2. Literature review on platinum-group minerals

2.1. Platinum-group element mineralogy

2.1.1. Introduction

The distribution of PGEs (platinum-group elements) in an ore is directly related to the type of ore, which in turn, dictates the mineralogical constitution. PGE ores can be divided into the following main classes (Stribrny *et al.*, 2000):

- Alluvial ores: These ores contain almost no sulphide and are composed of individual particles of rock and liberated minerals: an example is the Colombian deposit.
- Layered intrusions (e.g. Bushveld, Stillwater, Great Dyke)
- Magmatic nickel sulphide deposits (e.g. Noril'sk-Talnakh, Sudbury)

The layered intrusion ores contain by the far the world's largest reserves of PGE. The mineralization and occurrence of the PGEs are of utmost importance considering the very low concentrations of these elements in the ores (1-15 g/t).

PGE deposits can be divided into two categories: discrete platinum-group minerals (PGMs), and those hosted as "impurities" within other minerals. The latter category also includes the so-called "invisible" portion of the precious-metal distribution (Oberthür *et al.*, 2002a). The reason for the "invisibility" is not always known but can be twofold in nature: PGEs are present in submicroscopic particles or they occur as a dilute solid-solution. The understanding of the PGE associations is of utmost importance in order to construct mineralogical balances.

2.1.2. Hosted platinum-group elements

The PGE distribution between and content of the base-metal sulphides, sulpharsenides, oxides, and silicates are largely speculative, without substantial experimental evidence. However, the invention of the electron microprobe has led to

an explosion in the number of discrete PGM species being identified. It has also contributed to the understanding of the PGE distributions within other minerals as indicated by the results of the studies given below.

2.1.2.1. PGEs hosted in sulphides

There is little doubt at this stage that sulphides are a major repository of PGEs and these minerals can contain PGEs in variable amounts up to a few percent (by mass).

2.1.2.1.1. Pentlandite $(Fe,Ni)_9S_8$.

The best known carrier of PGEs is pentlandite (which can contain up to 12.1 wt% Pd). Pentlandite from Stillwater contains between 8.6-12.1 % Pd (Cabri, 1992). Reported maximum levels of Pd in pentlandite in (ppmw) (ppmw refers to parts per million by weight) are: J-M reef (46000), Platreef (20000), Lac des Iles (6500), Medvezhy Creek (2540), Great Dyke (1990), Penikat (1800) and Merensky reef (1164) (Cabri, 1992). Strirny *et al.* (2000) reported Pd and Rh partioning up to 2236 and 259 ppmw, respectively, in pentlandite from the Hartley Mine in the Great Dyke. In addition to this Prendergast (1990) reported a maximum of around 0.2 wt% Pd in pentlandite and that these low Pd concentrations could not account for the "missing Pd". "Missing" PGMs were also reported by Oberthür *et al.* (1998) from the Hartley Mine in the Great Dyke.

Lidsay *et al.* (1988) reported that the Pt content of the pentlandite from the Merensky reef is usually less than 36 ppmw and has a mean content of around 10-13 ppmw. Pentlandite from the Hartley Mine in the Great Dyke has a mean content of around 8.5 ppmw Pt. In contrast to this Prendergast (1988a) reported no association of Pt with pentlandite from samples taken at Mimosa Mine in the Great Dyke. The maximum reported solubilities of Pd, Rh and Ru in pentlandite are 12.5%, 12.4% and 12.9%, respectively, but no Pt could be detected at the analytical sensitivity value of 0.05% (Makovicky, 1986). This clearly indicates that pentlandite is mainly a Pd carrier and that high pentlandite recoveries are essential to optimise the Pd recoveries.

2.1.2.1.2. Pyrrhotite (Fe$_{1-x}$S)

Pyrrhotite can accommodate considerable quantities of PGE in solid solution at elevated temperatures, up to 11% Pd, 1.3 % Ru, 10.5% Rh and 2.2 %Pt, but upon cooling most of these PGM are expelled. A higher Fe content in the pyrrhotite is also detrimental to the solubility limit of PGMs in the mineral. Cabri (1988) reported a maximum of 47 ppmw Pd in pyrrhotite from the J-M reef. The contents of the rest of the PGEs in pyrrhotite from the most important PGE deposits are usually lower than 20 ppmw. The detection limit of many of the PGMs is of the order of 10 ppmw. These results indicate that pyrrhotite contains PGEs very close to the detection limit; indeed Oberthür *et al.* (1997) reported that pyrrhotite usually contains PGEs at concentrations close to or lower than the detection limit. Another important aspect is the occurrence of pentlandite as flame-shaped exsolutions in pyrrhotite (typical in ore from Mimosa Mine, Great Dyke). Hence the flotation characteristics of pyrrhotite will impact on the recovery of the PGEs, largely due to the occurrence of pentlandite within pyrrhotite.

2.1.2.1.3. Pyrite (FeS$_2$)

Pyrite does not accommodate appreciable quantities of PGM as shown by the experimental work performed by Makovicky (1986). However, Strirny *et al.* (2000) reported that pyrite from the Hartley Mine in the Great Dyke can contain on average about 36 ppmw Pt (range from 0.4 to 244; mean of 35.5 ppmw).

2.1.2.1.4. Chalcopyrite (CuFeS$_2$)

Chalcopyrite usually contains PGE at concentrations lower than the detection limit [(Oberthür *et al.*, 1997) and (Cabri, 1992)]. In addition to this, experimental studies also indicate the low solubility of PGMs in Cu-Fe sulphides (Lindsay *et al.*, 1988).

2.1.2.2. PGEs hosted in oxides

The most important oxides currently under investigation are chromite ($FeCr_2O_4$) and magnetite (Fe_3O_4). Cabri (1981) reported the presence of Pt in magnetite, but this needs verification (Cabri, 1981), since magnetite can be associated with Pt-Fe alloys. Parry (1984) reported PGE values of typically less than 1 ppmw for mixtures of magnetite and ilmenite.

2.1.2.3. PGEs hosted in silicates

There is little information on the PGE content of silicates. Michell *et al.* (1987) reported values less than 5 ppb and typically of the order of 1ppb. It is postulated that the Sudbury ores contains a significant portion of minute PGMs, which occur interstitially in silicates (Sizgoric, 1984) and that the Merensky reef contains PGMs in solid solution within oxides and silicates (Kinloch, 1982; Peyerl, 1983). It remains difficult to assess whether large or small quantities of PGEs are associated with the silicates.

2.1.2.4. PGEs hosted in sulpharsenides, arsenides and tellurides

These groups of minerals can contain appreciable levels of PGE. For example cobaltite (CoAsS) contains up to 600 ppmw Pt, 2800 ppmw Pd, 25000 ppmw Rh and 2600 ppm Ir (Cabri, 1981).

2.1.3. Platinum-group minerals

2.1.3.1. Platinum-group element mineralogy of the Merensky Reef, UG-2 Reef and the Great Dyke of Zimbabwe

Microbeam techniques enable the investigator to analyse the PGMs quantitatively to understand better the platinum-group element (PGE) distribution between discrete PGMs. As stated earlier, the number of identified PGMs exploded after the development of the microprobe. Broadly, PGMs can be grouped into metals, intermetallic compounds and alloys especially with Sn, Fe, Pb, Hg, Cu and Ni. The

remaining PGMs are formed with Bi, Te, As, Sb and S. The latter group of PGMs and compounds is of great interest and this study focused on characterising the flotation behaviour of two members of this group. Usually it is believed that the most common PGMs are the sulphides, arsenides and tellurides. The proportions and textures of these minerals vary considerably locally and regionally. Very informative surveys on PGMs and PGEs, covering all aspects of identification, composition, properties and recoveries may be found in Cabri (1981).

Table 1 and 2 list the most common Pt and Pd minerals in alphabetical order. The lists represent estimates of PGMs bearing Pt and Pd on a world basis, taking into consideration amounts produced from different deposits (Cabri, 1994). Although these lists are not intended to be highly accurate (Cabri, 1994), they do give a good account of the most common PGMs of Pt and Pd found in the world, with their ideal compositions and common substitutions in these PGMs. According to Cabri (1994) sperrylite is the most common PGM worldwide, and it can be found in every type of geological environment.

Table 1: Most common Pt minerals (Cabri, 1994).

Mineral	Ideal formula	Common substitutions
Braggite	$(Pt,Pd)S$	Ni
Cooperite	PtS	Pd, Ni
Isoferroplatinum	Pt_3Fe	Ru, Rh, Ir, Pd, Os, Cu, Ni
Moncheite	$PtTe_2$	Pd, Ni, Sb
Sperrylite	$PtAs_2$	Rh, Ir, Sb, S
Unknown, UG2	$Pt-Cu-S$	Rh, Ir, Pb

Table 2: Most common Pd minerals (Cabri, 1994).

| Mineral	Ideal formula	Common substitutions
Braggite	$(Pt,Pd)S$	Ni
Cabriite	Pd_2SnCu	Pt, Ag, Sb
Isomertieite	$Pd_{11}As_2Sb_2$	Te
Kotulskite	$PdTe$	Pt, Ni, Bi, Sb
Merenskyite	$PdTe_2$	Pt, Ni, Bi, Sb
Michenerite	$PdBiTe$	Pt, Ni, Sb
Plumbopalladinite	Pd_3Pb_2	Ag, Cu, Bi, Sn, Sb
Polarite	$Pd(Bi,Pb)$	Pt
Stannopalladinite	Pd_5Sn_2Cu	Pt
Sudburyite	$PdSb$	Ni, Te, Bi, As
Taimyrite	$Pd_9Sn_4Cu_3$	Pt
Vysotskite	PdS	Pt, Ni

In general the dominant platinum-group minerals (with their proportions by number) of the Merensky reef are the Pt-Pd sulphides (braggite, cooperite) at 60% (braggite and cooperite at 30% each), PGE tellurides (11%) and arsenides and sperrylite (6%) (the balance is mostly PGE alloys and Au/Ag phases) (Wilson, 1998). An average distribution of PGM for the Rustenburg facies (reef associated with potholes) is: PGE sulphides, 36%, Pt- and Pd-bearing bismuthotellurides, 32%, Ru phases, 15%, PGE alloys, 7%, and PGE arsenides 7% and Au/Ag phases 3% (Wilson, 1998). Potholes comprise about 15% of the total reef area. These areas are generally highly disturbed and represent areas of reef loss. UG-2 ores contain in general more PGE – sulphides such as braggite, cooperite, malanite and laurite. In sharp contrast to this the principal platinum-group mineral phases found in the Wedza-Mimosa platinum deposit in the Great Dyke of Zimbabwe are, in order of decreasing abundance, sperrylite ($PtAs_2$), Pt- and Pd-bearing bismuthotellurides (moncheite and merenskyite, respectively) and hollingworthite ($RhAsS$)   (Prendergast, 1990). These results were obtained from 47 precious-metal mineral grains and groups   (i.e. grains close together or clearly associated), or 111 individual grains in total. In contrast to this Weiser *et al.* (1998) suggested Pt- and Pd-bearing bismuthotellurides (michenerite, merenskyite,

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moncheite and kotulskite) to be the most frequent PGM whereas sperrylite is subordinate. However no indication was given of the number of samples analysed.

The proportions given in Table 3 for Mimosa Mine (data from Oberthür *et al.*, 2002a) are mostly in agreement with mineralogical investigations performed by Mintek (Van Wouw, 2000). The Mintek investigations showed that the most common PGMs are the Pt-Pd-Bi-Te minerals - including Pd-Bi-Te, Pt-Pd-Bi-Te and Pt-Bi-Te (probably michenerite, merenskyite, moncheite and kotulskite) - and sperrylite ($PtAs_2$) (Van Wouw, 2000). PGE sulpharsenides, cooperite (PtS), braggite ((Pt,Pd,Ni)S) and Au-Ag compounds were also detected (Van Wouw, 2000). Platinum occurs predominantly as $PtAs_2$, Pt-Bi-Te, Pt-Pd-Bi-Te and PGM sulpharsenides. In addition to occurring as bismuthotellurides of Pt and Pd, Pd also occurs in variable amounts in solid solution in pentlandite.

For these deposits, the Pd-bearing bismuthotellurides and to a lesser extent the Pt-bearing bismuthotellurides are the only PGMs containing appreciable amounts of palladium.

As an example, a back-scattered electron image of a sample of the concentrate of Mimosa mine is shown in Figure 1. This mineral (see white arrow) has been identified qualitatively by energy dispersive X-ray analysis (EDS-analysis) to belong to the class of Pd-Bi-Te.
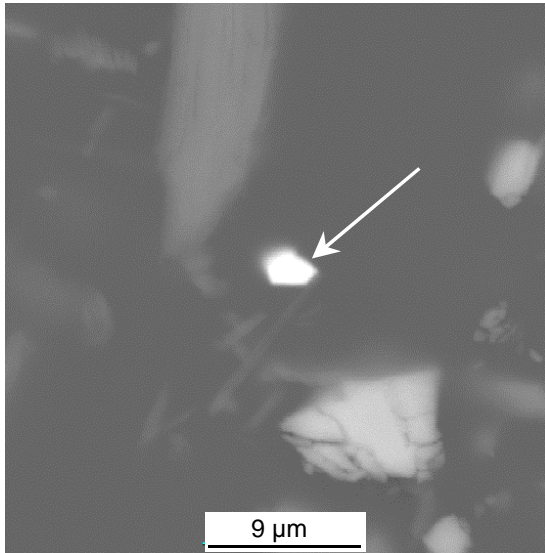
Figure 1: Back-scattered electron image (25kV) of a small liberated Pd-Bi-Te particle (arrowed) in the concentrator effluent stream of Mimosa platinum (Great Dyke, Zimbabwe).

The palladium recovery is on average about 5% lower than that of platinum (for the Mimosa Mine in Wedza-Mimosa platinum deposit) (Van Wouw, 2004). It seems, therefore, that the platinum and palladium recoveries are decoupled, which reflects differences in mineralisation. There is also a physical separation of the minerals in the ore deposit: Weiser *et al.* (1998) reported that the platinum peak lies 50-60 cm below the top of the reef profile whereas Pd peak lies 50-70 cm below the Pt peak. Similar profiles have been reported by Oberthür *et al.* (1998) for the Hartley mine (see Figure 2) and more generally on the Great Dyke (Oberthür, 2002b).

Type profile (CD-02, Hartley Mine) through MSZ
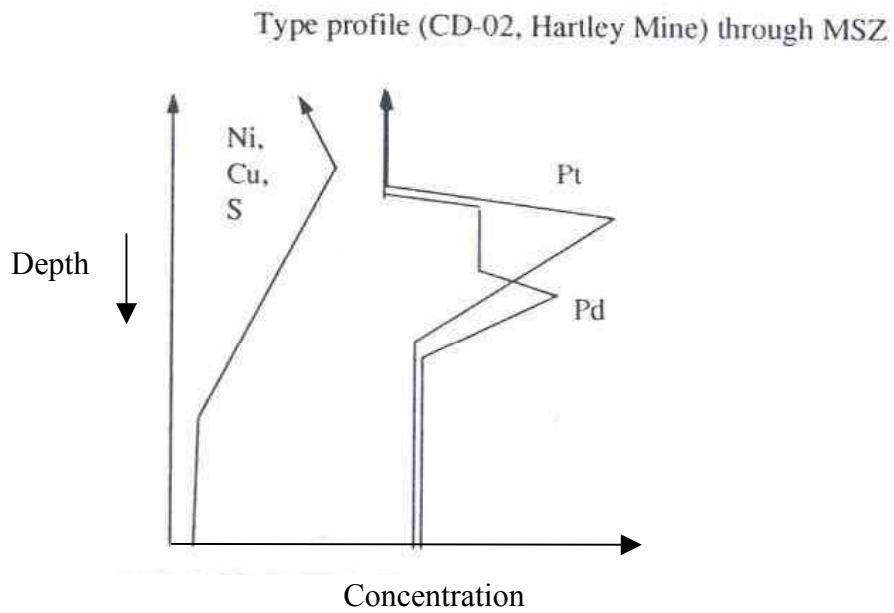
Figure 2: Schematic profile of the Main Sulphide Zone (MSZ) from the Hartley Mine (Oberthür *et al.*, 1998).

The proportions and textures of these minerals vary considerably locally and regionally. For instance the relative prevalence of Pt- and Pd-bearing bismutho-tellurides varies from 20 – 80% (See Table 3 and Appendix 1).

Table 3. The PGM proportions (proportions are by number) of a number of MSZ localities from the Great Dyke in Zimbabwe (Oberthür *et al.*, 2002a).

Locality →	Hartley	Mhondoro	Ngezi	Unki	Mimosa
PGM (n) → Type [%]	*181*	*43*	*199*	*250*	*134*
(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
Gold (n)	*26*	*7*	-	*12*	-

It is evident that PtAs$_2$ and (Pt,Pd)(Bi,Te) are the principal PGM classes along the Great Dyke in Zimbabwe, except at Mimosa where the PGE-AsS phase can also be found in appreciable quantities.

According to Weiser *et al.* (1998), the grain sizes of the PGMs are very small (< 20 μm diameter) and only rarely exceed 100 μm. The PGE and Au mineral grains of the Mimosa ore sample are smaller than 10 μm diameter, compared with the 10 - 31μm of the Merensky reef (Wilson, 1998). Prendergast (1990) reported that the mean grain size of sperrylite and moncheite is ~ 1000 μm^3, and of merenskyite, ~ 400 μm^3 corresponding to 12μm and 9μm equivalent diameters of spheres. Daily plant size-assay data from Mimosa Mine in Zimbabwe indicate that the -45 μm fraction has by far the highest PGM recovery (86.5%) compared to the recovery of the +45 – 75 μm fraction of 59%. This confirms that one of the possible reasons for low recoveries is that of insufficient liberation (Van Wouw, 2004).

The platinum-group minerals of the Merensky Reef (10-30 and 50-350 μm in diameter; these two ranges are for different PGMs) are in general larger than that of

the UG-2 Reef (6-10 μm in diameter) and Great Dyke (less than 10 μm). The textural association of the PGM will greatly influence their recovery potential during flotation. Good associations of base metal sulphides with PGMs are evident for the Merensky and UG-2 reefs. In contrast to this, ores from the Great Dyke show poorer association with the base metal sulphides and a significant portion is associated with the silicate minerals (Van Wouw, 2000). Regrinding of the ore is the only option to avoid significant losses to the tailings.

According to Weiser *et al.* (1998) and Prendergast (1990) the PGMs occur as inclusions in the base-metal sulphides, as irregular grains on the sulphide-silicate (also hydrosilicate) boundary, and interstitially in silicate minerals. No statistical indication was given of the number of grains analysed (for the Mimosa Mine sample) and the occurrence distributions. All the gold grains were located within the hydrosilicates. A mineralogical investigation of the Mimosa flotation feed samples showed that the major modes of occurrence in order of decreasing abundance, are as liberated grains, at the grain contact of base-metal sulphides and silicates, and at the grain contact of silicates (Van Wouw, 2003). A very small fraction of the PGMs is locked in the base-metal sulphides. Unfortunately, only about 86 grains were analysed during this investigation. Literally hundreds of PGM grains would have to be investigated to reduce the statistical uncertainty to acceptable levels (Merkle, 2004).

In addition to this, investigations performed by Mintek on the Mimosa Mine tailings indicated that the vast majority (70%) of the (unrecovered) PGMs are Pt-Pd-bismuthotellurides. Knowing that the PGMs belong to the class, the next question that should be answered is the textural association of these minerals in the tailings sample. Unfortunately, the results of the textural association of these minerals in the tailings are rather inconclusive and contradictory. One report stated that no liberated PGMs could be found in the tailings sample. In sharp contrast to this, investigations performed on the rougher and cleaner tailings indicated the presence of large quantities of liberated PGMs. The – 45μm fraction of the rougher and cleaner tailings contained respectively 33% and 15% liberated PGMs (expressed as percentages of total number of PGMs identified). The –10μm fraction of the cleaner tailings contained as much as 80 % liberated PGMs. The PGM assemblage of both the

rougher and cleaner tailings consisted mostly of Pt-Pd-Bi-Te and sperrylite. No indication was given of the number of PGMs analysed in each case (Van Wouw, 2000).

Given the inconclusive nature of the results a follow-up mineralogical investigation was conducted on the flotation tailings of Mimosa mine (Van Wouw, 2003). The following streams were subjected to the investigations: primary rougher (PRT) and cleaner tailings (PCT), secondary rougher (SRT) and cleaner tailings (SCT) and the combined recleaner tailings (RCT). The primary rougher and cleaner tailings, and the combined recleaner tailings are reground in the secondary mill, while the secondary rougher and cleaner tailings are discarded. All of these streams contained appreciable amounts of PGMs. The lowest quantity of PGE was found in the secondary rougher tailings (0.8 - 1.0 g/t PGE) while the largest concentration was found in the primary cleaner tailings (2 – 3 g/t PGE). The quantities found in the secondary rougher and cleaner tailings are indicative of the low recoveries that are obtained. Figure 3 indicates the relative amounts of PGM found in the different tailings samples (Van Wouw, 2003). Data on the liberation are discussed below.
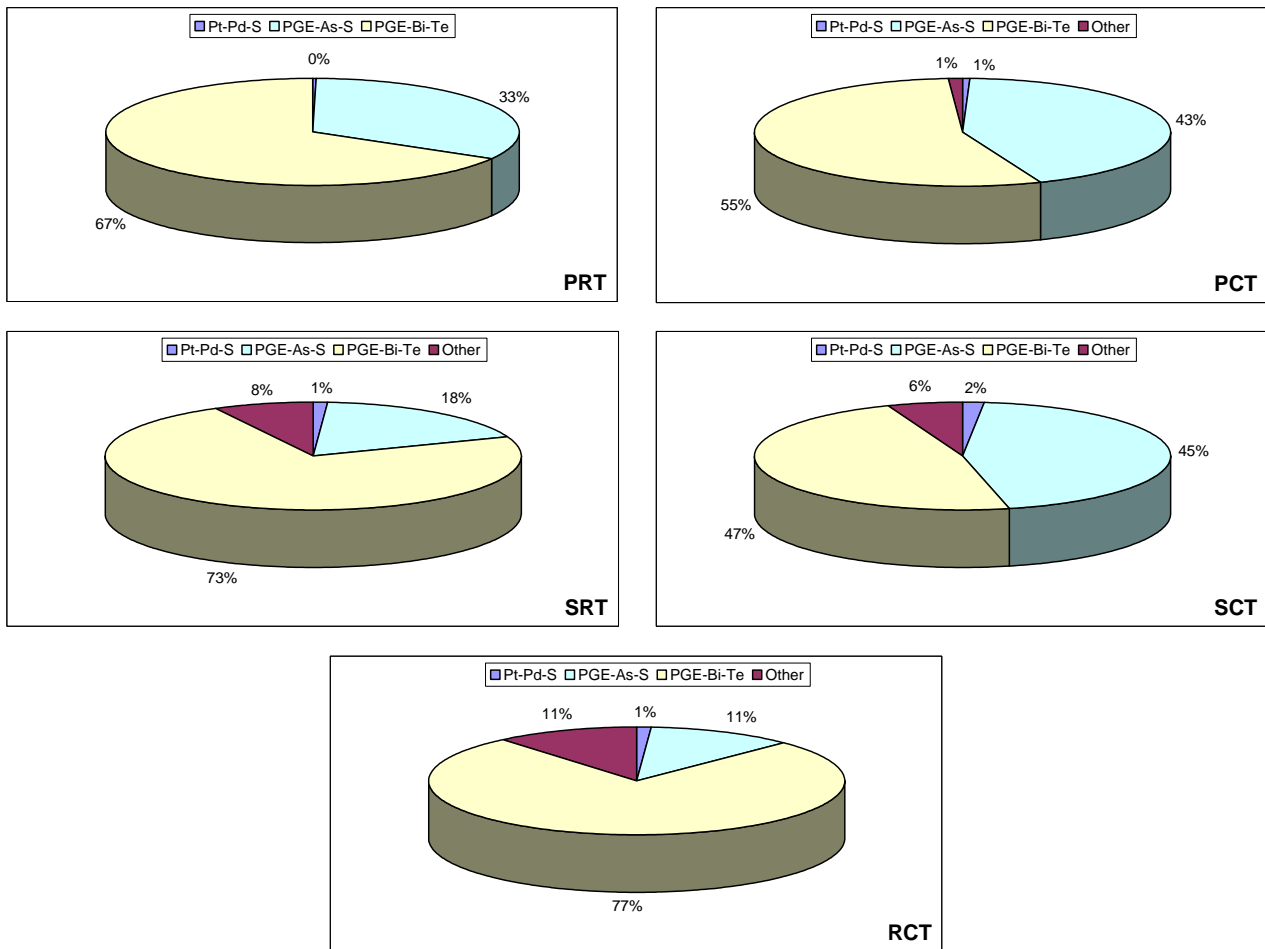
Figure 3: Relative quantities of PGMs in the tailings samples of Mimosa Mine (proportions are by number) (Van Wouw, 2003). (PRT: primary rougher tailings; PCT: primary cleaner tailings; SRT: secondary rougher tailings; SCT: secondary cleaner tailings;   RCT: combined recleaner tailings; PGE-Bi-Te: PGE-bearing bismuthotellurides; PGE-As-S: PGE sulpharsenides; Pt-Pd-S: Pt-Pd sulphides)

Figure 3 indicates that the PGE-Bi-Te and PGE-As-S are by far the most representative PGM types, generally forming more than 90% of all grains found. Especially the large proportion of the Pt-Pd-Bi-Te class in all the samples investigated is noteworthy. The reason for the low flotation response of this class of mineral can be threefold:

- minerals are locked in or attached to silicates,
- minerals are liberated but are too small to be recovered
- minerals are liberated but are not responding well to the flotation stimuli.

Data on liberation are given in Figure 4, which shows the modes of occurrence of the PGMs and base metal sulphide grains. The six different modes of occurrence used in the Figure are:

- Liberated (L)
- Locked in gangue (G)
- Attached to gangue (AG)
- Associated with liberated BMS (SL)
- Associated with BMS that is locked in gangue (SAG)
- Associated with BMS that is attached to gangue (SG)

These results confirm that a large portion of the PGMs is not associated with the base metal sulphides, unlike South African ores (UG-2 and Merensky). Generally more than 70% (by volume) of the grains identified in the tailings samples occur as discrete grains (not associated with base-metal sulphide particles) (Van Wouw, 2003). This phenomenon contributes to the lower recoveries typically found in ores from the Great Dyke; small liberated PGMs are not easily recovered. Liberated PGM grains occur in all the samples, but especially the primary rougher tailings and the combined recleaner tailings contain substantial amounts of liberated PGMs. Significant association of PGMs with liberated BMS is found only in the secondary cleaner tails. These PGMs may be associated with the slow floating pyrrhotite.

The average grain size of the particles located during the search is between 3 and 4 μm in diameter (Van Wouw, 2003). The small size of these particles may be the single most important factor affecting the low recoveries of these particles; this is one of the effects studied in this project.
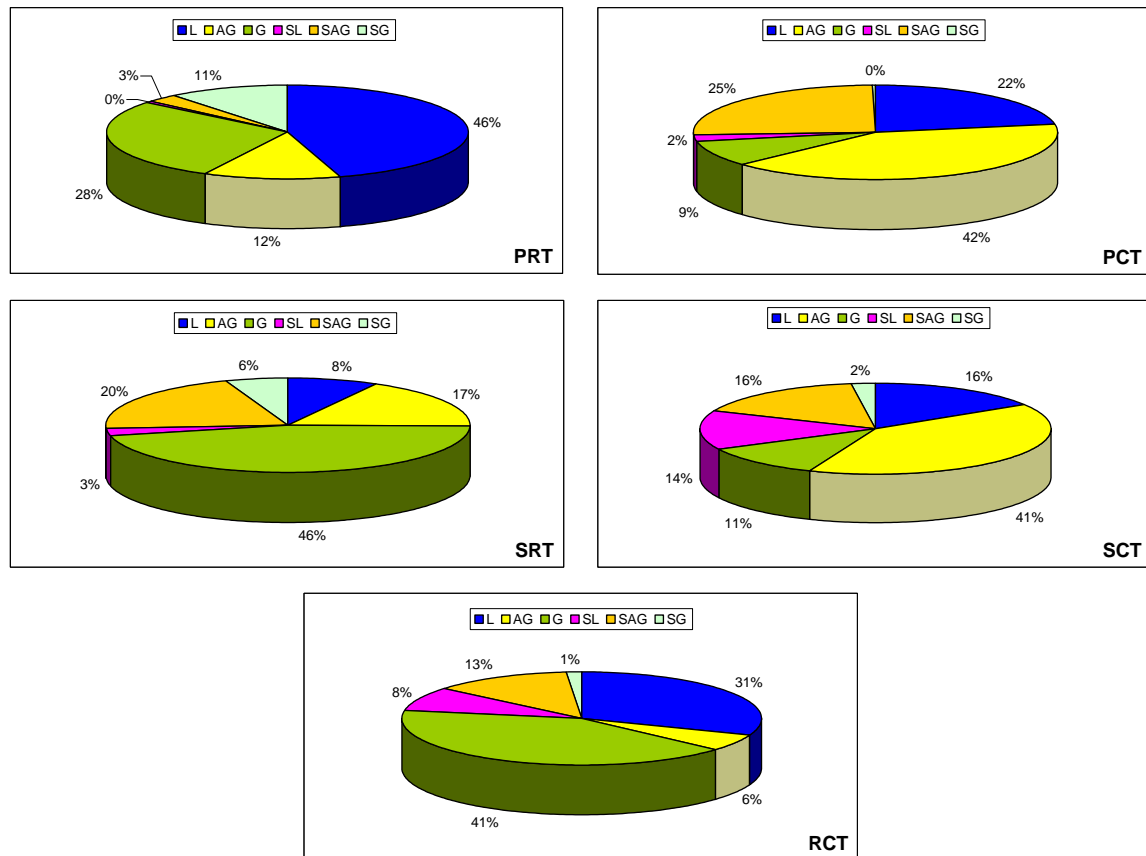
Figure 4: Modes of occurrence of PGM grains (proportions are by number) (Van Wouw, 2003) (L: liberated; G: locked in gangue; AG: attached to gangue; SL: associated with liberated BMS; SAG: associated with BMS that is locked in gangue; SG: associated with BMS that is attached to gangue).

2.1.3.2. Microprobe analysis of platinum-group minerals from Mimosa Mine (Great Dyke)

Although this has not been demonstrated, it is proposed that the Te and Bismuth contents of the Pd-Pt-Bi-Te class will affect the flotation behaviour of these particles. It is therefore important to establish the major types of PGMs in this class for the purpose of synthesis of samples used in experimental work.

Micro-probe analyses of minerals from the Great Dyke (Mimosa Mine) are shown in Figures 5-7 and in the Appendix 2. These analyses were kindly supplied by Thomas Oberthür (2002c) who has over the years studied the PGM mineralization of the Great Dyke in detail. The microprobe analyses were conducted with a Cameca Camebax

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instrument (15kV, 20nA and 1μm to 2 μm spot size). Natural and synthetic standards were used for calibration.
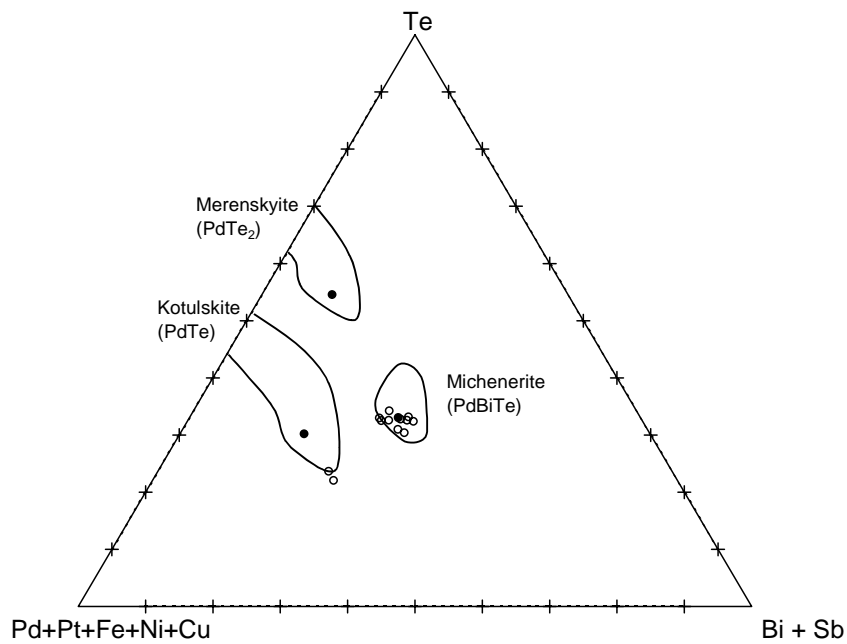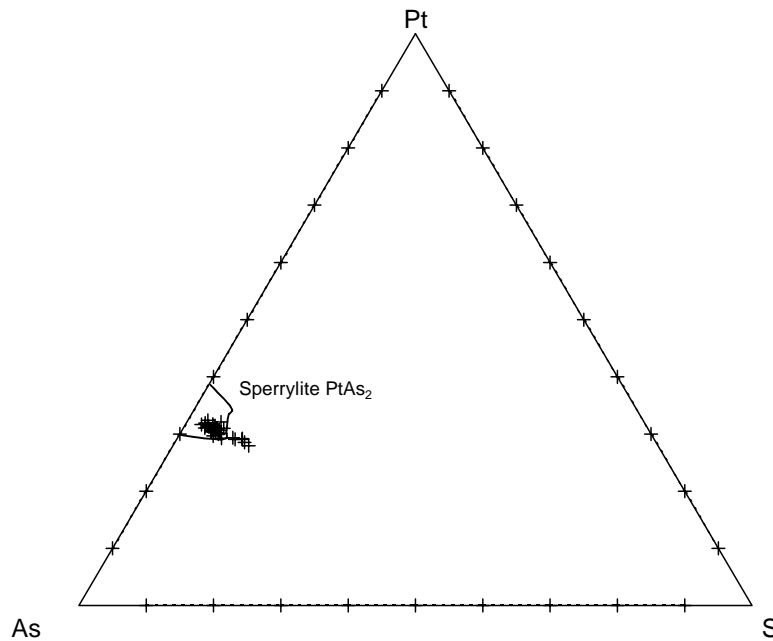

Figure 5: Composition (at %) of natural Pd-Pt-Bi-Te minerals from Mimosa Mine in the Great Dyke of Zimbabwe (Oberthür, 2002c). The curved lines enclose the compositional fields of the respective minerals reported in the literature (Wilson *et al.*, 1993).
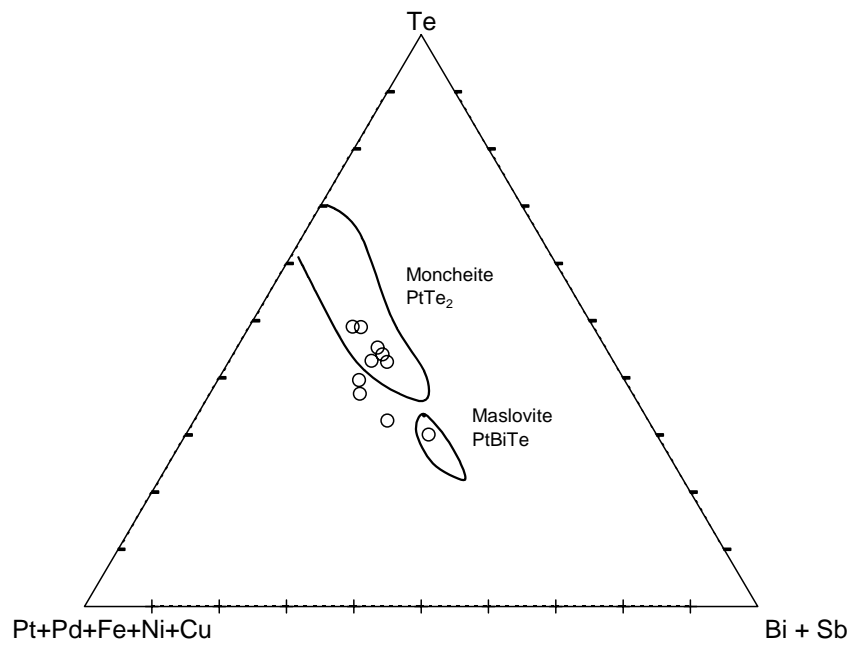
Figure 6: Composition (at %) of natural Pt-Bi-Te minerals from Mimosa Mine in the Great Dyke of Zimbabwe (Oberthür, 2002c). The curved lines enclose the compositional fields of the respective minerals reported in the literature (Wilson *et al.*, 1993).

Figure 7: Composition (at%) of natural Pt-As minerals from Mimosa Mine in the Great Dyke of Zimbabwe (Oberthür, 2002c). The curved line encloses the compositional field of sperrylite reported in the literature (Wilson *et al.*, 1993).

These results clearly show that michenerite is the predominant Pd-Bi-Te mineral and moncheite the predominant Pt-Bi-Te mineral. In addition to this the microprobe results of michenerite given in Appendix 2 indicates low Pt substitution for Pd, indicating that the Pt substitution can be neglected in this instance. This simplified the synthesis procedure and the interpretation of results, which are described later in this document. In contrast to this the moncheite analysis indicate the presence of appreciable quantities of Pd (up to 6 mass percentage Pd).

2.1.3.3. Platinum-group element mineralogy of the Platreef

The PGM mineralogy of the Platreef in South Africa is very similar to that of the Great Dyke. The Platreef has recently been classified as an economically viable reef (Merkle *et al.*, 2002). Various new plants have been commissioned to exploit the reef through open pit mining. The Platreef is a variably mineralised (PGE,Ni,Cu) composite pyroxinite zone. The distribution of discrete PGMs in the Platreef tends to be erratic but by far the predominant class of PGM is the Pt-Pd-tellurides (Wilson, 1998). Unfortunately no indication of the different types of minerals

constituting the Pt-Pd-tellurides class was given. The PGE-telluride content (given as fractions of the total number of PGM grains) can vary from 80% near Drenthe in the extreme north (see map in the Appendix 3) to 90% near Tweefontein Hill, to 30% at Swartfontein (Wilson, 1998). (The map in Appendix 3 also indicates the location of future pits along the Platreef).

The three other important classes of PGMs (in order of decreasing abundance) are PGE arsenides (21%), alloys and sulphides. The PGMs are on average coarser than those found in the Merensky, UG-2 and Great Dyke ores. Interestingly enough the tellurides and arsenides are predominantly enclosed in the silicate gangue. According to Wilson (1998) up to 62% of the PGMs can be associated with the silica gangue and 38% by volume with BMSs, hence high base-metal sulphide abundances do not necessarily indicate high PGM contents. It is been found that up to 70% of the Platreef PGMs can be liberated during the milling process (Dippenaar, 2002). Given the encapsulation by silica, liberation of these particles is therefore a prerequisite for good recoveries; this confirms the importance of the flotation behaviour of the liberated minerals.

2.1.3.4. Platinum-group element mineralogy of the oxidised MSZ of the Great Dyke of Zimbabwe

Oxidised MSZ ores that occur close to the surface differ from the deeper sulphide ores in both their physical state and precious metal content. The term oxidised refers to the alteration of the pyroxinites to form hydroxy-species such as magnesium silicate hydroxides (talc) and calcium magnesium iron silicate hydroxides. The brownish colour of the ore is a result of the formation of the iron hydroxides.

The average head grade of Pt in the oxidised reserve compares well to that of the pristine (unweathered) ore. In contrast, the Pd content of the oxidised ore is significantly lower than that of the pristine ore due to the weathering of the bismuth-tellurides, which is the most important Pd-carrying PGM (Prendergast, 1990); the Pt-Pd-bismuthotellurides are susceptible to chemical dissolution. Table 4 shows the PGE distribution of the Main Sulphide Zone (MSZ) and the oxidised ores from various

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localities, including the Hartley Mine, Ngezi project, Unki mine and the Old Wedza mine near Mimosa Mine (Oberthür *et al.*, 2002d).

Table 4: Summary of PGM data (Oberthür *et al.*, 2002d). The PGM proportions are by number.

|	Pristine MSZ	Oxide MSZ
PGM : Number of grains → Type ↓	801	1293
(Pt,Pd)(Bi,Te) %	50.1	11.4
PtAs$_2$ (%)	19.0	57.2
(Pt,Pd,Ni)S %	8.5	28.3
Pt-Fe alloys %	2.4	3.1
PGE-sulpharsenides	11.9	-
Others %	8.7	-

In contrast to the pristine MSZ, which contains mostly (Pt,Pd)-bismuthotellurides, the oxidised reserve contains mostly of sperrylite (PtAs$_2$) grains followed by cooperite/braggite ((Pt,Pd,Ni)S). The classes of PGM found in the oxidised ore from the Great Dyke compare well with the main classes found in the typical Merensky ore. The Pt-Pd-bismuth-tellurides of the oxidised ore show incipient alteration, in contrast with the sperrylite and cooperite/braggite which show little sign of alteration (Oberthür *et al.*, 2002d): sperrylite remains the main carrier of Pt in the oxidised MSZ because it is resistant to weathering (Prendergast, 1988a). In contrast the weathering of the bismuthotellurides causes loss of palladium, resulting in a Pt/Pd ratio of 2.4 in the oxidised ore, compared with the 1.3 in the pristine ore (Oberthür *et al.*, 2002d).

The Mimosa Mine's North Hill geological complex (See Appendix 4 for a geological map) strikes over 5 km in a NNE direction at a width of about 2 km. The total ore reserves of the Far South Hill and North Hill are estimated at 14MT and 20 MT, respectively. The North Hill deposit is a well-exposed surface deposit, which dips at 3 degrees making it suitable for shallow-open cast mining with a low waste to ore ratio. Mimosa mine plans to exploit this reserve in about 2-3 years time, after the

completion of the expansion projects which are currently underway. Economic ways have to be found to exploit this reserve; there have been unsuccessful attempts previously. A thorough understanding of the mechanisms governing the flotation of the PGMs found in the oxidised reserve will be of great value to the company once it is decided to extract PGEs from this reserve.

2.2. Phases and phase relations of the platinum-group elements

PGEs frequently substitute for one another in compounds with other elements. Pt-Pd-Bi-Te minerals are no exception: 1:1 substitution between Pt and Pd (Merkle *et al.*, 1990), as well as between Te and Bi is well documented (Hoffman *et al.*, 1976). The solid solution phase fields are shown in Figures 8 and 9.
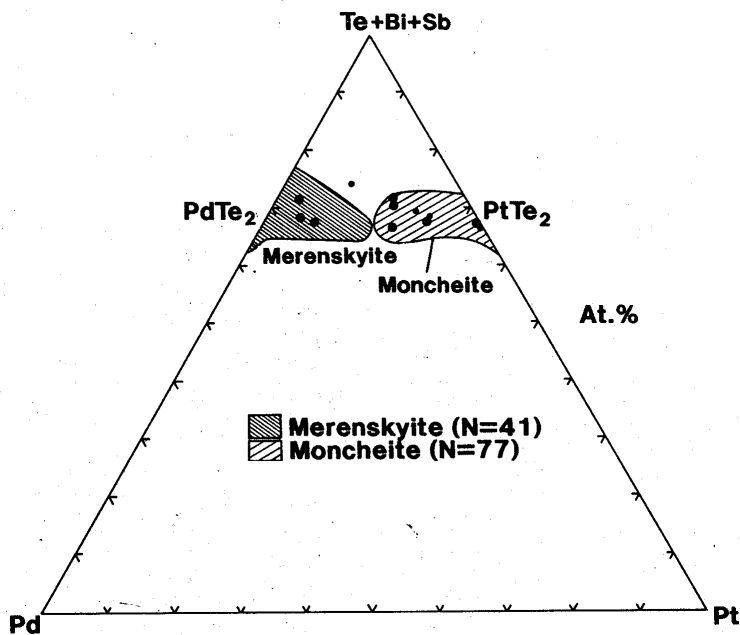
Figure 8: Pd - Pt – (Te + Bi + Sb) diagram showing the solid-solution (shaded areas) between merenskyite and moncheite (Merkle *et al.*, 1990). N represents the number of grains analysed.
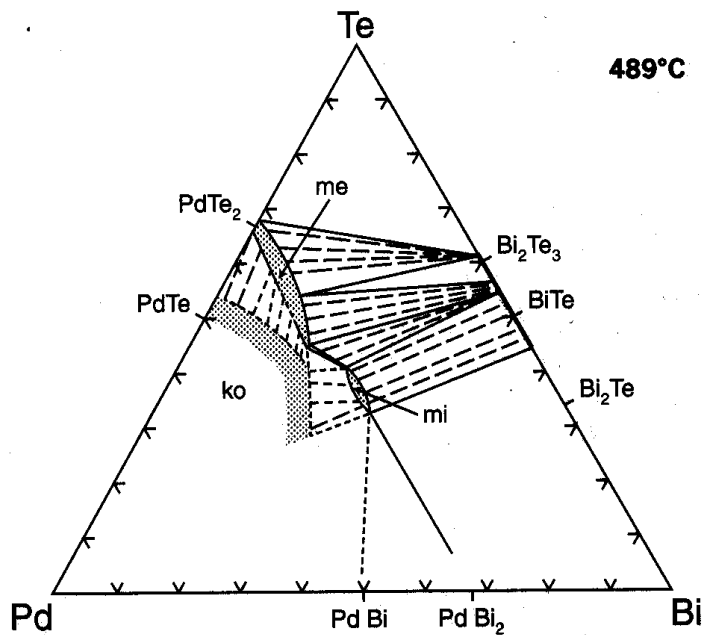
Figure 9: Synthetic phase relations (at %) in the Pd-poor portion of the system Pd-Bi-Te at 489°C. Solid solution phases are shaded; ko = kotulskite (PdTe), me = merenskyite ($PdTe_2$) and mi = michenerite (PdBiTe) (Hoffman *et al.*, 1976).

The bismuthotellurides of palladium also depart from the nominal composition: Figure 9 indicates the solid solution fields of synthetic merenskyite ($PdTe_2$) and michenerite (PdBiTe). Merenskyite shows a greater degree of Te-Bi substitution than does michenerite. The michenerite field is very narrow with the palladium content ranging from 31.3 - 33.2% (at %) (Hoffman *et al.*, 1976). Bi mainly substitutes Te in the merenskyite, but some substitution of Pd for Bi and Te is also possible. In addition to this, Pt can also substitute for Pd on a 1:1 basis. Figure 10 shows the solid solution fields of merenskyite, moncheite, michenerite and sperrylite as determined by microprobe analysis of natural minerals (Evans *et al.*, 1994) (N represents the number of analysis performed). The solid solution field of merenskyite as shown in Figure 10 (for natural minerals) is larger than that shown in Figure 9 (for synthetic minerals), in length (Bi substitution) and width (Pd or Pt substitution). Contaminants (Fe, S and Ni) are possibly responsible for the discrepancy in the width (Pd or Pt substitution) of the stability field. Cabri *et al.*(1979) suggested, albeit a quarter of a century ago, that all Pd-Te data in the literature require major revision. However, in the absence of other data the diagrams shown in Figure 10 were used to determine the alloy compositions for the work presented here.

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This work concentrated on michenerite, as this is the most prevalent Pd-bearing in many of the Great Dyke deposits and prominent in the Platreef, and on sperrylite as the second most prevalent mineral class of the Great Dyke deposits
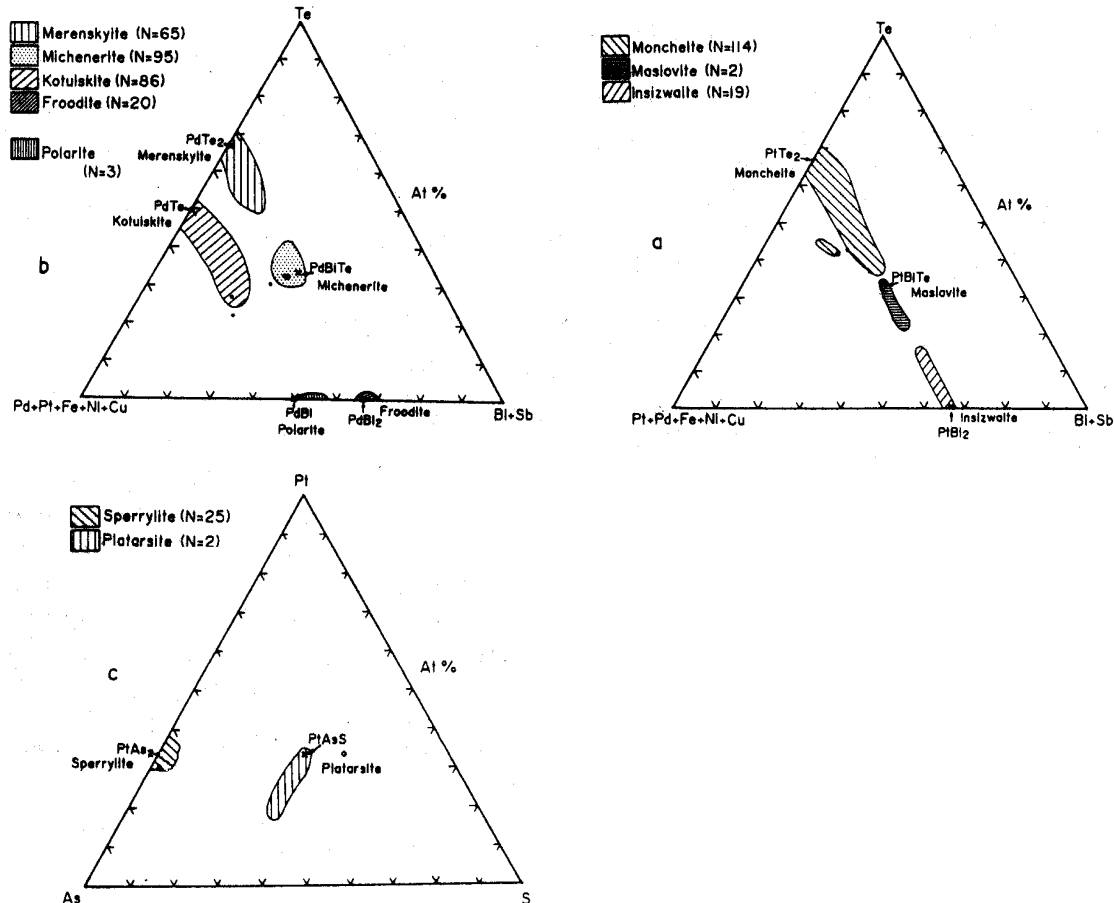
Figure 10. Ternary diagrams showing compositions of PGM phases based on the analyses of natural minerals (Wilson *et al.*, 1993).

2.3. Flotation behaviour of platinum-group minerals

Research on the flotation behaviour of selected platinum-group minerals is very limited. Volyanskii *et al.* (1985) investigated the reactions of two sulfhydryl collectors, namely potassium butyl xanthate (KX) and sodium dibutyl dithiophosphate (DTP), with sperrylite. The sperrylite contained 73.12% Pt, 0.11 % Ni, 0.04% Cu, 0.02% Fe and the balance As (in mass %). This composition of this "alloy" does not

correspond with the chemical composition of stoichiometric sperrylite, which contains 57% Pt by weight. No indication was given on whether this "sperrylite" was synthetically prepared or whether a natural sample was used. Nevertheless, the mass (1g) and particle size (+ 0.074 –0.44 mm) suggest that a synthetic sperrylite sample was employed.

The investigations were performed by employing electrochemical and spectrophotometric techniques. The organic species were extracted from the liquid phase of the pulp and were washed off the solid surface using n-hexane.   The potassium butyl xanthate and sodium dibutyl dithiophosphate distribution mass balance are shown in Table 5.

Table 5: Potassium butyl xanthate and sodium dibutyl dithiophosphate distribution mass balance (Volyanskii *et al.*, 1985) (KX: potassium butyl xanthate; DTP: sodium dibutyl dithiophosphate; DTP-dithiolate: oxidised species of DTP; M[C]n: metal xanthate species; solid phase: mineral sample; liquid phase : solution containing the collector).

System	pH	Initial amount of collector (mg)		Amount (mg)								Total Sum (mg)
				Liquid phase				Solid phase				
		KX	DTP	KX	DTP	X_2	DTP-dithiolate	M[C]n	DTP	X_2	DTP-dithiolate	
Sperrylite + KX	6.9	1.03	-	0.83	-	0.03	-	0.05	-	0.12	-	1.03
	8.0	1.03	-	0.80	-	0.03	-	0.04	-	0.16	-	1.03
	10.0	1.03	-	0.63	-	0.13	-	0.06	-	0.21	-	1.03
Sperrylite + DTP	6.9	-	1.05	-	0.90	-	0.03	0.01	0.04		0.05	1.03
	8.0	-	1.05	-	0.89	-	0.03	0.01	0.04		0.05	1.03
	10.0	-	1.05	-	0.79	-	0.03	0.01	0.14		0.06	1.03

The significance of these results is that they are consistent with the formation of dixanthogen on the surface of the "sperrylite". Dixanthogen can only form if the mineral surface attains a mixed potential higher than the xanthate-dixanthogen

equilibrium value. From the results given in Table 5 it appears that the metal xanthate species (M[C]n) can also exist on the surface of the "sperrylite". The authors of this study also mentioned the formation of platinum xanthate species as a result of the interaction of the "sperrylite" with the collector. Table 5 shows further that the pH has a definite effect of adsorption properties of the dixanthogen (more alkaline pH being favourable for X_2 formation). While these are interesting results, there are several discrepancies in the paper, including apparently erroneous interpretation of UV spectra. It hence seems warranted to re-investigate the flotation behaviour of sperrylite.

Penberthy *et al.* (2000) conducted a comprehensive study on the recovery of platinum-group elements from UG-2 chromite from the Bushveld Igneous Complex. As mentioned earlier, the platinum-group mineral assemblage of the UG-2 chromite consists mainly of PGE-sulphides (predominantly, cooperite, braggite, malanite and laurite) and a significant component of alloys (such as Pt-Fe alloy) or various tellurides. The PGMs were mainly associated with the base metal sulphides (>74 %), occurring either within or at the sulphide-gangue grain boundary. Fifty percent of the PGMs were liberated during milling. Most of the PGMs associated with the sulphides reported to the concentrate during flotation, while PGMs associated with the silicates were not recovered. The response of the liberated PGMs to the flotation stimulus was difficult to investigate due to their small size (< 10 μm). Most of the liberated grains did float, albeit at a lower rate than the base metal sulphides. In general the ranking of the PGM flotation rate was in decreasing order braggite, cooperite, malanite, ferroplatinum and laurite (See Figure 11). No indication was given of the rate at which sperrylite and (Pt,Pd)-bismuthotellurides float.
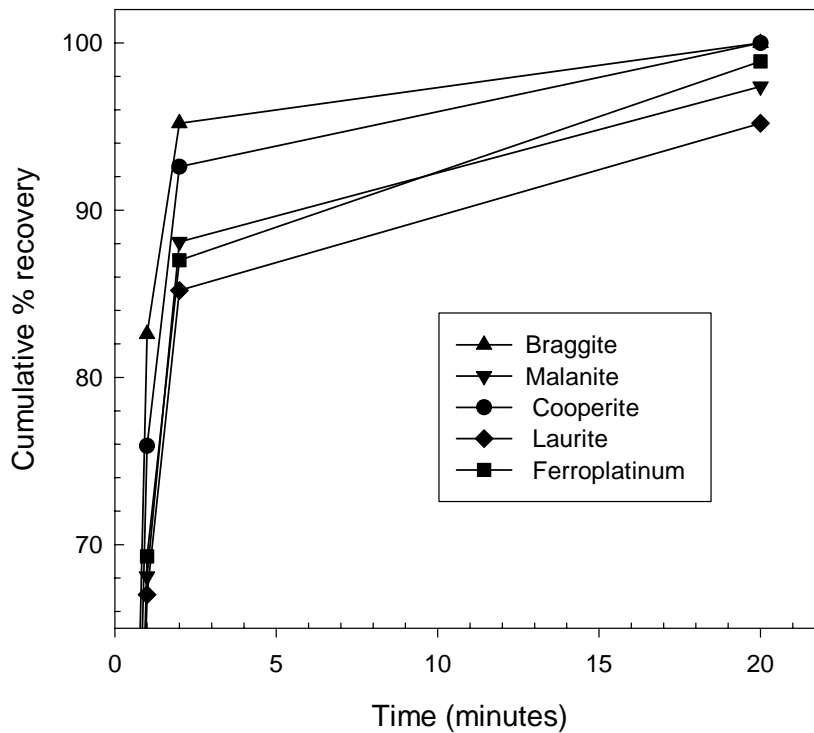
Figure 11: The recovery for selected liberated PGMs (redrawn from Penberthy *et al.*, 2000) in batch flotation tests.

According to staff of the Anglo Platinum Research Centre (ARC) (ARC, 2002), based on their experience, some physical characteristics and the recovery of the different classes of PGM can be summarised as follows:

Table 6: Some physical characteristics and the recovery behaviour of different classes of PGM (ARC, 2002).

Class	Size	Density	Gravity recovery	Flotation recovery
Sulphides	Often coarse	High	Good	Good
Tellurides	Variable	Low	Poor	Poor
Arsenides	Variable	Medium	Good	Good
Alloys	Often coarse	Very high	Excellent	Variable
Oxides	Fine	Low	Very poor	Very poor

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The inherent assumption of Table 6 is that all the minerals are liberated. This table underlines the importance of a good understanding of the flotation behaviour of the tellurides with the main aim to optimise the recovery of these minerals.

2.3.1. Platinum-group element recovery from the oxidised MSZ of the Great Dyke of Zimbabwe

Sperrylite is the principal platinum carrier in the oxidised MSZ of Mimosa mine (formerly known as Wedza mine) and previous attempts, which included flotation and gravity concentration, did not achieve better than 50% Pt recovery (Prendergast, 1988b). Metallurgical test work performed by Zimplats on the their oxidised ores only achieved recoveries of between 15-30% (Oberthür *et al.*, 2002d). Evans (1994) reported that PGE-bearing minerals in the weathered ore are predominantly platinum-iron alloys of variable composition containing variable amounts of bismuth, palladium and tellurium. Evans *et al.* (1994) suggested that the bismuthotellurides and Pt-Pd-sulphides have been altered *in situ* by the leaching of the sulphur, tellurium and bismuth. This hypothesis was not supported by Stribrny *et al*. (2000). However, Oberthür *et al.* (2002d) have shown the existence of ill defined "PGE-oxides or hydroxides " around altered (Pt,Pd)-bismuthotellurides. Preliminary results show the loss of Te and Bi and the increase in Pt and Pd contents from the oxides or hydroxides. The fact that these phases contain oxygen was verified by micro-probe analysis and corresponds to the work published by Evans *et al.* (2000). In addition to the formation of these PGE oxides or hydroxides, it was suggested by Stribrny *et al.* (2000) and Oberthür (2002d) that the PGEs are dispersed in the iron hydroxides or smectites. The weathering of the sulphides to goethite or limonite minerals, and the alteration of the pyroxenites, prevent the efficient concentration of precious metals by sulphide flotation (Prendergast, 1990). The textural association of the PGMs with the altered sulphides is not well known at this stage, but electron micro-probe investigations have revealed that the PGMs in the oxidised deposit are located at the goethite-limonite patches after the interstitial sulphides (Evans *et al.*, 1994; Oberthür, 2002b).

The possibility of applying an oxidic float to recover the altered sulphides is currently being tested at General Metallurgical Research and Services (GMRS). Prendergast

(1988) proposed the recovery of the PGM by fine grinding and flotation by altering the flotation conditions.


2.4. Chemical stability of Michenerite

All three elements in Michenerite (PdBiTe) are fairly noble, concerning the considerable overlap of their stability areas with that of water (See Figures 12 - 14) (Pourbaix, 1974). All the relevant reaction equations can be found in Pourbaix (1974). Palladium is thermodynamically stable in the presence of aqueous solutions free from strongly oxidising conditions at low pH values. Both Te and Bi oxidise in the bismuth-telluride minerals despite the fact that these elements do not oxidise readily, in their pure state, in air. Aerated water attacks bismuth to form Bi_2O_3, which is in turn very soluble in dilute acids. TeO_2 is formed in aerated water and forms a non-protective film if the TeO_2 is freshly precipitated. The kinetics of the oxidation in solution is not very well understood, but if oxidation proceeds at a high enough rate, oxidation could impact negatively on the flotation process.

The majority of sulphide flotation plants operate at pulp potentials (using air as carrier gas) between 200 mV (SHE) and 300 mV (SHE) (Ralston, 1991). Ores from the Merensky and UG2 reefs have a natural buffer capacity ensuring pH levels between 8 and 9 (Buswell *et al*., 2002; Ekmekçi et al., 2003). Considering the typical values of the pulp potential and pH (assuming the same values for the Great Dyke of Zimbabwe) Te and Bi are likely to be oxidised in industrial flotation circuits if the oxidation proceeds at a higher rate than competing reactions (possibly the oxidation of the collector).

Elvy *et al.* (1996) reported the incongruent oxidation (the migration of some metal atoms to the surface to form an overlayer of a metal-oxygen species) of minerals in the Pd-Te-Bi system leading to the formation of layer of tellurium and/or bismuth oxide covering the palladium-rich substrate The reactivity of the minerals increased in the order of: PdTe < PdTeBi < PdBi. This is in the same order as the reactivities of Pd, Te and Bi in the pure form. This implies that merenskyite should be more resistant

to oxidation than michenerite, since merenskyite has the higher tellurium content and lower bismuth content.

Figures 12, 13 and 14 represent the potential-pH diagrams respectively of bismuth, palladium and tellurium in water.
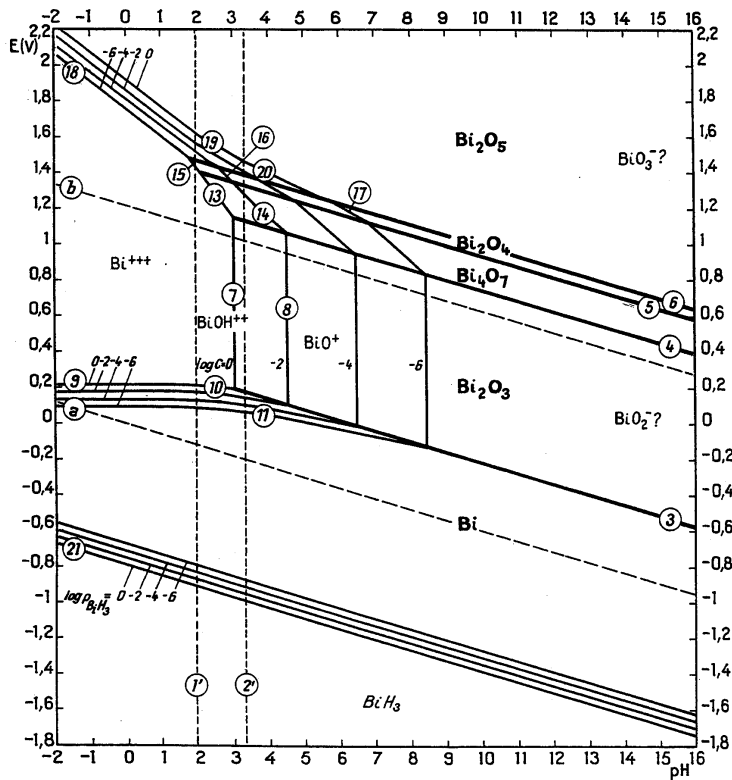
Figure 12: Potential-pH equilibrium diagram for the system bismuth-water for molar concentrations of dissolved species of 1M, 10^{-2}M, 10^{-4}M and 10^{-6}M, at 25°C (Pourbaix, 1974).

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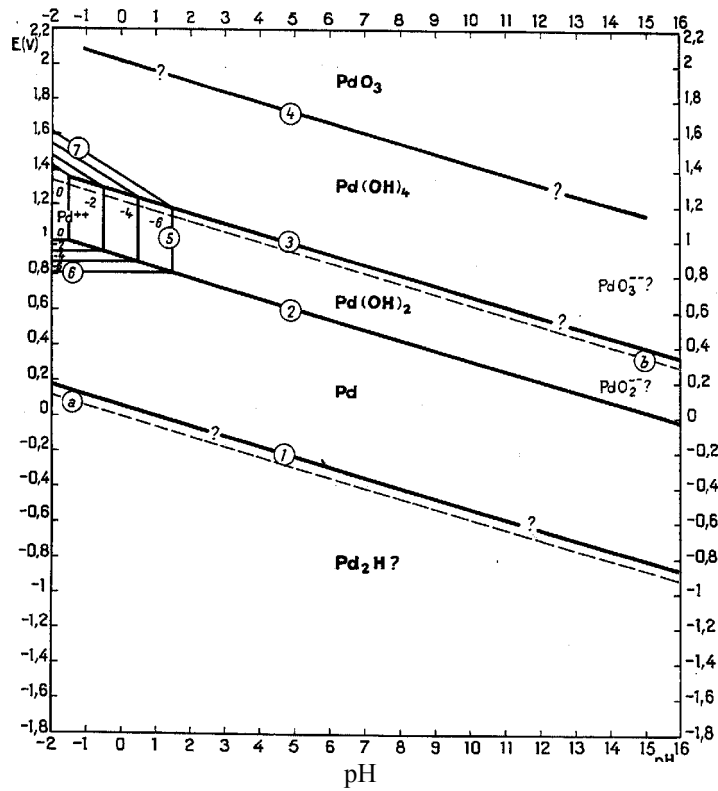
Figure 13: Potential-pH equilibrium diagram for the system palladium-water for molar concentrations of dissolved species of 1M, 10^{-2}M, 10^{-4}M and 10^{-6}M, at 25°C (Pourbaix, 1974).
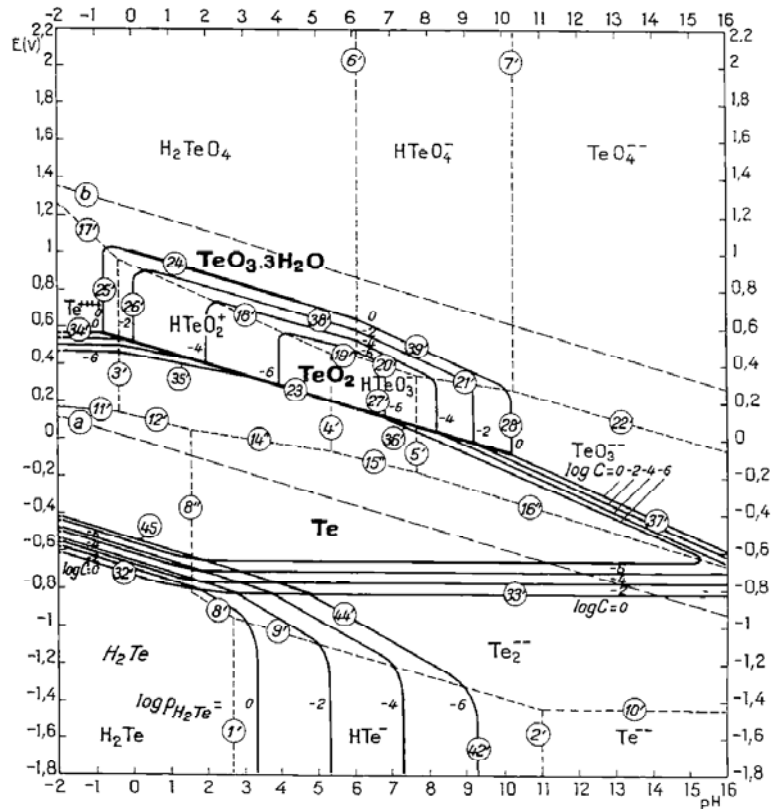
Figure 14: Potential-pH equilibrium diagram for the system tellurium-water for molar concentrations of dissolved species of 1M, 10^{-2}M, 10^{-4}M and 10^{-6}M, at 25°C (Pourbaix, 1974).

Investigations performed by Peyerl (1983) on the mode of occurrence of platinum-group minerals in the Merensky reef and UG-2 chromitite, revealed bismuthotellurides to be the PGM which was least resistant to chemical attack by HNO_3. None of braggitte, cooperite, sperrylite, laurite or platinum-iron alloys showed any chemical attack after been exposed to diluted and concentrated boiling HNO_3 for 10 hours. The bismuthotellurides showed dissolution behaviour similar to that of the base metal sulphides. The issue on the stability of bismuthotellurides in aqueous solutions must be investigated in order to predict their response in milling and flotation circuits. This issue was not studied in any detail in the present work, which concentrated on unoxidised samples.

2.5. Interaction of Thiols with metals

It was proposed that the interaction of thiols with metals (platinum, gold and copper) involves an electrochemical mechanism, with anodic oxidation of the collector supported by a cathodic (reduction) reaction (e.g. reduction of oxygen) (Woods *et al.*, 1974):

$$2X^- = X_2 + 2e^- \hspace{5cm} (1)$$

$$0.5O_{2(ads)} + H_2O + 2e^- = 2OH^- \hspace{3.5cm} (2)$$

In these equations X^- indicates the xanthate ion and X_2 dixanthogen. Woods *et al.* (1974) further proposed that reaction 1 proceeds via an initial chemisorption step and that the multi-layers of dixanthogen product are bound to the chemisorbed monolayer xanthate by the interaction of the hydrocarbon parts of the molecule. The main experimental advantage of the electrochemical nature of these reactions is that the reactions can be tracked by electrochemical techniques (potentiodynamic measurements and impedance measurements).

The possible oxidation of dithiocarbonate collectors was hence studied through potentiodynamic measurements in the present work; anodic and cathodic polarization diagrams were drawn for synthetic Pd-Bi-Te and PtAs$_2$ working electrodes, to investigate the anodic oxidation and oxygen reduction reactions. The possibility of the formation of a surface layer of the collector was determined through impedance measurements. Impedance measurements allow *in situ* detection of the formation of surface layers (of collector), by a decrease in the circuit capacitance.

Impedance measurements are based on the modelling of an electrode in solution as an electronic circuit containing resistors, capacitors and inductors. A simplified version of such a circuit is shown in Figure 15. The equivalent circuit contains a resistor in series with a parallel circuit containing a capacitor and resistor.

The capacitance effect is a result of the double layer charging effect (C_D) and possible surface layers (C_s). The electrode capacitance is the series combination of the two effects as shown below

$$\frac{1}{C} = \frac{1}{C_D} + \frac{1}{C_s} \tag{3}$$

As shown by equation (3), formation of a surface layer (with a non-zero value of C_s) will cause the electrode capacitance to decrease. In this way, the formation of surface layers can be detected when the mineral is anodically polarized in the presence of xanthate ions.
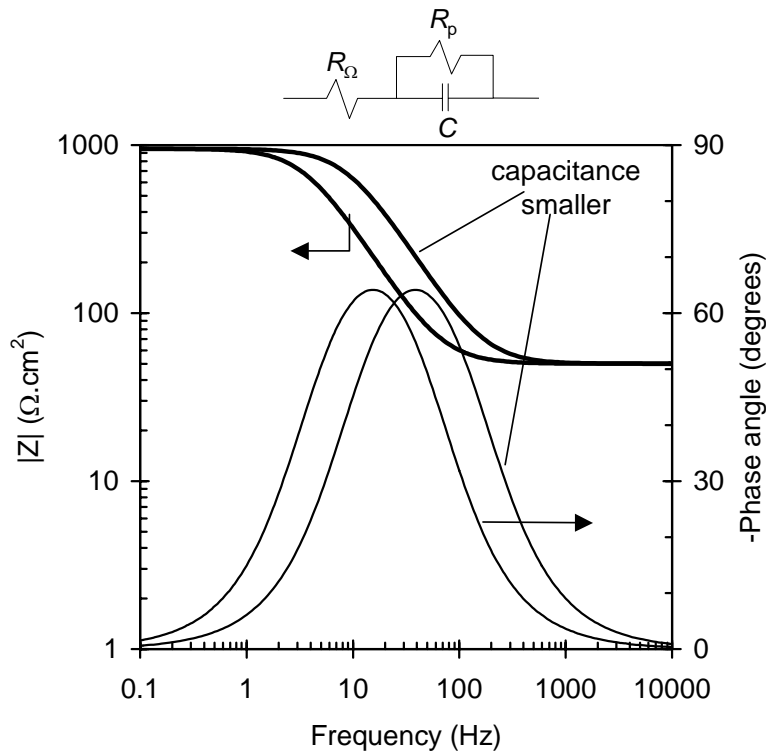
Figure 15: Bode plot of the impedance of a metallic electrode in a solution (with an equivalent circuit as shown). The effect of a decrease in capacitance is shown in the Bode plot. Drawn for $R_\Omega = 50$ $\Omega.cm^2$, $R_p = 900\Omega.cm^2$ and $C = 50$ $\mu F/cm^2$ or 20 $\mu F/cm^2$.