

**NUTRIENT LIMITATION IN THE PRECAMBRIAN.** Noah J. Planavsky<sup>1\*</sup>, Stefan Lalonde<sup>2</sup>, Kurt Konhauser<sup>2</sup>, Timothy W. Lyons<sup>1</sup> (\*noah.planavsky@ucr.edu). (<sup>1</sup>*Department of Earth Sciences, University of California, Riverside, Riverside, CA, 92521, USA*, <sup>2</sup>*Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB, T6G 2E3, Canada*)

In almost all modern aquatic systems, primary production of organic matter is typically thought to be limited by either phosphorus or bioavailable nitrogen<sup>1</sup>. Because temporally extended deficiencies in fixed nitrogen availability are buffered by a virtually limitless supply of atmospheric N<sub>2</sub> (via nitrogen fixation), while phosphorus is sourced primarily by weathering of continental materials, it is generally thought that phosphorus will ultimately limit net primary productivity on geologic timescales<sup>1,2</sup>. An estimate of marine phosphate reservoir size through time is therefore essential to unravel basic aspects of biological and geochemical evolution<sup>3</sup>.

The ratio of P to iron (Fe) in Fe oxide-rich sedimentary rocks can be used to track dissolved phosphate concentrations if the dissolved Si concentration of seawater is estimated<sup>4-7</sup>. Here, we present Fe and P concentrations from distal hydrothermal sediments and iron formations through time in order to evaluate the evolution of the marine P reservoir. The data suggest that phosphorous concentrations have been relatively constant over the Phanerozoic, the last 542 million years of Earth's history. In contrast, P concentrations appear to have been elevated in Precambrian oceans.

There is a pronounced spike in P/Fe ratios in Neoproterozoic iron formations dating from 750 to 640 million years ago, indicating unusually high dissolved P concentrations in the aftermath of the widespread, low latitude 'Snowball Earth' glaciations. We suggest that the combination of upwelling Fe-rich waters<sup>8</sup> and significantly elevated marine P concentrations in the time surrounding the 'Snowball Earth' glaciations would have caused a nutrient surplus, stimulating high rates of primary productivity and increased organic carbon burial. Extensive ferruginous marine settings in the mid-late Neoproterozoic would have provided conditions needed to meet the high metal demands of diazotrophic primary producers. High rates of organic carbon burial would have caused a shift to more oxidizing conditions. The 'Snowball

Earth' glaciations and a Neoproterozoic oxidation are both proposed triggers for the evolution and radiation of metazoans<sup>9,10</sup>. Our data suggest that these two factors are intimately linked; a glacially induced nutrient surplus would have led to an oxygen increase, paving the way for the rise of metazoan life.

In contrast, we propose that in the predominantly ferruginous Archean oceans bioessential metals (e.g. Zn, Co, Cd, and Mo), rather than P were the most important factors limiting carbon fixation. Trace element stress is likely to have been severe in early oceans given that under an essentially anoxic atmosphere there would be limited continental weathering and delivery of sulfide-associated metals. Muted authigenic Mo enrichments in Archean black shales provide empirical evidence for a dramatically different trace metal cycle prior to the rise of atmospheric oxygen<sup>11</sup>. We have also found that iron oxide-rich rocks preserve the signature of a small marine Mo reservoir in Precambrian oceans.

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