The oxidized ores of the Main Sulphide Zone, Great Dyke, Zimbabwe: turning resources into minable reserves—mineralogy is the key

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Synopsis

The Great Dyke of Zimbabwe constitutes the world's second largest reserve of platinum group elements (PGE) after the Bushveld Complex in neighbouring South Africa. Within the Great Dyke, economic concentrations of PGE are restricted to sulphide disseminations of the Main Sulphide Zone (MSZ), which are currently mined at the Ngezi, Unki, and Mimosa mines.

Near-surface oxidized MSZ ores have a large potential. Their total resources are in the range of 160–250 Mt; however, all previous attempts to extract the PGE from this ore type have proved uneconomic due to low PGE recoveries (<< 50 per cent) achieved by conventional metallurgical methods.

Within the ores of pristine, sulphide-bearing MSZ, the PGE are bimodally distributed. Platinum occurs mainly in the form of discrete platinum group mineral (PGM) grains (mainly bismuthotellurides, sulphides, and arsenides), whereas approximately 80 per cent of the Pd (and some Rh) is hosted in pentlandite.

Within the oxidized MSZ ores, the PGE are polymodally distributed. Whereas the arsenide- and sulphide-PGMs that make up approximately 25 per cent of the original Pt content of the ore largely remain stable (relict PGMs), the remaining PGMs are disintegrated. The base metal sulphides are destroyed, partly releasing their base metal and PGE contents, and are replaced by iron oxides or hydroxides. Unspecified amounts of the PGE are redistributed and either form secondary PGMs, are found in chemically and mineralogically ill-defined (Pt/Pd)-oxides or hydroxides, or in iron-hydroxides, Mn–Co-hydroxides, and in secondary silicates. The problematic processing of oxidized MSZ ores is attributable to their complex nature and polymodal distribution of the PGE, prohibiting a significant upgrading of the ores by conventional metallurgical methods.

Therefore, only bulk leaching methods are viable for ore treatment, and novel metallurgical methods have to be developed for the processing of these ores. Our ongoing work aims at locating the PGE in their mineralogical form in order to understand the mineralogical balance of the PGE in the ores and thereby facilitate the evaluation of metallurgical options for their recovery. A short overview on options and recent advances regarding the recovery of the PGE from oxidized ores is given.

Keywords
main sulphide zone, Great Dyke, Zimbabwe, oxidized ores, mineralogy, metallurgy.

Introduction

The Great Dyke of Zimbabwe constitutes the world's second largest reserve of platinum group elements (PGE) after the Bushveld Complex in neighbouring South Africa. Within the Great Dyke, economic concentrations of PGE are restricted to sulphide disseminations of the Main Sulphide Zone (MSZ). Currently, pristine sulphide-bearing MSZ ores are mined underground at the Ngezi, Unki, and Mimosa mines and are treated by conventional metallurgical practice (grinding, milling, flotation, smelting and matte production, chemical refining). Ngezi Mine milled 4 095 Mt of ore at a head grade of 3.56 g/t (5E+Au)§ in 2010, and platinum production in matte was 173 900 ounces (Impala Platinum, 2011). The Unki Platinum Mine is a 1 44 Mt/a operation, and equivalent refined platinum production was 51 600 ounces (Anglo American Platinum, 2011). Mimosa Mine milled 2 277 Mt of ore at a head grade of 3.86 g/t (5E + Au) and produced 101 000 ounces of platinum in concentrate (Impala Platinum, 2011). The 2011 production from the MSZ of the Great Dyke (340 000 oz.) is equivalent to about 5.2 per cent of the world production of platinum (Johnson Matthey, 2012).

Near-surface oxidized MSZ ores have a large potential; Prendergast (1988) estimated a resource of approximately 400 Mt of ore. A first effort to mine oxidized MSZ ores was undertaken at the Old Wedza mine (close to Mimosa Mine) between 1926 and 1928, and again at the Hartley Mine from late 1997 to 1999. However, all these attempts to extract the PGE from this ore type proved uneconomic

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§(5E + Au) = (ΣPt,Pd,Rh,Ir,Ru+Au)

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due to low PGE recoveries (<< 50 per cent) achieved by conventional metallurgical methods. At present, oxide ores of the MSZ and also of the Merensky Reef and the Platreef of the Bushveld Complex, are either left *in situ*, are stockpiled, or discarded as waste. Recent mining of surface ores of the UG2 Reef at e.g. Smokey Hills Mine in the eastern Bushveld and by Impala Platinum in the western Bushveld reportedly resulted in low PGE recoveries. However, oxidized PGE-bearing ores definitely represent an important resource that will be tapped in the near future.

The present contribution summarizes previous and ongoing work of our group on oxidized MSZ ores taken at the Hartley, Ngezi, Unki, and the Old Wedza/Mimosa mines (Figure 1). Vertical profiles across the MSZ and bulk samples were investigated and changes down-dip were followed. The geochemical and mineralogical studies pursue the (re)distribution of the PGE from the pristine sulphide-bearing ores into the supergene environment (oxidized ores).

The main aim is to locate the PGE in their mineralogical form in order to understand the mineralogical balance of the PGE in the ores and thereby facilitate the evaluation of metallurgical options for their recovery. Further, a new resource calculation based on mine data for the oxidized MSZ ores is presented, and an overview on options and recent advances regarding the recovery of the PGE from oxidized ores is given.

Geological setting

The Great Dyke layered intrusion is Archean (2575.4 ± 0.7 Ma; Oberthür *et al.*, 2002) in age. It is linear in shape and trends over 550 km NNE at a maximum width of about 11 km, and cuts Archean granites and greenstone belts of the Zimbabwe Craton (Figure 1). Stratigraphically, the layered series of the Great Dyke is divided into a lower Ultramafic Sequence and an upper Mafic Sequence. Economic concentrations of PGE, Ni, and Cu in the form of disseminations of mainly intercumulus sulphides are found in the Main Sulphide Zone (MSZ) hosted in pyroxenites, some metres below the transition from the Ultramafic to the Mafic Sequence (Wilson and Prendergast, 1989; Prendergast and Wilson, 1989). The MSZ is generally between 1.5 and 4 m wide. Pervasive oxidation of the sulphides often exceeds 30 m below surface in the Hartley open pits. In the Ngezi Mine area, the irregularly undulating boundary between the pervasively oxidized MSZ and ores showing incipient oxidation, i.e., containing relict sulphides, lies between 15 and 30 m below surface.

Samples and methods

Sampling in open pits and trenches showed that the oxidized ores comprise relatively competent rocks of light to dark brownish colour, which locally have a greenish or bluish staining caused by secondary Cu- and Ni-minerals (Figure 2). The grains of orthopyroxene making up the pyroxenites mostly show incipient alteration only, whereas the interstitial network is filled by iron hydroxides and brownish smectites. Vertical profiles and bulk samples of oxidized MSZ were taken in open pits at the Hartley Mine, from drill cores at the Ngezi Mine, and from trenches at the Unki and the Old Wedza mines.

Due to the fact that only small quantities of discrete platinum group minerals (PGMs) were found in polished sections of the oxidized samples, heavy mineral concentrates were prepared from a number of samples weighing between 1.1 and 1.7 kg. These were step-wise reduced in size using a RETSCH crusher at steps 8, 6, 4, 2, and 1 mm. After each step, the material <1 mm was sieved and collected. Finally, the total <1 mm material was transferred to a washing pan to concentrate the heavy mineral fraction. The concentrates
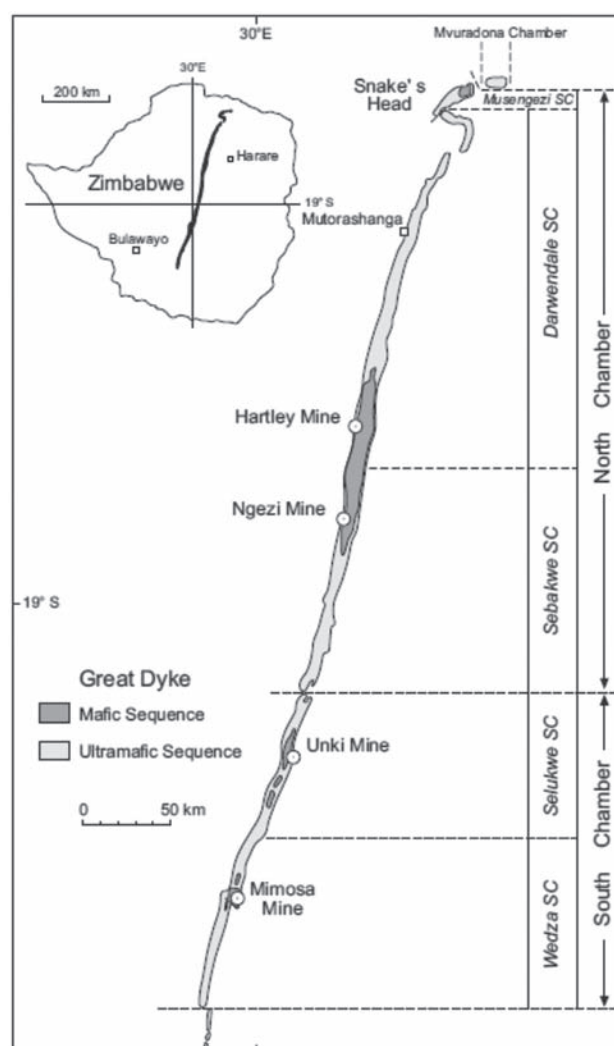

Figure 1—Generalized geology of the Great Dyke and its subdivision into chambers and sub-chambers (SC), after Wilson and Prendergast (1989). Also shown are the localities of platinum mines and prospects

Figure 2—Trial mining of MSZ oxide ores at Hartley Mine, ca. 1998, view south. Note flat dip of the oxidized MSZ (brownish, approx. 2 m wide layer) towards the east (left side of photo)

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were studied under a binocular microscope and grains of interest were extracted by hand picking and transferred onto sample holders. Additional polished sections were made from rock and concentrate samples and studied using a FEI Quanta 600 scanning electron microscope (SEM) equipped with an EDAX Genesis 6000 energy-dispersive analytical system (BGR). The whole-rock samples were analysed for major and trace elements by XRF (BGR), and PGE contents were determined by instrumental neutron activation analysis (INAA) after Ni-sulphide extraction (ACTLABS, Canada). The polished sections were investigated by reflected light microscopy and SEM/EDS. Mineral analyses were performed using the Camebax and the Cameca SX100 electron microprobes at the BGR. Both the routine analytical mode (20 kV, 20 nA, approx. 1 μm beam diameter and counting times 10–20 seconds on peak) and the trace element program (35 kV, 300 nA, approx. 5–10 μm beam diameter and counting times 600 seconds on peak) were employed.

Pristine Main Sulphide Zone

Geochemistry

Geochemical profiles across the pristine sulphide-bearing MSZ were studied extensively by our working group (e.g. Oberthür *et al.*, 2003a; Oberthür, 2002, 2011). Apart from minor variations of the MSZ metal profiles, all previous workers agree that the MSZ is characterized by a typical vertical pattern of base metal sulphide and PGE distribution (e.g., Prendergast, 1988; Prendergast and Wilson, 1989; Wilson, 2001; Oberthür, 2002, 2011). This pattern is charac-terized by a distinct zonation, also called 'offsets', i.e., a certain degree of decoupling, and separation of the respective element distribution patterns and peak concentrations, especially of Pd from Pt, and also of all PGE from the base metals. This has led to the subdivision of the MSZ into a lower PGE subzone and an upper BMS subzone, as proposed by Prendergast (1988, 1990), and the further subdivision of the PGE subzone into a lower (Pd>Pt) and an upper part (Pd<Pt). Wilson *et al.* (2000a, 2000b) showed that the MSZ is composed of a number of chemically distinct, consecutive layers, which they interpreted as resulting from minor emplacements of primitive magma into the chamber causing undersaturation of sulphur.

The typical vertical distribution pattern of the base metals and sulphur (BMS: Cu, Ni, and sulphur), Pt, and Pd is shown in Figure 3, which is a 2.70 m wide profile across the pristine MSZ from the Ngezi Mine (drill hole NG 36; MSZ at approx. 124 m depth of borehole). MSZ profiles from other localities show very similar patterns. Following the onset of sulphide mineralization (sulpur contents approximately 0.10 weight per cent S) at the bottom of the profile, the metal zonation within the MSZ is characterized by a number of consecutive peaks of the PGE, the base metals, and sulphur. From bottom to top, BMS contents increase continuously; the peak of Pd is reached first, whereas the peak of Pt follows further up in the sequence.

The main BMS peak either coincides with the Pt peak or is slightly displaced further up. From the BMS peak upwards, undulating values of Ni and Cu are observed, whereas the PGE contents drop to low levels.

PGMs and PGE carriers

The pyroxenites of the MSZ contain between 0.5 and 10 volume per cent of sulphides, mainly pyrrhotite, pentlandite, and chalcopyrite in about equal proportions, as well as subordinate pyrite. The sulphide grains and aggregates are up to several millimetres across, and occur mainly interstitial to grains of cumulus orthopyroxene and minor chromite, intercumulus clinopyroxene, plagioclase, and alteration products such as calcic amphibole, anthophyllite, magnetite, serpentine, talc, and chlorite. The PGMs are either included in pyrrhotite or chalcopyrite, rarely in pentlandite, or they occur at sulphide/sulphide or sulphide/silicate contacts, or within silicates. PGMs intergrown with pyrite are extremely rare.

The suite of PGMs found in the MSZ comprises (Pt,Pd)-bismuthotellurides (i.e., moncheite, maslovite, merenskyite, michenerite), sperrylite [PtAs$_2$], the (Pt,Pd)-sulphides cooperite [PtS] and braggite [(Pt,Pd,Ni)S], and some rarer phases (Prendergast, 1990; Coghill and Wilson, 1993; Evans *et al.*, 1994; Oberthür, 2002). In a summary encompassing all mining activities along the Great Dyke, Oberthür (2011) established that mineral proportions demonstrate the predominance of (Pt,Pd)-bismuthotellurides (50.1 per cent), followed by sperrylite (19.0 per cent), cooperite/braggite (8.5 per cent), the PGE-sulpharsenides hollingworthite [RhAsS], platarsite [PtAsS], irarsite [IrAsS], and ruarsite [RuAsS] (11.9 per cent), laurite [RuS$_2$], (5.0 per cent), Pt–Fe alloy (2.4 per cent), and some less common PGMs. The various PGMs are heterogeneously distributed within the MSZ sequence. Larger numbers of discrete PGMs are found from about 20 cm above to 60 cm below the Pt peak of the MSZ.
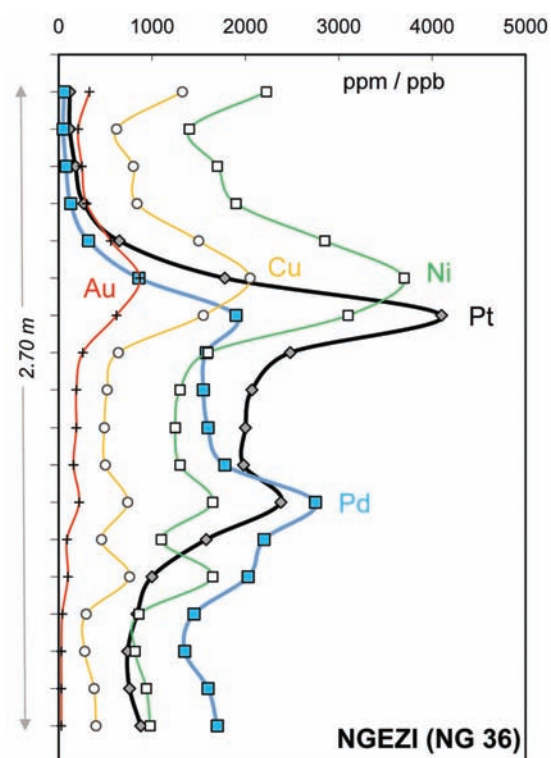

Figure 3—Geochemical profile (core NG 36) of selected elements (Cu and Ni in ppm; Pt, Pd, and Au in ppb) across the pristine MSZ at Ngezi Mine showing the zonation of the MSZ ('offsets')

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Further, regional trends of the PGM distribution are of note. The PGE occur mainly as bismuthotellurides and sulphides (together 77 per cent by number) in the north chamber, but preferentially combine with arsenic as sulfarsenides and arsenides (together 50 per cent) in the south chamber (Oberthür, 2011).

Grain sizes (apparent maximum diameters) of the PGMs range from < 5 to 50 μm in general, but may reach up to 480 μm in longest dimension (Oberthür 2002, 2011; Oberthür et al., 2008). The relatively small grain sizes of the PGMs observed in polished sections raised the question whether larger PGMs might be present. Therefore, one sample of pristine ore from the Pt peak of the MSZ, weighing about 1 kg, was treated by electric pulse disaggregation (EPD; Cabri et al., 2008). Altogether, 75 PGM grains larger than 50 μm were hand-picked from the heavy mineral fraction obtained. The observed maximum true diameters were 480 μm for (Pt,Pd) bismuthotellurides (moncheite), 85 μm for sperrylite, 195 μm for cooperite/braggite, and 300 μm for Pt-Fe alloy grains (Oberthür et al., 2008).

An additional point of interest is the proportions of PGE found in the different PGMs. Oberthür (2011) demonstrated that the PGM spectrum of the Great Dyke is Pt-dominated; about two-thirds of the PGMs are Pt-rich, followed by Pd (19.8 per cent) and Rh (6.6 per cent) compounds. The Ru and Ir minerals (laurite and irarsite) make up 3.7 per cent and 2 per cent respectively.

Consequently, at Pt/Pd ratios of pristine sulphide MSZ zone ores near unity (1.28 in the sample suite of Oberthür and Melcher, 2005), the mineralogical siting of the various PGE in the ores attracts some consideration also in view of the metallurgical treatment of the ores. If one assumes that most of the Pt is present in the form of individual PGMs, then about two-thirds of the Pd is not present in discrete PGMs but must be hosted in some other compound(s). This point will be followed up next.

Trace PGE contents in sulphides

Micro-PIXE studies (Oberthür et al., 1997) revealed that pentlandite from the lower PGE subzone of the MSZ at Hartley, Unki, and Mimosa mines has elevated contents of Pd (maximum value 2 236 ppm Pd) and Rh (max. 259 ppm Rh), and SIMS analysis showed that pyrite was a carrier of Pt (0.4–244 ppm, mean 35.5 ppm; n=37). Electron microprobe analysis revealed maximum contents of 2 506 ppm Pd and 562 ppm Rh in pentlandite (Oberthür et al., 2003a). Within the MSZ sequence, Pd contents in pentlandite appear to attain and stay at a plateau level of approximately 1000–1200 ppm Pd through most of the PGE subzone of the MSZ; maximum Pd contents in pentlandite recorded reached between 2000–3000 ppm Pd. Further up in the sequence, Pd contents in pentlandite drop to values below the detection limit of the method (about 40 ppm Pd) just before reaching the Pt peak. The data obtained underlines that most of the Pd is hosted by pentlandite in the lower and central parts of the PGE subzone (Oberthür et al., 2003a; Li et al., 2008; Oberthür, 2011).

Oxidized Main Sulphide Zone

Geochemistry

Geochemical profiles across the oxidized MSZ resemble those of pristine MSZ sequences with respect to their general shapes and Pt grades. However, the element distributions show wider dispersions and the different peaks appear less pronounced. In the profiles of oxidized MSZ, the offsets of Pd → Pt → base metals are often still discernible. In the example of a drill core from the Ngezi Mine (NRC 146), the Pt-peak is approximately 10 m below surface and weathering is observed down to 17 m (Figure 4); however, all peaks coincide in one sample, probably due to the large sample width of 50 cm. Compared to profiles of pristine MSZ (Figure 3), the conspicuous depletion of Pd relative to Pt is evident in Figure 4. Indeed, relative to Pt, a variable proportion of the Pd is 'missing' in the average data of the profiles of oxidized MSZ relative to those of the pristine sulphide-bearing MSZ. At the Hartley Mine, for example, average Pt/Pd ratios of 1.28 characterize pristine sulphide MSZ; pervasively oxidized MSZ ores have average Pt/Pd ratios of 2.43 (Figure 5). This result underlines and corroborates the findings of e.g. Wagner (1929) on the Merensky reef of the Bushveld Complex, and of Evans et al. (1994) on surface ores of the Great Dyke, that Pd is more mobile than Pt and is dispersed in the supergene environment. The present data from the Great Dyke demonstrates that relative to Pt, the concentration ranges of which are nearly identical in pristine and oxidized MSZ ores, about 50 per cent of the Pd is lost from the system.

On the other hand, cementation zones or supergene enrichment horizons in or around the oxidized MSZ ores were neither discovered during open pit mining at Hartley Mine nor in the course of extensive exploration drilling in the Ngezi project area (Brown, Wilhelmij, and Du Toit, pers. comm.).
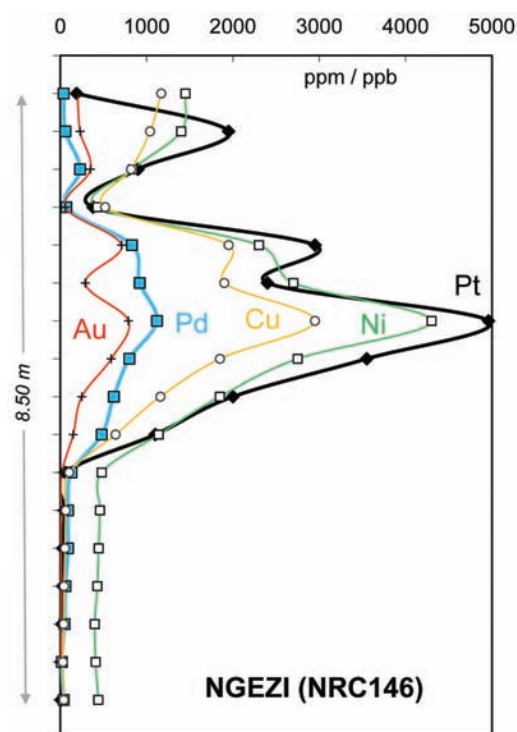

Figure 4—Profile NRC 146 across oxidized MSZ at Ngezi Mine (sample widths = 50 cm each) showing the distribution patterns of Cu and Ni (in ppm), Pt, Pd, and Au (in ppb)

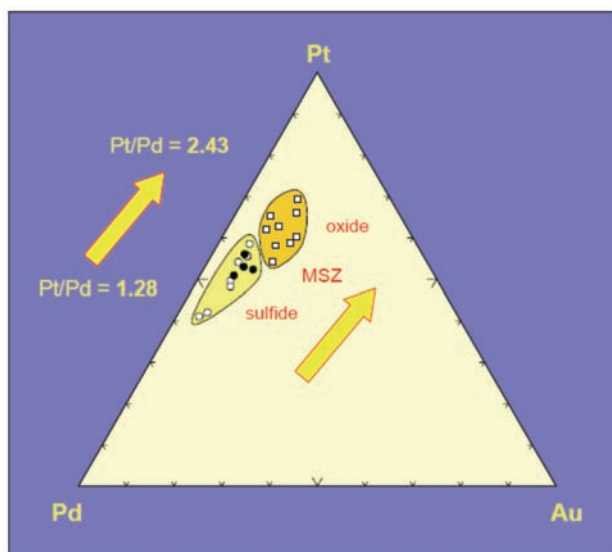# The oxidized ores of the Main Sulphide Zone, Great Dyke, Zimbabwe

Figure 5—Triangular plot of Pt, Pd, and Au contents of pristine sulphide MSZ and oxidized MSZ ores. ○ = pristine MSZ, official mine production or reserve data; ● = averages of profiles of pristine MSZ, own data; ▫ = □ averages of profiles of oxidized MSZ, own data

The obvious trend seen in Figures 4 and 5 is underlined by gain/loss calculations following equations given by Gresens (1967). At measured average specific gravities of 3.23 g/cm³ (pristine MSZ) and 3.05 g/cm³ (oxidized MSZ), and regarding Al_2O_3 (Al) as constant, the following principal gains and losses due to weathering are observed from pristine to oxidized MSZ (example from Hartley Mine; Figure 6).

Most major elements are relatively immobile; significant losses are observed for Na, K, and S (partial destruction of orthopyroxene, feldspar, phlogopite, and sulphides, respectively), combined with a large gain of LOI (formation of hydrous silicates, FeOOH). There is a conspicuous gain of Cu and Au, which may point to a certain supergene enrichment of these elements in the section studied. In general, PGE contents remain relatively constant except for Pd, which in this case shows a marked loss of 37 per cent.

PGMs and PGE carriers

Wagner (1929) reported sperrylite and cooperite in ores from the Old Wedza mine. Evans *et al.* (1994), Locmelis *et al.* (2010), Oberthür *et al.* (1999, 2000, 2002b, 2003b), Oberthür and Melcher (2005), Evans and Spratt (2000), and Evans (2002) studied oxidized MSZ ores and agreed that a large proportion of the primary PGE carriers, including PGMs, has been destroyed and that their PGE contents are now sited either in iron hydroxides, or in smectites, or occur as discrete 'PGE-oxides or hydroxides'.

The oxidized samples are characterized by equidimensional cumulus orthopyroxene and subordinate intercumulus clinopyroxene and plagioclase, all of which appear relatively unaltered. The former interstitial sulphides and sulphide aggregates of the pristine MSZ are totally decomposed to iron hydroxide clots that may often retain the original shape of the sulphides. An interstitial network of iron hydroxides and brownish smectites is commonly observed. Rare relict

sulphides, mainly pyrrhotite, are surrounded by rims of iron hydroxides. Although iron oxides/hydroxides may carry up to 5 weight per cent Ni and Cu respectively, they are not considered a major carrier of these elements in the oxidized MSZ. Instead, microprobe analyses showed that a large proportion of the Ni and Cu is hosted in chlorites and smectites. Relict primary sulphides are preserved only as small inclusions, usually <10 μm in size, in unaltered orthopyroxene grains.

Trace concentrations of Pd (usually some hundred ppm; and up to 6 500 ppm) and Pt (even up to 440 ppm) in pentlandite are in a grossly similar range as concentrations in unaltered samples of the MSZ. This indicates that a small proportion of the original PGE content is still 'in place'.

The inspection of numerous polished sections of oxidized MSZ samples yielded an unsatisfying amount of PGMs detected *in situ*. Therefore, heavy mineral concentrates were prepared and their study led to a certain quantification, particularly of relict PGMs and to the detection of a number of other PGE carriers. In the concentrates of the samples (starting sample weights between 1.1 and 1.7 kg; 50 cm samples on Pt peak each) from down-dip trending drill holes at the Ngezi Mine (MHR 194–197), 62 distinct PGM grains were detected with grain sizes between 25 μm and 60 μm. (Pt,Pd)-bismuthotellurides occur only in the deepest sample, which shows incipient oxidation only, but are non-existent (destroyed) in all samples nearer to surface. Sperrylite and cooperite/braggite, on the other hand, are stable PGMs in the supergene environment. This is a general rule in oxidized MSZ ores, as documented by our studies at the other localities of the MSZ.

Our complementary investigations of concentrates and polished sections by SEM and microprobe analysis revealed that the PGE show a polymodal distribution in the ores of oxidized MSZ, being present in a variety of different PGM and PGE carriers.

Relict PGMs and gold

Numerous discrete PGM grains were extracted from the concentrates. Sperrylite is most common (57.2 per cent), followed by cooperite/braggite (28.3 per cent) and Pt-Fe alloy
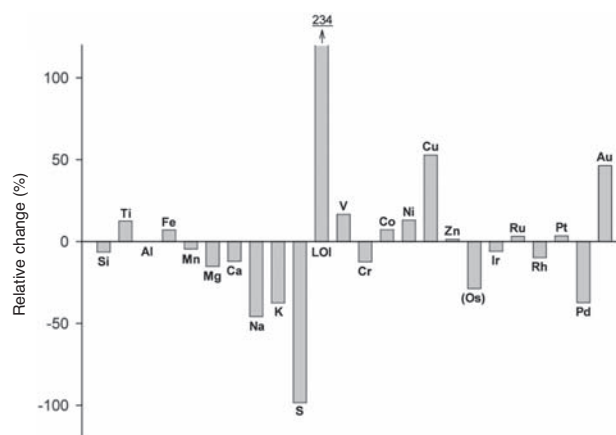

Figure 6—Relative gains and losses of selected elements (Al = constant) of the oxidized MSZ compared to pristine MSZ. Data from the Hartley Mine (Oberthür *et al.*, 2003a, b)

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grains (3.1 per cent). The ratio of sperrylite to cooperite/braggite is nearly identical to that of the pristine MSZ, indicating that these minerals are relicts of the pristine MSZ ores.

Sperrylite mostly shows idiomorphic crystal shapes (Figure 7a) with grain sizes up to about 100 μm. Cooperite/braggite grains, in contrast, are present as splinters of irregular shape or elongated grains with clean surfaces and grain sizes between <1 μm and 100 μm (Figure 7b). In general, the sperrylite and cooperite/braggite grains show no distinct features of alteration. Platinum-iron alloy grains are either compact, forming idiomorphic, cubic crystals, or they are porous. The porous grains of Pt–Fe alloy (close to Pt_3Fe in composition) probably represent replacements of other precursor PGMs of unknown chemical composition (see Figure 7f). Notably, Schneiderhöhn and Moritz (1939) showed texturally similar porous grains of 'native Pt' from oxidized Merensky Reef and proposed that these grains represent relicts of sperrylite or cooperite grains. Other rare relict PGMs comprise laurite [RuS_2] with grain sizes between 1 μm and 10 μm, and PGE-sulpharsenides (hollingworthite and irarsite with grain sizes < 5 μm). Relict (Pt,Pd)-bismuthotellurides (11.4 per cent) were found in only a few samples (MHR 197 and Adit A) from the Ngezi Mine, which show incipient alteration. Grain sizes of the PGMs (true maximum diameters, hand-picked grains from concentrates) range from approximately 50–400 μm.

As summarized in Table I, the oxide ore PGM assemblage thus strongly contrasts to that of the pristine MSZ ores, especially with respect to the proportion of (Pt,Pd)-bismuthotellurides. The fate of the Pd hosted in interstitial pentlandite is only partly known. With the exception of a few relict grains of Pd-rich (Pt,Pd)-bismuthotellurides and some secondary Pd-bearing phases, the ores of oxidized MSZ contain only discrete grains of Pt-rich PGMs (sperrylite, cooperite/braggite and rare Pt-Fe alloy grains). Notably, the proportion sperrylite to cooperite/braggite is nearly constant from pristine to oxidized MSZ ores, indicating the relative stability of these PGMs in the weathering environment.

Gold grains from concentrates of oxidized MSZ samples have various shapes (filigree, hooked, platy with crystal faces, e.g. Figure 7b) and far more resemble gold from primary deposits than rounded, detrital gold. Their sizes range from 40–300 μm, much larger than gold grains from pristine MSZ (usually <25 μm). The size distribution combined with their shapes indicates that the gold grains are products of remobilization processes and coagulated to larger grains in the oxidized MSZ, consistent with the relative gold enrichment in oxidized ores compared to pristine ores, as shown in Figure 6.

Secondary PGMs (neoformations)

In addition to unequivocally high-temperature magmatic PGMs, some PGE phases such as Pt–Fe alloy, zvyagintsevite, and ill-defined PGE oxides/hydroxides are considered secondary in origin based on textural and chemical reasons.

Zvyagintsevite [Pd_3Pb] occurs as euhedral to subhedral grains (less than 1 μm and 15 μm) in clusters and trails associated with Pt–Fe alloy and Pd-bearing goethite. Pt–Fe grains are abundant at Hartley Mine. The grains (<1 μm to 50 μm) are roundish or cubic and may be intergrown with
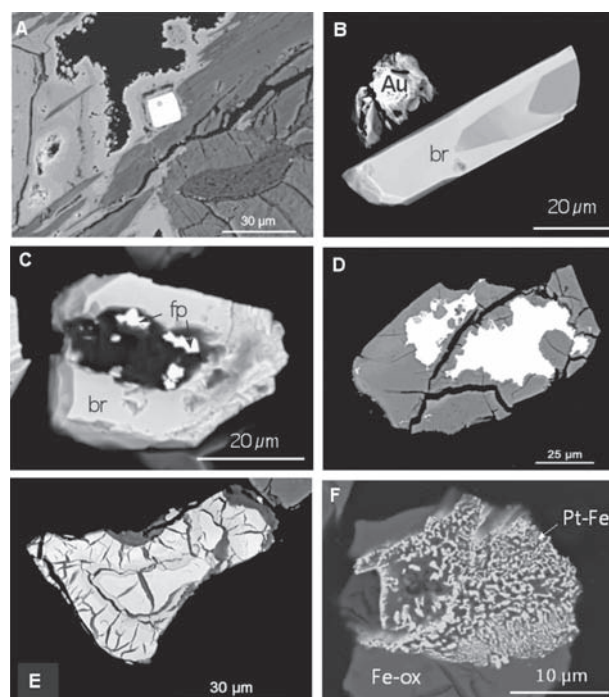

Figure 7—Backscatter electron (BSE) images of polished sections. A: Sperrylite grain (white) surrounded by iron-hydroxides (shades of light grey, to the left) and silicates (medium grey, right). Oxidized MSZ ore, Old Wedza mine. B: Zoned grain of braggite (br) and grain of gold (Au); composition of braggite ranges from [($Pt_{0.3}Pd_{0.5}Ni_{0.2}$)S] (darkest area) to [($Pt_{0.6}Pd_{0.2}Ni_{0.2}$)S] (brightest area). Hartley Mine open pit. C: Slightly corroded braggite (br) grain [($Pt_{0.5}Pd_{0.3}Ni_{0.2}$)S] with euhedral crystals of ferroan platinum (fp) [$Pt_{2.3}Fe$], in open space. Hartley Mine open pit. D: Grain of Pd-Bi-Cu-oxide (medium grey) with relict core of michenerite (white). Hartley mine open pit. E: Finely banded grain of PGE-oxide (composition ~[$Pt_{60}Pd_3Fe_{15}Cu_8Te_5Bi_3$]$_{\Sigma 94}$). Adit A, Ngezi Mine. F: Pt–Fe phase with spongy texture intergrown with iron-hydroxide. Ngezi

Table I

Proportions (by number of grains *n*, in %) of discrete PGMs in pristine MSZ ores as observed in polished sections, and in oxidized MSZ ores (concentrates)

Ore type →	Sulphide MSZ	Oxide MSZ
PGM (n) → type ↓ [%]	801	1293
(Pt,Pd)(Bi,Te)*	50.1	11.4
$PtAs_2$	19.0	57.2
(Pt,Pd)S	8.5	28.3
Pt and Pt-Fe alloys	2.4	3.1
PGE-AsS [+]	11.9	—
Others	8.7	x

(Pt,Pd)(Bi,Te)* = (Pt,Pd)-bismuthotellurides. (The number frequency of (Pt,Pd)-bismuthotellurides in oxide MSZ is considerably lower; 11.4% given includes some samples showing incipient oxidation only). (Pt,Pd)S = cooperite and braggite. PGE-AsS[+] = PGE-sulpharsenides. No estimate is given for the proportions of (Pt,Pd)-oxides/hydroxides and other PGE-bearing phases in the oxidized MSZ

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zvyagintsevite, goethite, and relict PGMs (Figure 7c). In the concentrates prepared by hydroseparation, moderately abundant porous Pt–Fe grains are intergrown with goethite (Figure 7f) and silicates (amphibole, chlorite, and smectite).

Although microprobe analysis of the porous, spongy-looking material is problematic, our data encompasses a range in compositions varying from Pt/Fe ratios of 0.5 to 2.63. The concentrations of other metals in the Pt-Fe grains may reach 7.6 weight per cent Co, 3.5 weight per cent Ni, 2.3 weight per cent Cu, and 1.5 weight per cent Pd. It is suspected that most of the porous material originally developed from or even represents Pt-(BM) oxides. The close association with Fe oxyhydroxides and secondary silicates attests to neoformation rather than replacement of a precursor phase.

The secondary PGE phases comprise very small (<5 μm) grains of poorly defined phases. Some of them may actually be oxides or hydroxides, others are alteration products of primary PGMs, or neoformations. 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 these PGM grains has a stoichiometric composition.

(Pt,Pd)-oxides and/or hydroxides

Evans *et al.* (1994) were the first to report 'Pt-alloys with low sums and weak reflectivity' from the Great Dyke. The presence of Pt and Pd in secondary PGE oxides or hydroxides in oxidized MSZ ores was substantiated later by various authors (e.g., Evans and Spratt, 2000; Oberthür *et al.*, 2003b; Oberthür and Melcher, 2005; Locmelis *et al.*, 2010). The PGE oxides/hydroxides are inconspicuous in reflected light; they are dark grey or brownish in colour and possess low reflectivity, often resembling Fe or Mn oxide/hydroxide phases. Some are characterized by internal textures such as concentric rings, alternating bands, and botryoidal textures (Figure 7e). Numerous small grains, commonly less than 10 μm in size, are dispersed in secondary minerals such as Fe and Mn oxyhydroxides, talc, chlorite, amphibole, and clay minerals (Figure 8e, 8f). The PGE oxides/hydroxides carry highly variable concentrations of Pt and/or Pd, Cu, Fe, O, and often contain Mn, Co, As, Sb, and S. Notable Bi and Te concentrations in some PGE oxide/hydroxide grains indicate that these phases formed directly from (Pt,Pd)-bismuthotellurides (Figure 7d), whereas the incipient alteration of some grains shows that the grain shapes of primary PGMs are often preserved during alteration.

The formation of mineralogically and chemically ill-defined 'PGE-oxides or hydroxides' was observed around relict, disintegrating (Pt,Pd)-bismuthotellurides (Figure 7d). These alteration phases are generally porous to various degrees and chemically inhomogeneous. They are characterized by relative losses of Bi and Te, an upgrade of Pt and/or Pd contents (e.g., from approx. 30–35 atomic per cent Pt in moncheite to 60–70 atomic per cent Pt in the alteration rims), and substantial gains in mainly Fe and Cu (up to a few weight per cent). The presence of oxygen in these phases was confirmed by electron microprobe analysis, underlining that these phases are oxides or hydroxides as also stated by Evans and Spratt (2000). In addition, individual, finely banded grains of (Pt,Pd)-oxides or hydroxide phases are also present (Figure 7e). Notably, some of these grains show

prominent shrinkage cracks indicating dewatering. Based on their stoichiometry and chemistry, a number of distinct groups of PGE-oxides/hydroxides were established by Locmelis *et al.* (2010).

PGE in iron hydroxides

Iron hydroxides form roundish aggregates, up to 0.5 mm in size, that are interstitial to orthopyroxene and other silicates and at least in part represent altered magmatic sulphide droplets (Figure 8a). They also occur as vein-like structures that crosscut the silicates. Both types of Fe hydroxides reveal characteristic layered and zoned internal textures. Iron hydroxides pseudomorphous after sulphide droplets may carry small grains of secondary PGMs (mainly Pt, but also relict PGMs, e.g., a Pd–S compound; see Figure 8b), whereas the vein-like hydroxides are barren of PGMs. Microprobe
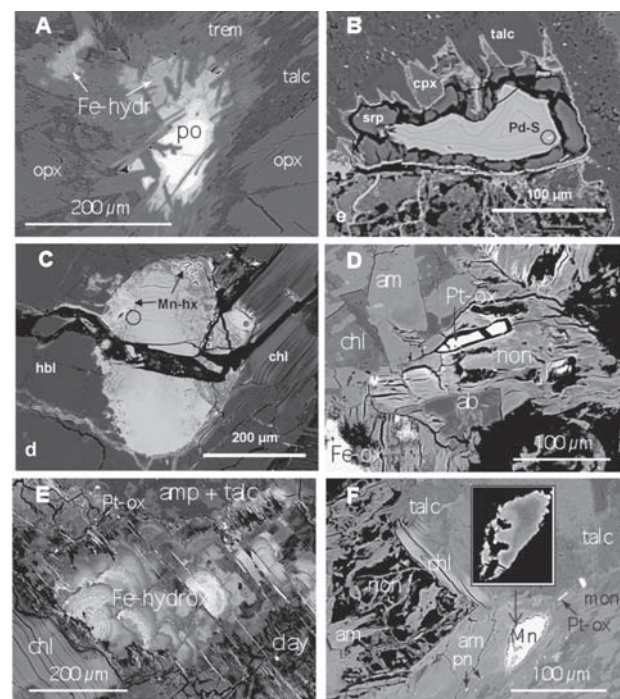

Figure 8—Backscatter electron (BSE) images of polished sections. A: Pyrrhotite (po) showing alteration to iron-rich weathering product (Fe-hydr), in matrix of orthopyroxene (opx), tremolite (trem), and talc. Hartley Mine open pit (HOP206). B: Fe-hydroxide with colloform texture and inclusion of Pd-S compound (circle) within a matrix of Fe-rich serpentine (srp), talc, and clinopyroxene (cpx). The Fe-hydroxide carries elevated contents of Ca, V, Cu and 30 ppm Pt. Old Wedza mine, AS 6828. C: Aggregate of iron-hydroxide enclosed by chlorite (chl) and hornblende (hbl). Areas of Mn-Co-hydroxide (Mn-hx) carry 150-400 ppm Pt. Note small PGM (Pt) in a crack (circle). Chlorite (chl) is Ni- and Cu-rich (up to 6 and 4 wt.%, respectively). Old Wedza mine, AS 5320a. D: Alteration assemblage of amphibole (am), chlorite (chl), albite (ab), nontronite (non), iron hydroxide (Fe-ox), and secondary Pt–(Bi–Fe–Cu) oxide (Pt-ox). Nontronite carries up to 0.36 wt.% Pt and 86 ppm Pd. Hartley open pit, HOP206. E: Aggregate of iron hydroxide (Fe-hydrox), crosscut by Fe hydroxide veinlets, in a matrix of Ni-rich chlorite (chl), nontronitic clay minerals (clay), as well as amphibole and talc (amp + talc). Note small grain of Pt–(Fe–Cu) oxide (Pt-ox; circled). Hartley Mine open pit, HOP207. F: Amphibole (am), Ni-rich chlorite (chl; 8–10 wt.% NiO), talc, (Pd-bearing) nontronite (non), pentlandite (pn), moncheite (mon, circled), Pt oxide (Pt-ox), and Mn–(Co–Ni–Cu–Fe) hydroxide (Mn) carrying up to 1.7 wt.% Pt; internal texture of the Mn oxide is outlined in the inset. Hartley Mine open pit, HOP207

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analyses reveal a distinct suite of minor and trace elements in the iron hydroxides. Most notable are highly variable concentrations of SiO_2 (5–25 weight per cent), correlating remarkably with V_2O_5 (up to 0.5 weight per cent), MgO (up to 0.8 weight per cent), CaO (up to 2 weight per cent), and CuO (up to 2.5 weight per cent). Additional significant impurities are Al_2O_3 (up to 4 weight per cent), NiO (up to 3 weight per cent), and Cl (up to 0.3 weight per cent). The extraordinary relationship of presumably silicate-bound elements and metals corroborates that mixtures of iron hydroxide with silica-rich material are present, probably amorphous or very fine-grained clayey substances. Microprobe analyses show that the iron hydroxide aggregates may carry up to 3 600 ppm Pt and 3 100 ppm Pd. In the iron hydroxide veinlets, however, the Pt and Pd concentrations are invariably below the detection limits (approx. 25-40 ppm) of the electron microprobe.

PGE in manganese hydroxides

Occasionally, iron hydroxides pseudomorphous after sulphides are veined by bluish/grey Mn–Co–Ni–Cu-oxides/hydroxides with highly variable compositions (30 to 56 weight per cent MnO_2, 2– 31 weight per cent Fe_2O_3) and appreciable amounts of cobalt (7–18 weight per cent Co), nickel (8–13 weight per cent Ni), and copper (4–23 weight per cent Cu). Manganese oxides/hydroxides occur mainly as roundish aggregates intergrown with Fe oxides/hydroxides (Figure 8c). Grain sizes are usually between 50 and 100 μm. The Mn oxides/hydroxides are significant carriers of Pt (up to 1.6 weight per cent) and Pd (up to 157 ppm).

PGE in clay minerals and chlorites

Secondary silicates are defined here as hydrothermal and/or supergene serpentine minerals, smectite (nontronite), and Ni–Cu-bearing chlorite-like phases. Smectite and chlorite carry up to several weight per cent Ni and Cu and occasionally PGE. At Hartley Mine, nontronite forms fine-grained, often porous aggregates of irregular shape (Figures 8d, 8f). Microprobe analyses detected up to approximately 2 weight per cent CuO, and high contents of Pt (up to 1 800 ppm) and Pd (up to 1 600 ppm). Apart from nontronite, mixtures of at least two clay minerals were found, consisting mainly of SiO_2 (26.7– 46.4 weight per cent) and Fe_2O_3 (19.7–42.4 weight per cent). These aggregates host notable amounts of Pd (up to 4 000 ppm) and Pt (up to 700 ppm Pt).

Summary of PGM and PGE carriers in the oxidized MSZ

In the oxidized MSZ, PGE occur in different modes:
  (1) As relict primary PGMs (mainly sperrylite, cooperite, and braggite)
  (2) In solid solution in relict sulphides, dominantly Pd in pentlandite
  (3) As secondary PGM neoformations (e.g., Pt–Fe alloy and zvyagintsevite)
  (4) As PGE oxides/hydroxides that either replace primary PGMs or represent neoformations
  (5) Hosted in secondary oxides/hydroxides and silicates like iron oxides/hydroxides, manganese oxides/hydroxides, and phyllosilicates.

The proportions of the various PGE-bearing phases vary considerably from mine to mine and between samples, probably reflecting both variations in primary ore mineralogy and depth within the weathering profile. Locmelis *et al.* (2010) attempted mass balance calculations using particle counts in a limited number of polished sections from different samples of the oxidized MSZ at Hartley Mine. These authors found that relict pentlandite contributes less than 1 per cent of the Pd to the whole-rock composition, whereas the major proportion of Pd is hosted by primary and secondary PGMs (55–92 per cent), and oxides/hydroxides (8–45 per cent). Platinum shows a nearly identical, though highly variable, distribution; 33–96 per cent of Pt is hosted in PGMs and 4–67 per cent in oxides/hydroxides. In conclusion, at the current stage of the investigation, mass balance calculations appear to be somewhat premature due to the extreme unpredictability of the mineralogical siting of the PGE in the ores, varying within the MSZ, down-dip, and from local to regional scale.

Resources of oxidized MSZ ores

Prendergast (1988) estimated a resource of 389 Mt of near-surface oxidized MSZ ores for the whole Great Dyke, based on total outcrop length of the MSZ, a depth of 30 m to unweathered rock, and 1 m thickness of the mineralized horizon (Prendergast, pers. comm. 2012). Our present recalculation is preliminary in character due to the fact that prospecting and mining leases for platinum on the Great Dyke have been granted to at least seven companies, and these projects are in different stages of progress. As published data of the various mining companies are rare, some estimates were brought in on the remaining properties.

In the Snake's Head area (north end of the Great Dyke, Figure 1), African Consolidated Resources (ACR) is in an early exploration phase and therefore, the company cannot outline any identified zones of oxidized PGE mineralization on either the MSZ or the LSZ (Lower Sulphide Zone), although the mineralization has been followed for at least 30 km along strike (Kellow, 2011).

The resources of oxide ores of the whole Hartley Complex of the north chamber (from north of Hartley Mine to the southern tip south of Ngezi Mine; approx. 130 km N-S) were evaluated by Zimplats in 2005. The mineral resource (indicated and inferred) stated amounts to 138 Mt at 3.4 g/t (Pt+Pd+Rh+Au) and a mining width of 2.3 m. The average depth of oxide ore was 19.9 m (standard deviation 27.9 m); however, locally a depth of oxidation down to approximately 100 m was observed. After the release of a significant portion of ground to the Zimbabwe Government in 2006, the most recent estimates for the remaining Ngezi property of Zimplats are 80 Mt of oxide ores (indicated and inferred) at a grade of 3.61 g/t (Pt+Pd+Rh+Au) and a mining width of 2.2 – 2.5 m (Impala Platinum, 2011). For the Unki Platinum Mine, Anglo American Platinum (2011) gives a total mineral resource (including reserves) of 123.4 Mt. No separate figures for oxide ores are given, and therefore, we estimate that the oxide ores comprise about 10 per cent of the total tonnage, i.e. 12.3 Mt. For the Mimosa concession (North and South Hill), Impala Platinum (2011) presented an inferred oxide resource of 13.9 Mt at a grade of 3.39 – 3.58 g/t (Pt+Pd+Rh+Au) and a mining width of 2.00 m. In a cautious

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summary, oxide ore resources (measured, indicated, and inferred) of the Great Dyke amount to a minimum of 164.2 Mt and, taking into account the unknown areas, may reach about 250 Mt. At the current prices of the PGE, the value of platinum alone in these ores would amount to about US$10–20 billion. Indeed, this ore type is a highly promising treasure chest to be opened in the near future, and this also applies for oxidized PGE ores of the Bushveld Complex (Merensky Reef, UG2 chromitite, Platreef), as described for the UG2 by Hey (1999), or Kapalagulu in Tanzania.

Metallurgical implications

Recovered grades of Pt and Pd from pristine MSZ ores were 86 per cent and 90 per cent, respectively, at Hartley Mine (Rule, 1998), and are slightly lower at Mimosa mine. Prendergast (1990) stated that all early attempts at processing oxidized MSZ ores resulted in Pt recoveries below 50 per cent by either gravity concentration or flotation. Metallurgical test work performed by Zimplats on pervasively oxidized MSZ ores (from surface down to approximately 10–15 m) from the Ngezi Mine achieved recoveries of only 15–30 per cent. These results indicate that probably only relict sperrylite and cooperite/braggite grains were recovered, as also suggested by the present mineralogical study. Evidently, novel methods have to be developed for the processing of oxidized MSZ ores. Prendergast (1990) and Evans (2002) have highlighted possible pyrometallurgical and hydrometallurgical methods capable of treating the ores and extracting the PGE.

However, in case of bulk treatment of the ores, conventional methods as discussed by Prendergast (1990) and Evans (2002) would require large-scale technical equipment or expensive chemicals, and are uneconomic at present. Bulatovic (2003) reported poor recovery of PGE from oxidized ores with conventional reagent schemes. By using various clay and gangue depressants/dispersants and PGE collectors during flotation, concentrate grades and recoveries were improved significantly. In general, however, some process of preconcentration of the PGE would be desirable to reduce the ore volumes to be processed.

Therefore, laboratory experiments were, and are still being, conducted at and on behalf of the BGR (Locmelis *et al.*, 2010) using different techniques to separate and upgrade PGM and PGE carriers from oxidized MSZ ore. The work revealed that the PGE are concentrated into the smaller grain size fractions compared to the coarser fractions by a factor of approximately 2. The highest concentrations of PGE reported to separates of the magnetic fraction. However, the volumes obtained by these techniques are too low to produce saleable concentrates. Furthermore, during electric pulse disintegration and hydroseparation, Pt and Pd fractionate and platinum becomes successively enriched in the fine fractions. However, all our test work showed (Locmelis *et al.*, 2010) that the volumetrically most important coarse fractions still carry almost bulk-rock PGE concentrations. Obviously, the complex nature and polymodal distribution of the PGE in the oxidized MSZ ores does not permit significant upgrading of the ores by conventional metallurgical methods (Becker and Wotruba, 2008). Therefore, only bulk leaching methods are viable and need to be developed for the treatment of these ores. Current studies at and on behalf of the BGR concen-

trates on single- and multi-step hydrometallurgical processes involving acids and various organic chelating agents (Bau *et al.*, 2012, Mohwinkel *et al.*, 2012). Although this laboratory-scale work is still in a pilot phase, some promising results with Pt recoveries > 50 per cent have been achieved already.

Summary and conclusions

The fundamental mineralogical and geochemical trends emerging from the oxidation of the pristine MSZ ores and observed in our previous and ongoing studies are summarized in Figures 9 and 10. Vertical profiles across oxidized MSZ showed that the general metal distribution and zonation patterns ('offset') of the pristine MSZ are grossly preserved. However, at similar Pt grades, up to about 50 per cent of the Pd is lost from the system during weathering, probably dispersed and transported away by acidic surface waters, as shown by the increasing Pt/Pd ratios from pristine (average 1.28) to oxidized (average 2.43) MSZ. This finding is corroborated by mass balance calculations, which highlight
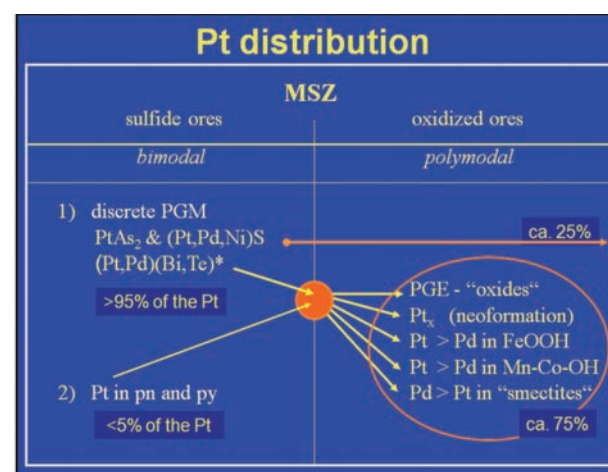

Figure 9—Summary graph showing trends of preservation of PGMs and redistribution of Pt from pristine to oxidized MSZ. (Pt,Pd)(Bi,Te)* = (Pt,Pd)-bismuthotellurides
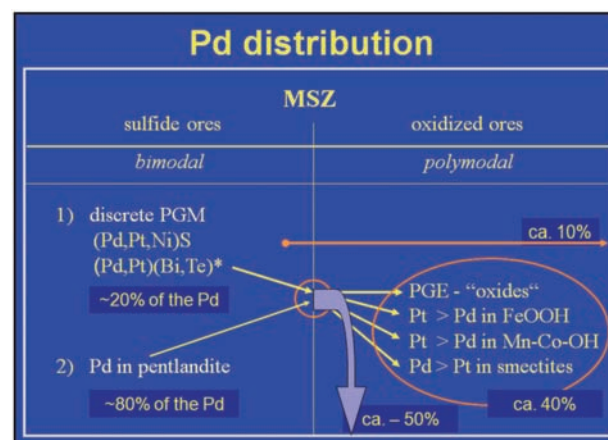

Figure 10—Summary graph showing trends of preservation of PGMs and redistribution of Pd from pristine to oxidized MSZ. (Pt,Pd)(Bi,Te)* = (Pt,Pd)-bismuthotellurides

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the fact that Pd (mainly released from disintegrating sulphides) is more mobile than Pt and is partly dispersed and removed, probably in solution (ground- and/or surface waters), in the exogenic environment.

Within the ores of pristine, sulphide-bearing MSZ, the PGE are bimodally distributed. Platinum occurs mainly in the form of discrete PGM grains (mainly bismuthotellurides, sulphides and arsenides), whereas approximately 80 per cent of the Pd (and some Rh) is hosted in pentlandite.

Within the ores of oxidized MSZ, the PGE are polymodally distributed. Major changes during weathering, from pristine to oxidized MSZ ores comprise the following. Sperrylite and cooperite/braggite grains, which make up about 25 per cent of the original Pt content of the ore, largely remain stable as relict PGMs, whereas the (Pt,Pd)-bismuthotellurides are disintegrated.

The base metal sulphides are destroyed during weathering, partly releasing their base metal and PGE contents, and are replaced by iron oxides or hydroxides. Largely unspecified amounts of the PGE are redistributed and are found either as secondary PGMs, in chemically and mineralogically ill-defined (Pt/Pd)-oxides or hydroxides (replacement and neoformation), in iron-hydroxides, in Mn–Co-hydroxides, and in secondary silicates (adsorbed or lattice-bound). Our ongoing work concentrates on the chemical and mineralogical characterization of these phases, and the establishment of their mineralogical balance in the ores.

Our estimate of the resources of oxidized MSZ ores of the Great Dyke is in the range of approximately 160–250 Mt. The current value of platinum alone in these ores (at 1.5 g/t recovered) would amount to approximately US$10–20 billion. Indeed, this ore type is a highly promising treasure chest that needs to be opened in the near future.

The problem encountered lies in the metallurgical processing of oxidized MSZ ores. The low platinum recoveries (< 30–50 per cent) achieved by either gravity concentration or flotation are uneconomic. Obviously, the complex nature and polymodal distribution of the PGE in the oxidized MSZ ores does not permit significant upgrading of the ores by conventional metallurgical methods. Therefore, only bulk leaching methods are viable for the treatment of these ores. Indeed, novel methods have to be developed for the processing of oxidized MSZ ores.

Our current work on the laboratory scale uses single and multi-step hydrometallurgical processes involving acids and various organic complexing ligands. Some promising results with Pt recoveries >50 per cent have been obtained already. In addition, we have started investigations into the chemical and mineralogical behaviour of the PGE in weathered Bushveld ores, concentrating primarily on the Platreef.

Acknowledgements

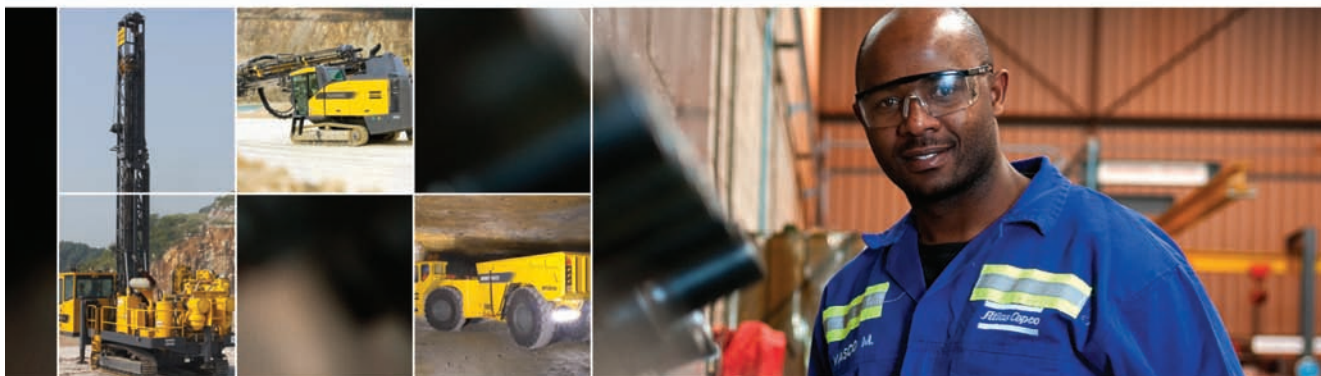## References

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