STUDIES ON THE MINERALOGY AND GEOCHEMISTRY OF THE WITWATERSRAND SUPER-GROUP

CLIVE E FEATHER

VOLUME ONE

MAIN TEXT AND APPENDICES

STUDIES ON THE MINERALOGY AND GEOCHEMISTRY OF THE WITWATERSRAND SUPER-GROUP

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Dissertation submitted for examination for the degree of
Doctor of Philosophy. Submitted to the University of Cape Town.

1st August, 1976.

This work was sponsored by the Anglo American Research Laboratories, and is presented, for examination, by kind permission of the Management of the Laboratories.

DECLARATION

I declare that the contents of this thesis has not been submitted previously for examination.

Clive E

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STUDIES ON THE MINERALOGY AND GEOCHEMISTRY OF THE WITWATERSRAND SUPER-GROUP

SUMMARY

Despite the large volume of literature which has appeared since 1886 concerning the mineralogy of the auriferous conglomerate reefs of the Witwatersrand super-group, much new information has been derived during this investigation, essentially due to the use of the electron microprobe. Also, the findings have confirmed the work of previous investigations and settled some old controversies.

Gold grains in the reefs were found to be coated with a very thin layer of iron sulphide and/or iron oxide. The thickness of this coating may increase rapidly during passage of the grains through the mills and recovery plants on the mines, due to decomposition of iron sulphides and metallic iron worn essentially from the crushers and mills. The coating may completely inhibit dissolution of the gold by cyanide solutions during recovery.

Enclosure of gold in carbon may also render the metal refractory during recovery. Evidence is presented which supports the theory that the carbon in its pre-fossil form grew in columnar colonies on the exposed flood planes in quiet periods between phases of sedimentological deposition.

Both free grains of uraninite and uraninite enclosed in carbon, are shown to be of primary placer origin, being derived from a multiple granitic or pegmatitic source. The UO_2/ThO_2 ratio varies over a wide range in the uraninite in individual reef samples. The presence of brannerite, undoubtedly a secondary mineral derived from detrital uraninite, is confirmed. Particularly in the far West Witwatersrand, and in the O.F.S., brannerite was found to be invariably the most abundant uranium-bearing mineral present. It is intimately associated with other secondary minerals,

notably/.....

notably phyllosilicates, pyrite and leucoxene. Enclosure protects the brannerite from dissolution during recovery, and together with uraninite enclosed in carbon, contributes significantly to the residues of the oxidising dilute sulphuric acid leach recovery process. The uranium-bearing minerals contain traces of scandium.

Temperatures of metamorphic activity in the vicinity of 400 - 600°C were indicated by the chemical compositions of mixed crystals of gersdorffite and cobaltite which were deposited at the same time as the gold was redistributed and uraninite was probably altered and recrystallised.

Twenty-five platinum group minerals (PGM) were investigated in heavy mineral concentrates prepared at several gold mines. The occurrence in the Witwatersrand of at least half of these PGM has not been recorded previously, and three are unnamed minerals. The nature of the relatively abundant (Ir,Os,Ru) alloys and the origin of the PGM are discussed in detail.

A new mineral, tučekite (Ni_9SbSbS_8), is described. It is extremely rare in the reefs, and occurs in close association with gold and secondary authigenic minerals.

In the appendices are discussed new and improved methods of X-ray fluorescence analysis, a computer programme to process major element intensity data, and methods which aid electron microprobe investigation.

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CONTENTS

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NOTE: Each Section is preceded by a detailed table of contents.

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FORWARD/.......

STUDIES ON THE MINERALOGY AND GEOCHEMISTRY OF THE WITWATERSRAND SUPER-GROUP

SECTION I - INTRODUCTORY NOTES

FORWARD

This thesis results from research, carried out during the past four years, by electron microprobe, scanning electron microscope, X-ray diffractometer, optical microscope and X-ray fluorescence spectrometer, of a number of selected ore mineral suites in the gold-bearing conglomerate reefs of the Witwatersrand System. It embodies the essential contents of the following papers which have appeared, or have been accepted for publication, in the scientific literature:

1. Feather, C. E., 1972 . Excitation of outer orbital electrons and conductive coating interferometry as aids to the mineralogist and metallurgist using the electron probe X-ray micro-analyzer. Proc. South. Afr. Electron. Microsc. Soc. Vol. 2, 53 - 54.

2. Feather,/.....

2. Feather, C. E. and Koen, G. M., 1973. The significance of the mineralogical and surface characteristics of gold grains in the recovery process. J. S. Afr. Inst. Min. Metall., vol. 73, 223 - 234.

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6. Feather, C. E., 1976. Mineralogy of the platinum group minerals in the Witwatersrand, South Africa.Econ. Geol.,(in press-expected in issue no. 7, 1976).

7. Feather, C. E. 1976. Some aspects of the mineralization of the Witwatersrand reefs. U. S. Geol. Surv. Prof. Paper (in press, expected Dec. 1976).

8. Feather, C. E. and Willis, J. P., 1976. A simple method for background and matrix correction of spectral peaks in trace elements determination by X-ray fluorescence spectrometry. X-ray Spectrometry, vol. 5, p.41-48.

It would be a pointless repetition of work to rewrite the contents of the above papers into the continuous form of a single thesis. Thus the drafts of these papers are reproduced here, with certain enlargements and additional illustrations. Each section (paper) is accompanied by a signed declaration by the co-author, if applicable, stating which part of the work was contributed by the co-author.

The sections on gold, carbon, tučekite and scandium are newly written and have not, as yet, been published.

Each section is treated in roughly the same manner. First the fundamental mineralogy and geochemistry of the minerals are described, followed by discussions of their origin and of their economic implications, if applicable. New and innovated analytical procedures which were used are appended.

The thesis is presented in two volumes to facilitate reading. Volume 1 contains the text, and volume 2 the Tables and Figures.

Each section is terminated by its bibliography (references). Methods of referencing differ in the sections due to differing requirements of the journals to which the papers were sent for publication.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the help of the following persons without which this investigation would have taken very much longer:

Messrs/.....

Messrs L.W. Duggan, B.E. Jackson and M.Harrison

- assistance with electron miscroprobe analyses,

Miss J.A. Snegg - assistance with X-ray diffraction analyses,

Mr. O.G. Garvie - reflectance and micro-indentation hardness determinations on tučekite, and

Mr. D.N. Robinson - assistance with scanning electron photomicrographs.

The help, with sample preparation, of the staff of the Geology Laboratory and of the X-ray Fluorescence Section of the Anglo American Research Laboratories (AARL), is also acknowledged.

The author would like to thank Dr. G.M. Koen, Mr. E.J.J. van Vuuren, Mr. C. van Zyl and Dr. L.J. Cabri for their guidance and encouragement, the mines of the Anglo American Corporation of South Africa and Gold fields of South Africa, and the Geology Laboratory of AARL for supplying samples, and, in particular, the management of the Anglo American Research Laboratories for their support and encouragement.

INTRODUCTION/.....

INTRODUCTION

Since the discovery of the Main Reef group in 1886, several hundred papers have appeared describing, among other geological features, the mineralogy of the gold-bearing reefs of the Witwatersrand System.

At first, the contributions were sparse because there were few qualified metallurgists, geologists, and mineralogists on the early diggings. The need for more sophisticated mining techniques as depth of mining increased, slowly brought qualified men to the Highveld, to the early mines of the Witwatersrand gold fields.

The early experts, and self-styled experts, expounded theories as to the origin of the gold-bearing conglomerates, with descriptions ranging from auriferous lavas and chemical deposits to steam bed gravels and ocean deposits (Ballot 1888). It is not intended that the many theories of the origin of the reefs, and the descriptions of the depositional environment, should be discussed here. These have been reviewed excellently and recently by Pretorius (1975).

The present investigation cocerns the mineralogy of the reefs, with the emphasis on those aspects where further research was clearly required.

Specific attention has been given to the following:

1) - to the geochemical characteristics of the gold grains in the reefs, with specific reference to surface characteristics.

2) - to the compositions and distribution of the uranium-bearing minerals, their age, and influence in the recovery process.

3) - /.......

3) - to the composition, size and shape of the platinum group minerals (PGM).

4) - to the study of certain secondary minerals, especially with regard to compositions, structure and temperature of formation.

5) - to the study of the geochemical and mineralogical associations of elements and minerals, respectively, in an attempt to establish the paragenetic sequence of mineralization.

Complete major and minor element analysis of most of the rock samples was carried out, and a number of trace elements in these samples were determined. Nearly all the ore minerals in the reefs were analysed by electron probe, and some surface studies were carried out on a scanning electron microscope.

SAMPLES EXAMINED

Samples of all the economically important reefs were examined, as listed in Table I - 1. In some cases, a number of samples of a particular reef were collected from different locations underground, e.g. close to dyke contacts, far from dykes, or at regular intervals underground.

Samples taken at various points in gold and uranium recovery plants, at various stages in the gravity concentration of the platinum group minerals, the residues of both recovery plants and

laboratory/.....

laboratory tests, and artificial products produced in the laboratory were also examined. These samples are listed in Table I-2.

The reef samples were examined in thin section, polished section and on freshly opened fractures (no polishing). Concentrates of various specific gravity fractions of deslimed -150 μm crushed reefs were also prepared. These include "Super-panned" very heavy mineral concentrates, bromoform heavy (sink) and light (float) mineral concentrates, and carbon ("thucholite") concentrates. A number of these concentrates were also cleaned chemically with acids to remove soluble common minerals, e.g. pyrite.

In all, 269 sections of reef samples, and 168 sections of the remaining samples were prepared and examined.

ANALYTICAL METHODS AND EQUIPMENT USED IN THE INVESTIGATIONS

Overall rock analyses were obtained on pressed powder pellets and fused glass discs using a Philips PW 1220 Sequential X-ray Spectrometer, and a Philips PW 1270 14-Channel Simultaneous X-ray Spectrometer (Table I - 3). Trace elements were determined by a rapid method described in Appendix 1, in which background and mass absorption coefficient are linearly related. Major and minor elements were determined by a fusion method, described in Appendix 2, based on the method of Norrish and Hutton (1969). Correction for interferences, matrix effects and instrumental drift were effected by the BASIC language computer programme detailed in Appendix 3.

Polished/......

Polished sections of reefs and heavy mineral concentrates were briefly studied by optical microscope before being coated with a conductive layer of carbon for electron microprobe and scanning electron microscope investigation. It was possible to optically examine coated sections using conductive coating interferometry, described in Appendix 4. Mineral identification in the microprobe was aided by cathodoluminescence colours which are documented in Appendix 5.

A JEOL JXA-5A Electron probe X-ray microanalyser was used for all quantitative analyses of mineral grains. The standards are listed in Table I - 4. Apart from pure elements, synthetic and natural compounds were used. Intensity data were collected on punch paper tape using a Canberra Instrumentation (U.S.A.) serialiser interface and teletype ASR 33 teleprinter. The data were transferred to BASIC language files of the Computer Sciences Sigma Limited (C.S.S.L.) Infonet System, using a telephone-line connected terminal situated at the A.A.R.L. Initially, the data were averaged, and corrected for dead-time, drift and background by a front-end BASIC language program written by Mr. D. Whitfield of C.S.S.L., who have copyright. The program presents its results in a format acceptable to the FORTRAN IV program TIM 1 of Duncumb and Jones (1969) which corrects for atomic number, matrix absorption and fluorescence to produce the final results which are listed in the mineral analysis Tables of this work.

A JEOL JSM-35 scanning electron microscope was used for detailed examination of the surface characteristics of mineral grains, freshly exposed in reef and in mineral concentrates and treated materials.

X-ray diffraction studies were all carried out in 57,3 mm Debye-Scherrer cameras using iron-filtered cobalt radiation.

COMPLETE ROCK ANALYSIS:/.......

COMPLETE ROCK ANALYSIS : DISCUSSION

Before considering the mineralogy, attention was given to the overall chemical composition of the reefs.

Major and minor element analyses by X-ray fluorescence are given in Table I-3, which are indicative of the relative proportions of the well-known abundant minerals in the reefs. In general terms, Fe content is essentially a function of pyrite and pyrrhotite content, Al_2O_3 and K_2O of the phyllosilicates, and TiO_2 of the leucoxene content. These elements thus constitute the significant ingredients of the matrix, and vary sympathetically with SiO_2 content, which is mainly in the form of quartz. Some of the SiO_2 occurs in the matrix e.g. in the phyllosilicates and in secondary quartz which has consolidated the reefs as a cement.

The minor elements show large variations between reefs, and even in the same reef sampled within the same mine. Due to the coarse nature of the pebbles in the conglomerate, it is extremely difficult to obtain, crush and split a representative sample for analysis.

The X-ray fluorescence scan for trace elements ($Z>26$) given in Figure I-1 is typical of a well mineralised reef, and the elements detected are indicative of the more important ore minerals present. (Analysis for some of these trace elements are given in Table I-3). They are as follows:

Element present/.....

Element present	Mineral
Uranium Thorium	Uraninite Brannerite
Lead	Galena (mainly radiogenic)
Gold Silver	Gold 10% silver alloy
Zirconium	Zircon
Yttrium	Zircon, xenotime
Arsenic	Gersdorffite, cobaltite, Arsenopyrite
Zinc	Sphalerite
Copper	Chalcopyrite
Nickel	Gersdorffite, pentlandite
Cobalt	Cobaltite

THE ORE MINERALS

Over 80 ore minerals, including the previously undescribed minerals in the present work, have been recorded in the reefs, as given in Table I - 5. The Table is used to depict the approximate paragenetic sequence of ore mineralization, as given by Feather and Koen (1975). The first stage represents the period of detrital mineralization, and includes reworking by wave action and currents on the shores of the ancient basin. The second stage corresponds to the main period of secondary pyrite formation, and the third stage to the period during which most of the gold was remobilized and most of the rare secondary sulphides were formed.

In Table I-5, the relatively more abundant ore minerals are given in bold type, and together they constitute perhaps as much as 99 percent of the ore minerals in most mineralized reefs. The

remainder/....

remainder are rare, even in heavy mineral concentrates. Several are extremely rare indeed: these include the rarer platinum group minerals, tučekite (a new mineral), and at least four minerals which the present author believes are doubtful identifications by previous investigators (see Table I-5).

The confirmation of known minerals, and the identification of new minerals was only made possible through the use of the electron microprobe during this investigation.

Although each section of this thesis is written as a self-contained paper, the ore minerals are discussed approximately in order of economic importance: gold, uranium-bearing minerals, platinum group minerals, and secondary base-metal ore minerals.

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NOTE: Tables and Figure are in Volume 2.

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SECTION II

GOLD

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GOLD.

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SECTION II.

GOLD.

SUMMARY.

Individual gold grains in the Witwatersrand are remarkably homogeneous, and there is very little variation in composition of gold grains within individual reefs. On average, the grains contain about 10 per cent silver, 0,1 per cent copper and 0,5 per cent iron. The average gold fineness of gold grains within rocks, and the fineness as determined by fire assay on the whole rock, gave no positive confirmation that silver occurs in minerals other than gold. Also, in a careful electron microprobe search for silver-bearing minerals, only a very rare silver-bearing palladium telluride was found. The silver was not found to be dispersed in solid solution throughout the abundant pyrite and pyrrhotite in the reefs.

Gold grains in the reefs are coated with iron sulphide and/or iron oxide. During passage through the gold recovery plants this coating was found to increase rapidly. A substantial proportion of the gold reporting to the residues is completely enclosed by iron oxide. An hypothesis is advanced in explanation of the origin of the coatings.

Because/.......

SECTION II.

GOLD.

Because of its economic importance, the gold in the reefs has been studied in great detail, especially by the earlier investigators of the Witwatersrand. After reviewing the literature, and in the quest for improving gold recoveries at the mines, in the present investigation some fundamental aspects of the gold mineralization were studied.

INTRODUCTION

In the Witwatersrand Super-Group gold mineralization is for all practical purposes confined to the conglomerate reefs and, to a lesser extent, to banded pyritic quartzites. Gold in the system is also found in thin films along parting planes between unconformities or disconformities, in quartz veins and in dykes (Pretorius 1964).

The bulk of the gold in the reefs occurs in the fine-grained matrix between the pebbles. This matrix, rich in phyllosilicates and quartz, is very similar to the mineralized portions of the pyritic quartzites referred to above (Young 1917, 1931, Liebenberg 1955).

Veinlets of gold passing from the conglomerate matrix may occasionally intersect the pebbles which may also be coated with thin films of the metal or even be replaced partially by it (Kransdorf, 1937, Du Toit 1954, Liebenberg 1955).

Gold is very rarely found as primary inclusions in the pebbles (Ramdohr, 1958),yet indirectly, they do seem to bear some relationship/......

relationship to the gold tenor of the reef. Several investigators have, reported that for a given reef a relationship may exist between pebble size and gold content: the larger the pebbles, the richer the reef (Young 1917, Reineke 1927, Pirow 1920, Davies 1950, Nel 1960, Pretorius 1964, Steyn 1964, Wilson 1964, Jacob 1966, Schidlowski 1968, Whiteside 1970). The shape and colour of the pebbles (Young 1917, Pirow 1920, Davies 1950) and their degree of sorting (Reineke 1927) have also been found to bear, on occasions, a relationship to gold content. Other features, claimed to be of importance in this respect, are the ratio of reef to finer sediments (Steyn 1964) and the lateral variation of reef width (Pretorius 1964).

For the most part, the gold grains in the reefs are remarkably homogeneous, which might be expected from the fact that some degree of metamorphic activity has certainly taken place since burial, and that a degree of migration of the gold has taken place. Table II-1 lists multiple electron microprobe analyses on an individual gold grain.

Within the reefs, there is generally very little variation in composition. On average the grains contain about 10% silver, 0,1% copper and 0,5% iron. Examples are given in Table II-2, and in Table II-3 average analyses by electron microprobe of a number grains in a variety of reef specimens are compared with the gold/silver fineness determined by fire assay and atomic absorption techniques.

Generally the fineness of the grains by microprobe and that for the rock are in good agreement, with a few exceptions where the fineness is lower in the rock. Graton (1930) and Fisher (1939) were among the first to draw attention to the possibility that silver-bearing minerals (they suggested silver-bearing base metal

sulphides)/......

sulphides) may occur in the reefs.

In later years Von Rahden (1964, 1965) came to very much the same conclusion as Graton and Fisher (op cit) but, together with other researchers (Prentice 1939, Hargraves 1961, Saager, 1969)discounted the possibility of base metal sulphides in the ore contributing anything but insignificant amounts of silver.

Using a novel method (apparently not generally accepted) to leach out silver not associated with gold in ore samples, he found that samples of Ventersdorp Contact Reef and Basal Reef contained quantities of silver (probably present as minerals predominantly silver in composition) ranging from about 4 per cent of the total silver content of the sample to as much as almost 25 per cent.

Von Rahden (1964) discovered a trace of native silver in the banket and, as de Kock (1964) in the Carbon Leader, found that some of the gold particles were coated with thin films of silver. Von Rahden concluded that variations in the gold-silver ratio encountered in the ore-horizons he had studied could be explained satisfactorily by the presence of silver minerals.

Saager (1969) carried out microprobe analyses of individual gold grains in the Basal Reef (O.F.S.) and obtained results compatible to those presented by Von Rahden (1964): whereas the silver contents of individual gold particles (6,53 to 9,37 per cent) were very constant, the silver contents of the ore samples have markedly higher values (up to 37,5 per cent). He suggested that the main portion of the free silver was present as dispersed silver minerals, traces of which he found (proustite and stromeyerite: Saager 1968).

Schidlowski/......

Schidlowski (1968) also carried out microprobe analyses of individual gold particles in Orange Free State gold reefs, but found the gold containing between 9,9 and 12,4 per cent silver. His mean silver content (about 10 per cent) agreed closely with bullion values published by Hargraves (1963) and he concluded that the amount of silver originally present in the reef as silver minerals, if present at all, must therefore have been negligible, thus contradicting the conclusions arrived at by Von Rahden (1964, 1965) and Saager (1969).

Viljoen (1971) carried out electron microprobe analyses of gold grains <u>in situ</u> in samples from a variety of reefs and localities, but his search for discrete silver minerals in these reefs gave negative results. The silver content of individual gold grains was found to vary from 0,3 to 32,1 per cent. Variations were even noted in one and the same sample, and gold grains were analysed that had been considerably enriched in silver along the periphery. This discovery contradicts the findings of Schidlowski (1968) and Saager (1969) who both had found that no significant variation of the silver content occurred within single grains. For most of the gold particles analysed by Viljoen (1971) an average figure of 10 per cent for the silver content seemed reasonable. The wide variations in silver content have probably resulted from association of the gold grains with different minerals (Liebenberg 1973).

Viljoen's results (1971) also show that the silver content of gold particles in the Monarch Reef, West Rand, diminishes from 11,6 percent to 0,52 percent when followed from North to South. A similar depletion in silver content of gold was reported by Pretorius (1964) to occur in Central Witwatersrand reefs, when traced from the western or eastern boundaries of the Witwatersrand basin towards the center. These findings contradict the conclusions of Hargraves (1961) that the

silver/.....

silver content of bullion in each Witwatersrand reef varies as a function of elevation: the reef in shallow areas having a higher silver content that the reef in deep areas.

As may be seen by studying Table II-3, little new information can in fact be gleaned. There is the same inconsistency of results, but the figures are quoted for the sake of completeness.

Although extremely rare, a silver bearing palladium telluride*, probably michenerite, was found as minute inclusions in pyrite in a sample of Carbon Leader reef from Western Deep Levels, Ltd.

Pyrite certainly does not contain any silver in its lattice. Gravity concentrates and tailings, and pyrite flotation concentrates and calcines were treated with hot concentrated nitric acid and the solutions were analysed for silver.

As may be seen from Table II-4, the pyrite concentrate contained somewhat less than average silver than did the gravity fractions. The silver reported in the concentrates is most probably derived from silver in the gold grains which are mainly contained in this fraction.

IRON OXIDE COATINGS ON THE GOLD

Samples of ore from the Carbon Leader, Basal and Vaal Reefs were crushed to approximately one inch diameter fragments, thereby providing fresh exposures of gold grains for examination. The surface of fragments selected for examination were cleaned in an ultrasonic cleaner bath using acetone, alcohol and methyl ethyl ketone successively.

The/......

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* See Section V, Figure 25.

The specimens were thereafter flash-coated with a conductive layer of pure carbon and examined in the electron microprobe.

Without exception, the outer surfaces of the alloy grains examined were found to possess a thin layer of iron sulphide and/or iron oxide (Figure II-1). In cases where the sulphide coating was thicker than average, the iron and sulphur were found to be present in constant proportions, probably as pyrrhotite or pyrite, as shown in figure II-2.

In some cases the alloy was seen to be coated so thickly with iron oxide as to be almost completely concealed from detection using the microprobe (Figure II-3). It is likely that many grains were so thickly coated as to have escaped detection altogether.

Where gold alloy grains were found in the proximity of zinc sulphide (sphalerite), the surface coatings on the alloy grains were found to contain zinc in addition to sulphur and iron (Figure II-4). Lead sulphide may coat the alloy grains when galena is abundant and in close proximity to the alloy grains.

DISCUSSION

The presence of coatings on gold grains is not a new discovery. From time to time, over the years for nearly a century, various investigators have made reference to these coatings, but paid little attention to them. This is partly because the coatings probably only cause the loss of at most 0,5 per cent of the total gold in the ore to

the tailings /....

the tailings, during recovery. But with the value of gold having increased substantially in recent years, it is worthwhile to pay attention to the coatings and find means of removing them, thereby winning the enclosed gold.

Mr. Nellmapius, in his early experiences in recovering gold at Pilgrim's Rest, noted that nuggets of gold were frequently encrusted with iron oxide. In 1934, Leaver et al. reported that iron oxide coatings on gold had adverse effects on recovery. Head (1935 and 1936) confirmed this finding. The National Institute for Metallurgy, S. Africa, published several reports (e.g. Viljoen and Mihálik 1968, Beukes 1968, Beukes and von Rahden 1968), some of which were initially restricted in circulation and only made public in 1975. However, in 1973, Anglo American Research Laboratories made public the findings of its researches into improving gold recovery at a special one day Symposium on "Developments in Gold Recovery Processes" (14 Mar. 1973).

The contribution which the present author made to the presentations at this symposium are discussed in detail below.

THE FORMATION OF COATINGS ON THE GOLD

Laboratory experiments were carried out using pure gold, pure silver and gold/silver alloy concentrated from the Witwatersrand Reefs. The metals were treated with Fe^{2+}, S^{2-}, H^+ and SO_4^{2-} ions in dilute aqueous solution at 40°C.

After 12 hours the silver was heavily coated with a layer of silver sulphide (Figure II-5) containing minor concentrations of iron.

The pure gold did not react (Figure II - 6).

A readily detectable sulphide coating formed on the gold/silver alloy (Figure II-6).

It thus appears that the silver in solution in the alloy becomes available for reaction with sulphide ions in solution, thereby forming a silver sulphide surface deposit.

HYPOTHESIS FOR THE FORMATION OF REFRACTORY COATED GOLD IN WITWATERSRAND GOLD ORE

Studies of the conglomerate reefs of the Witwatersrand System have proved that the age of the system is in the region of 2 600 million years.* There is also abundant evidence that during the vast expanse of time following its formation it has been subjected to metamorphic processes. There have been periods of high activity of sulphide ions, leading to alterations of some of the constituent minerals and the deposition and redistribution of a significant amount of sulphides. Presently there are appreciable quantities of pyrite and pyrrhotite in the reefs, as well as small amounts of other sulphides. Also, radioactive decay of uranium in uranium-bearing minerals, which produces radiogenic lead, has resulted in the formation of galena (lead sulphide). Thus, it may be concluded that, at least during the metamorphic history of the reefs, free sulphide ions were available, and sulphides were formed readily.

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* See Section IV.

In the/.....

In the laboratory experiments described above it has been demonstrated that silver-bearing gold is easily attacked by sulphide ions, whereas pure gold is inert. It is concluded that similar reactions have taken place in the reefs.

The hypothesis advanced is that in nature silver atoms in the peripheral regions of gold alloy grains are able to combine with available sulphur. Once sulphur atoms have been bonded to the alloy surface by this means, the alloy grains become excellent seeds for the growth of yet more sulphide, especially iron sulphides. To at least some extent such coatings have been observed on all the Witwatersrand gold grains studied.

By subsequent oxidation, the iron sulphide coatings have become capable of seeding further growth of iron oxides. In the course of mining and plant operations the process initiated in nature can be continued with extraordinary rapidity owing to the abundance of introduced metallic iron and the prevailing highly oxidising conditions.

The chemical and galvanic* decomposition of tramp iron and precipitation of ferric hydroxides in the alkaline milling and processing circuits is readily observable. In a similar manner introduction of calcium into the surface coatings, by the addition of calcium hydroxide to the pulp, has also been demonstrated.

It is interesting also to note that dilute nitric acid is found to be better than dilute hydrochloric acid for removing the coatings from the gold/silver alloy prior to mercury amalgamation on the gold plants. Silver in the surface of the alloy grains will react with the acids, and in the case of hydrochloric acid only, form a very thin coating

of insoluble/....

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* The galvanic corrosion of iron in the presence of gold is being investigated by the Chemistry Section of AARL.

of insoluble silver chloride on the surface of the alloy grains. In the case of nitric acid, no tarnish forms.

ECONOMIC IMPORTANCE

In addition to iron oxides coatings on the gold, the metal may be enclosed in gersdorffite, carbon and to a lesser extent in other secondary sulphides. Primary inclusions are very rare, mainly in pyrite. Where complete enclosure occurs, neither amalgamation with mercury or dissolution in cyanide can occur. This is an important means by which gold is lost to the residues.

More rigorous treatment of the ore in order to break down these coatings is necessary to improve recovery.

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NOTE: Tables and Figures are in Volume 2.

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SECTION III

CARBON

SECTION III.

CARBON.

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FIGURES (See Volume 2)

SUMMARY/.......

SECTION III.

CARBON.

SUMMARY.

Polished sections of Witwatersrand uraniferous carbon were examined in the electron microprobe, mainly in order to study the distribution of the inorganic elements within the carbon.

The columnar fabric and apparent internal structures of possible biogenic origin are confirmed.

U, Th and Pb occur within tiny crystals of uraninite which may be arranged in (growth?) rings. Gold occurs mainly in the material deposited along the column boundaries, together with Al,Si and Fe in clay minerals. S is ubiquitous throughout the carbon, and is possibly of organic origin. Ti is widespread within the boundary material, ocurring in leucoxene and brannerite.

During the recovery of gold and uranium, even in pressure leaching the carbon was found to be very refractory, and protects the uraninite and gold it encloses.

INTRODUCTION/......

SECTION III.

CARBON.

INTRODUCTION.

The nature of the carbon in the reefs was reviewed excellently and recently by Hallbauer (1975). Convincing evidence has been put forward in favour of the carbon being the fossil remains of a lichen-like plant which grew mainly in the form of columns. Large colonies of these columns covered great areas, and this investigation is intended to evaluate the role which the ancient "lichen" and its remains played in not only aiding the concentration of minerals during deposition but also in protecting gold and uranium minerals in the recovery process today.

ELECTRON MICROPROBE EXAMINATION

The electron microprobe is ideally suited to a study of the internal structures in uraniferous carbon. Both scanning secondary electron images and scanning-backscattered electron images display the inorganic inclusions in high contrast against the relatively low density carbonaceous material that forms the matrix of the substance.

Figure III - 1 illustrates sections of columnar carbon in various reefs. The material is similar to that photographed by Hallbauer (1973, Plate I) and Snyman (1965, plates I, II and III). It can be seen that the column divisions are filled with inorganic material. Within the columns are a multitude of tiny uraninite crystals, sometimes arranged in patterns possibly indicative of growth structures (Fig. III-2).

(It is important/......

(It is important to note the difference between these minute included and contemporaneous uraninite particles and the apparently detrital much larger grains which are to be found outside the carbon and commonly not associated with the carbon at all. The composition of both varieties of uraninite will be discussed in greater detail later - Section IV).

Hypha-like threads, discovered by Oberlies and Prashnowsky (1968) (see also Hallbauer (1973), Plates 3, 4 and 5), forming fibrous clusters (Figure III-3) are frequently emphasised by the presence of relatively heavier mineral particles deposited on the threads.

In massive carbon, many of these structures have been wholly or partly destroyed by the plastic yielding of the carbon to stresses during structural changes of the reefs (Fig. III-4). The fairly regular distribution of the enclosed uraninite generally remains, but the material which was once deposited along the walls of the columns has become squeezed along planes parallel to the shearing forces which were applied.

Detailed investigations were carried out on relatively unaltered columnar carbon, Typical inter-column boundaries are illustrated in Figure III-5. Within the well-defined column, uraninite forming a possible "growth ring" occurs. Uranium is also deposited along the boundaries and in lesser concentration in tiny crystals of brannerite. The uraninite within carbon, in addition to abundant uranium and thorium, generally was found to contain minor amounts of calcium and iron, and much radiogenic lead, mainly in the form of galena filling holes and cracks within the partly metamict grains, and on the periphery of the grains as the result of exsolution. The chemical evidence suggests that both "detrital" uraninite, and the uraninite included in carbon, had a common origin (See Section IV).

Silicon,/........

Silicon,aluminium and iron are generally concentrated along the boundary "membrane" and the hypha-like threads within the columnar carbon. In massive carbon these elements may be used to detect the sites of the original boundaries.

Sulphur is evenly distributed throughout the carbonaceous material. It is not known whether it occurs in organic or inorganic compounds.

Titanium, probably in brannerite and leucoxene, is fairly evenly distributed in relatively high concentrations along the column boundaries (see figures III-5 and III-6).

Various minerals, thought to be of detrital origin also occur in the boundary material. These include zircon, monazite and sphalerite. Although nugget-like gold grains are often found, most of the gold occurs as very finely divided particles (Figures III-5 and III-6) frequently so minute as to escape resolution by the 0,05 micron electron beam. Apart from occurring in the boundary material, the gold was also found as an infilling in the fossil hypha-like threads, confirming the findings of Hallbauer (1973), (see his plates 4 and 5) who studied the structures of gold in contact with columnar carbon.

DISCUSSION

On the strength of studies during the past few years, there seems little doubt that the carbonaceous material is the coal-like remains of organic matter. However, when the author recently attended a workshop on Precambrian Conglomerates in Golden, Colorado,

some doubt/.....

some doubt was cast on the possibility of a biogenic origin as Hallbauer has suggested, despite his excellent structural information. The palaeobiologists who were present (Prof. Schopf, Dr. and Mrs. Nagy) do not believe that life forms of such an advanced level as lichen had appeared on earth prior to about 2000 m.y. ago (The Witwatersrand is about 2600 m.y. old). In all the reefs examined the characteristics of the carbon are remarkably consistent and it appears that the particular species was extant throughout the long period of deposition of the Witwatersrand and the Ventersdorp Systems.

The presence of silicon, aluminium and iron in the boundary material suggests that either finely divided clay minerals settled onto the growing plants, or the fossil remains adsorbed these elements superficially in the subsequent long history of the Witwatersrand and related systems.

Titanium is regularly distributed throughout the boundary material and is believed to have been introduced during the period when solutions, probably formed by the decomposition of titanium-bearing minerals (see Ramdohr, 1957 and 1958), penetrated and altered other minerals in the conglomerates. It appears that these solutions were particularly reactive and were able to penetrate the carbon structures by partial dissolution of the boundary material. During this period abundant brannerite formed in the reefs (Section IV).

The surface of the colonies of columns must have resembled that of a corduroy table, acting to aid the concentration of heavy minerals which were washed over their surface,

Behaviour/........

BEHAVIOUR IN RECOVERY PROCESSES

Being non-wetting, carbon tends to float, especially in the presence of small amounts of grease and oil which are invariably present in the mill circuits of the uranium-recovery plants. Consequently the average particle size of the carbon exceeds the average for quartz and other minerals by many orders of magnitude. By virtue of their enclosure in the carbon, which itself is completely refractory to sulphuric acid leaching, the minute uraninite grains pass undissolved through the recovery plant (Figure III-7). Even pressure leaching causes only minor decrepitation of the carbon, and much of the enclosed uraninite is not dissolved even under the most vigorous and reactive conditions (Figure III-6).

Similarly, enclosed gold, often very abundant, is not released for cyanide leaching.

In the light of the present electron microprobe studies it is unhesitatingly recommended that the uraniferous carbon be separated by flotation from the ore pulp for separate treatment for both uranium and gold.

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NOTE: Tables and Figures in Volume 2.

SECTION IV/.......

SECTION IV

URANIUM-BEARING MINERALS
&
SECONDARY MINERALS

SOME ASPECTS OF WITWATERSRAND MINERALIZATION WITH SPECIAL REFERENCE TO URANIUM MINERALS

Clive Feather

Paper submitted for publication in a Professional Paper of the United States Geological Survey. Presented at the Workshop on "The Genesis of Gold- and Uranium-Bearing Precambrian Quartz Pebble Conglomerates", in Golden, Colorado, 13 - 15 October 1975.

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SOME ASPECTS OF WITWATERSRAND MINERALIZATION WITH SPECIAL REFERENCE TO URANIUM MINERALS

Clive E. Feather

ABSTRACT

Evidence is presented which suggests that temperatures of metamorphic activity in the vicinity of 400 - 600°C have been achieved in the Witwatersrand gold-bearing reefs. This temperature range is based on the chemical composition of mixed crystals of gersdorffite and cobaltite which are undoubtedly of authigenic origin, being deposited at the same time as the gold was redistributed and uraninite was probably recrystallized.

Sedimentological studies support the view that uraninite is of detrital origin, but it has been suggested that the mineral resulted also from precipitation from solution, since the "lichen-like plant" which is seen today as carbon ("thucholite") possibly also absorbed uranium from solution during its growth. However, the UO_2/ThO_2 ratio varies over a wide range in the grains from single reef samples, suggesting a multiple granitic or pegmatitic detrital source.

All original features of the uraninite grains have been destroyed by subsequent partial chemical dissolution and alteration to the uranium titanate mineral brannerite (confirmed by electron microprobe and X-ray diffraction studies).

Age determination by ion microprobe on minute volumes within the metamict crystals gives the same age (about 1 800 m.y.) for both uraninite and brannerite suggesting that recrystallization and

alteration took place at the same time. This is younger than results obtained on whole grains as determined by other investigators (about 2000 m.y.), possibly because whole grains may be contaminated with some radiogenic lead of a greater age which occurs in pits and cracks in the grains, and thus not completely purged from the grains at the time of recrystallization.

Electron microprobe analyses of a large number of gersdorffite, cobaltite, uraninite and brannerite grains are presented.

Losses to uranium extraction plant residues are essentially due to enclosure of minute uraninite crystals in carbon, and, especially in the west of the Witwatersrand basin, to enclosure of minute brannerite crystals in acid insoluble hosts, mainly phyllosilicates and leucoxene.

INTRODUCTION/....

SOME ASPECTS OF WITWATERSRAND MINERALIZATION WITH SPECIAL REFERENCE TO URANIUM MINERALS

INTRODUCTION

In recent years, mainly as a result of the development of sophisticated instrumentation such as the scanning electron microscope and electron microprobe, considerable advances have been made in our understanding of the processes responsible for the mineralization of the conglomerate reefs of the Precambrian Witwatersrand deposit. Our present knowledge of the ore mineralogy of the reefs has been collated and reviewed by Feather and Koen (1975), who indicated certain aspects which required further research.

With this in mind, the present paper considers; inter alia uranium mineralization and the temperature to which the reefs were subjected during the major period of metamorphic activity which they underwent.

Chemical compositions were determined with a JEOL JXA-5A Electron Probe X-ray microanalyser using pure metals, synthetic compounds and analysed minerals as standards. Data refinement was achieved by the computer program of Duncumb and Jones (1969). Fe-filtered CoKα radiation was used for all 57.3 mm Debye-Scherrer camera X-ray diffraction studies.

Samples of all the economically important reefs of the Witwatersrand stratigraphic sequence were examined. Polished sections of reef and heavy concentrates were prepared. In addition, a large number of mine recovery plant products were examined.

SECTION 1/....

PART 1: TEMPERATURES OF METAMORPHIC ACTIVITY

Introduction: The Modified Placer Theory

It is not intended that the arguments which were put forward for a hydrothermal (e.g. Davidson, 1960), and a placer origin for the mineralization of the conglomerates be discussed here. Recent evaluations by Pretorius (1974a, 1974b, 1975) among others, especially with regard to the sedimentology of the Witwatersrand basin, clearly support a placer origin for the mineralization of the reefs. In brief, it is believed that deposition took place along the interface between a fluvial system that brought sediments and heavy minerals from an elevated source-area to the northwest of the basin and a lucastrine littoral system that reworked the material and redistributed the finer sediments along the shoreline of an ancient inland sea. The heavy minerals were concentrated by gravity settling and subsequent winnowing by wave and current action. Some investigators, e.g. Hallbauer (1975) and Riemer (1975), support the view that some of the gold and uranium were carried into the basin in solution and deposited biochemically by an ancient lichen-like life-form that preferentially developed in quieter water conditions at the mouths of major rivers at the end of cycles of sedimentation.

There is little doubt that some of these ore minerals, notably the gold, base metal sulphides and arsenides, and uraninite underwent subsequent alteration and redistribution <u>in situ</u> in the reefs after burial, during at least one major epoch of metamorphic activity. The date of this epoch is set by the age of the uranium-bearing minerals which would have been purged of their radiogenic lead at this time.

This /...

This is the modified placer theory, which enjoys a fair degree of concensus especially among those who are familiar with the geology of the basin through mining activities.

Previous Work

Fuller (1958), using the method of Kullerud (1953), in which the iron content of sphalerite is used as a geothermometer to determine the temperature at the time of deposition, obtained an average temperature of 450°C for undoubtedly authigenic sphalerite in samples from the Bird Reefs Group taken just south of Krugersdorp on the Witpoortjie fault. Similarly, von Rahden (1964) obtained a temperature of 400°C on a grain of authigenic sphalerite from the Bird Reefs Group at Luipaardsvlei Gold Mine.

Barton and Kullerud (1957/58), however, point out that this method gives only a minimum temperature of formation and therefore the temperatures in the reefs may have been still greater than those indicated above. However, the iron content has been shown to be not only dependent upon temperature. This is born out by the fact that the iron content of secondary sphalerite in the reefs varies from 1 to 7% (Table 1), even when secondary pyrite and pyrrhotite are abundantly present.

The presence of various other secondary minerals in the reefs has been cited as giving information as regards temperature of formation. Pyrrhotite, which occurs sporadically throughout the reefs, occurs in occasional abundance in the vicinity of major dykes. Most investigators believe it to have been derived from pyrrhotization of primary pyrite. Exsolved pentlandite lamellae are common, and both monoclinic and hexagonal pyrrhotite occur in the reefs. Both these facts are indicative of fairly high temperatures of pyrrhotization (Ramdohr, 1955, and von Rahden, 1964). Similarly the presence of chloritoid replacing sericite in the matrix of the reefs has been considered by many (e.g. Ramdohr, 1955) to be an indicator of high temperature and pressure conditions. Mackinawite, although very rare, must have crystallized at a minimum temperature of 210-250°C, as cited by Schidlowski (1968). Graphite, occurring as bent and broken flakes, apparently formed in situ as a result of graphitization of carbon (Saager, 1968 and Schidlowski, 1967). X-ray diffractometric analyses of columnar and massive carbon, believed to be the fossil remains of an ancient lichen-like plant, frequently show signs of incipient graphitization (Feather and Koen, 1975), indicating that fairly widespread elevated temperatures were achieved during metamorphism.

These observations are, however, of a qualitative nature. Consequently, in the present investigation, quantitative information was sought of a more suitable mineral assemblage, notably of the cobaltite and gersdorffite which are widespread in the reef.

The Evidence of Cobaltite and Gersdorffite

The cobaltite-gerdorffite grains are of two distinct generations, allogenic and authigenic. The allogenic grains, all with Co> Ni> Fe, i.e. cobaltite, are well-rounded (Figure 1), may contain pyrrhotite inclusions, and have undergone little or no alteration since burial in the reefs.

Electron/....

Electron microprobe analyses of a large number of grains are plotted in the ternary diagram FeAsS-CoAsS-NiAsS (Table 2 and Figure 2). Superimposed on this diagram are the chemical isotherms of mixed crystal formation of Klemm (1965). Differing symbols are used to identify each reef. The temperatures at which the grains formed vary widely over the range of <300°C to about 600°C, and may have been derived from one or more possible hydrothermal deposit situated in the primary source rocks to the northwest.

Further evidence may be derived from the crystal structure of the cobaltite. X-ray diffraction analyses of a large number of grains of varying composition consistently gave the $Pca2_1$ space group of the orthorhombic system. According to Giese and Kerr (1965), and Gammon (1966), this is the low temperature ordered crystal form of cobaltite, having crystallized at temperatures below about 800°C.

The secondary (authigenic) (Ni, Co) sulpharsenides (Figure 3) are more variable in chemical composition (Table 3 and Figure 4). The majority have Ni> Co> Fe, and thus may be classified as gersdorffite. Indicated temperatures of formation of individual grains (Table 3 and Figure 4) vary within the individual reef samples, and in the Witwatersrand System as a whole, over the range of about 400°C to 600°C. Variation within reefs is explained by slow and zoned crystal growth. In some of the reef samples, the compositions may be plotted along a line which extends toward the pure NiAsS end member (see the dotted lines in Figure 4). Zoned crystal growth is commonly visible. For example, grain A201 from the Basal Reef has a core which is optically silver-white with a greyish tinge, and a composition indicating a temperature of crystallization of 450°C. It is immediately enclosed by a zone of higher nickel content, blueish in colour, which indicates a

temperature/.....

temperature of $<300^{\circ}C$. The outermost zone is even more blueish, has a higher nickel content, and thus was formed at an even lower temperature.

The above deductions are based on the premise that Co, Ni and Fe were freely available in the reefs at the time of crystallization. The zoned structure and crystallization trends (dotted lines in Figure 4) may also be explained as due to depletion of Co and Fe during crystal growth. For this reason, in all cases, the temperatures indicated must be regarded as minimum temperatures of formation.

Additional information was sought in the crystal structure of the authigenic gersdorffite. Both Pa3 (pyrite) and $P2_13$ (ullmannite) space groups of the cubic system are present. According to Bayliss and Stephenson (1967), and Bayliss (1969), these are the high and intermediate temperature forms of gersdorffite, and, as may be deduced from Figure 5, resulted from crystallization at temperatures in the region of 450-600°C. This is further confirmed by the fact that mixed crystals of the authigenic sulpharsenide, with $Co \approx Ni$, gave the $Pca2_1$ low temperature form of cobaltite, indicating that this cobaltite crystallized at temperatures of about 600°C (see figure 5).

To summarise, this study of the chemistry and crystal structure of secondary gersdorffite-cobaltite has indicated that minimum temperatures in the region of 400-600°C, and probably closer to 600°C have been achieved in the Witwatersrand reefs during metamorphism of the reefs. Samples which were taken close to dykes (e.g. sample 192-Basal Reef, see figure 4) indicated only slightly higher temperatures (about 500-600°C) than did reef samples not associated with dykes (the rest in figure 4 - about 400-550°C). It appears, therefore,

that/...

that these temperatures were widespread and not localised to the vicinities of cross-cutting dykes and related hydrothermal veins. However, a word of caution should be noted here. The work of Klemm (1965) has not been independently and critically examined. In addition to temperature, a variety of other factors might influence the mixed crystal formation. However, the excellent correlation with the temperatures indicated by the crystal structures does suggest that Klemm's isotherms are applicable to the metamorphism of the Witwatersrand System.

Optical Characteristics of Gersdorffite

Witwatersrand gersdorffite is cubic, thus shows no anisotropism or birefringence, and varies in colour from silver-white to white with a blueish tinge as Ni-content increases. The NiAsS end-member is strongly bluish and readily confused with skutterudite which has almost identical optical properties. There is additional chance of misidentification resulting from descriptions of gersdorffite in the literature. E.g., according to Uytenbogaardt and Burke (1971), gersdorffite is white with a yellowish or pinkish tint.

In the past, a number of references to the presence of skutterudite in the reefs have been made. Among others, Ramdohr (1955) found that the redistributed gold was often associated with skutterudite, which is of about the same age, though sometimes distinctly younger. Viljoen (1963) also noted the close association of gold and skutterudite.

In the present investigation, skutterudite could not be found, despite an extensive search by electron microprobe, and it is concluded that previous investigators have confused gersdorffite with skutterudite. The descriptions which both the above authors give for skutterudite could apply equally to gersdorffite.

Section 2/...

PART 2: URANIUM-BEARING MINERALS.

The important uranium-bearing minerals in the Witwatersrand and related reefs are uraninite, and the alteration product of uraninite. Lesser uranium-bearing minerals include zircon, monazite, columbite, betafite, uranothorite, euxenite and xenotime.

In this section, the result of an extensive electron microprobe examination of these minerals is presented, intending to complement the findings of previous investigators, to present new information, and notably to present quantitative microprobe analyses of the important uranium-bearing minerals.

Evidence is presented to confirm that the alteration product of uraninite is brannerite. Particular attention is drawn to this mineral, as it may be the main uranium-bearing mineral in the reefs, especially in the Vaal and Basal Reefs.

URANINITE

Introduction

Cooper (1923) was the first to record the presence of uraninite in the reefs. Ramdohr (1955) and Liebenberg (1955) published the first detailed studies of the mineral, and, in general, investigators have regarded it as being essentially of detrital origin. It invariably occurs in greatest concentration close to the footwalls of the reefs, or on the false footwalls (Ramdohr, 1955) within them, in apparent hydraulic equilibrium with other heavy minerals which are

definitely/...

definitely of detrital origin.

The grains have a limited size range (Liebenberg (1955) records that the average diameters range from 75-100 μm), and contain abundant galena inclusions, and may enclose gold, gersdorffite, pyrrhotite and chalcopyrite.

The grains are commonly rounded, tending to be oval in shape (Liebenberg, 1955), and surrounded by phyllosilicates, mainly sericite. Euhedral and subhedral grains are, however, not uncommon. During the present investigation, fractured sections of the reef (i.e. simply reef samples which were broken open and the freshly exposed surfaces studied) revealed the presence of uraninite grains which were often bounded by some or all crystal faces, as in figure 6. This might be expected from the fact that the grains were recrystallized and were purged of radiogenic lead during metamorphism. Rounded grains were invariably found to be accompanied by traces of minute crystals of an alteration product.

It is suggested, therefore, that the rounding is due to partial chemical dissolution rather than detrital rounding.

Uraninite also occurs as minute anhedral and subhedral inclusions in carbon. The carbon is believed to be the fossil remains of an ancient lichen-like plant (Hallbauer, 1975). Thus two distinctly different generations of uraninite occur in the reefs which will be referred to as free and included respectively, but each generation is remarkably uniform in texture throughout the reefs.

The UO_2/ThO_2 Ratio/.....

The UO_2/ThO_2 Ratio

Whereas most investigators of the reefs support a detrital origin for the uraninite not associated with carbon, some, e.g. Koen (1961), and Riemer (1975), have suggested that the uraninite may have precipitated from solution, aided by biochemical activity of the "lichen" or similar organisms.

Hallbauer and von Warmelo (1974) have pointed out that the "lichen" has certainly absorbed both uranium and gold, and other inorganic materials, during its growth. The question arises, however, as to whether the "lichen" "digested" detrital matter, or whether it actually absorbed these elements from solution. It is a common observation that the carbon (the fossil form of the "lichen") replaces partially, or almost wholly the uraninite grains.

Recrystallization during metamorphic activity has destroyed all the primary features of the uraninite. As noted above, the present state of rounding of the grains is probably due to partial dissolution rather than attrition, and evidence of crystallization as colloidal pitchblende, e.g. radial textures and cracks, is also absent.

During the progress of this investigation, Grandstaff (1974) published electron microprobe analyses of free uraninite grains in a sample of reef from Vaal Reefs West Mine. In common with the present author's findings at the time, he found that although the individual grains were fairly homogeneous, the overall UO_2/ThO_2 ratio of grains varied vastly in the assemblage of uraninite grains in the reef sample. He concluded that such heterogeneity favours a detrital, placer origin for the uraninite, having been derived from a number of primary sources.

He points out that the Witwatersrand grains contain appreciable thorium (up to 10% ThO_2), in common with a pyrogenetic (granitic or pegmatitic) source, rather than low-temperature, hydrothermally derived uraninite which is normally very poor in thorium content.

In the present investigation, uraninite from a number of reefs was analysed for U, Th, Pb, Fe, Ca and Ti by electron microprobe, using, as standards, sintered UO_2 and Th (prepared by the Atomic Energy Board, Pelindaba), Pb-metal, and analysed hematite, wollastonite and rutile. The results are summarised in Tables 4 and 5, and in figure 7 the UO_2/ThO_2 ratios of the grains are plotted against ThO_2 content. The data for free uraninite and uraninite included in carbon are plotted separately.

Within all the reefs examined great variation in the UO_2/ThO_2 ratio occurs in the free uraninite favouring, in each reef, a multiple primary source for the uraninite, in keeping with Grandstaff's (1974) findings. In addition, a similar variation occurs in the uraninite enclosed within the carbon. Although it may be possible that the UO_2/ThO_2 contents of the water which came into contact with the "lichen" may have varied so vastly, it seems more likely that the "lichen" "digested" detrital grains, hence the large and similar variation in UO_2/ThO_2 ratio.

Also, the overall compositions of the free and included uraninite are very similar (compare Tables 4 and 5), although the variations in all elements within each reef would require more analyses to be carried out and the data to be rigorously statistically treated before it could be proved that they are definitely of a common source.

Although/....

Although the evidence in favour of a detrital source for the uraninite appears to be most convincing, it is difficult to explain why it is only the well-mineralized reefs which contain the bulk of the uraninite. There are numerous conglomerate and sandstone layers in the succession which may contain other typical detrital grains, e.g., chromite, zircon, etc., which contain neither uraninite nor gold. In addition, in the reefs, uraninite is relatively much more abundant than zircon by several tens of times. This is contrary to what might be expected from granitic or pegmatitic source-rocks which are expected to have contained relatively more zircon than uraninite.

The mineralized reefs do contain one common ingredient which is virtually absent in the barren sediments, i.e. carbon. Despite the foregoing evidence it does seem possible that the ancient "lichen" played an obscure role in aiding the concentration of both gold and uranium. However, it may be argued that the presence of detrital uraninite was essential to the "lichen's" origin and development.

Also, cognisance should be taken of the fact that when each period of sedimentation came to an end, the newly deposited material was exposed to the elements for a long period before the next cycle of sedimentation. The sediments may have been reworked several times before complete burial took place. Such exposure may have resulted in weathering and resultant partial dissolution and alteration.

BRANNERITE/...

BRANNERITE

Introduction

As previously noted, the free uraninite grains are invariably partially dissolved and altered. Both Ramdohr (1955) and Liebenberg (1955) noted the presence of an alteration product. Liebenberg distinguished between two products: a common microcrystalline, relatively homogeneous phase somewhat similar in appearance to parent uraninite, which he called "secondary uraninite", and uraniferous leucoxene. The "secondary uraninite" forms encrustations (Figure 8) on, or may partially or wholly replace grains. Ramdohr called this material "ghosts" since the outline of the parent grain is frequently discernible in the crystal orientation of the altered material. Both "secondary uraninite" and uraniferous leucoxene may also be seen infiltrating neighbouring quartz, sericite, clay and sulphide grains (Figure 9).

When it was established that the "secondary uraninite" contained abundant titanium, it was speculated (e.g. Davidson, 1957; Davidson , 1960; Jacob, 1966; Schidlowski, 1966) that it might be the uranium titanate mineral called brannerite, derived from the combined reaction of uraninite and ilmenite or titaniferous magnetite. Pyritization of ilmenites is abundantly evident in the reefs, and titanium would have been freely available for reaction. Although Jacob (1966) obtained a refractive index value which was similar to that of brannerite, attempts to identify positively the mineral by X-ray diffraction failed, even when heating experiments were carried out (von Rahden and Hiemstra, 1967; Mihâlik, 1968; von Rahden, 1970).

Electron /...

Electron Microprobe and X-Ray Diffraction Investigation

Using back-scattered electron images, the mineral appears to be homogeneous, despite abundant galena inclusions. A number of grains were analysed for U, Th, Pb, Fe, Ti, Ca and Si, and the results are listed in Table 6. As in the uraninite analyses (Tables 4 and 5), the elements are expressed as oxides. The low totals probably result from metamictization and voids in the crystal "lattice structure", and possibly also from the fact that Fe may be present as Fe_2O_3 instead of FeO, and Pb as a sulphide rather than an oxide, since galena inclusions are abundant although visible inclusions were avoided during analyses.

In Table 6, the SiO_2 content of the grains varies from 1 to as much as 18%. It is probable that it is derived from the abundant authigenic silica which has invaded all fractures and pores in the reefs, having either entered the structure of the uranium titanate at the time of formation, or later when the grains became metamict and somewhat porous (in the same way, e.g. as sulphur entered the grains to form galena from radiogenic lead.

As in uraninite, the UO_2/ThO_2 ratio varies extensively in the alteration product (Figure 10), helping to confirm its derivation from the uraninite.

Selected grains were heated to 1000°C for one hour and examined by X-ray diffraction analysis. The results are given in Table 7. Although the diffraction data may partially fit a mixture of Pb_3O_4, quartz, and rutile, or the mineral may be contaminated with these three, there are a number of important lines of these proposed impurities which are absent (underlined in the table). Ignoring the

lines/...

lines of an unknown impurity, the best fit is with the data for brannerite given by Patchett and Nuffield (1960).*

It may be argued that a metamict micro-aggregate of TiO_2 and UO_2 would, on heating, synthesize brannerite, and that the original mineral may not have been brannerite at all. However, this is a problem inherent in all studies of metamict minerals.

As Ferris and Ruud (1971) have pointed out, because of the uncertainty of heating experiments and X-ray diffraction analyses, structure analyses cannot be considered essential for positive identification of metamict minerals such as brannerite.

What we do know is that we have in the Witwatersrand a homogeneous mineral similar in appearance (medium grey, medium reflectance) to descriptions of brannerite given in the literature (e.g. Pabst, 1954; Patchett and Nuffield, 1960; Ferris and Ruud, 1971). It is similar in composition to brannerite from other sources (Table 8, and Ferris and Ruud, 1971). For the overall average in Table 6, if the uranium content in increased to what it would have been before radioactive decay, and on the reasonable assumption that Th, Ca and Fe substitute for U in the structure, and SiO_2 is ignored, the average normalised composition would then be approximately 65% UO_2 and 35% TiO_2, close to the ideal formula $UO_2.2TiO_2$ (62.8% UO_2 and 37.2% TiO_2).

It is the opinion of the present author that the uranium titanate mineral in the Witwatersrand is indeed brannerite.

The uraniferous leucoxene described first by Liebenberg (1955) is found to be an admixture of leucoxene and varying amounts of tiny needles of/......

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* Since this paper went to press, numerous X-ray diffraction patterns confirming brannerite have been obtained.

of brannerite (Figure 9, grain 5).

Economic Importance of Brannerite:

Brannerite is most abundant in the reefs mined in the West and Far West Witwatersrand where it may be the most important uranium-bearing mineral, and of lesser abundance in the Orange Free State. In the Middle, East and Far East Rand it is relatively rare.

According to Liebenberg (1955), who refers to brannerite as "secondary uraninite", its rate of dissolution in the oxidising dilute sulphuric acid leach solutions of the uranium extraction plants is slightly greater than that of uraninite. However, on examination of many leach residues during the present investigation, in addition to uraninite enclosed in carbon, brannerite was frequently the most abundant uranium-bearing mineral in the plant tailings. This is due to enclosure of the brannerite by minerals which are themselves insoluble. Phyllosilicates, pyrite, quartz and leucoxene are common refractory hosts (Figure 9). Finer milling of the ore to release the tiny crystals of brannerite (generally <5μm) would be impractical. Only by dissolution of these refractory host minerals will recovery efficiencies significantly improve.

It has been suggested by Laxen (1973) that (U,P) compounds, if present, may be relatively refractory and slow to react with the leach solutions. Although Mihálik was able to identify a (U,P) compound in the Dominion Reef, no similar compound could be found during the present study in the reefs of the Witwatersrand and Ventersdorp Systems.

In/...

In an intensive search for phosphorus compounds associated with uranium, only monazite and a calcium phosphate mineral (presumably apatite) could be found, occurring as minute crystals in the matrix of the conglomerates, and sometimes associated as discrete grains, with brannerite, as illustrated in Figure 11. These discrete phosphate grains are not expected to interfere with the dissolution of the brannerite. Also, there is no evidence that the brannerite in the residues, compared with that in the plant feed, is in any way more closely associated with these phosphate minerals.

UO_2/ThO_2 RATIO IN THE REEFS AS A WHOLE

In Table 9 a comparison is made of the overall UO_2/ThO_2 contents of rock samples of the reefs determined by X-ray fluorescence spectrometry, with the average obtained on uraninite and/or brannerite grains in the same reef samples by electron microprobe. The ratio is always lower in the case of the overall rock samples which suggests that there are other thorium-bearing minerals in the reefs.

Investigation shows that zircon, monazite and uranothorite are present, although relatively rare, and all three contain varying and sometimes appreciable amounts of thorium and relatively lesser uranium.

AGE OF WITWATERSRAND URANIUM-BEARING MINERALS

Polished sections containing Witwatersrand uraninite, brannerite and zircon were sent to Drs. Hinthorne and Andersen at the

ARL Hasler Research Centre, Goleta, California, for age determination by ARL IMMA Ion Microprobe (for a description of the instrument and technique see, e.g., Andersen and Hinthorne, 1972). The results which they obtained are as follows:

MINERAL	Pb^{207}/Pb^{206} RATIO	AGE (million years)
Uraninite (average)	0.1078 ± 0.0002	1770 ± 60
Brannerite	0.1103 ± 0.007	1810
Zircon	0.2017	2845

The age values were calculated using the newly recommended decay constants of Tatsumoto et al. (1973). The average value for uraninite (1770 ± 60 million years) is somewhat lower than previously determined values [approximately 2000 million years - see e.g. Louw (1954)] . The difference might lie in the fact that the ion beam sampled the lead within the crystal structure of the uraninite eliminating any contamination from the environment of the grains.

The fact that the brannerite and uraninite are practically of the same age (limits of accuracy overlap) may indicate that the formation of brannerite by alteration of uraninite coincided with the period when the remaining uraninite recrystallized. This age (1800 m.y.) agrees with the last stages of emplacement of the Bushveld Igneous Complex (e.g. Davidson, 1960), which thus may have been the source of the metamorphic activity.

The zircon age (2845 m.y.) is somewhat older than that of the Witwatersrand System itself (approx. 2500 m.y.) and may be indicative of the age of crystallization or recrystallization of the source rocks.

The zircon age/......

The zircon age is also somewhat similar to the convergent age of 2680 m.y. reported by Ahrens (1955a), for the oldest Rhodesian monazites. The monazites occur in rocks that are believed to occur in the source terrain of the Witwatersrand sediments. It would be of great interest to investigate zircons from a number of reef samples in order to test the validity of this suggestion.

Ahrens (1955b) also notes that the convergent age for Witwatersrand uraninite, using the data of Louw (1954), is approximately 2000 m.y. The values given above for uraninite and brannerite are expected to be underestimates, according to Ahrens (1955b).

However, the information does confirm that during this ancient epoch of evolution of the earth's crust, two major events took place : one at about 2700 m.y. and one at about 2000 m.y. Obviously the latter was able to produce sufficient activity to recrystallize the Witwatersrand uraninite,alter the reefs and deposit secondary minerals at temperatures as high as 400 - 600°C.

PART 3/........

PART 3: PARAGENESIS OF GERSDORFFITE AND OTHER SECONDARY MINERALS

Temperatures of metamorphism in the vicinity of 600°C are fairly high, and medium grade metamorphism is expected to have occurred. Apart from very thorough cementing of the pebbles and matrix, mainly through the redistribution of quartz, a proportion of, if not all of the gold was redistributed, virtually in situ, and gersdorffite and other secondary minerals were formed from the alteration of pyrite and less stable detrital minerals which were present.

Gersdorffite is invariably associated with gold, as noted by Saager (1968), with which it is commonly intergrown. So regular is this association that gersdorffite may be used as an indicator of gold content. The association is even closer than that of carbon and gold, where carbon may be present in abundance without the gold content being sympathetically high. (In mining practice, carbon content is commonly used as an indicator of gold content).

Intergrowths of gersdorffite and gold often were seen to contain chalcopyrite (Figure 12) and, more rarely galena(Figure 13), pyrrhotite, sphalerite, tucekite (Ni_9SbSbS_8)*, pentlandite, stibiopalladinite and sudburyite, all clearly secondary minerals of the same generation. Intergrowths of gersdorffite, gold and sperrylite were also observed (see Section V, Figure 26). These intergrowths are generally xenomorphic, unlike free grains of the same generation. Pyrite and galena notably show euhedral crystal outlines (cf. intergrowth of galena and gersdorffite in Figure 13.).

At the same time, much rarer sperrylite, hollingworthite, ruthenarsenite and iridarsenite are believed to have formed from reconstitution of the remains of highly altered primary platinoid mineral grains. Alteration of phyllosilicates in the matrix, pyritization of iron oxides and ilmenite leading also to abundant needles of rutile, recrystallization of uraninite and crystallization of

brannerite/.....

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* See Section VI

brannerite, and the growth of tourmaline, bravoite, cubanite, proustite, stromeyerite, tennantite and mackinawite, all very rare, is expected to have taken place at this time.

GENERAL CONCLUSIONS

Investigation of the Witwatersrand cobaltite-gersdorffite assemblage has revealed, on the basis of crystal structure and chemistry, that temperatures in the vicinity of 400-600°C were achieved during metamorphism of the reefs.

It is apparent that at that time the gold was remobilized and secondary base metal sulphides, sulpharsenides and arsenides were formed. It appears that at the same time the uraninite was recrystallized, and was partially altered to a uranium titanate mineral which is confirmed to be brannerite.

Age determinations by ion microprobe show that the last period of recrystallization of uraninite, presumed to be the same period as gave rise to the metamorphic activity during which gersdorffite and related minerals were formed, took place about 1 800 million years ago. This coincides with the last stages of emplacement of the Bushveld Igneous Complex.

The variable UO_2/ThO_2 ratios in uraninite grains not associated with carbon suggest that the grains are of detrital origin having been derived from a number of granitic or pegmatitic sources. A similar variation in uraninite included in carbon suggests that the ancient "lichen", which is fossilised as the carbon, "digested" the detrital uraninite, rather than absorbed the UO_2 and ThO_2 from solution.

In /...

In addition to uraninite included in carbon, brannerite enclosed by refractory silicate minerals is an important source of uranium losses to uranium extraction plant residues.

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NOTE: Tables and Figures in Volume 2.

SECTION V/......

SECTION V

PLATINUM GROUP MINERALS

ADDENDUM.

Because of high printing costs, and the limits set by the editors, some interesting photographs were not included in the original text of this Section, which was submitted to Economic Geology for publication. These photographs have been included in this thesis, and are referred to in the footnotes. They appear as additional Figures 22 to 26.

SECTION V

MINERALOGY OF THE PLATINUM GROUP MINERALS IN THE WITWATERSRAND, SOUTH AFRICA

Clive E. Feather

Paper accepted for publication in "Economic Geology", in issue No. 7, 1976. Presented at the Society of Economic Geologists International Platinum Symposium, Denver, Colorado, U.S.A., 16 to 18 October 1975.

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ABSTRACT/.....

MINERALOGY OF THE PLATINUM GROUP MINERALS IN THE WITWATERSRAND, SOUTH AFRICA

Clive E. Feather

ABSTRACT

Approximately 80% of the platinum-group mineral (PGM) grains in the Precambrian Witwatersrand conglomerate reefs are (Ir,Os,Ru) alloys. Osmium, iridosmine, osmiridium, and iridium are most abundant; rutheniridosmine, ruthenosmiridium and ruthenian iridium are less abundant. Zoned grains are common, with Os-rich cores enclosed by (Ir,Pt)-rich outer zones filled with exsolution lamellae of (Pt,Fe) alloy. Discrete grains of this alloy proved to be isoferroplatinum of a composition close to Pt_3Fe. In addition, grains ranging in composition between Pt_3Fe and platiniridium are present.

Sperrylite commonly occurs as an outer coating on all the above grain types. Sperrylite and isoferroplatinum make up 15 to 20% of the PGM grains and account for nearly all the Pt present. Hollingworthite, iridarsenite, and ruthenarsenite occur in variable quantities (1 to 5%) as coatings on alloy grains, which in turn may be coated with sperrylite.

Euhedral and subhedral inclusions in the common PGM grains are michenerite, moncheite, laurite, geversite, and three new and unnamed minerals: RhS, RuAsS and (Pt,Rh,Ru) alloy. Free grains of geversite, moncheite, sudburyite, and stibiopalladinite are very rare. The last two may be intergrown.

Occasionally, partial or complete alteration of (Ir,Os,Ru) alloys has resulted in mixtures of erlichmanite, irarsite, osarsite, and phases that could not be identified.

The/...

The evidence suggests that the (Ir,Os,Ru) and (PGE,Fe) alloys and their inclusions underwent little or no alteration during weathering, transportation, and burial, or even during later metamorphism of the reefs when sperrylite, hollingworthite, and related phases probably formed from less stable PGMs, possibly tellurides and antimonides.

INTRODUCTION

Although the existence of iridosmine (sic) in the Witwatersrand gold-bearing conglomerate reefs has been known since 1896 (Wagner, 1929), only a few descriptions have been published. The first was by Young (1907), who observed iridosmine grains in heavy-mineral concentrates obtained from crushed ore at Rietfontein mine.

Horwood (1912) had two concentrates spectrographically analysed and concluded that osmium, iridium and ruthenium were essential constituents, and noted the marked relative deficiency of both platinum and palladium. He expressed the opinion that the iridosmine was of hydrothermal origin, a view that was strongly opposed by Young (1912), who maintained that the iridosmine was detrital.

Wagner (1929) noted that not only was iridosmine recovered in heavy concentrates being produced by the mines, but also were recovered "several distinct (platinum group) minerals, probably including native platinum". He recorded that the essential constituents were iridosmine and osmiridium, and that they were also present in the Black Reef of the Transvaal System. The platinum-group mineral (PGM) concentrates became popularly known as "osmiridium concentrates".

Koen (1964) examined chemically cleaned concentrates and suggested that two distinct iridosmine phases were present which he described as "iridosmine I" and "iridosmine II". He found that both phases had hexagonal symmetry, and differed distinctly from cubic osmiridium, which he noted was also abundant.

Hiemstra (1964) described sperrylite and an unidentified sulpharsenide of Ru and Rh from the reefs, and de Kock (1964) mentioned sperrylite, cooperite, braggite, native platinum, platiniridium and osmiridium.

Barrass/....

Barrass (Cousins, 1973a) recognized laurite, sperrylite, cooperite and iron-rich platinum, in addition to iridosmine and osmiridium. Both Barrass and Koen noted that the Witwatersrand grains may display crystal zoning and intergrowth structures.

In the present investigation carried out at Anglo American Research Laboratories the previously recognized minerals were examined in detail using a JEOL JXA-5A electron microprobe and JEOL JSM-35 scanning electron microscope. Quantitative analyses are presented, and a number of previously unrecognized minerals are described. At least one, a rhodium sulphide, is a newly discovered mineral. The abbreviations PGE and PGM will be used for platinum-group elements and platinum-group minerals, respectively. Element symbols are used to distinguish elements from minerals of the same name, and mineral names are unabbreviated

Quantitative electron microprobe results are based on standards of pure metals (Bi,Pt,Ir,Os,Pd,Rh,Cu,Ni,Co,Fe), synthesized alloys and compounds (Pt_9Ru, PdBi, PdTe, $PtBi_{1.4}Sb_{0.6}$, PdSb, Pt_3Fe, Pd_5As_2), and chalcopyrite. Data were refined by using the computer program of Duncumb and Jones (1969).

SOURCE OF MATERIALS

Samples of heavy-mineral concentrates from the gravity concentration circuits of ten gold mines of the Anglo American Corporation of South Africa Limited were used. In addition, samples were obtained from various stages of gravity concentration and chemical cleaning at two of these mines.

Although the heavy-mineral concentrates contained abundant PGM grains, they could not be classified according to the stratigraphic sequence, since at all these mines a number of reefs are being mined simultaneously.

Attempts/....

Attempts to concentrate PGM from crushed individual samples of reef proved unsuccessful, owing to very low abundances. Cousins (1973a) gives a value of 0,0035 ppm based on recovery values. Only two of more than thirty panned fractions yielded PGM grains. Consequently, a study of variations within reefs was not possible.

PLATINUM-GROUP MINERALS OBSERVED

The PGM identified in the Witwatersrand concentrates, and estimates of their average relative abundances, are given in Table 1. Mineral names and formulae which could not be determined positively are indicated by asterisk. The nomenclature of Harris and Cabri (1973) is employed for the (Ir,Os,Ru) alloys.

The platinum sulphides braggite and cooperite were not observed in the suite of samples examined, but both minerals were previously described by de Kock (1964), and cooperite was described by Barrass (see Cousins, 1973a).

THE ALLOYS OF IR,OS AND RU

Electron microprobe analyses of (Ir,Os,Ru) alloys are listed in Tables 2 and 3. The values are plotted in the ternary diagram Ir-Os-Ru (dots) (Figure 1), where they are classified using the nomenclature of Harris and Cabri (1973). Osmium and iridium are most abundant, followed by iridosmine and osmiridium. Ruthenosmiridium, rutheniridosmine and ruthenian iridium are minor constituents. Three operators were used intermittently in the analysis of the (Ir,Os,Ru) alloys, and owing to each operator's bias in selecting grains of specific appearance, Tables 2 and 3 contain analyses of distinct groups of alloys rather than of randomly selected grains. Subsequent re-examination of the concentrates revealed that the alloy suites are remarkably

similar./......

similar. They contain all the phases given above, which are present approximately in the proportions shown in Figure 1.

The compositional data were accumulated over two years, and initially, due to the use of an unsuitable Os standard (pure metal sponge), Os was determined by difference, the data being treated reiteratively by the computer program of Duncumb and Jones (1969). As a result, it appears that the Os may have been underestimated, since a few iridosmine analyses fall within the miscibility gap (hatched area in Figure 1) indicated by Harris and Cabri (1973). Cabri and Harris (1975), however, point out that the boundaries of the miscibility gap have not been accurately defined and, in addition, may vary with temperature and pressure of crystallization, as well as with the effect of the impurity elements.

Generally, Ru content appears to increase with increasing Ir content, Osmium was found to contain not more than 4 atomic percent Ru, and a great number of analyses of this phase revealed no Ru at all. In contrast, the Ir-rich phases vary over a wide range of Ru contents, as shown in Figure 1.

The affinity of Ru for Ir,* rather than for Os, is a geochemical anomaly, since Ru and Os are expected to show preferred association due to their having more similar chemical properties and common hexagonal symmetry. It is suggested that the anomaly may have some reflection on the genesis of these minerals, and thus warrants further investigation.

The hexagonal Os-rich alloys have a distinct basal cleavage (Figure 2)*, and cleavage cracks are commonly filled with authigenic matrix constituents of the reefs (e.g., phyllosilicates and quartz),

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* See Figure 23.

suggesting/......

suggesting that some parting took place while the alloy grains were in the reefs, during periods of tectonic stress. Chemical alteration parallel to the basal cleavage plane was observed in some grains (Figure 2). The nature of these alteration products is described later in this paper.

In contrast, the cubic Ir-rich alloys show few signs of cleavage, but they commonly contain exsolution lamellae of (Pt,Fe)alloy and inclusions (Figure 3).

Zoned grains are fairly common*. Iridosmine cores, often of hexagonal outline, may be surrounded by alloy both poorer in osmium and containing Pt. Some examples of this alloy are given in Table 4, and are plotted as open circles in Figure 1, although, because Pt>10 at. %, the nomenclature does not apply. Ideally, a three-dimensional diagram (Pt,Ir,Os,Ru) should be used.

This Pt-bearing alloy may be the hexagonal phase referred to as "iridosmine II" by Koen (1964), although, by virtue of its Ir and Pt contents, it is expected to have cubic symmetry. It is generally enclosed by Ir-rich alloy containing numerous Pt-rich exsolution lamellae* similar to the composition to the examples given in Table 5. The entire grain may, in turn, be enclosed by an arsenide or sulpharsenide of PGE, especially sperrylite.

ISOFERROPLATINUM

The Pt-rich exsolution lamellae referred to above contain varying concentrations of Fe (Table 5). Where distinct segregation as phases has taken place, as well as in free grains, compositions approaching Pt_3Fe were recorded (Table 6). Determined by X-ray diffraction analysis, the mineral has a primitive cubic structure and thus is isoferroplatinum, according to the nomenclature of Cabri and Feather (1975).

The/......

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*Addendum: See Figure 22, in which a typical zoned grain is illustrated.

The free grains are relatively rare and are smaller than the average platinoid grains (i.e., <80 μm). They commonly contain inclusions of other platinoid minerals: moncheite, michenerite, (Pt,Rh,Ru) alloy and a rhodium sulphide.

The chemical data in Tables 5 and 6 are plotted in the ternary diagram (Pt)-(Fe,Ni,Cu)-(Ir,Os,Rh,Ru) in Figure 5. A distinct trend is revealed which separates the end member Pt_3Fe from (Ir,Os,Ru) alloys. The Fe content decreases steadily from Pt_3Fe to (Ir,Os,Ru)alloy. The evidence suggests that this trend is possibly due to fractionation of the end members, and fractionation is confirmed by the presence of exsolution lamellae and intergrowth textures, as illustrated in Figure 3. Phase separation may have occurred during cooling in the source rock, or later during metamorphic activity in the Witwatersrand conglomerate reefs.

The evidence appears to support segregation in the source rocks,* since the free grains of isoferroplatinum contain inclusions common to ultrabasic source rocks and therefore appear to be of primary origin. This point will be discussed in detail later in this paper.

Isoferroplatinum grains coated with PGE-(As,S) minerals, notably hollingworthite and sperrylite, are also common.

SPERRYLITE

Sperrylite ($PtAs_2$) is a ubiquitous member of the PGM suite in the Witwatersrand reefs but appears to vary in concentration within the reefs. Generally, it forms an outer coating on (Ir,Os,Ru) alloy and isoferroplatinum grains. This coating varies in thickness from less than 0,1 μm, where it is composed of a layer of minute crystals, to 50 μm or greater. The coating may act to cement PGM and other grains together, including gold and base-metal sulphides (Figures 4 and 25).

In the /.......

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* Addendum: See Figure 24, in which a distinct intergrowth texture has developed. It is believed that this texture could only have developed upon crystallization in the source rocks.

In the mine concentrates, free grains of sperrylite are rare. They may represent fragments of coating which broke away during milling of the ore (Figure 4, grain 5). The frequency of uncoated grains can be similarly explained.

Chemical data for sperrylite are presented in Table 7. The mineral contains very little impurity and closely conforms to the formula $PtAs_2$. In some samples, e.g., concentrate 2 from Western Deep Levels Limited, Rh and S show a sympathetic relationship (Figure 6), and Ir may substitute for Pt in varying amounts up to about 11 weight percent.

HOLLINGWORTHITE AND ASSOCIATED MINERALS

Hollingworthite (RhAsS) occurs almost exclusively as a few μm thick intermediate layer in composites comprising an outer coating of sperrylite and a central grain of either (Ir,Os,Ru) alloy (Figure 3) or isoferroplatinum. Free grains are extremely rare, as are layers thick enough (>10 μm) for electron microprobe analysis. The best microprobe results obtained are summarized in Table 8. Stoichiometry is not always present, and other PGE, notably Pt and Ru, substitute freely for Rh. Similarly As appears to substitute for S. To test the apparent mutual substitution of PtAsS, RhAsS and RuAsS, the data have been plotted in the ternary diagram with these three as end-members, the small amounts of Ir,Cu,Ni and Fe being grouped with Pt. The results are illustrated in Figure 7. Grains H15 and H21 fall within the RuAsS field - that of an unnamed mineral - in which RuAsS > RhAsS > PtAsS. Grain H6 is similar to the ruthenian hollingworthite recorded by Genkin et al. (1966), and the rest are either Pt- or Fe-bearing varieties. Owing to high Fe (7,7%), grain H9 plots within the (Pt,Ir,-Cu,Ni,Fe)AsS field, but has more RhAsS than any other end-member sulpharsenide and therefore is still hollingworthite.

Hollingworthite is the main Rh-bearing phase in the platinoid suite of the Witwatersrand. Presumably this is the phase described by Hiemstra (1964) as containing Ni, Fe, Co, Ru, Rh, As and S, and having an X-ray diffraction pattern resembling that of arsenopyrite, although hollingworthite in the strict sense has a pyrite-type structure.

When present, the rare arsenides of ruthenium and iridium, namely ruthenarsenite and iridarsenite, are associated with hollingworthite, either as irregular exsolution lamellae (Figure 9, grain 1) or in an interstitial layer between alloy grains and hollingworthite. No suitable examples for electron probe analysis were found, but mixed X-ray diffraction patterns confirmed the presence of these two arsenide phases.

RHODIUM SULPHIDE AND RUTHENIUM SULPHIDE (LAURITE)

Sulphides of both rhodium and ruthenium are very rare in the reefs.These sulphides occur as minute inclusions in the PGE alloy grains, especially in isoferroplatinum. The inclusions range from euhedral to completely irregular or globular (Figure 8).

For the rhodium sulphide an average composition of 51,5 at .% Rh+(Pt,Ru,Ir,Os,Ni,Fe) and 48,5 at. % S+As was determined by electron microprobe analysis (Table 9). This corresponds to an ideal end member RhS, hitherto unrecorded in the literature. The smallness of the inclusions (<20μm) precluded reliable X-ray diffraction analysis.

Similarly, the structure of the ruthenium sulphide could not be investigated. The electron microprobe results indicate that two phases of ruthenium sulphide are present. In Table 10, grains R13 and R14 conform to an ideal end-member RuS_2, or laurite. However, the remaining grains are closer to RuS in composition.

Laurite occurs occasionally intergrown with Ir-rich (Ir,Os,Ru) alloy (Figure 9, grain 3). This association is considered to be related to primary crystallization in the source rock.

MICHENERITE, MONCHEITE AND GEVERSITE

Traces of michenerite Pd(Bi,Sb)Te were observed in sample 3 from Western Deep Levels Limited, usually as globular inclusions in isoferroplatinum (Figure 9, grain 6) and (Ir,Os,Ru) alloys, but also as minute acicular crystals in common sulphides (e.g., pyrite and pyrrhotite). Only one free grain was found,* and an electron microprobe analysis of it appears in Table 11. X-ray diffraction analysis confirmed that the grain has the structure of michenerite.

The acicular michenerite found in base-metal sulphides is considered to be of a younger generation than the globular variety. It contains minor Ag (<10 atomic %),* and less Sb and Bi.

Tellurium and antimony were frequently detected in the cores of the microcrystalline aggregates which appear to represent the highly weathered remains of primary PGM grains (Figure 4).

In addition to occurring as very rare inclusions in alloy grains, geversite occurs intermixed with sperrylite as a coating on these weathered primary grains (Figure 4). Where As and Te are present (Table 11), X-ray diffraction analysis nevertheless confirms that the mineral has the structure of geversite.

(PT,RH,RU) - ALLOYS

Alloys of Pt, Rh and Ru occur as minute irregularly shaped inclusions in isoferroplatinum grains (Figures 4 and 9), frequently concentrating towards the central areas of the grains. The smallness of the inclusions (<30μm) precluded X-ray diffraction studies. Electron microprobe analysis of the larger inclusions in isoferroplatinum from President Brand gold mine

revealed a/.......

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* Addendum: This free grain is ilustrated in Figure 26, as well as an acicular grain which contained Ag.

revealed a considerable variation in composition (Table 12). One example, grain R3, has Ru>Pt>Rh, and grains R9 and R11 have Pt>Rh>Ru and the rest have Pt>Ru>Rh. As illustrated in Figure 10, increasing Ru is not accompanied by a parallel increase in Rh content, which remains in the region of 13 to 26 atomic percent.

SUDBURYITE AND STIBIOPALLADINITE

Pd-bearing minerals in the Witwatersrand are extremely rare. Other than michenerite, only sudburyite (PdSb) and stibiopalladinite (Pd_5Sb_2) have been isolated by the author.

Sudburyite (Figure 11) was found in a superpanned heavy concentrate of a sample from a highly mineralized section of the Vaal Reef. Electron microprobe analyses are given in Table 13. The identification of the mineral was confirmed by X-ray diffraction analysis.

In a concentrate from President Brand gold mine, discrete grains of sudburyite were found, as well as fragmented grains of stibiopalladinite containing inclusions of chalcopyrite and sudburyite.

In all the grains observed, the palladium antimonides were partly or completely enclosed in gersdorffite, with which stibiopalladinite was also intergrown.

IRARSITE, OSARSITE AND ERLICHMANITE

It appears that some localized alteration of (Ir,Os,Ru) alloys grains has taken place. In general, Os-rich alloys are the more altered, and the alteration has been inwards and parallel to the basal cleavage (Figure 2), whereas in the Ir-rich alloys, the inward alteration is of an irregular pattern.

X-ray diffraction studies of selected altered grains reveal mixtures of a number of compounds. In Table 15 two examples are given. Some unaltered alloy remains (osmium, ASTM-6-0662, is given as a guide) and, of the seven possible alteration products listed (data taken from the literature), a mixture of erlichmanite (OsS_2) and irarsite (IrAsS) and/or hollingworthite (RhAsS) is deduced to be present. Osarsite (OsAsS), RuAsS (unnamed), or both minerals might be present, although some important lines are absent (d-values in parentheses). In examples where both Rh and Ru are only present in low concentrations (refer to microprobe analyses in Table 14), hollingworthite and RuAsS are not likely to be present. The lack of correlation with iridarsenite ($IrAs_2$) and ruthenarsenite (RuAs) precludes the presence of these two minerals. However, the irarsite in Table 13 contains only 8,2 at. % S instead of 33,3 at. % S of the ideal formula. Similarly, the osarsite contains only 2,4 to 9,2 at. % S. Genkin et al. (1966) and Snetsinger (1972) also reported As/S ratios exceeding unity for these minerals. Presumably, As substitutes for S without any change in crystal symmetry.

Although the alteration products generally form microcrystalline admixtures, delicate intergrowth textures resulting from distinct exsolution subsequent to alteration can be observed (Figure 2). The analyses given in Table 14 were obtained on exsolved bodies exceeding 20 µm in average diameter.

SHAPE OF THE GRAINS

Young (1907) briefly mentioned the occurrence of iridosmine in a concentrate obtained from Rietfontein mine and stated that the mineral was probably of detrital origin. Horwood (1912), in his more detailed study, felt that the iridosmine was "certainly of secondary origin", its source being basic dykes which intersect the reefs. Horwood expressed

the opinion /...

the opinion that, among other features that favoured a pneumatolytic origin, the grains were crystalline (sic) and showed no evidence for being waterworn.

This was not the conclusion which Young came to in 1912. By publishing photomicrographs (Young, 1912), which clearly showed rounded grains and crystals with worn corners, he challenged Horwood to present him with evidence of the crystalline grains the latter had described.

Young's views were largely subscribed to, despite challenges by Davidson (e.g., 1956, 1960, 1963) and others who supported a hydrothermal origin for the platinoid grains, until Koen (1964) carried out a detailed optical microscopic examination of chemically cleaned grains. He noted that the shapes of the grains varied from perfectly round to euhedral, and that many grains were completely irregular in shape. He reported nodular and dumbbell shapes, with embayments, concave curves and re-entrant angles, and suggested that these features were not characteristic of waterworn grains; since, e.g., it was difficult to explain how some grains were heavily abraded while others, which would have been tranported and deposited under identical conditions, were left apparently unaffected.

It should be noted, also, that it is the smaller grains which invariably display the highest degree of rounding, and the larger which are most irregular. Some of the irregularity is due to mechanical fracturing during crushing and milling of the ore, despite the prevailing smallness of the grains (<100µm).

In a discussion of Koen's paper, Hiemstra (1964) disagreed with the former's view since independent studies of detrital attrition (he quoted Kuenen, 1959) had shown, in fact, that great differences in roundness

could be /...

could be found in grains of the same mineral which had been transported under the same conditions.

Since the shapes of the grains had been investigated under the optical microscope only, it was decided that valuable evidence might be obtained if grains were examined with a scanning electron microscope as well. Because secondary coatings on the grains might be present, the concentrates were treated to varying degrees with acids and caustic soda. Both chemically treated and untreated samples were examined. The most interesting finding is that virtually every grain which was examined was coated with secondary PGM which probably formed subsequent to burial. Even Os-rich alloy grains, provided they have not undergone any alteration, appear in polished section to consist of only one phase, but they have thin coatings of microcrystals on the surface (Figure 12). Relatively thick coatings of sperrylite, undoubtedly a secondary mineral (see next section) produced perfectly rounded and nodular grains (Figure 13), which when fractured may be seen to enclose both euhedral (Figures 14 and 15) and rounded older PGM grains (Figure 14).

Evidence of detrital fracturing and pitting is rare and is seen only in iridosmine grains (Figure 12, possibly Figure 16). Surface patterns indicative of chemical etching are also present, e.g., along the basal cleavage planes of iridosmine (Figure 17) and on grains consisting of intergrown PGE alloys (Figure 18; although this may also be considered a coating texture).

In addition, there are a variety of surface textures which are difficult to interpret, e.g., the apparent shrinkage folds in Figure 19 and embayment in Figure 20.

The predominance of coating features, even on those grains which had been vigorously treated chemically, suggests that the grains, with

the exclusion /...

the exclusion of the Os-rich alloys which may display original detrital attrition characteristics, have lost their original appearance, and that it would be most invalid to draw conclusions as to their origin from their shapes alone.

For the most part, the present shapes would appear to have resulted instead from chemical overgrowths on originally detrital grains, and from alteration of unstable detrital grains.

ORIGIN OF THE WITWATERSRAND PGM SUITE

Practically everyone with extensive and direct experience in mining or research on the Witwatersrand gold-bearing reefs maintains that there is abundant geological and mineralogical evidence to indicate a placer origin for the precious-metal content of the reefs, whereas the contrary applies to many arguments of the protagonists of a hydrothermal origin (e.g., Horwood, 1912, and Davidson, 1960). Argument between the two schools of thought has stretched over many years and has often been subjective and acrimonious. In recent years, favour of the hydrothermal theory has steadily diminished. In particular, it is considered both unlikely in the extreme and also unnecessary to invoke hydrothermal mineralization, e.g., mineralization from the few isolated dykes to be found in the proximity of the reefs which occupy narrow planes of vast and remarkably consistent areal distribution.

Today, the so-called modified placer theory is largely accepted, since, among other factors, it is obvious to the placerist that low-grade metamorphism has brought about partial alteration or redistribution of the more susceptible detrital minerals present in the reefs. Fuller (1958) and Feather and Duggan (1974) have shown that temperatures in the vicinity of 400-600°C have prevailed in the reefs. During this period, the bulk of the gold was redistributed, the uranium minerals were re-

crystallized /...

crystallized and altered, and a number of secondary sulphide, sulpharsenide and arsenide minerals were formed.

Probably by virtue of their relative abundance and economic importance, attention has been given principally to the origin of the gold- and uranium-bearing minerals in the reefs, but much of the argument also applies to the considerably rarer PGM.

In the following discussion, the validity of the various proposals for the origin of the Witwatersrand PGM suite are examined in the light of the findings of this investigation.

The mineralized detritus, which included PGE, was carried into the Witwatersrand basin by rivers and was reworked by wave and current action along the shoreline of an ancient inland sea (see Pretorius, 1975).

Viljoen et al. (1970) have suggested that the source rocks were mafic and/or ultramafic rocks from belts which lay to the northeast of the basin. Köppel and Saager (1974) were able to produce quantitative evidence which indirectly supports this theory. They found that the isotopic composition of the lead in detrital pyrite in the Witwatersrand reefs is similar to that in sulphides from the primary gold deposits of the ancient greenstone belts of the Eastern Transvaal.

However, the relative proportion of the elements comprising the PGM suite in the Witwatersrand is virtually the converse of that characteristic of primary magmatic deposits. In the Witwatersrand, (Ir,Os,Ru) alloys predominate, Pt is less abundant (5 to 23 %), while Rh (0,5 to 1,2%) and Pd (<0,5%) are present only in very low concentrations. Whereas antimonides, tellurides, bismuthides, sulpharsenides, and arsenides of the PGM are widespread in primary sulphide-type deposits these minerals are significantly rare in the Witwatersrand. As in the recent Riam Kanan placer in Borneo, where vincentite, $(Pd,Pt)_3(As,Sb,Te)$, has only been

preserved /....

preserved within grains of native platinum (Stumpfl and Tarkian 1974), tellurides, antimonides and bismuthides of palladium and platinum have been preserved by similar enclosure in isoferroplatinum and (Ir,Os) alloy grains in the Witwatersrand assemblage. This suggests that free grains of these minerals were lost during weathering, transportation and burial.

Cousins (1973a, 1973b) has attributed this enrichment of Ir and Os, relative to the remaining PGE, to the relative chemical stability of Ir and Os during weathering, transportation and burial (Pd, Pt, Rh, Ru, Os, and Ir being the order of increasing chemical stability). Pd is expected to be completely lost in solution, and Pt and Rh lost to a lesser extent. Laboratory experiments indicated that double salts of the PGE may form under oxidizing conditions, and Cousins has suggested that this may have been the mode of dissolution of the more soluble PGE in a supposedly saline Witwatersrand sea. In addition, Stumpfl (1974) has suggested that PGE chloride-type complexes may have increased the solubility of the PGE, especially at elevated temperatures during burial and metamorphic activity.

Dissolution of the more soluble PGE and disintegration of tellurides and other unstable minerals, possibly would result in liberation of colloidal PGE metal particles which Cousins envisages, led by a process of accretion to growth of colloform and zoned grains. A similar process has been suggested by Ottemann and Augustithis (1967) for the formation of "platinum nuggets" in lateritic covers from ultrabasic rocks and birbirites in Ethiopia. They suggested that the decomposition of sperrylite during weathering of the source igneous rocks led to production by "element agglutination" of accreted "platinum nuggets" which contained an enrichment of osmium and iridium in the form of an (Os,Ir) sulphide, which they could not trace to the source rocks. In order to substantiate his theory, Cousins has demonstrated, by evaluating the records of over 70 Witwatersrand gold mines, that there is a steady decrease in PGE

content with /...

content with increasing distance from the shoreline, together with a relative increase of Ir and Os at the expense of other PGE. The maturity factor, which Cousins defines as (Ir + Os)/(Pt+Rh+Ru+Pd) shows only comparatively small compositional variations throughout more than 400 km of strike length, but aids in delineating the entry points of rivers which carried mineralized detritus to the Witwatersrand basin.

The concept of accretion of the alloy grains is lent support by the coatings identified on most grains (see previous section).

Some additional evidence, which may be given in favour of the idea of chemical accretion, was derived from the samples from Western Deep Levels Limited. These samples contain a relative abundance of minerals normally associated with primary deposits: michenerite, moncheite, geversite and laurite, as inclusions in alloy grains and also as free grains. A large number of apparently primary PGM grains in a state of alteration was observed, these grains now comprising microcrystalline aggregates of alteration products. Many grains had what appeared to be a relict enrichment of tellurium and antimony at their cores, and were invariably enclosed by an irregular coating of geversite and sperrylite (Figure 4).

In some cases, euhedral crystals of (Ir,Os,Ru) alloy were observed in the groundmass (Figure 21), where they may have formed by recrystallization of (Ir,Os,Ru) alloy present as one of the alteration products. (That (Ir,Os,Ru) alloy is present in the weathered groundmass of altered grains has been confirmed by X-ray diffraction analysis). If so, the accretion took place in situ in the weathered mass, a process which seems more likely than accretion from completely dispersed colloidal alloy particles, as Cousins has envisaged. The concentration of PGM in the source rocks and in the Witwatersrand depository is thought to have been far too low to have permitted "nugget-like accretion" of completely dispersed colloid-sized particles.

Of course, an alternative interpretation of the (Ir,Os,Ru) alloy crystals included in weathered primary grains is that they themselves may have been primary inclusions and not the result of secondary crystal growth.

Cabri (1974), from investigations he has in progress and by quoting a number of examples from the literature, has shown that (Pt,Fe) and (Ir,Os,Ru) alloys are present in primary PGM deposits and thus need not form by the process which Cousins has suggested. Cabri and Harris (1975) point out that experimental work on (Os,Ir) alloys indicates that these alloys are difficult to react and equilibrate at temperatures below 1000°C, and they suggest that "it seems more likely that non-homogeneous or zoned (Os,Ir) alloys are the result of non-equilibration during crystallization rather than 'element agglutination'".

Certainly, some of the evidence obtained in the present study of the Witwatersrand PGM alloys favours their suggestion. Apart from the features typical of detrital attrition discussed in the previous section, a significant proportion of the (Ir,Os,Ru) and (Pt,Fe) alloy grains, which are invariably zoned to some degree, have inclusions of minerals typical of the source rocks. If it were not for the protection afforded by the alloy hosts, the inclusions would have decomposed. In addition to the PGM inclusions mentioned above, nickel sulphides (Figure 9, grain 7) and silicate glass (possibly recrystallized) inclusions (Figure 9, grains 1 and 2) were observed. The silicate inclusions have a common globular shape (Figure 9), suggesting that they may have been included as a liquid during crystallization of the original PGMs in the source igneous body. By means of the electron microprobe these silicate inclusions were found to contain minor concentration of Cr and

Ni, and when analysed for major silicate rock-forming elements using a defocused electron beam (about 10μm electron spot diameter), gave a composition (Table 16) similar to that of basic or ultrabasic rock in composition. No free rock particles of similar composition have been found in the Witwatersrand sediments.

The evidence therefore seems to favour the theory that at least a significant proportion of the (Ir,Os,Ru)alloy and isoferroplatinum grains have been derived directly, without alteration, from the source rocks. No doubt the Pt- and Pd-bearing minerals, if they were abundant in the source rocks, have been lost completely, but they are not envisaged as the principal source of the (Os,Ir) alloys, forming by a process of accretion or "element agglutination". In fact, Cabri and Harris (1975) have suggested that deposits of the Witwatersrand type have derived their PGM suite from relatively unfractionated Alpine-type emplacements, such as those in New Guinea, Atlin, and Tasmania, which themselves are expected to have low Pt/(total PGE) ratios.

Small changes to the alloys may have occurred subsequent to burial, aided by the low-grade metamorphism. Further separation of (Pt,Fe) alloys from (Ir,Os,Ru) alloys (Figure 5), and the development of secondary PGM, such as sperrylite, hollingworthite, geversite, iridarsenite and ruthenarsenite, is expected to have taken place at this time. The sperrylite and related minerals are undoubtedly of secondary origin; may coat and cement together not only PGM but gold and secondary minerals, such as gersdorffite,* as well. It is likely that these secondary PGM resulted from the redistribution and recrystallization of the phases in the remains of altered primary, mainly Pt-rich, grains -- i.e., those primary PGM grains which, although altered, did not break up during transportation and become lost due to dispersal. Some of these altered primary grains have become coated themselves, the coating having obstructed further redistribution.

Very rare/.....

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* Addendum: See Figure 25.

Very rare minerals, such as stibiopalladinite and sudburyite, also formed during this period and are closely associated with both gold and gersdorffite, all of which may be intergrown.

At some late stage, the (Os,Ir) alloys underwent localized alteration to erlichmanite, irarsite, osarsite, and unidentified phases.

CONCLUSIONS AND RECOMMENDATIONS

This study has clearly demonstrated the usefulness of the electron microprobe both in aiding identification of PGM which had not been noted previously in the Witwatersrand and in providing abundant quantitative analyses of the minerals. The chemical data have demonstrated some distinct trends indicative of the origin of these minerals.

Although there is evidence favouring accretion of (Ir,Os,Ru) alloy crystals from the weathered remains of primary PGM, the investigation supports the theory that a substantial proportion of the alloy grains (if not all), and definitely the Os-rich grains, were derived directly from the source rocks and have undergone little change during weathering, burial and even subsequent metamorphism.

In contrast, the primary Pd- and Pt-bearing minerals, even if they were abundant in the source rocks, may have been lost completely owing to disintegration, dissolution and dispersion. Those PGM which are definitely of secondary origin, such as sperrylite, hollingsworthite, sudburyite and stibiopalladinite, were probably derived from the remains of these weathered and altered primary grains.

From the economic viewpoint, it should not be overlooked that the platinoid concentrates produced by the gold mines contain a previously undescribed suite of slightly acid-soluble PGM which are being lost to solution during chemical processes designed to clean the

heavy /..

heavy concentrates. The solutions obtained should not be discarded, but treated to win the valuable metals which they contain, e.g. by ion exchange columns.

Since not all the minerals have the very high specific gravity of iridosmine and osmiridium, greater care should be exercised in recovery during gravity concentration. It is recommended, also, that the gravity concentration equipment and methods be generally improved upon in order to increase PGM recovery.

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NOTE: Tables and Figure in Volume 2.

SECTION VI/.....

SECTION VI

TUČEKITE

SECTION VI

TUČEKITE IN THE WITWATERSRAND CONGLOMERATE REEFS

CLIVE E. FEATHER

COVERING NOTE

The new mineral Ni_9SbSbS_8 was simultaneously discovered by Dr J. Just of Australian Selection (Pty) Ltd., and Mr C.E. Feather of AARL. As will be seen in the attached notes from the Chairman of the Commission on New Minerals and Mineral Names, Dr Just's proposal for the new mineral reached the chairman only days before that of Mr Feather. Accordingly the name which Dr Just proposed, Tučekite, was accepted by the members of the Commission.

Tučekite, although rare, is intimately associated with gold in the Witwatersrand reefs, which it may enclose, rendering the gold refractory to recovery.

The attached report constitutes a draft of part of a paper on Tučekite being jointly submitted by the discovers of this unusual mineral.

ABSTRACT/.....

CONTENTS

Tables: See Part 1 of Volume 2.

Figures: See part 2 of Volume 2.

ABSTRACT/......

TUČEKITE IN THE WITWATERSRAND CONGLOMERATE REEF

ABSTRACT.

Tučekite occurs in the Witwatersrand gold-bearing conglomerate reefs as a very rare mineral of secondary, probably hydrothermal origin. It is intimately associated with the remobilised gold in the reefs, is white with a pale yellow-brown tinge, and is anisotropic. From electron microprobe analysis the average chemical composition is calculated to be $(Ni_{0,436}\,Fe_{0,036})\,(Sb_{0,096}As_{0,009}Bi_{0,003})\,S_{0,420}$ or $(Ni, Fe)_9\,(Sb, As, Bi)_2\,S_8$. X-ray diffraction analysis revealed a tetragonal crystal structure almost identical to that of hauchecornite ($Ni_9Bi_2S_8$), which has the space group P4/mmm. The average cell axes are a= 7,174 Å and c= 5,406 Å. The grains examined were too small to permit accurate determination of Vickers hardness numbers (VHN_{10g} Kg/mm^2 ranged from 302 to 613), or permit reflectance values to be measured in air. Reflectance values in oil ranged from 32,0 to 32,8 per cent, when measured in Cargille D liquid at 22°C.

Tučekite is the antimony end-member in the solid solution series $Ni_9SbSbS_8^{*}$ - Ni_9BiBiS_8

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* Prefered chemical formula based on valence differences, $Ni_9Sb^{VI}Sb^{VIII}S_8$.

INTRODUCTION/.....

INTRODUCTION.

Antimony-bearing minerals in the conglomerate reefs of the Witwatersrand and Ventersdorp Systems are extremely rare. According to the recent review by Feather and Koen (1975), rare amounts of dyscrasite (Ag_3Sb), tetrahedrite ($Au_3Sb\ S_{3,25}$) and stibnite (Sb_2S_3) have been reported from a few localised occurrences in the reefs. In addition the author has observed sudburyite (PdSb), (confirmed by X-ray diffraction analysis) in the Vaal Reef, and stibiopalladinite (Pd_5Sb_2) in a heavy mineral concentrate from President Brand Gold Mine.

A mineral containing nickel, sulphur and antimony was discovered in a Wilfley table concentrate from Western Deep Levels Ltd., where the Carbon Leader Reef of the Witwatersrand System and the Ventersdorp Contact Reef of the Ventersdorp System are mined. For the period during which this concentrate was prepared, the abundance of the mineral in the incoming ore was estimated at 5×10^{-5} p.p.m., but it is suspected to have been derived from a small localised abundance in one of the two reefs being mined. Careful examination of a large number of similar concentrates from the same mine and eight other Witwatersrand Mines, failed to reveal any further traces of the mineral. However, during the examination of concentrates prepared of individual reef samples, the mineral was found intergrown with gersdorffite in a sample of highly mineralized Vaal Reef taken close to the footwall contact.

COMPOSITION/.....

COMPOSITION AND STRUCTURE

The chemical composition of the mineral was quantitatively determined using a JEOL JXA-5A electron microprobe, and as standards, pure nickel (Ni), analysed chalcopyrite (Fe,S), and synthetic Pd_5As_2 (As) and $PtBi_{1,4}Sb_{0,6}$(Bi,Sb). The data was refined by means of the computer program of Duncumb and Jones (1969). The results of the analysis of six grains are summarised in Table 1 and the average composition is calculated to be:-

$(Ni_{0,436}Fe_{0,036})(Sb_{0,096}As_{0,009}Bi_{0,003})S_{0,420}$, or

$(Ni\text{-}Fe)_9(Sb,As,Bi)_2S_8$.

X-ray diffraction analysis by Debye-Scherrer camera revealed a tetragonal crystal structure (Table 2) almost identical to that of hauchecornite ($Ni_9Bi_2S_8$). Peacock (1950), and Kocman and Nuffield (1974) have assigned the space group P4/mmm to hauchecornite, and it is probable that this mineral has the same space group. The average cell axes are a=7,174 Å and c= 5,406 Å.

The same mineral was found by Dr. J. Just, in ultra-basic rocks near Kanowna, N. E. Coolgardie Goldfield, W.Australia. Having priority on a new mineral name (by a few days), he named it <u>tučekite</u> (for Dr. K. Tuček , Prague). The mineral represents the antimony end-member in the series Ni_9SbSbS_8* - Ni_9BiBiS_8, whereas the antimonian hauchecornite which has been described by Gait and Harris (1972), and Kocman and Nuffield (1974), has antimony less than 50 atomic per cent of (Bi, Sb).

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* $Ni_9Sb^{VI}Sb^{VIII}S_8$

OPTICAL/.....

OPTICAL AND OTHER PROPERTIES.

Tučekite is white with a pale yellow-brown tinge, and is distinctly anisotropic.

Approximately 20 grains were examined all of which were too small (< 80μm) for accurate determination of microindentation hardness values (Vickers Hardness Numbers) - VHN and for the measurement of reflectance values in air.

The VHN values were obtained using a pneumatically impelled Vickers 136° diamond indentor. All determinations were performed at standard loads of 10 grams. Values ranging from 302 to 613 were obtained, with an average value of 417 (Table 3).

Reflectance values were determined in oil with a Reichert microphotometer using a continuous dielectric filter. As a reflectivity standard, a basal section of black carborundum was used, for which a reflectance (R_o) in air at 546 nm of 20,5 per cent has been recommended by The National Physical Laboratory, England, and Firma Carl Zeiss, Germany. Applying the method given by von Gehlen and Piller (1964), the reflectance of the standard in oil was calculated at 7,4 per cent using the refractive indices of a basal section of carborundum as given by Thibault (1944). All measurements in oil were made in Cargille D liquid (n_i = 1,516) at 22 °C, using a 160/1,25 oil immersion Reichert lens. The results are presented in Table 4. The reflectance values (R_i) for stibiohauchecornite ranged from 32,0 per cent to 32,8 per cent, with an average value of 32,3 per cent. The reflectivity of the mineral in air could not be calculated as the refractive indices of the mineral are not known.

PARAGENESIS/.....

PARAGENESIS

In the table concentrate examined, the tučekite is almost invariably contained in grains which also contain gold. Only two free grains were found (Figure 1). Throughout the Witwatersrand and related reefs, gold is in a similar manner commonly associated with a variety of secondary minerals, such as gesdorffite, chalcopyrite and pyrrhotite. These minerals are usually believed to have formed during the period of metamorphic activity which remobilised the gold, leading to this intimate association. By the same process of deduction it is suggested that the tučekite is of a similar metamorphic history and, judging from its sporadic appearance during routine mineralogical examination of the reefs, is likely to occur most abundantly in close proximity to features of most intense metamorphism such as dykes or veins intersecting the reefs.

As with the other secondary minerals, tučekite may completely enclose the gold (e.g. grain 2 in Figure 1), rendering it refractory in gold recovery processes. In the concentrate which was examined the gold had escaped recovery by mercury amalgamation.

CONCLUSIONS/.....

CONCLUSIONS.

Tučekite is the end-member in the solid solution series $Ni_9(Sb,X)_2S_8$ - $Ni_9(Bi,Z)_2S_8$, where X is Sb, As, Te and/or Bi, and Z is Bi, As, Sb and/or Te. Arsenian, tellurian and bismuthian varieties of Tučekite may exist, but the substituting element (X) may not exceed 50 atomic per cent of (Sb,X).

The determination of reflectance values in air, and the accurate determination of microindentation hardness numbers will only be possible when larger grains of the mineral are found.

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ADDENDUM/.....

Tučekite $Ni_9Sb_2S_8$ (or $Ni_9Sb^{VI}Sb^{VIII}S_8$)
(75-22) Tetragonal, P4/mmm
a 7.26, c 5.28Å, Z=1

J. Just

Australian Selection(Proprietary) Limited
Box R 1274, G. P. O., Perth, Western Australia 6001, Australia

Electron microprobe analysis using pyrite, artificial CoSbS, NiS_2, InAs, Te, and Bi as standards, gave Ni 47.34, Co 1.06, Fe 3.61, As 0.86, Sb 21.62, Bi 1.84, Te 0.30, S 25.19, sum 101.82%. This corresponds to $(Ni_{8.21}Fe_{0.66}Co_{0.18})_{9.05}(Sb_{0.89}Bi_{0.09}Te_{0.02})_{1.00}(Sb_{0.92}As_{0.12})_{1.04}S_8$ on the basis of S=8. The ideal end member formula is $Ni_9Sb_2S_8$ or $Ni_9Sb^{VI}Sb^{VIII}S_8$ when the structural analysis of topotypic hauchecornite($(Ni,Co,Fe)_9Bi^{VI}(Sb_{0.7}Bi_{0.3})^{VIII}S_8$) by Kocman and Nuffield(1974) is taken into consideration.

X-ray powder diffraction pattern is very similar to that of hauchecornite(Peacock, 1950) and therefore indicates that the mineral is tetragonal, space group P4/mmm, a 7.26(5), c 5.28(6)Å, Z=1. X-ray diffraction lines are 3. 9(w)(120), 2.96(w)(021), 2.73 (s)(121), 2.35(m)(112), 2.26(m)(221,130), 1.841(m)(222), 1.787(m) (032).

Colour pale brass-yellow, luster metallic. Opaque, indistinguishable from adjacent millerite. Specific gravity 6.18(calc.).

In polished section, it is pale brownish yellow(against millerite); bireflectance very weak to absent; anisotropism very strong, colours between crossed Nicols change from deep brown to grayish blue. Reflectances: 470nm-43%, 546nm-48%, 590nm-50%, 650nm-52%(silicon and high reflectivity glass standard). Vickers hardness 718 kg/mm^2(20g load). Cleavage not observed in polished section. Brittle.

The mineral occurs as microscopic(max. 0.2 mm) rims around and inclusions in millerite in hydrothermal ores in altered ultrabasic rocks near Kanowna, North East Coolgardie Goldfield, Central Division, Western Australia. The other minerals found in the

section/.....

section are millerite, pyrite, violarite or polydymite(of supergene origin), magnetite, chlorite, quartz, and small amounts of chalcopyrite, gersdorffite, and pentlandite.

The name is for Dr. Karel Tuček, curator of minerals at the National Museum, Prague, Czechoslovakia. Type material will be deposited at the British Museum.

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NOTE(by A. K.)

This proposal was received by the chairman on June 11, 1975. On July 7, the chairman received a proposal of the same mineral from Witwatersrand from Mr. C. E. Feather of South Africa with his writing that he sent his proposal on April 2, 1975. But the chairman has not received it till now, his letter being strayed very probably. If his letter was not strayed, he might have the priorities about the new mineral and another name he proposed if they are approved by the Commission.

The chairman should deal with this matter according to the following rule appeared in the memorandum from Dr. M. Fleischer dated May 7, 1971.

> It has been the accepted rule of the Commission that problems of priority were dealt with on the basis of the date of receipt of an abstract by the chairman.

However, the present problem should be considered as a special case, and the chairman introduces the abstract of Mr. Feather, hoping that the best way to save him is to be considered. If the joint authorship is suggested by some Commission members, the chairman desires the Commission members to admit that Mr. Feather is one of the original author of this mineral when the mineral and name are approved by the Commission.

Clive E. Feather/.....

Clive E. Feather
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Electron microprobe analyses of 6 grains gave: Ni 45.3, 48.9, 48.6, 47.0, 48.2, 48.8; Fe 4.8, 3.5, 4.2, 3.5, 2.6, 3.9; Sb 22.8, 22.1, 22.5, 20.0, 22.9, 20.9; Bi 0.4, 0.9, 0.8, 3.0, <0.1, 1.0; As 1.8, 1.3, 1.5, 0.86, 1.1, 1.5; S 25.8, 25.0, 25.0, 24.6, 24.8, 25.6; total 97.9, 101.7, 102.6, 98.96, 99.7, 101.7%. The average corresponds to $(Ni_{8.31}Fe_{0.69})_{9.00}(Sb_{1.83}As_{0.18}Bi_{0.05})_{2.06}S_8$ on the basis of S=8.

X-ray diffraction study shows it to be tetragonal, space group P4/mmm, a 7.174, c 5.406Å, Z=1. The strongest lines in the x-ray powder diffraction pattern are 4.33(7)(011), 3.21(6)(120), 2.76(10)(121), 2.38(8)(112), 2.28(8b)(221,130), 1.850(8)(222), 1.793(7)(040,032).

It is opaque. Under the ore microscope, the colour is wihte with a pale yellow-brown tinge. Strongly anisotropic. Reflectances measured in oil(Cargille D liquid, 22°C) are 32.0-32.8% at 546nm. The grains were too small(<80 m) to permit measurement in air. Vickers hardness ranges from 302-613 kg/mm^2(10 g load).

It is found in Witwatersrand gold-bearing conglomerate as minute grains possibly of hydrothermal origin. It is intimately associated with the gold in the reefs.

NOTE(by A. K.)

If the result of structural analysis of hauchecornite from Westphalia by Kocman and Nuffield(1974)(Can. Min., 12, 269-274) is taken into consideration, the empirical formula becomes $(Ni_{8.31}Fe_{0.69})_{9.00}(Sb_{0.95}Bi_{0.05})^{VI}_{1.00}(Sb_{0.88}As_{0.18})^{VIII}_{1.06}S_8$. Both of 6- and 8-coordinated sites are dominantly occupied by Sb along with all the chemical analyses.

INTERNATIONAL MINERALOGICAL ASSOCIATION
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October 16, 1975

Mr. Clive E. Feather
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Dear Mr. Feather,

I inform you that the proposed new mineral Tucekite (=Stibiohauchecornite proposed by you) by Dr. Just has been approved by the Commission on New Minerals and Mineral Names, I. M. A. by a vote 14-1-1 and the name by 13-2-1. One dissenter stated that the compositional variation of hauchecornite is so small and the occurrence is so rare that all the minerals of hauchecornite group should be called hauchecornite, hauchecornite with very little bismuth, etc. One member desired the authors to give pronounciation of the mineral in their paper. Along with the name, one dissenter required the illustration on the connection between the author(Just) and Dr. Tucek. Two members preferred the name stibiohauchecornite (for SbSb material) after the reference to the names haucoecornite (for SbBi material) and bismutohauchecornite(for BiBi material) appeared in Dr. Just's proposal on the classification of hauchecornite series minerals.

The joint authorship of Dr. Just with Mr. Feather has been supported by nine members, all recognizing the priority of Dr. Just, although two of them questioned the significant difference between the unit cell constants of two materials.

Now I hope you and Dr. Just will write a good paper to describe the new mineral after mutual agreement.

Sincerely yours,

A. Kato

SECTION VII

SCANDIUM

SECTION VII

SCANDIUM IN THE WITWATERSRAND

Enlarged and revised version of "Geochemistry of Scandium in the gold-bearing reefs of the Witwatersrand gold fields" by C.E. Feather.

AARL Project No. D/27, Report No. 3, 1972, 2 pages.

CONTENTS/.....

CONTENTS

Figure: See Part 2 of Volume 2.

INTRODUCTION/......

INTRODUCTION: CRYSTAL CHEMISTRY OF SCANDIUM

Originally it was thought that, because of its ionic size (similar to iron) and known dispersion through the lithosphere, scandium was contained preferentially within ferromagnesian minerals of igneous rocks (see e.g. Goldschmidt and Peters (1931)). However, recent studies have shown that this element more commonly follows the heavier rare-earth elements. Norman and Haskin (1968) have shown that, in nature, scandium occurs as a positive trivalent ion (Sc^{3+}). It has a similar ionic size (0,81 Å) to the heavier lanthanides and the actinides, and belongs to the same group (Group III A) as these elements.

By virtue of these properties, it can be predicted that scandium can occur in lanthanide and actinide minerals (e.g. monazite, uraninite, uranothorite, brannerite, euxenite, zircon, etc.).

EXAMINATION OF THE WITWATERSRAND REEFS

The concentration of scandium in the reefs is very low, and could not be detected by scanning X-ray fluorescence spectrometry.

However, electron microprobe investigation of the essential uranium-bearing minerals, uraninite and brannerite, revealed low concentrations in the order of 100 p.p.m. Sc in these minerals.

Electron microprobe X-ray fluorescence scans of uraninite and brannerite are given in Figure VII - 1, and compared with those obtained on leucoxene, galena and pure UO_2. The scandium line, although very weak, is clearly defined.

The element was found to occur in uraninite, both free and enclosed in carbon, and in brannerite (which resulted from alteration of the uraninite). Samples from the Vaal Reef, Carbon Leader Reef, and Ventersdorp Contact Reef were examined.

Using/.....

Using Table 4 in Section IV, in which the overall average concentration of UO_2 in Witwatersrand uraninite is 67,2%, and ignoring the presence of brannerite for the moment, the Sc : UO_2 ratio is thus approximately 1 : 6720 in the reefs. Assuming an average abundance of about 400 p.p.m. UO_2 in the banket, the scandium content will be only approximately 0,06 p.p.m. which is very low indeed.

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SECTION VIII/......

SECTION VIII

GENERAL CONCLUSIONS

SECTION VIII

GENERAL CONCLUSIONS AND RECOMMENDATIONS

This investigation of the mineralized conglomerate reefs of the Witwatersrand Super-Group was made possible only by the use of the electron microprobe. It is a significant demonstration of the power and usefulness of this instrument as a mineralogical tool.

In addition to the abundant quantitative data which have been presented, simple qualitative investigation has revealed reasons for the refractory character of gold and uranium-bearing minerals which occur in the extraction plant residues. This is due to enclosure, rather than to slow dissolution, or the chemical character, of the minerals themselves.

Gold was found to be enclosed in iron oxide and/or iron sulphide coatings, in carbon where it commonly occurs along intercolumnar boundaries, and in such secondary minerals as gersdorffite, pyrrhotite, and tučekite. These secondary minerals were formed at the same time as the gold was redistributed, apparently during an epoch of metamorphic activity when the reefs were heated to minimum temperatures in the range of 400 - 600°C.

Tučekite (Ni_9SbSbS_8) is a new mineral, and its physical properties have been described in detail.

Uraninite enclosed in carbon, and brannerite enclosed in secondary minerals in the matrix of the conglomerates (e.g. phyllosilicates, pyrite and leucoxene), contribute significantly to the uranium extraction plant residues. Laboratory tests indicate that dissolution of the enclosing hosts by pressure leaching improves uranium recovery significantly, except for uraninite in carbon which requires separate treatment.

A/.....

A large proportion of the time taken for this investigation was spent in the study and analysis of the platinum group minerals (PGM) in the reefs. Twenty-five PGM were found to occur in the reefs, and the presence of at least twelve of these was recorded for the first time, three of which are unnamed.

(Ir,Os,Ru) alloys are the most abundant members of the PGM suite (about 80%). They vary widely in composition, and both hexagonal and cubic alloys are present. Osmium, iridosmine, osmiridium, and iridium are most abundant; rutheniridosmine and ruthenian iridium are less abundant. Zoned grains are common, with Os-rich cores enclosed by (Ir,Pt)-rich outer zones filled with exsolution lamellae of (Pt,Fe) alloy. Discrete grains of this alloy proved to be isoferroplatinum of a composition close to Pt_3Fe.

Sperrylite commonly occurs as an outer coating on all the above grain types. Sperrylite and isoferroplatinum make up 15 to 20 percent of the PGM grains and account for nearly all the Pt present.

Examination of the surface features of the PGM grains by scanning electron microscope, in conjunction with the information derived from electron microprobe analysis, indicates that a substantial proportion of the alloy grains are of detrital origin. They appear to have undergone little change during weathering of the source rocks, transportation and even during subsequent metamorphism. These primary grains were found to contain rare inclusions which would have become unstable if it were not for protection by enclosure : michenerite, moncheite, laurite, geversite, (Pt,Rh,Ru) alloy and RhS were observed in addition to basic and/or ultrabasic silicate glass and nickel sulphide inclusions.

It/.....

It is believed that most of the free grains of Pd and Pt-bearing minerals, even if they were abundant in the source rocks, appear to have been lost completely owing to disintegration, dissolution and dispersion. Those PGM which are definitely of secondary origin, such as sperrylite, hollingworthite, iridarsenite, ruthenarsenite, sudburyite, stibiopalladinite and RuAsS, were probably derived from the remains of these weathered primary grains.

Care should be taken when chemically cleaning PGM concentrates produced by the gold mines. Some of the PGM are slightly acid soluble, and thus the solutions should not be discarded, but treated for removal of the PGM, e.g., by ion exchange columns.

Many aspects of the Witwatersrand mineralogy await investigation by the techniques used in this study. Further examination of the secondary minerals might possibly provide still further information concerning the nature of the metamorphic activity which the reefs underwent. Minerals which should be investigated include pyrrhotite, pentlandite, chalcopyrite, galena and secondary silicates, notably the phyllosilicates. Useful information might also be derived from a detailed study of alteration and replacement of the primary detrital minerals.

In this investigation only reefs which belong to the Witwatersrand System and the Ventersdorp Contact Reef were examined, and it is logical that the Dominion reefs (Dominion Reef System) and Black Reef (Transvaal System) should also be examined.

APPENDIX 1/......

APPENDICES

1 TO 5

APPENDIX 1

DECLARATION

Mr. Clive E. Feather was responsible for the development, and initial testing, of the method described in Appendix 1: "A simple method for background and matrix correction of spectral peaks in trace element determination by X-ray fluorescence spectrometry". He subsequently discussed his findings with myself, and asked me to carry out additional testwork. Simultaneously we demonstrated its application to a wide range of instrumental conditions, and the analytical data given in the Tables in Appendix 1 results essentially from my testwork.

Appendix 1 constitutes the draft of a joint paper published by Mr. Feather and myself.

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A SIMPLE METHOD FOR BACKGROUND AND MATRIX CORRECTION OF SPECTRAL PEAKS IN TRACE ELEMENT DETERMINATION BY X-RAY FLUORESCENCE SPECTROMETRY

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Published in X-Ray Spectrometry, Vol. 5, p. 41-48, 1976.

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TABLES: See Part 1 of Volume 2

FIGURES: See Part 2 of Volume 2

(Except Figures 9, 10 and 11 which are illustrated on pages 1 - 13 and 1 - 14).

A SIMPLE METHOD FOR BACKGROUND AND MATRIX CORRECTION OF SPECTRAL PEAKS IN TRACE ELEMENT DETERMINATION BY X-RAY FLUORESCENCE SPECTROMETRY

C.E. Feather and J.P. Willis

ABSTRACT

Background intensities at differing wavelength positions were found to be related linearly between adjacent major element absorption edges. Also, background intensity at any position is linearly related to the reciprocal of the mass absorption coefficient for any wavelength between the absorption edges.

The method presented here allows for the determination of background, as well as mass absorption coefficient, by a single measurement at an interference-free background position (which can be the Compton scatter "peak"). If the mass absorption coefficient is already known, backgrounds may be calculated directly.

Tests on geological materials show that, while not as accurate as conventional methods of background determination, relative accuracies of 2 to 5 per cent are obtainable with a substantial saving in time, since intensity at only one background position need be measured. The use of low-dispersion high-reflectivity analysing crystals, e.g. LiF(200), is possible once more because it is no longer necessary to attain interference-free background positions between peaks.

The method is furthermore ideally suited for the determination of background intensities in energy dispersive systems where spectral resolution is a problem, and in multichannel spectrometers where only one channel need be used for determination of both mass absorption coefficient and backgrounds for a

group of trace elements.

The method has been used in the low cost determination of trace elements in large numbers of geochemical prospecting samples.

INTRODUCTION

The motivation behind this investigation was the need to develop a method for trace element analysis in pressed powder briquettes or uncompacted powders, which was more rapid than methods in current use, even if it resulted in slight losses in accuracy. When analyzing many thousands of samples for geochemical prospecting a rapid method of analysis is essential, and highly accurate results are not necessarily desired.

Accuracies of 2-5% relative can be achieved using the method presented here, combined with a considerable saving in instrument time (and therefore cost). Consequently the work load can be increased, or more time given to work demanding higher accuracies (1-2% relative).

The method is applicable to a large number of trace elements above atomic number 27(Co) in a wide range of geological materials. It includes a standard procedure for correction of matrix variation, and, in particular,provides for the rapid determination of background beneath element spectral peaks without the need to measure a number of off-peak background positions.

SAMPLE PREPARATION

Tests were carried out using pressed powder briquettes prepared of pure (undiluted) pulverised sample, sample milled with 10% polyvinyl alcohol binder (e.g. Hoechst Moviol N20-98) and sample milled with 10% boric acid. The briquettes prepared with boric acid were found to be the most rigid and can be rapidly prepared by unskilled operators. Tests were also carried out on sample powders poured directly into mylar-windowed sample holders.

It is essential to use sufficient sample to prepare an " infinitely thick" sample layer for the shortest wavelength under investigation. Tests

carried/.......

carried out using pure quartz indicated that, for MoKα radiation (0.711Å) a minimum of 8 grams was required for a boric-acid backed 40mm diameter briquette. However, at BaKα radiation (0.39Å), more than 20 grams of quartz was required for the same diameter backed disc. The tests were carried out on quartz (SiO_2) since it has the lowest mass absorption coefficient of geological materials investigated in common practice.

INSTRUMENTAL SETTINGS

Instrumental settings were chosen to suit the wavelength regions under investigation. As an example the following settings were used for the analysis of the commonly required elements which lie in the wavelength region 0.7 to 1.7Å. (MoKα to NiKα and ULα to HfLα).

Instrument:	Philips PW.1220 Sequential X-ray spectrometer.
X-ray tube:	Silver-target, 1,6 kW.
Excitation:	70kV.
Current:	20 mA.
Analysing crystals:	LiF (220) or LiF (200).
Detectors:	Flow plus scintillation, with pulse height discrimination.
Primary Collimator:	Fine(160 µm).

CONVENTIONAL METHOD OF BACKGROUND MEASUREMENT.

Figure 1 illustrates a typical spectrum obtained using a silver X-ray tube for excitation and a LiF(220) crystal. The characteristic lines

of/...

of trace elements are superimposed on a background which is most elevated at the Compton peaks of scattered primary radiation. Despite the use of a high dispersion crystal, there are few background positions which are completely interference-free.

In current practice two or more of the available interference-free background positions are read and the backgrounds beneath spectral peaks are interpolated graphically or mathematically. The method gives reliable results over a limited wavelength range, but tends to be time-consuming. It does not account for irregularities in the background caused by "spurious" reflections of primary and secondary radiation by the analyzing crystal, the so-called ghost peaks[1,2] (see Figure 2). For example, both molybdenum and silver X-ray tubes with a LiF(220) crystal yield "ghost peaks" in the region between ZrKα and PbLβ causing considerable difficulties in direct measurement of backgrounds by the current method.

It was necessary that a method be developed which would be less time consuming and at the same time, might eliminate some of the difficulties outlined above in determining background.

RELATIONSHIP OF BACKGROUND AND MASS ABSORPTION COEFFICIENT (μ)

Background originates essentially from two sources: scattering of primary radiation by the sample and general instrument noise. The scattering occurs in two forms: coherent or Rayleigh scattering and incoherent or Compton scattering[3].

Both/...

Both coherent and incoherent scattering are matrix dependent (e.g. Andermann and Kemp[4]), and Reynolds[5,6] has shown that Compton peak intensity and mass absorption coefficient are inversely related (Fig. 3). It is common practice to generate mass absorption coefficients of the samples of unknown major element composition by this method. Willis[7] has shown that the relationship is actually better than 1 per cent relative when Mo Kα Compton intensity and measured mass absorption coefficients (transmission method) are used, provided that an Y_2O_3 filter and LiF(220) analysing crystal are used with a Mo X-ray tube.

Since not only the characteristic lines of the X-ray tube target but also the continuum are scattered by the sample, any chosen background may be shown to be similarly inversely related to mass absorption coefficient (Fig. 4), as demonstrated by Hahn-Weinheimer et al.[8] It has also been shown that mass absorption coefficients at all wavelengths between adjacent major element absorption edges are linearly related (Table 1 and Hower[13]). It follows that any two backgrounds in this region are also linearly related.

The relationship was investigated at various wavelengths using briquettes prepared of a number of pure stable reagents, which served as "blanks" for trace elements under investigation. Linear relationships were obtained (Figures 5 and 6), but in none of the cases did the line pass through zero. Particular care was taken to check the blanks previously for contaminants, e.g. Sr in $CaCO_3$, Rb in K-salts, Zr in TiO_2, etc.

The intercept which the line makes with the background intensity axis, for convenience, will be referred to as residual background.

It is thought that this non-zero interception of the axes results from background contributed by the actual instrument, e.g. electronic noise and scattering and fluorescence from the analysing crystal, and from the crystal and sample chambers.

Such contributions to background are not matrix dependent, but crystal fluorescence and internal scattering is strongly influenced by the radiation energies which the sample fluoresces. For example in experiments carried out with the spectrometer set to measure intensity at a wavelength of 0.7Å, the contribution due to crystal scattering using a sample disc of RbCl {RbKα + Kβ radiation (0.93 and 0.87Å), absorption edge at 0.81Å} - ideally a very heavy absorber of 0.7Å radiation - was many times in excess of the actual sample scattered radiation diffracted by the crystal.

Ignoring crystal fluorescence and scattering, residual background at a given wavelength is constant for all samples in an analytical run, and if subtracted from background measured, the difference - referred to here as "true" background - is directly proportional to $1/\mu$ and the line passes through zero (Figure 7).

It follows that the ratio

$$\frac{\text{Total spectral peak intensity - total background intensity}}{\text{True background}}, \quad \text{i.e.} \ \frac{\text{Net peak}}{\text{True background}}$$

permits correction for matrix variations within samples. Since the μ's at all spectral positions between adjacent major element absorption edges are linearly related (Table 1), the true background used for matrix correction need not necessarily be that of a spectral line under investigation.

SIGNIFICANCE/.....

SIGNIFICANCE OF THE FINDINGS

Backgrounds beneath several spectral peaks may be determined by measurement of only one interference-free background position. Also, the true background at this position may be divided into all net spectral peaks under investigation to obtain matrix variation correction. If mass absorption coefficients are known, backgrounds may be calculated directly, obviating the need even to measure an interference-free background position. All calibrations may be set up at the beginning of a run by using blanks, the mass absorption coefficients of which can be calculated easily from tables published in the literature, or measured, preferably by a transmission method[9] or by using an X-ray tube Compton peak[5,6]. It is strongly advised that a number of different blanks should be used, which have been previously checked for contaminants.

Compton "peaks" are, correctly speaking, background regions of elevated intensity, and especially for the silver- and molybdenum-target X-ray tubes, residual background at these "peaks" is insignificantly small by comparison with total intensity, and its effect may be ignored when analysing ordinary silicate rocks and soils.

However, the method has the advantage of making it no longer necessary to measure Compton peaks where there are numerous interferences (e.g. AgKα Compton peak is subject to interference by ULγ and RuKβ, MoKα Compton peak by ULβ, NbKα and YKβ, and AuLα Compton peak by WLβ and ZnKβ - see Figures 1 and 8).

DATA/....

DATA PROCESSING

All the relationships described above may be handled mathematically (see Appendix) and thus data processing may be handled rapidly by a small computer.

In a particular application at Anglo American Research Laboratories a Digital Equipment Corporation PDP 11/05 computer is used to process data produced on punched tape from a Philips PW.1270 Multi-channel X-ray Spectrometer, which is equipped with a Philips PW.1266 automatic 160-sample changer. In 54 working days, approximately 25 500 samples were analysed for uranium, thorium and rubidium by this method with maximum economy.

RESULTS AND CONCLUSIONS

This method has been widely tested by the authors, and Tables 2 to 6 summarise results obtained for a number of elements. Of particular significance are the good results obtained for gallium using a Mo-target X-ray tube, as the GaKα peak (1.342Å) is far removed from the MoKα Compton peak (0.73Å) used for background determination and mass absorption correction.

While not always as accurate as the conventional method described, relative accuracies of 2 to 5 per cent are obtainable with a very considerable saving of time. However, the accuracy of the final result is critically dependent upon the accuracy of μ, or the counting statistics of the measurement of the reference background from which μ and/or all spectral peak backgrounds are being determined, because an error in μ leads to a combined error in background calculation and matrix correction, which is additive.

The/....

The main advantage of the method is that for a group of analytical elements only one background reading is used for both background and matrix variation correction of all the spectral peaks being measured, provided that no major or minor element absorption edges occur between the background wavelength and the spectral peaks. Apart from saving time, and, in the case of multi-channel units the saving of actual spectrometer channels, the method proved to take into account spurious analysing crystal reflections and other irregularities in the background.

The method has the added advantage of once again making possible the use of high-reflectivity low-dispersion crystals such as the LiF(200), which have previously fallen from favour because of the difficulty in obtaining interference-free backgrounds in the region of 0,5 to 1,5Å. It is also ideally suited for use with energy dispersive X-ray spectrometry, where the accurate determination of background is very difficult.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the co-operation and encouragement received from the Management of the Anglo American Research Laboratories. One of the authors, J.P. Willis, wishes to thank the C.S.I.R., Pretoria, for financial support, and Mrs Y. Abrahams for assisting with the analyses.

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ADDENDUM:/....

ADDENDUM: EXAMPLE OF ANALYTICAL RUN AND CALCULATIONS

1. Set up calibration using "blank" samples relating backgrounds beneath the spectral peaks to a nearby interference-free background (Figure 9), or to $1/\mu$, if μ is known (Figure 10).

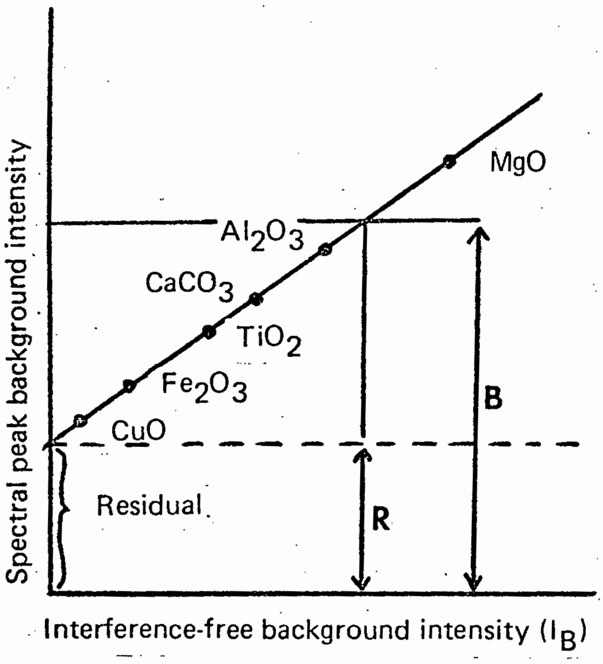

FIG. 9

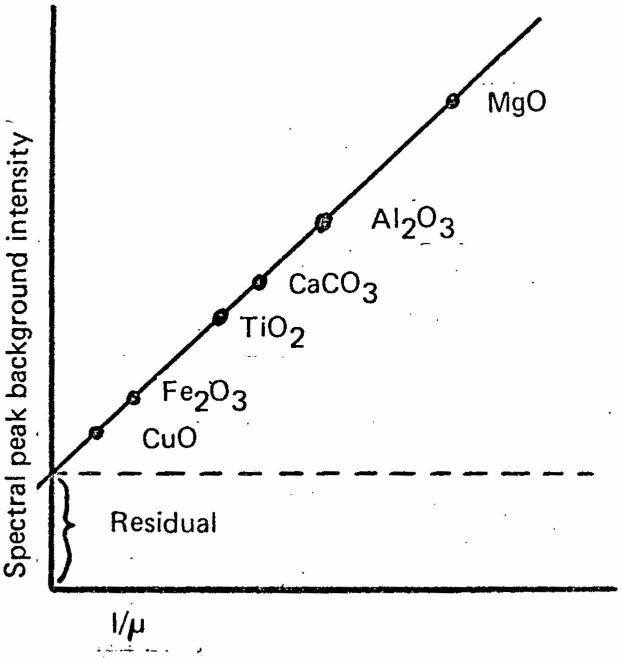

FIG. 10

2. Using either of the relationships, determine the backgrounds beneath the spectral peaks in both standards and unknowns, and calculate the net spectral peak intensities (P).

3. Divide the net peak intensities (P) by Compton peak intensity (if read) or by "true background" (i.e. total background (B) minus residual background (R)) (Figure 9), or multiply by μ, in order to correct for matrix effects.

4./.....

4. Plot these matrix corrected ratios, or (P x μ), for the standards against concentration to obtain concentration calibrations (working curves) (Figure 11).

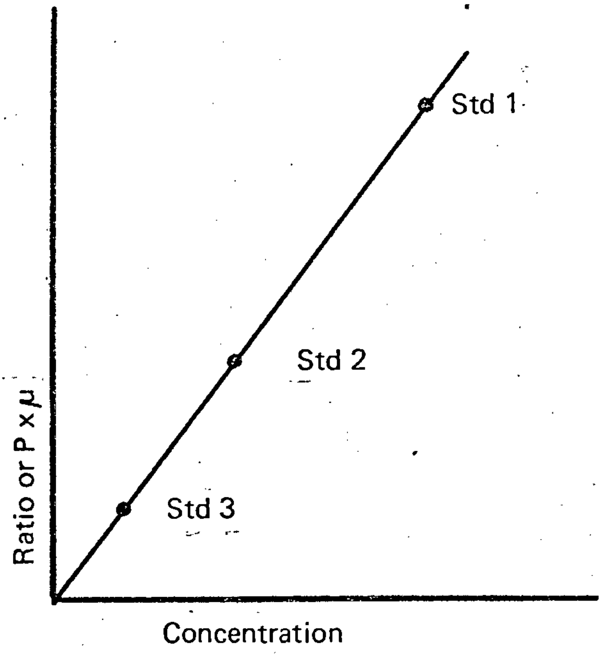

FIG. 11

5. Using the matrix corrected ratios, or (P x μ), obtained for the unknowns, calculate or read off the working curves, the concentrations in the unknowns.

For example, the calculations, if μ is not known, may proceed as follows:

In Figure 9, let m = slope
R = intercept (i.e. residual background)

For the unknown, measure the intensity of the interference-free

background/...

background (I_B), and the intensity of the spectral peak (I_P).

It follows that the background beneath the spectral peak is

$$B = m.\ I_B + R$$

and the net peak, $P = I_P - B$.

Thus the intensity ratio, $I_R = \frac{P}{(B-R)} = \frac{P}{m.I_B}$.

In Figure 11, if C = concentration and S = slope,

then $C = S \times I_R$

Therefore, for an unknown sample for which only I_B and I_P need be measured, the concentration can be calculated from:

$$C = \frac{S \times (I_P - (m.I_B + R))}{m.\ I_B}$$

where S, m and R are constants.

APPENDIX 2.

PROCEDURE FOR THE FUSION OF SAMPLES AND FLUX, AS USED AT THE ANGLO AMERICAN RESEARCH LABORATORIES.

This appendix describes, for the sake of completeness, the fusion procedure used at AARL. It is the result of a team effort over some years. The author, Mr. C. van Zyl, Mr. F.C. Baumgartner, Mr. G. Yeo, and laboratory assistants all contributed to its development and perfection.

CONTENTS:

REFERENCES (See end of Appendix 3)

APPENDIX 2: PROCEDURE FOR THE FUSION OF SAMPLES AND FLUX, AS USED AT THE AARL

INTRODUCTION

Limited understanding of the basic principles of X-ray emission has resulted in most methods of X-ray fluorescence (XRF) analysis being based on the premise that the sample is of uniform composition. But rocks are mineralogically heterogeneous, and there are finite limits to particle size reduction practicable upon milling, which are many hundreds of times greater than the average X-ray wavelength. Therefore, a pressed powder disc is not homogeneous, i.e. not of uniform particle composition.

X-rays of short wavelength (0,1A^{O}), characteristic of trace elements ($Z > 30$) in common rocks and ores, may pass through many grains in a powder disc before being seriously attenuated. Thus many grains are effectively averaged. Furthermore in trace element work fairly substantial relative errors are tolerable and consequently the disc may be assumed to be uniform. The converse applies for the common rock-forming elements ($Z < 31$), where long wavelength radiation is absorbed after only having penetrated a shallow depth of sample and only a small relative error is acceptable for these abundant elements. Effectively, only the grains virtually at the surface of the disc are sampled, where platy or soft minerals may be concentrated or assume a disproportionately large area of exposure because of preferred orientation.

Claisse (1956) was the first to publish a method for eliminating these effects of microheterogeneity by fusion of the sample together with a reagent (borax) enabling the formation of a glass disc suitable for X-ray analysis. Subsequently, lithium borate was found to be a more suitable glass-forming reagent in many instances.

Dilution/.....

Dilution in the flux provides the further advantage in that matrix effects are reduced. These are the absorption and enhancement phenomena that are a function of the elements present. If a sample is sufficiently diluted in a glass, the matrix effects become almost constant, and a simple linear relationship of intensity and concentration with a minimum of scatter is approached

Rose et. al (1962,1963) devised a glass-forming mixture incorporating lanthanum oxide in a lithium tetraborate glass. Lanthanum is a strong absorber of X-rays in the relevant wavelength range and thereby serves to suppress even more the variable matrix effects of the samples. However, the absorber also attenuates the characteristic wavelengths of the elements to be analysed. Therefore, in arriving at a recipe to be standardised upon for the range of samples likely to require analysis by the method, proportions of sample, heavy absorber and borate have to be selected to give the best compromise between loss of sensitivity and effective supression of matrix effects.

Although this type of glass disc enables increased accuracy in a diversity of samples, a theoretically perfect result is never attainable. However, results obtained can be improved upon by mathematical procedures. Using the indicated concentration values and published mass absortion coefficients it is theoretically possible to calculate matrix effects and correct the indicated values accordingly, i.e. by the application of so-called matrix correction factors. However, Norrish and Hutton (1969) found that these calculated factors were not completely satisfactory, for two important reasons.

First/.....

First, the published coefficients were not sufficiently accurate, since a variety of assumptions had to be made for their determination. Secondly, there were other lesser corrections which should have been applied, in addition to matrix correction. These concern the geometry of the X-ray spectrometer, fluorescent-yield coefficients, jump factors and the X-ray tube continuum. Austen (1974) has written a computer program for handling such corrections and has obtained satisfactory results.

For a variety of reasons including those given above many authorities consider it even preferable to derive matrix correction factors by empirical means, using suitably chosen standards. Lechance (1964, 1970), and Lucas-Tooth and Pyne (1963) were among the pioners in this field. Lechance and Trail (1966), Trail and Lechance (1965), Lucas-Tooth and Price (1961), Jenkins and Campbell-White-law (1970), Kodama, Brydon and Stone (1967), and Hughes et. al (1970), have all used this method successfully.
A large number of fusion discs (> 500) need to be made, if all the major and minor rock-forming elements are to be included, and mathematical data treatment requires a computer. Norrish and Hutton (1964, 1969) have determined factors (Table 3) for glasses prepared by fusing 15,56% sample and 1,11% sodium nitrate with a flux previously prepared by fusing 47,03% $Li_2B_4O_7$, 36,3% Li_2CO_3 and 16,34% La_2O_3. The sodium nitrate is added to ensure oxidation of small amounts of sulphide or highly reduced oxides which might be present. Both the matrix correction factors and the method of fusion of Norrish and Hutton, with minor variations, are practised widely. Their technique of fusion, like many others, involves the use of platinum alloy crucibles and special casting apparatus of some complexity.

For a number of practical reasons the method of fusion in graphite crucibles, developed at A.A.R.L. approximately five years ago, is still preferred

This report, describes in some detail the AARL methods of glass disc preparation and the adapation of the Norrish-Hutton mathematical treatment of data by by means of a Digital Equipment Corporation PDP 11/05 16 K Computer.

PREVIOUS WORK AT AARL

Following upon the work of Claisse (1956), Anderman and Allen (1961) and Rose et al. (1962), a fusion method was developed at AARL. The glass discs were fused of 15% sample, 25% lanthanum oxide and 60% $Li_2B_4O_7$, and became known as the 12th series composition. Initially the fusions were performed in platinum-5% gold alloy crucibles in a gas-air burner flame at approx. 1000°C and the glass was cast in a 32mm platon made of the same alloy. Annealing the glass, the most difficult part of the procedure, was performed on a hot-plate at about 250°C.

The method was tedious, and an experienced operator, with three burners, could produce a maximum of five discs per hour.

In 1970 graphite crucibles, manufactured from nuclear reactor graphite rods, were used with great success. The fusions were carried out in a globar furnace at 1000°C, for one hour, where they could be left unattended. The crucibles were cut to have the required diameter for introduction to the Philips PW1220 spectrometer, viz. 32mm, and had a flat base. Quenching and annealing was performed in the crucible. After cooling, the surface of the glass discs were cleaned and polished on emery powder and diamond laps. Later, diamond impregnated nickel and felt laps were used.

Using a small globar furnace into which only one salamander tray could be introduced, the production rate was approximately 15 discs per hour, during which time the operator could attend to other duties, e.g. weighing of the next batch of samples.

With the acquisition of the Philips PW1270 multichannel X-ray spectrometer, the fusion method was refined further, and by using a much larger furnace, up to fifty 40mm diameters discs per hour could be produced. In addition, the composition of the flux was changed, in order that the previously described correction factors of Norrish and Hutton might be used.

FUSION METHOD IN CURRENT PRACTICE

Norrish and Hutton produce a glass which has the following approximate composition:

16,7%	sample	
18,1%	La_2O_3	
52,0%	$Li_2B_4O_7$	or 68% $Li_2O.B_2O_3$
13,0	Li_2O	

$Li_2O.B_2O_3$ has a lower melting point (700°C) than $Li_2O.2B_2O_3$ ($Li_2B_4O_7$) (915°C), and forms a less viscous fluid. However, if high temperatures of fusion are used (>1100°C) then $Li_2B_4O_7$ is as fluid and reactive, and completely suitable.

In order to use the correction constants derived by Norrish and Hutton, at AARL the glass discs are made to be very similar in composition:

15%	sample
17%	La_2O_3
68%	$Li_2B_4O_7$

Instead of the use of sodium nitrate during fusion, the samples are oxidised by previous ignition at 1000°C.

CONCLUSIONS/.....

CONCLUSIONS

Thus, a glass disc, closely resembling that for which the Norrish-Hutton empirical correction constants were determined, was tailored to suit the needs of the Anglo American Research Laboratories.

By necessity, the processing of the intensity data, normally very tedious by hand operated electronic calculator, was accelerated by the use of a BASIC language computer programme written by C.E. Feather, which is described in the next section (Appendix 3).

REFERENCES

(See the end of Appendix 3).

APPENDIX 3

COMPUTER PROGRAM FOR THE REDUCTION OF INTENSITY DATA OBTAINED ON THE FUSION GLASS DISCS PREPARED BY THE METHOD DESCRIBED IN APPENDIX 2.

CONTENTS/.....

CONTENTS:

Tables (See Part 1 of Volume 2).

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DATA/.....

APPENDIX 3: COMPUTER PROGRAM FOR THE REDUCTION OF INTENSITY DATA OBTAINED ON FUSION GLASS DISCS PREPARED BY THE METHOD DESCRIBED IN APPENDIX 2.

DATA PROCESSING

Initially, a linear relationship between fluorescent intensity and concentration of the elements being determined was assumed. Best results were obviously obtained when standards used closely resembled the unknowns in composition.

Tedious graphical interpretation of intensities of unknowns was first used and later a desk calculator speeded up the data manipulation. A programmable desk calculator (max. of 250 machine steps) was later applied with considerable success. The present author wrote, for 11 recording cards, a simple program which used the Norrish-Hutton correction factors. First estimates were calculated using the sample calculator in the Philips PW1270 which had been acquired.

However, apart from being very time-consuming,data transfer errors were common, and no corrections could be made for short-term and long-term drift. Calculation by computer with 16K memory core, at least, was found to be desirable.

Edgar Schonvelder, of Computer Applications Section, wrote a program in FORTRAN V for the CSSL Infonet which proved to be highly successful and completely flexible. With the recent acquisition of a Digital Equipment Corporation PDP11/05 computer, on-line operation is possible, and calculating costs are reduced considerably.

The/.....

The program described in this report is designed to allow on-line and off-line calculation in the manner described above. It is written in BASIC, essentially Dartmouth College BASIC, with some additional functions which are described.

The program is limited to manipulation of data for a maximum of 13 standards, 4 blanks and 50 samples. Apart from the 9 elements determined by the PW.1270, additional nominal concentrations of Ni, Cr and S, and absolute concentrations of Na may be input on a prompt from the computer. Corrections for loss on ignition and fusion factors may also be applied.

PDP11 BASIC, VERSION 007A

The PDP11 BASIC language compiler is the copyright property of Digital Equipment Corporation of America. It contains the essential statements, commands, functions and operands of BASIC as compiled originally by Kemeny and Kurtz (1971), which has become generally known as the Dartmouth College BASIC language.

PDP11 BASIC utilizes the following commands:

DELETE
LIST
OLD (= TAPE)
RUN
SAVE (= PUNCH)

Statements/.....

Statements are as follows:

DATA*
DEF (ine)
DIM (ension)
END
FOR* (-NEXT)
GOSUB
GOTO
IF (-GOTO, -THEN)
INPUT
LET
NEXT* (FOR)
PRINT
RANDOMIZE
READ
REM (ark)
RESTORE
RETURN
STEP*
STOP
THEN (IF-, -GOSUB)

All the above statements may be used as commands in the immediate mode of operation, except those marked by asterisks. All commands and statements may be contained in programs for use in the deferred mode.

All PDP11 BASIC programs must have line numbers between 0 and 8191. The program is executed from the lowest line number to the highest. Multiple statements lines may be used, with certain rules which are described in the manual (PDP11 BASIC programming manual, DEC-11-AJPB-D, Digital Equipment Corporation, Maynard, Massachusetts, 1970).

Arithmetic operators in order of decreasing priority are as follows: ↑ (raise to power), *(multiply), / (divide), + and -. Parentheses, of highest priority, may be used to separate individual sections of an equation. Calculations proceed from the innermost parentheses outwards. Comparisons are limited to =, <> (not equal to), >, < , > = , < = Arithmetic functions are as follows:

SIN (X)/.....

SIN (X)	Sine of x
COS (X)	Cosine of X
ATN (X)	Arctangent of x
SQR (X)	Square root of x
EXP (X)	Exponential of x
LOG (X)	Natural logarithm of x
ABS (X)	Absolute value of x
INT (X)	Truncate fraction part of x
RND (X)	General random number between 0 and 1.
SGN (X)	Return a value indicating the sign of x

36 error messages, for prompting programming faults, are listed in Appendix 1. Errors numbered 0 to 27 are fatal (program stops).

The EXF statement may be used to address specific functions in programs loaded in core, but outside BASIC working area, thus known as external functions (EXF). Such programs are loaded using absolute binary notation, and assembled using an ASSEMBLER compiler. The statement takes the form EXF (X,Y). X may be a transfer address (number) or/a binary statement recognisable to the EXF program. Y may take the form of an instruction concerning handling of the data which result from the operation of the particular external program.

A program containing 19 external functions has been compiled by Applied Research Laboratories (ARL) for the operation on the ARL SEMQ electron microprobe. The functions constitute the soft-ware package called BLISS (BASIC Language Integrated Software System), which is the copyright and property of ARL. Some of these subfunctions, as listed below, are useful for general laboratory application, and are used in the program described in this report.

1) EXF (8,A(0)):/.....

1) EXF (8,A(0)): Permits teletype keyboard or punch tape reader input of data to 12-member list A.

2) EXF (10,Z): Prints atomic symbol from input atomic number (Z).

3) EXF (11,A(0), B(0)): Permits conversion of free field constants, input using 1 above, to floating point values. The data is read from list A to list B.

4) EXF (14): Ring teletype bell (alarm).

5) EXF (15, A(0)): Print ASCII string on teletype, previously input to list A using 1 above (Max. 72 characters in length).

6) EXF (18): Reset and start real time clock in computer.

7) EXF (19): Read real time clock

THE X-RAY SPECTROMETERS

At A.A.R.L. the Philips PW1270 14-channel simultaneous spectrometer has been hardware programmed to detect and print out the spectral intensities of nine major rock-forming elements, viz. Fe, Mn, Ti, Ca, K, P, Si, Al and Mg. An example of output format is given in Table 1. The remaining five channels are reserved for other routine analyses by completely different X-ray fluorescent methods.

Electronic instabilities, however small, are considered at all stages in a determination. First, all samples are compared to a reference glass disc, which is read alternatively with the samples. This corrects for small short-term drifts. Long term drifts and day-to-day changes are taken into account by reading a set of selected standard discs at the beginning of every run. If the run contains more than 20 samples, the standards are read at the end of the run also. Calibration constants are then adjusted linearly during calculation of the unknown concentrations (assumes a linear drift).

The Philips PW1220 Sequential X-ray Spectrometer is used in the determination of Na, S, Cr and Ni(hereafter "extra elements"). Na is determined on pressed powder pellets, and Cr and Ni on the fusion discs. S is lost during fusion in graphite crucibles. However, the reaction is slow and small amounts of SO_3 may be present, and determinable on the PW1220. This data are necessary for most accurate correction in the computer program.

Absolute S values may be obtained on discs by a separated method which will be described in a forthcoming report.

INTENSITY DATA OUTPUT FROM PW 1270

Each line of intensity data from the PW 1270 takes the form (e.g.) 10012, 03421, 02121, 00089, 00123, 01249, 10021, 07394, 0008, 00122 (see Table 1). Note that the line is preceeded by a comma and that the first field is indicative of the PW 1270 hardware program being used and the sample number as follows:

10012
↗ ↖
Programe 1   Sample No. 12

The/.....

The nine fields are intensity data for the elements determined by the PW 1270, in the order:

Ca, Fe, Si, Al, Ti, P, K, Mg, Mn.

THE BASIC PROGRAM FOR DATA REDUCTION USING THE CORRECTION CONSTANTS OF NORRISH AND HUTTON

1) - LOADING

By using the comand OLD, the punch paper tape reader is activated on the Teletype ASR 33 teleprinter. The program takes approximately 25 minutes to load, and occupies approximately 7 k of core storage.

After loading, the following steps may be taken:

i) If the first set of standards listed in Table 2 are to be used, type control/P. The teletype will print "READY".

ii) If an alternative standards "file" which is previously punched on tape, is to be loaded, ensure that the line numbers are the same as in table 2. The conc. data must be in the order of standards and elements to be read. Any undesired lines must be recorded on the tape, but left blank, e.g. 2000 Return/line feed, deletes line 2000 if previously loaded, or is ignored if referred to for the first time. If any changes are made to the order in which the elements are read, e.g. changes to the hardware configuration of the PW 1270, then a new standards "file" should be punched and loaded at this stage. At the end of the operation type control/P. The program will respond with "READY".

2) - RUNNING THE PROGRAM

a) Initial dialogue. Following the command RUN, the teletype will type:

```
CONTROL OPTIONS: 1ST EST=1, ON-LINE=2, OFF-LINE=3?1
```

Reply with numbers 1, 2 or 3 as indicated. Any other number will produce an error message and the dialogue will be repeated.

The program then prints `SAMPLE NOS? (1=YES,2=NO)?`

If the reply is positive, the sample numbers may be typed in 10 to a line, or read in off a punch tape, immediately after the initial control cards which are described in the next section. Any error in input will be reported in the program, e.g.,

```
CONTROL OPTIONS: 1ST EST=1, ON-LINE=2, OFF-LINE=3?2
SAMPLE NOS? (1=YES,2=NO)?3
                                WHAT?
SAMPLE NOS? (1=YES,2=NO)?
```

* An explanation of these control options, and of how each option may be used, is given in a later section of this report.

b) Control/.....

b) Control "cards" (or Control lines)

Following the prompt "INPUT CONTROL CARDS", both tape reader and keyboard are activated to receive information. The first control card fields are as follows:

First page No. of the report, date (given as day, month, year (numerically)), no. of standards, no. of blanks, no. of unknowns.

e.g. $\underset{\overset{\uparrow}{\text{page}}}{2},\ \underbrace{13,\ 8,\ 1974}_{\overset{\uparrow}{\text{date}}},\ \underset{\overset{\uparrow}{\text{No. of stds.}}}{10},\ \underset{\nwarrow\ \text{No. of blanks}}{4},\ 22 \leftarrow \text{No. of unknowns}$

e.g.

```
INPUT CONTROL CARDS

1,25,4,1975,12,3,5
```

If "1st ESTS" option is used, then no. of blanks is given as zero. The no. of stds. must always be as in the standards "file", if loaded, elsewise "ZERO".

The next control card concerns the blanks, except if the "1ST EST" option is used. It is prompted by the program as follows:

```
SPECIFY COLUMN NO. WHERE BLANKS NOT APPLICABLE
4,3,1
```

The numbers indicate, for the order of the blanks read, the column numbers of the array into which intensities are read, where the blank disc in question is not applicable. e.g. where a SiO_2 disc is used, 3 specifies that it is not a blank for the element silicon. (The order of input at present is $\begin{array}{ccccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ \text{Ca,} & \text{Fe,} & \text{Si,} & \text{Al,} & \text{Ti,} & \text{P,} & \text{K,} & \text{Mg,} & \text{Mn} \end{array}$). A CaO blank must be read always last. It is used to determine the interference factors for the interference of Ca on P and Ca on Mg. If the option to input sample numbers was exercised, the program will prompt therefor . They may be typed in or read from a tape, 10 numbers to a line, separated by commas:

INPUT/.....

```
INPUT SAMPLE NOS. TAPE
20,21,22,23,24
```

The 3rd control card encountered is:

```
INPUT EXTRA ELEMENTS CONTROL CARD
11,100,101,0,0,0
```

If a zero (0) is input the routine is ignored. Only information concerning the elements Na, S, Cr and Ni, and loss in ignition (L.O.I.) and fusion factors (F.F.) may be fed in at this stage. The control card must contain the atomic numbers of the extra element(s). The numbers 100 and 101 and used to indicate L.O.I. and F.F. respectively.

e.g. 11, 24, 16, 101, 100, 0

Note that the card must have six fields, if additional element information is to be input. Therefore, as in the example, a zero is given to complete the six field of the line. If any other number (s) other than 0, 11, 16, 24, 28, 100, and 101 is given, it will be ignored.

Then following a pause during which the Norrish-Hutton correction factors are read into arrays, the computer will prompt the operator to input the actual concentrations of the additional elements, as in Example 1. The prompts are as follows:

XNA_2O?/.....

XNA2O?
XSO3?
XCR2O3?
XNIO?
LOI VALUES:
FUSION FACTORS:

```
XNA2O?
.24,.25,.27,.28  ,.21

LOI VALUES:
10.45,10.43,13.98,5.32,5.46

FUSION FACTORS:

.9987,.9967,.9876,.9999,.9768
```

The values are input 10 to a line, separated by commas. LOI values are given as positive % for a loss and negative % for a gain on ignition. The F.F.s are normalised to 1.

Following upon the above, the actual run on the PW 1270 X-ray spectrometer is ready to begin. The program prompts

```
INPUT STANDARDS DATA (BEGINNING OF RUN)
```

and activates all reading devices (which may be a direct input data line from the PW 1270).

c) Intensity Data Input

For maximum accuracy, approximately twelve standards of widely varied composition are read, in the same order as in the standards "file" (Table 2). When the intensity data input is complete, the data is regressed against nominal concentration (i.e. concentration before matrix correction, if the standards are treated as unknowns, which can be calculated). On completion of the calculations, the program prompts

```
INPUT BLANKS DATA
```

The blanks are read in order as indicated by the blanks control card. The intensity data are used to determine the true zero intercepts of concentration calibration, expressed in terms of matrix, and calculated using the Norrish-Hutton correction factors.

The/.....

The program then prompts for unknowns intensity data;

```
INPUT UNKNOWNS DATA
```

Following each input, and using the concentration calibration constants and the calculated zero intercepts, first (nominal)intercepts are calculated for the unknowns.

Norrish-Hutton matrix correction constants (Table 3) are then applied to the unknowns. Several iterations may be performed, but little change is noted after the first. Oxide totals outside the range 96 to 102% are reported upon by the program (e.g. BAD TOTAL, SAMPLE 1).

A further program prompt is

```
INPUT STANDARDS DATA (END OF RUN)
```

which is applicable to the off-line mode of operation described in detail in the section entitled "Modes of operation".

d) - The Report

Upon completion of all calculations, a report is printed in two sections. First the calibration constants, blank values, interference factors and drift factors are tabulated. The program then prompts for a heading

```
INPUT HEADING
```

and the results reportfollows. It is typed with the format of 8 samples to an approximate A4 sized page (examples in Tables 5, 6 and 7). Upon

completion/.....

completion of the report, the total elapsed run time is printed, and the program stops.

3) MODES OF OPERATION:

a) - Off-Line operation (See appendix 2)

For off-line operation (option 3 - see "Initial dialogue"), a data tape is prepared previously. It must be constructed as follows:

i) Lead null frames (deletes are illegal!)
ii) Control cards (1st and 2nd)
iii) Sample numbers (if option exercised), ten to a line and separated by commas
iv) Standards intensity data.
v) Blanks intensity data
vi) Unknowns intensity data
vii) Standards intensity data
viii) Blanks intensity data
ix) Extra elements control card
x) Extra element concentration data (ten values to a line)

The tape must be loaded with the reader on the leader null frames. Following on the initial dialogue, the tape will be read into core, stopping between lines to permit calculations to take place. Poor oxide totals are reported upon.

At the end of processing the intensity data, the extra elements data is input, and finally the report is printed.

b) - On-line/.....

b) - On-line operation (see Table 6):

On-line operation differs only from off-line operation in that extra element information is given at the beginning of the run (after the control cards and sample numbers (if desired) instead of at the end). As the standards, blanks and unknowns are read by the PW 1270, the data are input, and the program calculates and report concentrations. The standards and blanks are not read again at the end of the run, thus drift during the run is not taken into account. If a result is unsatisfactory, the sample disc may rerun, or a new sample disc read by reading in the manual mode. This is done by using the edit call "99" described later in the section on "Correcting False Starts, and Editing".

Finally, after all discs have been read, the report is printed.

c) - First estimates only (see Table 7):

These are input, following upon the prompt "INPUT 1ST ESTS" as nominal concentrations, one sample to a line, and the elements in the same order as for intensity inputs in (a) and (b), above, viz. Ca, Fe, Si, Al, Ti, P, K, Mg and Mn.

Extra element information may be given also during the run, and a report is printed.

4) CORRECTING/.....

4. CORRECTING FALSE STARTS, AND EDITING (With working examples):

a) - To begin and begin again

Use the comand RUN,↵ (i.e. type the return key). To escape and restart, type control /P, and type RUN again,

```
RUN

CONTROL OPTIONS: 1ST EST=1, ON-LINE=2, OFF-LINE=3?1
SAMPLE NOS? (1=YES,2=NO)?↑P
READY
RUN

CONTROL OPTIONS: 1ST EST=1, ON-LINE=2, OFF-LINE=3?2
SAMPLE NOS? (1=YES,2=NO)?
```

b) - To restart reading in sample numbers

Escape first using control/P (P and the control key pressed simultaneously). Basic responds with ↑P, READY.

Then type GOTO 64 ↵

```
↑P
READY
GOTO64

INPUT SAMPLE NOS. TAPE
```

c) - To restart reading in extra elements information

i) Correct extra elements control card, but wrong data;

Escape, then GOTO 332 ↵

↑P/.....

```
↑P
READY
GOTO332

XNA20?
```

ii) Wrong extra elements control card: Escape, then RESTORE: GOTO 108 ↵

```
RESTORE:GOTO108


INPUT EXTRA ELEMENTS CONTROL CARD
```

d) - To restart reading in first set of standards data

Escape, then GOTO 116 ↵

```
↑P
READY
GOTO116

INPUT STANDARDS DATA (BEGINNING OF RUN)
```

e) - To restart reading in first set of blanks data

Escape, then GOTO 128 ↵

```
↑P
READY
GOTO128

INPUT BLANKS DATA
```

f) - To/.....

f) - To restart reading in unknowns data

i) Off-line : Escape, then GOTO 158 ↵

```
↑P
READY
GOTO158

INPUT UNKNOWNS DATA
```

ii) On-line : Escape, then GOTO 476 ↵

```
↑P
READY
GOTO476

INPUT UNKNOWNS DATA

EDIT CALL=99
             CA    FE    SI    AL    TI    P    K    MG    MN
```

Notes: To restart an individual sample read in the on-line mode of operation, escape, then GOTO 482 ↵ .

To restart from a point back in run, escape, then

LET I = n: GOTO 482 ↵

where n is the analysis number at restart. (If the numerator on the PW 1270 is started at zero, and two trays of standards are used, the value of will be present numerator value minus 20 minus the number of samples back from the point of escape (point where reading the next sample).

g) - To restart the input of first estimates

Escape, then GOTO 498 ↵

```
↑P
READY
GOTO498

INPUT 1ST ESTS.
```

h) - To/.....

h) - To restart reading in of standards intensity data at end of run (off-line mode only)

Escape, then GOTO 168 ↵

```
↑P
READY
GOTO168

INPUT STANDARDS DATA (END OF RUN)
```

i) - To restart reading in of blanks intensity data

Escape, then LET C1 = 1+n:GOTO 128; where n = number of blanks ↵

```
↑P
READY
LETC1=1+4:GOTO128

INPUT BLANKS DATA
```

j) - To rerun a sample immediately upon obtaining a suspect or bad result in the on-line mode of operation

Use the edit call 99 ↵ without escaping.

Since the computer takes approximately one minute to calculate an unknown's concentration, the PW 1270 will be reading the next sample. If a result of the present sample is unsatisfactory, and you wish to re-run the disc, or run an alternative disc, type 99 ↵ . The program will respond with "SWITCH PW 1270 TO 'MANUAL' AND WAIT". Having followed that instruction, when the present reading is complete, the "FREE" light on the PW 1270 will illuminate and the rerun can be made. The new result will overwrite the old, and control by the normal routine of the program will be restored. Press the "C" button on the PW 1270, and the run will continue from where it left off.

INPUT/.....

```
INPUT UNKNOWNS DATA


EDIT CALL=99

         CA     FE     SI     AL     TI     P      K      MG     MN
,10029,03762,02707,22349,00485,04641,00203,00611,04454,00335
UNK 1   4.38   8.89   41.71   4.68   1.93   .14   1.45   26.1   .18  0  0  0
.24 TOTAL= 100.16
99
SWITCH PW1270 TO 'MANUAL' AND WAIT
,10030,08663,02551,19516,00343,05428,00189,00541,04695,00325
UNK 2   10.28   8.47   36.24   3.25   2.35   .11   1.27   27.33   .16  0  0  0
  0 TOTAL= 99.9
,10031,08493,02564,19439,00317,05461,00195,00555,04722,00327
UNK 1   10.09   8.52   36.17   3   2.37   .12   1.31   27.57   .17  0  0  0  .
24 TOTAL= 100
,10032,08540,02563,19691,00313,05442,00188,00550,04693,00312
UNK 3   9.98   8.37   36.01   2.9   2.32   .11   1.27   26.92   .13  0  0  0
.27 TOTAL= 99.25
```

k) - To overwrite a false heading

Escape, then GOTO 620 ↵

```
↑P
READY
GOTO620
INPUT HEADING
```

1) - To print another copy of report

LET A1 = first page number: GOTO 621 ↵

↑P/.....

```
↑P
READY
LETA1=10:GOTO621
```

DISCUSSIONS AND CONCLUSIONS

Examples of off-line, on-line and "first estimate" runs of the program are given in Tables 5, 6 and 7. The program is listed in Table 8

The results obtained by using the revised method of glass disc preparation described, and the computer program, are highly acceptable, as demonstrated in Table 4.

The program provides complete flexibility, even when false starts and wrong instructions are given. Error messages are written into the program to prevent fatal errors during program execution.

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APPENDICES 2 & 3.

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APPENDICES 4 & 5

APPENDIX 4: CONDUCTIVE COATING INTERFEROMETRY

APPENDIX 5: VISIBLE LIGHT FLUORESCENCE, AND OTHER USEFUL AIDS IN ELECTRON PROBE MICROANALYSIS

The contents of these two appendices were presented at the 11th Annual Conference of the Electron Microscopy Society of Southern Africa, Johannesburg, 1972, in a paper entitled: "Excitation of outer orbital electrons and conductive coating interferometry as aids to the mineralogist and metallurgist using the electron probe X-ray microanalyser".

(Proc. Electron Microsc. Soc. South.Afr., Vol. 2, p. 53-54, 1972).

APPENDICES 4 & 5

INTRODUCTION

APPENDIX 4: CONDUCTIVE COATING INTERFEROMETRY

APPENDIX 5: VISIBLE LIGHT FLUORESCENCE, AND OTHER USEFUL AIDS IN ELECTRON PROBE MICROANALYSIS

INTRODUCTION

It is likely that the phenomena which are described in this paper are familiar to all experienced electron microprobe operators, but their usefulness in identifying phases under examination has not been assessed previously.

The most useful information which may be derived from an electron probe X-ray microanalyzer is undoubtedly the study of textures and the identification of elements in phases under examination. However, many are similar in composition, and, when using an instrument which has mechanical spectrometers, it is often a tedious procedure to scan through a wide wavelength range in order to ascertain qualitatively the chemical constituents of a phase.

The conductive coatings on polished sections alter the appearances of the phases in reflected light and, except in thin section with transmitted light, it is often difficult to identify transparent phases.

Therefore, it is advantageous for the microprobe operator to be able to identify metals and minerals utilizing some of the often less appreciated phenomena which are associated with electron beam excitation and with thin coating film interferometry.

The purpose of this paper is to describe these phenomena and their application, and to introduce these new methods in optical mineralogy and metallurgy.

APPENDIX 4/.....

APPENDIX 4

CONDUCTIVE COATING INTERFEROMETRY

CONDUCTIVE COATING INTERFEROMETRY

If a polished section has been flash coated with a conductive element in a vacuum evaporator, during subsequent optical examination visible light interferences occur between the phases and the coatings if the phases are electrical conductors. Thus all metals, many sulphides and some oxides show this phenomenon.

The interference colours which arise resemble the birefringence interference colours of transparent minerals observed between crossed polarizers of a conventional mineralogical microscope. The extent of interference (amount of retardation and the colour that results) is dependent upon coating thickness and the chemical composition of the phase under examination. The intensity of the colour (brightness) appears to be dependent upon the electrical conductivity properties of the phase. Group 1B elements (Cu, Ag and Au) are very good electrical conductors and give intense colours, whereas sulphides and oxides give pale colours dominated by the gray of the actual carbon. The colour of the uncoated phase does not affect the interference colour at all, and is completely obscured by coating.

Provided that coating thickness is controlled, interference colours are reproducible.

The simplest, but not the most accurate method of controlling coating thickness is done by placing the samples to be coated on aluminium foil and observing the interference colours that arise as the aluminium foil is coated. When flash-coating with carbon, just as the colour approaches the end of the first order of interference, at magenta (see the Michel-Levy colour chart in any text on optical mineralogy), the coating will be thick enough for efficient conduction.

A simple/.....

A simple and fairly accurate instrument for measuring and controlling coating thickness is illustrated in figure 4-1. It consists of a microscope glass slide held by two clamps at two corners dotted with conductive paint. The slide is placed in the vacuum evaporator with its face parallel to, and at the same height as the surface of the samples to be coated. As the coating thickness increases the resistances drops from infinity. A suitable thickness is usually achieved at a resistance of 150 ohms across a 50 mm x 25 mm glass slide. For a given vacuum evaporator, the correct resistance is found by trial and error.

Metals with similar chemical and electrical properties tend to give similar interference colours. As an example, copper, silver and gold are all group 1B elements and give varying hues of a common basic colour. In an experiment carried out by the author, a carbon coating giving a resistance of 150 ohms between two points at opposite corners of a 50 mm glass slide gave interference colours of sky-blue for copper, voilet-blue for silver and turquoise-blue for gold (interference retardations of approximately 700, 650 and 720 nanometers respectively).

The interference colours are different for a different coating thickness, but the relative retardations are the same, and are of diagnostic value.

Pyrite and gold are good examples of the application of this method. Uncoated, gold is a brighter yellow than pyrite, but the difference is small. Coated, they are distinctly different. The pyrite gives paler lower order interference colours than gold which gives intensely bright higher order interference colours.

The interference colours and their intensities which were recorded for a fixed thickness of carbon coating on various elements, oxides and sulphides are tablulated in Table 4-1 in order of increasing retardation. Popular terms are used to describe the colours, which may be observed in the Michel-Levy chart. Pale colour intensities are dominated by the gray colour of the carbon.

The most/.....

The most useful application of coating interferometry is in the identification of phases once they are coated, especially when viewing them through the microprobe's optical microscope attachment. Without application of this method it is virtually impossible to recognise the phases, as the coating tends to obliterate all the information which would normally be investigated by standard reflecting microscope techniques. A typical example is given in Figures 4 - 2 and 4 - 3.

APPENDIX 5/.....

APPENDIX 5

VISIBLE LIGHT FLUORESCENCE, AND OTHER USEFUL AIDS IN ELECTRON PROBE MICROANALYSIS

VISIBLE LIGHT FLUORESCENCE

Electrically non-conductive phases, especially the silicate minerals, may be identified by the phenomenon of visible light fluorescence arising from electron bombardment. The emissions appear when excited outer orbital electrons return to their ground (original) energy levels. They are often extraordinarily bright and the colours may be used in the identification of mineral species.

This phenomenon is exceptionally useful in identifying common silicate minerals in thick polished section. Normally, identification is often virtually impossible using a standard microscope, even before the minerals are coated with a conductive element.

The writer has recorded the colours of the visible emissions of a number of common minerals. Examples are given in Table 5 - 1.

As a very simple example of application, consider the very high intensity indigo emission of diamond; Steel sections submitted for examination are frequently polished by means of very fine diamond paste. Individual diamonds become embedded in the metal and may be mistaken for carbon, graphite or carbide crystals, which are true phase constituents of the steel. However, of these carbon compounds, only diamond fluoresces, and its colour is so bright and characteristic that it could not be mistaken for any of these other carbon-bearing phases expected in the steel.

Examples of two fluorescent minerals, as viewed through the optical microscope of the JEOL JXA-5A microprobe, are given in Figures 5-1 and 5-2.

It would/.....

It would be extremely useful to equip the microprobe with a small focussing optical spectrograph for observing these longer wavelength emissions which frequently convey information concerning orbital and bond structure, and valency.

LOW ENERGY X-RAY EMISSIONS

Further useful information may be derived from the low energy emissions of outer orbital electrons which are involved in electron bonding. As shown by White and Gibbs (1967)[1], the electrons in orbitals responsible for chemical bonding have energy levels that depend firstly upon atom structure and secondly, but less conspicuously, on the actual bonding orbital formed. Consequently, the wavelengths emitted by the outer orbital electrons of a given element may vary slightly, depending on the nature of the chemical bonding in the compounds that form. These variations, or "wavelength shifts", as they are referred to in the literature, are very small, but may be usefully applied to measuring bond lengths and in classifying bond types.

The measurement of "wavelength shifts" require a highly sensitive instrument with high resolution X-ray spectrometers. It is probably for this reason that very little work has been done in this field. White and Gibbs (1967)[1] found that the silicon-oxygen bond length may be measured using wavelength shifts in silicon K-beta radiation. Similar experiments were carried out, and the results are in agreement with the findings of White and Gibbs. Quartz, orthoclase and forsterite were chosen for the study, since, in all three, silicon is in tetrahedral co-ordination. The wavelength shift of silicon K-beta radiation was measured and a near-linear relationship was found between line shift and silicon-oxygen bond distance (see Figure 5-3).

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1. White E.W. and Gibbs G.U., Am. Min., Vol. 52, p. 985, 1967

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IONIC VALENCY

Outer orbital electrons may also be involved in ionic bonding, giving rise to spectral emissions which may contain information concerning ionic valency. The oxidation states of iron and manganese, for example, are often of considerable interest. Preliminary investigations into the use of the electron microprobe in determining the Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} ratios were made by A.L. Albee and A.A. Chodos (1970)[2] measuring the relative intensities of the iron L-alpha and iron L-beta X-ray emissions, the intensities of which depend upon the availability of electrons in outer-most valence shells of the atoms.

Albee and Chodos showed that these relative intensities may be used, but also found that besides valence state, many factors influence the actual intensities of these emissions, namely coordination number, the identity of the nearest neighbour atoms, the bond length, the bond angle and the bond type. It is difficult to separate the effect of oxidation state from these other effects. There are probably very few minerals in which there is a complete variation from divalent to trivalent iron or manganese without a systematic variation in other structural parameters. Divalent and trivalent iron and manganese differ in ionic radii as well as in charge and commonly play very different roles in rock-forming silicates and oxides. For example, very often, as in garnet and ilmenite, iron and manganese may occupy two six-fold coordinate sites in the same basic lattice structure, namely as divalent and as trivalent ions. It is therefore obvious that mineral species should be studied and calibrated separately.

In this study the method of measuring changes qualitatively in the iron L-alpha to iron L-beta ratio was applied usefully in a number of experiments. One of these applications is illustrated in Figure 5-4. Chromian spinel was roasted in a controlled chemical environment. Changes in the intensity ratios of the iron L-spectral peaks between the unroasted and roasted spinel showed that the oxidation state of the iron had changed, as was hoped for during this experiment.

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2. Albee A.L. and Chodos A.A. Am. Min., Vol. 55, p. 491, 1970.

The method enables positive identification of most iron oxide minerals: hematite, magnetite, goethite, etc., as illustrated in Figure 5-5 all give differing but characteristic iron L-alpha to L-beta ratios.