

Chapter 4

Geochemistry

4.1 Introduction

Representative samples (as defined in section 1.5, chapter 1) from the economic zone of the lower Mn orebody, including the lithostratigraphic zones M, C and N, from eight drill cores in the study area (Fig. 1.4) were selected for whole rock chemical analysis to represent all stages of supergene alteration. Although the X-zone has very good manganese grades, it was not used for modeling purposes, as it is eroded over large parts of the suboutcrop area below the Kalahari Formation and very few drill cores intersect strongly supergene altered X-zone. Among the 8 selected drill cores Rex 16, 44 and 85 represent the geochemistry of unaltered braunite lutite protore, Rex 70, 71 and Rex 74 represent weakly supergene, and Rex 2 and 24 strongly supergene altered braunite lutite (Fig. 4.1). It is important to note that for comparative purposes and mass balance calculations, it was necessary to link supergene altered samples to unaltered reference samples of the same lithostratigraphic zone from different core intersections (Table 4.1). To assure compatibility, unaltered reference samples were selected from drill cores located in close proximity to the altered drill cores to be evaluated. Consequently, samples from REX 16 are reference for REX 2, 24 and 74, and samples from REX 85 are used as reference for REX 70 and 71 (Fig.4.1).

It should be noted that the degree of alteration of any one specific ore zone depends very much on how deep below the Kalahari unconformity it was intersected in drill core. Highly altered M, C and N-zone samples are only available in cores Rex 24 and 2 which intersect these lithostratigraphic zones immediately below the Kalahari Formation (Fig. 4.1). This is clearly indicated in figure 4.1 where the cores with unaltered M, C and N material are located down dip to the west of the Kalahari unconformity.





4.2 Whole rock geochemistry of major and trace elements

Manganese, iron, silica, calcium and CO₂ represent the most abundant constituents in the low-grade manganese ores of the KMF (Preston, 2001) (Table 4.1). Minor but distinct concentrations of Mg occur in the unaltered braunite lutite, while an abundance of Na and K is characteristic for strongly supergene altered ore. For unaltered braunite lutite, the major element composition of all lithostratigraphic zones is fairly uniform throughout the study area and compares well with data reported by Ramos (2001) for the Mamatwan Mine area. Trace elements, in contrast, display considerable variations between the different unaltered reference boreholes (Table 4.2).

Systematic enrichment or depletion of major and trace elements related to supergene alteration along the Kalahari Unconformity can be deciphered by comparison with the geochemistry of unaltered reference drill cores. A decrease in Mn₃O₄ content (Fig. 4.2) is marked to the west of the suboutcrop of the Lower manganese bed against the Kalahari Formation. Mn enrichment is distinct for altered manganese ore along the suboutcrop compared to unaltered braunite lutite that is covered by banded iron formation (Fig. 4.2). Contour maps of whole rock geochemical analyses illustrate elevated Mn₃O₄ concentrations in the northern and eastern corner of the study area for the economic zones in the Lower Mn-orebody and confirm the latter statement (Fig. 4.2). The maps produced for M, C and N-zones illustrate similar trends, differences can be attributed to the lack of drill core data in specific areas (Fig.4.2). Elevated Mn₃O₄ concentrations are evident along the eastern perimeter of these contour maps and correspond to the suboutcrop of the Lower manganese ore bed against the Kalahari Unconformity. Two areas of particularly high grade can be identified in the contoured area: one at Rex 89 and the other from Rex 80 northwards (Fig. 4.2). Together with Mn, Fe concentrations are elevated (Table 4.1) in the strongly supergene altered ore and this is expressed as Mn/Fe ratios that are fairly consistent for unaltered and strongly supergene altered ore.



4.2.1 Unaltered ore

Major constituents of the Lower Mn-body are Mn_3O_4 , Fe_2O_3 and CaO. Greatest Mn concentrations occur in the X, M, C and N-zones, reaching an excess of 50wt% Mn_3O_4 . An inverse covariation is observed between Mn_3O_4 and all other major elements including Fe_2O_3 , CaO and also MgO (Fig's. 4.3 and 4.4). The carbonate-rich C-zone is an exception to this rule, as CaO has a positive correlation with Mn_3O_4 . Greatest iron concentrations are observed in zones constituting the transition of braunite lutite to BIF (B and L-zones) (> 10%) as reflected also by decreasing Mn/Fe ratios, making these zones uneconomic to mine. The greatest MgO concentrations (4-5 wt%) are restricted to the V, W and L-zones. The greatest CaO concentrations are present in the V, X1 and Y-zones (> 20 wt%). The concentration of SiO_2 increases dramatically only in the L-zone (> 10%). The major element data concur with the work done by Preston (2001), except for an on average 5 wt% drop in Mn_3O_4 concentration between G558 (reference drill core from Ramos, 2001) and REX drill cores (Figure 4.5 A). Other major element concentrations are rather uniform throughout the study area.

There are, some important vertical geochemical trends that can be recognised when comparing the trace element geochemistry of different lithostratigraphic zones in one specific drill core (Fig's. 4.3 and 4.4):

- B is elevated in the X2, X3, Z, M and C-zones (600-1000ppm).
- P is elevated in the Y, B and L-zones (255-333ppm).
- Concentrations of V, Rb, Sr and Ti appear to change randomly.
- Co is marked by elevated concentrations in the X2 and L-zones (61-69ppm).
- Ni is elevated in the X1-zone (179ppm).
- Cu concentrations are elevated in the X, Y and M-zones (4-52ppm).

The M, C and N zones in, particular, are marked by the following relative trends of enrichment or depletion (Fig.4.4):

- The M-zone has elevated B, Cu and Cr concentrations.
- The C-zone is marked by elevated concentrations of B, Ba, Zn and Pb.





Lateral geochemical trends for trace elements in specific lithostratigraphic zones in unaltered braunite lutite show little consistency, but can be summarised as follow (Fig. 4.5):

- Concentrations of P (131 to 277ppm) and Sr (130 to 540ppm) both increase towards the north.
- Ba concentrations vary randomly between 300 and 1300ppm.
- The concentrations of boron remains virtually constant.
- There are considerable differences in the trace element geochemistry for each drill core intersecting unaltered braunite lutite (Rex 16, 44, 85; Appendix 4 and fig's. 4.3 and 4.4).

4.2.2 Supergene altered ore

Petrographic studies illustrated (see Chapter 3) that weakly supergene altered ore represents the transition between unaltered ore and strongly supergene altered ore. It is thus not surprising that no consistent geochemical trends in major as well as trace element geochemistry were observed for the weakly supergene altered ore; it is thus not discussed in any further detail (Tables 4.1-4.2).

The strongly supergene altered ore, in contrast, displays distinct and consistent geochemical changes compared to unaltered braunite lutite. The M, C and N-zones display very similar lateral trends for major and also trace element concentrations as a response to supergene alteration (Tables 4.1-4.2). There is a definite increase in Mn_3O_4 , Fe_2O_3 , SiO_2 , K_2O and Na_2O and a corresponding decrease in MgO and CaO . K_2O and Na_2O , in particular, are very strongly enriched during supergene alteration (Table 4.1 and Fig's. 4.5 F, G, 4.6 D, E, 4.7 B and C). It is important to note that Mn/Fe ratios remain fairly unaffected by the alteration process (Table 4.1). Among the trace elements only boron decreases markedly during supergene alteration (Fig's. 4.6 A, G and 4.7 E). Enrichment is evident for Ba but also Zn, V, Cr, Rb, Sr, Cu, P and Pb (Table 4.2; Fig's. 4.5 H; 4.6 B, F, G, H and 4.7 D, E, F). Co, Ni, Ti, Y and Li concentrations stay rather







constant with reference to the unaltered ore (Table 4.2; Fig's. 4.5 H; 4.6 B, F, H and 4.7 D,E and F).

4.3 Whole rock density measurements

Densities for unaltered ore samples virtually devoid of porosity were determined using the following formula:

$$\rho_G = G_G / (G_G - G_W) * \rho_T$$

Where ρ_G = density of sample

G_G = weight of sample in air

G_W = weight of sample in water

ρ_T = density of water at temperature T

The density of supergene altered ore samples with distinct porosity was determined by first measuring the weight of selected block samples in air. The samples were then coated completely with candle wax (to prevent the abundant secondary pore space to be filled by water). The coated samples were also weighed first in air and then in water. The results were corrected for the contribution of the wax coating to the measurement taken. The density of the wax (0.96 g/cm³) was determined by measuring the weight of a 1cm³ block of candle wax (Gutzmer, 1996).

$$\text{Formula: } \rho_{cr} = (\rho_G * G_G / G_{cr}) - (\rho_{cw} * (G_G - G_{cr}) / G_{cr})$$

Where: ρ_{cr} = corrected density of sample (g/cm³)

G_G = weight of coated sample in air (g)

ρ_G = uncorrected density of sample (g/cm³)

G_{cr} = weight of sample without candle wax coating in air (g)

ρ_{cw} = density of candle wax (0.96 g/cm³)

The density of unaltered braunite lutite ($3.51 - 3.8 \text{ g/cm}^3$) is distinctly higher than that of altered ores. Densities exceeding 3.6 g/cm^3 were measured for samples of unaltered ore in the X2, X3, Z, M1, M2, M3, C1, C2 and N zones (Table 4.3 and Fig. 4.8). Weakly supergene altered ore has very variable densities, ranging between 2.8 g/cm^3 and 3.4 g/cm^3 , while strongly altered supergene ore has densities as low as 2.0 g/cm^3 . This is a reflection of the porosity developed during supergene alteration (Fig. 4.8 and Appendix 3).

4.4 Mass Balance Calculations

Mass balance calculations are often used to quantify true changes in chemical composition, porosity and volume that accompany alteration processes (Gresens, 1967). Although Gresens' (1967) classical method to estimate changes in volume and concentrations during metasomatism have been applied to many hydrothermal alteration systems, Brimhall et al. (1985) and Brimhall and Dietrich (1987) have illustrated that the same equation is well-suited to characterize the effects of supergene alteration. Brimhall and Dietrich (1987) used the relationship between whole rock density, porosity, mineral density and strain to quantify the effects of chemical weathering. The availability of an accurate geochemical data set and whole rock density data, and the identification of one (or several) elements that remained immobile during the alteration process constitute the foundation for all mass balance calculations.

Gresens' (1967) basis for "composition-volume" diagrams was modified and simplified by Grant (1986) to a linear relationship between the concentration of a chemical component in an altered rock and that of its unaltered precursor:

$$\Delta C_i = f_v \cdot (\rho^A / \rho^O) \cdot c_i^A - c_i^O$$

ΔC_i = gain or loss of component i (in wt% or ppm)

f_v = volume factor



- ρ^O = density of unaltered sample (g/cm^3)
 ρ^A = density of altered sample (g/cm^3)
 c_i^O = concentration of component i in unaltered sample (in wt% or ppm)
 c_i^A = concentration of component i in altered sample (in wt% or ppm)

The volume occupied by the material present in the unaltered sample can be obtained by multiplying the volume of altered material by a volume factor (f_v). Grant (1986) simplified Gresens' formula further by proving that $f_v \cdot (\rho^A/\rho^O)$ can be replaced by c_x^O/c_x^A , which represents the ratio of an immobile element in the unaltered rock to the same immobile element in the altered rock.

$$\Delta C_i = c_x^O/c_x^A \cdot c_i^A - c_i^O$$

- ΔC_i = Gain or loss of component I (in wt% or ppm)
 c_i^O = Concentration of component i in unaltered sample (in wt% or ppm)
 c_i^A = Concentration of component i in altered sample (in wt% or ppm)
 c_x^O = Concentration of immobile monitor x in unaltered sample (in wt% or ppm)
 c_x^A = Concentration of immobile monitor x in altered sample (in wt% or ppm)

The latter formula requires the identification of an immobile element, i.e., an element that has remained unaffected by the alteration process ($\Delta C_i = 0$). This immobile element will, in a XY-plot presenting C_i^A against C_i^O , define the so-called isocon, i.e. a line of zero concentration change that runs through the origin of the XY-plot. The slope of this isocon defines the mass change associated with the alteration, and the deviation of data points from the isocon defines the concentration change of the corresponding component (Grant, 1986). The isocon diagram thus enables us to determine immobile elements graphically and to monitor gains and losses.

Isocon diagrams (Fig. 4.9) were drawn in an attempt to identify elements that behaved immobile during supergene alteration of braunite lutite. This was a difficult task, as most



major and minor elements appear to have been mobilised during supergene alteration and constituents commonly regarded as being immobile in supergene and hydrothermal environments (Zr, Al, Ti) (Maclean, W.H. and Kranitiotis, P., 1987) are present only in very low concentrations in the chemical sedimentary rocks of the Hotazel Formation. However, the comparative study of all data revealed that TiO_2 appeared least affected by supergene alteration and this component was thus selected to construct the isocon, i.e., to establish the line of zero concentration change. The reciprocal of the slopes (Fig. 4.9) were then used to calculate the mass gain or loss during supergene alteration, following Olsen and Grant (1991). With reference to the isocon defined by Ti as immobile element, inconsistent mass changes are indicated for weakly altered braunite lutite, ranging from 18% mass loss (M-zone, Rex 71), to 14% mass gain (N-zone, Rex 71, Fig. 4.9). Strongly supergene altered ore, however, yields consistent mass losses, ranging from 17% (N-zone) to as much as 63% (C-zone, Rex 2, Fig. 4.9). Mass balance calculations were executed only for major and selected trace elements (with concentrations exceeding 5ppm) (Table 4.4 and 4.5). The gains and losses of trace elements are reported in ppm and for major elements in wt% (Tables 4.4 and 4.5, Fig. 4.10).



4.5. Summary

It was the aim of this investigation to describe the qualitative and quantitative changes of mineralogy and geochemistry associated with the alteration of carbonate-rich braunite lutite (Mamatwan-type ore) immediately below the Kalahari unconformity. The geochemical characterisation of the protore, i.e., braunite lutite of the M, C and N zones of the Lower Mn orebody, yielded results very well comparable to those reported by Ramos (2001) for the same lithostratigraphic zones in the Mamatwan mine lease area to the south of the present study area, the farm Rissik. This confirms the lateral continuity not only of the lithostratigraphic zonation but also of the chemostratigraphy of the Lower manganese orebody in the Kalahari deposit. It is, however, important to note that Mn-grades drop significantly (up to 5 wt% Mn_3O_4) in the unaltered braunite lutite from the Mamatwan Mine area into the Smartt-Rissik area. This drop in Mn-grade is not







associated with a significant change in Mn/Fe ratio. The decrease in Mn-grade is compensated by an increase in carbonate (Ca, Mg but also Sr) content. The concentration of phosphorous, possibly in the form of apatite, increases systematically with increasing carbonate concentrations. This may suggest that phosphate was co-precipitated with carbonates. Other trace elements vary randomly.

Incipient alteration of this carbonate-rich braunite lutite protore along the Kalahari Unconformity does not yield any significant geochemical trends and it appears most appropriate to regard this stage of supergene alteration as a simple transition of braunite lutite to strongly altered manganese ore.

The strongly altered ore is marked by the formation of microcrystalline todorokite and manganomelane on the expense of carbonates (Mn-calcite and kutnahorite) and braunite (see Chapter 3), and the corresponding geochemical changes are also apparent. Concentrations of alkali elements (Na_2O , K_2O) and of BaO increase dramatically; CaO and MgO, in contrast, decrease sharply. These changes are in obvious agreement with mineralogical transformations; carbonates decompose and CaO and MgO hosted by kunahorite and Mn-calcite are leached. Todorokite and manganomelane that form on the expense of the carbonates incorporate some earth alkali elements, but also significant concentrations of Na_2O , K_2O and BaO that must have been introduced during the alteration process. The formation of manganomelane and todorokite suggests widespread, but not complete oxidation of the braunite lutite from Mn^{2+} and Mn^{3+} (carbonates and braunite) to Mn^{4+} .

Boron is the only trace element that illustrates a decrease in concentration. Ba, but also Zn, V, Cr, Rb, P, Sr, Cu and Pb are enriched during supergene alteration. These qualitative changes in trace and major element concentrations were quantified using mass balance calculations.

Mass balance calculations aptly illustrate the effective leaching of CaO, MgO, Fe_2O_3 , Mn_3O_4 . Leaching of Fe_2O_3 and Mn_3O_4 occur to a very similar degree, resulting in

virtually unchanged Mn/Fe ratios. The latter results provide strong evidence that the observed increases of Fe_2O_3 and Mn_3O_4 in strongly supergene altered ore are indeed relative and attributable simply to a smaller degree of mobility of Mn and Fe in comparison to Ca and Mg. Mass balance calculations also confirm the observed introduction Na_2O and K_2O .

Another very significant geochemical change associated with alteration involves the removal of large concentrations of CO_2 (hosted by carbonate in braunite lutite) and the introduction of large volumes of H_2O (in todorokite and manganomelane). This very important change does not become apparent in the available geochemical data set as both components report into the loss of ignition (L.O.I.) value. The change is, however, self-evident from the observed mineralogical changes (Chapter 3).

Several trace elements display consistent trends of enrichment or depletion. These are quantitatively of no importance to the alteration process but may profoundly influence the suitability of the altered manganese ore for industrial applications. Phosphorous and boron, deleterious elements during the production of steel, are both efficiently leached. Trace elements that have been introduced during supergene alteration include Sr, Ba and Zn. All three are easily incorporated into the structure of supergene Mn^{4+} -oxyhydroxide minerals (Burns & Burns, 1979; Nicholson, 1992).

The generation of secondary porosity as a result of carbonate decomposition enabled the reaction progress. It is reflected by significantly lowered whole rock densities but may have also subsequently led to 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 (Table 4.4 and 4.5), and it is interesting to note that the most carbonate-rich zone, the C-zone (Fig. 2.12) displays the greatest degree of compaction, i.e., the greatest amount of carbonate dissolution/porosity generation.