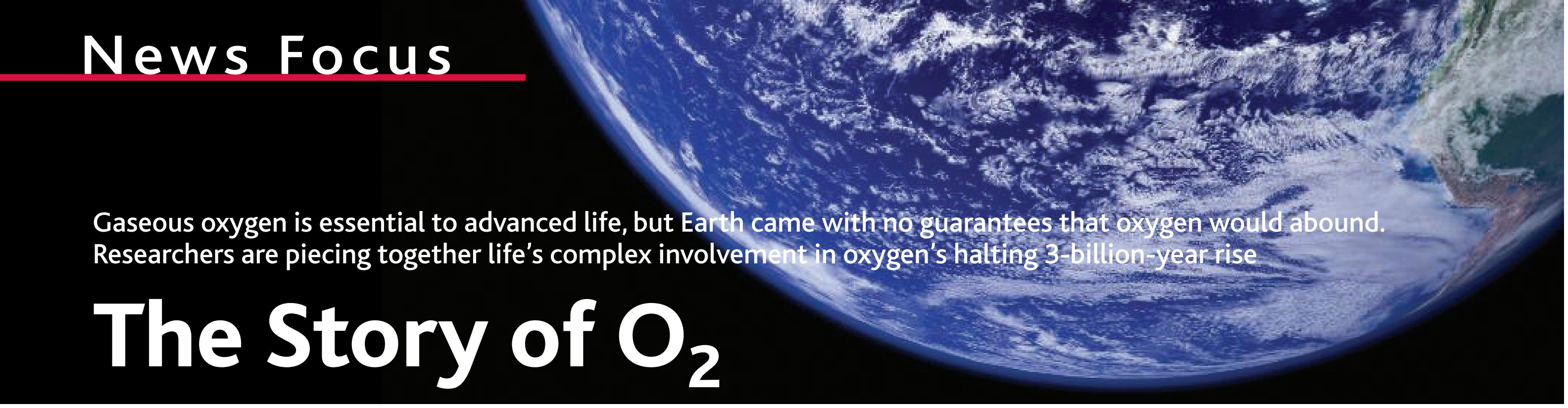


Gaseous oxygen is essential to advanced life, but Earth came with no guarantees that oxygen would abound. Researchers are piecing together life's complex involvement in oxygen's halting 3-billion-year rise

The Story of O_2

In the beginning, Earth was devoid of oxygen, and then life arose from nonlife. As that first life evolved over a billion years, it began to produce oxygen, but not enough for the life-energizing gas to appear in the atmosphere. Was green scum all there was to life, all there ever would be? Apparently, yes, unless life and nonlife could somehow work together to oxygenate the planet from the atmosphere to the deep sea.

Earth scientists are flocking to the emerging field of astrobiology to tease out the history of oxygen on Earth from a maddeningly subtle and fragmented rock record. The rise of atmospheric oxygen from nothing to abundance, they are finding, came in two big steps about 2 billion years apart. Relatively simple life probably facilitated the first step up and possibly the second, much to its own detriment but to the benefit of more complex life.

"The rise of oxygen changed the course of evolution," says astrobiologist David Catling of the University of Bristol, U.K. "Atmospheric oxygen was a precursor to advanced life on Earth, and, I would argue, to life elsewhere." With the new interest in 3 billion years of oxygen history, "there's been a great deal of progress," says geochemist Donald Canfield of the University of Southern Denmark in Odense. "The field has matured; it used to be a hobby area for most people. I credit NASA's [astrobiology funding] for much of that." An invigorated field is attacking a host of big questions: When did free oxygen first appear in Earth's atmosphere? What made it appear in the first place? What held it back for so long? And what caused the second, delayed surge of oxygen that allowed advanced animals to appear?

A certain beginning

Historians of oxygen have always agreed on one thing: Earth started out with no free oxygen—that is, diatomic oxygen, or O_2. It was all tied up in rock and water. For half a century, researchers have vacillated over whether the gases that were there favored the formation of life's starting materials (see sidebar, p. 1732). Without free oxygen, in any case, the first life that did appear by perhaps 3.5 billion years ago had to "breathe" elements such as iron, processing them to gain a mere pittance of energy.

For decades, scientists have argued about just how long the planet remained anoxic, and thus home to nothing but tiny, simple, slow-living microorganisms. Until recently, the idea that early Earth was anoxic for more than 2 billion years—as advanced primarily by geochemist Heinrich Holland of Harvard University—dominated the field but had not won the day. Its proponents pointed to diverse evidence. Minerals older than about 2.2 billion to 2.4 billion years found in ancient soils, streambeds, and other sediments seemed to show no sign of ever having been exposed to oxygen. There were no "red beds" of sediment stained with rusted iron minerals, for example. But a small but vocal opposition, headed by Holland's former student Hiroshi Ohmoto of Pennsylvania State University (PSU), University Park, had long believed that Earth's atmosphere was oxygenated back as far as geologists can peer. He and other opponents pointed to mineral bits here and there that they believed had been oxidized 3 billion years ago or longer.

> "The rise of oxygen changed the course of evolution."
> —David Catling

A step up

That teacher-student debate now appears to be resolved in the teacher's favor. Researchers have in hand an unequivocal method for determining the presence or absence of oxygen early in Earth's history. Introduced by geochemist James Farquhar of the University of Maryland, College Park, and his colleagues in 2000, the sulfur isotope method depends on the way sunlight breaks down sulfur dioxide in the atmosphere. These photochemical reactions can shuffle sulfur isotopes in weird ways, without respect to the mass of the isotopes. But free atmospheric oxygen wipes out such mass-independent fractionation (MIF) before the sulfur reaches Earth's surface, where the odd mix of isotopes could be preserved in sediments. Farquhar and colleagues found MIF of sulfur in rocks older than 2.4 billion years but not in younger rocks, apparently pinning down atmospheric oxygen's first appearance at levels of at least 1 part per million.

Slow leak. Escaping hydrogen (imaged as blue) would have slowly oxidized early Earth, but only if methane sped things up.

That discovery—now buttressed by theoretical work and studies of other rocks—pretty much clinches the case for a late "Great Oxidation Event," as Holland has dubbed it. "Skeptics would have to reinvent physics to counteract Farquhar's results," says atmospheric physicist James Kasting of PSU. Although Ohmoto and some associates have yet to give in, "there's a strong consensus in the rest of the community," says Catling. "In the MIF of sulfur, you have a clear signal that something changed at about 2.4 billion years."

And that permanent rise in oxygen to detectable atmospheric levels seems to have spurred evolution. The earliest known fossil of a eukaryote—the term for organisms, from yeast to humans, that have a cell nucleus and usually require oxygen—is about 2 billion years old. The first fossil big enough to be seen without a microscope—the spiral-chained algae *Grypania*—appeared 1.9 billion years ago.

Rumors of oxidation

So what about those signs of earlier oxygen that helped fuel years of debate? Some could be markers of ancient "oxygen oases" in which cyanobacteria—oxygen-producing blue-green algae—seem to have been capturing the sun's energy through photosynthesis for hundreds of millions of years before atmospheric levels exceeded the sulfur MIF limit.

In rocks from the Hamersley Basin of western Australia, researchers have found signs that such oxygen did manage to permeate at least small parts of the environment—perhaps just a sea-floor skim of microbial scum—while the rest of the world remained anoxic. When

CREDITS (TOP TO BOTTOM): NASA GODDARD SPACE FLIGHT CENTER; ISTP/GSFC/NASA

oxygen-producing microorganisms die, they leave behind a telltale mix of carbon isotopes biased toward the lighter isotope, as well as distinctive organic molecules such as steranes.

At the astrobiology meeting, geochemist Jennifer Eigenbrode of the Carnegie Institution of Washington's Geophysical Laboratory and colleagues reported finding those geochemical fingerprints in Hamersley rocks. The mix of isotopes and biomarkers changed as the researchers traced them into geologically more recent rocks. Eigenbrode said the shifts point to an increasing role for oxygen-dependent ecosystems, perhaps confined to thick films on the sea floor. In such oxygenated islands, eukaryotes may have appeared hundreds of millions of years earlier than their first recognized fossils, giving them that much more time to evolve their more sophisticated lifestyle.

What was the holdup?

Better records of the history of oxygen don't always make the historian's job easier. They can also make gaps in the timing harder to explain. For example, evidence from sterane and other biomarkers indicates that oxygen-generating cyanobacteria were in business by 2.7 billion years ago or earlier. Yet the Great Oxidation Event didn't come along for another 300 million years. Why the delay?

Researchers have suggested several possible reasons. Geobiologist Joseph Kirschvink of the California Institute of Technology in Pasadena and his doctoral student Robert Kopp note that early cyanobacteria didn't produce oxygen. They argue that the type of photosynthesis that liberated the gas did not appear until 2.4 billion years ago. The explanation discounts a number of geochemical indicators, such as steranes, which are commonly thought to require oxygen for their synthesis.

Other geoscientists suspect that the supply of oxygen-devouring volcanic gases such as hydrogen might have started petering out by 2.4 billion years ago, finally allowing oxygen levels to rise. But recent studies of trace metals in ancient rock derived from the deep Earth seem to show that the supply of reducing gases held steady right up to and through the oxidation event.

Catling and colleagues have proposed that high levels of methane (CH_4) in the early atmosphere greatly increased the rate at which hydrogen "leaked" into space, allowing photosynthetically produced oxygen to oxidize Earth. In 2001, they pointed out that 3 billion years ago methane produced by anoxia-loving bacteria was probably 100 to 1500 times more abundant than it is today. And hydrogen-bearing methane can freely diffuse to the atmosphere's outer fringes where its hydrogen can make the final jump to space; water's hydrogen gets condensed out at lower altitudes.

To test the idea, Catling, astrobiologist Mark Claire of the University of Washington, Seattle, and planetary physicist Kevin Zahnle of NASA's Ames Research Center in Mountain View, California, recently programmed methane into a computer model that keeps tabs on oxygen's comings and goings on early Earth. In the model, volcanic gases and reactions with crustal minerals sop up oxygen as fast as cyanobacteria can churn it out. Without abundant methane to carry hydrogen away to space, Earth remains anoxic indefinitely. But with high atmospheric methane, hydrogen losses to space eventually overwhelm the anti-oxygen forces, and oxygen levels begin to rise. So the lowly methane-generating bacterium may have unwittingly given oxygen—its deadly enemy—a leg up on the road to an oxidizing world.

The boring billion

Even more puzzling than the 300-million-year run-up to the Great Oxidation Event is what came next. The advent of oxygen ushered in geology's red beds and life's eukaryotes. Then, for a good billion years, the newcomer eukaryotic algae went nowhere evolutionarily, frozen in time as an advanced sort of green scum. And there is growing geochemical evidence that the Great Oxidation Event wasn't actually all that great. To understand why not, scientists look to the ocean.

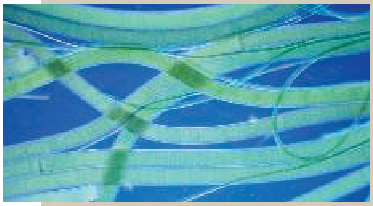
Doubts about the oxidation event's greatness arose in 1998 when geochemist Canfield first proposed—on the basis of sulfur isotopes—that all of the ocean's waters except the uppermost layer had remained anoxic for more than a billion years after atmospheric oxygen made its first appearance. In 2002, geochemist Ariel Anbar of Arizona State University, Tempe, and paleontologist Andrew Knoll of Harvard University linked Canfield's idea to the history of life. They suggested that what oxygen the atmosphere held during the time of the "Canfield Ocean"—perhaps 1% to 10% of present levels—had actually starved eukaryotic algae and held them back evolutionarily (*Science*, 16 August 2002,

PROTEROZOIC ERA

2.7 billion years ago

CYANOBACTERIA

Blue-green algae are producing oxygen before the world oxidized.



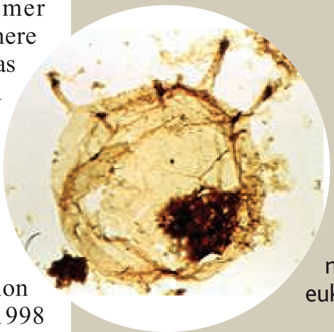
2.4 billion years ago

GREAT OXIDATION EVENT

1.9 billion years ago

GRYPANIA SPIRALIS

First eukaryote visible to the naked eye appears after oxidation.



1.4 billion years ago

EUKARYOTES

Nucleated, more-sophisticated eukaryotic algae arise but go nowhere evolutionarily.

0.6 billion years ago

EDIACARA

About the time oxygen rises to near-modern levels, large organisms first appear in the sea.

CREDITS (TOP TO BOTTOM): TOM ADAMS/VISUALS UNLIMITED; PAUL JANKE/PAN TERRA INC.; ANDREW KNOLL; CHASE STUDIO/PHOTO RESEARCHERS INC.

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p. 1104). The atmospheric oxygen, they noted, would have weathered sulfur off the land, dosing the ocean with deadly sulfides, which would have chemically removed the iron and molybdenum from seawater. The algae needed these elements to form enzymes essential to taking up nutrients; without them, they were malnourished and therefore evolutionarily listless.

The Canfield Ocean, and thus the Malnourished Earth hypothesis, has since gained ground. Several groups have extended Canfield's sulfur isotope analysis across the midsection of the Proterozoic era (2.5 billion to 0.54 billion years ago), confirming signs of anoxia. But those studies drew on marine rocks deposited from waters that were at least partially isolated from the open ocean, like today's Red Sea. Perhaps their anoxia was not typical of the ocean at large.

Last year Anbar, geochemist Gail Arnold, then at the University of Rochester, New York, and colleagues allayed many of those doubts. In *Science* (2 April 2004, p. 87), they reported on their analysis of molybdenum isotopes preserved in mid-Proterozoic rocks. The ratio of two molybdenum isotopes depends on the amount of oxygen in the ocean. And unlike many other dissolved elements, molybdenum remains in seawater so long before being removed to the sediment that it has a chance to mix throughout the ocean, even its backwaters. Samples from one place in the Proterozoic ocean, then, should reflect the amount of oxygen in the ocean as a whole. Arnold and colleagues found signs that far more of the ocean floor was anoxic 1.4 billion and 1.7 billion years ago than today. So, almost 4 billion years after the world began, the team of life and Earth that boosted oxygen from nothing to detectable levels still had a ways to go.

Breakout

What locked a billion years of the Proterozoic in geochemical and evolutionary stasis remains a mystery. But the bigger, more enticing mystery may be how oxygen finally rose to something like modern levels toward the end of the Proterozoic, 0.6 billion or 0.7 billion years ago. That's when multicellular animals first appeared, and then large animals such as the enigmatic Ediacara, creatures that must have required higher levels of oxygen. Canfield's sulfur isotopes hint that oxygen levels did in fact rise about then.

This second oxidation event is proving far more elusive than the great one. Most scientists agree that it hinged on some major change that started locking up more organic matter in sediments before it could decay. Instead of being consumed in the chemistry of decomposition, oxygen built up in the atmosphere and ocean. As to what triggered the mass carbon burial, explanations fall into two camps: geological and biological.

Proposed geological shifts capable of driving up oxygen levels include a jump in the production of clays able to adsorb organic matter and preserve it beneath the sea floor, and the assembly of a supercontinent whose weathering could stimulate ocean life and subsequent carbon burial by adding nutrients to the seas. Biological shifts include the arrival of lichens on land, which would have accelerated rock weathering as well, and the evolutionary innovation among zooplankton that produced dense, organics-laden fecal pellets able to sink into the deep sea.

Before the oxygen historians can sort out the truth from the just-so stories, they'll have to come to grips with the nature of the ancient record of life as well as oxygen. "There's less data the older you go [in the geologic record]," says Kirschvink, "so there's less chance of being proven wrong right off" if you're working 2 billion or 3 billion years in the past. That can make spinning yarns about the early days more fun, but it puts a premium on collecting what data can be retrieved from the oldest rocks.

–RICHARD A. KERR

A Better Atmosphere for Life

Thirty years ago, geochemists took away the primordial soup that biologists thought they needed to cook up the first life on Earth. Now, some atmospheric chemists are trying to give it back. They're suggesting that the early Earth could have held onto much more of its volcanic hydrogen—a key ingredient in the recipe for making the organic compounds that may have led to the first life.

Creating the primordial organic goo used to be easy. If you combined the methane and ammonia seen in the still-primordial atmosphere of Jupiter, passed lightninglike sparks through the mixture, and added some water, voilà, complex organic compounds such as amino acids formed. But then in the 1970s geochemists spoiled the party by insisting that Earth's earliest atmosphere was nothing like Jupiter's. Earth's carbon would have been part of oxygen-rich carbon dioxide, and its nitrogen part of inert nitrogen gas, they said. And hydrogen seeping from the planet's interior would have quickly escaped to space. That left chemists with a thin gruel indeed. It had far too much oxygen, which destroys organics, and not enough of the hydrogen that enables carbon atoms to link up to form the complex polymers needed for life. In the lab, such mixtures yielded few organics, and simple compounds at that.

Now, atmospheric chemist Feng Tian of the University of Colorado, Boulder, and his colleagues argue that hydrogen on early Earth would have escaped much more slowly than has been assumed (*Science*, 13 May, p. 1014). Lacking the oxygen that absorbs solar energy, they point out, the outer fringes of the early atmosphere would have been far colder than they are today. With less energy jittering its atoms, much less lightweight hydrogen would have "boiled" away into space.

The researchers also figured out how to calculate the rate at which hydrogen would have been lost as wisps of the atmosphere flowed away into space. The mathematics of such supersonic flow had frustrated all previous attempts. Overall, hydrogen would have escaped at 1/100 the rate previously assumed, the group says. Rather than building to concentrations of just 0.1%, hydrogen might have reached 30%. That would make for a far more productive atmosphere than chemists have been coping with for 30 years. "The end result is you drop vast amounts of organic compounds into the ocean to make a soup," says the group's Brian Toon of the University of Colorado, Boulder.

"On the face of it, what they have produced is quite reasonable," says atmospheric chemist Yuk Yung of the California Institute of Technology in Pasadena. "It's a nice piece of work. It's going to make the biologists a lot happier." Astrobiologist David Catling of the University of Bristol, U.K., isn't so sure. "It would be rather premature," he says, to shift emphasis back to the prebiotic chemistry of a hydrogen-rich atmosphere and organic-goo–laced ocean. Tian and his colleagues "haven't dealt with all the factors that lead to hydrogen escape," says Catling. He suspects that a more sophisticated model would show that hydrogen escaped the early Earth at least as fast as it does today. Time will tell whether too many cooks spoil the primordial broth.

–R.A.K.

Deep roots. A buildup of volcanic hydrogen may have helped form life's ingredients.

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