A STUDY OF THE TRACE ELEMENTS ASSOCIATED WITH GOLD FROM THE BARBERTON DISTRICT

by

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CONTENTS

ABSTRACT

Sixty eight samples of native gold were analyzed for their silver, copper, iron and trace element contents. Forty of the samples were collected from different localities in the Barberton district; twenty two from various levels along the Zwartkopje ore shoot, Sheba Mine; and six from localities on the Witwatersrand and in Southern Rhodesia.

The gold was extracted by either crushing the samples and then concentrating the gold using a superpanner, or by dissolving the rock in hydrofluoric acid. The particles of gold were thoroughly cleaned before analysis with hydrochloric, hydrofluoric and nitric acids. Great care was taken throughout the pre-analytical treatment to prevent contamination by extraneous material or by removal of trace elements from the gold.

Three analytical methods were used to determine the composition of the gold. Atomic absorption spectroscopy was used to determine the copper and iron contents, the fire assay the silver content and emission spectroscopy the trace element composition. The concentrations of the trace elements are given semi-quantitatively as log intensity ratios. All other results are quantitative.

Generally the composition of the gold samples is relatively simple. Silver, copper, iron and silicon were present in all the samples; magnesium was present in fifty-eight of them; aluminium in fifty-three; nickel in twenty-seven; lead in twenty-three; antimony in twelve; tin in eleven; bismuth in ten; cobalt in seven; mercury in six; zinc in four; titanium and molybdenum in three; beryllium and platinum in two;

..calcium/...

calcium, manganese, palladium and vanadium in one.

Of these trace elements, it is considered that beryllium, bismuth, cobalt, manganese, mercury, molybdenum, palladium, platinum, silver, tin and vanadium occur as alloy constituents in solid solution with the gold. Antimony, copper, iron, lead, nickel, titanium and zinc are also thought to be present in the gold lattice, though they may also occur as mineral inclusions. Aluminium, calcium, magnesium and silicon are probably present as mineral inclusions.

The results of the samples taken from the Zwartkopje shoot seem to indicate two different types of gold, occurring between the 20 and 26 and the 14 and 18 levels, respectively. Gold samples taken below the 20 level increased in fineness from 924 to 950 with increasing depth, while those samples from above the 20 level, had fineness values increasing from 915 to 935 between the 14 and 18 levels. The copper content of the samples decreased from 700 p.p.m. to 400 p.p.m. between the 14 and 18 levels and increased from 160 to 500 p.p.m. between the 20 and 26 levels. The iron content decreased from 500 to 300 p.p.m. between the 14 and 18 levels and from 1300 to 900 p.p.m. between the 20 and 26 levels. The increase in copper content with increasing depth in the gold from the lower levels, correlates with increasing chalcopyrite content with increasing depth in these levels. Trace elements occurring in the gold from the upper levels include aluminium, magnesium, mercury, nickel, while in the lower levels, aluminium, antimony, bismuth, magnesium and nickel are present.

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The main factors controlling the composition of the samples appear to be the temperature and pressure conditions prevailing at the time of deposition, the concentration of the elements in the ore fluids and the chemical and mineralogical environment.

The fineness values for the regional gold samples in the Barberton District show some regular distribution with the highest values around the Consort and Agnes Mines. The copper and iron contents show no systematic variation, nor do the trace elements. However, there does appear to be a definite association between trace elements from the same, or adjacent, groups in the Periodic Table.

From the few samples analyzed, it appears as if gold from the Witwatersrand mines, differs fundamentally from that of Barberton, being much more complex in composition.

The results appear to be of little economic importance.

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INTRODUCTION

A. GENERAL STATEMENT

As part of the general study of the geology of the Barberton Mountain Land by the Economic Geology Research Unit of the University of the Witwatersrand, the author undertook a study of the trace elements associated with free gold from the Barberton area. The work was begun in January, 1962, and completed 14 months later. This thesis embodies the results of the investigation and discusses their geological significance. The work was initially undertaken with a view to finding an element constantly associated with the gold which might serve as an indicator in a geochemical prospecting method. Unfortunately the work failed in this respect, though the results suggest that the degree of fineness of the native gold may indicate the economic potential of a particular ore deposit.

An initial survey of the previous work on the analysis of native gold revealed that very little was known about the composition of free gold and the factors which affected it. Therefore, a very detailed review of the associations and characteristics of gold in ore deposits was carried out, in order to assess fully the results obtained in the present investigation. This review is being published as an information circular by the Economic Geology Research Unit and is briefly summarized in this thesis.

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Samples containing native gold were collected from old workings and present day mines throughout the Barberton region. In addition, to study the variation in the composition of gold along an ore shoot, samples were collected from various levels along the Zwartkopje shoot at Sheba Mine. The gold from these samples was extracted with a minimum amount of contamination and analyzed to determine the trace element composition and the copper, iron and silver contents. The trace elements were determined semi-quantitatively using an optical spectrograph; the copper and iron contents were determined by atomic absorption spectroscopy and the fineness by fire assay.

The results indicated that two types of gold occur in the Zwartkopje shoot, above and below the 20 level respectively. This is shown by the marked change in the composition of the gold samples between the 18 and 20 levels. In both types the fineness increases with depth while the copper and iron contents decrease. The minor element composition is relatively simple and seems to be controlled by the chemical environment at the time of deposition of the gold.

The fineness of the regional samples is highest in the area around Agnes Mine and between the Consort and Sheba Mines and decreases away from these localities. This seems to indicate that the source of the mineralization occurs in these areas. The copper and iron contents seem to show no definite variation and the minor element content appears to be related to the original composition of

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the ore fluids and the chemical environment at the time of deposition.

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C. A REVIEW OF THE GEOCHEMICAL ASSOCIATIONS AND CHARACTERISTICS OF NATIVE GOLD

(a) Introduction.

Gold occurs sporadically in very small amounts throughout all phases of the earth. For example, the concentration of the element in the earth's crust is 0.0000n gm /ton (Woodtli, 1960): the average gold content for nickel-iron meteorites and troilites is 4 and 0.7 p.p.m., respectively (Goldschmidt, 1958); in the standard granite and diabase, G-1 and W-1, it is 0.01 and 0.018 p.p.m., respectively (Ahrens and Fleischer, 1960, quoted by Ahrens and Taylor, 1961); in sedimentary rocks the average gold content is 15 mgm/ton (Lincoln, 1911).

In ore deposits, however, gold tends to be concentrated in amounts greater than those quoted above and is associated with definite minerals and elements. Its composition varies with certain physical factors such as the depth of deposition.

In nature, gold occurs normally as the native metal, usually alloyed with some silver and containing small amounts of copper and other base metals. The only relatively common natural compounds of

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gold are the tellurides such as calaverite, sylvanite, mullerine and nagyagite. Maclaren (1908) reported that in addition to gold, silver and tellurium, the above four minerals contained copper, iron, lead, bismuth, zinc, antimony, selenium and sulphur, indicating the large variety of elements with which gold may be associated. Occasionally alloys of gold with other metals such as mercury, bismuth, copper and palladium are found.

(b) The associated minerals and elements in gold ore deposits.

The association between gold and certain ore minerals has been observed in almost all ore deposits Don (1897) noted a correlation between sulphide mineralization and the gold content of the ore in the South St. Mungo Mine, Bendigo, Australia and proved statistically that a high sulphur content indicated rich gold values. A similar association between the gold-silver ores of Gilpin Co., Colorado, and sulphides and quartz, was reported by Collins (1902). However, Hulin (1930) found that gold in the Kennedy Mine, California, tended to occur with galena, chalcopyrite, apatite and carbonates rather than with pyrite, sphalerite and quartz. In the ore of the Lake Shore Mine, Canada, the gold tends to be associated with either chalcopyrite or pyrite (Blomfield et al, 1936). Frankel (1939) reached a similar conclusion for gold in the Black Reef. Other authors who have reported associations between gold and definite minerals include Wilson (1944), who noted an association between gold and

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alunite at Goldfield, Nevada; Tapp (1948) who found that gold in the North Empire district of Colorado was related to the primary and secondary copper mineralization; Saksela and Heiskanen (1952) in the Valkealocki area, Finland; and Edwards (1955) who reported that the gold in the Hill 50 Mine, West Australia, was genetically related to the sulphide mineralization and showed a preference for pyrite and chalcopyrite even though pyrrhotite was the dominant sulphide.

Mineral associations from 585 gold deposits throughout the world were reviewed by Lincoln (1911) and he concluded that pyrite, galena, chalcopyrite, argentite, pyrrhotite and silver were the most common associates of gold. Schwartz (1944), in a similar review of all the data published after Lincoln, found that pyrite, arsenopyrite, galena, sphalerite, chalcopyrite, the bismuth minerals, pyrrhotite and tetrahedrite-tennantite occurred most commonly in contact with gold. The most common gangue minerals were quartz, carbonates, chlorite, graphite, carbonaceous material and tourmaline. He concluded that there was no definite evidence for the precipitation of gold by the host minerals though the possibility could not be ignored. Van Aubel (1935), Warren and Cummings (1937) and Boyle (1961) reviewed similar information on the ore deposits of Eastern Urega (Congo), British Columbia and the Yellowknife district, Canada, respectively.

De Villiers (1957) dealt with the chemistry and mineralogy of the Barberton gold deposits. Table I summarizes the results of the

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Table 1 Ore Minerals of the Barberton district. (after De Villiers, 1957)

Ore:	Arsenopyrite-pyrrhotite			Antimonial ore		Lead-bearing ore		Pyritic ore		
Mine:	Eagles Nest	Lily	New Consort	Amo deposit	Bellevue	Rosetta	Alfstrom	Alpine	Agnes	Three Sisters
Arsenopyrite	2	3	2	-	1	-	-	-	-	-
Antimony	-	-	1	-	-	-	-	-	-	-
Berthierite	-	-	1	-	-	-	-	-	-	-
Bismuth	-	-	tr	-	-	-	-	-	-	-
Bournonite	-	-	-	-	-	tr	-	-	-	-
Chalcocite	-	-	-	-	-	-	-	-	-	-
Chalcopyrite	-	1	3	-	tr	2	-	1	1	tr
Cobaltite	-	-	-	-	-	-	-	-	-	-
Corynite	-	-	-	-	-	tr	-	tr	-	-
Covellite	-	-	-	-	-	-	-	-	-	-
Enargite	-	-	-	-	-	tr	-	-	-	-
Galena	-	-	tr	-	-	3	3	1	-	-
Gold	-	1	2	-	tr	1	-	1	1	1
Jamesonite	-	-	-	tr	-	-	-	-	-	-
Magnetite	-	1	-	-	-	-	-	-	-	-
Marcasite	-	-	1	-	-	-	-	-	-	-
Maucherite	-	-	tr	-	-	-	-	-	-	-
Melinkovite-pyrite	-	3	-	-	-	-	-	-	-	-
Niccolite	-	-	tr	-	-	-	-	-	-	-
Pentlandite	-	-	1	-	-	-	-	-	-	-
Platinoid-minerals	1	-	-	-	-	-	-	-	-	-
Pyrite	3	-	-	1	2	3	1	2	3	2
Pyrrhotite	1	3	3	-	-	-	-	-	-	-
Silver	-	-	-	-	-	tr	-	-	-	-
Sphalerite	-	-	-	-	-	3	2	1	1	-
Stibnite	-	-	2	3	3	-	-	-	-	-
Tetradymite	-	-	-	-	-	-	-	-	-	-
Tetrahedrite	-	-	-	-	-	2	-	1	-	-
Trevorite	-	-	tr	-	-	-	-	-	-	-
Violarite	-	-	-	-	-	tr	-	1	-	-

N.B. 3 very abundant; 2 common; 1 rare; tr trace amounts; - not reported

Table I, continued.

Ore:	Pyritic ore									
Mine:	Fairview	Sheba	Golden Quarry	Sheba Queen	Comstock	Forbes Reef	Barbrook	Belfast	Clutha	Piggs Peak
Arsenopyrite	2	2	2	1	2	-	2	-	2	1
Antimony	-	-	-	-	-	-	-	-	-	-
Berthierite	-	-	-	-	-	-	..	-	-	-
Bismuth	-	-	-	-	-	-	tr	-	-	-
Bournonite	-	-	-	-	-	-	-	-	-	-
Chalcocite	-	1	-	-	-	-	-	-	-	-
Chalcopyrite	1	1	-	tr	1	1	tr	1	1	1
Cobaltite	-	-	-	-	-	-	-	-	-	tr
Corynite	-	-	tr	-	-	-	-	-	-	-
Covellite	-	1	-	-	-	-	-	-	-	-
Enargite	-	-	-	-	-	-	-	-	-	-
Galena	-	-	tr	-	-	-	-	-	-	-
Gold	tr	2	1	tr	tr	tr	1	1	tr	tr
Jamesonite	-	-	-	-	-	-	-	-	-	-
Magnetite	-	-	-	-	-	-	-	-	-	-
Marcasite	-	-	-	-	-	-	-	-	-	-
Maucherite	-	-	-	-	-	-	-	-	-	-
Melnikovite-pyrite	-	-	-	-	-	-	tr	-	-	1
Niccolite	-	-	-	-	-	-	-	-	-	-
Pentlandite	-	-	-	-	-	-	-	-	-	-
Platnoid-minerals	-	-	-	-	-	-	-	-	-	-
Pyrite	3	3	3	3	2	2	3	1	3	3
Pyrrhotite	1	-	1	tr	tr	-	1	1	1	1
Silver	-	-	tr	-	-	-	-	-	-	-
Sphalerite	-	-	-	-	-	-	-	-	-	-
Stibnite	-	-	-	-	-	-	-	-	-	-
Tetradymite	-	-	tr	-	-	-	-	-	-	-
Tetrahedrite	-	1	-	-	-	-	-	-	-	-
Trevorite	-	-	-	-	-	-	-	-	-	-
Violarite	-	-	-	-	-	-	-	-	-	-

N.B. 3 very abundant; 2 common; 1 rare; tr trace amounts; - not reported.

mineralogical study. The ore deposits are divided into four types, namely, the arsenopyrite-pyrrhotite ores, the lead-bearing ores, the antimonial ores and the pyritic ores. Native gold is found in nearly all deposits of all four types of ore. Arsenopyrite and pyrite, and to a lesser extent, chalcopyrite, are the most common sulphide minerals. Unusual minerals found in the region include tetradymite, in the Golden Quarry Mine; an unidentified platinoid-bearing mineral, in the Eagles Nest Mine; and native silver in the Rosetta and Golden Quarry Mines.

In addition to associated ore minerals, definite elements appear to occur with gold in ore deposits. Lincoln (1911) found that, excluding iron and lead in the form of pyrite and galena, the most common elements associated with gold are arsenic, bismuth, selenium and tellurium. Haycock (quoted by Blomfield et al, 1936) found that iron, copper, silicon, magnesium, calcium, gold, molybdenum, tellurium and lead constituted the ore concentrates of the Lake Shore Mine. In addition to these, Blomfield and his co-workers (1936) reported carbon, arsenic, sulphur and zinc.

At Goldfield, Nevada, Wilson (1944) found that a definite relationship existed between silver, gold, bismuth and tin on the 830' level of the Consolidated vein. Although this relationship persisted laterally along the vein, it had disappeared on the 225' level of the Clermont vein. At this level, and nearer the surface, tin and bismuth

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were either absent from the ore samples or were present in very small amounts. In addition, gold and silver varied independently of each other. Similarly, minor impurities such as silver, bismuth, lead and tin from gold veins in California showed no significant correlation with high grade values, according to Fuller (1942, quoted by Cooke, 1947).

In a survey of ores from some Russian mines, Zemel (1936) found that bismuth, tellurium, cobalt, molybdenum and tin tended to concentrate in the ores while thallium, gallium, germanium and indium did not. Prior to this, Zemel (1935) reported the presence of zirconium, tungsten, vanadium, titanium, molybdenum and thorium in gold slimes from Russian mines.

Concentrates of ores from various Barberton gold mines were analyzed by De Villiers (1957), whose results are given in tables II and III. In addition to the elements which seem to be commonly associated with gold such as arsenic, lead, silver and tin, De Villiers reported the presence of tungsten, selenium and tellurium, each in one concentrate. Steele and Carlton (1961) spectrographically analyzed samples of high and low grade pyritic ore from the Woodbine reef. The only difference in the trace element composition of the two ores was the absence of lead from the low grade ore, and even this element was detected on chemical enrichment of the low grade sample. Elements common to both samples included manganese, nickel, tin, bismuth, cadmium, cobalt, chromium, molybdenum, antimony and zinc.

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Table II. Composition of gold concentrates from the Barberton district (after De Villiers, 1957).

Concentrate	Ag	Au	Sb	As	Ni	Co	Bi	Zn	Pb	W	Mo	Te	Se	Sn
Rosetta Mine	6	4	4	0	1	1	0-1	6	4	0	0	0	0	0
Rosetta Mine, richest fraction	6	6	5	0	0	1	1	6	5	0	0	0	0	0
Agnes Mine	4	3	0	0	4	3	0	0	2	0	0	0	0	0
Fairview Mine	6-7	8	1	8	3	4	0	2-3	0	1	0	0	0	tr
Fairview Mine, gravity concentrate	3	4	2	8	1	1	0	0	2	0	0	0	0	0
Fairview Mine, flotation concentrate	2	3	0	5	2	3	0	0	0	0	0	0	0	0
Alpine Mine	5	6	4	1-2	6	6	0	0	3	0	0	0	0	0
Sheba Mine	5	5	1-2	2	5	5	0	0	0	0	0	0	0	0
Sheba Mine, richest fraction	7	7	1	4	4	3	0	0	1	5	0	0	0	tr
New Consort Mine	5	4-5	3	8	7	6	0	0	0	0	0	0	0	0
New Consort Mine, richest fraction	9	8	3	6	6	5	0	0	3	3	0	0	0	0
Golden Quarry Mine	6-7	8	0	2	2	1	0	0	1	0	0	0	0	0
Golden Quarry Mine	5	8	0-1	8	4	1	0	0	2	-	0	0	0	0
Three Sisters Mine, corduroy concen.	5	4	0	0	2	4	0	0	0	0	0	0	0	0
Three Sisters Mine, Midlings	6-7	7	0	0	1	3	0	0-1	0	0	0	0	0	0
Piggs Peak Mine	6	7	2	10	6	4	0	0-1	1	0	0	0	0	tr
Woodstock Mine	6	5	1	1-2	7	6	0	0	2	1	0	0	0	tr
Forbes Reef, Western workings	0	0	1	0	1	0	0	0	1	0	1	0	tr	0
Forbes Reef	0	0	0	0	0-1	0-1	0	0	0	0	0	0	0	0

N.B. Ge, Tl and the platinum metals were looked for but were not detected in any concentrate.

Numbers give the approximate order of concentration for the elements based on the intensity of the spectrographic lines.

Table III The chemical analyses of gold concentrates from Barberton (from De Villiers, 1957)

Concentrate	Ag	Sb %	Bi	Zn %	Pb %	Cu %	As %	Ni %	Co %	Fe %	S %	Au
Rosetta Mine, richest fraction .	tr	0.41	tr	0.17	8.9	0.3	-	-	-	-	-	-
Alpine Mine	tr	0.67	-	-	tr	0.17	tr	0.15	0.16	-	-	-
New Consort Mine	-	0.13	-	-	-	0.05	23.8	1.19	0.36	-	-	-
Three Sisters Mine, midlings. ..	tr	-	-	-	-	0.01	-	-	-	-	-	-
Fairview Mine.	tr	-	-	-	-	-	-	-	-	-	-	-
Rosetta Mine	tr	0.47	-	0.09	9.5	9.3	-	tr	-	43.12	30.38	88 ozs/ton

N.B. tr = trace amounts; - = not reported.

While relatively little work has been done on the trace elements in gold from ore deposits, several authors have published papers on the trace elements in ore minerals associated with gold in ore deposits. For example, Bruce (1934) spectrographically examined varieties of coloured quartz from Canadian gold veins in an attempt to explain the association between high gold values and blue and grey quartz. The minor elements in pyrite from Canadian gold deposits have been studied in detail by Auger (1941) and Hawley (1952). Auger found that samples of pyrite taken from localities within and outside the Pre-Cambrian shield had very similar qualitative and quantitative trace element compositions. However, within one district or mine the apparent supremacy of one element over another was very consistent and the rarer elements tended to be confined to a particular mine or district. In addition, the results indicated that the type of deposits had a definite bearing on the nature and proportion of the minor elements present in the pyrite, whereas the wall-rock and gangue material did not affect the trace element distribution. Auger therefore concluded that generally the total composition of the pyrite was mainly dependent on the nature of the ore fluids. However, from examination of pyrite from the individual deposits of the Hollinger, Noranda and Siscoe Mines, Auger found that local conditions at the time of deposition also affected the minor element composition and controlled variations in the composition along the ore bodies. Hawley (1952) examined pyrite from 4 different types of deposits, namely, the Powell-Rouyn quartz vein, the Kerr-Addison flow ore, seven

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Kirkland Lake mines and a mine in the Porcupine district. Trace elements common to all four types of deposits were gold, silver, nickel, copper, chromium, manganese, molybdenum, vanadium, lead and titanium. In each deposit there was a marked uniformity in composition with increasing depth, indicating relatively constant conditions of deposition.

A similar survey of the minor elements in sphalerite from Western Canadian mines by Warren and Thompson (1945) showed that manganese-rich sphalerite indicated shallow gold deposits, which did not persist to depths greater than 1500'. Boyle (1961) found that the chalcophile elements, including antimony, gallium, tin, indium, vanadium, silver, gold and lead, in addition to the more common ones, tended to concentrate in pyrite from the Yellowknife gold ores. Arsenopyrite also collected these elements, especially cobalt, nickel and antimony. However, pyrrhotite appeared to have a low tolerance for extraneous chalcophile elements and contained only cobalt, nickel and copper. Hawley and Nichol (1961) carried out a similar study on pyrite, pyrrhotite and chalcopyrite from Canadian ore deposits and found a preferential concentration of the minor elements, especially cobalt, nickel, silver and lead.

(c) The composition of native gold

Generally native gold contains a certain percentage of silver, copper and iron, together with the

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