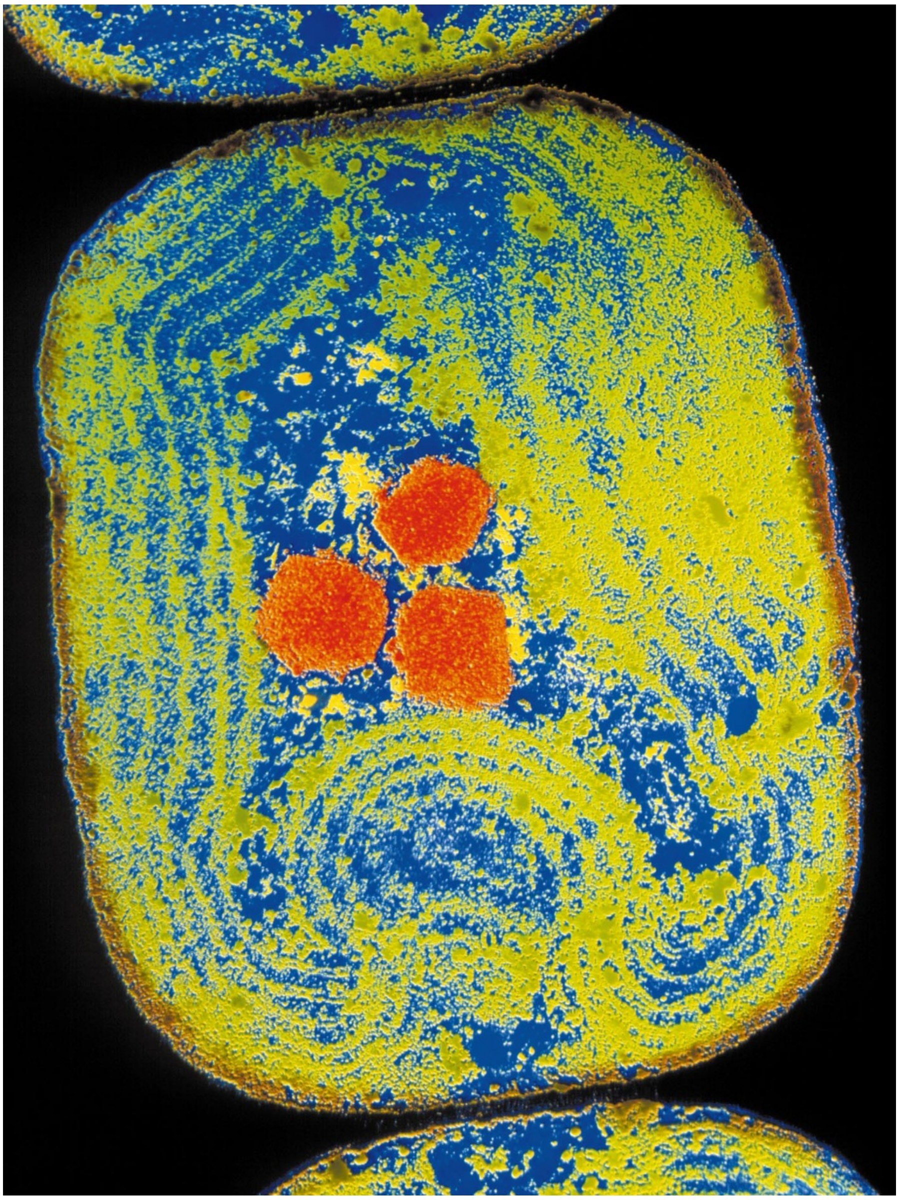
news feature

The story of O

Geochemists are having a hard time working out why the atmosphere of the early Earth appears to have lacked oxygen for so long. Jon Copley considers the competing theories.

Take a deep breath. A fifth of the air that fills your lungs is oxygen. But it was not always like this. Around 3.5 billion years ago, the Earth's atmosphere contained almost no oxygen. Simple microorganisms had evolved, but they were adapted for an atmosphere rich in nitrogen, carbon dioxide and the sulphurous gases poured forth by volcanoes.

Thankfully for us, cyanobacteria evolved. These primitive microorganisms, descendants of which survive to this day, were probably the first to photosynthesize, harnessing light from the Sun to power their own growth and generating oxygen as a by-product. As a result, they started a momentous evolutionary change — adding oxygen to the atmosphere and paving the way for the eventual evolution of multicellular life.



Early output: cyanobacteria were probably the first organisms to pump oxygen into the atmosphere.

Up in the air

But as geologists and geochemists studying the early Earth know, the story is not quite so simple. Fossil evidence for cyanobacteria can be seen in rocks dating from as far back as 3.5 billion years ago[1]. But there is a host of evidence suggesting that oxygen remained a trace element in the atmosphere until about 2.5 billion years ago. So if cyanobacteria were pumping out oxygen for at least 1 billion years before it reached detectable levels, what kept the concentration of oxygen so low?

This is a difficult question to answer because the events happened so long ago. Oxygen leaves its fingerprints almost everywhere, changing the composition of rocks that are exposed to it and altering the chemistry of the oceans. It is also intimately linked to cycles of other elements such as carbon and phosphorus. But unravelling this complex web of interactions to peer back through time has taxed the ingenuity of geochemists, and the techniques at their disposal.

Researchers are helped in their search by the fact that many biological reactions occur at different rates for different isotopes of the same element. Take photosynthesis, which combines carbon dioxide and water to produce organic matter and oxygen. Almost all carbon on Earth exists as one of two isotopes — carbon-12 and carbon-13. For photosynthesis, organisms prefer to use carbon dioxide that contains the lighter carbon-12 isotope, because this means the reactions then need less energy. This preference leaves its mark billions of years later: rocks formed from organic matter contain high levels of carbon-12, whereas those formed from inorganic material include more carbon-13.

This difference provides geologists with the earliest evidence for any kind of life. Rocks from Greenland dating from 3.8 billion years ago show suspiciously high levels of carbon-13, hinting that microbes which selectively extracted carbon-12 may have been at work[2–4]. And Western Australian rocks formed 300 million years later provide the first fossil evidence of cyanobacteria[1].

But these dates do not tally with the evidence for the rise in atmospheric levels of oxygen. Much of this evidence comes from palaeosols — rocks formed by the compression of ancient soils. The air and water of the early Earth would have left its mark on these soils and the palaeosols that formed from them, so geochemists use these rocks to test whether or not oxygen was present billions of years ago. The key to tracking oxygen is the way it reacts with iron. If there was little oxygen on the early Earth, minerals known as iron silicates would have dissolved in any water that was present, and washed straight through the soil. But oxygen converts iron silicates into insoluble iron hydroxides, which would have been trapped in the ancient soils.

Gas detectors

Iron hydroxides have so far only been found in palaeosols younger than 2.3 billion years old[5], indicating that before this time, the atmosphere did not contain much oxygen. Other mineral indicators in palaeosols seem to tell a similar story. A 2.5 billion-year-old Canadian palaeosol has been shown to contain the element cerium[6]. Had oxygen been present it would have reacted with the cerium to produce cerium oxide — but none of this oxide was found.

How can this apparent paradox between

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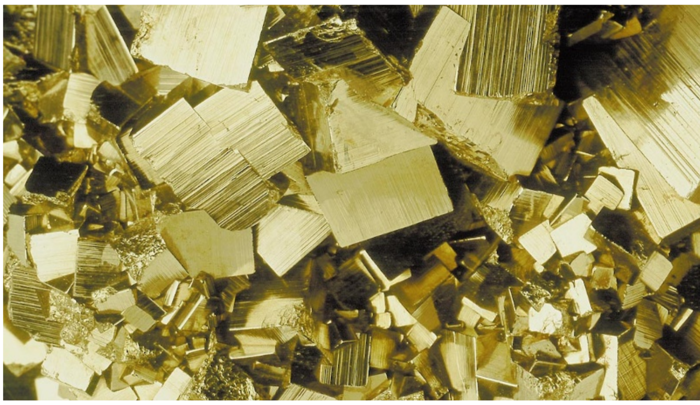

Puzzling evidence: the formation of pyrite (above) and banded iron formations (left) indicate that atmospheric oxygen levels did not rise until at least 1 billion years after photosynthesizing cyanobacteria had evolved.

NATURAL HISTORY MUSEUM, LONDON

the emergence of cyanobacteria and the rise in oxygen levels be explained? Some researchers argue that the paradox does not exist and that the interpretation of the evidence is wrong. Others invoke changes in the way that organic material released by dead microorganisms reacted with oxygen. And a new hypothesis suggests that changes in gases emitted by volcanoes could be the key.

Hiroshi Ohmoto, a geochemist from Pennsylvania State University, is one of those who thinks that there is no paradox, denying that oxygen emerged as late as the palaeosol evidence suggests that it did. Ohmoto argues that the lack of iron in palaeosols does not mean it was never there. It might have been removed by hot water from volcanoes[7].

Organic acids produced by bacteria might also have stripped iron from palaeosols. Ohmoto says he has seen a number of palaeosols where this might have happened. The organic acids may have been produced by cyanobacteria. Although cyanobacteria first evolved in the oceans, they could soon have colonized the land. Ohmoto says that a 2.6 billion-year-old South African palaeosol looks as if it may have had a large community of cyanobacteria living in it[8]. So these microorganisms could be confusing the geological record — creating the oxygen that fixed iron in soils and also producing the acids that removed it. Put these factors together, says Ohmoto, and the timing of the jump to high oxygen levels is "very, very difficult to clarify".

Ohmoto is currently working on a geochemical model that appears to back up his assertions. In unpublished studies conducted with Antonio Lasaga, a geochemist until recently at Yale University in New Haven, Connecticut, Ohmoto has modelled the cycles of oxygen, carbon, sulphur and iron for the early Earth. "The end result is very striking," he says. "Within 30 million years from the time cyanobacteria evolved, the atmosphere will contain very high oxygen content and will remain basically the same." Thirty million years is the blink of a geological eye, so if cyanobacteria appeared at 3.5 billion years ago or earlier, the atmosphere would have contained large amounts of oxygen from then onwards.

Rocky road to success?

But if Ohmoto is going to convince other researchers that he is right, he will have to account for a range of other evidence that points to low oxygen levels before 2.5 billion years ago. At that time, minerals such as pyrite and uraninite were being washed around by rivers. Contact with oxygen would have altered their composition, but sediments from 2.75 billion years ago and earlier contain the minerals in their unreacted form[9].

More evidence comes from deposits that cannot form if oxygen is present. Examples of one of these — banded iron formations — seem to be confined to rocks dating from more than 2.3 billion years ago, indicating that oxygen was not present at that time. But Ohmoto points to a similar banded iron formation dating from 1.8 billion years ago as evidence that such structures can form in the presence of oxygen. Other researchers argue that this formation is probably an anomaly, arising in water that contained little oxygen.

A new approach to the problem has further strengthened the case for the late emergence of oxygen. Developed by James Farquhar of the University of California, San Diego, the technique takes advantage of a quirk in the behaviour of different isotopes. Biological reactions such as photosynthesis leave clear signatures in rocks by selecting for lighter isotopes. Now it appears that some non-biological reactions also select for certain isotopes, although here, mass is not the governing factor. Although the selection mechanism — known as mass-independent fractionation — is not fully understood, the effects of it can be seen in the geological record.

Sulphur gases in the Earth's early atmosphere were subject to both biological and non-biological fractionation. Microorganisms that fed on sulphur preferred the lighter of the element's three isotopes and the resulting rocks reflect this. But some of the non-biological processes involved in the formation of other rocks can cause mass-independent fractionation of sulphur. Such rocks contain isotopes of sulphur in distinctive ratios that do not fit with those generated by biological processes.

Crucially, this mass-independent selection of sulphur is driven by ultraviolet (UV) light from the Sun. As oxygen appeared in the atmosphere it would have slowed the reaction down by forming a layer of ozone — a molecule containing three oxygen atoms — which blocked out much of incoming UV light. Oxygen would also have combined with sulphur and removed it from the atmosphere. Together, these effects would have stopped the mass-independent selection of sulphur. And according to Farquhar, evidence for mass-independent fractionation in the geological record ceases at 2.45 billion years ago[10].

For Jim Kasting, a geochemist at Pennsylvania State University, Farquhar's evidence is "the real clincher". Heinrich Holland, a geologist at Harvard University, agrees and says he will argue so when he reviews the evidence at a joint meeting of the Geological Societies of London and America to be held this summer in Edinburgh. "Every time somebody looks at something different, it's one more piece of evidence for low oxygen before 2.3 billion years ago," he says.

But Ohmoto is not willing to give up the fight just yet. He says that recent work[11] from Don Canfield of the Danish Center for Earth System Science in Odense backs his early oxygen theory. Canfield has found evidence for sulphate-devouring microorganisms at around 3.5 billion years ago. Oxygen in the atmosphere promotes the production of sulphate in the oceans, leading Ohmoto to argue that evidence of the microbes is evidence of oxygen. But other researchers, including Canfield himself, are not convinced that one implies the other, reasoning that other mechanisms could have produced the sulphate.

Into the black

But if the evidence does favour the late emergence of oxygen — and most geochemists believe it does — the original question remains unanswered: why did oxygen take so long to build up after cyanobacteria first emerged? The answer may lie not in the processes that create oxygen, but in the ones that mop it up. "It's like continually having your spending exceed your income — it does not lead to wealth," explains Holland.

The organic carbon left over after the decay of dead microbes can react with oxygen. The critical factor is how much of this organic matter gets buried underground, away from oxygen sources in the oceans and atmosphere. Rocks formed around 2.2 billion years ago show a peak in carbon-12 levels, indicating that the burial of organic carbon increased at this time[12]. Researchers believe that movement of tectonic plates may have opened up deep basins on the ocean floor that were free of oxygen, where organic material could have settled[13].

Volcanic gases could also have mopped up oxygen. According to new work from Kasting and his colleagues[14], a change in the composition of these gases about 2.7 billion years ago may have had a dramatic effect on oxygen concentrations.

Kasting's model depends on the composition of the Earth's mantle — the region below the crust and above the core, where volcanic gases originate. Before the emergence of oxygen, the mantle was rich in 'reducing' minerals such as iron silicates, which react with oxygen when exposed to it. A reducing mantle would have produced reducing gases which, when released into the atmosphere, extracted much of the oxygen produced by photosynthesis.

Smokin': changes in volcanic emissions could have tipped the balance and allowed oxygen levels to rise.

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Digging in: Hiroshi Ohmoto believes that oxygen levels rose around 3.5 billion years ago.

Late reductions

But the mantle is not static. At its bottom, heat from the Earth's core forces material upwards, whereas at the Earth's surface the crust and the mantle immediately below it slide back underground. Material that breaks the surface comes into contact with whatever oxygen is present in the atmosphere and oceans, reacts with it and loses some of its reducing strength. So over time, this 'oxidized' material would move back down to the base of the mantle where it would build up. According to Kasting, the mantle underwent a major switch around 2.7 billion years ago pushing the non-reducing material to the surface. As a result, the volcanic gases emitted by the mantle would have become less reducing. Kasting and his colleagues calculate that by 2.7 billion years ago these gases had lost much of their ability to mop up atmospheric oxygen, allowing its levels to rise.

Holland is currently working on a similar issue. He is looking at the contribution to volcanic gases arising from downward moving rocks in what are known as subduction zones. Subduction material emits gases that are less reducing than those coming from the mantle into which it sinks, and Holland believes that the contribution to volcanic gases from subduction zones was growing at just the time that oxygen levels started to increase.

The new work by Holland and Kasting may yet join more established theories such as carbon burial. Put together, they could explain how the atmospheric oxygen budget broke from the red into the black. The issue might not be settled yet, but the geological record is starting to make more sense.

But for life on Earth, the emergence of oxygen was only the beginning of the story. Oxygen's first effect was to make conditions harsher — combining with and removing much of the methane that had trapped heat in the atmosphere. Within a few million years, ice and snow covered the Earth, killing much of the primitive life that had evolved. Indeed, the emergence of oxygen was just the first step in the dance between life, geology and climate that continues to this day. ■

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