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Ni, Co AND Au CONTENTS OF PYRITES FROM  
ARCHAEAN GRANITE-GREENSTONE TERRANES AND  
EARLY PROTEROZOIC SEDIMENTARY DEPOSITS  
IN SOUTHERN AFRICA

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by

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ABSTRACT

A suite of hypogene pyrites from a variety of Archaeozoan granitoids, greenstones and gold deposits as well as allogenetic pyrites from various auriferous sedimentary deposits in the Kaapvaal and Rhodesia Cratons were analyzed for their Ni, Co, and Au contents.

The allogenetic pyrites are characterized by mean Co/Ni ratios of approximately one and exhibit a range in Au contents of 0,01 to 309 ppm. Similar Co/Ni ratios were found in hypogene pyrites from epigenetic gold deposits in the Murchison and Pietersburg greenstone belts and from a variety of country rocks including granitoids from the Archaeozoan basement adjacent to the Witwatersrand basin, and from the volcano-sedimentary greenstone succession of the Barberton Mountain Land. The hypogene pyrites exhibit a range in Au contents between 0,01 and 96,2 ppm.

Hypogene pyrites collected from epigenetic gold deposits in the Barberton greenstone belt, and from the Klipwal gold mine, possess mean Co/Ni ratios of 0,08 and 0,09, respectively. This contrasts markedly with the mean Co/Ni ratios determined for detrital pyrites in the Witwatersrand placer deposits and helps to preclude derivation of this material from a Barberton-type source area. The Witwatersrand pyrites, could, however, have originated in younger Murchison-Pietersburg type mineralizations, and from a granitoid basement.

A positive correlation is observed between the gold contents of allogenetic pyrites and the bulk gold contents of the conglomerate samples from which the pyrites were separated. This is explained by contamination of these pyrites due to the remobilization of gold during metamorphism/diagenesis.

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1. INTRODUCTION

The geochemistry of pyrites has been studied by many workers mainly in attempts to elucidate the genesis of pyritic ores (Loftus-Hills and Solomon, 1967; Mitchel, 1968; Bralia *et al.*, 1979; Roberts, 1982 and others) or to trace back the origin of allogenic pyrites in sedimentary successions (Saager, 1976, 1981; Utter, 1978; Hirdes, 1979; Hallbauer, 1981; Hallbauer and Kable, 1982). In particular, Co and Ni contents and Co/Ni ratios in pyrites have proved to be reliable indicators for fingerprinting pyrites, as well as for making statements regarding their genesis (Bralia *et al.*, 1979). The Co and Ni disulphides, cattierite and vaesite respectively, form solid solutions with pyrite and Co and Ni occur as isomorphous substitutions for Fe in the pyrite lattice. Thus, the distribution of Co and Ni in pyrite is governed by physiochemical conditions (Kullerud, 1964) as well as by the availability of these metals during pyrite formation (Loftus-Hills and Salomon, 1967).

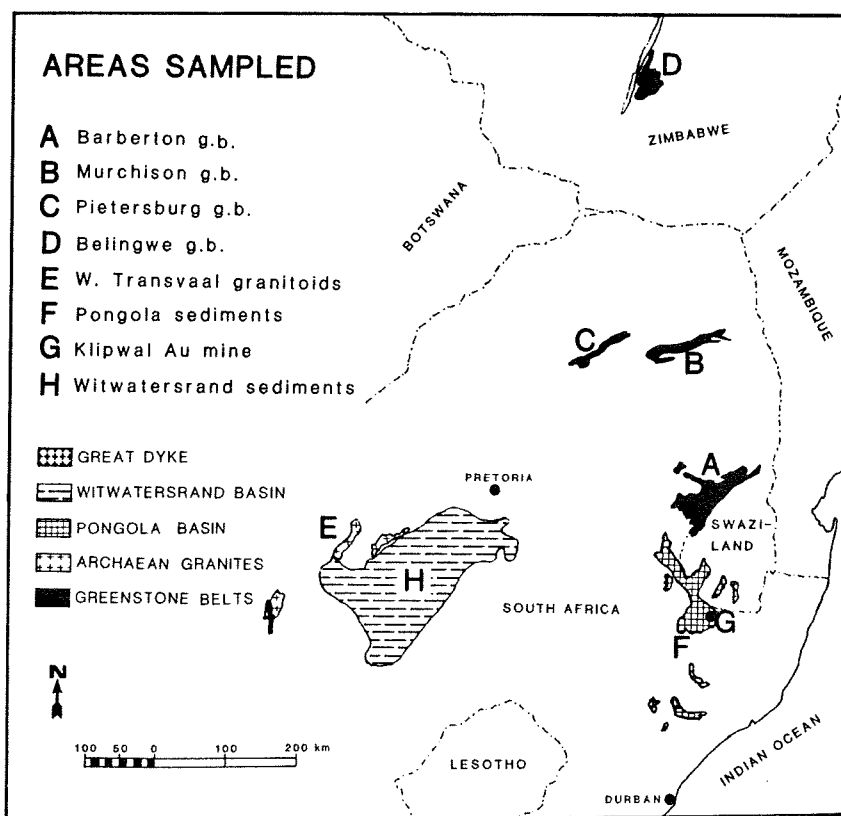
The siting of Au in pyrite is less well understood and still disputed. Kurauti (1941) investigated the nature of Au in pyrite and reported a Au-solubility of up to 2 000 ppm. On the other hand, McPheat *et al.* (1969) concluded that gold in auriferous pyrite exists in solid solution up to a concentration of 1 ppm, and that the balance of the metal occurs as finely dispersed grains throughout the mineral. Iwanoff (1951) studied the distribution of gold in pyrites containing up to 1 000 ppm Au and was able to demonstrate that the Au formed sub-microscopic inclusions with diameters of up to 0,01 microns.

The present study was undertaken firstly, to gather data on the geochemistry of allogenic pyrites in quartz-pebble conglomerates from various early Proterozoic sedimentary basins in southern Africa and, secondly, to compare this data with the geochemical characteristics of hypogene pyrites sampled from primary gold deposits in Archaean greenstone belts, and also from the granite-greenstone country rocks. From this comparison it was hoped to shed some light on the nature of the source rocks from which the detrital pyrites have been derived.

II. SAMPLE LOCALITIES

Samples containing hypogene pyrite were collected from numerous auriferous massive sulphide and lode deposits and prospects in the Barberton, Murchison, Pietersburg, and Belingwe (Mberengwa) greenstone belts of the Kaapvaal and Rhodesian cratons. Pyrites were also collected from the Klipwal mine located in northern Zululand (Figure 1).

Additionally, pyrite bearing samples were drawn from mafic and ultramafic rocks of the Swaziland Supergroup in the Barberton greenstone belt and from borehole intersections of the Archaean granitic basement adjacent to the Witwatersrand basin (Figure 1).



*Figure 1 : Sketch map of southern Africa showing sample areas.*

## A. Hypogene Pyrites

### (i) Komatiite-Related Gold Deposits

Detailed mineralogical and geochemical descriptions of pyrite from gold mines in the Barberton, Murchison, and Pietersburg greenstone belts are given in Saager and Koeppel (1976), Saager (1981), and Saager and Muff (in press). Genetic models on the formation of komatiite-related gold lode deposits rely mainly on the source bed theory, a model introduced by Boyle (1961) to explain the genesis of Precambrian epigenetic gold occurrences. The model assumes that gold, silver, and gangue elements, initially present in the country rocks, were mobilized and subsequently concentrated in suitable tectonic structures and chemical traps during metamorphism. The process of metamorphic secretion has been used in South Africa to explain many of the occurrences of Archaean gold deposits (Viljoen *et al.*, 1969; Saager, 1970; Anhaeusser, 1976). More recent investigations undertaken by Saager *et al.* (1982), Saager and Meyer (1984), Viljoen (1984), and Meyer and Saager (1985) have confirmed the validity of this theory, namely, that the ultimate source of the gold and accompanying elements in greenstone-related lode deposits is the adjacent greenstone volcanic assemblage.

The Belvedere mine is situated in the Lower Greenstones of the Belingwe belt. The ore is stratabound, the immediate host rocks comprising banded jaspilite as well as ultramafic and mafic volcanoclastics (Foster, 1980b). Foster *et al.* (in preparation) assume that basaltic pillow lavas provided the metals found in this deposit, the gold and other elements were leached from inter-pillow areas and fractures within the volcanic pile.

### (ii) Klipwal Gold Mine

The host rocks of the Klipwal gold mine are mainly made up of dark phyllites belonging to the upper succession of the Mozaan Group (Pongola Supergroup). The mineralogy and geochemistry of the ore was studied by Stupp (1984). According to this author the gold and sulphide mineralization is of epigenetic-hydrothermal origin. The ore bearing solution is considered to be derived from underlying volcanics of the Pongola Supergroup. Stupp (1984) further points out that, on mineralogical and geochemical grounds, considerable similarity exists between the Klipwal ore and those of the Barberton gold mines.

### (iii) Granite-Greenstone Country Rocks

The pyrites from rocks of the Barberton greenstone belt were obtained from a basaltic komatiite from the type locality of the Komati Formation, from a serpentinite at the Msauli asbestos mine, and from the Middle Marker along the Steynsdorp anticline. The granitoids from which pyrite separates were collected stem from borehole intersections of the sub-surface granite basement in the western Transvaal. The samples were obtained from the vicinities of the Hartbeestfontein dome, the Schweizer-Reneke dome, the Ventersdorp dome, the West Rand Anticline, and the Colesburg area. Granite compositions vary from tonalites through to granite (*sensu stricto*) with most samples exhibiting a form of hydrothermal alteration. Further information on the geology and petrography of these granitoids is provided by Robb (in preparation).

## B. Allogenic Pyrites

A total of 32 samples of compact, rounded, allogenic pyrites were collected from quartz-pebble conglomerates (i.e. Carbon Leader, Kimberley Reef, Intermediate Reefs, Kimberley Reef, Vaal Reef, Ventersdorp Contact Reef) of the Central Rand Group gold fields, and nine samples stem from the uneconomic Promise Reefs of the West Rand Group of the Witwatersrand Supergroup. Additionally, 15 pyrite separates were obtained from conglomerates of the Moodies Group in the Barberton greenstone belt, of the Nsuze and Mozaan Group of the Pongola Supergroup, and of the Uitkyk Formation in the Pietersburg greenstone belt (Figure 1). All the pre-Central Rand Group conglomerates only in a few places are known to contain erratic gold. Detailed petrographic and geochemical descriptions of the conglomerate samples as well as the pyrites studied here have been published by Stupp (1984), Oberthür (1983), Meyer (1983), Frey (1982), Saager (1982), Saager *et al.* (1982) and Koeppel and Saager (1974).

## C. Analytical Procedure

Pyrite and other heavy minerals were liberated from the silicate matrix by hydrofluoric acid treatment (Neuerburg, 1975). Pyrite concentrates were recovered by hand-picking under a binocular microscope. Only rounded, compact pyrites (i.e. detrital grains), were collected from the conglomerate samples. Considerable care was taken to prevent sample contamination caused by inclusions of other minerals, especially gold. Polished sections were prepared from each concentrate and investigated with an ore-microscope in order to study inclusions and inter-growths of the pyrites. For chemical analyses between 100 and 500 mg of powdered material was used. Au, Co, and Ni were determined by instrumental epithermal neutron activation analysis and/or by flameless atomic absorption-spectroscopy. Duplicate analyses using both methods were found to be in good agreement (Stupp, 1984; Meyer, 1983).

## III. RESULTS

### A. Ore Microscopic Studies

The hypogene pyrites from primary gold deposits contain inclusions of pyrrhotite and chalcopyrite and, to a lesser extent, sphalerite, magnetite, rutile, and gold. Many of the pyrites from the Barberton Au mines show a distinct zonal structure caused by variations in contents of Ni, Co, and Au (Saager, 1981).

In the allogenic pyrites from sedimentary deposits inclusions of pyrrhotite, arsenopyrite, magnetite, ilmenite, rutile, sphalerite, pentlandite, and gold are found in approximate order of decreasing abundance. Furthermore, secondary infiltrations of chalcopyrite, pyrrhotite, galena, gersdorffite, and gold can be seen along hairline cracks and in veinlets within the pyrite.

### B. Ni, Co, and Au Abundances in Allogenic Pyrites

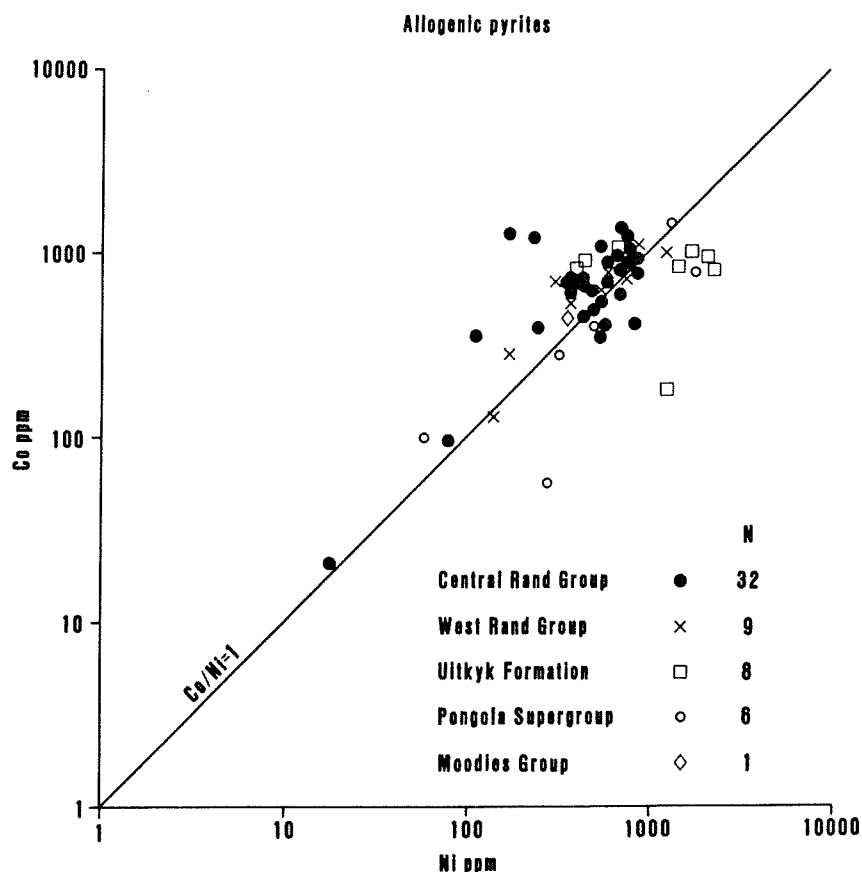
The Ni, Co, and Au contents in allogenic pyrites from the various sample areas are presented in Table 1.

The Ni and Co values range from 17,8 to 1957 ppm and from 20,5 to 1396 ppm, respectively. Two samples from the Uitkyk Formation (77/6, 77/7) and one from the Pongola Supergroup (93) are characterized by Ni and Co contents exceeding 1000 ppm. The majority of the remaining samples contain Ni and Co values in the range of 300 to 900 ppm. Sample 30 BR from the Vaal Reef is exceptionally low in both elements. The Co/Ni ratios vary between 0,24 and 7,0.

In Table 2 the geometric mean Ni, Co, and Au values and the mean Co/Ni ratios for the individual sample populations are summarized. With the exception of the Uitkyk Formation the detrital pyrites of the sedimentary successions examined contain mean Ni and Co contents in the range 300 to 600 ppm. The mean Co/Ni ratios for these samples vary between 0,85 and 1,26. The Uitkyk pyrites possess a slightly higher mean Co content and a mean Ni value exceeding 1000 ppm. They also have the lowest Co/Ni ratio of 0,79.

#### (i) Co/Ni Ratios

The Co and Ni contents of all 56 analyzed concentrates of allogenic pyrites are depicted in Figure 2. The data points plot in a narrow field and scatter around a straight line which defines Co/Ni ratios of 1. One sample from the Vaal Reef in the Central Rand Group (Table 1) is characterized by a distinctly lower Co and Ni content than the bulk of the other samples and, thus, is separated from the other data points.



*Figure 2 : Plot of Co versus Ni for allogenic pyrites*

#### (ii) Au Contents

Table 1 shows that the Au values found in allogenic pyrites range from 0,53 to 1190 ppm. The samples from the West Rand Group and the Uitkyk Formation are characterized by low Au values and a small range (0,53 to 10,2 ppm) whereas pyrites from the Central Rand Group and the Pongola Supergroup contain higher Au contents which vary from 0,78 to 1190 ppm.

**TABLE 1**  
**Ni, Co, AND Au CONTENTS IN ALLOGENIC PYRITES**

(a) Central Rand Group

SAMPLE	LOCALITY	REEF	Ni (ppm)	Co (ppm)	Au (ppm)
Wh2/1	Welkom	Intermediate	450,00	718,00	0,78
FSG9/2	Welkom	Intermediate	373,00	696,00	1,25
VRC/WDL	Carletonville	VCR	83,10	92,40	30,30
1186	Carletonville	Carbon Leader	599,00	533,00	26,30
ELAND	Carletonville	Carbon Leader	472,00	437,00	11,30
1155	Carletonville	Carbon Leader	280,00	394,00	14,40
RCS	Carletonville	Carbon Leader	748,00	775,00	309,00
1134 B2	Carletonville	Carbon Leader	540,00	680,00	35,00
1005 B1	Carletonville	Carbon Leader	490,00	460,00	210,00
1165 B3	Carletonville	Carbon Leader	550,00	400,00	250,00
117632	Carletonville	Carbon Leader	550,00	390,00	67,00
10666	Carletonville	Carbon Leader	825,00	920,00	425,00
100 2C	Carletonville	Carbon Leader	250,00	1160,00	5,00
9774	Carletonville	Carbon Leader	120,00	340,00	35,00
115046	Carletonville	Carbon Leader	820,00	900,00	24,00
118210	Carletonville	Carbon Leader	760,00	850,00	110,00
118527	Carletonville	Carbon Leader	820,00	660,00	31,00
118210 B	Carletonville	Carbon Leader	740,00	575,00	320,00
115421	Carletonville	Carbon Leader	180,00	1260,00	26,00
118744	Carletonville	Carbon Leader	850,00	800,00	125,00
ED 1103	Carletonville	Carbon Leader	800,00	1200,00	2,00
3103	Carletonville	Carbon Leader	835,00	550,00	30,00
964 E25	Carletonville	Carbon Leader	890,00	400,00	1190,00
1766	Carletonville	Carbon Leader	510,00	630,00	150,00
2141	Carletonville	Carbon Leader	380,00	610,00	135,00
EV1	Evander	Kimberley	919,00	906,00	11,30
EV2	Evander	Kimberley	438,00	679,00	62,00
EV3	Evander	Kimberley	408,00	636,00	11,20
EV4	Evander	Kimberley	749,00	1291,00	1,78
EV5	Evander	Kimberley	450,00	693,00	49,60
EV6	Evander	Kimberley	786,00	927,00	9,43
30BR	Klerksdorp	Vaal	17,80	20,50	1,75

(b) West Rand Group

KL12/7227	Kafferskraal	Promise	1175,00	965,00	2,16
KL12/7394	Kafferskraal	Promise	428,00	554,00	3,17
KL12/7530	Kafferskraal	Promise	542,00	629,00	3,03
KL7/707	Kafferskraal	Promise	136,00	126,00	0,56
KL7/820	Kafferskraal	Promise	872,00	1018,00	1,80
HB210	Randfontein	Promise	180,00	295,00	1,02
HB310	Randfontein	Promise	325,00	683,00	0,94
BFD1	Buffelsdoorn	Promise	858,00	781,00	2,13
BFD2	Buffelsdoorn	Promise	798,00	971,00	4,60

(c) Uitkyk Formation

77/1	Mount Robert		427,00	613,00	1,48
77/2	Mount Robert		538,00	744,00	1,38
77/3	Mount Robert		530,00	771,00	0,53
77/4	Mount Robert		1095,00	458,00	0,87
77/5	Mount Robert		1383,00	941,00	10,20
77/6	Mount Robert		1672,00	1045,00	1,71
77/7	Mount Robert		1810,00	1077,00	1,32
77/186	Mount Robert		1957,00	914,00	1,86

(d) Pongola Supergroup

42/79	Gunsteling		693,00	828,00	0,78
SP2	Denny Dalton		279,00	67,10	3,86
18/79a	Denny Dalton		317,00	284,00	81,60
18/79b	Denny Dalton		58,90	107,00	19,70
BP11	Denny Dalton		537,00	393,00	0,73
93	Vuleka		1259,00	1396,00	2,63

(e) Moodies Group

78/11a	Bearded Man		387,00	488,00	2,54
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TABLE 2

GEOMETRIC MEAN VALUES FOR Au, Co, AND Ni AND MEAN Co/Ni RATIOS FOR  
ALLOGENIC PYRITES FROM QUARTZ-PEBBLE CONGLOMERATES

SAMPLE LOCALITIES	N	G Au ppm	G Co ppm	G Ni ppm	Co/Ni
Central Rand Group	32	31,30	542,00	546,00	1,20
West Rand Group	9	1,80	573,00	478,00	1,20
Pongola Supergroup	6	4,57	312,00	367,00	0,85
Uitkyk Formation	8	1,59	793,00	1011,00	0,79
Moodies Group	1	2,54	488,00	387,00	1,26

N = number of samples  
G = geometric mean

The geometric mean Au values for the individual sample populations are summarized in Table 2. It is shown that the mean Au content found in the Central Rand Group pyrites is 31,3 ppm while the mean Au values for the remaining sample groups do not exceed 5 ppm.

Figure 3 illustrates a Au versus Co/Co + Ni x 1000 scattergram for pyrites from the Central Rand Group only. It is shown that with the exception of six points, all the data plot above the horizontal line defined by Au = 7 ppm. Two of the six samples stem from the subeconomic Intermediate Reefs in the Welkom goldfield.

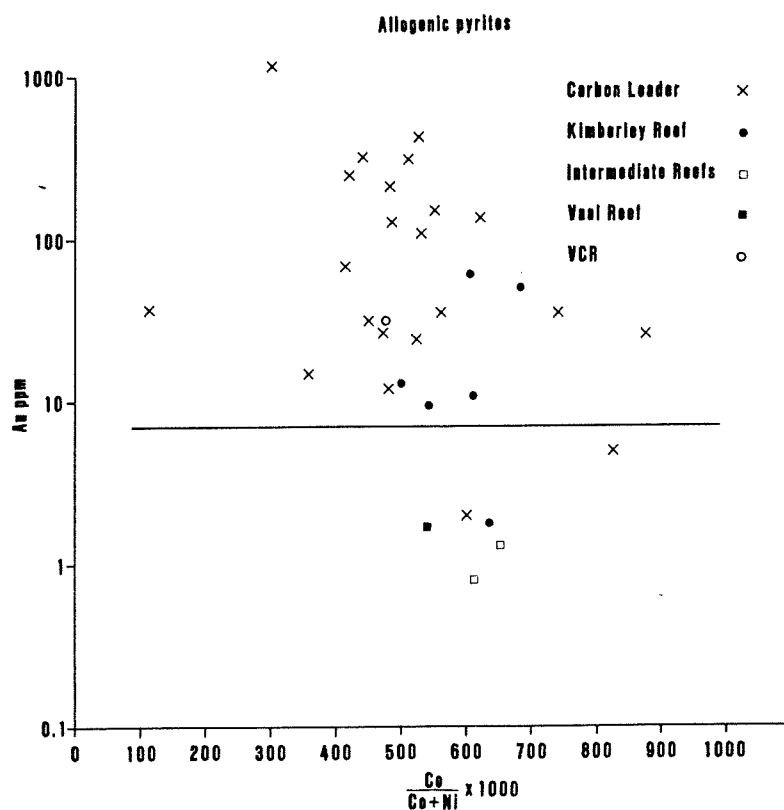


Figure 3 : Plot of Au versus Co/Co + Ni x 1000 for allogenic pyrites from various reefs of the Central Rand Group.

By contrast Figure 4 shows the Au versus  $\text{Co}/\text{Co} + \text{Ni} \times 1000$  values for pyrites drawn from the Moodies Group, the Pongola Supergroup, the Uitkyk Formation, and the West Rand Group. Again the data field can be demarcated by the horizontal line for Au = 7 ppm, but in this case only three of a total of 24 samples carry Au contents higher than 7 ppm. Two of these pyrites were sampled at the Denny Dalton Au mine where the conglomerates of the Mozaan Group have been exploited.

Furthermore, Figures 3 and 4 reveal that there is no meaningful statistical relationship between Au, and Co and Ni in the pyrites.

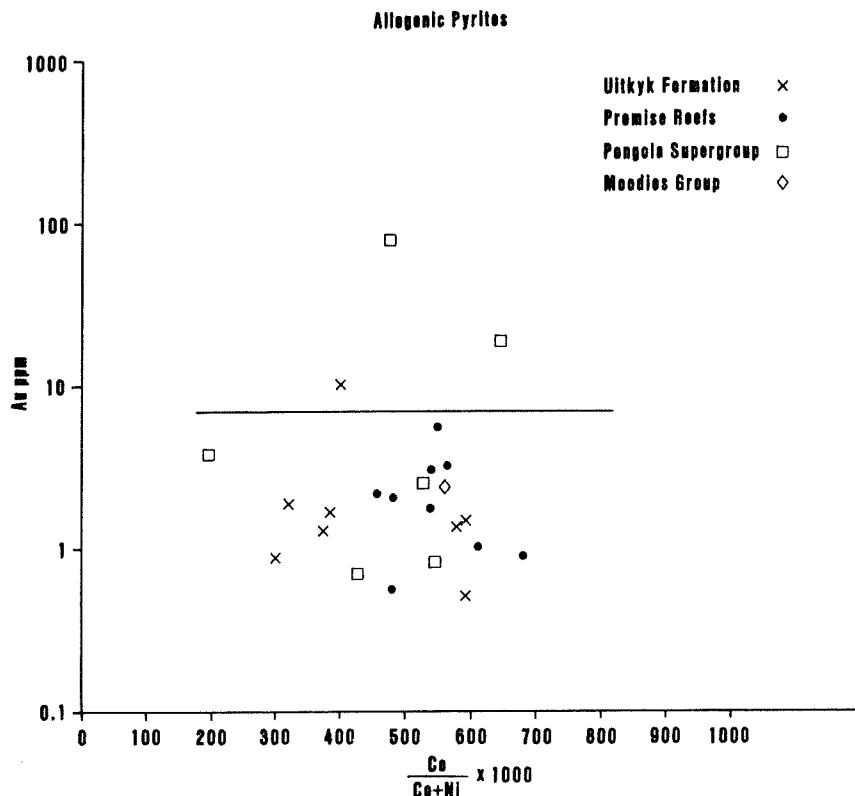


Figure 4 : Plot of Au versus  $\text{Co}/\text{Co} + \text{Ni} \times 1000$  for allogenic pyrites from various conglomerate horizons of pre-Central Rand Group sediments.

### C. Ni, Co, and Au Abundances in Hypogene Pyrites

Table 3 shows the Ni, Co, and Au contents in hypogene pyrites drawn from epigenetic Au mines and from the various non-auriferous country rocks sampled. The Ni values range from 19,2 to 8290 ppm whereas the Co contents vary between 1,10 and 2345 ppm. Samples SHEQUE and BEL from the Sheba Queen and Belvedere mines are unusually low in Ni and Co, whereas sample 117 from the Klipwal mine and sample LET from the Letaba mine carry the highest Ni and Co contents, respectively. The Co/Ni ratios range from 0,001 to 8,56. The geometric mean Ni, Co, and Au values and Co/Ni ratios calculated for the different sampled units are presented in Table 4.

The pyrites from the Barberton Au mines and the Klipwal mine possess similar mean Ni and Co values and Co/Ni ratios. Their Co/Ni ratios are an order of magnitude lower than those for the remaining sample populations. Close similarity exists between the mean Ni and Co values of the pyrites from the Murchison Au mines and from the granitoids, but the latter contain somewhat more Ni on average and, therefore, a lower mean Co/Ni ratio.

#### (i) Co/Ni Ratios

Figure 5 shows a Co versus Ni scattergram for the 51 hypogene pyrite concentrates. The field of data points delineated by the allogenic pyrites from the Central Rand Group (Figure 2) and two straight lines representing Co/Ni ratios of 1 and 0,1 are also shown. It is evident that the fields occupied by hypogene pyrites from the Barberton gold mines, from the Klipwal mine and from the Belvedere mine and by allogenic pyrites from the Witwatersrand sediments are quite discrete, not as much in terms of Ni contents, but certainly in terms of Co abundances and, hence, Co/Ni ratios. The hypogene pyrite concentrates from the epigenetic gold mines scatter around a line defining Co/Ni ratios of 0,1. The sample from country rocks of the Barberton greenstone belt are characterized by higher Co/Ni ratios as well as higher Ni and Co contents. Certainly, best overlap with the field of allogenic Witwatersrand pyrites exists for hypogene pyrites from the Murchison gold mines, from the Girlie mine and the granitoids of the western Transvaal basement.

TABLE 3

## Ni, Co, AND Au CONTENTS IN HYPOGENE PYRITES

## (a) Au Mines in the Barberton Greenstone Belt

SAMPLE	LOCALITY	Ni (ppm)	Co (ppm)	Au (ppm)
IVAN	Ivanhoe	525,00	93,00	35,60
B 24	Ivanhoe	2091,00	161,00	49,00
FAIR	Fair View	289,00	23,90	14,00
SHEQUE	Sheba Queen	19,20	1,10	16,30
29 B	Sheba Queen	4633,00	6,63	0,07
SG 29	Sheba Queen	1137,00	163,00	5,35
FORE	Forbes Reef	1066,00	93,90	96,20
EAG	Eagle's Nest	229,00	23,10	5,32
B 6	Eagle's Nest	69,60	3,87	42,00
EN	Eagle's Nest	1054,00	90,00	7,26
MTMO	Mount Morgan	66,70	8,60	49,50
ROCH	Rochford	268,00	78,50	8,89
AGN	Agnes	38,30	20,00	13,20
B 20	Agnes	180,00	66,90	5,58
DAYS	Daisy	399,00	45,80	0,01
SG 27	Unity	362,00	115,00	3,64

## (b) Au Mines in the Murchison Greenstone Belt

LET	Letaba	950,00	2345,00	0,55
Le 2	Letaba	142,00	1390,00	42,50
Le 4	Letaba	184,00	1576,00	0,07
M 7	Monarch East	86,30	100,00	0,01

## (c) Au Mines in the Belingwe Greenstone Belt

BEL	Belvedere	28,30	2,46	4,25
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## (d) Au Mine in the Pietersburg Greenstone Belt

GIE	Girllie	105,00	269,00	3,92
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## (e) Klipwal Au Mine

18		93,00	8,50	1,90
27		101,00	13,60	2,70
35		124,00	25,00	4,40
43		143,00	33,00	48,00
44		163,00	33,00	9,30
53		92,00	15,20	4,60
58		371,00	22,00	132,00
64		287,00	15,80	20,00
65		438,00	22,00	8,60
71		705,00	198,00	1,79
81		646,00	21,00	0,58
88		290,00	61,00	11,70
96		399,00	49,00	7,60
117		8290,00	193,00	6,59
124		117,00	0,60	3,30
125		219,00	17,70	72,00
128		294,00	30,00	120,00

## (f) Non-Auriferous Rocks of the Swaziland Supergroup

B17	Middle Marker	1802,00	2199,00	0,08
BASKO	Komati Valley	1786,00	773,00	0,20
K 16	Msauli	82,90	717,00	0,33

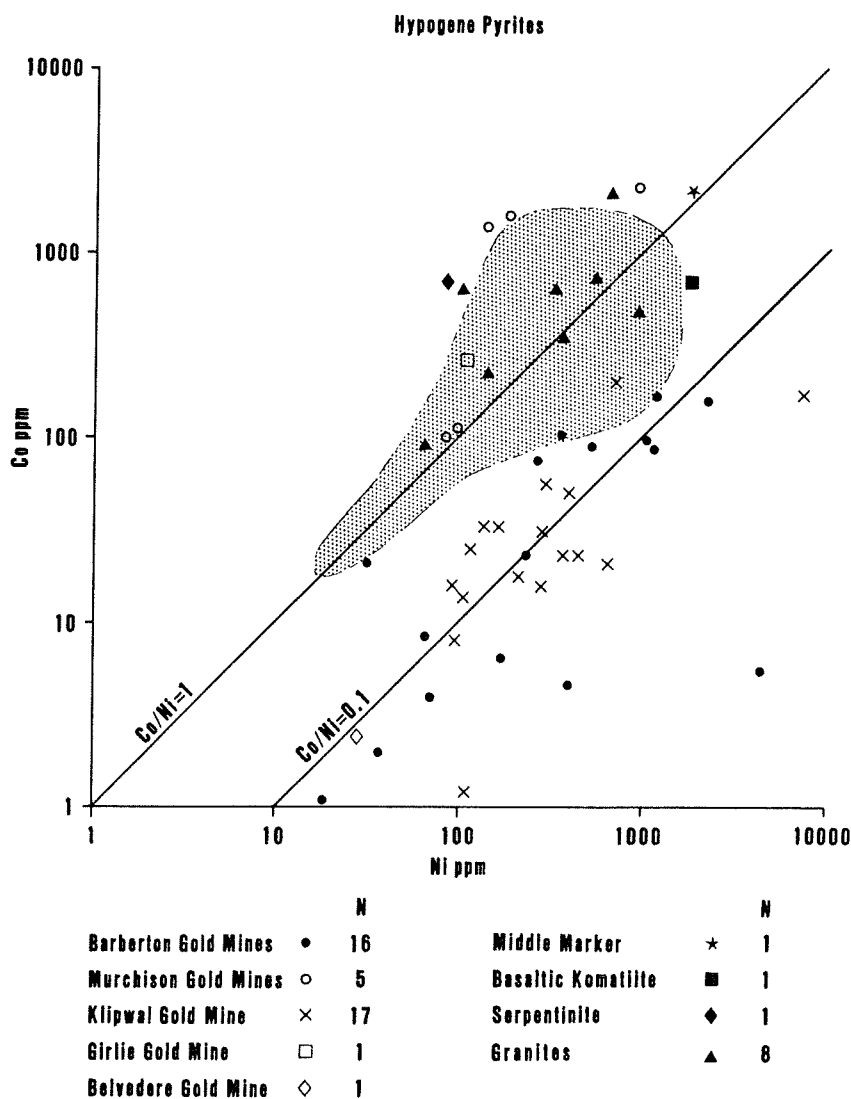
## (g) Granitoids from the Archaean Basement of the Western Transvaal

SF 7a	Hartebeestfontein	345,00	722,00	0,06
SF 7b	Hartebeestfontein	469,00	818,00	0,61
TA 2	Schweizer-Reneke	261,00	747,00	0,05
BMV 4	Ventersdorp	83,60	95,80	0,58
RAT 1	Ventersdorp	133,00	225,00	0,09
BSP 8	West Rand Anticline	765,00	560,00	1,12
N 2	West Rand Anticline	686,00	2164,00	0,24
CB 1	Colesberg	328,00	367,00	0,03

**TABLE 4**  
**GEOMETRIC MEAN VALUES FOR Au, Co, AND Ni AND**  
**MEAN Co/Ni RATIOS FOR HYPOGENE PYRITES**

SAMPLE LOCALITIES	N	G Au ppm	G Co ppm	G Ni ppm	Co/Ni
Barberton Au mines	16	7,07	32,10	422,00	0,08
Murchison Au mines	5	0,30	563,00	183,00	3,08
Belvedere Au mine	1	4,30	25,00	283,00	0,09
Girle mine	1	3,90	269,00	105,00	2,56
Klipwal Au mine	17	9,07	23,90	279,00	0,09
Middle Marker	1	0,08	2199,00	1802,00	1,22
bas. komatiite	1	0,20	773,00	1786,00	0,43
serpentinite	1	0,35	717,00	82,90	8,65
granitoids	8	0,17	505,00	308,00	1,64

N = number of samples  
G = geometric mean



*Figure 5 : Plot of Co versus Ni for hypogene pyrites from various greenstone-hosted gold deposits and country rocks. Stippled field shows Co and Ni values of allogenic pyrites from the Central Rand Group.*

(ii) Au Contents

The Au contents of the hypogene pyrites are listed in Table 3 and exhibiting a range between 0,01 and 96,2 ppm. Table 4 shows the geometric mean Au values for the individual sample populations. The pyrites from the Klipwal mine possess the highest mean Au values of 9,07 ppm while pyrites from the Barberton Au mines carry only slightly lower Au contents averaging 7,07 ppm.

The Au contents of the hypogene pyrites are also depicted in the plot of Au versus  $\text{Co}/\text{Co} + \text{Ni} \times 1000$  in Figure 6. This diagram reveals the close similarity between Au, Co, and Ni abundances in the Barberton and Klipwal pyrites which are characterized by  $\text{Co}/\text{Co} + \text{Ni} \times 1000$  values of less than 300 and Au contents, generally, exceeding 4 ppm. The majority of the remaining samples from all other sample localities carry Au contents less than 1 ppm and have  $\text{Co}/\text{Co} + \text{Ni} \times 1000$  values greater than 300.

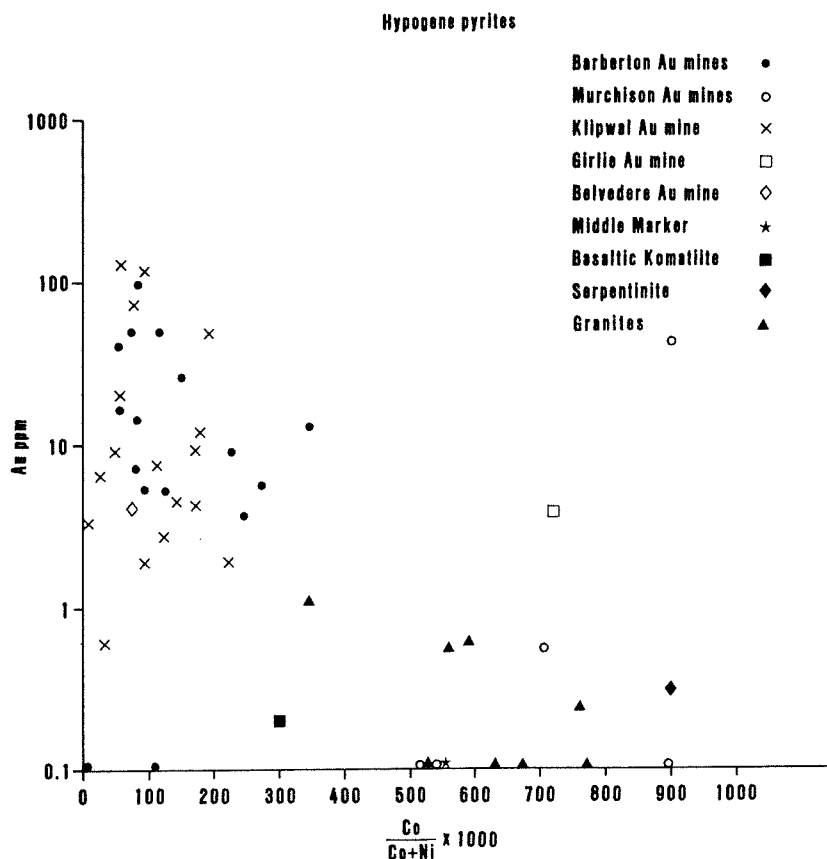


Figure 6 : Plot of Au versus  $\text{Co}/\text{Co} + \text{Ni} \times 1000$  for hypogene pyrites

#### IV. DISCUSSION

##### A. Genetic Implications

Hypogene pyrites from the Barberton gold mines, from the Belvedere mine and from the Klipwal mine are characterized by low Co/Ni ratios. The mean Co/Ni value for these samples is about 0,1, with the data ranging from 0,01 to 0,37. Co/Ni ratios as low as this are not commonly reported (Bralia *et al.*, 1979) and, thus, must be regarded as somewhat unusual. The origin of the metals concentrated in the Barberton and Klipwal deposits has been explained by the source bed theory, which envisages that gold and accompanying elements were leached from the country rocks, namely ultramafic and mafic volcanics.

Saager *et al.* (1982) concluded that sulphides are more easily attacked and dissolved by migrating hydrothermal solutions than are rock-forming silicate and oxide minerals and, thus, they regarded the sulphides hosted in the potential source rocks as the principal donators for Au (and other metals) concentrated in the adjacent epigenetic ore deposits.

The mean whole rock Co/Ni ratios for peridotitic and basaltic komatiites from the Barberton Mountain Land fall in the range 0,06 to 0,27 respectively (Saager *et al.*, 1982). Pyrites from the basaltic komatiite analyzed in the present study yielded a Co/Ni ratio of 0,43.

Bralia *et al.* (1979), for example, found that remobilized pyrites generally tend to be characterized by decreases in their Co/Ni ratios with respect to their primary equivalents. Complexity in pyrite genesis is substantiated by the study of Saager and Koeppel (1976) who suggested that three periods of ore-concentration occurred in the Barberton deposits, whilst Stupp (1984) cited evidence for several periods of shearing affecting the Klipwal ore.

A second group of hypogene pyrites is characterized by Co/Ni ratios greater than one. These samples stem from the Monarch East and Letaba mines in the Murchison greenstone belt, the Girlie mine in the Pietersburg belt, from a serpentinite and the Middle Marker in the Barberton greenstone belt, and from the Archaean granitic basement of the western Transvaal. The serpentinite sample was taken from a shear zone at the contact between the upper Onverwacht and Fig Tree groups, in which the pyrite mineralization is clearly of secondary origin. The Middle Marker pyrite concentrate contains high Co (2199 ppm) and high Ni (1802 ppm) and yields of Pb-Pb age of 3020 m.y. (Saager and Koeppel, 1976). This pyrite, therefore, is also of secondary origin formed some time after the deposition of the chemical sediments. Viljoen *et al.* (1969) found that the dark tuffaceous shale layers in the Middle Marker horizon contain elevated contents of Au, and up to 628 ppm Ni. Consequently, the high Co and Ni values in the Middle Marker pyrites are probably inherited from the environment of their formation.

A total of 45 granite samples from the western Transvaal basement have been analyzed for their whole-rock Ni and Co contents. The Ni contents of these rocks range from 0,69 to 33,7 ppm, the Co values vary between 0,85 and 23,9 ppm and the mean Co/Ni ratio is 1,57 (range 0,13 to 10,7). The eight pyrite concentrates separated from this sample suite possess a mean Co/Ni ratio of 1,64 (Tables 3 and 4) a value which is very close to the mean Co/Ni ratio of the host granitoids. The mean Ni and Co contents of the pyrite separates are approximately ten times higher than in the bulk rocks. Again, it would appear that the Ni and Co contents and Co/Ni ratios of the pyrites reflect the environment in which they were formed.

The pyrites from the Murchison gold mines possess Co/Ni ratios ranging from 1,16 to 9,79. These values correspond with the range of Co/Ni ratios in pyrites from volcanogenic-exhalative ores as reported by Bralia *et al.* (1979). Muff and Saager (1979) found a lack of covariance between Co and Ni in the rocks of the "Antimony Line" as well as in the ore itself. They concluded that the Co distribution is related to late-stage volcanic activity, whereas the Ni was derived from the host rocks as a result of metamorphic overprint. The paragenesis of the ore related to the "Antimony Line" is essentially a high-temperature assemblage comprising pyrite, pyrrhotite, chalcopyrite, and arsenopyrite followed by the low-temperature antimony ores comprising mainly Ni-rich berthierite (Muff and Saager, 1979). The elevated Co/Ni ratios of the Murchison pyrites are considered, therefore, to be a function of one of two parameters, either that the Ni and Co contents in the host rocks are uncorrelated or that solid solution between pyrite and vaesite is incomplete at temperatures envisaged for the pyrite crystallization (Nickel, 1970). It should also be pointed out that Rb-Sr isotope investigations (Barton, 1984) have suggested that remobilization of Murchison ores occurred during Proterozoic times and thus, in terms of the suggestion of Bralia *et al.* (1979) the Co/Ni ratios in the Murchison pyrites could originally have been even higher than the values presently recorded.

A single pyrite concentrate from the Girlie mine in the Pietersburg greenstone belt was analyzed, and this yielded a high Co/Ni ratio of 2,6. This value falls in the range of Co/Ni values for pyrites from the Murchison mines. However, little is known on the mineralogy and geochemistry of the Girlie mine and adjacent country rocks and, thus, a direct comparison with the Murchison ores cannot be made at this stage.

## B. Origin of Allogenic Pyrites

The mean Co/Ni ratio of allogenic pyrites from the various sedimentary horizons investigated is 1,1, with the Co and Ni values ranging from 20,5 to 1260 ppm and from 17,8 to 1810 ppm, respectively. The Co/Ni ratios vary from 0,13 to 7,0. No systematic differences were observed in the Co and Ni contents of pyrites collected from the various localities, despite their widespread geographic distribution and the differing sedimentary ages.

Similar Co and Ni values as well as Co/Ni ratios to those reported in this study have been obtained from the Klerksdorp and Evander goldfield by Utter (1978) and Hirdes (1979). However, Hallbauer and Kable (1982) have also found Co-depleted pyrites in the Ventersdorp Contact Reef of the Carletonville goldfield which yield an average Co/Ni ratio of 0,6.

Figure 5 demonstrates that a significant difference exists in the Co/Ni ratios of allogenic pyrites from the Witwatersrand basin and hypogene pyrites from komatiite-related Au deposits in the Barberton and Bellingwe greenstone belts and the Klipwal mine. This indicates that the bulk of the Witwatersrand depository was not derived from a predominantly Barberton-type source area and also militates against previous suggestions (Saager, 1981; Utter, 1978; Pretorius, 1976; Viljoen *et al.*, 1970) that the gold itself was derived from a Barberton-type greenstone belt assemblage. However, similarities in the Co/Ni ratios of pyrites from epigenetic gold deposits in the Murchison and Pietersburg greenstone belts and the detrital Witwatersrand pyrites indicate that this type of greenstone belt assemblage may well have contributed a significant amount of detritus (as well as gold) into the basin. It is also pertinent to point out that pyrites from the Archaean granite basement in the vicinity of the Witwatersrand basin have similar Co/Ni ratios to the allogenic pyrites studied. Clearly, therefore, pyrites in the Witwatersrand sediments could conceivably have been derived from a granitic source. The ratio of granite to greenstone in the Kaapvaal Craton exceeds approximately 5:1 which makes it axiomatic that granites provided a major component of the detritus into the depository. A more direct confirmation comes from the study of Hallbauer and Kable (1982) who deduced that granite pegmatites must have played a significant role as the source for allogenic pyrites in the Basal and "B" reefs of the Orange Free State goldfields. It is obvious, therefore, that the source of the Witwatersrand pyrites was diverse, comprising mainly granites, but also a greenstone belt component of the Murchison-Pietersburg type. Finally, it is pertinent to emphasize that allogenic pyrites from the Witwatersrand basin are not significantly different, at least in terms of Co/Ni ratios, from detrital pyrites in other horizons such as the Moodies, Pongola, and Uitkyk sediments. The constancy of Co/Ni ratios in allogenic pyrites from these diverse sedimentary deposits suggests that the source rocks from which they were derived must have been both widespread in extent as well as chemically homogeneous enough to have yielded the requisite pyrites.

### C. Gold Contents in Allogenic Pyrites and Host Rocks

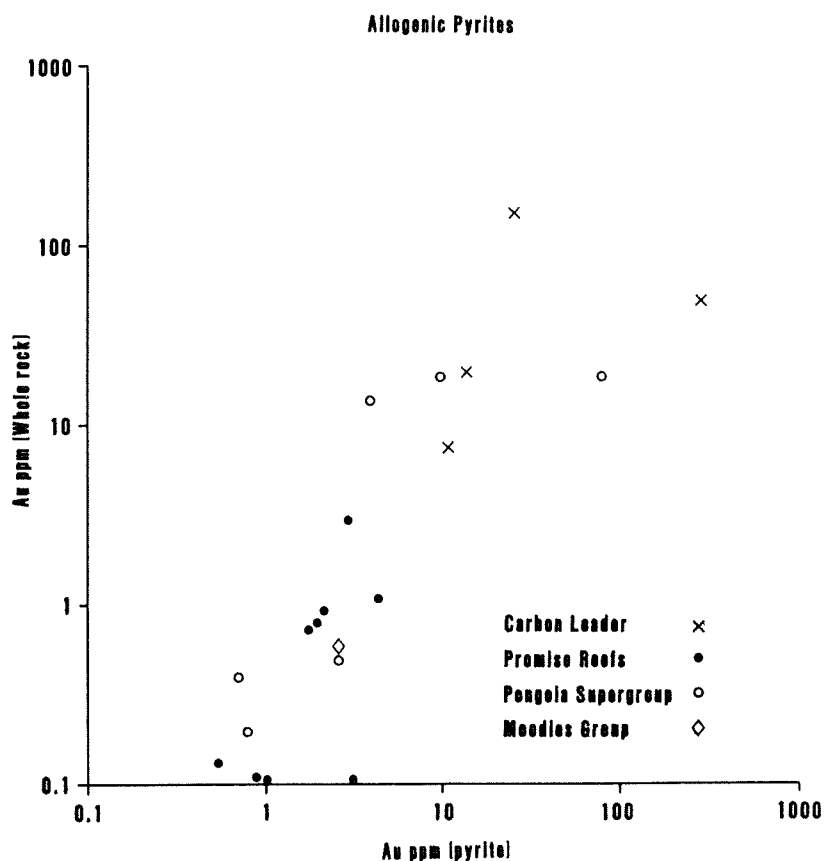
Comparison of Figures 3 and 4 indicates that allogenic pyrites from subeconomic auriferous reefs, generally, contain Au values lower than 7 ppm, whereas pyrites from economic horizons carry Au contents higher than 7 ppm.

Furthermore the relationship between Au contents in pyrite concentrates and Au contents in the corresponding whole-rock samples (Figure 7) reveals a broad positive correlation between the two variables, e.g. Au enriched conglomerate horizons also contain pyrites with elevated Au contents. This coherence can be interpreted in two ways.

- (i) Both the Au (as detrital gold grains) contained in these bulk samples as well as the Au-enriched pyrites were released from a gold-rich source in the hinterland and subsequently deposited together in a sedimentary basin, or
- (ii) the elevated Au tenor of allogenic pyrites occurring in Au rich conglomerate reefs is related to contamination due to Au remobilization caused by metamorphic overprint of the sediments.

In this context it is pertinent to discuss a paper by Bancroft and Jean (1982) who studied the reaction between  $\text{KAuCl}_4$  in solution and various sulphide minerals. They could show that Au(iii) was rapidly reduced to metallic Au on the surface of sulphide minerals. Consequently, it is assumed that an equivalent mechanism of Au deposition at low solution concentrations and temperatures is also applicable to geological environments similar to those of quartz-pebble conglomerates which suffered weak metamorphic overprint. Thus, the Au concentration in the studied allogenic pyrites may not only be a primary feature (i.e. primary Au inclusions in the pyrites) but, also a function of the Au availability, namely, the Au level in the particular environment of occurrence. In other words, the Au contents of the allogenic pyrites investigated here may reflect various amounts of adsorbed Au, and, consequently, may provide an indication of the amount of Au inherent in the specific conglomerate horizon, itself.

This suggestion is in accordance with the observation that detrital pyrites in the studied sediments very rarely contain microscopic Au inclusions. Oberthür (1983), for example, studied inclusions in detrital pyrites from the Carbon Leader reef with the aid of a scanning electron microscope and found in a total of 10 000 pyrite grains only five which contained primary gold inclusions. Furthermore, the suggested Au contamination explains the observed discrepancy in Au contents of allogenic pyrites and hypogene pyrites from the possible source rocks.



## V. SUMMARY AND CONCLUSIONS

1. Ni and Co contents and particularly Co/Ni ratios in hypogene pyrite reflect the specific environment of their formation and, therefore, can be regarded as useful parameters in explaining the genesis of sulphide ores.
2. Comparison of Co/Ni ratios in allogenic pyrites from various sedimentary deposits with hypogene pyrites from possible source rocks indicated a polygenetic origin of the detrital pyrites and led to the suggestion that they may have been derived from granitic and volcano-sedimentary rocks comprising the Archaean basement of the Kaapvaal Craton and from epigenetic gold deposits similar to those occurring in the Murchison and Pietersburg greenstone belts.
3. The Au contents of allogenic pyrites are broadly correlated with the bulk Au contents of the corresponding conglomerate samples. From this it is assumed that the original Au contents of the allogenic pyrites studied here is obscured by contamination caused by Au remobilization during diagenesis/metamorphism.

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