

## Do Cr isotopes really fingerprint Precambrian surface oxidation?

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Oxidation of Cr(III) to Cr(VI) by Mn oxides in soils and subsequent Cr reduction cause isotope fractionation. Isotopic excursions of Cr relative to the narrow and consistent ratio of igneous rocks have been reported for Precambrian paleosols and banded iron formation. Significantly, this includes strata older than the Great Oxidation Event (GOE) [1]. At face value, Cr isotopes in these latter deposits imply Cr(III) oxidation on continental land well before the GOE. This view has been challenged, however, based on the high atmospheric O<sub>2</sub> and kinetic requirements of surficial Mn oxide formation [2], and because it contradicts other sensitive redox indicators such as Fe speciation and pyrite preservation.

Here, we present a detailed Fe-Mn-Cr study of the ca. 1.85 Ga Flin Flon paleosol – one of the best preserved and unambiguous Proterozoic subaerial weathering profiles known. It shows progressive upwards alteration, formation of spheroidal weathering textures, and depletion of mobile elements. Consistent with its formation after the GOE, the paleosol shows Fe retention with systematic upward oxidation of Fe(II) to Fe(III) preserved in hematite. In clear contrast to Fe, however, following observations imply mobility of Mn and Cr in reduced state.

Upward Mn depletion in the profile suggests negligible Mn oxide formation. This is supported by *in situ* redox analysis of the paleosol failing to detect any Mn(III) or Mn(IV) compounds. Furthermore, the heavy isotopes of Cr become enriched in the oxidised, hematite-bearing horizons of the paleosol, opposite to modern weathering profiles. We propose that this heavy isotope enrichment occurred during Cr(III) interaction with pedogenic smectite and/or Fe oxides.

Regardless of the mechanism that led to the observed Cr isotope signature, our study shows that Cr isotope excursions in Precambrian surface deposits may have multiple origins and are not unique fingerprints of high levels of atmospheric O<sub>2</sub>.

[1] Crowe et al. (2013), *Nature* **501**, 535-539; [2] Konhauser et al. (2011), *Nature* **478**, 369-374