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THE MOBILITY OF THE PLATINUM-GROUP ELEMENTS IN THE SOILS OF THE FREETOWN PENINSULA, SIERRA LEONE

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ABSTRACT

Suggestions that platinum-group minerals (PGM) may develop in supergene environments have created controversy. The opposing view is that they act solely as resistate phases during weathering. There is, however, significant evidence that weathering processes can dissolve the platinum-group elements (PGE) and permit their transport and deposition of PGM in eluvial deposits, in which the PGM are significantly different in grain size and morphology from those derived from an igneous source. We present here three complementary lines of evidence relating to the formation of eluvial and alluvial PGM deposits using the Freetown deposits (Sierra Leone) as the principal example. There is unambiguous partitioning of the more soluble palladium and gold into ground and surface waters, and preferential deposition of platinum in soils and eluvial and alluvial deposits. There is no preference of the PGE in the soils dominantly for the coarse fraction, as there is in the eluvial deposits. Simple mechanical concentration from the soil cannot, therefore, account for eluvial or alluvial deposits downslope. Polymeric acids (humic acids) have been extracted from the soils and are shown to contain compounds that have a high affinity for the PGE. These organic compounds could well provide a potential means of PGE transport in solution. These observations provide eloquent support for the importance of controls by organic species during supergene weathering for the movement of gold and the PGE.

Keywords: aliphatic hydrocarbons, aromatic hydrocarbons, carboxylic acids, laterite, platinum, palladium, soils, weathering, Freetown, Sierra Leone.

SOMMAIRE

Toute proposition que les minéraux du groupe du platine peuvent se former dans un milieu supergène provoque la controverse. L'opinion contraire veut que ces minéraux soient demeurés passifs et donc inertes dans un milieu de lessivage. Pourtant, il existe un corpus important d'évidence que les processus de lessivage peuvent mener à la dissolution des éléments du groupe du platine (EGP), pour pemettre leur transfert, et la déposition de minéraux nécéssairement différents dans leur granulométrie et leur morphologie de ceux dont la filiation est ignée, et qui seraient concentrés par la suite en gisements éluviaux. Nous présentons trois types d'évidence pour appuyer notre hypothèse, en nous servant des gisements de Freetown, Sierra Leone, comme exemples principaux. D'abord, il y a répartition irréfutable de Pd et Au, plus solubles, dans les eaux de surface et souterraines, et déposition préférentielle du Pt dans les sols et les gisements éluviaux et alluviaux. Nous ne croyons pas qu'il existe dans les sols une préférence des éléments du groupe du platine pour la fraction à granulométrie grossière, contrairement au cas des gisements éluvionnaires. Une simple concentration mécanique des particules dérivées d'un sol ne pourrait donc expliquer la présence en aval de gisements éluvionnaires et alluvionnaires. Les acides polymériques (humiques) extraits des sols contiennent des composés reconnus pour leur affinité envers les EGP. Ces composés organiques pourraient bien assurer le transfert des EGP en solution. Ces observations appuient donc l'importance d'acides organiques dans un milieu de lessivage supergène pour expliquer le mouvement de Au et des EGP.

(Traduit par la Rédaction)

Mots-clés: hydrocarbures aliphatiques, hydrocarbures aromatiques, acides carboxyliques, latérite, platine, palladium, sols, lessivage, Freetown, Sierra Leone.

INTRODUCTION

Cousins & Kinloch (1976) noted that platinum placer minerals are commonly two orders of magnitude larger than those found in the source rocks. They also suggested that "biochemical leaching ... by complex organic acids ... are a part of the weathering process" and "humic acid leaching of platinoids appears feasible." Bowles (1986) provided mineralogical evidence that supergene solution, transport and deposition occur and suggested that weathering and "leaching processes, particularly those involving leaching by carboxylic acids and soil organic matter", may be relevant to nugget formation. Bowles (1986) also pointed out that the acid, high-Eh conditions of lateritic soils are within the bounds of significant solution of platinum and palladium as chloride species. In the same paper, Bowles noted the geochemical similarity of platinum to gold (for which element such processes are well accepted) and the possible involvement of organic complexing agents. In a later paper, (Bowles 1988), the hydrogeological mechanisms of solution, transport and deposition were considered.

Wood (1990) has shown that organic acids may have an important role in controlling platinum in natural, near-surface solutions. He considered that some form of complex or colloidal suspension appears a likely means of transport. That work and later studies (Wood *et al.* 1994) focused on the interaction of fulvic acid and synthetic analogues with platinum and palladium in solution as K_2PtCl_4 or K_2PdCl_4. In the later work, the authors showed that palladium, at least, forms dissolved complexes with simple carboxylic acids; this may also, by analogy, apply to platinum. Bowles *et al.* (1994, 1995) have conducted experiments in which they gently agitated platinum and palladium foils, synthetic PtS and natural platinum-group minerals (PGM) in natural humic and fulvic acids. These tests show an appreciable solubility (100–270 ppb) of Pd and Pt within 393 days under conditions designed to mimic weathering processes.

The present paper provides new data concerning the soil overlying a PGE-bearing horizon within the Freetown Layered Gabbro, Sierra Leone. This information includes (1) assay data for platinum, palladium and gold, which illustrate a stage in the differential dispersion of these elements intermediate between the source rocks and eluvial deposits, and (2) analyses of the actual organic material present in those soils, that may have had a role in the weathering and transport of the platinum-group elements (PGE).

THE WEATHERING OF PGE-BEARING DEPOSITS

Two explanations for the formation of eluvial deposits of PGM are current. The classical explanation is that the PGM are resistate phases derived as a heavy concentrate following breakdown of the enclosing silicates (*e.g.*, Hattori & Cabri 1992). This explanation is unsatisfactory in the Freetown Layered Gabbro and other areas, for several reasons that have been discussed previously (Bowles 1986, 1988). In brief, the size of the minerals (0.5 mm to several mm) is about two orders of magnitude larger than that found in the surrounding PGM-bearing, layered, silicate rocks. The crystals of PGM (Bowles 1981) display perfect faces with undamaged interfacial angles and corners, even on the scale revealed by the electron microscope. These minerals have clearly not suffered from abrasive transport. The mineralogical characteristics of the eluvial deposits have been considered more fully by Bowles (1995). In addition, there is no PGE-rich horizon underlying the mined deposit, the nearest known PGE anomaly being 0.5 km away. The intervening soils are very efficiently bound with long-established tree roots; thus soil creep is minimal. The argument that the PGM are weathered as resistate phases offers no reason for variations in Pt/Pd values between source rocks, soils and eluvial deposits. In the eluvial and alluvial suite, the bulk of the palladium is contained within the platinum nuggets (Bowles 1981), so that separation of small, platy alluvial Os–Ir–Ru phases from the larger, more equant nuggets, as documented by Mertie (1976), has little effect on the Pt/Pd ratio.

The alternative explanation (Bowles 1986, 1988) allows solution of the PGE during weathering of the enclosing silicates in the acid, high-Eh regime of lateritic soils, where the content of potential complexing species is high. The PGE source may be a mineralized horizon or disseminated mineralization, and transport is proposed in solution until the conditions change, at which point deposition occurs. An appropriate change in conditions can be found where soil waters interface with stream waters, with a significant change in Eh, pH and dilution of potential soil-derived complexing species. Deposition would then occur close to a stream bank. This is, in fact, where deposits commonly are found. Additional mineralogical support for this explanation is found in the presence of resorbed crystal surfaces and overplating due to renewed deposition (Bowles 1986). It is most significant that only differences in solubility can account for variations in the Pt/Pd and Pt/Au values among source rock, soils and eluvial deposits, whereas preservation of the PGM as resistate phases cannot provide a mechanism to explain systematic variations in Pt/Pd or Pt/Au.

SOIL SAMPLES FROM THE FREETOWN LAYERED COMPLEX

Soil samples were collected from soil horizon A overlying banded pyroxenites, troctolites and mottled anorthosites within the Freetown Layered Gabbro, Sierra Leone. This area is designated as a Forest

Reserve and consists of primary forest that has been protected from cultivation. There is hunting and gathering activity, and some wood is removed for fuel, especially from the fringes of the forest. Human interference with the forest soil has been minimal, and it is unlikely that there has been any addition of anthropogenic organic compounds, such as pesticides, near the sample site.

Tree cover is virtually complete in this area, and the soil is permanently shaded. Whereas there are some substantial trees, most of the area is covered with a woody undergrowth of saplings. Rainfall is heavy (about 1300 mm per month) in July and August, but the period from December to March is virtually arid. The result is that there is no succulent undergrowth; walking between saplings is generally possible without the need to cut a path. Tree species recorded in the area include *Kaya anthotheca*, *Guared cedrata*, *Mimusops heckelii*, *Entandrophragma utile* and *macrophyllum*, *Oldfieldia africana* and *Cordia platythyrsa* (Clarke 1969). Trees surrounding the sample sites have waxy, lanceolate leaves. Grasses are absent, and the soil cover is principally humic material derived from the trees.

Lateritic soils, such as those found in Sierra Leone, have a very thin layer of organic material and are very porous. Organic material in these soils is quickly washed away through the other soil horizons. The ability of such soils to support a luxuriant growth of vegetation is an anomaly that requires explanation, but the high temperatures and humidity, the rapid breakdown of organic material and the aeration of the soil by bacteria, insects, earthworms and other soil-dwelling organisms all contribute to a dynamic system (MacFarlane 1983).

The soil samples were obtained from the shallow soil cover above a platinum- and palladium-bearing horizon in the rocks of the Freetown Layered Gabbro. This horizon is parallel to the igneous layering of the intrusion; present indications suggest that it is continuous for at least several kilometers. At the sample point, this horizon is near the crest of a small hill, and rock samples have been obtained from adjacent outcrops. The hill is above the source of a small stream where working of eluvial and alluvial deposits have produced platinum concentrates in the past. The mining areas were designated by steel posts and plates set in concrete. Many of these remain, and can be found today and correlated with maps showing mining licence areas. The sample site is directly upslope of one such clearly defined mining area. The vertical separation is about 70 m, and the horizontal separation about 550 m. Although there has been human interference with the deposits near the stream, there is no indication of any interference with the soil of the hill slope. The soil and rock samples from the hill crest are, therefore, considered to be sufficiently close to the eluvial and alluvial deposits at the foot of the hill to provide the logical and undisturbed natural source of the PGE in the stream.

Two soil samples were obtained. Sample 51 is a red-brown, clay-rich laterosol from a depth of 5 to 10 cm. This sample contains abundant organic matter and saprolitic gabbro clasts. Sample 52 is a dark brown, organic-matter-rich soil obtained from a similar depth and overlying laterite or ferricrete. The ferricrete near sample 52 also was sampled (sample 53).

ANALYSES OF ORGANIC MATTER IN THE SOIL

Analytical method

Analyses of the organic matter in the soil were obtained for the complex polymers, the humic acids. Although the organic polymeric material in the soil can be subdivided into three fractions analytically (fulvic acids, humic acids and humins), the humic acids were targeted on the basis of analytical ease. The inherent assumption is that although the molecular weights and some structural details of the three fractions may differ, they will have been derived from the same biochemical debris. Consequently, a detailed analysis of the organic compounds in the humic acid structure is assumed to be applicable to the fulvic acids and humins.

The method of humic acid extraction was based on that of Ertel & Hedges (1983), which provides an ash-free yield. The humic acids were extracted from 200 g of dried soil after stirring for 48 hours at room temperature in 1 liter of a solution made to 0.1 M $Na_4P_2O_7 \cdot 10H_2O$ (Merck) and 0.1 N NaOH (Merck). The solutions were then adjusted to 0.1 M KCl (Merck) in order to flocculate the clays. The solutions were centrifuged at 4000 rpm for 1 hour, and the solutions decanted from the clays and other particulates. The solutions were slowly acidified to a pH of 1 with HCl (Analar, Merck), which precipitated the humic acids overnight. The solutions were then centrifuged at 4000 rpm for 1 hour, and the fulvic acids decanted to leave the humic acid precipitate. The humic acids were redissolved in a 0.1 N NaOH solution in an ultrasonic bath (1 hour) and then centrifuged as above for 1 hour. The humic acids in solution were decanted and reprecipitated as above. The precipitate was isolated and then freeze-dried. The procedure was performed on two soil samples, which gave final dried humic acid yields of 0.36 g (sample 51) and 0.44 g (sample 52).

Approximately 0.5 mg of the dried humic acid was analyzed by on-line pyrolysis gas chromatography – mass spectrometry. The sample was pyrolyzed in a helium atmosphere by being dropped into a glass tube furnace at 550°C (SGE Pyroinjector). The pyrolysate was cold-trapped (liquid nitrogen) at the head of an 8-m BP1 column (Hewlett Packard) in the gas chromatograph (HP 5890). The column was heated at 4°C min^{-1} to 300°C. The eluate was introduced into a VG Masslab Trio–1 quadrupole mass spectrometer, set to scan 35–450 a.m.u., with a scan time of 0.80 s and an interscan time of 0.08 s. The mass spectrometer source was set at 230°C, and the gas chromatograph – mass spectrometer transfer line at 300°C. Structural assignment was based on mass spectral interpretation alone, without co-injections of known standards.

Results

The pyrolysates from the two soils were found to be similar, with sample 52 being relatively enriched in long-chain hydrocarbons and acids.

Low-molecular-weight compounds predominate and fall into two groups of compounds, based on origin. The molecular structures of the compounds discussed in the text are shown in Figure 1. Where a

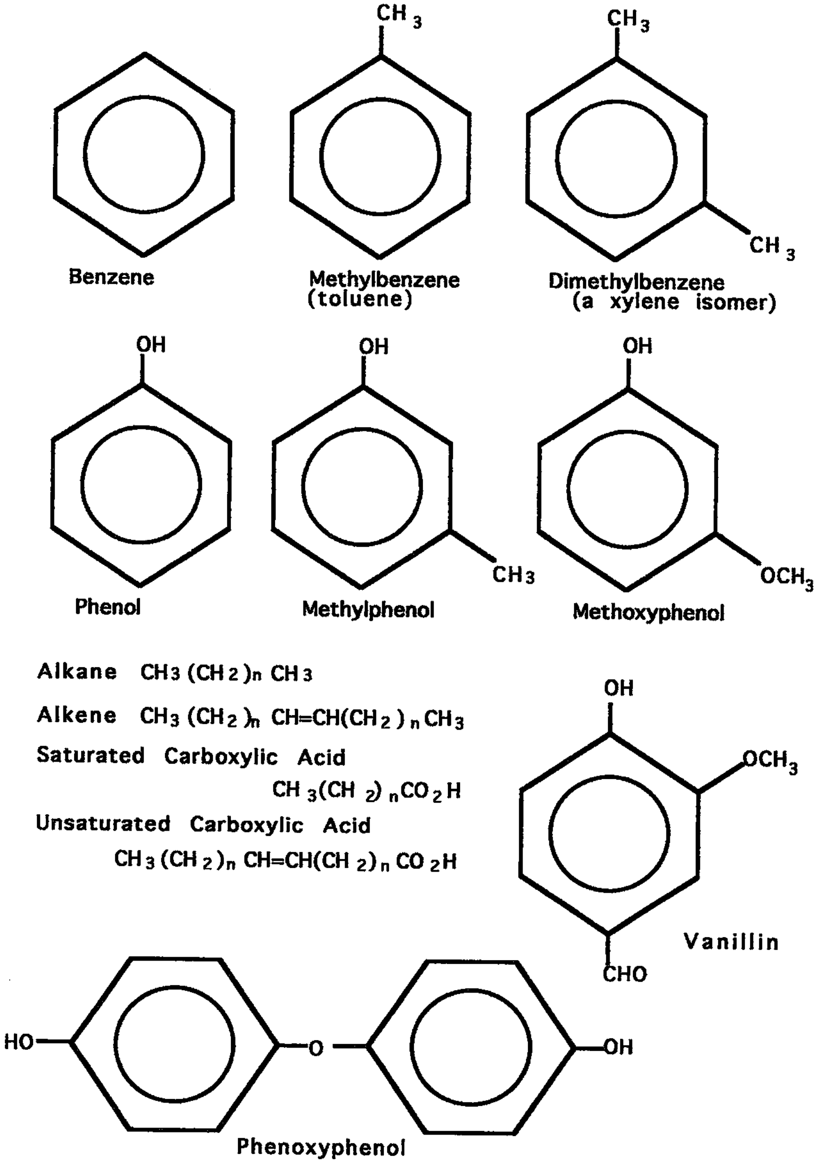

FIG. 1. Formulae and structures of compounds mentioned in the text.

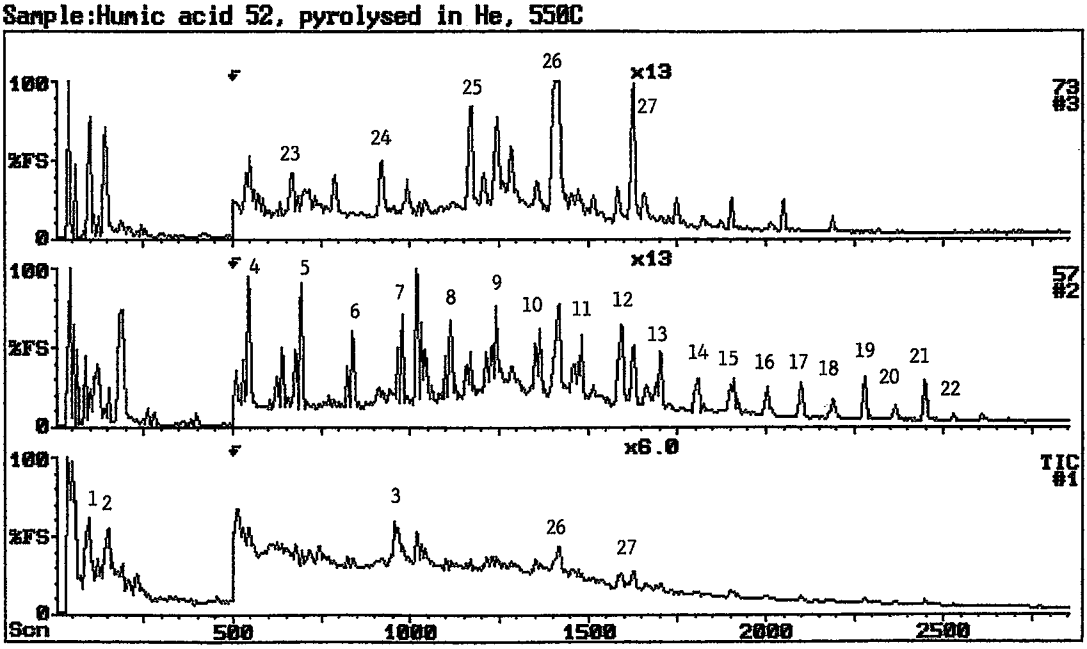

FIG. 2. Total ion-current chromatogram (lower trace) and selected ion traces (upper traces) of a humic acid pyrolysate (sample 52). The lower trace shows the total ion-current chromatogram with only a few peaks evident as a result of overlap from many compounds. The major peaks are: 1 toluene, 2 xylenes, 3 phenoxyphenol, 26 hexadecanoic acid (saturated carboxylic acid with $n = 15$, Fig. 1), 27 octadecanoic acid (saturated carboxylic acid with $n = 17$). The middle trace is of the intensity of the ion m/z 57 as a function of time (scan number), which enhances normal alkanes and alkenes. A homologous series of alkanes is shown, starting from peak 4 ($n = 12$) to peak 22 ($n = 30$). The small shoulder to the left of some of the numbered peaks is the alkene ($12 < n < 30$) with the same number of carbon atoms as the alkane. The upper trace shows the intensity of the ion m/z 73, indicative of carboxylic acids. In contrast to the normal alkanes, which show a peak for every number of carbon atoms, the carboxylic acids occur in increments of two carbon atoms. The range is from decanoic acid (peak 23, $n = 8$) to octadecanoic acid (peak 27, $n = 16$).

group comprises a carbon chain, this is abbreviated to $(CH_2)n$, where n is an integer. The low-molecular-weight compounds are those with low values of n. The first group comprises short-chain hydrocarbons (Fig. 1, alkane with n equal from 2 to 6, and alkene with n equal to 2) such as methane (CH_4), ethane (C_2H_6) and ethene (C_2H_4), together with benzene and derivatives. The benzene derivatives include toluene and xylenes (Fig. 1) and other hydrocarbon-substituted benzenes. These compounds were derived largely by thermal rupture of the humic acid, probably with a contribution from the breakdown of other products of pyrolysis. Also present in notable quantities is phenol (Fig. 1), together with isomers of methyl and dimethyl (or ethyl) phenols. One probable source for these compounds is phenolics such as vanillin (Fig. 1) in the woody tissue, and lignin (Ertel *et al.* 1984). Also detected was a methoxyphenol (Fig. 1), indicative of lignin (Fogel *et al.* 1989). Lignin is also suggested to be the source of phenoxyphenol (Fig. 1). The presence of toluene, xylene and phenoxyphenol in soil sample 52 is shown by peaks 1, 2 and 3, respectively, in Figure 2.

Higher-molecular-weight compounds are alkanes, alkenes and saturated and unsaturated carboxylic acids with $n > 10$ (Fig. 1). Compounds detected in the Sierra Leone soils fall into three groups: long-chain aliphatic hydrocarbons (Fig. 1, alkanes and alkenes), long-chain carboxylic acids (Fig. 1), and polynuclear aromatic hydrocarbons. The long-chain aliphatic hydrocarbons are present in the carbon range C_{9-31}, with a slight increase in the concentration of normal (unbranched) alkanes in the range C_{27-31}. Examples of the higher-molecular-weight compounds are shown in the three traces in Figure 2. The source of these compounds is presumed to be, in part, bacterial cell membranes, derived from the leaf litter, accounting for the normal alkanes of carbon number $C_{<20}$ (Han & Calvin 1969). The normal alkanes of carbon number $C_{>20}$ are suggested to be residues from the high-molecular-weight waxes in the leaf cuticles (Eglinton & Hamilton 1967). Associated with the normal alkanes is a suite of monounsaturated alkenes, in the range C_{9-16}. There are probably multiple sources for these compounds from naturally occurring unsaturated carboxylic acids and as artifacts of the pyrolysis technique.

Normal saturated carboxylic acids (Fig. 1) were detected in the range C_{8-18}, with the C_{16} and C_{18} acids in markedly higher concentrations. The sources for these compounds are again biochemical, either cell membranes or leaf waxes. The predominance of the C_{16} and C_{18} acids mirrors their predominance in biochemical systems. Undetected in the humic acid pyrolysates were unsaturated carboxylic acids (Fig. 1), which in biochemical systems are present in significant levels. One reason for their absence in the humic acid pyrolysates is the fact that they have been shown to be highly labile during the earliest stages of organic diagenesis, being rapidly altered microbially (Rhead *et al.* 1971).

The last group of compounds detected are polynuclear aromatic hydrocarbons, based on compounds derived from fusion of benzene rings, such as naphthalene (two benzene rings). Although they could be artifacts of pyrolysis, their concentrations were greater than usually encountered. One source of these compounds is from combustion; it is presumed that they represent residues from forest fires (Youngblood & Blumer 1975).

In summary, pyrolysis of the humic acid in two soil samples indicates derivation from the local forest litter. The predominant inputs are woody tissues (lignin) and leaf litter (leaf cuticular waxes). It is also extremely likely that a fraction of the organic matter was derived from micro-organisms in the soils. Although there may be some differences between the composition of the humic acids and the humins and fulvic acids, the same compounds are presumed to be present in all three fractions.

PLATINUM, PALLADIUM AND GOLD ASSAYS OF THE SOIL SAMPLES

The two soil samples 51 and 52 were sieved to provide –6 mm and –177 μm (–80 mesh) fractions. Both fractions of each of the two samples and the ferricrete were assayed for platinum, palladium and gold to permit comparison with other data. The assays were performed by Genalysis of Australia using fire assay with a lead collector followed by inductively coupled plasma – mass spectrometry (ICP–MS), giving a limit of detection of 1 ppb. The assays were bracketed by assays of the reference standard SARM 7, which produced values close to the certified values. The results are shown in Table 1. Samples of the host rocks and the heavy-mineral concentrates from the drainage were assayed by Lakefield of Canada using fire assay with a lead collector followed by ICP, giving a detection limit of 20 ppb. These results are listed in Tables 2 and 3. The results are plotted in Figure 3, along with other published assays of rocks, surface waters and sediments.

TABLE 1. RESULTS OF ANALYSES OF SOILS AND FERRICRETE FROM THE FREETOWN LAYERED COMPLEX

Sample	Fraction	Pt	Pd	Au	Pt/Pd	Pt/Au
Soil 51	-6mm+177μm	12	4	2	3	6
Soil 51	-177μm	11	6	1	1.8	11
Soil 52	-6mm+177μm	52	6	1	8.7	52
Soil 52	-177μm	62	7	5	8.9	12.4
Ferricrete		45	6	1	7.5	45

Results in ppb above a limit of detection of 1 ppb

	n	mean	median	1SD	max	min
Pt/Pd	5	6.0	7.5	3.0	8.0	1.8
Pt/Au	5	25.3	12.4	19.2	52	6

TABLE 2. RESULTS OF ANALYSES OF PAN CONCENTRATES FROM THE FREETOWN LAYERED COMPLEX

	Au	Pt	Pd	Pt/Pd	Pt/Au
1	n.d.	n.d.	0.02	n.d.	n.d.
2	0.02	0.02	0.02	1	1
3	n.d.	0.04	0.02	2	>2
4	0.02	0.04	0.02	2	2
5	0.02	0.03	0.02	1.5	1.5
6	n.d.	n.d.	0.03	n.d.	n.d.
7	0.08	29.5	n.d.	>1475	369
8	n.d.	1.0	n.d.	>5	>5
9	0.02	17.5	0.08	219	875
10	n.d.	1.04	0.11	9	>52
11	n.d.	n.d.	0.02	n.d.	n.d.
12	n.d.	0.07	n.d.	>3.5	>3.5
13	n.d.	0.16	n.d.	>8	>8
14	n.d.	2.5	0.06	83	>125
15	n.d.	5.14	0.04	129	>257
16	0.02	16.3	0.03	543	815
17	n.d.	0.12	n.d.	>6	>6
18	0.02	0.08	n.d.	>4	4
19	0.03	14.9	0.18	83	497
20	0.02	7.33	1.06	2	117
21	n.d.	0.07	0.03	2	>3.5
22	n.d.	n.d.	n.d.	n.d.	n.d.
23	n.d.	0.08	0.02	4	>4
24	n.d.	1.41	n.d.	>71	>71
25	n.d.	3.56	0.27	13	>178
26	0.02	n.d.	0.02	n.d.	n.d.
27	n.d.	0.65	0.06	11	>33
28	0.02	0.02	n.d.	>1	1

Results in ppm above a detection limit of 0.02ppm

	n	mean	median	1SD	max	min
Pt/Pd	15	74	10.2	140	543	1
Pt/Au	10	268	117	333	825	1

TABLE 3. RESULTS OF ANALYSES OF ROCK SAMPLES FROM THE FREETOWN LAYERED COMPLEX

	Au	Pt	Pd	Pt/Pd	Pt/Au
1	n.d.	0.07	0.03	2.3	>3.5
2	n.d.	0.15	n.d.	>7.5	>7.5
3	n.d.	0.02	0.03	0.7	>1
4	0.08	0.11	n.d.	>5.5	1.4
5	0.02	0.02	0.02	1	1
6	0.13	0.03	0.02	1.5	0.23
7	n.d.	0.02	0.02	1	>1
8	0.09	0.04	n.d.	>2	0.44
9	0.03	0.11	0.06	1.8	3.7
10	0.06	0.03	0.02	1.5	0.5
11	0.02	0.02	0.03	0.7	1
12	0.02	0.02	n.d.	>1	1
13	0.06	0.02	n.d.	>1	0.3
14	0.05	0.03	n.d.	>1.5	0.6
15	0.03	0.05	n.d.	>2.5	1.7
16	0.02	0.03	n.d.	>1.5	1.5
17	0.02	0.02	n.d.	>1	1
18	0.03	0.03	0.02	1.5	1
19	0.02	0.03	0.02	1.5	1.5
20	0.02	0.02	0.02	1	1
21	n.d.	0.05	0.03	1.7	>2.5
22	n.d.	0.02	0.02	1	>1
23	n.d.	0.04	0.02	2	>2
24	0.02	0.25	n.d.	>12	12.5
25	n.d.	0.15	n.d.	>7.5	>7.5
26	n.d.	0.14	n.d.	>7	>7
27	0.02	0.02	n.d.	>1	1
28	n.d.	0.05	0.02	2.5	>2.5
29	n.d.	0.05	0.11	0.45	>2.5
30	n.d.	0.17	n.d.	>8.5	>8.5
31	0.05	0.03	n.d.	>1.5	0.6
32	0.04	0.03	n.d.	>1.5	0.75
33	n.d.	0.02	0.02	1	>1

Results in ppm above a detection limit of 0.02 ppm

	n	mean	median	1SD	max	min
Pt/Pd	17	1.36	1.5	0.56	2.5	0.45
Pt/Au	20	1.64	1.0	2.6	12.5	0.23

TREATMENT OF THE ASSAY DATA

The data discussed here consist of assay values for platinum, palladium and gold. These are, in many cases, close to the detection limit, and the assay values are rather scattered owing to the "nugget effect". In order to describe the partitioning and relative solubility of these elements, it is intended to use Pt/Pd and Pt/Au ratios. Two problems arise: how to treat the scattered data in a meaningful way, and how to use those ratios where one value is known to be less than a stated detection-limit.

The following procedure has been adopted. Pt/Pd and Pt/Au ratios have been calculated. Where both elements in the ratio are above the detection-limit, the result is regarded as prime data. In cases where one element is known to be above a stated detection-limit, then the result can also be quoted as an inequality. Thus 50/<5 is expressed as >10. These data are regarded as secondary.

The data are illustrated by calculation of a mean and standard deviation from the prime data. The mean, standard deviation and range of the prime data are shown in Tables 1, 2 and 3 and illustrated on Figure 3. Inspection of the result usually shows that the secondary data fall within the range of the prime data. Where this is not the case, the secondary data are included in Figure 3 as outliers, and the additional range shown dotted.

COMPARISON OF Pt/Pd AND Pt/Au VALUES FROM DIFFERENT SUPERGENE ENVIRONMENTS

Samples of 80 platinum-bearing rocks from the Freetown Layered Complex show an average Pt/Pd ratio of 1.4, with Pt/Pd ratios in prime data between 0.45 and 2.5 (Fig. 3). These rocks are all fresh samples, but are from surface outcrops and may have suffered some leaching of Pd. The rocks are generally fresh and unaltered in thin section, and it seems unlikely that there has been significant alteration. Some samples, however, show enhanced platinum values, whereas palladium remains below detection, leading to Pt/Pd ratios as high as >12.5 in the secondary data.

The soil samples and the ferricrete (Table 1) have an average Pt/Pd value of 6.0, with a range from 1.8 to 8.9, all in prime data.

Assays of 23 heavy-mineral concentrates from alluvial samples from streams near the Freetown soil-sampling site show an average Pt/Pd value of 73.7, with a range in prime data of 1 to 543. The secondary data lie within this range, except for one sample, which shows Pt/Pd >1475. These results are also illustrated in Figure 3. An analysis of a concentrate produced from the area at the start of mining activity in 1928 was provided by the Imperial Institute (now Imperial College, London). This is recorded by Pollett (1931) and gives a Pt/Pd value of 44, within the above range.

These Pt/Pd values are similar to those reported from source rocks and alluvial deposits in other parts of the world. Mellor (1947), quoted in Capitán-Vallvey (1989), gave compositions of alluvial PGM concentrates from Colombia whose Pt/Pd values are in the range 53 – 159.

An analysis of variance between the populations has been calculated as shown in Table 4. This is based on the number of primary data-points (n) and the degrees of freedom of each population (n–1). The ratio of the variance between populations to be compared is judged against the value of the F-distribution, which describes the limiting variance ratio for the appropriate degrees of freedom. A value of the probability $p = 0.01$ has been used, *i.e.*, there is a 1% opportunity for an incorrect result. The population of Pt/Pd soil analyses can be distinguished from the rock analyses with this degree of confidence because the variance

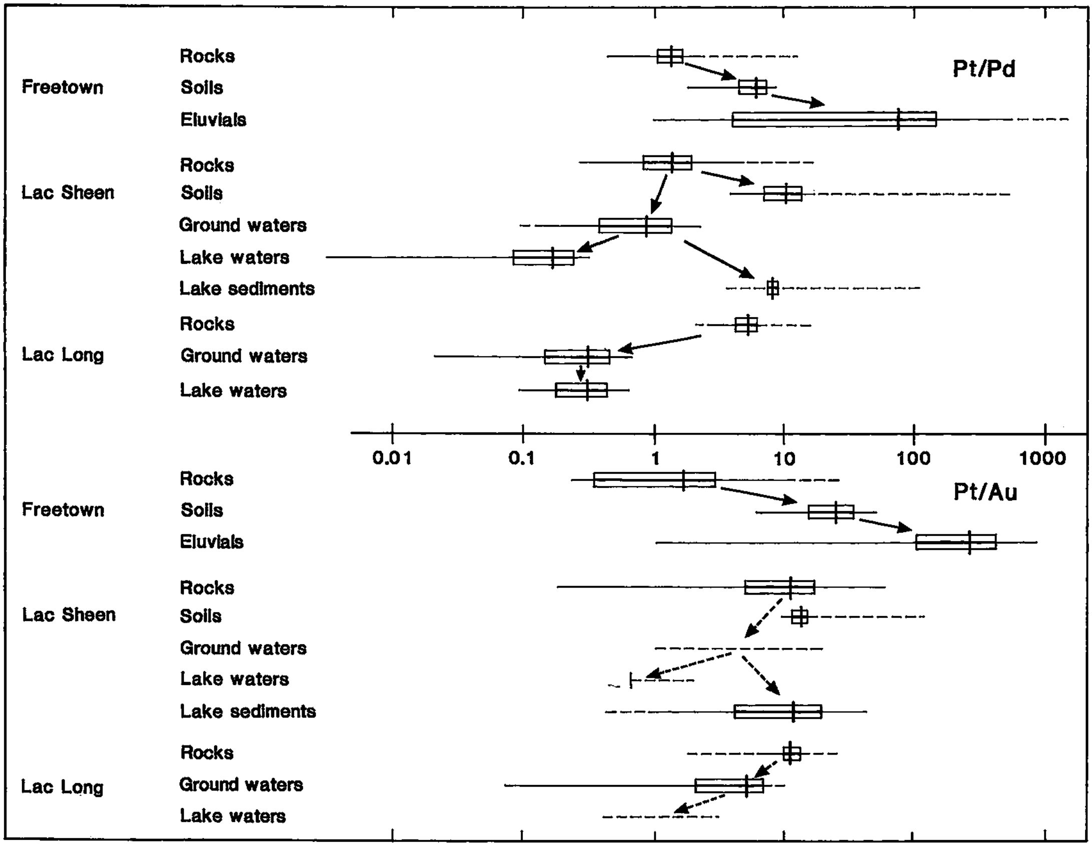

FIG. 3. Pt/Pd and Pt/Au ratios of rocks soils and sediments from the Freetown Intrusion and those at Lac Sheen and Lac Long. For each occurrence, the mean is shown by a vertical bar, one standard deviation by a broad strip, and the total range by a thin line. These are calculated from primary data, *i.e.*, where both Pt and Pd (or Au) are above the detection limit and the ratio can be calculated. Secondary data are represented by a dotted line where they exceed the range of the primary data; these are calculated as an inequality from data where Pd (or Au) are less than the detection limit. The results show progressive partitioning of Pt with respect to Pd and Au among rocks, soils and eluvial deposits in each of the areas and an opposite trend toward groundwater and lake waters.

ratio of these two populations is 5.6, which is greater than the limiting value for the F-distribution of 5.04. The distinction between the alluvial samples and the soils is in no doubt with a variance ratio of 11 329 compared with an F-distribution limiting value of 6.42. For Pt/Au, the distinction between soil and rock populations is 54.5 compared with a F-distribution limiting value of 4.77, and the comparison between the alluvial analyses and the soil analyses also is conclusive (16 404, well above the limiting value of 4.50).

Wood & Vlassopoulos (1990) have examined the platinum, palladium and gold content of rocks, soils, water and sediments from two platiniferous areas in Quebec, Lac Sheen and Lac Long. Their results also are displayed in Figure 3 using the same conventions.

TABLE 4. ANALYSIS OF VARIANCE TO DISTINGUISH THE POPULATIONS OF TABLES 1, 2 AND 3

Pt/Pd	Soils	Alluvial	Rock	Soil/Rock	Alluvial/Soil
Variance	1.73	19600	0.31	5.6	11329
n	5	15	17		
degs freedom	4	14	16		
F (0.01)				5.04	6.42
Pt/Au	Soils	Alluvial	Rock	Soil/Rock	Alluvial/Soil
Variance	368.6	110889	6.76	54.5	16404
n	5	10	20		
degs freedom	4	9	19		
F (0.01)				4.77	4.50

The lower part of Figure 3 shows the corresponding data for Pt/Au. Since the areas considered here are primarily platinum-bearing with a low gold content, many of the gold assay values are below the detection limit. Consequently, the Pt/Au results include fewer prime data and more secondary values. This is particularly true of the data from Quebec.

DISCUSSION OF THE ASSAY RESULTS

From the Freetown data, a clear sequence emerges from the rocks, through the soil to the eluvial–alluvial deposit (Fig. 3). The sequence shows enrichment of platinum with respect to palladium due to significant partitioning of platinum into the eluvial–alluvial deposits *via* the soil.

The explanation is clearly shown by the Lac Sheen results. Here there is a similar increase in Pt/Pd from the rocks to the soil. The complementary part of the story is shown by decreasing Pt/Pd between the rocks and the groundwater. It is clear that there is partitioning of the platinum and the more soluble palladium following weathering of the rocks; more palladium remains in the groundwater, more platinum in the soil. There is a second partitioning when the groundwater reaches the lake, as the palladium is further partitioned into the lake water, and the platinum, to the lake sediments. The Lac Long data follow the same pattern, with palladium preferentially partitioned into the waters.

The Pt/Au data for Freetown and the two occurrences in Quebec also conform to the same pattern, with the more soluble gold partitioned in favor of the waters. The gold data from Quebec contain fewer results above the detection limit, so that this interpretation would not stand alone. The relevance of the Pt/Au data is that it supports entirely the interpretation of the Pt/Pd results. This is especially clear from the Freetown assays.

Wood & Vlassopoulos (1990) appreciated that their results showed palladium and gold to be preferentially retained in surface waters, and platinum, to be partitioned into the sediments. The additional results presented here for the Freetown area, the treatment of the data and the presentation of Figure 3 support and elaborate this explanation. We note that Cook & Fletcher (1993) observed "very limited hydromorphic solubility of platinum and its accumulation in bogs" on the Tulameen Complex, British Columbia, where the climate is substantially different from that in Sierra Leone. They ascribed much of the movement of the PGM to glacial transport. Pt/Pd ratios in soil and till overlying the Stillwater Complex, Montana (Fuchs & Rose 1974), however, show similar values and clearly illustrate differential mobility of platinum and palladium in the surface environment.

In the mineral deposit down-slope from the Freetown soil sample, the PGM are notable for their large size. The grains are generally 0.5 to 1 mm across, though many are larger. The experience of those who mined these deposits was that virtually no fine-grained PGM were present (Pollett 1931).

The assays of each of the fractions of the soil samples shows no significant difference between the –6 mm to +177 µm fraction and the –177 µm fraction. If the soil represented a purely passive intermediary containing resistate PGM en route between the rocks and the eluvial–alluvial deposit, then the assay results would show a higher PGE content in the coarse fraction. This is not the case.

CONCLUSIONS

We have presented three complementary lines of evidence relating to the formation of eluvial and alluvial PGM deposits using the Freetown deposits as the principal example. These show that there is unambiguous partitioning of the more soluble palladium and gold into groundwater and surface waters, and preferential deposition of platinum in soils and eluvial–alluvial deposits. There is no division of the PGE in the soils dominantly into the coarse fraction as there is in the stream down-slope from the soil-sample site. The soil contains organic species that have a high affinity for the PGE, and these could provide a potential means of local transport in solution.

Sedimentary organic matter has been invoked frequently to play a variety of roles in the concentration of metals (for a review, see Disnar & Sureau 1990). Some investigators have argued that the organic matter acts as a reductant, whereas others consider that the organic matter complexes the metals. In the current study, we suggest that the organic matter may complex or chelate the metals initially, followed, possibly, by reduction. A similar approach has been proposed by Nash *et al.* (1981) with respect to uranium. The humic acid analyses were undertaken in this study in order to provide constraints on the possible initial interactions of organic matter with the PGE. In this study, we are concerned with the initial organic matter – platinum reactions. Although we realize that organic reduction is a potentially important stage (Baranger *et al.* 1991), it falls outside our current objectives.

The pyrolysis data are relevant to the suggestions by Cousins & Kinloch (1976) and Bowles (1986) that organic acids contribute to weathering, transport and deposition of the PGE. The humic acids in soils over the Freetown Complex have been shown to contain carboxylic acids. Consequently, there are no restrictions on possible organic matter–PGE complexes being formed. The main constraint is the pH. In order to act as a complexing agent, the carboxylic group must be present as the carboxylate anion. The dissociation constants (pKa) for the carboxylic acids are a function of chain length. The pKa for acetic acid at 25°C is 3.7, and increases to approximately 4.8 if the carboxylic group is attached to three or more carbon atoms. Consequently, carboxylic complexing is most likely to occur where the soil pH is above 4.8.

The other potential carboxylate compounds are those based on aromatic structures, for which the pKa is less than that of the non-aromatic acids. The advantage of considering the long-chain acids is that rotation can occur between carbon bonds, making them potential chelates, whereas such rotation cannot occur with the planar aromatics. Experimentally, platinum carboxylate salts can be formed, either when the platinum is in solution or present as an oxide or hydroxide (Hartley 1973).

A special aspect of the organic geochemistry of platinum is the ease with which it reacts with unsaturated carbon bonds. Of historical interest is the fact that the first organometallic compound synthesized was a platinum compound (Zeises's salt), formed by the reaction of a platinum salt with an unsaturated hydrocarbon. The humic acid pyrolysates contain unsaturated hydrocarbons that are potentially capable of reacting with platinum. Our data must be treated with caution, since some unsaturated hydrocarbons are a product of the pyrolysis technique, and they are also geochemically labile. We contend that unsaturated carbon–carbon bonds may be very important in geological situations, but this cannot be proven in the present study.

In the context of the details of mineralogy and occurrence, which have been reviewed above, it is clear that the most satisfactory explanation of the observations recorded here is to be found in supergene weathering. Platinum, palladium and gold are taken into solution, together with organic species. Differences in the solubility and stability of these complexes lead to partitioning of palladium and gold into the aqueous phase. Platinum is partitioned into the soils and eluvial deposits. In the soils, platinum is not held in the fine fraction, in which it is probably resident in the rock, neither is it in the coarse fraction, in which it predominantly occurs in the eluvial deposits. It is equally distributed between the coarse and fine fractions, possibly as organic species. These may relate to particles of decaying organic matter or coatings on other soil fragments. The remaining problem is the mechanism by which the nuggets are derived from the organic matter. At some stage, reduction to Pt° is required, presumably by the organic matter (Baranger *et al.* 1991). It may be that the concentration of Pt increases within the organic matter until nucleation can occur. Alternatively, some change in pH or other parameters may destabilize the platinum–organic matter complex and induce nugget formation.

Other PGE occurrences show similar properties, and the principles espoused here are not applicable only to the Freetown area. That the explanation given here provides the complete mechanism of formation of eluvial PGM deposits remains to be proven in detail. The present work has helped to define the conditions under which the solution and transport occur.

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