Sulphidation in the Witwatersrand Goldfields: evidence from the Middelvlei Reef

RUSSELL E. MYERS, TAIHE ZHOU, AND G. NEIL PHILLIPS

National Key Centre in Economic Geology, Geology Department, James Cook University, Townsville, Australia Q4811

Abstract

There is extensive textural evidence for sulphidation in the Middelvlei Reef of the Carletonville Goldfield, South Africa. Secondary iron sulphides have replaced sand- and pebble-sized clasts in conglomerate, as well as matrix material in both conglomerate and quartzite. Within the Middelvlei Reef there is a close correspondence between the intensity of sulphidation and areas of greater modal muscovite, and there is less sulphidation where chloritoid dominates. Both pyrite and minor pyrrhotite are widespread. The timing of the sulphidation appears to be post-depositional but the relative importance of diagenetic and syn-metamorphic processes cannot be determined using textural criteria. The absence of retrograde effects suggests that sulphidation occurred prior to or during peak metamorphism. The distribution and intensity of sulphidation and phyllosilicate alteration indicate that these processes may be more significant in the Witwatersrand than has generally been thought. These processes should be considered in all future genetic models.

KEYWORDS: sulphidation, goldfields, Witwatersrand, South Africa.

Introduction

The alteration/sulphidation debate. Out of recent discussions on the origin of the gold mineralisation in the Witwatersrand Basin (Fig. 1), the role of sulphidation has emerged as a central issue. Phillips and Myers (1989) suggested that widespread sulphidation of detrital iron minerals could be a major control on gold mineralisation. In response, Reimer and Mossman (1990*a*, *b*) present evidence to argue that widespread sulphidation of iron minerals is a 'myth'. Later Robb and Meyer (1991) use thermodynamic arguments to suggest that the complete alteration of magnetite to pyrite is physically impossible. Along the same lines, Sutton *et al.* (1990) have used geochemical evidence to argue that there is no evidence of widespread post-depositional alteration, and by inference no widespread sulphidation. Wallmach and Meyer (1990) use metamorphic phase equilibria to argue the same conclusion.

In contrast to the findings of these recent studies, earlier workers such as Ramdohr (1958) and Saager (1970) documented clear evidence of pseudomorphic replacement of iron-titanium oxide minerals in the Witwatersrand conglomerates. In addition they also reported partial pyrite replacement of a variety of clasts, including banded chert and shale (see also Hirdes and Saager, 1983). Unfortunately, these older petrographic studies were concerned primarily with documenting the variety of textures present and it is often difficult to assess the wider significance of the sulphidation textures they reported. Are the sulphidation textures common? Are they in any way related to gold mineralisation itself? The object of this paper is to demonstrate that sulphidation may be more common and widespread than has generally been thought and present data which must somehow be incorporated into all future genetic models.

Why the Middelvlei Reef? If other ore deposits are any guide, the place to look for evidence of sulphidation is the margins of ore deposits, or in marginally economic areas. Experience in greenstone gold deposits, for example, suggests that less than 10% of the exposures contain over 90% of the critical evidence (Robert *et al.*, 1991): in the heart of major ore deposits evidence for or against sulphidation is typically equivocal (i.e. is there complete replacement or no replacement?). Hence, while petrographic studies of well mineralised reefs in the Witwatersrand (e.g. Saager,

Mineralogical Magazine, September 1993, Vol. 57, pp. 395–405

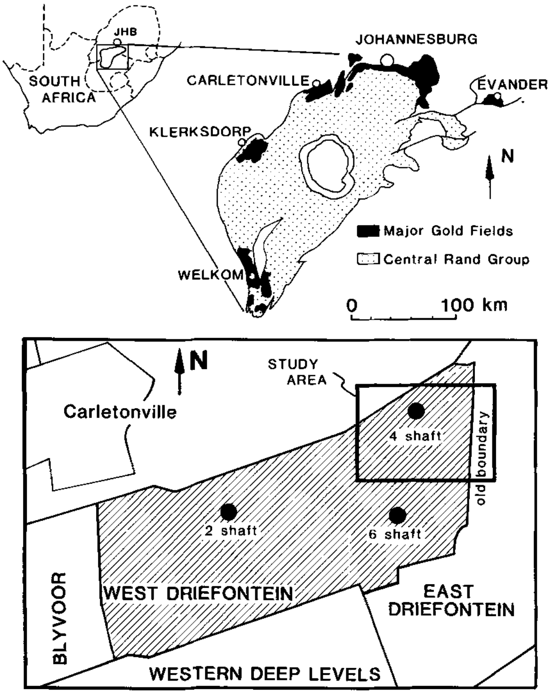


FIG. 1. General location of the Witwatersrand within South Africa and sketch of the Witwatersrand Basin showing locations of the major goldfields. The inset shows the location West Driefontein Gold Mine with respect to Carletonville and the location of the study area on West Driefontein.

1970; Hirdes and Saager, 1983) have documented the widespread presence of crystalline authigenic pyrites, partial replacement textures in detrital grains are only rarely seen. In order to examine the true extent of replacement it is necessary to move out of areas which may have been most intensely altered.

The Middelvlei Reef, selected for this study, is the lateral equivalent of the very rich South Reef (Englebrecht *et al.*, 1986) which supported much of the early mining in the Johannesburg area. Unfortunately for miners in the Carletonville Goldfield (Fig. 1), the gold grades in this horizon are generally patchy and on West Driefontein Gold Mine the Middelvlei Reef can only support selective mining of high grade areas (Fig. 2). On the other hand, the Carbon Leader, one of the single most important gold producers in the Witwatersrand Basin, lies stratigraphically less than one hundred metres below the Middelvlei Reef. It was hoped that in the economically marginal Middelvlei Reef environment partial replacement textures might be preserved and that contrasts in the mineralogy between low grade and very high grade areas might be present.

Geology of the Middelvlei Reef. The Middelvlei Reef is developed near the base of the roughly 3 km thick upper Witwatersrand succession (Central Rand Group) which consists primarily of quartzite, with conglomerate and minor shale (Fig. 3). The Middelvlei Reef was deposited on a well-defined regional unconformity which eliminates in excess of 70 m of footwall quartzite in the Carletonville Goldfield (Els, 1991). In the Carletonville area alone the Middelvlei Reef covers an area of more than 500 km^2. However, if its lateral equivalents in the West Rand and Central Rand Goldfields are considered the area would represent thousands of square kilometres.

The sedimentology of the Middelvlei Reef has been extensively studied (Els, 1987, 1991; Jolly, 1984), particularly on West Driefontein Gold Mine where this investigation has been undertaken. The Middelvlei Reef represents a braided fluvial system, deposited initially on a degradational surface which slowly became aggradational. Palaeocurrent measurements indicate that flow directions were from northwest to southeast across West Driefontein (Els, 1991).

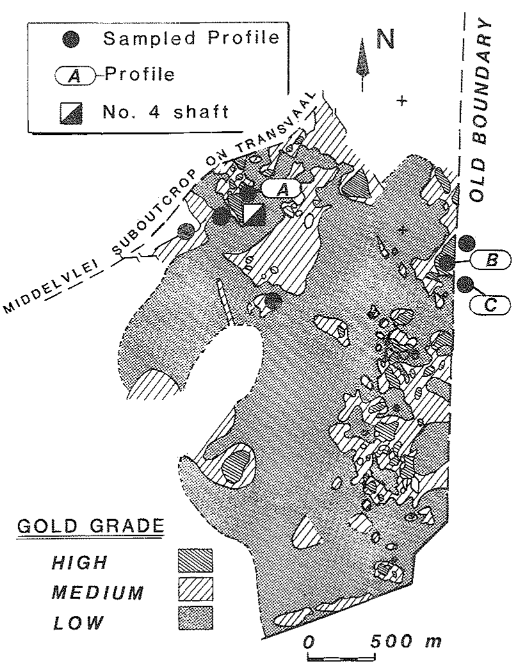


FIG. 2. Gold grade distribution in the Middelvlei Reef in the study area modified from Els (1991). Solid circles show the location of profiles sampled in this study. Profiles specifically referred to in the text are labelled A, B and C.

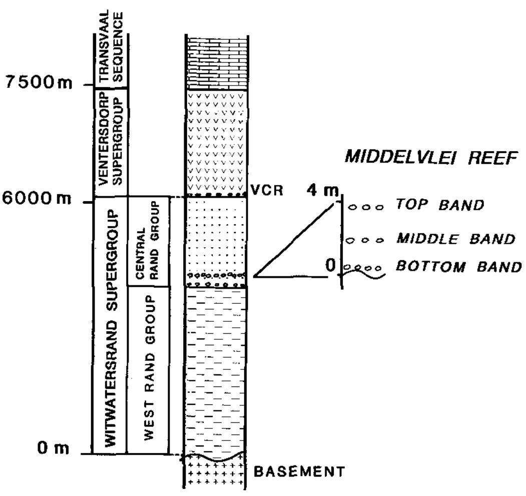


FIG. 3. Generalised Archaean stratigraphy in the Carletonville area illustrating the general position of the Middelvlei Reef in the Witwatersrand Supergroup. The subdivision of the Middelvlei Reef is indicated. The 'VCR' at the base of the Ventersdorp Supergroup is the Ventersdorp Contact Reef.

On West Driefontein the Middelvlei Reef package generally consists of three conglomerate bands with intercalated quartzite making up a package between 1 and 4 m thick (Fig. 3). The precise geometry of the three conglomerates can change as individual horizons pinch, swell and bifurcate but in general they can be correlated over the mine area.

The present distribution of the Middelvlei Reef is strongly affected by erosional elimination. To the east of the study area shown in Fig. 2, the Middelvlei reef suboutcrops beneath the VCR (see Fig. 3). The northern limit of the study area is defined by the suboutcrop of the Middelvlei Reef underneath the Transvaal Sequence (Fig. 3).

Sampling strategy. Because this study was specifically intended to evaluate the possible role of sulphidation in the Middelvlei Reef, great care has been taken to insure that no model-dependant bias was introduced in the sampling program. Our sampling program was based on the sedimentological study of Hesske (1989) in which he compiled reef assay values in conjunction with sedimentological profiles. Based on Hesske's grade distribution data, sample locations were selected by targeting areas of exceptionally low grade, normal grade and extremely high grade. Using Hesske's sedimentological data as a guide, vertical profiles through the Middelvlei Reef were sampled, with a sample taken from each lithological unit, including the footwall and hangingwall. Sample weights varied between 1.5 and 5 kg with a minimum of three kilograms for conglomerate horizons. In total over 90 samples were collected from seven profiles through the reef (Fig. 2). Detailed observations from three profiles are reported here.

Analytical techniques. Quantitative analyses of chlorite and chloritoid grains were conducted using an EDS system on a Jeol JXA-840A electron probe microanalyser at James Cook University. An accelerating voltage of 15 kV, and a beam current of 15 nA were applied. A standard counting time of 100 sec was used. ZAF corrections were carried out with the Tracor Northern MicroQ software. Calibration silicates were wollastonite (Si, Ca), titanite (Ti), corundum (Al), hematite (Fe), rhodonite (Mn), periclase (Mg), biotite (K), albite (Na) and chromite (Cr).

The general grain size heterogeneity of these rocks, particularly the presence of quartz pebbles, makes mineralogical volume estimates extremely difficult. In an effort to overcome this problem XRF, XRD and microprobe analyses have been integrated to calculate the mineral proportions (wt.%) in the samples (Fig. 4). The totals obtained using this technique appear to be quite adequate, ranging between 97 wt% and 104 wt.%.

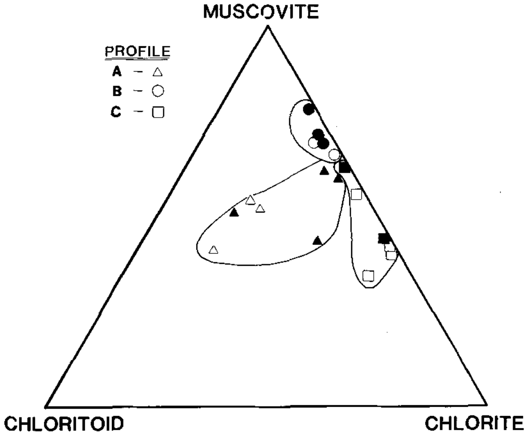


FIG. 4. Triangular diagram indicating the relative weight proportions of muscovite, chloritoid, and chlorite in profiles from the Middelvlei Reef. Open symbols represent sandstones, closed symbols represent conglomerates. This diagram illustrates how different the modal mineral assemblages are in each of the studied profiles. It is noteworthy that all the assemblages converge toward the muscovite rich assemblage characteristic of Profile B.

Mineralogy of the Middelvlei Reef

Silicate assemblage. All the samples from the Middelvlei Reef have the same basic silicate assemblage, comprising quartz, muscovite, chlorite and chloritoid. However, marked differences exist in the modal mineralogy of the sediment matrix, with three 'end member' assemblages recognised. In the northwestern profiles, such as profile A (Fig. 2), the predominant silicate mineral after quartz is generally chloritoid, with lesser muscovite and chlorite (Fig. 4). In contrast, profiles in the eastern section of the mine have a predominance of muscovite, with lesser chlorite and chloritoid. In the most extreme case, profile B, chloritoid is a minor constituent and chlorite is distinctly subordinant to muscovite. In profile C, dark coarse-grained chlorite, different from the fine-grained chlorite found elsewhere, is a major constituent in the phyllosilicate matrix of the sandstones and conglomerates. On the basis of their modal mineralogy, profiles A, B and C were selected for more detailed mineralogical and geochemical work. The mineralogical features of these profiles as observed in hand specimen are summarised in Table 1.

XRD data indicate that the white mica in these samples is a $2m_1$ muscovite. Microprobe analyses show that although the chlorite composition is uniform within a given sample, the composition varies considerably between samples (Table 2). In comparison, the chloritoid composition varies only slightly in response to shifts in the chlorite.

The atypical nature of the dark, coarse-grained chlorite in profile C is reflected not only in the high iron content of the chlorite but also the absence of chromium in comparison to the chlorite from the other profiles (Table 2).

Sulphide assemblage. The sulphide assemblage in every conglomerate and most sandstone samples comprises pyrite, minor pyrrhotite, and traces of chalcopyrite. At the handsample scale it is clear that pyrite is the dominant sulphide in all samples. Round pyrite grains on cross-bed surfaces in the quartzites, and in the matrix of the conglomerates (Fig. 5*e*) are the most abundant sulphide, followed by grains with euhedral morphologies (Table 1). However, anhedral matrix-replacive pyrite is present in many samples. Matrix-replacive pyrrhotite and chalcopyrite are rare in hand specimen (Table 1) but can be seen microscopically in most of the conglomerate samples.

Table 1: Mineralogy of selected Middelvlei Reef profiles as observed in hand samples. The sandstones and conglomerates have been separated to emphasise the differences in the sulphide mineralogy between these lithologies. "n" indicates the number of samples with round, euhedral, and matrix-replacive anhedral pyrite. Po, Cpy and Au represent the number of samples with visible pyrrhotite, chalcopyrite or gold.

Profile	n=	Py1	Py2	Py3	Po	Cpy	Au
A cong	4	4	4	3	1	0	1
sand	4	0	1	1	0	0	0
B cong	3	3	3	2	1	0	3
sand	2	1	1	0	0	0	0
C cong	3	3	3	1	1	1	0
sand	7	1	2	1	3	0	0
Total	23	12	14	8	6	1	4

Textural evidence for sulphidation

In terms of this investigation the word 'sulphidation' is used to describe the replacement of iron-bearing rock and mineral grains or phyllosilicate-rich sediment matrix by pyrite or pyrrhotite. The process specifically demonstrates that sulphur has been added to the rock or mineral grain. The sulphidation process may or may not be related to the development of euhedral pyrite grains and euhedral grain overgrowths since these textures could reflect the mobility of either iron or sulphur or both. In the following section textural evidence for the partial replacement of rock and mineral grains, matrix replacement by pyrite and pyrrhotite, and euhedral pyrite grain development will be presented.

Selective grain replacement. By far the most striking examples of sulphidation were observed in the top conglomerate band in profile B, where large clasts of chert and shale have been partially and totally replaced by pyrite (Fig. 5*a, b*, and *c*). In this particular sample the phyllosilicate portion of the conglomerate matrix is almost exclusively muscovite, with subsidiary chlorite. However, chloritoid is present inside the sulphidised clasts, and in at least two instances, the matrix around the sulphidised clasts has been replaced, by an intergrowth of anhedral pyrite and chloritoid (Fig. 5*c, d*). In contrast to intensely sulphidised examples above, shale clasts in the top conglomerate band of profile A, the chloritoid rich profile, show little macroscopic evidence of sulphidation (Fig. 5*e*). However, in thin section both pyrite and chloritoid can be seen (Fig. 5*f*).

Microscopically many examples of the partial replacement of silicate grains can be found (Fig. 6*a, b* and *c*). These are generally sand sized grains, made up of phyllosilicates, which probably represent rock fragments. In many cases pyrite replacement has very selectively highlighted the detailed internal structure of these grains (Fig. 6*b* and *c*).

No examples of partially replaced iron oxide grains were found in the Middelvlei Reef. However, in at least one example (Fig. 6*d*), the intimate intergrowth of pyrite and rutile reflects

Table 2: Microprobe analyses of chloritoid and chlorite from the Middelvlei Reef illustrating the compositional uniformity of minerals within profiles and the compositional differences between profiles. Sample numbers consist of the profile name and the position in the profile. "n" shows the number of mineral grains analysed in each sample.

CHLORITOID

SAMPLE	A-8	A-7	A-6	A-2	B-6	B-4	C-9
ROCK TYPE	CONG	SAND	CONG	CONG	CONG	CONG	SAND
n=	6	7	13	3	3	4	3
SiO2	23.9	23.5	23.6	24.1	24.2	24.3	24.6
TiO2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al2O3	41.4	41.4	41.3	40.4	40.5	40.6	41.1
Cr2O3	0.2	0.1	0.1	0.3	0.3	0.2	0.1
FeO	**23.6**	**23.9**	**23.6**	**24.2**	**24.3**	**24.5**	**25.3**
MnO	0.5	0.7	0.5	0.5	0.4	0.4	0.3
MgO	**2.0**	**1.6**	**1.9**	**1.8**	**1.8**	**1.9**	**1.3**
CaO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Na2O	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K2O	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	**91.5**	**91.2**	**91.1**	**91.4**	**91.5**	**91.9**	**92.8**
Si	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Al	4.1	4.1	4.1	4.0	4.0	4.0	4.0
Fe	1.6	1.7	1.7	1.7	1.7	1.7	1.8
Mg	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Total	7.9	7.9	7.9	7.9	7.9	7.9	7.9

CHLORITE

SAMPLE	A-8	A-7	A-6	A-2	B-6	B-4	C-9
n=	5	5	10	4	6	6	5
SiO2	23.4	23.4	22.9	23.6	23.2	23.4	23.3
TiO2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Al2O3	25.9	26.2	26.4	26.4	25.5	25.5	25.3
Cr2O3	0.2	0.2	0.2	0.3	0.3	0.3	0.0
FeO	**23.7**	**23.0**	**23.6**	**24.2**	**27.5**	**27.2**	**30.7**
MnO	0.0	0.1	0.1	0.1	0.1	0.1	0.1
MgO	**12.5**	**12.9**	**12.5**	**12.7**	**10.6**	**10.9**	**9.1**
CaO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Na2O	0.1	0.1	0.1	0.0	0.0	0.0	0.1
K2O	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Total	**85.8**	**86.0**	**85.9**	**87.3**	**87.3**	**87.3**	88.6
Si	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Al	3.3	3.3	3.3	3.3	3.2	3.2	3.2
AlIV	1.5	1.5	1.5	1.5	1.5	1.5	1.5
AlVI	1.8	1.8	1.8	1.8	1.7	1.7	1.7
Fe	2.1	2.1	2.1	2.1	2.5	2.4	2.7
Mg	2.0	2.0	2.0	2.0	1.7	1.7	1.5
Total	9.9	9.9	9.9	9.9	9.9	9.9	9.9

the sulphidation of hematite exsolution lamelle in an ilmenite grain as described by Dimanche and Bartholome (1976). It must be stated, however, that such intergrowths are rare and normally rutile and pyrite occur as discrete phases or with pyrite overgrowing rutile (Fig. 6*e*).

Matrix replacement. Some examples of matrix replacement by sulphides, such as the pyrite halo around sulphidised shale clasts, have already been discussed (Fig. 5*d*). In other cases, the matrix-replacive domains may be isolated (Fig. 6*f*) or associated with other sulphide grains (Fig. 6g). Because the replacement process begins in the sediment matrix, the matrix-replacive grains often enclose detrital quartz grains (Fig. 6*f*). However, the size of the matrix replacive domains are anomalously large when compared to the texture of the host sediment suggesting that quartz may be removed as the alteration proceeds. The recognition of this replacement process raises, but does not resolve, questions about the origin of many 'rounded' poikilitic pyrite grains (Fig. 6*h*).

Pyrrhotite occurs exclusively as a matrix-replacive mineral, and seems in general to coexist with pyrite (Fig. 6*f* and *g*).

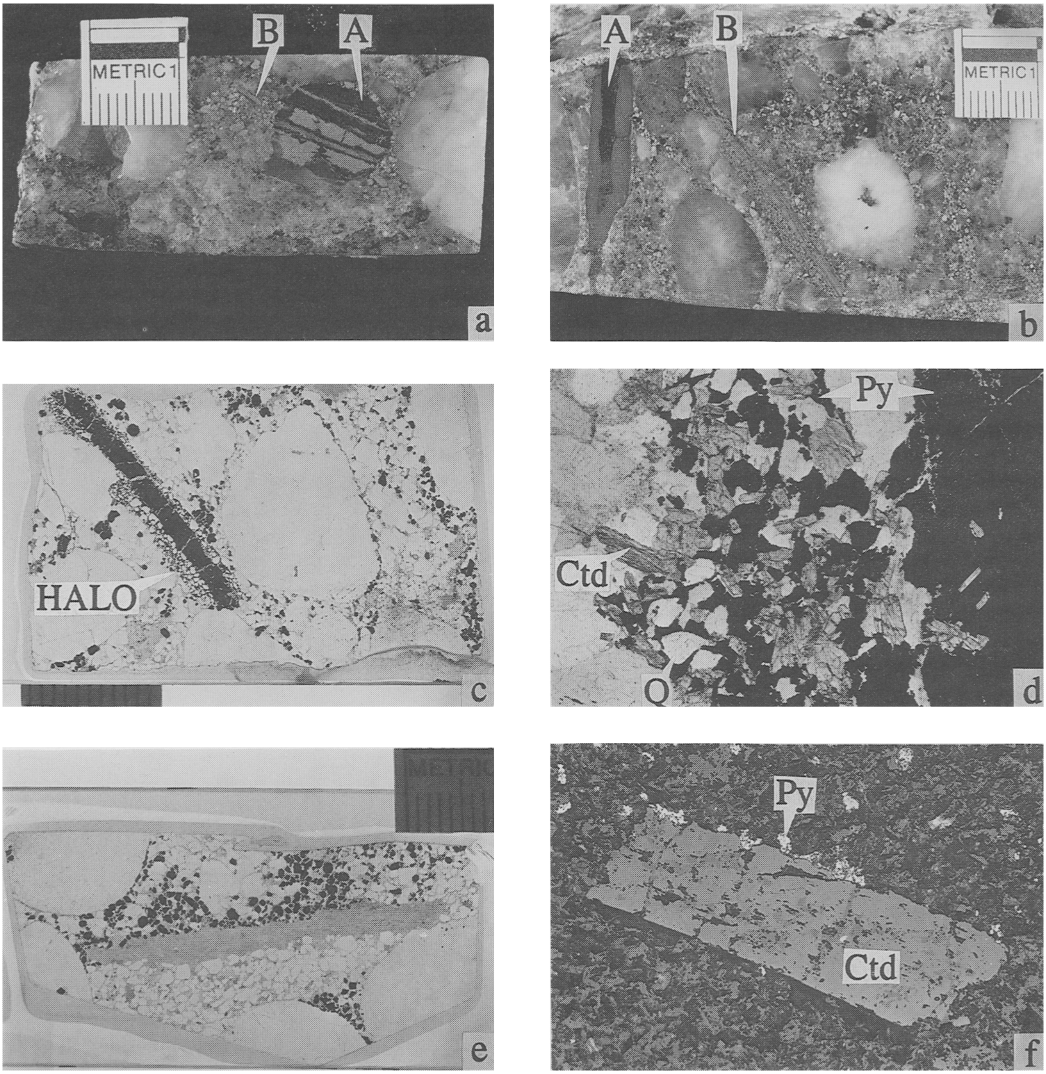


FIG. 5. Photographs illustrating sulphidation textures in the Middelvlei Reef. (*a*) Pebbles of banded chert partially replaced by pyrite. Clast A shows well defined banding and selective sulphidation. Clast B is also sulphidized banded chert, and illustrates the problem of recognition as the pebbles break down to smaller pieces. Top band conglomerate, profile B, sample 10-50-U08. (*b*) Two tabular shale clasts from the top band of profile B. Clast A has a core of chloritic shale with a concentric rim of fine grained pyrite. Clast B has been almost entirely replaced by pyrite. Clast A is 35 mm long. Sample 10-50-U08. (*c*) Pyritised shale clast from 5*b*, illustrating the halo of sulphidised matrix surrounding the clast. The clear, lath shaped, patches in the clasts (not the cracks) are chloritoid porphyroblasts. Width of section = 25 mm. (*d*) Detail of sulphidised halo from 5*c* showing the intergrowth of anhedral pyrite and chloritoid which surrounds the sulphidised shale clast shown in 5*c*. Transmitted light, plane polarized. Field of view = 2.1 mm. (*e*) Unsulphidised shale clast from the top band conglomerate of Profile A. The triangular concentration of opaque grains (pyrite) between quartz pebbles in the lower half of this section illustrates the process of heavy mineral entrainment on a 'rough' bed. The concentration of heavy minerals on the upper side of the shale clast shows that the shale clast acted as a barrier preventing the downward infiltration of heavy mineral grains. These features show clearly that there were original detrital concentrations of heavy minerals in this specimen. Width of section = 25 mm. Thin section 6-43-U08Y. (*f*) Detail from shale clast in Fig. 6*e* illustrating the presence of chloritoid and pyrite in a matrix of chlorite and muscovite. Field of view = 0.67 mm. Mixed transmitted and reflected light. Polars crossed on transmitted light.

Euhedral pyrite growth. Euhedral pyrite grains and overgrowths are relatively common in the Middelvlei Reef (Fig. 6*a*, *e*, and *g*) but at present there does not appear to be either a macroscopic or microscopic pattern to their development. In the Middelvlei Reef the crystal forms are more often pyritohedrons than cubes. Where euhedral pyrite is common in the conglomerate matrix, veinlets of euhedral pyrite have been observed in the quartz pebbles.

Discussion

The following questions arise from the observations described above. What is the extent of sulphidation? What are the relationships between sulphidation and the silicate mineralogy of the reef? When did the sulphidation occur? What are the implications of the observed mineral assemblages for the conditions under which sulphidation occurred? Finally, how do our observations compare with those of other workers?

Extent of sulphidation. We have found an example of either grain-selective replacement or matrix replacement in virtually every thin section with sulphides. In most conglomerates there are several examples of both grain-selective replacement and matrix replacement in a single thin section. However, even though sulphidation was observed in a large number of grains it is important to emphasise that the majority of the grains show no textural features which can be used as evidence for or against sulphidation.

The problem of determining the extent of sulphidation is well illustrated by the large sulphidised chert clasts (Fig. 5*a*). As long as a banded chert pebble is identifiable (Fig. 5*a*, clast A), the selective sulphidation of certain layers is easy to recognise. However, it would be virtually impossible to recognise a sand-sized fragment of one of the sulphidised bands because it would consist entirely of pyrite.

The same problem arises for sand-size fragments of iron-rich shale or grains of magnetite or hematite. The fact that the sulphidation can pick out very fine details of the internal structure of grains (Fig. 6*b*, *c*) means that near perfect pseudomorphism of grains must be considered as a real possibility.

From these observations we conclude that sulphidation has affected a large number of grains in the Middelvlei Reef and that what we observe represents a minimum estimate of the extent of sulphidation.

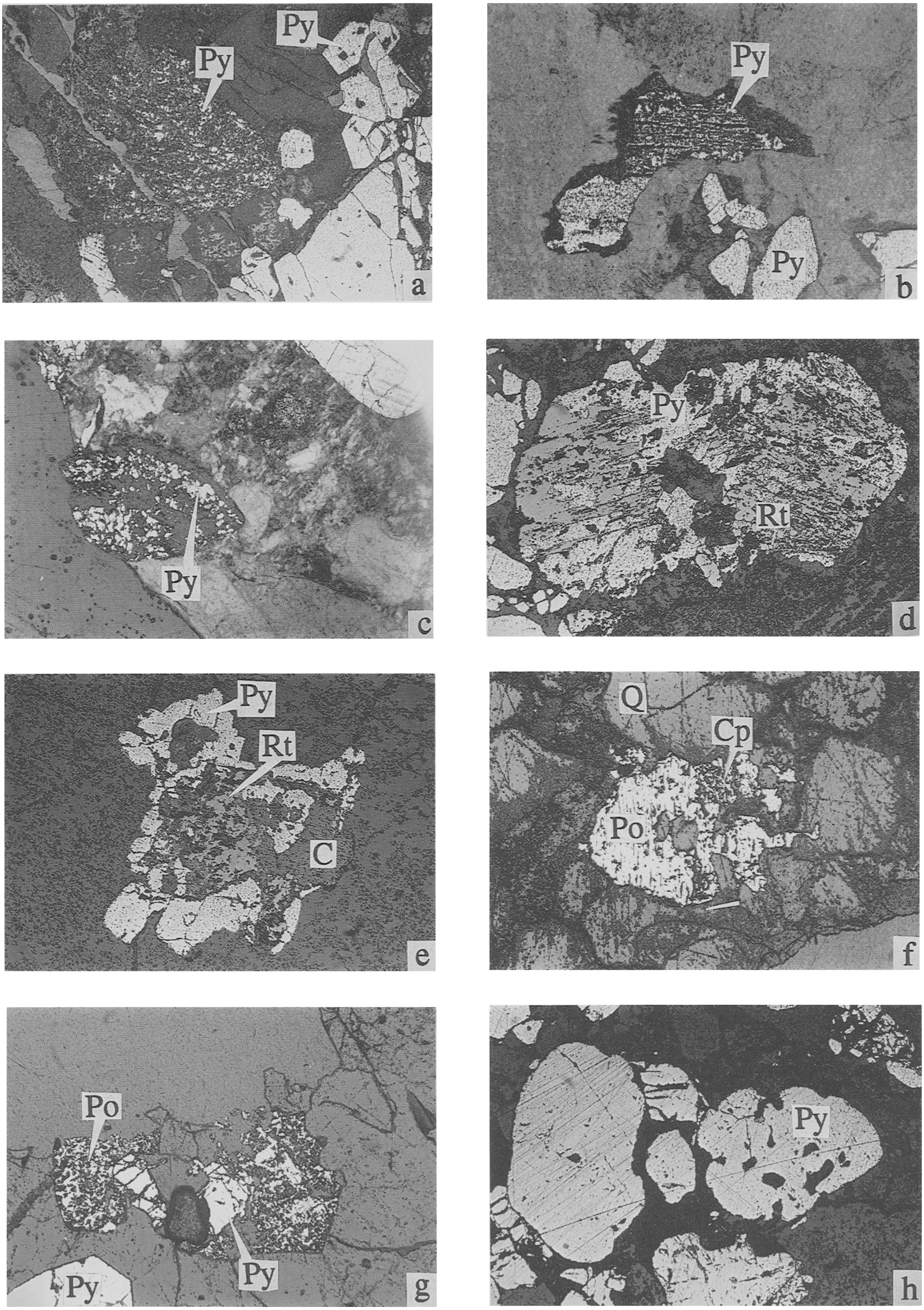
Sulphidation and the silicate assemblage. A few empirical observations can be made regarding the relationship between the intensity of sulphidation and the silicate mineralogy. First, it appears that the most intense sulphidation has occurred in profile B, which is muscovite rich (Fig. 4). This is evidenced by the wholesale replacement of chert and shale clasts as well as an abundance of matrix replacive pyrite. By comparison, profile A, which is rich in chloritoid, shows less intense sulphidation with little matrix replacive sulphide and no sulphidised shale clasts. Given that both grain and matrix replacement textures are common in the chlorite-rich profile C, it must be strongly sulphidised. However, nowhere has the wholesale replacement of clasts been observed in this profile. It is also interesting to note that pyrrhotite is visible at hand sample scale in 4 of the 10 samples collected from profile C.

These observations suggest that there may be a relationship between the phyllosilicate assemblage and the style of sulphidation. Unfortunately, using textures alone, the process(es) which control these relationships are poorly constrained at present. However, given the fact that five individual units within the Middelvlei Reef can be correlated over the entire study area it seems improbable that the variations in the phyllosilicate assemblage (Fig. 4) reflect primary depositional circumstances. This leads to the almost inevitable conclusion that the Middelvlei Reef has experienced relatively intense alteration of the silicate assemblage at some point in its history; an alteration which either directly or indirectly controls the style of sulphidation.

Timing of the sulphidation event. The history of the Middelvlei Reef can be subdivided into four periods during which grain-selective sulphidation could have occurred. These are prior to burial, during diagenesis, during regional metamorphism, or after regional metamorphism. Because there is no evidence for retrogression in either the microscopic textures or the phyllosilicate assemblage the last option can be eliminated immediately, leaving three serious alternatives. It is important to point out that these alternatives are in no way mutually exclusive. It is conceivable that sulphidation occurred during all three stages.

The widespread development of matrix replacive pyrite and pyrrhotite clearly indicates there has been some post-burial sulphidation but cannot be used to further constrain the timing.

Unfortunately, because of the very selective nature of the grain replacive sulphidation it is virtually impossible to prove that any individual grain was not sulphidised prior to its deposition. From all the examples of partially replaced grains, only the shale clasts in Fig. 5*b* and *c* can be used to argue confidently that they were replaced after burial. In the case of the partially replaced


Py
Py
a
Py
Py
b
Py
Py
c
Py
Rt
d
Py
Rt
C
e
Q
Cp
Po
f
Po
Py
Py
g
Py
h

clast (clast A in Fig. 5*b*) the alteration rim follows the present shape of the clast and has a virtually constant thickness suggesting that the sulphidation occurred after the clast obtained its current shape. In the case of the totally replaced grain (Fig. 5*c*) the alteration 'halo' in the sandy matrix around the clast clearly indicates that the sulphidation occurred after the deposition of the shale clast.

On the basis of these arguments it can be concluded that post-burial grain-selective replacement has occurred, and although additional pre-burial sulphidation cannot be ruled out, there is no unambiguous evidence for it.

There is no real criterion which could be used to distinguish between sulphidation textures developed during diagenesis and those developed during the low-grade metamorphism which has affected the Middelvlei Reef. Therefore, other lines of argument, possibly chemical criteria, will have to be used to distinguish between these two options.

It is possible to argue that the pyrrhotite formed during the metamorphic event because pyrrhotite is a relatively rare diagenetic mineral but is common in low-grade metamorphic terranes. Unfortunately, even if it is correct, this line of reasoning does not solve many problems. The coexistence of pyrite and pyrrhotite means that it is not possible to demonstrate that pyrrhotite formed by desulphidation as a consequence of metamorphism, or that the pyrite was present prior to the onset of metamorphism.

In summary, there is very good textural evidence to suggest that post-burial sulphidation has played an important role in the history of the Middelvlei Reef and that sulphidation occurred prior to or during regional metamorphism. It is not possible to distinguish between sulphidation during diagenesis and sulphidation during regional metamorphism, although the presence of pyrrhotite could suggest sulphur mobility during metamorphism.

Fluid conditions during regional metamorphism. Because the precise timing of sulphidation in the Middelvlei Reef cannot be constrained it is not possible to characterise the fluid(s) responsible. It is possible, however, to place certain constraints on the composition of the fluid present during metamorphism.

The silicate textures and the compositional uniformity of coexisting minerals in the Middelvlei Reef (Table 2) indicate that equilibrium or near equilibrium was established under regional metamorphic conditions of around 350 °C and 2 Kb (Phillips, 1987).

The coexistence of chlorite, chloritoid and muscovite and the absence of pyrophyllite and K-feldspar is consistent with the assemblage predicted in the system Fe–K–Si–Al–H_2O (Fig. 7*a*). Phase relations in this system indicate that the K^+/H^+ ratio of a fluid in equilibrium with the observed assemblage will be relatively high, approaching that required to stabilize K-feldspar.

The coexistence of four iron phases, chlorite, chloritoid, pyrite, and pyrrhotite fixes the activity of oxygen and sulphur in the fluid during peak metamorphism (Fig. 7*b*), indicating a relatively low oxygen activity and high sulphur activity. The presence of iron-rich chlorite precludes the coexistence of magnetite, pyrite and pyrrhotite in the Middelvlei Reef under peak metamorphic conditions.

It is only possible to speculate on the original proportion of magnetite in the detrital heavy mineral assemblage, and whether the absence of

FIG. 6. Microscopic examples of sulphidation. (*a*) Partial replacement of chloritic grain by pyrite. Note the presence of euhedral, poikilitic pyrite grains in the section. Reflected light. Field of view = 2.65 mm. Top Band profile C, thin section 12-32A-U08. (*b*) Fragment of chloritic grain now partially replaced by pyrite. Note detailed internal structure defined by pyrite. Reflected light. Field of view = 2.65 mm. Top band profile C, thin section 12-32A-U08. (*c*) Fragment of chloritic grain now partially replaced by pyrite. Note detailed internal structure highlighted by pyrite. Reflected and transmitted light. Field of view = 2.65 mm. Top band profile A, thin section 6-43-U08X. (*d*) Intergrowth of rutile and pyrite. This texture suggests that the grain may originally have been ilmenite with exsolution lamelle of hematite. Reflected light. Field of view = 1.32 mm. Top band profile C, thin section 12-32-U08. (*e*) Halo of pyrite surrounding intergrowth of rutile and carbon. Reflected light only. Field of view = 0.67 mm. Middle band profile A, thin section 6-43-UO4Y. (*f*) Matrix replacive growth of pyrrhotite and chalcopyrite. Note poikilitic enclosure of quartz grains. Reflected light. Field of view = 2.65 mm. Bottom band profile C, thin section 12-32A-U04X. (*g*) Matrix replacive growth of pyrrhotite and chalcopyrite. Note sharp contact between solid pyrite and porous pyrrhotite. Also note euhedral pyrite grain in lower left corner. Reflected light. Field of view = 1.32 mm. Bottom band profile B, thin section 10-50-U04Z. (*h*) Round poikilitic pyrite grain enclosing quartz grains. Large ovoid grain to the left has small quartz grain at its centre. Reflected light. Field of view = 2.65 mm. Bottom band profile B, thin section 10-50-U04Z.

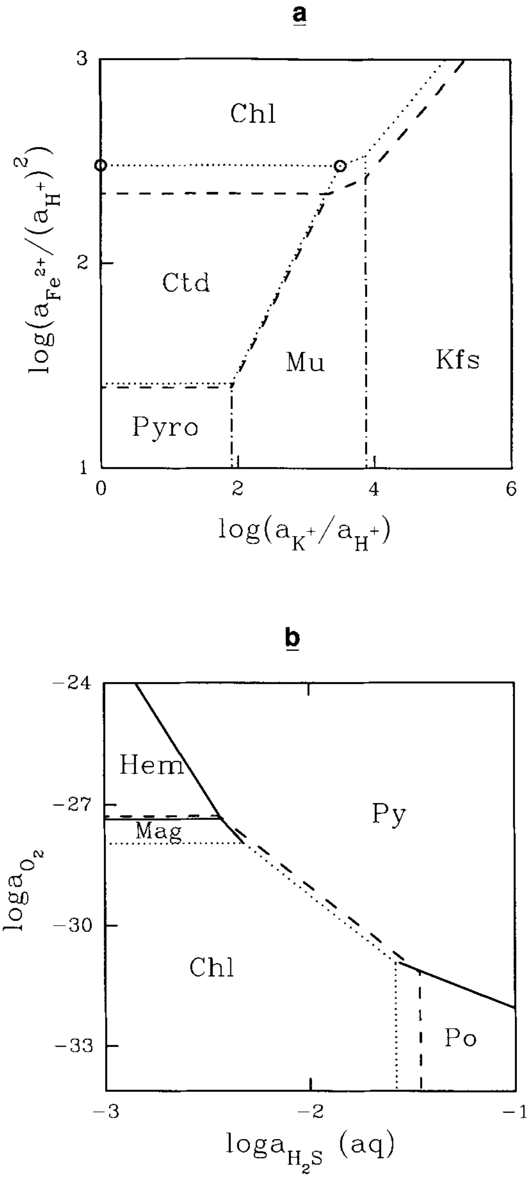


FIG. 7. Activity diagrams relevant to the Middelvlei Reef assemblages under peak metamorphic conditions of 350 °C, 2 kbars pressure and quartz in excess. Field boundaries have been calculated to represent the range of mineral compositions observed in the Middelvlei Reef. Most iron-rich chlorite/chloritoid compositions = dotted line. Least iron-rich = dashed line. The thermodynamic data of Holland and Powell (1990), Johnson *et al.* (1992), and Walshe (1986) were used in the calculations for these diagrams. (*a*) Log [Fe^{++}]/[H$^+$]^2 versus Log [K$^+$]/[H$^+$] for system $FeO–K_2O–Al_2O_3–SiO_2–H_2O$. (*b*) Log f_{O_2} versus Log a_{H_2S} for the system $FeO–MgO–Al_2O_3–SiO_2–H_2S–H_2O$.

magnetite from the present assemblage reflects destruction of the magnetite during diagenesis, or magnetite destruction during metamorphism.

Comparison with earlier workers. The features we have observed are in no way incompatible with those documented by earlier workers such as Ramdohr (1958) and Saager (1970). Our data merely serve to emphasise the abundance and distribution of sulphidation effects. On the basis of our observations it seems premature to relegate sulphidation of Witwatersrand black sands to the realms of mythology as Reimer and Mossman (1990*a*) would like to do. Interestingly, our results do not contradict the conclusion of Reimer and Mossman (1990*a*) that the majority of detrital iron–titanium oxide minerals were destroyed during diagenesis and/or metamorphism and that a substantial proportion of the iron released formed authigenic pyrite.

It appears then that the disagreement is not really about the observations, it is based on the significance of the observations. The primary difference of opinion centres on the origin of the round ‘allogenic’ pyrite grains. Workers such as Reimer and Mossman (1990*a*, b) and Robb and Meyer (1990) remain confident that the vast majority of these grains represent original detrital pyrite grains. In contrast, we feel that the grain-selective sulphidation we have observed demonstrates that pseudomorphism can occur. Thus, while we would not argue that there is no detrital pyrite, it seems that grain morphology is not a sufficient criterion to identify truly detrital pyrite. Unfortunately, we must conclude that this difference of opinion cannot be resolved microscopically.

The lateral variations in the bulk mineralogy of the Middelvlei Reef appear to reflect some post-depositional alteration either directly or indirectly related to sulphidation. This type of alteration would not have been detected by studies such as those of Sutton *et al.* (1990) which concentrate on chemical differences between stratigraphic units rather than within a single unit. Thus, a difference in methodology may account for the differences in our conclusions. Nevertheless, it is the recognition of the silicate alteration and its relationship to the sulphidation which may provide the critical information required to understand the wider significance of the observed sulphidation.

Conclusions

Textural evidence from the Middelvlei Reef demonstrates sulphidation involving both the replacement of clasts and matrix material in the conglomerates and quartzites. This is consistent with early petrographic studies of the Witwatersrand conglomerates but our study suggests that sulphidation may be more common and intense than has generally been thought.

The timing of the sulphidation to form pyrite can be broadly constrained as being post-burial and no later than the peak of metamorphism. The formation of pyrrhotite may coincide with the metamorphic event.

Coincident variations in the bulk silicate mineralogy of the Middelvlei Reef and the intensity of sulphidation suggest that the silicates also reflect post-depositional diagenetic or metamorphic alteration processes. We believe that the observations presented here should be incorporated into future discussions of alteration or mineralisation in the Witwatersrand.

Acknowledgements

This work has been made possible through the logistical support of Gold Fields of South Africa especially Mr. Chris Murray and Mr. Bill Kellwaway of West Driefontein Gold Mine. Additional support was provided by the Australian Research Council and the Key Centre in Economic Geology. Discussions with Mr. Eugene Siepker and Mr. Jean Body of the Gold Fields Sedimentology Unit were invaluable in the formulation of this project. The comments of two anonymous referees were greatly appreciated.

References

Dimanche, F. and Bartholome, P. (1976) The alteration of ilmenite in sediments. *Mineral Sci. Engineering*, **8**, 187–201.

Els, B. G. (1987) *The auriferous Middelvlei Reef depositional system, West Wits Line, Witwatersrand Supergroup*. PhD Thesis, Rand Afrikaans University, Johannesburg.

—— (1991) Placer formation during progradational fluvial degradation: the late Archean Middelvlei gold placer, Witwatersrand South Africa. *Econ. Geol.*, **86**, 261–77.

Englebrecht, C. J., Baumbach, G. W. S., Matthysen, J. L., and Fletcher, P. (1986) The West Wits Line. In *Mineral Deposits of Southern Africa, Volume II* (C. R. Anhaeusser and S. Maske, eds.), Geol. Soc. S. Afr., 599–648.

Hesske, S. (1989) *The sedimentology of the auriferous Middelvlei Reef in the 4 Shaft area of West Driefontein Gold Mine*. Gold Fields of South Africa, internal report, 37 pp.

Hirdes, W. and Saager, R. (1983) The Proterozoic Kimberley Reef Placer in the Evander Goldfield, Witwatersrand, South Africa., *Monograph Series on Mineral Deposits*, GeBruder Borntraeger, Berlin, **20**, 100 pp.

Holland, T. J. B. and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: the system K_2O–Na_2O–CaO–MgO–MnO–FeO–Fe_2O_3–Al_2O_3–TiO_2–SiO_2–C–H_2–O_2. *J. Metamorphic Geol.*, **8**, 89–124.

Johnson, J. W., Oelkers, E. H., and Helgeson, H. L. (1992) A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0° to 1000 °C. *Computers Geosci.*, **18**, 899–914.

Jolly, M. K. (1984) *The sedimentology and economic potential of the auriferous Middelvlei Reef on West Driefontein Consolidated Limited.* MSc Thesis, Rand Afrikaans University, Johannesburg.

Phillips, G. N. (1987) Metamorphism of the Witwatersrand goldfields: conditions during peak metamorphism. *J. Metamorphic Geol.*, **5**, 307–22.

—— and Myers, R. E. (1989) The Witwatersrand Gold Fields Part II: An origin for Witwatersrand gold during metamorphism and associated alteration. *Econ. Geol. Monograph*, **6**, 598–608.

Ramdohr, P. (1958) New Observations on the Ores of the Witwatersrand in South Africa and their Genetic Significance. *Trans. Geol. Soc. S. Afr.*, **Annex. to vol. 61**, 111 pp.

Reimer, T. O. and Mossman, D. J. (1990*a*) Sulphidization of Witwatersrand black sands: from enigma to myth. *Geology*, **18**, 426–9.

—— —— (1990*b*) The Witwatersrand controversy revisited. *Econ. Geol.*, **85**, 337–43.

Robb, L. J. and Meyer, F. M. (1991) A contribution to recent debate concerning epigenetic versus syngenetic mineralization processes in the Witwatersrand Basin. *Econ. Geol.*, **86**, 396–401.

Robert, F., Phillips, G. N., and Kesler, S. E. (1991) Greenstone gold and crustal evolution: scope and results of the conference. In *Greenstone Gold and Crutal Evolution*, Geol. Soc. Can., 2–7.

Saager, R. (1970) Structures in Pyrite from the Basal Reef in the Orange Free State. *Trans. Geol. Soc. S. Afr.*, **73**, 29–48.

Sutton, S. J., Ritger, S. D., and Maynard, J. B. (1990) Stratigraphic control of chemistry and mineralization in metamorphosed Witwatersrand quartzites. *J. Geol.*, **98**, 329–41.

Wallmach, T. and Meyer, F. M. (1990) A petrogenetic grid for metamorphosed aluminous Witwatersrand shales. *S. Afr. J. Geol.*, **93**, 93–102.

Walshe, J. L. (1986) A six component chlorite solid solution model and the conditions of chlorite formation in hydrothermal and geothermal systems. *Econ Geol.*, **81**, 681–703.

[*Manuscript received 20 September 1992: revised 5 February 1993*]