Oxygen made us. But what made oxygen, asks Nick Lane

Life's a gas

OXYGEN is life. That's true not just for us: all animals and plants need oxygen to unleash the energy they scavenge from their environment. Take away oxygen and organisms cannot produce enough energy to support an active lifestyle, or even make them worth eating. Predation, an essential driver of evolutionary change, becomes impossible.

It is easy to picture a planet without oxygen. It looks like Mars. Our nearest planetary neighbour was probably once a water world too, primed for life to evolve. But it lacked a vital ingredient: a protective shield of ozone derived from oxygen. Without an ozone layer, the sun's rays slowly atomised the Martian water. The hydrogen floated off into space while the oxygen oxidised the iron-rich Martian topsoil, turning it rust-red. Perhaps there is – or was – life on Mars. But if so it never progressed beyond the bacterial stage.

So how did Earth get lucky? Ten years ago, when I was writing my book *Oxygen*, it didn't seem too big a deal. Photosynthesising bacteria were the magic ingredient. These tiny organisms popped up in Earth's oceans early on, sometime between 4 and 3 billion years ago. In the couple of billion years that followed, their oxygenic exhaust fumes slowly did the job. By 600 million years ago, the air was primed for complex animal and plant life.

Now this cosy story has collapsed. We are no longer so sure how Earth's atmosphere got – and retained – its oxygen-rich atmosphere. "Photosynthesis by itself was not enough," says Graham Shields, a geochemist at University College London. "It was a complex dance between geology and biology."

Uncovering life's earliest origins is never an easy task. There are no large animal or plant fossils to draw on: these only make an appearance starting around 600 million years ago. Yet perhaps remarkably, hints of life's humble beginnings do survive in ancient rocks, crushed by the weight of sediment and time. With ardour, patience and skill, they can be marshalled into a convincing story.

William Schopf had those qualities. Two decades ago he thought he had the story, too. A palaeontologist at the University of California, Los Angeles, he was investigating the Apex cherts of Western Australia, 3.5-billion-year-old rocks that are among the oldest on Earth. In 1993, he announced that they contained 11 different types of "microfossil" that looked for all the world like modern photosynthesising cyanobacteria (*Science*, vol 260, p 640).

The finding fitted a global pattern. Other 3.5-billion-year-old Australian rocks contained rippling structures that looked like fossil stromatolites. A few examples of these structures, domed edifices up to a metre high built by cyanobacteria, still eek out a marginal existence in salty lagoons on the coast of Western Australia and elsewhere. Meanwhile, 3.8-billion-year-old rocks from Greenland had reduced levels of one of the two stable carbon isotopes, carbon-13, compared with the other, carbon-12 – a chemical signature of photosynthesis. It seemed that life had come early to Earth: astonishingly soon after our planet formed some 4.6 billion years ago, photosynthesising bacteria were widespread.

This emerging consensus lasted only until 2002, when palaeontologist Martin Brasier of the University of Oxford unleashed a barrage of criticisms. The Apex cherts, he claimed, were far from being the tranquil sedimentary basin evoked by Schopf. In fact, they were shot through with hydrothermal veins that were no setting for cyanobacteria. Other evidence that the rocks had undergone convulsions in the past made the rippling stromatolites no more biological in origin than ripples on a sandy beach. As for the microfossils Schopf had identified, they ranged from the "almost plausible to the completely ridiculous".

ANDREW HEN

"With all of oxygen's ups and downs, life on Earth was even luckier than we thought to get as far as it has"

Mind the gap

If, as seems increasingly likely, photosynthesising cyanobacteria first made an appearance in Earth's oceans around 2.7 billion years ago, why did they take so long to make a difference to Earth's air?

One possibility is that the oxygen's first chemical mission was to oxidise all the iron and compounds like hydrogen sulphide in the oceans. Only after it had done that was it free to escape into the atmosphere.

Perhaps the most persuasive answer, though, is purely geological. It comes from veteran geologist Heinrich Holland of Harvard University. He points the finger at gases such as methane and hydrogen sulphide that are constantly spouted out by volcanoes. They would have reacted with the first free oxygen to form carbon dioxide and sulphur dioxides, effectively removing the oxygen from circulation (*Geochimica et Cosmochimica Acta*, vol 73, p 5241).

Holland proposed that two processes took place over geological time. First, the supply of radioactive fuels in Earth's interior gradually dwindled, reducing its internal temperature. That in turn damped down the rate of volcanic emissions, and the rate at which oxygen-consuming gases entered the atmosphere gradually fell too.

Second, the volcanic gases themselves contained more oxygen. Oxygen produced by the first cyanobacteria would have steadily oxidised surface rocks. As those rocks cycle through the Earth's mantle through the standard processes of subduction and convection, rocks with an extra load of oxygen gradually fed through to the gases emitted by volcanoes.

As cyanobacteria continued to pump out oxygen, there came a point where the balance tipped inexorably towards oxygen, and the excess finally accumulated in the air. Perhaps it took the 300 million years leading up to the great oxygenation event to get to that tipping point.

This very public spat produced no clear outcome, but since then new evidence has been emerging. In 2006, Thomas McCollom of the University of Colorado in Boulder and Jeffrey Seewald of the Woods Hole Oceanographic Institution in Massachusetts found that reactions known as Fischer-Tropsch syntheses can occur in hydrothermal vents, leaving a carbon isotope signature that mimics photosynthesis with no need for a biological explanation. The mere possibility that hot water might have massaged the evidence in Australia and elsewhere was damning enough for the duo. "The possibility must be entertained that complex life was not present on Earth, or at least not widespread, until a much later date," they wrote (*Earth and Planetary Science Letters*, vol 243, p 74).

That conclusion was supported by a reanalysis of "biomarkers" found in 2.7-billion-year-old Australian shales. These organic molecules had been thought to indicate the presence of cyanobacteria, but in 2008 an Australian team concluded that the shales had been contaminated by ancient oil that had filtered down into the sediments some time after the rocks first formed (*Nature*, vol 455, p 1101). Even more damningly, in September 2009 a French team discovered living bacteria buried deep down in ancient rocks of a similar age (*PLoS One*, vol 4, p e5298).

Crumbling edifice

Perhaps the decisive blow came in August last year, when Daniele Pinti of the University of Quebec in Montreal, Canada, and his colleagues announced results from a survey of the Apex cherts using advanced microscopy techniques. They concluded that the rocks had formed in a hydrothermal vent at a searing 250 °C or more – way too hot for cyanobacteria. The "microfossils", they said, were mostly deposits of iron oxides and clay minerals (*Nature Geoscience*, vol 2, p 640).

These new lines of evidence mean that the oldest undisputed signs of cyanobacteria are now fossils found in rocks from the Belcher Islands in northern Canada dating from just 2.1 billion years ago. So where does that leave our ideas about how life evolved, and the part oxygen played in that evolution?

In one sense it is no bad thing: it removes an embarrassing billion-plus year delay between cyanobacteria arising and oxygen levels in the air first taking a significant upwards turn. In this "great oxygenation event" of around 2.4 billion years ago, levels rose from around 1 per cent of today's levels to perhaps 10 per cent.

Our best guess is still that cyanobacteria were around some time before this event. Persuasive evidence is converging on a date around 2.7 billion years ago (see diagram, right). Research from Linda Godfrey and Paul Falkowski of Rutgers University in New Brunswick, New Jersey, indicates that the modern nitrogen cycle kicked off around this time. This requires free oxygen to form nitrogen oxides, suggesting that a first whiff of oxygen – not even 1 per cent of today's levels – had just appeared (*Nature Geoscience*, vol 2, p 725).

That squares with evidence from Robert Frei of the University of Copenhagen, Denmark, and his colleagues that the oxidative weathering of rocks kicked off around this time too. They measured levels of chromium in ancient marine rock layers known as banded iron formations. Exposed to oxygen in the air, the metal is weathered from rocks and washed out to sea, where it reacts immediately with iron, settles to the ocean bottom and forms these layers. The chromium signature in them suggests there was essentially no oxidative weathering before 2.7 billion years ago, after which chromium became significantly more mobile (*Nature*, vol 461, p 250).

If these coordinated changes are the calling cards of the first photosynthesising bacteria, there is still a mysterious hiatus of 300 million years before the great surge in oxygen 2.4 billion years ago. The gap is less embarrassing than a billion years, but still needs explaining (see "Mind the gap", left). Yet this puzzle masks a more fundamental new twist to the tale.

It is that the great oxygenation event was perhaps not as decisive an event as we thought. It certainly happened – a suite of geochemical evidence leaves little room for doubt on that score – and it was traumatic, too. Evidence of a sudden drop in ultraviolet radiation penetrating to Earth's surface 2.4 billion years ago indicates it was enough to create the ozone layer – a pivotal event that ensured our planet's history diverged from that of Mars.

It also seems to have been the forerunner to a "snowball Earth". If Joe Kirschvink of the California Institute of Technology in Pasadena and many others are correct, the oxygen produced by cyanobacteria oxidised the potent greenhouse gas methane, precipitating a global freeze. "That raises the spectre of one mutant organism being able to destroy an entire planetary ecosystem – the first biogenic climate disaster," says Kirschvink.

And yet the great oxygenation was impermanent. The same chromium record that provides evidence for a first whiff of oxygen 300 million years before this event shows that, by 1.9 billion years ago, levels of breathable oxygen in Earth's atmosphere were back down to the merest trace.

We don't know why. It might have been a knock-on effect from a big freeze: if Earth did indeed enter a snowball phase, glaciers would have scoured huge amounts of nutrients from the underlying rock. When the ice eventually retreated, melted by the build-up of volcanic greenhouse gases in the atmosphere, those nutrients would have found their way into the oceans. One idea is that they nourished a huge transient bloom of cyanobacteria that quickly died and rotted, in the process consuming all the oxygen they had once produced.

Did lichens help oxygen to finally break free?

Stinking oceans

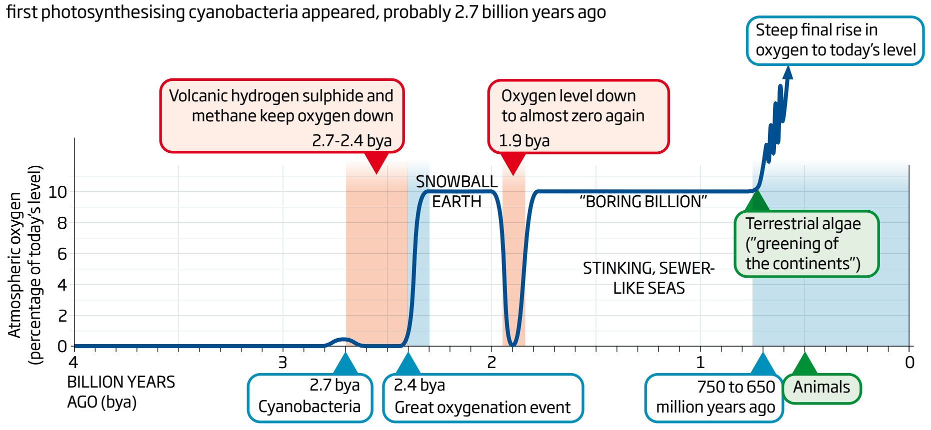
Oxygen levels in the atmosphere soon recovered again as rates of photosynthesis and weathering established a new equilibrium, at about 10 per cent of present-day levels. But this was no fresh dawn of a high-octane world: quite the reverse. This time, the oxidative weathering of sulphides on land filled the oceans with sulphate. That in turn fuelled a hardy group of bacteria that filled the oceans with sewer gas – hydrogen sulphide – turning them into stinking, stagnant waters almost entirely devoid of oxygen, rather like the deeper levels of the Black Sea today. It was the herald of an extraordinary stasis in Earth's environment lasting nearly a quarter of its history – a period dubbed the "boring billion".

But hang on: what happened to the oxygenic utopia in which life supposedly grew and prospered, evolving the complex cells that went on to make up animal and plant life? The answer is that it probably never existed. If cyanobacteria did produce the first oxygen in Earth's atmosphere, all the evidence is they lacked the oomph to push levels much above 10 per cent of present levels in the long term.

That has led William Martin, an expert in cell evolution at the University of Düsseldorf in Germany, and others, to come up with a controversial theory: that the boring billion was anything but boring. In fact, the stinking oceans were the true cradle of life. Evidence behind this idea includes the fact that mitochondria, the powerhouses of all complex, oxygen-respiring "eukaryotic" cells today, were once far more varied, sometimes "breathing" sulphur or nitrogen instead of oxygen, or even emitting hydrogen gas. It seems that these mitochondria originated in the stinking oceans of the boring billion, which were full of the chemical imbalances that power life today in places, like deep-sea hydrothermal vents.

O_2 on the up

The rise of oxygen in Earth's atmosphere has experienced many setbacks since the first photosynthesising cyanobacteria appeared, probably 2.7 billion years ago



Earth's anoxic stasis was broken in the end by a dramatic series of snowball Earths, indicating bursts of oxygen, beginning about 750 million years ago and recurring over the following 100 million years. They broke the eternal loop: soon afterwards, oxygen levels shot up and never looked back. Animal life soon exploded onto the scene.

What made the difference this time? One intriguing possibility is that it was down to the organisms that had evolved in a leisurely way during the boring billion: terrestrial red and green algae and the first lichens. "I suspect the final big rise in oxygen was caused by the greening of the continents from around 800 million years ago," says Shields. Terrestrial algae and lichens get their nourishment in part by breaking down the rocks on which they live. These nutrients flooded into the oceans, stimulating more and more photosynthesis by both cyanobacteria and the more advanced algae that had evolved in the meantime.

It did not all end in a "bloom and a bust" this time because lichens kept right on eating away at the rocks. They sustained a higher rate of erosion, and constant flow of nutrients into the ocean, even after the scouring glaciers of various snowball Earth phases had melted.

Life's story on Earth is a complex one, perhaps more complex that we ever imagined. After many false starts, a singular combination of chemistry, biology and geology finally came together to unleash the oxygen we breathe. Even then, many ups and downs were to come. To get as far as it has, life on Earth was even luckier than we thought. ■

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