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A detailed mineralogical investigation of the Ventersdorp contact reef at Venterspost and Libanon gold mines, West Rand with special reference to the mode of mineralization of this horizon

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RAHDEN

A DETAILED MINERALOGICAL INVESTIGATION

OF THE VENTERSDORP CONTACT REEF AT

VENTERSPOST.

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All assays quoted were carried out by Messrs. Gold Fields of South Africa Laboratories.

A DETAILED MINERALOGICAL INVESTIGATION OF THE VENTERSDORP CONTACT REEF AT VENTERSPOST AND LIBANON GOLD MINES, WEST RAND, WITH SPECIAL REFERENCE TO THE MODE OF MINERALIZATION OF THIS HORIZON.

H.V.R. VON RAHDEN.

Thesis
M Sc.
University of the Witwatersrand
1963.

DECLARATION

This is to certify that this dissertation, entitled "A detailed mineralogical investigation of the Ventersdorp Contact Reef at Venterspost and Libanon Gold Mines, West Rand, with special reference to the mode of mineralization of this horizon", has not been previously submitted as a dissertation or thesis for any degree by the undersigned.

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(Candidate for the degree of

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Thesis G.26168

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INTRODUCTION.

This work represents the results of a survey of the mineralogy and petrology of the Ventersdorp Contact Reef at Venterspost and Libanon gold mines. During this study, attention was paid to the mode of occurrence of gold in the ore, and to the relationships of the gold towards the other minerals. An attempt was also made to gather evidence concerning the physico-chemical conditions which prevailed during the mineral deposition, and to evaluate their effect on the mode of mineralization.

Ventersdorp Contact Reef.

De Kock (1940) has said that the name "Ventersdorp Contact Reef" is applied to the conglomeratic sedimentary layer which occurs at the base of the Ventersdorp Lavas and which itself rests on the Witwatersrand System. The V.C.R. is younger than the Witwatersrand System and older than the Ventersdorp volcanic rocks, but since it is conformable to the base of the latter and owes its preservation to the outpouring of the lavas, it can be regarded as a basal conglomerate of the Ventersdorp System. De Kock further pointed out that the name "Ventersdorp" was not intended to convey a genetic affinity with the Ventersdorp lavas, which have definitely not contributed any gold, but were responsible only for small additions of volcanic ash to the matrix of the reef. The name was originally chosen to indicate the stratigraphic position of the reef at the contact between the Ventersdorp and Witwatersrand Systems and also to distinguish it from a true Witwatersrand Banket.

A detailed description of the geological features and structural variations of the V.C.R. at

Venterspost has been given by Davies (1949) but is beyond the scope of the present study. A brief outline is however presented below.

The V.C.R. may best be described as a conglomeratic layer consisting of quartz pebbles varying in size from what may be called a pebbly grit to boulders reaching up to 15 inches in length. The pebbles and boulders constituting the V.C.R. vary considerably in their degree of sorting, depending on their location in the mine, and are invariably cemented together by dark green chlorite and various interstitial sulphides.

Petrography of the V.C.R.

Quartz in various forms constitutes over 80% by weight of the total mineral assemblage of the V.C.R. at Venterspost, and over 90% at Libanon, in the suite of samples examined.

The pebble types encountered were composed of vein quartz, quartzite and chertlike pebbles. Most of the pebbles examined were well-rounded ellipsoidal or muffin-shaped glassy varieties of quartz with subordinate amounts of milky white or dirty grey varieties, as well as numerous small pebbles of blue opalescent quartz. Lozenge-shaped and square pebbles showing little rounding were also found. A few angular greyish-black to dark brown banded chert pebbles were also seen. (Plate II).

The lengths and breadths of over 600 pebbles and cobbles were measured. The maximum size of cobble found in the present study was 150 mm. The length-breadth ratio varied between 1.26 and 3.03, with an overall average for all the pebbles measured of 1.59. This

indicates that the pebbles had most probably been transported for considerable distances.

The following quartz types, classified according to the scheme proposed by Pettijohn (1948), were encountered in the suite of samples examined. The size limits refer to the major axis.

Blue opalescent granules and pebbles	2 - 8 mm.
Muffin-shaped pebbles and cobbles	17 -95 mm
Brownish-green cherty types	10 -60 mm.
Blackish or greyish quartz grains and pebbles)	2 -20 mm
Ellipsoidal grains,pebbles and cobbles	2-150 mm.

The typically dark green matrix of the V.C.R.is composed mainly of phyllosilicates, the principal members of this group present in the suite of samples being chlorite and sericite. On the average, in the suite of samples from Venterspost, the phyllosilicates account for nearly 10% by weight of the total mineral assemblage, whereas in the samples from Libanon, the average percentage by weight of the phyllosilicates is of the order of 1%.

The average matrix to pebble ratio (by weight) obtained for the Venterspost samples is 1: 4.9, and for the Libanon samples 1: 24.0. It should, however, be pointed out that the suite of samples obtained from Venterspost showed a higher average degree of sulphide mineralization, approximately 8%, than those from Libanon, where the average was approximately 3%. This would obviously also affect the matrix to pebble ratio.

As can therefore be seen, the degree of sulphide mineralization varies considerably. Pyrite is the predominant sulphide present and can easily be seen in hand specimen. The overall pyrite content for the suite of

samples from Venterspost varies from less than 1% to over 30% by weight, with an average value of 6%, while in the samples from Libanon the pyrite varies from less than 1% to over 4% by weight, with an average value of 1.6%. The pyrite may occur as pyrite bands, showing parallel alignment to the bedding, or as completely haphazardly distributed grains throughout the reef. Another form in which the pyrite occurs is as so-called "buckshot" or pseudo-pebbles of pyrite. This occurs generally in the lower portions of the reef (Davies 1949). Davies also mentions that the presence of buckshot pyrite is generally taken as a rough indication of high ore values, due to the fact that gold is commonly found to be concentrated in areas containing such pyrite.

Pyrrhotite is the next most abundant sulphide present and occurs as xenomorphic grains and stringers or more rarely as fine pebbles of buckshot. The pyrrhotite content of the present suite of samples varies from less than 1% to over 8% by weight at Venterspost, and from less than 1% to nearly 2% by weight at Libanon. The presence of large amounts of pyrrhotite in the mine has generally been accepted as an indicator for high gold values of ore. Pelletier (1940) has in fact commented on this, and has stated that the pyrrhotite represents an enriching factor.

The other sulphides are generally only present in very minor amounts and are not readily seen in hand specimen. Chemical analysis of a composite sample prepared from equal portions of every sample in the present suite showed that the average content of lead, zinc and copper minerals did not exceed 0.04% respectively.

A particularly noticeable feature in the specimens of ore containing buckshot pyrite was the presence of particles of visible gold. In this feature the V.C.R. differs from most other horizons of the banket, where coarse visible gold is less readily seen, despite higher ore values (de Kock, 1940).

Origin of the V.C.R.

The V.C.R. may be considered to represent the erosion product of the immediately underlying Witwatersrand System, formed during the period intervening between the deposition of the latter and the outpouring of the Ventersdorp Lavas. The major portion of the components or minerals present in the V.C.R., including the gold and the large quartz pebbles so characteristic of the horizon, were unquestionably derived from the pre-existing Witwatersrand beds. This surface detritus derived from the underlying Witwatersrand beds was then deposited and reworked by physical agencies such as the wind and the rain, which resulted in the sorting of the various components and the subsequent infillings of the undulations in the older land surface. De Kock (1940) has shown that irregularities in the floor of the V.C.R. influenced the lateral distribution of the gold.

The tuffs which occur intermittently in the conglomerates point to an immediately pre-Ventersdorp Lava eruptive phase or phases, during which volcanic ash was deposited on the pre-existing land surface and became intermixed with the coarser debris. This volcanic ash is considered to have been responsible for imparting the characteristic dark colour to the V.C.R. The subsequent outpouring of nearly 1400 feet of lava then

resulted not only in the compaction and metamorphism but almost certainly in the preservation of the V.C.R.

The principal rock types encountered in descending order in borehole sections examined at Venterspost may be briefly summarized as follows:-

Ventersdorp Lavas.

The major features of the Ventersdorp lavas, which extend to nearly 1400 feet in a vertical direction above the V.C.R. proper, have already been described in detail by Davies (1949).

The lavas are andesitic in composition, and are in places amygdaloidal or porphyritic. The colour of the lavas in hand-specimen varies from a greenish colour to an olive-green with increase in depth.

Some of the less well-known features of the lavas are contained in an unpublished company report by P.J. Rossouw, at the time West Wits geologist, who prepared numerous thin sections from the 1390 feet of core recovered during the drilling of borehole 11 at Venterspost in 1934. According to Rossouw, a very striking feature of the thin sections examined was the abundance of zeolites present in the lavas. The zeolites either occurred as discrete grains or as infillings in cracks in the rocks or in amygdales. The zeolite content also appeared to show a pronounced increase with increase in depth from the top of the lavas. In the first 600 feet of lavas examined by means of thin sections by Rossouw, only scolecite was recognized, whereas numerous other zeolites, such as stilbite, phillipsite, laumontite and thompsonite, were identified in the next 700 feet of core examined, stilbite being the most common variety encountered.

The two varieties of chlorite identified in thin section in the lavas were light green, faintly pleochroic, penninite and clinochlore. These two varieties of chlorite occurred either as part of the matrix or as small patches apparently representing areas of intense localized alteration. The patches of chlorite seemed to be ophitic towards the plagioclase laths and appeared to represent the alteration products of an earlier ferro-magnesian mineral, probably augite.

The composition of the minerals filling and lining the amygdales may be briefly summarized as follows:

Type 1:

This type of amygdale showed a lining of chlorite on the inside periphery of the amygdale, followed in turn either by a zone consisting of intermixed mosaic-like grains of quartz and chlorite, or a few grains of chlorite and pyrite, or even just chlorite.

Type 2:

The second major type of infilling consisted of numerous small grains of quartz arranged around the periphery of the amygdale, followed by an intimate mixture of quartz grains and chlorite, which is again in turn followed by pure chlorite with a core of quartz grains which are significantly larger in size than those on the periphery. Calcite is another component which may or may not be present.

Rock Types immediately overlying the V.C.R.

The last thirty or forty feet of material overlying the V.C.R. is generally composed of metamorphosed lava containing scattered amygdales. The lava is often traversed by small veinlets of calcite and quartz.

This layer is followed by another layer consisting of a mixture of sedimentary material, lavas, volcanic breccia and tuffs, and this is in turn followed by a layer of black ashy tuffaceous material which may reach thicknesses of up to two feet (de Kock, 1940).

Footwall quartzites.

De Kock (1940) has stated that the V.C.R. may rest directly on clean light grey Witwatersrand quartzites, but that generally the footwall quartzites for a few inches, and rarely up to a few feet, below the contact, are coloured dark green by chloritic infiltrations from the tuffs above the reef.

SAMPLING TECHNIQUE AND TREATMENT OF SAMPLES.

Sampling.

Specimens were collected from currently accessible exposures of ore in the underground workings at Venterspost and Libanon gold mines. In each case the sampling sites were noted with respect to some known reference points. The positions and elevations of the sampling sites from which the present suites of samples were derived are shown on the accompanying mine plans and tables. (Tables Nos. I, II, III, IV, V.)

Specimens were collected in areas of payable ore, and also from mineralized rocks that were not of mill ore grade, these latter being the so-called low-grade specimens. In some cases, however, this designation was found to be completely erroneous. In each locality an attempt was made to collect a sample weighing 10 to 15 pounds that was representative of that particular region.

Treatment of Samples.

The samples taken consisted largely of coarse chips and lumps. Since it had previously been decided to examine the samples by means of polished sections, thin sections and crushes or pulp, a suitable method of subdivision of the samples had to be devised which would yield reasonably representative portions for assay purposes, yet which would not preclude the preparation of both thin and polished sections. For this purpose, all lumps of rock were first broken with a heavy hammer until the overall size of the lumps did not exceed approximately 2 inches, and the sample was then quartered in the normal way. One portion was reserved for polished sections, a second portion for thin sections and the third

portion for combined assaying and mineralogical examination. The fourth portion was kept in reserve for any further work which might be required. The portion of ore set aside for assay and mineralogical purposes was then put through a jaw crusher and finally through a laboratory disc crusher of the rotary type.

For heavy mineral studies the use of a disc crusher is generally not recommended. This fact was taken into consideration, and comparative studies were carried out on samples crushed in a percussion mortar and samples ground in the disc crusher. These studies showed that, in fact, a better control over the degree of comminution could be obtained by careful adjustment of the disc crusher than was possible with the percussion mortar, and the latter was accordingly not used.

The samples were ground to a degree of fineness such that approximately 50% of the sample passed through a 100 mesh Tyler screen. A screening analysis of a composite sample prepared from equal portions by weight of crushed V.C.R. ore showed the following size distribution:

Mesh Size (Tyler)	Percentage
+ 100	51.74
- 100 + 200	19.35
- 200	28.91
	100.00

Previous work carried out indicated that this degree of comminution would be likely to cause the least possible damage to the brittle accessory minerals such as zircon. On subsequent examination of the liberated particles of gold, it was found that less than 1% of the total number of grains of gold examined showed any noticeable degree of either flattening or deformation. (This

indicates that the use of the disc crusher in fact produced no serious deformation of the minerals.) Since all the samples were treated in the same way, any significant errors likely to have been introduced in the relative abundance of liberated heavy minerals due to variations in the crushing procedure may be discounted. (Tyler and Marsden, 1937).

A composite sample prepared from representative weighed portions of all the pulped samples was then screened through a series of standard Tyler mesh screens in order to see whether this procedure would aid in the concentration of any of the heavy minerals. This test indicated that, apart from the elimination of the coarser grains of pyrite, nothing could be gained by this procedure. Conventional methods therefore had to be used for the concentration of the heavy mineral suite.

Concentration of the heavy minerals.

Previous examination of a composite sample indicated that conventional procedures of mineral separation would have to be modified due to the presence of pyrrhotite in the ore. The pyrrhotite and tramp iron derived from the crusher were both found to be highly susceptible to alteration, especially when heavy liquids such as bromoform were used. Contact with such organic liquids resulted in the very rapid oxidation of the pyrrhotite, with the liberation of ferrous iron ions, which in turn coated all the sulphides and gold particles present with a dull reddish coating of iron oxides. Accordingly the pulverized ore was repeatedly exposed to a bar magnet in order to remove as much pyrrhotite and tramp iron as possible before carrying out conventional mineral separation procedures.

The pyrrhotite and tramp iron concentrates prepared in this way were then immersed in methylated spirits in a large flat glass dish, and a bar magnet was moved repeatedly over the surface of the liquid. By means of this method, it was possible to obtain an ostensibly pure pyrrhotite concentrate. These concentrates of pyrrhotite with admixed tramp iron were then rapidly washed with acetone, dried in an oven and placed in stoppered glass tubes to inhibit further oxidation.

The heavy liquids used throughout these investigations were Bromoform (S.G. 2.90) and Methylene Iodide (S.G.3.20). Separations were carried out using glass separating funnels. Since it was proposed to separate upwards of 100 grm. portions of pulverized ore, it was necessary to obtain some idea of the amount of material which could safely be treated in any one operation with the best possible separation of the heavy minerals. Ideal conditions would demand a layer one grain thick on the surface of the heavy liquid, but with the weight of material which had to be separated, such a condition would be impractical. Instead, very large separating funnels capable of holding nearly 500 grams of bromoform were used, and the contents were vigorously stirred with a thick glass rod until no further heavy minerals were liberated from the cake of light minerals floating on top of the bromoform. In order to check the efficiency of the separations carried out, the cake was washed free of bromoform and superpanned, or separated a second time with bromoform. The amount of material added to further lots of bromoform was then adjusted accordingly for the maximum recovery of the heavy minerals.

The bromoform sink or concentrate was then further re-treated with a large excess of methylene iodide. By virtue of the fact that the pulp had on an average been reduced to approximately 5% of its total previous bulk, clean separations could now be attained with relative ease. In those cases where it was desired to isolate a particular mineral, such as pyrite, for specific examination, the Franz Isodynamic Separator was used, whilst the Haultain Superpanner was used to concentrate any particles of uraninite and gold.

Quantitative mineral analysis.

Preliminary studies carried out on the heavy mineral concentrates obtained by the methods previously described, soon indicated that a purely quantitative mineralogical study of the heavy mineral suite might not give a true picture of the relative quantities of heavy minerals present. Whilst it was found that most of the chromite and zircon grains, with the exception of those already occurring as fractured grains in the host rock prior to crushing, were liberated virtually completely, the same could most certainly not be said for the sulphide minerals and gold particles. Both the gold and the sulphide minerals often occurred as fine attachments to quartz and other gangue minerals, and by virtue of their higher specific gravity altered the overall specific gravity of the "chats' to such an extent that these were concentrated in the heavier gravity fraction. The presence of such "chatted" particles would therefore render any results based purely on weight percentage open to suspicion.

Qualitative mineralogical studies.

Previous work carried out by the writer on other horizons in the Witwatersrand suggested that, in order to obtain the clearest picture of differences in morphology and size, the various minerals occurring in the V.C.R. could best be studied in the form of integral liberated grains by means of a binocular microscope, aided where necessary by polished section studies.

Cohen (1962) has stated that the measurement of sizes of gold particles visible in polished section is a risky practice, as a two-dimensional view is used and measurements are statistically not representative because the total number of grains measured is generally low. This latter point is readily borne out in the present study, where only approximately 600 grains of gold were seen in over 200 polished sections, whereas over 5000 grains were counted with relative ease in the pulped concentrates prepared. In addition, Cohen has carried out studies of the real and apparent sizes of gold in polished specimens using microradiographic techniques. These studies revealed that the size of the gold particles was often apparent rather than real, depending more on the accidental position of the plane of polishing in relation to the gold particles than on any other factor. Very small spots of gold exposed were found by Cohen to be the tips of large concealed grains, and apparently large "nuggets" were sometimes thin skins lying in the plane of the section and of negligible weight and thickness.

In the present study, therefore, measurements made on polished sections probably do not represent the true sizes of the grains. Krumbein (1935) has proved that the average diameter as shown in polished sections

of spheres distributed at random represents 0.785 of their true diameter. Accordingly, where measurements have been made on polished sections, the true dimensions of the grains can be taken as being larger than the measured dimensions.

All grain sizes measured in the present study may be defined as the distance between parallel lines that touch the outer contour of the grain and are parallel to a given direction, such as the vertical or horizontal lines of an ocular reticle. In each case, the maximum overall dimension or length has been quoted, unless otherwise stated. In the case of the gold particles, which only seldom showed rounded outlines, it was felt that the present method of measurement would give a better correlation with sieving (Packham 1955) and be of more practical use in actual metallurgical practice than measurements based on the breadth.

Apart from size, other factors of great practical and economical importance which can be studied far more readily on liberated grains by means of a binocular microscope than in polished section, are micron-thin coatings on particles and the condition of the gold. For example, micron-thin coatings of silver were seen on particles of gold when examined by means of a binocular microscope. Such coatings would almost certainly have been removed during the preparation of polished sections and would accordingly have gone undetected.

The "condition" of gold in mined ore is of great significance to the metallurgist, since this factor will to a large extent govern the most efficient recovery of the gold. Edwards (1947) has illustrated this feature and discussed its implications by showing a photograph of

a grain of gold which has become coated by a layer of iron oxides. Since the thickness of these coatings of iron oxide rarely exceeds more than a few microns, it is doubtful whether such coatings would be seen in polished section. The orange-red to brown iron-stained particles of gold may, however, readily be seen in heavy mineral concentrates by means of a binocular microscope. The latter technique is also preferable in those cases where "chats" representing intergrowths or inclusions of economic minerals with gangue occur. In the present study, for example, small particles of gold, whose maximum size never exceeded 5 microns, yet which numbered over 100 in a particle of quartz whose overall size did not itself exceed 5 microns, were seen with ease in three dimensions.

The obvious objection generally advanced by workers who prefer basing all their measurements on polished section studies, is that the method favoured by the writer involves the measurement of deformed grains, and therefore does not represent a true picture of the original size of the grains. In order to check the validity of this argument, special attention was paid to the degree of deformation caused to the particles of gold during the grinding of the ore. The present study, supported by many thousands of similar observations on liberated grains of gold, indicated that less than 1% of the total number of grains of gold examined showed any signs of flattening or deformation. Therefore any objections based on these grounds may, in the writer's opinion, be discounted for all practical purposes. The effects of grinding on the brittle minerals such as uraninite are described under their appropriate headings.

It should, however, be pointed out that the study of polished sections does possess some advantages. The polished section method is the only method whereby the interrelationships, mode of occurrence and paragenesis of ore minerals may be studied in situ, and it has been used for these purposes in the present study.

It may therefore be said that both methods have their advantages, and that the choice of method is dependent on the nature of the problems to be elucidated.

POLISHING METHOD.

At the start of the present study, the writer was faced with the necessity of producing polished sections which would be suitable for micro-photography if required, and yet which could be prepared using semi-skilled labour with the materials and equipment available in the minimum possible time. The position was complicated by the presence in the samples of hard minerals such as quartz and pyrite as well as soft minerals such as gold, both of which were required to show a high degree of polish without the production of an objectionable degree of relief. It is felt that the present method, devised by the writer, meets most of the essential requirements.

Details of abrasives used.

Abrasive Type	Average Size of Abrasive Grains (microns)
Carborundum - 220 grit	150
Carborundum - 400 grit	60
Carborundum - 600 grit	20
Carborundum --600 grit	12
Levigated Alumina	5
Zirconium Oxide	1-2
"Diadust" graded diamond abrasive	12-8
" " " "	6-3
" " " "	3-½

(The imported diamond abrasives are usually supplied in a tube with a fine nozzle. Locally produced diamond abrasives supplied in a suitable carrier paste were found to be equally effective.)

Preliminary hand-grinding stages.

The initial grinding and flattening of specimens prior to moulding in bakelite and subsequent polishing was found to govern, to a large extent, the time required to produce acceptable polished sections. It was found that this initial grinding and flattening of the ore chip could best be carried out using a 220 grit carborundum powder. The use of coarser grades merely resulted in the formation of deep scratches, which could often only be removed with accompanying loss of specimen. The chips of rock were initially ground flat on a rotating steel lap or stationary steel plate using 220 grit, with water as a lubricant. This stage was then followed by a further period of grinding using 400 grit, until all depressions and irregularities on the surface had been removed. After thorough washing with water, the specimen was moulded in bakelite at 150 degrees Centigrade for 3 minutes, using a Nash and Thompson metallurgical moulding press. The completed moulded specimen was then once more ground on a stationary sheet of thick plate glass with 400 grit,using water as a lubricant, until both the bakelite surrounding the section and the rock were completely level and an overall matte effect was produced over the entire surface to be polished.

Automatic polishing.

After the initial hand grinding on the glass plate with 400 grit, the mounted sections were transferred to the automatic polishing machine and ground with successively finer abrasives, starting with 400 grit and finishing with a 1:1 mixture of levigated alumina and zirconium oxide, which was applied as a thick slurry.

Water and detergent (Teepol) were used as the lubricating medium during these stages. The laps used were 3 inch diameter steel throughout, and the polishing cloth used was nylon taffeta tautly stretched over the new steel laps. The next three stages of polishing involved the use of 6-3 micron diamond abrasive, then 1 micron diamond abrasive and then zirconium oxide. During these three stages of polishing, paraffin and finely powdered spectrographic grade graphite were used as lubricants.

Separate laps were used for each grade of abrasive, and sections were carefully washed when a change of abrasive was made. The careful cleaning of the sections is particularly important, especially during the last three polishing stages. Sections are best cleaned by using copious quantities of carbon tetrachloride and wiping off with cotton wool, to minimize any possibility of contamination of the laps.

Equipment used.

In the machine used by the writer (Cooke Troughton and Simms Model M70 metallographic polishing machine) the specimen is held on the rotating lap by means of a peg which fits freely into a hole already centrally moulded into the back of the bakelite mount. The peg is weighted by, and connected to, an eccentric cam which may be adjusted so that the specimen moves over a major portion of the lap with an orbital motion, whilst revolving about its own centre due to the differential friction set up between the lap and the section. The eccentricity and weight are adjustable and may be fixed once the optimum conditions have been established.

Lap speeds.

During the preliminary machine-grinding stages, which involve the successive use of various graded carborundum abrasives prior to the last three polishing stages, the lap speed should not exceed 100 r.p.m. Any increase in lap speed merely results in the unnecessary loss of abrasive and consequent reduction in cutting speed. The last three stages may be carried out using the fastest lap speed available, 400 r.p.m. During the initial grinding stages, the cutting rate is greatly enhanced by using the maximum possible loading or weight, provided adequate lubrication is used to forestall any undue heating. The last three stages of polishing are carried out using preferably the least possible weight or loading.

Polishing times.

These vary considerably according to the type of specimen. The average maximum times required for each stage in the case of the present suite of minerals are shown below:

400 grit	2 minutes
600 grit	2 minutes
-600 grit	3 minutes
Mixture of levigated alumina and zirconium oxide)	5 minutes
Diamond abrasive, 6-3 microns	6 minutes
Diamond abrasive, 3-$\frac{1}{4}$ microns	6 minutes
Zirconium oxide	3 minutes

The most satisfactory way of controlling the progress of the grinding and polishing processes, is however, frequent recourse to a binocular microscope to study any noticeable improvement during each polishing stage. This helps to minimize the formation of excessive

relief caused by unnecessarily prolonged polishing on the cloth laps.

Nylon taffeta as a polishing cloth.

Initially lead tin laps, grooved in criss-cross fashion, which had been originally supplied with the polishing machine, were tried with graded diamond abrasives. Generally speaking, the results were found to be poor. In order to obtain a satisfactory degree of polish, it was found necessary to increase the loading on the section to such an extent that plucking of the softer minerals from the section occurred. The laps also soon became dished, resulting in the formation of domed specimens.

The method advocated by Hallimond (1954), using a solid nylon disc, was tried with a variety of graded diamond abrasives and a variety of lubricants. It was found, however, that severe scratching could not be avoided, and the method was consequently abandoned.

The method suggested by Sampson (1956), using silk bolting cloth and graded diamond abrasives, was tried next, with 12 to 8 micron, 6 to 3 micron and 3 to ½ micron diamond abrasives. The silk bolting cloth seemed to yield acceptable results, the major drawback being the very short polishing life of the cloth, necessitating the frequent changing of the cloth and the concomitant loss of expensive diamond abrasive. Nylon taffeta was finally selected as being suitable for the final polishing stages. The material has only a very slight nap and shows a high resistance to wear. It was found that, before the cloth became unserviceable, upwards of 25 sections containing both hard and soft

minerals could easily be polished without the production of undue relief.

Selection of diamond abrasives.

Extensive tests showed that the use of the 12 to 8 micron range diamond abrasive was not warranted, since the finish imparted by the 1:1 mixture of levigated alumina and zirconium oxide was not only superior but also considerably cheaper to produce. The 6 to 3 micron and 3 to ½ micron ranges of diamond abrasives were therefore finally selected as being the most suitable grades.

Application of diamond abrasive to the polishing lap.

The writer uses by preference a minimum of 1½ inches of diamond abrasive extruded from the tube. This is applied as small spots all over the lap and then lightly rubbed in with the tip of a clean finger. It was found that the use of smaller amounts of abrasive resulted not only in an inferior polish being obtained, especially in the case of quartz, but also unnecessarily shortened the life of the nylon cloth by increasing the polishing time required for a good finish.

Choice of lubricants.

Paraffin was chosen as the final lubricant in preference to a large number of oils, such as sewing machine oil and olive oil and others of a wide range of viscosity. It was found that the degree of relief or undercutting of the softer minerals was to a large extent dependent on the viscosity of the lubricant used, those of higher viscosity causing more undercutting.

During the final polishing stages, it became apparent that fine hair scratches were being imparted to

the softer minerals, especially by the 6 to 3 micron diamond abrasive. It was suspected that these scratches were caused by the movements of the diamond particles themselves on the polishing cloth, rather than being caused by a lack of lubricant (paraffin). It was found that these scratches could be successfully eliminated by adding small amounts of finely pulverized spectrographic grade graphite to the lap. Natural graphite proved to be unsuitable, as small amounts of impurities were usually present, and these merely led to the production of more scratches.

Final finish.

The final polish produced by the last diamond abrasive used (3 to ½ micron range) frequently imparts numerous fine hair scratches, especially to the sulphides. These scratches should be removed if the section is to be used for micro-photography. The finishing medium suggested by most other workers is magnesium oxide of reagent grade of purity, made into a slurry with water. Magnesium oxide does, however, suffer from the disadvantage that exposure to the atmosphere is likely to result in the formation of magnesium carbonate in the pores of the cloth, and this then ultimately scratches the sections. Cameron (1961) has proposed a technique whereby the formation of magnesium carbonate is minimized by storing the magnesium oxide under kerosene. This, however, does not offer any solution as regards the material already on the lap and in contact with the atmosphere. The writer has compared the finish imparted to similar sections finished with either magnesium oxide or zirconium oxide, and has found that the latter is free of

the latent disadvantages listed for magnesium oxide, and, in addition, imparts a superior finish.

Comparison of results obtained by the use of the present method with those from the Graton Vanderwilt type of polishing machine.

Advantages:

1. The writer's method is capable of producing finished polished surfaces suitable for micro-photography in less than half an hour using semi-skilled labour, in contrast to the Graton Vanderwilt machine, which requires constant attention and considerable experience to produce a good section in under one day.

2. Inexpensive steel laps are used with polishing cloths.

3. Since only steel laps are used, there is no possibility of the polished section becoming contaminated by pieces of lead polishing lap.

Disadvantages.

1. The writer's method cannot produce sections as free of relief as those produced by the Graton Vanderwilt.

2. Small inclusions of grains of uraninite embedded in "carbon", as well as the "carbon" itself, were polished to a higher degree by the Graton Vanderwilt than was possible by the writer's method.

SPECTROGRAPHIC METHODS FOR THE DETERMINATION OF GOLD, SILVER, COBALT AND NICKEL IN PYRITE AND PYRRHOTITE.

GOLD AND SILVER DETERMINATION:

Pyrite - Preparation of samples.

The pyrite to be analysed was concentrated from a composite prepared from equal weights of the original 18 crushed samples submitted from the V.C.R. at Venterspost for assay. The pyrite was initially separated from the gangue materials by means of heavy liquids, followed by a Haultain Superpanner and finally by the Franz Isodynamic Separator. The settings on the Franz Isodynamic Separator were as follows:-

Tilt 16°

Dip 26°

Current 1.00 amperes

Vibration control maximum.

In order to facilitate handpicking of the resultant pyrite concentrates, which represented both the oxidized and unoxidized forms of pyrite (described more fully under the heading of "Pyrite"), the pyrite was screened through a 65 mesh Tyler screen. All the particles retained on the screen were then handpicked, until no attached gangue or foreign particles could be detected under a binocular microscope. The two types of pyrite were then finely ground in an agate mortar with alcohol, and dried under a heat lamp in preparation for spectrographic analysis.

Pyrrhotite - Preparation of Samples.

The method adopted for the concentration and purification of the pyrrhotite concentrate has already been described in the section on "Sampling technique

and treatment of samples". The ostensibly pure pyrrhotite sample was then also finely ground in an agate mortar with alcohol and dried under a heat lamp prior to spectrographic analysis.

Pyrite - purity of samples.

Examination of the pyrite concentrate prepared by the method described above failed to show the presence of any contamination when the concentrate was viewed under a binocular microscope. When, however, some of the pyrite was treated with nitric acid, which destroyed the pyrite, thereby liberating any included materials, the following impurities were found: zircon, chromite and quartz. These impurities constituted less than 2% of the total weight of the sample, and were presumably entrapped at the time of formation of the pyrite.

Pyrrhotite - purity of samples.

The pyrrhotite concentrate was analysed chemically for pyrrhotite and total iron. (The estimation of pyrrhotite is based on the fact that pyrrhotite when reacted upon by hydrochloric acid liberates H_2S. This H_2S may then be quantitatively determined and the result recalculated in terms of pyrrhotite). Other impurities were found by treating the concentrate with concentrated hydrochloric acid, which takes both the tramp iron and pyrrhotite into solution, so that all other insoluble impurities may be estimated by difference.

Composition of pyrrhotite concentrate:-

Pyrrhotite	78.39%
Tramp iron	17.80%
Pyrite	1.17%
Quartz, chlorite & gold	2.64%
	100.00%

Spectrographic analysis of gold and silver in pyrite and pyrrhotite.

Esterhuizen, who carried out all the spectrographic analyses using a large Hilger Littrow-type spectrograph fitted with quartz optics, found the following conditions most suitable for the spectrographic analysis of pyrite and pyrrhotite. (Esterhuizen, personal communication).

Slit width:	0.025 mm.
Amperes:	3.00
Voltage:	250 D.C.
Polarity:	Sample positive
Time:	60 seconds
Film:	Ilford thin film half-tone 4" x 10"
Processing:	Kodak D19B developer. Plates developed for 5 minutes at 18°C, constant agitation.
Densitometer:	Jarrel Ashe
Calculations:	Calculating board used for determining intensity ratios.
Analytical Weight:	70 mg. approximately.
Electrodes	National Carbon Co. Cat.No.L 4018
Flux:	Graphite
Matrix:	Spectrographically pure Fe_2O_3
Standards:	Standards were prepared by adding 1.00, 0.10, 0.01, 0.001 % of both gold and silver to a matrix of pure Fe_2O_3.
Analytical Lines:	The following analytical lines were chosen:

$$\frac{\text{Au } 2675.95}{\text{In } 3039.36} \qquad \frac{\text{Ag } 3280.68}{\text{In } 3256.09}$$

Internal standard: Indium was chosen as an internal standard for the determination of gold and silver for the following reasons: (Ahrens 1954).

1. Considerations of volatility
2. Placement of lines suitable for measurement.
3. Excitation potentials of the analytical lines.

Qualitative results

Qualitative analysis showed the following elements to be present:

Pyrite: (both types): Ag, Al, Au, Co, Cu, Mg, Mn, Ni, Pb, Si, Ti.

Pyrrhotite: Ag, Al, Au, Co, Cu, Mg, Mn, Ni, Si, Ti.

Quantitative results

	Gold ppm	Silver ppm
Tarnished pyrite:	190	19
Untarnished pyrite:	150	14
Pyrrhotite:	130	12

Discussion of results

These results are discussed under the headings "Gold", "Pyrite" and "Pyrrhotite".

NICKEL AND COBALT DETERMINATION.

Spectrographic conditions for the determination of the cobalt and nickel contents of pyrite and pyrrhotite.

The conditions used by Esterhuizen for the determination of cobalt and nickel in pyrite and pyrrhotite were the same as those previously listed, with the following exceptions:

Polarity:	Sample negative
Analytical weight:	100 mg.
Electrodes:	Spectrotech Deep
Time:	3 amperes for 10 seconds followed by 5 amperes for 10 seconds followed by 10 amperes for 10 seconds.
Standards:	Standards were prepared by adding 1.00%, 0.30%, 0.10% and 0.01% of both cobalt and nickel to a matrix of Fe_2O_3. A further set of standards with cobalt-to-nickel ratios varying between 0.10 and 10.00 was also prepared.
Analytical lines:	The following analytical lines were chosen Ni 3414.77 / Fe 3422.67 Co 3453.51 / Fe 3422.67 Co 3453.51 / Ni 3414.77 Co 3405.12

Results

Direct method:	Cobalt: Nickel ratio
Tarnished pyrite	1.43:1
Untarnished pyrite	0.93:1
Pyrrhotite	0.20:1

Indirect Method:	Nickel %	Cobalt %	Co:Ni ratio
Tarnished pyrite	0.115	0.125	1.09:1
Untarnished pyrite	0.175	0.135	0.77:1
Pyrrhotite	0.235	0.053	0.23:1

Discussion of analytical methods used in determination of cobalt and nickel.

Two methods were used, the direct and the indirect method. The direct method is based on the determination of the ratio between the line intensities of cobalt 3405.12 and nickel 3414.77. The indirect method makes use of synthetic standards and matrix as well as an internal standard.

The indirect method is therefore inferior, since it depends on the absolute values of the synthetic standards being completely correct. Errors are also multiplied by the use of an internal standard. The results obtained by the direct method are therefore to be preferred.

It should, however, be pointed out that both methods show the same trend concerning the variations in the cobalt:nickel ratios of the two types of pyrite.

These results are discussed further under the headings "Pyrite" and "Pyrrhotite".

GOLD.

Common practice on the Witwatersrand often makes use of the term "gold" in cases where, in fact, an alloy of silver and gold is meant. Such an alloy should perhaps more correctly be called "electrum", but in this respect a certain amount of confusion exists. Dana (1946) states that gold forms a continuous series with silver, with a minimum cell edge at 20% silver, and restricts the name "electrum" to gold alloyed with 20% or more of silver. Ramdohr (1960), however, prefers to apply the term "electrum" to those alloys of silver and gold which contain between 30 and 45% of silver, and which are nearly pure white in colour.

In view of the confusion surrounding the use of the term "electrum", all alloys of silver and gold, irrespective of their silver content, will be referred to as "gold" in the present study.

Habit.

The gold observed both in polished sections and as liberated grains was generally found to show irregular outlines and to occur as hackly grains. (Plate 111). A few grains of gold showing rounded outline were, however, recovered from pyrite after the latter had been destroyed by treatment with nitric acid. These grains of gold occurred as tiny cylinders or seed-like grains and showed a roughened or pitted outer surface. The grains appeared to correspond in all respects to those illustrated by Dunn (1929) for undoubted detrital gold from Australia (Plate IV).

A few subhedral grains of gold were also located in the polished sections examined. Because of their small size and their frequent distortions, however,

it was found difficult to determine their crystal form with any degree of certainty, but some of the grains appeared to be fairly symmetrical octahedra and cubo-octahedra.

Optical character shown by the gold.

The gold in the V.C.R. occurred as isotropic grains. Grains showing any signs of anisotropism were invariably found to be those which had been improperly polished or had become stained.

Fisher (1939) attempted to develop the micro-structure of gold grains in ores from the Witwatersrand. He found that most of the minute particles of gold that he had etched appeared to be structureless and seemed to consist of only a single grain, but that occasionally twin bands could be seen in them. Fisher found,however, that larger grains in specimens containing visible gold showed what he termed "recrystallized structures".

Accordingly, polished sections were prepared from portions of rich ore containing visible gold from Venterspost. These were etched using dilute aqua-regia, as suggested by both Fisher (1939) and Edwards (1947). A 20% solution of potassium cyanide in water was also found by the writer to be equally effective.

Various effects due to etching were noted, which may be summarized as follows:

Under low power, many of the grains showed the presence of parallel aligned bands suggesting (111) twinning of the gold (Plate V). It could further be seen that most of the larger grains were in fact composed of numerous smaller grains. The boundaries shown by these smaller grains, which extinguish at

different rates under crossed nicols, took the form of either very sharp straight lines (Plate VI), or gentle curves. These phenomena appear to correspond to those described by Fisher (1939) as "recrystallized structures".

Under oil immersion, at magnifications in excess of 300 X, various hitherto unrecorded features were seen.(Plate VII)clearly shows a large grain of gold which not only shows the presence of included grains or "islands" of pyrrhotite, but also the presence of tiny crystalline inclusions of gold, standing out in relief with respect to the large grain of gold. Under oil immersion, these little grains of gold can clearly be seen to resemble octahedral and distorted octahedral crystals.

Some larger grains of gold, when examined under low power, appeared to show different orientations of adjacent portions within the same grain (Plate VI). When these grains of gold were examined under oil immersion, they were in fact found to show micro structures consisting of numerous parallel aligned layers of tiny grains with cubic outlines. Adjacent portions of the large grain could clearly be seen to have an identical micro structure, but differed in the direction of the alignment of the tiny grains (Plate VIII).

In order to verify that none of the observed effects could have been caused by the polishing method used, some of the sections containing etched grains of gold were repolished. Subsequent examination clearly showed that minute differences in relief still persisted between the smaller portions of the larger grains. The following facts also strongly suggest that the observed features were not caused by the polishing method used: firstly, the sharp boundaries which existed between the

various portions forming the larger grains and secondly, the randomly oriented rod-like inclusions in some of the gold grains.

Accordingly it can be said that the various microstructures revealed by etching suggest that the gold in the V.C.R. did in fact undergo recrystallization in situ, subsequent to its deposition.

Fisher (1939) concluded from his studies that little could unfortunately be learned from the micro-structures of the gold in the banket. He added that this was due to the fact that the Witwatersrand conglomerates during their history had been deeply buried, with a consequential rise in temperature sufficient to account for the recrystallized structure of the gold, whatever the origin of the gold might in fact have been.

In conclusion it should be added that the present writer failed to find any suggestion of "recrys-tallized structure" in particles of gold not visible to the naked eye.

Colour.

In polished section the gold in the V.C.R. appeared to show a reasonably uniform deep yellow colour. When, however, panned concentrates of gold were examined, an apparently much wider range of colours was seen. These could not be explained as mere coatings by other minerals, and showed colours ranging from a pale yellow to a reddish orange. Whilst it is generally accepted that an increase in the silver content of the gold-silver alloy reduces the characteristic tint of the gold, it is also accepted that the presence of copper heightens the colour. Coleman (1957) mentioned seeing grains of gold from Yellowknife, N.W.T., which showed a reddish

colour, and added that in all cases these grains were associated with copper-bearing minerals, and that this reddish gold occurred on particles having a normal hue. Coleman further added that it seemed reasonable to suggest that it was an Au-Cu alloy which had formed as a result of the reaction of fluids containing copper with pre-existing gold. Ferguson (1950), working on samples from Manitoba, has reported seeing similar red gold, which when analysed was found to contain copper. Copper is not an unknown trace element in Witwatersrand gold, and may therefore well be responsible for the ruddy colour imparted to some of the grains of gold.

Eales (1961) commented on the wide variation of the silver content of grains of gold in Rhodesian ores, and stated that the colour of the gold in polished section was an index of its fineness. According to Eales, nearly pure gold has a pure golden colour with a distinctive ruddy tint, and with increasing proportion of alloyed silver this colour changes to yellow and ultimately to a pale silvery yellow.

The present writer feels that the colour of the gold particles is, however, not sufficiently exact to be used as a quantitative indication of the silver content of the grains. The only reliable means of differentiating between grains of gold showing differences in colour is either by parting the grain for silver and gold in the conventional way, or alternatively by the use of the electron micro-scanner.

Coatings on gold particles.

Iron oxides and a substance believed to be silver were the only kinds of coatings which were identified on the gold particles in the present suite of samples.

Iridescent to dull orange coatings of iron oxide were often found on liberated grains of gold. These may readily be ascribed to the decomposition of unstable pyrrhotite in the ore, with the accompanying liberation of iron ions. This coating may easily be removed by heating the particle gently with dilute hydrochloric acid. The nature of such iron coatings and their effect on the economic recovery of gold have been well illustrated and discussed by Edwards (1947).

Panned concentrates of gold from Venterspost revealed the presence of thin greyish to almost black coatings on some of the gold particles. Since the coatings were not very much more than a few microns thick, the following method was devised for their removal and identification. The grains were first very carefully heated with a few drops of dilute nitric acid on a glass slide and the reaction observed under a binocular microscope. In all cases the thin coating disappeared and a bright yellow particle of gold was revealed. The nitric acid solution containing the insoluble gold grain was then exposed to ultra-violet radiation for short periods of time, and the effects were observed under a binocular microscope. Initially,the gold grain became covered with a purplish coating, which on further exposure to ultra-violet light ultimately blackened completely, thereby colouring the entire previously bright yellow grain of gold black.

Silver salts are known to blacken when exposed to ultra-violet light, a feature which is made use of in photography. It is therefore probable that silver was present in solution in the dilute nitric acid.

As will be shown under the heading "Fineness of Gold", gold-silver alloys containing less than 38.5% of silver are not attacked by dilute nitric acid. According to Ramdohr (1960), gold-silver alloys of this composition (electrum) are white in colour. Since, after heating with nitric acid, the gold grain had a bright yellow colour, the grain can be assumed to have contained considerably less than 30% silver. Hence, the silver present in the gold grain would not have been removed by the nitric acid, and accordingly any silver dissolved in the nitric acid must have originated from the coating only.

It is therefore possible that the coating originally present on the grain of gold, and subsequently removed by the nitric acid, could have been metallic silver or a compound of silver.

Sizes of gold particles observed.

Observations made in the present study showed that the coarser particles of gold appeared to be concentrated more generally with the sulphide minerals (Plate IX), whereas the finer grains were apparently associated more frequently with the phyllosilicates and quartz (Plate X).

This difference can most easily be shown by comparison of the sizes of grains of gold recovered from areas not carrying abnormally large pyrite grains (Sample 1) and those carrying coarse grains and pebbles of buckshot pyrite (Sample 2).

Size interval (microns)			Distribution per cent	
			Sample 1	Sample 2
0	to	15	37.00	15.67
15	to	30	19.86	6.82
30	to	60	18.33	8.49
60	to	90	13.63	9.93
90	to	120	6.65	12.20
120	to	250	3.32	19.14
250	to	500	1.19	20.93
500	to	1000	0.02	5.98
Over 1000			0.00	0.8
Total			100.00	100.00

(Sample 1: Composite of 18 samples of ore from Venterspost. Sample 2: Special sample rich in coarse "buckshot" pyrite. The above results are based on nearly 4000 individual estimations of grain size). See Figures 1 and 2.

The findings of von Aubel (1939) with regard to size distribution of gold particles appear to have a bearing on the results of the present survey. Von Aubel concluded that the particle size of native gold was commonly a function of the mode of formation of the associated minerals. When gold was contemporaneous with the enclosing mineral, it was extremely fine-grained, whereas those grains of gold which were formed later than their host were generally coarser. Since, therefore, in the present study, the finer grains of gold seem to be associated with the phyllosilicates and quartz (Plate X), it can be assumed that gold is contemporaneous with the phyllosilicates. On the other hand, the association of the coarser grains of gold with pyrrhotite (especially in areas containing buckshot pyrite) (Plate IX) indicates that the pyrrhotite must have been

deposited before the gold. This generalization is supported by the finding on numerous occasions of islands of pyrite and pyrrhotite in the gold, clearly indicating that the pyrite and pyrrhotite pre-dated the gold.

Variation in the composition of gold with respect to differences in grain sizes.

Young (1917) mentioned that the purity of the gold appeared to vary to some extent with the particle size in which the gold occurred in the rock, the coarser grains being the purer. The writer has not been able to check the validity of this statement in the present suite of samples. Fisher (1939), however, stated that he was unable to find any gold in the banket that appeared to be notably richer in silver than the average. He further remarked that he could find no confirmation of the suggestion that the composition of the finely divided gold was markedly uniform or less pure than the coarse gold.

When examined in polished section, all the grains of gold seen in the present survey, irrespective of particle size, appeared to show uniform colour, and were therefore presumably of reasonably uniform composition.

At present there therefore seems to be little support for the assertions made by Young (1917) concerning the variation of gold fineness with grain size. Any such variations could best be checked by means of the micro-scanner in polished section.

Gold and cobaltite.

The association of gold and cobaltite has already been reported on the Far East Rand by Mendelssohn (1932). Mendelssohn stated that gold could be seen in considerable quantity in polished sections prepared of

the cobaltite, mainly in the form of isolated small inclusions, and that in addition veins of gold were seen cutting through the cobaltite and evidently replacing it. The cobaltite described by Mendelssohn occurred in large irregular masses showing no crystal outlines. One or two small isolated crystals were, however, observed.

Keep (1939) also commented on the presence of cobaltite in a piece of banket from Government Gold Mining Areas which was rich in visible gold and contained much cobaltite in which innumerable grains of gold were disseminated. Keep was able to show from the appearance of the specimen that it had been obtained from the vicinity of a doleritic intrusion and that a leaching from, and redeposition of the gold in, the banket by the magmatic waters containing the cobalt, which most probably accompanied the intrusion, would have resulted in such an occurrence.

Sharpe (1955) stated that polished sections of cobaltite from Government Gold Mining Areas showed what appeared to be a distinct eutectic structure of the gold within the cobaltite. Sharpe considered that in this particular case the gold and cobaltite had crystallized simultaneously. Liebenberg (1955), however, who also examined specimens containing cobaltite from Government Gold Mining Areas, stated that the gold occurred as veinlets and small irregular patches, and that the gold was obviously later than the cobaltite and replaced this sulphide. Liebenberg added that, although his interpretation of the association of gold and cobaltite differed from that of Sharpe, he nevertheless agreed that the cobaltite had acted as a collector for the gold during thermal metamorphism.

Numerous fragments of cobaltite were found in the V.C.R. in the course of the present survey. The grains occurred mainly as jagged irregular fragments (Plate XI) and rounded grains (Plate XII), but a single grain showing sharp crystal outlines was also found. Most of the cobaltite grains found carried gold, which appeared to replace the cobaltite (Plate XI). These modes of occurrence of the cobaltite in the V.C.R. are very similar to those described by Mendelssohn (1932) on the Far East Rand.

The rounded outline shown by some of the cobaltite grains in the V.C.R. suggests that they are probably detrital components derived from an earlier horizon, and that they probably originated in the manner suggested by Keep. The replacement features shown by the present suite of samples containing cobaltite with associated gold appear to support the views of Liebenberg rather than those of Sharpe.

Gold and "Carbon".

There appeared to be no obvious relationship governing the association of gold and carbon in the polished sections examined. Some sections were found to be devoid of any visible particles of gold, yet to contain numerous particles of pyrite and "carbon". In other cases, sections were found which, apart from quartz and chlorite, were completely devoid of any other minerals except a few granules of "carbon". Some sections showed particles of gold within a few millimetres of "carbon" grains, or in direct contact with the "carbon", or even filling cracks in the "carbon". In all the cases cited, the period of gold mineralization

appeared to be totally independent of that of the "carbon". The fact, however, that numerous grains of "carbon" with associated uraninite often showed cracks filled in by fine stringers of gold certainly places the period of gold mineralization after that of the "carbon" in the paragenetic sequence. (Plate XIII).

Gold and pyrite.

The bulk of the gold mineralization of the V.C.R. appears to be totally independent of the pyrite mineralization, and the presence of high concentrations of pyrite seems to be independent of the amount of gold present. In the present suite of samples the small proportion of gold found associated with the pyrite occurred in two distinct ways: firstly, as totally enclosed (Plates IV, XIV) seed-like grains or cylinders of apparently detrital origin, and secondly as jagged stringers or veinlets, which represent infillings in cracks of the pyrite and are most certainly later in sequence than the pyrite.

These findings support those of Liebenberg (1955). He stated that although gold was a relatively constant and widespread associate of the pyrite in the banket, the pyrite was only of minor importance as a gold carrier. Liebenberg further mentioned that only comparatively few of the many thousands of pyrite grains that he had examined contained any included grains of gold.

It is interesting to note that the fineness of the gold included in the pyrite was found by the present writer to vary between 914 and 908.

Joralemon (1951) reported that L.C. Graton had found at Simmer and Jack and adjacent mines that a dependable sign of rather better than average gold values

in the reef was the rapidity of the tarnish of the pyrite at those places. Graton thought that this differential tarnish might have been brought about by the presence of gold in solid solution in some of the pyrite. Stilwell and Edwards (1946) pointed out that since pyrite was a non-stoichiometric compound, it seemed likely that any gold solid solution that occurred in it would be of the limited interstitial type of solid solution. This type is found in some metals, in which the solute atoms fill vacant spaces in the lattice structure rather than substitute for solvent atoms.

If Graton's theory concerning the possible presence of gold in solid solution with pyrite is valid, it could have important metallurgical implications. This theory could possibly be investigated by heating polished sections of pyrite from areas where the grade of ore was very low, in an inert atmosphere for a few hours, to see whether the "invisible" gold in the pyrite could not perhaps be made visible as a result of the segregation of the gold.

The present writer feels, however, that the reason for the tarnishing of the pyrite is most probably a function of the chemical composition of the pyrite itself, rather than a result of the possible presence of gold in solid solution in the pyrite. (This question is more fully discussed under the heading "Pyrite".) It is further felt that the undisputed particles of gold, which can be recovered easily after the pyrite has been destroyed by means of nitric acid, constitute the major portion of the gold included in the pyrite, and that while there may be some gold in solid solution in the pyrite, it certainly is of very minor importance. In

any case, the size distribution of the gold particles reported in this study, which takes into account all particles over 1 micron in size, does not indicate that the size distributions have been appreciably displaced towards the submicroscopic range. This would have been the case if gold were present predominantly in solid solution in pyrite.

Gold and "buckshot" pyrite.

In the V.C.R., the presence of coarse grains and pebbles of "buckshot" pyrite is generally indicative of high gold values (Davies, 1949). In addition, polished sections of V.C.R. ore have shown that the "buckshot" is usually accompanied by coarser grains of gold. Accordingly, in the present study, special attention was paid to polished sections containing both visible gold and buckshot pyrite in an attempt to see if any purely mineralogical reason could be found for their co-existence.

In the sections examined, the gold was found to occur mainly as intergrowths with the pyrrhotite or as discrete grains embedded in the phyllosilicates. No gold could be found either as inclusions in, or as stringers replacing, the buckshot pyrite. This finding differs from the findings of Liebenberg (1955), who reported the presence of minute roundish and irregular inclusions of gold in buckshot pyrite from the Vaal Reef at Buffelsfontein, which was apparently similar to that present in the Witwatersrand banket and other reefs.

Unfortunately, therefore, the present writer was unable to account for the co-existence of the gold

and the buckshot pyrite in the V.C.R. on purely mineralogical grounds.

Gold and chalcopyrite.

A very few grains of gold were found associated with small grains of chalcopyrite and pyrrhotite as minute inclusions in apparently old pyrite. The gold, chalcopyrite and pyrrhotite inclusions appeared to show mutual grain boundaries, thereby suggesting contemporaneous deposition. In those cases where chalcopyrite occurred as massive grains, no gold could be found associated with it.

Gold and pyrrhotite.

Pelletier (1940) and de Kock (1940) have commented on the association of gold and pyrrhotite at Venterspost. They remarked that in some specimens from Venterspost, the main portion of the gold was associated with pyrrhotite, and that abundance of pyrrhotite was usually an indication of high gold values. In the writer's opinion, this statement should be treated with some reserve.

Inspection of Figures Nos. 3 and 4, in which the pyrrhotite content is plotted against the gold values of the ore, shows widely scattered points, with no obvious trend. Microscopic examination of these samples also failed to disclose any close relationship between gold and pyrrhotite. In most cases it could quite clearly be seen that the pyrrhotite was being replaced by gold.

It should, however, be stated that Pelletier's views are perhaps warranted in those cases where buckshot pyrite is present. The samples referred to above, which

represented the bulk of the samples examined, did not contain significant amounts of buckshot pyrite. It was, however, found by the present writer that in those samples where large amounts of buckshot pyrite were present, rather coarser gold and pyrrhotite appeared to accompany the buckshot pyrite. Inspection of such sections, containing these larger grains of gold associated with the pyrrhotite, would certainly give the impression that pyrrhotite constitutes an enriching factor. In these sections, the gold characteristically occurred as large irregular grains in the pyrrhotite and on first inspection, the gold and the pyrrhotite apparently showed mutual grain boundaries, thereby suggesting contemporaneous deposition. On closer inspection, however, islands of pyrrhotite in gold were clearly seen (Plate IX), thereby disproving this assumption and definitely placing the gold after the pyrrhotite in the paragenetic sequence.

On the strength of these findings, the writer feels that the generalization that pyrrhotite represents an enriching factor, as suggested by Pelletier (1940), should perhaps be treated with some reserve.

Gold and phyllosilicates.

Most of the gold in the present suite of samples was found to be associated with chlorite and sericite. The gold grains occurred as jagged, irregular particles, or more rarely as tiny euhedral crystals, usually totally embedded in and surrounded by the chlorite and sericite. (Plate X). This mode of occurrence suggests that the deposition of the gold probably predated the formation of the phyllosilicates.

Gold and quartz.

Only minor amounts of gold were found associated with quartz. Where such an association did occur, the gold was found to occur in the form of secondary infillings apparently replacing the quartz. In such cases the gold often occurred as euhedral grains showing brilliant crystal facets. Due to the fact that these gold grains were usually very small and were embedded in the quartz, no detailed study of the crystallography of the gold could be undertaken.

Gold and uraninite.

Fine stringers of gold were occasionally found replacing some of the larger uraninite grains, which were themselves embedded in "carbon". Gold was also found as infillings in cracks present in such uraninite grains. (Plates XIII, XV).

In order to see whether any relationship existed between the gold and uraninite content of the samples, the gold content of the ore was plotted against the eU_3O_8 value. Inspection of these graphs (Figures nos 5 and 6) shows widely scattered points with no apparent trend, suggesting that no obvious relationship exists between the gold and uraninite values in the present suite of samples.

Summary.

The gold in the V.C.R. occurs in two forms, which are clearly of different age. The older variety of gold is represented by the seed-like or cylinder-shaped grains which occur embedded in the pyrite grains and are probably of detrital origin. The second or younger variety occurs in various forms and shows

numerous associations with minerals such as sulphides, uraninite, "carbon" and the phyllosilicates. The younger variety of gold was apparently taken into solution and recrystallized in situ. The angular nature of, and the micro-structures shown by, this gold strongly suggest that it has undergone no significant travel since its deposition.

FINENESS OF GOLD IN THE V.C.R.

Inspection of the accompanying assay results (Tables nos. I, II, III, IV, V), clearly reveals that the present suite of samples from the V.C.R. and underlying Main Reef at Venterspost and Libanon, and from the V.C.R. at West Driefontein, shows a wide range of "fineness". In the present study, the definition of "fineness" proposed by Fisher (1945) has been adopted. Any analysis of native gold will always show that the major components, gold and silver, are accompanied by lesser amounts of base metals. Fisher suggested that, in order to have some true basis for comparison between gold from various horizons or even within the same horizon, the base element content should be ignored, and the silver and gold contents should be recalculated to add up to 1000.

True fineness is therefore defined as:

$$\frac{\text{Au}}{\text{Au plus Ag}} \times 1000$$

As can be seen from the above definition, no provision is made for the presence of any other gold or silver in the sample, other than that occurring alloyed together. It is for this reason that all assay results quoted in the present study are reported as "apparent" and not "true" fineness, since the present suite of samples did in fact contain other argentiferous minerals.

In 1935 Lawn commented on the fact that he had found large variations in the silver content of bullion in every mine that he investigated, even where the samples had originated from the same stope.

In Government Areas, for instance, the silver content varied from 4.2 to 20.0%, whereas at Langlaagte variations from a trace to 25% were noted. A section at New State Areas was found to show a variation from 5.0 to 27.0%, whilst a lower leader showed 43.0%. Lawn was convinced that it would be impossible to find a single stope on the Rand which would show any uniformity in the fineness of the gold. (Lawn's results obviously also referred to apparent fineness, since no allowance was made for the presence of any silver-bearing minerals). The wide variation in apparent fineness, even in samples from the same stope, as reported by Lawn, has been confirmed in the present study.

Changes in the apparent fineness of the gold with variations in the tenor of the ore.

The apparent fineness values obtained for the present suite of samples were plotted against the gold content of the ores. The graphs are shown in Figures nos. 7,8,9,10,11. The data are admittedly scanty, but nevertheless indicate that samples containing larger amounts of gold show a high apparent fineness (low silver), whereas low apparent fineness (high silver) is more typical of low grade ores. These results support the findings of Prentice (1939-40) and Eales (1961). Prentice reported that he had found a definite correlation between the gold value and the silver percentage in ore from eleven Witwatersrand mines, with silver content decreasing as the gold content increased and vice versa. Eales has likewise shown that the same trend occurs in the hydrothermal gold deposits of Southern Rhodesia. Lawn (1924) reported that, although in individual samples there seemed to be a tendency for

low silver percentage to be associated with high gold values, the reverse not infrequently occurred.

Changes in apparent fineness of gold with increasing depth.

Hargraves (1961) has recently drawn attention to the variation in the fineness of the gold with increase in depth. He stated that, for a particular reef in any one mining area, the average silver content of the gold appeared to vary as a function of the present elevation of the reef in that area. Reef in "shallow" areas contained gold with a higher silver percentage (lower fineness) than reef in "deep" areas.

The validity of this theory has been carefully examined by the present writer. The elevations at which samples of the present suite were obtained have been set out in the accompanying tables. (Tables nos. I, II, III, IV, V). For purposes of comparison, the datum line for all the samples was taken as 6,000 feet above mean sea level. Inspection of the tables reveals that no clear trend seems to exist correlating fineness with depth, as suggested by Hargraves. Samples taken at the same elevation, but in different parts of the same stope, show a wide variation in apparent fineness, a feature which has already been commented on. Intrastope variations are in fact so large as to obscure any possible relationship between fineness and depth. (For example, samples nos. 28, 29 and 30, all taken at -4098 feet from the V.C.R. at Libanon, show the following apparent fineness values: 767, 389 and 643 respectively.)

It should be pointed out that many of Hargraves' observations, especially at Venterspost, were based on figures obtained from the Rand Refinery, and

refer only to the fineness of the actual gold bars (bullion) supplied to the Refinery by the mines. These figures do not bear any relation to the fineness of the gold occurring naturally in the ore for the following reason: the gold bars, before reaching the Refinery, have already been refined to a certain extent by the mine. During the course of this process, which is designed to remove as much base metal as possible, some gold and silver is also removed in the slag. The silver to gold ratio in the slag is exceedingly variable, and may reach values as high as 50:1, or more. Accordingly, Hargraves' use of such data is not warranted.

Fineness of gold-silver alloys as a measure of resistance to attack by nitric acid.

It is a known fact that the dissolution of silver from an alloy of gold and silver by dilute nitric acid, is broadly dependent on the fineness of the alloy. According to Smith (1913), the solubility of pure gold in nitric acid is 0.005 parts per thousand, whereas Au-Ag alloys with fineness values of 400 and less are parted virtually completely, i.e., all the silver is removed quantitatively from the alloy by the acid. This feature is made use of in everyday assay practice. Since, however, no information could be found concerning the behaviour in nitric acid of gold-silver alloys whose fineness exceeded 400, it was decided to investigate this feature more fully.

For this purpose, a series of gold-silver alloys, differing in fineness, were prepared as follows: Pure gold and silver, in approximately the correct final proportions required for the different alloys,

were carefully weighed out on an assay balance. The particles of gold and silver were then carefully transferred into National Carbon Company Type L4018 preformed spectrographic electrodes and clamped in the electrode holder of a large Hilger optical spectrograph. The arc was then struck at 7 amperes for 10 seconds and the resulting bead was reweighed after cooling. In no case was any loss of weight recorded during this initial process. The beads were then transferred to new Type L4012 preformed spectrographic electrodes, which are considerably shallower than the Type L4018 electrodes. The arc was then once more struck at 5 amperes for 2-3 seconds, at which time the carbon arc took on a green colour. The beads were then once more weighed and allowance was made for any losses due to the volatilization of small amounts of silver. These losses, in the case of the 100 mg beads prepared, were of the order of 0.2 to 0.3 mg.

The beads were then flattened with an assay hammer and refluxed for 1½ hours with a mixture of 1:1 nitric acid and water in a battery of flasks fitted with reflux condensors. The beads were then once more weighed and the loss of silver in the course of the treatment with nitric acid was calculated.

The accompanying table and graph (Figure no. 12) show the amount of silver (expressed as a percentage of the total amount of silver present) which was taken into solution by the nitric acid in each case.

Fineness of Gold-Silver Alloy.	Loss of Silver %.
1000	0.00
849	0.00
723	0.00
621	2.09
615	0.00
586	11.77
558	13.74
548	32.85
519	31.02
510	42.30
502	45.35
481	4[illegible] 03
459	78.63
444	97.35
425	100.00
393	100.00

(The above results are accurate to within 0.5%).

From these results, it would appear that the limiting value of fineness, above which no silver can be removed from a gold-silver alloy by dilute nitric acid, is approximately 615. This feature is made use of in a subsequent section.

SILVER.

In a previous section, mention has been made of the wide variations found by Lawn (1935) and the writer in the apparent fineness of samples from various horizons. These wide variations could best be explained if either silver-rich minerals, such as galena, sphalerite and chalcopyrite, or silver minerals themselves were known to occur in the horizon. Fisher

(1939) mentioned that the fact that practically all the gold which was detected by him on the Witwatersrand appeared to be of fairly uniform composition, indicated that some of the silver in the banket was not alloyed with the gold, but was present in other minerals, such as galena and other sulphides. Fisher felt that the wide variations in the silver content of individual samples might be due in part at least to variations in the amount of silver-bearing minerals other than gold that happened to be present in the samples.

Investigation of the silver content of sulphides.

In order to obtain some idea of the amount of silver which could be expected to be contributed by known argentiferous minerals such as galena, sphalerite and chalcopyrite, the following procedure was carried out. A composite sample, consisting of equal weighed portions representative of 18 samples of ore from the V.C.R. at Venterspost, was analysed chemically for lead, zinc and copper, and the results were expressed in terms of galena, sphalerite and chalcopyrite. The results were as follows:

Galena 0.036%

Sphalerite 0.047%

Chalcopyrite 0.046%

Unfortunately, no samples of any of these three minerals could be obtained from the V.C.R. at Venterspost and Libanon in sufficient quantities to permit individual analysis for silver. Therefore, in order to have some basis for calculation, a sample containing sufficient galena and sphalerite to permit hand-picking and subsequent assay was obtained from the Bird Reef at Luipaardsvlei.

The galena from the Bird Reef was found to contain 339 ppm of silver and the sphalerite 29.3 ppm. Unfortunately, no sample, or information concerning the silver content, of South African chalcopyrite could be found.

From these analyses it can be seen, however, that the amount of silver which is likely to be contributed by galena, sphalerite and chalcopyrite, which average only 0.04% in the samples examined, is really negligible, and may probably be discounted for all practical purposes.

According to Goldschmidt (1954) pyrite, which is the most common sulphide in the V.C.R., has never been proved to contain silver in solid solution. Prentice (1940) investigated the gold, silver and pyrite in ores from 11 Witwatersrand mines and was unable to establish any obvious relationship between the pyrite content and the silver percentage in the ore. Further support for Prentice's work has recently been supplied by Hargraves (1961), who carried out similar studies. Hargraves concluded that the amount of silver likely to be contributed by the various sulphides would not adequately account for the large variation which is found to occur in the gold-silver ratio.

"Free Silver"

Since it is therefore probable that only negligible amounts of silver are likely to be included in, and therefore donated by, the various sulphides such as galena, sphalerite, chalcopyrite and pyrite, the only obvious carriers of any major amounts of silver in the banket would be "gold" and any other mineral

composed predominantly of silver. To date, no reference has been made to the presence of any silver minerals on the Rand (Hargraves 1961).

The first indication of the possible presence of free silver on the Rand was the finding by Mr. F.C.M. Bawden of a particle of gold which had a distinct silver-grey coating. This particle was found in a panned concentrate prepared from freshly pulped ore from the Carbon Leader horizon at Doornfontein. During the present study of the V.C.R., grains of gold were found showing tarnished greyish-black encrustations, similar in appearance to the grain from Doornfontein. The encrustations were identified by the writer as silver by means of the ultra-violet-light method, which has already been described.

In addition, a fine stringer of greyish silver material associated with sericite was found in a carefully prepared polished section of ore from the V.C.R. This grain was found to be soft and sectile, yielding a bright silvery surface when freshly scratched. The grain showed a poor polish, a feature which is sometimes encountered in the polishing of native silver. (Ramdohr 1960). (See Plate XVI).

Work carried out by Weiss (1925), who prepared a complete series of silver-gold alloys varying in composition from pure silver to pure gold in steps of 10%, showed that the X-ray diffraction patterns of such alloys were so similar as to preclude the use of X-ray diffraction techniques in differentiating between silver, gold and alloys of the two. The constants for silver, gold and electrum quoted by Berry and Thompson (1962) support Weiss' original findings.

Accordingly, in order to identify the grain, microchemical tests were carried out using the scheme outlined by Short (1948). The results were as follows:-

Hardness:		Soft (B), very sectile
HNO_3	:	Effervescence, with the formation of a white coating.
HCl	:	Tarnishes
KCN	:	Tarnishes brown.
$FeCl_3$	:	Stains iridescent immediately.
KOH	:	Negative.
$HgCl_2$	:	Stains brown.
Optical character:		Isotropic

The above characteristics thus conform in all respects to the properties listed by Short (1948) and Ramdohr (1960) for native silver.

Unfortunately, in the course of the microchemical tests, the sample was destroyed, so that no other confirmatory work could be carried out.

Quantitative Aspects.

Since it was desired to obtain some idea of the relative proportion of silver present as silver unalloyed with gold (in the form of either integral grains or a coating on the gold particles), the following test was carried out.

Composite samples were prepared from portions of pulped ore which had previously been assayed for gold and silver content. Each of these composites was placed on a hot plate and an excess of a mixture of water and nitric acid in the proportion of 1:1 by volume was added. (Chemically pure nitric acid was used in order to minimize the amount of free chlorine, the presence of

which might otherwise be responsible for the dissolution of gold). The mixture was boiled for approximately 1½ hours until all visible traces of sulphides had disappeared. This procedure was designed to liberate any "gold" included in the sulphides, as well as to take into solution any silver mineral(s) present. (From the conclusive tests carried out by the writer, reported in an earlier section, it is quite clear that a natural gold-silver alloy with a fineness above 615 will not be attacked by the nitric acid). The digested samples were then filtered through two No. 542 Whatman filter papers under vacuum, and the pulp or insoluble residue was thoroughly washed with water numerous times. The "washings" and filtrate were then combined, and the resultant "solution", together with the "pulp", submitted for gold and silver assay.

Despite the obvious objection that the washing process may not necessarily have removed all the silver ions from the pulp, the assay results obtained for the "solution" and "pulp", which are set out in the attached table (no.VI), definitely show an excess of silver over gold in the solution. This clearly indicates that some source of silver other than that alloyed with "gold" must be present.

It can be seen that a certain amount of gold does in fact accompany the silver in the solution. There are three possible explanations for this phenomenon.

1. The gold may have passed through the filter paper as fine colloidal particles of gold-silver alloy.

2. The true fineness of the gold-silver alloy may have been less than 615, in which case limited parting might have occurred. This is unlikely, since no marked differences in the colour of the "gold" from the Witwatersrand were observed by Fisher (1939) or by the writer. According to Ramdohr (1960), grains of this degree of fineness would be white in colour, and no such grains were seen.

3. Native silver may have been present, and, according to Smith (1913), native silver is rarely found pure but is usually accompanied by minor amounts of gold, copper and platinum.

The gold-silver ratio, and the fineness of the "gold", in the acid-treated "insoluble residue or pulp" was then calculated, and the results are set out in the accompanying tables (nos VI, VII). If one assumes that all the silver ions were removed from the pulp during the washing process, then the gold and silver values obtained probably reflect the true fineness or gold-silver ratio of the actual gold. If this is a valid assumption, then the gold present in the solution may theoretically be reallocated to the pulp with the requisite amount of silver in the ratio of the newly-determined true fineness. The accompanying detailed calculation shows how this reallocation may be made and the proportion of the silver not alloyed with the gold calculated.

Inspection of the accompanying calculation clearly shows that, even after the gold with the requisite amount of silver has been reallocated to the pulp, excess silver remains in the solution. This

excess silver can best be accounted for by assuming that "free" silver is present in the various horizons listed, even though the nature of the silver-bearing mineral(s) has only been tentatively established for the V.C.R. at Venterspost. In this context, it should be noted that, despite the fact that the average apparent fineness of the gold from the V.C.R. at West Driefontein is 919, 4.19% of the total silver occurs as nitric-acid-soluble-silver. In view of the very conclusive tests carried out concerning the inability of nitric acid to dissolve silver from a gold-silver alloy whose fineness exceeds 615, it must be concluded that in the V.C.R. silver occurs in a form other than as an alloy with gold.

It seems apparent from the results that the same situation probably also obtains in the other horizons listed. For example, special attention should be paid to the results from the Main Reef at Libanon (Table no. VII). Here the lowest apparent fineness recorded is 791 (well above the figure of 615), but the percentage of free silver is 13.45.

Fisher (1945), discussing the fineness of gold in New Guinea, stated that he was not able to find an authenticated case where the fineness of gold, or more strictly, that of electrum, occurred naturally below 450 parts per thousand. Fisher further felt that the extreme variations in the gold-silver ratios found by him showed that the concentration of silver had little effect on the gold fineness and that, provided sufficient silver was present, the gold and silver would be deposited in the proportions appropriate to the physico-chemical conditions prevailing. Thus, bullion naturally formed was never below 450 fine, the remainder of the silver

going to form other minerals, while if insufficient silver was present to produce the requisite proportions, the fineness of the gold would of course be higher. Fisher further said that in the deeper zones, that is, at higher temperature and pressure, silver, no matter how concentrated in the ore-bearing solutions, would not form a low-grade alloy with gold, but would be deposited as either primary silver or silver-bearing minerals.

If Fisher's investigations and conclusions are valid, then the apparent fineness values of 500 and 389 obtained for ores from the V.C.R. at Venterspost and Libanon respectively (Table nos. I, II) strongly support the supposition that a silver-bearing mineral, other than "gold", must be present.

DETAILED CALCULATION SHOWING HOW AMOUNT OF "FREE SILVER" PRESENT IN A SAMPLE MAY BE CALCULATED.

After boiling with nitric acid and filtering:

	"Pulp"	"Solution"
Gold dwt/ton	22.44	0.09
Silver dwt/ton	3.90	1.29

Apparent gold/silver ratio:

Gold:	22.44	Silver:	3.90
	0.09		1.29
	22.53 dwt		5.19 dwt.

Apparent ratio $\frac{22.53}{5.19} = 4.33$

Apparent fineness 813

True gold/silver ratio:

This figure reflects the ratio of gold to silver in the pulp, after the "free silver" has been removed.

$$\frac{22.44}{3.90} = 5.75$$

True fineness 853

Silver Re-allocation:

All the gold in the "solution" (0.09 dwts) should theoretically be reallocated back to the "pulp" with the requisite amount of silver in the ratio of 5.75:1. This amounts to 0.01 dwt of silver.

Gold

Gold in pulp	22.44	Silver in pulp	3.90
Gold from solution	0.09	Silver from solution	0.01
Total gold present in pulp	22.53 dwt	Total silver present in pulp	3.91 dwt

Silver present in "solution" after re-allocation of 0.01 dwt to "pulp" equals 1.28 dwt.

Percentage of unalloyed or free silver expressed in terms of the total amount of silver in the ore:

$$\frac{1.28}{5.19} \times \frac{100}{1} = 24.65\%.$$

CARBON.

Despite the fact that, for nearly 70 years, a hydrocarbon associated with uranium has been known to exist in the banket, very little is yet known about its origin and exact nature, and its relationship to other uranium-containing hydrocarbons occurring elsewhere in the world, such as the thucholite of Canada and the carburan of Russia. In addition, considerable doubt still exists concerning the best name for the substance.

Historical outline.

In 1917, Young mentioned that small, black, opaque spheroidal or nodular grains with a dull warty outer surface were present in the banket. He referred to them as "carbon", and added that grains of this nature had first been noticed in the Buffelsdoorn Gold Mine near Klerksdorp in 1895 and had since been shown to be widely distributed.

Further mention of this material was made by Macadam in 1931, when he stated that "carbon" was plentifully distributed in the bankets of the Witwatersrand System and also occurred in all the bedded pyritic seams which were found in the beds of the quartzite from the lowest to the uppermost. He reported the presence of "carbon" at Modder B, Modder East, New Modder, New Kleinfontein, Van Ryn G.M. Estates and several other East Rand mines, as well as on Randfontein Estates, the Coronation workings on Luipaards Vlei No.10, Middelvlei No.6, the Afrikander, Buffelsdoorn and other mining areas on the Witwatersrand. Macadam stated further that, although "carbon" was found in most of the pyritic seams that lay within the quartzites, it occurred in

larger grains in the bankets. He said that it was not unusual to find "carbon" in grains up to one sixteenth and occasionally up to one eighth of an inch in diameter, and that where "carbon" was of exceptional size, it was accompanied by a corresponding amount of visible gold.

In 1936, yet another occurrence of "carbon" was discovered, when a small carbon-rich band with visible gold was first intersected at over 5,000 feet in depth on the West Rand. In view of the high carbon content and its generally narrow ribbon-or seam-like nature, the new horizon was called the Carbon Leader. The geology and mineralogy of the Carbon Leader have been fully described by de Kock (1948), who stated that the true chemical and physical nature of the "carbon" had not been fully determined.

Liebenberg (1955) sought to remedy this deficiency and carried out a large number of chemical, spectrographic and X-ray analyses to establish the nature of this so-called "carbon", to which he assigned the name of thucholite.

The term "thucholite" was originally proposed by Ellsworth (1928) to describe a radioactive constituent of a pegmatite in Conger Township, Parry Sound District, Ontario, and at the Wallingford felspar mine near Buckingham, Quebec, and is derived from the principal constituents of the material (Th, U, C, H, O, lite). According to Ellsworth, thucholite is a mineral of jet black colour, having a hardness of four and a specific gravity of about 1.8. The chemical composition of the material varies widely. It was reported to contain 40-60% carbon and 20-30% absorbed volatile gases, with the remainder consisting of ash. The material has, to

date, been found mainly in pegmatite dykes, associated with primary minerals such as uraninite, felspar and mica. The ash of the material from Conger Township is thorium-rich (ThO_2 48.48%, U_3O_8 5.80%) whereas that from Wallingford is uranium-rich (U_3O_8 18.20% ThO_2 10.40%).

Labuntzov (1927) described a radioactive carbonaceous material "carburan" found in pegmatites of northern Karelia, which appeared to be essentially similar to thucholite in both habit and association.

Spence (1930) further described the occurrence of the Besner Mine thucholite from Henvey Township, Parry Sound, with its liquid and solid hydrocarbons.

According to Hoekstra and Fuchs (1960), it has become apparent that the name "thucholite" has become rather indiscriminately applied to many types of organo-uranium associations, including hydrothermal vein deposits and sedimentary deposits containing no significant amounts of thorium. (For example, Davidson and Bowie in 1951 referred to a uraninite-hydrocarbon aggregate from Laxey, Isle of Man, as being of "thucholite type", despite the fact that no thorium could be detected -- U_3O_8 = 70.50%).

Liebenberg (1955) reported an ash analysis of U_3O_8 52.60%, ThO_2 1.70% on specimens from Blyvooruitzicht.

Polished Section Study.

The grains of "carbon" examined in the V.C.R. at Venterspost and Libanon occur as opaque blackish grains with very irregular outlines. Some of the carbon grains appear to have been plastic or mobile at some time in the past, as suggested by their tendency to mould themselves in between and around grains of apparently

older pyrite (Plates XVII, XVIII). Under crossed nicols, most of the grains show a greyish-brown colour, and appear to be anisotropic and made up of numerous fibre-like growths arranged in haphazard orientation. (Plate XIX). Where the grains have been moulded between older pyrite grains, careful examination of the grain edges of the carbon often showed a pronounced darkening of the colour of the carbon and an increase in the degree of anisotropism, suggesting the presence of strain. (Plate XX).

Uraninite is the most prolific inclusion present in the carbon grains (Plate XXI), but may on occasion be totally absent. The nature and association of the uraninite with the carbon are more fully discussed under the section on uraninite.

"Carbon" in the V.C.R. is often replaced by minerals such as gold, pyrrhotite and phyllosilicates, which appear to be considerably later in the paragenetic sequence.

Tests carried out.

In order to compare the chemical and physical composition of the "carbon" existing on the Witwatersrand with the Besner Mine thucholite, as investigated by Hoekstra and Fuchs (1960), and by Barthauer (1953), various tests were carried out. To obtain material for this purpose, concentrates were made from various horizons in different mines, both on the East and West Rand. The material was purified as far as possible by hand-picking, followed by heavy liquid separations.

Unfortunately only 100 milligrams of "carbon" could be concentrated from the Ventersdorp Contact Reef

at Venterspost, so that in this case, it was not possible to carry out a proximate analysis. Liebenberg (1955) stated, however, that thucholite was of common occurrence in the V.C.R., and that most of the thucholite was megascopically visible and occurred mainly as granules similar in appearance, size and occurrence to those in the Witwatersrand banket. He reported that mineragraphic work showed that the "carbon" in the V.C.R. consisted of thucholite similar to the three types in the Witwatersrand.

In order to establish whether the Witwatersrand "carbon" was soluble in various organic solvents, a composite sample of "carbon" was carefully weighed before and after boiling with benzene, toluene and pyridine for 5½, 5¾ and 5 hours respectively. After drying, no loss of weight could be detected, indicating that no loss due to the removal of soluble hydrocarbons had occurred. A further sample of "carbon" (S.G. 1.445) from West Driefontein was refluxed in a Soxhlet apparatus with carbon disulphide for 2½ hours. After drying, no loss of weight was noted. On the basis of these findings, the "carbon" may be classed as an insoluble pyrobitumen, using the method advocated by Hunt, Stewart and Dickey (1954), who proposed a scheme of classification of various carbonaceous minerals, based on their solubility in carbon disulphide. (Figure no.13).

The behaviour of "carbon" in organic solvents may be contrasted with that of a sample of solid bitumen from the New Primrose Gold Mine Ltd., which was found by Mr. F.C.M.Bawden to be completely soluble in cold toluene and pyridine.

Hoekstra and Fuchs (1960) found that the specific gravity of the thucholites examined by them

varied from 1.46 to 2.26 and that individual samples of approximately equal density showed a wide variation of ash content. The "carbon" samples examined by the writer varied in specific gravity from 1.32 to 1.88. The variation of ash content for samples of approximately equal density was likewise found to correspond to those of Hoekstra and Fuchs. The density of the "carbon" samples examined was extrapolated to zero ash content which gave a theoretical approximate density of 1.30 for the ash-free carbonaceous material. The 100 milligram sample of "carbon" separated from the V.C.R. at Venterspost was put into a separating funnel of bromoform which was progressively diluted with alcohol and the "sink" carefully run off. The specific gravity of the accompanying liquid was then determined, and the following is a list of the range of specific gravities obtained: 1.72, 1.63, 1.54, 1.49, 1.43, 1.38, 1.32. The last figure quoted probably represents a close approximation to the true specific gravity of the "carbon".

This wide variation of the specific gravities is, as was mentioned above, in accordance with the findings of Hoekstra and Fuchs (1960). These authors found that examination of analytical and X-ray data indicated that wide variations in thucholite composition exist and that residual fragments of the original uraninite are usually present. The wide range of specific gravities reported by the present writer indicates that the same must hold true for the Witwatersrand "carbon".

In order to establish the chemical composition of the actual hydrocarbon accompanying the uraninite, proximate analyses were carried out on highly purified samples of "carbon" from the following mines and horizons:

Luipaards Vlei	Bird Reef
Doornfontein	Carbon Leader
West Driefontein	Carbon Leader
Vogelstruisbult	Main Reef and May Reef

The results obtained are set out in detail in the attached table (Table no. VIII).

In order to have some basis for the comparison of the "carbon" from the various mines and horizons, the A.S.T.M. method for the classification of coals by rank was used. It is, however, very doubtful whether this classification may be used for the absolute identification of the "carbon", but it does at least provide a basis whereby it is possible to contrast the physical properties of the "carbon" on an ash-free basis.

The results obtained by the A.S.T.M. method, as set out in Table VIII, suggest that the "carbons" from the various horizons have very similar properties. This would therefore suggest that a common mechanism was probably responsible for the formation of the "carbon". The writer feels that the theory put forward by Sharpe (1949), envisaging an algal origin for the "carbon", is worthy of serious consideration.

As can be seen from the aforegoing results, the problem of what one calls the material commonly referred to as "carbon" in mining circles, or "thucholite" in others, is far from settled and merits more detailed mineralogical examination. The writer feels, with Liebenberg (1955), that the term "thucholite", has shortcomings due to its having been applied to a variety of carbonaceous materials of different

composition, but that none the less its use is now too well established for it to be easily discarded, unless a more satisfactory and exact classification can be proposed, based on a clearer understanding of the nature of the substance.

URANINITE.

Composition.

According to Ramdohr (1960) and Frondel (1958), the ideal formula for uraninite is UO_2 and not U_3O_8, as quoted in most text books. Material approximating to the formula UO_2 has, however, not been found in nature. Uraninite is always more or less oxidised with the conversion of the tetravalent uranium to hexavalent uranium. According to Frondel, this oxidation takes place without destruction of the crystal structures up to a not clearly defined limit.

Crystallography.

Uraninite is isometric and crystallizes in the hex-octahedral crystal class. Cleavages have not been observed in large crystals in nature, since these have generally been destroyed as a result of radioactivity. Ramdohr (1960) has, however, mentioned seeing (111) and less frequently (100) cleavages in material from the Witwatersrand.

Occurrence of the uraninite in the V.C.R.

In polished sections prepared from rich portions of V.C.R. ore from Venterspost, the uraninite occurred as ovoid, subhedral and euhedral grains, which were isotropic with a pinkish-brown colour. Numerous grains apparently showing (111) cleavage, as described by Ramdohr (1960), as well as many severely fissured grains, a feature which is apparently common to radioactive minerals, were found. Integral liberated grains of uraninite were also studied. These grains were concentrated by the use of the Haultain Superpanner followed by a series of further purifications using the Franz Isodynamic Separator.

These grains had a jet black colour and showed a wide range of angularity and rounding.

Etch reactions.

The uraninite grains examined in polished sectior appeared to conform to all the etch reactions listed by Short (1948). The technique advocated by Liebenberg (1955), involving the use of hydrofluoric acid as a stain for the uraninite, was used with great success during the present study. It was found, however, that the staining of the uraninite could best be controlled by diluting the hydrofluoric acid slightly, thus slowing down the rate of reaction with the uraninite and permitting a more satisfactory control over the rate of staining. It was found that, when concentrated acid was used, the uraninite grains very rapidly turned dark brown, unless care was exercised. The use of dilute acid makes it relatively easy to obtain the formation of an almost iridescent blue colour, which appears just before the uraninite grain turns brown. This blue colour is far easier to see in polished section than the dull brown, especially where the grains are associated with "carbon". The duration of etching is dependent on the strength of the hydrofluoric acid and the degree of staining desired, and may vary between one and five minutes.

Association of uraninite with other minerals.

The grains of uraninite examined in the present suite of samples were found to be mainly associated with "carbon" (Plate XXI), although a few rounded grains were seen embedded in quartz. Very often the quartz in the immediate proximity of such uraninite grains was found to be fractured in a radial manner. This feature has been

confirmed by Liebenberg (personal communication). Most of the other grains occurred as subhedral grains showing partial crystal outlines (Plate XXII), or as fragments of subhedral grains showing resorption by their "carbon" host (Plate XXI), or as anhedral grains. Some of the larger grains of uraninite were seen to have only a partially developed thin shell of "carbon", or to be transected by numerous small veinlets of anisotropic "carbon" (Plate XXIII). Some of these larger grains of uraninite, when examined under crossed nicols, showed the presence of a ring of apparently amorphous material, described by Ramdohr (1958) as "ghosts" and thought to be leucoxene.

After staining with hydrofluoric acid to facilitate recognition, many of the uraninite grains included in the "carbon" were seen to be severely fractured, with "carbon" filling the interstices (Plates XXIV, XXV). In some isolated cases, the entire grain was completely enveloped by the carbon, and the fragments of the included uraninite grain, which appeared to show {111} cleavages, would, if they could be fitted together, form a single grain with sharp crystal outline. There are three possible explanations for the origin of such grains: the grain could have been formed in the "carbon" and then shattered as a result of stresses set up within the horizon, or it might have shattered in situ as a result of the release of helium at a time when the "carbon" was plastic or fluid enough to cement the fractions together, or the "carbon" may be considerably younger than the uraninite and might have merely cemented the grain after it had become shattered.

Many of the uraninite grains examined in the present survey were found to contain inclusions of galena. Numerous uraninite grains showed fretted edges due to replacement by minerals such as gold, pyrrhotite and phyllosilicates (Plates XIII, XV). These findings are in accord with those of Liebenberg (1955), who observed similar features in the V.C.R. and commented on oval grains of uraninite from Venterspost and South Roodepoort which had almost completely been replaced by pyrrhotite.

A second variety of uraninite described by Liebenberg (1955) as secondary uraninite was also found. This variety was present only in minor amounts as fine brownish stringers generally associated with the phyllosilicates, and showed the normal reactions to etch reagents.

Size of the uraninite grains.

The size of the uraninite grains was determined in polished section as well as in concentrates of liberated grains. (Figure no. 14). The results obtained for the grains measured in the uraninite concentrate differ considerably from those quoted by Liebenberg (1955), who could find no concentration of grains smaller than 40 microns in the portions of ore he had examined from the V.C.R. at Western Reefs. This apparent difference between the two sets of results may easily be explained. The results quoted in the present study include all the fragments resulting from the fracture of the larger grains and will therefore show a bias with respect to the smaller grains.

In order to obtain some idea of the approximate size range of the uraninite in the ore prior to crushing, numerous polished sections were examined. Due to the paucity of uraninite in the sections examined, however, it was decided that the results would not be statistically significant, so that only the minimum and maximum grain sizes observed may be stated with any degree of certainty. The smallest remnant of uraninite observed in polished section was about 5 microns, and the maximum 520 microns.

Krumbein (1935) has shown that the average diameter indicated in polished sections of spheres distributed at random can be shown to be 0.785 of the true diameter. Liebenberg (1955), commenting on this feature, considered that use of the size shown by grains in polished section was justifiable, but that the distinction between true and measured dimensions of grains should, however, always be borne in mind.

Size distribution of uraninite grains in a heavy mineral concentrate.

Size interval in microns.	Distribution in per cent.
0 to 50	45.32
50 to 75	39.14
75 to 100	15.54
	100.00

Mechanism of association of uraninite with carbon.

It is suggested that the following mechanism may in part be responsible for the relatively constant association of uraninite with "carbon".

The presence in the V.C.R. of minerals such as rutile, which, according to Stringham (1952), are formed under acid conditions, suggests that at some stage acid conditions may have existed in the V.C.R. It is probable that these acid conditions existed in the period following the outpouring of the Ventersdorp lavas, which may have raised the temperature of the relatively unmetamorphosed V.C.R. sufficiently to allow any inherent moisture to react with the sulphides present, with consequent formation of sulphuric acid. This acid would then result in the dissolution of any pre-existing detrital uraninite.

Moore (1954) has shown that carbonaceous substances, such as subbituminous and bituminous coals, are able to remove uranium from solution quantitatively. The results of chemical analyses carried out on the "carbon" of the Witwatersrand, details of which are to be found under the heading of "Carbon", suggest that the chemical composition of the "carbon" is very similar to that of a medium to low volatile bituminous coal. Thus, the carbonaceous matter present in the V.C.R. might have adsorbed the uranium (in the form of uranyl sulphate) from solution and held it in an irreversible process. As the degree of metamorphism of the V.C.R. proceeded, the adsorbed uranium would then be converted into uraninite, and the "carbon" converted into a less plastic form as a result of the loss of volatile matter.

The feasibility of synthesizing uraninite under similar conditions has recently been illustrated by Sidorov and Rafal'skii (1958). These two workers found that it was possible to synthesize uraninite with a unit cell measurement of 5.44 Angstroms in two

to three days by heating the raw materials to 300°C in an autoclave, this process being followed by rapid cooling. The raw materials used were a slice of carbonaceous siliceous shale and a solution of uranyl sulphate with a concentration of 1 gram per litre.

Koen (1961) has recently reported the presence of both euhedral and subhedral grains of uraninite in the Witwatersrand, contrary to the previously published findings of other workers. Koen further said that little doubt existed that the recrystallization and reconstitution of the uraninite had taken place during more than one period of metamorphism, and that the effects of the later period superseded and partly obliterated those resulting from the earlier one.

It is felt that the present study indicates that at least some of the uraninite in the V.C.R. has been recrystallized in situ, as is shown by the presence of subhedral grains of uraninite located in the "carbon" host. The irregular nature of the "carbon" host itself, and its association with other minerals (Plate XVII), strongly suggests an authigenic origin for the "carbon" grains, and the included uraninite grains, both of which have obviously not undergone any significant degree of movement since their formation.

Uraninite and zircon.

Koen (1961) recently carried out a size analysis of uraninite, chromite and zircon fractions from the Vaal Reef, Carbon Leader and Kimberley Reef. The size distributions obtained for these minerals were well-matched, indicating that the uraninite grains had been deposited together with the zircon and chromite fractions from a suspension in water.

It was accordingly felt that a comparison of the zircon and uraninite contents of the present suite of samples from the V.C.R. might prove of interest.

Due to the small amounts of uraninite found in polished section, it was decided to determine the uraninite radiometrically. In polished section, zircon grains were often found to be fractured, and accordingly, in order to have some basis for comparison, all fragments of zircon recovered from samples of pulverized ore of equal weight were taken to represent individual grains. This would therefore take into account not only the grains originally occurring as shattered fragments, but also those shattered during the crushing process.

The number of zircon grains was then plotted against the radiometric assay (eU_3O_8) for each of the samples. The graphs, (Figures nos. 15 and 16) show no obvious trend between the zircon and uraninite contents of the samples, such as might have been expected. It is felt, however, that the fact that the uraninite had to be determined radiometrically, and that a compromise had to be adopted regarding the zircon grains, may have obscured any relationship which may have existed between these two minerals.

ZIRCONS

Zircons are a relatively constant constituent of the V.C.R., and it was accordingly felt that they would perhaps justify further detailed inve tigation. The advantages of such a study were summarized by Mathias (1962), who stated that, since in most magmatic rocks zircon was of early and short crystallization, its form therefore reflected the physico-chemical conditions prevailing during its crystallization. Since zircons showed relatively simple crystal forms and were tetragonal, it was immaterial whether the breadth was measured parallel to the "a" or the "b" axis. Also, in sedimentary rocks or metamorphosed sediments, zircons acted as provenance indicators. Since zircons had a high degree of durability, they were able to withstand more than one sedimentation cycle. Further, zircons derived from sedimentary rocks or granitized sediments could generally be distinguished from those of intrusive plutons by the rounding of their corners and edges, and/or the presence of outgrowths.

Occurrence in the V.C.R.

The zircons found in the V.C.R. occurred mainly as euhedral to subhedral grains showing prismatic and pyramidal faces. These grains varied considerably in their degree of preservation and occurred mainly as subangular and sub-rounded crystals when intact, or, more generally, as shattered fragments. (Plate XXVI) The average length of the intact zircon grains was about 200 microns. The zircons usually occurred as inclusions in quartz or pyrite. Numerous grains were observed

which showed a conspicuous zonal structure in polished section.

Colour

The zircon grains were usually transparent and showed a variety of colours, but concentrates of zircons from both Venterspost and Libanon showed that the same range of colours was present at both mines. The grains were mostly colourless or pinkish, although some grains showed a deep wine-red colour. No malacons were found. Zircons from the V.C.R. from West Driefontein, however, showed a slightly wider range of colours, such as pink, orange-red, colourless and greyish-purple.

Achutharao (1961) carried out a study of zircons from various metamorphic and granitic rocks in Mysore, India, and found that no rigid demarcation of colour types between groups and within rock types could be made with certainty. This was due to the fact that certain percentages of other colour types of zircons were usually also encountered, but they were not significant enough to permit division of groups. In the light of these findings, and also because the recognition of colour differences is largely subjective, this line of study was not pursued in the present survey.

Photoluminescence.

According to Horne (1951), zircons from any one igneous rock generally fluoresced with a uniform intensity and hue under a given source of ultra-violet radiation. Specimens from different igneous rocks, according to Horne, had recognizably different fluorescent

properties under long and short wave ultra-violet light, whilst sedimentary zircon concentrates could be expected to show a diversity of fluorescence from grain to grain. Foster (1948) considered this feature to be a useful tool in petrological studies. Accordingly, the zircons of the V.C.R. were examined by this method in the present study.

Concentrates of zircons prepared from samples from Venterspost, Libanon and West Driefontein were exposed to ultra-violet radiation from a "Mineralite", and the effect was observed by means of a low-powered binocular microscope. The bulk response shown was virtually negative. A very few grains of zircon from Venterspost were, however, seen to fluoresce with an intense golden colour. This yellow colour was probably caused by the presence of large amounts of hafnium in these zircons. Von Knorring and Hornung (1961) found a similar effect in the case of zircons containing between 2% and 3% per cent of HfO_2 taken from a pegmatite area.

According to George (1949), the presence of fluorescent zircons in placers was nearly always an indication of the co-presence of monazite. A careful study of heavy mineral concentrates prepared from the present suite of samples, however, failed to reveal the presence of monazite.

The above observations would, therefore, tend to suggest that the zircons in the V.C.R. were most probably derived from a common igneous source, as shown by their similar overall response to ultra-violet radiation.

Hafnium-zirconium ratio

Kosterin, Zuev and Shevaleevaskii (1958) found wide variations in the zirconium-hafnium ratios of zircons derived from different rock types. It was accordingly thought that an examination of the Zr-Hf ratios of the zircons from the V.C.R. might have some significance. Unfortunately, however, indifferent results were obtained in the present study. This was probably due to the fact that the determination of the Zr-Hf ratio was made by merely arcing powdered grains of zircon instead of first chemically precipitating the hafnium and zirconium prior to spectrographic analysis. It would therefore appear that the use of the method might be feasible in those cases where enough zircons are available for chemical treatment prior to spectrographic analysis. In the present suite of samples, however, zircons were not present in sufficiently large quantities for this procedure to be adopted.

Morphological features

Various attempts have been made in the past to utilize zircons as provenance indicators. These attempts have been based on the study of such features as form, degree of idiomorphism, outgrowths, overgrowths, inclusions, zoning and various aspects of the length-breadth relationships of the grains. Most of these features have been studied in the present survey.

Hoppe (1962) has investigated the use of variations in the crystallographic form of zircons as an indication of the source rocks from which the

zircons were derived. He found that this was generally only possible in the case of acid rocks, in which the zircons were often idiomorphic. Many of the other rock types examined by Hoppe, however, contained zircons which were not idiomorphic. Hoppe accordingly came to the conclusion that comparisons based solely on the crystal outlines shown by zircons were most unsatisfactory, since only a portion of the zircons could be considered and therefore only a portion of the zircon-containing rocks could be contrasted. He further felt that it was very important that features such as rounding and other irregular features should also be examined. In the past these features were generally considered to be due to either corrosion or abrasion. Hoppe, however, felt that zircons showing both rounding and irregular growth did not owe these features solely to the effects of corrosion and abrasion, but also to hindered growth. If Hoppe's observations are correct, then it is apparent that the widespread use of rounded zircons as indicators of sedimentary origin may in fact not be valid.

Form and degree of idiomorphism

A careful study of the individual euhedral types of zircons from the V.C.R., when compared with the forms illustrated by Dana (1909) (Figure no. 17), indicated that at least six crystallographically different forms were present.

Type 1. (111), (110).

Type 2. (111), (110), (331).

Type 3. (111), (110), (100).

Type 4. (101), (111), (311), (110), (100).

Type 5. (111), (110), (221), (331).

Type 6. (111), (100), (001), (311).

The present study indicated that types 2 and 3, that is, those grains showing (111), (331), (110); and (111), (100), (110); facets, are the most prevalent types present in the V.C.R.

Hoppe (1962) concluded that perfectly developed zircon crystals usually showed (111), (100), (110), (311). forms, and that other forms were less common, and in fact seemed to have very little real significance. He stated that eruptive rocks were characterized by the (111) and (110) forms, whereas the combination of (111) and (100) occurred more generally with deep-seated rocks, which also contained numerous grains showing (311) forms. Hoppe felt that the latter form was presumably caused by a lack of space during growth. Hoppe further stated that perfectly developed crystals of zircon were a rarity even in eruptive rocks, and that even granites contained numerous grains of anhedral zircon.

A few of the zircons examined in the present study showed the presence of both outgrowths and overgrowths. (Plates XXVIII, XXIX) These features have been described by Poldervaart and Eckelmann (1955). These workers found that zircons from autochthonous granites showed growth habits in between the predominantly rounded grains of siliceous sediments and the predominantly

euhedral zircons of intrusive granites. A high proportion of zircons with overgrowths and outgrowths seemed to be characteristic of autochthonous granites, although minor amounts of these forms (such as shown by the samples from the V.C.R.) appeared to be normal in intrusive granites. Further, if the rock was of sedimentary origin, then the cores of the zircons would be either fragmentary or rounded, while regenerated granites were in turn characterized by the presence of zircons showing euhedral cores.

Zonal growth and inclusions

Many of the zircon grains examined in the present study showed the presence of well-developed pronounced zoning. One case in particular clearly showed the presence of a euhedral centre core of zircon (Plate XXX), which, according to Poldervaart and Eckelmann (1955), is characteristic of a regenerated granite. Numerous other zircon grains examined showed what appeared to be tiny inclusions of fluid aligned in haphazard manner, as well as numerous tiny included grains of zircons, sometimes aligned parallel to the length of the host zircon crystals themselves. (Plate XXXI) According to Hoppe (1962), the presence of such included zircon grains aligned parallel to the length of the host zircon crystals suggests that the shell may have been formed under conditions different from those of the inclusion, and therefore may indicate a considerable difference in time of formation. Hoppe felt that, on the other hand, in those cases where the core and shell were

co-incident, there was most probably very little real difference in age.

Length-breadth studies

The length-breadth measurements in the present study were made with a calibrated eye-piece reticule and are correct to within 2 microns. The results obtained from this study have been represented in the manner suggested by Wyatt (1954), by plotting the elongation (the elongation is defined as the length divided by the breadth) against the frequency and drawing a histogram.

According to Wyatt, zircon assemblages of similar origin gave similar histograms even though the average size of the zircons varied greatly from rock to rock. It should however be pointed out that this procedure was merely designed to distinguish short zircons typical of sediments from long zircons typical of idiomorphic grains from igneous rocks. Hoppe (1962) felt that the method had limitations, since the size of the grains was often influenced by such factors as non-uniform overgrowths on zircon crystals. Wyatt (1954) obviously did not take this factor into account.

Since zircons are generally known to be able to withstand more than one sedimentation cycle (Mathias 1962), it was decided to investigate whether the zircons currently present in the V.C.R could have been derived from an underlying horizon such as the Main Reef. For this purpose, a pure concentrate of zircons from the Main Reef at Sub-Nigel on the East Rand was made. It was felt that since this mine was separated by a lateral distance of over 50 miles from Venterspost and Libanon,

any accidental similarities in the elongation-frequency histograms due to the samples being taken from the same mine would be minimized. The results obtained from these studies were then plotted in the manner suggested by Wyatt (1954), and are shown in the accompanying figures (No. 18) and table (No. IX).

As can be seen from Figure No. 18, the two histograms for the V.C.R. and the Main Reef compare very favourably. In the region of 1.50 to 2.25 elongation, the two histograms show frequency distributions of 66.66 and 59.57 per cent respectively, and thus, in addition, compare very favourably with the histogram of a coarse granite A 124, examined by Wyatt. This latter histogram Figure No. 19 is a typically "igneous" type histogram, and shows a frequency of 55% for the elongation range of 1.60 to 2.20.

Zircons from the V.C.R. and the Main Reef with elongations in excess of 3.50 showed frequencies of 1.08 and 1.44% respectively, which again compares favourably with elongated zircons with elongations in excess of 3.80 examined by Wyatt. He found that normal granites contained about 0.5% of such types, whereas contaminated granites contained about 3.8%.

The two histograms of the V.C.R. and the Main Reef respectively reveal a close co-incidence, which, according to the findings of Wyatt (1954), suggests that the zircons of these two horizons were probably derived from the same or similar source rocks. The histograms are further of the "igneous" type and correspond most closely with that illustrated by Wyatt

for a coarse granite. It may therefore be stated that the available evidence points not only to a common source rock for the V.C.R. zircons themselves, but also indicates that the zircons of the V.C.R. were probably derived from horizons at present underlying the V.C.R., such as the Main Reef.

In conclusion, it may be said that the various properties of the V.C.R. zircons investigated in the present survey, such as overgrowths, outgrowths, length-breadth relationships, crystal forms and photoluminescence, all point to an igneous, probably granitic, origin for the zircons of the V.C.R.

URANIFEROUS LEUCOXENE.

In the Blind River field in Canada, much of the uranium has been reported as the uraniferous titanate, brannerite. Uraninite is considered to play a lesser role. In the Witwatersrand, brannerite has not been specifically recognized, even as a minor accessory mineral of uraninite.

According to Traill (1954) and Rice (1958), the brannerite occurring at Blind River has generally been altered to a felted mixture of anatase and thorogummite. The unheated mineral gives the X-ray diffraction pattern of anatase, and a brannerite pattern after strong heating in the absence of air. Patchett and Nuffield (1960) have shown that natural brannerite regains its original structure on ignition.

Traill (1954) has described the brannerite from Blind River as having a deep brown colour and a vitreous to resinous lustre. In thin section the brannerite was found to be isotropic, dark brown in reflected light and reddish-brown in strong transmitted light. According to Robertson and Steenland (1960), typical brannerite grains in reflected light had a definite yellowish alteration product particularly heavy along the grain edges, and the interior of the grains was a mass of opaque material and transparent needles of (?) rutile. All brannerite grains seen by the authors were rounded to subrounded, and showed both the yellowish alteration product and the faint red colouration in oblique illumination which are

characteristic of the break-down of iron-bearing minerals.

In his study of the Witwatersrand ores, Ramdohr (1958) has mentioned the presence of a radioactive titaniferous mineral, which he has tentatively identified as brannerite or davidite, which is decomposed to a white aggregate of titanite, rutile or leucoxene associated with considerable amounts of radiogenic lead. Ramdohr also refers to the presence of numerous so-called "ghosts", consisting of an aggregate of a dull unidentified whitish material not unlike leucoxene.

The present study of the V.C.R. at Venterspost and Libanon revealed the presence of numerous rounded and anhedral orange to orange-yellow-brown grains of leucoxene. In polished section the leucoxene is grey (Plate XXXIII), under crossed nicols shades of orange and yellow are seen. Many of the grains show a dark brownish core, which appears to grade to a lighter, often yellowish, colour towards the periphery. Careful examination of the core material showed the presence of numerous felted euhedral grains similar to rutile in appearance. These grains of leucoxene correspond closely to those described by Liebenberg (1955) as uraniferous leucoxene.

Grains resembling those in the V.C.R. at Venterspost and Libanon, as described above, were concentrated in the course of previous work carried out at West Driefontein (Carbon Leader), and sent to Dr. Pabst at the University of California. He examined a few

dark resinous anhedral grains by means of X-rays. One of the grains apparently gave a weak pattern, which Pabst thought might be rutile, and on heating this to 850 degrees Centigrade, it was in fact found to be rutile. Pabst then examined a few of the grains showing a dark core and light yellowish outer film. These grains were found to be a mixture of fine grained quartz and rutile. Pabst further stated that the grain looked much like the yellow anatase crusts that he had frequently seen on brannerite, and this was what he had expected to find. It seemed likely that the fine grained yellow rutile quartz mixture was an alteration product, but it differed from the brannerite crusts that he had seen. Pabst was unable to find any brannerite in the concentrates sent to him by the writer.

The findings reported by Pabst appear to correspond with those of Liebenberg, who had similar X-ray investigations carried out by Hiemstra. Hiemstra found that the radioactive leucoxene showed X-ray patterns of the rutile type. Pabst mentioned that he was unable to obtain any signs of radioactivity after exposing the grains to sensitive photographic plates for five days. Faint traces of radioactivity were, however, found by the writer, after exposing polished sections prepared of the grains to sensitive film for 11 days. Liebenberg (1955) likewise found traces of radioactivity after exposing the grains to sensitive film for 19 days.

Liebenberg (1955) stated that the detrital mineral from which the uraniferous leucoxene had been derived was still unidentified, but that the available

evidence indicated that it may have consisted of uraniferous titanite which had been almost completely altered to microcrystalline rutile. Even the small remnants of the parent mineral were apparently severely altered, as could be shown by the X-ray investigations.

The present study therefore would tend to refute the statement made by Davidson (1957) concerning the nature of the material identified in this suite of samples as leucoxene. Davidson stated that there was little room for doubt that this leucoxene was precisely the same material as was recognized by the Canadian mineralogists to be altered brannerite.

TITANIUM MINERALS.

Rutile

Rutile was found in most of the polished sections prepared for the present study, and occurred in numerous forms and associations. The grains varied considerably in colour, from orange through to brownish-red, and were mainly subangular and subhedral. Pronounced furrows down the length of the crystals were a prominent feature. (Plate XXXIV) Twinning was generally geniculer. The grains often exceeded 500 microns in size, and usually averaged about 250 microns.

Many of the rutile grains were embedded in chlorite. These grains occurred either as isolated prismatic to acicular grains or as fine clusters showing geniculer habit, usually accompanied by yellow leucoxene. Other rutile grains occurred as fine included needles in quartz, imparting a characteristic blue colour to the latter. Rutile was observed included in pyrite, and fine euhedral grains of rutile were also often found to form the core material of rounded uraniferous leucoxene grains.

The angular nature shown by the rutile grains examined strongly suggests that the rutile grains, especially those embedded in chlorite, had not undergone any significant degree of transportation since their formation.

Anatase.

Numerous grains of anatase were located in both polished sections and heavy mineral concentrates.

The grains may best be described as acute bipyramids. In some cases not all the crystal facets were developed, probably due to hindered growth. The grains were invariably found associated with chlorite as inclusions, and varied from 80 to 280 microns in size. By reflected light the grains were a deep indigo blue colour, but when examined by means of a binocular microscope as integral grains, they appeared a paler blue.

Brookite

A few small dark brown grains were tentatively identified as brookite. These grains showed what appeared to be (122) and (120) faces when compared with illustrations in Dana (1909).

Temperatures and conditions of formation of rutile and anatase.

According to Stringham (1952), rutile is commonly formed under acid conditions at temperatures in excess of 350°C. Anatase, however, is known to invert to rutile at 400°C.

An interesting account of the co-existence of rutile and anatase in the Upper Devonian deposits of the Argichi River Basin has been given by Nisanyan (1959). The rutile and anatase were supposed to have been formed during epigenesis and early metamorphism of the sedimentary rocks. Nisanyan stated that the formation of rutile and anatase in the quartzites occurred by the dissolution of ilmenite, which was delivered into the basin with other clastic material and subsequently recrystallized. After the dissolution of the ilmenite, leucoxene was

formed in the presence of water. Later, during recrystallization, and as a result of dehydration, the leucoxene was transformed, either directly into rutile or at the beginning into anatase and then into rutile. The presence of both anatase and rutile in the V.C.R., accompanied by leucoxene, suggests that a similar mechanism may have operated in the Witwatersrand. A significant feature of the rutile in the V.C.R. is its crystalline habit with grains showing no signs of attrition, strongly supporting an authigenic origin. (Plate XXXIV).

PHYLLOSILICATES.

Chlorite

De Kock (1940) mentioned that the dark colour imparted to the matrix of the V.C.R. was caused by the presence of large amounts of chlorite, which he assumed had been formed as a result of the alteration of large amounts of volcanic ash.

Since chlorite forms such a major portion of the matrix of the V.C.R., it was thought necessary to determine the composition of the chlorite(s).

All refractive index measurements were carried out on crushed chlorite concentrates using the conventional immersion method. Measurements were carried out at 27°C using monochromatic sodium light and are correct to within ± 0.002. Only the intermediate refractive index Beta was determined, since, as Albee (1962) has pointed out, the platy habit, abnormal interference colours, fine grain size and colour of the chlorites make it difficult to measure all the indices of chlorite precisely.

Two chlorites with the following refractive indices were found in the V.C.R.:

B = 1.620 ± 0.002 Biaxially positive

B = 1.631 ± 0.002 Biaxially negative

Albee mentions (Albee 1962) that in general the higher index chlorites have a negative optic sign, and the lower index chlorites a positive sign, which is in agreement with the above findings.

The determination of the optic signs of the chlorites in the present study was made easier by Albee's

observation that the sign of the elongation of the chlorite grains was always opposite to that of the optic sign. This technique avoids the difficulties inherent in the conventional determination of the optic sign, which is hampered by the dark colour and fine nature of the chlorite grains.

In thin section the chlorite of the V.C.R. was found to occur characteristically as interstitial material confined to the matrix in the form of small scaly aggregates. (Plates XXXV, XXXVI). The mineral is green in colour and shows faint pleochroism in shades of green and greenish-yellow. The interference colours are dusky mauves and greenish browns. On rotation of the microscope stage, the isogyres showed very slight movement, so that the value of the axial angle probably does not exceed an estimated 5 degrees.

On the basis of the optical data obtained in the present survey, the chlorites of the V.C.R. may be classified as Ripidolite and Brunsvigite respectively, using the scheme of classification proposed by Hey (1954). The presence of the iron-rich variety of chlorite, Brunsvigite, has also been reported from the Jeppestown Series on the East Rand by Fuller (1958).

According to the diagram proposed by Stringham (1952), it is very probable that the chlorite group minerals present in the V.C.R. could have been formed under pH conditions which were virtually neutral, in the temperature region between 250 and 300°C.

Sericite

In the V.C.R., sericite and muscovite occur as fine tabular grains, or more generally as fine minutely crystalline shards, which are usually intimately intermixed with the chlorite (Plate XXXVII). Sericite appears to be very late in the sequence of minerals in the V.C.R. It generally occurs as fine interstitial material between the quartz grains, which it often replaces, thereby imparting a fretted or jagged outline to the quartz grains. (Plate XXXVII). According to Stringham (1952), it is probable that the sericite was formed under alkaline conditions in the vicinity of 200°C.

Biotite

Only a few small grains of very faintly pleochroic pale brown biotite were found in the thin sections examined. According to Stringham (1952), it is probable that these were formed under acid conditions at a temperature of about 450°C.

The biotite grains observed in the V.C.R. did not resemble in any way the grains which Koen (1962) has described in a recent paper as chlorite pseudomorphs after detrital amphibole, but which Willemse considers to be biotite with included needles of rutile.

PYRITE

Second only to quartz, pyrite is the most common mineral present in the V.C.R. It occurs mainly in the chlorite matrix, but also to some extent in the quartz pebbles, where it fills cracks and replaces the pebbles on their periphery. Most of the pyrite grains examined varied from a few millimetres in diameter to very small specks only visible with the microscope. Larger pebbles up to 15 mm. or more in size were, however, not uncommon.

The pyrite in the V.C.R. occurs in numerous forms. A full description of the various forms encountered has not been attempted, since it is felt that these are perhaps best illustrated by means of photographs. The footnotes accompanying the various attached micrographs (Plates XL to XLIX) list very briefly the salient features associated with the various forms.

Numerous pyrite pebbles, derived from earlier horizons, were seen, as well as banded ironstones which had apparently become hydrothermally pyritized in the present horizon. Numerous skeletal growths of pyrite were also present. These had either a compact or a porous nature, and appeared to have grown around older grains of pyrite in situ, during the period of consolidation and metamorphism of the V.C.R. Apart from these types, there were also numerous varieties of interstitial and stringer-like pyrite, which help to cement the smaller quartz grains together.

No attempt has been made in the present study to establish the sequence amongst the various pyrite

types themselves, or to correlate the individual pyrite types with any of the other authigenic minerals in the V.C.R. It is, however, quite apparent that some of the various forms of pyrite examined were formed at different times and were epigenetic. Whilst it would perhaps be possible to correlate a few forms with each other, it would be very difficult to propose any hard and fast rule concerning their sequence, certainly not one that would be valid for all the types. As a generalization, however, the following sequence is envisaged:

The abraded and rounded pyrite grains probably represent the oldest generation. This type is then followed in turn by a variety of intermediate age, which occurs as overgrowths on older grains and may take the form of either porous or clear overgrowths. The youngest generation is represented by the form generally referred to as juvenile pyrite and occurs as fine stringers or infillings between the quartz grains.

Optical properties of pyrite

Stanton (1957) has drawn attention to the variations in the optical properties of pyrite. He mentioned that the optical properties of sections containing pyrite could be greatly influenced by the method adopted for the final stages of polishing. Stanton found that it was possible to change the optical character of pyrite from isotropic to anisotropic, depending on whether a cloth or lead polishing lap was used. As early as 1942 Smith suggested that the apparently anomalous optical behaviour of pyrite might be a function of

both the composition and the secondary crystal structure of the pyrite. Stanton investigated Smith's suggestions, and found that pyrite was generally anisotropic and that double refraction was produced by any plane other than the octahedral. Stanton also found that pyrite could be rendered superficially isotropic by surface deformation during polishing, and that anisotropism was not necessarily due to the presence of arsenic or other trace impurities, as had been suggested by Smith. Ramdohr (1960) has also commented on the fact that he had noted pyrite which showed both optical characters, but offered no explanation to account for this phenomenon.

Since most of the polished sections in the present study contained varying amounts of pyrite and were polished by means of cloth laps, it was thought necessary to examine the optical character of the pyrite very carefully. The pyrite was all found to be isotropic. Many thousands of grains were carefully checked for anisotropism, but no marked tendency to anisotropism could be found. This suggests that, if Stanton's observations are correct, the present suite of pyrite has had its optical character superficially altered as a result of the use of cloth polishing laps.

Inclusions of other minerals in pyrite.

Numerous inclusions of other sulphides, such as chalcopyrite, sphalerite and galena, have been found in some of the pyrite grains. Other inclusions, such

as zircon and gold, have also been found in some of the apparently older pyrite grains. The gold occurs in two forms, either as jagged particles, representing gold which has replaced the pyrite subsequent to the deposition of the latter, or as cylinders or cornets. These cornets of gold are not unlike those reported by Dunn (1929) for undoubted detrital gold from Australia, and were entrapped in the pyrite at the time of formation of the latter. (Plate XIV)

A feature of some significance is the presence of numerous rutile inclusions in some of the pyrite grains. Closer examination further revealed the presence of small included cores of leucoxene in some of the grains of pyrite. Arnold (1954) has commented on the finding of grains of pyrite with centres of leucoxene at Blind River, Canada. Arnold believed that at least some of the pyrite there had resulted from the sulphidization of pre-existing titaniferous magnetites. The presence of considerable amounts of apparently authigenic rutile in the V.C.R. suggests that a mechanism similar to that suggested by Arnold may also have applied to the V.C.R. The rutile in the V.C.R. probably represents the excess titanium released during the formation of the epigenetic pyrite from titaniferous magnetite.

Pyrite geothermometer.

At the start of the present study, it was proposed to construct a replica of an instrument devised by Smith (1947) and named by him the "pyrite

geothermometer". With this instrument it was apparently possible to determine the temperature of crystallization of large pyrite grains in polished section by measuring the thermo-electrical potential of the pyrite against another reference metal. The project was eventually abandoned for technical reasons, partly because the instrument was suited only to the study of large pyrite grains, which were not always available in the present suite of samples. Hawley and Nichol (1961), on examining the varieties of pyrite that Smith (1947) had distinguished by means of the pyrite geothermometer as having distinctly different temperature effects, found that these varieties also varied considerably in composition. Further study by Nichol confirmed the fact that the higher temperature pyrites seemed to show significantly higher amounts of nickel and cobalt, and lesser amounts of silver, than the so-called low temperature types.

It was accordingly felt that more significant results would probably be obtained from a trace element study than could be obtained by the use of the pyrite geothermometer. In the present survey, however, the trace element study has been restricted to an investigation as to why some varieties of pyrite tarnish readily, whereas other varieties show no such tendency. The two types, referred to as "tarnished" and "untarnished" respectively, were isolated and analysed quantitatively for nickel, cobalt, gold and silver by the method described in the section on "spectrographic methods."

Trace elements in pyrite.

Qualitative results:

Both types of pyrite showed the identical trace element assemblage. The results are as follows:

Ag, Al, Au, Co, Cu, Mg, Mn, Ni, Si, Ti, Pb.

Quantitative results:

Direct method:-

	Co:Ni ratio	Gold ppm	Silver ppm
Tarnished pyrite	1.43:1	190	19
Untarnished pyrite	0.93:1	150	14

Indirect method:-

	Nickel%	Cobalt%	Co:Ni ratio
Tarnished pyrite	0.115	0.125	1.09:1
Urtarnished pyrite	0.175	0.135	0.77:1

(The relative merits of the two methods of analysis have already been discussed.)

The spectrographic analysis carried out on the tarnished variety of pyrite clearly shows a higher cobalt to nickel ratio than the untarnished pyrite. This feature would therefore suggest that the stability of the pyrite is apparently influenced to a larger extent by the cobalt, rather than by the nickel, content.

Kullerud and Yoder (1959) have drawn attention to the fact that the presence of cobalt and nickel in pyrite is generally thought to reduce the stability of the pyrite. According to Kerr (1945), the pyrite group apparently forms an isostructural series, with pyrite FeS_2, Vaesite NiS_2 and Cattierite CoS_2 as end

members, whilst Bravoite (Co, Ni, Fe)S_2 is intermediate. These minerals show virtually the same cell sizes when compared with pyrite (Berry and Thompson 1962), and may possibly account for the nickel and cobalt found in the pyrite.

It is interesting to note that, in the present study, analysis of the less stable variety of pyrite (tarnished) showed a greater amount of gold to be present (190ppm.) than the more stable (unoxidized) variety, which contained only 150 ppm. The present findings appear to coincide with those of Graton (quoted by Joralemon 1951), who found that at Simmer and Jack and adjacent mines, a dependable sign of better-than-average gold values in the reef was the rapidity of the tarnishing of the pyrite at such places. Graton further mentioned that the pyrite in the rich stretches of the conglomerates would develop strong iridescence on a freshly blasted face within a day or two. Graton felt that the reason for this behaviour of the pyrite was the presence of gold in solid solution in the pyrite. This theory has been discussed in an earlier section and discounted by the present writer.

The Co:Ni ratio

The cobalt:nickel ratio obtained for the tarnished variety of pyrite was 1.43:1. This figure is in close agreement with that obtained by Coetzee (1955) for pyrite from the Main Reef at Durban Roodepoort Deep Gold Mine. Coetzee used colorimetric methods of analysis, and reported a cobalt:nickel ratio of 1.33:1 for pyrite derived from areas that had been unaffected by basic dykes.

According to Hawley and Nichol (1961), cobalt appears to be preferentially enriched in pyrite rather than in pyrrhotite, whereas the opposite applies in the case of nickel. Hawley (1952) further stated that the preferential concentration of certain elements in particular sulphides could be assumed to be due to their being more acceptable in certain lattices than in others. This factor apparently holds true for cobalt and silver irrespective of the type of ore or the absolute amounts of the metal itself. Wager and others (1957) stated that the reason for pyrite showing errichment in cobalt 14 to 60 times that of pyrrhotite or chalcopyrite was the more chalcophile nature of the cobalt in comparison to that of nickel.

According to Carstens (1941), pyrites of sedimentary origin are characterized by the presence of less than 100 ppm of cobalt and a cobalt:nickel ratio of less than unity, whereas pyrite of hydrothermal origin shows a cobalt content of 200 to 2400 ppm, with an average of 500 ppm of cobalt, and a cobalt:nickel ratio of greater than unity. These generalizations have been confirmed by Hegemann (1943), who found that the cobalt:nickel ratio for sedimentary pyrites in 68 out of 74 samples was less than unity, and that the cobalt content was less than 100 ppm. Only two of the samples analysed by Hegemann contained more than 100 ppm of cobalt.

Accordingly, it would appear that both the tarnished and untarnished varieties of pyrite in the

present suite of samples were probably of hydrothermal origin, since both varieties had cobalt contents in excess of 100 ppm.

Hawley and Nichol (1961) considered that differences in temperature of formation of pyrites offered the only obvious explanation for consistent differences in composition. These authors further drew attention to the work of Nichol, who found that the pyrites formed at higher temperatures showed a higher cobalt and nickel content, but a lower silver content, than those formed at lower temperatures.

The results obtained in the present study, interpreted in the light of Hawley and Nichol's work, strongly suggest that the two varieties of pyrite (tarnished and untarnished), in the present suite of samples, were formed at different temperatures. The untarnished pyrite was probably formed at a higher temperature than the tarnished variety, as can readily be seen from the significantly higher cobalt and nickel, but lower silver, content of the untarnished variety.

PYRRHOTITE.

The pyrrhotite in the V.C.R. occurs mainly as xenomorphic grains (Plate IX), or very rarely as subhedral grains showing hexagonal outline (Plate L). Pyrrhotite replaces most of the earlier minerals such as pyrite and uraninite, and is in turn itself replaced by gold and later sulphides such as chalcopyrite, galena and sphalerite. (The association of gold with pyrrhotite has already been discussed in the section on "Gold"). The pyrrhotite of the V.C.R. showed no unusual optical properties. Under crossed nicols it was a common feature to see clusters of grains of pyrrhotite showing different orientations. The mineral was found to conform to all the etch reactions listed for its identification by Short (1948).

Inclusions

Many of the grains of pyrrhotite examined showed the presence of tiny flame-like lamellae of pentlandite aligned parallel to (0001). These lamellae have also been reported in an earlier study carried out at Venterspost by Davies (1949). According to Ramdohr (1958), the presence of these lamellae is normally limited to very high temperature "nickeliferous pyrrhotite" deposits and to a few pyrite occurrences of equally high temperature. He felt that the presence of these exsolution features in the Witwatersrand might also be attributed to the effect of high temperature. Hewitt (1958), on the other hand, reported that pentlandite dissolves in pyrrhotite at 425°C, and that

with slow cooling, exsolution and segregation of pentlandite occurs.

Lamellae of a different type, referred to as "beta lamellae", were found in a few grains of pyrrhotite in the V.C.R. in the course of the present survey (Plate LI). According to Kiskyras (1950), the occurrence of such lamellae is usually associated with high temperature types of pyrrhotite, which may or may not show them. According to Ramdohr (1958), these beta lamellae are usually absent in the Witwatersrand.

Trace elements in the pyrrhotite.

Both qualitative and quantitative spectrographic analyses were carried out on a composite prepared from equal portions of pyrrhotite extracted from representative samples of V.C.R. ore from Venterspost.

The purity of the pyrrhotite used for the spectrographic analysis has already been discussed under the heading "Spectrographic methods".

The following trace elements were detected on qualitative spectrographic analysis of the pyrrhotite by Esterhuizen:

Al, Ag, Au, Cu, Co, Mg, Mn, Ni, Si, Ti.

The quantitative results were as follows:

Gold:	130 ppm.
Silver:	12 ppm.
Gold:Silver ratio:	10.82:1
Cobalt:Nickel ratio:	1:5 (0.20:1) (Direct method)
Cobalt:Nickel ratio:	1:4.53 (0.23:1) Indirect method)
Cobalt:	0.053%
Nickel:	0.235%

Cobalt:

It is almost certain that the cobalt found to occur in the pyrrhotite in the present study is due to the presence of intergrown or exsolved pentlandite and occluded pyrite. According to Hegemann (1943), the limit of isomorphous replacement of iron by cobalt is not known, but it is apparently below 1 per cent.

Nickel:

Some uncertainty exists concerning the actual degree of isomorphous substitution of iron by nickel in the pyrrhotite lattice, due to the frequent occurrence of intergrowths of pentlandite in the pyrrhotite. The present sample of pyrrhotite does, however, show enrichment in nickel. According to Fryklund and Harner (1955), cobalt and nickel are the only common elements that substitute for iron in the pyrrhotite structure. If the cobalt or nickel content of the pyrrhotite exceeds 1%, then an included mineral may be assumed to be present. The studies of Fryklund and Harner seem to indicate that no consistent or significant relationship exists between the Ni:Co ratio, or nickel or cobalt contents, and the geological environments on a district-wide basis.

Origin of the pyrrhotite

Davies (1949) commented on the intensity of the sulphide mineralization of the Ventersdorp lavas when in direct contact with the V.C.R. and not separated from it by quartzite. He further mentioned

that under these conditions, pyrite predominates in the lava to the exclusion of all other sulphides, and may form up to 70% of the rock locally. Davies further stated that pyrrhotite occurred in the lavas as disseminated specks and irregularly shaped blebs, and sometimes formed up to 20% of the rock, though it seldom exceeded 1 to 2%. Davies further added that where the lava was transected by white quartz veins, the percentage of pyrrhotite increased and the pyrrhotite formed stringers up to 2 mm in width.

Ramdohr (1961) mentioned a suite of samples from South Roodepoort mine, taken from the contact region between the V.C.R. and the Ventersdorp lava, in which he found pyrrhotite formed from pyrite pebbles. Ramdohr stated that in that particular zone, at temperatures below the melting point of granite, pyrite had been changed into pyrrhotite. Ramdohr claimed that this inversion of pyrite to pyrrhotite at the direct contact with lava flows doubtless did not go deep, perhaps 5 to 10 cms.

According to Davidson (1960), the deduction that pyrrhotite represented inverted pyrite was radically wrong. He quoted the work of Kullerud and Yoder (1959), which had shown that the inversion of pyrite to pyrrhotite takes place at temperatures of 690°C at atmospheric pressure. At a pressure of 10 bars, however, this inversion takes place at 743°C, while at 1000 bars, equivalent to about 13,000 feet of burial, this inversion occurs at 755°C.

Macdonald (1954) has recorded that the temperature at which Hawaiian aa basaltic lava becomes immobile is between 700 and 780°C. Zies (1941) found that the temperature of andesitic lava extruded from the volcano of Santiaguito in Guatemala was about 700°C. This estimate was, however, probably low, since the measurements were made at the top of a slowly extruding dome. Jaeger (1957), who did a considerable amount of research on the cooling of dolerites, concluded that in an intrusion with the range of solidification of 800 to 1100°C, the contacts were never raised to more than 665°C, certainly far from the required temperature for the inversion of pyrite to pyrrhotite. The results obtained during the present study, from various geological thermometers, seem to indicate that the Ventersdorp lavas, which have an andesitic composition, did not raise the temperature of the V.C.R. very much more than 450°C as an upper limit.

Davidson (1960) felt that the formation of pyrrhotite occurred rather as a result of deposition from hydrothermal solutions in which the iron:sulphur ratio was higher than that needed to form pyrite. He added that the observed presence of higher concentrations of pyrrhotite in the neighbourhood of basic sills and dykes pointed to a possible higher concentration of iron in the hydrothermal fluid in the proximity of such sills and dykes. Kullerud and Yoder (1959) have commented on the presence or absence of pyrrhotite in a pyrite assemblage. They felt that this was a function

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