
Distribution of PGE and PGM in Oxidized Ores of 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. Economic concentrations of PGE are restricted to sulfide disseminations of the Main Sulfide Zone (MSZ). Pristine, sulfide-bearing MSZ ores are mined underground (Mimosa mine) or from surface (Ngezi mine). Near-surface oxidized MSZ ores have a large potential at an estimated resource of 400 Mt of ore (Prendergast 1988). However, all previous attempts to extract the PGE from this ore type proved uneconomic due to low PGE recoveries achieved by conventional metallurgical methods.

The present contribution reports on the study of vertical profiles and bulk samples of oxidized MSZ from Hartley mine, the Ngezi project area, Unki mine and the Old Wedza mine close to Mimosa mine (see Fig. 1 in Oberthür et al., this volume). The study follows the redistribution of the PGE and PGM in the supergene environment in order to locate the PGE mineralogically and to evaluate metallurgical options for their recovery. Direct relationships between primary and secondary PGE/PGM mineralization are established.

Geological setting

The Great Dyke layered intrusion has a linear 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. 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 sulfides are found in the Main Sulfide Zone (MSZ) hosted in pyroxenites, some meters below the transition from the Ultramafic to the Mafic Sequence. A first attempt to mine oxidized MSZ ores was undertaken at the Old Wedza mine between 1926 - 1928, and again at the Hartley mine as from late 1997. However, the operations at Hartley were terminated due to low recoveries early in 1999.

Samples and Methods

Sampling in the open pits and trenches

showed that the oxidized ores comprised relatively competent rocks of light to dark brownish colour which locally had some greenish or bluish staining caused by secondary Cu- and Ni-minerals. The orthopyroxenes of the pyroxenites mostly showed incipient alteration only, whereas the interstitial network is filled by iron-hydroxides and brownish smectites. Pervasive oxidation of the sulphides exceeds 30 metres below surface in the Hartley open pits. In the Ngezi project area, the irregularly undulating border between the pervasively oxidized MSZ and ores showing incipient oxidation, i.e. containing relict sulphides, lies between 15 - 25 metres below surface.

Vertical profiles and bulk samples of oxidized MSZ were taken in the open pits at Hartley mine, from drill cores of the Ngezi project, and from trenches at Unki mine and the Old Wedza mine. The whole rock samples were analyzed for major and trace elements by XRF, and PGE contents were determined by INAA after Ni-sulfide extraction. In addition, heavy mineral concentrates were prepared from the samples. Polished sections were made from the rock and concentrate samples. The sections were investigated by reflected light microscopy and SEM/EDS. Mineral analyses were performed using an electron microprobe.

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. In the profiles of oxidized MSZ, the offsets of Pd → Pt → Au are well discernable as exemplified by one of the sections from Hartley (Fig. 1). Notably, 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 sulfide MSZ. Whereas average Pt/Pd ratios of 1.28 (n=12) characterize pristine sulphide MSZ, pervasively oxidized MSZ ores have average Pt/Pd ratios of 2.43 (n=9). The trend is also obvious in Figure 2 and corroborates the findings of e.g. Wagner (1929) and Evans et al. (1994) that Pd is more mobile than Pt and is dispersed in the super-

gene environment.

PGM and PGE-Carriers

Wagner (1929) reported sperrylite and cooperite in ores from the Old Wedza mine. Evans et al. (1994), Oberthür et al. (1999, 2000) and Evans and Spratt (2000) studied oxidized MSZ ores and agreed that a large proportion of the primary PGE-carriers including PGM 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”.

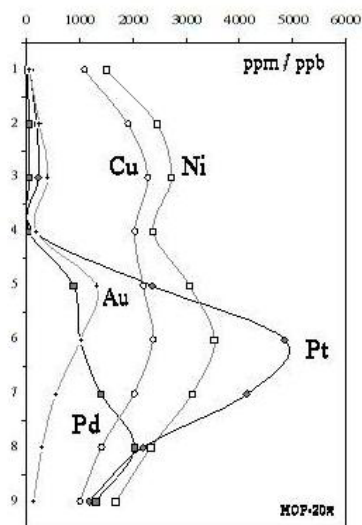


Figure 1. Profile HOP-20x (9 samples, each 20 cm wide) across oxidized MSZ showing the distribution patterns of Cu and Ni (in ppm), Pt, Pd and Au (in ppb).

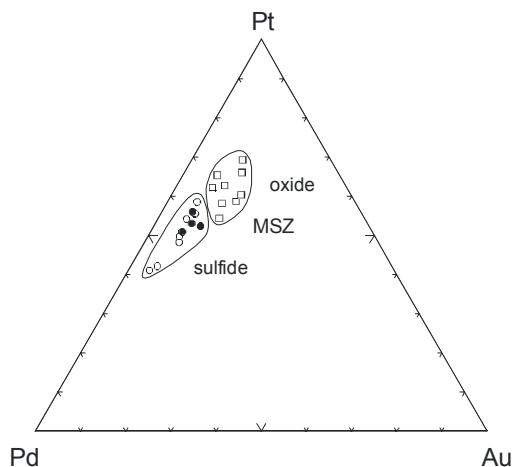


Figure 2. Triangular plot of Pt, Pd and Au contents of pristine sulfide MSZ and oxidized MSZ ores. (●) = pristine MSZ, official mine production or reserve data. (○) = profiles of pristine MSZ, own data. (□) = profiles of oxidized MSZ, own data.

Table 1. Proportions (by number of grains) of discrete PGM in pristine and oxidized MSZ ores. (Pt,Pd)(Bi,Te)* = (Pt,Pd)-bismuthotellurides. (Pt,Pd)S = cooperite and braggite. PGE-AsS⁺ = PGE-sulpharsenides. Proportions of (Pt,Pd)-oxides and -hydroxides in the oxidized MSZ cannot be estimated.

locality	sulfide MSZ	oxide MSZ
PGM type ↓ (n) → [%]	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	×

The samples are characterized by an interstitial network filled by iron-hydroxides and brownish smectites. Rare relict sulphides, mainly pyrrhotite, are surrounded by rims of iron-hydroxides. According to microprobe analyses, a large proportion of the Ni and Cu is hosted in smectites and not in the iron oxides/hydroxides. As only a few discrete PGM grains were found in polished sections, heavy mineral concentrates were prepared from the oxide MSZ samples, and altogether 1293 discrete PGM grains were extracted from the concentrates. Sperrylite is most common (57.2%), followed by cooperite/braggite (28.3%) and Pt-Fe alloy grains (3.1%). 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. Relict (Pt,Pd)-bismuthotellurides (11.4%) were only found in a few samples showing incipient alteration.

Sperrylite mostly shows idiomorphic crystal shapes. Cooperite/braggite, in contrast, are usually present as splinters of irregular shape with clean surfaces. In general, the sperrylite and cooperite/braggite grains show no distinct features of alteration. Rare 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 Pt₃Fe) probably represent replacements of other precursor PGM of unknown chemical

composition. 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. Grain sizes of the PGM (true maximum diameters) range from ca. 50 - 400 μm for hand-picked grains. However, in polished sections grain sizes of PGM down to 1 μm were also observed.

The PGM assemblage thus strongly contrasts to that of the pristine MSZ ores especially with respect to the proportion of (Pt,Pd)-bismuthotellurides (Table 1). The fate of the Pd hosted in pentlandite is not known. With the exception of a few relict grains of Pd-rich (Pt,Pd)-bismuthotellurides, the ores of oxidized MSZ only contain discrete grains of Pt-rich PGM.

A distinct variation in the proportions of discrete PGM grains was noted within vertical profiles of oxidized MSZ. For example, in profile HOP-20x (407 PGM grains) from Hartley mine (c.f. Fig. 1), the ratio of sperrylite to cooperite/braggite steadily increases from bottom to top. Similar relationships were also found in a profile across the MSZ close to Unki mine. The varying proportions of these PGM probably reflect original features of the respective pristine MSZ sequences as described by Oberthür et al. (this volume).

(Pt,Pd)-Oxides and/or -Hydroxides

The formation of mineralogically and chemically ill-defined “PGE-oxides or -hydroxides” was observed around relict, disintegrating (Pt,Pd)-bismuthotellurides (Fig. 3). These alteration phases are generally porous at various degrees and chemically inhomogeneous. Preliminary data show that they are characterized by relative losses of Bi and Te, an upgrade of Pt and/or Pd contents (e.g. from ca 30 – 35 at% Pt in moncheite to 60 – 70 at% Pt in the alteration rims, analyzed on an oxygen-free basis), and substantial gains in mainly Fe and Cu (up to some wt%). 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 to the alteration rims around disintegrating (Pt,Pd)-bismuthotellurides, individual, finely banded grains of (Pt,Pd)-oxides or -hydroxide phases were also detected (Fig. 4). Gold grains have various shapes (filigree, hooked, platy with crystal faces) and far more resemble gold from primary deposits than rounded, detrital gold. Their sizes range from 40 – 300 μm .

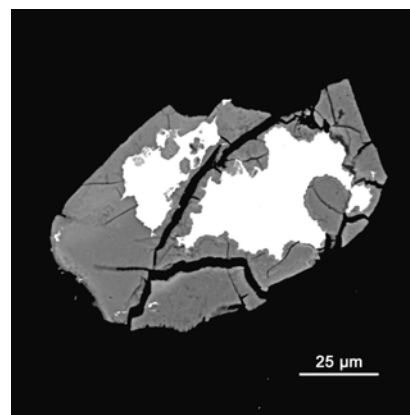


Figure 3. Grain of michenerite (white, centre) in disintegration. Alteration rim (grey) of probable (Pt,Pd)-oxide/hydroxide phases shows Pd, Cu and Fe as major elements. Polished section, backscatter electron image. Sample HOP-206a, ps 5910a.

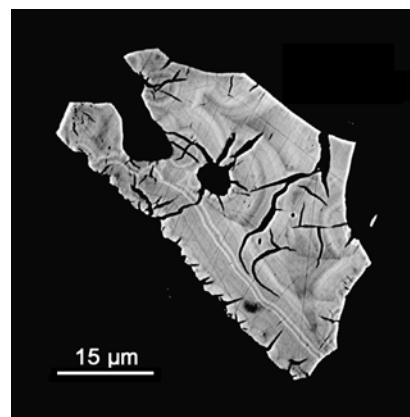


Figure 4. Colloform, banded grain of PGE-oxide/hydroxide phase. Polished section, backscatter electron image. Sample NGZ -1C from Adit A, Ngezi concession, ps 5711b.

Discussion and Conclusions

The processes of PGE redistribution and their mobilities in the supergene environment are much debated and cases of both dispersion and concentration have been proposed by various authors. In contributing to the discussion, it is fortunate that near-continuous underground and surface exposures of the MSZ allowed us to investigate some aspects of the fate of the PGE and PGM in the exogenic environment in detail.

Vertical profiles across oxidized MSZ showed that the general metal distribution and offset patterns of the pristine MSZ are grossly preserved. However, at similar Pt grades, some Pd has been lost from the system as shown by the increasing Pt/Pd ratios from pristine (average 1.28) to oxidized (average 2.43) MSZ, indicating that Pd

(mainly released from sulfides) is more mobile than Pt and was partly removed, probably in solution (ground- and/or surface waters), in the exogenic environment. Relict sperrylite and cooperite/braggite grains remain stable in the oxidized MSZ. Major changes from pristine to oxidized MSZ comprise the disintegration of the (Pt,Pd)-bismuthotellurides and the concomitant neo-formation of chemically and mineralogically ill-defined (Pt/Pd)-oxides or -hydroxides.

It is widely accepted that oxides or hydroxides of the PGE exist in the oxidized zone or in laterites of many deposits in the world (e.g. Augé and Legendre 1994, Hey 1999). Although the presence of Pt and Pd in the form of PGE-oxides or -hydroxides has been substantiated in ores of the MSZ by our recent studies and those of Evans and Spratt (2000) and Oberthür et al. (2000), more work is needed to characterize these phases chemically and mineralogically.

Metallurgical Implications

Recovered grades of Pt and Pd from pristine MSZ ores were 86% and 90%, respectively, at Hartley mine, and are slightly lower at Mimosa mine. Prendergast (1990) stated that all early attempts of processing oxidized MSZ ores resulted in Pt recoveries below 50% by either gravity concentration or flotation. Metallurgical test work performed by Zimplats on pervasively oxidized MSZ ores (from surface down to ca. 10 – 15 metres) from the Ngezi Project achieved recoveries of 15 – 30% only. 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. These have to be based on a better chemical and mineralogical characterization of the (Pt/Pd)-oxides or -hydroxides and on a precise knowledge of the proportions of PGE hosted in discrete PGM, being present as (Pt/Pd)-oxides or -hydroxides, or found in a dispersed form in iron-oxides/hydroxides or smectites.

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