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DETRITAL PLATINUM-GROUP MINERALS IN RIVERS DRAINING THE GREAT DYKE, ZIMBABWE

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ABSTRACT

The present work focuses on the description of the assemblage of detrital platinum-group minerals (PGM) found in rivers draining the Great Dyke. This PGM assemblage distinctly contrasts with the suite of PGM in the pristine, sulfide-bearing Main Sulfide Zone (MSZ) of the Great Dyke, the assumed source of the detrital PGM. Specifically, PGE-bismuthotellurides and -sulfarsenides, common in the MSZ ores, and PGE-oxides or -hydroxides present in the oxidized MSZ, are missing in the assemblage of detrital PGM in the fluvial environment. Instead, conspicuously high proportions of grains of Pt-Fe alloy are common in the sediments, followed by sperrylite, cooperite, braggite, laurite, rare Pd-Sb-As compounds, and Os-Ir-Ru alloys. Possibly, some of the Pt-Fe alloy grains originate from the MSZ, but the majority appear to represent true neo-formations that formed in the course of weathering of the MSZ ores and concomitant supergene redistribution of the ore elements. Sperrylite, cooperite/braggite, and laurite appear to be direct descendants from the primary MSZ. Rare Pd-dominated minerals (Pd-Hg ± As and Pd-Sb ± As) are considered to be neo-formations that probably formed from dispersed elements during supergene processes. Os-Ir-Ru alloy grains, present in the samples from the Umtebekwe River in the Shurugwi area, possibly originate from the Archean chromitite deposits of the Shurugwi greenstone belt and not from the Great Dyke. Geochemically, the Pt/Pd proportions increase from pristine via oxidized MSZ ores to the fluvial environment, corroborating earlier findings that Pd is more mobile than Pt and is dispersed in the supergene environment.

Detrital PGM can be expected to be present in rivers draining PGE-bearing layered intrusions, and economic placers may form under particular sedimentological conditions. Therefore, the work also highlights the fact that simple field methods have their value in mineral exploration, especially if they are combined with modern micro-analytical methods.

Furthermore, it is established that the PGE-bismuthotellurides, PGE-sulfarsenides, and PGE-oxides, dominating the PGM assemblages in the pristine and oxidized MSZ, are components that are unstable during weathering and mechanical transport. Including the genetically somewhat disputed Pt-Fe alloys, the order of decreasing stability in the supergene environment is as follows: (1) Pt-Fe and Os-Ir-Ru alloys (very stable) → (2) sperrylite (stable) → (3) cooperite/braggite (variably stable/"meta-stable") → (4) PGE-bismuthotellurides, PGE-sulfarsenides, and PGE-oxides (unstable).

Keywords: Great Dyke, Zimbabwe, alluvial sediments, Pt-Fe alloy, Os-Ir-Ru alloy, sperrylite, cooperite/braggite, Pd-bearing PGM, gold, awaruite, origin

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INTRODUCTION

Placer deposits were the only source of platinum-group elements (PGE) for over two thousand years. Colombia and the Urals constituted the main sources of PGE up to early in the 20th century, when the rich primary deposits of the Bushveld Complex of South Africa, the Sudbury district in Canada, and later Norilsk in Russia came into production (Mertie 1969, Cabri *et al.* 1996, Weiser 2002). Today, only about 1% of world PGE production originates from placers, mainly in the Russian Far East (*ca.* 5 t Pt; Piskulov 2012) and in Colombia.

The most productive PGE placer deposits are associated with “Alaskan” or “Uralian”-type ultramafic-mafic complexes in tectonic belts; smaller placer deposits are related to “Alpine-type” intrusions (ophiolite complexes) and are usually subeconomic (*e.g.*, Weiser 2002). Notably, the discovery of detrital platinum-group minerals (PGM) in gravels on the Maandagshoek farm, in the then eastern Transvaal, South Africa, led to the discovery of the largest known PGE deposits on Earth in the Bushveld Complex in 1924 (Merensky 1924, 1926, Wagner 1929, Cawthorn 1999, Oberthür *et al.* 2004). Despite this, only limited knowledge has emerged during the last 90 years regarding the mineralogy and mineral chemistry of detrital PGM in rivers draining the great layered intrusions (Bushveld, South Africa; Great Dyke, Zimbabwe; Stillwater, USA) that host the overwhelming proportion of mineable PGE. The present study intends to close this gap of knowledge on the Great Dyke of Zimbabwe.

The Great Dyke of Zimbabwe constitutes the world’s second largest resource of platinum group elements (PGE) after the Bushveld Complex in neighboring South Africa (Sutphin & Page 1986, Vermaak 1995, Zientek 2012). However, after a number of intermittent unsuccessful attempts of mining between 1926 and the 1970’s, production of PGE only commenced in the 1990’s at the Hartley Platinum Mine (now under care and maintenance), some 70 km SW of Harare; today, the Ngezi, Unki, and Mimosa mines are in production.

The Great Dyke (2575.4 ± 0.7 Ma; Oberthür *et al.* 2002) is a layered intrusion of linear shape that strikes over 550 km NNE with a maximum width of about 11 km, intruding Archean granites and greenstone belts of the Zimbabwe Craton (Worst 1960). Stratigraphically, it is divided into a lower Ultramafic Sequence with narrow layers of chromitite at the base of cyclic units, and an upper Mafic Sequence mainly consisting of plagioclase-rich rocks. Economic concentrations of PGE, Ni, and Cu are found *ca.* 10–50 m below the transition from the Ultramafic to the Mafic Sequence, in the several meters thick “Main Sulfide Zone” (MSZ), in pyroxenitic host rocks (Prendergast 1988, Prendergast & Wilson 1989).

The MSZ is characterized by disseminated intercumulus sulfides (pyrrhotite, pentlandite, chalcopyrite,

and rare pyrite). In the MSZ, the PGE are bimodally distributed; they are present as discrete PGM, and in solid solution in sulfides, mainly pentlandite (*e.g.*, Weiser *et al.* 1998, Oberthür 2002, 2011). In addition, subeconomic PGE concentrations occur within the chromitite layers of the Great Dyke (Slatter 1980, Evans *et al.* 1996, Germann & Schmidt 1999, Oberthür 2002, 2011).

Only sparse mention is found in the literature with respect to the possibility of placer accumulations of PGM in stream sediments along the Great Dyke (Maufe 1919, 1923, Gordon, 1923), as compiled by Prendergast (1988, p. 20–21). The latter author also comments on Pt and Au from the Moonie creek and the Umtebekwe River, SE of Shurugwi, and that the Moonie creek occurrence points to the Shurugwi chromitite terrain as the most likely source of the Pt. An early report on anomalous Pt contents obtained by fire assay in concentrates from rivers along the Great Dyke close to Shurugwi (Selukwe Subchamber) is from a prospecting campaign for gold and “platinum” performed by Gordon (1923). Results of a reconnaissance study on alluvial PGM in the environs of the Great Dyke were published by Oberthür *et al.* (1998, 2003b) who reported rare grains of sperrylite, Pt-Fe alloy, Os-Ir-Ru alloy, atheneite, and isomertieite in heavy mineral concentrates from various rivers along the Great Dyke.

One aim of the present work is to investigate the supergene mobility of PGE in the weathering environment. Therefore, it appeared promising to look into the final erosion products in sediments of rivers draining the Great Dyke in order to study the heavy mineral spectra and possibly identify detrital PGM. A sampling program along the Great Dyke was performed with the following objectives in mind: (1) Test the presence of detrital PGM, (2) Mineralogical characterization of the PGM, (3) Evaluation of their relationship to the suite of primary PGM of the MSZ, and (4) Obtain data on the stability of PGM and the supergene mobility of PGE in the weathering environment.

SAMPLES AND METHODS

All our sample locations are on or close to the Great Dyke (<1 km away). Sediment samples weighing between 25 and 100 kg (locally more as described below) of coarse to fine grained sediments were taken within streams or on river banks at 28 localities along the Great Dyke. The main sampling locations are shown in Figure 1 and are described here in brief:

Great Dyke – North

Fundumwi River (30°59’20.0”E, 16°26’09.7”S). Point 1 in Figure 1; north of Snake’s Head, flowing into the Zambesi valley. One grain of sperrylite (diameter 120 µm) from 36 kg of material < 2 mm.

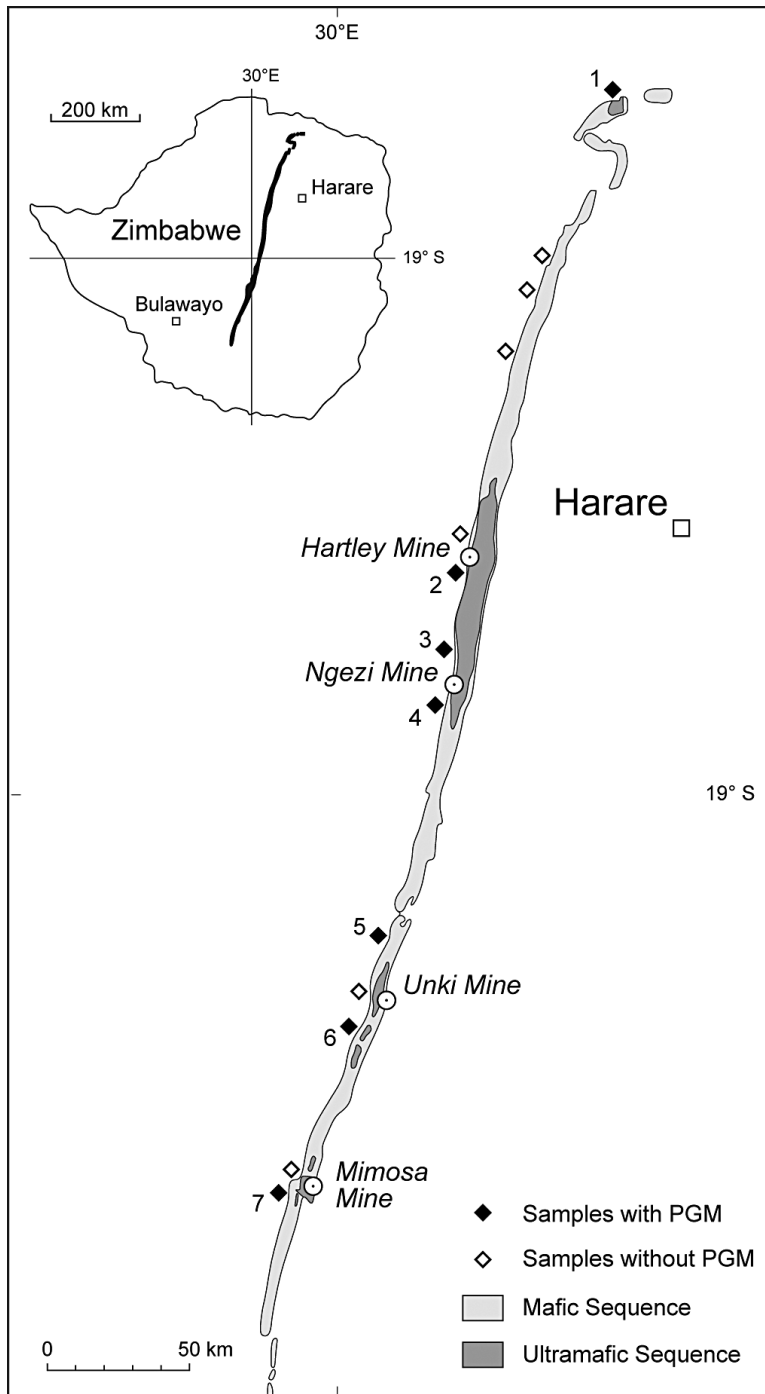


FIG. 1. Geology of the Great Dyke showing the distribution of the Ultramafic and the Mafic Sequence, after Wilson & Prendergast (1989). Stream sampling localities are also shown (heavy mineral concentrate sample with filled diamonds and without (open diamonds) PGM grains).

River at Caesar Chrome Mine (30°39'00.4"E, 17°14'11.4"S). The chromite-rich concentrate contained four grains of awaruite (Ni₃Fe), three grains of gold, but no PGM.

Hartley Mine area

Makwiro River (30°25'05.8"E, 18°02'27.6"S; 30°25'25.0"E, 18°04'00.0"S). Point 2 in Figure 1. During three sampling campaigns, some hundred kg of sediments <2 mm in total were treated. Heavy mineral concentrates from the Makwiro River comprised grains of chromite (>90%), magnetite, rutile, ilmenite, zircon, monazite, rare pyrite and pentlandite, an awaruite-like phase with composition [Ni₃(Fe,Cu)], as well as 161 PGM and 282 gold grains (Table 1). Taking into account grain sizes and Pt contents of the PGM, Pt contents between 0.005 and 0.022 g/t (ppm) were calculated for the gravel. Mineralogically, sperrylite and Pt + Pt-Fe alloy grains predominate, followed by cooperite/braggite and other PGM like potarite and atheneite (Table 1). PGM grain sizes range from 65–480 µm (mostly between 150–200 µm), and gold grains from 50–750 µm.

Ngezi Mine area

Umsweswe River (30°21'02.0"E, 18°29'48.3"). Point 3 in Figure 1. Pt and Pt-Fe alloy (20 grains), sperrylite (2), and unnamed ["RhS"] (1), as well as 65 gold grains from 73 kg of material <2 mm.

Ngezi River (30°19'56.6"E, 18°42'45.0"S). Point 4 in Figure 1. One grain of Pt-Fe alloy only from 60 kg of sediment <2 mm.

Unki Mine area

Umtebekwe River (North) (30°05'44.6"E, 19°30'40.0"S). Point 5 (3 near-by locations) in Figure 1. Nine PGM grains; Pt + Pt-Fe alloy (7), cooperite/braggite (1), and stibiopalladinite (1) from 84 kg of sediment <2 mm.

Umtebekwe River (South); terrace; close to Moonie Creek. (30°00'35.0"E, 19°46'18.0"S). Point 6 in Figure 1. At this highly productive location, a number of concentrates, together containing ca. 7 g of gold, were bought from artisanal miners working the gravels along the river. Observations at site, based on gravel quantities and gold contents, allow an estimate of the average gold tenor of 1.57 g/t Au for the gravels. The ratio by number of gold/PGM grains is probably about 1000/1. Altogether 151 PGM grains covering a wide range of compositions (see Table 2) and numerous gold grains were obtained for our studies. Notably, Os-Ir-Ru alloy grains are only found at this locality.

Moonie Creek (30°00'32.5"E, 19°44'56.6"S). This river drains the Mont d'Or area of the Shurugwi greenstone belt. It is a true gold placer, and again, a number of gold concentrates were bought from artisanal miners working the gravels along the river. The main heavy mineral component is chromite, followed by magnetite, rare hematite, pyromorphite (?), cassiterite, scheelite, monazite, and considerable amounts of zircon. Silver-rich gold (up to 3 mm in diameter) and gold-amalgam (in samples only from this location, probably produced by the local artisanal miners) were detected. Based on gravel quantities and gold output, the estimated grades of the gravels range from ca. 1.5 to 6 g/t Au. Notably, no PGM were found in the concentrates obtained from the Moonie creek occurrence whose placers were intensively mined for gold at the time of our sampling

TABLE 1. INVENTORY OF DETRITAL PGM IDENTIFIED IN SEDIMENT SAMPLES IN RIVERS DRAINING THE GREAT DYKE, ZIMBABWE, BASED ON SEM/EDAX DATA OF INDIVIDUAL GRAINS

Mine area Rivers	Hartley Makwiro	Ngezi Umsweswe	Unki Umtebekwe*	Mimosa Umts + Ma ⁺	SUM	%
Pt	24		15	2+3	44	11.3
Pt-Fe	29	21	58	10+2	120	30.8
PtAs ₂	76	2	76	13+11	178	45.6
PtS	24	1	1		26	6.7
PdHg(As)#	8		1	1	10	2.6
PdSb ⁺			3		3	.8
Os-Ir-Ru alloy			8		8	2.0
OsS ₂			1		1	.2
n PGM grains	161	24	163	25+17	390	
n gold grains	282	84	+++	++		

Remarks and abbreviations: Unki Mine area: Umtebekwe* = Umtebekwe (160) + Umtebekwana (3); Mimosa Mine area: Umts + Ma⁺ = Umshingwe(25) + Maholo (17). PdHg(As)# = potarite and atheneite. PdSb⁺ = Pd-Sb-(As) minerals.

TABLE 2. INVENTORY OF PGM (DETRITAL GRAINS AND INCLUSIONS) IDENTIFIED IN POLISHED SECTIONS AND ANALYZED BY ELECTRON MICROPROBE

Mineral	Formula	Mine areas [rivers]			
		Hartley [Makwiro]	Ngezi [Umsweswe (+ Ngezi)]	Unki [Umtebekwe]	Mimosa [Umtshingwe (+ Maholo)]
platinum	Pt	•		•	•
ferroan platinum	PtFe	•	•	•	•
ferroan platinum	(Pt,Pd)Fe		•	•	•
tetraferroplatinum	PtFe			•	
tulameenite	Pt ₂ FeCu		○	○	
ferronickelplatinum	Pt ₂ FeNi			○	
osmium	Os-Ir-Ru alloy			•○	
rhodium	Rh-Pt-Ru alloy			•	
cooperite	PtS	•		•	
braggite	(Pt,Pd)S	•			
laurite	RuS ₂	○	○		○
erlichmanite	OsS ₂			•	
bowieite	Rh ₂ S ₃				•
cuproiridsite	CuIr ₂ S ₄		○		
sperrylite	PtAs ₂	•	•	•	•
majakite	PdNiAs	○			
palladodymite	(Pd,Rh) ₂ As		○		
hollingworthite	RhAsS	○			
stibiopalladinite	Pd ₅ Sb ₂			•	
arsenopalladinite	Pd ₅ (As,Sb) ₃	•○			
isomertieite	Pd ₁₁ (Sb,As) ₄			•	
vincentite	Pd ₃ (As,Sb,Te)	○			
sobolevskite	PdBi			○	
rustenburgite	Pt ₃ Sn				•
potarite	PdHg	•		○	•
atheneite	Pd ₂ (As,Hg)	•		•	
gold	Au-Ag	•	•	•○	•
gold alloy	Au-Pd-Hg			•	
unnamed	(Ir,Pt)(Fe,Ni) ₂ S ₃	○			
unnamed	Pd ₂ (Ni,Cu)S		○		
unnamed	Pd ₃ Te		○		
unnamed	Pd ₃ (Pb,Hg)			•	
unnamed	RhS		•○		
unnamed	RhNi ₂ S ₃		○		
unnamed	Ni ₃ S ₂	○			
awaruite	Ni ₃ Fe	•			
Cu-bearing awaruite	Ni ₃ (Fe,Cu)	•			
Pt-bearing awaruite	(Ni,Pt,Ir) ₃ Fe	○	○		

• = single detrital grains. ○ = inclusions in and intergrowths with other PGM.

campaign. Platinum-group minerals are present only in the Umtebekwe River and its terraces. This indicates, in contrast to earlier assumptions (Zealley 1918, Worst 1960, Stowe 1968, and others in the compilation of Prendergast 1988), that the PGM in the Umtebekwe River likely originate from the Great Dyke, rather than from the Shurugwi greenstone belt.

Umtebekwana (30°03'05.6"E, 19°46'02.7"S). 3 Pt-Fe alloy grains in 69 kg of sediment <6.3 mm.

Mimosa Mine area - Point 7 in Figure 1

Umtshingwe River, 29°49'04.3"E, 20°21'56.7"S. Location ca. 4.3 km south of the Mimosa mine; 25 PGM grains (mainly Pt and Pt-Fe alloys, some sperrylite, and one grain each of rustenburgite and laurite) as well as 55 mg of gold (grade ca. 0.24 g/t) from 232.5 kg of sediment <6.3 mm. Gold probably originates from the near-by greenstone belts.

Chitedza River (Maholo?) 29°44'26.9"E, 20°20'52.6"S. Location ca. 9.1 km southwest of the Mimosa mine, west side of Great Dyke. The Chitedza River flows into the Umtshingwe River. 17 PGM grains (mainly Pt and Pt-Fe alloys, some sperrylite, and one grain each of potarite and bowieite) from 63.5 kg of sediment <6.3 mm.

The samples were screened in place to remove coarser material. After weighing, the finer grained (<6.3 mm; mostly <2 mm only) fractions were panned by hand to obtain heavy mineral pre-concentrates, which were collected in bottles in the field. Final treatment in the laboratories of BGR comprised panning and sieving into various <2 mm size fractions, and the investigation of the final concentrates was conducted under a binocular microscope. Altogether 390 PGM grains were recovered from the concentrates. The highest quantities of PGM were found in areas where the remnants of the Upper Mafic Sequence, and consequently, the Main Sulfide Zone, are present. Lightfoot (1926) previously remarked that the absence of flood plains or alluvial terraces of the perennial streams reduced the prospects of finding alluvial deposits of platinum.

The mineral grains were mounted on SEM sample holders and investigated with a scanning electron microscope (SEM) with an attached energy-dispersive X-ray system (EDAX). Following this step, grains of interest were embedded in resin and polished sections were prepared for subsequent electron-probe microanalysis (EPMA).

The instruments used were a CAMEBAX and a CAMECA SX100 electron-probe at the BGR. Analytical conditions were: Accelerating voltage 20 kV, specimen current 30 nA, and measurement times 10 s. Standards and X-ray lines were: RuL α , RhL α , OsM α , IrL α , AuL α , AgL β , NiK α , SeK α , TeL α , BiM α , SnL α (metals), PtL α and FeK α (Pt₃Fe alloy), PdL α (PdS), SK α (PtS), AsL α (GaAs), PbM α (galena), and SbL α (stibnite). Raw data were corrected using the PAP program (Pouchou & Pichoir 1991) supplied by CAMECA. Additional corrections were performed for overlaps of Rh, Pd, Ag, Cu, As, and Sb with secondary lines. Detection limits for the elements listed are ca. 0.1 wt.%. Altogether, 267 quantitative analyses were carried out on 153 grains of PGM.

RESULTS

The present work provides the first comprehensive description of the assemblage of detrital PGM found in rivers draining the Great Dyke. Detrital PGM were identified at the localities shown in Figure 1. In general, the heavy mineral spectrum of the rivers sampled along the Great Dyke comprises chromite, magnetite, hematite, ilmenite, rutile, leucoxene (all ubiquitous), and rarer Mn-columbite, cassiterite, scheelite, monazite, zircon, garnet, pyromorphite (?), pyrite, pentlandite, arsenopyrite, gold (common), an awaruite-like mineral

[Ni₃(Fe,Cu)] – “Cu-bearing awaruite”, and rare PGM. Obviously, some of these minerals, including variable proportions of the gold grains, originate from the granite-greenstone terrains surrounding the Great Dyke. Anthropogenic contamination consisted of gold-al amalgam (very common at Moonie creek), splinters of iron and brass, metallic Pb, and Zn.

Platinum-group minerals were found along the Great Dyke (from N to S in Fig. 1) in the areas close to Hartley Mine (Makwiro River), Ngezi mine (Umsweswe and Ngezi Rivers), Unki mine [Umtebekwe River N and S (north of Shurugwi = N; and south of Shurugwi, in terraces close to the confluence with Moonie Creek = S, and Umtebekwana (Little Umtebekwe) River], and in the Umtshingwe and Chitedza (Maholo) Rivers south of the Mimosa mine. On a regional scale, detrital PGM are only present in areas along the Great Dyke where the Mafic Sequence (stippled in Fig. 1) is exposed, *i.e.*, where the Main Sulfide Zone is present (just ca. 10–50 m below) the contact of the Mafic and the underlying Ultramafic Sequence).

SEM OBSERVATIONS

Platinum-group minerals grains identified in the concentrates were characterized by scanning electron microscope (SEM) investigations (Table 1). It must be noted, however, that although SEM investigations are valuable in the study of grain morphologies and allow obtaining semi-quantitative analytical data for mineral grains, the SEM analyses are performed on the surfaces of grains only. Therefore, thin crusts on the grains or overgrowths may produce compositions that differ from those of the internal cores of the grains. Indeed, polished section studies and the electron-probe microanalyses demonstrate that some PGM grains assigned to native Pt or Pt-Fe alloy had cores of cooperite, braggite, or, in rare cases, sperrylite. This must be taken into consideration regarding PGM proportions obtained by SEM in Table 1.

Mineral proportions were obtained by SEM surface analysis using the energy-dispersive analytical system (EDAX) attached to the SEM (n = 390 grains): The PGM assemblage is mainly composed of grains of sperrylite (45.6% by number of grains), native Pt and Pt-Fe alloys (together 42.1%), the Pt-Pd sulfides cooperite and braggite (6.7%), and a number of rarer Pd-bearing PGM (3.4%). Notably, cooperite and braggite are more common in the samples from the Hartley Mine area, and Os-Ir-Ru alloy grains (2.0%) were found only in samples from the Umtebekwe River south of the Unki mine. Remarkably, PGE-bismuthotellurides (*e.g.*, merenskyite, michenerite) and PGE-sulfarsenides (*e.g.*, hollingworthite, irarsite), common in the pristine MSZ ores (*e.g.*, Oberthür *et al.* 2003a, Oberthür 2002, 2011), are missing in the detrital PGM assemblage. Furthermore, the predominance of Pt-bearing PGM is conspicuous. Most PGM are monomineralic grains,

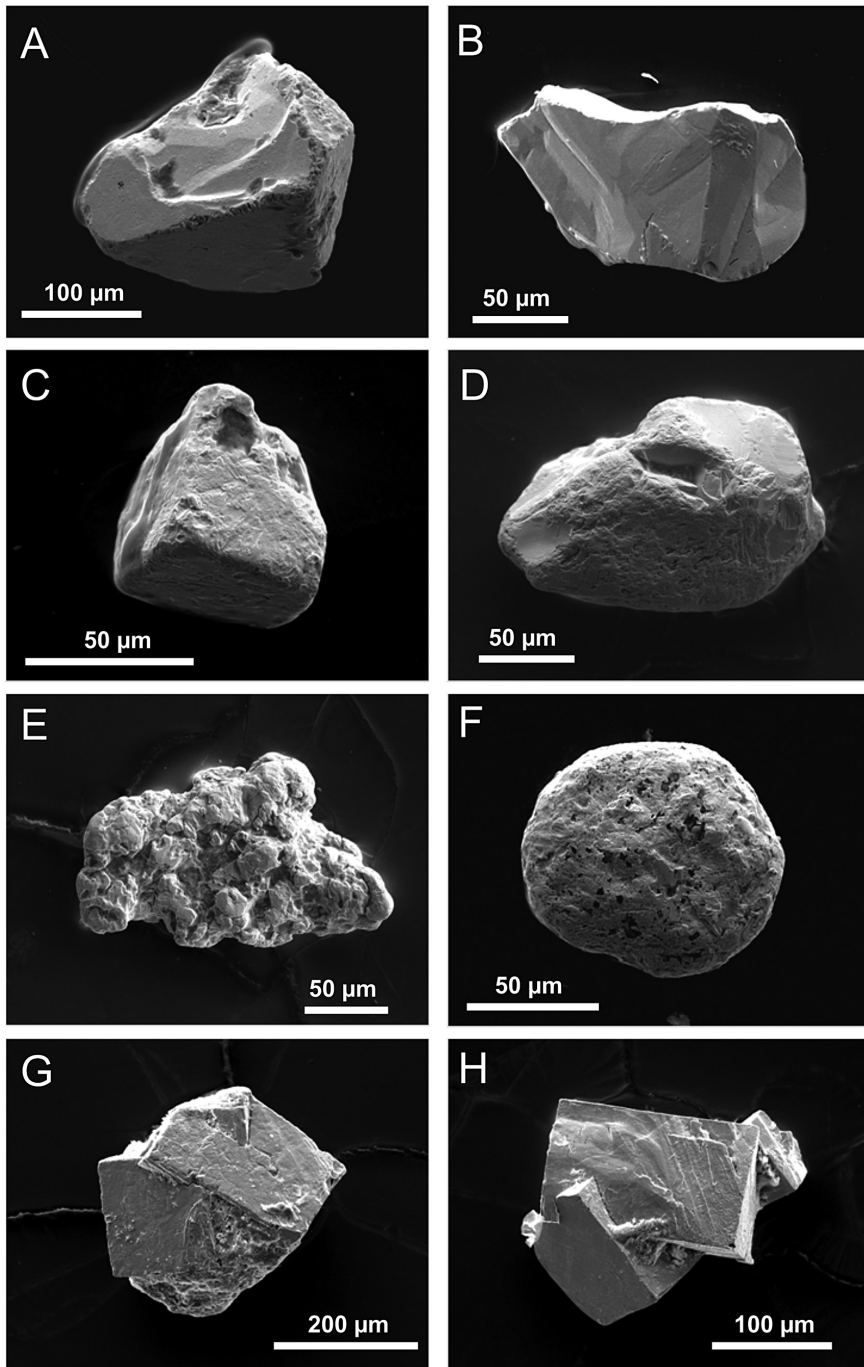


FIG. 2. Scanning electron microscope images (SEM) of individual PGM grains, Hartley Mine area (all Makwiro River). (A) Sperrylite grain with crystal faces showing little attrition. Grain 1131. (B) Well-crystallized grain of sperrylite. Grain 4443. (C) Grain of Pt-Fe alloy showing cubic crystal faces and smooth surface polish. Grain 4446. (D) Grain of cooperite with partly abraded surface. Grain 4406. (E) Aggregate of potarite (PdHg). Grain 4431. (F) Round gold grain with silicate inclusions (dark). Grain 1003. (G) Cubic crystals of “Cu-bearing awaruite” $[\text{Ni}_3(\text{Fe,Cu})]$. Grain 1301. (H) Cubic crystals of “Cu-bearing awaruite” penetrating each other. Grain 1305.

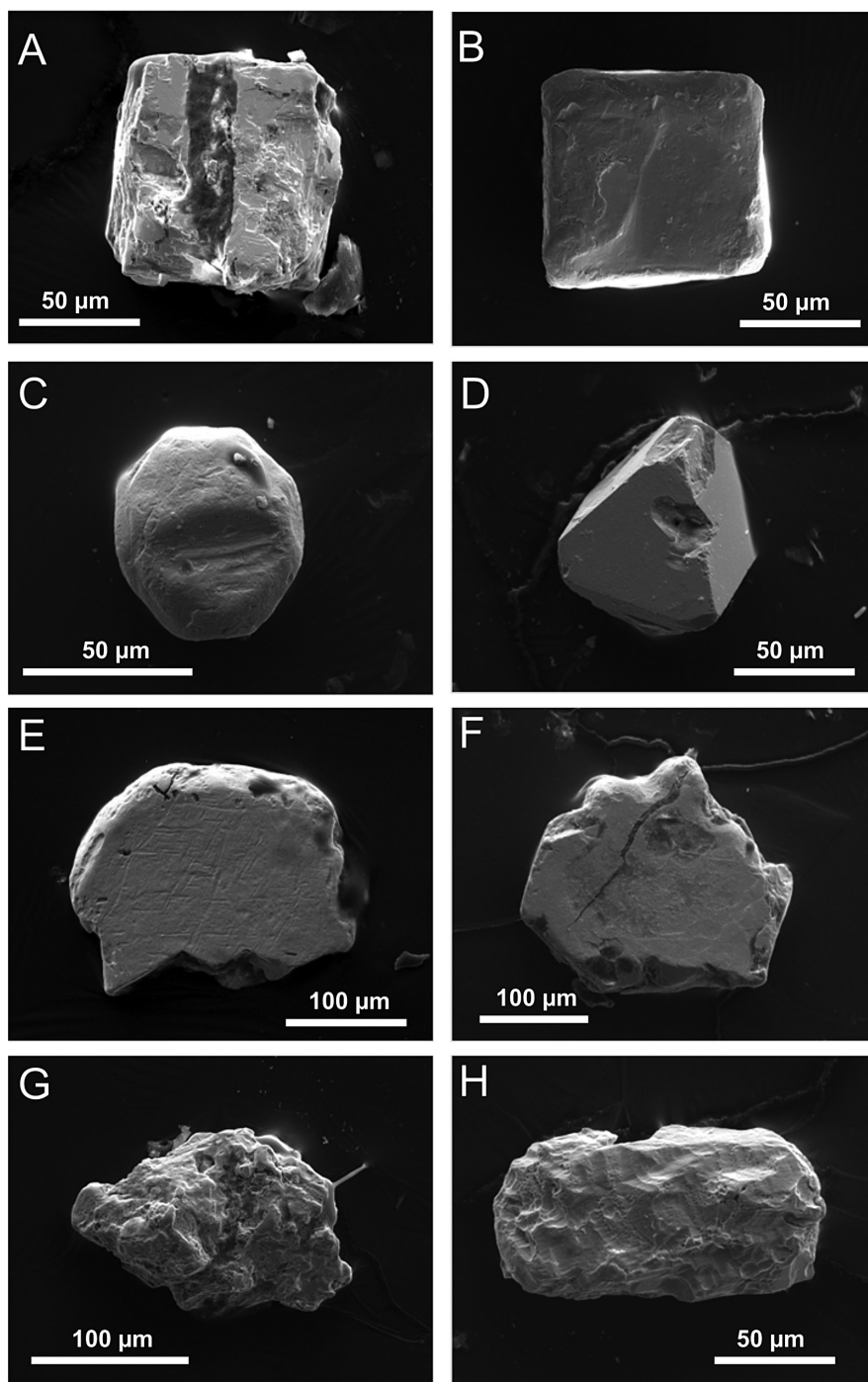


FIG. 3. Scanning electron microscope images (SEM) of individual PGM grains, Unki Mine area [Umtebekwe and Umtebekwana (B) Rivers]. (A) Cubic grain of Pt-Fe alloy with a silicate inclusion (darker; center). Grain 2106. (B) Well-crystallized grain of Pt-Fe alloy with smooth surface. Grain 5957. (C) Well-crystallized grain of Pt-Rh-Fe alloy. Grain 4362. (D) Sperrylite crystal. Grain 5836. (E) Os-Ir alloy grain. Note hexagonal surface linings. Grain 4224. (F) Os-Ir-Ru alloy. Grain 5871. (G) Aggregate of probable isomertiete $[\text{Pd}_{11}(\text{Sb,As})_4]$. Grain 2112. (H) Crystalline potarite (PdHg). Grain 2136.

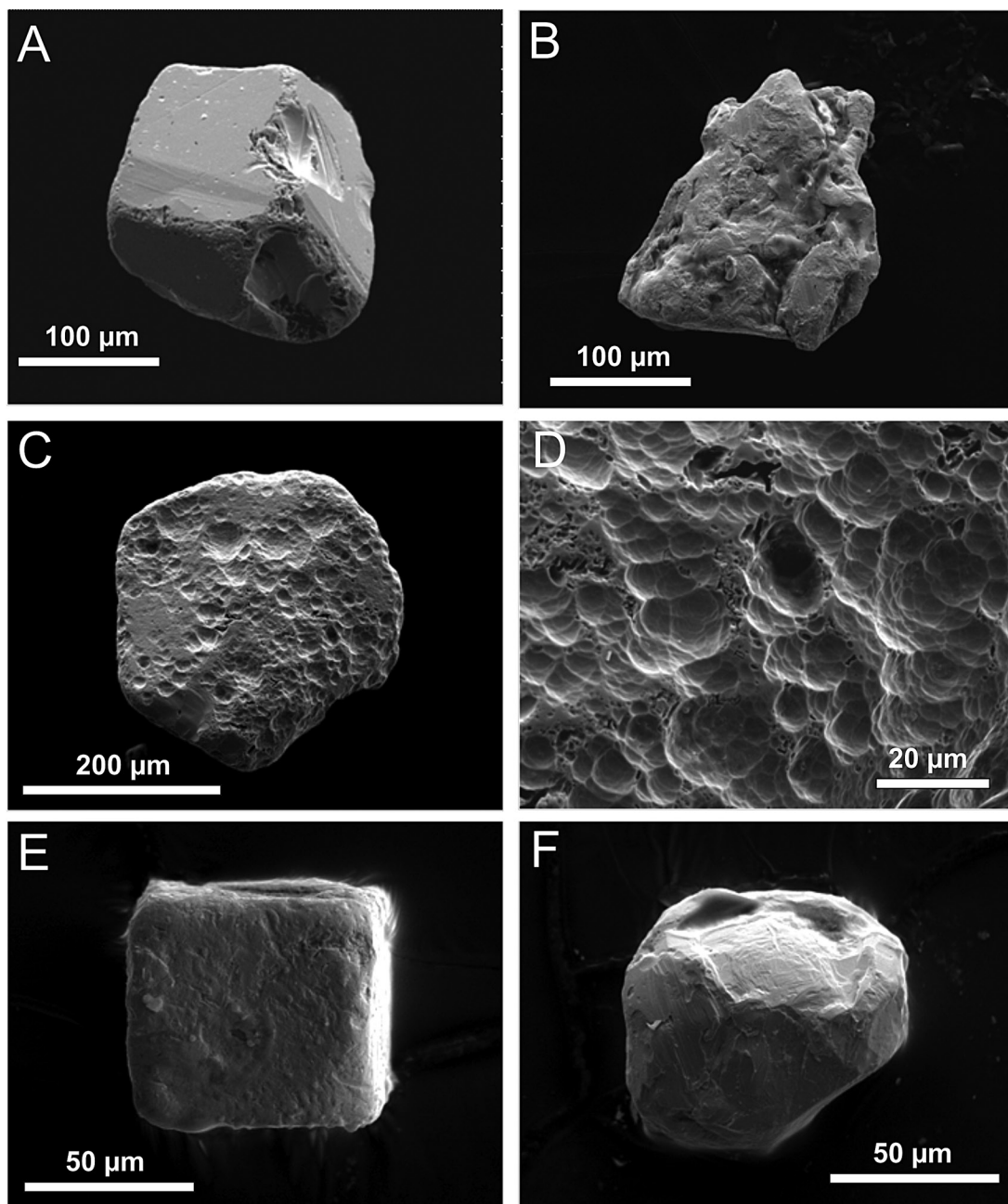
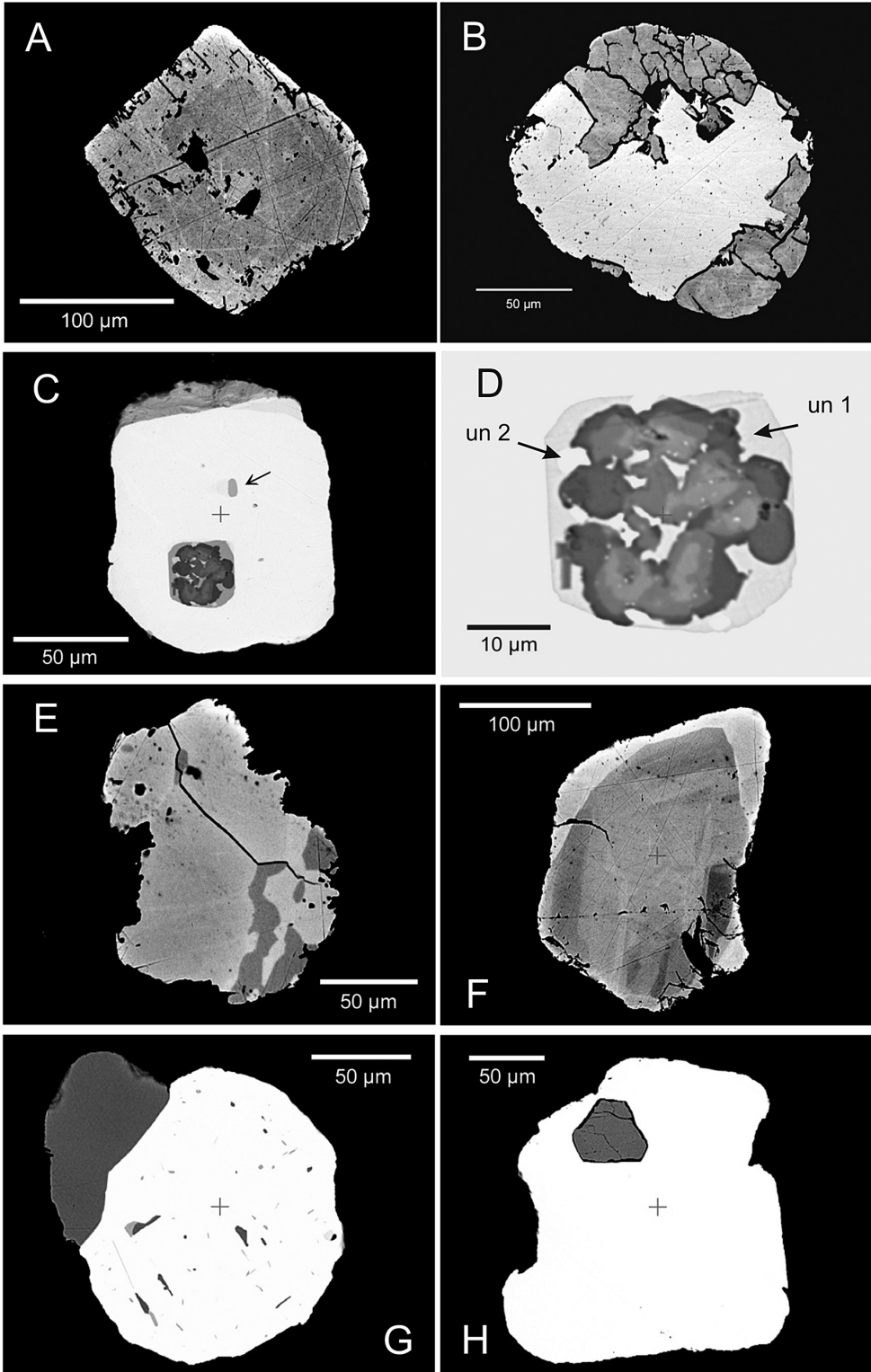


FIG. 4. Scanning electron microscope images (SEM) of individual PGM grains, Mimosa Mine area [Umtshingwe and Maholo (F) Rivers]. (A) Well-crystallized grain of sperrylite. Grain 1028. (B) Pt-Pd-Fe alloy. Grain 1029. (C) Large sperrylite grain with numerous pocks on the surface. Grain 1025. (D) Magnification of surface. Grain 1025 (C). (E) Cubic grain of Pt-Fe alloy with abraded surface. Grain 4885. (F) Grain consisting of Pt only. Grain 5935.



however, a number of intergrowths, mainly between Pt-Fe alloy and laurite, were observed, and also various inclusions of different minerals in the detrital PGM grains (details further below). Grain sizes of the detrital PGM range from 90 to 300 μm (mostly between 100–200 μm); maximum grain sizes measured are 480 μm (sperrylite), and 285 μm (Pt-Fe alloy grain). In comparison, the apparent grain sizes of PGM measured in polished sections range from <5 to 50 μm in diameter and exceptionally reach 200 μm in the longest dimension (Oberthür *et al.* 2003a, Oberthür 2002, 2011). However, a test using electric pulse disintegration on one sample of pristine MSZ, weighing about 1 kg, resulted in the recovery of 75 PGM grains larger than 50 μm (Oberthür *et al.* 2008). The observed maximum true diameters were 480 μm for (Pt,Pd)-bismuthotellurides (moncheite), 85 μm for sperrylite, 195 μm for cooperite/braggite, and 300 μm for Pt-Fe alloy grains. Examples of PGM grains from the Hartley, Unki, and Mimosas areas are shown in Figures 2, 3, and 4.

Pt-Fe alloy grains have various surface morphologies. Cubic crystal grains with abraded surfaces are common (Figs. 2C, 3A,B,C, 4E), but most grains show various degrees of attrition with rounded shapes and smooth grain surfaces (Fig. 4B) due to the physical softness of this mineral group.

Sperrylite grains are generally multi-faceted single crystals without obvious signs of corrosion or mechanical wear (Figs. 2A,B, 3D, 4A). Figures 4C and D show a somewhat unusual large grain with many pits on the surface.

FIG. 5. Backscatter electron images of PGM in polished sections. (A) Cubic, zoned grain of Pt-Fe alloy. Core has 0.75 wt.% Pd, rim is devoid of Pd. Makwiro River. (B) Pt-Pd-Fe alloy (light; 7.7 wt.% Pd) intergrown with ferrornickelplatinum (darker, partial rim; analysis No. 7 in Table 3). Umtebekwe River. (C) Pt-Pd-Fe alloy with various small and one large inclusion. Oval inclusion (medium gray; arrow) is palladodymite (Analysis No. 12 in Table 5). Umsweswe River. (D) Magnification of large, complex inclusion from Figure 5C. Included minerals are: outer rim, light gray (un 1) is unnamed $\text{Pd}_2(\text{Ni,Cu})\text{S}$ (Analysis No. 3 in Table 6). Un 2 (white) is unnamed Pd_3Te (Table 6, analysis 4). Main, worm-like mineral (medium gray in center and darker gray towards the rim) is unnamed RhNi_2S_3 (Table 6, analysis 7). (E) Vincentite $[\text{Pd}_3(\text{As,Sb,Te})]$ (dark grey; analysis 4 in Table 5) intergrown with atheneite $[\text{Pd}_2(\text{As,Hg})]$ (light grey; analysis 2 in Table 5). Makwiro River. (F) Zoned grain of cooperite-braggite; lighter areas have higher Pt/Pd ratios. Makwiro River. (G) Well-rounded grain of Pt-Fe alloy (white) with numerous inclusions of various PGM (palladodymite, unnamed RhS and unnamed Pd_3Te ; see text), intergrown with unnamed $\text{Rh}(\text{Ni,Cu})_2\text{S}_3$ (dark grey; top left). Umsweswe River. (H) Grain of Pt-Fe alloy (white) with idiomorphic inclusion of laurite. Umsweswe River.

The (Pt,Pd)-sulfides cooperite and braggite are mainly present as splintered, broken grains not illustrated here.

Other PGM recorded and shown here are aggregates of potarite (PdHg) (Figs. 2E, 3H), alloys with compositions in the system Ru-Os-Ir (Figs. 3E,F), isomertieite $[\text{Pd}_{11}(\text{Sb,As})_4]$ (Fig. 3G), and the well-crystallized phase with the composition $[\text{Ni}_3(\text{Fe,Cu})]$ - “Cu-bearing awaruite” (Figs. 2G,H). Gold grains are numerous and far more frequent than PGM grains. Larger gold grains are commonly flakes with bent edges, whereas smaller grains tend to be present as equidimensional grains with smooth surfaces (Fig. 2F).

ELECTRON-PROBE MICROANALYSIS

Proportions of PGM investigated by electron-probe differ from those investigated by SEM, also owing to preferential selection of rarer phases for analysis. Nomenclature and formulae given by Cabri (2002) are adapted for approved PGM. Table 2 summarizes PGM detected and their preferred mode of occurrence.

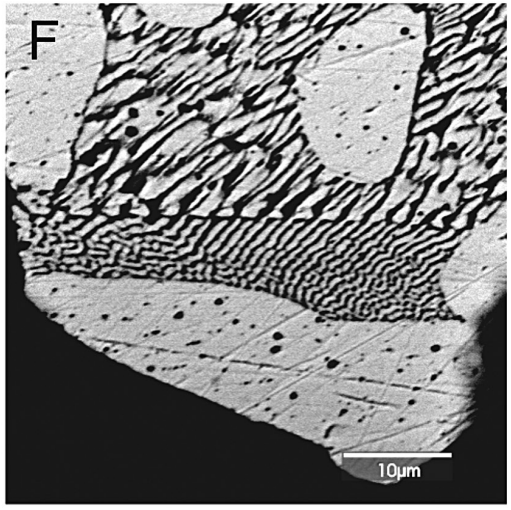
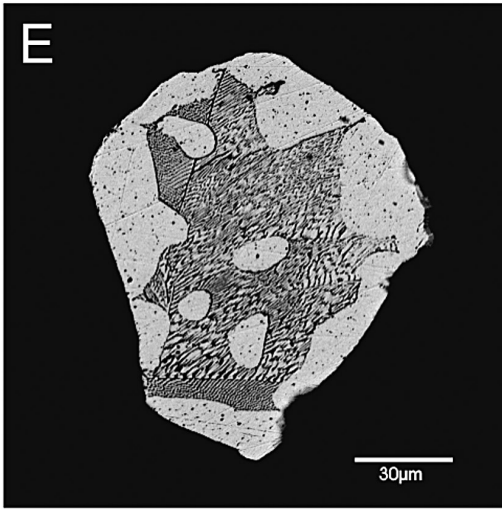
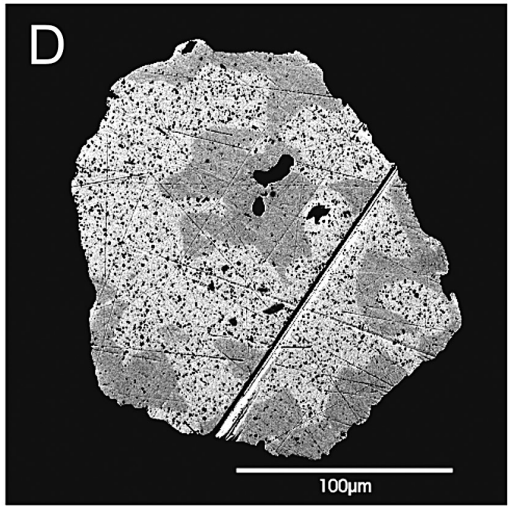
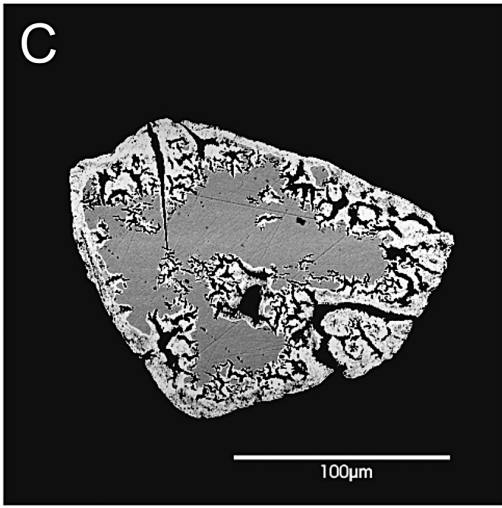
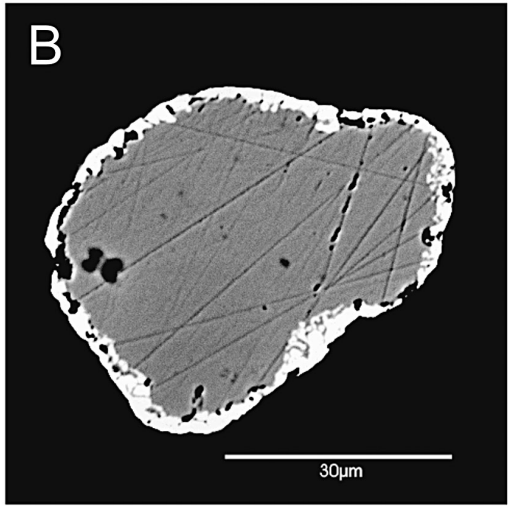
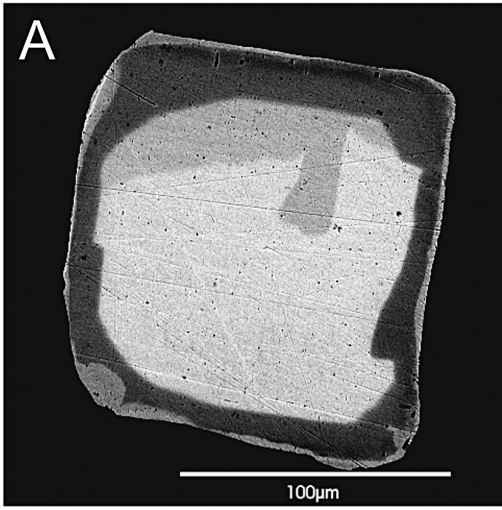
Platinum

Native Pt occurs mainly as porous grains, and also as compact grains (Fig. 4F and Table 3, analysis 1) at all localities investigated, except in the Ngezi area. In addition, thin films of native Pt form the outermost rim of some sperrylite and cooperite/braggite grains (Figs. 6B and 6C). Notably, Schneiderhöhn & Moritz (1939) showed texturally similar porous grains of native Pt from oxidized Merensky Reef and proposed that these grains represent relics of former sperrylite or cooperite grains. Native Pt is usually relatively pure and devoid of other elements; its chemical variation is shown in Figure 7.

Pt-Fe alloys [comprising “ferroan platinum”, isoferroplatinum (Pt_3Fe), tetraferroplatinum (PtFe), ferrornickelplatinum (Pt_2FeNi), and tulameenite (Pt_2FeCu)].

Pt-Fe alloy grains are mainly single crystals with variably rounded corners and commonly retain cubic outlines (Figs. 2C, 3A, 3B, 4E, 5A, 6A) with slightly abraded surfaces. Intergrowths with ferrornickelplatinum (Fig. 5B), laurite (Fig. 5H), and unnamed RhNi_2S_3 (Fig. 5G) are rare, as are partial replacements by tulameenite. Most of the grains are monophase and homogeneous, however, some grains are zoned with respect to Pt/Pd ratios (see Table 3, analyses 4 and 5; Fig. 6A), display unusual internal textures (Figs. 6E, 6F), or carry inclusions of a variety of other PGM (Figs. 5C, 5D, 5G), as described below.

As shown in Figure 7, most of the analyses reflect compositions ranging from Pt_3Fe to $\text{Pt}_{1.5}\text{Fe}$ (“ferroan platinum”). A certain amount of substitution of Pd for Pt is also obvious (not in the Pt-Fe alloy grains from the Hartley area) and quite common (up to 27.91 wt.% Pd). Some rare Pt-Fe alloy grains also carry



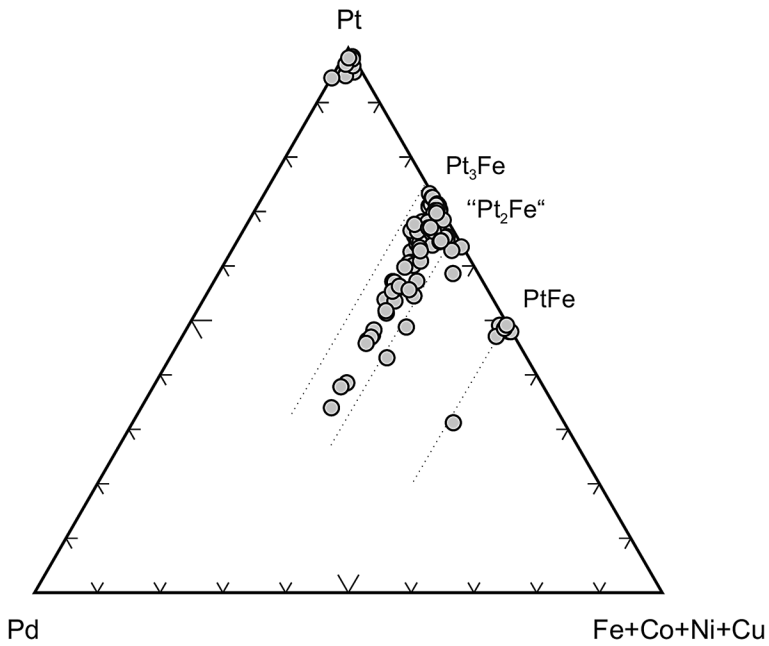


FIG. 7. Compositions (in at.%) of Pt and Pt-Fe alloys, projected in the triangular diagram Pt-Pd-(Fe+Co+Ni+Cu).

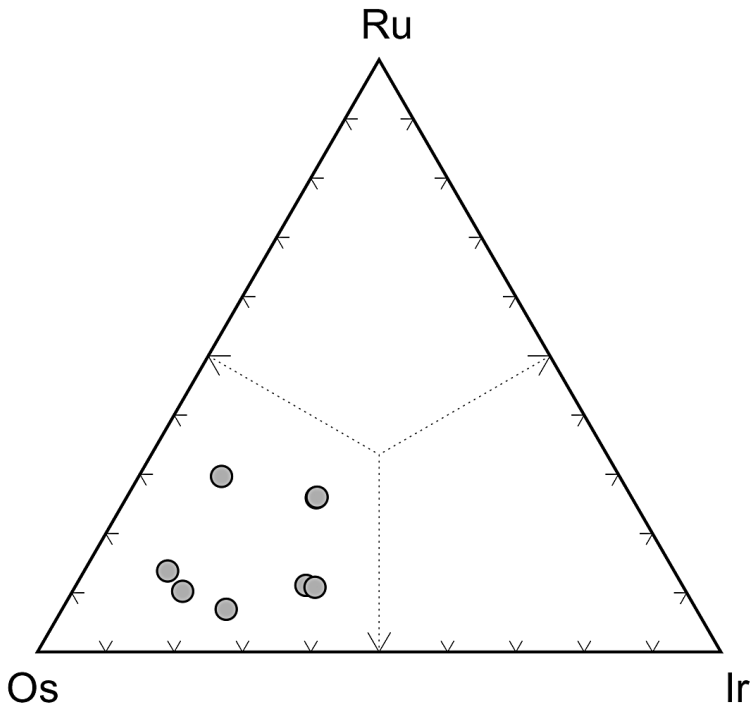


FIG. 8. Compositions (in at.%) of Os-Ir-Ru alloys, projected in the triangular diagram Ru-Os-Ir. Note all grains are osmium.

elevated contents of Rh (up to 5.97 wt.%) or Ir (5.55 wt.%). Furthermore, one grain with the composition $(\text{Pt}_{2.27}\text{Ir}_{0.52}\text{Pd}_{0.14}\text{Ru}_{0.10}\text{Rh}_{0.05})_{3.08}(\text{Fe}_{0.75}\text{Ni}_{0.04}\text{Cu}_{0.10})_{0.89}$ and the simplified formula $(\text{Pt},\text{Ir})_3\text{Fe}$ with inclusions of cuproiridsite was found in the mineral suite from the Umsweswe River. A minority of grains with Pt/(Fe + Co + Ni + Cu) ratios close to 1/1 represent solid solutions of tetraferroplatinum (PtFe), ferronickelplatinum (Pt_2FeNi), and tulameenite (Pt_2FeCu). Representative results of analyses are given in Table 3.

Os-Ir-Ru alloy

These PGM occur as monomineralic grains (Figs. 3E, 3F), and only in the Umtebekwe River. Chemically (Fig. 8), all grains must be termed osmium after Harris and Cabri (1991). Maximum contents of other PGE are 0.7 wt.% Rh and 3.5 wt.% Pt. The compositional variation of the various Os-Ir-Ru alloys is shown in Figure 8, and representative analyses are given in Table 3, analyses 8 and 9. An Os isotope analysis of one Os-Ir-Ru alloy grain gave an $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.110275 (Kramers, pers. commun. 2001), well within the range of initial $^{187}\text{Os}/^{188}\text{Os}$ ratios (average 0.1112) of the chromitites of the Great Dyke (Schoenberg *et al.* 2003). This indicates that at least this grain originates

from the Great Dyke, probably from a chromitite seam, and not from the Archean chromitite deposits of the Shurugwi greenstone belt.

Rh-Pt-Ru alloy

A single grain from Umtebekwe south with the simplified formula $\text{Rh}_{38}\text{Pt}_{37}\text{Ru}_{19}$ (Table 3, analysis 10). The analysis of the alloy is in the ternary diagram Pt-Rh-(Ru,Ir,Os) on the boundary between the fields of platinum and rhodium. However, according to the nomenclature of Nickel (1992), this PGM is rhodium due to the slight overweight of Rh over Pt.

Cooperite (PtS) and braggite [(Pt,Pd,Ni)S]

Cooperite and braggite are dealt with together, as these minerals are hard to distinguish microscopically and they form a chemically nearly continuous series (Cabri 2002, Merkle & Verryn 2003). Notably, cooperite was found in the Makwiro and Umtebekwe Rivers, and braggite in the Makwiro River alone. Cooperite/braggite mostly occur as rounded and internally homogeneous grains (Fig. 2D) or as splinters. The grains may be zoned internally (Pt/Pd variation), as shown in Figure 5F. Quite often, marginal to pervasive alteration features

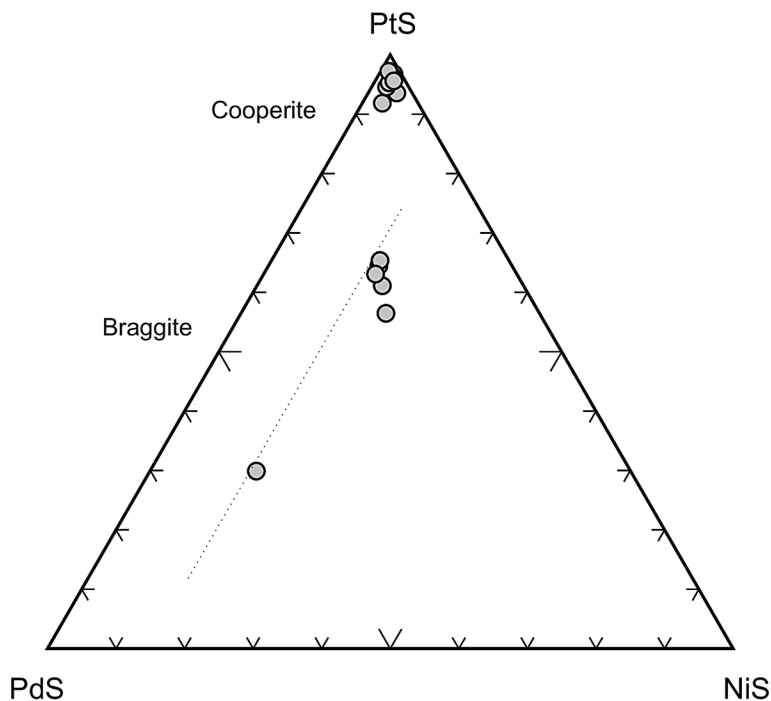


FIG. 9. Compositions (in at.%) of cooperite and braggite, projected in the triangular diagram PtS–PdS–NiS.

TABLE 4. ELECTRON MICROPROBE ANALYSES OF PGE-SULFIDES

No.	1	2	3	4	5	6	7	8	9	10	11
						wt.%					
Pt	82.99	83.77	66.84	37.45	0.19	1.18	1.83		0.39	8.11	1.31
Pd	1.56	0.77	10.97	37.31			0.40			4.41	
Os					4.50	2.66	2.61	61.50			
Ir					5.05	1.64	1.03	10.66	3.72	35.63	4.54
Ru					51.02	54.46	55.74	1.61			0.80
Rh					2.49	2.93	2.20		65.27	12.78	44.71
Fe					0.23					1.84	0.20
Cu									0.17	10.22	
Ni	0.58	0.31	5.04	5.86						1.45	0.21
S	14.71	14.46	16.77	19.36	34.16	34.57	34.83	23.78	28.59	22.48	14.71
As						0.26					31.58
Se											0.16
Te											0.17
Total	99.40	99.31	99.62	99.98	97.64	97.70	98.64	97.55	98.14	96.92	98.39
						apfu					
Pt	0.950	0.962	0.650	0.308	0.002	0.010	0.016		0.006	0.222	0.015
Pd	0.003	0.016	0.195	0.563			0.007			0.221	
Os					0.043	0.025	0.024	0.854			
Ir					0.048	0.015	0.010	0.146	0.063	0.989	0.052
Ru					0.918	0.964	0.978	0.042			0.017
Rh					0.044	0.051	0.038		2.064	0.663	0.956
Fe					0.007					0.176	0.008
Cu									0.009	0.858	
Ni	0.022	0.012	0.163	0.160						0.131	0.008
S	1.025	1.010	0.992	0.969	1.938	1.928	1.927	1.958	2.876	3.740	1.009
As						0.006					0.928
Se											0.004
Te											0.003

(1) Cooperite (PtS), Makwiro. (2) Cooperite, Umtebekwe. (3) Braggite [(Pt,Pd)S], Makwiro. (4) Braggite [(Pd,Pt,Ni)S], Umtebekwe. (5) Laurite (RuS₂), Makwiro. (6) Laurite, Umsweswe. (7) Laurite, Umtshingwe. (8) Erlichmanite (OsS₂), Umtebekwe. (9) Bowieite (Rh₂S₃), Maholo. (10) Cuproiridsite (CuIr₂S₄), Umsweswe. (11) Hollingworthite (RhAsS), Makwiro.

are visible on the surfaces (Fig. 6C), indicating chemical instability of cooperite/braggite grains in the supergene environment (*e.g.*, Oberthür *et al.* 2003a, Oberthür & Melcher 2005). The compositional variability of cooperite/braggite grains as shown in Figure 9 largely overlaps with data of cooperite/braggite from pristine MSZ ores (Oberthür *et al.* 2003a). However, the proportions of cooperite to braggite appear to have increased from pristine MSZ ores to detrital grains, indicating a higher stability of cooperite compared to braggite in the supergene environment. Representative analyses are presented in Table 4, analyses 1 to 4.

Laurite (RuS₂)

Laurite is rare and mostly occurs as inclusions in or attached to Pt-Fe alloy grains from the Makwiro and Umsweswe Rivers (Fig. 5H). Chemically, the mineral is mainly close to ideal (RuS₂) in composition; some grains contain up to 2.9 wt.% Rh, 4.5 wt.% Os, 5.0

wt.% Ir, and 1.2 wt.% Pt. Representative analyses are presented in Table 4, analyses 5 to 7.

Erlichmanite (OsS₂)

A single grain of erlichmanite with 10.7 wt.% Ir and 1.6 wt.% Ru was found in the mineral assemblage of the Umtebekwe River (Table 4, analysis 8).

Bowieite (Rh₂S₃)

One grain with 3.7 wt.% Ir, 0.4 wt.% Pt and 0.17 wt.% Cu was found in the Maholo River assemblage (Table 4, analysis 9).

Cuproiridsite (CuIr₂S₄)

One occurrence as an inclusion in idiomorphic Pt-Ir-Fe alloy from the Umsweswe River. The composition corresponds to (Cu_{0.86}Fe_{0.18}Ni_{0.13})_{1.17}(Ir_{0.99}Rh_{0.66}Pt_{0.22}Pd_{0.22})_{2.09}S_{3.74} (Table 4, analysis 10).

Sperrylite (PtAs₂)

Sperrylite mainly occurs in the form of unaltered monophase crystals (Figs. 2A, 2B, 3D, 4A). Some grain surfaces display etch pits, with partial replacements or overgrowths of pure Pt (Fig. 6B). An unusual grain from the Umtshingwe River is shown in Figures 4C and 4D. All sperrylite grains are close to stoichiometric (PtAs₂).

Majakite (PdNiAs)

This mineral was found once only as an inclusion in atheneite from the Makwiro River (Table 5, analysis 5).

Palladodymite [(Pd,Rh)₂As]

Palladodymite was identified as an inclusion in Pd- and Rh-bearing platinum from the Umsweswe River (Table 5, analysis 12).

Hollingworthite (RhAsS)

Hollingworthite was identified once only as an inclusion in a Pt-Fe alloy grain from the Makwiro River (Table 4, analysis 11).

TABLE 5. ELECTRON MICROPROBE ANALYSES OF PGE-ARSENIDES, -ANTIMONIDES, AND -STANNIDES

No.	1	2	3	4	5	6	7	8	9	10	11	12	13
	wt. %												
Pt									1.36		12.00	1.53	84.12
Pd	73.96	68.72	65.81	74.12	44.29	70.97	72.24	35.55	36.30	35.48	29.29	44.18	
Os													
Ir				0.26		0.24							
Ru													
Rh	0.35	0.54											31.75
Fe									0.33		0.76	0.14	0.20
Cu	4.12	0.54		0.16		1.23			0.92	0.13		0.24	
Ni	0.66	0.23	0.29		24.81				0.35				
As	20.01	17.62	20.16	9.31	29.68	10.65	3.13						23.44
Se					0.15								
Te				7.46							8.71	0.18	
Bi				3.30							48.65		
Sb			0.35	4.56		15.48	24.16						
Pb	0.28			0.96									
Hg	0.22	11.52	12.40		0.37			65.23	58.33	65.16			0.39
Sn													17.36
sum	99.60	99.17	99.01	100.13	99.29	98.57	99.53	100.78	97.59	100.8	99.41	101.5	102.1
	apfu												
Pt									0.021		0.189	0.022	2.958
Pd	7.323	1.943	1.938	2.961	1.008	10.456	5.171	1.013	1.025	1.010	0.845	1.184	
Os													
Ir				0.006		0.019							
Ru													
Rh	0.036	0.014											0.880
Fe									0.018		0.042	0.007	0.025
Cu	0.682	0.024		0.011		0.304			0.044	0.006		0.011	
Ni	0.118	0.011	0.016		1.023				0.018				
As	2.814	0.835	0.843	0.528	0.960	2.229	0.318						0.892
Se					0.005								
Te				0.248							0.209	0.004	
Bi				0.067							0.715		
Sb			0.009	0.159		1.992	1.511						
Pb	0.015			0.020									
Hg	0.012	0.173	0.194		0.004			0.987	0.874	0.984			0.013
Sn													1.004

(1) Arsenopalladinite [Pd₈(As,Sb)₃], Makwiro. (2) Atheneite [Pd₂(As,Hg)], Makwiro. (3) Atheneite, Umtebekwe. (4) Vincentite [Pd₃(As,Sb,Te)], Makwiro. (5) Majakite (PdNiAs), Makwiro. (6) Isomertieite [Pd₁₁(Sb,As)₄], Umtebekwe. (7) Stibiopalladinite (Pd₅Sb₂), Umtebekwe. (8) Potarite (PdHg), Makwiro. (9) Potarite, Umtebekwe. (10) Potarite, Maholo. (11) Sobolevskite (PdBi), Umtebekwe. (12) Palladodymite [(Pd,Rh)₂As], Umsweswe. (13) Rustenburgite (Pt₃Sn), Umtshingwe.

Stibiopalladinite ($Pd_{5+x}Sb_{2-x}$) and *Mertieite II*
 $[Pd_8(Sb,As)_3]$

According to Cabri (2002), stibiopalladinite (hexagonal) and mertieite II (rhombohedral) are "related". The two PGM are dealt with together here owing to the fact that both optical and chemical distinction between these PGM is difficult. Both minerals are cream-yellow to yellowish white and variably anisotropic. One platy, homogeneous grain of stibiopalladinite or mertieite II was identified from the Umtebekwe River. The calculated formula for stibiopalladinite is $(Pd)_{5.17}(Sb_{1.51}As_{0.32})_{1.83}$ (Table 5, analysis 7). In case of mertieite II, the calculated formula is $(Pd)_{8.13}(Sb_{2.37}As_{0.50})_{2.87}$.

Arsenopalladinite $[Pd_8(As,Sb)_3]$

This mineral was only found in the Makwiro River; a single grain contained 4.1 wt.% Cu, 0.7 wt.% Ni, 0.4 wt.% Rh, and traces of Hg and Pb (Table 5, analysis 1). A second occurrence as an inclusion in atheneite carried 1.3 wt.% Cu and 0.65 wt.% Hg.

Isomertieite and Mertieite I – (both $[Pd_{11}Sb_2As_2]$ or $[Pd_{11}(Sb,As)_4]$)

Isomertieite (cubic) and mertieite I (hexagonal) are difficult to distinguish optically (light yellowish white to brass or cream-yellow; anisotropy indistinct), have Sb/As ratios near unity and typically low contents of other elements besides Pd, As, and Sb. In the present study, one single, detrital grain carrying 1.2 wt.% Cu was detected in the mineral assemblage from the Umtebekwe River (Fig. 3G and Table 5, analysis 6).

Vincentite $[Pd_3(As,Sb,Te)]$

Vincentite was found as roundish inclusions in arsenopalladinite (carrying about 3 wt.% Bi) and in atheneite (without any Bi) in the samples from the Makwiro River (Table 5, analysis 4).

Sobolevskite ($PdBi$)

A single grain of sobolevskite was found as an inclusion in Pt-Fe alloy from the Umtebekwe River. The calculated formula is $(Pd_{0.84}Pt_{0.19})_{1.03}(Bi_{0.72}Te_{0.21})_{0.93}$ (Table 5, analysis 11).

Rustenburgite (Pt_3Sn)

One well rounded grain of rustenburgite was detected in the sample from the Umtshingwe River. The composition closely corresponds to the Pd-free rustenburgite endmember (Table 5, analysis 13).

Potarite ($PdHg$)

Four individual, stoichiometric grains of potarite ($PdHg$) were detected from the Makwiro River (Table 5, analysis 8), and one grain from the Maholo River (Table 5, analysis 10). Furthermore, an inclusion of potarite in tetraferroplatinum was identified from the Umtebekwe River (Table 5, analysis 9).

Atheneite $[Pd_2(As,Hg)]$

Three individual, platy, detrital grains of atheneite found in the Makwiro River contained traces of Fe, Cu, Ni, and Rh (Table 5, analysis 2). One single atheneite grain from the Umtebekwe River carried traces of Ni and Sb (Table 5, analysis 3).

Gold ($Au-Ag$)

Gold grains are ubiquitous in all samples, and far more common than PGM grains. Gold grains display various shapes; larger grains are commonly flat or disc-like, whereas smaller grains tend to roundish forms (Fig. 2F). Gold grains are mostly homogeneous internally, though usually somewhat porous, and commonly have an outer rim of variable thickness of silver-poor or pure gold. Distinction between gold grains originating from the MSZ of the Great Dyke or from greenstone-hosted mineralization is hardly possible by studying grain morphologies or mineral chemistry (see also McClenaghan & Cabri 2011). Therefore, it is assumed that the gold grains in our samples originate both from the Great Dyke and from gold mineralization in the greenstone belts, in proportions that vary depending on the source areas of the rivers.

Gold alloy ($Au-Pd-Hg$)

A single, porous grain of gold alloy was found in a sample from the Umtebekwana River. The composition of the homogeneous area is $Au(Pd,Hg)$ (Fig. 6D and Table 7, analysis 1), whereas the porous region is devoid of Pd and Hg.

Unnamed $[(Ir,Pt)(Fe,Ni,Cu)_2S_3]$

Some small inclusions of this mineral were found in Pt-Fe alloy grains from the Makwiro River. The composition corresponds to $(Ir_{0.57}Pt_{0.24}Rh_{0.09})_{0.90}(Fe_{0.91}Ni_{0.84}Cu_{0.31})_{2.06}S_{3.04}$ (Table 6, no. 1).

Unnamed $[Pd_2(Ni,Cu)S]$

One rounded grain intergrown with unknown $RhNi_2S_3$ and Pd_3Te was found as an inclusion in Pt-Fe alloy from the Umsweswe River. The composition corresponds to $(Pd_{2.11}Pt_{0.02})_{2.13}(Ni_{0.45}Cu_{0.43}Fe_{0.02})_{0.90}(S_{0.94}Te_{0.02}Se_{0.01})_{0.95}$ (Table 6, no. 2).

Unnamed (Pd₃Te)

This compound occurs as a single grain enclosed in Pt-Fe alloy or intergrown with Pd₂(Ni,Cu)S and RhNi₂S₃ as inclusion in Pt-Fe alloy (Fig. 5D). The analysis corresponds to (Pd_{2.90}Pt_{0.04}Ir_{0.01})_{2.95}(Te_{1.01}Bi_{0.03}Pb_{0.01})_{1.05} (Table 6, no. 3). An unnamed mineral with this composition was described earlier by Johan *et al.* (1991) from Fifield, Australia. Weiser & Schmidt-Thomé (1993) reported a similar mineral [Pd₃(As,Te)] from the Santiago River, Esmeraldas Province, Ecuador.

Unnamed [Pd₃(Pb,Hg)]

This compound with the composition Pd_{2.99}(Pb_{0.82}Hg_{0.18})_{1.00} was found as a rounded single grain in a sample from the Umtebekwe River (Table 6, no. 4). It might be zvyagintsevite (Pd₃Pb) containing some mercury. Cabri *et al.* (1996) described a similar phase with the composition (Pd,Pt)₂(Pb,Hg) from the Urals, Russia.

Unnamed (RhS)

This mineral occurs intergrown with or as inclusion in Pt-Fe alloy in samples from the Umsweswe River. The composition corresponds to (Rh_{0.90}Pt_{0.01}Ir_{0.01}Ni_{0.14}Cu_{0.03}Fe_{0.02})_{1.11}S_{0.89} (Table 6, analysis 5). RhS

TABLE 6. ELECTRON MICROPROBE ANALYSES OF UNNAMED MINERALS

No.	1	2	3	4	5	6	7
				wt.%			
Pt	12.28	1.35	1.87	0.00	1.30	0.82	
Pd		71.41	68.81	62.11	0.34	0.39	
Os							
Ir	28.27		0.26	0.14	1.45	0.80	
Ru							
Rh	2.28				65.17	30.94	
Fe	13.07	0.40			0.66	11.23	2.48
Cu	5.08	8.70			1.45	7.73	1.21
Ni	12.58	8.51			5.93	18.29	69.95
S	24.97	9.61			20.13	28.77	24.40
As							
Se		0.22					0.14
Te		0.62	28.76				
Bi			1.41	0.16			
Pb			0.19	33.26			
Hg				7.22			
Total	98.53	100.82	101.30	102.89	96.43	98.97	98.18
				apfu			
Pt	0.245	0.022	0.043		0.009	0.014	
Pd		2.106	2.904	2.986	0.004	0.012	
Os							
Ir	0.573		0.006	0.004	0.011	0.014	
Ru							
Rh	0.086				0.896	0.978	
Fe	0.912	0.022			0.017	0.654	0.110
Cu	0.312	0.430			0.032	0.396	0.047
Ni	0.835	0.455			0.143	1.013	2.953
S	3.035	0.941			0.888	2.919	1.886
As							
Se		0.009					0.004
Te		0.015	1.012				
Bi			0.030	0.004			
Pb			0.004	0.821			
Hg				0.184			

(1) (Ir,Pt)(Fe,Ni,Cu)₂S₃, Makwiro. (2) Pd₂(Ni,Cu)S, Umsweswe. (3) Pd₃Te, Umsweswe. (4) Pd₃(Pb,Hg), Umtebekwe. (5) RhS, Umsweswe. (6) RhNi₂S₃, Umsweswe. (7) Ni₃S₂ (inclusion in "Cu-bearing awaruite"), Makwiro.

TABLE 7. ELECTRON MICROPROBE ANALYSES OF GOLD ALLOYS AND Ni-Fe-Cu COMPOUNDS

No.	1	2	3	4	5	6
	wt.%					
Pt					20.45	
Pd	16.87	23.78			0.16	0.94
Rh						
Ru						
Os						
Ir					0.69	
Fe		1.40	24.68	10.76	10.94	6.89
Ni		13.87	76.43	77.53	58.17	78.33
Cu	0.17	58.31		9.61	8.91	14.19
Co		0.14	1.42			0.78
Au	56.00	8.92				
Ag	1.52					
Hg	26.28					
Total	100.84	106.42	102.53	97.90	99.32	101.13
	apfu					
Pt					0.292	
Pd	0.588	0.925			0.004	0.026
Rh						
Ru						
Os						
Ir					0.010	
Fe		0.104	1.000	0.463	0.546	0.362
Ni		0.977	2.946	3.174	2.758	3.917
Cu	0.010	3.797		0.363	0.390	0.656
Co		0.010	0.054			0.039
Au	0.865	0.187				
Ag	0.052					
Hg	0.485					

(1) Au(Pd,Hg) alloy, Umtebekwe River. (2) Inclusion of (Pd,Au)NiCu₄ in synthetic Ni₄(Fe,Cu), (analysis 6 below). (3) Awaruite (Ni₃Fe), river at Caesar Mine. (4) "Cu-bearing awaruite" [Ni₃(Fe,Cu)], Makwiro River. (5) Inclusion of (Ni,Pt)₃(Fe,Cu) in "Cu-bearing awaruite". (6) Synthetic Ni₄(Fe,Cu), product of the slow-cooling process of Anglo American Platinum (see text). Average of 19 individual analyses.

was earlier reported from the Witwatersrand gold ores in South Africa (Feather 1976), and from the Rogue River, Oregon, USA (Weiser 2004).

Unnamed (RhNi₂S₃)

This mineral was identified as small rounded inclusions together with the unnamed PGM Pd₂(Ni,Cu)S and Pd₃Te in Pt-Fe alloy from Umsweswe River (Fig. 5D). The composition corresponds to the formula (Rh_{0.98}Pt_{0.01}Pd_{0.01}Ir_{0.01})_{1.01}(Ni_{1.01}Fe_{0.65}Cu_{0.40})_{2.06}S_{2.92} (Table 6, no. 6). Barkov *et al.* (1999) mention this mineral from the Penikat layered complex in Finland.

Unnamed (Ni₃S₂)

Awaruite from the Caesar Mine (Table 7, no. 3) contained some droplike inclusions of unnamed Ni₃S₂

with the composition (Ni_{2.77}Fe_{0.07})_{2.84}S_{2.16}. Furthermore, "Cu-bearing awaruite" from the Makwiro River also contained some chemically similar roundish inclusions with a composition corresponding to (Ni_{2.95}Fe_{0.11}Cu_{0.06})_{3.12}S_{1.88} (Table 6, no. 7).

Awaruite (Ni₃Fe)

A number of awaruite grains were found in sediments of a small river close to the Caesar chromite mine, near Mutorashanga. Analyses are given in Table 7.

"Cu-bearing awaruite" [Ni₃(Fe,Cu)]

Well-crystallized monophase grains of this compound (Figs. 2G, 2H) were detected in sediment samples of the Makwiro River right behind, *i.e.*, west

of, the Hartley Mine. Furthermore, one grain of this compound was found intergrown with sperrylite. X-ray diffraction analyses of some grains gave XRD spectra identical to awaruite. Microprobe analyses, however, revealed the constant presence of Cu besides Ni and Fe (Table 7), largely corresponding to the formula $Ni_3(Fe,Cu)$. Therefore, this compound was tentatively named "Cu-bearing awaruite". Notably, zones enriched in platinum are present in some grains (e.g., Figs. 6G, 6H); maximum contents analyzed were 19.96 at.% Pt (substituting for Ni; see also Table 7).

In this context, Schouwstra (pers. commun.) pointed out that a compound similar to the above "Cu-bearing awaruite" is one of the products obtained during processing of platinum ores resp. matte using the slow-cooling process (Schouwstra 2000). For comparison, we obtained some of Schouwstra's material and analyzed a number of grains by EPMA; results are shown in Table 7. This synthetic product chemically largely resembles the "Cu-bearing awaruite" from the Makwiro River. At near-identical Ni contents, the Cu contents are slightly higher, whereas the Fe contents are lower. Occasionally, PGE concentrations reach up to 2.64 at.% Pt and 1.34 at.% Pd. A number of small, roundish inclusions consisted of a compound with a formula close to Cu_4NiPd .

It must be noted that the samples containing the phase $Ni_3(Fe,Cu)$ were taken before the smelter at Hartley Mine was operative. Therefore, it remains unclear whether this compound is a natural mineral or an anthropogenic product from possibly earlier ore processing activities for which no record is on hand.

Base metal sulfides

Rare inclusions of base metal sulfides, mainly in Pt-Fe alloy, are pyrrhotite and chalcopyrite.

DISCUSSION AND CONCLUSIONS

PGM in the pristine MSZ mainly comprise sperrylite $PtAs_2$, cooperite/braggite $[(Pt,Pd,Ni)S]$, (Pt,Pd)-

bismuthotellurides, and PGE-sulfarsenides (e.g., Haynes 1983, Prendergast 1988, 1990, 1991, Johan *et al.* 1989, Evans & Buchanan 1991, Evans *et al.* 1994, Coghill & Wilson 1993, Oberthür 2002, 2011, Oberthür *et al.* 2003a). Major regional differences in PGM proportions are known (Oberthür 2011): MSZ samples from the northern Great Dyke (Hartley to Ngezi) have higher proportions of (Pt,Pd)-bismuthotellurides (64%) and cooperite/braggite (13%), and lower proportions of sperrylite (11%), PGE-sulfarsenides (2.4%), and laurite (1.7%) compared to those of the MSZ of the southern Great Dyke (Unki and Mimosa), which have (Pt,Pd)-bismuthotellurides (35%), cooperite/braggite (4%), sperrylite (28%), PGE-sulfarsenides (22%), and laurite (8.6%). The elevated proportions of PGE-arsenides and -sulfarsenides in the southern Great Dyke (together 50%) most likely indicate higher fugacities of arsenic in the magmas of the southern Great Dyke at the stage of MSZ formation, possibly due to contamination of the magmas by assimilation of country rocks (Oberthür 2002). In addition, appreciable amounts of PGE are hosted in solid solution in sulfides, e.g., much of the Pd is sited in pentlandite (Oberthür *et al.* 1997, Weiser *et al.* 1998, Oberthür *et al.* 2003a, Oberthür 2011).

The apparent restriction of PGM-bearing sediments to areas of the Great Dyke where the Mafic Sequence, and consequently the MSZ, is present is a strong indication that the majority of the detrital PGM originate from the MSZ. The general trends of the PGE mineral assemblage observed from pristine via oxidized MSZ into the fluvial environment are shown in Table 8. Obviously, the PGM assemblage found in the various rivers draining the Great Dyke is distinctly different from that of pristine and oxidized MSZ (Table 8).

In contrast to the pristine MSZ ores, in the heavy mineral concentrates detrital (Pt,Pd)-bismuthotellurides, PGE-sulfarsenides, and PGE-oxides are absent, and cooperite/braggite grains are scarce. Besides sperrylite, ubiquitous Pt-Fe alloy grains are present as well as a suite of rare Pd-dominated PGM, and Os-Ir-Ru alloy grains were found in the Umtebekwe River south of Shurugwi.

TABLE 8. COMPARISON OF PGM ASSEMBLAGES IN THE PRISTINE MSZ, IN OXIDIZED MSZ, AND OF DETRITAL PGM IN SEDIMENT SAMPLES, GREAT DYKE, ZIMBABWE

locality	sulfide	oxide	Great Dyke
PGM (numbers)	MSZ	MSZ	rivers
	801	1293	390
<i>mineral groups</i> [%]			
(Pt,Pd)(Bi,Te) *	50.1	11.4	—
$PtAs_2$	19.0	57.2	45.6
(Pt,Pd)S	8.5	28.3	6.7
Pt and Pt-Fe alloys	2.4	3.1	42.1
PGE-AsS *	11.9	—	—
others	8.1	x	5.6

We deduce that sperrylite grains are relict minerals originating from the MSZ, thus indicating that sperrylite is generally stable in the supergene environment. Most of the cooperite/braggite grains show distinct features of external corrosion and partial internal leaching along irregular corrosion channels. The increasing ratio of sperrylite to cooperite/braggite from pristine via oxidized MSZ to the fluvial environment indicates that sperrylite is largely stable in the exogenic environment, whereas cooperite/braggite grains are progressively disintegrated in the course of prolonged oxidation (*i.e.*, they are “metastable” from oxidized MSZ ores to the placers).

(Pt,Pd)-bismuthotellurides and PGE-sulfarsenides, common in the pristine MSZ ores, and the porous and friable PGE-oxides or -hydroxides present in the oxidized MSZ, are missing in the suite of detrital PGM in the fluvial environment. Apparently, these minerals were chemically and physically disintegrated in the course of weathering and mechanical transport.

The rare Os-Ir-Ru alloy grains are present only in samples from the Umtebekwe River (South); Point 6 in Figure 1. This leads to the assumption that these grains originate from Archean chromitite deposits of the Shurugwi greenstone belt, and not from the Great Dyke. However, as documented above, an Os isotope analysis of one Os-Ir-Ru alloy grain gave an $^{187}\text{Os}/^{188}\text{Os}$ ratio well in the range of initial $^{187}\text{Os}/^{188}\text{Os}$ ratios of the chromitites of the Great Dyke (Schoenberg *et al.* 2003). This suggests that at least this grain originates from the Great Dyke, possibly from a chromitite seam. Therefore, the ultimate origin of the Os-Ir-Ru alloy grains remains open.

The high proportion of Pt-Fe alloy grains is conspicuous. The origin of Pt-Fe alloy, the most abundant PGM in most placers worldwide (Cabri *et al.* 1996, Weiser 2002, 2004), remains controversial. Textural and geochemical arguments, such as the presence of inclusions of other PGM and Os isotope compositions, are considered by most researchers to reflect an origin of many of the Pt-Fe grains from high-temperature (*i.e.*, magmatic) processes (*e.g.*, Cabri *et al.* 1996, Weiser 2002, Malitch & Thalhammer 2002, Melcher *et al.* 2005, Okrugin 2011).

Other authors, however, have proposed a secondary origin of PGM in placers and soils (Augusthitis 1965, Bowles 1986, 1990, 1995, Ottemann & Augusthitis 1967, Stumpfl 1974, Cabral *et al.* 2007). Cousins (1973) and Cousins & Kinloch (1976) pointed out that size, shape, composition, and microtexture of many eluvial and alluvial PGM differ from those observed in bedrocks and ores. They proposed formation of secondary PGM in a simplified process: (1) serpentinization or weathering leads to the decomposition of base-metal sulfides carrying PGE in solid solution; (2) PGE are removed and transported as colloidal particles; and (3) the colloids may coalesce or accrete

to form larger particles and aggregates of PGE alloys. Textures such as zoning and reniform and mammillary textures are considered evidence for accretion and secondary growth in a low-temperature environment (Stumpfl 1974, Cabral *et al.* 2007). Unconstrained three-dimensional growth, corrosion features on mineral faces, overplating of mineral faces, colloform and cyclic zonation, porous and spongy Pt-Fe nuggets, and overgrowths of one phase by another were considered unique to hydrothermal and supergene processes of formation (Bowles 1995).

Cabri & Harris (1975) disputed a supergene origin of PGM as proposed by Augusthitis (1965). Cabri *et al.* (1996) and Weiser (2002, 2004) cited only two likely exceptions where Pt nuggets may have formed in a surficial environment, namely palladian gold, potarite and native platinum in alluvial sediments from Devon, England, and botryoidal, zoned Pt-Pd nuggets from the Bom Sucesso stream in Brazil. The Brazilian example has been critically evaluated by Fleet *et al.* (2002), who concluded that the alluvial PGM most likely originated from detrital grains that crystallized from low-temperature hydrothermal fluids. In their study of gold and PGM (isoferroplatinum and Os-Ir alloy) in offshore placers near Goodnews Bay, Alaska, Mardock & Barker (1991) found textures related to both derivation of PGM grains from mechanically weathered primary ore (*i.e.*, typical assemblages of inclusions and exsolution phenomena) and subsequent accretion (*i.e.*, microcrystalline assemblages of PGM in grain-rim cavities, suggesting leaching and crystallization). This important observation pertains to many occurrences of placer PGM; therefore, a combination of primary and secondary processes has to be considered to explain textural and chemical attributes of PGM nuggets.

Accordingly, possible sources of the Pt-Fe alloy grains comprise:

(1) They are direct descendants from the MSZ. This is improbable for all of them, as they are rare in pristine and oxidized MSZ ores, and a prolonged concentration and upgrading of these grains in the fluvial environment appears unlikely. Furthermore, Pt-Fe alloy grains should be present in similar proportions relative to sperrylite as in the MSZ, which is not the case (see Table 8).

(2) The Pt-Fe alloy grains originate from disseminated occurrences in other rock units of the Great Dyke, *e.g.*, chromitites. This possibility is not supported by the present work, as no PGM were found in stream sediments of rivers draining the basal Ultramafic Sequence of the Great Dyke only, and Pt-Fe alloy grains have not been reported from chromitites of the Great Dyke (Germann & Schmidt 1999, Oberthür 2002).

(3) Pt-Fe alloy grains represent neo-formations that came into existence in the course of weathering of the MSZ ores and the concomitant supergene redistribution of the ore elements. Observations both in the oxidized MSZ ores and the river sediments (presence of porous Pt

and Pt-Fe alloy grains) and of PGM in ferralitic soils of Madagascar (Salpéteur *et al.* 1995) are in support of this hypothesis, but do not fully explain the quantity of Pt-Fe alloys present. Furthermore, some Pt-Fe alloy grains host a variety and in part numerous inclusions of other PGM indicating a consanguineous, magmatic origin.

At the current state of knowledge, it must be speculated that some of the Pt-Fe alloy grains originate from the MSZ, and others are true neo-formations that formed in the course of weathering of the MSZ ores and concomitant supergene redistribution of the PGE. Their precursor phases are either pre-existing, unstable PGM (note Pt coatings and partial replacements of cooperite/braggite, and also of sperrylite; Figs. 6B and 6C), or they may even have formed via a solution stage under low-temperature conditions

The suite of rare Pd-dominated minerals (Pd-Hg ± As and Pd-Sb ± As) found in the gravels, which are very rare in the MSZ ores, are regarded to be neo-formations that probably formed from elements dispersed (disintegration of Pd-bearing pentlandite, other sulfides and tellurides) during supergene processes.

The generally large grain sizes of the detrital PGM (*ca.* 50–870 µm; mostly between 100–200 µm) compared to those from the pristine MSZ ores, where apparent maximum diameters observed in polished sections range from <5 to 50 µm, and exceptionally reach 200 µm in the longest dimension, is striking. In order to solve the observed discrepancy in size distributions, one sample of pristine MSZ from the Hartley Mine, weighing about 1 kg, was treated by electric pulse disintegration. Altogether, 75 PGM grains larger than 50 µm were hand-picked from the treated material. The observed maximum true diameters were 480 µm for (Pt,Pd)-bismuthotellurides (moncheite), 85 µm for sperrylite, 195 µm for cooperite/braggite, and 300 µm for Pt-Fe alloy grains (Oberthür *et al.* 2008). These results emphasize that coarser PGM are present in the pristine MSZ, and that the observed differences in grain sizes mainly result from the different methods of sampling (only in rare cases, grains < 50 µm are recovered by panning) and investigation (depending on grade and grain size distribution, tens to hundreds of polished sections need to be investigated to find PGM with grain sizes > 100 µm).

Geochemically, it is notable that the Pt/Pd proportions increase from pristine via oxidized MSZ ores to the fluvial environment. For example, average Pt/Pd ratios of 1.28 characterize pristine sulfide MSZ, whereas pervasively oxidized MSZ ores have average Pt/Pd ratios of 2.43 (Oberthür *et al.* 2003a, 2003b, Oberthür & Melcher 2005, Locmelis *et al.* 2010). Regarding the detrital PGM assemblage, the Pt/Pd ratio is estimated to lie between *ca.* 30–50. This corroborates the earlier findings of, *e.g.*, Wagner (1929) on the Merensky Reef of the Bushveld and of Evans *et al.* (1994) and Oberthür *et al.* (2003b) on surface ores

of the Great Dyke, that Pd is more mobile than Pt and is dispersed in the supergene environment.

The present work further demonstrates that the PGE-bismuthotellurides, PGE-sulfarsenides, and PGE-oxides dominating the PGM assemblages in the pristine and oxidized MSZ are components that are unstable during weathering and mechanical transport. Including the genetically somewhat disputed Pt-Fe alloys, the order of decreasing stability in the supergene environment is as follows: (1) Pt-Fe and Os-Ir-Ru alloys (very stable) → (2) sperrylite (stable) → (3) cooperite/braggite (variably stable/"meta-stable") → (4) PGE-bismuthotellurides, PGE-sulfarsenides, and PGE-oxides (unstable).

Finally, the detection of PGM in stream sediments by the nowadays somewhat neglected simple field methods had their merits previously, as the PGM acted as indicator minerals for platinum mineralization (*e.g.*, Bushveld; Merensky 1924, 1926, Cawthorn 1999, Oberthür *et al.* 2004). The systematic recovery of PGM from stream sediments, soils, and till should regain wider application in mineral exploration, especially when combined with PGM characterization by modern micro-analytical methods (Oberthür *et al.* 2008, McClenagan & Cabri 2011).

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