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Review

The Fate of Platinum-Group Minerals in the Exogenic Environment—From Sulfide Ores via Oxidized Ores into Placers: Case Studies Bushveld Complex, South Africa, and Great Dyke, Zimbabwe

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Abstract: Diverse studies were performed in order to investigate the behavior of the platinum-group minerals (PGM) in the weathering cycle in the Bushveld Complex of South Africa and the Great Dyke of Zimbabwe. Samples were obtained underground, from core, in surface outcrops, and from alluvial sediments in rivers draining the intrusions. The investigations applied conventional mineralogical methods (reflected light microscopy) complemented by modern techniques (scanning electron microscopy (SEM), mineral liberation analysis (MLA), electron-probe microanalysis (EPMA), and LA-ICPMS analysis). This review aims at combining the findings to a coherent model also with respect to the debate regarding allogenic versus authigenic origin of placer PGM. In the pristine sulfide ores, the PGE are present as discrete PGM, dominantly PGE-bismuthotellurides, -sulfides, -arsenides, -sulfarsenides, and -alloys, and substantial though variable proportions of Pd and Rh are hosted in pentlandite. Pt–Fe alloys, sperrylite, and most PGE-sulfides survive the weathering of the ores, whereas the base metal sulfides and the (Pt,Pd)-bismuthotellurides are destroyed, and ill-defined (Pt,Pd)-oxides or -hydroxides develop. In addition, elevated contents of Pt and Pd are located in Fe/Mn/Co-oxides/hydroxides and smectites. In the placers, the PGE-sulfides experience further modification, whereas sperrylite largely remains a stable phase, and grains of Pt–Fe alloys and native Pt increase in relative proportion. In the Bushveld/Great Dyke case, the main impact of weathering on the PGM assemblages is destruction of the unstable PGM and PGE-carriers of the pristine ores and of the intermediate products of the oxidized ores. Dissolution and redistribution of PGE is taking place, however, the newly-formed products are thin films, nano-sized particles, small crystallites, or rarely µm-sized grains primarily on substrates of precursor detrital/allogenic PGM grains, and they are of subordinate significance. In the Bushveld/Great Dyke scenario, and in all probability universally, authigenic growth and formation of discrete, larger PGM crystals or nuggets in the supergene environment plays no substantial role, and any proof of PGM "neoformation" in a grand style is missing. The final PGM suite which survived the weathering process en route from sulfide ores via oxidized ores into placers results from the continuous elimination of unstable PGM and the dispersion of soluble PGE. Therefore, the alluvial PGM assemblage represents a PGM rest spectrum of residual, detrital grains.

Keywords: Bushveld Complex; South Africa; Great Dyke; Zimbabwe; platinum-group minerals; primary ores; oxide ores; placers; allogenic; authigenic

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Contributing to the Debate Allogenic versus Authigenic Origin of Placer PGM

1. Introduction

The world's prime sources of platinum-group elements (PGE) are layered intrusions of Proterozoic and Archean age (e.g., the Bushveld Complex, South Africa; the Great Dyke, Zimbabwe; the Stillwater Complex, USA). Placer deposits in Russia and in Colombia were the world's only providers of platinum-group elements up to early in the 20th century, when the rich primary deposits of the Bushveld Complex in South Africa, of the Sudbury district in Canada, and later Norilsk in Russia came into production [1–3]. Today, only about 1–2% of the world's PGE production originates from placers mainly in the Russian Far East, the Ural Mountains, and Colombia [4]. Remarkably, the identification of detrital platinum-group minerals (PGM) in alluvial gravels on the farm Maandagshoek, then eastern Transvaal, South Africa, led to the discovery of the largest PGE deposits on Earth in the Bushveld Complex in 1924 [5–8]. Today, South Africa is the dominant country in mining and supplying PGE to the world, entirely from the Bushveld Complex, followed by Russia's Norilsk-Talnakh field and modest contributions from Zimbabwe, Canada, and the USA.

The 2054.4 ± 1.3-Ma-old [9] Bushveld Complex in north-eastern South Africa is the largest layered intrusion on Earth, covering an area of at least 65,000 km^2 (Figure 1). The PGE ores are principally related to sulfide mineralization. Three major, laterally extensive ore bodies are mined, namely the Merensky and the UG-2 chromitite reef in the western and eastern Bushveld, and the Platreef in the northern Bushveld [10,11]. In addition, increasing amounts of PGE are extracted as by-products from the chromitite seams of the Bushveld Complex [12].

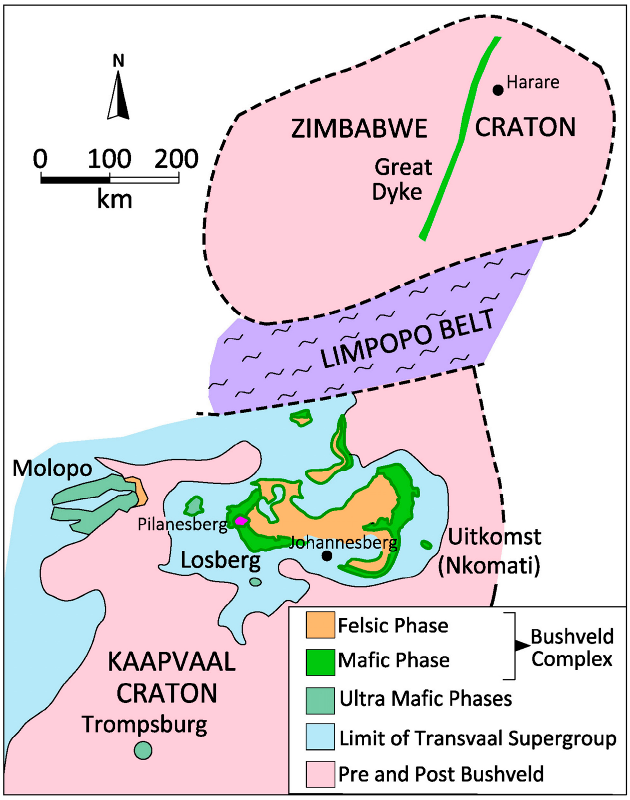

Figure 1. Location of the Bushveld Complex and the Great Dyke in southern Africa (Reproduced with permission from M. Viljoen, *Episodes* [10]).

The 2575.4 ± 0.7-Ma-old [13] Great Dyke of Zimbabwe (Figure 1) is a 550 km long mafic/ultramafic layered intrusion with a NNE strike and a maximum width of about 11 km that transects the Zimbabwe Craton [14]. Within the Great Dyke, economic PGE mineralization is restricted to sulfide disseminations in pyroxenites of the 1–5 m thick Main Sulfide Zone (MSZ), sited some meters below the transition of the Ultramafic and the Mafic Sequence of the Great Dyke [15,16]. The MSZ displays a regular geochemical and mineralogical fine structure which is regarded to reflect primary magmatic features of consecutive batches of sulfide accumulation, concomitant scavenging of PGE, and fractionation [16,17].

In both intrusions, the pristine PGE mineralization is related to sulfide accumulations (mainly pyrrhotite, pentlandite, chalcopyrite, and sporadic pyrite), in a manner typical of Ni–Cu-sulfide mineralization worldwide [18]. The PGE are bimodally distributed; they occur at variable proportions in the form of discrete PGM, and also in variable proportions substituting in the crystal lattices of sulfides (mainly Pd and Rh in pentlandite) [16,19–23].

Under the subtropical conditions encountered in the Bushveld Complex and along the Great Dyke, the outcropping PGE-rich sulfide ores are typically weathered to depths of ca. 20–30 m as observed in drill core and in open pit workings [16,24–26]. The most important features of the oxidation zone are the removal of sulfides and a significant loss of palladium concomitant with the extensive destruction of most species of the primary PGM assemblage. Large proportions of the PGE are dispersed, and either lost from the system or re-concentrated in secondary iron/manganese oxides/hydroxides. Currently, oxidized PGE ores are not being processed, neither in the Bushveld Complex nor in the Great Dyke nor in any other PGE-producing mine worldwide, as all previous attempts to recover PGE from this type of ore by conventional methods failed due to insufficient recovery rates [24].

In completion of the studies, the final step of changes of the PGM assemblage, the detrital PGM in stream sediments of rivers draining the Bushveld and the Great Dyke was investigated. This placer PGM assemblage differs starkly from that in pristine and oxidized ores; it is dominated by stable compounds, foremost Pt–Fe alloys, followed by sperrylite and cooperite/braggite [27–30].

During the past years, our working group at the BGR had access to underground exposures, cores, open pits, surface exposures, and stream sediments of rivers draining the Bushveld and the Great Dyke, and the research results were published in internal reports and in international journals. This contribution summarizes the findings of the individual studies and intends to combine these with the intention of following the fate of the platinum-group minerals in the exogenic environment. The work concentrates on the PGM and aims at advancing our understanding of the processes during weathering of the primary ores via oxidized equivalents and into placers mainly with respect to the redistribution of PGE and concurrent mineralogical changes.

2. Materials and Methods

Complete profiles of pristine ores were obtained from various mines and prospects of Impala Platinum in the western limb (Karee Mine; Merensky Reef and UG-2 chromitite), Anglo Platinum and Nkwe Platinum mainly in the eastern limb (Merensky Reef and UG-2; platinum pipes), and the northern limb (Platreef) of the Bushveld Complex in South Africa. Equivalent samples of the MSZ of the Great Dyke were taken underground and from drill core at the Hartley, Ngezi, Unki, and Mimosa mines as well as at the Mhondoro Concession in Zimbabwe.

Bushveld oxide ores comprised Merensky Reef from the eastern limb (farms Twickenham and Richmond) and Platreef material from surface exposures and drill core taken at Anglo Platinum projects and mines. MSZ oxide ores were taken on surface, in open pits, and from drill core at the Hartley, Ngezi, Unki, and Mimosa mines.

The placer sample campaigns in rivers draining the Bushveld Complex in South Africa yielded close to 6500 PGM grains in the samples from ten panning localities (one rich placer site with ca. 6000 PGM grains!), and 390 grains of detrital PGM were obtained by panning 28 (seven with output) samples in rivers draining the Great Dyke in Zimbabwe.

Some hundred polished sections of sulfide and oxide ores were prepared and investigated by reflected light and scanning electron (SEM) microscopy, as well as electron-probe microanalysis (EPMA). In selected sections of pristine ore samples, sulfides, and secondary phases (Fe–Mn-oxides/hydroxides, PGE-oxides) were analyzed in situ for their PGE contents by either EPMA or Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). Finally, some samples were treated by combined Electric Pulse Disaggregation (EPD) and Hydroseparation (HS).

More details on samples, sample localities, analytical procedures, instruments used, and analytical parameters of the studies are provided in the respective publications [12,17,20–22].

3. Results

3.1. Pristine Sulfide Ores

The pristine Merensky Reef, Platreef, and MSZ ores generally contain between about 0.1 and 10 vol % sulfides. Interstitial sulfides and sulfide aggregates, up to several mm and locally some cm across, consist of pyrrhotite, pentlandite, chalcopyrite, and subordinate pyrite. As a rule, the PGM are associated with the sulfides, commonly intergrown with or sited at sulfide–sulfide or sulfide–silicate grain boundaries, at the peripheries or at contacts of the sulfide grains. Most PGM occur as single grains, however, inter-PGM intergrowths are also present. Grain sizes of the PGM usually range from <5 to 50 µm but may reach up to about 400 µm in the longest dimension.

In the chromitite reefs (LG, MG, UG-2) of the Bushveld Complex, sulfide contents are usually below 0.1 vol %, however, a primary sulfide–PGE relation is indicated as elevated PGE contents are only encountered up-sequence from a point (LG-5) when sulfur saturation was achieved during differentiation [10,11,18,31]. The low sulfide contents are interpreted to result from sulfide–chromite reactions whereby sulfide iron was taken up by chromite and sulfur was expelled from the system [18].

The number of platinum-group minerals (PGM) accepted by the International Mineralogical Association (IMA) was 138 in June 2014, whereby Pd-dominated PGM prevail (62) followed by Pt-rich (31), Ir-rich (17), and Rh-rich (14) species; for Ru and Os, 8 and 6 PGM are on record [32]. However, in the primary sulfide ores studied, only a small number of PGM species is of greater significance, and these are mainly compounds with pnictogens (As, Sb, Bi) and chalcogens (S, Se, Te), or PGE alloys.

The following PGM groups are of relevance, and examples of the PGM and their associations are depicted in Figure 2:

- Bismuthides and tellurides mainly of Pt and Pd, called (Pt,Pd)-bismuthotellurides in the following, which show high degrees of Pt ↔ Pd and Te ↔ Bi substitution. A first group [MeX_2] comprises moncheite [$PtTe_2$], maslovite [PtBiTe], merenskyite [$PdTe_2$], and michenerite [PdBiTe], and a second, rarer group [MeX] consists of kotulskite [PdTe]-sobolevskite [PdBi] (Figure 2A,B,G).
- Sulfides, encompassing the Pt–Pd monosulfides cooperate-braggite-vysotskite [PtS–(Pt,Pd,Ni)S–PdS] and called (Pt,Pd)-sulfides in the following (Figure 2B,C); malanite-cuprorhodsite solid solution [$CuPt_2S_4$–$CuRh_2S_4$] (Figure 2C); and laurite [RuS_2], which often carries the bulk IPGE budget of the ores.
- Arsenides, the most ubiquitous representative being sperrylite [$PtAs_2$] (Figure 2D,E).
- Sulfarsenides with limited substitution comprise the common Rh-mineral hollingworthite [RhAsS], rarer platarsite [PtAsS], irarsite [IrAsS], and ruarsite [RuAsS].
- Antimonides like stibiopalladinite [Pd_5Sb_2].
- Zvyagintsevite [Pd_3Pb] and members of the solid solution rustenburgite-atokite [Pt_3Sn–Pd_3Sn] are locally abundant in the Bushveld ores.
- Alloys mainly of Pt with Fe, Cu, or Ni (Figure 2D,F), and inter-PGE alloys (e.g., Pt–Pd, Os–Ir–Ru).

The PGM assemblages of the pristine Bushveld ores vary within wide limits, and the compilation given here largely reflects the data presented in previous publications [20,21,25,33–51].

The Merensky Reef consistently has high contents of (Pt,Pd)-bismuthotellurides (~10–40%), (Pt,Pd)-sulfides (~5–70%) and sperrylite (~1–10%); sulfarsenides (up to 50%) and Pt–Fe alloys (up to 90%!) dominate locally [19–21,33–36].

Platinum-group minerals in the Platreef are mainly (Pt,Pd)-bismuthotellurides (20–40%), (Pt,Pd)-sulfides, and sperrylite (~10% each), zvyagintsevite (~10%), and PGE-sulfarsenides (~10%). Malanite, laurite, and Pt–Fe alloys are also present in smaller amounts [25,41–46].

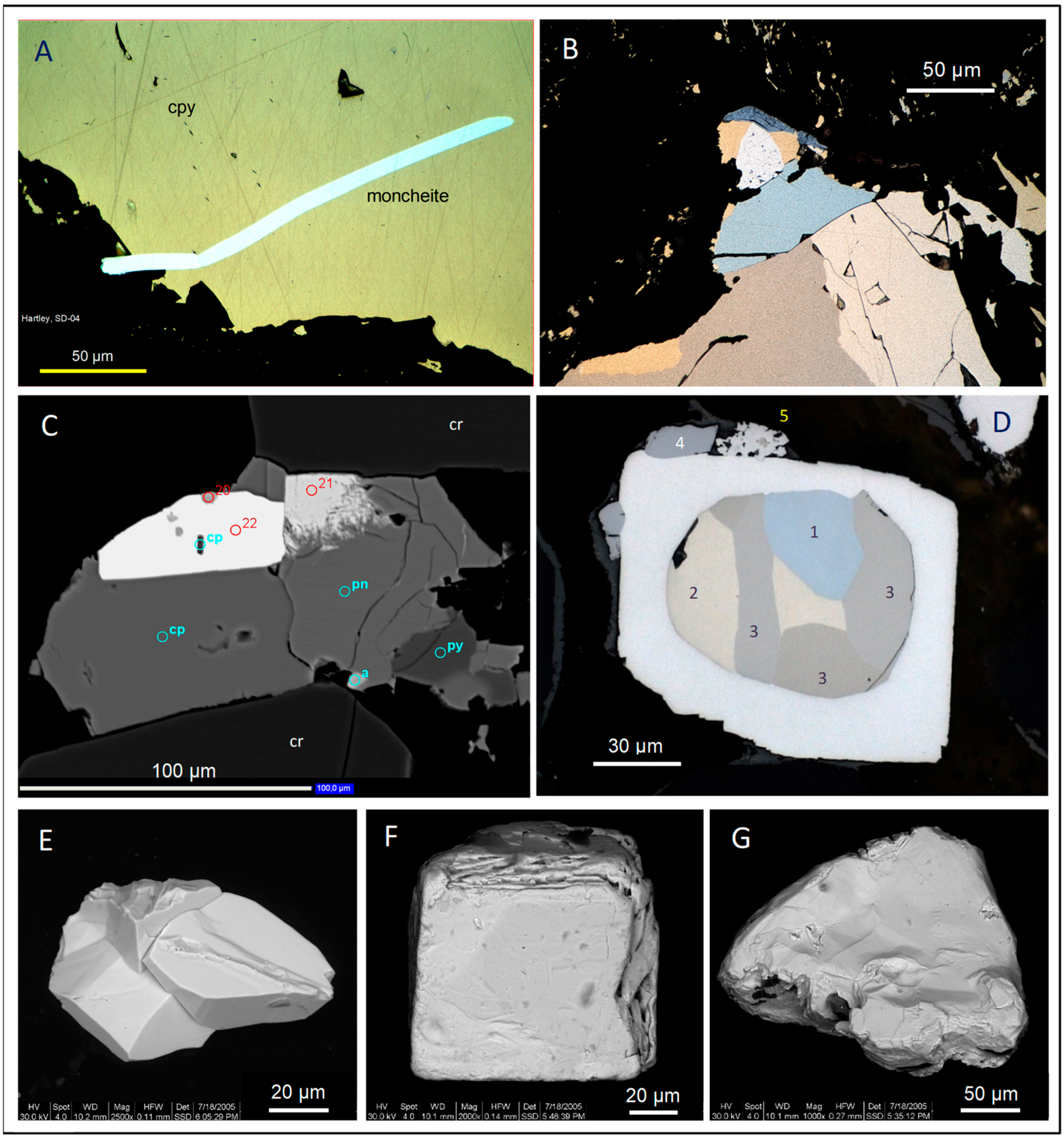

Figure 2. Platinum-group minerals (PGM), pristine ores, in reflected light, oil immersion (**A**,**B**,**D**), Backscatter electron (BSE) image (**C**), and BSE images of PGM grains from pristine ores of the Main Sulfide Zone, Great Dyke, extracted by electric pulse disaggregation, EPD (**E**–**G**). (**A**) Lath of moncheite in chalcopyrite (cpy). MSZ, Hartley Mine. (**B**) Aggregate of pyrrhotite (brownish) and pentlandite (cream-white) at bottom part, overgrown by braggite (bluish), grain of moncheite (white, soft) partly surrounded by chalcopyrite (yellow), and molybdenite (gray, crocodile-shaped). MSZ, Hartley Mine. (**C**) Sulfide aggregate between two chromite grains (cr) consisting of chalcopyrite (cp), pentlandite (pn), and pyrite (py). White grain on top is cooperite/braggite (22) intergrown with malanite (light grey, 21). Merensky Reef, Garatau, eastern Bushveld. (**D**) Composite grain of Pt–Fe alloy (white rim; $Pt_{65}Fe_{30}$), geversite [$PtSb_2$] (1, bluish), stumpflite [Pt(Sb,Bi)] (2, yellowish), genkinite [$(Pt,Pd)_4Sb_3$] (3, light brown), sperrylite (4), and tulameenite [Pt_2CuFe] (5). Driekop Pipe, eastern Bushveld. (**E**) Sperrylite crystal. (**F**) Pt–Fe alloy. (**G**) Moncheite.

The UG-2 is characterized by the dominance of (Pt,Pd)-sulfides and lesser amounts of malanite/cuprorhodsite, followed by Pt–Fe alloys. Laurite is common, and (Pt.Pd)-bismuthotellurides are generally rare though locally present.

Similarly, within the LG/MG chromitites, (Pt,Pd)-sulfides, namely cooperite-braggite, and also malanite-cuprorhodsite are abundant, as are laurite, followed by PGE-sulfarsenides, sperrylite, and Pt–Fe alloys. Notably, all chromitite PGE ores are characterized by elevated contents of zvyagintsevite [12,37,40].

The ultramafic Pt-pipes of the eastern Bushveld need to be mentioned here as we investigated eluvial and alluvial PGM in near-by placers [28,30]. Concentrates from the best-studied Driekop pipe contain about 50% Pt–Fe alloys (Figure 2D), 15% each of sperrylite and geversite [$PtSb_2$], 15% PGE-sulfarsenides (hollingworthite and irarsite), and 5% of other PGM. (Pt,Pd)-bismuthotellurides and (Pt,Pd)-sulfides are virtually absent [47–50].

Platinum-group minerals of the Main Sulfide Zone of the Great Dyke [16,17,51] comprise (Pt,Pd)-bismuthotellurides, sperrylite, the (Pt,Pd)-sulfides cooperite and braggite, and some rarer phases (Figure 2A,B). Mineral proportions by number show the predominance of (Pt,Pd)-bismuthotellurides (50.1%), followed by sperrylite (19%), cooperite/braggite (8.5%), the PGE-sulfarsenides hollingworthite, platarsite, irarsite, and ruarsite (11.9%), laurite (5.0%), Pt–Fe alloys (2.4%), and some rarer PGM [16]. Interestingly, the MSZ samples of the Great Dyke's North chamber (Hartley, Mhondoro, 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 MSZ samples of the South chamber (Unki and Mimosa) with (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 South chamber (together 50%) most likely indicate higher fugacities of arsenic in the South chamber magmas compared to the North chamber during MSZ formation. Further, the PGM spectrum of the Great Dyke is Pt dominated, as about two out of three PGM are Pt-rich (67.7%), followed by Pd- (19.8%) and Rh-rich (6.6%) compounds. Ru- and Ir-rich minerals make up 3.7 and 2 percent, respectively.

Notably, in the pristine sulfide ores of both the Bushveld and the Great Dyke, variable amounts of the PGE are hosted in sulfides. Apparently, Pd and Rh readily substitute for Ni and Fe in the crystal lattice of pentlandite, and accordingly, extensive proportions of the Pd and Rh budget of the ores are hosted in pentlandite [16,17,19–25,44,46,52,53]. Maximum concentrations of Pd and Rh in pentlandite are 757 ppm Pd and 649 ppm Rh for the Merensky Reef, 29,975 ppm Pd and 23,817 ppm Rh for the UG-2, and 746 ppm Pd and 405 ppm Rh for the Platreef. Pentlandite in the LG-6 and MG-1/2 chromitites constantly has maximum concentration levels above 1000 ppm of both Pd and Rh. Maximum contents are 7731 ppm Pd (LG-6) and 11,366 ppm Rh (MG-1/2). For the MSZ, maximum contents of 2506 ppm Pd and 562 ppm Rh were reported from the Hartley Mine. In all cases, PGE contents in chalcopyrite, pyrrhotite, and pyrite are in general insignificant, and the silicates and chromite usually contain no detectable amounts of PGE [19,20].

Mass balance calculations revealed that in the Merensky Reef, between 13 and 100% of the Pd and from 3 to nearly 100% of the Rh hosted by pentlandite [19,20]. In the UG-2, pentlandite consistently hosts elevated proportions of the whole-rock Pd (up to 55%) and Rh (up to 46%) budget, whereas Pt is almost absent in the base metal sulfides (BMS) [21]. In the Platreef, almost all Pd and Rh may be present in solid solution in pentlandite [54].

In summary, the source material of our study, the PGM assemblages of the pristine ores, have pronounced mineralogical similarities but the proportions of the various PGM vary within wide limits. The PGE are bimodally distributed; whereas Pt is dominantly present in the form of discrete PGM like (Pt,Pd)-bismuthotellurides, PGE-sulfides (cooperite/braggite and malanite/cuprorhodsite), sperrylite, and Pt–Fe alloys, large though variable proportions of the Pd and Rh are hosted in pentlandite. Part of the IPGE (Ru, Os, Ir) may be hosted in sulfides and sulfarsenides, however, a great deal of the IPGE budget of the ores is present in laurite.

This generalized inventory above is the basis of our examination of the fate of the abovementioned PGM and PGE-bearing sulfides during the weathering of the ores.

3.2. Oxidized Ores

The behaviour of the PGE in the exogenic cycle was examined in several profiles of oxidized Merensky Reef of the eastern limb and Platreef ores of the northern limb of the Bushveld and on oxidized MSZ ores. Geochemically, in the oxidized ores of both the Bushveld and the Great Dyke, the general metal distribution patterns of the pristine ores are grossly preserved. However, at similar Pt grades, significant proportions of Pd have been lost from the system [27,55–57]. This indicates that Pd is more mobile than Pt and is dispersed in the supergene environment as already shown for the Merensky Reef in the seminal book of Wagner [7]; Pt/Pd values of 2.7 for sulfide ore and 5.1 for oxidized ore were reported [58]. For the UG-2 from the Union section, Pt/Pd values of 2.2 for primary and up to 3.2 for oxidized ore were provided [56]. Pt/Pd ratios of 0.75 and 1.15 were reported for pristine and oxidized Platreef, respectively [25]. Similar relationships between pristine and oxidized PGE mineralization, namely average Pt/Pd values of 1.28 and 2.43, respectively, are on record from the MSZ of the Great Dyke [16,17,24,27].

Mineralogically, in the oxidized ores of both the Great Dyke and the Bushveld, rare relict sulfides, mainly pyrrhotite, are surrounded by rims of iron hydroxides (Figure 3A,B). In case of pervasive oxidation, weathering leads to the complete destruction of all base metal sulfides (BMS) and concurrent replacement by iron hydroxides, which may carry up to 5 wt % Ni and/or Cu. However, the iron hydroxides are not considered major carriers of Ni and Cu in the oxidized ores as, according to microprobe analyses, a large proportion of the Ni and Cu is hosted in chlorites and smectites [57].

In general, sperrylite and cooperite/braggite grains show no distinct features of alteration (Figure 3A). Pt–Fe alloy grains, both compact and porous ones, were found in samples from Hartley and Ngezi. The porous grains of Pt–Fe alloy (close to Pt_3Fe in composition; Figure 3C,D) probably represent replacements of other precursor PGM of unknown chemical composition, or they are relics of spongy to emulsion-like Pt–Fe alloys which were intergrown with other PGM or sulfides, as testified from the pristine MSZ [16] and the Merensky Reef ores [T. Oberthür, unpublished data]. As early as 1939, texturally similar porous grains of “native Pt” from oxidized Merensky Reef were reported and the early authors proposed that these grains represent relicts of sperrylite or cooperite grains [59].

The (Pt,Pd)-bismuthotellurides, common in the pristine ores, show features of alteration and decomposition at various degrees. At incipient oxidation, islands of (Pt,Pd)-bismuthotellurides are surrounded by somewhat porous secondary (Pt,Pd)-oxides/hydroxides (Figure 3E,F), occasionally with shrinkage cracks. In pervasively oxidized ores, all (Pt,Pd)-bismuthotellurides have disappeared and locally some colloform, banded grains of PGE-oxides/hydroxides may represent complete replacements of former PGM (Figure 3G). Further, only sparse relict PGE-sulfarsenides were encountered in the oxidized ores. “Pt-alloys with low sums and weak reflectivity” were first reported by Evans et al. [60] from the Great Dyke, and a first description of oxidation products of PGM from the Bushveld (UG-2) was presented by Hey [56]. Today, the existence of secondary (Pt,Pd)-oxides/hydroxides (“PGE-oxides”) has been established worldwide by a number of authors, however, their physico-chemical nature remains ill-defined [56,61–68]. The only PGE-oxide approved (but assigned “questionable”) by the IMA is palladinite [PdO], occurring as an ocherous coating on palladian gold (porpezite) in Itabira, Brazil [69].

The polished section studies of oxidized ores revealed the presence of some PGM grains of a seemingly secondary nature. They comprise small (<5 µm in size) grains of poorly defined phases. Some of them may actually be oxides or hydroxides, or alteration products of primary PGM, or neoformations (Figure 4A,C). Compounds of Pt–S, Pd–S, Pt–Pd–As–Cu, Pd–Cu–Fe, Pt–Fe, and Pt were also identified, either hosted by Fe hydroxides or by hydrous silicates, or commonly by amphibole, chlorite-, or smectite-like phases. None of the PGM grains had stoichiometric composition; concentrations of sulfur and arsenic, if present, are much lower than in their presumed precursor phases [61,70].

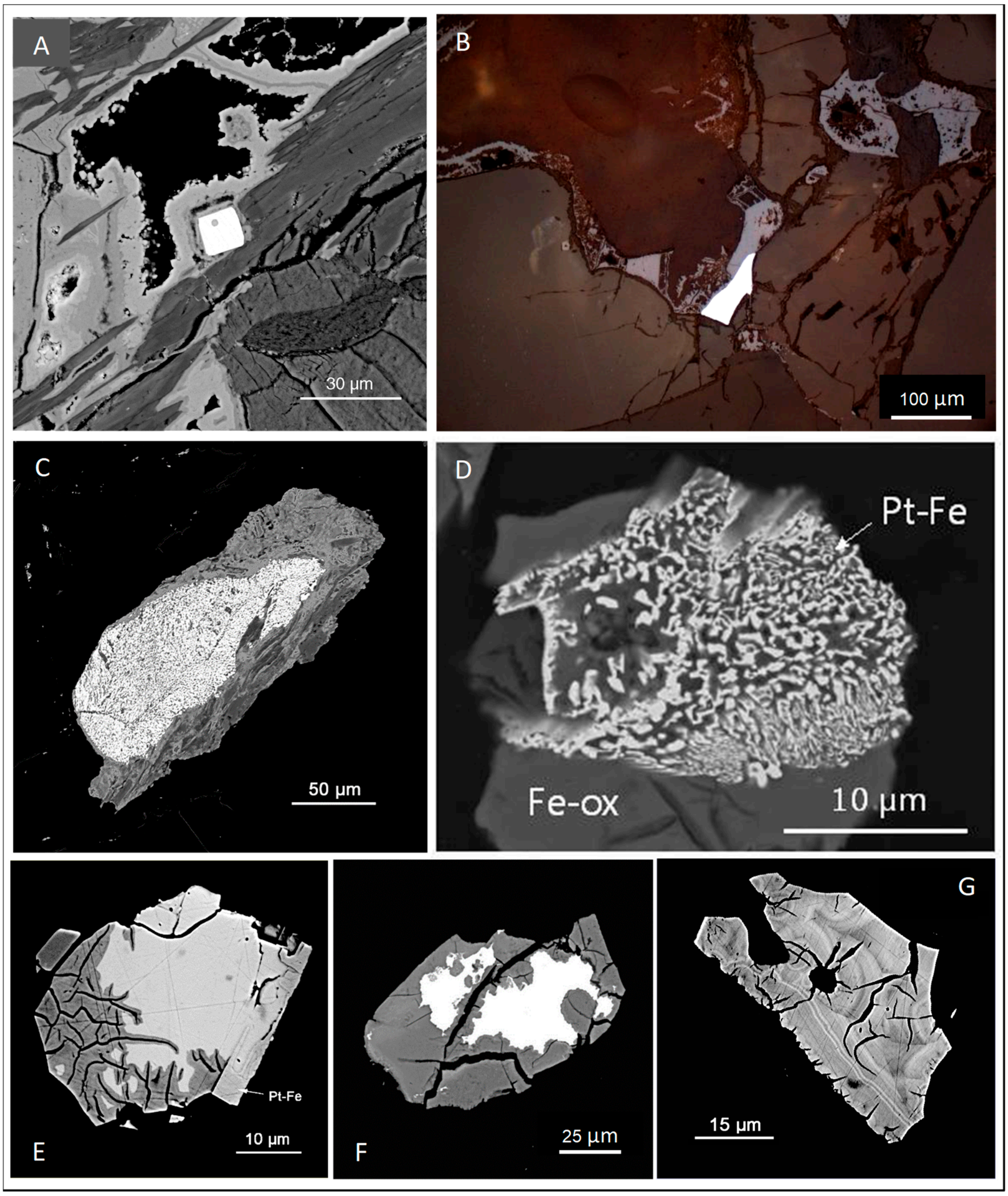

Figure 3. Relict platinum-group minerals, replacements, secondary formations, in oxidized ores. BSE images of polished sections, except (**B**) which is in reflected light. (**A**) Euhedral, relict sperrylite grain (white) in weathered MSZ ore consisting of iron-hydroxides (medium gray) and smectites (dark gray). HOP-05, ps 5663a, Hartley Mine. (**B**) Relict cooperite/braggite (white) surrounded by goethite (gray-bluish) and silicates (darkest phases). Merensky Reef, Richmond, eastern Bushveld [26]. (**C**) Porous grain of Pt–Fe alloy surrounded by a mixture of secondary oxides/hydroxides and silicates. HOP-206a, ps 5910a, Hartley Mine. (**D**) Pt–Fe phase of spongy texture intergrown with Fe hydroxide. Concentrate after hydroseparation, Hartley Mine. (**E**) Pt-bearing sobolevskite (light grey) being replaced by PGE-oxides/hydroxides (left and bottom). Note attached grain of Pt–Fe alloy (Pt–Fe). Adit A, Ngezi concession. (**F**) Grain of michenerite (white, center) in disintegration. Alteration rim (gray) of (Pt,Pd)-oxide/hydroxide phases shows Pd, Cu, and Fe as major elements. HOP-206a, ps 5910a, Hartley Mine. (**G**) Colloform, banded grain of PGE-oxide/hydroxide phase with shrinkage cracks. NGZ 1C, ps 5711b, from Adit A, Ngezi concession.

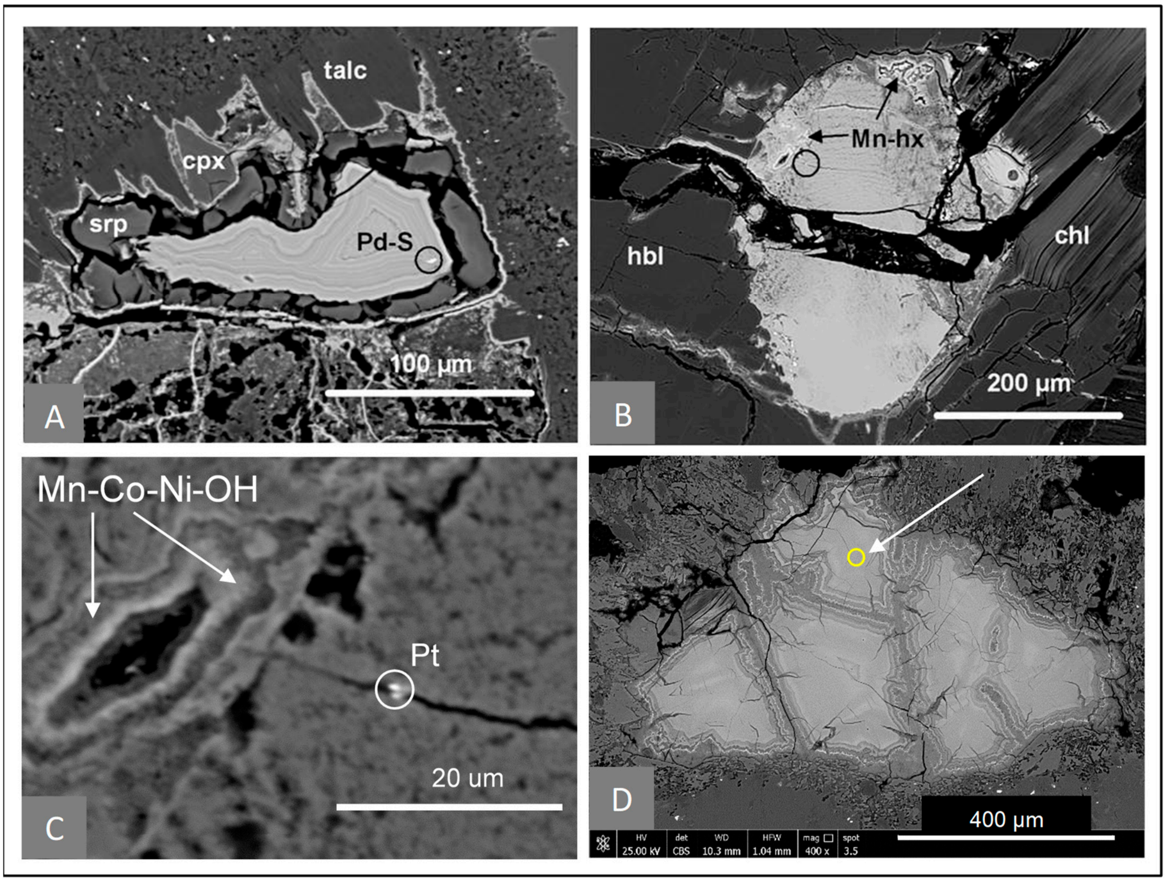

Figure 4. BSE images of secondary minerals in oxidized ores. (**A**) Iron-hydroxide with colloform texture and inclusion of Pd–S compound (circle:) in a matrix of Fe-rich serpentine (srp), talc, and clinopyroxene (cpx). The Fe-hydroxide carries 30 ppm Pt. AS 6828, Mimosa Mine. (**B**) Iron-hydroxide aggregate enclosed by chlorite (chl) and "hornblende" (hbl). Within the Fe-hydroxide, small areas and veinlets of Mn–Co-hydroxide (Mn–hx) carry 150–400 ppm Pt. Small PGM (Pt) in circle. The chlorite is rich in Ni and Cu (up to 4 and 6 wt %, resp.). AS 5320a, Mimosa Mine. (**C**) Porous Fe-hydroxide (matrix) with areas of Mn–Co–Ni-hydroxides (Mn–Co–Ni–OH) which contain ~200 ppm Pt. Small spec of PGM (Pt) in fracture. Ngezi Mine. (**D**) Interstitial iron-hydroxide with colloform textures. Analyzed point (circle, arrow) has 214 ppm Pt and 192 ppm Pd. Platreef, Overysel, Mogalakwena Mine. Reproduced with permission from Malte Junge [25].

Within the oxidized ores, substantial proportions of the PGE are hosted in Fe- and Mn-oxides/hydroxides. They also occur as vein-like structures that crosscut the silicates. Both types of Fe-/Mn-oxides/hydroxides reveal characteristic layered and zoned internal textures (Figure 4A). At Mimosa mine [61,70], Fe-hydroxides pseudomorphous after sulfide droplets may carry small grains of secondary PGM (mainly Pt, but also relict PGM), whereas the vein-like hydroxides are barren of PGM.

The unusual correlation of presumably silicate-bound elements and metals corroborates that mixtures of Fe hydroxide with Si-rich material are present, probably amorphous or very fine-grained clayey substances. In the Great Dyke oxide ores, the Fe hydroxide aggregates may carry up to 230 ppm Pt and 150 ppm Pd (EPMA trace analysis). In some cases, Fe-hydroxides, pseudomorphous after sulfides are veined by bluish/grey Mn–Co–Ni–Cu-hydroxides (17–47 wt % Mn, 7–18 wt % Co, 8–13 wt % Ni, 4–23 wt % Cu) that have elevated concentrations (40–400 ppm) of Pt, however, Pd contents are below the EPMA detection limit of 25 ppm [61,66]. In the Hartley mine ores, iron-oxides/hydroxides revealed highly variable concentrations of Pt (up to 3600 ppm) and Pd (up to 3100 ppm), and Mn-oxides/hydroxides are significant carriers of Pt (up to 1.6 wt %) and Pd (up to

157 ppm) [57]. From the Platreef ores (Figure 4D), up to 416 ppm Pd, 335 ppm Rh, and 803 ppm Pt are on record from secondary minerals [25].

Secondary silicates comprise serpentine minerals, smectite (nontronite), and chlorite-like phases. Smectite and chlorite carry up to several wt % Ni and Cu and occasionally PGE; trace analyses gave high contents of Pt (up to 1800 ppm) and Pd (up to 1600 ppm).

Summary—PGM and PGE Carriers in Oxidized Ores

Weathering of the pristine, sulfide-rich ores has a pervasive impact on the ores. Within the oxidized ores, the sulfides are destroyed, and the PGM assemblage suffers destruction especially of the (Pt,Pd)-bismuthotelluride and the PGE-sulfarsenide species. Pt and Pd, liberated from either PGM or sulfides, are now found in PGE oxides/hydroxides or in appreciable amounts in secondary iron and iron/manganese oxides/hydroxides, or in secondary phyllosilicates. A large proportion of the mobile Pd is carried away in solution. Neoformation of small, secondary PGM plays a subordinate role. In brief, the PGE are polymodally distributed in the oxidized ores and they occur in different modes:

(1) As relict primary PGM (mainly sperrylite, cooperite/braggite, and Pt–Fe alloys),
(2) in solid solution in relict sulfides (dominantly Pd and Rh in pentlandite),
(3) as secondary PGM neoformations (rare, mainly small grains, e.g., native Pt),
(4) as PGE oxides/hydroxides that either replace primary PGM or represent neoformations,
(5) in iron oxides/hydroxides (up to some thousand ppm Pt and Pd),
(6) in iron/manganese oxides/hydroxides (up to 1.6% Pt and 1150 ppm Pd) [57], and
(7) in secondary phyllosilicates (up to a few hundred ppm Pt and Pd).

The proportions of the various PGE-bearing phases vary considerably from mine to mine and between samples. This probably reflects both variations in primary ore mineralogy and depth within the weathering profile (incipient to pervasive oxidation). Semiquantitative mass balance calculations and findings related to the metallurgical treatment of oxides ores indicate survival of ca. 10–30% of the primary PGM assemblage, mainly Pt-rich PGM like sperrylite, cooperite/braggite, and Pt–Fe alloys. All (Pt,Pd)-bismuthotellurides and the PGE-sulfarsenides were destroyed and at least part of their PGE contents are located in secondary phases. Up to 50% of the original Pd is lost from the system, probably transported away by acid surface waters, and the remaining Pd is largely hosted in PGE oxides/hydroxides, iron and iron/manganese oxides/hydroxides, and secondary phyllosilicates [57,61]. The fate of Rh remains open, as only rare carriers of Rh (PGM or secondary phases) were detected in the oxidized ores.

3.3. PGM Grains in Alluvial Sediments of Rivers Draining the Bushveld Complex and the Great Dyke

3.3.1. SEM Observations of Single Grains—Morphology, Intergrowths, Alteration, Modification

The assemblages of detrital PGM found in rivers draining the Bushveld Complex and the Great Dyke indicate further mineralogical changes [27–30,71].

Within the Bushveld Complex, our first study [28] concentrated on the placers of the farm Maandagshoek in the eastern Bushveld, i.e., the locality where Dr. Hans Merensky, based on placer PGM, identified platiniferous pipes first and then the Merensky Reef in 1924 [5–8]. Our sampling localities were, at maximum, 1–2 km away from the probable sources (Merensky Reef, UG-2 and other chromitites, platiniferous dunite pipes). Accordingly, many grains of the detrital PGM assemblage are still rather unaffected (Figure 5a,b,d,f) whereas others have experienced some physical modification or chemical corrosion [28,30,71].

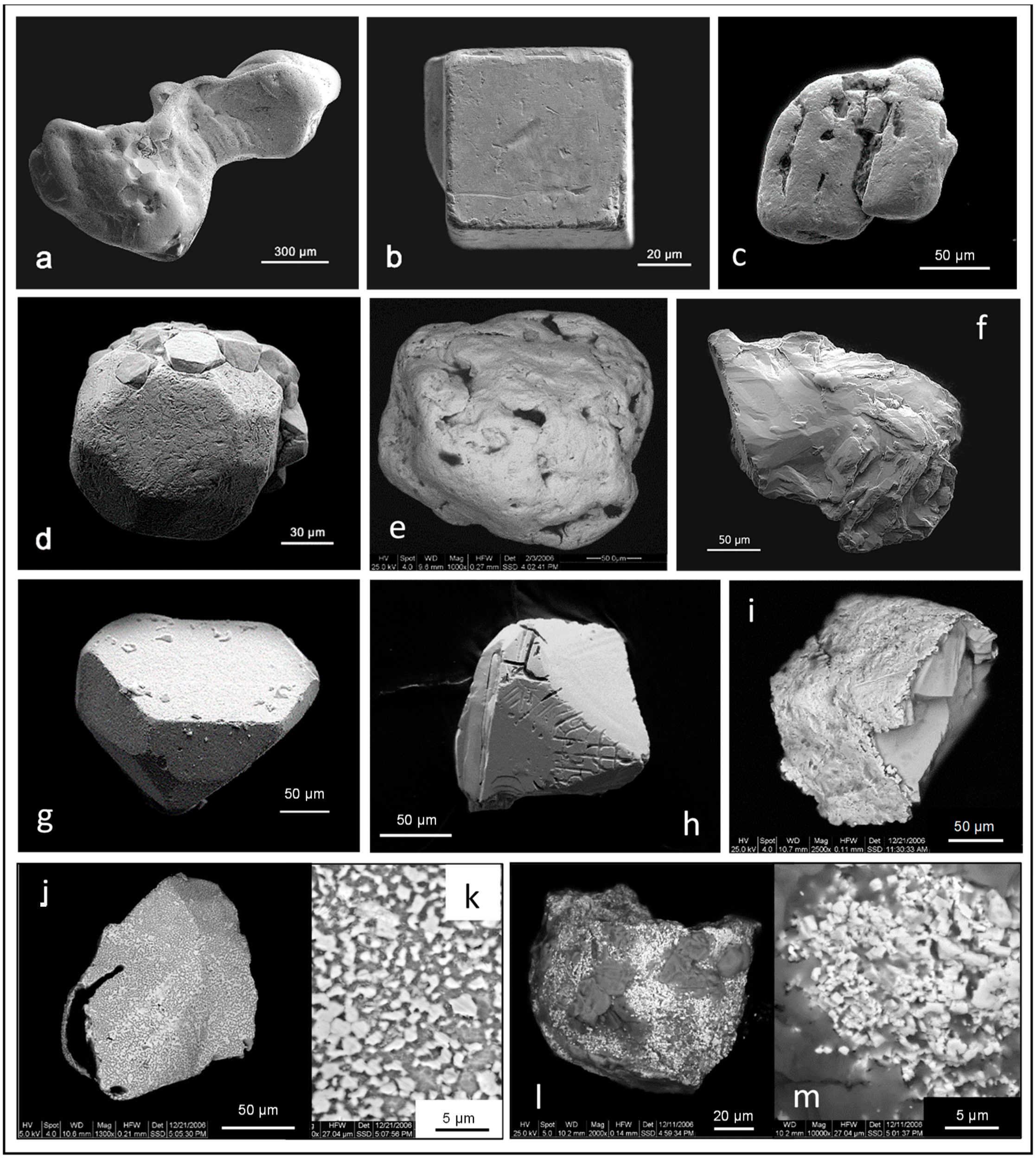

Figure 5. Detrital PGM, scanning electron microscope (SEM) images. (**a**) Pt–Fe alloy grain (1.6 mm in diameter) with smooth surface. Moopetsi river, Maandagshoek, eastern Bushveld. (**b**) Idiomorphic Pt–Fe alloy grain. Note slightly contorted edges. Locality as Figure 5a. (**c**) Well-rounded grain of Pt–Fe alloy. Makwiro river near Hartley Mine, Great Dyke, Zimbabwe. (**d**) Grain of Pt–Fe alloy with cubic crystal faces and smooth surface polish, intergrown with platelets of laurite (on top). Locality as Figure 5a. (**e**) Well-rounded grain of native Pt. Dithokeng river, northern Bushveld. (**f**) Splinter of large grain of cooperite. Locality as Figure 5a. (**g**) Sperrylite crystal showing little attrition. Locality as Figure 5a. (**h**) Well crystallized sperrylite grain with crystallographically oriented etch pits. Makwiro River, Hartley Mine. (**i**) Sperrylite with a thin surface coating of native platinum. Dwars river, eastern Bushveld. (**j**,**k**) Sperrylite surface overgrown by platelets of native platinum, (**k**) is surface magnification. Der Brocken, eastern Bushveld. (**l**,**m**) Tiny crystals of native Pt (light grey) on grain of pentlandite (dark grey). (**m**) Magnification from (**l**) showing crystals of native Pt (light grey). Brakspruit, western Bushveld.

SEM investigations of 1425 PGM grains provided an excellent overview and showed that the PGM assemblage is mainly composed of grains of native Pt, Pt–Fe and Pt–Fe–Cu–Ni alloys (together 73.2% by number of grains), cooperite/braggite (14.2%), and sperrylite (10.2%). The remainder (2.4%) consists of a variety of rarer PGM. Grain sizes range from 40 µm to 1.6 mm in diameter, and the highest numbers of PGM grains were found in the fraction <125 µm. Pt–Fe alloy grains are up to 1.6 mm in diameter (mostly between 100 and 200 µm) and have various surface morphologies. Grains with well-rounded shapes are most frequent, although cubic crystals are also present. Intergrowths with laurite embedded in or attached to Pt–Fe alloy grains are common (Figure 5d). Sperrylite grains are generally multifaceted single crystals without any signs of corrosion or mechanical wear (Figure 5g). Cooperite/braggite grains are mainly present as splintered, broken grains. Besides monomineralic PGM grains, many grains are intergrowths of between two and six different PGM, the most common association being Pt–Fe alloy intergrown with laurite (Figure 5d).

The other localities of the Bushveld studied [30] revealed similar gross PGM assemblages with minor variation (Figure 5e,i) also due to the smaller amount of PGM grains (n = 54) recovered. PGM grain sizes are mostly in the range from ~50 to 150 µm (maximum diameter 600 µm). The overall PGM proportions are: native Pt and Pt–Fe alloys (54%), sperrylite (33%), cooperite/braggite (11%), and stibiopalladinite (one grain). Accordingly, nearly 98% of the detrital PGM are Pt minerals.

In the river sediments along the Great Dyke [29], PGM mineral proportions by number of grains (n = 390) obtained by SEM are: sperrylite (45.6%; Figure 5h), native Pt and Pt–Fe alloys (together 42.1%; Figure 5c), cooperite and braggite (6.7%), and a number of rarer Pd-bearing PGM (3.4%). Notably, Os–Ir–Ru alloy grains (2.0%) were only found in samples from the Umtebekwe River south of Unki mine and probably originate from the economically important chromitite mineralization in the near-by Archean Shurugwi greenstone belt. Most PGM grains are monomineralic, however, several intergrowths, mainly between Pt–Fe alloy and laurite, were observed, and also various inclusions of different minerals in the detrital PGM grains. Grain sizes of the PGM range from 90 to 300 µm (mostly between 100–200 µm); maximum grain sizes determined are 480 µm for sperrylite, and 285 µm for a Pt–Fe alloy grain.

In summary and generalized, the Pt–Fe alloy grains span a large compositional range from [Pt_3Fe] to [$Pt_{1.5}Fe$] and have various surface morphologies. Grains with well-rounded shapes (Figure 5a,c) are common, although cubic crystals are also present (Figure 5b), as are occasional intergrowths mainly with laurite (Figure 5d). Grains of native Pt may contain elevated contents of Pd (%-range), are usually well-rounded and show mechanical wear on their surfaces (Figure 5e). Sperrylite grains are commonly multifaceted single crystals. Although some grains show etch pits, channels, or fractures, the majority of the sperrylite grains are without obvious signs of corrosion or mechanical wear (Figure 5g,h). Cooperite/braggite grains are mainly present as splintered, broken grains (Figure 5f). PGM neoformation is restricted to sporadic, thin coatings of native Pt on sperrylite and cooperite/braggite (Figure 5i–k). Deposition of tiny Pt crystals on a pentlandite grain was observed once (Figure 5l,m).

The above SEM studies provided an insight into grain morphologies and also allowed to obtain semi-quantitative analytical data of the mineral grains. However, SEM analyses are performed on the surfaces of grains only and therefore, thin crusts on the grains or overgrowths may show compositions that differ from the internal composition of the grains. Indeed, polished section studies demonstrate that some PGM grains assigned to native Pt or Pt–Fe alloy have cores of cooperite, braggite, or in rarer cases, sperrylite, as will be shown in the following.

3.3.2. Detrital PGM: Intergrowths, Inclusions, Alteration, Modification

Features of magmatic-hydrothermal alteration of Bushveld PGM were described in detail elsewhere [71]. Based on light microscopic and EPMA studies, this section will concentrate on the characteristics of secondary alteration of the detrital PGM in the weathering environment, from oxidized ores to final placer deposition. Further details on alteration, intergrowths, and inclusions will be disclosed, and the question of PGM neoformation will be illuminated.

As mentioned, in the Maandagshoek placer, many grains of the detrital PGM assemblage are still rather unaffected whereas others have experienced some physical and chemical modifications [28,71]. Figure 6a is an example showing well-crystallized grains of Pt–Fe alloy intergrown with other PGM, and a porous grain of native Pt. The PGM grain depicted in Figure 6b shows an unusual, complex intergrowth of some rather exotic PGM. This author is convinced that these textures cannot survive extended alluvial transport, corroborating the earlier notion of short transport distance.

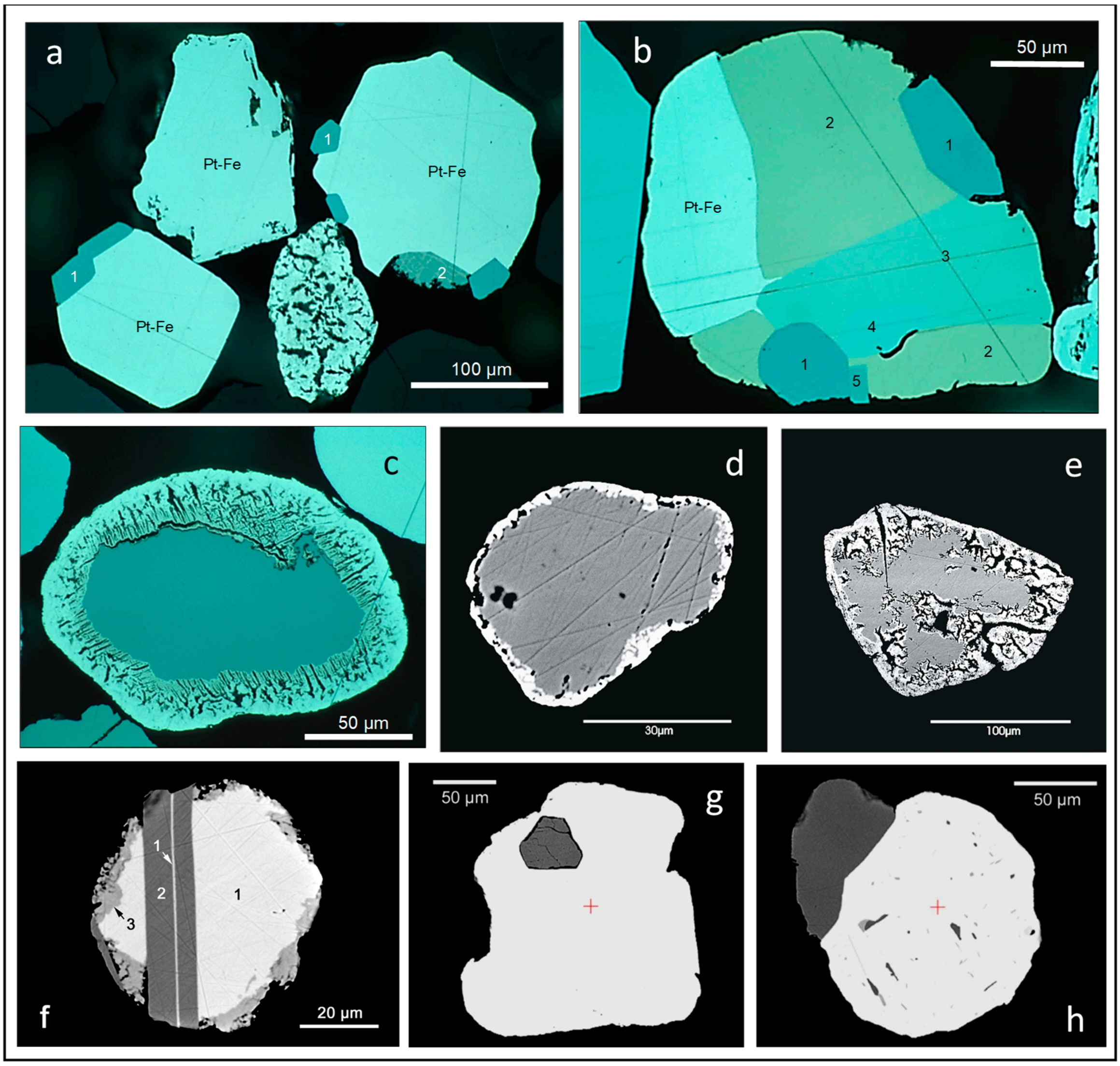

Figure 6. Detrital PGM in polished sections. Reflected light, oil immersion (**a**–**c**), and BSE images (**d**–**h**). (**a**) Three grains of Pt–Fe alloy (Pt–Fe), with attached laurite (1) and RhFeNi sulfide (2). Porous grain (lower half, center) is native platinum. Maandagshoek. (**b**) Composite grain consisting of Pt–Fe alloy, laurite (1), törnroosite [$Pd_{11}As_2Te_2$] (2), palladoarsenide [Pd_2As] (3), sperrylite (4), and irarsite (5). Maandagshoek. (**c**) Alteration of cooperate-braggite, replaced by platinum. Note intruding channels and outer, compact rim. Maandagshoek. (**d**) Sperrylite grain with rim of pure Pt. Umtshingwe River, Great Dyke. (**e**) Strongly corroded cooperite grain being replaced by pure Pt (white). Umtebekwe River, Great Dyke. (**f**) Polyphase grain of Pt–Fe alloy (1) with a lamellar Ru_{70} alloy (2), overgrown by a rim of [Ni_2PtFe] (3). Maandagshoek. (**g**) Grain of Pt–Fe alloy (white) with idiomorphic inclusion of laurite. Umsweswe River, Great Dyke. (**h**) Well-rounded grain of Pt–Fe alloy (white) with numerous inclusions of various PGM (palladodymite $(Pd,Rh)_2As$, unnamed RhS, unnamed Pd_3Te), intergrown with unnamed $Rh(Ni,Cu)_2S_3$ (dark grey; top left). Umsweswe River, Great Dyke.

In both the Bushveld and the Great Dyke samples, sperrylite is usually unaltered. However, a few grains have narrow (<10 μm), discontinuous to complete rims of pure platinum (Figure 6d) as also observed in the SEM studies (Figure 5i–k), or corrosion channels on their surface (Figure 5h).

Relics of primary Pt–Pd sulfides (cooperite/braggite) are rimmed by porous native platinum with abundant root-like channels that occasionally form a dense network penetrating into the Pt–Pd sulfide (Figure 6c,e). The platinum rims may have elevated concentrations of Ni (up to 5.2 at %) and Pd (up to 30 at %) which also point to the precursor phases. Therefore, it is assumed that many porous to compact grains of native platinum are the end-products of Pt–Pd–Ni sulfide alteration [71]. Accordingly, most of the native platinum grains detected in the SEM studies probably originate from the alteration of Pt–Pd–Ni sulfides.

Further modifications observed are local alteration of Pt–Fe alloy grains by inhomogeneous Pt–Fe oxide phases and replacement of laurite by Ru-rich oxides or hydroxides. Minor to trace concentrations of PGE in secondary phases such as Fe oxide and hydroxide, chlorite, and smectite forming a continuous rim around PGM grains are considered to have formed in situ within the placer deposits.

Intergrowths of the PGM mainly consist of Pt–Fe alloys intergrown with other PGM (Figure 6f,h), and inclusions detected mainly in Pt–Fe alloy grains comprise a wide spectrum of sulfides and PGM (Figure 6g,h). In all probability, the observed intergrowths and inclusion types point to early formation in the history of the grains, at the magmatic stage.

Unambiguous neoformations are the coatings of native Pt on cooperite/braggite, and more sporadic on sperrylite or pentlandite (Figures 5i–m and 6c–e). Visibly, these thin coatings source their metal contents from the enclosed grains (PtS, $PtAs_2$), following the simplified reaction (example: cooperite): $PtS + 3/2O_2 + H_2O = Pt^0 + SO_4{}^{2-} + 2H^+$ [71]

Dissolution takes place under oxidizing conditions, and reprecipitation of Pt may be assisted by electrochemical processes [72]. Note that a large proportion of native platinum grains is regarded to be the end-product of Pt–Pd–Ni sulfide alteration [71]. Chemically, the neoformations observed are native Pt, not Pt–Fe alloys. Further, small overgrowths and crusts of zvyagintsevite [Pd_3Pb] record the mobilization of Pd and reaction with stray Pb, however, the general trend of the placer PGM assemblage is a further increase of the Pt/Pd ratio, and now >95% of the PGM are Pt-minerals. The newly grown PGM occur as small platelets or crystals (Figure 5j–m), and any growth to larger crystals or nuggets was not observed. The common Pt–Fe alloy grains occasionally carry inclusions of sulfides and other PGM which most probably were included at the magmatic stage. Inclusions trapped in an oxidizing, secondary environment like iron/manganese oxides or hydroxides or silicates are absent.

4. Discussion

The paper reports on the PGM assemblages identified in the Bushveld and the Great Dyke, specifically in:

(1) the primary, pristine ores,
(2) the near-surface oxidized/weathered ores, and,
(3) associated placers.

One important aspect to be discussed on a wider base below aims at contributing to the debate allogenic versus authigenic origin of placer PGM, i.e., whether the placer PGM:

(1) originate from the primary ores (residual/allogenic/detrital grains), or,
(2) developed during weathering/oxidation of the primary ores (authigenic grains), or,
(3) were newly formed (authigenic grains/“neoformation”) in the alluvial placer environment.

4.1. Development of the Bushveld/Great Dyke PGM Assemblages in the Course of Weathering

The processes of PGE redistribution and the behavior of the PGM in the weathering cycle are much debated and cases of both dispersion and concentration, destruction and neoformation have been proposed by various authors (for details see Sections 4.3.1 and 4.3.2 below). In contributing to the discussion, it is fortunate that near-continuous underground and surface exposures of the Bushveld and Great Dyke reefs allowed us to investigate some aspects of the fate of the PGE and PGM in the exogenic environment in detail. The basic results of our studies were reported above and are depicted schematically in Figure 7.

In the pristine sulfide ores of both the Bushveld and the Great Dyke, the PGE are bimodally distributed: (i) Pt, the IPGE (Ru,Os,Ir) and variable proportions of Pd and Rh are present in the form of discrete PGM, dominantly PGE-bismuthotellurides, -sulfides, -arsenides, -sulfarsenides, and -alloys; (ii) Substantial though variable proportions of Pd and Rh are hosted in pentlandite.

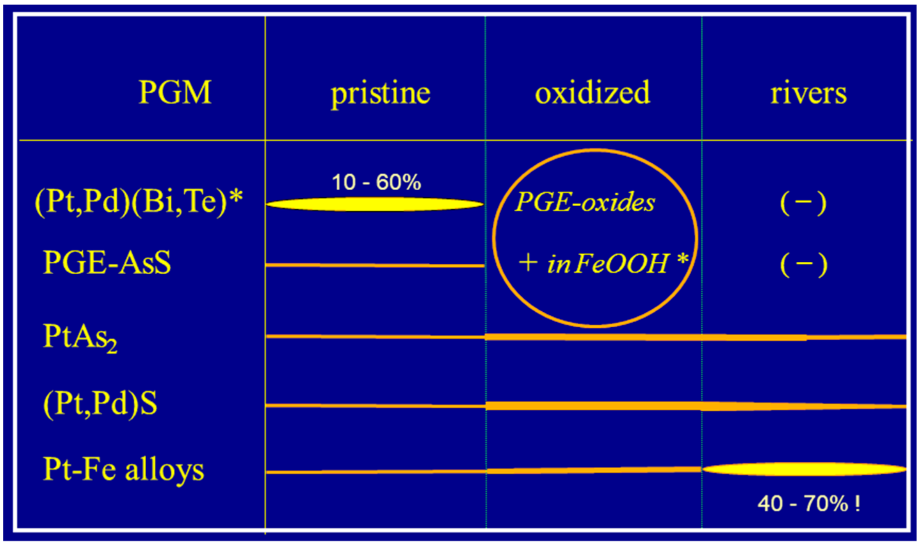

Figure 7. Schematic graph showing the principal changes of the PGM assemblages from pristine, sulfide ores via oxidized ores into placer accumulations. Abbreviations: (Pt,Pd)(Bi,Te)* = (Pt,Pd)-bismuthotellurides; FeOOH* stands for Fe,Mn,Co-oxides/hydroxides. Note that Pt–Fe alloys include native Pt.

In the weathered/oxidized ores, the PGE are polymodally distributed: PGE-sulfides, -arsenides, and Pt–Fe alloys remain the only relics of the pristine PGM assemblage. During weathering of the ores, all base metal sulfides, the (Pt,Pd)-bismuthotellurides and most PGE-sulfarsenides are destroyed. Part of their PGE contents are found in the form of ill-defined (Pt,Pd)-oxides or -hydroxides, and in secondary Fe/Mn/Co-oxides/hydroxides as well as smectites which carry elevated though variable contents of Pt and Pd. Possible PGM neoformations comprise rare and tiny (<3 µm) specks of native Pt or Pt oxide in Fe-hydroxides, and small (1–5 µm) grains of zvyagintsevite. Notably, a large proportion of the mobile Pd (up to 50%) is lost from the system. The weathering event is mainly characterized by destruction of primary sulfides and unstable PGM, and dispersion of the PGE.

Finally, the PGE are unimodally distributed in the alluvial sediments as only discrete PGM are present. Obviously, the often porous (Pt,Pd)-oxides or -hydroxides and secondary Fe/Mn/Co-oxides/hydroxides, important carriers of Pt and Pd in the oxidized ores, do not survive the mechanical transport into the rivers and their metal contents are either transported away as detritus in the fine sediment fraction or in solution. The remaining PGM assemblage is characterized by continued partial alteration or destruction of most PGE-sulfide grains. In contrast, sperrylite largely remains a stable mineral, and ubiquitous Pt–Fe alloy and native Pt grains have gained in importance. Notably, >95% of the placer PGM are Pt-rich, indicating a further loss of the mobile Pd.

Native Pt as crusts and overgrowths and forming porous or compact grains is a newcomer that mainly formed more or less in situ on and replaces pre-existing PGE-sulfide (cooperite/braggite) and to a lesser extent sperrylite grains. Rare, newly grown coatings of native Pt on pentlandite indicate a low-temperature solution state of Pt, however, the precipitates occur as small platelets or crystals only and any indications of growth to larger crystals or nuggets (mm size) are absent.

4.2. Placer PGM Worldwide—An Overview

Placers in Colombia and in Russia (Ural Mountains) were the major source of PGE for many years before the discovery of the rich deposits of the Bushveld Complex in South Africa. The initial major detection 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 [5–8,10]. Early reports describe several alluvial diggings in the Bushveld Complex that produced some platinum [7]. However, as mining commenced on the rich dunite pipes and reef-type deposits of the Bushveld, alluvial PGM soon became forgotten because prospecting work in the 1920s did not reveal any profitable placers of significance [7].

Indeed, economic accumulations of PGM in stream sediments draining PGE-bearing layered intrusions such as the Bushveld Complex or the Great Dyke are unknown [2,3,7,28–30]. Their PGM assemblages are dominated by Pt–Fe alloys, sperrylite, and cooperite/braggite (Table 1), distinctly contrasting to the spectra of placer PGM derived from Alaskan/Uralian type complexes, and also from PGM assemblages originating from ophiolitic, generally uneconomic PGE mineralization (Table 1). Therefore, the "layered intrusion" assemblage can be regarded to represent a useful proximity indicator of near-by platinum mineralization.

Table 1. PGM proportions (in %) of placers originating from layered intrusions (1 + 2), Alaskan-type intrusions (3–5), ophiolite-related localities (6–8), the Rhine River (9), and the Witwatersrand gold paleoplacer (10). At some localities, no exact numbers are available, and *x* means = present. Abbreviations: $PtAs_2$ = sperrylite; RuS_2–OsS_2 = laurite-erlichmanite; PGE-sulfides = various PGE-sulfides; PGE–AsS = various PGE-sulfarsenides.

	PGM Locality	**Ru–Os–Ir Alloys**	**Pt–Fe Alloys**	**$PtAs_2$**	**RuS_2–OsS_2**	**PGE Sulfides**	**PGE–AsS**	**Others**	**Ref.**
1	*Great Dyke Rivers*		**42**	**46**	*x*	**7**		**5**	[29]
2	*Bushveld Rivers*		**54**	**33**		**11**		**2**	[30]
3	*Tulameen, Canada*	**2**	**98**						[73]
4	*Choco, Columbia*	**1**	**97**		**1**	**1**	*x*	*x*	[2]
5	*Urals, Russia*	**2**	**97**		**1**				[74]
6	*Chindwin, Burma*	**96**	*x*	*x*	*x*	*x*	**4**		[75]
7	*Aikora River, PNG*	**88**	**12**						[76]
8	*Samar, Philippines*	**41**	**40**		**17**			**2**	[77]
9	*Rhine River*	**70**	**15**	**10**	*x*			**5**	[78]
10	*Witwatersrand*	**80**	**10**	**10**		*x*	*x*		[79]

The most productive PGE placer deposits are associated with "Alaskan" or "Uralian"-type ultramafic-mafic complexes in tectonic belts, the best-known examples being many locations in the Ural Mountains in Russia, the Tulameen Complex in Canada, and alluvials in the Chocó department of Colombia [1–3,73]. Their PGM assemblages are characterized by the dominance of Pt–Fe alloys (>95% of the PGM assemblage), followed by inter-IPGE (Ru–Os–Ir) alloys (Table 1).

Numerous PGM placer occurrences linked to "Alpine-type" intrusions (ophiolite complexes) are on record worldwide and are well-studied, however, they are generally uneconomic [2,3,78,80]. Their PGM assemblages mainly comprise Pt–Fe alloys and Ru–Os–Ir alloys in about equal though variable proportions (Table 1).

The comparison provided in Table 1 includes the enigmatic PGM assemblages of the Witwatersrand gold-uranium paleoplacers (sources are probably Archean komatiites), and of the Rhine river in Germany. The assessment demonstrates that different PGM assemblages prevail in relation to the various source rock types and between different localities with similar source areas. Therefore, care must be exercised in comparing PGM from these different PGM sources, and this will be kept in mind in the discussion following.

4.3. Placer PGM—Residual Grains (Allogenic/Detrital) or Authigenic ("Neoformation")?

4.3.1. PGM in Laterites

It is felt that topic Section 4.3 deserves some deeper going and extensive discussion, which will follow now. Those readers less attracted by this theme may proceed to Section 4.3.3.

In the context of the discussion on PGM "neoformation", several studies have shown that lateritization can lead to solution, transport, and concentration of Pt and Pd [64,65,81]. In lateritized ophiolitic pyroxenites from the Pirogues River area of New Caledonia, up to 2 ppm (although typically 400 ppb) Pt were analyzed and this enrichment has been attributed to the lateritization process [64,81]. Pt mobility in the lateritic environment was also investigated at Andriamena in Madagascar [81], where a variety of primary, magmatic PGE minerals were observed including arsenides, sulfides, and stibiopalladinite, however, only sperrylite appears to have been resistant and occurs in the weathered zone, together with Pt–Fe alloy which is suggested to be newly-formed from a pre-existing grain of Pt, Fe (Pd, Ni) sulfide [81]—grossly being reminiscent of replacements of cooperite-braggite grains in the Bushveld alluvials (Figure 6c–e). Equally, an almost complete removal of Pd is reported [81].

More recent work on PGM from Ni-laterites (with ophiolite parent rocks) of the Dominican Republic [82] led the authors conclude that PGE are mobile on a local scale leading to in situ growth of PGM within limonite, probably by bio-reduction and/or electrochemical metal accretion. Besides primary PGM inclusions in fresh Cr-spinel (laurite, bowieite), supposedly secondary PGM (e.g., Ru-Fe–Os–Ir compounds) from weathering of pre-existing PGM were described, and also PGM precipitated after PGE mobilization within the laterite ("neoformation"). One elongated Pt–Fe–Ni grain (20 μm) is characterized by delicate botryoidal textures interpreted as in situ growth at surface conditions. No larger or well-crystallized PGM were observed.

Follow-up research [83] revealed the presence of so-called multistage PGM grains, namely porous Os–Ru–Fe–(Ir) grains overgrown by Ni–Fe–Ir and Ir–Fe–Ni–(Pt) compounds which in turn are overgrown by Pt–Ir–Fe–Ni phases. A model for multistage PGM grain formation is proposed: (i) hypogene PGM are transformed to secondary PGM by desulphurization during serpentinization; (ii) at the stages of serpentinization and/or at the early stages of lateritization, Ir is mobilized and recrystallizes on porous surfaces of secondary PGM; and (iii) at the late stages of lateritization, biogenically mediated "neoformation" (and accumulation) of Pt–Ir–Fe–Ni nanoparticles occurs. It is suggested [83] that in situ growth of Pt–Ir–Fe–Ni alloy nuggets of isometric symmetry may be possible within Ni laterites from the Dominican Republic.

The observed multistage IPGE-rich PGM grains are porous, corroded, locally oxidized, and overgrown by PGM nanoparticles. Clearly, the PGM assemblage has experienced a series of overprints including serpentinization (strongly reducing) and lateritization (oxidizing), and the observations can also be interpreted as corrosion and dissolution of primary PGM (intergrowth of various inter-IPGE alloys, here Ru–Os–Ir ± Pt alloys, laurite—typical PGM from ophiolites) and direct re-precipitation of dissolved PGE. Further, the result of an XRD analysis of one Pt–Ir–Fe–Ni alloy grain, namely an X-ray pattern identical to awaruite [83], is an unequivocal indication that this grain formed under strongly reducing conditions during serpentinization [84,85], and not through supergene (oxidizing) processes. Notably, Pt-rich awaruite grains have been described from both the Bushveld and Great Dyke placers [29,71], and Ir-rich awaruite grains were reported from ophiolitic chromitites in Pakistan [86].

In conclusion, any indisputable and convincing mineralogical evidence of in situ growth of larger and chemically well-defined PGM grains in the lateritic environment and at low temperatures is still lacking. No evidence of well-crystallized newly-formed PGM is on hand; in fact, all products of "neoformation" are thin films, nanoparticles and/or crystallites on substrates of earlier, generally larger, pre-existing PGM.

4.3.2. PGM in Placers

As indicated above, the origin of certain alluvial PGM grains is a matter of controversial debate. Two major models are in vogue:

(i) Primary PGM formation within mafic/ultramafic intrusions, followed by weathering with no or only minor further alteration prior to alluvial concentration.
(ii) Solution of the PGE during weathering of the source rocks, probably aided by organic reactions, followed by the supergene growth of the macroscopic grains within the weathering zone and final alluvial concentration.

In the alluvial samples from the Bushveld and the Great Dyke, the largest proportion of the PGM assemblage (~40–70%) consists of Pt–Fe alloy and native Pt grains, compared to the scarcity (mostly ±10%) of these PGM in the primary ores (Figure 7 and Table 1). Indeed, explanations are needed for this discrepancy.

Based on textural and geochemical arguments such as the presence of inclusions of a variety of sulfides, spinels, silicates, and other PGM as well as Os isotope compositions, the origin of Pt–Fe alloy, the most abundant PGM in most placers worldwide [2,3,80], is considered by most researchers to reflect an origin from high-temperature (i.e., magmatic) processes [2,3,87–90].

In contrast, a secondary origin of PGM in placers and soils is anticipated by several authors [81,91–98]. As size, shape, composition and micro texture of many eluvial and alluvial PGM differ from those observed in bedrocks and ores, it was proposed that secondary PGM come into being 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; (3) The colloids may coalesce or accrete to form larger particles and aggregates of PGE alloys.

An examination of gold and PGM (Pt–Fe and Os–Ir alloys) in offshore placers near Goodnews Bay, Alaska [99], revealed textures related to both derivation of PGM grains from mechanically weathered primary ore (i.e., typical assemblages of inclusions of PGE-arsenides, -sulfides and -tellurides; exsolution phenomena), and subsequent accretion (i.e., micro-crystalline assemblages of PGM in grain-rim cavities, suggesting leaching and crystallization).

Similar features were also observed in and on PGM grains of the Bushveld/Great Dyke placer assemblage [27–30]. Indeed, the above observations [99] pertain to many occurrences of placer PGM. Surface corrosion features are obvious in many localities, and a certain degree of PGE mobility has been documented by newly-formed nm- to µm-sized crystalline PGM [27–30,100–102] or PGE-biofilms [103] on and in cavities of pre-existing residual PGM grains. However, relative to the total budget of the alluvial PGM assemblages, these PGM neoformations play an insignificant role.

Bowles and coworkers [93–98] studied alluvial PGM grains (mostly Pt–Fe alloys, laurite-erlichmanite, Os–Ir alloys) from Sierra Leone and reported contrasting features of the primary and placer PGM [97], a main reason for the proposal that the latter developed as a result of breakdown of the primary PGM during weathering, movement of the PGE in solution, and growth of new PGM in placers with a different mineral assemblage, mineralogy and mineral chemistry [97]. The processes postulated for PGM "neoformation" include [97]: (1) long term weathering in an area of warm climate and high rainfall; (2) destruction of the primary PGM and transport of the PGE in solution; (3) organic compounds, such as humic or fulvic acids that are abundant in tropical rain forest soils appear likely to be involved in solution and transport of the PGE; (4) differential movement of the PGE in solution; (5) concentration of the least mobile PGE in soils close to the rivers, the more mobile PGE (especially

Pd) being carried away in solution; (6) accretion of the remaining PGE to form a new PGM assemblage, possibly where there is a change in Eh and pH conditions favourable for deposition; and (7) bacterial action may assist, or be responsible for, the PGM growth.

The main evidence claimed that PGM grow in situ as "neoformations" is that they comprise a different mineral assemblage from the PGM in the source rocks. The differences are [97]: (1) PGE arsenides, tellurides, and sulfides present in the host rocks become less abundant in or disappear completely from the alluvial suite, and Pt–Fe alloys including tulameenite, Os–Ir alloys, and laurite—erlichmanite become more abundant; (2) oxidized PGM appear in weathered or oxidized rocks, Cloudy, porous, or filamentous altered PGM may also be present; (3) there is a loss of the more soluble Pd which is present in the host rocks, but is much less abundant in the alluvial mineral suite; (4) a considerable difference in size (typically three orders of magnitude) exists between micrometre-sized PGM in the host rocks and millimetre-sized PGM in the alluvial suite; (5) some PGM in an alluvial suite show delicate crystal features that would not survive mechanical transport, these features include dendritic growth, perfect crystal faces, and perfect edges and corners between crystal faces. The corners are the most susceptible to mechanical damage and the presence of undamaged corners provides evidence for the absence of abrasion. The dendritic PGM are not known to occur in the host rocks. (6) There is over plating of mineral faces, colloform, cyclic, and fibrous textures not characteristic of PGM in the host rocks.

The observations of points (1) to (3) mirror those of the Bushveld/Great Dyke case. Less stable PGM are partly altered or destroyed during weathering, combined with a relative increase in Pt–Fe alloys; PGE-oxides appear and a large proportion of the bulk Pd is lost.

Point (4), the observed discrepancy in size distributions of detrital PGM grains (mostly between 100–200 µm and larger) compared to PGM in pristine ores (<5 to 50 µm) has been resolved for the Great Dyke case by treatment of a pristine MSZ sample (ca. 1 kg) 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, 85 µm for sperrylite, 195 µm for cooperite/braggite, and 300 µm for Pt–Fe alloy grains [16,17,27], emphasizing that coarser PGM grains are present in the pristine MSZ ores. Notably, the presence of larger (~100 µm) and well-crystallized PGM grains extracted by careful crushing of primary Bushveld ores was reported recently [104,105], and wherever placer PGM were followed to their source rocks (e.g., Great Dyke, Bushveld, Urals, Colombia), chemically and size-equivalent precursor PGM were detected [16,17,27,87,106,107]. Evidently, larger PGM grains are present in the pristine ores and invalidate the argument of point (4).

It is claimed in point (5) that some alluvial PGM show delicate crystal features that would not survive mechanical transport. However, this generalized statement is not adequate as distinct differences exist in the chemical and physical stabilities of different PGM. Accordingly, detrital grains of the comparably soft native Pt and Pt–Fe alloys (e.g., Vickers hardness VHN_{50} of 303–321 for Pt_3Fe; [108]) often show evidence of physical abrasion such as bent and rounded corners and smooth, occasionally scratched or polished grain surfaces. In contrast, Os–Ir–Ru grains display little signs of corrosion or mechanical wear due to the great hardness (Os: VHN_{100} = 689–734; Ir: VHN_{100} = 841–900; Ru: VHN_{100} = 841–907; [108]) and chemical resistivity of this mineral group, and the same applies to the hardest PGM known, laurite (VHN_{100} = 1650 and 2012) and erlichmanite (VHN_{50} = 1358) [108]. Consequently, undamaged and perfect crystals of Os–Ir–Ru and laurite-erlichmanite [RuS_2–OsS_2] are on record from placers worldwide [2,3,77,78]. For example, the perfect hexagonal Os grains found in the Rhine river were probably transported up to some hundred kilometres [78]. Furthermore, well-crystallized or delicate alluvial grains could have well been transported within a protecting rock matrix, or alternatively not as bedload, but in suspension [2,3,77,78]. In conclusion, the argumentation of point (5) is faint.

Point (6), over plating of mineral faces, colloform, cyclic, and fibrous internal textures were described from a well-crystallized eluvial erlichmanite grain from Serra Leone and regarded as not characteristic of PGM in the host rocks, and "neoformation" by late-stage hydrothermal or secondary processes was proposed [96]. However, exactly this grain, which also carries bornite and chalcopyrite inclusions and displays a heterogenous internal distribution of Ru and Os, was analyzed for its Os isotope composition, and the authors conclude [109]: "that the nuggets were not formed during lateritization nor were they formed in-situ in sediments. The delicate morphology of PGM nuggets simply manifests very short transportation distances from the eroded site, as expected in eluvial (residual) deposits. The $^{187}Os/^{186}Os$ data are consistent with the formation of PGM nuggets in the melt and their detrital origin."

Recently, a Pt–Fe alloy grain from the Freetown Layered Complex, Sierra Leone, containing numerous and diverse inclusions of laurite, irarsite-hollingworthite (IrAsS–RhAsS), Pd–Te–Bi–Sb phases, Ir-alloy, Os-alloy, Pd-bearing Au, a Rh–Te phase, Pd–Au alloy, and Pd–Pt–Cu alloy was presented [98]. This grain was interpreted to be "neoform" growths in the organic- and bacterial-rich soils of the tropical rain forest cover of the Freetown intrusion [98]. However, such an assemblage of PGM, typical of magmatic, high temperature ores, is highly improbable to form from dispersed PGE, As, S, Te, Bi, etc. at ambient surficial conditions. In evidence to the contrary, previous work [27,57] and the present review (e.g., Figure 3E,F) have shown that the (Pt,Pd)-bismuthotellurides and -tellurides are the PGM species most susceptible to oxidation/weathering and are unstable in the supergene environment. PGM of this mineral group and the equally unstable sulfarsenide inclusions have only survived oxidation as they are well-shielded by the enclosing Pt–Fe alloy grain, and the described multi-PGM assemblage [98] as well as their Pt–Fe alloy host are definitely not products of supergene formation. Concentration of rare and stray elements should follow a chemical gradient which is not in evidence in this environment. Accordingly, an origin from the magmatic realm of this remarkable detrital Pt–Fe alloy grain is suggested. Its excellent state of preservation points to a near-by source. In fact, the external surface of the Pt–Fe alloy grain with intergrown PGM sticking out closely resembles eluvial grains (for example, similar grains from Onverwacht in South Africa [30].

An investigation of placer PGM surfaces [103] demonstrated the existence of biological PGE cycling in some environments, whereby microbial biofilms play a key role in transforming PGM into more mobile forms (for example, nanoparticles). The authors [103] suggest that the microbial biofilms may enable the aggregation of PGE nanoparticles to form secondary PGM grains. Again, the products are small and distributed on the surface layers of pre-existing PGM substrates, and any proof of PGM growth to larger grains or nuggets still remains to be furnished.

Opponents of the school of supergene PGM "neoformation" admitted 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 [2,3,87]. However, contrasting views on the Brazilian occurrences still exist: An evaluation of the Brazilian example [110,111] led to the conclusion [112] that the alluvial PGM most likely are detrital grains from mineralization formed by low-temperature hydrothermal fluids. In contrast, it is postulated [113] that they have a bio-organic origin, linking high levels of iodine in these grains to their formation from organic matter-rich waters. In conclusion, the origin of these Pt–Pd nuggets still remains enigmatic.

4.3.3. PGE Mobility and PGM Neoformation—Concluding Remarks

The above discussion demonstrates that the debate on the origin of PGM in placers—primary, detrital/allogenic grains versus authigenic "neoformation"—is not resolved. However, this is also partly due to a mix-up of terms and definitions, and dubious comparisons. For instance, the terms "PGM" or "Pt nuggets" embrace Pt–Fe alloys ("ferroan Pt") and native Pt (which may contain some % Pd) as in the Bushveld/Great Dyke case; the Brazilian example involves dendritic, mamillary or botryoidal grains of zoned Pt–Pd alloys of variable composition and partly containing potarite in the core [2,87,110–113], the PGM described from the Dominican Republic are Ru–Os–Ir ± Pt alloys [82,83], and in the Sierra Leone occurrences Pt–Fe alloys and erlichmanite-laurite [OsS_2-RuS_2] are the PGM studied [96–98]. The PGM dealt with need to be named unambiguously because, as shown above, different PGM will behave differently during weathering, Further, the definite relation of the placer PGM species to their source rocks—layered intrusions, Uralian/Alaskan complexes, or ophiolites (Table 1)—needs to be considered.

No doubt, the six PGE are in general though variably mobile in the supergene environment. First signs are detected in the weathering zone of the pristine ores, where oxidation in a hydrous environment leads to the destruction of the sulfides, releasing contained PGE (mainly Pd, Rh) and producing sulfuric acid, concomitant with the destruction of specific PGM, and "neoformation" more or less in situ of PGE-oxides/-hydroxides. PGE released from the destruction of sulfides and unstable PGM follow two paths: (i) Pt and part of the Pd are fixed (either adsorbed or in the crystal lattices) in iron- and iron-manganese oxides/hydroxides and smectites, and (ii) a great proportion of the dissolved Pd (up to 50%) is lost from the ores, taken away in solution. Rare newly-formed PGM in the Bushveld/Great Dyke oxidized ores consist of tiny (~1–5 µm) specks of Pt or Pt-oxides and zvyagintsevite usually on pre-existing residual PGM. Accretion to larger PGM crystals is not noted. The main effect of oxidation and weathering on the pristine PGM assemblage is continuous destruction of unstable compounds.

In the Bushveld and Great Dyke alluvial samples, breakdown and dissolution of the remaining PGM assemblage persists. Evidently, the often porous (Pt,Pd)-oxides/-hydroxides and the secondary Fe/Mn/Co-oxides/hydroxides, important carriers of Pt and Pd in the oxidized ores, do not survive the mechanical transport into the rivers and their metal contents were either transported away in the fine sediment fraction or in solution. The remaining PGM assemblage is characterized by continued partial alteration or destruction of most PGE-sulfide grains, as best seen in the immature Maandagshoek placer PGM assemblage [28,30,49,71], where some polyphase grains consisting of diverse PGM (various alloys, sulfides, sulfarsenides, tellurides) have survived, and simultaneously cooperite/braggite and rare Ru- and Rh-sulfides are still in disintegration [71]. Native Pt as crusts and overgrowths and forming porous or compact grains largely is a "neoformation" that mainly formed in situ by alteration of pre-existing cooperite/braggite grains. Sperrylite largely remains stable, and ubiquitous Pt–Fe alloy and native Pt grains have gained in prominence. In fact, ~40–70% of the PGM assemblage consists of Pt–Fe alloy and native Pt grains, compared to their scarcity (mostly ±10%) in the primary ores. Rare Pd-dominated minerals (Pd–Hg ± As and Pd–Sb ± As) probably are newly-formed compounds which may have formed during supergene processes.

Some Pt–Fe alloy grains are intergrown with or host a variety of inclusions of other PGM or sulfides, equivalent to grains in the pristine ores, and therefore indicate a consanguineous, magmatic origin. Based on comparable observations, similar deductions were put forward for placers of the Urals [87], Colombia [106,107], and worldwide [2,3,87].

The replacement of PGM-sulfides by native Pt and the newly grown coatings of native Pt on relict sulfides in the Bushveld alluvials indicate that low-temperature solution and redeposition of Pt is possible to a certain degree. The resulting precipitates occur as small (<1–5 µm) microcrystalline platelets or crystallites, or colloform, or porous grains, mostly deposited on or in cavities of pre-existing detrital PGM.

In the Bushveld/Great Dyke case, the predominance (~40–70%) of Pt–Fe alloy and native Pt grains of the PGM assemblage is explained in a satisfactory manner by the assumption that they are direct descendants from the pristine, primary ores (Merensky Reef, UG-2, Platreef, MSZ). Some Pt–Fe alloy grains host a variety of inclusions of sulfides and other PGM indicating a consanguineous, magmatic origin. Pt–Fe alloy and native Pt are the PGM most stable in the weathering environment. Therefore, the placer PGM assemblages represent a mineral rest spectrum that has survived physical and chemical attack. Demonstrably, the order of decreasing stability in the supergene environment is: (1) Pt–Fe alloys (very stable) → (2) sperrylite (stable) → (3) cooperite/braggite (variably stable/"meta-stable") → (4) PGE-bismuthotellurides and PGE-sulfarsenides (unstable).

Both in the oxidized ores and in the alluvial environment, the main impact of weathering on the PGM assemblages is destruction. Redistribution of PGE (PGM "neoformation") is taking place, however, on a very limited scale only. As a rule, the newly-formed products are nano-sized particles, small crystallites or rarely lowest range µm-sized grains, predominantly sited on precursor detrital/allogenic PGM grains, and they are of subordinate significance. Any growth to larger crystals or nuggets (mm size) was not observed, and in the Bushveld/Great Dyke case, any proof of PGM "neoformation" in a grand style is missing.

This finding can safely be extended to the common Pt–Fe alloys in placer occurrences worldwide. The missing link of the "neoformationists", a look into the cradle of PGM creation in the supergene environment, is still outstanding, as is any evidence of authigenic PGM formation and growth to larger crystals or nuggets.

5. Conclusions

The behavior of the platinum-group minerals (PGM) in the weathering cycle was studied in the Bushveld Complex, South Africa (Merensky Reef, UG-2 chromitite, Platreef) and the Great Dyke, Zimbabwe (Main Sulfide Zone). The main findings comprise:

- In the pristine sulfide ores of both the Bushveld and the Great Dyke, the PGE are bimodally distributed: Pt and variable proportions of Pd and Rh are present in the form of discrete PGM, dominantly PGE-bismuthotellurides, -sulfides, -arsenides, -sulfarsenides, and -alloys, and substantial though variable proportions of Pd and Rh are hosted in pentlandite.
- Near surface, in the oxidized ores, the PGE become polymodally distributed: In the course of weathering of the ores, PGE-sulfides, -arsenides and Pt–Fe alloys remain the only relics of the pristine PGM assemblage. The base metal sulfides and the (Pt,Pd)-bismuthotellurides are destroyed, and ill-defined (Pt,Pd)-oxides or -hydroxides develop. Further, elevated contents of Pt and Pd are found in Fe/Mn/Co-oxides/hydroxides and smectites.
- In the alluvial sediments, the PGE are unimodally contained in discrete PGM. The assemblages of detrital PGM are characterized by partial alteration or destruction of most remaining PGE-sulfide grains, whereas sperrylite largely survives as a stable phase, and Pt–Fe alloy grains predominate.
- Accordingly, 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).
- In the Bushveld/Great Dyke case, and in all probability also worldwide, "neoformation", i.e., authigenic growth, of discrete, larger PGM in both oxidized ores and placers plays no substantial role. Dissolution and redistribution of PGE is taking place, however, the newly-formed products are nano-sized particles, small crystallites, or rarely µm-sized grains primarily sited on substrates of precursor detrital/allogenic PGM grains, and they are of subordinate significance. Any growth to larger crystals or nuggets (mm size) was not observed, and in the Bushveld/Great Dyke case, any proof of PGM "neoformation" in a grand style is missing.
- The final PGM suite which survived the weathering process on route from sulfide ores via oxidized ores into placers results from the continuous elimination of unstable PGM and the dispersion of soluble PGE. Therefore, the alluvial PGM assemblage represents a PGM rest spectrum of residual, detrital grains.

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