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Where did the oxygen in the atmosphere come from?

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A breath that fleets beyond this iron world
Alfred Tennyson

Today the air consists of 21% molecular oxygen (O_2), but this was not always so. Indeed, for almost the first half of Earth history, the air contained less than one part per million of oxygen. With so little oxygen, animals and multicellular plants (p. 27) could not evolve, and only single-celled organisms existed.

The atmosphere first became oxygenated at 2.4–2.3 billion years ago. But at that time, oxygen concentrations probably only reached a few per cent of present levels. It was not until a second increase in oxygen, around 580 million years ago, that widespread animal respiration became possible. While oxygen appears to be essential for complex life, planets are constructed with chemicals that consume oxygen, so oxygen should not accumulate. Earth's oxygen-rich atmosphere is therefore rather mysterious. Fortunately, the comings and goings of oxygen on the modern Earth provide hints for solving this great puzzle.

The oxygen balance sheet: gains and losses

The principal source of oxygen is biological: it is a byproduct of a particular type of photosynthesis called oxygenic photosynthesis. This is a process whereby certain bacteria and green plants convert carbon dioxide and hydrogen extracted from water into organic matter such as carbohydrates, using the energy from sunlight. Oxygen is released from the process as a waste product:

Carbon dioxide + water + sunlight = organic matter + oxygen

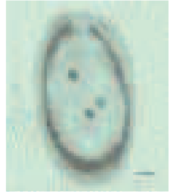
$CO_2 + H_2O$ + sunlight = $CH_2O + O_2$

The reverse process is aerobic respiration, whereby the organic matter is combined with oxygen to provide metabolic energy, releasing carbon dioxide and water.

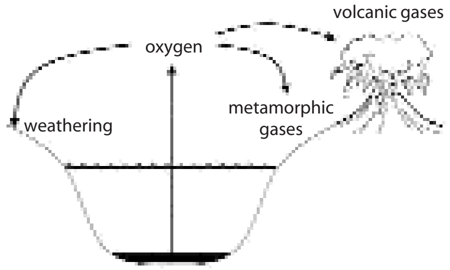
Cyanobacteria are the most numerous oxygenic photosynthesisers – the oceans teem with them, and their ancestors were probably just as plentiful. DNA analysis shows that chloroplasts – bacteria-sized sites of photosynthesis within plants and algae – are descendants of cyanobacteria. Evidently, long ago, a cyanobacterium took up symbiotic residence inside another cell that was the ancestor of modern plants and algae.

At first sight, then, we might suppose that when cyanobacteria evolved, oxygen would have accumulated as a result of photosynthesis. But geochemical evidence suggests that cyanobacteria produced oxygen for several hundred million years or more before oxygen levels rose at 2.4 billion years ago. To understand what happened requires us to consider carefully the loss of oxygen as well as its source.

Both respiration and the decay of organic matter consume oxygen, reversing the gains through photosynthesis, thus producing no net oxygen. But a tiny fraction (0.1–0.2%) of organic carbon escapes oxidation by being buried in sediments (mostly marine), leaving oxygen behind.



Prochlorococcus is the most numerous cyanobacterium in the oceans. Ancestral marine cyanobacteria on the early Earth were the architects of oxygen in the atmosphere.



Oxygen is produced when organic carbon and pyrite are buried, but is consumed by 'reductants', substances that react chemically with oxygen, which are released from hot rocks that melt (volcanism) or metamorphic rocks that do not melt. Other reductants include minerals on land.

In the Grand Canyon of Arizona, thick red beds of Permian-age Esplanade Sandstone form the top of this tower of rock, O'Neill Butte. Red beds are found only in rocks younger than 2.4–2.3 billion years ago when the atmosphere was oxygenated.

Thus, on geological timescales, the net gain of oxygen is actually equivalent to the burial rate of organic carbon.

Some organic matter is used by microbes to make pyrite (FeS_2) from seawater sulphate. Consequently, the burial of pyrite accounts for roughly 40% of net oxygen production today. The ancient oceans before 2.4 billion years ago were largely devoid of sulphate, so at that time organic carbon burial was the main cause of oxygen production.

Oxygen is easily lost. Geothermal activity and volcanoes release gases, such as hydrogen, which consume oxygen. In the ocean, oxygen reacts with dissolved minerals and gases from hot seafloor vents. Finally, oxygen dissolved in rainwater reacts with minerals in the process of weathering. For example, 'red beds' are riverbanks, deserts and floodplains with a reddish pigmentation arising from an iron oxide coating on mineral grains produced from the reaction of iron minerals with atmospheric oxygen.

When losses balance production, the amount of atmospheric oxygen remains steady. Today, about 80–90% of the oxygen produced from organic and pyrite burial is lost to oxidative weathering, while 10–20% reacts with reduced gases in the atmosphere and is also lost. 'Reduced' or 'reducing' gases are those that tend to react with oxygen and become oxidized, e.g., hydrogen, which oxidizes to form water vapour.

Anaerobic air and the advent of oxygenic photosynthesis

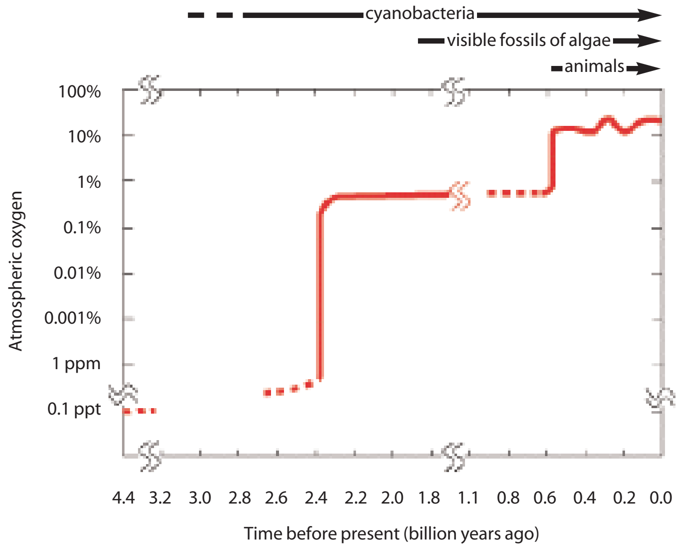
Before photosynthesis developed, the breakdown of water vapour (H_2O) in ultraviolet sunlight would have produced oxygen. This process is only a net source of oxygen when hydrogen subsequently escapes into space, so that the products of water decomposition cannot recombine. Notably, water vapour condenses in the lower atmosphere, preventing its hydrogen from escaping. Consequently, before life, volcanic gases would have scavenged oxygen down to less than one part per trillion.

Surprisingly, atmospheric oxygen did not accumulate as soon as photosynthesizers evolved. Biomarkers (diagnostic organic molecules) in 2.7 billion-year-old sedimentary rocks indicate the presence of cyanobacteria as well as eukaryotes (single-celled organisms with cell nuclei) that used local O_2 – some 300 million years before oxygen rose at 2.4 billion years ago.

A plausible explanation for why little atmospheric oxygen accumulated is that a glut of reductants – chemicals that consume oxygen – depleted it. Then, a time came when the oxygen produced from organic carbon burial exceeded the geological sources of reductants. At this tipping point, oxygen flooded the atmosphere until oxygen levels reached a plateau where oxygen production was balanced by losses to continental weathering.

But what caused this rise of oxygen? Either oxygen production increased or consumption decreased. Some favour the former idea, arguing that the growth of early continental shelves promoted organic carbon burial and thus oxygen production. Others question this hypothesis: organic matter extracts the light carbon isotope, carbon-12, from seawater, but seawater carbon, recorded in ancient limestones, does not show a steady decrease in carbon-12 content.

Instead, oxygen consumption by reducing gases could have abated. Proponents of this theory note that excess hydrogen-bearing reducing gases in the pre-oxygenated atmosphere would cause hydrogen to escape to space, which oxidizes the planet and diminishes further release of reductants. Perhaps methane was the key. In an anoxic atmosphere, methane reaches concentrations hundreds of times greater than today's 1.8 parts per million. Ultraviolet light decomposes methane in the upper atmosphere, causing hydrogen to escape and therefore Earth to oxidize. So high quantities of methane may have subtly encouraged oxygen to rise.



The red line shows estimated amounts of atmospheric oxygen over time, based on geological evidence and models. Before life existed, at 4.4 billion years ago, the oxygen concentration was less than 1 ppt (parts per trillion).

At 2.4 billion years ago, oxygen levels rose from less than 1 ppm (parts per million), up to 0.3–0.6%. Shortly after 0.58 billion years ago, oxygen rose to levels that supported animals. The history of fossils is shown above the graph.

The 'Great Oxidation Event'

The rise of oxygen 2.4–2.2 billion years ago is called the 'Great Oxidation Event'. Despite this name, oxygen levels remained limited and subsequent biological evolution progressed slowly. These years of stasis have been dubbed 'the boring billion'. During this time, much deep seawater perhaps remained anoxic, limiting biological evolution.

Oxygen finally rose a second time around 580 million years ago from a few per cent to greater than 15% of present levels. Afterwards, Ediacaran animal fossils (see p. 30) appear at 575 million years ago, and then Cambrian animals at 542 million years ago.

The cause of the second rise of oxygen remains unsolved, but various ideas have been suggested. Geological proposals include the enhanced production of clays that adsorbed and buried organic matter, or the construction of a supercontinent whose weathering flushed nutrients to the sea, encouraging more oxygen production. Biological proposals are that weathering was accelerated by lichen, or that fecal pellets from newly evolved zooplankton hastened organic burial. Alternatively, moderately high levels of biogenic methane throughout the 'boring billion' promoted hydrogen escape and oxidized the Earth.

In the Phanerozoic eon (542 million years ago to present), oxygen levels have probably varied between extremes of 10% and 30%. Thanks to high oxygen, the world has remained fit for animals, but exactly how oxygen rose from much lower Precambrian concentrations still remains somewhat enigmatic.

In the pre-oxygenated atmosphere, methane would decompose at high altitude allowing hydrogen to escape from the Earth, leaving corresponding amounts of oxygen behind. This has been proposed to explain how the Archaean Earth oxidized.