

Platinum-group mineral assemblages in the Platreef at the Sandsloot Mine, northern Bushveld Complex, South Africa

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ABSTRACT

Platinum group mineral (PGM) assemblages in the Platreef at Sandsloot, northern Bushveld Complex, in a variety of lithologies reveal a complex multi-stage mineralization history. During crystallization of the Platreef pyroxenites, platinum group elements (PGE) and base-metal sulphides (BMS) were distributed throughout the interstitial liquid forming a telluride-dominant assemblage devoid of PGE sulphides. Redistribution of PGE into the metamorphic footwall by hydrothermal fluids has formed arsenide-, alloy- and antimonide-dominant assemblages, indicating a significant volatile influence during crystallization. Serpentinization of the footwall has produced an antimonide-dominant PGM assemblage. Parts of the igneous reef were subjected to alteration by a late-stage, Fe-rich fluid, producing ultramafic zones where the telluride-dominant assemblage has been recrystallized to an alloy-dominant one, particularly rich in Pt-Fe and Pd-Pb alloys. A thin, small-volume zone of PGE-BMS mineralization along the base of the hangingwall contains a primary PGM assemblage that is locally altered to one dominated by Pt/Pd germanides. This is thought to have formed when the new pulse of Main Zone magma entered the chamber, and scavenged PGE from the underlying Platreef pyroxenites. That each major rock type at Sandsloot contains a distinctive PGM assemblage reflects the importance of syn- and post-emplacement fluid and magmatic processes on the development of Platreef mineralization.

KEYWORDS: PGM, Bushveld Complex, South Africa, Sandsloot mine, Platreef, Pt, Pd, base-metal sulphides.

Introduction

THE Bushveld Complex of South Africa is the largest layered igneous intrusion in the world and is the largest single host of platinum-group elements (PGE) yet discovered. The major PGE deposits of the Bushveld Complex are the stratiform Merensky Reef and UG2 chromitite layer, and the stratabound, but not stratiform, Platreef. The complex can be divided into an eastern and western limb of similar size; a southern limb, identified beneath cover rocks by gravity studies; and a smaller northern limb (Cawthorn *et al.*, 2002). The Platreef, located in

the northern limb, has an estimated Pt+Pd reserve of 16.3 million ounces (Cawthorn, 1999), and is currently being mined by open-pit methods by Potgietersrus Platinums Ltd., a subsidiary of Anglo Platinum, at the Sandsloot and Zwartfontein South pits ~30 km northwest of the town of Mokopane (formerly Potgietersrus; Fig. 1).

The northern limb of the Bushveld Complex strikes approximately north–south and is slightly sinuous in shape (Fig. 1). Mafic igneous lithologies of the Rustenburg Layered Suite (RLS) of the complex dip west-southwest with the pyroxenitic Platreef located at the base of the igneous package north of Mokopane, in direct contact with metamorphosed sedimentary and igneous country rocks. A thick sequence of fairly homogenous gabbro-norites and norites attributed

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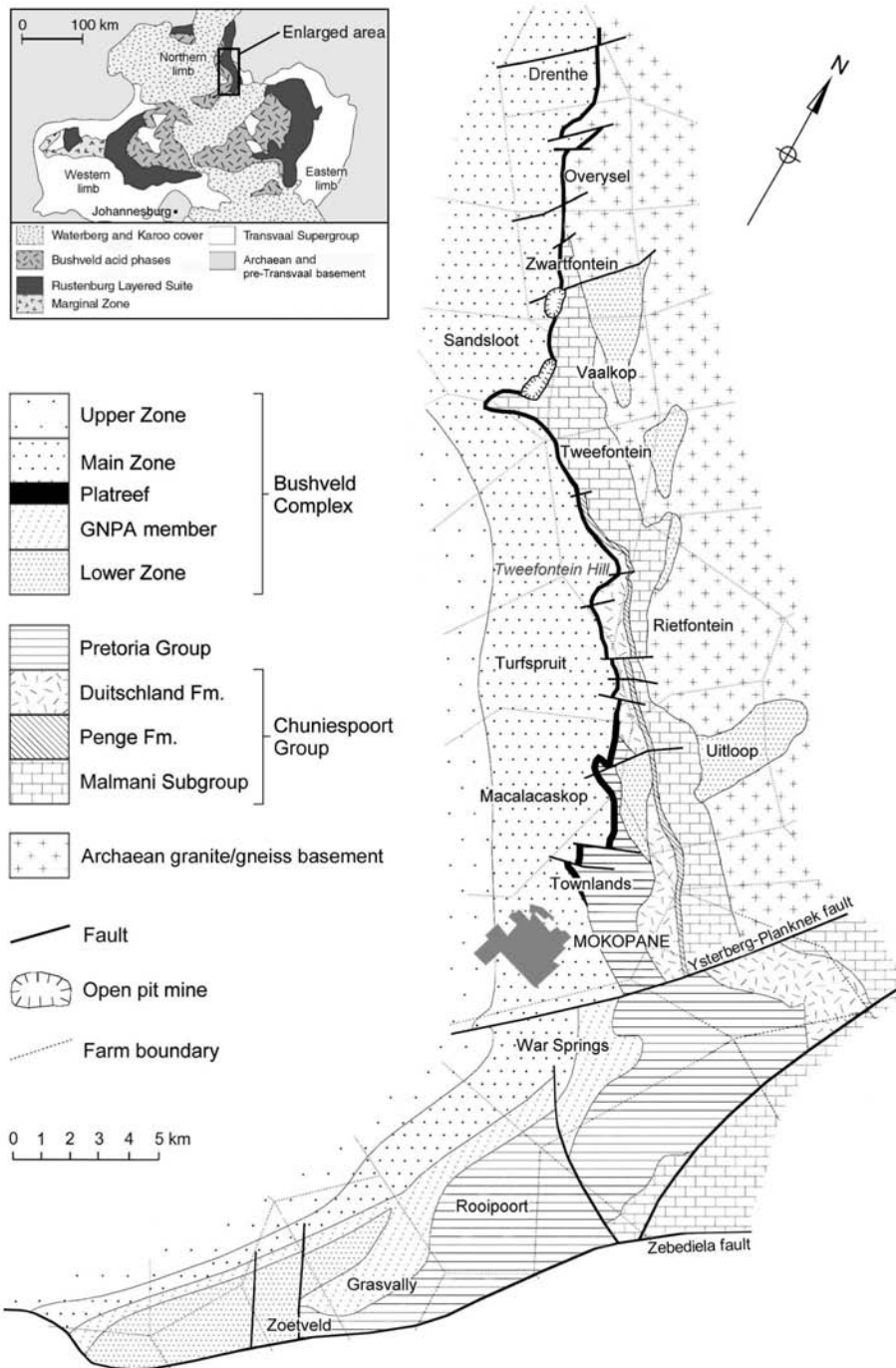


FIG. 1. Geological map of the central and southern sections of the northern limb of the Bushveld Complex, showing the Platreef and localities and lithologies referred to in the text (after Kinnaird and Nex (2003), von Gruenewaldt *et al.* (1989) and Hammerbeck and Schürmann (1998)).

to the Main Zone of the RLS overly the Platreef pyroxenites.

Other than brief references to the most common platinum-group minerals (PGM) by Schneiderhöhn (1929) and Gain and Mostert (1982), very few data on the PGM assemblages within the Platreef have been published. Kinloch (1982) summarized data from exploration boreholes on Zwartfontein and Overysel, north of the current Sandsloot mine and suggested that regional variations could be related to the amount of assimilation and contamination from the differing floor-rock lithologies. This was discussed further by Viljoen and Schürmann (1998), who summarized the overall abundances of PGM types in the Platreef as 30% Pt/Pd tellurides, 26% alloys, 21% PGE arsenides, and 19% sulphides, and highlighted the variations observed on different farms along strike. According to Viljoen and Schürmann (1998), from north to south, the most important PGM groups are: tellurides on the farm Drenthe; sulphides and tellurides on Overysel; alloys and tellurides on Zwartfontein and Sandsloot; sulphides on Tweefontein north; and tellurides at Tweefontein Hill. Recent work by Hutchinson *et al.* (2004) has shown the Platreef on Macalacaskop and Turfspruit to be rich in Pd bismuthides, tellurides and antimonides. Armitage *et al.* (2002) presented the results from a preliminary study of the PGE mineralization at Sandsloot, which found the PGM assemblage to be rich in alloys and tellurides and devoid of sulphides. This study builds on these findings and aims to provide further evidence of the processes governing the distribution of PGE in the Platreef.

Geology

From south to north, the northern limb of the Bushveld Complex rests upon a succession of progressively older sedimentary units of the late Archaean–early Proterozoic Transvaal Supergroup and Archaean granite/gneiss basement, in what has been termed an ‘igneous transgression’ (Wagner, 1929). The footwall units are, north from Mokopane: quartzites and shales of the Timeball Hill Formation; shales of the Deutschland Formation; the Penge Banded Iron Formation; dolomite of the Malmani Formation and, north of Zwartfontein, Archaean granite/gneiss basement (Fig. 1). Samples used in this study were taken from the Sandsloot mine, where the footwall is Malmani Dolomite. The hangingwall along the entire strike of the reef is

composed of gabbro-norites and norites ascribed to the Main Zone of the RLS.

The geology of the Platreef at Sandsloot Mine has been described by Harris and Chaumba (2001), Armitage *et al.* (2002), McDonald *et al.* (2005b), and Holwell *et al.* (2005) and is summarized below, together with the authors’ own observations on previously undescribed lithologies. The majority of the Platreef ‘package’ can be divided into hangingwall lithologies, igneous Platreef lithologies, and a variety of metamorphic footwall lithologies. There are variations in lithology on a metre scale along the length of the Platreef in the Sandsloot pit, and the variations are summarized in Fig. 2.

Footwall lithologies

The lowermost footwall lithology exposed in the Sandsloot pit is a series of highly altered and variably serpentinized, metamorphosed calc-silicate rocks, derived from the Malmani Dolomite. These generally retain some semblance of the original bedding and are often interbanded with more massive clinopyroxenites and thin serpentinites. In many places, the immediate footwall to the Platreef pyroxenites, separating the igneous reef and the calc-silicates, and are a series of clinopyroxenites, which are either green, grano-blastic diopsidites, often recrystallized with 120° grain boundary triple junctions, or more amorphous purple-grey clinopyroxenites. Olivine is present in variable amounts, and is usually serpentinized, occasionally to a stage where no relict olivine remains. The rocks are of metamorphic origin, as shown by a higher Ca content in the clinopyroxenes compared to those in the igneous pyroxenites, and a whole-rock Cr content much lower than the igneous reef (Harris and Chaumba, 2001). These rocks were termed ‘parapyroxenites’ by Wagner (1929). Xenoliths of clinopyroxenite and calc-silicate where all original features have been overprinted occur regularly throughout the igneous reef at Sandsloot and are usually serpentinized.

Igneous Platreef lithologies

The igneous reef pyroxenites are typically coarse-grained, occasionally pegmatitic, and made up of cumulus orthopyroxene, with intercumulus plagioclase and clinopyroxene. In many cases plagioclase makes up >10% of the modal

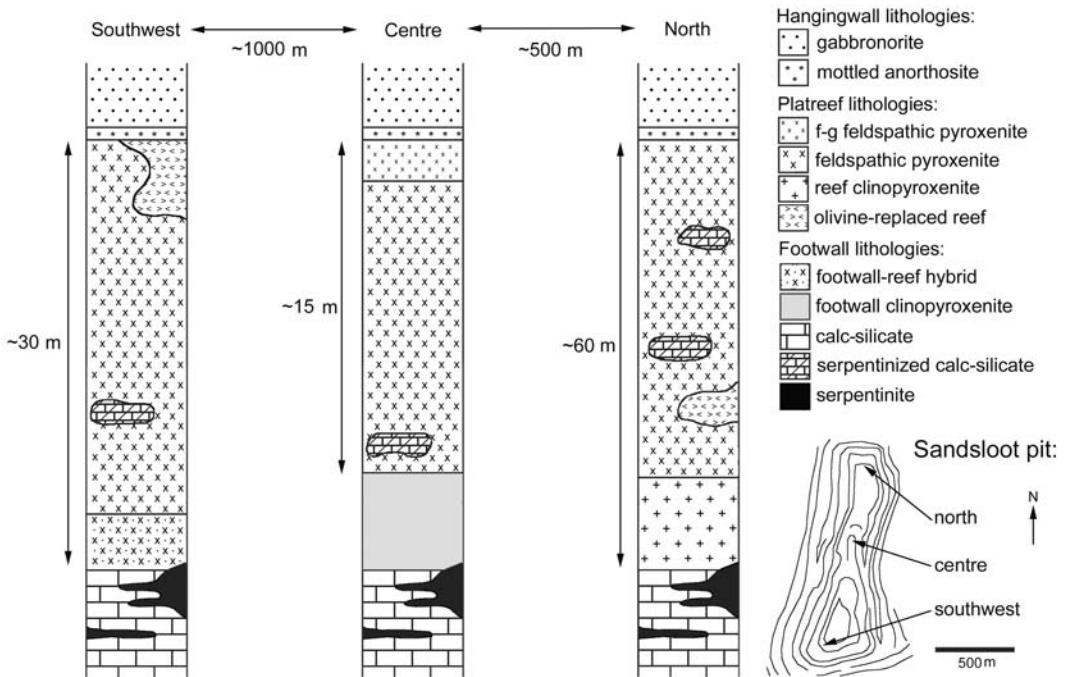


FIG. 2. Simplified stratigraphic representation showing all major rock units in the southwestern, central and northern parts of the Sandsloot pit.

mineralogy, and therefore the rock should be classified as gabbronorite under IUGS classification. However, in keeping with general Bushveld nomenclature in which names generally reflect the cumulus mineralogy, we refer to these rocks as feldspathic pyroxenites, and gabbronorites are rocks with both pyroxenes, and cumulus plagioclase. A fine-grained feldspathic pyroxenite barren of mineralization, located below the hangingwall contact, is present in the central part of the Sandsloot pit. Plagioclase is commonly altered to fine-grained white mica and epidote minerals. Base-metal sulphides (BMS) occur within the interstitial assemblage and are discussed below. Chromitites were not encountered, though chromite, ilmenite and rare armalcolite are present as minor phases, with ilmenite particularly common in the pegmatitic lithologies and most commonly found as inclusions along cleavage planes in interstitial clinopyroxene. Some areas of the igneous reef in the southwestern and northern parts of the pit contain a considerable amount of replacement olivine, which is Fe-rich (Fo_{62-67}) and overprints orthopyroxene, producing peridotitic zones with up to

60% olivine (Fig. 3a). This is thought to have formed from the reaction of a late-stage, Fe-rich, SiO_2 -poor fluid with the primary Platereef pyroxenites (McDonald *et al.*, 2005b), causing desilicification of orthopyroxene to form olivine. Parts of the igneous reef are also overprinted with a secondary, low-grade metamorphic assemblage that includes chlorite, sericite, actinolite and sphene highly suggestive of abundant fluid alteration. The basal part of the igneous reef in some sections in the southwest part of the pit is marked by a wehrlitic rock, with igneous, though not cumulus, textures, which is often partially serpentinized. This has been interpreted as a footwall-reef hybrid lithology by McDonald *et al.* (2005b), on the basis that geochemically, the rocks are intermediate between reef pyroxenite and footwall clinopyroxenite in terms of Ca and Cr content. In the northern part of the pit, the lower part of the igneous Platereef comprises clinopyroxenite, with cumulus clinopyroxene, and ~5% highly altered interstitial plagioclase. These rocks contain 1000–2000 ppm Cr and the clinopyroxenes have a composition of Wo_{45} which are consistent with the Platereef pyroxenites.

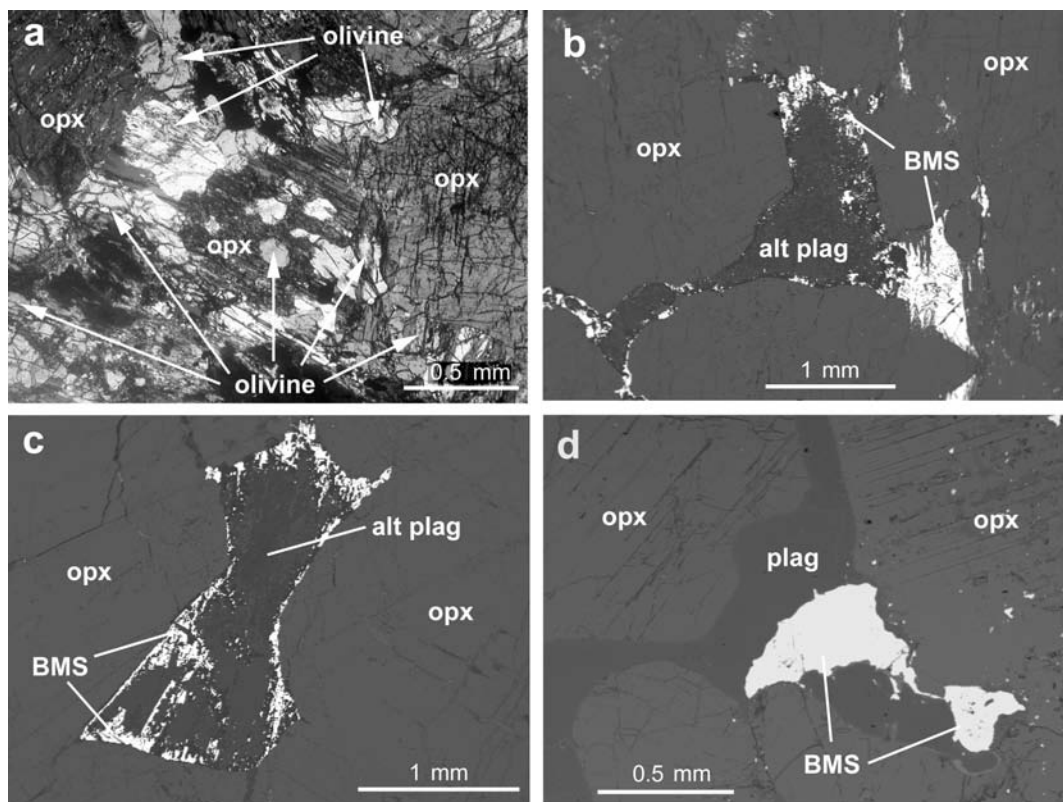


FIG. 3. (a) Thin section of olivine-replaced reef showing olivine overprinting orthopyroxene (opx); in cross-polarized transmitted light. (b–d) Backscattered electron photomicrographs of (b and c) typical associations of base-metal sulphides (BMS) intergrown with altered plagioclase (alt plag) at the edge of the interstitial region enclosing cumulus, sulphide-free orthopyroxene in Platreef pyroxenites at Sandsloot, and (d) typical association of discrete BMS grains with unaltered plagioclase (plag) from the Merensky Reef in the eastern Bushveld, for comparison.

In contrast, footwall clinopyroxenites contain <100 ppm Cr and have clinopyroxene compositions of Wo_{50} .

Hangingwall lithologies

The hangingwall to the Platreef pyroxenites is made up of norites and gabbronorites, resembling those of the Main Zone elsewhere in the Bushveld Complex. Plagioclase is the cumulus phase and makes up ~50–70% of the modal assemblage, with oikocrystic orthopyroxene and clinopyroxene making up the remainder in a crystallization sequence plagioclase-orthopyroxene-clinopyroxene. Base-metal sulphides (pentlandite, pyrrhotite and chalcopyrite) and oxides (almost exclusively ilmenite) are rare. A thin (<1 m) mottled anorthosite layer is often present at the

base of the hangingwall. The contact with the underlying pyroxenites is sharp and undulatory and is described in detail by Holwell *et al.* (2005).

Mineralization

Base-metal sulphides (primary pyrrhotite, pentlandite, chalcopyrite and minor secondary pyrite and bornite) are common throughout the reef pyroxenites, though heterogeneously distributed, and occur within the interstitial assemblage. However, the sulphides do not occur as well defined euhedral crystal aggregates with sharp linear contacts with surrounding silicates as, for example, they do in the Merensky Reef. They are invariably 'ragged' in morphology due to the common intergrowth with plagioclase and secondary amphiboles, particularly actinolite,

epidote and micas (Fig. 3*b,c,d*). In samples where plagioclase has been replaced by white mica, small blebs of sulphide commonly rim the outer edge of the interstitial region (Fig. 3*b,c*), and rarely encroach into orthopyroxene, though interstitial clinopyroxene often contains blebs of sulphide along cleavage planes. In the footwall, the assemblage is more diverse and contains the above assemblage along with minor amounts of sphalerite (ZnS), millerite (NiS), galena (PbS), chalcocite (Cu₂S) and alabandite (MnS).

Platinum group mineralization occurs throughout the igneous reef, its xenoliths, into the footwall and occasionally at the base of the hangingwall. Grades are variable within the igneous reef, and are more erratic through the footwall, though it is generally lower than in the igneous reef, however some serpentinized units carry very high grades. Table 1 shows Pt/Pd ratios for a range of reef, footwall and hangingwall samples together with an indication of grade. The Pt/Pd ratios in the igneous reef and hangingwall are around unity, which decrease slightly into the footwall, as would be expected if PGE were transported into the footwall via fluid activity, due

to the greater relative mobility of Pd compared to Pt and the other PGE (e.g. Wood, 2002). Conversely, Pt/Pd ratios >1 in some reef samples may indicate removal of greater amounts of Pd during remobilization of PGE into the footwall and therefore it is likely that the original Pt/Pd ratio of the igneous Platreef was probably unity or lower.

Platinum group minerals

Fifty-eight polished thin sections and blocks from the hangingwall, igneous reef and metamorphic footwall from the Sandsloot pit were analysed at Cardiff University using a Cambridge Instruments LEO S360 scanning electron microscope, coupled to an Oxford Instruments INCA energy dispersive X-ray analysis system. More than 1000 individual PGM grains were identified and are listed in Table 2. Each individual grain was classified by type and association. The vast majority of PGM were Pt and Pd minerals, while the only major carriers of Ir, Ru and Rh identified were members of the hollingworthite/platarsite/irarsite series. No carriers of Os were found, which may suggest that

TABLE 1. Pt/Pd ratios and relative grade for selected hangingwall (HW), reef and footwall (FW) samples. PGE grade based on Rh+Pt+Pd+Au. low: <2.0 ppm; intermediate: 2.0–6.0 ppm; high: >6.0 ppm.

Sample	Lithology	PGE grade	Pt/Pd
PA-N1-31	HW norite	low	1.36
PA-N3X4A	HW gabbro-norite	low	0.87
PA-SW1-47B	HW gabbro-norite chill	low	0.95
PA-SW1-32	Reef feldspathic pyroxenite	intermediate	0.81
PA-SW1-28	Reef feldspathic pyroxenite	high	1.28
PA-SW1-20	Reef feldspathic pyroxenite	intermediate	0.88
PA-N1-30	Reef feldspathic pyroxenite	high	0.93
PA-N1-22	Reef feldspathic pyroxenite	intermediate	1.04
PA-N1-24	Reef feldspathic pyroxenite	intermediate	0.98
PA-N1-26	Reef feldspathic pyroxenite	high	1.94
PA-SW2-49	Reef feldspathic pyroxenite	high	1.48
DH-G	Reef feldspathic pyroxenite	high	1.03
DH-P	Reef pegmatoidal pyroxenite	intermediate	0.79
PA-SW1-40	Olivine-replaced reef	intermediate	0.55
PA-SW1-43	Olivine-replaced reef	high	0.70
SNN1-68	Reef clinopyroxenite	low	0.81
PA-SW1-8	Serpentinized calc-silicate xenolith	high	0.99
PA-SW1-1	FW clinopyroxenite	high	0.86
PA-E55	FW clinopyroxenite	intermediate	0.98
PA-EX6	FW calc-silicate	intermediate	0.84
PA-SW1-4	FW serpentinized calc-silicate	low	0.65
PA-S2-12	FW serpentinized calc-silicate	low	0.55
PA-S0	FW serpentinite	low	0.54

Os may not be present in discrete minerals, but as a trace component in BMS, for example. The PGM identified were grouped as: (1) Pt/Pd tellurides; (2) Pt/Pd bismuthides; (3) Pt/Pd arsenides; (4) Pt/Pd antimonides; (5) Pt/Pd germanides; (6) PGE sulphides; (7) PGE sulpharsenides; (8) PGE alloys with Fe, Cu, Sn, Pb and Tl; and (9) Au and Ag bearing phases. Each occurrence was also classified by its association: enclosed in sulphide, at sulphide-silicate boundary, or enclosed by silicates, in keeping with other studies of the PGE deposits of the Bushveld Complex.

Grain size and morphology

Each PGM grain's long and short axes were measured in micrometres. Grains $<1\ \mu\text{m}$ were ignored due to their relative volumetric insignificance, and the difficulties in accurately determining their composition. Relative proportions of the various mineral phases and PGM species type are based on an estimation of area (and by inference, volume) of each grain. Using the long- and short-axes dimensions, the area of each grain was approximated to the area of an ellipse around the two axes. This therefore produces data which accurately reflect the relative proportions of each PGM type within an assemblage. This method of data presentation is preferable to proportions of PGM type by number of grains, which can be biased by a relatively large amount of very small grains, for example. This approach is particularly pertinent when comparing PGM data with Pt/Pd ratios. If, say, the Pt/Pd ratio of the whole-rock

sample is around unity, when using the proportion by number of grains method, there may appear to be a deficit of one particular PGE represented by discrete PGM phases, which may be wrongly attributed to its presence in BMS phases or silicates. Therefore we present all the assemblage data in percentage of total area of all PGM.

Grain-size data for all PGM grains $>1\ \mu\text{m}$ in their longest dimension are shown in Fig. 4. From Fig. 4, it can be seen that in most rock types, ~80% of grains were $<10\ \mu\text{m}$ in length, with the exception of pegmatitic reef rocks, which had a higher average grain size with 50% of grains $>5\ \mu\text{m}$. The units with the lowest average PGM grain sizes ($>70\%$ of grains $<5\ \mu\text{m}$) were the footwall calc-silicates, the reef clinopyroxenites and the hangingwall gabbro-norite. No grains of $>100\ \mu\text{m}$ were found.

The PGM morphology varies with individual phases and also with association. Where surrounded by sulphides, PGM, and particularly electrum, are commonly present as rounded blebs. Where surrounded by silicates, grains vary from anhedral to euhedral. Moncheite (PtTe_2) is commonly found as laths, Pt_2Fe as cubic crystals, and sperrylite as tetrahedra. Most PGM identified occur as single-phase grains, though they may occasionally occur as compositionally zoned (Fig. 5a) or polyphase grains (Fig. 5b).

Assemblages

The PGM mineralogy in the variety of host-rock lithologies studied are summarized in Table 3. The most notable characteristic of the Sandsloot

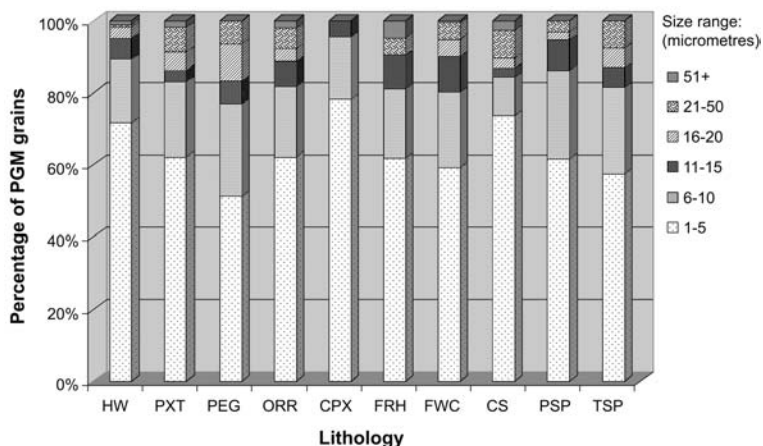


FIG. 4. Range of PGM grain size (longest axis) in the various host-rock lithologies at Sandsloot. See Table 2 for lithology abbreviations.

TABLE 2. Name and ideal formulae of all occurrences of PGM and Au-Ag minerals in the variety of host-rock types.

Name	Formula	HW	PXT	PEG	ORR	CPX	FRH	FWC	CS	PSP	TSP	Total
Kotulskite	PdTe	7	53	24	45	1	2	7	8	44	1	192
Sperrylite	PtAs ₂		30	6	6		2	52	18	13	4	131
Moncheite	PtTe ₂	1	50	36	18	6	1	5	1	9	1	128
unnamed	(Pd,Pt) ₂ Ge	65		3								68
Electrum	Au,Ag	1	15	4	9		1	5	1	20	2	58
Hessite	Ag ₂ Te		36					5	1	2		44
Sudburyite	PdSb							5	5		29	39
Zvyagintsevite	Pd ₃ Pb	4		2	21					1		28
Palladoarsenide	Pd ₂ As		2	1	1		18	4		1		27
Paolovite	Pd ₂ Sn	1						20		3		24
Geversite	PtSb ₂			4						5	14	23
unnamed	Pd ₃ Bi ₃ (Te,Sb) ₂							23				23
Pt-Fe alloy	Pt ₂ Fe	10			8					4		22
Froodite	PdBi ₂		1		2				1	16		20
Michenerite	PdBiTe	1	6			3		6				16
Sobolevskite	PdBi		2		3	3		3		5		16
unnamed	Pd ₂ (Sn,Sb)							15				15
Stibiopalladinite	Pd ₅ Sb ₂		2		3	1		4	1	3		14
Mertieite II	Pd ₈ (Sb,As) ₃		7						6			13
Atokite	Pd ₃ Sn				5		1	1	1			8
Native silver	Ag		5		1					2		8
Hollingworthite	RhAsS				1			2			4	7
unnamed	Pd ₃ Tl	7										7
Irarsite	IrAsS		2	1	2							5
Isoferroplatinum	Pt ₃ Fe		2	1				1				4
Merenskyite	PdTe ₂		2		2							4
Tulameenite	Pt ₂ FeCu			4								4
Platarsite	PtAsS		3									3
Rustenburgite	Pt ₃ Sn			3								3
Tetraferroplatinum	PtFe	1		2								3
Stillwaterite	Pd ₈ As ₃	1	1									2
unnamed	Pd ₅ Sb ₃									2		2
Auricupride	Au,Cu			1								1
Insizawite	PtBi ₂			1								1
Laurite	RuS ₂	1										1
Majakite	PdNiAs							1				1
Menshikovite	Pd ₃ Ni ₂ As ₃		1									1
Niggliite	PtSn										1	1
Palarstenide	Pd ₅ SnAs										1	1
Palladian gold	Au,Ag,Pd			1								1
Palladobismutharsenide	Pd ₂ (Bi,As)	1										1
Plumbopalladinite	Pd ₃ Pb ₂							1				1
Stannopalladinite	Pd ₅ Sn ₂ Cu			1								1
unnamed	PtAg ₂		1									1
unnamed	Pt ₂ SbSb										1	1
unnamed	PdTe ₃ Pb ₃							1				1
unnamed	Pd ₂ Bi							1				1
unnamed	Pd ₃ Bi ₂							1				1
unnamed	Pd ₂ (Sb,Bi,Te)							1				1

PGM assemblages identified here is the complete lack of PGE sulphides (also noted by Armitage *et al.*, 2002), with the exception of a single grain of laurite (RuS₂) in the hangingwall gabbronorite. This is unusual in that throughout the Merensky Reef, the UG2 chromitite and elsewhere in the

Platreef, namely Zwartfontein north, Overysel (Kinloch, 1982) and Drenthe (Gain and Mostert, 1982), PGE sulphides are ubiquitous in the form of cooperite (PtS), braggite [(Pt,Pd)S], laurite and other rarer minerals. The only other PGM found at Sandsloot containing any sulphur are a few

PGM ASSEMBLAGES FROM THE PLATREEF, BUSHVELD COMPLEX

Table 2 (contd.)

Name	Formula	HW	PXT	PEG	ORR	CPX	FRH	FWC	CS	PSP	TSP	Total
Unconstrained phases:												
	Pd-As-Sb			2								2
	Pd-Te-Bi				2							2
	Pt-Cu-Fe-Ag							2				2
	Pt-Pd-Sb-As								1		1	2
	Pt-Pb-Ag		1									1
	Pt-Fe-Te	1										1
	Pt-Au-Cu-Fe				1							1
	Pt-Pd-Pb-Te				1							1
	Pd-Pb-Te				1							1
	Pd-Pb-Pt				1							1
	Pd-Bi-Pb-Pt				1							1
	Pt-Pd-Te-Sb										1	1
	Pt-As-Sn-Sb										1	1
	Pt-Fe-Te-Pb										1	1
Composite polyphase grains, unconstrained compositions:												
	Pd-Sn-As-Te-Pb				1							1
	Au-Cu-Pt-Pd-Ag				1							1
	Pd-Pt-Fe-Cu-Sn-Te				1							1
	Pd-Pb-Te-Pt-Ir				1							1
	Pd-Pt-Te-Bi-Cu-Fe				1							1
	Pd-Bi-Sb-Sn-Te							1				1
	Ni-Bi-Pd-Ag-Au								1			1
	Pt-Sb-Te-Bi-Pb-As										1	1
	Pt-Sb-As-Au-Pb										1	1
	Pd-Sn-Sb-Pt-As										1	1
	Pt-Sb-Te-Bi-As										1	1
Total PGM grains:		102	222	79	156	23	23	163	44	132	64	1008

HW: hangingwall gabbro-norite; PXT: reef pyroxenite; PEG: reef pegmatite; ORR: olivine-replaced reef; CPX: reef clinopyroxenite; FRH: footwall-reef hybrid; FWC: footwall clinopyroxenite; CS: calc-silicate; PSP: partially serpentinized footwall; TSP: totally serpentinized footwall. Unconstrained phases were too small to determine formulae.

occurrences of the sulpharsenide hollingworthite/platarsite/irarsite series. As a whole, the Platreef at Sandsloot can be said to be dominated by Pt/Pd tellurides, alloys, and to a lesser extent, PGE arsenides and antimonides. In detail though, there is a great variation from one host rock type to another, particularly in terms of igneous reef versus metamorphic footwall, and several major trends in the PGM assemblage can be identified.

Reef pyroxenites and pegmatites

The igneous reef pyroxenites and pegmatites are dominated by Pt and Pd tellurides, particularly moncheite and kotulskite (PdTe). Hesseite (Ag₂Te) and electrum (Au,Ag) are common in the pyroxenites. Arsenides, particularly sperrylite, as throughout the deposit as a whole, are common, particularly in the pegmatites. The immediate

associations of the PGM are shown in Table 4. Most PGM in the pyroxenites and pegmatites are surrounded by silicates or located at the BMS-silicate boundary. However, even where surrounded by silicates, the PGM retain a strong spatial relationship with the BMS and many are in association with secondary amphiboles which replace BMS, and very few are found completely isolated from any BMS. The secondary assemblages of tremolite and actinolite around BMS grains in the primary Platreef pyroxenites are similar to those found in the Merensky Reef and UG2 chromitite, described by Li *et al.* (2004). The appearance of PGM as satellite grains around BMS grains may be due to the regression of the BMS boundary, with the PGM (originally at the edge of the sulphide blebs) remaining in their original positions. This association has also been noted in the Platreef at Macalacaskop and

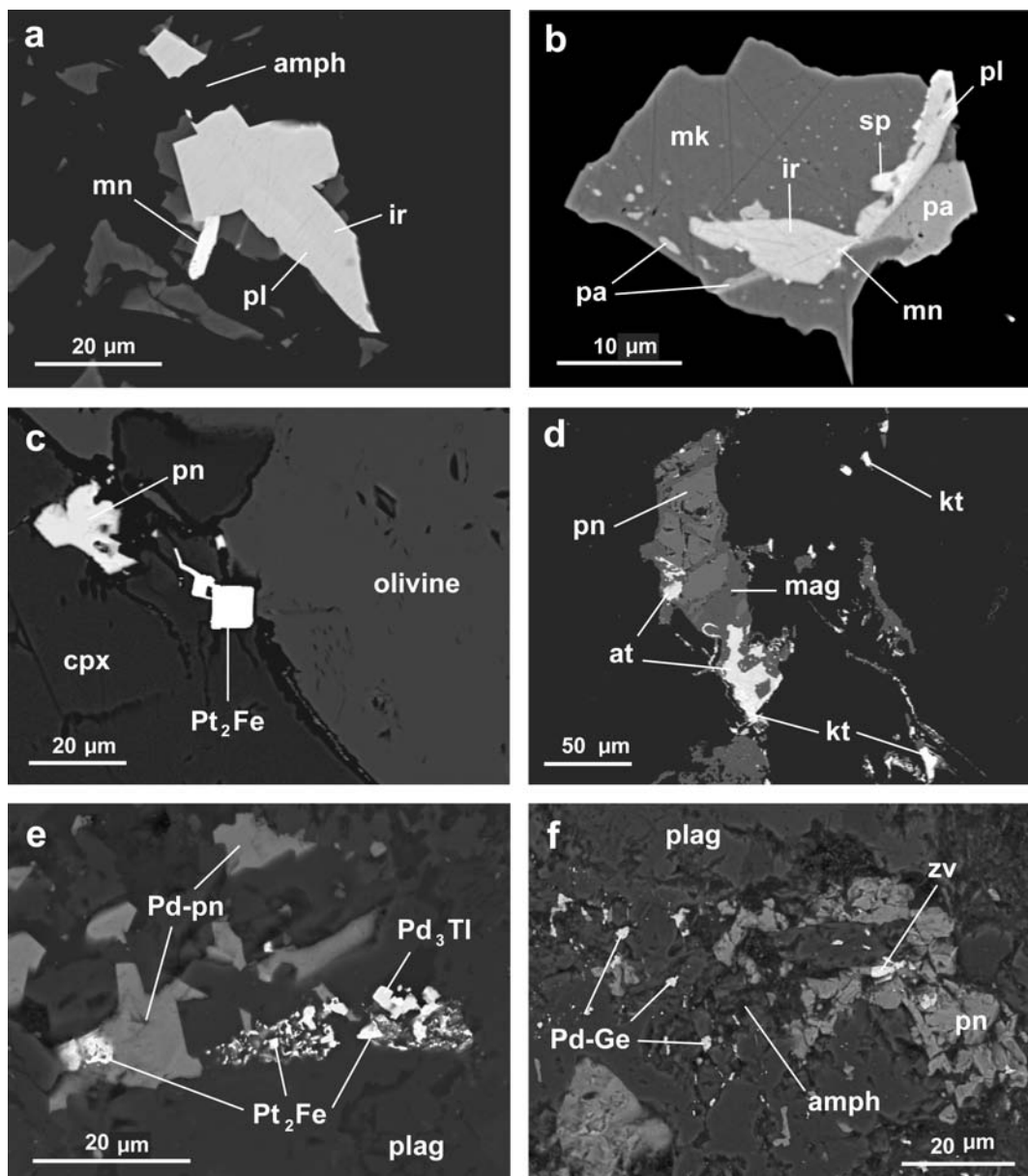


FIG. 5. Backscattered electron photomicrographs of PGM found in Sandsloot Platreef samples. (a) Zoned grain of irarsite (ir) and platarsite (pl) with moncheite (mn) from pegmatoidal pyroxenite reef. Note how the grain is cut by a secondary amphibole. (b) Polyphase PGM from pyroxenite reef consisting of menshikovite (mk), irarsite (ir), platarsite (pl), palladoarsenide (pa), sperrylite (sp) and moncheite (mn). (c) Typically cubic crystal of Pt_2Fe from olivine-replaced reef. (d) Association of atokite (at) and kotulskite (kt) with pentlandite (pn), oxidized to magnetite (mag) in a partially serpentinized sample of footwall. (e) Typical association of Pt_2Fe intergrown with palladian pentlandite (Pd-pn) and Pd_3Ti from hangingwall gabbronorite. (f) Cluster of Pd germanides surrounded by secondary amphiboles replacing non-Pd-bearing pentlandite with zvaigintsevite (zv) in the same hangingwall gabbronorite as in e.

TABLE 3. Proportions of PGM type within each lithology in percentage of the total area of PGM. See Table 2 for the lithology abbreviations.

PGM type:	HW	PXT	PEG	ORR	Lithology:		FWP	CS	PSP	TSP
					CPX	FRH				
Pt tellurides	0.6	40.1	38.8	4.9	11.6	0.3	10.3	0.2	6.8	0.2
Pd tellurides	6.0	19.2	18.2	31.1	26.6	3.6	1.6	6.1	26.4	
Pt bismuthides				0.1						
Pd bismuthides	0.4	0.8		3.5	4.0		22.3	0.1	21.8	
Pt arsenides		10.8	23.4	20.1	8.5	1.1	18.6	79.5	21.6	9.1
Pd arsenides	0.5	0.5	0.5			89.2	0.2		0.1	
Pt antimonides									2.6	46.3
Pd antimonides		0.9		2.7	39.4		4.9	2.8	0.6	35.0
Pd germanides	55.3		0.5							
PGE sulphides	0.4									
PGE sulpharsenides		0.8	14.5	0.1			0.3			4.4
Pt-dominant alloys	28.2	0.1		25.3			0.3		0.2	3.0
Pd-dominant alloys	8.6	3.8	0.3	9.1		5.8	40.1	11.3	0.6	0.2
Au/Ag-bearing phases		23.0	3.8	3.1	9.9		1.4		19.3	1.6
Total no. of grains	102	222	79	156	23	23	163	44	132	64

Turfspruit (Hutchinson and Kinnaird, 2005). The replacement by amphiboles and epidote appears to be paragenetically late as there is evidence of secondary minerals cross-cutting the PGM, such as in Fig 5a. Most electrum is found as rounded blebs within BMS grains. PGE antimonides were found to be extremely rare in the Platreef pyroxenites.

Olivine-replaced reef

Samples of reef pyroxenite which have undergone replacement by Fe-rich olivine have their own distinctive Pd-rich and alloy-dominant PGM assemblage, with abundant Pd tellurides, and Pt-Fe alloys. Table 3 indicates that Pt arsenides are also very abundant; however, Table 2 shows that only six sperrylites, in a total of 156 grains, were identified, though all were large relative to the other grains, which has caused the high percentage by area in Table 3. Table 1 shows that the Pt/Pd ratio in these rocks is ~0.6, therefore in this case, the proportion by area data in Table 3 appears to have been skewed by a small number of particularly large grains. We therefore consider that the true dominant species in this assemblage are Pd tellurides and alloys. The most common telluride, kotulskite, commonly contains much higher concentrations of Pb (up to 12 wt.%) than kotulskite in the unaltered pyroxenites, with a representative

composition in these rocks of $\text{Pd}_1\text{Te}_{0.74}\text{Bi}_{0.14}\text{Pb}_{0.12}$. The most common Pd alloy is zvyagintsevite (Pd_3Pb), which is particularly characteristic of this lithology. The Pt-Fe alloys have a typical composition of Pt_2Fe , which is intermediate between isoferroplatinum (Pt_3Fe) and tetraferroplatinum (PtFe), and is therefore referred to under the nomenclature of Cabri and Feather (1975) as Pt-Fe alloy. In these rocks, Pt-Fe alloys occur as discrete cubic crystals (Fig. 5c) rather than as intergrowths with BMS or magnetite, which is the more common mode of occurrence in the Merensky Reef (Kinloch, 1982; Kinloch and Peyerl, 1990). The other common Pt-dominant alloy in the olivine-replaced rocks is tulameenite (Pt_2FeCu), which was not found in any of the other lithologies. A few examples of PGE bismuthides and antimonides were also found in the replaced reef, which are absent or extremely rare in the unaltered pyroxenite reef. Arsenides and electrum are also present. Only 8% of PGM are included in BMS (Table 4) and many of the 43% which are surrounded by silicates do not show the close spatial relationship to BMS that those in the unaltered reef show, with some often isolated along veins.

Reef clinopyroxenites

The reef clinopyroxenites at the base of the Platreef in the northern part of the pit were found

TABLE 4. Textural associations of PGM (excluding Au/Ag alloy) in the variety of host-rock types and the percentage of grains. See Table 2 for lithology abbreviations.

All PGM, Au, Ag phases Association:	HW	PXT	PEG	ORR	CPX	FRH	FWP	CS	PSP	TSP
Enclosed in BMS (%)	10.3	12.6	9.1	8.2		77.8	10.4	6.4	21.2	
BMS-silicate contact (%)	29.9	38.1	16.9	49.0	30.4	11.1	27.6	14.9	60.6	11.5
Enclosed in silicate (%)	59.8	49.3	74.0	42.8	69.6	11.1	62.0	78.7	18.2	88.5
Pt-dominant phases Association:	HW	PXT	PEG	ORR	CPX	FRH	FWP	CS	PSP	TSP
Enclosed in BMS (%)	23.1	8.4	11.9	6.5			9.8	4.3		
BMS-silicate contact (%)	53.8	37.3	26.2	41.3			14.8	8.7	67.6	7.4
Enclosed in silicate (%)	23.1	54.2	61.9	52.2	100.0	100.0	75.4	87.0	32.4	92.6
Pd-dominant phases Association:	HW	PXT	PEG	ORR	CPX	FRH	FWP	CS	PSP	TSP
Enclosed in BMS (%)	8.0	8.5	3.1	6.1		72.2	10.5	8.7	29.2	
BMS-silicate contact (%)	22.7	34.1	3.1	51.0	40.0	16.7	34.7	21.7	55.6	16.1
Enclosed in silicate (%)	69.3	57.3	98.8	42.9	60.0	11.1	54.8	69.6	15.3	83.9

to be low grade (Table 1). The grade is also known to decrease with depth away from the contact with overlying feldspathic pyroxenites, such that the calc-silicate footwall is not exposed in the northern part of the pit. From Table 3 it appears that the 23 PGM grains found differed from the reef pyroxenites in that they contained a large proportion of antimonides. Table 2, however, reveals that this figure comes from a single, relatively large grain of stibiopalladinite, and other than this, the assemblage is similar to the reef pyroxenites, containing mainly tellurides. The small number of grains located requires any trends identified to be taken with caution, though it appears that the assemblage is similar to that of the reef pyroxenites, with a slight increase in the number of PGM containing Bi and Sb. None of the PGM is included in BMS, and all of the Pt phases and 60% of the Pd phases are located in silicates, which is much higher than in the reef pyroxenites (Table 4). Overall grain size was very small (Fig. 4), with most grains <5 µm long, and the largest being only 15 µm in its longest dimension.

Footwall clinopyroxenites

The footwall clinopyroxenites are dominated by Pd-dominant alloys, particularly paolovite

(Pd₂Sn) and the similar, but unnamed phase Pd₂(Sn,Sb), which contain Sn and Sb in equal proportions. Bismuthides, and in particular an unnamed phase with composition close to Pd₃Bi₃(Te,Sb)₂, are also common. Almost a third of all grains were sperrylite, making it the most abundant phase by occurrence, although sperrylite only made up 19% of the assemblage by area (Tables 2, 3). Other than sperrylite, very few of the PGM grains were Pt phases. A few tellurides and antimonides make up the remainder of the assemblage. Almost two-thirds of PGM in the footwall clinopyroxenites are surrounded by silicates (Table 4). This figure increases to three-quarters when only the Pt-dominant phases are considered, which reflects the preference of sperrylite to be isolated in silicate grains away from BMS grains.

Footwall calc-silicates

The calc-silicates, like the clinopyroxenites, are telluride-poor, and are rich in arsenides, particularly sperrylite, which makes up nearly 80% of the assemblage (Table 3). There are fewer alloys than in the clinopyroxenites, although Pd-dominant alloys are still the second most common PGM type. However, in contrast to the clinopyroxenites, bismuthides are very rare.

Table 4 shows 79% of all PGM grains being enclosed within silicate minerals, a figure probably enlarged partially by the relative paucity of BMS in the calc-silicates compared to the igneous reef. As in the clinopyroxenites, the Pt phases (largely sperrylite) show a strong preference to be associated with silicates.

Footwall-reef hybrid

A sample of footwall-reef hybrid rock contained a large number of palladoarsenide (Pd_2As) grains, concentrated in and along fractures in BMS grains. Comparatively few PGM were found elsewhere in the sample, which include a few tellurides. The small number of PGM grains in the sample means any trends must be viewed cautiously, though it does show a marked increase in arsenides and Pd minerals compared to the primary reef pyroxenites, possibly indicating a more volatile influenced environment more akin to the footwall assemblages than the igneous pyroxenites.

Footwall serpentinites

Two types of serpentinite were studied: partially and completely serpentinitized footwall. In the partially serpentinitized samples, where up to 60% fresh metamorphic olivine (Fo_{88}) is still present, the PGM assemblage is dominated by Pd tellurides and lesser amounts of Pd bismuthides and Pt arsenides. As in the olivine-replaced reef, kotulskite contains relatively high concentrations of Pb (often higher than Bi) which substitutes for Te in the ideal formula PdTe . Significantly, the PGM in this rock type are very much associated with BMS (Table 4) which are variably oxidized to Fe-oxide phases (Fig. 5d), an association also noted in serpentinitized parts of the Platreef on Drenthe by Gain and Mostert (1982). Li *et al.* (2004) describe BMS being replaced by magnetite in areas of serpentinitization in the Merensky Reef and UG2 in the western Bushveld. Nearly all of the kotulskite and electrum is found in association with these partially oxidized blebs of BMS. The PGM in the completely serpentinitized rocks, however, are almost completely silicate-associated (Table 4), with completely serpentinitized footwall containing very few BMS, with most altered to magnetite. This PGM assemblage has the most predominant enrichment in antimony in any of the assemblages and is characterized by the presence of gersversite (PtSb_2) and sudburyite

(PdSb). A few arsenides, tellurides and sulpharsenides make up most of the remainder of the assemblage.

Hangingwall gabbronorite

Samples from the base of the hangingwall were surprisingly found to contain appreciable occurrences of PGM. Sporadic BMS occur in both the mottled anorthosite and the basal part of the overlying gabbronorite in places where the hangingwall sits on coarse-grained mineralized reef (Holwell *et al.*, 2005). One sample of gabbronorite, taken from just above the basal contact with the thin mottled anorthosite that forms the base of the hangingwall in places, was considerably rich in PGM. Patches of Pt_2Fe intergrown with chalcopyrite and pentlandite are common (Fig. 5e), an association which differs from the discreet cubic crystals of Pt_2Fe found in the replaced reef. The only grain of PGE sulphide (laurite) found in the entire suite of samples studied was located in the centre of one of these Pt_2Fe alloy-BMS intergrowths. Also associated with the intergrowths were several grains of the unknown Pd-Tl alloy, Pd_3Tl (Fig. 5e). The only other published occurrences of any Pd-Tl minerals is a very rare, unconstrained Pd-Tl phase from the Platreef on Zwartfontein and the Merensky Reef in the eastern Bushveld (Kinloch, 1982) and a mineral close to the formula Pd_3Tl , with some substitution of Tl by Re, in the Wetlegs deposit of the Duluth Complex, Minnesota (Severson and Hauck, 2003). Significantly, the pentlandite which is intergrown with Pt-Fe and Pd-Tl alloys in Fig. 5e also contains up to 6 wt.% Pd, which is the highest recorded natural concentration of Pd in pentlandite (L. J. Cabri, pers. comm.). Overall, however, the sample was particularly rich in the unnamed Pd germanide phase with composition close to Pd_2Ge . Sixty four individual grains, plus many $<1\text{ }\mu\text{m}$, were found, of which 11 contained some Pt in place of Pd, and most contained some As in place of Ge. Typical analyses of this phase are shown in Table 5, together with the ideal compositions for Pd_2Ge and $\text{Pd}_{11}\text{Ge}_5$, the latter of which the analyses match more closely. Armitage *et al.* (2002) noted a single grain of $(\text{Pd,Pt})_2\text{Ge}$ in the Platreef, and the only other recorded occurrences of PGE-germanides anywhere in the world are an unconstrained Pd-Ge phase from the UG-2 chromitite (McLaren and de Villiers, 1982), Pd_2Ge recorded from the Noril'sk Ni-Cu-PGE

TABLE 5. Compositions of unnamed Pd-germanide phase from the base of the hangingwall gabbro-norite, together with the ideal compositions of Pd₂Ge and Pd₁₁Ge₅.

Grain no:	1	2	3	4	Pd ₂ Ge	Pd ₁₁ Ge ₅
Wt.% Pd	75.84	76.52	60.00	59.51	74.56	76.32
Pt			18.33	17.23		
Ge	21.80	20.42	21.96	21.44	25.43	23.67
As	2.54	3.53	0.77			
Total	100.18	100.47	100.28	98.95	100.00	100.00

orebody (Komarova *et al.*, 2002) and (Pd,Pb)₂Ge (Grokhovskaya *et al.*, 2005). The Pd₂Ge grains, and some rarer kotulskite and Pd arsenides are found as satellite grains around larger BMS minerals which are intergrown with secondary amphiboles (Fig. 5f). The association of Pd-bearing pentlandite, PGE alloy intergrowths and PGE sulphides with unaltered BMS does not hold any PGE germanides, whereas germanides are present in association with non-PGE-bearing, partially replaced BMS. The remainder of the hangingwall assemblage is made up of zvyagin-tsevit, kotulskite and a few arsenides.

Discussion

The results from this study show the Platreef to be a very complex PGE orebody both lithologically and mineralogically. The PGM mineralogy at Sandsloot is distinctive within the Platreef compared to other areas. In detail, we have shown that the variety of host rock types in the Platreef contain their own, characteristic PGM assemblages which reflect the processes involved in redistributing the PGE through the reef and into the footwall during the evolution of the Platreef, though the mechanism which led to the initial introduction of PGE into the Platreef has yet to be resolved.

The most characteristic feature of the Sandsloot PGM assemblage, in comparison to most other tabular Bushveld PGE orebodies, is the complete lack of PGE sulphides. Throughout the Merensky Reef, PGE sulphides make up a substantial proportion of the overall PGM assemblage (e.g. Kinloch, 1982; Mostert *et al.*, 1982; Mossom, 1986; Prichard *et al.*, 2004). In the Platreef, on the farms Drenthe and Overysel, to the north of Sandsloot, these minerals make up greater than or nearly half the volume percentage of the assemblage (Gain and Mostert, 1982; Kinloch,

1982). Kinloch (1982, Table 6) lists PGM from eight borehole cores on Zwartfontein, the first five of which are sulphide-poor, alloy- and telluride-dominant, the remaining three are sulphide-dominant and similar to the Overysel data in the same table. The footwall changes from dolomite in the southern and central part of Zwartfontein (Fig. 1) to Archaean basement in the northern part of the farm. The cores listed in Table 6 of Kinloch (1982) are shown in south to north order (P. Hey, pers. comm.) with the change from a dolomite footwall to one composed of granite and gneiss directly corresponding to the change in the PGM assemblage with respect to the presence of PGE sulphides. South of Sandsloot, on Tweefontein where BIF and shales of the Dutchland Formation form the footwall, sulphides are again reported (Viljoen and Schürmann, 1998). Immediately to the south though, on Turfspruit and Macalacaskop where the footwall is Dutchland Formation and Pretoria Group shales and sandstones, Hutchinson *et al.* (2004) describe a number of PGM assemblages with very few PGE sulphides. The lack of sulphides is probably due to low f_{S_2} which would have prevented any free S being available to combine with PGE. This appears to be directly related to footwall lithology, with low f_{S_2} conditions characteristic of areas where the Platreef magma has interacted with dolomitic footwall. Elsewhere in the Bushveld Complex, potholed Merensky Reef (Kinloch, 1982) and the platiniferous dunite pipes (Tarkian and Stumpfl, 1975) contain relatively few PGE sulphides and are dominated by alloys, tellurides and sperrylite. Volatile activity is thought to be important in both these mineralizing environments, which therefore suggests a link between volatile activity and sulphide-poor, alloy-dominated PGM assemblages. The Platreef at Sandsloot is certainly more alloy-rich and sulphide-poor than at Overysel and Drenthe (Gain and Mostert, 1982;

Viljoen and Schürmann, 1998) where the footwall is Archaean granite/gneiss basement. This would suggest that greater volatile activity affected the Platreef where it intruded the dolomites than where it intruded the granites and gneisses, which is manifested in distinctively different PGM assemblages.

The pyroxenites and pegmatites of the igneous reef contain a typical PGM assemblage dominated by Pt and Pd tellurides, electrum and some arsenides. Their presence in the interstitial regions, in a proximal association with BMS, indicates a spatial relationship with the sulphides. Typically, magmatic PGE associations are of Os, Ir and Ru with chromite (Lee, 1996), and Pt, Pd and Rh concentrated with sulphides (Naldrett and Duke, 1980). In a typical immiscible sulphide separating from a silicate magma and collecting base metals and PGE (e.g. Naldrett *et al.*, 1986), the sulphide liquid collects the PGE, and PGM are commonly found included in, or more commonly, at the margins of BMS grains. In our samples, most PGM are found either at the sulphide-silicate boundary, or are silicate-hosted as satellite grains around altered BMS. The intergrowth of BMS with plagioclase and the frequent distribution of small blebs of sulphide and PGM around the edge of interstitial areas suggests that if PGE were originally held in the sulphide liquid, redistribution of the PGE occurred during fluid fluxing after orthopyroxene crystallization, but before the interstitial fluid crystallized, unless the PGM crystallized directly from the melt. The fact that the pegmatitic rocks show a considerably larger average PGM grain size also suggests that the PGM crystallized at a similar, early stage, though their relative enrichment in Pd tellurides and sperrylite would suggest greater degrees of fluid activity, which would be expected if the pegmatoidal nature of the lithology is due to fluid interaction. The reef clinopyroxenites have a similar PGM assemblage, although do contain a few antimonides and bismuthides, more commonly found in the footwall. Texturally, the PGM in these rocks have less of an association with BMS, which is more characteristic of the footwall lithologies. This evidence, together with the fact that the PGE grade decreases away from the contact with the reef pyroxenites, may suggest that the PGE have been transported from the feldspathic pyroxenites by hydrothermal activity.

Base-metal sulphides in the igneous reef have been variably altered around their margins and replaced by actinolite, tremolite and epidote. The

appearance of PGM as satellite grains around BMS may be the result of PGM, originally at the edge of the sulphide grains, remaining *in situ*, as the BMS boundary regressed. A similar association was found in the Merensky Reef and UG2 chromitite by Li *et al.* (2004), who suggested possible reactions for the replacement of BMS by amphiboles and epidote. All of the reactions proposed by Li *et al.* (2004) involve the addition of aqueous Ca, Mg and Si, all of which are readily available from the assimilation of the siliceous Malmani dolomite. However, rather than the BMS being replaced directly by silicates, it is more likely that the hydrous fluids reacted with the BMS to form sulphuric acid, dissolving the BMS around its margins and hydrous silicates were able to grow into the voids around the regressed margins. The PGM appear to be paragenetically earlier than the episode of alteration that formed the hydrous silicates, as seen by the cross-cutting of PGM by the secondary minerals (Fig. 5a). This observation for the Platreef would appear to contrast with the conclusions of Li *et al.* (2004) who suggested that secondary hydrothermal alteration may have been important in redistributing PGE in the Merensky Reef. In the case of the Platreef at Sandsloot, it seems that fluid fluxing at or close to the time of crystallization, and not later hydrothermal alteration, was the most important factor in redistributing PGE through the primary reef.

The presence of Pt-Fe alloy in crystal form (rather than as intergrowths), Pd alloys and Pd tellurides in olivine-replaced portions of reef is analogous to the volatile-influenced ultramafic platiniferous pipes of the eastern Bushveld and pegmatoid-replaced Merensky Reef potholes (Kinloch and Peyerl, 1990). The olivine-replaced lithologies are thought to have formed from a late-stage Fe-rich, Si-poor fluid (McDonald *et al.*, 2005b) which percolated through parts of the pyroxenite, replacing orthopyroxene with olivine (Fig. 3a). At present, the origin of this fluid remains unclear, although it may have been derived from serpentinization of the olivine-bearing footwall lithologies. The fluid also appears to have been Pb-rich as seen by the formation of abundant zvyagintsevite (Pd₃Pb), and the replacement of some Te by Pb in kotulskite. If PGM were present in the protolith (probably reef pyroxenite), the Fe-rich fluid seems likely to have recrystallized Pt into Pt-Fe alloys, and the assemblage therefore post-dates the main episode of mineralization.

The difference in the nature of the PGM between the igneous reef and metamorphic footwall units that contain PGE mineralization is striking. The dominance of tellurides, alloys and electrum with a complete lack of antimony observed in the igneous reef, is reversed in the footwall, with arsenides, bismuthides and antimonides dominating. The dominance of PGM containing elements such as As and Sb in the footwall lithologies suggests a significant amount of volatile activity involved in the redistribution of PGE into the footwall. However, the role of elements such as As, Sb, Se and Te is believed to be to immobilize the PGE, rather than be transported with them, as reduced forms of these elements cannot be transported with Pt and Pd (Wood, 2002). The almost total absence of antimonides in the igneous reef is analogous to normal Merensky Reef, where PGE antimonides are very rare (Kinloch, 1982), whereas in areas where fluid activity has been prevalent, antimonides are common. For example, the type localities for the PGE antimonides genkinite, geversite, stibiopalladinite, stumpflite, sudburyite and naldrettite and ungavaite are, respectively: the Onvervacht pipe (Bushveld Complex, RSA); the Driekop pipe (Bushveld Complex, RSA); Tweefontein Hill (Bushveld Complex, RSA); the Driekop pipe; Copper Cliff (Sudbury, Canada), and the Mesamax Northwest deposit (Québec, Canada) (Cabri, 2002; Cabri *et al.*, 2005; McDonald *et al.*, 2005a), all of which have been fluid affected. This would imply that PGE antimonides are indicative of fluid transport of PGE, and are present in secondary assemblages. The fluid activity that redistributed the PGE would be expected to have preferentially transported the more mobile Pd into the footwall over Pt, therefore producing low Pt/Pd ratios in the footwall, and raising the Pt/Pd slightly in the igneous reef. Table 1 shows Pt/Pd ratios for reef samples in the range 0.79–1.94, whereas in footwall samples the ratio is 0.54–0.98, and in the replaced reef it is ~0.6, showing a relative enrichment in Pd over Pt in the areas where the greatest fluid activity appears to have taken place, indicating that the PGE were introduced by fluid activity.

Partial serpentinization of footwall olivine desulphurizes BMS to form magnetite, a feature also seen in the Merensky Reef and UG2 (Li *et al.*, 2004) and in its early stages appears to form a telluride-dominant PGM assemblage (often Pb-

bearing) which is not dissimilar to that found in the olivine-replaced reef. If there is a link between the two assemblages, it may be that the Fe-rich fluids that altered the reef originated from serpentinization of the footwall. Further degrees of serpentinization are associated with a generally fine-grained, disseminated, low-temperature PGM assemblage rich in volatile elements such as Sb and As. The antimonide-dominant assemblage formed is likely to represent recrystallization of the telluride dominant-assemblage.

The PGM assemblage at the base of the hangingwall is of particular interest, as until very recently (Holwell *et al.*, 2005) the hangingwall was not thought to contain any PGE mineralization, except around calc-silicate rafts (Kinnaird *et al.*, 2005). Holwell *et al.* (2005) concluded that the Platreef was almost completely crystallized when the hangingwall gabbro-norites were intruded. Localized assimilation of mineralized reef into the new magma incorporated PGE-rich sulphide into the hangingwall magma. The observed high Pd content in pentlandite requires rapid cooling, which would be likely if the hangingwall magma chilled against a crystallized and relatively cooled Platreef. The PGE-rich sulphide liquid cooled rapidly to form, first monosulphide solid solution (mss), then the 'primary' assemblage of Pd-pentlandite, Pt-Fe alloy-BMS intergrowths and laurite. In particular, the presence of Pt-Fe alloy-BMS intergrowths is a characteristic texture associated with primary BMS, present in Merensky Reef that has not undergone significant volatile interaction (Kinloch, 1982) and in other layered intrusions (Cabri, 2002). Here we refer to 'primary' magmatic sulphides as pyrrhotite and pentlandite derived from the recrystallization of mss on cooling from magmatic temperatures. The PGE mineralization seems to exhibit a two-stage crystallization history. The primary assemblage appears to have been locally altered on a centimetre-scale, with Pd apparently exsolved from pentlandite, BMS surrounded by secondary amphiboles, and the PGM assemblage altered to one rich in germanides.

Holwell *et al.* (2005) suggested that the PGE in the basal portion of the hangingwall originated in the Platreef, and was assimilated into the magma that formed the hangingwall gabbro-norites, forming an unusual, primary assemblage of PGM at the base of the hangingwall which is distinct from, and post-dates, the main episode of mineralization in the Platreef.

Conclusions

The variety of characteristic PGM assemblages in the host of rock types of the Platreef at Sandsloot reflects the fluid and magmatic processes which affected the Platreef during and after emplacement. The method of initial introduction of PGE is still to be resolved; however, from the data presented here, it is possible to describe a sequence of events which redistributed PGE and/or recrystallized PGM through the reef and its footwall and hangingwall, each of which producing a characteristic assemblage in distinct lithologies.

(1) During crystallization of the igneous reef, PGM crystallized around the margins of BMS within the interstitial liquid forming a telluride-dominant assemblage, in close spatial association with BMS. Fluids, originating from assimilation and metamorphism of the dolomitic floor, are likely to have circulated within the interstitial liquid during crystallization. The lack of PGE-sulphides suggests conditions during this time were characterized by low f_{S_2} .

(2) During emplacement of the reef, fluid activity was very significant in redistributing PGE into the footwall. The footwall contains characteristic arsenide-, alloy- and antimonide-dominant PGM assemblages, showing a significant volatile influence during crystallization of this secondary assemblage.

(3) Serpentinization of footwall olivine also appears to convert earlier BMS to oxides, with PGE-tellurides remaining in association with the remnant sulphides. Further degrees of serpentinization, where all olivine is replaced, produces a more volatile-enriched antimonide-dominant PGM assemblage, without the association with BMS.

(4) Late-stage, Fe-rich fluids percolating through certain parts of the igneous reef desilicified orthopyroxene to form olivine, producing peridotitic zones. PGM were also recrystallized by this fluid, to form an alloy-dominant PGM assemblage of Pt-Fe and Pd-Pb alloys, together with possibly pre-formed tellurides.

(5) After a period of cooling and almost total crystallization of the pyroxenitic reef, the hangingwall magma was intruded, locally assimilating PGE-rich pyroxenite reef and cooling quickly to form a separate, primary PGM-BMS assemblage of Pd-bearing pentlandite, Pt-Fe alloy-BMS intergrowths and laurite. Later, localized alteration has recrystallized PGM, producing a germanide-dominant PGM assem-

blage of satellite grains around altered BMS.

This paper summarizes the assemblages present in various rock types at Sandsloot. Elsewhere along the Platreef the rock types and PGM assemblages are known to be different (e.g. Kinloch, 1982; Viljoen and Schürmann, 1998; Hutchinson and Kinnaird, 2005) and the Platreef is obviously a highly complex orebody with a varied and complex magmatic and fluid history determined by several factors, most importantly, the interaction of the Platreef magma with the varying floor rocks. The results of this study reveal the importance of syn- and post-emplacement fluid activity on the mineralogy and distribution of PGE in the Platreef on a metre scale at this locality, with the presence of dolomite as the footwall rock producing a distinctively PGE sulphide-poor PGM assemblage. Further work is planned to attempt to constrain this footwall control by investigation into the PGM mineralogy in other sections along strike where the footwall is different.

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References

- Armitage, P.E.B., McDonald, I., Edwards, S.J. and Manby, G.M. (2002) Platinum-group element mineralization in the Platreef and calc-silicate footwall at Sandsloot, Potgietersrus District, South Africa. *Applied Earth Science (Transactions of the Institute of Mining and Metallurgy B)*, **111**, B36–45.
- Cabri, L.J. (2002) The platinum-group minerals. Pp. 13–129 in: *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements* (L.J. Cabri, editor). Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume **54**.

- Cabri, L.J. and Feather, C.E. (1975) Platinum-iron alloys: a nomenclature based on a study of natural and synthetic alloys. *The Canadian Mineralogist*, **13**, 117–126.
- Cabri, L.J., McDonald, A.M., Stanley, C.J., Rudashevsky, N.S., Poirier, G., Durham, B.R., Mungall, J.E. and Rudashevsky, V.N. (2005) Naldrettite, Pd₂Sb, a new intermetallic mineral from the Mesamax Northwest deposit, Ungava region, Quebec, Canada. *Mineralogical Magazine*, **69**, 89–97.
- Cawthorn, R.G. (1999) The platinum and palladium resources of the Bushveld Complex. *South African Journal of Science*, **95**, 481–489.
- Cawthorn, R.G., Merkle, R.K.W. and Viljoen, M.J. (2002) Platinum-group elements in the Bushveld Complex. Pp. 389–430 in: *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements* (L.J. Cabri, editor). Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume **54**.
- Gain, S.B. and Mostert, A.B. (1982) The geological setting of the platinoid and base metal sulphide mineralization in the Platreef of the Bushveld Complex in Drenthe, north of Potgietersrus. *Economic Geology*, **77**, 1395–1404.
- Grokhovskaya, T.L., Lapina, M.I., Ganin, V.A. and Grinevich, N.G. (2005) PGE mineralization in the Burakovsk Layered Complex, Southern Karelia, Russia. *Geology of Ore Deposits*, **47**, 283–308.
- Hammerbeck, E.C.I. and Schürmann, L.W. (1998) Nickel. Pp. 471–482 in: *The Mineral Resources of Southern Africa* (M.G.C. Wilson and C.R. Anhaeusser, editors). Council for Geoscience.
- Harris, C. and Chaumba, J.B. (2001) Crustal contamination and fluid-rock interaction during the formation of the Platreef, Northern Limb of the Bushveld Complex, South Africa. *Journal of Petrology*, **42**, 1321–1347.
- Holwell, D.A., Armitage, P.E.B. and McDonald, I. (2005) Observations on the relationship between the Platreef and its hangingwall. *Applied Earth Science (Transactions of the Institute of Mining and Metallurgy B)*, **114**, B199–207.
- Hutchinson, D. and Kinnaird, J.A. (2005) Complex, multi-stage mineralization history in the southern sector of the Platreef, Bushveld Complex, RSA. *Applied Earth Science (Transactions of the Institute of Mining and Metallurgy B)*, **114**, B208–224.
- Hutchinson, D., Kinnaird, J.A. and Schürmann, L.W. (2004) Complex, multi-stage mineralization history in the southern sector of the Platreef, Bushveld Complex, RSA. *Geoscience Africa 2004, Abstract Volume*, University of the Witwatersrand, Johannesburg, South Africa, pp. 293–294.
- Kinloch, E.D. (1982) Regional trends in the platinum-group mineralogy of the Critical Zone of the Bushveld Complex, South Africa. *Economic Geology*, **77**, 1328–1347.
- Kinloch, E.D. and Peyerl, W. (1990) Platinum-group minerals in various rock types of the Merensky Reef: genetic implications. *Economic Geology*, **85**, 537–555.
- Kinnaird, J.A. and Nex P.A.M. (2003) Mechanisms of marginal mineralization in the Bushveld Complex. *Applied Earth Science (Transactions of the Institute of Mining and Metallurgy B)*, **112**, B206–208.
- Kinnaird, J.A., Hutchinson, D., Schürmann, L., Nex, P.A.M. and de Lange, R. (2005) Petrology and mineralization of the southern Platreef: northern limb of the Bushveld Complex, South Africa. *Mineralium Deposita*, **40**, 576–597.
- Komarova, M.Z., Kozyrev, S.M., Simonov, O.N. and Lulko, V.A. (2002) The PGE mineralization of disseminated sulphide ores of the Noril'sk-Taimyr region. Pp. 547–567 in: *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements* (L.J. Cabri, editor). Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume **54**.
- Lee, C.A. (1996) A review of mineralization in the Bushveld Complex and some other layered mafic intrusions. Pp. 103–146 in: *Layered Intrusions* (R.G. Cawthorn editor). Elsevier Science, Amsterdam.
- Li, C., Ripley, E.M., Merino, E. and Maier, W.D. (2004) Replacement of base metal sulphides by actinolite, epidote, calcite and magnetite in the UG2 and Merensky Reef of the Bushveld Complex, South Africa. *Economic Geology*, **99**, 173–184.
- McDonald, A.M., Cabri, L.J., Stanley, C.J., Rudashevsky, N.S., Poirier, G., Mungall, J.E., Rossa, K.C. and Rudashevsky, V.N. (2005a) Ungavaite, Pd₄Sb₃, a new intermetallic mineral from the Mesamax Northwest deposit, Ungava region, Quebec, Canada: Description and genetic implications. *The Canadian Mineralogist*, **43**, 1735–1744.
- McDonald, I., Holwell, D.A. and Armitage, P.E.B. (2005b) Geochemistry and mineralogy of the Platreef and 'Critical Zone' cumulates of the Northern lobe of the Bushveld Complex, South Africa: implications for Bushveld stratigraphy and the development of PGE mineralization. *Mineralium Deposita*, **40**, 526–549.
- McLaren, C.H. and de Villiers, J.P.R. (1982) The platinum-group chemistry and mineralogy of the UG-2 chromitite layer of the Bushveld Complex. *Economic Geology*, **77**, 1348–1366.
- Mossom, R.J. (1986) The Atok Platinum Mine. Pp. 1143–1154 in: *Mineral Deposits of Southern Africa* (C.R. Anhaeusser and S. Maske, editors), vols I and II. Geological Society of South Africa, Johannesburg.

- Mostert, A.B., Hofmeyr, P.K. and Potgieter, G.A. (1982) The platinum-group mineralogy of the Merensky Reef at the Impala Platinum Mines, Bophuthatswana. *Economic Geology*, **77**, 1385–1394.
- Naldrett, A.J. and Duke, J.M. (1980) Platinum metals in magmatic sulphide ores. *Science*, **208**, 1417–1424.
- Naldrett, A.J., Gasparini, E.C., Barnes, S.J., von Gruenewaldt, G. and Sharpe, M.R. (1986) The Upper Critical Zone of the Bushveld Complex and the origin of Merensky-type ores. *Economic Geology*, **81**, 1105–1117.
- Prichard, H.M., Barnes, S.-J., Maier, W.D. and Fisher, P.C. (2004) Variations in the nature of the platinum-group minerals in a cross-section through the Merensky Reef at Impala Platinum: implications for the mode of formation of the reef. *The Canadian Mineralogist*, **42**, 423–437.
- Schneiderhöhn, H. (1929) The mineragraphy, spectrography and genesis of the platinum-bearing nickel-pyrrhotite ores of the Bushveld Complex. Pp. 206–246 in: *The Platinum Deposits and Mines of South Africa* (P.A. Wagner, editor). Oliver and Boyd, Edinburgh, UK.
- Seversen, M.J. and Hauck, S.A. (2003) *Platinum group elements (PGEs) and platinum group minerals (PGMs) in the Duluth Complex*. Technical Report NRRI/TR-2003/37. Natural Resources Research Unit, University of Minnesota, Duluth, USA, 296 pp.
- Tarkian, M. and Stumpfl, E.F. (1975) Platinum mineralogy of the Driekop Mine, South Africa. *Mineralium Deposita*, **10**, 71–85.
- Viljoen, M.J. and Schürmann, L.W. (1998) Platinum group metals. Pp. 532–568 in: *The Mineral Resources of Southern Africa* (M.G.C. Wilson and C.R. Anhaeusser, editors). Council for Geoscience.
- von Gruenewaldt, G., Hulbert, L.J. and Naldrett, A.J. (1989) Contrasting platinum-group element concentration patterns in cumulates of the Bushveld Complex. *Mineralium Deposita*, **24**, 219–229.
- Wagner, P.A. (1929) *The Platinum Deposits and Mines of South Africa*. Oliver and Boyd, Edinburgh, UK, 326 pp.
- Wood, S.A. (2002) The aqueous geochemistry of the platinum-group elements with applications to ore deposits. Pp. 211–249 in: *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements* (L.J. Cabri, editor). Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume **54**.

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