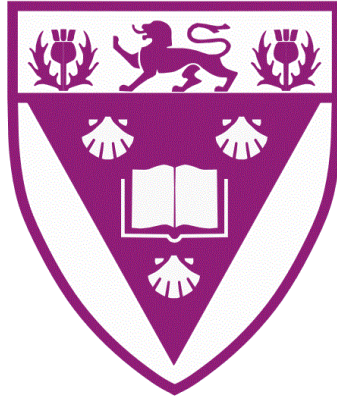


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GENESIS OF BIF-HOSTED HEMATITE IRON ORE DEPOSITS IN THE CENTRAL PART OF THE MAREMANE ANTICLINE, NORTHERN CAPE PROVINCE, SOUTH AFRICA

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This thesis is submitted in fulfilment of the requirements for the degree of

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Abstract

The Paleoproterozoic Transvaal Supergroup in the Northern Cape Province of South Africa is host to high-grade BIF-hosted hematite iron-ore deposits and is the country's most important source of iron to date. Previous work has failed to provide a robust and all-inclusive genetic model for such deposits in the Transvaal Supergroup; in particular, the role of hydrothermal processes in ore-genesis has not been adequately clarified. Recent studies by the author have produced evidence for hydrothermal alteration in shales (Olifantshoek Supergroup) stratigraphically overlying the iron-ore intervals; this has highlighted the need to reassess current ore-forming models which place residual supergene processes at the core of ore-genesis.

This thesis focuses on providing new insights into the processes responsible for the genesis of hematite iron ores in the Maremane anticline through the use of newly available exploration drill-core material from the centre of the anticline. The study involved standard mineralogical investigations using transmitted/reflected light microscopy as well as instrumental techniques (XRD, EPMA); and the employment of traditional whole-rock geochemical analysis on samples collected from two boreholes drilled in the centre of the Maremane anticline, Northern Cape Province. Rare earth element analysis (via ICP-MS) and oxygen isotope data from hematite separates complement the whole-rock data.

Iron-ore mineralisation examined in this thesis is typified by the dominance of Fe-oxide (as hematite), which reaches whole-rock abundances of up to 98 wt. % Fe_2O_3 . Textural and whole-rock geochemical variations in the ores likely reflect a variable protolith, from BIF to Fe-bearing shale. A standard supergene model invoking immobility and residual enrichment of iron is called into question on the basis of the relative degrees of enrichment recorded in the ores with respect to other, traditionally immobile elements during chemical weathering,

such as Al_2O_3 and TiO_2 . Furthermore, the apparently conservative behaviour of REE in the Fe ore (i.e. low-grade and high-grade iron ore) further emphasises the variable protolith theory. Hydrothermally-induced ferruginisation is suggested to post-date the deposition of the post-Transvaal Olifantshoek shales, and is likely to be linked to a sub-surface transgressive hydrothermal event which indiscriminately transforms both shale and BIF into Fe-ore. A revised, hydrothermal model for the formation of BIF-hosted high-grade hematite iron ore deposits in the central part of the Maremane anticline is proposed, and some ideas of the author for further follow-up research are presented.

DECLARATION

I, JARRED SVEN LAND, HEREBY DECLARE THAT THIS DISSERTATION IS ENTIRELY MY OWN WORK AND ALL THE SOURCES THAT HAVE BEEN QUOTED ARE ACKNOWLEDGED BY MEANS OF COMPLETE REFERENCES. NO PART OF THIS DISSERTATION HAS BEEN PRESENTED FOR ANOTHER DEGREE ELSEWHERE.

NO PORTION OF THIS THESIS, OR THE DATA PRESENTED WITHIN, MAY BE REPRODUCED OR PUBLISHED WITHOUT THE WRITTEN CONSENT OF THE AUTHOR

J.S. LAND

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1. INTRODUCTION

1.1 General

Iron (Fe) is the second most abundant metal, the fourth most abundant element and composes approximately 5% by mass of the earth's crust (Astrup *et al.*, 1998). Since 1200 B.C., iron production was relatively rare, however this changed with the commencement of the Iron Age in 800 B.C. The art of steel-making came into use about 800 years later and late in the 14th century the blast furnace further aided development (Taylor *et al.*, 1988). In Great Britain, coal was used to smelt iron ore in the 16th century until about 1710, when it was discovered that coal could be used as a reductant in iron-making (Taylor *et al.*, 1988). This was the beginning of the industrial age which saw iron at the forefront of development.

In South Africa, iron ore has been mined and smelted since pre-historic times with evidence of this found scattered all over the country, with a concentration found in the Northern Cape Province (Taylor *et al.*, 1988). The purpose of these small iron ore mines was either for specular hematite used in the manufacturing of body paint or for the use in smelting. Extensive local iron ore mining occurred in the Thabazimbi area and it was estimated that approximately 400 tons of ore were removed (Taylor *et al.*, 1988). However, the primitive technology used by the local people inhibited further exploitation of the ore reserves and it was the Europeans who had the technology to further develop and exploit these massive iron ore reserves in the country (Friede, 1980).

The core of the Earth is predominantly composed of metallic iron, however, the element has the opportunity to react with other substances in the earth's crust and is rarely found in the free metal form. Iron owes its widespread distribution to the fact that it easily combines chemically with many elements in different chemical and physical environments and is a constituent in hundreds of mineral species (Taylor *et al.*, 1988). Although iron is present in almost all sedimentary and igneous rock types only a few contain iron in significant quantities and in large enough masses to be sources of iron that can be mined economically (Taylor *et al.*, 1988).

The minerals that contain significant quantities of iron are listed below:

Magnetite	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$	72% Fe	} Most Important Economical Sources of Iron
Hematite	Fe_2O_3	70% Fe	
Goethite/Lepidochrosite	$\text{FeO} \cdot \text{OH}$	61% Fe	
Limonite	$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	59-63% Fe	
Siderite	$\text{FeO} \cdot \text{CO}_2$	48% Fe	

Economically exploitable iron ore deposits can be described as abnormal concentrations of iron in restricted zones where geological processes have successfully concentrated iron into a useable mineral form (Taylor *et al.*, 1988). The useable mineral form of iron must be capable of being easily separated from undesirable minerals and other deleterious chemical elements. The most undesirable constituents of iron ores are titanium, silica, aluminium, potassium, phosphorous and sulphur. The addition of these constituents into the ore can have serious implications for the characteristics of the steel that will be produced (Dub *et al.*, 2006).

Today, iron ore is the backbone of modern civilisation as it is used in the production of iron and steel. Iron ore is also used in the manufacturing of paint, as a catalyst in platinum production, as a desulphurizing agent in heavy-medium separation and in the production of high density concrete. The success of the metal can be attributed to a few factors which have led to its industrial popularity. Iron ore deposits are often large and can be exploited cheaply using open-pit methods. Iron ores are also easy to reduce to metal, and iron is cheap when compared to other metals.

The metal has been valued due to its physical properties such as strength, hardness, ductility, durability and malleability (Klemic *et al.*, 1973). These physical properties can be altered by combining iron with manganese, carbon, silicon, nickel, chrome or molybdenum to form various steel alloys (Dub *et al.*, 2006). Many of these steel alloys are used in the manufacturing of structural components in bridges, buildings, highways, aircrafts, automobiles and ships.

Although iron is mined from a variety of different rock types, the production of iron today is almost entirely from ores derived by secondary enrichment processes in Archean and Proterozoic banded iron formations (BIF).

In South Africa, the iron deposits associated with Superior-type banded iron formations of the Transvaal Supergroup, Northern Cape Province (Beukes *et al.*, 2003) are by far the most economically important sources of iron for the country, however there are other occurrences of sub-economic iron deposits in the country (Figure 1.1). There are countless vein and lode deposits which are located in the Northern Cape Province, North West Province and Limpopo that hold hematite or specular hematite (Astrup *et al.*, 1998). The specular hematite contained in these veins can be of economic interest to the pigment industry. There is also titaniferous magnetite in ultra-mafic magmatic rocks of the Bushveld Complex in the Gauteng, North West and Mpumalanga Provinces (Astrup *et al.*, 1998). The iron content of these ores ranges from 50-67 wt. % iron and has been previously considered as economical. The presence of magnetite in the felsic magmatic rocks in the Phalaborwa Complex, where magnetite accounts for approximately 27% of the main ore body, is another economically important source of iron in terms of South Africa (Astrup *et al.*, 1998).

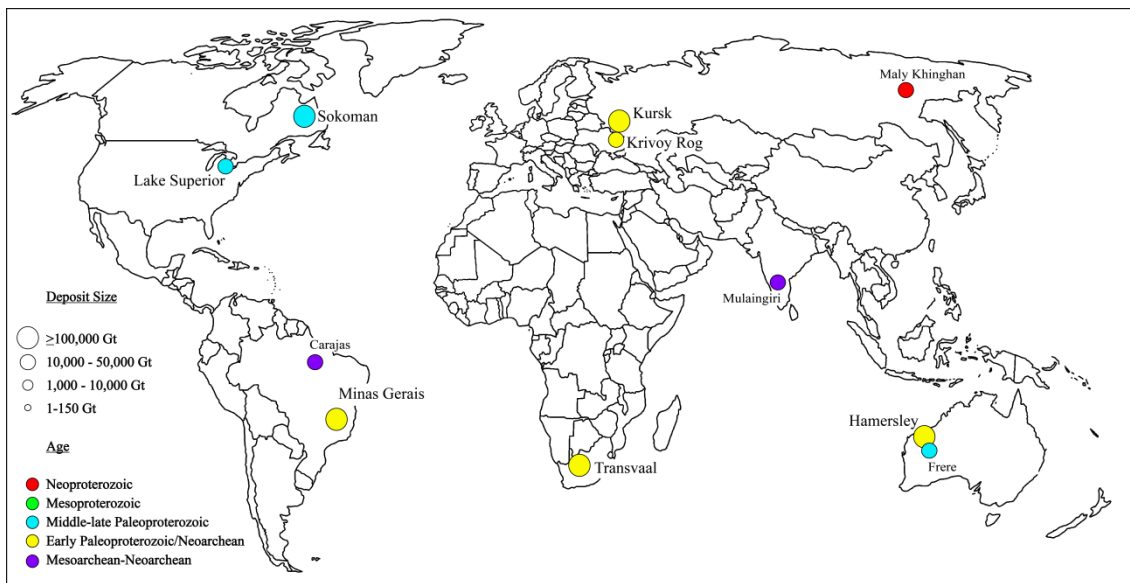


Figure 1.1. World map showing the distribution of banded iron formations based on their size and age. This illustration emphasizes the world-wide distribution of major iron formations and does not attempt to show all occurrences. Noteworthy deposits include those of the Transvaal basin (South Africa), Hamersley basin (Western Australia), Kursk and Krivoy Rog district (Ukraine), Minas Gerais (Brazil) and the Sokoman and Lake Superior region deposits (North America) (after Bekker *et al.*, 2010).

1.2 Banded iron formations and associated iron mineralisation

Banded iron formations (BIF) are chemically precipitated sedimentary rocks that are composed of thin (millimetre to centimetre scale) alternating layers of chert, iron oxides

and/or iron carbonates (Gross, 1980). James (1954) established a lower limit iron content of 15 wt. % in order for a rock to be classified as a banded iron formation. BIFs occur in a variety of different stratigraphic settings with no consistent lithological associations before or after BIF deposition; however, this has not discouraged researchers from attempting to categorise types of iron formations (Gole and Klein, 1981).

Gross (1980) recognised two principal types of iron formations based on the characteristics of the depositional basin, age and associated rock types:

1. **Lake Superior-type** iron formations are banded, cherty or oolitic iron deposited with quartz, dolomite, black shales and minor amounts of volcanic rocks in a near-shore continental-shelf environment (James, 1954; Gross, 1980; Astrup *et al.*, 1998). These iron formations lack spatial associations with volcanic rocks and are predominantly distributed in Proterozoic rocks (Gross, 1980; Figure 1.2). The high-grade iron ore deposits of Sishen and Kolomela (Sishen South) in the Northern Cape Province and Thabazimbi in the Limpopo Province are all considered to be altered Superior-type iron formations in South Africa. Other noteworthy Lake Superior-type iron ore deposits are the Krivoy Rog basin in Ukraine, Minas Gerais in Brazil as well as the Hamersley Basin deposit in Western Australia (Gross, 1980; Figure 1.1).
2. **Algoma-type** iron formations are banded cherty iron formations. Some authors believe that this type of iron formation is restricted to Archean greenstone belts (James, 1983; Klein, 2005). These types of iron formations are commonly associated with greywacke sedimentary units. Furthermore, Algoma-type iron formations have a genetic and spatial association with volcanic rocks and are deposited along volcanic arcs, rift zones and fracture systems (Gross 1980, Astrup *et al.*, 1998; Figure 1.2).

Banded iron formations are amongst the oldest rocks on Earth and have a considerable age-spread across the Precambrian time period. The vast majority of banded iron formations were deposited between 3.3 Ga and 1.5 Ga, prior to the end of the Paleoproterozoic age (Bekker *et al.*, 2010). The deposition of the early Paleoproterozoic Transvaal Supergroup banded iron formations coincides with a prolific peak in the deposition of BIF world-wide and it is these BIFs that host significant deposits of iron ore (Bekker *et al.*, 2010; Figure 1.2).

The occurrence of high-grade iron ore deposits hosted within banded iron formations is a process that is still poorly understood with certain aspects of the ore formation remaining

elusive (Gutzmer *et al.*, 2006). The controversy between a ‘hydrothermal’ and ‘supergene’ origin of various high-grade BIF-hosted hematite deposits has been the subject of debate for decades (Hagemann *et al.*, 2007). There are some iron ore deposits that are suggested to be hydrothermally-related, yet it is important to note that most BIF-related iron ore deposits also have a distinct supergene overprint due to deep lateritic weathering (Taylor *et al.*, 2001; Beukes *et al.*, 2003; Dalstra and Guedes, 2004; Gutzmer *et al.*, 2008; Hagemann *et al.*, 2008; Ramanaidou and Morris, 2010; Angerer *et al.*, 2012). It is also worth mentioning that there has been increased attention given to a syngenetic model, whereby chert-free BIF is formed during diagenetic processes (Lascelles, 2006a, 2006b).

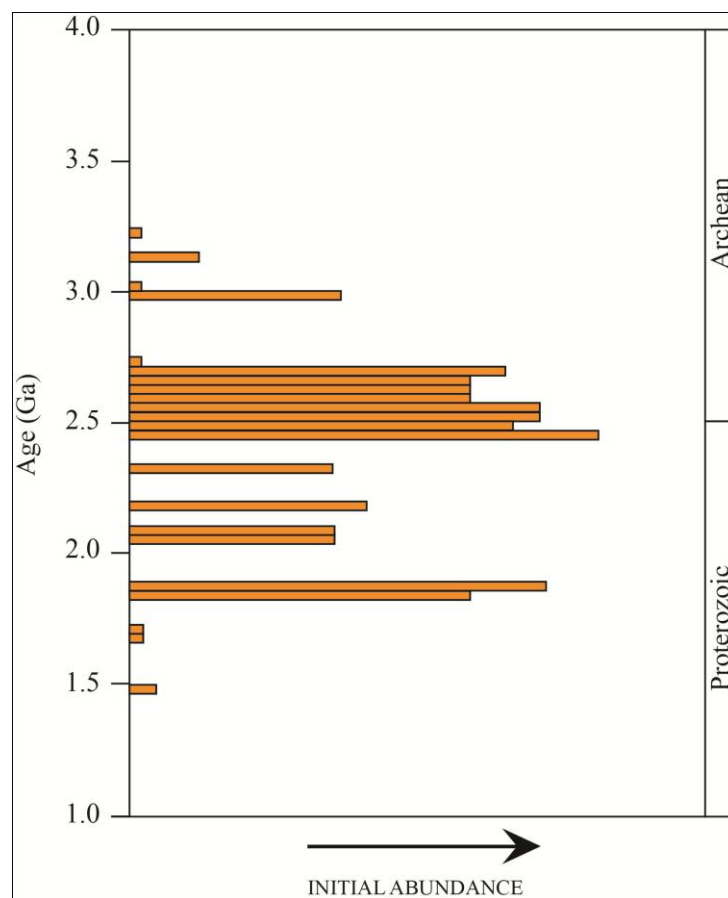


Figure 1.2. Schematic diagram showing estimated abundances of banded iron formations deposited between 4.0 Ga and 1.0 Ga. The distribution of the iron formations is plotted as the amount of iron formation in billion metric tons (modified after Bekker *et al.*, 2010).

Recent studies have suggested that too little whole-rock geochemical work has been conducted on BIF-hosted high-grade iron ores of the world (Gutzmer *et al.*, 2008). Detailed geochemical studies carried out on BIF-hosted iron ores are scarce in the past literature

(Gutzmer *et al.*, 2008; Figueiredo *et al.*, 2008; Angerer *et al.*, 2012) and near absent for the iron ores in the Maremane dome. The application of whole-rock geochemical data has contributed to the understanding of ore-forming processes in a wide range of geological environments (Gutzmer *et al.*, 2008). The authors further suggest that contributions to the understanding of whole-rock geochemical characteristics of BIF-hosted high-grade iron ores may aid in the understanding of the processes involved in ore genesis and render feasible exploration tools in the future.

1.3 Review of literature on BIFs and associated iron ores

From 1844 to 1904, there was little research carried out on iron formations, due to the belief that previous work suggested iron ore reserves were sufficient to support future industrial needs for several years (Morey, 1983). In 1922, John W. Gruner, a well-known pioneer in Precambrian geological research, published his first scientific paper on the origin of sedimentary iron formations in the Mesabi Range, northern Minnesota. Gruner went on to publish several other scientific papers on the origin of iron formations by weathering processes and hydrothermal processes (Gruner, 1924, 1926, 1930), the mineral composition and structure of greenalite (Gruner, 1936), stilpnomelane (Gruner, 1937) and minnesotaite (Gruner, 1944) as well as a paper on the discovery of micro-organisms in Archean chert pebbles (Gruner, 1925).

Harold James, another pioneer with regards to Precambrian banded iron formation research, was best known for his trail-blazing interpretations of the petrology of structurally complex banded iron formations (Barton, 2002). Harold James focused much of his research on northern Michigan BIFs which gave him the opportunity to publish three classic papers (James, 1954, 1955 and 1958). The paper titled “Sedimentary Facies of Iron-Formation” published in the journal “Economic Geology” (James, 1954) ignited renewed interest in banded iron formations and researchers once again began publishing papers on the origin, sedimentology, geochemistry and mineralogy of these unusual yet economically important rocks.

Following numerous publications by researchers on banded iron formations, UNESCO (1973) published a collection of these papers in a volume titled “Genesis of Precambrian Iron and Manganese Formations”. The Society for Economic Geologists (SEG) also published a special edition titled: “Precambrian Iron-Formations of the World” in 1973, which represents

a compilation of papers on regional distribution, research conducted by experts in various fields, and theories regarding the genesis of banded iron formations and their associated iron ore deposits.

Further research into the enigma of banded iron formations over the next 20 years resulted in the publication of two volumes in “Developments in Precambrian Geology”. The first volume, published in 1982, was titled: “Precambrian Banded Iron-Formations: Physicochemical Conditions of Formation” which was followed one year later by a volume titled “Iron-Formation: Facts and Problems” (1983). The latter publication includes research on the origin, genesis, chemical composition of BIF, rare earth element analysis, oxygen isotopes and paleontological evidence of BIFs from around the world.

In 2008, Steffen Hagemann, Carlos Rosière, Jens Gutzmer and Nicolas Beukes received enthusiastic support from the research community and industry to assemble a series of papers published in a special volume of *Economic Geology*, that captured the latest innovative research conducted on high-grade BIF-related iron ore deposits throughout the world (Hagemann *et al.*, 2008). This publication in “Reviews in Economic Geology 15” titled: “Banded Iron Formation-related High-Grade Iron Ore” contains a collection of papers with emphasis on the origin, timing of iron mineralization, hypogene alteration, structural control, mineralogy, geochemistry of iron ores and the importance of hydrothermal *versus* supergene processes from both established and newly discovered iron ore districts and deposits. This volume represents the latest summary of knowledge on high-grade BIF-related iron ore deposits.

A substantial amount of research has been carried out specifically on the BIFs of the Transvaal Supergroup, most notably work by La Berge (1966), Button (1976), Beukes (1983, 1984, 1986), Lamprecht and Hälbig (1988), Hälbig and Altermann (1992), Hälbig *et al.* (1992, 1993), Bau (1993), Tsikos (1994), Horstmann and Hälbig (1995), Tsikos and Moore (1997, 2005), Tsikos *et al.* (2003, 2010) and Beukes and Gutzmer (2008). There has been some research specifically carried out on the BIF-hosted iron ores of the Transvaal Supergroup, in the Northern Cape Province of South Africa, by Beukes *et al.* (2003), Carney and Mienie (2003), Gutzmer *et al.* (2005), Gutzmer *et al.* (2006), Alchin *et al.* (2008), de Kock *et al.* (2008) and Gutzmer *et al.* (2008).

Several researchers have proposed various metallogenic models for the genesis of high-grade BIF-hosted hematite iron ore deposits which are all in favour of epigenetic fluid-rock

interaction processes, of a supergene and/or hydrothermal nature (Taylor *et al.*, 2001; Beukes *et al.*, 2003; Morris, 2003; Dalstra and Guedes, 2004; Thorne *et al.*, 2004; Lascelles, 2006a; Lascelles, 2006b; Lobato *et al.*, 2008; Roy and Venkatesh, 2009). In this light, Beukes *et al.* (2003) recognise three general genetic types of high-grade iron ore deposits, namely hydrothermal, supergene and supergene-modified hydrothermal deposits, the latter being essentially a hybrid of the previous two.

The iron ores found on Maremane dome in South Africa, are thought to represent a type example of ancient supergene deposits (Figure 1.3). These ores are believed to be lithified ore from previous saprolitic soft ores that developed in the ancient supergene environment (Beukes *et al.*, 2003). The iron ores occur immediately below a major regional unconformity, which separates the Transvaal Supergroup from the overlying Olifantshoek Supergroup. This unconformity is host to numerous iron and manganese deposits and appears to have played a major role in the genesis of ore deposits in the Northern Cape region (Tsikos *et al.*, 2003, Moore *et al.*, 2010). This is due to the folded and tilted nature of the Transvaal Supergroup which results in the unconformity transecting a variety of rock types from the Transvaal Supergroup (Beukes *et al.*, 2003). High-grade iron ore deposits have developed in locations where the unconformity has transected the banded iron-formations (BIF) of the Transvaal Supergroup (Beukes *et al.*, 2003). However, large economically important deposits of high-grade iron ore (67 wt. % Fe) occur in karstic settings, where the BIF of the Asbestos Hills Subgroup has slumped into dissolution structures in the underlying Campbellrand carbonates (von Plehwe-Leisen and Klemm, 1995; Beukes *et al.*, 2003; Carney and Mienie, 2003). In areas outside of these karstic settings, thin layers (1-2m thick) of high-grade hematite ore are preserved below the Transvaal-Olifantshoek unconformity (Grobbelaar *et al.*, 1995; Beukes *et al.*, 2003).

These large high-grade hematite iron ore deposits were formed by a series of processes that have upgraded the Asbestos Hills BIF into an economically viable high-grade iron ore. The iron ores are thought to be the result of karstification and effective leaching of SiO₂ from the Asbestos Hills banded iron formation through circulation of meteoric waters during weathering (Grobbelaar *et al.*, 1995; von Plehwe-Leisen and Klemm, 1995; Beukes *et al.*, 2003; Carney and Mienie, 2003).

The hard hematite iron ores in supergene deposits are mainly characterised by laminated, massive and brecciated iron ore units (Beukes *et al.*, 2003). The karstic setting of these

deposits results in highly irregular thickness variations throughout the ore deposits. The unconformity-bound nature of these iron ore deposits and their association with these karstic structures forms the basis for their suggested supergene-related genesis by various workers (Beukes *et al.*, 2003; Dalstra and Rosière, 2008). The close link between the Maremane ores and supergene processes is strengthened by the fact that paleomagnetic data indicates that the ores were formed at low latitudes near the equator, where warm humid tropical conditions favour possible supergene enrichment processes (Evans *et al.*, 2001).

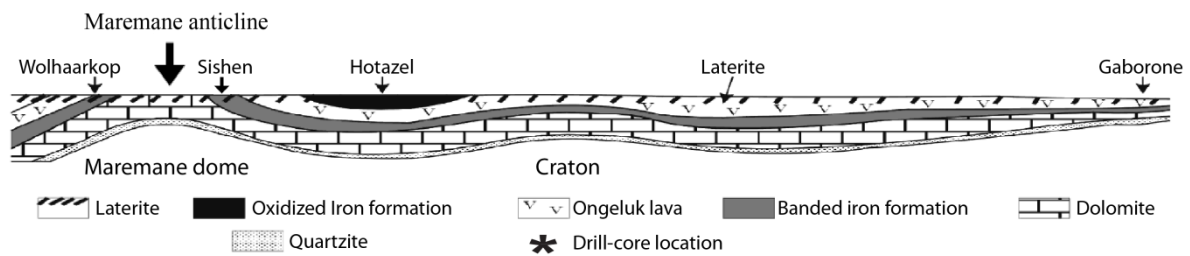


Figure 1.3. A cross-section of the Transvaal Supergroup illustrating the truncation of the stratigraphy by the regional unconformity. The Maremane anticline and associated iron ore deposits (Sishen and Wolhaarkop) are shown (modified after Beukes *et al.*, 2003).

The supergene-type ores differ from the hydrothermal ores. The Mount Tom Price (Australia) and the Thabazimbi (South Africa) represent type examples for hydrothermal deposits (Beukes *et al.*, 2003). These hydrothermal ores are not associated with any unconformity surfaces and mineralisation grades from the bottom upwards into an unmineralised banded iron formation (Figure 1.4; Taylor *et al.*, 2001; Beukes *et al.*, 2003). The main ore bodies usually occur above black shale units, and the mineralisation in hydrothermal-type ores is suggested to be associated with faulting (Taylor *et al.*, 2001; Thorne *et al.*, 2008). The high-grade hematite iron ores develop as a result of silica leaching from the BIF by warm, highly saline fluids (1st stage) and recrystallization of iron-rich phases to specular hematite and martite caused by moderately warm, low salinity, oxidized fluids (2nd stage) (Taylor *et al.*, 2001). Studies conducted on hydrothermal-type deposits reveal a relatively restricted temperature range of ore formation for all deposits. These temperatures range from 150°C to 320°C (Taylor *et al.*, 2001) during ore formation with the $\delta^{18}\text{O}$ of the hydrothermal fluid being estimated at approximately -2‰ relative to SMOW (Beukes *et al.*, 2003). It is thus suggested that the fluids involved are of shallow crustal origin (meteoric water) and have not interacted with any silicate rocks (Taylor *et al.*, 2001; Beukes *et al.*, 2003). A study conducted by Taylor *et al.* (2001) suggests that iron enrichment can be accounted for by

simple silica leaching and an increase in porosity. Intrusive igneous and shale units, present in most hydrothermal-type ore deposits, are believed to be important controls in the distribution of ore bodies.

The modified magmatic-meteoric hydrothermal and supergene-modified hydrothermal type ores are represented by the deposits from Brazil (Carajas district) and India (Noamundi district), respectively (Beukes *et al.*, 2008; Figueiredo *et al.*, 2008; Figueiredo *et al.*, 2013). The Noamundi deposit is regarded as being of hydrothermal origin but have later experienced deep chemical weathering in geologically recent times (Dalstra and Guedes, 2004; Gutzmer *et al.*, 2008). The supergene overprint is believed to have contributed significantly to the further upgrading of the ore in terms of both tonnage and grade. The supergene-related ores are usually comprised of soft saprolitic ores which are the direct consequence of supergene enrichment. The hydrothermal-related hard laminated or massive hematite iron ores occur beneath the soft saprolitic-type ores in supergene-modified hydrothermal deposits (Dalstra and Guedes, 2004). The modified magmatic-meteoric hydrothermal fluid model for the Carajas hard hematite ores was suggested by Figueiredo *et al.* (2013), whereby a saline, ascending modified magmatic fluid caused oxidation of magnetite to hematite. The authors then suggest this was followed by influx of meteoric water, mixing with ascending magmatic fluids, with the later stages of alteration being dominated by low-salinity meteoric water which maintained temperatures of 240° to 310°C forming late-stage tabular hematite.

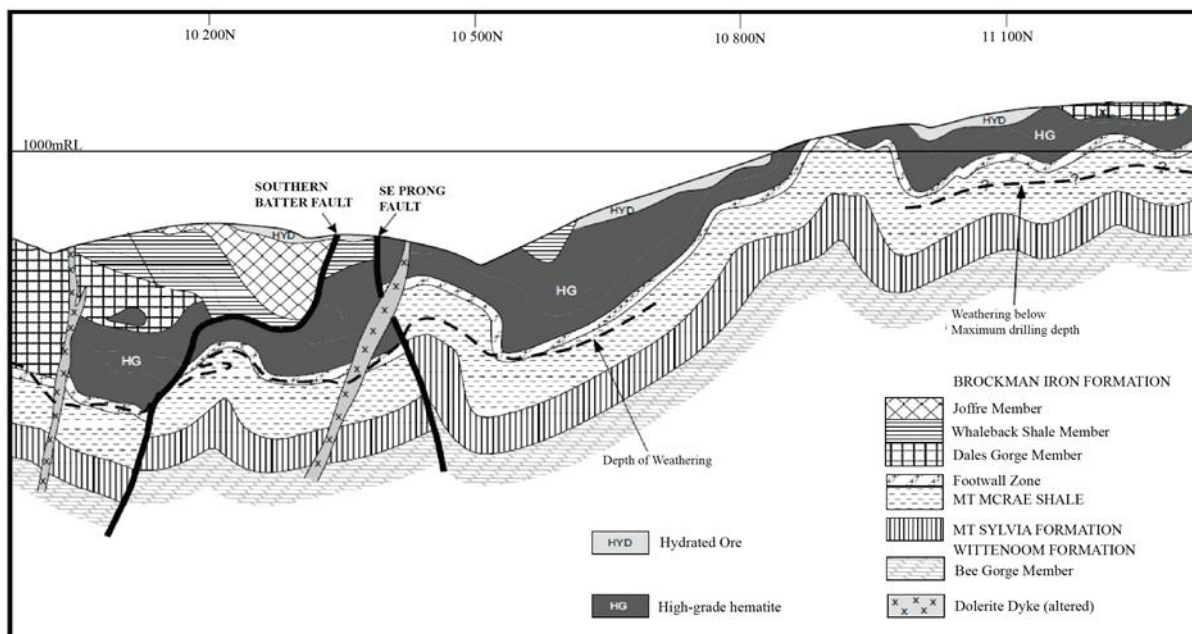


Figure 1.4. A cross-section through the Mount Tom Price mine illustrating the main mineralisation horizons that parallel the trend of the fault zones (modified after Taylor *et al.*, 2001).

1.4 Thesis outline and objectives

As a result of the paucity of geochemical data available for high-grade iron ore deposits, as highlighted previously in Gutzmer *et al.* (2008) and Angerer *et al.* (2012), there is an important question that arises concerning the potential of whole-rock geochemistry in aiding the understanding of such deposits. Furthermore, the current literature on iron ore deposits from the Northern Cape Province offers very little with respect to detailed geochemistry and a comprehensive genetic model for these ores, particularly with regards to the relative role of hydrothermal processes in ore genesis (Beukes *et al.*, 2003).

The need to re-assess the role of hydrothermal overprinting in such ores as well as adjacent rocks, arises from recent studies of the author which focused on geochemical evidence for hydrothermal alteration in the lowermost shales of the Olifantshoek Supergroup which overlie the iron ores (Mapedi Formation; Land, 2010).

In recent years, Kumba Iron Ore have made significant BIF-hosted iron ore discoveries adding to the already established resources at Sishen and Beeshoek in the Northern Cape Province, South Africa (Carney and Mienie, 2003). Using newly available exploration drill-core material from the centre of the Maremane anticline this study focuses on providing insights into the processes responsible for the genesis of these newly discovered iron ores. This study does not intend to fully elucidate the complex processes responsible for the formation of BIF-hosted high-grade iron ore deposits in the entire region in question. The main objectives of this study are summarised in the following three key points:

- to provide insights into the mineralogical composition of ores in the Maremane dome with particular focus on gangue mineralogy, its stratigraphic distribution and their origin
- to contribute new major and trace element geochemical data to the current literature on iron ore deposits with particular reference to the ores of the Northern Cape Province of South Africa
- to integrate all data produced with a view to constraining the genesis of the studied iron ores and specifically assessing the relative role of hydrothermal *versus* supergene processes

The above will be achieved through standard mineralogical studies (microscopy, XRD, EPMA) and employment of traditional whole-rock geochemical analysis (XRF, ICP-MS, GS-MS) on high resolution samples collected from two boreholes drilled in the centre of the Maremane anticline, Northern Cape Province. These aforementioned analytical procedures were all carried out by the author with the exception of the GS-MS used in oxygen isotope analysis, as described in Appendix A. Mineralogical and textural evidence together with geochemistry will enable the preliminary identification of possible protolith lithology's, whilst also allowing better constraints on the timing of the mineralisation. Additionally, oxygen isotope analysis from hematite separates complement the whole-rock data and yield insights in terms of the fluids responsible for the genesis of the high-grade iron ore and the physicochemical conditions thereof.

There are 5 chapters that form the main part of this thesis. The 1st chapter presented introductory aspects of the research such as general information regarding iron, banded iron formation-hosted high-grade iron ore deposits, a brief review of current literature as well as a summary of the objectives of the thesis and methodologies that were employed. The 2nd chapter provides a detailed account of the regional and local geology in the study area as well as a section on the economic geology of the Transvaal Supergroup. The 3rd chapter focuses on the mineralogy and petrography of the iron ores, as well as the overlying shales and underlying banded iron formation units. The chapter provides a detailed account of the mineralogy of each rock unit with particular emphasis placed on textures. The petrographic information obtained and sample groups derived in this chapter provide a key framework for the presentation and evaluation of the geochemical data presented later.

The 4th chapter of the thesis presents the whole-rock geochemistry of the iron ores as well as underlying banded iron formation. Major and trace element compositions are presented and evaluated. Additionally, this chapter includes the application of rare earth element and oxygen isotope geochemistry of hematite separates from the iron ore intersections.

The 5th chapter provides a detailed discussion of the results presented in the foregoing chapters. Here, emphasis is placed on providing suggestions with regards to the pre-ore lithologies and on highlighting specific physical and chemical factors that appear to be implicated in the genesis of these deposits. Finally, the 6th chapter will provide a succinct account of some of the more pertinent conclusions derived from the research as well as a

revised genetic model. The implications that this research may have on exploration strategies employed in the region as well as on future research directions conclude this thesis.

2. REGIONAL AND LOCAL GEOLOGY

2.1 The Transvaal Supergroup

The Paleoproterozoic Transvaal Supergroup rocks cover approximately 250 000km² and are preserved in two separate structural basins, the Transvaal basin which circumscribes the Bushveld Complex and the Griqualand West basin which occurs on the western margin of the Kaapvaal Craton (Moore *et al.*, 2001; Figure 2.1).

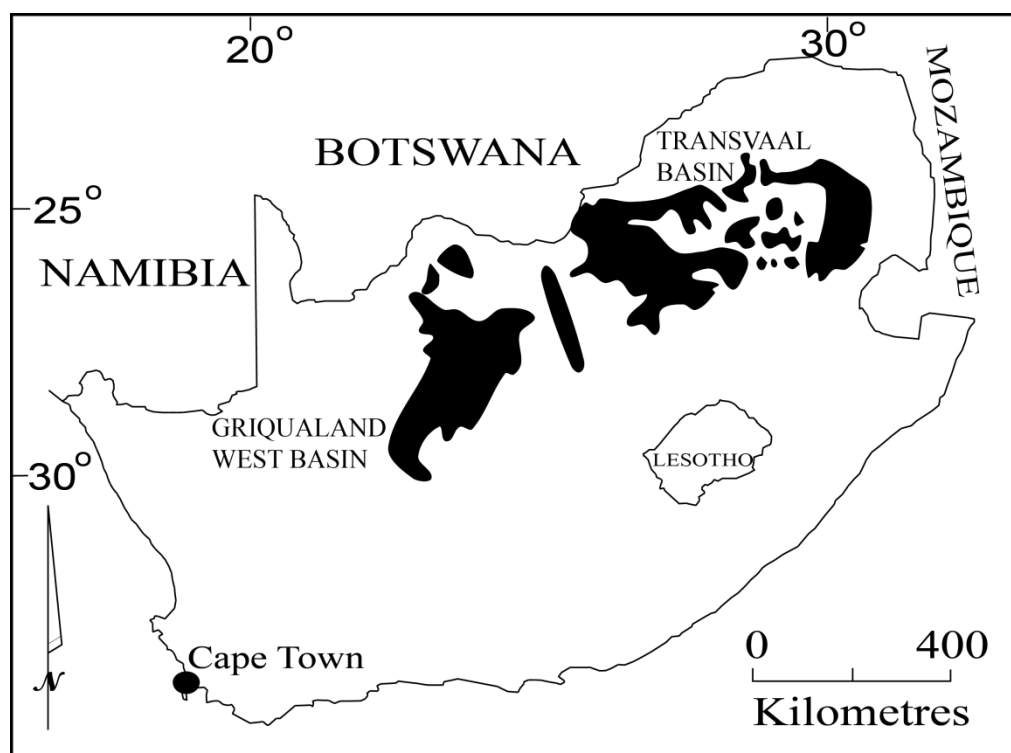


Figure 2.1. Map showing the distribution of the Griqualand West basin as well as the Transvaal basin (modified from Moore *et al.*, 2011).

The Transvaal Supergroup rocks are composed primarily of carbonate, chemical sedimentary, glacial and volcanic sequences which span an approximate period of ~2.5 to 2.2 Ga (Beukes and Smit, 1987). The Ghaap and Postmasburg Groups from the Griqualand West basin have been correlated with the Chuniespoort and Pretoria Groups in the Transvaal basin (Beukes, 1983; Figure 2.1; Table 2.1). Subsequent to the deposition of the Transvaal Supergroup sequences, the rocks underwent mild deformation (open folding), resulting in the formation

of the Maremane dome (Beukes, 1983; Figure 2.2). The Mapedi shales of the Olifantshoek Supergroup unconformably overlie the Transvaal Supergroup. Major tectonic events have caused thrust faulting and intense folding, post-Olifantshoek period, and have caused lithostratigraphic successions in some areas of the Griqualand West basin to be destroyed.

The Transvaal Supergroup consists of two major geological groups, the Ghaap and Postmasburg Groups. The Ghaap Group is composed of the Schmidtsdrif, Campbellrand, Asbestos Hills and Koegas Subgroups (Table 2.1).

Table 2.1. A simplified stratigraphy of the Transvaal Supergroup in the Griqualand West basin (modified after Beukes and Smit, 1987; Dorland, 1999).

SUPER GROUP	GROUP	SUBGROUP	FORMATION	LITHOLOGY	APPROXIMATE THICKNESS (IN METRES)
TRANSVAAL	POSTMASBURG	VOELWATER	Moodraai	Dolomite, Chert	250
			Hotazel	Mn, Fe-Formation	
			Ongeluk	Andesitic lava	900
			Makganyene	Diamictite	50-150
	GHAAP	KOEAS	Nelani	Shale	240-600
			Rooinekke	Fe-formation	
			Naragas	Quartz-wacke, shale	
			Kwakwas	Riebeckitic shale	
			Doradale	Fe-formation	
			Pannetjie	Quartz-wacke, shale	
		ASBESTOS HILLS	Griquatown	Clastic textured Fe-formation	200-300
			Kuruman	Microbanded Fe-formation	150-750
		CAMPBELLRAND	Gamohaam	Sparry limestone, shale	1500-1700
			Kogelbeen	Dolomite, limestone	
			Klippan	Cherty dolomite	
			Papkuil	Dolomite	
			Klipfonteinheuvel	Cherty dolomite	
			Fairfield	Sparry dolomite	
			Reivelo	Micritic dolomite	
			Monteville	Dolomite, limestone, shale	
		SCHMIDTSTDRIF	Lokammona	Shale	10-250
			Boomplaas	Dolomite, limestone, shale	
			Vryburg	Quartzite, lave, shale	

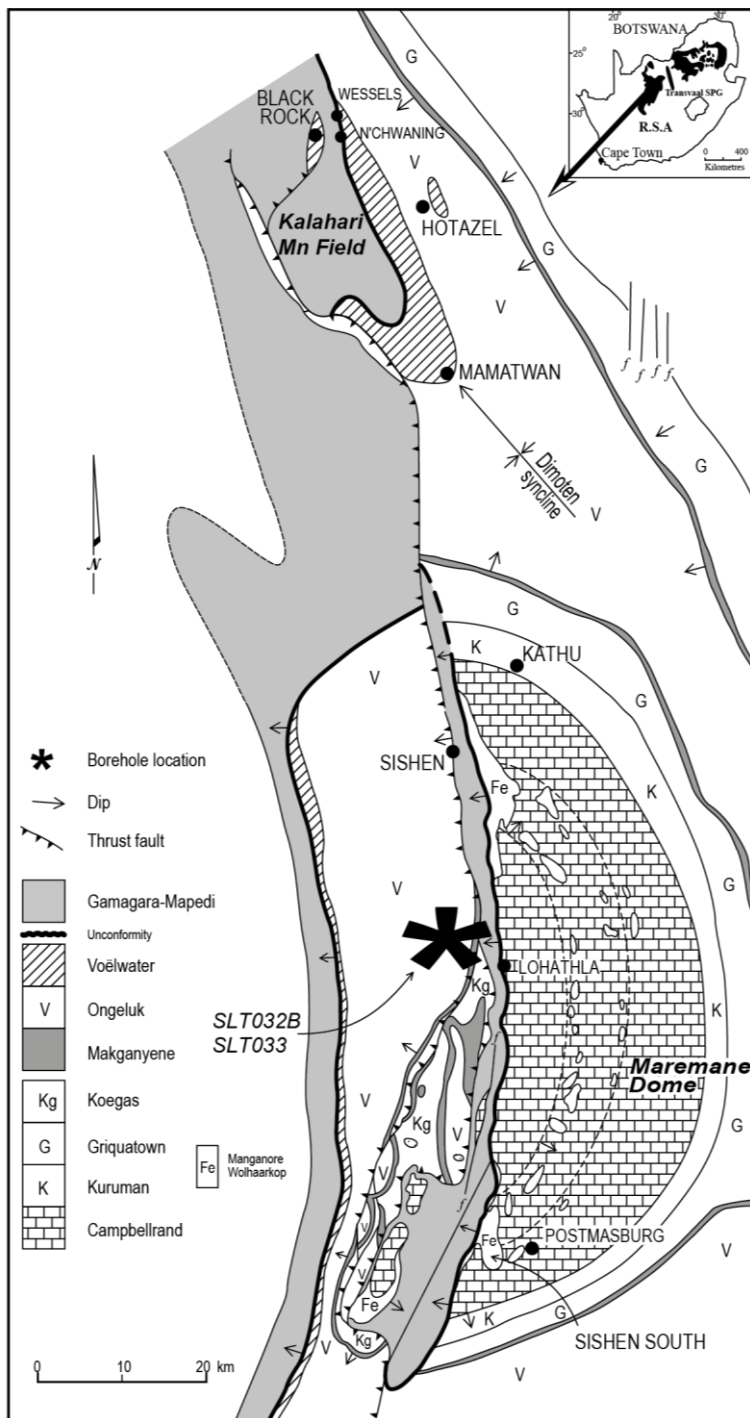


Figure 2.2. Detailed geological map showing the stratigraphic setting of the Transvaal Supergroup and the unconformably overlying Olifantshoek Supergroup, the position of the Kalahari manganese field (KMF), as well as the localities of boreholes SLT032B and SLT033, near Postmasburg. (modified after Moore *et al.*, 2011).

2.1.1 Ghaap Group

2.1.1.1 Schmidtsdrif Subgroup

The Schmidtsdrif Subgroup forms the basal unit of the Ghaap Group and unconformably overlies either the ~2.7 Ga lavas of the Ventersdorp Supergroup or crystalline Archean

basement rocks (Beukes, 1983). The Schmidtsdrif Subgroup has been subdivided into the basal Vryburg Formation, the central Boomplaas Formation and the upper Lokammona Formation (Beukes, 1979; Table 2.1). The basal Vryburg Formation consists of siltstones, shales, quartzites and carbonates and has been interpreted as fluvial to marine deposits (Beukes 1986). The central Boomplaas Formation is composed of oolitic and stromatolitic carbonates deposited in a carbonate platform environment (Beukes, 1979). The Lokammona Formation is composed of banded siderite lutites which overly the carbonates rocks of the central Boomplaas Formation (Beukes, 1983). The basal Vryburg Formation was dated by Walraven and Martini (1995) at 2642 ± 3 Ma.

2.1.1.2 Campbellrand Subgroup

The Campbellrand Subgroup represents the onset of widespread carbonate accumulation and conformably overlies the Lokammona Formation of the Schmidtsdrif Subgroup (Beukes, 1987). This subgroup has been further subdivided into two main facies, the basinal and platform facies (Beukes, 1980; Figure 2.3). The platform facies consists of the basal Monteville Formation, followed by the Reivilo, Fairfield, Klipfonteinheuwel, Papkuil, Klippan, Kogelbeen and the uppermost Gamohaam Formations (Altermann and Wotherspoon, 1995; Eriksson and Altermann, 1998; Table 2.1). These platform facies formations extend laterally into the basinal facies deeper water carbonates. The platform facies consists of shallow water stromatolitic carbonates which interfinger laterally into the deeper water basinal carbonates (Beukes, 1983; Figure 2.3). These basinal carbonates are composed of laminated, clastic textured dolostones and pyritic carbonaceous shales (Beukes, 1983). A U-Pb zircon age of 2521 ± 3 Ma, for a tuff bed in the platform succession of the Campbellrand Subgroup, was reported by Sumner and Bowring (1996).

2.1.1.3 Asbestos Hills Subgroup

The transition from carbonate deposition to BIF deposition has been attributed to a major marine transgression. The Asbestos Hills Subgroup has been subdivided into two formations, the lowermost orthochemical rhythmically banded Kuruman Iron Formation and the uppermost allochemical clastic-textured Griquatown Iron Formation (Beukes, 1983; Table 2.1; Figure 2.2).

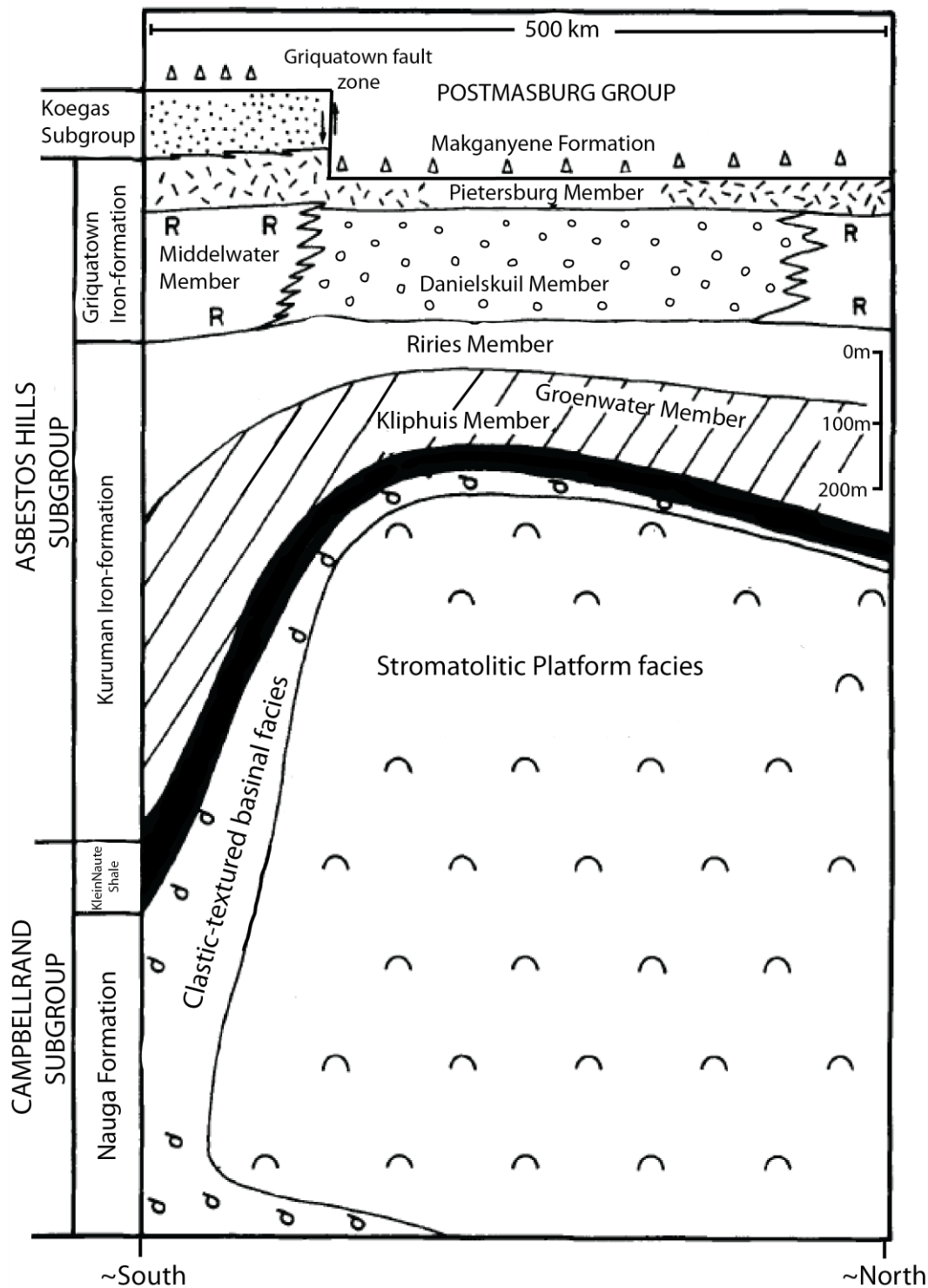


Figure 2.3. South-North section illustrating the paleodepositional environments and stratigraphic relationships of the Ghaap Group, Transvaal Supergroup, in Northern Cape Province (modified after Beukes, 1984).

The Kuruman Iron Formation is considered to have been deposited in an open shelf marine environment (Figure 2.3). The Kliphuis Member forms the basal unit of the Kuruman Iron Formation and is composed of chert mesobands alternating with ankerite mesobands, whilst the Groenwater Member overlies the ankerite-banded cherts and consists of bands of

stilpnomelane lutite, siderite-microbanded chert, siderite-magnetite rhythmite and magnetite-hematite rhythmite (Beukes, 1983). Beukes (1983) suggest that during periods of volcanic activity, silica and acidic ash beds were deposited and are now represented by chert and stilpnomelane bands. Thriving photosynthesising microbial life promoted the precipitation of siderite in the presence of oxygen, whereas the presence of magnetite may reflect the presence of intermediate oxygen fugacity levels (Beukes, 1983). The Riries Member overlies the chert-rich Groenwater Member and consists predominantly of siderite-greenalite rhythmite. Pickard (2003) dated a tuff bed within the Kuruman Iron Formation and a SHRIMP U-Pb age of 2460 ± 5 Ma was obtained.

The Griquatown Iron Formation conformably overlies the Kuruman Iron Formation and was deposited in a storm-dominated, shallow-water continental sea (Beukes, 1984). This Formation has been subdivided into three units, namely the Middlewater, Danielskuil and Pietersberg Members (Figure 2.3). Both the Middlewater and Pietersberg Members were deposited in the basinal facies whereas the Danielskuil Member was deposited in a sub-tidal platform environment (Beukes, 1983). The Danielskuil Member was deposited in a low energy environment below the normal wave base and consists of orthochemical-allochemical iron formation cycles. This member is interfingered with the Middlewater Member which was deposited in a shallow basin below the wave base and consists of riebeckite minnesotaite-greenalite lutites (Beukes, 1983). The Pietersberg Member consists of banded greenalite lutites deposited in a fresh water lake environment and marks the end of the Griquatown Iron Formation. This member overlies both the Danielskuil and Middlewater Members. A SHRIMP U-Pb age for tuff beds in the Griquatown Iron Formation dates this formation at 2431 ± 31 Ma (Trendall *et al.*, 1990).

2.1.1.4 Koegas Subgroup

The iron formations of the Koegas Subgroup conformably overlie the Griquatown Iron Formation of the Asbestos Hills Subgroup. The Koegas Subgroup consists of terrigenous clastic sediments and subordinate iron-formations (Beukes, 1983; Eriksson *et al.*, 2006). The Subgroup represents the upper part of the Ghaap Group and is subdivided into five formations, namely the Pannetjie, Doradale, Kwakwas, Naragas, and the Rooinekke Formations (Beukes, 1983; Table 2.1).

The Pannetjie Formation, which forms the lowermost part of the Koegas Subgroup, consists of quartz wackes deposited in a deltaic environment (Beukes, 1983). The Doradale Formation

is a thin banded iron formation, which is remarkably similar to the Kuruman Iron Formation, and progressively grades into the Kwakwas Iron Formation. Notably, the Kwakwas Iron Formation is geochemically similar to the Middelwater Member in the Griquatown Iron Formation. The overlying Naragas Formation consists of 10 to 20m-thick quartz-chlorite mudstone units (Polteau *et al.*, 2006). The Rooinekke Formation forms the uppermost part of the Koegas Subgroup and consists predominantly of BIF's (Polteau *et al.*, 2006). Kirschvink *et al.* (2000) obtained one Pb/Pb age for the Rooinekke Formation of 2415 ± 6 Ma.

In previous studies of the Transvaal Supergroup, the Ghaap and Postmasburg Groups are reported to be separated by a major regional unconformity (Beukes, 1983; Beukes and Smit, 1987). More recently, questions have arisen that challenge the unconformable relationship between the Ghaap and Postmasburg Groups of the Transvaal Supergroup (Moore *et al.*, 2001). Polteau *et al.* (2006) suggest that the change from the Rooinekke Formation to the overlying Makganyene Formation is transitional as diamictite beds are commonly interbedded with the upper parts of the Rooinekke BIF. The Postmasburg Group, which conformably overlies the Ghaap Group, is composed of the Makganyene, Ongeluk, Hotazel and Mooidraai Formations (Moore *et al.*, 2001).

2.1.2 Postmasburg Group

2.1.2.1 Makganyene Formation

The Makganyene Formation forms the basal unit of the Postmasburg Group and consists of glacial diamictites interlayered with shales, sandstones and BIF's (Table 2.1). The clasts contained in the Makganyene Formation consist mainly of chert, sandstone and BIF set in a fine-grained ferruginous matrix (Polteau *et al.*, 2006). These glacial diamictites are commonly intermixed with manganese-bearing carbonate bodies (Polteau *et al.*, 2006).

2.1.2.2 Ongeluk Formation

The Ongeluk Formation conformably overlies the Makganyene Formation and consists of a 900m thick succession of continental flood-type basaltic andesites (Polteau *et al.*, 2006). Presence of widespread pillow lavas indicates a sub-aqueous depositional environment (Cornell *et al.*, 1996). Lavas in the Ongeluk Formation reveal a Pb-Pb whole-rock age placing this extrusive event at 2222 ± 13 Ma (Cornell *et al.*, 1996). Upper parts of the Ongeluk Formation consist of hyaloclastites, volcanic tuffs and hematitic jaspilites interbedded with the BIF of the overlying Hotazel Formation (Polteau *et al.*, 2006).

2.1.2.3 Hotazel Formation

The Hotazel Formation predominantly consists of BIF which may vary from Fe-silicate-rich to Fe-oxide-rich and contains a significant calcareous component (Polteau *et al.*, 2006). The iron formations in the Hotazel Formation are geochemically similar to the iron formations of the Asbestos Hills and Koegas Subgroups (Tsikos and Moore, 1997). The basal part of the Hotazel Formation is composed of BIF and diamictite lenses which conformably overlie the Ongeluk lava (Kirschvink *et al.*, 2000). This basal part of the Hotazel Formation grades into the typical Hotazel Fe-Mn succession. Banding in the Hotazel Formation is defined by millimetre- to centimetre-scale (1mm to 1cm thick) bands of individual minerals (mainly magnetite) or combinations of silicate (chert, greenalite, minnesotaite, stilpnomelane, and riebeckite), carbonate (dolomite, ankerite, siderite and calcite) and oxide-sulphide (magnetite, hematite and pyrite) minerals (Tsikos and Moore, 1997; Polteau *et al.*, 2006). The lower member of the Hotazel Formation plays host to three discrete manganese-rich ore units. These manganese-rich ore units represent the largest land-based manganese deposits in the world (Tsikos and Moore, 1997).

2.1.2.4 Mooidraai Formation

The Mooidraai Formation conformably overlies the Hotazel Formation and represents the uppermost part of the Transvaal Supergroup in the Northern Cape Province. It is composed of microcrystalline banded Fe-bearing limestone, dolomite and subordinate chert (Polteau *et al.*, 2006). Tsikos *et al.* (2001) suggest that the Mooidraai Formation is the end member of the chemical sedimentation period that resulted in the Fe-Mn sequences of the Hotazel Formation. Bau *et al.* (1999) obtained a carbonate Pb-Pb age of 2394 ± 26 Ma from a dolomitized part of the Mooidraai Formation. Interestingly, this is significantly older than the ~ 2.2 Ga Pb-Pb age obtained by Cornell *et al.* (1996) for the underlying basaltic andesites of the Ongeluk Formation.

Subsequent to deposition, the Transvaal Supergroup was mildly deformed, resulting in the formation of the Maremane dome. This was followed by a ~ 200 Ma period of non-deposition and erosion, resulting in the development of a major regional angular unconformity. The red shales of the Olifantshoek Supergroup occur above this major regional angular unconformity.

2.2 The Olifantshoek Supergroup

2.2.1 Mapedi Formation

These red shales represent the ~2.2 Ga Mapedi Formation and form the basal unit of the Olifantshoek Supergroup. The Mapedi Formation is separated from the Postmasburg Group of the Transvaal Supergroup by a regional angular unconformity (Grobelaar *et al.*, 1995; Yamaguchi and Ohmoto, 2006). The Mapedi Formation consists predominantly of red shale units with minor green/white shale units intercalated (Land, 2010). In past studies (Evans *et al.*, 2001; Yamaguchi and Ohmoto, 2006), these red shales have been used to infer the presence of an oxygenated atmosphere, as they would have required an oxidizing environment where hematite (Fe_2O_3) is stable. Yamaguchi and Ohmoto (2006) suggest that the red shales of the Mapedi Formation formed during lateritic weathering and transport in an oxidizing environment ~2.2 Ga, rather than by the oxidation of the pre-existing Fe^{2+} bearing minerals in the shales. Yamaguchi and Ohmoto (2006) suggest the source rock for the shales is the underlying lateritic paleo-weathering profile of the Ongeluk Formation. The authors support this conclusion due to apparent chemical similarities between the Mapedi Formation and the underlying lateritic profiles in the Ongeluk Formation.

A recent study, by Land (2010), on the red shales of the Mapedi Formation has shown anomalous high field strength element (HFSE) concentrations near the basal section of the shales. Furthermore, the author suggests this is evidence for alkaline hydrothermal fluid flow.

2.3 Local Geology

The Kolomela or Sishen South deposit is located on the southern extremity of the Maremane anticline (Figure 2.2). In contrast to the larger ore bodies at Sishen mine, the ore bodies in the southern end and central part of the Maremane anticline (study area) are in the form of numerous, small isolated ore bodies spread over a large area (Carney and Mienie, 2003). Ore at the Sishen mine is much thicker, more extensive and laterally continuous, if compared with ores in the southern and central parts of the Maremane anticline (Carney and Mienie, 2003).

The bulk of the iron ore resource present is high-grade brecciated iron ore belonging to the Asbestos Hills Subgroup, which has slumped into karst structures present in underlying carbonate sequence (von Plehwe-Leisen and Klemm, 1995; Beukes *et al.*, 2003). The study

area is situated in the centre of the Maremane anticline, which is defined by the Campbellrand Subgroup and Asbestos Hills Subgroup dipping gently ($<10^\circ$) to the north, east and south (Figure 2.2; Gutzmer, 1996). In this area the lithologies have a North-South strike and plunge away from the centre of the anticline (Carney and Mienie, 2003).

The carbonates of the Campbellrand Subgroup are separated from the overlying iron ore, of the Asbestos Hills Subgroup, by the Wolhaarkop breccia which was developed on an irregular karst surface (Figure 2.4) (Gutzmer, 1996; Carney and Mienie, 2003). The Wolhaarkop breccia is a “manganiferous” siliceous chert breccia which marks the dissolution surface between the iron-enriched BIF of the Asbestos Hills and the underlying dolomites of the Campbellrand Subgroup (Beukes *et al.*, 2003). The Wolhaarkop breccia appears to have formed during the formation of karstic structures by carbonate dissolution in the Campbellrand Subgroup. It is suggested that the development of karstic structures beneath the Asbestos Hills Subgroup caused the overlying BIF to slump into these large sinkholes and it is at the base of these sinkholes that insoluble residual material has been preserved as the Wolhaarkop breccia (Carney and Mienie, 2003).

These karstic features are restricted to the Maremane anticline and are important feature in preserving the iron ore of the Asbestos Hills Subgroup (Beukes *et al.*, 2003; Carney and Mienie, 2003). It is common to find a highly altered, intrusive sill near the contact between underlying unaltered BIF and the overlying iron ore (Carney and Mienie, 2003). This sill can attain a thickness of up to 30m at Sishen South, whereas at Sishen mine it is usually less than 2m thick (Carney and Mienie, 2003). The iron ores are truncated by an erosional surface above which the sedimentary rocks of the Mapedi Formation have been deposited (Gutzmer, 1996; Yamaguchi and Ohmoto, 2006). These sedimentary rocks of the Mapedi Formation are locally covered by clays, calcrete and eolian sands from the Cenozoic Kalahari Formation (Gutzmer, 1996).

The exact processes involved in the genesis of these iron deposits and the manganiferous chert breccia is still vague. A simplified sketch of the stratigraphy in the study area is shown in Figure 2.4, which illustrates the relationship between the previously discussed stratigraphic units (Refer to Appendix B1, B2 for detailed borehole logs of the drill-cores used in this study).

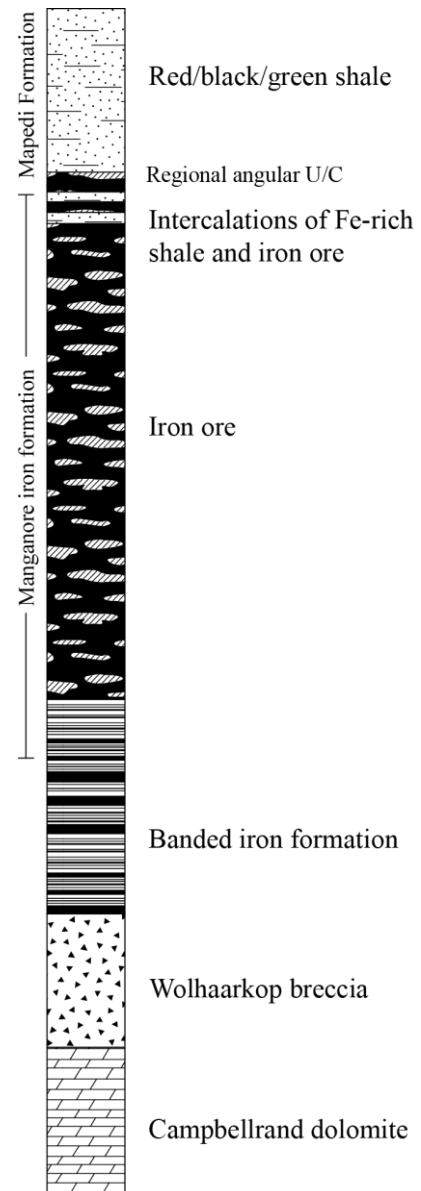


Figure 2.4. Simplified sketch of the typical stratigraphy (not to scale) from the Maremane anticline, Northern Cape Province. The sketch displays the shales of the Mapedi Formation unconformably overlying the iron ore with the underlying BIF. There are intercalations of Fe-rich shale and iron ore at the top of the iron ore unit. At the base of the BIF the Wolhaarkop breccia is found with dolomite occurring below.

2.4 Economic Geology of the Transvaal Supergroup

The rocks of the Transvaal Supergroup in the Griqualand West Basin are of major importance to South Africa's rich mining culture. According to Laznicka (1992), the BIF-hosted manganese deposits in the Kalahari Manganese Field accounts for approximately 50% of the world's total manganese reserves. Additionally, there are deposits of crocidolite (asbestos) hosted within the iron formations in the Transvaal Supergroup. The crocidolite deposits occur within the Kuruman Iron Formation which contained several economic crocidolite zones with thicknesses of several metres (Dreyer and Söngé, 1992; Gibbons, 1998). Within the BIFs

crocidolite has developed in riebeckite-rich mesobands in the presence of magnetite (Horstmann and Hälbig, 1995). The dolomites of the Campbellrand Formation contain economic MVT-type Pb-Zn mineralisation (e.g. Pering) which contained 18 Mt of ore with grades of 3.6% Zn and 0.6% Pb (Martini *et al.*, 1995; Kesler *et al.*, 2007). Additionally, the Campbellrand Subgroup is mined for primary limestone and dolomite which is consumed mainly by the cement industry (Altermann and Wotherspoon, 1995). The Campbellrand Subgroup also plays host to karst fill-type manganese ore deposits which are mined at Glosam, Beeshoek and Lohathla (von Plehwe-Leisen and Klemm, 1995; Beukes *et al.*, 2003). Lastly, the world-class high-grade iron ore deposits (e.g. Sishen, Beeshoek and Kolomela) hosted within the BIFs of the Asbestos Hills Formation, contribute significantly to the production of iron ore in South Africa and the global economy.

3. MINERALOGY AND PETROGRAPHY

3.1 Introduction

Sample analysis by optical microscopy is a convenient tool for obtaining information about the characteristics of rocks. It enables the identification of different minerals, mineral abundances, mineral associations, grain size, size distribution, porosity and mineral shapes. Information about different textures, specifically within ore-grade rocks, is vital for predicting downstream processing performance and final product characteristics (Donskoi *et al.*, 2007). The textures of ores can often be quite complex, however in the past they formed the basis for the interpretation of the genesis of iron ores, whether it be hydrothermal or supergene (Clout, 2003). Particularly in recent years, several authors have been involved in the studies of the mineral assemblages observed in BIF-hosted iron ore deposits from Hamersley, Australia (Dalstra and Guedes, 2004; Thorne *et al.*, 2004; Thorne *et al.*, 2008), Minas Gerais, Brazil (Dalstra and Guedes, 2004; Figueiredo *et al.*, 2008; Lobato *et al.*, 2008) and the Transvaal Supergroup, South Africa (Carney and Mienie, 2003; Gutzmer *et al.*, 2005; de Kock *et al.*, 2008; Gutzmer *et al.*, 2008).

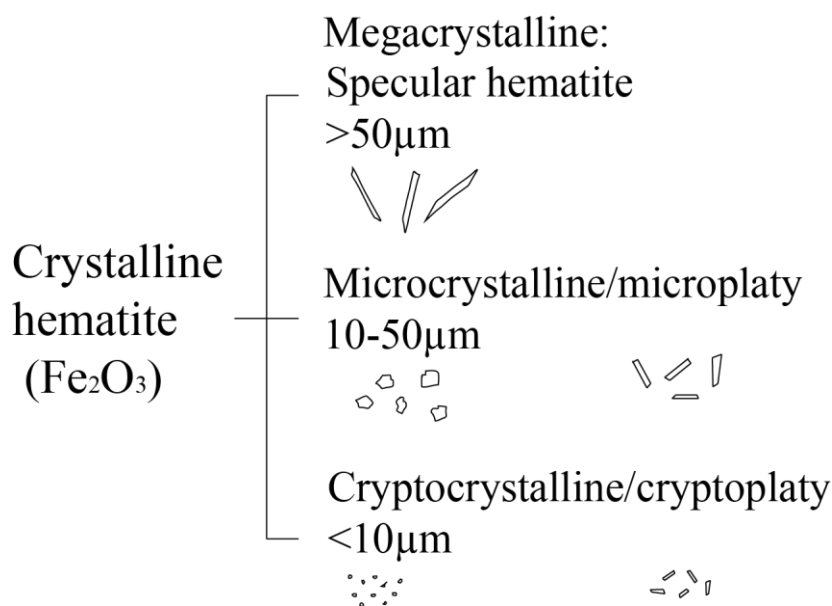


Figure 3.1. Hematite occurs in a variety of forms as illustrated. Crystalline hematite can be further subdivided into specular hematite (>50 μm), microcrystalline/microplaty hematite (10-50 μm) and cryptocrystalline/cryptoplaty (<10 μm) (Beukes *et al.*, 2008).

The predominantly monomineralic nature of the iron ores makes drawing petrographical interpretations difficult. However, the identification of different forms of hematite, ore textures and associated mineralogy can be used to further clarify processes responsible for ore formation (Beukes *et al.*, 2008; Mukhopadhyay *et al.*, 2008). There are 3 textural types of hematite present, as described by Beukes *et al.* (2008), namely crypto-, micro-, and megacrystalline hematite (Figure 3.1). Cyptocrystalline hematite can occur as anhedral/subhedral grains (<10µm) as well as in the form of euhedral platy crystals (cryptoplaty hematite, <10µm). Microcrystalline hematite (10-50µm) includes microplaty hematite, which is comparable to cryptoplaty hematite but slightly coarser (10-50µm). Megacrystalline hematite (>50µm) is represented only by euhedral, thin, platy specular hematite.

3.2 Macroscopic observations and methodologies

The following section describes the two selected borehole intersections as well as macroscopic properties of the samples used in this study. The exact locality* of the boreholes cannot be disclosed in this study due to confidentiality reasons, however the approximate location is shown in Figure 2.2. The two boreholes were recovered by Kumba near the centre of the Maremane anticline, in the Northern Cape Province of South Africa. A total of 81 samples were collected from the two boreholes (SLT032B and SLT033). The thicknesses of the rock units and the stratigraphic location of the samples collected for each borehole are illustrated in Figure 3.2.

The basal depth of borehole SLT032B is at 201.17m from surface, logging and sampling took place from a depth of 145m to 201.17m. A total number of 45 samples were collected from this borehole and are labelled 32-n (n = 1 – 45). The SLT032B intersection consists of a section of Mapedi Formation (shale, quartzite) which overlies a 30m thick intersection of iron ore (Figure 3.2). The contact between the Mapedi shale and the underlying iron ore is generally sharp. The iron ore interval can be broadly subdivided into two sections based on macroscopic properties. The upper part of the ore unit is comprised of ferruginised clasts set in a fine-grained ferruginous silicate matrix, whereas the lower part appears to be brecciated/laminated monomineralic hematite. The iron ore gradually changes to a siliceous BIF from around 182m in depth. Additionally, the borehole has an 80cm thick gabbro unit near the base of the borehole. Although this unit was sampled it was not the focus of this study and no mineralogical or geochemical analysis was completed on it. Throughout the iron

*The exact locality of the boreholes cannot be disclosed due to a confidentiality agreement between Rhodes University and Kumba Iron ore. These boreholes are part of an on-going exploration programme with the view to increase the iron ore reserves held by the company.

ore intersection there is the occurrence of apparent silicate-rich bands, which are more abundant in the upper part of the ore intersection than in the lower part.

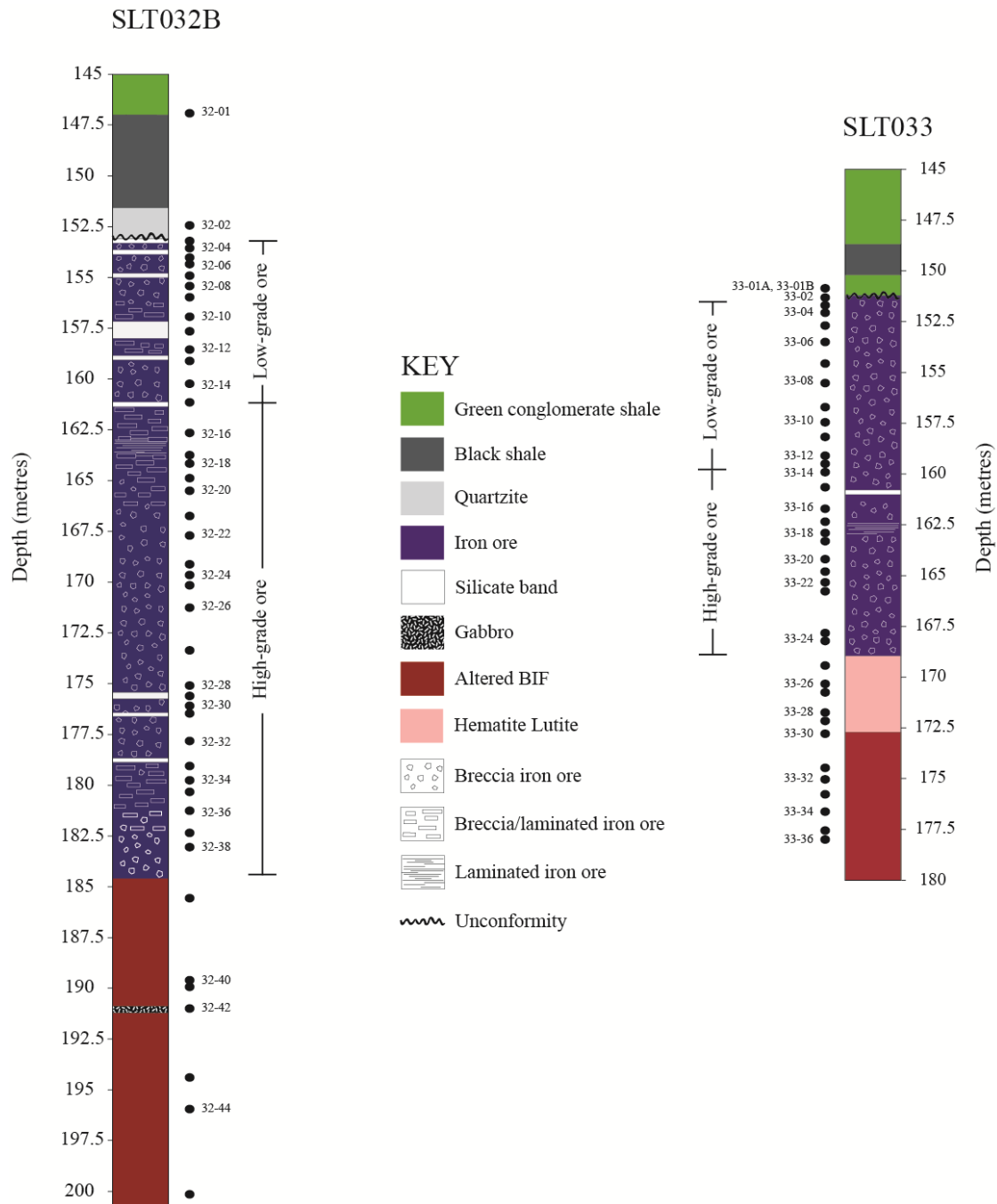


Figure 3.2. Lithostratigraphic columns for the logged boreholes SLT032B and SLT033. The various rock types and thickness variations between the two logged boreholes are illustrated. The hematite lutite unit occurs exclusively in borehole SLT033, whilst the gabbro unit occurs only near the base of borehole SLT032B. The approximate stratigraphic locations of samples taken from both logged boreholes are shown (Note: only every second sample has been labelled).

The depth of borehole SLT033 is 179.20m, with sampling and logging taking place from a depth of 145m to 179.20m. A total number of 36 samples were collected from borehole SLT033 and are labelled 32-n ($n = 1 - 36$). The intersection is comprised of a section of Mapedi shale overlying an 18m thick intersection of iron ore; the ore unit in this borehole is smaller in thickness when compared with borehole SLT032B (Figure 3.2). However, as in borehole SLT032B, the upper part of the iron ore unit differs from that in the lower part. The upper part consists of ferruginised clasts set in a fine-grained ferruginous silicate matrix, whereas the lower part is more monomineralic in nature. There are silicate-rich bands present in the borehole, albeit to a much lesser extent when compared to borehole SLT032B. At the base of the iron ore unit, there is a 3m thick hematite lutite unit (168.90 – 173.16m), of which the contacts with the overlying iron ore and underlying siliceous BIF are both sharp. Siliceous BIF occurs from 173.16m to the base of the borehole.

Petrographic observations of the iron ores and Mapedi shales were conducted using transmitted light microscopy and reflected light microscopy. Thin sections were cut from most of the samples used in the whole-rock geochemical analysis presented in Chapter 4 (See also Appendix B). In cases where the samples were very fine-grained, rendering mineral identification difficult, a JEOL electron probe micro analyser (EPMA) was used in order to accurately identify the phases. In addition to this, selected powder samples were analysed using x-ray diffraction analysis (XRD) to determine the major mineral constituents present. Samples that were found to be of ore-grade were set in polished briquettes, whereas partially hematitised samples and silicate-dominated samples were prepared as polished thin sections. More detailed descriptions of the analytical techniques applied are available in Appendix A, with detailed lithostratigraphic borehole logs, sample locations and numbers are also available in Appendix B.

For the purpose of mineralogical investigations, the samples collected from the two boreholes were initially grouped according to certain macroscopic properties. The samples were grouped based on properties such as hematite content (colour, density), texture (brecciated/laminated) and hematite/gangue mineral content (Refer to Appendix B; Figure B1 for representative photographs of the sample groups). These macroscopic observations allowed for the basic subdivision of samples into the following groups (Table 3.1):

- Mapedi shales and Fe-rich shales, essentially ferruginous aluminous shale containing detrital fragments of hematite. These shales unconformably overlie the

iron ore in the study area, and are locally found intercalated with the underlying low-grade iron ore in places;

- low-grade iron ore, comprising ferruginised fragments, that show apparent textural similarities to BIF, set in a fine-grained Fe-rich silicate matrix;
- high-grade iron ore, characterised by a shiny blue-grey monomineralic hematite ore with small amounts of gangue matrix. Additionally there are two textural end-members that can be identified in the high-grade iron ore samples, namely brecciated and laminated type ores;
- hematite lutite, occurring at the base of the iron ore in borehole SLT033 and characterised by a dusty red appearance. The hematite lutite samples appear to resemble iron ore, however, are significantly less dense and are thus more siliceous than iron ore samples. Additionally, hematite lutite appears to be mineralogically homogenous on a macro-scale;
- siliceous banded iron formation, containing large amounts of chert (cherty iron-formation) and lesser hematite. Macroscopically, the samples appear similar to traditional iron formations, yet more silica-rich. There is also abundant secondary hematite occurring in veins and fractures within these samples;
- gabbro, occurring at the base of borehole SLT032B (Figure 3.2) and approximately 80cm in thickness. This unit was sampled but not analysed.

Table 3.1. A summary table of characteristics for the different macroscopic sample groups. The samples were grouped based on colour, hematite content, silicate content and textural differences.

GROUP	COLOUR	HEMATITE CONTENT	SILICATE CONTENT	TEXTURAL DESCRIPTION
Mapedi shales and Fe-rich shales	light red	low	high	fine-grained, ferruginous aluminous shale with detrital fragments of hematite
Low-grade iron ore	dark red	moderate	moderate	ferruginised fragments in fine-grained Fe-rich silicate matrix
High-grade iron ore	shiny blue-grey	high	very low	monomineralic hematite, brecciated/laminated
Hematite lutite	dusty red	low	high	fine-grained, mineralogically homogenous
Siliceous BIF	white with veins of a dark red mineral	very low	high	BIF-like texture, mostly chert with hematite veining

The main petrographic characteristics of the above groups are discussed separately in the following sections.

3.3 Mineralogy and Petrography

3.3.1 Low-grade iron ore

The low-grade iron ore samples consist of ferruginised clasts (hematite; Fe_2O_3) (0.5mm-2mm) set in a very fine-grained matrix of quartz (SiO_2), sericite ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) and clinochlore ($(\text{Mg, Fe, Al})_3(\text{Si, Al})_2\text{O}_5(\text{OH})_4$) (Figure 3.3A, 3.4A). These lower grade samples are easily distinguishable in hand-specimen due to the large proportions of silicate matrix present relative to ferruginised BIF clasts.

The ferruginised clasts are randomly distributed within the samples and show apparent textural similarities to BIF. The clasts are mostly sub-angular to sub-rounded with clinochlore filled fractures (Figure 3.3A). Clasts are generally well-banded, with bands ranging from 0.25 - 1mm in thickness. This banding is rhythmic and consists of dull, porous hematite bands alternating with brighter hematite bands. The contacts between these bands are mostly sharp and laterally continuous within clasts. There is evidence of “crackle”-type breccia textures in these clasts, and the displacement along these fracture planes is mostly minimal (Figure 3.3A). There are also samples that show some degree of reworking of the ferruginised clasts before they are welded with the accompanying silicate matrix. These reworked clasts tend to be more sub-rounded in shape. As the underlying high-grade iron ore is approached, the ferruginised BIF clasts become progressively larger in size.

The matrix is comprised of a relatively homogenous combination of very-fine grained silicate phases (sericite, quartz and clinochlore) as well as disseminated fine-grained hematite. XRD studies have confirmed the presence of these silicate phases accompanying the hematite clasts (Figure 3.4). Further examination using the JEOL EPMA, confirms the presence of a magnesium-aluminium-silicate and quartz, as well as occasional zircon grains in the silicate matrix (Figure 3.4). Throughout the low-grade iron ore samples, there are both vertical and horizontally orientated clinochlore veins present (Figure 3.3B). In some samples, there are aggregates of clinochlore surrounded by a very fine-grained matrix of quartz and sericite (Figure 3.3C). As the underlying high-grade iron ore is approached, the relative abundance of silicate material present decreases as the matrix becomes increasingly iron-rich (Figure 3.3F).

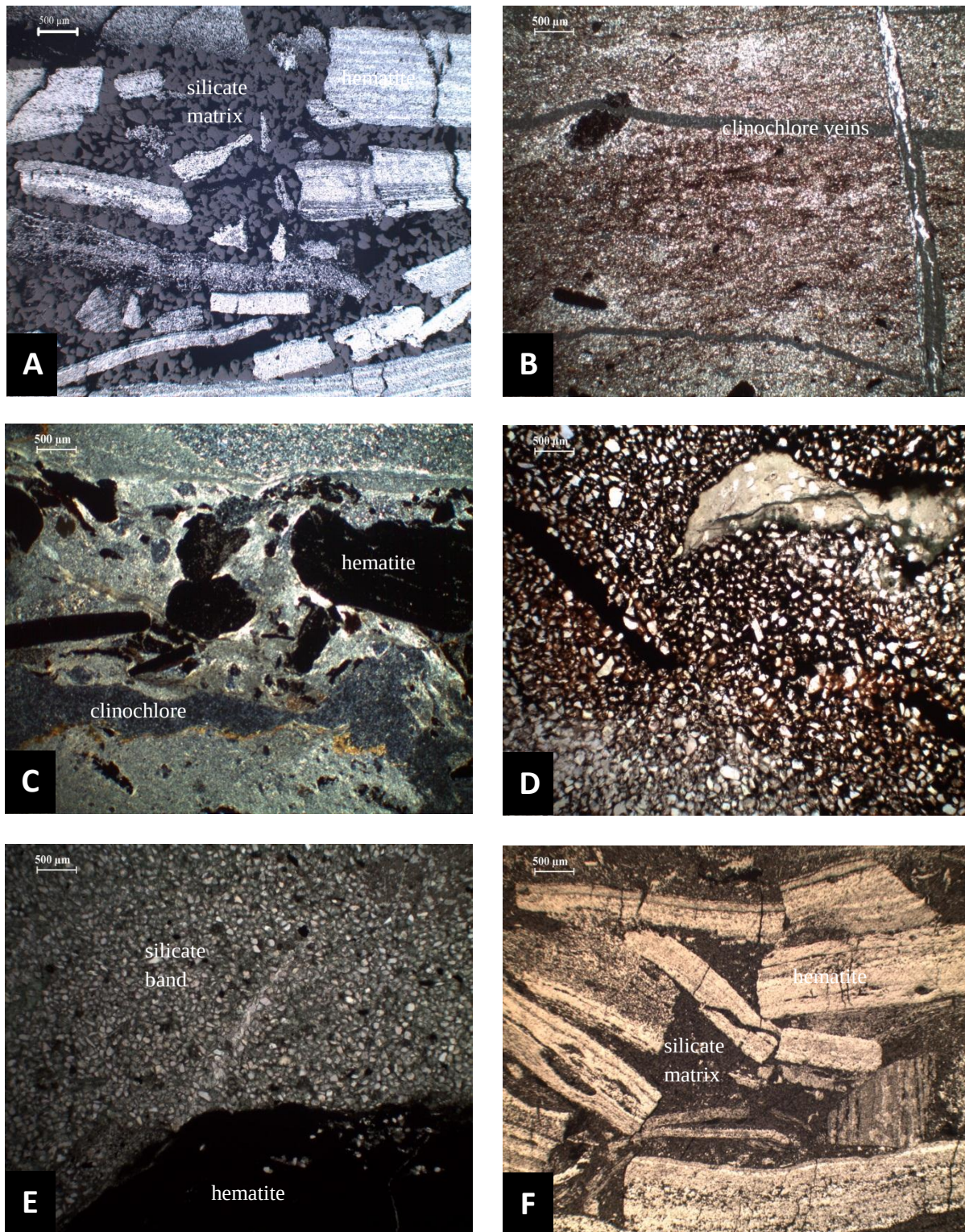


Figure 3.3. Photomicrographs of low-grade iron ore (All photomicrographs were taken under transmitted light, unless otherwise stated). **A.** Laminated hematite clasts (white) in a predominantly quartz matrix (grey) (Reflected light – PPL). **B.** Hematite clasts (opaque) in a very fine-grained matrix of sericite, clinocllore, quartz and hematite. Horizontal and vertical veins of clinocllore (CPL). **C.** Hematite clasts (opaque) in a very fine-grained quartz, sericite and clinocllore matrix. Aggregates of clinocllore (blue) are present in matrix (CPL). **D.** Very fine-grained hematite with apparent cross-cutting relationship in a quartz matrix (PPL). **E.** Silicate band consisting of fine-grained quartz, sericite and clinocllore (PPL). **F.** Brecciated laminated hematite clasts in a typical very fine-grained hematite, sericite and clinocllore matrix (Reflected light – PPL).

It is interesting to note that there are samples that show distinct zones of very fine-grained hematite in the silicate matrix. These zones of hematite seem to crosscut primary bedding planes with the hematite zones often being accompanied by large aggregates of clinochlore (Figure 3.3D). This crosscutting nature of hematite-rich zones is also noted in the overlying Mapedi shales, as will be demonstrated later in this chapter (Land, 2010).

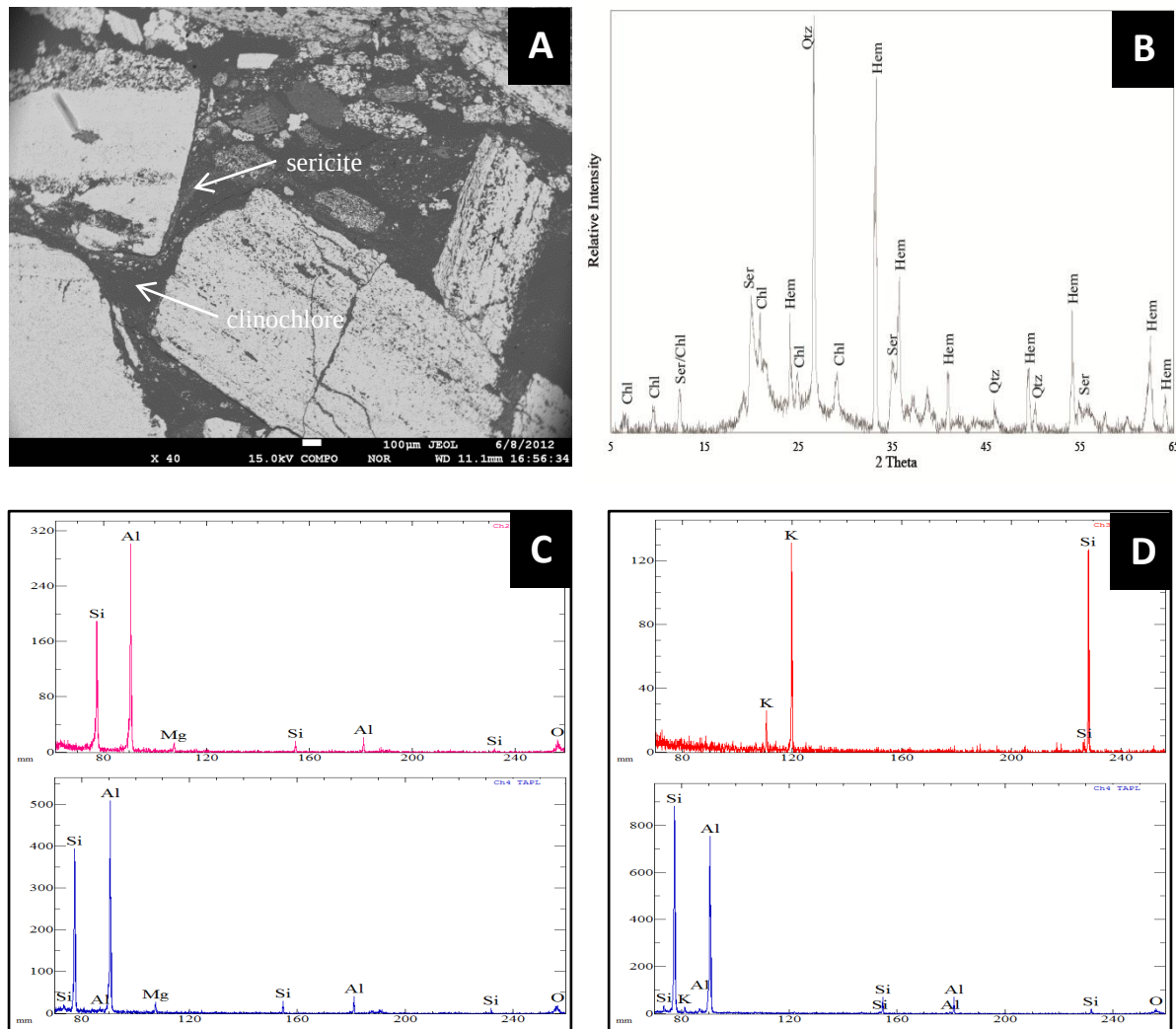


Figure 3.4. Back scatter electron image, XRD and WDS analysis of the low-grade iron ore. **A.** Back scatter electron image showing a representative image of the low-grade iron ore. The image shows brecciated ferruginised clasts set in a very fine-grained matrix of clinochlore and sericite. **B.** XRD spectra for a low-grade iron ore sample. Minerals present are clinochlore (Chl), sericite (Ser), quartz (Qtz) and hematite (Hem). **C.** WDS spectra (Ch2 TAP and Ch4 TAPL) of the dark grey phase (clinocllore) in Figure 3.4A. The semi-quantitative analysis shows the mineral consists of Al, Si and Mg and is most likely the clinocllore mineral identified in the XRD spectra. **D.** WDS spectra (Ch3 PETL and Ch4 TAPL) of the lighter grey phase (sericite) in Figure 3.4A. The analysis shows that the mineral contains K, Si, and Al. This mineral is likely to be the sericite identified in the XRD spectra.

Within the low-grade iron ore there are occasional silicate “bands”. These bands appear to have no definitive relationship with any other features present in the ore body. The silicate bands range in thickness from 1 to 1.5cm and are internally homogenous, both mineralogically and texturally. The bands are dominated by quartz, fine-grained clinochlore and minor amounts of sericite (Figure 3.3E) and have sharp wavy contacts with adjacent iron-rich domains. EPMA studies conducted on these silicate bands have confirmed the presence of quartz, clinochlore and sericite (Figure 3.5). Silicate bands are also found in the high-grade iron ore, in a similar fashion with the bands found in the low-grade portion of the ore but less abundant.

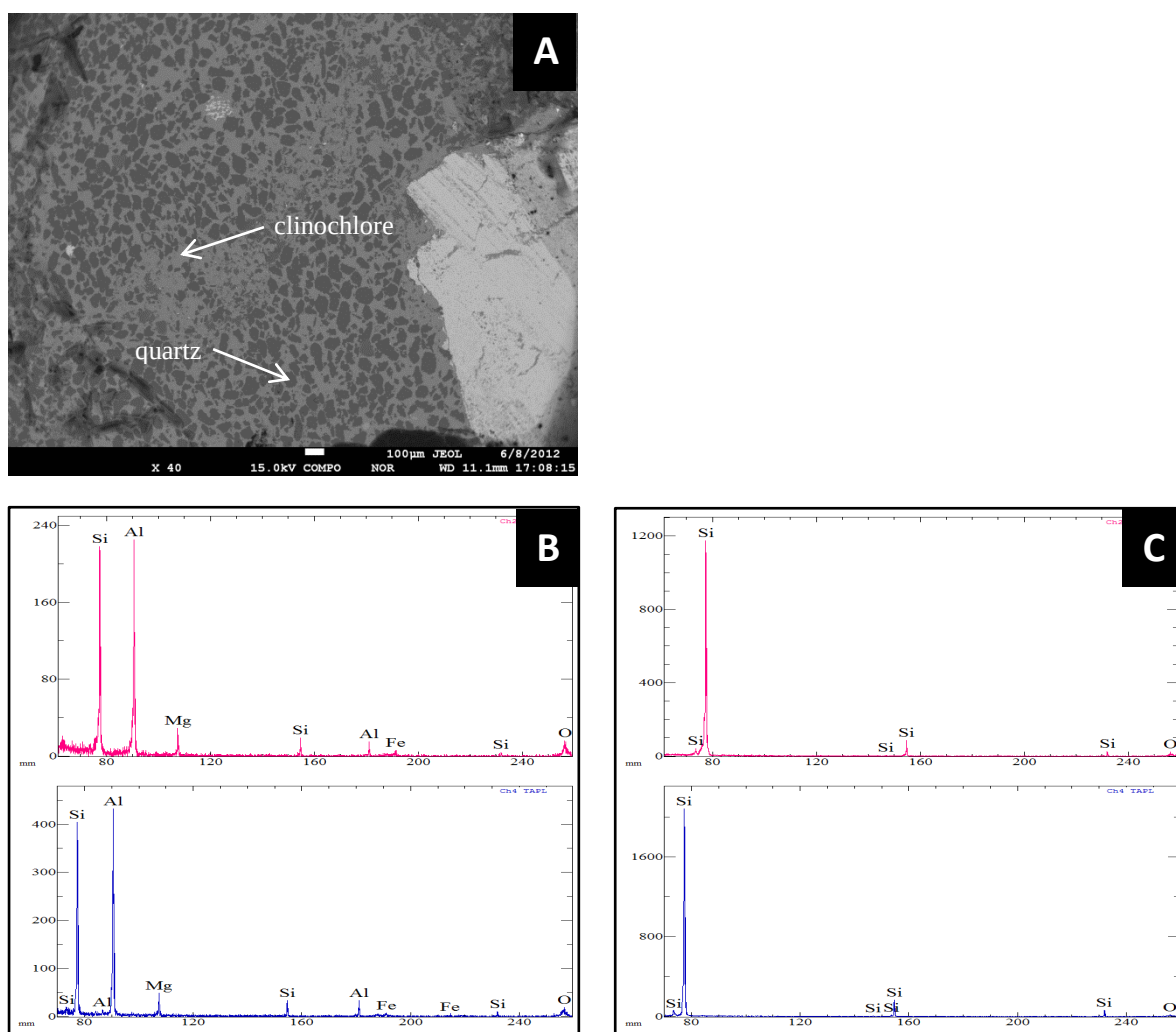


Figure 3.5. Back scatter electron image and WDS analysis of a silicate band. **A.** Back scatter electron image showing a representative image of a silicate band present in the iron ore. The image shows sub-angular quartz grains set in a very fine-grained matrix of clinocllore. **B.** WDS spectra (Ch2 TAP and Ch4 TAPL) of the lighter grey matrix phase (clinocllore) in Figure 3.5A. The semi-quantitative analysis shows the mineral consists of Al, Si and Mg and is most likely clinocllore. **C.** WDS spectra (Ch2 TAP and Ch4 TAPL) of the darker grey phase (quartz) in Figure 3.5A. The analysis shows that the mineral contains only Si and is likely to be quartz.

3.3.2 High-grade iron ore

Within the high-grade iron ore intersection, and on a core-scale of observation, there are two dominant types of ore textures, namely laminated iron ore and brecciated iron ore. Throughout both boreholes, the brecciated iron ore is far more abundant than laminated iron ore. The brecciated and laminated ore samples are essentially two textural end-members, with many samples falling within an intermediate continuum of textures. Some samples exhibit a very incipient breccia texture where the laminated ore is fragmented but the clasts experience little to no displacement/rotation and thus maintain a broadly laminated appearance.

The high-grade iron ore samples predominantly consist of various types of hematite clasts/laminae with discrete occurrences of vein hosted fine-grained clinochlore, quartz and minor sericite. The abundance of silicate minerals in the high-grade iron ore is significantly less than in the previously described low-grade iron ore samples.

3.3.2.1 Laminated iron ore

Laminated ore consists of dull, porous hematite mm-scale bands alternating with bright hematite-rich ones (Figure 3.6A, 3.6B). These bands are often internally microbanded. The thicknesses of the mesobands are on average 1-2mm, whereas the microbands thickness ranges from 0.25-0.5mm. The contacts between the bands are sharp and wavy, though they can be more diffuse in some samples.

The bright hematite-rich bands are typically composed of subhedral, microcrystalline hematite and microplaty hematite, whereas the dull porous bands contain cryptoplaty to microplaty hematite. Additionally, there is the presence of a secondary hematitic phase represented by coarser specular hematite. Specular hematite occurs in fractures, veins and secondary pores within the ore body (Figure 3.6B). Specular hematite is more coarse-grained and acicular when compared with microcrystalline hematite. The specular hematite present in the veins is accompanied by clinochlore in the centre of these veins. These veins occur both perpendicular and parallel to the banding (Figure 3.6B). Microscopic and XRD studies confirm quartz and clinochlore are present in the laminated iron ore samples, however the sericite which is present in the lower grade iron ore samples appears to be virtually absent here. These gangue minerals accompany the veins, mentioned above, as well as occur in pore

spaces within the laminated ore. In terms of grain size shape, these gangue phases are very fine-grained and usually subhedral to anhedral.

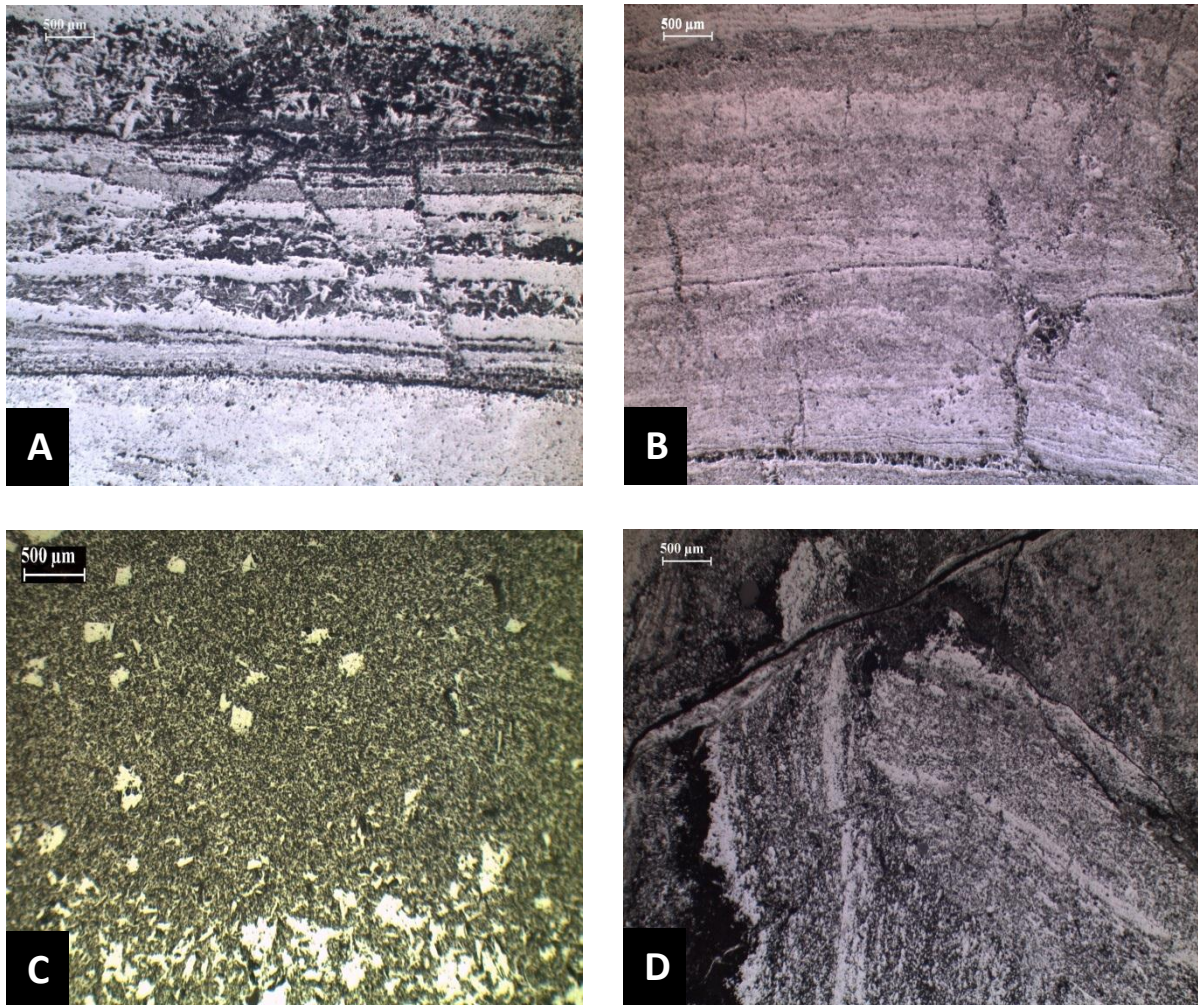


Figure 3.6. Photomicrographs of high-grade laminated iron ore (All photomicrographs were taken under reflected light). **A.** Typical laminated ore sample where the bright dense hematite-rich and dull porous hematite bands are shown. The difference in porosity between the bands is clearly evident. **B.** Laminated ore sample where the difference in porosity is not as clearly visible. The fracture through this sample is filled with specular hematite and gangue minerals, most likely clinocllore. **C.** Rhombohedral textures, preserved in dull porous hematite band, resembling iron carbonates from a typical banded iron formation. **D.** Kink structure in a laminated ore sample, where the hematite bands are fractured along the axial plane of the fold. There has been some micro-faulting of the kink structure.

The dull porous hematite bands sometimes contain apparent rhombohedral textures (Figure 3.6C). Rhombohedral-shaped hematite grains resemble textures usually associated with iron carbonate minerals (Klein, 1983). From the petrographic evidence gathered, it is difficult to determine exactly what iron carbonate mineral is pseudomorphed, but it is speculated to be siderite or ankerite, the most common carbonates in the Kuruman BIF (Beukes, 1983). This

attests to the likely origin of the clasts from BIF of the Asbestos Hills sequence in the Transvaal Supergroup. There are kink structures present in some of the laminated ore samples (Figure 3.6D), where the dull porous hematite bands appear to behave differently to the more competent bright hematite bands.

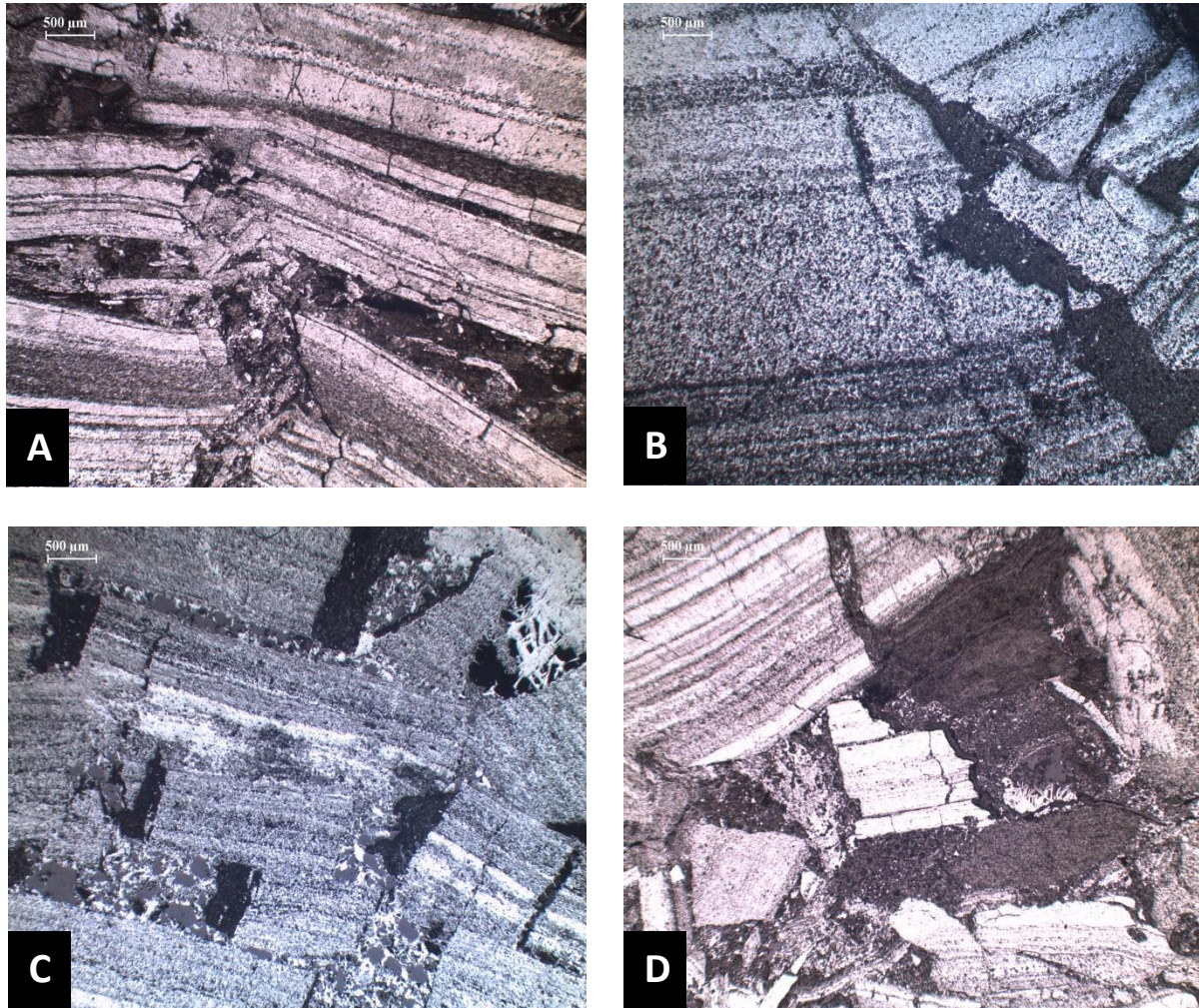


Figure 3.7. Photomicrographs of high-grade brecciated iron ore (All photomicrographs were taken under reflected light). **A.** Laminated hematite clasts with alternating porous and dense hematite bands. Sample shows some brecciation but still preserves the typical laminated ore textures. **B.** Laminated hematite clasts showing the typical banding with crackle brecciation. The pore space is taken up by disseminated hematite and gangue phases. **C.** Sub-angular brecciated laminated hematite clasts with specular hematite and gangue minerals in pore space. This sample shows a significant degree of brecciation. **D.** Sub-angular brecciated laminated hematite clasts with minor specular hematite and gangue phases between clasts. This sample shows a higher degree of brecciation with clasts of hematite sometimes being completely rotated.

3.3.2.2 Brecciated iron ore

Brecciated ore consists of poorly sorted sub-angular to angular clasts of banded laminated hematite ore within a ferruginous matrix (Figure 3.7A, 3.7B). These brecciated clasts have essentially the same composition and textures as the previously described laminated ores. Incipient (crackle) breccia textures are most common in the brecciated iron ores, whilst specular hematite is common in the porous breccia matrix (Figure 3.7C).

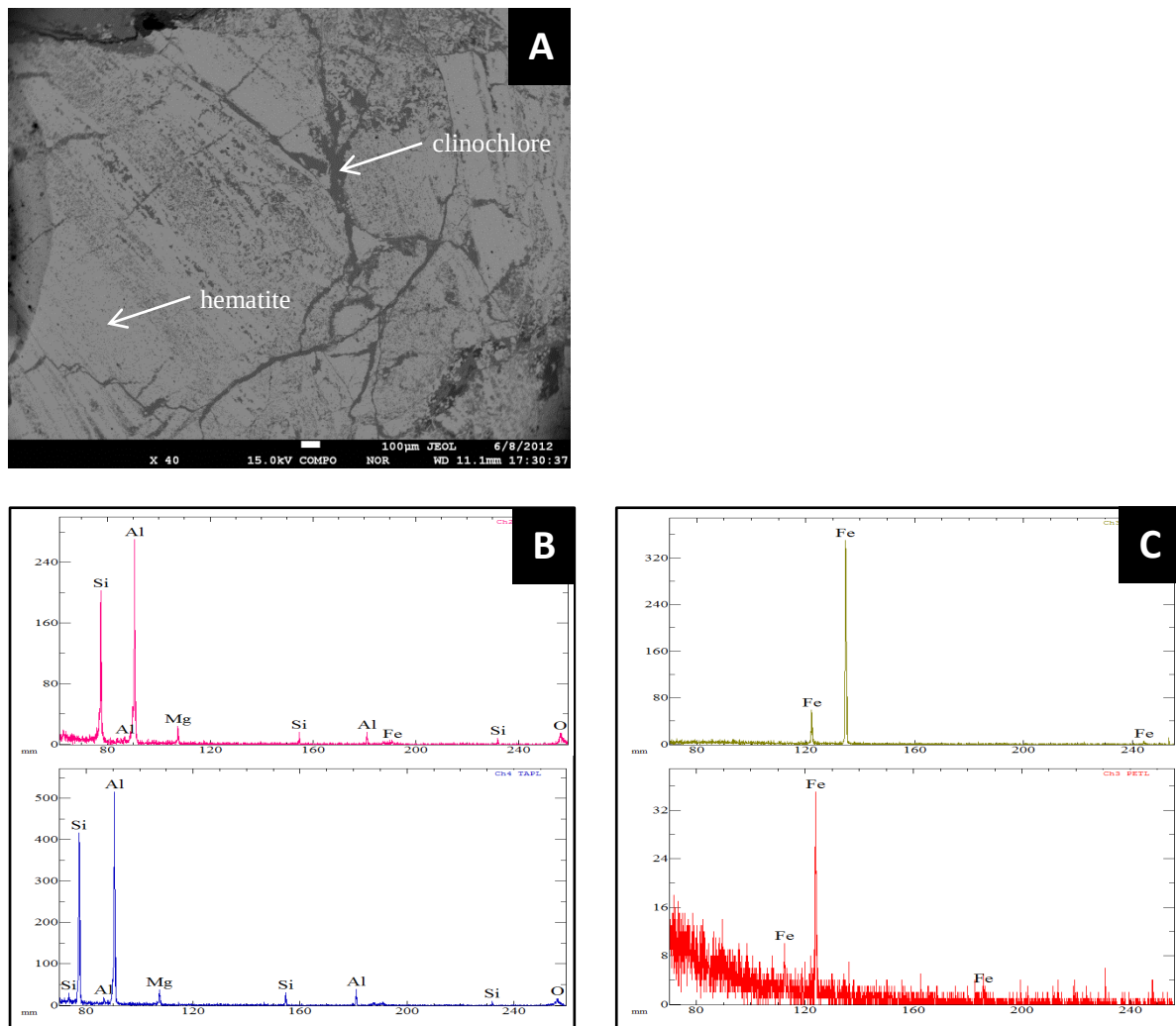


Figure 3.8. Back scatter electron image and WDS analysis of a high-grade iron ore sample. **A.** Back scatter electron image illustrating the characteristic high-grade iron ore texture. The microbanded nature of the hematite ore clasts is clearly evident with the characteristic silicate-filled fracture system. **B.** WDS spectra (Ch2 TAP and Ch4 TAPL) of the darker grey phase (clinocllore) in the fractures in Figure 3.8A. The semi-quantitative analysis shows that the mineral consists of Al, Si and Mg and is most likely clinocllore. **C.** WDS spectra (Ch3 LIFL and Ch3 PETL) of the microbanded light grey phase (hematite) in Figure 3.8A. The analysis confirms that the mineral is hematite, reading only Fe in the semi-quantitative analysis.

Pore space is often filled by specular hematite as well as minor quartz and clinochlore. Studies conducted on the high-grade brecciated iron ores using the EPMA have further confirmed the presence of vein-hosted clinochlore (Figure 3.8). Sericite appears to be absent from the silicate assemblage in the brecciated iron-ore samples. The matrix silicate minerals are very fine-grained, subhedral and appear to be more abundant in the brecciated ore samples than in laminated ones. Clasts are often fractured and these fractures are filled with gangue phases, microcrystalline hematite and specular hematite from the centre outward (Figure 3.7D, 3.8).

3.3.3 Hematite Lutite

The hematite lutite samples consist of very fine-grained hematite, quartz and sericite. The samples are characterised by hematite-rich domains that exhibit a direct relationship with fractures in the samples (Figure 3.9A). These hematite-rich domains are characterised by cryptocrystalline and microcrystalline hematite accompanied by minor quartz and sericite. Within the hematite lutite samples, there is some evidence of relict banding (Figure 3.9B). The banding in these samples is in the form of hematite-rich bands alternating with quartz-hematite-sericite bands. The contacts between these bands are mostly sharp, and there are veins that cut through the hematite lutite section at random orientations. These veins appear to be solely comprised of hematite, but further investigation reveals they consist of cryptoplaty hematite, very fine-grained quartz and sericite. This hematite lutite unit occurs exclusively in borehole SLT033 and has relatively sharp contacts with the overlying iron ore and underlying siliceous BIF.

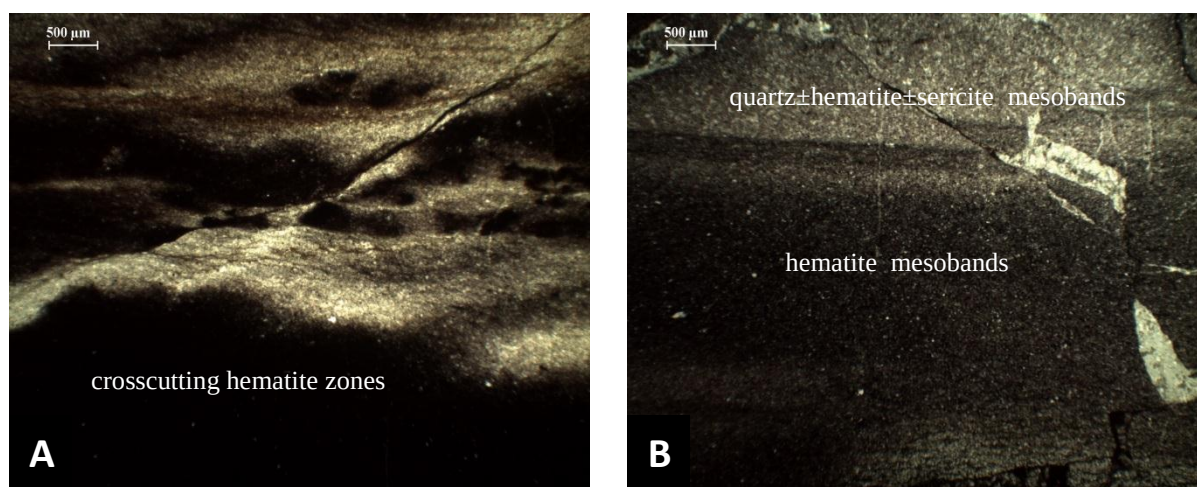


Figure 3.9. Photomicrographs of hematite lutite samples (All photomicrographs were taken under transmitted light, plane polarised light). **A.** Hematite-rich domains in a very fine-grained quartz and sericite matrix. Fractures predominantly filled with hematite are evident. Hematite-rich domains have diffusive contacts with the surrounding matrix. **B.** Hematite-rich bands alternating with quartz-hematite-sericite bands.

3.3.4 Siliceous Banded Iron Formation (BIF)

The contact between the siliceous BIF and the overlying high-grade iron ore is gradational. The overlying iron ore becomes increasingly cherty with a progressive decrease in hematite content as the underlying contact with the siliceous BIF is approached. Siliceous BIF samples are mineralogically dominated by microcrystalline quartz (chert) and hematite with minor amounts of clinochlore. Texturally, there are two different types of siliceous BIF present, namely cherty BIF and brecciated cherty BIF.

The cherty BIF samples are characterised by alternating chert-rich and hematite-rich mm-scale bands (Figure 3.10A). In some samples, these bands can be internally microbanded. The thickness of the bands ranges from 0.75mm to 1mm whereas the microbands within them are between 100µm to 200µm thick.

The chert-rich bands consist of subhedral to euhedral microcrystalline quartz accompanied by very fine-grained disseminated hematite (Figure 3.10A). These chert-rich bands may contain microbands of microplaty or microcrystalline hematite. Hematite-rich bands are comprised of microcrystalline hematite and disseminated chert. The contacts between the mm-scale bands and internal microbands are usually sharp, undulating and laterally continuous, however they can be diffusive in some samples. Throughout these samples there are fractures which are filled with microplaty hematite and lesser coarser specular hematite. In addition, there are quartz veins which crosscut primary bedding structures, with the quartz being fine-grained to very fine-grained (Figure 3.10D).

Brecciated cherty BIF samples are comprised of angular to sub-angular chert (microcrystalline quartz) clasts which are set in a matrix of fine-grained hematite (Figure 3.10B, 3.10C). The samples are clast-dominated, with chert clasts ranging in size from 0.25mm to 4mm. These chert clasts are often fractured with hematite filling these fractures (Figure 3.10B). The hematite in the matrix, as well as in the fractures, is comprised of crypto-platy hematite and lesser amounts of specular hematite. There are minor aggregates of very fine-grained clinochlore, although this is not a common occurrence (Figure 3.10C). Some of the chert clasts exhibit relict banding typical of BIF, but with little to no hematite present. There is a substantial degree of quartz veining that cuts through the chert clasts in random orientations; notably the veins do not cut through the ferruginous matrix. The quartz within

these veins is fine-grained to very fine-grained and similar to the quartz veining in cherty BIF.

Commonly within the chert clasts, there are hematite pseudomorphs after original iron-bearing carbonates which attest to the fact that the original rock was likely a BIF (Figure 3.10D). These rhombohedral hematite grains vary in size from 100µm to 250µm and exhibit the same shape of iron carbonates from the Kuruman Iron Formation (Klein and Beukes, 1989).

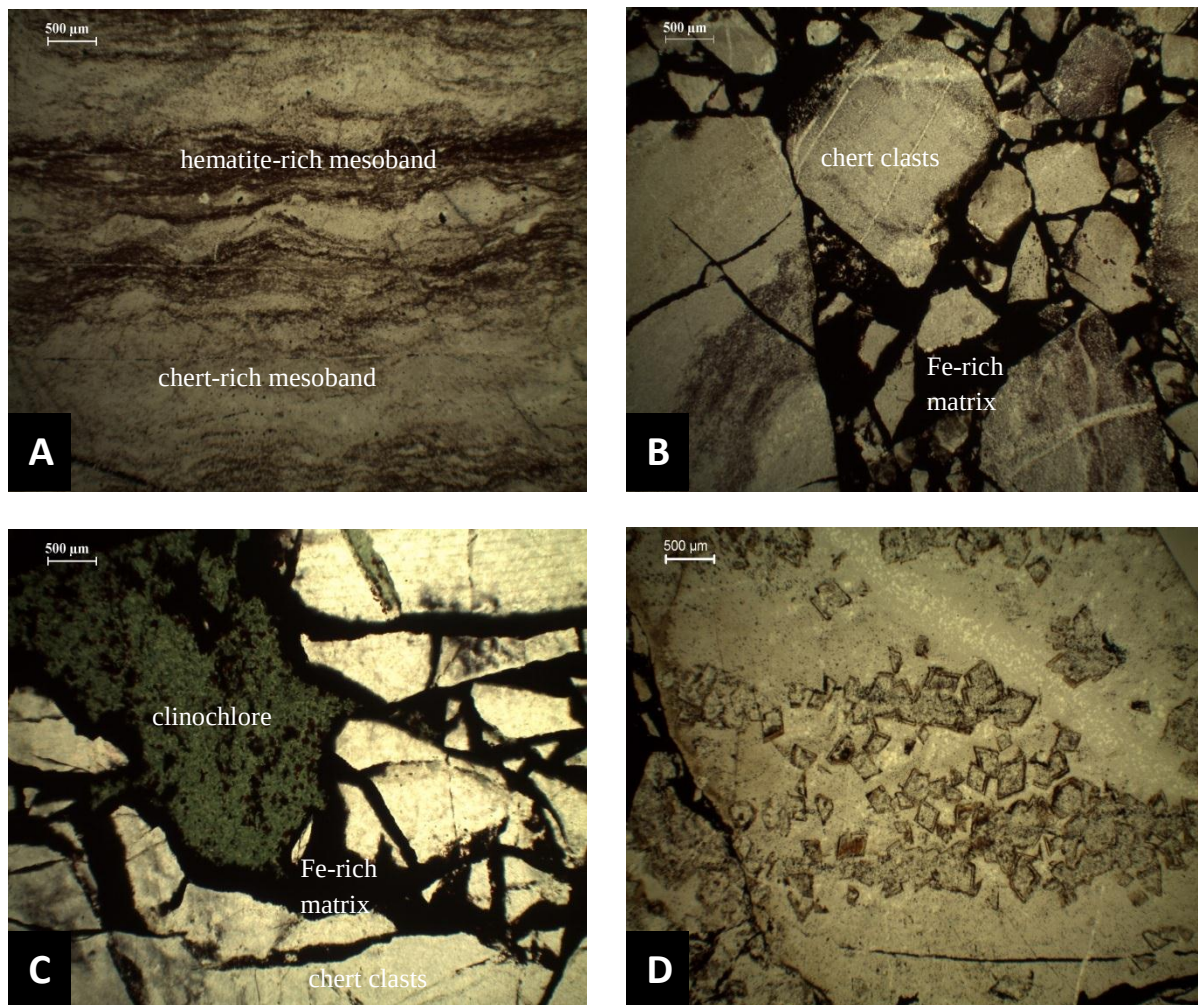


Figure 3.10. Photomicrographs of siliceous banded iron formation (All photomicrographs were taken under transmitted light, plane polarised light). **A.** Cherty BIF sample showing the alternating and undulating nature of hematite-rich and chert-rich bands. **B.** Brecciated cherty BIF sample characterised by angular to sub-angular chert in a very fine-grained matrix of hematite. The relict banding is evident in the chert clasts along with the quartz veining. **C.** An aggregate of very fine-grained clinochlore found in the very fine-grained hematite matrix. **D.** Hematite replacing original grains of a rhombohedral mineral, presumably an iron-carbonate. The quartz veining, which can be abundant, is evident in the sample.

3.3.5 Mapedi shales and Fe-rich shales

The author carried out an Honours study that examined the mineralogy and geochemistry of the Mapedi shales in the Beeshoek and Blackrock areas of the Northern Cape in 2010 (Land, 2010). Some of the main results are summarised here as they bear possible relevance to the genesis of the iron ores in the Maremane anticline. Mineralogical and petrographical evidence has suggested that the Fe-rich shales interbedded with the low-grade iron ore samples of this study are very similar to the Mapedi shales studied earlier despite the fact that the Mapedi shales unconformably overlie the iron ores. Thus these two lithology's are described together in this section.

The Mapedi Formation forms the basal part of the Olifantshoek Supergroup. The formation consists of red shales, green shales, white shales and quartzites. The minerals identified in the green shales are chlorite, quartz, sericite and hematite. Red shales are composed of fine-grained hematite, sericite and quartz (Figure 3.11A), whereas white shales contain quartz, sericite and only minor hematite.

Within the red shales there are hematite zones that crosscut primary bedding planes (Figure 3.11A, 3.11B). This is analogous to the crosscutting hematite zones identified in the matrix of the low-grade iron ore and the hematite lutite samples. Additionally, whole-rock geochemical analysis and scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) analysis on the red shales has confirmed anomalous concentrations of a TiO_2 rich phase (Figure 3.11C), determined to be mostly rutile using Raman spectroscopy (Figure 3.11F). The rutile grains are surrounded by a matrix of fine-grained quartz, sericite and hematite (Figure 3.11C). A back-scatter SEM image shows the abundance of rutile (bright phase) in the Mapedi shales (Figure 3.11D). Further examination of some of these bright phases reveals that the presence of ilmenite which is apparently replaced by rutile and hematite (Figure 3.11E).

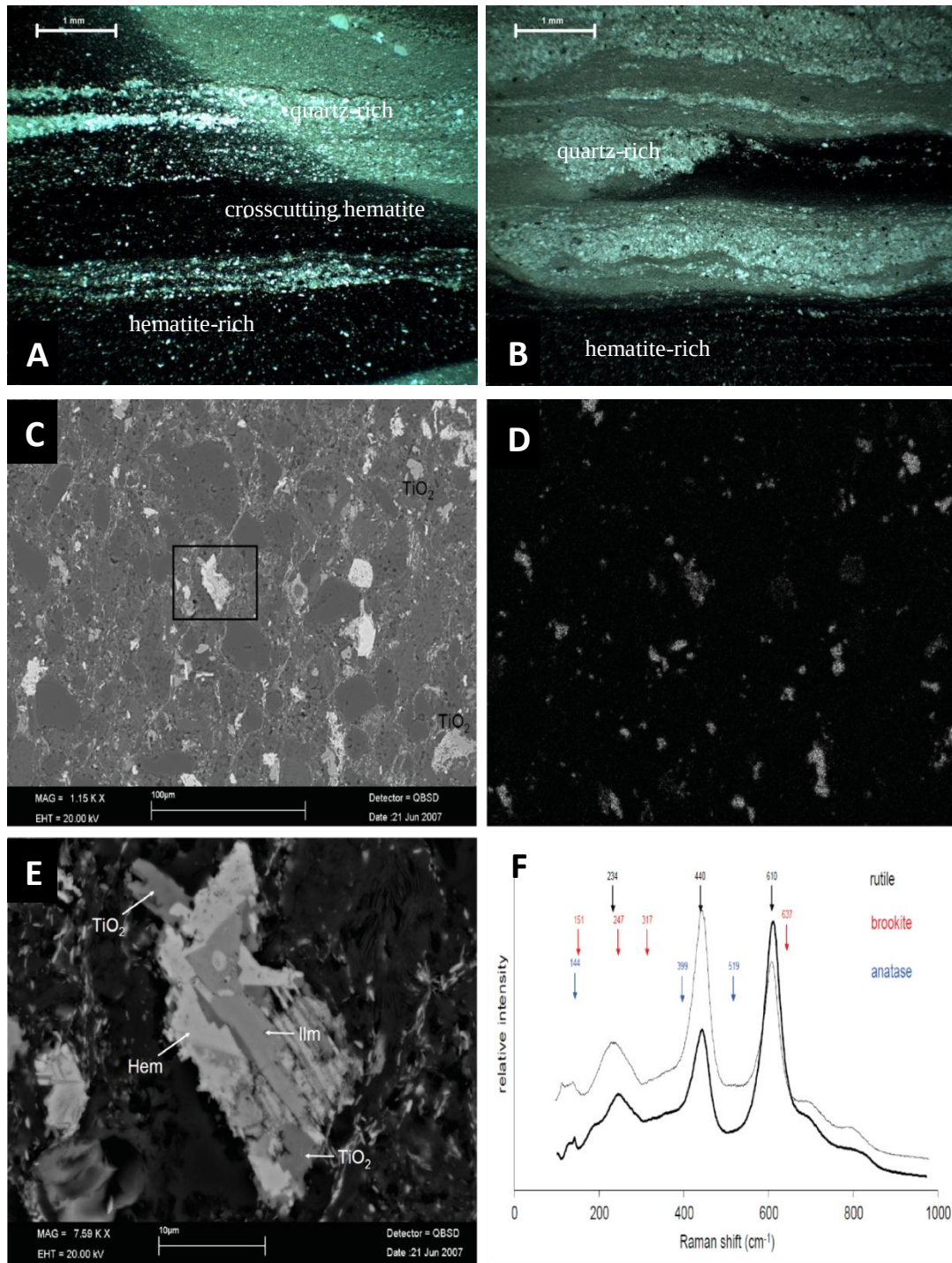


Figure 3.11. Photomicrographs, SEM-EDS and RAMAN analysis for the shales of the Mapedi Formation. **A.** Transmitted light photomicrograph of hematite (Hem) and quartz (Qtz) rich domains with apparent cross-cutting relationship. **B.** Transmitted light photomicrograph of the red shales of the Mapedi Formation comprised of microcrystalline hematite interbedded with fine-grained quartz. **C.** SEM image of the shales showing the presence of TiO_2 rich mineral phases (bright white) in a matrix of fine-grained hematite and quartz. Scale: 100 μm . **D.** Back scatter electron image showing the abundance of the TiO_2 rich phases in the shales. **E.** SEM image of ilmenite surrounded by rutile and hematite in a matrix of finer grained hematite and quartz. Scale: 10 μm . **F.** RAMAN spectra confirming that the dominant TiO_2 phase is rutile.

3.4 Summary of mineralogical characteristics

Macroscopic, petrographic and mineralogical observations presented in this chapter, suggest the iron ores in the studied boreholes can be divided into a low-grade and high-grade unit, with a siliceous BIF occurring beneath the iron ore horizon.

The low-grade iron ore samples consist of ferruginised BIF clasts set in a very fine-grained matrix of quartz, sericite, hematite and clinochlore. The ferruginised BIF clasts are mostly sub-angular to sub-rounded and are generally well-banded. The banding is rhythmic and consists of dull porous hematite bands alternating with brighter hematite-rich bands. The matrix surrounding these clasts is comprised of a relatively homogenous combination of very-fine grained silicate phases (sericite, quartz and clinochlore) as well as disseminated fine-grained hematite. Throughout the low-grade iron ore samples, there are both vertical and horizontally orientated clinochlore-rich veins present.

On a core-specimen scale, the high-grade iron ore body is dominated by two types of ore-textures namely laminated iron ore and brecciated iron ore. Laminated ore consists of dull porous hematite bands alternating with bright hematite-rich bands. These textures are very similar to the hematite clasts present in the low-grade iron ore. Specular hematite occurs in fractures, as veins and secondary pore-fillings within the ore body. Brecciated ore consists of clasts of brecciated laminated ore within a mostly ferruginous matrix. The brecciated ore has essentially the same composition and texture as the laminated ores. Specular hematite is common in the pore spaces within the breccia, with minor occurrences of quartz and clinochlore. The occurrence of vein-hosted specular hematite and fine-grained clinochlore is present throughout the high-grade iron ores. A key difference between the low-grade and high-grade iron ore is the relative abundances and distribution of silicate assemblages. In the low-grade iron ore the silicate minerals are present in the matrix amongst ferruginised BIF clasts, whereas in the high-grade iron ore the silicate assemblages are vein-hosted.

Siliceous BIF underlying the ore unit is dominated by chert and hematite, with minor amounts of clinochlore. There are two different textural types of siliceous BIF present, namely cherty BIF and brecciated cherty BIF. The cherty BIF samples are characterised by alternating bands of chert and hematite. The brecciated cherty BIF is comprised of chert clasts set in a matrix of fine-grained hematite.

4. WHOLE-ROCK GEOCHEMISTRY

4.1 Introduction

Traditional whole-rock geochemical data for high-grade iron ore deposits are relatively scant throughout the published literature (Gutzmer *et al.* 2008). There has been remarkably little use of whole-rock geochemical techniques in attempts to quantify the transformation process of iron-rich sedimentary rocks to high-grade iron ore (Gutzmer *et al.* 2008). It is possible that accurate, high quality whole-rock geochemistry could aid in elucidating processes involved in the formation of these world-class iron ore deposits and particularly ores that form the subject of this study.

Researchers have focussed much of their attention on petrographic and specialised geochemical techniques, such as rare earth element (REE) and stable isotopes, with little focus on the importance of whole-rock geochemistry (Gutzmer *et al.*, 2008). This is probably due to the largely monomineralic nature of these ores which reduce the significance that other elements may have on the overall geochemistry of the ore. The author believes that the application of whole-rock geochemistry may yet hold the key in furthering our understanding of the genesis of these ores, and thus forms the core of this thesis.

In this chapter, major and trace element data from the majority of the samples collected from the two boreholes are presented and evaluated. Initially, the data are presented in the form of simple chemostratigraphic profiles of major and trace elements, with more informative diagrams (such as spidergrams) presented later. Some early basic interpretations are made in conjunction with observations presented in the preceding chapter on the mineralogy and petrography of the ore and associated rocks.

4.2 Sample collection and analytical techniques

Details for sample collection, preparation, analytical techniques and raw analytical results are available in Appendix A and B. A total of 78 samples were analysed for both major and trace elements from the 81 samples collected during the fieldwork, as described in Chapter 3 earlier. These include shale-rich intervals as recorded within the iron ore intervals. Sampling across the iron ore intersections was carried out at a high resolution and sample selection was

done by avoiding, as much as possible, abundant secondary specular hematite veining which may impact sample homogeneity. For all iron ore samples, emphasis was placed on capturing, where possible, the silicate matrix that occurs interstitial to the hematite. Silicate bands were also sub-sampled from the iron ore intersection.

Whole-rock analytical data for ten major element oxides and sixteen trace elements were obtained via x-ray fluorescence (XRF) using the method outlined by Norrish and Hutton (1969). Major element (except Na_2O) analyses were obtained from fused lanthanum-bearing lithium borate glass disks whereas the trace element and Na_2O analyses were obtained from pressed powder pellets. The analyses were carried out on a Philips PW 1480 X-ray spectrometer housed in the Department of Geology, Rhodes University. Analysis of very Fe-rich samples proved to be somewhat problematical in terms of accurately determining Fe_2O_3 totals. Details regarding the issues surrounding accurate Fe_2O_3 analysis and how this was solved are available in Appendix A4.

4.3 Major element geochemistry – results

Mineralogy and petrography from chapter 3, has allowed for different sample groups to be defined. These groups provide the framework for the presentation and interpretation of the whole-rock geochemical data in this chapter. The macroscopic method used to define these groups has resulted in geochemical overlaps between the sample groups. Though a geochemical continuum exists between some of the groups the macroscopic properties of the samples are very different.

4.3.1 Major element chemostratigraphy

Chemostratigraphic plots were constructed for both boreholes SLT032B and SLT033, for all major element oxides that were analysed in this study. The chemostratigraphic plots allow for insights to be drawn into the vertical compositional variation of the iron ores, the underlying siliceous banded iron formations and the geochemical relationships and contrasts between the low-grade and high-grade iron ore intervals.

Chemostratigraphic plots for the two borehole intersections along with the sample groups already defined in chapter 3 are shown in Figure 4.1 and 4.2 for major element oxides. These plots depict a clear antithetic relationship in the iron ore between Fe_2O_3 and

($\text{SiO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}$), which is testament to the closure effect caused by such high concentrations of Fe_2O_3 . The remaining element oxides such as MnO , MgO , CaO , Na_2O and P_2O_5 are minor and generally low (usually <0.5 wt. % each) in most samples. However, whilst concentrations of MgO and Na_2O are also very low they do exhibit comparable chemostratigraphic behaviour as shown by SiO_2 , TiO_2 , Al_2O_3 and K_2O in the iron ore unit.

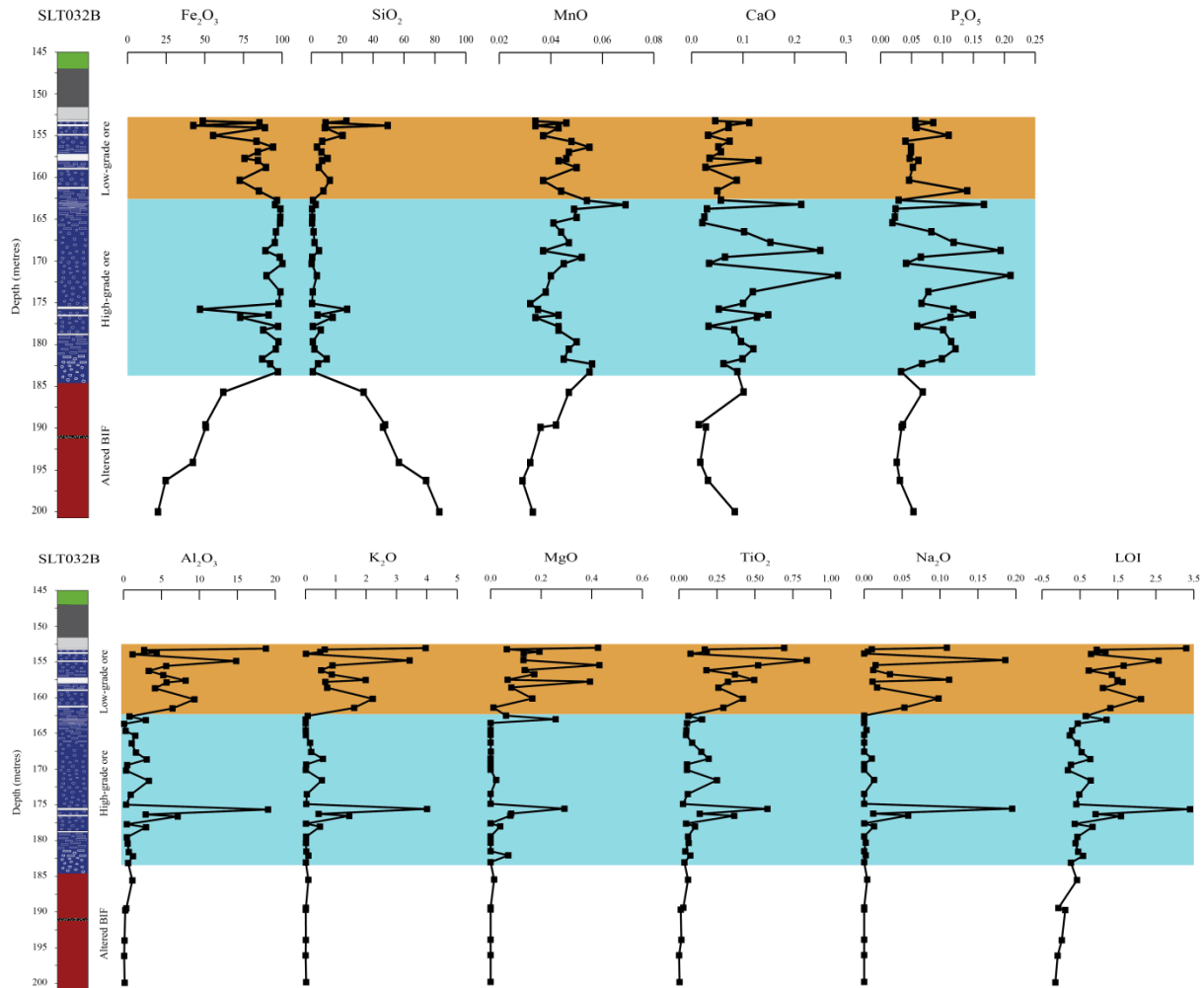


Figure 4.1 Variation plots of major element oxides (wt. %) for borehole SLT032B. Stratigraphic columns depict the approximate locations of the selected samples. The stratigraphic column shows the relative thicknesses of Mapedi shales (green, dark grey), quartzite (light grey), iron ore (purple), silicate bands (white), siliceous BIF (red) and the small gabbro unit (black with white dashes). Additionally, the low-grade iron ore samples are represented by the orange-fill and the high-grade iron ore samples by the blue-fill. Refer to Appendix B for detailed samples depths.

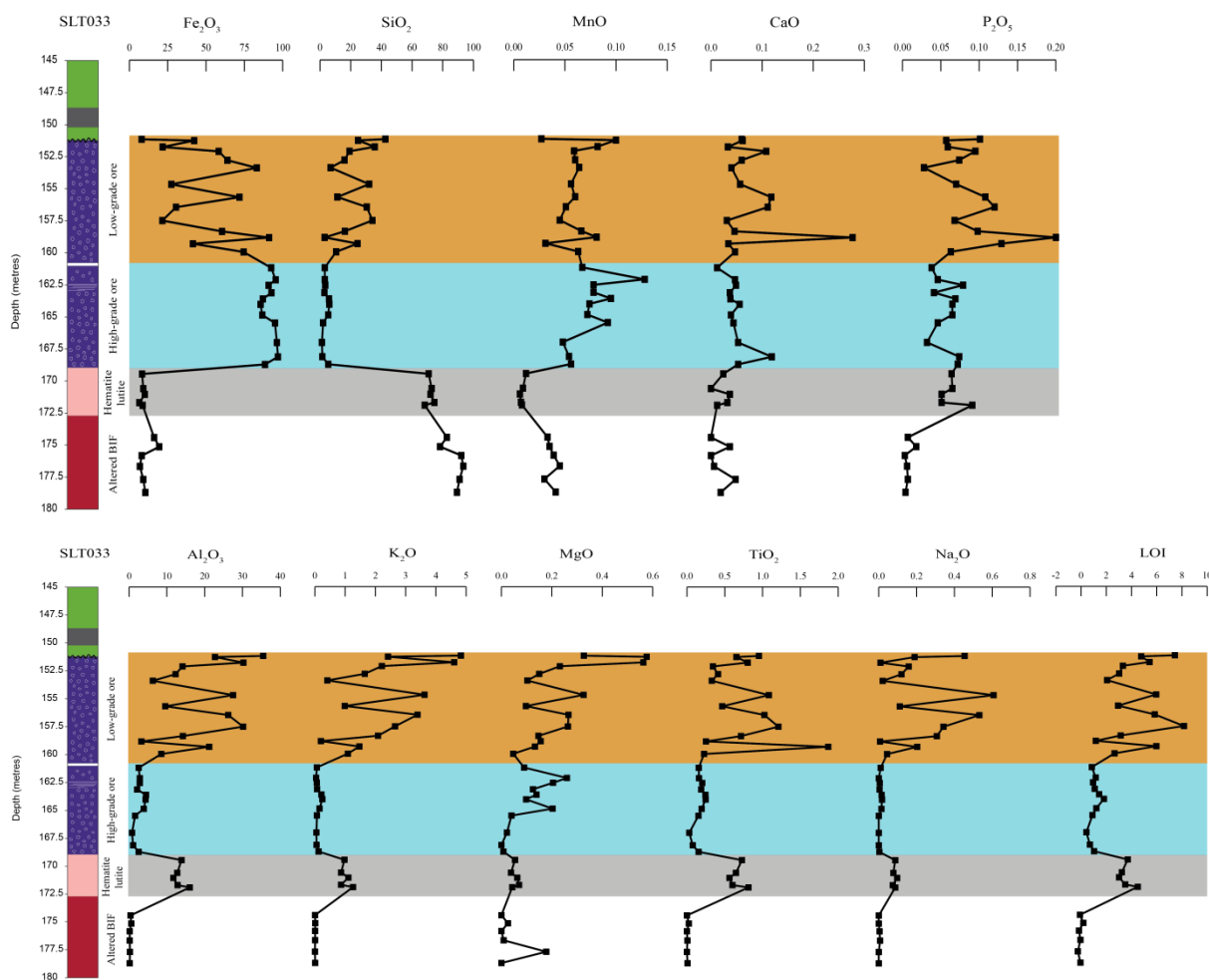


Figure 4.2 Variation plots of major element oxides (wt. %) for borehole SLT033. Stratigraphic columns depict the approximate locations of the selected samples. The stratigraphic column shows the relative thicknesses of Mapedi shales (green, dark grey), iron ore (purple), silicate bands (white), siliceous BIF (red) and the hematite lutite unit (pink). Additionally, the low-grade iron ore samples are represented by the orange-fill, the high-grade iron ore samples by the blue-fill and hematite lutite samples by the grey fill. Refer to Appendix B for detailed samples depths.

Geochemical variation plots for major element oxides across the iron ore indicate that values for Fe_2O_3 increase from an average of 78 wt. % to 93 wt. %, whereas the values for Al_2O_3 , SiO_2 , MgO , TiO_2 and K_2O show a general decrease (from a collective average of 16 wt. % to 5 wt. %) in concentration stratigraphically downwards within the ore unit.

In the two intersections, concentrations of SiO_2 , Al_2O_3 , K_2O , TiO_2 and MgO behave in a similar manner throughout both iron ore sections (Figure 4.1, 4.2). The low-grade portion (SLT032B, 153m to 162m; SLT033, 151.50m to 161m), contains highly variable concentrations of deleterious elements (Si, K, Al and Ti which collectively account for up to

25 wt. % bulk rock), whilst Fe_2O_3 concentrations range widely from 60 to 89 wt. % (Figure 4.1, 4.2).

In the high-grade ore, the deleterious elements account for up to 12 wt. % bulk rock and Fe_2O_3 concentrations are consistently higher than 85 wt. %. This decrease in deleterious element concentrations occurs sharply below the depths of 162m and 161m, respectively for boreholes SLT032B and SLT033. This chemical change is a reflection of an abrupt change in mineralogy and texture of the ore from a low-grade, matrix-rich ore containing relatively high abundances of sericite, quartz and clinocllore, to essentially a monomineralic high-grade hematitic ore with vein-hosted gangue minerals (clinocllore and quartz). K_2O values are also very low (<0.5 wt. %) in the high-grade iron ore, mainly due to the near complete absence of sericite. Notable exceptions are the samples within the high-grade iron ore that have elevated concentrations of SiO_2 , TiO_2 , Al_2O_3 , MgO and K_2O . These samples contain silicate bands, rich in quartz, sericite and clinocllore, locally introducing these deleterious elements into the high-grade ore unit.

The high-grade iron ore grades into the underlying siliceous BIF, at depths of 183m and 173m for boreholes SLT032B and SLT033, respectively. As mentioned earlier, the transition from high-grade iron ore to a silicified BIF is gradational. The samples become increasingly SiO_2 -rich and Fe_2O_3 -poor and basically become bimodal in composition. The concentrations of the remaining major element oxides are low and invariant (< 1.5 wt. % bulk rock) across the siliceous BIF samples owing to the dominant hematite and quartz mineralogy of the samples. Notably there is the occurrence of the hematite lutite unit exclusively in borehole SLT033, occurring at a depth of 169m to 172.6m. The hematite lutite unit, dominated by quartz, hematite and sericite, is generally geochemically homogenous and is predominantly composed of SiO_2 , Al_2O_3 , Fe_2O_3 and K_2O .

Table 4.1. Average composition and ranges of major element oxide whole-rock analytical data, from boreholes SLT032B and SLT033, for the Fe-rich shales, low-grade iron ore, high-grade iron ore, hematite lutite and the siliceous BIF. Data sources: Superior-type BIF (n=1073) from McClung (2006). n.a. = not available.

Rock Type (wt. %)	Fe-rich shale (n=7)		Low-grade iron ore (n=14)		High-grade iron ore (n=34)		Hematite lutite (n=5)		Altered BIF (n=12)		Superior-type BIF (wt. %)*
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	
SiO ₂	19.25 - 49.43	30.68	4.86 - 16.20	9.62	0.26 - 10.01	2.82	68.25 - 74.32	71.54	33.82 - 93.12	72.3	47.30
TiO ₂	0.18 - 0.95	0.64	0.08 - 0.72	0.36	0.03 - 0.25	0.12	0.56 - 0.81	0.67	0 - 0.06	0.01	0.04
Al ₂ O ₃	4.37 - 35.48	20.08	1.20 - 14.23	7.11	0.09 - 4.48	1.84	11.72 - 16.06	13.45	0.09 - 1.17	0.32	1.07
Fe ₂ O ₃	8 - 58.28	39.55	60.44 - 89.56	78.77	85.56 - 98.90	93.87	6.51 - 10.11	8.55	7.94 - 63.85	27.45	43.10
MnO	0.03 - 0.10	0.05	0.04 - 0.07	0.05	0.03 - 0.13	0.06	0 - 0.01	0.01	0.03 - 0.05	0.04	0.44
MgO	0.13 - 0.58	0.35	0.01 - 0.43	0.15	0 - 0.26	0.06	0.04 - 0.07	0.05	0 - 0.18	0.02	5.68
CaO	0.03 - 0.11	0.06	0.03 - 0.13	0.07	0.01 - 0.28	0.09	0 - 0.04	0.02	0 - 0.1	0.03	3.03
Na ₂ O	0.01 - 0.45	0.16	0 - 0.31	0.07	0 - 0.02	0	0.07 - 0.1	0.08	0 - 0.01	0	0.33
K ₂ O	0.49 - 4.83	3.14	0.02 - 2.22	1.13	0.01 - 0.58	0.14	0.87 - 1.26	1.02	0 - 0.1	0.02	0.27
P ₂ O ₅	0.06 - 0.11	0.08	0.03 - 0.14	0.07	0.02 - 0.21	0.08	0.05 - 0.09	0.06	0 - 0.07	0.02	0.10
LOI	1.17 - 7.44	4	0.79 - 3.14	1.87	0.18 - 1.81	0.71	3.01 - 4.50	3.59	-0.26 - 0.42	-0.02	n.a
H ₂ O ⁻	0.19 - 0.67	0.44	0.19 - 0.84	0.43	0.06 - 0.5	0.19	0.3 - 0.74	0.48	0.02 - 0.21	0.1	n.a

4.3.2 Whole-rock major element oxide signatures

Table 4.1 provides a summary of major element oxides (in wt. %) of the different lithological groups entirely on geochemical grounds. The table excludes the few silicate band samples which are discussed separately later.

4.3.2.1 Iron ore

Mineralogical and petrographical investigations presented earlier established the existence of ferruginous shale units above the iron ore bodies, as well as intercalated with low-grade iron ore. These shales are variable in major element oxide concentrations, mainly composed of SiO₂ (19.2 – 49.4 wt. %), Al₂O₃ (4.3 – 35.4 wt. %), Fe₂O₃ (8 – 58.2 wt. %) and K₂O (0.5 – 4.8 wt. %). Concentrations of TiO₂ (0.18 – 0.9 wt. %), MnO (0.02 – 0.1 wt. %), MgO (0.13 – 0.57 wt. %), CaO (0.03 – 0.1 wt. %), Na₂O (up to 0.45 wt. %) and P₂O₅ (0.056 – 0.11 wt. %) are of minor abundances in the samples. Loss of ignition (LOI) values range from 1.1 to 4.8 wt. % with one sample peaking at 7.4 wt. % LOI.

The major element oxide composition of the low-grade iron ore is also fairly variable, however concentrations of Fe₂O₃, SiO₂ and Al₂O₃ tend to dominate most samples. The concentrations of Fe₂O₃ range from 60.44 to 89.56 wt. %. Concentrations of SiO₂ range between 4.8 and 16.2 wt. %, whereas those of Al₂O₃ range from 1.2 to 14.2 wt. %. The other elements present in the low-grade iron ore are minor and account for less than 2.5 wt. % of the bulk rock. These include TiO₂ (0.075 – 0.715 wt. %), MnO (0.037 – 0.066 wt. %), MgO (0.011 – 0.430 wt. %), CaO (0.027 – 0.130 wt. %), K₂O (up to 2.2 wt. %), P₂O₅ (0.028 –

0.140 wt. %) and LOI (loss on ignition: 0.7 – 3.1 wt. %). Na₂O concentrations were below detection limit (bd) in most of the samples, but a few samples contained maximum measurable concentrations around 0.3 wt. % Na₂O.

High-grade iron ore samples are dominated by Fe₂O₃ (85.56 – 98.90 wt. %) followed by SiO₂ (0.25 – 7.8 wt. %) and Al₂O₃ (0.09 – 6.4 wt. %). K₂O concentrations range from 0 to 0.577 wt. % with one sample containing 1.6 wt. % K₂O. The remaining elements, TiO₂ (0.02 – 0.29 wt. %), MnO (0.03 – 0.12 wt. %), MgO (0 – 0.26 wt. %), CaO (0.012 – 0.284 wt. %), P₂O₅ (0.019 – 0.21 wt. %) and LOI (0.18 – 1.81 wt. %), are of very minor abundances. Na₂O was consistently below detection limit for a majority of the samples analysed. It is evident that the high-grade iron ore samples contain significantly less deleterious elements than the stratigraphically higher low-grade iron ore samples. Notably the high-grade iron ore contains slightly more CaO and P₂O₅ than the low-grade iron ore. Concentrations of CaO and P₂O₅ are likely linked to the presence of minor apatite.

4.3.2.2 Hematite lutite

The hematite lutite unit is approximately 2-metres in thickness and occurs at the base of the iron ore in borehole SLT033. The chemical composition of the hematite lutite is dominated by concentrations of SiO₂ (68.2 – 74.3 wt. %), Al₂O₃ (11.7 – 16 wt. %) and lower concentrations of Fe₂O₃ (6.51 – 10.11 wt. %). There are minor concentrations of TiO₂ (0.5 – 0.8wt. %), K₂O (0.8 – 1.2 wt. %) and LOI (3 – 4.5 wt. %). The remaining elements present in the hematite lutite are in trace amounts and account for less than 0.25 wt. % of the bulk rock. These are MnO (0.006 – 0.012 wt. %), MgO (0.037 – 0.07 wt. %), CaO (up to 0.036 wt. %), Na₂O (0.074 – 0.09 wt. %) and P₂O₅ (0.051 – 0.091 wt. %).

4.3.2.3 Siliceous BIF

The chemical composition of the siliceous banded iron formation is dominated by high concentrations of SiO₂ (ranging from 33.8 to 93 wt. %) and relatively high concentrations of Fe₂O₃ (ranging from 7.9 to 63.8 wt. %). The remaining elements are present in trace amounts and in most samples account for less than 1 wt. % of the bulk rock. These are TiO₂ (up to 0.059 wt. %), Al₂O₃ (0.091 – 1.16 wt. %), MnO (0.029 – 0.047 wt. %), MgO (up to 0.177 wt. %), CaO (up to 0.1 wt. %), K₂O (up to 0.097 wt. %) and P₂O₅ (up to 0.068 wt. %). Na₂O was

consistently below detection limit in most of the siliceous banded iron formation samples. LOI (loss on ignition) values range from -0.260 to 0.420.

4.3.2.4 Silicate bands

Silicate bands (Table 4.2) are composed of highly variable concentrations of SiO₂ (13.83 – 34.15 wt. %), Al₂O₃ (7.15 – 30.16 wt. %) and Fe₂O₃ (21.53 – 72.87 wt. %). These highly variable concentrations are most likely due to the variable Fe₂O₃ content across the different silicate bands present in the boreholes, as well as due to sample selection size when crushing the given samples. Low concentrations of TiO₂ (0.36 – 1.87 wt. %) and K₂O (1.45 – 4.01 wt. %) are present in the samples. The remaining major element oxides present in the silicate bands are minor and account for less than 1 wt. % of the bulk rock. These include MnO (0.03 – 0.06 wt. %), MgO (0.08 – 0.33 wt. %), CaO (0.03 – 0.13 wt. %), Na₂O (0.06 – 0.61 wt. %) and P₂O₅ (0.07 – 0.13 wt. %). LOI for the silicate band samples ranges from 1.58 to 8.16 wt. %.

Table 4.2. Average composition and ranges of major element oxide whole-rock analytical data, from boreholes SLT032B and SLT033, for 6 silicate bands.

(wt. %)	Silicate band samples (n=6)	
	Range	Average
SiO ₂	13.83 - 34.15	26.35
TiO ₂	0.36 - 1.87	1.02
Al ₂ O ₃	7.15 - 30.16	21.88
Fe ₂ O ₃	21.53 - 72.87	40.09
MnO	0.03 - 0.06	0.04
MgO	0.08 - 0.33	0.23
CaO	0.03 - 0.13	0.07
Na ₂ O	0.06 - 0.61	0.32
K ₂ O	1.45 - 4.01	2.77
P ₂ O ₅	0.07 - 0.13	0.1
LOI	1.58 - 8.16	5.15
H ₂ O ⁺	0.24 - 0.87	0.51

4.3.3 Major element geochemical compositions relative to Superior-type BIF

Average geochemical compositions were calculated for each sample group and normalized against the average composition of Superior-type BIF's as compiled by McClung (2006). The major element oxide data are normalized against Superior-type BIF's as the Kuruman Iron Formation is widely considered the protolith for the iron ore (Beukes *et al.*, 2003). The diagram allows for the visual evaluation of enrichment and depletion characteristics in relation to average Superior-type BIF. Enrichment in a particular element is expressed by the

normalization value being greater than one, whereas depletion trends are expressed by normalization values being less than one. A logarithmic scale is used in the spidergram as it conveniently presents different magnitudes of enrichment/depletion.

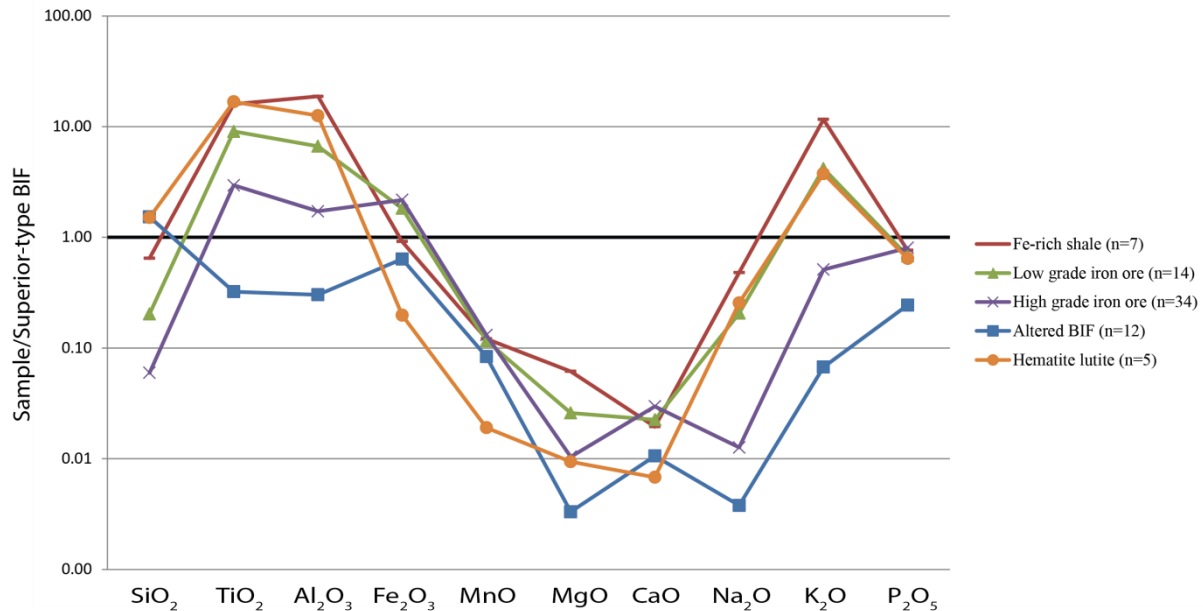


Figure 4.3. Average major element oxide geochemical spidergram of Fe-rich shales, low-grade iron ore, high-grade iron ore, hematite lutite and siliceous BIF, normalized to Superior-type BIF (McClung, 2006).

In the spidergram of Figure 4.3, the Fe-rich shale samples are enriched in TiO_2 , Al_2O_3 and K_2O relative to Superior-type BIF. The TiO_2 has an enrichment factor up to 16, Al_2O_3 up to 19, whereas K_2O is enriched by up to 12. Relative depletion in SiO_2 (0.65), MnO (0.12), MgO (0.06), CaO (0.02), Na_2O (0.48) and P_2O_5 (0.76) is observed in the Fe-rich shales. The Fe_2O_3 concentration in the Fe-rich shales is broadly equivalent to that of Superior-type BIF.

In the low-grade iron ore samples, there is a distinct enrichment in TiO_2 (9.05), Al_2O_3 (6.60) and K_2O (4.20) relative to Superior-type BIF protolith. The concentration of Fe_2O_3 is higher by a factor up to 1.78, whereas the concentration of P_2O_5 is slightly depleted at 0.68. Significant depletion is noticeable for SiO_2 and Na_2O , which are both depleted by a factor of up to 0.2. Concentration of MnO is depleted by 0.12 in the low-grade ore samples, whereas MgO and CaO are both depleted by a factor of 0.03.

The pattern for the high-grade ore samples appears to compare well with that of the low-grade ore samples, albeit at lower concentrations for most elements in the high-grade ore, apart from P_2O_5 , CaO and expectedly for Fe_2O_3 . The high-grade ore samples are enriched in

TiO₂, Al₂O₃ and Fe₂O₃ by factors of 2.95, 1.72 and 2.05 respectively. It is interesting to note that TiO₂ is effectively more enriched than Fe₂O₃, whereas Al₂O₃ is nearly as enriched as the Fe₂O₃. There are depletions in K₂O and P₂O₅ by factors of 0.5 and 0.8. There are significant depletions in SiO₂, MnO, MgO, CaO and Na₂O. SiO₂ is depleted by a factor up to 0.06, MnO by 0.13, CaO by 0.03, whereas both MgO and Na₂O are depleted by factors of 0.01. The concentrations of MgO, CaO and Na₂O compare well with the concentrations that are present in the siliceous BIF. Additionally, the high-grade ore sample curve seems to mimic the siliceous BIF curve apart from the SiO₂ concentration.

The hematite lutite curve is very similar to that of the Fe-rich shale curve, with enrichments in SiO₂ (1.51), TiO₂ (16.7), Al₂O₃ (12.5) and K₂O (3.76). Depletions are observable for Fe₂O₃, MnO, MgO, CaO, Na₂O and P₂O₅, relative to Superior-type BIF. P₂O₅ is depleted by a factor of 0.64, whereas CaO, MgO and MnO are depleted by factors between 0.01 and 0.02. Concentration of Fe₂O₃ is depleted by a factor up to 0.17 with Na₂O being depleted by a factor up to 0.26 relative to Superior-type BIF.

The pattern for siliceous BIF samples shows depletions for all major element oxides relative to Superior-type BIF, apart from the SiO₂ concentration which is enriched by a factor of up to 1.53. The concentration of Fe₂O₃ in the siliceous BIF is depleted by 0.64, relative to Superior-type BIF, which is a testament to their cherty nature described earlier in the mineralogy and petrography. TiO₂, Al₂O₃ and P₂O₅ are depleted by factors of 0.24 to 0.32 in the siliceous BIF samples. K₂O and MnO are depleted between factors of 0.07 to 0.08, whereas the concentrations of MgO, CaO and Na₂O are depleted by a factor up to 0.01.

4.4 Trace element geochemistry – results

The trace element geochemistry results are presented in a similar way to the major element oxides. However, the chemostratigraphy of trace elements will be subsequently described in the context of two major groups, namely silicate-associated and oxide-associated trace elements.

4.4.1 Trace element chemostratigraphy

Chemostratigraphic plots were constructed for both boreholes SLT032B and SLT033, for all the trace elements that were analysed in this study. The chemostratigraphic plots allow for

important insights into the trace element composition of the iron ores, the underlying siliceous banded iron formation and the trace element geochemical relationships and contrasts between the low-grade and high-grade iron ore. The chemostratigraphic plots for the trace elements are shown in Figure 4.4 and 4.5 for the two borehole intersections.

Silicate-associated trace elements are geochemically coupled to the silicate phases present in the iron ores, as shown earlier. The silicate-associated trace elements include Nb, Zr, Y, Rb, Th, Pb, Sr, Ba, Sc, V, Cr and Ni. The concentrations of Nb, Zr, Y, Rb, Th and Ba indicate high concentrations (up to 130ppm) in the upper part of the stratigraphy, i.e. Fe-rich shales and low-grade iron ore. These high concentrations dissipate down the stratigraphy into the high-grade iron ore, where concentrations are very low (< 50ppm) (Figure 4.4 and 4.5). These trace elements also show increased concentrations near the silicate bands, much like the behaviour of SiO_2 , TiO_2 , Al_2O_3 , MgO and K_2O .

Trace element concentrations of Pb, Sc and Cr seem to exhibit a similar chemostratigraphic pattern to the silicate phases, however this is slightly weaker due to lower concentrations. Mo concentrations are erratic across the stratigraphy. Sr concentrations in SLT032B show a clear silicate-related chemostratigraphic pattern, however in SLT033, concentrations behave erratically across the stratigraphy.

The concentrations of V appear to be invariant across the stratigraphy in both boreholes aside from anomalies at 175m in depth in borehole SLT032B and at 154m in borehole SLT033, which do not correspond with any other trace elements. Concentrations of Ni show a silicate-related chemostratigraphic trend in both boreholes.

Oxide-associated trace elements are coupled with Fe_2O_3 (hematite) concentrations. The oxide-associated trace elements include Co and Cu. Co and Cu concentrations behave in an antithetic way compared to the silicate-related trace elements, with concentrations being low (< 28ppm) in the upper part of the ore body and higher (> 30ppm) in the lower part. Cu concentrations can be highly variable but show an oxide-related relationship similar to Co. Furthermore, it is apparent that most trace elements exhibit extremely low concentrations and are invariant in the siliceous BIF units at the base of both boreholes.

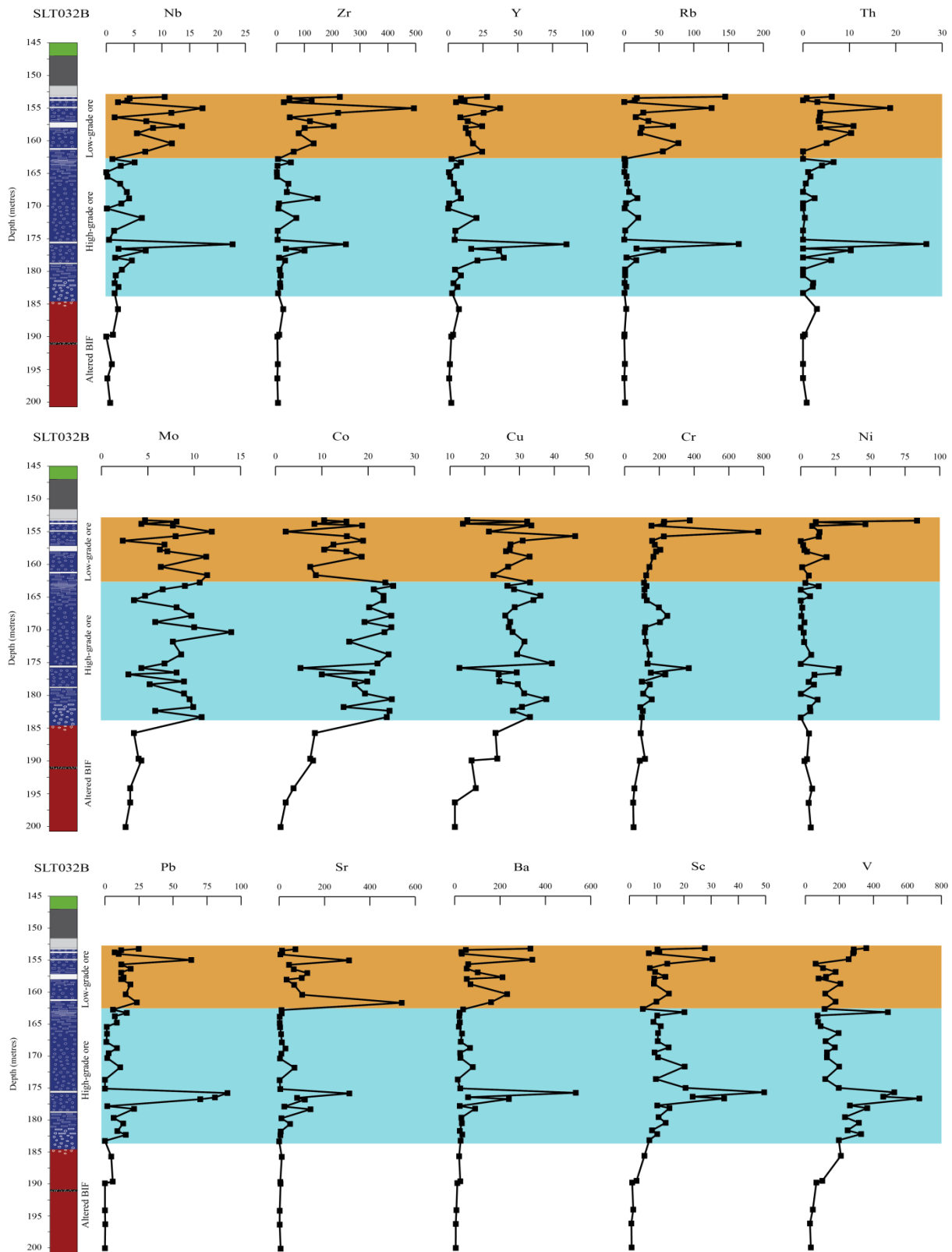


Figure 4.4. Variation plots of trace elements (ppm) for borehole SLT032B. Stratigraphic columns depict the approximate locations of the selected samples. The stratigraphic column shows the relative thicknesses of Mapedi shales (green, dark grey), quartzite (light grey), iron ore (purple), silicate bands (white), siliceous BIF (red) and the small gabbro unit (black with white dashes). Additionally, the low-grade iron ore samples are represented by the orange-fill and the high-grade iron ore samples by the blue-fill. Refer to Appendix B for detailed samples depths.

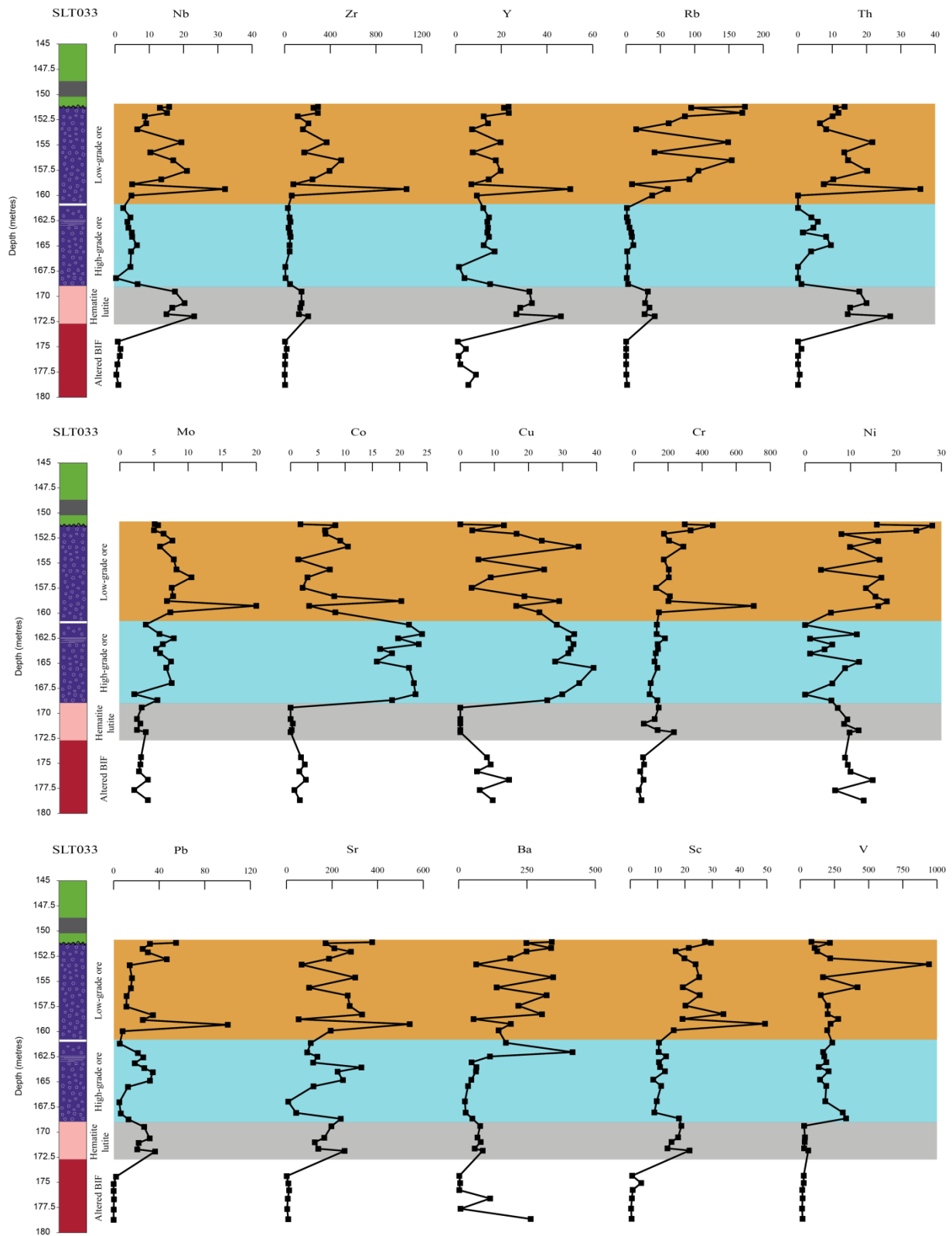


Figure 4.5. Variation plots of trace elements (ppm) for borehole SLT033. Stratigraphic columns depict the approximate locations of the selected samples. The stratigraphic column shows the relative thicknesses of shales (green, dark grey), iron ore (purple), silicate bands (white), siliceous BIF (red) and the hematite lutite unit (pink). Additionally, the low-grade iron ore samples are represented by the orange-fill, the high-grade iron ore samples by the blue-fill and hematite lutite samples by the grey fill. Refer to Appendix B for detailed samples depths.

4.4.2 Whole-rock trace element signatures

Table 4.3 provides a summary of trace element composition (in ppm) of the different lithological groups entirely on geochemical grounds. The table excludes the few silicate band samples which are discussed separately later. Furthermore, a summary of the trace element composition of Superior-type BIF is presented in Table 4.3.

Table 4.3. Average composition and ranges of trace element whole-rock analytical data, from boreholes SLT032B and SLT033, for the Fe-rich shales, low-grade iron ore, high-grade iron ore, hematite lutite and the siliceous BIF. Data sources: Superior-type BIF (n=1073) from McClung (2006). n.a. = not available.

Rock Type ppm	Fe-rich shale (n=7)		Low-grade iron ore (n=14)		High-grade iron ore (n=34)		Hematite lutite (n=5)		Altered BIF (n=12)		Superior-type BIF (ppm)*
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average	
Mo	4.30 - 11.90	6.14	5.90 - 11.40	7.87	2.10 - 14	7.23	2.50 - 3.80	3	2.10 - 4.30	3.32	n.a
Nb	3.80 - 17.30	12.06	2.10 - 13.60	8.26	0 - 6.60	2.99	15 - 23.10	18.52	0 - 2.1	0.93	3.00
Zr	114.70 - 493.60	256.89	26.30 - 244.50	131.56	1.10 - 147	30.67	126 - 206.20	153.08	1.3 - 24	7.15	38.00
Y	11.80 - 37.30	22.43	5.60 - 25.40	14.31	0 - 39.90	9.52	26.60 - 46.10	33.34	0.7 - 8.90	3.42	25.00
Sr	13.30 - 376.10	204.7	5.40 - 540.30	135.87	0 - 328.60	66.17	124.20 - 255	176.26	0.9 - 11.50	5.86	25.00
U	0 - 2.90	0.63	0 - 5.50	1.14	0 - 6.20	1.34	0 - 1.5	0.6	0 - 1.4	0.29	1.70
Rb	15.30 - 173.20	115.61	0 - 92.30	41.45	0 - 20	5.14	26.90 - 41.70	32.36	0 - 2.9	0.63	36.00
Th	0 - 18.80	10.21	0 - 13.50	5.68	0 - 9.60	2.25	14.50 - 26.90	18.9	0 - 3	0.48	3.00
Pb	7.10 - 63.40	33.93	0 - 92.30	17.66	0 - 80.80	13.53	20.80 - 36.40	27.54	0 - 5.70	1.08	5.00
Cu	0 - 21.20	11.81	18.80 - 46	28.54	24.20 - 39.30	30.77	0	0	4.90 - 23.60	12.82	12.00
Ni	8 - 83.60	31.41	1.00 - 18.60	8.35	0 - 26.90	5.33	7.20 - 11.80	9.34	2.70 - 14.90	8.07	18.00
Co	1.80 - 10.50	6.26	7.20 - 18.70	11.82	14.70 - 25.40	21.25	0 - 0.4	0.12	0.7 - 8.5	3.55	24.00
Cr	175.90 - 769	376.81	124.10 - 289.70	189.74	90.80 - 245.60	136.08	57.30 - 234.40	139.38	28.90 - 117.30	61.05	n.a
V	81.70 - 357.90	203.46	60.10 - 941.30	248.46	71.40 - 484.90	210.03	27.80 - 58.30	36.08	13.30 - 208.60	48.95	26.00
Ba	29.30 - 342.30	268.67	31.30 - 304.90	129.32	13.60 - 416.80	55.78	58.80 - 88.30	75.14	2.5 - 263.60	39.11	108.00
Sc	11 - 30.50	23.43	7.10 - 34.10	14.95	4.90 - 23.20	12.05	13.60 - 21.70	17.32	0.3 - 5.5	1.58	6.40

4.4.2.1 Iron ore

The trace element geochemistry of the Fe-rich shales is dominated by Zr (114.70 – 493.60 ppm), Sr (13.30 – 376.10 ppm), Rb (15.30 – 173.20 ppm), Cr (175.90 – 769 ppm), V (81.70 – 357.90 ppm) and Ba (29.30 – 342.30 ppm). There are low concentrations of Y, Pb, Ni and Sc ranging between 8 and 80 ppm, whilst concentrations of Mo, Nb, Th and Cu are extremely low ranging between 0 and 21.20 ppm. Concentrations of U and Co are consistently below detection limits and therefore negligible for the Fe-rich shale samples.

Low-grade iron ore samples are dominated by concentrations of Zr (26.30 – 244.50 ppm), Sr (5.40 – 540.30 ppm), Cr (124.10 – 289.70 ppm), V (60.10 – 941.30 ppm) and Ba (31.30 – 304.90 ppm). There are moderate to low concentrations of Rb (0 – 92.30 ppm), Pb (0 – 92.30 ppm) and Cu (18.80 – 46 ppm), whereas concentrations of Mo, Nb, Y, U, Th, Ni, Co and Sc are either very low or below the detection limit ranging from 0 to 34.10 ppm.

High-grade iron ore unit has moderate concentrations of Zr (1.10 – 147 ppm), Sr (0 – 328.60 ppm), Cu (24.20 – 39.30 ppm), Cr (90.80 – 245.60 ppm), V (71.40 – 484.90 ppm) and Ba (13.60 – 416.80 ppm) that account for a majority of the trace element composition. There are low concentrations of Mo (2.10 – 14 ppm), Y (0 – 39.90 ppm), Rb (0 – 20 ppm), Pb (0 – 80.80 ppm), Ni (0 – 26.90 ppm), Co (14.70 – 25.40 ppm) and Sc (4.90 – 23.20 ppm). Concentrations of Nb (0 – 6.60 ppm) present in the samples is very low, whereas concentrations of U and Th were below detection limit in most of the samples and therefore insignificant.

4.4.2.2 Hematite lutite

Hematite lutite samples appear to share similarities with the Fe-rich shale samples and are distinctly different from the iron ore and siliceous BIF samples. Hematite lutite samples are dominated by Zr (126 – 206.20 ppm), Sr (124.40 – 255 ppm) and Cr (57.30 – 234.40 ppm) with Mo, U, Cu and Co having concentrations that are consistently below the limit of detection in most samples. There are moderate to low concentrations of Nb (15 – 23.10 ppm), Y (26.60 – 46.10 ppm), Rb (26.90 – 41.70 ppm), Th (14.50 – 26.90 ppm), Pb (20.80 – 36.40 ppm), V (27.80 – 58.30 ppm), Ba (58.80 – 88.30 ppm) and Sc (13.60 – 21.70 ppm). Concentrations of Ni (7.20 – 11.80 ppm) present were only slightly above the lower limit of detection.

4.4.2.3 Siliceous BIF

Siliceous BIF samples are predominantly composed of Cu (4.90 – 23.60 ppm), V (13.30 – 208.60 ppm) and Ba (2.5 – 263.60 ppm), however these concentrations are low when compared with the overlying ore units. There are very low concentrations of Zr (1.3 – 24 ppm), Y (0.7 – 8.90 ppm), Sr (0.9 – 11.50 ppm) and Ni (2.70 – 14.90 ppm) present in the siliceous BIF samples. The trace elements Mo, Nb, U, Rb, Th, Pb, Co and Sc were regularly below the lower limit of detection and are thus negligible.

4.4.2.4 Silicate bands

Table 4.4. Average composition and ranges of trace element whole-rock analytical data, from boreholes SLT032B and SLT033, for 6silicate bands.

ppm	Silicate band samples (n=6)	
	Range	Average
Mo	2.90 - 20	8.87
Nb	7.10 - 32.10	19.88
Zr	100.6 - 1067.4	445.52
Y	17.60 - 85	38.12
Sr	113.20 - 540.70	301.78
U	0 - 3.8	1.25
Rb	56.30 - 164.60	115
Th	10.30 - 35.70	21.52
Pb	11.20 - 100.20	49.82
Cu	3.30 - 24	11.77
Ni	9.80 - 27.50	16.67
Co	1.40 - 10	4.25
Cr	129.60 - 702.90	302.62
V	149.60 - 669.70	321.6
Ba	191 - 533.80	308.28
Sc	20.20 - 49.50	34.07

Trace element geochemistry of the silicate bands (Table 4.4) is dominated by Zr (100.6 – 1067.4 ppm), Sr (113.20 – 540.70 ppm), Rb (56.30 – 164.60 ppm), Cr (129.60 – 702.90 ppm), V (149.60 – 669.70 ppm) and Ba (191 – 533.80 ppm). Silicate band samples have low to moderate concentrations of Nb (7.10 – 32.10 ppm), Y (17.60 - 85 ppm), Th (10.30 – 35.70 ppm), Pb (11.20 – 100.20 ppm), Ni (9.80 – 27.50 ppm) and Sc (20.20 – 49.50 ppm). There are also very low concentrations of Mo (2.90 - 20 ppm), Co (1.40 - 10 ppm) and Cu (3.30 - 24 ppm) present in the samples, whilst concentrations of U were negligible.

4.4.3 Trace element geochemical compositions relative to Superior-type BIF

The average trace element compositions for each sample group were normalized against Superior-type BIF and plotted on a spidergram (McClung, 2006). The spidergram allows for the visual assessment of enrichment and depletion trends in the samples. In the Superior-type BIF-normalized spider diagrams, the Fe-rich shale samples are enriched in Nb, Zr, Sr, Rb, Th, Pb, Ni, V, Ba (2.50 to 8) and Sc (3.66) relative to the Superior-type BIF (Figure 4.4). The Fe-rich shale samples are depleted in Y and Cu by factors of 0.9, whereas Co is depleted by a factor around 0.3.

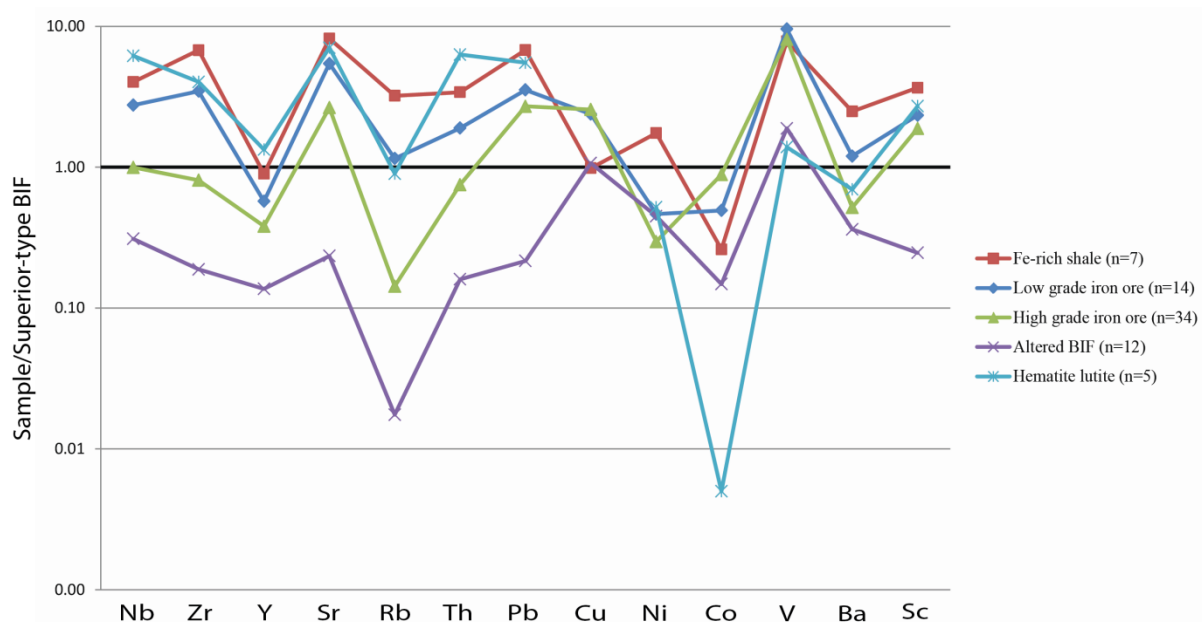


Figure 4.6. Average trace element geochemical spidergram diagram of Fe-rich shales, low-grade iron ore, high-grade iron ore, hematite lutite and siliceous BIF, normalized to Superior-type BIF (McClung, 2006).

In the low-grade iron ore samples there are distinct enrichments in Nb, Zr, Sr, Pb, Cu and Sc by factors between 2 and 4 relative to Superior-type BIF. Vanadium is enriched by up to 9 times when compared to the Superior-type BIF, whereas there are slight enrichments in Rb, Th and Ba between factors of 1.2 and 1.8. In the low-grade iron ore samples, depletions in Y, Ni and Co are observed by a factor of 0.50. The low-grade iron ore samples display very similar normalized patterns to that of the Fe-rich shale samples, however the trace elements are less enriched in the low-grade iron ore samples.

In the high-grade iron ore samples, a distinct enrichment is observed for V by a factor of 7 relative to Superior-type BIF. The concentrations of Sr, Pb, Cu and Sc are all enriched by factors between 2 and 3 relative to Superior-type BIF. There are depletions observed for Zr, Th and Co between 0.75 and 0.9, whereas concentrations of Y, Rb, Ni and Ba are depleted between factors of 0.15 and 0.50. The concentrations of Nb are similar to that found in Superior-type BIF samples. The high-grade iron ore samples seem to show a similar normalized pattern to the low-grade iron ore samples. A vast majority of the trace elements are lower in concentration in the high-grade iron ore when compared with the low-grade iron ore, except for Cu and Co, which are explained earlier as oxide-associated trace elements.

The hematite lutite samples show a unique trace element geochemical fingerprint, however the samples seem to have similarities to the normalized pattern for the Fe-rich shale samples.

The hematite lutite samples are enriched in Nb, Zr, Sr, Th and Pb between factors of 4 and 7, whereas Cu concentrations were undetectable. Concentrations of Y and V were enriched by factors of 1.3, whereas Sc shows enrichment by 2.71, relative to Superior-type BIF. Trace element concentrations were depleted in Rb (0.90), Ni (0.52), Ba (0.70) and Co (0.01), relative to Superior-type BIF samples.

The siliceous BIF samples display enrichment only in V by a factor of approximately 1.88. The remaining trace elements are all depleted by various magnitudes, except for Cu which has concentrations similar to Superior-type BIF. The concentrations of Zr, Y, Sr, Th, Pb, Co and Sc are all depleted between factors of 0.14 and 0.25, whereas Rb (0.02) is highly depleted. Concentrations of Nb, Ni and Ba are depleted by factors between 0.3 and 0.5 in the siliceous BIF samples, relative to Superior-type BIF. The siliceous BIF displays a similar pattern to the high-grade iron ore, albeit at lower concentrations, with the exception of Ni and Ba.

4.4.4 Summary of geochemical characteristics

In summarizing, the two borehole intersections contain sections of iron ore that are characterized by clear chemostratigraphic patterns showing input of a possible clastic-type sediment into the upper part of the iron ore unit. The deleterious elements behave in a similar manner due to the simple silicate mineral assemblages (clinocllore, quartz and sericite) present in the iron ore units. A key difference between the low-grade and high-grade iron ore is the relative abundances of silicate-related elements (Si, K, Al, Mg and Ti). In the low-grade iron ore there are high concentrations of deleterious elements present, whereas in the high-grade iron ore there are lower concentrations of silicate-related elements (Si, K, Al, Mg and Ti).

4.5. Rare earth element and oxygen isotope applications

4.5.1 Introduction

This section deals with the application of rare earth element (REE) geochemistry and stable oxygen isotopes of hematite on the iron ores of this study. In the recent past, some researchers have focussed on rare earth element (REE) and stable isotope analysis on iron ores, with literature being published on various iron deposits around the world (e.g. Powell *et al.*, 1999; Gutzmer *et al.*, 2006; Lobato *et al.*, 2007; Figueiredo *et al.*, 2008; Gutzmer *et al.*, 2008; Roy and Venkatesh, 2009; Thorne *et al.*, 2009).

Gutzmer *et al.* (2008) propose that unique rare earth element geochemical fingerprints are present in supergene high-grade hematite ores which allow them to be classified. The authors argue that there are distinct enrichments in light rare earth elements (LREE), relative to heavy rare earth elements (HREE) in all supergene high-grade iron ore deposits. This effect has been observed in modern low-temperature environments affected by intense chemical weathering where the mobilisation of HREE in weathering profiles and the concentration of LREE in the weathering residue is observed (Nelson *et al.*, 2003). In contrast, hydrothermal and magmatic deposits appear not to exhibit this unique geochemical fingerprint.

The use of stable oxygen isotopes are also suggested to be an important tool in differentiating between high-grade iron ore deposits of hydrothermal or supergene origin (Gutzmer *et al.*, 2006; Hagemann *et al.*, 2007). Iron oxides are present in all stages of the transformation of BIF to high-grade iron ore, hence a study of their oxygen isotopic compositions can potentially provide important constraints on fluid-rock interaction processes (Thorne *et al.*, 2009). Gutzmer *et al.* (2006) show that hematite $\delta^{18}\text{O}$ values from high-grade iron ores interpreted to be of supergene origin (-3.9 to 2‰) have a range which overlaps with the range that is defined by $\delta^{18}\text{O}$ values of hematite/magnetite from weakly metamorphosed Archean-Paleoproterozoic BIF protore (-4 to +5‰). In contrast, the $\delta^{18}\text{O}$ compositions of hematite obtained from deposits interpreted as hydrothermal, range from -7.3 to +0.9‰. The authors further suggest that supergene-processes have little to no effect on the $\delta^{18}\text{O}$ composition in high-grade iron ore deposits.

The aim of this part of the study is to:

- present rare earth elements (REE) and oxygen isotope results from the hand-picked hematite separates; and
- assess the results against similar data from the current literature

This section is subdivided into two parts. The first part deals with rare earth element variations of hematite separates from low-grade and high-grade ore, and the second part deals with oxygen isotope variations of the same separates. The importance of these two applications, with regards to genesis of the ore body, post-depositional processes and fluid interactions are discussed later in the thesis.

In accordance with the literature, oxygen isotope variations are reported as $\delta^{18}\text{O}$ values, according to the following equation:

$$\delta^{18}\text{O}_{\text{mineral}} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{mineral}} - ({}^{18}\text{O}/{}^{16}\text{O})_{\text{VSMOW}}] / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{VSMOW}}$$

In the above equation, VSMOW is the Vienna Standard Mean Ocean Water which is the standard that has approximately the same oxygen isotopic composition of modern ocean water (International Atomic Energy Agency, 2009).

4.5.2 Sample preparation and analytical techniques

For the purpose of both rare earth element and stable oxygen isotope studies, a total of 16 samples from the iron ore were selected and analysed from borehole SLT032B. The stratigraphic locations of the 16 selected samples for this study are illustrated in Figure 4.7. Hematite was hand-picked from each sample that was selected for REE and isotope analysis. This was done by picking out fragments of hematite from a coarse-crush of each sample using a binocular microscope. The hematite fragments were then crushed to a fine powder using a mortar and pestle. Care was taken to ensure that the separated sample was as mineralogically homogenous and pure as possible; to this end, each separate was tested for purity via XRD analysis.

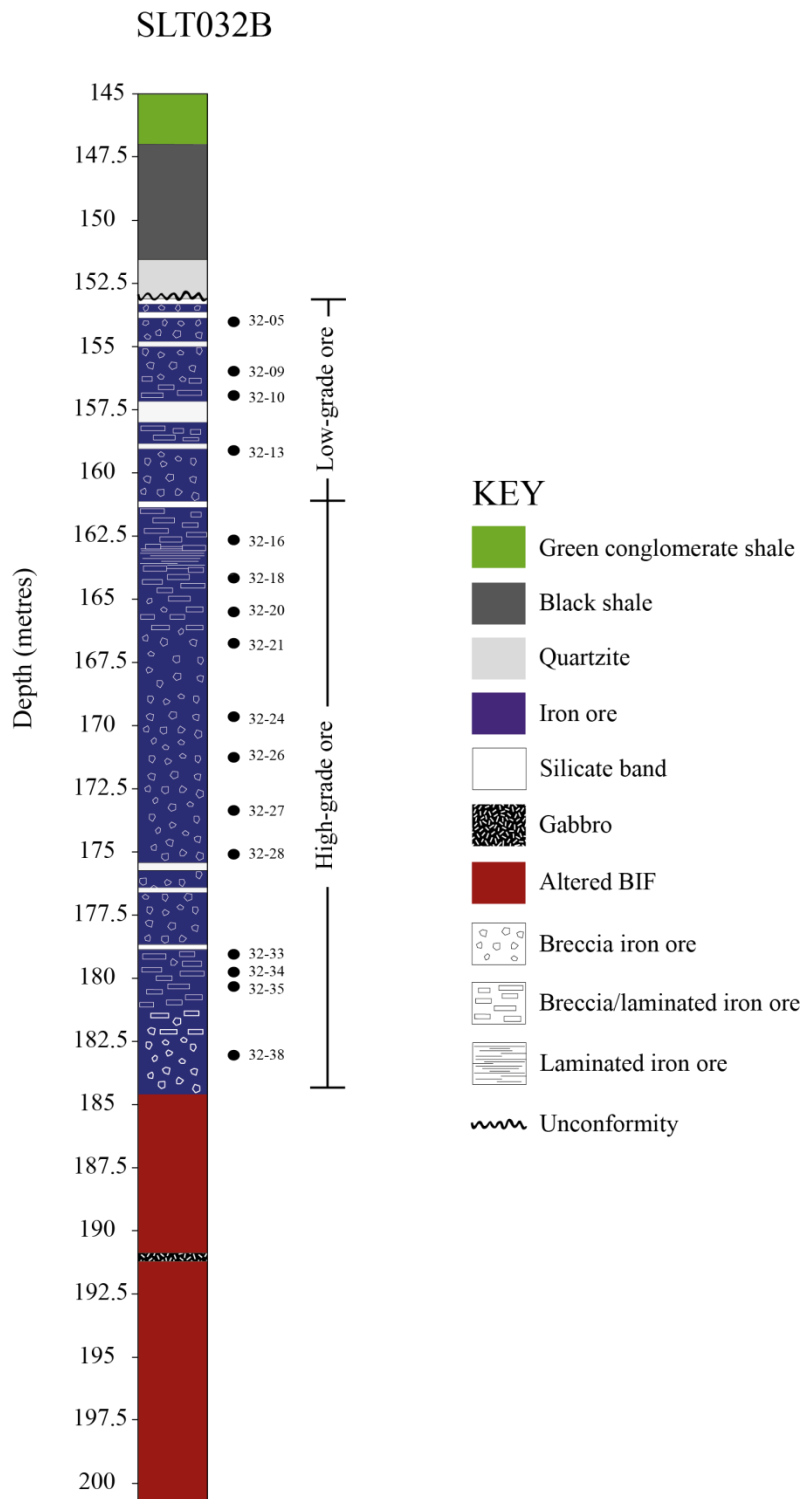


Figure 4.7. Lithostratigraphic column for the logged borehole SLT032B. The approximate stratigraphic locations of samples hand-picked for hematite are shown. There are 4 samples taken from the low-grade ore and 12 samples taken from the high-grade ore.

Stable oxygen isotope data for the 16 hand-picked hematites was obtained using the method outlined by Fourie and Harris (2011). The analyses were carried out using a gas-source Finnegan DeltaXP mass spectrometer in the Department of Geology, University of Cape Town. The REE analyses were carried out using an ICP-MS at the University of Cape Town. The approach for obtaining oxygen isotope data from hematite separates is standard procedure, whereas the analysis of REE contents in hematite separates is an unusual approach. This approach was taken to determine what concentrations of REE are hosted in the hematite. The analysis of hematite separates from the iron ore could potentially show whether the hematite records a BIF or shale REE signature. However, this approach does have a shortcoming in that the hematite separate REE data must be cautiously compared with whole-rock data due to the fact that traces of phosphates in iron ores have been demonstrated to be important carriers of REE signatures (Angerer *et al.*, 2012; Chetty and Gutzmer, 2012). Details of sample preparation, analytical techniques and x-ray diffraction spectra are available in Appendix A and Appendix C.

4.5.3 Rare earth element geochemistry – results

A total of 16 hematite separates were analysed for REE concentrations from borehole SLT032B. There were 4 samples selected from the low-grade iron ore and the remaining 12 samples from the high-grade iron ore unit (Figure 4.7). The rare earth element compositions of the samples is presented in Table 4.5, with the concentration (in ppm) of each element presented for all the hematite separates (n=16). Furthermore, a summary of the REE compositions of Mapedi shale (Land, 2010), Kuruman iron formation (Klein and Beukes, 1992) and Post-Archean Average Shale (PAAS; Taylor and McLennan, 1985) are presented in Table 4.5.

The REE data for the hematite separates can be divided into samples taken from the low-grade iron ore (n=4) and high-grade iron ore (n=12) (Figure 4.7). Overall, La concentrations range between 0.26 – 27.16 ppm, Ce between 0.28 – 63.27 ppm, Pr between 0.06 – 5.49 ppm, Nd between 0.21 – 22.67 ppm, Sm between 0.14 – 4.64 ppm and Gd between 0.27 – 3.65 ppm. There are lower concentrations of Eu ranging between 0.06 – 1.06 ppm, Tb between 0.04 – 0.45 ppm, Dy between 0.26 – 2.42 ppm, Ho between 0.06 – 0.46 ppm, Er between 0.18 – 1.45 ppm, Tm between 0.03 – 0.25 ppm, Yb between 0.18 – 1.88 ppm and Lu between 0.03 – 0.32 ppm present in the hematite separates.

Table 4.5. Absolute REE compositions for the hematite separate samples from the low-grade and high-grade iron ores of this study. Data sources: Mapedi shale* (n=8) from Land (2010), Kuruman iron formation (n=25) from Klein and Beukes (1992) and PAAS from Taylor and McLennan (1985).

Sample No. ppm	32-05	32-09	32-10	32-13	32-16	32-18	32-20	32-21	32-24	32-26	32-27	32-28	32-33	32-34	32-35	32-38	Mapedi shale (n=8)	Kuruman iron formation (n=25)	PAAS
La	0.31	9.19	11.7	27.2	1.77	0.56	0.48	2.48	1.53	16.5	0.26	0.69	1.54	2.28	4.57	0.32	38.34	2.29	38.2
Ce	0.61	20.0	27.9	63.3	4.61	1.39	1.45	8.42	3.77	61.8	0.28	3.03	2.62	5.85	12.6	0.89	90.05	3.22	79.6
Pr	0.07	1.93	2.69	5.49	0.36	0.08	0.09	0.58	0.31	4.29	0.06	0.24	0.40	0.50	1.10	0.08	8.38	0.38	8.83
Nd	0.34	7.90	10.7	22.7	1.39	0.37	0.37	2.33	1.11	18.3	0.21	1.16	1.72	2.00	4.63	0.36	30.46	1.63	33.9
Sm	0.16	1.65	2.20	4.64	0.28	0.15	0.14	0.52	0.24	4.24	0.17	0.44	0.62	0.53	1.04	0.14	5.41	0.34	5.55
Eu	0.07	0.43	0.59	1.06	0.08	0.08	0.06	0.13	0.08	1.06	0.09	0.17	0.22	0.18	0.28	0.07	1.14	0.17	1.08
Gd	0.33	1.55	2.22	3.15	0.32	0.33	0.27	0.53	0.36	3.65	0.32	0.78	0.79	0.68	0.99	0.33	4.10	0.55	4.66
Tb	0.05	0.20	0.30	0.37	0.05	0.05	0.04	0.07	0.06	0.45	0.10	0.12	0.10	0.09	0.11	0.06	0.61	0.09	0.774
Dy	0.29	1.05	1.88	2.05	0.26	0.33	0.27	0.49	0.48	2.42	0.39	0.72	0.49	0.48	0.53	0.33	3.75	0.66	4.68
Ho	0.06	0.20	0.39	0.41	0.06	0.07	0.06	0.11	0.11	0.46	0.11	0.14	0.09	0.09	0.09	0.07	0.72	0.18	0.991
Er	0.18	0.62	1.29	1.29	0.19	0.21	0.19	0.33	0.39	1.45	0.26	0.40	0.25	0.28	0.25	0.23	2.15	0.62	2.85
Tm	0.03	0.10	0.20	0.21	0.03	0.03	0.03	0.06	0.07	0.25	0.07	0.10	0.05	0.05	0.04	0.04	0.32	0.09	0.405
Yb	0.18	0.71	1.47	1.47	0.23	0.23	0.19	0.42	0.55	1.88	0.28	0.41	0.29	0.32	0.27	0.24	2.21	0.58	2.82
Lu	0.03	0.11	0.23	0.24	0.03	0.04	0.03	0.07	0.09	0.32	0.09	0.07	0.05	0.05	0.04	0.04	0.32	0.1	0.433
Σ LREE	1.5	40.6	55.2	123.2	8.4	2.5	2.5	14.3	7.0	105.2	1.0	5.6	6.9	11.2	24.0	1.8	172.6	7.9	184.8
Σ HREE	1.20	4.97	8.58	10.25	1.25	1.36	1.12	2.22	2.18	11.93	1.71	2.92	2.33	2.22	2.61	1.40	15.32	3.04	18.69
Σ REE	2.68	45.60	63.74	133.47	9.65	3.91	3.64	16.54	9.13	117.15	2.68	8.47	9.23	13.38	26.59	3.19	187.97	10.90	184.77
(Ce/Ce*) _{PN}	0.97	1.09	1.15	1.20	1.34	1.55	1.66	1.62	1.26	1.69	0.51	1.74	0.77	1.26	1.30	1.29	1.16	0.80	
(Pr/Pr*) _{PN}	0.87	0.90	0.92	0.85	0.83	0.62	0.68	0.77	0.89	0.75	1.55	0.74	1.11	0.87	0.85	0.82	0.94	0.98	
(Eu/Eu*) _{PN}	1.55	1.26	1.26	1.30	1.25	1.63	1.38	1.18	1.32	1.27	1.85	1.34	1.48	1.41	1.31	1.58	1.14	1.85	

Notes: (Ce/Ce*)_{SN} = Ce anomaly, (Pr/Pr*)_{SN} = Pr anomaly and (Eu/Eu*)_{SN} = Eu anomaly. The subscript “PN” indicates PAAS-normalized values were used to calculate the relevant anomalies.

The often anomalous behaviour of LREE can make the evaluation of the presence or absence of a La or Ce anomaly difficult (Bau and Dulski, 1996). In order to evaluate the true possibility of La and Ce anomalies, plots of Ce/Ce* against Pr/Pr* are often used as suggested by Bau and Dulski (1996) (Figure 4.8). Europium, Cerium and Praseodymium anomalies were defined quantitatively, in Table 4.5, as $Eu/Eu^* = Eu_{PN}/(Sm_{PN} * Gd_{PN})^{0.5}$, $Ce/Ce^* = Ce_{PN}/(La_{PN} * Pr_{PN})^{0.5}$ and $Pr/Pr^* = Pr_{PN}/(Ce_{PN} * Nd_{PN})^{0.5}$, respectively (Kato *et al.*, 2006; Chetty and Gutzmer, 2012). The subscript “PN” indicates PAAS-normalized values. In Figure 4.8, there is clustering of the hematite separates observed in field I. This suggests the samples exhibit a positive Ce anomaly, whereas it is important to note that the Kuruman BIF plots within field II displaying a positive La anomaly and no Ce anomaly. The hematite separate samples show a positive Eu anomaly ($Eu/Eu^* = 1.40$ average).

*Raw rare earth element data for the Mapedi shales (n=8), as studied by Land (2010), are available in Appendix B4

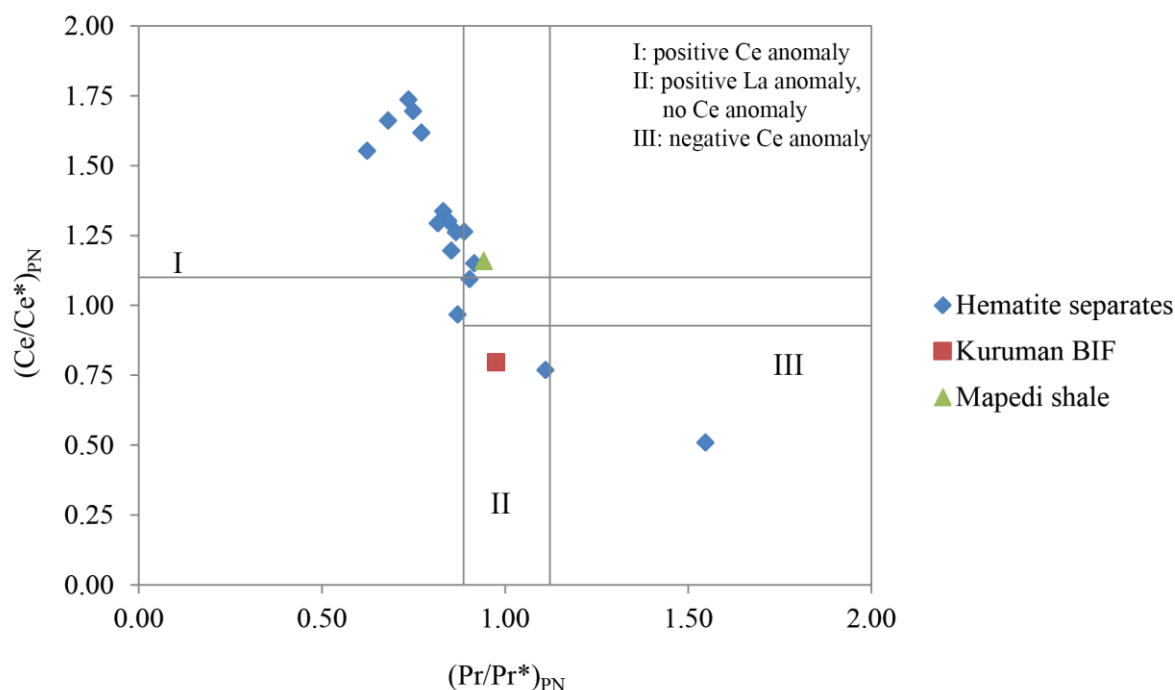


Figure 4.8. Plot of $(Ce/Ce^*)_{PN}$ versus $(Pr/Pr^*)_{PN}$ for the quantification of La and Ce anomalies. The plot illustrates the different anomaly fields, I, II and III, after Bau and Dulski (1996). A majority of the hematite separate samples plot in field I which suggests a positive Ce anomaly. The Mapedi shale samples ($n=8$) plot outside field I, whereas the Kuruman BIF samples ($n=25$) plot within field II suggesting an affinity towards a positive La anomaly and no Ce anomaly.

4.5.4 Rare earth element concentrations relative to PAAS

The concentrations of REE in each hematite sample were normalized and graphically presented in a spidergram against the Post Archean Average Shale (PAAS; Taylor and McLennan, 1985; Figure 4.9B). The diagrams facilitate comparisons with PAAS, as well as between different ore types and with Kuruman BIF and Mapedi shale. The Mapedi shales, from Land (2010), are dominated by LREE (5.4 - 90 ppm) whilst HREE are present in lower concentrations (0.3 - 4.1 ppm). The Kuruman iron formation samples, from Klein and Beukes (1992), have slightly higher concentrations of LREE (0.34 - 3.22 ppm), relative to the low HREE (0.09 - 0.66 ppm) concentrations.

In the PAAS-normalized spider diagrams, it is evident that there are two distinct groups of REE patterns present. Figure 4.9B shows that some samples exhibit relatively flat REE patterns with no appreciable variation in REE concentrations relative to PAAS. The same figure also shows REE patterns for samples displaying a distinct depletion in LREE (La-Sm) relative to HREE (Gd-Lu). The main difference between these two types of REE patterns is the concentrations of LREE. The ratio of La/Eu provides an indication of the slope of the

LREE. The samples with “flat” REE patterns have an average La/Eu ratio of 0.57, whereas the remaining samples have an average ratio of 0.22. The samples with “flat” REE patterns also show a small, albeit distinct, positive Eu anomaly.

It is interesting to note that the samples displaying “flat” REE patterns are mostly from the low-grade iron ore unit with the exception of samples 32-21, 32-26 and 32-35. By contrast, the samples displaying LREE depletion relative to HREE, represent mostly the high-grade iron ore interval with the exception of sample 32-05. The implications of this are discussed in more detail in chapter 5 later.

4.5.5 Comparisons with overlying Mapedi shales and protore BIF

In order to facilitate comparisons between the REE signatures of the hematite separates with the stratigraphically overlying Mapedi shales and the suggested protore for the iron deposit, i.e. the Kuruman Iron Formation the data are PAAS-normalized, average REE patterns for both, have been plotted in Figure 4.9A and C (Klein and Beukes, 1992). The average REE pattern of the Kuruman Iron Formation (n=25) is characterised by HREE enrichment relative to LREE and a positive Eu anomaly. The REE pattern of the Mapedi shales is generally flatter and thus shows similar REE concentrations to PAAS (Figure 4.9A), particularly with respect to LREE.

There is a striking similarity between the REE patterns of the Mapedi shales and hematite separates from the low-grade iron ore unit, while in terms of absolute REE concentrations the low-grade iron ore samples are less enriched compared to the Mapedi shales (Figure 4.9A; B). These patterns suggest that the low-grade iron ores record a REE signature similar to that of the overlying shales rather than the presumed protolith BIF.

Additionally, the REE patterns exhibited by samples from the high-grade iron ore (Figure 4.9B) show very similar REE patterns to the Kuruman Iron Formation (Figure 4.9C). In terms of absolute REE concentrations some of the hematite separates from the high-grade iron ore are depleted in LREE when compared to the Kuruman Iron Formation. These similarities suggest; (1) that the Kuruman Iron Formation could also constitute a plausible source of the REE patterns for the high-grade iron ore and (2) that the results partly conform to suggestions made by Gutzmer *et al.* (2008), whereby distinct enrichments in LREE relative to HREE are observed for all supergene high-grade iron ore deposits such as the supergene high-grade iron

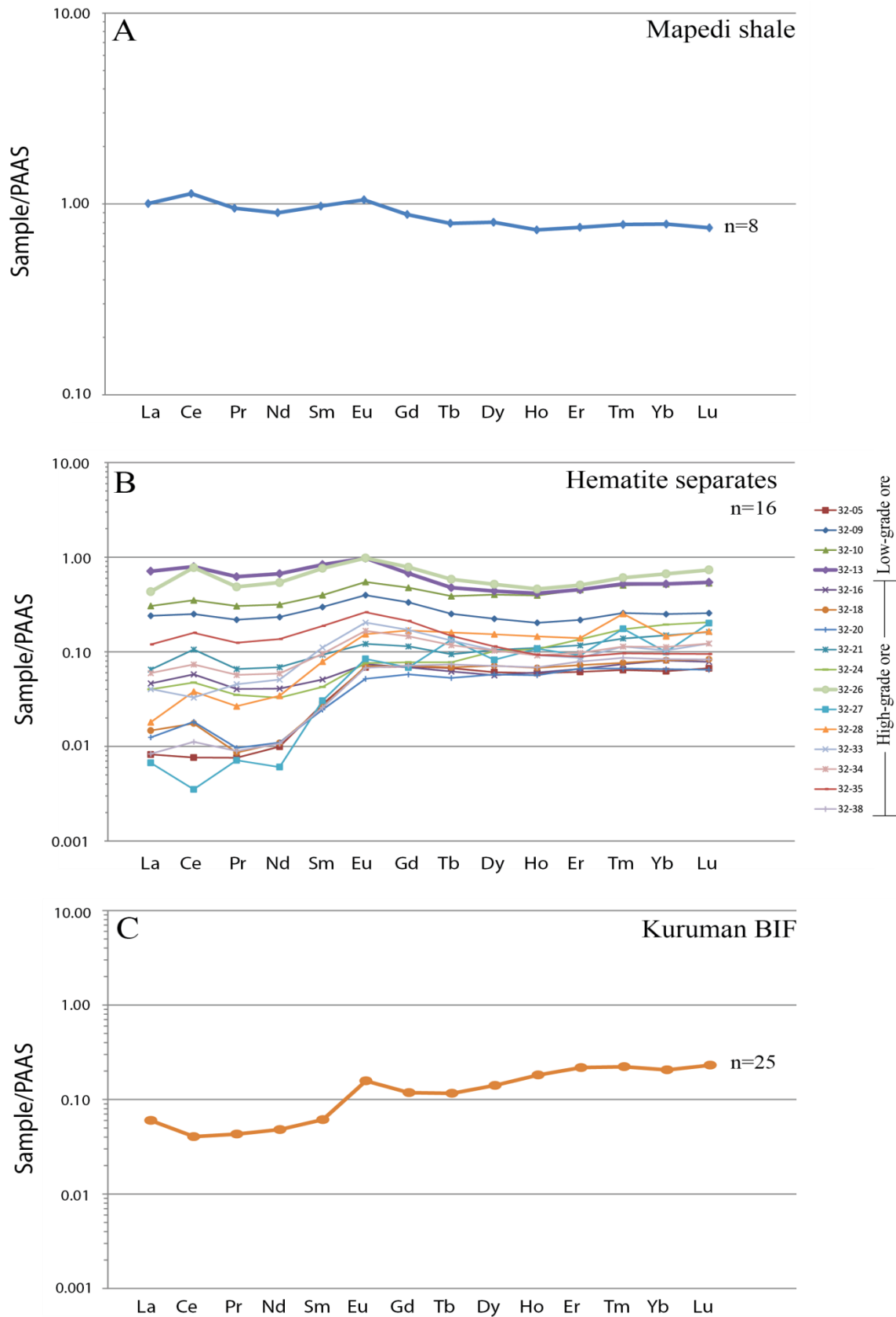


Figure 4.9. (A) PAAS-normalized average REE patterns for Mapedi shales (Land, 2010; n=8). (B) PAAS-normalized REE patterns from hematite separates from this study. (C) PAAS-normalized average REE signatures for the Kuruman iron formation. Data sources: Mapedi shale average REE data from Land (2010); Kuruman iron formation average REE data from Klein and Beukes (1992).

ores of the Maremane dome, as characterised by Beukes *et al.* (2003). These aspects will be investigated further in the final part of the thesis.

4.5.6 Oxygen isotopes – results

The $\delta^{18}\text{O}$ values for the hematite separates (Table 4.6, Figure 4.10) were obtained using the method as outlined by Fourie and Harris (2011), and ranged from -3.1 to 3.0‰, with an average of -0.7‰ (n=16). Most of the values reported in Table 4.6 gave yields between 90 to 105%, except two samples which gave a yield of 70.0% and 112.3%. The low yield value could have been due to an incomplete reaction during analysis or caused by a weighing error, whilst the high yield value is most likely due to silicate impurities in the hematite separate. These samples have not been excluded from the data set as the values are within the range of $\delta^{18}\text{O}$ values obtained for the remaining samples.

The $\delta^{18}\text{O}$ values of hematite from the iron ore of this study are shown in Figure 4.9 in comparison with other major iron ore districts from around the world. Notable here is a partial overlap between the range of $\delta^{18}\text{O}$ values presented in this study and the range shown for iron oxides from the protore BIF (Figure 4.10).

Table 4.6. Compilation of $\delta^{18}\text{O}$ isotope signatures and yield percentages from hematite separates of the iron ore from SLT032B.

Sample	$\delta^{18}\text{O}$	Yield %
32-05	-1.4	103.3
32-09	-0.4	92.5
32-10	3.0	92.3
32-13	-1.3	102.3
32-16	-3.1	92.4
32-18	2.1	70.0
32-20	-2.2	94.9
32-21	-0.9	97.4
32-24	-2.7	98.3
32-26	-0.2	105.1
32-27	-1.1	101.0
32-28	-0.2	112.3
32-33	0.3	102.0
32-34	0.1	92.8
32-35	-1.3	98.6
32-38	-2.2	101.2

Yield calculation assumes pure hematite @ 9.38 $\mu\text{mol/mg}$

$\delta^{18}\text{O}$ values normalized to VSMOW

The iron ore values from this study coincide with $\delta^{18}\text{O}$ values obtained from the Sishen iron ore deposit, located on the northern part of the Maremane anticline, which has been interpreted as an ancient supergene deposit (Beukes *et al.*, 2003; Carney and Mienie, 2003). The Thabazimbi, Hamersley, Carajas, Noamundi and Zeekoebaart deposits, which are interpreted to be hydrothermal or supergene-modified hydrothermal deposits, have significantly lower $\delta^{18}\text{O}$ values than both Sishen and the samples from this study. The $\delta^{18}\text{O}$ values for the hematite of hydrothermal origin can be as low as -7‰ and show a $\delta^{18}\text{O}$ depletion of at least 3‰ (and sometimes as much as 6‰) relative to iron oxides in the BIF protolith (Gutzmer *et al.*, 2006). The $\delta^{18}\text{O}$ values for hematite from this study are as low as -3.1‰ and show a $\delta^{18}\text{O}$ depletion of at least 1.5‰, relative to iron oxides in the Kuruman BIF protolith (Figure 4.10). The implications of the stable oxygen isotope results will be discussed further in the final part of the thesis.

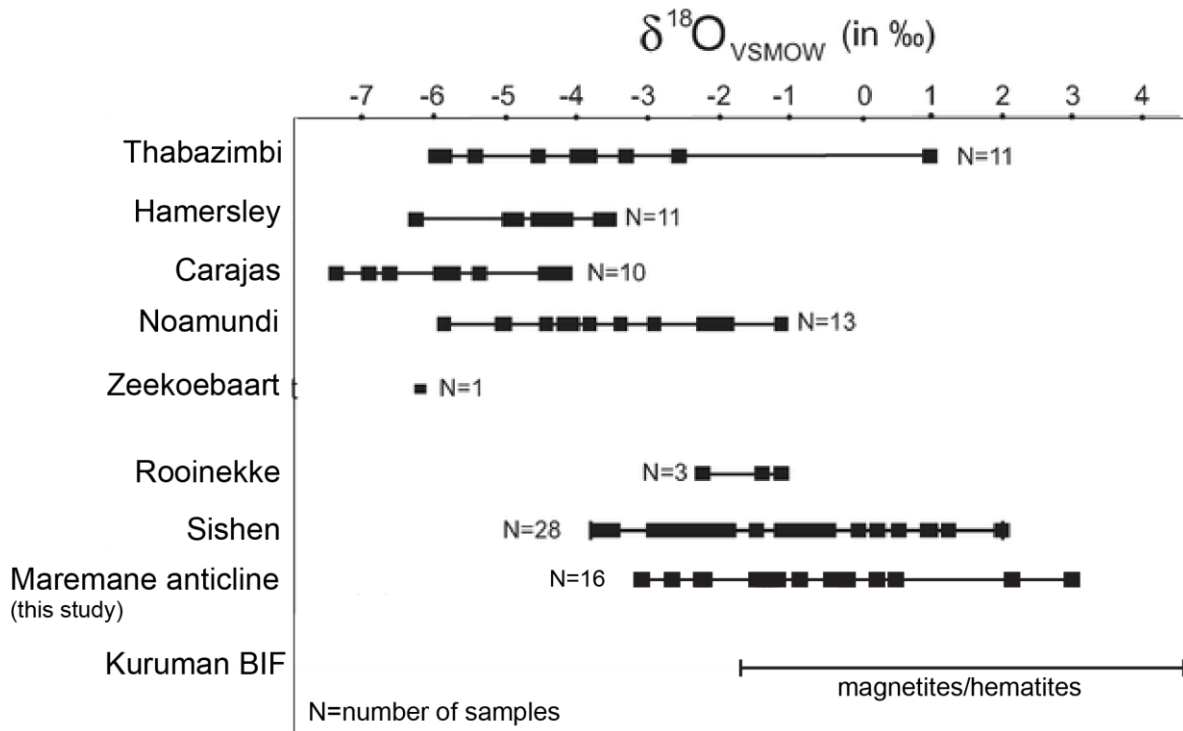


Figure 4.10. Oxygen isotope composition of hematite from various high-grade iron ore deposits (modified after Gutzmer *et al.*, 2006). The deposits have been divided into those that are interpreted as hydrothermal (Thabazimbi, Hamersley, Carajas, Noamundi and Zeekoebaart) and those that are interpreted as supergene in origin (Rooinekke and Sishen). The $\delta^{18}\text{O}$ values of Maremane anticline samples (this study) are plotted in conjunction with $\delta^{18}\text{O}$ values of the Kuruman iron formation. Data sources: Kuruman iron formation (Perry and Ahmad, 1983).

5. DISCUSSION

High-grade BIF-hosted hematite iron ore deposits are the world's most important source of iron to date. Although economically important their origin remains poorly understood. According to Klein (2005), a typical BIF is predominantly composed of Fe (up to 40 wt. %; varying proportions of FeO and Fe₂O₃), SiO₂ (up to 56 wt. %), CaO (up to 9 wt. %), Al₂O₃ (up to 1.8 wt. %) and MgO (up to 6.7 wt. %). In order to form a high-grade iron ore from a BIF protolith it would require the enrichment of iron predominantly at the expense of silica. This process would require all iron-bearing minerals (Fe-silicates, Fe-carbonates, Fe-oxides) present in the BIF to be transformed into hematite, which would be accompanied by practically complete loss of silica and carbonate material.

In order to shed light on the processes involved in the formation of the high-grade hematite iron ore from this study, the discussion will focus on the following aspects (in that order):

- (i) mineralogical and textural evidence for protolith identity;
- (ii) geochemical evidence for pre-ore lithologies, geochemical mobility and hydrothermal redistribution;
- (iii) REE geochemistry: constraints on pre-ore lithologies;
- (iv) oxygen isotope geochemistry: insights into the ore-forming process;

5.1 Mineralogical and textural evidence for protolith identity

Low-grade iron ore from this study consist of sub-angular ferruginised BIF clasts set in a very fine-grained matrix of quartz, sericite and clinocllore (Figure 5.1A). The samples are mostly matrix-supported, and the matrix mineralogically resembles the overlying Mapedi shales as described by Land (2010). The presence of hematite-rich matrix domains that appear random in orientation and crosscut apparent bedding planes (Carney and Mienie, 2003), may signify the mobilisation of Fe as well as the addition of Fe to the system through potential fluid-related processes (Figure 5.1B). Furthermore, the presence of pre-existing iron-bearing carbonates found in the ferruginised BIF clasts within the low-grade ore is suggested to represent ankerite or siderite (Beukes, 1983). This is important as it is known that carbonate minerals do not occur at all in the Mapedi shales (Land 2010), but are however found in abundance in the Kuruman Iron Formation and BIFs in general (Beukes, 1983).

Therefore, textural evidence from the low-grade iron ore suggests a combination of ferruginised BIF clasts and clastic-input from the overlying Mapedi shales (Carney and Mienie, 2003). It is possible that during brecciation of the BIF into underlying karstic depressions, overlying precursor silty material of the Mapedi shales physically infiltrated the upper parts of the slumped BIF, resulting in a combination of BIF clasts and soft, pre-cursor shale matrix. The infiltration of silt through the upper parts of the brecciated BIF would be expected to have been naturally limited further down the BIF profile. This would result in reduced dilution of BIF clasts by silicate material and the highest iron ore grades being found near the base of the BIF unit.

The bulk of the hematite in the high-grade iron ore portion occurs in the form of microcrystalline and microplaty hematite commonly accompanied by later specular hematite veins. The high-grade iron ore consists of two texturally different types namely laminated and brecciated ore. The brecciated ore is regarded here as laminated ore that has been brecciated during the collapse of BIF into underlying karst depressions. Within the high-grade iron ore, there is significantly less silicate material present when compared to the overlying low-grade iron ores.

The high-grade ore consists predominantly of dull porous hematite bands (microcrystalline and microplaty hematite) alternating with dense bright hematite-rich bands (microplaty and cryptoplaty; Figure 5.1C). The dull porous hematite bands commonly exhibit rhombohedral-shaped hematite grains closely resembling replaced carbonate minerals. The dull porous hematite bands in the ores are thought to represent earlier chert-rich bands that have been leached epigenetically, causing secondary porosity with subsequent precipitation of hematite in void space (Carney and Mienie, 2003). The dense hematite-rich bands are thought to represent oxidised equivalents of the iron-rich bands (i.e. magnetite) in the precursor banded iron formation. The bulk of the gangue mineralogy present in the high-grade iron ore is found within fractures and veins and is most likely linked to hydrothermal re-distribution during or after the ore-forming event.

The underlying siliceous BIF consists predominantly of microcrystalline quartz with disseminated fine-grained hematite. Within this unit, there appears to be loss of Fe-bearing minerals and/or addition of silica as there are only a few hematite-rich bands occurring in what was possibly a typical BIF. It is evident that in chert-rich bands, silica has replaced pre-existing medium-grained subhedral and euhedral minerals from the precursor BIF. This

siliceous BIF unit is most probably a banded iron formation due to the presence of pseudomorphed carbonate minerals as well as the relict textures of banded iron formation, which has undergone extensive silicification accompanied by some iron removal.

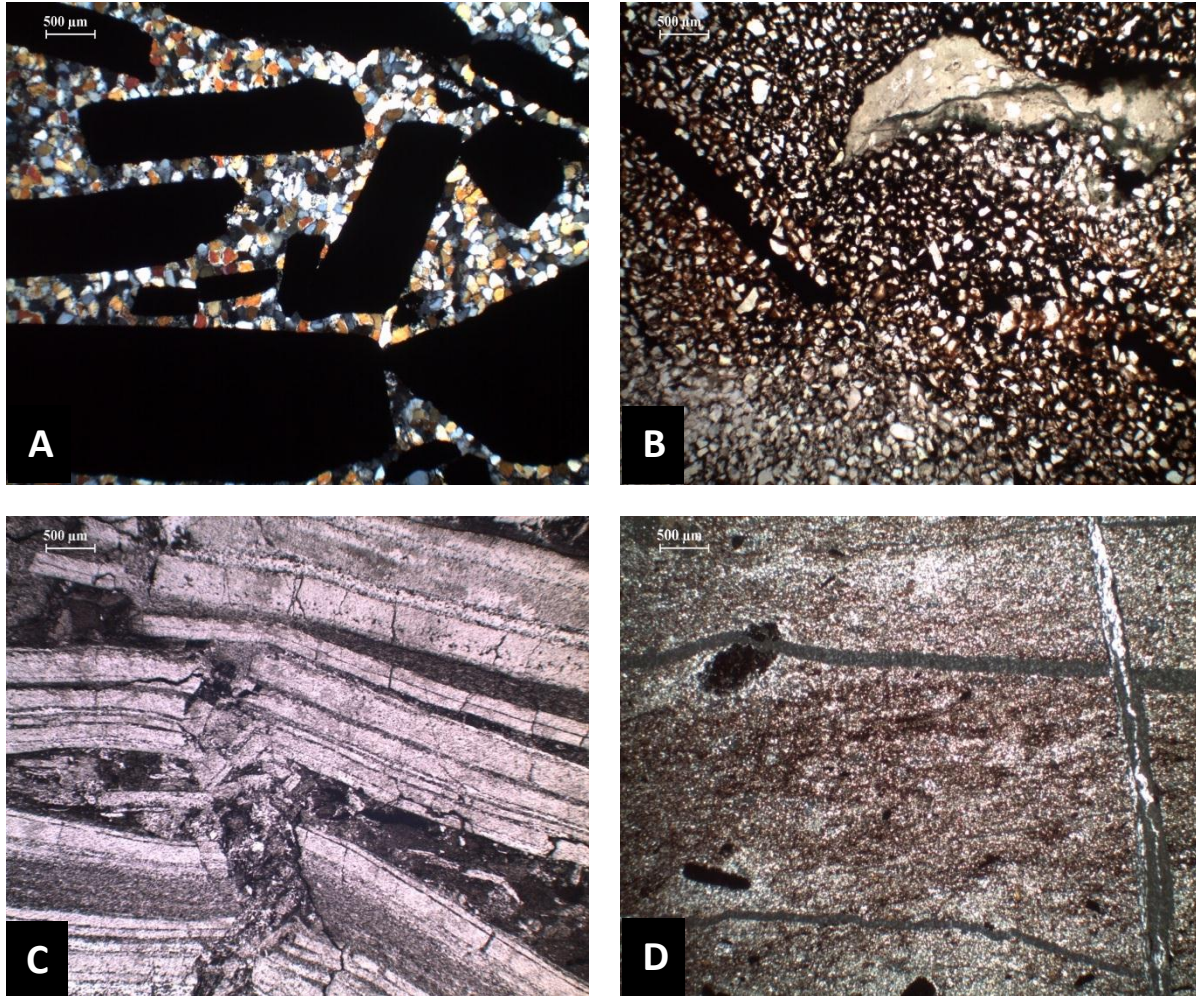


Figure 5.1. Photomicrographs of typical low-grade and high-grade iron ore textures. **A.** Typical textural example of low-grade iron ore. Hematite ore clasts (black) set in a predominantly quartz-rich matrix with some fine-grained sericite and clinocllore (Photomicrograph taken using transmitted light in CPL). **B.** Photomicrograph of low-grade iron ore illustrating massive hematite domains with apparent cross-cutting relationship (Photomicrograph taken using transmitted light in PPL). **C.** Typical example of high-grade iron ore. Brecciated laminated iron ore, almost entirely hematite, showing bright dense hematite bands alternating with dull porous hematite bands (Photomicrograph taken using reflected light). **D.** Photomicrograph of low-grade iron ore illustrating the horizontal and vertical veins of clinocllore in a very fine-grained matrix of sericite, clinocllore, quartz and hematite. (Photomicrograph taken using transmitted light in CPL).

Specular hematite-filled veins that crosscut the iron ore are thought to represent late-stage hydrothermal alteration and iron mobilisation. Such veins are present throughout the low-

grade and high-grade iron ores, and also include Al-silicates, with specular hematite precipitated on their margins (Figure 5.1D).

5.2 Geochemical evidence

5.2.1 Chemostratigraphic patterns and their relationship to pre-ore lithologies

The whole-rock geochemistry of the iron ore allows for important insights to be made with regards to the ore forming process. Identifying chemostratigraphic patterns for major and trace elements can provide information regarding the transformation of precursor iron-rich rocks into high-grade iron ore deposits as well as clues to pre-ore lithologies. The chemostratigraphic plots in Figure 5.2 are a summary of the most important signatures identified in the two selected intersections.

The upper low-grade iron ore interval is highly variable in terms of SiO_2 , Al_2O_3 , K_2O , MgO , TiO_2 , Nb and Zr, and Fe_2O_3 (Figure 5.2). A combination of sericite, quartz and clinocllore contribute to the SiO_2 , Al_2O_3 , K_2O and MgO concentrations present in the low-grade iron ore. In the iron ore unit the Fe_2O_3 concentration increases downward in the stratigraphy, with SiO_2 , Al_2O_3 , K_2O , MgO , TiO_2 , Nb and Zr all decreasing accordingly. This signals the onset of the high-grade iron ore interval, with a minimum Fe_2O_3 concentration of 85 wt. %, and very low concentrations of SiO_2 , Al_2O_3 , K_2O and TiO_2 , when compared to the overlying low-grade iron ore (Figure 5.2). Notable exceptions to this general trend are a few samples within the high-grade iron ore that have elevated concentrations of SiO_2 , Al_2O_3 , K_2O , MgO , TiO_2 , Nb and Zr. These samples contain silicate bands which are responsible for the increased concentrations in deleterious elements in the high-grade part of the ore unit. As the underlying siliceous BIF is approached, the samples become increasingly SiO_2 -rich and Fe_2O_3 -poor, with concentrations of the remaining major elements being very low and invariant across the underlying siliceous BIF (Figure 5.2).

Textural evidence from the low-grade iron ore as presented earlier in the discussion, along with the chemostratigraphic evidence, presented here, suggests that the low-grade iron ore is a combination of siliciclastic input and ferruginised BIF clasts. The silicate matrix in the low-grade iron ore samples is responsible for the concentrations of SiO_2 , Al_2O_3 , K_2O and MgO , whereas the ferruginised BIF ore clasts account for the high Fe_2O_3 concentrations. Other trace elements commonly associated with the overlying Mapedi shale, such as Zr and Nb (Land,

2010), also show elevated concentrations in the low-grade iron ore when compared to the high-grade iron ore. The high-grade iron ore thus appears to be a ferruginised BIF with the bulk of silicate assemblages hosted in veins lending support to the likelihood of hydrothermal fluid infiltration precipitating the specular hematite and silicate vein material.

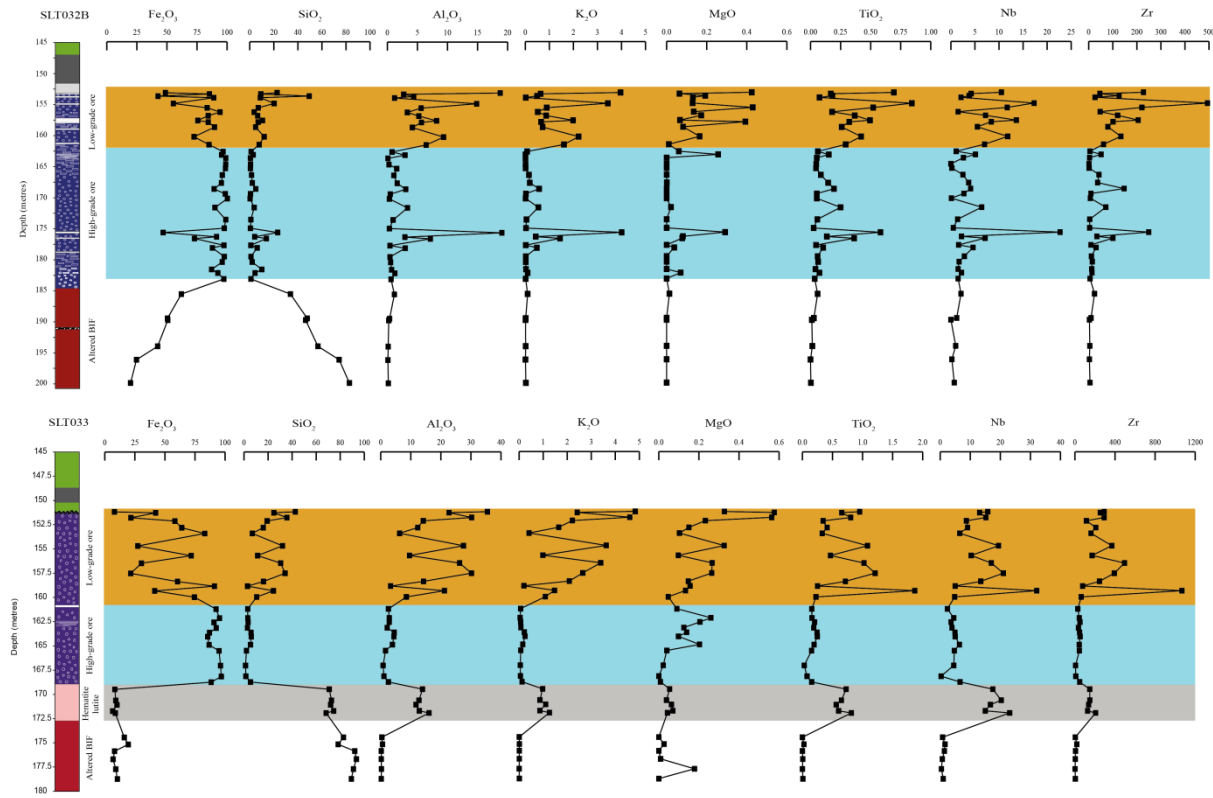


Figure 5.2. Variation plots of selected major element oxides (wt. %) and trace elements (ppm) for borehole SLT032B and SLT033. The stratigraphic column shows the low-grade iron ore, high-grade iron ore, hematite lutite and siliceous BIF. The orange-filled area corresponds to the low-grade iron ore, whereas the blue-filled area represents the high-grade iron ore.

5.2.2 Geochemical mobility during ore formation

In 1967, Gresens developed a mathematical method to establish element mobility during the transformation of a protolith to an altered rock in any given alteration process. Grant (1986) provided a simple graphical solution to Gresens' (1967) mathematical method, which requires no significant analytical data manipulation and can be easily accomplished graphically.

The basic notion behind Gresens' approach is that some elements are likely to have been immobile during the alteration process, and these can be used to determine any volume change that may have taken place. The gains and losses of various elements can then be

calculated, assuming that the calculated volume change is an influence common to the behaviour of all elements (Grant, 1986). A “constant mass isocon” can be drawn through the origin at 45° and this line assumes constant mass during the alteration from the original rock to the altered product. The immobile elements generate, through the origin, a straight line which may be called an “immobile isocon”. The deviation of element data points from the relevant isocon defines the concentration change for that element relative to the protolith (Grant, 1986).

Using Gresens’ (1967) method requires the identification of the original parent rock prior to alteration. Based on previously presented mineralogical and geochemical results (Chapter 3 and 4), there are two possible protoliths for the iron ore unit, namely the Kuruman Iron Formation (Klein and Beukes, 2002) and silty material of a source in the overlying Mapedi shales (Land 2010). Notably the results indicate that some of the hematite is also ferruginised silty material. With this in mind, isocon diagrams have been generated for the low-grade iron ore and high-grade iron ore for both such end-member protoliths, and these are presented in Figure 5.3. The four isocon graphs in Figure 5.3 were constructed for 10 major element oxides and 3 trace element components, and will allow insights into geochemical mobility and re-distribution during the ore-forming process. The isocon method was applied to samples from the low-grade iron ore (n=14), high-grade iron ore (n=34), as well as to samples from the Mapedi shales (n=25; Land, 2010) and Kuruman Iron Formation (n=25; Klein and Beukes, 2002). The data for selected major and trace elements was scaled so that they plot between the values of 0 and 30 on the x and y axes. The scaling of the data is mathematically valid and furthermore gives credence to the components considered to be trace elements relative to the major rock forming elements such as Al_2O_3 , SiO_2 and Fe_2O_3 . The isocon plots of Figure 5.3A and 5.3B also assume that the low-grade iron ore is an alteration product of a precursor geochemically similar to the Kuruman Iron Formation and Mapedi shale, respectively. By contrast, the isocon plots of Figure 5.3C and 5.3D assume that the high-grade iron ore is an alteration product of the Kuruman Iron Formation and Mapedi shale, respectively.

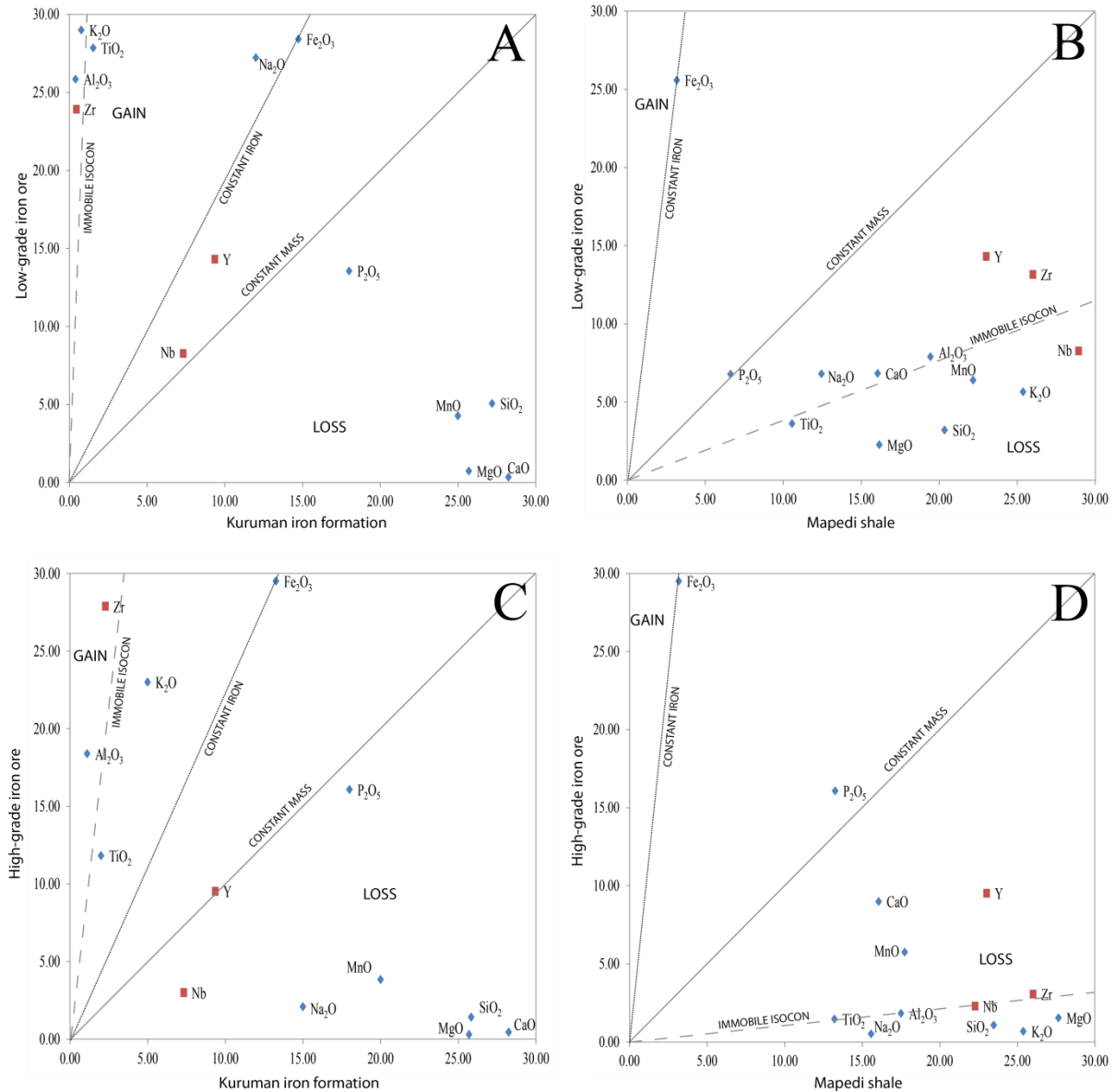


Figure 5.3. Isocon graphs illustrating average whole-rock geochemical relationships between: (A) Low-grade iron ore and Kuruman Iron Formation; (B) Low-grade iron ore and Mapedi shale; (C) High-grade iron ore and Kuruman Iron Formation; and (D) High-grade iron ore and Mapedi shale. Isocons for constant mass, constant iron and immobile elements are shown.

For the purpose of the isocon considerations, binary diagrams for selected major and trace element compositions were plotted for samples from the low-grade and high-grade iron ores. The bivariate diagrams A, B, C, E and F of Figure 5.4 illustrate the most characteristic geochemical differences between the low-grade and high-grade iron ores, which are mostly related to the relative abundance of silicate material present in the ores. The low-grade iron ore samples contain primarily quartz, clinocllore and sericite as the main silicate phases, whereas the high-grade iron ore samples contain the same silicate phases apart from sericite,

which is much less abundant. The linear correlation between K_2O and Al_2O_3 (Figure 5.4A) as well as SiO_2 and Al_2O_3 (Figure 5.4C) confirm that the silicate phases present in the low-grade and high-grade iron ores are practically the same i.e. quartz, sericite and clinocllore. These relationships also suggest that the matrix in the low-grade iron ore is largely homogenous from a geochemical viewpoint.

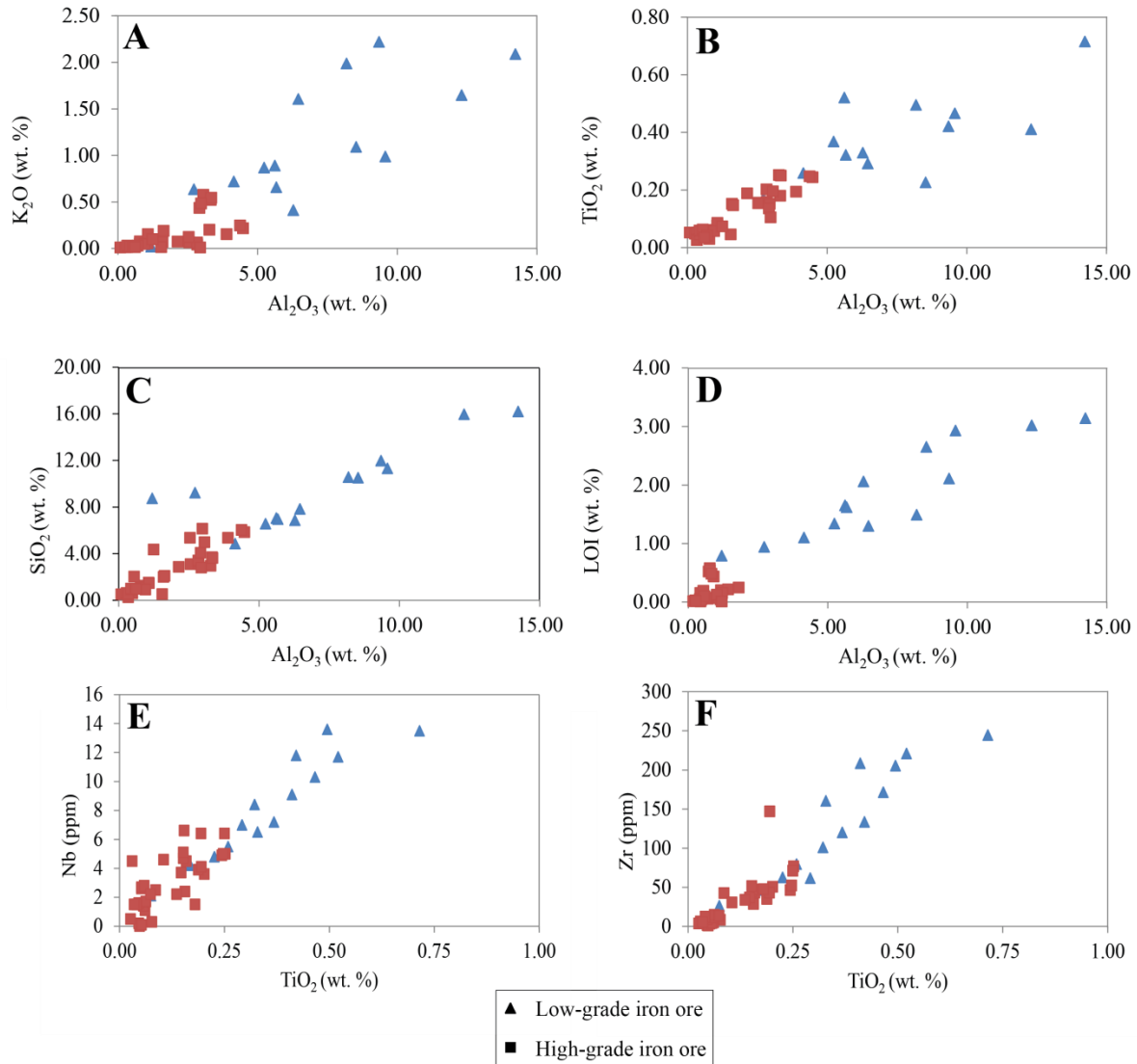


Figure 5.4. Bivariate plots of: (A) Al_2O_3 versus K_2O ; (B) Al_2O_3 versus TiO_2 ; (C) Al_2O_3 versus SiO_2 ; (D) Al_2O_3 versus LOI (loss on ignition); (E) Al_2O_3 versus Nb and (F) Al_2O_3 versus Zr for samples from low-grade and high-grade iron ores. Low-grade iron ore samples are illustrated as filled triangles, whereas high-grade iron ore samples are shown by filled squares.

The TiO_2 versus Al_2O_3 graph (Figure 5.4B) also illustrates the linear relationship and coupled behaviour between Ti and Al in the samples. Titanium and aluminium are considered to behave as immobile elements during low-temperature alteration processes, and this appears to

be the case here as well (Grant, 1982; Gutzmer *et al.*, 2008). This is important to note when defining a best-fit immobile isocon, where it is desirable to base the isocon on species that are geochemically immobile over a range of environments. It is worth noting that the LOI (loss on ignition) in Figure 5.4D corresponds essentially to the H₂O bound in the clinocllore and sericite of the samples. The linear correlation between Nb and TiO₂ (Figure 5.4E) as well as Zr and TiO₂ (Figure 5.4F) illustrates that these elements are essentially all related to the silicate fraction of the ore unit.

In light of the above, a constant mass isocon (45°), constant iron isocon and immobile element isocon have been plotted in the graphs of Figure 5.3. The three isocons represent three end-member scenarios: (1) constant mass; (2) constant iron, whereby iron was immobile and residually enriched during transformation process to form the iron ore, as suggested by most supergene-type models (Beukes *et al.*, 2003; Gutzmer *et al.*, 2008); and (3) immobility isocon, based on the assumption that aluminium, titanium and zirconium remained immobile during the alteration process.

There are a number of implications demonstrated by these isocon plots when considering the possibility of a supergene or hydrothermal model for the iron ores. It is well documented that in a supergene environment, zirconium, titanium and aluminium are immobile and concentrate in the weathering profile whereas alkali earth and alkali metal elements are typically mobile (Grant, 1982; McLennan *et al.*, 2003; Angerer *et al.*, 2012). Additionally, the immobility of iron and effective removal of silica, calcium and magnesium is often invoked in the formation supergene-related high-grade iron ore (Gutzmer *et al.*, 2008). In a supergene model it would thus be expected that zirconium, titanium, aluminium as well as iron would remain immobile and therefore should plot on or about on the same isocon. This is clearly not the case here, suggesting relative mobility of iron against immobile elements, or visa-versa.

It therefore becomes apparent that is not possible to produce a low-grade iron ore in a supergene environment, regardless of protolith, as it would require either the mobilisation of typically immobile elements or that of iron (Figure 5.3A and 5.3B). Simply speaking, if iron were assumed to be immobile during the alteration process, there would have to be a gain (Figure 5.3A) or loss (Figure 5.3B) of typically immobile elements. Similarly, if the immobile isocon held true during the alteration process, there would be either a loss (Figure 5.3A) or a significant gain (Figure 5.3B) of iron in the system.. This scenario is no different

when considering the alteration of Kuruman Iron Formation or Mapedi shale to a high-grade iron ore (Figure 5.3C and 5.3D). It is worth noting, Beukes *et al.* (2008) advocate the addition of iron by fluids in the Noamundi deposit, India

Based on the isocon diagrams alone, it appears that a simple, residual supergene model is not readily applicable, and that some sort of fluid-induced re-distribution is necessary. Such a process may implicate fluids other than meteoric water, with the ability to mobilise elements like Fe, Ti or Al (Jiang *et al.*, 2005; Evans *et al.*, 2013). The following section examines this possibility.

5.2.3 Hydrothermal redistribution during ore-forming process

The host mineralogy of the bulk of the Al_2O_3 present in the iron ore is the mineral clinochlore. The clinochlore, specifically in the high-grade iron ore, occurs in veins which are present in a variety of orientations. The clinochlore in these veins is medium-grained and subhedral, and is commonly accompanied by specular hematite.

For most of the samples in this study, iron is enriched relative to BIF by a factor that ranges between 2 and 2.4. Iron, however, is not the only element that is effectively enriched during the formation of this deposit. As indicated in the isocon diagrams of Figure 5.3., aluminium is enriched by factors between 3 and 4, whereas titanium is enriched by factors between 2 and 6 relative to BIF. Therefore, titanium and aluminium appear to be effectively more enriched than iron when compared with the precursor BIF. This is also true for the ores of the Thabazimbi, Carajas deposits and Hamersley iron ores (Taylor *et al.*, 2001; Gutzmer *et al.*, 2008). This enrichment in Al_2O_3 and TiO_2 is surprising, if in fact iron is believed to have been residually enriched during the ore-forming process (Beukes *et al.*, 2003). Although, aluminium is chemically reactive in nature, the metal reacts rapidly with oxygen to develop a layer of Al-oxide at the surface (Roberge, 2008). This layer of Al-oxide prevents the metal from reacting with water and hence aluminium becomes highly resistant to weathering (Roberge, 2008).

The Al_2O_3 and TiO_2 enrichment in the iron ores can either be attributed to (1) residual enrichment due to immobility, accompanied by iron loss; or (2) introduction of Al_2O_3 by fluids during or after the ore-forming event (Ridley, 1999; Gutzmer *et al.*, 2008). Simple residual enrichment of Al_2O_3 by the re-distribution of SiO_2 during ore formation could not account for the Al_2O_3 concentrations in the ores, unless there was considerable removal of Fe

during ore formation, as shown in the earlier presented isocon diagrams. Therefore, it appears likely that there has been an introduction of Al_2O_3 into the system either during or after the ore forming process. This is further supported by the presence of aluminium-silicate veins, particularly in the high-grade iron ore.

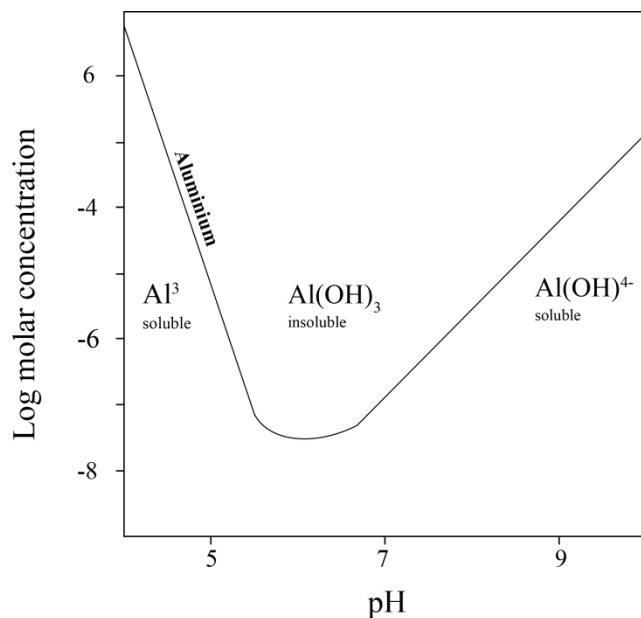


Figure 5.5. The solubility of Al as a function of pH. The diagram illustrates the relative solubility of aluminium in acidic conditions, but will precipitate and become insoluble due to hydrolysis in neutral conditions. Aluminium is again soluble in alkaline conditions (modified after Robb, 2005).

The elemental form of aluminium is never found in nature. Aluminium is soluble in extremely acidic and alkaline conditions, whereas it is insoluble in more neutral pH conditions typically present in supergene environments (Figure 5.5; Robb, 2005). Therefore, in order to mobilise any aluminium into the iron ore system, the fluids would have to be either very acidic or alkaline in order to transport it in solution.

The potential origin of these aluminium-silicates is interesting, given their similar mineralogy to the minerals found in the overlying shales and in the matrix of the low-grade iron ore. Table 5.1 shows a summary of the average whole-rock geochemical composition of the low-grade iron ore, high-grade iron ore, Mapedi shale and Kuruman Iron Formation. For comparative purposes, these average whole-rock compositions have been calculated and normalised based on a Fe_2O_3 -free basis. This allows the low-grade and high-grade iron ore silicate-related chemistry to be compared with that of the Mapedi shales and Kuruman BIF.

Table 5.1. A summary of the average whole-rock geochemical composition of the low-grade iron ore, high-grade iron ore, Mapedi shale (n=25; Land, 2010) and Kuruman Iron Formation (Klein and Beukes, 2002) normalised to Fe₂O₃-free concentrations.

wt. %	Low-grade iron ore (n=14)	High-grade iron ore (n=34)	Mapedi shale (n=25)	Kuruman BIF (n=25)
SiO₂	45.99	46.18	70.77	81.97
TiO₂	1.73	1.93	1.23	0.03
Al₂O₃	33.98	30.05	20.29	0.17
MnO	0.24	0.94	0.21	0.48
MgO	0.70	0.97	1.22	8.15
CaO	0.33	1.47	0.19	8.96
Na₂O	0.33	0.07	0.14	0.05
K₂O	5.41	2.26	5.89	0.05
P₂O₅	0.32	1.31	0.08	0.14
ppm				
Nb	33.05714286	24.85	28.94347826	18.3
Zr	526.2285714	254.5658824	260.0782609	6.25
Y	57.25714286	79.04529412	23.0173913	23.375

The TiO₂, Al₂O₃, K₂O, Nb, Zr and Y concentrations, in both the low-grade and high-grade iron ores, are very dissimilar to Fe₂O₃-free Kuruman Iron Formation. By contrast, these concentrations of deleterious elements are much more comparable to the Fe₂O₃-free geochemical signature of the Mapedi shales. It has already been suggested earlier that the matrix of the low-grade iron ore is essentially contamination from the overlying Mapedi shale, hence the similarity between the Fe₂O₃-free low-grade iron ore and Fe₂O₃-free Mapedi shale can be expected and accounted for.

Similarly, concentrations of deleterious elements in the high-grade iron ore are comparable to the Fe₂O₃-free geochemical signature of the Mapedi shales, yet the protolith has been confirmed to be BIF. It is therefore suggested here that the bulk of the deleterious components in the high-grade iron ore are possibly not residual concentrations from precursor BIF, but have in fact been derived externally and hydrothermally introduced into the system during/after the ore-forming event. It is possible that very alkaline fluids may have mobilised components from the overlying shale and subsequently transported them to the underlying high-grade iron ore, precipitating as veins in various orientations. This would result in

geochemical compositions of the Mapedi shale, low-grade and high-grade iron ores comparing remarkably well, when normalised to a Fe_2O_3 -free system.

It is well documented that Zr, Ti, Nb and Y are generally immobile elements (Grant, 1982; Fralick, 2003; McLennan *et al.*, 2003). Therefore, the average ratios of immobile elements between genetically related samples should remain relatively invariant. Immobile element bivariate plots can be used to substantiate the theory that the overlying Mapedi shales are contributors to the low-grade and the high-grade iron ore geochemistry. Figure 5.6 illustrates the strong correlation between TiO_2 and Nb in the low-grade iron ore, high-grade iron ore and Mapedi shale samples. This further elucidates the geochemical similarities between the silicates in the low-grade and high-grade iron ores as well as their genetic relationship with the overlying Mapedi shales.

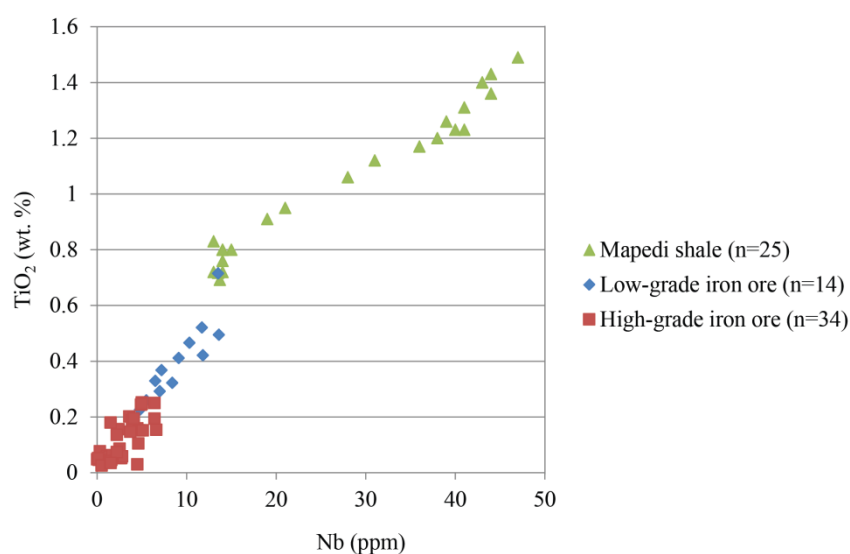


Figure 5.6. Bivariate plots of TiO_2 (wt. %) versus Nb (ppm) for low-grade iron ore (n=14), high-grade iron ore (n=34) and Mapedi shale samples (n=25; Land, 2010). The plot illustrates the strong positive correlation between TiO_2 and Nb in the iron ore samples as well as their relationship to the average TiO_2/Nb concentrations present in the Mapedi shales.

The formation of high-grade hematite iron ore from a BIF protolith essentially requires the near-complete removal of silica and effective enrichment and possible addition of iron (Evans *et al.*, 2013). The process of silica removal would have to be associated with the transformation of all iron-bearing minerals into hematite. The Kuruman banded iron formation protolith typically contains chert-rich bands and an abundance of Fe^{2+} -bearing

minerals such as carbonates (ankerite, siderite), silicates (greenalite, minnesotaite, and stilpnomelane), magnetite and only rare hematite (Beukes, 1983). Thus, in order to form a high-grade iron ore from the Kuruman Iron Formation there would have to be the transformation of Fe^{2+} to Fe^{3+} to form hematite during ore formation (Hagemann *et al.*, 2007).

The construction of an Eh-pH diagram for iron allows for the determination of conditions that would facilitate the transformation of Fe^{2+} to Fe^{3+} (Figure 5.7). The Eh-pH diagram illustrates the stability field of mineral and chemical species in terms of activity of hydrogen ions (pH) and the activity of electrons (Eh) (Rafferty, 2012). The reactions responsible for species change in Eh-pH space involve proton transfer (hydrolysis) and electron transfer (either oxidation or reduction). Figure 5.7 shows that an increase in pH, from acidic to alkaline conditions would result in Fe^{2+} oxidizing to Fe^{3+} , whereas a change in Eh, from a reducing to a more oxidizing environment, would bear the same result (Ohmoto, 2003; Takeno, 2005).

The other most important process, involving the transformation of BIF to high-grade iron ore, is silica removal (Evans *et al.*, 2013). The solubility of quartz is dependent on temperature, salinity and pH (Busey and Mesmer, 1977). The solubility of quartz increases with an increase in temperature, pH and salinity. The pH control is crucial; quartz is 4 orders of magnitude more soluble at pH 9 than in is at pH 6 (Figure 5.7; Busey and Mesmer, 1977).

The immense amount of silica removal needed for the formation of a large BIF-hosted high-grade iron ore deposit is not plausible given silica solubility in near neutral-pH meteoric waters. However, it could be produced by pervasive infiltration of a high pH ($\text{pH} > 9$) hydrothermal fluid (Dalstra and Guedes, 2004; Evans *et al.*, 2013). Alkaline hydrothermal fluids thus provide a plausible mechanism to transform Fe^{2+} to Fe^{3+} , transport SiO_2 out of the system, dissolve some carbonates as well as mobilise elements like Fe, Ti or Al (Figure 5.5; 5.7).

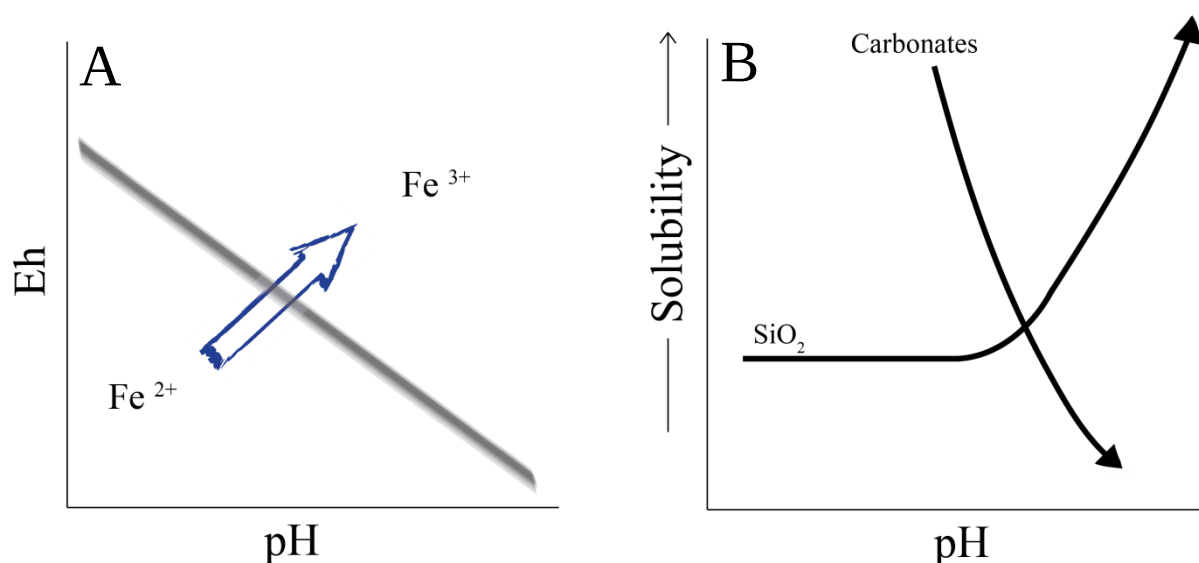


Figure 5.7. **A.** Eh-pH diagram illustrating the changes required to convert Fe^{2+} to Fe^{3+} . An increase in pH from acidic to alkaline conditions or a change in Eh from reducing to oxidizing conditions would result in the formation of Fe^{3+} -bearing minerals (modified after Takeno, 2005). **B.** The solubility of silica (SiO_2) at 25°C is shown to increase as pH increases. The diagram also illustrates the solubility curve of carbonate minerals. The solubility of carbonate species is shown to decrease as pH increases (modified after Robb, 2005; Busey and Mesmer, 1977).

5.3 Rare earth element geochemistry: constraints on pre-ore lithologies

Gutzmer *et al.* (2008) provide a comprehensive report and comparison of REE data from both supergene and hydrothermal iron ore deposits. These authors conclude that distinct enrichments in LREE relative to HREE, are observed in all supergene high-grade iron ore deposits (Figure 5.8). The concentration of LREE in the weathering profile and subsequent mobilisation of HREE are well documented in modern supergene environments (Nelson *et al.*, 2003). Greater HREE solubility relative to LREE is especially true for neutral to slightly alkaline waters; this is most likely due to the preferential complexation of HREE with ligands such as fluoride, carbonate or hydroxide anions (Nelson *et al.*, 2003). Therefore, the fractionation of LREE from HREE records the effects of chemical weathering. Additionally, Nelson *et al.* (2003) suggest that Ce anomalies in weathering environments can be explained by the preferential adsorption of Ce^{4+} onto Fe-Mn particles, which is especially common in slightly alkaline to alkaline fluids.

On the basis of the foregoing, Gutzmer *et al.* (2008) propose that REE can be used to differentiate between supergene and hydrothermal deposits. It has been documented that some hydrothermal hematite ore deposits show a marked enrichment in HREE relative to LREE, as REE are believed to behave conservatively in hydrothermal systems (Figure 5.8). Overall, the REE patterns of some hydrothermal ores remain similar to the precursor banded iron formations, suggesting that there is no preferential enrichment or introduction of REE taking place during ore formation (Figure 5.8). Essentially the REE appear to behave conservatively during hydrothermal high-grade hematite iron ore formation. However, this is not the case world-wide as it is worth noting that studies by Figueiredo *et al.* (2008) and Lobato *et al.* (2007) on the Carajas and Hamersley iron ores, respectively, show a dramatic change in the REE pattern from BIF to iron ores which is in contrast to Gutzmer *et al.* (2008).

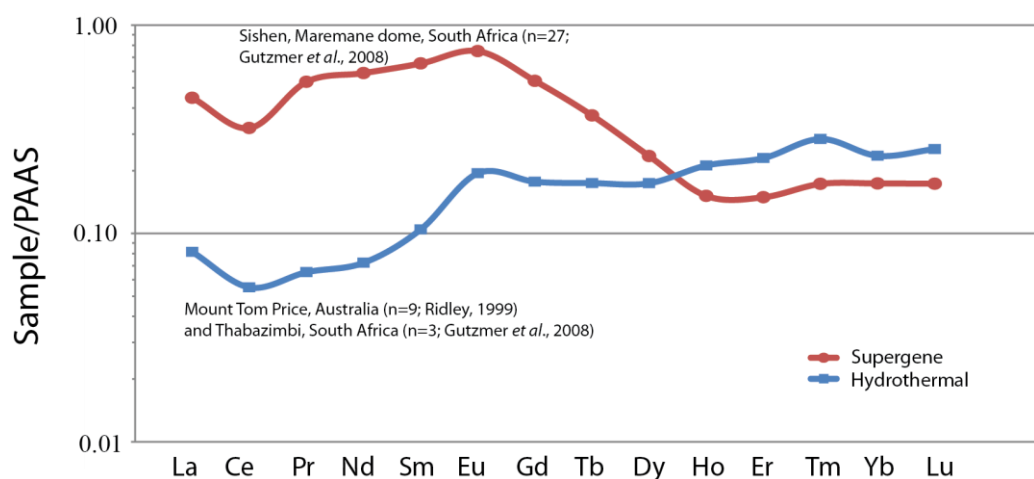


Figure 5.8. Spidergram illustrating the distinct REE compositional differences between supergene and hydrothermal high-grade hematite iron ore deposits. The supergene deposits (red) have a distinct enrichment in LREE relative to HREE. The direct opposite is observed for hydrothermal deposits (blue) where the HREE are enriched relative to LREE. Averages from each deposit type were normalized to PAAS.

The handpicked hematite samples used in this study were picked from a coarse-crush and analysed by XRD to ensure there was no contamination. Oxygen isotope yields of the same samples show that there is no silicate contamination in most of the samples analysed. Figure 5.9 shows the average REE patterns of Mapedi shale (Land, 2010; n=8), Kuruman Iron Formation (Klein and Beukes, 2002; n=25), the shale-type REE signature (mostly low-grade iron ore samples) and the BIF-type REE signature (mostly high-grade iron ore samples).

Figure 5.9 shows that low-grade iron ore has a REE signature which is remarkably similar to that of the Mapedi shale. This agrees with the mineralogy of the low-grade iron ore interval, where the samples contain significant amounts of ferruginous shale-type matrix. By contrast, the high-grade iron ore samples display an average REE signature that is strikingly similar to that of the Kuruman Iron Formation (Figure 5.9) suggesting that the high-grade iron ore has inherited a REE signature from the pre-cursor Kuruman Iron Formation.

The implications of the above are significant: if the REE behave conservatively in the iron ore, then the protolith is variable from ferruginous shale (dominantly in the low-grade iron ore) to a ferruginous BIF (dominantly in the high-grade iron ore). This would further imply that the unconformity which is thought to separate the Mapedi shales from the underlying iron ore is broadly located within the iron ore (as a gradational contact between the low-grade and high-grade ore) due to brecciation of BIF and insitu reworking with overlying shaly material. Moreover, the ferruginisation event would have to post-date the Mapedi shales and is most likely linked to a subsurface transgressive hydrothermal event which indiscriminately ferruginises both shale and BIF.

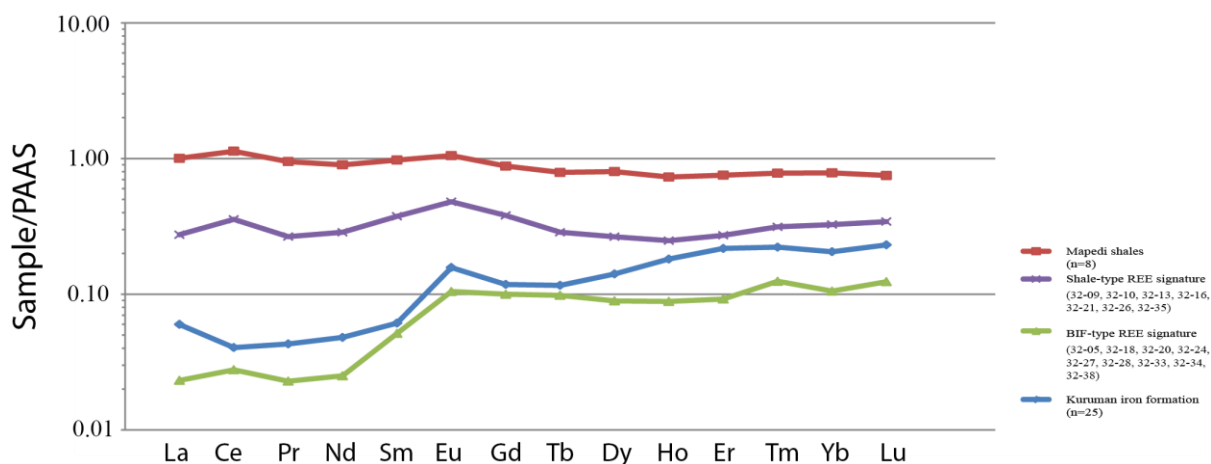


Figure 5.9. REE patterns of the Mapedi shales, low-grade iron ore, high-grade iron ore and the Kuruman Iron Formation, normalized to PAAS. The Mapedi shales REE signature (red) is an average of samples taken from Land (2010; n=8). The shale-type REE signatures (purple) come mainly from samples in the upper part of the iron ore unit. The BIF-type REE signatures (green) come predominantly from samples in the lower part of the iron ore. The REE signature of the Kuruman Iron Formation (blue) was obtained from Klein and Beukes (1992; n=25).

5.4 Oxygen isotope geochemistry: insights into the ore-forming process

High-grade iron ore deposits consist mostly of hematite which causes limitations in the types of geochemical analysis that can be used to determine the role of fluids in ore formation. Hematite is a mineral that has a wide stability field and its simple chemical composition yields little about its source. However, because iron oxides are present throughout the transformation from protore to high-grade hematite iron ore, studying their oxygen isotope compositions can provide researchers with a tool to determine the interaction of fluids with the protore (Thorne *et al.*, 2009).

At low temperatures (up to 250°C), the rate of isotopic exchange in mineral-fluid systems, that are originally far from chemical equilibrium, are mainly controlled by crystallization from the fluid phase or by the transformation of minerals to new phases (Cole *et al.*, 1983; Cole and Chakraborty, 1991). Whether the minerals crystallize directly from the fluid or are replaced by a new crystalline phase, it is certain that isotopic exchange will occur during the growth of the new mineral (Cole and Chakraborty, 1991). During the recrystallization of Fe-rich silicates, carbonates or magnetite to hematite, the Fe-O bonds are broken and reformed into new crystal structures. If this process occurs in the presence of a fluid, the oxygen incorporated into the new hematite crystal may be derived from the pre-existing mineral or from the fluid (Gregory, 1989; Thorne *et al.*, 2009). Therefore, the $\delta^{18}\text{O}$ values of the new iron oxide will be a function of the fluid to rock ratio. If the fluid-to-rock ratio is low or if the fluid is in isotopic equilibrium with the pre-existing minerals, then the newly formed phase will have similar $\delta^{18}\text{O}$ values to the original minerals. Alternatively, if the fluid to rock ratio is high, then the newly formed phase will inherit a $\delta^{18}\text{O}$ value closer to that of the fluid, and $\delta^{18}\text{O}$ values will be further removed from the $\delta^{18}\text{O}$ values of the pre-existing mineral.

The oxygen isotope compositions of iron oxides from this study are clearly depleted in $\delta^{18}\text{O}$ by at least 1.5 per mill when compared to the Kuruman Iron Formation. This depletion illustrates the importance of a fluid in the genesis of this ore deposit. In order to evaluate the significance of the $\delta^{18}\text{O}$ values in the iron oxides, one requires an understanding of the oxygen isotopic composition of the protolith, temperature of ore formation and the temperature-dependant oxygen isotope fractionation between iron oxide minerals (hematite) and water. It is suggested that the protolith for the high-grade iron ore is most likely geochemically similar to the Kuruman Iron Formation (Beukes *et al.*, 2003).

Currently the isotopic fractionation curves at low temperature for iron oxides are not entirely robust. This is due to the fact that mineral precipitates at low temperatures are usually fine-grained, poorly crystalline and can often contain large amounts of adsorbed water (Chacko *et al.*, 2001). However, for the purpose of this study it is important to note that oxygen isotope fractionation curves for iron-oxide/H₂O determined by Yapp (1990), and later by Bao and Koch (1999), compare reasonably well to the curve constructed from natural assemblages by Clayton and Epstein (1961). The temperature-dependant oxygen isotope fractionation for the hematite-water system which was experimentally determined by Yapp (1990) will be used in this study (Figure 5.10). Yapp (1990) experimentally determined the fractionation curve for the hematite-water system in the temperature range 20°C to 120°C and extrapolated it to 300°C (Figure 5.10). The hematite-water oxygen isotope fractionation curve based on the experiments is represented by the following equation:

$$1000 \ln ^{18}\alpha_{\text{min-H}_2\text{O}} = 1.63 \cdot 10^6 / T^2 - 12.3$$

The resultant curve illustrates an important crossover point at approximately 91°C. At temperatures above this point, hematite precipitating in isotopic equilibrium from a fluid should be depleted in $\delta^{18}\text{O}$, whereas below this point would result in enrichment in $\delta^{18}\text{O}$, relative to the fluid (Figure 5.10).

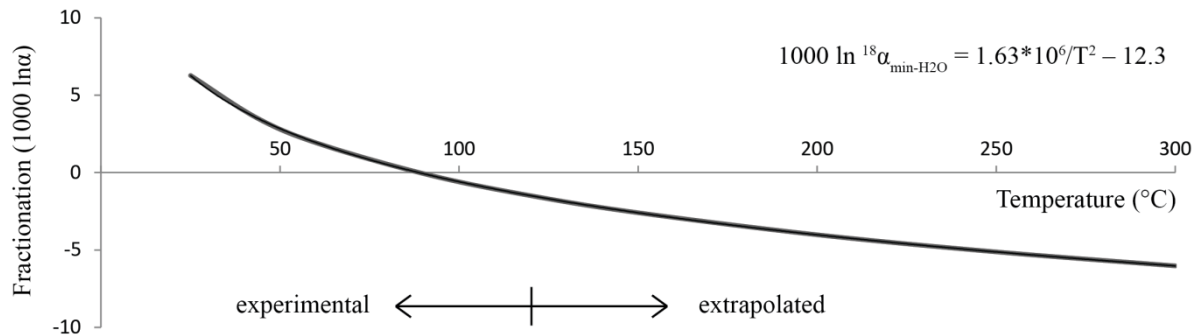


Figure 5.10. Temperature-dependant oxygen isotope fractionation curve for the hematite-water system. This fractionation curve was experimentally determined by Yapp (1990) for temperature ranges between 20°C to 120°C and extrapolated to 300°C.

An estimate of the maximum $\delta^{18}\text{O}$ value of the ore forming fluid is possible using the most $\delta^{18}\text{O}$ -depleted samples. The $\delta^{18}\text{O}$ isotope values furthest removed from the $\delta^{18}\text{O}$ values of iron oxides from the BIF protolith are regarded as the most fluid-dominated (Gutzmer *et al.*, 2008). Although, these samples are probably still comprised of a mixture of protore iron oxide and fluid-derived oxygen. It is important to note that this assessment is still based on

the assumption that there is equilibrium partitioning of oxygen isotopes. The $\delta^{18}\text{O}$ value of -3.1‰ from sample 32-16 is regarded as the furthest removed $\delta^{18}\text{O}$ value from BIF protolith (Figure 5.11). Perry and Ahmad (1983) determined that iron oxides in the Kuruman Iron Formation have $\delta^{18}\text{O}$ values between -1.5‰ to 4.5‰ (Figure 5.11).

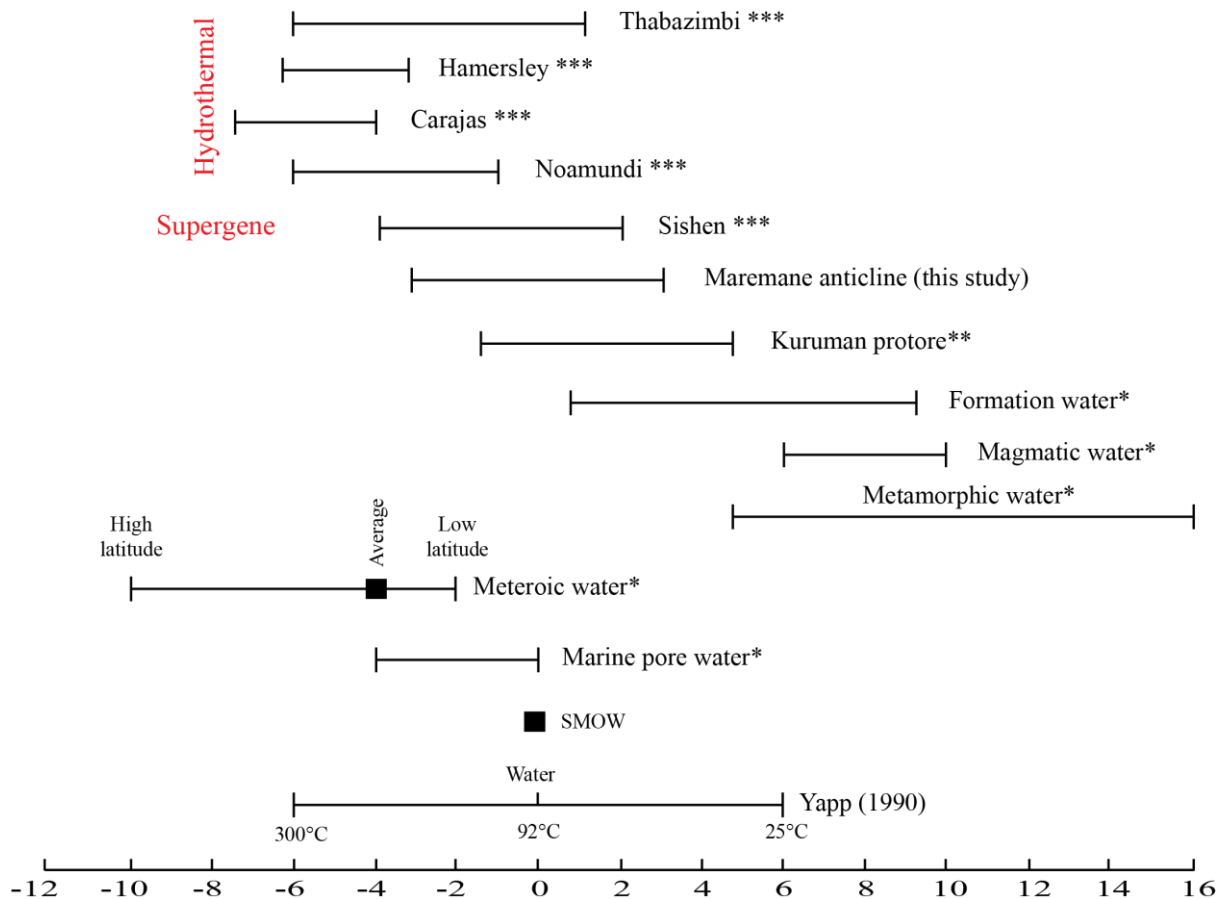


Figure 5.11. Diagram illustrating the $\delta^{18}\text{O}$ ranges of iron oxides from Thabazimbi, Hamersley, Carajas, Noamundi, Sishen and Maremane anticline (this study) iron ore deposits, the Kuruman Iron Formation and various water types. In addition the oxygen isotope fractionation factor between hematite and water, expressed as $\delta^{18}\text{O}_{\text{hematite}} - \delta^{18}\text{O}_{\text{water}}$, is shown for different temperatures as determined by Yapp (1990). Data sources: *Hoefs (2009), **Perry and Ahmad (1983), ***Gutzmer *et al.* (2008).

It has been speculated (Beukes *et al.*, 2003) that the ores found in the vicinity of the Maremane dome are of supergene origin. If this is the case, then temperatures during ore formation would be low, approximately 25°C to 30°C if at low paleo-latitudes. The temperature-dependant isotopic fractionation at 25°C results in the formation of hematite enriched in $\delta^{18}\text{O}$ by up to +6‰ (Figure 5.10; Yapp, 1990). If this fractionation factor is

applied to the $\delta^{18}\text{O}$ values of hematite from this study, the estimated maximum $\delta^{18}\text{O}$ value of the fluid from which the hematite precipitated is approximately -9‰. Figure 5.11 illustrates the $\delta^{18}\text{O}$ ranges of various water types. Based on this, if the temperature of ore formation is around 25°C it is suggested that the fluid is most likely meteoric water.

By contrast, if the hematite is hydrothermal, as earlier suggested, then a temperature of ore formation between 75°C and 150°C is plausible. The temperature-dependant isotopic fractionation at 75°C and 150°C results in the formation of hematite enriched in $\delta^{18}\text{O}$ by +0.8‰ and -2.6‰ relative to the fluid, respectively (Figure 5.10; Yapp, 1990). If these fractionation factors are applied to the $\delta^{18}\text{O}$ values of hematite from this study, the estimated maximum $\delta^{18}\text{O}$ value of the fluid is approximately -3.8‰ (at 75°C) or -0.4‰ (at 150°C). It is thus evident that with increasing fluid temperatures it is possible to advocate fluids in the genesis of the hematite which are isotopically heavier, such as formation or metamorphic fluids (Figure 5.11).

Nonetheless, it is clear that a better evaluation of the hematite oxygen isotope geochemistry is presently hindered by the lack of constraints with regards to the temperature of ore formation, as well as the fluid $\delta^{18}\text{O}$ composition. A study which assesses the temperature of ore formation independently based on possible fluid inclusions in hematite would greatly assist in a more comprehensive evaluation of oxygen isotope geochemistry for this deposit.

6. SUMMARY AND CONCLUSIONS

6.1 Possible genetic model

It has been established that the iron ore deposit in this study has a low-grade iron ore unit composed of a shale and BIF protolith component, whereas the underlying high-grade iron ore is established to have once been a BIF. The processes that lead to the formation of this iron ore deposit will now be discussed.

Many researchers, including Beukes *et al.* (2003), Carney and Mienie (2003) and Gutzmer *et al.* (2008), have concluded that these ores, of BIF protolith, are due to supergene enrichment. This was based mainly on: (1) the crosscutting nature of hematite mineralisation in the shales and iron ore; (2) gradational contacts between BIF and overlying iron ore; and (3) the relict BIF textures in the iron ore.

The crosscutting nature of hematite mineralisation in the overlying Mapedi shales suggests that there was a post-Mapedi ferruginisation event (Land, 2010). It is the author's opinion that these crosscutting relationships of hematite mineralisation in the iron ore and Mapedi shales cannot readily be attributed to supergene processes. Interestingly, the marked enrichment of HFSE in the iron ores relative to the protolith, is similar to HFSE enrichment documented by Land (2010) in the stratigraphically overlying Mapedi shales. In this study, the authors identified anomalous HFSE concentrations in the lower part of the Mapedi shales. This was suggested to be due to post-depositional metasomatic alteration as a result of alkaline hydrothermal fluid-flow.

The low-grade and high-grade iron ores of the central Maremane anticline are suggested to have been formed by alkaline hydrothermal fluids, which provide a plausible mechanism to transform Fe^{2+} to Fe^{3+} , transport SiO_2 out of the system, dissolve carbonates and mobilise elements like Fe, Ti or Al.

It is speculated that during brecciation of the Asbestos Hills BIF into underlying karstic depressions, the overlying precursor of the Mapedi shales physically infiltrated the upper parts of the slumped BIF, resulting in a combination of BIF clasts and soft, pre-cursor shale

matrix. The brecciated ore in this deposit is regarded as laminated ore that was brecciated during the collapse of BIF into underlying karst depressions.

A strictly supergene model would result in zirconium, titanium, aluminium as well as iron remaining immobile. The isocons constructed in this thesis suggest that a simple, residual supergene model is not applicable here, pointing to relative mobility of iron against immobile elements, or visa-versa, via some sort of fluid-induced re-distribution. This fluid-induced re-distribution is represented by the veins present throughout the iron ore which share geochemical characteristics with the overlying Mapedi shales. It is possible that very alkaline fluids may have mobilised components from the overlying shale and subsequently transported them to the underlying iron ore.

The geochemistry indicates that the REE behave conservatively in the iron ore and therefore a variable protolith from ferruginous shale (dominantly in the low-grade iron ore) to a ferruginous BIF (dominantly in the high-grade iron ore) is suggested. This implies that the unconformity, thought to separate the Mapedi shales from the underlying iron ore, is broadly located within the iron ore due to brecciation of BIF and insitu reworking with overlying shales. Moreover, the ferruginisation event would have to post-date the Mapedi shales and is most likely linked to a subsurface transgressive hydrothermal event which indiscriminately ferruginises both shale and BIF.

The following is a summary of the sequence of events that are suggested to be responsible for the formation of the Maremane anticline high-grade hematite iron ore deposit (Figure 6.1):

- Formation of Campbellrand dolomites and overlying Kuruman Iron Formation (Fig. 6.1A)
- Dissolution of dolomites to form ancient karst environments; researchers have long suggested that the karstification and subsequently formed Wolhaarkop breccia, which occurs at the base of the karsts, has played a critical role and is intimately related in the ore-forming process (Carney and Mienie, 2003). Groundwater, which played a role in the karstification process, would have been acidic in order to dissolve the Campbellrand dolomites (Carney and Mienie, 2003). This is an on-going process and occurs even today.
- Slumping of overlying Kuruman Iron Formation into underlying karsts and subsequent brecciation. Deposition of overlying Mapedi shales and some degree of

infiltration of silty material into upper part of iron ore horizon; some insitu reworking of BIF clasts with overlying shale material (Fig. 6.1B)

- Leaching of SiO_2 and carbonates from Kuruman Iron Formation by alkaline hydrothermal fluids and transformation of any Fe^{2+} -bearing minerals to hematite (Fig. 6.1C); it is possible that the fluid uses the Transvaal-Olifantshoek unconformity as a fluid conduit and subsequently flows through the brecciated BIF along pre-existing fracture systems
- Remobilisation of silica and aluminium by alkaline hydrothermal fluids and development of Al-silicate veins in underlying iron ores (Fig. 6.1C)
- Re-mobilisation of iron into the system to form specular hematite-chlorite veins and further upgrade the iron ores (Fig. 6.1D)

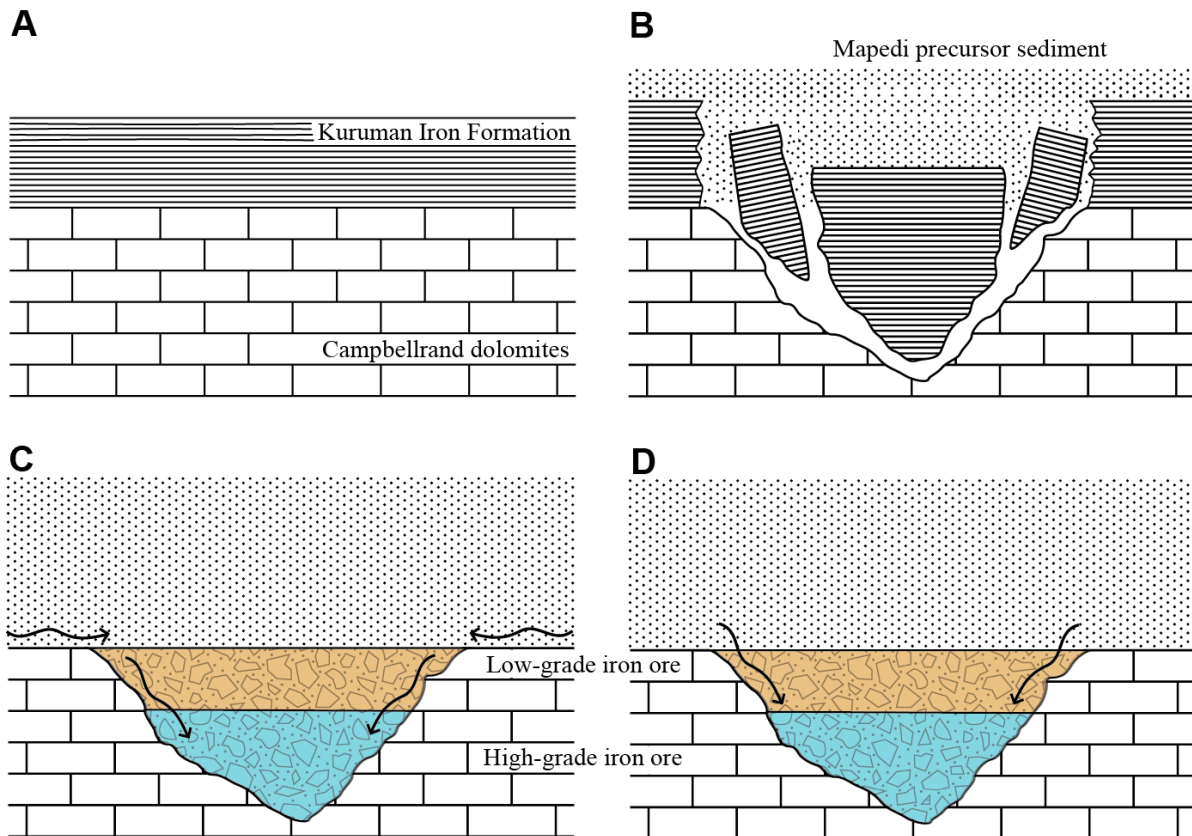


Figure 6.1. Illustration showing the sequence of events that are suggested to have led to the formation of the Maremane anticline high-grade hematite iron ore deposit.

6.2 Suggestions for further study

The strong possibility that the iron ore deposits located on the Maremane anticline are related to hydrothermal processes has several implications. Most importantly, further exploration for high-grade iron ore bodies, need not necessarily have to follow extensions of the pre-Mapedi unconformity, unless the hydrothermal event is structurally controlled by the unconformity. Research conducted on the structural control of the ore-forming fluids would help assess the importance of the unconformity as a key factor in ore genesis. There is scope for additional geochemical work to be carried out involving trace elements that were not analysed in this study, as well as potential work on iron isotopes of hematite with the view to identify different generations of hematite present in the ores. Moreover, constraints on the temperature of ore formation using fluid inclusion studies of the hematite, siliceous BIF and possibly the Wolhaarkop breccia would be useful in the interpretation of the isotope geochemistry. In addition, radiogenic isotope analysis of the silicate-rich low-grade iron ore may yield information on the source and age of the contamination in the iron ore.

7. REFERENCES

- Alchin, D., Lickfold, V., Mienie, P. J., Nel, D., & Strydom, M. (2008). An Integrated Exploration Approach to the Sishen South Iron Ore Deposit, Northern Cape Province, South Africa, and Its Implication for Developing a Structural and/or Resource Model for These Deposits. *Reviews in Economic Geology* 15, 317-338.
- Altermann, W., & Wotherspoon, J. M. (1995). The carbonates of the Transvaal and Griqualand West Sequences of the Kaapvaal Craton, with special reference to the Lime Acres limestone deposit. *Mineralium Deposita* 30, 124-134.
- Angerer, T., Hagemann, S. G., & Danyushevsky, L. V. (2012). Geochemical evolution of the banded iron formation-hosted high-grade iron ore system in the Koolyanobbing Greenstone Belt, Western Australia. *Economic Geology* 107, 599 - 644.
- Astrup, J., Hammerbeck, E. C., & van den Berg, H. (1998). Iron in The Mineral Resources of South Africa (M.G.C. Wilson and C.R. Anhaeusser, eds): Handbook. *Council for Geoscience* 16, 402-415.
- Bao, H., & Koch, P. L. (1999). Oxygen isotope fractionation in ferric oxide-water systems: Low temperature synthesis. *Geochimica et Cosmochimica* 63, 599 - 613.
- Barton, P. (2002). A Biographical Memoir: Harold Lloyd James. *Biographical Memoirs* 81, 19p.
- Bau, M. (1993). Effects of syn-depositional and post-depositional processes on the rare-earth element distribution in Precambrian iron-formations. *European Journal of Mineralogy* 5, 257-267.
- Bau, M., & Dulski, P. (1996). Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Research* 79, 37 - 55.
- Bau, M., Romer, R. L., Luders, V., & Beukes, N. J. (1999). Pb, O, and C isotopes in silicified Mooidraai dolomite (Transvaal Supergroup, South Africa): implications for the

- composition of Paleoproterozoic seawater and 'dating' the increase of oxygen in the Precambrian atmosphere. *Earth and Planetary Science Letters* 174, 43-57.
- Bekker, A., Slack, J. F., Planavsky, N., Krapez, B., Hofmann, A., Konhauser, K. O., & Rouxel, O. J. (2010). Iron Formation: The Sedimentary Product of a Complex Interplay among Mantle, Tectonic, Oceanic, and Biospheric Processes. *Economic Geology* 105, 467-508.
- Beukes, N. J. (1979). Litostratigrafiese onderverdeling van die Schmidtsdrif Subgroep van die Ghaap Groep in Noord-Kaapland. *Transactions of the Geological Society of South Africa* 82, 313-327.
- Beukes, N. J. (1980). Stratigrafie en litofasies van die Campbellrand-Subgroep van die Proterofitiese Ghaap-Groep, Noord-Kaapland. *Transactions of the Geological Society of South Africa* 83, 141-170.
- Beukes, N. J. (1983). Palaeoenvironmental setting of iron-formations in depositional basin of the Transvaal Supergroup, South Africa, in: Iron-formations: Facts and Problems, eds., A.F. Trendall and R.C. Morris. *Developments in Precambrian Geology* 6, 131-198.
- Beukes, N. J. (1984). Sedimentology of the Kuruman and Griquatown Iron-Formations, Transvaal Supergroup, Griqualand West, South Africa. *Precambrian Research* 24, 47-84.
- Beukes, N. J. (1986). The Transvaal Sequence in Griqualand West, in: Mineral Deposits of Southern Africa, eds., C.R. Anhaeusser and S. Maske. *Geological Society of South Africa* 1, 819-828.
- Beukes, N. J. (1987). Facies relations, depositional environments and diagenesis in a major early proterozoic stromatolitic carbonate platform to basinal sequence, Campbellrand Subgroup, Transvaal Supergroup, Southern Africa. *Sedimentary Geology* 54, 1-46.
- Beukes, N. J., & Gutzmer, J. (2008). Origin and Paleoenvironmental Significance of Major Iron Formations at the Archean-Paleoproterozoic Boundary. *Reviews in Economic Geology* 15, 5-47.

- Beukes, N. J., & Smit, C. A. (1987). New evidence for thrust faulting in Griqualand West, South Africa: Implications for stratigraphy and the age of red beds. *South African Journal of Geology* 90, 378-394.
- Beukes, N. J., Gutzmer, J., & Mukhopadhyay, J. (2003). The geology and genesis of high-grade hematite iron ore deposits. *Transactions of the Institute of Mining and Metallurgy B - Applied Earth Sciences* 112, B18-B25.
- Beukes, N. J., Gutzmer, J., & Mukhopadhyay, J. (2008). Genesis of high-grade iron ores of the Archean Iron Ore Group around Noamundi, India. *Economic Geology* 103, 365 - 386.
- Busey, R. H., & Mesmer, R. E. (1977). Ionization equilibria of silicic acid and polysilicate formation in aqueous sodium chloride solutions to 300C. *Inorganic Chemistry* 16, 2444 -2450.
- Button, A. (1976). Iron formations as an end member in carbonate sedimentary cycles in the Transvaal Supergroup, South Africa. *Economic Geology* 17, 193-201.
- Carney, M. D., & Mienie, P. J. (2003). A geological comparison of the Sishen and Sishen South (Welgevonden) iron ore deposits, Northern Cape Province, South Africa. *Transactions of the Institute of Mining and Metallurgy B - Applied Earth Sciences* 112, B81 - B88.
- Chacko, T., Cole, D. R., & Horita, J. (2001). Equilibrium Oxygen, Hydrogen and Carbon isotope fractionation factors applicable to geologic systems, in Valley, J.W., and Cole, D.R., eds., Stable isotope geochemistry, Reviews in Mineralogy and Geochemistry 43. 1 - 62.
- Chetty, D., & Gutzmer, J. (2012). REE redistribution during hydrothermal alteration of ores of the Kalahari Manganese Deposit. *Ore Geology Reviews* 47, 126 - 135.
- Clayton, R. N., & Epstein, S. (1961). The use of oxygen isotopes in high-temperature geological thermometry. *Journal of Geology* 69, 447 - 452.
- Clout, J. M. (2003). Upgrading processes in BIF-derived iron ore deposits: implications for ore genesis and downstream mineral processing. *Transactions of the Institute of Mining and Metallurgy B - Applied Earth Sciences* 112, B89- B94.

- Cole, D. R., & Chakraborty, S. (2001). Rates and mechanisms of isotopic exchange, in Valley, J.W., and Cole, D.R., eds., *Stable isotope geochemistry, Reviews in Mineralogy and Geochemistry* 43, 83 -224.
- Cole, D. R., Ohmoto, H., & Lasaga, A. C. (1983). Isotopic exchange in mineral-fluid systems. I. Theoretical evaluation of oxygen isotopic exchange accompanying surface reactions and diffusion. *Geochimica et Cosmochimica Acta* 47, 1681a - 1693.
- Cornell, D. H., Schutte, S. S., & Eglington, B. L. (1996). The Ongeluk basaltic andesite formation in Griqualand West, South Africa: Submarine alteration in 2222Ma Proterozoic sea. *Precambrian Research* 79, 101-124.
- Dalstra, H., & Guedes, S. (2004). Giant hydrothermal hematite deposits with Mg-Fe metasomatism: A comparison of the Carajas, Hamersley, and other ores. *Economic Geology* 99, 1793-1800.
- Dalstra, H., & Rosiere, C. A. (2008). Structural controls on the high-grade iron ores hosted by banded iron formations: A global perspective. *Reviews in Economic Geology* 15, 73 - 106.
- De Kock, M. O., Evans, D. A., Gutzmer, J., Beukes, N. J., & Dorland, H. C. (2008). Origin and Timing of Banded Iron Formation-Hosted High-Grade Hard Hematite Deposits - A Paleomagnetic Approach. *Reviews in Economic Geology* 15, 49-71.
- Donskoi, E., Suthers, S. B., Fradd, S. B., Young, J. M., Campbell, J. J., Raynlyn, T. D., & Clout, J. M. F. (2007). Utilization of optical image analysis and automatic texture classification for iron ore particle characterisation. *Minerals Engineering* 20, 461 - 471.
- Dorland, H. (1999). Paleoproterozoic laterite, red beds and ironstone of the Pretoria Group with reference to the history of atmospheric oxygen. MSc Thesis (unpublished), Rand Afrikaans University, Johannesburg.
- Dreyer, C. J., & Sohnge, A. P. (1992). The crocidolite and amosite deposits of the Republics of South Africa and Bophuthatswana: Handbook. *Geological Survey of South Africa* 12, 126.

- Dub, V. S., Dub, A. V., & Makarycheva, E. V. (2006). Role of impurity and process elements in the formation of structure and properties of structural steels. *Metal Science and Heat Treatment* 48, 279-286.
- Eriksson, P. G., & Altermann, W. (1998). An overview of the geology of the Transvaal Supergroup dolomites (South Africa). *Environmental Geology* 36, 179-188.
- Eriksson, P. G., Altermann, W., & Hartzler, F. J. (2006). The Transvaal Supergroup and its precursors, in: The Geology of South Africa, eds., M.R. Johnson, C.R. Anhaeusser and R.J. Thomas. *Geological Society of South Africa*, 237-260.
- Evans, D. A., Gutzmer, J., Beukes, N. J., & Kirschvink, J. L. (2001). Paleomagnetic constraints on ages of mineralization in the Kalahari Manganese Field, South Africa. *Economic Geology* 96, 621 - 631.
- Evans, K. A., McCuaig, T. C., Leach, D., Angerer, T., & Hagemann, S. G. (2013). Banded iron formation to iron ore: A record of the evolution of Earth environments? *Geology* 41, 99 - 102.
- Figueiredo e Silva, R. C., Hagemann, S., Lobato, L. M., Rosiere, C. A., Banks, D. A., Davidson, G. J., Vennemann, T., & Hergt, J. (2013). Hydrothermal Fluid Processes and Evolution of the Giant Serra Norte Jaspilite-hosted Iron Ore Deposits, Carajas Mineral Province, Brazil. *Economic Geology* 108, 739 - 779.
- Figueiredo e Silva, R. C., Lobato, L. M., Rosiere, C. A., Zucchetti, M., Hagemann, S., Baars, F. J., Morais, R., & Andrade, I. (2008). Hydrothermal origin for the jaspilite-hosted, giant Serra Norte iron ore deposits in the Carajas mineral province, Para State, Brazil. *Reviews in Economic Geology* 15, 255-290.
- Fourie, D. S., & Harris, C. (2011). O-isotope Study of the Bushveld Complex Granites and Granophyres: Constraints on Source Composition, and Assimilation. *Journal of Petrology* 52, 2221-2242.
- Fralick, P. (2003). Geochemistry of clastic sedimentary rocks: ratio techniques, in Lentz, D.R., ed., *Geochemistry of Sediments and Sedimentary rocks: Evolutionary Considerations to Mineral Deposit-Forming Environments. Geotext* 4, 85 - 103.

- Friede, H. M. (1980). Iron Age mining in the Transvaal. *Journal of the South African Institute of Mining and Metallurgy*, 156-165.
- Gibbons, W. (1998). The Exploitation and Environmental Legacy of Amphibole Asbestos: A Late 20th Century Overview. *Environmental Geochemistry and Health* 20, 213-230.
- Gole, M. J., & Klein, C. (1981). Banded Iron-Formation through much of Precambrian Time. *Journal of Geology* 81, 169-183.
- Grant, J. A. (1986). The isocon diagram - a simple solution to Gresens equation or metasomatic alteration. *Economic Geology* 81, 1976 - 1982.
- Gregory, R. T., Criss, R. E., & Taylor, H. P. (1989). Oxygen isotope exchange kinetics of mineral pairs in closed and open systems: applications to problems of hydrothermal alteration of igneous rocks and Precambrian iron formations. *Chemical Geology* 75, 1 - 42 .
- Gresens, R. L. (1967). Composition-volume relationships of metasomatism. *Chemical Geology* 2, 47 - 55.
- Grobbelaar, W. S., Burger, M. A., Pretorius, A. I., Marais, W., & van Niekerk, I. J. (1995). Stratigraphic and structural setting of the Griqualand West and the Olifantshoek Sequences at Black Rock, Beeshoek and Rooinekke Mines, Griqualand West, South Africa. *Mineralium Deposita* 30, 152-161.
- Gross, G. A. (1980). A classification of iron formations based on depositional environments. *Canadian Mineralogist* 18, 215-222.
- Gruner, J. W. (1922). The Origin of Sedimentary Iron Formations: The Biwabik Formation of the Mesabi Range. *Economic Geology* 17, 418p.
- Gruner, J. W. (1924). Contributions to the geology of the Mesabi range with special reference to the magnetites of the iron-bearing formation west of Mesaba. *Minnesota Geological Survey Bulletin* 19, 71p.
- Gruner, J. W. (1925). Discovery of Life in the Archean. *Journal of Geology* 33, 151-152.
- Gruner, J. W. (1926). The Soudan Formation and a new suggestion as to the origin of the Vermilion ores. *Economic Geology* 21, 629-644.

- Gruner, J. W. (1930). Hydrothermal oxidation and leaching experiments, their bearing on the origin of Lake Superior hematite-limonite ores. *Economic Geology* 25, 697-719.
- Gruner, J. W. (1936). The structure and composition of greenalite. *American Mineralogist* 20, 475-483.
- Gruner, J. W. (1937). Composition and structure of stilpnomelane . *American Mineralogist* 22, 885-860.
- Gruner, J. W. (1944). The composition and structure of minnesotaite, a common iron silicate in iron-formations. *American Mineralogist* 29, 363-372.
- Gutzmer, J. (1996). Genesis and alteration of the Kalahari and Postmasburg manganese deposits, Griqualand West, South Africa. Phd thesis (unpublished), University of Johannesburg, Johannesburg.
- Gutzmer, J., Beukes, N. J., de Kock, M. O., & Netshiozwi, S. T. (2005). Origin of high-grade iron ores at the Thabazimbi deposit, South Africa. *Australasian Institute of Mining and Metallurgy, Iron Ore 2005 conference, Fremantle, Western Australia*, 57-65.
- Gutzmer, J., Chisonga, B. C., Beukes, N. J., & Mukhopadhyay, J. (2008). The Geochemistry of Banded Iron Formation-Hosted High-Grade Hematite-Martite Iron Ores. *Reviews in Economic Geology* 15, 157-183.
- Gutzmer, J., Mukhopadhyay, J., Beukes, N. J., Pack, A., Hayashi, K., & Sharp, Z. D. (2006). Oxygen isotope composition of hematite and genesis high-grade BIF-hosted iron ores, in Kesler, S.E., and Ohmoto, H., eds., *Evolution of Early Earth's Atmosphere, Hydrosphere, and Biosphere - Constraints from Ore Deposits. Geological Society of America Memoir* 198, 257-268.
- Hagemann, S., Dalstra, H. I., Hodkiewicz, P., Flis, M., Thorne, W., & McCuaig, C. (2007). Recent Advances in BIF-related Iron Ore Models and Exploration Strategies. In *"Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration"*, 811-821.
- Hagemann, S., Rosiere, C., Gutzmer, J., & Beukes, N. J. (2008). Introduction: Banded Iron Formation-Related High-Grade Iron Ore. *Reviews in Economic Geology* 15, 1-4.

- Halbich, I. W., & Altermann, W. (1992). The genesis of BIF in the Transvaal Supergroup, South Africa, in: Source, Transport and Deposition of Metals, eds., M. Pagel and J.L. Leroy. Rotterdam. 841p.
- Halbich, I. W., Lamprecht, D., Altermann, W., & Horstmann, U. E. (1992). A carbonate-banded iron formation transition in the Early Proterozoic of South Africa. *Journal of African Earth Sciences* 15, 217-236.
- Halbich, I. W., Scheepers, R., Lamprecht, D., van Deventer, J. L., & De Kock, N. J. (1993). The Transvaal-Griqualand West banded iron formation: geology, genesis, iron exploitation. *Journal of African Earth Sciences* 16, 63-120.
- Harris, C., & Ashwal, L. D. (2002). The origin of low $\delta^{18}\text{O}$ granites and related rocks from the Seychelles. *Contributions to Mineralogy and Petrology* 143, 366 - 376.
- Hoefs, J. (2009). *Stable isotope geochemistry*. Berlin Heidelberg: Springer-Verlag.
- Horstmann, U. E., & Halbich, I. W. (1995). Chemical composition of banded iron-formations of the Griqualand West Sequence, Northern Cape Province, South Africa, in comparison with other Precambrian iron formations. *Precambrian Research* 72, 109-145.
- International Atomic Energy Agency. (2009). Reference Sheet for International Measurement Standards VSMOW2. SLAP2.
- James, H. L. (1954). Sedimentary facies of iron-formation. *Economic Geology* 49, 235-293.
- James, H. L. (1955). Zones of regional metamorphism in the Precambrian of northern Michigan. *Geological Survey of America Bulletin* 66, 1455-1488.
- James, H. L. (1958). Stratigraphy of pre-Keewenawan rocks in parts of northern Michigan. *United States Geological Survey Professional Paper* 314-C, 27-44.
- James, H. L. (1983). Distribution of banded iron-formation in space and time, in: Iron-Formations: Facts and Problems, eds., A.F. Trendall and R.C. Morris. *Developments in Precambrian Geology* 6, 471-486.
- James, H. L., & Sims, P. K. (1973). *Precambrian Iron-Formations of the World*. In: *Economic Geology* 68. St. Lawrence: Society of Economic Geologists Inc.

- Jiang, S., Wang, R., Xu, X., & Zhao, K. (2005). Mobility of high field strength elements (HFSE) in magmatic-, metamorphic-, and submarine-hydrothermal systems. *Physics and Chemistry of Earth* 30, 1020 - 1029.
- Kato, Y., Yamaguchi, K. E., & Ohmoto, H. (2006). Rare earth elements in Precambrian banded iron formations: Secular changes of Ce and Eu anomalies and evolution of atmospheric oxygen, in Kesler, S.E., and Ohmoto, H., eds., Evolution of Early Earth's Atmosphere, Hydrosphere, and Biosphere. *Geological Society of America Memoir* 198, 269 -289.
- Kesler, S. E., Reich, M., & Jean, M. (2007). Geochemistry of fluid inclusion brines from Earth's oldest Mississippi Valley-type (MVT) deposits, Transvaal Supergroup, South Africa. *Chemical Geology* 237, 274-288.
- Kirschvink, J. L., Gaidos, E. J., Bertani, L. E., Beukes, N. J., Gutzmer, J., Maepa L. N., & Steinberger, R. E. (2000). Paleoproterozoic snowball Earth: Extreme climatic and geochemical global change and its biological consequences. *Proceedings of the National Academy of Sciences* 97, 1400-1405.
- Klein, C. (1983). Diagenesis and metamorphism of Precambrian Banded Iron-Formations, in: Iron-formations: Facts and Problems, eds., A.F. Trendall and R.C. Morris. *Developments in Precambrian Geology* 6, 417-469.
- Klein, C. (2005). Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. *American Mineralogist* 90, 1473-1499.
- Klein, C., & Beukes, N. J. (1989). Geochemistry and sedimentology of a facies transition from limestone to iron-formation deposition in the early proterozoic Transvaal Supergroup, South Africa. *Economic Geology* 84, 1733-1774.
- Klein, C., & Beukes, N. J. (1992). Time distribution, stratigraphy, and sedimentologic setting, and geochemistry of Precambrian iron formations, in Schopf, J.W., and Klein, C, eds., The Proterozoic biosphere: Cambridge, Cambridge University Press. 139 - 146.
- Klemic, H., James, H. L., & Eberlein, G. D. (1973). Iron in: United States mineral resources, eds., D.A. Brobst and W.P. Pratt. *United States Geological Survey* 820, 291-306.

- La Berge, G. L. (1966). Altered pyroclastic rocks in South African iron-formations. *Economic Geology* 61, 572-581.
- Laetsch, T., & Downs, R. (2006). Software For Identification and Refinement of Cell Parameters From Powder Diffraction Data of Minerals Using the RRUFF Project and American Mineralogist Crystal Structure Databases. *Abstracts from the 19th General Meeting of the International Mineralogical Association, Kobe, Japan, 23-28 July 2006*.
- Lamprecht, D. F., & Halbach, I. W. (1988). A vertical transition from carbonates to banded iron-formation in the Griqualand West Sequence of the Transvaal Supergroup, at Finsch diamond mine, Northern Cape Province. *Abstracts, Geocongress 1988, Geological Society of South Africa*, 783-786.
- Land, J. S. (2010). The Geochemistry of Paleosols and "Red Beds" in the Transvaal and Olifantshoek Supergroups: Provenance versus Metasomatism. Honours Thesis (unpublished), Rhodes University, Grahamstown.
- Lascelles, D. F. (2006a). The Genesis of the Hope Downs Iron Ore Deposit, Hamersley Province, Western Australia. *Economic Geology* 101, 1359-1376.
- Lascelles, D. F. (2006b). The Mount Gibson Iron Formation-Hosted Magnetite Deposit: Two Distinct Processes for the Origin of High-Grade Iron Ore. *Economic Geology* 101, 651-666.
- Laznicka, P. (1992). Manganese deposits in global lithogenetic system: quantitative approach. *Ore Geology Reviews* 7, 279-356.
- Lobato, L. M., Figueiredo e Silva, R. C., Hagemann, S., & Thorne, W. (2007). Mineralizing fluid evolution and REE patterns for the hydrothermal Carajas iron ores, Brazil, and for selected Hamersley iron deposits, Australia. *In: 9th Biennial Society for Geology Applied to Mineral Deposits, SGA meeting, Dublin, Ireland*, 1227 - 1230.
- Lobato, L. M., Figueiredo e Silva, R. C., Hagemann, S., Thorne, W., & Zuchetti, M. (2008). Hypogene alteration associated with high-grade banded iron formation-related iron ore. *Reviews of Economic Geology* 15, 107-128.

- Martini, J. E., Eriksson, P. G., & Snyman, C. P. (1995). The Early Proterozoic Mississippi Valley-type Pb-Zn-F deposits of the Campbellrand and Malmani Subgroups, South Africa. *Mineralium Deposita* 30, 135-145.
- McClung, C. R. (2006). Basin analysis of the Mesoproterozoic Bushmanland Group of the Namaqua metamorphic province, South Africa. Ph.D. thesis (unpublished), University of Johannesburg, Auckland Park.
- McLennan, S.M., Bock, B., Hemming, S.R., Hurowitz, J.A., Lev, S.M., & McDaniel, D.K. (2003). The roles of provenance and sedimentary processes in the geochemistry of sedimentary rocks, in Lentz, D.R., ed., *Geochemistry of Sediments and Sedimentary Rocks: Evolutionary Considerations to Mineral Deposit-Forming Environments. Geological Association of Canada, GeoText* 4, 7 - 38.
- Mel'nik, Y. P. (1982). *Precambrian Banded Iron-Formations Physicochemical Conditions of Formation. In: Developments in Precambrian Geology* 5. Amsterdam: Elsevier Science Publishing.
- Moore, J. M., Kuhn, B. K., Mark, D. F., & Tsikos, H. (2011). A sugilite-bearing assemblage from the Wolhaarkop breccia, Bruce iron-ore mine, South Africa: Evidence for alkali metasomatism and ^{40}Ar - ^{39}Ar dating. *European Journal of Mineralogy* 23, 661-673.
- Moore, J. M., Tsikos, H., & Polteau, S. (2001). Deconstructing the Transvaal Supergroup, South Africa: Implication for Palaeoproterozoic palaeoclimate models. *Journal of African Earth Sciences* 33, 437-444.
- Morey, G. B. (1983). Animikie Basin, Lake Superior Region, U.S.A, in: Iron-formations: Facts and Problems, eds., A.F. Trendall and R.C. Morris. *Developments in Precambrian Geology* 6, 13-67.
- Morris, R. C. (2003). Iron ore genesis and post-ore metasomatism at Mount Tom Price. *Transactions of the Institute of Mining and Metallurgy B - Applied Earth Sciences* 112, B56 -B67.
- Mukhopadhyay, J., Gutzmer, J., Beukes, N. J., & Bhattacharya, H. N. (2008). Geology and Genesis of the Major Banded Iron Formation-Hosted High-Grade Iron Ore Deposits of India. *Reviews in Economic Geology* 15, 291-316.

- Nelson, B. J., Wood, S. A., & Osiensky, J. L. (2003). Partitioning of REE between solution and particulate matter in natural waters: A filtration experiment. *Journal of Solid State Chemistry* 171, 51-56.
- Norrish, K., & Hutton, J. T. (1969). An Accurate X-Ray Spectrographic Method for the Analysis of a Wide Range of Geological Samples. *Geochimica et Cosmochimica Acta* 431, 31p.
- Ohmoto, H. (2003). Nonredox transformations of magnetite-hematite in hydrothermal systems. *Economic Geology* 98, 157 - 161.
- Perry, E. C., & Ahmad, S. N. (1983). Oxygen isotope geochemistry of Proterozoic chemical sediments, in Medaris, L.G., Byers, C.W., Mickelson, D.M., and Shanks, W.C., eds., Proterozoic Geology: Selected papers from an international Proterozoic symposium. *Geological Society of America* 161, 253 - 263.
- Pickard, A. L. (2003). SHRIMP U–Pb zircon ages for the Palaeoproterozoic Kuruman iron formation, Northern Cape Province, South Africa: evidence for simultaneous BIF deposition of the Kaapvaal and Pilbara cratons. *Precambrian Research* 125, 275 - 315.
- Polteau, S., Moore, J. M., & Tsikos, H. (2006). The geology and geochemistry of the Paleoproterozoic Makganyene diamictite. *Precambrian Research* 148, 257-274.
- Powell, C. M., Oliver, N. H., Li, Z. X., Martin, D. M., & Ronaszeki, J. (1999). Synorogenic hydrothermal origin for giant Hamersley iron oxide ore bodies. *Geology* 27, 175-179.
- Rafferty, J. P. (2012). *Geology: Landforms, minerals, and rocks*. New York: Britannica Publishing.
- Ramanaidou, E. R., & Morris, R. C. (2010). Comparison of supergene mimetic and supergene lateritic iron ore deposits. *Transactions of the Institute of Mining and Metallurgy B - Applied Earth Sciences* 119, B35-B39.
- Ridley, M. (1999). Evidence for the hydrothermal origin of iron ore, Southern Ridge, Mt. Tom Price, Western Australia. BSc Thesis (unpublished), University of Western Australia, Perth. 82p.
- Robb, L. (2005). *Introduction to ore-forming processes*. Oxford: Blackwell Publishing.

- Roberge, P. R. (2008). *Corrosion Engineering: Principles and Practice*. Columbus: McGraw-Hill.
- Roy, S., & Venkatesh, A. S. (2009). Mineralogy and geochemistry of banded iron formation and iron ores from eastern India with implications on their genesis. *Journal Earth System Science* 118, 619-641.
- Sumner, D. Y., & Bowring, S. A. (1996). U-Pb geochronologic constraints on deposition of the Campbellrand Subgroup, Transvaal Supergroup, South Africa. *Precambrian Research* 79, 25-35.
- Takeno, N. (2005). *Atlas of Eh-pH diagrams: Intercomparison of thermodynamic databases*. Tokyo: National Institute of Advanced Industrial Science and Technology.
- Taylor, D. J., Dalstra, H. J., Harding, A. E., Broadbent, G. C., & Barley, M. E. (2001). Genesis of high-grade hematite orebodies of the Hamersley Province, Western Australia. *Economic Geology* 96, 837 - 873.
- Taylor, D. J., Page, D. C., & Geldenhuys, P. (1988). Iron and Steel in South Africa. *Journal of the South African Institute of Mining and Metallurgy* 88, 73-95.
- Taylor, S. R., & McLennan, S. M. (1985). *The continental crust: Its composition and evolution*. Oxford: Blackwell.
- Thorne, W. S., Hagemann, S., & Barley, M. E. (2004). Petrographic and geochemical evidence for hydrothermal evolution of the North deposit, Mount Tom Price, Western Australia. *Mineralium Deposita* 39, 766-783.
- Thorne, W., Hagemann, S., Vennemann, T., & Oliver, N. (2009). Oxygen isotope compositions of iron oxides from high-grade BIF-hosted iron ore deposits of the Central Hamersley Province, Western Australia: Constraints on the evolution of hydrothermal fluids. *Economic Geology* 104, 1019 - 1035.
- Thorne, W., Hagemann, S., Webb, A., & Clout, J. (2008). Banded iron formation-related iron ore deposits of the Hamersley province, Western Australia. *Reviews of Economic Geology* 15, 197-221.
- Trendall, A. F., & Morris, R. C. (1983). *Iron-formation: Facts and Problems*. In: *Developments in Precambrian Geology* 6. Amsterdam: Elsevier Science Publishing.

- Trendall, A.F., Compston, W., Williams, I.S., Armstrong, R.A., Arndt, N.T., McNaughton, N.J., Nelson, D.R., Barley, M.E., Beukes, N.J., De Laeter, J.R., Retief, E.A., & Thorne, A.M. (1990). Precise zircon U–Pb chronological comparison of the volcano-sedimentary sequences of the Kaapvaal and Pilbara Cratons between about 3.1 and 2.4 Ga. In: Glover, J.E., Ho, S.E. (Eds.), *Proceedings of the Third International Archaean Symposium*, Perth. p81 - 83.
- Tsikos, H. (1994). The mineralogy and geochemistry of the Voelwater banded iron-formation, Northern Cape Province: MSc thesis (unpublished), Rhodes University, Grahamstown.
- Tsikos, H., & Moore, J. M. (1997). Petrography and Geochemistry of the Paleoproterozoic Hotazel Iron-Formation, Kalahari Manganese Field, South Africa: Implications for Precambrian Manganese Metallogenesis. *Economic Geology* 92, 87-97.
- Tsikos, H., & Moore, J. M. (2005). Sodic metasomatism in the Palaeoproterozoic Hotazel iron-formation, Transvaal Supergroup, South Africa: implications for fluid-rock interaction in the Kalahari manganese field. *Geofluids* 5, 264-271.
- Tsikos, H., Beukes, N. J., Moore, J. M., & Harris, C. (2003). Deposition, Diagenesis, and Secondary Enrichment of Metals in the Paleoproterozoic Hotazel Iron Formation, Kalahari Manganese Field, South Africa. *Economic Geology* 98, 1449-1462.
- Tsikos, H., Matthews, A., Erel, Y., & Moore, J. M. (2010). Iron isotopes constrain biogeochemical redox cycling of iron and manganese in a Palaeoproterozoic stratified basin. *Earth and Planetary Science Letters* 298, 125-134.
- Tsikos, H., Moore, J. M., & Harris, C. (2001). Geochemistry of the Palaeoproterozoic Mooidraai Formation: Fe-rich limestone as end member of iron formation deposition, Kalahari Manganese Field, Transvaal Supergroup, South Africa. *Journal of African Earth Sciences* 32, 19-27.
- UNESCO. (1973). *Genesis of Precambrian Iron and Manganese Deposits*. Paris: UNESCO.
- von Plehwe-Leisen, E., & Klemm, D. D. (1995). Geology and ore genesis of the manganese ore deposits of the Postmasburg manganese-field, South Africa. *Mineralium Deposita* 30, 257-267.

-
- Walraven, F., & Martini, J. (1995). Zircon Pb-evaporation age determinations of the Oaktree Formation, Chuniespoort Group, Transvaal sequence: implications for Transvaal-Griqualand West basin correlations. *South African Journal of Geology* 98, 58 - 67.
- Wiggering, H., & Beukes, N. J. (1990). Petrography and Geochemistry of a 2000-2200-Ma-old Hematitic Paleo-Alteration Profile on Ongeluk Basalt of Transvaal Supergroup, Griqualand West, South Africa. *Precambrian Research* 46, 241-258.
- Yamaguchi, K. E., & Ohmoto, H. (2006). Geochemical and isotopic constraints on the origin of Paleoproterozoic red shales of the Gamagara/Mapedi Formation, Postmasburg Group, South Africa. *South African Journal of Geology* 109, 123-138.
- Yapp, C. J. (1990). Oxygen isotopes in iron (III) oxides 1. Mineral-water fractionation factors. *Chemical Geology* 85, 329 - 335.

Appendix A: Methodology

A1. Introduction

The techniques used in this study involved core logging, X-ray fluorescence analysis, X-ray diffraction analysis, electron microprobe analysis, inductively coupled plasma mass spectrometry and gas source DeltaXP mass spectrometer. In Appendix A, the analytical techniques used in this study are described in greater detail than in the text.

A2. Core logging and sample collection

The two drill cores, SLT032B and SLT033, were used in the study of the iron ore (Refer to Appendix B for detailed borehole logs). The drill cores were drilled on the Maremane anticline in the Northern Cape Province. The depth of the drill cores, SLT032B and SLT033, are 201.17m and 179.20m respectively. The drill cores were logged with a total of 81 samples being collected. Samples were labelled 32-n (n=1-45) and 33-n (n=1-36). The depth of the drill core SLT032B is 201.17m, but logging and sampling took place from a depth of 146.63m to a depth of 200.10m. The depth of drill core SLT033 is 179.20m, but logging and sampling took place from a depth of 151.20m to a depth of 178.60m. Both drill cores intersect a variety of shales, which overly the main iron ore body, following which a silicified banded iron formation occurs beneath the iron ore bodies.

The logging of the core was carried out by visual observation of the rock units present, changes in colour, textures and minerals present. These were the main features that were recorded. A measuring tape was used in order to correctly determine the depth at which recordable features were found and samples were taken.

A3. Pulverization, Loss on Ignition (L.O.I.) and X-ray fluorescence (XRF) analysis

The pulverization step involved crushing the samples into powder form for whole rock geochemical analysis. Prior to this the samples are cleaned to ensure no contamination. The samples were then crushed in a chrome swing mill continuously for 4 to 5 minutes to ensure thorough crushing and a homogenous fine powder. In order to prepare a pressed powder pellet for trace element analysis, 5 grams of each sample was mixed with 2 drops of Mowial,

which serves as a binding agent, and surrounded with 10 grams of boric acid in a steel container. A weight of 10 tons was then subjected to the sample in order to produce a pressed powder pellet. In order to prepare the samples for major element analysis, the samples must go through the Loss of Ignition (L.O.I.) process followed by the preparation of fusion disks for each sample. This involves 2 grams of each sample being placed in a crucible of known mass, and transferred into an oven for 2 hours at 110°C. Following this the samples were re-weighed in order to determine the loss of H₂O⁻ (wt. %). The L.O.I. was then carried out by placing each sample in a furnace at 1000°C for 8 hours. Thereafter, each sample was re-weighed in order to determine the mass of the material lost due to heating (L.O.I.). The process of fusion disk preparation was then carried out for each sample. This involves mixing 0.28 grams of the ashed sample, 0.02 grams of NaNO₃ and 1.50 grams of lithium tetraborate flux. The mixture is then heated in a platinum crucible over a bunsen burner in order to melt the mixture and produce a fusion disk. Trace element and major element concentrations, for each sample, were then determined by running the pressed powder pellets and fusion disks through a Philips PW 1480 X-ray fluorescence spectrometer housed in the Department of Geology, Rhodes University. The standards used during the analytical process include BCR-1, CAR-08, G-2, NIM-G, SCO-1, BHVO-1, G-2, BCR-1, GSN-005, JB-1, GSP-1, AGV-1, NIM-N, S-7, INS-79, INS-33, INS-79 as well as 3 in-house standards. The raw results obtained through XRF analysis can be found in Appendix B.

A4. Accurately determining Fe₂O₃ (wt. %) in very Fe-rich samples

The analysis of very Fe-rich Si-poor samples using the Philips PW 1480 X-ray fluorescence spectrometer following preparation techniques, as outlined by Norrish and Hutton (1969), proved to be problematical in terms of accurately determining Fe₂O₃ total. The totals obtained for such samples never exceed the values of 97%.

It was noticed that there was a systematic departure from the calibration curve in samples where Fe₂O₃ was greater than 30 wt. %. The departure of these samples from the calibration curve became greater as Fe₂O₃ increased, as any calibration curve which includes low and high Fe standards would not be linear. As a result a combination of low and high Fe standards were created ranging from 35 to 95 wt. % Fe₂O₃ (Table A1).

These samples were then used to determine the exact difference between measured Fe₂O₃ and actual Fe₂O₃ in very Fe-rich samples. This was done by using low Fe standards to determine

counts per second (cps) per % oxide. The cps per % oxide was determined to be 227.77. This cps per % oxide was then used to determine the theoretical cps for both the low and high Fe standards. The difference between the theoretical cps and measured cps for the high Fe standards was then calculated (Table A1). This difference in cps was converted to % oxide using the earlier calculated cps per % oxide ratio. The measured concentrations of Fe₂O₃ were then plotted against the difference between theoretical cps and measured cps converted to difference % oxide (Figure A1). A 2nd order polynomial curve can be fitted to these points and an equation can be determined.

Table A1. Samples of known Fe₂O₃ concentrations between 35 and 95 wt. % used to determine the equation used in the correction of Fe₂O₃ in very Fe-rich samples are shown. The samples respective theoretical cps, measured cps, Fe₂O₃ difference (wt. %) and actual Fe₂O₃ (wt. %) are presented.

	Theoretical cps	Measured cps	Difference in cps	Fe₂O₃ difference (wt. %)	Measured Fe₂O₃ (wt. %)	Actual Fe₂O₃ (wt. %)
S18	12559	12282	277	1.216	53.92	55.136
S16	7996	7913	83	0.364	34.73	35.094
S25	14838	14350	488	2.143	62.99	65.133
S17	10283	10093	190	0.834	44.3	45.134
S39	21655	20250	1405	6.169	88.89	95.059
S28	20509	19414	1095	4.807	85.22	90.027
S29	19370	18269	1101	4.834	80.2	85.034

This equation could be applied to the measured Fe₂O₃ values and would result in a true Fe₂O₃ value. When this equation was applied to the samples of known Fe₂O₃ it produced values which were expected from these standards. Once this equation was then applied to the Fe-rich samples it resulted in 95% of the samples totals being within an acceptable range of 100%. The 2nd order polynomial equation calculated is as follows:

$$y = 0.0015x^2 - 0.0882x + 1.59$$

In the above equation, x is the Fe₂O₃ measured by the XRF using low-Fe standards, whilst y is the Fe₂O₃ correction to be added to the x value. All Fe₂O₃ values presented in the geochemistry chapter, as well as in Appendix B are corrected Fe₂O₃ values. Additionally, the geochemical analysis of these samples, conducted by Kumba iron ore, using their in-house XRF facilities was made available to the researcher. The values obtained by Kumba compare well to the corrected values obtained in this study and provide confirmation that the XRF at Rhodes University was in fact underestimating the Fe₂O₃ concentrations. The geochemical

data from Kumba for comparative purposes cannot be made available in this thesis due to confidentiality issues, however can be made available if a specific request is made.

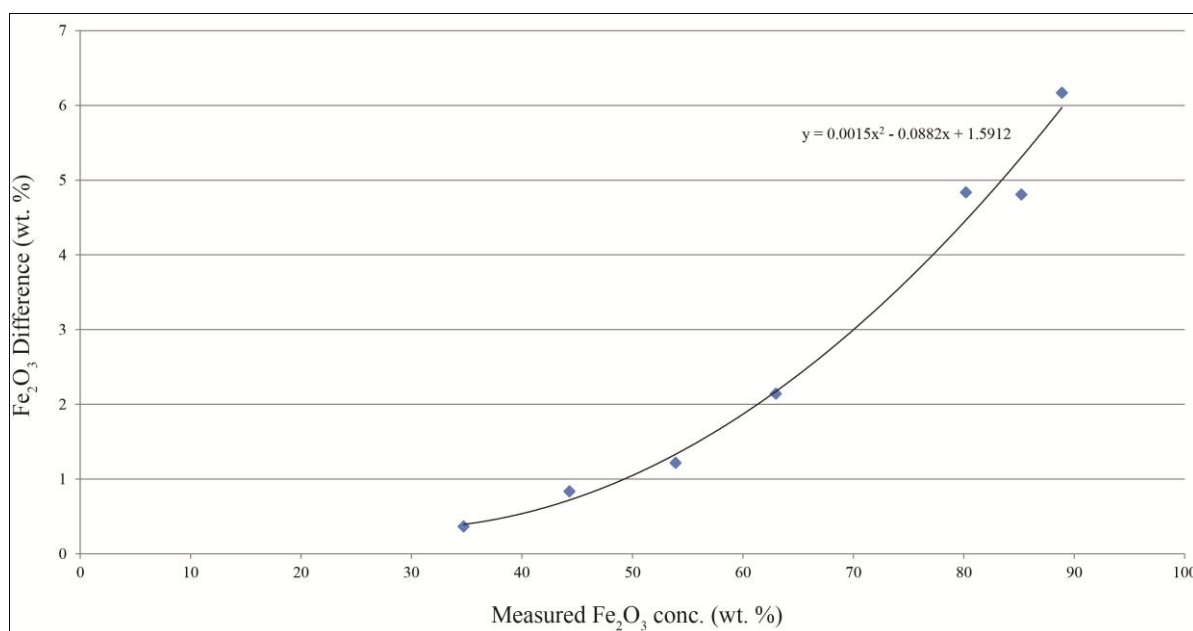


Figure A1. Measured Fe₂O₃ concentrations (wt. %) are plotted against Fe₂O₃ difference (wt. %). The equation from the resultant 2nd order polynomial curve was then used to correct the measured Fe₂O₃ values to produce actual Fe₂O₃ concentrations in very Fe-rich samples.

An alteration of the flux to sample ratio, as described by Norrish and Hutton (1969), could potentially eliminate this shortcoming. It is suggested that a lower flux to sample ratio could solve this problem and bring totals within a suitable range of 100%. However, this technique was neither tried nor proven during this study.

A5. Inductively coupled plasma mass spectrometer analysis

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometer that is extremely sensitive and capable of determining a wide range of trace elements at concentrations below one parts per billion (ppb). The ICP-MS technique was used in this study in order to measure the quantities of rare earth elements in hematite separates.

The hematite separates used to analysis for rare earth element concentrations were obtained by handpicking hematite fragments from a coarse crush of each sample using a binocular microscope. The hematite fragments were then crushed to a powder using a mortar and pestle. The hematite powder was then analysed using a XRD to ensure that the sample was pure hematite.

The ICP-MS used in this study is housed in the Department of Geology at the University of Cape Town. The sample preparation for ICP-MS analysis is carried out by weighing 50 mg of hematite sample powder into a clean, small Savillex beaker. In a fume-cupboard, in a wet chemistry lab, 4 ml of acid solution (3:1 HCl:HNO₃ aqua regia acid solution) was added to each sample. The beakers were closed and placed on hotplates at a temperature of 50-60°C to digest for 48 hours. Once the samples were fully digested the beakers were opened and the solutions were left on the hotplates and allowed to evaporate to complete dryness. Once the samples had dried down they were removed from the hotplates and allowed to cool. Using a 100-1000 µl pipette and a clean pipette tip, 2 ml of concentrated 2-bottled nitric acid (HNO₃) is added to each sample. The beakers were then closed and placed on the hotplates until the samples were completely dissolved. Once the samples had completely dissolved the beakers were opened and the solutions left on the hotplates to evaporate to complete dryness. The process of adding another 2 ml of concentrated 2-bottled HNO₃ to each sample is repeated, using a 100-1000 µl pipette. The samples were then allowed to evaporate to complete dryness, removed from the hotplates and allowed to cool. Using a 1-10 ml pipette and a clean pipette tip, 4 ml of internal standard stock solution was added to each sample beaker. The sample beakers were then placed in an ultrasonic bath for 60 minutes to dissolve completely. The dissolved sample was then quantitatively transferred to a 50 ml centrifuge tube. The sample beaker was then washed with 2 ml of internal standard stock solution, with care being taken to collect any droplets on the beaker walls, and quantitatively transferred to the centrifuge tube. On a microbalance, the dissolved sample was then made up to 50 g using internal standard stock solution. The sample solution represents a 1000-fold dilution of the original solid sample and was then ready for further dilution.

The hematite samples were diluted by a further 5-fold using the internal standard stock solution. The solutions then represented a 5000-fold dilution of the original solid hematite sample. The standards used during the analytical process include international standard BHV-02 and internal standard stock solution containing 5% HNO₃ with 4 additional standards. In addition, a total procedural blank (TPB) is run in order to establish the levels of contamination in the preparation and analytical processes.

A6. X-ray diffraction analysis

X-ray diffraction analysis is a common tool used in the mineralogical analysis of rocks. The x-ray diffraction (XRD) machine used in this study is a Bruker D8 Discover XRD equipped

with a Lynx Eye detector, housed in the Department of Chemistry at Rhodes University. Sample preparation is done by placing a thin layer of the crushed sample on a glass slide. This is then inserted into the cavity mount, made of aluminium, of the XRD machine. The XRD instrument uses a Cu-K α radiation ($= 1.5405 \text{ \AA}$, nickel filter) and is operated with power at 20mA and 40kV. The scanning is done from 5° to 65° (2θ) with scanning speeds of 1° per minute. The X-ray diffraction data is treated using the Eva (evaluation curve fitting) software with baseline corrections performed on each diffraction pattern. Diffraction patterns are then compared to the database hosted by RRUF (Laetsch and Downs, 2006). The measured peaks on the diffraction patterns obtained are compared to known peaks of minerals from the database using the computer software, Crystal Sleuth (Laetsch and Downs, 2006). A collation of the spectra obtained for each sample is available in Appendix C.

A7. Gas-source Finnegan Mat DeltaXP mass spectrometer

All oxygen isotope data in this study were obtained at the University of Cape Town using a gas-source Finnegan DeltaXP mass spectrometer. All results are reported in standard δ notation, where $\delta^{18}\text{O} = (\text{R}_{\text{sample}}/\text{R}_{\text{standard}} - 1) * 1000$ with $\text{R} = {}^{18}\text{O}/{}^{16}\text{O}$, and VSMOW is the standard, VSMOW stands for Vienna Standard Mean Ocean Water. The standards used during the analytical process include the internal standard MQ (Murchison line quartz) and the NBS-28 quartz standard, as described in Harris and Ashwal (2002).

Hematite separates were obtained by handpicking hematite fragments under a binocular microscope from a coarse crush of each sample. The hematite fragments were then crushed using a mortar and pestle. The hematite powder was then analysed using a XRD to ensure that the samples were pure hematite.

Approximately 10 mg of hematite powder for each sample was loaded into externally heated Ni tubes which were dried overnight at 50°C . The samples were then degassed under a vacuum at 200°C for a minimum of two hours. The samples were then reacted with ClF_3 at 550°C for about three hours. The liberated oxygen was then passed over a hot carbon rod, converting the oxygen to CO_2 gas which was then frozen into “break seal” tubes. The oxygen isotopes were measured off-line using a gas-source Finnegan DeltaXP mass spectrometer in dual inlet mode. This method is outlined in Fourie and Harris (2011).

A8. Electron Probe Micro Analyser (EMPA)

Major element analyses were performed on various minerals using a Jeol JXA 8230 Superprobe with 4 WD spectrometers housed in the Department of Geology, Rhodes University. The polished thin sections and briquettes were prepared for analysis by coating with carbon at a thickness of 30 μm . The analytical conditions for spot analyses as well as were as follows:

- Acceleration voltage: 15 kV
- Probe current: 20 nA
- Counting time: 10 seconds on peak and 5 seconds on background

Qualitative WDS scans were used to identify major elements in the unknown minerals. The majority of analyses were performed using a spot beam size of less than 1 μm . Yet, matrix analyses were performed using a beam radius of 10 μm to 20 μm so as to include all extremely fine-grained phases and attain an approximately homogenous, bulk analysis of the matrix. There were a variety of standard materials used depending upon the mineral analysed.

Appendix B: Results

This appendix contains photographs of representative core samples, detailed schematic illustrations of the logged boreholes used in this study (Figure B1 and B2), as well as tabulated whole-rock geochemical data and rare earth element data obtained for all samples analysed during this study. Additionally, a table is shown with sample numbers and corresponding stratigraphic depths for all samples analysed for geochemical purposes (Table B1).

Table B1. Sample numbers and the corresponding stratigraphic sample depths (in metres) for all samples selected for geochemical analysis during this study. The location of the sample depths for all the samples is shown in Figure B1 and B2. The prefix 32- indicates the samples are from borehole SLT032B, whilst the prefix 33- indicates the samples are from borehole SLT033.

32-03	153.22	32-31	176.77	33-01A	151.15	33-28	171.62
32-04	153.43	32-32	177.86	33-01B	151.25	33-29	171.83
32-05	153.77	32-33	178.28	33-02	151.75	33-31	174.33
32-06	154.03	32-34	179.69	33-03	152.09	33-32	175.05
32-07	154.96	32-35	180.57	33-04	152.78	33-33	175.74
32-08	155.66	32-36	181.76	33-05	153.37	33-34	176.57
32-09	156.35	32-37	182.34	33-06	154.65	33-35	177.59
32-10	156.94	32-38	183.30	33-07	155.65	33-36	178.60
32-11	157.71	32-39	185.74	33-08	156.43		
32-12	157.97	32-40	189.66	33-09	157.47		
32-13	158.79	32-41	189.94	33-10	158.31		
32-14	160.34	32-43	194.17	33-11	158.79		
32-15	161.61	32-44	196.34	33-12	159.27		
32-16	162.74	32-45	200.10	33-13	159.91		
32-17	163.25			33-14	161.14		
32-18	163.78			33-15	162.07		
32-19	164.77			33-16	162.50		
32-20	165.44			33-17	163.08		
32-21	166.52			33-18	163.56		
32-22	167.80			33-19	163.98		
32-23	168.77			33-20	164.81		
32-24	169.56			33-21	165.43		
32-25	170.32			33-22	166.95		
32-26	171.77			33-23	168.06		
32-27	173.72			33-24	168.65		
32-28	175.11			33-25	169.39		
32-29	175.80			33-26	170.53		
32-30	176.49			33-27	170.98		

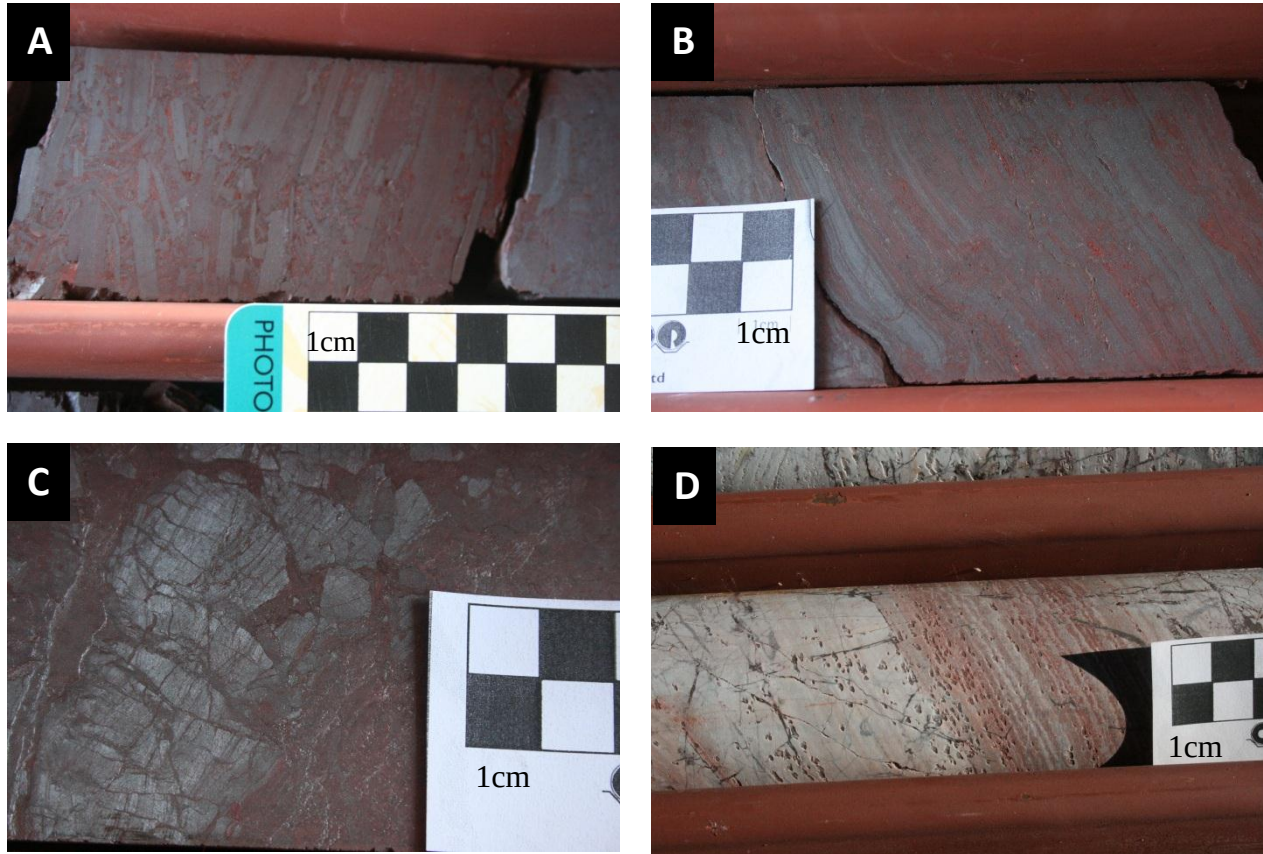
B1: Representative photographs

Figure B1. Representative core samples of major rock types investigated during this study. **A.** Low-grade iron ore (hematite clasts in an iron-rich silicate matrix). **B.** High-grade laminated iron ore. **C.** High-grade brecciated iron ore. **D.** Siliceous BIF.

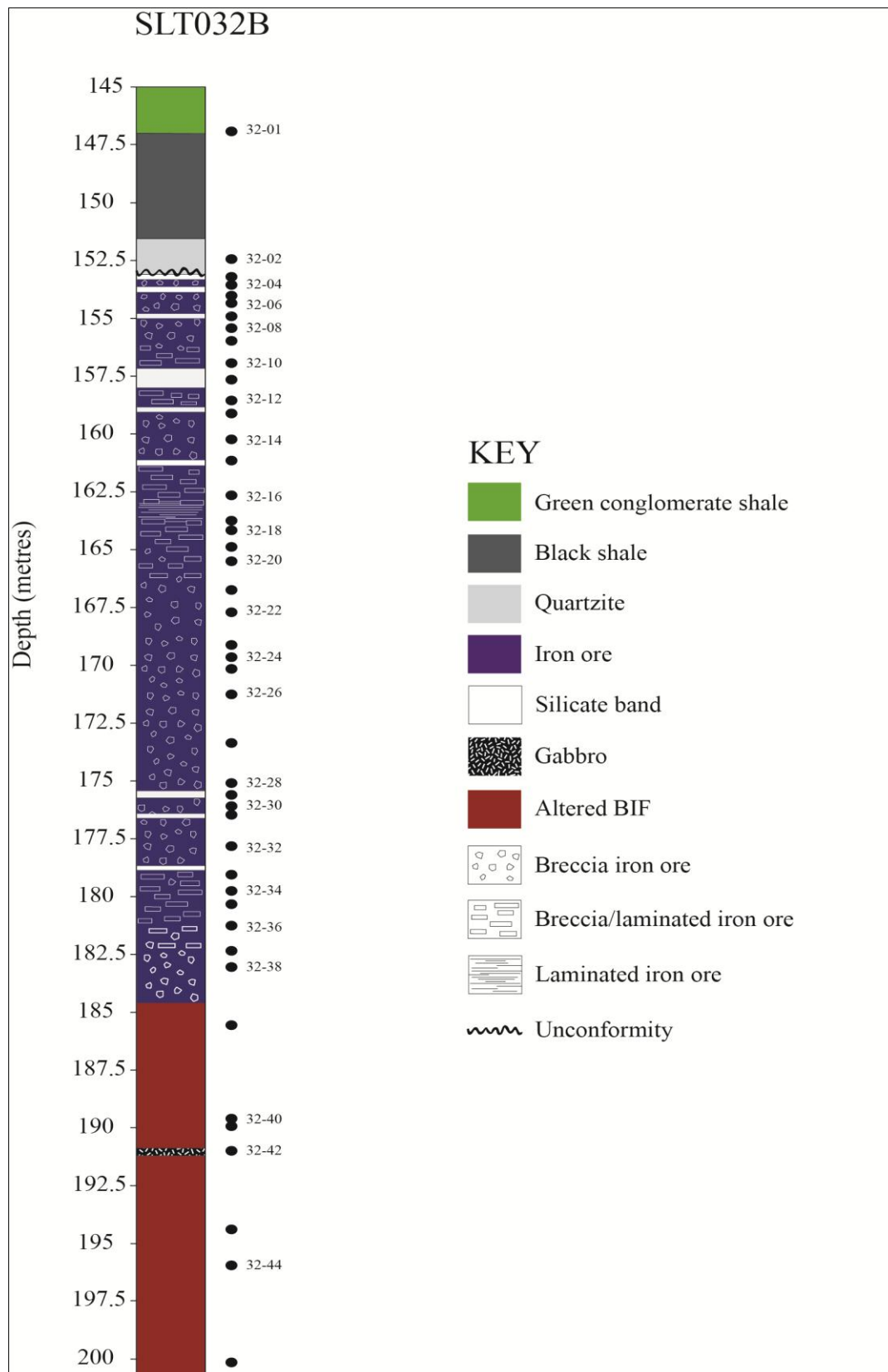
B2: Logged boreholes

Figure B2. Approximate stratigraphic locations for the samples selected for this study taken from borehole SLT032B.

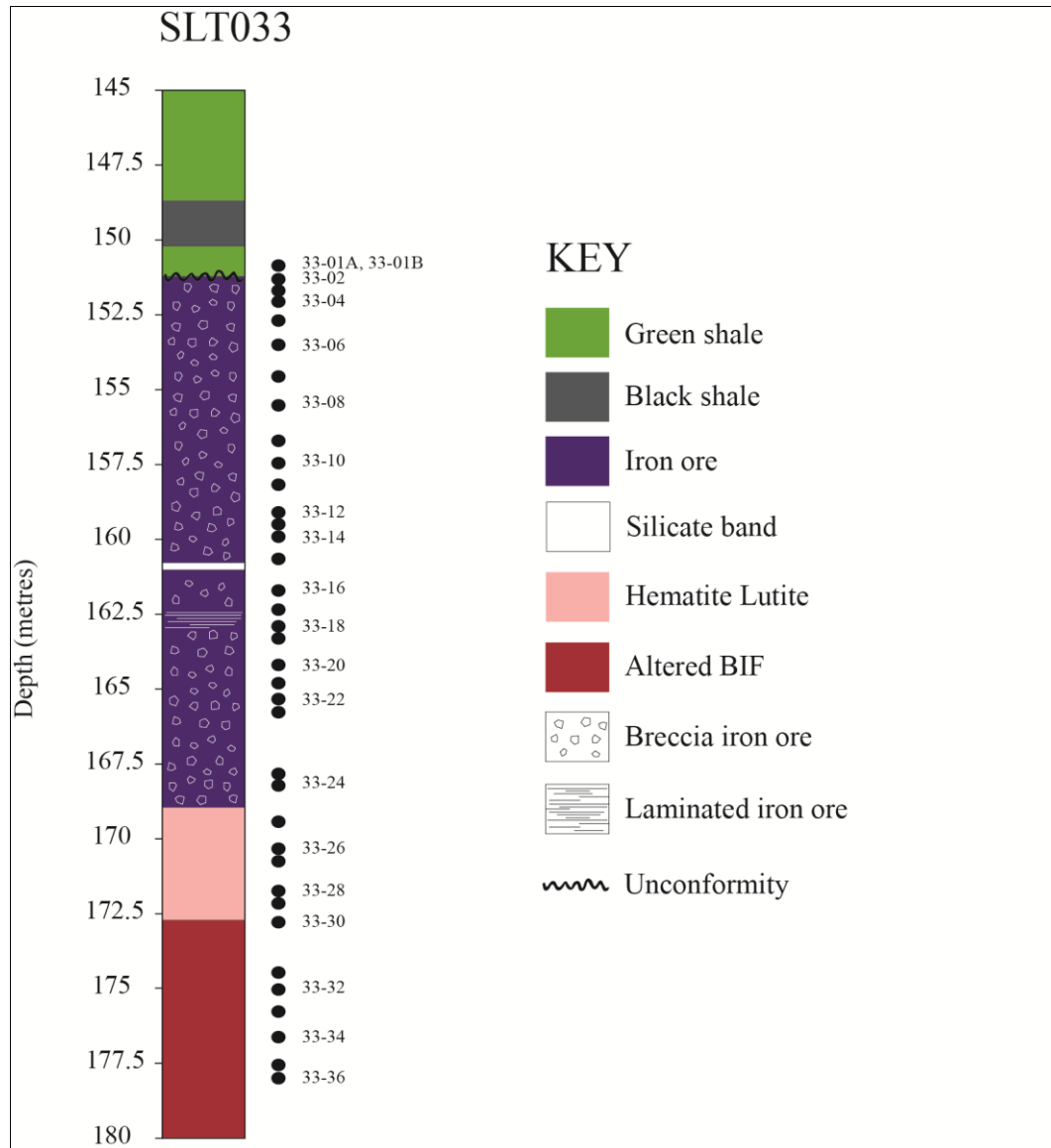


Figure B3. Approximate stratigraphic locations for the samples selected for this study taken from borehole SLT033.

B3: Major and trace element geochemical data

Appendix B3 contains raw tabulated whole-rock geochemical data for all samples analysed in this study. Major element data are expressed as weight percent (wt. %) whereas the trace element data are presented in parts per million (ppm). The analytical totals have been calculated by adding up the major element concentrations. The total iron-oxide concentrations are shown as Fe_2O_3 . The Fe_2O_3 concentrations presented in this appendix have been corrected according to the equations presented in appendix A4.

Abbreviations used:

LOI: Loss on ignition

nd: not determined

Sample No. wt. %	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	H ₂ O ⁻	Total
32-03	22.73	0.69	18.77	48.69	0.03	0.43	0.05	0.11	3.96	0.06	3.30	0.30	99.11
32-04	9.24	0.17	2.72	85.33	0.05	0.06	0.11	0.01	0.64	0.09	0.94	0.45	99.80
32-05	49.43	0.18	4.37	42.55	0.03	0.19	0.07	0.01	0.49	0.06	1.17	0.19	98.74
32-06	8.75	0.08	1.20	88.90	0.04	0.13	0.07	0.00	0.02	0.06	0.79	0.29	100.32
32-07	20.28	0.84	14.85	55.34	0.04	0.13	0.03	0.19	3.43	0.11	2.57	0.25	98.07
32-08	7.05	0.52	5.62	83.41	0.05	0.43	0.07	0.02	0.89	0.04	1.65	0.49	100.24
32-09	3.69	0.18	3.33	94.16	0.06	0.14	0.05	0.01	0.52	0.05	0.73	0.16	103.06
32-10	6.56	0.37	5.24	84.31	0.05	0.17	0.06	0.03	0.87	0.05	1.34	0.48	99.52
32-11	10.57	0.50	8.19	75.63	0.05	0.07	0.04	0.11	1.99	0.05	1.49	0.21	98.87
32-12	6.97	0.32	5.67	84.36	0.04	0.39	0.13	0.01	0.66	0.06	1.62	0.41	100.65
32-13	4.86	0.26	4.15	89.56	0.05	0.08	0.03	0.02	0.72	0.05	1.10	0.22	101.10
32-14	11.98	0.42	9.35	72.51	0.04	0.17	0.09	0.10	2.22	0.05	2.11	0.54	99.57
32-15	7.84	0.29	6.46	84.97	0.04	0.01	0.05	0.05	1.61	0.14	1.30	0.19	102.96
32-16	1.09	0.06	0.79	96.71	0.05	0.06	0.06	0.00	0.08	0.03	0.65	0.21	99.79
32-17	2.80	0.15	2.95	95.43	0.07	0.26	0.21	0.00	0.01	0.17	1.20	0.15	103.39
32-18	0.52	0.05	0.09	98.90	0.05	0.00	0.03	0.00	0.01	0.02	0.44	0.16	100.27
32-19	0.63	0.05	0.27	98.83	0.05	0.00	0.03	0.00	0.01	0.02	0.29	0.06	100.24
32-20	0.52	0.05	1.55	98.65	0.04	0.00	0.02	0.00	0.01	0.02	0.23	0.11	101.20
32-21	1.47	0.09	1.08	96.03	0.04	0.00	0.10	0.00	0.15	0.08	0.43	0.09	99.57
32-22	2.10	0.15	1.64	95.26	0.05	0.00	0.15	0.00	0.19	0.12	0.54	0.12	100.31
32-23	4.99	0.20	3.06	89.18	0.04	0.00	0.25	0.01	0.58	0.19	0.77	0.14	99.41
32-24	0.59	0.05	0.49	98.48	0.05	0.00	0.07	0.00	0.03	0.07	0.26	0.11	100.19
32-25	0.26	0.05	0.34	100.23	0.05	0.00	0.03	0.00	0.01	0.04	0.18	0.07	101.26
32-26	3.64	0.25	3.35	89.91	0.04	0.02	0.28	0.01	0.54	0.21	0.78	0.20	99.24
32-27	0.92	0.06	0.96	98.90	0.04	0.00	0.12	0.00	0.05	0.08	0.48	0.11	101.71
32-28	0.52	0.03	0.34	97.69	0.03	0.00	0.10	0.00	0.03	0.07	0.40	0.15	99.35
32-29	23.20	0.58	19.05	46.86	0.04	0.29	0.05	0.20	4.01	0.12	3.40	0.24	98.03
32-30	4.07	0.14	2.92	91.26	0.04	0.08	0.15	0.01	0.43	0.15	0.91	0.10	100.26
32-31	13.83	0.36	7.15	72.87	0.03	0.08	0.13	0.06	1.45	0.11	1.58	0.28	97.92
32-32	0.93	0.05	0.44	97.41	0.04	0.00	0.03	0.00	0.02	0.06	0.36	0.08	99.42

Sample No. wt. %	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	H ₂ O ⁻	Total
32-32	0.93	0.05	0.44	97.41	0.04	0.00	0.03	0.00	0.02	0.06	0.36	0.08	99.42
32-33	6.14	0.11	2.98	87.79	0.04	0.04	0.08	0.01	0.48	0.10	0.83	0.13	98.74
32-34	1.00	0.06	0.44	97.65	0.05	0.00	0.10	0.00	0.02	0.11	0.43	0.08	99.94
32-35	2.03	0.06	0.55	95.95	0.05	0.00	0.12	0.00	0.02	0.12	0.38	0.07	99.35
32-36	10.01	0.04	0.71	87.10	0.05	0.00	0.10	0.00	0.03	0.10	0.45	0.10	98.68
32-37	4.35	0.07	1.25	92.32	0.06	0.07	0.06	0.00	0.10	0.07	0.58	0.07	99.00
32-38	0.98	0.04	0.62	97.31	0.06	0.00	0.09	0.00	0.01	0.03	0.26	0.10	99.49
32-39	33.82	0.06	1.17	61.96	0.05	0.01	0.10	0.00	0.10	0.07	0.42	0.10	97.86
32-40	47.76	0.03	0.37	50.42	0.04	0.00	0.01	0.00	0.02	0.04	-0.07	0.09	98.70
32-41	46.43	0.01	0.23	50.71	0.04	0.00	0.03	0.00	0.01	0.03	0.11	0.08	97.69
32-43	56.68	0.02	0.14	42.26	0.03	0.00	0.02	0.00	0.02	0.03	0.02	0.09	99.30
32-44	74.28	0.00	0.09	24.68	0.03	0.00	0.03	0.00	0.01	0.03	-0.09	0.02	99.09
32-45	82.86	0.00	0.16	19.69	0.03	0.00	0.08	0.00	0.02	0.05	-0.15	0.10	102.85
Sample No. wt. %	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	H ₂ O ⁻	Total
33-01A	42.62	0.95	35.48	8.00	0.03	0.33	0.06	0.45	4.83	0.10	7.44	0.67	100.96
33-01B	24.80	0.65	22.72	42.31	0.10	0.58	0.06	0.19	2.42	0.06	4.77	0.57	99.22
33-02	35.67	0.80	30.24	21.71	0.08	0.56	0.03	0.01	4.60	0.06	5.43	0.45	99.65
33-03	19.25	0.34	14.14	58.28	0.06	0.23	0.11	0.16	2.22	0.10	3.32	0.67	98.87
33-04	15.97	0.41	12.31	63.95	0.06	0.15	0.06	0.12	1.65	0.07	3.02	0.43	98.19
33-05	6.87	0.33	6.28	83.09	0.06	0.10	0.04	0.02	0.41	0.03	2.06	0.35	99.65
33-06	32.01	1.08	27.51	27.40	0.06	0.33	0.06	0.61	3.62	0.07	5.96	0.51	99.22
33-07	11.32	0.47	9.57	71.85	0.06	0.10	0.12	0.11	0.99	0.11	2.93	0.83	98.45
33-08	30.48	1.02	26.23	30.44	0.05	0.27	0.11	0.53	3.40	0.12	5.84	0.31	98.80
33-09	34.15	1.21	30.16	21.53	0.05	0.26	0.03	0.34	2.65	0.07	8.16	0.87	99.48
33-10	16.20	0.72	14.23	60.44	0.07	0.15	0.05	0.31	2.09	0.10	3.14	0.26	97.75
33-11	2.97	0.25	3.28	91.14	0.08	0.16	0.28	0.01	0.20	0.20	1.17	0.42	100.14
33-12	24.44	1.87	21.18	41.45	0.03	0.13	0.03	0.20	1.47	0.13	5.97	0.86	97.77

Sample No. wt. %	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	H ₂ O ⁻	Total
33-13	10.52	0.23	8.53	74.52	0.06	0.05	0.05	0.04	1.09	0.06	2.65	0.84	98.63
33-14	3.09	0.16	2.56	92.49	0.07	0.09	0.01	0.01	0.07	0.04	0.85	0.27	99.70
33-15	3.12	0.16	2.84	95.40	0.13	0.26	0.05	0.00	0.04	0.05	1.16	0.26	103.46
33-16	3.41	0.20	2.83	90.79	0.08	0.21	0.05	0.01	0.06	0.08	0.95	0.23	98.90
33-17	2.86	0.19	2.14	92.65	0.08	0.13	0.04	0.00	0.07	0.04	1.08	0.38	99.65
33-18	5.84	0.24	4.48	87.06	0.10	0.14	0.04	0.02	0.22	0.07	1.43	0.35	99.98
33-19	6.04	0.25	4.38	85.56	0.07	0.10	0.06	0.02	0.25	0.07	1.81	0.50	99.09
33-20	5.36	0.19	3.90	86.69	0.07	0.20	0.04	0.01	0.15	0.07	1.21	0.27	98.17
33-21	2.00	0.15	1.60	94.97	0.09	0.04	0.04	0.00	0.07	0.05	0.90	0.37	100.28
33-22	1.25	0.03	0.78	96.21	0.05	0.02	0.05	0.00	0.05	0.03	0.42	0.17	99.06
33-23	1.51	0.08	1.07	96.90	0.05	0.00	0.12	0.00	0.06	0.07	0.70	0.41	100.97
33-24	5.37	0.15	2.54	88.45	0.06	0.01	0.05	0.00	0.12	0.07	1.03	0.34	98.19
33-25	70.60	0.73	13.90	8.33	0.01	0.05	0.02	0.09	0.98	0.06	3.70	0.74	99.22
33-26	72.76	0.65	12.73	9.10	0.01	0.04	0.00	0.08	0.87	0.07	3.23	0.34	99.87
33-27	71.77	0.56	11.72	10.11	0.01	0.06	0.04	0.10	1.11	0.05	3.01	0.54	99.06
33-28	74.32	0.60	12.83	6.51	0.01	0.07	0.03	0.07	0.87	0.05	3.50	0.46	99.32
33-29	68.25	0.81	16.06	8.70	0.01	0.04	0.01	0.09	1.26	0.09	4.50	0.30	100.12
33-31	82.68	0.00	0.39	16.17	0.03	0.00	0.00	0.00	0.01	0.01	-0.09	0.09	99.27
33-32	77.97	0.03	0.59	19.48	0.04	0.03	0.04	0.00	0.01	0.02	0.18	0.18	98.56
33-33	92.08	0.00	0.18	8.08	0.04	0.00	0.00	0.00	0.01	0.00	-0.17	0.07	100.29
33-34	93.12	0.00	0.17	6.88	0.05	0.01	0.01	0.00	0.01	0.01	-0.05	0.21	100.40
33-35	90.99	0.00	0.23	9.11	0.03	0.18	0.05	0.00	0.00	0.01	-0.26	0.05	100.37
33-36	88.94	0.00	0.18	10.44	0.04	0.00	0.02	0.00	0.01	0.00	-0.05	0.16	99.74

Sample No. ppm	Mo	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Cu	Ni	Co	Cr	V	Ce	Nd	La	Ba	Sc
32-03	4.7	10.5	227.6	27.9	71.6	nd	145.2	6.2	24.8	15	83.6	10.5	375	357.9	104.1	35.1	61.8	333.8	27.7
32-04	8.1	4.2	46.2	9.1	12.3	0.9	18.1	0.8	11.9	32.2	10.8	15.3	227.4	284.1	28.3	7.4	4	49.2	10.3
32-05	4.3	3.8	126.2	11.8	13.3	0.1	15.3	nd	7.1	13.7	46.5	8.4	225	285.6	23.7	5.2	9.3	29.3	11
32-06	7.7	2.1	26.3	5.6	5.4	nd	nd	3.1	10.1	33.4	8.2	18.7	154.7	280.8	18.6	nd	4.7	31.3	7.1
32-07	11.9	17.3	493.6	37.3	308	2.9	125.6	18.8	63.4	21.2	13.5	2.2	769	254.4	337.9	71.4	150.9	342.3	30.5
32-08	8	11.7	220.9	25.4	43.5	nd	27.4	3.7	12	46	13	15.4	225.4	60.1	76.5	25.1	32	59.6	13.9
32-09	2.3	1.5	47.5	8.7	64.1	3.2	16.5	3.6	18.9	30.9	0	18.9	158.2	103.9	87.6	28	30	52.9	7.5
32-10	6.8	7.2	120.1	14	123.9	1.3	34.7	3.4	11.9	27.4	1.7	12.5	173.5	177.9	70.5	18.4	22.6	101.3	9.4
32-11	6.3	13.6	205.4	24.4	99.7	0.8	70.1	10.9	13.7	27.2	2.6	10.5	205.4	121.4	71.1	22.8	36	210.9	13.2
32-12	7.1	8.4	100.9	12.6	32.4	2.3	25	3.7	11.9	26.1	4.5	15.3	180.7	77.4	46.3	12.4	11.8	53.1	9.1
32-13	11.3	5.5	79.6	14.4	66	1.1	23.1	10.4	18.7	32.9	18.6	18.6	165.7	205.9	98.2	29.9	37.7	69.6	9
32-14	6.4	11.8	133.5	17.8	101.4	0.7	78	5.1	15.2	26.7	1	7.5	142.6	117	79.9	18.7	22.3	231.4	14.5
32-15	11.4	7	61.6	24.4	540.3	5.5	55.5	nd	23.4	22.5	5.8	8.7	124.1	177.4	368.1	127.1	288	160.5	9.9
32-16	10.6	1.1	5	2.3	10.2	nd	0.3	nd	5.9	33	3.3	23.7	111.8	112.7	36.3	3.7	1.9	37.2	4.9
32-17	9	5.1	51.6	9.2	11.2	4.7	1.4	6.6	16	26.5	12.9	25.4	125.7	484.9	73.1	nd	5.3	22.2	20.2
32-18	6.6	2.6	3.4	6.1	2.3	nd	1.1	4.1	7.2	28.4	nd	21.2	114.4	71.4	13.4	nd	2.4	20.2	10.2
32-19	4.7	nd	1.1	0.5	2.3	nd	0.3	1.1	8.7	36	6.7	23.3	113.5	74.5	21.4	nd	nd	22.7	8.8
32-20	3.5	0.2	1.6	1.4	4	5.2	3.2	1.6	1.3	34	nd	23.3	127.9	90	12.3	nd	nd	18.2	11.5
32-21	8.1	2.5	42.5	4.1	8.5	3	4.5	0.6	1.5	28.6	1.1	20.2	197.3	195.2	27.8	6	nd	32.2	10.5
32-22	9.7	3.7	36.9	7	11.9	2.1	7.1	nd	1	25.9	0.4	25	245.6	118.7	39.6	5.1	6.4	26.5	10.4
32-23	5.8	4.1	147	9.1	27.8	1.3	18.9	2.5	8.8	27.3	2.6	19.2	203.4	173.2	60.6	3.1	6.9	67.7	14.4
32-24	10	2.7	8.9	0.7	9.7	nd	2.5	nd	2.7	26.9	nd	25	119.1	126.8	27.9	9.4	6.5	24.1	9.2
32-25	14	0.1	6.6	0	3.5	nd	0.7	nd	1.7	28	2.1	23.5	115.4	126.5	17.6	nd	nd	25.4	10.5
32-26	7.7	6.4	71	20.3	67.3	6.2	20	0.4	11.2	31.4	2.4	15.9	121	198.4	93.1	31.8	32.3	79.6	20.3
32-27	8.6	1.4	4.1	5.1	2.1	0.5	1.4	nd	nd	29.3	7.5	24.4	143.8	117	7.3	nd	0.2	13.6	9.7
32-28	6.8	0.5	3.7	4.6	5	nd	nd	nd	nd	39.3	nd	22	132	196.4	18.9	nd	nd	24.5	20.6
32-29	4.3	22.7	249.3	85	309.3	1.7	164.6	26.6	90	12.7	27.5	5.4	369.4	522.5	292.5	181.2	162.3	533.8	49.5
32-30	8.1	2.2	33.8	16.5	79	3.7	17.6	nd	80.8	29.2	26.9	20.9	151	457.4	140.1	47.8	37.6	59	23.2
32-31	2.9	7.1	100.6	36.5	113.2	3.8	56.3	10.3	70	24	9.8	10	234.4	669.7	226.9	72.2	64.6	238.8	34.8
32-32	8.9	1.6	8.9	39.9	22.6	5	3.2	nd	1.7	24.2	5.7	19.8	98.9	261.5	37.2	15.5	18.2	22.4	10.2
32-33	5.2	4.6	30.5	21	138.2	0.4	17.3	6.1	21.4	29.5	9.5	17.1	144.9	363.9	169.5	109.3	103.5	90.2	14.7
32-34	8.9	2.8	11.3	4.9	9.9	1.4	1.3	nd	6.4	31.3	0.1	19.3	107	232.7	21.1	3.9	0.6	29.3	10.7
32-35	9.5	1.7	14.7	9.1	48.1	4	1.3	nd	13.4	37.7	12.1	25.1	156.2	314.6	141	38	30.8	31.8	13.3
32-36	9.9	1.5	12.3	3.8	6.8	3.9	0.5	2.2	9.1	30.7	6.6	14.7	90.8	248.5	26.5	1	1.2	22.6	8.3
32-37	5.8	2.2	13.6	6.6	5.5	nd	3	2.1	15.3	28.1	6.9	24.6	104.5	327.7	23.6	nd	nd	33.4	10.2

Appendix B: Results

B10

Sample No. ppm	Mo	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Cu	Ni	Co	Cr	V	Ce	Nd	La	Ba	Sc
32-38	10.8	1.5	5.4	2.8	nd	nd	0.4	nd	nd	33	nd	24	99.2	196.6	22.2	2.4	nd	26.1	7.3
32-39	3.5	2.1	24	7.7	11.4	0.7	2.9	3	4.6	23.1	5.9	8.5	92.6	208.6	19.5	4	3.8	19.5	5.5
32-40	4	1.2	9.5	3.5	5	1.4	0.4	0.4	5.7	23.6	4.5	7.5	117.3	99.6	14.9	1.9	0	24.7	2.6
32-41	4.3	nd	2.9	2.2	6.2	nd	0.1	nd	nd	16.2	2.7	8.1	87.3	64.6	16.8	1.4	2.5	11.6	1
32-43	3.1	1	4.5	1.2	2.4	0.5	1	nd	nd	17.4	8.2	3.9	56.3	43.7	11.2	nd	nd	7.7	1.4
32-44	3.1	0.2	2.8	0.7	2.3	nd	0.2	nd	0.2	11.4	5.7	2.2	49.2	27	5.2	1.5	nd	4.8	0.7
32-45	2.6	0.7	5.1	2.2	6.4	nd	1.2	0.8	nd	11.4	7.2	1.1	51.7	32.3	8.3	2	2.2	4.6	0.8

Sample No. ppm	Mo	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Cu	Ni	Co	Cr	V	Ce	Nd	La	Ba	Sc
33-01A	5.1	15.8	292.1	23.2	376.1	0.3	173.2	13.6	54.8	0	15.8	1.8	298.2	81.7	168	41.5	62.3	340.7	27.3
33-01B	5.6	13.1	252.8	21.2	171.4	nd	94.8	11	31.9	12.8	28	8.2	462.5	216.5	124.9	32.3	47	247.9	29.5
33-02	5	15.2	291.2	23.3	209.6	1.1	169.5	11.8	25.5	3.5	24.5	6.3	332.1	104.6	78.3	22	41.5	338.2	21.4
33-03	6.4	8.7	114.7	12.3	282.9	nd	85.7	10.1	30	16.5	8	6.4	175.9	123.5	60.1	25.2	32.7	248.5	16.6
33-04	7.7	9.1	208.4	14.2	186.6	1.6	62.1	6.4	46.7	23.9	16.1	9.1	205.9	218.7	89.7	29.7	54	189	19.8
33-05	5.9	6.5	160.5	7.2	66.1	0.1	14.6	8.2	14.1	34.7	9.9	10.5	289.7	941.3	26.6	4.6	2.9	64.3	23.9
33-06	7.9	19.4	368	19.7	301.5	nd	148.8	21.7	16.1	5.3	16.4	1.4	175	165.9	63.7	20.2	30	345.9	25.2
33-07	8.3	10.3	171.4	7.5	99.2	0.2	41.4	13.5	15.2	24.6	3.5	7.2	204.2	419.2	38.7	9.3	17.3	139.2	19.2
33-08	10.5	17	494.8	17.6	268.6	1	154.1	14.6	11.4	8.9	16.8	3.1	204.4	149.6	58.1	16.1	28.8	321.9	25.4
33-09	7.6	21	393	19.7	277.4	nd	105.4	20.2	11.2	3.3	13.4	2.2	129.6	200.5	53.5	15.9	31.2	218.3	20.2
33-10	7.8	13.5	244.5	14.5	331.7	nd	92.3	10.3	34.6	18.8	15.5	8	210.6	200.3	130.2	23.6	55.1	304.9	34.1
33-11	6.9	5	76.7	6.9	53.3	nd	8.6	7.5	25.6	29	18	20.3	202.4	277	93.7	11.8	25.2	54.6	19.1
33-12	20	32.1	1067.4	50.2	540.7	1	60.8	35.7	100.2	16.4	16.1	3.4	702.9	221.4	212.7	78.4	107.2	191	49.3
33-13	7.4	4.8	62.5	9.3	193.7	1.5	38	nd	7.9	23.2	5.7	8.2	146.4	196.9	62.8	15.7	21.4	146.2	15.9
33-14	3.8	2.4	28.7	12.1	106.6	nd	1.2	nd	5.4	28.3	nd	21.7	134.3	234	57.3	8.4	21.4	172.7	10.5
33-15	5.8	4.5	43.1	14.6	90.7	nd	1	3.9	21.3	33.4	11.4	24.1	133	167.2	91.8	28.8	46.6	416.8	10.4
33-16	7.9	3.6	50.5	13.9	135.4	1	2.6	5.8	26	31.7	1.1	19.7	181.9	175.3	134.5	38	58.5	114.7	13.1
33-17	6.3	3.9	35.1	14.2	116.8	nd	4.9	4.5	18.6	33.2	6	23.5	138.9	190.6	82.5	23.1	41.5	47.4	10.5
33-18	5.3	4.9	46.2	13.9	328.6	nd	7.5	1.4	26.9	32.4	4.3	16.4	141.2	135	174	45.5	74.1	65	10.9
33-19	5.9	5	52.1	14.6	224.3	nd	8.4	8.2	34.4	31.7	1.1	18.6	128	206.7	152.2	44.9	75.3	63.6	12.7
33-20	7.5	6.4	43	12.3	247.6	nd	10.5	9.6	31.9	27.8	11.9	15.8	120.6	144.4	123.9	42.5	62.7	46.5	8.4
33-21	6.8	4.7	44.1	17.1	118.5	nd	1.5	3.8	12.6	39.1	8.8	21.7	137.4	190.1	72	23.3	39.1	34.3	11.3
33-22	7.6	4.5	6.3	1.5	7.7	nd	2.4	nd	5	34.9	6	22.6	98.3	182.5	13.8	4.4	0.8	23	9.7
33-23	2.1	0.3	8.3	3.9	42.3	nd	0.9	nd	6.3	29.9	nd	22.9	92.1	310.6	24	5	1.9	25.8	8.8
33-24	5.5	6.6	47.3	15.1	238.1	nd	2.8	1	13.1	25.5	5.8	18.6	137.1	335	76.4	40.7	50.4	50.3	17.8

Sample No. ppm	Mo	Nb	Zr	Y	Sr	U	Rb	Th	Pb	Cu	Ni	Co	Cr	V	Ce	Nd	La	Ba	Sc
33-25	3.2	17.5	147.6	32.3	197.1	0.3	31.7	17.9	26.8	nd	7.2	nd	145.2	27.9	112.4	52.4	63.1	78.8	18.7
33-26	2.5	20.3	148.6	33.4	165.5	nd	27.6	20	31.7	nd	9.3	nd	121.4	34.1	114.4	53.9	63.4	69	17.5
33-27	3	16.7	137	28.3	124.2	nd	33.9	15.2	22	nd	8.6	0.4	57.3	32.3	96.4	38.5	52.8	80.8	15.1
33-28	2.5	15	126	26.6	139.5	1.2	26.9	14.5	20.8	nd	11.8	0.2	138.6	27.8	85.3	36.3	48.3	58.8	13.6
33-29	3.8	23.1	206.2	46.1	255	1.5	41.7	26.9	36.4	nd	9.8	nd	234.4	58.3	165.1	67.4	89.9	88.3	21.7
33-31	3.1	0.8	3.6	1	0.9	0.2	nd	nd	2.1	7.8	8.8	1.9	53.4	25	2.3	nd	nd	2.5	0.7
33-32	3	1.6	18.6	4.5	8.1	nd	nd	1	nd	8.9	9.4	2.6	59.3	25.1	7.9	0.8	1.9	5.5	4
33-33	2.8	1.4	5.8	1.4	11.5	nd	nd	nd	nd	4.9	10	1.6	36.5	14.5	7.2	2.6	0.7	2.5	0.9
33-34	4.1	0.7	3.6	2.1	5.5	nd	nd	nd	0.3	14.3	14.9	2.8	56.3	16.9	4	0.1	0.4	115.3	0.6
33-35	2.1	0.4	1.3	8.9	3.1	nd	0.3	0.5	0.1	5.7	6.6	0.7	28.9	13.3	2.3	0.5	1.1	7	0.3
33-36	4.1	1	4.1	5.6	7.5	0.7	1.4	nd	nd	9.5	12.9	1.7	43.8	16.8	4.4	2	1.3	263.6	0.5

B4: Rare earth element geochemical data for Mapedi shales

Appendix B4 contains raw tabulated REE geochemical data for the shale samples from Land (2010). REE data are expressed as part per million (ppm).

Sample No. ppm	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
N2	42.37	102.7	9.622	35.57	6.353	1.414	4.729	0.668	3.982	0.737	2.124	0.299	2.03	0.294
N9	48.1	115.4	10.68	38.74	6.715	1.391	4.846	0.706	4.24	0.801	2.335	0.335	2.327	0.342
N15	47.45	109.9	10.12	36.69	6.381	1.296	4.743	0.687	4.17	0.785	2.284	0.334	2.329	0.342
N28	24.4	55.4	5.206	18.69	3.391	0.729	2.862	0.459	2.949	0.603	1.857	0.286	2.026	0.302
N32	29.38	66.86	6.285	22.63	4.195	0.846	3.324	0.54	3.418	0.694	2.145	0.326	2.342	0.343
L2	44.8	104	10.2	37.7	6.56	1.53	5.15	0.72	4.09	0.77	2.24	0.33	2.21	0.33
L8	46.2	99.6	9.91	35.6	6.22	1.35	5.03	0.75	4.53	0.87	2.59	0.38	2.56	0.39
ALK 4	53.6	124	11.8	42.9	7.51	1.62	5.84	0.88	5.27	1.03	2.96	0.45	3.00	0.44

Appendix C: X-Ray Diffraction (XRD) data

The following graphs (C1 to C16) present the XRD spectra for the 16 hematite separate samples that were analysed for rare earth elements and oxygen isotopes. The only mineral present in all of the spectra is hematite. Using the XRD technique, contaminant minerals could be identified by examining the peaks that occur in the XRD spectra obtained. The maximum peak of a particular mineral occurs at a specific 2θ on the x-axis of the graph. Thus the presence of a particular minerals maximum peak at a specific 2θ value is indicative of the presence of the mineral. However, the absence of a maximum peak at a specific 2θ value indicates the absence of that mineral.

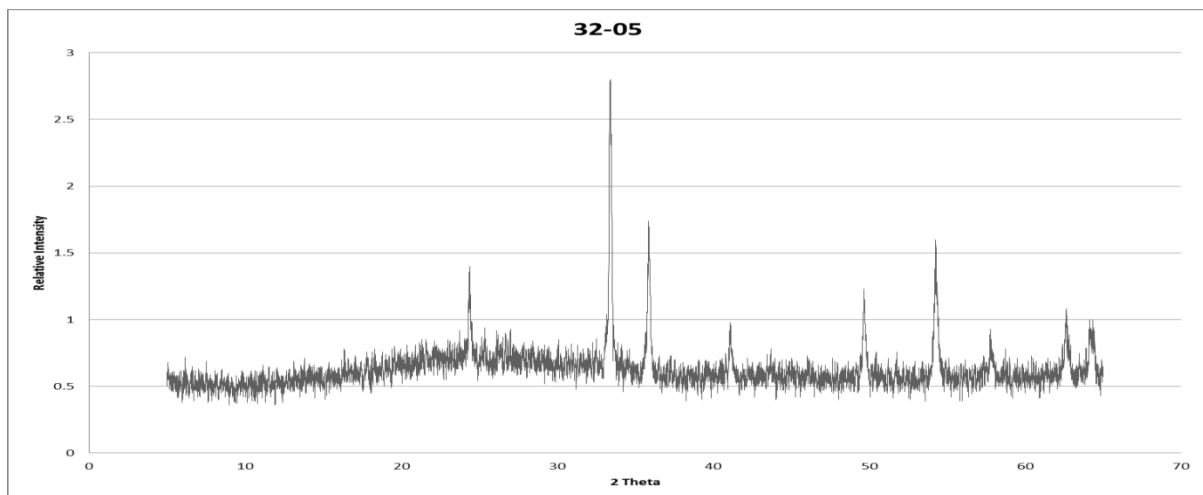


Figure C1. Sample 32-05. This is a sample from the low-grade iron ore.

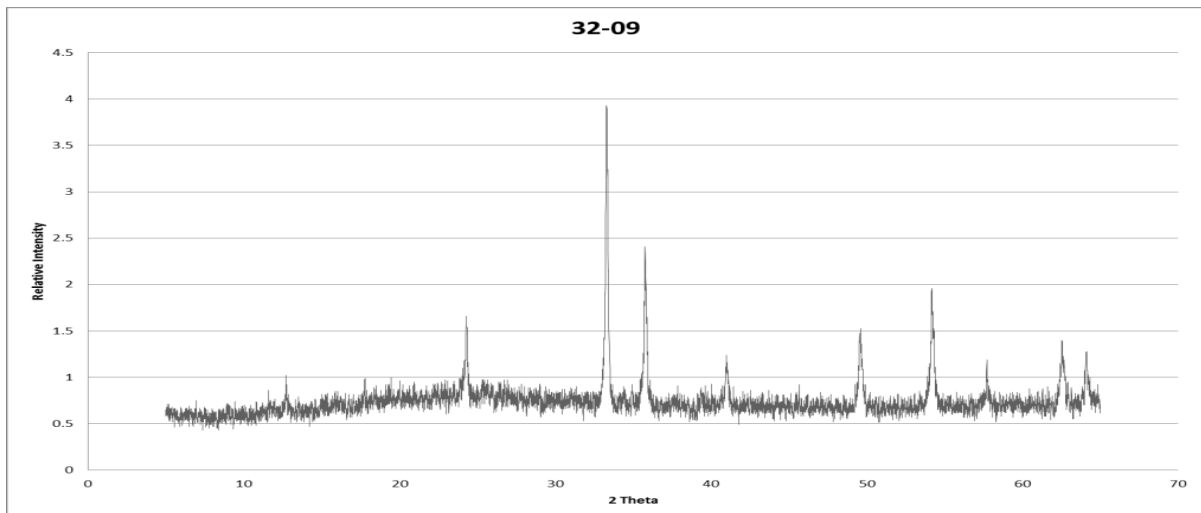


Figure C2. Sample 32-09. This is a sample from the low-grade iron ore.

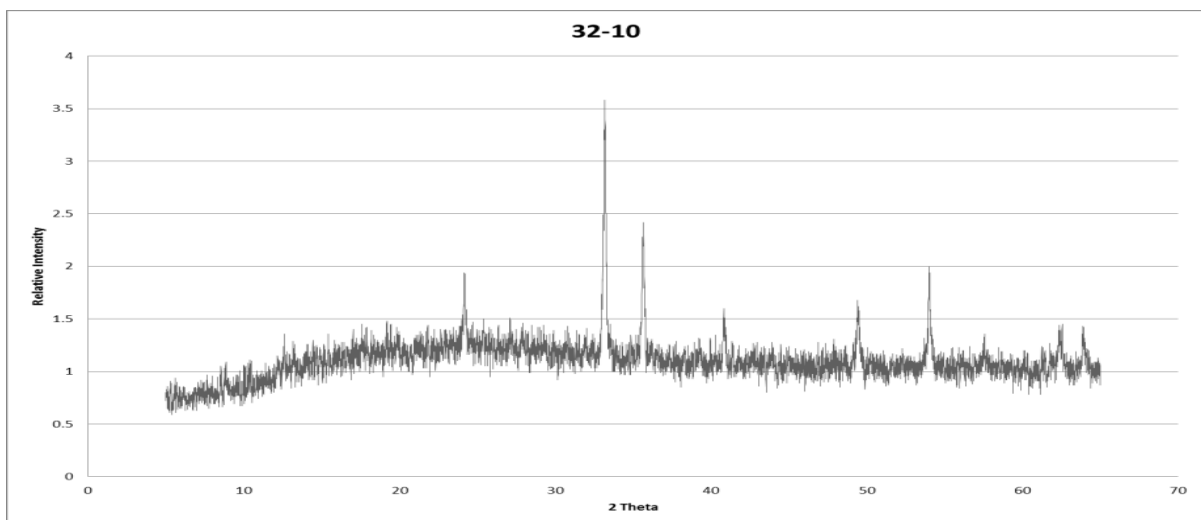


Figure C3. Sample 32-10. This is a sample from the low-grade iron ore.

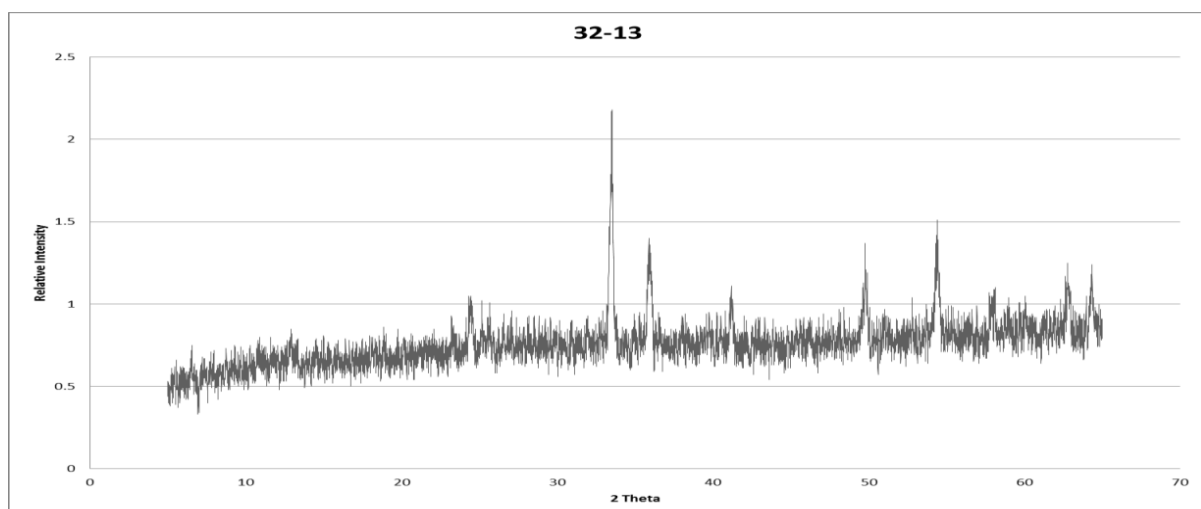


Figure C4. Sample 32-13. This is a sample from the low-grade iron ore.

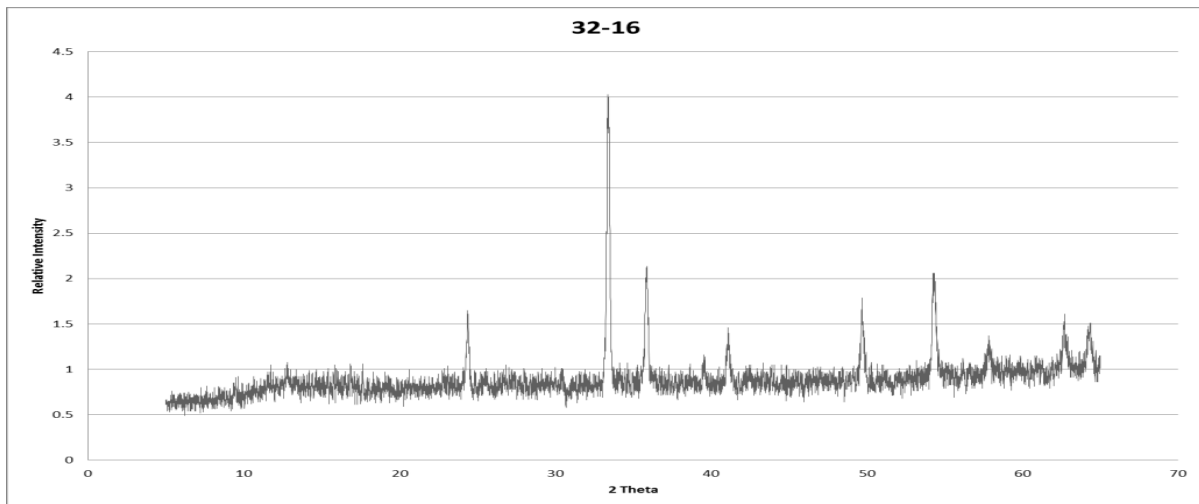


Figure C5. Sample 32-16. This is a sample from the low-grade iron ore.

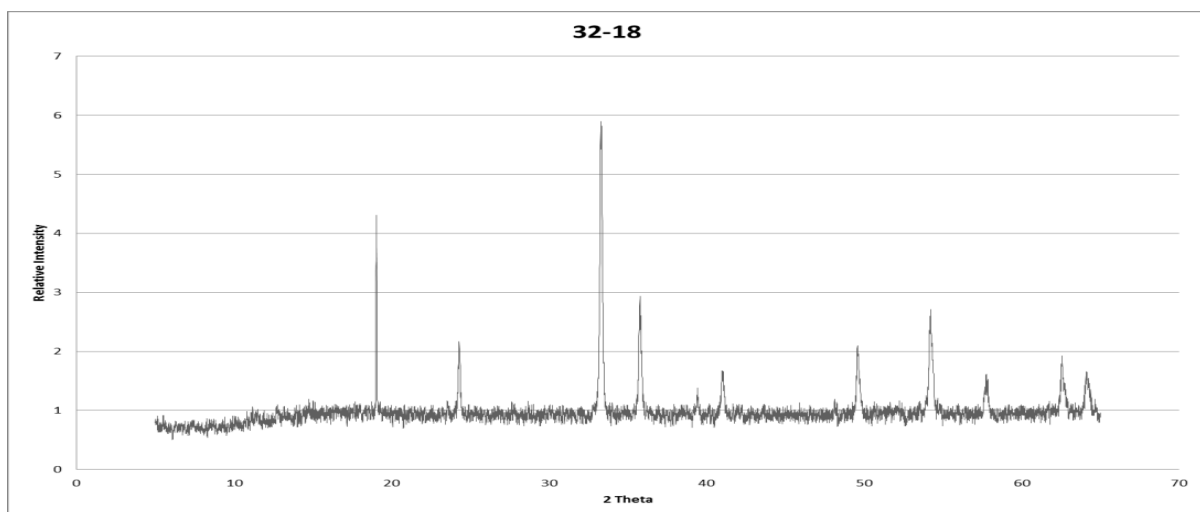


Figure C6. Sample 32-18. This is a sample from the high-grade iron ore.

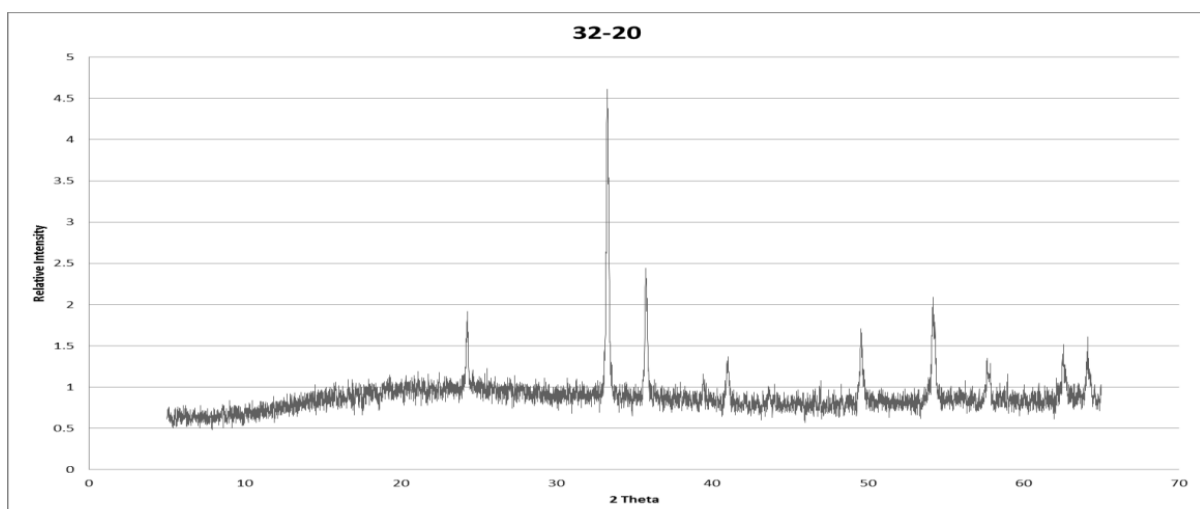


Figure C7. Sample 32-20. This is a sample from the high-grade iron ore.

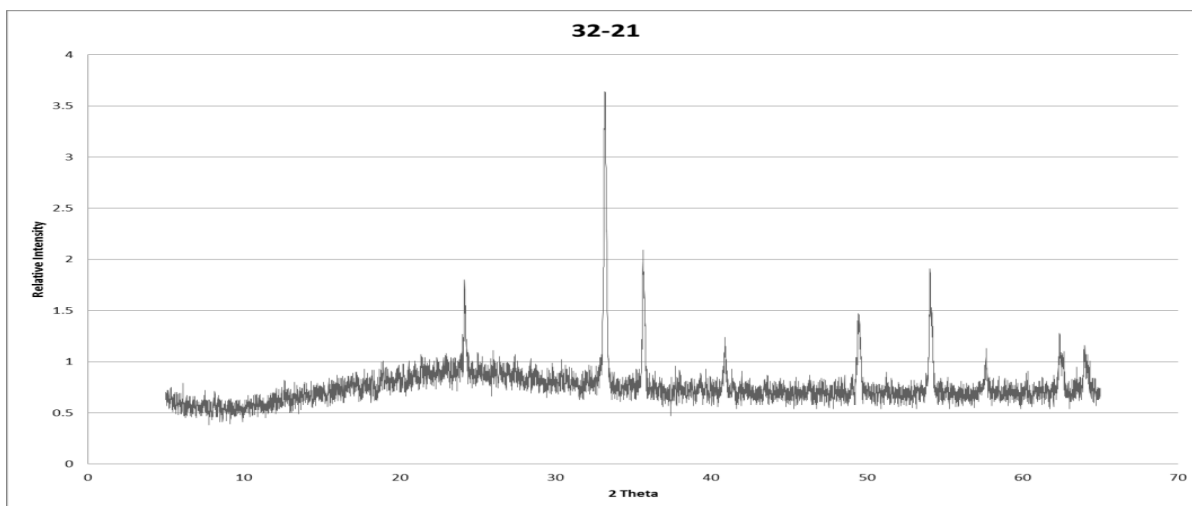


Figure C8. Sample 32-21. This is a sample from the high-grade iron ore.

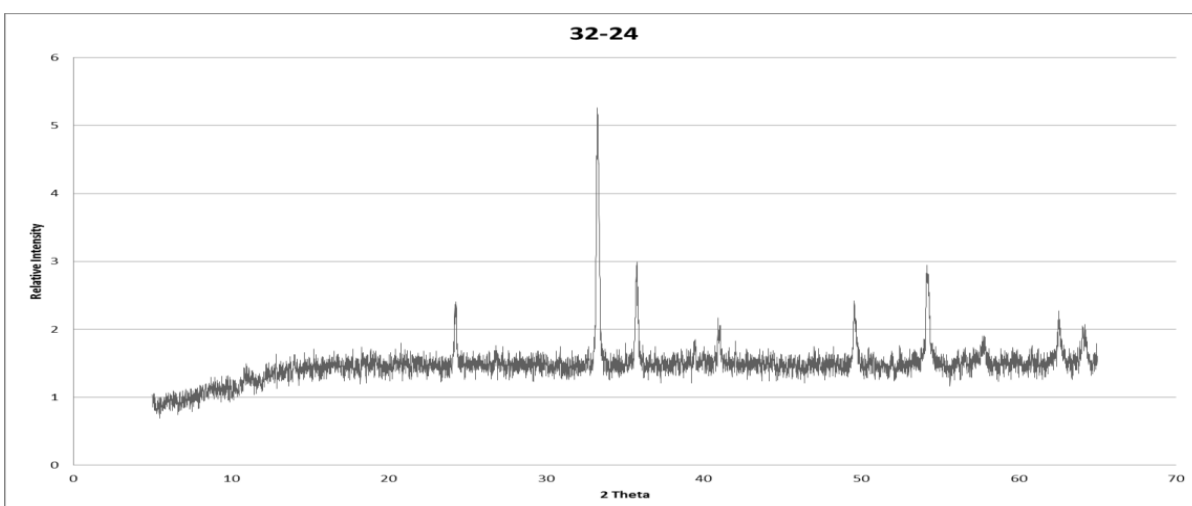


Figure C9. Sample 32-24. This is a sample from the high-grade iron ore.

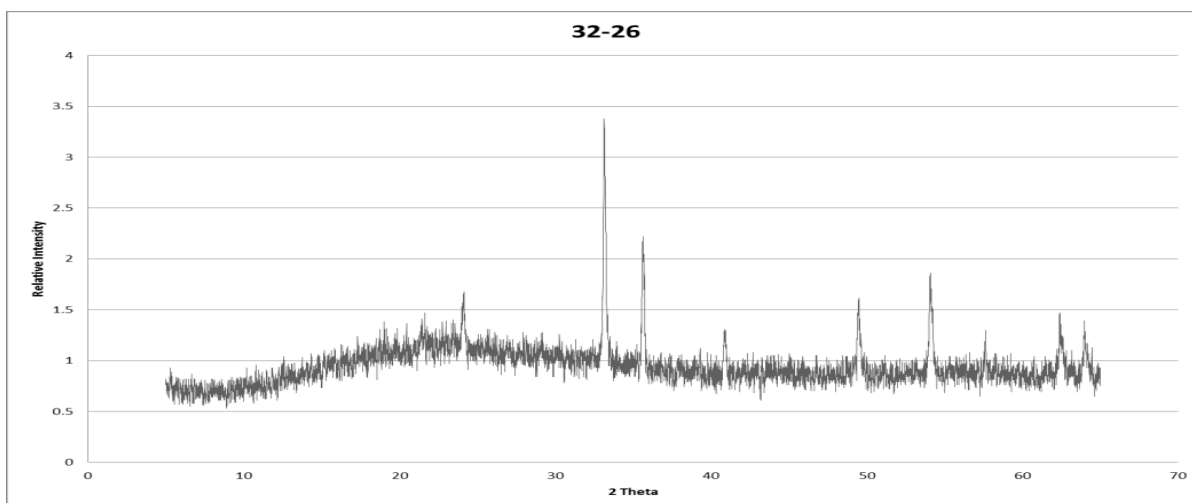


Figure C10. Sample 32-26. This is a sample from the high-grade iron ore.

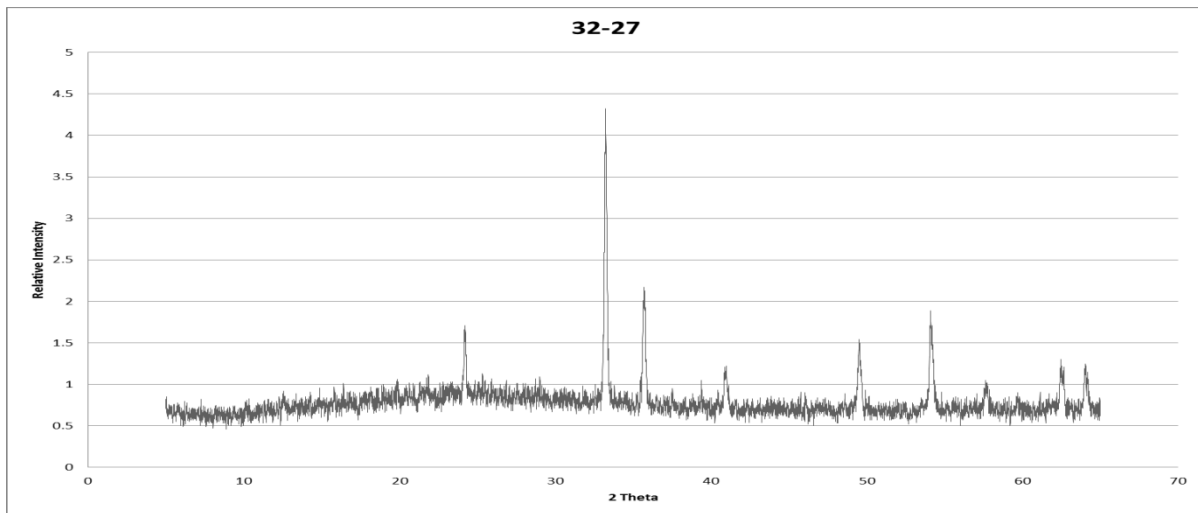


Figure C11. Sample 32-27. This is a sample from the high-grade iron ore.

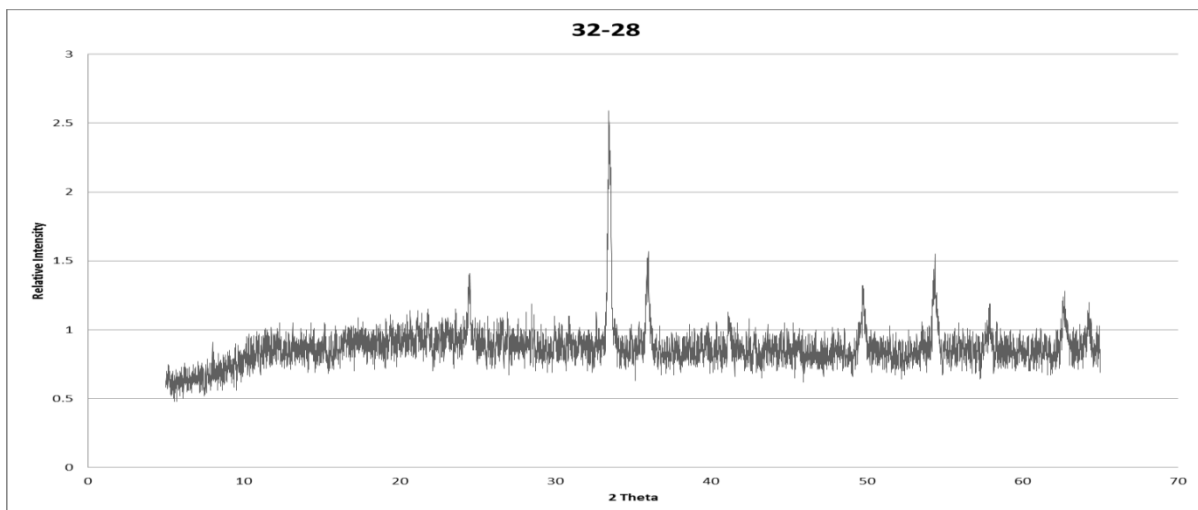


Figure C12. Sample 32-28. This is a sample from the high-grade iron ore.

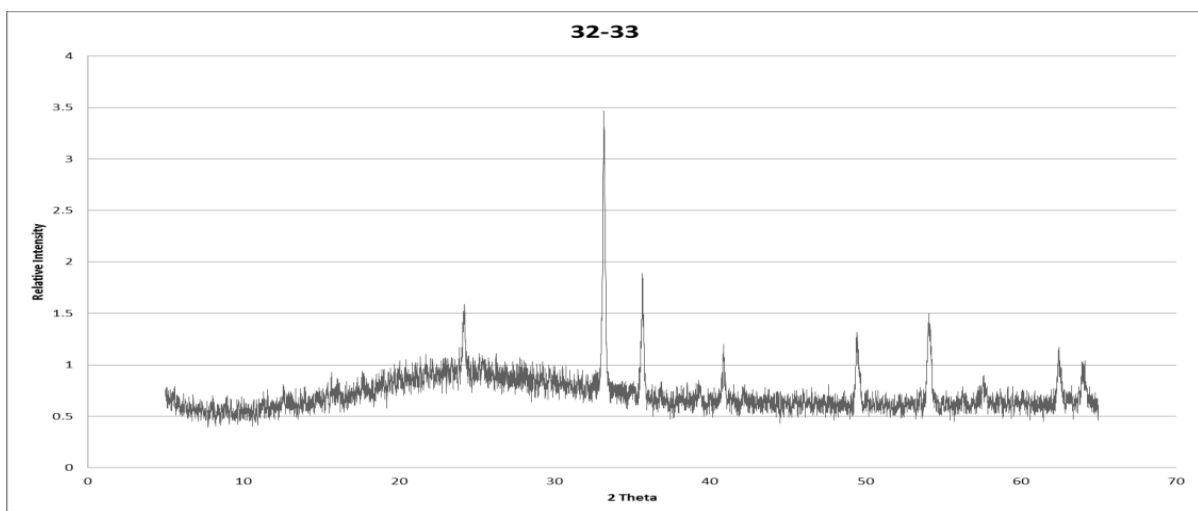


Figure C13. Sample 32-33. This is a sample from the high-grade iron ore.

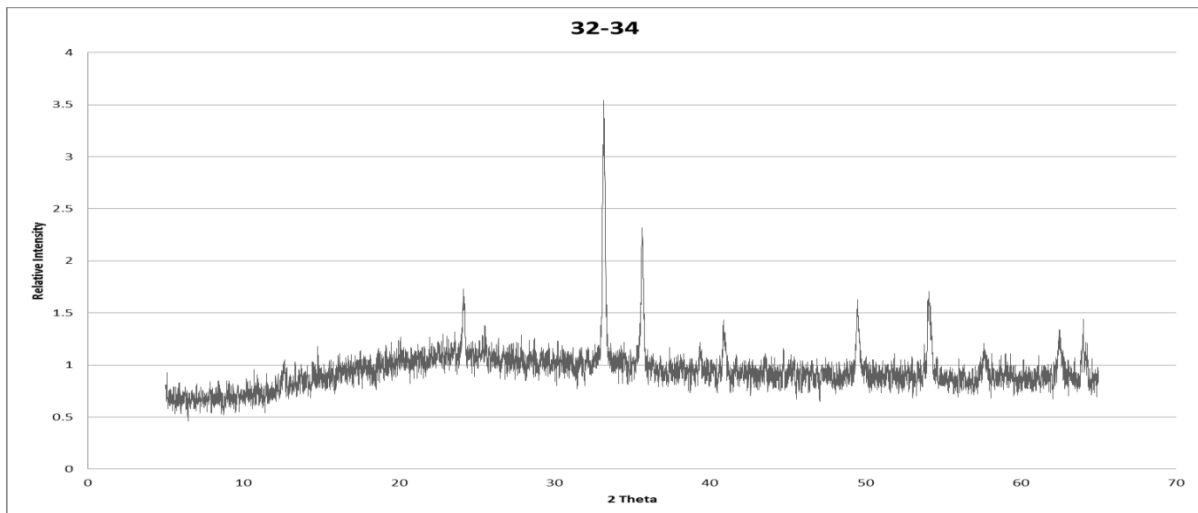


Figure C14. Sample 32-34. This is a sample from the high-grade iron ore.

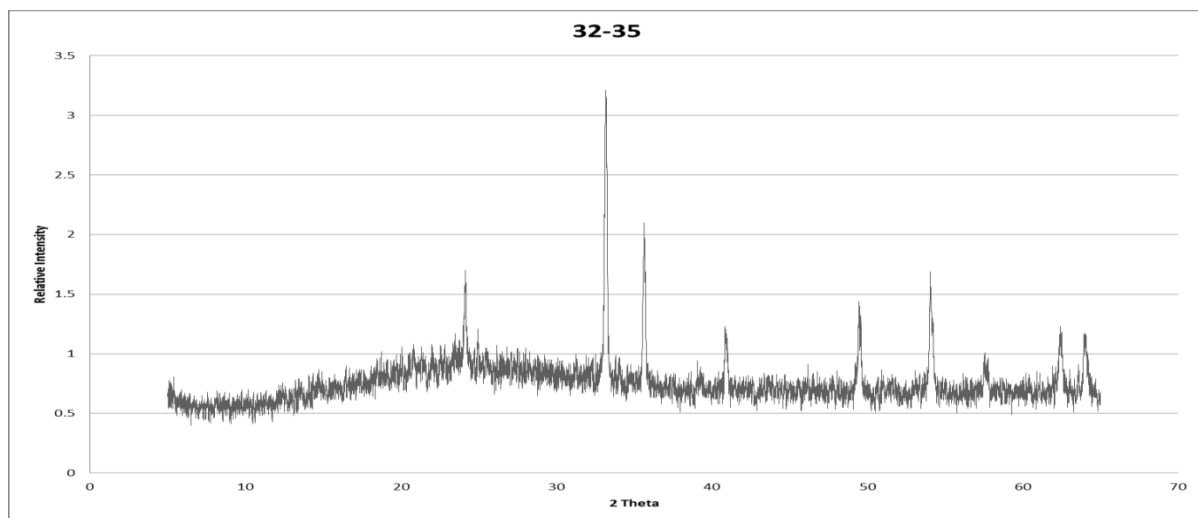


Figure C15. Sample 32-35. This is a sample from the high-grade iron ore.

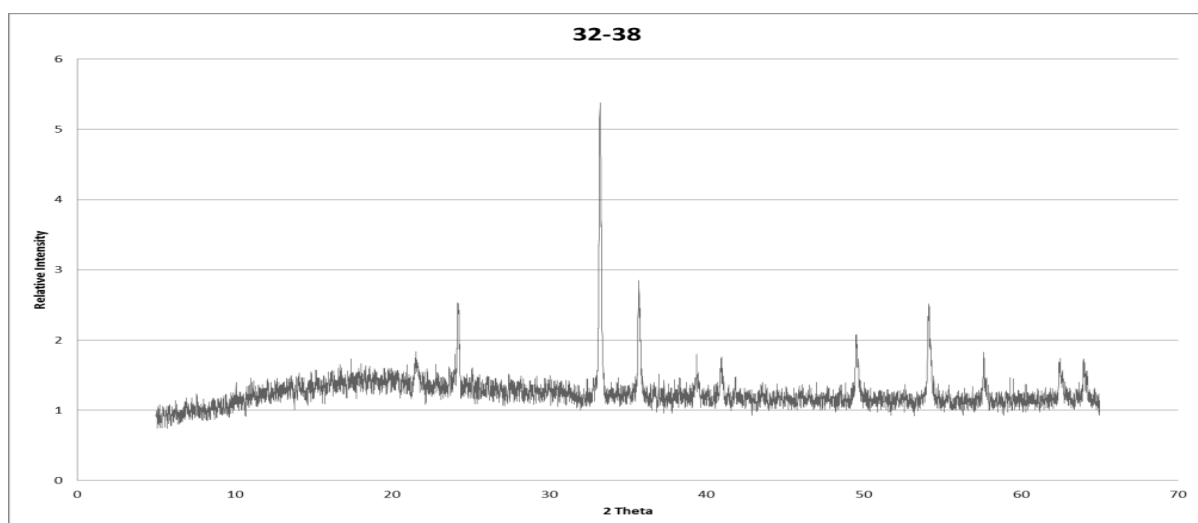


Figure C16. Sample 32-38. This is a sample from the high-grade iron ore.