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EXSOLUTION OF GOLD FROM DETRITAL PLATINUM-GROUP METAL GRAINS IN THE WITWATERSRAND AURIFEROUS CONGLOMERATES

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ABSTRACT

Some polymetallic grains of platinum-group metals (PGM) from the Klerksdorp area, Transvaal, South Africa show concentric layers of other minerals identified as gold, platinum-group element (PGE) sulfides and limonite. Small gold grains were also discovered to have outer coatings of limonite or PGE sulfides. A comparison of the compositions of the layers with the grain to which they are attached indicates that the sulfide and gold layers have been derived from the grain by a process of selective sulfidation of PGE at low to moderate temperatures. Grains representing different stages in the corrosion process have been identified; gold grains with PGE sulfide coatings are the terminal condition. Consequently, a small fraction of the gold of the Witwatersrand has a source in common with the PGM grains.

SOMMAIRE

Certains grains polymétalliques des métaux du groupe du platine, trouvés dans la région de Klerksdorp, Transvaal (Afrique du Sud) sont enrobés d'or, de sulfures d'éléments du même groupe et de limonite, en couches concentriques successives. De petits cristaux d'or sont aussi recouverts de limonite ou de sulfures. La comparaison de la composition de ces couches à celle du cristal enrobé indique que les sulfures et l'or résultent d'une sulfuration sélective à basse ou moyenne température. On observe des grains à différents stades de ce processus de corrosion dont les granules d'or gainés de sulfures représentent le stade ultime. Une faible partie de l'or du Witwatersrand aurait donc la même provenance que les grains de métaux du groupe du platine.

(Traduit par la Rédaction)

INTRODUCTION

The Witwatersrand gold-uranium deposits have been a source of controversy amongst mineralogists, economic geologists and others ever since the problem of their formation was first seriously considered (Pretorius 1975). Whereas the rocks themselves are clearly of detrital origin, the heavy-metal minerals are not characteristic of placer deposits either in composition or habit (Liebenberg 1960). An exception is the group of platinum-group metal (PGM) alloys found in small quantities in the reefs; these grains commonly show rounded shapes expected of abraded particles (Koen 1964).

Opinion as to the origin of the gold is divided into two broad categories. Some consider that the gold and certain other metals were introduced into the established formations at some time subsequent to their formation. Hydrothermal agencies are invoked to account for the introduction, and the mineralogy of the deposits is largely consistent with this mechanism (Graton 1930, Davidson 1961). For others, the gold is considered to be introduced into the deposits at or about the time of their formation (Liebenberg 1960, Ramdohr 1958). The evidence for this is that the gold and other heavy minerals are concentrated in foot-wall deposits of the conglomerate layers, and in positions which can be interpreted as those of braided-stream channels. Also, there is no obvious source for the proposed hydrothermal solutions that can credibly explain the widespread distribution of gold in deposits whose total thickness extends to several kilometres.

The consensus has shifted to support the latter hypothesis (Feather & Koen (1975), but the provenance of the gold is unknown. Ramdohr (1958) and Hallbauer (1975) have shown that (1) very little of the gold is in its primary form, and (2) most has been deposited in association with pyrite or carbon. Hallbauer (1975) has shown that the carbon has an organic origin, and reproduces the shapes of primitive plants. He suggested that the plants concentrated the gold from dilute aqueous solution in the presumed saline Witwatersrand sea. How the gold got into the sea is not known.

Koppel & Saager (1974) have demonstrated that pyrite found in the deposits was derived from the greenstone belts of the Kaapvaal craton; it is possible that the gold and PGM were derived from the same source.

The PGM grains are rare in the Witwatersrand reefs. They are very small, typically 70 μm in diameter, and are rounded to subrounded in shape. There is little doubt that these grains are detrital in origin, but Koen (1964) and Cousins (1973) have suggested that the shapes are due to processes other than stream abrasion. However, in a detailed study of the platinum-group minerals in the Witwatersrand, Feather (1976) concluded that most of the PGM grains are of primary origin, derived directly from the source rocks with little ensuing alteration. Small amounts of gold are found with some PGM grains, and it is the purpose of this paper to show that such gold is exsolved from the grains, and hence, that the primary source of the PGM contributed at least some gold to the Witwatersrand deposits.

MATERIALS AND TECHNIQUES

A small quantity of PGM concentrates from an unknown mine near Klerksdorp was obtained from the geological collection of the University of Wales, Cardiff, U.K. These were barrel residues from the amalgamation process. Ferromagnetic constituents were removed by magnetic separation, and the remainder was mounted in conducting bakelite. Following hand-grinding and diamond-polishing to obtain a smooth, planar section, the grains were examined using the reflecting optical microscope and a Cambridge Microscan Five electron-probe microanalyzer. Details of operating conditions and standards are listed in the Appendix.

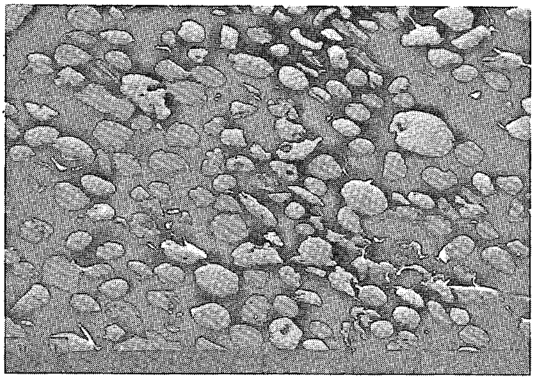

FIG. 1. Scanning electron micrograph of a polished section showing the size and shape of the PGM grains.

RESULTS

Many of the native PGM grains are rounded to subrounded in shape; all are very small, ranging from 15 μm to 60 μm in diameter (Fig. 1). Several small gold grains are also present, mantled with a layer of a grey mineral that presumably protected the gold from dissolution during the amalgamation treatment (Figs. 2, 3). Some of the PGM grains are also surrounded by one or more concentric layers of

FIG. 2. Gold grain with coating of limonite (x 720).

FIG. 3. Irregular gold grain with coating of limonite (x 720).

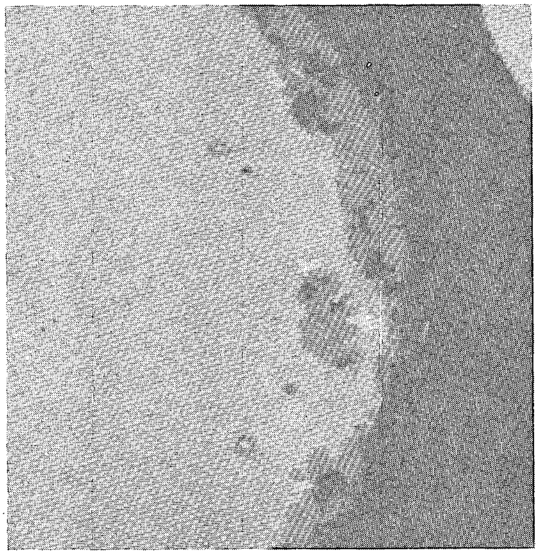

FIG. 4. PGM grain with coatings of sulfide and limonite. Small, bright particles at sulfide/PGM interface are gold (x 720).

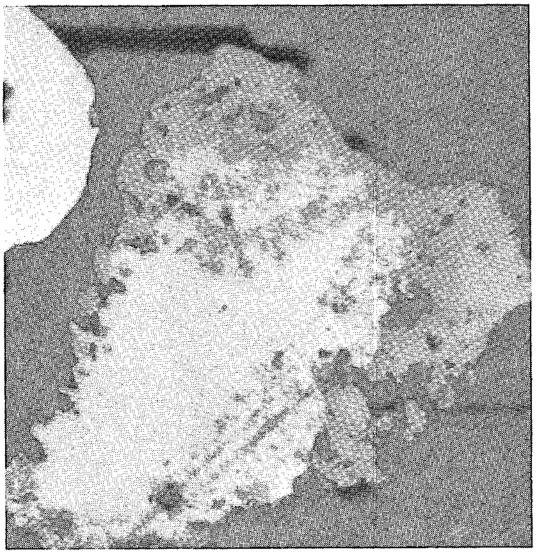

FIG. 5. PGM grain with thick coating of gold (poor polish) and outer layer of sulfide. This is grain 12 of Table 1 (x 720).

grey minerals. Electron-probe microanalysis showed that these layers are either platinum-group metal sulfides or limonite.

A rare but recurring feature of the layered structures on the PGM grains is the interposition of gold between the first layer and the PGM. The gold is usually particulate, but in cases forms a complete layer concentric with the outer layer. Typical examples are shown in Figures 4, 5 and 6. In Figure 4 the gold is present as small, discrete light-colored grains at the inner edge of a grey sulfide layer. Figure 5 shows an almost complete layer of gold around a PGM core, with an outer layer of sulfide. This grain is numbered 10 in Table 1. Figure 6 shows a grain similar to that in Figure 4, but with a thin limonite coating around the periphery. Electron-probe microanalysis on the grain in Figure 6 showed that the elements platinum, iron, gold, silver, sulfur and oxygen were present. Comparison of the X-ray distribution images (Fig. 7) shows that the core is a platinum-iron alloy; the gold layer contains dissolved silver only and the sulfide layer is cooperite. Limonite coats this and other grains.

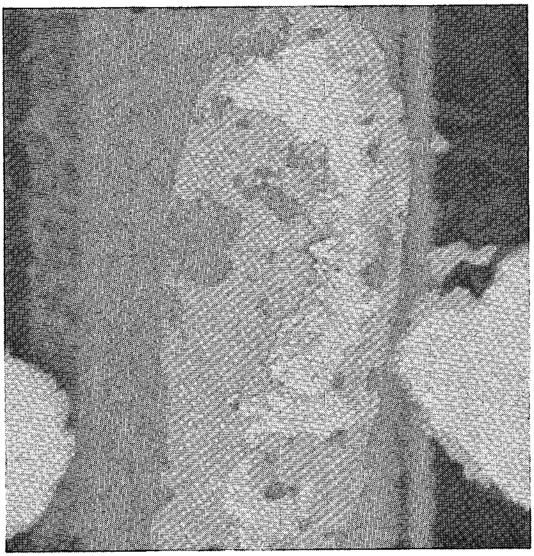

FIG. 6. Platinum-iron alloy grain with gold, sulfide and limonite layer (x 720).

Platinum-iron alloy is a relatively minor phase in the assemblage of platinum-group metal minerals found in the Witwatersrand, but is well-represented in the concentrates examined here. The bulk of the material comprises alloys of osmium, iridium, ruthenium and platinum with smaller amounts of rhodium, palladium, iron, nickel and copper (Feather 1976). Arsenic may be associated with the sulfide in the outer layer. Small amounts of mercury are commonly found in the gold particles, probably arising from the amalgamation process.

Grains were chosen for microanalysis with and without sulfide layers; gold grains without a core of PGM were also analyzed. Where possible, analyses were made at several different points on each phase with the object of collect-

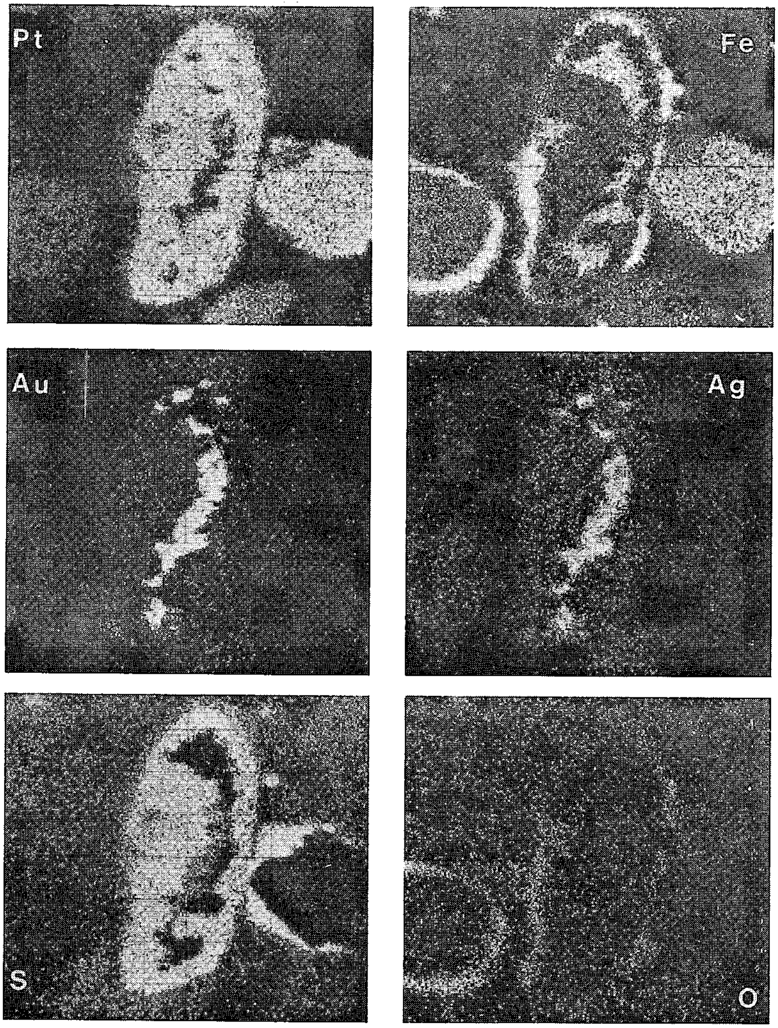

FIG. 7. X-ray distribution images of Pt, Fe, Au, Ag, S and O in the grain shown in Figure 6.

ing a total of the order of 10^6 counts and thus achieving a statistical precision of ± 0.1%. In many cases this was not possible as the gold or sulfide particles were too small for more than one or two analyses. For this same reason some of the analyses may not show the mean composition of the phase but are nevertheless probably representative. The results are presented in Table 1, together with a brief description of the grain. Low totals in the analyses of the sulfide layers are due to the extreme thinness of the layers and the tight curvature of the grain under the polished surface, which sometimes allowed the electron beam to pass through the sulfide and into the bakelite underneath. Where the summed concentrations of the elements differed significantly from unity, the analyses were normalized to 100%. Such analyses are marked in the Tables with an 'n' in the 'total' column, followed by the measured total in parentheses.

DISCUSSION

The limonite layer

This is always the outermost layer on the gold or PGM grain and is usually intact. Examination of Figures 2 and 3 shows that in section the coating has the irregular, wavy substructure and rounded outline of an overgrowth forming in a free space. Analysis of the layer showed than none of the PGM are present.

TABLE 1. MICROPROBE ANALYSES (WT.%) OF PGM GRAINS

Description	Ag	As	Au	Cu	Fe	Hg	Ir	Os	Pt	Rh	Ru	S	Other	Total
1. Pt-Fe alloy grain					6.1		5.0	2.9	65.8	12.5	6.3			98.6
sulfide envelope		2.1		0.8	2.8		8.6	5.2	18.3	26.9	10.4	24.9		n(96.6)
2. Pt-Fe alloy grain			0.1	1.1	5.7		1.1	1.1	86.4	2.5	0.3	0.4	Ni 1.1	99.8
irregular sulfide env.					1.6		1.3		40.7	33.1		21.0		97.7
3. Pt-Fe alloy grain				0.3	5.6		1.0		89.3	0.7	2.8		Pd 0.3	n(92.9)
sulfide envelope		1.5		0.4	0.6		6.8	12.5	52.4	0.6	5.6	19.0	Pd 0.3	99.7
4. Pt-Fe alloy grain			2.0		9.4				90.4					101.8
gold adjacent PGM	13.0		83.9		0.2				2.7			0.2		100.0
gold in sulfide	13.2		83.3		0.2				3.2			0.2		100.1
sulfide					0.1				85.5			14.4		100.0
5. Pt-Fe alloy grain				1.9	8.9				90.0					100.8
sulfide rim				6.6	4.9				14.7	35.6		37.5		100.0
gold interposed	3.0		94.0		1.0				2.0					n(95.7)
6. Pt-Fe alloy grain	0.1		0.7	0.1	8.6		3.3	0.3	88.7	0.9				102.0
sulfide rim				0.9	0.2		6.9	1.0	75.4	1.1		14.4	Ni 0.1	n(103.9)
gold interposed	12.6		74.6		0.5		4.0		6.5			1.8		n(93.9)
7. Pt-Fe alloy grain				0.5	11.3		0.3		84.0		0.4		Ni 0.2 Pd 0.5	97.2
thin gold layer	12.6		79.2		0.7				4.5					97.0
sulfide layer			0.9		0.6		0.1		33.0	39.2	0.9	25.0	Ni 0.1 Pd 0.2	n(65.5)
8. Pt-Fe alloy grain					10.4				88.8					99.2
thin gold layer	13.6		77.2						7.5			0.5		98.8
sulfide layer									85.4			13.1		98.5
9. Pt-Fe alloy grain					9.3				89.3					98.6
thin gold layer	10.8		77.1			3.8			8.3					n(96.3)
sulfide layer					0.1				85.4			14.1		99.6
10. Pt-Fe alloy core	2.1				8.6		0.2		84.9				Pd 4.8	100.6
sulfide angular grain					0.3		2.2		80.9			14.0	Pd 0.5	97.9
gold interposed	11.7		78.1		0.5		1.5		6.3			0.4	Pd 0.3	98.8
11. Pt-Fe alloy grain				0.8	10.3				84.5	3.4				99.0
thin gold layer	8.5		58.0		0.4	25.7			6.3	0.2		0.9		n(96.4)
sulfide layer					0.8				80.3	3.9		15.0		n(88.2)
12. Pt-Fe rounded grain				0.5	0.5		53.5	39.9	0.3		5.8			100.5
thin sulfide envelope				0.6	0.3		68.2	8.3	3.5	0.6	1.7	16.8		n(63.4)
13. Pt-Fe rounded grain				0.8	0.7		58.6	36.6			3.0			99.7
thin sulfide envelope				1.1	0.1		66.9	13.2			3.3	15.4		n(71.0)
14. Zoned Pt-Fe grain: core							18.9	72.1	1.5	0.4	7.1			n(104.3)
middle PGM grain							22.2	41.1	11.4	1.1	24.8		Ni 0.1	100.7
outer PGM grain				0.4			21.6	20.2	35.1	1.3	22.0			100.6
sulfide envelope							21.3	7.4	2.5	0.9	38.7	28.7		99.5
15. PGM grain							22.5	18.6	32.4	8.2	18.3			n(96.0)
sulfide envelope	0.7			0.5	0.1		28.2	18.0	4.4	10.6	23.7	13.4		99.6
16. PGM grain	2.4		17.9		1.2		49.7	6.1	17.7		4.8	0.3		100.1
thin gold layer	4.0		88.7		1.0	2.6			3.6					99.9
sulfide layer	1.4						38.9	4.6	10.9		16.8	26.5		99.1
17. PGM grain					2.0		32.5	30.1	31.9		1.3		Ni 0.5	98.0
sulfide envelope				0.5	0.7		51.2	26.2	6.4		3.1	11.9		n(81.0)
gold particles	1.5		10.8	0.4	0.9		38.2	26.4	19.5		1.6	0.5	Ni 0.2	n(92.5)
18. PGM grain					0.8		45.4	11.9	30.4	2.0	9.3		Ni 0.2	n(96.4)
sulfide coating					0.4		31.7	20.5		5.7	17.7	23.5	Ni 0.5	n(101.8)
19. PGM grain					0.4		23.0	38.6	10.7	0.7	24.9		Ni 0.2 Pd 0.1	98.6
sulfide coating					1.0		31.2	9.9	0.6		31.1	26.1	Pd 0.1	n(83.8)
20. small PGM grain				0.6	1.3		38.7	24.9	24.7	0.5	9.7			100.4
sulfide coating				0.7	3.2		41.3	30.8	6.3	0.3	9.7	7.7		n(92.4)
21. PGM grain				1.0	3.8		11.4	13.1	39.7	4.4	23.7		Pd 2.9	100.0
sulfide coating				0.4	2.3		14.2	18.3	4.9	1.2	35.0	23.7		n(88.7)
22. PGM grain					1.5		36.8	24.8	26.9		9.3		Ni 0.6	99.9
sulfide coating					1.3		40.2	31.3	0.5		15.5	12.6	Ni 0.2	101.6

Notation 'n(96.9)' indicates that the sum of element concentrations differs significantly from unity, and that the analyses are normalized to 100% (see text).

In one case (grain 29, Table 2) traces of silver and gold were observed but this is almost certainly due to penetration of the electron-probe beam into the underlying gold. The iron concentration changed significantly during the electron-probe microanalysis, starting at approximately 55% Fe and stabilizing at 60% after a few minutes. This is probably due to the

TABLE 2. MICROPROBE ANALYSES (WT.%) OF GOLD GRAINS

Description	Ag	As	Au	Cu	Fe	Hg	Ir	Os	Pt	Rh	Ru	S	Other	Total
23. irregular grain	11.7		82.1	5.2	1.1									100.1
24. irregular grain	12.9		85.9		1.2									n(92.3)
25. irregular grain	12.5		86.4		1.1									n(95.4)
26. irregular grain	11.4		78.8		1.0	8.7								99.9
27. irregular grain	10.9		75.7		0.4	13.0								n(95.0)
28. gold grain	12.1		87.1		0.1							0.1		99.4
limonite coating			1.4		54.2								O, H(?)	-
29. gold grain	11.2		88.7		0.1									n(96.9)
limonite coating	0.1		0.6		60.4								O, H(?)	-
30. angular gold grain	9.9	1.0	78.8	0.2	0.3		1.4		2.2	1.7	1.2	3.3		n(93.8)
arsenide/sulfide coating	2.0	19.2	18.5	0.1	0.3		1.5		22.9	19.8	2.1	13.6		n(96.8)
31. rounded gold grain	12.6		84.5		0.9	1.7			0.3					n(95.9)
sulfide coating	4.1								81.9			14.0		n(97.2)

Notation 'n(96.9)' indicates that the sum of element concentrations differs significantly from unity, and that the analyses are normalized to 100% (see text).

loss of combined or absorbed water, and corresponds to a change from $2Fe_2O_3 \cdot 5H_2O$ to $2Fe_2O_3 \cdot 3H_2O$, the composition of limonite.

It is not known at what stage the limonite was deposited, except that it followed the formation of the sulfide envelopes on the PGM grains. It may possibly have formed by alteration of pyrite, marcasite or pyrrhotite under oxidizing conditions. Feather & Koen (1973) have discussed the development of limonite as coatings on gold during the mining and milling of ore; the limonite coatings found here seem to be further examples of this effect. They will not be discussed further as they have no relevance to the *in situ* mineralogy of the deposits.

PGM grains with sulfide layer

Analyses of three platinum–iron grains with a coating of sulfide are given in Table 1, grains 1 to 3. Grain 1 is platinum–iron alloy with 12.5% rhodium and lesser amounts of ruthenium, iridium and osmium. The sulfide envelope shows markedly different ratios of the platinum-group elements (PGE) compared with the grain. All of the PGE other than platinum itself are in much greater concentration in the sulfide layer. Grain 2, which contains much smaller amounts of rhodium and ruthenium, shows a much larger content of rhodium in the sulfide compared with the grain. The third grain in Table 1 is also platinum–iron alloy, but with small amounts of iridium and ruthenium. The sulfide layer is platinum-rich with substantial amounts of osmium. In all cases the iron content of the sulfide is lower than that of the grain to which it is attached. Copper, where present, is higher in the sulfide.

Platinum–iron alloy grains with gold particles interposed between the core metal and the sulfide rim are numbered 4 to 11 in Table 1. Again, comparison of analyses of the core with the sulfide shows the same compositional differences as for grains 1 to 3. Exceptionally pure platinum–iron alloy grains 4, 5, 8 and 9, which contain negligible amounts of the other PGE, may have a pure cooperite rim (grains 4, 8 and 9) or, as in grain 5, a rim containing platinum and rhodium sulfides. Grains with more of the other PGE (6, 7 and 10) have greatly increased proportions of one or more of the elements Ir, Os, Ru and Rh in the rim.

The same general relationship between composition of the PGM core and the sulfide coating is found where the core material is not platinum–iron alloy. Grains 12 and 13 in Table 1 are osmiridium with smaller amounts of ruthenium and platinum. The sulfides are iridium-rich with substantial amounts of osmium. Platinum is either absent or occurs in low concentration. Grain 14 has a central iridosmine core with distinct layers of other PGM surrounding it which increase in platinum content towards the edge. The sulfide coating on this grain is rich in ruthenium and contains very little platinum.

Grains 15 to 22 are complex mixtures or alloys of the PGE and do not correspond to known minerals. They contain substantial amounts of iridium, osmium, ruthenium and rhodium in addition to platinum. The sulfide coating in each case is relatively high in iridium and very low in platinum.

One possible explanation for the existence of sulfide coatings on the grains of PGM is that these have acted as nuclei for the precipitation of sulfides from aqueous solution. This explanation could be used to account for the occurrence of associated gold grains also, as virtually all the gold is known to be in a state of secondary mineralization in the Witwatersrand deposits, and must therefore have been mobile at some period. However, the morphology of the gold particles is not consistent with deposition onto the surface of relatively smooth, rounded platinum-group metal grains. The gold always occupies embayments in the otherwise rounded grains; the inner grain-boundary is commonly very irregular or even degenerates into a mass of interlocking particles of PGM and gold. This is also true of the PGM/sulfide interfaces. The possibility that the gold is a primary intergrowth is negated by the fact that the gold is always located at the sulfide/PGM interface, a position unlikely to occur repeatedly by chance. Perhaps most significantly the nucleation mechanism does not provide an explanation for the observed paucity of platinum in the sulfide compared with the grain it encloses. The data in Table 1 show that the coatings are invariably richer in the non-platinum metals even where the absolute concentration of platinum is quite high.

Arguments as to the relative solubilities of platinum-group metals in the hypothetically saline depositional environment of the Witwatersrand sea (Cousins 1973) or during later metamorphic activity (Stumpfl 1974) predict that platinum should be preferentially dissolved from mixed platinum-group metals and thus would predominate in a precipitated layer. This is not in accord with the data obtained here, and strongly indicates that the layers were formed under conditions distinctly different to those envisaged by those authors.

A much more attractive hypothesis can account for both the morphology of the minerals and their composition: both the gold particles and the sulfide coating are derived from the PGM grain to which they are attached, by a process of selective corrosion in a sulfide environment. Toma & Murphy (1977) have shown that at low temperatures the free energy of formation of sulfides of Ir, Os and Ru is much lower than that of PtS, and strongly negative. On the basis of their free energy/temperature diagram, introduction of sulfide ions into a system containing a mixture of the PGE should result in the formation of sulfides of Ru, Os and Ir rather than of Pt. All these elements form sulfides extremely slowly, but the Witwatersrand deposits are very ancient and sufficient time must have been available for at least an approach to equilibrium.

Some caution is needed in the application of the free-energy diagram of Toma & Murphy, as no account is taken of the effect of pressure or of changes in free energy due to mixing as solid solutions. Some minor adjustments to the relative stabilities of Ir, Os and Ru sulfides may result from these effects, but Pt is certainly much more stable in a sulfide-bearing environment than Ir, Os or Ru. No data are available for rhodium sulfide, but its sulfur content would group it with Ir, Os and Ru in terms of stability. For similar reasons palladium would be expected to be similar to platinum, as both form a monosulfide.

Attack of the detrital PGM grains by limited concentrations of sulfide ion would be expected to form a coating of sulfide in which platinum is a minor constituent. Only on very pure Pt–Fe alloy grains would a cooperite layer be formed. These predictions are in exact accord with the data of Table 1, which thus lend strong support to the hypothesis. Selective corrosion which removes some elements preferentially must alter the composition of the corroded grain. In general the platinum content must increase, particularly near the encroaching sulfide. Grain 14 is considered an example of such an effect; if so, it was deposited as an iridosmine grain and the different layers represent a platinum-enriched zone extending to the surface.

Gold

The presence of gold at the base of the sulfide coating lends indirect support to the corrosion hypothesis. Gold can dissolve extensively in platinum at high temperatures; its solubility in other PGM is not known. Darling *et al.* (1952) and Darling (1962) show that the solubility of gold in platinum decreases sharply as the temperature is reduced. No figures are available for the solubility of gold at lower temperatures, but extrapolation of the data given by Darling (1962) indicates that a level of 0.1% Au is reached at about 400°C. If the primary platinum-iron alloy grain contained gold in excess of about 0.1 wt.% after its separation from a magma, this would exsolve gradually on cooling, either as an intergrowth or possibly in particulate form on the surface of the grain. Of the grains in Table 1, only two platinum–iron alloy grains contain detectable gold, even though many were contiguous with gold particles. This confirms the prediction that the equilibrium concentration of gold at room temperature is less than 0.1 wt.% (close to the detection limit for gold on the electron microprobe). The figures of 0.1 wt.% and 2.0 wt.% obtained for grains 2 and 4 are possibly due to the presence of fine intergrowths on a scale too small to resolve optically.

Some of the gold grains at the surfaces of PGM grains could be due to early exsolution on cooling from a magmatic temperature. However, even if hardened by platinum, gold is much softer than platinum–iron alloy and would have been preferentially worn away during transport of the grains to the Witwatersrand basin. Any rounded PGM grains must have lost a substantial portion of their original surface during transport, and with it any gold exsolved during cooling from a magmatic temperature.

Small gold particles imbedded in the surface of a rounded PGM grain would result from the sulfide corrosion which has been proposed to account for the composition of the sulfide envelopes on these grains. Gold is inert to sulfide attack, and removal of PGM by sulfide corrosion must increase the mean gold concentration of the grain, if it contained any gold at all. When the solubility limit was exceeded, gold would exsolve as a separate phase. Exsolution would occur at the point where the gold was at a maximum concentration, *i.e.*, at the edge of the encroaching sulfide layer, where in fact it is always found. This mechanism would apply whether the gold in the grain was in solid solution or exsolved as a fine texture. In the latter case the pre-existing gold particles dispersed in the PGM grain would be incorporated in the growing gold grains. Once one or more relatively large grains of gold were established in the PGM grain, fine particles of gold in an exsolution texture would become thermodynamically less stable and would ultimately disappear by an Ostwald ripening process (Hillert 1965, Greenwood 1969). For similar reasons a thin layer of gold formed by selective corrosion at the PGM/sulfide interface would migrate to join a nearby interfacial particle of gold rather than thicken; thus the gold layer is particulate rather than in the form of a smooth shell around the PGM grain.

An estimate of the original concentration of gold in the sedimented PGM grains can be made from the volume of gold liberated by selective corrosion. The largest PGM grains are near 100 μm in diameter, and a platinum grain of that size containing 0.1% Au is calculated to yield only 500 μm^3 of gold if corroded to half its original diameter, or a gold particle 10 μm in diameter if all the platinum were removed. The rounded grains, which appear to preserve their original outline, (*e.g.*, Figs. 4 and 6), have more gold than the 1:100 ratio expected between gold and sulfide areas even neglecting the much lower density of the sulfides compared with the PGM, suggesting a gold content somewhat higher than 0.1%. This does not necessarily mean that exsolution textures existed in some of the grains prior to corrosion. One iridium-rich grain was found to contain 17.9% Au (Table 1) with no sign of exsolution textures; it is possible that the presence of other PGE in solution could appreciably alter the equilibrium solubility of gold in platinum.

The composition of the gold particles suggests that the corrosion took place at low temperatures. The mean analysis of gold in grains large enough to analyze accurately is: 81.1% Au, 9.8% Ag, 0.5% Fe, 3.4% Hg, 5.2% Pt, with small amounts of other elements. The mercury is undoubtedly from the amalgamation treatment and varies widely from grain to grain. The silver content is somewhat variable: it is always substantial in the gold but was only found in three of the PGM (grains 6, 10 and 16) and in two of the sulfide coatings (grains 15 and 16). Reference to the free energy/temperature diagram of Toma & Murphy (1977) shows that Ag_2S is very much less stable than the platinum-group element sulfides at temperatures less than 950°C. Attack of a PGM grain containing silver by sulfide ions would thus increase the concentration of silver in a similar way to that described for gold, provided that the reaction temperature was low. Reaction temperatures above 950°C would first produce Ag_2S, then the PGE sulfides as coatings on the PGM grain. The outer coating of Ag_2S could be reduced back to silver if cooling was sufficiently slow. However in that case the silver would be expected to exsolve on the outside edge of the sulfide and should not be incorporated in the exsolved gold.

The compositional evidence thus indicates that sulfide corrosion took place at a temperature below 950°C. It has been shown by other workers that the temperature achieved in the Witwatersrand deposits was between 400°C and 600°C (Fuller 1958, Feather & Duggan 1974), and the evidence presented here broadly supports that figure.

The logical end-point for the scheme of selective corrosion in a sulfide-bearing environment would be a small gold grain thickly coated with PGE sulfides. Two examples of this were found: grain 30, in which the coating is actually a sulfide/arsenide, and grain 31 (Table 2). Grain 10 of Table 1 is similar to this also because the platinum–iron alloy core is very small. Furthermore this is one of the few grains in which significant amounts of palladium were encountered. Unlike gold or silver, palladium forms a continuous solid solution with platinum (Pearson 1958), and if concentrated by selective corrosion, does not form a separate exsolution texture. The near-absence of palladium in the sulfide coating of this grain indicates that palladium is more resistant to sulfide attack than platinum, and has therefore been concentrated by corrosion from the very low levels normal in Witwatersrand minerals.

Apart from grains 30 and 31 of Table 2, the gold grains were coated with limonite or were not coated. Most were very small as would be expected if they had been derived from PGM grains. It is possible that the bulky sulfide coating, if present, became detached at some stage in the separation process. The analyses of these grains do hint at their formation from PGM grains, as the mean silver-to-gold ratio of 0.14 is close to that of the gold attached to the PGM grains, *i.e.*, 0.13.

CONCLUSIONS

The habit, distribution and composition of gold and sulfide minerals associated with some platinum-group metal grains from the Witwatersrand basin are consistent with their formation by low-temperature corrosion in a sulfide-bearing environment. This mechanism requires that gold be dissolved or in the form of a fine texture in the detrital PGM grain prior to sulfide attack, and hence, that the gold and PGM have a common primary source.

It is not suggested that more than a small fraction of the Witwatersrand gold has been formed in this way, as the average tenor of PGM in these deposits is very much lower than that of gold. However, the source rocks from which the platinum-group metals were derived must also have contained gold, some of which was associated with the PGM. Both detrital gold and detrital PGM would eventually be incorporated in the Witwatersrand sea deposits. Following deposition, sulfide attack on the water-worn sediments occurred, with the formation of many different sulfide minerals. This, it seems, was followed by redistribution of the gold. Hydrothermal processes may have had a part to play in the events following deposition, but a hydrothermal source for the gold is not required.

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APPENDIX: OPERATING CONDITIONS AND STANDARDS USED FOR ANALYSIS

A Microscan V electron-probe microanalyzer with two fully-focusing crystal spectrometers was used for the microanalyses. This was operated at either 15 or 20 kV accelerating potential to minimize penetration of the beam into the sample. A beam current of 50 nA was used throughout. Diffracting crystals of either PET or LiF (200) were used for analysis of the elements; the X-ray lines, crystals, Bragg angles (2θ) and standards used are listed in Table 3.

TABLE 3. X-RAY LINES, CRYSTALS AND STANDARDS USED FOR ANALYSIS

Element	Line	Crystal	Angle 2θ	Standard
Ag	$L\alpha$	PET	56°42'	Ag
As	$K\alpha$	LiF	33°58'	As
Au	$L\alpha$	LiF	36°58'	Au
Cu	$K\alpha$	LiF	45°00'	Cu
Fe	$K\alpha$	LiF	57°29'	Fe
Hg	$M\alpha$	PET	80°25'	Hg/Ag amalgam
Ir	$L\alpha$	LiF	39°13'	Ir
Ni	$K\alpha$	LiF	48°38'	Ni
Os	$M\alpha$	PET	95°46'	Os
Pd	$M\alpha$	PET	59°53'	Pd
Pt	$L\alpha$	LiF	38°04'	Pt
Rh	$L\alpha$	PET	63°24'	Rh
Ru	$L\alpha$	PET	67°15'	Ru
S	$K\alpha$	PET	75°46'	FeS_2

Some overlap problems were encountered which required adjustment of the measured values. When Cu was being measured in the presence of Ir, overlap of the Ir$L\alpha$ line (45°00′) with the Cu$K\alpha$ line (45°00′) gave an apparent copper content of 2% of the iridium content. This was removed from all the analyses of Table 1. Similarly a weak unidentified Pt second-order line at 63°30′ gave an apparent rhodium content of 0.3% of platinum content if the Rh$L\alpha$ at 63°24′ was used for measurement. Overlap of the Ru$L\beta_2$ line at 59°27′ with the Pd$L\alpha$ at 59°53′ required the subtraction of 4.3% of the ruthenium content from the apparent palladium content. Overlap of the Ru$L\beta_1$ line at 63°45′ with the Rh$L\alpha$ line at 63°24′ required the subtraction of 1.5% of the ruthenium content from the apparent rhodium content. Overlap of the Pd$L\beta$ line at 56°34′ with the silver line at 56°42′ required the subtraction of 14.6% of the palladium content from the apparent silver content. All the above corrections refer to a 20 kV accelerating potential.