



UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG



**Petrographic, whole-rock geochemical and $\delta^{34}\text{S}$ isotope
characterisation of the Middelvlei Reef in the
Witwatersrand Basin**

Dissertation in Fulfilment of the degree of Master of Science in Geology

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Declaration

I, Mooa Phuthanang Faith declare that this dissertation titled “*Petrographic, whole-rock geochemical and multiple S isotope characterisation of the Middelvie Reef in the Witwatersrand Basin* “ is my own, unaided work. It is being submitted for the Degree of Master of Science (MSc) at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.

Mooa Phuthanang Faith

06/03/2025

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Abstract

Gold is still one of the greatest sought-after metals in the world. The Witwatersrand Basin in South Africa has historically been a key gold metallogenic province. However, the extensive exploitation of the Mesoarchean Witwatersrand Basin has led to the exhaustion of many of its primary, regionally persistent orebodies known as “reefs”. Consequently, the exploration of secondary composite orebodies within the Witwatersrand Basin has become a necessity. Composite reefs, characterised by multiple auriferous conglomerate beds, present significant opportunities for continued gold recovery in the Witwatersrand Basin. However, their origin and gold content have often been overlooked due to their restricted or localised mineralisation extent and lower gold tenor compared to thin conglomerate beds and gold-rich carbon seams.

The Middelveli Reef serves as an exemplary composite reef, that is found at the bottom of the Central Rand Group in the Witwatersrand Basin. The Middelveli Reef, along with its counterparts such as the Elsburg Reefs, exhibits distinctive features where gold is frequently interlinked with multi-stacked auriferous and pyrite-rich conglomerates. The quartz-pebble conglomerates of the Middelveli Reef are noted for their exceptional pyrite richness, relatively moderate gold grades (i.e., <5 g/t), and thin, alternating multicycle conglomerates, rendering them a complex subject for gold-bearing formation studies.

This research focuses on the morphology and chemical composition of pyrite grains within the Middelveli Reef to explain the depositional environment through comprehensive trace element chemistry and sulphur isotope ($\delta^{34}\text{S}$) analysis. The study identifies various pyrite morphologies based on textural distinctions, classifying them into detrital and authigenic types. Detrital pyrite can be classified as massive, inclusion-bearing (random, planar-laminated, concentrically laminated, and micro-spherical), and coarsely crystalline detrital pyrite. Authigenic pyrite is classified into euhedral/subhedral, overgrowth, infill, aggregates, and pseudo-morphic pyrite.

Conventional and advanced analytical techniques such as reflected light optical microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS), Tescan Integrated Mineral Analyser (TIMA), electron-probe microanalyses (EPMA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and virtual secondary ions mass spectrometry (vSIMS) were employed to investigate the in-situ trace element and $\delta^{34}\text{S}$ composition of pyrite grains.

Proxies such as Au, Au/As ratios, Co/Ni ratios, Ni, and Mo/Ni ratios were used to infer the process of gold enrichment in the Middelvlei Reef. Detrital pyrite grains are characterised by low Co/Ni (1.51 ppm) and high Au contents (3.05 ppm). Contrarily, high Co/Ni (29.96 ppm) and low Au (0.15 ppm) concentrations imply authigenic pyrite grains. The elevated Mo/Ni ratios (0.005 ppm) in these pyrite grains indicate a source from felsic to mafic rocks within the granitoid-greenstone belts of the Kaapvaal Craton.

Sulphur isotopic analyses from vSIMS reveal a broad range of $\delta^{34}\text{S}$ values (-15.39 to +38.25 ‰) in the pyrite grains of the Middelvlei Reef, suggesting multiple sources that include localised sulphurous pools and photochemical reactions. The broad range of high positive (+38.25 ‰) and negative (-15.39 ‰) $\delta^{34}\text{S}$ values are attributed to the high amounts of inclusions observed within the respective grains. Clusters of positive $\delta^{34}\text{S}$ values (-6.32 to +25.27 ‰) observed in detrital pyrite grains imply erosion of sedimentary deposits, whereas low $\delta^{34}\text{S}$ values (-2.18 to +3.87 ‰) in authigenic pyrite grains point towards metamorphic and hydrothermal fluid sources.

These findings suggest that the composite Middelvlei Reef was formed in a combination of high to low-energy braided riverine environments that allowed the accumulation of large sulphide group minerals, which were reworked into auriferous conglomerate channels. Pyrite morphology, chemistry, and isotopic composition indicate that the detrital pyrite grains were generated by a combination of sedimentary and diagenetic processes, while the authigenic pyrite grains recorded fluid mobilisation evidence and multiple re-deposition processes. Detrital pyrite, which is a fingerprint of the composite Middelvlei Reef, was created by erosion and reworking of diagenetic pyrite. This complex process resulted in the accumulation of fine-grained gold within various pyrite grains, alongside other metals like As, Ag, Cu, Ni, Co, and Mo. This study provides insights into the complex depositional and post-depositional processes that have governed gold accumulation in the Middelvlei Reef, in that way laying the groundwork for future exploration and exploitation of similar composite reefs within the Witwatersrand Basin.

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Abbreviations and Acronyms

AE	Euhedral/Subhedral
Au	Gold
Bt	Biotite
Br	Brannerite
Brt	Baryte (Barite)
Ccp	Chalcopyrite
Chl	Chlorite
DC	Coarsely crystalline
DIC	Concentrically laminated
DM	Massive pyrite
dm	decimetre
DIR	Random inclusion-bearing
EPMA	Electron Probe Micro-Analyses
Fl	Florencite
FW	Foot Wall
Ga	Billion years
Gn	Galena
HFSE	High Field Strength Elements
HREE	Heavy Rare Earth Element
HW	Hanging Wall
Hz	Hertz
J/cm ²	Joule per square centimetre
Kao	Kaolinite
Km	Kilometres
Km ²	Square kilometres
kV	Kilovoltage

LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LOI	Loss on ignition
LREE	Light Rare Earth Element
m	metre
Ma	Million years
mA	Milliampere
mm	millimetre
Ms	Muscovite
MVR	Middelvlei Reef
Pa	Pascals
pA	Picoampere
Po	Pyrrhotite
Py	Pyrite
PPB	Parts Per Billion
PPM	Parts Per Million
Qz	Quartz
SEM-EDS	Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy
TIMA	TESCAN Integrated Mineral Analyzer
Urn	Uraninite
µm	Micrometre
VCDT	Vienna-Canyon Diablo Troilite
VCR	Ventersdorp Reef
Wt%	Weight Percentage
XRD	X-ray Diffraction
XRF	Fluorescence

Element names

Ag	Silver
As	Arsenic
Au	Gold
Ba	Barium
Bi	Bismuth
Ce	Cerium
Co	Cobalt
Cu	Copper
Cr	Chromium
Cs	Caesium
Dy	Dysprosium
Er	Erbium
Eu	Europium
Fe	Iron
Ga	Gallium
Gd	Gadolinium
Hg	Mercury
Ho	Holmium
La	Lanthanum
Li	Lithium
Mg	Magnesium
Mo	Molybdenum
Mn	Manganese
Na	Sodium
Nb	Niobium
Nd	Neodymium
Ni	Nickel
P	Phosphorus
Pb	Lead
Pr	Praseodymium
Rb	Rubidium
S	Sulphur
Sb	Antimony
Sc	Scandium

Se	Selenium
Sm	Samarium
Sn	Tin
Sr	Strontium
Ta	Tantalum
Tb	Terbium
Te	Tellurium
Th	Thorium
Ti	Titanium
Tl	Thallium
Tm	Thulium
U	Uranium
V	Vanadium
Y	Yttrium
Yb	Ytterbium
Zn	Zinc

Mineral names and formulas

Almandine	$\text{Fe}_3\text{Al}_2\text{O}_{12}$
Aluminium oxide	Al_2O_3
Arsenopyrite	FeAsS
Baryte (Barite) : BaSO_4	BaSO_4
Biotite	$\text{K}(\text{Mg}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})\text{Si}_3\text{O}_{10}(\text{OH}, \text{F})_2$
Brannerite	UTi_2O_6
Calcium oxide	CaO
Chalcopyrite	CuFeS_2
Chlorite	$(\text{Mg}, \text{Fe})_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$
Chromite	FeCr_2O_4
Chromic oxide	Cr_2O_3
Electrum	$\text{Au}\pm(\text{Ag}, \text{Hg})$
Florencite	$\text{SmAl}_3(\text{PO}_4)_2(\text{OH})_6$
Galena	PbS
Ilmenite	FeTiO_3
Iron oxides	$\text{FeO} - \text{Fe}_2\text{O}_3$
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
K-Feldspar	KAlSi_3O_8
Magnesium oxide	MgO
Manganese oxide	MnO
Muscovite	$\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$
Nickel oxide	NiO
Phosphorus trioxide	P_2O_3
Potassium oxide	K_2O
Pyrite	FeS_2
Pyrrhotite	Fe_{1-x}S
Quartz	SiO_2
Rutile	TiO_2
Sodium oxide	NaO
Silica dioxides	SiO_2
Titanium dioxide	TiO_2
Uraninite	UO_2
Zircon	ZrSiO_4

Chapter 1: Background

1.1 Introduction

Gold (Au) has been a critical commodity throughout human history and its supply has controlled many economies and socio-economic status around the world (Neingo and Tholana., 2016). In some countries such as South Africa, gold mining has established metropolitan cities e.g., Johannesburg (Neingo and Tholana., 2016). For over a century, the global supply of gold was dominated by the Witwatersrand Basin (Figure 1) in South Africa, which to date has produced approximately one-third of all gold ever produced (>54,000 metric tonnes) (Frimmel., 2019; Nwaila *et al.*, 2020). However, gold production in the Witwatersrand Basin has steadily declined from 1000 metric tonnes at 12 g/t in the 1970s to the current levels of <200 metric tonnes per annum at <5 g/t (Neingo and Tholana., 2016). Several factors contribute to this decline, including a consistent decrease in ore quality (grade), depletion of high-grade deposits at shallow depths, extreme mining depths requiring high energy and labour costs, inadequate space for mechanised mining, and hazardous working conditions for workers at these great levels (Frimmel., 2019). As a result of these factors, there is a great deal of interest in discovering another gold deposit like the Witwatersrand Basin.

For over 100 years, debates have surrounded the origin of gold in the Witwatersrand Basin. Numerous published research (e.g., Phillips *et al.*, 1987; Meyer *et al.*, 1994; Law and Phillips., 2005; Agangi *et al.*, 2013; Frimmel., 2014, Frimmel., 2018; Fuchs *et al.*, 2016) have provided more insights into the source of gold in the Witwatersrand Basin, but still differ on the concentration mechanisms. It has now been well established that while the Witwatersrand Basin is not a distinctive deposit type, its size and gold content set it apart from other known deposits of the same type (Nwaila *et al.*, 2020). Several Witwatersrand-type deposits have been found in Brazil, Canada, Australia, and India (Nwaila *et al.*, 2020). Common factors in all the Witwatersrand-type gold deposits are ore constituents e.g., pyrite-uraninite for ore deposits formed before the Great Oxidation Event (GOE) and oxides (haematite + magnetite) for those formed after the GOE, the paragenetic sequence is related to atmospheric O₂ levels, etc (Frimmel., 2005). Gangue minerals such as phyllosilicates were mainly studied previously to constrain metamorphic and hydrothermal overprint in both mineralised horizons (auriferous conglomerates known as reefs and unmineralised regional persistent units e.g., shales; Phillips and Powell., 2015). Although many studies by Agangi *et al.* (2013); and Frimmel (2014) focussed on the Witwatersrand Basin, much attention has been on either high-grade reefs or unmineralised units. Limited studies by Neingo and

Tholana (2016) and Els (1983) have been done on low-grade reefs such as the Middelvlei Reef. The Middelvlei Reef represents a prominent orebody in the Carletonville goldfields of the Central Rand Group (Witwatersrand Supergroup) shown in Figure 1.

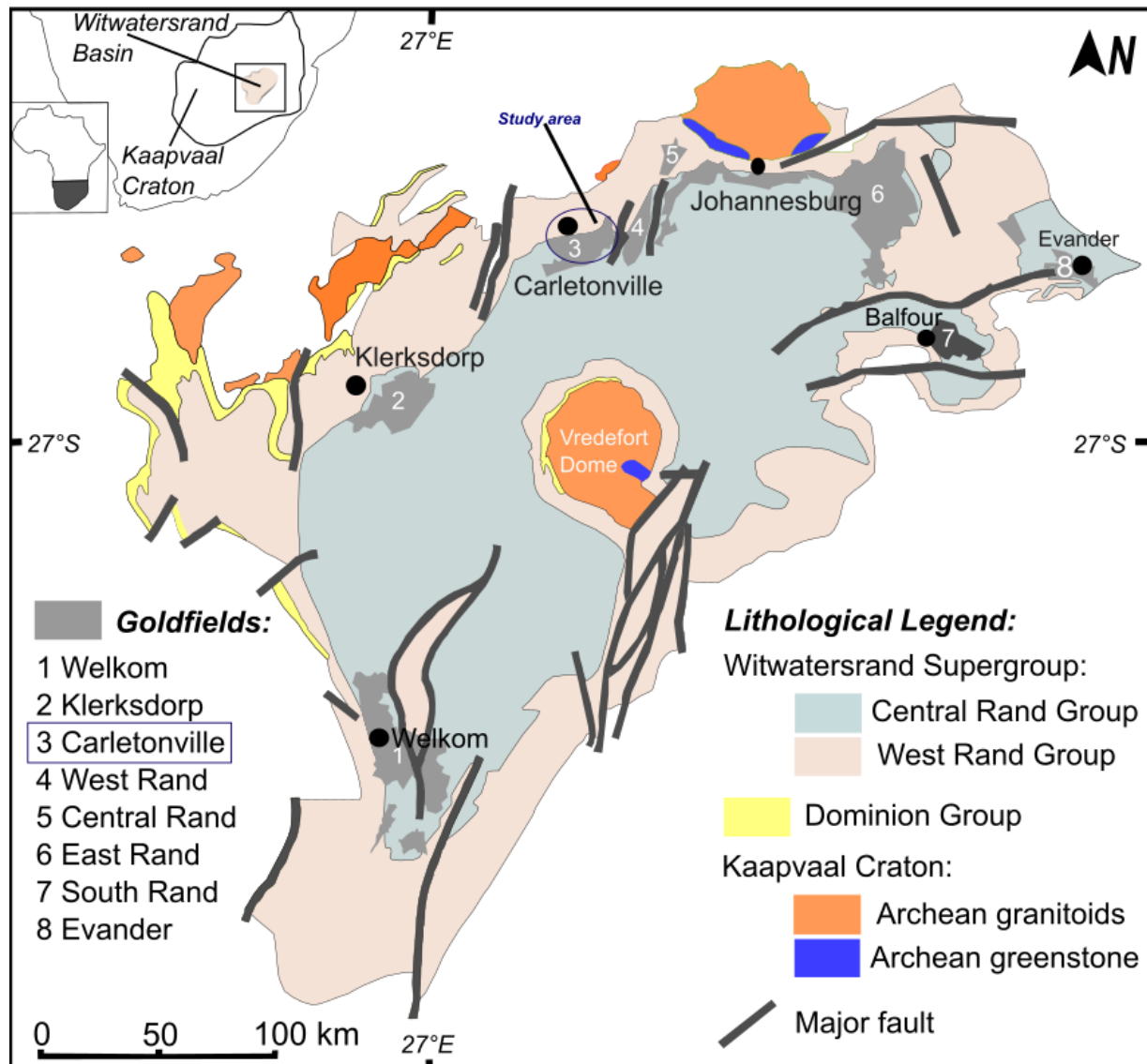


Figure 1: The geological map of the Witwatersrand Supergroup showing various goldfields and the study area which is relevant for this research (modified after Frimmel., 2005).

1.2 Problem Statement

Previous research on low-grade reefs has focused chiefly on sedimentology and geostatistics to convert mineral resources into mineable ore reserves (Els., 1983; Jolly., 1984). The Middelvlei Reef sedimentological facies were described in detail by Els (1983) and have since been updated by various gold mining companies. Jolly (1984) and more recently, Letanta *et al.* (2018) have assessed the spatial arrangement of gold in Middelvlei Reef and discovered that the primary controls on gold content are sedimentological

properties rather than secondary fluid infiltration. It is significant to remember that many previous studies did not take into account the genesis of the Middelvlei Reef. This is partly because it is carbon-poor and has a low gold tenor compared to carbon-rich reefs in the Witwatersrand Basin. The only known detailed reference of gold and pyrite ore-forming processes is Myers (1993), who focused on sulphidation and its importance on prevailing atmospheric conditions during the formation of Witwatersrand-type gold. Therefore, there is still a gap regarding the nature of the gold mineralisation in the Middelvlei Reef and similar low-grade orebodies.

1.3 Research scope

1.3.1 The research aims and objectives

This study's main aim is to critically assess the processes responsible for gold mineralisation in the Middelvlei Reef by examining the gold, pyrite, and associated ore components using the Carletonville goldfield as a case study. This study will investigate the composition of the Middelvlei Reef by incorporating petrology, mineralogy, and geochemical analyses. This will assist in determining the morphological composition and trace element concentration of the grains of pyrite in the Middelvlei Reef and its relationship with gold mineralisation. A second but equally important aim of this study is to use in-situ sulphur (S) contents of pyrite grains in the Middelvlei Reef to understand the nature and source(s) of ligands that facilitated the gold mineralisation.

To fulfil the aims of this study, the following fundamental objectives were addressed:

- Compare and contrast major characteristics between the Middelvlei Reef and other orebodies in the Witwatersrand Basin.
- Assessment of gold distribution relative to various lithologies of the Middelvlei Reef.
- Examination of trace element content per pyrite morphology.
- Assessment of sulphur composition based on isotopic fractionation.

1.3.2 Scope of the study

This study only covers the petrogenic, geochemical, and isotopic characterisation of the Middelvlei Reef. Geological modelling (whether 2D or 3D), resource estimation, and economic evaluation fall outside this study's scope.

1.4 Dissertation structure

There are six chapters in this dissertation. Chapter 1 is the background that gives an overview of the study including the problem statement, aim, objectives, and scope. A review of the literature on the stratigraphy and depositional setting of the research area is given in

Chapter 2. The hypothesis and main research questions of the study will be derived from the detailed discussion of mineralogy, alteration, and metallogenic models. Chapter 3 outlines in depth the research methods for this dissertation, including sample preparation, petrographic, chemical, and isotopic tests. The results for the latter test analyses are outlined in Chapter 4. Chapter 5 provides a thorough explanation of how all of the assessments relate to one another and how to interpret them. The results of the study are compiled in Chapter 6 along with recommendations for more research. The Appendix provides the full set of results. An overview illustration of the dissertation outline is found in the Figure 2 below.

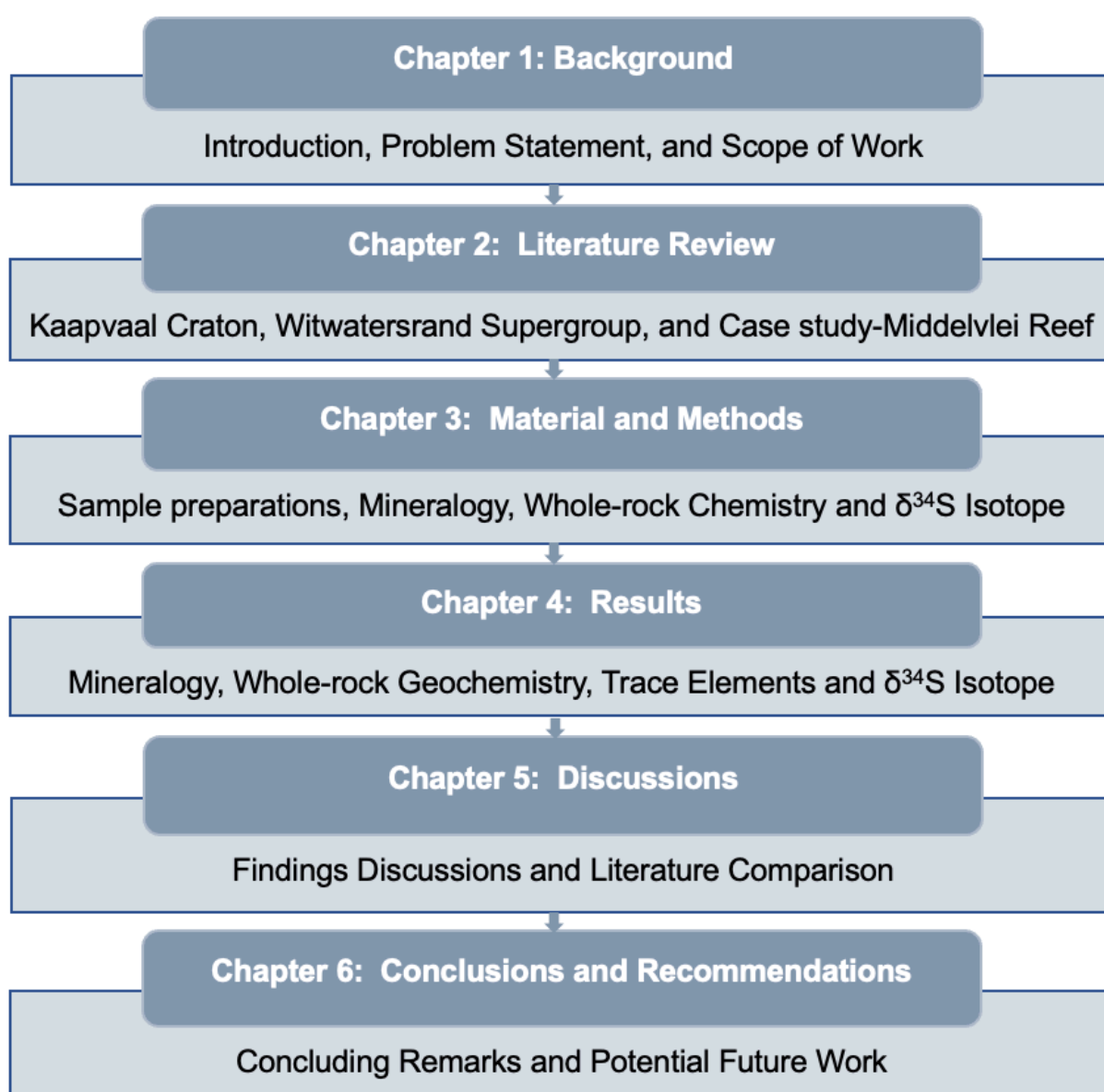


Figure 2: An illustration showing the workflow of the dissertation.

Chapter 2: Literature Review

2.1 Kaapvaal Craton

The Kaapvaal Craton (Figures 3A and 3B) in southern Africa is a representative of one of the oldest and well preserved cratonic blocks (Dirks *et al.*, 2003) and hosts several ancient rocks worldwide (De Wit *et al.*, 1992). However, 86% of the Kaapvaal Craton is covered by younger cover sequences (De Wit *et al.*, 1992). As per De Wit *et al.* (1992), the Kaapvaal Craton is roughly 1.2×10^6 square kilometres (km²). Towards the north of the Craton, the high-grade Limpopo Belt forms a barrier between the Kaapvaal Craton and the Zimbabwe Craton (Dirks *et al.*, 2003).

Granitoids intruded between 3.6 and 2.7 Ga, forming and stabilizing the Kaapvaal Craton (Kirk *et al.*, 2002). These granitoid intrusions settled the continental crust at the beginning levels of arc magmatism and sediment cycle (De Wit *et al.*, 1992). The craton comprises granite gneiss greenstone terranes intruded by granite plutons (De Wit and Ashwal., 1997). Later development of Kaapvaal Craton is from convergent continental arcs resulting in overlying sequences of basins containing volcano-sedimentary rocks (Dirks *et al.*, 2003). The episodes of extension and rifting occurred during the evolution of Gaborone-Khanye and Ventersdorp successions (De Wit *et al.*, 1992). This Craton holds many orogenic gold deposits in the Archean greenstone belts and conglomerate-hosted gold deposits which occur in the Dominion Group, Witwatersrand, Ventersdorp, and Transvaal Supergroups (Nwaila *et al.*, 2020). Economically, the Kaapvaal Craton contains large volumes of gold deposits (Witwatersrand Basin being the most prominent gold anomaly), uranium deposits, platinum group elements (PGE's) deposits, base metals, and non-ferrous metals (Kirk *et al.*, 2002; Nwaila *et al.*, 2020).

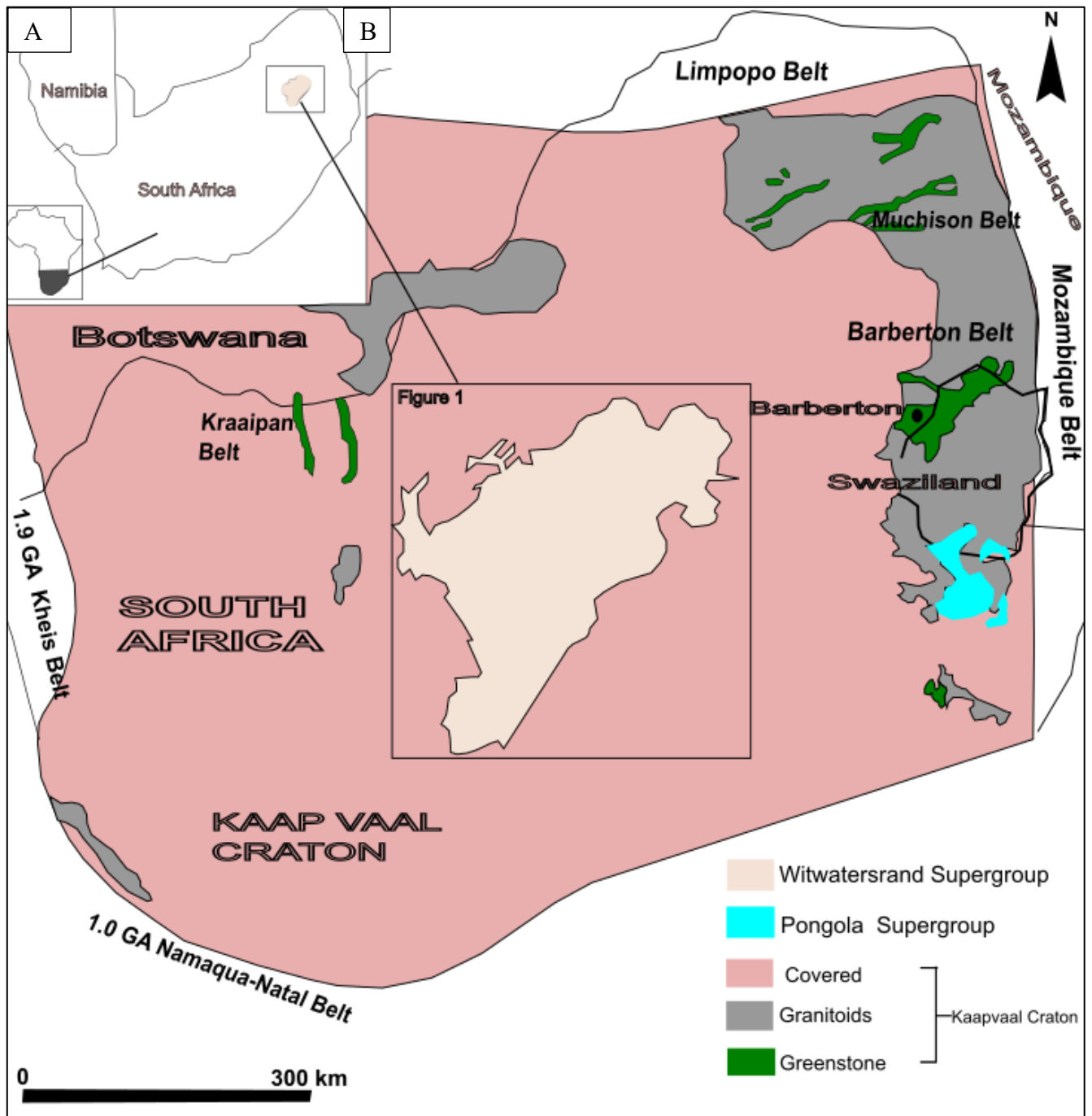


Figure 3: Images showing A) Location of the Kaapvaal Craton in the African continent (modified from Nwaila et al., 2017) and Geology of the Kaapvaal Craton with the Witwatersrand Supergroup occurring in the middle of the craton (modified from Tucker et al., 2016).

2.2 The Witwatersrand Supergroup

2.2.1 Stratigraphic setting of the Witwatersrand Supergroup

The Mesoarchean Witwatersrand Basin in the middle part of the Kaapvaal craton (Jolly., 1984) is the essential economically ore province for Witwatersrand-type gold resources (Figure 1). This structurally preserved basin appears to be stretched over 350 kilometres (km) in the north-easterly direction and 200 km in the north-western direction (Frimmel., 2019) with a maximum diameter estimated to be reaching 300 km (Tucker *et al.*, 2016; Frimmel., 2019). This thick sequence of quartzites, shales with interbedded conglomerates has been subjected to regional (low-grade) metamorphism (Jolly., 1984). The basin fill is composed of up to 7 km of primarily siliciclastic rocks from the Witwatersrand Supergroup, that lies on the bimodal volcanic and coarse-grained siliciclastic, uraninite-rich rocks from the 3074 Ma Dominion Group and rest upon a Palaeo- to Mesoarchean granitoid-greenstone basement (Tucker *et al.*, 2016; Nwaila *et al.*, 2020).

The pyrite quartz-pebble conglomerate layers of the Dominion Reef at the bottom of the Dominion Group is where the profitable Au-U mineralisation formed (Frimmel and Minter., 2002). The Ventersdorp Supergroup (3 km thick), Transvaal Supergroup (15km thick), and Karoo Supergroup sediments covers much of the Witwatersrand Supergroup and the Dominion Group (Jolly., 1984; Tucker *et al.*, 2016; Nwaila *et al.*, 2021). The base of the Ventersdorp is made up of gold-rich quartz-pebble conglomerate beds called the Ventersdorp Contact Reef (VCR) (Nwaila *et al.*, 2020). Deposition of the Transvaal Supergroup were ended by Rooiberg Group bimodal volcanism and emplacement of the layered igneous intrusion called the Bushveld Complex (Tucker *et al.*, 2016). Later, the Vredefort meteorite impact hit the central part of the basin (former Central Rand basin) resulting in a 90 km wide dome structure, vast network of cracks, and low-angle thrusts allowing fluid movement to spread through the Witwatersrand Supergroup stratigraphy (Tucker *et al.*, 2016; Nwaila *et al.*, 2021).

The lower West Rand Group (WRG) and the upper Central Rand Group (CRG) are the two groups of the Witwatersrand Supergroup (Nwaila *et al.*, 2021). Deposition of this notable clastic sedimentary basin commenced with the development of the West Rand Group (thickness of 5150 m) and it is occurring beneath the arenaceous Central Rand Group (thickness of 2880 m) (Frimmel., 2019). Age constraints from detrital zircon and xenotime grains (Kositcin and Krapez., 2004), and a volcanic block in the upper part of the West Rand Group (Armstrong *et al.*, 1991), imply sedimentation times in the West Rand Group between 2985 and 2914 Ma, and in the Central Rand Group between 2902 and 2840 Ma. For up to

5150 m thick sedimentary and minor volcanic rocks of the West Rand Group, a passive margin environment with a palaeoslope continuous to the south and southwest has been proposed (Frimmel and Minter, 2002). The extent of the Witwatersrand strata is obscured by a younger cover over most of the Witwatersrand Supergroup, which ranges in age from Neoarchean to Mesozoic. The Mozaan Group (Beukes and Cairncross, 1991) contains equivalents of the West Rand Group in the upper parts of the Pongola Supergroup (300 km southeast of the known Witwatersrand basin) (Figure 1). As a result, the West Rand Group's known relics represent only a tiny part of what must have been a probably larger basin.

a) West Rand Group

Iron-rich shales, shale, quartzites, and minor conglomerates make up majority of the West Rand Group (Tucker *et al.*, 2016). It comprises widespread magnetite-bearing shales (Law and Phillis, 2005) and extends from shallow marine to distal fluvio-deltaic (Nwaila *et al.*, 2017). This group is separated stratigraphically into the Hospital Hill, Government, and Jeppestown Subgroup as shown by the stratigraphic column in Figure 5 (Nwaila and Frimmel, 2019). Basin-wide unconformities split these subgroups and the division is dependent on various proportions of sandstone/shale (Frimmel and Minter, 2002). Shale dominates the Hospital Hill and Jeppestown subgroups and wacke dominates the Government and Jeppestown subgroups (Frimmel and Minter, 2002).

The base of the local stratigraphy comprising of interbedded quartzite and shale units is the Hospital Hill Subgroup (2.225 m thick) of the West Rand Group (Nwaila *et al.*, 2021). The Hospital Hill Subgroup holds one reef which is the Bonanza Reef occurring in the uppermost unit (Frimmel, 2005). Overlying the Hospital Hill Subgroup are interbedded quartzites and shales with little conglomerates and diamictite beds of the Government Subgroup (750 m thick) (Frimmel, 2019). The Government Subgroup comprises three auriferous subeconomic reefs: Coronation reef, Rivas reef, and Government reef (Frimmel *et al.*, 2005). Resting on the Government Subgroup is the Jeppestown Subgroup which consists of interbedded quartzites and shales with little conglomerate beds and volcanic units of basaltic andesite (Crown formation) (Frimmel, 2019; Nwaila *et al.*, 2021). Economic reefs hosted in the Jeppestown Subgroup are Buffelsdoorn, Outer Basin reefs; and Veldskoen, Inner Basin reefs (Frimmel and Minter, 2002). Other formations dividing the Jeppestown Subgroup are the Roodepoort (300 m thick) and the Maraisburg Formation (100 m thick) (Frimmel, 2019).

b) Central Rand Group

The Central Rand Group consists of coarse-grained siliciclastic rocks and shale (mudstone) with ordinary unconformity surfaces that represent the gradual uplift of the hinterland (Law and Phillips., 2005; Nwaila and Frimmel., 2019). This group was deposited in a retro-arc foreland basin and comprises gold-bearing conglomerates (Nwaila *et al.*, 2020). These conglomerate beds are unusually enriched with more than 90% of the overall gold yielded in the Witwatersrand Basin (Tucker *et al.*, 2014; Nwaila and Frimmel., 2019). Accumulation of this group started after a break of 10 million years in sedimentation which caused the observed unconformable contact in the Witwatersrand Basin (Nwaila *et al.*, 2021). The Central Rand Group is divided into the Johannesburg and Turffontein subgroups as shown in Figure 4 (Nwaila and Frimmel., 2019).

The Johannesburg Subgroup rests unconformably on the West Rand Group. The Johannesburg Subgroup comprises conglomerates of the Blyvooruitzicht Formation (25 m thick) (Frimmel and Minter., 2002; Tucker *et al.*, 2016). The latter formation is overlain by the Main Formation (475 m) consisting of quartzite with minor shale and conglomerates (Nwaila *et al.*, 2021; Frimmel., 2019). The conglomerate beds from the Main Formation are characterised by their heavy enrichment in Au, U, and carbonaceous material (seams) (Nwaila *et al.*, 2021). The bottom layer of the Main Formation contains the Carbon Leader Reef which rests on quartzite and shale (Jolly., 1984). Again, the same reef is overlain by the conglomerate unit called the Middelvlei Reef (Nwaila *et al.*, 2021). Other reefs hosted in the Johannesburg Subgroup are Ada May and Beisa reefs; North, South, and Commonage reefs; Livingstone reef; and Basal, Steyn, Vaal, Saaipias, Leader reefs (Frimmel., 2005).

Overlying the Johannesburg Subgroup is the Turffontein Subgroup (~ 625 m) consisting of quartzite and small conglomerate beds making up the top of the Central Rand Group (Frimmel., 2019). The basal unit of the Turffontein Subgroup is the Kimberly Formation and consists of three economic reefs which are Crystalkop, A, Kalkoenkrans, B, and Kimberly reefs (Frimmel and Minter., 2002). Following the Kimberly Formation is the Elsburg/Eldorado Formation consisting of Denny's, Beatrix, and Composite reefs (Frimmel and Minter., 2002). The Mondeor formation is made up of the Bastard, EA, and Upper Elsburg reefs (Frimmel., 2019).

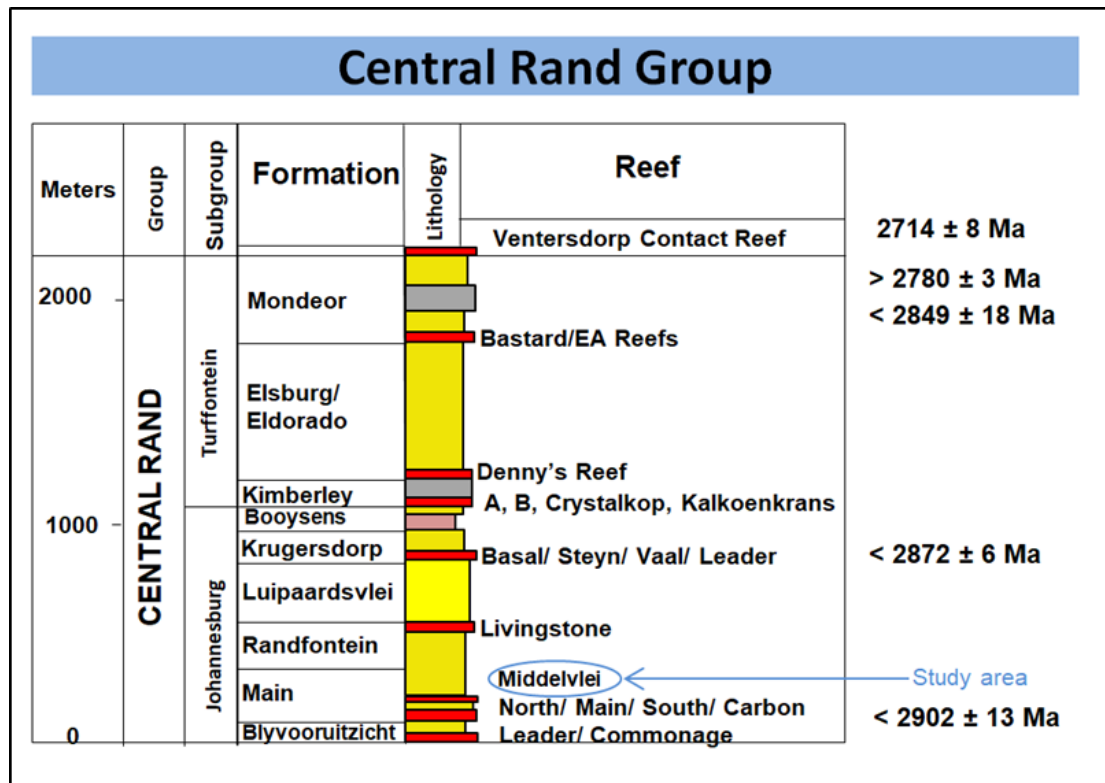


Figure 4: Stratigraphic column of the Central Rand Group illustrating the location of the Middelvlei Reef stratigraphically (ages taken from Robb and Meyer., 1995 and modified from Frimmel and Nwaila., 2020).

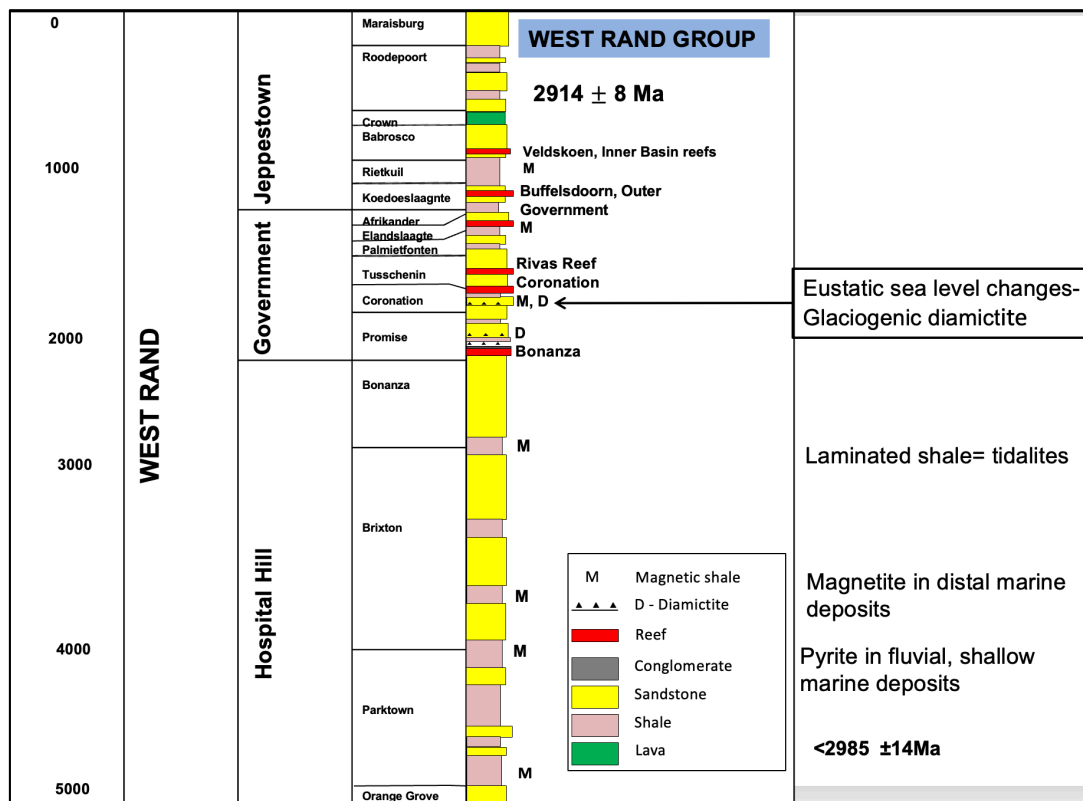


Figure 5: Stratigraphic column of the West Rand Group (ages from Robb and Meyer., 1995 and modified from Frimmel and Nwaila., 2020).

2.2.2 Metallogenic models

The Witwatersrand-style gold mineralisation is not unique to the Kaapvaal Craton (Frimmel., 2014). However, It is typical to many Archean and Paleoproterozoic landmasses (Law and Phillips., 2005; Frimmel., 2014). The unique nature of the Witwatersrand Basin can be clarified by its fortuitous conservation underneath a substantial layer of flood basalt that is resistant to erosion and the voluminous impact melt sheet (Frimmel and Nwaila., 2019). What makes these deposits distinguishable from other examples of this type of mineralisation is the gold that is occurring in various textural regions, the significant gold endowment, the bounty of gold-rich carbon seams that represent former microbial mats, the lack of gold nuggets and significantly enriched Os contents associated with Au (Minter *et al.*, 1993; Frimmel., 2014). The "big controversy" regarding the formation of the conglomerate-hosted gold deposits has been highly discussed for quite some time now (Tucker *et al.*, 2016; Nwaila *et al.*, 2021).

Several models that have been put forward are the placer model (Minter *et al.*, 1988), hydrothermal/ epigenetic processes (Barnicoat *et al.*, 1997), a blend of the two called the modified placer/local hydrothermal remobilisation (Frimmel *et al.*, 2005) and syngenetic model (Frimmel., 2014: 2018, Frimmel and Hennigh., 2015; Horscroft *et al.*, 2011). According to the placer model, sedimentary cycles brought gold and other associated minerals into the basin and deposited them there as detrital particles (Minter *et al.*, 1988, Law and Phillips., 2005). The hydrothermal model suggests that fluid movement and geochemical features of the host rocks influenced gold precipitation from aqueous solutions during post-post-depositional alterations (Barnicoat *et al.*, 1997; Law and Phillips., 2005; Fuchs *et al.*, 2017).

The modified placer/local hydrothermal remobilisation model proposes that gold and related minerals were presented as detrital particles (Minter *et al.*, 1993). They were fluidly remobilised during post-depositional alteration forming gold compositions and textures which clarify the explicit aqueous nature of the gold observed currently (Minter *et al.*, 1993; Frimmel., 2005). Syn-sedimentary/Syngenetic model (Horscroft *et al.*, 2011) infers that gold precipitated on the surfaces of early photosynthesising microbes (cyanobacteria) derived from rivers enriched with gold 2.9 Ga (Frimmel and Nwaila., 2019). When these microbes got eroded, they prompted the development of gold placers in the fluvial channels and on aeolian collapse surfaces (Frimmel and Nwaila., 2019). Younger placers with low gold grades resulted from the repetition of sedimentary reusing of older placers (Frimmel and Nwaila., 2019). The repetition of post-depositional fluid penetration set off incomplete

dissolution and re-precipitation of gold and ore minerals which in turn led to delayed paragenetic textural position of gold (Frimmel and Nwaila., 2019). However, this cycle was, notwithstanding, of minimal economic importance (Frimmel and Nwaila., 2019).

Proof for every origin model has been introduced throughout the years and the modified placer and hydrothermal model were the broadly accepted models (Tucker *et al.*, 2016; Nwaila *et al.*, 2021). The primary reasons proposed to support the latter models are summarised by Frimmel and Minter (2002). Evidence recognised in defence of the hydrothermal model is by Barnocoat *et al.* (1997) who deduced that (1) there is a bedding-parallel hydrothermal liquid invasion along host rock horizons; (2) the distribution of pyrophyllite in the basin is associated with large-scale metasomatism; (3) the basin is enriched with rounded pyrite and uraninite which are related to the gold metal of post-depositional aqueous genesis; (4) within the paragenetic succession, the gold is late; and (5) The atmosphere in the Neoarchaeon was necessary.

More evidence for the hydrothermal model from Phillips and Myers, 1989; Phillips and Law., 1994; Phillips *et al.* ., 1997, concluded that (6) the rounded pyrite came from sulfidation of “black sands” in the basin (Phillips and Myers., 1989); (7) Witwatersrand gold cannot be placer gold due to lack of suitable area of origin; (8) gold was hydrothermally deposited into the basin at peak metamorphism, and this occurred at the same time as the layered igneous intrusion event; and (9) the same hydrothermal gold deposit into the basin occurred during the Ventersdorp Supergroup volcanic eruption, which occurred between 2.7 and 2.6 Ga. Further evidence for this hypothesis was explored by Barnicoat *et al.* (1997) with Phillips and Myers (1989) and they came up with proof that (10) there is a relation between gold and acidic metamorphic alteration; and that (11) After deposition of sediments, that is when gold was deposited into the Witwatersrand; lastly (12) hydrothermal pyrobitumen is associated with gold (Nagy., 1993; Gray *et al.*, 1998).

Evidence for the modified placer model is that the (1) distribution of gold is controlled by sedimentology; (2) it is rare to see rounded gold micro nuggets and secondary hydrothermal gold together on a microscale (Minter *et al.*, 1993); (3) the atmosphere in the late Archean was acidic and ; (3) neutral to basic pH is represented by compositions of liquid inclusion in the auriferous hydrothermal quartz (Frimmel *et al.*, 1999); (4) under a decreasing environment, chemical weathering is linked to an elevated chemical index of alteration in the footwall near the reef (Sutton *et al.*, 1990); (5) Older ages prior to sedimentation (Re- Os age of 2.99 Ga for pyrite) are provided by the isotope results for rounded sulphides and uraninite (Kirk *et al.*, 2001); (6) the rounded pyrite with a perfect crystal shape (Fleet., 1998)

is clear proof for mechanical abrasion which is represented by zoning of the truncated oscillatory on the rounded pyrite grains (McLean and Fleet., 1989); (7) hydrothermal pyrobitumen is derived from local intrinsic oils, and this process is represented by bulk and molecule $\delta^{13}\text{C}$ (Spangenberg and Frimmel., 2001); (8) Gold composition variability in certain reefs indicate contrasts in the source regions (Frimmel and Gartz., 1997); (9) Re-depletion periods of 3.5 - 2.9 Ga acquired for gold are older than during sedimentation (Kirk *et al.*, 2001); (10) there is absence of secondary permeability post >600 million years of burial, diagenesis, and low-grade metamorphism (Frimmel and Minter., 2002); (11) the Witwatersrand- style gold deposits during the post-Ventersdorp Black Reef occurred after the reworking of sediments of the Witwatersrand gold deposits in the Ventersdorp diamictite (Frimmel and Minter., 2002); (12) the average gold composition of the Archean granite-greenstone crust relates with the determined background value for eroded source region (Loen., 1992).

2.2.3 Major geological structure in the Witwatersrand Supergroup

Geological structures are rare on the surface in the Witwatersrand Basin (Frimmel., 2019). Regardless of that, detailed underground structural mapping of all major goldfields and surveying by several mine geologists provides a clear understanding of the complicated faulting and folding within this basin (Tucker *et al.*, 2016). The findings also exhibited a unique history with compressional and extensional forces (Frimmel., 2019). In addition, recent studies of regional deep seismic and 3-D seismic surveys showed better evidence of major faulting (Tucker *et al.*, 2016). The information from these seismic surveys affirmed the unconformity amid the West Rand and Central Rand Group and the unconformable relationship between Witwatersrand and Ventersdorp Supergroups (Frimmel., 2019).

During the Central Rand Group, syn-depositional tectonism in the hinterland intensified from Johannesburg to Turffontein Subgroup periods, which shaped the Witwatersrand Basin's structure and sedimentation trends (Tucker *et al.*, 2016). The advancement of basin edge faults, uplifted blocks, and regional uplift of the basement domes in the hinterland became controlling elements for the area for river channels and the source of conglomerates within the overall compressional system (Frimmel., 2019). It prompted strike-slip fault dominating the eastern portion of the basin while initial folds, thrusts, and reversal faults were more so along the western basin margin (Frimmel., 2019).

2.2.4 Alteration in the Witwatersrand Supergroup

The Witwatersrand Basin represents a sedimentary sequence that underwent a few post-depositional shifts like metamorphism and hydrothermal alteration (Frimmel., 2019; Guy *et al.*, 2014). The tectonic development of the basin was associated with the two significant times of broad metasomatism in the Central Rand Group (Phillips and Powell., 2011). The early events include diagenesis and weathering cycles, and the late stage is the hydrothermal alteration throughout peak metamorphism (Law and Phillips., 2002; Frimmel *et al.*, 2005). The hydrothermal alteration differs from weathering by its geometry and inclusion of potassium (K), rubidium (Rb), and S (Law and Phillips., 2005).

Regional metamorphism has overprinted weathering and diagenetic minerals which can still be explained with younger sedimentary basins (Phillips and Law., 2000; Law and Phillips., 2005). Near the peak of metamorphism, hydrothermal alteration had already overprinted about 300 km of the Central Rand Group (Phillips and Powell., 2015). Several elements were lost as a result of hydrothermal alteration (e.g., Si, Fe, Mg, Ca, K, and Rb). It corresponds with economic gold and the regions with extensive sulphide distribution within the basin (Law and Phillips., 2005).

2.2.5 Auriferous lithofacies and ore mineralogy

The Witwatersrand Basin is representative of an extensive sedimentary basin loaded with shale, sand, and gravel ranging somewhere from 2.98 - 2.79 Ga (Frimmel., 2014). Most of the gold and uraninite occur in reefs which are thin layers of quartz-pebble conglomerate, coarse-grained arenites, and carbon seams (Frimmel and Minter., 2002). The latter beds address reworked sediments on the continental crust where braided rivers and shallow-water lakes were uncovered without sediment addition over time (Frimmel., 2019). Characteristics of the conglomerate beds were reported by the likes of Krendelev (1974) and Frimmel *et al.* (2005). Conglomerates that contain ore comprise rounded (usually well-arranged) pebbles while pebbles that vary in size and shape generally represent less auriferous conglomerates (Simanovich., 2009).

The conglomerate matrix mainly comprises quartz (dominates), unoxidized sulphides (predominantly pyrite) as seen in Table 1 and some non-metallic minerals such as sericite, chlorite, pyrophyllite, chloritoid, calcite, and dolomite (Simanovich., 2009). The ore contains more than 90% gangue minerals and just 45 parts per million (ppm) gold (Pulles *et al.*, 2005). Economic ore minerals in conglomerates are gold and uranium minerals such as uraninite, pitchblende, thucholite, osmiridium, and platinum group metals (PGMs) (Frimmel *et al.*, 2005). Observed sulphides in the conglomerate matrix are usually pyrrhotite, galena,

arsenopyrite, sphalerite, chalcopyrite, cobaltite, and linnaeite (Frimmel *et al.*, 2005). The substantial percentage typically incorporates chromite, ilmenite, garnets, spinel group, monazite, zircon, tourmaline, pyrochlore, rutile, cassiterite, and diamond which probably occur as an important clastic material (Frimmel *et al.*, 2005). In the unquestionably clastic minerals, an elevated level relation between gold and these elements is present i.e. Ti, Zr, Cr, Fe, Pb, As, Sn, Ag, Cu, Zn, Nd, Pr, Ce, La, Y, Nb, Mo, Co, and Ni (Krendelev., 1974). Conversely, uranium exhibits a particular connection with clastic-derived minerals (Krendelev., 1974).

Table 1: The mineralogy of a common Witwatersrand ore in bulk (Nwaila et al.,2013; Nwaila et al., 2020)

Mineral	Abundance (wt%)
Quartz	70-90%
Muscovite and other phyllosilicates	10-30%
Pyrite	3-4%
Other sulphides	1-2%
Grains of primary minerals: chromite, rutile etc	1-2%
Uriniferous Kerogen	1%
Gold	~ <0.01-0.04%

2.2.6 Pyrite in the Witwatersrand Supergroup

A highly abundant heavy mineral in the Witwatersrand gold-bearing quartz-pebble conglomerates is pyrite (FeS_2) which frequently occurs with gold (Da Costa *et al.*, 2020; Frimmel., 2005). Different pyrite morphologies have been observed in the Witwatersrand deposits, representing several formation processes (Tucker., 1980; Guy., 2012; Frimmel., 2014). Thus, numerous authors came up with various pyrite classification schemes from extensively studying the gold-bearing quartz-pebble conglomerates of the Witwatersrand Basin, to grasp the genesis of reefs, and the environmental settings better (Da Costa *et al.*, 2020). Major features used to classify these pyrite types are shape and texture of pyrite grains, the occurrence of inclusions within the pyrite grains, spatial configuration, trace element content, S and iron (Fe) isotope compositions (Hofmann *et al.*, 2009; Guy., 2012; Da Costa *et al.*, 2017; Da Costa *et al.*, 2020).

a) Classification and significance of pyrite

The recognised primary pyrite morphologies are allogenic (compact, rounded), syngenetic, diagenetic, and epigenetic pyrite (Tucker *et al.*, 2016; Da Costa *et al.*, 2020). The allogenic pyrite is a primary detrital ore mineral that ordinarily associates with detrital zircon and chromite (Kirk *et al.*, 2002). Syngenetic pyrite is frequently associated with high gold grades (Frimmel., 2014). Syngenetic pyrite alludes to reworked intrabasinal material (Frimmel., 2014). Due to that, it is detrital even though the intensity of reworking and transport was minor (Da Costa *et al.*, 2020). Diagenetic pyrite developed through the early diagenesis of the gold-bearing quartz pebble conglomerates (Guy., 2012). Prior to lithification and metamorphism, diagenetic pyrite formed in the sediments (Guy., 2012; Tucker *et al.*, 2016). And the epigenetic pyrite is well-crystallised euhedral to subhedral morphology and they allude to pyrite that developed post-consolidation of sediments (Da Costa *et al.*, 2020). This pyrite is younger and not associated with gold mineralisation (Large *et al.*, 2013). Their formation is interpreted to have been during a metamorphic or hydrothermal event (Tucker *et al.*, 2016).

Da Costa *et al.* (2020) developed a new pyrite scheme of classification (Figure 6) by reviewing the regularly cited previous studies of pyrite classification of detrital and authigenic pyrite. Pyrite in clastic sedimentary rocks can be reliably described petrographically using the modified classification scheme (Kirk *et al.*, 2002). The classification scheme is complex and permits the arrangement of pyrite grains in various textural types (Da Costa *et al.*, 2020). This scheme classified the detrital (allogenic) pyrite (Table 2) found in Witwatersrand gold deposits into three pyrite types: Massive, inclusion-bearing, and coarsely crystalline (Da Costa *et al.*, 2020) and the authigenic pyrite (formed in situ) into five pyrite types: euhedral, overgrowth, infill, aggregate and pseudomorphic as summarised in Table 3 (Da Costa *et al.*, 2020). The differentiation in the pyrite types accounts for the association between pyrite shapes, composition, depositional environment, and tectonic setting (Frimmel., 2014). The significance of pyrite grains is not only because of their association with gold mineralisation but it has the capability of giving valuable data on processes that formed the ores (Koglin *et al.*, 2010; Da Costa *et al.*, 2020).

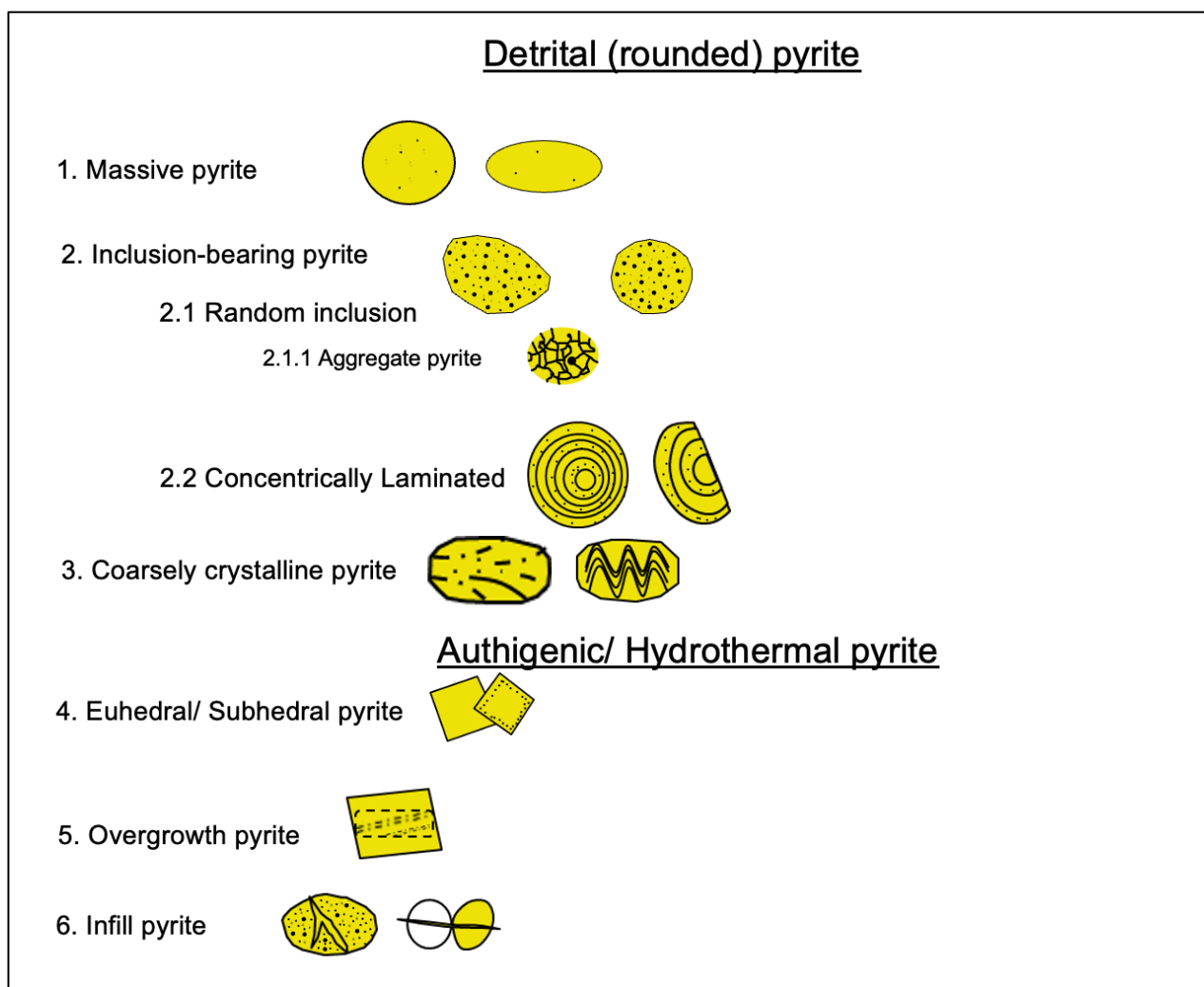


Figure 6: Schematic representation of detrital and authigenic (hydrothermal) pyrite grains (modified from Da Costa *et al.*, 2020).

Table 2: Classification scheme of detrital (allogenic) pyrite (Da Costa *et al.*, 2020)

Detrital (allogenic) pyrite types	Brief description	References
Massive detrital pyrite (DM)	Called “compact” pyrite and it is abundant in all conglomerate units. It lacks inclusions (holds < 10%) and has minor sulphide inclusions (chalcopyrite, sphalerite and galena). The grains are closely packed ranging from < 0.2 – 2 mm in size. They are equant and cubic with abraded edges in shape.	(Da Costa <i>et al.</i> , 2020; Frimmel., 2005)

Inclusion-bearing detrital pyrite (DI) i. Randomly distributed inclusions (DIR). ii. Planar laminated (DIP) iii. Concentrically (DIC) iv. Micro-spherical (DIM)	Referred to as “porous” pyrite and it is less abundant in conglomerate beds. They show different textures and loosely knit textures. Have inclusions (> 10%) which are euhedral to subhedral pyrite grains with random orientation in parallel-layered /concentric laminated crystals (rare) form. It is subdivided into four subtypes	(Da Costa <i>et al.</i>, 2020; Frimmel., 2005; Koglin <i>et al.</i>, 2010; England <i>et al.</i>, 2002)
Coarsely crystalline detrital pyrite (DC)	Made of massive/ inclusion-bearing grains with a size range of 0.2 – 1.5 mm (could get up to 5mm) diameter and pyrite crystals that are > 0.05 mm. The texture is the main feature (dendritic, branching, cone-in-cone, chevron and radiating). It appears in Basal, Steyn, Virginia, Upper Elsburg, Vaal and Black Reefs.	(Da Costa <i>et al.</i>, 2020; Hallbauer., 1986; England <i>et al.</i>, 2002b)

Table 3: Classification scheme of the authigenic pyrite (Costa and Agangi., 2019)

Authigenic pyrite (found <i>in-situ</i>) type	Brief description	References
Euhedral/Subhedral pyrite (AE)	Occurs as individual crystals or as aggregates and the crystals are cubic, pentagonal, octahedra/dodecahedral. With a diameter of ~ 80 µm - 3 mm. Inclusions are rare and if they occur (hold < 10%) and occur randomly/ as zonal configurations that are oriented toward crystals. The inclusions include chalcopyrite, chlorite, quartz, sphalerite, galena, pyrrhotite, U-	(Da Costa <i>et al.</i>, 2020; English <i>et al.</i>, 2002b; Agangi <i>et al.</i>, 2013)

	Ti mineral phase and Au.	
Overgrowth pyrite (AO)	Usually massive. However, occasionally there may be many inclusions. They form on rounded detrital grains producing core-rim shaped grains. About 30% of it is detrital pyrite. It consists of single idiomorphic crystals/ idiomorphic to hypidiomorphic pyrite aggregates. Have high amounts of As, Ni, Co, and Au.	(Da Costa <i>et al.</i> , 2020; English <i>et al.</i> , 2002b; Guy <i>et al.</i> , 2014; Koglin <i>et al.</i> , 2010)
Infill pyrite (AI)	Fills cracks and basic porosity. Primary veins cut detrital pyrite grains. It is trace-element poor. And is related to inclusions of sphalerite, galena, chalcopyrite and electrum.	(Da Costa <i>et al.</i> , 2020; English <i>et al.</i> , 2000b; Agangi <i>et al.</i> , 2013)
Aggregate pyrite (AA)	Largely detrital type.	(Da Costa <i>et al.</i> , 2020)
Pseudomorphs (AP)	Indicate non-sulphide grains replaced by pyrite. Contains relict structures and compositions. Represented by rutile laths and pyrite which is the size of sand.	(Da Costa <i>et al.</i> , 2020; English <i>et al.</i> , 2002b)

b) Trace element and isotopic composition of pyrite in the Witwatersrand Supergroup

Studies conducted over the years using LA-ICPMS and EPMA by (Reimold *et al.*, 2004) on trace-element distribution within the pyrite grains indicated that pyrite contains other elements in trace amounts (Koglin *et al.*, 2010). It's challenging to analyse and quantify trace elements in pyrite because their concentration levels are low (Koglin *et al.*, 2010). The trace element contents and ratios of S isotopes in the compact, rounded (massive) pyrite contrast with the euhedral (authigenic/hydrothermal) pyrite types (Frimmel., 2014). The variable amounts of trace elements like As, Ni, and Co in individual grains because of solid chemical zonation are features of authigenic (hydrothermal) pyrite (Agangi *et al.*, 2013).

The multiple S isotope studies on detrital pyrite from Witwatersrand conglomerates revealed that the three pyrite types in Table 2 represent detrital origin (Hofmann *et al.*, 2009). In addition, the study uncovered that the compact, rounded (massive) pyrite grains form a broader range of $\delta^{34}\text{S}$ values (-5.0 to +6.7) than reported in the past by bulk-grain analysis (Frimmel., 2005). This wide variety of $\delta^{34}\text{S}$ for the rounded pyrite grains from Steyn Reef affirms the heterogeneous array of sulphur compositions with adjoining grains that regularly

have different isotopic signatures and it supports the placer origin (Tucker *et al.*, 2016). A comparison of development processes and provenance is represented by the considerable heterogeneity of $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ of detrital pyrite (Hofmann *et al.*, 2009; Guy *et al.*, 2014; Agangi *et al.*, 2015). The authigenic/hydrothermal pyrite types analysed showed a restricted range of $\delta^{34}\text{S}$, $\delta^{33}\text{S}$, $\delta^{36}\text{S}$ amounts which propose that the euhedral and overgrowth pyrite grains were sourced from metamorphism and hydrothermal fluids (Guy *et al.*, 2014).

2.3 Case study- The Middelvlei Reef

2.3.1 Depositional setting and lithofacies

The Middelvlei Reef formed close to the base of the Central Rand Group (3 km thick) which forms part of the Witwatersrand Basin and consists of quartzite with conglomerate and minor shale (Myers *et al.*, 1993). This reef occurs in the Carletonville goldfields (As indicated in Figure 1) covering a surface of more than 500 km² regions in Carletonville only (Myers *et al.*, 1993). Deposition of the Middelvlei Reef was on a clear-cut regional unconformity which occupies more than 70 m of the footwall quartzite in the Carletonville Goldfield (Els., 1991). From the sedimentological data studied to a detailed degree by Els (1991) and Jolly (1984), it was decided that Middelvlei Reef is of a braided fluvial origin, deposited firstly on a degradational to aggradation surface (Myers *et al.*, 1993). The palaeocurrent direction shows the flow from northwest to southeast across west Driefontein Mine (Els., 1983). The Middelvlei Reef on Doornfontein Gold Mine in the Carletonville goldfields comprises a sheet-like deposit of interbedded quartz (pebbly) conglomerate and quartzite (Els and Beukes., 1987; Els., 1983). Similar silicate assemblages such as quartz, muscovite, chlorite, and chloritoid are observed in all samples of Middelvlei Reef (Myers *et al.*, 1993).

The Middelvlei Reef is consists of either a single conglomerate layer or interbedded conglomerate and coarse-grained quartzite combined with siltstone drapes (Els., 1983). The conglomerates are compositionally developed with over 80% pebble assemblage comprising smooth and smoky quartz, chert, and quartzite pebbles (Jolly., 1984). The silicate matrix of the conglomerate shows colour fluctuations of light to dark grey (Els and Beukes., 1987). Pyrite minerals commonly occur as aphanitic detrital grains filling the interstitial material (Els and Beukes., 1987). Several lithofacies are observed in this reef, summarised in Table 4 below.

Table 4: Classification of lithofacies observed in the Middelvlei Reef (Els., 1983)

Code	Code Miall (1977)	Equivalent Middelvlei Reef	Interpretation definition facies (Miall., 1977)
Gm	Massive clast-supported gravel	Clast-supported conglomerate	Longitudinal bars/channel lag deposits
Gp	Planar cross-bedded gravel	Planar cross-bedded conglomerate	Linguoid gravel bars
Gt	Trough cross-bedded gravel	Trough cross-bedded conglomerate	Minor channel fill
Gl		Single pebble layer conglomerate	Single- layer lag deposits
St	Trough cross-bedded sand	Trough cross-bedded quartzite	Dunes
Sp	Planar cross-bedded sand	Planar cross-bedded quartzite	Linguoid sand dunes
Fm	Massive mud/silt	Lenticular massive siltstone	Drape deposits formed in pools
FI	Laminated mud/silt	Blanket deposit of laminated siltstone/shale	Suspension deposits are found over extensive areas.

2.3.2 A critical review of previous studies

a) Sedimentological studies

Els (1983; 1991) examined the Middelvlei Reef's sedimentology to comprehend the mechanisms influencing the gold concentration. There are two categories for the Middelvlei Reef which is single cycle conglomerate and multicycle conglomerate. The palaeocurrent directions, size of the grain, and rocks stratification were examined and it was concluded that the sediments were of fluvial origin and were deposited by braided streams with various amounts of gold (Els., 1983). In the eastern portion of the Driefontein mine, the palaeocurrent directions are towards the south-southeast, and the western region is towards the east (Els., 1983). The palaeoenvironmental model concluded that the thin single-cycle conglomerates hold the highest concentrations of gold (Els., 1983). The study by Els (1991) concluded that the orebody consists of interbeds of the quartz-pebble conglomerate.

b) Geostatistical evaluation of gold distribution

Studies done by Jolly (1984) concluded that greater gold grades concentrate at the base of the Middelvlei Reef even though acceptable gold grades are in the upper conglomerates in the north-eastern portion of the Driefontein mine. The most significant grade of gold is found

in the eastern portion of the Driefontein mine in association with bigger pebbles, thin basal reef units, and low ratios of the conglomerate (Jolly., 1984). It was observed that gold contents appear throughout the entire reef and relative to the base unit, but the amounts are low and uneconomic to mine (Jolly., 1984). The interbedded quartzites are poor in gold grade except on a localised scale when processes leading to internal quartzites cross-stratification may have concentrations of pyrite and gold on the foresets (Jolly., 1984). The moderate to elevated gold grades occur in the far west of the Driefontein mine and are related to the rising ratios of conglomerates (Jolly., 1984). The gold grades exhibit the highest consistency, equal to the measured palaeocurrent occurring in the east and west of the Driefontein mine, described as a potential ore reserve for future gold extraction (Jolly., 1984).

c) Sulphidation studies

The Middelvlei Reef shows extensive textural evidence for alteration/sulphidation where sand and pebble-sized clasts in conglomerate and matrix in quartzite too have been substituted by secondary iron sulphides (Myers *et al.*, 1993). The degree of sulphidation in the Middelvlei Reef is correlated with areas of higher modal muscovite, while minor sulphidation is where chloritoid is more common (Myers *et al.*, 1993). Sulphides that appear extensively are pyrite and lesser pyrrhotite and their evolution might match the metamorphic event (Myers *et al.*, 1993). The significance of diagenetic and syn-metamorphic events cannot be distinguished with textural models, even though the timing of sulphidation gives off an impression of being post-depositional (Myers *et al.*, 1993). The lack of retrograde impacts shows that sulphidation happened before or during peak metamorphism (Myers *et al.*, 1993). According to Myers *et al.* (1993), the distribution and force of phyllosilicate alteration and sulphidation suggest that these processes may be more important in the Witwatersrand Basin than is commonly believed.

Chapter 3: Materials and Methods

The experimental tests conducted for this research are presented in this chapter. In the experimental study, samples were prepared and characterised for chemistry, mineralogy, and in-situ sulphur isotopes, as illustrated in Figure 7. Different test methods used to determine pyrite's physical and chemical features are also outlined in this chapter.

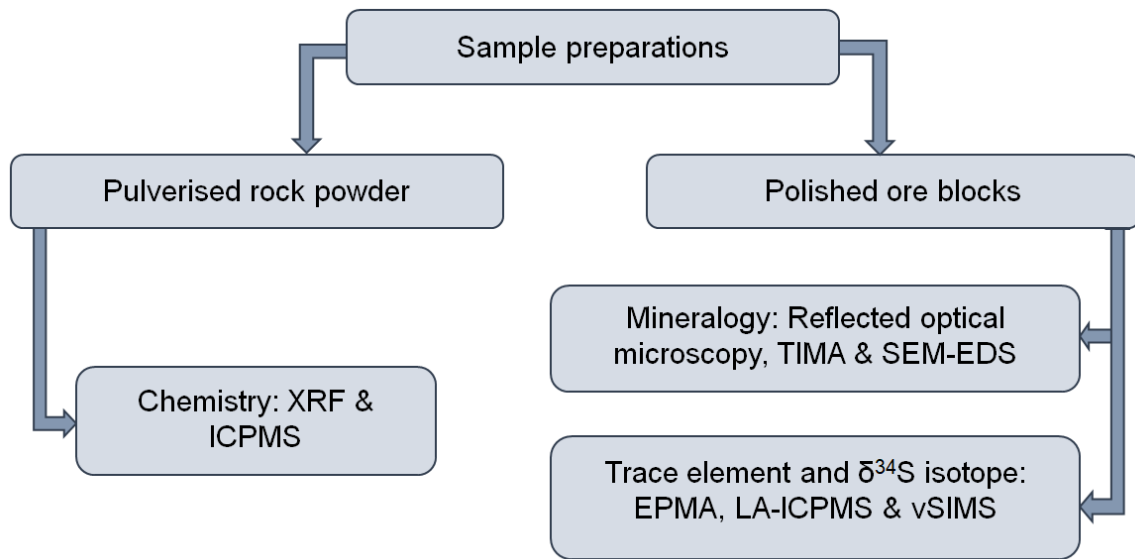


Figure 7: Schematic illustration of experimental procedures and methods.

3.1 Ore sampling and sample preparation

To sample and investigate the variations between the Middelvelei Reef's numerous facies, site visits were necessary to quantify the different ore textures, grade distribution, and mineralogical assemblage. A bulk composite sample amounting to a total of twenty-six samples of the reef ($n=17$), hanging wall ($n=5$), and footwall ($n=4$) were collected from Sibanye Stillwater mine Shaft 8 Driefontein. The samples were predominantly from the stope that was at 3200 m levels of the mine (Figure 8). The samples were described in detail to record the characteristics and mineralogy of the rock units according to the grain size; colour; clast size, type; pebble roundness, sorting, mineral assemblage; matrix component and mineralisation.

The classification of the rock samples followed the Wentworth scale. At the same time, mineralisation was determined using the observed amount of sulphide minerals (mainly pyrite) which were described as massive, disseminated, net-texture, and as veinlets. Measuring the stratigraphic sections permitted the stratigraphic profile to be drawn. The samples of a large mass of ore were taken for detailed geochemical and mineralogical

analyses. These bulk samples were prepared for two types of samples: pulverised rock powder and polished ore blocks. Sixteen of the samples underwent crushing and milling at the University of the Witwatersrand EarthLab to produce pulverised rock powder using a jaw crusher and agate mill. In the pulverised powder, three samples represented the hanging wall, four represented the footwall and ten was the reef. Due to the high mineralisation observed in the reef, only samples from the reef were prepared for polished ore blocks. They were sectioned for ten polished ore blocks (25 mm) at the School of Geosciences, University of the Witwatersrand.

The sample was prepared in an enclosed area to avoid contamination. Errors are omnipresent during the cutting, crushing, and milling in the lab. Hence, an essential issue to be aware of is the sample size, so it is important to use a large sample size to obtain a representative sample (Bartlett., 2002).



Figure 8: Image of the ore collected from Sibanye Stillwater mine Shaft 8 Driefontein.

3.2 Mineralogical Characterisation

3.2.1 Reflected light optical microscopy

The ten polished ore blocks (25 mm) prepared were studied using an Olympus petrographic microscope from Wits Imaging Lab (WIMLab) at the University of the Witwatersrand. This was to investigate the mineralogy, textural properties, and mineral association of the Middelvlei Reef gold ore. During this, the overview of the ore blocks in Plane Polarized Light (PPL) was captured under reflected light as images, focussing on sulphide minerals.

3.2.2 TESCAN Integrated Mineral Analyzer (TIMA)

The polished ore blocks that showed a more defined mineralisation and had big pyrite grains were selected and studied using TIMA at the School of Geosciences, University of the Witwatersrand, to obtain a modal composition and to better understand the mineral phases. TIMA is an automated SEM-based analysis system that yields quantitative and qualitative mineralogical and textural data. It is used to perform mineral characterisation in the mining and minerals industry (Aylmore *et al.*, 2019). This instrument can perform analytical analysis such as measuring and organising particles according to their size, composition, and texture. The technique performs image analyses through bright phase search (BSE) and X-ray analysis (Aylmore *et al.*, 2019). The BSE detects gold/silver deportment, mineral abundances, mineral associations, and liberation characteristics (Hrstka *et al.*, 2018). For the identification of minerals and compounds in a variety of sample types, the instrument also has a specially designed electron-beam platform with four energy-dispersive X-ray spectrometers (EDS).

This tool was deployed to establish gold occurrence and its association with other minerals because reflected light optical microscopy limits the information on the silicate phases. However, TIMA analyses tend to be biased in sampling since the samples analysed are related only to the mineralisation we are seeking. TIMA uses elements to calculate the minerals. Comparing TIMA-calculated assays with X-ray fluorescence (XRF) actual assays (Table 5) allowed for data cross-validation, which is visually displayed in Figure 9. The necessity for this validation was to check whether we could rely on the mineral proportions obtained from TIMA analyses because of the element-to-mineral conversions. The cross-validation shows that we can indeed rely on the minerals and elements from TIMA because many of the points fall on the gradient or ideal line of one. This means that the mineralogy from TIMA is correct because there are few outliers from the linear correlation. Those detected deviations (the high values observed in Table 5) are that of Fe content because the

selected samples are those that showed high sulphide mineralisation and Si concentrations reflecting the quartz pebbles in the samples.

Table 5: Comparison between TIMA calculated and XRF actual assays.

Elements	XRF average	TIMA average
Si	41.826	33.820
Al	1.695	0.720
K	0.555	0.322
Ca	0.019	0.003
Ti	0.096	0.180
Mn	0.010	0.000
Fe	2.647	10.254
Na	0.022	0.006
Mg	0.162	0.124
P	0.013	0.001
Cr	0.014	0.019
Ni	0.009	0.000

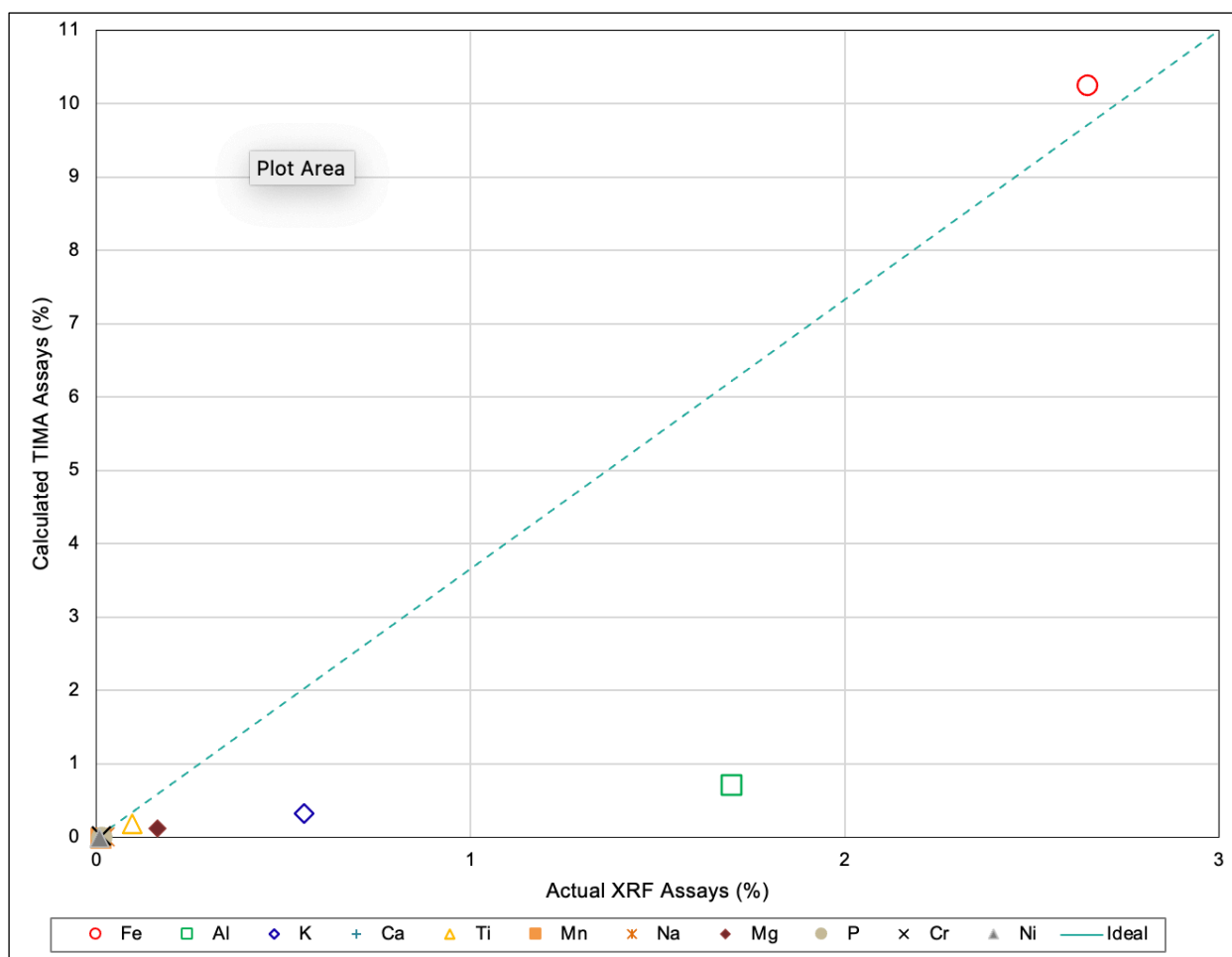


Figure 9: Cross validation plot of TIMA calculated and XRF actual assays depicting correlation in the Middelvlei Reef samples. The $x=y$ relation is represented by the ideal line.

3.2.3 Scanning election microscopy (SEM-EDS)

Four highly mineralised samples were analysed for SEM-EDS imaging using a scanning electron microscope (SEM) at the University of the Witwatersrand in the School of Chemical and Metallurgical Engineering. The area of interest was scanned with a focussed beam of electrons, phases that were included in the matrix and pyrite grains were identified and mineralogical association was described. These samples were chosen mainly because of their significant amounts of pyrite mineralisation, different pyrite morphologies, and for confirmation of other phases that were too complicated to detect with the reflected light optical microscopy. An Oxford x-act EDS detector with a spot size of 30 microns was employed with the Carl Zeiss Sigma FEG-SEM. The device analyses four ore blocks simultaneously, taking a 60-second analysis time per spot. It displays topography by first acquiring a backscattered electron (BSE) image and then a secondary electron image. The chemical content of the phases of the samples in question were obtained using energy dispersive X-ray spectroscopy (EDS).

3.3 Whole-rock chemistry

3.3.1 X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS)

Some of the ore substance underwent crushing and milling using a jaw crusher and agate mill at the University of the Witwatersrand's EarthLab to turn them into pulverised rock powder. Seventeen pulverised rock powder samples [8 grams(g) per sample] were produced and analysed for their whole-rock compositions using XRF for major elements and ICPMS for trace and minor elements.

a) Analytical Procedure for XRF major elements.

The Norrish Fusion 1 tool was used to identify the major elements using a Panalytical X-ray fluorescence spectrometer and internal correction techniques. At 50 milliamperes (mA) and 50 kilovoltages (Kv), the samples were examined. Using Johnson Matthey Spectroflux 105 at 1000 °C, major elements were fused, and internal software was used to rectify the raw data. International standard rocks, synthetic oxide combinations, and internal controls were used to create standard calibrations. The weights of the sample and flow were 0.35 g and 2.0 g, respectively. The principal International Reference Materials used for calibration were the NIM series (South Africa) and the USGS series (USA). For elements in abundance beyond 5% by weight, accuracy is defined as 1%, and for abundant elements which are below 5% by weight, precision is defined as 5%. The Panalytical Axios X-ray spectrometer was the device in use. BCR2, NIM-P, NIM-D, W-2, NIM-S, GSP-2, NIM-N, NIM-G, PCC1, BHVO2, AGV2, and G2 DTS are used in standard calibrations.

b) Analytical Procedures for ICP-MS trace elements

With the use of Thermo Scientific iCAP RQ tool, ICP-MS samples were examined in the University of the Witwatersrand's EarthLab. An open beaker/hotplate technique was used to weigh and digest 50 milligrams (mg) of the material since it is simpler to digest. Using the open beaker/hotplate approach, a 50 mg sample is put straight into a 15 ml Savilex beaker along with 3 ml of Ultra High Purity 2:1 HF: HNO₃. The hotplate was then set at 70 °C and left to evaporate. After drying, 3 ml of HF: HNO₃ was poured, sealed, and remained on the hotplate for 72 hours at 70 °C. Following a 70 °C drying process, 3 mls of HNO₃ were added to the sample and allowed to evaporate. The beaker was capped and another 3 mls of HNO₃ was added and set on the hotplate at 70 °C. After adding an additional 3 mls of HNO₃, the beaker is sealed and remained on the hotplate at 70 °C for a whole day. Upon evaporating

the acid, 3 mls of HNO₃ were added once more and let to evaporate. The samples were then kept in 300 microliters (ul) of HNO₃ till they were ready for analysis.

The samples were mixed to 50 ml (Dilution Factor 1:1000) with 5% HNO₃ with 100 parts per billion (ppb) Re, Rh and 50 ppb In and Bi. These elements were checked during the analyses and were considered in-house standards. By minimizing interaction between the sample and HF while still achieving complete digestion reduces fluorides levels. Fluorides, which appear as a precipitate after being diluted, were carefully examined in samples. Using bought International Certified Reference Materials, calibration standards were created at five distinct contents (10, 30, 50, 75, and 100 ppb) with all 40 elements that needed to be examined present.

Optimum counts of In and oxide amounts set to lower than 2%, and double charged ions adjusted to lower than 2%, were optimized for the Thermo Scientific iCAP RQ. The instrument averages each measurement, and any repeated deviation of more than 2% will be noted. All unknowns, typically BCR-1, BHVO-2, and BIR-1, were digested and analysed with Certified Reference Materials. All elements must pass the quality standards if the CRMs yield a deviation lower than 10% from the observed concentrations, which is typically about 5%. A Total Procedural Blank (TPB) underwent the analysis with all unknowns. It includes an empty container but subjected to the entire sample digestion process. This provides a measure of the preparation lab's cleanliness and blank levels. The TPB is deducted from all data.

3.4 Micro-beam analysis and in-situ S isotopes

Micro-beam analyses involve the comparison of electron probe microanalyses (EPMA) and Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). EPMA with wavelength dispersion spectrometers (WDS-EPMA) was employed to map the trace elements in pyrite. Cross-validation with LA-ICPMS is offered to check the consistency of the results. Even though the two approaches are different to a great extent in terms of the size of spot, limits of detection, and number of elements identified once. Their evaluation demonstrates how these methods complement one another and can be applied in tandem as mapping approaches. Elemental mapping was completed using the TIMA technique due to the loss of data with the EPMA tool. The disadvantage of EPMA is that certain elements like Ag, Au, Bi, Cu, Ni, Pb, V, Sb, Te and Zn are frequently below its limits of detection but can be detected with LA-ICP-MS since it gives more vigorous low concentration data.

3.4.1 Electron probe microanalysis (EPMA) trace elements of pyrite

After establishing and selecting mineral phases in the more mineralised ore blocks during TIMA and SEM-EDS analyses, a total of six ore blocks were examined by EPMA for their major and trace element contents of pyrite. Quantitative spot analyses of different pyrite grains were performed using a WDS detector equipped with Cameca SX-100 EPMA in the Microscopy and Microanalysis Unit (MMU) at the University of the Witwatersrand. EPMA total spot analyses of ~ 46 spots were used with maps showing composition to measure the trace-element composition of pyrite grains discovered during compositional mapping. All the analyses were carried out at operating conditions (detailed in Table 6) of 15 kV acceleration, a beam current of 20 nanoamperes (nA), and the dwell (peak) time per spot for Fe, S, Cu, Co, Fe, S, Sb, Mo, V, Te, Hg, Pb, Se and Zn were set at 20 s and 46 s dwell time per spot for Ni. Standards and emission lines such as Fe (Ka), S (Ka), Co (Ka), Ni (Ka), Cu (Ka), As (Ka), Se (Ka), Zn (Ka), V (Ka), Mo (La), Ag (La), Sb (La), Te (La) Au (La), Hg (La), Pb (La) and Bi (La) were analysed by WDS. A set of sulphides and native elements were used as reference material. Reference materials were a set of sulphides and elements. Limits of detection are between 200 and 950 ppm for majority of the trace elements except Zn and Mo which are between 2500 and 4500 ppm. There are trace element concentrations like As, Se, Hg, and Pb which were observed to be above the limits of detection. The probe was not able to detect elements such as Co, Cu, Ag, Sb, Au, and Bi.

Table 6: Analytical parameters of EPMA investigations.

Elements, spectral line	Mineral	Acceleration (kV)	Beam current (nA)	Diffraction crystal	Peak time (s)	Detection limit (ppm)
Fe Ka	Pyrite	15	19.95	LLIF	20	953
S Ka	Pyrite	15	19.95	PET	20	794
V Ka	Pyrite	15	19.95	LPET	20	207
Co Ka	Pyrite	15	19.95	LLIF	20	
Ni Ka	Pyrite	15	19.95	LLIF	20	528
Cu Ka	Pyrite	15	19.95	LLIF	20	
Zn Ka	Pyrite	15	19.95	LLIF	20	2478
As Ka	Pyrite	15	19.95	LLIF	20	12509
Se Ka	Pyrite	15	19.95	LLIF	20	20469
Mo La	Pyrite	15	19.95	LPET	20	4371
Ag La	Pyrite	15	19.95	LPET	20	
Sb La	Pyrite	15	19.95	LPET	20	

Te La	Pyrite	15	19.95	LPET	20	577
Au La	Pyrite	15	19.95	LLIF	20	
Hg La	Pyrite	15	19.95	LLIF	20	16001
Pb La	Pyrite	15	19.95	LLIF	20	30547
Bi La	Pyrite	15	19.95	LLIF	20	

3.4.2 Laser ablation ICP-MS (LA-ICPMS) trace-elements of pyrite

The established and selected mineral phases in highly mineralised ore blocks that were examined with EPMA for their trace element contents of pyrite underwent in-situ trace elements analysis using LA-ICPMS. Trace-element concentrations in pyrite grains from the Middelvlei Reef were measured by LA-ICPMS on polished ore blocks at the University of Stellenbosch. The microelement analysis instrument used to analyse trace elements in sulphide grains was an Agilent 7700 QQQ ICP-MS with a resolution of 193 nanometres (nm) Excimer laser from Applied Spectra and the ICP-MS software used is called Mass Hunter v 4.5. Ablation took place in a Helium (He) filled sample cell the ablated material is then combined with argon and a tiny quantity of nitrogen prior to being moved to the ICP-MS. When ablating on NIST612, the laser gas flow and ICP-MS parameters were first adjusted to get the highest sensitivity and low oxide ratios (<0.4%). Depending on the sensitivity or possible disturbances to be removed, all analyses were then conducted using a method that used oxygen as reactive cell gas at a flow of 0.68 ml/min, either on mass or mass-shifted (analyze mass +16).

The flow rates of He ablation gas, argon, and nitrogen were set at 0.5 litres per minute (L/min), 1 L/min and 0.004 L/min, respectively. ⁵⁷Fe was employed as an internal standard element (ISTD). Because sulphide material ablates completely different from the NIST silicate glasses typically used for LA ICPMS quantification, a matrix-matched standard MASS-1 produced by the United States Geological Survey (USGS), is therefore used. The analysis spot size was determined to be 20 and 30 micrometers (µm) and matrix-optimized ablation variables like laser energy and laser beam frequency were calibrated during spot ablation of MASS-1. To provide a steady signal with good sensitivity and introduce minimal laser-induced element fractionation, parameters were set at 3 joules per square centimetre (J/cm²) energy and 6 hertz (Hz). All laser and ICP parameters are summarized in Table 7. The equation (Equation 1) is used to determine each element's detection limit (LOD) from Longerich *et al.* (1996):

$$DetectionLimit = \frac{3\sigma}{S} \sqrt{\frac{1}{n_b} + \frac{1}{n_a}}$$

Equation 1

Table 7: Summary of all laser and ICP analytical parameters.

ICP-MS Instrument connected to laser	Agilent 7700
ICP-MS Software	Mass Hunter v 4.5
ICP-MS Settings	
RF Power (W)	1450
Carrier gas (L/min)	0.95
Sample depth (mm)	4.2
He Cell gas flow (ml/min)	n/a
H2 Cell gas flow (ml/min)	n/a
O2 Cell gas flow (ml/min)	0.68
Detector type	Photo multiplier
Laser Ablation Instrument	
	Applied Spectra Resolution SE 193nm Excimer laser
Controlling Software	Geostar v 10.12
Laser Settings	
Frequency (Hz)	6
Fluence (J/cm²)	2.8
Spot size (µm)	30
Ablation gas (He) flow (ml/min)	500
Additional gas (N2) flow (ml/min)	3
Background acquisition time (sec)	20
Ablation time (sec)	40
Washout time (sec)	25
Calibration stds	
	MASS-1 sulfide
Calibration method	Standard - Sample bracketing every 15 - 20 samples

3.4.3 Virtual Secondary-ion mass spectrometry (vSIMS) $\delta^{34}\text{S}$ isotopes of pyrite

The highly mineralised ore blocks (25 mm diameter) that underwent in-situ trace elements analyses under EPMA and LA-ICP-MS were subjected to an in-situ sulphur isotope of $\delta^{34}\text{S}$. A sample mount used to analyze two ore blocks was regularly swapped out for a different mount that contained the Balmat pyrite reference material. Detrital and hydrothermal pyrite grains were selected and underwent in-situ S isotope analyses to understand and obtain the source of S. This was done through the virtual SIMS facility at the University of the Witwatersrand using Cameca 1280-HR device which is housed at the Helmholtz Zentrum Potsdam.

The samples were put into sample holders with tension springs after being sterilized with ethanol in an ultrasonic bath prior to the analyses. After that, a motorized Nikon Eclipse LVDIA-N microscope was used to photograph the samples in order to help with navigation and point selection. Images of the samples were taken prior to their sputter coating with a high-purity gold layer at a thickness of 35 nm. ~ 500 pA (picoampere), $^{133}\text{Cs}^+$ primary ion beam was used. A -10 kV potential on the sample holder was used to recover negative secondary ions, and low-energy electron flooding and normal incidence were used for charge compensation.

The gold coating was removed and steady sputtering conditions were achieved by pre-sputtering with a 10 μm raster for 70 seconds prior to each experiment. The tool was run at a mass resolving power of $M/\Delta M \approx 5000$ and it was operated in multi-collection mode with $\delta^{32}\text{S}$ detected using the L'2 trolley and $\delta^{34}\text{S}$ detected using the mono-collection central position Faraday cup FC2. The ion count rate under these conditions was typically around 2×10^8 counts per second on ^{32}S and 9×10^6 on $\delta^{34}\text{S}$. About two and a half minutes were spent on a single analysis that included pre-sputtering and automatic centering procedures. On average, the sample chamber's pressure was 1.7×10^{-6} Pascals (Pa).

Data processing was carried out over the course of two days. The Balmat pyrite reference material was employed to calculate the Instrumental Mass Fractionation (IMF). This reference material was measured 38 times resulting in a combined analytical repeatability of 0.48 ‰. Finally, to determine the $\delta^{34}\text{S}$ values relative to the Vienna Canyon Diablo Troilite (VCDT) scale, we used the zero-point defined as 0.044163 by Ding *et al.* (2001), and the $\delta^{34}\text{S}$ value for the Balmat pyrite (15.1 ± 0.2 ‰) by Crowe and Vaughan (1996).

Chapter 4: Results

4.1. Mineralogical Characterisation

4.1.1. Stratigraphy and sedimentology features of the Witwatersrand ores

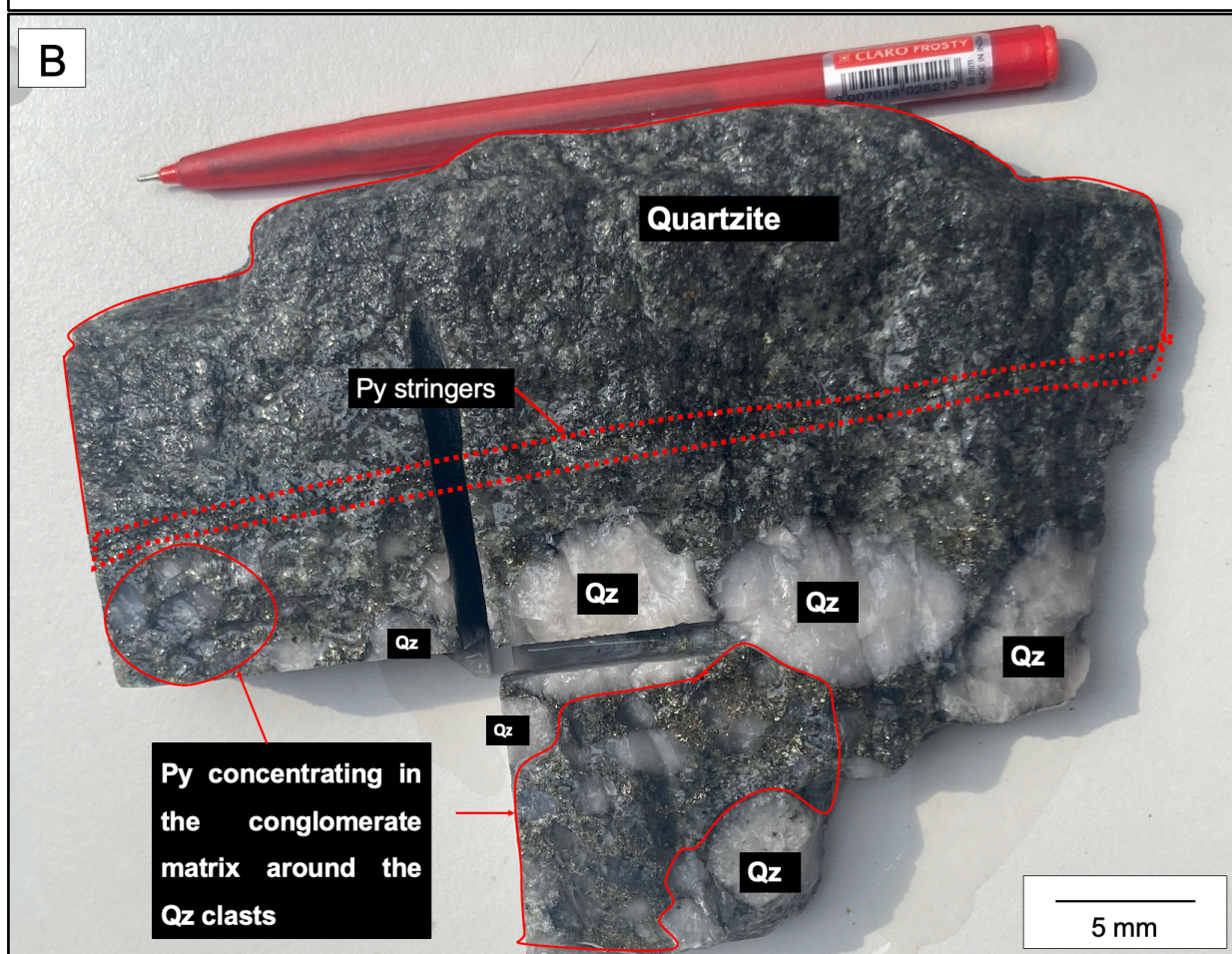
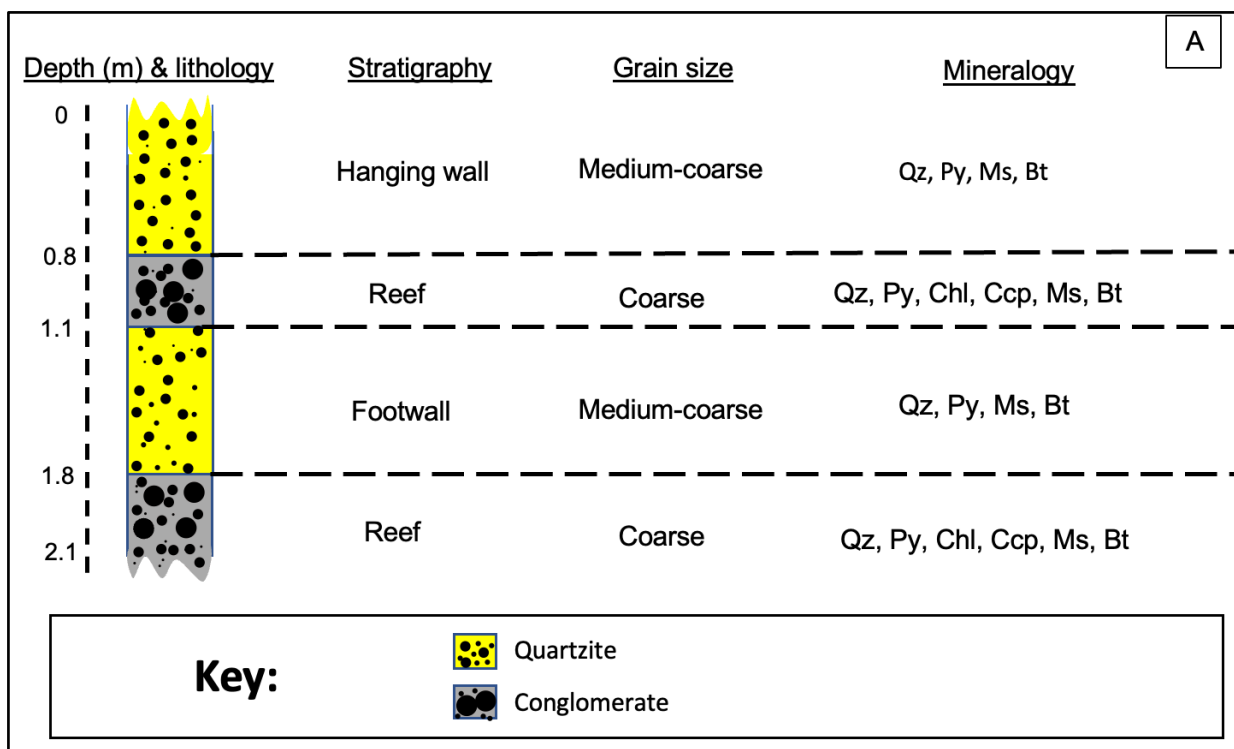
A stope and development visit at Driefontein Mine 8 Shaft indicated two main interbedded rock types of the Middelvlei Reef; (1) quartzite and (2) conglomerate. The conglomerate forms part of the reef and quartzite occurs as both the footwall and the hanging wall (as seen in Figure 13A). Each of these rock units varies in size, abundance, and textures but has a similar mineral assemblage. As a result, the stratigraphic column was deduced (Figure 10A).

Quartzite

Quartzite makes up the footwall and hanging-wall (~ 1 cm to 80 cm thick) strata of the Middelvlei Reef. It is grey with granular grains in the matrix. It is medium-to-coarse grained with grains that range from 0.5 mm - 1 mm in size and a shape that is sub-angular to angular (Figure 10B). Towards the reef, the quartzite unit is dark grey in colour, mature, and moderately mineralised with pyrite. Further from the reef, the grains are immature and poorly mineralised. The pyrite mineralisation is disseminated throughout the quartzite unit and forms stringers (Figure 13B) on the margins or along the cross beds of the reef and quartzite.

Conglomerate

The quartz-pebble conglomerate (reef) containing gold of the Middelvlei Reef is ~30 cm thick. The conglomerate is characterised by small-to-large, well-rounded, and well-sorted quartz pebbles which are smooth, smoky and milky in colour with a size range of 10 mm – 45 mm (Figure 10C). The conglomerate is oligomictic, clast-supported with a light grey matrix that is highly mineralised and shows tints of chlorite and mica group minerals across the matrix. The pyrite mineralisation tends to concentrate around the quartz pebbles on the margins where the conglomerate is overlain and underlain by the quartzite. The matrix comprises minerals such as quartz, pyrite, chlorite, and muscovite.



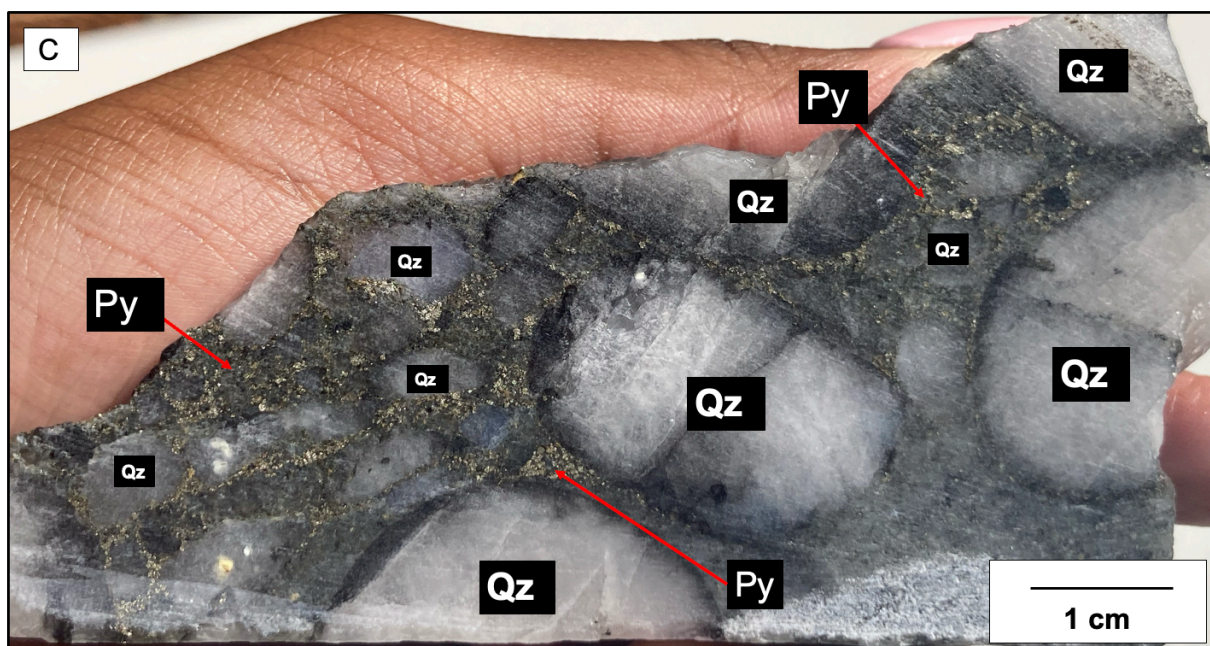


Figure 10: A) Stratigraphic column of the stope from Driefontein mine in the Middelvlei Reef with major minerals. B) Hand specimen showing Py stringer occurring as a margin between quartzite, and conglomerate rock units. C) Conglomerate rock unit showing Qz pebbles/clasts and the highly mineralised matrix which has Py concentrating around the Qz clasts/grains. (Qz = Quartz, Bt = Biotite, Ms = Muscovite, Chl = Chlorite, Py = Pyrite, Ccp = Chalcopyrite).

4.1.2. Mineralogical characterisation of the Middelvlei Reef

Understanding the difference in ore mineralogy of the Middelvlei Reef is important to deduce and determine sediment provenance. The mineralogy of the seven samples was assessed. A combination of techniques such as optical reflected light microscopy, TESCAN Integrated Mineral Analyser (TIMA), and scanning electron microscope (SEM-EDS) were utilised to evaluate bulk modal mineralogy, mineral association, gold distribution, and pyrite morphology distribution within the Middelvlei Reef.

4.1.2.1. Bulk modal mineralogy

To understand the mineral composition of the Middelvlei Reef, a TIMA mineral phase search was conducted, and the modal mineralogy is documented in Figure 11. It shows that quartz is the predominant silicate mineral (70%) in the Middelvlei Reef while the other minerals makes up 30%. Other observed minerals correspond to sulphides (18%), muscovite (4%), chlorite (1%), biotite (1%), and other minor minerals like gold, rutile, zircon and chromite (Figure 11). The most dominant sulphide mineral is pyrite (17%) and it occurs as various types of detrital and hydrothermal grains. Pyrrhotite, chalcopyrite, and galena are other

sulphides in the Middelvlei Reef ore, occurring in a relatively low percentage (<1%) relative to pyrite.

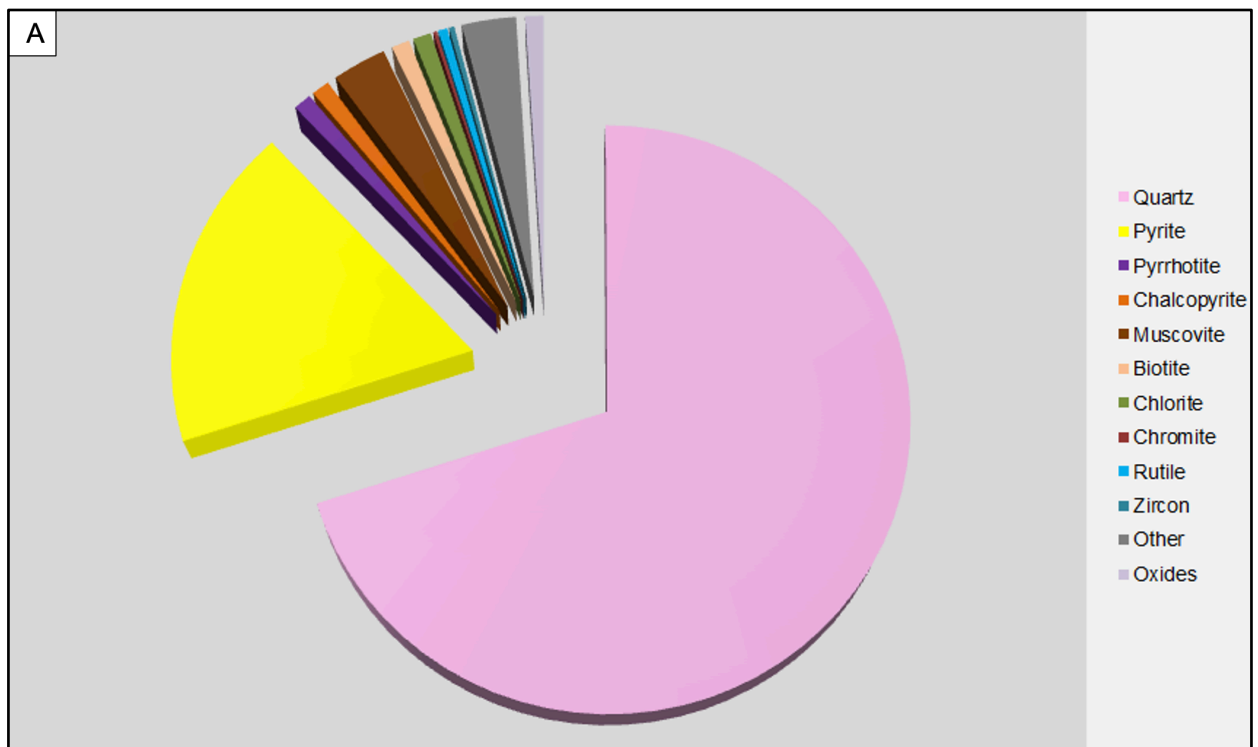


Figure 11: An overview of the Middelvlei Reef's modal mineralogy (%) in a pie chart as determined by TESCAN Integrated Mineral Analyser (TIMA).

4.1.2.2. Mineral association and characterisation of gold

Accessory minerals in the matrix of the pebble-quartz conglomerates were too complex to identify with optical microscopy. As a result, SEM-EDS and TIMA tools were utilised to identify complex small grains of gold, rutile, zircon, and chromite, etc., and to determine the mineral connection of sulphide, silicates and the mineralisation of gold of the Middelvlei Reef. The silicates form the matrix with micro fractures which are filled by minerals like quartz, pyrite, chalcopyrite, pyrrhotite, chlorite, biotite, and muscovite. The gold observed in the quartz conglomerates of the Middelvlei Reef is predominantly associated with quartz, pyrite, chlorite, muscovite, and other sulphide grains as shown in Figures 12 and 13. Figure 14 shows the irregularly shaped coarse gold grains disseminated in the matrix, filling the matrix fractures (Figure 14C). The gold also occurs irregularly, around the quartz grains and is included in the quartz and pyrite grains.

The gold grains are also linked to rutile and zircon as they sometimes occur as veinlets filling the fractures of the grains (Figure 14A). Rounded and sub-angular gold grains are also present in the Middelvlei Reef as depicted in Figure 13B and it is associated with chlorite which is included in the silicates. The majority of the electrum grains are composed of silver (Ag) and gold (Au) (Appendix A1.3). The rutile grains have inclusions of gold, galena, uraninite, and brannerite (Figure 14A). Chlorite is included in the matrix. Gold occur as inclusions in the quartz matrix (Figure 14C), the fractures of pyrite and quartz grains, and as inclusions in the pyrite grains. These compositions show that pyrite mineralisation dominates the Middelvlei Reef.

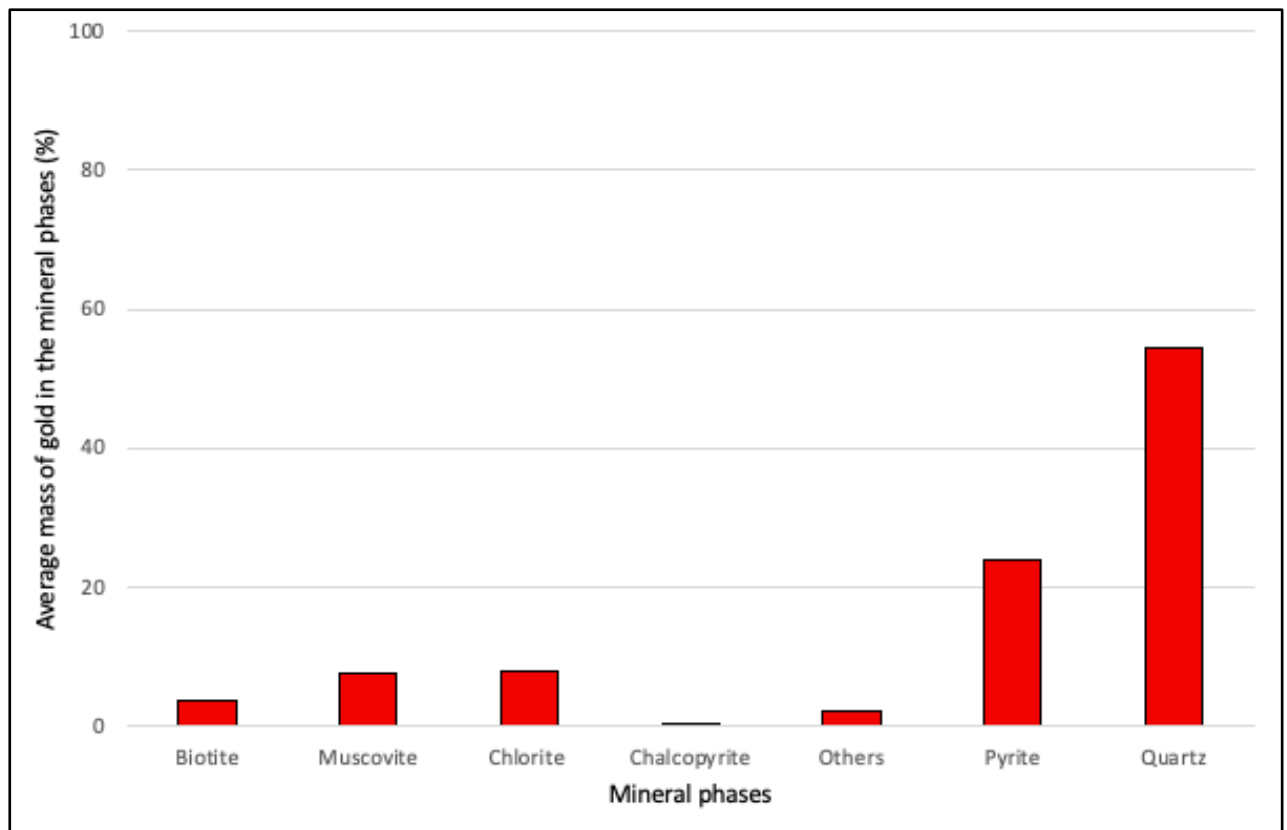


Figure 12: Mineralogical association of gold with gangue minerals obtained from TIMA.

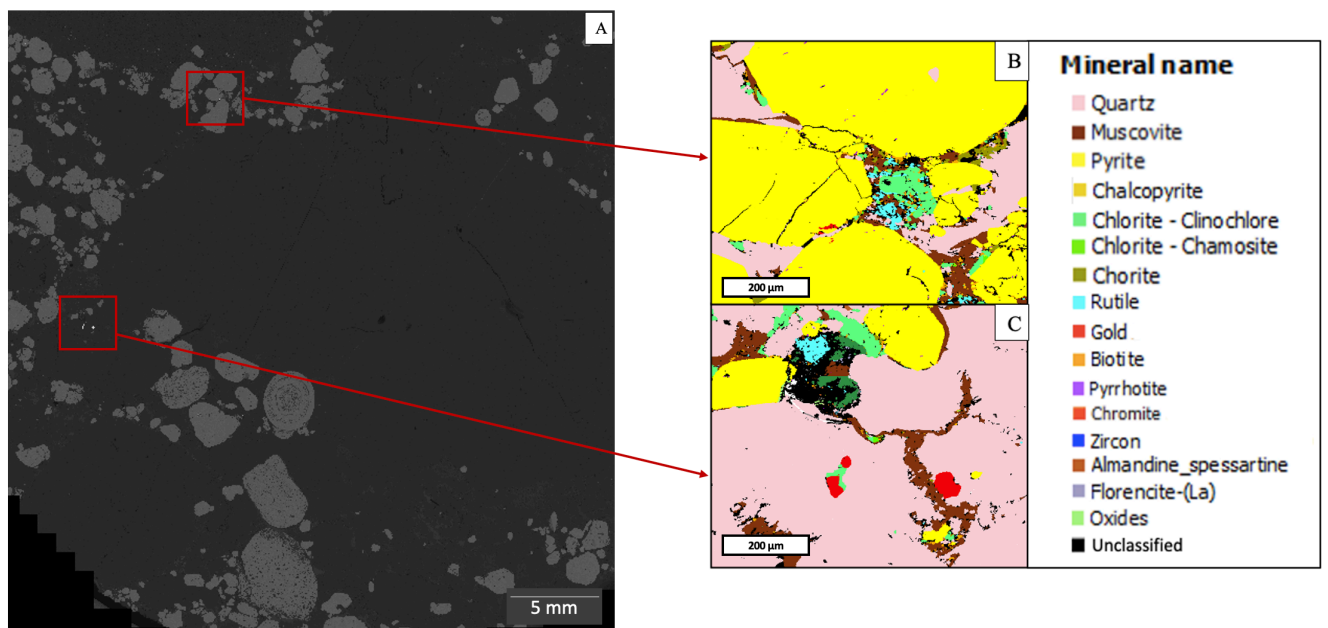


Figure 13: Mineral phases from TIMA analyses showing A) BSE image of analysed pyrite grains within the ore block B) Pyrite grains with chlorite, muscovite and gold and C) Mineral association between gold and chlorite and quartz.

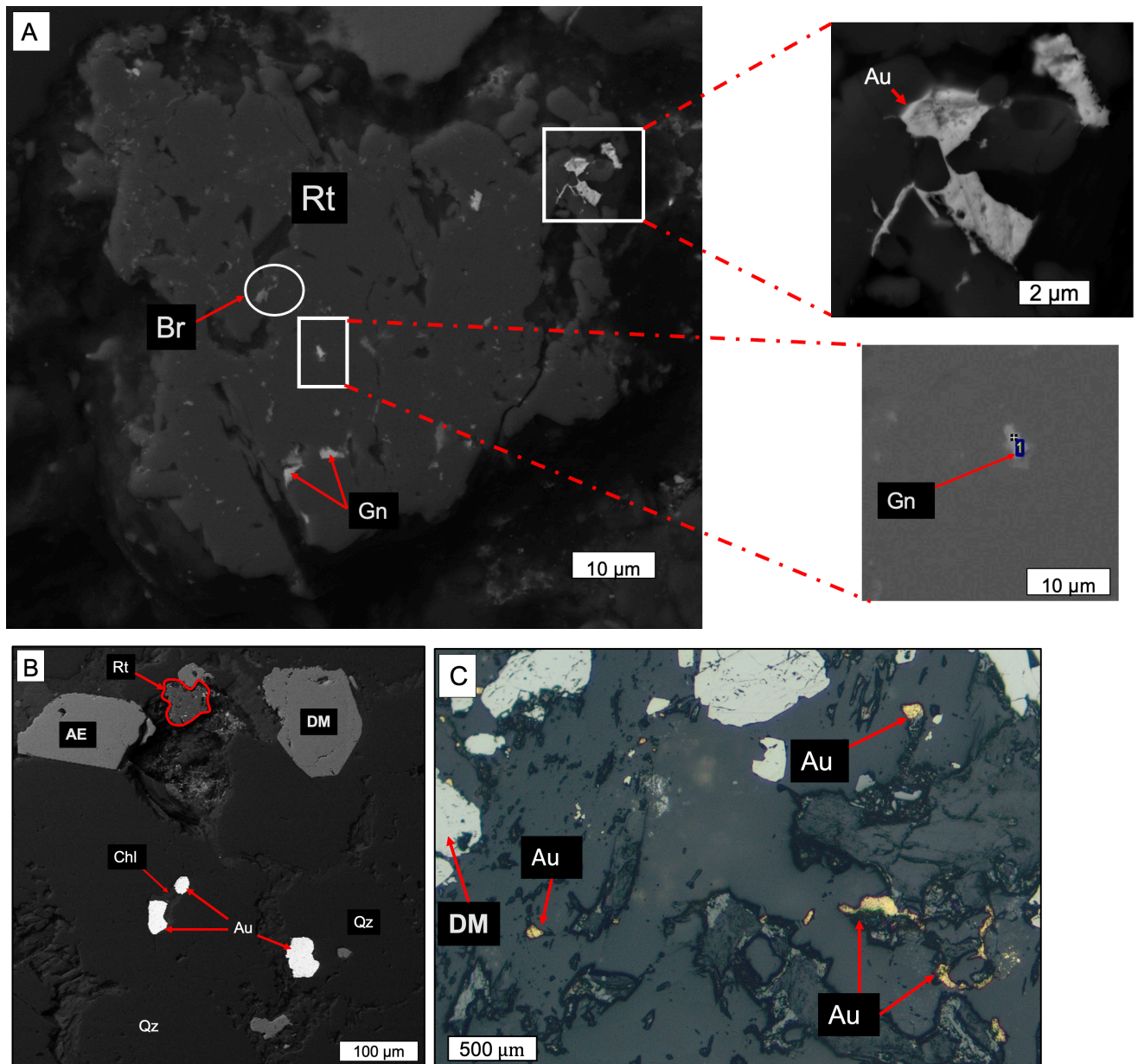


Figure 14: SEM-EDS images depicting A) Rutile grain with various inclusions like Au, Gn, Urn and Br. Au occurring as veinlets filling the fractures in the rutile grain. Spectrum 1 analysed on a grain of Gn. B) BSE image showing gold grains and the minerals it is associated with. C) Photomicrographs depicting gold grains in the silicate matrix. (Au = Gold, Br = Brannerite; Gn = Galena; Urn = Uraninite; Chl = Chlorite).

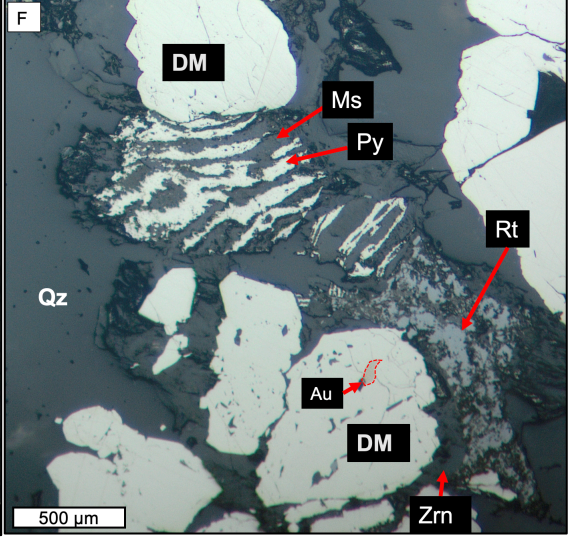
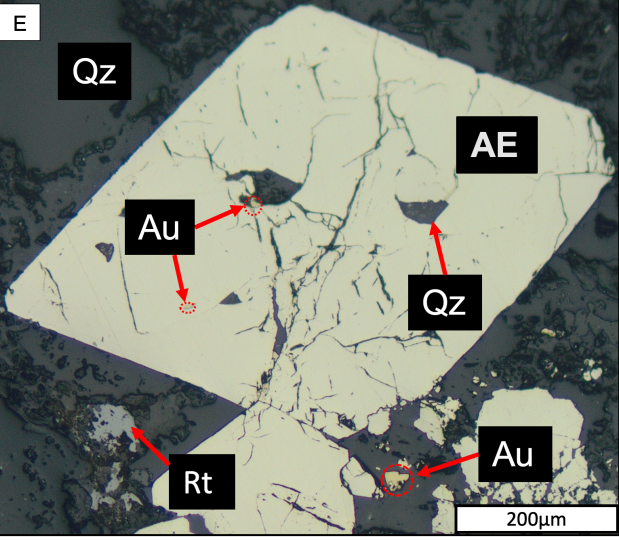
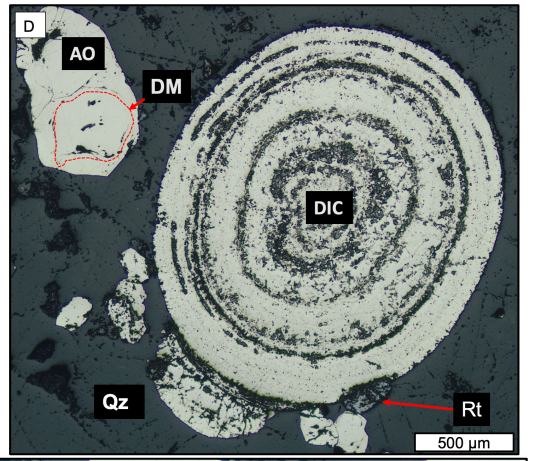
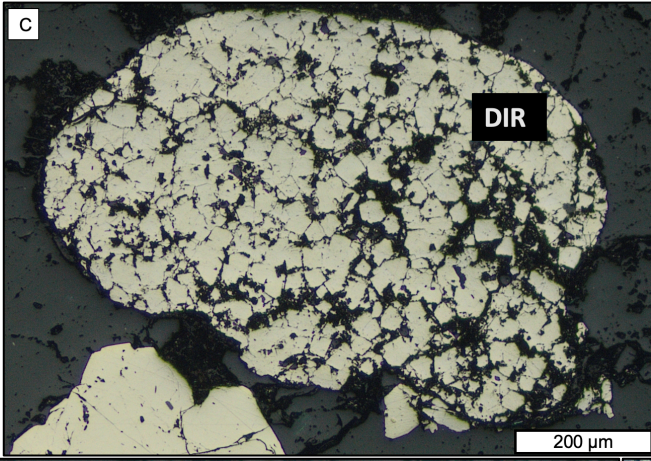
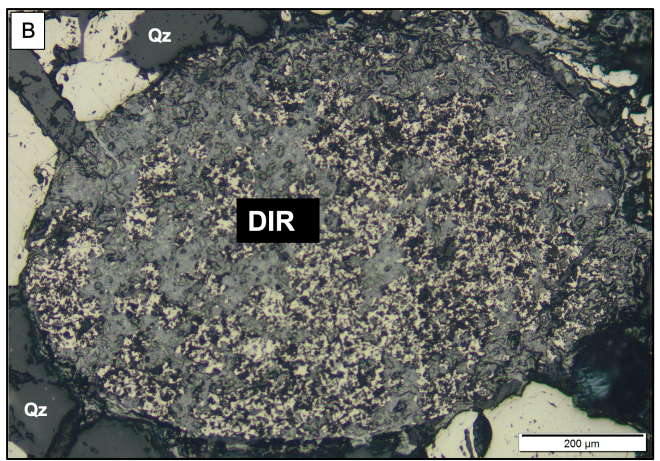
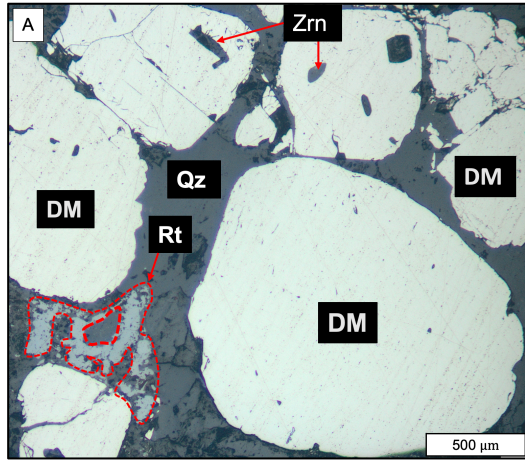
4.1.2.3. Sulphide minerals in the Middelvlei Reef

In the Middelvlei Reef orebody, sulphide mineralisation is widespread and occurs in conglomerates and quartzites. Sulphides observed include mainly pyrite, minor pyrrhotite with chalcopyrite, traces of galena, and sphalerite. Chalcopyrite occurs within the fractures of the matrix and as inclusions in the pyrite grains. The occurrence of pyrite is closely associated with gold mineralisation. Gold is disseminated as specks in the matrix, next to chalcopyrite, around the pyrite grains, and as inclusions within the pyrite grains. The pyrite grains make up about 20% of the modal abundance and more than 90% of sulphide minerals in the Middelvlei Reef with a general size range of about 0.01 - 1.6 mm. It occurs as different morphologies, predominantly as detrital (allogenic)/ syn-sedimentary and hydrothermal/ authigenic (formed *in situ*) pyrite. The Middelvlei Reef's quartz-pebble conglomerates include various kinds of pyrite (following the revised classification scheme in Figure 6 by Da Costa *et al.*, 2020).

- 1) Massive detrital pyrite (DM): It occurs as a closely packed massive, sub-rounded to rounded shape with a grain size range between 0.7 mm - 1.64 mm (Figures 15A and 15H). It is inclusions-poor, holding ~ < 10% inclusions such as chalcopyrite (Ccp), pyrrhotite (Po), quartz (Qz), rutile (Rt), florencite (Fl), biotite (Bt), muscovite (Ms), baryte (Brt), oxides and kaolinite (Ko). It makes up about 40% proportion of the sample.
- 2) Inclusion-bearing detrital pyrite (DI) is inclusion-rich with more than 10% of inclusions which occur either orientated randomly (Figures 15B and 15G), as concentric laminae (Figure 15D) and as aggregates of small (<50 µm) angular to sub-rounded pyrite grains (Figure 15C). Making up about 30% proportion of the sample. The porous pyrite grains observed are distinguished from each other because of the different arrangement of mineral inclusions in the different textures. They are:
 - i. Random inclusion-bearing pyrite (DIR): the grains are rounded-subrounded in shape with a size range between 0.12 mm - 1.66 mm. It is inclusion-rich (>10%) with inclusions such as chalcopyrite, pyrrhotite, quartz, gold, and galena that are randomly scattered throughout the grain and range in size from a few µm. In some areas, the random inclusions occur as aggregates of pyrite (Figures 15B and 15G). The aggregate pyrite (AA) occurs as multiple small (<50 µm) cubic to sub-angular grains which concentrate together as a singular sub-rounded grain as seen in Figure 15C.
 - ii. Concentrically laminated detrital pyrite (DIC): occurs as spherical grains which are 1.15 mm in size. It is made of concentric sets of alternating laminae and non-

laminated domains with micro-inclusions between interstices of laminae that are mainly chalcopyrite, pyrrhotite, rutile, muscovite, biotite, gold and chlorite (Figure 15D).

- 3) Coarsely crystalline detrital pyrite (DC): the grain is dominated by a zebra-like texture immersed in the muscovite matrix (Figure 15F). It makes up about < 1% proportion of the sample.
- 4) Euhedral/subhedral authigenic pyrite (AE) occurs as individual cubic, regular to sub-regular shaped grains (Figure 15E). They occur as single or clustered crystals with less ($\sim < 10\%$) to no inclusions. The grains are disseminated across the sample or appear closely packed in the fractures. The grains make up about 25% proportion of the sample. They are smaller than the detrital grains with a size range from 0.03 mm to 1.15 mm. They occur as aggregate inclusions in the structure of randomly distributed pyrite grains and contain inclusions such as quartz, pyrrhotite, chlorite, and gold.
- 5) Overgrowth authigenic pyrite (AO) forms overgrowths on and around the massive and subhedral grains (Figure 15H) forming grains with a core-rim structure. There are several inclusions observed. These pyrite grains make about 2% of the sample.
- 6) Infill authigenic pyrite (AI) fills the fractures within the compact pyrite grains cross-cutting the detrital grain (Figure 15G). The proportion they make up within a sample is about 2%.



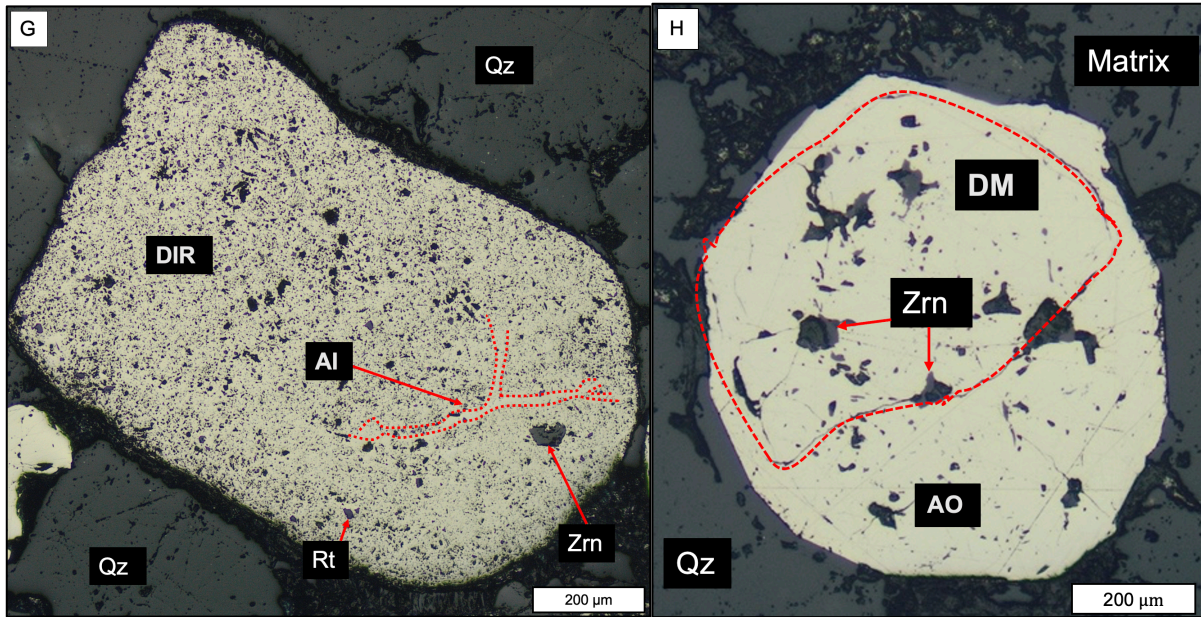


Figure 15:: Representative photomicrographs (reflected polarized light) of the Middelveit Reef showing A) Rounded to subrounded detrital massive pyrite (DM); B) and C) Shows inclusion-bearing pyrite (DI) with randomly distributed inclusions (DIR), aggregate pyrite (AA), respectively; D) Shows concentrically laminated (DIC) pyrite and overgrowth(AO) pyrite around massive pyrite type (DM); E) Euhedral/subhedral pyrite (AE) with Au inclusions in the grain and matrix; F) Coarsely crystalline pyrite (DC) with zebra-like /chevron texture. Pyrite mineral alternate with Rt (inclusions occupying fractures); G) DIR with veinlet of infill pyrite (AI) (showed by the arrow); H) Overgrowth pyrite (AO) on massive pyrite (DM).

4.2. Whole-rock geochemistry

4.2.1. Major element geochemistry

Understanding the mechanisms influencing the weathering, transport, and sorting of sediments could help determine where Middelvlei Reef successions originate (Taylor and McLennan., 1988). The average major element chemical concentrations of Middelvlei Reef's quartzite and conglomerate are displayed in Table 8 (LOI free), and a complete dataset is shown in Appendix A2.1. Table 8 shows the analysed sample results of the reef and average results of the hanging wall and footwall are represented by quartzite. Because the two walls showed similar features, the analysed data is averaged as one in the data analyses. The two rock units discussed in Section 4.1.1 have significant silicon dioxide (SiO_2) enrichment and low levels of most of the other oxides. Specifically, SiO_2 content ranges between 86.73 – 91.66 wt% and 78.28 – 90.61 wt% with equivalent mean values of 89.48 and 84.76 wt% in conglomerate and quartzite, respectively. The major elements composition of the Middelvlei Reef shows that the most abundant mineral in this reef is quartz, followed by pyrite, mica group minerals (muscovite and biotite), chlorite, and other minor minerals and sulphides.

SiO_2 and Al_2O_3 have a positive correlation ($r = +0.95$). The overall ore contains lesser amounts of MnO , MgO , and TiO_2 which have a very narrow to zero compositional range with mean and standard deviation (stdv) of <1 wt%. The correlation between Al_2O_3 , Fe_2O_3 and NiO is negative as shown in Figures 16F and 16H. There are some strong positive correlations (Figure 16B) observed between K_2O and Al_2O_3 with correlation efficiency ($r = +1$) due to these major oxides being hosted in illite/mica group minerals. Another strong correlation ($r = +0.97$) between MgO and Al_2O_3 can be attributed to chlorite (Figure 16D). The major oxides that show no correlation with Al_2O_3 are Na_2O , NiO , P_2O_3 and MnO (Figures 16C, 16F, 16G, and 16I).

The Chemical Index of Alteration (CIA) calculates the intensity of chemical weathering (Nesbitt and Young, 1982). Every value in the equation (Equation 2) is expressed in molar proportions. CaO^* is CaO that is only housed in silicates (Garzanti and Resentini., 2016). In this study, it was corrected using the correction from McLennan (1993). The empirical correction considers $\text{CaO}^* = \text{Na}_2\text{O}$ if the number of CaO moles is bigger than Na_2O (McLennan., 1993). On the geochemical ternary plot, presented in Figure 16A, the Middelvlei Reef shows a depletion of CaO , Na_2O and K_2O which indicates trends along the A-K compositional line towards kaolinite and chlorite. Conglomerate samples cluster just above illite, whereas quartzite contents cluster around muscovite. Conglomerate and quartzite rocks of the Middelvlei Reef yield 85% and 82% CIA value indicating intermediate to strong weathering.

$$CIA = \left(\frac{Al_2O_3}{Al_2O_3 + CaO^* + Na_2O + K_2O} \right) \times 100$$

Equation 2

Although the CIA can anticipate the weathering pathway and the formation of clay minerals, this study also calculates the Chemical Index of Weathering (CIW) (Equation 3) because modification in potassium is thought to impact weathering interpretations from the CIA method (Harnois., 1988 and Condie *et al.*, 1992). The conglomerate and quartzite from the Middelvlei Reef show 100% and 98% CIW values, respectively. These high CIW values correlate with the results of the CIA, suggesting intense weathering of the sedimentary rock units.

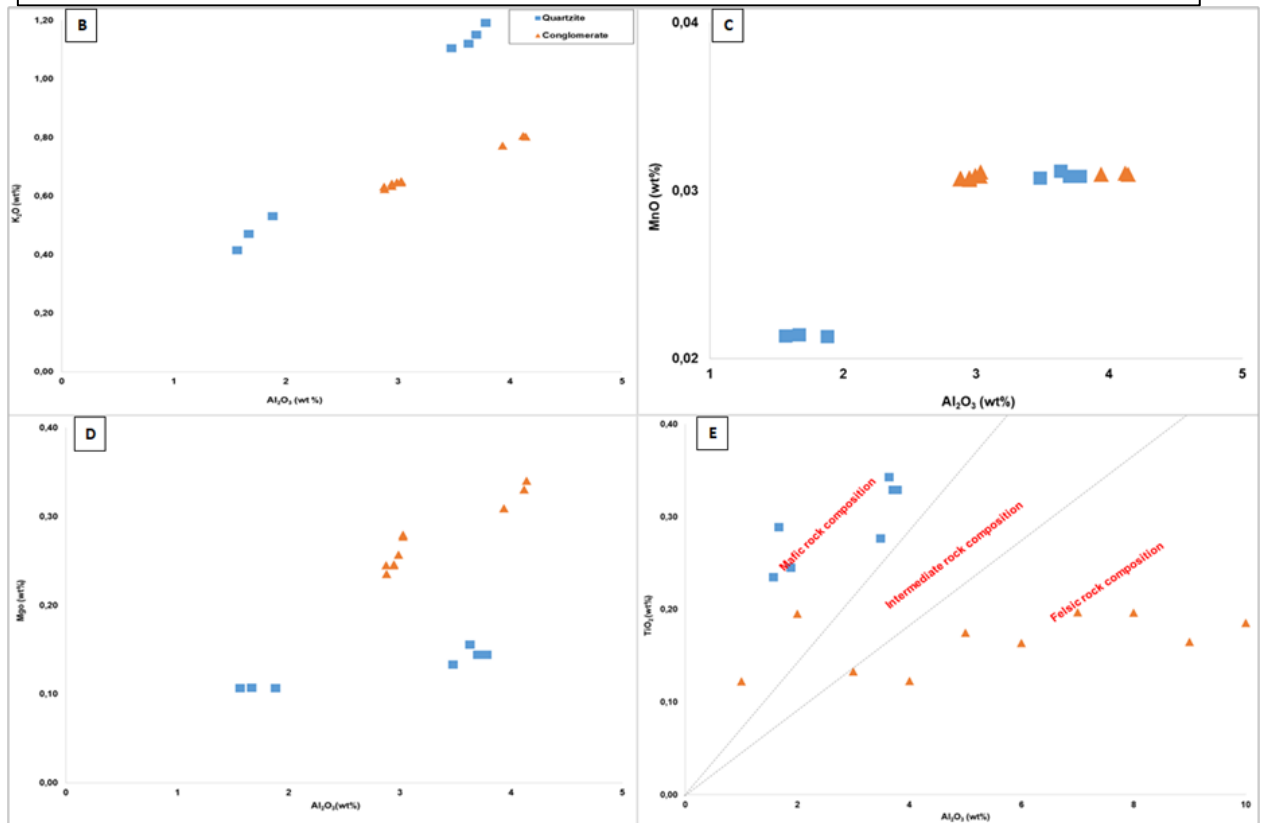
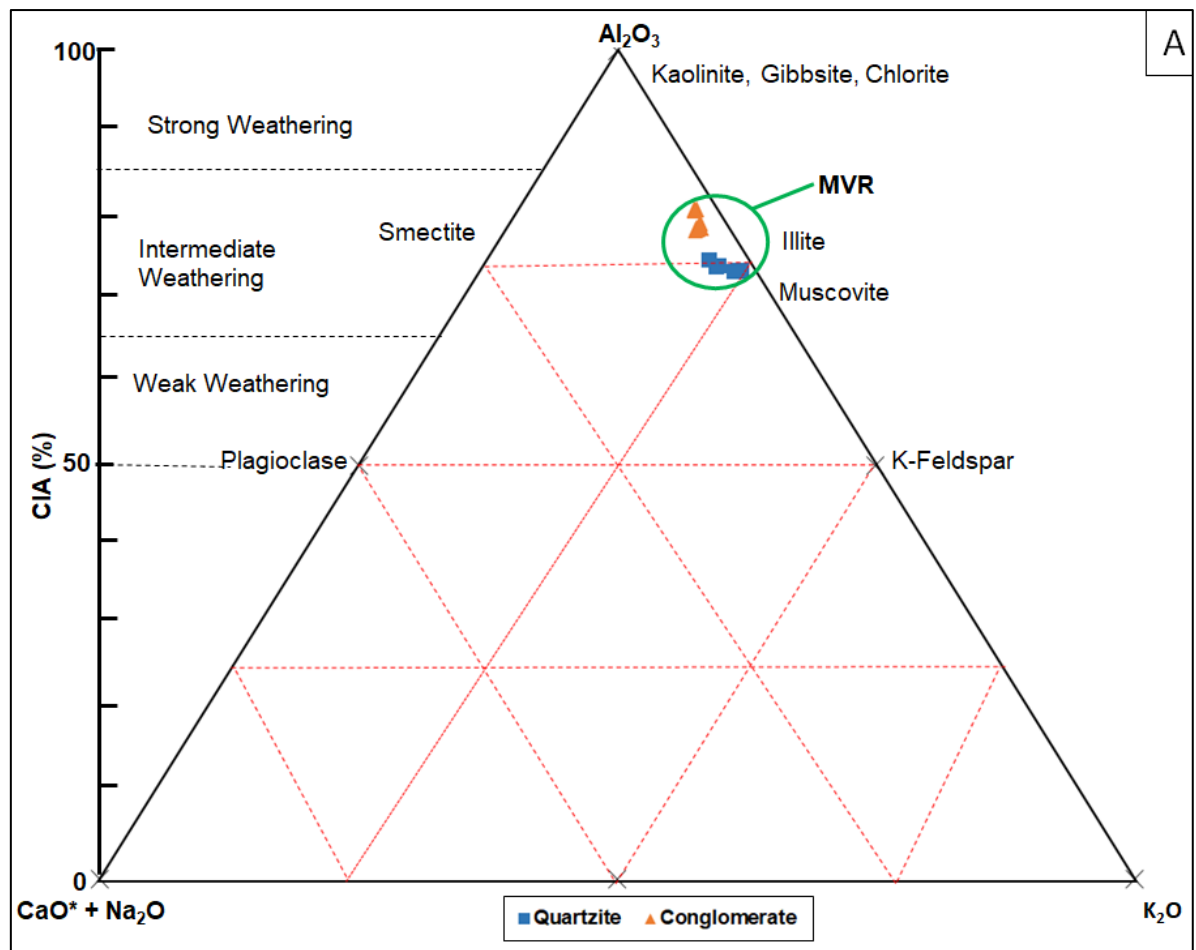
$$CIW = \frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O} \times 100$$

Equation 3

The Index of Compositional Variability (ICV) should also be taken into account simultaneously because it is indicative of resistance to processes of weathering (Cox *et al.*, 1995). The ICV is also used to quantify the amount of aluminium present in a rock relative to other major oxides (Perri., 2020). The ICV is believed to be strongly associated with CIA and CIW as stated by Cox *et al.* (1995). It was indicated that low ICV values (<1) are related to high values of CIA and CIW (vice-versa). In the Middelvlei Reef, the latter relation is not true. The conglomerate and quartzite samples of the Middelvlei Reef yield high ICV values of 2 and 3, respectively. This represents immature rocks that are less weathered while CIA and CIW values indicate intense weathering.

$$ICV = \frac{(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)}{Al_2O_3}$$

Equation 4



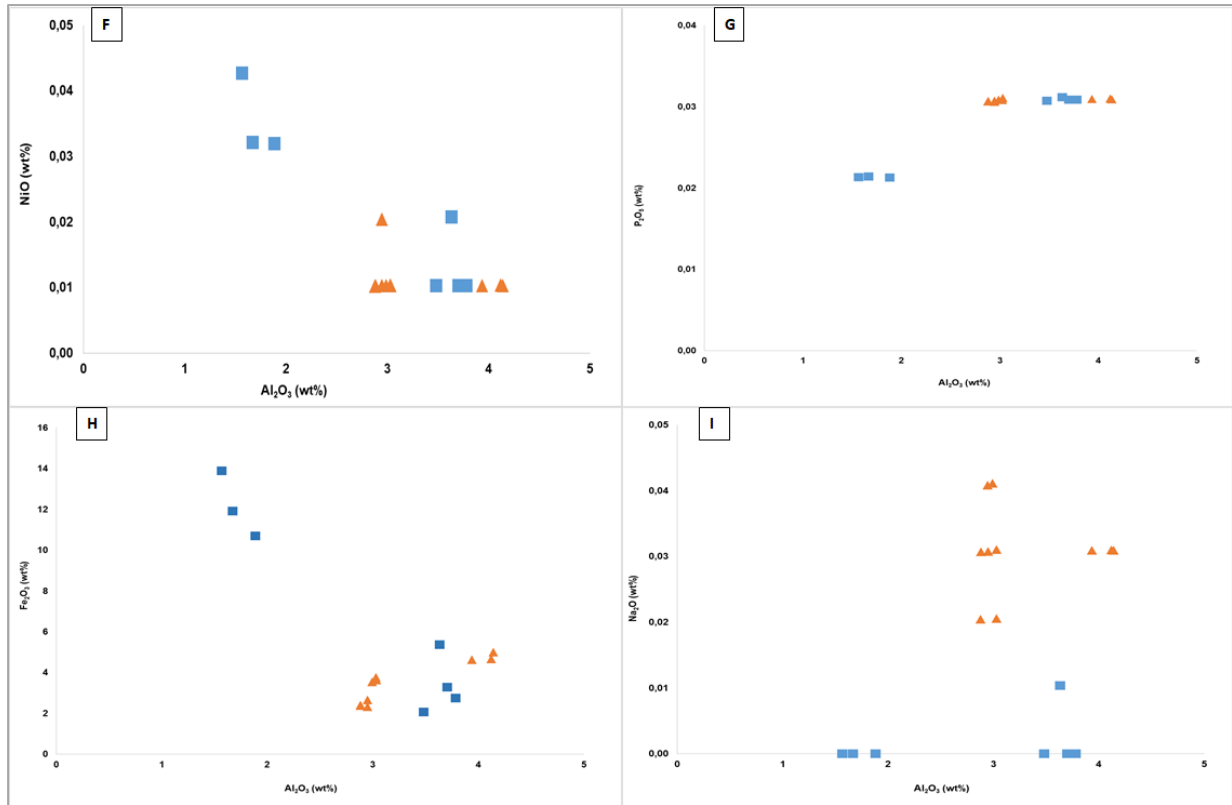


Figure 16: A) The A-CN-K ternary diagram ($A = Al_2O_3$; $CN = CaO + Na_2O$; $K = K_2O$) showing geochemical composition of the Middelvlei Reef emphasizing weathering trends in molecular proportions (Nesbitt and Young, 1982); B - I) Bivariate plots of major elements oxides of the Middelvlei Reef samples. E) Bivariate plots of major elements oxides with provenance identification.

Table 8: Mean of major element chemical compositions of the Middelvlei Reef rock types (Stdv= standard deviation).

Quartzite	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	NiO
Mean (wt%)	88.53	2.82	7.14	0.03	0.13	0.04	0.00	0.86	0.29	0.03	0.12	0.02
Stdv (wt%)	3.56	1.05	4.90	0.01	0.02	0.01	0.00	0.36	0.04	0.01	0.05	0.01
Conglomerate												
Mean (wt%)	91.62	3.25	3.83	0.03	0.26	0.03	0.03	0.70	0.18	0.03	0.03	0.01
Stdv (wt%)	1.66	0.54	1.03	0.00	0.04	0.00	0.01	0.08	0.03	0.00	0.01	0.00

4.2.2. Trace element geochemistry

The nature of the source rock can be inferred from trace elements. Trace element abundances result from a variety of factors such as origin, weathering, erosion, transport, diagenesis, and climate conditions. A complete dataset of the Middelvlei Reef trace element compositions of quartzite and conglomerate samples is presented in Appendix A2.2. The conglomerate and quartzite rock units show significantly different lithochemistry. The minor minerals and sulphide minerals such as gold, zircon, rutile, uraninite, chromite galena,

pyrrhotite, and chalcopyrite are reflected by the high concentrations of elements presented in Table 9. Quartzite from the Middelvlei Reef is enriched with both High Field Strength Elements (HFSE) and transition minerals (Cu, Co, and Ni). Light Rare Earth Elements (LREE) and Heavy Rare Earth Elements (HREE) appear in lower amounts in both quartzite and conglomerate.

Table 9: Average trace element chemical concentrations (ppm) of the Middelvlei Reef rock types.

Quartzite		Conglomerate	
Ti	737.709	Ti	373.80
Cr	315.841	Cr	68.96
Ni	154.380	Ni	67.72
Zr	260.168	Zr	65.32
Ba	39.159	Ba	104.67
Co	137.616	Co	53.69
U	103.433	U	24.56
Cu	106.879	Cu	36.37
P	45.665	P	54.29
Pb	83.559	Pb	18.89
Ce	32.379	Ce	41.86
La	17.045	La	22.96
Rb	16.141	Rb	13.57
Nd	11.721	Nd	15.25
V	17.934	V	9.75
Zn	66.11	Zn	26.09
Y	12.586	Sr	18.14

Some trace element concentration ratios can be used to predict the potential source of rock units. Those for the Middelvlei Reef are calculated and presented in Table 10. The quantities of mafic, intermediate, and felsic rocks in the sediment origin area can also be evaluated using ratio values. Besides chemical indices, provenance signatures such as i) Th/Sc vs Zr/Sc plot (Figure 17A), ii) TiO_2/Zr plot (Figure 17B), and iii) $\text{TiO}_2/\text{Al}_2\text{O}_3$ (Figure 16E) are used to quantify chemical changes of sediments resulting from weathering, diagenesis and terrane type.

The Th/Sc ratio values range between 2.62 - 5.15 and 2.28 - 6.63 with equivalent averages of 4.07 and 2.52 for conglomerate and quartzite samples, respectively. The Zr/Sc values range between 21.99 - 5.15 and 62.29 - 133.18 with averages of 38.18 and 84.16 for conglomerate and quartzite samples, respectively. Th/Sc vs Zr/Sc ratios suggest that the samples from the Middelvlei Reef belong in the felsic rock field. Following these results, the TiO_2/Zr diagram (Figure 17B) shows that the conglomerate belongs to the intermediate rock field and the quartzite in the felsic rock field. The $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio values of the conglomerate and quartzite from the Middelvlei Reef range between 0.04 - 0.07 and 0.08 - 0.17, with equivalent averages of 0.05 and 0.11, respectively. The $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio values (Figure 16E) demonstrate that most of the conglomerate belongs to a felsic rock composition while all quartzite samples indicate a mafic rock composition.

Table 10: Average trace element concentration ratio values of samples from the Middelvlei Reef. Rock provenance deduced following work from McLennan et al. (1993) and Ofili et al. (2022).

Ratios	Quartzite	Conglomerate	Potential rock Source
Nb/Ta	7.05	6.54	Felsic
Ti/Zr	2.84	5.72	Mafic
Gd/Yb	1.30	2.86	Mafic
Eu/Eu*	0.01	0.01	Felsic
La/Co	0.12	0.43	Mafic
Th/U	0.10	0.26	Mafic
Cr/Th	31.66	10.61	Mafic
La/Sc	6.10	13.82	Felsic
Zr/Sc	93.09	39.33	Felsic
Th/Sc	3.57	3.91	Felsic
Y/Ni	0.08	0.09	Felsic

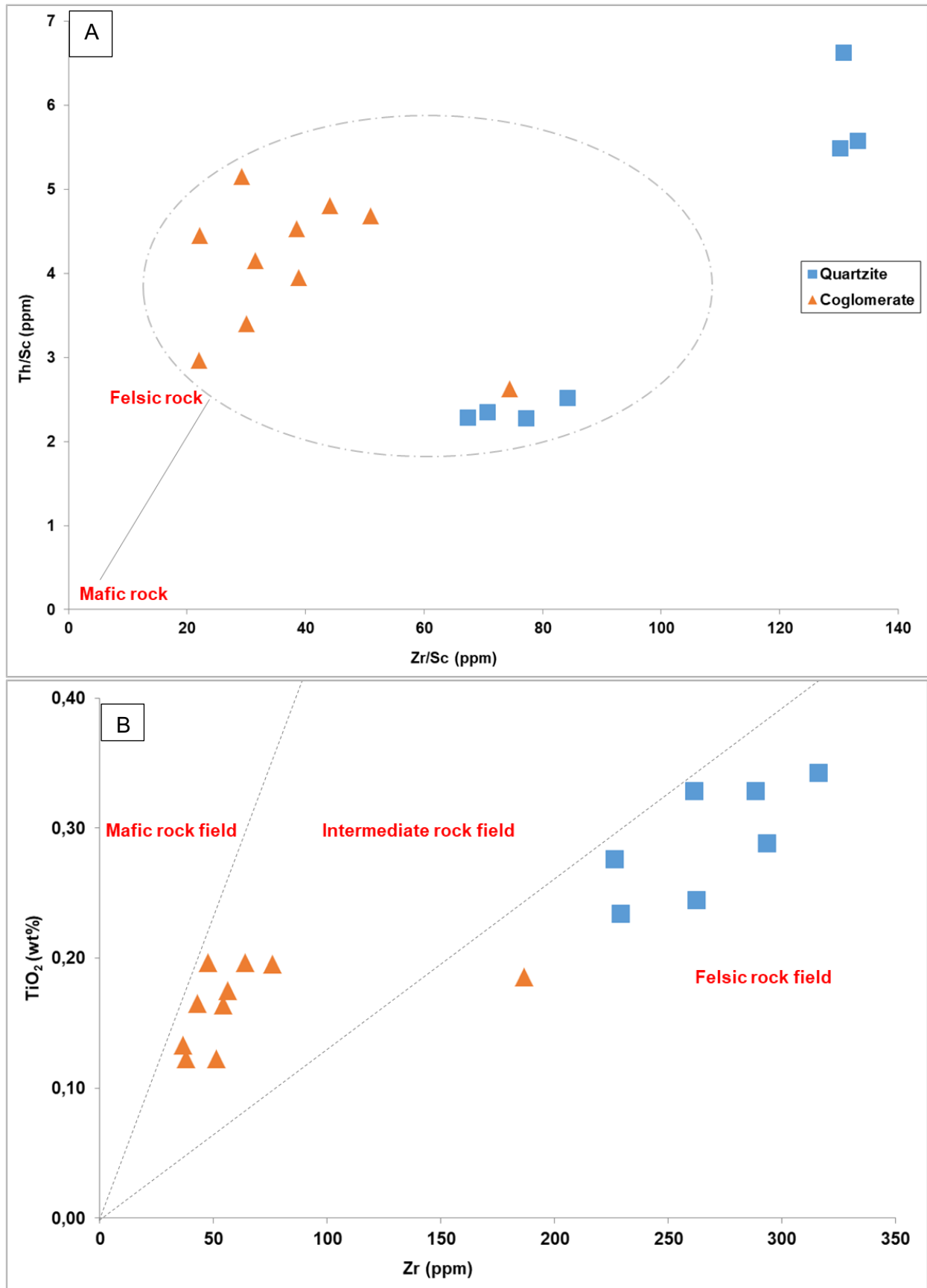


Figure 17: A) Th/Sc vs Zr/Sc, and B) TiO₂/Zr diagrams are used to depict rock provenance following work from Ofili et al. (2022).

4.3. Micro-beam analysis and $\delta^{34}\text{S}$ isotopes

4.3.1. Electron probe micro-analyses (EPMA) trace elements

EPMA results of massive “compact” detrital, random inclusion-bearing, concentrically laminated and euhedral/subhedral generations of pyrite grains are listed in Table 11 and a complete data set is presented in Appendix A3.1. For every pyrite grain, the Fe and S concentrations are the same. The pyrite grains of the Middelvlei Reef correlate with the composition of that of typical pyrite grains when measured by wt%.

Notably, both Fe and S content values are relatively high in massive detrital pyrite. Fe shows a range of 44.11 - 47.11 wt%, with an average of 45.21 wt%. S shows a range of 51.02 - 53.35 wt% and an average of 52.51 wt%. In random inclusion bearing “porous” pyrite, Fe ranges from 41.80 - 45.45 wt%, with an average of 44.12 wt% and S content ranges from 48.14 - 53.33 wt%, with an equivalent average of 51.03 wt%. The Fe and S contents of 40.87 – 46.35 wt% and 48.70 - 53.75 wt%, with averages of 44.63 wt% and 52.15 wt%, respectively. In euhedral/subhedral “cubic” pyrite, Fe and S concentrations range from 41.61 - 45.25 wt% and 50.88 - 53.36 wt%, with averages of 44.27 wt% and 52.69 wt%, respectively.

The contents of Co, Ni, As, Au, Ag, Au/Ag, and Co/Ni within the grains of pyrite show a huge variation. The composition of Co in detrital massive pyrite grains shows a range of 0.09 – 0.11 ppm with an average of 0.10 ppm. In addition, Ni shows a range of 0.09 – 2760.08 ppm and an average of 436.43 ppm. The concentrations of As, Au, and Ag are <10896.81 ppm, <1249.74 and 467.25 ppm with equivalent averages of 3125.07 ppm, 78.20 ppm and 175.90 ppm, respectively. The ratios of Co/Ni and Au/Ag are <1 and <3.66 with equivalent average values of 0.25 and 0.48, respectively.

The concentrations of Co and Ni are highest in inclusion-bearing pyrite grains. The composition of Co in random inclusion-bearing pyrite grains shows a range of 0.09 – 0.19 ppm with an average of 0.11 ppm. Ni shows a range of 70.01 – 8856.28 ppm and an average of 3453.79 ppm. The concentrations of As, Au, and Ag are <10571.25 ppm, <1102.13 ppm and 553.1 ppm with equivalent averages of 2666.88 ppm, 68.98 ppm and 181.59 ppm, respectively. The ratios of Co/Ni and Au/Ag show average values of 0.0002 and 689.02, respectively. The contents of Co and Ni in concentrically laminated inclusion-bearing pyrite grains range from 0.09 – 0.12 ppm and 445.15 – 5102.47 ppm, with averages of 0.10 ppm and 2946.62 ppm. The concentrations of As, Au, and Ag show ranges of 613.29 – 25132.68 ppm, 0.09 – 0.12 ppm and 0.10 - 413.27 ppm with equivalent averages of

10786.65 ppm, 0.1 ppm and 193.18 ppm, respectively. The ratio of Co/Ni and Au/Ag is <1 with an average of 0.17.

The composition of Co in euhedral pyrite grains shows a range of 0.09 – 4219.50 ppm with an average of 602.87 ppm. Ni shows a range of 0.09 ppm and an average of 951.43 ppm. The concentrations of As, Au, and Ag are <15690.50 ppm, <0.1 and 292.38 ppm with equivalent averages of 5181.10 ppm, 0.1 ppm and 52.77 ppm, respectively. The ratios of Co/Ni and Au/Ag are <42195 and <1 with equivalent average values of 6028.14 and 0.57 respectively.

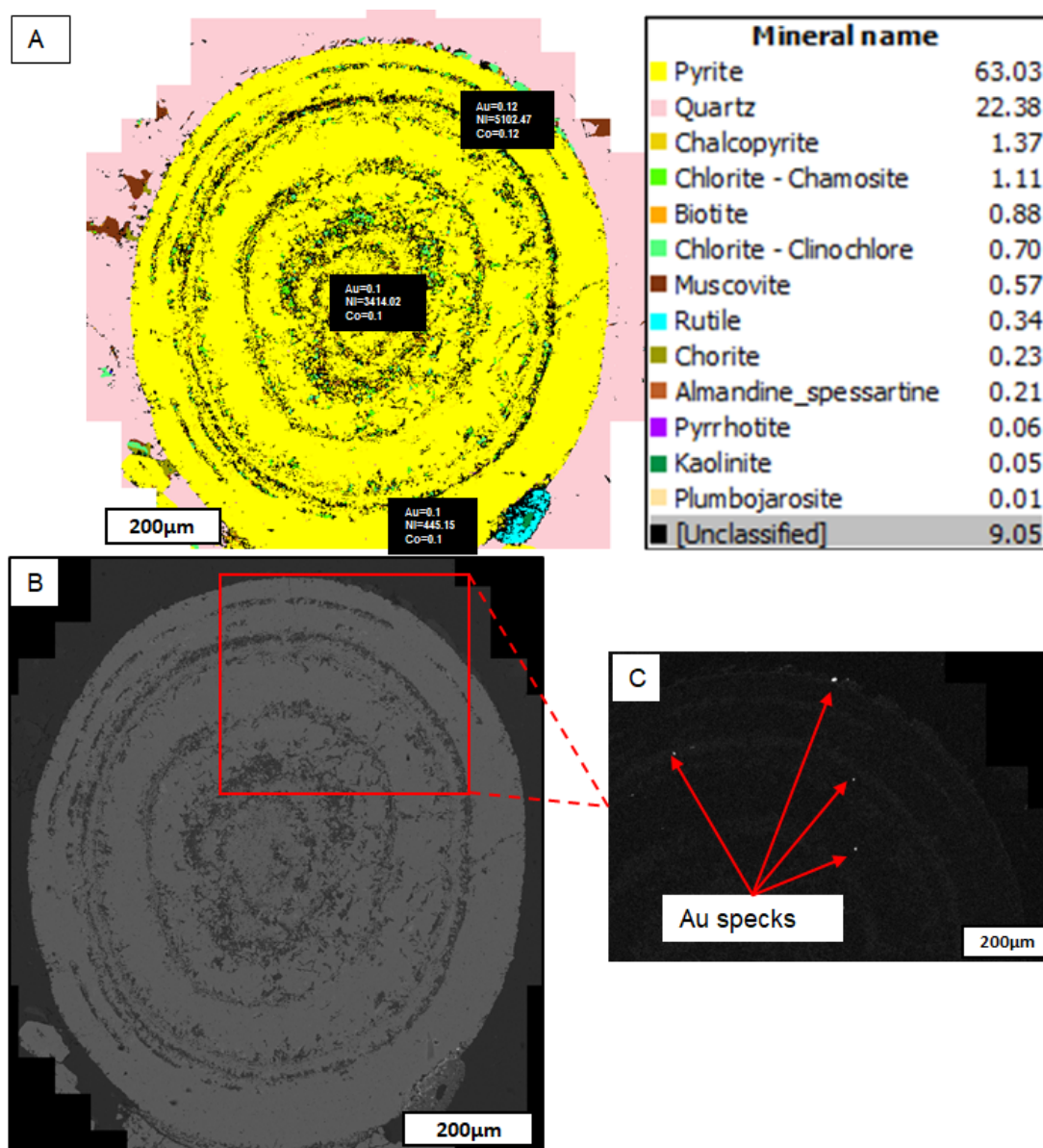


Figure 18: Petrographic and BSE micrographs depicting some of the spot analyses performed with EPMA tool on DIC grain. A) Mineral phases from TIMA showing Au, Ni, and Co (ppm) variation. (B) BSE image from SEM-EDS and C) Au compositional map from TIMA (white sparks represents Au).

Table 11: EPMA element compositions (ppm) for all pyrite types from the Middelvlei Reef deposits.[Massive detrital (DM), random inclusion-bearing (DIR), concentrically laminated (DIC) and euhedral/subhedral authigenic (AE)]

DM (n=16)	V	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Sb	Te	Au	Hg	Pb	Bi
Minimum	0.09	0.09	0.09	0.09	0.09	0.10	0.09	4275.17	0.09	0.09	0.09	0.09	0.09	0.09	0.10
Maximum	88.02	0.11	2760.08	991.68	1385.15	10896.81	8089.25	9423.94	467.45	400.08	233.51	1249.74	3909.26	13433.57	27251.01
Stdv	28.98	0.01	719.09	306.75	429.88	3166.53	2657.35	1359.74	175.16	105.76	95.59	312.41	1352.92	5066.49	6935.66
Average	25.49	0.10	436.43	190.15	314.22	3125.07	3029.54	6333.47	175.90	39.19	95.54	78.20	899.94	4475.75	3612.92
DIR (n=16)															
Minimum	0.10	0.09	70.01	0.10	0.10	0.10	0.10	2405.21	0.10	0.09	0.10	0.09	0.10	0.10	0.10
Maximum	123.64	0.19	8856.28	60283.96	1513.53	10571.25	9596.21	13434.37	553.10	187.14	367.41	1102.13	6049.07	19726.07	10857.28
Stdv	40.17	0.02	2096.98	14879.62	485.81	3053.15	3283.49	2337.61	176.73	55.16	117.41	275.51	1772.49	6114.36	4473.99
Average	36.42	0.11	3453.79	4548.11	323.58	2666.88	2177.82	5966.50	181.59	27.32	162.74	68.98	1225.23	6238.78	2911.64
DIC (n=6)															
Minimum	0.09	0.09	445.15	0.09	0.10	613.29	0.10	4968.11	0.10	0.10	0.10	0.09	0.09	0.10	0.09
Maximum	0.12	0.12	5102.47	1301.96	948.94	25132.68	11219.52	8565.54	413.27	759.16	203.91	0.12	0.12	54726.77	1454.85
Stdv	0.01	0.01	1687.91	544.35	412.66	9265.58	4531.73	1375.43	177.60	312.04	92.88	0.01	0.01	20939.24	593.90
Average	0.10	0.10	2946.62	450.72	480.45	10786.65	2814.67	6233.14	193.18	206.78	82.41	0.10	0.10	23985.44	242.56
AE (n=7)															
Minimum	0.10	0.09	0.09	0.10	0.09	0.10	0.09	5684.71	0.10	0.09	7.03	0.09	0.09	0.10	0.10
Maximum	119.39	4219.50	5914.44	555.98	806.61	15690.50	4488.57	7668.90	292.38	0.10	410.61	0.10	10154.18	31925.99	7696.13
Stdv	39.71	1594.78	2192.27	223.50	294.32	5733.18	1961.59	729.50	108.76	0.00	170.31	0.00	3669.58	11495.02	3265.87
Average	54.93	602.87	951.43	219.27	363.94	5181.10	1599.47	6728.18	52.77	0.10	245.08	0.10	5180.83	6643.51	2363.75

4.3.2. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) trace elements

LA-ICP-MS analyses reveal distinct trace element abundance in all different morphologies of pyrite as compared to EPMA results. The analytical compositions of the several generations of pyrite grains are listed in Table 12 and a complete data set is given in Appendix A3.2. The majority of elements examined were present in quantifiable amounts, mostly in inclusion-bearing pyrite grains. For some analyses, certain elements are occur in contents beneath the detection limit (LOD), especially in some areas within detrital massive and euhedral pyrite grains. Thus, these areas were not considered further.

4.3.2.1. Trace elements distribution

The concentration of elements such as Au and Ag are very low in all pyrite grains. The variation of Au and Ag within the different pyrite grains is shown in Figure 19A. In massive pyrite, the concentrations of Au and Ag range from 0.04 - 6.79 ppm and 0.02 - 7.48 ppm, with average values of 0.96 ppm and 1.23 ppm, respectively. The randomly distributed pyrite has high compositions of both Au and Ag. Notably, concentrations range from 0.73 - 11.48 ppm and 1.84 - 18.07 ppm with average compositions of 3.64 ppm and 5.49 ppm, respectively. The concentrically laminated pyrite has the highest Au and Ag concentrations with values of 0.79 - 12.46 ppm and 1.92 - 33.40 ppm with averages of 4.56 ppm and 8.77 ppm, respectively. The euhedral pyrite shows the lowest concentrations of Au and Ag. Specifically, the average Au concentration is 0.15 ppm, with a range of 0.03 ppm - 1.13 ppm. The average Ag content is 0.22 ppm, with a range of 0.03 - 0.57 ppm.

The contents of As range from 0.35 ppm - 3916.21 ppm, Pb ranges from 0.02 - 1040.73 ppm, and Zn range from 0.35 ppm - 798.83 ppm with average values of 647.45 ppm, 119.25 ppm, and 49.22 ppm, respectively, in massive pyrite. Euhedral pyrite has low concentrations of As, ranging from 0.24 - 38.30 ppm, Pb from 0.02 - 18.40 ppm, and Zn from 0.25 - 38.30 ppm. The averages of As, Pb, and Zn are 1772.90 ppm, 4.70 ppm and 4.95 ppm, respectively. The randomly distributed pyrite grains have high concentrations of As, Pb, and Zn. Notably, As ranges from 1181.55 - 13734.73 ppm with an average of 5024.39 ppm, Pb ranges from 35.39 - 2614.65 ppm with an average of 463.08 ppm and Zn ranges from 2.06 - 23.95 ppm with an average of 7.09 ppm. Finally, the concentrically laminated pyrite has As contents ranging from 234.76 - 5543.79 ppm with an average of 2238.09 ppm, Pb ranging from 24.29 - 1681.97 ppm with an average of 282.83 ppm, and Zn ranging from 1.04 - 178.17 ppm with an average of 46.53 ppm.

Trace elements Co, Ni, and Te are also found in pyrite. Co and Ni are both highly abundant in the pyrite grains from the Middelvlei Reef and interestingly exhibit a high variation (Figure 19B). In massive pyrite, Co and Ni concentrations range from 0.49 - 3034.98 ppm and 1.66 - 2590.92 ppm with equivalent averages of 431.04 ppm and 325.53 ppm, respectively. The concentration of Te ranges from 0.19 - 87.69 ppm with an average of 15.96 ppm. The randomly distributed pyrite has Co and Ni concentrations ranging from 111.11 - 2641.47 ppm and 385.65 - 6359.71 ppm with averages of 784.99 ppm and 2513 ppm, respectively. This pyrite type holds the highest concentrations of Te, ranging from 3.07 - 110.30 ppm, with an average of 51.97 ppm. Concentrically laminated pyrite has Co concentrations ranging from 49.14 - 1312.23 ppm with an average of 485.85 ppm. Interestingly, Ni concentrations are the highest, ranging from 1616.25 - 5847.68 ppm, with an average of 4031.97 ppm. The Te concentrations range from 3.41 - 68.29 ppm, with an average of 21.75 ppm. Massive pyrite has the highest Co concentrations ranging from 21.49 - 18221.55 ppm, with an average of 2154.80 ppm. The Ni concentration in the massive pyrite type ranges from 14.31 - 3523.24 ppm, with an average of 691.52 ppm. Finally, Te contents range from 0.26 - 11.38 ppm, with an average of 2.64 ppm.

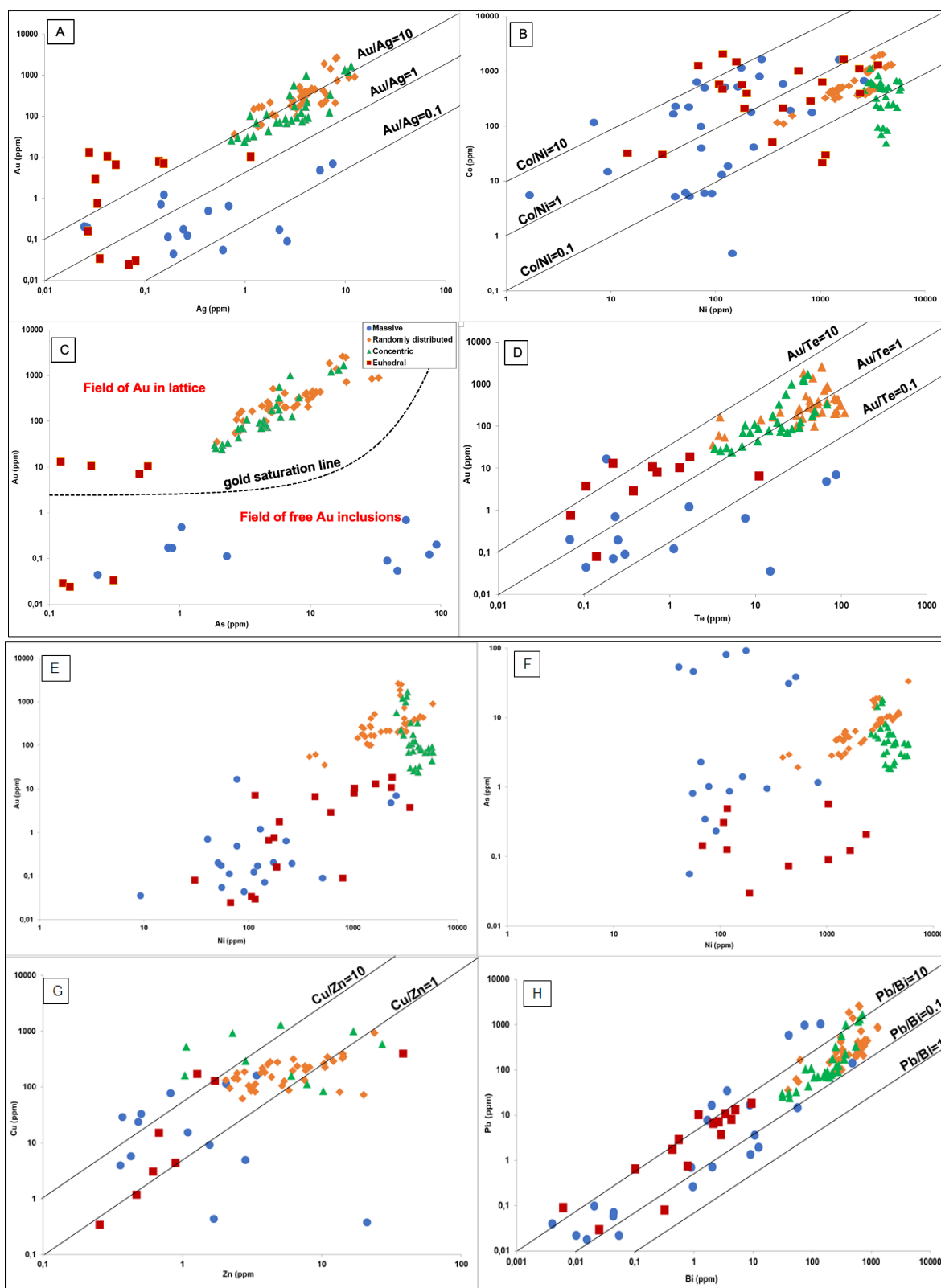


Figure 19: Bivariate plots of LA-ICPMS trace elements concentrations of detrital massive (DM), randomly distributed detrital (DIR), detrital concentric laminated (DIC), and authigenic euuhedral (AE) grains of pyrite from the Middelvlei Reef. The plots are element pairs A) Au – Ag; B) Co – Ni; C) Au – As; D) Au – Te; E) Au – Ni; F) As – Co; G) Cu – Zn; H) Pb – Bi. Reich et al. (2005) are the source of the gold saturation line in (A).

4.3.2.2. Comparisons to other Witwatersrand Reef: B, Elsburg, Vaal and Ventersdorp Reef

Trace element concentrations and calculated ratios from the Middelvlei Reef can be used to deduce the formation of the Middelvlei Reef. The results from the Middelvlei Reef analyses can be compared with other reefs in the Witwatersrand Basin. Here, the other reefs include the B-Reef, Elsburg, Vaal and Ventersdorp Reef (VCR) reefs which were studied by Koglin *et al.* (2010) (Table 14).

Overall, the concentrations of Au and Ni are most similar between all reefs and the Middelvlei Reef (Figure 19E). The Ni concentrations in the Middelvlei Reef for detrital massive, detrital randomly distributed, detrital concentric and authigenic euhedral pyrite grains are 355.53 ppm, 2513 ppm, 4031.97, and 691.52, respectively. In the Witwatersrand Basin reefs, Ni compositions across the reefs range between 88 - 325 ppm in detrital massive, 4.05 – 2285 ppm in detrital randomly distributed, 5351- 5712 ppm in detrital concentric and 153 – 639 ppm in authigenic euhedral pyrite.

The Au concentration from the Middelvlei Reef is also consistent with Au contents from the four Witwatersrand Basin reefs, which shows that Au is highest in the detrital randomly distributed (4.56 ppm) and concentrically laminated pyrite grains (3.64 ppm), and lowest in massive and euhedral pyrite grains (0.96 and 0.15 ppm, respectively). The other Witwatersrand Basin reefs follows a similar Au distribution pattern as the Middelvlei Reef where high Au concentrations are observed detrital randomly distributed (0.76 – 3.65 ppm) and concentrically laminated pyrite grains (3.12 – 4.09 ppm), and lowest in massive and euhedral pyrite grains (0.12 – 0.16 ppm and 0.06 - 1.54 ppm, respectively).

Interestingly, the detrital inclusion-bearing pyrite grains (randomly distributed and concentrically laminated) in the Witwatersrand Basin reefs chemically differ even though their specific ranges in Au and Ni contents match. Specifically, the concentric laminated pyrite grain is, on average, higher in both Au and Ni in the B-Reef, Elsburg, Vaal, and VCR reefs as compared to the Middelvlei Reef. However, in the Middelvlei Reef, the concentrically laminated pyrite grains are only richer in Ni, and the randomly distributed pyrite grains are richer in Au contents.

Table 12: Concentrations of elements and element/ Ni ratios for pyrite grains of the Middelvlei Reef.

Concentrations	Detrital massive (n=34)	Detrital randomly distributed (n=42)	Detrital concentric (n=30)	Authigenic Euhedral(n=25)
Au (ppm)				
Min-max	0.04 - 6.79	0.73 - 11.48	0.79 - 12.46	0.03 - 1.13
Median	0.17	2.99	3.86	0.05
Average (±SD)	0.96 (± 2.05)	3.64 (± 2.86)	4.56 (± 2.65)	0.15 (± 0.31)
Ni (ppm)				
Min-max	1.66 - 2590.92	2616.25 - 5847.68	385.65 - 6359.71	14.31 - 3523.24
Median	102.19	3794.43	2476.01	192.39
Average (±SD)	355.53 (± 611.04)	4031.97 (± 881.51)	2513 (± 1412.38)	691.52 (± 924.24)
Co (ppm)				
Min-Max	0.49 - 3034.98	49.14 - 1312.23	111.11 - 2641.47	21.59 - 18221.55
Median	181.91	479.14	508.12	578.57
Average (±SD)	432.04 (± 639.99)	485.85 (± 334.92)	784.99 (±614.21)	2154.80 (± 4315.70)
Mo (ppm)				
Min-Max	0.01 - 11.55	1.04 - 38.53	0.02 - 29.49	0.01 - 0.11
Median	0.05	3.54	4.50	0.03
Average (±SD)	1.62 (± 3.64)	6.93 (± 9.02)	6.35 (± 6.71)	0.05 (± 0.04)
Cu (ppm)				
Min-Max	0.17 - 240.07	84.48 - 26092	60.90 - 58212.07	0.22 - 394.35
Median	7.48	1897.17	183.55	1.31
Average (±SD)	35.77 (± 59.69)	4717.15 (±7099.84)	2320.47 (± 10042.24)	42.76 (± 103.13)
As (ppm)				
Min-Max	0.35 - 3916.21	234.76 - 5543.79	1181.55 - 13734.73	0.24 - 11159.79
Median	50.07	1856.40	3935.80	30.88
Average (±SD)	647.45 (±	2238.09 (± 1585.84)	5024.39 (±	1772.90 (±

	1136.98)		3123)	2895.48)
Ag (ppm)				
Min-Max	0.02 - 7.48	1.84 - 18.07	1.92 - 33.40	0.03 - 0.57
Median	0.28	4.33	6.44	0.13
Average (±SD)	1.23 (± 2.04)	5.49 (± 4.04)	8.77 (± 6.79)	0.22 (± 0.18)
Hg (ppm)				
Min-Max	0.51 - 13.54	2.11 - 21.32	1.38 - 18.46	0.52 - 0.82
Median	0.85	5.90	9.45	0.78
Average (±SD)	4.48 (± 3.66)	7.25 (± 5.07)	8.90 (± 4.31)	0.71 (± 0.16)
Pb (ppm)				
Min-Max	0.02 - 1040.73	24.29 - 1681.97	35.39 - 2614.65	0.02 - 18.40
Median	1.28	93.16	260.51	2.32
Average (±SD)	119.25 (± 288.56)	282.83 (± 433.68)	463.08 (± 585.57)	4.70 - 5.53
Co/Ni (ppm)				
Min-Max	0.003 - 45.92	0.14 - 0.55	0.01 - 0.40	0.02 - 593.01
Median	1.23	0.31	0.11	1.14
Average (±SD)	4.11 (± 8.31)	0.30 (± 0.10)	0.13 (± 0.11)	29.96 (± 120.43)
Mo/Ni (ppm)				
Min-Max	0 - 0.10	0 - 0.026	0 - 0.011	9.66 - 0.00
Median	0.0006	0.003	0.001	0.00
Average (±SD)	0.01 (± 0.03)	0.003 (± 0.005)	0.002 (± 0.003)	0 (± 0)
Pb/Ni (ppm)				
Min-Max	0.00 - 626.48	0.06 - 0.96	0.01 - 0.50	0.00 - 0.261
Median	0.01	0.11	0.02	0.004
Average (±SD)	30.27 (± 121.84)	0.18 (± 0.20)	0.08 (± 0.14)	0.021 (± 0.060)
Au/Ni (ppm)				
Min-Max	0.00 - 0.12	0.001 - 0.004	0.00 - 0.004	0.00 - 0.006
Median	0.00	0.002	0.001	0.00
Average (±SD)	0.01 (± 0.03)	0.002 (± 0.001)	0.001 (± 0.001)	0.001 (± 0.002)

4.3.3. Isotope composition of pyrite

The $\delta^{34}\text{S}$ analyses results of the morphological forms of pyrite from the Middelvlei Reef are listed in Appendix A3.1 and the spread of $\delta^{34}\text{S}$ values are presented in Figure 20 and Table 13 based on Vienna-Canyon Diablo Troilite (VCDT) standard. The generations of pyrite grains of the Middelvlei Reef show a broader range of S isotopes with a spread of -15.39 to +38.25 ‰.

Notably, massive pyrite grains yield $\delta^{34}\text{S}$ values ranging from -5.30 to +5.69 ‰ with an average of +1.83 ‰. Randomly distributed pyrite yields large positive $\delta^{34}\text{S}$ values showing an average of +7.59 ‰ and ranges from -1.70 to +25.27 ‰. Negative values of $\delta^{34}\text{S}$ are observed in concentrically laminated pyrite with an average of -3.33 ‰ and $\delta^{34}\text{S}$ values ranging from -15.39 to +4 ‰. The higher positive and negative counts of $\delta^{34}\text{S}$ in randomly distributed and concentrically laminated pyrite grains could be a result of numerous observed inclusions (see Figures 18D and 23C). The highest positive $\delta^{34}\text{S}$ values are observed in euhedral pyrite grains showing an average of +2.32 ‰ and ranging from -9.50 to +38.25 ‰. This outlier (+38.25 ‰) of high positive $\delta^{34}\text{S}$ value can also be attributed to inclusions observed within euhedral pyrite grains (as shown in Figures 18D, 18E, 18G, and 18H). Finally, euhedral pyrite grains show a narrow range of $\delta^{34}\text{S}$ values ranging from -1.58 to +3.87 ‰ with an average of +1.10 ‰.

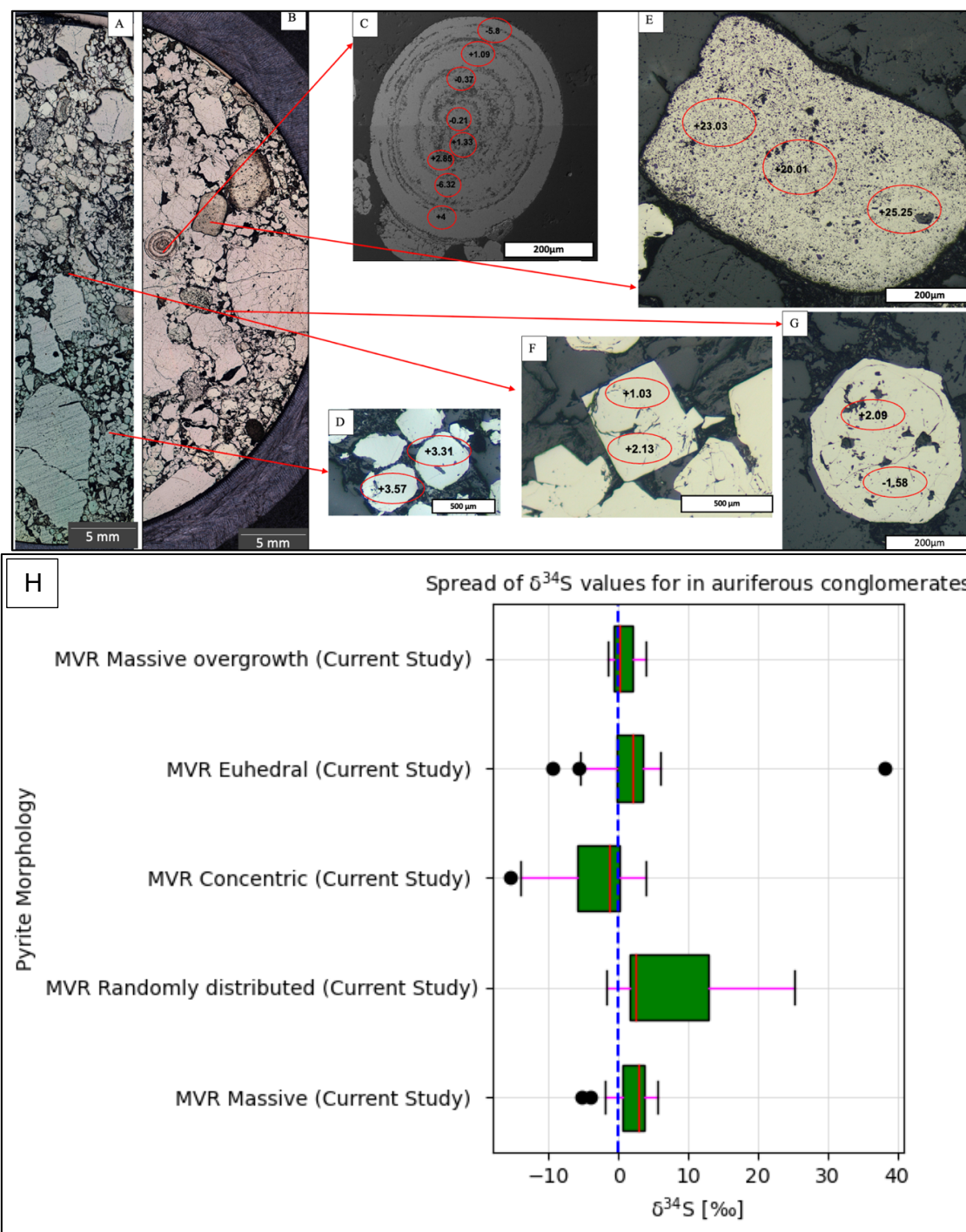


Figure 20: BSE micrographs and Reflected light micrographs of some of the pyrite grains from the Middelvlei Reef that underwent vSIMS for $\delta^{34}\text{S}$ isotope composition. The red circles within the images are the approximate analysis spots. C) Detrital concentrically laminated pyrite showing high variations of $\delta^{34}\text{S}$ values. D) Some of the analysed detrital massive pyrite grains. E) Detrital randomly distributed pyrite reflecting higher counts of $\delta^{34}\text{S}$ values. F) The analysed euhedral pyrite and G) overgrowth pyrite grain. H) Sulphur isotope concentrations of the Middelvlei Reef plotted as box and whisker plot. The first quartile (Q1) to the third quartile (Q3) are outlined by boxes with whiskers representing the lowest and highest while black dots indicates anomalies.

4.3.3.1. Comparisons to previous studies

Table 13 shows that isotopic $\delta^{34}\text{S}$ values from the Middelvlei Reef overlap with earlier research presented by Hofmann *et al.* (2009) and Guy *et al.* (2014). Specifically, average $\delta^{34}\text{S}$ values of grains of pyrite from the Middelvlei Reef best correspond with values obtained by Guy *et al.* (2014), especially between data from Middelvlei Reef and VCR as shown by Figure 21.

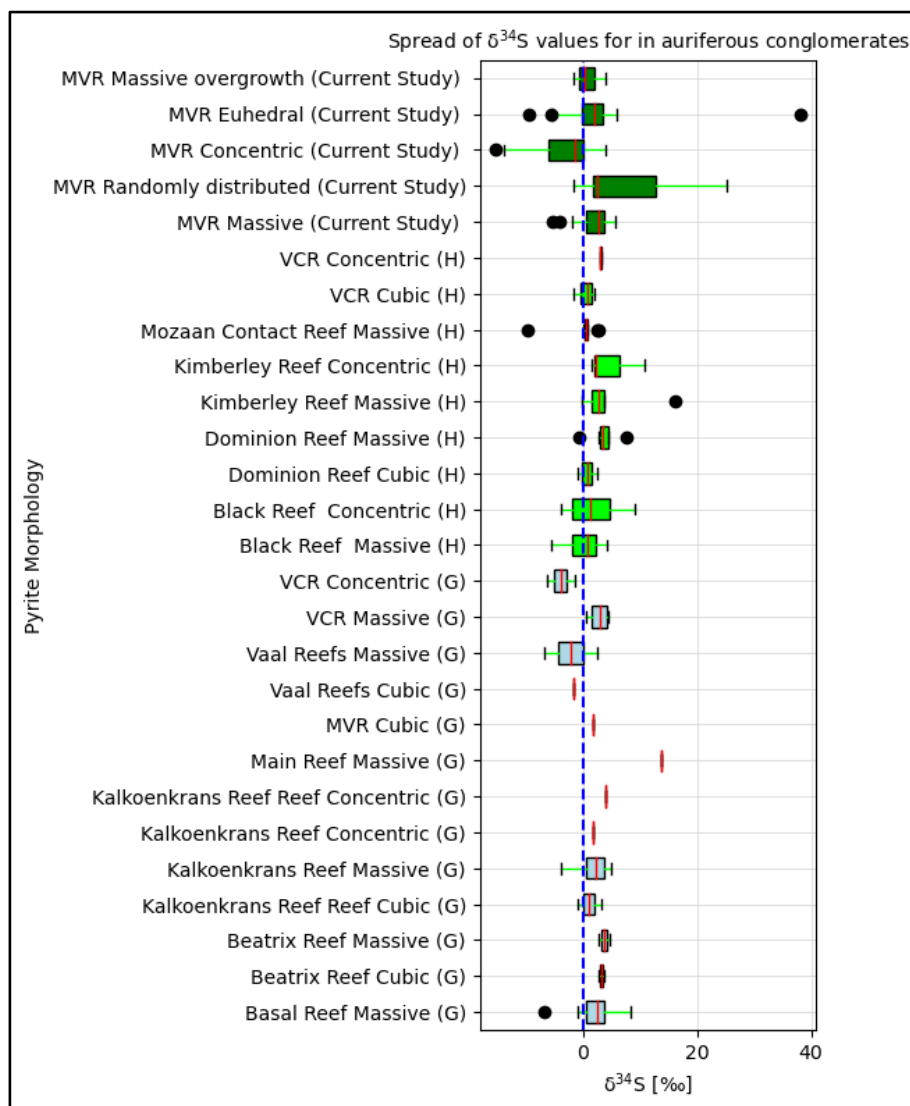


Figure 21: Sulphur isotope concentrations plotted as box and whisker graph of the various grains of pyrite in the Middelvlei Reef compared to those previously studied by Hofmann *et al.* (2009) and Guy *et al.* (2014). Current study pyrite grains: Massive detrital (DM), random inclusion-bearing (DIR), concentrically laminated (DIC), authigenic euhedral (AE) and authigenic overgrowth (AO). The first quartile (Q1) to the third quartile (Q3) are outlined by boxes with whiskers representing the lowest and highest while black dots indicates anomalies. (MVR = Middelvlei Reef; VCR = Ventersdorp Reef).

Table 13: Statistical distribution of $\delta^{34}\text{S}$ values of the Middelvlei Reef and previously studied mineral deposits by Hofmann et al. (2009) and Guy et al. (2014). (MVR=Middelvlei Reef; VCR=Ventersdorp Reef)

	Pyrite morphology	Minimum	Maximum	Q1	Median	Q3	Average
MVR (Current Study)	Massive	-5.30	5.69	0.64	2.85	3.64	1.83
MVR (Current Study)	Randomly distributed	-1.70	25.27	1.71	2.53	12.84	7.59
MVR (Current Study)	Concentric	-15.39	4.00	-5.94	-1.38	0.11	-3.33
MVR (Current Study)	Euhedral	-9.50	38.25	-0.16	2.13	3.46	2.32
MVR (Current Study)	Overgrowth	-1.58	3.87	-0.44	1.15	2.55	1.10
Basal Reef (G)	Massive	-6.80	8.30	0.47	2.41	3.77	2.04
Beatrix Reef (G)	Cubic	2.65	3.80	2.94	3.23	3.51	3.23
Beatrix Reef (G)	Massive	2.70	4.65	3.19	3.68	4.16	3.68
Kalkoenkrans Reef Reef (G)	Cubic	-1.00	3.13	-0.03	0.95	2.04	1.03
Kalkoenkrans Reef Reef (G)	Massive	-3.92	4.83	0.45	2.19	3.79	1.58
Kalkoenkrans Reef Reef (G)	Concentric	1.87	4.01	2.41	2.94	3.48	2.94
Main Reef (G)	Massive	13.79	13.79	13.79	13.79	13.79	13.79
MVR (G)	Cubic	1.86	1.88	1.87	1.87	1.88	1.87
Vaal Reef (G)	Cubic	-1.54	-1.54	-1.54	-1.54	-1.54	-1.54
Vaal Reef (G)	Massive	-6.66	2.42	-4.39	-2.12	0.15	-2.12
VCR (G)	Massive	0.65	4.40	1.56	3.11	4.17	2.81
VCR (G)	Concentric	-6.24	-1.46	-5.17	-3.75	-2.87	-3.90
Basal Reef (H)	Massive	-5.59	4.25	-1.82	0.88	2.15	-0.08

Basal Reef (H)	Concentric	-3.80	9.10	-1.98	1.37	4.64	2.00
Dominion Reef (H)	Cubic	-0.95	2.40	-0.12	0.72	1.56	0.72
Dominion Reef (H)	Massive	-0.55	7.56	2.98	3.48	4.39	3.60
Kimberly Reef (H)	Massive	-0.15	16.26	1.48	2.71	3.72	4.80
Kimberly Reef (H)	Concentric	1.57	10.71	1.94	2.31	6.51	4.86
Mozaan Contact Reef(H)	Massive	-9.60	2.86	0.31	0.53	0.70	-0.15
VCR (H)	Cubic	-1.52	2.11	-0.31	0.91	1.51	0.50
VCR (H)	Concentric	3.06	3.15	3.08	3.11	3.13	3.11

Chapter 5: Discussions

This chapter examines the findings from Chapter 4 with the objective of fulfilling the aims stated in Section 1.3.1. The first part of the discussion will summarise the mineralogical and textural characteristics obtained, the provenance of the rock composition and how the gold is distributed within the Middelvlei Reef. It is then followed by utilising the evaluated composition of trace elements to deduce the origin of pyrite, and gold within the Middelvlei Reef. Lastly, the sulphur composition from isotopic fractionation will be discussed to assess the source of sulphur and the mechanisms responsible for pyrite formation and gold association within the Middelvlei Reef. The following basic questions will be covered in this section:

- a) How does gold distribution vary per facies type?
- b) What is the sediment provenance of the Middelvlei Reef?
- c) How does trace element composition vary per pyrite grain type?
- d) What is the source of sulphur(S) in pyrite grains of the Middelvlei Reef?
- e) Was the gold contained in the Middelvlei Reef sourced from a single or multiple sources?

5.1 Lithology and mineralogical characteristics

The studied quartz-pebble conglomerate units of the Middelvlei Reef includes predominantly of interbedded quartzite and conglomerate as the main rock units occurring as alternating sheets (Figure 10A). The reef also comprises sulphides, muscovite, chlorite, biotite, and other minor minerals like gold, rutile, zircon, and chromite (Figure 13A). The bulk mineralogy of the current study matches the characteristics of a typical Middelvlei Reef studied previously by Els and Beukes (1987) ; Els (1983, 1988, 1991) and Myers *et al.* (1993). These observations indicate a braided fluvial origin which was deposited by braided streams with various amounts of gold and other metals. As shown in Figure 11A and mentioned by Nwaila *et al.* (2013; 2020), quartz grains are the main component of the Middelvlei Reef conglomerate ores. Tucker *et al.* (2016) described these conglomerate-hosted gold deposits as well-rounded and well-sorted oligomictic quartz pebbles. The nature of these clast-supported quartz pebbles conglomerate ores indicates reworked sediments from the Witwatersrand Basin and migration of great distances to reach their formation settings (Minter *et al.*, 1988; Law and Phillips., 2005; Tucker *et al.*, 2016).

5.2 Sediment provenance and weathering

Insight into the provenance of the Middelvlei Reef is influenced by numerous factors, such as weathering conditions, transport, diagenesis, climate, and tectonism. These factors affected the observed mineralogical and chemical compositions of sediments from the Middelvlei Reef. Since they were transported by the river streams before entering the basin where the quantities of major and trace elements in the sediments changed. Major elements in this research are more beneficial for measuring how much the source sediments have weathered. Based on changes in the chemical composition of the ore and proxies such as CIA, CIW, and ICV were utilised.

From this evaluation, the observed high values of CIA and CIW represent intense weathering with low rates of sedimentation that travelled further in warm/hot and humid tropical conditions. Hence the sediments of the Middelvlei Reef are well rounded and sorted. They are also enriched in clay minerals such as illite with feldspars as shown in Figure 19A. They cluster above and around the illite and muscovite zone and are consistent with the observed bulk mineralogy and strong correlation observed (Figures 19B and 19C) between K_2O/Al_2O_3 and MgO/Al_2O_3 . Since an increase in weathering decreases with the compositional maturity (ICV) of the rock (Cox *et al.*, 1995), the Middelvlei Reef was predicted to show low values of ICV. However, the results from these sediments show ICV values greater than one. Meaning they represent immature sediments that underwent low chemical weathering. However, the high abundance of the whole-rock elements is in agreement with the conclusion that the sediments of the Middelvlei underwent intense weathering.

Similar to the other Witwatersrand Basin reefs, the Middelvlei Reef also shows a large variation of its potential source. The felsic to intermediate volcanic rocks of the Dominion Group and the granitoid-greenstone belt of the Kaapvaal Craton are the main constituents of the pre-Witwatersrand basement (Poujol *et al.*, 2003; Robb *et al.*, 2006; Brandl *et al.*, 2006; Frimmel *et al.*, 2009). Hence the assessment of the geochemical characteristics indicates the origin of the Middelvlei Reef sediments being recycled sedimentary rocks with a mixture of mafic to felsic rocks from the granitoids and greenstone belts of the Kaapvaal Craton. This interpretation is corroborated by (i) High concentrations of SiO_2 content and the dark colour observed in the samples (Figure 8) indicates that the Middelvlei Reef samples as being mafic rock type; (ii) The ratios of certain trace elements (Table 9) which indicates mafic to felsic source rock; (iii) TiO_2 vs Al_2O_3 , TiO_2 (wt%)/ Zr (ppm) and Th/Sc vs Zr/Sc diagrams suggesting that the provenance of the Middelvlei Reef is a mix of felsic, intermediate and mafic source since the samples all belong in all source fields.

5.3 Gold concentration and distribution

The gold content observed shows different morphology and texture throughout the reef, though in low and uneconomic value. The gold is disseminated in the matrix filling the silicate micro-fractures, around the quartz pebbles and as inclusions filling pre-spaces of quartz and pyrite grains (Figure 14). Petrographic observations of this study revealed that visible and invisible gold are preserved in pyrite. The visible gold is observed as native gold and electrum (A1.3) gold occurring irregularly as subhedral to anhedral (Figure 14) grains. It also occurs irregularly as inclusions within and around the pyrite grains and along the quartz boundaries. This is also observed in the Au - As plot (Figure 15B) from LA-ICP-MS analyses where detrital pyrite occurs above the gold saturation line because of the elevated Au/As ratios. This indicates that there is gold in the form of free inclusions in detrital pyrite or in solid solution.

The invisible gold in the Middelvlei Reef is distributed within and on the surface of different pyrite grains mainly authigenic pyrite. Figure 22 shows this gold occurring below the gold saturation line. This can be explained by the observed low As/Au ratios and indicates that gold occurs as nano-to micro-particles locked in pyrite. The textural association of gold and pyrite can be attributed to the high-affinity gold has for pyrite as concluded by Large and Maslennikov (2020); Chingwaru *et al.* (2022).

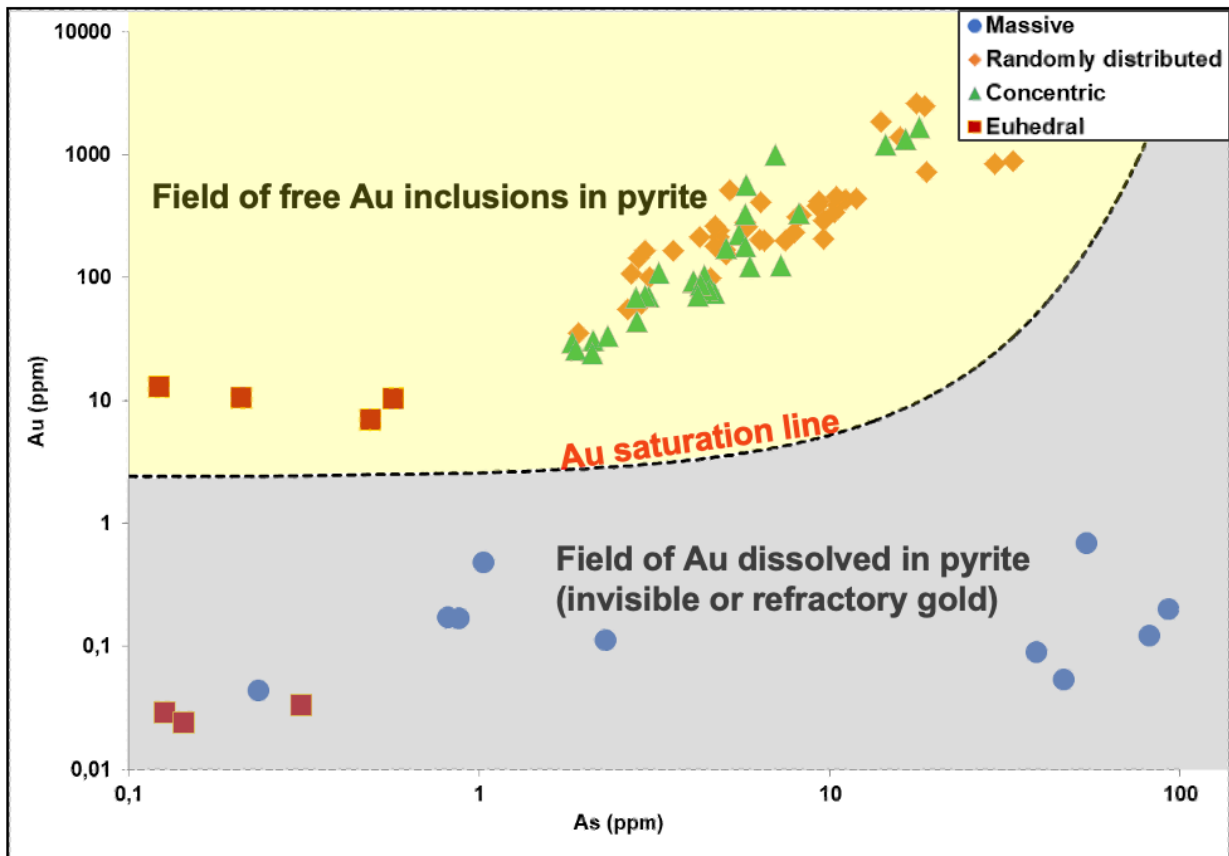


Figure 22: Au-As association (Large and Maslennikov., 2020) in pyrite grains of the Middelvlei Reef. Invisible gold dissolved in pyrite is represented by data plotted under the gold saturation line (grey region). Gold is found in pyrite as nano- to micro-gold inclusions above the line (yellow region) (modified after Large and Maslennikov., 2020; Chingwaru *et al.*, 2022).

Between 2.9 and 2.7 Ga, some of the gold that was created by sedimentary reworking of auriferous microbial mats was kept within the wealthiest gold palaeoplacers of the Witwatersrand Basin, although most of it was reworked straight after it was first deposited (Frimmel., 2014; Tucker *et al.*, 2016). Because the gold-rich microbial mats are delicate, it means those that had developed in shallow marine areas have been readily reworked by coastline regression, and those that had developed on riverbanks could have been flooded (Frimmel, 2018). This reworking of the gold-rich microbial mats created aphanitic gold particles that were either wind-blown on ancient erosion surfaces or mechanically settled downstream; giving rise to the extremely fine-grained gold placer that characterises the conglomerates of the Central Rand Group (Frimmel., 2018). The oldest auriferous conglomerates found in the lower Central Rand Group (Figure 4) with the highest gold production are Carbon Leader Reef (CLR) and Main Leader Reef (Tucker *et al.*, 2016). On the contrary, the lowest gold producers are the orebodies in the upper Central Rand Group and VCR at the bottom of the Ventersdorp Supergroup (Frimmel., 2018). The extraordinarily

high gold grades found in the old reefs are indicative of an alternative transport of gold (Tucker *et al.*, 2016). Due to the presence of carbon seams within these older auriferous conglomerates, it is interpreted that they are the source of the high gold endowment since it was preserved within the carbon seam (Hallbauer and Joughin., 1973; Tucker *et al.*, 2016).

The Middelvlei, Kimberly, and Elsburg Reef are also known as composite reefs because they have thin alternating sequences of conglomerates as studied by Tucker *et al.* (1980; 2016). These thin multicycle conglomerates formed from the re-deposition of coarse gravels and heavy minerals into the subsiding coastline (Minter *et al.*, 1996; Law and Phillips., 2005 and Tucker *et al.*, 2016). Transportation of these sediments lowered the fluvial surface in areas of high energy channelized flow (Tucker *et al.*, 2016). Gold concentrations were caused by a reworking mechanism of continuous fluvial movement (Minter *et al.*, 1996; Law and Phillips., 2005). The Middelvlei Reef is complex in that it is the oldest reef at the bottom of the Central Rand Group and sulphide mineralisation is common and intense (Tucker *et al.*, 1980). The sulphide mineralisation is observed due to the high levels of pyrite, minor pyrrhotite, and chalcopyrite. However, even with the observed high amounts of pyrite, it is the lowest gold producer in the Witwatersrand Basin and this is interpreted by Tucker *et al.* (2016) to be because of the lack of carbon seams in this orebody. The lack of carbon seams is due to zero remnants of microbial mats during the physical reworking of this orebody (Tucker *et al.*, 2016). Another reason for the low gold concentrations in this orebody is because it has thin multiple stacks of conglomerate and from the palaeoenvironmental model developed by Els.(1883), it was concluded that the thin single cycle conglomerates have the highest gold concentrations and multicycle conglomerates holds low contents.

5.4 Pyrite grains in the Middelvlei Reef

5.4.1 Classification of pyrite and description

Pyrite in this study is the dominating sulphide. It accounts for up to 90% of the sulphide minerals and it is consistent with previous studies by Myers *et al.* (1993), Tucker *et al.* (2016) and Da Costa *et al.* (2020). Several generations of pyrite grains were found, and they seem to be disseminated throughout the rock units of the Middelvlei Reef. Most of these grains concentrate on the margins/bedding of the conglomerate rocks, around the quartz pebbles of conglomerate units, and within the conglomerate matrix. Like the pyrite gains in the Witwatersrand Basin, the pyrite grains in the Middelvlei Reef occur predominantly as two main classes which are detrital and authigenic pyrite grains. The obvious abrasion that results from sedimentary transport on detrital pyrite allows it to be differentiated from authigenic pyrite.

The main types of detrital pyrite identified in the Middelvlei Reef are massive, inclusion-bearing, concentrically laminated, and coarsely crystalline pyrite grains. The massive detrital pyrite is the most resilient to physical damage and is thought to have originated from the granitic-greenstone erosion in the hinterland (da Costa *et al.* (2020). Inclusion-bearing pyrite grains contain inclusions (>10%) and the inclusions are randomly orientated (Figures 15B, 15C, and 15G) or/and arranged in concentric laminae (Figure 15D). According to da Costa *et al.* (2020), inclusion-rich grains of pyrite are thought to originate locally because of the preservation of texture, which serves as a record of the depositional environment.

Given the variety of textures and compositions observed, detrital pyrites was likely formed by range of source rock in the basin hinterland and/or intrabasinal reworking of early diagenetic or hydrothermal sulphide. Those potential sources are (1) sedimentary sources such as diagenetic pyrite found in sedimentary rocks that are fine-grained (Dimroth *et al.*, 1979; Guy *et al.*, 2010; Hofmann *et al.*, 2009); (2) sedimentary sources that are syn-genetic (reworked early diagenetic pyrite) (Hallbauer., 1986; Guy *et al.*, 2014, Agangi *et al.*, 2015); and (3) hydrothermal sources which include exhalative and syn-genetic sulphide deposits (Hutchinson and Viljoen., 1988), and vein mineralization (Saager *et al.*, 1982; Utter., 1978).

The euhedral to subhedral and cubic shape of authigenic pyrite is its defining characteristic. It is commonly massive, however inclusion-bearing authigenic pyrite (< 10% inclusions) is known to be present and can occur as an overgrowth of older pyrite generations (Figures 15D and 15H) as identified in the Middelvlei Reef. Post sedimentation, diagenetic and epigenetic (metamorphism and/or hydrothermal) activities are the main processes that formed authigenic pyrite (da Costa *et al.*, 2020; Hallbauer and von Gehlen., 1983). The cubic outlines and abraded edges of the euhedral/subhedral authigenic pyrite suggest that the grains have undergone very little reworking. These grains originate from hydrothermal sources or metamorphosed and consequently recrystallised sedimentary rocks. They might perhaps have originated from pyrite-filling porosity in early diagenetic sediments. Another pyrite morphology observed in the Middelvlei Reef is the authigenic infill pyrite (AI) which seen as veins piercing through detrital or other minerals (Figure 15G) indicating post-depositional origin. In this study, the Middelvlei Reef's origin is indicated by the morphology of the pyrite grains. In this sense, the connectivity of pyrite grains and trace element concentrations will be the main features that help us understand the chemistry of the depositional environment and the gold concentrating mechanism of this orebody.

5.4.2 Origin and provenance of pyrite

The two primary forms of pyrite found in the Middelvlei Reef show different sizes and textures. The trace element concentrations and the occurrences of gold in these two forms of pyrite are also different. These dissimilar features suggest that distinct hydrothermal fluid systems formed the authigenic and detrital pyrite grains that precipitated. The results in this study also show that the pyrite grains from the Middelvlei Reef when compared with previous palaeoplacer deposits studied by Koglin *et al.* (2010) (specifically deposits within the Witwatersrand Basin) exhibit major distinction in their trace element content. This is not only revealed by Ni and Au contents but also by Co, Mo, Cu, As, Ag, and Pb which indicate the origin and reveal the geological environment of the Middelvlei Reef formation.

There are ratios used by authors like Bralier *et al.* (1979) and Clark *et al.* (2004) as empirical indicators of depositional environment. Since pyrite's Co - Ni and Co/Ni ratio contents are sensitive to physicochemical circumstances and they can reveal information about the origin of pyrite (Tan *et al.*, 2022). High Co/Ni ratio values of more than one with high standard deviation are commonly acknowledged to indicate pyrite of hydrothermal origin and formation in medium and high temperature environments (Bralier *et al.*, 1979). Contrarily, low Co/Ni ratios of less than one with low standard deviation imply syn-sedimentary origin and low temperature environments (Bralier *et al.*, 1979). The content amounts of Co in the Middelvlei Reef are detectably highest (Table 10) in euhedral pyrite implying hydrothermal origin of the authigenic pyrite grains. The Co/Ni ratio values are greater than one with the highest standard deviation in massive and some euhedral pyrite grains (Table 13). This implies that it is formed by hydrothermal processes and inclusion-bearing pyrite grains support syn-sedimentary formation due to Co/Ni ratios of less than one and very low standard deviation.

The pyrite formed by hydrothermal processes is also distinguished by the extremely low Au concentrations and the discovery of native gold adjacent to this kind of pyrite (Koglin *et al.*, 2010). Figure 14B and Table 11 indicate that in the Middelvlei Reef, euhedral pyrite is of hydrothermal origin due to its proximity to native Au and the low Au contents. However, Koglin *et al.* (2010) revealed that detrital porous pyrite grains possess elevated Au concentrations. In the Middelvlei Reef (Tables 11 and 13), the highest Au concentrations are observed in inclusion-bearing pyrite indicating a sedimentary source. Within the Witwatersrand Basin reefs (Table 13) reported by Koglin *et al.*, 2010, the trace elements of the massive, inclusion-bearing, and euhedral pyrite grains are consistent with those from the Middelvlei Reef.

5.5 Implications for ore-forming environment

Insights gained from geochemical and $\delta^{34}\text{S}$ isotope composition research aid in understanding the conditions that lead to the formation of ore deposits. The implications include:

5.5.1 Geochemical signatures

The distribution patterns of Ni may reveal details about the pyrite formation environment because Ni is readily included in the crystal structure of pyrite and is not expelled during hydrothermal pyrite recrystallization (Huerta-Diaz and Morse.,1992; Morse and Luther., 1999; Tribovillard *et al.* 2006; Large *et al.*, 2009). High Ni is highly enriched in ultramafic and to some degree, mafic rocks. It is indicative of hydrothermal or magmatic sources. While the incompatible metal Mo is abundant in porphyry-type mineralisation systems and indicates high-temperature hydrothermal fluids. Consequently, the Mo/Ni ratio is employed as an empirical indicator of mafic to ultramafic rocks as opposed to felsic rocks in the source region (Koglin *et al.*, 2010). The Middelvlei Reef relative to other reefs in the Witwatersrand Basin reflects mafic to felsic source rocks because the detrital massive pyrite holds higher Mo/Ni ratio values. This is consistent with the documented makeup of the prior Witwatersrand Basin rocks in the Kaapvaal Craton.

Detrital inclusion-bearing pyrite of syn-sedimentary source in the Middelvlei Reef and the other Witwatersrand Basin reefs are classified as randomly distributed and concentrically laminated pyrite types. These detrital inclusion-bearing pyrite grains also exhibit elevated Ni, Co, Cu, very minimal Mo levels, and low Mo/Ni ratios that reflect a mafic to ultramafic environment. These findings are indicative of magmatic-hydrothermal origins. Traits of observed trace element patterns of the different pyrite grains can serve as proxies for various hydrothermal events. Authigenic pyrite grains which are euhedral, infill and overgrowth pyrite within the Middelvlei Reef give us information about post-depositional fluid-rock interaction. During the re-deposition and transport of the coarse Middelvlei Reef and heavy minerals, Au was deposited with other elements which are associated with sulphide minerals as seen in Table 11 and Figure 16.

The sulphide ores are represented by chalcophiles (As, Ag, Bi, Cu, Hg, Pb, Se, Sb, Te, S, Zn, etc.), lithophiles (Al, Ba, Cr, Cs, Li, Na, Ta, Ti, Th, Sr, U, V, Zr, etc.) and siderophiles (Au, Co, Fe, Mn, Mo, Ni, etc.) elements (Halder., 2017). Except for As, Cu, Ni, and Co, the euhedral pyrite is generally deficient in most elements in the Middelvlei Reef. For the transport of the metals, HS^- -complexes in neutral to moderately basic reducing fluids are thought to be the most significant in the Archaean (Huerta-Diaz and Morse., 1992;

Tribovillard *et al.*, 2006). Reports of these fluids have been made from the Witwatersrand Basin and are believed to be responsible for the short-range mobility of detrital gold there. As previously stated, the depletion of all trace elements is evident in post-sedimentary pyrite from the Witwatersrand deposits, which is explainable by the presence of post-sedimentary Ag and Hg bearing gold, chalcopyrite, galena, sphalerite, and Ni-Co phases (Koglin *et al.*, 2010). In the Middelvlei Reef, the depletion of most to all trace elements can be ascribed to the nano-sized inclusions of Ag-Hg gold and Cu-bearing minerals such as electrum/tellurium and chalcopyrite, respectively locked inside other minerals such as pyrite.

The same applies to other observed elements such as Pb and Zn. The presence of these elements is caused by the included nanoscale Pb-Zn-bearing minerals like sphalerite and galena. Galena is observed as an inclusion in Figure 14A while sphalerite is absent, hence the Zn concentrations are below the detection limit. This implies that these traces may have been transported by metamorphic-hydrothermal fluids during post-sedimentation. This indicates that the post-sedimentary pyrite type of the Middelvlei Reef still preserved some of the initial origin signatures. The comparison with the B, Elsburg, Vaal and VCR Reef (Table 13) shows that if the Middelvlei Reef precipitated from an external hydrothermal fluid instead of local mobilisation of detrital pyrite grains, it could have resulted in different metal ratios to those from the mentioned reefs in the Witwatersrand Basin. The various morphologies of pyrite of the Middelvlei Reef are consistent with the diverse Witwatersrand Basin reefs; nevertheless, there are minor variations in the composition of particular pyrite grains amongst the reefs.

Table 14: Laser ablation-ICPMS trace element content amount and element/Ni ratios for pyrite morphologies from the Middelvlei Reef deposit compared to B, Elsburg, Vaal and VCR Reef in the Witwatersrand Basin .(DM = massive detrital; DIR = random inclusion-bearing; DIC = concentrically laminated; AE = authigenic euhedral/subhedral and MVR=Middelvlei Reef].

Concentrations (ppm)	Witwatersrand Basin Reefs				
	B-Reef	Elsburg Reefs	Vaal Reef	VCR	MVR (Current Study)
Detrital massive					
Ni(ppm)	266	88	325.00		355.53
Au(ppm)	0.12	0.16	0.16		0.96
Co	1679	451	7555.00		431.04
Mo	56	25	81.00		1.62
Cu	528	257	288.00		35.77
As	1679	137	455.00		647.45

Ag	41	38	63.00		1.23
Hg	431	1160	119.00		3.66
Pb	282	1076	1518.00		119.25
Au/Ni	0.0004	0.002	0.00		0.01
Co/Ni	0.32	0.42	0.89		4.11
Mo/Ni	0.009	0.008	0.005		0.01
Detrital randomly distributed					
Ni(ppm)	4.047	1051	1332	2285	2513.00
Au(ppm)	3.65	0.76	1.32	1.21	4.56
Co	70622	11854	21346	7736	784.99
Mo	42	44	197	62	6.35
Cu	6494	904	2332	4710	2320.47
As	26629	3704	10755	11960	5024.39
Ag	613	184	307	121	8.77
Hg	968	935	412	1173	8.90
Pb	117177	19589	89249	122429	463.08
Au/Ni	0.001	0.0006	0.001	0.0005	0.002
Co/Ni	0.62	0.83	0.79	0.31	0.3
Mo/Ni	0.02	0.003	0.006	0.002	0.003
Detrital concentric					
Ni(ppm)	5712	5351			4031.97
Au(ppm)	3.12	4.09			3.64
Co	74153	14801			485.85
Mo	190	361			6.93
Cu	4462	7691			4717.15
As	41481	3965			2238.09
Ag	298	816			5.49
Hg	606	766			7.25
Pb	70034	15574			282.83
Au/Ni	0.0006	0.0004			0.001
Co/Ni	0.64	0.14			0.13
Mo/Ni	0.003	0.004			0.002
Euhedral					
Ni(ppm)	383	153	639	280	691.52
Au(ppm)	1.54	0.11	0.11	0.06	0.15
Co	4889	4127	14783	2034	2154.80
Mo	106	31	32	68	0.05
Cu	562	120	103	113	42.76
As	2695	67	816	1286	1772.90
Ag	81	43	61	27	0.22
Hg	222	979	118	113	0.71
Pb	10977	133	2145	832	4.70
Au/Ni	0.0002	0.0008	0.0001	0.0003	0.001
Co/Ni	0.09	1.39	1.23	0.78	29.96
Mo/Ni	0.009	0.09	0.001	0.01	0.00

5.5.2 Fluid origin/ Source of sulphur

Understanding the origin of sulphur is necessary to comprehend the genesis of the Middelvlei Reef, the development of the fluids that formed the ore associated with the gold source, and the source of gold itself in this orebody. The differences in the isotopic composition and origin of sulphur change depending on the form of pyrite, and depositional area (Guy *et al.*, 2014). The pyrite grains of the quartz-pebble conglomerates in the Middelvlei Reef exhibit a large range of $\delta^{34}\text{S}$ values, which suggests that the fluid source varies. The overall wide range of the $\delta^{34}\text{S}$ concentration of the Middelvlei Reef ore is reflective of mafic to felsic rocks. This is fairly corroborated by the whole-rock elements and geochemical element concentrations provenance signatures/proxies in sections 5.1 and 5.5.

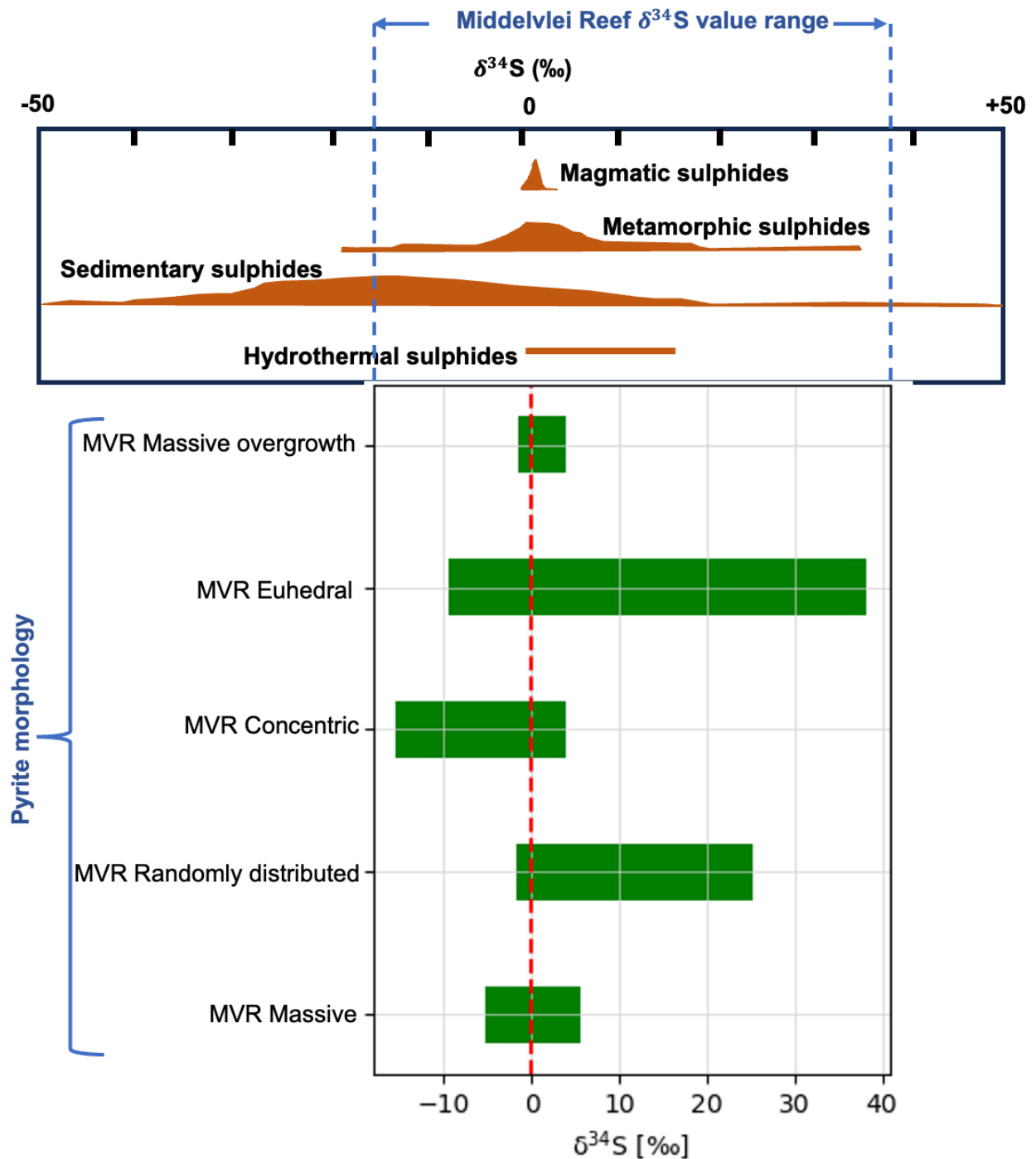


Figure 23: Sulphur isotopic characteristic used to interpret the Middelvlei Reef data analysis of each pyrite type (modified from Huston *et al.*, 2023).

The $\delta^{34}\text{S}$ values of Middelvlei Reef overlaps with those from the Kimberly Reef in the Witwatersrand Basin as studied by Hofmann *et al.*, 2009 and Guy *et al.*, 2014 (Figures 21 and 24) and they indicate that they come from both hydrothermal and sedimentary origins. Hofmann *et al.* (2009) reported that the Kimberly Reef shows two grains of pyrite with high positive $\delta^{34}\text{S}$ values that could be linked to sulphate reduction in a closed sulphate-limited

system which is a sedimentary source. Compared to the Middelvlei Reef, highly positive $\delta^{34}\text{S}$ values are observed in massive, randomly distributed, and concentrically laminated pyrite grains implying that the latter pyrite grains formed from sedimentary sources. As established in section 5.2, the Kimberly and Middelvlei Reef are also similar in that they are composite reefs that have thin multiple cycles of conglomerates with low concentrations of gold.

Detrital pyrite grains under discussion also exhibit a wide range in $\delta^{34}\text{S}$ values indicating that the source of the detrital grains is an erosion of a sedimentary deposit, which received its isotope composition over a brief period time from a unique photochemical process. The highest positive $\delta^{34}\text{S}$ (+38.25 ‰) and moderately negative $\delta^{34}\text{S}$ values are seen in euhedral pyrite of the Middelvlei Reef. These higher than average counts are outliers and most likely imply that the cubic grains contain a spherical pyrite core inside the cubic grains. This characteristic is commonly observed in the Ventersdorp Contact Reef (England *et al.*, 2002; Frimmel, 2005). Euhedral and overgrowth pyrite grains in the Middelvlei Reef show a restricted range of $\delta^{34}\text{S}$ values than that of massive grains indicating that these grains were sourced from metamorphism and hydrothermal fluids.

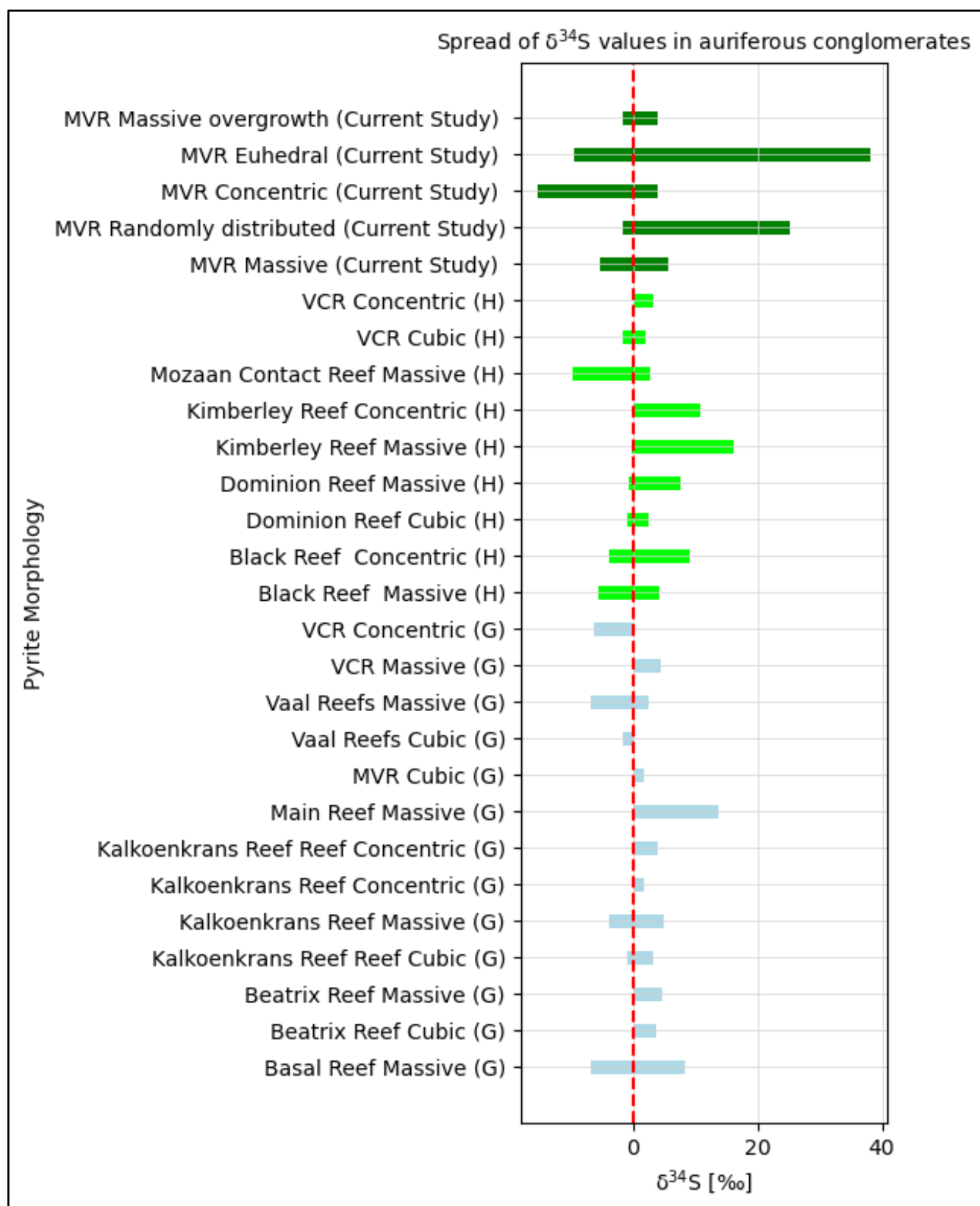


Figure 24: Comparison of $\delta^{34}\text{S}$ isotopic data for auriferous conglomerates from the Middelvlei Reef (current study) with those from by Hofmann et al., 2009 and Guy et al., 2014.

5.5.3 Ore deposit model of the Middelvlei Reef

From all data presented, the sulphide mineralisation of Middelvlei Reef is represented by both placer model and hydrothermal model (also known as the modified place model). The placer model that formed the conglomerated-hosted gold deposits of the Middelvlei Reef was proposed by Minter *et al.* (1988) and Law and Phillips (2005). They concluded that the Middelvlei Reef indicates braided fluvial origin where gold was deposited with associated minerals by sedimentary cycles within the detrital pyrites (Figure 25). This is corroborated the evidence observed:

1. The clast-supported, oligomictic quartz pebbles conglomerate (Figure 10C) ores which shows that the sediments that formed the Middelvlei Reef were reworked for long distances from the Witwatersrand Basin to their depositional environments (Tucker *et al.*, 2016).
2. The intense sulphide mineralisation alteration is observed because of the large quantities of sulphide group minerals like pyrite, minor pyrrhotite, and chalcopyrite. Pyrite occurs as different morphologies (massive, randomly distributed, and concentrically laminated) making it a stable heavy mineral during erosion and transport (Tucker *et al.*, 2016).
3. The high trace element compositions in detrital pyrite grains with little to zero mineral nuggets of copper, gold, chalcopyrite, galena, and sphalerite.
4. The significant variations in $\delta^{34}\text{S}$ of rounded pyrite confirms the heterogeneous sulphur compositions which supports a placer origin.

The hydrothermal model suggested by Barnicoat *et al.* (1997), Law, Phillips (2005), Tucker *et al.* (2016) and Fuchs *et al.* (2007) concluded that fluid movement and geochemical features of host rocks influenced gold precipitation from aqueous solution during post-post-deposition alteration. Evidence corroborating this that is observed in the Middelvlei Reef:

1. The enrichment of rounded pyrite grains that are closely associated with gold grains (Figures 13B and 14C).
2. The gold appears to be younger within the paragenetic sequence (Figures 13B and 13C).
3. The visible and invisible gold incorporated within and around the different pyrite grains is a clear indication of the high gold affinity for pyrite.
4. Depletion of trace elements in authigenic pyrite grains is attributed to the abundance of post-sedimentary mineral phases such as Ag and Hg-bearing gold, chalcopyrite, galena, sphalerite, and Ni-Co.

5. Metal ratios and isotope signatures of the Middelvlei Reef are similar to other studied Reefs from the Witwatersrand Basin and showed that the initial origin signatures were preserved within the authigenic pyrite grains.
6. In the Middelvlei Reef, authigenic pyrite grains show restricted $\delta^{34}\text{S}$ values indicating the product of metamorphism and hydrothermal alteration ((Tucker *et al.*, 2016).

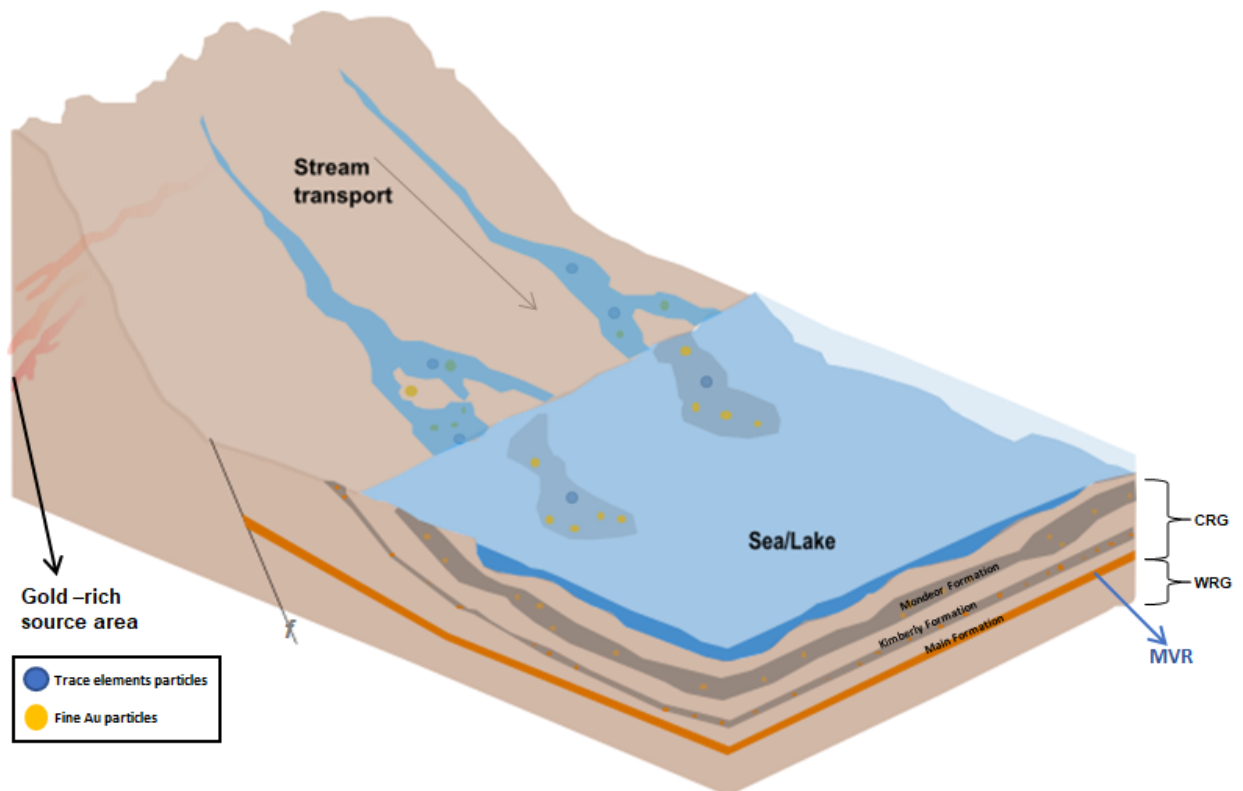


Figure 25: A depiction of the potential model for the gold mineralisation of the Middelvlei Reef (MVR). (CRG = Central Rand Group, WRG = West Rand) (Modified from Kirk *et al.*, 2003).

Chapter 6: Conclusions and Recommendations

6.1. Conclusions

To better understand the morphological distinction of pyrite grains in the Middelvlei Reef, a detailed mineralogical, geochemical, and isotopic characterisation was carried out. The formation environment of the Middelvlei Reef is drawn from the analyses of trace elements chemistry and in-situ sulphur isotopes of the pyrite morphologies observed. In assessing the connection between Middelvlei Reef's pyrite and gold, the current research study revealed that:

- The Middelvlei Reef orebody is a clast-supported conglomerate consisting of interbedded alternating layers of conglomerate and coarse-grained quartzite. These auriferous conglomerate beds comprise quartz, pyrite, chalcopyrite, pyrrhotite, galena, chlorite, muscovite, biotite, chromite, rutile, and zircon. The Middelvlei Reef comprises sedimentary pyrite grains identified as massive pyrite, randomly distributed, concentrically laminated, and coarsely crystalline. And post-sedimentary/hydrothermal pyrite is classified as euhedral/subhedral, overgrowth, and infill pyrite morphologies identified from textural differences.
- Variations of trace element concentrations such as Au and Co/Ni are used as empirical indicators to link the various pyrite morphologies to syn-sedimentary/diagenetic sources and hydrothermal/metamorphism processes. The Middelvlei Reef shows high values of Co/Ni and low Au contents in euhedral pyrite and is indicative of hydrothermal source formation in medium and high temperature environments. Contrarily, minimum Co/Ni and maximum Au contents are observed in detrital pyrite grains (massive, randomly distributed and concentrically laminated) representing the sedimentary origin and low temperature environments.
- Other trace element proxies that are used to deduce the origin of the Middelvlei Reef are Ni and Mo/Ni ratios. Mafic to felsic rocks in relation to felsic rocks in the source region are empirically indicated by the Mo/Ni ratio (Koglin *et al.*, 2010). The higher Mo/Ni ratio values observed in the massive pyrite of the Middelvlei Reef reflect ultramafic to mafic source rocks. These rock units are sourced from mafic to felsic rocks of the granitoid-greenstone belts of the Kaapvaal Craton. Trace elements found in inclusion-bearing pyrites are a reflection of the provenance of the material that

developed in the sedimentary transport environment of the river i.e. mafic to felsic. The enrichment of Ni and Co concentrations demonstrates that authigenic/hydrothermal pyrite grains preserved the origin features of detrital pyrite grains. The fact that these trace elements had strong enrichment in the hydrothermal pyrite grains indicates that the fluid composition after deposition was mainly internally buffered.

- The pyrite grains of the quartz-pebble conglomerates in the Middelvlei Reef exhibit a wide range of $\delta^{34}\text{S}$ values, which suggests that the fluid originated from metamorphic and hydrothermal sources. The $\delta^{34}\text{S}$ values of detrital pyrite grains are highly positive and exhibit a large range indicating an erosion of the sedimentary deposit. The authigenic pyrite grains show smaller $\delta^{34}\text{S}$ values indicating that they were sourced from metamorphism and hydrothermal fluids.

Based on the mineralogical characterisation, trace element, and in-situ S isotope concentration results obtained from the Middelvlei Reef. The intense sulphide mineralisation of the Middelvlei Reef is concluded to have formed within the braided fluvial environment with varying energies leading to the reworking of the sulphide minerals. This reef is a representation of modified placer model because some of the pyrite grains were derived from sedimentary provenance and others from hydrothermal provenance because they vary in texture and composition. The extensive range of pyrite generations suggests that the observed grains have high amounts of continentally derived sulphur (Tucker *et al.*, 2016). The genesis of the Middelvlei Reef is more complex because it is an older composite reef (Similar to Elsburg and Kimberly Reef), with thin multicycle alternating conglomerate sequences and it is pyrite-rich. However, regardless of the strong gold-pyrite association within the Witwatersrand Basin, the Middelvlei Reef has the lowest gold tenor due to a lack of microbial mats and being transported in areas of high energy channelised flow (Tucker *et al.*, 1980 Tucker *et al.*, 2016).

6.2. Recommendations

The insights into the complex syn-depositional and post-depositional processes that have controlled gold accumulation in the Middelvlei Reef are offered in this research study. As a result, it can be used as a foundation for future research and utilization of comparable composite reefs in the Witwatersrand Basin. I think further analysis of trace elements and isotopic data using modern technologies like artificial intelligence, data analytics, and machine learning will produce a more accurate provenance model of this orebody given the

gaps in the formation of the Middelvlei Reef. A more detailed analysis of pyrite to discuss major controls on sulphur isotope composition might be a study that can be explored in future. Numerous factors influenced the Middelvlei Reef's provenance, which in turn impacted this orebody's gold endowment. Further studies of the genesis of the Middelvlei Reef using advanced mineralogical, geochemical, isotope techniques and modelling software to assess the structural controls on this orebody can be explored. Understanding the timing of the Middelvlei Reef ore formation would be beneficial in the provenance studies. So, U-Pb radiometric dating of zircons could be a study that can also be explored.

References

- Agangi., Hofmann, A., Wohlgemut, U.C., 2013. Pyrite zoning as a record of mineralization in the Ventersdorp contact reef, Witwatersrand Basin, South Africa. *Economic Geology* 108(6), 1243-1272.
- Agangi, A., Hofmann, A., Rollion-Bard, C., Marin-Carbonne, J., Cavalazzi, B., Large, R. and Meffre, S., 2015. Gold accumulation in the Archaean Witwatersrand Basin, South Africa—Evidence from concentrically laminated pyrite. *Earth-Science Reviews*, 140, pp.27-53.
- Aylmore, M.G., 2019. Automated mineralogy. *SME Mineral Processing and Extractive Metallurgy Handbook*; Dunne, RC, Kawatra, SK, Young, CA, Eds, pp.43-68.
- Barnicoat, A.C., Henderson, I.H.C., Knipe, R.J., Yardley, B.W.D., Napier, R.W., Fox, N.P.C., Kenyon, A.K., Muntingh, D.J., Strydom, D., Winkler, K.S. and Lawrence, S.R., 1997. Hydrothermal gold mineralization in the Witwatersrand basin. *Nature*, 386(6627), pp.820-824.
- Bartlett, H.V.R., 2002. Variance relationships between the masses, grades and particle sizes for gold ores from the Witwatersrand. *Journal of the Southern African Institute of Mining and Metallurgy*, 102(8), pp.491-500.
- Barton, E.S. and Hallbauer, D.K., 1996. Trace-element and U-Pb isotope compositions of pyrite types in the Proterozoic Black Reef, Transvaal Sequence, South Africa: Implications on genesis and age. *Chemical Geology*, 133(1-4), pp.173-199.
- Beukes, NJ and Caimcross, B., 1991. A lithostratigraphic-sedimentological reference profile for the Late Archaean Mozaan Group, Pongola Sequence: application to sequence stratigraphy and correlation with the Witwatersrand Supergroup. *South African Journal of Geology*, 94(1), pp.44-69.
- Bralia, A., Sabatini, G. and Troja, F., 1979. A revaluation of the Co/Ni ratio in pyrite as geochemical tool in ore genesis problems: evidences from southern Tuscany pyritic deposits. *Mineralium Deposita*, 14, pp.353-374.
- Brandl, G., Cloete, M., Anhaeusser, C.R., Johnson, M.R. and Thomas, R.J., 2006. Archaean greenstone belts. In *The Geology of South Africa* (pp. 9-56). Geological Society of South Africa/Council for Geoscience Johannesburg/Pretoria.

Chingwaru, S., Von der Heyden, B. and Tadie, M., 2022. Invisible gold in the Archean detrital sulphides of the Witwatersrand tailings dumps: A large and under-exploited gold resource.

Clark, C., Grguric, B. and Mumm, A.S., 2004. Genetic implications of pyrite chemistry from the Palaeoproterozoic Olary Domain and overlying Neoproterozoic Adelaidean sequences, northeastern South Australia. *Ore Geology Reviews*, 25(3-4), pp.237-257.

Condie, K.C., Boryta, M.D., Liu, J. and Qian, X., 1992. The origin of khondalites: geochemical evidence from the Archean to Early Proterozoic granulite belt in the North China craton. *Precambrian Research*, 59(3-4), pp.207-223.

Da Costa, G.V., 2019. *Evaluation of syngenetic gold deposition in syn-sedimentary pyrite of the Witwatersrand Basin*. University of Johannesburg (South Africa).

Da Costa, G., Hofmann, A. and Agangi, A., 2017. Provenance of detrital pyrite in archean sedimentary rocks: Examples from the Witwatersrand Basin. In *Sediment Provenance* (pp. 509-531). Elsevier.

Da Costa, G., Hofmann, A. and Agangi, A., 2020. A revised classification scheme of pyrite in the Witwatersrand Basin and application to placer gold deposits. *Earth-Science Reviews*, 201, p.103064.

De Wit, M.J., de Ronde, C.E., Tredoux, M., Roering, C., Hart, R.J., Armstrong, R.A., Green, R.W., Peberdy, E. and Hart, R.A., 1992. Formation of an Archaean continent. *Nature*, 357(6379), pp.553-562.

De Wit, M.J. and Ashwal, L.D. eds., 1997. Greenstone belts. *Clarendon Press*.

Dimroth, E., 1979. Significance of diagenesis for the origin of Witwatersrand-type uraniferous conglomerates. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 291(1381), pp.277-287.

Dirks, P.H.G.M., Blenkinsop, T.G. and Jelsma, H.A., 2003. The geological evolution of Africa (Doctoral dissertation).

Els, B.G. (1983). *Sedimentology of the Middelvllei Reef on Doornfontein Gold mine*. MSc. (Geology). [Unpublished]: University of Johannesburg: retrieved from: <https://ujdigispace.uj.ac.za> (Accessed: 06 May 2020).

Els, B.G., 1988. Pebble morphology of an ancient conglomerate; the Middelvllei gold placer, Witwatersrand, South Africa. *Journal of Sedimentary Research*, 58(5), pp.894-901.

Els, B.G., 1991. Placer formation during progradational fluvial degradation; the late Archean Middelvllei gold placer, Witwatersrand, South Africa. *Economic Geology*, 86(2), pp.261-277.

Els, BG and Beukes, N.J., 1987. Sedimentology of the Middelvllei Placer, Doornfontein Gold Mine, Witwatersrand Supergroup. *South African journal of geology*, 90(1), pp.72-85.

England, G.L., Rasmussen, B., Krapez, B. and Groves, D.I., 2002. Paleoenvironmental significance of rounded pyrite in siliciclastic sequences of the Late Archean Witwatersrand Basin: oxygen-deficient atmosphere or hydrothermal alteration?. *Sedimentology*, 49(6), pp.1133-1156.

England, G.L., Rasmussen, B., Krapez, B. and Groves, D.I., 2002b. Archean oil migration in the Witwatersrand Basin of South Africa. *Journal of the Geological Society*, 159(2), pp.189-201.

Feather, C.E. and Koen, G.M., 1975. Mineralogy of the Witwatersrand reefs. Anglo American Research Labs., Crown Mines, S. Afr..

Fleet, 1998. Detrital pyrite in Witwatersrand gold reefs: X-ray diffraction evidence and implications for atmospheric evolution. *Terra Nova*, 10(6), pp.302-306.

Frimmel, H.E., 2005. Archean atmospheric evolution: evidence from the Witwatersrand gold fields, South Africa. *Earth-Science Reviews*, 70(1-2), pp.1-46.

Frimmel, H.E., 2008. Earth's continental crustal gold endowment. *Earth and Planetary Science Letters*, 267(1-2), pp.45-55.

Frimmel, H.E., 2014. A giant Mesoarchean crustal gold enrichment episode: possible causes and consequences for exploration. *Society of Economic Geologists* 18, 209-234.

Frimmel, H.E., 2018. Episodic concentration of gold to ore grade through Earth's history. *Earth Science Reviews* 180, 148-158.

Frimmel, H.E., 2019. The Witwatersrand Basin and its gold deposits. The Archean geology of the Kaapvaal craton, southern Africa, pp.255-275.

Frimmel, H.E. and Gartz, V.H., 1997. Witwatersrand gold particle chemistry matches model of metamorphosed, hydrothermally altered placer deposits. *Mineralium Deposita*, 32, pp.523-530.

Frimmel, H.E. and Minter, W.E.L., 2002. Recent developments concerning the geological history and genesis of the Witwatersrand gold deposits, South Africa.

Frimmel, H.E. and Hennigh, Q., 2015. First whiffs of atmospheric oxygen triggered onset of crustal gold cycle. *Mineralium Deposita*, 50(1), pp.5-23.

Frimmel, H.E., and Nwaila, G.T., 2019. Geological Evidence of Syngenetic Gold in the Witwatersrand Goldfields, South Africa. *Society of Economic Geologists*, no.23, pp. 645-668.

Frimmel, H.E., Le Roex, A.P., Knight, J. and Minter, W.E.L., 1993. A case study of the postdepositional alteration of the Witwatersrand Basal Reef gold placer. *Economic Geology*, 88(2), pp.249-265.

Frimmel HE, Hallbauer DK, Gartz VH (1999) Gold mobilizing fluids in the Witwatersrand Basin: composition and possible sources. *Mineral Petrol* 66:55–81

Frimmel, H.E., Groves, D.I., Kirk, J., Ruiz, J., Chesley, J. and Minter, W.E.L., 2005. The formation and preservation of the Witwatersrand goldfields, the world's largest gold province.

Frimmel, H.E., Zeh, A., Lehrmann, B., Hallbauer, D. and Frank, W., 2009. Geochemical and geochronological constraints on the nature of the immediate basement next to the Mesoarchaeon auriferous Witwatersrand Basin, South Africa. *Journal of Petrology*, 50(12), pp.2187-2220.

Fuchs, S., Williams-Jones, A.E., Przybylowicz, W.J., 2016. The origin of the gold and uranium ores of the Black Reef Formation Transvaal supergroup, South Africa. *Ore Geology Reviews* 72, 149-164

Fuchs, S.H., Schumann, D., Williams-Jones, A.E., Murray, A.J., Couillard, M., Lagarec, K., Phaneuf, M.W. and Vali, H., 2017. Gold and uranium concentration by interaction of immiscible fluids (hydrothermal and hydrocarbon) in the Carbon Leader Reef, Witwatersrand Supergroup, South Africa. *Precambrian Research*, 293, pp.39-55.

Garzanti, E. and Resentini, A., 2016. Provenance control on chemical indices of weathering (Taiwan river sands). *Sedimentary geology*, 336, pp.81-95.

Gray, G.J., Lawrence, S.R., Kenyon, K. and Cornford, C., 1998. Nature and origin of 'carbon' in the Archaean Witwatersrand Basin, South Africa. *Journal of the Geological Society*, 155(1), pp.39-59.

Guy, B.M., 2012. *Pyrite in the Mesoarchean Witwatersrand Supergroup, South Africa* (Doctoral dissertation, University of Johannesburg).

Guy, B.M., Beukes, N.J. and Gutzmer, J., 2010. Paleoenvironmental controls on the texture and chemical composition of pyrite from non-conglomeratic sedimentary rocks of the Mesoarchean Witwatersrand Supergroup, South Africa. *South African Journal of Geology*, 113(2), pp.195-228.

Guy, B.M., Ono, S., Gutzmer, J., Lin, Y. and Beukes, N.J., 2014. Sulphur sources of buckshot pyrite in the Auriferous Conglomerates of the Mesoarchean Witwatersrand and Ventersdorp Supergroups, South Africa.

Haldar, S.K. 2017. Chapter 1 – Introduction. *Platinum-Nickel-Chromium Deposits*, Isevier, Pages 1-35.

Hallbauer, DK and Joughin, N.C., 1973. The size distribution and morphology of gold particles in Witwatersrand reefs and their crushed products. *Journal of the Southern African Institute of Mining and Metallurgy*, 73(11), pp.395-405.

Hallbauer, D.K. and Von Gehlen, K., 1983. The Witwatersrand pyrites and metamorphism. *Mineralogical magazine*, 47(345), pp.473-479.

Hallbauer, D.K., 1986. The mineralogy and geochemistry of Witwatersrand pyrite, gold, uranium, and carbonaceous matter. In *Mineral deposits of Southern Africa. V. 1-2*.

Harnois, L., 1988. The CIW index: a new chemical index of weathering. *Sedimentary geology*, 55(3), pp.319-322.

Hofmann, A., Bekker, A., Rouxel, O., Rumble, D. and Master, S., 2009. Multiple sulphur and iron isotope composition of detrital pyrite in Archaean sedimentary rocks: A new tool for provenance analysis. *Earth and Planetary Science Letters*, 286(3-4), pp.436-445.

Horscroft, F.D.M., Mossman, D.J., Reimer, T.O. and Hennigh, Q., 2011. Witwatersrand metallogenesis: the case for (modified) syngeneses. *SEPM Spec Publ*, 101, pp.75-95.

Hrstka, T., Gottlieb, P., Skala, R., Breiter, K. and Motl, D., 2018. Automated mineralogy and petrology-applications of TESCAN Integrated Mineral Analyzer (TIMA). *Journal of Geosciences*, 63(1), pp.47-63.

Huerta-Diaz, M.A. and Morse, J.W., 1992. Pyritization of trace metals in anoxic marine sediments. *Geochimica et Cosmochimica Acta*, 56(7), pp.2681-2702.

Huston, D. and Gutzmer, J., 2023. *Isotopes in Economic Geology, Metallogenesis and Exploration* (p. 475). Springer Nature.

Huston, D.L., Trumbull, R.B., Beaudoin, G. and Ireland, T., 2023. Light stable isotopes (H, B, C, O and S) in ore studies—methods, theory, applications and uncertainties. In *Isotopes in Economic Geology, Metallogensis and Exploration* (pp. 209-244). Cham: Springer International Publishing.

Hutchinson, RW and Viljoen, R.P., 1988. Re-evaluation of gold source in Witwatersrand ores. *South African journal of geology*, 91(2), pp.157-173.

Jolly, M.K. (1984). Sedimentology and Economic potential of the auriferous Middelvel Reef on Driefontein. MSc. (Geology). [Unpublished]: University of Johannesburg: retrieved from: <https://uhdigispace.uj.ac.za> (Accessed: 06 Mar 2020).

Kirk, J., Ruiz, J., Chesley, J., Titley, S. and Walshe, J., 2001. A detrital model for the origin of gold and sulfides in the Witwatersrand basin based on Re-Os isotopes. *Geochimica et Cosmochimica Acta*, 65(13), pp.2149-2159.

Kirk, J., Ruiz, J., Chesley, J., Walshe, J. and England, G., 2002. A major Archean, gold-and crust-forming event in the Kaapvaal Craton, South Africa. *Science*, 297(5588), pp.1856-1858.

Koglin, N., Frimmel, H.E., Minter, W.L. and Brätz, H., 2010. Trace-element characteristics of different pyrite types in Mesoarchean to Paleoproterozoic placer deposits. *Mineralium Deposita*, 45(3), pp.259-280.

Kositcin, N. and Krapez, B., 2004. SHRIMP U-Pb detrital zircon geochronology of the Late Archaean Witwatersrand Basin of South Africa: relation between zircon provenance age spectra and basin evolution. *Precambrian Research*, 129, pp.141-168.

Krendelev, F.P., *Metallonosnye konglomeraty mira (Metalliferous Conglomerates of the World)*, Novosibirsk: Nauka, 1974.

Large, R.R., Danyushevsky, L., Hollit, C., Maslennikov, V., Meffre, S., Gilbert, S., Bull, S., Scott, R., Emsbo, P., Thomas, H. and Singh, B., 2009. Gold and trace element zonation in pyrite using a laser imaging technique: Implications for the timing of gold in orogenic and Carlin-style sediment-hosted deposits. *Economic Geology*, 104(5), pp.635-668.

Large, R.R., Meffre, S., Burnett, R., Guy, B., Bull, S., Gilbert, S., Goemann, K. and Danyushevsky, L., 2013. Evidence for an intrabasinal source and multiple concentration processes in the formation of the Carbon Leader Reef, Witwatersrand Supergroup, South Africa. *Economic Geology*, 108(6), pp.1215-1241.

Law, J.D.M. and Phillips, G.N., 2005. Hydrothermal replacement model for Witwatersrand gold.

Letanta, D.M., 2018. *A mining feasibility case study analysis of fuel cell technology application to stimulate platinum beneficiation in South Africa* (Doctoral dissertation).

Li, N., Deng, J., Yang, L.Q., Goldfarb, R.J., Zhang, C., Marsh, E., Lei, S.B., Koenig, A. and Lowers, H., 2014. Paragenesis and geochemistry of ore minerals in the epizonal gold deposits of the Yangshan gold belt, West Qinling, China. *Mineralium Deposita*, 49, pp.427-449.

Loen, J.S., 1992. Mass balance constraints on gold placers; possible solutions to "source area problems". *Economic Geology*, 87(6), pp.1624-1634.

Longerich, H.P., Jackson, S.E. and Günther, D., 1996. Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. *Journal of analytical atomic spectrometry*, 11(9), pp.899-904.

McLean PJ, Fleet ME (1989) Detrital pyrite in the Witwatersrand gold fields of South Africa: evidence from truncated growth banding. *Econ Geol* 84:2008–2011.

McLennan, S.M., Hemming, S., McDaniel, D.K. and Hanson, G.N., 1993. Geochemical approaches to sedimentation, provenance, and tectonics.

Meyer, F.M., Möller, P., Debruin, D., Przybylowicz, W.J., and Prozesky, V.M., 1994, The gold-pyrite association in Witwatersrand reefs—Evidence for electrochemical precipitation of gold: *Exploration and Mining Geology*, v. 3, p. 207–217.

Minter, W.E.L., Feather, C.E. and Glatthaar, C.W., 1988. Sedimentological and mineralogical aspects of the newly discovered Witwatersrand placer deposit that reflect Proterozoic weathering, Welkom gold field, South Africa. *Economic Geology*, 83(3), pp.481-491.

Minter, W.E.L., Goedhart, M., Knight, J. and Frimmel, H.E., 1993. Morphology of Witwatersrand gold grains from the Basal Reef; evidence for their detrital origin. *Economic Geology*, 88(2), pp.237-248.

Morse, J.W. and Luther Iii, G.W., 1999. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochimica et Cosmochimica Acta*, 63(19-20), pp.3373-3378.

Myers, R.E., Zhou, T., Phillips, G.N., 1993. Sulphidation in the Witwatersrand goldfields: evidence from the Middelvllei Reef. *Mineralogical Magazine* 57, 395-405

Nagy, B., 1993. Kerogens and bitumens in Precambrian uraniferous ore deposits: Witwatersrand, South Africa, Elliot Lake, Canada, and the natural fission reactors, Oklo, Gabon. In Bitumens in ore deposits (pp. 287-333). Berlin, Heidelberg: Springer Berlin Heidelberg.

Neingo, P.N. and Tholana, T., 2016. Trends in productivity in the South African gold mining industry. *Journal of the Southern African Institute of Mining and Metallurgy*, 116(3), pp.283-290.

Nesbitt, H. and Young, G.M., 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *nature*, 299(5885), pp.715-717.

Nwaila, G.T. and Frimmel, H.E., 2019. Highly siderophile elements in Archaean and Palaeoproterozoic marine shales of the Kaapvaal Craton, South Africa. *Mineralogy and Petrology*, 113, pp.307-327.

Nwaila, G., Frimmel, H.E. and Minter, W.E., 2017. Provenance and geochemical variations in shales of the Mesoarchean Witwatersrand Supergroup. *The Journal of Geology*, 125(4), pp.399-422.

Frimmel, H.E. and Nwaila, G.T., 2020. Geologic evidence of syngenetic gold in the Witwatersrand Goldfields, South Africa.

Nwaila, G., Becker, M., Ghorbani, Y., Petersen, J., Reid, D., Bam, L.C., De Beer, F.C. and Franzidis, J.P., 2013. A geometallurgical study of the Witwatersrand gold ore at Carletonville, South Africa. In The Second Ausimm International Geometallurgy Conference. Brisbane (pp. 75-83).

Nwaila, G.T., Durrheim, R.J., Jolayemi, O.O., Maselela, H.K., Jakaitė, L., Burnett, M. and Zhang, S.E., 2020. Significance of granite-greenstone terranes in the formation of Witwatersrand-type gold mineralisation—A case study of the Neoarchaean Black Reef Formation, South Africa. *Ore Geology Reviews*, 121, p.103572.

Nwaila, G.T., Ghorbani, Y., Becker, M., Frimmel, H.E., Petersen, J. and Zhang, S., 2020. Geometallurgical approach for implications of ore blending on cyanide leaching and adsorption behavior of witwatersrand gold ores, South Africa. *Natural Resources Research*, 29, pp.1007-1030.

Nwaila, G.T., Bourdeau, J.E., Jinnah, Z., Frimmel, H.E., Bybee, G.M., Zhang, S.E., Manzi, M.S.D., Minter, W.E.L. and Mashaba, D., 2021. The significance of erosion channels on gold

metallogeology in the Witwatersrand Basin (South Africa): evidence from the carbon leader reef in the carletonville gold field. *Economic Geology*, 116(2), pp.265-284.

Ofili, Sylvester, Alvar Soesoo, Elena G. Panova, Rutt Hints, Sigrid Hade, and Leho Ainsaar. "Geochemical reconstruction of the provenance, tectonic setting and paleoweathering of lower paleozoic black shales from northern Europe." *Minerals* 12, no. 5 (2022): 602.

Perri, F., 2020. Chemical weathering of crystalline rocks in contrasting climatic conditions using geochemical proxies: an overview. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 556, p.109873.

Phillips, G.N., Myers, R.E. and Palmer, J.A., 1987. Problems with the placer model for Witwatersrand gold. *Geology*, 15(11), pp.1027-1030.

Phillips, G.N., Zhou, T. and Powell, R., 1997. Metamorphic temperature variations among Witwatersrand goldfields: evidence from the pyrophyllite-chloritoid-chlorite mineral assemblage. *South African Journal of Geology*, 100(4), pp.393-404.

Phillips, G.N., 1988, Widespread fluid infiltration during metamorphism of the Witwatersrand goldfields: Generation of chloritoid and pyrophyllite: *Journal of Metamorphic Geology*, v. 6, p. 311–332.

Phillips, G.N. and Myers, R.E., 1989. The Witwatersrand gold fields: Part II. An origin for Witwatersrand gold during metamorphism and associated alteration. *Economic Geology Monograph*, 6, pp.598-608.

Phillips, G. Neil, and Jonathan DM Law. "Witwatersrand gold fields: geology, genesis, and exploration." (2000).

Phillips, G.N. and Powell, R., 2011. Origin of Witwatersrand gold: a metamorphic devolatilisation–hydrothermal replacement model. *Applied Earth Science*, 120(3), pp.112-129.

Phillips, G.N. and Powell, R., 2015. Hydrothermal alteration in the Witwatersrand goldfields. *Ore Geology Reviews*, 65, pp.245-273.

Poujol, M., Robb, L.J., Anhaeusser, C.R. and Gericke, B., 2003. A review of the geochronological constraints on the evolution of the Kaapvaal Craton, South Africa. *Precambrian research*, 127(1-3), pp.181-213.

Pulles, W, Banister, S and Van Biljon, M., 2005. The development of appropriate procedures towards and after closure of underground gold mines from a water management perspective. WRC report no 1215/1/05.

Reimold, W.U., Przybylowicz, W.J. and Gibson, R.L., 2004. Quantitative major and trace elemental mapping by PIXE of concretionary pyrite from the Witwatersrand Basin, South Africa. *X-Ray Spectrometry: An International Journal*, 33(3), pp.189-203.

Robb, L.J. and Meyer, F.M., 1995. The Witwatersrand Basin, South Africa: geological framework and mineralization processes. *Ore Geology Reviews*, 10(2), pp.67-94.

Robb, L.J., Brandl, G., Anhaeusser, C.R., Poujol, M., Johnson, M.R. and Thomas, R.J., 2006. Archaean granitoid intrusions. *The Geology of South Africa*, pp.57-94.

Saager, R., Meyer, M. and Muff, R., 1982. Gold distribution in supracrustal rocks from Archean greenstone belts of southern Africa and from Paleozoic ultramafic complexes of the European Alps; metallogenic and geochemical implications. *Economic Geology*, 77(1), pp.1-24.

Simanovich, I.M., 2009. Auriferous Precambrian conglomerates of Witwatersrand. *Lithology and Mineral Resources*, 44, pp.497-509.

SIMMONDS, S., 2009. The Nugget Effect: In describing the variability of an (Doctoral dissertation, Rhodes University).

Spangenberg, J.E. and Frimmel, H.E., 2001. Basin-internal derivation of hydrocarbons in the Witwatersrand Basin, South Africa: evidence from bulk and molecular $\delta^{13}\text{C}$ data. *Chemical Geology*, 173(4), pp.339-355.

Tan, H., Shao, Y., Liu, Q., Zhang, Y., Feng, Y., Zhang, Y. and Shah, S.A., 2022. Textures, trace element geochemistry and in-situ sulfur isotopes of pyrite from the Xiaojiashan gold deposit, Jiangnan Orogen: Implications for ore genesis. *Ore Geology Reviews*, 144, p.104843.

Taylor, S.R. and McLennan, S.M., 1988. The significance of the rare earths in geochemistry and cosmochemistry. *Handbook on the physics and chemistry of rare earths*, 11, pp.485-578.

Taylor, R.D. and Anderson, E.D., 2018. Quartz-pebble-conglomerate gold deposits: Chapter P in Mineral deposit models for resource assessment (No. 2010-5070-P). US Geological Survey.

Tucker, R. F., 1980. The sedimentology and mineralogy of the Composite Reef on Cooke Section, Randfontein Estates Gold Mine, Witwatersrand, South Africa. Master of Science Dissertation, University of Witwatersrand, Johannesburg, South Africa, 355 p.

Tucker, R.F., Viljoen, R.P. and Viljoen, M.J., 2016. A review of the Witwatersrand Basin- The world's greatest goldfields. *Episodes*, 39(2), pp.105-133.

Tribovillard, N., Algeo, T.J., Lyons, T. and Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chemical geology*, 232(1-2), pp.12-32.

Utter, T., 1978. Morphology and geochemistry of different pyrite types from the Upper Witwatersrand System of the Klerksdorp Goldfield, South Africa. *Geologische Rundschau*, 67, pp.774-804.

Viljoen, R.P., Saager, R. and Viljoen, M.J., 1970. Some thoughts on the origin and processes responsible for the concentration of gold in the early precambrian of southern-africa. *Mineralium Deposita*, 5, pp.164-180.

Wits Integrated Experience (2022) Plane Crash Investigation.
https://www.wits.ac.za/media/wits-university/study/schools-liason/documents/geochemistry_presentation.pdf

Zhang, S.E., Nwaila, G.T., Bourdeau, J.E., Ghorbani, Y. and Carranza, E.J.M., 2023. Machine learning-based delineation of geodomain boundaries: A proof-of-concept study using data from the Witwatersrand Goldfields. *Natural Resources Research*, 32(3), pp.879-900.

Appendix A: Experimental Results

A.1. Mineralogical characterisation

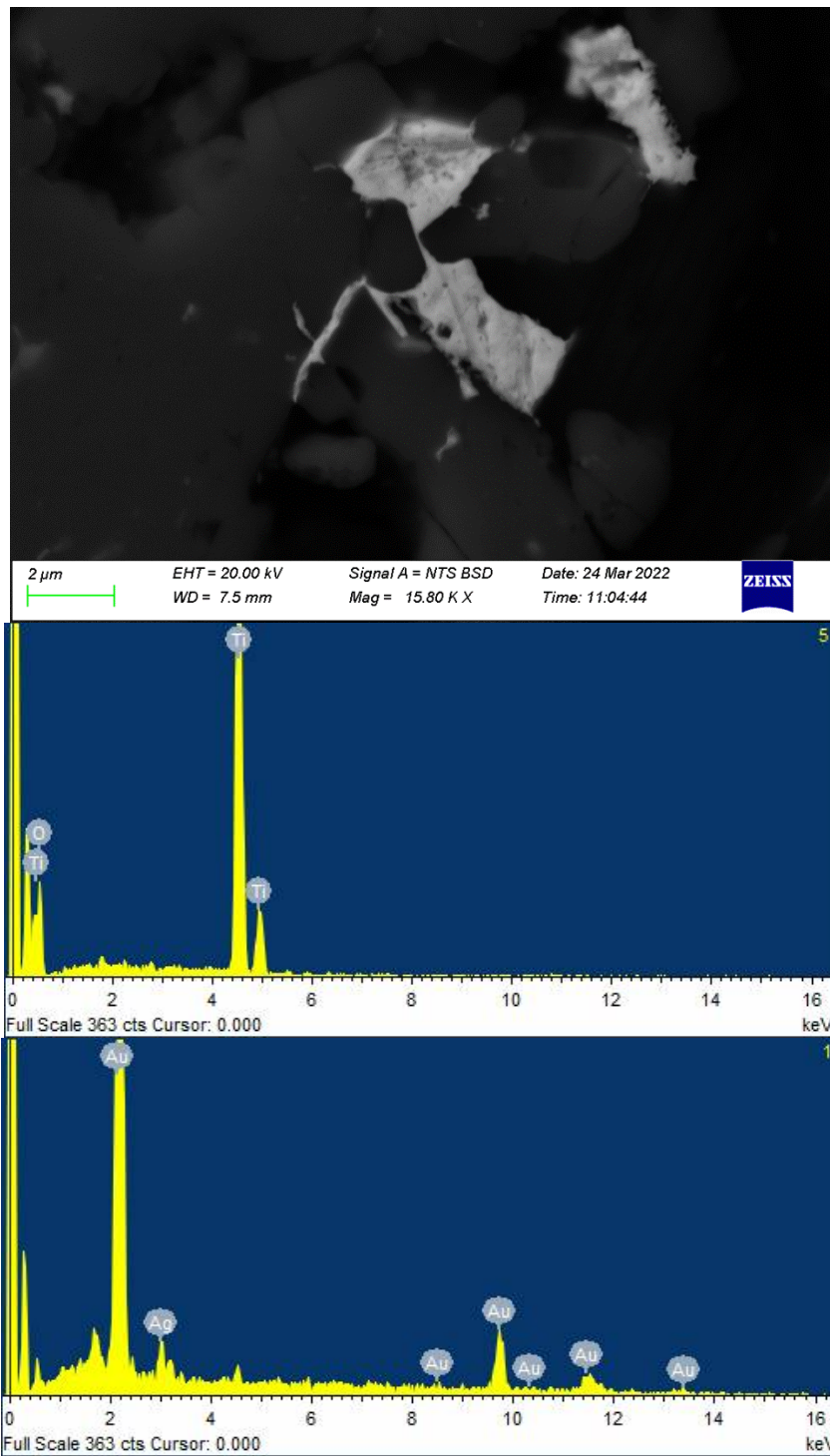
A1.1. Elemental composition of the samples in %

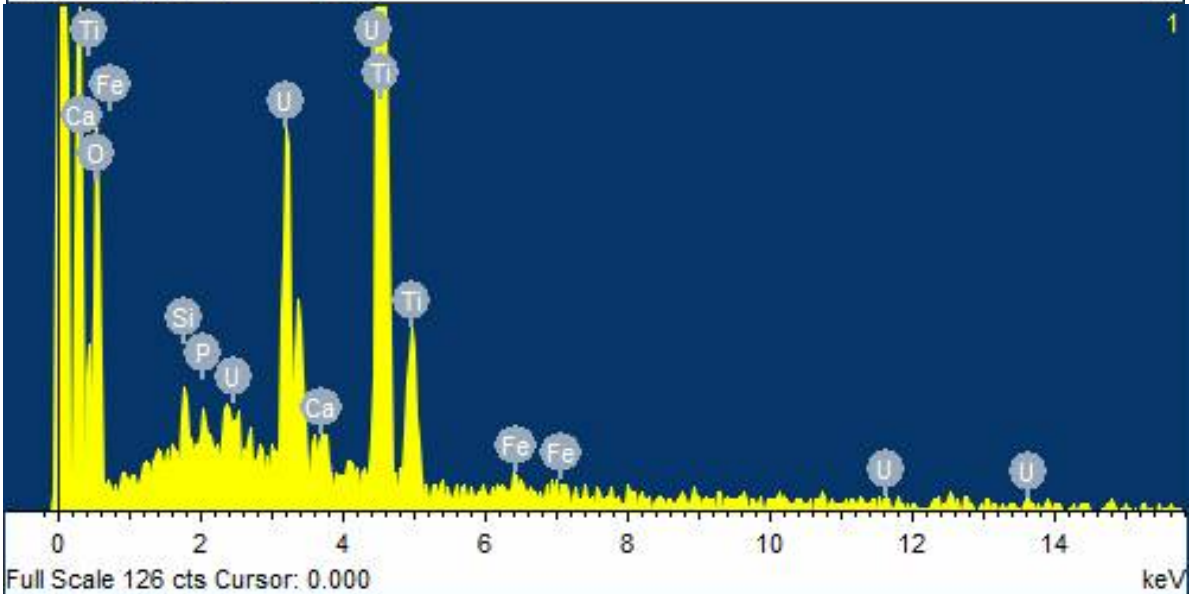
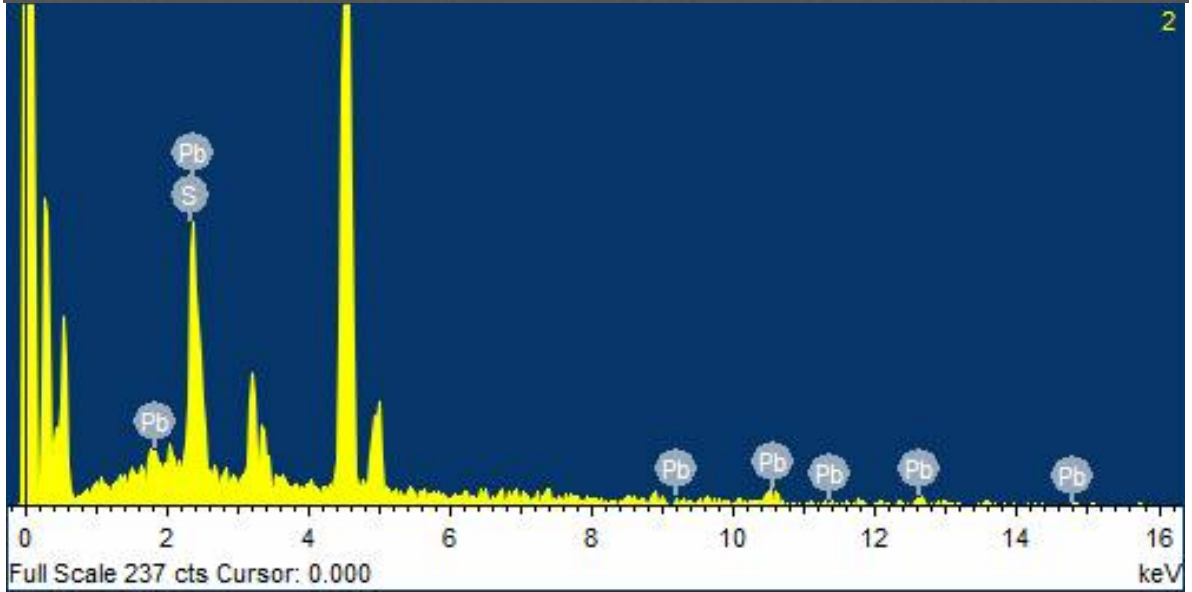
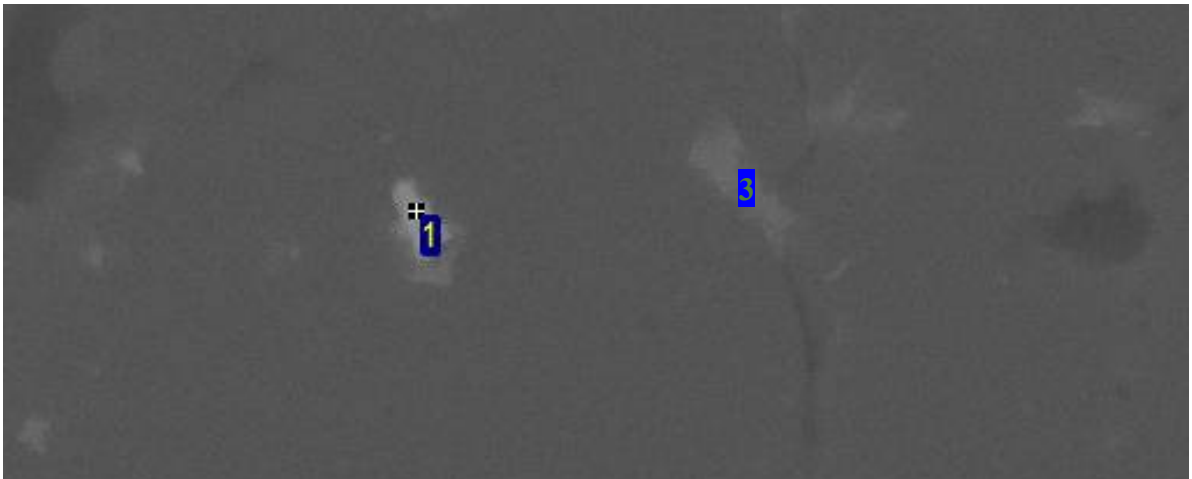
Elements	XRF Average	TIMA Average
Si	41.826	33.820
Al	1.695	0.720
K	0.555	0.322
Ca	0.019	0.003
Ti	0.096	0.180
Mn	0.010	0.000
Fe	2.647	10.254
Na	0.022	0.006
Mg	0.162	0.124
P	0.013	0.001
Cr	0.014	0.019
Ni	0.009	0.000

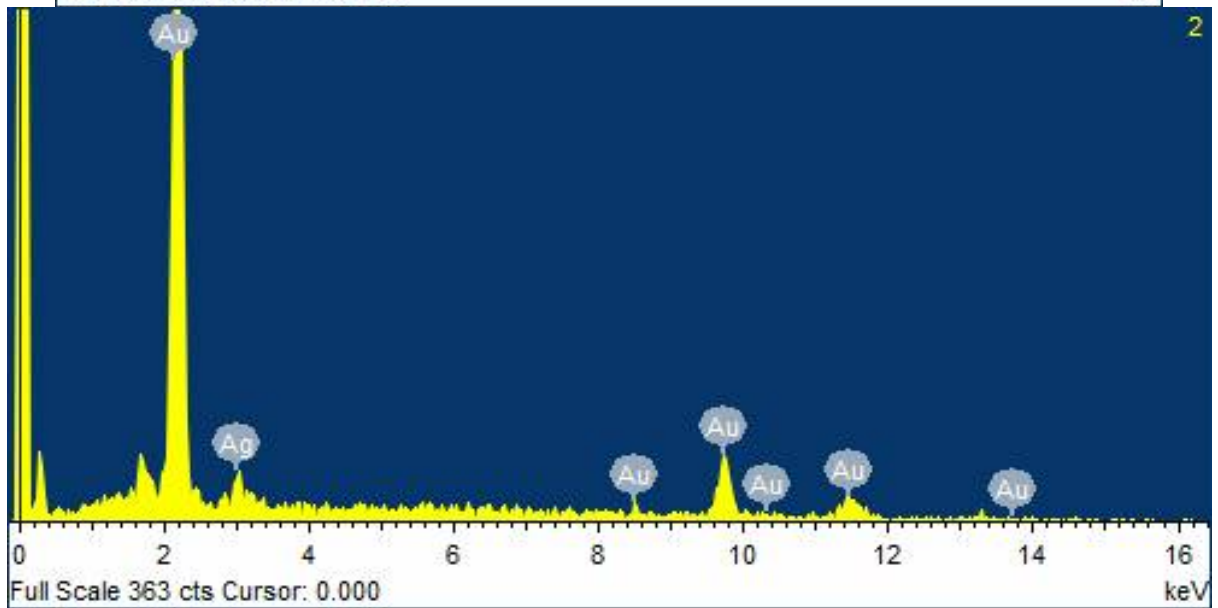
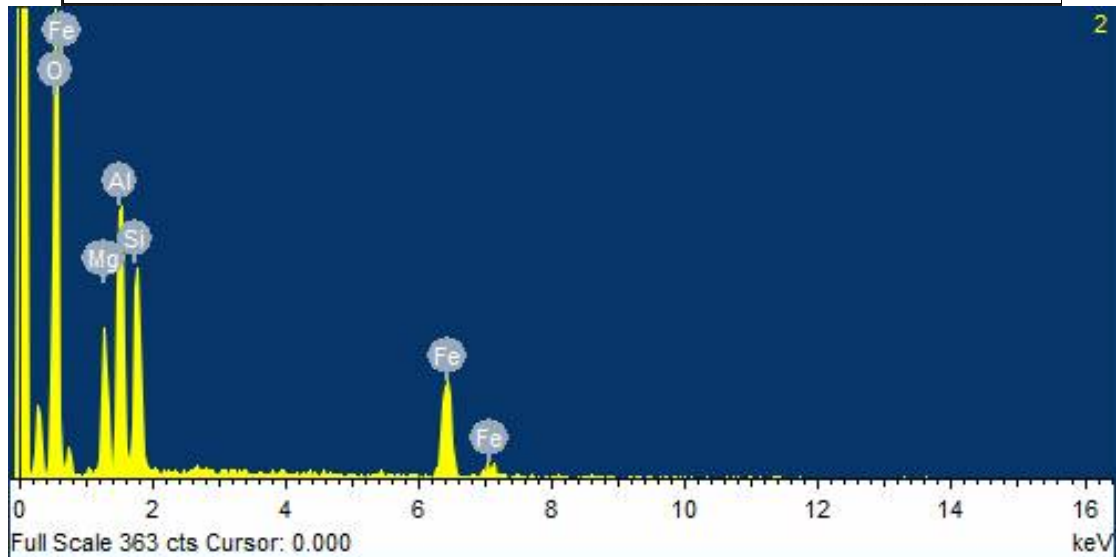
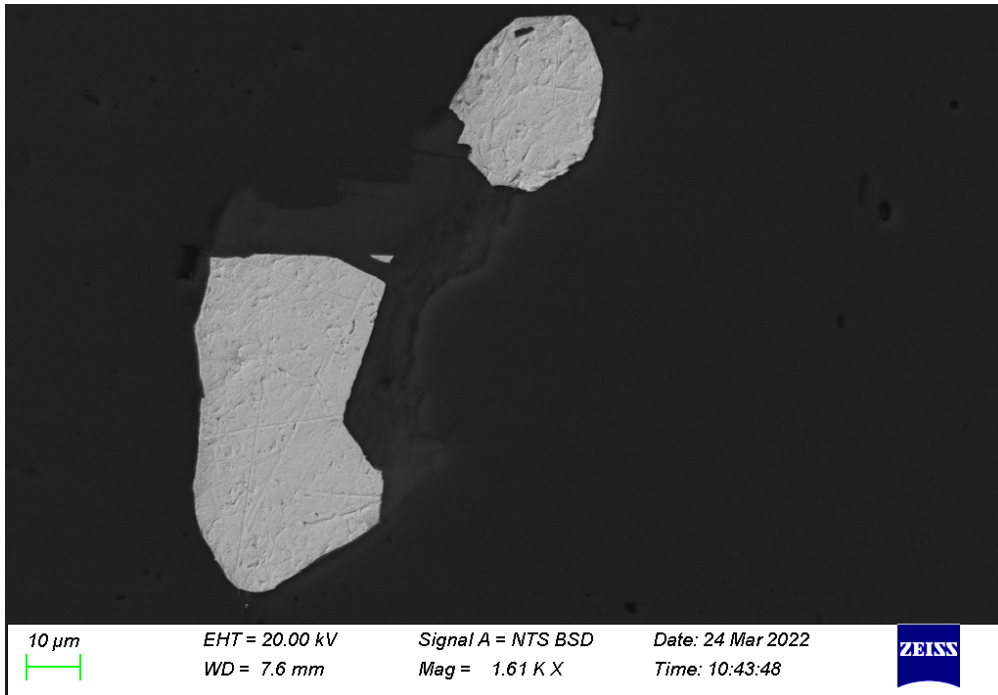
A1.2. TIMA Bulk mineralogy in %

Mineral	Bulk mineralogy
Quartz	70.03
Pyrite	16.65
Chalcopyrite	0.03
Pyrrhotite	0.10
Muscovite	4.37
Chlorite	1.35
Biotite	0.59
Chromite	0.08
Rutile	0.48
Zircon	0.14
Oxides	0.02
Others	6.10

A1.3. SEM-EDS images of ore minerals







A2. Geochemistry

A2.1. Major element chemistry

Rock type		Quartzite					
Sample	FW1	FW2	FW3	FW4	HW1	HW2	HW3
SiO ₂ (wt%)	85.26	86.26	83.48	89.13	91.18	92.76	91.62
Al ₂ O ₃	1.67	1.88	1.57	3.63	3.70	3.48	3.78
Fe ₂ O ₃	11.91	10.69	13.90	5.37	3.29	2.07	2.74
MnO	0.02	0.02	0.02	0.03	0.03	0.03	0.03
MgO	0.11	0.11	0.11	0.16	0.14	0.13	0.14
CaO	0.04	0.04	0.04	0.04	0.04	0.03	0.03
Na ₂ O	0.00	0.00	0.00	0.01	0.00	0.00	0.00
K ₂ O	0.47	0.53	0.42	1.12	1.15	1.11	1.19
TiO ₂	0.29	0.24	0.23	0.34	0.33	0.28	0.33
P ₂ O ₅	0.02	0.02	0.02	0.03	0.03	0.03	0.03
Cr ₂ O ₃	0.18	0.16	0.17	0.11	0.09	0.07	0.08
NiO	0.03	0.03	0.04	0.02	0.01	0.01	0.01

Rock Type		Conglomerate (Reef)								
Sample	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
SiO ₂ (wt%)	93.53	92.20	93.58	93.60	91.96	93.21	92.06	89.72	90.03	89.38
Al ₂ O ₃	2.95	2.99	2.88	2.88	3.03	2.95	3.03	4.12	3.94	4.14
Fe ₂ O ₃	2.33	3.55	2.40	2.38	3.77	2.65	3.63	4.67	4.64	5.00
MnO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
MgO	0.24	0.26	0.25	0.24	0.28	0.25	0.28	0.33	0.31	0.34
CaO	0.02	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.02	0.03
Na ₂ O	0.04	0.04	0.02	0.03	0.02	0.03	0.03	0.03	0.03	0.03
K ₂ O	0.64	0.65	0.63	0.62	0.65	0.63	0.65	0.81	0.77	0.80
TiO ₂	0.12	0.20	0.13	0.12	0.17	0.16	0.20	0.20	0.16	0.19
P ₂ O ₅	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Cr ₂ O ₃	0.04	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.02
NiO	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

A2.2. Trace elements

Quartzite (Hanging wall)			
Sample ID	HW1	HW2	HW3
Li(ppm)	3.8	3.31	3.341
P	47.907	49.839	52.571
Sc	3.736	3.365	3.697
Ti	858.875	871.25	1027.82
V	24.89	21.778	25.7
Cr	360.283	272.087	347.333
Co	55.064	31.736	44.062
Ni	87.299	61.433	73.184
Cu	70.962	63.708	75.63
Zn	60.271	14.577	10.455
Ga	4.449	4.714	5.788
As	2.835	1.559	2.662
Rb	23.19	21.58	23.305
Sr	3.647	3.502	3.809
Y	13.09	11.339	12.745
Zr	288.355	226.446	261.398
Nb	3.306	3.673	4.159
Sn	2.035	1.851	2.209
Sb	2.704	2.351	2.632
Cs	1.012	0.916	0.983
Ba	52.845	47.633	52.771
La	17.684	19.407	27.267
Ce	32.764	37.332	51.621
Pr	3.201	3.709	5.163
Nd	11.266	13.614	17.959
Sm	2.105	2.555	2.984
Eu	0.577	0.654	0.75
Gd	2.228	2.392	2.723
Tb	0.404	0.385	0.436
Dy	2.856	2.569	2.906
Ho	0.604	0.544	0.607
Er	1.877	1.641	1.839
Tm	0.303	0.265	0.294
Yb	2.036	1.771	1.998
Lu	0.307	0.253	0.295
Hf	8.732	7.11	8.034

Ta	0.419	0.444	0.5
W	0.377	0.407	0.532
Tl	0.232	0.189	0.226
Pb	37.535	33.686	34.181
Th	8.519	7.692	8.682
U	59.733	55.7	60.48

Quartzite (Footwall)			
Sample ID	FW1	FW2	FW3
Li(ppm)	3.437	3.628	3.511
P	43.378	39.582	40.714
Sc	2.203	2.016	1.751
Ti	617.796	582.186	468.325
V	12.242	12.624	10.37
Cr	312.409	305.37	297.564
Co	197.705	251.339	245.791
Ni	236.136	217.404	250.824
Cu	135.152	145.433	150.386
Zn	100.284	134.485	76.594
Ga	3.002	2.744	2.592
As	12.159	14.781	15.98
Rb	9.678	10.571	8.519
Sr	2.501	2.627	2.406
Y	14.278	12.249	11.812
Zr	293.401	262.399	229.011
Nb	2.08	1.993	1.544
Sn	2.705	2.487	2.672
Sb	4.854	4.867	5.056
Cs	0.809	0.842	0.804
Ba	26.439	29.398	25.868
La	14.288	12.286	11.335
Ce	26.728	23.277	22.553
Pr	2.621	2.406	2.348
Nd	9.752	8.702	9.031
Sm	2.215	1.921	2.167
Eu	0.643	0.549	0.642
Gd	2.596	2.226	2.412
Tb	0.489	0.435	0.443
Dy	3.258	2.943	2.929
Ho	0.665	0.596	0.581
Er	1.897	1.733	1.669
Tm	0.293	0.273	0.254

Yb	1.952	1.79	1.682
Lu	0.276	0.255	0.237
Hf	8.605	8.108	7.161
Ta	0.324	0.306	0.382
W	4.724	2.386	1.692
Tl	0.266	0.263	0.247
Pb	128.092	119.979	147.883
Th	12.286	11.066	11.606
U	158.505	141.049	145.131

Conglomerate (Reef)									
Sample ID	R1	R2	R3	R5	R6	R7	R8	R9	R10
Li (ppm)	2.345	2.551	2.533	2.599	3.03	2.549	5.212	4.792	5.626
P	52.621	56.19	51.936	57.311	55.59	53.143	57.555	47.509	58.969
Sc	1.204	1.487	1.252	1.875	1.409	1.446	2.164	1.945	2.507
Ti	316.051	345.722	315.187	428.91	272.502	451.309	446.347	401.027	545.553
V	6.896	7.528	6.913	9.004	7.534	7.867	14.645	14.148	15.961
Cr	52.667	65.802	51.28	60.681	64.236	71.07	86.651	88.462	96.334
Co	41.357	49.037	43.906	55.293	42.933	47.504	85.817	62.69	65.468
Ni	61.229	70.305	69.86	77.653	62.016	67.565	68.954	69.18	75.705
Cu	28.199	17.811	33.803	32.345	20.986	26.932	62.883	55.372	58.767
Zn	23.185	32.962	23.216	33.4	37.304	37.109	15.219	12.13	19.81
Ga	4.923	5.05	4.991	4.907	4.758	4.938	5.832	5.187	6.34
As	1.649	3.519	2.19	3.038	2.989	2.172	3.976	3.39	3.925
Rb	12.713	12.644	11.966	12.477	12.73	12.696	15.874	14.962	16.841
Sr	17.978	18.587	16.989	19.508	17.542	18.174	18.617	16.614	20.01
Y	4.415	6.714	4.808	7.632	5.79	6.5	6.177	5.13	7.706
Zr	37.94	75.859	36.644	56.289	54.303	63.802	47.583	43.046	186.536
Nb	1.243	1.299	1.079	1.383	0.988	1.477	2.701	2.486	3.061
Sn	1.346	1.564	1.554	1.762	1.639	1.601	1.775	2.322	1.96
Sb	3.022	3.328	4.351	2.944	2.832	2.223	6.492	7.096	6.379
Cs	0.45	0.455	0.439	0.418	0.46	0.459	0.851	0.796	0.906
Ba	95.463	93.39	90.73	92.175	95.306	94.423	128.989	122.88	137.492
La	23.39	23.133	23.687	22.723	21.098	22.062	23.6	19.896	26.305
Ce	40.932	41.71	44.548	39.647	38.814	39.835	42.985	36.621	49.992
Pr	4.263	4.199	4.527	4.032	3.922	4.036	4.371	3.7	4.581
Nd	15.684	15.288	16.283	14.93	14.188	14.971	15.842	13.329	16.382
Sm	2.553	2.537	2.696	2.486	2.337	2.519	2.807	2.354	2.94
Eu	0.566	0.601	0.558	0.586	0.55	0.571	0.672	0.555	0.73
Gd	2.04	2.237	2.208	2.298	2.043	2.204	2.307	1.915	2.434
Tb	0.236	0.299	0.267	0.318	0.273	0.287	0.309	0.251	0.335
Dy	1.199	1.635	1.358	1.835	1.517	1.612	1.735	1.402	1.92
Ho	0.22	0.315	0.24	0.343	0.279	0.308	0.33	0.265	0.377
Er	0.589	0.861	0.643	0.957	0.767	0.845	0.895	0.738	1.094
Tm	0.082	0.126	0.087	0.134	0.109	0.12	0.133	0.112	0.162
Yb	0.535	0.805	0.553	0.854	0.695	0.79	0.874	0.725	1.111
Lu	0.074	0.115	0.077	0.12	0.098	0.11	0.12	0.1	0.158
Hf	1.456	2.455	1.387	2.125	2.02	2.134	1.798	1.577	5.344
Ta	0.19	0.197	0.169	0.222	0.183	0.24	0.36	0.4	0.427

W	0.179	0.13	0.065	0.248	0.06	0.08	0.166	0.174	0.252
Tl	0.158	0.16	0.186	0.15	0.167	0.172	0.374	0.358	0.326
Pb	36.408	14.979	17.858	15.122	17.539	16.412	19.352	16.478	19.447
Th	5.001	6.957	6.452	6.382	6.385	6.942	6.41	8.66	6.58
U	20.403	21.161	21.432	19.237	21.434	23.686	34.548	28.16	33.8

A3. Micro-beam analyses

A3.1 EPMA Trace element

ppm	V	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Sb	Te	Au	Hg	Pb	Bi
Detrital massive	14.96	0.1	636.9	0.1	591.15	0.1	0.1	5312.46	89.97	0.1	131.07	0.1	637.4	10071.98	0.1
	0.1	0.1	402.76	0.1	83.71	1808.65	6320.05	5849.7	0.1	0.1	98.08	0.1	0.1	0.1	723.01
	5.52	0.1	215.47	0.1	0.1	0.1	2824.99	7647.47	341.59	0.1	0.1	1249.74	2347.63	1053.79	0.1
	0.1	0.1	20.18	30.85	0.1	1366.44	5396.03	6330.96	126.93	171.27	227.41	0.1	0.1	13433.57	0.1
	36.38	0.11	1409.93	74.54	144.12	3605.15	4891.84	9423.94	0.11	0.11	0.11	0.11	2717.92	12753.53	3491.92
	62.21	0.1	2760.08	103.5	1019.61	4080.62	1211.57	6862.28	415.02	400.08	196.15	0.1	217.34	12878	0.1
	29.71	0.09	0.09	282.58	111.86	2543	0.09	5934.66	0.09	0.09	63.53	0.09	401.92	5555.7	3785.98
	0.09	0.09	224.03	442.56	0.09	3400.84	4181.62	7149.87	334.97	0.09	168.42	0.09	0.09	3444.37	8463.2
	59.21	0.1	53.01	0.1	0.1	2701.06	0.1	4275.17	102.72	0.1	16.65	0.1	3909.26	0.1	1201.89
	0.09	0.09	128.21	771.22	769.33	5059.45	8089.25	8426.87	64.59	0.09	168.22	0.09	871.46	573.72	7961.36
	14.26	0.1	0.1	0.1	429.34	6390.87	2154.3	6104.8	430.96	54.35	0.1	0.1	0.1	0.1	0.1
	32.67	0.09	490.8	0.09	1385.15	7826.97	4806.76	6554.63	115.93	0.09	0.09	0.09	0.09	0.09	4927.47
	88.02	0.1	0.1	991.68	0.1	10896.81	2172.14	6145.01	312.03	0.1	233.51	0.1	0.1	3656.28	0.1
	0.1	0.1	0.1	0.1	15.87	0.1	0.1	5178.05	0.1	0.1	0.1	0.1	3295.25	5522.79	0.1
	64.36	0.1	504.32	344.67	476.74	0.1	536.42	4441.43	11.79	0.1	0.1	0.1	0.1	2667.81	27251.01
	0.1	0.1	136.86	0.1	0.1	320.9	5887.25	5698.17	467.45	0.1	224.95	0.1	0.1	0.1	0.1
	V	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Sb	Te	Au	Hg	Pb	Bi
Detrital randomly distributed	4.46	0.1	1830.89	0.1	0.1	0.1	0.1	4890.7	169.67	0.1	344.12	0.1	899.73	7109.13	6165.27
	63.42	0.1	615.82	897.12	0.1	4776.87	702.74	6628.64	164.46	0.1	20.13	0.1	2420.87	2390.75	0.1
	40.69	0.1	4601.87	543.77	655.95	1018.2	6953.58	6231.09	11.65	72.5	102.69	0.1	2974.23	10422.48	0.1
	0.12	0.12	8856.28	1043.65	0.12	4718.07	9596.21	5226.45	0.12	0.12	306.38	0.12	0.12	242.82	631.74
	123.64	0.1	4049.36	864.11	0.1	1897.14	0.1	5928.12	152.84	0.1	131.42	0.1	2626.81	7783.02	0.1
	0.1	0.1	3970.28	746.32	0.1	488.08	0.1	5695.4	0.1	187.14	162.37	1102.13	0.1	3936.3	0.1
	49.31	0.1	1986.27	467.4	212.21	853.8	3576.79	6407.67	553.1	117.91	173.43	0.1	0.1	19726.07	10262.33
	35.07	0.1	2166.57	2266.5	908.31	3057.97	0.1	7023.49	262.33	0.1	32.84	0.1	0.1	7398.96	0.1
	40.02	0.1	4984.25	0.1	95.04	0.1	0.1	6557.36	495.79	0.1	0.1	0.1	0.1	3345.37	9216.42
	122.21	0.1	2482.83	1097.09	969.57	10571.25	0.1	4121.4	329.81	58.27	218.47	0.1	3155.58	15904.15	0.1
	47.6	0.09	5201.33	60283.96	1513.53	3643.95	1932.21	6268.33	72.58	0.09	223.68	0.09	6049.07	8220.05	10857.28

	13.25	0.1	4751.03	1802.12	0.1	7068.04	294.08	4631.81	0.1	0.1	150.67	0.1	0.1	0.1	0.1
	42.38	0.1	3385.22	0.1	821.73	4304.36	3086.94	6113.05	0.1	0.1	250.52	0.1	1476.44	12914.31	0.1
	0.1	0.1	2571.54	698.99	0.1	271.81	309.2	3900.86	339.89	0.1	367.41	0.1	0.1	0.1	0.1
	0.1	0.1	3737.14	2015.76	0.1	0.1	8392.53	2405.21	129.56	0.1	0.1	0.1	0.1	0.1	9452.17
	0.19	0.19	70.01	42.72	0.19	0.19	0.19	13434.37	223.39	0.19	119.56	0.19	0.19	426.7	0.19
	V	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Sb	Te	Au	Hg	Pb	Bi
Detrital concentric	0.1	0.1	445.15	351.75	474.19	5636.66	0.1	5337.89	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	0.09	0.09	3787.08	0.09	948.94	5460.83	437.34	5515.24	82.98	759.16	154.9	0.09	0.09	25396.3	0.09
	0.1	0.1	3414.02	0.1	0.1	613.29	11219.52	7196.25	64.92	400.73	203.91	0.1	0.1	5937	0.1
	0.1	0.1	1477.47	1301.96	0.1	9184.37	0.1	5815.78	413.27	80.45	135.3	0.1	0.1	16773.58	1454.85
	0.11	0.11	3453.51	119.03	577.69	18692.05	4903.12	4968.11	196.33	0.11	0.11	0.11	0.11	41078.86	0.11
	0.12	0.12	5102.47	931.4	881.69	25132.68	327.81	8565.54	401.48	0.12	0.12	0.12	0.12	54726.77	0.12
	V	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Sb	Te	Au	Hg	Pb	Bi
Euhedral/subhedral	44.4	0.1	256.33	0.1	806.61	5039.67	277.46	5964.2	0.1	0.1	206.25	0.1	4082.14	7079.72	0.1
	0.1	0.1	5914.44	370.36	549.67	15690.5	3437.1	6447.93	292.38	0.1	372.73	0.1	10154.18	31925.99	0.1
	15.95	0.1	0.1	354.16	472.44	0.1	0.1	6927.48	0.1	0.1	20.51	0.1	8819.9	0.1	0.1
	119.39	4219.5	0.1	0.1	439.13	0.1	2992.88	5684.71	0.1	0.1	345.32	0.1	5935.82	0.1	5960.7
	58.63	0.1	185.32	0.1	0.1	4225.94	0.1	7668.9	70.24	0.1	7.03	0.1	5808.58	0.1	0.1
	72.59	0.09	0.09	254.06	0.09	9636.93	0.09	7386.78	6.37	0.09	410.61	0.09	0.09	2289.73	2889.03
	73.46	0.1	303.64	555.98	279.57	1674.46	4488.57	7017.26	0.1	0.1	353.13	0.1	1465.1	5208.84	7696.13

A3.2. LA-ICPMS Trace elements

Detrital massive (n=34)	ppm	51V	55Mn	59Co	60Ni	65Cu	66Zn	75As	77Se	95Mo	107Ag	121Sb	125Te	128Te	197Au	202Hg	208Pb	209Bi
	Minimum	0.04	0.77	0.49	1.66	0.17	0.35	0.35	0.45	0.01	0.02	0.03	0.07	0.19	0.04	0.51	0.02	0.00
	Maximum	3.12	52.70	3034.98	2590.92	240.07	798.83	3916.21	25.40	11.55	7.48	491.94	86.00	87.69	6.97	13.54	1040.73	602.26
	Stdv	1.02	20.65	639.99	611.04	59.69	193.23	1136.98	7.31	3.64	2.04	139.26	23.98	28.19	2.05	4.48	288.56	149.53
	Average	0.70	16.00	431.04	325.53	35.77	49.22	647.45	8.52	1.62	1.23	71.63	10.95	15.96	0.96	3.66	119.25	57.58
Detrital randomly distributed (n=42)																		
	Minimum	0.17	1.50	111.11	385.65	60.90	2.06	1181.55	5.06	0.02	1.92	29.25	3.28	3.07	0.79	1.38	35.39	39.57
	Maximum	65.97	84.75	2641.47	6359.71	58212.07	23.95	13734.73	42.18	29.49	33.40	755.59	109.95	110.30	12.46	18.46	2614.65	1302.94
	Stdv	14.94	17.77	614.21	1412.38	10042.24	5.10	3123.15	9.75	6.71	6.79	209.52	28.86	28.87	2.65	4.31	585.57	293.35
	Average	12.85	18.16	784.99	2513.00	2320.47	7.09	5024.39	15.65	6.35	8.77	384.24	51.82	51.97	4.56	8.90	463.08	486.68
Detrital concentric (n=30)																		
	Minimum	0.17	2.78	49.14	2616.25	84.48	1.04	234.76	1.39	1.04	1.84	19.96	3.31	3.41	0.73	2.11	24.29	31.29
	Maximum	25.94	137.60	1312.23	5847.68	26092.33	178.17	5543.79	33.70	38.53	18.07	404.82	68.67	68.29	11.48	21.32	1681.97	715.23
	Stdv	8.21	34.98	334.92	881.51	7099.84	46.53	1585.84	8.01	9.02	4.04	95.66	15.73	15.73	2.86	5.07	433.68	185.67
	Average	6.15	25.77	485.85	4031.97	4717.15	34.64	2238.09	7.59	6.93	5.49	151.09	21.79	21.75	3.64	7.25	282.83	240.99
Euhedral(n=25)																		
	Minimum	0.07	0.94	21.59	14.31	0.22	0.25	0.24	0.39	0.01	0.03	0.03	0.07	0.26	0.03	0.52	0.02	0.00
	Maximum	2.69	3.17	18221.55	3523.24	394.35	38.30	11159.79	105.35	0.11	0.57	4.43	10.61	11.38	1.13	0.82	18.40	9.38
	Stdv	1.07	1.02	4315.70	924.24	103.13	12.52	2895.48	32.77	0.04	0.18	1.54	3.23	3.68	0.31	0.16	5.53	2.45
	Average	1.14	1.75	2154.80	691.52	42.76	4.95	1772.90	29.33	0.05	0.22	1.74	2.03	2.64	0.15	0.71	4.70	1.75

A4. Sulphur isotope analyses

A4.1. Middelvlei Reef sulphur isotope data

Pyrite Morphology	$\delta^{34}\text{S}$
MVR Massive	2.91
MVR Massive	4.06
MVR Massive	1.62
MVR Massive	-5.30
MVR Massive	0.78
MVR Massive	2.53
MVR Massive	0.48
MVR Massive	-4.03
MVR Massive	2.85
MVR Massive	3.11
MVR Massive	5.15
MVR Massive	1.03
MVR Massive	0.49
MVR Massive	3.96
MVR Massive	-1.81
MVR Massive	0.18
MVR Massive	5.69
MVR Massive	0.97
MVR Massive	3.31
MVR Massive	3.57
MVR Massive	3.73
MVR Massive	3.22
MVR Massive	3.70
MVR Random inclusion bearing	23.03
MVR Random inclusion bearing	20.01
MVR Random inclusion bearing	25.27
MVR Random inclusion bearing	5.66
MVR Random inclusion bearing	1.18
MVR Random inclusion bearing	0.28
MVR Random inclusion bearing	-1.70
MVR Random inclusion bearing	2.24
MVR Random inclusion bearing	2.53
MVR Random inclusion bearing	2.61
MVR Random inclusion bearing	2.41
MVR Concentrically laminated	-0.21
MVR Concentrically laminated	-1.33
MVR Concentrically laminated	2.85
MVR Concentrically laminated	-6.32
MVR Concentrically laminated	4.00

MVR Concentrically laminated	-0.37
MVR Concentrically laminated	1.09
MVR Concentrically laminated	-5.81
MVR Concentrically laminated	-3.02
MVR Concentrically laminated	-1.43
MVR Concentrically laminated	-13.96
MVR Concentrically laminated	-15.39
MVR Euhedral	3.46
MVR Euhedral	3.76
MVR Euhedral	3.82
MVR Euhedral	3.14
MVR Euhedral	-2,18
MVR Euhedral	5,96
MVR Euhedral	3,95
MVR Euhedral	-0,16
MVR Euhedral	38,25
MVR Euhedral	-0,74
MVR Euhedral	0,47
MVR Euhedral	2,18
MVR Euhedral	1,18
MVR Euhedral	2.13
MVR Euhedral	1.03
MVR Euhedral	-1.87
MVR Euhedral	3.62
MVR Euhedral	-9.50
MVR Euhedral	1.61
MVR Euhedral	2.20
MVR Euhedral	2.35
MVR Euhedral	-5.67
MVR Euhedral	-5.41
MVR Euhedral	1.82
MVR Euhedral	2.70
MVR Massive overgrowth	-0.66
MVR Massive overgrowth	3.87
MVR Massive overgrowth	2.09
MVR Massive overgrowth	-1.58
MVR Massive overgrowth	0.22