Abstract
Du Plooy, A.P., 2002, Geochemistry and mineralogy of supergene altered manganese ore below the Kalahari unconformity in the Kalahari manganese field, Northern Cape Province, South Africa. M.Sc. dissertation (unpubl.), Rand Afrikaans University, P.O. Box 524, Auckland Park, 2006, 96pp.

It is the focus of the study to qualitatively describe and then quantify the mineralogical and geochemical changes associated with the supergene alteration of carbonate-rich braunite lutite (Mamatwan-type ore) immediately below the Kalahari unconformity along the southeastern suboutcrop perimeter of the Hotazel Formation in the Kalahari deposit. It was also the objective of this study to determine the timing and duration of supergene alteration.

Samples for polished thin sections were carefully selected from eight representative boreholes to be representative of all the lithostratigraphic zones and ore types. The thin sections were used to study mineralogy by means of reflected light microscopy and scanning electron microscopy. X-ray powder diffractometry on representative powder samples were used to study the mineralogy and geochemistry of the samples. Microprobe analyses were also performed on the representative samples. Finally the samples were submitted for $^{40}$Ar/$^{39}$Ar geochronology.

In this supergene enrichment zone carbonates are leached (associated with an increase in porosity) and Mn$^{2+}$/Mn$^{3+}$-bearing minerals (kutnahorite, Mn-calcite an braunite) are altered to supergene Mn$^{4+}$-bearing mineral phases (todorokite and manganomelane) and minor quartz. This process upgrades ore from 38 wt% Mn to ore with more than 40 wt% Mn.

Element fluxes, enrichment and depletion of major and trace elements were quantified by mass balance calculations. Na$_2$O, K$_2$O, Sr, Ba, Zn and H$_2$O were enriched, while Mn$_3$O$_4$, Fe$_2$O$_3$, CaO, MgO, P, B and CO$_2$ were leached from the ore during supergene alteration. Results of this study suggest that the development of Post African I erosional surface may have taken place 45 Ma ago. The bottom of the weathering profile gives a well-defined
peak at ca. 5 Ma that may possible coincide with the development of Post African II erosional surface.

The major characteristics of the alteration process of the unaltered Mamatwan-type ore to supergene altered braunite lutite can be summarized as follow:

- 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 Mn$_3$O$_4$, Fe$_2$O$_3$, CaO, MgO, P, B, CO$_2$.
- Enrichment of Na$_2$O, K$_2$O, Sr, Ba, Zn, H$_2$O.

Chemical weathering processes along the Cenozoic Kalahari unconformity appear to have affected the manganiferous lithologies of the Hotazel Formation from 45 Ma onwards to 5 Ma. The weathering front processes very slowly through the Mn-rich braunite lutite (<10m in 40 Ma; <0.25m/Ma); producing a very uniform and microcrystalline supergene mineral assemblage with distinct characteristics.
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