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Arguments for the late evolution of Oxygenic Photosynthesis at ∼2.3 Ga: A Trigger for the Paleoproterozoic Snowball Earth

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The evolution of oxygenic photosynthesis and the oxygenation of the atmosphere are two of the most important events in Earth history. While biomarker, trace element, and isotopic evidence have been used to claim that oxygenic photosynthesis evolved by 2.8 Ga (1-3), and perhaps as early as 3.8 Ga (4), a skeptical examination raises considerable doubt about how strongly this earlier evidence actually demands the presence of oxygen. Although the Present is sometimes the key to the Pleistocene, it might *not* be a good key to the Archean.

Many of the lines of evidence used to argue for early oxygenic photosynthesis come with significant caveats. The redox potentials of Fe and U, the behavior of which is often claimed as a tracer of environmental oxygen, are sufficiently low that their behavior can also be explained by anoxygenic photosynthesis (in the case of Fe), photo-oxidation, or interaction with mildly more oxidizing compounds. The presence of organic-rich shale in the Isua metasediments in Greenland, although strongly suggestive of life, provides no constraints on deposition rates, biological productivity, or metabolism. Massive stromatolitic reefs may reflect carbonate deposition in an ocean supersaturated with respect to $CaCO_3$ (5) rather than the high productivity of O_2 photosynthesis as has been claimed (2). While 2-methyl-bacteriohopanepolyol is produced copiously by cyanobacteria, nothing in hopanol synthesis demands the presence of oxygen and, indeed, *Geobacter sulfurreducens* has been shown to produce hopanols anaerobically (6). Although all known biosynthetic pathways for sterol synthesis have a few steps involving O_2 as a substrate, the organic chemistry of sterol synthesis does not demand oxygen, and the one-for-one replacement of anaerobic enzymes with those using O_2 is a common evolutionary transition (7). An ancient, or perhaps modern but currently unknown, microbe might well have produced sterols without O_2-dependent enzymes.

The occurrence of numerous geological oxygen indicators immediately before and after the Paleoproterozoic Makganyene Snowball Earth at ca. 2.3-2.2 Ga supports an alternate history, in which the evolution of oxygenic photosynthesis triggered the geologically rapid destruction of a methane greenhouse and Earth's first global glaciation. New age constraints from the Transvaal Supergroup in South Africa demonstrate that all three of the Huronian glaciations in Canada, which are unconstrained in latitude and may therefore be mid-latitude rather than global events (8), predate the oxygenation and the Snowball event. A simple flux model of nutrient-limited cyanobacterial growth that incorporates the range of P and Fe fluxes expected during the Huronian glacial episodes indicates that cyanobacteria could have destroyed a methane greenhouse and triggered the Paleoproterozoic Snowball Earth on timescales as short as 1 My. As the geological expression of oxygen does not appear during the Pongola glaciation at 2.9 Ga or in the earlier part of the Huronian interval, when these fluxes should also have been high, we argue that oxygenic cyanobacteria may not have evolved and radiated until shortly before the Makganyene Snowball at $\sim$ 2.3 Ga. In addition to removing need to explain how PS-II could have been 'bottled up' for 500-1500 My before the surface expression of oxygen became apparent, this scenario raises the specter of one mutant organism being able to destroy an entire planetary ecosystem: perhaps the first biogenic climate disaster.

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