# Detrital Platinum-Group Minerals (PGM) in Rivers of the Bushveld Complex, South Africa – A Reconnaissance Study

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### Introduction

The initial major discovery of platinum in the Bushveld Complex, which subsequently led to the discovery of the Merensky Reef, was made in 1924 by panning in a river bed on the farm Maandagshoek in the Eastern Bushveld (Merensky 1924, 1926, Wagner 1929, Cawthorn 1999a, 1999b, 2001). Wagner (1929) also reports on a number of alluvial diggings in the Bushveld Complex that produced some platinum. However, as mining commenced on the rich pipes and reef-type deposits of the Bushveld, alluvial PGM soon became forgotten and no published information on the placer PGM is available. Cawthorn (1999b, 2001) performed geochemical investigations of streamsediments at and close to the 1924 discovery site and found Pt concentrations up to 0.79 ppm. Our experience with alluvial PGM in rivers along the Great Dyke in Zimbabwe (Oberthür et al. 1998, Oberthür 2002) indicated that, at the above grades, the stream sediments investigated by Cawthorn (1999b, 2001) should contain discrete PGM. Guided by G. Cawthorn, we performed reconnaissance sampling in the Eastern Bushveld in July 2000 (Gast and Wittich 2001). In the following, we provide a first comprehensive, though preliminary description of the assemblage of detrital PGM based on SEM and electron microprobe work.

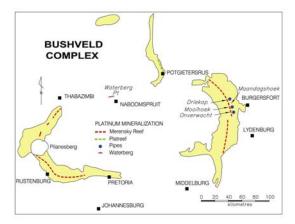


Figure 1. Geology of the Bushveld Complex showing the exposure of the Mafic Phase (Rustenburg Layered Suite), and location of the farm Maandagshoek in the Eastern Bushveld. Modified after Cawthorn (2001).

## Regional geology

Sampling concentrated on stream sediments of rivers in the vicinity of the original discovery of the Merensky Reef on the farm Maandagshoek close to Burgersfort in the Eastern Bushveld (Fig. 1). The localities investigated by Cawthorn (1999b, 2001), i. e. those documented by Merensky (1924) as Pt-bearing, and additional places along the Moopetsi river were sampled. The river valley runs approximately north-south, subparallel to the layering of the Mafic Phase of the Bushveld Complex, and is between 2 and 3 km wide. On the farm Maandagshoek, the Merensky Reef and the UG2 are about 2 km apart and crop out on the western and eastern side, respectively, of the Moopetsi river. Smaller ultramafic pipes occur to the east, and the better-known Mooihoek and Driekop pipes to the east and north, respectively, between about 3 and 8 km away from the sampling

#### **Samples and Methods**

Between 50 - 100 kg of sand- to gravelsized sediment each were taken, weighed and sieved at 15 different sample points. Fractions >2mm were checked by panning, however, as PGM or gold grains were absent, this fraction was discarded later and only the fraction <2mm was treated further. After weighing, the material was panned 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 size fractions <2mm, and the investigation of the final concentrates under a binocular microscope. Altogether, 1127 kg of sediment was treated, resulting in 5.232 kg of pre-concentrates and 6.4 g of final concentrates. The final heavy mineral concentrates mainly consisted of grains of chromite and magnetite (95 - 99%) and grains of ilmenite, rutile, zircon, baddeleyite, monazite, PGM and gold. PGM and gold grains were extracted from the final concentrates by hand, transferred to a sample holder and studied using a scanning electron microscope (SEM) with an attached energydispersive analytical system. Selected PGM grains

were mounted, polished sections were prepared, and the PGM grains were analyzed using a CAMECA SX100 electron microprobe.

#### **Detrital PGM**

The 15 final concentrates contained 6036 grains of PGM and 406 grains of gold. The richest sample had a content of 1.29 g PGM/t and 0.13 g Au/t. The largest PGM grain was a Pt-Fe alloy with a maximum diameter of 1.6 mm (Fig. 2a), the largest gold grain was 0.9 mm in diameter.

SEM investigations are valuable in the study of grain morphologies and allow to obtain semiquantitative analytical data of mineral grains. However, SEM analyses are performed on the surfaces of grains only, and therefore, thin crusts on grains or overgrowths may compositions that differ from the internal mineralogy of the grains. Indeed, polished section studies and the electron microprobe analyses demonstrated that especially a number of PGM grains assigned to Pt or Pt-Fe alloy had cores of cooperite/braggite. This fact must be taken into consideration regarding the PGM proportions obtained by SEM.

The semiquantitative overview by SEM (1425 PGM grains studied) showed that the PGM assemblage is mainly composed of grains of Pt and Pt-Fe alloy (together 73.2%), the Pt- and Pd-sulfides cooperite and braggite (14.2%) and sperrylite (10.2%). The remainder (2.4%) consisted of a variety of rarer PGM. The highest proportion of PGM grains was found in the fraction <125  $\mu$ m. The largest grain attained 1.6 mm, the smallest grain was 40  $\mu$ m in diameter. Besides monomineralic PGM grains, a large number of grains are intergrowths of between 2 and 5 different PGM, the most common association being laurite embedded in Pt-Fe alloy grains.

Pt-Fe alloy grains are up to 1.6 mm in diameter (mostly beween 100 – 200 µm) and have various surface morphologies. Grains with well-rounded shapes (Fig. 2a) are most common, however, cubic crystals are also present (Fig. 2b). Sperrylite grains are generally multi-facetted crystals without corrosion or mechanical wear (Fig. 2c). The (Pt,Pd)-sulfides cooperite and braggite are mainly present as splintered grains. Other PGM are laurite and chemically different Ru-Os-Ir-alloy (always intergrown with Pt-Fe alloy), atheneite, stibiopalladinite, and some undetermined phases consisting of various combinations Pt, Pd and/or Rh with Sb, As, and/or S. Common intergrowths are laurite and Ru-Os-Ir alloy embedded in or attached

to Pt-Fe alloy grains (Fig. 2d). The gold grains are flakes with bent edges or equidimensional grains with smooth surfaces.

Microprobe analyses were conducted on a total of 252 PGM and 12 gold grains. About 68% of the PGM consisted of single or polyphase, variably altered grains of Pt-Fe alloy. More than 78% of the Pt-Fe alloy grains have compositions ranging from Pt<sub>3</sub>Fe to Pt<sub>1.5</sub>Fe ("ferroan platinum") with 56-73 at% PGE, and up to 31 at% Pd, 14 at% Rh, and 12 at% Ru. The remaining 22% are solid solutions of (tetraferroplatinum), (ferronickelplatinum) and Pt<sub>2</sub>FeCu (tulameenite). A large number of grains of ferroan platinum are mantled by Pt(Fe,Cu,Ni), interpreted to be an alteration rim (Figs 2e, f). Many of these rims have an additional outermost rim consisting of a Ni-rich phase close to Ni<sub>2</sub>FePt in composition (Fig. 2g). Pd-Pb and Pd-Hg phases are occasionally also present in these rims. In a few cases, grains of Pt-rich (Fig. 2 h) or Ru-rich oxides are present, probably representing alteration products.

Polyphase Pt-Fe alloy grains occur as two textural varieties: (i) as homogeneous grains with either lamellar (Fig. 2f) or euhedral inclusions of other PGM, or (ii) as agglomerates of several PGM. In decreasing order of abundance, the following minerals are present in polyphase grains: laurite, Rh-Ir sulfides (bowieite-kashinite and prassoite), cooperite, braggite, alloys dominated by Ru (usually Ru<sub>70</sub> - see Fig. 2f), Pt or Os (rare), Pd-Te (Fig. 2e) and Pd-Sb-(As) phases, hollingworthite and irarsite, RhNiAs, PdRhAs, Pd<sub>3</sub>Fe, (Cu,Pd)<sub>5</sub>S<sub>2</sub>, atokite (Pd,Pt)<sub>3</sub>Sn, Ni-Ir-Rh monosulfide, and gold.

Pt-Pd-Ni sulfides (cooperite, braggite) comprise 14% of the investigated PGM. More than 50% of the Pt-Pd-Ni sulfide grains are severely corroded and rimmed by a porous phase of pure Pt, indicating removal of Pd and S during weathering. Intergrowth with prassoite, bowieite and laurite are observed in polyphase grains. Sperrylite (7% of the PGM grains) mainly occurs in the form of monophase crystals of which in excess of 90% are unaltered. Large single grains of stibiopalladinite, isomertieite and mertieite II, in rare cases overgrown by sperrylite and pure Pt, or associated with kotulskite Pd(Bi,Te), represent 3% of the PGM grains. The remainder comprise laurite (3%) and a number of various alloys.

Examples of unusual polyphase PGM are:

(i) The phase  $(Cu,Pd)_5S_2$  with inclusions of  $Pd_3Fe$  intergrown with  $Pd_3(Te,As)$  which contains lamellae of  $Pd_3Te$  (keithconnite).

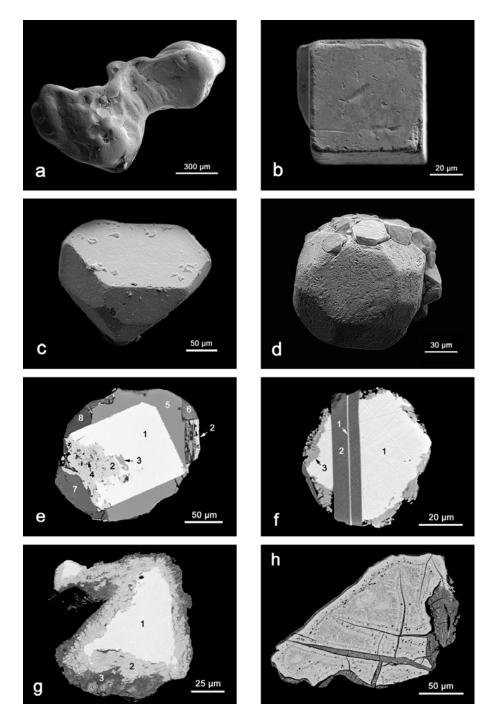


Figure 2. Scanning electron microscope images (SEM) of individual PGM grains and backscatter electron images (BSE) of PGM in polished sections. 2a) Pt-Fe alloy grain (1.6 mm in diameter) with smooth surface. Grain 9801/SA1005. SEM. 2b) Well-crystallized cubic Pt-Fe alloy grain. Note slightly contorted edges. Grain 9531/SA1004. SEM. 2c) Sperrylite crystal showing little attrition. Grain 7747/SA1001. SEM. 2d) Grain of Pt-Fe showing cubic crystal faces and smooth surface polish, intergrown with hexagonal grains of laurite (on top). Grain 9354/SA1004. SEM. 2e) Polyphase grain of (1) ferroan platinum corroded by (2) Pt(Fe,Cu) and overgrown by (5) telluropalladinite, an unknown (6) Pd-Te-Fe-Si-O phase, (7) Fe hydroxide and (8) a Ca-Mn-Fe silicate. The Pt-Fe alloy phases carry inclusions of (3) kotulskite PdTe and (4) keithconnite Pd<sub>3</sub>Te. Grain AS6392/29. BSE image. 2f) Polyphase grain of (1) ferroan platinum with (2) a lamellar Ru-rich alloy, overgrown by (3) Pt(Fe,Cu). Grain AS6392/111. BSE image. 2g) Ferroan platinum (1) showing two-stage alteration to (2) Pt(Ni,Fe) and (3) Ni<sub>2</sub>PtFe. Grain AS6444/9. BSE image. 2h) Pt-Fe-Cu alloy (brightest colour) replaced by Pt-Fe-Cu oxide phases (light grey). Crack filling and rim consist of an undefined Pt-Fe-Si-O phase. Grain AS6444/31. BSE image.

(ii) Unnamed Pd(Cu,Te) with drop-like inclusions of PdHg. (iii) The phase  $(Pt,Rh)_{2.7}$ Fe intergrown with  $Ru_{67}Ir_{10}Pt_9Rh_6(Os,Ru,Fe)_8$  and  $Ru_{43}Pt_{28}Rh_{19}(Os,Ru,Fe)_{10}$ , one grain of RhNiAs, and having a rim of  $Ni_2$ FePt.

The gold grains are internally homogeneous and silver-rich (between 17-40 at% Ag) and have variably thick outer rims of of silver-poor or pure gold. One grain contained numerous tiny (1-5  $\mu$ m in diameter), round to oval inclusions of atokite (Pd<sub>3</sub>Sn), another one had a larger inclusion of stibiopalladinite.

#### **Discussion and Conclusions**

Our preliminary data show that the assemblage of detrital PGM is far more complex than anticipated regarding (i) the large number of different PGM identified, (ii) the complex and multiple intergrowths of various PGM, (iii) the wide range of Pt-Fe alloy compositions, and (iv) secondary alteration features which are especially prominent on cooperite/braggite and Pt-Fe alloy grains.

Based on Pt:Pd:Au ratios of the <250 µm sediment fraction, Cawthorn (2001) hypothesized that the most probable source of the PGE is the Merensky Reef. However, the present study has shown that the relationship is not that straightforward, as secondary alteration of PGM in the weathering environment preferentially removes Pd relative to Pt and Au. Furthermore, Cawthorn (2001) remarked that the sedimentological history of the sand and gravel deposits at Maandagshoek is not yet understood due to Pliocene to recent changes in the geomorphology of the area. Therefore, no definite decision can be made vet on the origin of the detrital PGM(one specific source only or multiple sources), also in the light of the high variability of PGM assemblages recorded from the Merensky Reef and the UG2. An additional problem is posed by the differences in grain sizes of the primary PGM (usually <50 μm) and the detrital PGM (all >40 µm, up to 1.6 mm in diameter). Our ongoing studies specifically concentrate on some of the open questions. Further studies aim at sampling the major rivers draining the Bushveld Complex.

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