O_2 variability in Archean environments: Do whiffs trump tiffs?

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High-resolution chemostratigraphy in a drill core from the late Archean Mt. McRae Shale, Western Australia, reveals correlated variations in multiple redox-sensitive geochemical tracers, including concentrations of Mo and Re, $\delta^{34}S$, $\Delta^{33}S$, $\Delta^{36}S$, $\delta^{56}Fe$ and $\delta^{98}Mo$. These variations are interpreted as reflecting an increase in environmental oxygenation, at least locally, whereby small amounts of O_2 in the water column, and possibly the atmosphere, affected the sulfur cycle and enhanced the rate of oxidative weathering [1, 2].

This "whiff of oxygen" was precisely dated using Re-Os geochronology, obtaining an age of 2500 ± 8 Ma [1]. The timing indicates that the oxygenation episode recorded in the Mt. McRae Shale significantly preceded the Great Oxidation Event at the beginning of the Proterozoic Eon. The accumulated data suggest that typical PO_2 remained $< 10^{-5}$ PAL during this time, and did not persistently cross this threshold until after 2450 Ma.

These findings hint at the possibility that atmospheric O_2 behaved as a biogenic trace gas before the Great Oxidation Event. Results from 1D photochemical models predict short tropospheric O_2 lifetimes (minutes to hours) under a variety of conditions, and the Archean atmosphere may have experienced strong diurnal flux variations because cyanobacterial mats release O_2 during the day and reductants primarily at night [3]. In addition, short O_2 lifetimes would have precluded significant horizontal mixing of O_2, so that Archean ground level O_2 concentrations may have been negligible distant from local "plumes" of biogenic O_2.

The notion of O_2 as a spatially and temporally variable, trace gas in the Archean is, on the one hand, unremarkable. On the other hand, this concept has not been well-integrated into interpretations of Archean redox evolution. Heterogeneity among redox proxies seems likely. As a result, some of the debates that have animated this field over the past decade may prove to have been over false dichotomies.

[1] Anbar *et al.* (2007) *Science* **317**, 1903. [2] Kaufman *et al.* (2007) *Science* **317**, 1900. [3] Hoehler *et al.* (2001) *Nature* **412**, 324.

Redox renaissance

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The oxygen content of the oceans is intimately connected with the geochemical cycles of carbon and other elements in a complex network of feedbacks. Hence, biogeochemists are interested in reconstructing how redox conditions in the oceans – and in the broader environment – have changed with time. In the wake of recent analytical advances, this decade has seen the invention of several new isotopic paleoredox proxies that may provide information about ocean redox conditions, catalyzing a renaissance of research on this topic. Much of this effort has focused on the Precambrian, an era that witnessed at least two very large, stepwise increases in ocean oxygenation, but these tools are now also being extended into the Phanerozoic. This talk will provide an overview of current research frontiers for Mo and Fe isotopes, two of these new proxies that are now relatively well-established, and an introduction to the insights that may come from U and other complementary isotopic proxies that are still in their infancy.