The Paleoproterozoic snowball Earth: A climate disaster triggered by the evolution of oxygenic photosynthesis

Robert E. Kopp*, Joseph L. Kirschvink, Isaac A. Hilburn, and Cody Z. Nash

Division of Geological and Planetary Sciences, California Institute of Technology 170-25, Pasadena, CA 91125

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Although biomarker, trace element, and isotopic evidence have been used to claim that oxygenic photosynthesis evolved by 2.8 giga-annum before present (Ga) and perhaps as early as 3.7 Ga, a skeptical examination raises considerable doubt about the presence of oxygen producers at these times. Geological features suggestive of oxygen, such as red beds, lateritic paleosols, and the return of sedimentary sulfate deposits after a ≈900-million year hiatus, occur shortly before the ≈2.3–2.2 Ga Makganyene "snowball Earth" (global glaciation). The massive deposition of Mn, which has a high redox potential, practically requires the presence of environmental oxygen after the snowball. New age constraints from the Transvaal Supergroup of South Africa suggest that all three glaciations in the Huronian Supergroup of Canada predate the Snowball event. A simple cyanobacterial growth model incorporating the range of C, Fe, and P fluxes expected during a partial glaciation in an anoxic world with high-Fe oceans indicates that oxygenic photosynthesis could have destroyed a methane greenhouse and triggered a snowball event on timescales as short as 1 million years. As the geological evidence requiring oxygen does not appear during the Pongola glaciation at 2.9 Ga or during the Huronian glaciations, we argue that oxygenic cyanobacteria evolved and radiated shortly before the Makganyene snowball.

oxygen | Makganyene glaciation | Huronian glaciations | cyanobacteria

After the rise of life itself, the most radical transformation of Earth's biogeochemical cycles occurred in the transition from an anoxic to an oxic world. This transformation took place in three phases. First, oxygenic photosynthesis evolved and brought into the world locally oxic environments. Second, oxygen became a major component of the atmosphere; some authors (1, 2) have suggested that this period was a protracted phase during which the ocean became euxinic. Finally, the whole ocean–atmosphere system took on its modern oxygen-dominated cast.

Although the timing of and relationship between the three stages have been topics of active research for many decades, there is still a wide divergence of opinion. Evidence from organic biomarkers (3–5) and arguments concerning trace element mobility (6) and biological productivity (7) have convinced many that O_2-generating cyanobacteria and aerobic eukaryotes evolved no later than ≈2.78 giga-annum before present (Ga) and perhaps as long ago as 3.7 Ga. Meanwhile, the developing record of mass-independent fractionation (MIF) of sulfur isotopes in the sedimentary record, as well as some other geochemical tracers, has been interpreted as supporting a protracted atmospheric oxygenation over the period of ≈2.5–2.2 Ga (8).

An early origin for oxygenic photosynthesis demands an explanation of how surface oxidation was muted for perhaps as long as 1,500 million years (My), until cyanobacteria finally surmounted some geochemical, environmental, or ecological barrier and successfully oxidized the planet. Perhaps this scenario is correct, and some abiotic change, such as the long-term escape of hydrogen to space (9), was the direct cause of planetary oxygenation. We suggest, however, that the data are also consistent with scenarios without oxygenic photosynthesis in the Archean. Herein we discuss an alternate hypothesis, one in which the evolution of cyanobacteria destroyed a methane greenhouse and thereby directly and rapidly triggered a planetary-scale glaciation, the ≈2.3–2.2 Ga Makganeyene "snowball Earth."

Geological Setting

The earliest evidence for glaciation comes from the late Archean and early Proterozoic, which suggests Earth at this time experienced global temperatures not much different from those today. The oldest known midlatitude glaciation, recorded in the Pongola Supergroup diamictite, occurred at 2.9 Ga (10). The period from 2.45 Ga until some point before 2.22 Ga saw a series of three glaciations recorded in the Huronian Supergroup of Canada (11) (Fig. 1). The final glaciation in the Huronian, the Gowganda, is overlain by several kilometers of sediments in the Lorrain, Gordon Lake, and Bar River formations (Fms.). The entire sequence is penetrated by the 2.22 Ga Nipissing diabase (12); the Gowganda Fm. is therefore significantly older than 2.22 Ga.

In its eastern domain, the Transvaal Supergroup of South Africa contains two glacial diamictites, in the Duitschland and Boshoek Fms. The base of the Timeball Hill Fm., which underlies the Boshoek Fm., has a Re-Os date of 2,316 ± 7 My ago (13). The Boshoek Fm. correlates with the Makganyene diamictite in the western domain of the Transvaal Basin, the Griqualand West region. The Makganyene diamictite interfingers with the overlying Ongeluk flood basalts, which are correlative to the Hekpoort volcanics in the eastern domain and have a paleolatitude of 11° ± 5° (14). In its upper few meters, the Makganyene diamictite also contains basaltic andesite clasts, interpreted as being clasts of the Ongeluk volcanics. The low paleolatitude of the Ongeluk volcanics implies that the glaciation recorded in the Makganyene and Boshoek Fms. was planetary in extent: a snowball Earth event (15). Consistent with earlier whole-rock Pb–Pb measurements of the Ongeluk Fm. (16), the Hekpoort Fm. contains detrital zircons as young as 2,225 ± 3 My ago (17), an age nearly identical to that of the Nipissing diabase in the Huronian Supergroup. As the Makganyene glaciation begins some time after 2.32 Ga and ends at 2.22 Ga, the three Huronian glaciations predate the Makganyene snowball.

In contrast to the Makganyene Fm., the three Huronian diamictites are unconstrained in latitude. Poles from the Matachewan dyke swarm, at the base of the Huronian sequence, do indicate a latitude of ≈5.5° (18), but ≈2 km of sedimentary deposits separate the base of the Huronian from the first glacial unit (19), which makes it difficult to draw conclusions about the latitude of the glacial units based on these poles.

Abbreviations: Ga, giga-annum before present; My, million years; BIF, banded iron formation; Fm., formation; MIF, mass-independent fractionation.

*To whom correspondence should be addressed. E-mail: rkopp@caltech.edu.

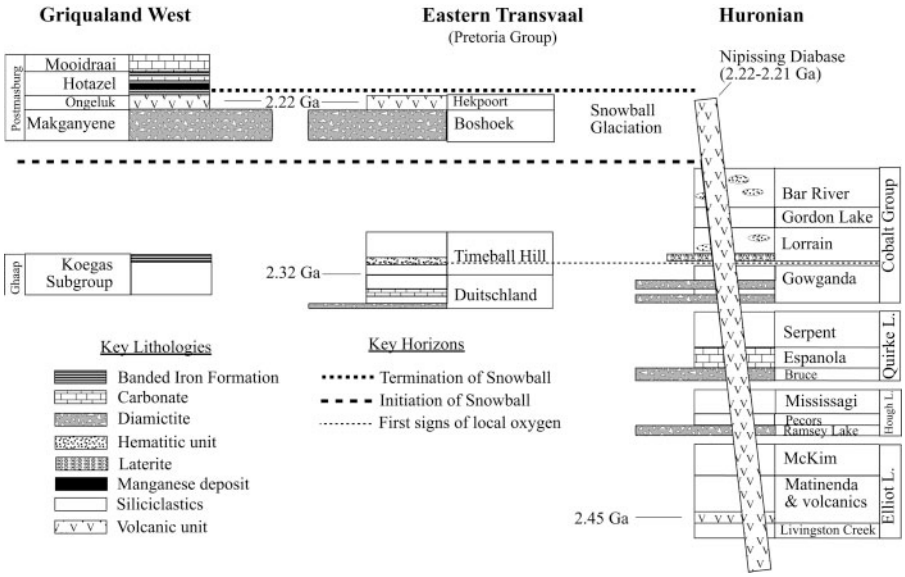

Fig. 1. Proposed correlation of the Huronian Supergroup and the upper Transvaal Supergroup. The three Huronian glacial units, penetrated and capped by the Nipissing diabase, predate the Makganyene diamictite in the Transvaal. The uppermost Huronian glacial unit, the Gowganda Fm., is overlain by hematitic units, perhaps reflecting a rise in O_2. The basal Timeball Hill Fm. contains pyrite with minimal MIF (26), whereas the upper Timeball Hill Fm., which we suggest is correlative to the Lorrain or Bar River Fms., contains red beds. The Makganyene diamictite records a low-latitude, snowball glaciation (29), perhaps triggered by the destruction of a CH_4 greenhouse. It is overlain by the Kalahari Mn Field in the Hotazel Fm., the deposition of which requires free O_2. Transvaal stratigraphy is based on ref. 17; Huronian stratigraphy is based on ref. 19.

Low latitude poles in the Lorrain Fm. (20, 21), which conformably overlies the Gowganda diamictite, are postdepositional overprints (22).

MIF of Sulfur

The recent discovery of MIF of S isotopes in Archean and early Proterozoic rocks has provided a major constraint on atmospheric O_2. Large MIF of S (up to several hundred permil) is produced by photolysis of SO_2 to S by light of wavelengths of <200 nm, which would have been unable to penetrate to the lower atmosphere had O_2 levels been above a few percent of the present atmospheric level (23). To preserve MIF, multiple atmospheric S species must be maintained as partially isolated reservoirs rather than being homogenized by oxidation of reduced species like hydrogen sulfide and polysulfur, as would occur at greater than $\approx 10^{-5}$ present atmospheric level O_2 (24). Mixing and dilution of the atmospherically fractionated component, both in the atmosphere and in the oceans, presumably yields the observed Archean MIF values of up to $\approx 10‰$ (25). An active oceanic S cycle, as would exist at moderately high O_2 levels, also would likely prevent the preservation of MIF.

Before the deposition of the ≈2.32 Ga Rooihogite and Timeball Hill Fms. in the Transvaal Supergroup (13, 26) and the McKim Fm. in the Huronian Supergroup,[†] sedimentary sulfides often display MIF (8, 26, 27) over an order of magnitude larger than the largest values observed in modern sulfate aerosols (25, 28). One plausible interpretation of the diminished MIF observed in the Rooihogite, Timeball Hill, and McKim Fms. is a rise in atmospheric O_2. At present, only glaciers record the MIF sometimes present in sulfate aerosols; in the marine environment, with riverine input composing ≈90% of sulfate input and aerosols composing ≈10%, MIF is not preserved (25). The small range of MIF could reflect an environment in which atmospheric chemistry began to approach modern conditions, decreasing the magnitude of MIF, but in which aerosols formed the major component of marine sulfate input, allowing its preservation.

The small range of MIF also permits an opposite interpretation. Rather than a decrease in atmospheric fractionation, the diminution could be a product of increased continental input and ocean/atmosphere mixing driven by glacial conditions. The period of 2.5–2.2 Ga was a time of glaciations. Enhanced glacial weathering could have made unfractionated S from igneous sources a larger part of the marine S budget, whereas sharper thermal gradients would have driven homogenization of the S pool. Both effects would have decreased sedimentary MIF. If this interpretation is correct, only the final decrease of MIF after ≈2.09 Ga may reflect the rise of atmospheric O_2, and the oxygenation event may have been more rapid than the length of Farquhar and Wing's (8) MIF Stage II (2.45–2.09 Ga) indicates.

Appearance of Local O_2

Both the Huronian and the Transvaal Supergroups contain features suggestive of, but not demanding, the first appearance of O_2 in the period between the Gowganda and Makganyene glaciations. As noted in ref. 8, MIF in the Huronian rocks examined so far is at diminished values compatible with either increased atmospheric O_2 or enhanced glacial weathering and ocean/atmosphere mixing. The Lorrain Fm. contains red beds, as well as a hematitic paleosol at Ville-Marie, Quebec, and the Bar River Fm. contains pseudomorphs after gypsum, consistent with an increase in sulfate levels from oxidative weathering of sulfide minerals on land. In the Transvaal Supergroup, the upper Timeball Hill Fm., like the Lorrain Fm., contains red beds.

Stronger evidence for O_2 appears after the Makganyene glaciation. The Ongeluk Fm. is overlain by the Hotazel Fm., which consists predominantly of banded iron formation (BIF). The basal half meter of the Hotazel Fm. contains dropstones (29) (see *Supporting Text*, which is published as supporting information on the PNAS web site), which suggests it was deposited toward the end of the glacial period. The Hotazel Fm. hosts a massive Mn member (29): a blanket of Mn deposition unmatched by any other known in the world, ≈50 m thick and with an erosional remnant, the Kalahari Mn Field, measuring $\approx 11 \times 50$ km in extent (30).

The Kalahari Mn Field indicates the release of large quantities of O_2 into the ocean and therefore suggests a highly active postglacial aerobic biosphere. In seawater at circumneutral pH, only NO_3^- and O_2 can chemically oxidize soluble Mn^{2+} to produce insoluble Mn(IV) (31) (Table 1). Although a Mn^{2+} oxidizing phototroph also could produce Mn(IV), no such organism has ever been identified. Given the high redox potential of the Mn(IV)/Mn(II) couplet, it is likely that no such organism exists. The unexcited P_{870} reaction center in purple bacteria has a redox potential too low to accept electrons from Mn(II) (Table 1), but no known photosystem reaction center aside from

[†]Wing, B. A., Brabson, E., Farquhar, J., Kaufman, A. J., Rumble, D., III, & Bekker, A. (2002) *Geochim. Cosmochim. Acta* **68,** A840 (abstr.).

Table 1. Midpoint potentials of relevant redox couplets

Redox couplet	E, mV pH 7	E, mV pH 8
CO_2/CH_4*†	−230	−289
SO_4^{2-}/HS^-‡	−217	−284
$Fe(OH)_{3\ (ferrihydrite)}/Fe^{2+}$‡	−5	−183
$UO_2(CO_3)_2^{2-}/UO_{2\ (uraninite)} + CO_2$*§	−18	−137
NO_3^-/NH_4^+‡	+366	+292
P_{870}/P_{870}^+ (purple bacteria)	≈+450	
$MnO_{2\ (pyrolusite)}/Mn^{2+}$‡	+490	+372
NO_3^-/N_2‡	+717	+646
O_2/H_2O	+815	+756
P_{680}/P_{680}^+ (Photosystem II)	≈+1,100	

All reactants not specifically noted are at standard state. Thermodynamic constants are from refs. 76 and 77. Photosystem potentials are from ref. 78.

*Calculated for pCO_2 = 100 mbar.

†Calculated for pCH_4 = 1 mbar.

‡Calculated with all aqueous reactants at 1 mM.

§Calculated with dissolved U species at 20 nM.

the P_{670} reaction center of photosystem II has a higher redox potential. Photosynthetic reduction of Mn(IV) therefore would likely require a two-part photosystem akin to that involved in oxygenic photosynthesis.

One plausible interpretation of the sequence of events leading up to the Paleoproterozoic snowball Earth is shown in Fig. 1 and is as follows.

1. Three glaciogenic units were deposited in the Huronian. The extent of the glaciations is not constrained, but they generally lack the lithographic features associated with snowball Earths, such as a sharp transition from a diamictite to a cap carbonate (32). Although the Espanola carbonate (33) could be a cap for the Bruce glaciation, without paleomagnetic data or additional lithographic features, its presence alone is insufficient to conclude that the Bruce glaciation was a snowball event.
2. Some of the earliest continental red beds were deposited in the Firstbrook member of the Gowganda Fm. and in the Lorrain and Bar River Fms. in Canada, as well as in the upper Timeball Hill Fm. in South Africa. The basal Timeball Hill Fm. has recently been dated at 2,316 ± 7 My ago (13). In our proposed correlation, all of the red bed-bearing units were deposited after the last Huronian glaciation and before the Makganyene glaciation. The formation of the red beds could involve local O_2, although it does not demand it (34). Syngenetic pyrite from the basal Timeball Hall Fm. shows only slight MIF of S (26), consistent with the initiation of planetary oxygenation or enhanced glacial activity.
3. The low-latitude glaciation that formed the Makganyene and Boshoek diamictites (14) was initiated when the production of O_2 triggered the collapse of a methane greenhouse. Although Pavlov *et al.* (35) proposed a similar trigger, they assumed a delay of at least ≈400 My between the onset of oxygenic photosynthesis and its surficial expression. We suggest a more immediate linkage.
4. The Nipissing diabase intruded into the Huronian sequence (36), and the Ongeluk and Hekpoort volcanics were deposited (16).
5. The Hotazel Fm., which includes BIF and Mn members, was deposited in oxygenated waters in the aftermath of the snowball.
6. The upper siderite facies of the Hotazel Fm. and perhaps also part of the overlying Mooidrai dolomite were deposited as cap carbonates in the process of removing CO_2 from a thick postsnowball greenhouse (29).

Timescale for Methane Greenhouse Collapse

For cyanobacteria to be directly responsible for triggering a planetary glaciation, they must have been able to produce enough O_2 to destroy the methane greenhouse before the carbonate–silicate weathering cycle could compensate. On sufficiently long timescales, global cooling would slow silicate weathering and carbonate precipitation, thereby allowing CO_2 to build up in the atmosphere (37). The response time of the carbonate–silicate weathering cycle is generally estimated at ≈1 My (38), although the time to replace the greenhouse capacity lost in a methane greenhouse collapse may be longer. To estimate the timescale for destruction of the methane greenhouse, we constructed a steady-state ocean biogeochemistry model based on the assumptions that biological productivity was controlled by P and N and that Fe(II) oxidation was the main inorganic O_2 sink (see *Supporting Text*).

The critical P/Fe flux ratio for net oxidation of the surface ocean increases with the burial rate of C (see Fig. 2*a*, which is published as supporting information on the PNAS web site). For a P flux similar to today's value of $\approx 8 \times 10^{10}$ mol/y (39) and a burial fraction of 2×10^{-2}, similar to modern anoxic environments, the model results indicate that the critical value is ≈1/50. The current ratio of P flux to hydrothermal Fe flux is ≈1/2, whereas the ratio of P flux to hydrothermal and terrigenous Fe flux is ≈1/64 (1). Rare earth element patterns of BIFs (40) and the stability of terrestrial ferrous sulfides in an anoxic atmosphere suggest that the main source of reactive Fe in the Archean was hydrothermal, so the P/Fe ratio may have been closer to 1/2 than 1/64.

When the P/Fe ratio falls below the critical value, essentially all O_2 produced is captured by Fe^{2+}. Above the critical P/Fe value, there is a net release of O_2 (Fig. 2*a*). Other dissolved O_2 sinks, such as Mn^{2+}, H_2, and CH_4, will consume some O_2, but hydrothermal fluxes of these reductants are up to an order of magnitude less than the flux of Fe^{2+} (41). At today's levels, these are capable of consuming $\approx 7 \times 10^{10}$ mol of O_2 per y, equivalent to 4×10^{-10} bar/y. Although the flux of H_2S from vent fluids in today's high sulfate oceans is comparable to that of Fe^{2+}, in an ocean where Fe^{2+} is the main electron donor, H_2S levels would be lower. A formaldehyde rainout flux of $\approx 10^{12}$ mol/y (24) would be the largest O_2 sink, capable of adsorbing $\approx 6 \times 10^{-9}$ bar of O_2 per y, but would be nullified by H_2O_2 rainout once even a small amount of O_2 accumulated in the atmosphere. O_2 production in excess of $\approx 6 \times 10^{-9}$ bar/y (1 bar = 100 kPa) would therefore be sufficient to initiate CH_4 oxidation, and, once begun, net O_2 production in excess of $\approx 4 \times 10^{-10}$ bar/y would suffice to continue it. At the rates predicted by our model, destruction of a 1-mbar methane greenhouse, if it occurred at all, would likely occur within a few My, a timescale comparable with the carbonate–silicate weathering cycle. Therefore, either cyanobacteria did not evolve until shortly before the oxygenation event, or the nutrient flux did not reach sufficiently high levels at any point after the evolution of cyanobacteria until then.

If cyanobacteria were present during the Huronian glaciations, the increased P flux into the oceans generated by glacial weathering (42) should have triggered the oxygenation event. Instead, the oxygenation event seems to correlate with the later Makganyene glaciation; this finding suggests the evolution of cyanobacteria occurred in the interval between the Huronian glaciations and the Makganyene glaciation.

Whether N limitation could have delayed the destruction of a methane greenhouse‡ depends on the Fe demand of the N_2 fixers and the ability of cyanobacteria to capture Fe before it reacted with O_2 and sank beneath the photic zone as a ferric precipitate. With anoxic deep waters

‡Falkowski, P. G., Follows, M. & Fennel, K. (2003) *EOS Trans. Am. Geophys. Union* **84,** Suppl., abstr. U52C-01.

providing a large source of Fe to the photic zone, life for an early Proterozoic diazotroph would have been easier than for modern diazotrophs that must subsist off of Fe transported from the continents. C/Fe ratios in N_2-fixing populations of *Trichodesmium* range from <2,000 to 50,000 (43). If early cyanobacteria were inefficient at both capturing and using Fe (e.g., C/Fe = 2,000; capture efficiency = 1%), then N limitation could have protected the methane greenhouse, but under more optimistic assumptions (either a higher capture efficiency or a higher C/Fe ratio), it would not have done so (Fig. 2*b*). The geologic record, not computational models, must ultimately decide.

Implications of the Possible Late Evolution of Cyanobacteria

The interpretation presented here suggests that planetary oxygenation began in the interval between the end of the Huronian glaciations and the onset of the Makganyene glaciation and that the Paleoproterozoic snowball Earth was the direct result of a radical change in the biosphere. In the Archean and earliest Proterozoic oceans, life may have been fueled predominantly by Fe, with Fe(II) used as the electron donor for photosynthesis and Fe(III) as the main electron acceptor for respiration. The sediments therefore would be moderately oxidizing and the surface waters reduced (34). Because the redox potential for Mn^{2+} oxidation is much higher than that of Fe^{2+}, Mn would have to be removed from the oceans in reduced form. The carbonates precipitated at this time contain up to ≈2% Mn (30), indicating that Mn^{2+} reached shallow waters and coprecipitated with Ca^{+2}; oxidized Mn is extremely rare. The atmosphere was likely reducing. Astrophysical models predict the Sun was substantially dimmer than today, but a CH_4 greenhouse (44) produced by methanogens living in a reduced upper ocean would have kept the planet warm enough to allow for the presence of liquid water without leading to massive siderite precipitation (45).

This world would have been overthrown when cyanobacteria capable of oxygenic photosynthesis evolved, which molecular phylogenies indicate occurred later than the main bacterial radiation (46). The surface waters became oxidizing and more productive. Reduced C accumulated in the sediments; methanogenesis moved from the surface ocean to the deep ocean, where it was isolated from the atmosphere. Methanotrophy in the ocean and photochemistry in the atmosphere used O_2 to transform atmospheric CH_4 to CO_2, a less effective greenhouse gas. The rise of O_2 thus might have triggered a glacial interval without the ≈400 My delay assumed by others (35).

Phosphate flux into the oceans correlates with increased continental weathering during glacial intervals (42), so increased continental weathering produced by the glaciations may have increased nutrient availability above the threshold for net O_2 release into the atmosphere. Because of the relatively low global temperature, it would have taken only a trace of OH radicals from the oxygenic bloom produced when cyanobacteria appeared in a high-P ocean to damage the CH_4 greenhouse enough to bring average global temperatures to <0°C. During the at least ≈35 My (29, 47) it took to build up a sufficient CO_2 greenhouse to escape from the snowball, hydrothermal fluxes would have built up a rich supply of nutrients in the oceans. When the planet finally warmed, the oceans were ripe for a cyanobacterial bloom. The O_2 produced by the bloom cleared out tens of My worth of accumulated reductants and thus produced the Kalahari Mn field (29).

Biomarker Counterevidence for Archean O_2

Despite the parsimony of cyanobacterial evolution occurring within a few My before the onset of the Paleoproterozoic snowball Earth, some organic biomarker evidence and indirect sedimentological and geochemical arguments have been used to suggest that the origin of cyanobacteria dates to far earlier times: at least 2.78 Ga and maybe as long ago as 3.7 Ga.

The critical piece of evidence placing the origin of cyanobacteria and locally oxic environments in the Archean is the discovery in bitumens from rocks as old as 2.78 Ga of organic biomarkers apparently derived from lipids used by cyanobacteria and eukaryotes in their cell membranes. Although Brocks *et al.* (48) concluded that the bitumens were likely syngenetic, they could not exclude the possibility that they were postdepositional contaminants. Even if the biomarkers are as old as their host rocks, however, the uniformitarian extrapolation of modern lipid distributions to the Archean should be viewed cautiously.

Hopanes. Among modern organisms, 2-methyl-bacteriohopanepolyol is produced predominantly by cyanobacteria and in trace quantities by methylotrophs like *Methylobacterium organophilum* (3). Hopanes derived from 2-methyl-bacteriohopanepolyol can be preserved in sedimentary rocks, where they have been used as tracers for cyanobacteria (3). Hopanol synthesis has traditionally been assumed, based on the understood modern distribution of hopanols, to occur only in aerobic organisms. Fischer *et al.* (79) recently demonstrated, however, that *Geobacter sulfurreducens* can synthesize diverse hopanols, although not 2-methyl-hopanols, when grown under strictly anaerobic conditions. Thus, fossil hopanes do not necessarily imply the presence of O_2-producing organisms, and nothing about 2-methyl-hopanols suggests that they are any different in this respect. Archean 2-methyl-hopanes also might have been produced by ancestral cyanobacteria that predated oxygenic photosynthesis.

Steranes. Produced by eukaryotes for use in the cell membrane, sterols are preserved in the rock record as steranes. Brocks *et al.* (4, 5) recovered steranes, along with 2-methyl-bacteriohopanepolyol, from 2.78 Ga Pilbara Craton shales. Because there is no known anaerobic sterol synthesis pathway, they used their discovery to argue for the presence of O_2.

Cholesterol biosynthesis in modern organisms is a long biochemical pathway that employs the following four O_2-dependent enzymes: (*i*) squalene epoxidase, (*ii*) lanosterol 14-α-methyl demethylase cytochrome P450, (*iii*) sterol-4-α-methyl oxidase, and (*iv*) lathosterol oxidase (49). These O_2-dependent enzymes perform reactions that, although not currently known to occur biochemically in anaerobic organisms, could feasibly occur without O_2. Moreover, the substitution of an O_2-dependent enzyme for an anaerobic step in a biosynthetic pathway appears to be a common evolutionary occurrence. Raymond and Blankenship (50) found that, of the 473 O_2-dependent enzymatically catalyzed reactions in the BioCyc database (www.biocyc.org), 20 have at least one O_2-independent counterpart that performs the same reaction. For instance, AcsF catalyzes an O_2-dependent cyclization step in the synthesis of chlorophyll and bacteriochlorophyll, a pathway that must have existed before the evolution of oxygenic photosynthesis. The O_2-independent enzyme BchE performs the same reaction as AcsF but uses vitamin B_{12} in place of O_2 (50). The assumption that sterol synthesis is always O_2-dependent and always has been therefore merits close inspection.

Indeed, the Hamersley bitumens include their own cautionary message about the application of uniformitarian assumptions to fossil lipids. Dinosterane is generally accepted to be characteristic of dinoflagellates and is interpreted as a dinoflagellate biomarker in Phanerozoic rocks (51). Yet even though an Archean origin for dinoflagellates seems implausible, because it would indicate the Ar-

chean origin of modern eukaryotic group not known in the fossil record until at least the Paleozoic (52), Brocks *et al.* (5) found dinosterane. They interpreted the molecule as being produced by eukaryotes of unknown affinities, although an alternative explanation is that these modern-style putative Archean biomarkers are contaminants.

Indirect Counterevidence for Archean O_2

Although organic biomarkers may be difficult to interpret, they are a significant improvement on several other geological tracers that have been used to argue for the presence of cyanobacteria and environmental O_2, including microfossils, stromatolites, BIFs, and assorted isotopic fractionations.

Microfossils. Before 2 Ga, when diversified assemblages with affinities to major groups of cyanobacteria first appear in the fossil record, the microfossil record is murky (53). Some have interpreted filamentous forms in earlier rocks as cyanobacterial remains (54–56), but Brasier *et al.* (57) recently questioned the biogenic nature of these objects. Moreover, cyanobacteria cannot be identified solely by a filamentous form. Many nonoxygenic bacteria are also filamentous, including some mat-forming green nonsulfur and purple sulfur bacteria (58, 59) and a methanogenic archeon (60). The wide variety of filamentous prokaryotes highlights a problem in identifying fossil microbes lacking clear evidence of cell differentiation based on morphology: Any given form has probably arisen many times in Earth history, both in extant and extinct organisms.

Stromatolites and BIFs. Two types of late Archean rock Fms. have often been interpreted as indicating cyanobacterial activity: stromatolites and BIFs. Des Marais (7) argued that large stromatolite reefs indicate the presence of cyanobacteria and therefore a locally aerobic environment, but large reefs also can form under anaerobic conditions. Populations of anaerobic methane oxidizers, for instance, have built massive reefs at methane seeps in the Black Sea (61). In addition, the Archean and Paleoproterozoic oceans were likely more supersaturated with respect to calcite and aragonite than the modern oceans (62), which would have facilitated the precipitation of large reefs even without biological participation. Indeed, abiotic processes may have played a major role in the formation of many Precambrian stromatolites (63). Moreover, although the deposition of ferric iron in BIFs has traditionally been taken to imply the presence of free O_2 (40, 64, 65), BIFs also could have formed in a O_2-free environment, either by photooxidation (66) or by Fe(II)-oxidizing phototrophic bacteria (67, 68).

Isotopic Evidence. Rosing and Frei (6) argued based on isotopic evidence that >3.7 Ga metashale from West Greenland preserves signs of an aerobic ecosystem. They found organic C with $\delta^{13}C$ values of $-25.6‰$ in the same sediments as Pb with isotopic ratios indicating that the samples were originally enriched in U with respect to Th and interpreted this finding as reflecting an environment in which U could be cycled between its reduced, insoluble U(IV) form and its oxidized, soluble U(VI) form. They concluded the light C was produced by oxygenic phototrophs and that biogenic O_2 had permitted the redox cycling of U. However, all biological C fixation pathways and some abiotic mechanisms can produce light C, and, just like the Fe(III) in BIFs, U(VI) can form in the absence of O_2. At circumneutral pH values, the midpoint potential of the U(VI)/U(IV) couplet is ≈0 V, similar to the Fe(III)/Fe(II) couplet and considerably less oxidizing than Mn(IV)/Mn(II), NO_3^-/N_2, or O_2/H_2O (see Table 1).

A strong negative $\delta^{13}C$ excursion in organic C at ≈2.7 Ga has been interpreted as evidence for the evolution of aerobic methanotrophy (69). Such light C suggests repeated fractionation: first in the production of CH_4 subsequently oxidized to CO_2, then in re-reduction by a primary producer; similar fractionations are observed today in environments with methanotrophs. But although CH_4 oxidation was once thought to require O_2, geochemical measurements (70) and recent microbiological work (71, 72) have demonstrated that CH_4 oxidation also can occur with alternative electron acceptors, so O_2 is not needed to explain the isotopic excursions. Although the anaerobic methane oxidizing bacteria studied today rely on sulfate, which is unlikely to have been available in a high-Fe Archean ocean, thermodynamics permits a variety of electron acceptors, including Fe(III), to be used for CH_4 oxidation.

S isotope data indicate local spikes in sulfate concentration starting ≈3.45 Ga (73, 74). Canfield *et al.* (75) argued that these spikes were produced in high-O_2 environments. But given the low redox potential of the sulfide/sulfate couplet, local sulfate spikes can be explained by scenarios that do not involve O_2. Moreover, sedimentary sulfate deposits, which disappear in the rock record after ≈3.2 Ga (75), do not reappear until after the Huronian glaciations, which suggests that high sulfate conditions were rare.

None of these indirect lines of evidence necessitate oxygenic photosynthesis. The case for cyanobacteria and locally oxic environments existing before the disappearance of MIF of S isotopes and the massive deposition of Mn in the Kalahari Mn Field rests, at the moment, solely on steranes.

Future Directions

Our model for a Paleoproterozoic origin of cyanobacteria is testable by several methods. It suggests that sterols in Archean rocks, if they are original, were synthesized by anaerobic reactions. It therefore should be possible to find or engineer enzymes capable of synthesizing cholesterol under anaerobic, biochemically plausible conditions. In addition, a continuous biomarker record that stretches back from time periods when O_2 is definitely present into the Archean might reveal transitions in community composition. Current work with samples from recent drilling programs targeting the late Archean and the Paleoproterozic has begun this task. An intensive search for biomarkers with definite relationships to metabolism, such as those derived from the pigment molecules of phototrophic bacteria, also would produce a more convincing record. A search for cyanobacterial or eukaryotic fossils that predate 2.0 Ga yet have affinities to modern groups would complement the geochemical approaches.

With respect to the record of MIF of S, the timeline we propose for a rapid oxygenation scenario suggests that decreased fractionation during the interval of the Huronian glaciations may be a byproduct of enhanced glacial weathering and ocean/atmosphere mixing. If this scenario is correct, a similar phenomenon should have occurred in association with the Pongola glaciation at ≈2.9 Ga. Investigation of the Huronian deposits where low-MIF S is found should reveal these deposits to be sedimentologically immature, reflecting glacial input. Additionally, the syngenicity of the MIF values should be tested through techniques such as the paleomagnetic search for significantly postdepositional formation of sulfides.

Finally, our model predicts that the Makganyene snowball Earth was a singular event. Convincing paleomagnetic evidence (including positive syn-sedimentary field tests) that demonstrated the Huronian glaciations were low-latitude would contradict our model and instead support a protracted episode of planetary oxygenation with multiple snowball events not directly triggered by a singular event, the evolution of cyanobacteria.

Summary

Because of the importance of the evolution of cyanobacteria and the planetary oxygenation event in Earth history, it is particularly useful to consider multiple working hypotheses about these events. We propose a model that takes a skeptical attitude toward the evidence for Archean cyanobacteria and a protracted early Proterozoic planetary oxygenation. In our alternative scenario, an evolutionary accident, the genesis of oxygenic photosynthesis, triggered one of the world's worst climate disasters, the Paleoproterozoic snowball Earth. Intensive investigation of the time period of the Paleoproterozoic glaciations may reveal whether a novel biological trait is capable of radically altering the world and nearly bringing an end to life on Earth.

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Observations of dropstones in the basal Hotazel Formation

As reported previously (1), the contact between unweathered pillow basalts of the Ongeluk volcanics and the overlying ironstones of the Hotazel Fm. usually includes 10-20 cm of fine-grained, immature and unsorted volcaniclastic sandstone. The sandstone unit is overlain by ~50-100 cm of jaspilitic iron formation, which contains occasional small dropstones, observed in 7 of 19 industrial drill cores that penetrating the contact (1). The dropstones were interpreted as recording the rapid deglaciation at the end of the Makganyene Snowball Earth. As all the observed clasts are composed of volcanic material, they might alternatively have been emplaced by volcanic activity; with data form isolated drill cores, it is not easily possible to distinguish between these two hypotheses.

In October of 2004, two of us (JLK and CZN) visited an access shaft of the Nchwaning Manganese mine in which the Ongeluk/Hotazel contact is exposed for a lateral distance of ~100m. In-situ examination of this layer revealed that the dropstones occur in isolation in different layers, not clustered in specific layers as would be expected if they were deposited by explosive volcanism. Hence, we conclude that the dropstones were glacially deposited and that this unit records the termination of the Makganyene Snowball.

An Ecological Stochiometry Model of Planetary Oxygenation

In order to determine the minimum timescale on which oxygenic photosynthesis could destroy a methane greenhouse, we constructed two models, one in which productivity was P-limited and one N-limited, and took the minimum of the two productivities. Results are shown in Fig. S2.

P-limited ocean model. Following Bjerrum and Canfield (2), we assumed in the P-limited case that P was removed from the ocean either adsorbed onto Fe(III) particles or in organic matter and organic-derived carbonate fluroapatite. We also assumed P fluxes into and out of the photic zone were balanced and iterated toward a steady state solutions of the equations

$$F_{\mathrm{P,out}} = F_{\mathrm{P,in}} = \gamma \eta_{\mathrm{C:P}} P_{\mathrm{CH_2O}} + K_{ads} F_{\mathrm{FeIII,out}} [\mathrm{P_d}] \quad (1)$$

$$P_{\mathrm{CH_2O,anoxy}} = \mathrm{Min}[\eta_{\mathrm{C:P}} u [\mathrm{P_d}] f_{\mathrm{anoxy}}, \tfrac{1}{4} F_{\mathrm{Fe,in}}] \quad (2)$$

$$P_{\mathrm{CH_2O,oxy}} = \eta_{\mathrm{C:P}} u [\mathrm{P_d}] - P_{\mathrm{CH_2O,anoxy}} \quad (3)$$

$$F_{\mathrm{FeIII,out}} = \alpha \,\mathrm{Min}[F_{\mathrm{Fe,in}}, 4\gamma P_{\mathrm{CH_2O,oxy}} + P_{\mathrm{CH_2O,anoxy}}] \quad (4)$$

$$P_{\mathrm{O_2}} = \gamma (P_{\mathrm{CH_2O,oxy}} + P_{\mathrm{CH_2O,anoxy}}) - \tfrac{1}{4} F_{\mathrm{FeIII,out}} \quad (5)$$

where γ is the ratio of organic C production to organic C burial, $\eta_{\mathrm{C:P}}$ is the ratio of carbon to phosphate in buried organic matter, K_{ads} is equilibrium constant for the adsorbtion of P onto Fe(III) particles, u is the velocity of upwelling bringing nutrient-rich waters into the surface oceans, f_{anoxy} is the maximum fraction of C production for which anoxygenic, Fe(II)-oxidizing photosynthesis can be accountable, and α is the maximum fraction of Fe buried as Fe(III). $F_{\mathrm{Fe,in}}$ is the flux of Fe into the oceans, $F_{\mathrm{FeIII,out}}$ is the flux of Fe(III) out of the oceans, $F_{\mathrm{P,in}}$ is the flux of P into the oceans, $F_{\mathrm{P,out}}$ is the flux of P out of the oceans, P_{CH2O} is the rate of primary productivity, P_{CH2O} is the net rate of surface ocean oxidation in O_2 equivalents, and $[\mathrm{P_d}]$ is the concentration of dissolved P in the oceans.

N-limited ocean model. In a locally aerobic environment, denitrification may have compelled cyanobacteria to engage in the Fe-demanding process of N_2 fixation (3). We modeled this using C/Fe ratios observed in field populations of *Trichodesmium* (4). We assumed the upwelling flux of Fe to be removed from the photic zone either as ferric particles or in organic matter, through the following modifications:

$$P_{CH_2O,oxy} = \eta_{C:Fe}\beta F_{Fe,in} - P_{CH_2O,anoxy} \quad (6)$$

$$F_{FeIII,out} = \mathrm{Min}[(1-\beta)F_{Fe,in}, 4\gamma P_{CH_2O,oxy} + P_{CH_2O,anoxy}] \quad (7)$$

where $\eta_{C:Fe}$ is the ratio of carbon to iron and β is the efficiency of the cyanobacteria in capturing iron.

Figures

Figure S1: (a) Modeled O_2 production at different levels of P and Fe flux into the photic zone. Contours are labeled in bar net O_2/y. Following (2), we assumed a carbon burial efficiency of 0.019, a C/P ratio of 185, a P adsorbtion onto Fe(III) constant of 0.07 μM^{-1}, and mixing velocity of 1.26 x 10^{18} L/y. All the P flux and 10% of the Fe flux were assumed available for biological use. The upper, diagonal portions of the contours represent P limitation, while the lower, horizontal portions represent Fe limitation. (b) Modeled O_2 production at varying C burial efficiency and C/Fe ratio. Except for carbon burial efficiency, parameters are as in part a, with P and Fe flux fixed. Observed C/Fe ratios for modern field populations of *Trichodesmium* range from <2,000 to 50,000.

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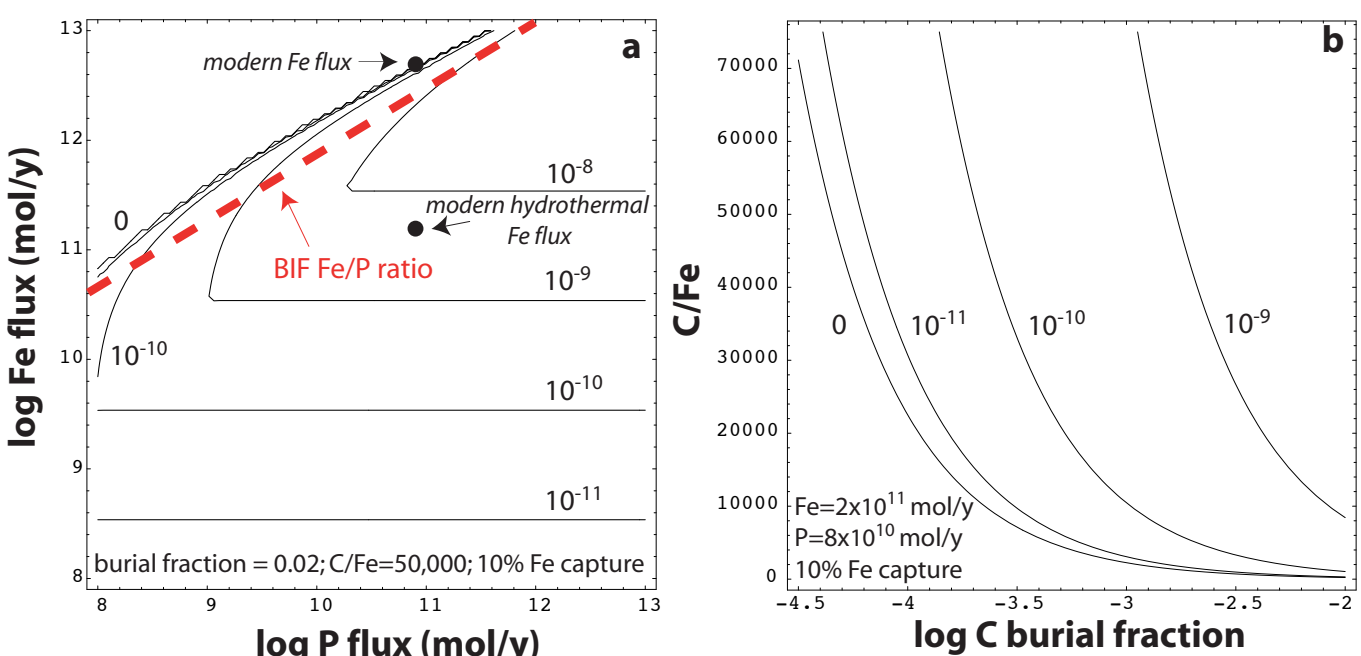

Kopp et al. Figure S3