

THE DISPERSION OF Pt, Pd AND Au IN SURFICIAL MEDIA ABOUT TWO PGE-Cu-Ni PROSPECTS IN QUEBEC¹

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ABSTRACT

Soils, lake sediments, groundwaters and lake waters in the vicinity of two Cu-Ni-Pt-Pd occurrences in Quebec (Lac Sheen and Lac Long - Lac Montauban), were sampled and analyzed for Pt, Pd and Au. In both areas the Pd content of lake waters ranges from 0.1 to 0.3 $\mu\text{g/L}$, and this appears to be in true solution. However, the suspended particulate fraction dominates in groundwaters, with total Pd ranging between 0.25 and 17 $\mu\text{g/L}$. In all waters, Pt and Au contents are generally below the detection limit of 25 ng/L, although Pt occasionally reaches higher values, especially in groundwaters. The Pt/Pd ratio in outcrop and boulder samples collected at Lac Sheen is nearly uniformly 1:1, but the soils are depleted in Pd relative to Pt, suggesting that Pd is preferentially mobilized in solution. This is consistent with the water analyses. The Pd contents of the lake sediments are very low (<3 ppb). The Pt contents are also relatively low, but sporadically attain high values (up to 200 ppb). The Au content in the lake sediments is also extremely variable, ranging from <1 ppb to 213 ppb, but with high values more common than is the case for Pt. The results of the study substantiate the idea that platinum-group elements are mobile in surficial environments, Pd being preferentially transported in solution. Furthermore, the sampling of lake water may offer some promise either as an alternative or a complement to sampling of lake sediments for reconnaissance exploration.

Keywords: analyses, exploration, gold, lake sediments, mobility, natural waters, palladium, platinum, soils, solubility, Quebec, Grenville Province, Superior Province.

SOMMAIRE

Les sols, les sédiments lacustres, les eaux souterraines et les eaux de lac autour de deux indices de Cu-Ni-Pt-Pd situés au Québec (lac Sheen et lac Long - lac Montauban) ont été échantillonnés et analysés afin de déterminer leurs teneurs en Pt, Pd et Au. Dans les deux régions, la teneur en Pd des eaux de lac varie de 0.1 à 0.3 $\mu\text{g/L}$, et la plupart du Pd semble être vraiment en solution. Cependant, la proportion des particules en suspension est plus importante dans les eaux souterraines, le Pd total variant entre 0.25 et 17 $\mu\text{g/L}$. Dans toutes les eaux, les teneurs en Pt et en

Au sont en dessous du seuil de détection (25 ng/L), bien que les teneurs en Pt soient parfois plus élevées, surtout dans les eaux souterraines. Le rapport Pt/Pd des échantillons d'affleurements et de blocs erratiques prélevés au lac Sheen est de 1:1 presque sans exception, mais les sols sont enrichis en Pt par rapport au Pd, ce qui fait penser que le Pd se dissout préférentiellement. Ceci concorde avec les analyses d'eaux. Les teneurs en Pd des sédiments lacustres sont toutes très faibles (moins de 3 ppb). Les teneurs en Pt sont généralement aussi faibles, mais atteignent parfois des valeurs élevées (jusqu'à 200 ppb). Les teneurs en Au dans les sédiments lacustres sont très variables, de moins de 1 ppb à 213 ppb, mais les valeurs élevées sont plus fréquentes que dans le cas du Pt. D'après les résultats de l'étude, les éléments du groupe du platine seraient transportables dans les milieux de surface, le Pd étant transporté préférentiellement en solution. D'ailleurs, l'échantillonnage des eaux de lac constituerait une méthode efficace d'exploration et de reconnaissance, soit comme substitut, soit comme complément à l'échantillonnage des sédiments lacustres.

Mots-clés: analyses, eaux naturelles, exploration, mobilité, or, palladium, platine, sédiments de lac, sols, solubilité, Québec, province du Grenville, province du Supérieur.

INTRODUCTION

Considerable evidence now suggests that Pt and Pd are mobile in surficial environments (Ottman & Augustithis 1967, Fuchs & Rose 1974, Cousins & Kinloch 1976, Cousins & Vermaak 1976, Travis *et al.* 1976, Dissanayake & Kritsotakis 1984, Bowles 1986, Riese & Arp 1986, Taufen & Marchetto 1989). A greater understanding of the mobility of Pt and Pd in surficial media is crucial to the successful application of geochemical sampling of waters, soils and lake sediments to mineral exploration. A number of studies of the behavior of metals such as Cu, Pb, Zn and Au in lake sediments have been conducted, and the potential of geochemical sampling of such media in the exploration for these metals has been well documented (Allan *et al.* 1973, Allan & Timperley 1975, Coker & Nichol 1975, Davenport *et al.* 1975, Nichol *et al.* 1975, Hornbrook & Garrett 1976, Cameron 1977, Coker *et al.* 1979, 1982, Schmitt 1989). However, the possibility of using lake sediments for geochemical exploration for Pt and Pd has not yet received much attention. The potential use

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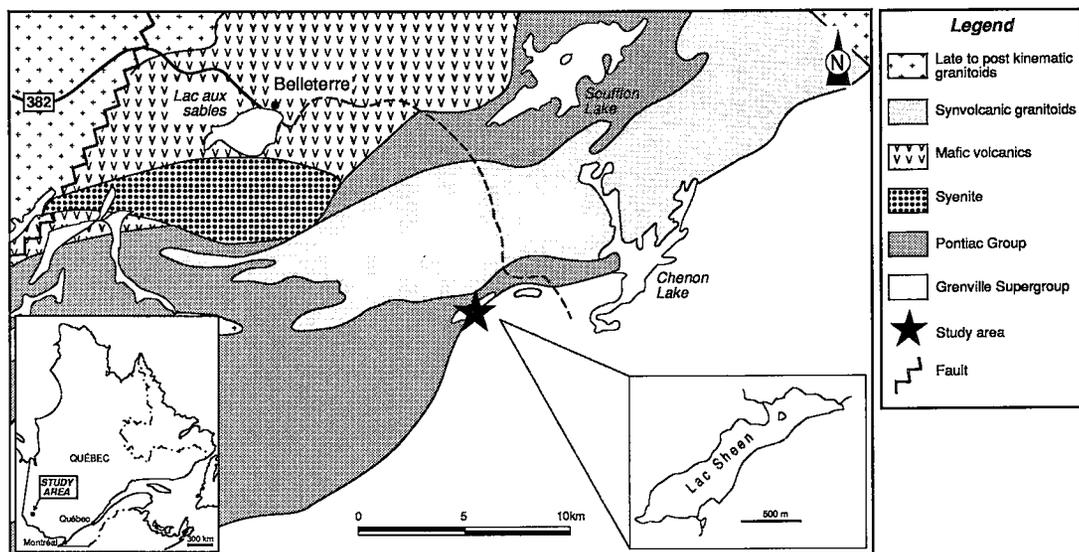


FIG. 1. Geological map of the Belleterre region of Quebec showing the location of the Lac Sheen Pt-Pd-Cu-Ni showing.

of Au, Pt and Pd concentrations in surficial waters as an exploration tool has been hampered by the paucity of reliable information (e.g., Pogrebnayk *et al.* 1984, McHugh 1988) on background and anomalous concentrations of these metals in surface and groundwater.

This investigation addresses the question of the dispersion of Pt, Pd and Au in surficial media around two previously recognized Pt-Pd showings in Quebec: the Lac Sheen and the Lac Long - Lac Montauban occurrences. We provide here a preliminary assessment of the nature of this dispersion by presenting analytical data for samples of bedrock, soil and lake sediments, as well as lake water and groundwater, taken from the two showings in the Autumn of 1988.

LOCATION AND GEOLOGY

Lac Sheen

This occurrence is located in Guillet Township, Quebec, approximately 22 km southeast of the town of Belleterre (Fig. 1). Previous exploration work included trenching, drilling, float sampling, geophysical surveys and analysis of lake sediments for Cu. The following geological description is largely derived from company reports (Gray 1962, Gleeson 1970, Gagnier 1979, Mutch 1982, Brault & Hobbs 1984, Mosher & Gittings 1987).

The Lac Sheen property occurs in the contact zone between the Grenville and Superior tectonic provinces, within the Pontiac Group of the Superior Province (Fig. 1). The Grenville Front passes just to

the south of Lac Sheen, where the contact takes the form of mylonitic zones in several locations. An elliptical body of Archean metasediments (biotite gneiss, biotite-hornblende gneiss and schist) occurs adjacent to the northeast end of Lac Sheen. The metasediments in turn lie within a sequence of orthogneisses (granite, pegmatite and aplite) cross-cut by diorite and granite. Within the biotite gneisses, lenticular bodies of amphibolitized gabbro and pyroxenite are found. These mafic and ultramafic rocks host disseminated sulfide mineralization (<1% up to, locally, 10% by volume). Petrographic examination (*vide infra*) indicates that the sulfides consist of, in order of abundance: chalcopyrite, pyrrhotite, pyrite, marcasite and minor pentlandite. Previous work (see reports listed above) has shown that the highest Cu-Ni-Pt-Pd-Au contents occur in glacial erratics, whose source has not been located, in spite of considerable efforts. However, the angular nature and large size of the boulders suggest a relatively proximal source (Gleeson 1970).

In addition to the Cu-Ni-PGE showing at Lac Sheen, there are several known occurrences of Au and Ag mineralization in metabasalts and metagabbros north of Belleterre, as well as on the west side of Lac aux Sables.

Lac Long - Lac Montauban

This occurrence is located in Montauban Township, Quebec, approximately 12 km south of the town of Perthuis (Fig. 2). The area studied is located on a hill surrounded by three lakes: Lac Long, Lac Montauban and Lac Nadeau. There has been less

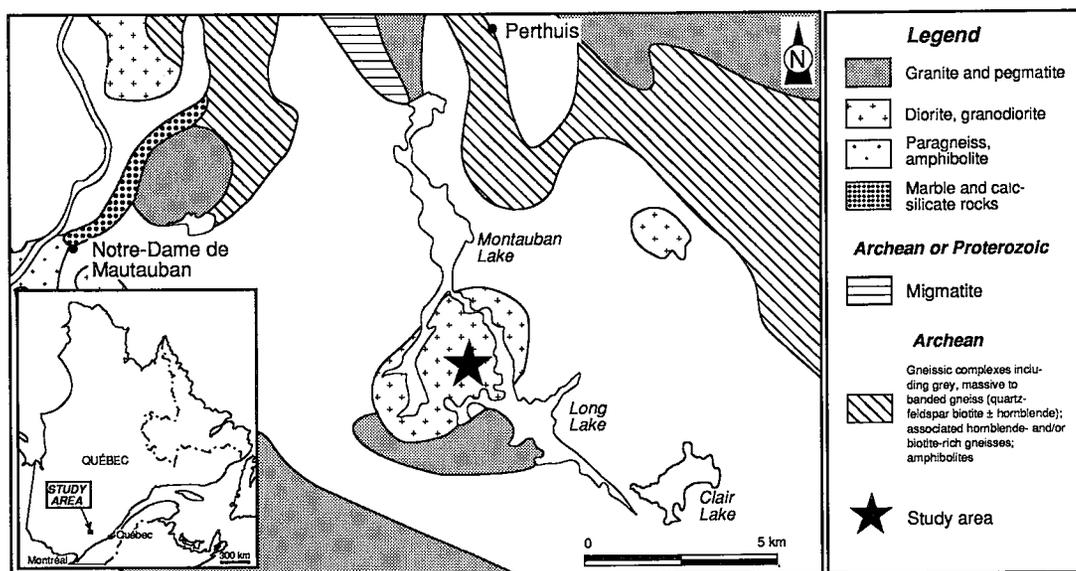


FIG. 2. Geological map of the Lac Long - Lac Montauban region, Montauban Township, Quebec.

exploration at this prospect than at Lac Sheen, but a few sketchy descriptions of the local geology are nevertheless available (Pyke 1963, Gledhill 1972).

The Lac Long - Lac Montauban area is underlain by Grenville series metasedimentary rocks (biotite-hornblende gneisses with quartzofeldspathic bands) and mafic metavolcanic units (Fig. 2). These rocks are folded and are intruded by synorogenic igneous rocks (granites to peridotites). From the reports of Pyke (1963) and Gledhill (1972), it was impossible to determine the exact locations at which rock samples with elevated Pt-Pd-Au contents had been previously collected. No trenches or drill holes were found, and only minor sulfide mineralization was observed. Therefore, the nature of the Pt-Pd-Au mineralization described by previous workers could not be verified. However, some mafic rocks sampled in the present study do exhibit anomalous Pt-Pd values (*vide infra*) and, therefore, analyses of lake water were performed in order to make the comparison with Lac Sheen. We have not yet executed a petrographic study of the rocks sampled from the occurrence in Montauban Township.

It is also interesting to note the presence of several known occurrences of Zn, Pb, Au, and Ag mineralization in Montauban Township southwest of the lakes studied here, including the Montauban Cu-Au deposit.

SAMPLING METHODS

The locations of samples of rock, soil, lake sediment and water collected at Lac Sheen are indicated

on Figure 3. The locations of water samples taken from Lac Long are given in Figure 4. At Lac Sheen, bedrock samples were obtained from trenches and outcrops. Several boulders also were sampled. At Lac Long - Lac Montauban, there is very little exposure; all of the rock samples collected from this prospect consist of boulder float.

Lake sediments were recovered using a coring device described by Hornbrook & Garrett (1976). The length of the core obtained varied from approximately 15 to 30 cm depending on the depth of penetration of the corer, which in turn depended on the nature of the sediment and the depth of the lake (*i.e.*, distance of free fall of the corer) at a given sampling point. Upon recovery of the sediment sample, the upper few centimeters were discarded. Several hundred grams of wet sediment were removed from the corer and placed into a paper sample bag, and the bag was sealed using iron wire. Replicate samples were taken from as near as possible to the first sample at each site. In the tables of data, replicate samples from the same location on the lake are given the same sample number but are distinguished from one another with a letter suffix (*i.e.*, a,b,c,...).

Soil samples were taken from pits dug as deep as possible before either bedrock, large boulders or the water table was encountered. These pits ranged from 30 to 60 cm in depth. Samples of the humus (A₀) and C layer were taken at every site (the B layer was taken in most cases as well) and then stored in paper sample bags.

Samples were taken of both lake water (from 10 meters depth or less) and groundwater. Two liters

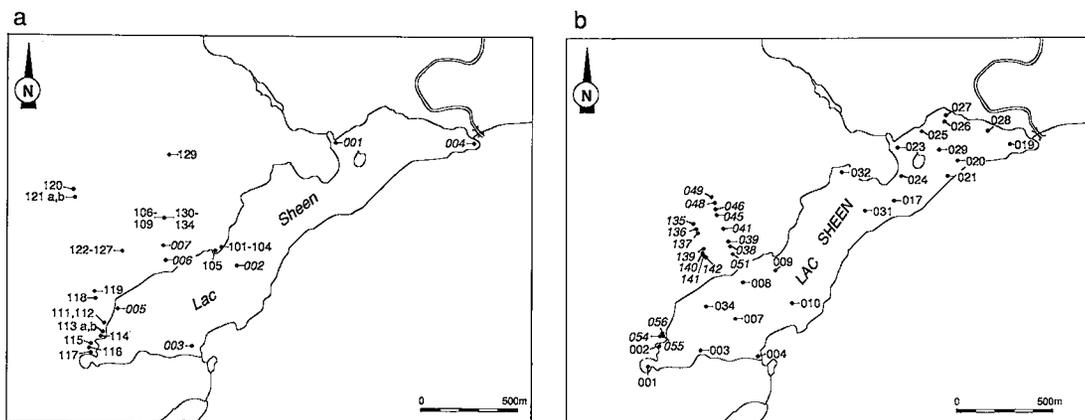


FIG. 3. a) Map of the Lac Sheen area showing the location of rock samples (101-134) and water samples (001-007). b) Map of the Lac Sheen area showing the location of soil (038-056, 135-142) and lake sediment (001-034) samples.

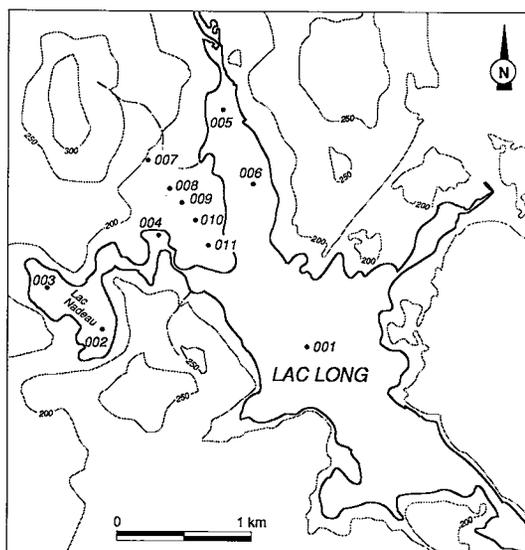


FIG. 4. Map of Lac Long area showing the location of groundwater and lake water samples (001-011).

of water were sampled for determination of Au, Pd and Pt. One liter of water was forced through a 0.45 μm Millipore filter in the field using a syringe, and the other liter remained unfiltered. These samples were then stored in 1-L acid-washed polyethylene bottles after acidification with 40 mL of concentrated HCl. The high acid concentration was deemed necessary to maintain the PGE and Au in solution until analysis (Chao *et al.* 1968). A third, unfiltered, acidified sample of water also was collected for Cu and Ni analysis. Finally, a 250-mL sample of unfiltered, unacidified water was taken for subsequent measurements of conductivity and chloride concentration.

Temperature measurements were made in the field using a portable digital thermometer and a chromel-alumel thermocouple.

Measurements of Eh and pH of the waters were performed in the field within hours after collection of the sample. The pH was measured with a glass electrode calibrated using NBS standards at ambient temperatures. The Eh was measured using a Pt electrode with a saturated calomel reference electrode. The Eh cell was calibrated at ambient temperatures using a standard ferricyanide-ferrocyanide buffer. Relatively long periods of time, up to 30 minutes, were required to obtain stable Eh and pH readings.

DETAILED SAMPLE DESCRIPTIONS

Rock samples

Several of the rock samples collected at Lac Sheen were examined petrographically. A summary of the results follows. More detailed descriptions may be found in Wood & Vlassopoulos (1989).

The amphibolite, both in trench and boulder samples, generally consists of fine- to coarse-grained hornblende in equant, tabular or prismatic crystals locally altered to biotite and epidote. Plagioclase occurs in trace amounts only. Quartz exhibits undulose extinction. This quartz is usually fine- to medium-grained and is located in the interstices between amphibole crystals as well as in small veins. It is accompanied by fine-grained epidote.

Pegmatite veins are composed of albite, microcline, quartz, biotite and, locally, apatite and epidote.

The opaque phases usually occur at silicate grain boundaries, in cleavage planes and locally in small fractures. Sulfide minerals are more common in the amphibolite, but also have been observed in the peg-

matite veins near contacts with the amphibolite. The opaque content in the rocks examined varies between 3 and 10% by volume. Chalcopyrite and pyrrhotite are the dominant original sulfide phases, but these are partially replaced by pyrite, magnetite and, in some samples, marcasite and goethite. Sphalerite, covellite and pentlandite occur in trace amounts. Marcasite, goethite and covellite are interpreted to be the result of supergene alteration. No individual Au, Pt or Pd phases were observed under routine petrographic examination.

Soils

Only a general description is given here. For more details on individual samples, see Wood & Vlasopoulos (1989). The soil profiles at the two prospects are poorly developed. In general, B and C layers as well as a thin humus (A_0) layer are present. The humus layer is typically only a few centimeters in thickness. The B layer is typically brownish orange to red in color and sandy to silty in grain size. The C layer contains grey to green, slightly altered rock fragments with interstitial clay.

The question as to whether these soils represent residual or transported overburden is clearly of relevance to the present study. Although the presence of allochthonous boulders on the surface and in the soil profile attest to some transport of materials from elsewhere, there are also some direct indications of a residual origin. For example, in the C horizon, the type of rock fragment present is correlated with the type of bedrock underneath. Furthermore, rusty coloration is more prevalent in the soils over sulfide-bearing amphibolites than over felsic pegmatites. Finally, the strongest indication of a largely residual origin is that, as pointed out below, anomalous (with respect to Pt, Pd and Au contents) soil samples from the trenches are correlated with anomalous bedrock underneath.

Lake sediment samples

Both Lac Sheen and Lac Long are rather typical Canadian glacial lakes and may be classified as dimictic and mesotrophic. The maximum depth of water measured at Lac Sheen was approximately 20 meters, whereas that at Lac Long was 45 meters. In general, the sediments in both Lac Sheen and Lac Long are quite similar. The profundal sediments usually consist of several decimeters of dark brown mud and silt, occasionally containing larger sand-size particles, rock fragments and plant debris. Organic content visually appeared to be relatively uniform throughout the core; loss on ignition ranged from about 20 to 40%. The littoral sediments tend to be coarser and less organic-matter-rich (loss on ignition generally <20%) than the profundal sedi-

ments. Tiny black particles are widespread (magnetite, ilmenite, Fe or Mn hydroxides?), and faint banding as defined by slight color changes was observed. Occasionally, a grey sticky clay layer was encountered below the above-mentioned sediment.

ANALYTICAL METHODS

Rock samples

Hand specimens were crushed using a puck grinder, resulting in approximately 100 g of pulp; care was taken to thoroughly clean the crushing apparatus between samples by crushing clean quartz sand. Crushed samples were sent to X-ray Assay Laboratories of Don Mills, Ontario for analysis. A 30-g split was initially analyzed. In the case of the Lac Sheen samples, a second split of 30 g or less was submitted at a later date to check for reproducibility of analysis. The analytical method employed was fire assay followed by DCP (direct current plasma) emission spectrophotometry. Stated detection limits (30-g sample) were 1, 2, and 10 ppb for Au, Pd, and Pt, respectively.

Water samples

The 1-liter water samples collected for Au, Pd, and Pt analysis were gently boiled down in stages in 400-mL beakers with the constant addition of HCl and HNO₃ and washing down the sides of the beakers. The solutions were boiled until less than 25 mL remained, and the remaining solution was quantitatively transferred to a 25-mL volumetric flask and diluted to volume with HCl. All solutions were analyzed for Au, Pd and Pt using ICP-MS (inductively coupled plasma - mass spectrometry) at the Université du Québec à Montréal. The detection limit for all three metals using this method was about 25 ng/L, although the detection limit varied somewhat from sample to sample owing to slight differences in volume of the initial sample. Although this detection limit is somewhat high compared to that obtainable by other methods (*e.g.*, McHugh 1983, 1984, 1986, 1988, Hall *et al.* 1986), it was considered adequate for the present study, where the main objective was the preliminary screening for anomalous values. The analytical imprecision was 5-10% for these metals.

The Cu and Ni contents were determined by Zeeman graphite-furnace atomic absorption spectrometry using the unfiltered, acidified 250-mL water samples. These metals were also determined in the filtered concentrates remaining after determination of Au, Pt and Pd. Conductivity was determined in the laboratory on the unacidified, unfiltered, 250-mL water samples using a portable conductivity meter.

These same samples were then analyzed for chloride content using a chloride ion specific electrode.

Soil and lake sediment samples

After air drying, both the soil and lake sediment samples were manually disaggregated and sieved. The $-160\ \mu\text{m}$ fraction (lake sediments) or the $-80\ \mu\text{m}$ fraction (soils) was retained for further processing. After sieving, approximately several tens of grams of material were weighed out and then dried overnight at 105°C to remove adsorbed and loosely bound water; the samples were then reweighed. Next, the samples were charred at $550\text{--}600^\circ\text{C}$ for several hours in a muffle furnace and reweighed. The difference in weight before and after the charring step is recorded as the loss on ignition (LOI) and is taken to represent primarily the content of organic matter (although some structurally bound water, carbon dioxide from carbonates and sulfur from sulfides may be included). Finally, the charred samples were digested by treating approximately 10 grams of sample with 10–30 mL HF and gently heating, followed by the addition of 50–100 mL aqua regia. The aqua regia was slowly boiled off until precipitation started to occur. The residue was then redissolved in concentrated HCl, and this was diluted to 100 mL with a 1:1 aqueous solution of HCl.

The solutions thus obtained were analyzed for Au, Pt and Pd by Zeeman graphite furnace – atomic

absorption spectrometry (GFAAS). However, the high content of total dissolved solids in the sample solutions prevented direct analyses in the furnace. Furthermore, without preconcentration, the expected detection limit for the diluted solutions would have been greater than 10 ppb for the metals of interest, resulting in a detection limit for the sediments and soils of approximately 100 ppb. Therefore, it was considered necessary to both preconcentrate Au, Pt and Pd and separate them from most of the other elements using a technique of organic solvent extraction, which involved the chelation of the metals by dibutyl sulfide (DBS) and then extraction into toluene (Rubeska *et al.* 1977). The procedure is as follows:

First, 5 mL of a 0.2 M DBS solution in toluene were combined with 100 mL of the sample solution in a separatory funnel and shaken vigorously for a minute or so. After allowing the phases to separate, the aqueous phase was drained off, and the toluene phase was stored in a capped polyethylene tube to be analyzed by GFAAS for Au and Pd. Platinum is not extracted using this technique (probably as a result of its slow ligand-exchange kinetics), and so the remaining aqueous solution was treated with 20 mL of a 1 M SnCl_2 solution in 3 M aqueous HCl (Wood *et al.* 1990). The SnCl_2 apparently renders Pt more readily complexed by the chelating agent (Brackenbury *et al.* 1987a, b), in this case DBS, and hence more easily extracted into toluene. The SnCl_2 -treated sample solutions were allowed to stand in the presence of light (Wood *et al.* 1990) for at least 2 hours. Then 2 mL of 0.2 M DBS in toluene were added to the aqueous solution, and the phases were mixed, allowed to separate, and the organic phase was retained for Pt analysis. Aqueous standard solutions were taken through exactly the same procedure as the samples, and the resultant organic extracts were used to construct the calibration curve for the GFAAS analysis. Although the detection limit varied somewhat from day to day and with initial weight of sample, the average detection-limits for Au, Pd and Pt in the soil and sediment samples were approximately 1, 2 and 10 ppb, respectively. Most of the variation in detection limits is due to variations in the initial weight of samples. In addition, detection limits tended to improve as the analytical technique was further refined throughout the course of the study. The analytical imprecision for replicate analyses varied between 2 and 20% and was usually $<10\%$.

RESULTS AND DISCUSSION

Rock samples

The analytical results for rock samples from Lac Sheen are given in Table 1. In the 36 rock samples

TABLE 1. Au, Pt AND Pd CONTENTS OF ROCKS FROM THE LAC SHEEN Cu-Ni-PGE OCCURRENCE

Sample No.	Au (ppb)		Pt (ppb)		Pd (ppb)		Rock type
	1	2	1	2	1	2	
GT88-101	2100	1900	1700	2300	6300	4600	amph.
-102	50	69	300	310	390	330	vein amph.
-103	7100	10000	1500	1800	990	840	vein amph.
-104	480	490	2300	3500	2500	2100	vein amph.
-105	3	<3	10	<30	15	10	amph.
GT88-106*	110	73	2300	1500	2500	2400	alt. amph.
-107	2	7	20	50	22	14	amph.
-108	62	150	340	450	150	110	amph.
-109	6	9	10	30	9	10	peg.
-110	<1	4	20	<30	22	12	alt. amph.
GT88-111	2	5	20	<30	25	20	amph.
-112	<1	3	10	<30	21	11	vein amph.
-113a	2	<3	20	<30	20	8	amph.
-113b	3	<3	<10	<30	10	<2	peg.
-114	2	14	<10	<30	3	3	vein amph.
GT88-115	<1	4	10	<30	18	10	alt. amph.
-116	11	12	90	100	150	130	vein amph.
-117	3	<3	10	<30	12	3	amph.
-118	2	<3	<10	<30	14	4	amph.
-119	2	<3	<10	<30	17	9	alt. amph.
GT88-120	1	<3	20	30	18	10	vein amph.
-121a	6	3	<10	40	5	<2	Bt gneiss
-121b	4	12	<10	40	4	<2	Bt gneiss
-122	18	18	<10	<30	4	<2	vein amph.
-123	3	<3	10	30	20	16	amph.
GT88-124*	4	<1	150	150	190	170	amph.
-125	12	25	360	450	460	390	alt. amph.
-126	2	<3	10	<30	14	6	amph.
-127	170	220	650	520	500	460	alt. amph.
-128	<1	6	10	50	21	11	vein amph.
GT88-129	1	4	20	50	17	10	alt. amph.
-130	25	20	1200	1200	960	900	alt. amph.
-131	96	100	890	1200	990	770	alt. amph.
-132	7	2	20	50	37	18	amph.
-133	2	<3	<10	40	<6	<2	peg.
-134	2	8	20	50	37	3	peg.

Note: Headings 1 and 2 refer to different splits (see text). * denotes bedrock samples, all others boulder float. Abbreviations: amph.: amphibolite, peg.: pegmatite; "vein": cross cut by small quartz veins, alt.: chloritized, oxidized, or weathered, Bt: biotite.

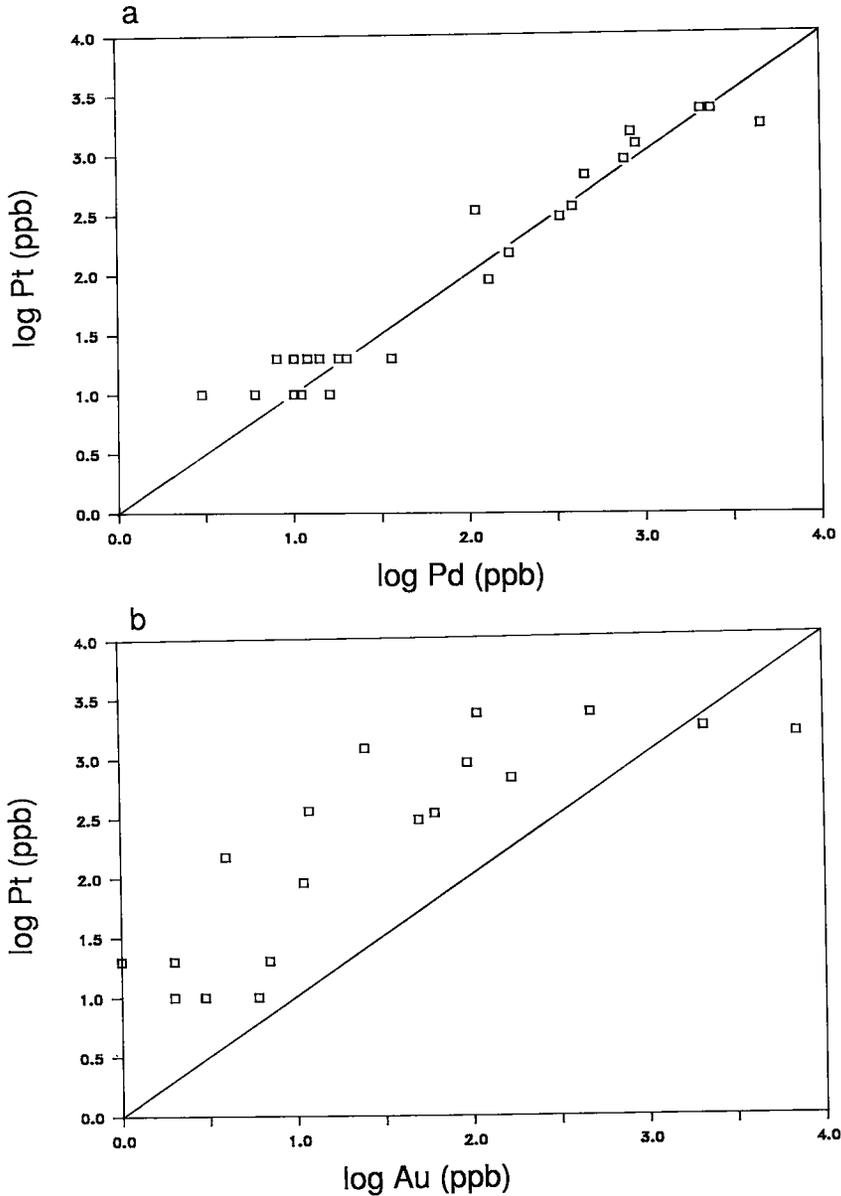


FIG. 5. a) Plot of log ppb Pt *versus* log ppb Pd for rock samples collected at Lac Sheen, showing the nearly invariant ratio Pt:Pd of 1:1. b) Plot of log ppb Pt *versus* log ppb Au for rock samples collected at Lac Sheen, showing the variable Pt:Au ratio, with Pt generally greater than Au.

analyzed from Lac Sheen, Au, Pt and Pd contents range from <10 to 10,000 ppb, <10 to 3500 ppb and <2 to 6300 ppb, respectively. Replicate analyses are generally in good agreement. The Pt and Pd values are remarkably well correlated, and the Pt/Pd ratio is approximately 1, but the Au/Pd and Au/Pt

ratios are far more variable (Fig. 5). For the most part, the highest precious-metal contents were found in boulders, whose origins are unknown. This finding is in agreement with the findings of other investigators (*e.g.*, Gray 1962). However, high values also occur sporadically in rocks taken from trenches. In

TABLE 2. Au, Pt AND Pd CONTENTS OF ROCKS FROM THE LAC LONG AREA

Sample No.	Au (ppb)	Pd (ppb)	Pt (ppb)	Rock type
MT88-34	5	<6	30	serp. gabbro
-35	5	11	80	vein. gabbro
-36	<3	6	<30	gabbro
-37	<3	11	<30	gabbro
-38	<10	37	220	gabbro w. sulf
MT88-39	<3	6	<30	gabbro
-40	<3	<6	<30	gabbro
-42	<3	10	<30	gabbro
-47	<3	2	<30	gabbro
-48	<3	13	<30	gabbro
MT88-50	<3	3	<30	gabbro
-88	17	22	<30	gabbro
-95	<3	3	<30	Bt gneiss
-96	<3	12	30	gabbro
-98	<3	<6	<30	Bt gneiss

serp. = serpentized; vein. = veined; w. sulf. = with specks of sulfide (<1%).

TABLE 3. ELEMENT CONCENTRATIONS IN WATER SAMPLES FROM LAC SHEEN

	Sample # GT88-						
	001	002	003	004	005	006	007
Temp (°C)	1.6	4.9	5.2	4.3	5.0	4.4	2.4
Depth (m)	0	10	1	0	1	gw	gw
pH	5.3	5.8	5.9	5.6	5.7	5.0	4.9
Eh (mV vs. SHE)	245	236	233	240	238	263	252
Cl ⁻ (mg/L)	1.2	4.6	12.1	<1	<1	<1	2.1
Metals							
Pt(t) (ng/L)	<25	51	<25	51	<25	75	500
Pt(d) "	<25	<26	<25	<26	<26	<41	43
Pd(t) "	120	155	163	17400	135	351	218
Pd(d) "	138	137	170	166	179	412	363
Au(t) "	<25	76	<25	<26	<25	<25	<25
Au(d) "	<25	<26	<25	<26	<26	<41	<43
Cu(t) "	14	20	3	5	5	6	115
Cu(d) "	5	3	2	1	2	17	108
Ni(t) "	1	<1	<1	2	1	1	---
Ni(d) "	<3	<3	<3	<3	<3	33	303

gw: groundwater, d: dissolved, t: total, ---: not determined.

general, the precious-metal content of the pegmatites is very low: Au, 2–6 ppb; Pd, <2–36 ppb; Pt, ≤10 ppb.

As indicated by the results summarized in Table 2, the precious-metal contents of the rocks sampled from the Lac Montauban – Lac Long area are considerably lower than those of the Lac Sheen rocks. Only Pt may be considered anomalous in a few samples, the highest Pt content (220 ppb) occurring in the only sulfide-bearing rock, a gabbro, sampled at Lac Montauban – Lac Long. As mentioned above, the sites from which previous samples with high PGE contents were taken (Pyke 1963, Gledhill 1972) could not be located in the present study, but the possible existence of such rocks cannot be ruled out.

Water samples

Results of water analyses are given in Tables 3 and 4. Reagent blanks analyzed for Au, Pt and Pd all gave ICP-MS signals barely detectable above background, which suggests little or no sample contamination due to the procedures and reagents employed. In almost all cases the Au concentrations of the lake and ground waters were below the detection limit (25 ng/L) in filtered as well as unfiltered samples from both the Lac Sheen and the Lac Long – Lac Montauban areas. This is not surprising, in light of the fact that most recent estimates of the background concentration of Au in surficial waters average about <1 to 5 ng/L, and anomalous concentrations near Au deposits may be less than a few hundred ng/L (McHugh 1988).

The concentration of Pd in filtered Lac Sheen waters averaged 158 ± 19 ng/L, whereas filtered

TABLE 4. ELEMENT CONCENTRATIONS IN WATER SAMPLES FROM LAC LONG

	Sample # MT88-										
	001	002	003	004	005	006	007	008	009	010	011
Temp (°C)	7.7	5.9	6.1	4.6	6.7	6.6	4.8	5.4	5.7	5.1	7.1
depth (m)	10	10	10	3	0.1	10	gw	gw	gw	gw	gw
pH	6.9	6.0	6.2	6.5	6.2	6.3	4.2	4.3	4.1	4.5	5.0
Eh (mV vs. SHE)	385	334	334	353	375	422	194	190	186	191	184
Cl ⁻ (mg/L)	<1	<1	<1	<1	<1	3	<1	<1	<1	<1	<1
Metals											
Pt(t) (ng/L)	<25	<25	<43	<25	50	25	25	<25	50	250	75
Pt(d) "	<48	<41	75	<40	<43	<42	<25	<43	<73	<25	200
Pd(t) "	213	212	261	150	275	275	250	425	3250	375	2500
Pd(d) "	260	187	118	257	262	267	205	562	220	250	300
Au(t) "	<25	<25	<43	<25	<25	<25	<25	<25	75	<25	<25
Au(d) "	<48	<41	<25	120	<43	<42	<25	<43	<73	<25	25
Cu(t) "	10	2	5	2	2	2	3	9	13	4	16
Cu(d) "	9	5	2	3	<1	<1	3	5	6	2	3
Ni(t) "	1	1	1	<1	<1	<1	1	1	11	<1	5
Ni(d) "	7	<3	<3	<3	<3	<3	71	<3	<6	<3	<3

gw = groundwater; d = dissolved; t = total.

waters from the main part of Lac Long averaged somewhat higher 262 ± 4 ng/L. At both locations the concentration of Pd in the filtered lake water appears to be relatively uniform throughout the entire lake, as evidenced by the relatively low standard deviations quoted above. However, in the Lac Long area the Pd concentrations fall off slightly in the smaller Lac Nadeau (153 ± 48 ng/L), which is isolated from the main part of Lac Long by a narrow, partially dammed stream and two stagnant ponds (Fig. 4). In general, the Pd contents of the filtered groundwaters in both field areas are slightly greater than those of the corresponding lake waters. Filtered groundwaters from the Lac Sheen area average 388 ± 35 ng/L Pd, and those from the Lac Long area average 307 ± 150 ng/L Pd. The measured Pd concentrations in all waters are about two orders of magnitude higher than the only other data on Pd contents in natural waters known to us: Pogrebnnyak *et al.* (1984) found

a mean of 2.4 ng/L Pd, mainly in dissolved forms, in groundwaters near a PGE occurrence in Transbaikal, USSR. At Lac Sheen the Pd appears to be mainly present in true solution in both the lake waters and groundwaters, inasmuch as the results for filtered and unfiltered samples are more or less identical, with the exception of one spuriously high Pd determination in an unfiltered water sample from the northeast part of the lake. In many cases, however, the filtered samples appear to yield slightly higher Pd contents than the unfiltered ones. The reason for this is unclear, but may be due to analytical imprecision or minor variation in the homogeneity of the water samples. At Lac Long - Lac Montauban, Pd probably occurs largely as suspended particles in the groundwaters because some of the unfiltered waters yield much higher Pd (up to an order of magnitude) than do the filtered waters. Furthermore, the high Pd content in the unfiltered groundwaters suggests

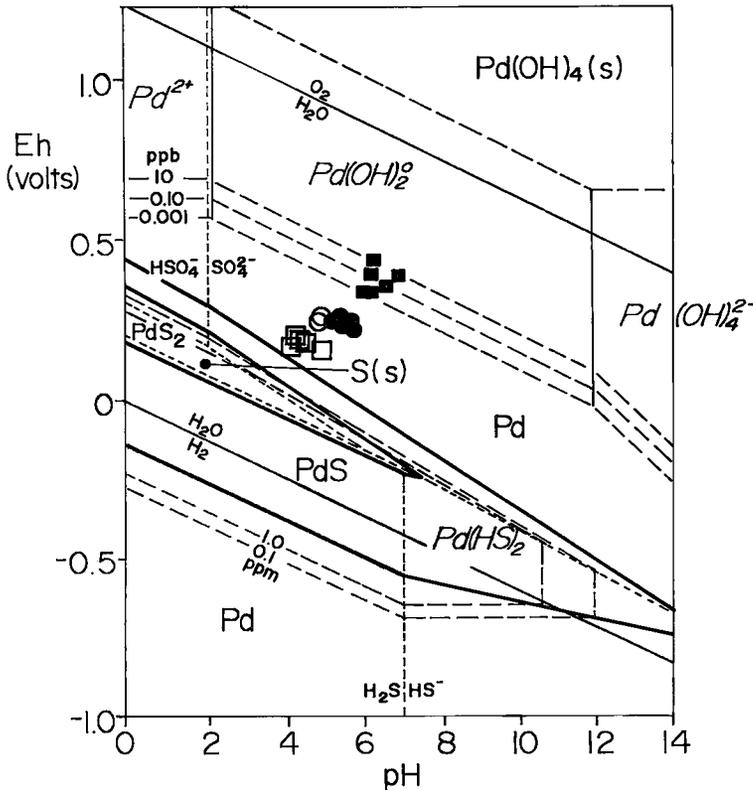


FIG. 6. Eh versus pH diagram for the system Pd-O-H-S-Cl at 25°C, $\Sigma S = 0.005$ m and $\Sigma Cl = 1$ mg/L. Heavy solid lines separate stability fields of solid Pd phases. Light solid lines separate fields of predominance of dissolved Pd species and limits of water stability. Short dashed lines separate fields of predominance of dissolved S species. Long dashed lines represent solubility contours labeled in either ppm or ppb as indicated. Solid symbols represent measured Eh-pH values of waters from Lac Long, and open symbols represent Eh-pH values of waters from Lac Sheen. Circles denote groundwaters, and squares denote lake waters.

a nearby Pd anomaly, in spite of the lack of anomalous values in the rocks sampled from the area.

The content of Pt in the filtered samples of lake water from both field areas is generally below the detection limit of approximately 25 ng/L. Platinum contents are higher in the groundwaters than in the lake waters, ranging up to 0.5 µg/L in unfiltered groundwaters. Furthermore, both the Pt and Pd contents of the groundwaters appear to increase with proximity to the showing in each case. Much of the Pt in the groundwater from both field areas is present mainly in the particulate fraction, in accord with the findings of Pogrebnyak *et al.* (1984). The analytical results, however, clearly indicate that at least Pd is significantly soluble in natural waters.

The Ni contents of unfiltered waters are also usually extremely low, less than 2 µg/L in most samples. However, there is a significant but erratic increase in Ni in the unfiltered groundwaters from Lac Long. Thus, Ni concentrations are commonly of the same order of magnitude as Pd. The Cu content of the unfiltered waters ranges from <2 µg/L up to 115 µg/L and appears to have a weakly positive correlation with both Pd content and proximity to the showings. Although a significant amount of the Cu contents of the waters may be present in dissolved form, content of this metal in unfiltered samples is often higher than the dissolved content, sug-

gesting an important contribution from particulate matter as well.

The measured temperatures of the waters ranged from 2 to 8°C. The measured pH of the waters in both lakes was between 5 and 7, whereas the groundwaters at Lac Long were more acidic (4 < pH < 5). The Eh values of the lake waters and groundwaters at Lac Sheen were more or less the same at 0.00 V *versus* SCE (saturated calomel electrode), but at Lac Long the groundwaters were slightly more reducing (Eh -0.05 V) than the lake waters (Eh 0.18 to 0.09 V). The chloride contents of all waters measured were less than or equal to 12 mg/L.

The above information on the character of the natural waters sampled may be used to make inferences on the speciation of the metals in these solutions. The most likely dissolved inorganic species of Au, Pt and Pd present in the waters studied here are the neutral hydroxide complexes (Vlassopoulos & Wood 1990, Wood *et al.* 1989). The dominant chloride complexes of Pd at low temperatures at the measured chloride concentrations (<1 to 12 mg/L) are the PdCl⁺ and PdCl₂⁰ species (Mountain & Wood 1988). The calculated solubility of Pd as these chloride complexes does not exceed 3 × 10⁻¹⁴ µg/L in the Lac Sheen waters and 3 × 10⁻⁹ µg/L in the Lac Long waters, even at the highest chlorinity measured (12 mg/L). The solubility of Pd as chloride complexes in the groundwaters is less, owing to the generally lower Eh. Thus, chloride complexes cannot be responsible for the observed concentration of dissolved Pd. Although not measured directly in this study, dissolved sulfide is expected to be very low (the Eh-pH conditions of all waters are well into the *sulfate* field). Therefore, bisulfide complexes of Au, Pt and Pd are also probably not significant in these waters.

Figure 6 is an Eh-pH diagram constructed at 25°C for the system Pd-S-Cl-O-H with a total Cl⁻ concentration of 10^{-4.8} m (1 mg/L) and a total S concentration of 10^{-2.3} m. The Lac Long waters appear to be close to saturation with respect to Pd metal as hydroxide complexes, whereas the Lac Long groundwaters and both the lake waters and groundwaters of Lac Sheen are apparently supersaturated by several orders of magnitude. This is an indication that either the thermodynamic data presently available for the hydroxide species are incorrect or that organic complexes of Pd contribute to the solubility and are responsible for the apparent supersaturation. Some support for the latter hypothesis is provided by the fact that the groundwaters were often tea-colored after filtration, suggesting the presence of natural dissolved organic acids.

Soils

Analytical results of soil samples from Lac Sheen

TABLE 5. PLATINUM, PALLADIUM, GOLD, COPPER AND NICKEL CONTENTS OF SOILS FROM THE LAC SHEEN OCCURRENCE

Sample	LOI	Pt	Pd	Au	Cu	Ni
GT88-	%	ppb	ppb	ppb	ppm	ppm
A0 Horizon (humus)						
041	64.3	<127	<13	<3	----	76
048	20.6	<48	<5	4	11	29
049	23.6	36	<2	<1	32	29
051a	46.3	<66	<7	<1	----	42
054	63.2	66	<2	6	150	75
055	76.5	1600	<3	150	124	109
056	42.7	19	5	2	49	35
135	16.9	116	<6	<1	21	35
136	8.8	---	<2	3	21	22
B Horizon						
038	7.6	<10	<2	<1	178	31
039	12.5	560	33	31	770	93
046	8.4	<10	<2	<1	20	27
051b	5.8	35	<2	2	27	22
137b	11.0	<10	<2	<1	25	34
139	16.0	<57	<6	<1	14	32
140b	16.1	96	<5	<1	19	33
142	7.9	17	<2	<1	49	32
C Horizon						
045	10.5	<31	<3	<1	---	25
137c	2.1	23	<2	2	33	26
140c	1.8	<30	<3	2	52	34
141c	3.6	<15	3	<1	66	24

Note: metal concentrations calculated on volatile-free weight basis. LOI: weight loss on ignition; ---: not determined. Suffixes a, b and c refer to soil horizon in locations where more than one horizon was analyzed.

are presented in Table 5. Although the number of samples collected and analyzed is limited, some preliminary conclusions can be made on the basis of these data. Contents of Pt range from < 10 to as high as 1600 ppb (typically < 50 ppb), whereas Pd contents vary from < 2 to 33 ppb and are typically < 5 ppb. Where analyses are available for both soils and the immediately underlying rocks (*i.e.*, in the trenches), Pt and Pd contents in the two media are directly related. For example, B layer soil samples 039, 140 and 142 are the only ones with Pt and Pd contents significantly higher than the detection limit. These all overlie amphibolite; that with the highest Pt and Pd content, 039, overlies the highly anomalous amphibolite in the most heavily mineralized trench. On the other hand, all other B-horizon soil samples were taken from profiles overlying pegmatite or gneiss, and these have little or no detectable Pt or Pd. These relationships suggest that the soils are at least partially residual in nature. Limited C-horizon analyses show no additional anomalies, but some humus layer samples from the southwestern shore of the lake exhibit extremely high anomalies in Pt and Au. The source of these anomalies is not entirely clear, but they may be related to some anomalous boulders found in this area.

The Pt/Pd ratios in the anomalous B-horizon samples overlying amphibolite are considerably higher than in the amphibolites themselves. The direct comparison of Pt and Pd analyses for the soil and rock samples is complicated by the different respective analytical methods used. Indeed, Hall *et al.* (1989) have demonstrated that a bias does exist among the analytical results for Au obtained by neutron activation, fire assay and aqua regia digestion, respectively, for geological samples. This bias was shown to be a result of the incomplete release of Au from rock and soil samples during acid attack and fire-assay procedures (Hall *et al.* 1989). Such a bias also undoubtedly exists among analytical techniques for Pt and Pd. Nevertheless, although the absolute concentrations of Pt and Pd may not be directly comparable between the soils and the rock samples, the Pt/Pd ratio will be less affected by the differences in analytical techniques. Furthermore, Hall *et al.* (1989) suggested that the differences in analytical results for Au among the various techniques are on the order of 20–40%. If the presumed bias for Pt and Pd is similar in magnitude, such differences could not be responsible for an increase in Pt/Pd from 1 in the rock samples to 10–1000 in some soil samples. Furthermore, the relationship between the Pt/Pd ratios in rocks and soils is complementary to the much lower Pt/Pd ratios found in groundwaters. These findings suggest preferential leaching of Pd relative to Pt during decomposition of the bedrock. Although clearly more data are required to substantiate the above hypothesis, such preferential mobil-

TABLE 6. PLATINUM, PALLADIUM, GOLD, COPPER AND NICKEL CONTENTS OF -160 MESH FRACTION OF LAKE SEDIMENTS FROM LAC SHEEN

Sample # GT88-	LOI (%)	Pt (ppb)	Pd (ppb)	Au (ppb)	Cu (ppm)	Ni (ppm)	depth (meters)
001	34.7	36	4	113	---	---	2.5
002	30.6	<15	<2	1	434	60	6.5
003a	25.7	<63	<6	<1	---	57	6.5
b	12.2	<8	2	213	---	---	"
006	5.9	<6	<2	<6	---	---	5.0
007	35.1	7	<2	2	305	62	11.5
008	39.9	54	8	29	401	54	12.0
009	21.5	<10	<2	61	100	30	6.5
010	26.6	<10	<2	16	53	40	14.0
017	3.4	15	<2	4	15	22	3.0
019	35.1	25	<2	3	619	60	7.0
020	40.1	<14	<2	2	80	66	11.5
021a	36.5	220	<2	5	95	46	7.0
b	41.6	<14	<3	<14	---	---	"
022a	42.4	<39	3	20	205	50	9.0
b	40.4	<31	<3	9	201	66	"
023a	16.5	<39	<4	1	25	31	2.0
b	16.1	<8	<2	2	25	29	"
024a	28.4	<11	2	67	---	---	7.0
b	31.6	<12	<3	<12	---	---	"
025a	35.5	<12	2	<1	79	51	7.0
b	34.6	<65	<7	2	55	56	"
026	17.3	<11	<2	128	32	53	4.5
027a	32.2	<15	<2	3	78	66	6.5
b	27.4	<13	<2	8	190	51	"
028a	6.9	<5	<2	1	36	20	2.0
b	3.0	<4	<2	10	35	27	"
029a	3.7	<15	<3	<15	---	---	7.0
b	38.3	<16	3	138	---	---	"
030	34.2	<14	<3	<1	---	---	8.0
031	38.5	<10	<2	<2	209	63	13.0
032a	4.2	13	<2	1	18	16	2.0
b	4.1	<4	<2	<4	---	---	"
034a	39.5	<8	<2	1	88	53	16.0
b	37.1	<10	<2	<2	247	68	"

Note: Metal concentrations calculated on a volatile-free weight basis. LOI = weight loss on ignition; --- = not determined. Letters a & b denote replicate samples at the same location and water depth.

ity of Pd compared to Pt has also been noted in weathered zones of the Stillwater Complex, Montana (Fuchs & Rose 1974, Riese & Arp 1986).

Lake sediments

Only the lake sediments from Lac Sheen have been analyzed to date, and the results are given in Table 6. None of the lake-sediment samples analyzed contain Pd in excess of 8 ppb. Most samples contain less than 3 ppb Pd. The Pt contents of most lake-sediment samples also are generally at or below the detection limit. This limit was as high as 15–20 ppb (except for very low-weight samples, where it was even higher) owing to the lower sensitivity of atomic absorption for Pt compared to Pd or Au. However, a few high values of approximately 10–30 ppb and one highly anomalous value of 220 ppb were encountered. Alternative methods for the analysis of Au, Pt and Pd are presently being investigated in order to establish reasonable background concentrations for these metals. Even 10 ppb of Pt or Pd could be considered anomalous when background concentrations of these metals in most common rocks are probably < 10 ppb (Goldschmidt 1954, Crockett 1978). Nevertheless, there is some indication that lake-sediment anomalies do occur for Pt, based on the

Lac Sheen data. The question is not yet settled for Pd.

The results obtained for Au are typically higher than for either Pt or Pd. The detection limit for Au determined by the method described above is <1 ppb, and many samples had significantly higher measured Au contents. Several samples were measured that contain >100 ppb Au. This compares favorably to a range of 0.5 to 190 ppb Au measured in lake sediments near gold occurrences in Saskatchewan by Coker *et al.* (1982) and up to 30 ppb Au measured by Schmitt (1989) in sediments from a lake in Manitoba located near a Au-bearing shear zone in a greenstone belt. However, the marked predominance of Au over Pt and Pd in the Lac Sheen sediments is somewhat surprising, given the relative

contents of these metals in the clearly autochthonous rocks (in the trenches $Pt \approx Pd > Au$). It is possible that some of the Au in the Lac Sheen sediments does not come from the same source as the Pt and Pd. In this regard, it is interesting to recall the proximity of Lac Sheen to several Au-Ag showings (see geology section above). Furthermore, it should be noted that the contents of Au relative to Pt and Pd in the boulder float at Lac Sheen are much higher than those in the trenches, which suggests that these boulders may represent a source different from the bedrock in the trenches. These facts support the idea of an additional source for much of the gold in the lake sediments.

Note that whereas the precious metal contents of the lake sediments apparently follow the order Au

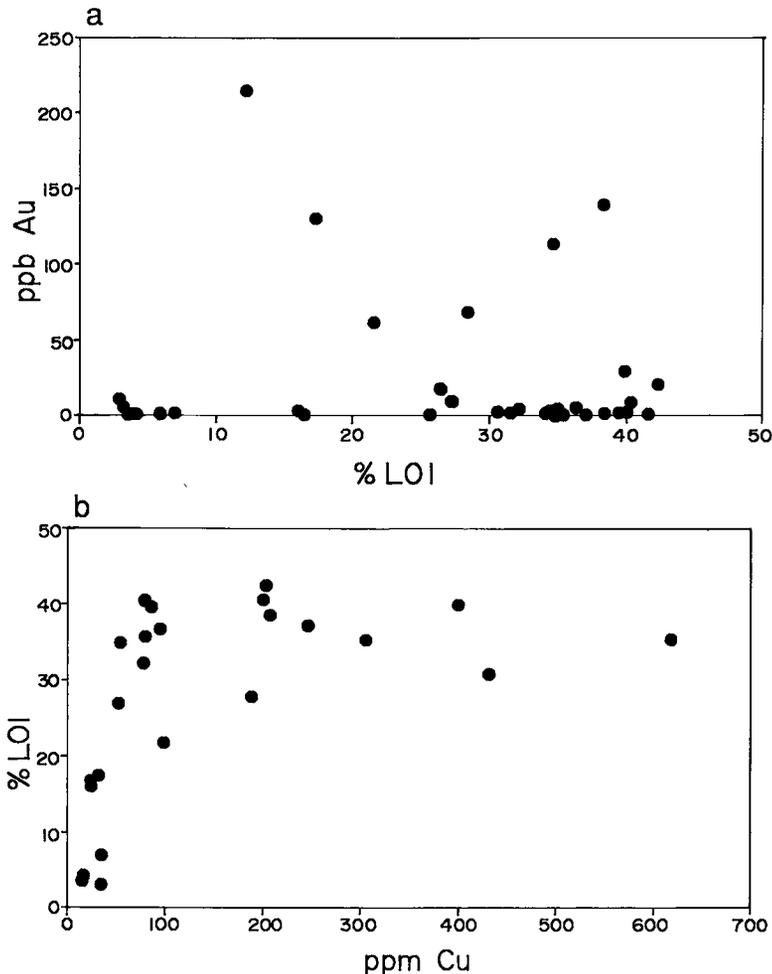


FIG. 7. a) Plot of Au content (ppb) versus LOI (wt.%) for Lac Sheen sediments; b) plot of LOI (wt.%) versus Cu content (ppm) for Lac Sheen sediments.

> Pt > Pd, the lake waters follow the order Pd >> Pt, Au. The reason for this behavior is not entirely clear, but it may be that Pd remains in solution and is not fixed in the sediments, whereas Au and (to a lesser extent) Pt are fixed. This is in agreement with the theoretically predicted higher solubility of Pd relative to Pt and Au under the given conditions. It is also possible that a large proportion of the transport of Au and Pt into the lake sediments is mechanical rather than chemical in nature.

Figure 7a reveals that there is little or no correlation between Au content and LOI in the lake sediments. This finding suggests that at Lac Sheen, organic matter and Au do not appear to be associated. This is in contrast to the finding of Coker *et al.* (1982) that Au in lake sediments in Saskatchewan is associated with organic matter. Alternatively, it may be that LOI is not a reliable indicator of organic matter content at Lac Sheen owing to strong contributions from bound water, *etc.* A mild correlation appears to exist between Pt, Pd and LOI (not shown), but the issue is clouded by the large number of analyses for Pt and Pd below the detection limit. As is evident from Figure 7b, and in contrast to Au, Pd and Pt, high Cu contents are restricted to sediments with higher LOI, but a high LOI does not necessarily imply a high Cu content.

In cases where replicate lake-sediment samples were analyzed, the replicates generally have closely corresponding LOI values, and the Cu and Ni contents often also correspond closely. However, the measured Au contents usually vary by a factor of 2 to 200 between replicates. This finding illustrates that Au is inhomogeneously distributed in the sediments. Its erratic behavior probably is a consequence of the well-known "nugget effect". Although the limited number of analytical results above the detection limit precludes a definitive statement at this time, it appears that similar behavior is also exhibited by Pt.

CONCLUSIONS

Some preliminary conclusions follow:

- 1) Pd is present in true solution in relatively high concentration (100 to 400 ng/L) in lake and groundwaters from both showings, perhaps as hydroxide or organic complexes (or both), although contributions from the particulate fraction may be locally important.
- 2) Dissolved Au and Pt contents of lake waters and groundwaters are generally below the detection limits of the present analytical technique (25 ng/L). Occasional high values can be attributed to particulate forms of these metals.
- 3) At Lac Sheen, Pd appears to be preferentially leached relative to Au and Pt from soils overlying anomalous bedrock, ultimately leading to

anomalously high Au and Pt concentrations in the sediments accumulating in the adjacent lake, probably by means of mechanical transport. At least some of the Au in the lake sediments may have originated from beyond the immediate environs of the lake.

4) These observations indicate markedly different behaviors of Pd *versus* Pt and Au in the supergene environment. Whereas Pt and Au seem to be dispersed mainly in particulate form by mechanical processes and are thus accumulated in the lake sediments, Pd is dispersed mainly in true solution, and is probably ultimately drained away from the lake.

5) Analyses of natural waters for dissolved Pd may hold some promise for delineating target areas, in addition to lake sediment and soil sampling, during reconnaissance exploration for PGE deposits. If reliable background values for Pd in natural waters can be established, lake-water analyses may be more useful for reconnaissance exploration than lake sediments, owing to: 1) the greater ease of collection of water samples, 2) the lesser degree of sample preparation necessary, and 3) the greater probability of sample media being homogeneous in composition. A disadvantage of using water samples in routine exploration is the requirement for analytical techniques with very low detection limits.

6) In the case of lake sediments, Au and perhaps Pt determinations seem to be more promising as exploration tools than Pd determinations, because Pd is evidently not fixed in lake sediments to the same extent that Au and Pt are.

Clearly, further work is required in order to substantiate these conclusions and to develop the techniques for application in mineral exploration. Seasonal variations in the metal contents of lake water and groundwater need to be investigated. More extensive sampling and analysis of soil and lake sediments are required. The general applicability of the results found here needs to be tested by carrying out similar studies of dispersion about other PGE occurrences in different geological and climatic environments. The nature of PGE and Au in the rocks, lake sediments and soils should be further investigated using techniques of selective extraction as well as SEM, microprobe and other microanalytical studies. Finally, experimental measurements of the ability of various natural organic ligands to dissolve and transport Pt, Pd and Au are required. Work has already begun on some of these problems, and the results should be forthcoming shortly.

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