

Constraining the evolution of atmospheric O₂ levels using the isotope geochemistry of paleosols

DAVID AUERBACH¹ AND NOAH PLANAVSKY¹

¹Department of Geology & Geophysics, Yale University, New Haven, CT, 06511, USA

The redox state of the Precambrian atmosphere and ocean has been widely studied to better understand the evolution of biogeochemical cycling and complex life early in Earth history. Given their direct contact with the atmosphere, the morphology and geochemistry of paleosols has been used to provide a variety of constraints on Precambrian environments, e.g., [1], [2]. Furthermore, significant paleosols develop over $\geq 10^6$ years, making them ideal archives of integrated long-term atmospheric composition.

Stable isotopes of chromium and uranium are fractionated by redox reactions, providing a measure of atmospheric O₂ concentrations through time. Uranium can be oxidized at O₂ levels less than $10^{-7} \times$ present atmospheric levels (PAL). Chromium fractionation, by comparison, begins at O₂ levels of $\sim 10^{-3}$ PAL. Using these two isotope systems together provides a way to make semi-quantitatively constrain atmospheric O₂ levels through Earth history, particularly when combined with S-MIF (sensitive at 10^{-5} PAL).

However, studies of modern soils indicate that the oxidation reactions that result in fractionation of these isotopic systems are not ubiquitous. Soils only become measurably fractionated at high degrees of weathering. Thus many modern soils appear unfractionated despite contact with our strongly oxidizing atmosphere. It is not yet clear the role what, if any, role reduced organic matter in modern soils may play in slowing oxidative weathering.

With this limitation in mind, we studied the $\delta^{53}\text{Cr}$ and $\delta^{238}\text{U}$ of a series of strongly weathered paleosol profiles with ages ranging from 2.97 Ga to ~ 0.3 Ga in order to better understand the oxidation state of the terrestrial realm during that time span. Each paleosol shows textural, mineralogical, and geochemical evidence confirming it is a true terrestrial weathering profile. Isotopic data remain unfractionated until the Neoproterozoic, indicating that either chemical weathering rates were extremely low or atmospheric O₂ levels remained below at least 10^{-3} PAL prior to that time. Data also indicate that terrestrial oxygenation (e.g., [3]) may have been spatially variable, suggesting a possibly significant role for terrestrial photosynthesizers in the production of atmospheric O₂.

[1] Holland & Zbinden (1988), in *Physical and chemical weathering in geochemical cycles*, 61-82.; [2] Rye & Holland (1998), *American Journal of Science* **298**, 621-672.; [3] Crowe *et al.* (2013), *Nature* **501**, 535-538.