Nutrient limitation in ferruginous, silica-rich Precambrian oceans

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The history of bio-essential trace metal availability is inextricably linked to the redox evolution of Earth's ocean-atmosphere system. A number of studies have hypothesized that shifts in ocean-atmosphere redox may have impacted micronutrient budgets in Precambrian basins, in turn delaying the rise of eukaryotes to ecological dominance. However, we lack a detailed mechanistic understanding of processes that would have regulated trace metal availability in dominantly ferruginous oceans. Here, we build upon recent evidence that anoxic and silica-rich waters frequently triggered the basin-scale precipitation of greenalite, an authigenic Fe(II)-silicate mineral, and assess its impact on trace metal cycling during nucleation, growth and diagenesis.

Anoxic nucleation experiments indicate significant and sometimes quantitative uptake of trace metals into the solid, including Zn, Cu, V, Co and Ni. X-ray absorption spectroscopy (EXAFS and XANES) confirms that these metals are structurally incorporated into Fe-octahedral sites. In addition, the metals remain locked-up in the greenalite structure during hydrothermal treatment, simulating late-stage diagenetic reactions. Incorporating experimental data into advective transport models shows that upwelling-derived greenalite precipitation could have acted as an effective gatekeeper, preventing vital nutrients such as Zn and Cu from reaching near-shore habitats.

Although greenalite is a ubiquitous component of Precambrian iron formation, is also occurs as a dominant constituent in ironstones interbedded with Mesoproterozoic black shales [Cochrane & Edwards, 1960]. Thus, we propose that upwelling of ferruginous silica-rich waters would have marginalized early eukaryotes to inner shelf and coastal habitats. This previously unrecognised control on trace metal availbility is testable with further scrutiny of Proterozoic clastic successions, and is consistent with emerging models of Precambrian ocean chemistry, inferences from the fossil record, and comparative genomics [Dupont et al. 2010].

Cochrane, G. W. & Edwards, A. B. (1960) *CSIRO Minerographic Investigations Technical Paper* No. 1
Dupont C. L. et al (2010) *PNAS*, 107(23) p. 10567