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Osmium isotope ratios of PGM grains associated with the Freetown Layered Complex, Sierra Leone, and their origin

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Abstract. Osmium isotope ratios for two types of platinum group mineral (PGM) nuggets of eluvial (residual) origin, associated with the Freetown Layered Gabbro Complex, were determined in-situ using an ion microprobe. The values for erlichmanite nuggets are ~1.08. Those for PGM inclusions in Pt–Fe alloy nuggets are higher, ranging from 1.2 to 2.1. Ratios of $^{187}Os/^{186}Os$ vary between the nuggets, but they are consistent within individual nuggets. The data suggest early formation of the erlichmanite nuggets, prior to a postulated substantial contribution of crustal Os. The Pt–Fe alloy nuggets, on the other hand, were formed later in a residual melt which was contaminated by crustal Os due to the assimilation ($<10\%$) or the gaseous/fluid transport of Os from Archaean host rocks into the magma. The lack of systematic mineralogical and chemical changes of the Complex and extensive granulitization in the adjacent host rocks and xenoliths may favor the latter process.

The lack of high $^{187}Os/^{186}Os$ ratios, consistent $^{187}Os/^{186}Os$ values within individual nuggets and their textures and mineralogy suggest that the studied PGM nuggets were not formed during lateritization or in low-temperature depositional environments.

Introduction

The origin of platinum nuggets is controversial. Proposed models for the genesis of PGM nuggets include their formation from silicate melt, in pegmatite, from subsolidus hydrothermal fluids, and during sedimentary processes. Difficulties in finding a nugget-size platinum group mineral (PGM) in mafic igneous rocks and some PGM nuggets in stream gravels exhibiting the delicate morphology and a lack of abrasion have led some researchers to propose an in-situ formation of nuggets in placers under sedimentary environments. A recent study of the solubility of platinum group elements (PGE) suggests that they may be soluble in very saline solutions, even at low temperatures (e.g., Mountain and Wood 1988). The PGM grains in Sierra Leone occur in laterites covering a layered ultramafic intrusion and in gravels along nearby streams. Some are large in size and they display branching shapes without surface abrasion. The tropical climate in the area was proposed to be conducive to the formation of PGM nuggets at low temperatures (Bowles 1986). This paper presents $^{187}Os/^{186}Os$ ratios of some PGM nuggets from Sierra Leone to constrain their possible origin.

Geology and sample description

Platinum group mineral (PGM) grains from Sierra Leone occur in the area underlain by the Freetown Layered Complex in the Freetown Peninsula, which extends from the capital, Freetown, southeast for ~40 km into the Atlantic Ocean (Fig. 1). The eastern half of the Layered Complex is exposed on land, forming rugged, highly dissected mountains, with an elevation up to 900 m above sea level. The Complex extends seaward and the southern tips are exposed on the Banana Islands. The original area is estimated to have been ~1,000 square miles (Wells 1962).

The site of the intrusion was once located in the central core of an Archaean craton, which is now separated into the Liberian Craton in Africa and the Guyana Shield of northern South America (e.g., Hurley et al. 1967). The Layered Complex (193 ± 3 Ma; Beckinsale et al. 1977) is one of many tholeiitic intrusions, including the dyke swarms in Africa, eastern North America and northern South America, and the mafic igneous activity is linked to the opening of the Atlantic Ocean (May 1971). The craton consists of a supracrustal sequence of ultramafic, mafic and sedimentary rocks older than 3.0 Ga (Morel 1979). The Kasila Group supracrustal rocks, which host the Layered Complex, form a wide NW-trending belt and they are overlain by a thin cover of Pleistocene-Recent sediments (Fig. 1). The lithologies of the Group are dominantly fine- to medium-grained mafic gneiss and granulite with minor sedimentary rocks, gabbros and gabbro-anorthosites. All rocks are metamorphosed and deformed during the late Archaean, 2,700 Ma, and Pan-African orogeny, ~600 Ma (Williams and Williams 1976).

Five major zones, totalling >6,000 m in thickness, are recognized in the Complex (Fig. 2). The basal zone at the bottom of

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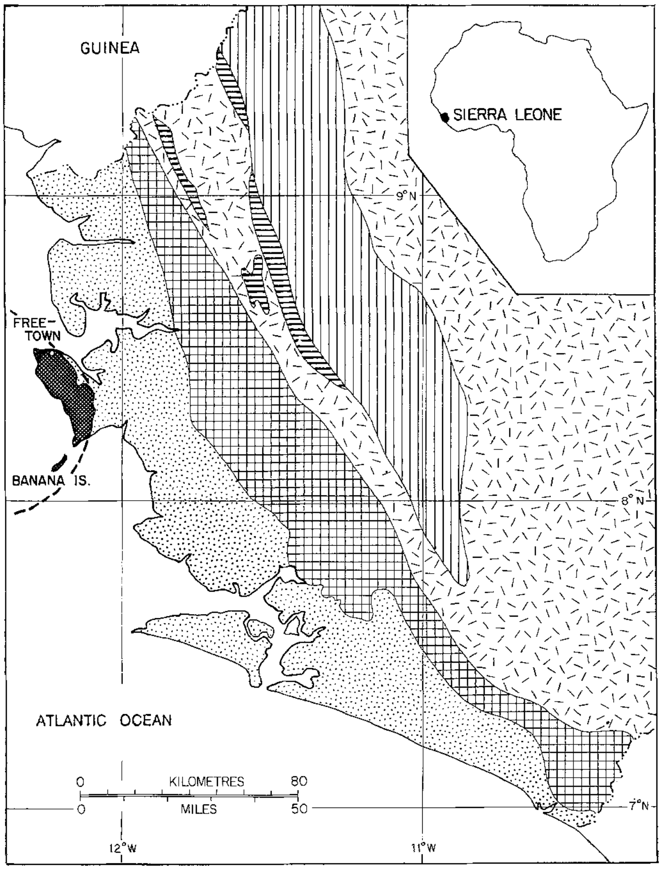

Fig. 1. General geology of Sierra Leone and the location of the Freetown Layered Gabbro Complex. After Geological Map 1081 (1:50,000), Directorate of Overseas Surveys (1960). *Close-diagonal cross-hatched area*, Freetown Layered Gabbro Complex, *dashed line*, limit of the Complex; *dotted area*, Bullom Series, Pleistocene-Recent sediments thinly covering the Kasila Group; *open vertical cross*, Kasila Group, highly metamorphosed and deformed mafic supracrustal rocks; *random-dashed area*, Archaean granite/gneiss terrain; *horizontal-lined area*, Archaean supracrustal rocks; *vertical-lined area*, Upper Proterozoic Rokel River Series

Unit	Thickness (m)	Lithology	Remarks
Zone 4	2000	Troctolite	Occurrences of gabbro pegmatites
		Olivine-gabbro	Abundant granulite xenoliths
Zone 3	2000	Anorthosite with pyroxenite layers	PGM occurrences Magnetite-ilmenite mineralization
		Troctolite	
		Olivine-gabbro	PGM occurrences
Zone 2	1000	Anorthosite	
		Hypersthene-gabbro	
		Hypersthene-gabbro	
		Troctolite	Abundant granulite xenoliths
Zone 1	600	Anorthosite	
		Augite-troctolite	
Basal (transitional)	500	Hypersthene gabbro	Olivine-free
		Norite	Olivine-free
		Mafic granulite	

Fig. 2. Schematic cross section of the Freetown Layered Complex (summarized from Wells 1962)

the sequence is considered to be transitional between the Complex and mafic granulite of the Kasila Group. In the upper four zones, each zone represents a single pulse of magma injection and displays rhythmic layering of troctolite, olivine-bearing norite, gabbro and anorthosite (Wells 1962). The PGM nuggets are found only in the area underlain by zone 3 (Fig. 2).

Attempts to find PGM grains in the igneous rocks have not been successful because of the rugged topography, dense jungle and deep weathering due to the tropical climate in the area. A thick laterite has developed over the Layered Complex and most of the PGM grains rest on the bedrock and are embedded in the laterite (Pollett 1951). Placer PGM nuggets are high in Pt and consist principally of Pt–Fe alloys, with minor Os–Ir–Ru alloys, and erlichmanite/laurite and tulameenite (Bowles 1981). The PGM

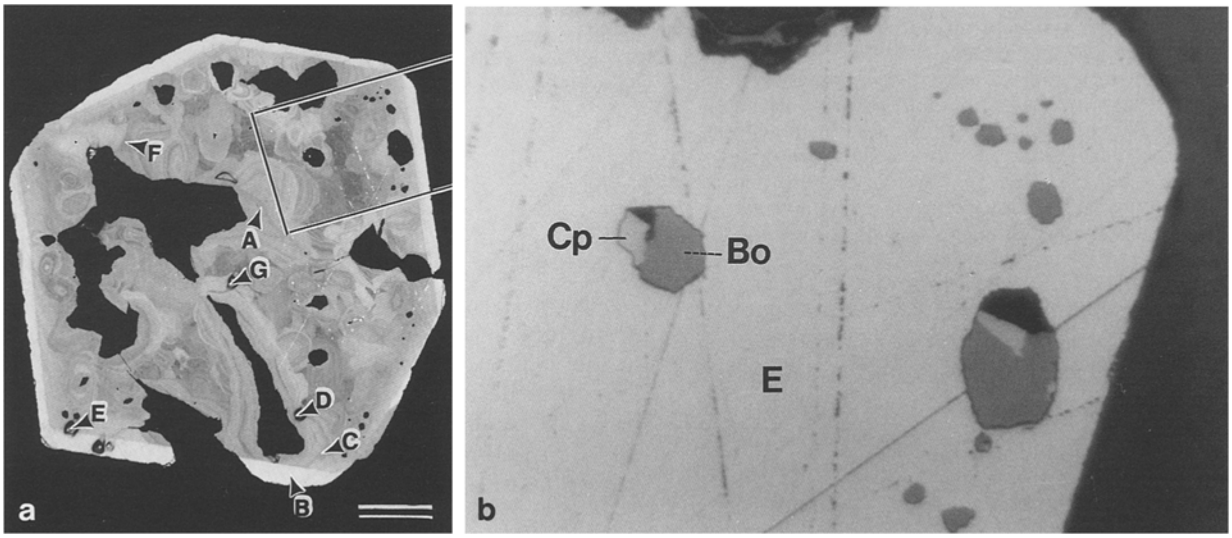

Fig. 3. a. Backscattered-electron image of erlichmanite nugget, SL-L2, showing intricate chemical zoning. Os-rich part is *brighter* and Ru-rich part is *darker*. The Os contents vary from 47 to 58 wt% (see Table 2). *Squared area in the upper right corner* is shown in **b**. *Dark rounded holes* in the grain are a mixture of sulphides shown in Fig. 3. a. *A* to *G* indicate the sites for $^{187}Os/^{186}Os$ analysis listed in Table 2. *Scale bar* represents 100 μm. **b** Photomicrograph of a portion of the nugget, SL-L2. *Bo*, bornite; *Cp*, chalcopyrite; *E*, matrix of erlichmanite

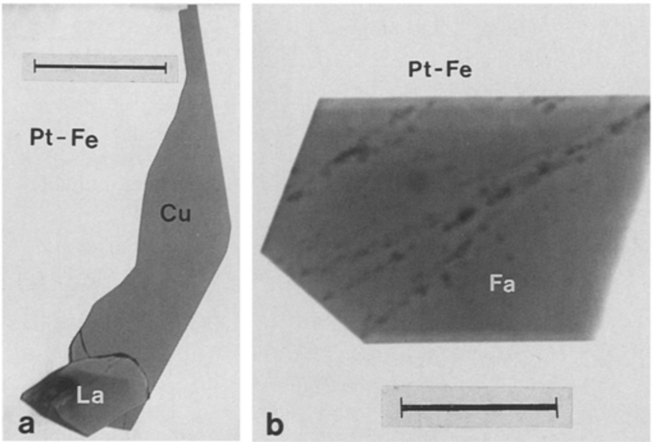

Fig. 4. a Backscattered-electron image of cuprorhodsite and laurite inclusions in Pt–Fe nugget, SL-UP3. Laurite exhibits Os-rim (*brighter*). *La*, laurite; *Cu*, cuprorhodsite; *Pt–Fe*, matrix part of Pt–Fe alloy. *Scale bar* represents 50 μm. **b** Backscattered-electron image of laurite inclusion in Pt–Fe nugget, SL-UP3. Euhedral laurite inclusion shows compositional zoning with Os-rich rim (*brighter*). *Scale bar* represents 10 μm

nuggets have mineralogical characteristics similar to PGM nuggets derived from Alpine- and Alaskan-type ultramafic intrusions (Cabri 1981a), except for the occurrence of erlichmanite nuggets. The occurrence of erlichmanite nuggets has not been reported elsewhere.

The PGM nuggets examined were of two kinds: (1) loose pyritohedra crystals of erlichmanite (OsS_2); (2) Pt–Fe alloys. Electron-probe analysis suggests that the latter is probably isoferroplatinum (Pt_3Fe). The nuggets studied were collected from an eluvial (residual) deposit on the hill slope of Guma Water at No. 2 village, Sierra Leone, and they are from the same heavy mineral concentrate that was originally described by Bowles (1981). The Guma Water runs southeast between high mountain ranges of zone 3 to the east and the mountains of zone 4 to the west (Wells 1962). The erlichmanite crystals prior to being mounted in polished sections are illustrated in Cabri (1981a, p. 104). The erlichmanite crystals are complexly zoned with large variations between Os and Ru (Fig. 3a), and contain a few oval inclusions of bornite and chalcopyrite (Fig. 3b). It is interesting that the Os-rich rims of the erlichmanite nuggets give them a pyritohedron morphology.

In contrast, Pt–Fe alloy nuggets exhibit varying degrees of abrasion, and contain inclusions of other PGM phases, such as laurite (RuS_2), cuprorhodsite ($CuRh_2S_4$), and iridian ruthenian osmium. The osmium alloy occurs as both very fine (~1 μm) crystallographically oriented exsolutions and coarser, less well-oriented inclusions, some of which stick out from the Pt–Fe alloy matrix. Laurite inclusions in the Pt–Fe alloy nuggets also have a compositional zoning which shows Os-rich rims (Fig. 4a, b) similar to the zoning in erlichmanite nuggets (Fig. 3a).

The general geology of the areas is found in Pollett (1951) and Morel (1979), and Macfarlane et al. (1981), detailed petrology of the Freetown Complex is described by Wells (1962), and the occurrence of PGM nuggets is reported in Bowles (1981).

Analytical procedures

Osmium isotope ratios were determined on individual grains, mounted in araldite and coated with Au, using the MIT-Harvard-Brown Cameca 3f ion microprobe. Operating conditions were essentially the same as those described in Hart and Kinloch (1989). The primary O^- beam current was 4–20 nA and secondary ions of 50–110 V excess energy were selected. A single analysis took an average of 25–30 min. Masses 185, 186, 187, 188, and 189 were determined for each analysis in order to correct the ratios of $^{187}Os/^{186}Os$ for the contribution of ^{187}Re, hydrides and mass fractionation. In this study, correction for ^{186}W was not necessary because ^{183}W was not detected before or after each analysis. The Re correction of the grains ranged from 0 to 6%. Some grains with heterogeneous Re contents, required Re correction up to 20%. After correction, calculated $^{187}Os/^{186}Os$ values were consistent within the nugget, certifying that the Re correction does not introduce additional uncertainty in the measurement of $^{187}Os/^{186}Os$. The hydride fractions and mass fractionation were calculated by normalizing the ratios of $^{186}Os/^{188}Os$ to 0.12035 (Luck and Allègre 1983). The hydride fraction was normally less than 0.5%. The mass fractionation factor ranged from 0.5 to 1% per atomic mass unit. The 2 σ of the measurement of 187/186 peak ratios was normally below ±0.2%. Replicate analysis of the same grains made over a 10 month period show a precision (2 σ) of ±0.6% (Table 1). The precision of each result, therefore, was given as ±0.6% or the in-run measurement of the peak ratios, whichever was larger.

Table 1. $^{187}Os/^{186}Os$ ratios of two osmian iridium working standards

No.	Analysis	$^{187}Os/^{186}Os$	No.	Analysis	$^{187}Os/^{186}Os$
101209	1	1.060	10120-11	1	1.086
	2	1.068		2	1.079
	3	1.065		3	1.083
	4	1.064		4	1.078
	5	1.066		5	1.083
	6	1.061		6	1.081
	7	1.067		7	1.081
	8	1.066		8	1.081
	9	1.067		9	1.081
	10	1.074		10	1.083
Average		1.0646	Average		1.0838
2σ		0.72%	2σ		0.42%

The chemical compositions of PGM were determined using a JEOL 733 electron microanalyzer system by energy-dispersion spectrometry at 20 kV with beam currents of ~10 nA. The semi-quantitative analyses were carried out using the X-rays of RuLα, IrMα, CuKα, PtMα, RhLα, PdLα and OsMα and the standards of pure metal for each element. The absence of Re in the minerals, including Pt–Fe alloys, was verified by scanning the ReLα peak with a wavelength-dispersion spectrometer at 20 kV, and 25 nA at a speed of 0.4 s/point.

Results

$^{187}Os/^{186}Os$ ratios of the PGM nuggets are listed in Table 2. The Re peak was not detected by wavelength-dispersion spectrometry, and therefore the Re content in the studied samples should be below 0.06 wt%. Since the Re contents are low, a decay product, ^{187}Os, does not constitute a significant proportion of the ^{187}Os in the PGM grains. The measured $^{187}Os/^{186}Os$ ratios of the PGM phases, therefore, are the initial values at the time of their formation.

Erlichmanite nuggets show a narrow spread from 1.08 to 1.10. Laurites in the Pt–Fe alloys, on the other hand, have higher values, ~1.41. Cuprorhodsite and Os metals in the Pt–Fe alloys show high $^{187}Os/^{186}Os$ ratios, from 1.39 to 1.43 and from 1.28 to 2.06, respective-

Table 2. Os isotope ratios of PGM from Sierra Leone

Nugget No.	Description	Os (wt%)	$^{187}Os/^{186}Os$[a]
L-L2	(Erlichmanite nugget containing rounded inclusions of mixtures of sulphides, chalcopyrite and bornite, shown in Fig. 3b. The nugget has heterogeneous distribution of Os and Ru as shown in Fig. 3a)		
	Centre, moderately Os-rich part, point A in Fig. 3a	54.4	1.089±0.007
	Margin of Os-rich rim, point B in Fig. 3a	61.7	1.096±0.007
	Low Os part, point C in Fig. 3a	53.4	1.084±0.012
	Low Os part, point D in Fig. 3a	54.5	1.094±0.010
	Low Os part, point E in Fig. 3a	54.8	1.089±0.008
	Low Os part, point F in Fig. 3a	51.5	1.087±0.032
	High Os part, point G in Fig. 3a	55.5	1.084±0.007
SL-L1	(Rounded erlichmanite nugget containing small oval chalcopyrite inclusions. Composition is heterogeneous with Os-rich centre and Os-rich rim)		
	Low Os part of erlichmanite	53.5	1.094±0.011
	Low Os part of erlichmanite	47.8	1.081±0.013
	Low Os part of erlichmanite	49.3	1.080±0.013
	Low Os part of erlichmanite	51.4	1.084±0.016
	Low Os part of erlichmanite	51.3	1.080±0.012
	High Os part of erlichmanite	55.8	1.089±0.009
	High Os rim of erlichmanite	58.0	1.089±0.007
	High Os rim, other side of erlichmanite	57.6	1.089±0.007
SL-UP3	(Semi-rounded irregular surfaced Pt–Fe alloy, containing laurite and cuprorhodsite		
	Rod-shaped cuprorhodsite inclusion in the alloy (Fig. 4a)	<0.5	1.412±0.021
	Chemically zoned laurite inclusion with Os-rich rim attached to cuprorhodsite grain (Fig. 4a)	31.5	1.418±0.011
	Euhedral laurite inclusion, chemically zoned with high Os rim (Fig. 4b)	13.5	1.414±0.022
	Semi-rectangular cuprorhodsite inclusion "A"	<0.5	1.387±0.024
	Semi-rectangular cuprorhodsite inclusion "B"	<0.5	1.430±0.025
SL-UP7	Osmium lamellae A in Pt–Fe alloy		1.253±0.020
	Osmium lamellae B in Pt–Fe alloy		1.249±0.012
	Osmium lamellae C in Pt–Fe alloy		1.251±0.060
L1088/21-5	(Semi-rounded Pt–Fe alloy with very thin oriented osmium lamellae, 1 µm wide		
	Osmium lamella		1.800±0.025
L1088/21-8	(Semi-rounded Pt–Fe alloy, 300 µm long, containing total 5 laths of Ru–Ir–Os metal alloy. One osmium rod is partially sticking out from the nugget)		
	Ruthenian iridian osmium[b] ($Os_{69}Ru_{17}Ir_{12}Rh_{1}$) rod inclusion in Pt–Fe alloy	75.6	1.743±0.012
	Long rod of ruthenian iridian osmium (~100 µm; $Os_{75}Ru_{12}Ir_{11}$) partially sticking out from the nugget	84.8	1.663±0.010
	Different spot of the long rod of the centre of osmium	80.8	1.671±0.010
	Round inclusion of ruthenian iridian osmium		1.642±0.010
L1088/21-9	(Semi-rounded Pt–Fe alloy nugget, ~600 µm long, containing 4 inclusions of osmium. One osmium rod is attached to the rim of the nugget)		
	Square iridian ruthenian osmium inclusion (30 µm long; $Os_{81}Ir_{10}Ru_{6}Rh_{2}$) in the centre	81.4	1.903±0.01
	Semi-rounded iridian ruthenian osmium inclusion (60 µm long; $Os_{81}Ir_{10}Ru_{6}Rh_{2}$)	84.6	1.904±0.01
	Iridian ruthenian osmium rod (~100 µm long; $Os_{84}Ir_{11}Ru_{4}Rh_{1}$) on the rim of Pt–Fe alloy	84.2	1.900±0.01
L1088/21-18	(Porous Pt–Fe alloy with rugged, angular surface, 500 × 800 µm, containing extremely fine oriented osmium lamellae, few in number)		
	Very fine osmium lamella		2.058±0.01
L1088/21-21	(Rounded Pt–Fe alloy, 350 × 500 µm, containing ~20 oriented osmium lamellae and one large osmium rod. The osmium rod, 100 × 220 µm, is partly sticking out from the nugget)		
	Ruthenian iridian osmium rod ($Os_{73}Ru_{13}Ir_{12}Rh_{2}$) partially sticking out from Pt–Fe	78.3	1.329±0.01
	Base on the osmium rod ($Os_{84}Ru_{9}Ir_{7}$)	87.8	1.334±0.01
	Another part of the osmium rod ($Os_{83}Ru_{10}Ir_{7}$)	86.9	1.313±0.01
	Oriented ruthenian iridian osmium lamella (100 µm long; $Os_{69}Ir_{15}Ru_{15}Rh_{1}$)	74.5	1.282±0.03

[a] Precision is calculated from ratio counting statistics or 0.6%, whichever larger; further explanation in the text

[b] Nomenclature of PGE alloys from Harris and Cabri (1991)

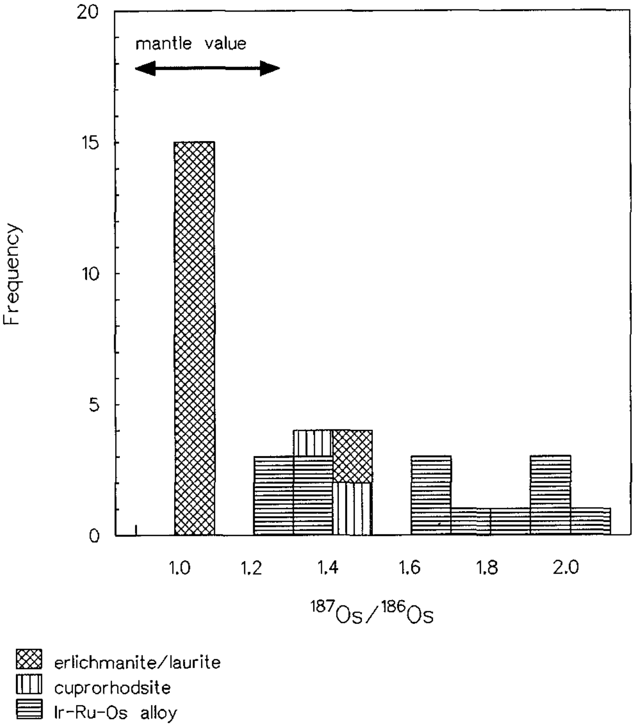

Fig. 5. Histogram of observed $^{187}Os/^{186}Os$ ratios of PGM phases from Sierra Leone in this study. The *arrow* shows the possible range of $^{187}Os/^{186}Os$ ratios of the 190 Ma mantle (see detailed explanation in the text)

ly. The total range of $^{187}Os/^{186}Os$ ratios, plotted in Fig. 5, is from 1.08 to 2.06. The spread is compatible with the variation observed in other layered mafic bodies, such as the Bushveld and Stillwater Complexes: from 0.938 to 1.509 in the Bushveld Complex (Hart and Kinloch 1989) and from 0.84 to 1.75 in the Stillwater Complex (Lambert et al. 1989; Martin 1989).

Contrary to the inter-nugget variation, the variation of $^{187}Os/^{186}Os$ within individual nuggets is statistically insignificant and is independent of chemical heterogeneity observed in any one phase. For example, a rod-shaped cuprorhodsite grain and several laurite inclusions in the Pt–Fe alloy nugget of sample SL-UP3 (Fig. 4a) show similar $^{187}Os/^{186}Os$. A large inclusion of Os metal and a small inclusion of the iridian osmium in Pt–Fe nugget of the sample L1088/21-8 have similar Os isotope ratios. One nugget sample (L1088/21-21) has a rod of osmium, 100 × 200 μm, sticking out from the Pt–Fe alloy matrix and also contains osmium lamellae inclusions. The $^{187}Os/^{186}Os$ values of these two occurrences of osmium are again similar, within the analytical error.

Several grains of erlichmanite display complicated compositional zoning with Os-rich rims (Fig. 3a). Small laurite inclusions in the Pt–Fe alloy of sample SL-UP3 (Fig. 4a, b) also show similar chemical zoning. The chemical variations do not appear to be related to the $^{187}Os/^{186}Os$ ratios; high-Os and low-Os portions in the erlichmanite nuggets have similar $^{187}Os/^{186}Os$ ratios. Chemically zoned laurite and non-zoned cuprorhodsite inclusions in the Pt–Fe nugget have similar $^{187}Os/^{186}Os$ ratios.

Discussion

Osmium isotope ratios of mantle-derived rocks indicate that the present-day mantle is heterogeneous in $^{187}Os/^{186}Os$ ratios, and that the values range from 0.905 to 1.11 (Martin and Turekian 1987; Pegram et al. 1988; Walker et al. 1989). Recently, Walker et al. (1990) suggested that the mantle along the break-up of Pangea was enriched in ^{187}Os, 1.13–1.26, based on $^{187}Os/^{186}Os$ values of 155 ± 43 Ma komatiite from Gorgona Island. The high values were attributed to the ancient incorporation of tholeiitic rocks into that particular portion of the mantle. The Freetown Layered Complex was also emplaced along the boundary of the break-up of Pangea and the site of the intrusion was near Gorgona Island. Therefore, the source magmas for the Freetown Complex would have been also enriched in ^{187}Os, although it is unlikely that the magmas for the Freetown Complex were derived from the same mantle source as the Gorgona komatiites. The $^{187}Os/^{186}Os$ ratio of 1.26 is the maximum possible value for the contemporaneous mantle in consideration of the difficulty of raising $^{187}Os/^{186}Os$ ratios in mantle peridotite.

A possible minimum value of the mantle may be obtained from the study of mantle xenoliths. Mantle xenoliths from southern Africa suggest that sub-continental lithospheric mantle may have been depleted in ^{187}Os due to earlier magma generation (Walker et al. 1989). The Freetown Complex intruded the core of the craton, therefore, the source mantle was part of sub-continental lithospheric mantle, which may have been depleted in Re relative to Os due to early Archaean magmatism (Morel 1979). The data by Walker et al. (1989) and the primordial values of the mantle gives a minimum $^{187}Os/^{186}Os$ ratio of the contemporaneous mantle of ~0.90. The two sets of data provide $^{187}Os/^{186}Os$ ratios for the 190 Ma mantle ranging from 0.90 to 1.26 (Fig. 5).

The $^{187}Os/^{186}Os$ values of erlichmanite/laurite nuggets fall within the range of the mantle Os isotope ratios, suggesting that the PGE essentially were derived from the mantle without a significant contribution of crustal Os (Fig. 5). The chemical zoning with Os-rich rims observed in erlichmanite nuggets is similar to that reported in laurite grains enclosed in chromite from mafic rocks (Ohnenstetter et al. 1986). This suggests that such cryptic compositional zoning may be formed under magmatic conditions. The cause of the zoning is not fully understood, but it may be due to an increase in f_{S_2} and/or a lowering of the crystallization temperatures. The presence of sulphide droplets in erlichmanite nuggets is consistent with the early magmatic formation of the nuggets because Cu-sulphide droplets are reported in olivine crystals in the gabbroic phase of the Freetown Complex (Bowles 1978). The resulting interpretation is that the erlichmanite nuggets were formed in the magma prior to substantial crustal assimilation and that the source mantle had $^{187}Os/^{186}Os$ ratios, ~1.08 at ~200 Ma.

The PGM phases within and associated with Pt–Fe alloys show higher $^{187}Os/^{186}Os$ ratios than the range of the possible mantle values, although these are much lower than the values of the average crust, ~30 (Palmer and Turekian 1986). High ^{187}Os coupled with low-Re content possibly may be interpreted due to the in-situ decay of ^{187}Re in the Pt–Fe alloys and later removal of Re from the grains by surface waters. Ravizza and Turekian (1989) documented that Re, which is loosely combined with organic matter in shales, may be leached preferentially out by oxidized surface waters. This is, however, rejected as a possible cause for high ^{187}Os in the samples based on the following reasons. First, no systematic zonings of Re peaks were observed in PGM grains during the Os-isotope analyses in the ion microprobe. If leaching of Re took place at low temperatures, higher Re contents should be observed towards the cores of PGM grains. Second, natural Pt–Fe alloys in igneous rocks do not contain any detectable Re, <0.06 wt%. Examples include isoferroplatinum grains completely enclosed in sulphides from the Stillwater Complex (analysis no. 6, Table 8.75; Cabri and Laflamme 1981), Pt–Fe alloy grains enclosed in olivine from the Mooihoek and Onverwacht dunite pipes in the Bushveld Igneous Complex (Cabri and Feather 1975) and tetraferroplatinum grains in Uralian dunite (Cabri and Genkin 1991). Therefore, it is reasonable to assume that the Pt–Fe alloys formed in the Freetown Layered Complex were also free of Re at the time of magma crystallization and that the high ^{187}Os content is not due to in-situ radioactive decay of Re in the grains.

The high ^{187}Os/^{186}Os ratios, therefore, suggest that the Pt–Fe alloy grains contain significant amounts of crustal Os, implying that they were formed later than the erlichmanite nuggets. Later formation of Pt–Fe alloys after erlichmanite/laurite is in accordance with the general observation of the occurrences of PGE in mafic igneous rocks. Osmium, together with Ir and Ru, precipitates at an early stage of magma crystallization, whereas Pt, Pd and Rh may remain in residual magmas until S saturation (e.g., Keays and Crocket 1970; Barnes et al. 1985; Talkington and Lipin 1986). If separation of S takes place, all PGE preferentially would be incorporated into the sulphide melt. If S is deficient, then Pt, Pd and Rh would remain in the silicate melt throughout crystallization (e.g., Nixon et al. 1990). Because the Freetown Layered Complex does not contain major occurrences of sulphides, Pt, Pd and Rh likely remained in the residual tholeiitic magma and gradually crystallized in the igneous rocks. The ^{187}Os/^{186}Os ratios of such low-Os melts would be highly susceptible to contamination of crustal Os.

The cause for the ^{187}Os enrichment of PGM grains in Pt–Fe alloys may be discussed in connection with their possible origin:

1. PGM grains were formed from a melt which was enriched in radiogenic Os either (1a) by assimilation of crustal rocks, (1b) by volatile transport of Os as OsO_4 or (1c) by fluid transport of Os into the magma.
2. Radiogenic crustal Os was transported by sub-solidus hydrothermal fluids; the fluids leached Os from the host rocks as well as from solidified intrusions: (2a) PGM nuggets formed from the sub-solidus hydrothermal activity; (2b) radiogenic Os was added to existing alloys possibly by amalgamation.
3. PGM nuggets were formed during weathering processes to form laterite or during sedimentation processes in placers (Bowles 1986). Osmium with high ^{187}Os/^{186}Os ratios may have been incorporated from the intrusion itself or from the host rocks.

Models (1a, b, c), which involve the contamination of magma, are a viable option considering the geological setting of the Freetown Layered Complex. The ^{187}Os/^{186}Os ratios of the >3.0 Ga host rocks would have been >15 (assuming average crustal ^{187}Re/^{186}Os$=300$) at the time of intrusion. Assimilation of small amounts of crustal rocks is required to raise the ^{187}Os/^{186}Os ratios of tholeiitic magmas of the Freetown Layered Complex. If it is assumed that the magma contained the average Os contents of tholeiite (0.025 ppb Os; Chou et al. 1983) and that the host gneiss contained 0.01 ppb Os, assimilation of 10% of the weight of the magma would results in an increase in ^{187}Os/^{186}Os from 1.1 to 1.64. Less than 20% assimilation would be sufficient to explain the observed ^{187}Os/^{186}Os ratios. If, as suggested above, the erlichmanite crystallized early and the silicate magmas were deficient in S, no separation of the sulphide melt would occur and PGE in the residual magma would remain in the silicate melts. The Os content of the residual magma would have been very low and assimilation of much smaller amounts of rocks ($\ll 20\%$) would have had a profound effect on the ^{187}Os/^{186}Os ratios of the magma. The ^{187}Os/^{186}Os ratios of the residual magma would be sensitive to the contamination of crustal Os. Varied ^{187}Os/^{186}Os values of PGM inclusions in Pt–Fe nuggets are again consistent with the model. the Os-isotopic composition of each nugget reflects the degree of incorporation of crustal Os into the residual magma. If this is correct, then it follows that the later-crystallized Pt–Fe alloys would show higher ^{187}Os/^{186}Os ratios and that the later-formed Pt–Fe alloys would not contain large amounts of Os. It is interesting to note that the highest ^{187}Os/^{186}Os values is observed in the Pt–Fe alloy enclosing very fine lamellae of Os, which is consistent with this interpretation.

Several granites in the basement are known to contain economic concentrations of molybdenite (Morel 1979). Rhenium has geochemical affinity with Mo, and ^{187}Os/^{186}Os ratios of Mo-rich old rocks would be phenomenal (e.g., Luck and Allègre 1982). Small percentages of assimilation of such ores or pegmatitic portions of granites would significantly increase ^{187}Os/^{186}Os ratios of the magma.

Contamination of crustal Os by the magma may have been accomplished through the gaseous transport of OsO_4 instead of by the assimilation of bulk host rocks (1b). Osmium occurs disseminated in rocks mainly as the native metal or as PGE alloys (Cabri 1981b). Radiogenic Os would reside as a foreign element in Re-bearing minerals. Such radiogenic ^{187}Os may be released preferentially during metamorphic reactions associated with the intrusion because ^{187}Os does not occupy a stable site in minerals. Because the host rocks to the Complex are mainly metamorphosed igneous rocks containing mainly hematite and minor magnetite (Morel 1979), the f_{O_2} of gas or fluids equilibrated with these rocks would have been relatively high. Osmium in the host rocks may have been oxidized to OsO_4 under such relatively high f_{O_2} during the intrusive activity and moved upward toward the magma. Abundant xenoliths in the Complex may have supplied radiogenic Os to the magma by this mechanism. The presence of excess ^{40}Ar, which gives falsely old ages of the intrusion (Beckinsale et al. 1977), is consistent with gaseous transport of ^{40}Ar.

Osmium in the host rocks may have been driven off with H_2O during the granulization and incorporated into the magma. Host-rock amphibolites of the Kasila Group and xenoliths, which are abundant in the lower sequence of the Layered Complex, are extensively granulitized to form orthopyroxene (Wells 1962). Recrystallization of pyroxenes in the basal unit of the Layered Complex (zone 1) has also been attributed to high-temperature hydrothermal activity at magmatic temperatures (Wells and Bowles 1981). Radiogenic Os may have been released during the granulization and then driven off together with H_2O toward solidified intrusions.

Osmium in the host rocks may have been introduced into the Complex by hydrothermal fluids after the solidification of the magma, as proposed for PGE mineralization in the Bushveld Complex by Hart and Kinloch (1989). It is well known that large intrusions produced large hydrothermal convective cells (e.g., Taylor and Forester 1979). Stumpfl (1966) proposed hydrothermal mineralization of Pt, Au and Cu-sulphides in the Freetown Layered Complex based on replacement textures of Fe–Ti-oxides by Cu-sulphides. Thermodynamic calculations appear to support significant mobility of Pt in fluids at temperatures higher than 300° C (Mountain and Wood 1988). Low-temperature hydrothermal activity is, however, discounted from the following evidence; the lack of retrograde alteration in the host rock granulites, the occurrence of pristine olivine and pyroxene, and the high-anorthite components in the plagioclase in the Complex and in the granulitized immediate host rocks beneath the limit of the laterite horizon. The evidence altogether suggests that the hydrothermal activity would have taken place at very high temperatures, at least $\sim 700°$ C, and would not have continued at low temperatures.

If Pt–Fe alloys were formed from such fluids, then the $^{187}Os/^{186}Os$ ratios would not have any systematic variation because the ratios are entirely dependent upon the $^{187}Os/^{186}Os$ ratios of rocks through which the fluids passed. As mentioned, radiogenic ^{187}Os would be preferentially mobile during metamorphism and hydrothermal activity because of its location in crystallographically unstable sites. The observed $^{187}Os/^{186}Os$ values, ranging from 1.1 to 2.1, suggest that the major component came from the intrusion, and a small fraction of Os from the Arachaean host rocks. Because PGE wouldhave been concentrated in basal sequences, the fluid had to percolate through the cumulate layers to dissolve the PGE. It would be difficult to dissolve, transport and precipitate PGE without altering the primary igneous textures and mineralogy. In addition, the fluid had to dissolve the right amount of Os from host rocks to form a narrow range of $^{187}Os/^{186}Os$ ratios, and had to precipitate PGM nuggets only within the Layered Complex. Such a process appears to be too fortuitous. Furthermore, the model does not explain the reasons why erlichmanite nuggets are low in ^{187}Os and PGM inclusions in Pt–Fe alloys have higher $^{187}Os/^{186}Os$ ratios. Hydrothermal formation of PGM nuggets (model 2a), therefore, is discounted as the principal process of their origin.

Radiogenic Os may have been transported by a high-temperature fluid and amalgamated to existing alloys which were originally formed from the melt (model 2b). Osmium in the fluids may have been incorporated into the alloys, but not into erlichmanite, which would result in higher and varied $^{187}Os/^{186}Os$ ratios in Pt–Fe nuggets. In this model, laurite, cuprorhodsite, and osmium inclusions in Pt–Fe alloys should have nucleated as exsolution products of the alloy during the cooling of the Layered Complex, thus exhibiting similar $^{187}Os/^{186}Os$ ratios within individual nuggets. The presence of compositional zoning in laurite inclusions (Fig. 4a, b) and the morphology of PGM inclusions in Pt–Fe nuggets (Fig. 4a) do not appear to be consistent with this interpretation. The hydrothermal enrichment of ^{187}Os in some Pt–Fe nuggets, however, still may be considered as a remotely plausible mechanism. As mentioned above, the pristine igneous mineralogy of the Complex suggests that the hydrothermal activity must be constrained to high magmatic temperatures.

Remaining possible processes to produce high $^{187}Os/^{186}Os$ ratios in PGM phases are: (1) the low-temperature formation of the PGM nuggets; (2) growth of PGM nuggets during serpentinization; (3) formation during lateritization; (4) supergene growth in placers. The relatively pristine silicate mineralogy of the Complex below the limit of lateritization (Wells 1962) does not permit serpentinization to be the primary cause for PGM formation.

It has been suggested that tropical weathering conditions, such as those which occur in Sierra Leone, may produce highly saline acidic solutions which may transport PGE at low temperatures (Bowles 1986). The argument against a low-temperature sedimentary origin of PGM nuggets is based on the following evidence. First, surface waters in ultramafic terrains are usually alkaline ($pH > 10$) due to buffering of the solutions by silicate minerals (e.g., Barnes et al. 1978). Alkaline solutions would not dissolve significant PGE. Second, the mineralogy of PGM nuggets is not favorable for a low-temperature origin. It is difficult to form crystallographically oriented iridian osmium lamellae in Pt–Fe alloys at low temperatures. The texture is attributed to the exsolution of osmium from Pt–Fe alloys during the cooling (Cabri et al. 1981). Furthermore, sulphide inclusions in Pt–Fe alloy nuggets of placer origin, including laurite, sometimes show the effect of low-temperature alteration, which is probably due to instability of the sulphide in surface environments (Cabri and Genkin 1991). It is highly unlikely that euhedral laurite and cuprorhodsite inclusions in Pt–Fe alloys were formed under such low-temperature environments. Third, large variations in $^{187}Os/^{186}Os$ ratios in individual nuggets would be expected if they were formed at low-temperatures because

^{187}Os/^{186}Os ratios of surface waters would not necessarily be constant. The ^{187}Os/^{186}Os ratios of the bulk of the gabbros would be >6 at present (initial ^{187}Os/^{186}Os ratios of 1.1 and Re/Os = 34.8; Chou et al. 1983). The ^{187}Os/^{186}Os ratio of 6 is a minimum because Re/Os ratios of silicate phases would be much higher than the bulk gabbro due to concentration of Os in PGM nuggets. If the nuggets were growing in-situ during lateritization, they would be high in ^{187}Os due to incorporation of Os released from decomposing silicate phases. If the PGM formation took place in-situ, at least rims of grains or one of the grains would display high ^{187}Os/^{186}Os ratios. Lack of such data precludes the low-temperature growth of PGM nuggets as the principal process of their formation.

If may also be argued that isotopic homogenization took place within the individual nuggets at low temperatures. We believe that it is highly unlikely to assume isotopic equilibriation with surface waters while preserving their primary mineralogy and chemical zoning. The evidence presented above, although none is individually conclusive, is at least consistent in supporting the proposal of primary formation of PGM.

Summary

PGM nuggets associated with the Freetown Layered Complex, Sierre Leone, have ^{187}Os/^{186}Os ratios ranging from 1.08 to 2.06. The values for erlichmanite nuggets are low with a narrow range (1.08–1.09), but Os-bearing inclusions within Pt–Fe alloy nuggets have higher ^{187}Os/^{186}Os values (1.25–2.06). The results are consistent with the high and varied values observed from other layered mafic intrusions, such as the Bushveld (Hart and Kinloch 1989) and Stillwater Complexes (Martin 1989). The data, however, are different from the narrow spread in Os isotope ratios of PGM nuggets from Alpine-type ultramafic bodies (Hattori and Hart 1990). The high ^{187}Os/^{186}Os values of some PGM nuggets in the Freetown Layered Complex are attributed to relatively low Os contents in the original tholeiitic magmas compared with ultramafic magmas, low S contents in the magma, and the old age of the host rocks.

The data are consistent with the model that erlichmanite nuggets were formed early in the magma, as observed in many other mafic intrusions. Their ^{187}Os/^{186}Os ratios of ~ 1.08 reflect the values of source mantle at 200 Ma. Pt-group elements remained in the Os-depleted residual silicate melts because of low S in the melt. Due to low Os concentrations of the melts, the ^{187}Os/^{186}Os ratios may vary sharply in response to the degree of crustal contribution either by assimilation ($<10\%$) or by gaseous or fluid transport of Os from the Archaean host rocks. Although any one mechanism is possible, the lack of progressive change in mineralogy and chemistry of the Layered Intrusive Complex may suggest that the latter processes may have been more significant. The occurrence of abundant granulitized xenoliths in the lower sequences of the Freetown Layered Complex and extensive granulitization of the host-rock amphibolites near the Complex may support the release of Os from these rocks.

Sub-solidus hydrothermal activity for the formation of PGM nuggets is discounted on the basis of petrographic evidence and ^{187}Os/^{186}Os data. The lack of Os-isotopic variation within individual nuggets in spite of large variations in compositions and chemical zoning, the presence of oriented lamellae of osmium, the lack of inclusions of low-temperature minerals, the lack of weathering effects on sulphide grains, and the absence of high ^{187}Os/^{186}Os ratios, expected for the present-day formation, suggest that the nuggets were not formed during lateritization nor were they formed in-situ in sediments. The delicate morphology of PGM nuggets simply manifests very short transportation distances from the eroded site, as expected in eluvial (residual) deposits. The ^{187}Os/^{186}Os data are consistent with the formation of PGM nuggets in the melt and their detrital origin.

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References

Barnes I, O'Neil JR, Trescases JJ (1978) Present-day serpentinization in New Caledonia, Oman and Yugoslavia. Geochim Cosmochim Acta 42:144–145

Barnes S-J, Naldrett AJ, Gorton MP (1985) The origin of the fractionation of platinum-group elements in terrestrial magmas. Chem Geol 53:303–323

Beckinsale RD, Bowles JFW, Pankhurst RJ, Wells MK (1977) Rubidium-strontium age studies and geochemistry of acid veins in the Freetown Complex, Sierra Leone. Mineral Mag 41:501–511

Bowles JFW (1978) The geochemical role of primary copper-sulphur mineralization in the crystallization of the Freetown (Sierra Leone) Layered gabbro. Mineral Mag 42:111–116

Bowles JFW (1981) Distinctive suite of platinum-group minerals from Guma Water, Sierra Leone. Bull Mineral 104:478–483

Bowles JFW (1986) The development of platinum-group minerals in laterites. Econ Geol 81:1278–1285

Cabri LJ (1981a) The platinum-group minerals. In: Cabri LJ (ed) Platinum group elements: mineralogy, geology, recovery. CIM Spec Vol 23, pp 83–150

Cabri LJ (1981b) Nature and distribution of platinum-group element deposits. Episodes 1981-2:31–35

Cabri LJ, Feather CE (1975) Platinum-iron alloys: a nomenclature based on a study of natural and synthetic alloys. Can Mineral 13:117–126

Cabri LJ, Genkin AD (1991) Re-examination of Pt-alloys from lode and placer deposits, Urals. Can Mineral 29 no 3 (in press)

Cabri LJ, Laflamme JHG (1981) Analysis of minerals containing platinum-group elements. In: Cabri LJ (ed) Platinum group elements: mineralogy, geology, recovery, CIM Spec Vol 23, pp 151–173

Cabri LJ, Rosenzweig A, Pinch WW (1977) Platinum-group minerals from Onverwacht. I: Pt–Fe–Cu–Ni alloys. Can Mineral 15:380–384

Cabri LJ, Criddle AJ, Laflamme JHG, Bearne GS, Harris DC (1981) Mineralogical study of complex Pt–Fe alloy nuggets from Ethiopia. Bull Mineral 104, pp 508–525

Chou C-L, Shaw DM, Crocket JH (1983) Siderophile trace elements in the Earth's oceanic crust and upper mantle. J Geophys Res 88:A507–518

Harris DC, Cabri LJ (1991) Nomenclature of platinum-group-element alloys: review and revision. Can Mineral 29:231–237

Hart SR, Kinloch ED (1989) Osmium isotope systematics in Witwatersrand and Bushveld ore deposits. Econ Geol 84:1651–1655

Hattori K, Hart SR (1990) Osmium isotope ratios of PGM from Alpine-type ultramafic rocks and associated placers: EOS Trans Am Geophys Union 71:1713–1714

Hurley PM, de Almeida FFM, Melcher GC, Cordani UG, Rand JR, Kawashita K, Vandoros P, Pinson WH Jr, Fairbairn HW (1967) Test of continental drift by comparison of radiometric ages: Science 157:495–500

Keays RR, Crocket JH (1970) A study of precious metals in the Sudbury nickel irruptive ore. Econ Geol 65:439–450

Lambert DD, Morgan JW, Walker RJ, Shirey SB, Carlson RW, Zientek ML, Koski MS (1989) Rhenium-osmium and samarium-neodymium isotopic systematics of the Stillwater Complex. Science 244:1169–1174

Luck JM, Allègre CJ (1982) The study of molybdenites through the ^{187}Re-^{186}Os chronometer. Earth Planet Sci Lett 61:291–296

Luck JM, Allègre CJ (1983) ^{187}Re-^{187}Os systematics in meteorites; early chronology of the solar system and the age of the galaxy. Nature 283:256–259

Macfarlane A, Crow MJ, Arthurs JW, Wilkinson AF, Aucott JW (1981) The geology and mineral resources of northern Sierra Leone. Inst Geol Sci Overseas Mem 7

Martin CE (1989) Re-Os isotopic investigation of the Stillwater Complex, Montana. Earth Planet Sci Lett 93:336–344

Martin CE, Turekian KK (1987) Osmium isotopic systematics in abyssal peridotits: Implications for mantle evolution (abstract) Geol Soc Am Abstr 19:761

May PR (1971) Pattern of Triassic-Jurassic diabase dikes around the North Atlantic in the context of predrift position of the continents. Geol Soc Am Bull 82:1285–1292

Morel SW (1979) The geology and mineral resources of Sierra Leone. Econ Geol 74:1563–1576

Mountain BW, Wood SA (1988) Chemical controls on the solubility, transport and deposition of platinum and palladium in hydrothermal solutions; a thermodynamic approach. Econ Geol 83:492–510

Nixon GJ, Cabri LJ, Laflamme JHG (1990) Platinum-group element mineralization in lode and placer deposits associated with the Tulameen Alaskan-type Complex, British Columbia. Can Mineral 28:503–535

Ohnenstetter D, Watkinson DH, Jones PC, Talkington R (1986) Cryptic compositional variation in laurite and enclosing chromite from the Bird River Sill, Manitoba. Econ Geol 81:1159–1168

Palmer MR, Turekian KK (1986) ^{187}Os/^{186}Os in manganese nodules and the constraints on the crustal geochemistries of rhenium and osmium. Nature 319:216–220

Pegram WJ, Luck JM, Allegre CJ (1988) Osmium isotopic ratios from basalts. EOS Trans Am Geophys Union: 69:510

Pollett JD (1951) The geology and mineral resources of Sierra Leone. Colon Geol Miner Resour 2:3–28

Ravizza G, Turekian KK (1989) Application of the Re–Os system to black shale geochronometry: Geochim Cosmochim Acta 53:3257–3262

Stumpfl EF (1966) On the occurrence of native platinum with copper sulphides at Congo Dam, Sierra Leone. Overseas Geol Miner Resour 10:1–10

Talkington RW, Lipin BR (1986) Platinum-group minerals in chromite seams of the Stillwater Complex, Montana. Econ Geol 81:1179–1186

Taylor HP, Forester RW (1979) An oxygen and hydrogen isotope study of the Skaergaard intrusion and its country rocks: a description of a 55 M.Y. old fossil hydrothermal system. J Petrol 20:355–419

Walker RJ, Carlson RW, Shirey SB, Boyd FR (1989) Os, Sr, Nd, and Pb isotope systematics of southern African peridotite xenoliths: implications for the chemical evolution of subcontinental mantle. Geochim Cosmochim Acta 53:1573–1595

Walker RJ, Echerverria LM, Shirey SB, Horan MF (1990) Re–Os isotopic constraints on the origin of volcanic rocks, Gorgona Island, Columbia. EOS Trans Am Geophys Union 71:1696

Wells MK (1962) Structure and petrology of the Freetown Layered basic Complex of Sierra Leone. Overseas Geol Min Resour Bull Supp, 4

Wells MK, Bowles JFW (1981) The textures and genesis of metamorphic pyroxene in the Freetown Intrusion; Mineral Mag 44:245–255

Williams HR, Williams RA (1976) The Kasila Group, Sierra Leone, an interpretation of new data. Precambrian Res 3:505–508

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