

Tracing the Evolution of Oxygen on the Archean Earth

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A remarkably coherent ensemble of evidence point to a significant accumulation of atmospheric oxygen for the first time in Earth's history beginning ca. 2.45 Ga, the so-called Great Oxidation Event (GOE). Briefly, this includes the disappearance of detrital pyrite, uraninite and siderite from fluvial and deltaic deposits, an increase in the retention of iron in paleosols, an enrichment of Cr and U in iron formations, and perhaps most importantly, the disappearance of sedimentary sulphur isotope mass-independent (S-MIF) anomalies indicative of atmospheric SO₂ processing in the absence of appreciable ozone. However, several trace element and isotopic proxies have recently suggested oxidative weathering hundreds of millions of years earlier¹⁻². The superposition of pre-GOE signals for oxidative weathering at a time of global anoxia represents a conundrum for which the most accepted explanation is that pre-GOE oxidative weathering is the result of transient oxygenation events driven by 'oxygen oases' in the marine realm. We propose here an alternative model, that being intense O₂ generation – and immediate consumption – at sub-meter scales by benthic oxygenic photosynthesis in the terrestrial realm. Despite the absence of a UV-protective ozone layer in the Archean, a terrestrial phototrophic biosphere may have existed in various sheltered environments, including biological soil crusts and freshwater microbial mats covering riverbed, lacustrine, and estuarine sediments. We calculate that the rate of O₂ production via oxygenic photosynthesis in these ecosystems provides sufficient oxidising potential to mobilise sulphate and a number of redox-sensitive trace metals from land to the oceans while the atmosphere itself remained anoxic with its attendant S-MIF signature. An intriguing question that follows from this hypothesis is if cyanobacteria were conceivably metabolising at modern rates on land by perhaps 3.0 Ga, what happened in the hundreds of million years between the first, rare signals of oxidative weathering and the first significant accumulation of atmospheric oxygen, i.e., the GOE? While the exact confluence of factors controlling the success of Earth's earliest oxygenic phototrophs remains an open question, several factors may have depressed areal coverage or photosynthetic efficiency of cyanobacteria, and thus masked their potential presence prior to the GOE, including the lack of colonisable surface area for oxidative weathering.

[1] Crowe et al (2013), *Nature* 501, 535-539.

[2] Planavsky et al (2014), *Nature Geoscience* 7, 283-286.