Chapter 6

Discussion and Conclusions

6.1 Controls of supergene alteration

It is the objective of this study to report the changes in mineralogical, petrographical and geochemical characteristics associated with supergene alteration of braunite lutite of the Lower manganese ore body in the Kalahari manganese field below the sediments of the Kalahari Formation. The reason and framework for this study was the Smartt-Rissik exploration project of SAMANCOR that targeted the altered ores on the farm Rissik in the southern part of the KMF.

Several geological parameters control the supergene alteration of carbonate-rich braunite lutite of the Lower manganese ore bed in the southern part of the Kalahari deposit. The most obvious of these is the exposure of the ore bed along the erosive unconformity overlain by the Cenozoic sediments of the Kalahari Formation. The degree of supergene alteration decreases rapidly with increasing depth below the Kalahari unconformity. It is usually minimal wherever a cover of cherty iron-formation separates the manganese ore beds from the overlying Kalahari Formation (Boardman, 1964).

In the study area, the manganese bed dips to the southwest and is affected by slight warping (folding) and local E-E-W trending dykes and faults (Fig. 2.5). The influence of faults, dykes and downward migrating meteoric water are illustrated by the fact that the thickness of supergene altered ore increases from 5m up to 25m in the vicinity of faults and dykes. The latter structures are thus an important control in supergene alteration processes probably by providing pathways for the downward migration of meteoric water from the Kalahari unconformity down into the Mn ore bed.

The carbonate-rich braunite lutite of the Lower manganese ore bed is altered to a micro- to cryptocrystalline, carbonate poor assemblage composed of todorokite, manganomelane, little pyrolusite, residual braunite and minor quartz. Former white and pink carbonate ovoids and laminae in primary sedimentary ore are altered to silver metallic ovoids and laminae composed of Mn^{4+}-oxyhydroxides. Locally, stratiform veins filled by asbestiform manjiroite, todorokite, calcite and quartz occur in this altered zone (Gutzmer and Beukes, 2000). Invasion of calcrete along fractures and bedding planes is restricted to the immediate erosional contact with the Kalahari Formation. These calcrete-filled fractures crosscut supergene altered manganese ores as well as manganomelane-todorokite veins.

6.2 Mineral Paragenesis

A decrease in carbonate abundance and an increase in the abundance of todorokite and manganomelane and quartz are associated with increasing proximity to the actual physical Kalahari unconformity and the associated increase in the degree of supergene alteration. Microcrystalline todorokite (Ca-Mg-rich) and Na-K-Ba-poor manganomelane form during the early stages of weathering, suggesting predominance of carbonate-derived Ca and Mg in the weathering solution possibly at low fluid/rock ratios. The abundance of Na, K and Ba-rich manganomelane, often concentrated in veinlets, during advanced stages of weathering, may be used to suggest that these large cations were introduced by meteoric fluid and that higher fluid rock ratios prevailed during their formation. All three elements, Na, K, and Ba, can be transported in significant concentrations by meteoric, SO_4-deficient meteoric water at low temperature (Burns & Burns, 1979). These elements are also known to be efficiently incorporated into supergene Mn^{4+}-oxyhydroxides during weathering ((Burns & Burns, 1979) Fig. 6.1). Their formation thus indicates the degree of interaction between former braunite lutite and descending weathering solutions.

An increase in abundance of veinlet-hosted manganomelane close to the Kalahari unconformity can be attributed to infiltration of meteoric water along available pathways whether it was fractures, joints or secondary porosity. Abundant secondary porosity generated during weathering enabled more efficient lateral penetration of meteoric water during the advanced stage of weathering, i.e., chemical weathering may be regarded as a self-accelerating process. In the presence of large concentrations of Na, K and Ba, manganomelane group minerals appear much more stable than Ca-Mg-rich todorokite or pure MnO_2-phases (especially pyrolusite). Hematite (iv) (Fig. 6.1) represents hematite of supergene origin and occurs as microcrystalline aggregates of anhedral to colloform appearance.

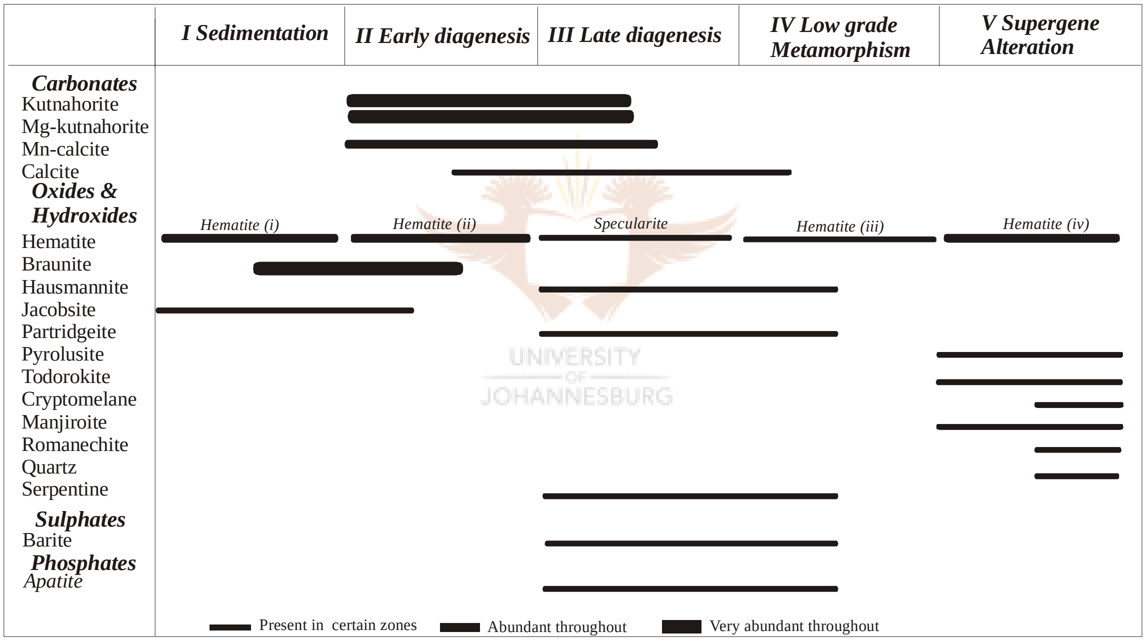

Figure 6.1 Mineral paragenetic table illustrating the effects of diagenesis, low-grade metamorphism and supergene alteration of braunite lutite (modified from Preston, 2001).

6.3 Geochemical Changes

Element fluxes, enrichment and depletion of major and trace elements were quantified by mass balance calculations. A preliminary assessment of the amounts of CO_2 reserved and the H_2O introduced during supergene alteration suggests that between 100 – 200 kg/t CO_2 was removed and a similar mass of water was introduced during supergene alteration of the carbonate-rich braunite lutite (Fig. 6.2). These two components are thus probably the most mobile constituents in the supergene altered zone below the Kalahari unconformity.

M, C and N-zone

Enriched			**Leached**	
Na_2O	3kg/t		**Mn_3O4**	129kg/t
K_2O	6kg/t		**Fe_2O_3**	22kg/t
Sr	306g/t		**CaO**	127kg/t
Ba	247g/t		**MgO**	16kg/t
Zn	67g/t		**P**	128g/t
H_2O	100-200kg/t*		**B**	510g/t
			CO_2	100-200kg/t*

* no actual geochemical data available, estimates only.

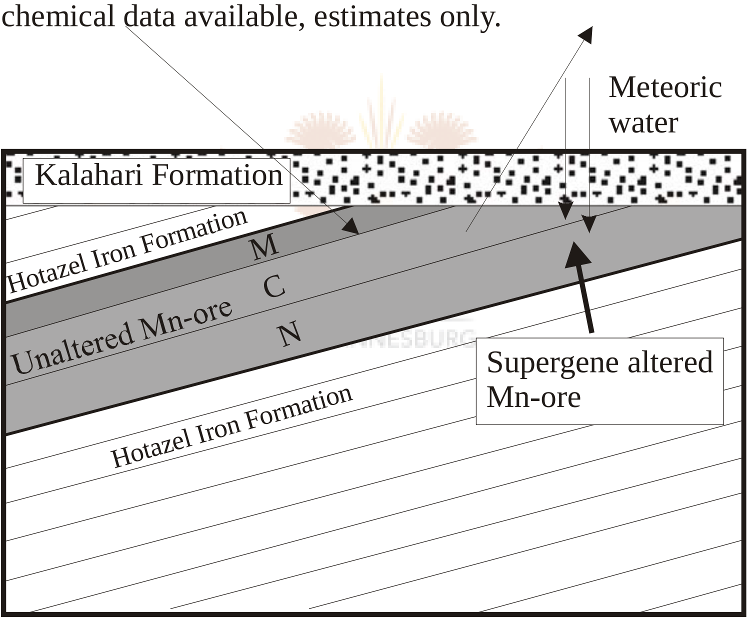

Figure 6.2 Schematic summary illustrating the enrichment and leaching of major and trace elements as a result of meteoric water influx into the M, C and N-zones of the lower Mn orebody along the Kalahari suboutcrop of the Hotazel Formation.

Results of mass balance calculations illustrate also that the leaching of CaO (127kg/t), Fe_2O_3 (22kg/t) and Mn_3O_4 (129kg/t) reach similar magnitudes to the mobility of H_2O and CO_2 (Fig. 6.2). The net removal of manganese is certainly surprising and leads to the conclusion that the observed enrichment of manganese is indeed a relative one, i.e., it is enriched only because other constituents are more efficiently leached. Although Mn_3O_4 and Fe_2O_3 are leached during supergene alteration, Mn/Fe ratios appear to be consistent with those in the unaltered ore. A possible explanation for this phenomena is that Mn_3O_4 and Fe_2O_3 were leached in similar proportions. Leaching of MgO (16kg/t) and introduction of Na_2O (3kg/t) and K_2O (6kg/t) are significant but quantitatively of little importance as element fluxes are only in the order of 3-6 kg/ton of manganese ore (Fig. 6.2).

Phosphorous (128g/t) and boron (510g/t), deleterious elements during the production of steel, are both efficiently leached during supergene alteration of the primary manganese ore. The depletion of phosphorous may point to the dissolution of apatite, whereas leaching of boron is most probably due to the decomposition of braunite (Wasserstein, 1943).

Trace elements that have increased in abundance during supergene alteration include Sr (306g/t), Ba (247g/t) and Zn (67g/t). All three are known to be easily incorporated into the structure of supergene Mn^{4+}-oxyhydroxide minerals (Burns & Burns, 1979; Nicholson, 1992).

It is difficult to pinpoint the source(s) for elements such as K_2O, Na_2O, Sr, Zn and Ba, introduced or enriched during alteration of braunite lutite. Kleyenstüber (1993) suspected clays of the basal Kalahari Formation as the source for K_2O enrichment in the altered ore. Whatever the source, descending meteoric water and ground water migrating along the erosional contact between the Kalahari Formation and the underlying Hotazel Formation can certainly be regarded as the transport medium. Such meteoric fluids should have been, oxidizing (high Eh) and of low temperature (25-50ºC). They would also have been undersaturated with respect to CaO, MgO and CO_2. Over geological time scales such a fluid would have been able to interact efficiently with the braunite lutite, resulting in the decomposition of Mn-rich carbonates, uptake of CaO and MgO and the formation of highly oxidised water-bearing Mn^{4+}-oxyhydroxides of typical supergene origin (Nicholson, 1992). The generation of secondary porosity as a result of carbonate decomposition enhanced the reaction progress. The generation of secondary porosity is reflected by significantly lower whole rock densities in supergene altered ore relative to unaltered ore. Porosity may have subsequently been alleviated by compaction, as indicated by negative values for strain derived during mass balance calculations (Table 4.5). Strains vary considerably (from values close to zero ranging between –10 and 10% up to 57% compaction) and it is interesting to note that the most carbonate-rich zone, the C-zone (Fig. 2.3) displays the greatest amounts of compaction, i.e., the greatest amount of carbonate dissolution (Table 4.5).

6.4 Geochronology

Since the breakup of Gondwana the South African Subcontinent has been submitted to a complex history of uplift and physical erosion. The African surface with its deep weathering profiles can be used as a datum for all structural influences on the subcontinent. The first landscape cycle (Post African I) was initiated by uplift and a slight westward tilt at 18 Ma (Partridge and Maud, 1987) or 30 Ma (Burke, 1996) (Fig. 6.3). The second landscape cycle (Post African II) followed at 2.5 Ma (Partridge and Maud, 1987) or 2.8 Ma (Burke, 1996) (Fig. 6.3) and was marked by further uplift and westward tilting. Deep physical erosion followed by chemical weathering are associated with these two landscape cycles. $^{40}Ar/^{39}Ar$ age dating was done on samples from a strongly supergene altered reference borehole (Rex 2) (Fig. 6.4) to determine the onset of chemical weathering and the vertical dimension of chemical weathering. The weathering process may have coincided with or may have predated the onset of deposition of the now calcretized lacustrine and terrestrial sediments of the Kalahari Formation. Furthermore, the demise of physical erosion can be expected to have postdated a final pulse of uplift of the South African Subcontinent, and the development of the Post African I erosional surface. Results presented in this study suggest that the latter event may, in fact, have taken place at about 45 Ma ago. The complexity of the age distribution for both the M and C-zones indicate that the development of the weathering profile below the Kalahari unconformity was a long-lasting multi-stage process. The amount of data available at this stage appears insufficient to discriminate between different stages of

more enhanced (humid) and more subdued (semi-arid and arid) climatic periods. However, the observation that the weathering front progressed very slowly through the Mn-rich braunite lutite (<10m in 40Ma, <0.25m/Ma), producing a very uniform and microcrystalline supergene mineral assemblage, strongly suggests that a more detailed geochronological study involving a larger set of more closely spaced samples, could perhaps yield a very good record of Cenozoic climate change for the interior of the South African subcontinent in Post Gondwana times.

The lithostratigraphic zone near the bottom of the weathering profile (N-zone) gives a very well defined peak at ca. 5 Ma. This age may mark the last episode of prominent chemical weathering and the formation of abundant supergene Mn-oxyhydroxides. This may possibly coincide with the development of the Post African II land surface (Fig.6.4), preceding widespread desertification and deposition of the uppermost wind blown Hutton sands that cover the calcretes of the middle Kalahari Formation (Fig. 2.6).

6.5 Conclusions

The major characteristics of the alteration process of unaltered Mamatwan type ore to supergene altered braunite lutite is summarized in figure 6.5. The process proceeded as follows:

- Leaching of Mn-carbonates and Mn^{2+}/Mn^{3+} oxides.
- Formation of Mn^{4+}-oxyhydroxides and quartz.
- Decrease in relative density of the ore.
- Increase in porosity of the ore.
- Leaching of CO_2, Mn_3O_4, Fe_2O_3, CaO, MgO, P, B form the ore. Enrichment of H_2O, Na_2O, K_2O, Sr, Ba, Zn in the ore.
- Enrichment of H_2O, Na_2O, K_2O, Sr, Ba, Zn in the ore.

A preliminary geochronological study of microcrystalline todorokite and manganomelane mixtures of supergene origin in the Kalahari manganese field yield complex yet very promising results. Chemical weathering processes along the Cenozoic Kalahari

Unconformity appear to have been more affected the manganiferous lithologies of the Hotazel Formation from 45 Ma onwards to 5 Ma ago. During this time physical peneplanation of the area must have been minimal and chemical weathering (supergene alteration) of the ore apparently peaked at about 26 Ma ago (Fig. 6.3). The weathering front processes very slowly through the Mn-rich braunite lutite (<10m in 40Ma; <0.25m/Ma); producing a very uniform and microcrystalline supergene mineral assemblage with distinct characteristics. Age distributions are complex and suggest that chemical weathering and recrystallisation processes were ongoing over the entire period of time from 5 Ma up to 45 Ma ago. Ar-Ar geochronology results are promising and more detailed investigations in future could potentially reveal climatic modulation between more arid (less intense chemical weathering) and more humid (more intense chemical weathering) climatic pulses in post Gondwana times in southern Africa. Given the microcrystalline and very uniform compact character of the supergene manganese ores developed and the obvious slow progression of the weathering front (Fig. 6.5), it appears very likely that a more detailed study of the chemical weathering of the manganese ores of the Hotazel Formation will yield much more conclusive paleoclimatic results than previous ^{40}Ar-^{39}Ar geochronological studies. Investigation reviewed by Vasconcelos (1999) have all focused on lateritic weathering caps in modern or ancient tropical settings. These weathering profiles are texturally and mineralogically much more complex, than the weathering profile developed below the Kalahari unconformity in the Hotazel Formation.