

# Life and the Evolution of Earth's Atmosphere

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### What's Life to a Geochemist?

Thinking about it, there's a subtle kind of poetry involved with its scientific definition. Life can be said to be a self-replicating, encapsulated, chemical system that undergoes Darwinian evolution. In other words, groups of related organisms have evolved in response to changes in the environment through natural selection. This process has been in effect ever since life began from simple organic molecules in water, over four

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### Stromatolites in Western Australia, today. Did ancient Earth look like this?

billion years ago. So, the origin of life is probably the origin of evolution. Life is resourceful and entrepreneurial. It takes advantage and it changes the chemistry of its surroundings. Life is a fantastically complex system, the emergence of which remains the greatest mystery in science.

Long-term changes in the composition of the atmosphere and oceans are intimately linked to both the geophysical changes in the solid Earth itself and with the ongoing evolution of life. The atmosphere and oceans first appeared about 4.5 billion years ago, soon after the Earth and Moon completed their formational phase. This was the time when gases escaping through volcanoes made an envelope of atmosphere around the young Earth, and a primitive crust solidified and cooled to the point where liquid water could condense. Water began pooling into the first lakes, seas, and oceans. The interaction of water, heat, and rock set the stage for the origin of life.

From the beginning, a number of factors have affected the makeup of the atmosphere to change it from its initial state to what we have today. Several of these factors, such as plate tectonics, weathering (which recycle rocks, water, and gases), and chemical changes induced by the byproducts of life itself, are internal to the planet. However, external factors such as the slowly but ever-increasing luminosity of the Sun over billions of years, gradual changes in the Earth's orbit over many tens of thousands of years, and the rare but catastrophic impacts of giant meteorites and comets, have also played an important role.

The atmosphere of our planet did not originally contain all the free, breathable oxygen it does now. The first permanent atmosphere arose when gases that had been dissolved in the molten planet during its assembly from smaller bodies, called "planetesimals," were released to the surface by volcanism. That first, primitive atmosphere was probably several times denser than what we have now, and was dominated not by oxygen, but by carbon dioxide—a major greenhouse gas. Other gases, such as molecular nitrogen, water vapor, and small amounts of carbon monoxide, sulfur gases, and trace quantities of methane, and hydrogen were also present.

Astrophysical computer models based on the study of young stars and of star-forming regions in the galaxy strongly suggest that the Sun was much dimmer when the first life emerged on Earth, over 4 billion years ago. A dimmer Sun would have supplied less solar radiation to warm the early Earth. To keep the Earth from starting out as a frozen wasteland, with no hope for beginning life to take hold, an atmospheric "greenhouse" must have kept the surface zone warm enough to maintain water in liquid form. Liquid water is the prerequisite for life. Greenhouse gases in much higher abundance than today, primarily water vapor, carbon dioxide, and methane, would have formed a thermal blanket over the surface of the early Earth that strongly absorbed outgoing thermal radiation. This leads to a significantly enhanced, warming "greenhouse effect" that offset the dimmer Sun. Without this very different, greenhouse gas-rich and oxygen-poor early atmosphere to begin with, life would have gotten a frozen start. (See the essay by Charles F. Keller in Section Five, which discusses greenhouse gases and global warming.)

The composition of this early atmosphere, so different from the one we have now, would be deadly for most life that is not a primitive bacterium. Soon after the emergence of the first life more than 4 billion years ago, the activities of organisms began to influence the composition of the atmosphere. As Earth's biosphere and atmosphere co-evolved over billions of years, the product of photosynthesis, mainly, free oxygen, has come to dominate the chemistry of the atmosphere. Without the byproducts of crucial biological processes such as photosynthesis, there would be little or no free oxygen for animals to breathe, nor enough to form a protective ozone layer in the upper atmosphere. Ozone  $(O_3)$  is formed by the recombination of oxygen  $(O_2)$  by solar radiation in the upper atmosphere into the new molecule with three oxygen atoms. This molecule screens harmful ultraviolet sunlight and prevents most of it from reaching the surface. Without an effective ozone layer in the upper atmosphere. more advanced life would not have been able to emerge from the seas to colonize the land. We can safely say that the vast amount of ozone needed to permit the colonization of land became possible only after significant free oxygen accumulated from photosynthesis beginning early in Earth's history.

Since little evidence from the Earth's formational time has survived for scientists to study, it is possible to only make a few basic conclusions about the nature of the first atmosphere and the conditions in which life originated. Most of what is known about early planetary history comes from three sources: the sparse geologic record remaining from more than 3.5 billion years ago, computer models of atmospheres changing with time, and comparing Earth to its planetary neighbors, Mars and Venus, which evolved along very different paths. Scientists have also recently started to study the sophisticated biochemical machinery of primitive photosynthetic bacteria to learn more about their early evolution. These primitive bacteria are descended from the pioneering microorganisms that forever changed the chemistry of the atmosphere from a primitive unbreathable mix to oxygen-rich air.

#### How Earth's Atmosphere Originated

The elements and compounds that make up the atmosphere and oceans evaporate readily under normal surface conditions; that's the definition of "volatile." Elsewhere in the universe, these volatiles would assume very different physical states. In the space between planets and stars, where it is very cold, they would be present mostly as solid ices; however, near stars or in regions where new stars are being formed, where it is hot, they would be present as plasma.

Plasma is a fourth state of matter after solid, liquid, and gas. It exists only at extremely high temperatures when electrons are stripped off atoms to form charged particles. Plasma is in fact the most common state of matter in the universe, yet this state is useless for life; only solid bodies like planets can support matter in the usable solid-liquid-gas states. Life as we know it can occur only where a volatile such as water is stable in the liquid state, and where energy resources like sunlight or chemical energy are available for exploitation for making or supplying food. Such special conditions for life seem to be satisfied only on planetary

Table 1: Comparison of atmospheric compositions of Venus, Mars, Earth						
	pressure (bars)*	CO <sub>2</sub> (%)	N <sub>2</sub> (%)	Argon-36 (%)	H <sub>2</sub> 0 (%)	0 <sub>2</sub> (%)
Venus	92	96.5	3.5	0.00007	<0.00003	trace
Earth	1.013	0.033	78	0.01	<3	20
Mars	0.006	95.3	2.7	0.016	<0.0001	trace

\*A bar is a measure of pressure. One bar equals 1.013 atmospheres, or the atmospheric pressure at sea level.



#### Partial Pressure of CO<sub>2</sub> in the Atmosphere Over Time

surfaces. On Earth, volatiles that constitute the atmosphere are principally represented by the gases nitrogen, which makes up seventy-eight percent, oxygen (twenty percent), water vapor (percentage varies according to weather and geography), argon gas (about one percent), and carbon dioxide, or  $CO_2$  (about 0.03 percent), and trace amounts of other gases. This mixture is vastly different from the lifeless atmospheres of nearby Venus and Mars, both of which have no free oxygen and are completely dominated by carbon dioxide (Table 1). This comparison of the atmospheres of our planetary neighborhood illustrates the role of life in maintaining surface conditions amenable for habitation.

The air and oceans probably represent most of the surface reservoir of the volatile compounds Nitrogen (N<sub>2</sub>) and water (H<sub>2</sub>0) on Earth. Oxygen is dominantly locked in minerals in the crust and the Earth's interior, and would remain so entirely if not for the actions of photosynthesizers. As for carbon, the amount that is present as  $CO_2$  in the atmosphere is small compared to the majority of the Earth's carbon which is sequestered in carbonate rocks such as Figure 1: Changing concentrations of atmospheric carbon dioxide with time on Earth in response to the steady increase in solar luminosity (after Kasting 1993). The amount of past  $CO_2$  that has been calculated in this figure (using the model of J.F. Kasting, 1993) is the concentration required to keep the surface warm enough for liquid water to exist even with past lower solar output. PAL = present atmospheric level of  $CO_2$ . The Moon formed between 4.5 and 4.45 billion years ago (dark blue field). The Earth could have started with an atmosphere extremely enriched in carbon dioxide (gray field). The rise in land plants after 500 million years ago ("C3" on the figure) defines a minimum limit for  $CO_2$  in the air after that time.

limestone and marble, organic matter in sediments, fossil fuels, and biomass on or near the surface. If all of this carbon were oxidized into  $CO_2$  and put into the atmosphere, it would overwhelm all other gaseous components. The amount of  $CO_2$  released in such a case would give our planet a surface pressure of about sixty bars, and result in an atmospheric composition very similar to that of Venus. There would also be a massive greenhouse effect, like the one that keeps the surface of Venus so hot (greater than 460°C). This massive greenhouse effect would result in temperature increases that were more than enough to vaporize the oceans. If the enormous volume of water in the ocean were vaporized, a heavy (250 bar) and deadly greenhouse blanket would push temperatures up beyond even the melting point of rocks. Therefore it is easy to understand how a delicate balance is necessary among the biosphere, atmosphere, crust, and the oceans to keep the Earth habitable over long time scales.

Over the past few hundred million years, the amount of  $CO_2$  in the atmosphere has decreased from high levels to stabilize near its present relatively low level (Figure 1). This appears to be a response of the environment to the steady increase in solar luminosity, which has kept the surface within an equitable temperature range for life to flourish over time.

## Photosynthesis Produces the Oxygen in the Atmosphere

Photosynthesis is the process through which certain bacteria and plants use carbon dioxide, water, and light energy to make food and oxygen. The first life on Earth was probably not photosynthetic, as conditions on the surface were harsh because of multiple meteorite impacts early on, and a deadly bath of ultraviolet radiation before the establishment of an ozone screen. Without an ozone layer, there might still be a biosphere, but it would be tiny and struggling to eke out an existence deep in the crust away from the surface. The bottom of the sea was protected from the realities of a dangerous surface zone on the young Earth, so life might have originated and subsequently evolved there, only to later migrate upwards. In the darkness of the ocean depths, it would have had to rely on chemical rather than light energy. An environment where this is possible—the deep-sea hydrothermal vent environments-has existed throughout much of Earth's history along the mid-ocean ridges (to learn more about this

environment, read Deborah S. Kelley's essay in Section Six). We don't know how long it took for photosynthetic life to evolve and begin the production of oxygen, but we do know that photosynthesis is the dominant metabolic process that sustains the biosphere today.

Photosynthesis, although a cornerstone of the present biosphere, is a complex process that as yet remains poorly understood. In order to convert light energy into chemical energy, photosynthetic organisms use molecular pigments that absorb sunlight of different wavelengths and reflect others. Different colored molecules in plants absorb light energy from different parts of the solar spectrum. The principal light-collecting pigment in plants is chlorophyll, which gives them their green color. Interestingly, the Sun's output is dominated by blue-yellow light, making this the most intense part of the visible solar spectrum. So, chlorophyll is green because it absorbs all of the intense, visible, blue-yellow light and reflects the green. Plants, like all forms of life, are efficient, so they make special use of their pigments to reflect the least intense parts, including the green light of the solar spectrum. The intense light energy is used by the chlorophyll in plants to make carbohydrates or food, with oxygen as a waste product.

#### How the Biosphere Affects the Atmosphere

Organisms affect the composition of the atmosphere in several significant ways. Most of us are aware that animals inhale oxygen and exhale carbon dioxide when they breathe. These gases are exchanged between the biosphere, the atmosphere, the hydrosphere (oceans) and the lithosphere (crust) in enormous quantities. Only a tiny proportion of the oxygen in the atmosphere is made when ultraviolet light splits water molecules high in the atmosphere in a process known as photolysis. The vast bulk of oxygen is continuously replenished via plant

photosynthesis. The high concentration of oxygen needed to keep the contemporary biosphere going, including all of the humans breathing it, is maintained despite its continual removal through oxidative processes like weathering of rocks (which tend to give them a reddish color as in the Grand Canyon), rusting, burning, and so on. In fact, if all photosynthesis were to cease, which would be a catastrophic event indeed, the oxygen in the atmosphere of the Earth would be mostly gone in less than a million years, along with the protective ozone layer. In the absence of photosynthesis, the oxygen present in the atmosphere would combine with carbon in organic matter at the surface to make carbon dioxide, or react with iron in minerals, to soon be removed from the atmosphere altogether. In 1979, in his book Gaia: A New Look at Life on Earth, James Lovelock emphasized that the atmospheric composition of the Earth is far from achieving chemical equilibrium with the surface and must be sustained by biological processes. According to Lovelock's Gaia Hypothesis, life is responsible for making the unique conditions for habitability on Earth; life regulates the global environment. The other planets near the Earth provide a useful measure of how different our planet is from places that are in equilibrium. Again, take a look at the lifeless planets of Mars and Venus in Table 1. They have negligible amounts of oxygen in their atmospheres, and are dominated by carbon dioxide. The same would be true for the Earth if life had never appeared and changed the atmosphere to keep the planet habitable.

#### The Build-up of Oxygen

When oxygen began to first accumulate on Earth billions of years ago, it caused a crisis for primitive anaerobic bacterial life, which is actually poisoned by excess oxygen in the environment. Such life still exists today in organic-rich soils, swamps, deep in sediments, and lake bottom muds where levels of oxygen are low. This early oxygen crisis, however, created an opportunity and led to important new evolutionary changes as life responded to this challenge with metabolic innovations that made use of the newly-available oxygen. Organisms evolved which used oxygen in their metabolic cycles to get more energy out of their food—twenty times more than anaerobic organisms get.

A coupled biological and geological mechanism termed the "carbon cycle" began to manifest itself early in the history of life on Earth, as life took over the production of organic matter and oxygen and began to regulate the balance of carbon between the atmosphere and the oceans. This cycle has helped to regulate the planet's surface temperature by balancing CO<sub>2</sub> output from volcanoes with weathering, burial of organic matter in sediments, and other means of removing CO<sub>2</sub> from the atmosphere. (To learn more details about how this works, read Rachel Oxburgh's essay on the carbon cycle in Section Six). In a sense, industrialization and the burning of fossil fuels, which have released vast amounts of carbon dioxide into the atmosphere, represent a small reversal of the general trend toward higher oxygen concentrations and lower carbon dioxide concentrations with geologic time. Human activity, the long-term actions of plate tectonics. and variations in Earth's orbit will inevitably cause large fluctuations in the amount of carbon dioxide in the atmosphere again, and perhaps changes in oxygen concentration as well.

#### When Did These Changes Occur?

Life originated more than 4 billion years ago. How soon after the origin of life did oxygen levels begin to rise? This is a question that scientists have been exploring for some time (Figure 2). Data gleaned from ancient soils (paleosols) and a variety of other geological evidence indicates that starting about 2.5 billion years ago, sedimentary rocks began to become increasingly affected by higher amounts of oxygen in the atmosphere, and appear red, as though "rusted." Scientists believe that oxygen concentration began to rapidly increase at that time because more oxygen began to be produced by photosynthesis than could be whisked away by reactions with the atmosphere, oceans, and rocks. A threshold had been reached, and the rise of oxygen had begun. At around that same time, more complex bacterial life evolved in response to the oxygen-rich conditions, including organisms with a true cell nucleus (Eukaryotes) from which all plants, animals, and fungi are descended.

The final significant section in the emergence of an oxygen-rich atmosphere on Earth began about 700 million years ago, when the fossil record documents the emergence of multicellular organisms. When oxygen levels became high enough, a little more than one percent of the present level, a powerful ozone screen started to form in the upper atmosphere that protected the first land-dwelling creatures from the Sun's harmful ultraviolet radiation. Abundant oxygen in the atmosphere was essential to the rise of animal and plant life on land.

#### A Hot Future

Knowing what we do about the past trends in atmospheric evolution of the Earth, what can we say about the distant future for life on this planet? The Sun will continue to grow brighter over the 5 billion years or so that remain in its stellar life span. Its luminosity has been increasing on a near-linear path for more than 4.5 billion years because hydrogen is continually converted into the heavier element, helium, by nuclear fusion. This conversion releases tremendous amounts of energy every second and is responsible for sunlight. As helium accumulates, the average density of the Sun increases over time, which in turn causes pressures and temperatures in the Sun's interior to increase. These higher pressures and temperatures increase the rate of fusion, and the extra energy that is generated leads to increased luminosity. As this positive feedback continues, the Sun will continue to increase in intensity by about six percent or more in the next billion years.

One of two things needs to happen to keep the Earth from slowly going the way of deadly hot Venus. Either almost all of the greenhouse gases have to be removed from the atmosphere, or the planet's albedo-the amount of sunlight the surface can reflect back into space—must increase. Unless new plants evolve a type of photosynthesis that requires very little carbon dioxide, or some future culture somehow protects the Earth from a brighter Sun, life on land will have to be abandoned. In the end, some 5 billion years from now, much of the Sun's fuel will be exhausted. The Sun will begin to grow as it approaches the Red Giant phase of its stellar life cycle. By then, the oceans on Earth will have long since boiled away. The last life, primitive bacteria much like the first that appeared, residing in deep crustal rocks and sediments, will have perished. As the surface temperature rises, all of the volatile gases stored over many eons in the Earth's crust will be released to form a thick, hot, blanketing atmosphere. Finally, there will be twin Venuses from that time until the end of the solar system.

#### Summary

A great deal can be learned by approaching the history of life on Earth from the standpoint of geology. The rocks that make up the geologic record preserve changes in the planet's crust, oceans, and atmosphere that have accompanied the history of the evolution of life. Studies of the geologic record help us fine-tune theoretical models that attempt to shed light on conditions at the Earth's surface when life emerged. Studying neighboring worlds is also relevant because it allows us to compare the very different paths taken by these planets in the absence of life. It is also necessary to keep in mind the immense expanse of time involved. Geologists approach the geologic record much like a detective tackles problems in a detective story; the plot thickens as new evidence is uncovered, but it often yields more questions than answers. In science, theories evolve as evidence accumulates. But theories must be grounded in the solid principles of physics, mathematics, and chemistry that describe the behavior of matter in the universe. We are now on the threshold of being able to evaluate the place of Earth in the universe; we may discover that we are not all that unique in having a water-rich planet with abundant life and oxygen. The search for other worlds that contain, or contained, life stands as the grand quest for the next millennium.



#### Partial Pressure of O<sub>2</sub> in the Atmosphere Over Time

Figure 2: This plot (after Kasting, 1993) shows estimates of changing concentrations of free oxygen in the atmosphere over geologic time. The area (in light blue) represents the range in possible concentrations of oxygen based on model calculations, and the study of ancient soils (paleosols), fossil organisms, and marine sediments that only form in the absence of oxygen. These sediments are preserved as Banded Iron Formations (BIF) and only appear in the geologic record up to about 1.8 billion years ago. Although it is not known when photosynthesis began, it is clear that photosynthesis only became an important producer of oxygen in the atmosphere late in Earth's history. PAL = present atmospheric level of  $O_2$ .