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Cerium anomaly and Th/U fractionation in the 1.85 Ga Flin Flon Paleosol: Clues from REE- and U-rich accessory minerals and implications for paleoatmospheric reconstruction

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ABSTRACT

The 1.85 Ga paleosol at Flin Flon, Manitoba, Canada, was one of the first paleoweathering profiles taken as evidence for a dramatic rise in the oxygen content of the Paleoproterozoic atmosphere. Diagenesis and greenschist-facies metamorphism have modified the abundances of some major elements (e.g., K and Fe) in the Flin Flon paleosol. Inductively coupled plasma-mass spectrometry (ICP-MS) analyses reveal a positive Ce anomaly on both chondrite- and Amisk basalt-normalized REE patterns and marked Th/U fractionation in the uppermost maroon paleosol. The Ce anomaly is confirmed by the occurrence of cerianite and by the compositions of other REE- and U-rich accessory minerals (i.e., secondary monazite and uraninite) in the uppermost maroon paleosol. Th/U fractionation is supported by the presence of uraninite in both the paleosol and overlying Missi sedimentary rocks. Chemical ages of uraninite (1.85 to 1.0 Ga) suggest that this mineral might have formed during weathering or diagenesis but was susceptible to disturbance. Although igneous monazite and zircon are well preserved in even the uppermost maroon paleosol, primary fluorapatite exhibits variable degrees of weathering in the basal green paleosol and has been obliterated completely in the upper maroon paleosol.

Published paleomagnetic data suggest a tropical paleolatitude for the Flin Flon region at the time of formation of the paleosol. The positive Ce anomaly in the Flin Flon paleosol confirms previous studies for an oxic atmosphere ($P_{O_2} \geq 10^{-1.5}$ to 10^{-2} PAL) at 1.85 Ga. However, extreme caution must be exercised in the interpretation of Th/U fractionation in paleosols. Moreover, this study demonstrates the advantage of a detailed characterization of REE- and U-rich accessory minerals in the application of trace-element geochemistry of paleosols for paleoatmospheric reconstruction. Eh-pH diagrams for the stabilities of cerianite and uraninite in their respective systems Ce-P-C-H-O and U-P-C-H-O at 25 °C and 1 bar reveal the importance of phosphate complexes in the formation of Ce anomalies and Th/U fractionation in both modern and ancient weathering environments.