

## Nutrient-O<sub>2</sub> feedbacks and Proterozoic pO<sub>2</sub> regulation

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Earth's O<sub>2</sub> evolution was not unidirectional. Despite major oxygenation during the GOE and subsequent Lomagundi Event, proxy records collectively suggest that atmospheric pO<sub>2</sub> fell precipitously and remained low, perhaps as low as 0.1% of the present atmospheric level (PAL), during the mid-Proterozoic. The level at which pO<sub>2</sub> stabilized during this time remains controversial because long-term maintenance of exceptionally low pO<sub>2</sub> during this 'Boring Billion' interval is difficult to reconcile with photochemical models that predict O<sub>2</sub> bistability and a tendency for 'runaway' oxygenation post-GOE. The current generation of photochemical models, however, assume static O<sub>2</sub> production and do not account for the possibility that biospheric O<sub>2</sub> fluxes are sensitive to atmospheric pO<sub>2</sub>.

We suggest that feedbacks within the N cycle may allow the stabilization of atmospheric pO<sub>2</sub> at a much lower level than today, independent of atmospheric processes. Under O<sub>2</sub> deficient conditions, an increase in O<sub>2</sub> concentrations in surface environments translates to an increased capacity for the conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup> via nitrification and, therefore, greater potential for the loss of bioavailable N via denitrification and NO<sub>3</sub><sup>-</sup>-dependant methanotrophy. The result is a negative feedback in which oxygenation tends to promote N scarcity and disfavor O<sub>2</sub> accumulation [1].

Meanwhile, mid-Proterozoic surface ocean conditions would have been suboptimal for cyanobacterial N fixation and may have impeded the replenishment of biospheric N—further disfavoring oxygenation. Potential obstacles to N fixation include: (1) O<sub>2</sub> inhibition of nitrogenase and (2) metal cofactor limitation, which is suggested by muted Mo enrichments in Proterozoic shales. Widespread N scarcity, therefore, may provide a mechanism to throttle O<sub>2</sub> accumulation in Earth's atmosphere despite the photochemical instability of low O<sub>2</sub> atmospheres.

[1] Fennel, K., Follows, M., and Falkowski, P.G. (2005) The co-evolution of the nitrogen, carbon and oxygen cycles in the Proterozoic ocean, *American Journal of Science*.