than Pt and Pd.

The Western Australia examples represent old, mature laterite terrain. Elsewhere, different results have been obtained. In Madagascar, Salpeteur *et al.* (1995) describe an earlier stage in

TABLE 13-7. DISTRIBUTION OF MEAN CONCENTRATIONS OF PT, PD, CU AND NI IN A LATERITIC WEATHERING PROFILE OVER MINERALIZED ULTRAMAFIC ROCK, MOUNT KEITH, WESTERN AUSTRALIA.

Zone	# Samples	Pt, ppb	Pd, ppb	Cu, ppm	Ni, ppm	Pd/Pt
Ferruginous	5	70	115	995	4760	1.6
Manganiferous	2	125	295	1505	21595	2.4
Quartz-Dolomite	12	40	95	690	14420	2.4
Dolomite	3	14	37	260	8275	2.6
Supergene	6	27	63	360	6020	2.3
Primary	5	19	47	295	4495	2.5

The profile is covered by transported overburden. From Butt (1986).

the development of ferralitic soils on hydrothermally altered pyroxenite that is weakly mineralized with Cu, Ni and PGE (Fig. 13-10). As in Australia there is an upward enrichment in Fe, the Fe_2O_3 content increasing from 10 to 35% and increases in Al_2O_3 (11 to 18%) and Cr (0.3 to 1.5%). But there are upward depletions in Pt (210 to 30 ppb) and Pd (130 to 35 ppb) and in MgO (13 to 5%), Cu (1200 to 200 ppm), and Ni (4000 to 800 ppm). This is a hilly region and erosion and colluvial transport has caused the formation of complicated profiles, including truncated ferralitic profiles and Pt- and Pd-enriched colluvium on top of residual soils. Although the environment is very different, the analogy to the complex soil profiles developed in the hilly Tulameen district of British Columbia should be noted. Maurizon *et al.* (1995) examined laterite–saprolite profiles up to 40 m thick in ophiolite terrain in New Caledonia. Maximum values tend to occur in yellow laterite, near the base of the profile and PGE are depleted near the surface. As noted in earlier sections, Pt-alloys may be present in lateritic soils (Salpeteur *et al.* 1995; Bowles 1995) and thus present an opportunity for collection and analysis in the HMC.

Use of Other Indicator Elements for PGE-Bearing Mineralization

Platinum-group minerals commonly contain Te, As, Sb, and Bi, but their concentrations are not necessarily significantly elevated in the bulk rocks, as shown in the Lac des Iles area (Hattori & Cameron 2004). Their precise analysis is not easy, which lessens their suitability as pathfinder elements.

PGE occur in association with a variety of base elements, most notably Ni, Co and Cu even in Lac des Iles-type sulfide-poor ore (Pettigrew and Hattori 2002, Hinchey *et al.* 2005). Therefore, the concentrations and distributions of base metals may assist in exploration for PGE deposits. However, base metal anomalies need to be carefully evaluated for PGE exploration. First, their mobility and fixing in the surface environment is different from Pd and Pt. Thus base metal anomalies may be spatially separated from those of Pd and Pt, which can either be an advantage or a disadvantage. Second, not all base metal sulfides are associated with significant PGE. It is not uncommon to have a PGE-rich zone with less sulfides. A good example is the newly discovered Suhanko deposit in Finland, that

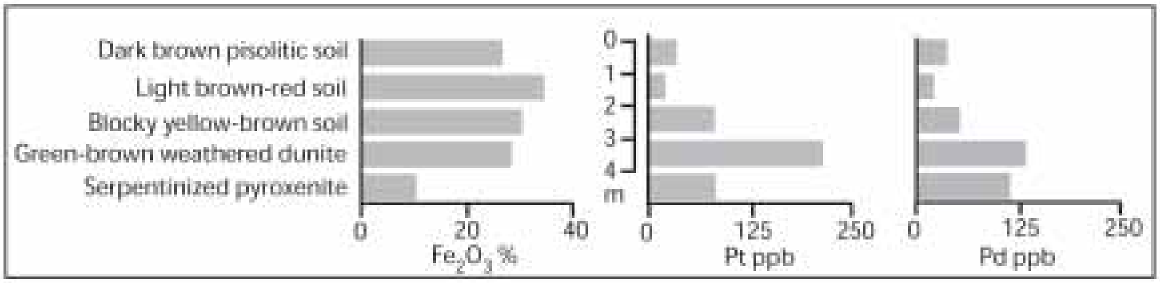

FIG. 13-10. Vertical distribution of Fe_2O_3 in lateritic soils overlying PGE-mineralized pyroxenite, Madagascar. Modified from Salpeteur *et al.* (1995).

contains massive sulfides on the margin of the complex, and a high PGE zone in the middle section of the intrusion.

ANALYTICAL CONSIDERATIONS AND QUALITY CONTROL

By far the most common method of analyzing solid samples for Pt and Pd is lead collection fire assay, followed by dissolution of the bead and analysis of the solution by ICP–MS. This provides detection limits for Pt of 0.1 ppb and 0.5 ppb for Pd. In addition, Au is determined to 1 ppb. Lead collection fire assay provides total dissolution of the sample, including alloys and PGE inclusions in chromite, which are not dissolved by aqua regia. Large samples are fluxed, typically 30 to 50 g in weight; this reduces the nugget effect to which PGE are prone. An important advantage of fire assay is that it removes elements which can cause isobaric interference during ICP–MS analysis. PGE occur in such low concentrations that several elements can potentially cause interference. For example, Sr present in carbonates and in gypsum is readily dissolved by acids and by some selective leaches. During analysis, $^{88}Sr^{16}OH$, which has mass 105, may be formed in the plasma. High peak at mass 105 is erroneously interpreted as high concentrations of Pd because ^{105}Pd is most commonly used to measure the concentration of Pd. An alternative to fire assay is aqua regia–ICP–MS. Detection limits are higher and variable because of interferences. However, aqua regia analyses are often considered a routine part of geochemical exploration programs because they provide data on up to 50 elements.

Selective leaches are widely used in geochemical exploration (Hall 1998). Leaching may enhance the signal to noise ratio, which is particularly important when trying to detect low concentrations of metals. The use of selective leaches has been proven to be effective in exploration of buried base metal deposits (Cameron *et al.* 2004). Enzyme Leach and MMI are proprietary leaches, Enzyme Leach providing analyses for Pt and Pd, with detection limits of 1 ppb; MMI providing analyses for Pd to a detection limit of 0.1 ppb. Non-proprietary leaches include ammonium acetate, that dissolves carbonate-bound elements, and hydroxylamine hydrochloride, which dissolves Mn and Fe oxides.

The most intensive study of selective extraction of Pt and Pd was on samples of lateritic soils over the Ora Banda and Mt. Carnage prospects, Western Australia by Gray (2001). The results should be considered specific to this environment, since the form that Pt and Pd take elsewhere may be different. Scanning electron microprobe examination plus physical and chemical extractions show that Pt and Pd are mostly present in the <2 µm fraction (Gray *et al.* 1996). Neither Pt nor Pd are extracted by reagents that dissolve exchangeable metals, carbonates, Mn oxides or poorly crystalline Fe oxides, indicating that they are not present in these phases. Most of the Pt and 25–50% of the Pd were dissolved by citrate–dithionite reagent, which dissolves Fe oxides, including goethite and hematite. Palladium shows an affinity for Al-rich Fe oxides and aqua regia was required to extract the largest fraction of this element (Gray *et al.* 1996).

The swamp humus sampled around Shorty Lake (Figure 13-5) near Lac des Iles is black and reduced. Hattori and Cameron (2004) experimented with a number of selective leaches to extract the Pd (Fig. 13-11). Cyanide leach removed the most Pd, but less than fire assay. Enzyme and Terrasol leaches removed only very small amounts of Pd from the humus. These data indicate that Pd is strongly bound. More than reduction of Pd may have been involved in its precipitation, with the formation of compounds resistant to dissolution, including organic complexes. Further experiments are required. Gregoire (1985) found that an oxidizing agent, sodium hypochlorite, was effective in extracting Au from organic-rich samples.

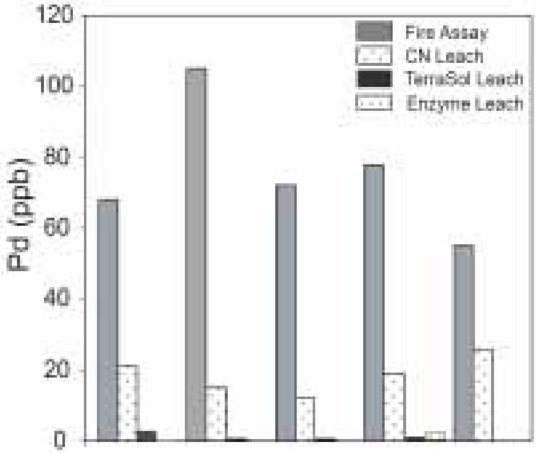

FIG. 13-11. Experiments on extracting Pd from five samples of swamp humus from around Shorty Lake using CN leach (NaCN-NaOH) TerraSol^{TM} and Enzyme Leach^{TM} in comparison to analysis by fire assay - ICP-MS. From Hattori and Cameron (2004).

Quality control on sampling and analytical precision is particularly important for surveys involving PGE, given the potential for the "nugget effect" and the low detection limits required for analysis. A recommended procedure is that a field duplicate should be collected at 10% of the sampling sites. This involves collection of a second sample several metres away from the first. Once the samples are prepared for analysis, *e.g.*, by sieving, one of the field duplicate pairs is split into two to provide an analytical duplicate. The Relative Standard Deviation (RSD) may then be calculated for the field duplicates and for the analytical duplicates:

$$s^2 = (\Sigma(xi_1 - xi_2)^2)/2N$$

$$\mathrm{RSD} = 100.s/Xd$$

where the squares of the differences between the duplicate pairs are summed, then divided by 2N, N being the number of pairs, to produce the variance estimate s^2. The RSD, which is equivalent to the Coefficient of Variation, and is expressed as a percentage, is then calculated, where Xd is the mean of all duplicates. Standards of known composition should be included when sample batches are submitted for analysis. A number of these are available (Hoffman and Dunn 2002).

CONCLUSIONS

In Western Australia there has been extensive sampling of residual soils and gossans and their analysis for PGE in the search for PGE-bearing Ni–Cu deposits below thick lateritic cover. PGE are retained in the upper, ferruginous layer of these soils, even where Ni and Cu have been lost during weathering. The laterites were developed over a long period of time on a land surface of low relief. In some cases there has been subsequent erosion and truncation of the profiles, or the PGE-enriched ferruginous layer may be covered by transported overburden (Butt 1992), features that add complication to survey applications. Nevertheless, the large literature on soil PGE geochemistry in this region attests to the value of the method.

In other regions of the world, both tropical and temperate, there has been a marked separation of Pd from Pt in the surface environment. Platinum remains as PGM in detrital fragments, mainly Pt-rich alloys and sperrylite, which mostly formed at high temperatures (Hattori *et al.* 2004). Palladium, by contrast, enters solution when its primary minerals are weathered. Except for environments with abundant chloride- and sulfur-bearing ligands, Pd(II) dissolves as neutral or negatively charged hydroxide complexes or as metal–organic complexes. Unlike positively charged base metal cations, Pd(II) hydroxide and organic complexes are not fixed by the negatively charged Fe oxyhydroxide coatings of B-horizon soils and stream sediments. Instead, Pd is fixed by organic matter, such as is present in swamps, in basins along streams, in lake sediments, in vegetation, and in the humus of soils.

The differing behaviors of Pt and Pd in the surface environment affect strategies applied to geochemical exploration. At the reconnaissance stage of exploration Pt may be sought in the HMC of stream sediments; separation of this concentrate achieves a magnification in the abundance of Pt relative to the bulk sample and an improvement in anomaly/background contrast. Where streams are poorly developed, as in the Canadian and Fennoscandian shields, sampling and analysis for Pd in organic lake sediments and humus from swamps provides a distal indicator of PGE mineralization. For the follow-up of anomalies obtained during the reconnaissance stage, sampling can focus on Pt within the HMC of tills and C-horizon soils or the Pd that accumulates in the humic layers of soil or vegetation growing on the soil. The recent development of methods that measure Pd and Pt directly in waters add a further option for more detailed levels of exploration.

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