

## Toxic levels of Fe(II) in Archean seawater delayed the Great Oxidation Event

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Multiple lines of evidence indicate temporally and spatially limited oxygen production by at least 2.6 Ga [1,2], prior to the Great Oxidation Event (GOE) at ca. 2.4-2.32 Ga [3]. Did abundant oxygen sinks in the Archean cause a protracted and episodic rise of atmospheric oxygen, or were early cyanobacteria initially limited in their ability to produce oxygen? We propose that the activity of early cyanobacteria was inhibited by toxic reactive oxygen species (ROS). Indeed, in experiments we observed significant toxicity when the marine cyanobacterium *Synechococcus* PCC 7002 was incubated in initially anoxic conditions with tens of  $\mu\text{M}$  Fe(II). Fe(II) caused an increase in ROS within the cell, and a reduced capacity to produce oxygen. We calculate that Fe(II) supplied to late Archean upwelling zones would have poisoned cyanobacteria. Semi-restricted carbonate platforms, such as the Gamohaam formation of the Griqualand West basin in South Africa, which formed between 2.6-2.5 Ga, sheltered cyanobacteria from upwelling Fe(II) in spatially-restricted oxygen oases. Shales deposited along the slope of such platforms contain evidence of oxygen [1,2]. Emplacement of large igneous provinces (LIP) periodically drowned carbonate platforms with Fe(II)-rich water [4], poisoned cyanobacteria, and turned off oxygen production. Cyanobacteria expanded throughout the oceans with the end of LIP activity after 2.4 Ga, coincident with the GOE.

[1]Godfrey & Falkowski (2009) *Nature Geosci.*, **2**, 725-9.  
[2]Kendall *et al* (2010) *Nature Geosci.*, **3**, 647-52. [3]Bekker *et al* (2004) *Nature*, **427**, 117-20. [4]Barley *et al* (2005) *EPSL*, **238**, 156-71.