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 \( (P_{\text{O}_2} \geq 10^{-1.5} \text{ to } 10^{-2} \text{PAL}) \) 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.

INTRODUCTION

Paleosols, which are ancient soils formed by interactions with both the atmosphere and the hydrosphere, have been used extensively for the reconstruction of Earth’s atmospheric evolution, particularly for estimating the atmospheric oxygen levels in Earth’s early history (Holland 1984; Rye and Holland 1998 and references therein). Most studies of Precambrian paleosols (e.g., Holland et al. 1989; Holland and Beukes 1990; Gutzmer and Beukes 1998; Rye and Holland 1998) support the theory that there was a major rise in the atmospheric oxygen level at about 2.2–1.9 Ga (Cloud 1972; Kasting 1993). Ohmoto (1996), however, examined selected occurrences of Precambrian paleosols and suggested that there was no significant change in the atmospheric oxygen content from about 3.0 Ga to 1.8 Ga. In a critical review of over 50 pre-1.7 Ga paleosols in the literature, Rye and Holland (1998) identified only 15 definite occurrences of paleosols and concluded that some of those examined by Ohmoto (1996) were of suspect origin and, therefore, not suitable for paleoatmospheric reconstruction. This ongoing debate underscores the need for further characterization of Precambrian paleosols for the reconstruction of Earth’s early atmosphere.

The 1.85 Ga Flin Flon paleosol of Manitoba, Canada, is one of the 15 definite occurrences in Rye and Holland (1998), and is exceptionally well-preserved (Holland et al. 1989), except for overprinting by greenschist-facies metamorphism (Digel and Gordon 1995). This paleosol was one of the first paleoweathering profiles taken as evidence for an increasing oxygen content of the Paleoproterozoic atmosphere (Holland et al. 1989; Holland and Beukes 1990). In their pioneering study, Holland et al. (1989) used mainly whole-rock, major-element oxide data (e.g., FeO and Fe₂O₃) of the Flin Flon paleosol to quantify the oxygen content in the Paleoproterozoic atmosphere. Ohmoto (1996) suggested that the Flin Flon paleosol belongs to his M-type, which is characterized by a redistribution of Fe within the weathering profile.

Rare-earth elements (REE, Z = 57–71) behave almost in-