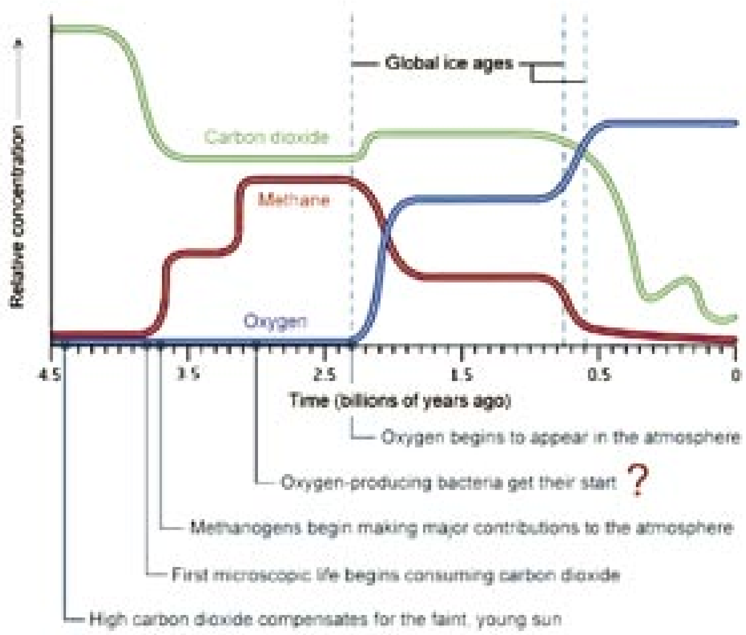
Red Earth, White Earth,

by Joseph L. Kirschvink

Oxygen drives the biosphere—we can't live without it. But most scientists now agree that there was no free oxygen in the air during the earliest portion of Earth's history. The first oxygen came from a group of bacteria—the cyanobacteria—that had developed a new method of photosynthesis. Their method was so efficient that they spread rapidly throughout the oceans of the world and overtook their less-efficient predecessors. But their success may have created a catastrophic climate disaster that plunged Earth into a global deep freeze for tens of millions of years and almost wiped out life on the planet forever. That, at least, is a scenario I have developed in collaboration with geobiology grad student Bob Kopp.

Our planet formed about 4.6 billion years ago, at a time when the young sun was only 70 percent as bright as it is today. With such a weak sun, Earth should have been very cold, but that doesn't seem to have been the case; no evidence of glaciers has (so far) been found for the first 1.5 billion years of the planet's history. It's possible that the greenhouse effect of carbon dioxide produced by volcanic eruptions kept the young planet warm, but it would have required enormous amounts of this gas to stop Earth's surface from freezing—amounts that the geologic record suggests could not have been present for much of the planet's first 2.3 billion years. Unless, that is, it was aided by methane, which is a much more powerful greenhouse gas than carbon dioxide. Methane is produced as a metabolic by-product by a group of primitive bacteria that feed on hydrogen and carbon dioxide—gases emitted in abundance by volcanoes. These bacteria could easily have produced the levels of atmospheric methane needed to make an effective insulating layer.

The cyanobacteria were the first organisms on Earth to produce oxygen, and their evolution led to a rise in atmospheric oxygen levels and a drop in methane levels. Kirschvink's team thinks the cyanobacteria evolved shortly before the first global ice age rather than at the earlier time shown here—hence the question mark.



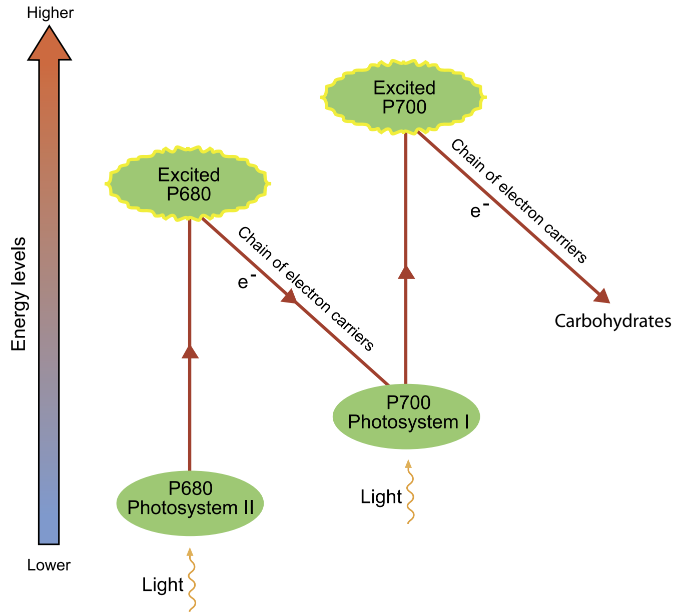
J. Johansen (John Carroll Univ.), M. Schneegurt (Wichita State Univ.) & Cyanosite (www-cyanosite.bio.purdue.edu).

Green Earth, Black Earth

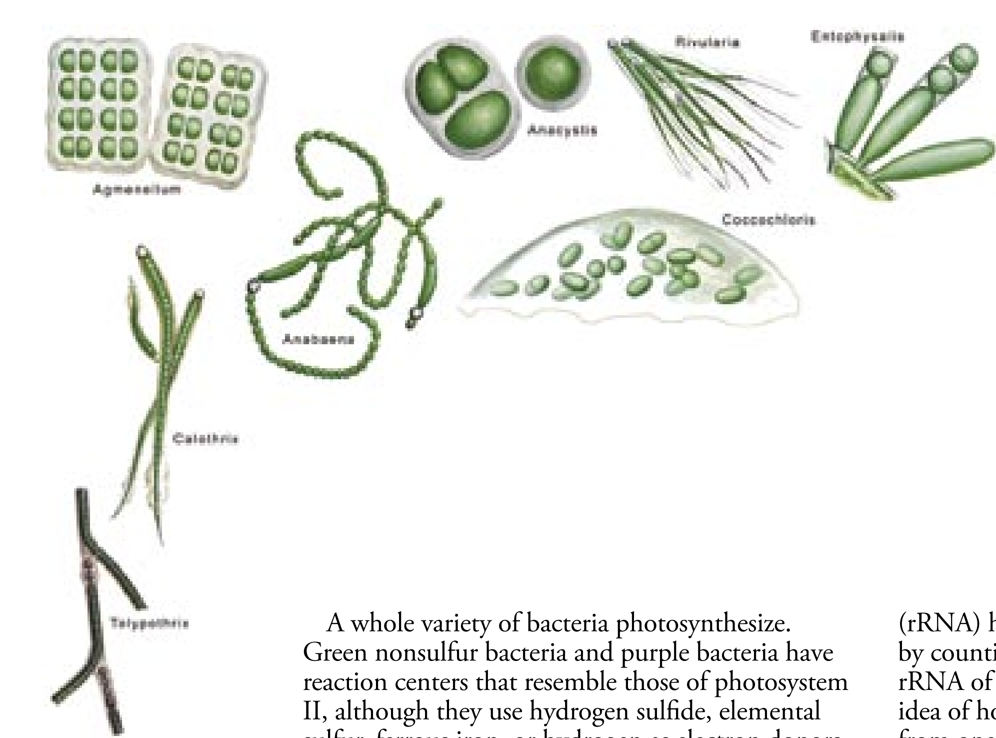
Then along came oxygen. Jim Kasting at Pennsylvania State University, and many other earth scientists, including Bob and myself, think that oxygen arose on our world about 2.3 billion years ago. But other scientists think there was prolific oxygen production much earlier than that, so it's a subject of hot debate. We do agree, however, that copious quantities of this gas were first produced by the cyanobacteria, which evolved a more efficient method of photosynthesis that released energy from a ubiquitous source—water—and produced oxygen as a waste gas. The cyanobacteria used to be called blue-green algae, until they turned out not to be algae at all and were found to come in yellow, brown, and red as well as blue-green.

In photosynthesis, the energy from sunlight starts a chain of events that eventually splits hydrogen atoms off from water molecules and combines them with carbon dioxide molecules to make sugars. These sugars, often converted to insoluble carbohydrates, store energy for the organism, while the remaining oxygen from the water molecules is given off as a waste product. The sequence of events begins when a green pigment, chlorophyll P680, absorbs energy from sunlight and releases an electron. This electron is passed along a chain of electron carriers (which store energy by pumping protons across a membrane) until it reaches a second type of chlorophyll, P700, which can also be excited by sunlight. When that happens, the P700 is able to transfer an electron into a pathway that ultimately results in the transformation of carbon dioxide into organic carbon. To replace the electron that left chlorophyll P680, an enzyme splits water into protons (H^+), oxygen, and electrons.

The diagram above right shows the changes in energy levels that occur during the process. Its Z shape reflects the fact that oxygenic photosynthesis is a two-stage process in which the two chlorophylls work together to raise energy levels higher than either could manage separately. The stage involving chlorophyll P680 is known as photosystem II, and the one using chlorophyll P700 is photosystem I. This dual photosystem evolved in the cyanobacteria. Incidentally, the reason it is also used by all green plants is that the photosynthetic organelles of green plants, the chloroplasts, are descended from cyanobacteria that once lived in a symbiotic relationship with an early ancestor of plants—chloroplasts still contain a residual loop of DNA inherited from their cyanobacterial ancestors.



The chain of events in the light-dependent stage of photosynthesis used by the cyanobacteria and all green plants begins when sunlight hits a molecule of chlorophyll P680, bottom left.



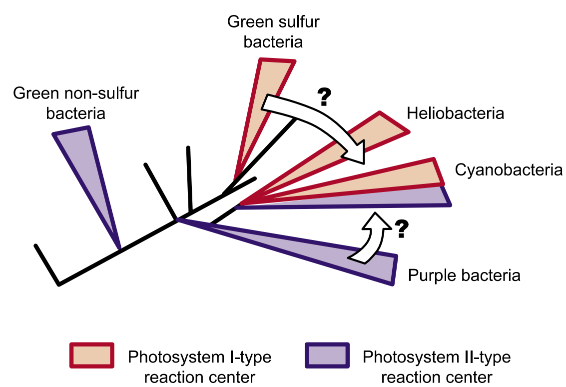
Cyanobacteria are both the heroes and villains of life on Earth. When they evolved, they—or rather, their oxygen—killed off most of the existing organisms and almost made Earth permanently uninhabitable. But without them, we would not be here today. Mistakenly classified as blue-green algae until it was realized that they were bacteria, they're a large and varied group. The paintings of cyanobacteria above were done by C. Mervin Palmer for a 1952 Public Health Service publication.

A whole variety of bacteria photosynthesize. Green nonsulfur bacteria and purple bacteria have reaction centers that resemble those of photosystem II, although they use hydrogen sulfide, elemental sulfur, ferrous iron, or hydrogen as electron donors rather than water, and do not produce oxygen. The reaction centers of green sulfur bacteria and heliobacteria resemble those of photosystem I and use a similar array of electron donors. Although many genes appear to have moved around among photosynthetic bacteria, the simplest interpretation of their genetic architecture suggests that the ancestor of the first oxygen-producing cyanobacterium arose from a chance fusion between a green sulfur bacterium and a purple bacterium (see below right).

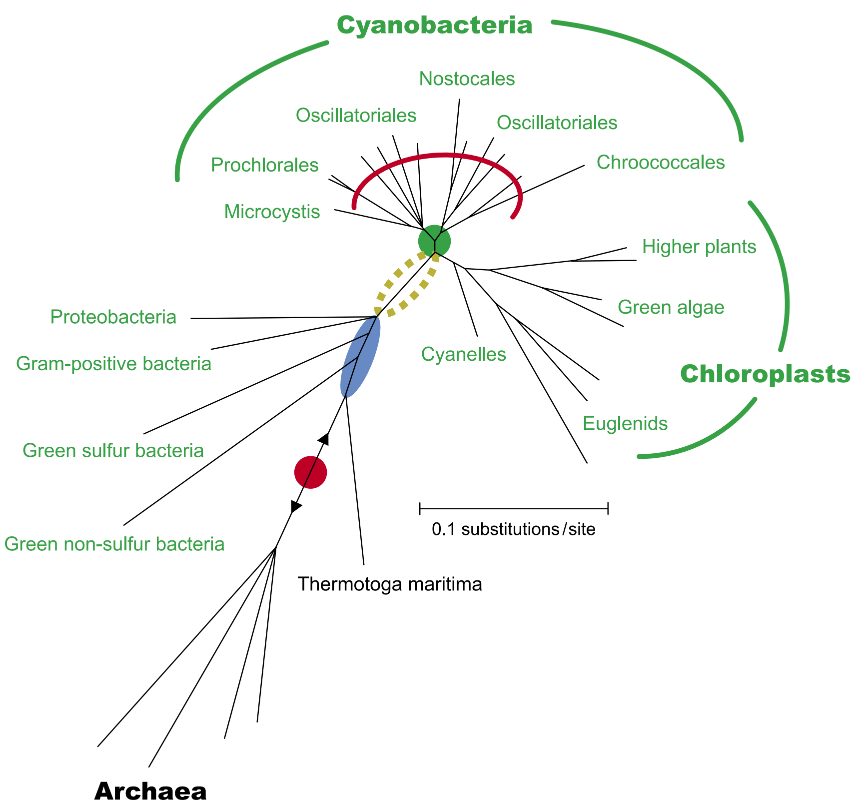
Why do we think it was a whole-cell fusion and not a mutation? The shift in energy levels of chlorophyll P680 when it captures a photon is among the largest of any known organic molecule, yet it is still not enough to couple directly into the electron transport chain following chlorophyll P700. This is presumably why a two-stage process is needed, and why such a process is unlikely to have arisen via a chance mutation in a bacterium with only one of these photosynthetic machines.

Furthermore, in an organism sustained by two photosystems, evolution would have had more flexibility to experiment until, ultimately, natural selection modified the ancestral photosystem II so that it could use water rather than other, less abundant molecules, as an electron donor. It's a very standard way for evolution to work—bits and pieces that have evolved separately combine and make a new system that does something novel. But whole-cell fusion events like this are *extraordinarily rare*, and wouldn't necessarily happen on any given planet.

Are there any clues as to when this fusion happened? We can get some idea by looking at the genomes of bacterial species and drawing up a phylogenetic tree. Mutations in ribosomal RNA (rRNA) happen at a fairly steady but slow rate, so by counting the number of differences between the rRNA of different bacterial species, we can get an idea of how long ago the two species diverged away from one another. The red dot in the phylogenetic tree on the facing page indicates the position of the last common ancestor of all living things. The blue ellipse highlights a radiative burst for the bacteria—a time when many different types evolved. And the branch surrounded by the dashed line leads to the cyanobacteria. It's a fairly long branch, indicating that the cyanobacteria had evolved away from the other bacterial groups for some time before a starburst of different groups suddenly appeared. The green dot, we believe, represents the point when photosystems I and II combined—the



This phylogenetic tree of the photosynthetic bacteria based on rRNA differences also shows the type of reaction center possessed by each group. It's likely that the cyanobacteria, with both reaction centers, are the result of the chance whole-body fusion of a green sulfur bacterium and a purple bacterium. Diagram courtesy of Bob Blankenship, Arizona State University.



This rRNA phylogenetic tree shows the relationships between the Archaea (a group that includes the methane-producing organisms), the bacteria, and chloroplasts. Groups that photosynthesize are labeled in green. The red dot indicates the last common ancestor of all living things (the higher organisms also branch off here but haven't been included to save space); the blue ellipse highlights a radiative burst of bacterial groups; and the green dot is the point at which oxygenic photosynthesis most likely evolved. No clearly identifiable fossils of cyanobacteria have been found earlier than the red line, 1.9 billion years ago.

start of the cyanobacterial success story. While bacteria that used hydrogen, ferrous iron, sulfur, or hydrogen sulfide could only live close to the sources of their electron donors, there was no longer any such constraint on the cyanobacteria. Their electron source, water, was everywhere. They could now radiate all over the world and diversify into many groups. The starburst occurs well after the main bacterial radiation, which places the start of oxygenic photosynthesis quite a long time after the evolution of the first bacteria.

So the evolution of oxygenic photosynthesis was, in fact, not very close to the origin of life, but about halfway through the evolution of the biosphere. Many scientists argue that it happened 2.7 billion years ago, based on the evidence from organic biomarkers—molecules such as fatty acids and lipids that only living organisms make. They fossilize as petroleum. But petroleum moves around through the geological strata, so it's hard to pin down the age at which it formed.

In 1999, Jochen Brocks and Roger Summons at MIT found derivatives of methylhopanol, a type of lipid, in Australian sediments that were 2.7 billion years old. These compounds are predominantly produced today by a number of cyanobacteria, but their function is not understood and their biosynthesis does not appear to require oxygen. Even if these compounds were produced by early cyanobacteria, we don't know if these organisms had yet evolved the ability to split water and make oxygen.

Brocks also found derivatives of sterols—molecules used in the cellular membranes of all known higher organisms—in the same sediments. Sterol synthesis, it is argued, requires oxygen. But these sterols may have formed more recently and moved down into the ancient sediments. Among the molecules present were ones produced today only by dinoflagellates, a type of algae with no fossil record until around 400 million years ago. Large parts of Australia were covered by limestone with reef complexes (a good source rock for petroleum) at about this time, so there are many possible sources of contamination in the present and past environments.

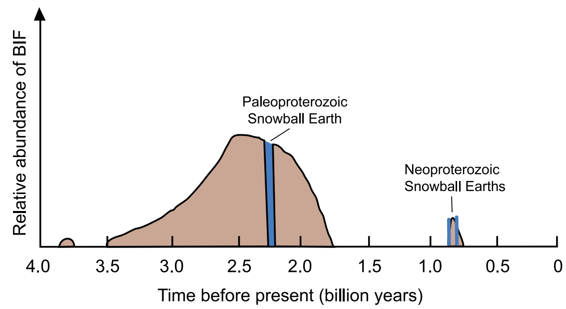
In addition, the assumption that oxygen has always been needed to produce sterols may be wrong. Bob Blankenship of Arizona State University and Jason Raymond of Lawrence Livermore National Laboratory checked out the BioCyc database, a collection of metabolic pathways for hundreds of organisms, for instances where completely oxygen-free reactions, using anaerobic enzymes, could perform the same work as oxygen-dependent enzymes. They found a real beaut: The synthesis of chlorophyll requires oxygen. But to make oxygen, you need chlorophyll. Where did the oxygen to make chlorophyll come from if oxygen wasn't there before chlorophyll evolved? Blankenship and Raymond found that anaerobic photosynthetic organisms had a different enzyme that catalyzed exactly the same chlorophyll-making step—closing a small ring in the carbon backbone—without needing oxygen. *Two completely unrelated enzymes were doing exactly the same chemical conversion.*

Of over 400 known oxygen-dependent reactions, there were more than 80, in at least 20 metabolic pathways, for which there was a direct anaerobic-to-aerobic substitution. It seems that once oxygen came in, many of the old enzymes were replaced with more efficient oxygen-dependant versions. The extrapolation of modern biochemistry to the early Earth must therefore always be handled with extreme caution.

Let's see if we're on firmer ground when we look at the geological record. The presence of sedimentary banded iron formations (BIFs for short) has often been claimed as evidence that locally oxygen-rich environments were present as long as 3.8 billion years ago. With their beautiful banding, BIFs are stars of the Precambrian rock world. The oldest BIFs formed about 3.8 billion years ago, peak formation time was about 2.5 billion years ago, and they stopped forming 1.75 billion years ago, apart for a small blip at 700 million years ago that I'll tell you about later.

BIFs form when something happens to change highly soluble ferrous iron, Fe^{2+}, to insoluble ferric iron, Fe^{3+}, which then drops to the ocean floor as a rain of rust. For a long time, many argued that this "something" was the interaction of dissolved iron—carried through oxygen-free bottom waters—with oxygen produced by small communities of cyanobacteria living in surface waters.

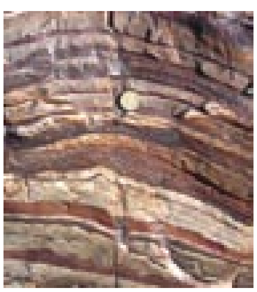
But does the deposition of BIFs actually demand oxygen? Both UV light and iron-oxidizing photosynthetic bacteria could also be responsible. Some strains of green sulfur, purple nonsulfur, and purple sulfur bacteria can use ferrous iron, rather than water, as the electron donor in photosynthesis. Strong support for this has come from my colleague Dianne Newman, associate professor of geobiology and environmental science and engineering. Newman and former postdoc Andreas Kappler simulated water of the chemistry that we think was present in the Precambrian, and put some iron-oxidizing photosynthetic bacteria into it. Even at a light level equivalent to that found at a depth of 100 meters, the bacteria received enough light for photosynthesis, and oxidized ferrous iron to ferric iron so rapidly that they used it all up (facing page). So it seems quite likely that the BIFs were formed by these bacteria, which makes sense; their lineage is much more ancient than that of the cyanobacteria. BIFs are not good indicators of free oxygen.



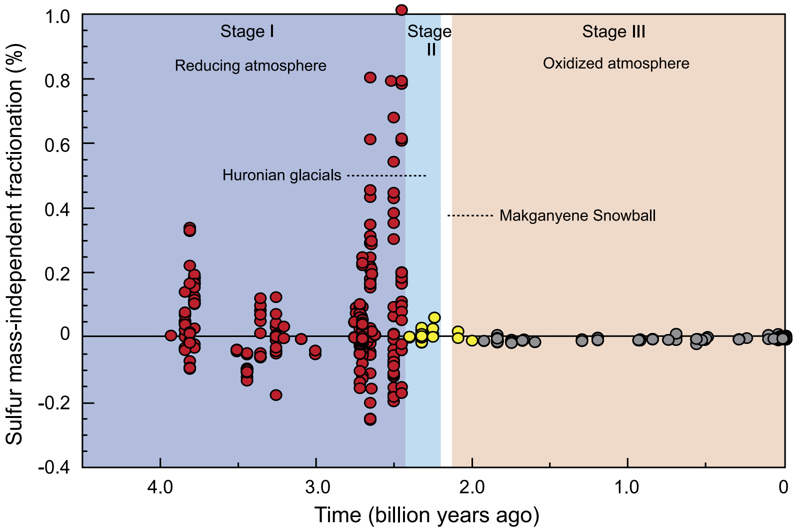
Aside from a few more recent deposits, banded iron formations (BIFs) are confined to the period of Earth's history ending around 1.8 billion years ago. Periods when Earth was in a global ice age, or "snowball" state, are also shown.

Evidence for the *absence* of oxygen in Earth's early atmosphere comes from pyrite, FeS_2. Pyrite is unstable in an oxygen-rich environment, but river deposits almost anywhere in the world that are older than 2.3 billion years contain pyrite grains. They show signs of having been carried for long distances by water—something that would be impossible in today's oxygenated world, because the sulfide would quickly oxidize to sulfate, and the iron would rust.

Another reliable line of geological evidence is the study of sulfur isotopes, of which there are four: ^{32}S, ^{33}S, ^{34}S, and ^{36}S. Most chemical reactions involving sulfur produce what's called mass-dependent fractionation—the reaction separates ^{34}S from ^{32}S twice as strongly as it separates ^{33}S from ^{32}S, and separates ^{36}S from ^{32}S twice as strongly again, proportional to the difference in masses. But this isn't true when gaseous sulfur species, particularly sulfur dioxide, are struck by photons of UV light. James Farquhar at the University of Maryland has shown that this produces something called mass-*independent* fractionation. It doesn't happen much today, both because the ozone layer blocks high-energy UV light from most of the atmosphere, and because sulfur dioxide tends to be oxidized



Western Australia has extensive banded iron formations; in some areas, individual layers of deposition can be traced for more than 300 kilometers. The dark bands in the close-up above are iron oxides, and the red bands are chert stained with fine-grained iron oxides. The coin is for scale. These photos were taken in Karijini National Park.



Plotting the ratio of different sulfur isotopes in rock samples against the age of the planet gives a good insight into the evolution of the atmosphere. A phenomenon known as mass-independent fractionation (MIF) only happens in an oxygen-free atmosphere, which indicates that the Earth was oxygen-free during the early years. Much less MIF is found in Stage II, perhaps due to the rise of oxygen, or maybe because glacial conditions enhanced the mixing of sulfur isotopes. No MIF is found after 2.2 billion years ago, a good indication that the atmosphere was fully oxygenated from that time on. Diagram courtesy of J. Farquhar.

The purple nonsulfur bacterium *Rhodopseudomonas* produces rust in the absence of oxygen.

pretty quickly to sulfate aerosols, which is why we don't see it in recent deposits of pyrite and other sulfides. But mass-independent fractionation *is* found in rocks older than 2.2 billion years. As the effect can only happen in a reducing ("reduction" being the chemical opposite of "oxidation") atmosphere, it's a good indication that the change from an oxygen-free to an oxygenated atmosphere happened at about this time. Our research is now focused on the period between 2.45 and 2 billion years ago (Stage II in the diagram above), when there appears to have been a transition between the two types of atmosphere.

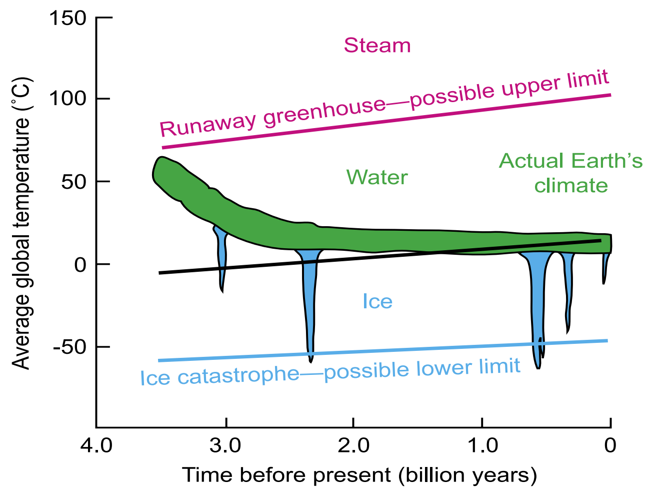
Every now and again in Earth's history, there's a geological event that happens once and is never repeated. The Kalahari manganese field in South Africa is one of those. It's the world's largest manganese deposit by far. Mostly buried beneath the sands of the Kalahari Desert, it's 11 kilometers wide, 50 kilometers long, and about 50 meters thick—and that's just what's left after erosion. The deposit formed about 2.2 billion years ago when insoluble manganese precipitated out of ocean water in vast quantities. It's a unique deposit, and a very valuable one. Without manganese, skyscrapers would fall down, because you need about a tenth of a percent manganese to be alloyed with iron to make steel. But there's no need to worry about that; there's so much here, it will be a long, long time before it ever runs out.

Manganese is a powerful indicator of the presence of oxygen because, electrochemically, it's as close as you can get to oxygen with a metal—much closer than iron. The only way you can oxidize soluble Mn^{2+} to insoluble Mn^{4+} is with nitrate (NO_3^-) or oxygen. Since nitrate itself requires oxygen to form, it's pretty clear that when sedimentary manganese starts to come out of solution in copious quantities, molecular oxygen has to be present. Anoxygenic photosynthetic bacteria couldn't be responsible for the manganese

A vast deposit of manganese lies below the sands of the Kalahari desert in South Africa.

deposit, the way they were for the BIFs, because Mn^{2+} is not a good electron donor for the one-part photosystems used in anoxygenic photosynthesis. So this is the earliest time for which we are certain that copious quantities of free oxygen were available, most likely from oxygenic photosynthesis. What caused this dramatic precipitation of manganese, and when did it happen?

Before I outline a possible scenario to explain this manganese deposit, I'd like to make a small detour into "snowballology." Back in the 1980s, it was known that over time the sun has been getting



The green band shows Earth's climate range over the past 4 billion years, and icicles indicate the major ice ages. Earth has managed to avoid getting so hot that a runaway greenhouse effect occurs, but there were periods—the icicles that extend below the ice catastrophe line—when it got cold enough for the entire planet to freeze over and become a snowball. The ice ages are, from left to right, the Pongola, the Huronian plus Makganyene, the Neoproterozoic, the Gondwana, and the Pleistocene. Adapted from a diagram by James Lovelock.

warmer, that the planet had had liquid water for most of its geological history, and that there had been four or five major ice ages. But all the global climate models that people were using had a persistent problem: the runaway ice-albedo effect. "Albedo" is a fancy word for brightness or, in this case, reflectivity. The landmasses and oceans of a planet absorb sunlight, but ice reflects it back into space. When the ice sheets only cover the north and south caps of the planet, this isn't a problem, but if everything above 30 degrees latitude—that's about the position of Houston or Perth—was frozen, the planet would reflect more heat than it could absorb. Earth would cool rapidly and unstoppably, floating pack ice would reach the equator in about 10 years, and sea ice at the equator would eventually be about a mile thick. Earth would become a snowball.

In all of these early climate models, there was no way Earth could escape from this ice catastrophe once the globe had frozen over. For this reason all of the climate modelers and most of the scientific community assumed that this had never happened. Then, in the late 1980s, our lab was dealing with some puzzling paleomagnetic data that showed there had been widespread ice on the equator about 700 million years ago. I must have been chewing on this in my sleep, because I woke up one night and realized that if it *had* happened, it would explain a lot of things, including that small blip of BIFs at 700 million years ago in the diagram on p. 14. If the oceans had indeed completely frozen over, hydrothermal vent fluids pumping reduced metals like ferrous iron into the ocean would have stripped the water beneath the ice sheets of oxygen (by converting it to rust) after a few million years. Once all the oxygen was gone, these reduced metals, still pumping out of the vents, would build up in the water. Then, once the ice melted and oxygen levels increased again, all that ferrous iron in the water would be oxidized again. Vast amounts of rust would precipitate out and form the BIFs.

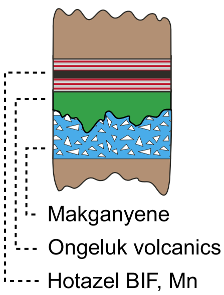
But what could possibly stop the ice-albedo effect once it had started? Volcanoes. The climate modelers had forgotten to put them into the models. Volcanoes wouldn't become inactive when all the land and oceans were covered in ice—they would still erupt and emit carbon dioxide, which would slowly build up in the atmosphere. And once the insulating greenhouse effect of this carbon dioxide kicked in, it would reverse the cooling. Carbon dioxide levels would have had to build up to four or five hundred times the present levels before there was enough warming to melt the ice, but our calculations showed that this could have happened in as short a time as 10 million years.

Today, the idea that Earth was a snowball at least twice between 800 and 600 million years ago, in the Neoproterozoic period, is gaining widespread acceptance. Most of the debate now is about how complete the snowballs were, and whether there were bits of open ocean around the equator. Was it a snowball or more of a slushball?

These snowballs happened well after the period that may have seen the rise of the cyanobacteria, but there's good evidence that Earth was also encased in a snowball between 2.3 and 2.2 billion years ago, in the Paleoproterozoic. And this snowball was directly related to their evolution. The evidence comes from the Makganyene glaciation in the Kalahari area of South Africa. When you walk in the field there, you find stones scratched in multiple parallel directions on both sides, a sign that they've been dragged across the bottom of a glacier. We've been able to estimate the latitude these rocks were at during the glaciation because a huge series of eruptions, the Ongeluk volcanics, flooded the area with basalt 2.22 billion years ago, and the lava intermingled with rocks carried along by the glaciers. When lava cools, tiny magnets made of iron oxide crystals within it get frozen in alignment with Earth's magnetic field, and we can tell the latitude of the eruption by the dip of their preserved magnetism to the horizontal. The Ongeluk eruptions were just 11 degrees from the

Dropstones like this one were embedded in the bottom half-meter of the Nchwaning manganese mine.

equator, the present-day level of Costa Rica. The runaway ice-albedo effect that causes a snowball kicks in when ice sheets get below about 33 degrees latitude, so finding signs of glaciers much closer to the equator, at 11 degrees latitude, is good evidence that Earth was entirely frozen over.



A section through the Precambrian strata of the Kalahari area.

The Precambrian geology of the Kalahari (left) is very interesting. We start with rocks that are 2.415 billion years old, above which lie the glacial deposits of Makganyene, intermingling with and covered by the 2.22-billion-year-old Ongeluk flood basalts. Above that is a BIF that includes the enormous manganese deposit, named the Hotazel formation after a local mining town (which, I can vouch, lives up to its name). It occurred to me that the Hotazel formation could be related to the Makganyene snowball, but to pursue my theory, I had to know when the glaciation ended.

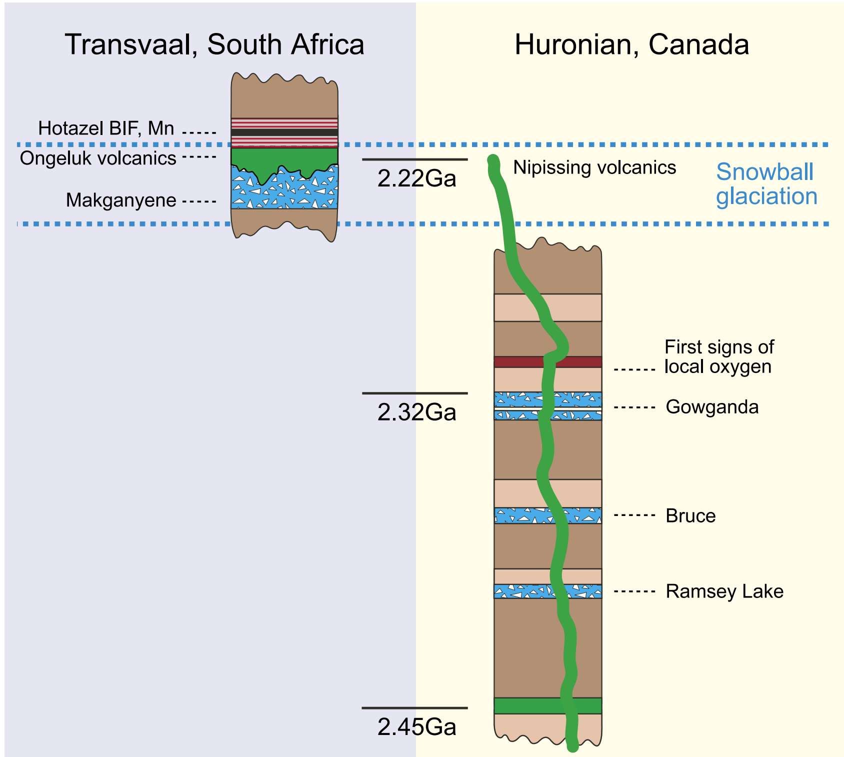
The prevailing view is that the Ongeluk eruptions marked the end of the ice age. But we know from other places where flood basalts have occurred, such as the Deccan Traps in India, that lava comes out of Earth's interior in enormous quantities over no more than one or two million years. That's much shorter than the time required to build up enough carbon dioxide to melt a snowball. In this early Earth, with its much weaker sun, it would take 70–100 million years to build up enough carbon dioxide to reverse the ice-albedo effect. So let's step back and look—could it be that the Hotazel BIFs, like the 700-million-year-old BIF blip in the Neoproterozoic, are related to the snowball?

Geologists use dropstones as evidence of melting glaciers. These are stones carried along in the ice as the glacier travels, and by icebergs after they calve off into the sea. When the ice melts, the stones drop down one by one and become embedded in the sedimentary layers. To see if the Hotazel BIF contained any dropstones, we looked at some drill cores. There were stones in the bottom meter or so of the BIF, on top of the volcanic layer, that might have been dropstones, but we couldn't be sure. They could equally well have been ejecta—rocks thrown up into the air by little explosions from a volcanic vent. But there is a way to tell the difference: ejecta are all in the same geological layer, while dropstones are arranged randomly, wherever they drop when the glacier melts. The drill cores couldn't tell us that, so we just had to go look at them *in situ*.

The best place to examine this contact between the Ongeluk lavas and the Hotazel formation is in the Nchwaning mine on the Kalahari manganese field, where the base of the ironstone and manganese deposits just happens to be exposed along an access tunnel, about 200 meters below ground. It wasn't easy working in the dark looking at rocks covered with many years' worth of diesel soot. We had to spray the rocks with soapy water to see what we were looking for, but there, in the bottom half-meter or so of the Hotazel formation, were dropstones. Not in discrete layers, as ejecta would have been, but dropped randomly here and there, as from a melting glacier. This, to me, shows that the snowball glaciation ended here, after the Ongeluk eruptions. And this melting is somehow tied up with the massive deposition of BIFs and manganese that came immediately after.

We know there were a number of earlier ice ages, including three known as the Huronian glacials (named after rock exposed around Lake Huron). There's no evidence from magnetization data that the Huronian glaciations occurred at low latitude. As far as we can tell, they may well have occurred at midlatitudes, further than 33 degrees from the equator. So they might not have been snowballs. Nevertheless, the Huronian strata have been very helpful in our attempts to discover the reason for the Makganyene snowball. By a lucky chance, the whole Huronian formation is overlaid and cut through by a volcanic dike stemming from an

Knowing they wouldn't look this clean afterward, the dropstone-detection team posed for a photo before descending into the manganese mine. Kirschvink (second from right) and geobiology grad student Cody Nash (third from right) were accompanied by a driver (next to Cody), and mine manager A. Pretorius's son and daughters.



A possible chronological correlation between the Kalahari (left) and Huronian (right) strata is shown above. The blue and white areas are glacial deposits from ice ages. Lava (green) from the Ongeluk volcanoes erupted during the Makganyene glaciation 2.22 billion years (Ga) ago, while lava from the Huronian Nipissing volcanics that occurred at about the same time erupted through the lower strata.

eruption that happened at the same time as the Ongeluk eruptions. This gave Bob and me a way to correlate the South African rock strata with the Huronian ones. When we put the two areas in chronological order, as in the diagram above, we could see that the final Huronian glaciation, the Gowganda, predated the Makganyene snowball. Before Gowganda, there is little evidence for oxygen. After Gowganda, there is; sulfates (from the oxidation of sulfides like pyrite) and ferric iron appear in the strata. And then the Makganyene snowball happens.

Is this just a temporal coincidence, or did planetary oxidation start just after the last Huronian glaciation and before the snowball? Did the mutant cyanobacterium, the one that combined photosystems I and II, do something bad? It's a possibility: an exponentially growing bacterium that releases oxygen into an anaerobic world could quite rapidly create a very unstable situation, eventually leading to a snowball.

When did the critical mutation happen? Was it during the Huronian glaciations? As I said earlier, cyanobacterial growth isn't limited by the availability of electron donors, only by the availability of nutrients like phosphorus and iron. This is true today—it's why you get cyanobacterial blooms from phosphorus- and nitrogen-rich agricultural runoff—and it would also have been true in Huronian times.

Bob constructed a simple cyanobacterial growth model using the sort of carbon, phosphorus, and iron fluxes that might have been present during a partial glaciation in an anoxic world. Phosphorus, which originates in the rocks of the continents and is carried into the oceans by rivers and glaciers, is the main nutrient limiting their growth, and the

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A bloom of *Anabaenopsis* on Bodetti Lake, Argentina; the bubbles are likely oxygen.

cyanobacterial bloom would increase rapidly until it was all used up. The oxygen the cyanobacteria released during photosynthesis would initially be taken out of solution by the ferrous iron, and other reductants, from the hydrothermal vents, or locked up in organic matter in sediments on the ocean floor. But eventually, there would be so many cyanobacteria that excess oxygen would build up in the atmosphere and affect the methane greenhouse.

According to Bob's model, this could happen in around a million years if the phosphorus input was pumped up enough. And guess what? Enhanced weathering during a glaciation is just the thing to pump up the flux of phosphorus into the ocean and spur the proliferation of the cyanobacteria. So if there *were* cyanobacteria around during the Huronian ice ages, these glaciations might well have been the trigger that pushed the system over the edge.

The cyanobacteria changed the planet forever . . . . But it all so nearly went wrong, and it's a sobering thought that a single mutant cell—the first oxygen-releasing cyanobacterium—could have destroyed the entire ecosystem of planet Earth.

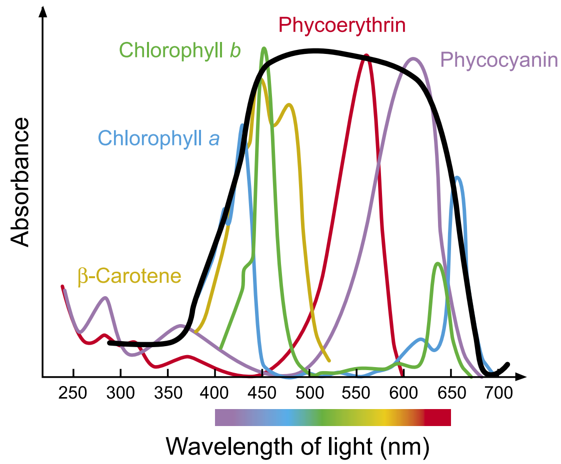
But we don't see any evidence of cyanobacterial oxygen production affecting sediments until *after* the three Huronian glaciations, and before the Makganyene. If Earth was experiencing glacial cycles in Huronian times the way it does today, the Makganyene ice age may have been just the fourth ice age in the series. If the cyanobacteria evolved just before it started, the extra phosphorus pumped into the ocean by the glaciers would have caused the huge bloom that oxygenated the oceans and the atmosphere. Even today there are mini-blooms in the wake of melting icebergs.

In attempting to cope with the influx of oxygen, many species died, others evolved the ability to breathe it, and some, like the methane-generating bacteria, survived in deeper parts of the ocean that were still anoxic. The methane from these bacteria no longer reached the atmosphere, but oxygen from the cyanobacteria, who live near the surface, did. Aided by sunlight, the oxygen would have reacted with the methane, changing it to water and carbon dioxide—a much less effective greenhouse gas, as I said earlier. With the destruction of the methane greenhouse, the planet would have lost heat rapidly. Global temperatures would have plummeted to -50 degrees C, Earth would have become a snowball, and most living things would have died.

It was a close call. If Earth had been a bit farther from the sun, temperatures at the poles could have dropped enough to freeze the carbon dioxide into dry ice, robbing us of the greenhouse escape route. The planet would never again have been able to support life. (Did something like this happen to Mars?) As it was, it likely took at least 70 million years for the planet to warm up again. But when the swing from freezing to warming came, it would have been rapid. Once enough carbon dioxide had built up in the atmosphere to start melting the glaciers, the extra water vapor released would have compounded the greenhouse warming, and temperatures would have jumped rapidly up to perhaps +50 degrees C**.**

While the oceans were frozen over, the hydrothermal vents continued to release large amounts of trace elements and minerals, including ferrous iron and soluble manganese, so by the time the ice melted, the waters were again rich in nutrients. Particularly in upwelling zones on continental margins, the cyanobacteria would have given off an abundance of oxygen, and this would have reacted with all that dissolved iron and manganese, and precipitated it out. That is the unique event that created the Kalahari manganese field.

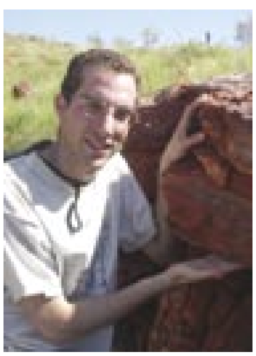
The pigments that plants and photosynthetic bacteria use to absorb sunlight during photosynthesis respond to all the wavelengths of visible light except green, which is reflected. That's why plants appear green. Photosynthesis would be more efficient if the green photons were harnessed as well (black line), but then the green parts of our planet would look black.



The cyanobacteria changed the planet forever. Living things were able to increase in size and become multicellular, as respiration using oxygen produces more energy than respiration with other electron acceptors. A few methane-excreting bacteria survived, but only in places well away from oxygen, such as the mud under rice paddies, and the stomachs of cows. But it all so nearly went wrong, and it's a sobering thought that a single mutant cell—the first oxygen-releasing cyanobacterium—could have destroyed the entire ecosystem of planet Earth.

Could it happen again? I remember attending a Chem 1 lecture back in a 1971 freshman class given by Harry Gray, now the Beckman Professor of Chemistry, in which he showed us a slide of the absorption spectrum of the various photosynthetic pigments. Gray, a chemist trying to find better ways of harnessing solar power, complained how inefficient the system was, because all those green photons in the middle of the spectrum were going to waste.

Which leads me to think, what if some clever genetic engineer made a bacterium that could photosynthesize those green photons as well? And what if it got out and spread? If all the green photons were captured, our green planet would look black. Imagine the albedo effect of a black planet—every living thing would fry. If one cyanobacterium 2.3 billion years ago could destroy most of life on Earth, it could happen again. We've got to watch those chemists. □



Bob Kopp is holding some of the oldest evidence for life on this planet, a stromatolite that formed 3.5 billion years ago.

Joe Kirschvink is the Van Wingen Professor of Geobiology. His research focuses on the way in which major events on the surface of Earth, and possibly Mars, have influenced biological evolution, and how biological evolution has affected the climate and geology. As a high-school student in Phoenix, Arizona, a talk by a visiting professor—Kip Thorne—so impressed him that he decided he wanted to study at the speaker's university. Working with the late paleoecologist Heinz Lowenstam, the discoverer of biomagnetism, he earned his Caltech BS in biology and MS in geology in 1975, followed by a PhD in geology/geobiology from Princeton in 1979. Returning to Caltech in 1981 as an assistant professor, he became an associate professor in 1987, a full professor in 1992, and the Van Wingen Professor in 2004.

Kirschvink has a knack for proposing controversial hypotheses that subsequently gain acceptance and lead to new ways of thinking. They include the Snowball Earth hypothesis; the proposal that polar wander led to the Cambrian evolutionary explosion; and the idea that bacteria could have traveled to Earth from Mars in meteorites. He discovered that some magnetized sedimentary rocks contain the fossilized remains of magnetotactic bacteria, and his idea that the higher animals can sense magnetic fields by using biogenic magnetite led to the discovery of these sensory organelles and provided a biophysical basis for the understanding of magnetic effects on animal behavior.

A fellow of the American Association for the Advancement of Science, the American Geophysical Union, and the American Academy of Arts and Sciences, Kirschvink is an enthusiastic and popular teacher who was awarded the Richard P. Feynman Prize for Excellence in Teaching in 2002. There is even an asteroid 27711 Kirschvink, which orbits between Mars and Jupiter with an unusually high eccentricity.

This article is adapted from a talk given in May at the 68th Annual Seminar Day. Bob Kopp is the lead author of a paper on this subject that appeared in the August 2005 issue of PNAS*, vol. 102, p.11131.*