## Boron isotope and REE signatures and their sources in manganese ores of the Kalahari Manganese Field

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The manganese (Mn) ores of the Kalahari Manganese Field developed as two chemical sedimentary layers alternating with banded iron-formation [1], and are categorised into low- and high-grade ores, rich in Mn carbonate and braunite, and braunite and hausmannite, respectively. Hydrothermal alteration formed the high-grade ores, removing carbonate, Si, Ca and Mg, and introducing Fe and Mn [2]. Both ascending saline fluids via normal faults, and descending meteoric water along the overlying unconformity contributed to hydrothermal fluid-rock interaction and alteration of the ores [3]. Low-grade ores decrease in Fe and Si concentrations and increase in Mn and Ca with depth, due to changes in primary marine precipitation of the protores, and/or incipient secondary oxidation, Fe addition and carbonate leaching. As a result of vertical variations in protore chemistry, aided by meteoric alteration, most high-grade ores have ferruginised, carbonate-free upper layers, with Fe decreasing with depth. Mn grade increase is attributed to carbonate loss from the protolith and replacement by newly-formed Mn oxides.

Increasing ore grade displays enrichment in Cu, Pb, Zn, Ba, Sr, Li and B. B is detrimental to the steel quality when in high concentrations and is mineralogically contained in braunite, gaudefroyite, tephroite, carbonates and serpentinegroup minerals. B isotope analyses reveal a range of values, which reflects mixing of different B sources and isotopic fractionation during hydrothermal evolution of the ores. High  $\delta^{11}$ B values are dominant, and are inferred as recording preservation of a primary seawater signal through the hydrothermal overprint; or interaction with an external B source that itself carried a seawater signature [4]. HREE enrichment is dominant, with positive La and negative Ce anomalies. The REE appear to retain the primary seawater signature along with a small hydrothermal component.

[1] Tsikos, H, Moore J.M. (1997) *Econ Geol*, 92, 87-97. [2] Evans, D.A.D. *et al.* (2001) *Econ Geol*, 96, 621-631. [3] Tsikos, H. et al., (2003) *Econ Geol*, 98, 1449-1462. [4] Spivack, A.J, Edmond, J.M (1987) *Geochim Cosmochim Acta*, 51, 1033-1043.