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The Delay in Oxidation of Earth's Atmosphere Following the Emergence of O_2-producing Photosynthesis: An Explanation

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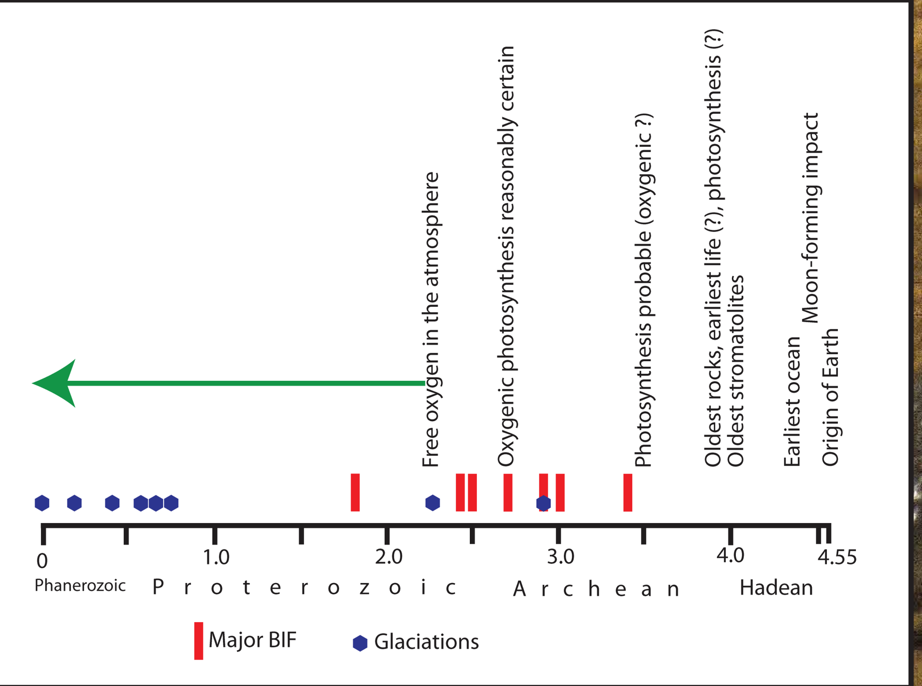
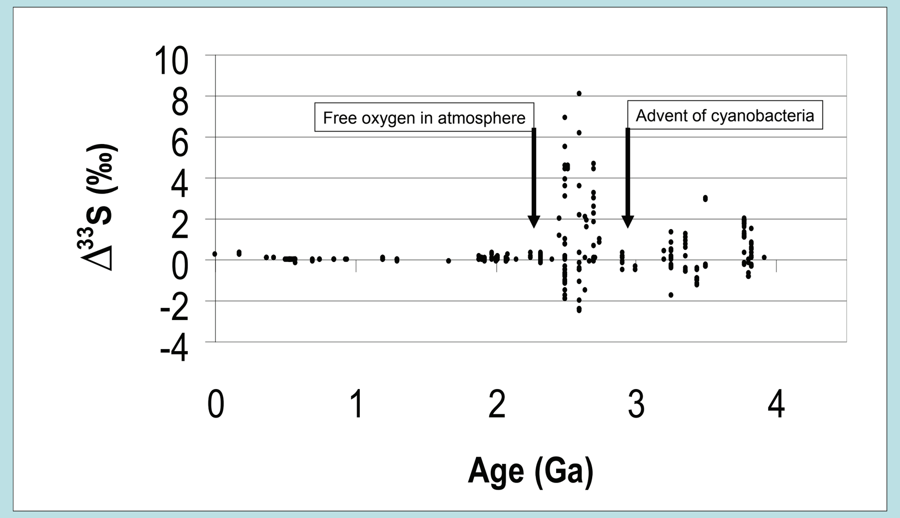
Abstract

The time of origin of oxygenic photosynthesis appears to be at least as early as 2.7 Ga, and possibly as early as 3.5 Ga, if stromatolitic fossils of those ages were produced by cyanobacteria. The record of mass-independent fractionation of sulphur isotopes indicates an abrupt rise in atmospheric oxygen at about 2.2-2.3 Ga, at least 400 Ma after the advent of oxygenic photosynthesis. This delay in atmospheric oxygen in the face of the likely productivity of cyanobacteria has been a puzzle for several years, particularly if the main carbon species in the surface environment was CO_2 as is widely assumed. Various possible nutrient limitations on cyanobacterial productivity have been suggested including Fe, Mo, fixed N and P. Examination of the geochemical availability of these limiting nutrients, and/or intrinsic biochemical inefficiency (i.e. primitive enzyme systems), suggests that none are capable of explaining the delay in surface oxidation. Consumption of photosynthetic oxygen by a surface reservoir of reducing substances appears to be insufficient as well, unless there was a large surface reservoir of reduced carbon compounds. However, with a large surface reservoir of reduced carbon compounds, the problem is more directly resolved by the limited carbonate reservoir available for photosynthesis. The presence of such a reduced carbon reservoir appears to be not only possible, but likely, based on conditions attending late accretion and planetary degassing during the Hadean.



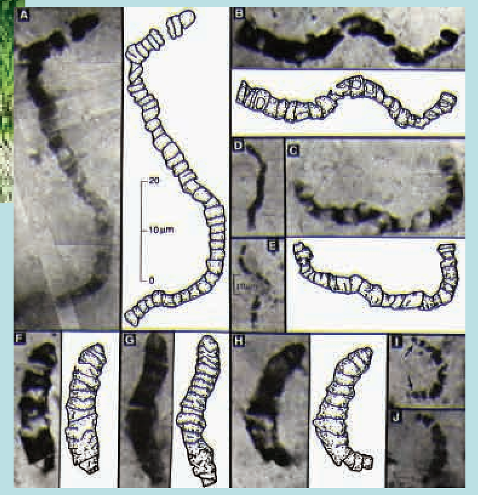
The gap in time between the origin of oxygenic photo-synthetic cyanobacteria and the presence of an oxygenated surface environment is at least 400 million years, and might be more than a billion years. How can this be?



Cyanobacterial bloom

http://www.botany.hawaii.edu/faculty/webb/BOT311/Cyanobacteria/BloomMicrocystisB.jpg

III.Cyanobacteria (or something strikingly like them) have been extant since at least 2.9 BYBP, probably since 3.5 BYBP and maybe since 3.9 BYBP. (The earlier dates are highly controversial). (Schopf and Walter, 1983).



• The Problem

• Cyanobacteria have reproduction rates of about one division/day. Even at lower rates they are capable of producing enough fixed carbon to liberate sufficient oxygen to result in free oxygen in the atmosphere in a matter of years, not a billion years. This issue has long been recognized (e.g. deDuve, 2002, Veizer, 1983; Walker, 1977). Attempts to address this problem have looked mainly at three considerations:

• **1)** Oxygen sinks, especially ferrous iron, the oxidation of which gave rise to BIF (Walker. 1977; de Duve 2002, Canfield, 2005).

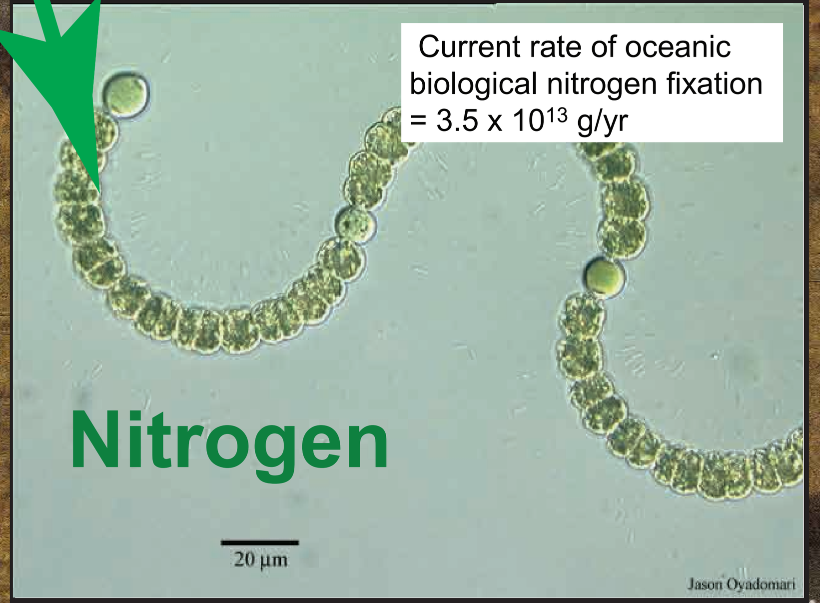
• **2)** Inefficient metabolic pathways in early cyanobacteria. (But inefficient metabolism only slows reproduction rates, and even orders of magnitude lower rates of cell division have insignificant effects on geological time sclaes.)

• **3)** Nutrient limited cyanobacterial reproduction (e.g. Canfield, 2005).

Nutrient limitations are the "classical" approach to limiting bacterial productivity (and hence cyanobacterial oxygen production)

But cyanobacteria are the major nitrogen fixers on Earth, and can produce this essential nutrient at high rates.

While weathering, even at probably lower modern rates, can provide abundant phosphorus.

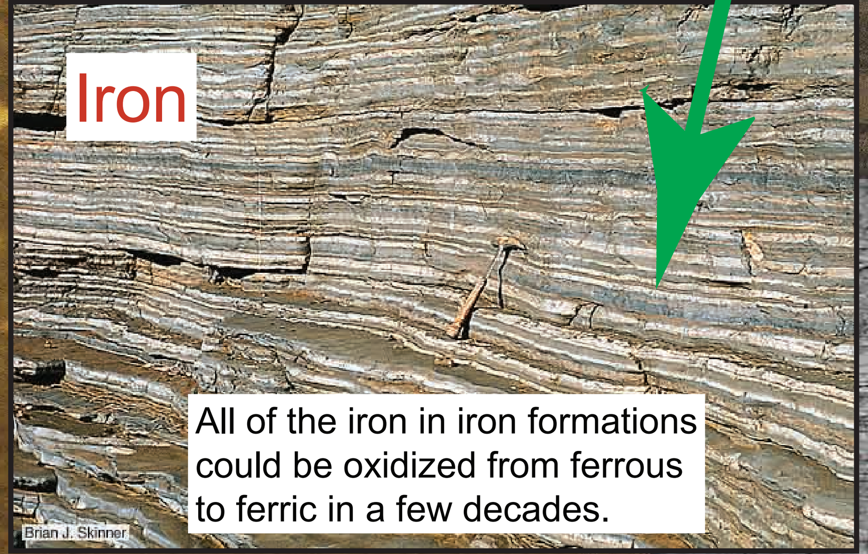


Current rate of oceanic biological nitrogen fixation = 3.5×10^{13} g/yr

Phosphorus

Phosphorus is provided to the biosphere by weathering of crustal rocks. The rate of phosphorus delivery is about 3.9×10^{13} g/yr.

Anoxic weathering produces ferrous iron, an important component of Archean oceans. It also releases reduced sulfur. Both of these can consume photosynthetic oxygen, but production rates from weathering, and accumulated reducing capacity in the oceans is readily ovewhelmed by bacterial oxygen productivity.



All of the iron in iron formations could be oxidized from ferrous to ferric in a few decades.

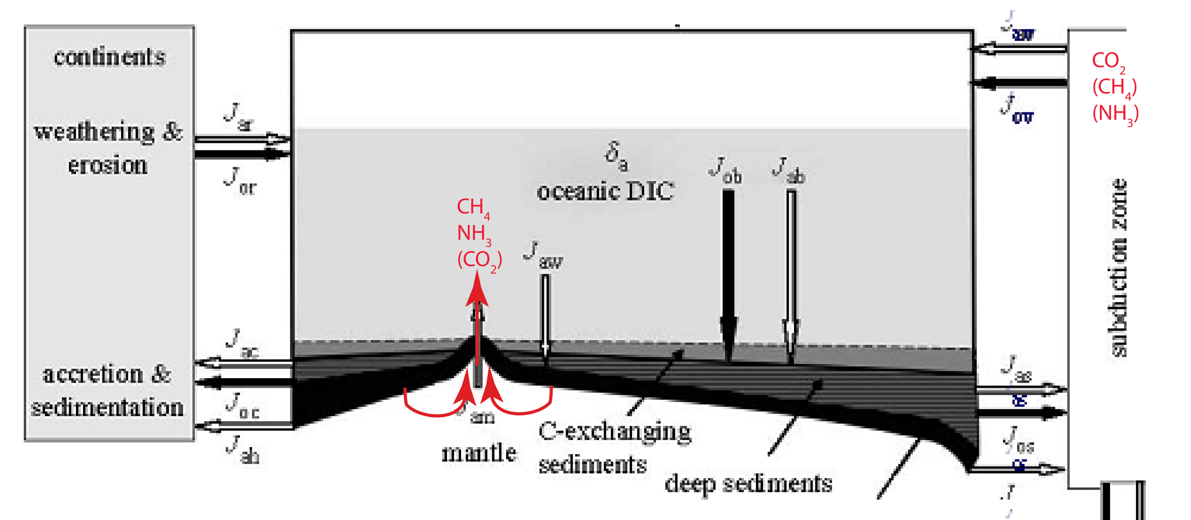
Carbon dioxide was the limiting nutrient !!!!!!

"If every other hypothesis has been excluded, the remaining explanation, however unlikely, must be the correct one."

Sir Arthur Conan Doyle (using the voice of Sherlock Holmes)

But, if CO_2 was the limiting nutrient, and by implication the surface carbon reservoir was mainly reduced carbon compounds, what is the source of the CO_2 for photo-synthesis, and how did the surface finally become oxidized?

Answer: Deep subduction of reduced carbon leads to carbon equilibration during magmagenesis, with production of CO_2. This slow production of CO_2 over geologic time provides the raw material for oxygenic photosynthesis, but at a rate that prolongs a reduced surface environment.



Modified from Hayes and Waldbauer, 2006

Conclusions

1) The high reproduction rate of cyanobacteria requires an explanation for the delay in oxidation of Earth's surface environment.

2) Metabolic inefficiency cannot be an explanation because reproduction rates even orders of magnitude lower than modern cyanobacteria result in delay of the buildup of the cyanobacteria populations short in geological terms.

3) Cyanobacterial nitrogen fixing essentially removes this nutrient as a limiting resource on oxygen production, at least on the necessary geologic time scale.

4) Weathering of crustal rocks delivers phosphorus at rates fast enough that it cannot be the limiting nutrient, again on the necessary geologic time scale. This is especially true for these early times when there were fewer biogeologic sinks for phosphate.

5) Inorganic carbon sinks, from weathering of rocks (ferrous iron and sulfur), are insufficient to prevent surface oxidation by unconstrained photosynthesis. This is obvious because such sources have clearly been overcome. The prior buildup of reduced surface reservoirs (prior to oxygenic photosynthesis) such as oceanic ferrous iron were insufficient to absorb enough oxygen to cause the delay. For example, the iron contained in BIF (and even assuming orders of magnitude larger deposits than those currently known) would be oxidized in a very short period of time by unconstrained photosynthesis by cyanobacteria.

6) Carbon dioxide was in short supply in the early terrestrial surface environment, limiting the amount of oxygen that could be produced by photosynthesis.

7) Most of the surface carbon was in reduced form, thus constituting a large reservoir to absorb photosynthetic oxygen.

8) Subduction of reduced carbon compounds, followed by equilibration of the carbon during magmagenesis (either in subduction environments or at ocean ridges), yields CO_2 which is emitted from volcanos, providing a slow delivery of CO_2 for long-term oxygen production through photosynthesis at *geologic* rates. Earth's early carbon cycle differed from the modern cycle, with reduced carbon reservoirs and transfers of reduced carbon compounds dominating over carbonates.