David Catling

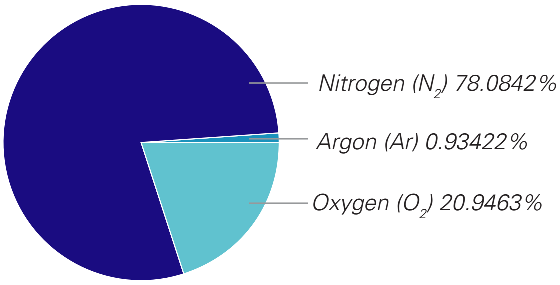
Earth's early atmosphere

The image above shows the Moon rising beyond the blue haze of the Earth's atmosphere. The Earth is the only planet in the solar system which can support life. In this article, David Catling of Bristol University describes how the composition of the atmosphere has changed through its history, and the link between atmospheric composition and life.

Key words
Earth's atmosphere
oxidation
reduction

When I was a secondary school pupil, my main impressions about chemistry were those of the industrial processes, particularly the Haber process to make ammonia and the manufacture of fragrant esters. But my perspective broadened. In the 1980s, the chemistry of the atmosphere and its link to life became prominent through two topical environmental issues: the ozone hole over Antarctica and global warming. It was around this time that my interest in the chemical composition of the Earth's atmosphere took hold. I found myself wondering why the Earth's atmosphere has the bulk chemical composition that we find around us. To put the question another way, how did the atmosphere evolve?

1000 million = 1 billion = 10^9



The composition of the Earth's atmosphere today – but it hasn't always been like this.

The oxygen story

On the modern Earth, living organisms regulate every key constituent of the air with the exception of the inert gas, argon. By far the most unusual constituent is oxygen (O_2), which is not found in abundance in the atmosphere of any other planet. Until around 2.4 billion years ago, the Earth's atmosphere had negligible oxygen and, without oxygen to respire, the large life forms that seem so familiar to us, such as multicellular plants and animals, could not exist. Indeed, there are no fossils visible to the naked eye in rocks from before 2.5 billion years ago, an aeon known as the Archaean. Instead, all you can find are the tiny microscopic fossils of single-celled microbes which make up stromatolites, laminated mineral mounds left behind by microbial communities.

David Catling

Giant stromatolites in South Africa. These formed about 2500 million years ago, in a group of rocks known as the Lyttleton Formation. Note the person's dangling legs at the top of the picture for scale. This enormous mound of laminated minerals was deposited by a slimy community of microbes (and possibly algae) that lived in the tidal zone on an ancient coastline.

ESA/NASA

Box 1 Sulfur and its ions

Sulfur has the atomic symbol S. It can form several ions. The simplest is sulfide, S^{2-}. This can be oxidised to form sulfate, SO_4^{2-}.

Crystals of the mineral stibnite, a form of antimony sulfide.

Charles D. Winters/SPL

The chemical history of Earth's atmosphere is largely the story of oxygen. Ozone (O_3) derives from oxygen and so when the atmosphere had little oxygen there was no stratospheric ozone layer. By looking at the chemistry of old rocks, scientists have established that oxygen levels increased dramatically twice during Earth history. The first rise of oxygen, called the Great Oxidation Event (GOE), was around 2400 million years ago, while a second rise of oxygen happened about 580 million years ago.

After the GOE, the Earth literally changed colour, like an indicator experiment in a test tube. Before the GOE, continental surfaces were the grey or black colour of volcanic rocks, such as basaltic lavas and granites. Afterwards, oxygen that was dissolved in rainwater reacted with iron minerals in the rocks on the Earth's surface to produce reddish-coloured iron oxides, somewhat like the way that your bicycle rusts.

The chemistry of seawater also changed. Today, sulfate is an abundant anion in seawater at a concentration of around 29 millimoles per dm^3. But before the GOE, the analysis of sulfur compounds in ancient marine sediments shows that sulfate concentrations were over a hundred times lower than today's level. Rivers ultimately supply sulfate to the ocean by washing sulfate off the land where it is produced by the oxidation of sulfides in rocks by oxygenated rainwater. Similarly, prior to the GOE, a chemical analysis of ancient soils shows that iron was leached out of soils in its soluble ferrous form ($Fe^{2+}_{(aq)}$) by rainwater. But following the GOE, iron didn't go anywhere; the iron was oxidized to insoluble ferric (Fe^{3+}) oxides, such as haematite (Fe_2O_3), by the small amounts of O_2 dissolved in the rain.

In the absence of oxygen, reducing gases such as methane (CH_4) would have reached very high concentrations compared to today. Today, methane exists at a level of 1.7 parts per million by volume (1.7 ppmv) but in the oxygen-free Archean atmosphere, it probably would have attained a level of several hundred ppmv. Volcanoes and seafloor volcanic vents produce some methane but by far the most important source is biology. Microbes in muds on the seafloor and in lakes decompose organic matter and continually produce methane. Today, nearly all seafloor methane is oxidised by bacteria that use downward-diffusing sulfate or oxygen as oxidants before the methane even gets out of the mud. But in the absence of oxygen or sulfate, such methane would have escaped out to the atmosphere in abundance. There, methane would have been subject to photochemical reactions that produced some other heavier hydrocarbon gases such as ethane (C_2H_6).

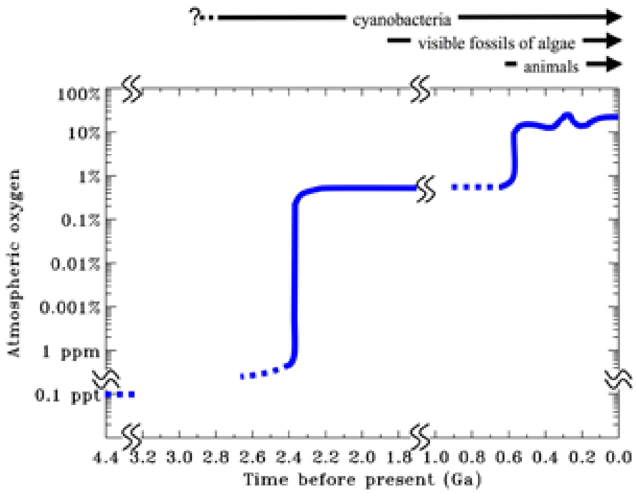
Atmospheric methane and its hydrocarbon derivatives in the early atmosphere would have been powerful greenhouse gases. Indeed, it is widely thought that methane and associated hydrocarbon gases likely account for how the Earth remained warm and habitable despite the fact that the Sun was less luminous by about 25-30% some 4 billion years ago. If it were not for ancient methane, the world's seas could have frozen over permanently. In fact, it perhaps comes as no surprise that signs of major glaciation are found in rocks ages 2450-2220 million years, at a time when oxygen rose and methane should have dropped through oxidation. Glaciers even extended into tropical regions at this time. Eventually, the establishment of an ozone layer prevented the Sun's powerful ultraviolet rays from reaching the underlying atmosphere, which would have slowed the photochemical destruction of methane and allowed methane levels to rise slightly again, permitting the Earth to warm up.

The Archean period was from 3.5 to 2.5 billion years ago.

A photochemical reaction is a reaction which is started by light.

Producing oxygen

Oxygen comes from a type of photosynthesis whereby bacteria or plants extract hydrogen from water and use it to reduce carbon dioxide to make organic matter; oxygen is released as waste. A vast number of photosynthetic bacteria, called cyanobacteria, live in today's oceans. Long before plants appeared, it was the ancient ancestors of cyanobacteria that first produced the oxygen that flooded Earth's atmosphere. Indeed, specific organic compounds that once made up the cell walls of ancient cyanobacteria have been found in black, carbon-rich sediments that were deposited on the seafloor 2750 million years ago. These sedimentary rocks predate the first rise of oxygen in the Earth's atmosphere.



The blue line shows estimated amounts of atmospheric oxygen over time in Ga (Giga anna = 1000 million years) based on a combination of geological evidence and models. Before life existed, at 4.4 Ga, theory predicts that oxygen concentration was less than 1 part per trillion. At 2.4 Ga, geological evidence shows that oxygen levels rose from less than 1 part per million, up to 0.3-0.6%. Shortly after 0.58 Ga, oxygen levels supported animals. The history of some forms of life is shown above the graph.

To explain the delay of oxygenation, it is theorized that the oxygen was initially used up during the oxidation of chemicals coming out of the solid Earth, such as hydrogen released from geothermal and volcanic regions. Also the oxygen would have been mopped up in oxidizing iron that was dissolved in largely oxygen free seawater. Effectively, the Earth underwent a global redox reaction until the production of oxygen exceeded the production of chemicals that consumed oxygen. At this tipping point, oxygen was able to flood the atmosphere.

After the GOE, the Earth's atmosphere and climate appear to have been relatively stable for over a billion years. Some scientists have even dubbed this period of time "the boring billion". Oxygen levels remained limited to a few percent of present levels and biological evolution was slow, being restricted to forms no more exotic than algae or tiny fungi. Then, around 580 million years ago, oxygen levels rose a second time up to 15% or more of present concentrations. We infer that this happened because sulfate levels in the ocean once again increased, this time from around 2-4 millimoles per dm^3 to levels that were perhaps close to modern. The idea is that higher amounts of atmospheric oxygen supported greater oxidation of sulfides on land and a bigger flow, via rivers, of sulfate to the oceans.

High concentrations of oxygen are necessary for animal respiration. We find that around 575 million years ago, the first animals appear in the fossil record during a time known as the Ediacaran period (630-542 million years ago) and then a profusion of animals occur around 542 million years ago at the beginning of the Cambrian period. From this time forward, oxygen levels have probably varied between extremes of 10% and 30%. Thanks to high oxygen and the unique chemistry of our atmosphere, the world has remained suitable for animals. Ultimately, then, we owe our own existence to atmospheric evolution.

The recent history of the atmosphere has been discovered from air trapped in Antarctic ice – see the article on pages 9-12.

Box 2
Observing the atmosphere

Orbiting spacecraft are used to monitor the Earth's surface and atmosphere. This picture, taken by the European Envisat spacecraft, shows the coast of Western Europe. A large 'bloom' of phytoplankton can be seen off the coast of Spain. These microscopic algae absorb atmospheric carbon dioxide and release oxygen.

__David Catling__ began his career by studying atmospheric physics and is now an Astrobiologist. He spent 6 years working for NASA (the US National Aeronautics and Space Administration) in California and is currently an affiliate professor at the University of Washington in the USA and a professor in the Department of Earth Sciences at the University of Bristol. His main research interests include how the evolution of planets' surfaces and atmospheres are related and he is also involved in the exploration of Mars.