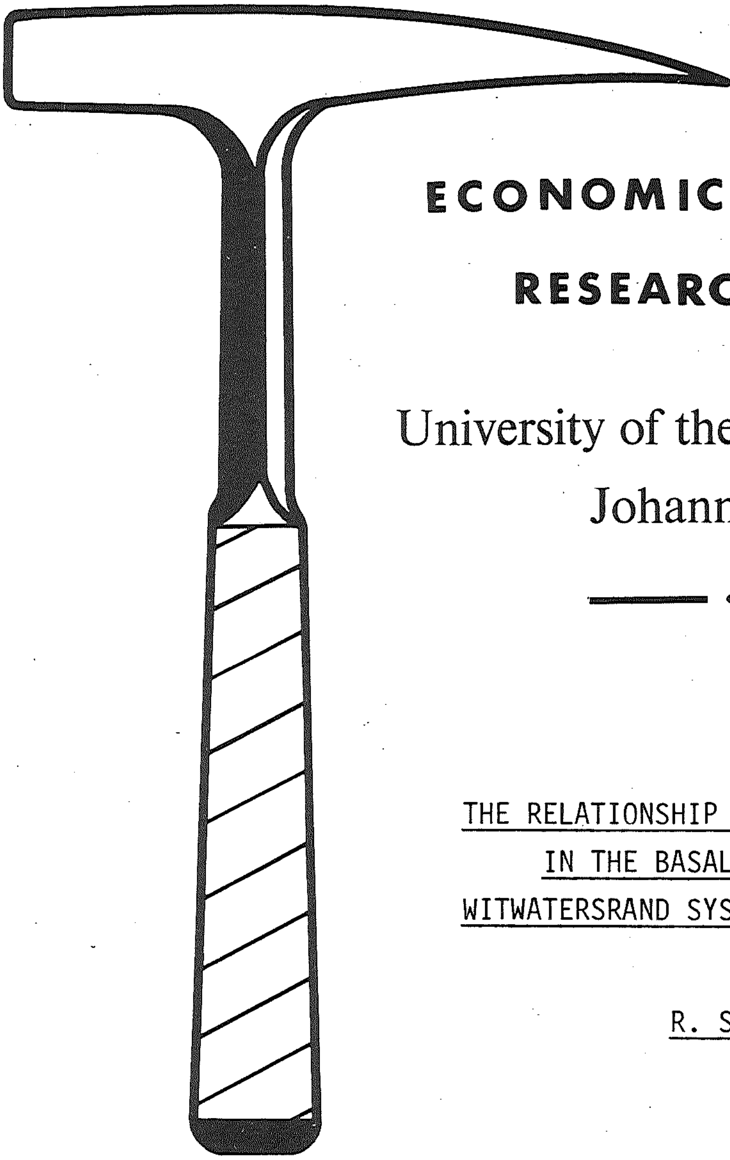

ECONOMIC GEOLOGY RESEARCH UNIT

University of the Witwatersrand
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THE RELATIONSHIP OF SILVER AND GOLD IN THE BASAL REEF OF THE WITWATERSRAND SYSTEM, SOUTH AFRICA

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INFORMATION CIRCULAR No. 52

UNIVERSITY OF THE WITWATERSRAND

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ABSTRACT

Ag/Au ratios of individual gold particles and of ore-samples, obtained from the Basal Reef conglomerate horizon of the Upper Witwatersrand System in the Orange Free State Goldfield (South Africa), are discussed. The Ag/Au values of individual gold grains were found to be exceptionally constant at about 0.0812, whereas the Ag/Au ratios of ore-samples have markedly higher values and show a large variation. These values indicate that the detrital gold has been homogenized during transportation and sedimentation and that part of the original silver content has been redistributed. It is likely that the first refining of detrital gold particles occurred in streams which eventually drained into the Witwatersrand basin. Further redistribution of the silver relative to the gold took place in the littoral zone of the basin, where the conglomerates were reworked by wave action and erosion. It is contended that supergenic enrichment of gold might also have taken place close to the original shoreline. These processes are believed to account for an increase in the Ag/Au values of ore-samples towards the northwest in the area investigated. The gold is considered to have homogenized during the metamorphic period of the Witwatersrand System, when pseudo-hydrothermal transport and redeposition of certain constituents took place. It is suggested that the main portion of the silver content of the original alloy, which was redistributed during the various processes outlined above, is now present as finely dispersed silver-minerals. The hypothesis of an elevation control of the Ag/Au values has been found to be improbable.

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THE RELATIONSHIP OF SILVER AND GOLD IN THE BASAL REEF OF THE WITWATERSRAND SYSTEM, SOUTH AFRICA

INTRODUCTION

The distinct variations of the Ag/Au values found in many gold deposits throughout the world have attracted the attention of many students of gold ores. In the Witwatersrand Goldfield this subject has been studied with particular interest since mining operations started more than 80 years ago. Several papers dealing with genetical, structural, and mineralogical aspects, which might cause changes in the Ag/Au values, have been published.

Lane Carter, in 1902, first reported a 9 to 19 per cent variation in the silver content of mine assay samples. This observation was later confirmed by Dures (1913) who found that the silver on different mines in the Witwatersrand Goldfield varied from 8.5 to 14.5 per cent of the bullion content of the assay prills. Young (1917) suggested that the fineness of Witwatersrand gold varied with its grain-size, the coarser gold generally having a lower silver content. Lawn (1924) reported that in individual samples there was a tendency for low silver percentages to be associated with high gold values.

Graton (1930) for the first time, drew attention to the occurrence of potentially argentiferous base metal sulfides in the conglomerate horizons. Such minerals could dilute the recovered gold in bullion with silver and could thus be responsible for the variation of the Ag/Au ratios between individual ore-samples.

Fisher (1939), studying Witwatersrand bankets with an ore-microscope, found "that all the coarse gold in the samples was of nearly uniform composition, the silver content being approximately 10 per cent". He came to the same conclusions as Graton (1930), suggesting that varying amounts of silver-bearing base metal sulfides account for the variation in silver percentage between samples.

Prentice (1939), after a detailed investigation of the variation of the Ag/Au ratios in the Witwatersrand Goldfield, confirmed the earlier findings of Young (1917) concerning a correlation between the grain-size of gold and its silver content. Prentice (1939) could find no relationship between the pyrite content and the silver percentage in the ore, but observed "a definite correlation between the gold values of the ore and the silver percentage, the latter decreasing as the former rises and vice versa". This observation has been confirmed by later workers (Richards and Rubidge, 1950 and von Rahden, 1965) all of whom were unable to offer any explanation for this trend.

Microscopic investigations of the Witwatersrand ores (Frankel, 1939; Liebenberg, 1955; Ramdohr, 1958; Saager, 1968 and 1969) revealed that gold inclusions in rounded grains of pyrite, cobaltite, and linnaeite, interpreted as being detrital, not infrequently possess a paler colour and higher reflectivity than the ordinary (remobilized) gold. This indicates a higher silver content. Ramdohr (1958) considered the gold inclusions of higher reflectivity to be a primary feature, originating from the source deposits and still exhibiting the original Ag/Au values.

Recently Hargraves (1963) and von Rahden (1965) discussed the variation of fineness in Witwatersrand ores. Hargraves (1963) studied the variation of silver in collections of bullion beads from mine samples obtained from all producing Witwatersrand mines in the Transvaal and Orange Free State. He interpreted the results as suggesting that in each Witwatersrand reef the silver content of the bullion varies as a function of sample depth relative to the surface. Thus, a particular reef in deep areas appears to contain gold with a lower average silver percentage than the same reef in shallow areas. This apparent elevation control of the Ag/Au ratio was regarded by Hargraves (1963) as a geochemical distribution pattern imposed, or superimposed, by "some physico-chemical process" subsequent to the deposition of the conglomerates.

Von Rahden (1965), who studied the Ventersdorp Contact Reef and the Main Reef, concluded that in these ore-horizons variations in apparent fineness could satisfactorily be explained by the presence of silver minerals. Contrary to the suggestions of Graton (1930) and Fisher (1939), von Rahden (1965) considered that argentiferous base metal sulfides could not have contributed to the wide spread of the Ag/Au values since he found such minerals occurring only in extremely minor amounts. In agreement with Prentice (1939) and Richards and Rubidge (1950), von Rahden (1965) also reported an antipathetic trend between the ore grade and its Ag/Au value. He concluded, however, that "the reason for the markedly lower apparent fineness shown by ore containing less than an apparently critical amount of gold is not understood". His studies, moreover, in no way support an elevation control of the silver as envisaged by Hargraves (1963).

In this investigation, Ag/Au values obtained by fire assay of 130 ore-samples from the Basal Reef in the Orange Free State are compared with the Ag/Au values of 47 individual gold particles determined with the aid of an electron-microprobe analyser. It was hoped that such a study might yield new information relevant to the conclusions drawn by earlier workers who were handicapped by a lack of knowledge of the true fineness of the gold particles within the ore. The results of an intensive microscopic investigation by the author on the Basal Reef of the Free State Geduld Mine (Saager, 1968a, 1968b, 1969) are incorporated in the study.

THE OCCURRENCE OF GOLD IN THE BASAL REEF

The Basal Reef is the most important ore-horizon in the Orange Free State Goldfield. With respect to reef thickness, pebble-size, and carbon content, it has more in common with the Carbon Leader of the Far West Rand than with the banket-type conglomerates of the Central Rand. Its mineral paragenesis, however, is closely similar to that of most other Witwatersrand auriferous conglomerates. The Basal Reef lies in the upper half of the Main-Bird Series, within the lower portion of the Upper Witwatersrand System.

The gold in the Basal Reef occurs in much the same way as in other ore-horizons of the Witwatersrand Goldfield. It varies considerably in grain-size from 1 micron to over 1,000 microns, commonly averaging between 5 and 100 microns. Macroscopically visible gold is only very rarely encountered. Usually the gold occurs as irregular, jagged particles among the matrix constituents of the conglomerate and is intimately intergrown with secondary, reconstituted sulfides, or it fills fractures and cavities in earlier formed minerals. Frequently the gold, during its reconstitution, has migrated into the marginal areas of porous pyrite grains where it now forms secondary inclusions. Primary inclusions and myrmekitic intergrowths of gold with detrital pyrite and linnaeite have occasionally been observed (Ramdohr, 1958; Saager, 1968a, 1969). Rarely, rounded gold grains are found in the matrix. According to a suggestion by Liebenberg (1955), these possibly represent detrital gold particles which still exhibit the abraded morphology obtained during transportation.

The close relationship between gold and thucholite in many Witwatersrand ores has been known for a long time, suggesting precipitation by the latter on gold taken into solution. The common close association also of uraninite with gold, led Liebenberg (1955) to suggest that the uraninite may have exerted a precipitating effect of gold from solution.

A vast array of incontrovertible macroscopic and microscopic evidence, now accumulated from all areas of the Witwatersrand and associated subsidiary basins, leaves little doubt that the gold is essentially of placer origin. The mode of occurrence of the gold and especially its relationship and association with other minerals clearly indicates subsequent mobilization and redeposition during the metamorphism of the Witwatersrand sediments. The mise en place of the gold and other minerals has been described in detail by Liebenberg (1955) and Ramdohr (1958). According to Ramdohr (1958) "all the indications are that the pseudohydrothermal transport of material has been effective over only a very small distance and is to be measured in fractions of an inch rather than in hundreds of feet". A true hydrothermal origin of the major portion of the gold now appears to be completely refuted.

SAMPLING AND TREATMENT OF DATA

130 ore-samples were collected from the Basal Reef in currently accessible stopes in the Free State Geduld Mine, near Welkom in the Orange Free State, the exact locality and elevation of all the samples being accurately recorded. Elevations are referred to a datum line of 6,000 feet above sea-level, as is common practice on Witwatersrand gold mines. The silver- and gold-contents of the ore-samples from which the Ag/Au values are calculated were determined to an accuracy of 0.05 dwt. per ton or approximately to 0.09 ppm by the conventional fire assay method at the Anglo American Research Laboratory in Johannesburg.

From the 130 ore-samples, 11 of different ore-grade were selected for examination with an electron-microprobe. One to three polished sections were prepared from each of the ore-samples and carefully examined under the ore-microscope. In each polished section one to ten gold particles of differing development and association were selected and their gold and silver percentages determined by means of an Applied Research Laboratories model EMX electron-microprobe at the Department of Crystallography and Petrology of the Federal Institute of Technology in Zürich. Pure gold and pure silver were used as standards, and on each particle between 5 and 10 point analyses were carried out. The standard deviations were usually less than 2 per cent of the amount of gold or silver determined. Ag $L\alpha$ and Au $L\alpha$ were measured at an accelerating voltage of 25 Kv and the sample current employed was 0.01 μA. To correct the resulting data for dead-time, drift, background, absorption and fluorescence, use was made of the computer programs EMX and EMX2 for electron-microprobe data processing published by Fraser et al. (1967).

The electron-microprobe is ideally suited for the determination of the composition of small in situ grains in the ore. The silver and gold percentages obtained from individual gold particles therefore reflect the true fineness of the particular grain analysed. Prior to the present study, true fineness values of gold were unknown from Witwatersrand ores, evaluated assessments hitherto being obtained by indirect methods, such as comparison of colours, or reflectivity measurements (Fisher, 1939; von Rahden, 1965).

The silver and gold content of the ore-samples obtained by fire assay yield the fineness of the total ore analysed. This value generally differs from the true fineness of the individual gold particles in the ore, unless gold and silver occur in no minerals other than in the natural alloy of rather homogeneous composition. Since this is certainly not the case in Witwatersrand ores, the data obtained from crushed ore-samples by the fire assay method represent the apparent fineness.

The formula for the fineness given by Fisher (1945) shows that small changes in very low silver percentages do not show up as clearly as when direct Ag/Au values are used. This can be seen in Table 1, where the fineness values and the Ag/Au values are listed side by side. Therefore, when comparing small silver percentages, the Ag/Au values were usually employed in preference to the fineness values.

THE SILVER AND GOLD CONTENTS OF INDIVIDUAL GOLD PARTICLES

In most of the electron-microprobe analyses the silver and gold percentages added up to approximately 100 and the Ag/Au ratio, as well as the true fineness value, could be determined directly. Exceptions were found only in two slightly reddish gold grains which totalled 93.4 and 94.2 per cent respectively. A qualitative analysis with the electron-microprobe revealed that this discrepancy was partly caused by the presence of a relatively substantial amount of Cu in the silver-gold alloy. The results of the electron-microprobe determination are given in Table 1.

The Ag/Au values for the 47 gold particles vary from 0.0689 to 0.1029, the mean value being 0.0812. The range of true fineness is from 906 to 935 with a mean value at 925. Comparison with the Ag/Au ratios and apparent fineness values of the present suite of ore-samples, which range from 0.600 to 0.0646 and from 625 to 930 respectively, indicates clearly that the small variations found in the silver content of individual gold particles cannot account for the larger variation in silver percentages observed in the 130 ore-samples. This larger variation is, furthermore, clearly borne out by the coefficients of variation which, in the case of the individual gold particles are approximately 10 times smaller than for the ore-samples (see Table 2).

Several investigators have suggested that the Witwatersrand gold was at least partially derived from gold-quartz vein deposits (Ramdohr, 1958; Viljoen, 1967; Saager, 1968b, 1969). If this is the case, there must have been, in the source ore-deposits, a substantial primary variation in the fineness of the gold, as exemplified by studies of lode deposits in New Guinea, Rhodesia, and Canada by Fisher (1945), Eales (1961), and Fitzgerald et al. (1967). Lindgren (1933) and Fisher (1945) observed that corrosion, leaching, and reprecipitation processes take place during stream transport of gold, resulting in an increase in fineness down-stream from the lode deposit. It can therefore be assumed that the fineness of the primary Witwatersrand gold must have been subjected to change, and was probably increased to a certain extent, during the transportation and sedimentation stages of its history. It is, however, unlikely that this removal of silver would have resulted in such an extraordinarily constant silver content as revealed by the individual gold particles investigated. The writer therefore considers that the far-reaching homogeneity of the gold must have been attained subsequent to its deposition, most likely during the metamorphism of the sediments, when by far the major portion of the detrital gold was reconstituted and redeposited under pseudohydrothermal conditions.

TABLE 1

Ag/Au Ratios and True Fineness Values of
47 Individual Gold Particles

		Ag/Au	Fineness
Sample 103	P11	0.0761	930
	P12	.0856	921
	P13	.0778	929
	P21	.0788	927
	P22	.0789	927
Sample 108	P31	.0814	925
	P32	.0816	924.5
	P33	.0802	925
	P34	.0810	926
Sample 109	P41	.0861	921
	P42	.0869	920
	P43	.0875	920
	P44	.0864	921.5
	P45	.0853	920.5
	P46	.0865	921
Sample 110	P51	.0828	923.5
	P52	.0878	930
	P53	.0861	920
Sample 113	P61	.0795	926.5
	P62	.0788	927
	P63	.0706	934
	P64	.0772	928
	P65	.0735	931.5
Sample 113	P71	0.1029	906.5
	P81	.0762	929
	P82	.0741	931
	P83	.0805	925
	P84	.0789	927
Sample 112	P91	.0817	924.5
	P92	.0822	924
	P101	.0913	916
Sample 115	P111	.0846	922
	P121	.0869	920
Sample 116	P131	.0769	926
	P132	.0783	927.5
	P133	.0733	932
	P134	.0758	929.5
	P141	.0689	935
	P142	.0768	925.8
	P143	.0801	925.8
	P144	.0786	927
Sample 117	P151	.0840	922.5
	P152	.0839	922.5
Sample 124	P162	.0826	924
	P163	.0772	928
	P164	.0749	930
Sample 129	P171	.0861	921

TABLE 2

Means, Standard Deviations and Coefficients of
Variation of the Ag/Au Ratios and Fineness Values from
47 Gold Particles and 130 Ore-Samples

	Individual Gold Particles				Ore-Samples			
	N	$\bar{x}$	s	C	N	$\bar{x}$	s	C
Ag/Au	47	0.0812	0.0057	0.070	130	0.0995	0.0605	0.608
Fineness	47	925	5	0.0054	130	875	63	0.072

N = number of samples

$\bar{x}$ = mean

s = standard deviation

C = coefficient of variation

A. Ag/Au Values of Gold Particles with Different Mineralogical Association

In order to establish whether the position of the gold particles within the ore, and their association with other minerals have any bearing on the amount of silver which was 'lost' during the homogenization process, the gold grains were grouped into the following four categories -

Group I — Primary gold inclusions in detrital rounded pyrite.

Group II — Reconstituted gold which has migrated into porous grains of other ore-minerals, mainly pyrite.

Group III — Gold particles associated with gangue - generally quartz - and which do not border on any ore-minerals.

Group IV — Gold particles associated with uraninite, thucholite, and galena.

The mean values and the standard deviations of the silver percentages of the four groups are given in Table 3. The paucity of primary gold inclusions in detrital pyrite grains made it difficult to examine a statistical number of such inclusions and only one inclusion of primary gold was measured in the present study. However, Frankel (1939), Liebenberg (1955) and Ramdohr (1958) showed that the sporadically occurring primary gold inclusions possess an exceptionally high silver content.

TABLE 3

Mean Values and Standard Deviations of Four Groups of Gold Grains Showing Different Associations with Bordering Minerals of the Basal Reef

	Group I	Group II	Group III	Group IV
N	1	14	23	9
$\bar{x}$	9.37%	7.87%	7.41%	7.15%
s	-	0.35%	0.38%	0.34%

N = number of gold grains

$\bar{x}$ = mean value

s = standard deviation

The means of Group II, III and IV are closely similar, and the cumulative frequency distributions of these three groups were plotted (Figure 1) and a graphical nonparametric Kolmogorov-Smirnov test was carried out to test the hypothesis that the three sample cumulative frequency distributions were drawn from populations having the same frequency distributions (Miller and Kahn, 1965). The determined values for Group II and Group III (G_2 and G_3), as well as for Group II and Group IV (G_2 and G_4), exceed a fixed value obtained from tables, which enabled a rejection of the null hypothesis H_0 (that there is no difference between the Groups) at a 0.05 level of significance. Due to a relatively smaller α value between Group III and Group IV (G_3 and G_4) the hypothesis H_0 could in this case only be rejected at a 0.1 level of significance. In fact, the three comparisons are not significant at the specified levels because a two-sample test is being used instead of a three-sample test and no correction has been made for multiple comparisons. Nevertheless, it can reasonably be assumed, that the three groups represent three populations and that the grouping of the gold particles according to their association is geochemically significant.

It appears that the different silver percentages observed in the four groups can be explained in the following way :

(a) Group I represents a primary inclusion of gold completely surrounded by unmobilized (detrital) pyrite and which therefore was not affected by the homogenization processes. The determined silver content of 9.37 per cent must still represent the original silver percentage of that particular gold individual in the source ore-deposit. It is interesting to note that its Ag/Au value of 0.1029 (Table 1, sample 113/P71) is by far the highest Ag/Au ratio obtained

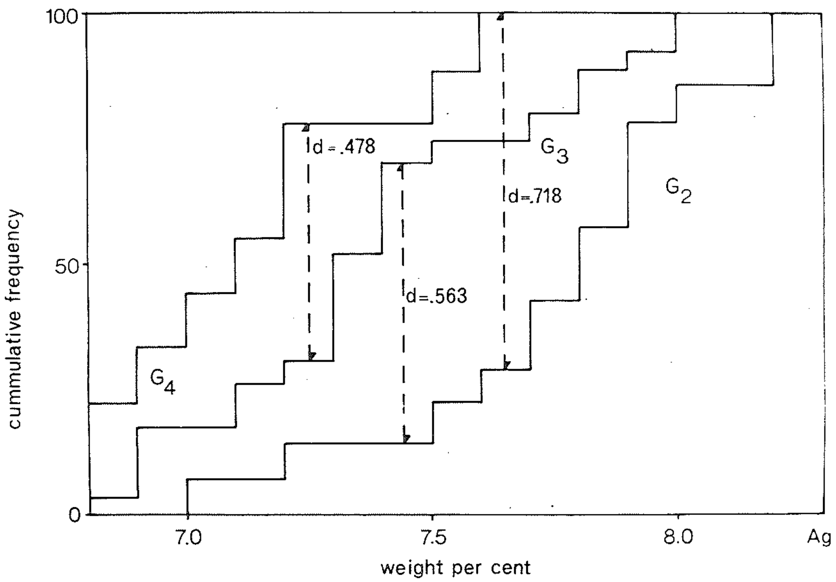

Figure 1 : Graphical solution of Kolmogorov-Smirnov statistics. G_2 - gold particles forming secondary inclusions in ore-minerals, G_3 - gold particles associated with gangue, G_4 - gold particles associated with uraninite, thucholite and galena.

from an individual gold particle and also exceeds the Ag/Au value (0.0942) of the total silver and gold produced at the Free State Geduld Mine over the last 5 years.

(b) Group II includes gold particles which infiltrated into the marginal areas of other porous minerals during the period of metamorphism and which are thus not primary. The distinctly lower mean silver content of the secondary gold inclusions (7.87 per cent) as compared with that of the primary gold inclusion (9.37 per cent) indicates that silver must have been removed during transportation and reconstitution of the gold, but not to such an extent as in the gold of Group III (7.41 per cent) and Group IV (7.15 per cent). This can probably be accounted for by the shielding effect of the surrounding ore-minerals which made the removal of the silver more difficult after the redeposition of the alloy. It also suggests that the homogenization process must have continued after the main phase of metamorphism and reconstitution, albeit to a much lesser extent.

(c) Group III represents reconstituted gold occurring along the grain boundaries and in cavities, as well as in fractures of gangue minerals. The mean silver percentage (7.41 per cent) of this group is lower than that of the two earlier discussed groups. This indicates a more prolonged influence of the homogenization process, resulting in a more pronounced loss of silver. It would seem that gangue minerals alone were a less effective "shielding" agent than ore-minerals.

(d) Group IV embraces gold associated with, or at least in close proximity to uraninite, thucholite, and predominantly radiogenic galena. The mean silver percentage found in this group (7.15 per cent) is the lowest observed in all the four groups. This particular association must, therefore, have involved the most effective means of silver abstraction. The thucholite possibly precipitated gold from solution more readily than silver which is known to be far more susceptible to solution and migration than gold. Since the galena is predominantly of radiogenic origin the well-known affinity of galena for silver will be most marked within and near uraninite. The generally finely divided galena was apparently the most effective silver acceptor, acting as a type of "sponge" for the silver which became free during the homogenization of the alloy. Such restricted and selective incorporation of silver into the lattice of galena appears feasible since galena is known to take silver readily into solid solution. Ramdohr (1960), for example, reported galena commonly containing silver in amounts of up to 1,000 ppm in solid solution. With the exception of chalcopyrite, galena has been found to be the only sulfide present in the Basal Reef which can take silver into solid solution in any significant amount. To check the outlined theory a semi-quantitative investigation of galena in the immediate neighbourhood of the gold was carried out with the electron-microprobe. This appeared to show a higher silver content (200 ppm) than galena not associated with gold (200 ppm).

B. Ag/Au Ratios of Gold Particles Having Different Morphologies and Grain-Size

Figure 2 shows the variation of true fineness in a profile across a distinctly rounded, possibly detrital gold particle (Liebenberg, 1955) and across an irregular unequivocally reconstituted gold particle. The fineness values were obtained with the electron-microprobe by

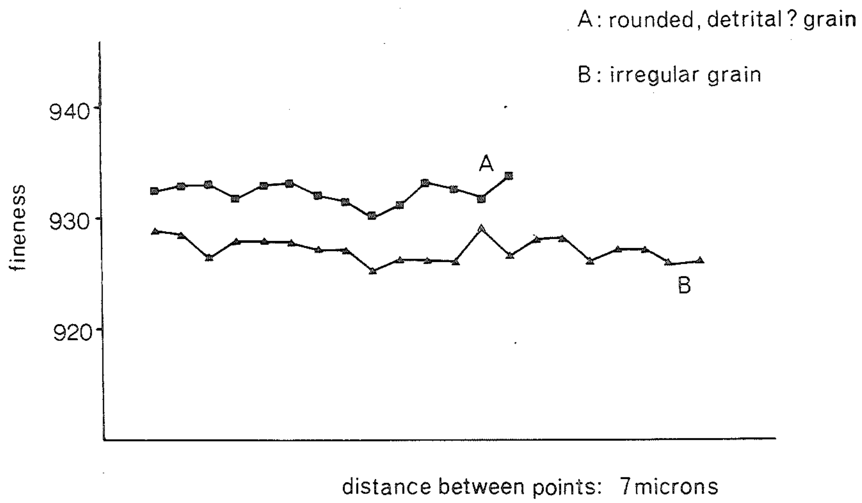

Figure 2 : Profiles of the true fineness through a rounded and an irregular gold grain.

step-scanning along the longer axis of the two grains. Gold and silver were simultaneously determined. The interval between measuring points was approximately seven microns. No pattern in the distribution of gold and silver was found in the two grains. Detrital gold grains should, however, according to the investigations carried out by Fisher (1945), exhibit a marginal rim of particularly pure gold. In alluvial gold particles from New Guinea he found that during transport, both gold and silver are dissolved by a corrosion process. Gold, however, is immediately reprecipitated to form a thin, extremely pure rim on the surface of the gold grain. The absence of a finer gold rim in the present study confirms the observation made by von Rahden (1965) on gold particles from the Venterspost Mine. He investigated the gold and silver distribution on a visual basis and did not find any layers of purer gold. In this discussion it is assumed, however, that in Witwatersrand times, chemical conditions of alluvial gold transport were identical to those of more recent times.

The variances of the fineness of the two gold grains were investigated by means of a statistical F-test to check the hypothesis that the two variances are equal. This hypothesis could not be rejected at a 0.05 level of significance. This feature, it would seem, may be explained by one or other of the following interpretations :

(a) The homogenization process, which must have affected both grains to more-or-less the same extent, has completely obliterated zones of different silver content. Therefore, a finer marginal area in the rounded (detrital) gold grain cannot be recognized any longer, and both gold particles exhibit approximately the same fineness, and the same homogeneity.

(b) Both grains are reconstituted gold particles, which were homogenized, and deprived of silver during their pseudohydrothermal transport within the ore. The rounded outline of the "detrital" grain was, therefore, not caused by abrasion during stream transport, but represents a chance intersection of an otherwise irregular particle, by the plane of the polished section. Such an interpretation appears to be more feasible, since it is unlikely to suppose that some detrital gold grains survived the metamorphic period without exhibiting any change in their morphology, while the bulk of the gold was reconstituted, thereby attaining completely different forms.

In Figure 3 the silver percentages of gold grains are plotted against their grain-size.

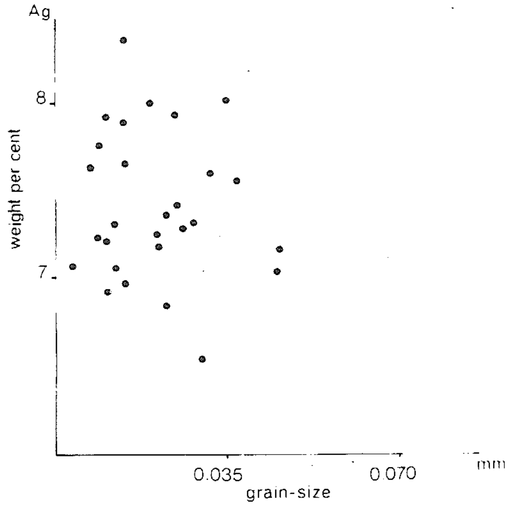

Figure 3 : Scatter diagram showing the relations between grain-size and silver content of gold particles.

The plot suggests no trend between the two variables. This impression is confirmed by a calculation of the correlation coefficient (+0.12) between the two sets of values. The writer is aware of the fact that the estimation of grain-size from polished sections can be extremely misleading. Since the habit of the gold is granular, rather than flaky, it appears justifiable to assume that at least the order of grain-size is indicated (Packham, 1955). The correlation obtained, therefore, does not support the observations of Young (1917) and Lawn (1924), who both suggested that, in the Witwatersrand ores, the coarser gold is generally purer than the finer grained gold.

DIFFERENCE BETWEEN TRUE AND APPARENT FINENESS

As illustrated in Table 2, there is a marked difference in the true fineness of individual gold grains and the apparent fineness determined on ore-samples. The difference between apparent fineness and true fineness is also clearly visible in Figure 6 where the two values obtained from the same ore-samples are plotted against the ore grade. The diagram also demonstrates the higher value of the true fineness obtained with the microprobe. This indicates that in the ore-sample assays, silver must have been incorporated from sources other than the natural silver-gold alloy. Since the coefficient of variation (Table 2) is approximately 10 times smaller for the individual gold grains than for the ore-samples, the other sources of silver must also contribute to the wide range in the Ag/Au values reported from Witwatersrand ores, and also established in the present suite of samples. Investigations of Fitzgerald et al. (1967) appear to rule out the possibility of a systematic error in the two analytical methods employed (fire assay and electron-microprobe), as well as in the cyanide circuit in the mills, to explain the difference found in the Ag/Au value.

The average ore grade of the Free State Geduld Mine over the last five years has been 20.72 dwt. gold and 1.95 dwt. silver per ton. This amounts to approximately 35.2 ppm gold and 3.3 ppm silver. The mean Ag/Au value obtained from the 47 electron-microprobe readings on individual gold particles is 0.0812, the standard deviation being 0.0057. If this ratio is valid for all the gold in the Free State Geduld Mine area it seems likely that only 2.8 ppm of the recovered silver derives actually from the natural silver-gold alloy. The remaining 0.5 ppm must derive from other silver-bearing minerals. The following modes of occurrence can be considered for such silver-bearing minerals :

(a) Galena, chalcopyrite, and, to a lesser extent, sphalerite, are potentially argentiferous sulfides which detailed microscopic investigation has shown to occur in small amounts throughout the ore-horizon. These minerals could, therefore, have taken some silver into solid solution during their pseudohydrothermal transport when the homogenization of the gold and the redistribution of the silver also took place. Cu, Pb, and Zn analyses carried out on the ore-samples from the Basal Reef revealed that chalcopyrite, galena, and sphalerite, on average, do not form more than 0.05 per cent of the total ore. In order to account for the "missing silver" (0.5 ppm) these three base metal sulfides should contain approximately 1,000 ppm silver. Such a conclusion seems highly unlikely since silver has not been detected either in the chalcopyrite or in the sphalerite using the electron-microprobe, which has a lower limit of detection of about 200 ppm. Silver, however, has been determined with the electron-microprobe in galena crystals which juxtapose redeposited gold. It can therefore be reasonably assumed that the silver content of galena, chalcopyrite, and sphalerite could account, at best, for only a small proportion of the "missing silver", but not for the variation in the Ag/Au values established between different ore-samples.

(b) Fitzgerald et al. (1967), who encountered a similar discrepancy between the Ag/Au values obtained by electron-microprobe analyses of gold grains and by fire assay from stope samples in the Val d'Or region in Quebec, showed the "missing silver" to be located in pyrite, the most common sulfide in the ore-body and which clearly contained more silver than gold.

In the Basal Reef, too, pyrite is the most abundant sulfide, constituting about 3 per cent of the total ore. If the findings of Fitzgerald et al. (1967) are also applicable to the Witwatersrand pyrite, its silver content must be approximately 17 ppm higher than its gold content in order to account for the 0.5 ppm "missing silver" in the total ore.

The history of the Witwatersrand pyrite, however, is particularly complicated and at least eight varieties of pyrite of differing genesis have been distinguished (Ramdohr, 1958; Saager, 1969). These pyrite varieties can be grouped basically into allogenic detrital and authigenic remobilized pyrite. At least 60 per cent of the pyrite in the Basal Reef is detrital and was apparently unaffected by the metamorphism. It therefore, probably did not absorb any silver during the homogenization process of the natural alloy. The secondary reconstituted pyrite, however, took part in the pseudohydrothermal transport during metamorphism, together with the silver-gold alloy, and most of the base metal sulfides (Liebenberg, 1955; Ramdohr, 1958; Saager, 1969). It is possible that this secondary pyrite could have "dissolved" some silver, since it was mobile more or less at the same time as the silver was removed from the gold. According to Fleischer (1955), silver contents in pyrite of up to 100 ppm have been reported. It therefore seems probable that silver, either in solid solution with secondary pyrite, or in the form of finely dispersed sub-microscopic inclusions could account for a large portion of the "missing silver". Since the content of secondary pyrite has been found to vary considerably in the Basal Reef (Saager, 1969), a relatively higher Ag/Au ratio in secondary pyrite could also explain the variations in the silver percentages between different ore-samples.

Prentice (1939) observed that there was "no obvious relationship between the pyritic content and the silver percentage of the ore". This seemingly contradictory statement can be explained by taking into account the fact that Prentice (1939) did not distinguish between detrital (unmobilized) pyrite - the latter being the only variety which could have affected the Ag/Au value of ore-samples to any appreciable extent. A quantitative analysis of the secondary pyrite is, however, an extremely difficult operation since it usually forms minute crystals, often finely dispersed in the gangue or occurring closely associated and intergrown with the unmobilized detrital pyrite variety. Therefore, only semi-quantitative silver determinations with the electron-microprobe were carried out, all of which showed negative results.

(c) A third possibility to account for the "missing silver" is the presence of finely dispersed silver minerals reported in the Witwatersrand ores by von Rahden (1965) and Saager (1968b). Since silver minerals such as native silver, argentite, proustite, stromeyerite, etc., all possess high silver contents, only small amounts of such minerals would be necessary to account for the difference observed between the true fineness and the apparent fineness. Small amounts which would lie in the range of 0.5 to 1 ppm, could very easily be overlooked under the ore-microscope, especially if the silver minerals occur as minute inclusions in other ore-minerals or if they are finely dispersed in the gangue. According to von Rahden (personal communication) finely dispersed submicroscopic silver minerals appear to be concentrated in the phyllosilicates which are generally present in Witwatersrand ore-horizons.

To summarize, it can be said that the last explanation outlined above seems to be the most probable, since silver minerals have actually been observed in the ore. They all possess a very high silver content and only extremely small amounts are sufficient to account for the "missing silver". Small changes in the amount of silver minerals present in the ore also satisfactorily explain the variation in the Ag/Au values between different ore-samples. A possibly higher silver concentration in the secondary pyrite or the presence of silver-bearing base metal sulfides could theoretically explain the variations of the Ag/Au ratios and also account for the difference between the true fineness and the apparent fineness. Since, however, the amount of base metal sulfides in the Basal Reef has been found to be insignificant and relatively high silver contents in secondary pyrite have not been unequivocally proved, it is considered that these two explanations are not as acceptable as the former interpretation. The conclusion reached, therefore, agrees largely with observations made by von Rahden (1965), who found that the wide interstope variations in apparent fineness can be reconciled, most probably, with the presence of silver minerals.

ORE GRADE AND VARIATION IN FINENESS

Figure 4 shows the scatter diagram and the least square line of best fit of the gold and silver contents obtained from the present suite of ore-samples plotted against each other. The

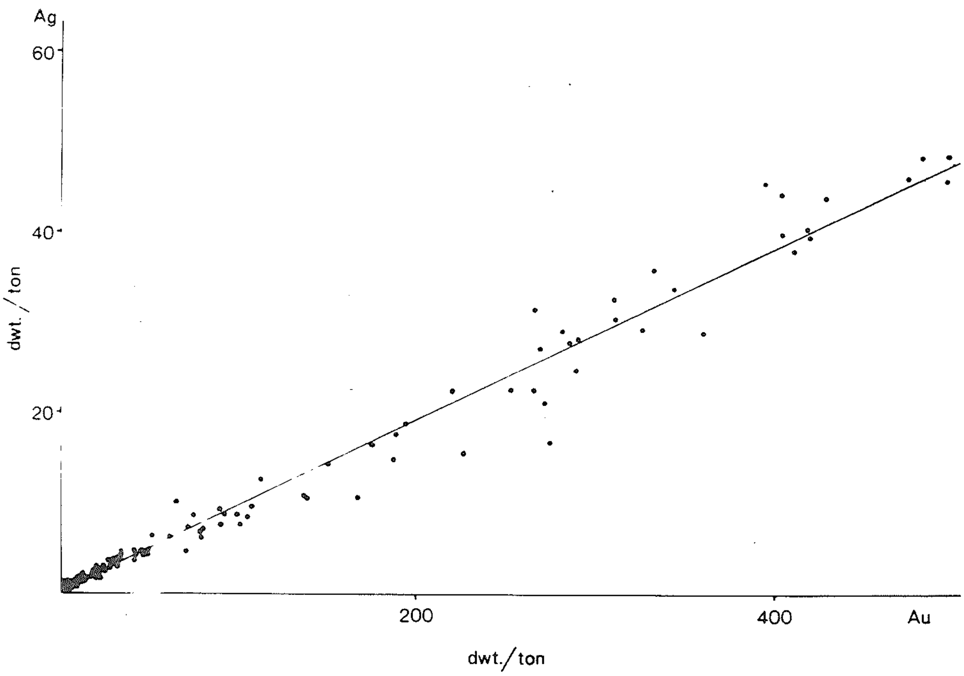

Figure 4 : Scatter diagram showing the relations between the silver and the gold content of ore-samples.

standard error of estimate of the silver content from the line of best fit has been calculated at 4.5 dwt. per ton. The plot indicates a distinct sympathetic variation between the values for silver and gold. Since neither of the two metals forms a normal distribution, a Spearman Rank Correlation Analysis was carried out to compute the correlation coefficient, for which a value of +0.99 was obtained. The high correlation is a result of the close mineralogical relationship which exists between silver and gold.

Prentice (1939), Richards and Rubidge (1950) and von Rahden (1965) observed that, in general, ore-samples containing large percentages of gold possess a low silver content, whereas for low-grade ore, higher silver contents appear to be more typical. However, no explanation for such a trend was given by any of these authors. Richards and Rubidge (1950), who studied the gold and silver content of several thousand ore-samples from the Main Reef Leader and the South Reef suggested a critical ore grade of 10 dwt. per ton below which the silver content seems to increase considerably.

In order to determine whether or not such an antipathetic trend is also present in the Basal Reef, the apparent fineness values of the present suite of ore-samples were plotted against their ore-grade (Figure 5). Such a plot shows changes in the silver content at low ore grades better than the scatter diagram of the silver and gold content (Figure 4). The resulting graph

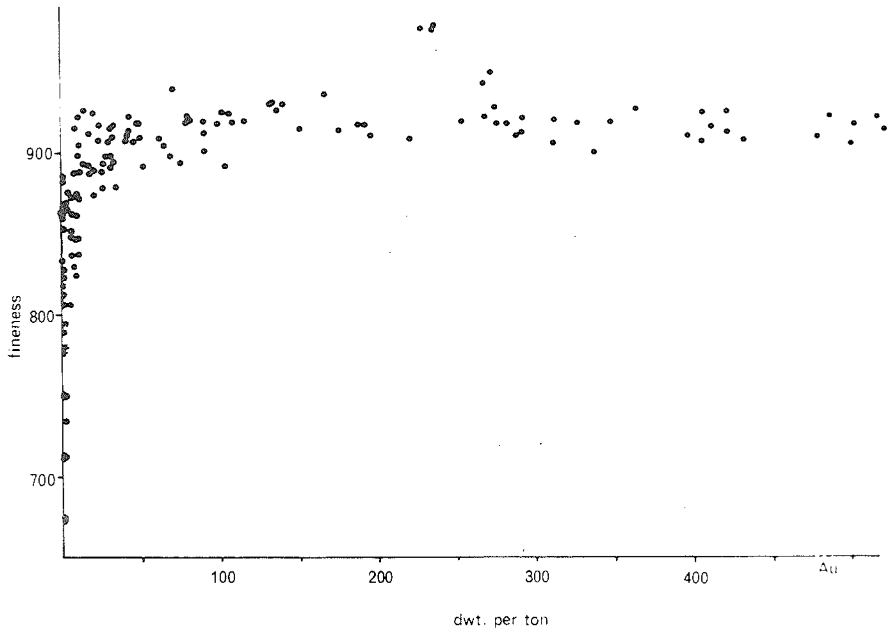

Figure 5 : Scatter diagram showing the relations between the apparent fineness and the ore grade of ore-samples.

closely resembles the observations made by Richards and Rubidge (1950) - samples with high gold content possess a fineness of about 910 to 920, and this value stays fairly constant down to an ore grade of 10 dwt. per ton, below which the fineness of the ore seems to drop, the lowest recorded fineness value being 660. The complete absence of points in the lower right hand corner of the diagram shows clearly that low silver values together with high gold values have not been found at all. The plot indicates not only a similar trend to that found by Richards and Rubidge (1950), but also suggests a similar critical ore grade.

In Figure 6, the apparent fineness values of 10 ore-samples are compared with the mean values of the true fineness of gold grains obtained with the electron-microprobe from the same 10 ore-samples. As in Figure 5, the fineness values are plotted against the gold grade of the ore. For the ore-samples the plot indicates a trend similar to that shown by the total population in Figure 5. The fineness values of the gold grains, however, do not seem to change with the ore grade but stay remarkably stable between a value of 928 and 916. It appears, therefore, that the distinct drop in fineness which seems to occur in the Witwatersrand ores below a critical ore grade of 10 dwt. per ton cannot be explained by a decrease in the true fineness of the native gold particles. It could, however, be explained by the assumption that a more or less constant silver "background" is present in the ore, irrespective of its grade. With such a silver "background" the least square line of best fit in Figure 4 has to intersect the y-axis at a positive value. The computation of the regression line revealed that the intersection lies, in fact, at a silver value of 0.16 dwt. per ton, or approximately 0.3 ppm. Such a very low "background" has a considerable influence on the apparent fineness at extremely low ore grades, whereas at high gold grades it becomes insignificant.

In Figure 7 the calculated "background" of 0.16 dwt. silver per ton has been subtracted from the silver values obtained by the fire assay method. The graph demonstrates a better linear spread of the points than in Figure 5. It therefore appears possible, that a silver "background" may account, at least partially, for the drop of the fineness values below a critical ore grade in Witwatersrand ores. The value of 0.16 dwt. per ton obtained from the suite of samples investigated cannot be taken as final and has merely been calculated to obtain some idea of the order of magnitude for such a possible silver "background".

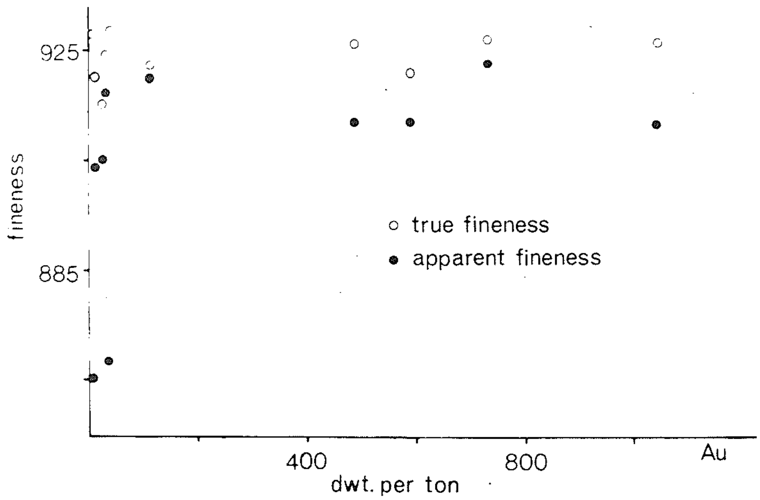

Figure 6 : Scatter diagram showing the relations between the apparent fineness of ore-samples, the true fineness of gold grains in the same ore-samples and the ore grade.

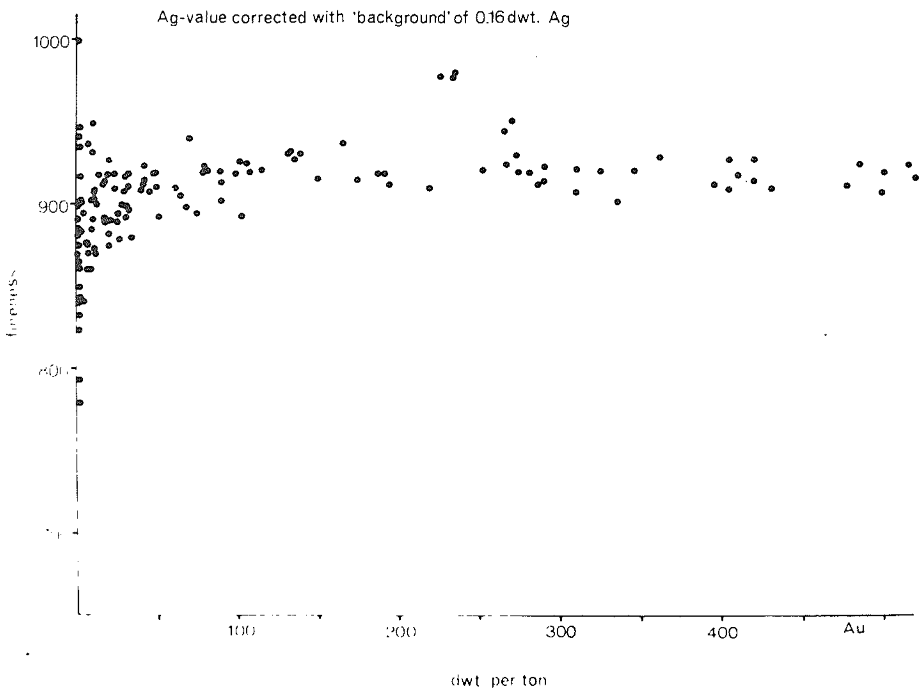

Figure 7 : Scatter diagram showing the relations between the apparent fineness corrected with a constant "background" of 0.16 dwt. silver per ton ore and the ore grade of ore-samples.

It is, however, not known whether such a "background" is constant, or whether it is influenced by factors such as ore grade, presence of base metal sulfides, or distance from the entry point of the conglomerates into the basin of deposition. A further possibility that could evoke a silver "background" could be a systematic, but very small positive error in the analytical method used for the determination of silver.

From these remarks it is apparent that, although a silver "background" might very well explain the drop in fineness at low ore grades, its origin is not known and much more work is required to solve this problem satisfactorily.

APPARENT FINENESS AS A FUNCTION OF THE SAMPLE ELEVATION

The present experimental data obtained from in situ gold grains, as well as from total ore-samples (with known locality and elevation) provide an excellent opportunity to check Hargrave's (1963) theory of an elevation control of the silver. He stated that a reef in "shallow" areas contains a higher Ag/Au value than the same reef in deeper areas. This deduction is based on data supplied by the Rand Refinery on the silver content of bullions from 12 mines over the period from 1922 to 1960. No information was available concerning the average elevation of the samples. Hargraves (1963) assumed that, since over the years mining operations became progressively deeper on average, the gold must have been produced from progressively greater depths. A chronological plot of the data showed a "distinct", if sometimes irregular, decrease in the average Ag/Au ratio of the bullion as a function of time or, according to Hargrave's (1963) assumption, as a function of depth.

To test this supposition, the Ag/Au ratios of the analyzed ore-samples from the Basal Reef were plotted against their elevation (Figure 8). The plot in no way suggests any

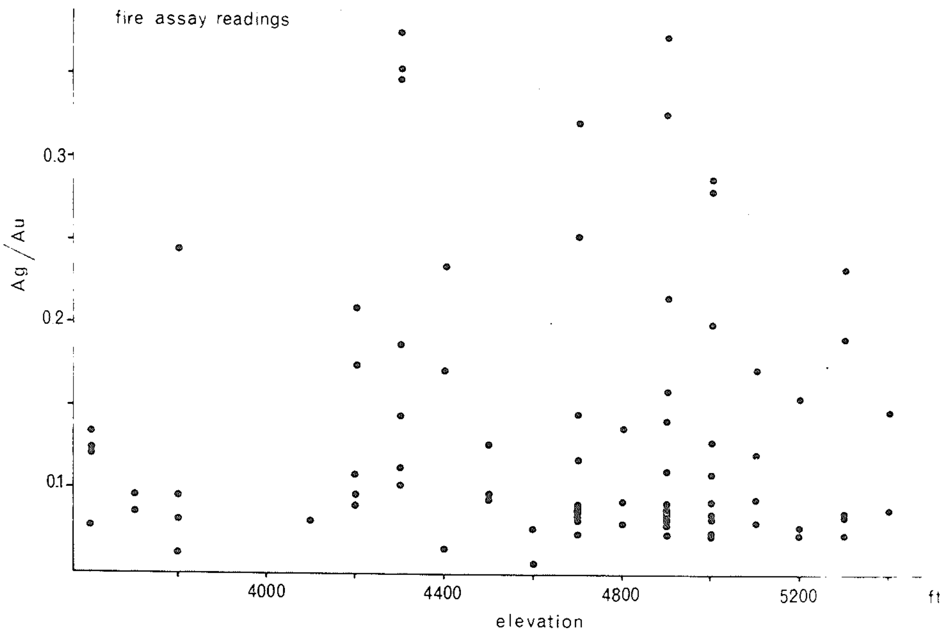

Figure 8 : Scatter diagram showing the relations between the Ag/Au ratio and the elevation of ore-samples.

correlation between Ag/Au values and elevation. This impression is confirmed by a calculation of the correlation coefficient between the two sets of variables. The value obtained is +0.057. An elevation control of silver, as proposed by Hargraves (1963), is, therefore, unsubstantiated in the present suite of ore-samples from the Free State Geduld Mine.

In Figure 9 the Ag/Au values of the 47 gold particles investigated were plotted against the elevation of the grains. As anticipated from the evidence quoted above, no increase or decrease of the silver content of individual gold grains, according to their elevation, could be observed. The Ag/Au ratio remains relatively stable.

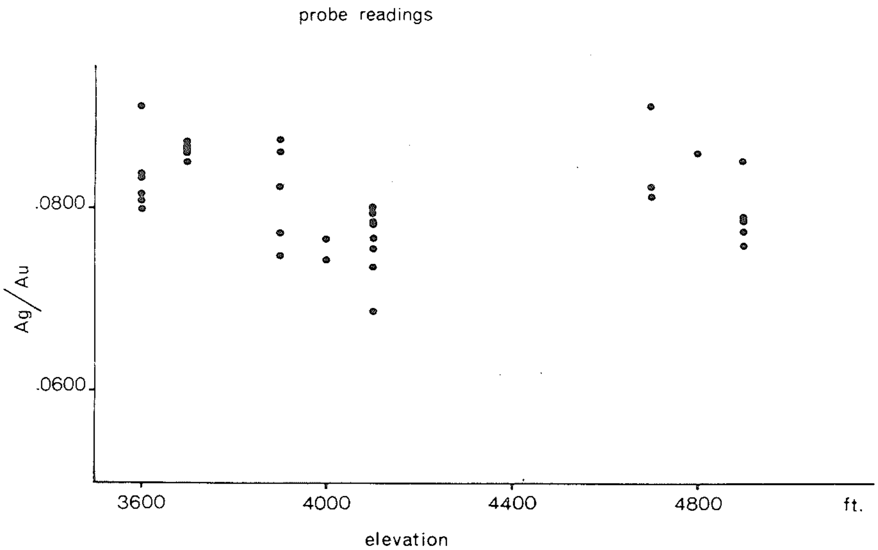

Figure 9 : Scatter diagram showing the relations between the Ag/Au ratio and the elevation of individual gold grains.

As pointed out, the small variation of the Ag/Au values appears to be due to the far-reaching homogenization of the natural alloy during the metamorphism of the sediments. Since metamorphic conditions were probably more or less uniform over the entire Witwatersrand basin, it is to be expected that a relatively constant proportion of silver would everywhere be removed from the original silver-gold alloy, resulting in fairly homogeneous Ag/Au values, as revealed in Figures 6 and 9. The relatively late homogenization of reconstituted gold during metamorphism is also the reason why investigations of the silver content of gold particles do not yield any information on its pre-metamorphic history.

Von Rahden (1965), examining Hargrave's (1963) deduction critically, questioned the elevation control of silver. Among other features, he pointed out that Hargrave's (1963) data could have been affected not only by the intermixing of ores from different elevations and from different reefs, but also by the differing recovery methods employed.

To investigate the behaviour of the Ag/Au values over the entire area studied, and also to test the theory of Hargraves (1963) in two dimensions, a trend surface analysis was carried out. The trend surfaces were computed with an IBM 360 computer using a Fortran program. On Hargrave's (1963) theory, some relationship between the contour map of the mine and the trend surfaces of the Ag/Au values should be expected. However, no correlation whatever, between sample elevation and Ag/Au trend surfaces, was found. The trend surfaces indicate a definite increase of the Ag/Au values in a northwesterly direction (Figure 10).

Several authors, using sedimentological data, concluded that the main source of the conglomerates lay to the southwest of the Orange Free State Goldfield, and that the entry point of the sediments, into the basin, must have lain to the south of the presently investigated area (Brock and Pretorius, 1964; Winter, 1964; McKinney, 1964). According to Brock and Pretorius (1964), the general transport direction in the area of the Free State Geduld Mine was from south-east towards the northwest (Figure 11). It is immediately apparent that the main transport direction is more or less parallel to the increase in Ag/Au values of the investigated ore-samples as shown by the trend surface (Figure 10). These results contradict the observations of Lindgren (1933) and Fisher (1945), that the fineness of alluvial gold appears to increase down-stream from the lode source. As pointed out earlier, this feature is due to the fact that during erosion and stream transport of gold particles, silver is preferentially removed from the alloy, whereas gold

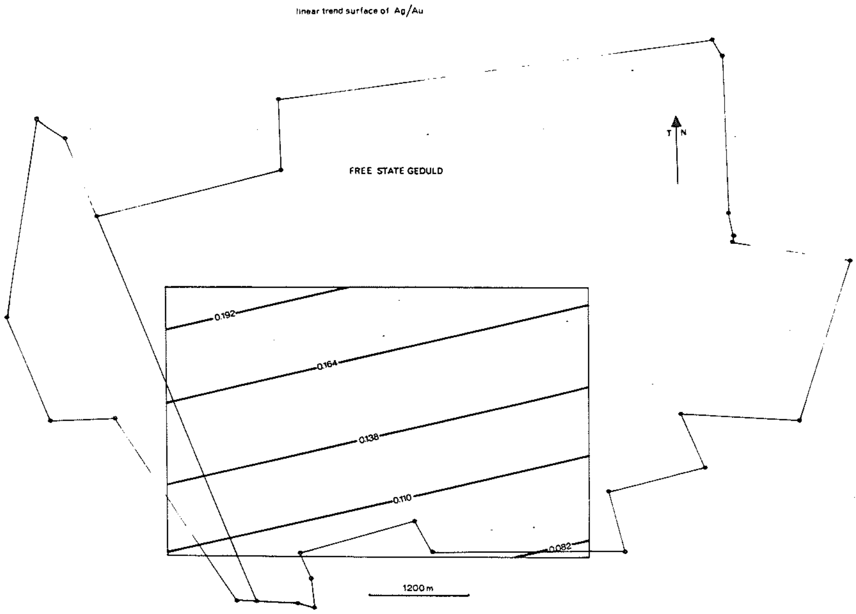

Figure 10 : Linear trend of Ag/Au values of ore-samples in the area of the Free State Geduld Mine.

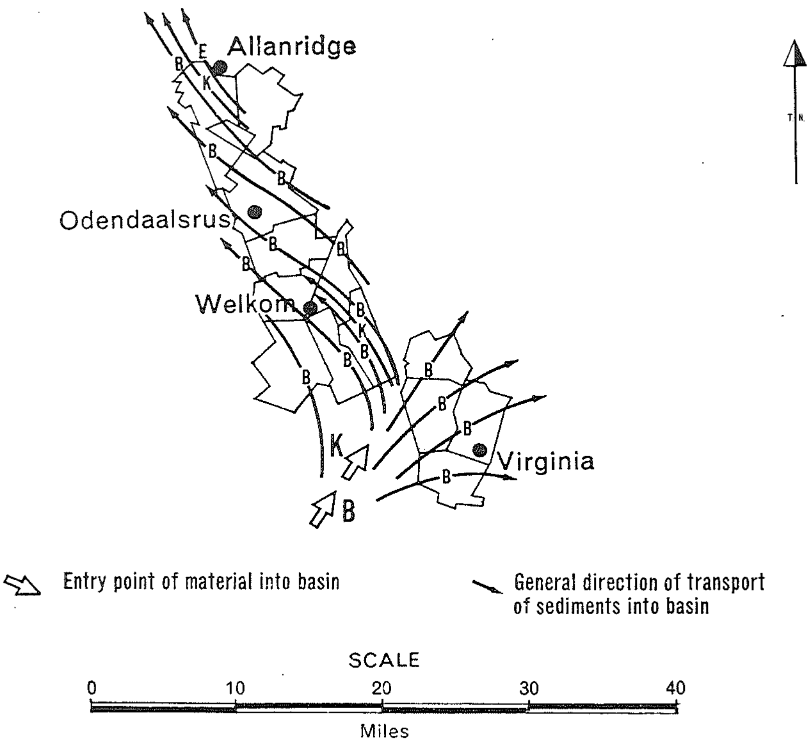

Figure 11 : Main transport directions in the Orange Free State Goldfield (Brock and Pretorius, 1964). Area of the Free State Geduld Mine hatched.

is redeposited on the surface of the grains as a thin film of pure gold. The removed silver migrates further away and is probably redeposited in the form of silver-bearing minerals.

It can be envisaged that in the relevant portion of the Witwatersrand basin the main transport direction roughly coincided with increase in the depth and was approximately perpendicular to the shore line. This is also valid for the direction in which the Ag/Au values increase, since it corresponds with the main transport direction. Brock and Pretorius (1964) pointed to the possible existence of a narrow littoral zone with persistent wave action. They further suggested that subsidiary basins could temporarily have become filled to the brim, allowing sub-aerial conditions to prevail, resulting in local marginal unconformities with a high degree of reworking on the eroded surface. McKinney (1964) suggested that the Basal Reef represents a cycle of transgression followed by regression. He assumed that, following the deposition of the Basal Reef, a long stable stage was initiated during which the Leader Quartzites were deposited in a shallow-water environment, probably a tidal flat. The Leader Quartzites, in turn, are rapidly truncated by the Leader Reef Formation, thus indicating a transgressional phase which continued until Elsburg times, at the very end of the Upper Witwatersrand period.

The models outlined above satisfactorily explained the increase of Ag/Au values to the northwest, which was, most likely, in a direction perpendicular to the shore line. Close to the latter, in the tidal flats, the reworking of the gold particles must have been much stronger than in less agitated, deeper portions of the basin, away from the littoral zone. The reworking and "milling" processes, which to a large extent took place under water, must have corroded and leached the gold in a manner similar to that of stream transport, thereby reducing the silver content of the gold. It is thus envisaged that the further away from wave action the less pronounced the removal of silver must have been; in other words, the Ag/Au values of gold particles must progressively increase in a direction approximately perpendicular to the shore line. This trend was probably further augmented by the removed silver migrating in the transport direction, thereby increasing the silver content to the northwest.

An observation made by Mackay (1944) must also be considered. He found that under present atmospheric conditions supergene processes tend to result in purer gold near the surface of gold deposits. This feature could also explain a relative increase in silver away from the shore line, since during later regressive periods, the littoral zone of the Basal Reef would have been closer to the surface where supergene processes may have been active.

To summarize, it is suggested that a pre-metamorphic redistribution of silver occurred as a result of reworking and "milling" in a narrow littoral zone of the basin of sedimentation, and/or as a result of supergene processes taking place in the more exposed areas of the Basal Reef, shortly after its deposition. Both processes could have resulted in an increase of the Ag/Au values of ore-samples as well as of individual gold-grains in a direction to the northwest (Figure 10). In the ore-samples this trend was apparently preserved to a large extent during subsequent metamorphism which indicates that the pseudohydrothermal transport of material was effective only over extremely short distances (see also Ramdohr, 1958). The correlation of Ag/Au values and elevation suggested by Hargraves (1963), and thought to have been produced by some "physico-chemical process" after the conglomerate had been deposited, could not be observed in the Basal Reef.

CONCLUSIONS AND SUMMARY

The analytical data assembled in this investigation indicates that the gold of the Basal Reef has been somewhat refined, and also homogenized, during its transportation from the source deposits into the basin of deposition, as well as during the actual process of sedimentation and mise en place into its present position within the auriferous ore-horizon. The homogenization processes can be considered essentially as a redistribution of silver relative to gold, resulting eventually in a rather constant and high Ag/Au value. Refining of alluvial gold during transport is by no means unusual and is widely reported. The relatively low grade metamorphism of the Witwatersrand ores, during which period the gold was reconstituted, led to a further removal of silver from the alloy. This obliterated earlier distribution patterns of silver and gold, and complicated the relationship between the two precious metals to some extent. It is also reflected in the contradictory statements and explanations made, not only on the silver-gold distribution in the Witwatersrand ores, but also on the ultimate source of the gold.

In the present study, the writer was able to distinguish between three different events during which silver was removed from the natural alloy :

(a) The first redistribution of silver relative to gold must have occurred during stream transport of the gold from its source into the basin of deposition. Gold, as well as silver, were dissolved by corrosion and leaching, but the gold was immediately reprecipitated on the surface of the grains forming thin marginal rims of very pure gold. It is considered, however, that this refining process was active for only a relatively short period and that only a limited amount of silver was removed in this way. The fate of the dissolved silver is unknown. It was probably transported into the basin of sedimentation and redeposited in the form of minutely disseminated silver minerals. Definite signs of this first silver substitution were not found in the samples investigated, indicating that they were completely veiled by later events.

(b) A second, and more important, removal of silver apparently took place within the Witwatersrand basin in the narrow littoral zone where, due to wave action and erosion, substantial reworking of the sediments must have taken place. The processes which removed silver from the gold during this period of reworking are believed to be roughly identical to those which occurred during stream transport. It is clear that in progressively deeper areas reworking became less and less intensive, thus imposing a progressively increasing Ag/Au ratio on the gold particles in a direction away from the littoral zone towards greater depth.

Furthermore, it seems possible that supergene processes, which have a tendency to produce purer gold nearer to the surface, intensified the trend outlined to an even greater extent. Supergene processes probably took place soon after deposition, during intervals of regression and/or much later, during the strong regression period at the end of Elsburg times.

Very little can be said about the fate of the silver removed during this period of refining. It is thought that the silver in solution migrated further outwards into the basin where it was redeposited as extremely minute, disseminated silver minerals. This second period of silver removal probably led to an increase of the Ag/Au ratios of the gold particles, as well as to an increase of the Ag/Au values of the total ore in a direction coinciding with an increase in the depth of water. This was more or less parallel to the main transport direction from south-east to northwest in the Free State Geduld Mine.

(c) The last, and certainly most conspicuous, redistribution of the silver took place during the metamorphism of the Witwatersrand sediments (solution stage of the modified placer theory). In this period, the gold was mobilized and redeposited, together with a portion of the pyrite and other sulfides, obtaining thereby its present structure and position. The removal of silver from the alloy has resulted in an exceptionally constant Ag/Au value of the gold particles and has evidently completely obliterated the gradient of <u>true</u> fineness from the shore-line outwards into the basin, attained during the previous periods of silver redistribution. The gradient in <u>apparent</u> fineness, was, however, preserved, as is seen from the trend surface analysis. This indicates that only extremely short distances of transport were involved during the metamorphic redeposition of the gold.

It is believed that the silver removed from the gold during this stage is now present mainly in the form of finely dispersed silver minerals, in addition to those formed earlier, and to a lesser extent, as minute silver contents in sulfides reconstituted during metamorphism. From the difference between average true fineness found in individual gold particles and average apparent fineness of the ore milled during the last five years, it was calculated that silver of the order of 0.5 dwt. per ton is recovered at the Free State Geduld Mine, from sources other than the natural gold-silver alloy. This figure represents the total amount of silver removed from the native gold during the three stages of silver redistribution and subsequent redeposition in that part of the reef covered by the mine area, provided there were no other sources of silver than the original detrital gold.

The last, and very intensive, homogenization process has affected, without exception, all reconstituted gold particles investigated, and has obliterated all pre-metamorphic features. Earlier statements concerning variations of the Ag/Au values of gold particles as a function of their grain-size, or ore grade, and of sample elevation, could for this reason, not be confirmed.

The general elevation control of silver as envisaged by Hargraves (1963), could not be observed in the suite of ore-samples investigated from the Basal Reef.

A decrease in apparent fineness below a critical ore grade (a feature reported by many students of Witwatersrand ores) was also encountered in the present investigation. An indisputable explanation of this feature cannot be given although there are some indications suggesting that an independent silver "background" could account for the lower fineness values typical of extremely low gold contents. This "background" was possibly introduced during the second period of silver redistribution in the littoral zone, where silver was removed and was able to migrate away from the shore-line towards the deeper portions of the basin. Further investigations, which would also have to cover the field of ore dressing and assaying, seem to be necessary to solve this interesting problem.

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