



RHODES UNIVERSITY

Grahamstown • 6140 • South Africa

**DISTRIBUTION OF IRON-TITANIUM OXIDES IN THE VANADIFEROUS MAIN
MAGNETITE SEAM OF THE UPPER ZONE: NORTHERN LIMB, BUSHVELD
COMPLEX.**

Demand Gwatinetsa

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Geology Department

Rhodes University

P.O. Box 94

Grahamstown 6140

South Africa

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DECLARATION

I, Demand Gwatinetsa, declare this dissertation to be my own work. It is submitted in partial fulfilment of the Degree of Master of Science at Rhodes University. It has not been submitted before for any degree or examination in any other University or tertiary institution.

Signature of the candidate:

Date:

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ABSTRACT

The main magnetite seam of the Upper Zone of the Rustenburg Layered Suite (SACS, 1980) on the Bushveld Complex is known to host the world's largest vanadium bearing titaniferous iron ores. The vanadiferous titanomagnetites, contain vanadium in sufficient concentrations (1.2 - 2.2 per cent V_2O_5) to be considered as resources and vanadium has been mined historically by a number of companies among them Anglo-American, Highveld Steel and Vanadium and VanMag Resources as well as currently by Evraz Highveld Steel and Vanadium Limited of South Africa. The titanomagnetites contain iron ore in the form of magnetite and titanium with concentrations averaging 50-75 per cent FeO and 12-21 per cent TiO_2 . The titaniferous iron ores have been historically dismissed as a source of iron and titanium, due to the known difficulties of using iron ore with high titania content in blast furnaces.

The economic potential for the extractability of the titaniferous magnetites lies in the capacity of the ores to be separated into iron rich and titanium rich concentrates usually through, crushing, grinding and magnetic separation. The separatability of iron oxides and titanium oxides, is dependent on the nature in which the titanium oxide occurs, with granular ilmenite being the most favourable since it can be separated from magnetite via magnetic separation. Titanium that occurs as finely exsolved lamellae or as iron-titanium oxides with low titania content such as ulvospinel render the potential recoverability of titanium poor. The Upper Zone vanadiferous titanomagnetites contain titanium in various forms varying from discrete granular ilmenite to finely exsolved lamellae as well as occurring as part of the minerals ulvospinel (Fe_2TiO_4) and titanomagnetite (a solid solution series between ulvospinel and magnetite). Discrete ilmenite constitutes between 3-5 per cent by volume of the massive titanomagnetite ores, and between 5-10 per cent by volume of the magnetite-plagioclase cumulates with more than 50 per cent opaque oxide minerals.

The purpose of this research was to investigate the mineralogical setting and distribution of the iron and titanium oxides within the magnetite layers from top to bottom as well as spatially along a strike length of 2 000m to determine the potential for the titanium to be extracted from the titanomagnetite ores. The titanomagnetites of the Upper Zone of the Bushveld Complex with particular reference to the Northern Limb where this research was conducted contains titanium oxides as discrete ilmenite grains but in low concentrations whose potential for separate economic extraction will be challenging. The highest

concentration of titanium in the magnetite ores is not contained in the granular ilmenite, but rather in ulvospinel and titanomagnetite as illustrated by the marked higher concentration of TiO_2 in the massive ores which contain less granular ilmenite in comparison to the disseminated ores which contain 3 to 8 percentage points higher granular ilmenite than the massive ores.

On the scale of the main magnetite seam, the TiO_2 content increases with increasing stratigraphic height from being completely absent in the footwall anorthosite. The V_2O_5 content also increases with stratigraphic height except for in one of the 3 boreholes where it drops with increasing height. The decrease or increase patterns are repeated in every seam. The titanomagnetites of the main magnetite seam display a variety of textures from coarse granular magnetite and ilmenite, to trellis ilmenite lamellae, intergranular ilmenite and magnesian spinels and fine exsolution lamellae of ulvospinel and ferro-magnesian spinels parallel to the magnetite cleavage. The bottom contact of the main magnetite seam is very sharp and there is no titanium or vanadium in the footwall barely 10cm below the contact. Chromium is present in the bottom of the 4 layers that constitute the main magnetite seam and it upwards decreases rapidly. In boreholes P21 and P55, there are slight reversals in the TiO_2 and V_2O_5 content towards the top of the magnetite seams.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
ABSTRACT	III
TABLE OF CONTENTS	V
LIST OF FIGURES	IX
LIST OF TABLES	XIII
CHAPTER 1 INTRODUCTION AND REGIONAL SETTING	1
1.1. Location of the study area	3
1.2. Fe-Ti-V mineral potential and occurrence in the Bushveld Complex	5
1.3. Outline of intended research	9
1.4. Purpose of research	11
CHAPTER 2 GEOLOGY AND REGIONAL SETTING	13
2.1. Historical work	13
2.2. The Geology of the Bushveld Complex	15
2.2.1. Age of the Bushveld	16
2.2.2. Tectonic Setting and Floor Rocks	17
2.2.3. Transvaal Supergroup	19
2.2.4. Rooiberg Group	19
2.3. Bushveld Stratigraphy	19
2.3.1. The Marginal zone	21
2.3.2. The Lower Zone	21
2.3.3. The Critical Zone	21
2.3.4. The Main Zone	22
2.3.5. The Upper Zone	22
2.3.6. The Lebowa Granite Suite	23
2.3.7. The Rashedoop Granophyre Suite	23
2.4. The geology of the Northern Limb	25

2.4.1.	Introduction.....	25
2.4.2.	The Rustenburg Layered Suite.....	27
2.5.	Local Geology.....	28
CHAPTER 3	MINERALS OF THE FE-TI-V SYSTEM	31
3.1.	The spinel series - magnetite, titanomagnetite and ulvospinel.....	31
3.2.	The rhombohedral series - ilmenite and hematite	32
3.3.	Phase relations.....	33
3.4.	Textural and exsolution features in titaniferous magnetites.....	35
3.4.1.	Macroscopic Textural features.....	36
3.4.2.	Microscopic Textural features	37
3.5.	Geochemistry of the titanomagnetite ores.....	40
3.6.	Origin of the vanadium bearing titanomagnetites of the Upper Zone.....	41
3.7.	Global Vanadium production	43
3.8.	Global Titanium production	43
3.9.	Recovery of vanadium from titaniferous magnetites	45
3.10.	Recovery of iron and titanium from titaniferous magnetites.....	45
CHAPTER 4	METHODOLOGY	47
4.1.	Introduction	47
4.2.	Problem statement	47
4.2.1.	The Titanium problem in Blast furnaces	48
4.3.	Research outline	49
4.4.	Sample collection and treatment	50
4.5.	Petrography	54
4.6.	Optical Microscopy	54
4.7.	Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry.....	54
4.8.	Electron Probe Micro-Analyser (EPMA).....	55
CHAPTER 5	RESULTS.....	57

5.1. TEXTURAL VARIATIONS	57
5.1.1. Granular ilmenite	58
5.1.2. Exsolved ilmenite and ulvospinel	59
5.1.3. Magnesian and ferromagnesian spinels (pleonaste and hercynite).....	60
5.2. PETROGRAPHY	62
5.2.1. P 21	62
5.2.2. P 55	66
5.2.3. P 57	70
5.3. VERTICAL DISTRIBUTION OF OXIDES, SULPHIDES AND TRACE ELEMENTS.....	74
5.3.1. Introduction.....	74
5.3.2. P21	74
5.3.3. P55	78
5.3.4. P 57	81
5.4. LATERAL DISTRIBUTION OF TiO ₂ , V ₂ O ₅ , SILICATES, SULPHIDES AND TRACE ELEMENTS.....	84
5.4.1. Introduction.....	84
5.4.2. TiO ₂	84
5.4.3. V ₂ O ₅	84
5.4.4. Silicates, sulphides and trace elements	84
5.5. Interpretation	85
CHAPTER 6 DISCUSSION.....	87
CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS	90
7.1. Conclusions	90
7.2. Recommendations	91
REFERENCES.....	93
APPENDIX A – QUARTER CORE SAMPLES.....	101

APPENDIX B – POLISHED THIN SECTIONS OF SAMPLES FROM P21, P55 AND P57	107
APPENDIX C - SAMPLE POSITIONS FOR THE BOREHOLES P21, P55 AND P57	110

LIST OF FIGURES

Figure 1 Generalised geological map of the study area on the Bushveld Complex. Adapted from (Roelofse, 2012).....	3
Figure 2 Location of the study area showing the farms constituting the study area GZ=Gezond 235KR, CM=Commandodrift 228 KR, ML=Molendraai 811 LR, MZ=Mozambique 807 LR and IN=Inhambane 802 LR.....	4
Figure 3 Borehole profiles from the Northern Limb in the study area showing the magnetite layers, TiO_2 as well as V_2O_5 content. Dark areas represent areas with more than 50% magnetite by weight while mottled areas represent areas less than 50%. Adapted from (Cawthorn and Molyneux, 1986).....	7
Figure 4 Borehole profiles showing magnetite layers and V_2O_5 content after (Raal, 1965) from boreholes drilled on farm Rhenosterfontein. Modified after (Cawthorn and Molyneux, 1986)	8
Figure 5 Quarter core samples which were prepared into polished thin sections. (a) Magnetite anorthosite parting between MAG 04 and MAG 03 in P57 (b) magnetite-plagioclase cumulate (c) massive magnetite with minor plagioclase (d) massive magnetite with plagioclase laths.....	10
Figure 6 Contrasting textures of titanium bearing magnetite [a] discrete ilmenite grains (dark grey) in magnetite (light grey). [b] fine ulvospinel exsolution lamellae (cloth texture) in titanomagnetite (grey background). Black laths are the spinel pleonaste.....	12
Figure 7 Outcrop of titanomagnetite seam in the Upper Zone of the Rustenburg Layered Suite at Magnet Heights in the Eastern Limb of the Bushveld Complex.	14
Figure 8 Simplified geological Map of the Bushveld Complex. Adapted from (Scoates and Friedman, 2008).....	16
Figure 9 Generalised tectonic map of Southern Africa showing the ENE trending major tectonic lineaments. Adapted from (Klemm et al., 1982).....	17
Figure 10 Tectonic Map of the Bushveld Complex showing the Murchison, Crocodile River and Steelpoort lineaments. Adapted from (Clarke et al., 2009).....	18
Figure 11 Simplified stratigraphy of the Rustenburg Layered Suite showing the Marginal Zone up to Upper Zone. Adapted from (Clarke et al., 2009).....	20
Figure 12 Simplified geological map of Northern Limb: Bushveld Complex. The position of a continuous borehole drilled at Belleveue is shown as BV 1. Adapted from (Ashwal et al., 2005)	26

Figure 13 Generalised geology of the study area. Modified after (Van der Merwe, 1978)....	30
Figure 14 The phases in the FeO-Fe ₂ O ₃ -TiO ₂ system, with the major solid solution series shown. Modified after (Buddington and Lindsley, 1964).....	33
Figure 15 The phase areas at 1300 ⁰ C in the FeO-Fe ₂ O ₃ -TiO ₂ system showing the three solid solution series. Adapted from (Taylor, 1964).....	34
Figure 16 Massive (adcumulate) titanomagnetite ore from the Upper zone magnetitite.....	35
Figure 17 Orthocumulate titanomagnetite-silicate ore from the Upper Zone. The light silicates are largely plagioclase. Note the preferential orientation of plagioclase.....	36
Figure 18 Magnetite grains showing the triple junction and exsolved ulvospinel showing cloth texture. The scale bar is 20µm Adapted from (Reynolds, 1986).....	38
Figure 19 Pleonaste, Ilmenite and ulvospinel exsolution textures (A) pleonaste and ulvospinel boxwork (B) Trellis ilmenite in magnetite. Adapted from (Von Gruenewaldt et al., 1985)	39
Figure 20 Ilmenite intergrowths in titanomagnetite. Note the magnetite triple junctions.	39
Figure 21 Microscopes used during the study (a) Optical Microscope (b) SEM with EDS...	49
Figure 22 Quarter core and corresponding thin section.	50
Figure 23 Borehole P 21 strip log showing the positions of the samples P21-01 to P21-15..	51
Figure 24 Borehole P55 strip log showing the positions of the samples P55-01 to P55-11...	52
Figure 25 Borehole P57 strip log showing the positions of the samples P57-01 to P57-14...	53
Figure 26 Area spectral scanning utilising Energy dispersive spectroscopy for major element analysis. The scanned area is approximately 15mm x 15mm.....	55
Figure 27 (a) Electron microprobe analyser used for point analysis (b) Diagram representing the Microprobe electron column showing the filament at top, sample stage, deflecting crystal and detector. Adapted from JEOL website	56
Figure 28 Backscatter image of ilmenite grains in oxide-silicate cumulate occurring in proximity to silicates.....	58
Figure 29 Backscatter images of (a) trellis ilmenite in titanomagnetite (b) ulvospinel exsolutions in titanomagnetite. Note the ulvospinel free zone surrounding the ilmenite grain. Ilm= ilmenite, ulvo= ulvospinel, tit.mag= titanomagnetite, sulph= sulphide.....	59
Figure 30 Backscatter image of a titanomagnetite grain showing ulvospinel cloth textures. Note the transparent magnesian spinel pleonaste as well as ilmenite filled intergranular space. Pleo= pleonaste, ilm= ilmenite	60

Figure 31 Backscatter image of titanomagnetite showing pleonaste as well as sub-micrometre ulvospinel exsolution lamellae forming a cloth texture. Pleo= pleonaste. Note the 10µm scale bar at bottom left.	61
Figure 32 Magnetite, ilmenite and plagioclase grains observed in borehole P21 under reflected light, PPL. Mag= magnetite, ilm= ilmenite, plag= plagioclase	63
Figure 33 Backscatter images of sections P21-06, 10 and 11. (a) and (b) Note the granular ilmenite in P21-06 in close proximity to silicate phases as well as a rim around an ilmenite grain with no ulvospinel exsolutions. (c) a massive magnetite grain showing ulvospinel exsolutions. (d) Granular ilmenite in magnetite within the vicinity of silicates. Mag= magnetite (titanomagnetite), ilm= ilmenite.	64
Figure 34 Backscatter images of sections P21-12-15. (a) Granular ilmenite in massive magnetite. (b) and (c) magnetite with ilmenite and ulvospinel. Note absence of ulvospinel around ilmenite grain. (d) Magnetite with trellis ilmenite exsolutions, silicate phases with chalcopryrite. Mag= magnetite (titanomagnetite), ilm= ilmenite, chalco= chalcopryrite.....	65
Figure 35 Scatter plot of TiO ₂ and V ₂ O ₅ across the main magnetite seam.....	66
Figure 36 Reflected light microscopy images of P55 titanomagnetites. Note the small nature of ilmenite grains. Mag= magnetite, ilm= ilmenite, plag= plagioclase	67
Figure 37 Backscatter images of titanomagnetite from MAG 03 (a); (b) ilmenite grains in titanomagnetite developed near silicates (c) massive titanomagnetite with shattered magnetite grains (d) large ilmenite grain in titanomagnetite. Mag= titanomagnetite, plag= plagioclase, ilm= ilmenite.....	68
Figure 38 Backscatter images of the samples from MAG 04 (a) ilmenite grains in close proximity to plagioclase (b) large ilmenite grain showing the ulvospinel free zone in the titanomagnetite (c) small ilmenite grains in massive titanomagnetite (d) elongated ilmenite grains in titanomagnetite. Mag= titanomagnetite, plag= plagioclase, ilm=ilmenite.	69
Figure 39 Scatter plot of TiO ₂ and V ₂ O ₅ across the main magnetite seam in P55.	70
Figure 40 Reflected light microscopy images of titanomagnetites in P57. Mag= magnetite, ilm= ilmenite, plag= plagioclase, sulph= sulphides.....	71
Figure 41 Backscatter images of sample P57-08 (a) titanomagnetite grains showing triple junctions and intra-granular ilmenite (b) titanomagnetite, ilmenite, silicates and sulphides (c) titanomagnetite with ulvospinel exsolutions (d) titanomagnetite grain boundaries with disappearing ulvospinel and triple junction.	72
Figure 42 SEM backscatter image of P57-11 showing magnetite (light grey), granular ilmenite (grey) and silicates (dark grey). Scale bar at bottom left is 10mm.	73

Figure 43 Strip log of borehole P21 with plots of TiO_2 and V_2O_5 content in the samples.....	76
Figure 44 Strip log of borehole P 55 with plots of TiO_2 and V_2O_5 content against depth.....	79
Figure 45 Strip log of P 57 with plots of TiO_2 and V_2O_5 against depth	82

LIST OF TABLES

Table 1 Description of the titaniferous magnetite layers of the Eastern Limb. Adapted from Reynolds (1986).....	6
Table 3 The currently accepted nomenclature and subdivisions of the Bushveld Complex of South Africa. Adapted from (Cawthorn et al., 2006)	24
Table 4 The stratigraphy of the Northern Limb of the Bushveld Complex after SACS (1980). Adapted from Walraven (1986).....	27
Table 5 USGS global vanadium production estimates as at 2011. Adapted from (Polyak, 2012)	43
Table 6 USGS global titanium production estimates as at 2011. Adapted from Bedinger (2013)	44
Table 7 P21 Energy dispersive X-ray spectroscopy pseudo-section sample analysis.....	77
Table 8 P55 Energy dispersive X-ray spectroscopy (EDS) pseudo-section sample analysis...	80
Table 9 P57 Energy dispersive X-ray spectroscopy (EDS) pseudo-section sample analysis...	83

Chapter 1 INTRODUCTION AND REGIONAL SETTING

The Bushveld Complex of South Africa is a Paleoproterozoic (~2.06 Ga). intrusion, which constitutes the most voluminous layered mafic complex in the world (Eales and Cawthorn, 1996; Maier et al., 2013), covering a surface area of approximately 29 450km² in outcrop and *ca.* 36 550km² in sub-outcrop which together is *ca.* 65 000km² (Eales and Cawthorn, 1996). The Bushveld Complex according to Lee (1996), Molyneux (1964), and Willemse (1969a) forms the largest repository of magmatic ore deposits in the world. It was intruded into supracrustal rocks of the Transvaal supergroup (Ashwal et al., 2005) of the Archean Kaapvaal Craton. Regionally, the Kaapvaal Craton is separated by the Proterozoic Limpopo Mobile Belt from the Zimbabwe Craton upon which another layered intrusion the Great Dyke sits together forming the Kaapvaal-Limpopo-Zimbabwe stable platform block (Du Plessis and Walraven, 1990).

The Bushveld Complex is host to the world's largest resources of platinum group elements, chrome and vanadiferous titanomagnetite as well as associated nickel, copper, gold, tin, fluorite, dimension stone and iron ore (Maier et al., 2013; Willemse, 1969a). Iron, titanium and vanadium are largely hosted in the Upper Zone of the Rustenburg Layered Suite (SACS, 1980) and this study is meant to determine the relationship between iron and titanium oxides in the Upper Zone of the Bushveld Complex's Northern Limb.

Iron is one of the first metals used by mankind and at present, it is the most commonly used metal in steel and ferro-alloys manufacture for structural and mechanical applications (Astrup et al., 1998). Titanium is a lightweight silver-white metal which falls in the group IV B of the periodic table of elements and was discovered by William Gregor in 1790 constituting about 0.62% of the earth's crust making it the ninth most abundant element in the earth's crust (Wipplinger, 1998). Titanium is utilised economically in the pigment industry as titanium dioxide (TiO₂) and also in the manufacture of various alloys. Vanadium, named after the scandinavian goddess of beauty 'Vanadis' (Schurmann and Marsh, 1998) is a soft, non-magnetic and ductile metal that is easily malleable and is the thirteenth most-common metallic element in the earth's crust, used in refractories and as an alloying metal for the impartation of strength and corrosion resistance to steel (Schurmann and Marsh, 1998).

Iron and titanium oxides are abundantly occurring within the earth's crust, with iron being the fourth most abundant element at 5% crustal average (Astrup et al., 1998) and concentrations

of these oxides are known to occur from igneous to sedimentary and metamorphic rocks. The Bushveld Complex of north-east South Africa is host to the largest resources of vanadium bearing titaniferous iron ores in the world (Willemse, 1969a; Wagner and Reinecke, 1930) with South Africa holding 17% of the world's titanium resources (Wipplinger, 1998). According to Reynolds (1985a) and (Harne and Von Gruenewaldt, 1995), the Upper Zone of the Rustenburg Layered Suite (SACS, 1980) in the Bushveld Complex has between 10 to 30 layers of vanadium bearing magnetitites.

The titaniferous magnetite ores of the Upper zone appear in literature from the 1900s with the Annual Reports of the Transvaal Geological Survey of 1903-1909 reporting them. Wagner and Reinecke, (1930), refer to the "great stratiform segregations of titaniferous magnetite occurring in the upper part of the Bushveld Complex" pg.189. The Upper Zone titanomagnetites have received not much attention as sources of iron as a result of their unsuitability for smelting in blast furnaces (Reynolds, 1986) after it had been discovered that they have high titanium content which ranges from 12 to 19 per cent (Wagner and Reinecke, 1930). According to Reynolds, (1986), the ores were known to be vanadiferous by the 1920s with (Hall, 1932) giving a comprehensive account of the Bushveld Complex.

The main magnetitite seams of the Upper Zone have a relationship between vanadium content as (V_2O_5) and titanium content as (TiO_2) that is referred to by (Wipplinger, 1998) as antipathetic. The TiO_2 content decreases from about 21% in the upper layers to 12% in the lower layers while the vanadium content as V_2O_5 increase from 0.2% in the upper layers to 2.0 in the lower layers (Schurmann and Marsh, 1998). The main magnetite layer in the Upper zone is the thickest with four important magnetite seams namely MAG 01 to MAG 04 named from top to bottom (Van der Merwe, 1976). The main magnetite layer according to (Schurmann and Marsh, 1998) occurs about 230m above the first appearance of magnetite in the sequence. There are no apparently discrete minerals of vanadium in the magnetite layers and the magnetite shows evidence of recrystallization and exsolution (Cawthorn and Molyneux, 1986).

1.1. Location of the study area

The study area is the prospecting right belonging to the CEI Group South Africa (Pvt) ltd. The prospecting right is located in the Limpopo province of South Africa on the Northern or Potgietersrus Limb of the Bushveld Complex see **Figure 1**. The study area is approximately 25km north-west of the Limpopo town of Mokopane. Farms Gezond 235 KR, Commandodrift 228 KR, Molendraai 811 LR, Mozambique 807 LR and Inhambane 802 LR as shown in **Figure 2** constitute the study area. The study area is bounded on the west by the Mogalakwena River and lies approximately 5km west of the platreef outcrop.

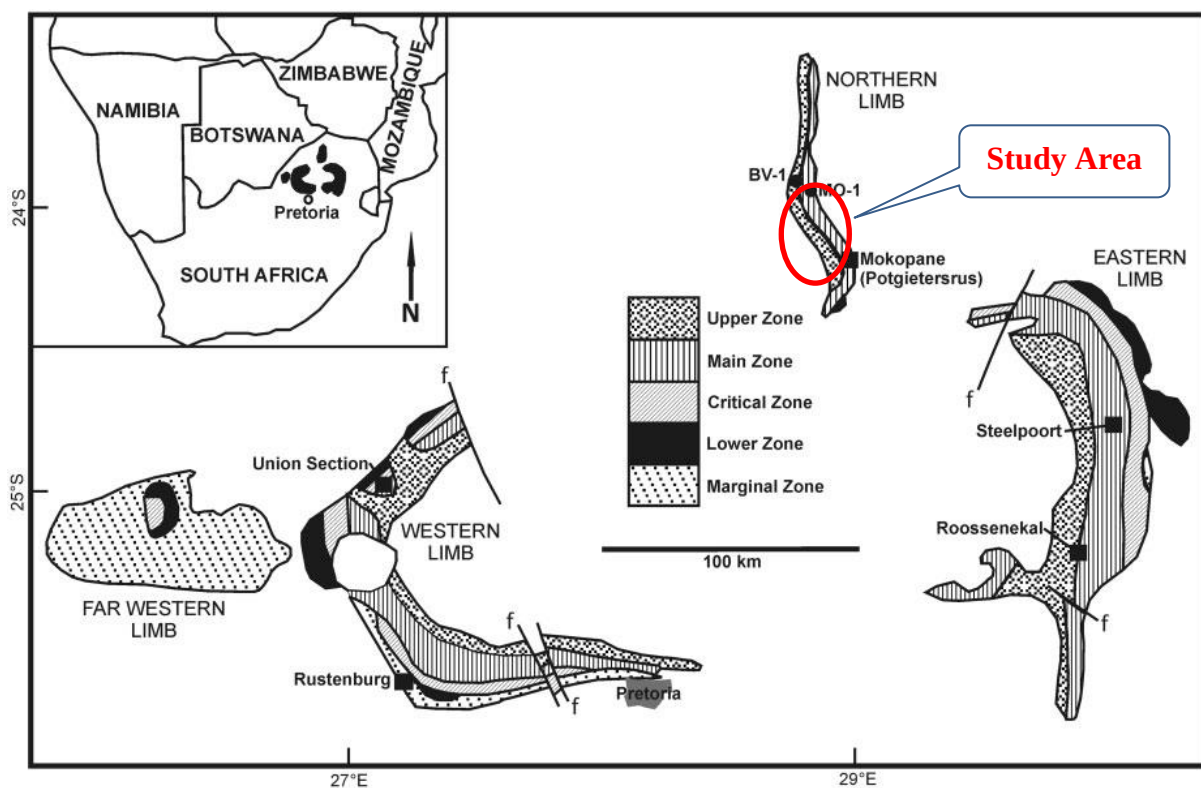


Figure 1 Generalised geological map of the study area on the Bushveld Complex. Adapted from (Roelofse, 2012)

1.2. Fe-Ti-V mineral potential and occurrence in the Bushveld Complex

The Bushveld Complex is the largest repository of the magmatic deposits in the world (Willemse, 1969a) with; Reynolds (1986) referring to the complex as the largest resource of vanadium bearing titaniferous iron ores. The vanadiferous iron ores (magnetites) are found in coarse grained plug-like bodies, referred to as iron rich ultramafic pegmatites (IRUPS) or as seams of magnetite and magnetite gabbro. The ore in the IRUPS is generally low grade owing to the presence of coarse grained silicates such as olivine and amphiboles (Willemse, 1969b).

Several workers among them (Molyneux, 1964; Molyneux, 1969; Coertze, 1966; Groeneveld, 1970) and Von Gruenewaldt (1973) in their work in the Eastern Limb of the Bushveld Complex identified up to 30 discrete layers of titaniferous magnetite dipping at about 12 to 30 degrees westwards in the vicinity of Magnet Heights, some of which are composite layers, consisting of a number of closely spaced layers. There are four layers of titanomagnetite below the Main magnetite layer which are numbered 1 to 4 from bottom to top, above which sits the main magnetite seam which averages 1.5 to 2.5m thick (Molyneux, 1969) see **Table 1**. Above the main magnetite seam are further magnetite layers that were numbered 1 to 21 by Molyneux (1969) and Von Gruenewaldt (1973) which were named with increasing stratigraphic height, see **Table 1**. It must be noted that some of the layers are composite layers and the most economic layers are the main magnetite layer as well as the layer 21 which is reported by Von Gruenewaldt (1973) to be up to 10m thick. The main magnetite layer in the Eastern Bushveld has V_2O_5 of 1.6 to 2.2 per cent (Molyneux, 1969; Molyneux, 1970).

Table 1 Description of the titaniferous magnetite layers of the Eastern Limb. Adapted from (Reynolds, 1986)

Subzone (Molyneux, 1970a, b, 1974)	Stoffberg Area (Groeneveld, 1970)			Roossenekal Area (Von Gruenewaldt, 1973)		Magnet Heights Area (Molyneux 1970a, b, 1974)			South of Olifants River (Coertze, 1966)		
	Layer	Thick- ness (m)	V ₂ O ₅ (%)	Layer	Thick- ness (m)	Layer	Thick- ness (m)	V ₂ O ₅ (%)	Layer	Thick- ness (m)	V ₂ O ₅ (%)
D	21	10	0,2– 0,3	21 20 19 18 17 — 15	10 0,2 0,3 — 0,6 — 0,25	21 20 19 18 17 16 15	9 1,2 0,3 0,7 0,4 0,3 0,3	0,3 0,3 — — 0,3 — —	six closely spaced layers	—	0,27
C	five to six layers	0,3 to 0,6	0,6– 0,8	14 13 12 11 10 9 8	0,1 0,4 0,7 0,45 0,3 0,2 0,2	14 13 12 11 10 9 8	0,28 0,35 0,57 0,50 0,22 0,22 0,17	0,55 0,55 0,60 0,65 — 0,75 —	one layer		0,76
B	2 1	0,45 0,35		7 6 — — — 2 1	1,18 0,72 — — — 0,27 0,25	7 6 5 4 3 2 1	0,72 0,52 0,2 0,45 0,15 0,75 0,35	1,35 1,35 1,35 1,5 — 1,5 —			
	MAIN MT.	1,80	1,8–2,0	MAIN MT.	2,2	MAIN MT.	2,5	1,6	MAIN MT.	1–3	1,75
A	three layers	0,25– 0,40 0,25– 0,40 0,25– 0,40	2,3 2,3 2,3	3 2 1	1,0 0,8 0,8	3 2 1	1,5 0,3 0,35	2,0 1,99 2,1	two layers	1,3 0,3	1,56

Van der Merwe (1976; 1978) in his work in the Potgietersrus/Northern Limb identifies 20 seams of titanomagnetite as shown in **Error! Reference source not found.**, with the vanadium content as V₂O₅ ranging from 0.3 to 1.6 per cent and titanium content as TiO₂ ranging from 12 to 21 per cent, see **Figure 3**, which is comparable to what is described by (Willemse, 1969b). There are 4 major magnetite layers identified in the Upper Zone of the Northern Limb and these are named from bottom to top the Lower, Main, Upper and magnetitite layers. The main magnetite layer has four individual magnetite seams named from top to bottom MAG 01, MAG 02, MAG 03 and MAG 04. The major resources for vanadium bearing titaniferous iron ores are the seams MAG 03 and MAG 04 with both seams averaging 1.5-2.5m in thickness and separated by a parting magnetite gabbro that is 1-2.5m. MAG 01 and 02 are on average less than 0.5m in thickness.

Table 2 Thicknesses of the individual titanomagnetite layers in the Northern Limb. Adapted from (Van der Merwe, 1978)

Layer Number	Thickness (cm)	Layer Number	Thickness (cm)
1	7	11	9
2	200	12	24
3	30	13	7
4	10	14	16
5	15	15	20
6	5	16	37
7	1	17	10
8	40	18	10
9	37	19	18
10	12	20	25

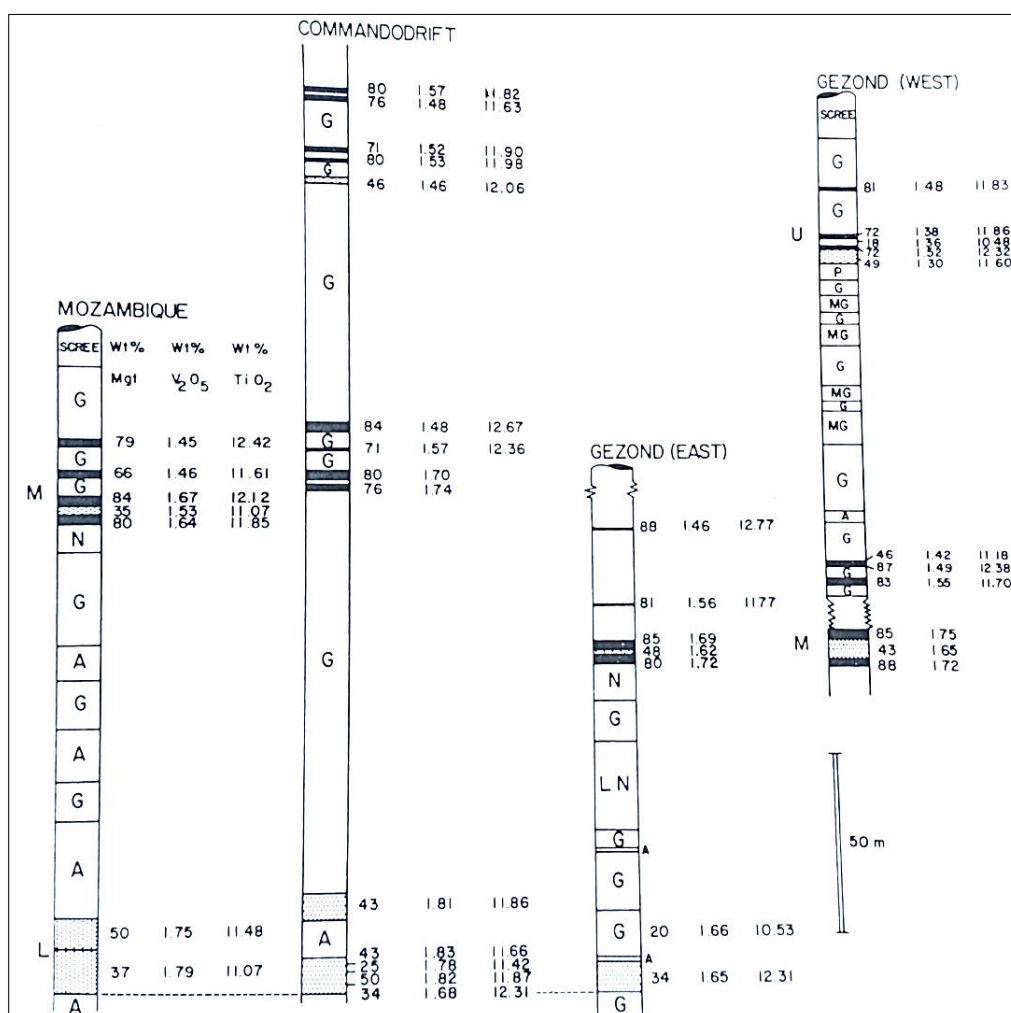


Figure 3 Borehole profiles from the Northern Limb in the study area showing the magnetite layers, TiO₂ as well as V₂O₅ content. Dark areas represent areas with more than 50% magnetite by weight while mottled areas represent areas less than 50%. Adapted from (Cawthorn and Molyneux, 1986)

The titaniferous magnetite occurrences of the Western Limb of the Bushveld Complex were mapped by (Coertze, 1970; Coertze, 1974) and are poorly exposed although magnetite rubble could be identified as evidence of the presence of magnetite layers (Cawthorn and Molyneux, 1986). The magnetite layers strike west towards the Pilanesburg from north of Pretoria and terminate against the intrusion, before re-appearing north of the Pilanesburg complex towards Thabazimbi (Reynolds, 1986). There are about 15 layers of titanomagnetite identified in the Western Limb of the Bushveld Complex (Cawthorn and Molyneux, 1986) with the most important economically being the Upper main magnetite layer at approximately 1.6m thick and averaging 1.42 per cent V_2O_5 (Raal, 1965) see **Figure 4**.

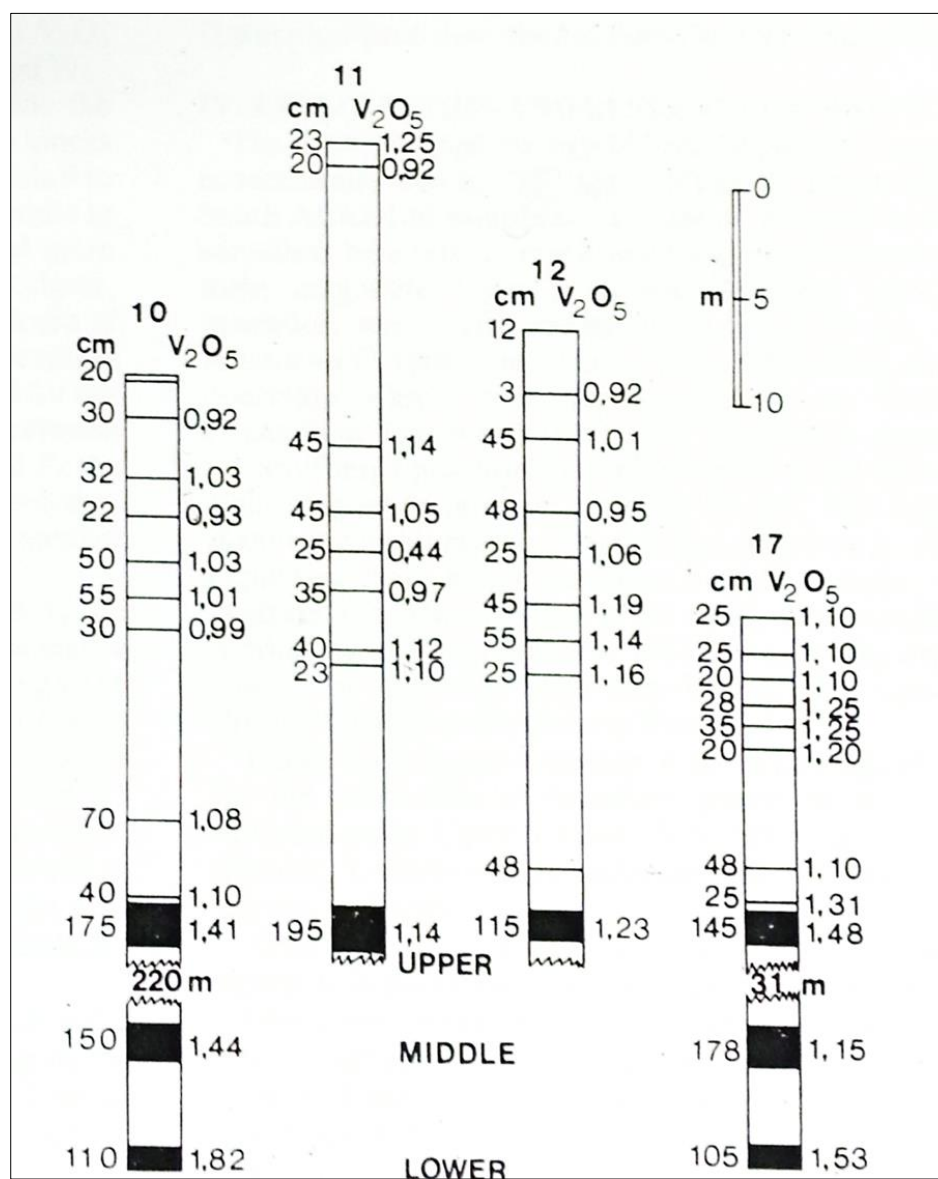


Figure 4 Borehole profiles showing magnetite layers and V_2O_5 content after (Raal, 1965) from boreholes drilled on farm Rhenosterfontein. Modified after (Cawthorn and Molyneux, 1986)

The resources of the vanadium bearing titaniferous magnetite have been estimated differently by various workers with Wagner (1928) estimating them at 2 000 million tonnes. Willemse (1969b) estimated the open castable resources of the Eastern Bushveld Complex at 200million tonnes averaging 1.6 per cent vanadium. Von Gruenewaldt (1977) estimated the resources at 1 030 million tonnes at an average of 1.6 per cent V_2O_5 to an open castable depth of 30m. (Cawthorn and Molyneux, 1986) estimated the open castable resources at more than 580 million tonnes, divided as 150million tonnes in the Eastern Limb, 45million tonnes in the Western Limb and 350million tonnes in the Northern Limb averaging 1.6 per cent V_2O_5 , 12-21 per cent TiO_2 and 54 per cent Fe. (Von Gruenewaldt et al., 1985). Astrup et al. (1998) estimated the Bushveld titaniferous magnetite resources at 26 400 million tonnes with the grades as 50-57 per cent Fe, 8-22 per cent TiO_2 and 0-2 per cent V_2O_5 .

1.3. Outline of intended research

The research will be conducted by way of petrographic study of rock samples collected from boreholes drilled for resource evaluation as well as elemental analysis by energy dispersive spectroscopy and electron micro-probing. The rock samples were collected on the intersections of the magnetite seams belonging to the main magnetite horizon and the sample locations within the boreholes can be seen illustrated in Figure 23, Figure 24 and Figure 25. The samples were collected as quarter cores of NQ (60.3mm) diamond drill core as shown in **Figure 5** and were studied petrographically first by hand as hand specimens by naked eye and with the aid of magnifying hand lenses. The samples were prepared into polished thin sections in preparation for study under transmitted and reflected light microscopy.

The research is meant to determine the mineralogical relationship of the iron and titanium oxides both in macroscopic scale and at microscopic scale. High resolution microscopy was carried out utilising scanning electron microscopes (SEM), while major element studies were carried out utilising the energy dispersive X-ray spectroscopy coupled with an electron microscope as well as utilising an Electron Probe Micro-analyser (EPMA) Geochemical studies were carried out utilising the electron microprobe analyser.



Figure 5 Quarter core samples which were prepared into polished thin sections. (a) Magnetite anorthosite parting between MAG 04 and MAG 03 in P57 (b) magnetite-plagioclase cumulate (c) massive magnetite with minor plagioclase (d) massive magnetite with plagioclase laths

Petrographic relationships of the iron and titanium oxides were determined by the microscopy, both optical and electron microscopes. Optical microscopes were utilised on minerals and textures that could be viewed under lower magnifications, such as magnetite-ilmenite-silicate relationships, while the scanning electron microscopes were utilised for visualisation of minerals and textures that could only be viewed under high magnification. Relationships and variations between the iron and titanium oxides and the associated vanadium were sought in the vertical column of the main magnetite seam as well as their variations laterally along the farm Gezond 235 KR. Other relationships that were studied include the chromium content from base to top of the magnetite seam as well as the change in the anorthite of the feldspars from base to top. The behaviour of granular ilmenite was also studied in areas or zones with massive titanomagnetite against areas or zones with magnetite-plagioclase cumulate. The behaviour of ulvospinel exsolutions was also studied with particular reference to the presence or absence of ulvospinel exsolutions on the grain boundaries of the titanomagnetite with other titanomagnetite as well as with granular ilmenite and silicates.

1.4. Purpose of research

The purpose of this research is to determine the mineralogical and petrographic relationship of the main magnetite layers of the Upper Zone of the Rustenburg Layered Suite on the farms Gezond 235 KR, Commandodrift 228 KR, Molendraai 811 LR, Mozambique 807 LR and Inhambane 802 LR. The mineralogical relationship of the iron and titanium oxides determines the economic recoverability of the two metals as discrete granular ilmenite (ferro-titanium oxide) can be separated from magnetite through crushing and magnetic separation. This research therefore seeks to explore the potential for main magnetite seams as ores of titanium and iron.

The aim of this study is to determine the petrographic and textural relationship between iron and titanium oxides within the vanadium bearing magnetitites of the Upper zone of the Rustenburg Layered Suite with particular reference to the prospecting right of the CEI group in the Northern Limb of the Bushveld. The study intends to develop an understanding on the relationship of the oxides with the intention of establishing the potential for recovery of titania (TiO_2) and metallic iron from the magnetite as separate products from the vanadiferous ores. The study also aims to determine the mineralogy of the titanium or titaniferous oxides and differentiate between oxides of titanium from which titanium can be recovered such as ilmenite against ulvospinel and titanomagnetite which may not be amenable to conventional crushing and magnetic separation followed by blast furnace smelting.

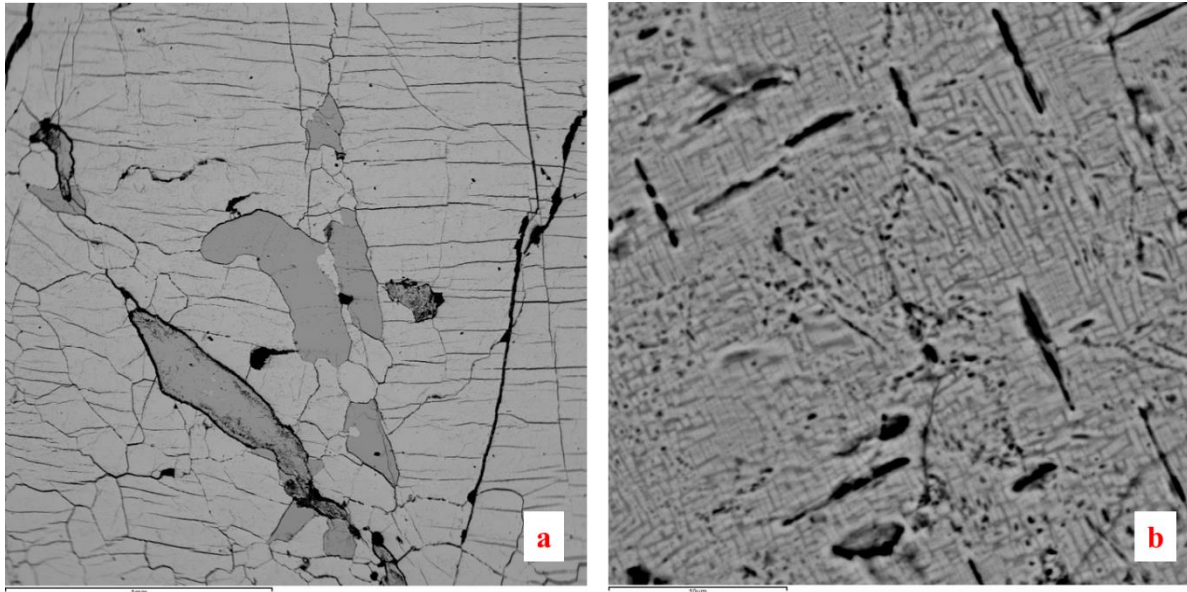


Figure 6 Contrasting textures of titanium bearing magnetite [a] discrete ilmenite grains (dark grey) in magnetite (light grey). [b] fine ulvospinel exsolution lamellae (cloth texture) in titanomagnetite (grey background). Black laths are the spinel pleonaste.

Titanium is a deleterious element in the conventional blast furnace processing of iron ore and its presence is undesired as it causes clogging of blast furnaces hearths and its slag erodes the refractory linings (Wu and Ho, 2009; Gavriluk et al., 1998) through the formation of titanium carbides and nitrides. Titanium ores that have titanium oxides occurring as individual grains as shown in **Figure 6 (a)** can be crushed and the titanium recovered by sending the crushed ore through magnetic separation where the non-magnetic ilmenite separates from magnetite, and the two minerals can be treated separately. Titanium oxides that exist as fine exsolution and immiscibility lamellae as shown in **Figure 6 (b)** may not be easily separated from magnetite as the ores would have to be ground extremely fine sizes (micron to sub-micron sizes).

Ulvospinel (Fe_2TiO_4) is a widely distributed constituent of the magnetite fraction of magmatic ore segregations. Its presence can reduce considerably the amount of recoverable titanium (Ramdohr, 1953), as it has a tendency to be weakly magnetic and will follow magnetite during separation. The presence of titanomagnetite, the solid solution intermediate of ulvospinel and magnetite also greatly increases the difficulty of separating iron and titanium through conventional smelting (Ramdohr, 1953) and (Gavriluk et al., 1998).

Chapter 2 GEOLOGY AND REGIONAL SETTING

2.1. Historical work

The occurrence of magnetite rich iron ores in the rocks of the Bushveld Complex according to Reynolds (1986) has been known, since the turn of the 20th century with mention in the Annual Reports of the Transvaal Geological Survey of 1903-1909. Molengraaff (1904) reported the titaniferous nature of the magnetite with Hall (1909) corroborating that assertion. The titaniferous nature of the magnetite rich layers rendered their potential as blast furnace feed to be considered poor (Reynolds, 1986; Willemse, 1969b). The first account that was comprehensive of the nature and mineralogy of the ores was presented by Wagner (1928) in his work 'The iron deposits of the Union of South' followed by his work in another publication 'Mineral deposits of the Union of South Africa' (Wagner and Reinecke, 1930) and concluded that the ore reserves could be in excess of 2 000Mt which resulted in Anglo American carrying out a regional study of the grades and tonnages for open casting (Cawthorn and Molyneux, 1986). The work on the complex and its associated mineral resources continued in the 1920s culminating in Hall (1932) publishing his article 'The Bushveld igneous complex of the Central Transvaal'.



Figure 7 Outcrop of titanomagnetite seam in the Upper Zone of the Rustenburg Layered Suite at Magnet Heights in the Eastern Limb of the Bushveld Complex.

Since then, significant work has been done on the vanadium bearing titaniferous magnetites of the Bushveld Complex with (Schwellnus and Willemse, 1943) establishing the antipathetic relationship between TiO_2 and V_2O_5 . Molyneux (1964) did a thorough study of the mineralogy and field relations of the ores in the then Eastern Transvaal within the Magnet Heights vicinity, see picture of outcrop of magnetite seam in **Figure 7**. The work of Molyneux (1964) resulted in the division of the Upper Zone into four sub-units (zones) based on the vanadium content as V_2O_5 . Other workers that have investigated the Bushveld titaniferous magnetites include (Willemse, 1969a; Reynolds, 1985a; Harne and Von Gruenewaldt, 1995; Reynolds, 1986; Van der Merwe, 1976; Willemse, 1969b; Molyneux, 1969; Klemm et al., 1985; Butcher and Merkle, 1987; Reynolds, 1978) having reviewed the nature and origin of the ores as well as the mineralogy, textures and petrography. Cawthorn and Molyneux (1986) reviewed the distribution, general geology and vanadium content of the ores.

According to Cawthorn and Molyneux (1986), the first attempt of the economic exploitation of the Bushveld titaniferous magnetite was by the Minerals Engineering of South Africa Ltd in 1957, through the establishment of a vanadium salt-roast and leach process plant in the Witbank area. The operation was partly successful and led to the taking over of the operation

by Anglo American Corporation of South Africa. Between 1968 and 1983, Mapochs Mine mined 22 496 686 tonnes of vanadium bearing titanomagnetite resulting in 638 260 tonnes of vanadium slag being recovered (Cawthorn and Molyneux, 1986).

2.2. The Geology of the Bushveld Complex

The Paleo-Proterozoic Bushveld Complex in the Northern Kaapval Craton of South Africa is the world's largest and most voluminous layered mafic intrusion in the world (Eales and Cawthorn, 1996; Maier et al., 2013; Scoates and Friedman, 2008). The complex is host to some of the richest platinum group element (PGE), chromium, and vanadium deposits on Earth (Willemse, 1969a; Cawthorn and Molyneux, 1986; Von Gruenewaldt, 1977) and (Scoates and Friedman, 2008). It covers a surface area of approximately 65 000km², separated as *ca* 29 450km² in outcrop and *ca.* 36 550km² in sub-outcrop (Eales and Cawthorn, 1996). The Bushveld Complex comprises of five Limbs or lobes, and these are the Western Limb, the Eastern Limb, the Far Western Limb, the Bethal Limb and the Northern Limb (also known as the Potgietersrus or Mokopane Limb) with the smaller Bethal Lobe to the south which is covered underneath younger sediments and only mapped out on the basis of Bouger gravity anomalies (Buchanan, 1976).

The Bushveld can be considered tabular (Eales and Cawthorn, 1996) and has been emplaced on the older supracrustal rocks of the Pretoria group which belongs to the Transvaal Supergroup (Ashwal et al., 2005; Cawthorn and Walraven, 1998). The stratified mafic rocks of the Bushveld Complex are known as the Rustenburg Layered Suite (SACS, 1980), which nomenclature supersedes the stratigraphy based on zones that was developed by (Hall, 1932). There is an unconformity above the Pretoria group above which the 2.061 Ma. Rooiberg group lavas sit (Walraven, 1997). In some places the rocks of the Rustenburg Layered Suite come in direct contact with the underlying older rocks of the Transvaal Supergroup or the Archean granites implying that the Rooiberg group is not always continuous (Clarke et al., 2009). The generalised geological map of the Bushveld as well as the floor rocks and major structures can be seen in Figure 8.

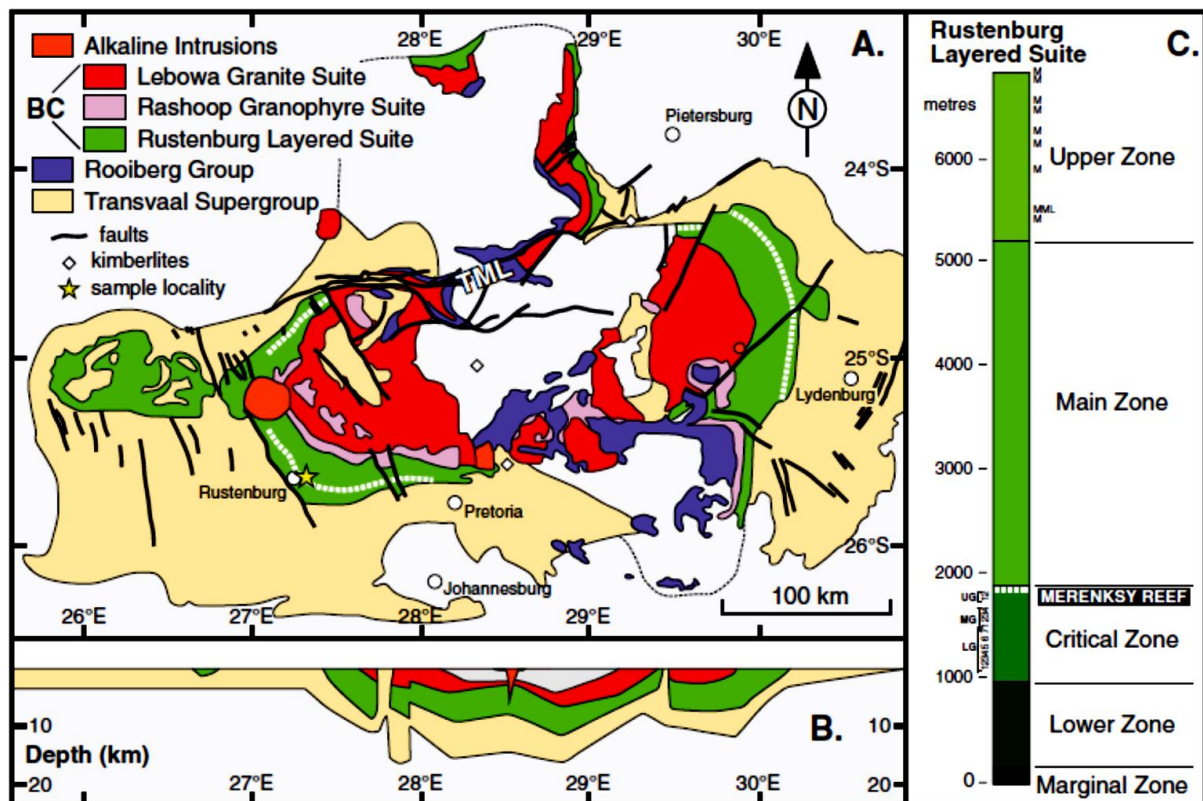


Figure 8 Simplified geological Map of the Bushveld Complex. Adapted from (Scoates and Friedman, 2008)

2.2.1. Age of the Bushveld

The age of the Bushveld Complex was up until the late 1950s thought to be of Late Precambrian age when the independent work of (Nicolaysen et al., 1958) and Schreiner (1958) determined that the complex was *ca.* $1,950 \pm 50$ Ma., much to the astonishment of most geologists of the time (Willemse, 1964). Hamilton (1977) determined the Rb-Sr age of the Rustenburg Layered Suite (SACS, 1980) of the Bushveld Complex at 2095 ± 24 Ma.

(Buick et al., 2001) came up with an age of $2,058.9 \pm 0.8$ Ma for a retrogressed xenolith in the Upper Zone. Recent work by (Scoates and Friedman, 2008) has determined the U–Pb age of the Merensky Reef at 2054.4 ± 1.3 Ma from zircons obtained from the West mine (Townlands shaft; level 22), Rustenburg mining section. (Scoates et al., 2012) put the major magma emplacement of the complex at *ca.* 2060 and 2055 Ma and suggest that the Bushveld Complex spans ~ 7 million years from 2061 to 2054 Ma.

2.2.2. Tectonic Setting and Floor Rocks

The Bushveld Complex was emplaced onto stable Cratonic environment of the Kaapvaal Craton of South Africa, much like other large layered mafic intrusions in the world which are associated with stable Cratons such as Great Dyke on the Zimbabwe Craton and the Stillwater Complex on the Wyoming Craton (Maier et al., 2013). The complex sits within the Transvaal basin see Figure 8, which is a Paleo-proterozoic sedimentary basin filled with a thick succession of chemical and clastic sediments (Cawthorn and Walraven, 1998) ranging in age from 2 551Ma to 2 204Ma (Walraven, 1997).

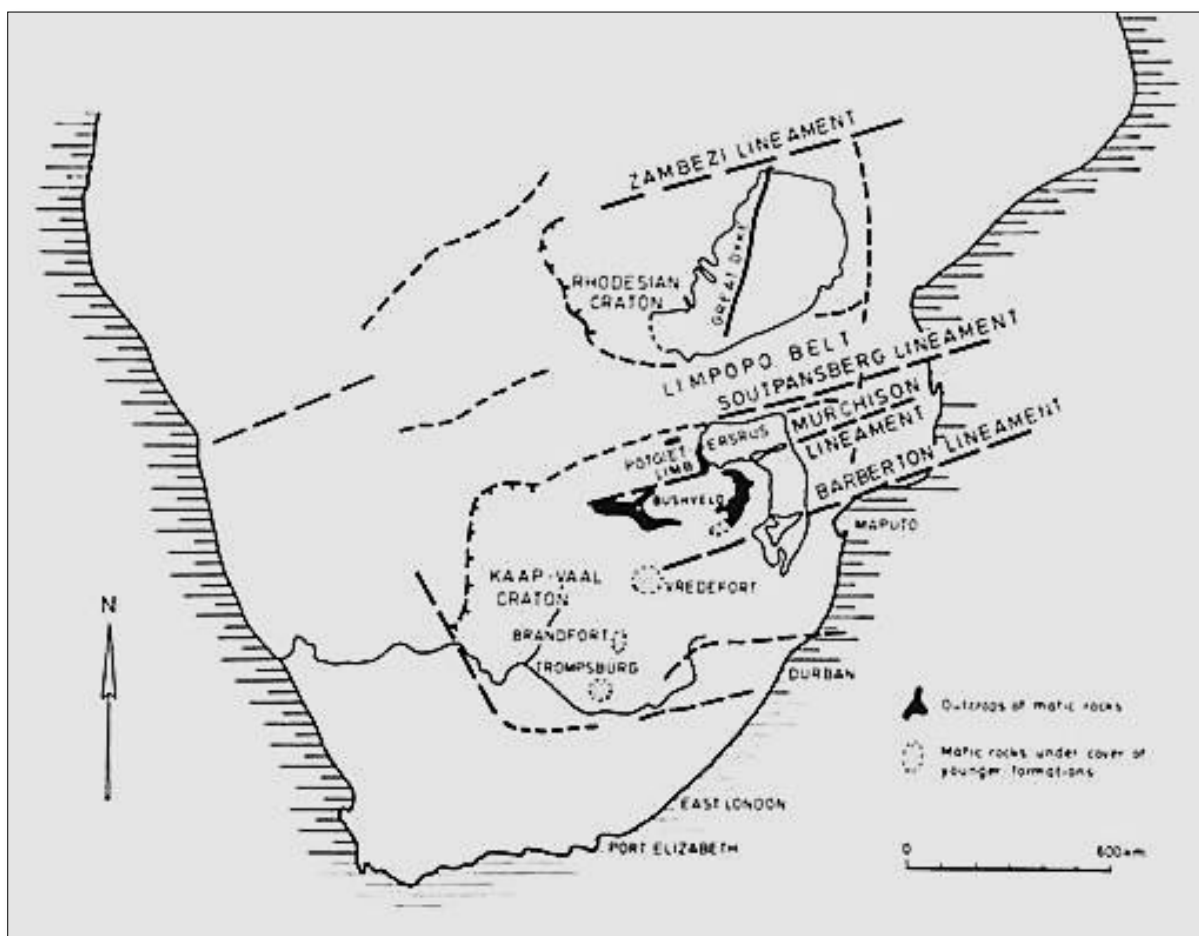


Figure 9 Generalised tectonic map of Southern Africa showing the ENE trending major tectonic lineaments. Adapted from (Klemm et al., 1982)

The major tectonic features that were present and active during the period 2,500 Ma to 1,800Ma are the Thabazimbi-Murchison, Barberton and Soutpansberg lineaments (Klemm et al., 1982) as shown in **Figure 9**, and other structural features that are thought to have been in place during the Bushveld emplacement include the Crocodile River and Steelpoort faults

(Maier et al., 2013) as shown in **Figure 10**. The lineaments and structures are said by (Olsson et al., 2011) to represent possible trans-lithospheric suture zones along the assembly lines of proto-cratonic nuclei. (Maier and Eales, 1997) suggest that the Thabazimbi-Murchison lineament and the Steelpoort fault were active during Bushveld Complex emplacement times with the Thabazimbi-Murchison lineament thought to have been present from as early as 2700Ma, (Clarke et al., 2009).

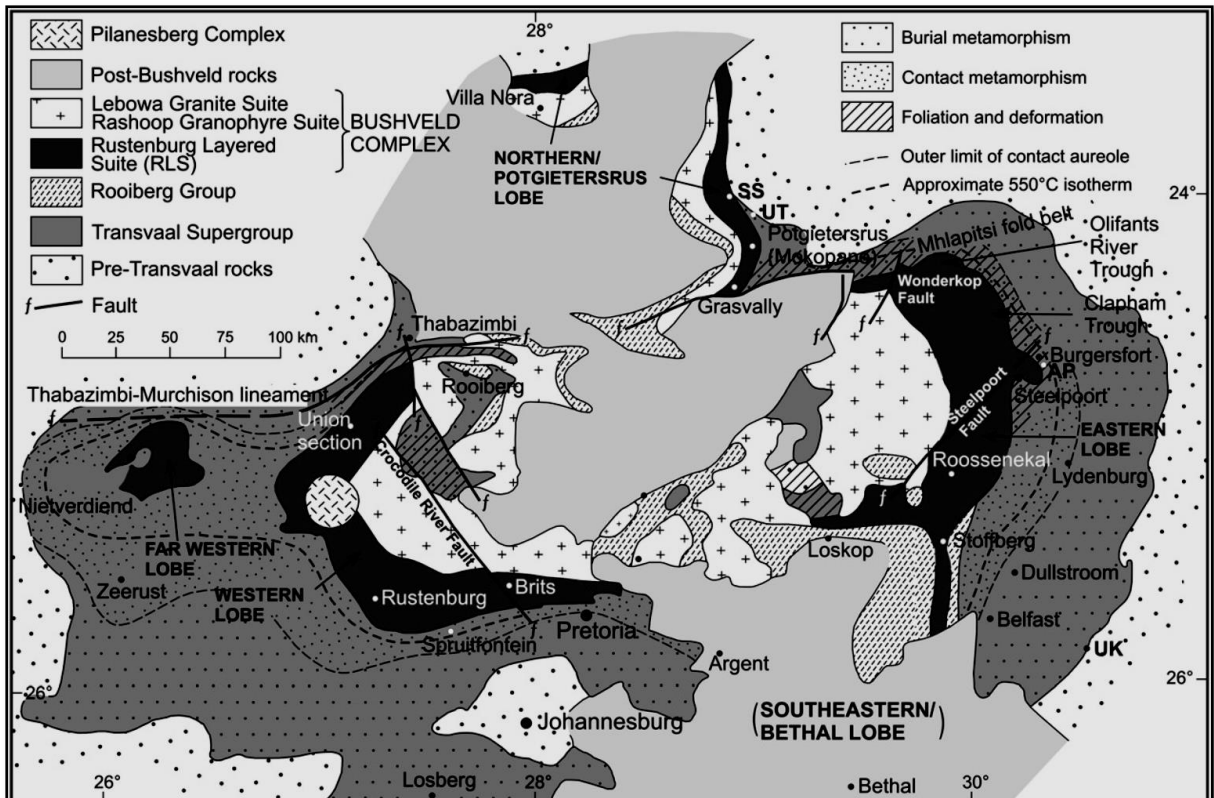


Figure 10 Tectonic Map of the Bushveld Complex showing the Murchison, Crocodile River and Steelpoort lineaments. Adapted from (Clarke et al., 2009)

The Kaapvaal Craton is also thought to have been under transpressional extension especially along re-activated lineaments and structures as collision with the Zimbabwe Craton in a Northwest to southeast direction would have resulted in a compressional tectonic regime (Holzer et al., 1999). The Northern Limb and the Villa Nora body of the Bushveld Complex are separated from the Limpopo Mobile belt by the Zoetfontein fault.

2.2.3. Transvaal Supergroup

The Bushveld Complex sits intruded into the approximately 20km thick succession of Late Archean to Paleo-proterozoic Transvaal Supergroup rocks (Eriksson et al., 1995), which consists of chemical as well as clastic sedimentary rocks (Cawthorn and Walraven, 1998; Walraven, 1997). The Transvaal Supergroup sediments are preserved within the Transvaal and Griqualand West basins on the Kaapvaal Craton of South Africa (Eriksson et al., 1995). The Bushveld Complex was intruded largely into the preserved Transvaal Basin with the rocks of the Rustenburg Layered Suite cross cutting the clastic sedimentary rocks of the Pretoria Group of the Transvaal Supergroup in places (Kinnaid, 2005). The surficial extent of the Transvaal Super group within the Transvaal Basin can be seen together with the generalised map of the Bushveld Complex in Figure 8 where the sediments are shown in yellow.

2.2.4. Rooiberg Group

The volcanic rocks of the Rooiberg Group form the floor and roof to the Bushveld Complex. The rocks have been dated at 2.061 Ma by (Scoates and Friedman, 2008; Walraven, 1997; Vantongerren et al., 2010) and are just older than the $2,058.9 \pm 0.8$ Ma Bushveld Complex (Scoates et al., 2012). The Rooiberg Group rocks consist of andesites and basalts which unconformably overlie the Pretoria Group clastic sediments (Kinnaid, 2005). It has been postulated that the Rustenburg Layered Suite rocks may have been emplaced along or just above the unconformity between the Rooiberg volcanics and the Pretoria Group rocks thereby preserving the Rooiberg volcanics both in the roof and the floor (Eriksson et al., 1995). The Rooiberg has been divided into four formations, namely the Dullstroom, Damwal, Kwaggasnek and Schrikkloof formations (Vantongerren et al., 2010).

2.3. Bushveld Stratigraphy

The Bushveld Complex was emplaced onto the Paleo-Proterozoic rocks of the Transvaal Supergroup (~2.5 to 2.06 Ga.) which include quartzites, dolomites, banded iron formations, basalts and rhyolites (Ashwal et al., 2005). The Rooiberg group volcanics (2.061 Ma) which according to (Kinnaid, 2005) is one of the largest pyroclastic provinces on earth forms both the floor and roof of the Bushveld and unconformably overlie the Transvaal Supergroup (Walraven, 1997) and the Rustenburg Layered Suite is thought to have been emplaced along or above the unconformity between the volcanics and the Pretoria group rocks of the Transvaal Supergroup (Walraven, 1997).

The Rustenburg Layered Suite is overlain or cross cut by the 2054 ± 2 Ma Lebowa Granite Suite which are in turn overlain by the felsic volcanics of the Rooiberg group and the Rashoop Granophyre Suite (Kinnaird, 2005). The Rustenburg Layered Suite has been subdivided into five stratigraphic zones and these are the Marginal Zone, Lower Zone (LZ), Critical Zone (CZ), Main Zone (MZ) and Upper Zone (UZ) (SACS, 1980) with the Critical zone further divided into the Lower critical and Upper critical zones (Maier et al., 2013) as illustrated in Figure 11.

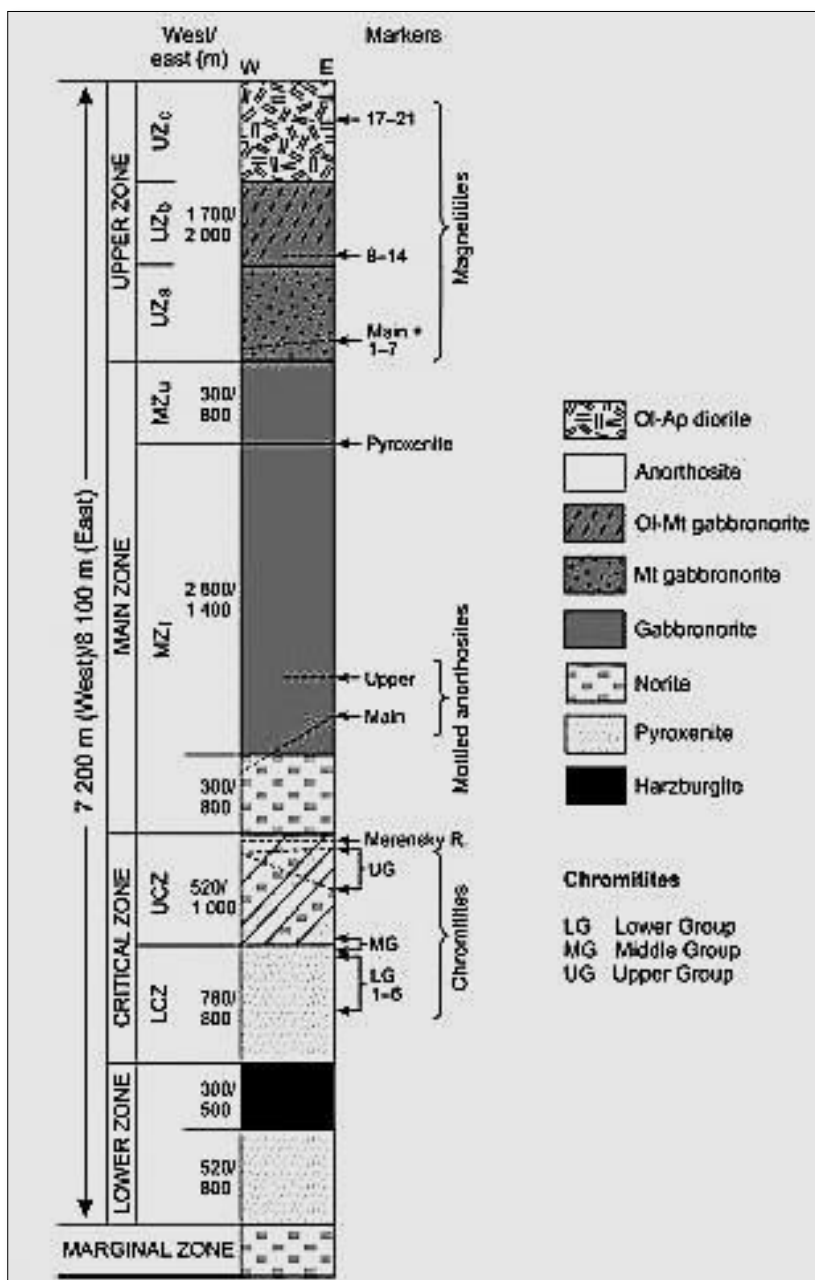


Figure 11 Simplified stratigraphy of the Rustenburg Layered Suite showing the Marginal Zone up to Upper Zone. Adapted from (Clarke et al., 2009).

2.3.1. The Marginal zone

The Marginal Zone of the Rustenburg Layered Suite (SACS, 1980) is not always present, however when it occurs, the rocks are commonly noritic with minerals such as clinopyroxene, biotite, hornblende and even quartz occurring in variable proportions reflecting varying degrees of crustal contamination by the underlying Transvaal Supergroup sediments (Kinnaird, 2005). The marginal zone ranges in thickness from 0m to 400m between the contact of the main mass (which comprises of the Lower, Critical, Main and Upper zones) and the floor (Van der Merwe, 1976). In the Northern Limb, inclusions of floor rocks which range from carbonates, quartzites, hornfels and granite can be found in the rocks of the Marginal Zone with an olivine –bearing chilled margin traceable sometimes (Van der Merwe, 1976; van der Merwe, 2008).

2.3.2. The Lower Zone

(Willemse, 1964) referred to the Lower Zone as the “Basal Zone” following the nomenclature of (Hall, 1932). The unit comprises essentially of ultramafic rocks mostly orthopyroxenites and harzburgites (Maier et al., 2013) and occurs with one or more layers of interbedded peridotite. (Eales et al., 1993) refers to the Lower Zone as being dominated by olivine rich cumulates and orthopyroxenites. In the Northern Limb, the Lower Zone orthopyroxenites and olivine show a clear trend of differentiation from being magnesian at the base of the sequence to being iron rich at the top (Van der Merwe, 1976). The thickness of the Lower zone is reported by Kinnaird (2005) to go up to 1.3km elsewhere in the complex while Van der Merwe (1976) and De Villiers (1970) suggest that the Lower Zone is between 4 to 6 km in the Northern/Potgietersrus/Mokopane Limb, an assertion which De Villiers (1970) concurs with.

2.3.3. The Critical Zone

The Critical Zone which overlies the Lower Zone is defined by clear layering (Eales et al., 1993). The zone has been sub-divided into Lower Critical Zone (C_LZ) and Upper Critical Zone (C_UZ) and its thickness goes up to 1.5km (Kinnaird, 2005). The rocks of the Critical zone consist of dunites, harzburgites, pyroxenites, chromitites, norites and anorthosites (Eales and Cawthorn, 1996). Traditionally, the first appearance of cumulus plagioclase was used to separate the Lower Critical Zone from the Upper Critical Zone, but this was shown by (Teigler et al., 1992) to be invalid in other parts of the Bushveld Complex. The boundary of

the Lower and Upper Critical Zones is now defined by the norite or anorthosite layer that is found between the Middle Group (MG) 2 and 3 chromitite layers (Eales et al., 1993). The Critical Zone is host to the largest resources of chromite and platinum on earth through its chromitite seams and the Merensky Reef (Crowson, 2001).

Nine cycles with nine chromitite seams, these the Lower Group (LG) 1 to 6 and Middle Group (MG) 1 and 2 have been recognised in the Lower Critical Zone (Maier et al., 2013). The Upper Critical Zone rocks comprise of orthopyroxenites, norites and anorthosites with about 4 major chromite seams and these are the Middle Group (MG) 3 and 4 seams as well as the Upper Group (UG) 1 and 2 seams. The Upper Critical Zone is overlain by the Main Zone (Eales and Cawthorn, 1996).

2.3.4. The Main Zone

The base of the Main Zone is placed by various authors in different places with Kruger (1990) placing the boundary at the level of the Merensky Reef based on Sr isotope change while De Klerk (1992) puts the boundary on the top of the Bastard Reef. The thickness of the Main zone can be in excess of 3km and according to Kinnaird (2005) , the Main Zone forms almost half the thickness of the Rustenburg Layered Suite. The Main Zone attains a thickness of about 2.2km in the Northern Limb and consists of gabbro, anorthosite, pyroxenite, norite, harzburgite and lherzolite and the base of the Main Zone in the North is formed by the Platereef unlike elsewhere in the Bushveld Complex (Van der Merwe, 1976).

2.3.5. The Upper Zone

The Base of the Upper Zone is defined by the first appearance of cumulate magnetite (SACS, 1980; Eales et al., 1993). The Upper Zone unlike the Main Zone displays a variation in rock types which range from gabbro to olivine diorite and granodiorite (Willemse, 1964). The Upper Zone is known to host in excess of 20 discrete magnetite seams in the Northern Limb (Van der Merwe, 1978), 15 in Western Limb (Raaijmakers, 1965) and up to 30 in the Eastern Limb as illustrated in **Table 1**, (Molyneux, 1964; Groeneveld, 1970) and (Von Gruenewaldt, 1973). In the Eastern Limb, the Upper Zone is developed over a strike length of approximately 160km (Reynolds, 1986) and 25 magnetite layers are exposed at Magnet Heights and Roosenekal with the thick uppermost layer (seam 21) forming prominent outcrops (Cawthorn

and Molyneux, 1986). The Upper zone magnetite seams have been divided into Lower, main (MAG) and Upper magnetite seams in the Northern Limb with the main magnetite seams being the most important economically and comprising of four seams named from top to bottom MAG 01 to MAG 04 with MAG 03 and 04 being about 1.5m to 2.5m thick each and separated by about 2.5m of magnetite gabbro (Van der Merwe, 1978).

2.3.6. The Lebowa Granite Suite

The Lebowa granites are referred to by Willemse (1969a) as the red granites and are a late plutonic phase of the complex that occupy extensive areas of the central portion, occupying two large lobes that are roughly semi-circular within the Eastern and Western Limbs (Cawthorn et al., 2006). The suite comprises a series of sheeted intrusives which range from 1.5km to 3km thick (Kinnaird, 2005). The granites have a surface extent of *ca.* 30 000km² and they underlie the felsic Rooiberg volcanics as well as the Rashoop Granophyre Suite (Eales and Cawthorn, 1996). The Lebowa Granite Suite have been sub-divided into the Nebo, Bobbejankop, Klipkloof and Makhutso granites with the Nebo making up the bulk of the granitic suite while the Makhutso is the least abundant (Cawthorn et al., 2006).

2.3.7. The Rashoop Granophyre Suite

The Rashoop Granophyre Suite is intrusive into the Rustenburg Layered Suite and the Rooiberg Group volcanics (Eriksson et al., 1995) and are referred to by Eales and Cawthorn (1996) as being predominantly composed of homogenous granophyre as well as associated granophyric granite and granophyre porphyry. Two types of rocks have been identified on petrographic bases and these have been recognised as magmatic and metamorphic types with the magmatic type being named the Stavoren granophyre (Cawthorn et al., 2006). The metamorphic types are the Zwartbnk Pseudogranophyre and the Diepkloof granophyre. A number of extensive sills are also included in the Rashoop Granophyre suite and these are known as the Rooikop Porphyritic Granite (Kinnaird, 2005; Cawthorn et al., 2006).

A summary of the currently accepted nomenclature and subdivisions of the Bushveld Complex is shown as **Table 3**.

Table 3 The currently accepted nomenclature and subdivisions of the Bushveld Complex of South Africa. Adapted from (Cawthorn et al., 2006)

Lebowa Granite Suite	Nebo, Makhutso, Klipkloof, Bobbejaankop and Verena Granites	
Rashoop Granophyre Suite	Staroven and Diepkloof Granophyres, Rooikop Porphritic Granite, Zwartbank Pseudogranophyre	
Rustenburg Layered Suite	Upper Zone	Subzone C (Ol-Ap diorite) Subzone B (Ol-Mt gabbronorite) Subzone A (Mt gabbronorite)
	Main Zone	Upper Subzone (gabbronorite) Lower Subzone (gabbronorite, norite)
	Critical Zone	Upper Subzone (norite, anorthosite, pyroxenite) Lower Subzone (pyroxenite)
	Lower Zone	Upper Pyroxenite Subzone Harzburgite Subzone Lower Pyroxenite Subzone
	Marginal Zone	Norite
Rooiberg Group	Schrikkloof Formation (flow-banded rhyolite) Kwaggasnek Formation (massive Rhyolite) Damwal Formation (dacite, rhyolite) Dullstroom Formation (basaltic andesites)	

2.4. The geology of the Northern Limb

2.4.1. Introduction

The Northern or Potgietersrus Limb of the Bushveld Complex is a roughly buffalo-horn shaped area covering ca. 2000km² (Van der Merwe, 1976) lying west of the Limpopo town of Mokopane formerly Potgietersrus, from about 30km southwest of Mokopane to about 25km north of Gilead (Ashwal et al., 2005), see **Figure 12**. The layered sequence in the Northern Limb comprises of the Marginal, Critical, Main and Upper Zones with a PGE and Ni-Cu bearing horizon known as the Platreef forming the base of the Main Zone (Van der Merwe, 1978). The Upper zone in the Northern Limb stretches over a strike length of ca. 110km while being approximately 1 100m thick (Reynolds, 1986). The layered rocks of the Northern Limb strike northeast and dip 15 to 27 degrees to the west with van der Merwe (2008) suggesting progressive increases in dip from top to bottom and geophysical surveys suggesting that the Northern Limb layered rocks also become progressively thinner and end up as a dyke like feature at depth (van der Merwe, 2008).

The layered sequence of the Northern Limb has a transgressive nature with the rocks sitting on progressively older basement rocks northwards, a point that was noted by Hall (1932) and (Ashwal et al., 2005). To the south the town of Mokopane, the Bushveld Complex rocks sit on the Transvaal clastic sediments while the dolomites and banded iron formations of the Transvaal Supergroup form the footwall in the central portion of the Limb and the older Archean granites forming the footwall in the north (Van der Merwe, 1976).

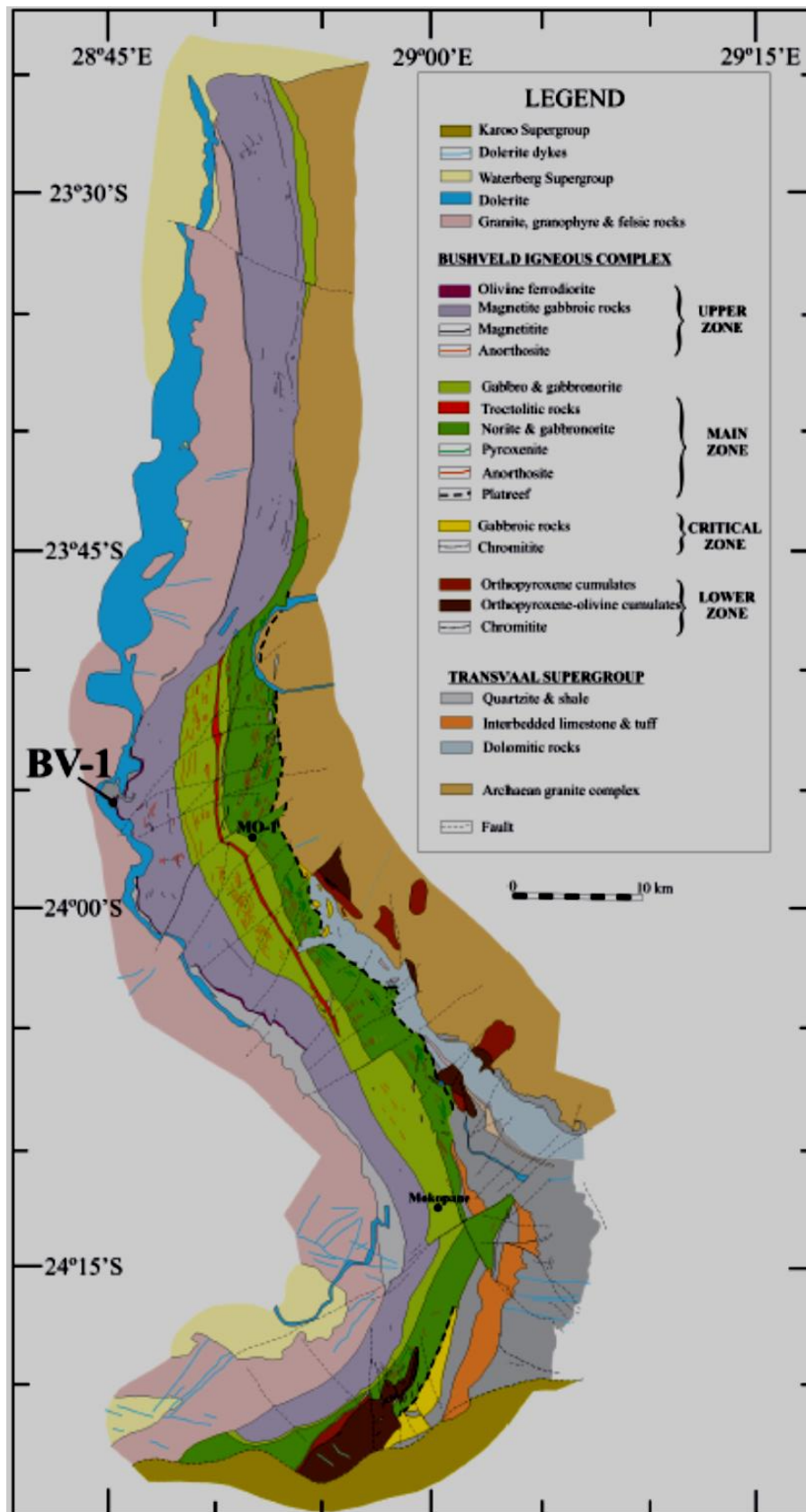


Figure 12 Simplified geological map of Northern Limb: Bushveld Complex. The position of a continuous borehole drilled at Bellevue is shown as BV 1. Adapted from (Ashwal et al., 2005)

2.4.2. The Rustenburg Layered Suite

The Rustenburg Layered Suite in the Northern Limb is approximately 8000m thick (Van der Merwe, 1978). The rocks of the Rustenburg Layered Suite strike 15 to 27 degrees west south of the town of Mokopane, and change to northwest and eventually due north strikes to the north of Mokopane (Ashwal et al., 2005). Hall (1932) recognised the transgressive nature of the rocks over progressively older footwall rocks northwards, beginning with clastic sediments of the Pretoria Group in the south, followed by the dolomites and banded iron formations of the Transvaal Supergroup in the central portion of the Limb and lastly the Archean granites of the Kaapvaal Craton in the north.

Table 4 The stratigraphy of the Northern Limb of the Bushveld Complex after SACS (1980). Adapted from (Walraven, 1986)

Lithological Units in the Northern Limb of the Bushveld Complex SACS (1980)				
Zonal division	Subdivision by SACS (1980)		Lithology	Approximate thickness (m)
	<i>Subsuits</i>	<i>Formations</i>		
Upper Zone		Molendraai Magnetite Gabbro	Magnetite gabbros with layers of magnetite	±1 000
Main Zone		Mapela Gabbro-norite	Gabbro and Norite	±1 600
Critical Zone		Grasvally Norite-Anorthosite	Norite, anorthosite, pyroxenite with chromitite layers	±200
Lower Zone	Zoetveld	Moorddrift Harzburgite-pyroxenite	Harzburgite, pyroxenite with chromitite layers	490
		Drummondlea Harzburgite-chromitite	Harzburgite with chromitite layers	210
		Volspruit Pyroxenite	Pyroxenite with chromitite layers	700

2.4.2.1. The Marginal zone

The Marginal Zone is not always present and in places where it occurs, its thickness ranges from less than a metre to hundreds of metres between the contact of the main mass (which comprises of the Lower, Critical, Main and Upper zones) and the floor (Van der Merwe, 1976). The rocks of the marginal zone are most commonly noritic to doleritic and they display an intrusive nature. Inclusions of floor rocks which range from carbonates, quartzites,

hornfels and granite can be found in the rocks of the marginal zone with an olivine –bearing chilled margin traceable sometimes (Van der Merwe, 1976).

2.4.2.2. The Critical Zone

According to Van der Merwe (1976), the critical zone has a thickness of 400m which outcrops in the Northern Limb of the Bushveld Complex. The zone comprises of rocks that range from chromitite layers, pyroxenites, norites and anorthosites. The base of the platiniferous horizon has been chosen as the top of the critical zone (Willemse, 1969a).

2.4.2.3. The Main Zone

The rocks of the Main Zone in the Northern Limb consist of gabbro, norite, anorthosite, pyroxenite, harzburgite and lherzolite and have a thickness of up to 2 200m (Van der Merwe, 1976). The main zone is thinner in the Northern Limb than elsewhere in the Bushveld Complex with a comparative thickness of 3 940m in the Roossenekal area (Willemse, 1969b) with markers that occur elsewhere in the Bushveld sometimes absent in the Northern Limb. The base of the Main Zone according to Van der Merwe (1976; 1978) is formed by the Platreef which attains a thickness of up to 200m where developed fully.

2.4.2.4. The Upper Zone

The Upper zone, which forms the zone of interest for this study is marked by the first appearance of cumulate magnetite and apatite in the rocks of the Rustenberg Layered Suite (Van der Merwe, 1976). It consists of layers of gabbro, magnetite-gabbro, anorthosite, magnetite and olivine diorite alternating with a thickness of approximately 1100m (Reynolds, 1986) with strike length of approximately 110km.

2.5. Local Geology

The local geology of the study area is interpreted from the geological mapping work and accompanying explanatory notes of (Van der Merwe, 1976; Van der Merwe, 1978; van der Merwe, 2008) as well as (Kinnaird et al., 2005). The far Eastern side of farms Gezond, Molendraai and Inhambane are covered in the rocks of the Mapela gabbro-norite which belongs to the Main Zone. The contact of the Mapela gabbro-norite with the overlying Molendraai magnetite-gabbro is an inferred one and runs almost along the Eastern edge of the farm Commandodrift as seen in **Figure 13**. The Molendraai magnetite-gabbro belongs to the Main Zone and is the host to the titanomagnetite deposits in the area. The magnetite gabbro continues all the way beyond the Western boundaries of the farms Gezond, Commandodrift

and Molendraai where they are bounded by the Mogalakwena River whose alluvium forms the recent cover along the channel. On farm Mozambique, the contact of the Molendraai magnetite gabbro and the overlying Nebo granite is inferred and from that point going west, the Nebo granite is the dominant geology with a small portion covered in sediments that have not been classified.

A total of 20 magnetite seams have been identified in the Northern Limb (Van der Merwe, 1976). The magnetite seams are divided into three units which are the Upper, Main and the Lower magnetite seams (Cawthorn and Molyneux, 1986). The upper seam is comprised of about four to seven layers which have variable thicknesses and they have been correlated to the layers described as layers 3-8 by (Van der Merwe, 1978). The main magnetite seam occurs about 65m below the upper seam and is close to 8m thick comprising of four seams named MAG 01 to MAG 04 from top to bottom, with MAG 03 and MAG 04 constituting the economic resource, each approximately 2m thick and separated by a magnetite gabbro parting (Cawthorn and Molyneux, 1986; Van der Merwe, 1978). The lower magnetite seam is the thickest at approximately 20m, but consists mostly of magnetite rich gabbro with about 20-50 per cent magnetite and occurring about 100m below the main magnetite seam (Cawthorn and Molyneux, 1986). The vanadium content of the main magnetite layer has been noted to decrease laterally from the north to the south, with (Cawthorn and Molyneux, 1986) noting the V_2O_5 grade of the main seam at farm Hamburg 737 LR in the north of the Limb at 1.5 per cent, while being 1.62 per cent at Mozambique, 1.77 at Gezond and 2.2 per cent about 50km south of Gezond.

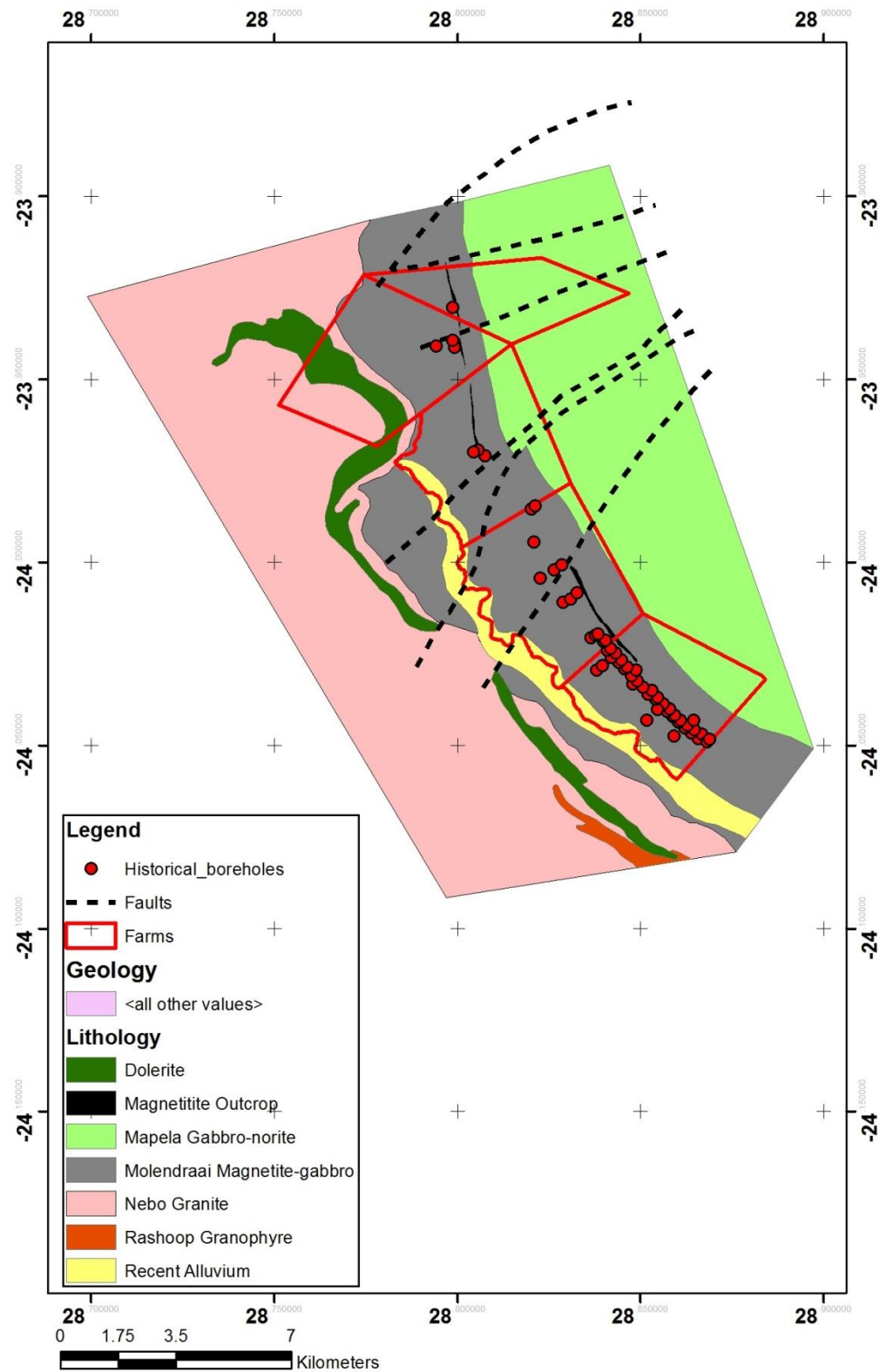


Figure 13 Generalised geology of the study area. Modified after (Van der Merwe, 1978)

Chapter 3 MINERALS OF THE FE-TI-V SYSTEM

Buddington and Lindsley (1964) did extensive work regarding the minerals of the FeO-Fe₂O₃-TiO₂ system and came up with a ternary diagram that shows the theoretical end members of the system as shown in Figure 14. According to Reynolds (1978), the minerals only rarely approximate the theoretical end members as they are parts of sometimes very complex solid solutions. Vanadium has a partition coefficient of 15 to 20 into magnetite and exists in the magnetite lattice as V₂O₃, with the highest concentrations at the base of the magnetite seams and the partition coefficient decreases with increase in oxygen fugacity (*f*O₂) (Cawthorn and Molyneux, 1986).

For the purposes of this study, the minerals magnetite, ilmenite, Ulvospinel, hematite and titanomagnetite are of importance. The magnesian spinels pleonaste and hercynite are not part of the FeO-Fe₂O₃-TiO₂ system but are discussed owing to their significance as exsolution phases in the titanomagnetites. The TiO₂ end of the system comprises of the polymorphs of TiO₂ namely rutile, anatase and brookite and together with pseudobrookite (Fe₂TiO₅) and ferro-pseudobrookite (FeTi₂O₅) are not of much interest, and are not the subject of discussion in this study.

3.1. The spinel series - magnetite, titanomagnetite and ulvospinel

Magnetite and Ulvospinel are members of the spinel mineral group with both being cubic with the formula of magnetite being Fe₃O₄ (FeO.Fe₂O₃) and that of ulvospinel Fe₂TiO₄ (Buddington and Lindsley, 1964). Titanomagnetite is a number of intermediate members of the magnetite-ulvospinel solid solution which are essentially iron rich titanium bearing spinels that are encountered normally in igneous rocks that were rapidly cooled (Reynolds, 1978). Naturally occurring titanomagnetite can contain varying but minor amounts of Mg²⁺, Mn²⁺, Zn²⁺, Ni²⁺, Al³⁺, Cr³⁺ and V³⁺. Ulvospinel named after the Södra Ulvön locality in Sweden by (Mogensen, 1946) is an end member of the spinel mineral group with a cubic crystal system and the chemical formula Fe₂TiO₄ (2Fe²⁺O.Ti⁴⁺O₂). The mineral according to Barth and Posnjak (1932) has an inverse spinel structure similar to that of magnetite, but with the Fe³⁺ ions being replaced by Ti⁴⁺ and Fe²⁺. Reynolds (1978) quotes Verhoogen (1962) and concedes that ulvospinel is extremely rare as a discrete mineral, but occurs commonly as a solid solution of other minerals of the spinel group such as magnetite and chromite (Posnjak and Barth, 1918).

Pleonaste and hercynite are members of the spinel group of minerals falling under the spinel series. Pleonaste is the term given to the spinel in which Fe^{2+} replaces Mg such that the Mg:Fe ratio ranges from 3 to 1 while hercynite is the aluminium bearing spinel in with the formula $\text{Fe}^{2+}\text{Al}_2\text{O}_4$ with potential for Mg replacing Fe^{2+} and Fe^{3+} replacing Al (Deer et al., 1966).

3.2. The rhombohedral series - ilmenite and hematite

Hematite with the name derived from the Greek “haema” meaning blood is a rhombohedral oxide of iron with a normal formula Fe_2O_3 . It is an uncommon phase in igneous rocks and is usually present as a secondary oxidation product of magnetite (Reynolds, 1978). Ilmenite is a rhombohedral oxide of iron and titanium with the formula FeTiO_3 ($\text{FeO} \cdot \text{TiO}_2$) and has the same crystal system as hematite, however there is some distortion of oxygen layers resulting in reduced O-O distances (Barth and Posnjak, 1911). At elevated temperatures, there exists complete solid solution between hematite and ilmenite, with a miscibility gap at low temperatures (Lindsley and Lindh, 1974). According to Posnjak and Barth (1918), substitution for Fe^{2+} by Mg^{2+} , Mn^{2+} , Ni^{2+} , Co and Cd can occur in ilmenites. Ilmenite contains about 40-60 per cent TiO_2 depending on its geological origin and history (Zhang et al., 2011).

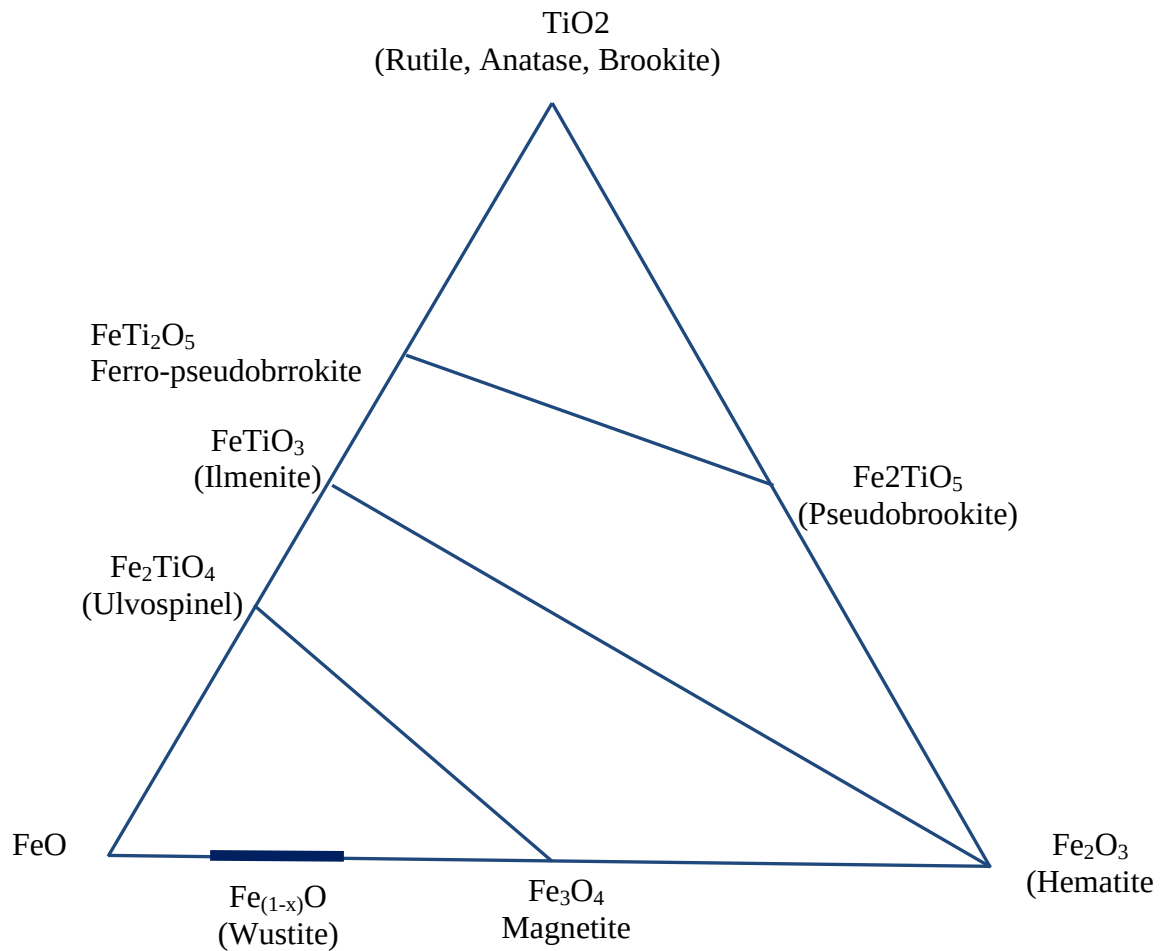


Figure 14 The phases in the FeO-Fe₂O₃-TiO₂ system, with the major solid solution series shown. Modified after (Buddington and Lindsley, 1964).

3.3. Phase relations

The FeO-Fe₂O₃-TiO₂ system is very complex with phase relations that are known to have three solid solution series at high temperatures following the work of (MacChesney and Muan, 1961; Webster and Bright, 1961) and (Taylor, 1963). At 1300⁰C the system has three solid solutions, as shown in **Figure 15** and these are:

- i) Ulvospinel-magnetite (Cubic)
- ii) Ilmenite-hematite (Rhombohedral)
- iii) Ferropseudobrookite-pseudobrookite (Orthorhombic)

The three solid solution series have limited solid solution at elevated temperatures and exsolution commences as the temperatures drop (MacChesney and Muan, 1961), (Reynolds, 1978). The work of Buddington and Lindsley (1964) found out that oxygen fugacity during

3.4. Textural and exsolution features in titaniferous magnetites

The Upper Zone rocks of the Rustenburg Layered Suite contain magnetite and ilmenite as discrete phases, except for the uppermost 200m in the Rustenburg area (Cawthorn and Molyneux, 1986). The portions of the Ti-magnetite layers that are silicate free, are essentially coarse grained with individual grains often exceeding 10mm in diameter (Reynolds, 1986). The massive magnetite rocks contain less than 5 percent volume silicates and are classified as adcumulus following the nomenclature of (Wager et al., 1960). According to Reynolds (1985a) the massive magnetite seams that are silicate free as shown in **Error! Reference source not found.** are composed almost entirely of Ti-magnetite and contain usually less than 6 per cent granular ilmenite by volume. The magnetite content by volume is variable in the orthocumulate portions of the magnetite seams and can range from plagioclase mesocumulate to magnetite heteradcumulate (Reynolds, 1986; Wager et al., 1960); see **Figure 17.**



Figure 16 Massive (adcumulate) titanomagnetite ore from the Upper zone magnetite.



Figure 17 Orthocumulate titanomagnetite-silicate ore from the Upper Zone. The light silicates are largely plagioclase. Note the preferential orientation of plagioclase.

3.4.1. Macroscopic Textural features

The Bushveld Complex titanomagnetite from the Upper zone consist of closely packed, almost equant grains of magnetite, with interstitial accessory silicates such as feldspars, pyroxenes and in some cases olivine with rare sulphides (Rohrmann, 1989). According to Reynolds (1985a), the silicate free portions of the titanomagnetites form massive polycrystalline aggregates in which the crystals of the titanomagnetite form triple junctions with the interfacial angles at 120° and straight to curved grain boundaries. The ores show a significant drop in grain size from the massive titanomagnetites which are essentially adcumulates to the zones that contain intercumulus phases (Reynolds, 1986). The grain sizes of the titanomagnetite markedly decreases in the immediate vicinity of silicates or ilmenite inclusions (Reynolds, 1985a).

Ilmenite occurs as elongate grains or as thin exsolution lamellae parallel to the octahedral planes of the magnetite (Von Gruenewaldt et al., 1985; Rohrmann, 1989). The ilmenite grains when present as discrete coarse granular phases are usually smaller than the surrounding co-existing titanomagnetite grains (Reynolds, 1986). Wagner (1928) in his Iron deposits of the Union of South Africa noted that the magnetite contained fine ilmenite intergrowths. Molyneux (1969) noted exsolution of titanium and magnesian spinels phases and makes particular mention of the magnesian spinel pleonaste which he noted to exsolved parallel to the 100 plane of the magnetite and he further suggests that the pleonaste grains are older than the fine ilmenite lamellae. The ilmenite can occur as discrete grains or grain aggregates which are typically elongate and occurring along the margins of magnetite and Ti-magnetite.

3.4.2. Microscopic Textural features

Molyneux (1969) states that the magnetite ores occur as largely monominerallic ores (adcumulates) or as interstitial ore in silicate rocks. The titaniferous magnetites have ilmenite occurring as exsolved lamellae and the abundant cloth-pattern ulvospinel exsolutions (Reynolds, 1986; Willemse, 1969b and Von Gruenewaldt et al., 1985) as can be seen in **Error! Reference source not found.** The ulvospinel exsolutions are sub-micrometre to micrometre in size which are oriented parallel to the (100) plane of the magnetite and dividing the magnetite into small rectangles and cubes of micrometre size and sometimes less. The fine ulvospinel exsolutions are suggested to be as a result of the exsolution products of a possible original magnetite-ulvospinel solid solution under low oxygen fugacity (fO_2) conditions (Reynolds, 1986; Buddington and Lindsley, 1964 and Verhoogen, 1962). According to Reynolds (1986), the ulvospinel exsolutions are generally absent or poorly developed in zones surrounding ilmenite grains for distances of between 5 to 20µm around the ilmenite grains, while being persistently present in the magnetite where it borders other titaniferous magnetite grains or silicates.

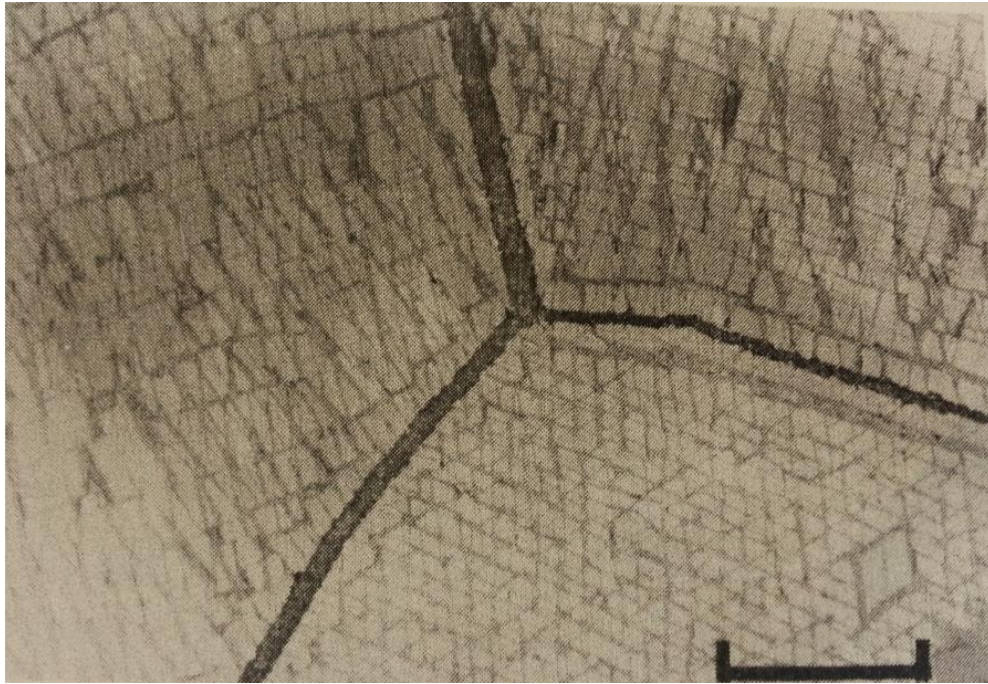


Figure 18 Magnetite grains showing the triple junction and exsolved ulvospinel showing cloth texture. The scale bar is 20 μ m Adapted from (Reynolds, 1986)

Ilmenite within the titanomagnetites occurs in several forms with discrete grains constituting anywhere between 2 to 10 per cent by volume and also as fine intergranular and lamellae ilmenite present in variable amounts. Intergranular ilmenite occurs sparingly and is usually developed along grain boundaries of the titanomagnetite and often shows outer rims that are spinelliferous (Reynolds, 1986; Howarth et al., 2013). Lamellae ilmenite although present, is not well developed and according to Reynolds (1986) and (Von Gruenewaldt et al., 1985), it is usually restricted to the higher levels of the sequence. Where present, the ilmenite forms trellis networks as shown in **Error! Reference source not found.** and **Error! Reference source not found.**

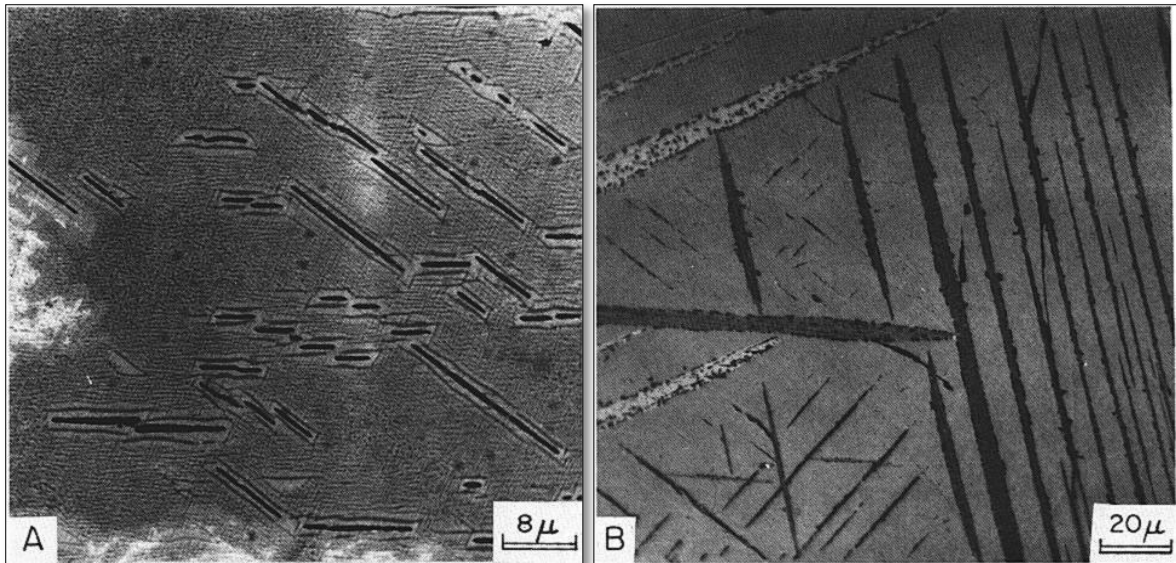


Figure 19 Pleonaste, Ilmenite and ulvospinel exsolution textures (A) pleonaste and ulvospinel boxwork (B) Trellis ilmenite in magnetite. Adapted from (Von Gruenewaldt et al., 1985)

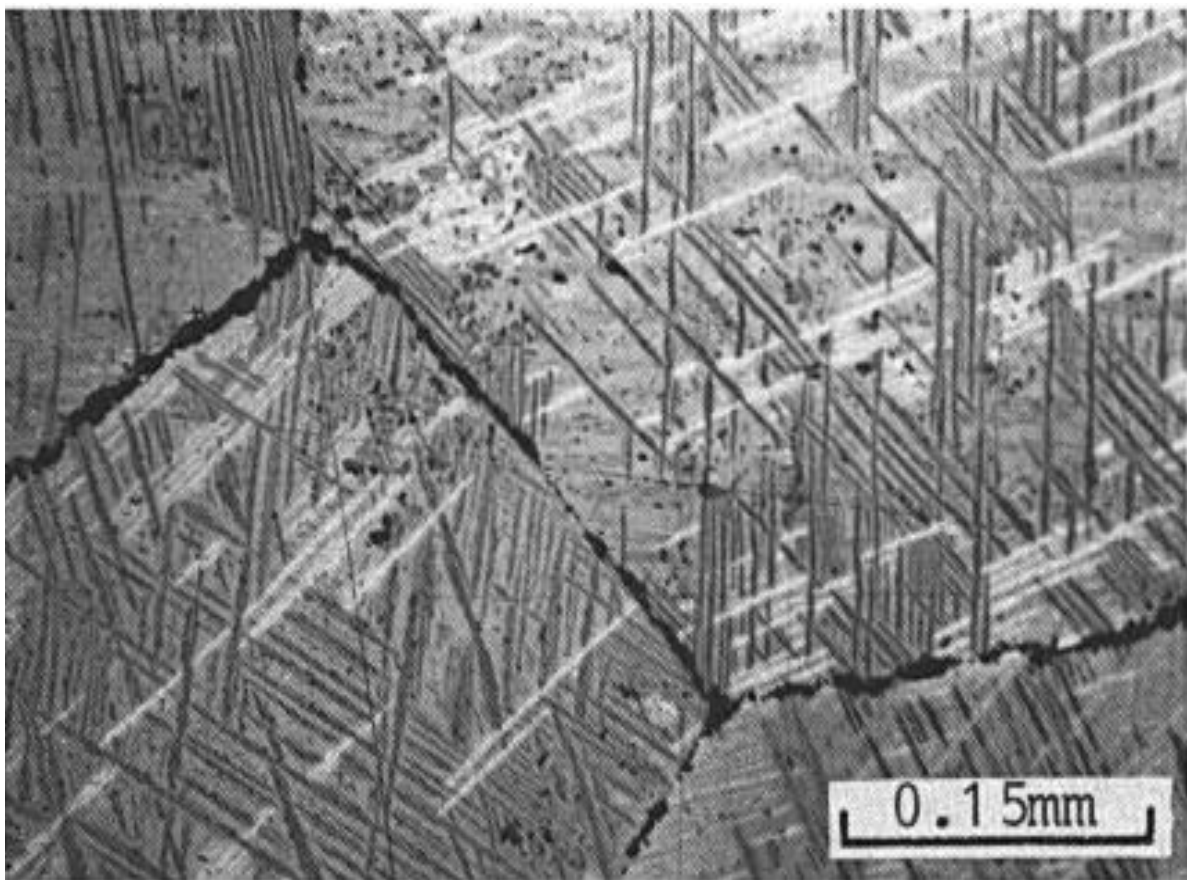


Figure 20 Ilmenite intergrowths in titanomagnetite. Note the magnetite triple junctions.

Smaller lamellae of ilmenite which hardly ever get to 25µm in length are also developed in the titanomagnetite from the base to the upper layers forming extensive trellis networks parallel to (111) of the magnetite and may take the place of the ulvospinel (Reynolds, 1986). The two sets of ilmenite exsolutions have been regarded as two distinct generations with the larger broad and not so widespread lamellae considered the first generation while the smaller ones are considered the second generation. Pleonaste and hercynite, which are transparent spinels are commonly exsolved in the titanomagnetite **Error! Reference source not found.**) and they are more apparent towards the base of the upper zone (Reynolds, 1985a; Willemse, 1969b). According to Molyneux (1969) and (Von Gruenewaldt et al., 1985) the magnesian spinels are more abundant in the zones that are silicate poor and shows variable distribution with vertical height within the Upper Zone.

3.5. Geochemistry of the titanomagnetite ores

The geochemical work that has been carried out on the titanomagnetites of the Upper zone both for major and trace element analyses are comparatively few and most of the work has been done by mining companies (Reynolds, 1985a; Cawthorn and Molyneux, 1986). The first major point to note in the whole of the upper Zone is the decrease in the anorthite (An%) content of the plagioclase from the base of the Upper Zone towards the top, with an An₅₀₋₆₀ at the base dropping to An₄₀₋₅₀ at the top (Van der Merwe, 1978; Cawthorn and Ashwal, 2009). The TiO₂ content in the magnetite seams increases progressively with stratigraphic height beginning with an average of approximately 12 per cent at the base of the Upper Zone to approximately 20 per cent at the top of the layered sequence (Reynolds, 1985a; Willemse, 1969b; Von Gruenewaldt et al., 1985; Klemm et al., 1985) and (Cawthorn and Ashwal, 2009).

Vanadium is known to exhibit an antipathetic relationship to TiO₂ with the bulk V₂O₅ content of approximately 2 per cent at the base and approximately 0.2cent at the top (Willemse, 1969b; Molyneux, 1969; Reynolds, 1985b) and (Von Gruenewaldt et al., 1985). Chromium content is of interest in the magnetite seams as it is known to decrease with stratigraphic height. Willemse (1969b) suggests that the chromium (Cr₂O₃) content at the base of the magnetite seams at magnet heights in the Eastern Limb is about 2.32 to 2.42 per cent. Later workers including Molyneux (1969) and (Reynolds (1986) report Cr₂O₃ contents of approximately 2.5 per cent.

Minor elements that are known to occur in the titanomagnetite seams include magnesium, manganese and aluminium with the MgO and the Al₂O₃ being represented by the magnesian and aluminous spinels pleonaste and hercynite that form exsolution lamellae together with ulvospinel and ilmenite (Reynolds, 1985a; Von Gruenewaldt et al., 1985). The distribution of the elements Mg and Mn according to Reynolds (1985a) is controlled by their partition coefficient into ilmenite relative to titanomagnetite during the crystallisation process and subsolidus re-equilibration as illustrated by (Neumann, 1974). Silicate mineral constituents SiO₂, CaO, NaO as well as silicate Al₂O₃ complete the package of the bulk rock compositions of the titanomagnetite ores (Reynolds, 1986).

3.6. Origin of the vanadium bearing titanomagnetites of the Upper Zone

Several authors have proposed a number of possible origins of the titanomagnetite seams of the Upper Zone of the Rustenburg Layered Suite and they are among others (Reynolds, 1985a; Klemm et al., 1982; Philpotts, 1967; Cawthorn and McCarthy, 1980; Cawthorn and McCarthy, 1981), and (Cawthorn and Molyneux, 1986). The earliest models for the origin of the titanomagnetite seams as discussed by authors like Molengraaff (1904) proposed magmatic segregation and Wagner (1928) concurred with this proposition while further suggesting that the magnetite seams formed as a result of the settling due to gravity of titanomagnetite crystals within a magma chamber. The work of Hall (1932) suggested that a magnetite liquid which will be much denser than the rest of the magma could accumulate at the base of the magma chamber and thereby forming the magnetite seams. He further went on to propose that the plagioclase grains that are common in the magnetite seams would have been displaced by the oxide liquid and concentrated towards the top where they form magnetite-plagioclase cumulates.

The work of Bateman (1951) further expanded on these ideas and came up with the conclusion that the titanomagnetite seams formed through gravitational settling of an immiscible oxide liquid which then percolated downwards through interstices of the silicates that crystallised earlier and Philpotts (1967) further developed the liquid immiscibility model through the demonstration that an iron rich liquid in equilibrium with a dioritic liquid can contain up to 35 per cent apatite, which was later shown by Reynolds (1985a) and Von Gruenewaldt (1993) to be present in significant quantities in the top magnetite layers of the

Upper Zone. Cawthorn and McCarthy (1980; 1981) and McCarthy et al., (1985) through their work on chromium content and diffusion control however have proposed that the rapid depletion in Cr in short vertical distances does not conform to the idea of gravitational settling.

Other models that have been proposed for the potential origin of the titanomagnetite layers include crustal contamination by Irvine (1974) and multiple magma injection although the silicate phases above and below the magnetite seams show consistency and no trace element reversals (Cawthorn and McCarthy, 1980). Change in oxygen fugacity can have an effect on the liquidus phases such that oxide rich layers can be produced (Hill and Roeder, 1974), (Howarth et al., 2013) however the V_2O_5 content of the magnetite seams contradict this proposition as the partition co-efficient of Vanadium in magnetite decreases with increasing oxygen fugacity and as such should result in low V_2O_5 contents which is not the case (Cawthorn and McCarthy, 1981; McCarthy et al., 1985). Changes in pressure in the magma chamber was proposed by Cawthorn and McCarthy (1980) to may have resulted in the formation of the titanomagnetite seams either through new magma injection, volcanic tapping or magma migration to lateral or deeper magma reservoirs.

The envisaged formation process of the formation of the titanomagnetite layers as presented by Reynolds (1986) is as follows:

- i) Fractional crystallisation that results from a lengthy period with several magma injection having resulted in sufficient accumulation of Fe, Ti and V in the residual magma which results in large scale precipitation of titanomagnetites at a large scale.
- ii) Growth through nucleation of the primocrysts of titanomagnetite as the temperatures decreases to intersect the ulvospinel-magnetite solid-solution series with diffusion controlled growth of the phases (Cawthorn and McCarthy, 1981).
- iii) Further precipitation of oxide minerals of the FeO-TiO system through changes in oxygen fugacity either by crustal contamination (Irvine, 1974) or through volatiles incorporated from thermal metamorphism of floor rocks (Klemm et al., 1982).

3.7. Global Vanadium production

South Africa contributes about 40% of the global production of vanadium pentoxide which stood at 60 000 metric tonnes per annum as of 2003 (Moskalyk and Alfantazi, 2003). China produces about 25 per cent of vanadium pentoxide annually while Russia contributes about 20 per cent. According to Rohrmann (1989), 98% of the world's vanadium resources are hosted in titanomagnetites, which makes the Bushveld Complex the largest resource of vanadium in the world (Reynolds, 1985a). Vanadium production in South Africa began in 1957 with the establishment of a plant in Witbank by Minerals Engineering of South Africa Limited (Cawthorn and Molyneux, 1986). South Africa's vanadium resources are estimated to contain 12.5 million tonnes of vanadium metal (Schurmann and Marsh, 1998).

The United States Geological Survey as of 2011 estimated that the world resources of vanadium stood at more than 63 million tonnes with production coming largely from China, Russia and South Africa (Polyak, 2012) as shown in **Table 5**.

Table 5 USGS global vanadium production estimates as at 2011. Adapted from (Polyak, 2012)

<u>World Mine Production and Reserves:</u>			
	Mine production		Reserves⁵
	<u>2010</u>	<u>2011^e</u>	(thousand metric tons)
United States	W	W	45
China	22,000	23,000	5,100
Russia	15,000	15,000	5,000
South Africa	19,000	20,000	3,500
Other countries	<u>1,600</u>	<u>1,500</u>	<u>NA</u>
World total (rounded)	57,600	60,000	14,000

3.8. Global Titanium production

Globally, most titanium dioxide (TiO₂) is produced from beach sands, where ilmenite is smelted in electric arc furnaces to produce pig iron and high titanium slag which typically contains about 85–90% TiO₂ (Zhang et al., 2011). The high titania slag is then crushed and screened before being mixed with petroleum coke and chlorine gas and heated to a temperature of between 800-1 000⁰C to form liquid titanium tetrachloride which is further purified by fractional distillation (Wipplinger, 1998). Production of titanium from titanomagnetites can be achieved through smelting, direct acid leaching, selective chlorination and reduction (Yuan et al., 2006). According to Wipplinger (1998), the global resources for titanium metal stood at 430 million tonnes with South Africa contributing 17% of that figure with most of the South African production coming from the Richards Bay

Minerals operations. In South Africa as at 1998, the titaniferous magnetite seams of the Upper Zone of the Bushveld were being exploited only for vanadium and not for titanium while the magnetite plugs which contain granular ilmenite were exploited for vanadium and titanium (Wipplinger, 1998).

According to the United States Geological Survey (USGS), global resources of ilmenite, anatase and rutile as of January 2013 stood at more than 2 billion tonnes with ilmenite accounting for 92 per cent of titanium production (Bedinger, 2013). Below is a compilation of the USGS titanium production data for the years 2011 and 2012 with South Africa being the largest producer (Bedinger, 2013).

Table 6 USGS global titanium production estimates as at 2011. Adapted from (Bedinger, 2013)

TITANIUM MINERAL CONCENTRATES			
<u>World Mine Production and Reserves:</u>			
	Mine production		Reserves⁵
	<u>2011</u>	<u>2012^e</u>	
Ilmenite:			
United States ²	⁶ 300	⁶ 300	2,000
Australia	960	940	100,000
Brazil	45	45	43,000
Canada ⁷	750	700	31,000
China	660	700	200,000
India	330	550	85,000
Madagascar	280	280	40,000
Mozambique	380	380	16,000
Norway ⁷	360	350	37,000
South Africa ⁷	1,110	1,030	63,000
Sri Lanka	31	60	NA
Ukraine	300	300	5,900
Vietnam	550	500	1,600
Other countries	40	40	26,000
World total (ilmenite, rounded)	6,100	6,200	650,000
Rutile:			
United States	(⁸)	(⁸)	(⁸)
Australia	440	480	18,000
Brazil	3	5	1,200
India	24	25	7,400
Mozambique	6	8	480
Sierra Leone	64	100	3,800
South Africa	122	131	8,300
Ukraine	56	60	2,500
Other countries	18	17	400
World total (rutile, rounded)	⁸ 730	⁸ 830	42,000
World total (ilmenite and rutile, rounded)	6,700	7,000	700,000

3.9. Recovery of vanadium from titaniferous magnetites

Vanadium recovery usually involves a number of both pyro-metallurgical and hydro-metallurgical processes (Fu et al., 2011). Vanadium can be recovered from titaniferous magnetite ores through a number of processes which among others include the direct pyro-metallurgical reduction of the titanomagnetite ore in an electric arc furnace. In this process, the vanadium goes into the iron phase and a subsequent process of oxygen blowing moves the vanadium to the slag phase which is then roasted, leached and the vanadium recovered as ammonium-polyvanadate which is then used to make ferrovanadium (Jena et al., 1995; Moskalyk and Alfantazi, 2003).

The other method involves the direct soda ash roast and leach process where the vanadium bearing titanomagnetite is processed directly without smelting with recoveries of approximately 85 per cent (Jena et al., 1995; Hukkanen and Walden, 1985). In the second process, the titanomagnetite ore is pelletised and mixed with sodium carbonate and roasted which leads magnetite to oxidise into hematite while vanadium moves out of the magnetite lattice and form sodium vanadate through oxidation. The sodium vanadate is leached with hot water and the vanadium is later precipitated with sulphuric acid or liquid ammonia (Jena et al., 1995; Hukkanen and Walden, 1985). In South Africa, another process has been developed that recovers vanadium from titanomagnetite by way of pelletisation of the ore which is then roasted in a grate-kiln cooler system and sodium sulphate used as a chemical reagent followed by the evaporation of the vanadium containing solution (Hukkanen and Walden, 1985).

3.10. Recovery of iron and titanium from titaniferous magnetites

The recovery of titanium and iron ore from titanomagnetite can be achieved through a number of ways which among others include mechanical separation of the iron oxides, usually magnetite from the titanium oxides through magnetic separation (Hukkanen and Walden, 1985). This process involves the crushing of the ore, followed by grinding to fine sizes to allow granular ilmenite to be separated from magnetite as it is passed through a weak magnetic field which attracts the magnetite as what is being practiced by Evraz Highveld Steel and Vanadium in South Africa. The other process involves the reduction of the titanomagnetite through the Direct Reduction process to produce sponge iron, which can then be smelted in an electric furnace to produce pig iron as well as high titania slag, a feedstock

for TiO_2 production through chloridisation (Rohrmann, 1989). The second process involves sending the ore through a rotary sponge iron kiln, before smelting in an electric arc furnace which increases the handling of the ore before titania slug can be produced (Hukkanen and Walden, 1985).

Recovery of iron from iron ores is usually through the conventional blast furnace smelting, where the iron ore is reduced by carbon from the metallurgical coke (Morizane and Fruehan, 1999). The metallic iron forms a separate liquid which is tapped away from a slag of impurities (Lekontsev and Shkumatov, 1980). The other commonly used method of iron processing is the direct reduction method, where the ore is sent through a rotary sponge iron kiln and the iron is reduced by carbon which is supplied as pulverised coal (Rohrmann, 1989).

The Bushveld titaniferous iron ores are difficult to process through the blast furnace smelting process due to the high TiO_2 content in the slag which can end up as high as 20-25 per cent (Fu et al., 2011; Lekontsev and Shkumatov, 1980). Titaniferous iron ores are usually dressed by crushing and magnetic separation where the magnetite which is magnetic is separated from the titanium oxides, usually ilmenite which is non-magnetic (Ramdohr, 1953). Problems may arise though in the processing of titaniferous iron ores if there are iron-titanium oxides that are fairly magnetic like ulvöspinel which will be difficult to separate by magnetic separation or if the ilmenite and other titanium bearing oxides exist as finely exsolved lamellae which could be sub-micron in size therefore rendering the ores difficult to mechanical crushing and separation (Ramdohr, 1953). Following reduction of titanium bearing ores, usually ilmenite in an electric arc furnace, the titania slag is crushed and further processed to produce TiO_2 or titanium metal through the thermo chemical reduction processes using TiCl_4 as feed material (Zhang et al., 2011). Pigment grade TiO_2 can be produced from the high titania slag through leaching by hydrochloric acid or H_2SO_4 (Zhang et al., 2011).

Chapter 4 METHODOLOGY

4.1. Introduction

The purpose of this study as outlined in the Section 1.4 is to determine the nature and occurrence of the vanadium bearing titanomagnetites of the Upper Zone within the prospecting right of the CEI group. The focus of the study is determining the relationship between the titanium oxides and magnetite, in order to evaluate the potential for recovery of iron as a metal for use in the steel industry as well as titania slag for use in the production of pigment grade TiO_2 or titanium metal.

4.2. Problem statement

The Upper Zone of the Bushveld Complex is according to (Eales and Cawthorn, 1996; Willemse, 1969a; Cawthorn and Molyneux, 1986) host to the largest vanadium bearing titaniferous magnetites in the world. The vanadium content within the main magnetite layers ranges from as low as 0.2% at the top layers to as high as 2% at the bottom layers (Cawthorn and Molyneux, 1986) which makes the Upper Zone main magnetite layer an important and economic resource for vanadium with South Africa producing about 40% of global vanadium (Moskalyk and Alfantazi, 2003). Recovery of vanadium from the titaniferous magnetite is possible through salt roasting and leaching process (Schurmann and Marsh, 1998; Moskalyk and Alfantazi, 2003)).

The vanadium resource that is the Upper Zone magnetite also contains titanium which ranges from 12% in the bottom magnetite layers to 21% in the top layers and iron ore in the form of magnetite (Schurmann and Marsh, 1998; Cawthorn and Molyneux, 1986; Von Gruenewaldt, 1977). The titanium occurs in the form of ilmenite (FeTiO_3), ulvospinel (Fe_2TiO_4) and titaniferous magnetite, where the ilmenite occurs as discrete grains or as exsolved lamellae while the ulvospinel occurs as finely exsolved lamellae parallel to the (111) magnetite cleavage (Reynolds, 1986; Von Gruenewaldt et al., 1985), . The presence of ulvospinel in the ores has the effect of reducing the total recoverable titanium because ulvospinel is weakly magnetic and will likely follow magnetite instead of ilmenite during magnetic separation (Ramdohr, 1953).

Thin lamellae of ilmenite will reduce the amenability of the ilmenite to separation from magnetite by crushing and grinding as some of the exsolution lamellae can be sub-micron in

size and thus will be almost impossible fine grinding required to mechanically separate the lamellae from the magnetite (Hukkanen and Walden, 1985).

4.2.1. The Titanium problem in Blast furnaces

The recovery of titanium and iron ore from other titaniferous magnetite deposits in the world depends to a very large extent on magnetic separation of the ilmenite and magnetite where they occur as discrete phases (Hukkanen and Walden, 1985). The magnetite and ilmenite will have to be treated separately as they are not easily amenable to processing using one processing method. Iron ore is conventionally processed using the blast furnace, while ilmenite is processed using an electric arc furnace (Jena et al., 1995). Titanium is a deleterious constituent in iron ores for conventional processing (Rossi, 1890) through the blast furnace smelting process, because if carbon in the form of coke is used to reduce the titaniferous iron ores in a conventional blast furnace, the carbon reduces the TiO_2 to titanium sesquioxide instead of reducing the iron oxide. The titanium sesquioxide then combines with the furnace blast to form titanium nitrides and carbides which precipitate, reduce the viscosity of the slag and agglomerate thereby clogging the blast furnace hearths and shutting it down (Gavrilyuk et al., 1998). The titanium carbides and nitrides are high melting compounds which then get deposited on the lower part of the blast furnace hearth refractory lining and effectively erode the lining by diffusion (Wu and Ho, 2009; Gavrilyuk et al., 1998). Titanium bearing iron ores that have titanium oxides which cannot be separated by mechanical means are not suitable for as blast furnace feed as the campaign life of the blast furnace is significantly reduced by the effect of titanium oxides in the slag (Morizane and Fruehan, 1999).

In as much as the Upper Zone of the Rustenburg Layered Suite of the Bushveld Complex is host to the largest vanadium bearing titaniferous magnetite deposits in the world (Cawthorn and Molyneux, 1986), the resource could be limited to being a vanadium resource only due to the difficulties that may arise from the potential processing of the titanium and iron due to the effects of titanium in iron. The Upper Zone titanomagnetite ores have been dismissed as potential iron and titanium ores by (Molengraaff, 1904; Hall, 1909) and (Willemse, 1969b) among other workers.

The mineralogical setting of the iron and titanium oxides within the vanadium bearing titanomagnetites on the farms under study will therefore determine the potential for separate extractability of iron and titanium over and above the vanadium. Discrete separate phases of

iron and titanium oxides in the form of magnetite and ilmenite therefore favour potential extractability through mechanical crushing, grinding and magnetic separation. The existence of the oxides of iron and titanium as indiscrete phases through exsolution, micro-intergrowths and solid solutions will thus limit the suitability of the ores as sources of iron and titanium through the blast furnace smelting process.

4.3. Research outline

The research was carried out on boreholes drilled as part on farm Gezond 235 KR distributed along the strike length of the farm. The boreholes selected are P21, P55 and P57 which were drilled as part of a measured resource evaluation. The study focused on both the macroscopic mineralogical relationship of the oxide minerals and the associated gangue silicate minerals as well as the microscopic relationship and setting of the minerals of the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system. The study involved observation of samples in hand specimen, under optical microscopy as well as under scanning electron microscopy (SEM). The study also entailed analysis of the samples through SEM coupled energy dispersive X-ray spectroscopy as well as electron microprobe analysis.

Optical microscopy was used to study the micron to millimetre size mineralogical relationships while the scanning electron microscopes were used to study the sub-micron to micron sized relationships and settings. Electron backscatter images of the samples were acquired for analyses of the relationship of the titanomagnetite with its co-existing oxide phases such as ilmenite, ulvospinel, pleonaste and hercynite. The chemical compositions of individual mineral grains were studied using the electron microprobe analyser, while the chemical composition of the polished sections were measured utilising the energy dispersive X-ray spectrometer that is coupled with a scanning electron microscope.

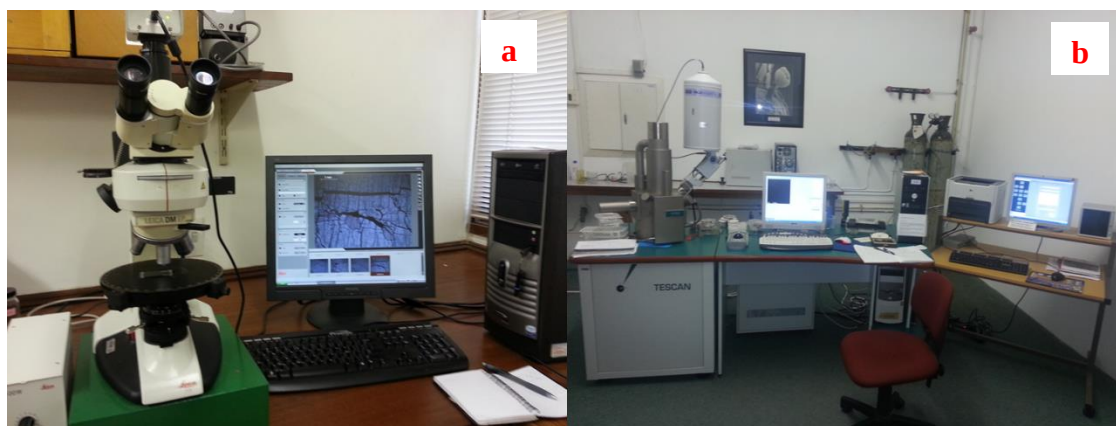


Figure 21 Microscopes used during the study (a) Optical Microscope (b) SEM with EDS

4.4. Sample collection and treatment

Three diamond core boreholes from the farm Gezond 235 KR were sampled in this study and they are P21, P55 and P57. The three boreholes were drilled as part of the exploration for Vanadium on the farm Gezond 235 KR and they all intersected the main magnetitite seam of the Upper zone. The borehole cores were sampled across all the intersected magnetitite seams as shown in **Figure 23**, **Figure 24** and **Figure 25** and quarter cores were obtained for preparation of thin sections. The quarter cores were cut using a diamond saw, labelled and stored separately with two name cards kept for each sample. Borehole P21 had 15 quarter core samples taken, while boreholes P55 and P57 had 11 and 14 samples collected respectively. The sample names, depth and remarks are attached as Appendix C.

The cut cores were prepared into polished thin sections as shown in **Figure 22** for study under the optical microscope as well as under scanning electron microscopes and no cover slips were used. The same polished thin sections were carbon coated for study under the electron microprobe as well as the energy dispersive spectroscopy machine after optical microscopy work. The prepared quarter cores are shown in Appendix A, while the associated thin sections are shown in Appendix B. The thin sections were observed under reflected light for the oxides and opaque minerals as well as under transmitted light for the transparent minerals. The Electron dispersive X-Ray spectroscopy technique was used for major element mapping while the electron micro-probe analysis technique was used for geochemistry and trace element analysis.

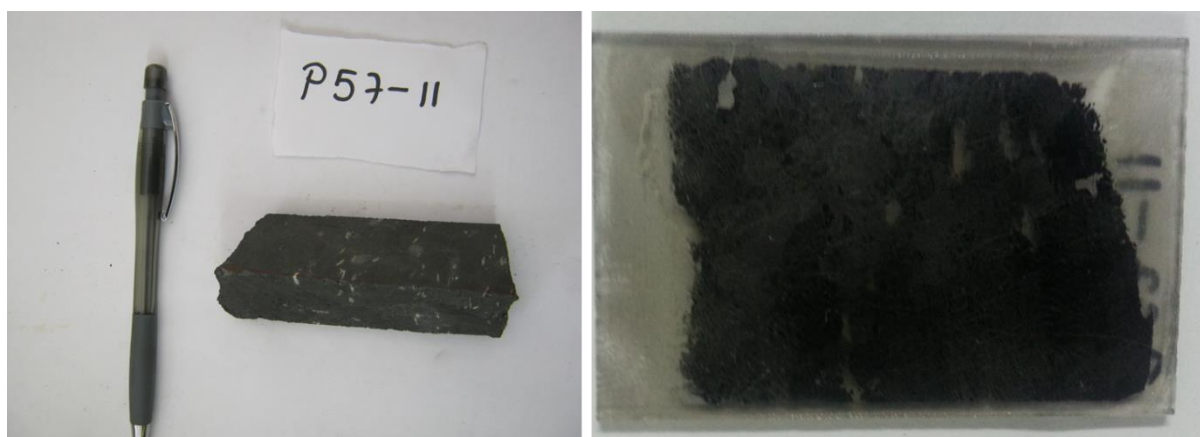


Figure 22 Quarter core and corresponding thin section.

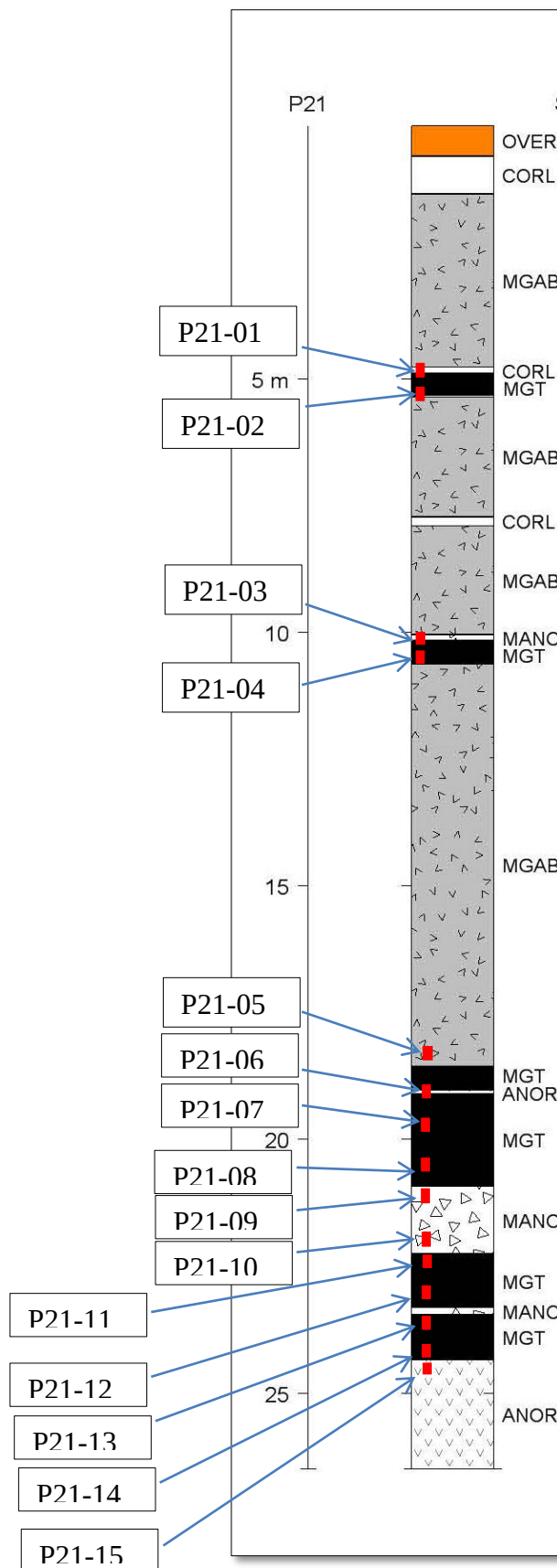


Figure 23 Borehole P 21 strip log showing the positions of the samples P21-01 to P21-15.

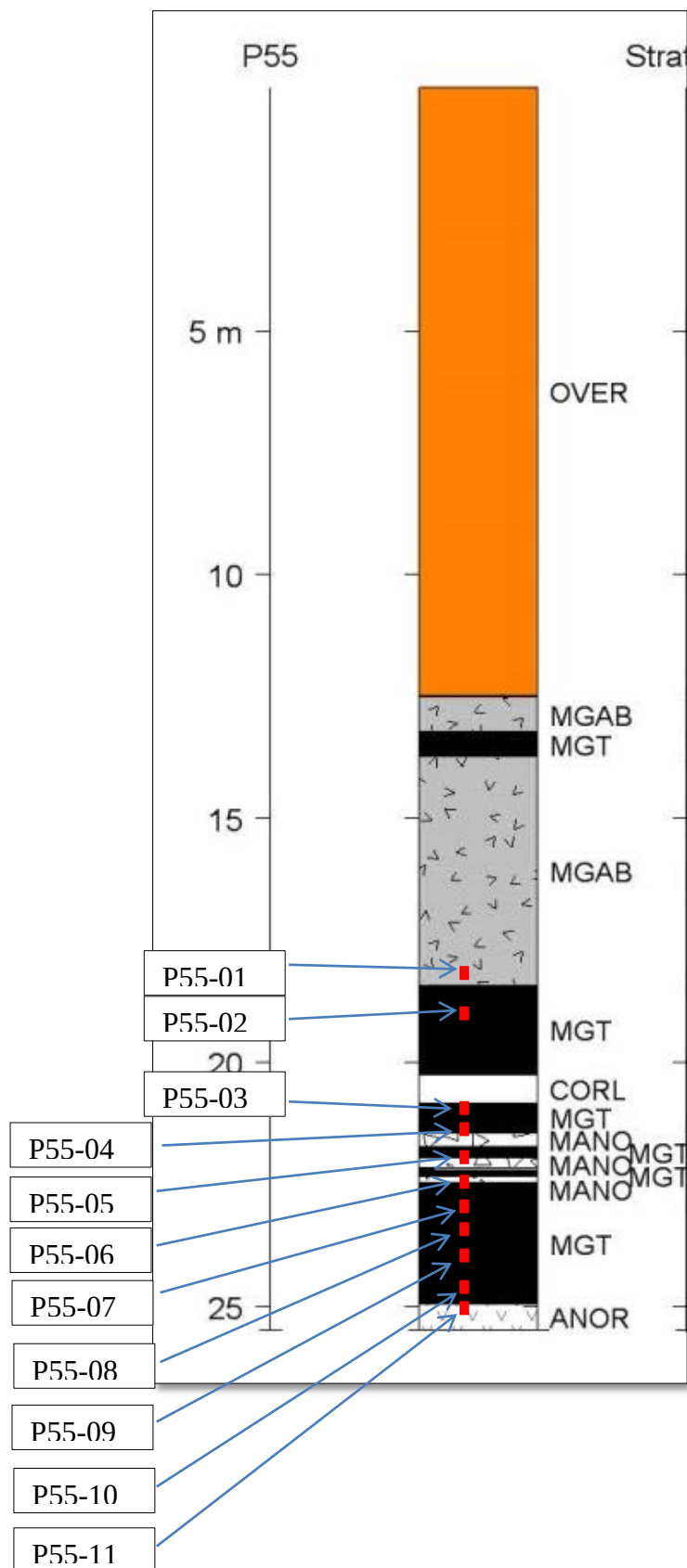


Figure 24 Borehole P55 strip log showing the positions of the samples P55-01 to P55-11

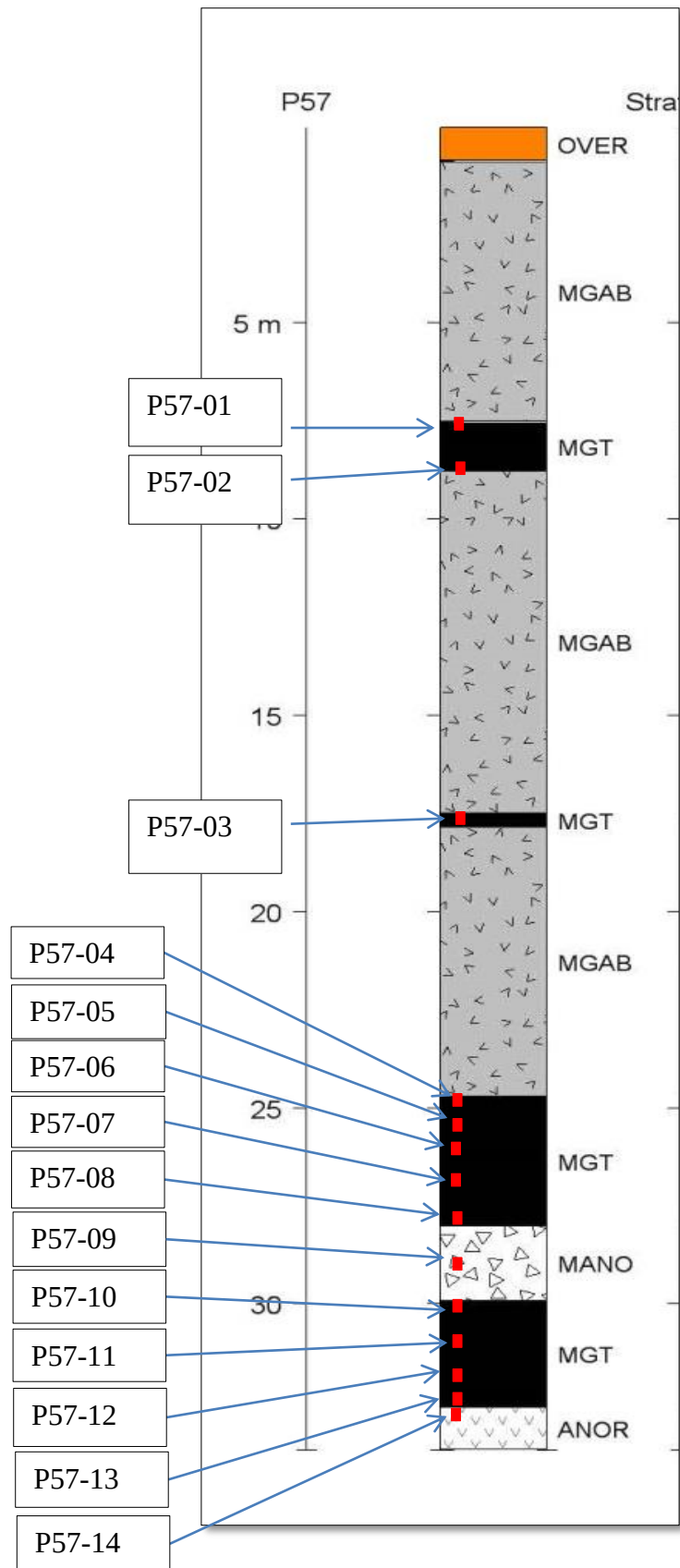


Figure 25 Borehole P57 strip log showing the positions of the samples P57-01 to P57-14.

4.5. Petrography

The samples collected were all prepared into polished thin sections as described above and studied using reflected light microscopy for the oxide ore minerals (iron, titanium oxides and subordinate sulphides). Gangue silicate minerals were studied under transmitted light microscopy. The quarter core samples of the coarse massive ore as well as the disseminated magnetite plagioclase cumulates were studied as hand specimens by naked eye and also under hand lense magnification.

4.6. Optical Microscopy

The polished thin sections which were not covered by glass cover slips were observed and studied with an optical microscope. The ore minerals which are mainly oxides of iron and titanium such as magnetite, ilmenite, ulvospinel and other transparent spinels together with rare associated sulphides were studied under reflected light microscopy while the gangue silicate minerals were studied under transmitted light microscopy. Spry and Gedlinske (1987)'s Table for the determination of common opaque minerals was used for reference with regards to ore mineral identification.

4.7. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry

The polished thin sections were studied using a TESCAN Vega TS 5136LM scanning electron microscope for visualisation under high magnifications of up to x10 000. The scanning electron microscope works by forming a sample image through the irradiation of a sample with a predetermined electron beam (Kanda, 1991). The scanning electron microscope also works with an Oxford Instruments EDS (Energy dispersive X-Ray spectroscopy) which was used to analyse the thin section samples. Areas of approximately 20mm x 20mm were analysed by EDS spectral scanning for all major elements as shown in **Figure 26**, and the data recorded as elemental weight percent which could be later transformed into Molar per cent or compound per cent using software called INCATM that comes coupled with the EDS machine.

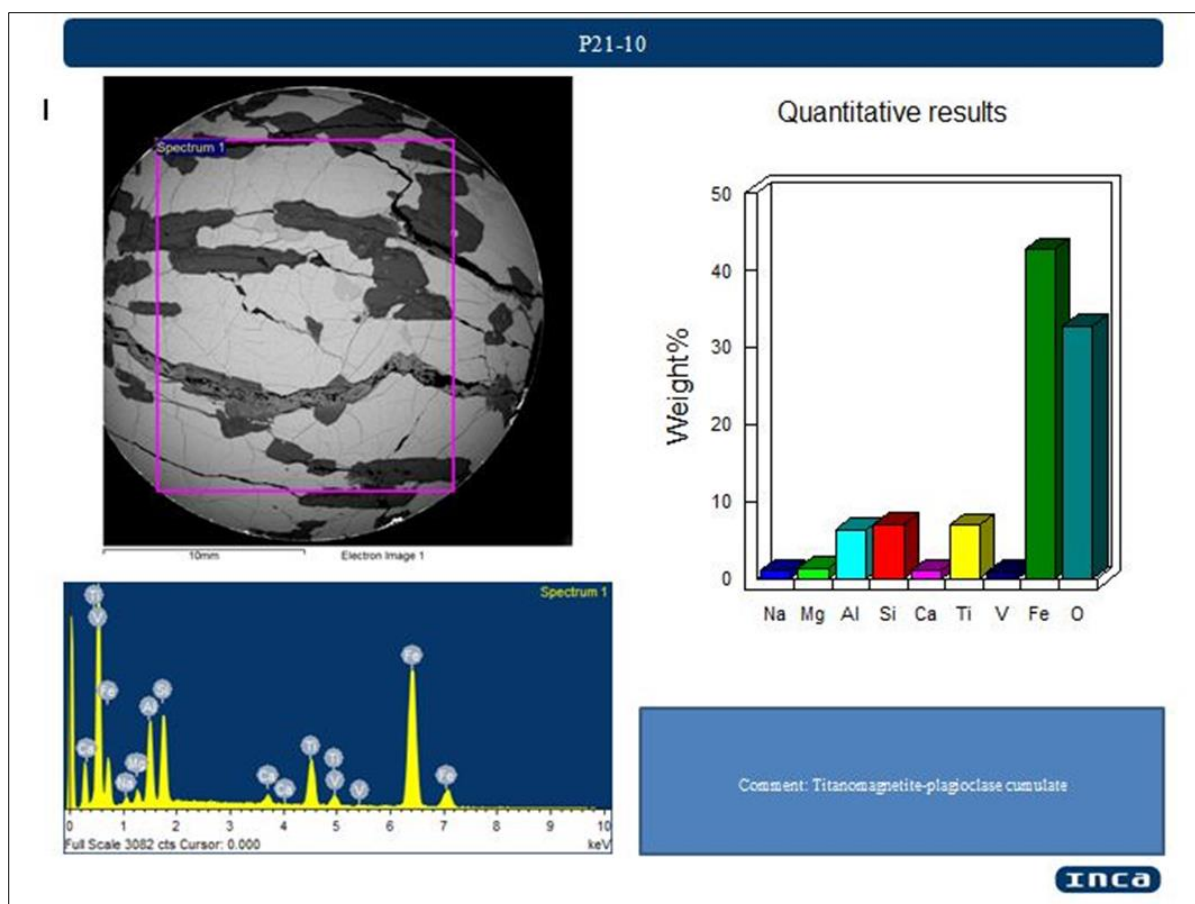


Figure 26 Area spectral scanning utilising Energy dispersive spectroscopy for major element analysis. The scanned area is approximately 15mm x 15mm.

4.8. Electron Probe Micro-Analyser (EPMA)

The JEOL™ JXA-8230 Electron Probe Micro-Analyser (EPMA) was used for quantitative analysis of the samples. The samples were polished thin sections that were carbon coated. The EPMA used utilises four wavelength dispersive spectrometers which were used for point analyses. The EPMA works by creating a focused beam of electrons utilising a tungsten (W) or (LaB₆) filament which interacts with the samples resulting in electron dispersion, and the dispersive energy is then measured by detector as illustrated in **Figure 27**. Grains of titanomagnetite, ilmenite and accessory silicates were chosen under the optical microscope and marked for spot analytical probing. Zones of magnetite with visible ulvospinel exsolutions were probed separately and so were zones with no visible ulvospinel exsolutions. The samples chosen for microprobe work represented a pseudo-vertical section with emphasis for the study being placed on the behaviour and concentrations of the iron and titanium oxides from the base of the main magnetite seam 1 (MAG 04) to the top seam of the

main magnetite (MAG 03) as well as relative vanadium and chromium concentrations with depth.

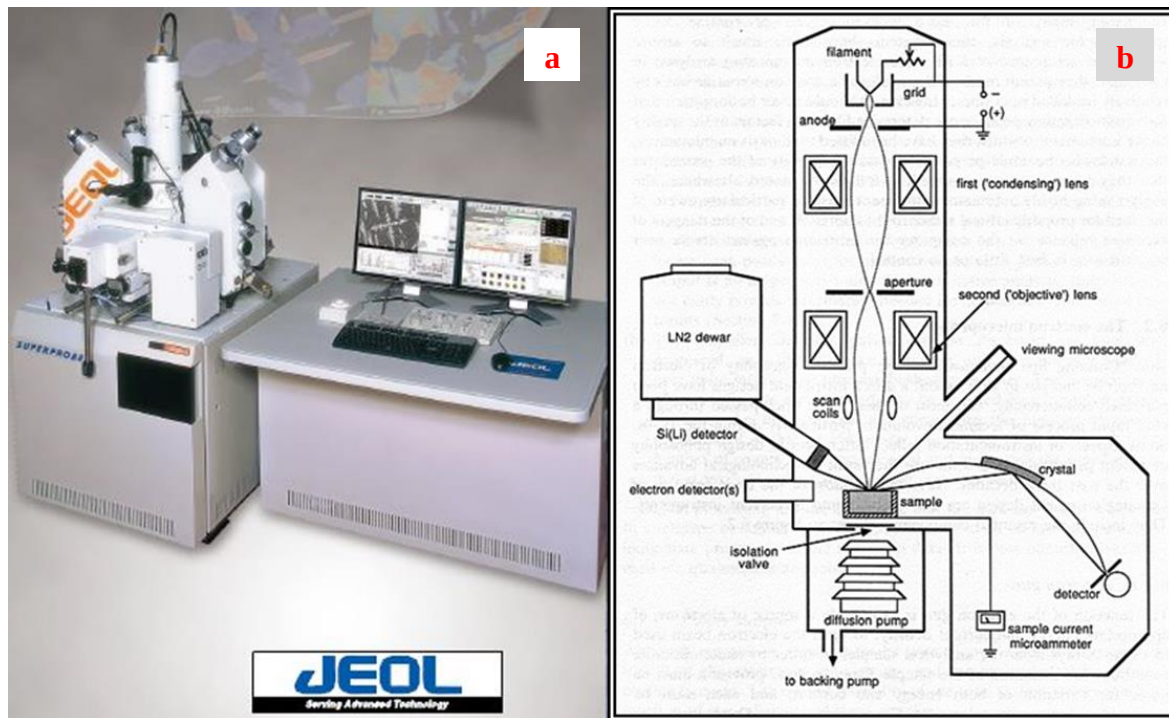


Figure 27 (a) Electron microprobe analyser used for point analysis (b) Diagram representing the Microprobe electron column showing the filament at top, sample stage, deflecting crystal and detector. Adapted from JEOL website

Chapter 5 RESULTS

5.1. Textural variations

The samples studied in all the boreholes showed a variety of textures both on a large scale and at micrometre to sub-micrometre scales. The massive titanomagnetite ores of the seams MAG 03 and MAG 04 are coarse grained with average grain sizes being larger than 5mm across as was reported by Reynolds (1986) and (Von Gruenewaldt et al., 1985). Granular ilmenite is present in the massive ores and can be seen by the naked eye, being considerably darker than the surrounding magnetite, but the grain sizes are considerably less than the titanomagnetite grains with an average of less than 2mm across. The magnetite grains decrease in size towards the magnetite-plagioclase cumulate (disseminated) ores with grain sizes dropping to an average of 3mm across while the plagioclase grains are on average 5mm across. The granular ilmenite grain sizes increases slightly in the disseminated ores and the modal concentrations of granular ilmenite increases from an average of less than 2-5 per cent in the massive ores to between 5 to 10 per cent in the disseminated ores.

The ilmenite grains are generally elongate and follow the grain boundaries of the titanomagnetite grains in the massive ores but become sub-hedral to euhedral in the disseminated ores. Plagioclase grains show preferential orientation in the layered cumulates and the longer axis of the grains is usually sub-horizontal to horizontal. Several cracks and gashes exist in both the massive and disseminated ores and these cracks have been filled by late stage minerals with hydrated iron oxides such as goethite very dominant. A crack in sample number P55-01 tested by EDS analysis showed the filling material to be high magnesium oxide, which was interpreted to be pleonaste.

The TiO_2 content of the massive ores is almost always 2 to 5 weight per cent higher in the massive ores than in the disseminated ores even though the relative abundance of granular ilmenite is more abundant in the disseminated ores than the massive ores. This trend seems to suggest that the majority of the TiO_2 content of the titanomagnetite ores is not contained in ilmenite, but rather in ulvospinel and titaniferous magnetite, a phenomenon which was also recognised by (Von Gruenewaldt et al., 1985).

5.1.1. Granular ilmenite

The discrete ilmenite grains observed in all the boreholes could be visualised from the base of the main magnetite seam to the top, with a general increase in grain size and modal concentration from bottom to top. The ilmenite grains are generally elongate and sub-hedral in most cases occurring in close proximity to silicate minerals especially plagioclase as can be shown in **Figure 28**, a feature which was described by Molyneux (1970). In the massive ores, the ilmenite grains are often found along the margins of the titanomagnetite grains filling the intergranular spaces, a phenomenon described by Reynolds (1985a; 1986) and (Von Gruenewaldt et al., 1985).

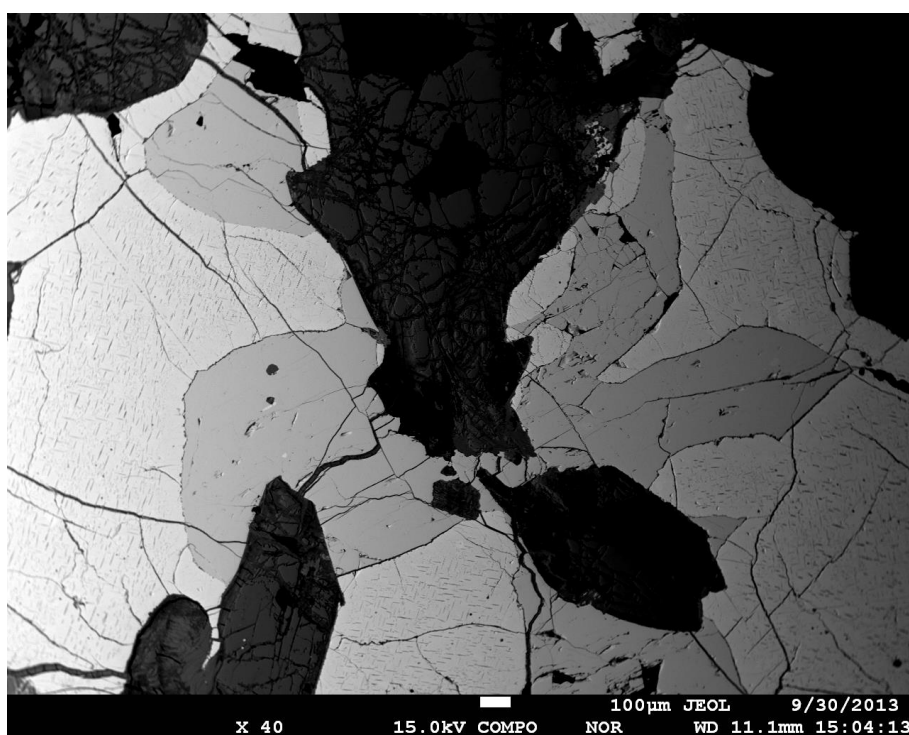


Figure 28 Backscatter image of ilmenite grains in oxide-silicate cumulate occurring in proximity to silicates.

The grain boundaries of the discrete ilmenite and the surrounding titanomagnetite are in most cases curved as can be seen in **Figure 28**, while the grain boundaries with the associated silicates are irregular and often jagged. The composition of the ilmenite grains was shown by microprobe point analysis to change from being more magnesian in the massive ores to less magnesian in disseminated ores which was attributed to the preferential substitution of Mg in the ilmenite phase by Speidel (1970) whereby the small volume of granular ilmenite in the massive ores result in their higher uptake of Mg in comparison to the ilmenite in the disseminated ores which are relatively more abundant (Reynolds, 1986).

5.1.2. Exsolved ilmenite and ulvospinel

Ilmenite also occurs as exsolution lamellae although this type of ilmenite is not widespread. In places where it exists as exsolution lamellae, the ilmenite is restricted to the intergranular spaces between titanomagnetite grains, or occurs as trellis lamellae in titanomagnetite but usually in the disseminated ores. Trellis lamellae of ilmenite occur preferentially along the magnetite cleavage as can be shown in **Figure 29** below.

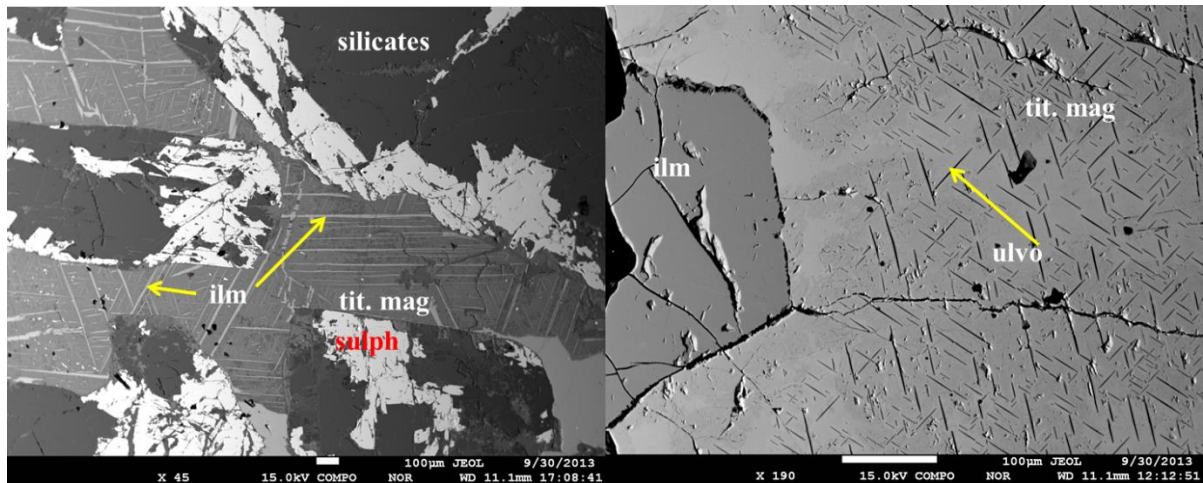


Figure 29 Backscatter images of (a) trellis ilmenite in titanomagnetite (b) ulvospinel exsolution lamellae in titanomagnetite. Note the ulvospinel free zone surrounding the ilmenite grain. Ilm= ilmenite, ulvo= ulvospinel, tit.mag= titanomagnetite, sulph= sulphide.

The more abundant exsolved phase in the titanomagnetites is by far ulvospinel with exsolution lamellae ranging in size from sub-micrometre to micrometre scale. The ulvospinel exsolution lamellae vary from cloth patterns as described by Von Gruenewaldt et al. (1985) to fine lamellae parallel to the (100) of the titanomagnetite, which are usually sub-micrometre in size. The ulvospinel exsolution lamellae are usually absent in zones of approximately 5-25µm from ilmenite grain boundaries as shown in **Figure 29**. The ulvospinel has an effect of dividing the titanomagnetite into small polygons that are sub-micrometre to micrometre sized, a feature which was described by Reynolds (1986). The lamellae though abundant in the massive ores, they are of different sizes with some being large enough to be visible under optical microscope magnification (x20 and x50), while some are only visible at magnifications of more than (x500) and in most cases, the lamellae preferentially follow the magnetite cleavage although complex patterns were also observed as shown in **Figure 30** and **Figure 31**. Ulvospinel cloth textures are in some cases well developed around or in close proximity to the transparent spinels, where the ulvospinel is more abundant than in the surrounding titanomagnetite, a feature which was described by Reynolds (1986) and ascribed

to the possibility of it representing the ulvospinel that exsolved first and resulted in nucleation in sites that were close to the transparent spinels and therefore energetically favourable.

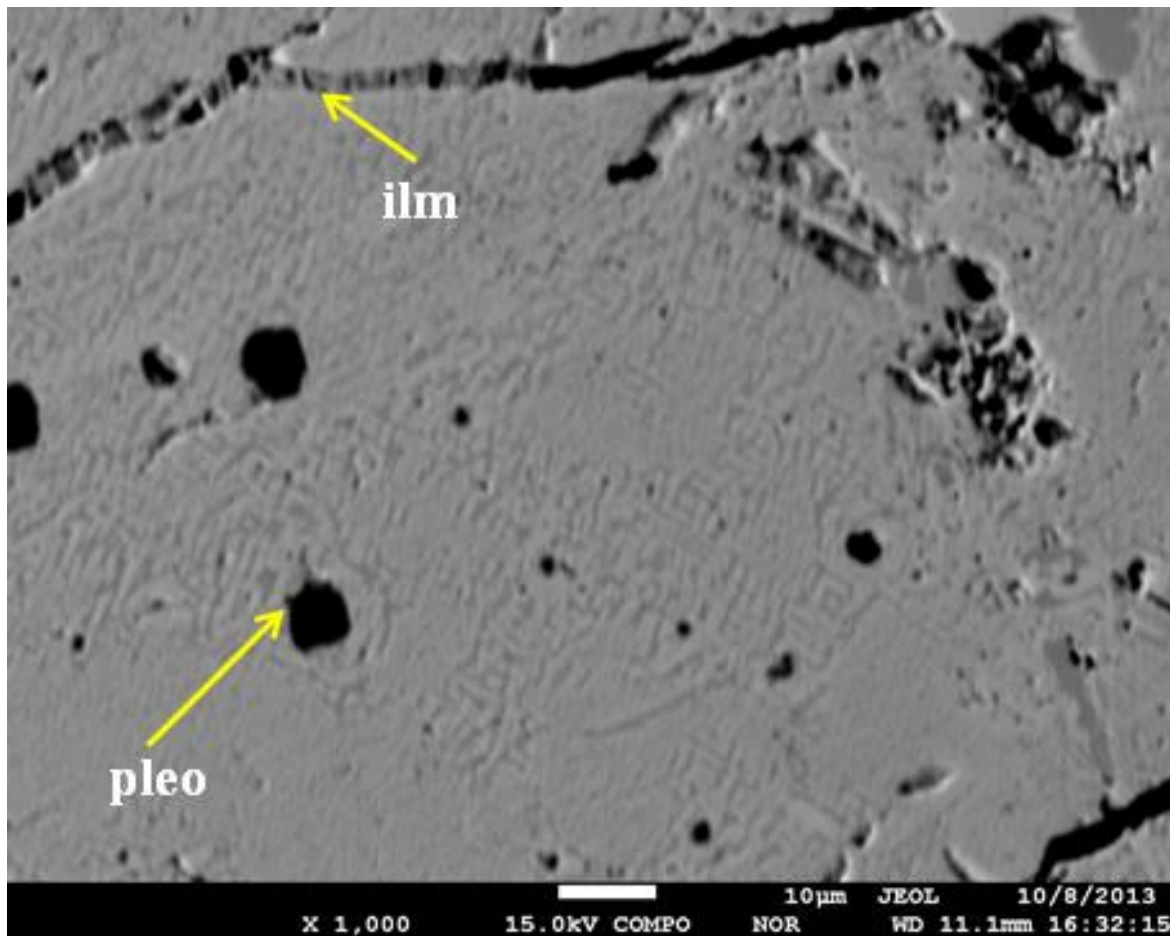


Figure 30 Backscatter image of a titanomagnetite grain showing ulvospinel cloth textures. Note the transparent magnetite spinel pleonaste as well as ilmenite filled intergranular space. Pleo= pleonaste, ilm= ilmenite.

5.1.3. Magnesian and ferromagnesian spinels (pleonaste and hercynite)

The titanomagnetites show a variety of complex textures which were studied and explained in great detail by (Von Gruenewaldt et al., 1985) as well as Reynolds (1986; 1978). Two important phases were observed and studied during the course of this study and these are the transparent spinels pleonaste and hercynite. The pleonaste exists both in granular form as shown in **Figure 30** as well as in lamellae form as shown in **Figure 31**. The presence of the transparent spinels shows a preferential existence in the massive ores in comparison to the magnetite-plagioclase culutae (disseminated ores), and the exsolutions of pleonaste usually follow the (100) magnetite cleavage as described by Molyneux (1964) and Reynolds (1986), and occur within the same titanomagnetite grains as ulvospinel as can be seen in **Figure 31**.

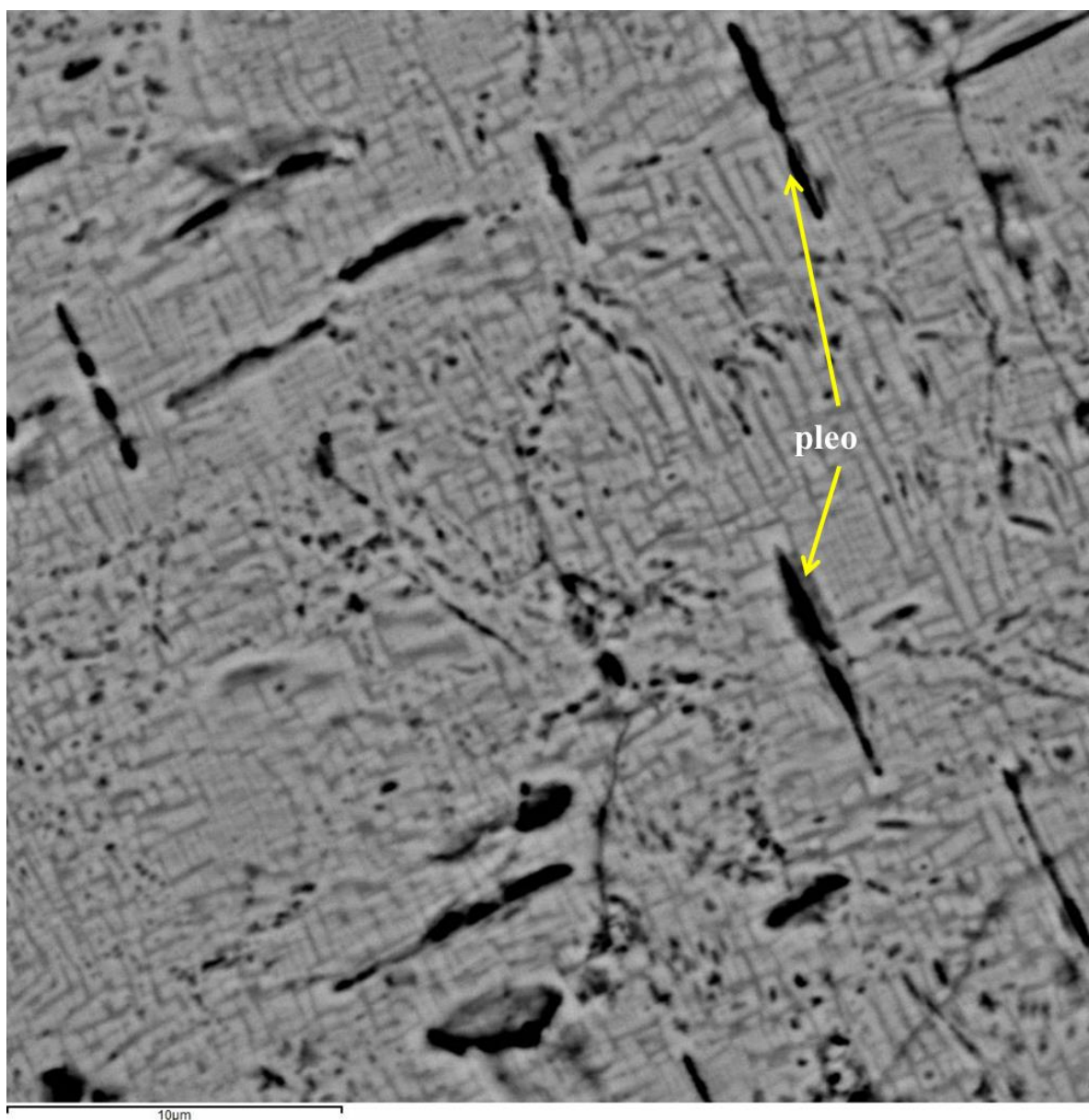


Figure 31 Backscatter image of titanomagnetite showing pleonaste as well as sub-micrometre ulvospinel exsolution lamellae forming a cloth texture. Pleo= pleonaste. Note the 10µm scale bar at bottom left.

A gash analysed using the EDS on sample P55-01 showed the composition of the filling material to be a ferromagnesian spinel which was interpreted as hercynite following the work of (Von Gruenewaldt et al., 1985). The magnesian spinels also show relative absence towards the grain boundaries of the titanomagnetites in much the same way as the ulvospinel exsolutions, with some small granules of pleonaste that are usually less than 100µm in diameter being exsolved along the grain boundaries together with intergranular ilmenite, see the dark coloured phase occurring together with exsolved ilmenite in **Figure 30**.

5.2. PETROGRAPHY

5.2.1. P 21

Borehole P21 had 14 samples studied that is P21-02 to P21-15, sample P21-01 was too weathered for section preparation and a thin section could not be made for the sample. The 14 samples that were prepared into sections are shown in Appendix A as quarter core samples and the corresponding thin sections are shown in Appendix B. Petrographic work done on P21 showed a number of mineralogical and textural variations from the base of the magnetite seams through disseminated magnetite-gabbro and magnetite-anorthosite partings towards the top of the main magnetite seam.

The most obvious is the presence of thick massive ore at the base which grades upwards into oxide-silicate cumulates (disseminated ore) with the minerals plagioclase and pyroxenes as the major silicates. The bottom two seams, MAG 03 and MAG 04 are the thickest with thicknesses of approximately 2.5m and 2.0m respectively while separated by a magnetite-anorthosite parting that is approximately 1.0-1.5m thick. The titanomagnetite grains range in size at the base from more than 10mm across at the base of MAG 04 to around 5mm across at the top of MAG 03. Silicate phases, largely plagioclase show a preferential orientation with most grains oriented either horizontally or sub-horizontally.

5.2.1.1. P 21 - Petrography

The footwall to the main magnetite seam which sits below titanomagnetite seam MAG 04 is an anorthosite with plagioclase as the dominant phase and an An% of An₇₁. The footwall mineralogy is dominated by plagioclase which constitutes more than 70 per cent by volume of the sample, with pyroxene accounting for 10-20 per cent. The accessory minerals are the sulphides pyrite, pyrrhotite as well as minor chalcopyrite. Sparse grains of magnetite exist which have trellis ilmenite lamellae exsolved in them

The titanomagnetite seams comprise of magnetite grains which range in size from 2mm across to about 10mm across and these polygonal titanomagnetite grains show triple junctions with angles nearing 120°. The magnetite grains form the primocrysts in the massive ores and the accessory silicates exist as interstitial material.

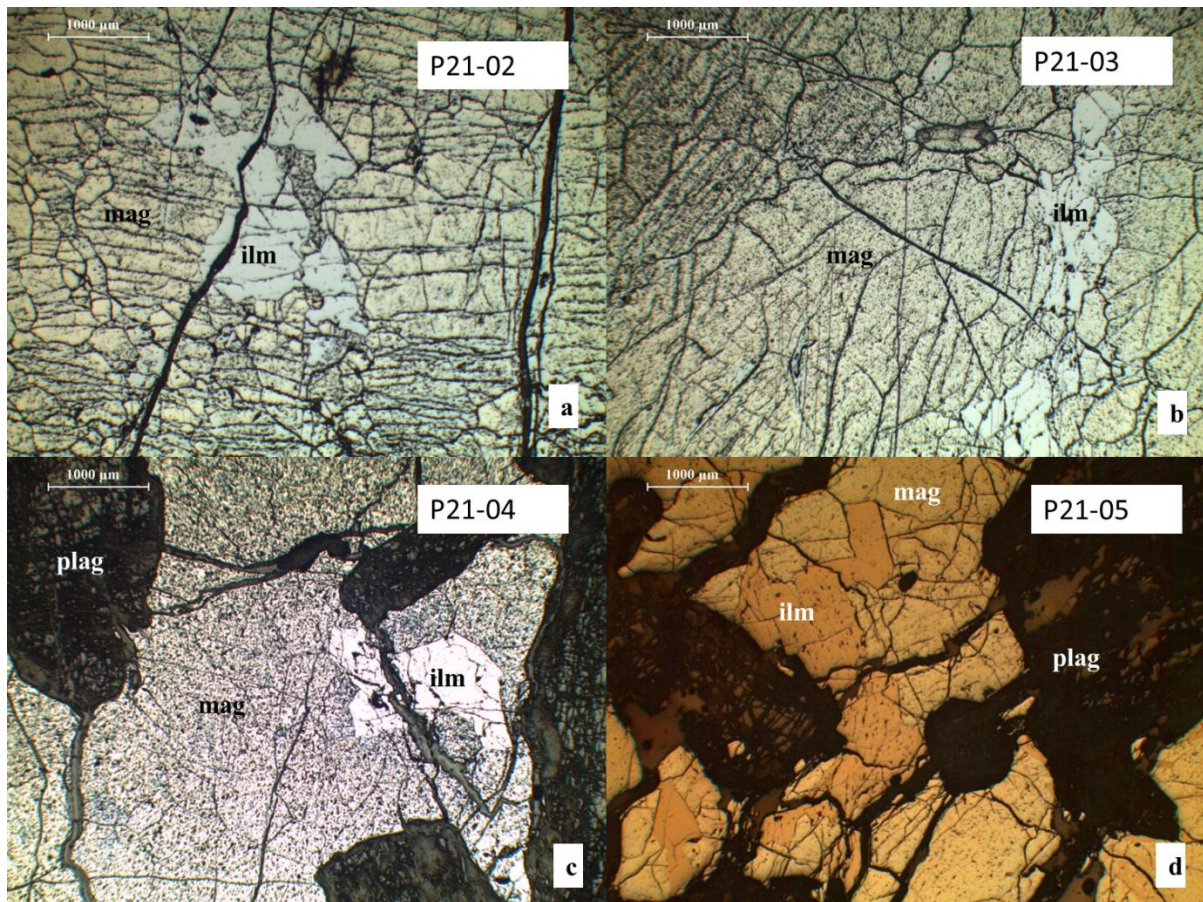


Figure 32 Magnetite, ilmenite and plagioclase grains observed in borehole P21 under reflected light, PPL. Mag= magnetite, ilm= ilmenite, plag= plagioclase.

Ilmenite occurs as few elongate discrete grains usually along grain boundaries or filling intergranular space and accounting for not more than 5 per cent by volume of the massive ores and less than 10 per cent of the disseminated ores. The ilmenite grain boundaries are usually curved as can be seen in **Figure 33** and **Figure 33** (b) and (d) in the massive titanomagnetite and irregular to jagged where they border plagioclase. Discrete ilmenite preferentially occurs in close proximity with the silicates where they occur as shown in **Figure 33** (a). The study of the samples under higher power magnification showed lamellae of ulvospinel, pleonaste and sometimes ilmenite that are micrometre to sub-micrometre in size as is shown in **Figure 33** (c).

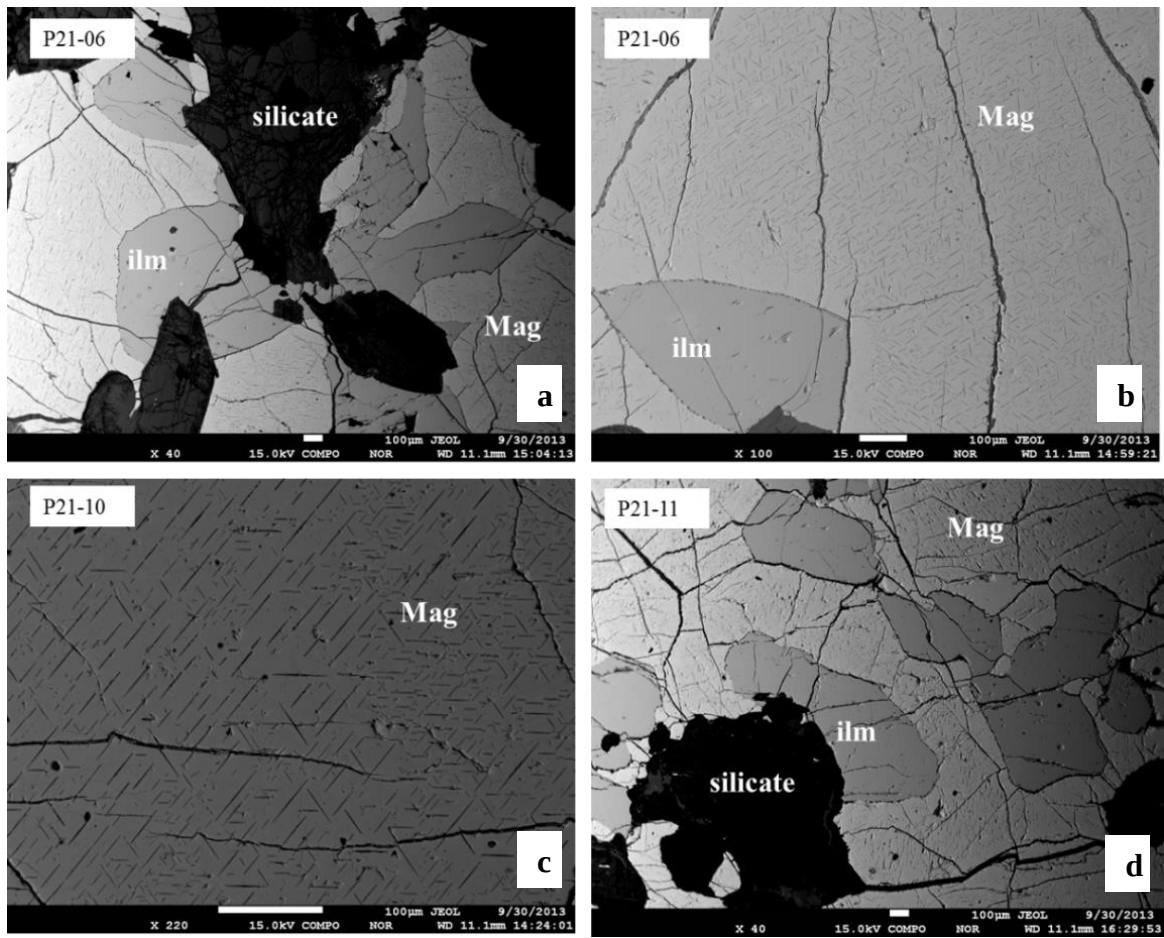


Figure 33 Backscatter images of sections P21-06, 10 and 11. (a) and (b) Note the granular ilmenite in P21-06 in close proximity to silicate phases as well as a rim around an ilmenite grain with no ulvospinel exsolutions. (c) a massive magnetite grain showing ulvospinel exsolutions. (d) Granular ilmenite in magnetite within the vicinity of silicates. Mag= magnetite (titanomagnetite), ilm= ilmenite.

Ulvospinel exsolutions form box-work textures, which divides the titanomagnetite into small polygonal compartments ranging in size from sub-micrometre to micrometre in size as can be seen **Figure 33 (c)** and **Figure 34 (c)**. The relative abundance of ulvospinel exsolutions decreases and sometimes completely absent in the vicinity of titanomagnetite grain boundaries with ilmenite as can be seen **Figure 34 (c)**.

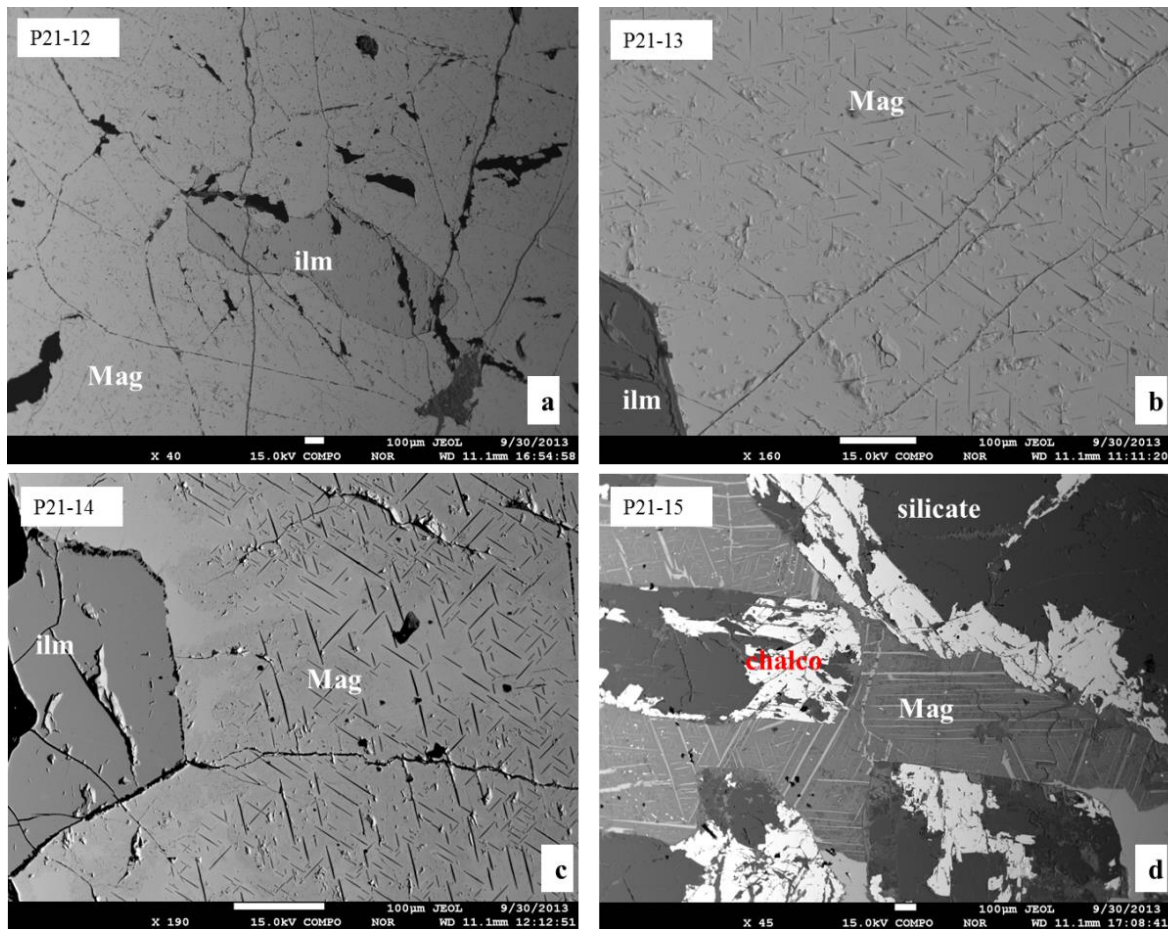


Figure 34 Backscatter images of sections P21-12-15. (a) Granular ilmenite in massive magnetite. (b) and (c) magnetite with ilmenite and ulvöspinel. Note absence of ulvöspinel around ilmenite grain. (d) Magnetite with trellis ilmenite exsolutions, silicate phases with chalcopyrite. Mag= magnetite (titanomagnetite), ilm= ilmenite, chalco= chalcopyrite.

Within the main magnetite seam as represented by the four seams MAG 01 to MAG 04 in the borehole P 21, the relationship between TiO_2 and V_2O_5 has a positive correlation as shown in **Figure 35** with both compounds increasing with increasing stratigraphic height and decreasing in the hanging walls which are a magnetite anorthosite in the case of MAG 04 and magnetite-gabbro in the case of MAG 03.

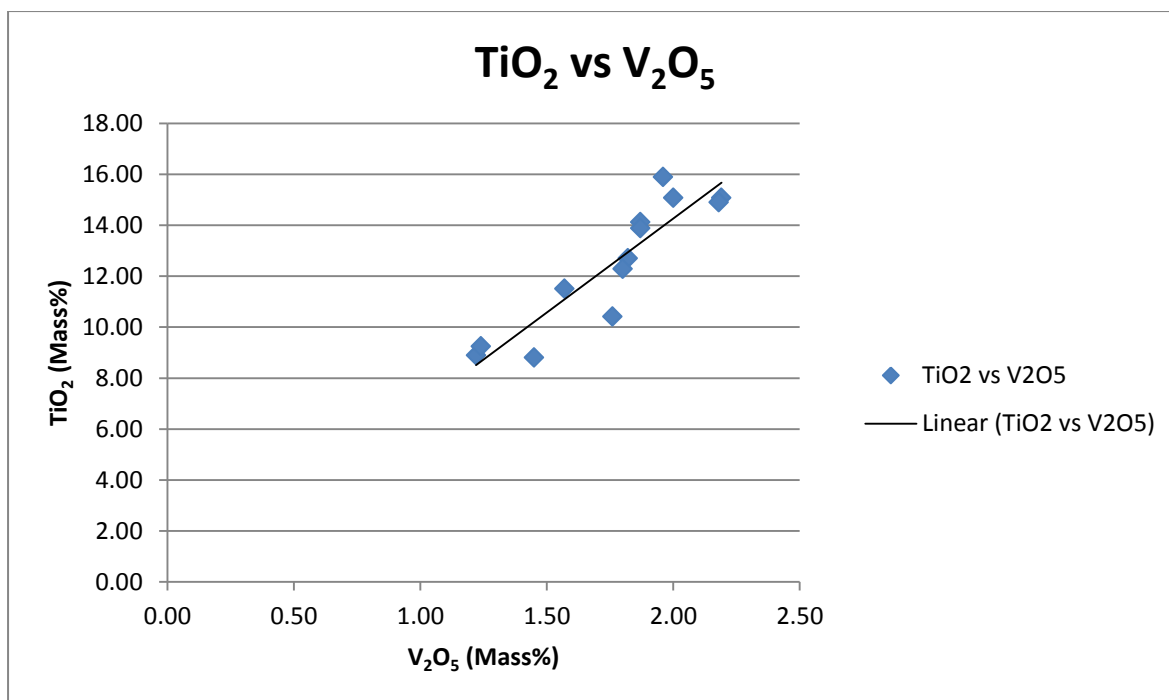


Figure 35 Scatter plot of TiO₂ and V₂O₅ across the main magnetite seam.

5.2.2. P 55

A total of 11 samples were collected and studied from the borehole P55 from the magnetite seams MAG 03 and MAG 04 and the quarter core samples are shown in Appendix A. The seam MAG 02 although intersected in the borehole was too weathered to be sampled for thin section preparation while sample MAG 01 was eroded and not intersected during the drilling exercise. The corresponding polished thin sections for borehole P55 are shown in Appendix B. The magnetite seams in P55 exhibit the coarsening of titanomagnetite grains in the massive ores as in P21 with a gradual decrease in titanomagnetite grain size towards disseminated ores while ilmenite grain sizes gradually increase away from the massive ores.

5.2.2.1. P 55 - Petrography

The footwall is an anorthosite with the dominant phase being plagioclase with minor pyroxene. Magnetite is present in the footwall but constitutes less than 3 per cent by volume and pyrite and chalcopyrite represent the sulphide phases. The magnetite grains in the massive ores as in P55-08 shown in **Figure 36** and **Figure 37** (c) show triple junctions and intergranular material which was shown by probing to be ilmenite or secondary iron oxides such as goethite. The ilmenite grains in P55 range in size from less than 100µm to as large as greater than 3mm as seen in P55-06 in **Figure 37** (d) with the grains increasing in size away from the massive ores. The ilmenite grains are more developed near or around silicates as can be seen in **Figure 37** (a) and **Figure 38** (a).

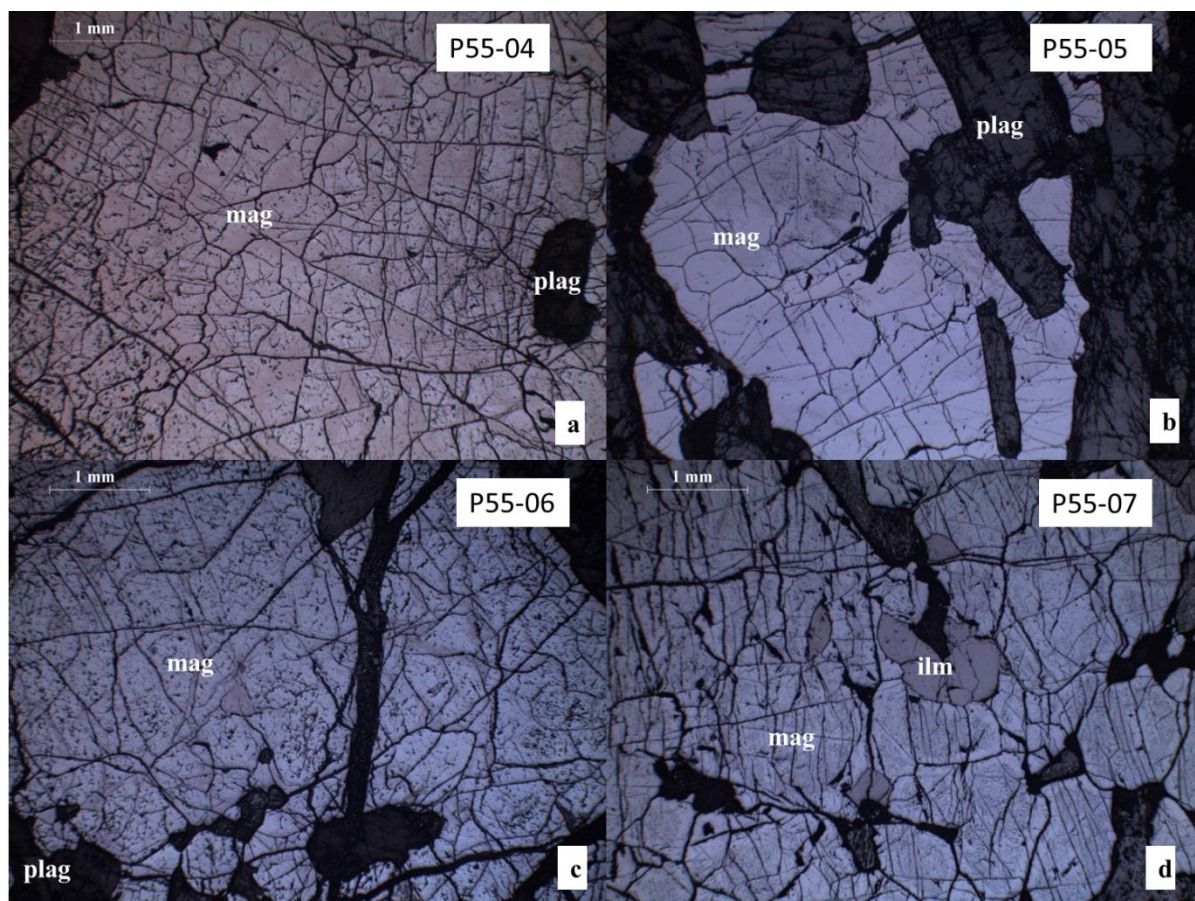


Figure 36 Reflected light microscopy images of P55 titanomagnetites. Note the small nature of ilmenite grains. Mag= magnetite, ilm= ilmenite, plag= plagioclase.

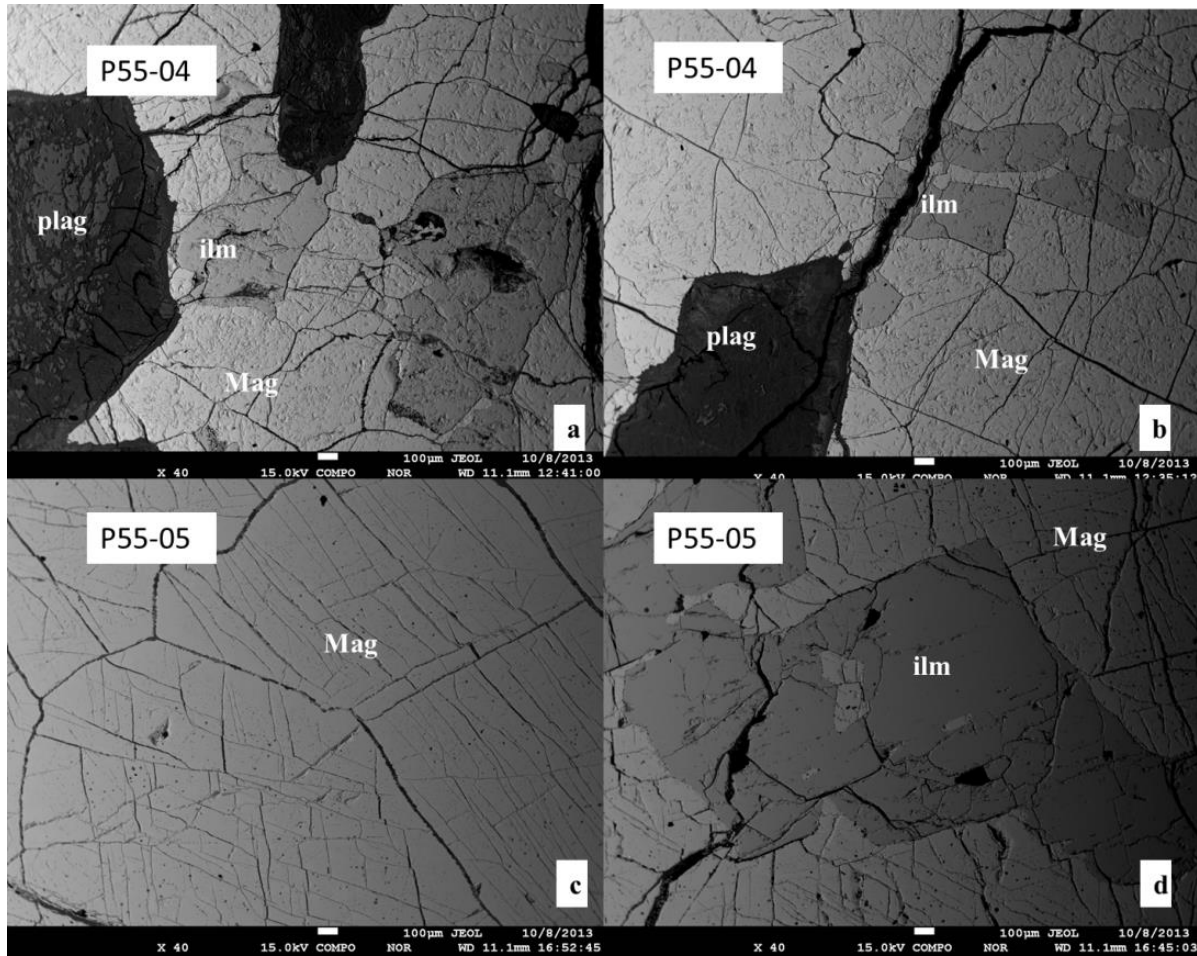


Figure 37 Backscatter images of titanomagnetite from MAG 03 (a); (b) ilmenite grains in titanomagnetite developed near silicates (c) massive titanomagnetite with shattered magnetite grains (d) large ilmenite grain in titanomagnetite. Mag= titanomagnetite, plag= plagioclase, ilm= ilmenite.

The titanomagnetite seams are generally massive at the bottom, becoming more disseminated towards the top and the corresponding decrease in grain size of the titanomagnetite as in P21. The magnetite grains are polygonal with triple junctions as seen in **Figure 37** (c) and sometimes show shattering within the individual grains. The transparent spinel is in most cases restricted to intergranular spaces with granules of the spinel rarely exceeding 10µm in diameter exsolved within the titanomagnetite grains as is shown in **Figure 38**.

Ulvospinel is present in most massive titanomagnetite samples but occurs as smaller lamellae in comparison to in borehole P 21 and only becomes apparent under high power magnifications of up to x200. The ulvospinel exhibits a cloth texture, again dividing the titanomagnetite into small box-work polygons, each a few microns across. It was noted that the ulvospinel as well as the transparent spinels generally disappear in zones close to the

titanomagnetite grain boundaries with ilmenite but continue to the grain edges where the titanomagnetite borders another titanomagnetite grain as is shown in **Figure 38** (a) and (b).

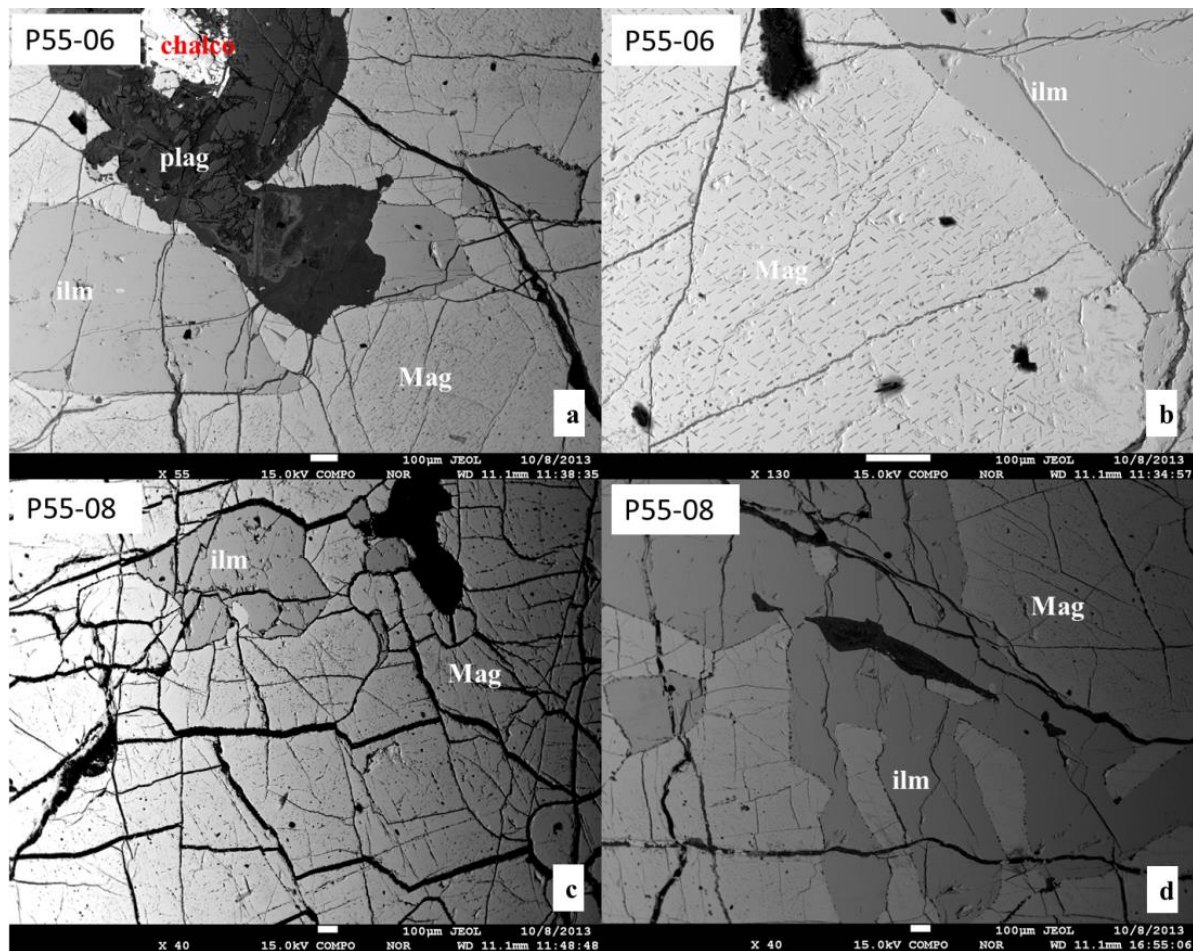


Figure 38 Backscatter images of the samples from MAG 04 (a) ilmenite grains in close proximity to plagioclase (b) large ilmenite grain showing the ulvospinel free zone in the titanomagnetite (c) small ilmenite grains in massive titanomagnetite (d) elongated ilmenite grains in titanomagnetite. Mag= titanomagnetite, plag= plagioclase, ilm=ilmenite.

The relationship between TiO_2 and V_2O_5 , much as in P 21 shows a positive correlation as shown in **Figure 39** and plotting the two compounds against depth as is shown in **Figure 44** shows that they increase together with increasing stratigraphic height from the footwall anorthosite towards the top of MAG 04 before dropping off in the parting magnetite-anorthosite and increasing again together in the seam MAG 03.

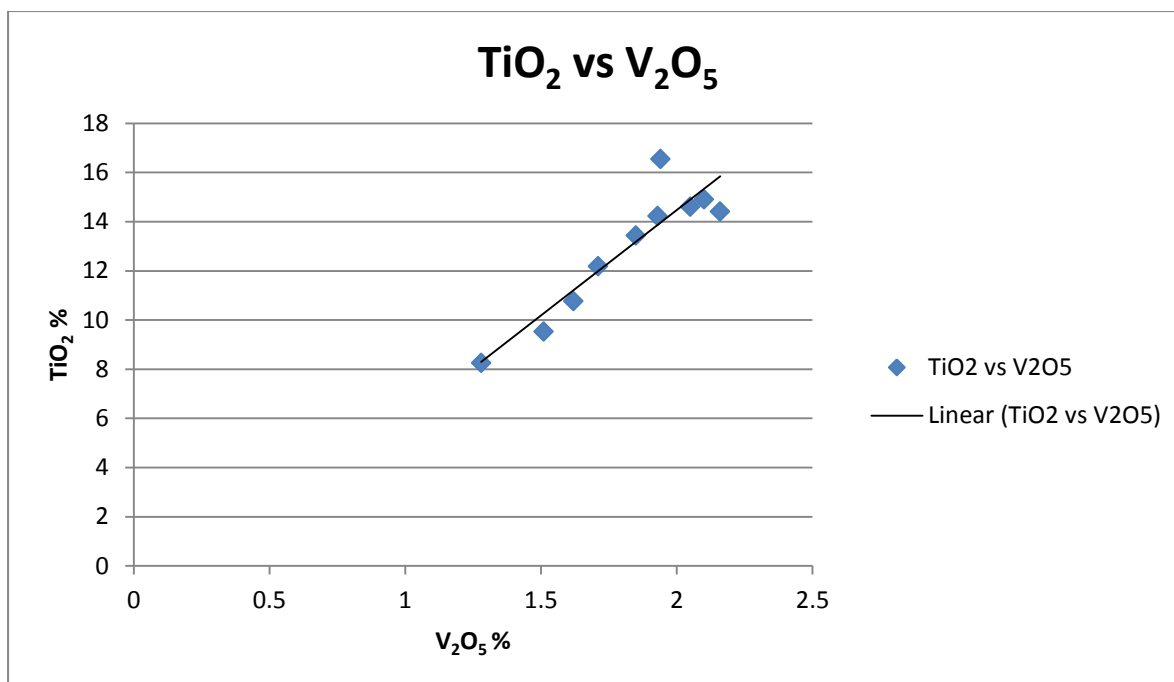


Figure 39 Scatter plot of TiO₂ and V₂O₅ across the main magnetite seam in P55.

5.2.3. P 57

The borehole P57 had 14 samples collected and 13 were studied as sample P57-02 was destroyed in the process of polished thin section preparation. The samples collected and analyses represent a pseudo-section across the main magnetite seam from MAG 04 at the bottom to MAG 01 at the top. The petrography of the borehole is in no way different from the other two boreholes except for the slightly higher abundance of augite in the footwall anorthosite. The titanomagnetites as in P21 and P55 are massive at the base becoming disseminated towards the top and they are as well coarser at the bottom with magnetite grain sizes decreasing with stratigraphic height. Ilmenite grains increase in size with increasing height, and becoming relatively more abundant in the magnetite-plagioclase cumulates (disseminated ores).

5.2.3.1. P 57 - Petrography

The footwall is an anorthosite with An% content of An₇₀, and although plagioclase in the dominant phase, clinopyroxenes especially augite make up close to 10 per cent by volume of the rock. The sulphide phases in the footwall are pyrite and pyrrhotite with pyrite being the more dominant. The titanomagnetite samples are dominated by titanomagnetite grains which accounts for about 40-50 per cent in the disseminated ores while accounting for 80-95 per

cent in the massive ores. Titanomagnetite grains coarsen downwards in the magnetite seams with grain sizes 10mm across in sample P57-12. Granular ilmenite occurs although as a minor phase in both the massive and the disseminated ores, accounting for about 3-3 per cent by volume in the massive ores while representing about 5-10 per cent by volume in the disseminated ores. Ilmenite grains increase in size away from the massive ores although some exceptions were noted and they tend to be more developed near or around silicate grains and they tend to be restricted to intergranular spaces in the massive ores as shown in **Figure 40** and **Figure 41 (d)**.

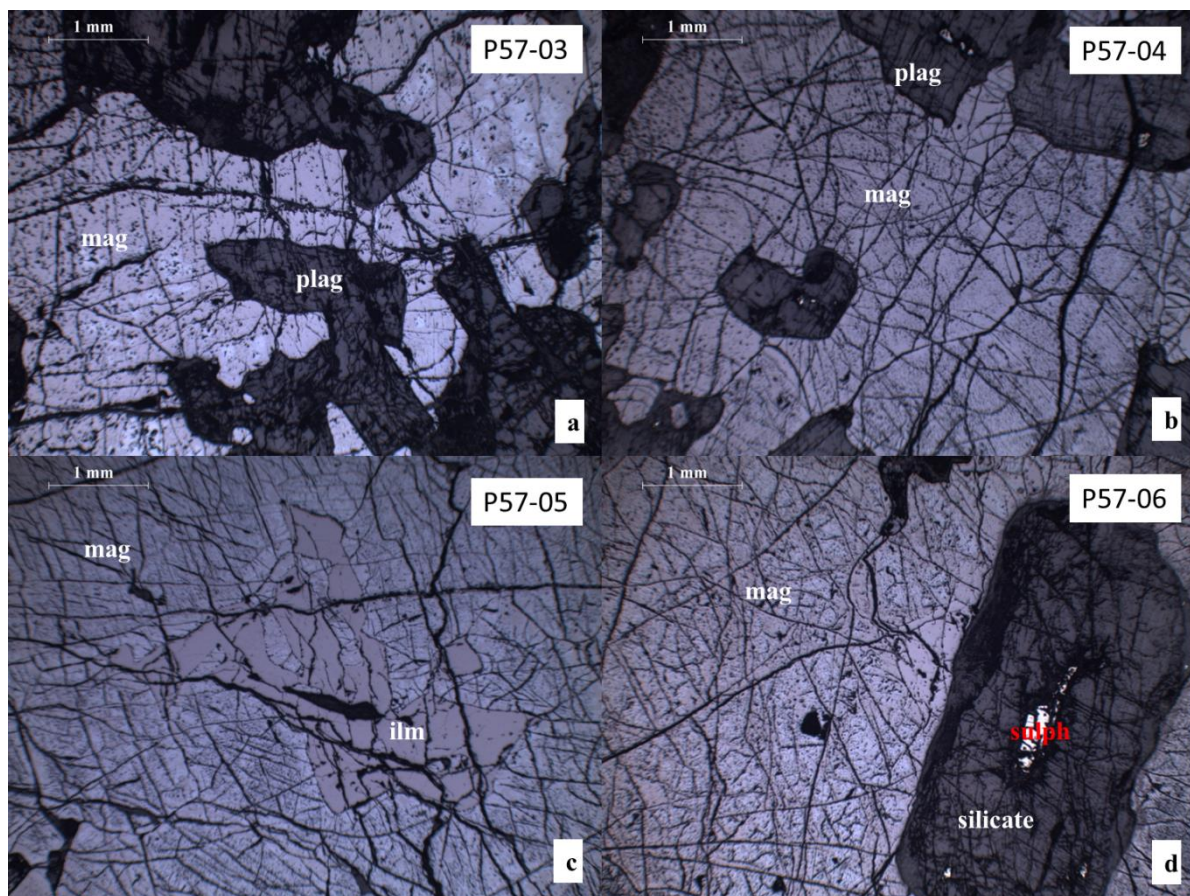


Figure 40 Reflected light microscopy images of titanomagnetites in P57. Mag= magnetite, ilm= ilmenite, plag= plagioclase, sulph= sulphides

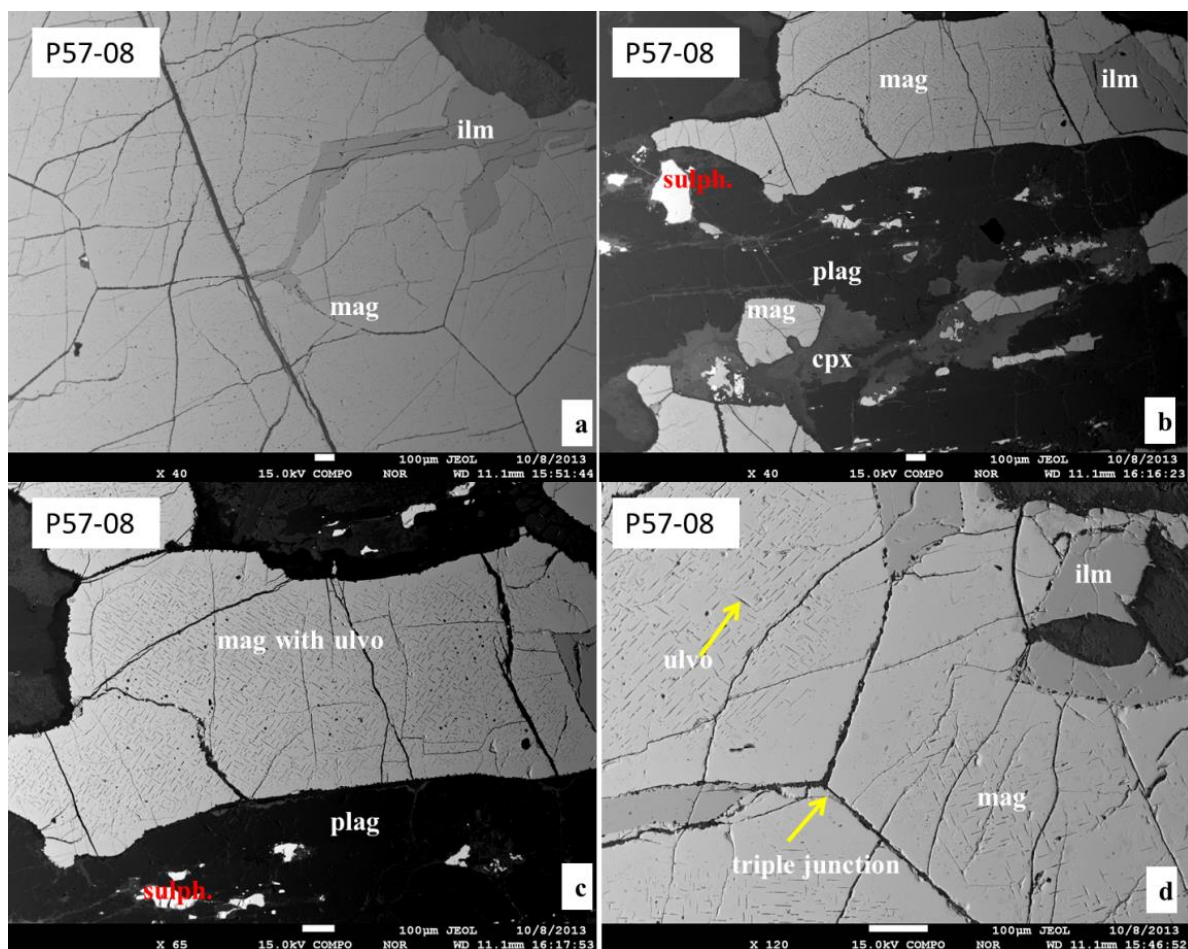


Figure 41 Backscatter images of sample P57-08 (a) titanomagnetite grains showing triple junctions and intra-granular ilmenite (b) titanomagnetite, ilmenite, silicates and sulphides (c) titanomagnetite with ulvospinel exsolutions (d) titanomagnetite grain boundaries with disappearing ulvospinel and triple junction.

The relative abundance of granular ilmenite although it is high in close proximity to silicates is in general low, with total granular ilmenite never exceeding 10 per cent by volume of any samples and in most cases averaging between 3-5 per cent as is shown in **Figure 41**. Plagioclase grains show preferential orientation with a preferred sub-horizontal to horizontal orientation as is shown in **Figure 41**.

The silicate phases are dominated by calcic and sodic plagioclase which often shows preferential orientation towards the sub-horizontal direction. The Anorthite content of the plagioclase ranges from An₅₅ to An₇₂. The clinopyroxene augite is present in the footwall anorthosite and also occurs in modal concentrations of less than 2 per cent in the disseminated ores as in P57-08 shown in **Error! Reference source not found.** Plagioclase grains have resorption rims and the sulphides which include pyrite and pyrrhotite occur as inclusions in the plagioclase grains. Ulvospinel occurs as exsolution lamellae in the titanomagnetite grains; see **Figure 41** with a tendency to disappear near magnetite grain boundaries with ilmenite or with silicates. This effect was also noted where the intergranular material between titanomagnetite grains is ilmenite.

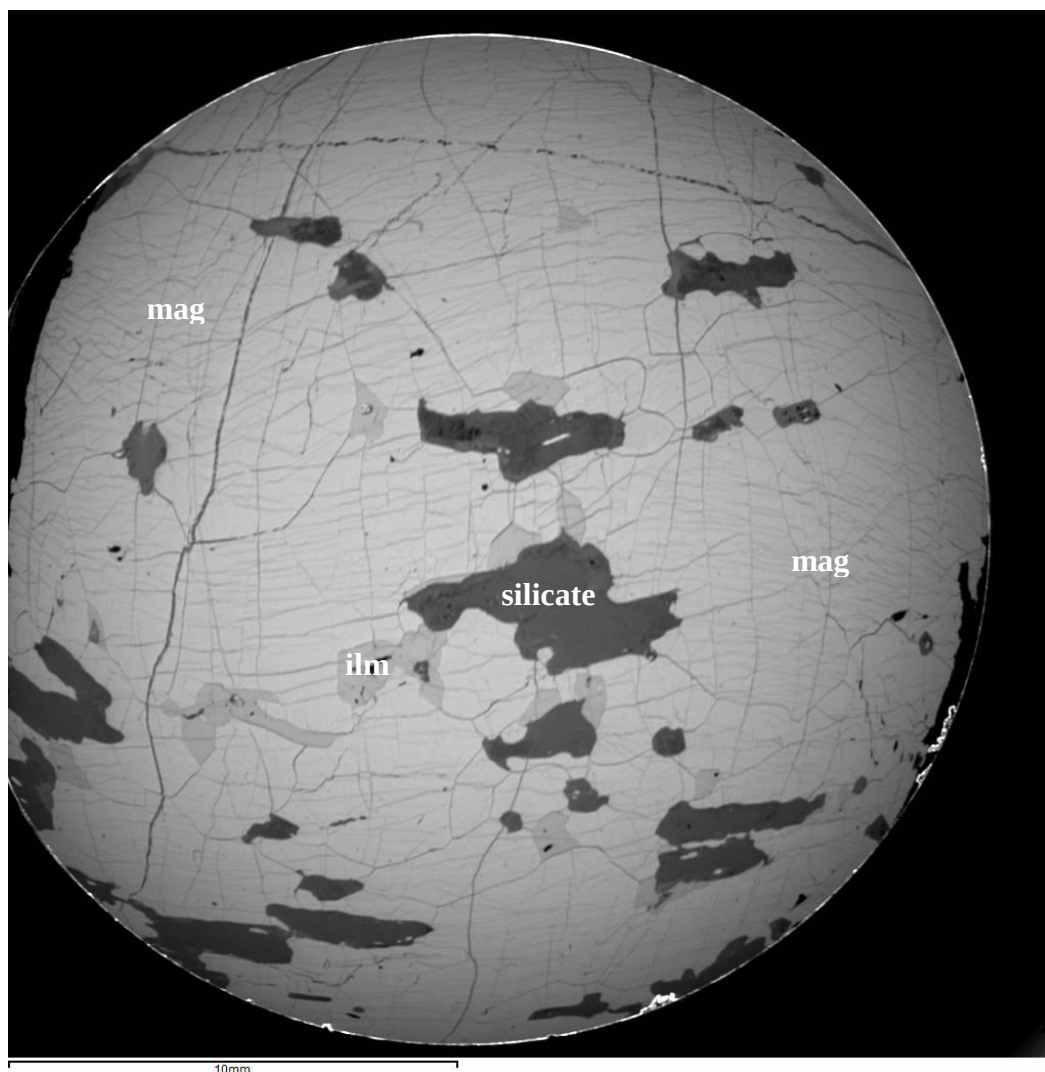


Figure 42 SEM backscatter image of P57-11 showing magnetite (light grey), granular ilmenite (grey) and silicates (dark grey). Scale bar at bottom left is 10mm.

5.3. VERTICAL DISTRIBUTION OF OXIDES, SULPHIDES AND TRACE ELEMENTS

5.3.1. Introduction

The main magnetite seam as studied on the farm Gezond comprises of four seams named MAG 01 to MAG 04 from top to bottom with the seams MAG 03 and MAG 04 being the thickest and thus constituting the important resource. The distribution of oxide minerals as well as associated silicates and subordinate sulphides was studied both by EDS and by EPMA. The elemental compound distribution within the oxide and silicate minerals was also studied to determine the relationship of the related oxide minerals and their accessory elements. The key compounds studied were FeO, TiO₂, V₂O₅, Cr₂O₃, MgO, Al₂O₃, CaO, Na₂O and K₂O. The elemental compound distribution as studied by EDS is presented in **Table 7**, **Table 8** and **Table 9**.

5.3.2. P21

Borehole P21 had 14 samples studied by EDS, namely P21-02 to P21-15 and the quantitative results are shown in **Table 7**. The results at a glance show that the TiO₂ content of MAG 04 increases steadily from 10.41 per cent at the seam-footwall contact to 14.90 at the seam parting magnetite-gabbro contact, while V₂O₅ also increases from a low of 1.76 at the seam-footwall to 2.18 per cent at the top of the seam. The TiO₂ and V₂O₅ content drops significantly in the parting magnetite-anorthosite to 8.50 and 1.45 per cent respectively.

Seam MAG 03 shows the increase in both TiO₂ and V₂O₅ content towards the top of the seam, both dropping abruptly in the hanging wall magnetite-gabbro above the seam. Seam MAG 02 also shows the increase in TiO₂ and V₂O₅ while seam MAG 01 had only one sample analysed but with TiO₂ and V₂O₅ contents of 15.89 and 1.96 respectively, which are both considerably higher. Cr₂O₃ was detected in significant quantities only in MAG 04 and it declines abruptly towards the top of the seam and re-appears in MAG 02. The relationship of the compounds TiO₂ and V₂O₅ are illustrated in the **Figure 43** which plots the compounds against depth.

The TiO₂ content when plotted against the V₂O₅ content showed a positive correlation which can be seen visually in **Figure 35** where TiO₂ and V₂O₅ increase steadily together in the seams

MAG 03 and MAG 04. The TiO_2 content at the scale of the individual seams does not show an antipathetic relationship with V_2O_5 .

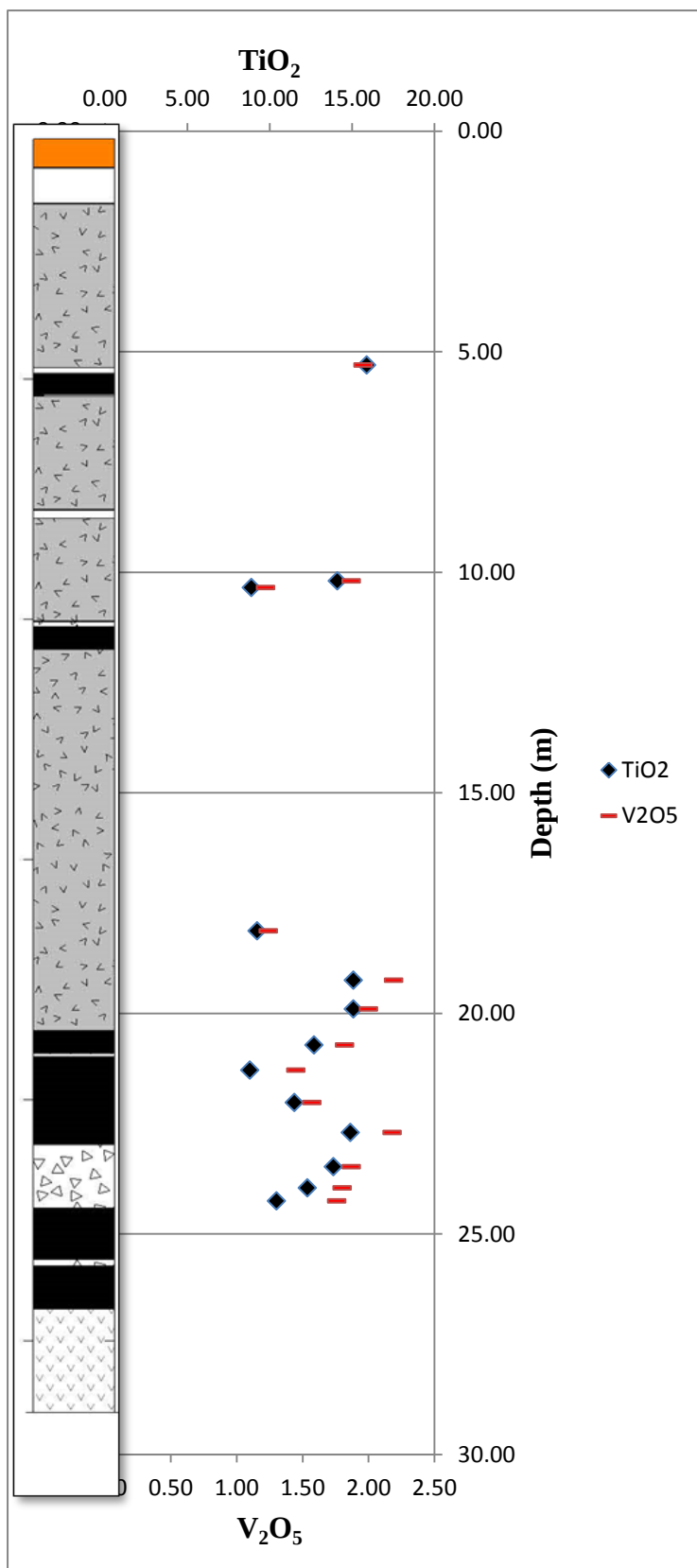


Figure 43 Strip log of borehole P21 with plots of TiO_2 and V_2O_5 content in the samples from EDS results.

Table 7 P21 Energy dispersive X-ray spectroscopy pseudo-section sample area analysis

Sample	Depth	FeO	TiO ₂	V ₂ O ₅	MgO	Al ₂ O ₃	Cr ₂ O ₃	MnO	CaO	Na ₂ O	SiO ₂	As	K ₂ O	S	Total
P21-02	5.30	75.27	15.89	1.96	1.52	3.96	0.00	0.00	0.00	0.00	1.39	0.00	0.00	0.00	100.00
P21-03	10.20	73.41	14.12	1.87	1.96	5.46	0.34	0.27	0.00	0.00	2.58	0.00	0.00	0.00	100.00
P21-04	10.35	50.05	8.89	1.22	2.02	14.58	0.00	0.00	1.86	1.43	19.94	0.00	0.00	0.00	100.00
P21-05	18.13	49.27	9.24	1.24	1.68	14.48	0.00	0.00	0.84	0.55	22.70	0.00	0.00	0.00	100.00
P21-06	19.25	73.28	15.08	2.19	1.91	5.49	0.00	0.00	0.00	0.00	1.42	0.00	0.00	0.63	100.00
P21-07	19.90	73.70	15.08	2.00	1.68	6.05	0.00	0.00	0.00	0.00	1.49	0.00	0.00	0.00	100.00
P21-08	20.72	70.05	12.70	1.82	3.38	7.72	0.00	0.31	0.00	0.00	4.02	0.00	0.00	0.00	100.00
P21-09	21.29	48.50	8.81	1.45	1.50	15.20	0.00	0.00	1.96	1.43	21.16	0.00	0.00	0.00	100.00
P21-10	22.02	55.02	11.50	1.57	2.13	12.10	0.00	0.00	1.30	1.33	15.05	0.00	0.00	0.00	100.00
P21-11	22.70	73.39	14.90	2.18	2.18	5.40	0.36	0.00	0.00	0.00	1.59	0.00	0.00	0.00	100.00
P21-12	23.48	74.40	13.88	1.87	1.95	5.92	0.71	0.00	0.00	0.00	1.08	0.00	0.00	0.00	99.82
P21-13	23.96	68.45	12.29	1.80	2.70	7.18	1.16	0.46	0.63	0.49	4.84	0.00	0.00	0.00	100.00
P21-14	24.25	62.24	10.41	1.76	2.11	10.11	1.35	0.34	1.16	0.96	8.93	0.00	0.00	0.63	100.00
P21-15	24.38	1.69	0.00	0.00	0.00	26.49	0.00	0.00	11.79	4.35	53.71	0.38	0.40	1.20	100.00

5.3.3. P55

Samples from borehole P55 were sampled from the titanomagnetite seams MAG 03 and MAG 04 only, owing to the weathered nature of MAG 02 and the absence of MAG 01 due to erosion. TiO_2 and V_2O_5 are absent in the footwall immediately below the titanomagnetite seam MAG 04 but are immediately in the sample P55-10 at 12.18 per cent and 1.71 per cent respectively which sits less than 30cm from the footwall sample P55-11, which represents a very sharp contact in between the titanomagnetite seam and the underlying footwall. From the base of MAG 04, both TiO_2 and V_2O_5 increase steadily to the top of MAG 04 where they both drop significantly in the parting magnetite-anorthosite as illustrated in **Figure 44**. MAG 03 also has high TiO_2 and V_2O_5 contents which both steadily increase to the top of the seam before tapering into the magnetite gabbro. The quantitative analytical results for the EDS analysis are presented in **Table 8**.

The relationship of TiO_2 content and V_2O_5 content shows a positive correlation as illustrated in **Figure 39** and also as can be deduced from **Figure 44**. This relationship is at the scale of the singular main magnetite seam not showing the antipathetic relationship. MgO content starts low in the footwall before jumping to a high of 2.80 per cent followed by a decline in sample P55-09 which is followed by a steady increase towards the top of MAG 04. In the seam MAG 03, the MgO content is relatively abundant in the massive sections and low in the disseminated sections as described by (Reynolds, 1986).

Sulphides are only present in the footwall anorthosite as pyrite, pyrrhotite and chalcopyrite. The parting magnetite anorthosite between MAG 04 and MAG 03 contains some tungsten and chromium is present in the seam MAG 04 where it decreases rapidly with increasing stratigraphic height almost disappearing completely in MAG 03. The iron content as Fe_2O_3 is fairly constant averaging approximately 70 per cent in the titanomagnetite seams except for the parting magnetite-anorthosite and the hanging wall magnetite gabbro.

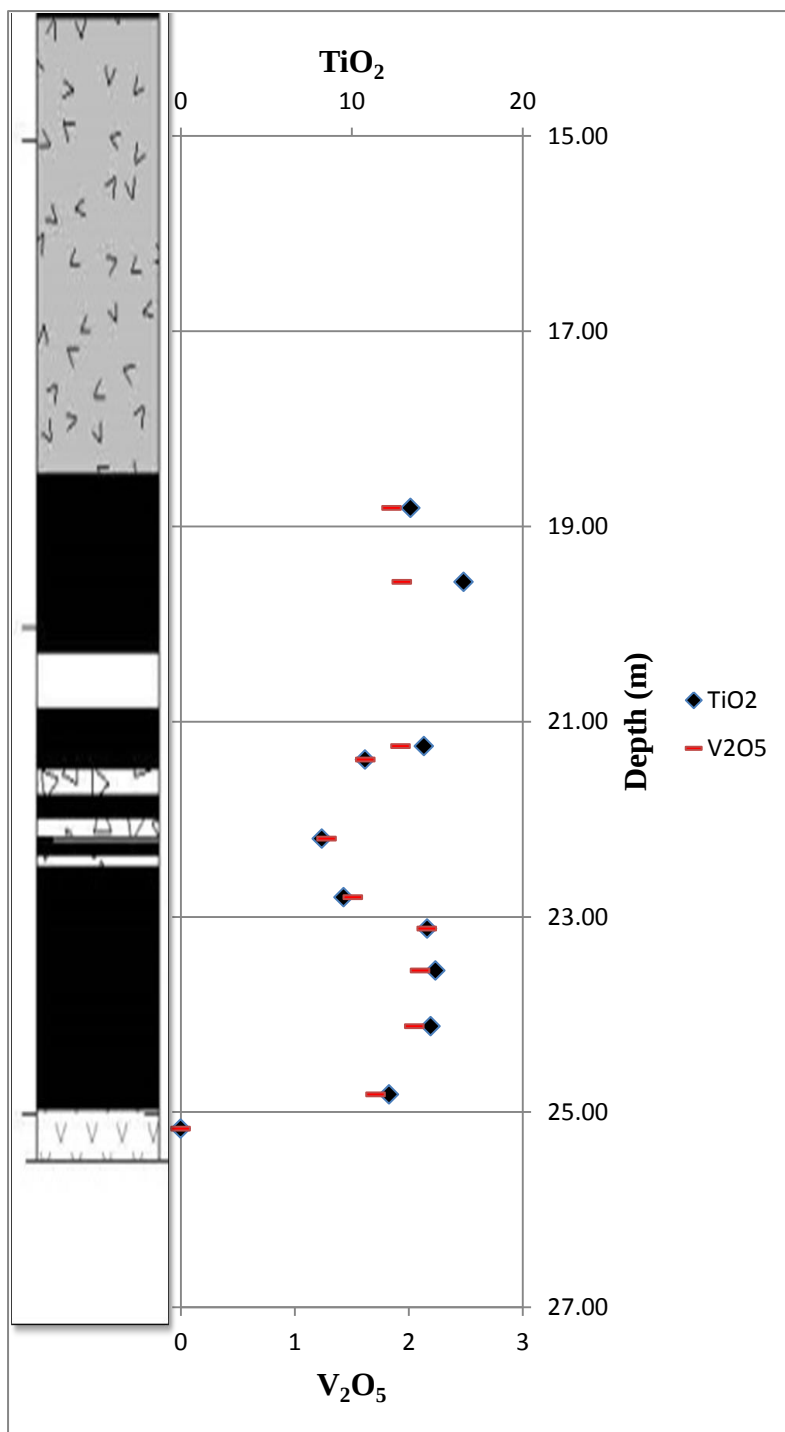


Figure 44 Strip log of borehole P 55 with plots of TiO_2 and V_2O_5 content against depth from EDS results.

Table 8 P55 Energy dispersive X-ray spectroscopy (EDS) pseudo-section sample area analysis.

Sample	Depth	FeO	TiO ₂	V ₂ O ₅	MgO	Al ₂ O ₃	Cr ₂ O ₃	MnO	CaO	Na ₂ O	SiO ₂	Cu	K ₂ O	S	W	Total
P55-01	18.81	68.89	13.43	1.85	3.2	7.19	0.00	0.00	0.00	0.00	5.24	0.00	0.00	0.00	0.00	99.79
P55-02	19.57	71.53	16.55	1.94	1.85	4.76	0.00	0.34	0.00	0.00	3.02	0.00	0.00	0.00	0.00	100
P55-03	21.25	71.70	14.23	1.93	1.66	6.66	0.35	0.00	0.00	0.00	3.47	0.00	0.00	0.00	0.00	100
P55-04	21.39	53.44	10.77	1.62	3.04	13.41	0.00	0.00	0.97	0.71	16.05	0.00	0.00	0.00	0.00	100
P55-05	22.20	46.73	8.25	1.28	1.72	14.63	0.00	0.00	2.84	1.48	21.76	0.00	0.00	0.00	1.32	100
P55-06	22.80	50.34	9.53	1.51	2.69	14.96	0.00	0.36	0.56	0.00	20.04	0.00	0.00	0.00	0.00	100
P55-07	23.12	72.11	14.41	2.16	1.74	6.12	0.33	0.00	0.00	0.00	3.14	0.00	0.00	0.00	0.00	100
P55-08	23.55	71.80	14.90	2.10	1.19	6.06	0.41	0.00	0.00	0.00	3.53	0.00	0.00	0.00	0.00	100
P55-09	24.12	70.49	14.61	2.05	0.72	7.23	0.63	0.00	0.00	0.00	4.28	0.00	0.00	0.00	0.00	100
P55-10	24.82	70.31	12.18	1.71	2.80	7.63	1.56	0.00	0.00	0.00	3.82	0.00	0.00	0.00	0.00	100
P55-11	25.17	4.75	0.00	0.00	0.55	23.78	0.00	0.00	12.71	3.66	48.96	1.37	0.33	3.89	0.00	100

5.3.4. P 57

The borehole P 57 had 14 samples collected named P57-01 to P57-14, and of these 13 were analysed except for sample P57-02 which was accidentally destroyed during thin section preparation. The footwall to the main magnetite seam sitting below MAG 04 is an anorthosite with An_{70} and contains less than 0.60 per cent TiO_2 and no V_2O_5 , with minimal iron most of which exists in pyrite as evidenced by the sulphur content of 2.07 per cent see **Table 9**. The TiO_2 content is fairly low at the base of the MAG 04 seam at less than 8 per cent and increases slightly to remain fairly constant at around 13 per cent with no marked decline or increase with a very sharp decline in the parting magnetite-anorthosite as illustrated in the **Figure 45**. The V_2O_5 content starts off at 1.21 per cent at the base of the MAG 04 seam and jumps to 2 per cent before declining steadily towards the top of the seam with a sharp drop as well in the magnetite anorthosite that separates it from MAG 03. The seam MAG 03 starts off with TiO_2 content of just over 13 per cent declining slightly to just over 11 per cent before rebounding 1m from the top of the seam to over 13 per cent and then sharply declining at the MAG 03 hanging wall contact.

V_2O_5 content in seam MAG 03 decreases slightly from bottom to top before jumping up again at sample P57-05 which sits almost a metre from the top of the seam, almost following the same trend as TiO_2 . The highest TiO_2 content of 15.13 per cent in the borehole is in sample P57-01 which came from the top of seam MAG 01 with a corresponding V_2O_5 content of 1.82 per cent. Of note is the presence of Molybdenum (Mo) in sample P57-05. Samples P57-13 and P57-04 had tungsten (W) amounts of more than 1 per cent and they are the samples with the lowest TiO_2 and V_2O_5 contents in MAG 04 and MAG 03 respectively as can be seen in **Table 9**. CaO , Na_2O and K_2O have their highest concentrations in the footwall anorthosite and the parting magnetite anorthosite between MAG 03 and MAG 04. A positive correlation was observed between TiO_2 content and V_2O_5 content in each individual seam and in the entire main magnetite seam comprising of all the MAG seams from MAG 01 to MAG 04. Cr_2O_3 is present only in MAG 04 and it declines sharply from bottom to top and disappears all together in MAG 03 and MAG 02 only to re-appear in MAG 01. MgO increases from bottom to top in MAG 04 but decreases with height in MAG 03, being relatively higher in the massive ores in comparison to the disseminated ores.

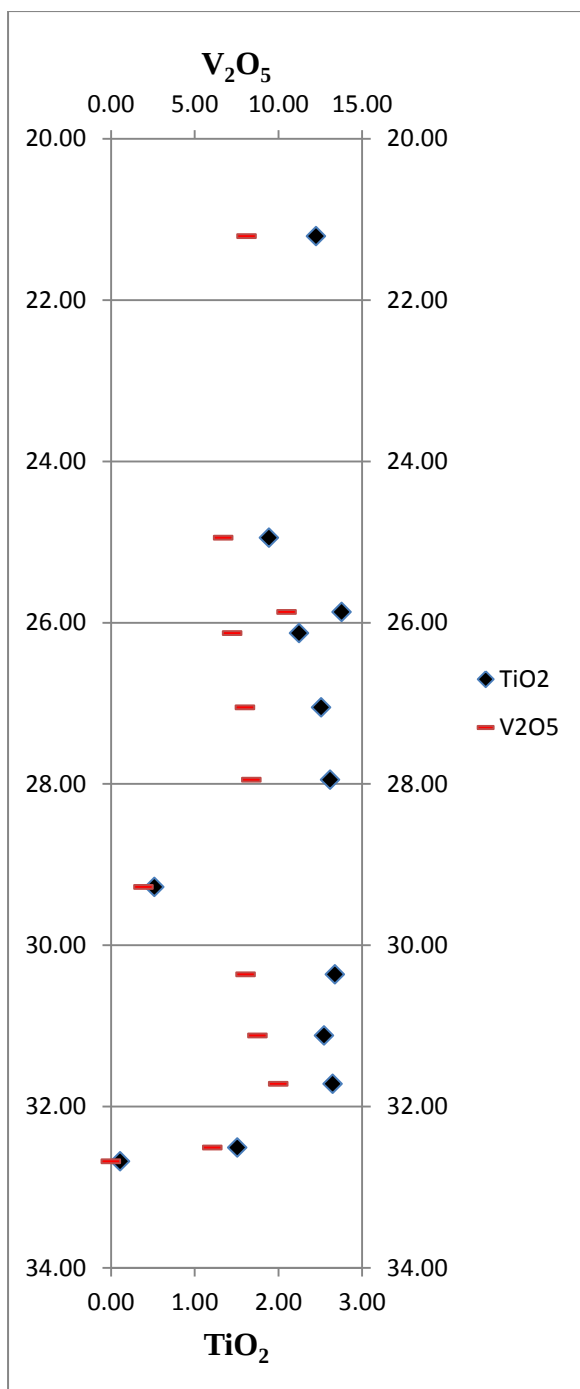


Figure 45 P 57 with plots of TiO_2 and V_2O_5 content against depth from EDS results.

Table 9 P57 Energy dispersive X-ray spectroscopy (EDS) pseudo-section sample area analysis.

Sample	Depth	FeO	TiO ₂	V ₂ O ₅	MgO	Al ₂ O ₃	Cr ₂ O ₃	CaO	Na ₂ O	SiO ₂	Mo	W	K ₂ O	S	Total
P57-01	7.97	72.71	15.13	1.82	1.94	5.67	0.33	0.00	0.00	2.39	0.00	0.00	0.00	0.00	100
P57-03	21.21	62.66	12.26	1.62	2.71	8.99	0.00	1.07	0.99	9.70	0.00	0.00	0.00	0.00	100
P57-04	24.95	51.00	9.44	1.34	2.79	12.94	0.00	2.62	1.69	16.59	0.00	1.14	0.00	0.46	100
P57-05	25.87	73.36	13.78	2.10	2.26	5.58	0.00	0.00	0.00	1.61	1.32	0.00	0.00	0.00	100
P57-06	26.13	59.11	11.23	1.45	2.35	10.85	0.00	1.41	1.05	11.50	0.00	0.00	0.00	1.05	100
P57-07	27.05	70.56	12.55	1.60	2.85	7.64	0.00	0.28	0.00	3.71	0.00	0.00	0.00	0.81	100
P57-08	27.95	58.39	13.10	1.68	3.27	10.22	0.00	1.72	1.00	10.62	0.00	0.00	0.00	0.00	100
P57-09	29.28	14.94	2.60	0.39	0.58	23.61	0.00	8.99	3.83	44.01	0.00	0.00	0.31	0.73	100
P57-10	30.36	62.85	13.38	1.61	3.54	9.01	0.00	0.95	0.69	7.47	0.00	0.00	0.00	0.49	100
P57-11	31.12	72.26	12.73	1.75	3.37	6.74	0.49	0.23	0.00	2.06	0.00	0.00	0.00	0.36	100
P57-12	31.72	74.53	13.25	2.00	2.56	5.81	0.84	0.21	0.00	0.80	0.00	0.00	0.00	0.00	100
P57-13	32.51	41.89	7.55	1.21	3.19	14.33	0.92	3.70	2.29	23.18	0.00	1.33	0.00	0.42	100
P57-14	32.68	7.76	0.56	0.00	0.52	23.92	0.00	11.14	4.14	49.04	0.00	0.00	0.53	2.07	99.69

5.4. LATERAL DISTRIBUTION OF TiO₂, V₂O₅, SILICATES, SULPHIDES AND TRACE ELEMENTS

5.4.1. Introduction

The boreholes analysed during the course of this study are situated on the farms Gezond 235KR and form part of the resource being developed for potential mining by the CEI group. The boreholes chosen are situated along the strike of the main magnetite seam. In light of the potential for mining operations to be carried out, the lateral distribution of the important oxide mineral ores as well as associated silicates and sulphides is presented for purposes of noting any differences in the ores laterally.

5.4.2. TiO₂

The TiO₂ content as average within the titanomagnetite seams with the footwall and parting gabbros or anorthosite left out is fairly consistent with an average just above 12 per cent. P55 which is the southern-most has an average of 12.89 weight per cent TiO₂, while P21 in the middle has 12.52 weight per cent and P57 has 12.22 per cent. P57 does not show much variance in the average TiO₂ content across the seams while the highest variance in TiO₂ content is illustrated in borehole P21. It can be deduced that the TiO₂ content decreases from south to north, but the decrease is of limited magnitude.

5.4.3. V₂O₅

V₂O₅ is highest in the South in the borehole P 55 which has an average of 1.81 weight per cent V₂O₅ in the titanomagnetite seams excluding the footwall and parting magnetite-anorthosite. Borehole P 21 in the central part of the farm has an average V₂O₅ content of 1.76 while borehole P 57 has an average of 1.65. In borehole P 55, the vanadium content increases in both MAG 03 and MAG 04, only dropping in the parting anorthosite. The same trend was observed in P 21 with steady increases in vanadium content from bottom to top with decreases at the titanomagnetite seam-hanging wall interfaces. In the borehole P57 however, the vanadium content decreases from bottom to top, as can be seen in **Figure 45**. The relationship between V₂O₅ and TiO₂ laterally can be interpreted as being antipathetic from south to north.

5.4.4. Silicates, sulphides and trace elements

The footwall in all the boreholes is anorthosite with plagioclase as the dominant silicate. The Anorthite content of the footwall decreases from south to north with P55 having An₇₆, while

P 21 and P 57 have An_{71} and An_{70} respectively. There are sulphides in the footwall and in the case of P 57 in the titanomagnetite as well. The sulphides in P55 are mostly chalcopyrite with very little pyrite, while in P 21 pyrite and arsenopyrite are the dominant phases. In borehole P 57, the sulphide phase is predominantly pyrite especially in the footwall anorthosite. Tungsten (W) is present in P 55 and P 57 while molybdenum (Mo) is present P 57 only and in one sample, P57-05. In all boreholes, Chromium is present in the seam MAG 04 where it rapidly declines with increasing height and is also present in the seam MAG 01 in boreholes P 21 and P 57.

5.5. Interpretation

The results of this study have indicated a number of trends and patterns that are interpreted in the context of the research interests. The main magnetite seam as intersected in the boreholes P21, P55 and P57 comprises of four seams namely MAG 01 to MAG 04 with the bottom two, MAG 03 and MAG 04 being the thickest at approximately 2.5 and 2.0m thick respectively. The two bottom seams constitute the most important resource for the minerals vanadium, titanium and iron ore. The ores sit above a footwall anorthosite that is often completely devoid of titanium and vanadium, but instead dominated by sulphides phases which range from pyrite to chalcopyrite and pyrrhotite.

The seam MAG 04 begins with relatively low amounts of titanium and vanadium immediately above the footwall, quickly increasing in content and gradually increasing all the way to the top of the seam where a significant drop in both elements is experienced into the parting magnetite-anorthosite. The seam MAG 03 also exhibits the same trend as in MAG 04 where the compounds TiO_2 and V_2O_5 increase with increasing height before declining in the hanging wall magnetite gabbro.

Granular ilmenite is restricted in the massive ores to intergranular spaces with relatively smaller grain sizes which has been interpreted in the course of this study as being the result of the oxidation of titanomagnetite-ulvospinel exsolution which was expelled to the grain boundaries as described by (Von Gruenewaldt et al., 1985) and Reynolds (1986). Grains of ilmenite that are free of titanomagnetite association start appearing in the disseminated ores and they are in general larger than the ilmenite grains associated with the titanomagnetite grains in the massive ores, which have been interpreted in this study as primary ilmenite that

may have crystallised in comparison to the ilmenite in the massive ores which is regarded by Buddington and Lindsley (1964) and Reynolds (1978) to be contemporaneous products of the oxidation of titanomagnetite-ulvospinel solid solution.

MgO content of the samples showed a general decrease away from the massive ores as can be seen in Table 7, 8 and 9, a phenomenon described by Reynolds (1986) as being associated to the partition of magnesium in ilmenite and the relative low amount of ilmenite in the massive ores resulted in higher concentrations of MgO in the ilmenite in comparison to the slightly higher ilmenite content in the disseminated ores where the MgO goes into more ilmenite.

Chapter 6 DISCUSSION

Petrographically, the dominant mineral in the main magnetite seam is titanomagnetite which constitutes in excess of 90 per cent by volume in the massive ores, representing a period of crystallisation of an oxide melt with the phases magnetite and ulvospinel crystallising above the magnetite-ulvospinel solidus. Ulvospinel occurs as fine lamellae parallel to the (111) magnetite cleavage or as fine cloth-pattern exsolutions as described by Reynolds (1985a) and (Von Gruenewaldt et al., 1985) which might be a reflectance of the variations in oxygen fugacity (fO_2) during the crystallisation process (Willemse, 1969b; Molyneux, 1969; Howarth et al., 2013).

Ulvospinel which is the major exsolution phase followed by the transparent spinels pleonaste and hercynite form cloth textures which are developed right to the grain boundaries between titanomagnetite grains, but absent or poorly developed in boundaries bordering ilmenite and silicates. Reynolds (1986) ascribes the absence of ulvospinel in the immediate vicinity of ilmenite grains to the fact that the development of discrete intergranular ilmenite may have depleted the titanomagnetite of its TiO_2 -rich components, and thus resulting in the absence of ulvospinel within the vicinity of ilmenite grains. Ulvospinel also occurs within the titanomagnetites in close proximity to the transparent spinels as broader and larger lamellae, an effect which Yund and McCallister (1970) and Reynolds (1986) suggest represents the heterogeneous nucleation of the earliest exsolved ulvospinel around dislocation sites that were energetically favourable.

Ilmenite occurs in a number of forms, from discrete granular ilmenite both in the massive ores and in the disseminated ores to intergranular ilmenite restricted to intergranular spaces in titanomagnetites and also as trellis exsolution lamellae. The granular ilmenite occurs in the massive ores at a number of times smaller than in the magnetite-plagioclase cumulates where individual ilmenite grain sizes may exceed 3mm across. The modal concentration of the ilmenite grains shows an increase with increasing silicate content concurrently with an increase in grain size, an effect which is described by several workers among them Molyneux (1970) and (Von Gruenewaldt et al., 1985). The relative lower modal concentrations of ilmenite in the massive ores can be explained by the fact that, the ilmenite is a result of the oxidation of the titanomagnetite-ulvospinel exsolution and not primary ilmenite, and that during the crystallisation; most of the TiO_2 in the system went into the ulvospinel as crystallisation was occurring above the magnetite-ulvospinel solvus.

Ilmenite that occurs as intergranular lamellae is less compared to the granular form, but is usually in occurrence as small grains along titanomagnetite grain boundaries as small grains. (Von Gruenewaldt et al., 1985) explains this phenomenon as being ilmenite that was exsolved from within the titanomagnetite grains such that the ilmenite now occurs outside of the magnetite grains, thus leaving the magnetite devoid of internal ilmenite exsolutions. (Reynolds, 1978; Reynolds, 1985b) explain this as an effect of the external granule exsolution, much the same way as (Von Gruenewaldt et al., 1985) or as the result of contemporaneous oxidation/exsolution of the titanomagnetite-ulvospinel solid solution. Ilmenite in lamellae form is not in common occurrence and is regarded by Buddington and Lindsley (1964) and Reynolds (1986) to be a result of the contemporaneous oxidation/exsolution of the solid solution of magnetite and ulvospinel.

During the course of this study, it was recognised that the TiO_2 content of the massive ores is almost always 2 to 5 weight percent higher than that of the disseminated ores, as in P 55 samples P55-06 and P55-07 where former is disseminated and has a TiO_2 content of 9.53 per cent while the latter is massive and has a TiO_2 content of 14.41 as shown in **Table 8**. The possible explanation for this scenario is that the majority of the TiO_2 content of the titanomagnetite ores is not in the form of granular ilmenite, but rather occurs as ulvospinel and titanomagnetite, from which the granular ilmenite originated as oxidation/exsolution products.

The vanadium content as V_2O_5 which ranges from approximately 1.2 to 2.2 observed during the course of this study is in conformance with what has been mentioned by a number of workers for the vanadium content of the Upper Zone magnetitites, among others (Molyneux, 1969; Willemse, 1969b; Reynolds, 1986; Cawthorn and Molyneux, 1986; Von Gruenewaldt, 1973; Van der Merwe, 1978). The vanadium content decreases with height in the seams MAG 04 and MAG 03 in borehole P57, but increase with stratigraphic height in the boreholes P21 and P55. The decrease in V_2O_5 with height was attributed by Reynolds (1986) to be in conformance with normal fractional trends. The increase in V_2O_5 with height might be a reflection of the small scale at which this current study was conducted which was over a four magnetite seams namely MAG 01 to MAG 04, all belonging to the main magnetite seam rather than the entire cross section of the Upper Zone of the Rustenburg Layered Suite. The variance in V_2O_5 and TiO_2 content within the confines of the main magnetite seam has been shown by many workers among them Coertze (1966), Groeneveld (1970), Von Gruenewaldt

(1973) and Molyneux (1970) to be not reflective of the variance within the entire Upper Zone.

The transparent spinels pleonaste and hercynite form exsolution lamellae and micron size granules within the titanomagnetite and is generally more abundant in the massive ores than in the disseminated/ silicate rich zones. The spinels are either poorly developed or completely absent close to the grain boundaries of the titanomagnetite and Reynolds (1986) and Von Gruenewaldt et al., (1985) suggest that it is as a result of low Al and Mg contents in those areas as a result of the possible preferential exsolution outside of the titanomagnetite grains into the intergranular spaces of the transparent spinels. This assertion could be supported by the apparent occurrence of the transparent spinel in the intergranular spaces where they occur together with intergranular ilmenite as is shown in **Figure 30**.

The MgO content as weight per cent is relatively higher in the massive ores in comparison to the disseminated ores.

Chapter 7 CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

The main magnetite seam of the Upper Zone of the Rustenburg Layered Suite in the Northern Limb of the Bushveld Complex is a resource for vanadium, titanium and iron ore as well as holding low potential for sulphide hosted mineralisation. The vanadium content as V_2O_5 ranges from 1.2 per cent to 2.2 per cent in conformance with what has been observed by previous workers among others (Molyneux, 1964; Willemse, 1969a; Reynolds, 1985a; Reynolds, 1986; Cawthorn and Molyneux, 1986; Willemse, 1969b; Molyneux, 1969; Von Gruenewaldt, 1973; Molyneux, 1970; Von Gruenewaldt, 1977). While no discrete vanadium minerals were identified during the course of this study, which may imply that the vanadium occurs in the magnetite lattice as V^{3+} which will be substituting for Fe^{3+} . The above mentioned workers also report the TiO_2 content to be in the range of 12-20 per cent, values which have been largely reproduced in the course of this study.

The vanadium content of the main magnetite seams renders it a potential resource for the economic extraction of vanadium through the roast and leach process. Borehole P57 is the only one that shows the decrease with stratigraphic height as is reported by Reynolds (1985a) and (Cawthorn and Molyneux, 1986), with the other two boreholes showing an apparent gradual increase in vanadium with stratigraphic height, probably due to the localised scale at which the study was carried out (only one composite magnetite seam of four layers). Layer MAG 04 of P57 is the only one that shows the antipathetic relationship between V_2O_5 and TiO_2 , while V_2O_5 decreases in MAG 03 in P57; it does so together with TiO_2 as can be seen in **Figure 45**. Boreholes P21 and P55 show an increase in both TiO_2 and V_2O_5 with stratigraphic height in both the major seams MAG 04 and MAG 03, with sharp drops at the seam hanging wall interfaces.

The investigation has revealed some textural and compositional trends in conformance with earlier work as can be summarised as follows:

- a) The TiO_2 content of the main magnetite seam of the Upper Zone of the Rustenburg Layered Suite on the farm Gezond 235 KR ranges from approximately 8 to 16.5 weight per cent, with the majority of the titanium occurring as ulvospinel and titanomagnetite and not as granular ilmenite.

- b) Granular ilmenite occurs in modal concentrations of 3 to 5 per cent by volume in the massive ores and just over 5 per cent in the disseminated ores, but the total TiO_2 content decreases by between 2 to 5 percentage points by weight from the massive ores to the disseminated ores, which validates the point that most of the titania occurs as ulvospinel rather than ilmenite.
- c) The bulk rock composition of the magnetite layers as analysed by energy dispersive X-ray spectroscopy shows that the TiO_2 content increases with increasing height, with exceptions of the parting magnetite-anorthosite and the hanging wall gabbro.
- d) The V_2O_5 content of the main magnetite seam ranges from 1.2 to 2.2 weight per cent on the farm Gezond 235 KR. While the V_2O_5 content does not decrease with increasing height, it also does not vary by more than 1 percentage points across the main magnetite seam, rendering the layers MAG 03 and MAG 04 potentially extractable without the need for selective mining of the massive and disseminated ores.

7.2. Recommendations

The results of this study have revealed the same textural and compositional trends as recognised by earlier workers on the Upper Zone vanadiferous titanomagnetite ores. In light of these results, the following recommendations are made with regards to the potential economic extraction of the titanomagnetite ores:

- 1) Vanadium as a product can be recovered through the crushing, pelletisation and roast leach process. This process of vanadium extraction is currently in practice by Evraz Highveld Steel and Vanadium of South Africa and is independent of the textures and mineralogy of the titanomagnetites and therefore can be pursued with economic potential. Feasibility studies should be carried out on the resource, backed by geological models and metallurgical bench tests to evaluate the economic extractability of the vanadium in light of other factors such as infrastructure, size of resource, mining method to be employed, labour, environmental concerns as well as the project's potential for return on investment.
- 2) The titanium content of the main magnetite seam is high enough to be attractive to the potential of recoverability. However, the nature and existence of the majority of the titanium is in the form of very fine exsolutions of ulvospinel instead of granular ilmenite which might be difficult to separate by mechanical means or by

conventional metallurgy. It is however recommended that the Direct Reduction process of iron be investigated first at small scale to test the recoverability of iron and titanium as separate products. The direct reduction method or sponge iron manufacture involves the reduction of iron oxides in their solid state by use of coal as the carbon reductant in a rotary kiln. The reduced iron or sponge iron will then be later smelted in an electric arc furnace leaving behind a titania rich slag, which can then be crushed and further treated for titanium either as pigment grade TiO_2 or as metallic titanium.

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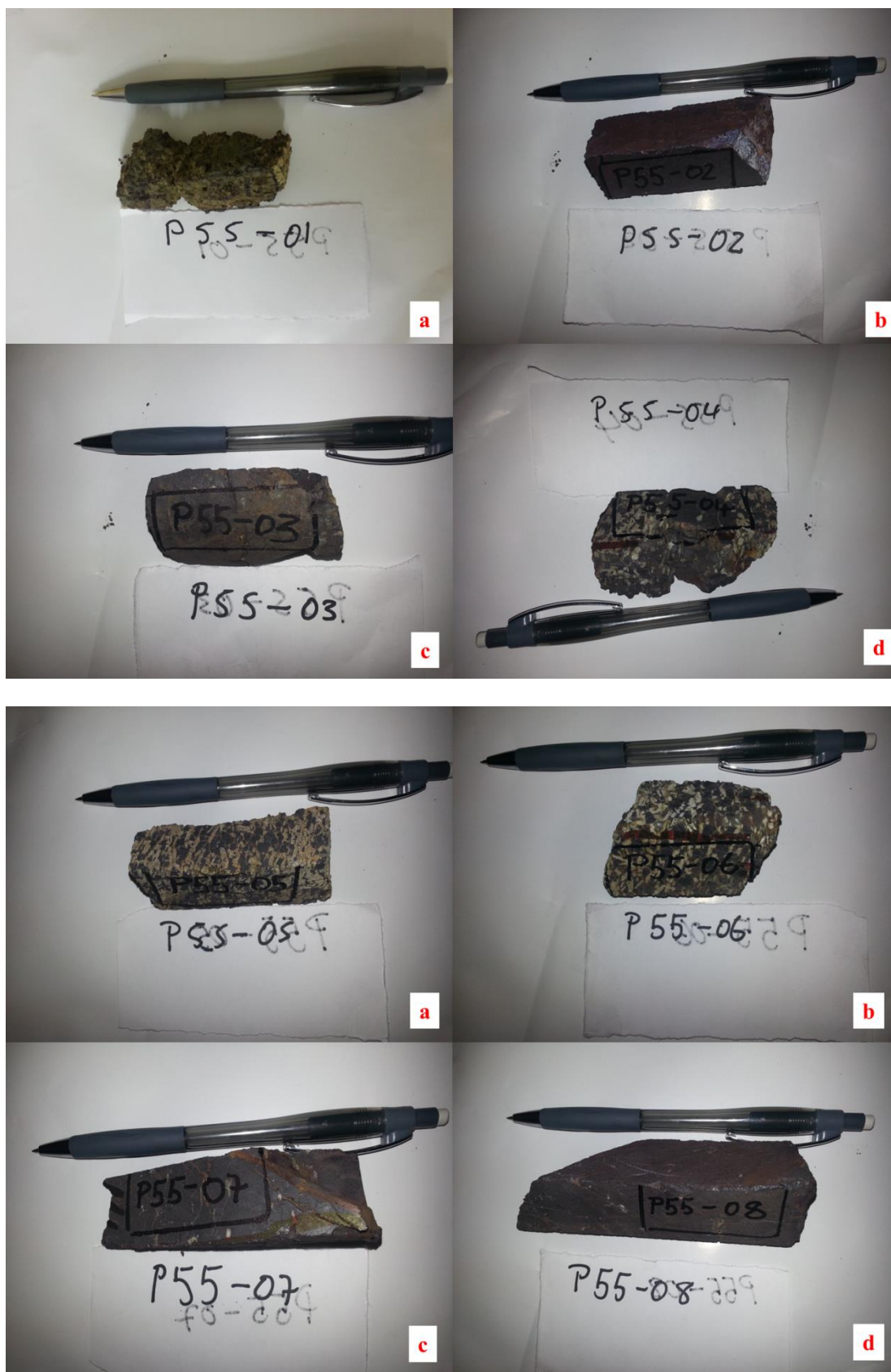
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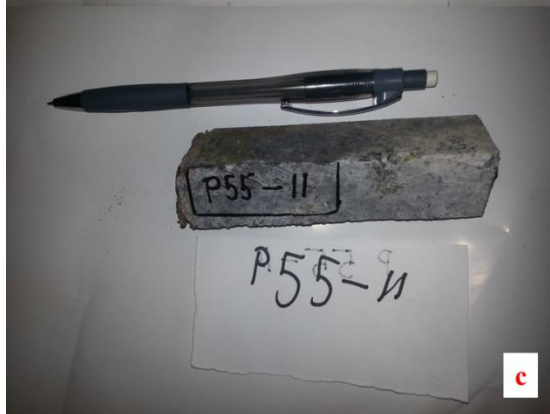
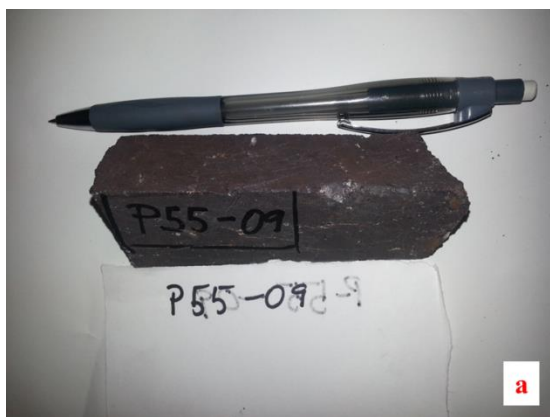
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APPENDIX A – QUARTER CORE SAMPLES





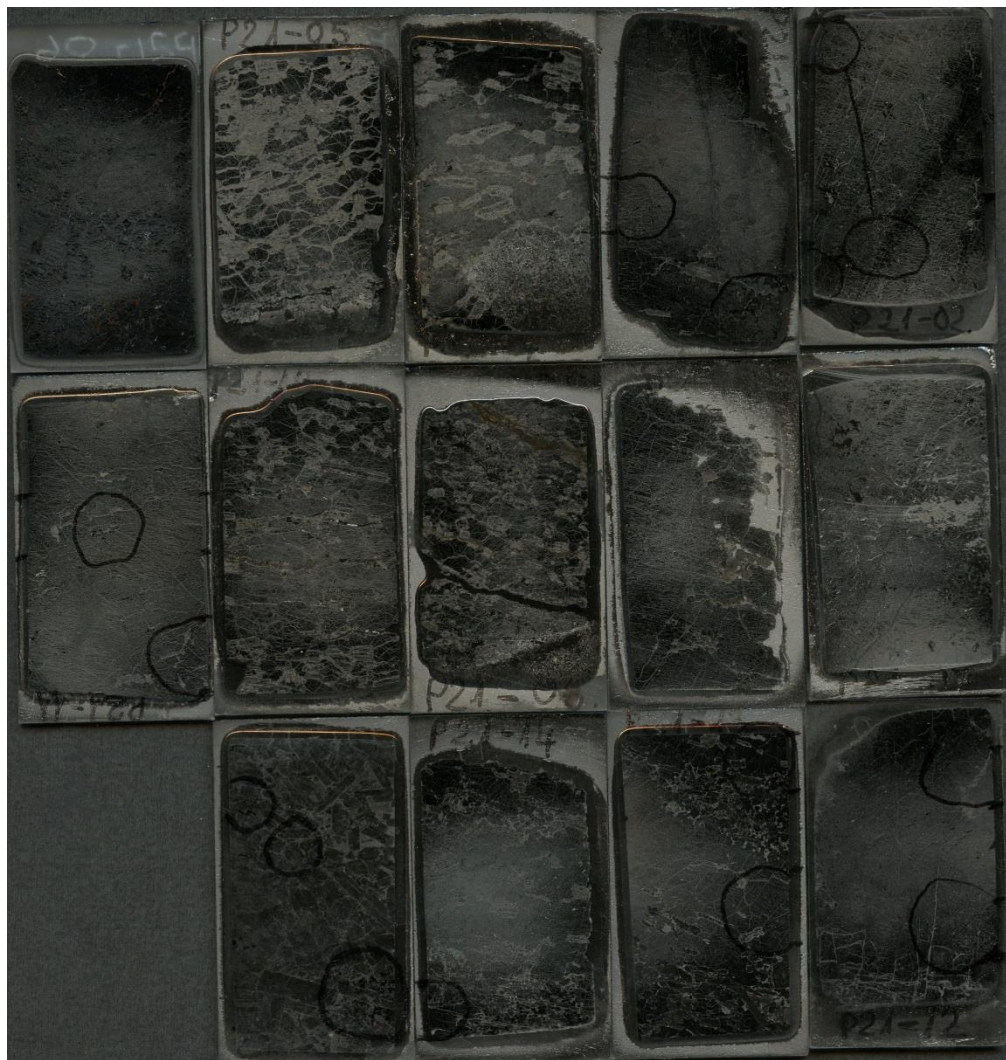




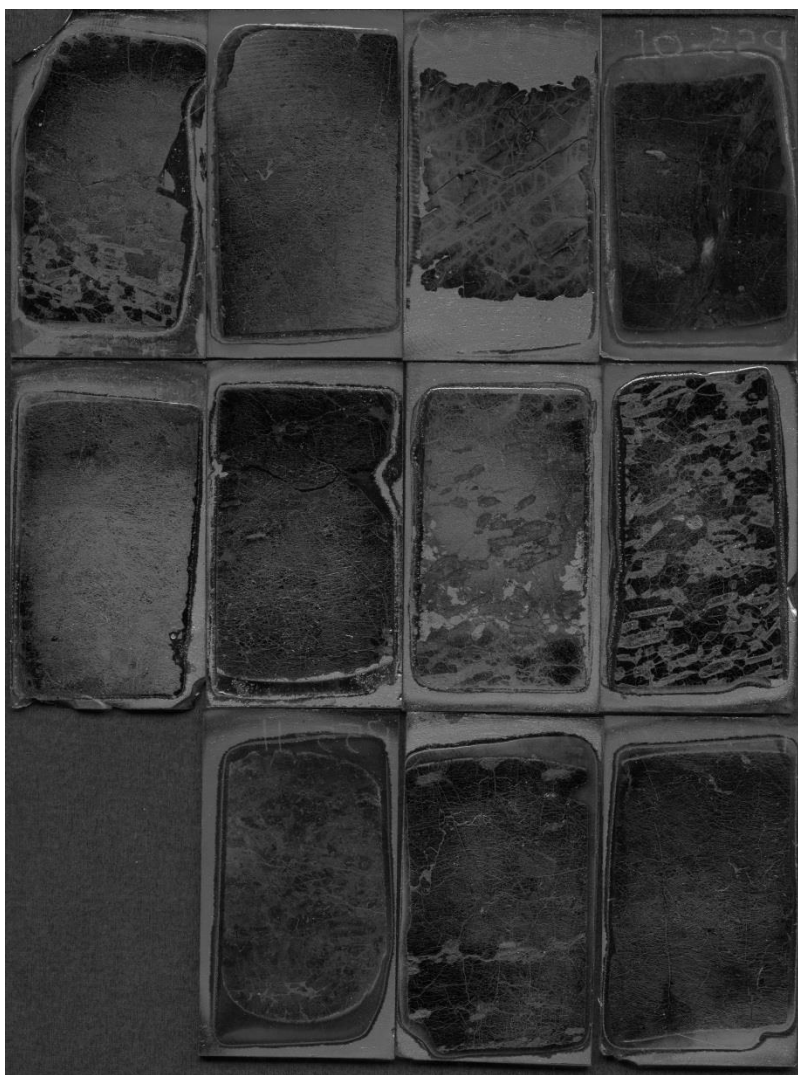




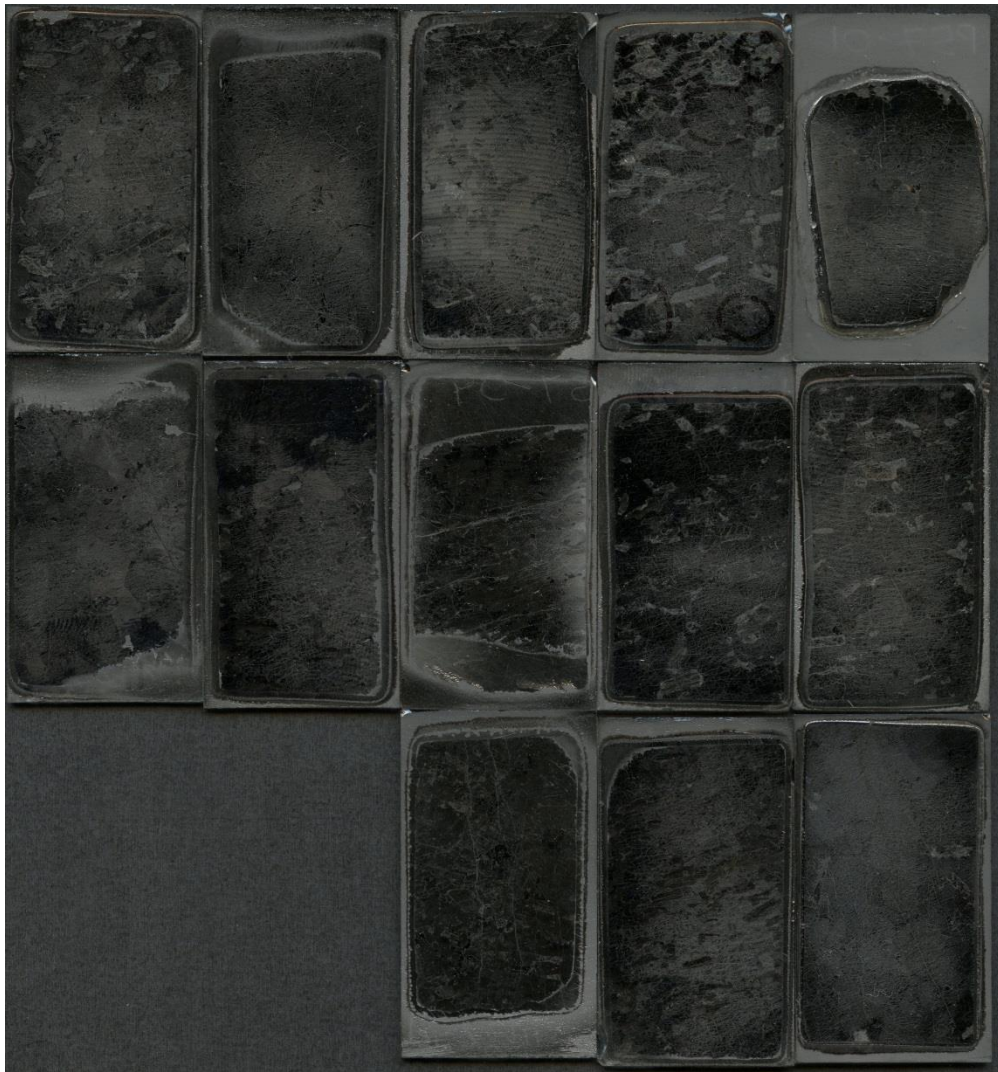
APPENDIX B – POLISHED THIN SECTIONS OF SAMPLES FROM P21, P55 AND P57



Polished thin sections of samples from borehole P 21



Polished thin sections of samples from borehole P 55



Polished thin sections of samples from borehole P 57

APPENDIX C - SAMPLE POSITIONS FOR THE BOREHOLES P21, P55 AND P57

Borehole Name	Sample Number	Lithoological Unit	From	To	Remarks
P21	P21-01	MAG-01	4.90	5.00	HW
P21	P21-02	MAG-01	5.25	5.35	Reef
P21	P21-03	MAD-02	10.16	10.23	HW
P21	P21-04	MAG-02	10.30	10.39	Reef
P21	P21-05	MAG-03	18.08	18.17	FW
P21	P21-06	MAG=03	19.20	19.30	HW
P21	P21-07	MAG-04	19.85	19.95	Reef
P21	P21-08	MAG=04	20.77	20.77	Reef
P21	P21-09	MAG-03/04	21.24	21.33	Reef
P21	P21-10	MAG-03/04	21.98	22.06	Parting Top
P21	P21-11	MAG-04	22.64	22.75	Parting
P21	P21-12	MAG-04	23.43	23.53	HW
P21	P21-13	MAG-04	23.92	24.00	Reef
P21	P21-14	MAG-04	24.18	24.30	Reef
P21	P21-15	MAG-04	24.33	24.43	FW
P55	P55-1	MAG-03	18.78	18.85	HW to MAG-03
P55	P55-2	MAG-03	19.52	19.62	Reef
P55	P55-3	MAG-03	21.20	20.30	MAG-03 Bottom
P55	P55-4	MAG-03	21.35	21.42	FW/Contact
P55	P55-5	MAG-03/04	22.16	22.24	Parting
P55	P55-6	MAG-04	22.76	22.85	Top
P55	P55-7	MAG-04	23.07	23.17	Reef
P55	P55-8	MAG-04	23.50	23.60	Reef
P55	P55-9	MAG-04	24.07	24.17	Reef
P55	P55-10	MAG-04	24.77	24.87	FW/Contact
P55	P55-11	MAG-04	25.12	25.22	FW
P57	P57-01	MAG-01	7.92	8.02	MAG01 Top
P57	P57-02	MAG-01	8.41	8.48	Reef
P57	P57-03	MAG-02	21.16	21.26	Reef
P57	P57-04	MAG-03	24.90	25.00	Reef Top
P57	P57-05	MAG-03	25.82	25.92	Reef
P57	P57-06	MAG-03	26.08	26.17	Disseminated
P57	P57-07	MAG-03	27.00	27.10	Reef
P57	P57-08	MAG-03	27.90	28.00	Reef Bottom
P57	P57-09	MAG-03/04	29.23	29.33	Parting
P57	P57-10	MAG-04	30.31	30.41	Reef Top
P57	P57-11	MAG-04	31.07	31.17	Reef
P57	P57-12	MAG-04	31.67	31.97	Reef
P57	P57-13	MAG-04	32.46	32.56	Reef Bottom
P57	P57-14	MAG-04	32.63	32.73	FW to MAG-04