Chapter 3
Petrography and Mineralogy

3.1 Introduction

Based on mesoscopic appearance, the manganese ores examined during the course of this study have been subdivided into those unaffected, weakly affected, and strongly affected by supergene alteration processes along the Kalahari unconformity. Downward from the Kalahari unconformity, strongly altered, weakly altered and unaltered manganese ores occur in close spatial association and the transition between these different degrees of alteration is gradual.

The unaltered ore in the study area can be described as braunite lutite (Table 3.1), commonly referred to as Mamatwan-type ore (Nel et al., 1986). Detailed descriptions of Mamatwan-type ore are available in Nel et al. (1986), Kleyenstüber (1993), Gutzmer and Beukes (1996), Preston (2001) and Van Staden (2002). It is typically composed of microsparitic carbonates (kutnahorite and Mn-calcite), intimately intergrown with microcrystalline braunite and hematite. The mineral assemblage that constitutes the braunite lutite (Table 3.1) is very similar throughout the lower manganese ore bed of the Hotazel Formation (Nel et al., 1986; Gutzmer and Beukes, 1995; Van Staden, 2002) and is widely accepted to be of sedimentary to diagenetic origin. Locally, this diagenetic mineral assemblage is affected by a mild metamorphic-metasomatic overprint, resulting in the formation of small amounts of Mn-calcite, hausmannite, partridgeite and manganite, at the expense of kutnahorite (Kleyenstüber, 1985; Gutzmer and Beukes, 1996; Van Staden, 2002).

In the zone of supergene alteration, below the Cenozoic Kalahari unconformity, the Mn-carbonates and braunite are altered to a crypto- or microcrystalline assemblage of Mn^{4+}-oxyhydroxides, mostly todorokite, with subordinate manganomelane and pyrolusite (Table 3.1). Concentrations of todorokite and manganomelane increase sympathetically with increasing degree of supergene alteration in any specific lithostratigraphic zone (Table 3.1). On the other hand, a distinct increase of manganomelane relative to todorokite is apparent with increasing proximity to the Kalahari unconformity, irrespective of which lithostratigraphic zone is cut by the pre-

Kalahari erosion surface. Microcrystalline quartz, a product of mild silification, is restricted to the upper part of the supergene altered zone, immediately below the pre-Kalahari unconformity (Table 3.1). Manganomelane, either K-, Na- or Ba-rich, is concentrated in microscopic veinlets that crosscut supergene altered ore.

It is important to note that these general description and characteristics of the supergene altered braunite lutite, in direct contact with the Kalahari Formation, are applicable to all of the 22 cores logged in the study area.

3.2 Definition of terms

In order to avoid misunderstandings, a few terms commonly used in the mineralogical and petrographical descriptions below need to be defined. The term “stringer” refers to horizontally elongated aggregates of inter-connected, amalgamated ellipsoidal carbonate ovoids. The term “stylolite” refers to irregular suture-like boundaries in the ore. The stylolites display a typical “teeth” and “socket” structure and are filled by braunite and/or hematite in the unaltered ore. They are typically developed in carbonate rocks as a result of compaction and dissolution (Tucker, 1992). A late diagenetic formation of stylolites in the Mn orebody of the Hotazel Formation is indicated by crosscutting relationships with early diagenetic carbonate ovoids. The generally parallel disposition of the stylolite seams implies that dissolution was caused by an interaction between overburden pressure and pore waters. In the text reference is also made to “mineral (i)” which implies the first generation of a specific mineral and then “mineral (ii), mineral (iii) and mineral (iv)” which implies the second, third and fourth generations of a specific mineral, respectively.

3.3 Petrography

3.3.1 Unaltered braunite lutite

Detailed petrographic descriptions for the different lithostratigraphic zones in braunite lutite (Fig. 2.3) unaffected by supergene alteration can be found in Preston (2001). Observations made during this study are in very good agreement with those presented by Preston (2001). The unaltered braunite lutite has a microcrystalline matrix that is finely laminated (1-3mm) with small (<1mm) to medium-sized (1-3mm) ovoids and locally abundant carbonate laminae. Kutnahorite and calcite veinlets (Fig. 3.1A) (20 - 30µm) as well as braunite, haumannite and hematite stylolites (Fig.3.1B) are present in the unaltered braunite lutite.

The mesoscopic appearance of many of the lithostratigraphic zones is similar and transitions between zones are gradational (Fig. 2.3). However, there are several zones with very distinct features that can be easily identified in core and mine exposures. For example, the X3 and C-zones (Fig. 2.3) have very characteristic cloudy accretions of Mn-calcite pseudospar ovoids of small size and few thin calcite and Mn-calcite laminae that result in a distinctly banded appearance (1-5mm) (Fig. 3.1C). The M-zone (Fig. 3.1D), in contrast, has a unique mottled appearance with medium- size (1-3mm) carbonate ovoids and again only few thin carbonate lenses and laminae (1mm). The N-zone (Fig. 2.3) is characterized by a distinct decrease in ovoid size (> 1mm) and an abundance of unusually thick carbonate laminae (1-3mm).

The microcrystalline lutite matrix is the paragenetically earliest component present in the braunite lutite, its formation predates that of carbonate ovoids and carbonate laminae (early diagenetic) (Nel at al., 1986 and Gutzmer and Beukes, 1996). The matrix of braunite lutite of all lithostratigraphic zones in the Lower manganese ore bed is fine-grained (4-16µm) and consists mainly of kutnahorite and Mn-calcite pseudospar, microspar and micrite. The matrix carbonates are finely intergrown with microcrystalline anhedral braunite (i) (2-8µm), hematite (i, ii and iii) (1-10µm) and locally hausmannite (ii) (>10µm) (Fig. 3.2A). Ovoids of kutnahorite and Mn-calcite pseudospar to microspar are ellipsoidal with braunite (i), hematite (i, ii and iii) and hausmannite (ii) (>10µm) inclusions. They can have a massive or zoned

internal texture. Zoned ovoids have a rim or core of late diagenetic hausmannite (ii) (>10µm) or braunite (ii) (>10µm) that are finely intergrown with carbonate (Fig's. 3.1E and 3.1F). In zone M, ovoids have a very characteristic irregular shape, while in zones X3 and C ovoids occur as accretions. Some carbonate ovoids in the unaltered braunite lutite matrix occur as interlinked and amalgamated ovoids to form stringers. Carbonate laminae and lenses (1-3mm wide) are also composed of kutnahorite and Mn-calcite pseudospar to microspar with braunite (i), hematite (i, ii and iii) and hausmannite (ii) (>10µm) inclusions in the unaltered ore. The laminae may also have a zoned appearance with a late diagenetic hausmannite (ii) (>10µm) rim or core. The hausmannite in the ore is considered to be of late diagenetic/low-grade metamorphic origin. Euhedral apatite and barite are associated with late diagenetic hausmannite formation.

3.3.2 Weakly supergene altered braunite lutite

Weakly supergene altered ore is marked by 5-10 vol% porosity increase, micro-faulting along subvertical veinlets filled by supergene minerals, and the formation of microcrystalline todorokite and manganomelane at the expense of Mn-bearing carbonates, hausmannite and braunite (Fig's. 3.3A, B and C). However, the mineralogy of incipiently altered braunite lutite remains to be dominated by braunite and Mn-carbonates. Todorokite typically form along pre-existing stylolites (Fig. 3.3D). There is also the development of crosscutting and bedding-parrallel veinlets filled with microcrystalline todorokite and manganomelane. This suggests that meteoric fluid movement was controlled by pre-existing fractures or laminae of carbonate that were chemically most reactive. The matrix in weakly altered ore remains essentially unaltered (Fig. 3.3 E). Minor amounts of microcrystalline todorokite occur finely dispersed in carbonate ovoids and laminae in weakly supergene altered ore (Fig's 3.3 A, D, E and F).

3.3.3 Strongly supergene altered braunite lutite

Photographs of representative core samples of strongly supergene altered braunite lutite from the M, C and N zones (Fig. 2.12) illustrate the profound effects supergene alteration has on the macroscopic appearance of the manganese ore. Strongly altered braunite lutite immediately below the Kalahari unconformity (Fig. 2.13) is marked by an abundance of fractures filled by sparitic calcite or calcrete of the Kalahari Formation. These fractures constitute a network that, when very densely developed, results in complete disintegration of the braunite lutite. Advanced alteration is also marked by a large increase in secondary porosity (10-20%) (Fig's. 3.4 A and B), abundant micro faults (Fig's. 3.4 C and D) and the formation of finely interspersed microcrystalline quartz (1-8µm) (Fig's. 3.4 E and F), todorokite (<10µm) and manganomelane (<10µm) at the expense of all pre-existing mineral phases in the braunite lutite protore. Crosscutting and bedding-parallel veinlets, filled with intimately intergrown microcrystalline todorokite and manganomelane, are very common (Fig's. 3.4F and 3.5A).

Microscopic observations illustrate that remnants of kutnahorite microspar, the protore mineral most susceptible to weathering, are sometimes preserved even in zones of very strong supergene alteration (Fig. 3.5B). Former carbonate ovoids and laminae are partially to totally altered to Mn^{4+}-oxyhydroxides. Partially altered ovoids contain calcite or Mn-calcite rims, while ovoid cores are replaced entirely by a dense mass of todorokite and manganomelane (Fig's. 3.4 A, B and 3.5C). During advanced alteration former carbonate ovoids and laminae are replaced by microcrystalline quartz and/or manganomelane and todorokite that may constitute a very porous boxwork texture (Fig. 3.4B). Mn-bearing carbonates (kutnahorite and Mn-calcite) and hausmannite in matrix, ovoids and laminae are the first Mn-minerals to be affected during the early stages of supergene alteration. Kutnahorite, Mn-calcite and hausmannite are partly or totally replaced by porous aggregates of microcrystalline todorokite (Ca-Mg-rich) and Na-K-Ba-poor manganomelane.

Calcite, braunite and jacobsite are less susceptible to supergene alteration than Mn-carbonates. However, the presence of microcrystalline quartz associated closely with

Mn^{4+}- oxyhydroxides strongly suggests that it was derived from the decomposition of braunite during advanced stages of alteration. K- or Ba-rich manganomelane is especially adundant immediately below the Kalahari unconformity, and is finely intergrown with todorokite and quartz. With increasing distance from the unconformity Na-K-Ba-poor manganomelane predominates, next to todorokite (Ca-Mg-rich).

3.4 Mineralogy

3.4.1 Protore mineral assemblage

3.4.1.1 Oxides

Braunite ($Mn^{2+}Mn_6^{3+}SiO_{12}$) is the most abundant oxide mineral present in the unaltered ore (Table 3.1) and is microscopically interspersed with hematite and micritic to pseudosparitic Mn-carbonates. Braunite (i) is anhedral, fine to very fine-grained (grain size 5-10µm) and intimately intergrown with kutnahorite, Mn-calcite and hematite. A small amount of braunite occurs as anhedral inclusions in carbonate ovoids and laminae. Coarser-grained recrystallised braunite (ii) (>10µm) occurs as euhedral crystals in carbonate ovoids and laminae or as rims around ovoids and laminae.

Microcrystalline hematite (i) is present in the matrix, ovoids and laminae in various amounts and increases in abundance towards the top and the bottom of the Lower Mn-body (Table 3.1 and Fig. 3.2B). The hematite occurs as needles (1µm) (B and L zones) (Fig. 3.2B). and dusty anhedral hematite [hematite (i)] (1-2µm). The dusty hematite (i) is present in matrix, ovoids and laminae and occurs in all lithostratigraphic zones of the Lower Mn-body only. Hematite (ii) (3-5µm) is finely intergrown with braunite. Recrystallized hematite [hematite (iii)] is distinctly more coarse-grained (up to 10µm) than hematite (i) and (ii) and occurs as platy crystals (Fig. 3.2C) in carbonate ovoids and matrix (Ramos, 2001).

Jacobsite ($MnFe_2O_4$) (Fig. 3.2D) is restricted to the transition zone from manganolutite (B-Zone) to hematite lutite (L-Zone) in the lower Mn-body (see borehole Rex 44 in Table 3.1) (Kleyenstüber, 1985).

3.4.1.2 Carbonates

Kutnahorite is a member of the dolomite group with three distinct compositional varieties known from the Mamatwan-type ore (kutnahorite, Ca-kutnahorite and Mg-kutnahorite; Kleyenstüber, 1985). Kutnahorite ($Ca(Mn^{2+},Mg,Fe^{2+})(CO_3)_2$) is the most abundant carbonate mineral present in unaltered braunite lutite ore (Table 3.1). It is finely intergrown with braunite and hematite (Fig. 3.2B). Pseudosparitic, microsparitic and micritic kutnahorite are present in the matrix, ovoids and laminae, often closely intergrown with Mn-calcite. Some kutnahorite ovoids appear zoned with a Mg-poor kutnahorite core and Mg-bearing kutnahorite rim (Nel et al., 1986).

Mn-calcite can be found finely intergrown with Mg-poor kutnahorite or as large subhedral crystals in the core of ovoids and laminae (Ramos, 2001; Kleyenstüber, 1985). Calcite was observed in fractures (Fig. 3.2E) in Mn-calcite ovoids as well as in crosscutting veinlets. This calcite is regarded to be of late diagenetic origin (Fig. 3.1A). Kutnahorite and Mn-calcite are replaced by metasomatic hausmannite (Fig. 3.2A). This alteration can be observed as coarse-grained hausmannite (ii) rims (Fig. 3.2E) and aggregates replace carbonate ovoids and laminae.

Hematite, braunite and jacobsite stylolites occur along the border of some carbonate laminae and are thought to be the product of late diagenetic compaction (Fig. 3.1B).

3.4.1.3 Sulfates

The occurrence of barite ($BaSO_4$) in the Mamatwan area was reported first by Preston (2001). Results of the latter study suggested that barite may have formed during supergene alteration of braunite lutite (Fig. 3.5D). In the present study, however, barite was also observed as minute (2µm) anhedral grains that are enclosed in hausmannite aggregates in unaltered Mamatwan-type ore (Fig. 3.2F), i.e., barite is rather of metasomatic/metamorphic than supergene origin.

3.4.2 Late diagenetic to early metamorphic mineral assemblage

The formation of serpentine and hausmannite is tentatively attributed to late diagenesis and/or incipient metamorphism. Trace amounts of serpentine ($Mg_3SiO_5(OH)_4$) (<5µm grain size) occur intergrown with kutnahorite, Mn-calcite and braunite in the unaltered ore (Fig. 3.1E). The serpentine forms accretions of anhedral grains (1-2µm) in carbonate ovoids and in the unaltered braunite lutite matrix; it appears to be of late diagenetic or low-grade metamorphic origin (Preston, 2001). Kleyenstüber (1985) observed the alumino-serpentines only in the hematite lutite, however, it was observed throughout the unaltered manganese ore in this study. Hausmannite (Mn_3O_4) (>10µm) occurs in small amounts as metasomatic-metamorphic replacement product of Mn-bearing carbonate ovoids and laminae (Fig. 3.2A). Hausmannite is usually associated with pseudosparitic Mn-calcite, kutnahorite, hematite, braunite and rarely also with barite. In some instances, hausmannite occurs as spherical coarse-grained hausmannite (>10µm) accretions with barite inclusions (Fig's. 3.1A and 3.5A). Apatite ($Ca_5(PO_{4,}CO_3)_3(F,OH,Cl)$) (5-10µm) inclusions are observed in late diagenetic hausmannite in kutnahorite micrite laminae (Fig. 3.2A).

3.4.3 Supergene mineral assemblage

3.4.3.1 Oxides

Todorokite (Ca, Na, K)$(Mg,Mn^{2+})Mn^{4+}{}_5O_{12}\cdot xH_2O$ is arguably the most important neoformed constituent in the weakly and strongly supergene altered ore, with the amount of todorokite increasing sympathetically with the degree of supergene alteration. Microcrystalline fibres or needles of todorokite (Fig. 3.5A) constitute dense and porous masses that replace kutnahorite, Mn-calcite, braunite and hausmannite. Todorokite is always intimately intergrown with manganomelane and residues of pre-existing minerals, most notably hematite (Fig. 3.5E). Fibrous to asbestiform todorokite occurs also as infill of veinlets that crosscut weakly to strongly supergene altered ore in the study area (Gutzmer and Beukes, 2000).

The term manganomelane refers to a group of closely related supergene Mn^{4+}-oxyhydroxides with the general formula $(Na, K, Ba)_{2-y}(Mn^{4+}, Mn^{2+}, Fe^{3+})_{8-z}O_{16-x}\bullet (H_2O)_x$ (Gutzmer, 1996). End members in this group include cryptomelane (K), manjiroite (Na), romanèchite (Ba) and coronadite (Pb). Manganomelane forms at the expense of braunite lutite along the Kalahari unconformity. It varies considerably in composition, and may be either K, Ba or Na- rich. Microcrystalline manganomelane (<1µm) occurs finely intergrown with todorokite (<1µm) in all supergene altered ores. Its abundance, however, increases considerably in close proximity to the Kalahari unconformity surface. Cryptomelane (1µm) and romanèchite (1µm) were identified as aggregates of thin needles filling microscopic veinlets that crosscut the supergene altered ore. The occurrence of asbestiform manganomelane and todorokite was studied in detail by Gutzmer and Beukes (2001) at Smartt mine. Minor amounts of pyrolusite and quartz occur finely intergrown with manganomelane and todorokite. The intergrowth is submicroscopic so that pyrolusite could only be identified by means of XRD, and quartz only by XRD and SEM.

Hematite (iv) (5µm) forms as a result of supergene processes from anhedral or needle-shaped hematite (i). Hematite (iv) appears to form microcrystalline aggregates of anhedral to collomorphous appearance (Fig. 3.5 E).

Quartz (SiO_2) – Microcrystalline quartz is present in strongly supergene altered ore in close proximity to the Kalahari unconformity. It is always intimately intergrown with todorokite and manganomelane and it may have formed by advanced decomposition of braunite (Fig's. 3.4F and 3.5D).

3.5 Summary

A detailed discussion of the petrography and mineral paragenesis of unaltered braunite lutite has been presented recently by Preston (2001), and there are only few new observations/corrections that arise from the present study. Braunite, hematite and Mn-carbonates (kutnahorite and Mn-calcite) are the main mineral constituents of unaltered braunite lutite (Preston, 2001). Hematite and braunite stylolites occur in several lithostratigraphic zones, suggesting that these oxide minerals formed prior to final lithification. Hausmannite stylolites occur as a result of the alteration of braunite stylolites present in the matrix during late diagenetic processes, with fluid migration focused along the pathways provided by stylolites**.** Serpentine occurs in trace amounts in all lithostratigraphic zones of the Lower Mn-Body and appears to be cogenetic with hausmannite and calcite that are widely regarded to be of late diagenetic to early metamorphic in origin.

Minute anhedral grains of barite, closely intergrown with hausmannite, were observed in the matrix of unaltered braunite lutite in several samples. Barite appears thus to be cogenetic with hausmannite, i.e., late diagenetic or metamorphic in origin and not supergene, as suggested by Preston (2001). Apatite was for the first time observed in unaltered braunite lutite and may be regarded as the source of minor, but measurable phosphorous concentrations in braunite lutite.

Systematic and consistent mineralogical transformations mark the transition of unaltered braunite lutite to strongly supergene altered ore along the Cenozoic Kalahari Unconformity. The supergene alteration is marked in particular by carbonate dissolution, associated with the generation of abundant secondary porosity, and the formation of microcrystalline todorokite and manganomelane and minor amounts of pyrolusite and quartz. Mn-bearing carbonates (kutnahorite and Mn-calcite) and hausmannite in matrix, ovoids and laminae are most susceptible to weathering; they are partly or completely replaced by porous aggregates of microcrystalline todorokite and manganomelane. Calcite, braunite and jacobsite appear less susceptible during the incipient stages of weathering, but the occurence of microcrystalline quartz during advanced weathering strongly suggests braunite decomposition. Among the major mineral phases least affected by weathering appears to be hematite. Although ramsdellite was observed in earlier studies (De Waal, 1969), it was not observed during the course of this study.