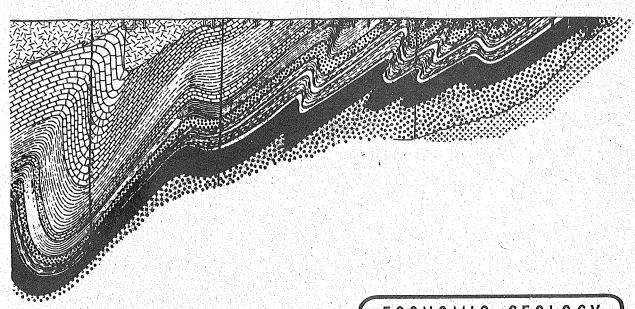UNIVERSITY OF THE WITWATERSRAND

JOHANNESBURG

ECONOMIC GEOLOGY

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INFORMATION CIRCULAR # 19

UNIVERSITY OF THE WITWATERSRAND

JOHANNESBURG

THE COMPOSITION OF GOLD FROM THE BARBERTON MOUNTAIN LAND

by

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Research Scholar

INFORMATION CIRCULAR No. 19

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THE COMPOSITION OF GOLD FROM THE BARBERTON MOUNTAIN LAND

ABSTRACT

Samples of visible, native gold were obtained from 40 localities over the shole of the Barberton Mountain Land, and from 20 localities at different levels in the Zwartkopje Shoot of the Sheba Mine. As checks, three samples of free gold from Southern Rhodesia, three from the Witwatersrand, and two from the Birthday Pipe in the Sheba Mine were also studied. Spectrographic analyses were carried out on all samples, and atomic absorption spectroscopy and fire assaying on most of them. As a result the fineness, copper and iron contents, and the trace element composition were determined. Of the 22 elements identified in the gold, it is thought that aluminium, calcium, magnesium and silicon are present as mineral impurities; that beryllium, bismuth, cobalt, manganese, mercury, molybdenum, palladium, platinum, silver, tin and vanadium are in solid solution with the gold; and that antimony, copper, iron, lead, nickel, titanium and zinc may be present either in the gold lattice or as mineral inclusions.

The samples from the area as a whole reveal the presence of copper, iron, silver and silicon in all 40 samples, of magnesium in 35, of aluminium in 30, of lead in 18, of nickel in 12, of tin in 10, of antimony and cobalt in 6, of bismuth and zinc in 4, of molybdenum in 3, of beryllium, mercury and titanium in 2, and of calcium, manganese and platinum in one only. In the Zwartkopje Shoot copper, iron, silver and silicon were found in all 20 samples, aluminium and magnesium in 17, nickel in 13, antimony and mercury in 4, bismuth and lead in 2, and cobalt and vanadium in one only.

The results indicate that two distinct types of gold occur in the Zwartkopje Shoot, one above 20 Level and the other below. The change from one type to the other can be correlated with a pronounced change in the structural disposition of the shoot. The main factors controlling the variation in the composition of the free gold down the ore-shoot appear to have been the temperature and, to a lesser extent, the pressure at the time of deposition, the concentrations of the individual elements in the ore fluids, the chemical and mineralogical environment, and the nature of the wall-rock. Because of the large number of variables controlling the composition of the gold at a particular locality, it has been found that the composition of individual grains varies markedly from grain to grain, and this variation casts some doubt on the statistical reliability of the observed differences.

A regional plot of the fineness values reveals the outlines of a possible pattern. The highest values occur in the vicinities of the Agnes, Sheba and Consort mines, and it is thought that this phenomenon indicates that the source of the gold mineralisation lies beneath these areas. It is concluded that the results of the present investigation favour the Kaap Valley Granite pluton, and not the Nelspruit gneisses and granites, as the probable source of the auriferous solutions. Most of the deposits investigated seem to be of a hypothermal nature, and, consequently, there is no readily apparent zoning of the mineralisation. Unlike the fineness values, the copper and iron contents of the samples do not appear to show any systematic regional variation, nor to indicate any possible source of the mineralising solutions.

Three samples of visible gold from Southern Rhodesia show a simpler trace element pattern than is associated with the Barberton gold which is believed to be a product of similar mineralisation that occurred in similar rock-types at about the same time in the Archean epoch. The three samples from the Witwatersrand show a trace element pattern no more complex than that found in some of the Barberton gold, but there is a suggestion that the gold from the former area might, in general, contain more trace elements.

It is concluded that silver and copper, because of their degree of concentration in the gold, might be the only elements which could satisfactorily be used as indicators of concealed gold mineralisation during geochemical prospecting. The fineness of the gold itself might provide another useful exploration tool, as it would appear that the higher the fineness the richer and more extensive the mineralisation. The gold : silver ratio of random samples of gold from a certain locality might indicate whether that locality can be considered a likely host of significant ore-bodies or of small occurrences of limited economic importance.

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THE COMPOSITION OF GOLD FROM THE BARBERTON MOUNTAIN LAND

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THE COMPOSITION OF GOLD FROM THE
BARBERTON MOUNTAIN LAND

INTRODUCTION

In the search for concealed ore-bodies in the Barberton Mountain Land, geochemical and geophysical prospecting techniques have been applied to a limited extent and with only limited success. In both cases the methods have been directed towards finding associated sulphide mineralisation, and not the gold itself. The development of pyrite has been sought after by geophysical means, and of arsenopyrite by geochemical means. It was anticipated that the location of anomalies indicating the presence of these sulphides might also lead to the discovery of new auriferous deposits. However, pyrite and arsenopyrite are also commonly present in disseminations or concentrations without any readily discernible amounts of gold, and, consequently, a sulphide anomaly really provides, in itself, no positive evidence as to whether or not it should be further investigated for gold.

It was reasoned that, if direct evidence was wanted of the presence of gold, then it would be advisable to search for elements which occur in the gold itself and not in the associated sulphides and gangue material. Information is available for a number of mines concerning the mineralogical composition of the auriferous reefs, but virtually no work has previously been undertaken on the composition of the gold. It was decided, therefore, to collect a representative suite of specimens of free gold from the whole of the Mountain Land, and to determine the amounts of various minor and trace elements in the actual gold. It was thought that a certain element, or combination of elements, might be characteristic of Barberton gold, and that it might be present in sufficient quantities to be detectable by normal geochemical prospecting techniques, once the ore had undergone oxidation, weathering and erosion, and the constituents of the gold had been shed into the soil or stream sediments.

A second objective of the research involved the problem of the origin of the gold in the conglomerates of the Witwatersrand Basin. It is commonly, but not universally, accepted that this gold is of a detrital nature and was derived from the erosion of earlier mineralisation of the type prevalent in the Barberton Mountain Land. It was thought that, if subsequent investigations of Witwatersrand gold showed a trace element pattern similar to that of the gold from Barberton, then considerable weight would be added to the theory of a placer origin of the Witwatersrand reefs.

This Information Circular is a report on the minor and trace element analyses of 40 samples of visible, free gold from 34 localities on the Transvaal and Swaziland sides of the Barberton Mountain Land. The localities were selected in order to give an indication of the pattern, if any, of areal variation in the composition of the gold. A further 22 samples from various levels in one particular locality - the Sheba Mine - were investigated to determine variations in composition in a vertical plane. The program formed part of the Barberton Project in which an attempt is being made by the Economic Geology Research Unit to establish the pattern, origin and causes of localisation of gold mineralisation in the Barberton Mountain Land.

The investigations were commenced in January, 1962, and completed in June, 1963.

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B.   PREVIOUS WORK

As a prelude to the laboratory studies, the author undertook a review of published material dealing with the mineralogy of gold deposits from many parts of the world, and a separate Information Circular was prepared on the geochemical characteristics of gold in ore deposits (Gay, 1963). In this mention was made of

previous work on the mineralogy and chemistry of the Barberton gold ores.

De Villiers (1957), on the basis of polished-section work, divided the ore deposits of the Barberton Mountain Land into four categories : (i) ores with arsenopyrite and pyrrhotite, (ii) lead-bearing ores, (iii) antimonial ores, and (iv) pyritic ores. Arsenopyrite and pyrite, with lesser amounts of chalcopyrite, were found to be the most common sulphides. Visible, free gold occurs in all four types of ore. The paragenetic sequence for the first category is (1) arsenopyrite, (2) pyrrhotite, (3) chalcopyrite; for the lead-bearing ores (1) pyrite, (2) sphalerite, (3) tetrahedrite, (4) chalcopyrite and galena; for the antimonial ores (1) pyrite or arsenopyrite, (2) berthierite and marcasite, (3) stibnite, (4) metallic antimony; and for the pyritic ores (1) arsenopyrite, (2) pyrite, (3) second-generation arsenopyrite, (4) pyrrhotite and chalcopyrite. Free gold occurs late in the paragenetic sequence, except in the arseno-pyrite ores where the gold is usually enclosed in this sulphide.

The same author spectrographically analysed mill concentrates from Rosetta, Agnes, Fairview, Alpine, Sheba, New Consort, Golden Quarry, Three Sisters, Piggs Peak and Woodstock mines. Gold, silver, nickel and cobalt were found in the samples from all ten mines, lead in nine, antimony in eight, arsenic in seven, zinc, tungsten and tin in four, and bismuth in one. The only other elements sought, but not found, were tellurium, selenium, germanium, thallium, copper, and the platinum minerals. Chemical analyses of the concentrates from some of these mines revealed the additional presence of copper, iron and sulphur.

Steele and Carlton (1961) carried out spectrographic analyses of high- and low-grade pyritic ores from the Barberton area, and found that iron and silica were present in very large amounts, magnesium in large amounts, aluminium, manganese and tin in moderate amounts, silver and arsenic in small amounts, copper and nickel in very small amounts, and gold and lead in trace amounts. The presence of boron, bismuth, cadmium, cobalt, chromium, molybdenum, antimony and zinc was also determined.

The only previous investigations into the composition of the gold itself were carried out by Warren and Thompson (1944), and by Steele and Carlton (1961). The former reported that gold from the Barberton area contained silver in quantities greater than 0.5%, and copper, iron, vanadium, titanium and mercury in amounts less than 0.1%. Other elements which were sought, but not detected, included lead, bismuth, tellurium, arsenic, antimony, zinc, cadmium, tin, palladium and platinum. The latter pair of investigators found that silica was present in moderate amounts, silver, lead, iron and tin in small amounts, copper and nickel in very small amounts, and arsenic and manganese in trace amounts only. They were not able to detect the presence of aluminium, antimony, boron, bismuth, cadmium, cobalt, chromium, indium, magnesium, molybdenum, vanadium or zinc.

Steel and Carlton (1961) also studied samples of gold specifically from the Trichardt's Luck and Lily mines. In the former sample silica was present in moderate amounts, silver, arsenic, iron and tin in small amounts, copper and nickel in very small amounts, and manganese in trace amounts only. The gold from the Lily Mine contained large amounts of silver, moderate amounts of silica, small amounts of iron and manganese, very small amounts of copper and nickel, and trace amounts of arsenic and antimony. In neither of the samples were aluminium, boron, bismuth, cadmium, cobalt, chromium, indium, magnesium, molybdenum, lead, vanadium, or zinc detected. In addition, no antimony was found in the Trichardt's Luck gold, and no tin in the Lily gold.

C.   GEOLOGICAL SETTING OF BARBERTON GOLD OCCURRENCES

The Barberton Mountain Land is composed of a mass of Archean sediments, lavas and intrusive basic and ultrabasic rocks which accumulated in a geosyncline that underwent orogenesis between 3000 and 2600 million years ago. This deformation produced a sequence of broad, isoclinal synclines separated by narrow anticlines, the axial plane traces of which strike northeastwards. Extensive faults occur near and parallel to the anticlinal axes. These displacements were originally high-angled thrust faults, but subsequent movements along the same planes have resulted in strike-slip movements as well. The latter movements have given rise to second-order faults and fractures adjacent, but oblique, to the major longitudinal faults. The majority of the ore-bodies are in the first- and second-order faults and fractures, and away from such structural features gold mineralisation is either very poorly developed or totally absent.

A second control on the localisation of ore-bodies is the proximity of the faults to the contact between the sediments and lavas of the Swaziland System and the granites and gneisses which bound the Mountain Land on all sides. The more significant mineralisation lies in a zone adjacent to this contact, and successive faults away from this zone become progressively less well mineralised so that the centre of the Mountain Land is totally barren of gold occurrences.

At least two main varieties of granitic rocks - the Kaap Valley Granite and the Nelspruit Gneiss - occur adjacent to the Mountain Land on the Transvaal side. Their origin and age are the subject of a long-standing controversy, but the most recent structural investigations suggest that the Nelspruit Gneiss, at least, formed the floor of the Barberton geosyncline. The original age of the gneisses and migmatites remains unknown. The Kaap Valley pluton, dated at 3000 million years, is intrusive into the rocks of the Swaziland System, and, hence, the formation of the geosyncline must predate this figure. At 2600 million years the Nelspruit gneisses and also possibly the Kaap Valley Granite, were remobilised along their contact with the sediments and lavas, and, at the same time, were intruded by at least one pluton of a third granitic variety - the Mpageni Granite - at some distance from the contact.

All the gold mineralisation appears to be epigenetic in origin and hydrothermal in nature. Hall (1918) classified the deposits as being either impregnation reefs or true reefs. The former appear to be replacements of the country rock and do not have sharp boundaries. They are the more common and more important of the two varieties, and examples of such deposits from which samples were collected for the present investigations include the Three Sisters, Fairview, Sheba, Clutha, Fortuna, Agnes, Wyldesdale, Forbes Reef and Consort mines. The true reefs are represented by quartz-filled fractures with well-defined contacts against the country rock. From the Alpine Mine ore of this type was obtained for trace element analysis. Hall's classification is generalised and simplified in the extreme.

De Villiers (1957) concluded that all the deposits seemed to have originated at moderate to great depths, but that various temperatures of formation were represented. Hypothermal, mesothermal and epithermal occurrences are to be found. The ores with arsenopyrite were formed at great depth and high temperature. The pyritic ores also appear to be hypothermal in origin, while the lead-bearing ores belong to the mesothermal class. The antimonial ores seem to have been deposited during the last stages of hydrothermal activity, and exhibit characteristics of both the mesothermal and hypothermal zones.

All previous investigators have concluded that the source of the gold-bearing fluids was the granites. Differences of opinion have been expressed as to which of the three granites actually was responsible. Hall (1918) thought that the Kaap Valley and Nelspruit granites were formed during the same period, and, hence, contributed equally to the formation of the gold deposits. Van Eeden (1941) recognized the greater

age of the Kaap Valley Granite, and believed that only a small portion of the mineralisation could be related to the intrusion of this pluton, while the bulk could be shown to be associated with the emplacement of the younger Nelspruit granites and gneisses. Hearn (1943) believed the opposite to be true, and stated that the gold mineralisation, at least in the Consort - Sheba area, was the product of the intrusion of the Kaap Valley Granite. Ramsay (1963) put forward another hypothesis to the effect that both the Kaap Valley and Nelspruit granites and gneisses were older than the rocks of the Mountain Land, and had formed the basement upon which the latter had been deposited. The gold was not related to the emplacement of either of these varieties, but had been introduced during the period of remobilisation of the basement granites along their contact with members of the Swaziland System. This remobilisation was possibly contemporaneous with the intrusion of the Mpageni Granite 2600 million years ago.

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THE ANALYSIS OF THE GOLD SAMPLES

A.   PRE-ANALYTICAL TREATMENT OF SAMPLES

(a)   Locations of Samples

Forty samples of visible gold were collected from mines and abandoned workings in the Barberton Mountain Land to determine the areal variation in gold composition. The samples consisted mainly of panned concentrates and chip samples, and are referred to in the text as the "G" series of samples. For comparison and check purposes a further six samples from Witwatersrand and Southern Rhodesian localities were added to this series. Figure 1 is a simplified geological map showing the location of the localities from which gold was collected. The following list gives the locality, nature of associated material, the appearance of the gold, and the analyses to which each sample of the "G" series was subjected (sg. - spectrographic analysis; aa - atomic absorption analysis; fa - fire assay; coarse-grained $>$ 1.5 mms. diameter; medium-grained 0.5 - 1.5 mms.; fine-grained $<$ 0.5 mms.) :-

G.1
- (i)   Agnes Mine, 14 Level - chip sample
- (ii)   associated material : pyrite, quartz
- (iii) gold : fine-grained; bright yellow to rich gold colour; few grains with brown coating
- (iv)   analysis : sg, aa.

G.2
- (i)   Albion Mine - chip sample
- (ii)   associated material : quartz, covellite, chalcopyrite, chalcocite, pyrite
- (iii) gold : fine- to medium-grained; yellow colour
- (iv)   analysis : sg, aa, fa.

G.3
- (i)   Alpine Mine - chip sample
- (ii)   associated material : quartz, galena, pyrite
- (iii) gold : fine-grained; yellow colour
- (iv)   analysis : sg.

G.4
- (i)   Beaver Trap Mine, North Reef - chip sample
- (ii)   associated material : quartz, pyrite
- (iii) gold : very fine-grained; bright yellow colour
- (iv)   analysis : sg, aa, fa.

G.5
- (i)   Beaver Trap Mine, South Reef - chip sample
- (ii)   associated material : quartz, pyrite
- (iii) gold : fine-grained; yellow colour; some grains coated with iron oxide
- (iv)   analysis : sg, aa, fa.

G.6
- (i)   Behind-the-Scenes Mine - chip sample
- (ii)   gold : very fine-grained; yellow colour
- (iii) analysis : sg, fa.

G.7
- (i)   Black Diamond Creek Mine - chip sample
- (ii)   associated material : quartz, sericite, chlorite, pyrite
- (iii) gold : fine- to coarse-grained; coarse material rich gold colour; finer material yellow to pale yellow colour
- (iv)   analysis : sg, aa, fa.

G.8
- (i)   Clutha Mine - chip sample
- (ii)   associated material : quartz, pyrite, magnetite
- (iii) gold : fine- to coarse-grained; fine grains yellow colour; coarse grains gold colour
- (iv)   analysis : sg, aa, fa.

G.9
- (i)   New Consort Mine, 38 West Drive - chip sample
- (ii)   associated material : quartz, iron oxides, arsenopyrite
- (iii) gold : very fine-grained; bright gold colour
- (iv)   analysis : sg, aa, fa.

G.10
- (i)   Dreyer's Imperial Mine - chip sample
- (ii)   associated material : quartz, magnetite, pyrite
- (iii) gold : fine- to medium-grained; yellow colour
- (iv)   analysis : sg, aa, fa.

G.11
- (i)   Fairview Mine - chip sample
- (ii)   gold : fine-grained; yellow colour with a few, larger, reddish grains
- (iii) analysis : sg.

G.12
- (i)   Fairview Mine - chip sample
- (ii)   associated material : grey quartz, pyrite, arsenopyrite
- (iii) gold : medium-grained, yellow colour
- (iv)   analysis : sg, aa.

G.13
- (i)   Forbes Reef Mine - chip sample
- (ii)   gold : fine-grained; yellow colour
- (iii) analysis : sg.

G.14
- (i)   Fortuna Mine - chip sample
- (ii)   associated material : pyrite, quartz, chalcopyrite, iron oxides
- (iii) gold : fine- to medium-grained; yellow to bright yellow colour
- (iv)   analysis : sg, aa, fa.

G.15
- (i)   French Bob's Mine, Martin's Reef - chip sample
- (ii)   gold : fine-grained, yellow colour
- (iii) analysis : sg, fa.

G.16
- (i)   Golden Quarry Mine, shallow level - chip sample
- (ii)   associated material : quartz, pyrite, arsenopyrite
- (iii) gold : fine-grained; yellow colour
- (iv)   analysis : sg, aa, fa.

G. 17   (i)   Golden Quarry Mine, deep level - chip sample
      (ii)   associated material : quartz, pyrite, arsenopyrite
      (iii)   gold : fine- to medium-grained; pale yellow to reddish colour
      (iv)   analysis : sg, aa, fa.

G. 18   (i)   Independent Mine - chip sample
      (ii)   associated material : pyrite, chalcopyrite, magnetite, quartz
      (iii)   gold : fine- to coarse-grained; yellow to bright yellow colour
      (iv)   analysis : sg, aa, fa.

G. 19   (i)   Ivy Mine, Lester Reef - chip sample
      (ii)   associated material : quartz, iron oxides
      (iii)   gold : fine- to medium-grained; yellow to reddish colour
      (iv)   analysis : sg, aa, fa.

G. 20   (i)   Ivy Mine, Ivy Lead Reef - chip sample
      (ii)   gold : fine- to medium-grained; mainly yellow colour with a few reddish grains
      (iii)   analysis : sg, aa, fa.

G. 21   (i)   Ivy Mine, Ivy Reef, 900-ft. Level - chip sample
      (ii)   associated material : pyrite
      (iii)   gold : fine-grained; bright yellow colour
      (iv)   analysis : sg, fa.

G. 22   (i)   Ivy Mine, Ivy Reef, bottom levels - chip sample
      (ii)   associated material : quartz, pyrite
      (iii)   gold : fine-grained; bright yellow colour
      (iv)   analysis : sg, aa, fa.

G. 23   (i)   Lily Mine - chip sample
      (ii)   associated material : quartz, arsenopyrite, pyrite
      (iii)   gold : fine- to coarse-grained; pale yellow to yellow colour
      (iv)   analysis : sg, aa, fa.

G. 24   (i)   Madeline Mine - chip sample
      (ii)   associated material : quartz, iron oxides, pyrite
      (iii)   gold : fine- to medium-grained; pale yellow colour
      (iv)   analysis : sg, aa, fa.

G. 25   (i)   Maid of de Kaap Mine - chip sample
      (ii)   gold : fine-grained; yellow colour
      (iii)   analysis : sg, fa.

G. 26   (i)   Maid of the Mountains Mine - chip sample
      (ii)   associated material : quartz, pyrite, iron oxides
      (iii)   gold : fine-grained; yellow colour
      (iv)   analysis : sg, aa, fa.

G. 27   (i)   Montrose Mine - chip sample
      (ii)   gold : fine- to coarse-grained; yellow colour
      (iii)   analysis : sg, aa, fa.

G. 28   (i)   Olga Mine - chip sample
      (ii)   gold : fine-grained; pale to bright yellow colour
      (iii)   analysis : sg, aa, fa.

G. 29   (i)   Rosetta Mine - panned concentrate
      (ii)   associated material : quartz, iron oxides, galena
      (iii)   gold : fine-grained; mostly bright yellow colour with a few reddish grains
      (iv)   analysis : sg, aa, fa.

G. 30   (i)   Thomas Mine - chip sample
      (ii)   associated material : pyrite, quartz, iron oxides, galena
      (iii)   gold : fine- to medium-grained; bright yellow colour
      (iv)   analysis : sg, aa, fa.

G. 31   (i)   Three Sisters Mine - chip sample
      (ii)   gold : fine- to medium-grained; pale yellow colour
      (iii)   analysis : sg, fa.

G. 32   (i)   Tiger Trap Mine - chip sample
      (ii)   associated material : magnetite, pyrite, quartz
      (iii)   gold : fine- to coarse-grained; yellow colour with a few large golden grains
      (iv)   analysis : sg, aa, fa.

G. 33   (i)   Tiger Trap Mine - borehole core
      (ii)   associated material : milky quartz, covellite, chalcocite, tennantite
      (iii)   gold : medium-grained; pale yellow colour
      (iv)   analysis : sg, fa.

G. 34   (i)   Verdite Mine - chip sample
      (ii)   associated material : pyrite, iron oxides, quartz
      (iii)   gold : fine- to coarse-grained; yellow colour
      (iv)   analysis : sg, aa, fa.

G. 35   (i)   Verdite Extension Mine - chip sample
      (ii)   gold : fine- to medium-grained; bright yellow colour
      (iii)   analysis : sg, aa, fa.

G. 36   (i)   Weltevreden (Queens) Mine - chip sample
      (ii)   associated material : pyrite, quartz
      (iii)   gold : fine-grained; bright yellow colour; few large grains of golden colour
      (iv)   analysis : sg, aa, fa.

G. 37   (i)   Woodbine Mine - chip sample
       (ii)   gold : fine- to medium-grained; yellow colour
       (iii)   analysis : sg, aa, fa.

G. 38   (i)   Worcester Mine - chip sample
       (ii)   associated material : magnetite, quartz, pyrite, galena
       (iii)   gold : fine- to coarse-grained; yellow colour
       (iv)   analysis : sg, aa, fa.

G. 39   (i)   Wyldesdale Mine - panned concentrate
       (ii)   associated material : iron oxides, pyrite
       (iii)   gold : fine-grained; pale to bright yellow colour
       (iv)   analysis : sg, aa, fa.

G. 40   (i)   Sheba Mine, Zwartkopje Shoot, deep level - chip sample
       (ii)   gold : fine- to coarse-grained; bright yellow colour
       (iii)   analysis : sg, aa, fa.

G. 41   (i)   Globe and Phoenix Mine, Southern Rhodesia - chip sample
       (ii)   associated material : pyrite, magnetite, quartz, galena
       (iii)   gold : very fine- to coarse-grained; golden colour
       (iv)   analysis : sg, aa, fa.

G. 42   (i)   Selukwe Mine, Southern Rhodesia - chip sample
       (ii)   associated material : magnetite, pyrite, quartz
       (iii)   gold : fine- to coarse-grained; bright yellow colour
       (iv)   analysis : sg, aa, fa.

G. 43   (i)   E.R.P.M. Mine, Cason Section, Central Rand, banket - chip sample
       (ii)   gold : medium-grained; golden colour
       (iii)   analysis : sg, aa, fa.

G. 44   (i)   Market Square, Johannesburg, quartz vein - chip sample
       (ii)   gold : fine- to medium-grained; bright yellow colour
       (iii)   analysis : sg, aa, fa.

G. 45   (i)   West Rand Consolidated Mine, West Rand, grit - chip sample
       (ii)   gold : fine- to medium-grained; yellow to bright yellow colour
       (iii)   analysis : sg, aa, fa.

G. 46   (i)   Angwa River, Southern Rhodesia - alluvial nugget
       (ii)   gold : bright yellow to golden colour
       (iii)   analysis : sg, aa, fa.

Twenty-two samples were, in addition to the above, collected along the Zwartkopje Shoot in the Sheba Mine, between the 14 and 26 levels, covering a length along the shoot of 1271 feet. These are all chip samples and have been called the "S" series. Material was collected at different levels along the shoot

to study any vertical variation in composition, three samples being collected at different positions on each level, where possible. Details of the samples collected are as follows :-

S. 1   (i)   14 Level, Z 1 Stope
       (ii)   sample : free gold in green schist with quartz, pyrite, arsenopyrite, iron oxides
       (iii)   gold : fine- to medium-grained; yellow colour; irregular grains with granular surface
       (iv)   analysis : sg, aa, fa.

S. 2   (i)   14 Level, Z 1 Stope
       (ii)   sample : gold in green schist with pyrite, quartz, arsenopyrite
       (iii)   gold : large, irregular grains; bright gold colour
       (iv)   analysis : sg, aa, fa.

S. 3   (i)   14 Level, C 4 Stope
       (ii)   sample : gold in milky-white and grey quartz with pyrite, arsenopyrite, a little chalcopyrite
       (iii)   gold : fine- to very coarse-grained; partly crystalline; yellow colour
       (iv)   analysis : sg, aa, fa.

S. 4   (i)   17 Level
       (ii)   sample : gold in quartz-chlorite rock with pyrite and iron oxides
       (iii)   gold : fine- to medium-grained; yellow colour; grains irregular or filiform in shape
       (iv)   analysis : sg, aa, fa.

S. 5   (i)   17 Level
       (ii)   sample : gold in quartz-chlorite rock with pyrite, arsenopyrite
       (iii)   gold : fine- to medium-grained; pale yellow colour
       (iv)   analysis : sg.

S. 6   (i)   17 Level
       (ii)   sample : gold in quartz with pyrite, chalcopyrite
       (iii)   gold : fine- to medium-grained; yellow colour
       (iv)   analysis : sg.

S. 7   (i)   18 Level
       (ii)   sample : gold in milky quartz with pyrite, arsenopyrite
       (iii)   gold : coarse-grained; pale yellow colour
       (iv)   analysis : sg, aa, fa.

S. 8   (i)   20 Level, Z 1 Stope
       (ii)   sample : gold in quartz-chert breccia with pyrite, iron oxides, arsenopyrite
       (iii)   gold : fine-grained; yellow colour; irregular grains with a granular surface
       (iv)   analysis : sg, aa, fa.

S. 9 (i) 20 Level, Z 1 Stope
   (ii) sample : gold in quartz-chert breccia with pyrite, arsenopyrite, iron oxides
   (iii) gold : fine-grained; yellow colour; irregular grains with a granular surface
   (iv) analysis : sg, aa, fa.

S. 10 (i) 22 Level
   (ii) sample : gold in quartz with pyrite, arsenopyrite, chalcopyrite, stibnite
   (iii) gold : fine- to coarse-grained; yellow colour
   (iv) analysis : sg, aa, fa.

S. 11 (i) 22 Level
   (ii) sample : gold in quartz with pyrite, arsenopyrite, stibnite, a little
     chalcopyrite
   (iii) gold : very fine- to coarse-grained; yellow colour
   (iv) analysis : sg, aa, fa.

S. 12 (i) 22 Level
   (ii) sample : gold in quartz with pyrite, arsenopyrite, a little stibnite
     and chalcopyrite
   (iii) gold : fine-grained; yellow colour
   (iv) analysis : sg.

S. 13 (i) 23 Level, Z 1 Stope
   (ii) sample : gold in grey and white quartz with pyrite, iron oxide, arsenopyrite
   (iii) gold : fine- to coarse-grained; yellow colour; grains irregular with some
     crystal faces
   (iv) analysis : sg, aa, fa.

S. 14 (i) 25 Level
   (ii) sample : gold in chert with pyrite
   (iii) gold : fine- to medium-grained; yellow colour
   (iv) analysis : sg.

S. 15 (i) 25 Level
   (ii) sample : gold in green schist with pyrite, arsenopyrite, a little chalcopyrite
   (iii) gold : fine- to medium-grained; yellow colour; some grains crystalline
   (iv) analysis : sg, aa, fa.

S. 16 (i) 25 Level
   (ii) sample : gold in green schist with pyrite, arsenopyrite, chalcopyrite
   (iii) gold : medium-grained, yellow colour; most grains irregular with few
     crystal faces
   (iv) analysis : sg, aa, fa.

S. 17 (i) 26 Level, East Drive
   (ii) sample : gold in chert with pyrite, arsenopyrite, iron oxides
   (iii) gold : medium- to coarse-grained; pale yellow colour
   (iv) analysis : sg, aa, fa.

S. 18 (i) 26 Level
   (ii) sample : gold in chert with pyrite
   (iii) gold : medium-grained; pale yellow colour; filiform and arborescent
     grains mostly
   (iv) analysis : sg, fa.

S. 19 (i) 26 Level
   (ii) sample : gold in chert with arsenopyrite, pyrite
   (iii) gold : medium-grained; yellow colour
   (iv) analysis : sg, aa, fa.

S. 20 (i) 26 Level
   (ii) sample : gold in chert with pyrite, arsenopyrite, chalcopyrite
   (iii) gold : medium- to coarse-grained; yellow colour; irregular grains with
     granular surface
   (iv) analysis : sg, aa, fa.

S. 21 (i) Birthday Pipe, 24 Level, Birthday Winze
   (ii) sample : gold in milky quartz with pyrite, chalcopyrite
   (iii) gold : fine- to coarse-grained; yellow colour
   (iv) analysis : sg, aa, fa.

S. 22 (i) Birthday Pipe, 24 Level, Birthday Winze
   (ii) sample : gold in quartz with pyrite, iron oxides, graphite
   (iii) gold : medium-grained; yellow colour
   (iv) analysis : sg, aa, fa.

The method of sampling is open to criticism in that it has been shown by Eales (1961) that the fineness of native gold varies markedly from one particle to another, and, therefore, single samples of visible gold may not be representative of the area from which they are taken. Unfortunately, many of the samples in the "G" series were collected many years ago from mines no longer in existence, and additional samples could not be obtained. However, in an investigation of the type carried out, random samples taken over a whole region might be statistically representative. The "S" series of samples were collected as systematically as possible to allow for changing physical conditions of deposition. Unfortunately, the sporadic occurrence of grains of native gold did not permit a more complete coverage of the shoot.

(b) Microscopic Examination of Native Gold

Polished-sections of samples were examined with a view to establishing the relationship between gold and the associated minerals. However, it was not possible to study the actual gold analysed because of the limited amount of material available in each sample, all of which was required for the three analytical procedures. Additional specimens were selected from the same deposits, and are assumed to illustrate the general relationships.

In all the specimens examined, visible gold seemed to be late in the paragenetic sequence. It occurred mainly in irregular grains and flakes which enclosed the adjacent gangue minerals. Veins of gold were also observed to fill cracks in the associated minerals. The size of the individual grains varied

considerably from a few microns to 1.5 mms or more. The smaller grains tended to occur as irregular flakes enclosed in the sulphides and quartz, while the larger particles completely enveloped the surrounding minerals. This relationship between the larger grains and the associated minerals was substantiated during the extraction of the gold by dissolution of the samples in hydrofluoric acid, when it was found that the particles released in this way were riddled with small fragments of quartz and sulphides. Sulphide grains were even found in the centre of what seemed to be solid gold.

Furthermore, it was seen in polished-sections that minute inclusions were very common in gold grains of all sizes. These inclusions occurred either on the grain boundaries or in the actual crystals themselves, and, in some specimens, were regularly spaced parallel to the cleavage directions in the gold. The inclusions were normally too small to be identified, but occasionally were recognizable as quartz, pyrite or chalcopyrite. Native gold from Barberton is thus intimately associated with the surrounding minerals, and minute inclusions of impurities are generally present in the actual gold crystals themselves. These observations agree with those of Crook (1939).

The ubiquitous presence of inclusions in gold must be considered when discussing the mode of occurrence of trace elements in native gold. Whereas the larger inclusions and adhering particles of quartz and sulphides can be removed from the gold grains by treatment with acids, it seems unlikely that any method can be devised which will remove completely those minute inclusions which occur in the gold crystals themselves and, possibly, in the actual gold lattice. Therefore, while arguments can be advanced to suggest that certain trace elements occur in solid solution with gold, the possibility of their being present as mineral inclusions must not be overlooked. However, it is believed that the cleaning processes subsequently devised were sufficiently effective to ensure a negligible amount of contamination by the inclusions.

(c)   Extraction of Gold

The gold was extracted from the samples in such a way that the maximum amount was obtained with a minimum amount of contamination by extraneous material. The "G" samples were crushed in an iron percussion mortar, thus limiting the contamination to surface iron on the gold. The gold was then concentrated and extracted by panning on a super-panner.

In the "S" samples, however, much larger grains of gold were encountered, and it seemed obvious that, if these samples were crushed, considerable contamination from the gangue material would occur. To overcome this, it was decided to liberate the gold by dissolving the remainder of the sample in hydrofluoric acid. Examination of solubility tables showed that this acid dissolved quartz and silicates, but had little effect on the noble metals and metallic sulphides.

(d)   Cleansing of Gold Particles

A study of the gold concentrates under a binocular microscope revealed that most of the gold grains had particles of sulphides, oxides and quartz adhering to them, and that occasionally the gold had a dull, reddish surface due to a coating of iron oxide. The quartz and some of the sulphides were removed by washing the samples in a mixture of equal parts of distilled water and concentrated hydrochloric and hydrofluoric acids for 24 hours at 60°C. To remove pyrite, arsenopyrite and other more resistant sulphides, the samples were boiled in 50% nitric acid for 10 minutes. Tests showed that the loss of silver and other trace elements, which are soluble in nitric acid, was negligible during this treatment. A gold alloy containing 42.5% silver was cut into 15 different portions, each of which was subjected to the above nitric acid treatment. The amount of silver lost was determined by weighing the samples before the after treatment. The maximum loss was 1.96% in a sample weighing 450 mgms., and the average loss for all the samples was 0.6%.

For those gold grains which enclosed a large amount of sulphides, and which required stronger treatment than nitric acid, a process was devised of pressure oxidation of the sulphides by passing oxygen under pressure into an autoclave enclosing the samples. After removal from the autoclave, the coating of oxides remaining on the grains was removed with dilute hydrochloric acid.

(e)   Homogenisation of Samples

To obtain reproducible results for each sample, it was decided to melt together the individual grains in the sample to form one homogenous bead. The method described by Esterhuizen (1962) was used to form the beads, the grains being placed in a large cup electrode, and allow current arc of 4 amps being struck on the edge of the cup and allowed to burn for a time interval just sufficient to melt the grains (5 - 8 seconds). The spectra emitted during the melting were recorded to detect any significant losses from the samples by volatilization.

After homogenisation, the beads were washed in boiling 2-normal hydrochloric acid. They were then weighed and rolled into strips to be cut for analysis. The degree of homogeneity was checked by spectrographically analysing five portions of one sample, and measuring the intensities of certain silver, copper and iron lines. The results indicated that, within the limits of accuracy of the spectrographic method, all five samples contained the same amounts of copper, silver and iron. The validity of the method of homogenisation was further substantiated when it was later found that the reproducibility of the line intensity ratios for the majority of the trace elements was satisfactory.

(f)   Precautions Taken to Prevent Contamination of Samples

As the analytical methods used were extremely sensitive, being capable of detecting concentrations down to 1 ppms, great care was taken to prevent contamination of the samples. Crushing was carried out with an iron mortar only, and the samples were sieved through a nylon mesh-perspex screen. Only analar grade chemical reagents and distilled water were used for the cleansing of the samples. High purity graphite electrodes were employed for the spectrographic analyses. The gold beads were flattened and rolled on an anvil and roller used only for this purpose. At each stage during the preparation of the samples for analysis, the gold was carefully examined under the binocular microscope to check the purity.

B.   QUANTITATIVE DETERMINATION OF COPPER, IRON AND SILVER IN NATIVE GOLD

Because of limited time and facilities it was decided to determine only copper, iron and silver quantitatively in the gold samples, and to express the concentrations of the other elements as intensity ratios obtained from spectrographic analyses. Initially it was hoped to determine the copper and iron contents simultaneously with the semi-quantitative spectrographic analysis of the other trace elements, but it was found impossible to prepare homogenous gold-silver-copper-iron alloys to act as reliable spectrographic standards. Therefore, the copper and iron concentrations were ascertained through the use of atomic absorption spectroscopy. The silver content of the ores was found by fire assay as the metal was present in too large amounts to be determined by indirect methods.

(a)   Determination of Copper and Iron by Atomic Absorption Spectroscopy

(i)   Analytical Method

The method used for the quantitative analysis of copper and iron was based on that described by Schuler, Jansen and James (1962). Definite amounts of gold (from 10 to 100 mgms. depending on the size of the sample) were dissolved in aqua regia, evaporated to incipient dryness, and then redissolved in 20% hydrochloric acid. For the smaller samples, ethanol (ethyl alcohol) was added to the final solution, giving a mixture of 70 parts acid and 30 parts alcohol, to enhance the sensitivity. Standard solutions of copper and iron were also prepared using the same solvents, and were diluted to form a concentration range of 0 - 10 ppm. copper and 5 - 70 ppm. iron. These standard solutions were introduced into the flame, and the absorbances given by them were plotted against the relevant concentrations. By comparison with the graph thus obtained, the absorbances of the sample solutions were converted to concentrations of copper and iron.

(ii)   Apparatus and Experimental Conditions

The apparatus used was that described by Schular and Jansen (1962). It consisted of a Zeiss monochromator and indicator unit for line isolation and intensity measurement; a specially designed, water-cooled glass burner with a titanium grid; a titanium atomizer; and a standard Hilger and Watts atomic absorption unit with a hollow cathode lamp holder. "Handigas" was used as fuel for the burner.

The experimental conditions were as follows:

Element	Wavelength	Slit Width	Lamp Current	Air Pressure
Copper	3247 $\overset{o}{A}$	0.07 mm.	12 mA.	20 lbs./sq. in.
Iron	2483 $\overset{o}{A}$	0.10 mm.	32 mA.	20 lbs./sq. in.

(iii)   Results

Three readings of the absorbance for each sample solution were corrected for instrument drift and then meaned. This mean was then further corrected for the copper concentration in the hydrochloric acid - aqua regia blank. By reading off from the graph for the standard solutions, the mean absorbance was converted into ppm. of the metal in solution. By considering this figure in conjunction with the weight of the sample in a particular volume of solution, the concentration of the metal in the sample was obtained in ppm. according to the following calculation:

Weight of sample dissolved in solution = 100 mgms. = 0.1 gm.

Volume of solution = 10 ccs.

Therefore, concentration of sample in solution = 0.01 gms./cc.

From measurement of absorbance, concentration of metal in solution = 5 ppm.

$$= 5 \times 10^{-6} \text{ gms./cc.}$$

Therefore, concentration of metal in sample $= \dfrac{5 \times 10^{-6} \text{ gms./gm.}}{0.01}$

$$= 500 \text{ ppm.}$$

The concentrations of copper and iron in the "G" samples are shown in Table 1, and in the "S" samples in Table 2. It can be seen that the copper content varies from 71 ppm. in G.40 to 6168 ppm. in G.34, with most of the samples having a concentration of less than 1000 ppm. The iron fractions vary from 73 ppm. in G.42 to 3261 ppm. in G.45. Generally, the iron concentrations seem greater than those of copper, especially in the "S" samples.

The reproducibility of the method was investigated by carrying out a series of absorbance measurements on the standard solutions and a check solution. The coefficients of variation obtained for replicate measurements on the solutions varied from 0.59% to 9.27%, the average being 2.32%.

(b)   Determination of Silver by Fire Assay

(i)   Cupellation of Samples

Amounts varying from 5 to 20 mgms. were accurately weighed out for each sample, and the required quantities of silver wire were added to give a gold to silver ratio of 1 : 3. This ratio is higher than that normally used (2 : 5), but is recommended by Rose and Newman (1937) for the assay and cupellation of small samples. Portions of proof gold (999.7 fine) were also weighed out and combined with silver to serve as controls during cupellation. Duplicate assays were carried out for each sample where possible. The gold and the silver wire were wrapped in lead foil, and cupelled in the furnace at approximately 900°C for 25 minutes.

(ii)   Parting of Assay Buttons

After cupellation was complete, the gold-silver beads were removed from the furnace, and flattened on an anvil. They were then annealed in the furnace at low red heat to prevent them from breaking up during parting, and to reduce the surcharge.

Parting was carried out using 50% nitric acid. The gold-silver beads were placed in the boiling acid, and allowed to remain there for half an hour. The acid was then decanted off, and the samples were washed twice with distilled water. After annealing in the furnace at red heat, the samples were re-weighed.

(iii)   Results

This final weight indicated the amount of gold present. The difference between the weights of the bead before and after parting was equivalent to the quantities of silver plus base metals dissolved in the acid. Assuming that the base metals were represented essentially by copper and iron, their concentration, previously determined by atomic absorption, was subtracted from this difference, and the weight of actual silver present thus obtained. The correction for the surcharge was ascertained from the gains in weight of the control samples included in each batch of assays.

The fineness of each sample was calculated as follows (Fisher, 1945):

$$\text{Fineness} = \frac{Au}{Au + Ag} \times 1000$$

Tables 1 and 2 give the results for those "G" and "S" samples respectively which were assayed. Where duplicate assays were carried out, the results agreed to within 1% for most of the samples, and to within 2.5% for all of them. For the "G" samples, the fineness varied from 757 (G.34) to 980 (G.41), while along the Zwartkopje Shoot, the range was between 846 (S.1) and 983 (S.16). Most samples had fineness values greater than 900.

C. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF NATIVE GOLD

The method used to analyse the gold samples was similar to that described by Hawley (1952) who expressed the concentrations of the minor elements in pyrite as log intensity ratios of the analysis element line against suitable iron lines as internal standards. Iron was chosen as the internal standard because it was present in approximately constant amounts in all the samples. The same argument was applied for the use of gold as an internal standard in this investigation.

Tables 3 and 4 show the elements detected in the analysis of the gold samples. The elements were selected after considering those previously reported in native gold, the possible alloys with gold, as shown by metallurgical evidence, and the gangue minerals commonly associated with gold. Beryllium, as far as is known, has not been previously reported in gold, and was not initially looked for. However, strong beryllium lines were detected in one sample, and re-examination of the other spectra showed it to be present in a second sample.

The lines used for identification were the most sensitive ones which were free from interference, and which fell within the wavelength range used. The analytical lines used for the determination of the intensity ratios were chosen after considering sensitivity, line width, self-reversal and diffuseness.

The suitability of gold as an internal standard was tested by comparing the relative rates of volatilization of gold and the elements sought in the samples. The volatilization curves obtained showed that the gold and most of the trace elements behaved in approximately the same way in the arc. Only two gold lines could be chosen for use as internal standard lines because of the simplicity of the gold spectrum and the fact that, under the arcing conditions employed, most of the weak gold lines were too intense for accurate measurement.

(a) Analysis of Samples

Duplicate amounts of approximately 10 mgms. were weighed out for each sample, where possible, and were fused into beads of uniform size following the method of Esterhuizen (1962). The beads were then firmly embedded in small cavities drilled into the tips of high purity graphite rods. The holes were just deep enough to allow half of the bead to protrude above the surface of the electrode. The beads were then arced using the following conditions :

Spectrograph : a large Hilger-Watts, Littrow-type spectrograph with quartz-glass optics.

Excitation : anode excitation; d.c. arc; 6 amps.; 220 volts.

Exposure : Hartmann diaphragm used to record an iron reference spectrum, followed by the sample spectrum.

Electrode Gap : 4 mms.

Slit Width : 20 microns.

Time : 4 seconds pre-arcing, followed by 25 seconds arcing, i.e. the time required to burn the samples to completion.

Wavelength Region : 2360 - 3200 $\overset{o}{A}$.

Emulsion : Ilford N.50 thin film half-tone plates.

Photographic Processing : Kodak D.19B developer for 5 minutes with constant agitation.

The lines of the individual elements were identified using master spectra containing the most sensitive lines of the elements. For positive identification of an element at least two sensitive lines had to be present in the sample spectrum (except for mercury and bismuth which have only one strong line in the given wavelength range). The intensities were measured on a Jarrel-Ash comparator-densitometer.

(b) Results

The intensities of the analytical and internal standard lines were converted to the log intensity ratios using a spectro-calculating board. Au 2932 was used as the internal standard line for analytical lines with wavelengths in the upper half of the wavelength region covered, and Au 2590 for those in the lower half. The intensity for silicon was not measured as its presence was probably due to particles of dust or impurities associated with the gold. For a few samples (G.3, G.11, G.13, S.6, S.9, and S.14) the results are given qualitatively, as they were analysed using different conditions from those given above.

Tables 3 and 4 contain the log intensity ratios for the samples analysed. These ratios indicate the orders of concentration of the elements, and comparisons can be made of the variations in concentration of a particular element from sample to sample. However, it is not possible to compare the concentrations of different elements in one particular sample.

Summarizing the results qualitatively, it is seen that copper, iron, silver and silicon are present in all 68 samples; magnesium in 58; aluminium in 53; nickel in 27; lead in 23; antimony in 12; tin in 11; bismuth in 10; cobalt in 7; mercury in 6; zinc in 4; titanium and molybdenum in 3; beryllium and platinum in 2; and calcium, manganese, palladium and vanadium in one. Considering only the "G" series from the Barberton Mountain Land, it is indicated that copper, iron, silver and silicon occur in all 40 samples; magnesium in 35; aluminium in 30; lead in 18; nickel in 12; tin in 10; antimony and cobalt in 6; bismuth and zinc in 4; molybdenum in 3; beryllium, mercury and titanium in 2; and calcium, manganese and platinum in one. The "S" series from Zwartkopje Shoot shows the presence of copper, iron, silver and silicon in all 20 samples; aluminium and magnesium in 17; nickel in 13; antimony and mercury in 4; bismuth and lead in 2; and cobalt and vanadium in one.

The reproducibility of the log intensity ratios for most of the elements was determined by analysing a sample of native gold known to contain a large number of trace elements under the same conditions as described above. The coefficients of variation ranged between 11.5% for tin and 33.6% for magnesium, with the average for aluminium, antimony, bismuth, cobalt, copper, iron, lead, magnesium, nickel, silver, tin and zinc being 17.3%.

Sample	Cu ppm.	Fe ppm.	(Cu+Fe) %	Ag %	Au %	Fineness	Cu - ppm. Au %	Fe - ppm. Au %	Cu - ppm. Fe - ppm.
G. 1	276	251	0.05	-	-	-	-	-	-
G. 2	3121	1159	0.43	18.16	81.41	817.6	38.33	14.24	2.69
G. 3	-	-	-	-	-	-	-	-	-
G. 4	310	673	0.10	5.30	94.60	946.9	3.28	7.12	0.46
G. 5	2897	2525	0.54	5.95	93.51	940.2	30.98	27.01	1.14
G. 6	-	-	-	-	86.53	-	-	-	-
G. 7	421	159	0.06	13.63	86.31	863.6	4.88	1.84	2.65
G. 8	202	311	0.05	8.80	91.15	912.0	2.22	3.41	0.65
G. 9	1586	258	0.18	5.15	94.66	948.4	16.75	2.72	6.14
G.10	82	105	0.02	10.34	89.63	896.6	0.92	1.17	0.78
G.11	-	-	-	-	-	-	-	-	-
G.12	538	1774	0.23	-	-	-	-	-	-
G.13	-	-	-	-	-	-	-	-	-
G.14	462	226	0.07	9.29	91.64	917.0	5.04	2.47	2.04
G.15	-	-	-	-	85.76	-	-	-	-
G.16	152	330	0.05	7.40	92.55	926.0	1.64	3.57	0.46
G.17	336	725	0.11	11.07	88.82	889.2	3.78	8.17	0.46
G.18	442	219	0.07	21.27	78.66	787.2	5.62	2.79	2.02
G.19	416	260	0.07	7.04	92.88	929.8	4.47	2.80	1.60
G.20	239	390	0.06	5.40	94.54	946.0	2.52	4.13	0.61
G.21	-	-	-	-	88.45	-	-	-	-
G.22	672	565	0.12	4.67	95.21	953.2	7.06	5.93	1.19
G.23	177	1917	0.21	11.47	88.32	885.1	2.00	21.71	0.09
G.24	879	1302	0.22	16.70	83.08	832.6	10.58	15.67	0.67
G.25	-	-	-	-	89.00	-	-	-	-
G.26	187	141	0.03	9.48	90.48	905.2	2.06	1.56	1.33
G.27	135	215	0.03	9.64	90.32	903.6	1.49	2.38	0.63
G.28	604	393	0.10	7.39	92.51	926.1	6.53	4.24	1.54
G.29	304	204	0.05	14.85	85.10	851.4	3.57	2.39	1.49
G.30	279	359	0.06	2.03	97.91	979.7	2.79	3.67	0.78

Table 1 : Gold, Silver, Copper and Iron Contents of Native Gold Samples from Various Localities in the Barberton Mountain Land, together with Calculated Fineness, Copper : Gold Ratio, Iron : Gold Ratio and Copper : Iron Ratio of Each Sample

Sample	Cu ppm.	Fe ppm.	(Cu+Fe) %	Ag %	Au %	Fineness	Cu - ppm. Au %	Fe - ppm. Au %	Cu - ppm. Fe - ppm.
G.31	-	-	-	-	78.07	-	-	-	-
G.32	527	179	0.07	12.18	87.74	878.1	6.00	2.04	2.94
G.33	-	-	-	-	88.75	-	-	-	-
G.34	6168	237	0.64	24.10	75.26	757.4	81.96	3.15	26.04
G.35	378	262	0.06	10.99	88.95	890.0	4.25	2.95	1.44
G.36	131	126	0.03	12.54	87.42	874.6	1.50	1.44	1.04
G.37	207	185	0.04	11.57	88.39	884.3	2.35	2.10	1.14
G.38	124	175	0.03	10.70	89.27	893.0	1.38	1.96	0.71
G.39	473	1754	0.22	11.42	88.36	885.6	5.35	19.85	0.27
G.40	71	137	0.02	7.12	92.86	928.8	0.76	1.48	0.52
G.41	167	82	0.02	1.99	97.99	980.1	1.70	0.84	2.04
G.42	156	73	0.02	11.99	88.79	888.1	1.76	0.82	2.14
G.43	77	1068	0.11	9.59	90.30	904.0	0.85	11.82	0.07
G.44	211	127	0.03	9.35	90.62	906.5	2.11	1.40	1.66
G.45	171	3261	0.34	5.69	93.97	942.9	1.82	34.76	0.05
G.46	380	78	0.05	5.27	94.67	947.3	4.01	0.82	4.88

Table 1 : Gold, Silver, Copper and Iron Contents of Native Gold Samples from Various Localities in the (Contd.) Barberton Mountain Land, together with Calculated Fineness, Copper : Gold Ratio, Iron : Gold Ratio and Copper : Iron Ratio of Each Sample

Sample	Cu ppm.	Fe ppm.	(Cu + Fe) %	Ag %	Au %	Fineness	Cu – ppm. / Au %	Fe – ppm. / Au %	Cu – ppm. / Fe – ppm.
S.1	612	223	0.08	15.39	84.53	846.0	7.24	2.64	2.75
S.2	821	263	0.11	6.95	92.93	930.4	8.84	2.83	3.12
S.3	246	1063	0.13	5.47	94.40	945.2	2.61	11.26	0.23
S.4	670	333	0.10	7.77	92.12	922.2	7.23	3.61	2.01
S.5	–	–	–	–	–	–	–	–	–
S.6	345	278	0.06	6.84	93.10	931.6	3.71	2.98	1.24
S.7	139	1492	0.16	6.81	93.03	931.8	1.50	16.04	0.09
S.8	176	1088	0.13	8.74	91.13	912.5	1.93	11.94	0.16
S.9	304	1140	0.14	4.08	95.78	959.1	3.18	11.91	0.27
S.10	286	1285	0.16	7.08	92.76	929.1	3.08	13.86	0.22
S.11	–	–	–	–	–	–	–	–	–
S.12	274	1026	0.13	6.08	93.79	939.1	2.92	10.94	0.27
S.13	–	–	–	–	–	–	–	–	–
S.14	207	1035	0.12	8.03	91.84	920.2	2.25	11.27	0.20
S.15	491	502	0.10	1.70	98.20	983.0	5.00	5.11	0.98
S.16	1005	688	0.17	5.51	94.31	944.8	10.66	7.29	1.46
S.17	–	–	–	–	–	–	–	–	–
S.18	341	596	0.09	7.02	92.89	929.7	3.68	6.41	0.57
S.19	290	1187	0.15	6.32	93.52	936.7	3.10	12.69	0.24
S.20	–	–	–	–	–	–	–	–	–
S.21	371	2023	0.24	4.49	95.20	955.0	3.89	21.25	0.18
S.22	647	202	0.08	6.11	93.81	938.9	6.89	2.15	3.20

Table 2 : Gold, Silver, Copper and Iron Contents of Native Gold Samples from Various Levels on the Zwartkopje Shoot, Sheba Mine, together with Calculated Fineness, Copper : Gold Ratio, Iron : Gold Ratio and Copper : Iron Ratio of Each Sample

THE SIGNIFICANCE OF THE RESULTS

A. OCCURRENCE OF TRACE ELEMENTS IN NATIVE GOLD

(a) Theoretical Considerations

In considering the modes of occurrence of trace elements in gold, several factors must be taken into account, viz. the possibility of these elements entering into the gold lattice, i.e. of solid solution between gold and its trace elements; the metallurgical evidence for alloys being formed between gold and the trace elements; and the associated ore and gangue minerals which could be present as inclusions.

Solid solution between two elements is controlled by three factors: (i) the size factor; (ii) the relative valency effect; (iii) the electrochemical factor. Complete solid solubility of two elements is only possible if the elements have the same crystal structure and similar atomic radii. When the atomic radii differ by less than about 15%, the size factor is favourable for solid solution formation. For example, silver and gold which form a complete solid solution series have the same structure (face-centred cubic), and their atomic radii differ by only 0.2%. Molybdenum and silver, however, have a limited solid solubility, even though the size factor is favourable, since the structure of molybdenum is body-centred cubic. If the sizes differ by 8 - 15%, there is usually a continuous series of solid solution with a minimum in the liquidus curve, representing a tendency towards eutectic formation.

With regard to the electrochemical effect, it is found that, the more electronegative the solute element and the more electropositive the solvent (or vice versa), the greater is the tendency to restrict solid solution ranges, and to form inter-metallic compounds. For example, elements such as S, Se, Te (Group VI B in the Periodic Table), which have a high electronegativity, tend to form stable compounds with the electropositive metals, and have only very limited solid solubility in them. The Group V B elements (P, As, Sb, Bi) are less electronegative in character than those of Group VI B, and tend to dissolve, up to a few atomic percent, in the electropositive metals. As the elements approach each other in the electro-chemical series, so the degree of solid solubility between them increases.

Solubility is also affected by the valencies of the metals, and it is found that, generally, a metal of lower valency will more readily dissolve a metal of higher valency. For example, silicon dissolves less than 2 atomic percent copper, while copper dissolves 14 atomic percent silicon; magnesium dissolves less than 0.2 atomic percent gold, but dissolves in gold to the extent of 20 - 30 atomic percent. Thus, it is seen that a solvent element has a definite capacity to absorb the valence electrons of a solute element when the size factor is favourable. However, the amount dissolved decreases as the valency increases. Maximum solubility corresponds to a ratio of valence electrons to atoms of 1.4 to 1. The ratio of valence electrons to atoms is known as the electron concentration.

Of the several types of solid solution discussed by Barrett (1952), two seem to be pertinent to the mode of occurrence of trace elements in the gold lattice. These are the substitutional and the interstitial solid solutions. The former occurs when the solute atoms actually substitute for the solvent atoms in the crystal lattice. The solute atoms can replace the solvent atoms in all proportions, and do not alter the crystal structure. Interstitial solid solutions occur when atoms with small radii are accommodated in the interstices of the lattice of a solvent. Only those atoms with radii less than 1Å are known, or are likely, to form interstitial solutions.

The above generalisations on solid solubility are based on discussions by Barrett (1952), Evans (1952), and Pearson (1958).

Sample	Al	Sb	Be	Bi	Ca	Co	Cu	Fe	Pb	Mg	Mn	Hg	Mo	Ni	Pd	Pt	Ag	Si	Sn	Ti	V	Zn
G. 1							1.31	0.90	1.13	0.13							+0.12	P				0.80
G. 2							0.31	0.40		0.38			0.83	0.95			0.07	P				1.21
G. 3						P	P	P	P			P		P			P	P				
G. 4		1.46					1.47	0.60	0.89	0.07							0.34	P		1.40		
G. 5	1.61	0.71					0.41	0.29	1.91	0.16			1.52	1.90			0.20	P	1.30			
G. 6	0.72				1.71		0.95	0.99									+0.07	P				
G. 7	1.40						1.27	1.06		+0.61							+0.09	P				
G. 8	1.13						1.55	0.88		0.53	1.14						0.27	P				
G. 9	0.97			1.06			0.52	0.84		0.07							0.31	P	0.49			0.81
G.10	1.22						2.15	1.54		0.34							0.20	P				
G.11	P						P	P		P		P		P			P	P				
G.12						P	P	0.35		+0.31							+0.29	P				
G.13	P					P	P	P		P				P			P	P				
G.14	1.25	1.75				2.00	1.21	1.01	1.48	0.27				0.78			0.81	P				
G.15							1.30	1.20	0.81								0.24	P				
G.16	1.20						1.75	0.80		+0.35							0.41	P				
G.17	1.09						1.49	0.60	0.74	0.64							0.50	P				
G.18	1.10			1.71			1.10	1.03		0.04							0.04	P				
G.19	1.33						1.10	0.80	1.13	0.23							0.53	P				
G.20	1.26						1.67	0.78	1.33	+0.10							0.46	P				
G.21	1.38						1.57	0.35	1.57	0.49							0.63	P				1.62
G.22	1.24		0.79				0.94	0.70		+0.09							0.56	P				
G.23	1.16						1.60	0.40		0.40							0.08	P				
G.24	0.97						0.77	0.51		+0.13				0.99			0.14	P	0.16			
G.25				1.65		1.03	1.27	0.46		+0.16				0.43			0.32	P				
G.26	1.17						1.58	1.50		0.68							0.32	P				
G.27	1.27						1.88	1.05									0.03	P				
G.28	1.45						0.90	0.80		0.45				1.71			0.63	P	1.18			
G.29							1.29	1.18	0.34	0.71							0.14	P	0.68	1.24		
G.30	0.44						1.30	0.58		+0.20							0.25	P	0.58			

Table 3 : The Minor and Trace Elements Present in Native Gold Samples from Various Localities in the Barberton Mountain Land

(figures represent log intensity ratios of elements to gold as an internal standard, and are all prefixed by a minus sign, except those shown with an actual plus sign; P = element present but not determined quantitatively)

Sample	Al	Sb	Be	Bi	Ca	Co	Cu	Fe	Pb	Mg	Mn	Hg	Mo	Ni	Pd	Pt	Ag	Si	Sn	Ti	V	Zn
G.31	1.17						1.29	0.80		0.42							0.46	P				
G.32	1.43						0.90	1.05						1.68			0.66	P				
G.33	1.24	1.95				1.95	1.27	1.57	0.73	0.35				0.20			0.55	P	1.24			
G.34	1.22						+0.07	1.09		0.25			0.68				1.06	P				
G.35	0.53						1.12	0.90		+0.64							0.02	P				
G.36							1.80	1.30	0.10	+0.01							+0.72	P				
G.37							1.50	1.36	1.34	0.59							0.28	P	1.12			
G.38	1.03		1.11	1.16			1.90	1.41	1.50	0.56							0.16	P	0.74			
G.39	1.00	1.74					1.05	0.44	1.37	0.50				1.48		1.14	0.69	P	0.71			
G.40	0.95	0.71				1.67	2.20	1.24		0.67							+0.09	P				
G.41	1.37	1.45					1.78	1.50	1.76	0.88							1.06	P				
G.42	1.08						1.90	1.60									0.32	P				
G.43	1.10	1.60					2.10	0.52	0.79	0.06				0.95	1.32		0.32	P				
G.44				1.52			1.60	1.18	0.56	1.71							0.20	P	1.08	1.44		
G.45	1.15			1.18			1.70	0.45		1.00						1.27	0.63	P				
G.46							1.16	1.30		0.48							0.20	P				

Table 3 : The Minor and Trace Elements Present in Native Gold Samples from Various Localities in the (Contd.) Barberton Mountain Land

(figures represent log intensity ratios of elements to gold as an internal standard, and are all prefixed by a minus sign, except those shown with an actual plus sign; P = element present but not determined quantitatively)

Sample	Al	Sb	Be	Bi	Ca	Co	Cu	Fe	Pb	Mg	Mn	Hg	Mo	Ni	Pd	Pt	Ag	Si	Sn	Ti	V	Zn
S.1	1.24						0.90	0.96		0.68				1.35			0.53	P				
S.2		1.10					0.78	0.90		0.30				1.23			0.73	P				
S.3	1.34						1.51	0.50		0.61							0.27	P				
S.4	1.32			1.56			0.80	0.83						0.44			0.45	P				
S.5	1.14	1.61					1.20			1.03				1.16			0.31	P				
S.6							P	0.55		P		P		P			P	P				
S.7	1.15						1.30	0.80		1.26				1.55			0.42	P				
S.8	1.18						2.00	0.29		1.25				1.41			0.75	P				
S.9	P			0.60			P	P		P							P	P				
S.10	1.68	1.12					1.30	0.50		1.71				1.73			0.66	P				
S.11	1.41	1.43					1.53	0.46						1.36			0.47	P				
S.12	1.60						1.45	0.85	0.84	0.33		1.62		0.94			0.30	P			1.60	
S.13	P						1.40	0.52		1.05		P		1.59			0.26	P				
S.14							P	P		P							P	P				
S.15	1.11						1.60	0.55		0.85				1.48			0.53	P				
S.16	1.23					1.08	1.01	0.75	1.18	0.93							0.27	P				
S.17	1.51						0.60	0.59		0.83							0.57	P				
S.18	1.12						1.22	0.51		0.63							0.15	P				
S.19	1.37						1.32	0.70						1.24			0.38	P				
S.20	1.41						1.43	0.43		1.41		1.90					0.57	P				
S.21	1.39			1.49			1.70	0.40		0.32				0.80			0.39	P				
S.22	1.23						0.90	1.00									0.63	P				

Table 4 : The Minor and Trace Elements Present in Native Gold Samples from Various Levels on the Zwartkopje Shoot, Sheba Mine, as Determined Spectrographically

(figures represent log intensity ratios of elements to gold as an internal standard, and all are prefixed by a minus sign, except those shown with an actual plus sign; P = element present but not determined quantitatively)

The maximum solid solubility in gold of each of the various trace elements detected has been determined from previous metallurgical investigations (Hansen, 1958; Pearson, 1958) as follows (figures represent atomic percent) :-

aluminium	15.50	iron	65.00	platinum	100.00
antimony	1.12	lead	0.09	silicon	limited
arsenic	0.20	magnesium	32.50	silver	100.00
beryllium	negligible	manganese	32.00	tellurium	negligible
bismuth	0.07	mercury	19.30	tin	6.80
calcium	< 1.80	molybdenum	1.25	titanium	8.50
cobalt	24.00	nickel	100.00	vanadium	17.50
copper	100.00	palladium	100.00	zinc	33.60

(b)   Mode of Occurrence of Individual Elements

(i)   Aluminium

Aluminium was one of the most frequently encountered constituents in the gold samples, being detected in 53 of the 68 analysed. The intensity ratios varied from -1.68 in S.10 (22 Level Zwartkopje Shoot) to -0.44 in G.30 (Thomas).

This common occurrence of aluminium in gold suggests the possibility of its occurring as a trace alloy constituent, in support of which it has been shown that up to 15.5 atomic percent aluminium can enter into the gold lattice. However, aluminium is present in large amounts in the common gangue minerals, such as chlorite and sericite, and there might be contamination by these minerals. This possibility is supported by the fact that, despite the precautions taken to ensure the purity of the samples analysed, silicon was found in all of them. Therefore, it is considered that part, if not all, of the aluminium is present in the form of gangue inclusions. This agrees with the findings of Crook (1939) and Warren and Thompson (1944).

(ii)   Antimony

Antimony was detected in 12 of the samples analysed, with the intensity ratio varying from -1.95 in G.33 (Tiger Trap) to -0.71 in G.5 (Beaver Trap, South Reef) and G.40 (Zwartkopje, deep levels).

Metallurgical evidence indicates that, despite a favourable size factor, antimony is only taken into the gold lattice with difficulty, having a solid solubility of 1.12 percent. The possibility of the antimony being present as inclusions of stibnite must, therefore, be considered, especially when it is remembered that antimonial gold ore is quite common in the Barberton area. However, stibnite was seen only in 3 samples - S.10, S.11, S.12 (22 Level, Zwartkopje Shoot). Two of these, S.10 and S.11, contained antimony, with intensity ratios of -1.12 and -1.43 respectively, and there is a possibility of antimony being present as inclusions of stibnite. Generally, however, it is considered that the cleaning process was efficient with respect to stibnite, since it is soluble in both hydrochloric and nitric acids. Antimony, therefore, appears

to be chemically associated with the gold, and it is considered possible for it to be in the gold lattice.

(iii)   Arsenic

Arsenic was not detected in any of the gold samples analysed, despite the fact that Steele and Carlton (1961) reported it in all three of the gold samples from the Barberton area, which they examined.

Metallurgical evidence indicates that arsenic enters into solid solution with gold only in very small amounts, even though arsenopyrite is one of the most common host minerals of gold (Lincoln, 1911; Schwartz, 1944). Arsenopyrite was observed in almost all the gold samples investigated, and the absence of arsenic from the samples is considered to be a measure of the efficiency of the cleaning process. However, the failure to identify arsenic might be due to the fact that the detection limit of arsenic in the d.c. arc is very high - 100 ppm. - (Ahrens and Taylor, 1961), and that the element is present in smaller amounts than this. It is suggested that arsenic does not occur alloyed with native gold, and that previously reported occurrences of the metal in gold are due to inclusions of arsenopyrite.

(iv)   Beryllium

Beryllium was detected in two samples, G.21, (Ivy Reef, 900' Level) and G.38 (Worcester), the intensity ratios being -0.79 and -1.11 respectively. As far as could be ascertained, beryllium has not been previously reported in native gold, though Degtyareva and Ostrovskaya (1960) did recognise it in chemically recovered gold.

The mode of occurrence of beryllium in the gold is uncertain. There appears to be no possibility of gangue inclusions, since no beryllium minerals have been reported in the Barberton area, and metallurgical data do not indicate the presence of beryllium in the gold lattice. The beryllium atom has a relatively small radius (1.12 Å), compared with that of gold (1.44 Å), and it might be present as an interstitial solid solution. Barrett (1952) mentions that the formation of interstitial solid solutions is, however, restricted to those atoms with radii less than 1 Å.

(v)   Bismuth

Bismuth was detected in ten samples, with intensity ratios varying from -1.71 in G.18 (Independent) to -0.58 in G.43 (Cason Section, E.R.P.M.).

No bismuth minerals were observed in the heavy concentrates of the samples analysed, and despite the fact that metallurgical evidence is against the presence of bismuth in solid solution with gold, it is suggested that the trace amounts of bismuth detected are chemically associated with the gold. This conclusion is supported by the existence in nature of a gold-bismuth alloy known as maldonite.

(vi)   Calcium

Calcium was recognised only in sample G.5 from the South Reef of the Beaver Trap Mine. Metallurgically, solid solubility of calcium in gold is not indicated, and it is suggested that the element is present as a gangue inclusion of some calcium-bearing mineral.

(vii)   Cobalt

In the present investigation, seven samples were shown to contain cobalt, the intensity ratios varying from -2.00 in G.14 (Fortuna) to -1.03 in G.25 (Maid of de Kaap).

It has been proved that up to 20 per cent cobalt in capable of entering into the gold lattice. This, together with the fact that no cobalt minerals were observed, suggests that the cobalt detected is chemically associated with the gold and in solid solution with it.

(viii)   Copper

Copper was found to be present in all samples, in amounts varying from 71 ppm. in G.40 (Zwartkopje) to 6168 ppm. in G.34 (Verdite). These observations confirm the conclusions of Crook (1939) and Warren and Thompson (1944) that it is a constant constituent of native gold.

Metallurgical data indicate that copper is capable of complete solid solubility in gold, but the possibility of at least some of the copper taking the form of inclusions of copper minerals cannot be discounted since chalcopyrite, covellite, chalcocite and tennantite were identified in the heavy mineral concentrates of the samples. Polished-sections showed that some gold grains contain minute inclusions of chalcopyrite. This mineral was present in sample S.16, which contained 502 ppm. copper, and chalcopyrite, covellite and chalcocite in sample G.2 (Albion) which revealed a copper content of 3121 ppm. On the other hand, the gold of sample G.34 (Verdite) contained 6168 ppm., but no copper minerals were found in the associated sulphides.

It is thought that the majority of the copper detected in the gold samples is present in solid solution with the gold, as concluded by Crook (1939).

(ix)   Iron

Iron, like copper, was found in all the gold samples in the present investigation, in amounts varying from 73 ppm. (G.42, Selukwe) to 3261 ppm. (G45, West Rand Consolidated).

Even though up to 65 per cent iron is capable of entering the gold lattice, it seems possible that some of the iron detected might be present as inclusions of pyrite, in agreement with the conclusions of Crook (1939). This mineral is one of the dominant sulphides identified in the heavy mineral concentrates, and, even though it is considered that the cleaning process was reasonably efficient in the removal of the sulphide minerals, pyrite inclusions in gold grains were observed under the ore microscope.

(x)   Lead

Lead was found in 23 of the 68 samples analysed, the intensity ratios varying from -1.91 in G.5 (Beaver Trap, South Reef) to -0.10 in G.36 (Weltevreden).

Metallurgical evidence indicates that only minute amounts of lead can be accommodated in the gold lattice, suggesting that much of the lead might be present as mineral inclusions. However, in the heavy mineral concentrates of the 68 samples galena was present in five samples only - G.3 (Alpine), G.29 (Rosetta), G.30 (Thomas), G.38 (Worcester), and G.41 (Globe and Phoenix). Lead was spectrographically detected in G.3, G.29, G.38 and G.41, and it is possible that some of the lead in these four samples occurs

in the gold as sulphide inclusions. The fact that lead is such a common constituent of native gold, even when no lead minerals appear to occur with it, favours the contention that the relationship is one of a more fundamental nature, and that much of the lead is actually chemically associated with the gold. Gerlach and Schweitzer (1928) have shown that lead tends to be deposited on the boundaries of gold grains.

(xi)   Magnesium

Magnesium, like aluminium, is one of the most common elements detected in the gold samples, occurring in 58 of them, with intensity ratios varying from -1.71 in G.44 (Market Square, Johannesburg) and S.10 (22 Level Zwartkopje Shoot) to +0.64 in G.35 (Verdite Extension).

The frequency of occurrence, together with the fact that up to 32 per cent magnesium can be accommodated in the gold lattice, favours some chemical association between the two elements. However, magnesium-bearing minerals, such as chlorite and talc, were seen to be very common in the samples studied, and, as silicon was identified spectrographically in all the samples, it is quite possible that the magnesium occurs as inclusions of a gangue mineral in the gold.

(xii)   Manganese

Manganese was found in one sample only - G.8 (Clutha). The element is capable of entering into solid solution with gold in fairly large concentrations (up to 32 per cent), and, as no manganiferous minerals were observed in the samples, it seems likely that the manganese is present in the gold lattice.

The relative paucity of manganese is not in accordance with the findings of previous investigators. Steel and Carlton (1961) reported its presence in gold from the Lily and Trichardt's Luck mines, and Warren and Thompson (1944) detected it in 40 of the 66 samples which they analysed. This feature might be due to the removal of the element during the cleaning of the samples, as manganese is soluble in all the acids used. However, as has been mentioned in the discussion on the cleaning process, it is unlikely that any trace elements were removed by dissolution during the washing of the samples. The detection limit of manganese in the d.c. arc is 10 ppm. (Ahrens and Taylor, 1961), and it is possible that, if the element is present in amounts less than this, it would not have been identified.

(xiii)   Mercury

Mercury was recognised in six of the samples analysed. It is capable of entering into partial solid solution with gold, and as no mercury minerals were observed, it seems likely that the element is alloyed with the gold. This conclusion is supported by the discovery of natural gold-mercury amalgam at Mariposa in California.

(xiv)   Molybdenum

Molybdenum was found to be present in three samples, G.2 (Albion), G.5 (Beaver Trap, South Reef) and G.34 (Verdite), with intensity ratios of -0.83, -1.52 and -0.68 respectively.

Metallurgical findings indicate that, despite a favourable size factor, only 1.25 per cent molybdenum can be taken into the gold lattice. However, as no molybdenum-bearing minerals were

identified in the samples, it is thought that the molybdenum is present in solid solution with the gold.

(xv)   Nickel

Nickel was identified in 27 samples, including most of those from the Zwartkopje Shoot. The intensity ratios varied from -1.90 in G.5 (Beaver Trap, South Reef) to -0.20 in G.33 (Tiger Trap). The element is capable of forming a complete solid solution series with gold and, as no nickel minerals were observed in the heavy concentrates, it is suggested that the element occurs in the gold lattice. However, both pyrrhotite and pyrite may contain nickel atoms in their structures, and it is possible that the nickel is present in inclusions of these minerals.

(xvi)   Platinum and Palladium

Platinum was recorded in two of the samples analysed, G.39 (Wyldesdale) and G.45 (West Rand Consolidated), while palladium was detected in sample G.43 only (Cason Section, E.R.P.M.). Both the elements are capable of complete solid solution with gold. The three elements are associated in nature, and alloys of palladium and gold (porpezite), and of palladium, silver and gold are known. The possibility of platinum and palladium being present as mineral inclusions is very unlikely, and it was concluded that they are actually in the gold lattice.

(xvii)   Silicon

Silicon was found in all samples, despite the vigorous cleaning treatment designed to remove inclusions of quartz and silicates adhering to the grains. However, as chert and quartz were by far the most common gangue minerals recognised, and as metallurgical data have shown that silicon and gold are only capable of very limited solid solution, it must be accepted that the silicon is present as gangue inclusions.

(xviii)   Silver

Silver occurred in all samples in amounts varying from 1.7 per cent (S.16, 25 Level, Zwartkopje Shoot) to 24.1 per cent (G.34, Verdite). There is complete solid solubility between gold and silver, though Zemczuzny (1926) found that, in nature, gold-silver alloys tend to have definite compositions. Native gold alloys containing up to 30 per cent silver are common, while electrum (30 - 43 per cent silver) is rare. Natural alloys containing 72 - 81 per cent silver are also common, while pure native silver usually contains less than 1 per cent gold. No silver minerals were observed in the samples, and it was concluded that the silver is alloyed with the gold. The results confirm Crook's (1939) and Warren's and Thomson's (1944) findings that silver is a constant associate of native gold.

(xix)   Tellurium

Tellurium was not detected in any of the samples analysed, despite the fact that the element is considered by Lincoln (1911) to be one of the most common associates of gold. However, metallurgical evidence indicates that only negligible amounts of tellurium are soluble in gold, and this suggests that

previously reported occurrences of tellurium in gold may be due to inclusions of minerals such as calaverite and sylvanite.

It should be mentioned that the detection limit of tellurium in the d.c. arc is 200 ppm. (Ahrens and Taylor, 1961), a fact which may account for the element not being identified in the native gold samples.

(xx)   Tin

Tin was identified in 11 samples, none of which came from the Zwartkopje Shoot. The intensity ratio varied from -1.30 in G.5 (Beaver Trap, South Reef) to -0.16 in G.24 (Madeline). It has been established that tin is capable of partial solid solution in gold, and because no tin-bearing minerals were observed in the gold concentrates, it was decided that the element is probably present in native gold as an alloy constituent.

(xxi)   Titanium

Titanium was detected in three samples only - G.4 (Beaver Trap, North Reef), G.29 (Rosetta) and G.44 (Market Square, Johannesburg), with intensity ratios of -1.40, -1.24 and -1.44 respectively.

The element is capable of partial solid solution in gold. However, iron oxides, including ilmenite, were fairly common in the heavy mineral concentrates of the samples, and it can be taken that titanium might be present in the gold either as a mineral inclusion or as an alloy constituent. The absence of titanium from the majority of the gold samples is in marked contrast to the results obtained by Warren and Thompson (1944) who found that titanium was so wide-spread in gold that its absence was of more interest than its presence.

(xxii)   Vanadium

Vanadium was identified in one sample only, viz. S.11 from 22 Level of the Zwartkopje Shoot. The element is capable of partial solid solution in gold, and, as vanadium minerals were found to be relatively rare, the element is thought to be present as an alloy constituent of the gold. However, Barberton gold seems to be vanadium-poor, compared to that from other occurrences as Warren and Thompson (1944) reported it in 28 of the gold samples selected from occurrences throughout the world.

(xxiii)   Zinc

Zinc was observed in four samples - G.1 (Agnes), G.2 (Albion), G.8 (Clutha) and G.21 (Ivy Reef, 900' Level). Metallurgical information reveals that up to 30 per cent zinc can enter into solid solution with gold. Although no zinc minerals were seen in the heavy mineral concentrates, sphalerite was identified in polished-sections of ore from the Agnes Mine and the Ivy Reef. Therefore, the possibility does exist of the presence of zinc being due to mineral inclusions, though it is probable that some of it, at least, is alloyed with the gold.

(c)   Summary and Conclusions

From the above discussion on the individual elements in the gold, it is evident that a large number of them are probably present as mechanical inclusions. Aluminium, calcium, magnesium and silicon are the main elements which fall into this category. Of the other elements detected, beryllium, bismuth, cobalt, manganese, mercury, molybdenum, palladium, platinum, silver, tin and vanadium are thought to occur solely as alloy constituents in solid solution with gold. Antimony, copper, iron, lead, nickel, titanium, and zinc are thought to be present both in the gold lattice and as mineral inclusions.

Generally, these conclusions agree with those of Crook (1939), Warren and Thompson (1944), and Boyle (1961). Crook considered that only copper and silver are definitely alloyed with the gold, the other elements occurring as non-metallic inclusions, either on the grain boundaries or in the actual gold crystals. Boyle believed that titanium and vanadium are present as mineral contaminators and that arsenic occurs in the gold lattice. Warren and Thompson argued that both arsenic and tellurium are chemically associated with native gold, but the present investigation appears to indicate that these two elements occur in gold as mineral inclusions.

B.   VARIATION IN COMPOSITION OF GOLD IN THE ZWARTKOPJE ORE-SHOOT

(a)   Reliability of Results

An attempt has been made to correlate the observed variations in the composition of the samples of native gold taken in the Zwartkopje Shoot with varying physical factors, such as depth of deposition and associated gangue minerals. It must be emphasised that the results obtained are by no means statistically sound, and need not necessarily apply to other samples of gold in the same ore-shoot. In the first place, it was not possible to collect sufficient samples from each level of the mine to allow for a statistically satisfactory determination of the mean composition. On 17, 18 and 23 levels only one sample was obtainable which could be subjected to all three types of analysis, and the maximum number of samples collected on any one level were the four on 26 Level.

Another factor which detracts from the statistical reliability is the variable composition of individual grains of gold. Eales (1961) noted that the colour of the individual grains from the Olympus Mine, Southern Rhodesia, varied from ruddy gold (approximately 950 fine) to pale yellow (600 fine), and that the widest variations could be seen in grains only a few hundred microns apart. Other workers who have remarked on the difference in colour of grains from a single sample include Russell (1929), Mather (1937) and Edwards (1958). Fineness variations within a single grain have been observed by Head (1935) who noted that individual grains had gold-rich cores, and by Eales (1961) who observed the reverse, i.e. silver-rich cores.

From Tables 2 and 4 it can be seen that the composition of gold samples from the individual levels varies markedly. For example, on 14 Level the fineness varies from 846 to 945 parts per thousand; the copper-gold ratios from 2.61 to 8.84, and the iron-gold ratios from 2.64 to 11.26. The trace elements also vary from sample to sample. On 20 Level, the differences in the composition of the two samples are not so marked. On 22 Level the copper and iron contents and the finenesses agree fairly well, but the trace element composition varies. On 25 Level, the fineness ranges from 920 to 983, and there are also noticeable variations in the copper-gold and iron-gold ratios, and in the trace element composition, cobalt and lead

being present in one sample, mercury in another, nickel in the third, while aluminium and magnesium are common to all three. On 26 Level the variations in the fineness are not as marked as those in the copper and iron contents. In the two samples from 24 Level of the Birthday Shoot there is a very distinct difference in composition. The finenesses, copper and iron contents differ widely in the two samples, and while S.21 contains aluminium, bismuth, magnesium and nickel, S.22 contains only aluminium.

From the above it would appear doubtful whether any systematic variation in the mean composition for each depth level would have any significance unless a large number of samples were collected to make the results statistically sound. However, it is suggested that the systematic changes in composition described in the following sections might have some significance, and are not merely the products of coincidence.

(b) Variations in Fineness

To determine the change in the gold : silver ratio with depth, the mean fineness on each level was plotted against increasing depth in Fig. 2. The vertical lines represent the range of fineness in the individual samples. It appears that there is an increase in fineness from 14 Level to 18 Level. Between 18 and 20 levels there is a slight decrease, after which the values increase steadily to 26 Level. Whether the lower fineness value for 20 Level really exists cannot be definitely stated from the small number of determinations made. However, both the copper and iron contents show a sharp break on 20 Level, and it can be expected that some change takes place in the silver content as well, assuming that all three elements were deposited in the gold simultaneously.

Fineness of gold from a single shoot has been found to vary according to the lateral position of the gold on a particular level, the grain size, and the grade of ore. Unfortunately, it was not possible to obtain sufficient samples of visible native gold from each level to allow for a systematic study of the lateral variation.

Similarly, no detailed investigation was made of the variation of fineness with grain size. Generally, there appeared to be no correlation between fineness, size, and colour of the grains. In addition, no marked colour change was observed for different grain sizes in a particular sample. In both S.2 and S.7 the gold was all coarse-grained, yet the colour was gold in S.2 and pale yellow in S.7. Very fine grains in S.12 had a gold colour, while somewhat coarser gold in S.14 was pale yellow. The colour seemed to bear little relation to the fineness, as determined by fire assay, though this was not conclusive since the colour variations were estimated visually, without reference to a particular standard. For example, in S.1 yellow-coloured gold had a fineness of 846, while in S.16 gold of a similar colour was 983 fine.

It was not possible to obtain any comprehensive data on the variation of fineness with grade of ore. Mining in the Zwartkopje Shoot has shown that the grade in a particular stope varies markedly from year to year, but no information is available on the associated changes in the silver content of the gold.

(c) Variation in Copper and Iron Concentrations

To illustrate the variation in copper and iron contents of the samples taken in the ore-shoot, the mean copper and iron concentrations on each level were plotted against the depth. The resultant curves are illustrated in Figs. 3 and 4. The vertical lines on the curves represent the range in values for individual samples on each level.

It is evident that the copper content decreases markedly from approximately 700 to 160 ppm. between 14 and 20 levels. Below the 20 Level the concentration increases steadily until it is approximately 500 ppm. on the 26 Level.

Between 14 and 18 levels the iron content of the samples behaves in a similar manner to that of copper, and decreases from 500 to 300 ppm. Between 18 and 20 levels there is an abrupt increase in the iron concentration of the gold, and at 20 Level the iron content is approximately 1200 ppm. From 20 Level down to 26 Level the concentration gradually decreases to about 900 ppm.

After comparing the ratios for copper to iron with increasing depth, Fig. 5 was prepared. From this curve it appears that the copper content decreases relative to the iron content between 14 and 18 levels. Between 18 and 20 levels this decrease becomes much more abrupt, while from 20 Level to 26 Level the copper increases regularly compared to iron.

(d) Trace Element Content

Generally, the samples of gold from the Zwartkopje Shoot appeared to have a relatively simple composition. Silver, copper and iron are present in all of them, and aluminium, magnesium and nickel in most. The presence of other elements, such as bismuth, antimony, mercury, lead and cobalt, serve to distinguish the individual samples from each other. Apart from copper, silver and iron, only aluminium, magnesium and nickel are present in at least one sample from each level. An attempt was made to relate the variations in log intensity ratios of these elements with depth by plotting Fig. 6. The horizontal lines represent the variation in intensity ratios in the individual samples.

The curve for aluminium is the only one which appears to show any consistant variation, the concentration increasing from 14 Level to 20 Level, decreasing to 22 Level, and then increasing again to 26 Level. Magnesium diminishes in concentration from 14 Level to 18 Level, and then increases slightly to 26 Level. The nickel content decreases to 17 Level, improves to 18 Level, and then remains relatively constant. However, there are wide variations in the amounts of nickel and magnesium in the individual samples on each level, and this casts some doubt on the validity of the overall variation in the shoot.

Of the other trace elements in the samples, antimony is present in S.2 (14 Level), S.7 (18 Level), and S.10 and S.11 (22 Level). The intensity ratios show no systematic variation with increasing depth, and the antimony in S.10 and S.11 may be correlated with the presence of stibnite on 22 Level. Bismuth was found in S.7 from 18 Level, S.12 from 22 Level, and S.21 from 24 Level (Birthday Shoot). Cobalt is a constituent of S.16 (25 Level) only, and lead of S.12 (22 Level) and S.16 (25 Level). Mercury was detected in four samples - S.6 (17 Level), S.13 (23 Level), S.14 (25 Level), and S.20 (26 Level). Once again, the intensity ratios showed no systematic variation. Vanadium is present in S.11 on 22 Level.

(e) Discussion of Results

(i) Variations in Fineness

Considering the usual sequence of ore deposition, as initially proposed by Emmons (1924), the fineness would be expected to increase with depth since gold tends to be deposited at greater depths than silver. The results obtained in the Zwartkopje Shoot are in agreement with this generalisation. Substantiating the argument, Fisher (1945) reported that gold from shallow, epithermal deposits normally has a much higher silver content than mesothermal or hypothermal gold. However, Eales (1961) concluded

from his study of the Olympus, Lonely and Horn mines that the composition of gold changed during precipitation from silver-rich in the early stages to silver-poor in the late stages.

Increase in fineness of gold ores with depth has been determined for many deposits from bullion assays and mine production records. Whether such results can be compared with fineness determined for free gold is a matter of conjecture. Fisher (1945) reviewed the available data for hydrothermal deposits throughout the world, and concluded that, in general, fineness of gold showed an increase with increasing depth of deposition. His conclusions have been supported by the later work of Colin (1946) in the Macequece Goldfield, Madagascar; of Mills (1954) in the O'Brien Mine, Quebec; and by Edwards (1958) in the Maude and Yellow Girl mines, Victoria.

Contrary opinions about the increase in fineness with depth have been expressed by Sharwood (1911) and Zviagintsev, et al (1938). The former found that the gold-silver ratio of gold from the Homestake Mine decreased with increasing depth from 400 feet to over 1000 feet. Zviagintsev and his co-workers found that gold samples collected from different levels in the Baleisk Mine, Transbeikalia, showed no change in composition with increasing depth from surface to 120 metres.

Several examples of decreasing fineness with depth are provided by secondary enrichment of gold in the oxidized zone. Anhaeusser (1963) found that, in the Lily Mine, Barberton, the gold-silver ratio in the sulphide ore is approximately 8 : 1, while that in the oxidized zone is 11 : 1. In the present investigation, a sample from the shallow levels of the Golden Quarry Mine revealed a fineness of 926 compared to one with a fineness of 889 from the deeper levels (G. 16 and G. 17 respectively). Don (1897), Knopff (1913), Mackay (1944), Fisher (1945) and Colin (1946) recorded similar observations, though Sharwood (1911) found that oxidized free gold from the Homestake Mine was richer in silver than unoxidized gold.

Decreases in the fineness of primary gold ores with depth have been reported by MacGregor (1928) from the Lonely Mine, Southern Rhodesia, and by Bruce (1943) for several Ontario gold mines.

With respect to the possible correlation between grain size and fineness, Sharwood (1911), Prentice (1939-40) and Mackay (1944) all found that coarser grains of gold were purer than finer particles. The opposite relationship of increasing fineness with decreasing particle size has, however, been reported by Mills (1954) and Eales (1961).

The general increase in fineness of visible gold with increasing depth down the Zwartkopje Shoot is in accordance with the normal order of deposition of elements from ore fluids. The irregularity in the pattern of fineness on 20 Level may indicate a change in the nature of the gold above and below this level.

(ii) Variations in Copper and Iron Contents

The differences in the copper and iron contents seem to indicate two different types of gold mineralization in the Zwartkopje Shoot. Accepting that the variation in copper and iron concentrations should follow the normal sequence of ore deposition, as postulated by Emmons (1924), then iron would be expected to precipitate first, followed by copper. This is the case between 14 Level and 18 Level where iron is progressively impoverished relative to copper from the lowest level upwards. However, the variation below 20 Level does not follow this pattern.

Table 5 gives the associated sulphide minerals found in the individual samples, and from this it can be seen that pyrite and arsenopyrite are distributed evenly down the ore-shoot, pyrite being the

Sample	Level	Host-Rock	Sulphide Minerals	Trace Elements
S. 1	14	quartz in green schist	py, ap	Al, Cu, Fe, Mg, Ni, Ag, Si
S. 2	14	quartz in green schist	py, ap	Sb, Cu, Fe, Mg, Ni, Ag, Si
S. 3	14	milky and grey quartz	py, ap, cp	Al, Cu, Fe, Mg, Ag, Si
S. 4	17	quartz-chlorite rock	py	Al, Cu, Fe, Ni, Ag, Si
S. 5	17	quartz-chlorite rock	py, ap	Al, Cu, Fe, Mg, Ni, Ag, Si
S. 6	17	quartz	py, cp	Cu, Fe, Mg, Hg, Ni, Ag, Si
S. 7	18	milky quartz	py, ap	Al, Sb, Bi, Cu, Fe, Mg, Ni, Ag, Si
S. 8	20	quartz-chert breccia	py, ap	Al, Cu, Fe, Mg, Ni, Ag, Si
S. 9	20	quartz-chert breccia	py, ap	Al, Cu, Fe, Mg, Ag, Si
S. 10	22	quartz	sb, py, ap, cp	Al, Sb, Cu, Fe, Mg, Ni, Ag, Si
S. 11	22	quartz	ap, py, cp, sb	Al, Sb, Cu, Fe, Ni, Ag, Si, V
S. 12	22	quartz	py, ap, sb, cp	Bi, Cu, Fe, Pb, Mg, Ni, Ag, Si
S. 13	23	grey and white quartz	py, ap	Al, Cu, Fe, Mg, Hg, Ni, Ag, Si
S. 14	25	chert	py	Al, Cu, Fe, Mg, Hg, Ag, Si
S. 15	25	green schist	py, ap, cp	Al, Cu, Fe, Mg, Ni, Ag, Si
S. 16	25	green schist	py, cp, ap	Al, Co, Cu, Fe, Pb, Mg, Ag, Si
S. 17	26	chert	py, ap	Al, Cu, Fe, Mg, Ag, Si
S. 18	26	chert	py	Al, Cu, Fe, Mg, Ag, Si
S. 19	26	chert	py, ap	Al, Cu, Fe, Ni, Ag, Si
S. 20	26	chert and quartz	py, ap, cp	Al, Cu, Fe, Mg, Hg, Ag, Si
S. 21	24*	milky quartz	py, cp	Al, Bi, Cu, Fe, Mg, Ni, Ag, Si
S. 22	24*	quartz	py	Al, Cu, Fe, Ag, Si

Table 5 : Host-Rocks, Associated Sulphide Minerals, and Trace Elements in Native Gold from the Zwartkopje Shoot, Sheba Mine

(* samples from the Birthday Pipe; py : pyrite, ap : arsenopyrite, cp : chalcopyrite, sb : stibnite)

dominant sulphide. Chalcopyrite occurs in only one sample (S.3) above 18 Level, but in five samples - S.10 and S.11 (22 Level) S.15 and S.16 (25 Level), and S.20 (26 Level) - below 20 Level. Thus, there seems to be a tendency for chalcopyrite to occur more abundantly in the deeper levels of the ore-shoot, a feature which might be correlated with the increase in copper content, relative to iron, of the gold. It is also possible that the variations in copper and iron content may be due to variations in the number of chalcopyrite inclusions present in the gold crystals. This would accord with the fact that chalcopyrite becomes more common in the deeper levels. Inclusions of both pyrite and chalcopyrite could also affect the amounts of copper and iron. A decrease in the number of inclusions of pyrite relative to chalcopyrite could explain the observed increase of copper relative to iron in the gold below 20 Level. However, it seems unlikely that the number of inclusions, if present at all, would vary systematically with variable physical factors such as increasing depth.

(iii)   Variations in Trace Element Content

Too little statistically reliable information is available to draw any definite conclusions as regards the variation in the trace element composition of the gold samples from the Zwartkopje Shoot.

The relatively small variation in the amount of aluminium is noteworthy since it was concluded that the element was present in the gold as a gangue inclusion, and not as an alloy constituent. The apparently consistent development of nickel in the gold from all levels, except 17 Level, agrees with the observations made by Auger (1941) and Hawley (1952) for the nickel content of sulphides from some Canadian gold deposits.

Unlike the pattern for copper, iron and silver, the trace element composition does not indicate a marked change in the nature of the gold between 18 Level and 20 Level. The only observable and unexpected difference between the samples from the upper and lower levels, is the more frequent occurrence of mercury, lead and cobalt below 20 Level. Assuming that the trace elements in the gold are of primary origin, and were precipitated in a similar sequence to that shown by the sulphide minerals along a vein, the elements lead and mercury would be expected to occur higher up in the shoot. Emmons (1924), Lindgren (1926), Newhouse (1928), and many other workers have shown that, in hydrothermal veins, the expected order of deposition for the minerals of the minor elements detected in the gold samples would be Co, Ni, Bi, Pb, Sb and Hg. Therefore, the apparently anomalous appearance of lead and mercury in the deeper levels might indicate a change in mineralization. However, it should be mentioned that Auger (1941) observed that the trace elements in pyrite from the Hollinger Mine did not obey the normal sequence of deposition.

(iv)   General Considerations

The variations in the composition of the samples with differing physical factors, such as depth, grade of ore, and grain size (in the case of fineness), are probably expressions of the differences in condition of deposition of the gold. The most obvious physical factors likely to influence the composition of the gold at a particular point would be the prevailing pressure and temperature conditions, the concentration of the various elements in the ore fluids, the chemical environment, and, possibly, the degree of permeability of the host rocks.

That the prevailing temperature and pressure conditions at the time of deposition are important in the determination of the fineness has been demonstrated by Fisher (1945) and Colin (1946). The former found from a world-wide survey of hydrothermal deposits that it was possible to classify the type of deposit by

the fineness of the gold it contained. Hypothermal gold is always greater than 800 fine, mesothermal gold varies from 750 to 900 fine, and epithermal gold ranges from 500 to 800 fine. Colin (1946) drew the same conclusions from a study of gold veins in the Macequece field, Madagascar. Applying these results to the Zwartkopje Shoot, it is evident that the deposit is hypothermal in character.

Whether temperature or pressure plays the more dominant role in controlling the relative rates of deposition of the various elements is uncertain. Fisher (1945) considered that both were important, with temperature probably being the controlling factor, while Scherbina (1956) believed that the vapour pressure of the elements was the main controlling factor. Edwards (1958), however, decided that the pressure over a single ore-shoot could be assumed constant, and that the temperature was more important.

Possibly the most essential factor in determining the composition at a particular point is the concentration of the various elements present in the ore fluids. With regard to fineness, Edwards (1958) pointed out the fundamental importance of the amounts of silver and other elements with which it could combine instead of alloying with the gold. Provided sufficient silver were available, a factor such as temperature could control the fineness of the gold. Fisher (1945) and Eales (1961) have both suggested that ore fluids should be basically silver-poor for the silver concentrations to affect the fineness of the gold. Fisher (1945) mentions that, in the deeper early-Tertiary deposits in the Cordilleran region of the United States, the gold is deposited relatively pure, even though silver is abundant. However, at shallow levels in these deposits silver and gold combine to form a low-fineness alloy. The overall composition of the ore fluid can also affect the fineness, and Scherbina (1956) found that deposits formed from more alkaline hydrothermal solutions were richer in gold than in silver.

Most of the free gold occurring in ore-shoots is deposited late in the paragenetic sequence, and it seems obvious that the chemical or mineralogical environment may affect the composition of the gold deposited. Palmer and Bastin (1913) have shown that nearly every mineral which precipitates gold from a solution will precipitate silver as well, except for galena, pyrite, stibnite and millerite. Eales (1961) indicated that, in the Olympus Mine, the fineness may bear some relation to an associated sulphide mineral, such as chalcopyrite which is generally associated with pale yellow gold of low fineness, especially if the gold is early in the paragenetic sequence. In the Zwartkopje Shoot the reverse is apparent, as the gold has its maximum fineness in the samples from the deeper levels where chalcopyrite is more abundant.

That the chemical environment affects the trace element composition of gold from the Zwartkopje Shoot seems likely, since the copper concentration is enriched (relative to gold and iron) in the samples which contain chalcopyrite. Similarly, antimony is found in gold from samples rich in stibnite, such as S.16 and S.17 from 22 Level.

The nature of the wall-rock could also be expected to affect the composition of the gold, and Gribnitz (1961) has pointed out that the character of the ore in the Zwartkopje Shoot is clearly influenced by the host-rock. For example, the ore in shale consists mainly of massive, auriferous pyrite concentrations, and the ore in chert mainly of free gold accompanied by irregular patches of pyritic mineralization, while the ore in green schist resembles that in the chert, but with free gold being less abundant. Comparing the minor element composition (other than silver, copper and iron) of the individual samples with the host-rock (see Table 5), it appears as if some relationship might exist. All the gold samples which contained quartz only (S.6, S.7, S.10, S.11, S.12, S.21) revealed trace elements other than aluminium, magnesium and nickel, which are common to all types of host-rock. There do not appear to be any differences in the composition of gold removed from other types of host-rock.

(v)   Conclusions

From the above discussion it appears that the composition of native gold will depend largely on the local conditions prevailing at the time of deposition. Although temperature and pressure may, in general, be assumed to control the fineness of gold in a single deposit, local conditions such as the concentration of silver and minor elements in the ore fluids, the mineralogical environment, and the nature of the wall-rock, will affect the composition of the gold at a particular point. Emphasis is thus given to the statement previously made to the effect that variations in the composition of grains of free gold from certain levels need not necessarily reflect the overall variation in composition of gold along the shoot.

Even allowing for this limitation, the results obtained do seem to indicate two distinct types of gold along the Zwartkopje Shoot, which might be related to different period of mineralization.

It is suggested that the fineness and copper and iron contents for the two different types are compatible with the generally accepted sequence of deposition in veins, as proposed by Emmons (1924). From the 18 Level to 14 Level, the mean silver, copper and iron contents all increase upwards, with the copper concentration increasing at a greater rate than that for iron. In the gold from the lower levels, the mean silver and iron concentrations become progressively greater upwards from 26 Level to 20 Level, but the mean copper concentration decreases upwards between these levels, contrary to what would be expected in a normal depositional sequence where iron is considered to precipitate out before copper. The enhanced copper concentration of the gold in the deep levels, however, correlates with an increase in the chalcopyrite content of the associated ore minerals. This suggests that the high copper content of the gold may be due to local enrichment in copper from the surrounding minerals, possibly by absorption, and may not reflect the original concentration of copper in the auriferous ore fluids. The other minor elements observed in the gold possibly reflect the chemical environment of the gold at the time of deposition. This last observation agrees with the conclusions drawn by Auger (1941) that, in pyrite from gold deposits, the variations in the minor element content do not follow the general paragenetic sequence in ore deposits, but reflect changes in the environmental conditions.

The results assume considerable significance when the changes in composition of the gold, as outlined above, are studied in relation to the structural disposition of the Zwartkopje Shoot. Fig. 7 clearly shows that the marked change in the attitude of the shoot below 20 Level, and the spacing of the drives reveals that the dip is much steeper above this same level. Below 20 Level the shoot is oriented approximately parallel to the strike of the contact between the chert bar and the shale, while higher up it cuts across the different horizons, and ore is found in chert, shale and green schist. This change in attitude might have been responsible for the changes in depositional conditions which are now reflected in the change in the composition of the gold.

C.   VARIATIONS IN COMPOSITION OF GOLD FROM THE BARBERTON MOUNTAIN LAND

(a)   Reliability of Results

In this section an attempt is made to analyse the significance of the results obtained for the 40 samples collected from various localities over the whole of the Barberton Mountain Land. As with the samples along the Zwartkopje Shoot, it must be emphasised that any systematic variation in the composition of these samples cannot be taken as necessarily applying to the general variation in the nature of gold from

the Barberton area. Panned concentrates or chip samples were collected at random in a particular locality, and it does not follow that they can be regarded as representative of the particular occurrence. No allowance has been made for secondary enrichment of the gold, which has undoubtedly occurred in many of the samples from the more shallow workings, nor for the prevailing conditions at the time of deposition. In the previous section it was shown that the trace element pattern of gold from the Zwartkopje Shoot was affected by environmental conditions, and did not necessarily reflect the composition of the ore fluids. The variations in fineness, however, could generally be correlated with the overall conditions of deposition, and with the composition of the ore fluids. Therefore, it can be expected that variations in the fineness of the 40 samples will be more indicative of regional conditions of mineralization than will the trace element results which are summarised in Table 6.

(b)   Variation in Fineness

To see if there is any regular variation in fineness of the gold samples, the results from Table 6 were plotted at their respective localities, and an attempt was made to contour the values. The resultant diagram is shown in Fig. 8. It must be emphasized when considering this diagram that the contours are based on very scanty data, and represent purely subjective extrapolation and interpretation. No attempts were made to determine the spread in fineness of a large number of samples at any point, and the distance between sampling points, particularly on the Steynsdorp and Swaziland sides, is far too great for any claim to be made that the contouring is statistically valid. These severe limitations render the diagram an illustration of possible interpretation, and not a representation of factual evidence.

In the area to the south of Barberton, the fineness is interpreted as increasing regularly from 860 on the edge of the Kaap Valley Granite to 960 in the vicinity of the Agnes Mine. Proceeding further south, towards the Montrose Mine, the values decrease again to 880. For the samples collected to the northeast of the Kaap Valley Granite, it is seen that there is a similar increase in fineness from 820 to 940 away from the granite. The highest values seem to be confined to a narrow zone extending from the Sheba Mine northwestwards past the Consort Mine. Beyond this zone the fineness values diminish again towards the Nelspruit gneiss.

(c)   Variations in Copper and Iron Concentrations

In an attempt to detect any regional pattern of variation in the copper and iron contents of the native gold samples, the copper-gold and iron-gold ratios were plotted on a locality map (Fig. 9). Generally, the concentrations of copper and iron are so small that the gold contents, relative to them, may be assumed constant, and the ratios will show the same variations as the actual concentrations.

It can be seen that the samples collected from the mines occurring in the belt of Jamestown Complex rocks between the Consort and Madeline mines, generally have a much higher copper-gold ratio than those from elsewhere in the Mountain Land. Sporadic and uneconomic copper mineralization has been found in this area, particularly around the Albion Mine, and it seems possible that the high copper values in the gold may be due to the copper-rich environment. No other generalisations can be made about the distribution pattern of copper in the gold.

The arrangement of iron-gold ratios is even more haphazard than that of the copper-gold ratios, and seems to show no systematic variation. The predominance of fairly low ratios indicates that the iron concentration is relatively uniform in most of the samples. Of the exceptions, G.5 (Beaver Trap, South

Sample	Locality	Fineness	Sulphide Minerals	Trace Elements
G.1	Agnes - 14 Level	-	py	Cu, Fe, Pb, Mg, Ag, Si, Zn
G.2	Albion	817.6	co, cp, cc, py	Cu, Fe, Mg, Mo, Ni, Ag, Si, Zn
G.3	Alpine	-	ga, py	Co, Cu, Fe, Pb, Mg, Hg, Ni, Ag, Si
G.4	Beaver Trap - North Reef	946.9	py	Sb, Cu, Fe, Pb, Mg, Ag, Si, Ti
G.5	Beaver Trap - South Reef	940.2	py	Al, Sb, Ca, Cu, Fe, Pb, Mg, Mo, Ni, Ag, Si, Sn
G.6	Behind-the-Scenes	-	-	Al, Cu, Fe, Ag, Si
G.7	Black Diamond Creek	863.6	py	Al, Cu, Fe, Mg, Ag, Si
G.8	Clutha	912.0	py	Al, Cu, Fe, Mg, Mn, Ag, Si, Zn
G.9	New Consort - 38 W. Dr.	948.4	ap	Al, Bi, Cu, Fe, Mg, Ag, Si, Sn
G.10	Dreyer's Imperial	896.6	py	Al, Cu, Fe, Mg, Ag, Si
G.11	Fairview	-	-	Al, Cu, Fe, Pb, Mg, Hg, Ni, Ag, Si
G.12	Fairview	-	py, ap	Cu, Fe, Mg, Ag, Si
G.13	Forbes Reef	-	-	Al, Co, Cu, Fe, Pb, Mg, Ni, Ag, Si
G.14	Fortuna	917.0	py, cp	Al, Sb, Co, Cu, Fe, Pb, Mg, Ni, Ag, Si
G.15	French Bob's - Martin's Reef	-	-	Cu, Fe, Pb, Ag, Si
G.16	Golden Quarry - shallow	926.0	py, ap	Al, Cu, Fe, Mg, Ag, Si
G.17	Golden Quarry - deep	889.2	py, ap	Al, Cu, Fe, Pb, Mg, Ag, Si
G.18	Independent	787.2	py, cp	Al, Bi, Cu, Fe, Mg, Ag, Si
G.19	Ivy - Lester Reef	929.8	-	Al, Cu, Fe, Pb, Mg, Ag, Si
G.20	Ivy - Ivy Lead Reef	946.0	-	Al, Cu, Fe, Pb, Mg, Ag, Si
G.21	Ivy - Ivy Reef, 900 ft.	-	py	Al, Be, Cu, Fe, Pb, Mg, Ag, Si, Zn
G.22	Ivy - Ivy Reef, bottom	953.2	py	Al, Cu, Fe, Mg, Ag, Si
G.23	Lily	885.1	ap, py	Al, Cu, Fe, Mg, Ag, Si
G.24	Madeline	832.6	py	Al, Cu, Fe, Mg, Ni, Ag, Si, Sn
G.25	Maid of De Kaap	-	-	Bi, Co, Cu, Fe, Mg, Ni, Ag, Si
G.26	Maid of the Mountains	905.2	py	Al, Cu, Fe, Mg, Ag, Si
G.27	Montrose	903.6	-	Al, Cu, Fe, Ag, Si
G.28	Olga	926.1	-	Al, Cu, Fe, Mg, Ni, Ag, Si, Sn
G.29	Rosetta	851.4	ga	Cu, Fe, Pb, Mg, Ag, Si, Sn, Ti
G.30	Thomas	979.7	py, ga	Al, Cu, Fe, Mg, Ag, Si, Sn

Table 6 : Fineness of and Associated Sulphide Minerals and Trace Elements in Native Gold from Various Localities
in the Barberton Mountain Land

(cc : chalcocite, co : covellite, cp : chalcopyrite, ga : galena, m : tennantite, py : pyrite,
ap : arsenopyrite)

Sample	Locality	Fineness	Sulphide Minerals	Trace Elements
G.31	Three Sisters	-	-	Al, Cu, Fe, Mg, Ag, Si
G.32	Tiger Trap	878.1	py	Al, Cu, Fe, Ni, Ag, Si
G.33	Tiger Trap	-	co, cc, m	Al, Sb, Co, Cu, Fe, Pb, Mg, Ni, Ag, Si
G.34	Verdite	757.4	py	Al, Cu, Fe, Mg, Mo, Ag, Si, Sn
G.35	Verdite Extension	890.0	-	Al, Cu, Fe, Mg, Ag, Si
G.36	Weltevreden (Queen's)	874.6	py	Cu, Fe, Pb, Mg, Ag, Si
G.37	Woodbine	884.3	-	Cu, Fe, Pb, Mg, Ag, Si, Sn
G.38	Worcester	893.0	py, ga	Al, Be, Bi, Cu, Fe, Pb, Mg, Ag, Si, Sn
G.39	Wyldesdale	885.6	py	Al, Sb, Co, Cu, Fe, Pb, Mg, Ni, Pt, Ag, Si, Sn
G.40	Sheba - Zwartkopje, deep	928.8	-	Al, Sb, Cu, Fe, Mg, Ag, Si

Table 6 : Fineness of and Associated Sulphide Minerals and Trace Elements in Native Gold from Various Localities
in the Barberton Mountain Land

(cc : chalcocite, co : covellite, cp : chalcopyrite, ga : galena, m : tennantite, py : pyrite,
ap : arsenopyrite)

Reef) not only has a high iron content, but has the most notable copper-gold ratio outside the Consort-Madeline belt. The only other sample to have such high iron and copper contents is G.2 (Albion).

(d) Trace Element Composition

Plotting the trace element composition, excluding copper, iron, silicon, aluminium and magnesium, of the samples on a locality map (Fig. 10) shows no obvious pattern of arrangement. Nearly all the samples have at least one trace constituent, in addition to those not plotted. However, the samples from Behind-the-Scenes (G.6), Black Diamond Creek (G.7), Dreyer's Imperial (G.10), Fairview (G.12), Golden Quarry (G.16), Ivy (G.22), Lily (G.23), Maid of the Mountains (G.26), Montrose (G.27), Three Sisters (G.31), and Verdite Extension (G.35), do not contain any unusual constituents. It is known that the ores from Montrose and Maid of the Mountain are similar to those from the Barbrook Line (French Bob's, Dreyer's Imperial), and it has been suggested that they are genetically related. The fact that the trace element composition of gold from these occurrences is relatively simple may substantiate the previous conclusions.

Eleven of the 40 samples reveal the presence of no elements other than silicon, copper, iron, magnesium, aluminium and calcium. Nine contain only one additional element, seven two elements, eight three elements three four elements, one five elements, and one six elements. Lead was the most common minor constituent, occurring in 18 of the samples, while nickel was present in 12, and tin in 10 samples from the Mountain Land.

In 70 per cent of the samples where nickel was detected lead was also present. Fifty per cent of the tin-bearing samples contained lead, both of which elements belong to Group IV B of the Periodic Table. Where cobalt was found, nickel also occurred in all samples, and lead in 80 per cent of the samples, thus showing that the common association between cobalt and nickel in nature is present in free gold. Of the Group V B elements, antimony was accompanied by lead in 80 per cent, and by nickel in 70 per cent, of the samples in which the metal was detected, but bismuth and lead were co-constituents in only 25 per cent of samples containing bismuth. However, 50 per cent of bismuth-bearing samples were found to harbour tin as well. The common association between zinc and lead, observed in many hydrothermal deposits, was disclosed in only 50 per cent of the zinc-bearing samples.

(e) Discussion of Results

(i) Variations in Fineness

Regional variations in the silver content of gold ores have been recorded by Collins (1902), Sharwood (1911), Lawn (1924), and Prentice (1939-40). Fisher (1953) has suggested that such changes in fineness may indicate the magmatic source of mineralisation, and may permit the more reliable delineation of zoning of deposits, provided that the fineness values are truly representative of each particular locality.

From a consideration of Fig. 8, it appears as if the fineness of the gold samples to the northeast and south of the Kaap Valley Granite pluton bears some relationship to the granite itself. However, if the granite were the source of the mineralisation, it would be expected that the fineness would decrease away from the granite contact, in accordance with the normal lateral zoning of ore deposits. Instead, the fineness has its highest value in zones some distance in from the granite, and decreases outwards in both directions away from these zones. This would suggest that the source of the auriferous ore fluids was

situated beneath these zones around the Agnes, Consort and Sheba mines.

Some previous workers have considered the Nelspruit Granite to be the source of the gold mineralisation (Van Eeden, 1941; De Villiers, 1957). The latter supported this view on the grounds that the different types of ore-bodies in the area seem to be related to each other and to the granite, but Gribnitz (1961) pointed out that such evidence was not very convincing. Hearn (1943) favoured the Kaap Valley pluton as the source of the gold.

Assuming that the data obtained reflect the variation in overall fineness of the gold in the region, the present investigation appears to support the contention that the Kaap Valley Granite is the more likely source of the mineralisation. Fisher (1945) observed that, in the majority of ore deposits which he reviewed, the associated magma was andesitic or granodioritic im composition. Visser et al (1956) have shown that the Kaap Valley Granite is really a granodiorite in composition, and it follows that it is more probably associated with the emplacement of the gold than the Nelspruit rocks which are closer to a true granite.

Zoning of the gold occurrences is not readily apparent from the results of the present investigation, though the high fineness values around the Consort and Sheba mines indicate this area to be the centre of high-temperature mineralisation. Gribnitz (1961) quotes C.A. Strauss as suggesting the following zonal arrangement of the ores : (i) the concentration of the arsenopyritic ores around the Consort Mine, with a rapid decrease in the amounts of arsenic to the south and southwest; (ii) then a zone of pyritic ores in which the pyrite crystals are very small; (iii) a third zone of coarse-grained pyritic ores; (iv) the concentration of the gold-quartz veins around the Kaap Valley Granite. However, the majority of the deposits have been shown by the present study to be hypothermal in character, having a gold fineness greater than 800 (Fisher, 1945). The most notable exception is the Rosetta Mine which is mesothermal in character, according to De Villiers (1957), and which has a gold fineness of 850.

(ii) Variations in Copper and Iron Contents

Unlike the fineness values, the copper and iron contents of the samples do not seem to show any systematic regional variation, or to suggest any possible source of the mineralising solutions. If the samples represent gold deposited during the same period of mineralisation, then it would appear that local environment, and not regional controls, governed the composition of the ore-bearing fluids, at least with respect to copper and iron.

(iii) Variations in Trace Element Content

The observed association between elements with similar properties, as indicated by the Periodic Table, suggests a more fundamental relationship between gold and its trace elements than can be explained by environmental conditions alone. It is probable that most of the elements were present in the original ore fluids, though the prevailing local physical and chemical conditions undoubtedly influenced their deposition at a particular point. The effects of chemical environmental control can be seen in gold from the lead-rich Rosetta Mine which contains the second highest amount of lead in the samples, and in tin-bearing gold from the Forbes Reef area where economic cassiterite deposits are found.

The fact that the majority of the samples show similar minor element contents, tends to support Warren's and Thompson's (1944) conclusion that it is the metallogenetic zone or province which determines the nature of minor elements in native gold.

(f) Comparison between Compositions of Free Gold from the
     Barberton Area and Other Localities

Only six samples of native gold from localities outside the Barberton area were analysed, and it is unlikely that they are representative of the occurrences from which they were collected. The analytical results of samples G.41 - G.46 are shown in Tables 1 and 3.

It is difficult to compare these samples with gold from the Barberton Mountain Land because of their very small number. All the elements, except palladium, which are recorded in the Southern Rhodesian and Witwatersrand samples, were detected in gold from the Barberton area.

The three Rhodesian samples have a very simple trace element pattern, and contain a lesser number of elements than the Barberton gold which is believed to be the product of similar mineralisation that occurred in similar rock-types at about the same time in the Archean epoch. Warren and Thompson (1944) also reported very simple compositions for free gold from Matloui and Golden Valley in Southern Rhodesia, silver, copper, iron and mercury being the only elements present.

The Witwatersrand samples show a pattern no more complex than that associated with some of the Barberton gold. However, there is a suggestion of two possible characteristics which might distinguish one pattern from the other. Bismuth occurs in all three of the Witwatersrand samples, but in only 10 per cent of the Barberton samples. Platinoids are present in two out of three Witwatersrand samples, but were found in only one out of 40 samples analysed from Barberton. If the three samples are representative, then it is suggested that, in general, Witwatersrand gold might contain more trace elements than that obtained from most of the Barberton mines.

D. APPLICATION OF RESULTS

Of the six elements found to be present in all, or nearly all, samples from both the Zwartkopje Shoot and the whole of the Mountain Land, three - silicon, aluminium and magnesium - probably represent inclusions of gangue material. Consequently, they do not necessarily reflect the presence of gold mineralisation, and there is no possibility of such elements constituting guides to ore-bodies in any application of geochemical prospecting techniques. Of the remaining three, iron is far too common a constituent of minerals and rocks to be used as an indicator of gold. Not only will it be found where bodies of barren pyrite occur, but the numerous horizons of banded ironstone will also contribute to the dispersion of iron in the soil.

It would appear then that copper and silver might be the metals to be sought geochemically in any future exploration for concealed ore-bodies. The problem is whether sufficient concentrations of these metals will accumulate in the soils and stream sediments as a result of weathering and leaching of the auriferous reefs. Sufficient data exist to show that silver, at least, will be liberated from its solid solution with gold under the normal conditions of rock disintegration. There is no record of either of these elements being determined in previous prospecting, and it is suggested that a limited amount of experimental geochemical surveying be carried out to test whether silver and copper can be detected in the soils surrounding known ore-bodies.

None of the other 15 trace elements identified is present either in sufficient quantities or with adequate persistency to merit its consideration as an indicator to be sought geochemically. If anomalies

are revealed during exploration for silver and copper, the quantities of lead, nickel and tin in such localities might also be established as confirmatory evidence of the anomalies indicating the possible presence of underlying gold mineralisation.

Warren and Thompson (1944) found that, in British Columbia, native gold which contained mercury or tin tended to occur in areas in which minerals of these two elements were concentrated in economic quantities. It is, therefore, possible that certain trace constituents in the Barberton gold might also indicate the possible presence of hitherto undetected deposits of other elements. Cassiterite has been recovered from the Forbes Reef area where tin has been shown to be in the gold as a minor constituent.

The results suggest that the fineness of free gold might be of use in prospecting for further gold deposits. Samples of native gold from the areas around three of the largest mines in the district - Agnes, Consort and Sheba - have consistently high fineness values. Therefore, if isolated specimens of native gold from a locality under investigation are found to be very fine, it might indicate that detailed prospecting operations are justified because of the relatively greater possibility of finding extensive, high-grade ore. The possibility of secondary enrichment of the gold must not be overlooked when trying to assess the significance of the specimens with a high gold : silver ratio.

Eales (1961) has suggested that small amounts of silver-rich gold are initially deposited from the ore fluids, followed by rapid precipitation of finer gold in places with a high degree of permeability. In this way, he explains the relationship between the grade of ore and fineness, and suggests that a marked drop in fineness and grade indicates bottoming of the ore-shoot. It is doubtful whether this generalisation can be employed when considering the significance of the results from the Zwartkopje Shoot. It has been pointed out that two types of gold occur, and that the break takes place between 18 Level and 20 Level. The depth range on either side of this break is too small to allow of any specific trends being clearly discernible. However, there does appear to be an overall increase in the fineness from 14 Level to 26 Level, indicating that this portion of the shoot might still be well above the zone of silver-rich gold which Eales (1961) believes to indicate the bottoming of ore-bodies. Although there is a drop in grade between 26 Level and 27 Level, there is no undoubted decline in fineness at the bottom of the present workings. Consequently, the results of the present investigations do not provide any definite indication as to the possible depth to which the Zwartkopje Shoot might persist.

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