

THE SULPHIDES IN THE LAYERED SEQUENCE OF THE BUSHVELD IGNEOUS COMPLEX

by

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ABSTRACT

The Bushveld Complex, which is the largest mafic and ultramafic complex of its kind in the world does not contain copper and nickeliferous ores, with the exception of the Merensky Reef and the sulphide pegmatoids of the Western Transvaal. Ores belonging to the latter type have almost been worked out. However, minor quantities of disseminated sulphides are found throughout the whole sequence of layered rocks of the Main Plutonic Phase, the Hypabyssal Phase, the Late Plutonic Phase and the Volcanic Phase. The investigation reported here is restricted to the rocks of the Main Plutonic Phase and the Late Hypabyssal Phase.

From field observations and bore-hole investigations it is clear that cross-cutting relationships exist between the rocks of the Basal Zone and the sediments of the Pretoria Series in the Western Transvaal. Huge blocks of metasediment were lifted from the floor to form inclusions in the plutonic rocks. The bore-hole results reveal that in the deepest parts of the basin the floor of the Complex has not yet been explored, particularly in the region west of the Pilanesberg.

It was found that disseminated sulphide seldom exceeds 2 per cent by volume of the rock. Abnormal concentrations of sulphide are known only from certain parts of the Basal Zone, from sulphide-bearing pegmatoids, from the Merensky Reef and from the mineralized anorthosites below the Main and the Uppermost Magnetitite Seams. Generally the sulphides constitute approximately O. 05 per cent by volume of the layered rocks. The sulphides are the three modifications of pyrrhotite (troilite, hexagonal and monoclinic pyrrhotite, distinguished from one another by X-ray diffraction and etching methods), pentlandite, chalcopyrite, cubanite, pyrite, mackinawite, zinc-blende, bornite, galena(?), safflorite-loellingite, linaeite, millerite, chalcopyrrhotite(?) and the nickel-arsenic-bearing minerals, gersdorffite, maucherite, niccolite, rammelsbergite(?) and ullmannite(?). The secondary minerals are valleriite, melnikowite-pyrite, bravoite and covellite. Not much attention was paid to the minerals containing the platinum group metals, although a few have been identified; sperrylite, braggite, cooperite and michenerite(?) .

A differentiation trend was established in the mineralogical composition of the sulphide phase. From the base to the top of the Main Plutonic Phase there is a decrease in pentlandite and an increase in chalcopyrite. The latter

 $I_{\text{vac},\text{max}}$ its maximum in the mineralized anorthosite below the Main Magnetitite Seam. In the Upper Zone chalcopyrite decreases with an increase of pyrrhotite. The sulphides in any pegmatoid, which is considered to be a differentiation product of the host-rock, are also enriched in copper sulphide and pyrrhotite in comparison with the adjoining country-rock. In addition to this differentiation trend, the sulphide of the mafic rock, which contains little sulphide (0.1%) , consists mainly of chalcopyrite. Mackinawite in pentlandite appears in these rocks below the Merensky Reef, in association with metal-rich sulphides such as troilite and cubanite. Galena $(?)$ is present only in higher horizons of the layered sequence.

All the sulphides involved in the Fe-Ni-S system exsolved from a solid solution of the monosulphide (FeNi) $_{1-x}$ S, above 863[°]C. The coarse-grained pentlandite in the sulphur-deficient sulphide phase formed by reaction between (NiFe) $\frac{3+x}{2}$ and pyrrhotite at 610 °C. Exsolution flames and bodies of pentlandite, as well as coarse-grained pentlandite, the latter being found in association with sulphur-rich sulphides, are exsolved from the solid solution of the monosulphide below $\pm 845^{\circ}$ C. It would appear that mackinawite exsolved only from pentlandite that originated by reaction between (NiFe) 3^+X^S and (FeNi) 1^-X^S . According to Kullerud (1962) pyrrhotite exsolved from pentlandite below 580[°]C. It is suggested instead that mackinawite exsolved at this temperature, perhaps at higher pressures. Yund and Kullerud (1966) mentioned that 4-5 per cent by weight of Cu could be in solid solution in $Fe_{1-x}S$ at 700^oC. A great deal of the copper sulphide in the ores in the Bushveld Complex thus also exsolved from the solid solution of monosulphide. Cubanite is not stable above \pm 440[°]C and would exsolve from a solid solution of chalcopyrite. A degree of solid miscibility exists between nickeliferous ores from volcanic rocks (e.g. the Igdlukunguaq extrusive basaltic "dyke"), hypabyssal rocks (e.g. the Petolahti diabase) and plutonic rocks (e.g. the Bushveld, Insizwa and Sudbury), decreasing in the order given.

At certain localities, in the Western Bushveld, south of Potgietersrus and in the vicinity of Burgersfort, disseminated sulphides are found in the Basal Zone mainly in those regions where a definite cross-cutting relationship exists between the plutonic and the metasedimentary rocks. Sedimentogenetic sulphides are known from the Pretoria Series. The metasediments in the Western Transvaal and at Potgietersrus also contain some sulphide, mainly

pyrrhotite or pyrite, of possible sedimentogenetic origin. Arsenic minerals and graphite are present in the metasediments and in the adjacent plutonic rocks, as well as in the sulphide pegmatoids in the Western Bushveld. To account for the abnormal quantity of disseminated sulphide and sulphide pegmatoids in the regions mentioned, it is postulated that assimilation took place of S, As and C from the metasediments by the plutonic rocks. Where the Merensky Reef is in contact with metasediments (north of Potgietersrus and south-east of Groblersdal) abnormal quantities of compounds containing the platinum group metals, arsenic and bismuth (?) have been noticed. This phenomenon is attributed to the assimilation of As and Bi (?) from the metasediments. The As and Bi apparently reacted with the platinum group metals which were in solid solution in the Cu-Ni-Fe sulphides to produce arsenides and bismuthides.

To test the reliability of this hypothesis of sulphur assimilation a sulphur isotope investigation was carried out. It was found that sediments far away from the Bushveld Complex have δS^{34} per mil values which are relatively high positive (± 46) and high negative (± 48) . The sulphides in the metasediments above the Magaliesberg quartzite have low negative values (± -10) . The plutonic rocks in contact with the different sedimentary horizons have comparable values. The δS^{34} per mil values of the sulphides in the layered rocks of the Complex far away from any metasedimenis have values in the vicinity of zero. This is more or less the same as the values for magmatic sulphur derived from the Upper Mantle. The sulphur isotope investigation thus confirms that sulphurization took place where the plutonic rocks are in contact with sulphide-bearing metasediments. A fractionation of sulphur isotopes was observed in the Bushveld Complex. The early differentiates at the base of the Complex are enriched in S^{32} whereas the later differentiates towards the top of the intrusion are $\,$ enriched in $\mathrm{S}^{34}.$ The sulphides in the pegmatoids also show an enrichment of s^{34} in comparison with the sulphides of the host-rock.

The intercumulus material in certain rock types in the Western Transvaal consists largely of sulphide. It is thus expected that a pegmatoidal fluid which originated out of the intercumulus liquid would be sulphur-rich and would give rise to fairly massive sulphide pegmatoid.

Owing to the fact that Ni^{2+} replaces Fe^{2+} diadochically in the early ferromagnesian silicates, the Ni content decreases from the bottom to the top

of the layered sequence. The Upper Zone which is relatively Fe-rich has, however, also a fairly large Ni content. Cu, Co and Zn vary sympathetically but remain more or less constant throughout the layered sequence. These elements also tend to replace Fe in the silicates and oxides. Cu, Ni, Co and Zn vary sympathetically with S.

Most of the disseminated sulphide in the Bushveld Complex crystallized from an immiscible sulphide liquid trapped in the intercumulus pores. In the Skaergaard intrusion it was found that Cu sulphides crystallized when the sulphur content of the magma was relatively low, whereas Fe sulphides are accompanied by a relatively high sulphur content. By examining the Bushveld Complex on the basis of these facts, certain concentrations of sulphide in the layered rocks of the Complex are explained. During the crystallization of the mafic rocks in the Critical Zone the S content in the magma was relatively low and consequently mainly chalcopyrite was formed. Not enough Cu was present to remove all the S in the magma and its content thus gradually increased. Soon after a change in the composition of the magma in the zone of crystallization, a copper-nickeliferous immiscible liquid formed, representing the Merensky Reef. The Merensky Reef could also be explained by crystallization of a sulphide-oxide- silicate eutectic at a high oxidation potential. During the crystallization of the Main Zone the conditions were the same as those in the Critical Zone, except that the oxidation potential of the magma during the crystallization of the upper part of the Main Zone was relatively high. The last liquid crystallized at a sulphide-oxide-silicate eutectic. Immediately after this event introduction of a new surge of magma or a change in the composition of the magma took place whereby the Main Magnetitite Seam crystallized. The mineralized anorthosite below the Uppermost Magnetitite Seam is a repetition of the former mineralized anorthosite.

A mafic-ultramafic intrusion could be classified as a potential nickeliferous ore-bearer with the aid of certain geochemical criteria. By applying these criteria to the rock-types of the Bushveld Complex, it appears that the ultramafic rocks are the only ones with which nickeliferous ores could be associated - excluding the Merensky Reef and abnormally mineralized zones.

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1. INTRODUCTION

This investigation of the sulphides in the layered sequence of the Bushveld Complex serves as an introduction to the study of the sulphides in the mafic and ultramafic plutonic rocks of the Complex. As indicated by the title, the investigation was restricted to the sulphides of the layered plutonic rocks of the Bushveld. The sulphides of certain hypabyssal rocks, especially the Late Hypabyssal (quartz) norites, were also included. No attention was paid to the sulphides associated with the Volcanic (andesitic lavas) and Late Plutonic (granitic rocks) Phases of the Bushveld Complex.

Wagner (1929) described the sulphides from several localities and stratigraphical horizons known at that time in the Bushveld Complex. A section dealing with the mineragraphy, spectrography and genesis of some Bushveld ores by Schneiderhohn is also included in Wagner's publication. Since then not very much work has been done on the sulphides. Of importance is the investigation of the Vlakfontein and Middellaagte ores carried out by Schwellnus (1936) and by De Bruyn (1944) respectively. In a number of unpublished M.Sc. theses, especially those dealing with some aspects of the Merensky Reef, sulphides are described, although very superficially.

It was thus found necessary to re-investigate the sulphides throughout the layered sequence of Bushveld rocks. Although the Bushveld Complex is the largest mafic-ultramafic intrusion of its kind in the world, no important copper-nickeliferous ore is associated with this Complex, with the exception of the Merensky Reef and the sulphide-bearing pegmatoids of the Western Transvaal. The latter have already been largely worked out. Considering the large volume of mafic-ultramafic rocks, the known occurrences of cupriferous and nickeliferous ores are comparatively small.

The Main objects of the research reported in this thesis are:

Firstly, a mineragraphic investigation of the sulphide phase, with reference to the mutual textural relationships of the ore-minerals and a determination of the variation in the mineralogical composition of the sulphide phase on different stratigraphical horizons, if present. The results are compared with other nickeliferous deposits and especially with experimental phase-chemistry of the sulphide systems in question. Secondly, as a result of the investigation mentioned above and with the aid of analyses of the chalcophile elements and S, as well as determina-

tions of sulphur isotopes, an attempt is made to clarify the causes of sulphide concentrations on different stratigraphical horizons in the Bushveld Complex.

For the purpose of this study more than 400 polished sections were made from samples taken over the entire eastern part of the Bushveld Complex and the Potgietersrus sector. Owing to a lack of proper outcrops in the Western Transvaal, samples in this area were obtained from several shallow and deep bore-holes and from the Vlakfontein Nickel Mines. A location list of all the samples is given in the appendix (table 63). The positions of the samples and the bore-holes are indicated on Maps I, II and III (inserted in pocket at the back). All the numbers of the samples from the bore-holes in the Western Transvaal are accompanied by a prefix which indicates the borehole number, e.g. KA1-234. The number at the end refers to the depth at which the sample is taken. Samples from the Vlakfontein Nickel Mines have the prefix "Vl".

2. AN OUTLINE OF THE GEOLOGY OF THE BUSHVELD COMPLEX 2. 1 Introduction

From an investigation of the sulphides of the Bushveld Complex it is clear that they are igneous differentiates which form part of the intercumulus material. The sulphides vary in quantity and in composition from layer to layer. There is also a close relationship between the major change in composition of the rock and the concentration of the disseminated sulphides. It is thus necessary to outline the general geology and the origin of the different rock types in the Bushveld Complex.

2. 2 The Phases of emplacement

According to Visser (1967, p. xxxiii) the plutonic rocks of the Bushveld Complex represent a magmatic phase at the end of a cycle of events which started with the deposition of sediments representing the geosynclinal phase.

As far as the eruptive rocks are concerned the following sequence of emplacement could be distinguished:

- 1. Volcanicity
- 2. A Hypabyssal Phase
- 3. The Main Plutonic Phase
- 4. A Late Plutonic Phase

The first phase was emplaced contemporaneously with the deposition of

the Pretoria Series. There are indications that some sills had already been in place during the outpouring of the Machadodorp volcanics (Willemse, 1959, p. xxxii).

2. 2. 1 Volcanicity

The volcanic activity, contemporaneous with the deposition of shales and quartzites, started with the extrusion of the Ongeluk lava, followed by the Machadodorp agglomerate, the Dullstroom lava and the lavas in the upper part of the Smelterskop Stage. These lavas are andesitic in composition but Willemse (1959, p. xxx) mentions that the lavas mentioned last are actually soda-trachyandesites. The felsites, extruded after the deposition of the sediments of the Pretoria Series, are referred to as the Epicrustal Phase by Willemse (1964, p. 99). The total thickness of these felsitic rocks may be up to 15,000 feet according to recent work in the Nylstroom area.

2. 2. 2 A Hypabyssal Phase

A great thickness of diabase sills intruded into the Pretoria Series. It appears as if there are essentially two groups of these rocks which differ in chemical composition (Willemse, 1959, pp. xliii-xlviii) and in age. The Early Hypabyssal Phase is gabbroic, whereas the Late Hypabyssal Phase is more noritic in composition. The latter is found at or near the contact with the Main Plutonic rocks of the Complex. The Late Hypabyssal Phase is often differentiated, with a peridotite layer at the base and a thick quartz norite at the top. The latter contains appreciable amounts of quartz and biotite and all gradations between norite, quartz-biotite norite, cordierite-biotite-quartz norite and cordierite-biotite-plagioclase hornfels could be observed. This clearly points to assimilation of sedimentary material by the quartz norites. Willemse (1959, p. xlvi) explained the difference in composition of the Late and Early Hypabyssal Phases by the assimilation of argillite by the gabbroic magma to form plagioclase and orthopyroxene.

The sills, which are quartz noritic in composition, are called the Maruleng norite. A sill-like layer, 1,000 feet thick at places and probably the last intrusive of the Late Hypabyssal Phase, is separated in its typical development from the Pretoria Series by a considerable thickness of ultramafic rock belonging to the Basal Zone. The norite layer is considered to have been lifted up from the sediment by the ultramafic rocks of the Main Plutonic Phase. The norite sill, generally called the Hendriksplaats norite is characterised by numerous inclusions of carbonate- and quartzitic rock.

The Hendriksplaats norite differs further from the Maruleng type in the absence of quartz and biotite. The Maruleng and Hendriksplaats norites were grouped in the Chill-zone of Hall or in the Diabase-norite zone of Lombaard. In the Marone Mountain where the Hendriksplaats norite has its thickest development, all gradations between anorthosite, norite, feldspathic pyroxenite and pyroxenite are present. At other places only a fairly massive norite is present. The author regards the composition of this norite to be the same as that of the original Bushveld magma.

In the Western Transvaal the Hendriksplaats norite is also developed but it is found directly above the Magaliesberg quartzite. It may be quartzand biotite-bearing at places but still with inclusions, thus grading into the Maruleng norite.

2. 2. 3 The Main Plutonic Phase

For the purpose of this study the Main Plutonic Phase of the Bushveld Complex is divided into the zones indicated in table 1, which is the classification most generally applied by geologists.concerned with Bushveld geology.

Table 1. The zones and the rock-types of the Main Plutonic Phase

illtramafic and Mafic Pegmatoid is present in the Basal, the Critical and the lower part of the Main Zone

The thickness of 15,000 feet for the Basal Zone may appear excessive, but this is the true thickness of the Basal Zone in the Burgersfort area. In some places (north of Pretoria, and west of Dullstroom and Belfast) the Basal Zone is absent at the present erosion-surface. This is due to the discordant intrusive relation between the Bushveld Complex and the Pretoria Series. More mafic, or mainly ultramafic, rocks may thus be present at greater depths which are not exposed at the present erosion-surface.

The modern tendency is to explain the heterogeniety of mafic intrusions, i.e. the phase layering, according to the Jackson nomenclature (Jackson, 1967, p. 2), in terms of crystal settling in situ from an ore-magma. Convection-currents could have played an important role as was the case inter alia at Stillwater (Hess, 1960, pp. 135-136; Jackson, 1960, pp. 94-99) and at Skaergaard (Wager et al, 1939, p. 332).

The following phenomenon in the Bushveld Complex forces us to postulate at least two separate injections of magma:

1. Harzburgite plutons intrusive into the metasediments of the Pretoria Series definitely indicate an intrusion of a harzburgite magma. These bodies link up with the ultramafic rocks of the Basal Zone at depth or in some places, e.g. the Aapiesdoorndraai body, at the surface (Liebenberg, 1966). They are thus regarded as an integral part of the Basal Zone and the Aapiesdoorndraai body is thus the lowest exposed horizon of the Bushveld Complex.

2. In the Potgietersrus area the Main Zone cuts across the Critical Zone and part of the Basal Zone so that the lower part of the last zone is in contact with the gabbro of the Main Zone.

3. In the Western Transvaal the Upper Zone and about 1,000 feet of the topmost part of the Main Zone, cut across the remainder of the Main, the

Critical and the Basal Zone (Map II). This extensive cross-cutting of rocks can also be explained by faulting simultaneous with the emplacement of the Upper Zone. In the Stoffberg area a leptite inclusion, 10 miles long, is found, also more or less 1, 000 feet from the top of the Main Zone without causing any disturbance of the layered sequence above and below the inclusion (Map I).

Much more factual evidence is actually necessary before any definite . deduction can be made of the number of magma surges which constitute the Main Plutonic Phase.

As far as the origin and the concentration of sulphides in the Bushveld are concerned, it would seem not to make any difference whether the change in the composition of the magma was brought about by convection or by an influx of fresh magma.

To explain certain phenomena we can assume that the layered rocks formed as cumulus crystals which separated from an overlying liquid and settled like a sediment. Separate surges of magma could be called upon to explain some of the discordant relationships. The crystal cumulate would retain some liquid in the interstices at the time of its formation and this necessarily would have the composition of the magma existing at that particular stage. As cooling progressed, the interstitial liquid would crystallize to form outer zones to the cumulus crystals or additional mineral phases, for example quartz, biotite and sulphide. Immiscible droplets of sulphide would remain liquid up to a very late stage of crystallization and would therefore appear as interstitial material.

2. 2. 4 A Late Plutonic Phase

This phase is represented by the Bushveld granite which builds the central part of the intrusion and which is also found as very thick dykes in the mafic rocks in the Eastern Transvaal (Map I).

2. 3 The Structural Form of the Intrusion

A knowledge of the structural form of a mafic intrusion is very important in the search for Ni-Cu mineralization. This mineralization is present mostly at or near the base of such intrusions and an understanding of the contact-relationships with the floor is thus essential. From the mineralized intrusions found in Canada and Norway it appears that, apart from the formation of an immiscible sulphide liquid which could have settled into basin-like structures in the floor, remobilization of ores along faults or breccias some-

times played an equally or even more important role. In the case of sulphurization (as proposed by Kullerud and Yoder, 1963), discordant intrusive relations with sulphide-bearing strata have to be looked for.

The structural relationships of the Bushveld Complex have intrigued many geologists in the past. Earlier research workers considered the intrusion to be concordant and lopolithic in character. Recent work done on the Complex indicates a definite cross-cutting relation between·the igneous and the metasedimentary rocks. Wilson (1956, pp. 289-300) and Willemse (1959, p. lxxvii) have independently come to the conclusion that the Complex is more funnel-shaped than basin-shaped.

In comparison with other parts of the Complex, an abnormal quantity of disseminated sulphides is present in the rocks of the Basal Zone near the foot-wall contact of the Complex in the Western Transvaal. In addition to these disseminated sulphides, bodies of sulphide pegmatoid cut through the layered rocks. On the basis of the classical theory of Vogt, whereby a sulphide pool is formed as a result of liquid immiscibility at the base of a mafic-ultramafic massif, 5 bore-holes were put down in the Western Transvaal at localities where depressions in the floor of the Complex were expected. These depressions were determined gravimetrically.

Columnar sections of these bore-holes are given in fig. 1 (inserted at the back). It will be noted that bore-holes KAl, KA2, KA4, KA5, KA6 show some correlation. Metasediments are found at depths between 1000 and 2000 feet below surface. In bore-hole KA5, which was the deepest in the area west of the Pilanesberg, a feldspathic pyroxenite, 1500 feet thick, is present below a layer of metasediments, \pm 1000 feet thick. Immediately above the ! metasediments a norite layer, 500-750 feet thick, is present. Above this norite are feldspathic pyroxenite and pyroxenite with intercalated harzburgite.

No sulphide concentrations were found "on the floor of the Complex" i. e. immediately above the metasediments which are present at depths between 1000 and 2000 feet. The problem arises: what constitutes the floor of the Bushveld Complex. The norite above the metasediments contains quartz, zoned plagioclase and biotite and therefore resembles the Maruleng norite of the Eastern Transvaal. Inclusions of carbonate- and quartzitic rocks were also struck in bore-hole KA6; this points to a correspondence with the Hendriksplaats norite. The relationships in the field and in bore-holes, as

well as the macroscopic and microscopic properties of the norite immediately above the metasediments thus strongly point to the fact that this norite belongs to the Late Hypabyssal Phase. The norite is thus older than the overlying ultramafic rocks which belong to the Basal Zone of the Main Plutonic Phase. The floor of the Main Plutonic Phase is thus apparently formed by a layer of the Late Hypabyssal norite in the Western Bushveld Complex. Higher than usual concentrations of disseminated sulphide $(1/2)$ per cent) were accordingly found in bore-holes KA6 and KA5 in the feldspathic pyroxenite, which forms the base of the Basal Zone in these bore-holes. These concentrations were by no means of any economic importance.

The relations are, however, somewhat more complicated. Schwellnus (1935, pp. 94-97) described a bore-hole (the Vlakfontein 902 bore-hole) which was put down 1 mile south of the mining-area of Vlakfontein, where bore-hole KA5 was recently drilled (Map II). In the former bore-hole no sediments were encountered in contrast with the KA bore-holes, except three small inclusions of quartzite. Drilling was stopped at a depth of 3000 feet, in harzburgite. It is thus clear that the deepest depressions in the "floor" of the Bushveld were not explored by the recent bore-holes.

Unfortunately outcrops in the Western Transvaal are very poor, but with the aid of these incomplete field relationships, the bore-hole records and our knowledge of the contact-relationships with the floor in the Eastern Transvaal we can reconstruct the structural development of the Bushveld Complex.

The sequence of intrusion of the different phases of the Bushveld Complex and their effects on, together with some slight folding of the floor, are given in the diagrammatic sections through the Bushveld Complex west of the Pilanesberg (fig. 2). The sequence of events are visualized:

1. The normal sedimentary succession consisted of shale with intercalated quartzite.

2. Intrusions of (quartz) norite in the form of sills took place on certain horizons in the vicinity of the Magaliesberg quartzite, which was nearly horizontal at this time and not inclined as indicated in a simplified manner in fig. 2a. The sills cut across the strata from one horizon to the other, yielding discordant relationships typical of sills here and there. These sills belong to the Late Hypabyssal Phase.

3. Slight diastrophism could have taken place at this stage -

Fig. 2. Diagrammatic sections illustrating the development of the contact-relationship of the mafic and the ultramafic rocks with the floor of the Bushveld Complex in the Western Transvaal.

Fig. 2a. Intrusion of (quartz) norite in the form of sills

Fig. 2b. Intrusion of the Main Plutonic Phase

Fig. 2c. Folding of all the type of rocks

particularly folding.

4. Intrusion of magma, mainly feldspathic pyroxenite in composition and belonging to the Main Plutonic Phase now followed. This intrusion took place on several horizons as indicated by arrows in fig. 2a. Discordant relationships developed on a much more extensive scale than during the intrusion of the Late Hypabyssal Phase. Large as well as small blocks of metasediment together with portions of the sills of Late Hypabyssal norite were lifted up (fig. 2b). Contemporaneous and subsequent folding took place and the metasediments, the uplifted blocks of norite and the plutonic rocks were slightly folded (fig. 2c).

5. The effect of the younger faults of Pilanesberg age and of the Rustenburg fault are not indicated on fig. 2c.

The positions of the bore-holes are also indicated in the diagrammatic section (fig. 2c). The exact position of bore-hole V902 (which was described by Schwellnus, 1935) is not known, seeing that no metasediments were encountered in it and consequently no correlations with the findings in the more recent bore-holes could be made. The metasediments recorded at 2000 feet in bore-hole KA4 definitely belong to a stratigraphical horizon encountered in KA1 at 2638 feet and in KA5 at 4020 feet, \pm 400 feet below the Magaliesberg quartzite. This correlation was made with the aid of sulphidebearing sedimentary stratum which has a texture and a mineralogical composition similar to those encountered in KA4. The sulphur isotope ratios were also in agreement with the stratigraphic correlation.

At Burgersfort in the Eastern Transvaal, field relationships also clearly indicate a discordance of the Basal Zone relative to the metasediments and the consequent uplift of a thickness of 1000 feet of Late Hypabyssal norite (Hendriksplaats norite), with a quartzite layer adhering to the base of the norite.

One deep bore-hole (Gl) was drilled in a separate basin of the Basal Zone situated north of Zeerust in the far Western Transvaal. The bore-hole ended in hornfels. The problem is whether this hornfels belongs to a horizon above the quartzite; the latter has to dip at an angle of at least 30° towards the centre of the basin. The real dip at the surface, although variable, is of the order of 15° . This clearly indicates that the mafic-ultramafic rocks are in contact with sediments below the Magaliesberg quartzite in bore-hole Gl. The mafic rocks therefore cut across the Magaliesberg quartzite at depth.

3. STATISTICAL ANALYSES

Statistical analyses were carried out to determine the reliability of point-counting techniques on the ore-minerals which are disseminated in a host of silicate minerals or which are present as fairly massive ore.

A statistical study was made of the following factors which could influence the reliability of the results obtained by point-counting:

- 1. The error in measurement;
- 2. The effect of grain-size of the sulphide blebs;
- 3. The representativeness of polished surfaces of samples from a given locality.

The factors mentioned above are expressed in terms of the standard **^Arf r~,c; ..,_"'-f-cl':I** deviation which is given by the well-known formula:

$$
s^{2} = \frac{1}{N} \sum_{i=1}^{n} (x_{i} - \bar{x})^{2}
$$

where $S = Standard deviation$

 $N =$ Number of analyses on the same or different polished sections

 \bar{x} = Arithmetic mean of percentages of a particular mineral

 x_i = Percentage of mineral.

3. 1 The Error in Measurement

The method used to determine the error in measurement was to obtain 10 volumetrical analyses on the same polished surface. This error was determined for a total of 500 as well as 1000 points counted.

It was found that the experimental values correspond closely with the theoretical results of Van den Plas and Tobi (1965, pp. 87). The experimental values satisfy the equation

quite well. This is clearly illustrated in fig. 3.

A comparison of the experimental and the theoretical values of 25 given in table 2 shows that the experimental value for the silicate mineral is much higher than the theoretical value, whereas the experimental and theoretical values of the sulphide minerals show a better agreement. The reason for this deviation is that a part of the polished section was point-counted and that the

- Fig. 3. Graph for determining the error in measurement (solid line) of point-counting results in terms of 2 X standard deviation (2S) which is plotted against the percentage of a mineral (p) for a total of 500 and 1000 points counted. The relative error in measurement $\left(\frac{2S}{p} \times 100\right)$ is also given (stippled line). The values for solid theoretical curves were calculated from the equation $s^2 = \frac{p(100 - p)}{N}$, given by Van den Plas and Tobi (1965, p. 87) where $N =$ total points counted.
	- **Ci)** Experimental results using Swift automatic point-counter

 $\ddot{\cdot}$ Experimental results using a Zeiss integrating eye-piece

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sulphides are distributed homogeneously in the polished section. The silicate, on the other hand, is heterogeneously scattered over the polished surface.

If the greater part of the polished surface is volumetrically analysed the experimental and theoretical values are comparable (table 3). It is thus necessary to determine whether only a part of, or the whole polished surface should be point-counted. This can be done macroscopically.

An attempt was also made to ascertain whether there is a difference in the point-counting values obtained with a Swift automatic point-counter or with an integrating eye-piece. The standard deviations of the results obtained with the integrating eye-piece (table 5) are somewhat higher than those which were obtained by using an automatic point-counter. This difference could be explained by the fact that the distance between the points in the integrating eye-piece was smaller than the average grain-size of the minerals, whereas the movement of the automatic point-counter was more or less equal to their mean grain-size.

3. 2 The Effect of the Grain-Size of the Sulphide Blebs

It was observed from the results, given in table 6 and fig. 4, that polished surfaces which contain predominantly large blebs of sulphide yield a relatively high percentage of pyrrhotite (78. 5%) and a low percentage of chalcopyrite (13. 5%), whereas those which carry mainly small grains of sulphide yield a relatively low percentage of pyrrhotite (51.2%) and high chalcopyrite (36. 4%). The amount of pentlandite remains fairly constant. This alternation in the percentage of the sulphide minerals could be attributed to the late crystallization of chalcopyrite compared with the other sulphides. Chalcopyrite is therefore much more intergrown (as small specks) with the silicate minerals than the pyrrhotite. Accordingly care should be taken in point-counting to analyse both fine and coarse granular ore.

From fig. 4 it appears that the histograms of chalcopyrite and pyrrhotite show a positive and a negative skewness respectively. The explanation for this phenemenon is that the sulphide minerals occur in a semizoned arrangement within a bleb whether the bleb be large or small. Chalcopyrite is predominant in the outer zone. If a polished section contains only a few blebs of sulphide and if only one or two of them are cut through the outer zone, a rather high value for chalcopyrite would be obtained. A percentage-histogram of a number of the polished surfaces of the type men-

Table 2. Point-counting results, in percentages, on a polished section (VI. 4), analysed 10 times for a total of 500 points, with a Swift automatic point-counter. Only a part of the polished surface was covered. The error in measurement is expressed in terms of the standard deviation (S).

Arithmetic

Table 3. Point-counting results, in percentages, on a polished section (VI. 4), analysed 10 times for a total of 500 points, with a Swift automatic point-counter. The whole polished surface was covered. The error in measurement is expressed in terms of the standard deviation (S).

Table 4. Point-counting results, in percentages of a polished section (VI.4), analysed 10 times for a total of 1000 points, with a Swift automatic point-counter. The whole polished surface was covered. The error in measurement is expressed in terms of the standard deviation (S).

Table 5. Point-counting results, in percentages, for a polished section (VI. 4), analysed 10 times for a total of 1000 points, with an integrating eye-piece. The whole polished surface was covered. The error in measurement is expressed in terms of the standard deviation (S).

Table 6. Point-counting results, in percentages, of disseminated sulphide in three grain-sizes, from samples 45, from a locality south-east of Groblersdal.

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Fig. 4. The effect of grain-size on the volumetric quantities of pentlandite, chalcopyrite and pyrrhotite. Distribution diagrams on the left indicate the three grain-sizes of the disseminated sulphide.

Table 7. *of total salphide*
Point-counting results (in percentages) obtained on polished sections of the mineralized anorthosite below the Main Magnetitite Seam, from three different localities. The reliability of a volumetric analysis of one polished surface from this mineralized zone is expressed in terms of the standard deviations (S) of the different minerals.

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- Table 8. Point-counting results, in percentages, obtain on polished sections of the Merensky Reef from five different localities. The reliability of a volumetric analysis of one polished surface from the Merensky Reef is expressed in terms of the standard deviations (S) of the different minerals .

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Table 9. Point-counting results (in percentages) obtained on polished sections of coarse- and fine-grained poikilitic ore from the Rock Shaft, Vlakfontein Nickel Mine. The reliability of a volumetric analysis of one polished surface of a certain ore type is expressed in terms of the standard deviations of the different minerals. The silicate mineral is determined separately and is given as a percentage of the ore.

Fig. 5. Graph for determining the representativeness of a volumetric analysis of one polished surface of a sample from a particular locality. Experimental 2 X standard deviation values (2S) are plotted against the percentage of a mineral (p).

> **form** Mineralized anorthosite below Main Magnetitite Seam \times Merensky Reef Curve A X Merensky Reef

Curve B \bullet Ore-body, Rock Shaft, Vlakfontein Nickel Mine

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tioned above would then yield a positive skewness. Accordingly, a histogram for pyrrhotite would indicate a negative skewness.

3. 3 The Representativeness of Polished Surfaces of Samples from a Particular Locality.

In order to investigate the representativeness of a polished section of a particular locality and also, of a specific stratigraphical horizon, the mineralized anorthosite below the Main Magnetitite Seam was studied. For this purpose 25 polished sections were made of a core obtained from a borehole drilled just north of Pretoria and of samples collected from localities 5 miles north of Roossenekal and 2 miles south of Magnet Heights. The volumetric percentages of the sulphides in the 25 polished sections are given in table 7. On comparing these percentages it is found that cubanite is developed in only the core-samples from north of Pretoria. Pyrite occurs sporadically at all the localities.

It is clear from the histograms that there are no major differences in the percentages of pyrrhotite, pentlandite and chalcopyrite from the three localities.

If the standard deviations of the core-samples from north of Pretoria are compared with those of all the 25 polished sections (table 7) it will be noted that the standard deviations of the samples mentioned first are greater than those mentioned last. A polished surface of any sample of the mineralized anorthosite is thus representative, within the limits of the standard deviations of the different minerals which were obtained from the core-samples north of Pretoria.

Seeing that the standard deviations for the sulphide-bearing anorthosite were high, the Merensky Reef was investigated with the same object in mind in order to determine whether the anorthosite is not an abnormal case. The results given in table 8 were, however, in quite good agreement.

An ore-body on the Vlakfontein Nickel Mine was also statistically analysed with respect to the representativeness of a polished section of samples from a locality. The standard deviation values (table 9) were found to be almost half of those obtained on the Merensky Reef and on the mineralized anorthosite. An explanation for this phenemenon is that in the two mineralized zones mentioned last the sulphide constitutes a major part of the interstitial material of the rock. The segregation of different sulphides into monomineralic interstitial patches, several centimeters in diameter,

was possible in the liquid state of the interstitial sulphide. In the poikilitic ore from Vlakfontein this effect was not observed.

Fig. 5 was used to determine the standard deviation of the volumetric percentages of samples investigated. In all investigations curve B was used; in circumstances where there was the possibility that curve A would be more applicable more than one polished section was made.

4. THE DESCRIPTION OF THE ORE-MINERALS AND THEIR• TEXTURES

4.1 The Sulphides in General

The sulphides in the layered mafic rocks represent a minor mineral constituent; they seldom exceed two per cent by weight . The relatively high values have been found in specimens from the following localities: (1) Some Late Hypabyssal norite and quartz norite in the Eastern and the Western Transvaal. (2) The ultramafic and the mafic rocks of the Basal Zone in the Western Transvaal, south of Potgietersrus and in the Burgersfort vicinity. (3) Some of the ultramafic and mafic pegmatoids in the Basal, the Critical and the lower part of the Main Zone. In the Western Transvaal these pegmatoids in the Basal Zone contain massive or fairly massive sulphide. (4) The Merensky Reef. (5) The anorthosite below the Main Magnetitite Seam. (6) The anorthosite immediately below the Uppermost Magnetitite Seam.

In the rocks that do not contain an abnormal quantity of sulphide, the sulphide percentage is about 0. 1 per cent, for the ultramafic rocks and 0. 05 per cent for the mafic rocks. This was deduced from sulphur analyses of the whole succession of Bushveld rocks. A norite layer in ultramafic rocks contains less sulphide than the neighbouring rock. Where a pyroxenite is intercalated with norite or gabbro (an example of this is on Fernkloof 539 KS, Lydenburg District), the former contains more sulphide than the norite or gabbro. Pegmatoid material, where sulphide-bearing, would be comparatively rich in sulphides.

The particle size of the sulphides is very variable - even in the same rock. Rocks with a high sulphide content (+ 2 per cent) have a great range of particle sizes. A histogram of the particle sizes of the sulphides in the ordinary Bushveld rocks (fig. 6) shows that the modus grain-size is between 0. 01 and 0. 025 mm.

Fig. 6. Histogram of the grain-size of the sulphides in the rocks of the Bushveld complex that do not contain an abnormal quantity of sulphide

The textural relation between the sulphides and the silicates is very complicated. In the hand-specimen four different textural relationships between sulphide and silicate have been observed in the rocks:

- 1. Roundish or semi-roundish blebs with irregular as well as smooth round edges. These globules are known from the Late Hypabyssal norites and from some feldspathic pyroxenites of the Basal Zone in the Western Transvaal and from the base and the top of the peridotite body on Aapiesdoorndraai 298 KT, Lydenburg District.
- 2. The most common type, found throughout the whole succession of the Bushveld Complex, is in the form of irregular interstitial patches, concave towards the early ferromagnesian silicates.
- 3. Angular patches, with some characteristic straight edges, which form the interstitial material between feldspar laths. This type is known from the mineralized anorthosites below the Main and Uppermost Magnetitite seams. The difference between the last two types is brought about by the silicate mineral which predominates.

4. Euhedral or subhedral grains of pyroxene or olivine are present in massive or fairly massive ore from the Vlakfontein Nickel Deposits. It appears that the first type (above) is found in plutonic rocks bordering on metasediments; in other words, those parts of the intrusion that crystallized relatively rapidly and thus captured the sulphide blebs.

Under the microscope the difference in the textural relation between the sulphides and the silicates is no longer obvious. All the sulphides are interstitial to the silicates and the contacts are noticeably irregular. Only in the harzburgite from Aapiesdoorndraai are some of the globules round, although the edges of the globule are still irregular particularly where there are late silicate minerals, e.g. chlorite. Examples of intergrowths of sulphide and, possibly chlorite, are known inter alia from the Merensky Reef south-east of Groblersdal.

Where the sulphide specks in any of the rocks mentioned are very small, (0.05 mm) they are mostly well rounded. This can be ascribed to the fact that they are too small to be really affected by the growing crystals of silicate minerals and therefore remain as round specks, still interstitial to the silicates.

Small crack-fillings and veins of sulphide in the silicates were ohserved in rocks with a relatively high sulphide content $(+ 0.5$ per cent), e.g. in the Merensky Reef.

Olivine and pyroxene often show convex boundaries towards the sulphides which are still interstitial. Van Zyl (1960) attributes this feature to replacement of the silicate by the sulphide. Other textures similar to a peg-texture, as between melilite and magnetite, are found where the sulphide has corroded the orthopyroxene. In the sulphide-bearing anorthosite just below the Main Magnetitite Seam, where the sulphides are interstitial to plagioclase laths, small specks of sulphides are found in the feldspar next to a sulphide patch. The plagioclase is altered to secondary minerals, for example sausurite and hydrogrossularite, in the vicinity of the sulphides. Replacement of lamellae of orthopyroxene in clinopyroxene by sulphide has been observed in this anorthosite. Magnetite has been replaced in some specimens by chlorite and simultaneously or subsequently by sulphides. It is interesting that lamellae of ilmenite in the replaced magnetite have not been q ffected at all (photos 103, 104).

4.2 Pyrrhotite

In general pyrrhotite is the principal sulphide in the ores of the Bushveld Complex, although in some localities this mineral may be subordinate to pentlandite, e.g. on Aapiesdoorndraai 298 KT, Lydenburg District, or to pyrite, e.g. in the mineralized pegmatoid above the Main Chromitite, Winterveld Chrome Mine. It is present as disseminations in the mafic and the ultramafic rocks or as massive sulphide in the Vlakfontein deposit. In the disseminated ore the pyrrhotite forms the core of a sulphide bleb, with pentlandite and/or chalcopyrite forming the mantle in a semi-zoned arrangement.

Pyrrhotite is seldom found on its own but is always in association with pentlandite, pyrite, chalcopyrite and/or cubanite.

Pyrrhotite takes a good polish except in some ore from the Vlakfontein deposit, in which the pyrrhotite is intensively deformed (photos 1, 2, 3) and the bent crystals show a pronounced cleavage. Deformed grains, are, in fact, encountered over the entire stratigraphical succession of the Bushveld Complex. Not necessarily the whole pyrrhotite grain, but only a part may be deformed. The deformed pyrrhotite is easily observed under crossed nicols and shows an undulatory extinction. The more deformed material is usually translated parallel to (0001). Translations cutting the basal cleavage have also been encountered in specimens from Vlakfontein. These translations are difficult to distinguish from irregular polysynthetic twins of pyrrhotite, which are also the result of stress. These twins do not show an undulatory extinction. On the other hand twinning and undulose extinction have been observed together. The more regular type of twinning (photo 34, 35) is fairly common in all the pyrrhotite of the Bushveld. The twinning direction could not be determined but, according to Hawley (1962, p. 44), it is parallel to (1012). The present writer does not attribute the regular twinning to deformation.

4.2.1 The three Modifications of Pyrrhotite

Wagner (1924) published three analyses from the pyrrhotite from Vlakfontein. He did not clean the pyrrhotite of contaminating pentlandite and chalcopyrite, but allocated all the Ni and Cu in the analyses to these two minerals respectively. He concluded that the formula of pyrrhotite ranges between $Fe_{13}S_{14}$ and $Fe_{16}S_{17}$ - not a very reliable deduction as it is now known that some Ni and Cu can be accommodated in the pyrrhotite structure.

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An accurate X-ray method was followed to determine the composition and the different phases of pyrrhotite in the Bushveld Complex, viz. the method described by Arnold (1958) and by Arnold*i*Reichen (1962). Hägg and Sucksdorff (1933, p. 448) have shown that the decrease in the ratio of Fe to S is due to the omission of iron from random structural positions, with concomitant reduction in the unit cell dimensions. Arnold (1958) published the curve which relates the strongest X-ray reflection, $d(102)$, to the composition of pyrrhotite. The curve used in this study is given in fig. 7. Arnold's values have been revised by Toulmin and Barton (1964, p. 664). By using the latter $d(102)$ -values and by expressing the mol. fraction of FeS in terms of atomic per⁻centages of metals, the values were resmoothed on a computer using the method of the least square fit. The values are given in table 10. This was necessary because the values of Toulmin and Barton were not sufficiently smoothed for the scale used in fig. 7.

Hexagonal pyrrhotite (2A, 5C type of structure) and troilite **(3A,** 2C type of structure) give sharp peaks whereas monoclinic pyrrhotite (2B, 4C type of structure) gives a double peak - (202) and (202). The composition of hexagonal pyrrhotite and troilite could easily be determined from fig. 7. As far as the monoclinic pyrrhotite is concerned, Desborough and Carpenter (1965, p. 1442) found that the d-value between the two peaks of monoclinic pyrrhotite does not differ from the d-value of the one peak obtained on heated monoclinic pyrrhotite (2A, 7C type of structure).

In this study the writer used a Guinier camera in the 0^{O} position, in which it has a very good resolution. Normally in diffractometric analyses (scan and chart speed $\frac{1}{2}^{\circ}$ per minute and one inch per degree 20 respectively) the one peak of monoclinic pyrrhotite coincides with the single peak of hexagonal pyrrhotite, if the two modifications are present together. If the compositions of the hexagonal and the monoclinic pyrrhotite differ slightly, the double peak of the latter, and also the single peak of hexagonal pyrrhotite, could be identified on a Guinier film. This is not the case with diffractograms. It was found that the arithmetic mean of 7 measurements of the difference in the double peaks values is 0.005 \hat{R} . The value used to determine the composition of the monoclinic pyrrhotite was obtained by using the centre of the (202) and $(\bar{2}02)$ lines if both were visible. If the (202) line of monoclinic pyrrhotite and the (102) line of hexagonai pyrrhotite coincided and only (202) and (102) of the two pyrrhotites were visible, 0.005 $\frac{\cancel{0}}{\cancel{0}}$ was added to d(202) of the monoclinic

Table 10. The corrected d(102)-values and the corresponding compositions (in atom per cent metals) of pyrrhotite recorded by Toulmin and Barton (1954, p. 664). The estimated d(102)values are also given.

Fig. 7. The d(102)-value plotted against the composition of pyrrhotite. The composition **of** the Bushveld pyrrhotites and others are given in the form of histograms

pyrrhotite. This procedure was followed to determine the composition of monoclinic pyrrhotite.

The X-ray analyses were carried out under the following conditions: a respresentative rock sample was crushed to a grain size depending on the particle size of the disseminated sulphide. From this pulverized material the sulphides were concentrated by repeated flotation. In coarse disseminated sulphide the pyrrhotite was drilled out with a dentist's drill. In the case of the massive sulphides and the poikilitic ore from Vlakfontein, chipsamples were taken at random from a bulk sample. The samples were $+80\%$ pure pyrrhotite. Silicon was used as an internal standard and three photos were taken of each pyrrhotite sample. It was found that the error in measurement was 0.0005 \AA for the d(102)-value. By analogy with the work done by Toulmin and Barton (1964, pp. 664-645) an error of $+$ 0.15 atom per cent metals in pyrrhotite could be accepted.

Histograms of the three different phases of pyrrhotite from the Bushveld are given in fig. 7. For purposes of comparison the histogram published by Arnold (1958, p. 221) of 61 analyses of pyrrhotite and the range of the composition of the three phases, according to Desborough and Carpenter (1965, p. 1433), are also given. It should be noted that the composition of the three pyrrhotite phases of the Bushveld occupies 3 fields separated from one another. This agrees with the work of Des borough and Carpenter (1965) and with that of Von Gehlen (1966). The fact that monoclinic and hexagonal pyrrhotite are not properly separated on Arnold's histogram could be attributed to the lack of sensitivity of their methods of determination.

The properties of the three modifications, which are compared below, were determined after the modifications had been identified by means of Xray analyses.

Reflectivity: Troilite hexagonal monoclinic. The difference is illustrated by the measurements of Ro by Desborough and Carpenter (1965,

p. 1445).

Hardness: Troilite > hexagonal *>* monoclinic Birefringence and anisotropism: Troilite > hexagonal > monoclinic Cleavage: Troilite < hexagonal < monoclinic Magnetic properties: Toilite < hexagonal < monoclinic Separation of pyrrhotite from a mixture containing silicates and also

other sulphides by means of magnetic methods resulted in an enrichment of the monoclinic variety at the expense of the hexagonal variety

Etching with chromic acid (50%): For $3/4$ hour - the monoclinic polymorph is stained, the hexagonal polymorph is slightly affected and troilite is not affected. Troilite oxidizes rapidly on exposure to the atmosphere and this results in a film which produces a lower reflectivity than other modifications of pyrrhotite. These two pyrrhotites could thus be identified easily in troilite and hexagonal pyrrhotite assemblages. Monoclinic pyrrhotite is much more difficult to distinguish from the hexagonal modification. This could however be done by slightly uncrossing the nicols (photos 4, 5, 6, 9, 10, 11) which causes the monoclinic pyrrhotite to show up lighter than the hexagonal variety.

Regarding the textural relationships between the different modifications, it should be noted that troilite and monoclinic pyrrhotite have not been found together, with the exception where monoclinic pyrrhotite originated as an oxidation product from the hexagonal variety (photos 4, 5, 6). Where troilite and hexagonal pyrrhotite are found together (photo 12), the texture resembles that of monoclinic and hexagonal pyrrhotite. The lamellar intergrowth of the two modifications of pyrrhotite is the same as that of the ∞ and β components described inter alia by Scholtz (1936, p. 152) and by Ramdohr (1960, p. 550). The lamellae of any modification of pyrrhotite within another variety are regular or irregular, lenslike bodies which form a network, parallel or semi-parallel to (0001) in some specimens but mostly parallel to a pyramidal plane (?) of the host-pyrrhotite. Phenomena illustrated by monoclinic pyrrhotite and not by troilite in a host of hexagonal pyrrhotite are:

Firstly, monoclinic pyrrhotite has a tendency to be present along cracks in and around crystal boundaries of hexagonal pyrrhotite (photos 9, 10, 11) and

secondly, in the case of the deformed Bushveld pyrrhotite, monoclinic pyrrhotite is developed as separate, rounded or elongated grains (e.g. in the ores from Vlakfontein).

Slight deformation-textures of pyrrhotite have no influence on the lamellae of monoclinic within hexagonal pyrrhotite. The lamellae cut through translation-planes displayed by the latter (photo 9).

4. 2. 2 Association of the Different Modifications of Pyrrhotite with other Sulphides

Troilite is not found together with monoclinic pyrrhotite and/or pyrite. Even where supergene conditions exist, pyrite does not form as an intermediate phase between troilite and the oxidized product (magnetite) in the Bushveld sulphides (samples 12, 19, 20). The following associations in the Bushveld ores have been identified:

- 1. If only troilite is present, the only copper sulphide which is stable in the assemblage is cubanite (sample 19 from Aapiesdoorndraai 298 KT, Lydenburg District). Pentlandite and mackinawite are also stable in this assemblage.
- 2. Troilite and hexagonal pyrrhotite are found together with cubanite and/or chalcopyrite and with pentlandite, with (sample 29 from Tweefontein 360 KT, Lydenburg District) or without (sample 103, from Zwartfontein LR, Potgietersrus District) mackinawite in the pentlandite.
- 3. Monoclinic and hexagonal pyrrhotite are also stable in the presence of chalcopyrite and/or cubanite, together with pentlandite and exsovled mackinawite, but not necessarily so. If cubanite and mackinawite (in pentlandite) are present, pyrite is incompatible with this assemblage.
- 4. Monoclinic and hexagonal pyrrhotite, together with chalcopyrite and pyrite, are very common in the rocks of the Bushveld Complex above the Merensky Reef and also in the oreminerals in the Late Hypabyssal norites in the Eastern as well as the Western Transvaal.

2. 3 Generations of Pyrrhotite

Three different generations of pyrrhotite could be recognised in the sulphide ores from the Bushveld Complex. These are:-

- 1. Coarse pyrrhotite
- 2. Round or lamellar bodies of pyrrhotite in chalcopyrite, cubanite, pentlandite and pyrite.
- 3. Pyrrhotite as replacements in silicates and in magnetite.

4. 2. 3. 1 Coarse Pyrrhotite. The coarse generation is the most common type of pyrrhotite, which also serves as a host for various types of intergrowths of pentlandite, chalcopyrite, cubanite and pyrite.

The particle size of the pyrrhotite is very variable and ranges from 0. 05 mm to several centimeters across. The crystals are always anhedral, although macroscopically, pyrrhotite occurring as coarse disseminations as well as in the massive ore from Vlakfontein **K** may display a pinacoidal habit. Under the microscope the boundaries between adjoining grains are al ways irregular. In places the grains are somewhat rounded and impart a granular texture to the specimen.

In the disseminated sulphide ore the pyrrhotite is restricted to the central parts of sulphide blebs, with pentlandite and chalcopyrite developed towards the margins of the bleb. The textural relationship between the pyrrhotite and any other sulphide is xenomorphic. Irregular contacts between pyrrhotite and the other sulphides are a common feature. Grain boundaries between pyrrhotite and pyrite, chalcopyrite, pentlandite, gersdorffite and platiniferous minerals, which are smooth and curved, were also frequently observed. The minerals mentioned last could have an euhedral shape when found in or next to pyrrhotite of the Merensky Reef (photos 36, 37, 83).

The only mineral which is replaced by pyrrhotite along cracks is pyrite (photos 58, 59). Corrosion of pyrite by pyrrhotite is frequently observed (photo 60).

4. 2. 3. 2. Round or Lamellar Bodies of Pyrrhotite in Chalcopyrite Cubanite, Pentlandite and Pyrite. Bodies of pyrrhotite in chalcopyrite, cubanite, pentlandite and pyrite, which represent products of exsolution, are found in small quantities not more than 0. 1 per cent of the host-sulphide. In some polished sections it is difficult to distinguish between pyrrhotite which is a replacement-remnant and pyrrhotite due to exsolution.

Lamellae of pyrrhotite have been observed only in chalcopyrite, parallel to (111) (photo 13). Their size varies considerably from 0. 01 mm to 0. 05 mm wide and 0. 03 mm to 0. 5 mm long. The larger lamellae are found in the

massive chalcopyrite from the Vlakfontein ore-deposits. Round particles of pyrrhotite, 0. 01 to 0. 05 mm in diameter, are also developed in chalcopyrite but rarely in cubanite, in which they were observed only in one polished section.

Pentlandite and pyrite seldom contain pyrrhotite as products of exsolution. In the case of pentlandite, tetragonal FeS (mackinawite) is present on horizons below the Merensky Reef. Round bodies of pyrrhotite were observed in pentlandite in only a few specimens from above the Merensky Reef. The only pyrrhotite within pyrite is known from the Merensky Reef and from the quartz norite in the vicinity of Burgersfort where round grains of pyrrhotite are scattered throughout the pyrite (photo 58). This represents replacement of pyrite by pyrrhotite rather than the exsolution of the latter.

Near the grain boundaries between pyrrhotite and chalcopyrite and between pyrrhotite and cubanite, and to a much lesser degree between pyrrhotite and pentlandite, round or angular inclusions of pyrrhotite are found, which have the same optic orientation as the surrounding pyrrhotite. This points to a re· placement of pyrrhotite by the minerals mentioned.

4. 2. 3. 3 Pyrrhotite as replacements in Silicates and in Magnetite. In the vicinity of the magnetite gabbro and the mineralized anorthosite below the Main Magnetitite Seam, replacements of silicates and magnetite by pyrrhotite are a general feature. Firstly the magnetite is replaced in part or completely, by silicates (chlorite). The remaining magnetite is then in part or entirely, oxidized to hematite. Thereafter pyrrhotite replaces some of the silicates and the magnetite and/or hematite. It is interesting to note that ilmenite, present as separate grains and as lamellae parallel to (111) of magnetite, remains unaffected and represents a relictstructure (photos 103, 104). According to Hawley (1962, p. 66) magnetite in the Sudbury ores is also more readily replaced by sulphide than ilmenite. Pyrrhotite which forms in this way has a colloid-structure and is very porous. The whole mass of pyrrhotite has the same optical orientation. Chalcopyrite could to a lesser degree also take $p_{\text{face}}^{\text{per}}$ in the replacement. These replacements are definitely later than the crystallization of the coarse pentlandite.

Another interesting replacement-texture was observed in specimens from the Vlakfontein Nickel Deposit, in which euhedral crystals of olivine are replaced by colloidal pyrrhotite along cracks and margins of the grains. This will be discussed in detail in the section dealing with the Vlakfontein deposit $ln \left(110 \right)$

4. 2. 4 Exsolution in, Replacements of and Secondary Alterations of Pyrrhotite

The most common product of exsolution in pyrrhotite is pentlandite, generally parallel to the basal plane of the former. Chalcopyrite is present as euhedral, round (photo 47) or irregular particles in grains of pyrrhotite, whereas cubanite is usually found between the grains of pyrrhotite. Replacement of pyrrhotite, along cracks and crystal boundaries, by the two Cubearing minerals is a common phenomenon (photos 15 and 124 and samples Vl. 5 and 12).

All the textures which are the result of exsolution in and replacement of pyrrhotite will be discussed in detail in the section dealing with the minerals participating in those processes.

Secondary alteration of pyrrhotite takes place in three stages under the influence of surface agencies (ground-water).

- 1. Troilite alteres to hexagonal pyrrhotite. This takes place along crystal boundaries, basal cleavages and cracks.
- 2. Pyrite and/or melnikowite-pyrite foloms along cracks and basal cleavages which provided access for oxidizing agents (photo 14). It was observed in one polished section (12) that mackinawite formed as an intermediate phase; no pyrite is visible in this section (photo 6).
- 3. Magnetite (photo 73) or ilvaite (photo 97) replaces the melnikowite-pyrite, which then assumes a grey colour. Where extensive secondary alteration has taken place, magnetite replaces the monoclinic pyrrhotite directly, the melnikowite-pyrite stage being eliminated. No pyrite forms as an intermediate phase when troilite is subjected to supergene alterations (photo 73).

4. 2. 5 A Comparison with Pyrrhotite from other Mafic Intrusions

As far as the three modifications or pyrrhotite (troilite, monoclinic and hexagonal pyrrhotite) from other intrusions are concerned, these have not been investigated in sufficient detail to justify a comparison with the pyrrhotite from the Bushveld Complex. From the descriptions by Scholtz (1936) of pyrrhotite from Insizwa the **same textural** relationships exist between the two modifications, which are probably monoclinic and hexagonal pyrrhotite. Troilite has not been recorded although it is very difficult to distinguish an

intergrowth between troilite and hexagonal pyrrhotite, and an intergrowth of monoclinic and hexagonal pyrrhotite. From Sudbury both monoclinic and hexagonal pyrrhotite have been described by Hawley $(1962, p. 45)$. Intergrowths of the different modifications have not been reported from the Petolahti diabase and the Igdlukunguaq intrusion.

The coarse pyrrhotite from the Bushveld is in fair agreement with pyrrhotite reported from other deposits. Hawley (1962, p. 45) described lamellar pyrrhotite in chalcopyrite and cubanite and also round grains of pyrrhotite in pentlandite $(p. 58)$ from the Sudbury intrusion. Ervamaa (1962, p. 51) reported 5-15 per cent exsolved pyrrhotite in pentlandite. Scholtz (1936) does not describe any pyrrhotite exsolutions in the sulphides from Insizwa.

4. 3 Pentlandite

The main Ni-bearing ore-mineral in the Bushveld Complex is pentlandite. Its mode of occurrence and its association with the other sulphide minerals, pyrrhotite, chalcopyrite and mackinawite is remakably similar to that found in ores from Insizwa (Scholtz, 1936) and to a lesser degree to those from ores from Sudbury (Hawley, 1962) Petolahti (Ervamaa, 1967) and Igdlukunguaq (Pauly, 1958).

Pentlandite always polishes readily. Pits which originate as a result of the octahedral cleavage serve as a distinguishing feature. Some polished pentlandite (sample 103, from Zwartfontein 818 LR, Potgietersrus District) shows the same pitted surface as pyrite which is badly polished. Under these circumstances the pentlandite was distinguished from pyrite by means of X-rays.

Fresh pentlandite varies from pale cream to distinctly cream in colour. The pentlandite which has undergone alteration by supergene agencies may have a brownish tint, especially specimens containing exsolved mackinawite, the latter being then completely altered. X-ray investigation of this type of pentlandite gave lines for pentlandite only. Scholtz (1936, p. 158) attributes the variation in colour of pentlandite to a difference in Fe content.

4. 3.1 Mode of Occurrence

A twofold classification based on the various modes of occurrence of pentlandite in the sulphide ores of the Bushveld is suggested. The two modes of occurrence are:

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- 1. Relatively coarse pentlandite.
- 2. Fine pentlandite within pyrrhotite, chalcopyrite and cubanite.

4. 3.1.1 Relatively Coarse Pentlandite. Coarse pentlandite is seldom found enclosed , in crystals of pyrrhotite. In the ore blebs, interstitial to the silicate minerals the coarse pentlandite is mostly restricted to the rims of the sulphide bleb, with or without chalcopyrite occurring as an outer zone. In the poikilitic ore from Vlakfontein where euhedral orthopyroxene and less frequently olivine are disseminated in a ground-mass. of sulphide (photos 112, 113, 114), pentlandite is also found adjoining the silicate crystals, mostly with chalcopyrite or cubanite. In the massive ore from Vlakfontein single grains of pentlandite (1 mm in diameter) are scattered through a ground-mass, mostly of pyrrhotite which exhibits a poikilitic texture (sample VI. 202). Pentlandite is also found as aggregates of crystals and patches, several centimeters in diameter, within the massive ore (sample VI. 78).

In all the massive ores pentlandite has a somewhat rounded, though euhedral appearance and is interstitial to pyrrhotite. Generally speaking, pentlandite is present as rounded or angular masses in the Bushveld ores. Less frequently pentlandite is idiomorphic towards pyrrhotite (photo 36), chalcopyrite and cubanite.

Coarse pentlandite is occasionally enclosed by pyrrhotite. The most common pentlandite of this nature forms veins of blocky crystals cutting across the basal cleavage of pyrrhotite (photo 36). These veins always follow former cracks in pyrrhotite which is sometimes completely filled with pentlandite and, but not necessarily, chalcopyrite or cubanite. These cracks acted like the crystal boundaries of pyrrhotite, as venues along which pentlandite could seggregate. The origin of the textures of the sulphides are discussed later on $(p. \quad 89)$. Roundish grains of pentlandite \pm 0.3 mm in diameter are found in grains of pyrrhotite $(V1, 10, V1, 131, V1, 187)$. Some of the bodies show a scalloped edge instead of a sharp, smooth boundary. It is very difficult to decide whether this type of pentlandite belongs to the fine or the coarse type.

Coarse pentlandite contains sporadic inclusions of angular or rounded pyrrhotite. These inclusions are located near the contact between pentlandite and pyrrhotite and in some specimens have the same optic orientation as the surrounding pyrrhotite. This clearly indicates a replacement of pyrrhotite by pentlandite.

4. 3. 1. 2 Fine-grained Pentlandite within Pyrrhotite. Fine-grained pentlandite is generally found as lamellae parallel to the basal cleavage of pyrrhotite. The quantity of these lamellae within pyrrhotite varies considerably but does not exceed 5 per cent of the amount of pyrrhotite. However, in this study on the sulphide pipes in the Western Transvaal, C. M. Schwellnus (1936) . photographed pyrrhotite with much more pentlandite. In a few specimens it is practically absent, for instance in the pyrrhotite of the Merensky Reef on Tweefontein 360 KT, Lydenburg District, Dwarsriver area (sample 29).

Fine-grained pentlandite in pyrrhotite clearly represents a product of exsolution. The following classification is applicable to the different types of exsolution bodies in pyrrhotite.

- 1. Small, globular or irregular bodies (photos 24, 25).
- 2. Small, regular lamellae parallel to (0001) of pyrrhotite (photos 19, 21, 26).
- 3. Feathery or brush-like lamellae (photos 19, 20, 21, 22, 23, 25, 27, 28, 30) parallel or subparallel to (0001) of pyrrhotite.
- 4. Lamellae parallel to the pyramidal crystallographic directions of pyrrhotite (photos 19, 20).
- 5. Irregular veinlets in pyrrhotite.

4. 3.1. 2.1 Small globular or irregular bodies. Small round bodies 0. 005 mm in diameter, is present anywhere within pyrrhotite crystals. These globular bodies grade into bigger, irregular bodies, 0. 05 mm in diameter, which are restricted to the central parts of pyrrhotite crystals (Vl. 78). They sometimes form an intergrowth with pyrrhotite.

4. 3.1. 2. 2 Small regular lamellae parallel to (0001) of pyrrhotite. Quite small, regular lamellae parallel to (0001) of pyrrhotite, vary in width from 0. 001-0. 01 mm, with a length of approximately 0. 03 mm, although somewhat longer lamallae have also been observed (photos 19, 21). They are not restricted to cracks in, or crystal boundaries of pyrrhotite, but are also found in the central part of crystals of pyrrhotite. The globular and irregular bodies, mentioned under 1 and this regular type of lamellae are developed in pyrrhotite where the feathery or brush-like lamellae are not so frequently observed, e.g. in the Vlakfontein Nickel Deposits.

4.3.1.2.3 Feathery or brush-like lamellae parallel or subparallel to (0001) of pyrrhotite. These occur as single minute flames or aggregates of flames and consist of fine, almost subparallel flames intimately intergrown with pyrrhotite, which also has a feathery appearance. The form of this feathery intergrowth varies considerably. In the centre of a pyrrhotite crystal, where they are not frequently developed, these aggregates of flames are small in dimensions - 0. 001 mm wide and 0. 2 mm long. In occurrences of this type they do not form large aggregates. This feather-like pentlandite may flare out from boundaries of pyrrhotite crystals, from the contact of pyrrhotite with other minerals (photos 31, 33) or from cracks (photo 28). It is often found in pyrrhotite along the contact with large pentlandite crystals (photo 32) and it may be difficult to determine the contact between the two generations of pentlandite. Near the crystal boundaries of pyrrhotite they are often large (0. 05 to 0.1 mm in diameter) and abundantly developed.

When twinning is present in pyrrhotite, feathery pentlandite flares out from the twinning plane (photos 34, 35) into both individuals to form a herring-bone texture. The same phenomenon has been described by Hawley (1962, p. 57) from Sudbury. In some specimens it is clear that the pentlandite formed after twinning had taken place, e.g. in the massive sulphide from the potholes in the Merensky Reef, whereas in other occurrences, e.g. the Vlakfontein ore-bodies, twinning has taken place after the development of the pentlandite. Stress-effects, especially in pyrrhotite, are noticeable in the latter occurrence.

The feathery intergrowth of pentlandite and pyrrhotite is roundish with the appearance of a rosette 0.2 mm in diameter (photos $29, 30$), if the polished section is cut parallel to (0001) of pyrrhotite. Another feature of these rosettes is that the blades tend to have a radiating appearance.

The rounded or irregular bodies, the regular lamellae and the feathery type of aggregates, show all gradations into one another. The form of the pentlandite within the pyrrhotite depends also along which crystallographic direction the pyrrhotite is cut.

4.3.1.2.4 Lamellae parallel to the pyramidal crystallographic directions of pyrrhotite. Irregular lamellae of pentlandite $(0.01 \text{ mm in width})$ parallel to $(10\overline{1}1)$ of troilite were observed in one specimen and should be considered as a rare phenomenon in the Bushveld Com-

plex, e.g. sample 19, from Aapiesdoorndraai 298 KT, Lydenburg District. Massive troilite from other localities or mixtures of troilite and hexagonal pyrrhotite or hexagonal and monoclinic pyrrhotite do not contain this type of lamellae.

4. 3. 1. 2. 5 Irregular veinlets in pyrrhotite. These irregular veinlets (0. 005 mm in width) are seldom found in pyrrhotite crystals of the Bushveld Complex and were seen only in troilite from Aapiesdoorndraai 2 98 KT, Lydenburg District.

Wide irregular veinlets (0. 1 mm thick) are more plentiful in all the modifications of pyrrhotite (photo 36). They are mostly in the vicinity of cracks and probably represent coarse-grained pentlandite which does not belong to the same generation as the fine-grained pentlandite within crystals of pyrrhotite.

$4, 3, 1, 3$ Fine-grained Pentlandite within Chalco-

pyrite and Cubanite. Pentlandite is uncommon within grains of chalcopyrite and of cubanite. The percentage of pentlandite in chalcopyrite or cubanite does not exceed 2 per cent of the Cu-bearing mineral. Mostly, however, it amounts to a tenth of a per cent.

Two types of pentlandite in chalcopyrite or cubanite could be distinguished, viz.:

- 1. There are small round or irregular grains, feathery in some places, (0. 01 mm in diameter) in chalcopyrite (Gl-4802. 2) or cubanite (V1.69). Near the boundary between a Cu sulphide and coarse pentlandite, small grains of pentlandite are often noticed. In specimens from, inter alia, Vlakfontein fairly large grains (0. 08 mm in diameter) of pentlandite together with mackinawite are distributed through cubanite in particular. This clearly indicates a replacement of the pentlandite by the cubanite. In contrast with the latter, some large grains (0. 1 mm in diameter) do not contain mackinawite and are found within cubanite. These grains are not necessarily replacement-relicts of pentlandite in cubanite.
- 2. Lamellae of pentlandite, with or without a feathery habit, are found parallel to (111) of chalcopyrite (photo 38). The feathery type varies in size. Generally the feathery lamellae are 0. 02 mm in width and 0.2 mm long, whereas the regular lamellae are $+0.005$

mm in width. The lamellae are in fine intergrowth with chalcopyrite, giving a feathery appearance to the lamellae.

Fine-grained lamellae or lenticular bodies (0. 001 mm thick) are common in the cubanite from Vlakfontein (photo 44). Coarse-grained lamellae of pentlandite, with (photo 42) or without (photo 37) mackinawite, in cubanite indicate a replacement of the pentlandite by cubanite.

It has been mentioned that fine-grained pentlandite due to exsolution, often protrude from the boundary between chalcopyrite and pyrrhotite into the latter. If no cracks are present between chalcopyrite and pyrrhotite, these exsolution bodies of pentlandite also protrude into chalcopyrite but to a lesser degree than into pyrrhotite (photo 33).

In contact with chalcopyrite coarse pentlandite may show a fine intergrowth with each other (photo 49). This could also be a replacement texture .. Hawley (1962, 0. 57) observed the same texture in the Sudbury ores.

4.3.2 Exsolution Bodies of other Sulphides in Pentlandite

Exsolution of other sulphides is present only in the coarse pentlandite. The fine-grained pentlandite in grains of other minerals (pyrrhotite, chalcopyrite and cubanite), which could be considered as exsolution products, do not contain exsolutions of any mineraL

Exsolution phases of mackinawite, chalcopyrite and pyrrhotite is present in pentlandite. These exsolutions are fully discussed under the sections dealing with the minerals (pp. 51, 46 and 35)

4.3.3 Replacement of Pentlandite by other Sulphides

Pentlandite is replaced by bravoite (photo 39, 40), chalcopyrite, cubanite and mackinawite. There is an uncertainty whether mackinawite replaces or has exsolved from pentlandite obtained from the Mooihoek pipe. The replacement-textures will be dealt with under the minerals involved in the replacement.

4. 3. 4 A Comparison of Pentlandite from the Bushveld Complex with Pentlandite from other Intrusions

The pentlandite found in the Bushveld Complex and its textural relationships with other minerals is very much the same as that from Insizwa (Scholtz, 1936) and Sudbury (Hawley, 1962). In the Petolahti diabase (Ervamaa,

1962) up to 40 per cent of pentlandite flames occur in pyrrhotite and along the boundary of the latter with grains of coarse pentlandite. Flames are often so abundant that it is difficult to determine the contact between the flames and the coarse pentlandite. From description of the pentlandite from the Igdlukunguaq intrusion (Pauly, 1958), flames are even more abundant in the rocks from that locality.

As far as the pentlandite flames in chalcopyrite and cubanite are concerned, it would appear that the amount of pentlandite within only the Cu-bearing minerals of the Bushveld, Insizwa and Sudbury intrusions is somewhat less than the amount in the Petolahti and Igdlukunguaq intrusions.

4.4 Chalcopyrite

4.4.1 General

Chalcopyrite is the most abundant **Cu** ore-mineral in the Bushveld Complex. It is found in varying quantities throughout the entire succession of mafic rocks. When present in association with troilite, cubanite is always associated with it, whereas when pyrite is present cubanite is absent. The assemblage - chalcopyrite, cubanite, monoclinic and/ or hexagonal pyrrhotite - is very common.

Chalcopyrite is always present as granular aggregates, the grain size of which varies from 0. 01 to several milimeters across, with a modus grain size of about 0. 1 mm. The grains have roundish shapes with irregular boundaries. A feature easily overlooked is the twinning of the chalcopyrite, which is only visible when the nicols are slightly uncrossed, or when the polished surface is etched with $H N_g^2 + K C 10_g$, or with chromic acid. Polysynthetic twinning parallel to the cubanite lamellae in chalcopyrite i.e. parallel to (111) is very common (photo 51). The twinning lamellae are very regular and straight and vary in thickness from 0. 01-0. 05 mm in different grains. Another type, often observed, is wedge-shaped twinning lamellae cutting one another, probably parallel to (110) (photo 50). They are very irregular and it is difficult to decide according to which crystallographic direction the twinning has taken place. From the work done by Buerger and Buerger (1934), Ramdohr (1960' , p. 492) concluded that three types of twinning in chalcopyrite may be distinguished: (i) grid twinning on (110), (ii) fine polysynthetic twinning on (101) and (iii) polysynthetic twinning on (111). Twinning of chalcopyrite is frequently developed in the ores where

the pyrrhotite exhibits deformation-textures. The twinning of chalcopyrite thus possibly took place under the influence of deformation (photo 50).

4.4.2 Types of Chalcopyrite

Three types of chalcopyrite could be distinguished:

- 1. Coarse chalcopyrite
- 2. Exsolution bodies of chalcopyrite in cubanite, pyrrhotite and pentlandite.
- 3. Veinlets of chalcopyrite.

4.4.2.1 Coarse Chalcopyrite. Whenever present in the disseminated ore of the Merensky Reef, chalcopyrite is restricted to the rim of a sulphide bleb. The chalcopyrite is then also much more intergrown with the silicates. The smaller specks of sulphide in the disseminated ore consist generally of chalcopyrite. Another phenomenon displayed by the chalcopyrite in the disseminated ore is its tendency to segregate as monosulphide patches, interstitial to the silicates. In the massive ore from the Vlakfontein deposits veins of chalcopyrite cut through pyrrhotite (photo 124). These veins are also found in the host-rock of the ore-body (e.g. in No. 4 shaft). The chalcopyrite in the veins replaces the pyrrhotite (photo 15).

The grin boundaries between chalcopyrite and pyrrhotite are very irregular and embayments of the latter in the former are very common. In places the chalcopyrite contains irregular or semi-rounded inclusions of pyrrhotite near these irregularities. The relationships between chalcopyrite and pyrrhotite mentioned above clearly illustrate to a certain extent the replacement nature of chalcopyrite. The grain boundaries between pentlandite and chalcopyrite are also scalloped and irregular. Inclusions of pentlandite in chalcopyrite are also found. In association with aggregates of pentlandite crystals, chalcopyrite grains are interstitial towards pentlandite, $e.g.$ in sample 17, from the Groothoek Chrome Mine. Coarse-grained pentlandite is sometimes intergrown with chalcopyrite (photo 49).

Where pyrite and chalcopyrite are found together, an eutectic relationship between the two minerals is observed (photo 45) e.g. in the Merensky Reef, Rustenburg Platinum Mine. Generally speaking, pyrite is surrounded by pyrrhotite and is seldom in contact with chalcopyrite.

4.4.2.2. Exsolution Bodies of Chalcopyrite in

Cubanite, Pyrrhotite and Pentlandite. Lamellae of chalcopyrite parallel to (111) (photo 56) or (110) (photo 62) of cubanite are frequently observed where these two minerals are found together. The thickness of the lamellae varies considerably - from O. 001 to O. 05 mm. Grains of chalcopyrite O. 005 **mm in** diameter also exsolved from cubanite granules towards the borders of the latter. Lamellae of chalcopyrite in the cubanite are often in optical continuity with the chalcopyrite grains (e.g. in the ore from the Vlakfontein Nickel Deposits).

Two types of exsolution of chalcopyrite in pyrrhotite were noticed:

- 1. The most abundant type in the pyrrhotite of the Bushveld Complex are grains of chalcopyrite, 0. 002-0. 05 mm in diameter (photo 47). Rounded grains or euhedral crystals with a (111) habit have been observed. The number of these grains in pyrrhotite is generally less than one per cent. The dividing line in the classification between coarse chalcopyrite and exsolved chalcopyrite grains is an arbitrary one because it is sometimes difficult to distinguish between the two types.
- 2. In certain ores of the Bushveld Complex, notably the poikilitic ore from the Rock Shaft (Vlakfontein Nickel Deposits), the pyrrhotite contains chalcopyrite as irregular shuttle-shaped lamellae. These are 0. 002 mm thick and are parallel to the pyramidal plane of pyrrhotite (photo 46). They are actually very rare and differ in this respect from the ores from Petolahti (Ervamaa, 1962, p.43).

In the ores from Vlakfontein a phenemenon that is worth mentioning is the thin veinlets of chalcopyrite between the grains of pyrrhotite and between the grains that have resulted from deformation (photo 48).

It is doubtful whether grains of chalcopyrite in pentlandite are due to exsolution and they should rather be classified as due to replacement.

4.4.2.3 Veinlets of Chalcopyrite. Chalcopyrite was observed in pentlandite parallel to (111) or (100) and also along cracks as very fine veins or lamellae, \pm 0.001 mm thick (photos 43, 41). These fine veins of chalcopyrite are found only in the presence of cubanite in some ores from Vlakfontein.

4.4.3 Exsolution of other Minerals in Chalcopyrite

Exsolution of the following minerals, viz. pyrrhotite, pentlandite, zinc-blende, galena, mackinawite, bornite and the platinum-bearing minerals in chalcopyrite is discussed fully in the sections dealing with these minerals . Some of the chalcopyrite-rich ores are the host of platinum-bearing minerals, e.g. sperrylite, braggite and other unknown minerals. The same association exists in Sudbury (Hawley, 1962, p. 62) and at Insizwa (Scholtz, 1936, p. 169). The platinum minerals are, however, not always surrounded by chalcopyrite, but are present mostly on the boundary of the silicates and the chalcopyrite. On Tweefontein 360 KT, Lydenburg District, chalcopyrite was found intergrown with sperrylite (photo 87). According to analyses of the Vlakfontein Nickel Deposits on the other hand (Schwellnus, 1939), Cu-rich ores do not contain abnormally high concentrations of precious and semiprecious metals.

4.4.4 The Alteration of Chalcopyrite

Under the influence of supergene agencies chalcopyrite alters to covelite. This takes place along grain boundaries, cracks and in places along the (111) crystallographic direction of chalcopyrite (photos 93, 94).

4.5 Cubanite

4.5.1 Abundance and Association

Cubanite is not developed very frequently in the ores of the Bushveld Complex and where it is present it is generally subordinate to chalcopyrite. In the sulphide phase from Aapiesdoorndraai and certain ore-bodies from Vlakfontein (No 27 ore-body), cubanite is the main Cu bearer. In the presence of pyrite, cubanite is absent. Troilite, mackinawite, monoclinic- and hexagonal pyrrhotite are all stable in the presence of cubanite.

4.5.2 Texture

Two types of cubanite could be distinguished, viz.:

- 1. Lamellar cubanite, and
- 2. Massive cubanite

4.5.2.1 Lamellar Cubanite. Cubanite lamellae exsolved from chalcopyrite parallel to (111) of the latter, yet a triangular **ever** arrangement of the lamellae is very seldom if \widetilde{I}_k seen. The lamellae are

always parallel to one another. The size of the lamellae varies considerably, from 0. 005 mm to 0. 5 mm wide and several mm in length. All gradations from a pure chalcopyrite to pure cubanite, forming lamellae in each other, have been observed.

4.5.2.2. Massive Cubanite. Massive cubanite is very common in the massive, poikilitic and disseminated ores from the Vlakfontein Nickel Deposits, where this mineral is concentrated along the contact of the ore-body with the host-rock. The massive type is dominant when the cubanite exceeds chalcopyrite in quantity, otherwise the lamellar type predominates. The grain size of the cubanite is up to 1 cm across.

Aggregates of cubanite grains have highly irregular borders (photo 41). Some contain minute laths of chalcopyrite which follow the (111) crystallographic direction of cubanite (photo 56). Fine polysynthetic twinning is also on (111) (photo 57). A feature displayed by the massive cubanite is its habit to replace the other sulphides, e.g. pentlandite (photo 41, 42, 37) and chalcopyrite. Inclusions in cubanite of the two minerals mentioned last is thus often observed. Grain boundaries between cubanite and these minerals are also irregular and of a corroded nature. The grain boundaries between chalcopyrite and cubanite are much more regular and straight-edged and represent the (111) crystallographic face of both chalcopyrite and cubanite. Round, corroded inclusions of chalcopyrite are found in the cubanite from the Mooihoek pipe (Eastern Transvaal).

In nature three modifications of cubanite are known, viz. the orthorhombic, the tetragonal and the cubic type, although fourtypes were described from Insizwa (Scholtz, 1936, p. 1 76). The orthorhombic cubanite is practically the only modification from the Bushveld ores. However, lamellae of an anisotropic cubanite (orthorhombic) are developed in a more isotropic type (tetragonal) from the Mooihoek pipe (photo 53, 54). In some specimens the tetragonal cubanite is completely isotropic - in these specimens the polished sections are taken to be perpendicular to the c-axis of the tetragonal cubanite crystal. The cleavage of the tetragonal cubanite is parallel to (001), and the lamellae of the orthorhombic modification exsolved parallel to (110) and (001) of the tetragonal cubanite. An isotropic, redish-brown cubanite has also been observed in the tetragonal cubanite. It is easily

distinguished from the latter by its darker colour and isotropism (photo 55). This cubanite is taken as cubic cubanite or chalcopyrrhotite (?) - described in section (p. $\not\!\phi$ 4) dealing with the latter mineral.

4.5.3 Exsolution Bodies of Cubanite in other Sulphides

Exsolution-lamellae of cubanite in chalcopyrite have been dealt with fully above. Very irregular bodies, $+0.05$ mm in diameter, of cubanite in pyrrhotite or in pentlandite have been observed in the ores from Vlakfontein. They are found very sporadically and are interstitial to grains of pyrrhotite and pentlandite or developed along cracks, which would rather suggest an origin due to replacement than due to exsolution for the cubanite. On the other hand it is difficult to visualize an isolated body of cubanite in pyrrhotite as due to replacement.

4.5.4 Exsolution Bodies of other Sulphides

The following minerals are found as products of exsolution in cubanite, generally parallel to (111) and (100): Chalcopyrite, mackinawite, pentlandite, zinc blende (round bodies) and chalcopyrrhotite (?) . These phenomena are discussed in the sections dealing with these minerals.

4.6 Pyrite

Pyrite is present usually as round grains or as cubic and octahedral crystals, 0. 001 mm to 3 mm in diameter. Pyrite always polishes badly, with a high relief and a pitted surface. Good polished surfaces were obtained by using the Brehner machine.

Pyrite is found in contact with pyrrhotite, chalcopyrite and pentlandite. It is never found associated with troilite or with cubanite, except in the mineralized anorthosite below the Main Magnetitite Seam north of Pretoria, where chalcopyrite, pyrrhotite, pyrrhotite, cubanite and pyrite are found together. The pyrite is clearly metastable and has been corroded by cubanite and pyrrhotite.

Round or corroded grains with embayments of pyrrhotite (photos 58, 60) are a common feature of pyrite which is in contact with pyrrhotite, e.g. in sample 119, from the Rustenburg Platinum Mine. Veins of pyrrhotite cutting pyrite have also been observed, e.g. sample 6, from Wildebeestkraal 354 KT, Lydenburg District. An extreme case of the replacement effects of pyrrhotite on pyrite was observed in specimens from the Merensky Reef (sample 119) and in a quartz norite from Wildebeestkraal 354 KT,

Lydenburg District (photo 58), where the central parts of pyrite crystals were altered to pyrrhotite.

A semi-eutectic intergrowth of chalcopyrite and pyrite was also observed in ore from the Merensky Reef and from the Maruleng type of norite from the Western Transvaal (photo 45).

Pinkish pentlandite from the Potgietersrus Platinum Field, which has a polished surface similar to that of pyrite was proved by means of an X-ray examination not to be nickeloan pyrite but a true pentlandite. Clark and Kullerud (1959, p. 143) found that by increasing the Ni content in Fes_o the a_0 -value is enlarged. This is represented diagrammatically in their fig. 37. The pyrites of the Bushveld Complex have values ranging from 5.416 \pm 0.002 to 5.418 \pm 0.002 and are accordingly Ni-poor. The method is however not very reliable. Wagner (1929, p. 208) described nickeliferous pyrite in fairly large quantities from the sulphides of the Bushveld (most of which could be secondary pyrite).

The pyrite of the Bushveld Complex resembles that of Sudbury (Hawley, 1962, pp. 66-73). However, no "reaction pyrite" or "hypogene replacement pyrite" could be identified.

4. 7 Mackinawite

4.7.1 Introduction

This Fe sulphide was recently named in a paper by Evans, et al (1964) . Natural occurrences from Finland were described by Kouvo et al (1963) and from the Muskox intrusion in Canada by Chamberlain and Delabio (1965).

The mackinawite from the Bushveld was originally described by Wagner (1929) , Schwellnus (1939) and Ramdohr $(1960, p. 636-638)$ as valleriite Also in the case of Insizwa, Scholtz, (1936, pp. 169-173) and Ramdohr (1960, p. 633) confused valleriite with mackinawite. From the description by Hawley (1960, p. 85) of the Sudbury ores it is clear that the valleriite he refers to is actually mackinawite.

4.7.2 The Properties of Mackinawite

The physical and the optical properties of mackinawite from the Bushveld Complex are in close agreement with the properties given for the same mineral from the Muskox intrusion by Chamberlain and Delabio (1965, p. 685).

The mineral takes a fairly good polish, although it tends to polish out and this badly polished surface has the same appearance as that of valleriite. It is due to this fact that mackinawite was in the past mistaken for valleriite.

Both the anisotropism and the bireflectance are very high. The bireflectance ranges from light pink to grey and the anisotropism from white to black when the nicols are completely crossed.

The black and white anisotropic colours of mackinawite serve to distinguish it from valleriite, of which the anisotropic colours vary from a very light bronze to a grey bronze. Mackinawite also has a higher reflectiv= ity than valleriite.

The identification of mackinawite in pentlandite and chalcopyrite was confirmed by X-ray powder-diffraction patterns (table 11).

Chemical analyses of mackinawite from the Outokumpu mine (Kouvo et al, 1963) and from the Muskox intrusion (Chamberlain and Delabio, 1965) indicate that the mineral has a composition close to FeS, but that it contains from 0. 2 to 8. 26 per cent nickel.

4. 7. 3 Paragenesis

Pentlandite from the Bushveld Complex contains abundant mackina~ wite, which takes up from 10 to 80 per cent of the area occupied by the pentlandite grains; in most specimens it is less than 30 per cent).

Four textural varieties of mackinawite have been distinguished in pentlandite from the Bushveld Complex:

- 1. Feathery lamellae which range from about 0. 002-0. 03 mm in length (photo 65).
- 2. Unorientated as well as orientated networks of very fine lamellae (0. 0005 to 0. 05 mm wide) parallel to (100) and (111) of pentlandite (photo 66, 67, 68). A rather coarse, unorientated network of mackinawite was found to replace (?) pentlandite or chalcopyrrhotite $(?)$. The latter is present as a network in pentlandite from the Mooihoek pipe (photos 16, 17 18). Scholtz (1936, photo 66) describes a similar texture displayed by pent= landite from Insizwa (1936, photo 66).

3. Mackinawite of patchy occurrence:

- (i) Small irregular patches (0. 03 mm in diameter; photos 67, 70, 71).
- (ii) Irregular patches (0. 05-0. 2 mm in diameter) mostly in the vicinity of cracks (photos 67, 68).
- (iii) Irregular, lenticular bodies (0. 5 x 0. 15 mm wide with their major axes parallel to (111) of pentlandite (photo 66).

4. Lamellae which are oriented very regularly parallel to (100) of pentlandite.

Most of the textures mentioned above have been described by Van Rensburg and Liebenberg (1967, p. 1030) from the Bushveld Complex.

Whereas the coarse pentlandite grains contain one or more of the textural varieties of mackinawite in abundance, flames rosettes and lamellae of pentlandite in pyrrhotite are free of mackinawite.

Two, or sometimes three different orientations of mackinawite in pentlandite have been distinguished.

Mackinawite is also present as orientated lamellae in chalcopyrite parallel to (111) (photo 50, 61). Ramdohr (1960, p. 636) described lamellae parallel to (100). In the Bushveld ores mackinawite has seldom been found parallel to (100) (photo 64). The lamellae have regular boundaries and are more or less tabular in outline. Where twinned chalcopyrite is present, herring-bone textures have also been observed (photo 72). The optical properties of the mackinawite found in pentlandite and in chalcopyrite are apparently identical. Mackinawite with exsolution lamellae of chalcopyrite has very rarely been observed (photo 63).

Cubanite in some specimens from the Vlakfontein Nickel Deposits contains abundant exsolution-lamellae of mackinawite parallel to (111) (photos 57, 62). Small bodies of mackinawite (0. 05 mm in diameter) are also found between the cubanite grains and an intergranular film (photo 57). These bodies of mackinawite are also due to exsolution. Patches of mackinawite, 0.01 mm in diameter, as well as lamellae \pm 0.005 mm wide and parallel to (001) of cubanite have been observed (photo 55) in the ore from Mooihoek 2 55 KT, Lydenburg District.

In pyrrhotite from some specimens a highly anisotropic mineral is pres~ ent parallel to (0001) of the former, as very fine lamellae (0. 0001 mm in

Table 11. X -ray data for $\frac{1}{\sqrt{N}}$ with the second construction and chalcopyrite 53 I/I₁ estimated visually. Co-K_{α}-radiation, Fe filter, $*$ hk1 from Chamberlain et al (1965, p. 686)

Mackinawite	Mackinawite $+$ Pentlandite (sample 20)		Mackinawite Mackinawite $+$ Pentlandite (sample V1.130		$\ddot{}$ Chalco- pyrite (sample V1.131)		Mackinawite Chamberlain et al (1965, p.686)		Pentlandite A.S.T.M. $8 - 90$ $\rm \stackrel{\circ}{X}$	Chalcopyrite A.S.T.M. No. 9-423
$ hk1*$	I/I_1	$\mathbf d$	I/I_1	$\mathbf d$	I/I_1	d		d(obs.) d(calc.)		
	20	5.80	50	5.83					5.78	
001	100	5.03	50	5.04	100	5.05	5.03	5.035	5.01	
			30	3.57					3.55	
	60	3.04	100	3.03	80	3.05			3.03	3.03
101	40	2.94	70	2.91	80	2.98	2.96	2.967		
									2.90	
110	-		10	$\left 2.63\right\rangle$	30	2.64	2.60	2.597		2.63
002	30	2.52	20	2.51				2.518	2.51	
111	60	2.31	70	2, 31	100	2.31	2.31	2.308	2.30	
									2.25	
102	$-\cdot$.		20	2.06	30	2.07		2.077		
	40	1.937	70	1.937	-				1.931	
					20	1.864				1.865
200	20	1.836	30	1.841	50	1.838	1.84	1.8365		1.854
112	20	1.813	30	1.801	50	1.805	1.81	1.8077		
	70	1.778	100	1.778					1.775	
201	${\bf 20}$	1.727	20	1.726	40	1.728	1.73	1.7253		
003	10	1.676	$\overline{}$		10	1.673	1.68	1.6784	1.697	
					10	1.595				1.591
211	20	1.561	10	1.561	20	1.562	1.56	1.5616		1.573
103	20	1.534	30	1.522	20	1.526	1.52	1.5265	1.530	
	20	1.501							1.514	1.518
202								1.4837		
113	30	1.405	20	1.406	10	1.412	1.41	1,4096		
212 $\overline{}$	20	1.310	40	1.312	-			1,3757	1.307	1.323
220	20	1.298			-	1.300	1.29	1.2986		1.303
004			40	1.261	20	1.259	1.26	1.2588	1.255	
221	۰.							1.2588		
203	20	1.249	10	1.229			1.24	1.2389		
										1.214
										1.205
104								1.1908		
301								1.1897		
213					20	1.173		1.1739	1.160	
310 222	$\overline{}$ 50	1.156	20	1.160				1.1615 1.1511		
114			10	1.131	20	1.133	1.13	1,1327		
311	50	1.126						1.1318		
302	-		10	1.105				1.1010	1.105	
$\overline{}$	\overline{a}								$\overline{}$	$\begin{smallmatrix} 1. & 077 \ 1. & 069 \end{smallmatrix}$
312	20	1.052	30	1.053	40	1.055	$1.05 -$	1.0547	1.052	
204					20	1.038		1.0383		
223	20	1.025	60	1.028	20	1.027	1.03	1.0271	1.025	
										1.018 1.014
005								1.0070		1.005
			\mathbf{a}	0.070					0.070	

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width). In the vicinity of the large cracks this mineral is absent (photos 6, 7, 8), whereas near small cracks an increase in the mineral is noticed. This clearly points towards exsolution of this mineral. In some specimens this mineral is restricted to hexagonal pyrrhotite only, whereas in others it appears in monoclinic pyrrhotite and not in the former (photo 6). This mineral could be either mackinawite or valleriite. In the ores from the 0' okiep Copper Mine, mackinawite is present in pyrrhotite (personal com~ munication: W. C. J. van Rensburg). The association of pyrrhotite and mackinawite is seemingly not incompatible. The author thus favours the idea that the mineral mentioned above is mackinawite.

4.8 Zinc-Blende

Zinc-blende is a common minor constituent of the chalcopyrit e or cubanite-bearing sulphides of the Bushveld Complex. It has also been described previously by Schwellnus (1939, p. 129) and by De Bruyn (1944, p. 80) from the rocks of the Basal and the Critical Zone in the Western Transvaal. The zinc-blende grains are always easily identified by means of the characteristic grey colour of the mineral. A slight internal reflection under oil immersion and crossed nicols is visible $_{\circ}$ in some specimens. This indicates a high Fe · content.

Although Barton and Toulmin (1966, pp. 815-849) maintain that the X-ray method, described originally by Kullerud (1953), is not entirely suitable for determining of sphalerite an attempt was nevertheless made to determine whether there is a difference between the a_0 -value ofzinc-blendein equilibrium with pyrrhotite and that of ZnS in equilibrium with chalcopyrite and/or pentlandite.

Sphalerite from different stratigraphical horizons in the Bushveld Complex was also investigated in this way. Very little material was available and consequently only the Debye-Scherrer photos obtained from a 57.3 mm diameter camera yielded measurable lines. The a_0 -values of the Bushveld zinc-blende was found to be of the order of 5.408 \pm 0.005 \AA . The error in measurement exceeded the range of the a_0 -values of (ZnFe)S and the method is therefore considered to be of no value.

Zinc-blende is mostly found in association with chalcopyrite and/or cubanite (sample 19). Grains of zinc-blende intergrown with silicates, but still in the vicinity of the Cu-bearing minerals mentioned, have also been

found (sample 45). Zinc-blende in pyrrhotite has been observed quite frequently, whereas sphalerite in pentlandite is a rare phenomenon. From the Merensky Reef, southeast of Groblersdal, asterisk-shaped zinc-blende within chalcopyrite have been observed. Irregular (samples 32, 45, G. 4802, photo 96) or roundish (samples 25, 45) grains within chalcopyrite, cubanite, pyrrhotite, silicates and pentlandite are commonly developed. In chalcopyrite these grains tend to arrange themselves in stringers (photo 96). Round bodies of chalcopyrite $(+0.005$ mm in diameter) exsolved from zinc-blende grains (photo 95) in the vicinity of, or in a host of chalcopyrite, cubanite and/or pyrrhotite. These small bodies of exsolved chalcopyrite are also arranged in stringers.

4. 0 Minerals **containing** Ni and As

The three Ni - As -bearing minerals gersdorffite, maucherite and niccolite are rare constituents of the ores of the Bushveld Complex. They are usually found in association with pyrrhotite and not with chalcopyri te as in the ores from Sudbury (Hawley, 1962, p. 7 4). Platiniferous minerals are often found in the immediate vicinity of these minerals (sample 105, from the skarn rock, Zwartfontein 818 LR). It is important to note that the **Ni-As** minerals are commonly found in the pyrrhotite ores from the horn= fels of the Western Transvaal or the plutonic rocks in contact with the metasediments. Examples are the Merensky Reef north-west of Potgietersrus (especially the skarn rock) and south-east of Groblersdal and also the ores in the Basal Zone and in the Late Hypabyssal Norites from the Western Transvaal. The Vlakfontein Nickel Deposits contain also sporadic, although sometimes abundant, Ni-As minerals. In the poikilitic ore they are usually concentrated on the contacts of the sulphides with the euhedral silicates (Rock Shaft, 300 feet level). An exception to this relation of **Ni-As** minerals with the metasediment is an occurrence of disseminated sulphide above the Main Magnetitite Seam one mile south of Magnet Heights (sample 25f).

$4, 9, 1$ Gersdorffite

Gersdorffite, (Ni, CqFe) As S, was easily identified by its high reflectivity and white colour with a somewhat bluish tint. Ramdohr (1960, p. 768) described gersdorffite as isotropic. The specimens from the Bushveld Complex and also from Sudbury (Hawley, 1962, p. 76) are anisotropic,

with colours ranging from dark blue-grey to dark brown-grey. Under crossed nicols the mineral reveals irregular twin structures. The grain-size of gersdorffite varies considerably within the range 0. 05-L 15 mm.

Yund (1959, pp. 151-152) points out the wide range in composition which gersdorffite has with respect to the As/S ratio. Gersdorffite has a cubic lattice and he plotted the length of the cell edge as a function of composition. The a_0 -value of three gersdorffite grains, each having a different relation to the surrounding arsenides and sulphides, were found to be within the range 5.690 \pm 0.01 \AA . (The determinations were made with the aid of a 57.3 mm Debye-Sherrer camera.) According to Yund's diagram the Bushveld gersdorffite contains less than 48. 55 by weight per cent of As or more than 87, 5 weight per cent of NiAsS in NiAs₂ - this is a relatively dorffite. s rich gers-

Gersdorffite shows a strong tendency towards idiomorphism (photo 83) which thus also serves as an distinguishing feature. In the Busveld Complex two types of gersdorffite are found: 1. Crystals of gersdorffite in the absence of other arsenides, mostly developed towards the border of pyrrhotite grains, e.g. sample 25, from Magnet Heights. Generatly speaking, these gersdorffite crystals are idomorphic but it is not uncommon to see a gersdorffite crystal showing sharp terminations on one side and deep embayments of pyrrhotite on the other (photo 83). 2. Especially in the Vlakfontein Nickel Deposits gersdorffite is present in an outer zone around the other arsenides maucherite and/or niccolite (photos 78, 79, 80, 81, 82, 84). This gersdorffite zone is developed around maucherite in some specimens but always around niccolite, when the latter is found in the presence of other sulphides. The rim of gersdorffite is usually rather thin (+ 0.003 mm) but thicker zones of gersdorffite were observed. Crystals of gersdorffite with euhedral grain boundaries towards niccolite (photo 80), maucherite and/ or pyrrhotite (photo 82) are also present. In comparison with the euhedral gersdorffite found on its own, the zoned gersdorffite is mostly isotropic. The zoned arsenides have a round appearance and no difference in the relation between the arsenides and pyrrhotite and that between the arsenides and chalcopyrite.

4.9.2 Maucherite

Maucherite, $Ni₁₁As₈$, generally next in abundance compared with gersdorffite, is however the only Ni arsenide in some samples from the mineralized skarn north-west of Potgietersrus and the in massive or poikilitic ore from Vlakfontein where grains of this mineral are up to 1 mm in diameter and are visible with the naked eye.

The reflectivity of maucherite is high. The colour varies according to the surrounding minerals. When on its own, the mineral is white with a light pink-grey tinge. Next to gersdorffite the pink tint is more pronounced. When maucherite is found together with niccolite or pyrrhotite, a greyishwhite colour is more conspicuous, but still with a pinkish tint. The aniso-1ropism is quite weak.

As far as the textural relationship between maucherite and the other arsenides and sulphides are concerned, two types could also be distinguished:

- 1. Single, rounded maucherite crystals in the absence of other nickel arsenides. Where these crystals are not enclosed within the massive sulphide, which is rarely the case, they are restricted to the contact between the sulphides and the silicates. A feature often observed in this type of maucherite is the pseudo-eutectic intergrowth in some places where this mineral is in contact with pyrrhotite (e.g. in the ore from Vlakfontein, photo 85). This type of intergrowth has also been described by Hawley (1962, pp. 81-82) and he also mentioned that a whole gersdorffite crystal is in some places replaced by an inter-· growth of maucherite and pyrrhotite. A similar texture was observed in some samples from the Vlakfontein Deposits (Vl. 208), but the intergrowth is very fine and only a faint indication of an intergrowth as such is visible. This maucherite exhibits a pinkish-brown tint due to the presence of pyrrhotite. The X-ray data for pure macherite and the data for the macherite-pyrrhotite intergrowth are given in table 12.
- 2. Maucherite is arranged in a zoned or semi-zoned texture with respect to niccolite (which is in the centre) and gersdorffite which forms the outer margin (photos79, 81, 82, 86). Either niccolite or gersdorffite may be absent (photo 82). Veinlets of pyrrhotite were found to cut across maucherite and gersdorffite (sample 105

Table 12 X-ray data for maucherite and maucherite intergrown with pyrrhotite. Intensity of the lines were estimated visually. Co-K_x-radiation, Fe filter.

Table 12. (continued)

Maucherite sample 105		Maucherite $+$ Pentlandite sample V1 208		Maucherite ASTM 8-85		Maucherite Yund (1961, p. 1283)			Pyrrhotite Carpenter et al (1964, $p.1360-3)$ strong lines only		
$\mathbf d$	I/I_1	$\mathbf d$	I/I_1	$\mathbf d$	I/I_1	h k 1	$\mathbf d$	I/I_1	hk1	$\mathbf d$	Inten- sity
1.454	${\bf 50}$	1.455	30	1.449		50 048					
1.404	5	1.435	40							1,439	W
1.364	10			1.361		10 00.16					
1.352	$\bf 5$										
1.295	$\bf 5$			1.299		5 249					
1.271	$\bf 5$										
1.250	$\overline{5}$			1.247		10 412					
1.235	$\overline{5}$										
1.215	50			1.212		60 440					
1.201	5			1.202	$\overline{5}$	02.17					
1.132	30			1.133	40	24.13					
1.109	30	1.106	10	1.108		50 448					
1.088	10										
1.082	20			1.083		50 22.18					
1.067	20			1.068		40 04.16					
1.041	20			1.039	30	226					
1.021	10			1.023	10						
				1.009	$\overline{5}$						
0.991	10			0.993	5						
0.973	20			0.973	x30						
0.944 0.932	$2\sqrt{0}$ $2\sqrt{0}$			0.946 0.932	20 $2\sqrt{0}$						
0.921	10			0.920	$\overline{5}$						
				0.915	$\bf 5$						
0.908	$2\sqrt{0}$			0.908	40						
0.890	$\bf 5$			0.893	10						
0.859	$10\,$			0.861	40						
				0.851	10						
0.835	$\overline{5}$										
0.829	$2\,0$			0.828	30						
0.819	$2\sqrt{0}$			0.819	40						
				0.808	40						
				0.804	40						

from the mineralized skarn, Zwartfontein 818 LR, Lydenburg District). The plae violet isotropic mineral A described by Scholtz (1936, pp. 181-182), which surrounds niccolite could be either maucherite or gersdorffite. Maucherite was definitely found to replace niccolite (sample 105).

4.9.3 Niccolite

Niccolite, $Ni_{1+x}As$, is a common minor constituent of the ores from the Western Transvaal. It is readily distinguished by the normal salmonpink colour, the marked pleochroism and the strong·anisotropism. Niccolite was previously identified by Schwellnus (1939, p. 135) as breithauptite, which has more or less the same properties. For this reason a few grains of niccolite from different samples of the hornfelses from the Western Transvaal and from the ore from Vlakfontein were drilled out and the identity confirmed by means of X-ray analysis $(\theta f + \theta h)$.

Niccolite is always surrounded by either gersdorffite (photos 78, 80, 84) or maucherite (photo 86) or both (photo 79). The same association was described from Sudbury (Hawley, 1962, p. 79), from Insizwa (Scholtz, 1936, p. 178, fig. 12a, b, d, e) and from Pisek, Czechoslovakia (Lensh et al, 1966, pp. 233-234). It is clear that niccolite is replaced and corroded by maucherite (photo 86) and to a lesser degree by gersdorffite. In a sample from the Rock Shaft (300' level), Vlakfontein Nickel Deposit, niccolite is bounded by gersdorffite on the one side and by mackinawite on the other. In massive chalcopyrite from Vlakfontein (V1. 5) niccolite is present, however, all on its own.

Yund (1961, p. 1285) plotted the variation ind (103) as a function of the Ni/ As atomic ratio of niccolite. Unfortunately a film from a Debye-Sherrer camera, 114. 6 mm in diameter, did not reveal measureable lines. The error in measurement on films taken with the 57. 3 mm diameter camera is much greater than the limits of the variation of the d(l03)-values and as a result no deductions with regards to the Ni/ As ratio could be made. Buseck (1963, p. 204) has compiled a diagram from which it is possible to determine the weight per cent of FeAs in niccolite, by using the $d(110)$ -value. From two measurements on different niccolite grains $d(110) = 1.815 + 0.01$ and 1.810 *.±.* 0. 001) from the Vlakfontein Nickel Deposit, it appears as if the niccolite has less than 15 per cent by weight of FeAs.

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4.9.4 Rammelsbergite (?)

Rammelsbergite (?), NiAs₂; was found in only one polished section (sample 45) from the Merensky Reef south of Groblersdal. The rammelsbergite grains were very small, 0. 002 mm in diameter, and could therefore only be identified with the aid of the optical characteristics of the mineral, which may be summarized as follows: A higher relief than gersdorffite or niccolite and relatively high reflectivity with a very weak pleochroism, the colours varying between a slight yellow-white and a blue-white. The anisotropism is quite strong.

The rammelsbergite was found in close association with the other Ni arsenides, where it occurs on the contact between niccolite and gersdorffite (photo 78).

4.9.5 Ullmannite $(?)$

Ullmannite, Ni Sb S, has been found only in the same polished section as the rammelsbergite (photo 78) and also in certain ores from the Vlakfontein Nickel Deposits (photo 82). The ullmannite was also identified by means of its optical properties. Next to gersdorffite, ullmannite has very much the same white colour, with a higher reflectivity, but under oil-immersion a blue-grey colour (somewhat like galena) is visible. Another distinguishing feature of ullmannite is its isotropic character although in a sample from the Potgietersrus Platinum Field (sample 105) a bireflectant anisotropic ullmannite (?) was found with exactly the same relation to niccolite and gersdorffite as the isotropic ullmannite grains mentioned above, Ramdohr (1960, p. 771) also described anisotropic ullmannite from Huel Gorland.

4.10 Bornite

Bornite is also a very unimportant mineral in the Bushveld Complex and in the course of the investigation the mineral was found in two localities. In a polished section from the Merensky Reef from Tweefontein 360 KT, Lydenburg District (Dwars River area) small grains (0. 003 mm in diameter) of bornite are found between the silicates in the vicinity of chalcopyrite and covellite. The bornite in this case could thus be a secondary product. Bornite constitutes a greater percentage of the sulphides in the magnetitite seams where it is mainly concentrated towards the borders of the laths of euhedral plagioclase (sample 134). The bornite is also intimately associated with chalcopyrite with which it can be in lamellar intergrowth (photo 93). Separate grains were also seen.

The optical properties of the bornite may be summarized as being very slightly bireflectant and anisotropic, exhibiting the typical reddishbrown colour. Bornite can also be isotropic.

4.11 Galena

Galena is present as a very minor constituent of the sulphides in the mineralized anorthosite below the Main Magnetitite Seam, single roundish grains, $+$ 0.003 mm in diameter, in the chalcopyrite. One sample, 321 , contains however, a few grains of galena. Owing to the smallness of the grains the galena could not be identified by means of X-rays, but the grey colour, the lack of anisotropism, the softness (relative to chalcopyrite) and positive etching with $HNO₉$, indicate that this mineral is galena. In Sudbury, galena was found in association with chalcopyrite and other minerals (Hawley, 1962, p. 99).

Galena was found only in the higher horizons, i. e. the upper part of the Main Zone and in the Upper Zone, of the layered sequence of the Bushveld Complex. This corresponds with a differentiated olivine diabase from Missouri in which Desborough (1967, p. 608) reported PbS from the upper horizons of the intrusive.

4.12 Minerals of the Safflorite-Loellingite Series (FeCo)As. The optical properties of the minerals in the safflorite-loellingite group are very similar to those described by Ramdohr (1960, pp. 781, 787). The (FeCo)As₂ of the Bushveld Complex is found in the absence of other arsenides. It is therefore difficult to identify and distinguish safflorite and loellingite from other arsenides such as glaucodot, arsenopyrite and rammelsbergite. Consequently the mineral was identified by means of X-rays.

No (FeCo) As_2 was found in the plutonic rocks; it was restricted to the metasediments. From Kuilsriver 31 JG, Groblersdal District, the safflorite, as euhedral or mostly subhedral grains (0.1 mm in diameter), is a constituent of $a^{'}$ quartzite forming the bonding material of the metasediment in places. The safflorite is replaced along (100) by erythrite. One grain of (FeCo) As₂, 0.1 mm in diameter, was observed in the hornfels in bore-hole KA5. The (FeCo)As₂ is zoned by linnaeite (?) which is in turn a host of pyrrhotite.

According to Clark (1960, pp. 131-132) the substitution of Sand Co for As and Fe in loellingite has an effect on the interplanar spacings. He

thus compiled a diagram in which the interplanar spacings (210) and (111) or (120) and (101) are plotted as a function of the S $(1-3\%)$ and Co content (1-10%) of the safflorite-loellingite series. The values for the Bushveld Complex's (Fe, Co)As₂ unfortunately fall outside the limits of the diagram (table 13). It could thus be concluded that the mineral in the metasediments surrounding the Bushveld Complex is S-poor and Co-rich.

Table 13. X-ray data for safflorite-loellingite, I/I_1 estimated visually. Cu- K_{α} -radiation, Ni-filter.

hkl	Safflorite Kuilsrivier 31 JS		Safflorite- Loellingite KA5 5028		Range of Clark's Values	Safflorite ASTM $11 - 59$		$Co-$ loellingite ASTM $11 - 699$	
	$d+0.005$ I/I ₁		$d + 0.005$ $1/I$		d	d	$\rm l/L$	d	$\rm{I/I}_{\ast}$
101	2.625	80			$\left 2.534 - 2.562 \right 2.65$		80		
120	2.524	100	2.586		$100 2,582-2,604 2,56 $		90	2.58	100
210	2.381	100			$2.390 - 2.422 2.41$			100 2.40	30
111	2.327	50	2.328		$80 2,334-2,352 2,35 $		40	2.35	80

4.13 Linnaeite

Linnaeite, $Co_3^{\text{ }S_4}$, is a subordinate constituent of the ore-minerals of the Bushveld Complex. In the plutonic rocks it exsolved from millerite along the prismatic crystallographic directions of the latter (photo 92). Other minerals in the same association are chalcopyrite and zinc-blende. The sulphides are developed in a vein and are therefore secondary. At another locality (sample KA5-5028) where linnaeite was found, it is difficult to assume a secondary origin, as it is present in a concentric zone around loellingite, all in a host of pyrrhotite in a hornfels (KA5-5028). The identity in the latter case is not positive. The optical properties are white with a reddish tint and an isotropic character. The reflectivity is higher than that of pyrrhotite but lower than loellingite. The linnaeite in the millerite, mentioned above, has the same features.

4. 14 Millerite

Millerite, NiS, is also a very subordinate mineral in the Complex and is considered secondary where it is present in a vein together with chalcopyrite, zinc-blende and linnaeite on the Farm Roodewal 193 JS, Groblersdal

District (photo 92). The latter exsolved from millerite along $(10\bar{1}0)$. In borehole G1 anhedral grains of millerite, 0.1 mm in diameter, are found in association with pyrite, chalcopyrite and pentlandite at a depth of 5566 feet. The texture of the millerite and that of the other ore-minerals are proof against any secondary origin of millerite - no secondary alteration effects were seen. The millerite from the latter locality shows polysynthetic twinning (photo 91), probably along (0112), according to r Ramdohr (1960, p.576). In the serpentinized harzburgite small specks of millerite, 0. 001 mm in diameter, are frequently seen.

Millerite is easily identified by its bireflectance in bright yellow (E-ray) and greyish-yellow (O-ray) together with its high anisotropism in yellow and iris-blue-violet. The identity of millerite was nevertheless confirmed by an X-ray investigation.

4.15 Chalcopyrrhotite (?)

The existence of chalcopyrrhotite as a natural mineral is not beyond any doubt. According to Ramdohr (1960) chalcopyrrhotite is a high-temperature mix-crystal of CuFeS₂ and FeS (p. 504) possibly including 'NiS (p. 492). According to Yund and Kullerud (1966, pp. 481-482) chalcopyrrhotite could most probably be a tetragonal or isometric isotype of orthorhombic cubanite.

Ramdohr (1960) described chalcopyrrhotite from the Mooihoek (p. 635) and Driekop (p. 506) pipes in the Eastern Transvaal. The mineral which the author would describe as possibly chalcopyrrhotite was also found in the Mooihoek pipe. The optical characteristics are very near to those of pyrrhotite but it is isotropic and somewhat browner. It is present as a replacement (?) network in pentlandite (photos $16, 17, 18$) where it is in turn replaced by mackinawite. The same mineral replaces tetragonal cubanite or vice versa (photo 55). If we considered that chalcopyrrhotite is either tetragonal or isometric cubanite, as suggested by Yund and Kullerud (1966, p. 482), then we would have three modifications of cubanite next to one another. The main mass would be tetragonal cubanite (very slightly anisotropic) with patches of cubic cubanite (this is now chalcopyrrhotite which is isotropic) and lamellae of normal ortho~rhombic cubanite - quite anisotropic (photos 53, 54, 55). Peculiarly enough, where the lamellae of orthorhombic cubanite are present in cubic cubanite (chalcopyrrhotite), they are rimmed by a whitish anisotropic mineral E. (photo 52).

X-ray work has been carried out on chalcopyrrhotite (or cubic cubanite) but no conclusion has been arrived at, seeing that no d-values exist for chalcopyrrhotite or for cubic cubanite.

4.16 Mineral E

Very thin rims of this mineral surround lamellae of orthorhombic cubanite (photo 52) where the latter is present in chalcopyrrhotite (described above) but not where the lamellae are developed in tetragonal cubanite. The mineral is anisotropic with a reflectivity somewhat higher than that of pentlandite.

4.17 Minerals containing the Platinum Group Metals

Before discussing the minerals which contain the platinum group metals the author wishes to state clearly that these minerals were not studied in detaiL Only the minerals which were observed in the course of the investigation are described. The platinum group metals will henceforth be referred to as P. G. M.

Minerals containing the $P_{\bullet}G_{\bullet}M_{\bullet}$ were observed quite often in specimens from the Merensky Reef and from the platinum-bearing pipes in the Eastern Transvaal, but very sporadically in the other rocks of the Bushveld Complex. Mostly the disseminated sulphides from other horizons contain no minerals which contain the P. G. M.

The P. G. M. have three modes of occurrence in the Bushveld Complex:

- 1. As Pt or its associated elements in solid solution in the sulphides, e.g. pyrrhotite, pentlandite and chalcopyrite (refractory **ore){wa.5 nu** *I l '¥2.'l).*
- 2. As definite sulphides, arsenides, antimonides, bismuthides, etc. containing major amounts of the P . G. M.
- 3. As native P , G , M , or ferro-alloys containing P , G , M , (nonrefractory ore).

Whichever category is the main P , G , M , bearer in the Merensky Reef is difficult to say and it is also supposed to be a secret at the Rustenburg Platinum Mine. During the present investigation, however, the most common mode of occurrence of the P. G. M. is that in which these metals are bonded to S, As, Sb, Bi, etc. Native P.G.M. is a very rare substance. Ferroplatinum, although an important Pt bearer at the Rustenburg Mine,

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was not observed. It may be mentioned that pieces of massive sulphide from a "pothole" in this mine gave a high assay-value for Pt. Investigations of these sulphides in polished sections did not show any minerals which contain the P.G.M. According to Wagner (1929) the ore from the platinum-bearing pipes in the Eastern Transvaal is non-refractory - native P. G. M. are a very common constituent.

The minerals containing the P , G , M , are mostly present near the sulphides and the silicates, usually in both (mainly chalcopyrite and pyrrhotite). Minerals which contain the P. G. M. and which are enclosed in the sulphide near the border of the sulphide with the silicates, are also common. Maucherite or gersdorffite are also found in some specimens in association with minerals containing the P, G, M , e.g. in the skarn rock from the Potgietersrus Platinum Field (photo 82) .The time ofcrystallization of the minerals which contain the $P_{\bullet} G_{\bullet} M_{\bullet}$ is very difficult to determine. Euhedral sperrylite with sharp edges against chalcopyrite but also including the latter was observed (photo 87). "Veins" of minerals containing P. G. M. cutting across the sulphide and the silicates are common (photos 89, 90). It thus appears as if the minerals were the last minerals to crystallize. The native platinum or the ferroplatinum included in chalcopyrite as small roundish grains is even much more problematic as far as the time of crystallization is concerned.

The following minerals which contain $P_{\alpha} G_{\alpha} M$, were distinguished: Sperrylite, braggite, mineral A (BiPd₃?), mineral C (cooperite?), mineral D (michenerite ?) and other minerals of high reflectivity.

4.17.1 Sperrylite

Of all the minerals which contain the P, G, M , sperrylite, PtAs, was the most frequently observed in the Merensky Reef (photo 87, 89, 90). In the Rustenburg Platinum Mine it is, however, subordinate to braggite.

Under the microscope sperrylite is easily identified on account of its high relief, high reflectivity and isotropism. The grains are up to 0.15 mm in diameter but are generally smaller. The particles are interstitial to the silicates or have cross-cutting relationships towards the sulphides and the silicates (photos 87, 89, 90). Well-developed crystal faces have also been observed (sample 29, from Tweefontein 360 KT, Lydenburg District.

Sperrylite encloses chalcopyrite (sample 29); this indicates a later crystallization of the former relative to the sulphides. No positive conclu-

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sion could be drawn as far as the time of crystallization of sperrylite, relative to other minerals which contain the P. G. M., is concerned. On photo 89 it appears to be later than BiPd_3 .

Enough material was available for an X-ray investigation with the aid of a 57. 3 mm diameter Debey-Scherrer camera. The data are given in table 14.

4.17.2 Braggite

From an investigation of representative polished sections from the Rustenburg Platinum Mine, it appears that braggite, (Pt, Pd, Ni) S, is the main platinum bearer (excluding perhaps the P. G. M. in solid solution in the sulphides). The braggite is generally present on its own, no other minerals which contain the P_{\cdot} G, M. have been observed. It is usually situated on the contact of a sulphide bleb with the silicates (photo 88). Separate small grains completely surrounded by silicates or by chromite are also present. The grains are subhedral and about O. 5 mm in diameter; the mean grain-size being $+0.03$ mm. Braggite is mostly free of mineral inclusions. On the other hand, a pentlandite "vein" cutting through a fairly large grain was noticed.

The braggite is easily identified on account of \exists its high reflectivity, very low bireflectance (differing only in shades of light grey) and anisotropism. Twinning in braggite was observed (photo 88). The identity of the mineral was confirmed by means of an X-ray investigation (table 15). It appears as if the intensity of the lines as well as the d-values vary with ehemical composition,

4.17.3 Mineral A - Unnamed Mineral BiPd₃?

This mineral is present in the mineralized skarn north-west of Potgietersrus (photo 89) and in the Merensky Reef south-east of Groblersdal. At these localities BiPd_3 may be the most common mineral containing the P. G. M., besides sperrylite.

The grains $(-0.1 \text{ mm}$ in diameter) are interstitial to the silicates but may be euhedral towards pyrrhotite. Mineral A has the following optical features: Relatively high reflectivity (50-55%) compared with the surrounding sulphides and arsenides. The bireflectance is very weak in yellow, with a slightly reddish tint and a somewhat lighter yellow, also with a reddish tint (very much the same as for millerite but much less bireflectant). Anisotropism is not very strong. The relief is higher than for mineral D.

Table 14. X-ray data for sperrylite. (Intensity estimated visually) Cu-K_{α}-radiation, Ni filter

 $a_{\rm o}$ = 5. 965 \pm 0. 005 $\rm \AA$

Braggite, sample 119 (Rustenburg Platinum Mine)			Braggite ASTM 9-421 (Rustenburg)		Braggite ASTM 10-429 synthetic			
Intensity $\mathbf d$		Intensity	d	hk1	Intensity	d	h k 1	
10	4.53	10	4.58	011				
20	3.72	5	3.75	111	10	3.74	111	
50	3.25	$\overline{5}$	3.21	020	10	3.21	200	
10	3.17							
80	2.91		2.93	012	80	2.936	102	
						2.886	201	
100	2.85	100	2.86	120	80	2.869	210	
		5	2.66	112	60	2.669	112	
90	2.62	30	2.64	121	100	2.631	211	
20	2.15	10	2.16	122	30	2.166	212	
$\overline{5}$	2.07	10	2.01	130				
50	1.853	30	1.852	222	60	1.871	222	
30	1.801	10	1.807	023	30	1.816	203	
					30	1.796	302	
30	1.769	10	1.771	230	80	1.781	320	
					80	1.747	213	
20	1.731	10	1.731	123	80	1.730	312	
40	1.713	20	1.713	231	30	1.720	321	
${\bf 30}$	1.637	$10\,$	1.642	004	30	1.650	004	
30	1.588	20	1.595	040	60	1.605	400	
20	1.545	$\overline{5}$	1.547	041	10	1.558	410	
10	1.502	$\overline{5}$	1.506	330				
10	1.456	$\sqrt{5}$	1.463	024	10	1.443	402	
40	1.420	30	1.423	124	30	1.430	214	
					30	1.408	412	
40	1.395	20	1.391	$\mathbf{1}$	10	1.403	421	
					30	1.384	323	
		$\overline{\mathbf{5}}$	1.375		10	1.376	332	

Table 15. X-ray data for braggite. Intensity estimated visually, Cu-K_{α}-radiation, Ni-filter.

Table 16. X-ray data for mineral $A - BiPd_q$ (unnamed). Intensity estimated visually, Cu- $K_{\rm ex}$ -radiation, Ni-filter.

Fortunately enough material was available for an X-ray investigation on a 57. 3 mm diameter Debye-Scherrer camera. The data are given in table 16 and the correspondence with the mineral $BiPd₃$ describe from Russia is quite remarkable, except for the weak lines and radiations.

4.17.4 Mineral B

Only one particle of this mineral was come across, where it is present next to other minerals containing the P. G. M. (photo 88) in the mineral~ ized skarn north-west of Potgietersrus (sample 105). Mineral B is slightly more brown than mineral A, displaying a light brown-yellow colour with a distinct anisotropism. It also has a higher relief than mineral D. X-ray data for mineral B are given in table 17. Contamination of mineral A could have taken place, seeing that some d-values coincide with those of mineral A $(cf. table 16)$.

$4.17.5$ Mineral C - Cooperite *(* ?)

This mineral, which is considered to be cooperite, PtS, was also discovered in the skarn rock from north-west of Potgietersrus (photo 88), in the Merensky Reef south-east of Groblersdal and from the Rock Shaft on Vlakfontein (photo 82). The mineral is always found in the presence of other minerals which contain P, G, M , and Ni-bearing arsenides. As a matter of fact cooperite (?) is enclosed in both niccolite and gersdorffite. Cooperite and michenerite (?) appear also as pseudo-eutectic intergrowths. The grains are generally small, 0. 005 - 0. 1 mm in diameter.

The mineral is characterised by a remarkable brown colour which could qualify for Ramdohr's (1960, pp. 388 and 641) "Kaffeebraun bis olivleder braun". The reflectivity is very much the same as that for the 0-ray of pyrrhotite, perhaps somewhat lower. The anisotropism varies from fair to rather weak, depending on the orientation of the mineral.

The X-ray results are given in table 18. Contamination with $BiPd_q$ must have taken place when a sample was drilled out for X-ray analysis; this is clear from the presence of strong lines belonging to the latter mineral. Some of the lines give a double reflection which could possibly indicate the presence of two varieties of cooperite of different composition al though not much difference is noticeable between the natural cooperite, (Pt, Pd, Ni)S, and synthetic cooperite, PtS.

4017.6 Mineral D - Michenerite (?)

Mineral D, Michenerite (Pd Bi₂), is associated with other minerals which contain the P.G.M. (photo 88) in the mineralized skarn rock of the Potgietersrus Platinum Field. A noteworthy texture is the pseudo-eutectic intergrowth of mineral D and mineral C. Under the microscope mineral D has a dull white colour with a reflectivity comparable with that of maucherite. It is very slightly anisotropic (this could also be an optical illusion due to the surrounding anisotropic minerals). The possibility is not excluded that this mineral is maucherite.

4.1707 Mineral F

This mineral was found in the ore from the Merensky Reef in the vicinity of Groblersdal and at Potgietersruswhere it is present as very small grains, O. 01 mm in diameter. This mineral is also present together with cooperite, gersdorffite and niccolite. The colour displayed by mineral F is actually a golden yellow with a slightly reddish tint and a very high reflectivity. Under crossed nicols a distinct anisotropism is visible. The latter feature excludes gold as a possible alternative.

$4, 17, 8$ Minerals of a very high Reflectivity

Minerals of a very high reflectivity are present in some samples seen as small roundish bodies in chalcopyrite or less commonly in other sulphides or silicates. They are generally very small $(0.002 \text{ mm in diameter})$ and under high magnification they appear to be an intergrowth of different minerals. These minerals could be native P. G. M.

4.18 Secondary Minerals

The secondary minerals which will be discussed under this heading are those which originated under the influence of supergene effects. The secondary minerals are developed in somewhat weathered samples or in serpentinized olivine-bearing rocks. Some minerals which originated as a result of supergene effects have already been discussed and will not be re~ peated in this section, for example, the hexagonal pyrrhotite which originate from troilite along cracks.

The following secondary minerals will now receive attention: 1. Valleriite. 2. Melnikowite-pyrite. 3. Bravoite, 4. Covellite.

4.18.1 Valleriite

Valleriite and mackinawite have previously been confused with each other. The first paper which indicated two different minerals is that by Evans et al (1964) . Chamberlain and Delabio (1965) gave a table summarizing the differences in the properties of the two minerals. The present author agrees with these authors as far as the properties of mackinawite and valleriite in the Bushveld Complex are concerned. In a recent publication Antun_1 El Goresy and Ramdohr (1966, p. 117) described the reflection-pleochroism of valleriite as follows: "0 ist viel heller, von licht graubraun bis erheblich dunkler 'graurosaviolett', E is blaulichgrau bis recht dunkel grau - alles in 01 .". According to the description of Chamberlain and Delabio (1965) properties given by Antun et al (1966) fit mackinawite quite well but not valleriite. The mackinawite in the Bushveld also shows the properties mentioned above which Antun et al (1966) ascribed to valleriite. Valleriite in the Bushveld Complex exhibits the following properties in oil: Reflection pleochroism - 0 bronze (yellow-brown), E grey Anisotropism - 0 light brown yellow, E grey. Reflectivity - O-ray much lower than for mackinawite.

Mackinawite (as a product of exsolution in pentlandite) that is somewhat badly polished shows exactly the same properties as valleriite and it may be that the confusion of the two minerals is due to this fact (as already men= tioned).

An X-ray investigation (table 19) was done on valleriite from several localities with the aid of a 57. 3 mm diameter Debye-Scherrer camera. It was very difficult to obtain measureable lines - this may be the result of the very fine intergrowth between valleriite and serpentine.

The mode of occurrence of mackinawite and valleriite in the Bushveld Complex is completely different. Mackinawite is present as an exsolution product in other sulphides, whereas valleriite is present as a secondary mineral which replaces pyrrhotite (photo 75) and pentlandite, with exsolved mackinawite, especially along cleavage directions in the case of the latter (photos 76, 77). Valleriite is also more restricted to cracks in the sulphides (photo 74) or along the outer rims of sulphide globules where it tends to replace the sulphide. Valleriite was observed in those rocks subjected to

Valleriite sample 29		Valleriite sample V1 202		Valleriite Chamberlain et al (1965)				
Intensity	d	Intensity	$\mathbf d$	hk1	Calculated $\mathbf d$	$\mathbf d$	Muskox Valleriite Intensity	
				00.3	11.367	11.53	Vs	
		100	5.72	00.6	5.68	5.74	VS	
		20	4.84					
		30	4.15					
		40	3.80	00.9	3.787	3.81	W	
		80	3.25	10.1	3.267	3.25	S	
				10.2	3.225			
		10	3.16					
				10.4	3.06			
100	2.99	30	2.97	10.5	2.959			
		30	2.84	00.12	2.482	2.87	W	
				10.7	2.723			
		10	2.63	10.8	2.601			
80	2.51	60	2.53			2.51	W	
		30	2.36	10.10	2.365	2.37	W	
		30	2.27	00.15	2.273	2.29	W	
	2.23			10.11	2.254			
		40	2.10					
50	2.08	30	2.05	10.13	2,050	2.06	m	
				10.14	1.956			
		100	1.883	00.18	1.894	1.89	m	
				11.3	1.870	1.865		
30	1.83	20	1.791	11.6	1.799	1.800	m	
30	1.74			10.16	1.788			
		20	1.714	10.17	1.712			
				11.9	1.696			
		30	1.643	20.1	1.640	1.635	VW	
				20.2	1.634			
		50	1.619	00.21	1.624			
				20.4	1.612			
				20.5	1.596			
				11.12	1.577			
				10.19	1.575			
				20.7	1.556			
30	1.54	20	1.533	20.8	1.532	1.54	W	
		60	1.487					
		$10\,$	1.325					
		$2\sqrt{0}$	1.303					
		10	1.265					
		$30\,$	1.234					
		10	1.212					
		20	1.122					
		40	1.092					
		$2\sqrt{0}$	1.047					
		$30\,$	0.9694					
		20	0.9387					

Table 19. X-ray data for valleriite. Intensity estimated visually, Co-K $_{\alpha}$ -radiation, Fe-filter.

Table 20. X-ray data for melnikowite-pyrite. Intensity estimated visually. Cu-K_x -radiation, Ni-filter.

serpentinization (samples 29, 104 and from Vlakfontein). It thus appears that the formation of serpentine stabilized the growth of valleriite. Chemical analyses of valleriite show that Mg and Al hydroxyl phases are important constituents. According to Evans et al (1964) , these phases are interlaminated with valleriite on a submicroscopic scale. The fact that valleriite in the Bushveld is always associated with serpentine confirms this theory. According to Ramdohr (1960, p.632) Cr-bearing valleriite is also known. In this respect it appears that certain chromite grains which crystallized relatively late, are replaced by valleriite (photo 108). Peculiarly enough, early euhedral chromite situated within valleriite is not effected.

$4.18.2$ Melinkowite-pyrite

Secondary pyrite is a common mineral in slightly weathered samples of the Complex (samples 6, 25, 32, 31) and also in the serpentinized harzburgite from the Western Transvaal, where it is present as an alteration product of the pyrrhotite. This pyrite always flares out from cracks and grain boundaries and shows the typical concentric "birds-eye" texture (photo 14).

This alteration product is not always a pure pyrite but also contains marcasite. An X-ray powder photograph (obtained with a 57.3 mm diameter camera) contains lines belonging to marcasite and pyrite (Table 20). The designation melnikowite-pyrite is thus applicable to this material. The extremely altered samples contain a porous pyrite which has a bluish colour due to the formation of magnetite, where the assemblage contains a certain amount of marcasite it is anisotropic and twinning is also noticeable.

4. 18. 3 Bravoite

This secondary mineral is found along cracks and grain boundaries in slightly altered pentlandite (photo $39, 40$). This alteration is conspicious in the ores which are weathered and in serpentinized olivine-bearing rocks. Although the mineral is isotropic, it could readily be distinguished from pentlandite on account of its brown-pinkish colour, which is very similar to that of pyrrhotite. In extremely weathered rocks or in the mineralized, serpentenized harzburgites (from bore-hole KA3) all the pentlandite is con= verted to bravoite. The original grain boundaries as well as the cleavage of pentlandite were preserved in some specimens. Where a great deal of the pentlandite is converted to bravoite, small irregular cracks (photo 40), due to the

volume change, are visible. Unit-cell determinations carried out on bravoite from different localities gave a value of $a_{\rm o} = 5.690 \pm~0.05$ Å.

4.18.6 Covellite

Covellite has only been observed in weathered rocks, where it replaces chalcopyrite and rarely bornite. The sulphides of the Main Zone, and especially those in the magnetitite, contain considerable amounts of covellite. The chalcopyrite is replaced along grain boundaries (photo 93), cracks and the (111) crystallographic directions (photo 94). The covellite is characterized by its well-known, typically high bireflectance in shades of blue, and high anisotropism in shades of red.

5. THE DISTRIBUTION OF THE SULPHIDES

The variation in the mineralogical composition of the sulphide phase of the Bushveld Complex is plotted against stritigraphical horizon (fig. 8, inserted in the pocket at the back). The results were determined by ordinary point-counting methods. Where enough sulphides were present 500 points were counted, otherwise a visual estimation was made.

Generally speaking, pyrrhotite is the most abundant sulphide in the Bushveld Complex, followed by pentlandite, chalcopyrite, pyrite, cubanite and mackinawite. This sequence may vary with the stratigraphical horizon (fig. 8). The localities of all the samples are given on Maps I, II and III as well as'_l table 63.

In the mineralized hornfelses of the Western Transvaal pyrrhotite is always in excess of 90 per cent whereas chalcopyrite, pentlandite and pyrite are of very subordinate occurrence. It is important to note that in some biotite granulites, arsenide minerals are common minor constituents. The diopside hornfels of Potgietersrus contains an abnormally high quantity of pentlandite in comparison with the hornfelses of the Western Transvaal. The Magaliesberg quartzite contains mainly pyrite.

In the late hypabyssal rocks of the Busveld, the percentage of pyrrhotite is also relatively high (fig. 8, 9 and table 21.) The mean value of pentlandite for these rocks is higher than the value of chalcopyrite. It also appears that rocks containing only chalcopyrite are present in the Bushveld Complex (sample 83). Arsenides are present in some (quartz) norites from the Western Transvaal.

In the Basal Zone itself the ratio of pyrrhotite to pentlandite and chalcopyrite shows considerable variation (fig. 8), even in the harzburgites from different localities this is the case. In samples from Aapiesdoorndraai pentlandite is in excess of pyrrhotite; in the harzburgites from the Western Transvaal and from Potgietersrus the opposite relationship appears. A norite layer (sample 67) between harzburgites and pyroxenites, contains only chalcopyrite. The other oscillations in the values (i.e. samples 15 and 99) could probably be attributed to polished sections which are not typical of the Basal Zone. Pyrite is actually an exception in rocks of the Basal Zone. In comparison with rocks from other zones, mackinawite (mainly within pentlandite) and cubanite, are quite abundant.

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Table 21. Mean percentages of the sulphide minerals in polished sections from the main sulphide-bearing stratigraphical horizons of the Bushveld Complex. Mineral ratios are also given. (The percentage of pentlandite is expressed as 100 and the other percentages adjusted accordingly.)

In the Critical Zone the percentage of the sulphide minerals also fluctuate to a remarkable extent. This may also be attributed to the diversity of the rock types. The anorthosites and norites (sample 28, 97, 89, 88, 87 and 86) contain mainly chalcopyrite, whereas the other rock types (harzburgite, pyroxenite and dunite) contain pentlandite and pyrrhotite as the major minerals. A noteworthy feature of the pipe-like bodies in the Critical Zone (e.g. the Mooihoek pipe) is that the Fe-rich ultramafic rocks of these bodies (samples 91 and 90) contain more pyrrhotite and less pentlandite than would be expected of ultramafic rocks from this stratigraphical horizon, whereas in the Mg-rich dunites the opposite was noted. The peridotite pegmatoid (sample 12) is an exception to this rule. The point-counting results of De Bruyn (1944, p. 83) on sulphide-bearing hortonolite dunite (pyrrhotite = 58. 6 per cent, pentlandite 7. 5 per cent chalcopyrite 1. 1 per cent and cubanite 5. 8 per cent from the Critical Zone in the Western Transvaal, however, confirm the statement made above. Some samples from the Mooihoek pipe (sample 90B) contain a fairly large percentage of cubanite, which indicates an enrichment in Cu sulphides. Pyrite is an exception in the Critical Zone. Mackinawite, as a very minor constituent of the sulphide phase, is also present (sample 12). A striking phenomenon with regard to this zone is the thick layer of norite and anorthosite (upper third of the Critical Zone), directly below the Merensky Reef, which containsonly chalcopyrite.

The Merensky Reef contains pyrrhotite as the chief sulphide, followed by pentlandite, chalcopyrite and pyrite. Cubanite and mackinawite are present only at localities where the sulphide phase is relatively Fe-rich and S-poor. The mineralogical composition of the sulphide phase of the rocks in the immediate vicinity of the Merensky Reef and of the Bastard Reef $\frac{15}{47}$ in agreement with that of the Merensky Reef.

Over the greater part of the Main Zone, chalcopyrite is the dominant sulphide mineral, followed by pyrite which is conspicuously developed in its lower parts. Pyrrhotite and very little pentlandite are also present. The uppermost pyroxenite seam in the Bushveld Complex, contains, in contrast with the surrounding anorthosites and gabbros, fairly abundant pentlandite and little chalcopyrite. The author is not so sure whether the pyrite in the upper part of the Main Zone is not a supergene alteration product of pyrrhotite. The enrichment of chalcopyrite in the upper part of the Main Zone, below the

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mineralized anorthosite, corresponds with the enrichment of the same mineral in the Critical Zone below the Merensky pegmatoid.

The mineralized anorthosite below the Main Magnetitite seam contains pyrrhotite as the most abundant sulphide mineral, followed by chalcopyrite and then pentlandite and pyrite. Peculiarly enough, cubanite js also present with pyrite. Mackinawite is only found in association with chalcopyrite. Zincblende is a common minor sulphide, whereas specks of minerals containing P. G. M. and galena (?) are very rare.

In the Main Magnetitite Seam as well as in other magnetitite seams chalcopyrite is the common sulphide. This corresponds with the findings in the (Main) Chromitite. Pyrrhotite is very subordinate. In the magnetitite seams containing feldspar laths, especially in the upper parts of those seams, chalcopyrite, pyrrhotite and bornite have been recorded (sample 134).

The normal anorthosites and gabbros of the Upper Zone are also rich in chalcopyrite, with little or no pyrite and pyrrhotite. Pentlandite is completely absent. The mineralogical composition of the sulphides in the anorthosite above the Main Magnetitite(sample 25), which is found locally south of Magnet Heights, corresponds very closely with that of the anorthosite below the Main Magnetite Seam. The troctolite seam (sisal horizon) contains pyrrhotite and pentlandite and no chalcopyrite, in contrast with the surrounding gabbro. An olivine diorite contains fairly abundant pyrrhotite and, relative to the common rocks of the Upper Zone, little chalcopyrite. The mineralized anorthosite immediately below the Uppermost Magnetitite Seam contains pyrrhotite with a few per cent of pentlandite and chalcopyrite. The horizons above the latter magnetitite become progressively enriched in pyrite and impoverished in pyrrhotite and chalcopyrite.

It is difficult to get a clue to the differentiation of the sulphides in the Bushveld Complex from fig. 8. For this reason the mean percentages of sulphides in a large number of polished sections from the main sulphidebearing stratigraphical horizons were calculated (table 21) and plotted in fig. 9.

Pyrrhotite decreases from the Basal Zone towards the Merensky Reef where it reaches the lowest percentage. Towards the Upper Zone it increases and attains a maximum in the mineralized anorthosite below the Uppermost Magnetitite Seam. Pentlandite shows a general decreasing tendency towards higher stratigraphical horizons, whereas chalcopyrite increases, except

near the roof (in the Upper Zone) of the Bushveld where it shows a sudden drop. It is perhaps noteworthy that the Skaergaard intrusion also shows an enrichment in pyrrhotite in the last rocks that crystallized (Wager et al, 1957, p. 867). In the Sudbury intrusion pentlandite and pyrrhotite decrease and pyrite increases towards higher horizons in the intrusion i.e. in the order mafic norite, felsic norite, micropegmatite (Naldrett and Kullerad, 1967, p. 507). A differentiated intrusion in Missouri also shows a decrease in pentlandite towards the top of the intrusion (Desborough, 1967, p. 608). Pyrite varies considerably. Cubanite varies sympathetically with chalcopyrite. The ore from Vlakfontein, situated in the rocks of the Basal Zone, shows no correlation with the latter as far as the mineralogical composition is concerned. The pyrrhotite is rather high and the other minerals, cubanite and chalco-pyrite, are low. The mineralogical composition of the sulphide phase of the late hypabyssal rocks and the feldspathic pyroxenite show a good correlation. The pyrrhotite percentage is high, whereas that of pentlandite and chalcopyrite is relatively low.

The effect of the differentiation is also clearly illustrated in the diagram showing the ratios of sulphide mineral $(fig. 10)$. Pyrrhotite is always higher than pentlandite with a peak value in the magnetite-bearing rocks. Up to the Merensky Reef chalcopyrite is lower than pentlandite, but exceeds the latter in the mineralized anorthosite below the Main Magnetitite Seam. The behaviour of the other minerals is clear from fig. 8.

A clearer view of the trend of differentiation is presented in fig. 11. For purposes of comparison the diagram of De Bruyn (1944, p. 86) is given in which he plotted the possible trend of differentiation of the sulphides in the Bushveld and the Insizwa ores (fig. 12). Owing to the lack of polished sections from all the stratigraphical horizons in the Bushveld Complex, his values are only partially correct. The Middellaagte ore is situated in a hortonolite dunite and is pyrrhotite-rich as discussed previously. The Insizwa oreshows an enrichment in chalcopyrite and, to a lesser degree, in pentlandite. This is not an effect of differentiation, initiated by the composition of the magma, but could be attributed to the late crystallization of the Cu-rich minerals relative to pyrrhotite and pentlandite. The same effect was observed in the Frood Mine (Sudbury) where there is, according to Hawley (1965), an enrichment of chalcopyrite in the sulphides which formed later. Hawley called this a zoning phenomenon. Veins of chalcopyrite which

Fig. 11. Plots of pyrrhotite-pentlandite-chalcopyrite ratios from different mineralized stratigraphical horizons in the Bushveld Complex, showing the trend of differentiation in the sulphides. Points LH, FP, VM, VP, U, MR, MA and MAU represent a mean value obtained from numerous polished sections from different localities (Table 21).

- LH Late Hypabyssal Rocks
- FP Feldspathic Pyroxenite, Western Transvaal
- VM Massive Ore, Vlakfontein
- VP Poikilitic Ore, Vlakfontein
- u Ultramafic Rocks of the Basal Zone.
- 17a Mineralized Pegmatoid Above Main Chromite Seam
- MR Merensky Reef
- MA Mineralized Anorthosite Below Main Magnetitite Seam
- MAU Mineralized Anorthosite Below Uppermost Magnetitite Seam

Fig. 12. The trend of differentiation of the Insizwa Ores and the possible trend of differentiation of the Bushveld ores, according to De Bruyn (1944, p. 86).

- MR Merensky Reef
- V Vlakfontein Ore
- M Middellaagte Ore (Hortonolite Dunite Critical Zone)
- 1 Disseminations in Olivine Hyperite
- 2.. Pyrrhotite-rich Ore
- 3.. Chalcopyrite Cubanite Ore

replace other sulphides, were also observed in the Vlakfontein ores. Chalcopyrite is thus clearly later than most of the sulphides.

The mineralogical composition of the Sudbury ores (fig. 13) is in close correspondence with that of the Vlakfontein ores (fig. 10). In fig. 13 the enrichment of chalcopyrite in some samples of the Sudbury ores is clearly illustrated and agrees in this respect with the ores from Insizwa (fig. 12) and Vlakfontein.

Fig. 13. Plots of pyrrhotite-pentlandite-chalcopyrite ratios of total sulphides in random samples from Sudbury: (a) Creighton mine, (b) Stobie mine, (c) Falconbridge mine, (d) Onaping Area mine. (According to Hawley, 1962, p. 117.)

From the above discussion it follows that a clear and definite differentiation trend in the mineralogical composition of the sulphide phase of the Bushveld Complex exists. The early differentiates of the layered sequence are relatively rich in pentlandite. In the later differentiates i. e. towards the top of the layered Main Plutonic Phase, pentlandite decreasesprogressively with an accompanying increase in Cu sulphide and/or pyrrhotite. The pegmatoids with massive and poikilitic sulphide in the Basal Zone and the disseminated sulphide in the pegmatoids of the Critical Zone (i.e. the hortonolite dunite, diallage pyroxenite etc.) also show an enrichment in pyrrhotite and/or Cu sulphide relative to the rocks in which they occur. The pegmatoids are considered as late differentiation products of their host-rock and the differentiation trend displayed by the sulphide phase consequently agrees with the trend of the layered rocks given above.

6. THE PHASE RELATIONSHIPS OF THE SULPHIDES AND THE ORIGIN OF THE TEXTURES

The relationships between the different minerals and the origin of the texture can be explained in terms of phase-diagrams. During the last 10 years about all the phase-relations involved in the orthomagmatic ores found in mafic and ultramafic rocks have been investigated or re-investigated in detail, especially by the Carnegie Institution. Nearly all the sulphide minerals of the Bushveld Complex should fit the system Cu-Fe-Ni-S. For reasons of simplification the phase-relations in the ternary systems Fe-Ni-S and Cu-Fe-S, or even in binary systems will be applied to the sulphides of the Bushveld Complex. The different sulphides will be dealt with in order of their relative abundance in the Bushveld Complex.

6.1 Minerals involved in the Binary Fe-S System

The relationship between pyrite, monoclinic pyrrhotite, hexagonal pyrrhotite and troilite can easily be explained by the phase-diagrams of a portion of the system FeS-FeS_2 (fig. 14).

The maximum amount of pyrite in solid solution in pyrrhotite saturated with sulphing is about 10 per cent, which will, upon cooling to 320° C, exsolve from the pyrrhotite (Naldrett and Kullerud, 1967, p. 501). The pyrite in the Bushveld ores seldom exceeds 10 per cent of the pyrrhotite and could thus have formed by exsolution from a solid solution of pyrrhotite and pyrite.

A pyrrhotite with a composition of 46. 7 atom per cent of metals or less, will upon cooling cause pyrite to exsolve along the po-py solvus, down to about 315° C where some pyrite will re-enter the pyrrhotite structure with slow cooling until the pyrrhotite has the composition $Fe_{7}S_{8}$ (i.e. 46.7) atomic per cent metals). This could account for the replacement of pyrite by pyrrhotite (photo 58). This reaction is very slow (Naldrett and Kullerud, 1967, p. 502) and is thus in accordance with the rarity of this phenomenon in the Bushveld ores. The pyrite is present mostly as euhedral, subhedral or roundish grains.

If the cooling in the case mentioned above is too fast, so that the reentering of pyrite in the pyrrhotite structure is incomplete, the pyrrhotite would have an intermediate composition between monoclinic and hexagonal pyrrhotite. Upon further cooling to below 315° C, lamellae of the one pyrrhotite phase would form in the other. The same phenomenon can of course be attain-

Fig. 14. A tentative phase-diagram of a portion of the system FeS-FeS_2 . After Desborough and Carpenter (1965, p. 1433) and Naldrett and Kullerud (1967, p. 502).

Atomic percentage of metals

- 1. Pyrrhotite metastable with 2A, 7C structure
- 2. Hexagonal pyrrhotite $(F e_9S_{10})$ with 2A, 5C structure
- 3. Monoclinic pyrrhotite (Fe₇S₈) 2B, 4C structure

ed when the initial composition of the pyrrhotite is between $\mathrm{Fe}_{7}\mathrm{S}_{8}$ and $Fe_{9}S_{10}$, when upon slow cooling all the exsolved pyrite will re-enter pyrrhotite which would also yield lamellae of the monoclinic phase in the hexagonal phase.

In the Bushveld sulphides, troilite is never found in association with monoclinic pyrrhotite or pyrite, unless supergene alteration has taken place. From fig. 14 it is clear that this is also impossible because monoclinic pyrrhotite and pyrite are separated from troilite by a field in which hexagonal pyrrhotite alone is stable. When troilite alone is found in the absence of hexagonal pyrrhotite, cubanite, and not chalcopyrite, is the stable coexisting Cu sulphide. Where lamellae of troilite were noticed in hexagonal pyrrhotite, both cubanite and chalcopyrite appear to be stable. Arnold (1958,

p220) has reported the same association.

Troilite lamellae within hexagonal pyrrhotite (the opposite was not observed in the Bushveld sulphides) exsolved from the latter, probably when the alpha-transformation took place.

A very common phenomenon during oxidation of the Bushveld pyrrhotite is the occurrence of the monoclinic phase along cracks and cleavages in the hexagonal phase (photo 4, 5, 6) or in troilite, although in the latter case hexagonal pyrrhotite is a very common, but only an intermediate product. An advanced stage of oxidation is where magnetite appears. This monoclinic pyrrhotite is explained by ordinary oxidation of the pyrrhotite as a result of supergene alteration. In heating experiments Desborough and Carpenter (1965, p. 1443) changed hexagonal pyrrhotite to monoclinic pyrrhotite and magnetite by heating the first to 600° C in air and by cooling slowly to room temperature. Naldrett and Kullerud (1967, p. 503) obtained the same results by conducting the experiment below 310° C. The monoclinic phase present along cracks in the Bushveld pyrrhotites is therefore a product which has resulted from supergene alteration rather than being due to heating. This oxidation is initially accompanied by an enrichment in sulphur. The presence of melnikowite-pyrite can be explained by the same process.

No experimental results are available about the unknown, highly anisotropic mineral, occurring as very fine lamellae parallel to the basal cleavage of pyrrhotite. It may, possibly be mackinawite.

6.2 The Pyrrhotite Geothermometer

The composition of pyrrhotite, where deposited in equilibrium with pyrite, could be a useful indicator of the temperature that existed when the assemblages was formed. This temperature is obtained from the pyrrhotitepyrite solvus, originally determined by Arnold (1958). The usefulness of this geothermometer is that the composition of the pyrrhotite can be readily determined by making use of the d (102)-line.

The pyrrhotite geothermometer has the following drawbacks, especially in the case of basic intrusives:

6.2.1 The effect of pressure on the pyrrhotite-pyrite solvus

Arnold (1957, p. 197) investigated the influence of total pressure on the pyrrhotite-pyrite solvus and found that at temperatures above 400 $^{\mathrm{O}}\mathrm{C}$ the solvus curve shifted measurably with pressure. At 600° C the effect of a dif-

ference in pressure of 1000 bars would have resulted in a difference in temperature of 50° C at a certain composition (46.40 atomic per cent Fe).

The S fugacity (S pressure) also has a measurable influence on this solvus. The change of the pyrrhotite-pyrite solvus with $\mathbf{u} \cdot \mathbf{S}$. \cdots fugacity was evaluated by Toulmin and Barton (1964). They found that the S pressure is proportional to the composition of the pyrrhotite in equilibrium with pyrite.

6.2.2 The effect of impurities

In this respect there are the elements Co, Ni, Mn and Cu which substitute Fe in $Fe_{1-x}S$. Arnold (1957, pp. 194–195) investigated the effect of Co replacing Fe in Fe_{1-x}^-S on the d(102)-value and found measurable differences where more than 2 per cent by weight of Co is accommodated in pyrrhotite. Ni could have a similar effect, according to this author.

The influence of other minerals in the assemblage would change the binary solid solution of pyrrhotite and pyrite to a ternary or even more complex system if pyrrhotite could take these minerals in solid solution. Von Gehlen et al (1961, pp. 154-155) consequently investigated the influence which chalcopyrite (a common mineral associated with pyrrhotite and pyrite) has on the $d(102)$ -value of pyrrhotite, seeing that pyrrhotite can take up 2 per cent of Cu in solid solution at 600 $^{\sf o}{\rm C}.$ Measureable differences have been reported. According to these authors zinc-blende and galena should not affect the pyrrhotite-pyrite solvus measurable. On the contrary, Fe oxides may affect the composition of pyrrhotite significantly, since pyrrhotite is very susceptible to oxidation.

As far as the orthomagmatic ores in noritic rocks are concerned, they do contain pentlandite, and according to Kullerud (1950, p. 176-177) there is a change in the composition of pyrrhotite when pentlandite is formed by exsolution. Bodies of pentlandite in hexagonal pyrrhotite, formed by exsolution, in some Bushveld ores (sample Gl-4028) were surrounded by monoclinic pyrrhotite (photo 29), which thus indicates an enrichment of S in the pyrrhotite surrounding the pentlandite.

6. 2. 3 The rate of cooling

The pyrrhotite geothermometer is based on the assumption that pyrrhotite maintained its original Fe/S ratio in the presence of pyrite, during subsequent cooling, According to fig, 14 and according to suggestions by Desborough and Carpenter (1965, p, 1446) this would only be the case where rapid cooling has taken place, which is improbable in basic intrusives. On

slow cooling exsolution of pyrite would take place, with consequent change in the composition of pyrrhotite along the pyrrhotite-pyrite solvus.

In order to determine the temperature of formation of mixtures of monoclinic and hexagonal pyrrhotite, samples of these mixtures of minerals are heated at 315° C for 0.1 hour, where both phases of pyrrhotite have the same structure (fig. 14). The composition of this phase is then determined and applied to the pyrite-pyrrhotite solvus to determine the temperature of formation. The temperature of formation of any mixture of Fe_9S_{10} and Fe_7S_8 is below 470°C. According to Desborough and Carpenter (1965, p. 1446) pyrrhotites containing S in excess of Fe_7S_8 (\pm 46.70 atom per cent Fe) do not exist in nature. In the Bushveld ores, although of a very high temperature, pyrrhotite richer in S than $Fe_{7}S_{8}$ was not observed. The pyrrhotite geothermometer is thus effective only below 470° C. In contrast with the finding of Desborough and Carpenter, of Arnold (1958, pp. 220-221) determined a pyrrhotite with a composition of 46. 40 atom per cent Fe. The only explanation for this, if we consider that the finding of Desborough and Carpenter is true, is that the cooling was rapid and that no proper exsolution of pyrite took place along the pyrrhotite· pyrite solvus.

6.3 Minerals Involved in the Fe-Ni-S System

The experimental phase relations at different temperatures will be discussed first and thereafter the textural relationships between the different minerals will be explained in terms of the experimental datal.

Kullerud (1963, pp. 175-189) investigated the phase-relations in the Fe-Ni-S system in detail up to 1100° C. At 1100° C the system is characterized by a large field of liquid immiscibility between a S-rich liquid and a more Fe-rich liquid, which occupies the central part of the system. At 1100° C the monosulphide solid solution (henceforth it will be abbreviated as mss), i.e. a solid solution between Fe_{1-x}^S and Ni_{1-x}^S , has only about 13 per cent by weight of Ni in solid solution. At temperatures below 900[°]C the monosulphide solid solution forms a complete series between Fe_{1-x}^S and Ni_{1-x}^S . The central liquid field which is now more metal-rich than the mss phase, no longer spans the ternary system. A locus of the composition of the relative metal-rich sulphides in the Bushveld Complex would lie in the field mss + liquid (L) + vapour (V) . The more S-rich ores of the Bushveld fall in the mss field. These loci were plotted on the Fe-Ni-S system (fig. 15) by making use of micrometric analyses (table 21).

On further cooling the monosulphide solid solution narrows and two phases (FeNi) $_{1-x}$ S (mss) and (NiFe) $_{3+x}$ S occur together below 862 °C. The metal-rich liquid is still present in the system at 860° C. The sulphurdeficient ores of the Bushveld would lie in the field mss + $(NiFe)$ _{3±} S_2 + V. The (NiFe) $_{3\pm x}^{}s_2^{}$ phase which exsolved from the mss, would occupy the outer rims of sulphide blebs. The S-rich ores of the Bushveld still lie in the mss field.

At temperatures below 860°C, the (NiFe) $\frac{S_{\pm X}S_{2}}{3^{+X}}$ field widens with increasing metal/S ratio. At the same time it also approaches the Ni-S boundary. The central liquid field diminishes gradually and disappears at $635\mathrm{^0C}$. At 650°C (FeNi)_{1-X}S, with about 1.0-1.5 per cent by weight of Ni and about 38 per cent by weight of S, coexists with $(NiFe)_{3+x} S_2$ and contains about 25.5 per cent by weight of S. Pyrite becomes stable at 743° C.

At 610[°]C (fig. 15) the (FeNi)_{1-x}S (pyrrhotite) phase reacts with the high-temperature, non-quenchable (NiFe) $\frac{1}{3+x}S_2$ phase to form (FeNi) $_9S_8$ (pentlandite). The pentlandite coexists with the mss in which the Ni content varies from less than 0. 5 to 40 per cent by weight. Seeing that pentlandit e has a rather large thermal expansion of the unit cell dimensions it was considered at first by Kullerud (1963, p. 189) that increasing pressure may increase the breakdown temperature. Work done by Bell et al (1964, p. 206) showed that the temperature of the reaction $Fe_{45}Ni_{4.5}S_8 \rightleftharpoons (FeNi)_{1-x}S$ (FeNi) $3+x^2$ decreases with increasing pressure and that at 25 Kb it takes place at 425° C.

At still lower temperatures pentlandite forms limited solid solutions towards the boundaries of Fe-S and Ni-S. Its maximum metal to S ratio appears at about 580 $\mathrm{^0C}.$ This is also believed to be the temperature of the maximum solubility of pyrrhotite in pentlandite. Below this temperature, pyrrhotite will exsolve from pentlandite. At the same time the pyrrhotite solid solution decreases in width and results in the exsolution of pentlandite from pyrrhotite.

At temperatures above 450° C pyrite and pentlandite cannot coexist: Below 450°C the solid solution between Fe_{1-x}^-S and Ni_{1-x}^-S is incomplete and tie-lines between pentlandite and pyrite may be possible at this temperature.

The (NiFe) $\frac{3+x}{3+x}$ high-temperature phase starts to disappear on lowering the temperature to below 550 °C, with the formation of $\text{Ni}_{3}\text{S}_{2}$ (heazlewoodite).

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- Fig. 15. The phase relations in the Fe-Ni-S system at 600° C. The composition of the sulphide phases from a few mineralized zones in the Bushveld Complex are plotted on the diagram.

Metal-rich sulphide phases

- 1. Harzburgite from Aapiesdoorndraai 298 KT, Lydenburg District.
- 2. Merensky Reef, Tweefontein 360 KT, Lydenburg District, (Dwars River)
- 3. Certain ultramafic rocks from the Western Transvaal
- 4. Certain massive ores, Vlakfontein 207 JP, Rustenburg District

Sulphur-rich sulphide phases

- 5. Merensky Reef, Rustenburg
- 6. Poikilitic ore, Vlakfontein 207 JP, Rustenburg District
- 7. Mineralized anorthosite below Main Magnetitite Seam
- 8. Late Hypabyssal rocks from the Western Transvaal
- 9. Mineralized anorthosite below Uppermost Magnetitite Seam

Applying the experimental results discussed above to the Bushveld ores, some textural phenomena between pyrrhotite, pentlandite and mackinawite can be explained: At 610 $^{\circ}$ C and at low pressures, say below 1Kb the (NiFe) $_{3+x}^{\qquad S}$ $_{2}^{\qquad S}$ phase present along the border of a sulphide bleb (in the case of the sulphurdeficient disseminated ores falling in the field mss + (FeNi) ${}_{9}S_{8}$ + V, fig 15) will react with some of the $(FeNi)_{1-x}S$ (pyrrhotite) to form pentlandite (fig. 15). This would account for the semi-zoned arrangement of pentlandite and pyrrhotite in disseminated and coarse pentlandite in S-deficient ore. This pentlandite forms grains and belongs to another generation as the pentlandite which exsolved parallel to the basal cleavage of pyrrhotite aslamellae.

Naldrett and Kullerud (1967, p. 504) determined that a locus of the composition of the ore from Strathcona, Sudbury, in the Fe-Ni-S system falls within the limits of the mss field at 600° C. They concluded that both the granular pentlandite around pyrrhotite grains and flames of pentlandite in pyrrhotite exsolved from nickeliferous pyrrhotite below 300° C. In a recent paper by Naldrett et al (1967, p. 884) they determined the pyrrhotite-pentlandite solvus accurately and deduced that in the ore from Alexo pentlandite started to exsolve between 350° C and 400° C.

The composition of certain ores from the Bushveld, e.g. the mineralized anorthosistes and ores from the Late Hypabyssal rocks, would also fall within the mss field at 600 $^{\mathrm{O}}\mathrm{C}$ (cf. fig. 15 - this was deduced from micrometric analyses of the ores). In the sulphide-rich ores of the Bushveld, the coarse pentlandite and lamellae of pentlandite which are parallel to the (0001) crystallographic directions of pyrrhotite, as well as the small roundish or irregular bodies in pyrrhotite, exsolved from the monosulphide solution. The loci of the points of the ores of the Bushveld are too inaccurate to make any definite deductions about the temperatures at which the exsolution started. The exsolution of this pentlandite took place with decreasing temperature where the pyrrhotite solid solution decreases. According to Kullerud (1956, p. 157P177) this takes place below 845° C. Owing to the exsolution of pentlandite from pyrrhotite the remaining pyrrhotite contains less Ni and more S than the original pyrrhotite. In this connection monoclinic pyrrhotite which surround bodies of exsolved pentlandite in hexagonal pyrrhotite were observed in some specimens_iores of the Bushveld (photo 29).

In the ores from Aapiesdoorndraai the pyrrhotite/pentlandite ratio is smaller than 1 and an "eutectic" relationship between the two minerals was noticed. As a result of experiments Kullerud (1956, p. 176) reported an eutectic in the binary system $\text{(FeNi)}_{15}\text{S}_{16}^{}\text{-(FeNi)}_{9}\text{S}_{8}^{}$ at 845 $^{\circ}\text{C}$. More recent experiments showed that pentlandite breaks down to pyrrhotite and (NiFe) $_{3+x}^{\vphantom{1}}$ S₂ at 610°C, as discussed above.

The mackinawite in the pentlandite (and chalcopyrite) is explained by exsolution rather than by replacement, on account of its very fine nature. A look at fig. 8 indicates that mackinawite in pentlandite is restricted to horizons below the Merensky Reef. The mackinawite in the mineralized anorthosite below the Main Magnetitite Seam is associated mainly with chalcopyrite. It appears that the bulk composition of the sulphide phase played an important role in the appearance of mackinawite. In this connection it is important to note the occurrence of mackinawite in pentlandite, in association with cubanite and troilite (i.e. S-deficient sulphides) from the Merensky Reef on Tweefontein 360 KT, Lydenburg District, (Dwars River area), whereas at certain other occurrences of the Merensky Reef which were investigated, no mackinawite was observed. In general more S-rich minerals were then developed (e.g. pyrite, hexagonal pyrrhotite, chalcopyrite, etc.) The sulphide phase in the zones below the Merensky Reef is also metal-rich, where mackinawite is present, e.g. the ores from Aapiesdoorndraai 298 KT, Lydenburg District and Vlakfontein 207 JP, Rustenburg District, (fig. 15).

Seeing that mackinawite appears only on the lower horizons of the Bushveld, total pressure could also have played a role. The total pressures at the stritigraphical horizons under discussion would be in the vicinity of 3 to 5 Kb. According to the experimental results the maximum solubility of Fe_{1-x}^S in pentlandite, although rather small, is at 580° C. Below this temperature Fe_{1-x}^S would exsolve from pentlandite. This phenomenon was observed in some pyrrhotite-pentlandite ores e.g. by Ervamaa (1962, p. 51) and also in some meteorites (Sztrokay, 1960, p. 1288). Instead of pyrrhotite mackinawite could have exsolved from pentlandite below 580° C. Pressures of 4 Kb, on the Basal and Critical Zones, reduce, the breakdown temperature of pentlandite from 610°C to approximately 580°C where $\text{Fe}_{1-\text{X}}$ S has its maximum solubility in $(FeNi)_{9}S_{8}$. At lower pressures the temperature of formation of pentlandite is higher and the solibility of Fe_{1-x}^S in pentlandite smaller. Conditions of this nature existed on the higher stratigraphical horizons of the Bushveld Complex.

The large quantities (up to 70%) of mackinawite in the pentlandite from the Vlakfontein deposit is difficult to explain in terms of the experiments done so far.

It has already been pointed out that mackinawite is present in pentlandite only when in association with metal-rich and S-deficient minerals. It is interesting to note that the loci of the composition of these ores on the Fe-NiS system (deduced from micrometric analyses)^{{"}
which mackinawite is found in pentlandite, fall in the field mss + pentlandite + vapour (fig. 15). The loci of the compositions of the ores in which no mackinawite is present in the pentlandite fall in the mss field. From this it may be deduced that mackinawite exsolved only from those pentlandites that originate by reaction between the $(\mathrm{NiFe})_{3\times} \mathrm{S}_2$ phase and $(FeNi)_{1-x}S$. The pentlandite which exsolved from the mss phase contains no mackinawite. The composition of the ores from Strathcona also falls in the mss field. The pentlandite in those ores contains no mackinawite, according to the description by Naldrett and Kullerud (1967, p. 495-506).

The loci of the composition of the Bushveld ores on the Fe-Ni-S system (fig. 15), deduced from micrometric analyses, are however not very accurate and chemical analyses of the sulphide phase should be plotted instead. In the case of the massive ore from Vlakfontein a volumetric and a partial chemical analysis of pyrrhotite (given by Wagner, 1924) were used.

6.4 Minerals involved in the Cu-Fe-S System

Yund and Kullerud (1966, pp. 454-488) summarized the phase relations in the Cu-Fe-S system which exist up to 700 $^{\mathrm{o}}$ C. Only those phaseswhich are of importance in the Bushveld Complex will be discussed in the section below.

Above 739[°]C chalcopyrite and pyrite invert to Fe-rich chalcopyrite, a Cu-rich pyrrhotite and a S-rich vapour. The latter relation is clearly illustrated in the diagram (fig. 16) of Roseboom et al (1958, • p. 224).

The pyrrhotite in equilibrium with chalcopyrite has a maximum of 4, 3 per cent by weight of Cu in solid solution at 700° C. The pyrrhotite in equilibrium with chalcopyrite + bornite is more metal-rich but contains only 2 per cent by weight of Cu in solid solution.

At temperatures below 700° C chalcopyrite is isometric and inverts very quickly to tetragonal chalcopyrite (with maximum S) at 547° C (fig. 18). Pressure has an marked influence on the transformation; at 40 Kb the transformation takes place at 400° C (Kullerud et al, 1965, p. 197).

Fig. 16. A part of the solidus in the system Cu-Fe-S.

The lowest temperature at which solid solution between chalcopyrite and cubanite is possible is between 500 $^{\mathrm{O}}\mathrm{C}$ and 600 $^{\mathrm{O}}\mathrm{C}.$ At 500 $^{\mathrm{O}}\mathrm{C}$ a miscibility gap exists and both cubanite and chalcopyrite are stable (fig. 18). Two transformations in cubanite were recorded. Isometric cubanite inverts to tetragonal cubanite very rapidly at 252° C. The latter inverts to the orthorhombic form 0 , **p**, i i , i at \pm 213[°]C. Pyrite_t cubanite are stable only above 328[°]C. Below this temperature tie-lines are installed between chalcopyrite and pyrrhotite as indicated in fig. 17. The fields that are occupied by chalcopyrite, cubanite and pyrrhotite decrease considerably at temperatures below 500 $^{\mathrm{O}}$ C, and result in the exsolution of bornite (photo 93) or cubanite and also of pyrrhotite below 334° from chalcopyrite, chalcopyrite and pyrrhotite from cubanite, and chalcopyrite or cubanite $(?)$ from pyrrhotite (fig. 17). The exsolution relationships between chalcopyrite and cubanite are also clearly illustrated in fig. 18.

In applying the phase-relations at elevated temperatures, discussed above, to the natural occurrences of sulphides in the Bushveld Complex most of the mineral assemblages and textures can be explained: The "eutectic" relation between chalcopyrite and pyrrhotite (photo 45) originated by the crystallization of chalcopyrite and pyrite at the eutectic point (fig. 16) from a Cu-rich pyrrhotite (monosulphide solid solution) in the presence of a vapour at 739° C.

It is suggested that the regular polysynthetic twinning of chalcopyrite (photo (photo 51) originated during the inversion of cubic chalcopyrite to tetragonal chalcopyrite at temperatures between 547° C and 400° C, but depends on the pressure. The grid-twinning on (110) (photo 50) could be the effect of deformation. In accordance with this surmise, the latter type of twinning was observed more frequently, but not exclusively, in ores which have suffered deformation,

Fig. 17. A part of the Cu-Fe-S system at 200^oC. (After Yund and Kullerud, 1966, p. 473).

c - cubic modification

t - tetragonal modification

o - orthorhombic modification

e.g. the ore from Vlakfontein, whereas the regular polysynthetic twinning is present mainly in undeformed ore, (e.g. the ore from the Merensky Reef). The polysynthetic twinning in deformed cubanite from Vlakfontein is probably also due to deformation. An example in which the orthorhombic-tetragonal inversion did not take place properly is from the Mooihoek pipe (photos 52, 53, 54) where lamellae of orthorhombic cubanite parallel to (110) and (001) are found in tetragonal cubanite (less anisotropic than the former).

If the composition of the Cu sulphide lies much more towards the pyrrhotite side in the solid solution field of chalcopyrite, i.e. above + 540° C, then massive cubanite would form, otherwise the lamellar cubanite exsolves from chalcopyrite parallel to (111) .

At 328[°]C tie-lines are installed between a rather S-rich chalcopyrite and pyrrhotite (fig. 17). On lowering the temperature to below 328° C any decrease of temperature would reduce the size of the chalcopyrite field, which will then result in the exsolution of pyrrhotite as lamellae along (111) of chalcopyrite or as roundish bodies. It is suggested that lamellae of

mackinawite along the same crystallographic direction of chalcopyrite could have originated under the same conditions but perhaps under different conditions of pressure.

Cubanite is stable together with pyrite above 328° C. At this temperature the reaction cubanite + pyrite \implies pyrrhotite + chalcopyrite takes place. Examples in which this reaction did not take place completely are from the mineralized anorthosite below the Main Magnetitite Seam north-west of Pretoria, where cubanite is found in association with pyrrhotite, chalcopyrite and pyrite.

Cubanite also exsolves from chalcopyrite below \pm 540 $^{\mathrm{O}}$ C. Seeing that tie lines exist between cubanite and pyrrhotite below temperatures which varies between 500 $^{\mathrm{o}}$ C and 600 $^{\mathrm{o}}$ C, exsolution of mackinawite (which was very frequently observed in some sulphides of the Bushveld - photos 55, 57), is possible below these temperatures. This takes place when the cubanite ffeld diminishes in size with lowering of temperature. The reason why mackinawite and not pyrrhotite exsolved is not known, although pressure may have perhaps have played a role. If the composition of the sulphide phase is metal-rich,mackinawite is frequently observed, e.g. in the ores rich in cubanite, from Vlakfontein.

At 700° C + 4.25 per cent by weight of Cu can be in solid solution in pyrrhotite. This Cu may account for the chalcopyrite which would exsolve at lower temperatures from pyrrhotite. This chalcopyrite is present as round or euhedral bodies or as lamellae parallel to the pyramidal plane of pyrrhotite. Chalcopyrite veinlets along the borders of deformed lamellae of pyrrhotite (photo 48) could also have originated by exsolution from the pyrrhotite during and/or after deformation. These bodies of exsolved chalcopyrite are found only in the monoclinic and hexagonal pyrrhotites. S-poor pyrrhotite takes much less Cu in solid solution.

Chalcopyrrhotite could not be synthetized by Yund and Kullerud (1966) below 700 $\mathrm{^0C}.$ The temperatures were perhaps still too low. The two authors mentioned stated that chalcopyrrhotite and isometric cubanite can be the same mineral.

A feature that is difficult to explain is the replacement of various other minerals by chalcopyrite and/or by cubanite. In the Vlakfontein ores pentlandite is impregnated with chalcopyrite along cracks, cleavage directions and along (001) (photo 43). This small-scale replacement always takes

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place in the vicinity of massive cubanite. It is suggested that on lowering of the temperature, chalcopyrite which exsolved from cubanite impregnated the pentlandite and the material in the immediate vicinity.

In the Bushveld Complex valleriite is a secondary mineral, and is found only in the presence of serpentine. The analyses of "pure" valleriite from Kaveltorp, Sweden and from Phalaborwa, South Africa, show $MgO, A1\over 2O_3$ and H_2 O as additional components. As mentioned previously (p. 78) Evans et al (1964) concluded that an unidentified Mg hydroxide phase is interlaminated with the $CuFeS₂$. While heating natural valleriite, Yund and Kullerud (1966, p. 482) found that high pressures, probably due to the breakdown of the hydroxyl phases, developed when the valleriite was heated above 500°C . The valleriite of the Bushveld ores are generally interlaminated with serpentine.

6.5 The Origin of Zinc-blende and its Unsuitability for Geothemometry in the Bushveld Complex

In the sulphides of the Bushveld sphalerite is always associated with chalcopyrite and seldom with cubanite. It takes the form of small bodies or stars due to exsolution. Even if zinc-blende is present in pyrrhotite it is nevertheless found in the vicinity of chalcopyrite. Bodies of chalcopyrite due to exsolution_t inc-blende are a very common phenomenon (photo 95), even sphalerite within pyrrhotite contains chalcopyrite in some places.

At 547° C tetragonal chalcopyrite inverts to cubic chalcopyrite and at $600\mathrm{^oC}$ almost 40 per cent of CuFeS₂ dissolves in ZnS (Kullerud, 1956, p. 180). Zinc-blende is present in such small quantities that it is considered to have been in complete solid solution with chalcopyrite at high temperatures and therefore exsolved upon cooling. The solubility of ZnS in pyrrhotite is negligible (Kullerud, 1953).

Very little material was available for X-ray investigation and consequent ly no accurate determinations of the Fe content were possible which could be applied to any solvus curve, used as a temperature indicator. A microprobe would solve the problem.

The variation of the Fe content of (Zn, Fe)S was investigated only where the mineral is in the presence of pyrrhotite and pyrite (Kullerud, 1953, Barton and Kullerud 1958, Barton and Toulmin 1966, Boorman 1967). The effect of chalcopyrite, cubanite and pentlandite on the temperature indicator curves were not investigated. Seeing that these minerals are very

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weight per cent As

commonly associated with zinc-blende in the Bushveld, those curves would not be of any value.

6. 6 The Arsenide Minerals

Some of the textures displayed by the arsenide minerals in the Bushveld Complex can be explained by means of the experimental results obtained in a part of the binary system Ni-As, given above in fig. 19.

A liquid in coexistence with vapour having a composition between $\frac{Ni}{11}As_{8}$ and NiAs, would start to crystallize between 962[°]C and 829[°]C with the exsolution of niccolite ($Ni_{1+x}As$). At 829[°]C the niccolite reacts with

the liquid to produce maucherite. Generally speaking, an excess of niccolite is present in the ores of the Bushveld and not all the niccolite has reacted with the liquid. These replacement-textures of niccolite by maucherite are very common (photo 86). From fig. 19 it is also clear that the composition of niccolite may vary considerably at higher temperatures (at 800 $^{\circ}$ C from 55.4 to 57.2 per cent by weight of As). The Ni $_{1+\mathbf{\chi}}^{\mathbf{A}\mathbf{S}}$ - NiAs $_{2}$ solvus has a slope and thus at lower temperatures the composition range of niccolite decreases with the resulting exsolution of rammelsbergite. In the Bushveld Complex tammelsbergite is in close association with niccolite. If any S is present gersdorffite will crystallize which could then account for the zoned arrangement of the gersdorffite and the niccolite. Sb preseni at that stage would result in the development of ullmannite.

Another possible explanation of a rim of gersdorffite surrounding niccolite is given by Hawley (1962, p. 78) where he mentions the results of experiments carried out by A. Y. Smith, who heated niccolite in close contact with pyrrhotite at 750 $^{\circ}$ C for 18 hours in a current of $\rm H_2^{\,}S.$ The niccolite was converted to irregular grains of gersdorffite along the grain boundaries. To explain the pseudo-eutectic intergrowth of maucherite and pyrrhotite in the Sudbury ores, also displayed by the sulphides from the Vlakfontein Nickel Deposts (photo 85), Hawley et al (1961, p. 547) suggested the breakdown of ferroan gersdorffite according to the formula.

11 Ni_(1-y)Fe_yAsS \rightleftharpoons (1-y) Ni₁₁As₃ + 11y FeS + (3+8y)As

ferroan gersdorffite maucherite pyrrhotite This reaction was also determined experimentally by A. Y. Smith.

The age relationship between the arsenides and the sulphides is very difficult to establish. It is suggested that the ars enides crystallized before the sulphides, seeing that most of the textures (such as the euhedral form of gersdorffite) favour this assumption. The high temperatures of crystallization of the arsenides also support this idea. In the ore from Vlakfontein the arsenides are found in contact with the early euhedral silicates. The latter could have acted as nuclei for the early crystallization of arsenides in a sulphide liquid which may have been partially solidified as a monosulphide. In the Lainijaur deposit, however, Grip (1961, p. 47) consideres the arsenides as definitely later than the sulphides.

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Another difficulty to overcome is the crystallization of arsenic-rich minerals (maucherite and niccolite) in the place of sulpharsenides at a low As and high S pressure. An explanation for this phenomenon could be that Ni is much more arsenophile than sulphophile, Ni is quite siderophile and As has more metallic properties than S, which could then explain the formation of Ni arsenides in the presence of S.

6.7 The Paragenetic Differences in the Pyrrhotite, Pentlandite and Chalcopyrite Ore from Volcanic, Hypabyssal and Plutonic Rocks

The textures displayed by the ores which crystallized under volcanic, hypabyssal and plutonic conditions show remarkable differences, especially as far as the degree of unmixing of the minerals is concerned. The conditions responsible for these differences are temperature, pressure and rate of cooling. Ervamaa (1962) already drew attention to the differences between the ores crystallizing under volcanic and under hypabyssal conditions,

The only example in the literature of ore which crystallized under almost volcanic conditions, is the ore from the Igdlukunguaq basaltic "dyke" de*ti* scribed by Pauly (1958), The best example of a nickeliferous pyrrhqte ore which crystallized under hypabyssal conditions, is from the Petolahti diabase described by Ervamaa (1962). The Bushveld Complex, Sudbury and Insizwa serve as examples in which the ores originated under plutonic conditions.

The major differences between the ores are given in table 22. The solid miscibility of pyrrhotite, pentlandite and chalcopyrite has been considerably more extensive in the case of the Igdlukuguaq deposit, than in the Petolahti diabase or in the plutonic rocks; in the latter the miscilibility was incomplete .

In the case of the Igdlukunguaq basaltic "dyke" the miscibility between the different sulphide phases was almost complete according to Pauly (1958). A great deal of the exsolution started at a relative high temperature, namely at 858 $^{\mathrm{o}}\mathrm{C}$ at which chalcopentlandite exsolved to form rims around the pyrrho tite crystals. Chalcopyrite exsolved in addition along certain crystallographic directions in pyrrhotite. According to the recent experimental data of Naldrett et al (1967) , the temperatures quoted by Ervamaa (1962) and by Pauly (1958) may be optimistic.

In the Petolahti diabase the mix-crystals of the sulphides were not so extensively developed as in the Igdlukunguaq "dyke" case, especially in certain

Table 22. A comparison of the textures of the sulphides from the volcanic Igdlukunquaq "dyke", the hypabyssal Petolahti diabase and the plutonic Bushveld, Sudbury and Insizwa intrusions compiled from data given by Pauly (1958), Ervamaa (1962), Hawley (1962) and Scholtz (1936).

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parts of the ore-body. According to Ervamaa (1962, p. 75) only a little unmixing started at 850° C, with the exsolution of chalcopentlandite. Chalcopyrite separated mainly at lower temperatures. Pentlandite also separated as flames in the pyrrhotite at relative low temperature. Ervamaa (1962, p. 63) explained the zoned arrangement of the sulphides by the almost complete separation of the components exsolved from the mix-crystals, with pyrrhotite in the centre. Although he attributed this type of texture mainly to the order of crystallization of the sulphides, namely pyrrhotite, pentlandite chalcopyrite, this is not strictly correct, because pentlandite does not exist above 610°C (at rather low pressures) at which temperature it changes to heazelwoodite and pyrrhotite. Not enough is known about the chalcopyrite solid solution above 700° C to speculate on the order of crystallization of the minerals.

In the plutonic rocks the ores display a much .more simple textural relationship. This is mainly due to the fact that the temperature was not so high and the formation of a complete, or nearly complete solid solution of the sulphides has not been possible. The intergrowth of mackinawite and pentlandite in the Bushveld and at Insizwa poses a problem. It could however be explained by higher pressures and more metal-rich ores in the intrusions mentioned previously.

The rate of cooling has also played an important role. Hewitt (1938) cooled an ore, composed of pyrrhotite and chalcopyrite, rapidly and found lamellae parallel to (0001) of pyrrhotite. This illustrates that the rate of cooling in the case of the Igdlukunguaq and Petolahti intrusions, with their extensive lamellae of chalcopyrite in pyrrhotite, was much more rapid than that of plutonic ores where lamellae of this nature are a very rare phenomenon. The chalcopyrite dissolved in the pyrrhotite $(+ 12$ per cent at 700°C , according to Yund and Kullerud 1966) has a much greater chance to exsolve as discrete grains than as lamellae. Grains of chalcopyrite in the pyrrhotite from the Bushveld are a common feature. Ervamaa (1962, p. 46) pointed out that exsolution lamellae of pentlandite parallel to (0001) , segregated mainly towards i**s**
-the grain boundaries of pyrrhotite, or towards points where pyrrhotite_iad jacent to a grain of free pentlandite. In the case of the latter type the exsolved pentlandite, is often so abundant in the ores from the Petolahti diabase that it is difficult to distinguish the boundary of the grains of original pentlandite. In the Bushveld ores the same tendency has been observed, but to a

lesser extent. As a matter of fact, pentlandite flames parallel to (0001) of pyrrhotite are rarely found in grains of pyrrhotite they are all scattered along cracks and grain boundaries. Rapid cooling of the Petolahti diabase contributed to the fact that diffusion of pentlandite towards the grain boundaries of pyrrhotite was interrupted and a considerable portion of the pentlandite remained in the pyrrhotite grains as bodies resulting from exsolution. (40 per cent of pentlandite compared with the Bushveld's 5 per cent table 22.)

No experimental work has been done recently on mix-crystals of pentlandite and chalcopyrite at temperatures above 700 $^{\mathrm{O}}\mathrm{C}$ and any discussion on this aspect would be too speculative.

7. THE SULPHIDE BODIES IN THE BASAL ZONE, WITH SPECIAL REFERENCE TO THE VLAKFONTEIN NICKEL DEPOSITS

Sulphide bodies are a very common feature of the Basal Zone in the Western Transvaal and also of the separate basins of mafic and ultramafic rocks north of Groot Marico. In the Potgietersrus area sulphide bodies are found in the rocks of the Basal Zone - judging from the presence of gossan, whereas in the Eastern Transvaal only one gossan dyke is known from Aapiesdoornddraai 298 KT, Lydenburg District, The sulphide bodies are mostly intimately associated with pegmatoid (coarse grained norite-pyroxenite) which may be free of sulphide in some places. These pegmatoids resemble the pegmatoid bodies of diallage pyroxenite, dunite or hortonolite dunite, situated in the Critical Zone and in the Lower part of the Main Zone or in the magnetite plugs and bodies in the Main and the Upper Zone.

7.1 The Host-rock of the Sulphide Bodies and the Pegmatoids

In the Western Transvaal the sulphide pegmatoids are mainly found in a zone ± 600 to 1500 feet above the Late Hypabyssal norite or ± 4300 feet below the Main Chromitite Seam. The host-rock of the sulphide pegmatoids is a feldspathic pyroxenite and pyroxenite with two groups of serpentinized harzburgite interbedded with the pyroxenite. Layers of anorthositic norite are also developed particularly towards the top of the zone which contains most of the sulphide bodies. Above this zone in which the sulphide pegmatoids are prominent, the rocks consist mainly of pyroxenite and two groups of layers of harzburgite with an occasional (sulphide) pegmatoid. According to N. D, Harte (oral communication) a histogram of the number of pipes found on a certain stratigraphical horizon, revealed that most of the pipes are associated with the two groups of harzburgite layers. According to the mapping of C. Vermaak, harzburgite and pyroxenite are extensively interbedded with each other. The sulphide bodies often cut across the layered rocks and consequently the immediate rock types are harzburgite, pyroxenite or norite. From Schwellnus' (1935, p. 15-28) description of some of the ore-bodies and also from description of bore-holes on the No. 27 ore-body (logged by C. Vermaak) it appears as if the main host-rock is pyroxenite and harzburgite with norite as subordinate.

7. 2 The different Types of Ore

In general four types of ores, associated with and genetically related to the sulphide pegmatoids, have been recognised:

- 1. Disseminated ores
- 2. Sulphide-bearing (noritic or pyroxenitic) pegmatoid.
- 3. Massive ore
- 4. Poikilitic ore

Granite pegmatoids have no genetic relation to the ore and are of somewhat later age.

7. 2. 1 Disseminated Ores

Disseminated sulphides in the layered rocks of the Basal Zone are a very common phenomenon and will be fully discussed in the following section $(p, 1,38)$. In the vicinity of some sulphide bodies the disseminated sulphides increase towards the body. They remain interstitial to the silicates. The disseminated ore consist mainly of pyrrhotite, pentlandite, chalcopyrite and mackinawite. Graphite and arsenide minerals in the immediate vicinity of the sulphide bodies are a common feature (samples Vl. 35, Vl. 96, Vl. 94).

7. 2. 2 Sulphide-bearing (Noritic or Pyroxenitic) Pegmatoid

At some places this type of rock carries no disseminations of sulphide and grades into massive or poikilitic ore. The rock consists mainly of coarse-grained pyroxene, anhedral plagioclase, clusters or flakes of biotite and crystals of chromite:... : A, pegmatoid in which the pyroxene crystals exceed 12 cm in length is intimately associated with the massive sulphide of the No. 1 ore-body. According to Schwellnus $(1935, p. 17)$ these pyroxene grains enclose or surround some sulphides, indicating the later introduction of the pegmatoid.

7.2.3 Massive Ore

The massive ore is composed entirely of sulphides. Pyrrhotite showing slickenslides and deformation effects $i₄$ very common. The grain size of the pyrrhotite varies from a tenth of a millimetre to several centimetres in diameter, depending mainly on the effect of deformation. Pentlandite is present mainly as clusters. Very little exsolution of pentlandite parallel to (0001) of pyrrhotite has taken place, roundish or irregular blebs are the most common type of exsolution. Chalcopyrite and cubanite are present in rather small amounts and are interstitial to the pyrrhotite and pentlandite. A replacement relationship of the Cu-bearing sulphides, especially cubanite, to the other sulphides is often observed.

In the massive ore from Vlakfontein mackinawite is the most frequently developed of all the Bushveld ores and constitutes up to 70 per cent of the pentlandite. Other opaque minerals include arsenides,, mostly maucherite, and early chromite crystals which have a brecciated appearance. The latter chromite may be situated in undeformed pyrrhotite, implying that brecciation took place during

Silicate minerals, mainly serpentine, are found in some specimens in the massive ore. Serpentine veins, with or without valleriite, traversing the massive ore, occur frequently.

Veins of massive chalcopyrite (samples Vl. 5, Vl. 133), several centimetres wide, are found in the No. 4 ore-body on the edge of the pipe. The chalcopyrite clearly replaces and resorbs the pyrrhotite. Chalcopyrite which replaces pyrrhotite along cracks and along the basal cleavage in the massive ore from the No. 1 shaft, should also be mentioned (photo 124).

The contact between the massive ore and the country-rock is usually sharp. Poikilitic ore forms an outer zone, a few centimetres to several metres in thickness, surrounding the massive ore (photo 115, 116). The relation between the poikilitic ore and the massive ore is always gradational within a distance of less than 3 cm. Sharp contacts have been observed, indicating the "intrusion" of the massive ore into the poikilitic ore. The massive ore then always shows deformation structures and it is difficult to make any deduction one way or the other.

7.2.4 Poikilitic Ore

This is the main ore-type in the sulphide pegmatoids in the Western Transvaal and it may constitute 80 per cent or more of the ore in a single body. It is a peculiar ore, with massive sulphide forming the ground-mass in which euhedral crystals of pyroxene or olivine are scattered. The pyroxene crystals vary in size and are 1-15 mm long and 1-3 mm in width. A variety with orthopyroxenes up to 4 cm in length is also known (sample Vl. 92). The pyroxene crystals are always somewhat rounded (photo 112) and orientated crystals are occasionally met with, indicating a certain amount of flowage (photo 114), Although the rock exhibits a fine-? or medium-grained texture, some samples were found which contain pyrrhotite crystals up to 8 cm in diameter.

The poikilitic ore containing olivine crystals (photo 113) is actually exceptional and is present in the Rock Shaft (lB Ore Body) on the 300 feet level. The olivine consists of euhedral crystals, but is replaced by pyrrhotite (photos $113,109$, 110 , 111). The sharp terminations and straight edges of the euhedral olivine are clearly visible in the hand-specimens (photo 113). The olivine is replaced by two phases of pyrrhotite:

- 1. Massive pyrrhotite
- 2, "Colloidal" pyrrhotite

7.2.4.1 Massive Pyrrhotite. This pyrrhotite forms embayments in the olivine and is in optical continuity with the massive pyrrhotite of the ground-mass in which the olivine is situated.

7.2.4.2 "Colloidal" Pyrrhotite. This type of replacement is also visible macroscopically along the margins and cracks of the olivine grains (photos 113, 109, 110, 111). In places this reaction zone is 4 mm wide and small olivine grains are completely replaced by colloidal pyrrhotite. The colloidal nature of this pyrrhotite is clearly visible under oil immersion at .:!:_ 250 magnifications (photo 110). Mackinawite is also a minor replacement product, especially, but not necessarily, in the vicinity of chalcopyrite. An X-ray investigation was carried out with the aid of a Guinier camera on this replacement phase. Only lines of pyrrhotite and olivine were recognised, the latter with a very low intensity. Although the optical properties of the replacement product resemble those of marcasite, no lines of marcasite could be identified. Lines of magnetite and spinel are also absent.

A noteworthy phenomenon in the olivine-bearing poikilitic ore is that a pyroxene-bearing poikilitic ore, with rather fine-grained orthopyroxene, is intrusive in the olivine-bearing type (photo 113). Furthermore, it would appear that the olivine is replaced only by colloidal pyrrhotite on those sides where the pyroxene-bearing poikilitic ore is in contact with the olivine-bearing poikilitic ore. At places the pyroxene-bearing ore is in direct contact with the replaced olivine or the massive sulphides which belong to the latter type of ore. It thus appears as if the olivine was replaced by a phase (S vapour or FeS) derived from the pyroxene-bearing poikilitic ore. The composition of the colloidal pyrrhotite was found to be the same as that of the pyroxene-bearing poikilitic ores (determined by means of the $d(102)$ method and with the aid a Guinier camera in the 45° position).

The composition of the olivine in the poikilitic ore was determined by means of the method suggested by Smith and Lambor (1964) and was found to be 65 mol per cent Fe. According to Schwellnus (1939, pp. 15-24) the composition of the olivine in the layered harzburgites found in situ in the pipes is

above 80 mol per cent Fo in all cases. The composition of the olivine in these pipes is then more or less the same as that of the pipes of hortonolite dunite and wehrlite from higher stratigraphical horizons (Critical Zone). The composition of the pyroxene in the sulphide pipes is of the order of 70-78 mol per cent En, whereas the composition of the pyroxene from the host-pyroxenite, harzburgite and norite varies between 83 and 88 mol per cent En (data from Schwellnus, 1939, p. 90-91). Thus the pyroxenes from the sulphide bodies are more Fe-rich than those from the surrounding host-rock. The composition of the plagioclase in the pegmatoid bodies varies between 7 5-85 mol per cent anorthite whereas that of the plagioclase in the norite surrounding the bodies is above 90 mol per cent. An. The plagioclase of the pegmatoid bodies is thus more alkali-rich than that of the surrounding rocks. Schwellnus (1936, pp. 91-94) declared that the only layered rocks which have the plagioclase and pyroxene with a corresponding composition are the rocks which crop out at the base of the Basal Zone in the Wes tern Transvaal.

The sulphides are the same as those of the massive ore, namely pyrrhotite, pentlandite, chalcopyrite, cubanite and mackinawite. Other opaque minerals are the arsenides (niccolite, gersdorffite and maucherite), chromite and graphite. The silicate crystals are situated in grains of pyrrhotite, $+2 \text{ cm}$ in diameter and form a typical poikilitic texture. The pentlandite and chalcopyrite are arranged as grains surrounding the silicates. The arsenides (0.1-2 mm in diameter and usually visible with the naked eye) are in general also found in contact with the silicates. Chromite of a definite later generation than the brecciated chromite in the massive ore, crystallized in regular or irregular zones (tenths of a millimetre thick), also surrounding the silicates (photo 100), or seggregated as discrete grains $+8$ mm in diameter (photo 106) with the silicates (mostly pyroxene) in an ophitic or subophitic relationship towards the chromite (photo 105, 106). Anhedral grains of chromite of a late generation, \pm 0.1 mm in diameter, are a common phenomenon.

Inclusions of norite were observed. They have a more or less roundish shape, with a diameter of $3 + 1$ cm, and are situated in the poikilitic ore. Arsenide grains generally surround these inclusions. The composition of the pyroxene in the inclusion is 74 mol ner cent En and of the plagioclase 78 mol per cent An and thus also corresponds with that of the minerals in the rocks which crop out at the base of the Basal Zone in the Western Transvaal.

The contact between the poikilitic ore and the host-rock is usually gradational over less than 3 cm (photos 117 , 118) with a finer-grained variety of poikilitic ore developed on the contact.

7.3 The Volumetric Composition of the Different Types of Ore in Relation to the Sulphide Phase of the Host-rock

The composition of the sulphide phase varies considerably from specimen to specimen of the same ore-type. Therefore the mean volumetric composition, as derived from several polished sections (20 or even more) are given in table 23, below.

The composition of the sulphide phase of the massive ore differs from that of the poikilitic ore mainly in a higher percentage of pyrrhotite and a lower percentage of chalcopyrite and pentlandite. Although it appears from table 23 that mackinawite is in general more prominentely developed in the massive ore than in the poikilitic ore, this is not necessarily the case (fig. 20), Maucherite and the other arsenides appear in greater quantities in the poikilit· ic ore. On the other hand, graphite was more generally observed in the massive ore.

By comparing the olivine- and orthopyroxene-bearing poikilitic ore from the Rock Shaft, it is quite clear that pyrrhotite is present in smaller amounts in the pyroxene-bearing ore than in the olivine-bearing ore. Pentlandite, chalcopyrite and arsenides are present in larger percentages in the ore type mentioned first than in the latter.

A correlation of the massive ore and the poikilitic ore with the disseminated sulphides in the adjacent host-rock, i.e. harzburgite and pyroxenite (table 23) reveals that the massive and poikilitic ores are more pyrrhotiterich whereas the disseminated sulphides have a higher percentage of pentlandite. However, the total Fe sulphide in the harzburgite (72. 7 per cent) is exactly the same as the total quantity of pyrrhotite in the poikilitic ore. The total percentage of Cu sulphide in the poikilitic and the disseminated sulphides are more or less the same. The massive ore has a rather low content of Cu sulphide. The correlation between the ores in the pegmatoids and the disseminated sulphides in the feldspathic pyroxenite and in the Late Hypabyssal rocks is quite good, if pyrite is taken as pyrrhotite. The last two rock-types; are from stratigraphical horizons 500 feet below the bottom of the sulphide pipes in the Vlakfontein mining-area. Other ore-bodies. for example No. 27, may be even 200 feet above this feldspathic pyroxenite.

Table 23. Volumetric composition of the sulphide phase of the various oretypes in the sulphide pegmatoids on Vlakfontein 207 JP, Rustenburg District, and the disseminated sulphides in the layered hostrocks in which the pegmatoids are situated.

Table 24. The volumetric compositions of massive ore, poikilitic ore and disseminated sulphides in the pyroxenite near the contact of an ore-body with the host-rock.

Fig. 20. Bore-hole DD 1/27 shows the relationship between the different ore-types and the country-rock in a part of the No. 27 ore-body. Volumetric compositions of the sulphides, Cu-Ni analyses and Cu/Cu+Ni ratios are also given.

Poikilitic Sulphide

Massive Sulphide

. Pyroxenite Feldspathic in places

%) Dots are Sulphide .
 Disseminations

 \rightarrow

 λ $\,$

Cu Mean Cu+ Ni Ratio Massive ore 0.13

Poikilitic ore 0. 28

filII] Harzburgite

 $\sqrt{\frac{1}{2}}$ Pegmatite

The feldspathic pyroxenite is mineralized to a fair extent at its top and this mineralized zone may be up to 150' thick in places.

The sulphide pegmatoids are zoned. A marked increase in the quantity of the Cu sulphides was noticed towards the marginal zones of the pegmatoids with the country-rock (fig. 20, table 24). These zones, richer in Cu sulphide, are between 1 cm and several meters thick. In addition to this, the disseminated sulphides in the host-rocks are also richer in Cu sulphide in the immediate vicinity (2 cm to $+$ 5 meters) of the sulphide pegmatoids. Farther away the composition of the sulphide phase in the host-rock is again the normal of the rock. In many places the outer zone of a body of massive sulphide consist of a zone of poikilitic ore, 1 cm to $+3 \text{ meters}$ thick. This poikilitic ore is al ways richer in Cu sulphide than the massive sulphide (table 24), Fig. 2 O shows the tendency for the enrichment of Cu sulphides on the borders of the pegmatoid - samples V1. 146 and V1. 152. The enrichment of Cu in the pegmatoid is illustrated by sample V1. 155, fig. 20 and samples V1. 94 and V1. 96, table 24. Farther away the composition of the disseminated sulphide is normal to that of the rock type $-$ sample 161, fig. 20.

7.4 The Structure of the Sulphide Pegmatoid

The structure of the bodies of sulphide pegmatoid is generally pipelike. They cut vertically across the layering of the host-rocks and may be up to 400 feet in length (fig. 21, 22). They definitely disappear at depth. They are roughly circular in plan (fig.21), although at some depths they may be elongated along an east-westerly axis. This was especially the case with the No. 1 body (fig. 21 - plan 300' level) and the No. 3 ore-body (fig. 23), in which the massive sulphide core is elongated along an east-west axis (Schwell nus, 1935, p. 15, 24, 26). A small vertical vein of sulphides about 150 feet away from the No. 1 ore-body (fig. 21), is also roughly parallel to the direction mentioned. Pockets of sulphide pegmatoid are found especially in the vicinity of larger pipes (fig. 21),

According to the mapping of Schwellnus (1936) the major joint directions, not only on Vlakfontein, but also in the areas to the north, are NNW-SSE and WNW-ESE. This has been confirmed by the mapping of C. Vermaak on Vlakfontein 207 JP. The directions of the major faults in the Vlakfontein area are also parallel to those given above. The younger faults radiate from the Pilansberg Alkaline Complex and consequently change their directions in the areas to the north (Map II).

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The rocks forming the floor of the Bushveld Complex, the layered rocks of the Basal Zone as well as inclusions of sedimentary rocks are folded. The axes of these folds are roughly NS and in addition to this direction, also E-W in the quartzites south of the Pilanesberg Complex (J.B. Gresse, personal communication). Some of the pipes are situated on the crests and in the troughs of these folds. In this respect all the pipes of the Vlakfontein mining-area (ore bodies No. 3, 2, 4, 1, lB, 3B and 3A) are situated on the crest of a prominent anticline. It would therefore appear that the folding preceeded the joints, because the latter were not disturbed by the folding.

The intimate association of sulphide pegmatoids with the structural elements of the area suggests that emplacement of the bodies took place during and/or after the deformation of the area. The important deduction to be made from the facts enumerated above is that the emplacement of the sulphide pegmatoids were controlled structurally.

7. 5 The Chemistry of the Sulphide Pegmatoids and their relation to other Nickeliferous Ores

The S/Ni ratio is equivalent to the pyrrhotite/pentlandite ratio in nickeliferous pyrrhotites, seeing that the dominant S mineral is pyrrhotite (70-80%) and the dominant Ni mineral is pentlandite $(10-30\%)$. In table 25 the pyrrhotite pentlandite ratios of the sulphide pegmatoids are given, together with those of some Canadian deposits. The S/Ni ratio of the massive ore in the Vlakfontein area is comparible with the occurrences at Frood and Falconbridge, whereas the ratio of the poikilitic ore lies between those of the Creighton and Garson deposits. This confirms the general statement made

Table 25. Pyrrhotite/pentlandite ratios of the sulphide pegmatoids (determined volumetrically) and of a few Canadian deposits (From Wilson and Anderson, 1959, p. 328)

by Wilson and Anderson (1957 , p. 328) that the S/Ni ratios are usually characteristic of each ore-body and/or ore-type.

Enough analyses of Cu and Ni were available from the sulphide pegmatoids (tables 26 and 27) for statistical analyses and for comparison with Canadian deposits, as given by Wilson and Anderson (1959). The values given in table 28 are not included in the calculations for they are not very reliable.

A frequency-diagram showing the $Cu/Cu+Ni$ ratios of the sulphide pegmatoids (fig. 24) tends to have a double peak. These two peaks corresponds with the two major ore types in the sulphide pegmatoids, namely the poikilitic and massive ores. The poikilitic ore from the 27 ore-body has a mean $Cu/Cu+Ni$ ratio of 0.28 and that of the massive ore is 0.13 (fig. 20). These values are in close correspondence with the two peaks of fig. 24. Unfortunately not enough separate analyses are available from the two different ore types to investigate this double peak effect in more detail. This influence of a more Cu-rich poikilitic ore is also displayed by a volumetric analysis of the sulphides of the two ore types. Cu-bearing minerals are present in larger quantities in the poikilitic ore than in the massive ore (table 23). The $Cu/Cu+Ni$ ratios of the host-rocks (harzburgite, pyroxenite and feldspathic pyroxenite - table 27) are comparable with the values obtained for the sulphide pegmatoids in fig. 24. E. Grip (1961, p. 34) found, however, that in the Lainijaur deposit in Sweden the median $Cu/Cu+Ni$ ratio of the fairly massive ore is 0.1, whereas the ratio of the disseminated ore is 0. 43. For comparative purposes frequencydiagrams of the Canadian deposits are given in fig. 25. The main difference is that the sulphide pegmatoids of the Bushveld are more Ni-rich.

The $Cu/Cu+Ni$ ratios show a slight decrease with increasing depth in the sulphide pegmatoid pipes - fig. 26 and table 31. A general decrease in the Cu/Ni ratio with depth is also recorded in the disseminated ores in the Lainijaur deposit (E. Grip, 1961, table V). The opposite phenomenon is displayed by the Frood ore-body, where an increase in the ratio takes place with increasing depth (table 32). Other Canadian mines, e.g. Kenbridge and Falconbridge show a rather constant ratio at different levels of the mines. In the sulphide pipes of the Bushveld Complex there has been no enrichment of massive ore with depth, which would be accompanied by a decreasing $Cu/Cu+Ni$ ratio as discussed above, to account for this phenomenon.

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Fig. 21. Sections and plans of the No. 1 Ore-body, Vlakfontein Nickel Mine (After Schwellnus 1935, p. 16).

Fig. 23. Plan 300 feet level, No. 4 Ore-body, Vlakfontein Nickel Mine

Table 26. Analyses for Cu, Ni and precious metals from the sulphide pegrnatoids from the Vlakfontein Nickel Mine, after Schwellnus (1935). Cu/Ni ratios are also given

Rock type	Cu	Ni	$Cu + Ni$	Cu $Cu + Ni$
Harzburgite	0.06	0.45	0.51	0.12
Pyroxenite	0.03	0.25	0.28	0.11
Feldspathic pyroxenite	0.06	0.16	0.22	0.27
Late Hypabyssal norite	0.07	0.12	0.19	0.37
Late Hypabyssal norite				
Y1.	0.18	0.25	0.43	0.42

Table 27. Analyses for Cu and Ni of the host-rocks of the sulphide pegmatoids. Cu/Ni ratios are also given.

The decrease in the $Cu/Cu+Ni$ ratio with grade is a very common feature displayed by ore-bodies of nickeliferous pyrrhotite from Canada (table 34) and also by the sulphide pegmatoids of the Bushveld (table 33).

The Ni/Co ratios of the sulphide pegmatoids are quite low, e.g. 12. 50 (table 29), 12.15 (table 30)and 10.6 (mean values in table 28 are not too reliable) for the associated rock types, namely harzburgite pyroxenite and feldspathic pyroxenite. The low Ni/Co ratio is comparable with that found in a gabbro as an associated rock type (table 35). However, according to the data given by Grip (1961, table XIII) for the Swedish deposits, the Ni/Co ratios for the same rocktype is quite variable, although an increase in this ratio is noticeable in the rocks in the sequence diorite, gabbro, norite, peridotite, This agrees therefore with the Canadian deposits (table 35).

Two analyses of bulk-samples (table 29 and 30) revealed the presence of As, which is present as definite arsenic minerals. Co is mostly in solid solution in the pyrrhotite; only a small amount is bonded in gersdorffite. Pb and Fe are probably also in solid solution in the sulphides. $\mathrm{Cr}_2^{\phantom 0}$ accounts for the chromite and C for graphite.

7. 6 The Genesis of the Sulphide Pegmatoids

Regarding the genesis of the sulphide pegmatoids, is Wager (1924) , Schwellnus (1935), Coertze (1962). Sohnge (1963) and Vermaak (personal communication) have formulated theories. Some of the theories have very much in common, which is clear from the condensed ideas given below.

Table 28. Analyses for Fe, Co, Ni, Cu and precious metals in the sulphide pegmatoid ores from the Vlakfontein Nickel Mine. Cu/Ni ratios are also given (Analyses after Schwellnus, 1939, p. 140).

(Ni + Cu = 4.61,
$$
\frac{Cu}{Ni + Cu} = 0.17
$$
, Ni/Co = 12.50)

Table 31. Vertical distribution of Cu/Ni ratios in the sulphide pegmatoids from Vlakfontein 207 JP, Rustenburg District

Table 32. Vertical distribution of Cu/Ni ratios in some Canadian deposits (After Wilson and Anderson, 1959, p. 331).

Mine and Level	Cu Median Ratio $Cu + Ni$		
Kenbridge Mine	800-1100'	0.44	
	1250-1550'	0.45	
	1700-2000	0.45	
Falconbridge Mine	1000-1500'	0.33	
	1500-2000'	0.32	
	2000-2500'	0.31	
	4000	0.33	
Frood:			
Upper disseminated mineral	$0 - 500$	0.43	
Lower disseminated mineral	1800-2700	0.50	
Heavy sulphide of foot- and hanging wall of disseminated mineral	2000-2700	0.52	
Heavy sulphide below disseminated $\left \rm{mineral}\right\rangle$	2700-3300	0.63	
Cubanite horizon	3200'	0.87	

Table 33. Effect of grade on the Cu/Ni ratios of the sulphide pegmatoids from the Vlakfontein Nickel Mine

Table 34. Effect of grade on the Cu/Ni ratios of some Canadian Cu-Ni deposits, (After Wilson and Anderson 1959, p. 332)

Grade	Median Ratio [®] Cu/Cu + Ni					
	Falconbridge Kenbridge		Werner Lake	Bird River	Norpax	
$\mathbf{0}$ -0.75% Ni	0.47	0.43	0, 55	0.50	0.46	
$0.75 - 1.5\%$ Ni	0.33	0.35	0, 40	0.21	0.25	
$1.5 + \%$ Ni	0.26	0.25	0.26	0.13	0.15	
$\vert 0.25 - 0.50\%~{\rm Cu} + {\rm Ni}$	0.53					
$0.50 - 1.00\%$ Cu + Ni	0.47					
$ 1.00 - 2.00\% \mathrm{Cu} + \mathrm{Ni} $	0.40					
$ 2,00 - 3,00\% \mathrm{Cu} + \mathrm{Ni} $	0.30					
$\left 3.00 + \% \right $ Cu + Ni	0.28					

Table 35. Ni/Co ratios in ores compared with that found in the associated rocktype. (After Wilson and Anderson, 1959, p. 330).

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Fig. 25. Frequency distribution of Cu/Ni ratios in some Canadian Cu-Ni sulphide ores (after Wilson and Anderson, 1959 , p. 329).

Fig. 26. Vertical distribution of Cu/Ni ratios in some sulphide pegmatoid bodies on Vlakfontein 207 JP.

Wagner (1924, p. 148) proposed that a direct gravity-settling of a Ni-Fe-Cu matte took place, mainly in a bronzitite environment. Filterpress effects helped to concentrate the sulphides. Fracturing of the consolidated rock took place, in which a partially concentrated sulphide, with a lower melting point than the silicates, remained in liquid form. The sulphide liquid concentrated further during injection along the fracture-zones. Not much could be said against this theory except that Wagner thought that the distribution of the sulphide pegmatoids were limited to the bands of anorthositic norite.

Since Wagner's time many more gossans have been discovered on different stratigraphical horizons.

Schwellnus (1935, pp. 102-110) favoured the idea of differentiation in situ from the emplaced lower part of the Complex. Gravitative settling of sulphides took place at sites on the floor of the Complex where conditions were suitable for the concentration of the sulphide liquid. Crystallization of the

silicates then set in, which was followed by jointing and fracturing of the consolidated rocks. Under the influences of increasing vapour pressure the residual pegmatoid and sulphide liquid intruded along the fissures, thus accounting for the sulphide pegmatoids. Owing to the large volume of volatile constituents which formed part of the sulphide pegmatoid, hydrothermal alteration took place of the country-rock.

This theory is not supported by evidence from certain bore-holes which were drilled in those areas where a gravimetric survey indicated the presence of basins in the floor of the Complex. No concentration of sulphide, correspondding in composition with the sulphide pegmatoids were found.

According to Vermaak (personal communication) sulphides concentrated as disseminated specks within the heaviest and lowest member of the differentiated series, namely the harzburgite. Tectonic distrurbance of the consolidated rocks gave rise to faults, fractures and joints. This was followed by the intrusion of pegmatite along the zones of weakness, which circulated acidic waters through the sulphide-bearing harzburgite and as a result thereof caused the serpentinization of the latter. The change of volume led to the filkrpressing of the sulphides in localized "magma chambers". Injection of the pegmatoids and the sulphide took place along zones of weakness with an accompanying relief of pressure.

The objections against this theory are that serpentinization of the harzburgites is purely a supergene phenomenon and not a heat effect. In this respect the peridotite of the Great Dyke is serpentinized to a depth of 940 feet in a certain bore-hole in the Wedza area (Worst, 1956). Below this, fresh olivine is found. Near a fault-zone at 1200 feet the olivine is serpentinized again. Furthermore, investigation of polished sections of serpentinized harzburgite from the Western Transvaal and the Potgietersrus area, revealed that the disseminated sulphide is highly oxidized and altered to magnetite and hematite whereas a highly serpentinized harzburgite consist mainly of serpentine, magnetite and very finely disseminated pyrrhotite, pentlandite and millerite, the latter being sometimes the dominant sulphide. The sulphide phase is thus destroyed and/or redistributed as very fine disseminations. Only in one polished section investigated, are signs of mobilization present (photo 119).

Coertze (1962) suggested the hypothesis that the plugs or pipes of dunite, magnetitie-diallage pegmatoid and bronzite pegmatoid, with or without sulphides, intruded along a zone of weakness. He pointed out that the Rustenburg fault provided this zone of weakness for the intrusion of the dunite, the magnetite and the diallage pipes south of Pilanesberg. His conclusions are however erroneous because the Rustenburg fault does not pass through Vlakfontein. Its real position is indicated on Map II.

Söhnge (1963, pp. x1iii-x1vi) draws attention to the relationships between the diallage, the dunite, the magnetite and possibly the sulphide pipes in the Bushveld Complex. He postulated that pockets of a hydrous femic residuum segregated from the highly differentiated layers of Bushveld rocks. From them, barren irregular dykelets and pipes were injected as pegmatoid. Other bodies could have formed mainly by lateral and local upward diffusion of the Fe and Mg toward "hydrous" centres. Metasomatic reaction would convert pyroxenite into dunite, hortonolite dunite and magnetite. The l atter is an expression of a final enrichment in Fe. The sulphide bodies of the Western Transvaal are explained as a residuum relatively more enriched in Fe, Ni, Cu and enough S-rich fluid to effect the metasomatic replacement of the host-rock, and to form pipe-like bodies in this way.

Wilson and Anderson (1959, p. 332) suggested a theory according to which the deposits of Cu-Ni sulphide, associated with mafic intrusions, could have originated in a twofold manner. Firstly, an immiscible liquid, rich in sulphide, settled as it separated, "but the process may be stopped by freezing at any time, so that the early segregated portions of sulphide ore are relatively richer in copper". The early sulphides are enriched more in Cu than in Ni because the former is more chalcophile than the latter. According to the authors mentioned above the deposits at the Frood Mine are examples where the early sulphides are enriched in Cu, owing to an increase of this element towards deeper levels of the ore-body (table 32). If the metal ratio of a deposit remains constant at different levels of the deposit, such as at the Kenbridge and Falconbridge Mines, it is a typical example of a sulphide pool which accumulated at the base of basic intrusions and was injected afterwards along zones of weakness. In this way the early as well as the late sulphides accumulated in the pool and gave a constant metal ratio to the sulphide.

In the sulphide pipes of the Bushveld there is a slight enrichment in Ni towards lower horizons. This feature is very difficult to explain. However,

the author feels that Wilson and Anderson's deduction that the early sulphides are enriched in Cu is not entirely correct. They made this assumption on the basis of the work of Wager and Mitchell(1951) from which it appeared that there is an enrichment in Cu in the rocks of Skaergaard which crystallized early. This deduction is not justified as the lower members of the differentiated series are not exposed. In contrast with their assumption, pentlandite is much more ex-**1.le.u~.lopi!J** $tensively_t$ than' Cu-bearing minerals in the peridotites of the Bushveld Complex. In a more recent investigation by Wager et al (1959) on Skaergaard the conclusion was reached that a controlling factor in the enrichment of Cu in the early sulphide phase was the lack of S.

Wilson and Anderson (1959, p. 332-333) also found that where 'the grade of the Cu-Ni ore increases Cu decreases (table 34). The same effect was observed in the sulphide pegmatoids (table 33). Wilson and Anderson explained this observation by the fact that pyrrhotite with nickel in solid solution would crystallize first in a sulphide liquid and consequently there will be an enrichment of Cu in the residual liquid. This residual liquid then migrates into the fringe-areas of the ore-bodies where a low-grade ore is formed with a high Cu-content. This possibility .would explain the enrichment of Cu in the sulphides of the outer zones and in the disseminated ore in the immediate vicinity of the bodies of sulphide pegmatoid of Vlakfontein. The veins of massive chalcopyrite along the edge of the No. 4 ore-body is a typical example of this process. Veins of massive chalcopyrite replacing massive pyrrhotite-pentlandite ores (photo 124) in the No. 1 ore-body could also be explained in this way. According to Hawley (1965, p. 563), this is also what actually happened at Frood, where the upside-down zoning effect was brought about by the injection of a sulphide-silicate liquid from above. The enrichment at the higher levels, relative to the lower levels, of the sulphide pegmatoids in the Vlakfontein Mining area indicates an injection of a sulphide pegmatoidal fluid from great depths. The Cu sulphides which crystallize late were thus enriched in those parts of the pegmatoid farthest away from the source.

Further to the actual genests of the (sulphide) pegmatoids a few general features displayed by the pegmatoid bodies will be discussed. Over the whole succession of the layered Bushveld'. rocks there is generally a strong tendency in these bodies, relative to the host-rock, towards an Fe-rich residuum in either silicates, oxides or sulphides. The olivine (65 mol per cent Fo) and the orthopyroxene (74 mol per cent En) in the sulphide pegmatoids are much more

Fe-bearing than the same minerals $(+ 80 \text{ mol per cent Fo and } 82 \text{ mol per})$ cent En) in the neighbouring rocks. The plagioclase is more albite-rich in the pegmatoid than in the host-rocks. On higher stratigraphical horizons the pegmatoid bodies show an increase in the Fe-content of the silicates. Some of these bodies have cores of hortonolite dunite and diallage is also a very common mineral in them, in comparison with the hyalosiderite and the bronzite of the country-rocks. Under high oxygen pressures, magnetite and· ilmenite started to crystallize from the residuum enriched in Fe, to form plugs and irregular bodies of magnetite.

It was found that the trend of differentiation of the sulphide phase in the layered rocks of the Bushveld is towards a pentlandite-pyrrhotite phase which gradually enriched in the Cu-bearing sulphides and finally suffers, a considerable increase in pyrrhotite (fig. 11). Pyrrhotite is also the dominant minera! in the rocks of Skaergaard which crystallized late (Wager et al, 1957). When comparing the percentages of pyrrhotite, pentlandite and chalcopyrite in the Vlakfontein ores with those of the country-rock (harzburgite) in table 23, it is clear that the poikilitic ore is enriched in chalcopyrite and pyrrhotite in relation to the host-rock. The massive ore, which could be considered as a later product of differentiation than the poikilitic ore,is quite pyrrhotite-rich. The differentiation trend displayed by the bodies of sulphide pegmatoid therefore corresponds with that of the sulphide phase in the layered rocks. This has atready been mentioned in the section dealing with the distribution of the sulphides in the Bushveld Complex.

The Ni/Co ratio of the ore also corresponds, not with the ratio of sulphides in ultramafic rocks, but with that found in a gabbro (table 35), thus indicating that the differentiation also caused an enrichment of Co in the sulphide pegmatoids.

The (sulphide) pegmatoids resemble granite pegmatites. The latter correspond with the residua system in petrology, whereas the former tend towards an Fe-rich residuum in gabbroic magmas. Under a high S pressure sulphides would crystallize, as in the sulphide pegmatoids, and under a high oxygen pressure Fe oxides would crystallize to form a magnetite plug or a magnetite and Fe-rich silicate body. High oxygen pressure existed during the crystallization of the Critical, Main and Upper Zones. In the rocks of the Basal Zone in the Western Transvaal the S pressure was initially low during the crystallization of the major rock-forming minerals (olivine,

orthopyroxene and plagioclase), Because of the low melting point of the sulphides they are enriched in the intercumulus liquid, During progressive crystallization and adcumulative growth of the cumulus crystals, olivines and pyroxene, the S pressure increased, A residual magma rich in Fe and with a high S pressure started to develop interstitially to the cumulus and adcumulus crystals of the harzburgite and perhaps also the pyroxenite and the feldspathic pyroxenite. This residual magma was a sulphide liquid in which different phases, inter alia silicates, chromite, arsenides and water, were in solution in the sulphide liquid. The composition of this liquid could have been more or less the same as that of the liquid at point 4 in fig. 31. In some cases the residual magma initially had a low S pressure and the composition was mainly that of hypersthene, plagioclase and biotite. At a later stage the S pressure increased, which would account for a later sulphide-rich liquid.

The residual magma started to segregate and under the influence of tectonism (which was present before, during and after the crystallization of the rocks of the Basal Zone in the Western Transvaal) and the high vapour pressure of the residual magma, intruded along zones of weakness to give rise to transgressive, pipe-like bodies. It is not certain how important the role of tectonism has been in the formation of these bodies, because in the Critical Zone in the Eastern Transvaal numerous pegmatoids composed of hortonolite dunite and diallage, are present and no tectonic effects are visible.

The residual magma was injected as different liquids:

1. a silicate pegmatoid with very little or no sulphides, followed by an olivine-bearing poikilitic ore (if present) and

2. a pyroxene-bearing poikilitic ore and simultaneously with it, or afterwards massive sulphide.

Evidence of the replacement of the silicates of the pegmatoid by ore is clearly visible according to Schwellnus (1939, p. 106). A definite intrusive relationship between the olivine-and the pyroxene-bearing poikilitic ore can be reported from the Rock Shaft at the Vlakfontein Nickel Mine (photo 113),

The silicates in the poikilitic ore crystallized first from the sulphide liquid in which little silicates were dissolved, according to the views of Smith (1961, p. 667). In some pegmatoids they have been in suspension in the sulphide liquid during its intrusion as revealed by the occasional orientation of the pyroxene laths (photo 114). Very little chromite crystallized, as zones around the silicates, from the sulphide liquid in which it was in solution. This

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chromite crystallize at a time different from that of host-rock, which was in some places incorporated and brecciated by the pegmatoid. The arsenides followed the chromite, because the grains adhere to the silicates. The sulphides, pyrrhotite, pentlandite, chalcopyrite and cubanite were the last to crystallize.

Hydrothermal alteration of the pyroxene in the poikilitic ore took place to a very small extent. On the contact between the sulphide pegmatoid and the host-rock only a few hydrothermal minerals (hornblende, biotite and chlroite) developed.

Although miscibility of the silicates in a sulphide liquid is commonly accepted by research workers e.g. Wager et al (1957) , Smith (1961) and Hawley (1962), their diagrams of the sulphide-silicate systems, with or without _{er}

oxide, do not make provision_Amore than 20 per cent by weight of silicate in solution in a sulphide-rich liquid (Hawley, 1962, p. 161 and Smith, 1961, p. 666) at \pm 1050[°]C. The solution of the silicates in the sulphide-rich liquid is also possible only above \pm 800 $^{\mathrm{o}}$ C. Another indication that the temperature was above 800 $^{\textsf{O}}\textsf{C}$ is the fact that niccolite is replaced by maucherite, which takes place above 829°C. These high temperatures contradict the theory mentioned above that the sulphide bodies are emplaced as a pegmatoidal fluid. The diversity of components in the fluid or liquid, including S and volatile constituents, could of course have lowered the termperature mentioned above considerably.

8. DISSEMINATED SULPHIDE AT THE BASE OF THE BUSHVELD COMPLEX

Disseminations of sulphide are developed at some localities at or near the base of the Complex. There are three areas in which sulphides are present as minor constituents of the rocks of the Basal Zone, e.g. in the area west of the Pilanesberg and farther to the west on the farm Goudini and vicinity, south-east of Potgietersrus and in the Burgersfort area, especially on the farm Aapiesdoorndraai 298 KT. Disseminated sulphide in the Late Hypabyssal rocks, mainly quartz norite, is also developed in the Eastern Transvaal (south of Burgersfort and west of Belfast). Up to 20 per cent of disseminated sulphide has been observed in the quartz norites in the cores from bore-holes KAl, KA4 and KA5 drilled in the Western Transvaal.

8. 1 The Disseminated Sulphide in the Rocks near the Floor of the Bushveld Complex in the Western Transvaal

In the Western Transvaal, the metasediments in contact with the Bushveld Complex, are the Magaliesberg quartzite and the hornfels above and below it. Deep bore-holes and field-relationships indicate that the rocks of the Bushveld Complex cut across a part of the hornfels above the Magaliesberg quartzite, the Magaliesberg quartzite itself and has intruded into the hornfels below the quartzite.

Immediately below the Magaliesberg quartzite two bands of marble (diopside-plagioclase hornfels) are present. In places they contain sulphides - mainly pyrrhotite with little chalcopyrite and pentlandite (table 36). The nature of the occurrence of the sulphides is very much the same as in the layer(s) above the Magaliesberg quartzite discussed farther on in this section. About 350 feet below the Magaliesberg quartzite a rather prominent sulphidebearing layer of cordierite-plagioclase-biotite-quartz hornfels is present. The volumetric composition of the sulphide phase is given in table 36. Gersdorffite constitutes about O. 1 per cent of the sulphide phase. Garnet is a major mineral especially in these metasediments which were mobilized as a result of the intrusion of the Complex. A noteworthy outcrop of a mobilized garnetbiotite-quartz-plagioclase granulite is found on the farm Bierkraal 134 JP in which rounded inclusions of another unmobilized, layered hornfels are present. An occasional speck of sulphide, 1 cm in diameter, was also observed in the granulite. Mobilized metasediments, with or without garnet and sulphide, were

Fig. 27. Diagrammatic profile across the floor of the Bushveld Complex in the Western Transvaal showing the position of the samples from which the data in table 36 and 37 were derived

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Table 36. Volumetric composition of the sulphide phase in the plutonic and the metasedimentary rock-types at the base of the Bushveld Complex in the Western Transvaal

seen in bore-holes KAI and KA5. A hornfels with thin lens-like layers of sulphide was found at $+400$ feet below the Magaliesberg quartzite. This intercalated layer of sulphide has real sedimentary characteristics which are also illustrated by the volumetric composition of the sulphides (table 36). No pentlandite and very little chalcopyrite are present. Co arsenide minerals (safflorite, loellingite and linnaeite) are very rare (KA5-5028). Graphite was also observed together with sulphide, mainly pyrrhotite, in one polished section (KA5-4971). For convenience the position of the different samples, which were investigated are inserted on a generalized diagrammatical profile in fig. 27.

In the Western Transvaal the Magaliesberg quartzite also contains sulphides, although very sparsely. The major sulphide mineral is pyrrhotite with minor amounts of chalcopyrite (table 36).

Directly above the Magaliesberg quartzite a sulphide-bearing diopsideplagioclase hornfels is present. The sulphides are concentrated in thin (1 mm) or thick (3 cm) layers which are intercalated with layers, of equal thickness, containing smaller quantities of sulphide (photo 121). These sulphides are also poor in pentlandite and chalcopyrite. In the norite layer above this diopsidefels, inclusions of the same type of rock are found (photos 122, 123). The composition of the sulphide phase and its mode of occurrence are nearly identical with that in the hornfels above the quartzite.

Sills of (quartz) norite have intruded along several stratigraphical horizons in the upper part of the Pretoria Series, mainly directly above the Magaliesberg quartzite and also along a few horizons in and below the quartzite, inter alia along the sulphide-bearing layer $+$ 400 feet below the Magaliesberg quartzite. This influx of magma took place as a Late Hypabyssal Phase, noritic in composition. However, all gradations between a norite, quartz-biotite norite, a contaminated quartz-biotite norite and a metasediment (cordierite-plagioclase-biotite-quartz hornfels) may be seen. Contamination by assimilation of the metasediments by the norite clearly took place along the contacts of the sills. It is often difficult to distinguish between quartz norite and metasediment.

The composition of the sulphide phase varies considerably from place to place in the quartz norite and the contaminated quartz norite (table 36). The major sulphide is pyrrhotite, but pentlandite is also present in quantities from $0-20$ per cent and chalcopyrite from $4-11$ per cent. As-bearing minerals -

niccolite, maucherite and gersdorffite - were also observed (table 30). On or near the contacts of the quartz norite with the sulphide-bearing metasediment the sulphides are generally pentlandite-poor (KA5-1624), whereas those farther away are richer in pentlandite and chalcopyrite (table 36). An exception to this rule is the sulphides in a quartz norite on the contact with a sulphide-bearing hornfels (KA5-3963, -3936) containing about 20 per cent pentlandite. This quartz no rite is at the base of a sill of feldspathic pyroxenite, 1500 feet thick.

Fig. 28 represent the contact of an inclusion of diopside hornfels in norite which contains sulphides. The norite intruded as stringers into the hornfels (photo 123) and sulphides are prominently developed in these stringers. The volumetric composition of this sulphide phase is: Pyrrhotite 72. 2 per cent, pentlandite 3. 5 per cent, chalcopyrite 9. 7 per cent and pyrite 14. 6 per cent. The sulphides are thus poorer in pentlandite than the norite which contains 13. 2 per cent of pentlandite (table 36).

In bore-hole Gl two small stringers of graphite and sulphide are present at 4416.5 and 4422.4 feet in norite. Both are about 2 inches wide. The graphite is generally fine-grained and fine-grained pyrrhotite (0. 001 mm in diameter) is disseminated through it.

Although a discussion of the oxides are beyond the scope of this treatise it should be mentioned that chromite, in eutectic intergrowth with the silicates, was found in the norites (photo 107). In some specimens a mineral with a higher reflection than chromite is intergrown with grains of chromite. Rutile has also been observed.

The magma of at least the Basal Zone, which belongs to the Main Plutonic Phase of the Bushveld, intruded after the (quartz) norite. This gave rise to feldspathic pyroxenite and pyroxenite with intercalated harzburgite. Below the Magaliesberg quartzite a thick sill of feldspathic pyroxenite has intruded at some places e.g. in the Vlakfontein area (Fig. 2).

A prominent layer of disseminated sulphide, 150 feet thick, is found on top of a feldspathic pyroxenite, the latter representing the base of the Basal Zone in this area. The same mineralized layer was found in bore-hole KA6, which shows that it is quite persistent along the strike (fig. 1). In other bore-holes the feldspathic pyroxenite is not mineralized. Disseminated sulphide appears interstitial to the silicates in the harzburgites (photo 120). The pyroxenites are not mineralized to the same extent as the harzburgites.

The form of the sulphides in the rocks of the **Basal** Zone is generally as irregular patches interstitial to the silicates, whereas in the Late Hypabyssal (quartz) norites they are present mostly as roundish blebs. As soon as the sulphides in the latter rocks are concentrated to some extent (+ 1. 0 per cent by weight S) the sulphide blebs are generally irregular in shape.

By investigating the analytical values of Ni, Cu and S in the different rock types near the base of the Bushveld Complex (table 37), the change in mineralogical composition of the sulphide phase of the different rock types is confirmed to be as follows: The harzburgite, pyroxenite and feldspathic pyroxenite are relatively rich in Ni and Cu. The quantity of Ni and Cu decreases in the various rock types in the order ultramafic rocks, contaminated quartz norite and metasediment (table 37). Seeing that the percentages of Ni and Cu are a function of the rock type as well as of the S content of the rock, the Ni:S and Cu:S ratios will be considered. The percentage of S is expressed as 100 and the percentages of the other elements are adjusted accordingly (cf. table 37). The rocks of the Basal Zone (harzburgite, pyroxenite and feldspathic pyroxenite) have a Ni/S ratio above 10 and Cu/S ratio above 2. The Late Hypabyssal norite and the quartz norites and contaminated quartz norites have Ni/S ratio above 4 and Cu/S ratio above 2. The metasediments have relative low Ni/S and Cu/S ratios, namely, below 4 and below 2 respectively.

A noteworthy phenomenon is As which was detected in the hornfelses and also in the adjacent quartz norite.

The Cu and Ni content of the sediments in general (table 38) are too low to account for the values reported in table 37. Under reducing conditions Ni and Cu show a tendency to become concentrated in muds rich in organisms and owing to their high affinity for S, are precipitated as sulphides in these sediments, according to Rankama and Sahama (1950, pp. 658 and 698). The presence of graphite in the hornfels (KA5-4971) and the graphitic shale just above the Daspoort quartzite could indicate that organisms have played a role in the precipitation of some of the sulphides in the metasediments. Analyses of sedimentary pyrite or marcasite in general (table 39), deposited in shale in fresh-water, show up to 1000 ppm of Ni and Cu, and +1000 ppm of Ni if the sulphide is present in limestone. These values could be responsible for the Ni and Cu anomalies in the assays (table 37) of the sulphide-bearing hornfelses. Although the Ni and Cu had been in solid solution in the sedimentary

Table 37. Analytical values of Ni, Cu, Zn, S and As in some sulphide-bearing rocks of the Western Transvaal. The ratios of the elements in terms of $S = 100$ are also given.

Table 38. Average Ni, Cu and S content in ppm of different sediments. (After Rankama and Sahama, 1950, pp. 658, 700 and 752)

Table 39. Ni, Cu and As content of sedimentary pyrite or marcasite in fresh-water sediments. (After Degens)

pyrite the latter two minerals could have formed as a result of the metamorphism produced by the Bushveld Complex.

Seeing that the As content of sedimentogenetic pyrite in shale or limestone is + 1000 ppm (table 39) and even 3000 ppm according to Rankama and Sahama (1950, p. 741), the presence of As-bearing minerals, which also formed under metamorphic conditions, could be readily explained. Co is also enriched in sedimentary sulphide (table 39) which is then built into gersdorffite.

The average S content of sediments are given in table 38. However the Magaliesberg shales have an average of 300 ppm S (personal communication: G Mr. R. N. Bohmer, Department of Inorganic and Analytical Chemistry, University of Pretoria) as previously described, but horizons are found where sulphides are concentrated to a considerable degree.

8. 2 The Disseminated Sulphides in the Rocks near the Base of the Bushveld Complex South-east of Potgietersrus

A discordant relationship between the plutonic rocks of the Bushveld and the underlying sediments is clearly illustrated in the vicinity of Potgietersrus (Map III). South-east of Potgietersrus the Bushveld Complex is in contact with the Magaliesberg quartzite, but the Complex gradually cuts across

the Pretoria Series as well as across the Dolomite Series towards the northwest and 15 miles north-west of Potgietersrus the Complex rests on the Archaean granite. Several inclusions of quartzite are present in the ultramafic rocks south and south-east of Potgietersrus (Map III). This also indicates a discordant relationship between the quartzite and the ultramafic rocks in depth.

The quartzites in the area south-east of Potgietersrus contain roundish or euhedral crystals of pyrite. The octahedral grains are clearly a product of recrystallization. Outcrops of pyrite-bearing Magaliesberg quartzite are known from the north- eastern corner of Grasvally 2 93 KR.

Directly in contact with this mineralized quartzite, a sulphide-bearing norite with about 10 per cent of sulphide is found.

Table 40. Volumetric composition of the sulphide phase of the rocks at and near the floor on Grasvally 293 KR, Potgietersrus District

The composition of the sulphide phase (table 40) is in accordance with that of a norite except that the zinc-blende is present in abnormally high quantity. Volumetric compositions of the sulphides in a norite, a feldspathic pyroxenite and a harzburgite farther away from the contact show no abnormalities (table 40). The percentage of pentlandite in the harzburgite may be somewhat too low in comparison with other harzburgites of the Bushveld (table 41).

8. 3 The Disseminated Sulphides in the Peridotite from Aapiesdoorndraai

The Aapiesdoorndraai peridotite is a body which cuts across the Magaliesberg quartzite and intrudes into the hornfels below the quartzite, although Willemse (1959, p. lxvii) suggested a pipe-like body. As a result of a gravimetric survey of this body (Liebenberg, 1964), the author prefers a more

Fig. 29. Diagrammatic profile of the Aapiesdoorndraai peridotite

sill-like form. The foot-wall contact becomes increasingly steeper with depth, which implies that it is actually ethmolitic in form as indicated in fig. 29. It is considered to be an integral part of the Basal Zone. This body of ultramafic rock is exposed on the lowest stratigraphical horizon in the Bushveld Complex and consequently it contains quite a high percentage of pentlandite, compared with sulphide-bearing peridotites (table 41). In fact, this is the only place in the Complex where the percentage of pentlandite exceeds that of pyrrhotite. Another exceptional feature of the sulphides is the very common mineral associations of troilite, pentlandite, mackinawite and cubanite, but still the association indicates a S-deficient and metal-rich sulphide phase. Such a S deficiency in the sulphides was not encountered in other rocks of the Complex. Troilite is found at least in the presence of hexagonal pyrrhotite. Two small euhedral, crystals of gersdorffite were found in a sample (20a) from a bore-hole·drilled for water on Aapiesdoorndraai 298 KT.

Compared with other peridotites (fig. 36) the Aapiesdoorndraai occurrence is quite rich in Ni and Cu. A similar body on Groothoek 256 KT has revealed comparable values. However, the forsterite dunite from the platinum-bearing pipes may have even higher values for Ni and Cu.

In the hornfelses at the floor of this peridotite body a sulphide-bearing cordierite-biotite hornfels is found on the farm Dresden 304 KT. This sulphidebearing hornfels is correlated with the same kind of hornfels $+350$ feet below the Magaliesberg quartzite in the Western Transvaal.

Table 41. Volumetric composition of the sulphide phase in the harzburgite from different localities

8. 4 Other Occurrences of Disseminated Sulphide at or near the Base of the Bushveld Complex

West of Belfast the Main Zone of the Complex rests on a quartz norite which in turn is in contact with the Dullstroom volcanics. The quartz norite contains numerous inclusions of metasedimentary rock and the composition of the norite varies from a melanocratic, through anorthositic to quartz noritic. Specks of sulphide occur here and there in the norite.

South of Burgersfort on Wildebeestkraal 354 KT, a differentiated Late Hypabyssal sill crops out immediately below the Magaliesberg quartzite. At the base a layer of harzburgite is developed. This is followed by pyroxenite and quartz norite, which constitute the major part of the sill. Just above the pyroxenite a mineralized layer is present in the quartz norite. The sulphides constitute less than 2 per cent of the rock. The volumetric composition is: Pyrrhotite 66. 4 per cent, pentlandite 19. 3 per cent, pyrite 9. 0 per cent and chalcopyrite 5. 3 per cent, which corresponds with that of some pentlanditerich quartz norites from the Western Transvaal (table 36, samples KA5-3936, -3963).

8. 5 The Origin of the Disseminated Sulphides

In the previous part (immediately above) the factual data bearing on the disseminated sulphide have been presented. The interpretation of these facts are now considered.

It is known that the layers of marble immediately above the Magaliesberg quartzite, the Magaliesberg quartzite itself and the metasediments below the quartzite contain appreciable amounts of sulphide at certain places. The origin of the sulphides in the metasediments will therefore be discussed first.

The presence of sulphides in diopside-plagioclase hornfels in the contact-metamorphic aureole of the Bushveld Complex and in some localities in direct contact with the plutonic rocks supports the idea of a mineralized skarn. The sulphides in these skarn rocks were thus metasomatically introduced by the magma into the neighbouring sediments, especially the marble strata. The fact that most of the sulphides appear in the norite stringers and not to the same extent in the hornfels itself (fig. 2 8) is also in favour of this theory.

North-west of Potgietersrus a rock, taken as a real skarn, is in contact with Merensky Reef. The sulphides in this skarn have a patchy appearance and are rather Ni- rich. It is thus clear that these sulphides were derived from the Merensky Reef by means of a meta somatic process. However, in the diopside hornfels in the Western Transvaal the sulphides are poor in Ni and Cu, compared with sulphides which have been derived from a basaltic magma. As shown above the Ni and Cu contents are within the limits of the composition of sedimentary sulphides. Furthermore, the structure of the diopside hornfels, with layers richer in sulphide (photo 121) indicates a sedimentogenetic origin. The sulphides in the diopside hornfels from the Western Transvaal are thus of real sedimentary origin.

Two stratigraphical horizons are known so far in which the diopside hornfelses are sulphide-bearing, viz. one immediately above and the other below the Magaliesberg quartzite.

The sulphides in the cordierite-plagioclase-biotite-quartz hornfelses have a different mode of occurrence. Some appear as lens-like intercalations in the hornfels (sample KA5-5028). Others are found together with graphite (sample KA5-4971). In other occurrences they have been mobilized as a result of the intrusion of an adjacent quartz norite (samples KAl-2581, -2638 , -2641). These sulphides are also Ni-poor, except in sample KA1- 2641 in which $+3.0$ per cent of pentlandite has been recorded. Also all these features indicate a sedimentary origin of these sulphides, which have formed under reducing conditions, probably with the aid of organisms, to account for the presence of graphite. The relatively high Ni content of the sulphides in the hornfels adjacent to the quartz norite can be attributed to Ni-metasomatism by the norite magma. Two sulphide-rich layers are known from + 350 and +450 feet below the Magaliesberg quartzite.

The only way in which the pyrite, with its roundish form, in the

quartzites can be explained, is that pyrite grains were deposited together with the sand grains to form a sandstone. The pyrite in the Magaliesberg quartzite south of Potgietersrus was not derived from the Bushveld magma, seeing that examples are known where pyrite is present in quartzite of the Pretoria Series (e.g. in a bore-hole north of Potchefstroom) in the absence of a metamorphic aureole.

The origin of the sulphides in the Late Hypabyssal (quartz) norites will now be discussed. The thick sills, especially the one above the Magaliesberg quartzite in the Western Transvaal contains little or no quartz and biotite. Near the contact with the metasediments the contents of quartz and biotite increase. Thin sills contain appreciable amounts of quartz and biotite and, as stated previously, all gradations between a norite and a metasediment can be seen. The assimilation of material from the metasediments by the sills can thus be easily accepted. The Late Hypabyssal sills intruded into the sediments above and below the Magaliesberg quartzite and also in places into those horizons where sedimentary sulphides were present in appreciable amounts. Assimilation of S subsequently took place, which would account for the abnormal amounts of sulphide in these rocks. The mechanism of the process, commonly called sulphurization will be discussed later. As and graphite are common constituents of sedimentary sulphides and sediments, and the assimilation of As and C is postulated to account for the arsenic-bearing minerals in the norites adjacent to the sediments. The graphite in the norites in bore-hole G1 at 4416 feet and 5401 feet could thus be of sedimentary origin.

In the extremely contaminated quartz norite the sulphides are pentlandite-poor and therefore also Ni-poor (KA6-1624). An explanation for this phenomenon is that the assimilated sulphide or S vapour did not react properly with the magmatic phase and therefore no more Ni could be extracted. Chemical equilibrium was therefore not attained in these cases. Another example is known where the sulphides in a contaminated quartz norite on the contact with metasediments contain 20 per cent pentlandite (samples KA5-3936, -3963). This occurrence is, however, at the base of an intrusion of feldspathic pyroxenite, 1500 feet thick. Consequently, high temperatures existed for a longer period and thus the possibility was greater for chemical equilibrium to be attained. Although it is assumed that the sills of feldspathic pyroxenite is of a later age than the Late Hypabyssal norite and therefore a part of the Basal Zone, it will not affect the argument in any way. The feldspathic

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pyroxenite in any case supplied enough heat for the reaction.

With regard to the sulphides in the differentiated sill on Wildebeestkraal 354 KT, Lydenburg District, it is not possible to decide whether the sediments acted as a source of S. The sulphide liquid was miscible with the silicate magma during the crystallization of the lower harzburgite and pyroxenite, but as soon as the magma became oversaturated with respect to silica, the sulphide started to form an immiscible liquid. This sulphide liquid sank to the bottom of the magma body just above the already solidified pyroxenite and harzburgite. This view is supported by the finding of Vogt (1921) that 1 per cent FeS can be dissolved in a norite magma and that the solubility decreases as the silica content of the magma increases.

The sulphide-bearing quartz norite west of Belfast is full of inclusions of metasedimentary and volcanic rock. Pyrite was observed in the Dullstroom volcanics. The latter could thus have acted as a source of S.

The most striking feature in the distribution of the disseminated sulphides in the rocks of the Basal Zone is the agreement between the presence of disseminations of sulphide in these rocks and the discordant intrusion of the Bushveld rocks into the Magaliesberg quartzite and the underlying (meta) sediments. This is illustrated by the three major occurrences of disseminated sulphide, i.e. in the Western Transvaal, to the south of Potgietersrus and in the vicinity of Burgersfort. The discordant intrusion into higher stratigraphical horizons is not important as far as the occurrence of disseminated sulphide is concerned.

The rocks of the Basal Zone intruded after the Late Hypabyssal Phase had been emplaced. As a result the plutonic rocks of the Basal Zone could not have been in proper contact with the metasediments in the Western Transvaal, seeing that they were emplaced to a large extent above the hypabyssal norite. A thick sill of feldspathic pyroxenite, which is probably part of the Basal Zone, intruded below the Magaliesberg quartzite into the hornfelses. Disseminations of sulphide were encountered in this layer, especially near the contact with hornfels (KA5-4521 to 4562). It thus appears that S was also assimilated by the feldspathic pyroxenite. Owing to the cutting of the rocks of the Basal Zone across the Magaliesberg quartzite and the hornfelses just below (the process is illustrated in fig. 2), which contain sedimentary sulphide, assimilation of S from the latter sediments by the magma of the Basal Zone could have taken place. It is, however, difficult to account for

the large amounts of interstitial sulphide in some rocks of the Basal Zone in the Western Transvaal. In this respect a layer of feldspathic pyroxenite, 15 0 feet thick, containing 1-2 per cent of interstitial sulphide, is found in bore-hole K.A5. In addition to this the harzburgites and some pyroxenites also contain interstitial sulphide. It would therefore appear that some magmatic S contributed to these large quantities of interstitial sulphide.

The composition of the magma of the Basal Zone in the Western Transvaal is considered to be that of a feldspathic pyroxenitic. This follows from the fact that the dominant rock type in the Basal Zone, and the total composition of all the rocks in the Basal Zone, is a feldspathic pyroxenitic. The feldspathic pyroxenite immediately above the Late Hypabyssal norite is taken as the base of the Basal Zone (bore-hole KA1, KA2, KA4, KA6 - fig. 1).

The sulphide disseminations on top of this feldspathic pyroxenite could be explained in the following way: Kullerud (1963, p. 186) stated that "in general, liquid miscibility existing under PT conditions in the magma chamber, followed by liquid immiscibility under changed PT conditions existing after intrusion, without accompanying change in magma composition, is not physically impossible, but highly improbable". Thus we have to assume that the sulphide liquid was in solution in the silicate liquid, which is possible according to the classical theory of Vogt (1921). In addition Smith (1961, pp. 666-667) found that a two-liquid field of sulphide and silicate exists in the system FeS-magnetite-gabbroic silicates (fig. 31). This will be dealt with in detail in the section on the Merensky Reef (p. 161). The extent of the miscibility gap between the two liquids depends on the chemical composition of the magma. A magma with a low oxidation potential and very little dissolved sulphide (composition a in fig. 31) would start to crystallize as silicates. In the Basal Zone this happened when pyroxene crystallized and settled to the bottom of the Basal Zone to initiate the build-up of the feldspathic pyroxenite. The remaining liquid became enriched in sulphide until a point was reached where the liquid was saturated with sulphide and silicates, a silicate liquid and a sulphide liquid were in equilibrium with each other. In the case of the Bushveld Complex in the Western Transvaal this event happened when the pyroxenes of the pyroxenite, lying immediately above the feldspathic pyroxenite, started to crystallize. As soon as the sulphide blebs formed they quickly sank to the bottom. The settling speed of the sulphide

liquid is much higher than that of the pyroxenes which formed simultaneously with the sulphides, with the result that the sulphide liquid came in contact with silicates which crystallized some time before the exsolution of the sulphide liquid from the silicate magma took place. Scholtz (1936, p. 205) calculated with the aid of Stokes' formula that ore pellets 2 mm in diameter settle four times faster than olivine crystals of the same dimensions. Thus the sulphides are now found near the top of the feldspathic pyroxenite. The pyroxenes which crystallized at the time when the sulphide liquid exsolved, now build up the pyroxenite immediately above the feldspathic pyroxenite.

The magma continued to change its composition. Sulphide liquid exsolved constantly from the magma to give rise to the interstitial sulphide in the pyroxenite and the harzburgite. The fact that greater quantities of interstitial sulphide are found in the harzburgite than in the pyroxenite could be explained by gravity control in the settling process of olivine, pyroxene and sulphide. The harzburgites are the heaviest members of the rocks of the Basal Zone and it would thus be expected that the heavy sulphide would be concentrated in the harzburgites. In all these rocks the sulphide blebs are completely modified by the intercumulus growth of the silicates and they consequently build up the intercumulus material.

In the area south of Potgietersrus the Magaliesberg quartzite, which contains up to 10 per cent of pyrite at places and in contact with the rocks of the Basal Zone, could act as a source of S in addition to the magmatic sulphide. Interstitial sulphides are very common in the harzburgites. Most of the sulphides are completely oxidized to magnetite, and/or hematite or were dispersed as very fine roundish disseminations between the silicates during serpentinization. Interstitial sulphide is also found in the feldspathic pyroxenite and the norite intercalated with the ultramafic rocks.

In the Eastern Transvaal very little disseminated interstitial sulphides are known from the rocks of the Basal Zone. In fact, the sulphides in the peridotite of Aapiesdoorndraai are at present the only disseminations known which are concentrated to a certain extent. These sulphides occur mostly along the foot-wall and hanging wall contacts of the peridotite body and it thus appears that the S was introduced by the sediments, although no sulphides were found in the latter. Interstitial sulphide, in contrast with the roundish blebs on the contacts of the body, is present in a dunite from the core of a bore-hole drilled for water in the central part of the body.

The reason for this can be sought in the fact that crystallization on the contacts was faster and that the sulphide droplets were trapped between the olivine crystals. In the central part of the body, on the other hand, crystallization was much slower and the sulphide droplets were modified by adcumulative growth of the olivine crystals and thus were pressed into the interstices.

This would indicate that some sulphide blebs settled to the base of the body and that the existence of an ore-body at the base, where the dip is not so steep (fig. 29) should not be excluded.

The rocks of the Basal Zone in the Eastern Transvaal cut across the same sedimentary layers as those of Western Transvaal. Very little disseminations of sulphide are found in the areas where discordant intrusion took place in the Burgersfort area. If the metasediments immediately above the Magaliesberg quartzite, the Magaliesberg quartzite itself and the hornfels below the quartzite introduced S to the rocks of the Basal Zone in the Western Transvaal, there is no reason why the same metasediments which are sulphide-bearing near the base of the Aapiesdoorndraai body, should not have acted similarly in the Eastern Transvaal. In this respect the rocks in the Eastern Transvaal have the advantage that the Late Hypabyssal norite did not shield them from the metasediments as happened to a certain extent in the Western Transvaal. If we assume that the quantity of magmatic S is the same in the Basal Zone of the Eastern and the Western Transvaal and that the amounts of introduced S is the same in both cases, the absence of the sulphide disseminations in the Eastern Transvaal is difficult to account for. The rocks of the Basal Zone in Burgersfort area are stratigraphically much lower than the lowest horizons intersected by the KA bore-holes. Furthermore, the layers of the individual rock types are much thicker.

This evidence suggests that the sulphides settled towards the base of the Complex in the Burgersfort area and that a concentration of sulphide could be expected at or near the floor of the Complex. The sulphides were thus not trapped during crystallization and solidification of the silicates as was the case in the Western Transvaal.

Depressions in the floor of the Bushveld Complex were proved to exist by gravity-surveys and field- relationships. Basins were found in the Burgersfort-Aapiesdoorndraai area, as well as in the area occupied by the farms De Grooteboom 340 KT, Welgevonden 338 KT and Wildebeestkraal 345

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KT. The synclinal structure displayed by the Pretoria Series and indicated by the Magaliesberg quartzite on Map I south of the Marone Mountain, could have had an influence on the structure of the floor of the Bushveld in this area, which would indicate the presence of a basin structure.

In quite a number of Ni deposits in Canada (Hawley, 1962 and Nalldrett and Kulerud, 1967) and in Sweden (Grip, 1961) brecciation is intimately associated with the massive sulphide at the base of these deposits.

It would therefore appear that the formation of these Ni deposits cannot be explained by gravitative differentiation in a liquid state alone, but that it has been controlled to a certain extent by tectonism during the cooling of the intrusion, whereby the sulphide liquid is squeezed out into certain structures (e.g. breccias). Boudinage structures, intensive folding and rheomorphic breccias are known in the metasediment of the floor of the Aapiesdoorndraai peridotite which would indicate tectonic movement. This tectonism could have had a favourable influence on the concentration of massive sulphides where these had been present.

8. 6 The Mechanism of Assimilation of S from the Pretoria Series by the Magma

The sedimentary rocks of the Pretoria Series contain S in the form of the sulphides pyrite and pyrrhotite. In some localities graphite is found together with pyrrhotite in the shales and hornfelses, whereas pyrite is found in the shales, hornfelses and quartzites. The pyrite in the latter **1s d e+..-;t.._l** rock type, represents a psammitic sediment of mochanical origin whereas the sulphides in the shales originated under biochemical conditions, as indicated c arbon now present as by the presence of the graphite in some cases.

Three processes were of importance during the assimilation of S from the meta sediments by the Bushveld magma:

- 1. Ordinary heat and pressure-distillation of S
- 2. Reaction between the magma and metasediments
- 3. Sulphurization.

8. 6. 1 Ordinary Heat- and Pressure-distillation of S

At first it is necessary to investigate the physical conditions to which the metasediments were subjected in the aureole of the Bushveld Complex. The total pressure in the foot-wall rocks of the Complex could have been as high as 4 Kb. The pyroxene hornfels contact-metamorphic facies was

identified by Willemse (1959) and by Liebenberg (1964) in these rocks on or near the contact with the ultramafic rocks. The temperature of this facies ranges between 650° and 800° C at 1000 bar fluid pressure according to Turner and Verhoogen (1960, p. 525), and biotite, quartz, potassium feldspar and hypersthene probably belong to the granulite facies which represents a maximum temperature of regional metamorphism, perhaps of the order of 700° to 800°C (Turner and Verhoogen, 1960, p. 557). Inclusions of metasediment in the Hendriksplaats norite suffered temperatures equivalent to the sanidinite facies i.e. $+800^{\circ}$ C, although the pressures at the base of the Bushveld Complex were too high for this facies. Metasedimentary sulphidebearing inclusions are found especially in the Western Transvaal.

The following breakdown reactions of pyrite is possible at these high temperatures (Kullerud and Yoder, 1959, pp. 554-555).

$$
\text{FeS}_2 \rightleftharpoons \text{Fe}_{1-x} \text{S} + \text{Liquid} + \text{Vapour, } 743^{\circ}\text{C}, \pm 10 \text{ bar}
$$
\n
$$
\text{FeS}_2 \rightleftharpoons \text{Fe}_{1-x} \text{S} + \text{Liquid} + \text{Vapour, } 796^{\circ}\text{C}, \pm 4000 \text{ bar}
$$

The vapour and gas phases which are almost pure S (neglecting the effect of H₂O at first) could be derived from the metasediments and could be assimilated by the magma. Evidence that this reaction has taken place comes from the foot-wall hornfelses and quartzites from the deep bore-holes in the Western Transvaal (samples KAl-2658, KA4-2083), in which pyrite is exceptional in the rocks belonging to the granulite facies. In the Magaliesberg quartzite south of Potgietersrus pyrite was still stable on the present erosion-surface. But on deeper horizons higher temperatures existed and pyrrhotitization of pyrite could have taken place. The S which was set free, was then assimilated by the magma.

Graphite and arsenic in the metasediments were also distilled from these rocks and assimilated by the magma.

8. 6. 2 Reaction between the Magma and Sulphide-bearing (Meta)sediment

Reaction of metasediments with the magma clearly took place during the intrusion of the Late Hypabyssal (quartz) norites. In thin sections all gradations between a norite, a quartz-biotite norite with or without cordierite and a cordierite hornfels have been observed. The quartz content of the (quartz) norite also increases towards the contact with the metasediment, both in the Eastern and in the Western Transvaal. Thinner sills also contain much more

biotite, quartz and even cordierite, than the thicker sills. It is thus clear that assimilation of the metasediments by reaction between the magma and the metasediments took place. Where the rocks of the Bushveld Complex cut across metasedimentary horizons containing sedimentogenetic sulphides, assimilation of sulphide took place.

8. 6. 3 Sulphurization

On the basis of the theory that immiscibility of sulphide and silicate resulted in the enrichment of sulphides at or near the base of gabbroic bodies, Kullerud (1963, p. 186) reckoned that if immiscibility existed under the PTconditions in the magma chamber, gravity-settling would already have taken place during the generation of the magma. He also stated that liquid miscibility in the magma chamber followed by liquid immiscibility after intrusion is "not physically impossible but highly improbable". As a result of these findings Kullerud and Yoder (1963, pp. 216-218; 1964, pp. 218-222) investigated experimentally a mechanism whereby sulphur could react with the magma. A series of experiments was conducted by heating synthetic ferromagnesian minerals with various amounts of sulphur in collapsible gold tubes at 650° C and 800° C and under pressures of 2000 bars. It was found that olivine containing equal amounts of Fe and Mg would react with S at 800° C as follows:

$$
4 \text{FeMgSiO}_4 + S \longrightarrow \text{FeS} + \text{Fe}_3\text{O}_4 + 4 \text{MgSiO}_3 \dots (2)
$$

If more than 20 but less than 25 per cent by mole S reacted with this olivine, the following results were obtained:

$$
3\,\text{FeMgSiO}_4 + S \longrightarrow \text{FeS} + \text{Fe}_2\text{O}_3 + 3\,\text{MgSiO}_3 \dots (2)
$$

More than 25 per cent by mole S has the effect that no Fe oxide is produced:

$$
2\,\text{FeMgSiO}_4 + 3\text{S} \longrightarrow 2\,\text{FeS} + 2\,\text{MgSiO}_3 + \text{SO}_2 \text{ (gas)} \dots \text{ (3)}
$$

An experiment with fayalite, containing a small amount of Ni yielded pyrrhotite with intergrown pentlandite showing textures similar to those observed in natural nickeliferous ores (Kullerud and Yoder, 1963, p. 217).

A troctolite with 50 per cent of plagioclase and 50 per cent $Fe₁ Mg₁ SiO₄$ reacted with only 2.3 per cent by weight of S to produce 48.88 per cent unchanged plagioclase, 28.45 per cent $\mathrm{MgSiO}_3^{}$, 16.42 per cent $\mathrm{Fe}_3\mathrm{O}_4^{}$ and 6. 25 per cent FeS.

At 650° C the reactions are much slower and pyrite is also stable, being formed instead of pyrrhotite in the three reactions above with $33^{1}/3$, 40 and $71^3/7$ per cent by mole S respectively (Kullerud and Yoder, 1964).

They found that S also extracted the Fe^{2+} out of hedenbergite, almandite and cordierite to produce Fe sulphide and more Mg- or Ca-rich derivatives of the silicates, with or without Fe oxide (Kullerud & Yoder, 1964, pp. 218-222).

Hydrous silicates react with S at still lower temperatures $(500-600^{\circ}\text{C})$ for periods ranging from 2 days to 6 months. Biotite reacts with an excess of S to produce oxymica + pyrite + hematite + $_{2}S$. Hornblende produced oxyhornblende after reaction with S.

The association of disseminated sulphide in the magma and sulphidebearing sediments in the Western and the Eastern Transvaal indicate that the sulphurization process probably took place at the base of the Bushveld Complex. On the other hand the metasediments contain large amounts of Fe-rich metamorphic minerals which would react with the excess of S so that actually little sedimentary S would be available for the sulphurization process in the magma itself.

In the Noril'sk District of Siberia, the Noril'sk and Talnakh plutons are intrusive in sedimentary strata consisting of, inter alia, sandstone, evaporites (gypsum) and coal beds. The Mt. Chernaya pluton is intrusive in the same strata except that coal is absent. Sulphur isotopic study proved that assimilation of sedimentary S by all three plutons had taken place. This indicates that C did not play a role in the reduction of s^{6+} in the CaSO₄ to s^{2-} . According to Cheney and Lange (1967, p. 90) this confirms indirectly that Fe^{3+} , was the major reducing agent. Vinogradov and Grinenko (1964, p. 473) determined that C^o, Fe^o and H^o reduce S^{6+} to S^{2-} at 600^o-800^oC.

In the Bushveld Complex biotite is abundant in the plutonic rocks adjacent to metasediments, especially in the Basal Zone in the Western Transvaal. This biotite could easily accommodate the Fe $^{3+}$ in its structure. If S $^{\rm o}$ was introduced to the magma, as indicated by reactions (1), (2) and (3), which are oxidation-reduction reactions, Fe^{3+} is a reaction product. Seeing that magnetite is nearly absent in the rocks of the Bushveld where sulphurization has possibly taken place, it is reasonable to assume that the Fe $\overset{3+}{}$ is accommodated in the biotite.

Hydrous minerals are some of the major constituents of the hornfelses and even of some of the quartzites. Under these high water pressures, S

would be largely present as H_2S , SO_2 and very little S^O , as confirmed by experiments carried out by Ellis (1957, pp. 415-417) given in table 42.

Table 42. Mole fractions of the different gases in the system H_0O-SO . in a molecular ratio 100:1 at different pressures and 2^2 temperatures (x = mole fraction x 10^3) - after Ellis (1957)

T^0K	P (bar)	xH_oO	xH_2S	XSO_{α}	xH_{α}	XS_{0}
600		980.2	13.2	6.6	0.016	0.007
1000		975.3	11.5	8.2	4.9	0.063
1200	1000	979.0	11.6	7.0	2.4	0.010

Wilson and Brisbin (1961, p. 476) found that $\text{H}_{2} \text{S}$ will react with peridotite to produce nickeliferous pyrrhotite. Magnetite is also altered to pyrrhotite at temperatures ranging from 400 to 600°C and at standard pressures.

9. THE MERENSKY REEF

The Merensky Suite of rocks (fig. 30) are at the top of the Critical Zone and consist mainly of two layers of feldspathic pyroxenite, together with spotted or mottled anorthosite and/or norite. In the lower feldspathic pyroxenite, pegmatoid and chromitite layer(s) are found.

The foot-wall rocks of the Merensky Reef are spotted and/or mottled anorthosite and/or norite (fig. 30). The spotted and mottled anorthosites or norites are plagioclase cumulates in which the pyroxene has an intercumulus relationship, except in the norites in which the pyroxene is also a cumulate. When the pyroxene crystals or clusters of pyroxene crystals are less than $+1$ cm in diameter the adjective "spotted" is applied and when they are more than *±.* 1 cm in diameter the adjective "mottled" is applied to the rock type. The top of the foot-wall rocks consist of a thin layer of anorthosite which is almost barren of pyroxene. In the Eastern Transvaal on Zeekoegat 421 KS, Lydenburg District a foot-wall leader of pyroxenitic norite, 3 feet thick, is also developed.

The feldspathic pyroxenite was generally called the Merensky Reef. Nowadays the Merensky Reef is defined as a norite, a pyroxenite or an olivine-bearing pegmatoid layer, which is present at the base of the feldspathic pyroxenite in the Rustenburg and Schilpadnest areas (fig. 30). In the Eastern Transvaal this pegmatoid appears near or at the top of the pyroxenite (fig. 30). The data presented in fig. 30 are based on the author's own observations on drilling cores from Umkoanesstad 419 KS, Lydenburg District and the Rustenburg area. Data given by Wagner (1929) and Cousins (1964) are also used. More than one layer of pegmatoid is developed in some localities e.g, three were observed **nn** Umkoanesstad 419 KS, Lydenburg District. Chromitite seams (usually not more than 2 inches thick) are also developed on different horizons in the pyroxenite as indicated in fig. 30. They are, however, mostly restricted to horizons above and/or below the pegmatoid (fig. 30). The thickness of the feldspathic pyroxenite and the pegmatoid is mostly between 3 and 9 feet. At the Union Platinum Mine the thickness of the Merensky Suite of rocks is exceptional. The thickness of the various rock types, from the different areas, is indicated in fig. 30.

The platinum and sulphide mineralization is mostly associated with the pegmatoid or is confined to the vicinity of a chromitite seam in the feldspathic

Fig. 30. Generalized diagrammatic profile through the Merensky Suite of rocks. Figures in parenthesis are the thicknesses at the Union Platinum Mine

pyroxenite (fig. 30). The chromitite seams always show high platinum values.

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The hanging wall rock is mainly a spotted norite or an anorthosite 5-10 feet thick. Above this layer a spotted norite or a mottled anorthosite of 30-50 feet thick is present. The Bastard Reef is developed immediately above this rock type and consists mainly of feldspathic pyroxenite $+12$ feet thick. Disseminations of sulphide with accompanying low Pt values are usually noticed near the top or the base of the Bastard Reef. A chromitite seam is also developed in some localities in the Schilpadnest area. The Bastard Reef is, therefore, a repetition of the Merensky Reef with a less intense mineralization.

9.1 The Composition of the Sulphide Phase and the Associated Minerals

The variation in the mineralogical composition of the sulphide phase of the Merensky Reef, the pegmatoid, the chromitite, the foot-wall and hanging wall rocks in the Rustenburg Mine are given in table 43. In general the percentages of pyrrhotite and pentlandite remain more or less constant. The fluctuations are due to the lack of representativeness of the sample. The only major variation is the appearance of pyrite and the simultaneous decrease in the percentage of chalcopyrite in the pegmatoid as well as near the top of the feldspathic pyroxenite (table 43). The volumetric composition of the sulphides of the Bastard Reef is approximately the same as those of the Merensky Reef and the pegmatoid (table 43). The platinum minerals sperrylite, braggite and cooperite were mostly observed in the chromitite and the pegmatoid. An occasional speck was also noticed in the feldspathic pyroxenite. Cousins (1964, p. 230) mentioned the presence of ferroplatinum as the principal mineral containing the P. G. M. with very little laurite and stibiopalladinite.

The composition of the sulphide phase is also fairly constant from locality to locality (table 43), although pyrite is absent and cubanite present at certain localities, e.g. on Tweefontein 360 KT, Dwars River area and north-west of Potgietersrus, table 43). Together with this variation lamellae of troilite appear in the hexagonal pyrrhotite instead of in the hexagonal and the monoclinic pyrrhotite which are found together with pyrite. In the latter case the sulphide phase is thus more S- rich, whereas the troilite-cubanite association is metal-rich. Mackinawite in pentlandite is present only in the latter association. The percentage of pentlandite is seldom less than half of

Table 43. Volumetric composition of the disseminated sulphides in the Merensky Suite of rocks

that of pyrrhotite and may even exceed it in some specimens (table 43), though this is actually high in comparison with the Vlakfontein deposit and other disseminated ores in the Bushveld Complex (fig. 8).

The different minerals oontaining the P. G. M. are not homogeneously distributed along the strike of the Merensky Reef. In the Rustenburg area braggite, $(Pt, Pd, Ni)S$ is the main mineral which contains the P.G.M. (excluding perhaps the platinum alloys) with subordinate sperrylite and cooperite. On Tweefontein 360 KT, Lydenburg District, and near Groblersdal and Potgietersrus sperrylite is not only the chief mineral, which contains the P, G, M , but the development is fairly prominent and much more so than in the Rustenburg Platinum Mine (table 43). It is worthy of note that where the minerals which contain the P, G, M , are present in relatively large amounts the Merensky Reef are in contact with or near sedimentary rocks e.g. at Potgietersrus, Groblersdal and Tweefontein 360 KT, Lydenburg District. The greatest concentration of minerals containing the P. G. M. (sperrylite, cooperite, BiPd_3) were found in the mineralized skarn at Potgietersrus. Usually the minerals containing the P. G. M. are in association with chalcopyrite.

As far as the oxides in the Merensky Reef are concerned, a quite Ferich chromite is the most common oxide. Two generations of this mineral are present: firstly, roundish or euhedral grains of chromite which were the first to crystallize and, secondly, euhedral grains which crystallized more or less simultaneously with the sulphides. Rutile was also observed in the ores from Rustenburg and from Potgietersrus (photo 101, 102).

9.2 Some aspects of the Geochemistry of the Merensky Reef

Although the Cu/Cu + Ni values $(0.06 - 0.45)$ are comparable with those of other deposits in the world (table 45), the Ni content of the Merensky Reef, which carries disseminated sulphide, is quite high. Only some ultramafic rocks of the Basal Zone have a higher Ni content, which becomes apparent when comparing the Ni and S values in fig. 36. This effect is also illustrated by the relatively high percentage of pentlandite of the Merensky Reef. As and Sb were also found in some specimens and the highest values were recorded in the Schilpadnest area (table 44).

The P. G. M. content of the pegmatoid, the chromitite and the feldspathic pyroxenite is very variable. Generally the chromitite has the highest values,

Table 44. Analytical values of S, As, Sb, Ni, Cu, Pt and Au in the Merensky Reef and the associated rocks from some localities. (The first 13 values are from Wagner, 1929).

Table 46. The ratios of the P.G.M. from different localities and ore types of the Merensky Reef (Wagner, 1929, pp. 110-111)

	Klipfontein Kroondal Rustenburg		Schilpadnest 385 KQ, Rustenburg		ore Sulphide Ğ,	ore	ore	Potgie- ore	PoH ore LR,	Pot- ore	
	ore Oxidized	ore Sulphide	ore Oxidized	gm Bullion 347	69 Elandsfontein Rustenburg:	Oxidized 117 JQ, Lydenburg: Hill Forest	Sulphide ፲፲ Lydenburg: \circ Helena	Oxidized KR, 325 tersrus: Vaalkop	Oxidized 818 Zwartfontein gietersrus:	Zwartfontein 818 LR, gietersrus: Sulphide	Concert of the Potentian or the Potentian concentration concentrates
Pt	77.5	66	76.3	73.4	70.0	73.0	74.13	38	55	48	53.3
Pd	15.2	25	11.8	20.8	20.0	20.0	24.91	62	44	50	40.6
Rh	2.0	$\overline{\mathbf{4}}$	1.70	5.3							
Ir	1.3	$\qquad \qquad \blacksquare$	1.18								2, 2
Os	0.95	$\mathbf 1$	4.50	0.5	5.0	$2\, .$ $0\,$	0.90				
Au	2.57	$\overline{\mathbf{4}}$	1.90	-	5.0	4.0					3.9
	99.42	100	97.38	100.0	100.0	99.0	99.94				100.0

 $\hat{\boldsymbol{\mu}}$

	Chromite	Olivine	Diallage	Nickeliferous pyrite	Pyrrhotite	Pentlandite	Chalcopyrite	serpentine Millerite
$\boldsymbol{\mathrm{V}}$				$\boldsymbol{+}$				
$\rm Fe$	$++$	$++$	$^{+++}$	$^{+++}$	$^{+++}$	$++$	$+ + +$	$++$
Co	tr	tr	tr	$\boldsymbol{+}$	$\boldsymbol{+}$	$\boldsymbol{+}$	tr	$\boldsymbol{+}$
$\rm Ni$	$\mathop{\rm tr}\nolimits$	tr	tr	$+++$	$^{+++}$	$^{+++}$	tr	$^{+++}$
Cu					$\ddot{}$	$\ddot{}$	$++$	tr
$\mathbf{R}\mathbf{u}$				$1 - 0.1$	$1 - 0.1$	$1 - 0.1$		
$\rm Rh$				$1 - 0.1$	$1 - 0.1$	$1 - 0.1$		
Pd				$100 - 10$	$100 - 10$	$10 - 1$		
$\rm Os$				${\rm tr}$	tr	${\rm tr}$		tr
$\mathop{\rm Ir}\nolimits$				$1 - 0.1$	$1 - 0.1$	$1 - 0.1$		
$\mathop{\rm Pt}$				$100 - 10$	$100~\textcolor{red}{\scriptstyle \sim}~10$	$10 - 1$	\equiv	tr
${\rm Au}$					$10 - 1$			
Ag								

Table 48. Partial, semi-quantitative analyses of some minerals of the Merensky Reef, Schilpadnest 385 KQ (From Wagner, 1929, p. 235)

The figures given are in gm per metric ton

- +++ signifies in large amounts (>+0%)
- + signifies measurable quantities (ca \pm 0.1%)

 $\hat{\mathcal{A}}$

- tr signifies trace (0.0001%)
- signifies not detectable ÷

 \mathbb{R}^2

 \bar{z}

Table 49. Partial, semi-quantitative analyses of the major sulphides in the mineralized skarn, central part of Zwartfontein 818 LR (After Wagner, 1929, p. 236)

The figures given are in gm per metric ton

- +++ Signifies in large amounts (10%)
- + signifies measurable quantities (ca \pm 0.1%)
- tr signifies trace $(0. 0001\%)$
- signifies not detectable $\overline{}$

Table 50. The ratios of the P. G. M. in ore-minerals and ore, Sudbury (Hawley, 1962, pp. 124 - 126)

which are up to 20 dwts/ton (table 47) or even more. The pegmatoid directly above or below the chromitite also carries up to 20 dwt/ton of $P, G, M,$, although usually less than 13. 5 dwts/ton, which has been recorded in the Kroondal vicinity (table 47). The feldspathic pyroxenite above or below the pegmatoid usually contains lower Pt values which are less than 2 dwts/t on. The average value reported by Wagner (1929, p. 109) for the Merensky Reef in general in the Rustenburg district is 6 dwts P. G. M. over a stoping width of 30 inches and an average of between 10 and 12 dwts over a milling width of 12 inches. It appears that the values in th_e Eastern Transvaal are generally lower than 5 dwts (table 47) and are thus lower than the values in the Western Transvaal. The coarse feldspathic pyroxenite in the Potgietersrus Platinum Field is the richest in the Bushveld and often assays above 7 dwts/ ton over a stoping width of several feet.

The Pt/Pd ratio of the Merensky Reef is rather high in the case of the deposits in the Western and the Eastern Transvaal. The sulphide ore has Pt/Pd values ranging between 66 : 25 and 74.13 : 24.91, whereas the Pt/Pd ratio for the oxidized ore is about 10 per cent higher, indicating an enrichment of Pt over Pd in the oxidized zone. In contrast with this, a Pt/Pd ratio of 2. 6 : 2. 5 was recorded from Rooibosbult 168 KS, Pietersburg District. Cousins (1964, p. 230) reported the following percentages of the P . G. M. :-Pt 60%, Pd 27%, Ru 5%, Rh 2. 7%, Ir 0. 7%, Os 0. 6% and Au 4%. These values are probably from the Rustenburg and Union Mines, both in the Western Transvaal. The ores in the Potgietersrus Platinum Field have a Pt/Pd ratio of about 1 or less.

The relation between Pt and the other P . G. M. in the Merensky Reef. in the Eastern and Western Transvaal, is very high (cf. table 46) in comparison with magmatic sulphides in general (cf. table 50), given by Nodack and Nodack (1931) and those of the Sudbury deposits (Hawley, Pt). The Potgietersrus deposit shows a better correlation with the average values of Nodack and Nodack. When comparing the results in tables 50 and 46 the Rh content of the Merensky Reef is comparable with that present in the magmatic sulphides, as determined by Nodack and Nodack (1931). Ir is somewhat lower in the Merensky Reef. Os, on the other hand, is higher.

The P. G. M. have a three-fold mode of occurrence in the Merensky Reef:-

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- 1. As S, Sb, Ci and As minerals, e.g. sperrylite, cooperite, stibiopalladinite and braggite.
- 2. As alloys of the P.G.M. or in combination with Fe and other metals, e.g. Au, Ni, Cu and Co (Wagner, 1929, pp. 13-14). According to Cousins (1964, p. 230) Au is alloyed with Zn and Ag.
- 3. As a solid solution of the P. G. M. in the sulphides.

Semiquantitative analyses of the sulphides in the Merensky Reef were carried out by Schneiderhöhn (Wagner, 1929, p. 235) and are given in table 48 and 49. It is clear that appreciable amounts of the P. G. M. are present in the sulphides and, according to Schneiderhöhn (op. cit.), the P.G.M. decrease with decreasing age of crystallization of the sulphides. This is clear from table 48. The main sulphides in the contact-zone on Zwartfontein 818 LR, Potgietersrus District, contain much less P. G. M. Furthermore, it also appears as if the Pt/Pd ratio in the sulphides from the Merensky Reef is about unity, whereas the ratio in the contact-zone on Zwartfontein 818 LR, Potgietersrus District, is very small. An analysis of Cu and Fe sulphides of a sample from a pothole in the Merensky Reef proved that the P. G. M. are in solid solution in the sulphide.

Polished sections of mineralized skarn from Potgietersrus contain numerous specks (0. 5 mm in diameter) of sulpharsenides containing P. G. M. or Bi compounds containing P. G. M. A great deal of the P. G. M. are thus present as the latter compounds.

In the Merensky Reef of the Eastern and the Western Transvaal, sulphides and arsenides containing P. G. M. (sperrylite, braggite and cooperite) were occasionally come across. No Ferro-alloys containing P. G. M. were seen, although the mineralized chromitite seam in the vicinity of the pegmatoid contain the highest value of Pt. Small specks (0. 02 mm in diameter) of sperrylite (?) are a very rare phenomenon. Most of the platinum must then be present as ferroplatinum, seeing that the chromitite contains very little sulphide in which the Pt could be in solid solution. Some of the sperrylite in the chromitite may have been wrongly identified and may be ferroplatinum.

The composition of the $P.G.M.$ in the dunite deposits in the Lydenburg district given in table 52. The Pt/Pd ratio is very high $-97.50 : 1.23$. If we assume that the Pt/Pd ratio of the metals in the Merensky Reef is more or less the same as that of the dunite deposits, it becomes clear that the rather high

Pt/Pd ratio recorded in the Eastern and the Western Transvaal is caused by the alloys.. This is substantiated by the fact that the Pt/PA ratio of the P.G.M. in solid solution in the sulphides is more or less unity. Furthermore, the oxidized ore, which is richer in metals than the fresh ore, has a higher Pt/Pd ratio than the fresh ore.

The ferro- alloys containing P. G. M. , which are concentrated in the chromitite, do not contribute to the P. G. M. content of the Merensky Reef in the Potgietersrus area, for no chromitite has been found there, nor has any been described by Wagner from that area. The absence of a small quantity of native P. G. M. could also explain the low Pt/Pd ratio in this area in comparison with that of the Eastern and the Western Transvaal. The ratio recorded in the Potgietersrus Platinum Field is thus more or less the same as that of the P. G. M. in solid solution in the sulphide together with the arsenides and sulphides containing $P.G.M.$ in the Merensky Reef in the Eastern and the Western Transvaal.

Compared with the Sudbury ores and minerals (table 50), the largest quantity of P. G. M. in solid solution in the sulphides is in the pentlandite and chalcopyrite and not in the pyrite and pyrrhotite, as is the case in the Bushveld. The Pt/Pd ratio varies considerably and is between $+1$ and 3 for pyrrhotite and pyrite, whereas the ratio for pentlandite and chalcopyrite is smaller than 1.

It has already been mentioned that where the Merensky Reef is developed near the contact with metasedimentary rocks, arsenide and bismuth (?) minerals are developed, e.g. at Potgietersrus, Groblersdal and Tweefontein 360 KT, Lydenburg District. The common sulphides in the mineralized skarn in the Potgietersrus area, carry much smaller quantities (table 49) of P. G. M. than those from Schilpadnest (table 48), far away from the metasediments. Pt itself is almost absent in the sulphides from the former locality. The whole association indicates that As, derived from the sediments, extracted most of the P. G. M. in solid solution in the sulphides, to form, inter alia sperrylite. According to Rankama and Sahama (1950, p. 688), the P. G. M. are siderophile and consequently they are enriched in the arsenide, antimonide and bismuthite phases in the presence of a sulphide phase, for As, Sb and Bi are more metal-like than S. It would thus appear that Pt is even more siderophile than Pd and some of the other $P.G.M.$ to account for its complete extraction from the sulphides in the mineralized skarn in the Potgietersrus

Platinum Field (table 49). The high Pt/Pd ratio in the alloys in relation to the ratio in the copper and nickeliferous sulphides also indicates a bigger siderophile affinity of Pt over Pd. The increase of the Pt/Pd ratio during oxidation of the ore, which is accompanied by an enrichment of metals in the ore, also points to the bigger siderophile affinity of Pt in relation to Pd.

The Bushveld Complex cuts across the Dolomite Series, on the top of which ironstones are found. The Merensky Reef is thus at places in direct contact with the ironstones. According to Rankama and Sahama (1950, p. 741) **As** · is enriched in the oxidates by adsorpsion on ferric hydroxide. Several carbonates of Bi are known and it is thus reasonable to assume that dolomite is enriched in Bi. The Bi of the Pd-Bi compounds in the mineralized skarn at Potgietersrus was then probably derived from the dolomite.

In the Potgietersrus area the content of the pentlandite and the Nicontent of the mineralized skarn area is quite high (table 43 and 44 respectively). It is thus necessary to suppose not only the metasomatism of S, Fe, P. G. M. , etc. to form the mineralized skarn, but also of Ni. These elements were mainly derived from the Merensky Reef which is in contact with the skarn.

9. 3 The origin of the Merensky Reef

The origin of the Merensky Reef and the relationship of the mineralized pegmatoid to the associated rock types have repeatedly been debated amongst geologist working on the Bushveld Complex, but a complete explanation incorporating all the facts is not yet available.

Willemse (1964, p. 123) gave a summary of the existing theories on the genesis of the Merensky Reef. To summarize, Cousins (1964, p. 237), Schmidt (1952, p. 235) and Van Zyl (1960, p. 101) favour the idea of crystal settling during magmatic differentiation. The author mentioned last suggested that the pegmatoid is a product of coarse crystallization at the base of a subunit during which the physical conditions and the presence of Cr and S influenced the crystallinity of the pegmatoid. Schwellnus (1956, p. 162) and Coertze (1958, p. 390) consider the Merensky Reef as a younger pegmatoid intrusion which followed a thin chromitite band, and split it into two bands in places on either side of the pegmatoid.

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Fig. 31. The system gabbroic silicates-pyrrhotite-magnetite. (After F. G. Smith,1961, p. 666.) $S =$ silicates and $M =$ magnetite or oxide. Sometimes in the text it refers to chromite.

Dr. H. S. Yoder (personal communication) mentioned some results of experiments carried out by the Carnegie Institution in connection with the crystallization of silicates, oxides and sulphides from a liquid. These results agree with the views of Smith, given below.

Smith (1961, p. 663-669; 1962, p. 204-211) deduced from the system FeS- SiO₂ - FeO, in which the exact phase relations are known, the qualitative relations in the system pyrrhotite-gabbroic silicates-magnetite (fig. 31). According to him, sulphides could originate under two sets of conditions prevailing in gabbroic rocks, viz.

1. When the oxidation potential of the magma is quite high and some Fe is present as Fe , an oxide such as magnetite, or a silicate would crystallize first (liquid compositions c and b respectively in fig. 31). This crystallization is followed by silicate and magnetite along the liquidus track and finally sulphide, magnetite and silicate crystallize at point e, the ternary eutectic.

2. If the oxidation potential of the magma is low and the iron is present as Fe $^{2+}$, a liquid with a composition indicated by the point a (fig. 31) would start to crystallize as silicate and the composition of the residual liquid moves to point 1 , fig. 31. At this temperature a sulphide liquid with composition 2 appears. During the further crystallization of silicates, the sulphide liquid moves towards 4 and the silicate liquid moves to 3 where it disappears. Silicates followed by silicates + magnetite now crystallize from the sulphide which moves along towards the point where sulphide, magnetite and silicate crystallize at a ternary eutectic.

In the disseminated ore from the Bushveld Complex, e, g , the Merensky Reef and the mineralized anorthosites, the crystallization of sulphides, silicates and oxides took place from the intercumulus liquid.

The first set of conditions mentioned above, appears at first sight to fit the origin of the Merensky Reef quite well. In the first instance there is the chromite in the Merensky Suite of rocks; this is about the highest stratigraphical horizon on which chromite appears in the Bushveld Complex. The layers above this chromitite seam contain magnetite and ilmenite. Actually two generations of chromite are observed in the Merensky Reef, viz·

- 1. the euhedral or roundish grains of chromite found mainly in the chromitite seams above or below the pegmatoid, or in the feldspathic pyroxenite, and
- 2. a coarser, more irregular type of chromite which is mainly developed in the pegmatoid.

It will now be necessary to refer to the origin of the rocks of the Critical Zone. The anorthosite may be considered as a plagioclase cumulate and the spotted norite as a plagioclase-pyroxene cumulate. Therefore the plagioclase and the pyroxene crystallized simultaneously and settled to build up the spotted anorthosite and/or norite. The remaining liquid became enriched in chromite and sulphide (the cause of this enrichment of sulphide is discussed in the section dealing with the behaviour of the chalcopile elements, $pp.208$), the latter of which is miscible with the silicate-oxide magma. The next mineral to crystallize together with the silicates is chromite and with the aid, probably, of convection-currents the chromitite seam at the base of the pegmatoid was formed. A high oxidation potential existed in the magma at this

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time. The minerals of the pegmatoid $i.e.$ the silicates, the coarse chromite and the sulphides, crystallized next at an eutectic point. This eutectic crystallization took place from the intercumulus liquid situated between silicate and chromite cumulus crystals. If we take into consideration that the pegmatoid crystallized at an eutectic point, at which the last liquid in the zone of crystallization solidified, we have to assume that immediately after the crystallization of the pegmatoid an influx of magma must have taken place, or that a change in the composition of the magma could also have taken place as a result of convection-currents. The feldspathic pyroxenite and the norites above the pegmatoid crystallized from this new magma.

The origin of the Merensky Reef and its relationship to the associated rock types could also be explained with the aid of the alternative possibility suggested by Smith (given above). During the crystallization of the norite and the spotted or mottled anorthosite of the Critical Zone~ the chief sulphide which formed was chalcopyrite. The mean S content of the Bushveld magma was between 250 and 300 ppm, whereas the mean S content of the norite and the anorthosite in the upper part of the Critical Zone is below 100 ppm. Thus an enrichment of S took place in the magma during the crystallization of the upper part of the rocks of the Critical Zone. Immediately before the Merensky Suite of rocks (chromitite, pegmatoid and feldspathic pyroxenite) **formed**
were found, a period intervened during which no crystallization and accumulation of crystals took place. It is immaterial whether this break was caused by a new influx of magma, in addition to the magma, which was enriched in S, or by a convection-currents, which is the most acceptable mechanism to explain this break in the accumulation of crystals.

Jackson (1960, pp. 96-99) gives details of the mechanism whereby a break originated in which no crystallization took place and which was accompanied by a convection current. A modification of this theory is now presented. When the adiabatic gradient of the temperature of the magma crosses the melting-point gradient as in fig. 32a, crystallization would take place. Owing to the latent heat of crystallization the temperature of the crystallization zone would slowly rise until the temperature gradient curve has the same slope as the melting-point curve (fig. 32b). At this stage crystallization would stop and the already crystallized products would settle to build up the upper part of the Critical Zone. The lower part of the warmer (lighter) magma would mix with the higher, heavier magma and a convection

Fig. 32. Diagrams illustrating the mechanism of the formation of a convection current and a break in the crystallization of a magma (After Jackson, 1960, pp. 96-99)

current would be induced. Fresh, cooler magma will then be brought to the bottom and an adiabatic gradient is again created with consequent crystallization (as in fig. 32c). This convection current could also tend to "erode" a part of the already partially solidified rock to explain the cross-cutting relationship of the Merensky Reef relative to the anorthosites of the Critical Zone, as reported by Feringa (1959).

The first mineral to crystallize after this period of formation of convection currents was chromite at a high oxidation potential, during which most of the Cr³⁺ and Fe³⁺ were removed as chromite, which settled to form the chromitite. The oxidation potential of the magma then dropped. Due to the change in composition of the magma the sulphide liquid which was miscible with the silicate-oxide liquid starts to form droplets of immiscible liquid which accumulate, together with crystals of silicates.

This sulphide liquid which contained dissolved oxide (chromite) and silicate with a composition more or less the same as at point 4 in fig. 31, filled up the intercumulus spaces in the pegmatoid. Silicates and chromite exsolved from the sulphide liquid. The coarse chromite in the pegmatoid belongs to this generation. As a result of this crystallization of coarse chromite, the sulphide (-oxide-silicate) liquid approached the eutectic point where sulphide, oxide and silicates crystallized simultaneously (point e, fig. 31).

The coarse texture of the Merensky Reef could be attributed to the sulphides, although pegmatoid, without sulphide mineralization is also known. It was found that silicates (olivine and pyroxene) which crystallized in the

presence of sulphide in the poikilitic sulphide ore from Vlakfontein are quite coarse-grained. Another explanation for this texture is that the difference between the temperature of the magma and the melting point was initially very small. This was especially the case after the adiabatic gradient was reestablished, subsequent to the convection-current, as illustrated in fig. 32c. The conditions in the zone of crystallization could thus be described almost as a two-phase liquid-crystal equilibrium. These conditions resulted in the crystallization of a coarse rock.

The minerals of the feldspathic pyroxenite crystallized next. The oxidation potential of the magma was again relatively high, so that chromite could crystallize. Chromite is a common accessory constituent of this latter rock and it is expected that this mineral would concentrate at the base of the feldspathic pyroxenite, owing to its greater density, to form the chromitite seam between the pegmatoid and the feldspathic pyroxenite. The pegmatoid could also be near or at the top, or as small layers within the feldspathic pyroxenite. The equilibrium between liquid and crystals could easily be established by the latent heat of crystallization of the feldspathic pyroxenite below, so that coarse layers could crystallize again.

In the anorthositic rocks which form the foot-wall of the Merensky Reef, disseminations of sulphide are present. The mineralogical composition of these sulphides is more or less the same as that of the Merensky Reef (table 43) and differs completely from the composition of the sulphide phase in the anorthosites. The sulphides in the foot-wall rocks are thus either a product of crystallization of trapped intercumulus liquid with the same composition as the sulphides in the overlying magma enriched in sulphide, or, the sulphides in the foot-wall rocks may be ordinary impregnations derived from the overlying mineralized pegmatoid.

It has been mentioned already that the chromitite has the highest Pt values and that it appears as if the main mineral which contains the P. G. M. is ferro-platinum. Because the heavy P. G. M. are concentrated in the heaviest member of the Merensky Suite of rocks, gravimetric control could have played a role in the concentration. On the other hand, in the Onverwacht pipe in the Eastern Transvaal "inclusions" of the Main Chromitite Seam also showed the highest Pt values and the theory was put forward by Wagner (1929, p. 68) that this chromitite could have acted as a sponge as far as the Pt is concerned. It is possible that the same conditions are applicable to the chromitite

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of the Merensky Reef.

The possibility exists that Pt $^{2+}$ replaced Fe $^{2+}$ diadochically in daubréelite (Fe $\,Cr_{2}\,S_{4}^{}\,$) in the mantle. In a magma derived from the mantle, this mineral would oxidize to form chromite and the Pt would be expelled - Pt is sulphophile but not oxyphile.

10. THE SULPHIDES IN THE PEGMATOIDS OF THE CRITICAL ZONE AND THE LOWER PART OF THE MAIN ZONE

10.1 Distribution and Composition of the Pegmatoids

The pegmatoid bodies are most commonly found in the lower part of the Critical Zone, although bodies may also be present in the Basal Zone, the upper part of the Critical Zone and the lower part of the Main Zone. As mentioned previously the pipes of sulphide pegmatoid found in the Basal Zone in the Western Transvaal and the magnetitite plugs developed in the Main and the Upper Zone are genetically closely related to the pegmatoids of the Critical Zone.

The composition of the pegmatoids varies considerably being diallage pyroxenitic or diallage noritic, with or without phlogopite. Ultramafic types with pure forsteritic olivine or hortonolite are known. Chromite, magnetite and ilmenite are frequently observed in these rocks. These bodies are mostly barren of sulphides and it is only an occasional one that contains disseminations of sulphide.

The shape of these bodies are dyke-like, pipe-like or generally irregular. A zoned arrangement of the different rock-types is also a general phenomenon. The Onverwacht pipe serves as an ideal example to illustrate this zoned arrangement, with hortonolite dunite forming the core, followed by a rim of forsteric dunite and then an outer zone of diallage pyroxenite. The host- rock is pyroxenite.

10. 2 The Sulphides of the Pegmatoid

Sulphides are actually very rare in the pegmatoids. To date a bore-hole in a pegmatoid on Middellaagte 382 KR, Rustenburg District, has revealed the highest percentage of disseminated sulphides. This deposit was described in detail by De Bruyn (1944, pp. 69-96). A volumetric analysis of these ores is given in table 51.

Generally speaking, the sulphides in the hortonolite dunite are pyrrhotiteand cubanite-rich as indicated by the first two analyses and the last analysis in table 51. The other analyses of the hortonolite dunites show the same tendencies. The forsterite dunite from Onverwacht and Mooihoek contain, however, mostly pentlandite. Most of the analyses are based on samples which are not representative of the deposit as a whole and they are therefore not very reliable and may deviate by about $+15$ per cent from the normal. The

sulphides in the pyroxenitic host- rocks of these pipes and bodies are much richer in pentlandite.

The sulphide phase in the hortonolite dunite corresponds with the silicate phase in that both are enriched in Fe in comparison with the neighbouring rocks,

From the Mooihoek pipe two modifications of cubanite and probably also isometric cubanite were identified. A full description of their relationship to each other is given in chapter 4, dealing with the mineragraphy of the Bushveld sulphides.

10. 3 The Platinum Mineralization of the Pegmatoids

The P. G. M. in the pipes of hortonolite dunite are present as platinum alloys or ferro-alloys containing P.G.M. This is in contrast with the Merensky Reef where the P. G. M. is found in solid solution with the ordinary Fe-Cu-Ni sulphides, as separate sulphides, as arsenides and as alloys.

Analyses of these alloys from the three platinum-bearing pipes in the Eastern Transvaal (table 52) indicate that the Pt/Pd ratio is much higher than that of the Merensky Reef (table 46).

The Pt content of the hortonolite dunite of Onverwacht varies from nil to 1213 dwts/ton with an average of 1 oz/ton in the upper parts of the pipe (Wagner, 1929, p. 68). At the Onverwacht and Mooihoek pipes the values

gradually increased towards the centre of the pipe and towards higher leves levels of the hortonolite dunite part of the pipe. The highest values were recorded from chromitite xenoliths in the hortonolite of the Onverwacht pipe, whereas phlogopite and black hornblende were associated with the highest value in the hortonolite core of the Mooihoek pipe (op. cit. p. 74). In the latter occurrence the Pt values ranged between 0 and 100 dwts/short ton. In the Driekop pipe, on the other hand, Pt-rich schlieren of hortonolite occurred in forsterite dunite (op. cit. p. 80). from 1.5 to 54 dwts in Fe-rich olivine veins. The : Pt content varied

	I	\mathbf{I}	III	${\rm IV}$
Pt	84.75	84.00	98.30	97.50
\mathbf{Os}			1.00	0.40 Ť
Ir	0.95	2.30		0.20
Rh	n.d.	0.20	0.30	0.67
Pd	0.53	0.30	0.40	1.23
Ni	0.48			
Cu	1.28	trace		
Fe	11.98	12.80		
	99.97	99.60	100.00	100.00

Table 52. Analyses of alloys of the P. G. M. from Onverwacht 292 KT, Mooihoek 255 KT and Driekop 253 KT (Wagner, 1929, p. 19)

- I Picked grains from hand-crushed dunites, Onverwacht
- II Picked crystals from outcrop, Onverwacht
- III Sample of crude platinum, Onverwacht
- IV Crude platinum alloy recovery from crushed dunite of Mooihoek and Driekop pipes.

10.4 The Genesis of the Pegmatoid Pipes

As already stated (p. 135) the genesis of these pipes in the Critical Zone is similar to that of the sulphide-bearing pegmatoids from the Basal Zone in tbe Western Transvaal. In short, they crystallized from a pegmatoidal fluid which originated in the intercumulus spaces of the rocks of the Critical Zone. The pegmatoidal fluid is a differentiation product of the pyroxenites and the norites of the Critical Zone. It could be expected that these fluids would be

more Fe-rich and Na-rich than the surrounding layered rocks. This difference in composition is illustrated by the pegmatoid bodies with their Fe-rich olivine and pyroxene. The sulphides in the pipes of hortonolite dunite are generally more Fe- and Cu-rich than the sulphides in the surrounding layered pyroxenite. They thus also display the effect of differentiation, It has been deduced in a previous section $(p_1, 80)$ that the differentiation trend in the sulphides is towards Cu-rich and finally Fe-rich sulphides.

11. THE MINERALIZED ANORTHOSITES BELOW SOME MAG-NETITITE SEAMS

Two layers of anorthosite with 5 per cent or more of disseminated sulphide are developed below some magnetitite seams. They are

- A. The mineralized anorthosite immediately below the Main Magnetitite Seam.
- B. The mineralized anorthosite just below the Uppermost Magnetitite Seam.
- 11.1 The Mineralized Anorthosite immediately below the Main Magnetitite Seam

This layer of mineralized anorthosite varies in thickness from about 2 feet to 20 feet or more and is very persistent along the strike. In the thicker parts the mineralization is more scattered than in the thin layers (about 2 feet thick) in which greater concentrations of sulphides are found. About one mile south of Magnet Heights a small occurrence (3 0 feet in diameter) of mineralized anorthosite is present $+ 200$ feet above the Main Magnetitite Seam.

The sulphides have an intercumulus relationship to the cumulus plagioclase crystals. Magnetite and ilmenite also form the intercumulus material. In certain cases the magnetitie is replaced by silicate (chlorite) and to a lesser extent by sulphide. Ilmenite which exsolved from magnetite along (111) and also as discrete grains is not affected by replacement and a beautiful relict-texture is thus formed (photo 103, 104).

The volumetric composition of the sulphide ore-minerals, from several localities, are given in table 53. The composition of the sulphide phase is quite uniform along the strike, although cubanite is present at some localities. This indicates that at certain localities the sulphide phase is more metal-rich than in others. In some polished sections from a core obtained from a borehole north of Pretoria the cubanite and the pyrite are present in the same section, which represents an unstable association below 334°C.

The volumetric composition of the sulphides from the local occurrence above the Main Magnetitite Seam in the Magnet Heights area is about the same as that below the Main Magnetitite Seam, except that gersdorffite is also present (table 53).

The sulphide phase in the anorthosite below the Main Magnetitite Seam is the richest in chalcopyrite compared with all other stratigraphical horizons

Table 53. Volumetric composition of the sulphide-bearing anorthosites immediately below the Main Magnetitite Seam and in the Upper Zone

Table 54. Partial chemical analyses in ppm of the mineralized anorthosite below the Main Magnetitite (first two analyses) and the Uppermost Magnetitite Seam. Metallic elements in ppm, Sand *As* in percentages

on which sulphide is concentrated to a certain degree (fig. 8). This enrichment in Cu-rich minerals is also reflected in the high Cu-content of the rock compared with Ni and S (table 54). The Pt content of this rock is about 2 dwts per short ton.

11. 2 The Mineralized Anorthosite just below the Uppermost Magnetitite Seam

In contrast with the sulphide-bearing anorthosite below the Main Magnetitite Seam that below the Uppermost Magnetitite Seam is not so persistent along the strike. The anorthosite containing disseminated sulphide is more lens-shaped immediately below the magnetitite. Actually only two localities are known where these sulphides are present, namely on Duikerkrans 173 JS, Middelburg District, (in the bed of the Steelpoortriver) and on Diepkloof 186 JS, Groblersdal District. This absence is due to the fact that these rocks crop out very poorly.

In some localities the anorthosite contains hornblende and sulphide with access accessory plagioclase and magnetite (or ilmenite). The sulphidesin the latter case are also present as roundish blebs and as a result of the high concentration of the sulphide a fairly massive sulphide is sometimes found.

The volumetric analysis of the sulphide (table 53), indicates that the sulphide phase is very rich in pyrrhotite. Chalcopyrite and pentlandite are present in only small quantities. The partial chemical analysis of the rock also illustrates the deficiency in Ni and especially in Cu in comparison with the mineralized anorthosite below the Main Magnetitite Seam.

Above the Uppermost Magnetitite Seam, mainly pyrite is present in the diorite. It may well be that some of this pyrite originated from pyrrhotite by supergene alteration.

11. 3 The Genesis of the Sulphides below the Magnetitite Seams

The disseminated sulphides are present in anorthosite directly below the Main and the Uppermost Magnetitite Seams. The base of the Magnetitite Seams is almost always very sharply defined, whereas the top is gradational into anorthosite and gabbro above.

We may therefore vizualise that the same conditions existed repeatedly, whereby the magnetitite seams were formed to give a cyclic appearance to the Upper Zone, in which the magnetitite seams occur. It is immaterial whether these cycles were produced by a repeated influx of fresh Fe-rich

magma, or by convection currents, or by both. A magnetitite seam indicates the beginning of a cycle.

The appearance of sulphides below the Main and the Uppermost Magnetitite Seams can be explained in terms of the ternary phase diagram of FeS-magnetite-gabbroic silicates (fig. 31) of Smith (1961): Each cycle started with the crystallizatjon of magnetite (point c, fig, 31) to form the magnetite seam ... This was followed by the simultaneous crystallization of magnetite and silicates to give rise to the magnetite gabbro. The composition of the magma changed as a result thereof and became enriched in sulphide. At a certain composition, sulphide, magnetite and silicate started to crystalize at a ternary eutectic from the residual intercumulus liquid. This took place at the end of a cycle, to account for the sulphide-bearing magnetite anorthosite. If we assume that the cycles were brought about by convection-currents, only the liquid in the zone of crystallization (fig. 32a) moves towards the eutectic whereas the composition of the overlying liquid remains unchanged.

The fact that sulphides are not present below each magnetite seam could be attributed to the disturbance of the cycle before its end by either a new influx of magma or by a convection-current.

Small specks of sulphide are, however, present in all the rock-types, even in the magnetitite. These sulphides could have crystallized from trapped intercumulus liquid.

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12. SULPHUR ISOTOPE INVESTIGATION

12. 1 Introduction

In the previous chapters of this treatise it has already been shown that disseminated sulphides are present throughout the whole succession of the Bushveld Complex; \int_{0}^{9n} certain horizons e.g., the Merensky Reef and the mineralized anorthosites below the Main and the Uppermost Magnetitite Seams, sulphides are concentrated to a considerable degree. The Basal Zone in the western sector of the Bushveld, south of Potgietersrus and also near Burgersfort in the Eastern Transvaal, contains intercumulus sulphide. Sulphidebearing pipes with a pegmatoidal character are found particularly in the Western Transvaal and indications of these pipes are known from the area south of Potgietersrus.

The suggestion has been put forward by Willemse (1964, p. 122) that the sulphide in the Basal Zone in the Western Transvaal originated by assimilation of sedimentary material by the intrusive magma. This conclusion is based on the fact that the mafic and the ultramafic rocks of the Complex cut across the sedimentary rocks of the Transvaal System in this particular region. These sedimentary rocks contain sulphides of possible sedimentary origin. Graphitic shales are also known from horizons below the Magaliesberg quartzite (cf. p.144).

In bore-holes sunk in the western sector of the Bushveld Complex, sulphides are present in the plutonic rocks as well as in the hornfels belonging to the Transvaal System. The sulphides in the plutonic rocks are ordinary pyrrhotite, pentlandite and chalcopyrite normally associated with mafic rocks. The sulphides in the hornfels consist mainly of pyrrhotite and chalcopyrite with very little pentlandite (almost only as flames) in the pyrrhotite. Near the contact between the metasediments and the mafic rocks larger quantities of pentlandite are present. No signs of hydrothermal action are evident in the hornfels. It thus appears that the sulphides in the hornfels are of sedimentary origin, whereas the Ni in these sulphides is also probably sedimentogenetic (analyses of sedimentary sulphiide in shale indicated the presence of up to 1000 ppm of Ni) or of metasomatic origin i. e. introduced by the magma.

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On Grasvally 293 KR, Potgietersrus District and also on Aapiesdoorndraai 298 KT, Lydenburg District, disseminated sulphides are present in the rocks of the Basal Zone of the Bushveld Complex as well as the adjacent sedimentary rocks. The association of disseminated sulphide in the plutonic rocks of the Bushveld Complex, where *the* latter cut across sulphide-bearing sedimentary strata, is thus clear.

The main purpose of this part of the investigation was to compare the sulphur isotope ratios of true sedimentary sulphides, far away from the Complex, with the sulphur isotope ratios of the sulphides in the hornfels and the sulphide in the plutonic rocks of the Basal Zone, especially in the western part of the Bushveld Complex, to see whether assimilation of S had taken place.

In other differentiated layered intrusions, e.g. the Sudbury intrusive (Thode et al, 1962) the Leitch sill (Shima et al, 1963, p. 2842), the Insizwa intrusive (Shima et al, 1963, p. 2841), the Gettysburg sill, the Belmont stock, the Saint Peters sill and the Palisade sill (Smitheringale and Jensen, 1963, pp. 1196-12 *oo)* it was found that there is a tendency for the late-stage products of magmatic crystallization to be enriched in $\text{S}^{34}.$ Another aim of the determination of sulphur isotopes on the Bushveld Complex was to establish whether fractionation of the sulphur isotopes had taken place durmg differentiation. For this purpose, samples were collected from different horizons in the layered sequence of the Complex.

12. 2 Experimental Part

Fresh samples were taken which were representative of a certain layer with respect to texture and mineral composition. From the cores of the boreholes drilled in the Western Transvaal, samples were taken across a layer enriched in sulphides. The location of the samples are given on Maps I, II and III.

Samples ranging from 0. 5 to 10Kg, depending on the sulphide content, were crushed to -80 mesh and treated in a flotation cell to concentrate the sulphides. Further purification was done by elutriation and by magnetic methods. Care was taken not to separate the different sulphides.

The sulphide concentrates contained between 30 per cent and 100 per cent of sulphides. Smitheringale and Jensen (1963, p. 1190) state that contamination by the xanthate used in the flotation process does not take place to such an extent that a change in the $\,$ oS 34 $\,$ per mil values of several specimens, each

prepared with the aid and without the aid of flotation, could be observed. The concentrates were nevertheless treated with 20 per cent nitric acid for about 20 seconds and thereafter washed with water, alcohol and acetone to remove the flotation reagents.

The isotope ratios and δS^{34} per mil were very kindly determined by Mr. Aikira Sasaki of the Department of Physics, University of Alberta, Canada.

12. 3 Results and Discussion

The results of the sulphur isotope determinations are given in table 55, together with a comprehensive description of the different samples. For the rocks of the Bushveld, 39 δs^{34} per mil values are given as well as the value for a meteorite from Okahandja S. W. A.

Although many more $\,\mathrm{^{834}}$ per mil values are necessary in order to approach the problems statistically, certain tendencies which are discussed below, are evident from the data available.

A diagram of all the $_{\delta}S^{34}$ per mil values, in the form of a histogram, for the rocks of the Bushveld Complex and for the neighbouring metasediments, is given in fig. 33. The sulphides of the layered rocks of the Complex far away from any metasediments have values in the vicinity of 0. According to Smitheringale and Jensen (1963, p.1192 -1195) magmatic S, and therefore S derived from the Upper Mantle,has a δS^{34} per mil value of + 0.1 and meteoritic sulphur has a value of $+ +0.2$, The layered rocks of the Basal Zone in the western sector of the Complex have relatively large positive values (+7. 8 and $+7.5$, except one value (-1.2) , which could be considered normal for the layered rocks. The norites (Hendriksplaats type) belonging to the Late Hypabyssal Phase of the Bushveld Complex also have relatively large positive values $(+7.8$ and $+10.3)$ except in one case in which the value is $+2.1$. It is also clear from fig. 33 that the values of the layered rocks of the Basal Zone, as well as for the Late Hypabyssal Phase, correspond with the values of the metasedimentary rocks above the Magaliesberg quartzite which are also high positive (+8. 6, +8. 0 and +9. 2). These latter plutonic rocks are mostly, but not always, in contact with the metasedimentary rocks above the Magaliesberg quartzite. One of the values for the sedimentary rocks far away from the Complex is also high and positive $(+7.8)$.

$$
\delta S^{34} \text{ O}_{00} = \frac{(S^{34}/S^{32}) \text{ sample} - (S^{34}/S^{32}) \text{ standard}}{(S^{34}/S^{32}) \text{ standard}}
$$
x 1000

Standard: sulphur in Cañon Diablo Troilite, in which the $\mathrm{S}^{32}/\mathrm{S}^{34}$ = 22.220 Experimental precision: \pm 0.2 $\%$ oo or better.

-
- Fig. 33. A histogram compiled for the $\,\,\overline{\mathrm{6S}}^{34}$ per mil values of the rocks of the Bushveld Complex and the Pretoria Series, showing the relationship between the values of some rocks of the Basal Zone, the Late Hypabyssal Phase and those of the hornfelses and the sediments

Layered rocks of the Bushveld Complex

Layered rocks of the Basal Zone in the Western Transvaal

Norites and quartz norites in contact with metasediments above the Magaliesberg quartzite

Feldspathic pyroxenite, (quartz) norite and other layered rocks in contact with metasediments below the Magaliesberg quartzite

Vlakfontein; massive sulphides

Metasediments above the Magaliesberg quartzite

Metasediments below the Magaliesberg quartzite

- Sedimentary sulphur far away from the Complex. Negative values, Magaliesberg \downarrow shale; positive value, Daspoort quartzite
- \downarrow Aapiesdoorndraai peridotite: Negative value, foot-wall contact; positive value, hanging wall contact

On the other hand, the plutonic rocks (feldspathic pyroxenites, harzburgites and (quartz) norites) which intruded, or cut across metasedimentary rocks below the Magaliesberg quartzite, have relative large negative values (ranging from -4. 3 to -11. 7). The hornfelses in contact with these plutonic rocks have comparable values $(-10.9, -10.7, 200, -15.3)$. The sediments far away from the Complex, which are from the same stratigraphical horizon as the latter hornfelses (i.e. Magaliesberg shale) also have similar values $(-8.5, -11.6 \text{ and } -6.4).$

The values for the sulphide-bearing pegmatoids situated in the rocks of the Basal Zone, vary between -4. 3 and -5. 1. These values are thus in agreement with values for plutonic rocks which have intruded into horizons below the Magaliesberg quartzite. The values for the neighbouring rocks i.e. harzburgite, pyroxenite and feldspathic pyroxenite, are positive.

A diagrammatic profile of the floor-contact showing the relationship of the Bushveld Complex to the host- (meta) sediments is presented in fig. 34. At some places there may be a complete discordant relationship between the rocks of the Basal Zone and the Magaliesberg quartzite (fig. 2c) and not only a concordant intrusion of a large sill below the Magaliesberg quartzite as is illustrated in fig. 34 and in borehole KA5. The δS^{34} per mil values and the sample positions in the stratigraphical succession are also plotted in the diagram - fig. 34. The association of relatively large negative values of the S in the plutonic rocks which intruded into the hornfels below the Magaliesberg quartzite and the corresponding values of the hornfels itself are indicated in the diagram. The relatively high positive values for the plutonic and the metasedimentary rocks above the Magaliesberg quartzite are also plotted. Worthy of mention is a sulphide bearing inclusion of diopside hornfels which has a s^{-34} per mil value of +8.6. The norite 13 feet away from this inclusion has a value of $+7.8$ and on the contact (fig. 28) the value is $+10.3$. Two samples of the plutonic rocks above the Magaliesberg quartzite have relatively low values:-

- 1. a sample from the Late Hypabyssal norite (KA4-1381) with δ S^{34} per ,mil of +2. 1, and
- 2. sample KA5-850 which was taken from a layer of mineralized feldspathic pyroxenite, 150 feet thick, belonging to the Basal Zone, has a $\, \scriptstyle \delta \, {\rm S}^{34}$ per mil value of -1.2.

These two values are more or less within the range of the layered rocks far away from any metasediments.

Fig. 34. Diagrammatic profile of the floor of the Bushveld Complex in the Western Transvaal. The $5S^{34}$ per mil values for some rocks of the Basal Zone and for the Late Hypabyssal Phase of the Bushveld Complex and their relationship to the values of the floor are given. Metasediments are indicated with open circles. The values (indicated with arrows) for sedimentary sulphur in the Magaliesberg shale (negative) and the Daspoort quartzite (positive) are also given.

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The values for the massive sulphide from a sulphide pegmatoid and for sedimentary sulphur away from the Complex (indicated with arrows) are also given.

The above description and the data supplied in diagrams, fig. 33 and 34, leave no doubt that contamination by sedimentogenetic S from the hornfels had taken place. Further evidence from sulphur isotopes to prove this is the δS^{34} per mil values from the same sediments 90 miles south of the Complex, near Potchefstroom, which show a close correspondence with the values for the sulphides in the hornfelses and the intrusive plutonic rocks.

The δS^{34} $\%$ o values on the foot-wall and the hanging wall contacts of the Aapiesdoorndraai peridotite body are -9. 3 and +10. 2 respectively. The former value corresponds with the metasedimentary S of the Magaliesberg shales with which the peridotite is in contact. The hanging wall is in contact with the Magaliesberg quartzite and the value is also more or less the same as for sedimentogenetic S. It is thus clear that assimilation of S by the peridotite from the sediments also took place in the Eastern Transvaal.

The fact that sample KA4-1381 has a relatively low value whereas other samples from the same layer have relatively high positive values could be explained by the fact that the former was taken further away from the metasediments than the latter. Very little contamination thus took place in the case of sample KA4-1381. From the same borehole, evidence in favour of contamination is obtained from a harzburgite layer (KA4-682), 7 00 feet above sample KA4-1381 and thus further away from the metasediments. The harzburgite belongs to the Basal Zone of the Complex and intruded later than the Late Hypabyssal norite. It could therefore have assimilated sedimentary S during the course of the intrusion of the Basal Zone.

In fig. 35 the 6 s^{34} per mil values obtained from different stratigraphical horizons in the Bushveld Complex are plotted against their actual position in the stratigraphical succession. An enrichment in $\,$ s 32 in the early sulphides took place with a consequent impoverishment in the products of later crystallization as is indicated by the stippled line. Values deviating from this curve have also been plotted.

The $\,\mathop{\updelta}\, \mathop{\rm S}\nolimits^{34}$ per mil value of sample KA5–850 has probably been affected by contamination by sedimentary S in the same manner as described above. The contamination is in any case small seeing that it does not deviate much

Fig. 35. Diagram showing the effect of fractionation of the sulphur isotope (indicated by broken line) caused by the differentiation of the Bushveld magma.

from its theoretical value, indicated by the stippled curve. Samples 17a and 12 are from later pegmatoids which originated from the intercumulus liquid of the rocks in which they occur. They are thus products of later crystallization of the host-rocks, as already mentioned previously. The sulphides in these pegmatoids are also differentiation products of the sulphides of the host-rock, and are more enriched in Cu and/or Fe. It may thus be expected that this pegmatoidal sulphide should be enriched in S^{34} . Their δS^{34} per mil values lie on the positive side of the theoretical fractionation line. The value for the Merensky Reef (sample 119) in the Rustenburg area is taken as representative of magmatic sulphur at this stratigraphical horizon, seeing that it is far away from any metasediments. Where the Merensky Reef is in contact with diopside hornfels (sample 103) the effect of contamination is illustrated. Sample 105 is from the mineralized skarn. The values for samples 24a, 46a and 60 fall more or less on the fractionation curve. The value for sample 117, which is from a diorite, does not fall on the curve. This may be attributed to supergene alteration of pyrrhotite to pyrite.

It can be deduced from the fractionation curve that no concentration of pure magmatic S, i.e. S derived from the Upper Mantle, where the Bushveld Magma probably originated, is present on the floor of the Complex. A removal of an early immiscible sulphide liquid which would be enriched in $\,$ $\,$ s^{32} , would have caused an accompanying enrichment in $\,$ $\, {\rm s}^{34}$ in the later differentiation products at higher horizons of the Bushveld Complex. The latter enrichment did not take place according to the fractionation curve.

It was calculated that if a third of the amount of the magmatic S in the Bushveld magma (taken as 300 ppm) was removed as an early immiscible sulphide liquid, it would produce a massive sulphide layer of 17 feet on the floor of the Complex. Such an enrichment of S is not reflected by the fractionation curve. The concentration of sulphides which originated by the introduction of sedimentary Sat the base of the Complex would, of course, have no effect on the fractionation curve.

The author wishes to repeat that the curve in fig. 35 is based on too few results and many more results are necessary for the problem to be dealt with statistically,

As far as the sulphide pegmatoids in the Basal Zone are concerned, their range in values between -4. 3 and -5. 1 could be explained by the liquidation of very early sulphide droplets which sank to the base of the

Bushveld Complex. These sulphides are enriched in s s^{32} and the δS^{34} per mil values differ considerably from the intercumulus sulphide in sample KA5-850, which is considered to be magmatic.

The sulphide pegmatoids with the sulphide are considered to be differentiation products of the host-rock (this is fully discussed in the section dealing with the Vlakfontein deposits, pp. 110). Because the products of late crystallization are enriched in s s^{34} , it should thus be expected that the sulphide pegmatoids originated from rocks which have a $\,\delta\, {\rm S}^{\rm 34}$ per mil value more negative than the pegmatoids themselves. This was the case with samples 17a and 12. The values for the host-rock are, however, more positive (δS^{34} per mil values of KA5-850 = -1.2, of KA3-130 = +7.8 and of KA4-682 = $+7.5$). It could thus also be concluded that at least some of the S in these pegmatoids was derived from the sedimentary horizon below the Magaliesberg quartzite. This idea is supported by the presence of C as graphite and As as arsenic minerals which were also assimilated from the sediments. The host-rocks contain very little or no As and C. Arsenic minerals and graphite are commonly observed in the hornfelses and in the neighbouring plutonic rocks below the Magaliesberg quartzite. A much more detailed knowledge of the structure of the floor-contact of the Bushveld Complex is necessary to decide whether these assimilation processes are possible.

The chalcopyrite is clearly later than the pyrrhotite (photo 124) and the enrichment of the heavy isotope in the products of later crystallization also shows its effect in this respect. Chalcopyrite has a $\,\delta\,\textrm{S}^{34}$ per mil value of -4. 3 whereas pentlandite and pyrrhotite have values of -5. 0 and -5. 1 respectively.

A bore-hole Gl was put down in a separate basin of the Bushveld Complex north of Zeerust. The sulphur isotope measurements of three samples Gl-4034, -5401 and -5421 indicate that sulphur was assimilated from horizons below the Magaliesberg quartzite. The presence of graphite in these samples supports this view, seeing that graphite is known from horizons below the Magaliesberg quartzite. The borehole thus ended in Magalies berg shale without intersecting the overlying Magaliesberg quartzite. At the surface however the plutonic rocks are in contact with the Magaliesberg quartzite. This evidence indicates a discordant relationship of the Bushveld Complex and the underlying sediments at depth. (Structural evidence, presented previously, also points to crosscutting in this basin.)

12. 4 A Comparison with other Mafic and Ultramafic Intrusions

Ault and Kulp (1959) obtained an average δS^{34} value of +2.4 per mil for sulphides in, and associated with mafic bodies. Larger mafic bodies which whould be less affected by contamination have an average of +4. 2 per mil. Smitheringale and Jensen (1963, p. 1185) criticise some of the values from which Ault and Kulp's average was calculated, mainly on account of the fact that the sulphides were concentrated to a certain degree, whereas normal mafic rocks contain only small amounts of sulphide. This would point to abnormal conditions in the formation of the sulphides.

When these criteria are tested against the values obtained from the Merensky Reef and from mineralized anorthosites below the magnetitite bands (table 55), which represent an abnormal concentration of pure magmatic sulphide, it becomes apparent that the criteria are not quite correct. The criteria set by Cheney and Lange (1967, p. 84) fit the values of the Bushveld Complex very well, namely: "sulphur isotopic values differing by a few per mil from the meteoritic value must be due either to extreme magmatic differentiation or to contamination (i. e. sulphurization)".

Smitheringale and Jensen (1963, p. 1195) calculated the average $\, \frac{}{}\, \mathrm{s}^{34}$ per mil value for undifferentiated Triassic diabases in the Eastern U.S. A. as +0.1 with a standard deviation of \pm 1.6. According to them this is the value for the Upper Mantle from which the diabases were derived. The value for meteorites are $+0.2 + 0.1$ (Smitheringale and Jensen, 1963, p. 1192).

These authors (1963, pp. 1196-1200) also recorded a fractionation of sulphur isotopes in 4 differentiated sills, including the Palisade sill, of Triassic age in New Jersey, Eastern U.S. A. The best example in the literature so far of isotopic fractionation of sulphur during differentiation was recorded by Thode et al (1962) from the Sudbury intrusive (table 56). Shima et al (1963) , pp. 2841-2840) recorded fractionation in the Leitch sill, Ontario. The Insizwa sill shows a vague tendency towards fractionation (table 56).

The sulphides which crystallized last in the paragenetic sequence are enriched in S^{34} in the case of the Bushveld ores (samples 120, 121 and 122). The same phenomenon was observed by Jensen (1957, p. 271) in the ores from Frood, where pyrrhotite has $\,$ a $\,$ $\,6\rm{S}^{34}$ per mil value of +1.4 and bends of chalcopyrite a value of +l. 6. In seven specimens of the Newark group of igneous rocks Smitheringale and Jensen (1963, fig. 2) reported an enrichment of s^{34} in chalcopyrite over pyrite.

Table 56. Sulphur isotopic data for the Sudbury-type deposits and adjacent rocks (modified after Cheney and Lange 1967, p. 86). References: (1) Shima_et al 1963, (2) Smitheringale and Jensen 1963, (3) Ault & Kulp 1959 , (4) Jensen 1957 , (5) McNamara $et al 1952 (6) Goldevskii & Grinenko 1963 (corrected), (7) Jensen 1959, (8) Thode et al 1962,$ </u> (9) Naldrett 1966, (10) Vinogradov & Grinenko 1964

The enrichment of the heavy $ \text{S}^{34}$ isotope in products of late crystallization from a mafic magma is thus a common phenomenon. The O^{18}/O^{16} ratio also increases also in the differentiation sequence from ultramafic to granitic rocks and granite pegmatites, according to Taylor and Epstein (1 962).

Cheney and Lange (1967, pp. 84-88) summarized the sulphur isotopic evidence available in the literature up to 1967. The most important data are reported in table 56 which is a modification of their table 2.

A phenomenon which clearly points to an assimilation of sulphur, but not recorded by Cheney and Lange, is the similarity of the values for the micropegmatite, the Cu-Pb-Zn deposits and the sediment lying above the Sudbury intrusive. The view is expressed by Thode et al (1962, p. 572) that the ores were derived from the micropegmatite. The deposits in the Noril'sk district, Siberia, namely the Noril'sk pluton (Godlevskii and Grinenko, 1963), the Talnakh pluton and the Mt. Chernaya pluton (Vinogradov and Grinenko, 1964), which are intrusive in coal, evaporite (gypsum) and other sediments are perhaps the best examples of sulphurization (table 56). Relatively high, positive $_\mathrm{6}$ s^{34} per mil values were recorded in the disseminated ore from the intrusions, corresponding with the values in the adjacent strata. According to Vinogradov and Grinenko (1966, p. 1) 30-50 per cent of the total Sin the Noril'sk intrusives was assimilated from sedimentary $CaSO_A$ and that accounted for 1.5 per cent of the mass of the intrusives. The reduction of S^{6+} to S^{2-} was caused by the oxidation of Fe²⁺ to Fe³⁺ and not by C^o to C⁴⁺. This follows from the fact that the Mt. Chernaya pluton is intrusive in sediments and evaporites but not in coal beds, according to Cheney and Lange (1967, p. 90).

The $\,\delta\, {\rm s}^{34}$ per mil values of the sulphides in the Dovyren intrusive in Siberia (Vinogradov and Grinenko, 1964) also show similarities with the sulphides in the sediments of the floor of the intrusion. The nickel deposits in the Porcupine District (Naldrett, 1966) show the same comparison.

Other evidence of S addition from sediments to intrusives is presented by the Palisade sill in New Jersey, which has a mean value of +0. 95 in the central parts and at the top and the basal contact the values were determined as +5. 3 and +3. 6 respectively by Shima et al (1963, p. 2842). Ault and Kulp (1959, p. 218) recorded a value of +7. 2 in the upper part of the sill. Cheney and Lange (1967, p. 87) reported high positive values from the base of the Duluth gabbro in comparison with lower values in the central parts of the intrusive itself. The same variation of values was noticed in the Mellen gabbro, Wisconsin.

The sulphide pegmatoids in the Basal Zone in the Western Transvaal, in the Basal ore-deposits in the Sudbury irruptive and in the Insizwa sill are similar, for the $\,\delta\,\textrm{S}^{34}$ per mil values of these deposits are fractions or a few per mil more negative than the associated rocks. This points either to the separation of a very early sulphide (enriched in $\,$ S $^{32})$ as an immiscible liquid, which accumulated at the base of the intrusive, or to the introduction of S from the neighbouring sediments by means of the sulphurization process. If we consider the former alternative first and we assume that the ^6 s^{34} per mil value of magmatic S is +0.1, a removal of a large amount of S^{32} in the early immiscible sulphides would have resulted in an equivalent enrichment of S^{34} in the later crystallization products at the top of the intrusion. This latter enrichment was not observed in the Bushveld, in the Sudbury or in the Insizwa intrusives. We are thus forced to accept the other alternative, postulating the addition of sedimentary S to the magma. A reaction took place between the silicates and S, perhaps according to the sulphurization proces and sulphides were formed. An immiscible liquid formed and settled at the base. Alternatively the sulphides were trapped as an intercumulus liquid, which intruded as pegmatoids at a later stage after the layered rocks were nearly solidified, to form discordant bodies, as in the Bushveld, Stillwater and Hope (Aho, 1956, p. 474-476) intrusions.

12: 5 Conclusions

The following conclusions arising from the sulphur isotope study of the rocks of the Bushveld Complex, in the light of isotope studies of other mafic intrusions, can now be drawn:

- 1. Assimilation of S by the magma from strata containing sedimentogenetic S is a frequent occurrence in nature and accounts for the enrichment of sulphides at or near the base of some intrusions. Also in the case of the Bushveld, introduction of sedimentary S took place at localities where the plutonic rocks cut across the sediments of the Pretoria Series, especially the Magaliesberg quartzite and shale.
- 2. The fractionation of the sulphur isotopes by the enrichment of the heavier isotope in the products of later crystallization during the differentiation of a mafic magma, which played a role in other differentiated bodies, also took place in the Bushveld Complex. This fractionation was not only observed in the layered rocks of the Com-

plex but also in the intrusions of later pegmatoid in the layered rocks. A considerable enrichment of $S³⁴$ is found in these pegmatoids. According to the fractionation curve, concentrations of magmatic S would not be expected on the floor of the Bushveld Complex.

12. 6 Economic Considerations

The sulphur isotopic study indicates that assimilation of sedimentary S by the Bushveld magma was, at least partially responsible for the concentration of both disseminated sulphide and pegmatoidal bodies of sulphide in the Basal Zone in the Western Transvaal. It is thus important to restrict future exploration for Ni-Cu ores in the Bushveld Complex to areas where the latter rocks are in contact with sulphide-bearing (meta)sediments - whether in a discordant or a conconrdant relationship is immaterial.

In the Western Transvaal assimilation clearly took place and from discussions in previous sections (p. 138) it appears as if most of the sulphide was trapped by the cumulus crystals and consequently crystallized as intercumulus material.

The area south of Potgietersrus needs investigation, seeing that up to 10 per cent of pyrite is present in the Magaliesberg quartzite adjacent to the mafic and the ultramafic rocks. Thus pyrite could act as a source of S whereby Ni and Cu ores could have formed by means of the sulphurization process.

Although the rocks of the Basal Zone cut across the same sedimentary strata in the vicinity of Burgersfort as in the Western Transvaal, the enrichment in disseminated sulphide of the plutonic rocks in outcrop appears to be much less in the former area than in the latter. According to the sulphur isotope investigation assimilation of sedimentary S took place on the contacts of the Aapiesdoorndraai peridotite. All these data point to the accumulation of an immiscible sulphide liquid at the base of the Complex in this area.

Considerable discordant relations of the Late Hypabyssal rocks to the Magaliesberg quartzite took place south-east of Rustenburg (Buffelspoort dam area) and between Rustenburg and Boshoek (Map II). These areas could well bear investigation, should it be found that the quartzite contain sulphide.

13. THE BEHAVIOUR OF CERTAIN CHALCOPHILE ELEMENTS DURING THE DIFFERENTIATION OF THE BUSHVELD MAGMA

The main purpose of this investigation was to evaluate the geochemical behaviour of Sand certain chalcophile elements during differentiation of a layered intrusion, 30,000 feet thick, such as the Bushveld Complex. A further aim was to determine the additional geochemical influences on the crystallization and the disappearance of certain sulphide phases and the concentration of magmatic sulphides.

C. J. Liebenberg (1961) determined the major elements and some trace· elements present in a great number of Bushveld rocks. From his data 61 analyses of Ni, Co and Cu were used (table 62, inserted in the appendix). An additional 52 samples from different stratigraphical horizons were analysed for Ni, Cu and Zn by the Department of Geochemistry, University of Cape Town. Analyses of S of the latter samples as well as determinations at Ni, Co, Cu, Zn, Fe, Sand As on 41 samples, mainly from the Basal Zone of the Bushveld Complex in the Western Transvaal were done by the Anglo American Research Laboratory.

13. 1 The Variation of S. Ni, Cu, Co, Zn and Pb on different Stratigraphical Horizons

The analyses of S and of some chalcophile elements are plotted in fig. 36, (inserted at the back). Some of these values represent averages obtained for a certain rock type. A more generalized diagram (fig. 37, inserted at the back), which clearly illustrates the effect of differentiation on these elements has also been compiled. Fig. 38 is a still more simplified version of fig. 37.

13. 1. 1 Sulphur

The average S content of ultramafic and mafic rocks is given as 3000 and 2000 ppm respectively (table 57). The values for the rocks of the Bushveld Complex are much lower and an average value for the ultramafic rocks of the Basal Zone is about 200 ppm and for the mafic rocks about 100 ppm (obtained from fig. 37 and 38). The Late Hypabyssal norites, and the ultramafic rocks in he Western Transvaal, which contain disseminated sulphide, have values which are very much higher than their unmineralized equivalents in the Eastern Transvaal. The S content gradually decreases from the Aapiesdoorndraai harzburgite (900 ppm) which is the lowest exposed member of the Complex, to the upper part of the Critical Zone (30 ppm). A sudden increase

is noticed in the rocks of the Merensky Reef. The greater part of the Main Zone has values below 50 ppm. In the uppermost pyroxenite layer in the Complex (sample 49) the S content increases suddenly to 300 ppm, A maximum value in the normal layered rocks of the Complex is recorded in the mineralized anorthosite below the Main Magnctitite Seam. A gradual decrease is again noted in the Upper Zone, and below the Uppermost Magnetitite Seam a repetition of the conditions below the Main Magnetitite appears. The diorites contain 1300 ppm of S. In comparison with the Critical and the Main Zone, The Upper Zone is quite S-rich (average of $+350$ ppm).

The most striking phenomenon of the variation curve for S is the repeated decreases in the Critical, Main and Upper Zones, which are followed by abrupt increases at the top of each of the zones respectively.

Wager et al (1957, pp. 873-877) also reported low values for S for the greater part of the Skaergaard rocks, followed by a high value in the Upper Purple Band.

13. 1. 2 Nickel

The Ni-content of the mafic and the ultramafic rocks of the Bushveld Complex is $+100$ and $+700$ ppm respectively and is lower than the average values for same rock groups, given in table 57. Only the harzburgites have values comparable with those of Vinogradov. Nickel shows a gradual decrease from ultramafic rocks to the rocks of the Upper Zone. C. J. Lieberberg (1960, fig. 23) already showed the good correlation between Ni and Mg. Some kind of correlation also exists between Ni and Fe (Liebenberg, C. J., 1960, fig. 26c). Ni is, however, much more enriched in the forsterite dunite (1423 ppm) than in the hortonolite dunite (400 ppm) of the pipes in the Critical Zone. Harzburgites (samples 102, Lieb 42) have higher values than the surrounding pyroxenites. The olivine in samples 102 and Lieb 42 is more Ferich than the pyroxenite, thus supporting the diadochy of Fe by Ni. A norite (sample 67) in a pyroxenitic environment tends to be lower in Ni. The pyroxenite in the Gabbro of the Main Zone shows a high Ni content which would be expected. The capturing of Ni by Fe is also clearly illustrated by the high Ni content (600 ppm) of the magnetitites and magnetite gabbros of the Upper Zone. Otherwise, owing to the chalcophile properties of Ni, this element varies sympathetically with S (fig. 37 and 38).

13. 1. 3 Copper, Cobalt, Zinc and Lead

In the Bushveld Complex the average content of Cu, Co and Zn of the ultramafic rocks are $+35$, $+90$ and $+70$ ppm and of the mafic rocks \pm 25, \pm 25 and \pm 30 ppm respectively. All these values (except Zn) of the ultramafic rocks of the Bushveld Complex are lower than the average value given for the corresponding rock groups (table 57).

The data for Co are unfortunately not so complete as for the other two elements, but it is clear from figs. 37 and 38 that these three elements vary sympathetically during differentiation. C. J. Liebenberg (1960 fig. 26b, 29b) determined a correlation between Co and FeO and also between Co and MgO.

There is a slight decrease in these elements from the base of the Complex towards the upper part of the Main Zone. High values of Co and Zn are once more found in the Fe-rich Upper Zone. Cu on the other hand, shows rather low values in some rock types.

Norite (sample 67) intercalated with pyroxenite has a lower Cu and Zn content than the pyroxenite. The harzburgites at the base of the Complex have larger Cu, Co, and Zn contents than the pyroxenites higher up. The hortonolite dunite is enriched in Zn, Co and Cu compared with the forsterite dunite (fig. 36 and table 62, in appendix). The Fe-rich dunites are the most enriched in Co followed by Zn and Cu. In the Fe-rich rocks of the Upper Zone (magnetitite and troctolite) Co has the highest value, followed by Zn and Cu (fig. 38).

Lead occurs in small quantities in the Main Zone.

13.1. 4 Discussion

According to Ringwood (1954, p. 198) the correlation between $Ni²⁺$ and Mg²⁺ is misleading because as a result of the differences in ionic radii between Ni²⁺, Mg²⁺ and Fe²⁺, Ni²⁺ (radius = 0.96 \hat{A}) is captured preferentially by Fe²⁺ (radius = 0.74 \AA) instead of by Mg²⁺ (radius = 0.66 \AA) in the ferromagnesiam silicates. The electronegativity of Ni $^{2+}$ (EN = 220) is nearer to that of Fe^{2+} (EN = 185) than that of Mg²⁺ (EN = 174) which thus explains the diadochy of Ni $^{2+}$ by Fe $^{2+}$ (radii and electronegativities from Smith, 1962, table 2-1).

The ionic radii of Co²⁺, Zn^{2+} and Cu²⁺ are very much the same as that of Fe^{2+} which they replace diadochically. Owing to the fact that the

difference in electronegativity between Fe^{2+} (EN = 185) and Co^{2+} (EN = 200) $\int_{\mathbb{R}}$ smaller than between Zn^{2+} (EN = 208) and Cu²⁺ (EN = 235), it may be expected than the ability of diadochy between Fe^{2+} and the three ions would decrease in the order Co^{2+} , Zn^{2+} and Cu^{2+} . This is also reflected by the hortonolite dunite.

The chalcophile affinity of these three elements is illustrated by their sympathetic variation with S especially in the norites and the ul tramafic rocks of the Western Transvaal, the Merensky Reef and the mineralized anorthosite below the Main and the Uppermost Magnetitite Seams (fig. 37, 38). An unsympathetic variation is shown by the diallage pyroxenite. By taking into account the increase in the content of Cu, Ni, Co and Zn in the mineralized zones, relative to the unmineralized neighbouring rocks, or the related unmineralized rocks in fig. 37, the relative chalcophile affinity of the elements could be deduced. The chalcophile affinity decreases in the order Cu, Ni, Co, Zn. This order corresponds with the well-known order determined during the smelting of sulphide ore (Rankama and Sahama, 1950, p. 696).

Mn, Cu, Ni, Co, Fe, Sn, Zn, Pb, Sb, Ag highest affinity lowest affinity In the mineralized ultramafic rocks of Western Transvaal and the mineralized anorthosites below the Main and the Uppermost Magnetitite Seams, Zn shows no or a very slight chalcophile affinity. According to Smith (1967, p. 415) chalcophile **reduces**
| elements with both oxy- and chalcophile tendencies are more enriched in' systems with low oxidation potentials, provided that the sulphur concentration remains high". The presence of oxides such as magnetite and ilmenite in the upper part of the Bushveld Complex indicates, however, a high oxidation potential which existed in these) parts of the magma. Zn was oxyphile under these conditions and was removed as \rm{Zn}^{2+} in fourfold co-ordination in the oxides and in sixfold coordination in the ferromagnesian silicates.

Desborough (1966) found some difficulty with a magmatic concentration of sulphide such as the Sudbury type of deposits. He indicated that the Ni:Cu:Zn ratio, in ordinary basaltic rocks, is more or less unity, whereas in the Sudbury deposit Zn is present only in small amounts, compared with the other two elements. The low S affinity of Zn in relation to the other elements Cu and Ni, and even the oxyphile properties of Zn under conditions of high oxidation potential could possibly be a reason for the low content of Zn

in the Sudbury type of deposit. To illustrate this the mineralized zones in the Bushveld Complex are examples. The Zn:Cu or the Zn:Ni ratio of the rocks above and below the Merensky Reef is about unity, whereas in the Merensky Reef itself, these ratios are smaller than 0. 1. More or less the same conditions exist in the mineralized anorthosites below the Main and the Uppermost Magnetitite Seams. Desborough (1966, p. 374) mentioned selective extraction of Ni, Cu and Fe without affecting Zn during the sulphurization process (proposed by Kullerud and Yoder, 1963). The concentration of sulphides in the ultramafic rocks of the Western Transvaal are attributed to sulphurization or definitely to some process of S assimilation from metasediments by the magma. These rocks are not enriched in Zn (fig, 37) owing to its weak chalcophile properties.

Small quantities of Pb are found mainly in the Main Zone. Rankama and Sahama (1955, p. 733) mentioned the diadochical replacement of Ca^{2+} (ionic radius = 0. 99) by Pb^{2+} (ionic radius = 1.24, coordination number 8) in monoclinic pyroxene. Nearly all the Pb is thus in the pyroxene of the gabbro. Only a few specks of galena (?) were found in the mineralized anorthosite below the Main Magnetitite Seam.

13.2 The Ni, Cu, Co, Zn and S Content of the Original Bushveld Magma

- $1 + 4$ Turekian and Wedepohl (1961).
- $2 + 5$ Vinogradov (1956)
- $3 + 6$ Vinogradov (1962)
- 7 Average Bushveld magma deduced from fig. 37 and table 58,
- 8 Hendriksplaats norite (3 analyses)
- 9 Maruleng norite (2 analyses)
- 10 Ultramafic rocks of Bushveld Complex deduced from fig. 37 and table 58.
- 11 Aapiesdoorndraai harzburgite (4 analyses)
- 12 Skaergaard, chilled marginal gabbro (Wager et al, 1957).
- 13 Greenstone flow, Keweenaw penisula, Michigan, U.S.A. (Wager et al, 1957).

The Maruleng norite is almost always present between the rocks of the Main Plutonic Phase and the Pretoria Series and is generally considered to be a chill-phase of the Complex. But is has exactly the same composition as the Late Hypabyssal norites intrusive as sills in the Upper part of the Pretoria Series (Willemse,1959, pp. xliii-1). The Maruleng norite could thus not be considered a chill phase of the Bushveld Complex, representative of the original composition of the Bushveld magma. The Hendriksplaats norite was the last magma to intrude as part of the Late Hypabyssal Phase, before the Main Plutonic Phase of the Complex was emplaced. The Hendriksplaats norite shows all gradations between an anorthosite and a pyroxenite in the area where it has its best development, namely, the Marone Mountain. At other places this norite is a massive norite (actually a hyperite). The author thus feels that the composition of this norite compares more favourably with that of the Bushveld magma.

It is clear from table 56 that the average content of Ni, Co, Cu and Zn of the rocks of the Bushveld Complex as a whole corresponds closely with that of the Hendriksplaats norite, whereas it differs from that of the Maruleng norite. Except for S and Cu the average values for Ni, Co and Zn of the Bushveld Complex are more or less the same as the average for mafic rocks (the values given for Zn in all cases are not accurate). Wager et al (1957, p. 37 5) determined the average S content of the Skaergaard magma (table 57) and concluded that: "The average figure of 0. 1 per cent S for basic rocks given by Tröger is likely to be totally unrepresentative of average undifferentiated magmas". The values given by Vinogradov (1956) are even more optimistic. The values given by Vinogradov (1956) are even more optimistic. The more recent data of Turekian and Wedepohl (1961) and of Vinogradov (1962), appear to be more correct if compared with those for the Bushveld Complex. The value of 238 ppm of S for the Hendriksplaats norite can be considered as the actual S content of the Bushveld magma. This is higher than the average value of 150 ppm for the Complex as a whole, but some ultramafic members, from deeper horizons of the Complex, which do not crop out at the present surface, could be enriched in S. The possibility of contamination by sedimentary S, by assimilation of sedimentary inclusions by the Hendriksplaats norite, should therefore not be ignored. The sample was however taken from massive norite far away from any inclusions.

e 58. Mean values of Ni, Cu, Co, Zn, Pb and S (values of individual analyses are represented in table 62 in the appendix) from the different rock types of the Bushveld Complex arranged from the floor to the roof of the Complex.

There is no correlation of the Ni, Cu, Co, Zn and S contents of the ultramafic rocks of the basal part of the Bushveld Complex with the values presented by Turekian and Wedepohl or by Vinogradov. Some of the values of the Aapiesdoorndraai harzburgite are in better agreement (table 57).

13.3 The Relationship between the Variation of S and Chalcophile Elements and the Crystallization of the Different Sulphides

In the Skaergaard intrusion, Wager et al (1957) found that during the crystallization of 90 per cent of the magma the S content remained below 300 ppm. Although the Ni content was higher than that of Cu in the beginning, a copper matte formed (Ni entered the silicates). The S content gradually increased in the successive liquids until it reached a concentration of 600 ppm at which stage the solubility of Fe sulphide was exceeded and a immiscible sulphide liquid composed mainly of Fe sulphide separated in the Upper Purple Band and on higher horizons. Most of the Ni was removed in the early silicates and only very little was available to enter the Fe matte. No Ni entered the Cu sulphides.

Unfortunately the conditions during the differentiation of the Bushveld Complex were too complex to allow any calculations of the S content of the magma. Furthermore, the analytical data on the rocks of the Bushveld Complex are far from complete.

The results of the study of Wager et al (1957) could, however, be applied to the Bushveld Complex. During the crystallization of the rocks of the Basal Zone and those of the lower half of the Critical Zone, the concentration of sulphur in the magma was high enough to allow the crystallization of pyrrhotite, pentlandite and chalcopyrite (the interstitial sulphide throughout the Bushveld Complex could have crystallized from an immiscible sulphide liquid which was trapped as part of the intercumulus fluid, excluding some mineralized zones in which sulphides crystallized directly from a silicate-oxide-sulphide fluid at an eutectic). From fig. 38 it is clear that the S content in the rocks of the Basal and the Critical Zone decreased during differentiation and it may thus be deduced that this was the result of a decrease in the S content of the magma. The S content of the magma was eventually so low that only chalcopyrite formed in the upper half of the Critical Zone, i.e. during the crystallization of the norites and the anorthosites (fig. 38). Not enough Cu was present in the magma to remove all the S, with the result that the magma became enriched in $S \cdot \iint_{\mathcal{U}}^N$ and not enter the structure of the chalcopyrite and limited fer-

Fug. 38. Variation of Ni, Cu, Co, Zn and S on different stratigraphical horizons in the Bushveld Complex. Diagram simplified from fig. 36 and 37

romagnesian minerals were available to remove the Ni from the magma during the crystallization of the 2000 feet of anorthositic norites, as illustrated by the low Ni-content of the rocks concerned (fig. 38). The residual magma was therefore enriched in Ni.

During the crystallization of the Merensky Reef, the concentration of S exceeded the solubility of the nickeliferous pyrrhotite in the magma and an immiscible sulphide liquid separated, which crystallized to form pyrrhotite, pentlandite and chalcopyrite. This separation of sulphide liquid was favoured by the change in the composition of the magma when the Merensky Reef started to crystallize. The crystallization of sulphides, oxides and silicates directly from one liquid at a high oxidation potential was also possible.

The S concentration in the magma was initially high enough during the crystallization of the norites in the lower part of the Main Zone to form Fe sulphide and chalcopyrite. The content of S in the magma decreased gradually and during the greater part of the formation of the Main Zone the concentration was so low that only chalcopyrite crystallized. As indicated in fig. 38, Cu was removed in progressively smaller amounts from the magma during the crystallization of rocks of the Main Zone, resulting in a considerable increase of this element in the residual magma. Ni was extracted from the magma mainly by the ferromagnesian minerals but during the late stages of the crystallization of the rocks of the Main Zone only very small amounts entered clinopyroxene and accessory magnetite. The magma was enriched in S, Cu, Ni, Co and Zn (in this order of abundance) to such a degree that crystallization of sulphides, magnetitie and silicates at an eutectec was possible according to the views of Smith (1961 and 1962), which have already been fully discussed in the section dealing with the sulphides immediately below the Main Magnetitite Seam (cf. p. 186). The S concentration was high enough to allow the crystallization of nickeliferous pyrrhotite. These sulphides were not very rich in pentlandite as a result of the extraction of Ni by the early ferromagnes ian minerals and the sulphides in the lower part of the Complex. Cu was not extracted to the same degree as Ni was by the latter minerals and consequently the sulphides below the Main Magnetitite Seam are Cu -rich.

After the crystallization of this mineralized zone at an eutectic it is necessary to postulate a change in the composition of the magma in the zone of crystallization, brought about possibly by either convection currents or a new influx of magma, to account for the Main Magnetitite Seam which then formed.

The data for the Upper Zone are even more incomplete than those for the rest of the Complex but a repetition of the variation in the chalcophile elements and of S of the Main Zone has apparently taken place in the Upper Zone (fig. 38). S was removed in decreasing amounts from the magma during crystallization of the rocks of the Upper Zone, as illustrated by fig. 38. Ni, Cu and Co behaved in the same way as S. Apparently the concentration of S was again high enough to allow a eutectic crystallization of sulphide magnetite and silicate. The sulphide is mainly nickeliferous pyrrhotite. The magma was much more depleted in Cu than during the crystallization of the mineralized horizons below the Main Magnetitite Seam, so that Cu sulphide played a minor role in the composition of the sulphide phase. Owing to the low concentration of S in the magma during the crystallization of the Upper Zone, chalcopyrite is the only or main sulphide in the gabbros and the magnetitites of this zone.

The S concentration in the magma was relatively high while the diorites were being formed and this resulted in the separation of mainly pyrite from the magma.

13. 4 Geochemical Criteria for Potential Nickel Mineralization in Mafic-Ultramafic Intrusives

Some Russian investigators (Polferov and Suslova, 1966 and Nyuppenen, 1966) have provided geochemical criteria for determining potential and economic mineralization in mafic and/or ultramafic intrusions. These criteria are based on the application of:

- 1. The petrochemical parameters b, m' , n and a:c of Zavaritskii.
- 2. The concentration coefficients of ore-forming elements.
- 3. The Ni and $SiO₂$ contents.

13.4.1 The Petrochemical Parameters b, m', n and a:c

Polferov and Suslova (1966) have put forward a method whereby it is possible to distinguish between nickeliferous and nickel-poor mafic and ultramafic b, m', and a:c. These parameters are given in table 59 for unmineralized as well as for mineralized mafic and ultramafic intrusions in

Table 59. Some petrochemical parameters of mafic and ultramafic rocks of niceliferous and non-nickeliferous regions.

The data of the Russian, Siberian, Norwegian and Sudbury rocks and some typical rocks (which were calculated from the world's average) are from Polferov and Suslova, 1966, p. 489.

* Parameters for typical diorite, picrite and dunite calculated from Daly's average (1933, pp. 9-28).

Siberia, Russia, Norway and Canada. The Zavaritskii parameters for a number of rocks from the Bushveld Complex and for Insizwa were calculated and are also included in table 59.

The following scheme was used to calculate the parameters from the chemical analyses after the latter had been converted to molecular proportions (Zavaritskii and Sobolev, 1966, Translator's appendix p. 214).

Conditions

B = FeO' + MgO + CaO' + $A1_2O_3$

No conditions

$$
s = \frac{S}{S + A + C + B}, \ a = \frac{A}{S + A + C + B}, \ b = \frac{B}{S + A + C + B} \quad c = \frac{C}{S + A + C + B}
$$

$$
m' = \frac{MgO}{B} \times \frac{100}{1} \qquad n = \frac{Na_2O}{1} \times \frac{100}{1}
$$

A total of 61 analyses of the different rock types from the Bushveld Complex, mainly from the Eastern Transvaal, were made by C. J. Liebenberg (1960). Two additional analyses of harzburgite from the Western Transvaal, taken from an unpublished thesis by Schwellnus (1939, p. 17), were also included, as well as one analysis of picrite from Insizwa (Scholtz, 1936, p. 117).

In comparing the petrochemical parameters of rocks from nickeliferous and non-nickeliferous mafic and ultramafic massifs in the U.S. S. R. , Norway and Canada (table 59), Polferov and Suslova (1966, p. 488) draw the following conclusions: In the case of the nioeliferous massifs as compared with the typical rocks, 84 per cent have a higher parameter b, 77 per cent have a higher parameter m', 84 per cent have a lower parameter n and most of them have a low a:c ratio. The nickeliferous massifs contain a greater quantity of femic minerals, Mg and K.

Some important conclusions could be drawn from a comparison of the mentioned parameters of the rocks of the Bushveld Complex with those of the typical rocks, calculated from the world's average. It has already been shown that the composition of the Hendriksplaats norite could be considered as typical of that of the Bushveld magma. The parameters b, m' and a:c are in accordance with those of a nickeliferous norite. The magma of the Bushveld Complex could therefore have been nickelfferous. However, all the ultramafic members have values for these parameters which are not in accordance with those of mineralized rocks, in spite of the fact that the harzburgites of the Western Transvaal contain sulphide pegmatoids which have been mined in the past. The dunite and the diallagite which form the pipe-like bodies in the Critical Zone appear to be of economic importance but these rocks are almost barren of sulphides (except for the normal intercumulus specks of sulphide).

Of the olivine-free rocks, only the norites and the quartz norites of the Bushveld Complex have values of the four parameters which suggest sulphide mineralization. They contain, however, only accessory sulphide.

The unmineralized Merensky Reef is the only rock in the Bushveld Complex which is in agreement with the idea of Polferov and Suslova that a **o\;stihc.i,'im** distruction may be drawn between nickeliferous and non-nickeliferous intrusions, according to the petrochemical parameters. (The Merensky Reef is classified here as a norite; it may be ultramafic at some localities.)

The picrite from Insizwa appears to be nickeliferous. Subjection and possible economic sulphide deposits are found at the base of this intrusion,

The applicability of this method of Polferov and Suslova to distinguish between nickeliferous and non-nickeliferous mafic and ultramafic rocks, as found in typical layered intrusions, is thus not beyond doubt. Even in most of the intrusions in the U.S. S. R., Vinogradov and Grinenko (1966, p. 1) as well as Cheney and Lange (1967, p. 87) have shown that definite assimilation of S from the surrounding sediments has taken place. The availability of S rather than only the composition of the original magma would thus determine whether a mafic or ultramafic intrusive would contain Ni-bearing sulphides.

According to Polferov and Suslova (1966, p. 491) the deviations in the parameters b, m' and a:c between the typical rocks and the nickeliferous massifs are exactly the same as those between achondrites or plutonic eclogites and basalts or eclogites of the metamorphic complexes. This may

serve as indirect proof that nickeliferous intrusions were generated in the Upper Mantle, below the Mohorovivic-discontinuity.

13.4.2 The Concentration Coefficients of Ore-forming Elements

It was found that rocks in the upper zones of the π :¹Ni-bearing intrusives of Norway, Noril'sk, Kola and the Northern Baikal region contain Ni, S and other ore-forming elements in relative abundance (Polferov and Suslova, 1966, p. 492). On account of this fact the authors mentioned investigated the concentration of several ore-forming elements in the unmineralized rocks of nickeliferous intrusions. The concentrations are expressed in terms of their concentration coefficients, Kc, i. e. the ratios of the actual contents of the elements to their clarkes in the corresponding rock-types, calculated by Vinogradov. (The word clarke is used by Russian geochemists for the average content of a certain element in a certain rock-type in the earth's crust.).

Polferov and Suslova found that mineralized intrusives give Kc values for Ni, Co, Cu, Cr. Ti and S which are higher than unity and for Zr lower than unity. The water content of these intrusions is also relatively high (table 60).

The concentration coefficients of the different rock-types in the Bushveld Complex were calculated using the analyses in the table in the appendix and the average content of the elements given by Vinogradov (1956) for mafic and ultramafic rocks. The data are presented in table 60.

All the rocks in the Western Transvaal gave Kc values larger than unity for Ni, Cu, Co and S (table 60). The sulphide content of these rocks is probably somewhat optimistic so that high values for the chalcophile elements may be expected. The harzburgites of the Eastern Transvaal and especially those of the Aapiesdoorndraai body have high Kc values for Ni. These rocks could thus be considered as potential Ni ore-bearers.

Polferov and Suslova (1966, p. 492) stated that Cr and Ti are principal indicators of Cr and Ti mineralization respectively, in mafic and ultramafic intrusives. The Bushveld Complex is well known for its enormous chromite de~ posits in the Critical and the Basal Zone. The Kc values for Cr. in the mafic and ul tramafic rocks of the Critical and the Basal Zone are relatively high, whereas rocks in the Upper and the Main Zone have values below unity. For Ti, which is also concentrated in large amounts in the Upper Zone, low Kc values were recorded in the Basal, Critical and Main Zones, whereas high values are reported from the Upper Zone.

* Late Hypabyssal Phase, The norite from Eastern Transvaal is Hendriksplaats norite.

All the harzburgites,dunites andpyroxenites are classified as ultramafic rocks, the remaining rocks are classified as mafic.

This behaviour of Cr and Ti in the Bushveld Complex places a restriction on this method of determining whether an intrusive would be chromiferous *¹* titaniferous or nickeliferous, particularly with regard to layered intrusions, A low Kc value of a certain element on a certain stratigraphical horizon of the intrusion would not be an indication of no enrichment of this element at another stratigraphical horizon in the intrusion.

Another drawback of this method is the classification of the different rock-types into mafic and ultramafic groups. For instance, a feldspathic pyroxenite with $+ 10$ per cent feldspar can be classified as ultramafic or mafic Furthermore, pyroxenites contain much less Ni than a harzburgite. It would thus not be correct to calculate the concentration coefficients of both rock-types by using the same clarke.

To overcome this difficulty Nyuppen₁ suggested the method given below,

13.4.3 The Ni and SiO₂ Contents

It is well known that the Ni content increases regularly from felsic to the ultramafic rocks, i.e. in sympathy with the gradual decrease in the SiO₂ content. Nyuppen $\binom{3n}{1966}$ determined the equation for the relationship between Ni and $SiO₂$ by using data given by Unksov and Lodochnikova as well as by Vinogradov. The logarithmic form of this relation is

 $\log \ C_{\rm gion}$ 2 = $\log 30 - 0.125 \log C_{Ni}$

All rocks with a high Ni content, i.e. potentially nickeliferous rocks, would have a positive value if the right hand side of the equation is deduced rocks
from the left hand side. Intrusive/with no economic Ni mineralization would have a value of 0 or a negative value. The uncertainty of this logarithmic equation is in the vinicity of $+0.03$.

In table 61 values, determined from the above equation, are given for mineralized and unmineralized intrusives in the U, S, S, R . It is clear that the mineralized intrusions have values larger than $+ 0.03$.

Testing the rocks of the Bushveld Complex against the criteria set by the logarithmic equation (table 61), all the harzburgites and bornzitites are potential Ni ore-bearers. The Hendriksplaats norite, which is possibly representative of the average Bushveld magma, has a very high positive value which indicates that the Bushveld Complex is a potential nickeliferous intrusion. It should be noted that the barren norites and dunites which were classified as potentially nickeliferous by the method using the petrochemical parameters are now excluded, as being of no economic importance. Testing the validity

of these criteria against the unmineralized Merensky Reef, it should be noted that a positive value is obtained - which is then also correct.

The main objection against this method is that pyroxenites and the norites have more or less the same $SiO₂$ content but their Ni content varies considera bly. The author thus suggest $\frac{1}{2}$ s that the relationship between Ni and the silica function $({}^{1}/3 \text{ SiO}_{2} + \text{K}_{2}\text{O})$ - (CaO + MgO), should be used, rather than between Ni and SiO_2 . A much better relationship exists in the former case than in the latter according to C. J. Liebenberg (1960, fig. 22 and 24).

13.4.4 Conclusion

When applying the criteria set out above to the Bushveld Complex, the following conclusions may be drawn:

- (a) All three methods are in agreement that the Hendriksplaats norite, which may be considered as representative of the original Bushveld magma, could have caused Cu-Ni mineralization, although the $: \mathbb{R}^s$ concentration may be too low. If enough S could have been supplied to the magma, by means of the sulphurization process, all conditions would then have been ideal for the formation of nickeliferous ores.
- (b) Of all the rocks throughout the whole succession of Bushveld rocks, the harzburgites in the Basal Zone, in both the Eastern and the Western Transvaal, have the best chances of being the host-rock of sulphide ores.

14. CONCLUDING REMARKS

Some important conclusions may be drawn, as far as the distribution and the concentration of sulphides in the different Phases of the Bushveld are concerned:

1., From field relationships it is clear that the Main Plutonic Phase of the Bushveld intruded at least as two separate surges of magma. Convectioncurrents and gravity-settling of minerals took place and gave rise to the phaselayering in the Bushveld Complex. The discordant intrusion of the Late Hypabyssal and the Main Plutonic Phase into some sedimentary strata of the Pretoria Series, caused the lifting of large and small masses of metasediments from the floor. As a result of this phenomenon a local "false" floor of metasedimentary inclusions were intersected in some of the KA bore-holes. From the bore-hole put down on Vlakfontein 207 JP and described by Schwellnus (1935), it is obvious that the deepest part of the basins in the area west of the Pilanesberg have not been explored completely by the recent drilling.

2. Micrometric analyses of the sulphides from different stratigraphical horizons, in the Bushveld Complex revealed a definite trend in the differentiation of the major sulphides. The sulphides in the ultramafic rocks of the Basal Zone are rich in pentlandite and poor in Cu sulphide. Towards higher horizons the percentage of pentlandite decreases and the percentage chalcopyrite increases to a maximum below the Main Magnetitite. In the Upper Zone the chalcopyrite becomes progressively less towards higher horizons. The sulphides near the top of the Upper Zone are very rich in pyrrhotite and consist only of pyrite in the diorites. The mafic rocks throughout the whole succession of the Bushveld Complex contain only chalcopyrite when the sulphide content is relatively low. The mafic and ultramafic pegmatoids in the Basal, the Critical and the Lower part of the Main Zone are regarded as products of differentiation of the host-rocks. The sulphides in these rocks are richer in Cu sulphide and in pyrrhotite than the disseminated sulphide in the host-rock, which may be regarded as due to differentiation. This is also the case with the massive and relatively massive ores from Vlakfontein which originated as a pegmatoidal fluid from the intercumulus liquid of the host-rock, the latter having been sulphide-rich (this is

deduced from the fact that the intercumulus material consists of a large percentage of sulphide). This pegmatoidal fluid, containing appreciable amounts of sulphide, intruded along structurally controlled zones of weakness, to form the discordant sulphide pegmatoids.

3. In the light of experimental phase relations of the Cu-Fe-Ni-S system, it was established that all the minerals involved in the Fe-Ni-S system existed as a monosulphide solid solution (mss) above 860° C. The pyrite content of all the Bushveld sulphides is relatively low (10 per cent) and it has therefore exsolved below 743° C along the pyrrhotite-pyrite solvus from the mss. The nonquenchable (Ni, Fe) $_{3+\rm x}$ S₂ phase exsolved from the mss below 863 $^{\circ}$ C. Compositions of relatively S-deficient sulphides in the Bushveld (e.g. , those from Aapiesdoorndraai, The Merensky Reef from Tweefontein and Potgietersrus,, as well as certain ores from ultramafic rocks, and the sulphide pegmatoids of the Western Transvaal) fall in the field mss + (Ni, Fe) $\frac{3+x}{52}$ + vapour in the Fe-Ni-S system. Coarse grains of pentlandite in these ores formed by reaction between (Ni, Fe) $S_3 + x S_2$ and pyrrhotite. Flames and other exsolution bodies in pyrrhotite exsolved from the mss below \pm 845^oC. The composition of the relatively S-rich ores (e.g. , the mineralized anorthosites, the Merensky Reef from Rustenburg and the ores in the Late Hypabyssal rocks) fall in the mss-field, The coarse pentlandite as well as the flames and roundish bodies of pentlandite exsolved from the monosulphide solid solution.

It is interesting to report that mackinawite occurs only in pentlandite in Sdeficient ores and thus appears to have exsolved from coarse pentlandite that originated by reaction between (Ni, Fe) $_{3+x}S_2$ and pyrrhotite. Kullerud (1962) determined that the pentlandite field in the Fe-Ni-S system has its maximum width at 580°C. Below this temperature the width decreases and this results in the exsolution of pyrrhotite. The author suggests that under certain chemical and pressure conditions mackinawite would exsolve instead of pyrrhotite.

Yund and Kullerud (1966) mention that pyrrhotite will hold 4-5 per cent of Cu in solid solution at 700 $^{\mathrm{o}}$ C. At lower temperatures this Cu would exsolve as chalcopyrite and/or cubanite. A large quantity of the chalcopyrite or cubanite in the Bushveld ores exsolved from pyrrhotite, especially the lamellae or grains within grain boundaries of pyrrhotite. Cubanite is not stable above \pm 440 $^{\mathrm{O}}$ C. Owing to the decrease of the cubanite and chalcopyrite fields in the Cu-Fe-S system these minerals exsolved from each other as lamellae. Pyrrhotite

and/or mackinawite also exsolved from these minerals. Phase transformations in the chalcopyrite and cubanite structures with lowering temperatures caused some twinning in these minerals in the Bushveld.

Paragenetic differences exist between Cu-nickeliferous ores from volcanic rocks (e.g. the Igdlukunguaq basaltic "dyke", described by Pauly, 1959), hypabyssal rocks (e.g. the Petolahti diabase, described by Ervamaa, 1962) and plutonic rocks (e.g. the Bushveld Complex, Sudbury and Insizwa). These differences may be summarized as the degree of solid miscibility between pyrrhotite, pentlandite and chalcopyrite, increasing in the order plutonic, liypabyssal and volcanic rocks. This is mainly due to temperature differences and cooling rates of the magmas which increase in the same order.

4 .. Disseminations of sulphide are frequently observed in the rocks of the Basal Zone in the Western Transvaal, south of Potgietersrus and in the vicinity of Burgersfort. In these regions the rocks of the Basal Zone cut across the sediments of the Pretoria Series, especially the Magaliesberg quartzite and the metasediments above and below it. Sedimentogenetic sulphides are present in the metasediments in the Western and the Eastern Transvaal and in the Magaliesberg quartzite south of Potgietersrus. The association of disseminations of sulphide in the Basal Zone and its discordant intrusion into sulphidebearing strata point to assimilation of S by the magma from the adjoining metasediments.

Although the Bushveld Complex in the vicinity of Burgersfort cuts across the same sedimentary layers as in the Western Transvaal, disseminated sulphide~, are only known from near the contacts of the Aapiesdoorndraai body. It is postulated that the greater part of the disseminated sulphides settled towards the floor of the Complex and that the sulphide blebs near the contacts were captured by a rock that cooled faster than the rest of the body farther away from the contact.

The presence of graphite and accessory arsenide minerals in the sediment ogenetic ores in the metasedimentary strata and also in the adjacent plutonic rocks, also indicates the assimilation of As and C from the metasediments. The sulphide pegmatoids also contain As minerals and graphite, which are also of possible sedimentary origin.

The mechanism of assimilation is either by chemical reaction between the magma and the metasediments or by a modification of the sulphurization process suggested by Kullerud and Yoder (1963) whereby $_{12}^{\circ}$ S reacted with the silicates, the water-pressure having been too high for the existence of S vapour.

5. The P. G. M. in the Merensky Reef, far away from any sediments, e.g. in the Rustenburg Platinum Mine, is present as ferro-alloys containing the P. G. M., sulphides and arsenides which contain the P. G. M. and the P. G. M. in solid solution in the Cu-N-Fe sulphides. Where the Merensky Reef is in contact with or near metasediments (north-west of Potgietersrus, Tweefontein 360 KT, Lydenburg District and south-east of Groblersdal), a consider-P. G. M. able increase in arsenides and bismuthites (?) which contain the $\frac{r}{R}$. $\frac{m}{R}$. was observed. The Cu-nickeliferous sulphides in the Merensky Reef north-east of Potgietersrus contain relatively small amounts of the P. G. M. in solid solution, compared with the Rus tenburg area (Wagner, 1929). It is thus suggested that the P. G. M., owing to their siderophile properties, were extracted from the sulphides to react with As and Bi, which have more marked metallic properties than S. Assimilation of these elements by the Merensky Reef from metasediments thus also took place at certain localities, e.g. north-west of Potgietersrus.

6. To test whether the introduction of S from the metasediments to the magma had taken place, a sulphur isotope investigation was carried out. It was found that metasediments above the Magaliesberg quartzite have relatively high positive δs^{34} per mil values (+ +8) whereas those below the quartzite have relatively high negative values $(† -10)$. Sediments from the same stratigraphical horizon far away from the Complex show the same variation. Plutonic rocks in contact with these metasediments have corresponding values. The plutonic rocks far away from the metasediments (e.g. the Merensky Reef and the mineralized anorthosites) gave values more or less the same as that of S which was derived from the Upper Mantle (i.e. $+0$). These values indicate that assimilation of S by the magma has taken place.

Fractionation of sulphur isotopes during the differentiation of the Bushveld Complex took place. This is illustrated by the enrichment of the S^{34} isotope in the higher horizons of the Complex and also in the later discordant (sulphidebearing) pegmatoids in the Basal and the Critical Zone. From the isotope fractionation curve it was deduced that no concentrations of magmatic S , which formed as an early immiscible sulphide liquid, occurred at the base of the Complex.

7. It was determined that the Ni, Cu, Co, Zn and S contents of the Bushveld magma were about 150, 41, 40, 48 and 238 ppm respectively. In accordance with the views of Ringwood (1956) Ni^{2+} replaces Fe^{2+} in the early ferromagnesian silicates in the Bushveld. The early ultramafic rocks and the

Fe-rich rocks of the Upper Zone show an enrichment of Ni. Cu, Co and Zn also tend to replace Fe in the silicates. Otherwise, the elements mentioned vary sympathetically with S. The chalcophile affinity of Cu, Ni, Co and Zn decreases in this order, which agrees with that given by Rankama and Sahama (1950).

The variation of the S content of the magma was responsible for the concentrations of sulphide in the layered sequence of the Complex. During the greater part of the crystallization of the ultramafic rocks of the Basal Zone, the S content of the magma was relatively high (in comparison with the Critical, Main and Upper Zones) and a nickeliferous immiscible sulphide liquid formed under a low oxidation potential of the magma, in accordance with the views of Smith (1961). This immiscible sulphide liquid was trapped in the intercumulus pores between the silicate crystals. The S content of the magma gradually decreased until it was so low that immiscible liquid, composed mainly out of Cu-sulphide, formed during the crystallization of the norite and the anorthos ite of the Critical Zone (following the ideas of Wager et al (1957)). Not enough Cu was present to remove all the S which resulted in an increase of the S in the magma. Just after a change in the composition of the magma and at a low oxidation potential, $_{k}^{\alpha_{\mathrm{W}}}$ mmisicle liquid composed mainly \bullet ut of coppernickdiferous sulphide, formed in the zone of crystallization to fill up the intercumulus spaces of the Merensky Reef. The Merensky Reef ·could also be explained by crystallization at a sulphide-oxide-silicate eutectic at a high oxidation potential of the magma.

During the crystallization of the Main Zone the S content in the magma was again very low, which resulted in the formation of a Cu-rich matte. The S content in and the oxidation potential of the magma increased very slowly and when the upper part of the Main Zone was formed, magnetite also crystallized. Finally, during the formation of the mineralized anorthosite, sulphide, magnetite and silicate crystallized at a ternary eutectic (according to the phase diagram of Smith, 1961). Immediately after this the magma's composition changed and the Main Magnetitite Seam was formed.

The sulphides in the mineralized anorthosite below the Uppermost Magnetitite Seam are the same of those below the Main Magnetitite Seam.

According to some geochemical criteria whereby the potential of mafic and ultramafic intrusions as Ni ore-bearers may be tested (Polferov and Suslova, 1966 and Nyuppenen, 1966), only the ultramafic rocks of the Bushveld are apparently of economic importance.

15. ECONOMIC CONSIDERATIONS

Excluding the Merensky Reef and the mineralized anorthosites, it appears that no true concentration of magmatic s, derived from the Upper Mantle, is present in the layered sequence of the Bushveld Complex. The introduction of sedimentary S to the ultramafic rocks of the Basal Zone was responsible for the somewhat above normal concentration of disseminated sulphide in these rocks. This was not only the case with the Bushveld Complex but also in certain intrusions in the U.S. S. R. and the Porcupine District of Canada, in which sedimentary S seems to have been assimilated.

In the Bushveld Complex the disseminated sulphide, known thus far in the Basal Zone has been observed only in regions where the plutonic rocks have intruded discordantly into the Magaliesberg quartzite and the hornfelses immediately above and below it. In this connection the following areas are of direct importance:

- 1. The Western Transvaal
- 2. South of Potgietersrus
- 3. The vicinity of Burgersfort

In the Western Transvaal (Vlakfontein region) the deepest parts of the basins have not been explored fully and the possibility exists that concentrations of sulphide may be present near the floor. In the area south of Potgietersrus, up to 10 per cent of sedimentary sulphides are known from the Magaliesberg quartzite, which could have acted as a source of S for the magma tic rocks.

Two separate basins were determined gravimetrically in the Burgersfort region, where the rocks of the Basal Zone cut across the Magaliesberg quartzite and some of the hornfelses below it. The two basins are on Aapiesdoorndraai and the neighbouring farms, and on Welgevonden and the farms in the immediate vicinity.

Attention should also be given to the area around Rustenburg where plutonic rocks cut across parts of the Magaliesberg quartzite.

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Explanation of Photos

Abbreviations used in description below:

- XN Nicols crossed PXN Nicols partially crossed
- 1. Deformed pyrrhotite from No. 27 ore body, Vlakfontein (Sample Vl. 187). RL, PXN, PL 2. 8 mm.
- 2. Deformed pyrrhotite from No. 27 ore body, Vlakfontein (Sample VL.187). RL, PXN, PL 2. 8 mm.
- 3. Deformed pyrrhotite from Vlakfontein. RL, PXN, PL 0. 8 mm.
- 4. Hexagonal pyrrhotite altered to monoclinic pyrrhotite along cracks and basal cleavage. Sample VL. 78 from Rock shaft, Vlakfontein, RL, PXN, PL 2.8 mm.
- 5. The same as photo 4. RL, PSN, PL 0. 8 mm.
- 6. The same as photo 4, unknown anisotropic mineral (mackinawite ?) developed along basal cleavage of pyrrhotite. RL, PXN, PL 0. 8 mm.
- 7. Unknown mineral (mackinawite ?) parallel to the basal cleavage of pyrrhotite, absent in the vicinity of cracks. Sample Vl. from Vlakfontein. RL, PXN, PL 0.43 mm.
- 8. The same as photo 7, PL 0. 8 mm.
- 9. Lamellae of monoclinic pyrrhotite (dark grey) in hexagonal pyrrhotite (grey). Deformation structure is also seen. Sample Vl. 92 from 3A shaft, Vlakfontein. RL, PXN, Pl 0. 8 mm.
- 10. The same as photo 9.
- 11. The same as photo 9.
- 12. Lamellae of troilite (dark grey) in hexagonal pyrrhotite (grey), pentlandite (white) parallel tobasal cleavage of pyrrhotite. Sample 103 from Potgietersrus Platinum Field. RL, PXN, PL 0. 8 mm.
- 13. Lamellae of pyrrhotite(with fine cracks, somewhat lighter) in chalcopyrite. Sample Vl. 5 from No. 4 shaft, Vlakfontein, RL, PL 0. 43 mm.
- 14. Pyrrhotite altered to melnikowite-pyrite along crakcs. Sample 6 from differentiated quartz nortie sill, Burgersfort vicinity. RL, PL 0. 43 mm.
- 15. Pyrrhotite (dark) replaced by chalcopyrite. Sample Vl. 5 from No. 4 shaft, Vlakfontein. RL, PL 0. 8 mm.
- 16. Pentlandite with darkish network of chalcopyrrhotite (or isometric cubanite). The latter mineral goes over in whitish mackinawite. Sample 90c from Mooihoek platinum-bearing pipe. RL, PXN, PL 0.6 mm.

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- 17. Pentlandite with light grey network of chalcopyrrhotite (?). The latter mineral goes over in mackinawite of three orientations - whitish, grey (more so than chalcopyrrhotite) and black-grey. Sample 90c from Mooihoek platinum-bearing pipe. RL, PXn, PL 0. 6 mm.
- 18. Pentlandite with darker grey network of chalcopyrrhotite (?). Mackinawite (white and dark) occurs in larger concentrations at the borders of the crystals of pentlandite. Tetragonal cubanite with lamellae of orthorhombic cubanite (?) in lower left corner. Sample 90c from Mooihoek platinum-bearing pipe. RL, PXN, PL 0. 8 mm.
- 19. Troilite with lamellae of pentlandite (whitish). Three types of lamellae a. brush-like lamellae parallel to (0001),
	- b. regular lamellae parallel to (0001) and

c. irregular lamellae parallel to the pyramid (?) crystallographic planes. Sample 19 from peridotite, Burgersfort. RL, PL 080. 8 mm.

- 20. The same as 19. PL 0. 43 mm.
- 21. Small regular, long straight and brush-like lamellae of pentlandite in troilite. Sample 19 from peridotite, Burgersfort. RL, PL 0. 43 mm.
- 22. Brush-like lamellae of pentlandite arranged in an en echelon texture in pyrrhotite. Sample 119 from "pothole", Merensky Reef, Rustenburg, RL, PXN, PL 0. 8 mm.
- 23. Lamellae of and irregular coarse grains of pentlandite with pyrrhotite Sample 119 from "pothole" Merensky Reef, Rustenburg. RL, PXN, PL 0.8 mm.
- 24. Roundish and irregular bodies of pentlandite in pyrrhotite. Sample Vl. 78 from Rock shaft, Vlakfontein. RL, PL 0. 8 mm.
- 25. Irregular grains of pentlandite and brush-like lamellae in pyrrhotite. Sample Vl. 10 from the Rock shaft, Vlakfontein. RL, PXN, Pl O. 8 mm.
- 26. Small regular and somewhat irregular lamellae of pentlandite parallel to (0001) of pyrrhotite. Sample Vl. 44 from Vlakfontein. RL, PXN, PL *Oo43* mm.
- 27. Lamellae of pentlandite in pyrrhotite parallel to (0001). Sample 119 from Merensky Reef, Rustenburg. RL, PXN, PL 0. 43 mm.
- 28. Brush-like lamellae of pentlandite concentrated next to a crack in pyrrhotite. Sample 119 from Merensky Reef, Rustenburg. RL, Pl 0. 43 mm.

- 29. Rosette of pentlandite, cut parallel to (0001) of pyrrhotite. Monoclinic pyrrhotite, darker than the host of hexagonal pyrrhotite, developed around pentlandite. Sample G1-4802.2. RL, PL 0.8 mm, sample etched with chromic acid.
- 30. Same as 29, sample not etched, PL O. 43 mm.
- 31. Brush-like lamellae of pentlandite fringing out from a vein of chalcopyrite in pyrrhotite. Sample Gl-4802. 2. RL, PL 0. 43 mm.
- 32. Coarse vein of pentlandite together with brush-like pentlandite cuts across pyrrhotite twins. Lamellae of pentlandite in pyrrhotite concentrated along the twinning plane of the latter. Sample 119 from pothole in the Merensky Reef, Rustenburg. RL, PXN, PL 2. 8 mm.
- 33. Flames of pentlandite in pyrrhotite (dark grey) on the contact with pyrrhotite and chalcopyrite (light grey) protrude also in chalcopyrite grain. Sample Gl-4802, RL, PXN, PL 0. 43 mm.
- 34. Flames of pentlandite on twinning plane of individuals of pyrrhotite forms a herringbone texture. Sample 119 from "pothole" in the Merensky Reef, Rustenburg. RL, PXN, PL 0. 43 mm.
- 35. Flames of pentlandite concentrated along twinning planes in pyrrhotite. Sample 119 from "pothole" in the Merensky Reef. RL, PXN, PL 2. 8 mm.
- 36. Vein of euhedral grains of pentlandite and brush-like pentlandite cuts across pyrrhotite. Sample 119 from "pothole" in the Merensky Reef, Rustenburg. RL, PXN, PL 0. 8 mm.
- 37. Pentlandite (whitish) replaced along (111) by cubanite. Sample 12, ultramafic pegmatoid eastern Transvaal. RL, PXN, PL 0. 43 mm.
- 38. Pentlandite (light grey) and mackinawite (black) in chalcopyrite. Sample Gl-4802. RL, PXN, PL 0.43 mm.
- 39. Pentlandite altered to bravoite along cracks. Pyrrhotite (same colour as bravoite) is at the top of the photo. Sample 6, from quartz norite, Burgersfort. RL, PL 0. 43 mm.
- 40. A certain part of a pentlandite grain is completely altered to bravoite, remnants of pentlandite are still to be seen at the bottom of photo. The rest of the pentlandite grain on the left is not affected. Pyrrhotite occupies right hand side of photo. Sample 6 from differentiated quartz norite, Burgersfort. RL, PL 0. 43 mm.

- 41. Pentlandite grains in groundmass of cubanite. Irregular bodies of three different orientations of mackinawite in pentlandite (three shades of grey). Chalcopyrite lamellae (very faint) parallel to (111) of pentlandite. Sample Vl. 146 from No. 27 ore body, Vlakfontein. RL, PL 0. 43 mm.
- 42. Cubanite host with grains of and straight lamellae of pentlandite. Sample Vl. 146 from No. 27 ore body, Vlakfontein. RL, PL 0. 43 mm.
- 43. Pentlandite with irregular bodies of mackinawite (darker grey and black) and lamellae of chalcopyrite, very faint, mostly parallel to (111). Pyrrhotite with basal cleavage contain small roundish pentlandite. Sample from No. 27 ore body, Vlakfontein. RL, PL 0. 43 mm.
- 44. Twinned cubanite with small lenticular bodies of pentlandite semiparallel to twinning planes i.e. (111) . Coarse pentlandite with mackinawite (white and black). Sample from No. 27 ore body, Vlakfontein. RL, PXN, PL 0.43 mm.
- 45. Pyrite (whitish) in eutectic intergrowth with chalcopyrite. Sample 119 from Merensky Reef, Rustenburg. RL, PL 0.8 mm.
- 46. Chalcopyrite occurs along pyramid cleavage of pyrrhotite, brushlike lamellae of pentlandite parallel to (0001) are also present along crack. Sample V1. 131 from Rock shaft, Vlakfontein. RL, PL 0.8 mm.
- 47. Euhedral and roundish grains of chalcopyrite in pyrrhotite. Sample Gl-4802. RL, PL 0.43 mm.
- 48. Chalcopyrite veins (black-grey) along the borders of deformed grains of pyrrhotite. Unknown mineral (mackinawite ?) occurs as white stripes along basal cleavage of pyrrhotite. Sample Vl. 187 from No. 27 ore body, Vlakfontein. RL, PXN, PL 0. 8 mm.
- 49. Chalcopyrite in intergrowth with pentlandite (whitish) on the contact of these two minerals. Sample Gl-4082. RL, PL 0. 43 mm.
- 50. Chalcopyrite twins according to (110) ? with lamellae of mackinawite (white). Sample V1, 5 from No. 4 ore body, Vlakfontein. RL, PXN, PL 0.8 mm.
- 51. Polysynthetic twinning on (111) ? in chalcopyrite. Sample Vl. 5 from No. 4 ore body, Vlakfontein. RL, PXN, PL 0. 8 mm.
- 52. Lamellae of orthorhombic cubanite (darkest) surrounded by mineral E (whitish), both occuring in isotropic, isometric, cubanite (chalco-

pyrrhotite ?) . Sample 90c from Mooihoek platinum-bearing pipe. RL, PXN, PL 0. 43 mm.

- 53. Lamellae of orthorhombic cubanite (whitish) along (100) and (110) in tetragonal cubanite. Sample 90 c from Mooihoek platinum-bearing pipe. RL, PXN, PL 0.43 mm.
- 54. Same as 53 (white is mackinawite).
- 55. Mackinawite lamellae (white) in darker isometric cubanite (chalcopyrrhotite ?). Light grey host is tetragonal cubanite with cleavage parallel to (001). Sample 90 c, from Mooihoek platinum-bearing pipe. RL, PXN, PL 0.43 mm.
- 56. Cubanite twinned polysynthetically according to (111) (very faint shades of grey) with chalcopyrite lamellae along twinning planes of the former. Sample 154 from No. 27 ore body, Vlakfontein, RL, PXN, PL 0. 43 mm.
- 57. Polysynthetic twinning according to (111) in cubanite with mackinawite lamellae (white and black) parallel to this direction. Small grains of mackinawite are also present between cubanite crystals. Sample V1. 189, from No. 27 ore body Vlakfontein. RL, PXN, PL 0. 8 mm.
- 58. Pyrite, white, corroded by pyrrhotite. Sample 6 from quartz horite, Burgersfort vicinity. RL, PL 0. 43 mm.
- 59. Pyrite veined by pyrrhotite (grey). Sample 6 from quartz norite, Burgersfort. RL, PL 0. 8 mm.
- 60. Pyrite grains (white) surrounded by pyrrhotite. Sample 119, Merensky Reef, Rustenburg. RL, PL 2. 8 mm.
- 61. Mackinawite (white lamellae) in chalcopyrite. Sample KA4-2088. 5. RL, PXN, PL 0.43 mm.
- 62. Cubanite with lamellae of chalcopyrite (darker and lighter grey than the cubanite) parallel to (111) and (110). White mackinawite is also present. The grain is surrounded by gange. Sample Vl 10 from Rock shaft. Vlakfontein. RL, PXN, PL 0. 43 mm.
- 63. Mackinawite white and grey in central part of photo. Faint chalcopyrite lamellae visible in white mackinawite. The mackinawite is surrounded and replaced by valleriite (spotted grey) and serpentine black. Sample V1. 208 from No. 27 ore body, Vlakfontein, RL, Xn, PL 0.43 mm.
- 64. Lamellae of mackinawite (white) parallel to (100), (110) or (111) in chalcopyrite which is somewhat twinned. Sample Vl. 5 from No. 4 ore body, Vlakfontein. RL, XN, PL 0. 43 mm.

- 65. Feathery mackinawite of three different orientations (white and two shades of grey) in pentlandite. Sample Vl. 78 from Rock shaft, Vlakfontein. RL, PXN, PL 0. 43 mm.
- 66. Irregular lenticular bodies of mackinawite (black, white and grey) parallel to (111) of pentlandite. Very fine network of mackinawite also in intergro'wth with p'entlandite. Sample 19, peridotite, Burgersfort. RL, PXN, PL 0.8 mm.
- 67. Orientated as well as unorientated network and patchy mackinawite (white) in pentlandite. Sample 19 from peridotite Burgersfort. RL, PXN, PL 0. 2 mm.
- 68. Unorientated very fine network and patchy mackinawite in pentlandite. Sample 19 from peridotite Burgersfort. RL, PXN, PL O. 43 mm.
- 69. White mackinawite as small irregular patches and lamellae parallel to (111) of pentlandite. Sample Vl. 187 from No. 27 ore body, Vlakfontein. RL, PXN, PL 0.43 mm.
- 70. Small irregular white patches of mackinawite in pentlandite. Deformed pyrrhotite occupies a part of the photo. Sample V1. 187 from No. 27 . ore body Vlakfontein. RL, PXN, PL 2. 8 mm.
- 71. Irregular small patches of mackinawite (white, light and dark-grey) in groundmass of pentlandite (grey). Sample $V1$, 187 from No. 27 ore body, Vlakfontein. RL, PXN, PL 0.43 mm.
- 72. Mackinawite forming herringbone texture along chalcopyrite twinning plane. Sample 24a mineralized anorthosite, Magnet Heights. RL, PXN, PL 0. 43 mm.
- 73. Lamellae of mackinawite (white) in grey host (secondary magnetite) both are an alteration product of troilite, white. Sample 12 from ultramafic pegmatoid. RL, PL 0. 43 mm.
- 74. Valleriite vein, cutting pyrrhotite. Sample VL 202 from No. 27. ore body, Vlakfontein. RL, PXN, PL 2. 8 mm.
- 75. Valleriite replacing pyrrhotite, light grey. V1. 202 from No. 27 ore body, Vlakfontein. RL, PXN, PL 0. 43 mm.
- 76. Valleriite (light grey) replacing pentlandite (white) along (111). Dark grey is serpentine. Sample Vl. 202. RL, PL 0. 8 mm.
- 77. Valleriite (grey black) replacing pentlandite (white) along (111). Mackinawite patches (light grey) in pentlandite are still present. Sample Vl. 202. RL, PL 0. 43 mm.

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- 78. Niccolite (N), gersdorffite (G), rammeslbergite (R) and ullmannite? (U) in a semi-zonal arrangement. Pyrrhotite (P) is also present. Sample 45, Merensky Reef, Groblersdal. RL, PXN, PL 0. 48 mm.
- 79. Niccolite (white) maucherite (light grey) pyrrhotite (dark grey) and a rim of gersdorffite between maucherite and pyrrhotite. Sample V1. 131 from Rock shaft, Vlakfontein. 'RL, PXN, PL 0.43 mm.
- 80. Niccolite (white) surrounded by gersdorffite (grey). Sample Vl. 131 from Rock shaft, Vlakfontein. RL, PXN, PL O. 43 mm.
- 81. Maucherite (light grey) zoned by gersdorffite (darker grey) in pyrrhotite. Sample KA5-5028. RL, PXN, PL 0. 8 mm.
- 82. Niccolite (N), gersdorffite (G), maucherite (M), ullmannite ? (U) and cooperite ? (C) in pyrrhotite and chalcopyrite (c) with mackinawite (m). Sample Vl. 10 from Rock shaft, Vlakfontein. Rl, PXN, PL 0.43 mm.
- 83. Subhedral gersdorffite (white) in pyrrhotite with flames of pentlandite Sample KAl-2640. RL, PL 0. 8 mm.
- 84. Niccolite surrounded by gersdorffite, situated in pyrrhotite. Sample KA4-2088. RL, PXN, PL 0. 8 mm.
- 85. Maucherite in "eutectic" intergrowth with pyrrhotite (grey) in central part of photo. Pentlandite (white grey). Sample Vl. 78 from Rock shaft, Vlakfontein. RL, PL O. 43 mm.
- 86. Remnants of niccolite (grey) in maucherite (light grey). Sample 105 from Potgietersrus Platinum Field. RL, PXN, PL 0. 43 mm.
- 87. Sperrylite (white) in intergrowth with chalcopyrite (somewhat darker than sperrryllite). Sample 29, Merensky Reef, Tweefontein 360 KT, Dwars River area. RL, PL 0. 43 mm.
- 88. Twinned braggite. Sample 119 from Rustenburg Platinum Mine. RL PXN, PL 0.43 mm.
- 89. Mineral A, Mineral B, Mineral C (cooperite), Mineral D (michenerite) and sperrylite (S). Sample 105 from Potgietersrus Platinum Field. RL, PXN, PL 0.43 mm.
- 90. Mineral A (whitish), Mineral B (light grey) and sperrylite vein (high relief) cuts through pyrrhotite (badly polished). Sample 105 from Potgietersrus. Platinum Field. RL, PXN, PL 0. 43 mm.
- 91. Polysynthetic twinned millerite. Sample Gl-5566. RL, PXN, PL O. 8 mm.

- 92. Millerite (grey) exsolved linnaeite (white) along prismatic crystallographic directions. Chalcopyrite darkest grey. Sample 42, Roodewal 193 JS, Middelburg district. RL, PXN, PL 0.43 mm.
- 93. Chalcopyrite with lamellae of bornite (grey) and covellite (grey), surrounding bornite. Sample 134, magnetitite, Magnet Heights. RL, PL0.43mm.
- 94. Chalcopyrite replaced according to (111) and (100) by covellite. Sample 138 from Kennedy's Vale. RL, PL 0. 43 mm.
- 95. Zinc-blende (grey) with chalcopyrite (white). Sample lllb from Grasvally 293 KR, Potgietersrus. RL, PL 0. 43 mm.
- 96. Zinc-blende (black) in chalcopyrite. Sample Gl-4082. RL, PL 0. 43 mm.
- 97. Graphite flake, pyrrhotite (dark grey), silicate (black). Sample VI. 128 a, No. 1 shaft, Vlakfontein. RL, PXN, PL 0. 43 mm.
- 98. Graphite. Sample VI. 35 from No. 3A shaft, Vlakfontein. RL, PL 0.43 mm.
- 99. Pyrrhotite (whitish) replaced by melnikowite-pyrite (irregular grey white) and ilvaite (dark grey patches within sulphide), silicates (dark grey surrounding sulphide. Sample 36 from Mapochsgronde RL, PL 0.43 mm.
- 100 Chromite (grey) surrounding silicate (darkest grey). Pyrrhotite (light grey) and pentlandite (lightest grey) surround chromite and silicate. Sample V1. 92 from No. 3A shaft, Vlakfontein. RL, PL 1.4 mm.
- 101. Twinned grains of rutile (grey and dark grey) in chalcopyrite. Sample 103 from Merensky Reef, Potgietersrus Platinum Field, RL, PL 0. 43 mm.
- 102. Ru tile (grey) in intergrowth with chalcopyrite (white grey) Sample 103 from Merensky Reef Potgietersrus Platinum Field. RL, PL 0. 8 mm.
- 103. Relict ilmenite, magnetite completely replaced by silicate (dark grey). White is sulphide. Sample 32 from mineralized anorthosite, north of Pretoria. RL, PL 1. 4 mm.
- 104. Magnetite (light grey) replaced by silicate (dark grey) and sulphide (white). Ilmenite (grey) is not very much affected. Sample 32 from

mineralized anorthosite north of Pretoria. RL, Pl 0. 43 mm.

- 105. Orthopyroxene crystal (central part of photo) in subophitic intergrowth with chromite (light grey). White is sulphide. Sample 44 from Vlakfontein Nickel Mines. RL, PL 2. 8 mm.
- 106. Chromite grain (grey) in host of sulphide (white) and orthopyroxene (dark grey) which is arranged subophitically towards chromite. RL, PL 2. 8 mm.
- 107. Chromite in eutectic intergrowth with silicate. Sample KA1-1526, RL, PL 0.43 mm.
- 108. Chromite (grey) replaced by valleriite (?) darker grey zone surrounding the chromite especially where in contact with sulphide (white). Silicates is dark grey. Sample Vl. 10 from Rock shaft, Vlakfontein. RL, PL O. 8 mm.
- 109. Olivine (grey) replaced by colloidal pyrrhotite (whitish and grey) where the former is in contact with pyrrhotite (white with basal cleavage). Replacement also took place along cracks in olivine. Sample V1. 131 from Rock shaft, Vlakfontein RL, PL L 4 mm.
- 110. Olivine replaced by colloidal pyrrhotite (greater part of photo) where it is in contact with sulphide (white). Sample Vl. 131 from Rock shaft, Vlakfontein. RL, PL 0. 43 mm.
- 111. Olivine replaced by colloidal pyrrhotite. Roundish grey grains are orthopyroxene which are not effected by replacement. Sulphides are white and the high reflecting minerals in the sulphide are arsenides in a zonal arrangement.
- 112. Thin section of poikilitic ore from Vlakfontein. Euhedral to Subhedral crystals of orthopyroxene embedded by sulphide (black). PL 1. 4 mm.
- 113. Poikilitic ore samples from the Rock shaft, Vlakfontein. Coarse olivine-bearing poikilitic ore with intrusive fine-grained orthopyroxene- bearing poililitic ores. The euhedral olivine crystals are corroded by massive sulphides (embayments in crystals) as well as colloidal pyrrhotite (faint lighther grey) forming an outer zone in the olivine crystals. PL 16 cm.
- 114. Poikilitic ore from No. 3 shaft, Vlakfontein, with orthopyroxene laths in a semi-parallel arrangement, PL 12 cm.

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- 115. Massive ore, white poikilitic ore in the outer zone, in contact with feldspathic pyroxenite. No. 27 ore body, Vlakfontein. Pl 9 cm.
- 116. The same as 115.
- 117. Poikilitic ore in contact with pyroxenite with disseminated sulphide. Sample from No. 3A shaft, Vlakfontein PL 9 cm.
- 118. The same as 117.
- 119. Mobilized nickeliferous pyrrhotite (grey) in serpentine (black, grey and white). Sample KA5-668. PL 12 cm.
- 120. Sulphides (highest reflectivity) in an intercumulus arrangement towards olivine (dark grey grains) and poikilitic pyroxene (grey). Sample KA5-648. PL 12. 5 cm.
- 121. Diopside hornfels with grains of sedimentary sulphide (highest reflectivity) concentrated parallel to the original bedding planes of the sediment. Sample KA6-526. PL 12 cm.
- 122. Inclusion of diopside hornfels (fine-grained) with small sulphide specks (whitish-grey) in norite with small grains of sulphide here and there. Sample KA6-484. PL 15 cm.
- 123. An inclusion of diopside hornfels with sedimentary sulphide grains (highest reflectivity) concentrated along bedding planes of the original sediment, The central coarser grained part is intrusive norite, also with sulphide specks here and there. The contact between the norite and diopside hornfels is gradational. Sample KA6-484. PL 15 cm.
- 124. Massive sulphide, pyrrhotite (dark grey) with pentlandite grains (lighter grey) and veins of chalcopyrite cutting the pyrrhotite. Sample from No. 1 ore body, Vlakfontein.
- 125. Merensky pegmatoid with intercumulus sulphide (white) and chromitite (white-grey) at the base of the pegmatoid (right hand side of photo). Sample from Rustenburg Platinum Mine. PL 8 inches.

FIG 8. THE VARIATION OF THE VOLUMETRIC MINERALOGICAL COMPOSITION OF THE SULPHIDE PHASE ON DIFFERENT STRATIGRAPHICAL HORIZONS IN THE

BUSHVELD COMPLEX. MEANING OF THE SYMBOLS: x Percentage smaller than oil

xx Percentage between 0.1 and 0.4

Reliable values - more than 500 points counted

· Percentages estimated visually

(w) Samples) from the Western Transvaal

* Mean of several polished sections

 α , α , α , α , α

 \mathcal{A}^{max}

FIG 36. VARIATION OF Ni (o), Cu (o), Zn (+), Co (--) AND S (O) ON DIFFERENT STRATIGRAPHICAL HORIZONS IN THE

=1G 37. VARIATION OF Ni (SOLID LINE), Cu (BROKEN LINE, SHORT DASHES), Zn (DOTTED LINE) AND S (BROKEN LINE,

LONG DASHES) ON DIFFERENT STRATIGRAPICAL HORIZONS IN THE BUSHVELD COMPLEX

