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PLATINOID MINERALS IN THE GOLD REEFS OF THE

WITWATERSRAND BASIN

P. F. BARRASS



## ABSTRACT

From a study of twenty six platinoid mineral concentrates from different gold mines around the Witwatersrand sedimentary basin, seven alloys of osmium and iridium, two alloys of platinum and iron, and five arsenide, sulpharsenide or sulphide minerals of the platinum group elements were identified and are described. The minerals include osmium, iridosmium, rutheniridosmium, osmiridium, ruthenosmiridium, iridium, rhodiridium, ferroplatinum, rhodoferroplatinum, sperrylite, laurite, one arsenide of osmium and iridium, one complex sulpharsenide of osmium, iridium and ruthenium, and a rhodium sulphide mineral. Where possible, optical properties and quantitative values for chemical composition, reflectivity, microhardness and structure are given for each mineral. The intergrowth textures and shapes exhibited by the platinoid particles are described and discussed. From a grain count study under the electron microprobe of six, selected platinoid mineral concentrates, the distributions in mineralogy and grain size of the particles from different parts of the Witwatersrand basin were determined and are compared. Only minor variations could be detected in both mineralogy and size of the particles across the basin. Four platinoid mineral grains were found in situ within the reef and these are described and illustrated. Photomicrographs showing a wide variety of grain shapes, intergrowth textures and compositions are provided as an appendix, to supplement the descriptions and discussion in the text of the thesis.

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## INTRODUCTION

Quartz-rich, oligomictic conglomerate bands, containing gold, uranium and minute quantities of platinoid minerals,\* contribute to a succession of precambrian quartzites, conglomerates, shales and lavas overlying the archaean schists and granite gneisses of the South African Basement Complex. The succession forms a basin, known as the Witwatersrand Sedimentary Basin, which covers an area of approximately 25,000 square miles and incorporates at its rim the gold mining areas of the Witwatersrand proper, Klerksdorp and the Orange Free State. (see Maps I and II).

The auriferous conglomerate bands, known locally as reefs or blanket, were first mined for gold in 1886 (1). The presence of platinoid minerals in the bands was noted by Bettel as early as 1892 (2), but concentration of the platinoids as a byproduct of gold mining operations did not commence until 1919. The term "byproduct" is an appropriate one since, notwithstanding the fact that platinoid mineral concentration has been carried out on a regional scale since 1923, the average recovery of the minerals from the conglomerates in 1956 was only  $3\frac{1}{2}$  milligrams per ton of ore, or 1 oz. per 2000 czs. of recovered gold (3). Production figures for later years are not available.

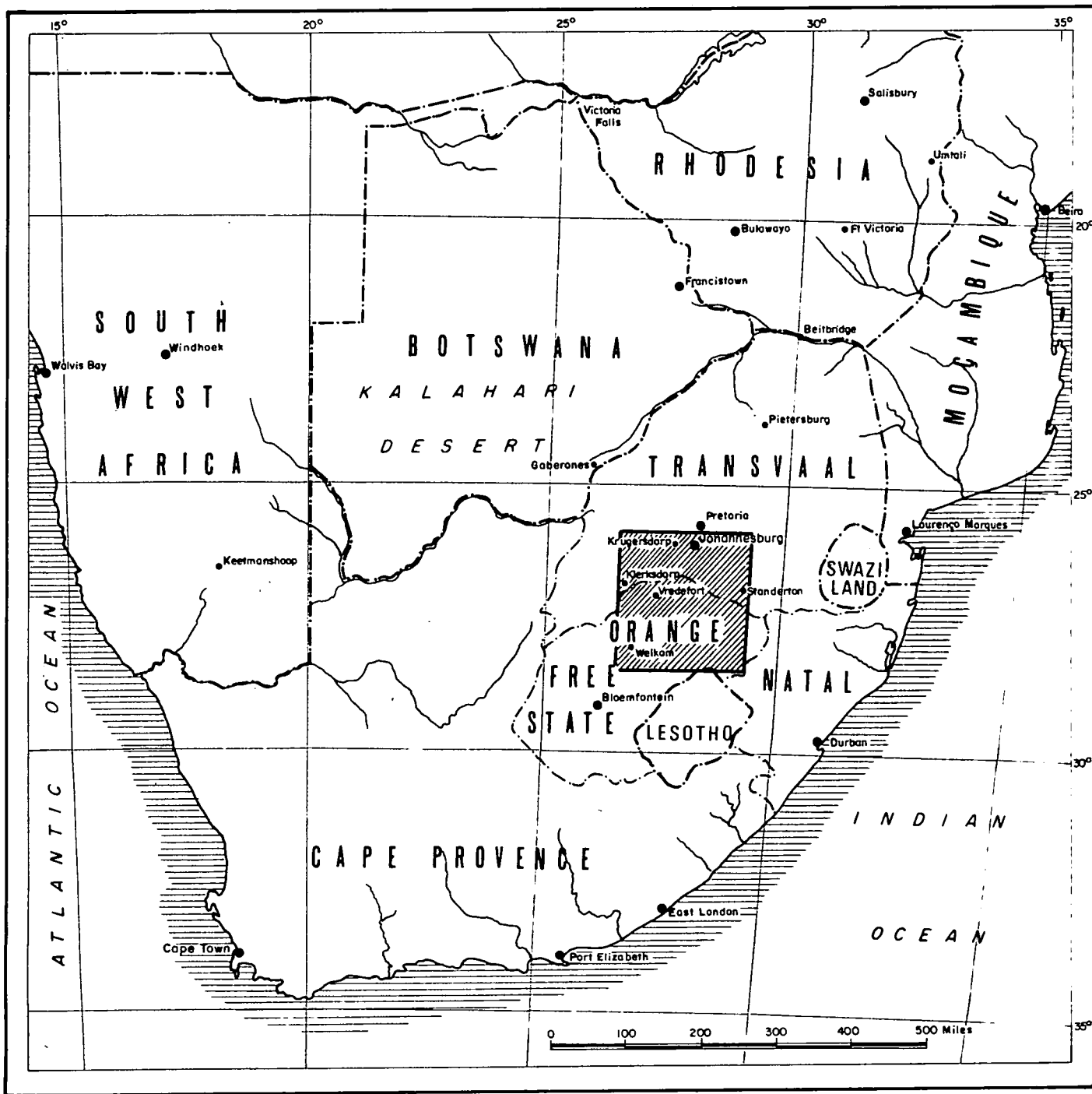
The platinoid minerals occur within the ore as minute particles associated with gold, uraninite and other heavy minerals (4,5,6), the particles mainly comprising alloys of osmium and iridium containing subsidiary amounts of ruthenium, platinum, rhodium and iron. Arsenides and sulphides of the platinum group elements have been reported (6,7),

\* Minerals of the platinum group elements:- osmium, iridium, platinum, ruthenium, rhodium, palladium.



but no positive identification of a palladium mineral has been made. In general, the individual platinoid particles are subspherical in shape and frequently comprise intergrowths of two or more discrete mineral phases. Owing to the small size, optical similarity and complex intergrowth textures of the minerals, quantitative data concerning the individual minerals and their distribution within the Witwatersrand reefs are nonexistent. The results of previous research work have been based mainly on microscopic observations and have inevitably generated controversy as to the identity and composition of the various, closely related platinoid minerals (3,5,6,7). The development of the electron probe microanalyser, however, has made possible the positive identification of such minerals (8). It is the aim of this thesis to define, with the aid of sophisticated instruments such as the electron probe, the properties of the individual platinoid minerals, their intergrowth textures and their distribution within the auriferous reefs of the Witwatersrand Basin.

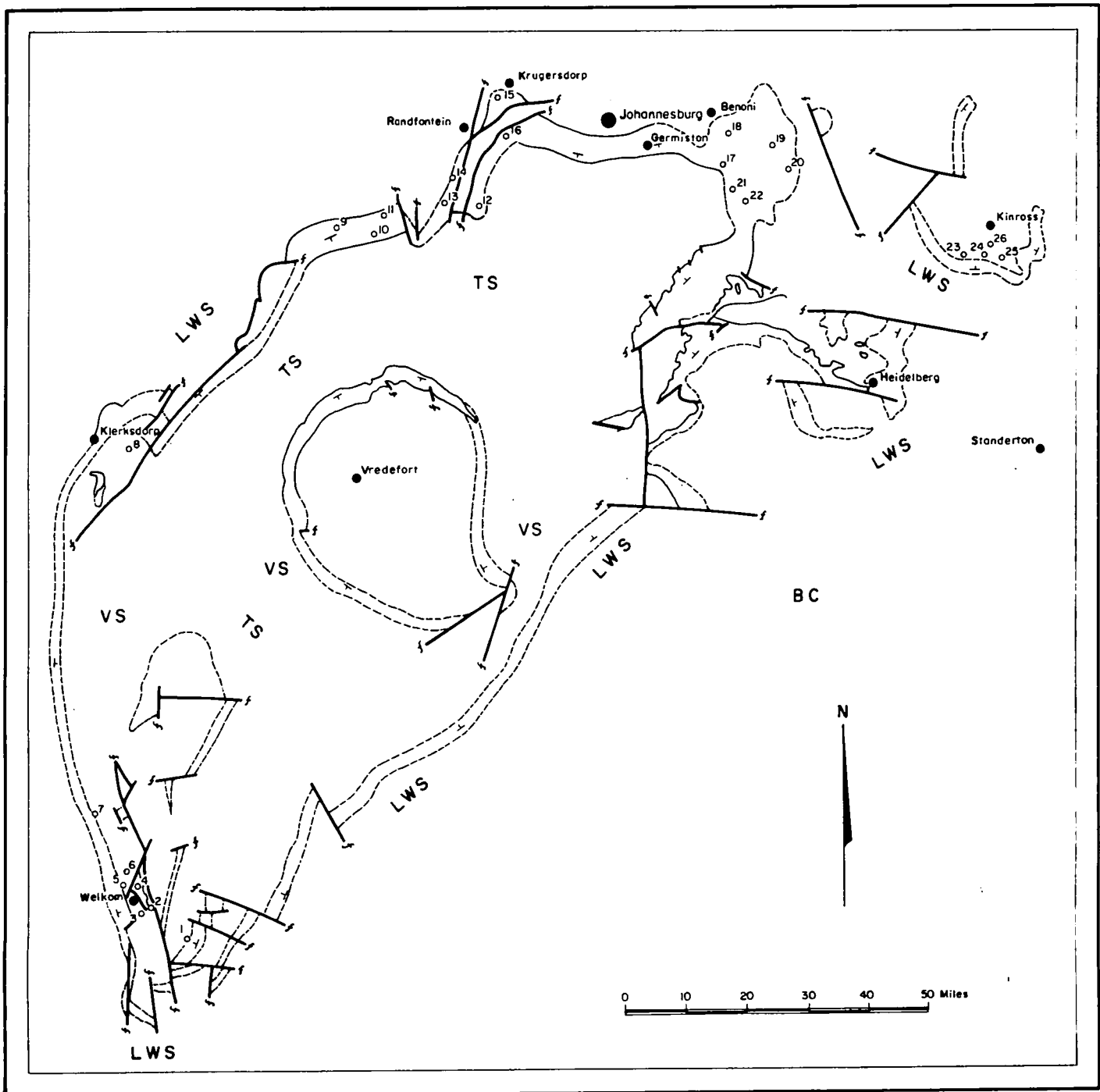
# SOUTHERN AFRICA



Outline (Approx.) of the Witwatersrand Basin ( See Map II overleaf )

THE WITWATERSRAND BASIN

DISTRIBUTION OF THE UPPER DIVISION OF THE WITWATERSRAND SYSTEM



**LEGEND**

- |                        |                      |     |   |
|------------------------|----------------------|-----|---|
| 1. Virginia            | 14. Venterspost      | —   | Outcrop   |
| 2. President Steyn     | 15. West Rand Cons.  | --- | Concealed boundary (Conjectural in places)                      |
| 3. President Brand     | 16. S. Roodepoort    | f—f | Fault   |
| 4. Welkom              | 17. S. A. Lands      | o6  | Gold Mines from which platinumoids were examined (see Schedule) |
| 5. Western Holdings    | 18. Government Areas | TS  | Transvaal System  |
| 6. Free State Geduld   | 19. Grootvlei        | VS  | Ventersdorp System  |
| 7. Loraine             | 20. E. Daggafontein  | --- | Upper Division of Witwatersrand System with strike and dip      |
| 8. Vaal Reefs          | 21. Viakfontein      | LWS | Lower Division of Witwatersrand                                 |
| 9. Doornfontein        | 22. Sub Nigel        | BC  | Basement Complex  |
| 10. West f Deep Levels | 23. Leslie           |     |   |
| 11. West Driefontein   | 24. Bracken          |     |   |
| 12. Western Areas      | 25. Winkelhaak       |     |   |
| 13. Libanon            | 26. Kinross          |     |   |



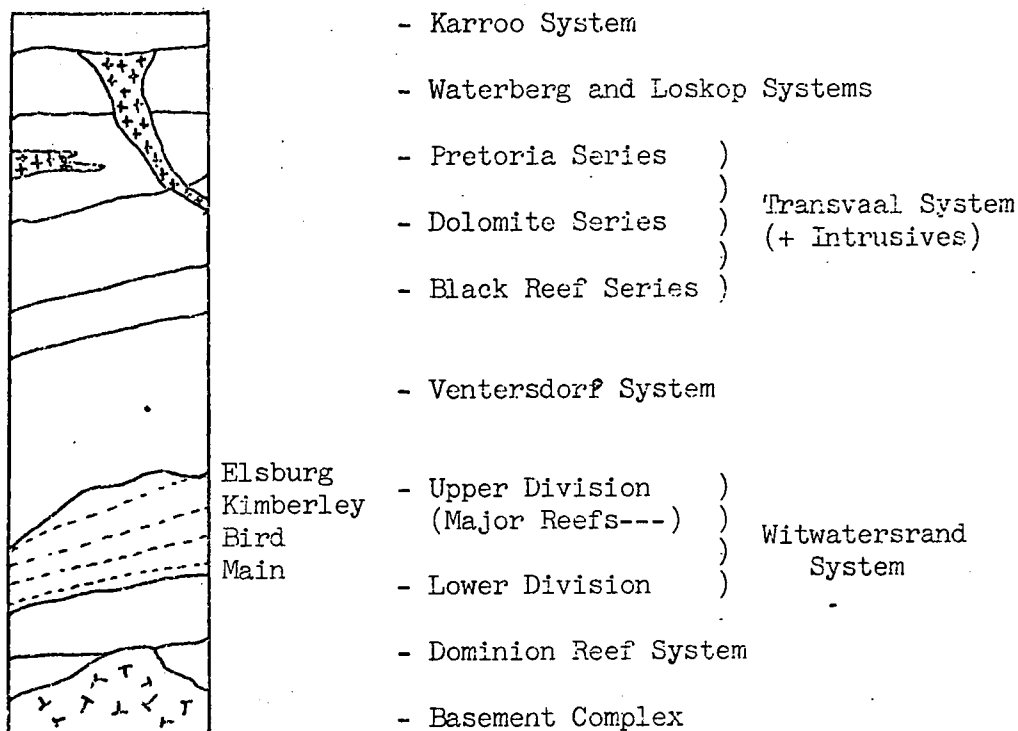
SECTION 1. The Witwatersrand Basin

1. (i) General Geological Features

Within the Witwatersrand Basin, the oldest rocks of the succession belong to the Dominion Reef system, resting directly on the Basement Complex. This system is overlain successively by the rocks of the Witwatersrand system, the Ventersdorp system and the Transvaal system, all of which are mutually unconformable. The succession, together with the younger Waterberg, Loskop and Karroo systems is illustrated in diagram 1.

DIAGRAM 1. (After Borchers (1))

Generalised Geological Succession in the Witwatersrand Basin (Not to scale)



The Dominion Reef system consists of a series of acid lavas, with basal sediments which include the gold- and uranium-bearing Dominion

Reef Conglomerate. In some areas, denudation completely removed the rocks of this system and, in these areas, the Basement rocks are in contact with the sediments of the Witwatersrand system. The latter system, some 7,400 metres thick, comprises a lower division,  $\pm$  4,600 metres thick, made up essentially of alternating quartzites and shales, and an upper division,  $\pm$  2,800 metres thick, of quartzites and conglomerates with only one major shale band, the Kimberley shale. It is within this upper division of the Witwatersrand system that the principal auriferous reefs and reef groups occur. These all contain gold and uranium minerals, together with minute quantities of platinoid minerals.

The principal reefs and reef groups can be described briefly as follows:

The Main Reef group occurs near the base of the Upper Witwatersrand formation and includes the Main Reef proper, the Main Reef Leader, the Carbon Leader and the South Reef. All reefs are worked in the central Rand area except the Carbon Leader which is a prominent source of gold in the Carletonville area. The Main Reef group as a whole is of no interest in the Orange Free State goldfields.

The Bird Reef group is found at the top of the Main-Bird series, approximately 900 metres above the Main Reef group. The reefs are worked under the names White Reef and Monarch Reef in the Krugersdorp-Randfontein area of the West Rand, as the Vaal Reef in the Klerksdorp area, and, in the goldfields of the Orange Free State, as the Basal Reef (1).

The Kimberley Reefs, higher in the succession above the Kimberley Shale, are worked in the Evander area at the Leslie, Bracken, Winkelhaak and Kinross mines, in the East Rand area at the Durban Deep goldmine and

also in the West Rand.

The Elsburg Reefs are developed throughout the basin near the top of the Witwatersrand system, but are of economic value in only a few areas, notably at the Western Areas goldmine southeast of Randfontein.

The sediments of the Upper Witwatersrand were overlain during a period of earth movement, erosion and volcanic activity by the rocks of the Ventersdorp system. These consist mainly of andesitic lavas, more than 3,000 metres thick in places, which incorporate localised basal sediments among which the gold-bearing Ventersdorp Contact Reef is notable. Overlying the Ventersdorp system, with marked unconformity, are the thick sediments of the Transvaal system, which once again include a basal, auriferous conglomerate known in this case as the Black Reef. During subsequent geological activity, the Bushveldt Igneous Complex, the Loskop and Waterberg sediments and finally the extensive beds of the Permo-Carboniferous Karroo system, now covering much of the Witwatersrand Basin, were formed. Although some of these younger deposits are of major interest from both an academic and economic viewpoint, they are of little relevance to this thesis.

#### 1.(ii) General Mineralogical Features of the Reefs

The auriferous reefs of the Upper Witwatersrand formation consist in general of well-rounded and well-sorted pebbles of quartz, quartzite and chert set in a fine-grained matrix of quartz and phyllosilicates. The latter are for the most part authigenic and include sericite, muscovite, pyrophyllite and chlorite. The conglomerate matrices also enclose a series of heavy minerals (S.G. > 2.89) remarkable in its variety, though representing only a very minor proportion of the rock as a whole. The minerals are both primary (detrital) and secondary

(authigenic). They occur mainly as rounded grains isolated in the conglomerate matrix and include the following individual species (9):

Algodonite, arsenopyrite, cassiterite, chalcopyrite, chromite, cobaltite, corundum, diamond, euxinite, galena, garnet, gersdorffite, gold, ilmenite, linnaeite, magnetite, millerite, monazite, pentlandite, platinoids, pyrite, pyrrhotite, rutile, sphalerite, thucolite, tourmaline, uraninite, xenotime, zircon.

The minerals of most economic importance are gold, uraninite and, to a relatively minor extent, the platinoid minerals. The nature, mode of occurrence and genesis of gold and uraninite in the reefs have been discussed repeatedly in the literature (3,4,9,10,11,12) and, at present, the majority of interested parties favour a detrital origin for both minerals, although a minority group, led by the late Professor Davidson (12), supports a hydrothermal origin for the Witwatersrand gold. The gold is found mainly as minute particles and veinlets associated with quartz, phyllosilicates and, to a lesser degree, with other heavy minerals in the conglomerate matrix. Uraninite occurs most frequently as rounded grains, although irregular patches and veinlets of secondary uraninite and thucolite (a uraninite alteration product) have been observed (9).

Owing to their extremely low concentration in the reefs, few platinoid particles have been described in situ (4,13). The limited amount of research work carried out on the Witwatersrand platinoids has been on granular concentrates obtained from the mining companies, and a summary of the results of this work is given in the following section.

## SECTION 2. Previous Work on the Platinoid Minerals

The existence of naturally occurring alloys of osmium and iridium has been known since 1805 (14). However, although research has been carried out on placer platinoid minerals (15, 16, 17), and the behaviour of the platinum group elements under artificial melt conditions has been reported (18, 19, 20), few publications are available which deal specifically with the platinoid minerals in the Witwatersrand reefs. The minerals were first noted by Bettel in 1892 (2),\* who succeeded in extracting a sample from the gold ore at the New Rietfontein mine (later to become part of the Rietfontein Consolidated gold mine north of Germiston). The first published account of the Witwatersrand platinoids was by Professor R. B. Young in 1907 (21), who described particles, obtained from the same source as Bettel, as probably detrital constituents of the banket, occurring in rounded and flattened grains and in tabular, six-sided crystals averaging 0.12 mms. in diameter. A paper by Baring Horwood followed in 1912 (22), in which platinoid minerals from the Rietfontein Consolidated mine were described as "certainly of secondary origin", originating in the banket by hydrothermal activity associated with diabase dykes. Baring Horwood included the results of two spectrographic analyses of platinoid concentrates in his work, but no mineralogical data were given.

\* This is uncertain. A letter appeared in the South African Mining Journal of 25th May, 1912 from Mr. Lewis Watkins, in which he claimed to have found platinum group metals in the tailings from the Aristan mine in Klerksdorp in 1888 and 1889.

Since 1912, several publications have appeared which were concerned mainly with the Witwatersrand gold and uranium, but in which some reference was made to the platinoid minerals. Prentice (23) described the method of concentration of the platinoids from the ore and gave mine production statistics for the years 1921 to 1938. He offered no description of the minerals. Liebenberg (4,9) described several platinoid grains in situ associated with pyrite, one grain of which enclosed gold specks. He also recorded the existence of sperrylite in the reefs and cited the rounded shape of this mineral, and of the osmium/iridium alloy grains as evidence that their emplacement in the reefs was detrital. Cousins (24) demonstrated a close correlation between gold, uraninite, the platinoid minerals, pyrite and chromite and concluded that these minerals were concentrated by a similar agency involving gravity control. de Kock (6) identified osmiridium, platiniridium, platinum, sperrylite, cooperite and braggite in concentrates from the western Witwatersrand but, as Cousins pointed out (3), his identification of braggite, a palladium-rich sulphide, was almost certainly incorrect.

In 1964 Koen (5) reported the results of an examination of Witwatersrand platinoid grains in polished section. Although emphasis was laid on the grain shapes and their genetic significance, Koen gave qualitative optical and structural data for one cubic alloy and two hexagonal alloys of osmium and iridium. No analyses of the alloys were carried out, owing no doubt to the lack of suitable facilities at that time, but Koen did suggest that "a detailed study of the (Witwatersrand platinoid) material, using electron microprobe techniques, will undoubtedly provide a wealth of additional information". Hiemstra, in his discussion of Koen's paper (7), did in fact quote the results of a microprobe

examination of one platinoid particle, in which a complex sulpharsenide of Ni, Fe, Co, Ru and Rh was identified.

In the most recent work on the Witwatersrand platinoids, Cousins (3) made a statistical comparison of platinoid assay values from various parts of the Witwatersrand basin. Information concerning the minerals, however, was restricted to a summary of previously published data, together with a brief summary (with acknowledgement) of the preliminary results of the present work.

### SECTION 3. The Scope of the Thesis

Through the efforts of my ex-colleague Mr. C. A. Cousins, and the generosity of the South African gold mining companies, a series of platinoid mineral concentrates was obtained from twenty six gold mines operating around the Witwatersrand basin (see table 1). In addition, a grab sample of platinoid-rich Kimberley Reef ore weighing about three kilograms was supplied from the Bracken gold mine (Map II, no. 24).

The bulk of the practical work on these samples was carried out in the mineralogical section of the Johannesburg Consolidated Investment Co. Ltd. Minerals Processing and Research Laboratory, situated near Germiston in the Republic of South Africa. Facilities were available at the laboratory for polished section preparation, reflected light microscopy, electron probe microanalysis, microhardness determinations and X-ray diffraction studies. In addition, facilities for reflectivity measurements were provided for a short time at the South African National Institute for Metallurgy in Johannesburg.

In defining the scope of the work to be carried out on the samples, clearly the available instrumental facilities were of paramount importance. In addition, the following factors were considered:

There is a paucity of information about the Witwatersrand platinoid minerals and both qualitative and quantitative data concerning the individual minerals and their intergrowths would be valuable.

Variations in the mineralogy and grain size of the minerals from one part of the Witwatersrand basin to another, or from one group of reefs to another have never been investigated. Since the origin of the mineral particles has been the subject of considerable



TABLE IGOLD MINES FROM WHICH PLATINOID MINERAL CONCENTRATES WERE EXAMINED

<u>Gold Mine</u>	<u>Map II - Reference</u>	<u>Reef Group(s) Worked</u>
Virginia	1	Bird
President Steyn	2	Bird
President Brand	3	Bird
Welkom	4	Bird
Western Holdings	5	Bird
Free State Geduld	6	Bird
Lorraine	7	Bird, Elsburg
Vaal Reefs	8	Bird
Doornfontein	9	Main
Western Deep Levels	10	Main, Ventersdorp Contact
West Driefontein	11	Main, Ventersdorp Contact
Western Areas	12	Elsburg
Libanon	13	Main
Venterspost	14	Main, Ventersdorp Contact
West Rand Consolidated	15	Main, Kimberley, Bird
South Roodepoort	16	Ventersdorp Contact
S.A. Lands	17	Main
Government Areas	18	Main, Kimberley, Black
Grootvlei	19	Main, Kimberley
East Daggafontein	20	Main, Kimberley
Vlakfontein	21	Main
Sub Nigel	22	Main
Leslie	23	Kimberley
Bracken	24	Kimberley
Winkelhaak	25	Kimberley
Kinross	26	Kimberley

controversy, such variations (or absence of variation) might be significant.

In any mineralogical investigation it is important, if possible, to examine the minerals in situ and to describe their associations with the other constituents of the rock or ore. However, the extremely low concentration of the mineral particles in the reefs makes negligible the possibility of encountering a representative selection of the platinoid minerals in situ. Work on the in situ minerals would, therefore, be restricted to the examination of a few, chance particles.

It was decided to divide the research work into three parts as follows:

General Mineralogical Examination.

To carry out a general mineralogical examination of platinoid minerals from a wide selection of gold mines, to identify the individual minerals and to describe these minerals as quantitatively as possible. Platinoid mineral concentrates from each of the twenty six gold mines listed in table 1. were available for this purpose.

Examination of the Variations in Platinoid Mineralogy and Grain Size across the Witwatersrand Basin.

To compare, by grain counting methods, the composition and size of platinoid mineral grains from the same reef group and similar geographical locations; from the same reef group but widely separated geographical locations; from different reef groups and different geographical locations. It would have been particularly interesting to compare mineral grains from different reef groups in the same geographical location (i.e. from the same mine). However, although several mines do

extract such minerals (see table 1.), they do so non-selectively, producing a composite concentrate useless for comparative purposes. ah

Owing to the impure and fragmentary nature of many platinoid concentrates, the selection of concentrates suitable for grain counting was limited. After careful scrutiny under the stereomicroscope, the concentrates from the six gold mines listed in table 2 were chosen for comparison.

TABLE 2

PLATINOID CONCENTRATES SELECTED FOR MINERALOGICAL COMPARISON

<u>Gold Mine</u>	<u>Reef Group</u>	<u>Local Reef Name</u>	<u>Map II Reference</u>
Welkom	Bird	Basal	4
Western Holdings	Bird	Basal	5
Free State Geduld	Bird	Basal	6
Vaal Reefs	Bird	Vaal	8
Libanon	Main	Main	13
S.A. Lands	Main	Main	17

Examination of Platinoid Minerals in situ.

To search for platinoid mineral grains in situ and, if successful, to examine the grains with particular reference to their associations with the other reef constituents. The Kimberley Reef grab sample from the Bracken gold mine was obtained for this part of the investigation.

In the descriptions of experimental procedures and results given in the following sections, frequent reference is made to a series of illustrative photomicrographs. These can be found in appendix I at the rear of the thesis.

#### SECTION 4. The General Mineralogy of the Platinoids

##### 4. (i) Experimental Procedures

Most of the work on the platinoid minerals was carried out on granular concentrates. It is appropriate, therefore, before describing the methods employed for the examination of the minerals, to outline the general procedure adopted by the gold mining companies to separate the minute platinoid particles from the ore. The following outline is based on the procedure employed by the Government Gold Mining Areas gold mine, and is considered to be fairly standard.

During the extraction of gold from the crushed ore, the platinoid mineral grains concentrate in the residues of the gold amalgamating barrels. These residues are treated in the following stages:

- (a) The residues are washed over corduroy blankets and riffled-rubber tables to concentrate the heavy minerals.
- (b) The heavy mineral concentrate is panned to remove pyrite, etc.
- (c) Thorough treatment of the concentrate with a powerful magnet is carried out to remove contaminants such as tramp iron (from crusher jaws) and cobaltiferous tungsten carbide (from drill bits).
- (d) The non-magnetic residue is digested with nitric acid, after which only unamalgamated gold and platinoid minerals should remain.
- (e) The gold/platinoid concentrate is treated with sodium cyanide solution to render "rusty" gold amenable to amalgamation.\*

\* A recent edition (1973) of the Anglo American Corporation publication, Optima, recorded that a significant increase in the recovery of "rusty" gold (i.e. gold coated thinly with iron oxide) is obtained simply by treatment with dilute acid (HCl) before amalgamation

All gold is then removed with mercury, and the platinoid mineral concentrate remaining is cleaned with acid, washed and then dried.

The final concentrate should, in theory, be pure but in fact, of the twenty six concentrates examined, most contained between 5% and 15% non-platinoid material, mainly as gold and tungsten carbide, and some concentrates contained a very much higher proportion of impurities.

The effects of the concentration process outlined above on the bulk composition of a platinoid mineral assemblage are considered for the most part to be insignificant. The platinoids are highly resistant to chemical attack (25). However, the magnetic susceptibility of ferroplatinum, a mineral found in minor quantities in the Witwatersrand concentrates, is known to vary with iron content and can be high (26). Whether the scarcity of ferroplatinum in the concentrates is attributable to the magnetic treatment (stage (c)) during concentration can only be determined by examining either the minerals taken directly from the amalgam barrels or those extracted (if any) by the magnet. These minerals are not available for examination.

Following a preliminary examination of the twenty six platinoid mineral concentrates in the raw state under the stereomicroscope (see photomicrographs plate I) a polished section of each concentrate was prepared as follows:

One half of each concentrate was separated by microriffling, washed in benzene and embedded, under pressure, in thermoplastic (Buehler AB 20 - 3400). Preferred orientation, although unlikely with the generally spheroidal platinoid particles, was minimised by mixing the particles with a small quantity of thermoplastic powder before proceeding with the mounting process. The 1 inch diameter mounts were then sectioned with 500 grade alumina on a glass plate,

Brief semipolishing was carried out on a 600 carborundum wet paper lap and the sections were polished on a grooved, lead alloy lap with an aqueous suspension of 0.3 micron alumina. Final polishing for a few seconds on Buehler microcloth with 0.3 micron, then 0.05 micron alumina produced a fairly scratch-free surface of low relief, adequate for microprobe work or hardness and reflectivity measurements.

During a careful examination of each polished section in reflected light, a selection was made of a series of apparently homogeneous particles representative of the individual platinoid minerals. The selection was made on the basis of colour, polishing hardness and qualitative reflectivity. The particles chosen were the largest that could be found. The composition and homogeneity of each particle was then checked under the electron microprobe and, on this basis, each particle was either accepted or rejected for complete mineralogical description. Homogeneous grains of some of the less-common minerals were never found, the minerals always occurring intergrown with other phases. Consequently, the description of these minerals in the results is limited.

After marking the position of each selected particle, by lightly circling with a diamond marker, the following systematic examination was carried out:

#### Optical Examination in Reflected Light.

Using a Leitz Ortholux Pol polarising microscope with daylight-filtered tungsten light and both air- and oil-immersion objectives, the shape, colour, cleavage, apparent reflectivity, bireflectance and anisotropy were noted for each particle.

### Electron Probe Microanalysis.

Under the electron probe, each particle was examined for inhomogeneity and was then analysed quantitatively.

After being cleaned with benzene, the relevant polished sections were coated in groups of three with a thin, conductive layer of evaporated carbon. Standards required for quantitative analysis were coated simultaneously with each group.

The effect of a thin carbon layer on the colour of the platinoid minerals in polished section is interesting. Hiemstra (27) noted that a zinc selenide coating on a platinoid mineral intergrowth enhances the colour contrast between the different phases. A similar interference effect was produced with carbon, although enhancement of contrast is rather limited (photomicrographs 4,5 and 6). Osmium-rich alloys acquire a very pale brown colour which darkens with increasing iridium and/or ruthenium. Ferroplatinum and sperrylite take on a pale pinkish-brown tint and base metal sulphides become chocolate brown. The interference effects were of some assistance in determining grain homogeneity, but only as a supplement to microprobe examination.

Following the application of a conductive film, each of the selected grains was examined and analysed under the electron probe. The relevant instrumental data and techniques are outlined below.

#### Instrument:

Japan Electron Optical Co. (JEOL) J x A - 3 SM.

Electron probe stability (real):  $3.9 \times 10^{-3}$  per hour.

Electron beam size: 1 micron.

Take-off angle: 20 degrees.

Goniometers: Two (20 - 79 degrees two theta), gas flow proportional counters (P.10), with PET, LIF, KAP and Mica crystals.

Chart recorder: monitoring each channel and specimen current.

Scanning electron beam display: four C.R.T. displays monitoring two X-ray signals and backscatter electrons (B.E.I.)

Electron photomicrography: Pentax (35 mm) and Polaroid cameras.

#### Determination of Grain Homogeneity:

High contrast B.E.I's were examined. All elements in each grain were identified by a chart scan. These elements were then measured (30 second counts) on several points across the grain surface.

#### Quantitative Microanalysis:

Spot analysis of each mineral was carried out using 25 KV accelerating voltage, 0.1 microamp. absorbed current, sets of three 20 second counts for each element and standard, and for background at each side of the peaks. Standards and peaks used were the elements: Os ( $L\alpha$ ,  $M\alpha$ ), Ir ( $L\alpha$ ), Pt ( $L\alpha$ ), Ru ( $L\alpha$ ), Fe ( $K\alpha$ ), Co ( $K\alpha$ ), Ni ( $K\alpha$ ) and Zn ( $K\alpha$ ) and the compounds: Galena, PbS, stoichiometric (for  $SK\alpha$ ) and Gallium Arsenide, GaAs, stoichiometric (for  $AsK\alpha$  and  $AsKB_1$ ). Raw data were corrected for background, machine dead time, atomic number, secondary fluorescence and absorption effects using a computer programme adapted from the programme by Mason, Frost and Reed (28). Mass absorption coefficients etc. were those calculated by Dewey, Mapes and Reynolds (29).



Difficulties were encountered in the quantitative determination of rhodium in the presence of ruthenium. Resolution of the Rh  $L\alpha$  and Ru  $L\beta_1$  peaks was impossible and, for minerals containing both elements in significant amounts, rhodium was calculated by difference. In all other analyses, an element total of between 99% and 101% was regarded as acceptable.

#### Reflectivity Measurements.

A Leitz MPV microphotometer attached to an Ortholux microscope was kindly made available for a short time at the National Institute for Metallurgy in Johannesburg. The standard used was a polished silicon carbide block (Leitz). After removal of the carbon film from each section, reflectivity values for the platinoid minerals were determined in air for the wavelengths 480 nm, 546 nm, 589 nm and 656 nm. For unoriented anisotropic sections only  $R_p$  was determined. Throughout the work, the usual precautions were taken to record reflectivity values from level, scratch-free surfaces (30,31). All reflectivity values given in the results are percentages.

#### Microhardness Determinations.

The Vickers microhardness number and range was determined, for each mineral whenever possible, following the procedure described by Young and Millman (32). Conditions were standardised as follows:

Instrument: Leitz Durimet (Miniload) Hardness Tester +  
Vickers Diamond.

Calibration: Manufacturers stainless steel block.

(VHN 566-579 for 100g load)

Temperature: 68 to 72 degrees F.

Indenter lowering time: 15 seconds.

Indentation time: 15 seconds.

Load: 100 grams. For very small grains a 50 gram load was applied.

Orientation of Indentations: Circular.

Distance between indentations: At least one indentation diagonal.

Microhardness values quoted in the results are in  $\text{Kg/mm}^2$

It was noted in Section 4(i) that the platinoid particles were mounted under pressure in thermoplastic. The pressure and temperature applied during mounting were 4,000 lbs/sq.in. and  $160^{\circ}\text{C}$  respectively. Young and Millman (32) reported that a soft mineral, galena, when mounted under these conditions gave anomalously high hardness values. Although the platinoid minerals under investigation are extremely hard and dense, a series of test indentations was made on chalcopyrite, a mineral harder than galena but considerably softer than the platinoids. Grains of chalcopyrite similar in size to the platinoid grains under investigation (100-160 microns) were mounted and polished following the procedure described earlier in this section. A total of ten indentations were then made using a 100 gram load, and the range and mean hardness values determined were compared with the published data for chalcopyrite (33).

	Mean VHN	Range
Chalcopyrite (Test):	210	201 - 216
Chalcopyrite (published):	Not given	195 - 218

Since the values obtained for the test chalcopyrite fall within the published range, the microhardness values obtained for the platinoid minerals mounted in thermoplastic are considered to be valid. Young and Millman (32) noted that "for hard minerals, the temperature-pressure effect is probably negligible, since any difference (in microhardness) due to deformational stress will be less than the probable error of the measured values".

Two difficulties were encountered in the testing of the platinoid particles, viz:-

- X
- (a) Although most particles selected for testing were relatively large (100 - 160 microns) and gave satisfactory results, smaller particles or minerals occurring as small patches intergrown with other phases frequently shattered on indentation even with a 50 gram load. Loads less than 50 grams applied to the hard platinoid minerals yield indentations too small for accurate measurement. Consequently, microhardness values for minerals occurring only as small particles or in intimate intergrowths could not be determined.
- (b) Some hexagonal osmium/iridium alloys have a perfect basal cleavage. Flakes of these alloys in polished section are, in some instances, extremely thin and give anomalously low microhardness values. Thin flakes were therefore avoided for this stage of the work.

#### X-Ray Diffraction Studies.

This final phase in the examination of the platinoid

mineral particles necessitated the extraction of each particle from section, pulverisation of the particle and the determination of d-spacings from a Debye-Scherrer film.

Extraction of each small particle from section was carried out by covering the particle with a film of collodion or rubber solution. The particle could then be prised loose with a sharp needle with little chance of it being lost in the process. Crushing of the platinoid particles proved difficult. A hardened steel percussion mortar was totally inadequate, since many particles were simply embedded, undamaged, in one of the steel surfaces. Success was eventually achieved by hammering the particles between two tungsten carbide drill-bit inserts. Pulverisation was adequate for ball-mount preparation and X-ray powder photography, although films of several of the harder minerals included diffraction lines of tungsten carbide ( $W_2C$ ). For recording of films, a Debye-Scherrer powder camera (57.3 mm. diameter<sup>\*</sup>), a Philips PW 1130 X-ray generator and iron-filtered Co  $K\alpha$  radiation were used throughout. Line measurements were corrected for film shrinkage as described by Azaroff and Buerger (34), and line intensities were graded visually.  $\theta$  to  $d$  conversions were obtained from the tables of Parrish and Mack (35). All d-spacings quoted in the results of this study are in Angstrom units.

\* A 114.6 mm. camera was unavailable. All patterns were fairly simple, however, and d-spacings are considered to be of good accuracy. Some back reflections ( $d < 0.9$ ) were unmeasurable.

4.(ii) Results.

In this subsection, the individual platincid minerals found in concentrates from the auriferous reefs of the Upper Witwatersrand system are described. Intergrowth textures are not discussed in any detail, these being dealt with fully in Section 5. In cases where brittleness, size limitations or intergrowth textures have prevented a full description of some minerals, notes to this effect have been made in the relevant parts of the text.

The platinoid minerals identified and described include seven alloys of osmium and iridium, two alloys of platinum and iron and five arsenide, sulphide or sulpharsenide minerals of the platinum group elements.

A study of the systems of nomenclature proposed for the osmium-iridium alloys leads to some confusion, and several alloys are either poorly defined or have not been defined at all. In 1938, Zvyagintsev (36) proposed that cubic osmium-iridium alloys with 0 to 35% osmium be classified in the native iridium group, that hexagonal alloys with 35 to 50% osmium be called nevyanskite and that hexagonal alloys with 50 to 70% osmium be called sysertskite. Osmium-iridium alloys with osmium > 70% were unknown at that time. In 1961, Lévy and Picot (37), in a paper primarily describing an almost pure natural osmium, applied the name iridium osmifère to the cubic alloys, and osmium iridifère and osmiridium respectively to the hexagonal alloys containing <50 atomic% or > 50 atomic% of osmium. Hey (38), in a critical account of the nomenclature of the natural osmium-iridium alloys, proposed the following system:

Cubic Series

Osmiridium (Os &lt; 32%)

Iridium (unknown in nature)

Platiniridium (Hey gave no composition for this alloy).

Hexagonal Series

Iridosmine (Os &gt; 32%) = Nevyanskite

Osmium (Os ≥ 80%) = Sysertskite

Aoyama (39) described an hexagonal alloy of osmium, iridium and ruthenium, containing 40% Os, 40% Ir and 20% Ru, as ruthenosmiridium. Uytenbogaardt and Burke (40), who for the most part employ the system of nomenclature proposed by Hey in their textbook, use the name rutheniridosmium for Aoyama's mineral in deference to its hexagonal structure. For Hey's iridosmine, they use the more explicit name iridosmium. Snetsinger (15) described an osmium-iridium alloy, containing 29.8% ruthenium, as iridosmine, giving no recognition to its high ruthenium content. In 1972, Cabri (41) published a general review of the mineralogy of the osmium-iridium alloys and of the osmium-iridium-ruthenium alloys. He concluded firstly that a general system of nomenclature be proposed for these natural alloys and secondly, that a miscibility gap probably exists in the natural Os-Ir-Ru system, basing this latter conclusion on published data for the synthetic alloys (18,19).

Harris and Cabri (42, personal communication) have proposed a system of nomenclature for the Os-Ir alloys and the Os-Ir-Ru alloys, in which they modify the system of Hey (38) and define all the alloys in terms of structure and composition.\* It is unfortunate that the new system proposed is complex, requiring very detailed information about the individual minerals. Such information on the platinoids

\* It is unknown to the writer if the nomenclature has been accepted by the I.C.M.M.N. or publicised. The present writer's reference to the work is therefore confidential and not for publication.

is frequently impossible to obtain owing to their small grain size and complex intergrowth textures.

However, the description of the Witwatersrand platinoid minerals given in this section is fairly comprehensive. The platinoid alloys identified are listed in table 3, together with the system in which they crystallise, and their compositional limits. The system of nomenclature used in the table and in the mineral descriptions is based extensively on the system proposed by Hey as modified by Uytendogaardt and Burke and supplemented by Harris and Cabri (42). The system has been extended here to include the alloys of platinum and iron and the alloys found in the Witwatersrand concentrates which have not previously been defined either in previous publications or by Harris and Cabri.

In table 4, the arsenides, sulpharsenides and sulphides of the platinum group metals identified in the concentrates are listed. Where possible, established names are used for these minerals, but minerals of uncertain nomenclature are described according to their chemical composition, possible names being discussed in the appropriate part of the text.

TABLE 3

PLATINOID ALLOY MINERALS

<u>Mineral</u>	<u>Symmetry</u>	<u>Composition (Atomic %)</u>
Osmium	Hexagonal	Os $\geq$ 80% of the total elements
Iridosmium	Hexagonal	Os < 80% of (Os + Ir) with no other element > 10% of the total
Rutheniridosmium	Hexagonal	Os < 80% of (Os + Ir + Ru) Ru 10% to 80% of (Os + Ir + Ru) No other element > 10% of the total
Osmiridium	Cubic	Ir < 80% of (Os + Ir) No other element > 10% of the total
* Ruthenosmiridium	Cubic	Ir < 80% of (Os + Ir + Ru) Ru > 10% of (Os + Ir + Ru) No other element > 10% of the total
* Iridium	Cubic	Ir > 80% of the total elements
* Rhodiridium	Cubic	Ir < 80% of (Ir + Rh) No other element > 10% of the total
<sup>x</sup> Ferroplatinum	Cubic	Pt < 80% of (Pt + Fe) No other element > 10% of the total
* Rhodoferroplatinum	Cubic	Pt < 80% of (Pt + Fe + Rh) Rh 10 to 80% of (Pt + Fe + Rh) No other element > 10% of the total

\* Minerals not previously identified in the literature. Most other alloys have been described incompletely.

<sup>x</sup> The nomenclature applied in the literature to the Pt-Fe alloys is far from systematic.



Uytenbogaardt and Burke (40) describe ferroplatinum as a variety of platinum containing 16 - 21% Fe, and polyxen as platinum containing 6 - 11% Fe with some Ir, Os, Rh, Ru. They further describe platiniridium as iridium-rich platinum. Their description of platiniridium is clearly unsuitable.

Cabri (41), in a discussion of the Pt-Fe alloys, indicates that there are probably three distinct Pt-Fe phases, namely  $Pt_3Fe$  (cubic), Pt Fe (tetragonal) and  $Fe_3Pt$  (cubic). The Pt-Fe alloys examined in the Witwatersrand concentrates are consistently isotropic (cubic), and the two alloys described in detail in this section correspond approximately in composition to the formula  $Pt_3Fe$ , one alloy being rhodium-rich. No name for  $Pt_3Fe$  is in general use and, in the descriptions of these alloys, the name ferroplatinum or rhodoferroplatinum has been applied according to the limits of composition detailed in table 3.

TABLE 4

PLATINOID ARSENIDE, SULPHARSENIDE AND SULPHIDE MINERALS

<u>Mineral</u>	<u>Symmetry</u>	<u>Composition (Atomic %) or Formula</u>
Sperrylite	Cubic	$PtAs_2$
Unnamed 1	?	33% Os, 36% Ir, 29% As + minor Ru and Fe
Unnamed 2	?	10% Os, 9% Ir, 10% Ru, 40% As, 27% S + minor Pt, Ni and Fe
Unnamed 3	Cubic	38% Rh, 57% S + minor Os, Ir, Pt and Ru. Poor analysis
Laurite	Cubic	$Ru S_2$

The minerals in table 4 almost invariably occur in intimate association with other platinoïd minerals. Consequently, the descriptions of the minerals given later in the section are in most

cases incomplete.

During grain counting of selected platinoid concentrates (see Section 5), a few small particles were identified semi-quantitatively as platiniridosmium, platinosmiridium and platiniridium. However, owing to the small size and poor surface quality of the particles, no description of these minerals was attempted. A rhodium sulpharsenide rich in cobalt, identified qualitatively by Hiemstra (5), was also identified during the investigation but on one occasion only (see photomicrograph 61). Hiemstra's description of the mineral as "quite abundant" in the Witwatersrand platinoid concentrates is erroneous and can be attributed to the close similarity in optical properties between this mineral and the much more common sulphosalts of osmium and iridium.

## DESCRIPTION OF THE PLATINOID MINERALS

### THE ALLOYS

#### OSMIUM

Homogeneous particles of osmium occur as angular to subangular, hexagonal basal cleavage plates of varying thickness (see photomicrographs 45,46).

#### Optical Properties

##### In air:

Section:	Perpendicular to c-axis	Parallel to c-axis
Cleavage:	Nil	0001 indistinct
Colour:	Pale blue-grey	Pale blue-grey
Bireflectance:	Nil	Indistinct
Anisotropy:	Isotropic	Strong; deep blue-grey to orange-red

The orientation of the grains in section is approximate.

In oil, the properties are similar. Anisotropy parallel to 0001 is vivid with purple-red colours.

The colour of osmium becomes paler with increasing iridium.

Most osmium particles were optically continuous. However, one roughly hexagonal grain consisted of numerous randomly orientated osmium laths.

Composition. Three osmium grains were analysed.

	Grain 1		Grain 2		Grain 3	
	Wt%	At%	Wt%	At%	Wt%	At%
Osmium	97.1	96.8	92.1	92.8	80.3	80.8
Iridium	3.2	3.2	7.3	7.2	17.9	17.8
Ruthenium	-	-	-	-	0.8	1.4
Total	100.3	100.0	99.4	100.0	99.0	100.0

Reflectivity (air). Grain 1 (section perpendicular to c-axis) and grain 3 (section parallel to c-axis) were measured. Exact orientation of sections is uncertain.

		480 nm.	546 nm.	589 nm.	656 nm.
Grain 1. R		62.9	60.1	58.2	55.0
Grain 3	Rp	62.9	61.5	60.3	56.5
	Rq	63.6	62.0	60.8	59.8

Reflectivity increases with increasing iridium.

Microhardness. Grain 1 was tested. On indentation, grain 3 split along the basal cleavage and grain 2 was shattered.

	VHN (Mean)	Range	Load	Indentations
Grain 1	1461	1378 - 1561	100g	12 Pcc*

\* Perfect, concave.

Structure. Identical d-spacings were recorded for grains 1, 2 and 3.

The structure of natural osmium is close to that of pure hexagonal osmium.

hkl	Wits. Osmium d	I*	Pure Osmium (43a) d
100	2.363	M	2.367
002	2.155	M	2.160
101	2.071	S	2.076
102	1.593	MW	1.595
110	1.362	MW	1.3668
103	1.227	MW	1.2300
200	1.183	VW	1.1840
112	1.154	MW	1.1551
201	1.140	MW	1.1416
004	1.081	VW	1.0799
202	1.039	VW	1.0383
104	0.983	VWB	0.9827
203	0.914	VWB	0.9145

\* Visual intensities: S - Strong, M - Medium, MW - Medium weak  
VW - Very weak, B - Broad.

#### IRIDOSMIUM

Homogeneous particles vary in shape from spherical through to subangular. Hexagonal cleavage plates are fairly common. (see photomicrographs 47 - 50).

#### Optical Properties.

##### In air:

Section (approx.)	Perpendicular to c-axis.	Parallel to c-axis
Cleavage:	Nil	Not observed
Colour:	White with blue-grey tinge	Blue-grey tinge is stronger
Bireflectance:	Nil	Distinct
Anisotropy:	Nil	Moderate to strong. Deep blue-grey to orange-red.

All properties are similar but more distinct in oil.

Colour of iridosmium becomes whiter with increasing iridium

Composition. Four iridosmium grains were analysed

	Grain 1		Grain 2		Grain 3*		Grain 4	
	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%
Os	74.6	75.0	75.3	73.8	51.6	49.1	36.6	35.6
Ir	24.0	23.9	24.1	23.4	39.2	36.9	52.0	50.1
Pt	-	-	-	-	2.9	2.7	8.4	8.0
Ru	0.6	1.1	0.6	1.1	4.5	8.1	1.1	2.0
Ni	-	-	0.1	0.3	0.2	0.6	0.3	1.0
Fe	-	-	0.4	1.4	0.8	2.6	1.0	3.3
Total	99.2	100.0	100.5	100.0	99.2	100.0	99.4	100.0

\* Grain 3 forms one half of a twin-like particle similar to those illustrated in photomicrographs 30 and 31. Both halves of the particle were of apparently homogeneous iridosmium. Structural examination was inconclusive.

Reflectivity (air). Grain 1 (isotropic) and grain 4 (anisotropic) were measured.

		480 nm.	546 nm.	589 nm.	656 nm.
Grain 1. R		63.6	62.0	60.8	59.8
Grain 4	Rp	61.7	65.7	67.1	70.4
	Rq	68.2	65.2	68.3	71.7

Reflectivity increases with increasing (Ir + Ru + Pt)

Microhardness. Grain 2 and grain 3 were tested. Grain 1 shattered on indentation and grain 4 split along 0001 cleavage plane. Grain orientations are unknown.

	VHN (Mean)	Range	Load	Indentations
Grain 2	1314	1246 - 1403	100g	10 Pcc
Grain 3	1110	1064 - 1187	100g	10 Pcc

Hardness decreases as (Ir + Pt + Ru) increases

Structure. d-spacings for iridosmium grains 1 and 2 were determined accurately. Poor patterns were obtained from grains 3 and 4 but these confirmed an hexagonal structure similar to grains 1 and 2 and to pure osmium.

hkl	Grain 1	Grain 2	I	Pure Osmium (43a)
100	2.355	2.357	M	2.367
002	2.155	2.155	M	2.160
101	2.066	2.068	S	2.076
102	1.591	1.590	MW	1.595
110	1.361	1.362	MW	1.3668
103	1.232	1.228	MW	1.2300
200	N.O.*	N.O.*	VW	1.1840
112	1.155	1.153	MW	1.1551
201	1.139	1.140	MW	1.1416
004	1.084	1.078	VW	1.0799
202	1.037	1.036	VW	1.0383
104	0.984	0.982	VW	0.9827
203	0.914	0.912	VW	0.9145

\*Not observed

The structures of grains 1 and 2 are virtually identical and are slightly more compact than the structure of pure osmium. As would be expected, variations in the ratio of the similarly size atoms of Os and Ir produce only slight variations in the lattice dimensions of the hexagonal alloys.

#### RUTHENIRIDOSMIUM

Homogeneous particles of rutheniridosmium are mainly subspherical.

Optical PropertiesIn air:

Section (Approx.):	Perpendicular to c-axis.	Parallel to c-axis
Cleavage:	Nil	Not observed
Colour:	White	Same
Bireflectance:	Nil	Indistinct
Anisotropy:	Nil	Deep purple-blue to bronze.

In oil: properties are similar but more distinct.

Composition. Two grains of rutheniridosmium were analysed.

	Grain 1		Grain 2	
	Wt%	At%	Wt%	At%
Os	29.8	22.1	46.5	42.0
Ir	22.0	16.1	39.0	34.8
Pt	12.2	8.8	4.1	3.6
Ru	30.4	42.1	10.1	17.2
Rh	2.1*	2.9	-	-
Zn	2.2	4.7	-	-
Ni	0.4	1.0	-	-
Fe	0.9	2.3	0.8	2.4
Total	100.0	100.0	100.5	100.0

\* By difference.

The presence of Zn in grain 1 is unusual. No other platinumoid particle was found containing Zn even in trace amounts.

Reflectivity (Air). Grain 1 (isotropic) was measured.

	480 nm.	546 nm.	589 nm.	656 nm.
Grain 1.R	66.8	67.1	67.1	67.8

Microhardness. Grain 1 and Grain 2 were tested. Grain 2 was parallel to the c-axis in section.

	VHN (Mean)	Range	Load	Indentations
Grain 1.	1344	1267 - 1436	100g	10 Pcc
Grain 2.	1224	1150 - 1267	100g	7 Pcc

No fracturing of grain 2 along cleavage planes was detected.

Microhardness of rutheniridosmium appears to increase with increasing ruthenium content.

Structure. d-spacings for grains 1 and 2 were measured.

hkl	Grain 1	Grain 2	I	Pure Osmium (43a)
100	2.339	2.354	M	2.367
002	2.138	2.166	M	2.160
101	2.052	2.064	S	2.076
102	1.585	1.587	MW	1.595
110	1.354	1.360	MW	1.3668
103	1.229	1.231	MW	1.2300
200	1.173	1.176	VW	1.1840
112	1.150	1.153	MW	1.1551
201	1.134	1.139	MW	1.1416
004	1.078	1.080	VW	1.0799
202	1.033	1.036	VW	1.0383
104	0.981	0.984	VW	0.9827
203	0.910	0.915	VW	0.9145

Contraction of the lattice of the ruthenium-rich grain 1 is evident when compared with grain 2 and pure osmium

#### OSMIRIDIUM

Homogeneous particles of osmiridium are almost invariably well-rounded and rarely show subhedral crystal outlines (see photomicrographs 50, 53).



Optical Properties. (Orientation unknown)In air and oil:

Colour:	Creamy white. Yellowish against osmium and iridosmium.
Cleavage:	Nil
Bireflectance:	Nil
Anisotropy:	Isotropic

Composition. Two grains of osmiridium were analysed. Grain 1 is extremely close in composition to native iridium.

	Grain 1		Grain 2	
	Wt%	At%	Wt%	At%
Os	1.2	1.1	20.6	20.0
Ir	88.9	79.9	73.9	70.7
Ru	5.6	9.6	4.4	8.0
Ni	1.2	3.5	-	-
Fe	1.9	5.9	0.4	1.3
Total	98.8	100.0	99.3	100.0

In both minerals, the presence of small amounts of rhodium is suspected but could not be confirmed.

Reflectivity (air). Grain 2 was measured.

	480 nm.	546 nm.	589 nm.	656 nm.
Grain 2.R	68.0	69.6	70.3	72.5

Microhardness. Grain 1 and grain 2 were tested.

	VHN mean	Range	Load	Indentations
Grain 1	676	585 - 803	100g	10 Pcc
Grain 2	953	835 - 1064	100g	10 Pcc

Hardness decreases with increasing Ir.

Structure. Identical d-spacings were determined for grains 1 and 2. The structure corresponds fairly well to the pure iridium structure.

hkl	Grains 1 & 2	I	Pure Iridium (43b)
111	2.205	S	2.220
200	1.910	M	1.9197
220	1.351	M	1.3575
311	1.152	M	1.1574
222	1.103	W	1.1082
400	0.957	VW	0.9598

#### RUTHENOSMIRIDIUM

This alloy is similar to osmiridium both in its shape as free particles and in its optical properties in reflected light. It is creamy white in colour and isotropic.

Composition. Two grains were analysed.

	Grain 1		Grain 2	
	Wt%	At%	Wt%	At%
Os	15.3	13.1	0.2	0.2
Ir	55.8	46.9	84.1	71.4
Pt	9.3	7.7	1.1	0.9
Ru	17.1	27.3	12.5	20.2
Rh	1.6*	2.5	-	-
Ni	0.3	0.8	0.6	1.7
Fe	0.6	1.7	1.9	5.6
Total	100.0	100.0	100.4	100.0

\* By difference

Grain 2 is extremely close in composition to rutheniridium, a mineral not described from the Witwatersrand concentrates or identified by previous workers.

Reflectivity (air). Ruthenosmiridium grains 1 and 2 were measured.

Orientation of grains is unknown.

	480 nm.	546 nm.	589 nm.	656 nm.
Grain 1. R	69.4	71.1	71.1	72.6
Grain 2. R	68.3	71.6	71.8	73.0

Microhardness. Grains 1 and 2 were tested.

	VHN mean	Range	Load	Indentations
Grain 1	1027	946 - 1132	100g	10 P
Grain 2	872	792 - 946	100g	12 P

Grain 1, richer in Os and Ru, is harder than grain 2.

Structure. d-spacings were recorded for grains 1 and 2. Both grains are similar in structure and correspond well with pure iridium

hkl	Grain 1	Grain 2	I	Pure Iridium (43b)
111	2.199	2.200	S	2.220
200	1.911	1.904	M	1.9197
220	1.350	1.348	M	1.3575
311	1.152	1.149	M	1.1574
222	1.103	1.099	W	1.1082
400	0.955	N.M.*	VW	0.9598

\* Too diffuse for measurement

### IRIDIUM

No optical distinction could be made between iridium, osmiridium and ruthenosmiridium either as loose grains or in polished section.

Iridium is creamy white in section, yellowish compared to osmium, iridosmium or the platinoid sulphosalts, and is isotropic.

Composition. One grain has been analysed.

	Grain 1	
	Wt%	At%
Ir	89.7	83.6
Pt	3.3	2.7
Ru	6.2	11.0
Fe	0.8	2.7
Total	100.0	100.0

Os was not detected.

It is noteworthy that, according to the proposed nomenclature of Harris and Cabri (41), ruthenium > 10% receives no recognition in this mineral name, whereas when ruthenium > 10% in iridosmine and osmiridium the prefix ruthen- is attached to the mineral name. This seems to be inconsistent.

Reflectivity. No quantitative data were obtained. Visually, the reflectivity of iridium is  $\gg$  osmium,  $>$  iridosmium and approximately equal to osmiridium and ruthenosmiridium.

Microhardness. Grain 1 was tested.

	VHN mean	Range	Load	Indentations
Grain 1	820	777 - 858	100g	7 P

It is notable that the microhardness of this native iridium grain is greater than that recorded for the osmiridium grain 1. Either the minor differences in Ru and Pt, or the orientation of the grains in section seems to be responsible.

Structure. The d-spacings of iridium grain 1 correspond very closely to those of osmiridium and ruthenosmiridium. Relative line

intensities (visual) are the same:

hkl	Osmiridium 1
111	2.199
200	1.905
220	1.348
311	1.151
222	1.103
400	0.957

#### RHODIRIDIUM

Rhodiridium is optically identical to osmiridium, ruthenosmiridium, and iridium. The mineral is isotropic.

Composition. One grain was analysed.

	Grain 1	
	Wt%	At%
Ir	74.5	59.3
Pt	5.4	4.2
Ru	0.4	0.6
Rh	16.7	24.8
Ni	0.9	2.4
Fe	3.2	8.7
Total	101.1	100.0

The contribution of Ru  $L\beta_1$  to the Rh  $L\alpha$  peak is considered to be negligible, and the high analytical total is not accounted for.

Reflectivity (air). Grain 1 (unknown orientation).

	480 nm.	546 nm.	589 nm.	656 nm.
Grain 1. R	68.6	71.2	72.4	73.6

These are the highest reflectivities recorded for any of the platinoïd minerals. The native iridium alloy may show slightly higher reflectance.

Microhardness. Rhodiridium grain 1 was tested.

	VHN mean	Range	Load	Indentations
Grain 1	868	782 - 1003	100g	10 P

The mean hardness number and range are slightly higher than for native iridium.

It was noted during the testing of this grain that the indentations show elastic recovery of up to 20% over a period of several hours. No measurable variations in indentation diagonals could be detected, however, over the two to three minute period required for the measurement of each indentation.

Structure. d-spacings determined for rhodiridium grain 1 indicate a slightly more compact structure than osmiridium, ruthen-osmiridium and iridium. Relative line intensities are similar.

hkl	Rhodiridium 1
111	2.196
200	1.896
220	1.343
311	1.148
222	1.099
400	0.954

#### FERROPLATINUM

Few homogeneous particles of this alloy were found in the Witwatersrand concentrates. The mineral occurs most commonly either finely intergrown with other platinoid minerals or as particles enclosed in a sperrylite or sulpharsenide shell (see photomicrographs 59, 61).

Optical Properties (Unknown orientation).

Air and Oil:

Colour: White. a faint creamy yellow tint is apparent compared with iridosmine, osmiridium, sperrylite or the sulphosalts of Os - Ir.

Bireflectance: Nil

Anisotropy: Isotropic

The Witwatersrand ferroplatinum does not show complete extinction.

Composition. One example of this mineral was analysed. The ferroplatinum formed an intricate intergrowth with a sulpharsenide mineral of osmium and iridium.

	Grain 1	
	Wt%	At%
Pt	73.6	59.6
Fe	5.7	16.1
Os	6.8	5.6
Ir	3.8	3.2
Ru	5.3	8.3
Rh	4.8*	7.3
Total	100.0	100.1

\* By difference.

Semiquantitative analyses of other ferroplatinum grains indicate a considerable variation in the content of Os, Ir and Ru.

No data on reflectivity, microhardness or structure could be obtained. The alloy is cubic with a formula close to  $Pt_3Fe$ .

RHODOFERROPLATINUM

This alloy is extremely rare. Its general mode of occurrence and optical properties are the same as for ferroplatinum. It is isotropic and presumed to be of cubic symmetry.

Composition. One example of rhodoferroplatinum, enclosed in a platinoid sulpharsenide and sperrylite, was analysed.

	Grain 1	
	Wt%	At%
Pt	78.7	57.6
Fe	8.7	22.2
Os	0.2	0.2
Ir	0.7	0.5
Rh	13.5	18.7
Ni	0.3	0.8
Total	102.1	100.0

The high analysis total is unexplained.

No ruthenium could be detected in the alloy.

The alloy formula approximates to  $Pt_3FeRh$ .

Reflectivity (air). Grain 1 was measured.

	480 nm.	546 nm.	589 nm.	656 nm.
Rhodoferroplatinum				
1.R	64.1	66.7	67.5	70.6

Normal ferroplatinum shows slightly higher reflectivity in white light than rhodoferroplatinum.

Microhardness. Grain 1 was tested.

	VHN mean	Range	Load	Indentations
Rhodoferroplatinum 1.	454	420 - 478	100g	4 P

The microhardness range for platinum (unspecified composition) was given by Young and Millman (32) as 229 - 274. The high hardness value of rhodoferroplatinum can only be attributed to the rhodium content of this alloy, since Uytendogaardt and Burke (40) state that the hardness of platinum is lowest for the iron-rich specimens.

Structure. Attempts to obtain a satisfactory powder pattern for rhodoferroplatinum were unsuccessful owing to its close association with other minerals.



THE PLATINOID ARSENIDES, SULPHARSENIDES AND SULPHIDESSPERRYLITE

A few, small angular particles of sperrylite were encountered in the concentrates. However, the mineral occurs most commonly as an outer shell enclosing other platinoid minerals and appears, in some instances, to be replacing those minerals (see photomicrographs 17 - 20, 23). The possibility that the sperrylite shells were deposited around platinoid alloy particles in situ in the reefs cannot be dismissed, although the geochemical environment necessary for such an occurrence would be highly unusual.

Optical Properties.

Colour: White with a grey tinge. In oil and compared with osmiridium, iridium and ferroplatinum, a distinct blue tint is visible. Sperrylite is lighter than the arsenides, and sulpharsenides of osmium and iridium.

The mineral is isotropic.

Only microprobe and X-ray diffraction work was possible on the sperrylite. Hardness tests were unsuccessful owing to grain fracturing.

Composition. Three sperrylite grains were analysed. Grains 2 and 3 form the rim of in situ grain A, described in section 6.

	Grain 1		Grain 2		Grain 3	
	Wt%	At%	Wt%	At%	Wt%	At%
Pt	55.7	32.6	41.3	19.7	31.9	13.7
As	42.0	63.8	37.2	46.4	31.4	35.1
Ru	-	-	6.6	6.1	14.2	11.7
S	0.7	2.6	8.2	24.0	13.3	34.8
Ir	-	-	5.4	2.6	7.6	3.3
Rh	-	-	1.1*	1.0	1.5*	1.2
Co	0.3	0.6	-	-	-	-
Fe	0.7	2.6	0.2	0.2	0.1	0.2
Total	98.9	100.0	100.0	100.0	100.0	100.0

\* Rh by difference.

Grain 1 is a normal sperrylite with the formula  $PtAs_2$ . Grains 2 and 3 are considered to be solid solutions of laurite in sperrylite, although the (As + S) total in each case is excessive for stoichiometric  $RuS_2 + PtAs_2$ .

Structure. A ball mount of sperrylite grain 1 was prepared. Although an exposure of several hours was given, the powder film produced was too light to give accurate values for all except one of the back reflections. The front reflections were measured accurately, however, and show very close correspondence to the published data for sperrylite.

hkl	Grain 1	I	Pure sperrylite (43c)
111	3.440	M	3.43
200	2.980	M	2.98
210	2.665	W	2.67
211	2.430	W	2.43
220	2.104	M	2.11
311	1.794	S	1.801
222	1.720	W	1.719
	?		+ 26 other lines

UNNAMED MINERAL 1. OSMIUM IRIDIUM ARSENIDE

(See photomicrograph 24)

× A mineral corresponding in composition to an osmium iridium arsenide was observed on several occasions, forming a rim around platinoid alloys, and as an intermediate zone between a platinoid alloy core and a sperrylite or sulpharsenide rim in composite, concentrically zoned particles. In some such composite particles, the arsenide of osmium and iridium is finely intergrown with, or grades into a sulpharsenide of osmium and iridium. Small patches of gold are common between the alloy core and the intermediate arsenide zone.

Optical Properties (unknown orientation)

Cleavage: Nil

Colour: In air: Grey-white; with a slight blue tinge compared with the iridium-rich platinoid alloys.

In oil: Pale grey with a distinct blue tinge.

Bireflectance: Distinct in oil.

Anisotropy: Strong. In air: Light grey-blue to dark grey.

In oil: Medium grey-blue to grey-brown.

A number of small crystal aggregates of osmium iridium arsenide were found comprising a mosaic of unoriented, anhedral crystals 3 to 5 microns in diameter. No significant variation in composition was found between one crystal and another.

Composition. One small patch of chemically and optically homogeneous osmium iridium arsenide was analysed.

	Grain 1	
	Wt%	At%
Os	39.8	32.7
Ir	44.6	36.3
As	13.8	28.9
Ru	1.1	1.7
Fe	0.2	0.4
Total	99.5	100.0

From the analysis, the formula for the mineral is  $(\text{Os, Ir})_{2.4}\text{As}$ .

The analysis was checked and seems good, and no error either in measurement or calculation can be found. No reference to an osmium iridium arsenide was found in the literature.

Reflectivity (air). Measurements were carried out on the analysed grain. Only minimum values (Rp) was determined.

	480 nm.	546 nm.	589 nm.	656 nm.
Rp	56.2	55.6	54.6	54.1

The mineral corresponds fairly well to sperrylite in minimum reflectivity (39).

Microhardness. The analysed grain was tested.

VHN mean	Range	Load	Indentations
1025	985 - 1049	50g	4 Pcc.

Structure. Efforts to separate a reasonably pure sample of the arsenide for powder diffractometry were unsuccessful.

In the absence of structural data, no attempt has been made to name the mineral. It possibly represents the pure arsenide end-member

of a series which includes the sulpharsenide described below.

UNNAMED MINERAL 2. OSMIUM IRIDIUM RUTHENIUM SULPHARSENIDE

This mineral was found intimately associated with the arsenide of osmium and iridium and is considered to be closely related. The intergrowths surround, and seem to replace osmiridium or more rarely iridosmium (see photomicrographs 22, 23 and plate X).

Optical Properties (Unknown orientation)

In air and oil:

Colour: Light grey without a blue tint. Sperrylite is lighter in contrast. Colour is slightly darker in oil.

Bireflectance: Not observed.

Anisotropy: Some sections are isotropic, while others show slight to moderate anisotropy. Variations in the As:S ratio are believed to contribute to the variation in anisotropism, but orientation in section is probably the major factor.

Several crystal aggregates of this mineral were seen, similar to those described for the osmium iridium arsenide.

Composition. Phase 1 of the in situ grain B, described in section 6, was analysed.

	<u>Wt%</u>	<u>At%</u>
Os	21.3	10.4
Ir	18.0	8.7
Pt	5.0	2.2
Ru	11.4	10.4
As	32.1	39.9
S	9.4	27.4
Ni	0.4	0.7
Fe	0.2	0.3
	<hr/>	<hr/>
Total	97.8	100.0

The low total probably represents undetected rhodium.

Several grains of the mineral examined semiquantitatively show considerable variations in the As:S ratio and in the relative proportions of Os, Ir, Ru and sometimes Pt. However, no pure sulphide mineral was found.

From the analysis detailed above, an approximate formula for the mineral is (Os, Ru, Ir) AsS. The correspondence, therefore, of this mineral, in both optical properties and composition, to the monoclinic mineral osarsite described by Snetsinger (44) is fairly good. The formula given for osarsite is (Os, Ru, Ni, Ir, Pd, Pt, Rh) AsS. Irasite, described by Genkin et. al. (45) has the formula (Ir, Rh, Ru, Pt) AsS and is isotropic.

Unfortunately, no data were obtained on the reflectivity, microhardness and structure of the Witwatersrand mineral. Damage to the in situ particle was avoided and other examples of the mineral were unsuitable, either in size, polish or intergrowth, for quantitative testing.

#### UNNAMED MINERAL 3. RHODIUM SULPHIDE

Only one occurrence of this mineral was positively identified. The mineral was found as flakes along the 0001 cleavage planes of iridosmium (see photomicrograph 58).

The mineral is white in air with a distinct grey tint. In oil, a faint blue tint is present. Rhodium sulphide is isotropic with

reflectivity <iridosmium, <osmiridium, <sperryllite and > osmium iridium arsenide. No reliable, quantitative data on either reflectivity, hardness or structure could be obtained. A quantitative microanalysis of the mineral gave the following results:

	Wt%	At%
Rh	62.2	37.9
S	29.2	57.1
Os	3.5	1.2
Ir	8.7	2.8
Pt	1.2	0.4
Ru	1.1	0.7
Total	106.0	100.1

The high element total is attributed to the poor surface quality and to the thinness of the analysed mineral flake.

Similarity in optical properties is apparent between this rhodium sulphide and Hollingworthite,  $(\text{Rh,Pt,Pd})(\text{As,S})_2$ , described by Stumpfl and Clark (46). However, the absence of arsenic suggests that the mineral is the rhodium equivalent of laurite,  $\text{RuS}_2$ .

#### LAURITE

Several grains of laurite were identified in the Witwatersrand concentrates (see photomicrographs 40 and plate X). The mineral is white with a pale grey-blue tint (darker in oil), isotropic and extremely hard; hardness  $>$  osmium,  $\gg$  iridosmium and  $\gg$  osmiridium. In composition, the Witwatersrand laurite is similar to the Merensky

Reef laurite and to some laurites described by Leonard et. al. (47). Ruthenium and sulphur are the predominant constituents and osmium, iridium and platinum were detected in minor amounts. No structural evaluation of the Witwatersrand laurite was possible.



SECTION 5. Variations in Platinoid Mineralogy and Grain  
Size across the Witwatersrand Basin

5. (i) Experimental Procedures.

Platinoid mineral concentrates from six gold mines (see section 3, table 2) were chosen for comparison. The selection of samples suitable for grain counting was subject to the following limitations:

The samples must originate in mines exploiting only one reef group.

The mineral grains in each sample must not have been artificially fragmented. Many samples, among which the East Daggafontein, Government Areas and Venterspost gold mine concentrates are notable examples, have clearly been fragmented during crushing and concentration. Such samples are unsuitable for the description of mineral intergrowths and natural grain sizes and were rejected for grain count purposes.

The samples must be free from excessive contaminant material such as gold, tungsten carbide and tungsten lamp filaments. Very impure concentrates were obtained from the Vlakfontein, Sub Nigel and Grootvlei gold mines. Severe acid treatment to remove the non-platinoid impurities was specifically avoided since the effects on the overall mineralogy of the concentrates could not be predicted.

The mineral and grain size distributions for each of the six samples were determined by grain counting. Because the identification

of many of the minerals is impossible microscopically, grain counting was carried out under the electron microprobe. A highly automated approach to probe counting, for the modal analysis of a simple silicate assemblage, was described by Keil (48). However, the lack of facilities and above all the mineralogical complexity of the platinoid concentrates dictated a manual approach to the grain counting, and the basic procedure described by Barringer (49) was followed. By moving the polished sections over an imaginary 36 x 36 grid ( $\frac{1}{2}$  mm intervals), a total of 1296 points were counted in each section. The intersection of the cross-hairs incorporated in the probe optical microscope was used as the reference point. A total of 2799 platinoid particles were intersected, made up of between 450 and 500 particles in each of the six sections and the properties of every particle were recorded according to the following scheme:

#### Intergrowth Texture.

Each particle was placed into one of five categories according to the intergrowth texture it exhibited.

Homogeneous particles.

Concentric intergrowth.

Linear intergrowth.

Inclusions.

Irregular intergrowth.

Definitions of each textural category are given in the results (section 5(ii)).

Composition.

Accurate chemical and structural analyses of 2799 particles, many comprising two or more minerals, were clearly impractical. Instead, each mineral in every grain was identified on the basis of semiquantitative chemical composition. For the most part, the system of nomenclature detailed in section 4, table 3 was used, but, for the distinction between iridosmium and osmiridium (based on structure in table 3), Hey's definitions of iridosmium and osmiridium were applied, taking 32% Os (of Os + Ir) as the point of division between the two minerals.

The classification of platinoid alloys close in composition to a phase boundary was of relatively low accuracy.

Similarly, the accuracy with which ruthenium- and rhodium-rich alloys were classified is limited. High Z.A.F. correction factors are involved in the microprobe determination of these elements in a matrix of the heavy platinum group elements, as the following example demonstrates:

e.g.	<u>Wt% (Uncorrected)</u>	<u>Wt% (Corrected)</u>
Os	45.5	46.5
Ir	38.4	39.0
Pt	4.0	4.1
Ru	<u>3.6</u>	<u>10.1</u>
Fe	0.8	0.8
		<hr/>
		100.5

Absorption of Ru  $L\alpha$  at a takeoff angle of  $20^\circ$  is strong, and is the main reason for the high correction factor necessary. Notwithstanding the limitations involved, identification of the platinoid minerals can be carried out with much higher precision under the probe than could be achieved using the microscope. As noted earlier, some minerals can not be resolved at all optically. Photomicrographs 7 and 8 illustrate the point well.

The semiquantitative microanalysis of each mineral was carried out by accumulating counts for 20 seconds at one point on the mineral for the elements Os, Ir, Pt, Ru and Fe. Rh, S and As were looked for and determined when present. Inclusions of base metal sulphides and silicates were easily distinguished on the B.E.I. scanning image and these minerals, together with the sulphides, sulpharsenides and arsenides of the platinoid elements, were classified according to their major constituent elements. Counts on standard elements were taken at ten-particle intervals and background values for elements and standards were recorded visually from the ratemeters. Microprobe operating conditions were standardised for each mineral, at 25 KV accelerating voltage, 0.1 microampere sample current. For the platinoid alloys, observed concentrations of the constituent elements were corrected by comparison with an alloy of similar composition described in section 4.

#### Grain Shape.

No statistical determination of roundness or sphericity were carried

out. Only the general features of the platynoid grain shapes are discussed in the results, reference being made to photomicrographs in which grain shapes of particular interest are illustrated.

#### Grain Size.

To compare the grain size distribution of the platynoid particles from one concentrate to another, the nominal sectional diameter ( $d_n$ ) of each particle was determined (50). This size parameter, more realistic than sieve size, is equivalent to the diameter of a circle equal to the area of the particle in section and is given by the formula:  $d_n = L \times B$ , where  $L$  is the maximum diameter of the particle in section, and  $B$  is the diameter at right angles to  $L$ . A graticule in the ocular of the microprobe optical system allowed measurements of length to be made to within one micron. A small error is introduced by the measurement of particles in section, rather than as loose grains in profile. Packham (51) has described a laborious procedure for the correction of this error using cumulative size frequency distribution curves. However, the error is small and, since the grain size distribution of the six concentrates was determined for the purposes of comparison, a correction for sectioning error can be safely ignored. The possibility of preferred orientation affecting the particle size measurements was considered. Some tabular particles, notably of osmium and iridosmium, do occur in the concentrates and these could show preferred (maximum area) orientation in section, particularly if mounted in a cold-setting liquid

resin. With the mounting process described in section 4(i), however, orientation of particles is considered to be close to random.

#### 5.(ii) Results.

##### Platinoid Mineral Intergrowths.

Results were provided by the mining companies of analyses of platinoid mineral batches typical of those from which the mineralogical concentrate samples were taken. These results are given in table 5. All values are weight %, corrected to 100% for the platinum group elements.

TABLE 5.

##### Typical Platinoid Mineral Batch Analyses

Mine	Reef	Os	Ir	Pt	Ru	Rh
Welkom	Bird	33.4	32.8	17.8	14.4	1.6
Western Holdings	Bird	38.1	36.9	9.2	14.5	1.3
Free State Geduld	Bird	41.3	36.6	8.2	12.8	1.1
Vaal Reefs	Bird	42.9	36.4	7.2	12.7	0.8
Libanon	Main	36.6	35.5	10.8	16.2	0.9
S.A. Lands	Main	44.0	39.5	5.5	10.6	0.4

A total of 2799 platinoid mineral grains were examined from the six gold mines. Of these grains, 1925 (68.8 vol.%) were monomineralic and each grain has been classified according to composition under the appropriate mineral name (see table 7). The remaining 874 grains (31.2 vol.%) comprise two or more intergrown mineral phases

which differ in composition to varying degrees. These grains have been classified, in the first instance, according to the type of intergrowth texture they exhibit (see table 6), and secondly according to the minerals they comprise (see table 8 + notes). Percentage figures given in tables 7 and 8 are corrected to the nearest whole number, reflecting the semiquantitative nature of the mineral identifications. Correction of volume % to weight % is impossible owing to the uncertainty in density of the minerals or mineral grains.

Including the monomineralic particles, the types of intergrowth texture encountered are defined as follows:

No Intergrowth. Mineral grains in which no inhomogeneity in composition could be detected either optically (under carbon coating) or with the electron microprobe (see photomicrographs, plates VII and VIII).

Concentric Intergrowth. Grains which comprise a central core surrounded or partly surrounded by one or a succession of zones of different composition (see photomicrographs, plates II, III, IV and X).

Linear Intergrowth. Three sub-types can be recognised. Photomicrographs 6, 25, 26 and 27 show grains in which two mineral phases form alternating, more or less parallel, curving bands with a eutectoid-like texture.

Photomicrographs 28, 29, 30 and 31 show grains in which phase boundaries are straight. Many of these grains are similar in appearance (but not in composition) to simple twins. Photomicrograph 32 illustrates a structural intergrowth between osmium-iridium sulpharsenide and iridosmine, the

sulpharsenide forming stringers along crystallographic directions of the iridosmine alloy. The latter texture is rare.

Inclusions. Grains in which small mineral inclusions or empty cavities are enclosed (see plate VI).

Irregular Intergrowth. Grains in which the interrelationship between phases is haphazard, with no visible regularity in the orientation of the interphase boundaries. Some grains are undoubtedly of a fragmentary nature. Other grains were found in which four or five distinct zones, all of iridosmine of slightly different composition, are intergrown.

Examples of grains in which two types of intergrowth are present were seen rarely (see photomicrographs 41, 42, 43 and 44).



TABLE 6

Intergrowth Textures Exhibited by the Witwatersrand Platinoid Grains

Intergrowth Texture	Gold Mines and Volume % of Platinoid Grains							
	Welkom	Western Holdings	Free State Geduld	Vaal Reefs	Libanon	S.A. Lands	Mines Combined	
Homogeneous	63.7	65.9	71.3	67.1	72.9	72.1	68.8	
Concentric	23.4	19.6	17.4	18.3	14.3	20.0	18.9	
Linear	4.2	5.3	4.2	5.9	2.9	3.9	4.4	
Inclusions	3.0	1.7	2.7	4.2	3.3	2.2	2.8	
Irregular	5.7	7.5	4.4	4.5	6.6	1.8	5.1	
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
Grains Counted	474	469	477	471	453	455	2799	

TABLE 7

Mineralogy of the Homogeneous Platinoïd Grains

Mineral	Gold Mines and Volume %						Mines Combined
	Welkom	Western Holdings	Free State Geduld	Vaal Reefs	Libanon	S.A. Lands	
Osmium	10	9	13	11	5	9	10
Iridosmium	62	64	65	67	63	74	66
Rutheniridosmium	5	5	3	5	7	3	5
Platiniridosmium	2	1	1	1	1	2	1
Osmiridium	12	16	15	14	18	9	14
Ruthenosmiridium	1	2	1	1	2	Trace	1
Platinosmiridium	1	1	Trace	1	1	1	1
Iridium	1	1	-	-	Trace	2	1
Rutheniridium	1	-	2	Trace	1	-	Trace
Platiniridium	Trace	-	-	-	-	Trace	Trace
Sperrylite	3	1	-	Trace	2	Trace	1
Pt-Fe alloys	2	-	-	Trace	Trace	Trace	Trace
Os-Ir sulpharsenides	-	-	-	Trace	Trace	-	Trace
Total	100	100	100	100	100	100	100

TABLE 8

Mineralogy of the Platinoid Grains with Concentric Intergrowth Texture

Grains Comprising	Gold Mines and Volume % of Grains						Mines Combined
	Welkom	Western Holdings	Free State Geduld	Vaal Reefs	Libanon	S.A. Lands	
Alloys only*	80	85	70	77	66	44	71
Alloys + Os, Ir, As, S*	10	9	17	6	13	14	11
Alloys + Os, Ir, As, S* + Sperrylite	5	3	8	3	7	5	5
Alloys + Sperrylite	5	3	4	12	10	37	12
Fe-Pt + Sperrylite	Trace	-	Trace	Trace	2	-	Trace
Alloys + Ru, S, Pt, As	-	-	1	2	2	-	1
Total	100	100	100	100	100	100	100

\* No distinction is made between the alloys of osmium and iridium, or between the arsenides, sulpharsenides and sulphides of osmium and iridium.

The mineralogy of the platinoid grains showing linear and irregular intergrowth textures, or of those grains with inclusions have not been tabulated. These grains are consistent in composition from one concentrate to another and are described, for the six concentrates in general, in the following pages.

Alloys of the platinum group elements make up a large majority of the particles exhibiting concentric intergrowth textures. In these particles, the element osmium is always more abundant in the core than elsewhere and decreases in quantity in successive zones outwards. Ir is antipathetic to Os while Pt, Ru, Rh and Fe either increase towards the peripheral zones or remain in the same proportions. A good example of such an intergrowth is shown in photomicrograph 16. The particle comprises an hexagonal osmium core, an intermediate iridosmium zone and a shell of osmiridium. The shell, although of a cubic alloy, has an hexagonal outline dictated by the internal structure of the particle, an effect which has been noted previously by Koen (5). Photomicrographs 7 and 8 show a similar particle, but in which the outer zone is rutheniridosmium. Photomicrograph 60 illustrates a particle in which osmium, iridosmium and rutheniridosmium are intergrown concentrically. The outer rutheniridosmium phase has a distinct fibrous texture not uncommon in the Ru-rich, platinoid alloys.. The osmium or iridosmium core is not always hexagonal, as is illustrated in photomicrographs 10 and 15 in which round and irregular forms respectively are exhibited. In other grains, the central osmium crystal is incompletely formed

(see photos. 7, 12, 13) and several particles were seen in which the core forms a typical skeletal crystal. Photomicrographs 4 and 5 show a grain in which the composite counterpart of a negative crystal occurs within an osmium core. The composite comprises ferroplatinum and an unidentified iron nickel sulphide. Several grains of similar texture were found (photo. 33 and photos. plate X). Diffuse boundaries between the core and surrounding phases are uncommon. A compositional gradient exists in such grains, in which one element (usually ruthenium) gradually increases in quantity from the core outwards (see photo. 15).

Concentric intergrowths, in which platinoid alloys and other platinoid minerals take part, are not uncommon. The alloys invariably form the core of such grains and may be surrounded and sometimes replaced by sperrylite (see photos. 17, 18, 19, 20). A thin Rh-rich reaction (?) rim between ferroplatinum and sperrylite was seen in some particles (see photo. 59). Other minerals found surrounding and replacing an alloy core were the arsenides and sulpharsenides of Os and Ir (see photos. 22, 24 and Plate X), and one grain, in which both sulpharsenide and sperrylite phases form successive layers around ruthenosmiridium, is shown in photomicrograph 23. It is interesting to note that non-alloy minerals were never found in contact with, or replacing osmium. This infers that the formation of the non-alloy mineral is dependant on the presence in the alloy it surrounds or replaces, of significant amounts of Pt or Ru, elements notably minor in the osmium alloy.

Linear intergrowths occur in the Witwatersrand minerals almost

exclusively between two or, more rarely, three alloy phases.

Furthermore, the phases are usually of the same mineral, iridosmium, the only distinguishing features between the phases being variations in the Os:Ir ratio or in their relative proportions of Pt or Ru.

In general, one phase is close to osmium in composition and optical properties, and the other phase is more iridium-rich and whiter in colour. Particles in which osmium or osmiridium is intergrown with iridosmium are not very common. Particles comprising a linear intergrowth of alloy and non-alloy minerals are even more uncommon.

Various examples of linear intergrowth textures are shown in photos.

6, 25, 26, 27 ("eutectoid" texture), photos. 28, 30, 31 (twin-like texture) and photos. 32, 57 (alloy/non-alloy intergrowths).

Inclusions were found only in the platinoid alloy minerals.

Inclusions identified most often in all concentrates were of Os-Ir sulpharsenide, laurite, calcium iron silicate\* and an anisotropic iron nickel sulphide. Inclusions identified on only one or two occasions in each concentrate consisted of chalcopyrite or a rare earth phosphate, probably monazite. Undoubtedly, many base metal sulphide, phosphate and silicate particles appearing as inclusions in section represent material filling embayments in the platinoid grain surfaces. However, particles of sulpharsenide, laurite and iron nickel are undoubtedly true inclusions and form an inherent part of the grains

\* With moderate/minor amounts of Mg and Al. It is probably phyllosilicate in most cases, similar to the minerals found in the matrix of the conglomerates.

in which they are enclosed. Osmium iridium sulpharsenide was found as small, spherical bodies in iridosmium (see photo. 38); laurite was found as angular blebs in osmiridium (see photo. 40) and in iridosmium (see plate X). The unidentified iron nickel sulphide was also found as spherical inclusions, in osmiridium (see photo. 36), and intergrown with ferroplatinum as a hexagonal "negative crystal" (see photos. 4, 5, 33). The base metal sulphide bears some optical resemblance to pyrrhotite, though its colour, pale yellowish green-grey, is unusual. It is comparable in approximate composition to an unnamed iron nickel subsulphide,  $(\text{Fe,Ni})_2\text{S}$  described by Stumpfl (8), which occurs intergrown with platinoid minerals in the ultrabasic rocks of the Bushveld Igneous Complex.

Platinoid particles in which one or more small cavities occur have been classified under "inclusions" in table 6. The cavities are sometimes hexagonal and were probably formed when an hexagonal osmium crystal was dislodged at some point in the particle's history (see photos. 3, 35). In other particles, spherical or tubular cavities were seen, almost certainly after gaseous or liquid inclusion in some cases, and of a typical vesicular nature (see photos. 37, 39). No distinct lineation of the tubes is apparent.

Irregular intergrowths consist almost exclusively of the platinoid alloys. Individual particles are usually monomineratic, the intergrowth texture being created by irregular zones of slightly different composition. The rare particles in which alloy and non-alloy minerals

are intergrown are all certainly fragments broken from larger particles of unknown texture.

The majority of intergrowth textures exhibited by the Witwatersrand platinoid grains is considered to have been created during crystallisation in a magmatic environment. The presence of vesicular and eutectoid-like textures and negative crystal structures are fairly convincing. The relationships between the platinoid arsenides and sulpharsenides with the alloys, however, are of an uncertain nature. The texture is certainly one of replacement in some particles, while in others (photos. 17, 23), sperrylite forms a well-defined shell of uniform thickness. Although the relationships may be primary, the possibility that both the sperrylite and the sulpharsenides are secondary minerals deposited in the reefs cannot be dismissed.

#### Platinoid Grain Shapes.

The shapes exhibited by the Witwatersrand platinoid grains are diverse. According to the roundness scale of Pettijohn (52), the shapes range from sharply angular and generally hexagonal, through to well-rounded (see photos. 45, 46, 47, 48, 49, 50). As was noted by Koen (5), concave curves and reentrant angles frequently complicate the grain outlines and many examples of such outlines are illustrated in plates I - X. Among the osmium and iridosmium alloys, hexagonal outlines are commonplace but, although osmiridium is fairly abundant in the concentrates, anything remotely resembling a cubic outline is rare (see photo. 53). Several particles have outlines which vary from



angular to round on different parts of the surface (see photos. 1, 54).

The shapes of the Witwatersrand platinoids and their genetic significance have been discussed by Koen (5) and Cousins (3). Koen concluded that the great variety of grain shapes to be found in a single concentrate "casts serious doubt on the popular view that the roundish grains were shaped by aqueous rounding". He quoted as evidence the facts that some grains appear heavily abraded while others do not, and that some of the well-rounded particles are too small to have been abraded in natural waters. He further stated that features such as embayments, concave curves and reentrant angles could hardly be the result of aqueous attrition, and that many shapes may be those assumed by the grains on crystallisation or those produced by chemical action. Cousins supports the latter hypothesis.

It is not intended to discuss in detail the shapes of the particles or their genetic significance in this thesis. However, some comments based on the observations of the writer are of interest.

The anomalies in degrees of rounding exhibited by platinoid mineral grains of similar size and composition within the same concentrate have five possible explanations.

- (a) The distance of transportation or degree of reworking of the particles has varied from one grain to another. This is highly unlikely.
- (b) Differences in grain hardness, or resistance to chemical attack have influenced the roundness of individual particles. Differential

rounding of the platinoid particles would certainly be expected, and the lack of crystal outlines in particles of the relatively soft osmiridium alloy has already been noted. However, the presence of both sharply angular and well-rounded particles of the same mineral in the same concentrate can not be explained either by differential aqueous attrition or by selective chemical attack (see photos. 47 to 50).

- (c) Dislocation along mineral boundaries, or irregular fracturing of larger particles has produced some of the angular, subangular and rounded homogeneous grains found in the concentrates. That dislocation has taken place is convincingly demonstrated in photomicrographs 48 and 55. The grains illustrated were undoubtedly composite particles at some stage in their history. The dislocation of hexagonal crystals (probably osmium) has produced hexagonal inlets in the remaining particles, the dislodged crystals now existing as monomineralic, angular/subangular particles such as those shown in photomicrographs 45 and 46. Photomicrograph 54 shows a grain which probably formed half of a twin-like linear intergrowth. The partial disintegration of the iridosmium particle in photomicrograph 51, if completed, would produce numerous, small angular particles unrelated to the subangular hexagonal particle from which they derived.

Fracturing has also produced rounded particles in the concentrates. Photomicrograph 17 shows a well-rounded iridium

particle around which only a remnant of a sperrylite mantle remains. While the rounded outer surface of the remnant might have been produced by attrition, the roundness of the alloy could be a primary feature acquired on crystallisation. Conversely, if it is assumed that the alloy was rounded during aqueous or aerial transportation, then the sperrylite must be authigenic. Photomicrograph 34 shows an osmiridium particle from which a round iridosmium inclusion is partially detached. Numerous, small, concave curves on the surface of the particle indicate that several such inclusions have already been lost and now exist, in the reef or concentrate, as rounded particles too small, according to Koen, to have been rounded by aqueous attrition. Reentrant angles and concave curves in other grain outlines could also be explained assuming that a process of fracturing or dislocation has taken place. The particle in photomicrograph 56 shows a remarkable resemblance to the one shown in photomicrograph 19, except that the latter retains a partial coating of sperrylite. The particle in microphotograph 52 may have had a peripheral sperrylite zone at one time, though the radial cracks are more likely to have been formed during cooling and crystallisation.

The point in their history at which dislocation or fracturing of these platinoid particles occurred is unknown. It may have been during transportation, reworking or during the extraction and

concentration of the particles from the ore. The latter possibility is considered to be the most likely one in the case of many particles, and many concentrates were rejected as unsuitable for grain counting for just this reason.

- (d) The particles possess their original outlines acquired on crystallisation, which outlines have subsequently undergone little or no modification. If shape and intergrowth textures are considered together, possible examples of such particles can be found. Photomicrographs 13 and 14 illustrate particles comprising a core of osmium enclosed in an iridosmium shell. In each case, the thickness of the shell is remarkably consistent and no evidence of attrition, in the form of differential thinning at the grain corners, can be found. The possibility raised by Cousins (3) that such zoning was produced chemically, either by leaching or accretion is improbable. If leaching of the osmium alloy is assumed, it must be further assumed that Os has been leached, resulting in a concentration of Ir, Ru, Pt and Fe in the peripheral zone. Although chemical data are sparse on the behaviour of these alloys under natural conditions, Os is the most chemically resistant of the elements involved (53) and is unlikely to have been preferentially leached. Furthermore, widespread leaching or chemical accretion does not explain the presence in a single concentrate of homogeneous particles and particles exhibiting linear, irregular and concentric intergrowth textures.

Photomicrographs 6, 18, 25, 59, in particular, illustrate grain shapes unlikely to have been formed by attrition or fracturing. Corrosion or replacement in situ may have been appreciable or the shapes may be similar to those acquired on crystallisation.

- (e) Mechanical deformation of the platinoid particles has taken place in situ in the reefs. This final possibility is discussed in section 6.

It is concluded from a general examination of the Witwatersrand platinoid grain shapes that, although many grains may have been shaped by aqueous or aerial attrition and may have been subjected to chemical corrosion or accretion in situ, no concrete evidence can be found to show that these processes had more than a minor effect on the grain shapes. Some particles appear to exhibit outlines they acquired on crystallisation, and this could be equally true of many round, nodular and irregularly shaped particles shown in the photomicrographs.

Dislocation of mineral grains from composite particles, either naturally during transportation, or artificially during metallurgical concentration, has played some role in the formation of the present grain shapes. It is considered therefore that an angular or sub-angular grain outline has doubtful genetic significance and that the presence of some concave curves and reentrant angles is not remarkable in the detrital platinoid particles. Furthermore, it

is believed that the use of the rounded outlines of some homogeneous platinoid particles as positive proof of a detrital origin or, in the case of extremely small grains, as evidence against a history of aqueous attrition is unjustified.

#### Grain Size Distribution of the Platinoid Minerals.

For each of the six concentrates, a cumulative size frequency distribution curve has been drawn. Grain size (dn - nominal sectional diameter) has been plotted against cumulative number percentage, equivalent to volume percentage for the grain count procedure followed. Size range midpoints used in plotting the curves are based on a  $\sqrt[4]{2}$  scale adapted from the Udden  $\sqrt{2}$  scale (52), the size intervals being selected such that no single size range includes more than  $\frac{1}{3}$  of the total grains measured (51).

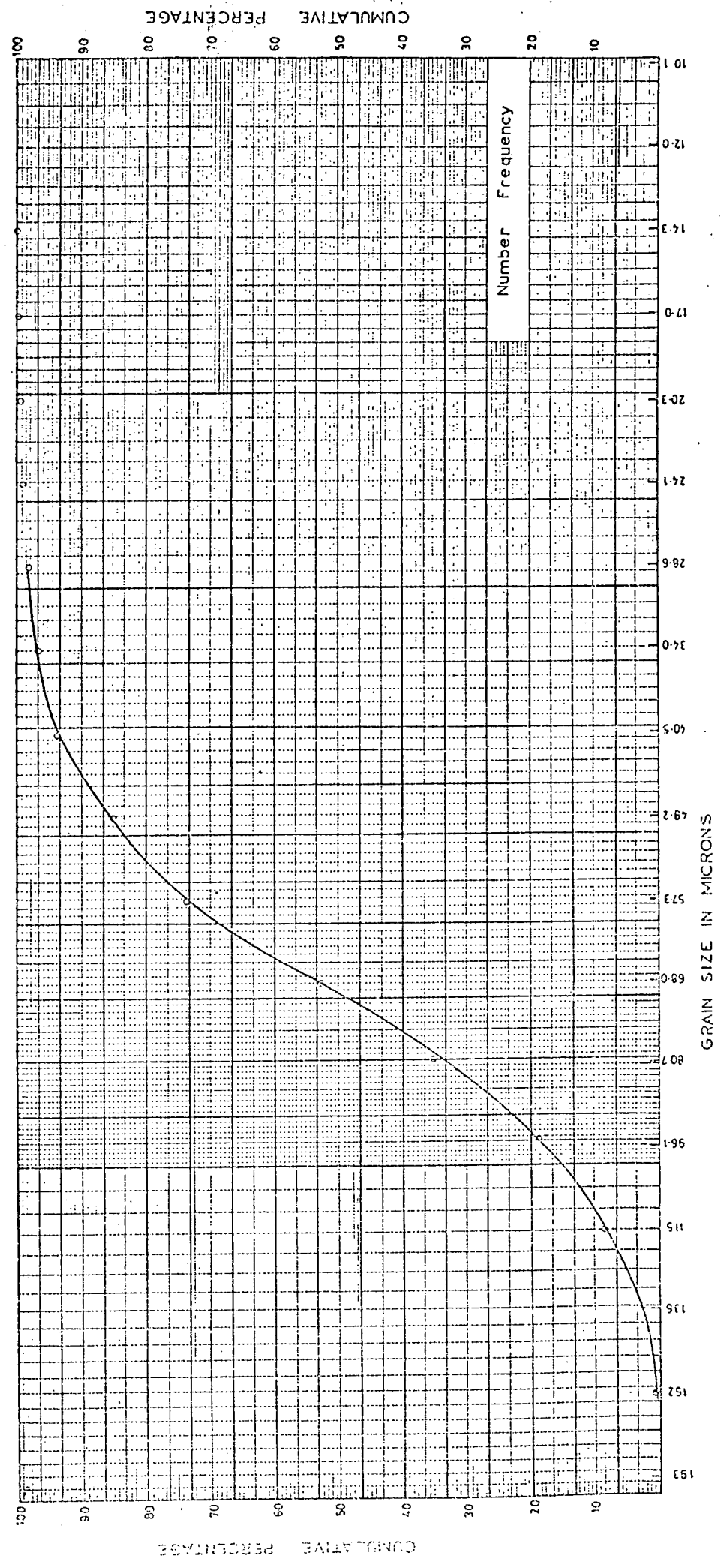
Grain size parameters for each concentrate, read from the frequency curves, are given in table 9. All sizes are in microns.

TABLE 9

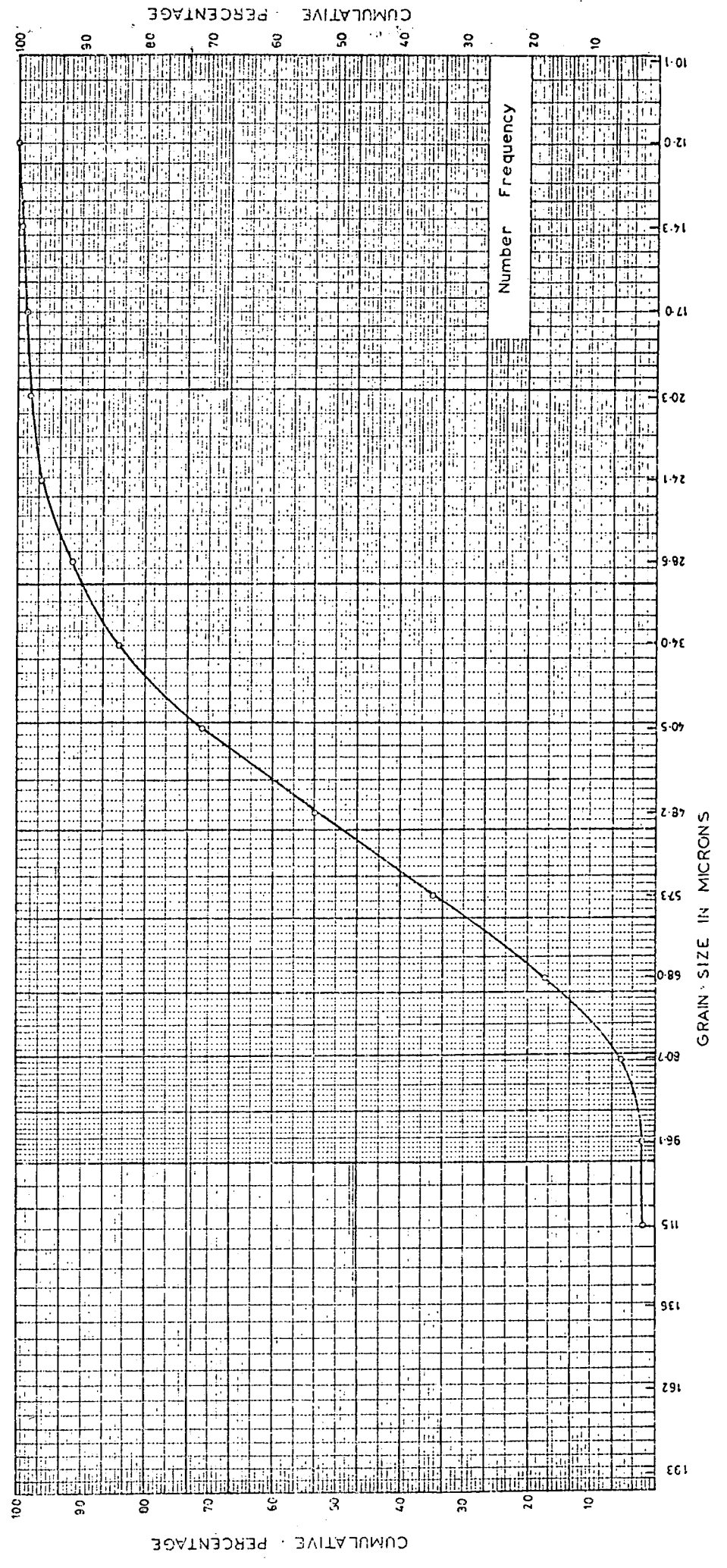
#### Size (dn) Parameters for Six Platinoid Concentrates

Mine	Reef	Median Size	First Quartile	Third Quartile	Grains Measured
Welkom	Bird	69.2	56.2	87.9	474
Western Holdings	Bird	49.5	38.8	62.9	469
Free State Gedult	Bird	64.7	51.6	79.9	477
Vaal Reefs	Bird	64.1	50.9	79.9	471
Libanon	Main	59.4	47.8	77.9	453
S.A. Lands	Main	49.7	38.6	63.1	455

GRAIN SIZE DISTRIBUTION OF PLATINOIDS MINE: WELKOM REEF: BASAL

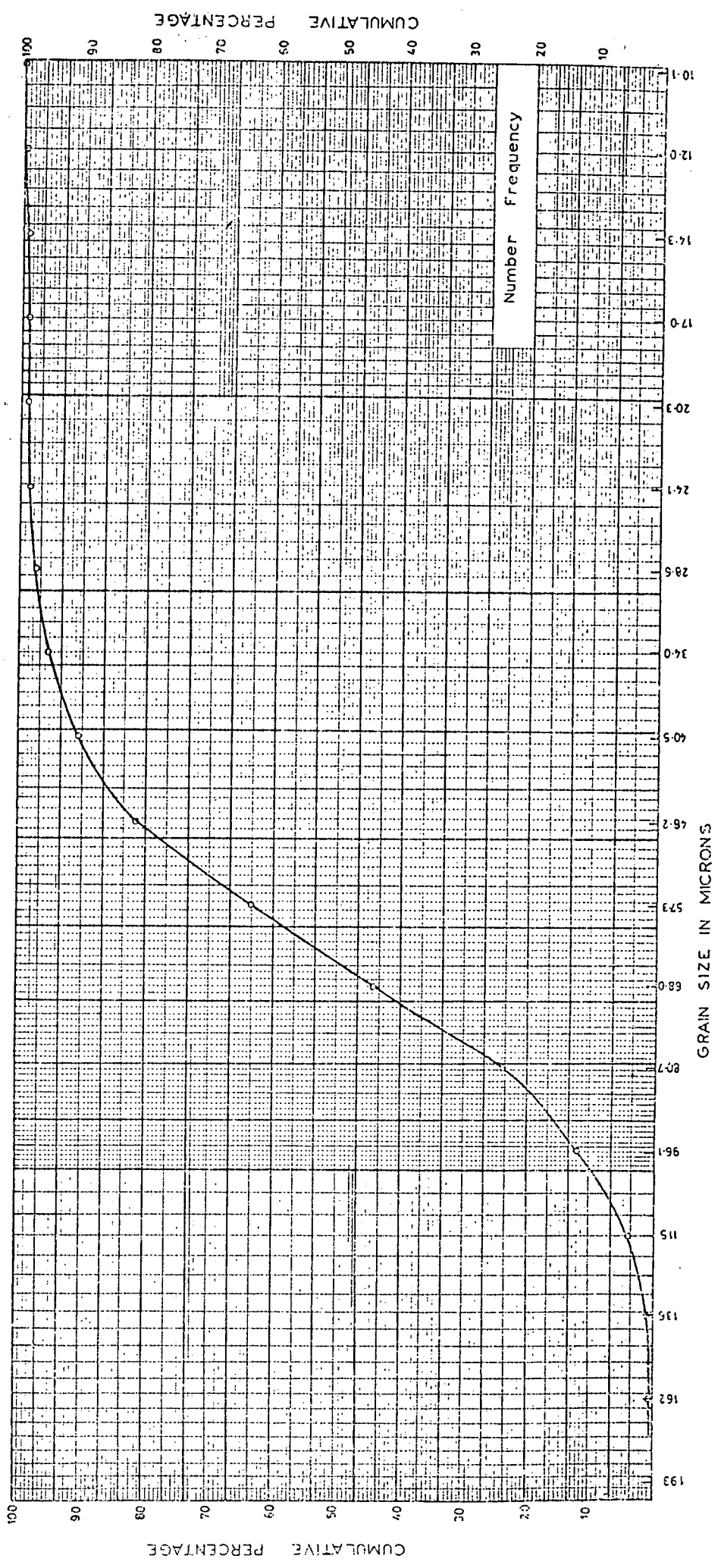


GRAIN SIZE DISTRIBUTION OF PLATINOIDS MINE : WESTERN HOLDINGS REEF : BASAL





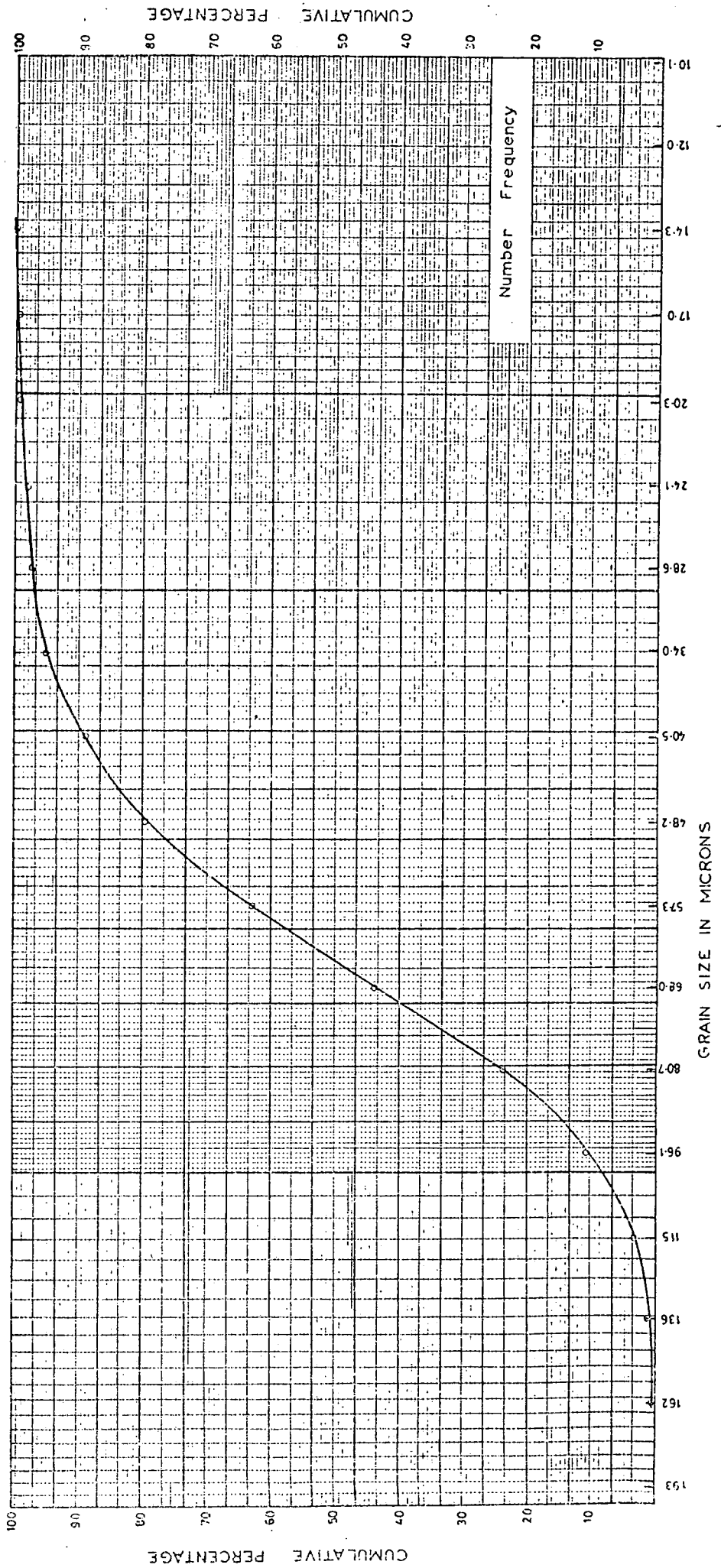
GRAIN SIZE DISTRIBUTION OF PLATINOIDS MINE : FREE STATE GEDULD REEF : BASAL



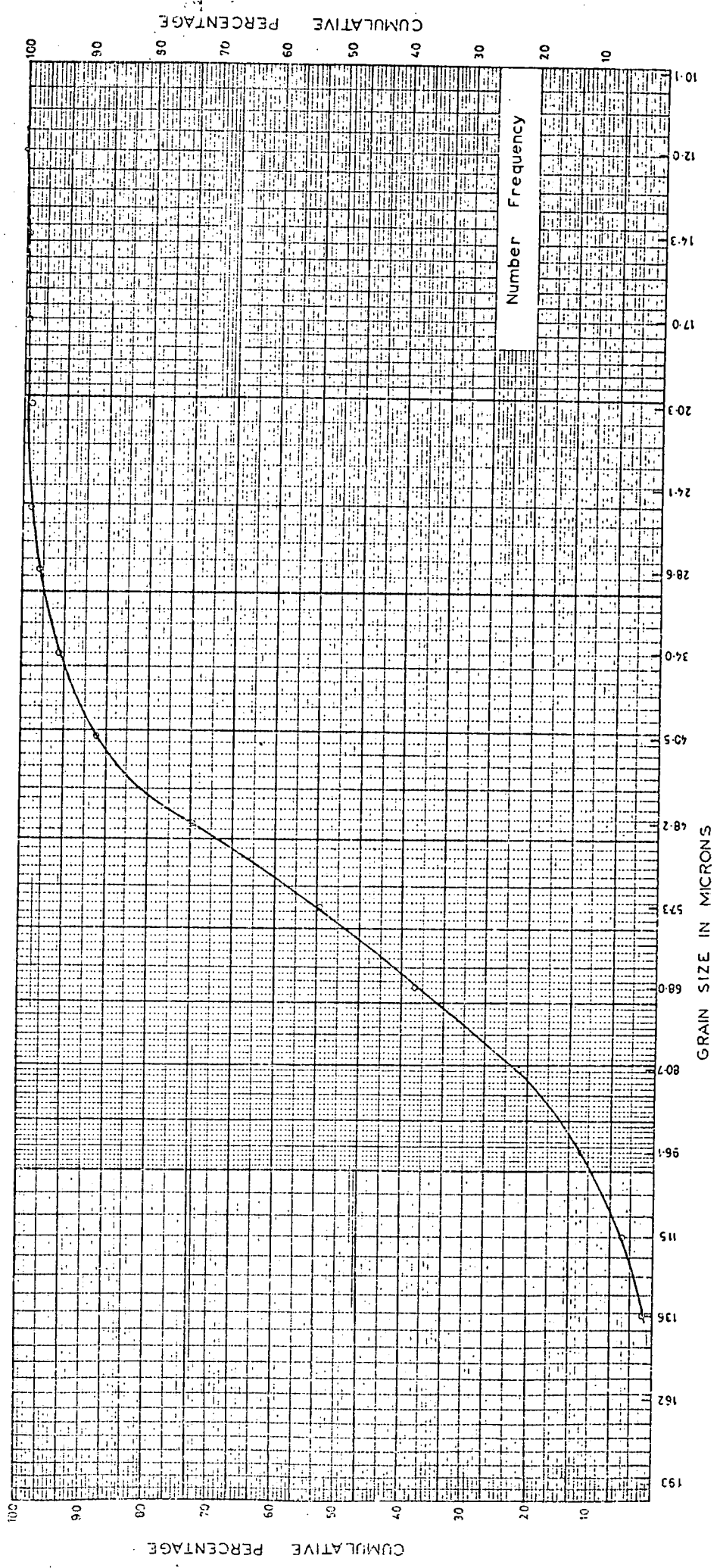
REEF : VAAL (≡ BASAL)

MINE : VAAL REEFS

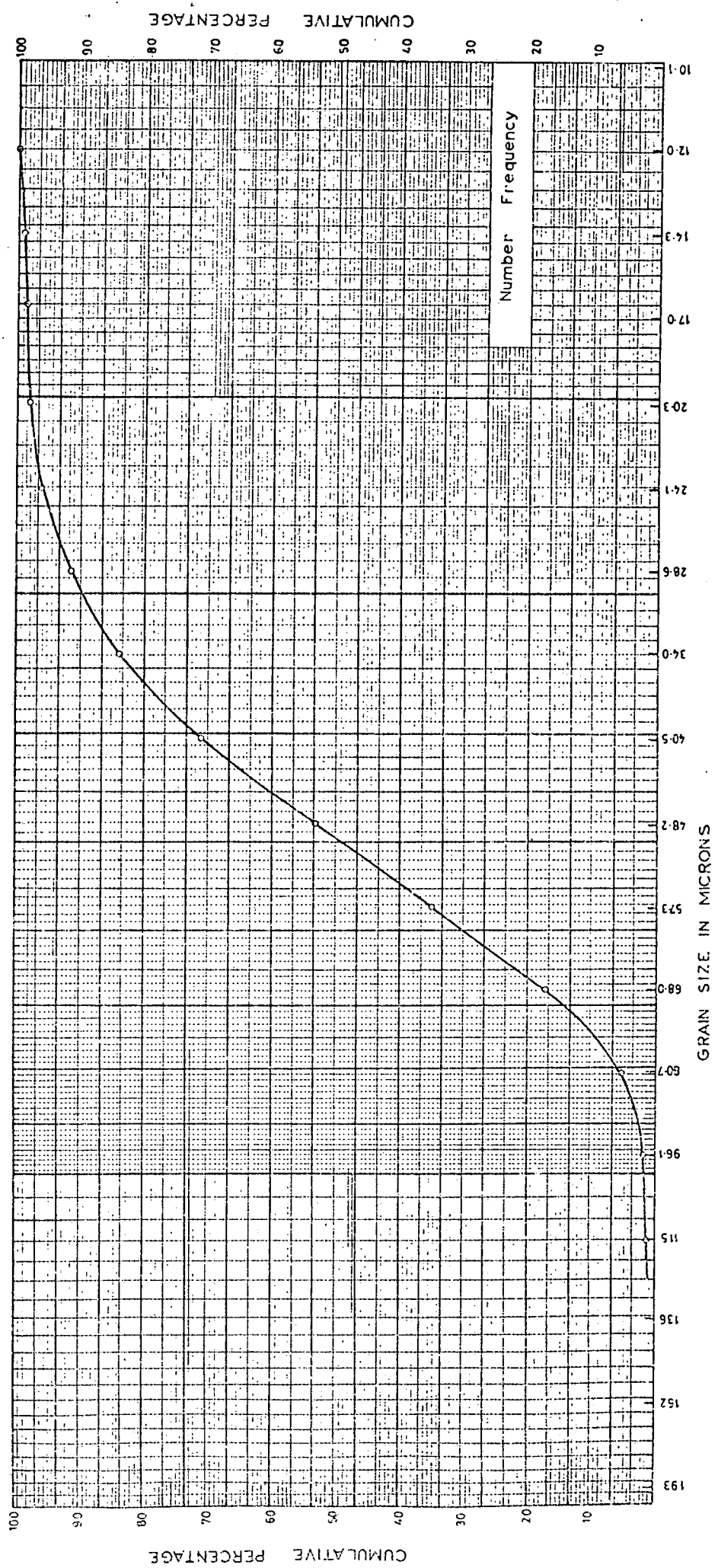
GRAIN SIZE DISTRIBUTION OF PLATINOIDS



GRAIN SIZE DISTRIBUTION OF PLATINOIDS      MINE: LIBANON      REEF: MAIN



GRAIN SIZE DISTRIBUTION OF PLATINOIDS MINE : S.A.LANDS REEF : MAIN



From an examination of the distribution curves and of the data in table 9, the following conclusions can be drawn.

The platinoid mineral grains examined from various positions in the Witwatersrand gold reefs are extremely small both in median grain size and grain size range.

Differences in median grain size and size distribution of the minerals from both adjacent and widely separated positions in the Witwatersrand basin are small.

The median size and size distribution of grains in the Bird Reef at Western Holdings gold mine and in the Main Reef at S.A. Lands gold mine are virtually identical. The mines are situated on opposite sides of the basin. Platinoid grains in the Bird Reef from the Welkom and Western Holdings gold mines show greater differences in grain size parameters. These two mines are geographically adjacent.

The variations, therefore, in median grain size and grain size distribution between platinoid particles in different parts of the Witwatersrand sedimentary basin appear to be small, random variations unrelated to their geographical or stratigraphic position in the sediments.

If it is assumed that the presence of the particles in the conglomerate reefs results from some detrital process, then the particles as a whole are either extremely well-sorted throughout the basin, or the particle sizes are similar to those they exhibited as primary platinoid grains before transportation. In the first event, the degree of attrition of the extremely hard grains need not have been

large, while in the second event attrition would certainly have been minor.

## SECTION 6. Platinoid Minerals in situ

### 6. (i) Experimental Procedures

The platinoid-rich Kimberley Reef ore sample from the Bracken gold mine, which assayed 2.22 grams of platinum group elements per ton of ore, was used to search for platinoid minerals in situ.

A preliminary search was made on semipolished rock slabs about 4" x 2" in size. These were cut with a diamond saw, ground smooth on the two main surfaces with successive grades of carborundum grit, and then semipolished on a wet, 600-grade carborundum paper lap. The semipolished surfaces were covered with a film of light oil and examined under the stereomicroscope. The positions of possible platinoid grains (silvery in appearance) were marked and the enclosing rock particles were cut out, mounted and polished following the procedure described previously in section 4(i).

Four platinoid mineral grains were found in situ. These grains have been examined optically and under the electron probe. With the aid of photomicrographs and electron photomicrographs, each grain is described in the following sub-section. Where possible, qualitative chemical data have been supplemented by quantitative or semiquantitative microanalyses. However, the rarity of in situ grains and their susceptibility to plucking during the polishing process necessitated that polishing be kept to a minimum. Consequently, some sections are unsuitable for quantitative microanalysis. In the descriptions, particular emphasis has been placed on the

relationships of the platinoids with the other conglomerate constituents.

6.(ii) Results

The four platinoid grains all occur in the soft, phyllosilicate matrix of the conglomerate. They each have rounded outline, which may have been modified by in situ deformation, and all grains comprise complex intergrowths of platinoid minerals which include at least one arsenide or sulpharsenide. However, the four grains described can not be regarded as in any way representative of the in situ platinoid particles as a whole.



IN SITU GRAIN A

IN SITU GRAIN A

The composite platinoid grain (Pd) occurs, together with soft, magnesium iron aluminium phyllosilicate (c), in the interstitial area between competent quartz pebbles (q). The white specks at the quartz/silicate boundaries are pyrite and gold. One gold speck also occurs within the silicate matrix close to the platinoid (see backscatter electron image).

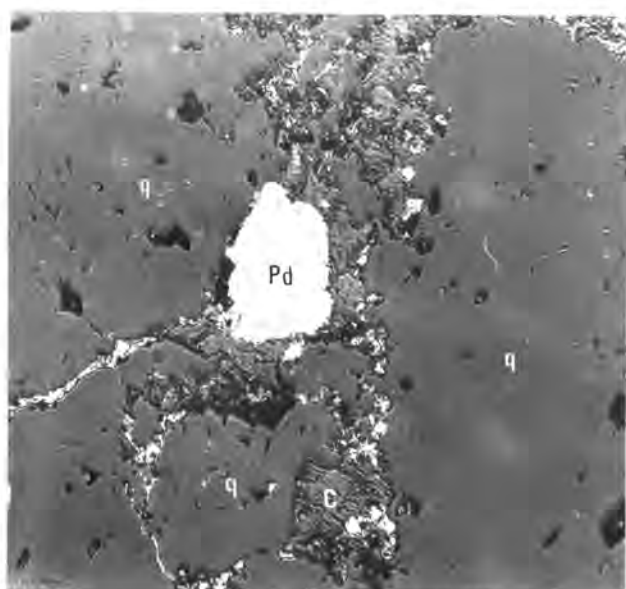
The platinoid grain is concentrically zoned, with a core comprising a network of iridosmium laths (1) set in a groundmass of osmium iridium arsenide (light grey unnumbered). A few patches and stringers of an iron sulphide (black) form part of the groundmass. The peripheral zone consists of sperrylite (4) in which diffuse patches richer in ruthenium and sulphur are common (3). One minute gold speck is also enclosed.

The iridosmium phase (1) contains osmium and iridium in a ratio of 1.2:1 with minor ruthenium and iron and trace amounts of platinum.

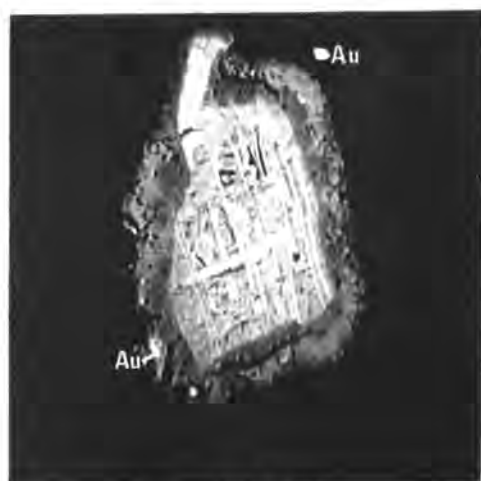
No useful, semiquantitative data could be obtained from phase 2 (osmium iridium arsenide).

The sperrylite phases 3 and 4 were analysed in full and complete data have been given in section (Results). Phase 3 contains 7.6%, 14.2% and 13.3% by weight of iridium, ruthenium and sulphur respectively, together with major platinum and arsenic. Phase 4 contains 5.4%, 6.6% and 8.2% by weight of iridium, ruthenium and sulphur respectively, again with major platinum and arsenic.

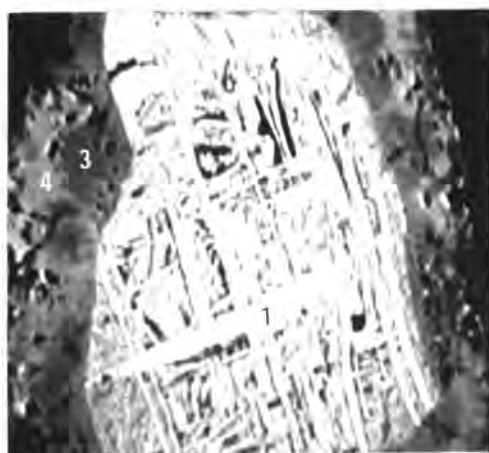
The bright white tongue at the top of the particle is iridosmium with Os:Ir = 1.1:1. The cracking at the base of the tongue, as well as the curvature of some of the iridosmium laths is considered to be a result of in situ deformation. The grain outline has probably also been modified in this way.



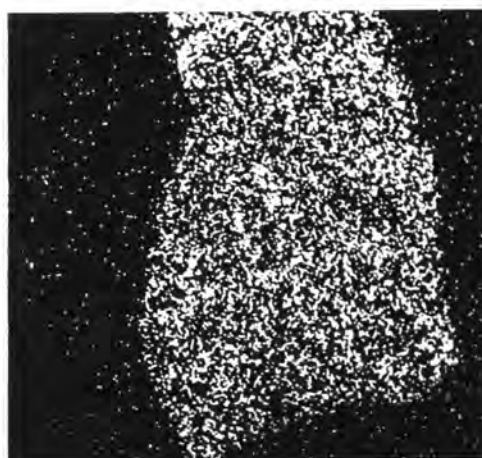
Photomicrograph x 168



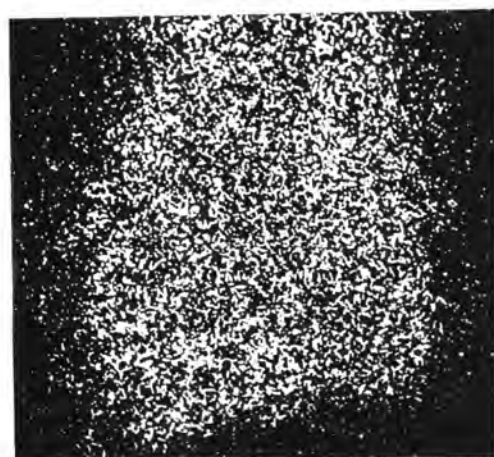
b.e.i. x 420



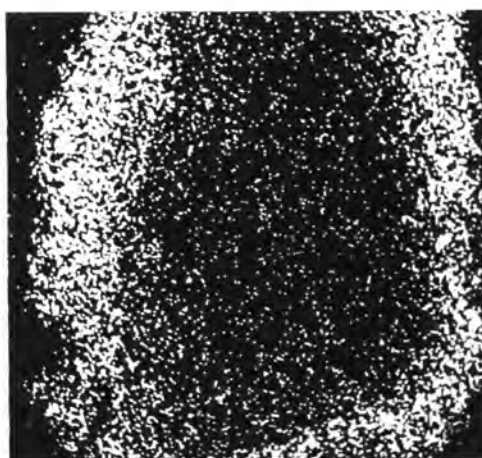
b.e.i. x 840



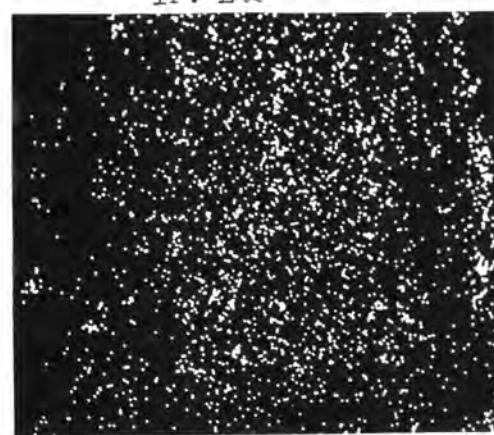
Os.Lα



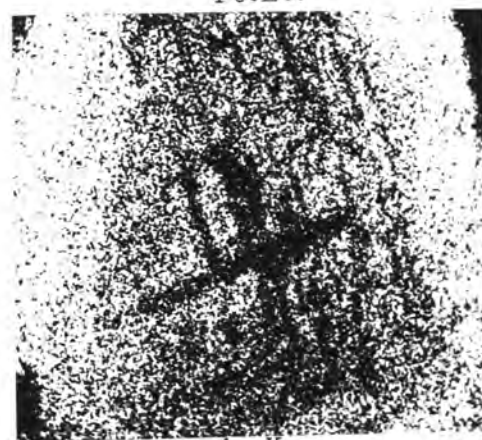
Ir.Lα



Pt.Lα



Ru.Lα



As.Kα

IN SITU GRAIN B

IN SITU GRAIN B

The rounded platinoid grain (Pd) is enclosed in a conglomerate matrix of magnesium iron aluminium phyllosilicate (c) and rests against an irregular quartz pebble (q). The pebble has been molded around the platinoid grain. Other patches within the matrix include thucolite (Th) (enclosing gold specks (white)), a rare earth phosphate (P), which is probably monazite in part, and large irregular patches and particles of a magnesium-poor phyllosilicate (white). Small specks of pyrite, galena, chalcopyrite and gold are disseminated throughout (white).

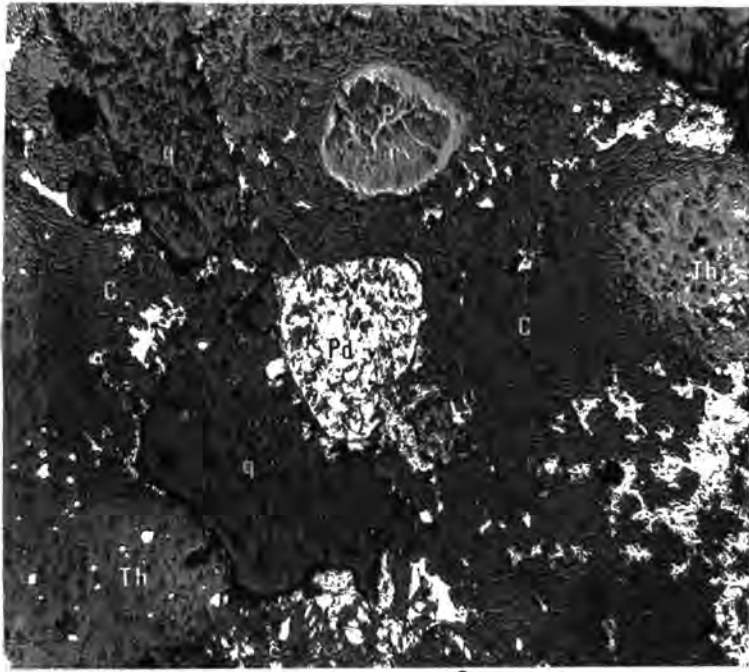
The platinoid particle comprises a complex, irregular inter-growth of an osmium iridium platinum ruthenium sulpharsenide (1) with an osmium ruthenium sulpharsenide (2). Small patches (light grey) in phase 1 contain slightly more arsenic and less sulphur than phase 1.

A full probe analysis of phase 1 was carried out, the results of which have been detailed in section 4(ii)(Results). The mineral contains 50.7% (Os + Ir + Ru), 32.1% As and 9.4% S by weight.

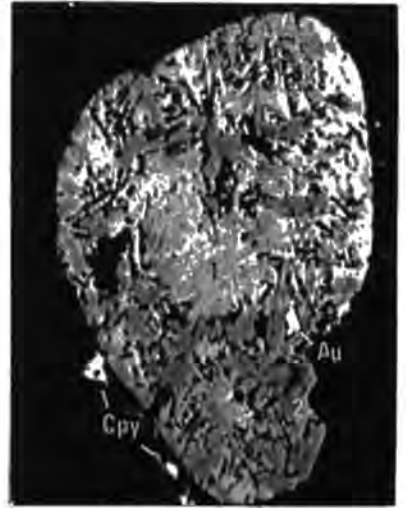
In phase 2, Osmium, ruthenium, arsenic and sulphur are major elements (owing to the low x-ray take-off angle and high absorption, the Ru x-ray image is weak). Iridium is present in minor quantities and iron is negligible.

A small speck of gold was observed enclosed in the platinoid grain. However, the abundance of gold in the surrounding matrix indicates that the speck could have been emplaced by smearing during the polishing process.

The concave curve at bottom right of the platinoid grain may have been formed by the in situ deformation of the grain due to pressure from the adjacent quartz particle.



Photomicrograph x 168



b.e.i. x 420



Os.L $\alpha$



Ir.L $\alpha$



Pt.L $\alpha$



Ru.L $\alpha$



As.K $\alpha$



S.K $\alpha$

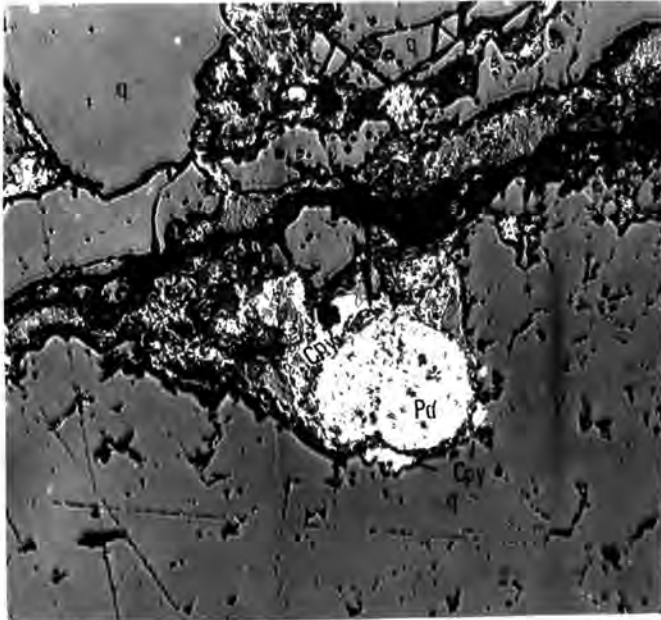
IN SITU GRAIN C

IN SITU GRAIN C

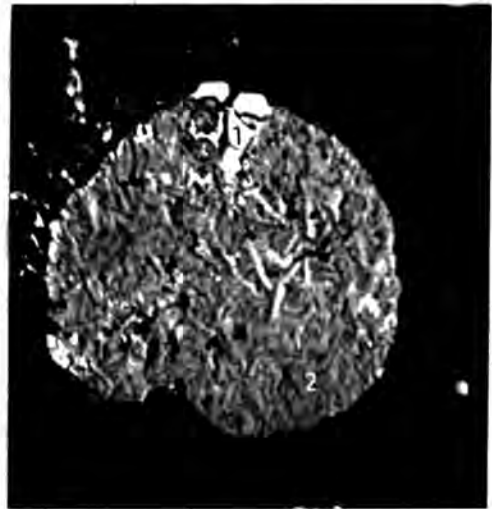
In this section, a well rounded platinum grain (Pd) rests within an embayment in a large quartz pebble (q). The grain is almost surrounded by chalcopyrite which is partly of a fine, granular nature. The conglomerate matrix again comprises a magnesium aluminium iron phyllosilicate (c) in which rare specks of zircon, pyrite and gold, difficult to define in the photomicrograph, are enclosed. The small embayment at the bottom of the platinum grain may have been created in situ by pressure from the adjacent quartz.

Two platinum mineral phases can be identified within the grain. Phase 1, which forms nodules and small laths, corresponds to osmiridium in composition. Os:Ir = 1:100 and ruthenium, platinum and iron are all very minor. Arsenic and sulphur were not detected, although a high background signal for each of these elements was recorded on the X-ray images. Phase 2 is a ruthenium iridium osmium sulpharsenide in which the Os:Ir ratio shows irregular, patchy variations, but where ruthenium is always the major platinum group element. The platinum content of this phase is barely detectable. Owing to the irregular surface and minutely-scaled compositional variations, no quantitative data were collected on phase 2.

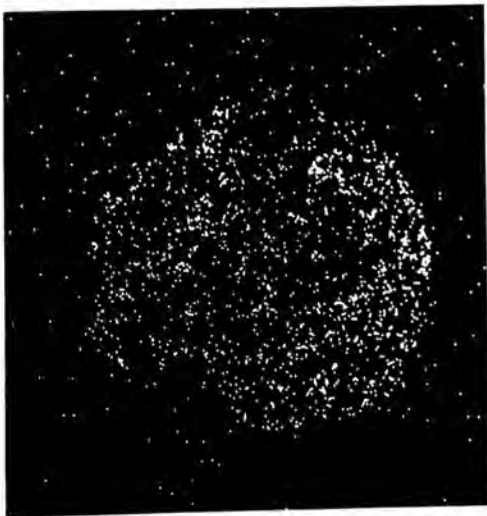




— Photomicrograph x 168



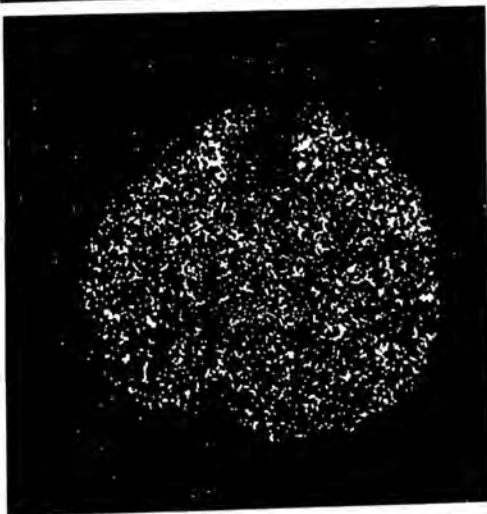
b.e.i  
x 420



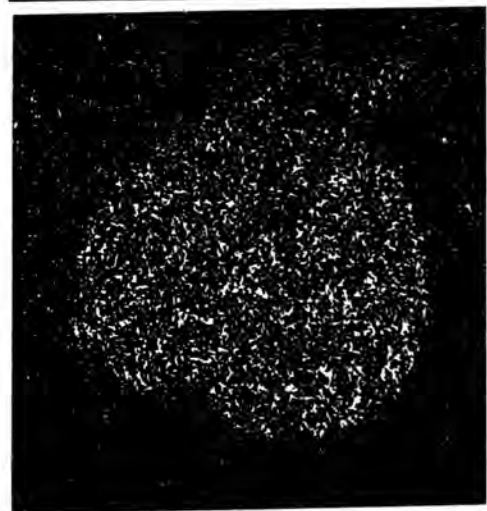
— Os.L $\alpha$



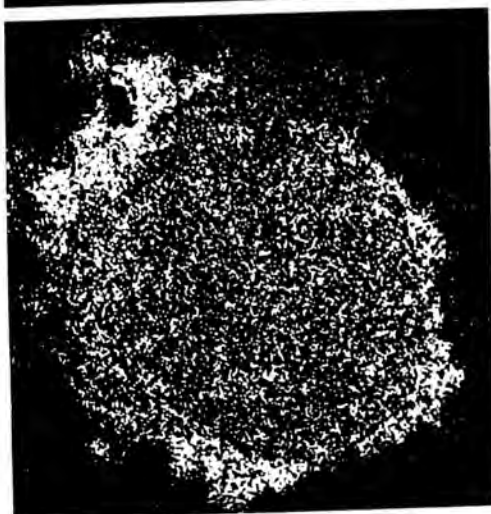
Ir.L $\alpha$



— Ru.L $\alpha$



As.K $\alpha$



— S.K $\alpha$

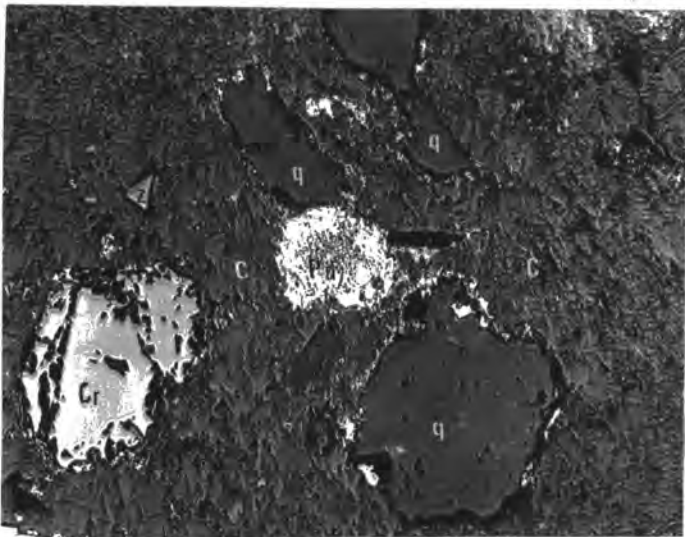
IN SITU GRAIN D

IN SITU GRAIN D

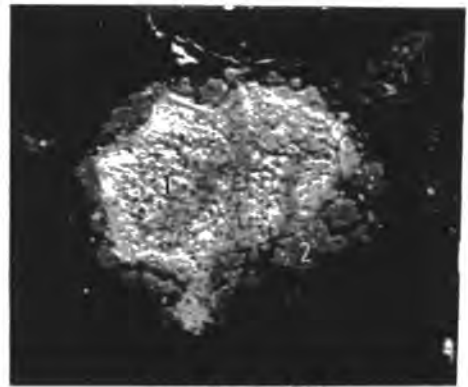
The poorly polished platinoid mineral grain (Pd) rests, together with particles of quartz (q), chromite (Cr) and zircon (z), in a groundmass of magnesium aluminium iron silicate (c). Specks of chalcopyrite occur around the large quartz particle, and a copper antimony sulphide (tetrahedrite) borders the top of the platinoid grain. The black lath to the right of the platinoid is a cavity containing tetrahedrite remnants.

Owing to the poor polish, the composition of the platinoid grain is badly defined. The grain shows concentric intergrowth texture with a core (1) of an iridium platinum osmium sulpharsenide. The dark irregular areas within the core are rich in antimony and probably result from contamination, during polishing, from the neighbouring tetrahedrite. The shell of the platinoid grain consists of ruthenium osmium sulpharsenide in which iron is a minor constituent and traces of iridium, platinum, cobalt and nickel were detected. The minute, white specks enclosed in the shell are of an osmium-rich alloy.

No deformation of the platinoid grain in situ is apparent, and the protruding tongue at the bottom of the grain is difficult to explain by a process of aqueous attrition. Chemical processes may have played a significant role in the formation of the present shape.



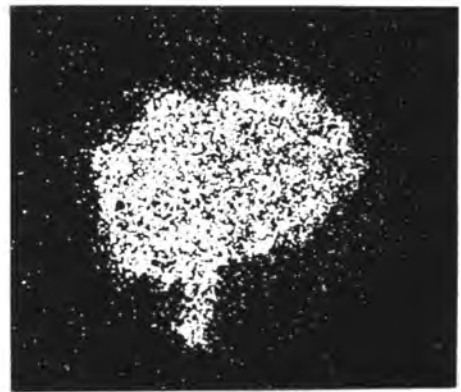
Photomicrograph x 168



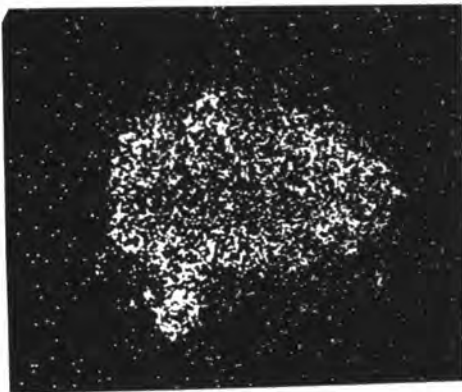
b.e.i. x 420



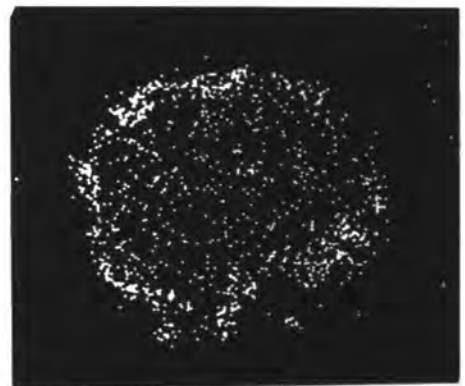
Os.L $\alpha$



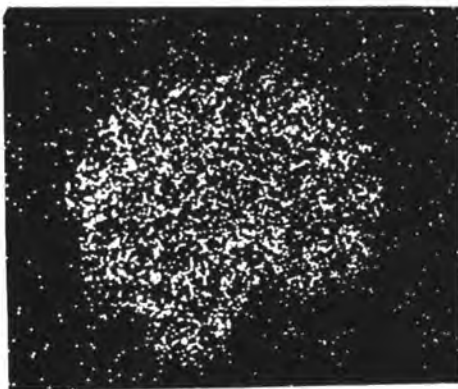
Ir.L $\alpha$



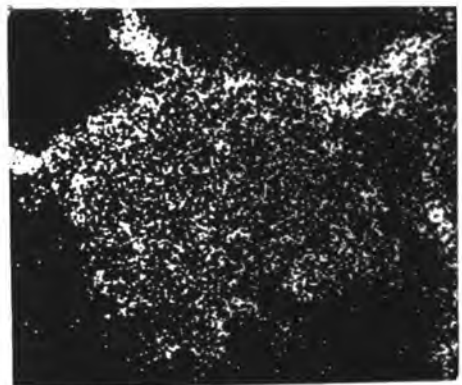
Pt.L $\alpha$



Ru.L $\alpha$



As.K $\alpha$



S.K $\alpha$

SECTION 7. Conclusions

1. Microscopically, the Witwatersrand platinoid grains appear to present a fairly simple mineral assemblage. Two hexagonal alloys, osmium and iridosmium, can be identified. One is a pale grey-blue alloy of extreme hardness, and the other is more or less paler in colour and of inferior hardness. Distinction between the alloys when they occur in mutual intergrowth is fairly simple. However, the positive identification of either alloy when examined as homogeneous particles is considerably more difficult, particularly if the composition of the alloy is marginal. Cubic osmiridium can be distinguished from the hexagonal alloys on the basis of reflectivity and polishing hardness, but optical distinction between either osmiridium or iridosmium and their ruthenium-rich counterparts, ruthenosmiridium and rutheniridosmium respectively, is generally impossible. Similarly, the distinction between osmiridium, iridium and rutheniridium can be extremely difficult unless the differences in composition between the minerals are extreme.

Among the arsenide, sulpharsenide and sulphide minerals of the platinum group elements, sperrylite and laurite can be identified fairly readily under the microscope. The arsenides and sulpharsenides of osmium and iridium can be isolated as distinct mineral species.

An examination of the platinoid concentrates under the electron

probe, however, reveals a mineral assemblage of considerable complexity. The ruthenian and rhodian varieties of some alloys are detectable and most minerals show remarkable variations in composition and intergrowth textures. Only by microanalysis, supplemented by accurate determinations of hardness, reflectivity and structure can many minerals be characterised with certainty.

2. Some general relationships between the composition and physical properties of the platinoid alloys can be defined with confidence.

For the alloys of Os + Ir and Os + Ir + Ru:-

Reflectivity↑ as Ir%↑

Reflectivity↑ as (Pt + Ru)%↑

Colour changes from pale blue-grey to creamy white

as Os%↓ and Ir%↑

Microhardness↑ as Os%↑ and Ir%↓

Microhardness↑ as Ru%↑

Contraction of the crystal lattice of hexagonal alloys

occurs as Ru%↑ . Contraction of the cubic alloy lattice

under similar conditions is barely definable, for either

osmiridium or iridium. For variations in the Os:Ir ratio

of either the hexagonal alloys or cubic alloys, corresponding

changes in the crystal structure are minimal.

For the Pt + Fe alloys:-

Hardness of ferroplatinum↑ as Rh↑

3. The system of nomenclature proposed by Harris and Cabri (42) for the Os + Ir alloys and the Os + Ir + Ru alloys adequately covers those alloys identified in the Witwatersrand concentrates. The system can also be successfully applied to the alloys of Fe + Pt and, until more detailed structural data on the Fe/Pt system are available, a system of nomenclature based on composition is necessary.

However, the distinction made by Harris and Cabri between osmium and iridosmium is based on Ir exceeding 20 at % of (Os + Ir), for iridosmium. Their criterion for distinguishing iridosmium and rutheniridosmium is that ruthenium exceeds 10 at % of (Os + Ir + Ru) for rutheniridosmium. Some inconsistency is apparent here. A limit of either 20 at % content or 10 at % content should be applied consistently as the criterion for including an element, as a prefix, in the names of all the alloys. It is clearly preferable that a 10 at % limit be applied and that osmium be redefined as an alloy with  $\geq 90$  at % Os. Similarly, native iridium should be redefined as an alloy with  $\geq 90$  at % Ir. No obstacles, in the form of structure or optical properties are present to prevent this standardisation of the nomenclature.

4. No further light has been thrown on the position of the compositional boundary between iridosmium and osmiridium. The point of division was placed at 32% Os by Hey (38). Cabri (41), however, has indicated the possibility that a miscibility gap exists in the Os + Ir + Ru system, basing his opinion on published data for the synthetic Os - Ir and Ir - Ru systems. Cabri's ternary diagram,

showing the postulated area of immiscibility has been reproduced (see diagram 2). On the diagram, the compositions of the alloys described in section 4 have been plotted, and serve to confirm the existence of an immiscibility gap.

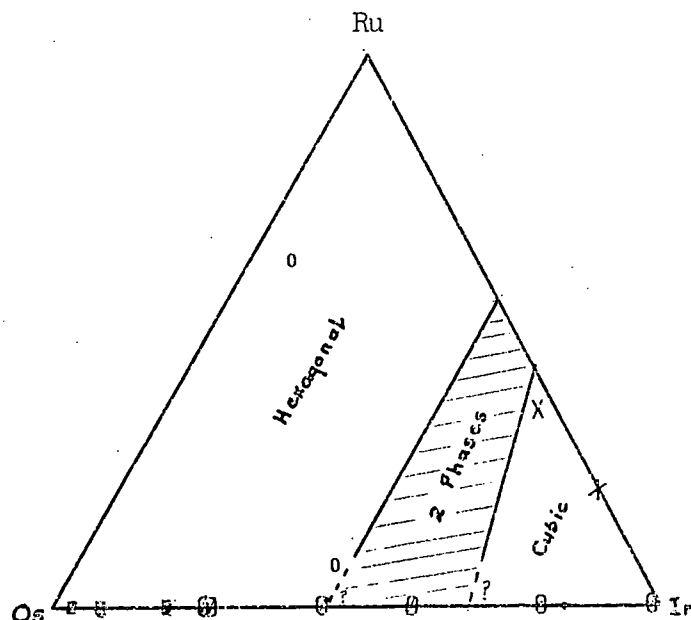
5. Intergrowth textures exhibited by the platinoid alloys are varied and complex. In most cases, any interpretation of the genetic significance of the textures would be conjectural. However, the existence of composite bodies identical in texture to negative crystals, of vesicular cavities and of eutectoid-like intergrowths indicates that the platinoid minerals crystallised under magmatic conditions.
6. Examination of the shapes and sizes of the platinoid grains provides little positive evidence as to their origin. The use of rounded or angular shapes and concave curves and reentrant angles for or against a detrital provenance is dubious. Both deformation in situ and fracturing during metallurgical concentration of the particles have probably played a significant part in the formation of the present grain shapes. The mean size and size distribution of the particles remains remarkably constant from one part of the Witwatersrand basin to another, and show only small random variations. The consistency in grain size may reflect either an efficient process of sorting of detrital particles, or a lack of attrition during transportation of evenly sized primary grains.
7. Owing to their complex intergrowths with other platinoid minerals, the arsenides and sulpharsenides of Os and Ir are only partly defined. The minerals are chemically complex and there is some evidence to indicate that a continuous mineral/compositional series



exists between the arsenide on the one hand and a sulpharsenide, rich in sulphur, on the other. The pure sulphide end-member, if it exists, was not identified. Most occurrences of these minerals were observed as coatings around, and sometimes replacing the alloys of osmium and iridium (with the exception of the native osmium alloy). The possibility exists that the minerals are authigenic. The occurrence of a sperrylite shell around a well-rounded iridium particle (photomicrograph 17) shows that if the iridium was rounded during transportation, then the sperrylite is authigenic. Alternatively, if the sperrylite was formed before transportation as a primary mineral, then the rounded shape of the iridium grain is primary and owes nothing to a process of physical attrition.

8. The descriptions of the platinoid minerals given in the thesis cover those minerals occurring as minor to major constituents in the Witwatersrand reefs. Observations of extremely rare minerals, such as rhodoferroplatinum and rhodiridium, were fortuitous, and it is certain that other, rare constituents of the reefs have escaped notice.

DIAGRAM 2. The Natural Os-Ir-Ru System (Cabri (41))



- |   |                            |
|---|----------------------------|
| ≡ | Postulated miscibility gap |
| ■ | Osmium                     |
| ◻ | Iridosmium                 |
| ○ | Rutheniridosmium           |
| ◊ | Osmiridium                 |
| X | Ruthenosmiridium           |
| . | Iridium                    |

Only one mineral falls in the field of immiscibility. This mineral formed one half of a twin-like iridosmium particle for which only a poor powder diffraction film was obtained. The structure, therefore, of this mineral is uncertain. All other analyses are of single phase, hexagonal or cubic alloys.

ACKNOWLEDGEMENTS

This investigation was undertaken at the suggestion of Mr. C. A. Cousins, who is thanked for supplying the platinoid samples and for the interest and enthusiasm he has shown throughout the work.

Thanks are also due to Mr. L. P. Hendriks, who was always willing to discuss and elucidate problems, and to Mr. W. Krompkamp, who draughted the maps.

The Johannesburg Consolidated Investment Co. Ltd. is thanked for allowing the facilities at their research laboratory to be used for the investigation, and Johnson Matthey Co. Ltd., Wembley, England, is thanked for supplying microprobe standards for the platinoid elements.

Finally, I wish to thank the South African National Institute for Metallurgy for making available facilities for reflectivity measurements.

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## APPENDIX I

### PHOTOMICROGRAPHS

The photomicrographs and electron photomicrographs in the following plates (I to X) illustrate a general cross section of the shapes, zonal or intergrowth textures and composition of the Witwatersrand platinoid grains. Since the variations are almost infinite, only the more common features or features of particular interest have been illustrated. Brief descriptive notes are given for each photograph and all minerals except those shown in plate I were identified with the electron probe.

Unless specified otherwise, the grains were photographed in polished section with plane polarised, oil immersion objectives and using Ilford FP4 35 mm. film. The exceptions were photographed using 9 x 12 cms. plate film (FP4) or polaroid film. The latter was used for all backscatter electron images (b.e.i.). The corresponding x-ray images are 35 mm. copies of polaroid originals. All negatives were developed in Johnson's Acutol.

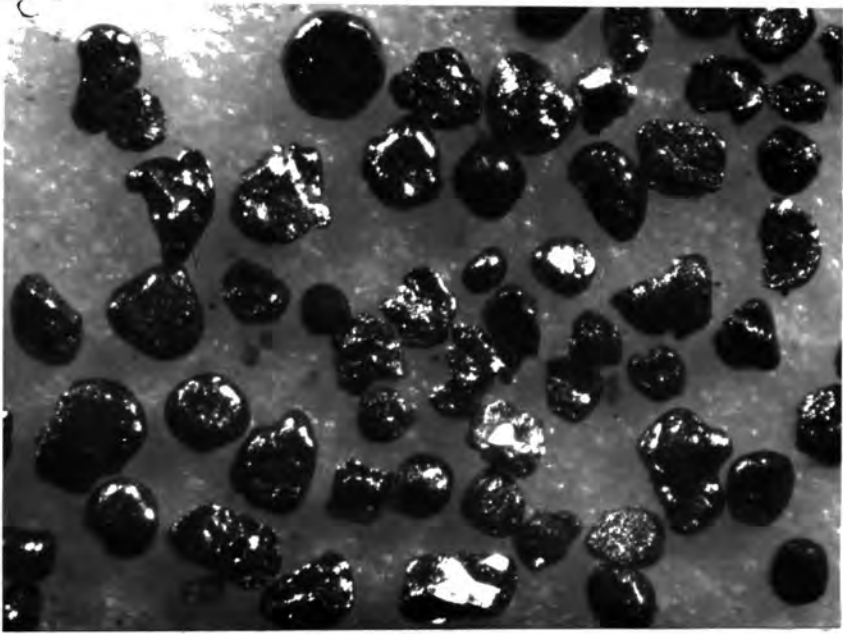


PLATES I - X

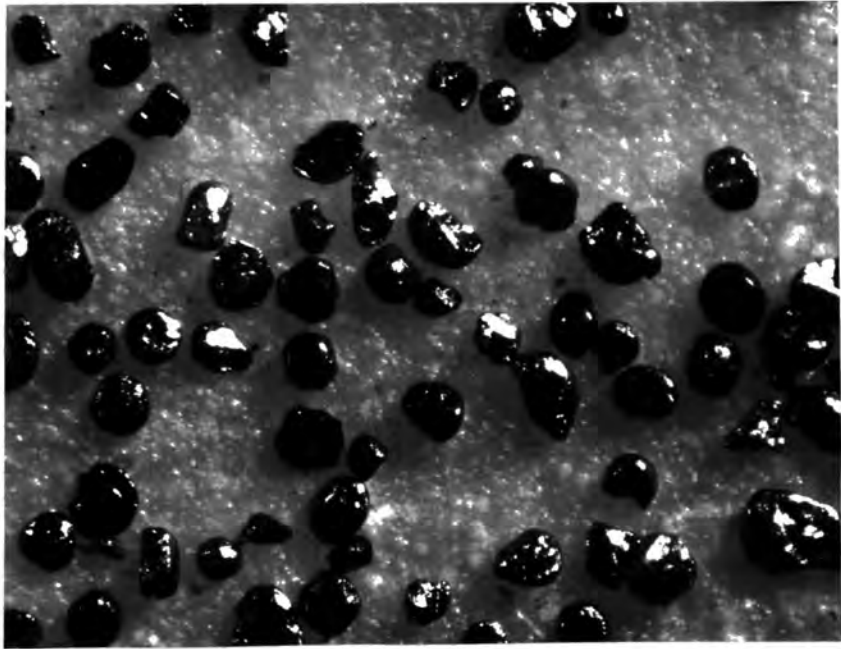
PLATE I

1. A random selection of loose platinoid grains. Western Holdings Mine. x 120 (Air Objective, Plate film).
2. A random selection of loose platinoid grains. S.A. Lands Mine. x 95 (Air Objective, Plate film).
3. Platinoid grains after dislocation of a central phase. (see arrows). The hexagonal outline of the core in the grain on the left is well defined. South Roodepoort Mine. x 150 (Air Objective, Plate film).

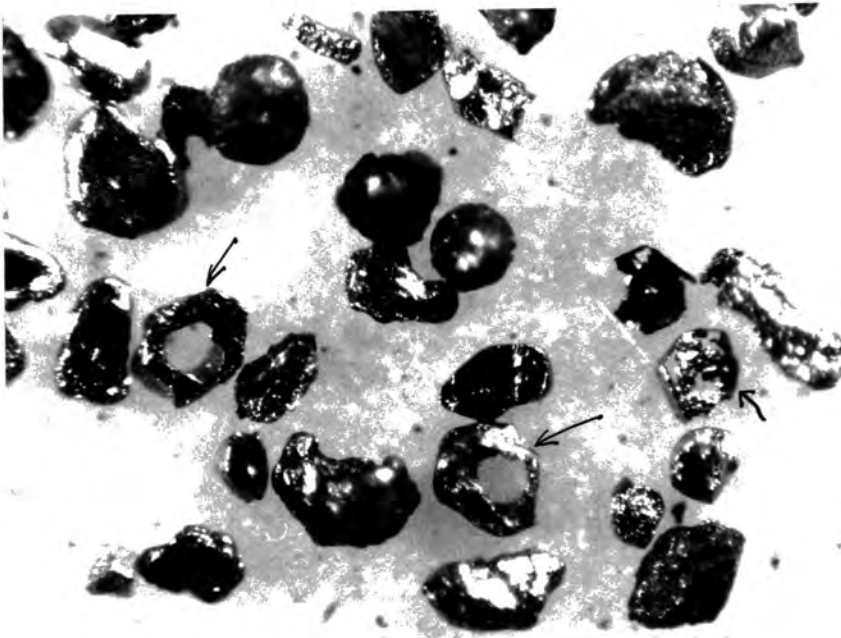
PLATE I



1



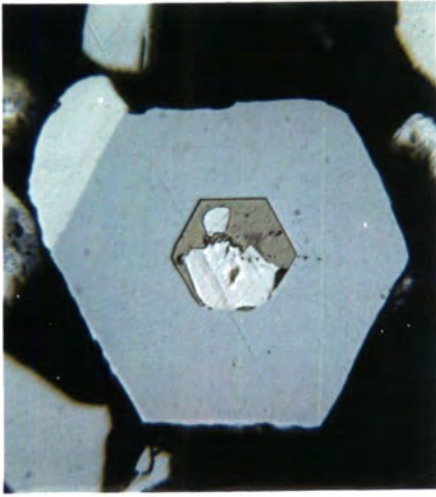
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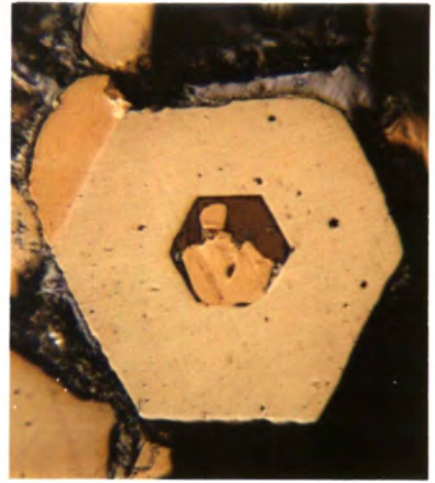
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PLATE II

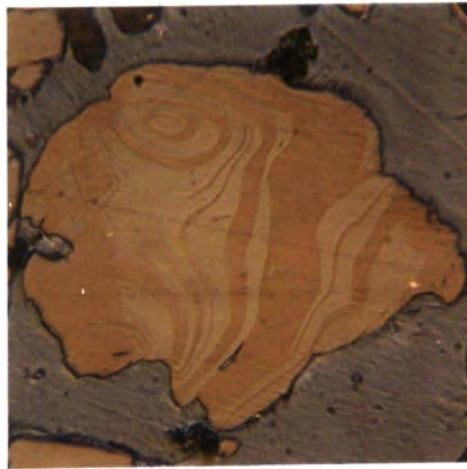
4. An angular, hexagonal crystal of osmium (blue) enclosing a "negative crystal" composite of iron nickel sulphide (grey-green) and ferroplatinum (white). An iridosmium remnant (white) is attached at upper left. Welkom mine. x 450 (Polaroid).
5. The same grain as 4, coated with a thin carbon film (Polaroid).
6. A linear intergrowth of iridosmium (light brown) and a more iridium and ruthenium rich iridosmium (dark brown). Carbon coating enhances contrast. Western Holdings mine. x 450, (Polaroid).
7. A concentric intergrowth of osmium (white), iridosmium (light grey) and rutheniridosmium (dark grey). Welkom mine, B.E.I. x 420.
8. The same grain as 7. Photomicrograph in oil. Note the lack of contrast between the two outer minerals. x 420.



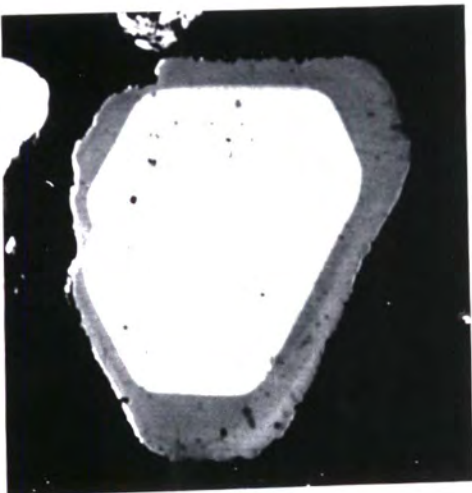
4



5



6



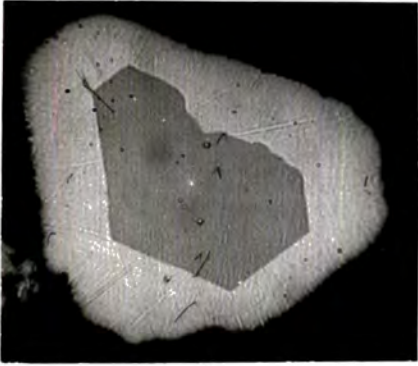
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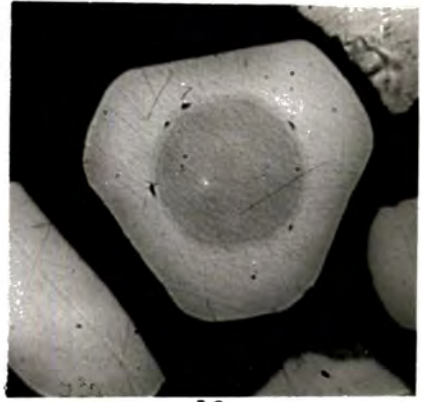
8

PLATE III

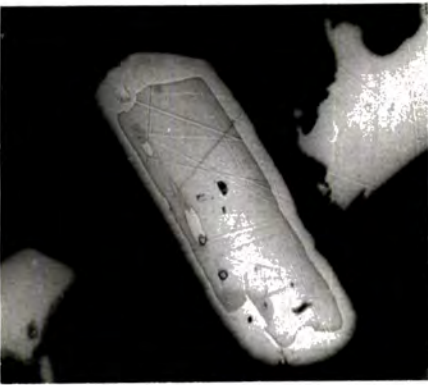
9. An imperfectly formed osmium crystal in iridosmium/rutheniridosmium. Same grain as photomicrographs 7 and 8. Welkom mine, x 380.
  
10. A concentric intergrowth with a round core of osmium (grey), a thin intermediate zone of Os-rich iridosmium (pale grey) and an outer zone of iridosmium (white) with  $Os \approx Ir$ . Grain rounding is minor. Libanon mine, x 530.
  
11. A concentric intergrowth of iridosmium (grey) and iridium-rich iridosmium, sectioned parallel to c-axis. Small patches of osmium (dark grey) are visible. Welkom mine, x 400.
  
12. An incompletely formed osmium crystal (grey) in iridosmium (white). Winkelhaak mine, x 400.
  
13. Osmium (incomplete at centre) in iridosmium (white). Central black patch is a cavity. Note the sympathetic outlines of the osmium and iridosmine. Libanon mine, x 400.
  
14. A similar grain to 14 with a thin iridosmine rim. S.A. Lands mine, x 770.
  
15. Several irregular nuclei of osmium grading compositionally into rutheniridosmine. Welkom mine, high contrast B.E.I. x 840.
  
16. A concentric intergrowth of osmium (dark grey), iridosmine (light grey) and osmiridium (white). Western Deep Levels mine, x 280. Poor polish.



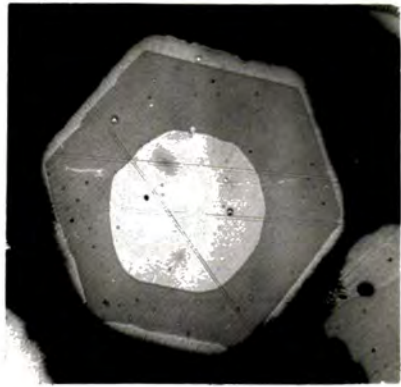
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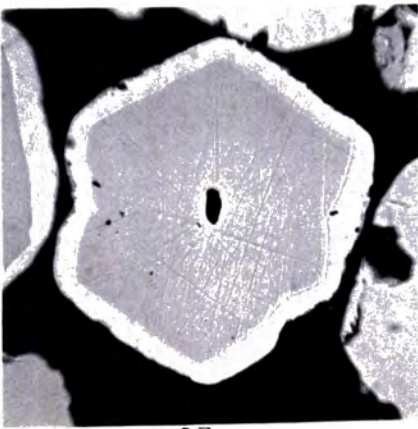
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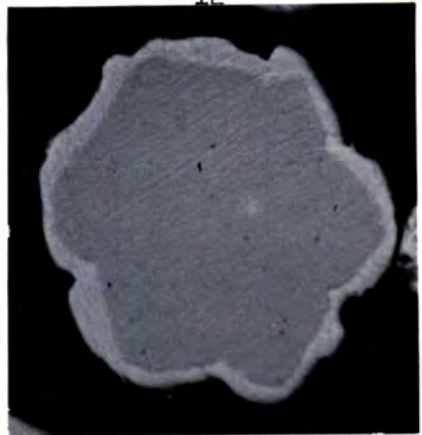
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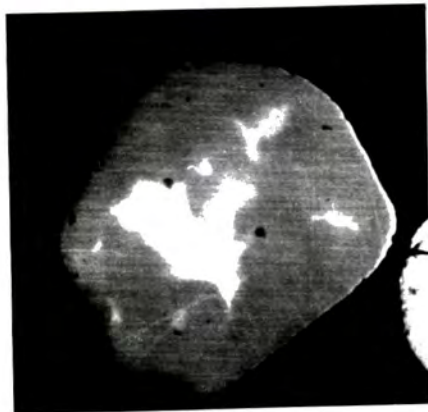
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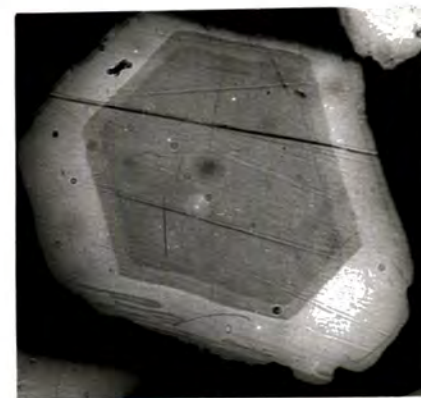
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14



15



16



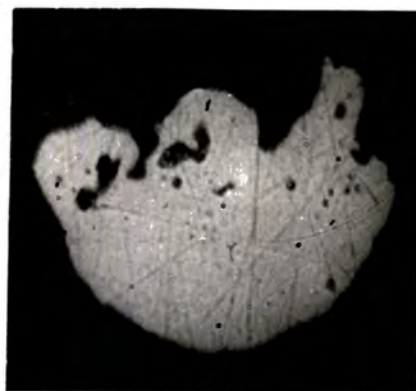
PLATE IV

17. Iridium (white) with a broken sperrylite rim. Both the iridium and sperrylite are well rounded. Free State Geduld mine, x 530.
18. Osmiridium (white) being replaced by sperrylite (grey). Welkom mine, x 770.
19. Osmiridium (white) being replaced by Sperrylite (grey). Welkom mine, x 770.
20. Similar grain to 19. Osmiridium in the core is ruthenium-rich and fibrous in texture. Libanon mine, x 770.
21. Hexagonal crystal of iridosmium (white) in which cavities occur, possibly after displacement of a skeletal crystal of osmium. Cavities are partly lined with a platinoid sulpharsenide (grey). Western Holdings mine, x 770.
22. Osmiridium (white) finely intergrown with a platinoid sulpharsenide. The sulpharsenide forms a porous shell (dark grey). Welkom mine, x 770.
23. Ruthenosmiridium (white) extensively replaced by platinoid sulpharsenide (medium grey), all enclosed in a uniform sperrylite shell (light grey). East Daggafontein mine, x 530.
24. Ruthenosmiridium (white) replaced by a sulpharsenide of osmium and iridium (medium grey) and then partly coated with an arsenide of osmium and iridium. Libanon mine, x 530.

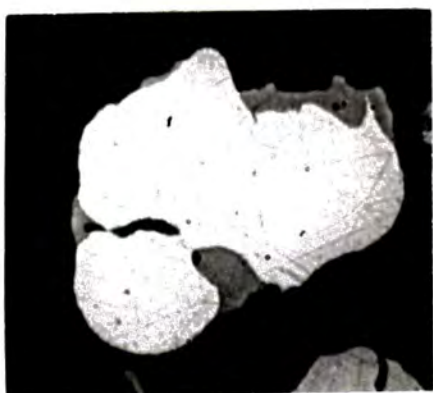
PLATE IV



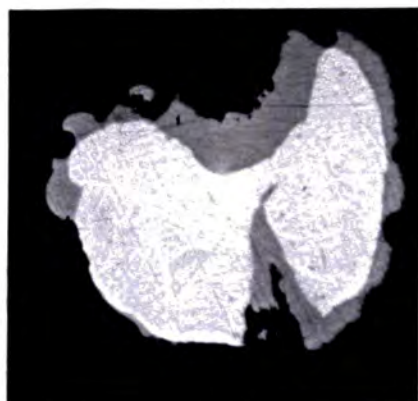
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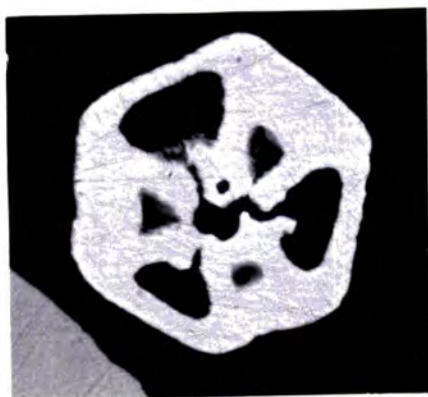
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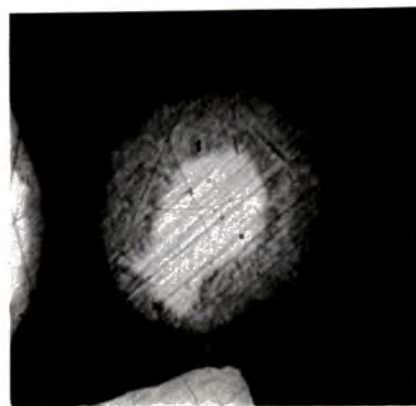
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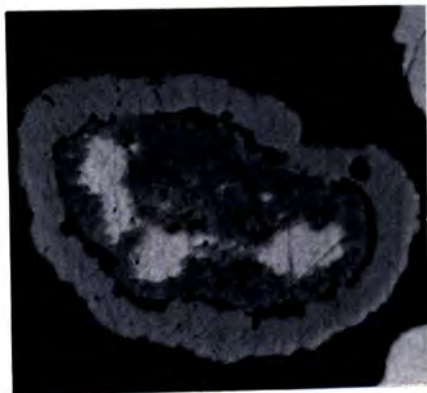
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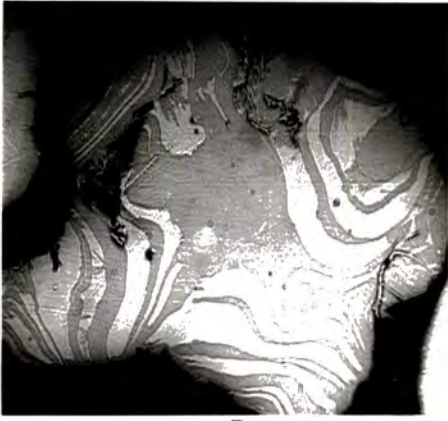
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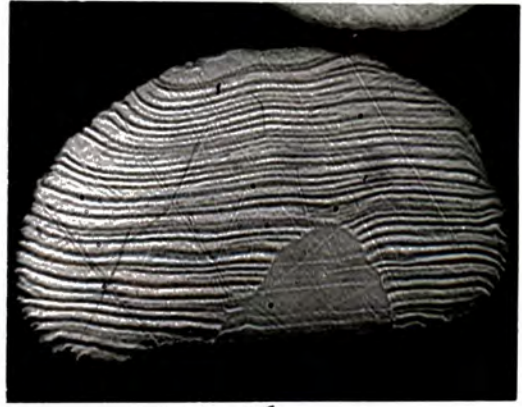
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PLATE V.

25. A linear intergrowth of osmium-rich iridosmium (grey) and iridium-, platinum- and ruthenium-rich iridosmium (white). Western Areas mine, x 400.
26. Similar intergrowth to 25. Polishing relief accentuates the osmium-rich phase. Western Areas mine, x 400.
27. Iridosmium (grey) and iridosmium near osmiridium in composition (white) in linear intergrowth. Kinross mine, x 400.
28. A bizarre twin-like intergrowth of osmium (grey) and iridosmium (white). The cause of the deformation is unknown. Libanon mine, x 770.
29. Concentric intergrowth of osmium (medium grey), iridosmium (light grey) and osmiridium (white), sectioned parallel to the osmium c-axis. Sperrylite remnants (dark grey) are present at grain surface. Vaal Reefs mine, x 600.
30. A twin-like linear intergrowth of osmium-rich iridosmium (grey) and iridium-rich iridosmine (white). Welkom mine, x 530.
31. Similar to grain 30. The two phases appear to have grown in crystal continuity. Vaal Reefs mine, x 500.
32. A linear (structural) intergrowth of a platinoid sulpharsenide along crystallographic directions of iridosmium (white). The sulpharsenide partly coats the composite. Welkom mine, x 530.



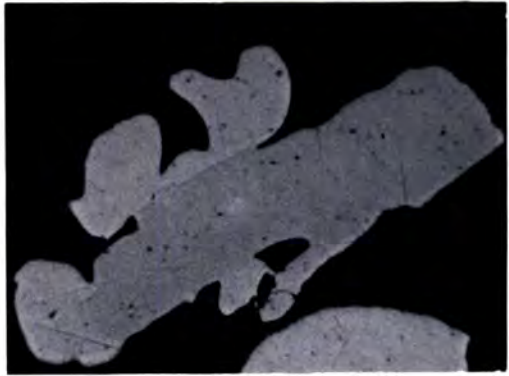
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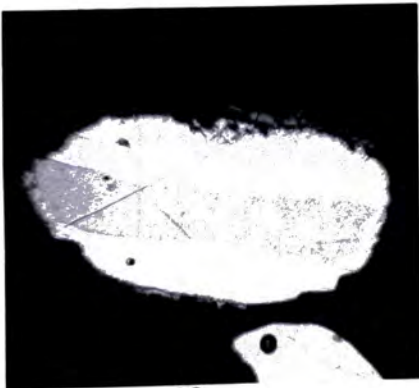
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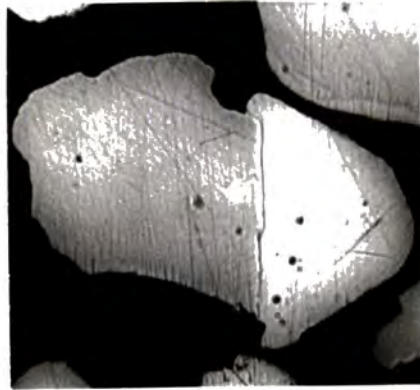
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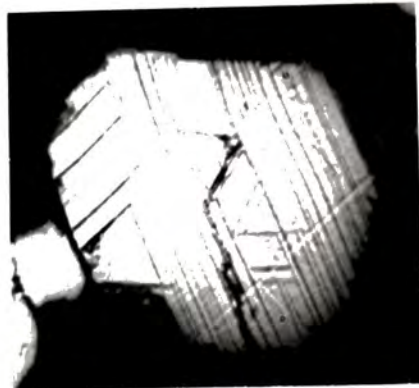
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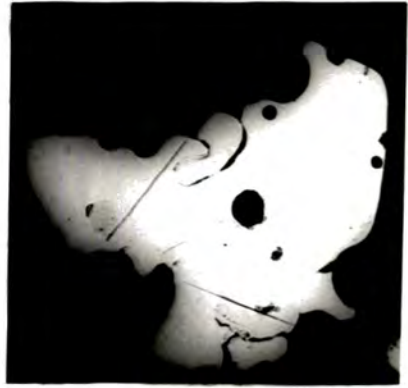
32

PLATE VI

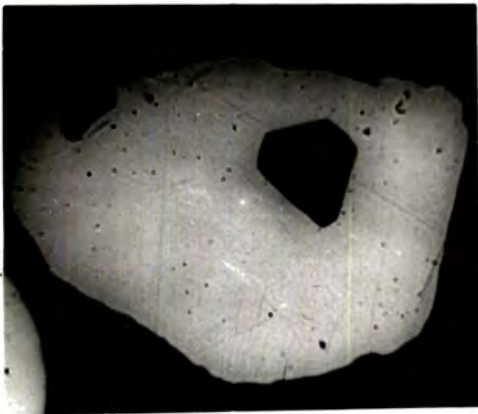
33. Iridosmium (white) enclosing a "negative crystal" composite of finely intergrown ferroplatinum and iron nickel sulphide. The black patch with the composite is iron-rich silicate. Welkom mine, x 770.
34. Inclusions of iridosmium (pale grey) in osmiridium (white). One inclusion is partly detached. Black discs are cavities. Western Areas mine, x 330.
35. Iridosmium with an hexagonal cavity, probably after osmium. Libanon mine, x 770.
36. Osmiridium with spherical inclusions of iron nickel sulphide (grey). A few inclusions near the grain edge have been detached. Free State Geduld mine, x 400.
37. Iridium with oval and tubular vesicles. Traces of a rhodium sulphide mineral can be seen (grey) lining several cavities. Vaal Reefs mine, x 770.
38. Iridosmium with peripheral inclusions of platinoid sulpharsenide. Some vesicular cavities are also present. Leslie Mine, x 330.
39. Osmiridium with vesicles, elongated at random in some cases. Welkom mine, x 530.
40. Angular inclusions of hard, fractured laurite (grey) in osmiridium (white). Libanon mine, x 700.



33



34



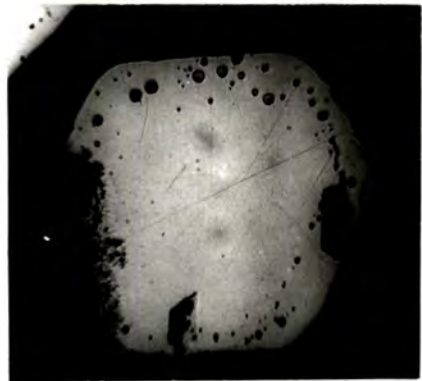
35



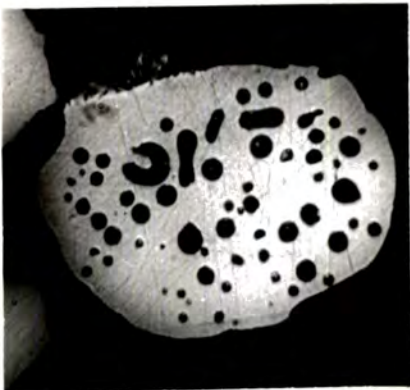
36



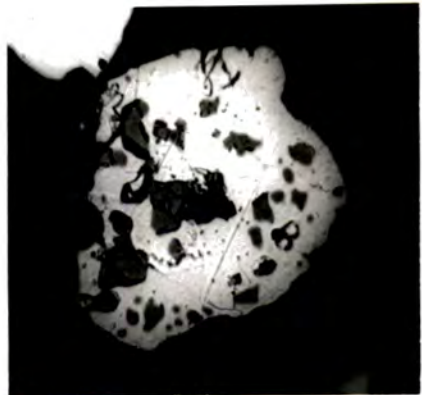
37



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PLATE VII

41. Osmium (dark grey) grading into iridosmium of variable composition (light/medium grey). The iridosmium forms a linear intergrowth with osmiridium (white). Western Areas mine, x 400.
42. A linear intergrowth of osmiridium (white) and a platinum/iron-rich alloy of uncertain identity (no As or S detected). The intergrowth is partly enclosed by sperrylite (dark grey). Western Areas mine, x 330 (Polaroid).
43. Concentric intergrowth of two varieties of iridosmium. The twin-like association is distinct. South Roodepoort mine, x 530.
44. Rutheniridosmium, extremely well-rounded and showing an indistinct linear texture. Inclusions of iron nickel sulphide are aligned with the lineation direction. President Brand mine, x 530.
45. An angular osmium crystal. Welkom mine, x 600.
46. A subangular osmium crystal. Welkom mine, x 530.
47. A subround iridosmine crystal. Welkom mine, x 600.
48. A subround iridosmine crystal with a subangular, hexagonal embayment. Welkom mine, x 530.

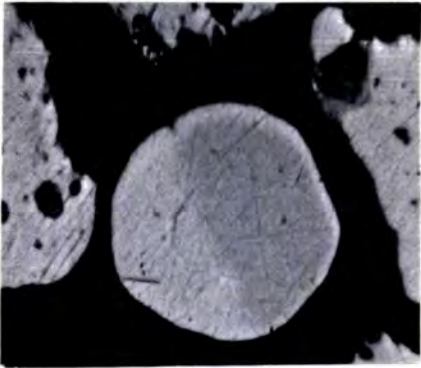
PLATE VII



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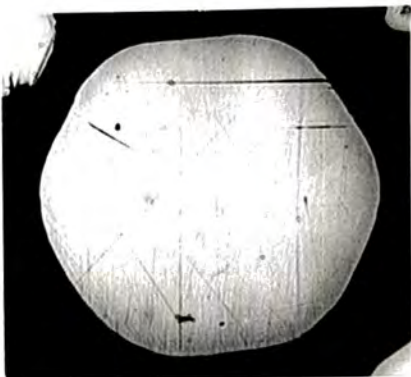
44



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46



47

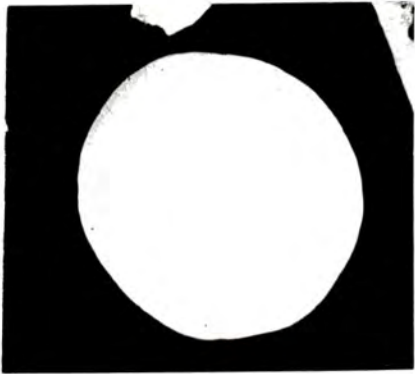


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PLATE VIII

49. A rounded iridosmium grain. Welkom mine, x 400.
  
50. A well-rounded osmiridium grain with concave curves. The small circle is an air bubble. Welkom mine, x 600.
  
51. Iridosmium fractured along crystallographic directions. Undamaged iridosmium shows no cleavage parallel to the c-axis. Libanon Mine, x 400.
  
52. Iridium with radial fractures or cracks. Vaal Reefs mine, x 770.
  
53. Osmiridium showing a crude subhedral outline. Vaal Reefs mine, x 770.
  
54. An hemispherical particle of iridosmium probably broken from a twin-like intergrowth. Libanon mine, x 770.
  
55. Iridosmium with angular hexagonal embayments. Libanon mine, x 450.
  
56. Iridosmium with dumbbell shape. S.A. Lands mine, x 770.



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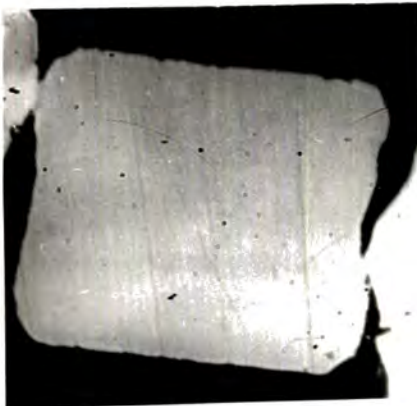
50



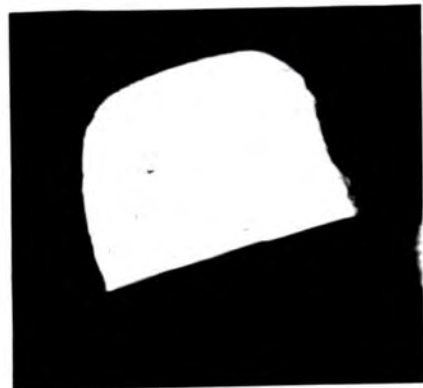
51



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53



54



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56

PLATE IX

- 57.a, b. Iridosmium (white) in concentric and structural intergrowth with an osmium iridium sulpharsenide (arsenic minor).

For iridosmium - Ir:Os = 1:1.1

Pt > 10 at %

For the sulpharsenide - Ir:Os:S = 1:1:4 (approx.)  
with minor Ru, As.

Western Areas mine, x 840 (Polaroid).

- 58.a,b,c. Iridosmium with cleavage flakes of rhodium sulphide.  
Welkom mine, x 420 (Polaroid).

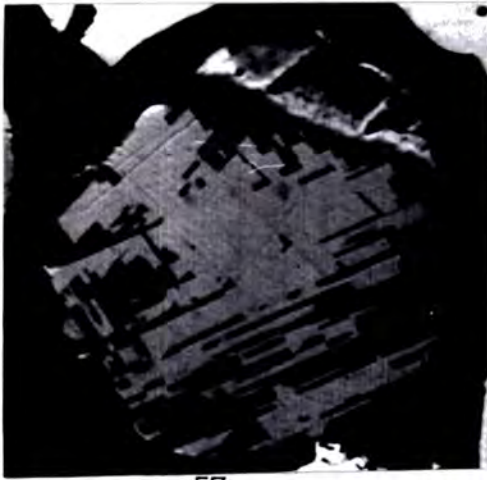
59. Ferroplatinum (white) enclosed in sperrylite (medium grey). A discontinuous zone (dark grey), intermediate between core and shell, comprises major Rh and S with moderate/minor Ru, Pt, As. Small grey patches in the ferroplatinum are enriched in Pt, As. Similar patches in the sperrylite are enriched in Rh,S. Western Areas mine, x 420 (Polaroid) B.E.I.

60. Osmium (white), iridosmium (dark grey) and rutheniridosmium (dark grey, fibrous) in concentric intergrowth. Vaal Reefs mine, x 840 B.E.I. (Polaroid).

61. Ferroplatinum (white) partly replaced by a complex mineral of rhodium, cobalt, arsenic and sulphur. With minor Ru, Fe and Ni (dark grey). Light patches within the rim are ferroplatinum remnants. Western Areas mine, x 420 (Polaroid).

62. Pt L $\alpha$  X-ray image.

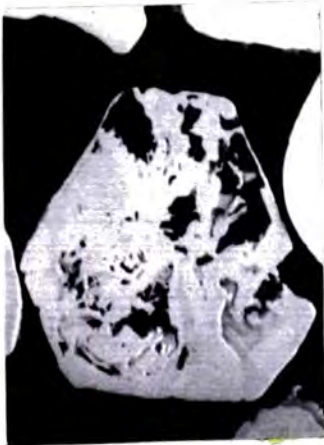
PLATE IX



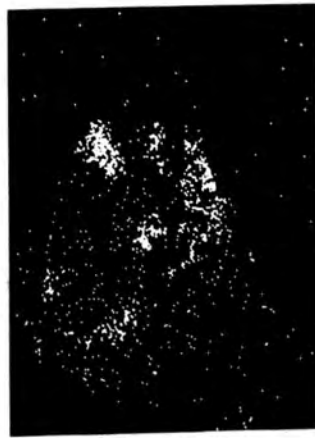
57.a



57.b. S.K $\alpha$



58.a



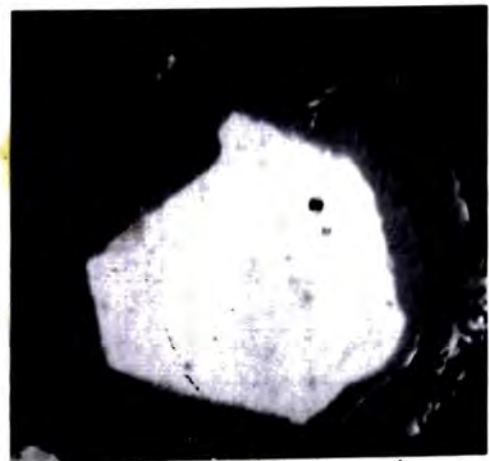
58.b. Rh.L $\alpha$



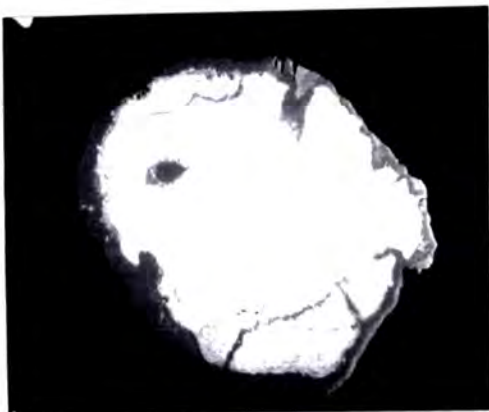
58.c. S.K $\alpha$



59



60



61



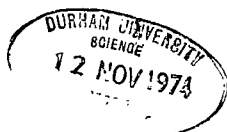
62

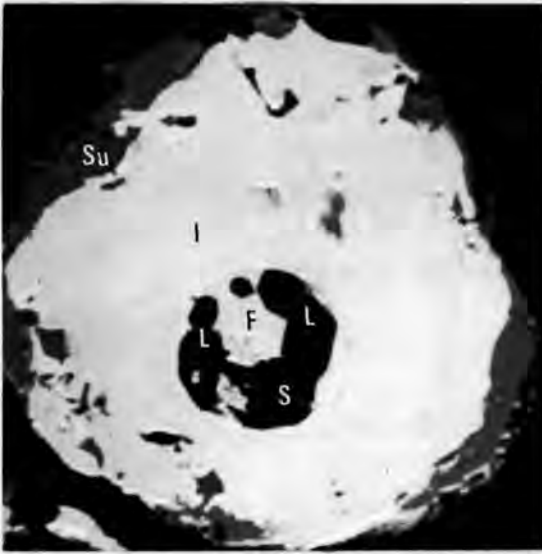
PLATE X

The backscatter electron image and corresponding x-ray images illustrate a complex concentric intergrowth in which five minerals can be identified.

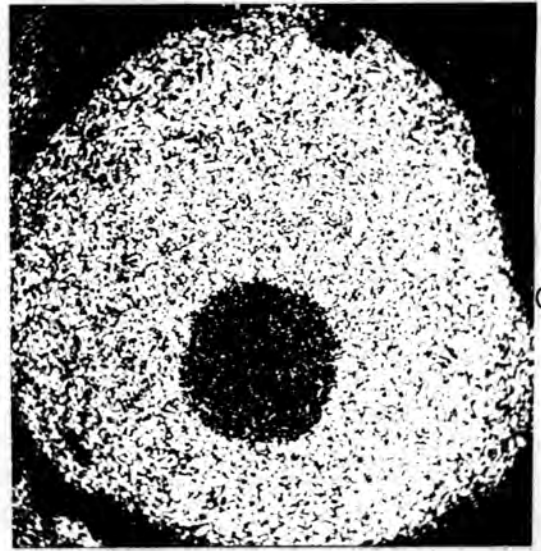
The round composite core of the grain comprises laurite (L), ferroplatinum (F) and a magnesium iron aluminium silicate (S). The composite is enclosed by a broad intermediate zone of iridosmium (I) in which Os and Ir are present in equal proportions and Pt is approximately 10% by weight. Ru and Fe are minor constituents of the alloy. The irregular outer zone of the intergrowth is of an osmium iridium sulphide mineral (S) in which Pt, Ru and As are minor constituents. This outer zone is probably replacing the iridosmium alloy. The occurrence of a small grain of laurite in the rim (top right) is, however, peculiar.

Kinross mine, x 840 (Polaroid).

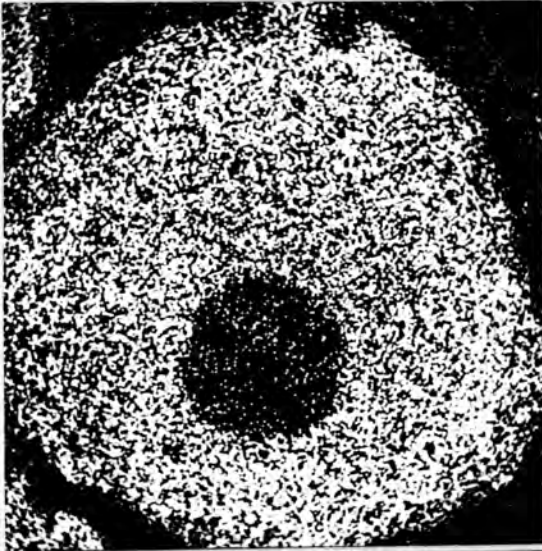




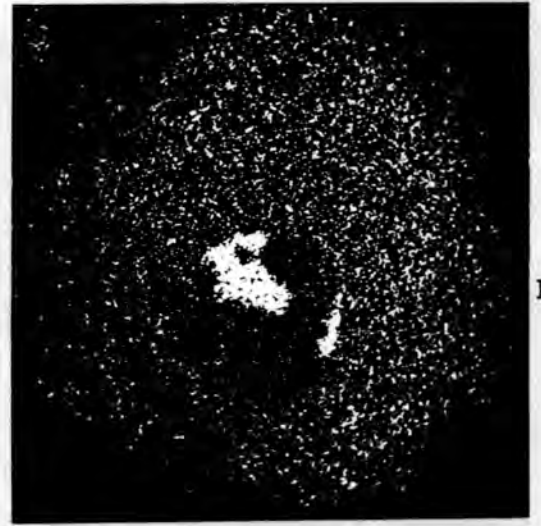
b.e.i.



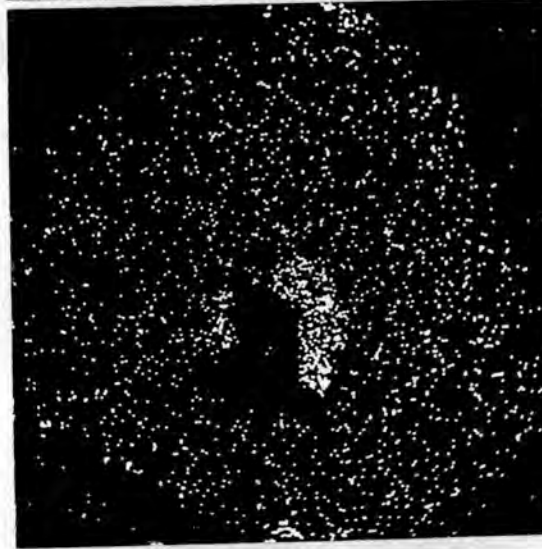
Os.L $\alpha$



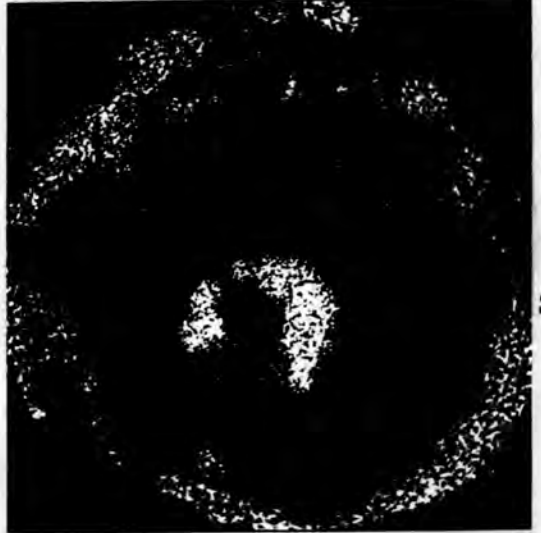
Ir.L $\alpha$



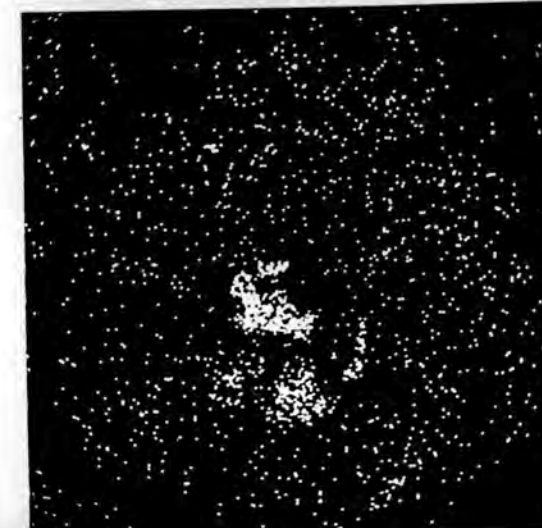
Pt.L $\alpha$



Ru.L $\alpha$



S.K $\alpha$



Fe.K $\alpha$



Si.K $\alpha$