THE COMPOSITION OF GOLD FROM THE BARBERTON MOUNTAIN LAND

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ECONOMIC GEOLOGY RESEARCH UNIT
INFORMATION CIRCULAR No. 19
MAY, 1964
INFORMATION CIRCULAR No. 19
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ABSTRACT

Samples of visible, native gold were obtained from 40 localities over the whole of the Barberton Mountain Land, and from 20 localities at different levels in the Zwartkopje Shoot of the Sheba Mine. As check samples, 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 there are distinct types of gold in the Zwartkopje Shoot, one above 20 Level and the other below. The change from one type to the other can be correlated with an 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 Archaean 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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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 metals concerning the mineralogical composition of the auriferous rocks, 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 Rheba 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.
A. ACKNOWLEDGEMENTS

The author would like to thank the following people for their assistance during the various stages of the project. Without their help it would have been impossible to begin, let alone complete, the research undertaken:

The General Manager of Eastern Transvaal Consolidated Mines, Limited, and Barberton Myre Beperk, for permission to collect samples of gold from their mines;

Dr. K. H. Grobbels, Chief Geologist for Eastern Transvaal Consolidated Mines; Mr. M. van R. Steyn, former Resident Geologist at Fairview Mine; Mr. D. A. Pretorius, Senior Research Fellow of the Economic Geology Research Unit, University of the Witwatersrand; Mr. P. Veillette, Geologist at Shaba Mine; and Mr. P. Vogler, Geologist at New Consort Mine, for assistance with the collection of samples;

Professor L. H. Abrams and Mrs. M. Kaye of the Department of Geochemistry, University of Cape Town, for instructing the author in the basic techniques of spectroscopy, and for advice on how to undertake the research;

Miss C. Carlson and Mr. A. Watson of the Spectrographic Department of the Government Metallurgical Laboratory, Johannesburg, for allowing the author to use their spectrographic equipment, and for their constant advice and help;

Mr. A. Adian of the Government Metallurgical Laboratory for help with the pressure oxidation of some gold samples;

Dr. D. D. Howat, Director of the Central Metallurgical Laboratory, Johannesburg, and Acting Professor of the Department of Metallurgy, University of the Witwatersrand, for enabling the author to use his laboratory's apparatus;

Mr. V. C. O. Schuler, of the Central Metallurgical Laboratory, for supplying the author with standard samples of high purity gold, and for assistance, together with Mr. A. V. Jansen, with the atomic absorption spectroscopic analyses;

Dr. N. P. Eichkorn of the Central Metallurgical Laboratory, for advice on the preparation of gold alloys, and for supplying the author with translations of many Russian references;

The members of staff of the Department of Metallurgy, University of the Witwatersrand, for allowing the author to use their assaying equipment;

The laboratory technician of the Department of Geology, University of the Witwatersrand, for help with the preparation of apparatus, polished sections and photographs;

Dr. W. R. Liebsenberg of the Government Metallurgical Laboratory; Professor W. J. van Biljon, Department of Geology, University of the Orange Free State; and Mr. C. Roentgen, Economic Geology Research Unit, University of the Witwatersrand, for their advice and encouragement.

B. PREVIOUS WORK

At 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 (Ogy, 1965). 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) sulfiite, (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 arsenopyrite ores where the gold is usually enclosed in this sulphide.

The same author spectrographically analyzed mill concentrates from Rosetta, Agnew, Patview, Alpine, Shaba, New Consort, Golden Quarry, Three Sisters, Pigg 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, manganite 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 group metals. Chemical analyses of the concentrates from some of these mines revealed the additional presence of copper, iron and sulphur.

Steele and Carlson (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 bismuth, cadmium, cobalt, lanthanum, 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 (1964), and by Steele and Carlson (1965). 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 0.5%. 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.

Steele and Carlson (1965) 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. 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 orogeny 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 northeast-southwest. Extensional faults occur near and parallel to the anticlinal axis. These displacements were originally high-sagged 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 Granite - 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 Granite, at least, formed the floor of the Barberton geosyncline. The original age of the granites and migmatites remains unknown. The Kaap Valley granite, 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 remodelled along the contact with the sediments and lavas, and, at the same time, were intruded by at least one phase of a third granitic variety - the Mponi 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, Shoba, Chloiba, Formosa, Agnew, Wyndelale, 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 one of this type was obtained for trace element analysis. Hall's classification is generalised and simplified in the extreme.

De Villiers (1887) 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 fluid 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 Vreden (1941) recognized the greater
A. PRE-ANALYTICAL TREATMENT OF SAMPLES

(a) Locations of Samples

Forty samples of visible gold were collected from mines and abandoned workings in the Barren Mountain Land to determine the assay variation in gold composition. The samples consisted mainly of pan 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 assay to which each sample of the "G" series was subjected (pg. - spectrographic analysis; aa - atomic absorption analysis; fa - fire assay; coarse-grained > 1.5 mm; medium-grained 0.5 - 1.5 mm; fine-grained < 0.5 mm.) :-

G. 1  (i) Agnes Mine, 10 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, fa.

G. 2  (i) Albion Mine - chip sample
     (ii) associated material: quartz, corteillite, 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, arsenic, 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) Chalk Mine - chip sample
     (ii) associated material: quartz, pyrite, manganite
     (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, hornblende
     (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, manganite
      (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, chalcocite, 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, manganite
      (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, aneneopyrite  
|   |   |   |   |   |   | (iii) gold; fine- to medium-grained; pale yellow to midddish 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, Lower Reef - chip sample  
|   |   |   |   |   |   | (ii) associated material: quartz, iron oxides  
|   |   |   |   |   |   | (iii) gold; fine- to medium-grained; yellow to midddish colour  
|   |   |   |   |   |   | (iv) analysis: sg, aa, fa.  
|   |   |   |   |   | G. 20 | (i) Ivy Mine, Ivy Load 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, aneneopyrite, pyrite  
|   |   |   |   |   |   | (iii) gold; fine- to coarse-grained; pale yellow to yellow colour  
|   |   |   |   |   |   | (iv) analysis: sg, aa, fa.  
|   |   |   |   |   | G. 24 | (i) Majdaline 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 the 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) Moutonne 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 - ground 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 - boehleite corn  
|   |   |   |   |   |   | (ii) associated material: milky quartz, celestite, 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 (Queen) 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.  

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Twenty-two samples were, in addition to the above, collected along the Zwartkops mine 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 "N" series. Material was collected at different levels along the shoot.

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S. 1
(i) 14 Level, Z 1 Stope
(ii) sample; fine 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 filliform 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.
The method of sampling is open to criticism in that it has been shown by [reference] (1901) 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 sheet.

(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 mm or more. The smaller grains tended to occur as irregular flakes
closed in the sulfides 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 hydrochloric acid, when it was found that the particles released in
this way were ridged with small fragments of quartz and sulfides. 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 pyrite, pyrrhotite 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 sulfides can be removed from the gold grains by treatment with acids, it seems unlikely that any method
can be devised which will remove completely these 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
pulveriser mortar, then leaching the contamination to surface iron on the gold. The gold was then concentrated
and extracted by passing over 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 hydrochloric
acid. Examination of solubility tables showed that this acid dissolved quartz and silicates, but had little effect
on the noble metals and metallic sulfides.

(d) Cleaning of Gold Particles

A study of the gold concentrates under a binocular microscope revealed that most of the gold grains
had particles of sulfides, 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 sulfides were removed by washing
the samples in a mixture of equal parts of distilled water and concentrated hydrochloric acid for 24 hours at 60°C.
To remove pyrite, arsenopyrite and other more resistant sulfides, the samples were boiled in 5% nitric acid for 16 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 43.56% 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 and after treatment. The maximum loss was 1.39%, in a sample weighing 450 mgnms., and the average lost for all the samples was 0.6%.

(e) Homogenisation of Samples

For three gold grains which enclosed a large amount of sulfides, and which required stronger
treatment than nitric acid, a process was devised of pressure oxidation of the sulfides 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.

(f) Precautions Taken to Prevent Contamination of Samples

At the analytical methods used were extremely sensitive, being capable of detecting concentrations
down to 1 ppm.; 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-punched screen. Only anilin-grade
chemical reagents and distilled water were used for the cleaning 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.

8. 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
taken 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 homogeneous 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 spectrometry. The silver content of the ore was found by fire assay as the metal was present in
too large amounts to be determined by indirect methods.
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 Jansen (1969). Definite amounts of gold (from 10 to 100 nagum, depending on the size of the sample) were dissolved in aqua regia, evaporated to incipient dryness, and then redissolved in 10% 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 0.7 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 Schuler and Jansen (1969). It consisted of a Zeiss monochromator and incandescence unit for line isolation and intensity measurements; 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. "Nadigas" was used as fuel for the burner.

The experimental conditions were as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength</th>
<th>Slit Width</th>
<th>Lamp Current</th>
<th>Air Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>3247 Å</td>
<td>0.07 mm</td>
<td>12 mA</td>
<td>20 lbs./sq in.</td>
</tr>
<tr>
<td>Iron</td>
<td>2483 Å</td>
<td>0.01 mm</td>
<td>32 mA</td>
<td>20 lbs./sq in.</td>
</tr>
</tbody>
</table>

Results

Three readings of the absorbance for each sample solution were corrected for instrument drift and then averaged. 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 calculations:

\[ \text{Weight of sample dissolved in solution} = 100 \text{ mg}, \quad \text{0.1 gm.} \]

\[ \text{Volume of solution} = 10 \text{ c.c.} \]

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

From measurement of absorbance, concentration of metal in solution = 6 ppm.

\[ 5 \times 10^{-6} \text{ gms./gms.} = 5 \times 10^{-6} \text{ gms./c.c.} \]

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

= 50 gppm.
Tables 1 and 2 give the results for those "G" and "S" samples respectively which were assayed. When duplicate assays were carried out, the results agreed to within 1% for the most of the samples, and to within 2.9% for all of them. For the "G" samples, the fineness varied from 767 (G. 84) to 908 (G. 41), while along the Zwartkopsie Shoot, the range was between 868 (G. 7) and 903 (G. 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 pyrolytic 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 it was not initially looked for. However, strong beryllium lines were detected in one sample, and the 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 intensities.

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 as internal standard lines because of the simplicity of the gold spectrum and the fact that, under the arcinvolving 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 bead of uniform size following the method of Blackett (1912). The beads were then firmly embedded in small cavities drilled into the tops 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 arc'd 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.

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(b) Results

The intensities of the analytical and internal standard lines were converted to the log intensity ratios using a spectro-calculating board. A 1000 was used as the internal standard line for analytical lines with wavelengths in the upper half of the wavelength region covered, and a 2550 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 (6.2, 6.3, 6.10, 6.11, 6.12, 6.13, and 6.19) 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 analyzed. These ratios indicate the order 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 58 samples; magnesium in 58; aluminium in 58; nickel in 57; lead in 29; antimony in 15; tin in 11; bismuth in 10; cobalt in 7; mercury in 6; zinc in 4; tantalum 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 30; aluminium in 30; lead in 18; nickel in 15; tin in 10; antimony and cobalt in 9; 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 Zwartkopsie Shoot show 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 5; 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 17.5%.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu ppm.</th>
<th>Fe ppm.</th>
<th>(Cu + Fe) %</th>
<th>Ag %</th>
<th>Au %</th>
<th>Fineness</th>
<th>Cu ppm.</th>
<th>Fe ppm.</th>
<th>Cu ppm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. 1</td>
<td>276</td>
<td>311</td>
<td>0.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>G. 2</td>
<td>215</td>
<td>252</td>
<td>0.49</td>
<td>7.71</td>
<td>81.42</td>
<td>887.6</td>
<td>28.37</td>
<td>16.34</td>
<td>2.82</td>
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<td>G. 3</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>G. 4</td>
<td>319</td>
<td>679</td>
<td>0.19</td>
<td>5.30</td>
<td>92.60</td>
<td>946.9</td>
<td>3.58</td>
<td>7.12</td>
<td>0.46</td>
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<tr>
<td>G. 5</td>
<td>389</td>
<td>593</td>
<td>0.54</td>
<td>8.86</td>
<td>98.31</td>
<td>940.3</td>
<td>30.98</td>
<td>27.02</td>
<td>1.14</td>
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<td>421</td>
<td>116</td>
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<td>12.63</td>
<td>86.53</td>
<td>856.8</td>
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<td>G. 8</td>
<td>202</td>
<td>311</td>
<td>0.05</td>
<td>8.80</td>
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<td>3.41</td>
<td>0.65</td>
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<td>G. 9</td>
<td>190</td>
<td>268</td>
<td>0.18</td>
<td>5.15</td>
<td>94.66</td>
<td>948.4</td>
<td>16.75</td>
<td>2.72</td>
<td>0.14</td>
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<tr>
<td>G. 10</td>
<td>83</td>
<td>105</td>
<td>0.02</td>
<td>10.54</td>
<td>89.46</td>
<td>896.6</td>
<td>0.99</td>
<td>1.17</td>
<td>0.78</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu ppm.</th>
<th>Fe ppm.</th>
<th>(Cu + Fe) %</th>
<th>Ag %</th>
<th>Au %</th>
<th>Fineness</th>
<th>Cu ppm.</th>
<th>Fe ppm.</th>
<th>Cu ppm.</th>
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<td>G. 12</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>G. 13</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>G. 14</td>
<td>426</td>
<td>218</td>
<td>0.07</td>
<td>9.29</td>
<td>91.64</td>
<td>937.0</td>
<td>5.04</td>
<td>2.47</td>
<td>2.04</td>
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<td>-</td>
<td>-</td>
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<td>G. 16</td>
<td>152</td>
<td>336</td>
<td>0.05</td>
<td>7.40</td>
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<td>920.0</td>
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<td>3.57</td>
<td>0.46</td>
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<td>725</td>
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<td>G. 19</td>
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<td>1.60</td>
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<td>G. 20</td>
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<td>590</td>
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<tr>
<td>G. 21</td>
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<td>-</td>
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<td>G. 22</td>
<td>679</td>
<td>565</td>
<td>0.12</td>
<td>6.67</td>
<td>93.21</td>
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<td>7.06</td>
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<td>177</td>
<td>201</td>
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<td>925.6</td>
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<td>4.24</td>
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<tr>
<td>G. 29</td>
<td>304</td>
<td>304</td>
<td>0.05</td>
<td>14.85</td>
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<td>853.4</td>
<td>5.57</td>
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<td>G. 30</td>
<td>279</td>
<td>369</td>
<td>0.00</td>
<td>5.50</td>
<td>94.50</td>
<td>945.7</td>
<td>2.79</td>
<td>3.67</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Table 2: 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.
### The Significance of the Results

#### A. Occurrence of Trace Elements in Native Gold

**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 size difference is 8% - 15%, there is usually a continuous series of solid solutions 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 range, and to form inter-metallic compounds. For example, elements such as Ag, Bi, Pb (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 VIII B elements (Fe, Ni, Co) 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 electrochemical 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 0.5 atomic percent gold, but dissolves in gold to the extent of 20 - 30 atomic percent. Thus, it is seen that a solute 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.

#### Table 1: Gold, Silver, Copper and Iron Contents of Native Gold Samples from Various Countries

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Of the several types of solid solution discussed by Barrett (1965), 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 small radii less than 1.0 are known, or are likely, to form interstitial solutions.

The above generalizations on solid solubility are based on discussions by Barrett (1965), Evans (1962), and Pearson (1968).
### Table 2: The Minor and Trace Elements Present in Native Gold Samples from Various Localities in the Barazona 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)

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### Table 2: (Cont'd.)

The Minor and Trace Elements Present in Native Gold Samples from Various Localities in the Barazona 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)

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<td>G. 38</td>
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The maximum solid solubility in gold of each of the various trace elements detected has been determined from previous metallurgical investigations (Hansen, 1965; Pearson, 1958) as follows (figures represent atomic percent):-

- **Aluminium**: 15.50
- **Antimony**: 1.12
- **Arsenic**: 0.20
- **Beryllium**: negligible
- **Bismuth**: 0.07
- **Calcium**: < 1.80
- **Cobalt**: 24.00
- **Copper**: 100.00
- **Iron**: 65.00
- **Lead**: 0.09
- **Magnesium**: 32.50
- **Manganese**: 32.00
- **Mercury**: 18.30
- **Molybdenum**: 1.35
- **Nickel**: 100.00
- **Palladium**: 100.00
- **Platinum**: 100.00
- **Silver**: limited
- **Tellurium**: negligible
- **Tin**: 6.60
- **Titanium**: 8.50
- **Vanadium**: 17.50
- **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 39 of the 68 analysed. The intensity ratio varied from -1.06 to 0.67 (Level 2, Zwartkopje-Shoot) to -0.46 in G.30 (Thomas).

This common occurrence of aluminium in gold suggests the possibility of its occurring as a trace element constituent, in support of which it has been shown that up to 1.5 atomic percent aluminium can enter into the gold lattice. However, a mixture 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 Thomson (1944).

(ii) Antimony

Antimony was detected in 12 of the samples analysed, with the intensity ratio varying from -1.95 in G.30 (Tiger Trap) to -0.73 in G.5 (Beaver Trap, South Reef) and G.66 (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 1.13 percent. The possibility of the antimony being present as inclusions of stibnite must, therefore, be considered, especially when it is remembered that antimonials gold ore is quite common in the Buttermere area. However, stibnite was seen only in 3 samples - S.10, S.33, S.13 (Shale 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 those 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. - (Alcides and Taylor, 1901), 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. 36 (Worcester), the intensity ratios being 0.95 and 3.51 respectively. As far as could be ascertained, beryllium has not previously been reported in native gold, though Deyganova and Ovostakaya (1969) did recognize 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 (1.19 Å), compared with that of gold (1.44 Å), and it might be present as an interstitial solid solution. Barrett (1960) mentions that the formation of interstitial solid solutions is, however, restricted to those atoms with odd l less than 1 Å.

(v) Bismuth

Bismuth was detected in ten samples, with intensity ratios varying from 1.71 in G. 18 (Independent) to 0.98 in G. 40 (Cason Section, F.R.M.). No bismuth minerals were observed in the heavy concentrates of the samples analysed, 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 recognized 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 0.06 in G. 14 (Fortuna) to 0.09 in G. 25 (Maal de Kaap). It has been proved that up to 20 cent cobalt is 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 1.8 ppm. in G. 40 (Zwartkopje) to 0.18 ppm. in G. 34 (Verdict). These observations confirm the conclusions of Cook (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 bornite 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 582 ppm. copper, and chalcopyrite, covellite and chalcocite in sample G. 3 (Albina) which revealed a copper content of 321% ppm. On the other hand, the gold of sample G. 34 (Verdict) contained 678 ppm. copper, 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 Cook (1939).

(ix) Iron

Iron, like copper, was found in all the gold samples in the present investigation, in amounts varying from 7.33 ppm. (G. 42, Selkirk) to 5261 ppm. (G. 45, West Rand Consolidated). Even though up to 65 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 Cook (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 essentially 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 25 of the 68 samples analysed, the intensity ratios varying from 1.91 in G. 5 (Beaver Trap, South Reef) to 0.19 in G. 26 (Wolvenrode). 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. 2 (Alpines), G. 29 (Rosetta), G. 36 (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. Geitach and Schweitzer (1928) have shown that lead tends to be deposited on the boundaries of gold grains.

(xii) 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 -3,71 in G.44 (Market Square, Johannesburg) and 5,10 (22 Level Zwartkopje Shoot) to -9,44 in G.38 (Verdine 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 spectrophotographically in all the samples, it is quite possible that the magnesium occurs as inclusions of a gangue mineral in the gold.

(xiii) Manganese

Manganese was found in one sample only - G.3 (Clutha). The element is capable of entering into solid solution with gold in fairly large concentrations (up to 33 per cent), and, as no manganeseous 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 Carton (1963) reported its presence in gold from the Lily and Trichard's Luck mines, and Warren and Thompson (1964) 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, 1951), and it is possible that, if the element is present in amounts less than this, it would not have been identified.

(xiv) 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 amalgams at Mariposa in California.

(xiv) Molybdenum

Molybdenum was found to be present in three samples, G.3 (Albion), G.5 (Beaver Trap, South Reef) and G.36 (Verdine), with intensity ratios of -0.83, -2.22 and -0.92 respectively.

Metallurgical findings indicate that, despite a favourable size factor, only 1.09 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 1.86 in G.5 (Beaver Trap, South Reef) to 2.20 in G.36 (Tiger Reef). 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.32 (Wyldesdale) and G.46 (Watt Rand Consolidated), while palladium was detected in sample 4.85 only (Capeon, 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 (palladians), 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.

(xvi) 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 quartz and quartzite 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.

(xvii) Silver

Silver occurred in all samples in amounts varying from 1.7 per cent (G.16, 33 Level, Zwartkopje Shoot) to 34.1 per cent (G.34, Verdine). There is complete solid solubility between gold and silver, though Zenouztov (1920) 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 euctectoid (80 - 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 Cook'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 500 ppm. (Ahrens and Taylor, 1963), 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 Zwartkopsie Shoot. The intensity ratios varied from -1.30 in G.5 (Beaver Trap, South Reef) to 0.16 in G.26 (Madelonwe). 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 component.

(xi) Titanium

Titanium was detected in three samples only - G.4 (Beaver Trap, North Reef), G.29 (Grootfontein) and G.44 (Marler 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 widespread in gold that its absence was of more interest than its presence.

(xii) Vanadium

Vanadium was identified in one sample only, viz. C.11 from 22 Level of the Zwartkopsie 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 26 of the gold samples selected from occurrences throughout the world.

(xiii) Zinc

Zinc was observed in four samples - G.1 (Agnes), G.2 (Albion), G.8 (Clitha) 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, galena was identified in polished-sections of one 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 Croix (1909), Warren and Thompson (1944), and Boyle (1961). Croix 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 at mineral concentrations and that arsenic occurs in the gold lattice. Warren and Thompson argued that both arsenic and tellurium were 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 ZWARTKOPSE ORI-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 Zwartkopsie 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 area.

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 25 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. Scales (1911) noted that the colour of the individual grains from the Olympus Mine, Southern Rhodesia, varied from reddish gold (approximately 860 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), Marler (1937) and Edwards (1946). Fineness variations within a single grain have been observed by Head (1950) who noted that individual grains had gold-rich cores, and by Scales (1911) 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 2.81 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 25 Level the copper and iron contents and the fineness agree fairly well, but the trace element composition varies. On 26 Level, the fineness ranges from 890 to 985, 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 distinct difference in composition. The finenesses, copper and iron contents differ widely in the two samples, and while 8, 21 contains aluminium, bismuth, magnesium and nickel, 6, 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. 9. 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 these 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 8, 4 and 8, 7 the gold was all coarse-grained, yet the colour was gold in 8, 4 and pale yellow in 8, 7. Very fine grains in 8, 13 had a gold colour, while somewhat coarser grain in 8, 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 8, 1 yellow-coloured gold had a fineness of 846, while in 8, 12 gold of a similar colour was 902 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) Variations 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.

(d) Trace Element Content

Generally, the samples of gold from the Zwartkopje Shoot appear 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 variation 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 constant variation, 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 nickel and magnesium in the individual samples on each level, and this casts some doubt in the overall variation in the shoot.

Of the other trace elements in the samples, antimony is present in 8, 4, 2 (14 Level), 8, 2 (18 Level), and 5, 10 and 5, 11 (22 Level). The intensity ratios show no systematic variation with increasing depth, and the antimony in 5, 10 and 5, 11 may be correlated with the presence of sinterite on 22 Level. Bismuth was found in 5, 7 from 18 Level, 5, 12 from 22 Level, and 5, 24 from 24 Level (Birthday Shoot). Cobalt is a constituent of 5, 16 (25 Level) only, and lead of 5, 12 (22 Level) and 5, 10 (25 Level). Mercury was detected in four samples - 8, 6 (17 Level), 8, 13 (23 Level), 8, 14 (25 Level), and 8, 20 (26 Level). Once again, the intensity ratios showed no systematic variation. Vanadium is present in 5, 11 on 22 Level.

(e) Discussion of Results

(i) Variations in Fineness

Considering the usual sequence of one deposition, as initially proposed by Emsom (1904), 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 monothermal or hypothermal gold. However, Salom (1941) concluded 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 1500 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.
Table 6: Host-Rocks, Associated Sulphide Minerals, and Trace Elements in Native Gold from the Zwardiopike Shoot, Sheba Mine

<table>
<thead>
<tr>
<th>Sample</th>
<th>Level</th>
<th>Host-Rock</th>
<th>Sulphide Minerals</th>
<th>Trace Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. 1</td>
<td>14</td>
<td>quartz in green schist</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 2</td>
<td>14</td>
<td>quartz in green schist</td>
<td>py, ap</td>
<td>Sb, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 3</td>
<td>14</td>
<td>milky and grey quartz</td>
<td>py, ap, ab</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 5</td>
<td>17</td>
<td>quartz-chlorite rock</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 6</td>
<td>17</td>
<td>quartz-chlorite rock</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 7</td>
<td>18</td>
<td>quartz</td>
<td>py, ap</td>
<td>Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 8</td>
<td>20</td>
<td>quartz-chole broccia</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 9</td>
<td>20</td>
<td>quartz-chole broccia</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 10</td>
<td>22</td>
<td>quartz</td>
<td>ab, py, ap, cp</td>
<td>Al, Sb, Cu, Fe, Mg, Ni, Ag, Si</td>
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<tr>
<td>S. 11</td>
<td>22</td>
<td>quartz</td>
<td>ap, py, cp, ab</td>
<td>Al, Sb, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 12</td>
<td>22</td>
<td>quartz</td>
<td>ap, py, cp</td>
<td>Bi, Cu, Fe, Pb, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 13</td>
<td>23</td>
<td>grey and white quartz</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Hg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 14</td>
<td>25</td>
<td>chart</td>
<td>py, ap</td>
<td>Cu, Fe, Mg, Hg, Ag, Si</td>
</tr>
<tr>
<td>S. 15</td>
<td>25</td>
<td>green schine</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 16</td>
<td>25</td>
<td>green schine</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 17</td>
<td>28</td>
<td>chart</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ag, Si</td>
</tr>
<tr>
<td>S. 18</td>
<td>28</td>
<td>chart</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Hg, Ag, Si</td>
</tr>
<tr>
<td>S. 19</td>
<td>38</td>
<td>chart</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 20</td>
<td>38</td>
<td>chart and quartz</td>
<td>py, ap</td>
<td>Al, Cu, Fe, Mg, Hg, Ag, Si</td>
</tr>
<tr>
<td>S. 21</td>
<td>38</td>
<td>milky quartz</td>
<td>py, cp</td>
<td>Al, Bi, Cu, Fe, Mg, Ni, Ag, Si</td>
</tr>
<tr>
<td>S. 22</td>
<td>44</td>
<td>quartz</td>
<td>py</td>
<td>Al, Cu, Fe, Mg, Ag, Si</td>
</tr>
</tbody>
</table>

(* samples from the Birthday Pipe, py: pyrite, ap: arsenopyrite, cp: chalcopyrite, ab: sulfides)
dominant sulphide. Chalcopyrite occurs in only one sample (6,3) above 18 Level, but in five samples - S,10 and S,11 (12 Level), S,15 and S,s1 (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 Zwartrandpunt 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 Hasie (1902) 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. Emmott (1904), Lindgren (1905), Newhouse (1928), and many other works 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 Cu, Ni, Pb, Ag, 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 remembered 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 rock.

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 Collins (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 800 fine, and epithermal gold ranges from 500 to 800 fine. Colin (1949) drew the same conclusions from a study of gold veins in the Nanayacisco field, Madagasar. Applying these results to the Zwartrandpunt 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) concluded that both were important, with temperature probably being the controlling factor, while Scherbinina (1965) believed that the vapour pressure of the element was the main controlling factor. Edwards (1988), 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 (1988) pointed out the fundamental importance of the amount 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 Sales (1943) 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 Cordillera region of the United States, the gold is deposited relatively late, even though silver is abundant. However, at shallow levels in these deposits silver and gold combine to form a low-finessness alloy. The overall composition of the ore fluid can also affect the fineness, and Scherbinina (1965) 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 Stas (1918) have shown that nearly every mineral which precipitates gold from a solution will precipitate silver as well, except for galena, pyrite, sphalerite and micalette. Sales (1943) 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 Zwartrandpunt 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 Zwartrandpunt 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 8,16 and 8,17 from 22 Level.

The nature of the wall-rock could also be expected to affect the composition of the gold, and Gigliseet (1961) has pointed out that the character of the ore in the Zwartrandpunt Shoot is clearly influenced by the host-rock. For example, the ore in shale consists mainly of massive, massive 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 compositions (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 cady (S,7, S,10, S,11, S,12, S,23) revealed trace elements other than aluminium, magnesium and nickel, which are common to all types of host-rock. These 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 Zwaartkopje Shoot, which might be related to different periods 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 Illinivoski (1964). From the 38 Level to 24 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 Anger (1962) 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 Zwaartkopje 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 chest bar and the shale, while higher up it cuts across the different horizons, and ore is found in chest, 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 analyze the significance of the results obtained for the 60 samples collected from various localities over the whole of the Barberton Mountain Land. As with the samples along the Zwaartkopje Shoot, it must be emphasized 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 Zwaartkopje 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 60 samples will be more indicative of regional conditions of mineralization than will the trace element results which are summarized 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 interpolation. 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 Steynslaan and Snowdon 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 north of Barberton, the fineness is interpreted as increasing regularly from 800 on the edge of the Kaap Valley Granite to 900 to the vicinity of the Agnes Mine. Proceeding further south, towards the Montrose Mine, the values decrease again to 800. 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 Sheep Mine northwards past the Consort Mine. Beyond this zone the fineness values diminish again towards the Nelspoort granges.

(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 concentration 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 Jamieson Complex rocks between the Consort and Madeline mines, generally have a much higher copper-gold ratio than those from elsewhere in the Mountain Land. Speculative and uneconomic copper mineralization has been found in this area, particularly around the Abbots Mine, and it seems possible that the high copper values in the gold may be due to the copper-rich environment. No other generalizations 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. 6 (Beaver Trap, South
<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Fineness</th>
<th>Sulphide Minerals</th>
<th>Trace Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>G, 1</td>
<td>Agnes - 14-Level</td>
<td>-</td>
<td>Cu, Fe, Pb, Mg, Ag, S, Zn</td>
<td></td>
</tr>
<tr>
<td>G, 2</td>
<td>Albion</td>
<td>817.6</td>
<td>Cu, Fe, Pb, Mg, Ag, S, Zn</td>
<td></td>
</tr>
<tr>
<td>G, 3</td>
<td>Alpsite</td>
<td>-</td>
<td>Cu, Fe, Pb, Mg, Ag, S, Zn</td>
<td></td>
</tr>
<tr>
<td>G, 4</td>
<td>Beaver Taps - North Reef</td>
<td>948.2</td>
<td>Pb, Cu, Fe, Pb, Mg, Ag, S, Tl</td>
<td></td>
</tr>
<tr>
<td>G, 5</td>
<td>Beaver Taps - South Reef</td>
<td>949.5</td>
<td>Cu, Fe, Pb, Mg, Mo, Ni, Ag, S, Sn</td>
<td></td>
</tr>
<tr>
<td>G, 6</td>
<td>Behind-the-Scenes</td>
<td>-</td>
<td>Cu, Fe, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 7</td>
<td>Black Diamond Creek</td>
<td>843.6</td>
<td>Cu, Fe, Mg, Ag, S</td>
<td></td>
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<tr>
<td>G, 8</td>
<td>Clitha</td>
<td>817.0</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 9</td>
<td>Coffs 90 - R.W. Dr.</td>
<td>948.4</td>
<td>Cu, Fe, Pb, Mg, Ag, S, Sn</td>
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</tr>
<tr>
<td>G, 10</td>
<td>Deepak's Imperial</td>
<td>848.6</td>
<td>Cu, Fe, Mg, Ag, S</td>
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<tr>
<td>G, 11</td>
<td>Fairview</td>
<td>-</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 12</td>
<td>Fairview</td>
<td>-</td>
<td>Cu, Fe, Mg, Ag, S</td>
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<tr>
<td>G, 13</td>
<td>Forsbee Reef</td>
<td>-</td>
<td>Cu, Fe, Mg, Pb, Mg, Ni, Ag, S</td>
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<tr>
<td>G, 14</td>
<td>Formula</td>
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<td>G, 15</td>
<td>French Bob's - Martin's Reef</td>
<td>-</td>
<td>Cu, Fe, Pb, Ag, S</td>
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<tr>
<td>G, 16</td>
<td>Golden Quarry - shallow</td>
<td>928.0</td>
<td>Cu, Fe, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 17</td>
<td>Golden Quarry - deep</td>
<td>889.2</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
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<tr>
<td>G, 18</td>
<td>Indeanslide</td>
<td>787.3</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 19</td>
<td>Ivy - Lester Reef</td>
<td>939.8</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 20</td>
<td>Ivy - Ivy Lead Reef</td>
<td>940.0</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 21</td>
<td>Ivy - Ivy Reef, 900 ft</td>
<td>908.2</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 22</td>
<td>Ivy - Ivy Reef, bottom</td>
<td>888.1</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 23</td>
<td>Lily</td>
<td>829.6</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
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<tr>
<td>G, 24</td>
<td>Mabeline</td>
<td>929.6</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 25</td>
<td>Maid of De Karp</td>
<td>-</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 26</td>
<td>Maid of the Mountains</td>
<td>905.3</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
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<tr>
<td>G, 27</td>
<td>Montrose</td>
<td>909.8</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
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<tr>
<td>G, 28</td>
<td>Olga</td>
<td>929.1</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 29</td>
<td>Rosetta</td>
<td>941.4</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
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<tr>
<td>G, 30</td>
<td>Thomas</td>
<td>929.7</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Fineness of and Associated Sulphide Minerals and Trace Elements in Native Gold from Various Localities in the Baberko Mountain Land (cc: chalcocite, co: corellite, cp: chalcopryite, ga: galena, m: tennantite, py: pyrite, sp: arsenopyrite)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Fineness</th>
<th>Sulphide Minerals</th>
<th>Trace Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>G, 31</td>
<td>Three Sisters</td>
<td>-</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
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<tr>
<td>G, 32</td>
<td>Tiger Trap</td>
<td>878.1</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 33</td>
<td>Tiger Trap</td>
<td>-</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 34</td>
<td>Verdike</td>
<td>757.4</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 35</td>
<td>Verdike Extension</td>
<td>890.0</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 36</td>
<td>Weltevreden (Queen's)</td>
<td>874.6</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 37</td>
<td>Wodhams</td>
<td>884.3</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 38</td>
<td>Wodhams</td>
<td>885.0</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
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<tr>
<td>G, 39</td>
<td>Wyndimere</td>
<td>884.6</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
<tr>
<td>G, 40</td>
<td>Zebka - Zwartkopie, deep</td>
<td>928.8</td>
<td>Cu, Fe, Pb, Mg, Ag, S</td>
<td></td>
</tr>
</tbody>
</table>

Table 6: Fineness of and Associated Sulphide Minerals and Trace Elements in Native Gold from Various Localities in the Baberko Mountain Land (cc: chalcocite, co: corellite, cp: chalcopryite, ga: galena, m: tennantite, py: pyrite, sp: 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 (Alice).

(d) Trace Element Composition

Plotting the trace element composition, excluding copper, iron, silicon, aluminum and magnesium, of the samples on a locality map (Fig. 18) 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.19), Parlier (G.13), Colleen Quarry (G.16), Ivy (G.20), Lily (G.33), Maid of the Mountain (G.38), Montrose (G.27), Three Sisters (G.31), and Vestite 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 Sixbrooke 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, aluminum and calcium. Nine contain only one additional element, seven two elements, eight three elements, 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 15, and tin in 10 samples from the Mountain Lead.

In 76 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. This 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 20 per cent of samples containing bismuth. However, 50 per cent of bismuth-bearing samples were found to contain tin as well. The common association between zinc and lead, observed in many hydrothermal deposits, was disclosed in only 60 per cent of the tin-bearing samples.

(e) Discussion of Results

(i) Variations in Fineness

Regional variations in the silver content of gold ores have been recorded by Collins (1903), Sharwood (1911), Lawn (1924), and Prentice (1939-40). Fisher (1963) has suggested that such changes in fineness may indicate the magmatic source of mineralization, and may permit the more reliable determination of the ages 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 mineralization, 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 values in zones some distance to from the granite, and decreases inwards in both directions away from these zones. This would suggest that the source of the auriferous ore fluids was situated beneath those 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 Staden, 1941; De Vliegen, 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 Grice (1961) pointed out that such evidence was not very convincing. Hsiau (1960) favored 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 most likely source of the mineralization. Fisher (1949) observed that, in the majority of ore deposits which he reviewed, the associated magmas were andesitic or granodioritic in composition. Finlay et al (1965) have shown that the Kaap Valley Granite is essentially a granite in composition, and it follows that it is more probably associated with the emplacement of gold than the Nelspruit rocks which are closer to a true granite.

Zoning of the gold occurrence 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 mineralization. Grice (1961) quotes C.A. Cress in suggesting the following zonal arrangement of the ores: (i) the concentration of the arsenopyrite 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; (iii) then a third zone of coarser-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 hydrothermal in character, having a gold fineness greater than 800 (Fisher, 1949). The most notable exception is the Rosetta Mine which is isothermal, in character, according to De Vliegen (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 mineralizing solutions. If the samples represent gold deposited during the same period of mineralization, 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 ore-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 suggest Warren's and Thompson's (1944) conclusion that it is the metallogenic zone or province which determines the nature of minor elements in native gold.
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 analyzed, 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 South 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 Matlou 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. Platinum is present in two out of these Witwatersrand samples, but were found in only one out of six samples analyzed from Barberton. If these 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 Zwartkops Shoot and the whole of the Mountain Land, three - silicofluorite, aluminium and magnetite - 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 constraining 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 banded 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 sulphide 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 10 trace elements identified is present either in sufficient quantities or with adequate persistence 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 those of the largest mines in the district - Agnes, Cossen 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 specimen with a high gold: silver ratio.

Saylor (1951) 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 applied when considering the significance of the results from the Zwartkops 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 34 Level to 38 Level, indicating that this portion of the shoot might still be well above the zone of silver-rich gold which Saylor (1951) believes to indicate the bottoming of ore-bodies. Although there is a drop in grade between 28 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 Zwartkops Shoot might persist.
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