

Local Variations and Regional Trends in PGE Geochemistry and Mineralogy in the Main Sulfide Zone of the Great Dyke, Zimbabwe

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Introduction

The Great Dyke of Zimbabwe constitutes the world's second largest reserve of PGE after the Bushveld Complex in neighbouring South Africa. In the Great Dyke, economic concentrations of PGE are restricted to sulfide disseminations of the Main Sulfide Zone (MSZ). The present work is based on the study of samples from new exposures of economic grade primary ores of the MSZ created in the course of exploration and mining at Hartley, Mhondoro, Ngezi, Unki and Mimosa (Fig. 1). New findings are reported on the geochemical distribution and the mineralogical siting of the PGE, the mineralogy of the PGM, and the regional variations of these parameters. The findings are discussed in view of the contrasting "magmatic sulfide" and "hydrothermal fluid" genetic models.

Geologic Setting

The 2575.4 ± 0.7 Ma Great Dyke layered intrusion has a linear shape and strikes over 550 km NNE at a maximum width of about 11 km, cutting Archean granites and greenstone belts of the Zimbabwe craton. Stratigraphically, it is divided into a lower Ultramafic Sequence of dunites, harzburgites, olivine bronzitites and pyroxenites, together with narrow layers of chromitite, and an upper Mafic Sequence mainly consisting of plagioclase-rich rocks (norites, gabbro-norites, olivine gabbros). Economic concentrations of PGE, Ni and Cu in the form of disseminated sulfides occur some meters below the transition from the Ultramafic to the Mafic Sequence, in the several meters thick "Main Sulfide Zone", in pyroxenitic host rocks.

Samples and Methods

Twenty-one vertical profiles across the MSZ, between 1.5 and 5 m long, were taken from drill cores (Hartley, Mhondoro, Ngezi, Unki) or were cut underground (Hartley, Mimosa). The whole rock samples were analysed by XRF and ICP-MS. PGE contents were determined by INAA after Ni-sulfide extraction. Polished sections were investigated by reflected light microscopy, XRD, SEM/EDX, and electron microprobe.

Geochemical Distribution of PGE in the MSZ

Our study of 21 MSZ sections corroborated that, apart from minor variations, the MSZ is characterized by a typical vertical pattern of base metal sulfide and PGE distribution as known from the work of e.g. Prendergast (1988), Prendergast and Wilson (1989), and Wilson (2001). This pattern is characterized by "offsets", i.e. a certain degree of decoupling, and separation of the respective element distribution patterns and peak concentrations, namely of Pd from Pt, and also of all PGE from the base metals. Our data also confirm the subdivision of the MSZ into a lower PGE subzone and an upper BMS subzone, and the further subdivision of the PGE subzone into a lower (Pd>Pt) and an upper part (Pd<Pt).

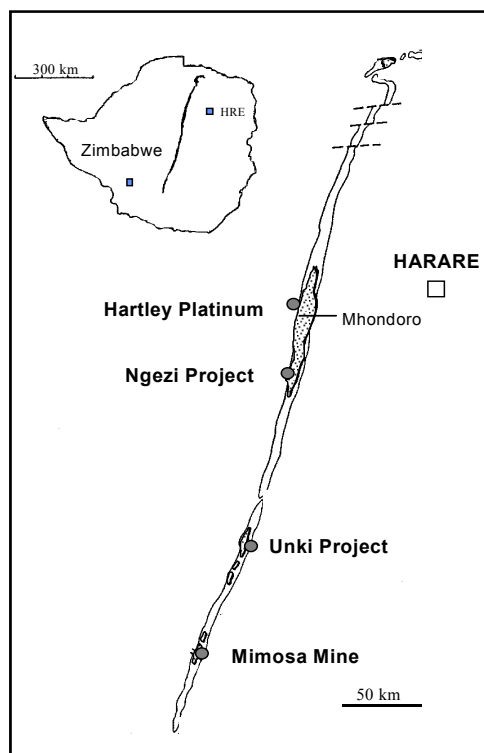


Figure 1. Sketch of the Great Dyke showing the localities of mines and prospects mentioned in the text.

The vertical distributions of the base metals and sulfur (BMS; Cu, Ni, S), Pt and Pd are shown in Fig. 2, which is an idealized profile across the MSZ, about 3 metres wide, mainly based on data from Hartley mine. Notable are three variably pronounced peaks in the PGE subzone. (i) PGE-1 close to the base is a broader area characterized by slightly increasing PGE contents at low levels of base metals and sulfur, Pd > Pt, and low contents of Σ PPGE relative to Σ IPGE (Σ PPGE/ Σ IPGE ratios are ca. 9 at PGE-1 compared to ca. 20 at positions PGE-2 and PGE-3 at Hartley mine). Further upward, Σ IPGE remain at nearly constant levels, Pd values exceed those of Pt, and the base metal and sulfur contents continue to increase slightly. (ii) At position PGE-2, the peak of Pd is reached, which coincides with a subsidiary peak of Pt and slightly elevated BMS contents. (iii) PGE-3 is the peak of Pt, distinctly offset from the peak of Pd. At this position, shortly before or overlapping with the strongest BMS peak, Pd shows a subsidiary peak and Rh, Ru, Ir and Os reach maxima. The elevated contents of Σ IPGE relative to Σ PPGE (low Σ PPGE/ Σ IPGE ratios) in the PGE-1 area indicate a certain offset of the IPGE group from Pt and Pd. This justifies a further refinement of the structure of the PGE subzone (basal, centre and top part; indicated by the peaks PGE-1, PGE-2 and PGE-3).

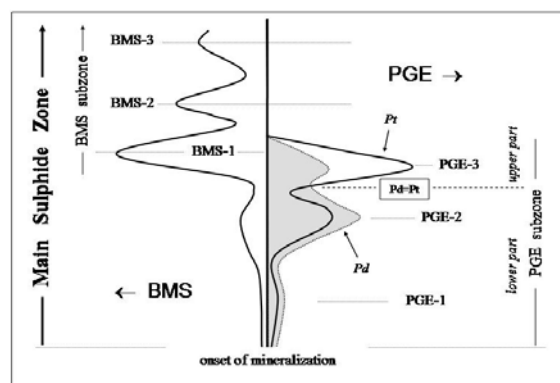


Figure 2. Sketch of key features of element distributions and subdivision of the MSZ. BMS = base metal sulfides.

Chondrite-normalized patterns of the averages of the PGE subzone of the MSZ show steep upward trending curves from Os to Pd (Fig. 3). This type of pattern is regarded typical for PGE mineralization produced by magmatic scavenging of PGE through segregating sulfides. The tight array displayed by the various MSZ localities indicates consistent contents and proportions of PGE within the MSZ over wide areas.

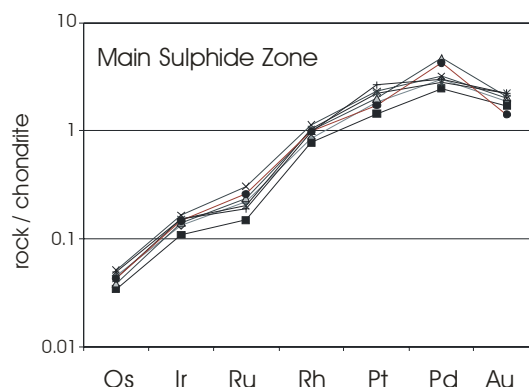


Figure 3. C-1 normalized average PGE contents of the MSZ (PGE subzone) from various Great Dyke localities.

Platinum-Group Minerals (PGM)

The pyroxenites of the MSZ contain between 0.5 and 10 vol% of sulfides – pyrrhotite, pentlandite, chalcopyrite and subordinate pyrite – which mainly occur interstitially to cumulus orthopyroxene. The PGM are usually included in pyrrhotite or chalcopyrite, rarely in pentlandite, or they occur at sulfide/sulfide or sulfide/silicate contacts or within silicates. PGM intergrown with pyrite are extremely rare. PGM grain sizes (apparent maximum diameters) range from < 5 to 50 μ m in general, but may reach up to 373 μ m in the longest dimension.

Altogether, 801 grains of PGM were analyzed by electron microprobe. The suite of PGM (proportions by number) comprises (Pt,Pd)-bismuthotellurides, mainly moncheite, maslovite, merenskyite, and michenerite (50.1%), followed by sperrylite (19%), the PGE-sulfarsenides hollingworthite, platarsite, irarsite and ruarsite (11.9%), the (Pt,Pd)-sulfides cooperite and braggite (8.5%), laurite (5.0%), and some rarer phases.

The various PGM are heterogeneously distributed within the MSZ sequence. At Hartley for example, sperrylite occurs throughout the PGE subzone of the MSZ, whereas cooperite/braggite only occur in samples from and below the Pt peak. The (Pt,Pd)-bismuthotellurides concentrate in the upper portion of the PGE subzone of the MSZ only, mainly in the regions around PGE-3 and BMS-1.

Trace PGE Contents in Sulfides

Micro-PIXE studies had shown that pentlandite from the lower PGE subzone of the MSZ at Hartley, Unki and Mimosa had elevated contents of Pd (maximum value 2,236 ppm Pd), and Rh (max. 259 ppm Rh), and SIMS analysis revealed that pyrite was a carrier of Pt (0.4-244, mean 35.5 ppm; n=37). Electron microprobe

analysis using the CSIRO-Trace program was performed on pentlandite from Hartley, Unki and Mimosa. Maximum Pd and Rh contents measured are 2,506 ppm Pd and 562 ppm Rh. In the example below (Fig. 4; core CD-02, Hartley mine), Pd contents in pentlandite appear to attain and stay at a plateau level of ca. 1,200 ppm Pd through most of the PGE subzone of the MSZ (maximum average value = 1,379 ppm Pd), interrupted by a return to lower values (\approx 300 ppm Pd) between PGE-1 and PGE-2. Further up-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 (PGE-3). The data therefore underline that most of the Pd is generally hosted by pentlandite in the lower and central parts of the PGE subzone.

Figure 5 summarizes the major geochemical and mineralogical variations and trends in the MSZ. Note the elevated contents of Pd in pentlandite in the lower part of the PGE subzone, overlapping distributions of the various PGM groups in the profile, and the preferred concentration of laurite in the basal part of the PGE subzone. Gold and the tellurides of Bi, Ag, Ni and Pb mainly occur in the transition from the PGE to the BMS subzone of the MSZ. Changes in pyrrhotite compositions, and the presence of pyrite in the upper part of the PGE subzone and the BMS subzone indicate increasing fS_2 up sequence.

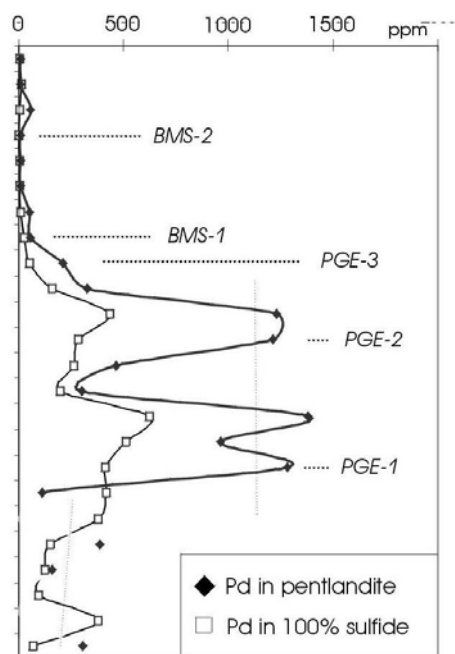


Figure 4. Vertical distribution of Pd in pentlandite (ppm) analyzed by electron microprobe, and Pd in 100% sulfide (ppm) calculated from whole rock data.

Regional Variations in PGM Proportions

Major regional differences were observed in PGM proportions (Table 1) and grain sizes. The MSZ samples of the North Chamber (Hartley + Mhondoro + Ngezi) have higher proportions of (Pt,Pd)-bismuthotellurides (63.8%) and cooperite plus braggite (12.7%), and lower proportions of sperrylite (11.0%), PGE-sulfarsenides (2.4%), and laurite (1.7%) compared to those of the South Chamber. The respective South Chamber (Unki + Mimosa) values are: (Pt,Pd)-bismuthotellurides (35.2%), cooperite/braggite (3.9%), sperrylite (27.6%), PGE-sulfarsenides (22.1%) and laurite (8.6%). The different PGM proportions and accompanying different apparent average PGM grain sizes (39 μ m in the North Chamber versus 18.5 μ m in the South Chamber) must be considered in the metallurgical treatment of the ores.

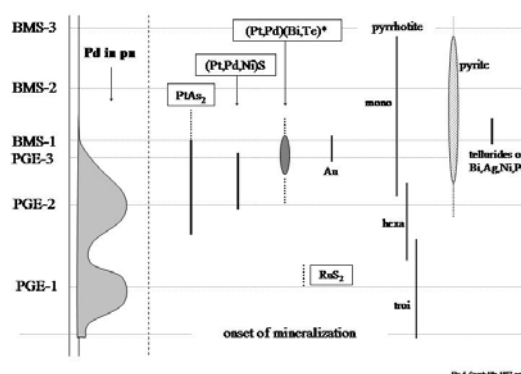


Figure 5. Summary of key geochemical and mineralogical features of MSZ profiles as exemplified at Hartley mine. Pd in pn = Pd contents in pentlandite. (Pt,Pd)(Bi,Te)* = (Pt,Pd)-bismuthotellurides. Pyrrhotite: mono = monoclinic; hexa = hexagonal; troi = troilite.

Table 1. Comparison of PGM proportions by number of various MSZ localities. (Pt,Pd)(Bi,Te)* = (Pt,Pd)-bismuthotellurides. PGE-AsS⁺ = PGE-sulfarsenides.

locality →	Hartley	Mhondoro	Ngezi	Unki	Mimosa
PGM (n) →	181	43	199	250	134
type [%] ↓					
(Pt,Pd)(Bi,Te)*	71	58	60	39	28
PtAs ₂	11	9	11	28	26
(Pt,Pd)S	11	5	16	4	3
PGE-AsS ⁺	2	4	2	16	33
Pt-Fe alloys	1	11	6	—	—
others	4	11	5	12	13

Discussion and Conclusions

The combination of geochemical and mineralogical data suggests the following model for the formation of the PGM in relation to PGE distributions. It is postulated that all PGE were primarily scavenged by sulfide in the magmatic stage due to their high partition coefficients in favour of sulfide. The metal profiles indicate sulfide accumulation in a number of distinct successive layers, each with its own geochemical characteristics. The general trend within the MSZ is one of upward increases in $\Sigma\text{PPGE} / \Sigma\text{IPGE}$, Pt/Pd and Cu/Ni ratios, as well as $f\text{S}_2$. Apparently, the various elements were extracted from the magma in consecutive batches which show successive enrichments of the chalcophile elements according to their apparent D values (in case of the MSZ, $D_{\text{Pd}} > D_{\text{Pt}}$, for example). Upon cooling, in the subliquidus stage, the PGE-bearing sulfide droplets recrystallized to form aggregates of pyrrhotite, pentlandite, chalcopyrite and some pyrite. The development down-temperature was accompanied by continuous subsolidus annealing of the sulfides and their internal crystal ordering. Ballhaus and Ryan (1995) demonstrated that Pd and Rh are accommodated within the crystal lattice of pentlandite down to low temperatures, a finding corroborated by our direct measurements of these elements in pentlandite. In contrast, Pt is incompatible with any of the sulfides forming (except for low levels in pyrite) and was thus expelled from their crystal lattices. Pt released from sulfides during the annealing process readily reacted with As, Bi and Te due to the high affinity of these metalloids for Pt, to form sperrylite and bismuthotellurides. Although occasional intergrowths of cooperite/braggite and (Pt,Pd)-bismuthotellurides indicate that these mineral groups do not exclude each other, their distribution patterns within the MSZ are antipathetic.

Furthermore, the high concentrations of Bi and Te combined with the availability of Bi and Te at the position of the main BMS peak (BMS-1) led to a pronounced competition also for Pd. It is postulated that a chemical gradient existed between sulfide-bound Pd in pentlandite and Te and Bi which favoured the formation of Pd-rich bismuthotellurides. It is assumed that these reactions largely took place under isochemical conditions on a sample scale, and interstitial magmatic-hydrothermal fluids probably aided the mass transfer. It can also be speculated that a general upward gradient within the MSZ (peak concentrations of reactive Te and Bi at BMS-1) led to a certain chromatographic control, which may have supported the small-scale redistribution, the separation of certain metals, and the reactions that

formed the PGM in a vapor-refining zone as fluids evolved during solidification of the cumulus pile (Boudreau and Meurer 1999). Furthermore, the elevated $\Sigma\text{IPGE} / \Sigma\text{PPGE}$ ratios at the base of the MSZ, closely following the onset of mineralization, are conspicuous. They may be explained by the preferential extraction of IPGE first, probably due to the formation of laurite, as indicated by elevated proportions of laurite in the basal part of the MSZ.

PGE distribution patterns and average contents in the MSZ are near-identical at the various localities studied. In contrast, PGM proportions differ widely between the ores of the North and South Chambers. This finding underlines that the formation of the PGM is mainly controlled by the local availability of reaction partners for the PGE. The elevated proportions of PGE-arsenides and -sulfarsenides in the South Chamber (together 49.7%) probably indicate higher fugacities of arsenic in the South Chamber magmas at the stage of MSZ formation, possibly due to contamination of the magmas by assimilation of country rocks (e.g. Oberthür et al. 2002).

The findings provide new indications towards the mechanisms that led to the distinct vertical element and mineral distribution patterns of the MSZ. Sulfide segregation appears to be the most important factor in the primary magmatic concentration of the PGE. It is concluded here that the orthomagmatic model elegantly explains the observed metal zonation patterns in principle. The degree to which internal fluids and certain metalloids (As, Te, Bi) have influenced the redistribution of the PGE and the formation of PGM still has to be ascertained.

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