

## Geochemistry of the Nsuta Mn deposit in Ghana: Implications for the Paleoproterozoic ocean redox state

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Oxygenation of the atmosphere and oceans may have influenced the ocean chemistry and diversified contemporaneous life. A number of large manganese (Mn) deposits are distributed in the Paleoproterozoic sedimentary successions that were formed during the great oxidation event (GOE) around 2.4-2.2 Ga (Maynard, 2010 *Econ. Geol.*). Due to the high redox potential of Mn, occurrences of Mn deposits have been regarded as important evidence for a highly oxidized environment during the Paleoproterozoic (Kirschvink et al., 2000 *PNAS*). Furthermore, because Mn oxides are efficient scavengers of various elements, including bio-essential elements such as Mo, formation of large Mn deposits may have affected the seawater chemical composition and ecology during the Paleoproterozoic. However, due to lack of detailed geochemical records constraining the genesis of each Mn deposit, the relationships among the formation of Mn deposits, the evolution of atmospheric and ocean chemistry, and the diversification of early life are still ambiguous.

In this study, we report the Re-Os isotope compositions, rare earth element (REE) compositions, and abundance of manganophile elements in the Mn carbonate ore and host clastic sedimentary rock samples collected from the Nsuta Mn deposit of the Birimian Supergroup, Ghana. The Nsuta deposit is one of the largest Paleoproterozoic Mn deposits, although its genesis remains controversial (Melcher et al., 1995 *Mineral. Mag.*; Mucke et al., 1999 *Miner. Deposita*). The composite Re-Os isochron age (2149 ± 130 Ma) of the Mn carbonate and sedimentary rock samples is consistent with the depositional age of the sedimentary rocks (?2.19 Ga) obtained from U-Pb zircon age of the volcanic rocks (Hirdes and Davis, 1998 *J. Afr. Earth Sci.*), suggesting that the timing of Mn ore deposition was almost equivalent to the host rock sedimentation. The PAAS-normalized REE patterns show positive Eu anomaly in all samples and a positive Ce anomaly only in the Mn carbonate ore. These REE patterns suggest possible contribution of Eu-enriched fluids derived from hydrothermal activity and Ce enrichment due to the oxidation of Ce(III) by Mn(IV) during ore formation. Among the manganophile elements, only Mo is enriched in the Mn carbonate ore compared to the host sedimentary rocks. The profile of manganophile elements is similar to that of modern hydrothermal Mn oxide (Kuhn et al., 2003 *Chem. Geol.*), although the Mo/Mn ratio is much lower. These geochemical lines of evidence provide the following plausible genetic model for the Nsuta deposit: (1) Mn(II) was derived from hydrothermal fluids, (2) Mn(II) was oxidized to Mn(IV) oxide by the oxygenated seawater, (3) the precipitation of Mn oxide is almost concurrent with the deposition of the host sedimentary rocks, (4) Mn oxide was diagenetically transformed to Mn carbonate ore by the reaction with organic matter.

The geochemical features of the Nsuta deposits suggest that, as in the present oxic oceans, Mn oxide was a potential sink for several trace elements in the Paleoproterozoic oceans. The low Mo/Mn ratio in the Mn carbonate ore may reflect the large difference between the chemical compositions of Paleoproterozoic and present seawater. As the Paleoproterozoic black shales also tend to show low Mo abundance (Scott et al., 2008 *Nature*), the observed low Mo/Mn in the Mn carbonate ore suggests low Mo inventory in the Paleoproterozoic seawater. In the presentation, we will also discuss the oceanic redox condition responsible for the low Mo inventory during the Paleoproterozoic.

Keywords: Paleoproterozoic, Great Oxidation Event, Mn ore, Re-Os isotope, manganophile elements, Birimian Supergroup