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**THE GOLD-PYRITE ASSOCIATION IN WITWATERSRAND  
REEFS: EVIDENCE FOR ELECTROCHEMICAL  
PRECIPITATION OF GOLD**

**F.M. MEYER, P. MÖLLER, D. de BRUIN,  
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by

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## **THE GOLD-PYRITE ASSOCIATION IN WITWATERSRAND REEFS: EVIDENCE FOR ELECTROCHEMICAL PRECIPITATION OF GOLD**

### **ABSTRACT**

The common style of gold mineralization in the Basal Reef and other auriferous conglomerates of the Witwatersrand Supergroup comprises clusters of gold grains occurring interstitially to quartz and pyrite pebbles as well as gold accumulations attached to the surface of and infilling hairline cracks and fractures in round, compact, detrital pyrite. The latter textural association is generally interpreted as a result of remobilization of originally detrital gold during regional metamorphism and related hydrothermal fluid circulation. There is general agreement that, although gold solubility was low, ore modification occurred during the metahydrothermal event, but uncertainty exists about the magnitude and scale of gold remobilization.

Micro-textural and chemical investigation of compact, round, pyrite and associated gold accumulation has established that gold is preferentially deposited on chemically heterogeneous pyrite surfaces. Combinations of alternating high- and low-As zones in pyrite result in mixed np-type conductivity accompanied by electron exchange and the reduction-driven deposition of gold at the cathode. This model does not explain gold accumulations which are not immediately linked to chemical heterogeneities and it is inferred that an additional control on the deposition of gold was exerted by physical defects which lead to zones of increased charge density and/or areas of focused conductivity. The inferred precipitation mechanisms suggest that sub-microscopic physical and chemical controls are the important factors that determined the sites of gold nucleation and that precipitation mechanisms based on physicochemical changes of the hydrothermal system were not involved. The Basal Reef contains on average close to 5% of round, detrital, chemically zoned pyrite which provides a large number of electrochemically active pyrite surfaces. The extremely effective electrochemical precipitation mechanism, together with the low solubility of gold in Witwatersrand fluids, is the main reason for the spatially restricted remobilization of gold in the conglomerate reefs.

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## **THE GOLD-PYRITE ASSOCIATION IN WITWATERSRAND REEFS: EVIDENCE FOR ELECTROCHEMICAL PRECIPITATION OF GOLD**

### **INTRODUCTION**

The Witwatersrand Basin is remarkable for its prodigious concentration of gold and uranium; in more than a century of commercial exploitation some 42 000 tons of gold and almost 150 000 tons of  $U_3O_8$  have been produced (Handley, 1990). Quartz-pebble conglomerates, kerogen seams and to a lesser extent pyritic quartzite are the main mineralized lithologies that host particulate gold and uraninite together with accumulations of pyrite and other heavy minerals. The gold-bearing reefs occur almost entirely in the upper portion of the Witwatersrand Supergroup, i.e. the Central Rand Group which was deposited over a period of  $\approx 200$  Ma, from  $\approx 2914$  Ma to  $\approx 2714$  Ma (Robb et al., 1992, 1990; Armstrong et al., 1991). The nature of the geological factors which contributed to the enormous enrichment of the Witwatersrand depository with gold and uranium is still debated after more than a century of mining. Most questions of the origin of the mineralization revolve about the source, genesis and mode of occurrence of essentially four components of the ore, namely gold, uraninite, pyrite and kerogen (Pretorius, 1991). Many ore genesis studies have been carried out since the discovery of the goldfields and they are marked by a continuing debate which, in its simplest form, revolves around syngenetic models on the one hand and epigenetic models on the other. The placerist school sees the distribution of gold tenor in the reefs controlled by primary palaeoflow patterns and subscribes to a placer interpretation of the stratabound mineralization, while the epigenetic models resort to mineralogical, textural and geochemical evidence to propose a post-sedimentation, hydrothermal origin of at least some of the ore constituents. Attempts at resolving these discrepancies resulted in the modified placer theory which envisages the reconstitution of detrital minerals by hydrothermal fluids during post-depositional, metamorphic events. Detailed mineralogical studies by Liebenberg (1955), Ramdohr (1955), Feather and Koen (1975), MacLean and Fleet (1989) and others recognized and distinguished between a suite of both allogenic and authigenic minerals in the Witwatersrand reefs. Mineragraphic observations as well as geochemical evidence leave little doubt that round chromite and zircon are unequivocally allogenic in origin, that pyrite, sphalerite, rutile, and cobaltite show both round detrital as well as secondary recrystallized characteristics while associations such as uraninite-brannerite, ilmenite-rutile-leucoxene, and arsenopyrite-gersdorffite have paragenetic features that span the range from allogenic to authigenic. Morphological evidence for the detrital origin of gold is scarce and mostly circumstantial, but Minter et al. (1993), Hallbauer and Utter (1977), and Utter (1980) were able to demonstrate that detrital gold nuggets are preserved in some of the reefs. The bulk of the Witwatersrand gold, however, is associated with paragenetically-late phases such as authigenic sulphides, kerogen and secondary chlorite. Primary gold inclusions in allogenic pyrite are rare and the metal occurs, preferentially in fractures in pyrite or as overgrowths on grain boundaries (Meyer et al., 1990a). Ramdohr (1955), in particular, recognized that gold is frequently attached to compact, round, pyrite surfaces and that in very rich reefs replacement of pyrite by gold is a common feature. Robb and Meyer (1991) reviewed the distribution of gold contents between the three principle pyrite types in the reefs and noted that the round, compact, detrital pyrite holds the highest concentrations followed by the round, porous variety,

whereas the authigenic, recrystallized type contains the lowest gold values. Texturally, authigenic gold is older than authigenic pyrite and postdates also the radiation-induced polymerization and accumulation of kerogen at  $\approx 2300$  Ma (Robb and Meyer, 1994; Robb et al., 1994; Meyer et al., 1991).

All advocates of the modified placer theory acknowledge that pervasive post-depositional dissolution of gold and other minerals by hydrothermal solutions took place, but their general belief is that reconstitution of the ore minerals occurred on a local scale. Undoubtedly, the dissolution of gold in a fluid phase and its inferred, almost instantaneous, reprecipitation from the same fluid is difficult to envisage. This process requires drastic changes, over very short distances, in various intensive and extensive properties of the hydrothermal system to facilitate either fluid undersaturation (dissolution) or supersaturation (precipitation) with respect to gold. It is clear, if gold remobilization indeed occurred virtually *in situ*, precipitation mechanisms other than fluid supersaturation in response to physicochemical changes have to be invoked.

In this paper the authors attempt to demonstrate that the widely documented gold-pyrite association in Witwatersrand reefs is the result of electrochemical, reduction-driven, deposition of gold on pyrite and that the effectiveness of the process is the main reason for of gold remobilization on a local scale.

## FLUID CONDITIONS AND GOLD SOLUBILITY

Both the modified placer theory as well as the epigenetic hydrothermal models require conditions of fluid flow and a solution chemistry favourable for metal transport. A summary of fluid characteristics, metal solubilities and thermal conditions that prevailed in the Witwatersrand Basin during postburial metahydrothermal events was presented by Robb and Meyer (1994, 1991) and Meyer et al. (1991, 1990b). These authors modelled fluid conditions using constraints provided by stable ore and silicate mineral assemblages as well as information from fluid inclusions. The inferred physicochemical conditions are indicated by the hatched field in Figure 1 which also shows that at peak-metamorphic temperatures of  $350^\circ\text{C}$  (Wallmach and Meyer, 1990) and a pH corresponding to muscovite stability, the total gold solubility in Witwatersrand fluids was not more than 30 ppb and that the principal soluble gold species was the  $\text{HAu}(\text{HS})_2^\circ$  complex and to a lesser degree the  $\text{AuCl}_2$  complex.

## ELECTROCHEMICAL ACCUMULATION OF GOLD

Over the past decade major advances have been made in the field of mineral-solution interface geochemistry and the mechanisms involved in the deposition of precious metals on sulphides and oxides have been studied by a number of workers. There is general agreement on the magnitude and extent of the accumulation of gold on sulphides, but not on the nature of the actual mechanism. For example, Cardile et al. (1993), Schoonen et al. (1992) and Renders and Seward (1989) subscribed to the process of physical adsorption without subsequent electrochemical reduction of the soluble Au species, whereas Knipe et al. (1991, 1992), Starling et al. (1989), Jean and Bancroft (1985) and Bancroft and Jean

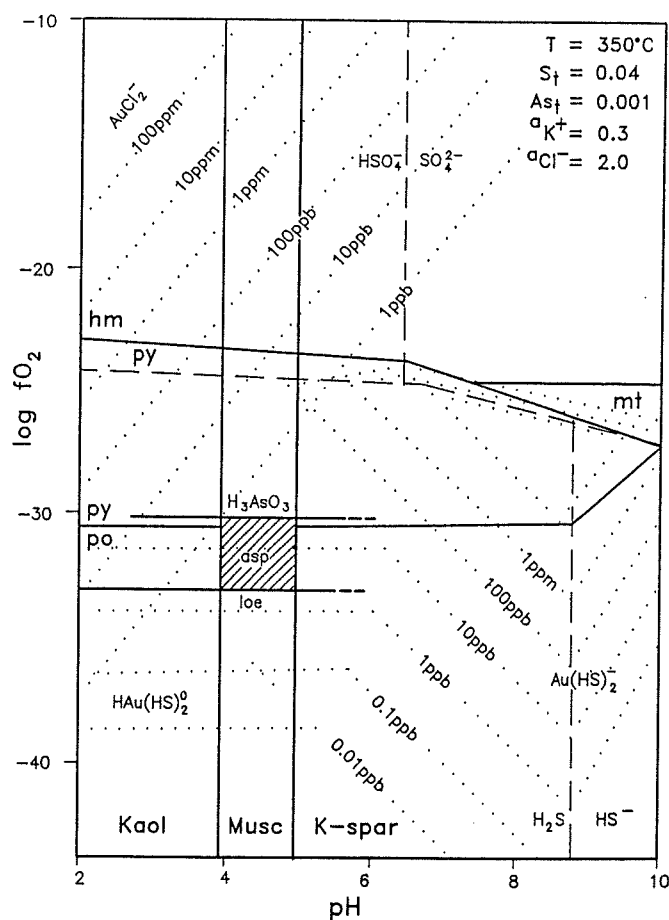


Figure 1:  $fO_2$ -pH diagram showing solubility contours for  $Au(HS)_2^-$ ,  $H_3AsO_3$ , and  $AuCl_2$  complexes. The hatched field indicates Witwatersrand fluid conditions during regional metamorphism (modified after Robb and Meyer, 1991).

(1982) proposed a two-stage mechanism which involves an initial physical adsorption of the aqueous metal species followed by a reduction-driven chemical adsorption at sites of high surface charge densities. A third group of researchers, e.g. Möller (1993), Möller and Kersten (1994) and Mironov et al. (1981) attributed the accumulation and reduction of gold on pyrite surfaces mainly to the semiconductive properties of the mineral. Chemical zoning of pyrite with As, or Ni and Co, which can substitute for S and Fe, respectively, results in mixed, n-p type semiconductors and, thus, in the generation of self-driving galvanic cells. In this configuration, the As-rich growth bands represent p-type semiconductors (cathodes) whereas the As-poor (or Co- and Ni-rich) zones are the n-type semiconductors (anodes). The experimental results of Möller and Kersten (1994) showed that at p-n junctions in a pyrite crystal, differences in the electric potential are in the order of 10 mV, and that such potentials are sufficient for the electrochemical precipitation of gold, even from very dilute solutions.

The fact that round detrital Witwatersrand pyrite is often oscillatory-zoned in As content (MacLean and Fleet, 1989; see later), and that the mineral is also one of the preferred substrates for secondary gold deposition suggests that gold precipitation occurred in response to its semiconductive properties.

## SAMPLING AND SAMPLE DESCRIPTION

The conglomerate samples studied were collected from the the Steyn facies of the Basal Reef at the Unisel Gold Mine in the Welkom Goldfield (Fig. 2). The conglomerate reef which has yielded more than 80% of the gold mined in the Welkom Goldfield, is unconformity-based, laterally persistent, and constitutes the basal unit of the Harmony Formation (Fig. 3).

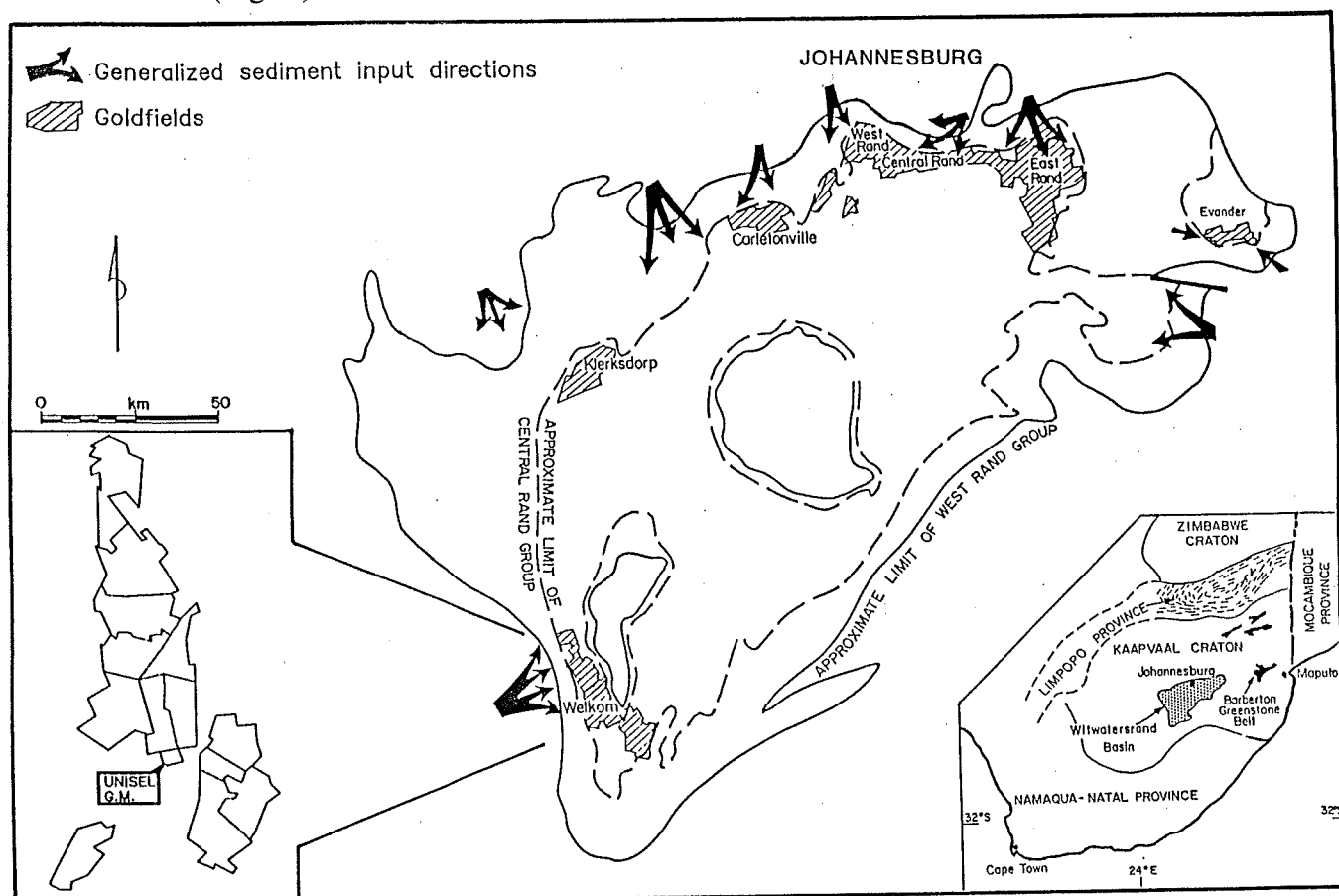


Figure 2: Simplified geologic map of the Witwatersrand Basin showing the locality of the Unisel Gold Mine.

The Basal Reef comprises two separate, but laterally coalescing conglomerate facies which are known as the northern, oligomict Basal facies and the southern, polymict Steyn facies (Minter et al., 1986). The 10 to 200 cm-thick polymict reef is, in general, a moderately-sorted, small-to-large-pebble conglomerate interbedded with cross-bedded quartz arenites. Clast composition comprises quartz, chert, quartzite, yellow shale and schist.

The conglomerate is well mineralized with round pyrite, gold, and uraninite. Kerogen is present in places. Gold is mainly concentrated along the erosional bottom contact (Bailey, 1991; Minter et al., 1986). At Unisel Gold Mine gold occurs in two distinctive mineralogical associations (Hofmeyr and Potgeiter, 1983). One type is similar to the style of mineralization normally observed in Witwatersrand reefs where gold occurs as clusters of irregular grains interstitially to quartz and pyrite pebbles or is attached to and occupies




























REEF		FORMATION	SUBGROUP	GROUP	
		Eldorado (430m)	Turffontein	CENTRAL RAND	
					
					
					
					
					
					
					
					
					
VS5 "A"		Aandenk (14m)			
BPM					
		Spes Bona (20m)			
"B"					
					
		Dagbreek (40m)	Johannesburg		
Leader					
Middle		Harmony (15m)			
Basal					
		Welkom (240m)			
					
Intermediate		St. Helena (320m)			
					
		Virginia (780m)			
Adg. May					

Figure 3: Stratigraphic column of the Central Rand Group of the Witwatersrand Supergroup showing the position of the Basal Reef (after Bailey, 1991).

minute cracks and fractures in round, compact pyrite. This textural association is generally interpreted as conclusive evidence of the remobilization of originally detrital gold during regional metamorphism. The second mode of gold occurrence at the Unisel Gold Mine is typified by the abundance of idiomorphic to hypidiomorphic, authigenic pyrite, in which case most of the gold can be found attached to and included in the secondary pyrite. This type of mineralization is spatially restricted to areas where hydrothermal fluid circulation and metal remobilization occurred as a result of the intrusion of a lamprophyric sill. Hofmeyer and Potgeiter (1983) found that the affect of the intrusion on the gold distribution is only recognizable in areas where the sill is thicker than 1m and occurs not further than 2m away from the Basal Reef. For the present study samples were taken from those portions of the reef which are not thermally overprinted by later sill or dyke intrusions. The ore textures described here are, therefore, interpreted to reflect textural associations between gold and pyrite resulting from gold remobilization during regional metamorphism and related fluid circulation.

### GOLD-PYRITE ASSOCIATION AND THE CHEMISTRY OF PYRITE

Textural associations of gold and pyrite were studied in polished sections and pyrite chemistry was analyzed with an electron microprobe at the Geological Survey in Pretoria and with a proton microprobe at the National Accelerator Centre (NAC) in Faure. Chemical analyses were carried out mainly to study the distribution of As in pyrite and to possibly



*Figure 4: Photomicrograph showing two round, detrital pyrite grains (grey) cemented and partly replaced by gold (white). Length of field of view is about 0.1mm.*

relate As-rich zones to sites of gold deposition. The electron microprobe data are illustrated in the form of compositional profiles while the proton microprobe results are depicted in the form of element distribution maps. Figures 4, 5A, 6, 7A and 8A illustrate typical gold-pyrite intergrowths which occur together in one polished section, but similar textures were also frequently observed in other samples taken from a number of localities throughout the Unisel Gold Mine.

The photomicrograph (Fig. 4) and the corresponding camera lucida drawing (Fig. 5A) depict two, round, compact pyrite grains cemented by gold. It is obvious that gold has partially replaced pyrite, particularly the larger grain on the left in Figure 4. Lines B to E across the pyrite grains (Fig. 5A) refer to electron microprobe traverses with the compositional analyses of the profiles being shown in Figures 5B-E. A value of 0.01% was arbitrarily assigned as the detection limit for As, Co and Ni. Profiles B, C and D (across larger grain in Fig. 5A) illustrate that besides Fe and S the third most abundant element is Co and that its abundance is inversely correlated with that of Fe. Nickel concentrations are below 0.5% and the mean Co/Ni ratio is about 8. Arsenic contents vary from below detection limit to 0.1 % and display a distinctly erratic distribution, probably indicating the presence of As-enriched zones or sectors. The smaller pyrite grain in Fig. 5A is characterized by much lower Co concentrations and a mean Co/Ni ratio of about 0.4 (Fig. 5E). Arsenic contents, however, are much higher, reaching up to 0.3 %, and the As distribution is more homogeneous than in the neighbouring grain. Proton microprobe scans provide a more complete image of the As distribution (Fig. 5F). The larger grain is characterized by three areas of different As contents which, according to combined proton

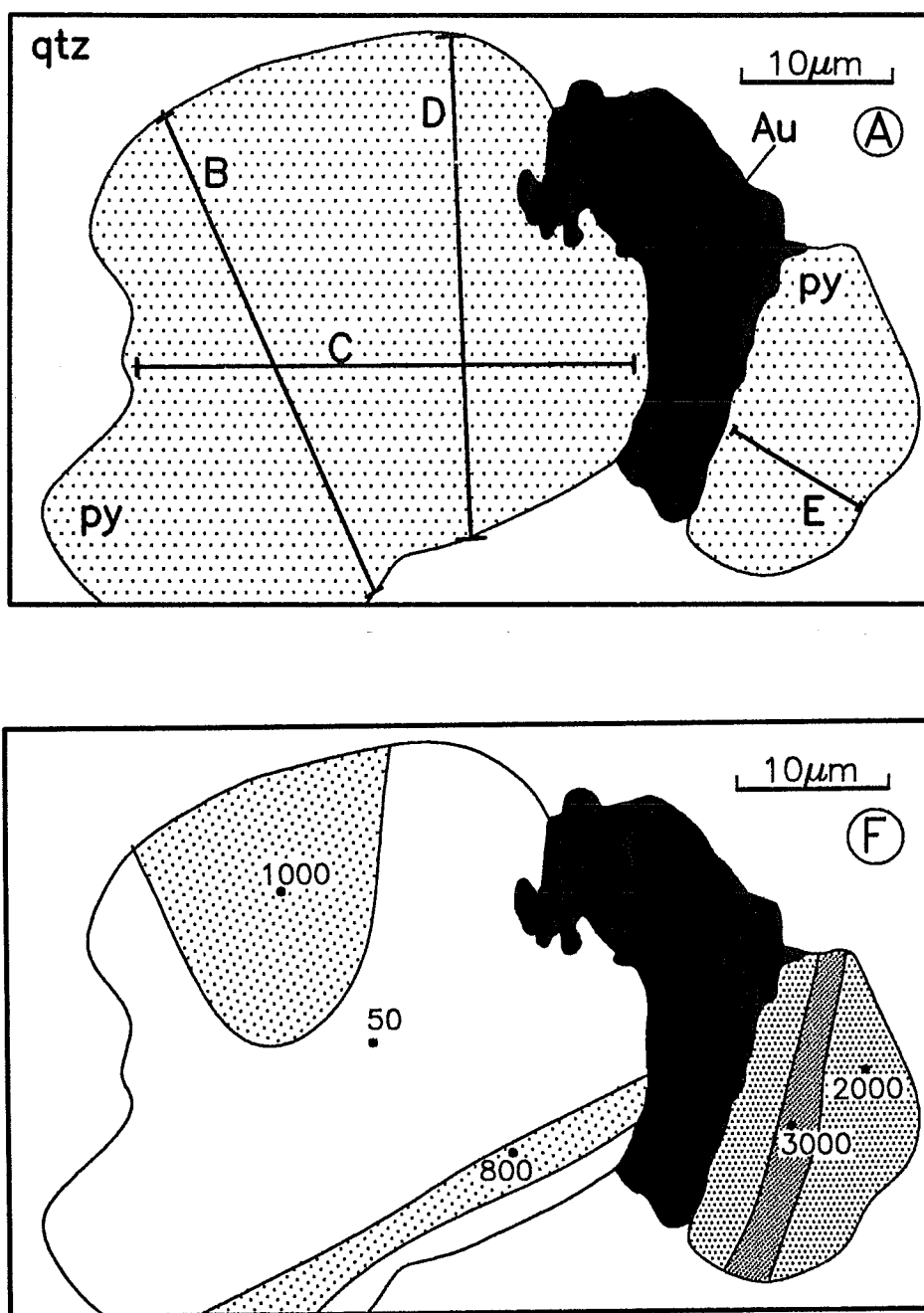
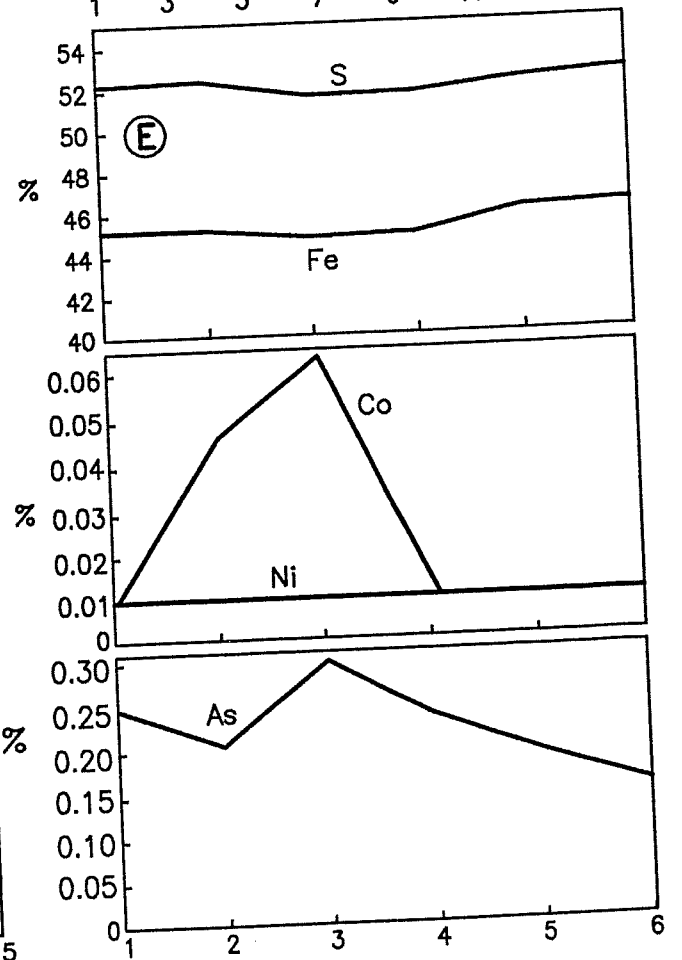
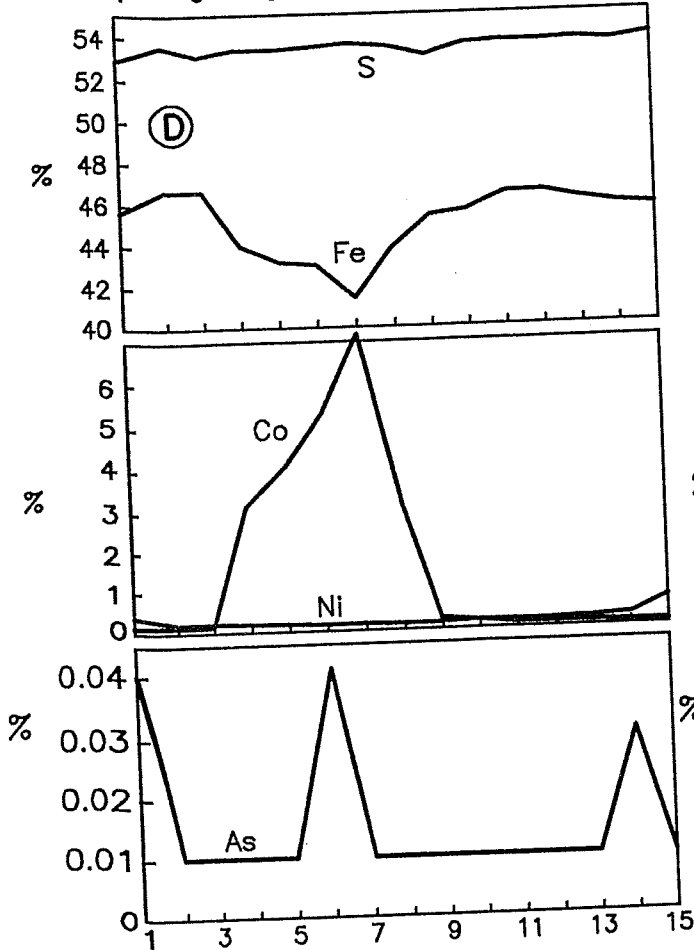
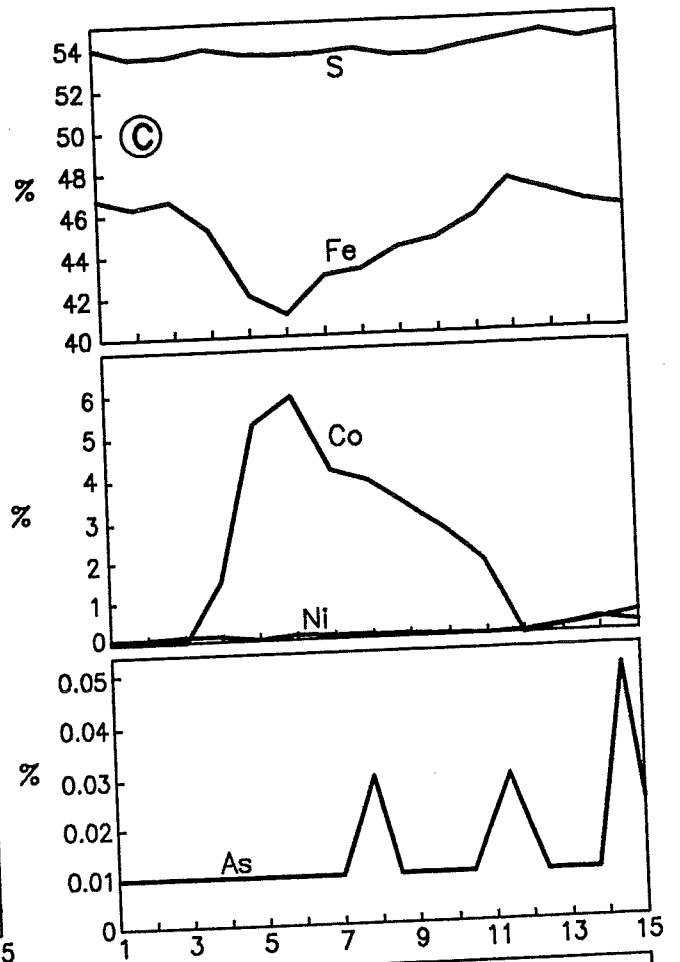
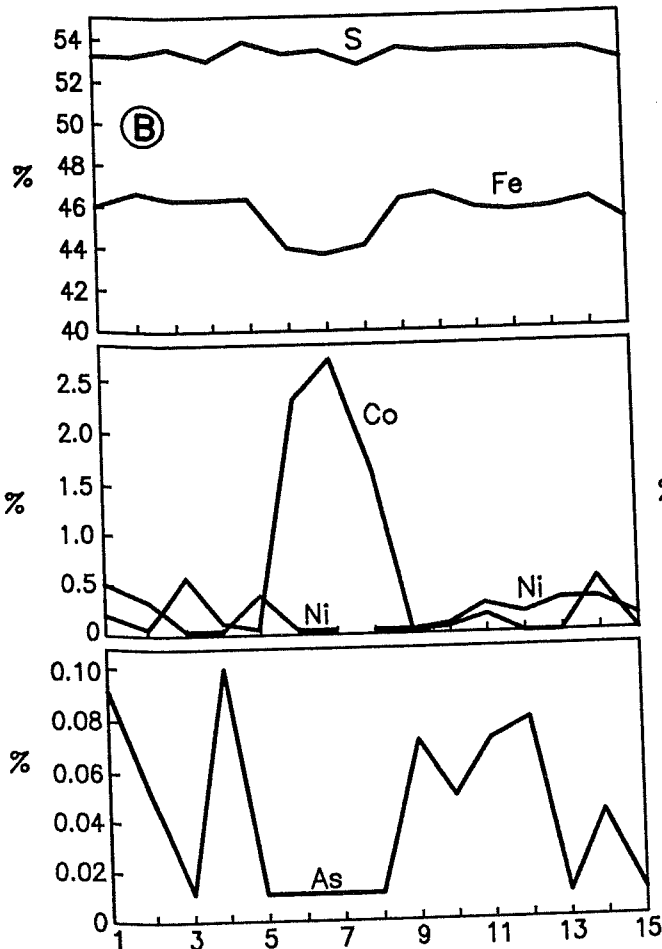


Figure 5. A. Camera lucida reproduction of Figure 4 showing the positions of electron microprobe traverses. B, C and D and E. Electron microprobe profiles showing the distribution of Fe, S, Co, Ni, and As. F. Proton microprobe map of As distribution. Numbers indicate mean As contents.



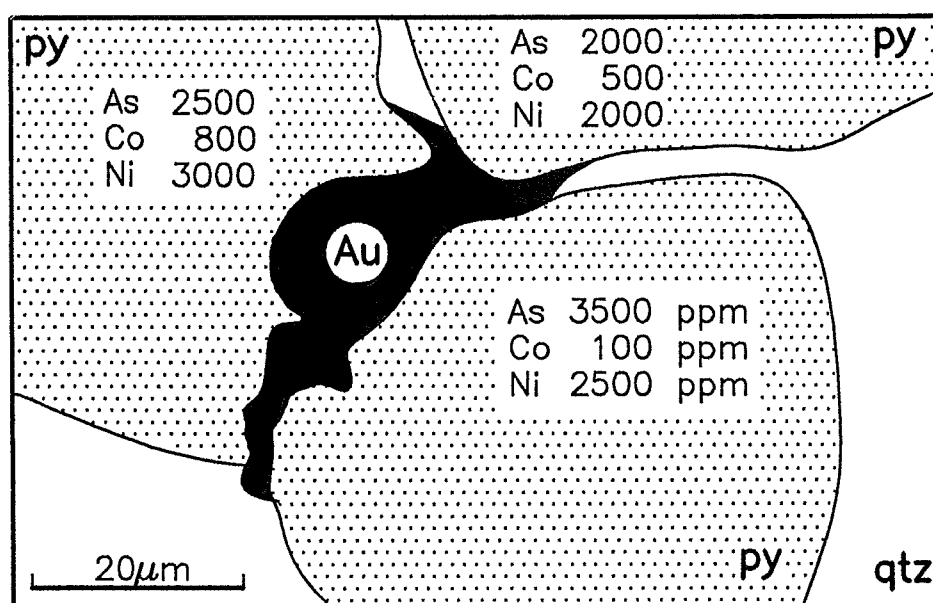


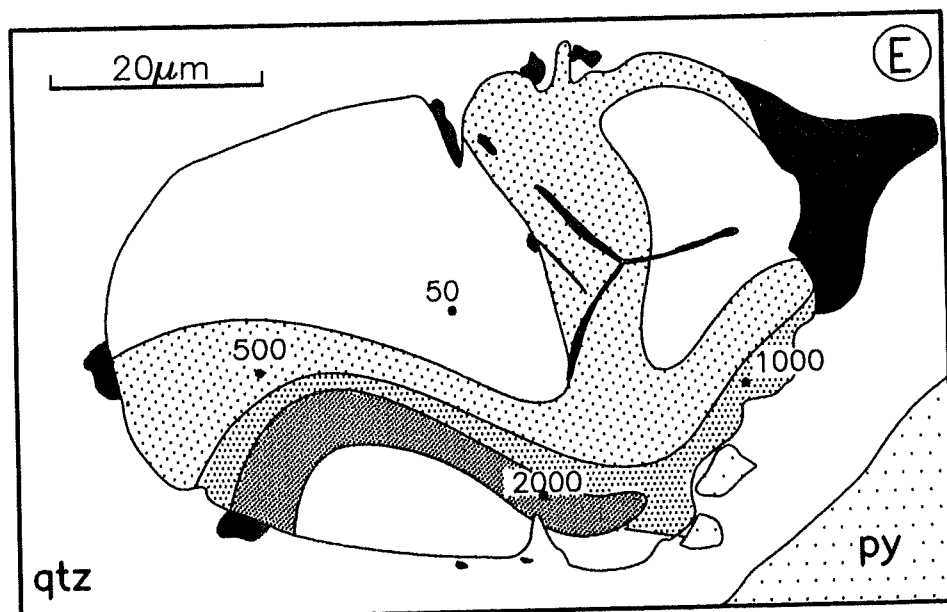
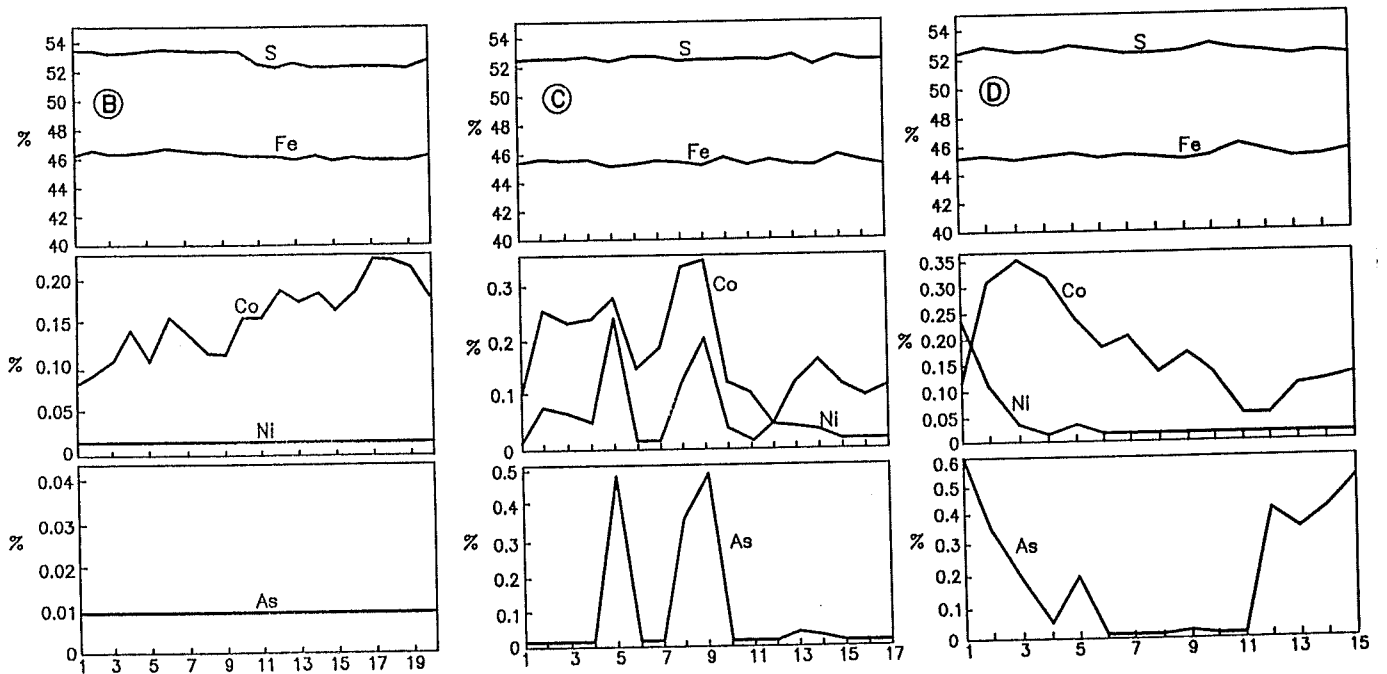
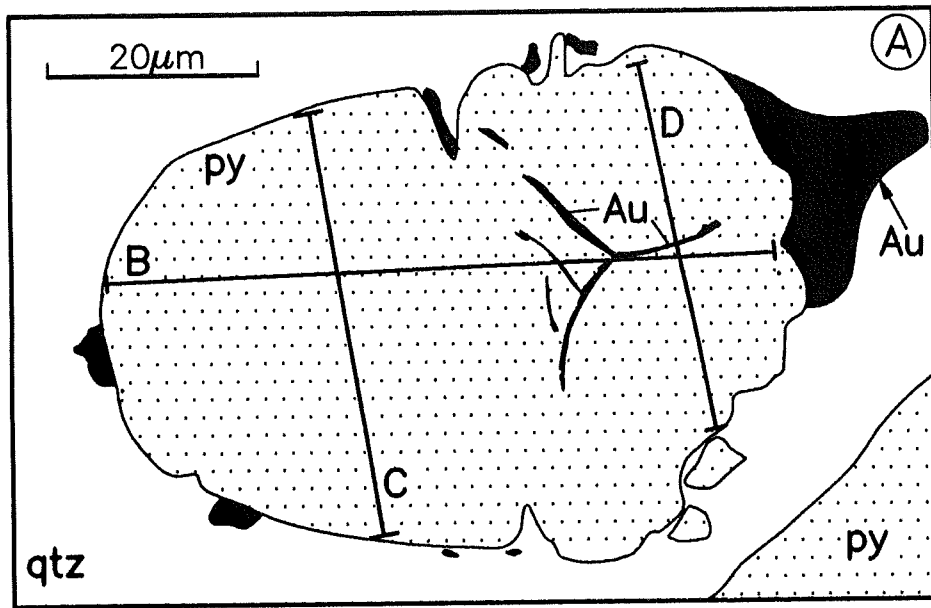
Figure 6: Camera lucida drawing showing three round, detrital pyrite grains cemented and partly replaced by gold. Mean Co, Ni and As contents are also given.

and electron microprobe spot analyses, range from 50 to about 1000 ppm. Most of the grain has As concentrations in the range of 50 ppm, a small band shows enhanced values of 800 ppm, while a larger segment contains the highest As concentrations of about 1000 ppm. The smaller grain in Figure 5F is distinctly higher in As than the larger grain and is divided into two parts separated by a band of As concentrations of about 3000 ppm. The remainder of the grain shows a homogeneous distribution of As with contents in the range of 2000 ppm. A direct spatial relationship between As concentrations and the site of gold precipitation is not immediately visible. It is clear, however, that the gold is located between two pyrite grains which are distinctly different with respect to As contents.

A similar example of partial replacement of pyrite by gold is shown in Figure 6. Electron microprobe scans indicate a fairly homogeneous As distribution throughout the grains. The mean As concentrations are, however, significantly different for each of the three pyrite grains, ranging from 2000 to 3500 ppm. Nickel and Co are less evenly distributed. In all grains Ni is considerably more abundant than Co with mean Co/Ni ratios ranging from 0.04 to 0.03.

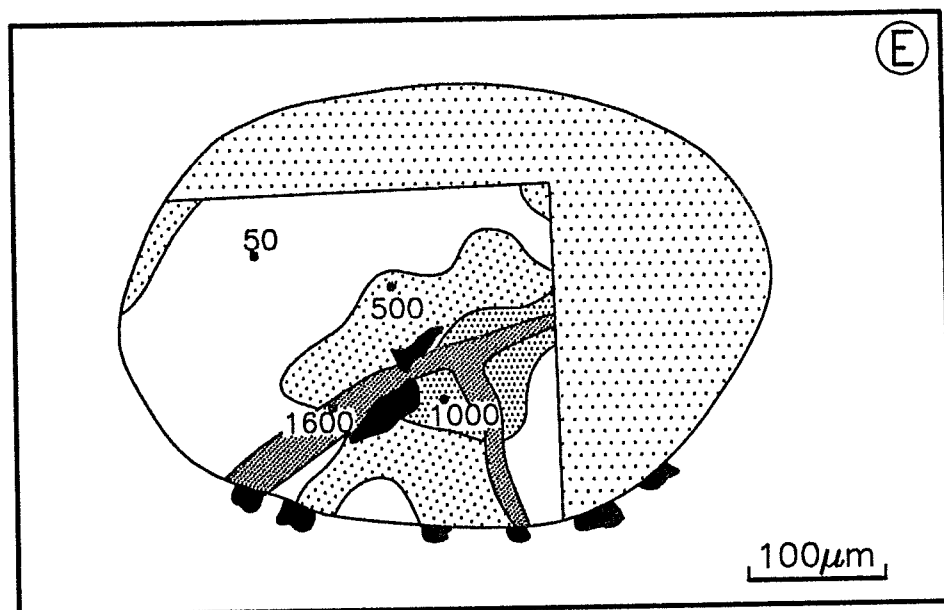
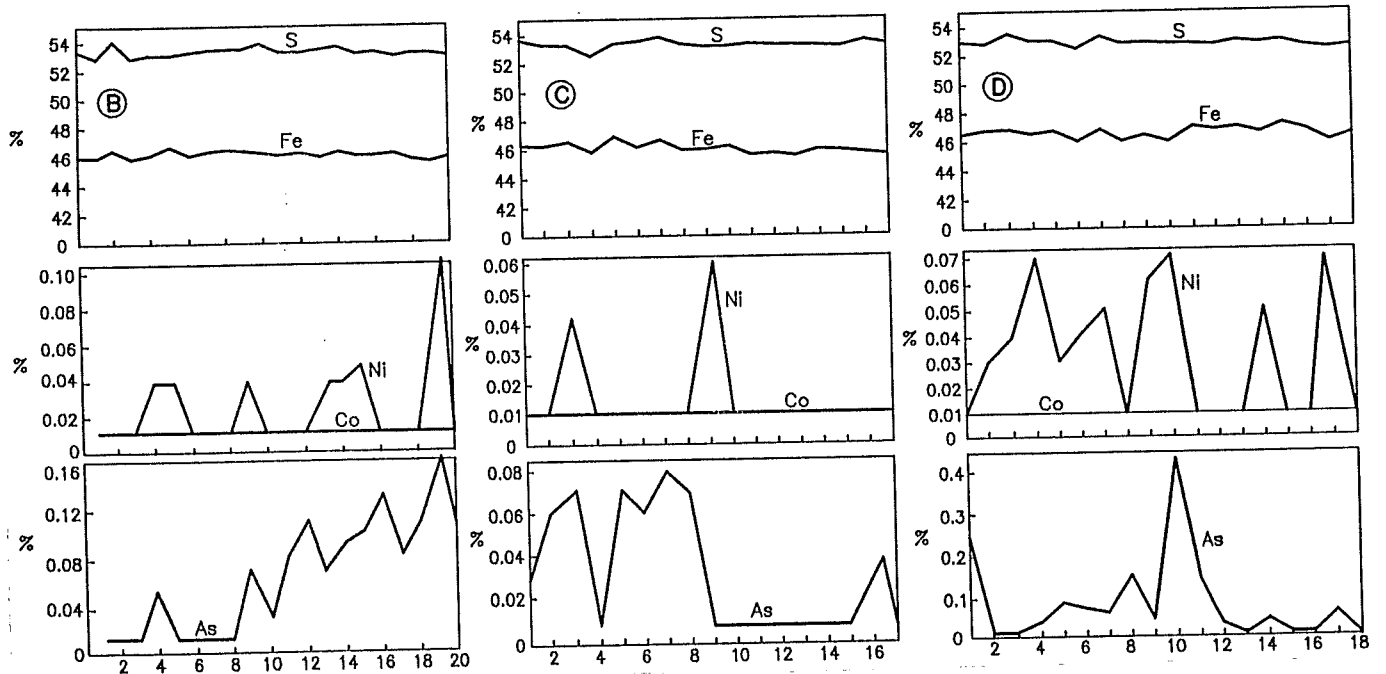
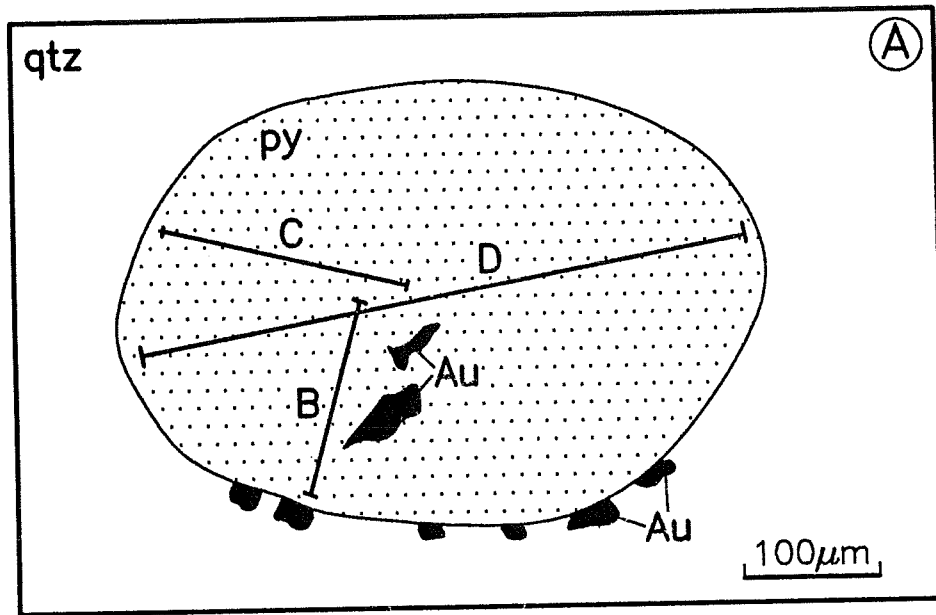
Another example of gold-pyrite intergrowth is provided in Figure 7A. Four small gold grains ( $\leq 5 \mu\text{m}$ ) are nucleated on the pyrite surface while a much bigger gold grain partially replaces pyrite. In addition, a Y-shaped hairline crack in the pyrite is filled with gold. The corresponding chemical profiles (Figs. 7B-D) show erratic and independent Co and Ni distributions with Co being consistently more abundant than Ni, which is reflected in the overall Co/Ni ratio of about 9. Arsenic concentrations are below detection limit across the long axis of the grain (Fig. 7B), but in traverses C and D the element can reach up to more than 0.5 %. For most parts of the chemical profiles C and D, As is consistently below detection limit, but a number of distinct peaks with increased concentrations do also occur which may indicate the presence As-enriched growth zones. The proton microprobe map

*Figure 7: A. Camera lucida drawing showing four small gold grains attached to round, detrital pyrite. One side of the pyrite is partly replaced by a large gold grain and a T-shaped hairline crack in the centre is filled with gold. The positions of electron microprobe traverses (B, C and D) are also indicated. B, C and D. Electron microprobe profiles showing the distribution of Fe, S, Co, Ni, and As. E. Proton microprobe map of As distribution. Numbers indicate mean As contents.*



*Figure 8: A. Camera lucida drawing of a large ( $\pm 1\text{mm}$ ) round, detrital pyrite. Small gold grains are attached to the pyrite surface and two cracks are filled with gold. The positions of electron microprobe traverses (B, C and D) are also shown. B, C and D. Electron microprobe analyses of Fe, S, Co, Ni and As distributions. E. Proton microprobe map showing the distribution of As. Numbers indicate mean As contents.*





reveals a rather complex As distribution (Fig. 7E). An S-shaped band with As concentrations around 2000 ppm is parallel to a band containing about 1000 ppm of As. They, in turn, lie adjacent to another zone with As contents in the range of 500 ppm. This zone parallels the two previously mentioned bands, but also branches off at right angles separating the rest of the pyrite grain into two parts possessing a homogeneous As distribution with values in the range of 50 ppm. The position of the four small gold grains appears to be related to the As distribution. Gold accumulations are situated close to the boundaries between high- and low-As zones, but occur in the high-As areas. The large gold grain is also located at the margins of adjacent zones with different As concentrations.

Figure 8A portrays a pyrite grain about 1.2 mm in diameter. Six gold grains, with diameters between 10 and 40  $\mu\text{m}$ , are attached to one side of the pyrite while two larger grains (50 to 60  $\mu\text{m}$ ) occur as fracture fillings. Chemically, the pyrite is conspicuous by the very low abundance of Co and a corresponding Co/Ni ratio below 0.1. Nickel contents are distinctly higher than Co, ranging from below detection limit to about 0.07%, but the distribution is highly erratic. Arsenic concentrations vary between <0.01 and 0.4% (Figs. 8B-D) and As distributions show distinct peaks which delineate areas of low and high As contents. A portion of the pyrite grain was also scanned with the proton microprobe and the results are shown in Figure 8E. Highest As contents (1600 ppm) are confined to a narrow, T-shaped band which is enveloped by two irregular zones containing progressively lower As contents of about 1000 and 500 ppm, respectively. The remaining area of the pyrite grain contains As in the 50 ppm range. Gold is noticeably concentrated in areas of alternating high- and low-As zones, where the high-As zones are truncated by grain boundaries. The siting of the attached gold grains on the pyrite surface appears, again, to be controlled by the As distribution.

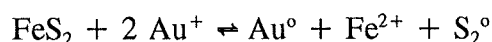
## MECHANISMS OF GOLD DEPOSITION

The conspicuous nucleation of gold on the surface of pyrite is not only known from Witwatersrand ores but has also been documented also for a number of mesothermal lode-gold deposits (e.g. Knipe et al., 1992). In the Basal Reef the observed gold-pyrite intergrowths suggest that gold is texturally younger than round pyrite and that the metal was deposited on As-rich sites on pyrite surfaces during metahydrothermal fluid circulation. Similar textures also occur in mesothermal lode-gold deposits, but in these deposits arsenopyrite and arsenian pyrite can, in addition, contain submicroscopic ppm-levels of gold exclusively associated with As-rich lamellae where it may have substituted for Fe during mineral growth (e.g. Fleet et al., 1993; Wu and Delbove, 1989).

Both textural associations described above are characterized by conspicuous Au-As relationships in pyrite which according to Möller (1993) and Möller and Kersten (1994) can be explained by an electrochemical precipitation mechanism. Based on experimental results the authors conclude that Au mainly accumulates on p-type zones in mixed np-type sulphides and that the type of conductivity is determined by the abundance and distribution of As and, thus, the As/S ratio. Spatial variation of As content in pyrite often occurs as oscillatory-zoned microstructures which may reflect disequilibrium growth conditions resulting from episodic fluctuation in fluid composition during crystal formation (Fleet et al., 1989).

Tectonic fracturing of the pyrite or truncation of its growth zones by grain boundaries during sedimentary transport facilitates the exposure of electrochemically active np-junctions to circulating fluids and, thus, the electrochemical deposition of gold.

MacLean and Fleet (1989) showed that round, detrital pyrite from the Basal Reef is oscillatory-zoned in As content and that the growth zones exhibit polygonal to colloform forms. Round pyrite from the Basal Reef investigated in this study displays rather irregular-shaped As distribution patterns and some of the grains appear to be almost featureless. The precipitation of gold on adjacent pyrite grains and their partial replacement by gold is shown in Figures 5 and 6. In these cases, pyrite is conspicuous by the absence of pronounced intragrain variations in As content. However, adjacent grains are distinctly different with respect to As concentrations. Since the minerals are not in immediate contact this configuration does not result in the formation of a galvanic cell and there is no obvious link between As distribution (i.e. the position of np-junctions) and the sites of gold nucleation. Chemical profiles shown in Figure 5B-D suggest zonation in Co content and major substitution of Fe by Co, whereas the grains in Figure 6 are characterized by high Ni contents. As mentioned above, zonation in Co and/or Ni content also results in the formation of np-junctions in pyrite which, in turn, can cause electrochemical deposition of gold. The partial replacement of pyrite suggests that gold deposition was accompanied by electrochemical corrosion and it may be suggested that even small differences in As concentrations may be sufficient to prompt gold precipitation. The electrochemical corrosion may be expressed by the following reaction:



The equation implies that the electrochemical reduction of Au resulted in the oxidation of Fe and in the leaching of soluble Fe species. A more unequivocal spatial relationship between As zonation and gold precipitation is provided in Figures 7E and 8E. In these examples, gold accumulations are located at low- and high-As boundaries (i.e. np-junctions) with the metal being preferentially concentrated in the high-As areas (i.e. p-type conductor). Possible redox reactions that can take place at the mineral-fluid interface are diagrammatically presented in Figure 9A and B. Estimations of environmental conditions during metahydrothermal gold remobilization of Witwatersrand reefs suggest that  $\text{HAu}(\text{HS})_2^0$  was the dominant soluble complex and that  $\text{AuCl}_2$  was far less important (Fig. 2). In mixed np-type pyrite, high-As zones represent p-type conductors (cathodes), while low-As zones are n-type conductors (anodes). In the case of the neutral  $\text{HAu}(\text{HS})_2^0$  complex it is envisaged that it dissociates at the cathode and/or that it is in thermodynamic equilibrium with  $\text{Au}^+$ -ions in solution and that the transfer of electrons at the cathode causes reduction of  $\text{Au}^+$ -ions to metallic gold. Oxidation of the  $\text{HS}^-$  complex at the anode favours deposition of native S and a decrease in fluid pH (Fig. 9A). The  $\text{AuCl}_2$  complex can be directly oxidized at the anode, but it is also conceivable that cathode-reactions may lead to a dissociation of the complex with the resulting  $\text{Au}^+$ -ion being reduced to metallic gold (Fig. 9B).

The mechanism of gold deposition that has been suggested above differs from the findings reported by Knipe et al. (1992) who were unable to establish any correlation between sites of gold deposition and the size, chemistry, and morphology of sulphide grains. Similarly, gold-pyrite textures shown in Figures 5 and 6, also do not suggest that areas of

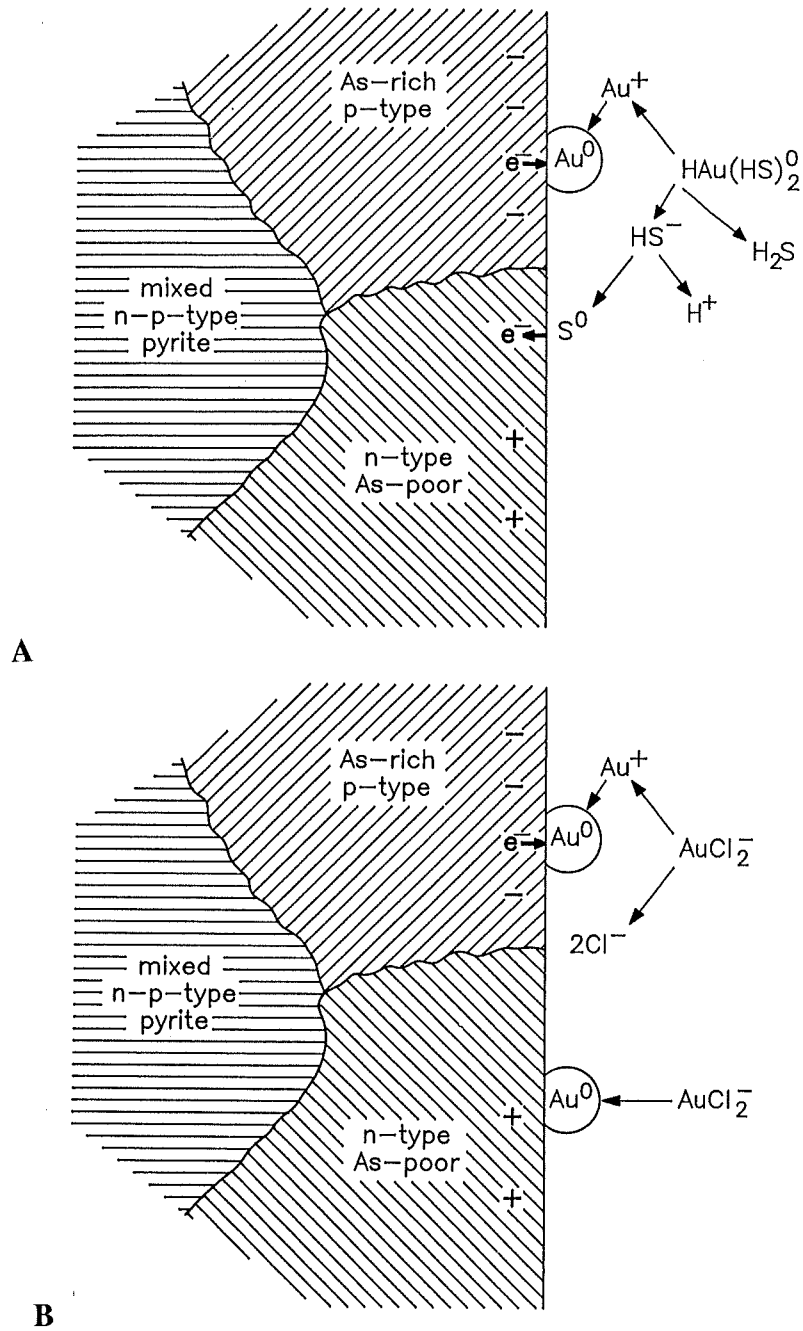


Figure 9: Model of a mixed np-type pyrite. (A) It is assumed that the neutral  $\text{HAu}(\text{HS})_2^0$  complex is in thermodynamic equilibrium with  $\text{Au}^+$  ions and that electron-transfer at the cathode results in reduction to native gold. (B) The  $\text{AuCl}_2^-$  complex can be directly oxidized at the anode to form native gold. Reduction of the dissociated  $\text{Au}^+$  -ions at the cathode leads also to gold precipitation (modified from Möller and Kersten, 1994).

gold nucleation are necessarily underlain by zones of high As contents. Consequently, it is necessary to assume that there may be more than one mechanism of gold deposition on pyrite, including the electrochemical reduction proposed by Möller and Kersten (1994) as well as physiosorption and chemisorption processes favoured by Knipe et al. (1992), Bancroft and Hyland (1990), and Jean and Bancroft (1985). However, most research into processes of gold precipitation on sulphide substrates results in the common conclusion that submicroscopic-scale physical and chemical controls are the factors that determine gold precipitation sites.

Detrital Witwatersrand pyrite is thought to have originated from a number of diverse geological environments in the Witwatersrand hinterland and it is believed that this is the main reason for the inhomogeneous chemical composition of the mineral as indicated by wide ranges in As contents and Co/Ni ratios (Meyer et al., 1990a). The above discussion has emphasized the importance of chemical inhomogeneities as well as the chemical and physical conditions of pyrite surfaces in controlling the precipitation of gold. It appears unlikely, therefore, that there was any involvement of conventional precipitation mechanisms such as the destabilization of gold complexes due to changes in internal and external properties of the hydrothermal system. The Basal Reef as well as many other Witwatersrand reefs contain up to 5% pyrite, on average, which provides a high abundance of electrochemically active surfaces. This phenomenon, together with the low gold solubility during metahydrothermal fluid circulation, is the main reason why gold was remobilized only over very short distances within the conglomerate reefs.

## CONCLUSIONS

This study reports the results of a petrographic analysis of the association of gold on detrital, round, pyrite in the Basal Reef of the Witwatersrand Supergroup. Textural relationships observed include nucleation of gold on pyrite surfaces, the infilling of hairline cracks and partial replacement of pyrite. Chemical micromapping of pyrite shows that in some instances a spatial association exists between the sites of gold accumulation and zones of high As content. This association is explained by the electrochemical model of Möller and Kersten (1994) which proposes that alternating high- and low-As zones in pyrite result in mixed np-type conductivity accompanied by electron exchange and the reduction-driven deposition of  $\text{Au}^+$  ions at the cathode. However, not all gold accumulations on pyrite are immediately linked to chemical heterogeneities and, in keeping with Knipe et al. (1992), it is inferred that an additional control on the deposition of gold was exerted by physical defects such as growth terraces, etch-pits and fractures, which create zones of increased charge density and/or areas of focused conductivity. Both models suggest that sub-microscopic physical and chemical controls are the important factors that determined the sites of gold nucleation and that physicochemical precipitation mechanisms, such as changes in pressure, temperature, or fluid composition, were not involved. The high abundance of round, detrital, chemically zoned pyrite in the Basal Reef provides a large number of electrochemically active pyrite surfaces which represent an extremely effective mechanism for gold deposition. This fact, together with the low solubility of gold in Witwatersrand fluids, is the main reason for the spatially restricted remobilization of gold in the conglomerate reefs.

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## REFERENCES

- ARMSTRONG, R.A., COMPSTON, W., RETIEF, E.A., WILLIAMS, I.S. and WELKE, H.J., 1991. Zircon ion-microprobe studies bearing on the age and evolution of the Witwatersrand Triad. *Precambrian Research*, **53**, p. 243-266.
- BAILEY, A.C., 1991. The stratigraphy and sedimentology of the upper Johannesburg and Turffontein Subgroups in the southwestern portion of the Welkom goldfield. MSc thesis (unpubl.), University of the Witwatersrand, Johannesburg, 145 pp.
- BANCROFT, G.M. and HYLAND, M.M., 1990. Spectroscopic studies of adsorption/reduction reactions of aqueous complexes on sulphide surfaces. *In: Mineral-Water Interface Geochemistry*. M. Hochella and A. White (Eds.), Mineralogical Society of America, *Reviews in Mineralogy*, **23**, p. 511-558.
- BANCROFT, G.M. and JEAN, G., 1982. Gold deposition at low temperatures on sulphide minerals. *Nature*, **298**, p. 730-731.
- CARDILE, C.M., CASHION, J.D., MCGRATH, A.C., RENDERS, P. and SEWARD, T.M., 1993. <sup>193</sup>Au Mössbauer study of Au<sub>2</sub>S and gold adsorbed onto As<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> substrates. *Geochimica et Cosmochimica Acta*, **57**, p. 2481-2486.
- FEATHER, C. E. and KOEN, G.M., 1975. The mineralogy of the Witwatersrand Reefs. *Minerals Science and Engineering*, **7**, p. 189-224.
- FLEET, M.E., CHRYSOULIS, S.L. and MACLEAN, P.J., 1993. Arsenian pyrite from gold deposits: Au and As distribution investigated by SIMS and EMP, and color staining and surface oxidation by XPS and LIMS. *The Canadian Mineralogist*, **31**, p. 1-17.
- FLEET, M.E., MACLEAN, P.J. and BARBIER, J., 1989. Oscillatory-zoned As-bearing pyrite from strata-bound and stratiform gold deposits: an indicator of ore fluid evolution. *In: The Geology of Gold Deposits: The Perspective in 1988*. R.R. Keays, W.R.H. Ramsay and D.I. Groves (Eds.). *Economic Geology Monograph*, **6**, p. 356-362.
- HALLBAUER, D.K. and UTTER, T. (1977). Geochemical and morphological characteristics of gold particles from recent river deposits and the fossil placers of the Witwatersrand. *Mineralium Deposita*, **12**, p. 293-306.

- HANDLEY, J.R.F. (1990). World gold resources review at the end of the 1980 decade. University of the Witwatersrand, Johannesburg, Economic Geology Research Unit, Information Circular, **227**, 37 pp.
- HOFMEYR, P.K. and POTGEITER, G.A., 1983. The occurrence of pseudo-hydrothermal gold in pyrite at Unisel Gold Mines Limited. Special Publication of the Geological Society of South Africa, **7**, p. 271-274.
- JEAN, G.E. and BANCROFT, G.M., 1985. An XPS and SEM study of gold deposition at low temperatures on sulphide mineral surfaces: concentration of gold by adsorption/reduction. *Geochimica et Cosmochimica Acta*, **49**, p. 979-987.
- KNIPE, S.W., FOSTER, R.P. and STANLEY, C.J., 1991. Hydrothermal precipitation of precious metals on sulfide substrates. In: Brasil Gold'91. E.A. Ladeira (Ed.), Balkema, Rotterdam, p. 431-435.
- KNIPE, S.W., FOSTER, R.P. and STANLEY, C.J., 1992. Role of sulphide surfaces in sorption of precious metals from hydrothermal fluids. Transactions of the Institution of Mining and Metallurgy, Section B: Applied Earth Sciences, **101**, p. 83-88.
- LIEBENBERG, W.R., 1955. The occurrence and origin of gold and radioactive minerals in the Witwatersrand System, the Dominion Reef, the Ventersdorp Contact Reef, and the Black Reef. Transactions of the Geological Society of South Africa, **58**, 101-227.
- MACLEAN, P.J. and FLEET, M.E., 1989. Detrital pyrite in the Witwatersrand gold fields of South Africa: Evidence from truncated growth banding. *Economic Geology*, **84**, 2008-2011.
- MEYER, F.M., DRENNAN, G.R., ROBB, L.J., CATHELINEAU, M., DUBESSY, J. and LANDAIS, P., 1991. Conditions of Au-U mineralization in Witwatersrand reefs. 681-684. In: Source, Transport and Deposition of Metals. M. Pagel and J.L. Leroy, (Eds.), Balkema, Rotterdam, p. 681-684
- MEYER, F.M., OBERTHÜR, T., ROBB, L.J., SAAGER, R. and STUPP, H.D., 1990a. Cobalt, nickel, and gold in pyrite from primary gold deposits and Witwatersrand reefs. *South African Journal of Geology*, **93**, 70-82.
- MEYER, F.M., WALLMACH, T., HENKEL, J. and SCHWEITZER, J.K., 1990b. Chlorite composition and fluid conditions in some Witwatersrand reefs. Geocongress '90, 23rd Earth Sciences Congress of the Geological Society of South Africa, Cape Town, p. 391-394.
- MINTER, W.E.L., GOEDHART, M., KNIGHT, J., and FRIMMEL, H.E., 1993. Morphology of Witwatersrand gold grains from the Basal Reef: evidence for their detrital origin. *Economic Geology*, **88**, p. 237-248.

- MINTER, W.E.L., HILL, W.C.N., KIDGER, R.J., KINGSLEY, C.S. and SNOWDEN, P.A.. 1986. The Welkom Goldfield. *In: Mineral Deposits of Southern Africa*, Volume 1. C.R. Anhaeusser and S. Maske (Eds.). Geological Society of South Africa, Johannesburg, p. 497-539.
- MIRONOV, A.G., ZHMODIK, S.M. and MAKSIMOVA, E.A., 1981. An experimental investigation of the sorption of gold by pyrites with different thermoelectric properties. *Geochemistry International*, **18**, p. 153-160.
- MÖLLER, P., 1993. Why is gold accumulated in pyrite- and arsenopyrite-rich mineralizations? An electrochemical approach. *In: Current Research in Geology Applied to Ore Deposits*. P. Fenoll Hoch-Ali, J. Torres-Ruiz and F. Gervilla, (Eds.). University of Granada, Granada, Spain, p. 503-506.
- MÖLLER, P. and KERSTEN, G., 1994. Electrochemical accumulation of gold on pyrite and arsenopyrite surfaces. *Mineralium Deposita* (in press).
- PRETORIUS, D.A. (1991). The sources of Witwatersrand gold and uranium: A continued difference of opinion. *Economic Geology Monograph*, **8**, p. 139-163.
- RAMDOHR, P., 1955. Neue Beobachtungen an Erzen des Witwatersrandes in Südafrika und ihre genetische Bedeutung. Abhandlungen der deutschen Akademie der Wissenschaften zu Berlin, Klasse für Mathematik and allgemeine Naturwissenschaften, Nr. 5., 43 Seiten und 130 Abbildungen.
- RENDERS, P.J. and SEWARD, T.M., 1989. The adsorption of thio gold(I) complexes by amorphous As<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> at 25 and 90 °C. *Geochimica et Cosmochimica Acta*, **53**, p. 255-267.
- ROBB, L.J. and MEYER, F.M., 1991. A contribution to recent debate concerning epigenetic versus syngenetic mineralization processes in the Witwatersrand Basin. *Economic Geology*, **86**, p. 396-401.
- ROBB, L.J. and MEYER, F.M. (1994). Geological environments and mineralization processes applicable to the Witwatersrand Au-U deposits. Proceedings Volume of the XV Congress of the Council of Mining and Metallurgical Institutions (in press).
- ROBB, L.J., DAVIS, D.W. and KAMO, S.L. 1990. U-Pb ages on single detrital zircon grains from the Witwatersrand Basin, South Africa: constraints on the age of sedimentation and on the evolution of granites adjacent to the basin. *Journal of Geology*, **98**, p. 311-328.
- ROBB, L.J., DAVIS, D.W., KAMO, S.L. and MEYER, F.M. 1992. Ages of altered granites adjoining the Witwatersrand Basin with implications for the source of gold and uranium. *Nature*, **357**, p. 677-680.



- ROBB, L.J., LANDAIS, P., MEYER, F.M. and DAVIS, D.W., 1994. Nodular hydrocarbons in granites: implications for the origin of kerogen in the Witwatersrand Basin, South Africa. *Exploration and Mining Geology* (in press).
- SCHOONEN, M.A.A., FISHER, N.S. and WENTE, M., 1992. Gold sorption onto pyrite and goethite: a radiotracer study. *Geochimica et Cosmochimica Acta*, **56**, p. 1810-1814.
- STARLING, A., GILLIGAN, J.M., CARTER, A.H.C., FOSTER, R.P. and SAUNDERS, R.A., 1989. High-temperature hydrothermal precipitation of precious metals on the surface of pyrite. *Nature*, **340**, p. 298-300.
- UTTER, T., 1980. Rounding of ore particles from the Witwatersrand gold and uranium deposit (South Africa) as an indicator of their detrital origin. *Journal of Sedimentary Petrology*, **50**, p. 71-76.
- WALLMACH, T. and MEYER, F.M., 1990. A petrogenetic grid for metamorphosed aluminous Witwatersrand shales. *South African Journal of Geology*, **93**, p. 93-102.
- WU, X. and DELBOVE, F., 1989. Hydrothermal synthesis of gold-bearing arsenopyrite. *Economic Geology*, **84**, p. 2029-2032.

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