EVOLUTION OF ATMOSPHERIC OXYGEN

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Introduction

Abundant free oxygen in the atmosphere distinguishes our planet from all others in the solar system. Earth's oxygen-rich atmosphere is a direct result of life. The current atmosphere contains (by volume) 78.09% N_2, 20.95% O_2, 0.93% Ar, 0.036% CO_2, and additional trace gases. Apart from argon, all of the quantitatively important gases are at least in part biologically controlled, but oxygen in particular has no significant abiotic source. Diatomic oxygen is generated by oxygenic photosynthesis, the biological process in which water molecules are split using the energy of sunlight. Today, green plants, single-celled phytoplankton (free-floating organisms in the ocean, incl. cyanobacteria (chlorophyll-containing bacteria)) all perform oxygenic photosynthesis. Of these, cyanobacteria are the most numerous, with $\sim 10^{27}$ in the oceans, and probably their ancient ancestors were just as plentiful. However, geological differences between the ancient and modern Earth show that there was insufficient O_2 in the early atmosphere to leave traces of oxidation that today are ubiquitous, such as the reddening of exposed iron-rich rocks. The transition from the ancient anoxic atmosphere to a more modern oxic atmosphere appears to have occurred at about 2.3 Ga (where Ga $= 10^9$ years ago). Although this "rise of O_2" has been seen by some as controversial, there is more than enough evidence in its favor for it to have come to be regarded as the standard history of the Earth's atmosphere. This history has been a major influence on life. All animals, multicellular plants, and fungi rely on free oxygen to maintain their energy intensive lifestyles. Life on the planet's surface also became protected from harmful ultraviolet radiation once O_2 levels exceeded 0.2–0.6%, causing an ozone

(O_3) layer to form in the stratosphere. But why free oxygen should have become abundant on a planet that is overall chemically reducing, or exactly why it first appeared about half-way through Earth's 4.5 billion-year history, are still open questions. Nor is there yet any firm understanding of what regulates O_2 at today's level. However, the modern oxygen cycle can at least elucidate some basic concepts of oxygen production and loss before we turn to the history of O_2.

The Modern O_2 Cycle

Oxygenic photosynthesis can be summarized by the following schematic equation [I], where "CH_2O" represents the average stoichiometry of organic matter.

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2 \qquad [I]$$
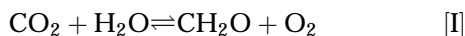
Respiration and decay rapidly consume virtually all (99.9%) of the oxygen produced by photosynthesis, and regenerate CO_2 from organic carbon and O_2. But photosynthesis does not completely reverse, because a small fraction (0.1%) of organic carbon escapes oxidation through burial in sediments (see Table 1). From eqn [I], the burial of one mole of organic carbon will generate one mole of O_2. However, the oxygen cycle is complicated by the burial and weathering fluxes of two other important redox elements, sulfur and iron. Pyrite (FeS_2) contains both elements in reduced form. During weathering, reduced minerals exposed on the continents react with oxygen dissolved in rainwater. Pyrite oxidizes to form soluble sulfate (SO_4^{2-}) and the chemically bound oxygen is then carried to the oceans in rivers. Bacteria in the ocean use sulfate and ferric iron (Fe^{3+}) to regenerate pyrite, and when pyrite is buried in sediments, oxygen is freed again (eqn [II]).

$$2Fe(OH)_3 + 4H_2SO_4 \rightarrow \\ 2FeS_2 + 15O_2 + 7H_2O \qquad [II]$$
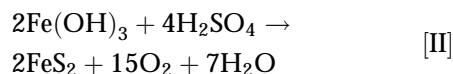
An analysis of the average composition of modern sediments by Heinrich Holland shows that organic carbon and pyrite burial contribute the equivalent to oxygen fluxes of $(10.0 \pm 3.3) \times 10^{12}$ mol O_2 y^{-1} and $(7.8 \pm 4.0) \times 10^{12}$ mol O_2 y^{-1}, respectively. The reduction of oxidized iron and the burial of ferrous iron ($2Fe_2O_3 = 4FeO + O_2$) also adds a minor flux of oxygen, $(0.9 \pm 0.4) \times 10^{12}$ mol O_2 y^{-1}. The burial of sulfate minerals in sediments removes $(0.3 \pm 0.1) \times 10^{12}$ mol O_2 y^{-1} through the oxidation

Table 1   Modern oxygen fluxes in the Earth system

Oxygen fluxes	Magnitude (10^{12} mol O_2 y^{-1})	Effect
Organic carbon burial flux[a]	10 ± 3	Production
Pyrite (FeS$_2$) burial flux[a]	7.8 ± 3.6	Production
Sulfate burial flux[a]	$-(0.3 \pm 0.1)$	Loss
Reduced iron burial flux[a]	0.9 ± 0.4	Production
Continental oxidative weathering flux[a]	$-(15.5 \pm 6.7)$	Loss
Flux of reduced volcanic and metamorphic gases[a]	$-(3 \pm 1)$	Loss
Net O_2 photosynthetic flux to the atmosphere (assuming that burial fluxes and oxidative losses are balanced by negative feedbacks)	~ 0	Net change
Effective oxygen gain from hydrogen escape to space	0.02	Absolute gain for whole Earth

[a]Derived from data in Holland (1978).

Table 2   Reduced and oxidized reservoirs in Earth's continental crust. The Earth's exterior contains Fe_2O_3 and SO_4^{2-} that arose via oxidation, and free atmospheric O_2. Oxidized species are expressed in terms of the moles of O_2 required for their production; e.g., each mole of Fe^{3+} needed $\frac{1}{4}$ mole O_2 to be produced from Fe^{2+} via $FeO + \frac{1}{4}O_2 = \frac{1}{2}Fe_2O_3$. Reduced species are expressed in terms of O_2 moles required for their consumption; e.g., each mole of reduced carbon can be consumed by one mole of O_2

Species and reservoir	Magnitude (10^{21} mol O_2 equivalent)	Size (R) comparisons[a]
Oxidized species		
O_2 in the atmosphere and ocean	0.0378	0.07 R_{AOS}
Fe_2O_3, SO_4^{2-}, and O_2 in the atmosphere–ocean–sedimentary (AOS) system	0.55	R_{AOS}
Total Fe^{3+} in the continental crust[b]	1.7–2.6	$(3.1-4.7)R_{AOS}$
Total oxygen locked up in the continental crust	2.0–2.9	$(1.5-2.2)R_{redC}$
Reduced species		
Reduced carbon in the AOS system	0.56	
Reduced carbon in felsic instrusives, gneisses, schists and felsic granulites	<0.78	
Total reduced carbon in the continental crust, R_{redC}	<1.3	R_{redC}

[a]AOS, atmosphere–ocean–sedimentary system; redC, reduced carbon in the centimental crupt.
[b]Most crustal oxidized iron, Fe^{3+}, resides not in sedimentary rocks but in continental basalt. Fe^{3+} derives from metamorphic or hydrothermal oxidation processes within the crust.

of SO_2 in the atmosphere. Summing these fluxes, the total O_2 production is $(18.4 \pm 7.8) \times 10^{12}$ mol O_2 y^{-1} (Table 1).

On long time scales, oxidation must balance O_2 production to leave a steady amount of O_2 in the atmosphere. About 80–90% of O_2 production is consumed during oxidative weathering, while 10–20% reacts with reduced gases in the atmosphere. Both volcanism (associated with the molten rocks) and metamorphism (associated with hot rocks that do not melt) release reduced gases into the atmosphere. Such gases include H_2, CO, SO_2, and H_2S, which react with O_2, albeit through photochemical intermediates. Consequently, the release of reductants from the solid Earth, either by continental uplift and weathering or by geothermal degassing, controls oxygen consumption. Atmospheric O_2 is not controlled, as is sometimes believed, by respiration and decay. Measured in moles, the amount of organic carbon in the biosphere is $\sim 10^2$ times smaller than the atmospheric reservoir of O_2 and therefore respiration and decay can modulate no more than 1% of total amount of atmospheric O_2.

Over the last 350 million years, a continuous record of charcoal in continental sedimentary rocks suggests that O_2 has always comprised at least $\sim 15\%$ of the atmosphere, because wood cannot burn below this threshold. Yet the residence time of O_2 in the atmosphere–ocean system is far shorter. Dividing the atmosphere–ocean oxygen reservoir (3.78×10^{19} mol O_2) (Table 2) by the source flux (1.8×10^{13} mol O_2 y^{-1}) gives ~ 2.1 million years for the average amount of time an O_2 molecule spends in the atmosphere–ocean system. Evidently, O_2 levels must be controlled by long-term negative feedbacks.

In broad outline, oxygen is regulated because an increase in oxygen increases the consumption of oxygen and/or decreases the rate of oxygen production. A decrease in oxygen has opposite effects. Because the oxidation of exposed continental surfaces appears to be saturated, many researchers have favored a negative feedback on the O_2 source as a primary control on the modern level of O_2. This control is not thought to act directly, by oxidizing newly produced organic carbon and preventing its burial, but indirectly through phosphorus. Most organic carbon is buried in the ocean on continental shelves. Phosphorus acts as a limiting nutrient for marine photosynthesis because the only source of phosphorus is from continental weathering and river runoff. In the ocean, the burial of phosphorus bound to iron hydroxides becomes less efficient under anoxic conditions. Thus a decrease of oxygen increases the amount of phosphorus available for the production and burial of new organic matter. However, this mechanism is not particularly effective against rising levels of oxygen. Instead, some workers have hypothesized that the above 21% oxygen frequency of forest fires will increase, triggering ecological shifts from forest to grassland. Vascular plants like trees amplify the rate of rock weathering by about an order of magnitude relative to simpler plant life. Rising oxygen will thus throttle the supply of phosphorus to the ocean, ultimately lowering the rate of organic carbon burial, the oxygen source. However, while such controls on modern oxygen concentrations are borne out by simple biogeochemical models, they are still hypothetical.

Oxygen in the Prebiotic Atmosphere

In all likelihood, the atmosphere started out with an oxygen partial pressure $pO_2 \leq 10^{-13}$ bar before life existed because reduced gases overwhelmed the abiotic source of O_2. In the absence of photosynthesis, free O_2 arises only from the photolysis of water and the subsequent escape of hydrogen to space. By itself, photolysis of H_2O does not provide a net source of oxygen because the photolysis products recombine. Although Earth's atmosphere has changed over time, a "cold-trap" for water generally exists at the (tropical) tropopause. Because water is cold-trapped to only a few parts per million, the rate of production of oxygen from the photolysis of water and escape of hydrogen is very small. The O_2 so produced can react with hydrogen through a series of photochemical reactions that add up to a net reaction eqn [III].

$$O_2 + 2H_2 \rightarrow 2H_2O \qquad [III]$$
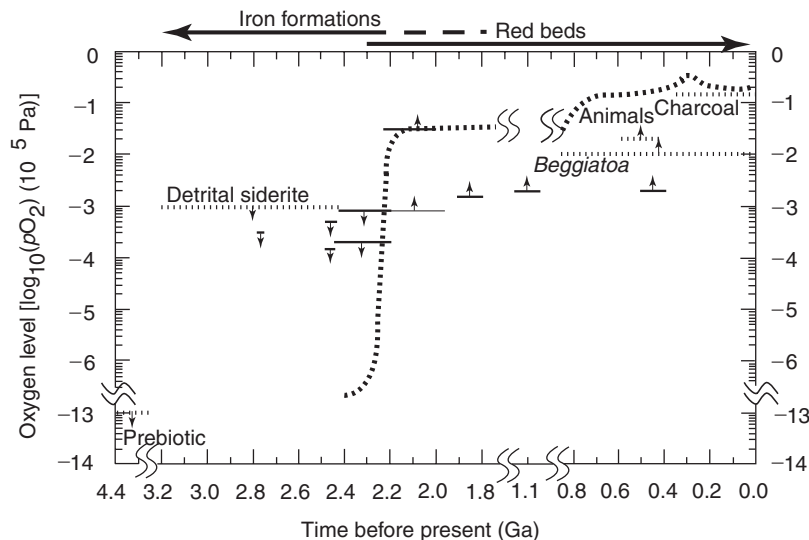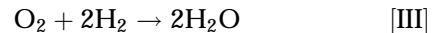
Figure 1   The history of atmospheric oxygen. The thick dashed line shows a possible evolutionary path for atmospheric oxygen that satisfies geochemical and biological constraints. Dotted horizontal lines show the duration of geochemical and biological constraints, such as the occurrence of detrital siderite ($FeCO_3$) in ancient riverbeds. Downward-pointing arrows indicate upper bounds on the level of oxygen, whereas upward-pointing arrows indicate lower bounds. Unlabeled solid horizontal lines indicate the occurrence of specific paleosols, with the length of each line showing the uncertainty in the age of each paleosol. Bounds on pO_2 from paleosols are taken from Rye and Holland (1998). Biological lower limits on pO_2 are based on estimates for the requirements of the marine sulfur-oxidizing bacteria *Beggiatoa*, and also the requirements of macroscopic animals that appear around 0.59 Ma. An upper bound on the level of pO_2 in the prebiotic atmosphere at c. 4.4 Ga (shortly after the Earth had differentiated into a core, mantle, and crust) is based on photochemical calculations. Similarly, a constraint of <10-6 bar before 2.4 Ga is suggested by mass-independent sulfur isotope evidence.

With volcanic outgassing rates similar to those of today, H_2 fluxes would be $\sim 10^2$ times larger than the abiotic O_2 flux in the primitive atmosphere. If anything, outgassing rates were greater on early Earth because of increased heat flow from a hotter, more radioactive interior.

Geochemical Evidence for a Rise of O_2 about 2.3 Ga

Once life arose, it must have modulated the cycling of all gases in the atmosphere–ocean system containing chemical elements of biological importance. The most dramatic atmospheric change evident in the rock record is an increase in the level of O_2 around 2.3 Ga (Figure 1). This event occurred in the Paleoproterozoic era (2.5–1.6 Ga), the first of three eras within the Proterozoic eon (2.5–0.544 Ga), which follows the Archean eon (before 2.5 Ga).

Evidence from Continental Environments

Paleosols, detrital grains, and red beds, all from continental environments, suggest very low levels of O_2 before about 2.3 Ga. Paleosols are ancient surfaces that were exposed to the atmosphere during weathering. Geochemical studies of paleosols indicate that around 2.4–2.2 Ga, atmospheric pO_2 rose from <0.0008 atm to >0.002 atm, possibly to >0.03 atm. Paleosols before ~ 2.4 Ga show that iron was leached during weathering, but after ~ 2.2 Ga, iron was not leached. Ferrous iron (Fe^{2+}) is soluble, whereas ferric (oxidized) iron (Fe^{3+}) is not. Consequently, iron will be flushed through a soil if rainwater has little dissolved O_2 but will be immobilized otherwise. Another sign of abundant oxygen in soils is that cerium is fractionated from the other rare-earth elements. Cerium is oxidized from Ce^{3+} to Ce^{4+} to form cerianite (CeO_2). The presence of Ce^{3+}-rich minerals in paleosols from the Archean eon (> 2.5 Ga) implies an early anoxic atmosphere. Other evidence for ancient anoxic air includes detrital grains from Archean riverbeds, which commonly contain reduced minerals that would only survive at low pO_2. Detrital grains of pyrite (FeS_2), uraninite (UO_2), and siderite ($FeCO_3$) place upper bounds on Archean pO_2 of roughly 0.1 atm, 0.01 atm and 0.001 atm, respectively. In oxic waters, uraninite dissolves to form soluble U^{6+} ions, pyrite oxidizes to sulfate (SO_4^{2-}) and ferric iron (Fe^{3+}), and siderite oxidizes to produce ferric iron (Fe^{3+}). Red beds provide further evidence for atmospheric redox change. They derive from wind-blown dust or river-transported grains coated with red-colored hematite (Fe_2O_3). Before ~ 2.3 Ga, red beds are very rare, whereas afterwards red beds are ubiquitous. Pre-2.3 Ga red beds result from ground water contamination by the post-2.3 Ga atmosphere.

Evidence from Iron Formations

An atmospheric O_2 increase at ~ 2.3. Ga is consistent with the temporal distribution of banded iron formations (BIFs). BIFs are laminated marine sedimentary rocks containing ≥ 15 wt% iron, usually with alternating iron-rich and silica-rich layers. The iron, in large part, originated from hydrothermal sources in the deep ocean, such as mid-ocean ridges. Today, iron is oxidized immediately and deposited on the flanks of the ridges. In the anoxic Archean oceans, ferrous iron circulated to the continental shelves where it was (microbially) oxidized and precipitated. In the Paleoproterozoic, BIFs decline in abundance and disappear after ~ 1.8 Ga. This has usually been attributed to a rise in atmospheric oxygen ventilating the deep ocean. However, it is also plausible that the deep ocean remained anoxic until the late Proterozoic and that sulfide was responsible for removing iron from the deep ocean. Increased oxidative weathering would have led to greater sulfate concentrations in the ocean, promoting microbial sulfate reduction. Because sulfate reduction produces sulfide (S^{2-}), the deep ocean could have been swept free of iron by the precipitation of insoluble pyrite, FeS_2.

Evidence from Carbon and Sulfur Isotopes in Marine Sediments

Marine carbon isotopes indicate drastic environmental change in the Paleoproterozoic, consistent with the rise of O_2. Of the two stable carbon isotopes, ^{12}C and ^{13}C, photosynthetic organisms kinetically concentrate ^{12}C into organic matter, leaving inorganic carbonate relatively enriched in ^{13}C. Isotope compositions are expressed as $\delta^{13}C$, where $\delta^{13}C = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1] \times 1000$, in parts per thousand (‰). From ~ 3.5 Ga, with only a few brief variations, sedimentary organic carbon is found to be about 30‰ (3%) lighter than marine carbonate carbon that has $\delta^{13}C \approx 0$‰. This mainly reflects biological fractionation. Carbon entering the atmosphere–ocean system from volcanism, metamorphism, and weathering has $\delta^{13}C_{in} \approx -6$‰. On time scales greater than the residence time of carbon in the ocean ($\sim 10^5$ years), the same number of atoms entering the atmosphere–ocean system must exit the system, implying the following balance shown in eqn [1].

$$\delta^{13}C_{in} = f_{carb}\delta^{13}C_{carb} + f_{org}\delta^{13}C_{org} \qquad [1]$$

Here f_{carb} is the fraction of carbon buried in carbonate minerals with isotopic composition $\delta^{13}C_{carb}$, and f_{org} is

the fraction of carbon buried in organic carbon with isotopic composition $\delta^{13}C_{org}$. Solving eqn [1] with the observed $\delta^{13}C$ values gives $f_{org} \approx 0.2$. Thus, over geological time, 20% of the carbon in CO_2 entering the ocean–atmosphere system has exited as buried organic carbon, whereas the remaining 80% has exited as carbonate.

The largest excursions in $\delta^{13}C_{carb}$ in Earth's history occur between 2.4 and 2.1 Ga, with positive and negative oscillations between $+10‰$ and $-5‰$. Three low-latitude glacial, or "Snowball Earth," episodes during 2.4–2.2 Ga together with sparse data complicate the interpretation of $\delta^{13}C_{carb}$ fluctuations. Clearly, major perturbations in the carbon cycle and climate system occurred. The rise of O_2 would have destroyed greenhouse gases like methane, inducing global cooling and decimating any early land biota. Oxygen would have been catastrophic to some anaerobic organisms, for which O_2 is toxic. In combination with inducing significant oxidative weathering, rising oxygen would have dramatically affected the carbon cycle.

Marine sulfur isotopes indicate an increase in sulfate concentrations at ~ 2.3 Ga consistent with a rise of O_2. Today, sulfate-reducing bacteria (SRB) produce most of the sulfide in marine sediments. SRB reduce $^{32}SO_4^{2-}$ in preference to $^{32}SO_4^{2-}$ so that the sulfide produced is depleted in ^{34}S. However, this fractionation ceases in waters with sulfate concentration <1 mmol l^{-1}. Archean sulfides display $^{34}S/^{32}S$ ratios that cluster around the unfractionated mantle value, implying Archean oceans with <1 mmol l^{-1} sulfate, compared to 28.9 mmol l^{-1} in today's surface sea water. Lack of sulfate is consistent with low pO_2, which would induce little oxidative weathering of sulfides, limiting the river supply of sulfate to the oceans. By 2.3–2.2 Ga, sulfides with significant ^{34}S depletions formed ubiquitously in the ocean, reflecting abundant sulfate and the rise of O_2.

Measurements of a third less-abundant sulfur isotope, ^{33}S, in addition to ^{34}S and ^{32}S, show a major change in the sulfur cycle between 2.4 and 2.1 Ga. In modern rocks, ^{32}S, ^{33}S, and ^{34}S obey "mass-dependent" fractionation, in which the difference in abundance between ^{33}S and ^{32}S is approximately half that between ^{34}S and ^{32}S. Many aqueous chemical and biochemical reactions, such as microbial sulfate reduction, produce mass-dependent isotope fractionation. In contrast, the full suite of stable sulfur isotopes in pre-2.3 Ga rocks show "mass-independent" fractionation, which is thought to result exclusively from photochemical reactions such as photolysis of SO_2. In this case, the relative abundance of different isotopes deviates from what is expected of mass-dependent fractionation. In a high-O_2 atmosphere, sulfur gases

are rapidly oxidized and rain out as dissolved sulfate. But in the absence of O_2, sulfur exits the atmosphere as sulfide, elemental sulfur, or sulfate, which allows the mass-independent fractionation produced by anoxic photochemistry to be transferred to sediments.

A Second Rise of O_2 in the Neoproterozoic Era?

Some researchers argue that there was a second rise of pO_2 in the Neoproterozoic era (1. 0–0.544 Ga) from about 1–3% to greater than 5–18% of present levels. From ~ 1.05 to 0.64 Ga, sulfides are increasingly found with ^{34}S-depletions exceeding the fractionation threshold of sulfate-reducing bacteria. This can be explained if sulfide was reoxidized at the sediment–water interface to SO_4^{2-} and reduced again by bacteria, cyclically increasing the isotope fractionation. Possibly, O_2 increased to the point where it penetrated marine sediments, making the deep ocean aerobic for the first time. This could corroborate an increase of oxygen thought necessary to explain the appearance of macroscopic animals in the fossil record around 590 Ma.

Phanerozoic Changes in pO_2

In the Phanerozoic eon (0. 54 Ga to present), pO_2 has probably always been in the range 0.15–0.35 bar (1 bar $\approx 10^5$ Pa). After the land was colonized by plants around ~ 420 Ma, large amounts of organic carbon were buried on the continents in the Carboniferous (362–290 Ma). Lignin, a structural compound in trees, was difficult to decompose until organisms like fungi evolved means of doing so. Because organic carbon burial is accompanied by a stoichiometric release of O_2 (eqn [I]), Carboniferous organic burial may have led to peak $pO_2 \sim 0.3$ bar at ~ 300 Ma. This would explain the presence of giant Carboniferous insects, like dragonflies with 0.7 m wingspan, which rely on the diffusion of O_2 for respiration.

Biogeochemical Change: Explaining the History of Oxygen

There are several lines of evidence suggesting that oxygenic photosynthesis pre-dates the rise of O_2. Biomarkers are organic molecules that are diagnostic of the organisms from which they were derived. Only cyanobacteria are known to synthesize 2-methyl bacteriohopanepolyols (specific five-carbon-ring compounds), which are transformed in sediments to 2-methyl hopanes. Similarly, only eukaryotes (single-celled organisms with cell nuclei) synthesize certain

sterols (four-carbon-ring alcohols) in a process that requires molecular oxygen. Steranes, derived from sterols, and 2-methyl hopane biomarkers have both been found in ancient sedimentary rocks from western Australia, providing unambiguous evidence of oxygenic photosynthesis at 2.7 Ga. Stromatolites, which are laminated mineral structures produced by microbial growth, provide further evidence. These are present in 2.72 Ga paleolakes that had no hydrothermal sources of reductant, implying oxygenic photosynthesis as the only means of organic synthesis. Isotopic fractionation of carbon between sedimentary organic carbon and inorganic carbonates is about 30‰ back to 3.5 Ga and characteristic of photosynthetic fractionation, which suggests an earlier origin for oxygenic photosynthesis but is not, on its own, conclusive.

Theories for the Paleoproterozoic rise of O_2

Once oxygenic photosynthesizers evolved, they very likely dominated the biosphere. In their absence, all other carbon-fixing organisms required reductants supplied by geothermal processes, such as H_2, to reduce CO_2 to organic carbon, restricting habitats to places like hydrothermal vents. In contrast, the source of hydrogen for oxygenic photosynthesis is ubiquitous H_2O. Why then, was there a delay of 0.3–1 billion years between the earliest oxygenic photosynthesis and the rise of O_2?

One explanation is that as geothermal heat declined owing to the decay of radioactive materials inside the Earth, the flux of volcanic gases dwindled, lessening the sink on O_2. However, increased past volcanic outgassing would have also injected proportionately more CO_2. Carbon isotopes from 3.5 Ga onward show that roughly 20% of the CO_2 flux into the biosphere was fixed biologically and buried as organic carbon, with the remainder buried as carbonate. Increased outgassing in the past, on its own, cannot explain the oxic transition because, as one goes back in time, O_2 production due to organic burial would have risen in parallel with O_2 losses. A second hypothesis suggests that large positive carbonate isotope excursions from 2.4 to 2.1 Ga were due to a massive pulse of organic burial that caused the rise of O_2. However, given the geologically short residence time of O_2, a pulse of organic burial would merely cause atmospheric O_2 to rise and decay, not to remain in the atmosphere. A third explanation of the rise of O_2 invokes a gradual shift of volcanic gases from reduced to oxidized. This hypothesis is promising, because a secular change would make the atmosphere more conducive to higher O_2 levels. However, data from redox-sensitive elements in igneous rocks show that

the mantle's oxidation state, which controls the redox state of volcanic gases, only permits an increase in H_2 relative to CO_2 by a factor ≤ 1.8, which cannot account for a sufficient change in the sink on O_2.

The rise of O_2 can be considered more generally. The rate of change of the number of moles of O_2, R_{O_2}, in the atmospheric reservoir is given by eqn [2].

$$\frac{d(R_{O_2})}{dt} = F_{source} - F_{sink}$$
$$= F_{source} - (F_{volcanic} + F_{metamorphic} + F_{weathering})$$
$$[2]$$

F_{sink} is the removal flux of O_2 from the atmosphere (in moles y^{-1}) due to numerous oxidation reactions and F_{source} is the source flux of oxygen (in moles y^{-1}) due to burial of organic carbon and pyrite. The sink fluxes are the reaction of O_2 with reduced volcanic gases ($F_{volcanic}$), reduced metamorphic gases ($F_{metamorphic}$), and reduced material on the continents ($F_{weathering}$). During any particular epoch, R_{O_2} will be in "steady state," which means that O_2 will have accumulated in the atmosphere to some value of R_{O_2} where the O_2 sink (F_{sink}) will be equal to the O_2 source (F_{source}). In this case, $d(R_{O_2})/dt = 0$. Such a balance of source and sinks is how O_2 remains stable today. O_2 levels have evolved because the terms on the right-hand side of eqn [2] have altered over Earth history. The sink due to oxidative weathering was apparently smaller in the Archean, but the source due to organic burial appears to have been relatively constant on the basis of carbon isotopes. This evidence implies that the sink from reduced gases was greater in the Archean relative to the source of O_2. For O_2 to rise, this sink must have diminished.

Unlike volcanic gases, reduced metamorphic gases provide an oxygen sink that is not determined by the oxidation state of the mantle and so could have changed greatly. The metamorphic recycling of more reduced Archean crust would have produced more reducing volatiles than the recycling of today's more oxidized crust, as a matter of redox conservation. That the early crust was more reduced than today is suggested by evidence showing no oxidized surfaces. A decrease by a factor of ∼3 in the H_2/CO_2 ratio of volatile fluxes is all that is required to flip the atmosphere from a state dominated in redox terms by hydrogen-bearing species like CH_4 to an O_2-rich state. Crustal redox change, perhaps in combination with a small change in mantle redox, could plausibly have effected such a change in the redox state of gaseous emissions. But why would the crust oxidize?

Just a small excess of hydrogen would have tipped the redox balance of the atmosphere to an anoxic, "hydrogen-rich" state. For thermodynamic reasons,

the biosphere is prone to convert metabolically desirable hydrogen to CH_4, which would accumulate to levels 10^2–10^3 times present values. The photolysis of methane in the stratosphere would promote rapid escape of hydrogen to space, at $\sim 10^2$ times today's escape rate. When hydrogen escapes to space, the Earth as a whole is oxidized. The severe depletion of noble gases in the composition of the Earth compared to solar composition shows that the Earth did not retain gaseous volatiles from the original solar nebula when it formed. Hydrogen was originally incorporated into the Earth in an oxidized, solid form such as in ice (H_2O) or water of hydration ($-OH$). If hydrogen is lost from such solids, the matter left behind is oxidized. Thus, when hydrogen originates from gases in the crust (or mantle) and escapes to space, the crust (or mantle) is irreversibly oxidized.

Consequently, a plausible explanation for the 2.3 Ga rise of O_2 is that excess reductants scavenged O_2 in the Archean. Hydrogen escape, promoted by methane, then oxidized the Earth, lowering the sink on O_2 from gaseous emissions until an oxic transition occurred. Explaining a second, Neoproterozoic rise of O_2 in the same way is problematic, unless methane persisted throughout the Proterozoic at a moderate level of order 10 parts per million by volume and shifted a redox buffer beyond another critical threshold. However, details are still obscure.

A large uncertainty is the time-integrated export of reduced and oxidized material from the crust to the mantle. Net export of reduced material to the mantle could have perhaps oxidized the crust, essentially with the same effect as hydrogen escape to space. However, we know little about how much reduced material has been subducted versus how much oxidized material over Earth history.

The Emergence of the Ozone Layer

The Paleoproterozoic rise in oxygen would have created an ozone layer, shielding surface life from ultraviolet (UV) radiation. Even before the rise of O2, radiation below 200 nm is absorbed by CO2. O3 shields biologically harmful radiation in the 200–300 nm range. Photochemical models show that harmful UV is mostly absorbed with an ozone layer that would form with O_2 levels about 1–3% of present, similar to those after 2.3 Ga.

Summary

The most significant biological event in the history of the Earth's atmosphere was the evolution of oxygenic photosynthesis. However, there was a long delay between the appearance of oxygenic photosynthesis before 2.7 Ga, possibly as early as 3.5 Ga, and the oxygenation of the atmosphere at 2.3 Ga. This delay reflects a secular change in the oxygen sink. The long-term consumption of oxygen is ultimately controlled by the release of reductants from the Earth's crust and mantle. A plausible explanation for the 2.3 Ga rise of O_2 is that excess reductants scavenged O_2 in the early atmosphere. Such conditions would have stabilized abundant biogenic methane in the atmosphere. Methane photolysis would have led to significant escape of hydrogen to space, oxidizing the Earth's lithosphere and lowering the sink on free O_2 until an oxic transition occurred. A second rise of O_2 at about 1.0–0.6 Ga is suggested by increased sulfate concentrations in the ocean, although the cause remains obscure. The progressive increase of atmospheric oxygen levels set the stage for multicellular life to develop. Ultimately, we owe our own existence to the growth in atmospheric oxygen levels.

Cyanobacteria Single-celled bacteria containing chlorophyll-*a* and capable of oxygen-producing photosynthesis.

Ga 10^9 years ago.

Hydrogen escape The process in which hydrogen atoms in the exosphere exceed the escape velocity of the Earth and escape into space.

Ma 10^6 years ago.

Oxidation state The degree of oxidation of an atom, molecule, compound, or quantity of matter. Substances with a low oxidation state have a large number of available electrons, whereas substances with a high oxidation state do not.

Oxidizing A process or environment (oxidizing environment) in which a chemical element or ion loses electrons and is changed from a lower to a higher valence state.

Oxygenic photosynthesis The process in which an organism uses sunlight, water, and carbon dioxide to synthesize organic matter, releasing O_2 as a waste product.

Paleosol A buried, commonly lithified, soil horizon of the geological past.

Phanerozoic An Eon of Earth history, 0.544 Ga to present.

Proterozoic An Eon of Earth history, 2.5 to 0.544 Ga. It is composed of three eras, the Paleoproterozoic

(2.5–1.6 Ga), the Mesoproterozoic (1.6–1.0 Ga), and the Neoproterozoic (1.0–0.544 Ga).

Red bed Sediment or sedimentary rock that is red or reddish-brown in color owing the presence of ferric oxide materials usually coating individual grains.

Reduction A process or environment (reducing environment) in which a chemical element or ion gains electrons and is changed from a higher to a lower valence state.

Snowball Earth An event in Earth history when low-latitude glaciation occurred and the whole Earth may have been covered in ice.

Stromatolite A lithified, commonly laminated, sedimentary structure produced as a result of the growth and metabolic activities of aquatic, bottom-dwelling communities of microorganisms.

Sulfate reduction A process used by some bacteria to derive energy by reducing sulfate ions (SO_4^{2-}) to H_2S.

See also

Biogeochemical Cycles: Carbon Cycle (0014); Sulfur Cycle (0015). **Chemistry of the Atmosphere:** Principles of Chemical Change (0098). **Evolution of Earth's Atmosphere** (0038). **Gaia Hypothesis** (0040). **Ozone:** Ozone Depletion Potentials (Halogen Loading) (0293); Ozone as a UV Filter (0296); Role in Climate (0297); Surface Ozone Effects on Vegetation (0295). **Tropospheric Chemistry and Composition:** H_2 (0427). **Volcanoes:** Composition of Emissions (0447).

Further Reading

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