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The copper, cobalt and nickel content of some South African pyrites

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COETZEE

THE COPPER, COBALT AND NICKEL CONTENTS

THE COPPER, COBALT AND NICKEL CONTENT

OF SOME SOUTH AFRICAN PYRITES

DISSERTATION PRESENTED FOR THE DEGREE OF MASTER OF SCIENCE
IN THE FACULTY OF SCIENCE, UNIVERSITY OF THE WITWATERSRAND,
JOHANNESBURG.

BY: G. L. COETZEE, B.Sc.,HONS.

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A B S T R A C T

A survey of the literature concerning the trace element content of pyrite is given. Descriptions of pyrite specimens analyzed are provided. Colorimetric analyses of 43 pyrites from Southern Africa show a range from 2·16% to < 0·001% for Cobalt and from 0·37% to 0·00% for Nickel. Some differences in in trace element content of sedimentary and hydrothermal pyrite reported from areas in Northern America and Europe are shown to be valid for South African pyrites. Cobalt-Nickel values for pyrite in some Witwatersrand "Bankets" are quoted. Analyses of pyrite from Kilembe, Uganda indicate an unusually high Cobalt content. Most pyrites are shown to contain Copper and some to contain Manganese.

A B S T R A K

'n Oorsig van die bibliografie in verband met die spoor-element inhoud van piriet word gegee. Beskrywings van piriet monsters wat geanaliseer is word aangegee. Kolorimetriese analises van 43 piriete uit Suidelike Afrika toon dat die Kobalt gehalte varieer vanaf 2·16% tot < 0·001% en die Nikkel gehalte vanaf 0·37% tot 0·00%. Sekere verskille in spoor-element gehalte van sedimentêre en hidrotermale piriete wat gerapporteer is uit gebiede in Noordelike Amerika en Europa word bevestig vir Suid-Afrikaanse piriete. Kobalt-Nikkel waardes vir piriete in sekere Witwatersraandse „Bankette" word aangegee. Piriet--analises van Kilembe, Uganda, dui op 'n buitengewoon hoë Kobalt inhoud. Daar word aangetoon dat meeste piriete koper en sommige Mangaan bevat.

I. INTRODUCTION

European and Canadian geochemists have shown that the trace-element content of pyrite, especially the Cobalt-Nickel content, often has a bearing on the genesis of the pyrite. As no data on this subject are available for South African pyrites, it was decided to undertake the present investigation, which is in reality a "reconnaisance" survey.

Originally, the intention was to obtain quantitative data for Copper in pyrites too. But, due to the great frequency with which Chalcopyrite appears with pyrite, admittedly in small amount, only qualitative tests were carried out for Copper.

The Cobalt-Nickel determinations were made colorimetrically, as this method requires relatively simple apparatus. Approximately 150 determinations each were made for Cobalt and Nickel, on 43 specimens of pyrite.

The author realizes that any value this investigation may have lies in the fact that it indicates certain trends, and suggests possibilities for much more intensive research.

To avoid confusion concentration figures were expressed on a percentage basis. In some instances concentrations were expressed in γ's, where $1\ \gamma = 10^{-6}$ grms, and thus $1\ \gamma$ /grm = 1 p.p.m.

II. REVIEW OF LITERATURE CONCERNING THE TRACE ELEMENT CONTENT OF PYRITE

The literature concerning the trace element content of pyrite is not as extensive as may be desired.

CARSTENS (1)(2)(3), in an investigation of Norwegian pyrite deposits found that pyrites of hydrothermal origin generally contain 0·01 to 0·07% Co and, very little Nickel, so that the ratio Co : Ni always exceeds 1. In one instance he reports a Co : Ni ratio of from 20 : 1 to 30: 1. In pyrite of sedimentary origin, e.g., at Leksdal, the relation is the reverse, here the Nickel content is from 10 to 20 times greater than the Cobalt content. These relations hold for pyrrhotite too, with the exception, that, when these two sulphides occur in contact, the pyrrhotite has the larger Nickel content and the pyrite contains the most Cobalt. Other differences between sedimentary and hydrothermal pyrites according to Carstens, are as follows: Hydrothermal pyrites are enriched in Cu, Ag, Zn and Se whereas sedimentary pyrites are enriched in C, P, Mn and As.

AUGER (4) has studied a considerable number of pyrites from mines in the Canadian Shield, and, a few from other mines in Northern America. His results are not expressed in absolute quantities but are spectrographic intensity ratios, which only afford an indication of relative concentrations. Auger reports Mg, Al, Si, Ca, Sc, Ti, V, Mn, Co, Ni, Cu, Zn, Sr, Y, Mo, Ag, Cd, Sn, In, Ba, Au, Pb and Bi in pyrites. He adduces evidence to show that Co, Ni and Mn are included in the pyrite structure in substitutional solid solution.

In one mine, district, or even region some trace elements are consistently more concentrated than in other areas - e.g., in the Hollinger and Montezuma, Calif., mines Nickel predominates over Cobalt while at the Kenora, Michipicoten, North Star, Calif., and Aldermac mines Co $>$ Ni. Similarly Mn, Cr and Ti vary in different mines.

The high temperature "shield" pyrites all contain Cr, Mn, Ni and Co in some amount, whereas these elements are absent, or occur only as traces in the lower temperature deposits of California and Mexico. On the other hand, Pb, Zn and Ag are present in the low temperature deposits while they are absent or occur only in minute traces in the "Shield" pyrites.

Auger further investigated variation with depth of trace element content at the Hollinger, Noranda and Siscoe mines in Canada

At Hollinger, in the Porcupine District, Ontario, in a high temperature gold-quartz deposit, Ag and Cr decrease strongly with depth, Nickel slightly while Zn increases gradually and Cobalt very slightly downward.

At Noranda (massive sulphides), Ag, Ti and V increase downward, Pb and Ni show no variation, Zn decreases slightly and in one particular ore-body Cobalt decreases from 0·5% at the top to 0·001% over a vertical range of 1700'. Here pyrrhotite shows a reverse relation as far as Cobalt is concerned. Ni occurs in greater amount in pyrrhotite, but again shows little vertical variation.

At the Siscoe Mine, Ni, Mn, Ti, Sr and Ag increase downwards while Co and Ba show a vague suggestion of a similar trend.

Auger states that there is no relation between the trace element content of pyrite and variations in gangue or wall rock.

In general, massive sulphides have more consistent values for minor constituents than the gold-quartz vein deposits.

HAWLEY (5) combined a spectrographic study of pyrites with "pyrite-geothermometer" determinations.

Relative concentrations of Au, Ag, Te, Pb, Zn, Sn, Mo, Mn, Cr, Ti, V, Bi and As and absolute amounts of Co and Ni were determined.

Four mining areas in Eastern Canada were investigated in detail.

In the Lowell Rouyn quartz vein, Quebec, Cobalt varies from 0·001% to 0·038% and Nickel from 0·005% to 0·1%. Au, Ag, Bi, Cr, Mn, Pb, Mo, V, Sn, Zn and occasionally Ti were detected in pyrite. Determinations of the temperature of deposition of the pyrite vary from 426°C to 520°C. Au, Ag, Bi, Cr, Pb and Mo decrease vertically while Co and Ni both show an increase with depth. The overall averages for Cobalt and Nickel are respectively 0·02% and 0·04%, thus Co : Ni = 1 : 2. Fine-grained pyrite is enriched in Co, Cr, Mo and Sn while the coarser variety contains more Ag, Pb and Bi.

Pyrite is associated with chalcopyrite, galena and sphalerite in the Kerr-Addison Gold Mine, Ontario. In the "21" ore-body Cobalt varies from 0·021% to 0·062% and Nickel from 0·021% to 0·082%, with a slight decrease of both Co and Ni with depth. Cr, Mn, Pb, Mo, Sn, As, Au and Ag, especially the latter two elements, increase downwards. There is little difference between pyrite in quartz veins and pyrite in the wall-rock. Except for the Gold-Silver content, fine-grained pyrite (290°C) and the coarse-grained pyrite (approximately 400°C) show very little difference. There is little variation between individual deposits. Hawley concludes that the pyrite was deposited under very similar conditions from one fluid with subsequent introduction of Au and Ag.

In the Kirkland Lake gold belt, Ontario, gold and pyrite occur with Tellurides of Pb, Hg and Ag. The pyrite contains Au, Ag, Te, Pb, Cu, Ti, Al, Mg, Cu, Ba and Sr [illegible] ake Shore mine, Cobalt varies from 0·029 - 0·101% and [illegible] m 0·06 to 0·10%, with an average Co : Ni ratio of 1 : 2. The Cobalt content is constant laterally, but increases downwards while silver decreases in depth. Variations in individual elements with grain size, wall-rock and different veins are mentioned.

Temperature studies on pyrite of the Porcupine Gold District, Ontario, indicate two stages of mineralisation, the first at 10 Km. depth and 650 - 400°C and the second at 150°C and much shallower depth. Cobalt is more concentrated in fine-grained pyrite and Nickel shows a similar but less marked relationship. High temperature (650 - 400°C) pyrite contains more Co and Ni and less Au, Ag, As, Pb and Zn than low temperature pyrite. There is also a variation between different host rocks, in one case cited Cobalt is more concentrated in the wall rock than in a nearby quartz vein, while the reverse applies to Nickel. The Cobalt content is higher in veins outside an intrusive quartz porphyry while Nickel is more enriched in the same veins, in the porphyry. There is little difference in trace element content between individual veins when other conditions are equal. The average values for the two types of pyrite are :-

High Temperature	0·04% Co	0·036% Ni
Low Temperature	0·013% Co	0·027% Ni

Cobalt values range from 0·002% to 0·055% and Nickel from 0·01% to 0·064%.

In all pyrites, excepting hi[illegible] temperature pyrite from Porcupine, Ni exceeds Co in amount an[illegible] Hawley points out, these values are not in agreement with values reported by Carstens (1)

To summarize, Cobalt and Nickel [illegible]ry from 0·02% to 0·10% each, in the four areas studied and in all, except Porcupine "high temperature" pyrite Co : Ni = 1 : 2 (approx.). Au, Ag, Co, Ni, Cu, Cr, Mn, Mo, V, Pb and Ti were present in all pyrites examined.

In three of the four deposits the only consistent variation with depth is a slight increase in Cobalt. Hawley states that, because Cobalt and Nickel are probably present in solid solution, variations in content of these elements in pyrite are directly related to the temperature of deposition.

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MINGUZZI (6) examined forty Italian pyrites of primary and secondary origin spectrographically. All contained Al, Co, Cu, Mg, Mg, Si and, in addition, pyrites of prima y origin contain Ag, As, Pb, Su, Sb and Zn. Ti is found in most secondary pyrites.

MINGUZZI and TALLURI (7) studied quantitative variations in 35 "magmatic" and 12 sedimentary pyrites from Italian occurrences. Both types of pyrite contain very little Copper, at most 10 p.p.m., but sedimentary pyrite contains slightly more than magmatic pyrite. Magmatic pyrites contain up to 2400 p.p.m. Co and a maximum of 180 p.p.m. Ni. Manganese reaches a maximum of 100 p.p.m. in magmatic pyrites whereas the sedimentary pyrites contain slightly more Manganese. There is a great enrichment of Co with respect to Nickel in magmatic pyrites. On the other hand, pyrites of sedimentary origin contain more Nickel. Talluri and Minguzzi point out that the length of the unit cell of CoS_2 and FeS_2 is 5·4 Å whereas that of NiS_2 is 5·74 Å. They consider that this explains the enrichment of Cobalt in magmatic pyrites.

NICKEL (8) has given a very ingenious demonstration of the application of geochemistry to the solution of problems of orogenesis.

In the Michipicoten district, Ontario, pyrite occurs in the wall-rock and in zones parallel to quartz-scheelite veins. When pyrite is present, biotite is the only ferromagnesian mineral; if pyrite is absent, chlorite and hornblende, often to the exclusion of biotite are present. In sixteen pyrites examined Co varies from 0·13 to 0·76%, Ni from 0·08 to 0·14% and Mn from 0·0007 to 0·0036%.

Nickel considers that, if at the time of formation of the pyrite, there was an exchange of ions between pyrite and biotite, then the presence or absence of pyrite should be reflected by variations in the composition of the biotite.

The results show that the Iron and Cobalt content of biotite decreases in the neighbourhood of pyrite. This suggests that there was a transfer of cations between biotite and pyrite. From the ratios of Co in pyrite and Co in biotite, in the same specimens, and similarly for Ni and Mn it emerges that Co is from 25 to 600 times more concentrated in pyrite than in biotite. Nickel is only from 1 to 2 times as abundant in pyrite as compared to biotite. Manganese again, is at least 10 times more concentrated in biotite. The Co ratio is the greatest where there is the "heaviest" pyrite development. At the same time, extensive pyrite development is accompanied by a sharp decrease in the amount of Iron and Cobalt in the biotite. These results strongly suggest that sulphurous fluids, acting on Potash-Felspars and iron-rich aluminous hornblende have altered these minerals to biotite, talc, pyrite, quartz and a different amphibole. This suggestion is given additional credence by field observations.

The results demonstrate that Co is the most sulphophile, nickel less and manganese least of the three elements. This observation may be explained on the basis of the sulphur-cation distance, which inversely relates to the polarity, of the sulphides of the three metals. The distances are:

$CoS_2 = 2{\cdot}33$; $NiS_2 = 2{\cdot}42$ and $MnS_2 = 2{\cdot}59$.

We may summarize the conclusions reached by the various authors as follows :

Pyrites of different origin have a different trace element content. This applies especially to pyrites of sedimentary, hydrothermal and magmatic origin. (Carstens, Hawley, Minguzzi)

In addition, the following factors have been shown to influence the trace-element content of hydrothermal pyrite:-

a. Temperature of Deposition. (Hawley)

b. Change in wall rock. (Hawley)

c. Vertical and lateral variations within one ore-body. (Hawley, Auger)

d. Differences between individual ore-bodies in one mine. (Hawley, Auger)

e. Regional or district differences. (Auger)

f. Variation in crystal habit of pyrite. (Auger)

g. Certain coexisting minerals, e.g. Pyrrhotite. (Carstens) and Biotite (Nickel) (Carstens)

h. Changes in grain-size. (Hawley)

Some of the variables mentioned also influence the trace element content of sedimentary and magmatic pyrite.

SAMPLING AND PREPARATION OF PYRITES FOR ANALYSIS

Samples of pyrite-bearing rock were obtained from mines and field-exposures scattered over Southern Africa. The author collected approximately half of these specimens personally while the remainder were donated by various geologists.

The samples varied in weight from a few grammes to several Kilogrammes, depending upon the amount of pyrite in the specimen.

An attempt was made to use only material in which there were no other sulphides. This was not always possible and hence quite a few specimens contain minor amounts of chalcopyrite. Other sulphides, such as galena, were removed by hand picking under a binocular microscope. In any case, traces of sulphides other than those of Copper, Cobalt and Nickel would not affect the results very seriously.

The pyrite-bearing rocks were crushed, ground and screened. Some rocks were ground to -28 mesh, others to -35, -48, -64 and occasionally to -90 meshes to the inch. The screen-size used was determined by the nature and size of the pyrite in the rock. Standard mesh on Tyler screens was used.

The screened rock-powder was "panned" in an ordinary prospecting pan to concentrate the pyrite. This preliminary concentrate was washed with acetone and dried in an oven. The acetone washing removes the greater part of the water and prevents oxidation of the pyrite. A heavy-medium separation, using Bromoform was then carried out on the "panned" concentrate. Usually the product of this separation consisted of 90% or more pyrite, the remainder being made up of non-sulphide heavy minerals, e.g., zircon, magnetite, chromite, apatite, etc.

After the pyrite had been washed with acetone and dried, any magnetic material, mainly metallic iron from the crusher, was removed electro-magnetically. This ensured that the samples were free from magnetite, pyrrhotite and other highly electro-magnetic minerals. In some instances, with a high content of non-magnetic non-sulphide heavy mineral in the rock, recourse was made to an elementary froth flotation procedure The sulphide present was floated with pine-oil in aqueous medium containing a xanthate. This method, although somewhat laborous when ordinary laboratory facilities only are available, yields pyrite of exceptional purity, when pyrite is the only sulphide present. In the few cases when other sulphides were present in quantity, the pyrite was separated by hand-picking under a binocular microscope. All the pyrite concentrates were inspected under a binocular microscope before analysis for the presence of contaminants and for the proportion of diluents.

The purity of the pyrites in all cases was in excess of 90%, often 95% and occasionally 100%.

With a few exceptions polished sections were made of the original material and occasionally of the pyrite concentrates. The polished sections served to ascertain whether sulphides, other than pyrite, were present.

ANALYTICAL METHODS

The procedure followed for the Colorimetric analysis of Cobalt and Nickel is essentially as described by Sandell (9).

Standard solutions:

Reagents. Nickel sulphate: $NiSO_4H_2O$

Cobalt chloride: $CoCl_26H_2O$

Both these salts were of "Analytical Reagent" quality. Macro-analyses were carried out on both salts to determine the amount of Nickel and Cobalt present in the respective compounds. Standard aqueous solutions containing 100 p.p.m. by weight, of metal were prepared.

Solution of the Pyrite:

Reagents : Nitric A.R.Q.

Hydrochloric Acid A.R.Q.

Samples of pyrite weighing roughly 1 gm were weighed out to the nearest 0·1 mg. The pyrite was then boiled with 1 : 1 Nitric Acid until the evolution of red fumes of nitrogen peroxide had ceased, more 1 : 1 Nitric Acid was added and the process repeated until all the pyrite had dissolved, and the solution was clear. Some solutions were cloudy, due to the incomplete oxidation of the sulphur, but, boiling with conc. Hydrochloric Acid, cleared these solutions.

The solutions were then filtered and made up to 100 ml. volume in a standard flask. Aliquots of 10 ml. each were then used for the subsequent determinations.

Separation of Iron from Cobalt and Nickel:

The most efficient and simple means of separating iron from copper, nickel and cobalt was found to be by precipitation with ammonium hydroxide. The copper, nickel and cobalt form soluble

ammines in excess of ammonia, but are retained to some extent by the precipitate of ferric hydroxide. This difficulty may be overcome by solution of the ferric hydroxide in acid and reprecipitation with ammonia.

Reagents : Ammonium Hydroxide C.P.

Nitric Acid A.R.Q.

Concentrated ammonia in excess was added to a 10 ml. aliquot of a solution as described above. The materials was filtered, the precipitate washed with distilled water, the ferric hydroxide precipitate dissolved in 1 : 1 Nitric Acid and re-precipitated with excess ammonia. The filtrate was added to the original ammoniacal filtrate.

The iron-free filtrate was boiled to a final volume of approximately 20 ml. At this stage the solution is slightly acid. The solution was now ready for either a cobalt or nickel determination. It was impracticable to determine both Cobalt and Nickel in the same solution.

Determination of Nickel:

Reagents : 1% Dimethylglyoxime in ethyl alcohol (w/v)

Liquid Bromine A.R.Q.

Ammonium hydroxide A.R.Q.

Ammonium nitrate C.P.

In the presence of a strong oxidizing agent, such as Bromine, in ammoniacal solution, Nickel ions produce a wine red solution with dimethylglyoxime.

If the concentration of the Nickel in the solution exceeds 6 γ/ml, nickelous dimethylglyoxime is precipitated. Sandell states that Cobalt and Copper in equal amount to the Nickel do not interfere. The author found that solutions containing ten times more Copper and Cobalt than Nickel produced deviations of

only 7% and 9% respectively as compared to a solution containing an equal amount of Nickel only.

The sample solution boiled down to about 20 ml. and iron free was transferred to a Nessler's Tube. Two to three drops of liquid Bromine were added to the solution.

One ml. of a 100 p.p.m. Ni solution was measured into another Nessler tube and it was made up to about 20 ml. with a saturated solution of ammonium nitrate. The same quantity of liquid Bromine was also added to this solution. The Bromine was then allowed to dissolve in the solutions. Two to three ml. of conc. ammonia were added to each solution, on shaking the colour of the Bromine disappeared. One ml. of dimethylglyoxime was then added to each solution. It is important that the dimethylglyoxime be added within one minute of the addition of ammonia.

The more intensely hued solution was diluted with distilled water until the colours and intensities of the two solutions were visually matched. The volumes of both solutions were then measured.

Frequent blank determinations were run to check the purity of the reagents used. Large amounts of copper were separated by precipitation of the sulphide, while large amounts of Cobalt were separated by precipitation with a. Nitroso b-Naphthol.

Determination of Cobalt:

Reagents : Acetone C.P.

Ammonium Thiocyanate A.R.Q.

50 gm/100 ml. of water

Sodium Fluoride A.R.Q.

Stannous Chloride A.R.Q.

20 gm. $SnCl_2 \cdot 2H_2O$/100 ml of 2 N HCl.

Cobalt forms a blue solution with an alkali thiocyanate in an acetone-water solution. The relative concentrations of thiocyanate, water and acetone affect the intensity of the colour

produced. Hence it is imperative that the concentrations of these substances be kept constant in both standard and unknown. Ferric iron, even in minute amounts, produces a bright red colour under the same conditions. The colour can be destroyed by addition of sodium fluoride, which complexes the iron as a colourless ferri-fluoride (10).

Copper and Nickel form green solutions under the above conditions. Sandell (9) states that Nickel in ten times larger amount than Cobalt does not interfere, at low concentrations. With larger amounts of Nickel a yellow filter is useful when making a colour comparison. Copper in small amounts does not interfere when stannous chloride is present. Larger amounts of Copper may be removed by precipitation with sodium sulphide in acid solution. Molybdenum, if present in some amount also produces a red colour, intensified by stannous chloride. This colour is not as easily dispelled as that caused by ferric iron and may completely mask the cobalt-blue.

Acetone was added to a sample of about 20 ml, prepared as described above. Sufficient acetone was added so that the solution contained acetone and water in equal volume. The solution was transferred to a Nessler tube. One ml. of 100 p.p.m. Cobalt, in a similar tube was made up to 20 ml. with saturated Ammonium nitrate solution.

Acetone and thiocyanate were added in the same proportions as in the case of the "unknown" solution. Approximately 0·1 grm. Sodium Fluoride and a few ml. of Stannous chloride solution were added to each sample.

The intensities of the solutions were then compared and the more intensely coloured solution was diluted with acetone, water and thiocyanate, so that their respective concentrations remained the same. When a colour match was obtained the volumes of both solutions were measured.

The results for Nickel were available at this stage and when necessary this metal was extracted with dimethylglyoxime in chloroform.

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Accuracy:

Sandell (9) states that a colour difference between two colour . lutions of which the one is 7% more concentrated than the other can be observed by a person with a normal vision. This figure applies regardless of whether concentrated or dilute solutions are used. It would appear that dilute solutions can actually be matched more closely than concentrated solutions with more intense colours.

When a number of comparisons are made the accuracy will of course increase.

Some results will be 7% (±) too high and others 7% (±) too low. But the average will approximate the true result within at most 2 or 3%. In practice it was found that with several results available, the mean of the highest and lowest figures was very close to the mean of all the results but, in view of the fact that it is difficult to obtain 100% pure pyrite, it may be safer to assume a maximum error of 10%, even though the analysis figures indicate a greater accuracy than this.

At least three determinations were carried out on each sample and in many cases four or five.

THE QUALITATIVE ESTIMATION OF COPPER AND MANGANESE

Manganese:

Manganese in the pyrites was detected by oxidizing this metal to permanganate.

Silver Nitrate solution was added to a hydrochloric-nitric acid solution of a pyrite, to suppress the action of chloride ions, because this element interferes in the oxidation of Manganese to the permanganate. Additional Nitric Acid was added, and Sodium Phosphate solution to remove the yellow colour caused by Ferric Iron. Solid Potassium Periodate was added to the solution and it was then boiled for about two minutes. Solutions which contain manganese

developed a pink colour, under these conditions.

All samples were treated under standard conditions, so that even though no actual quantitative measurement is involved, the results may still be compared.

Copper:

A "spot" test technique described by Feigl (11) was used to detect the presence of copper.

The reagent used was a 1% alcoholic solution of Rubeanic Acid acidified with acetic acid. A drop of the solution, to be tested, was placed on a filter paper and a drop of reagent was then added. The copper compound which is green to black remains in the position of the original drop, whereas the soluble cobalt and nickel compounds, which are respectively brown and blue, migrate to the outside of the drop.

DESCRIPTION OF SPECIMENS

The following prefixes were used to denote samples of similar affinities, or from the same area :

H - Hydrothermal pyrites

S - Pyrite of sedimentary origin

B - Pyrite associated with basic igneous rocks

W - Pyrite from Witwatersrand "banket" reefs or from intrusives

K - Pyrite from the Copper-Cobalt ore-body at Kilembe, Uganda.

A description of each sample is given below, based on an examination of hand specimens, crushed pyrite concentrate under a binocular microscope and polished sections.

Occasionally reference is made to some relevant aspects of the geology of the mine or area from which a particular specimen comes.

HYDROTHERMAL PYRITE.

Specimen H1

Massive pyrite was obtained from the Leeuwbosch Lead Mine, which is situated 10 miles north of Thabazimbi. Galena-pyrite mineralisation occurs in the Transvaal dolomite at this mine. Microscopically the massive pyrite is seen to be veined by later quartz-carbonate gangue.

Specimen H2.

This specimen, from the "Marico Lead Belt" in the Western Transvaal consists of a large octahedron of pyrite which is slightly veined by fluorite and galena. The specimen may be regarded as typical of these mesothermal deposits.

Specimen H3.

Cubes of pyrite from a Kimberlite pipe in the Kimberley area were analyzed. A small amount of gangue occurs as fragments and thread-like inclusions in the pyrite.

Specimens H4 - H6.

Specimen H4 is a pyrite concentrate from the flotation plant at the Pilgrimsrest Gold Mine in the Eastern Transvaal.

Specimen H5 is a grey quartzite which contains disseminated anhedral grains of pyrite and a small amount of magnetite, from the Sable-Pilgrimsrest area.

Specimen H6 consists of massive pyrite in a quartz vein, showing later magnetite and quartz microscopically, from Columbia Hill, Pilgrimsrest. Swiegers (12) regards the Pilgrimsrest Gold deposits as mesothermal.

Specimens H7 - H10.

Four specimens, from the Bourke's Luck Mine, Pilgrimsrest area, represent both generations of pyrite observed in this mine. Barnard (13) states that the later generation, a fine grained pyrite is generally associated with much higher gold values than the earlier pyrite. Specimen H7, an extremely fine-grained massive type of pyrite, veined with gangue and small amounts of chalcopyrite is of the later generation and contains 10 dwt. Au/ton. H8 and H10 are both clearly of the first generation of pyrite. Both are coarse grained pyrites with quartz. Microscopically these two specimens display extensive fine quartz veining, simulating cracked porcelain.

This deposit is probably related genetically to the Pilgrimsrest deposits. Barnard (13) considers the deposit to be mesothermal.

Specimens H11, H12.

Two pyrites, H11 and H12 from the Leeuwpoort Tin Mine, Rooiberg, N.W.Tvl., were analyzed. The deposit consists of pyrite-chalcopyrite-cassiterite mineralisation in Rooiberg quartzites (14). The mineralogy suggests a high temperature deposit. Specimen H11 consists of an aggregate of subhedral pyrite crystals with a small amount of gangue. Simple and twinned pyritohedrons and octahedrons, up to $\frac{1}{2}$" in size, in ankerite constitute specimen H12.

Specimen H12.

Specimen H13 consists of small crystals of pyrite in a black chert "bar" from the Eagles Nest Mine, Barberton.

A polished section reveals cubes of pyrite, much smaller arsenopyrite laths of rhombic cross-section and larger masses of pyrrhotite. The sulphides show a distinct concentration in bands. Some bands contain only pyrite and arsenopyrite and are free of pyrrhotite, whereas others contain all three ore-minerals. The arsenopyrite which is often completely enclosed by the other sulphides retains its crystal outlines. Close examination reveals slight corrosion of the arsenopyrite, suggesting that it was the earliest sulphide.

Hall (15) has remarked on the great similarity between ores from the Eagles Nest and New Consort Mines, the latter being a high temperature deposit.

Specimen H14.

Minute cubes, octahedrons and pyritohedrons of pyrite occur in small amount with some arsenopyrite and gold in fractures in talc schists of the Primitive System at the Woodstock Mine, at Noordkaap, Barberton District. The mineralisation is typically high temperature. The sample is a composite one, composed of pyrite from fractures all over the mine.

Specimen H15.

Film and spongy pyrite, in a silicified greenstone on the contact of the Ranga Pegmatite, Bikita Tinfields, Southern Rhodesia. This is probably a high temperature pyrite.

SEDIMENTARY PYRITES, S1 - S4.

Four specimens containing pyrite of sedimentary origin, all from different horizons in the Karroo system were included in this investigation.

In Specimen S1, very fine pyrite forms the matrix of a fine-grained sandstone, from the Karroo outlier at the old Cyferfontein Coal Mine, near Zuurbekom, Johannesburg.

Specimen S2 contains pyrite in blobs on the bedding planes of a carbonaceous shale. Microscopically the blobs consist of polygonal carbonaceous shale. Microscopically the blobs consist of polygonal Band" in grains with sutured contacts. The specimen is from the "White Ran

Specimen S3 consists of marcasite concretions from the base of the Cave Sandstone, Fouriesburg district, O.F.S. The strongly anisotropic marcasite occurs in raggedly intergrown grains which are elongated radially.

Transverse and bedded veins of pyrite in coal, from the floor of the No.2 Seam, Navigation Colliery, Witbank, provided the material for Specimen 4.

PYRITE ASSOCIATED WITH BASIC IGNEOUS ROCKS - B1, B2

Although some of the pyrites, discussed under other headings should be included here, it was decided, for the sake of continuity, to include only two isolated specimens in this category.

B1 is a specimen of a discordant veinlet of pyrite and pyrrhotite in a diabase sill intrusive into the Government Reef Series on Elandsheuvel, near Klerksdorp. The sample was obtained from a drill-hole core.

Simple and twinned cubes of pyrite in talc-chlorite schist, a few 100' in the footwall of a chromitite body at Selukwe Peak Mine, Selukwe constitutes sample B2. Most geologists favour an origin by magmatic segregation for the chromite deposits of Selukwe and the pyrite could well have originated through a similar mechanism. No pyrites of early magmatic origin, e.g., those at Insizwa, Vlakfontein, etc., were studied. Pyrite is not very common in these ores, while sulphides of nickel are quite c mon.

PYRITES FROM "WITWATERSRAND SYSTEM" GOLD MINES

Specimen W1.

Banket from the Battery Reef, one of the Kimberley Reefs, from West Rand Consolidated Gold Mine, near Krugersdorp. The specimen contains "buckshot" pyrite, with replacement, occasionally complete, of waterworn

pebbles. Some pebbles exhibit preferential replacement of certain bands of pyrite.

Specimen W2.

Pyrite in dyke, West Rand Consolidated Mine. Microscopically, an aggregate of cubes and octahedrons, isolated crystals and veinlets of earlier quartz. A few very small blobs of chalcopyrite were observed.

Specimen W3.

Pyrite disseminated in banket, East Geduld Mine, Springs.

Specimen W4.

Pyrite, very sparsely disseminated through banket of the Dominion Reef, Dominion Reefs Mine, Klerksdorp. In addition this specimen contains chalcopyrite and pyrrhotite in small amount.

Specimens W5 - W12.

Eight specimens of rock containing pyrite were obtained from the Durban Roodepoort Deep Gold Mine, in the area near No.6 Shaft. One specimen, W9, was taken on 26 Level and consists of oval aggregates, of pyrite crystals, developed in homogeneous quartzite, 2' below the contact of a basic sill. The remaining specimens were taken on 28 Level.

W5, W6, W7, W10, W11, W12 are all specimens of Main Reef Banket, with pyrite scattered through the matrix, replacing pebbles or, on the edges of pebbles. Specimen W10 is slightly different in that it contains small amounts of pyrrhotite as elongated blotches.

Specimen W5 was taken 50' from a basic dyke.

" W6 " " 8' " " " "

" W7 " " 1' " " " "

Specimen W6 consists of pyrite from the dyke. The pyrite occurs in this specimen as anhedral grains or as regularly shaped individuals moulded on pre-existing gangue.

Specimen W12 was taken 35' from a syenite dyke

" W10 " " 25' " " " "

" W11 " " 15' " " " "

These three specimens, i.e., W10-W12, were more than 50' away from a basic dyke.

Specimen W13.

W13 is a specimen of banded pyritic quartzite from the Crown Mines, Johannesburg. Unfortunately it is not known which horizon the specimen was taken from, or its relation to basic dykes or sills.

PYRITES FROM KILEMBE, UGANDA. K1 - K6.

Kilembe is situated in the foothills of the Ruwenzori mountains, Uganda.

The main ore minerals are chalcopyrite and nickeliferous linnaeite accompanied by pyrite, pyrrhotite, and magnetite which occur in highly metamorphosed "Basement" amphibolites, granulites and schists.(16) The origin of this deposit is enigmatic and it has previously been assumed to be hydrothermal although recent exploration based on an assumed sedimentary origin has been fairly successful.*

Specimen K1.

Irregular masses of pyrite, veined by magnetite. In the veinlets occur wisps of chalcopyrite, mainly replaced by the magnetite.

Specimen K2.

Fine-grained massive pyrite in amphibolite, veined by magnetite and gangue. The amphibolite has fine stringers of pyrite and pyrrhotite.

Specimen K3.

Portion of a very large octahedron, one edge measures approximately 30 mm. Microscopically the crystal is traversed by veins of magnetite containing fragments of chalcopyrite and rarely pyrrhotite crystals.

Specimen K4.

A fine-grained pyrite of sugary appearance.

Specimen K5.

Very fine-grained pyrite in granulite.

Specimen K6.

Disseminated, irregularly shaped grains of pyrite in schist.

*Personal communication, Dr G.R.Davis.

OTHER SPECIMENS OF PYRITE, 01 - 03.

Specimen 01.

Cubes of pyrite, from 5 to 10 mm. long, in the "White Dolomite" less than 200' above a copper ore -body at Mufulira, Northern Rhodesia.

Specimen 02.

Irregular masses of pyrite in the foot-wall dolomite at Thabazimbi Iron Mine, N.W.Tvl. The polished section shows one generation of pre-pyrite carbonate and another of post-pyrite carbonate.

De Villiers (17) has suggested a hydrothermal origin for the iron ores of Thabazimbi, but the majority of geologists are inclined to view this deposit as the result of enrichment by iron-bearing meteoric solutions.

Specimen 03.

Altered Karroo dolerite with scattered specks and little veinlets of pyrite. The rock consists of cloudy plagioclase, altered pyroxene, chlorite and a fair amount of Leucoxene. Many of the larger individuals of pyrite are rimmed by thin coverings of zeolite. This specimen was taken in the Bethlehem District, O.F. S.

THE COBALT NICKEL CONTENT OF SOME SOUTH AFRICAN PYRITES

Spec. No.	Locality	Description	%Ni	%Co.	Co:Ni ratio	Other elements
H1	Leeuwbosch	Galena-Pyrite mineralisation	0·012	0·012	1:1	Cu,Mn
H2	Maricc,W.Tv.	Pb-Zn,fluorite "	0·017	0·063	4:1	
H3	Kimberley	Pyrite from Kimberlite	0·068	0·062	1:1	Cu,Mn
H4	Pilgrimsrest	Flotation concentrate	0·05	0·020	1:2½	Cu,Mn
H5	Sabie Area	Pyrite in quartzite	0·047	0·043	1:1	
H6	Columbia Hill	Massive pyrite with quartz	0·079	0·014	1:5⅝	Cu
H7	Bourke's Luck	Fine grained auriferous/ pyrite	0·16	n.d.		Mo,Cu
H8	" "	Coarse-grained pyrite	0·077	0·021	1:4	Cu
H9	" "	Disseminated, fairly fine-grained	0·060	0·054	1:1	Cu
H10	" "	Coarse grained pyrite	0·049	0·019	1:2½	Cu
H11	Leeuwpoort	Coarse crystalline	0·056	0·10	2:1	Mn
H12	"	Coarse, with ankerite	0·20	0·027	1:7	Mo,Mn
H13	Eagles Nest	Pyrite from chert bar.	0·014	0·014	1:1	Mn,Cu
H14	Woodstock	Fine pyrite in fractures	0·37	0·16	1:2	Mn,Cu
H15	Bikita, S.R.	On contact of pegmatite	0·094	0·020	1:5	Cu
S1	Cyferfontein	In Karroo sandstone	0·003	<0·001		Cu,Mn
S2	Rietpan	In black carbonaceous shale	0·02	<0·001		Cu,Mn
S3	Fourieburg	Karroo Marcasite concretion	0·008	<0·001		Mn
S4	Navigation Clly	Karroo coal	0·006	<0·001		Cu,Mn
B1	Klerksdorp	Pyrite veinlet in diabase	0·014	0·029	2:1	Cu
B2	Selukwe	In footwall of chromite	0·094	0·22	2:1	Cu
W1	West Rand Cons	Banket pyrite,Battery Reef	0·043	0·034	4:5	Cu
W2	" " "	Pyrite from dyke	0·12	0 10	1:1	Cu
W3	East Geduld	Composite Reef	0·062	0·031	1:2	Cu
W4	Dominion Reefs	Normal banket	0·10	0·083	4:5	Cu,Mn
W5	Durban Roodepoort Deep	Banket 50' from basic dyke	0·064	0·079	5:4	Cu
	" " "	" 8' " " "	0·054	0·085	3:2	Cu
W6	" " "	" 1' " " "	0·073	0·096	4:3	Cu
W7	" " "	Pyrite from basic dyke	0·022	0·061	3:1	Cu,Mn
W8	" " "	2' below sill	0·027	0·020	3:4	Cu
W9	" " "	25' from syenite dyke	0·067	0·084	5:4	Cu
W10	" " "	15' " " "	0·063	0·083	4:3	Cu
W11	" " "	35' " " "	0·063	0·086	4:3	Mn
W12	" " "	Banded pyritic quartzite	0·11	0·070	2:3	Cu
W13	Crown Mines	Cubes from near ore-body	0·004	0·045	10:1	Cu
O1	Murullira	Masses in footwall dolomite	0·018	0·012	1:1½	Mn
O2	Thabazimbi	Banded pyritic quartzite	0·012	0·014	1:1	Cu
O3	Bethlehem		0·014	1·917	137:1	Cu
K1	Kilembe,Uganda	Massive, with magnetite				
K2	" "	Semicrystalline with pyrrhotite	0·021	1·928	92:1	Cu
			0·044	2·162	49:1	Cu
K3	" "	Large octahedron	0·028	1·728	62:1	Cu
K4	" "	Very fine grained	0·010	1·500	137:1	Cu
K5	" "	Fine grained in granulite	0·13	1·500	12:1	Cu
K6	" "	Semicrystalline in schist				

The cobalt contents of specimens S1, S2, S3 and S4

were determined spectrographically by Dr W.R.Liebenberg, Government

Metallurgical Laboratory, Johannesburg.

DISCUSSION OF RESULTS

The results obtained show to some extent that pyrites from one area are often very similar in trace element content, although there are several exceptions to this statement.

The results, incomplete as they are, do indicate that there are fundamental differences between many genetically different pyrites.

THE HYDROTHERMAL PYRITES:

The content of Cobalt in the 14 hydrothermal pyrites, analyzed for this metal, varies from 0·008% to 0·1% while the nickel content varies from 0·012% to 0·37%. Taking the arithmetic mean of the Cobalt and Nickel concentrations in all the hydrothermal pyrites, we find

$$Ni = 0{\cdot}09\%$$

$$Co = 0{\cdot}045\%,$$

that is a Co : Ni ratio of 1:2, which means that in all the hydrothermal pyrites taken as a whole there is twice as much Nickel as Cobalt. This agrees well with results obtained by Hawley (5) who found Co : Ni = 1:2 (approximately) for all the mines he investigated, with the sole exception of Porcupine "high temperature" pyrite. On the other hand both sets of results disagree with the statement made by Carstens (1) and quoted by Rankama and Sahama (18). Carstens states that hydrothermal pyrite he investigated always contains more Cobalt than Nickel.

If we accept 0·01% Ni and 0·04% Co, i.e., Co : Ni = 4 : 10 as quoted by Goldschmidt (19), then the hydrothermal pyrites do not represent a phase with Cobalt enriched with respect to Nickel as greatly as some of the work by Scandinavian and German geochemists would indicate. Even if we accept a slightly different value for Cobalt in the upper lithosphere, namely Co : Ni = 3 : 10, as suggested by Sandell and Goldich, the relative enrichment of Co is still not as striking as one would expect.

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It is quite apparent that Cobalt and Nickel are enriched in hydrothermal pyrites as a rule, but the relative enrichment of Cobalt as compared with Nickel does not appear to be of any great magnitude.

The ionic radii of Cobalt and iron, and the unit cell lengths of the di-sulphides of these two metals are practically identical whereas these constants are slightly different for Nickel. Nickel (8) has adduced data to show that Cobalt is more chalcophile than Nickel. But the relation between Cobalt and Nickel in the upper lithosphere is rather complex, as indicated by Rankama and Sahama. Cobalt is generally supposed to be enriched relative to nickel in residual and late magmatic deposits.

The results for South African hydrothermal deposits suggest that high temperature pyrites tend to contain the most Nickel and Cobalt. This is not always true, e.g., the low results for the high temperature Eagles Nest deposit.

The mean results of five high temperature pyrites (H11-H15) is 0·14% Ni and 0·05% Co. Similarly, for three lower temperature pyrites (H1, H2, H3) Nickel = 0·032% and Cobalt = 0·04%. This comparison is strictly not very sound. Even so, it does seem to suggest that the Nickel content of pyrite is more sensitive to temperature changes than the Cobalt content.

An interesting fact emerges when we consider the trace element characteristics of different generations of pyrite in the same deposit. Bourke's Luck pyrite is the best example available. At this mine there is an earlier coarser grained pyrite and a later generation, much finer grained and auriferous. (13)

Specimens H8 and H10 represent the earlier, Specimen H7 the later and possibly H9 represents an intergrowth of both generations. The earlier generation is characterized by a Cobalt content of about 0·02% and about three times more Nickel while the later auriferous generation is characterized by a relatively high Nickel content and a fair amount of Molybdenum.

A similar explanation could also be advanced for the two radically different pyrites from Leeuwpoort Tin Mine, Rooiberg. The one pyrite contains 0·2% Ni and only one seventh of that amount of Cobalt, while also containing some Molybdenum. In the other pyrite Molybdenum was not detected and there was actually twice as much Cobalt as Nickel in this pyrite.

The two ore-samples from the Pilgrimsrest area, H5 and H6 contain Cobalt and Nickel in quite different proportions. But, the Canadian investigators have detected so many factors which may influence the trace element content of pyrite, even in one mine, that this discrepancy is not surprising. The flotation concentrate from the T.G.M.E. plant at Pilgrimsrest, may conceivably give an indication of the bulk composition of pyrite from the entire area.

Most of the hydrothermal pyrites contain copper and some contain manganese.

It should again be emphasized that with so few results from so many areas, the results at best can only indicate trends or possibilities.

SEDIMENTARY PYRITES:.

Although only three pyrites and one marcasite, of sedimentary origin were analyzed these few samples have provided very interesting results. The Nickel content of these four specimens varied from 0·02% to 0·003%.

Repeated colorimetric tests failed to show the presence of Cobalt. Dr W.R.Liebenberg of the Government Metallurgical Laboratory, carried out a spectrographic examination of the specimens and could not detect Cobalt in any one. The smallest amount possible of detection under the conditions of the examination is approximately 10 p.p.m. Thus, the pyrites and the marcasite contain at least several times more Nickel than Cobalt, the Co : Ni ratio may well be of the order of 1 : 10 or even greater, in favour of Nickel. These results are in excellent agreement with those of Carstens (1) who reports less than 10 p.p.m., or 0·001% of Cobalt and amounts of Nickel approximately twenty times larger.

All four specimens contain Manganese, some in appreciable amount. Yet only one third of all the other pyrites analyzed contain manganese. Carstens (2) and Minguzzi and Talluri (7) report from 0·01 to 0·1% Mn in sedimentary pyrites, and usually much less in hydrothermal pyrites.

The three pyrites all contain traces of Copper while this metal is not present in the specimen of marcasite.

It is difficult to explain the marked preponderance of Nickel over over Cobalt in sedimentary pyrites, even though Nickel is 2 to 3 times more abundant than Cobalt in the upper lithosphere.

PYRITE ASSOCIATED WITH BASIC IGNEOUS ROCKS:

The following results were obtained from pyrites in basic igneous rocks, or, obviously genetically related to them:-

Specimen	Area	Description	% Ni	% Co.	Co : Ni
B1	Klerksdorp	Veinlet in diabase	0·014	0·029	2 : 1
B2	Selukwe	In Talc-Chlorite ,	0·094	0·21	2 : 1
W2	West Rand Cons.	Pyrite in dyke	0·11	0·10	1 : 1
W8	Durban Deep	" " "	0·022	0·061	3 : 1
W9	" "	2' below sill	0·027	0·020	3 : 4

None of these pyrites can, without fear of contradiction, be regarded as the result of magmatic differentiation, i.e., magmatic pyrites. Most probably represent a hydrothermal phase, associated with basic igneous rocks.

The mean Cobalt content of the five specimens is 0·08% and the mean Nickel value is 0·05%, thus Co : Ni = 3 : 2, a substantial enrichment of of Cobalt relative to Nickel.

The trend displayed by these specimens is not inconsistent with higher values reported by Minguzzi (7) for magmatic pyrites, which show even greater enrichment of Cobalt.

Rankama and Sahama (18) p.679 state: "Generally speaking, Cobalt has a higher tendency to remain in residual melts and solutions during magmatic differentiation than Nickel".

PYRITES FROM KILEMBE, UGANDA.

These pyrites from Uganda display an unusually high Cobalt content, from 1·50% to 2·13 Co. The Nickel content is quite low, it varies from 0·01% to 0·12%, with Co : Ni ratios from 137 : 1 to 12·5 : 1. The mean values are 1·80% Co and 0·04% Ni giving a Co : Ni ratio of 38 : 1.

It may be said that the high Cobalt values are due to contamination by linnaeite, but this is unlikely due to the following reasons :

(a) The only other sulphide seen in polished sections, apart from pyrite was chalcopyrite, and that mineral only in small amount in two of the polished sections.

(b) The Linnaeite from this mine is nickeliferous and with one exception the Nickel values are low; 0·01 - 0·04%. Specimen K6 contains 0·12% Ni, but the Cobalt content is the second lowest of the six specimens analyzed.

(c) The Cobalt values are very much of the same order, with only about 30% variation.

(d) Björlykke has reported up to 1·25% Cobalt in a Norwegian pyrite (19).

Regardless of whether we consider this deposit to be hydrothermal or sedimentary in origin, it seems that the Co : Ni ratio of the pyrite is genetically quite irrelevant. It is likely that this extreme enrichment of Cobalt compared to Nickel is conditioned by the great availability of Cobalt in the ore.

The author suggests tentatively that after the deposition of the ore, during the intense metamorphism of the area, some migration of the metals took place, and thus the pyrite acquired its high Cobalt content. PYRITES FROM "WITWATERSRAND SYSTEM" MINES

PYRITES FROM "WITWATERSRAND SYSTEM" MINES

This group comprises only 13 samples and very few definite conclusions can be drawn. At best, the results indicate only trends.

The pyrite is of two types :-

(a) Pyrite in or near dykes

(b) Pyrite in banket, some distance away from dykes or sills.

The following are results obtained, incomplete as they are, which indicate the effect of a dyke. This "traverse" was carried out on the 28 Level, No.6 Shaft, Durban Roodepoort Deep Gold Mine.

		% Ni	% Co	Co : Ni Ratio
W8	Pyrite in basic dyke	0·022	0·061	3 : 1
W7	Pyrite in banket, 1' away	0·073	0·096	4 : 3
W6	Pyrite in banket, 8' away	0·054	0·085	3 : 2
W5	Pyrite in banket, 50' away	0·064	0·078	5 : 4

Three specimens, W10, W11 and W12, which were taken from 15 to 35' away from a syenite dyke have rather consistent results and these probably represent pyrite unaffected by the action of basic dykes. In these three specimens Nickel varies from 0·063% to 0·087% and Cobalt from 0·083 - 0·086%. These results agree quite well with those obtained in the specimen 50' away from the basic dyke. The mean values for these four specimens are 0·064% Ni and 0·083% Co. The Nickel values are very similar and specimen W10, which was slightly different (0·003% Ni) was found to contain a small amount of pyrrhotite, which may account for the deviation. It seems logical to assume that the pyrite in Main Reef Banket, at Durban Deep Gold Mine, where unaffected by basic dykes contains amounts of the order of 0·064% Nickel and 0·083% Cobalt, with a Co:Ni ratio of 4 : 3.

Three other specimens of Banket yielded results as follows:-

			%Ni	%Co	Co : Ni
W1	West Rand Cons.	Battery Reef	0·043	0·034	4 : 5
W3	East Geduld	Composite "	0.062	0·031	1 : 2
W4	Dominion Reefs	Dominion "	0·10	0·083	4 : 5

It is not known whether any of these three specimens were taken from near basic dykes. The rather high results for Dominion Reefs pyrite may possibly be due to the proximity of a hanging wall sill which occurs at the mine.

Similarly, for the banded pyritic quartzite from Crown Mines, with 0·10% Ni and 0·07% Co, it is not known which horizon the specimen represents.

All the pyrites from dykes and banket contain traces of copper.

OTHER PYRITES 01 - 03

One specimen from the Northern Rhodesian Copper Belt gave fairly interesting results. The specimen, from Mufulira, has a Co : Ni ratio of 10 : 1, which is the only other pyrite analyzed which approaches the high Co : Ni ratios of Kilembe.

A pyrite from the footwall at Thabazimbi, 02, contains 0·018% Co and 0·012% Ni. It also contains a trace of Manganese.

Pyrite from an altered dolerite in the Free State contains pyrite closely associated with zeolite and this suggests that it could have been deposited by the late thermal solutions which are known to have affected some dolerites.

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SUMMARY OF DISCUSSION

Hydrothermal Pyrite : Co : Ni = 1 : 2 (±)

Hydrothermal phase with basic igneous rocks

Co : Ni = 3 : 2 (±)

Sedimentary Pyrites : Co : Ni = 1 : 10, or greater.

The results obtained on pyrites from the Witwatersrand suggest the following lines for further research:-

(a) *The effect of intrusives on pyrite in the banket.*

(b) Lateral and vertical variations in Cobalt-Nickel content of pyrite in a specific "banket" reef.

(c) The possibility of correlating "banket" reefs on the basis of their trace element content.

(d) The influence on the Co : Ni content of pyrite by co-occurring minerals, e.g., "carbon", pyrrhotite, etc.

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BIBLIOGRAPHY

1. C.W. Carstens - "Uber den Co-Ni gehalt norwegischer Schwefelries Schwefelkiesvorkommen."

   Kgl. Norske Videnskab. Selskabs. Forh. 15,p.165-168, 1942.

2. C.W.Carstens - "Ein never Beitrag zur geochemischen Characteristik Norwegische Schwefelkieserze".

   Kgl. Norske Videnskab.Selskabs.Forh.15, p 1-4,1942.

3. C.W.Carstens - "Uber Kupferhaltige Kiesvorkommen des Leksdaltypus".

   Kgl. Norske Videnskab. Selskabs.Forh.15, p.161-163, 1942.

4. P.E.Auger - "Zoning znd District variations of the minor elements in pyrite of Canadian Gold Deposits".

   Econ.Geol. Vol. 36, 1941 p.401-423.

5. J.E.Hawley - "Spectrographic Studies of pyrite in some Eastern Canadian Gold Mines".

   Econ. Geol.Vol.47. 1952. p.260-304.

6. C. Munguzzi - "Ricerche Sui Costituenti Minori di Piriti Italiane".

   Soc.Miner. Italiana. Rend an 5, p.59-60, 1948.

7. C.Minguzzi and A. Talluri - A."Dosatura spettrograffica del Nichel, del Cobalto, del rame e del Manganese in Piriti Italiane.

   Soc. Miner. Italiana. Rend. an 7. p. 48-50, 1951.

8. E.H.Nickel - "The Distribution of Iron, Manganese, Nickel and Cobalt between coexisting pyrite and biotite in wall rock alteration".

   Am. Mineral Vol. 39, 1954. p.494-503.

9. E.B.Sandell - "Colorimetric Determination of Traces of Metals"

   Interscience Publishers, New York, 2nd Ed. 1950.

10. A.I. Vogel - "A Textbook of Qualitative Chemical Analysis"

    Longmans, Green and Co. 3rd Ed. 1945.

11. F. Feigl - "Qualitative Analyse mit Hilfe von TÜpfelreaktionen/

    Leipzig. 1931.

12/...

12. J.U. Swiegers - "Gold Deposits of the Pilgrims Rest Gold Mining District, Transvaal.

Trans.Geol.Soc. S.Afr. Vol.51. p. 81.

13. K. J. Barnard - "The Geology of the Bourke's Luck Mine, E.Tvl."

M.Sc. Thesis, in preparation, Witwatersrand University.

14. ---------- "The Mineral Resources of the Union of South Africa"

Dept. of Mines, 1940, Govt. Printer.

15. A.L.Hall - "Eagles Nest Mine"

Trans.Geol.Soc.S.Afr. Vol. 37.

16. W.C.Simmons and H.F.Harwood - "Petrology of the Kilembe Copper Deposit".

Geol.Survey of Uganda. Bull. No.2, 1935.

17. J.E. de Villiers - "The origin of the Iron and Manganese Deposits in the Postmasburg and Thabazimbi areas".

Trans.Geol.Soc.S.A. Vol. 47, p. 123-137.

18. Rankama and Sahama - "Geochemistry"

University of Chicago Press, 1950, p.677-647.

19. V.M.Goldschmidt - "Geochemistry"

Oxford University Press, 1954, p.647 - 676.

D E C L A R A T I O N

I hereby declare that the dissertation entitled:

"THE COPPER, COBALT AND NICKEL CONTENT OF SOME SOUTH AFRICAN PYRITES"

has not been submitted for the Master's degree in any other university.

G. L. COETZEE.

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