



See also

- ▶ Fractionation, Mass Independent and Dependent
- ▶ Interstellar Chemical Processes
- ▶ Isotopic Fractionation (Interstellar Medium)
- ▶ Isotopic Fractionation (Planetary Process)
- ▶ Isotopolog
- ▶ Photochemistry
- ▶ Photodissociation Regions
- ▶ Protoplanetary Disk, Chemistry
- ▶ Stellar Nucleosynthesis

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Oxygen Respiration

- ▶ Aerobic Respiration

Oxygenase

Definition

Oxygenases catalyze the transference of oxygen from molecular oxygen to an oxidized substrate. They are a group of ▶ **enzymes** that form a class of oxydoreductases (enzymes that catalyze the transference of electrons from one molecule (called reductant) to another (the oxidant)). There are two classes of oxygenases: monooxygenases, which transfer an oxygen atom from molecular oxygen to the substrate and reduce the other atom to water, and dioxygenases, which are able to transfer both oxygen atoms to the substrate.

See also

- ▶ Enzyme
- ▶ Oxidation

Oxygenation

- ▶ Oxygenation of the Earth's Atmosphere

Oxygenation of the Earth's Atmosphere

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Synonyms

Atmospheric redox change; Earth's atmosphere, oxygenation; Great oxidation event; Oxygenation; Rise of oxygen

Keywords

Great oxidation event, rise of oxygen, oxygenation

Definition

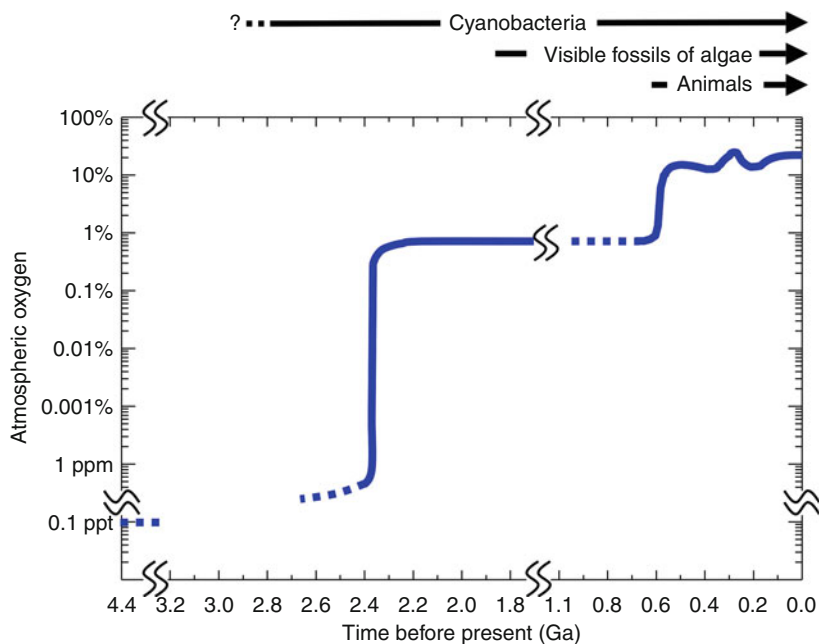
Earth's oxygenation is an increase in the concentration of atmospheric molecular oxygen (O_2) from levels of less than 1 ppmv before 2.45 Ga to 21% by volume today. Larger amounts of atmospheric oxygen became possible because of shifts in the competition between the production of oxygen derived from ► [photosynthesis](#) and the rate of consumption of oxygen by different geological processes. Evidence from ancient rocks suggests that oxygenation happened in steps, with a first rise of O_2 at 2.45–2.32 Ga and a second around 0.75–0.58 Ga. The latter increase was a precursor to the appearance of macroscopic animals.

Overview

The present atmosphere contains (by volume) 78.05% N_2 , 20.95% O_2 , 0.93% Ar, 0.038% CO_2 , and various trace gases. With the exception of argon, the concentrations of all of major gases are biologically modulated. Oxygen, in particular, is almost solely biogenic because it has no significant abiotic source. Consequently, before life existed, the atmospheric partial pressure of O_2 is estimated to have been $<10^{-13}$ bars. The importance of O_2 cannot be overstated: without sufficient O_2 , the Earth would have

no large multicellular plants, no land animals, and no humans or consciousness. A particular type of photosynthesis, ► [oxygenic photosynthesis](#), is responsible for supplying O_2 to the atmosphere. Jan Ingenhousz, a Dutch physician and botanist, discovered oxygenic photosynthesis in 1779, by showing that when green plants are exposed to sunlight they produce oxygen. In the nineteenth century, many single-celled photosynthesizers were identified in addition to plants, which included algae and organisms that were initially called *blue-green algae*. Like other algae, the blue-green ones were assumed to have the same cellular structure as plant cells, as a matter of definition. However, in the 1970s, blue-green algae were recognized as bacteria and were reclassified as *cyanobacteria* through the efforts of Roger Stanier, a Canadian microbiologist. Our modern description of oxygenic photosynthesis is a process by which green plants, algae, and cyanobacteria split molecules of water into hydrogen and oxygen. The hydrogen is used inside cells to chemically reduce carbon dioxide to organic matter, while the oxygen is released as O_2 waste gas.

In the twentieth century, geochemistry uncovered the history of Earth's atmospheric O_2 levels, showing that for roughly the first half of Earth history, up until about 2.4 Ga, O_2 concentrations were less than 1 ppmv (parts per million by volume) (Fig. 1). The first person to describe



Oxygenation of the Earth's Atmosphere. Figure 1 A schematic history of atmospheric oxygen according to geologic constraints discussed in the text

evidence that O₂ levels were significantly different on the early Earth was the geologist Alexander MacGregor. In the 1920s, MacGregor examined Archean (pre-2.5 Ga) sedimentary rocks in modern-day Zimbabwe and deduced that they formed in an atmosphere devoid of O₂ because they lacked the reddish-colored, oxidized iron minerals that are ubiquitous in analogous modern sediments. MacGregor's conclusion greatly influenced Preston Cloud, an American geologist, who further investigated the geologic record for information on past atmospheric O₂. Cloud also championed a suggestion originally made in 1959 by the marine biologist John Nursall that the relatively late appearance of macroscopic fossils animals in the geologic record reflected the slowness in reaching a sufficiently O₂-rich atmosphere.

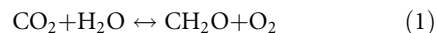
Modern geochemical research shows that an initial transition to an oxygenated atmosphere occurred in the period 2.45–2.32 Ga, but the O₂ levels attained were probably only 0.2–2% by volume and apparently insufficient for supporting macroscopic animals. This first “rise of oxygen” is also called the *Great Oxidation Event* (GOE). Although much less than today's 21% by volume, the post-GOE O₂ levels were enough to dominate the redox chemistry of the atmosphere. Such O₂ levels were also ample for producing a stratospheric ozone (O₃) layer, which ever since has protected life on the Earth's surface from biologically harmful ultraviolet radiation. The first fossils visible to the naked eye occur after the GOE at 1.87 Ga and are thought to represent a seaweed, *Grypania spiralis*. In a second increase in O₂, over the period 750–580 Ma, O₂ rose to levels of at least tens of percents of modern, that is, a concentration between 2% and present levels. The first animal fossils appear in the Ediacaran Period (635–542 Ma), with the oldest soft-bodied fossils of Ediacaran fauna at ~575–565 Ma. While there is a consensus that sufficient O₂ was a necessary physiological precursor to animal life, there remains considerable debate among paleontologists about whether an increase in O₂ caused large animals to appear or whether other evolutionary and ecological factors were crucial.

Explaining why O₂ increased is more elusive than it might first appear. We might suppose that when cyanobacteria evolved, O₂ would have accumulated in the atmosphere. But the consensus interpretation of geochemical evidence (discussed below) is that cyanobacteria produced O₂ for several hundred million years or more before 2.4 Ga, while atmospheric O₂ levels remained <1 ppmv. A pertinent consideration is that the Earth's overall chemical composition is reducing, so that reactions of O₂ with geothermal gases in the atmosphere or certain cations in the ocean (e.g., Fe²⁺) in an initially reducing

environment must have acted as a powerful chemical buffer opposing the accumulation of atmospheric O₂. Consequently, we need to carefully consider the losses of O₂ as well as its source for understanding past changes in O₂ levels. In this regard, the modern oxygen cycle helps to elucidate some of the basic concepts of source and sink fluxes before discussing how sources and sinks were probably different on the ancient Earth.

The O₂ Balance Sheet: Gains and Losses

The theoretical subtleties of how photosynthesis can influence long-term atmospheric O₂ levels were not fully appreciated until the 1970s, in spite of the fact that a French geologist, Jacques Ebelmen, correctly described the key ideas in 1845. Ebelmen implicitly realized that photosynthesis is nearly a zero-sum activity. Oxygenic photosynthesis can be summarized by the following schematic equation:



where “CH₂O” represents the average stoichiometry of organic matter. Oxygen consumption by respiration or decay of organic matter reverses Eq. 1, and produces no net oxygen on timescales greater than about 10² years. Oxygen only escapes respiration or oxidative decay on geologic timescales because a tiny fraction (0.1–0.2%) of organic carbon is buried, mainly in marine sediments, which segregates the oxygen from the organic matter. Some organic matter is also used in biogeochemical processes to make pyrite (FeS₂) from seawater sulfate ions (SO₄²⁻(aq)) as follows:

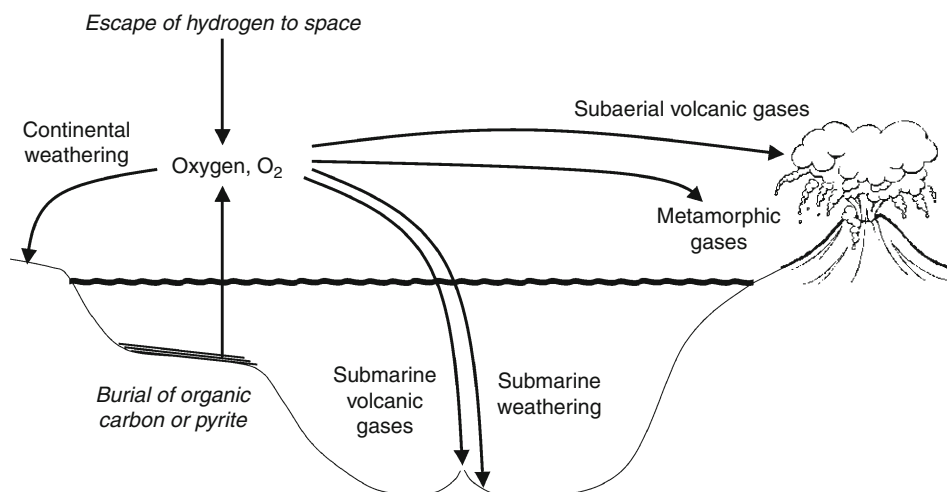
Oxygenic photosynthesis: $\text{CO}_2 + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{O}_2 \times 15$

Anaerobic decomposition: $15\text{CH}_2\text{O} + 8\text{SO}_4^{2-} + 2\text{Fe}_2\text{O}_3 + 16\text{H}^+ = 4\text{FeS}_2 + 15\text{CO}_2 + 23\text{H}_2\text{O}$

 Net reaction: $8\text{SO}_4^{2-} + 2\text{Fe}_2\text{O}_3 + 16\text{H}^+ = 15\text{O}_2 + 4\text{FeS}_2(\text{buried}) + 8\text{H}_2\text{O}$ (2)

Consequently, pyrite burial also liberates oxygen into the atmosphere or ocean. Remarkably, Ebelmen correctly identified both organic carbon burial and pyrite burial as the long-term sources of atmospheric oxygen. Unfortunately, his ideas went unnoticed and the same concepts had to be reinvented.

While it is useful to think of the burial of organic carbon and pyrite as a “net source” of O₂, it is important to appreciate that this “net” O₂ is lost to numerous other sinks for O₂ besides the reversal of eq. [1]. The geological sinks and sources of O₂ are shown in Fig. 2. By reviewing



Oxygenation of the Earth's Atmosphere. Figure 2 Schematic diagram of source and sink fluxes of oxygen on geologic timescales

Oxygenation of the Earth's Atmosphere. Table 1 Modern source fluxes of O_2 (Holland 2002)

Oxygen fluxes	$\times 10^{12}$ mol O_2 year $^{-1}$	Effect on O_2
Organic carbon burial flux	10.0 ± 3.3	Production
Pyrite (FeS_2) burial flux	7.8 ± 4.0	Production
Sulfate burial flux	$-(0.3 \pm 0.1)$	(Loss)
Reduced iron burial flux	0.9 ± 0.4	Production
Total rate of oxygen production $\sim (18.4 \pm 7.8) \times 10^{12}$ mol O_2 year $^{-1}$		

the average composition of new sediments, American geochemist Heinrich Holland has estimated that burial fluxes of organic carbon and pyrite produce oxygen at rates of 10.0 ± 3.3 Tmol O_2 year $^{-1}$ and 7.8 ± 4.0 Tmol O_2 year $^{-1}$, respectively, where 1 Tmol = 10^{12} mol (Holland 2002). The reduction of oxidized iron from its +3 oxidation state to the +2 state ($2Fe_2O_3 = 4FeO + O_2$) and subsequent burial also adds a minor flux of O_2 , whereas the burial of sulfate minerals in sediments removes O_2 . Summing these burial fluxes, the total O_2 net source is 18.4 ± 7.8 Tmol O_2 year $^{-1}$ (Table 1). Dividing the current amount of oxygen in the atmosphere-ocean reservoir (3.78×10^{19} mol O_2) by the source flux (1.8×10^{13} mol O_2 year $^{-1}$) gives ~ 2.1 million years for the average amount of time an O_2 molecule spends in today's atmosphere-ocean system. Consequently, over such timescales, the net source of O_2 must be closely balanced by losses or O_2 levels would wildly fluctuate. We know that

centimeter- to meter-sized animals, which require O_2 to grow and breathe, have been continuously present in the Phanerozoic eon (542 Ma to present) so that concentrations of atmospheric O_2 must have been within 0.2 ± 0.1 bar. The O_2 source is balanced by O_2 losses that include reactions in the ocean with dissolved minerals and gases from hot seafloor vents, and reactions of O_2 dissolved in rainwater with continental minerals, principally those containing elemental carbon, sulfide, and ferrous iron (Fig. 1). Gases that consume O_2 in the atmosphere or ocean are CH_4 , H_2 , CO , SO_2 , and H_2S . These are released either from hot rocks that melt (volcanism) or hot rocks that do not melt (metamorphism). Estimates of their fluxes are shown in Table 2. The O_2 sink from submarine and subaerial volcanic gases is ~ 2.3 Tmol O_2 year $^{-1}$, metamorphic gases consumes ~ 3.1 Tmol O_2 year $^{-1}$, and subduction of oxidized seafloor causes a loss of ~ 0.2 Tmol O_2 year $^{-1}$. The sink due to continental weathering is

Oxygenation of the Earth's Atmosphere. Table 2 Modern sink fluxes of O₂ (Holland 2002; Catling and Kasting 2012)

Type of flux	$\times 10^{12}$ mol O ₂ year ⁻¹	Effect
Continental oxidative weathering	-(15.5 ± 6.7)	(Loss)
<i>Surface volcanic gases</i>		
H ₂	-(0.5 ± 0.3)	(Loss)
CO	-(0.05 ± 0.03)	(Loss)
H ₂ S	-(0.06 ± 0.03)	(Loss)
SO ₂	-(0.9 ± 0.3)	(Loss)
Total sink from surface volcanic gases $\sim -(1.5 \pm 0.7) \times 10^{12}$ mol O ₂ year ⁻¹		
<i>Submarine volcanic gases</i>		
H ₂	-(0.05 ± 0.03)	(Loss)
H ₂ S	-(0.7 ± 0.4)	(Loss)
CH ₄ (axial)	-(0.02 ± 0.01)	(Loss)
CH ₄ (off-axis)	-(0.5 ± 0.3)	(Loss)
Total sink from submarine volcanic gases $\sim -(0.8 \pm 0.7) \times 10^{12}$ mol O ₂ year ⁻¹		
<i>Surface metamorphic gases</i>		
CH ₄ (abiotic)	~0.6	(Loss)
CH ₄ (thermal breakdown of organics)	~2.5	(Loss)
Total sink from metamorphic gases $\sim -3.1 \times 10^{12}$ mol O ₂ year ⁻¹		
<i>Seafloor oxidation and subduction</i>		
Fe ²⁺ conversion to magnetite	~0.2	(Loss)
Total rate of oxygen loss $\sim (21.1 \pm 8.1) \times 10^{12}$ mol O ₂ year ⁻¹		

15.5 ± 6.7 O₂ year⁻¹, which is estimated from the composition of average rock undergoing weathering (Table 2). Thus, within the large ~40% uncertainty of the data, the source flux of O₂ from organic carbon and pyrite burial of 18.4 ± 7.8 Tmol O₂ year⁻¹ is matched by the total sink flux of 21.1 ± 8.1 Tmol O₂ year⁻¹. In the past, changes in the relative proportions of source and sink fluxes evidently caused O₂ levels to change.

Evidence for Earth's Oxygenation

The Great Oxidation Event at 2.45–2.32 Ga occurred in the Paleoproterozoic era (2.5–1.6 Ga), the first of three eras within the Proterozoic eon (2.5–0.542 Ga), which follows the Archean eon (before 2.5 Ga). After the Paleoproterozoic, the Mesoproterozoic (1.6–1.0 Ga) and the Neoproterozoic (1.0 Ga–542 Ma) eras follow. The second rise of O₂ (750–580 Ma) occurred in the Neoproterozoic. We can tell that O₂ levels changed by studying at the chemistry of rocks from these eras. The Great Oxidation Event (GOE) produced binary geochemical changes in the Paleoproterozoic because the atmosphere changed the oxidation states (from weakly reducing to oxidizing), whereas the Neoproterozoic changes are subtler because an oxic atmosphere merely

became more oxygenated. Let us consider evidence for the GOE and Neoproterozoic increase of O₂ in turn.

Evidence for the Great Oxidation Event (GOE)

The different oxidation state of continental minerals that were formed before and after the GOE records a change from an atmosphere essentially devoid of O₂ to one redox dominated by O₂. The presence or absence of O₂ changes the chemistry of minerals that are formed because O₂ dissolves in rainwater and reacts with minerals. Three continental indicators are red beds, paleosols, and detrital grains (Holland 1984). *Red beds* are riverbanks, deserts, and floodplains with a reddish pigmentation that arises when an iron oxide coating on mineral grains is produced from the rusting of iron minerals. Before the GOE, no red beds are found in the geologic record, indicating a lack of O₂, whereas afterward red beds are common. *Paleosols* are lithified soils. Before the GOE, paleosols show a loss of iron, which is consistent with leaching by ancient anoxic rainwater, whereas after ~2.2 Ga, iron is not leached. Iron will be flushed through a soil in the form of soluble ferrous iron ions (Fe²⁺) if rainwater has little dissolved O₂ but if the air contains >0.2% O₂, iron will be oxidized into

insoluble and immobile oxides such as **▶ hematite** (Fe_2O_3). Cerium is another redox-sensitive element that has also been examined in paleosols. Cerium oxidizes from Ce^{3+} to Ce^{4+} to form cerianite (CeO_2), so the presence of Ce^{3+} -rich minerals in paleosols from the Archean implies an early anoxic atmosphere. *Detrital grains* in sediments are those that are never completely dissolved during the process of weathering. Rounded detrital grains from sediments deposited by turbulent Archean rivers commonly contain minerals that would only survive at very low levels of O_2 . Detrital grains of pyrite (FeS_2), uraninite (UO_2), and siderite (FeCO_3) place bounds on the concentration of Archean O_2 of roughly $<2\%$, $<0.2\%$, and $<0.02\%$, respectively, compared to today's 21% O_2 . In modern oxygenated waters, uraninite dissolves to form soluble U^{6+} ions, pyrite oxidizes to soluble sulfate (SO_4^{2-}) and hematite, and siderite rusts to produce insoluble hematite.

The chemistry of seawater also changed after the GOE, with increased levels of sulfate and much decreased levels of redox-sensitive elements such as manganese and iron that are insoluble when oxidized. Marine sulfur isotopes are the data that indicate an increase in sulfate concentrations. Today, sulfate-reducing bacteria produce most of the sulfide in marine sediments. These bacteria reduce $^{32}\text{SO}_4^{2-}$ in preference to $^{34}\text{SO}_4^{2-}$ so that bacterial sulfide is enriched in ^{32}S . However, this fractionation ceases in waters with <0.2 mM sulfate concentration. Archean sulfides have $^{34}\text{S}/^{32}\text{S}$ ratios close to an unfractionated mantle value, implying Archean oceans with <0.2 mM sulfate, compared to 28.9 mM in today's surface seawater. Rivers ultimately supply sulfate to the ocean by washing sulfate off the land where it is produced by the oxidation of sulfides by oxygenated rainwater. Consequently, the low concentration of seawater sulfate before the GOE is consistent with low atmospheric O_2 . By 2.3–2.2 Ga, sulfides with significant ^{34}S depletions formed ubiquitously in the ocean, reflecting increased sulfate and the rise of O_2 . When O_2 rose, it also oxidized and titrated manganese out of the ocean, producing the world's largest manganese deposit found in the 2.2 Ga Hotazel Formation in South Africa. The presence of **▶ banded iron formations** (BIFs) provides evidence that the deep ocean was devoid of O_2 in the Archean, unlike today. By definition, BIFs are laminated marine sedimentary rocks containing ≥ 15 wt% iron, with alternating iron-rich and iron-poor layers. The iron mainly originated from hydrothermal sources in the deep ocean, such as midocean ridges. Today, iron is oxidized in the deep ocean and deposited on the flanks of the ridges. But in the anoxic depths of Archean oceans, ferrous iron was transported to the continental shelves where it

was (microbially) oxidized and precipitated as iron minerals in the BIFs. In the Paleoproterozoic, BIFs decline in abundance and disappear after ~ 1.8 Ga. Chromium (Cr) isotopes in the BIFs also record changes in atmospheric O_2 . When insoluble Cr^{3+} is oxidized to soluble Cr^{6+} during oxidative weathering, the heavy isotope ^{53}Cr is preferentially oxidized relative to ^{52}Cr . After transport from rivers to the ocean, the Cr isotopic fractionation is preserved in ocean sediments. An increase in the abundance of ^{53}Cr after 2.4 Ga compared to Archean samples further confirms the GOE.

The strongest evidence for the GOE is a large amount of mass-independent fractionation (MIF) of **▶ sulfur isotopes** in sedimentary rocks older than 2.45 Ga compared to little or no sulfur isotope MIF in rocks younger than 2.32 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 , that is, a linear relationship with mass difference. Most processes, such as microbial sulfate reduction, produce mass-dependent isotope fractionation. In contrast, mass-independent fractionation in sulfur isotopes is where the relative abundance of different isotopes deviates from linear, mass-dependent fractionation. Laboratory studies show that large MIF is produced exclusively from photochemical reactions, such as the photolysis of SO_2 . Three conditions are needed for the production and preservation of the sulfur isotope MIF: O_2 levels below about 1 ppmv, sufficient sulfur gas in the atmosphere, and relatively large concentrations of reducing gases. In a high- O_2 atm, sulfur gases are rapidly oxidized and rained out as dissolved sulfate. But in the absence of O_2 and in the presence of reducing gases such as 10^2 – 10^3 ppmv methane, sulfur exits the atmosphere as sulfide, elemental sulfur, or sulfate, which allows the mass-independent fractionation produced by anoxic photochemistry to be segregated and preserved in different sedimentary minerals. In summary, the sulfur isotope MIF provides evidence for an Archean atmosphere with both low O_2 and high methane.

Donald Canfield (of the University of Southern Denmark) has proposed that a significant fraction of the deep ocean remained sulfidic rather than oxygenated during much of the Proterozoic, after 1.8 Ga (Canfield 2005; Lyons et al. 2009). In this model, BIFs declined because increased sulfate in the surface ocean caused sulfate-reducing bacteria to provide a flux of sulfide to the deep ocean, which scavenged ferrous iron into insoluble iron sulfides. This is an alternative to a model where the disappearance of BIFs at 1.8 Ga is explained by the oxygenation of the deep ocean and the formation of insoluble iron

oxides (Holland 2006). In today's ocean, <0.5% of the seafloor is *euxinic*, meaning oxygen free with H₂S. Molybdenum (Mo) isotopes are useful indicators of oxygenation and euxinia because oxic uptake of Mo on marine solids preferentially removes ⁹⁵Mo relative to ⁹⁸Mo, leaving the ocean isotopically heavy. In contrast, in times of low oxygenation, marine Mo is isotopically light. In highly euxinic deep waters, Mo is scavenged efficiently and tends to capture the Mo isotope composition of seawater. Rocks that are ⁹⁵Mo-enriched from the 1.7–1.4 Ga MacArthur Basin in Australia suggest that the deep ocean in the mid-Proterozoic seafloor was commonly oxygen-poor, with a greater proportion of euxinia than today. The data suggest that the euxinia was probably only several percent of the ocean's area, but this is enough to have had a significant effect in depleting trace metals in the Mesoproterozoic Ocean, which may have impacted marine ecology for a billion years until the Neoproterozoic.

Evidence for a Neoproterozoic “Second Rise” in Oxygen

Sulfur and chromium isotopes in marine sediments indicate that O₂ increased in the late Neoproterozoic. At this time, marine sedimentary sulfides occur with ³²S-enrichment exceeding the isotope discrimination of sulfate-reducing bacteria. The interpretation is that isotopically light sulfide was re-oxidized at the sediment-water interface and cyclically re-reduced by sulfur-disproportionating bacteria, which increased the isotope fractionation. The greater sulfur isotope fractionation is therefore related to oxygenation of the near-shore seafloor. Canfield (2005) has estimated that the oxygenation required atmospheric O₂ concentrations in excess of 1–4%. A large increase in the abundance of marine ⁵³Cr relative to ⁵²Cr after 750 Ma also confirms an increase in atmospheric O₂. Oxygen would have mobilized greater amounts of chromium during continental oxidative weathering, which is the mechanism of isotopic fractionation mentioned earlier. Fossil evidence for animals greater than a few millimeters or more in size also suggests that O₂ concentrations exceeded 2%, which is the minimum level that can support aerobic metabolism in such animals via O₂ supplied by diffusion.

When Did Oxygenic Photosynthesis Evolve?

In order to understand the early history of atmospheric O₂, we need to examine the evidence for the advent of oxygenic photosynthesis. In particular, the geologic record suggests that oxygenic photosynthesis arose 300 Ma or more before the GOE. This timing is inferred from a variety of proxies including biomarkers, nonmarine

stromatolites, redox-sensitive metals, and sulfur isotopes, which we discuss in turn.

Biomarkers are recognizable derivatives of biological molecules, which are usually in the form of certain hydrocarbons found in kerogen (noncrystalline sedimentary organic matter) or oil. Chemical changes induced when sediments convert into rock strip biological molecules of functional groups but can often leave a distinctive molecular backbone, in a way that is analogous to the more familiar macroscopic process that removes flesh to leave fossilized skeletons that we can associate with particular life forms. Biomarkers from the Archean have been the subject of controversy because of the possibility of contamination from modern molecules or fluid migration over geologic time and uncertainties regarding their specificity for particular organisms and metabolisms. Recent advances in ultraclean drilling and the ability to analyze oil-bearing fluid inclusions help to address concerns about contamination. Biomarkers for cyanobacteria are 2- α -methylhopanes, which are derived from compounds in cell membranes. Long chain varieties of these particular molecules (i.e., >C₃₁) occur very rarely outside the cyanobacteria. In addition, steranes derive from sterols, which are found in the membranes of eukaryotes and synthesized in a pathway that requires free molecular oxygen. For example, 11 molecules of O₂ are required to produce one molecule of cholesterol. No bacteria are known to synthesize C₂₆–C₃₀ sterols and archaea do not synthesize sterols at all. The simultaneous co-detection of long chain (>C₃₁) 2- α -methylhopanes with eukaryotic sterols is thus a reasonable biosignature for oxygenic photosynthesis. Such a combination of biomarkers has been found in fluid inclusions in the 2.45 Ga Matinenda Formation at Elliot Lake, Canada, which consists of sandstones deposited prior to the GOE (Dutkiewicz et al. 2006). Also, meticulous measurements of biomarkers from 2.72 to 2.56 Ga rocks in the Hamersley Province of northwest Australia (Eigenbrode et al. 2008) and 2.67–2.46 Ga rocks from the Transvaal of South Africa (Waldbauer et al. 2009) suggest the presence of microbial ecosystems that produced O₂ as well as consumed it.

Stromatolites (laminated rocks formed by microbes) from a 2.72 Ga lake in the Tumbiana Formation in northwest Australia possibly confirm the presence of O₂ production. Geologic evidence shows that the lake lacked sulfate and hydrothermal reductants needed for non-oxygen-producing photosynthesis. Consequently, a process of elimination suggests that microbial communities using oxygenic photosynthesis may have constructed these particular stromatolites (Sakurai et al. 2005).

Furthermore, the mobility of redox-sensitive metals indicates the presence of some O₂ before the GOE, and therefore the presence of oxygenic photosynthesis. Molybdenum (Mo), rhenium (Re), and chromium (Cr) are soluble only when oxidized. Consequently, a spike in Mo and Re concentrations found in 2.5 Ga sedimentary rocks in the Hamersley district of northwest Australia suggests that a transient “whiff” of O₂ occurred in the atmosphere about 100 million years prior to the GOE (Anbar et al. 2007). The whiff is confirmed by contemporaneous evidence of sulfur isotopic fractionation indicating a spike of sulfate. Enrichments of ⁵³Cr relative to ⁵²Cr (which are induced by oxidative weathering) are also found in banded iron formations at low levels for at least 300 million years prior to the GOE, which is consistent with the biological production of O₂ (Frei et al. 2009). In summary, multiple lines of evidence suggest that oxygenic photosynthesis existed at least 0.3 billion years before the GOE.

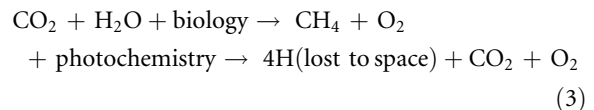
Theories for Oxygenation

At present, a framework has been developed for understanding why the GOE occurred, but the cause of the second rise of O₂ in the Neoproterozoic remains very obscure (Catling and Claire 2005).

The GOE happened because either O₂ production increased or O₂ consumption declined. The ancient, pre-2.45 Ga oceans were largely devoid of sulfate, so that organic carbon burial dominated O₂ production prior to the GOE, while pyrite burial was unimportant. Consequently, it has been argued that O₂ rose because the rate of organic carbon burial (O₂ production) increased, either as a pulse or long-term trend. One suggestion is that the growth of early continental shelves promoted organic carbon burial and oxygen production. But there are grounds for skepticism about this proposal. Organic matter extracts the light carbon isotope, ¹²C, from seawater, but marine carbon, recorded in ancient limestone, does not significantly decrease in ¹²C content between mid-Archean and Mesoproterozoic rocks. Notably, at 2.3–2.1 Ga, many marine carbonates are unusually depleted in ¹²C relative to ¹³C, which could be explained if there was a large pulse of burial of organic carbon, but then the ¹²C content returns to its previous value. A burial pulse would merely generate a parallel pulse of O₂, given the short residence time of O₂ and not a persistently increased level of O₂. Instead, the pulse was more plausibly an effect of increased O₂ because the Paleoproterozoic excursions in the ¹²C of limestones follow the rise of O₂ before 2.32 Ga.

A widely accepted explanation for why little atmospheric O₂ accumulated in the Archean is that a large

flux of volatile and aqueous reductants, that is, chemicals that consume oxygen, scavenged the O₂. In time, the geological sources of reductants declined to the point where the O₂ flux produced from organic carbon burial exceeded the kinetically rapid consumption flux. At this tipping point, oxygen flooded the atmosphere until O₂ levels reached a new plateau where continental weathering became the predominant balance for O₂ production. Various suggestions have been made for why the proportion of reductants in volcanic or metamorphic outgassing might diminish and cause such a tipping point. One suggestion is that a change in the style of outgassing from submarine to subaerial volcanism favored a decline in the proportion of reductants. Another consideration is that an anoxic atmosphere would always allow a relatively high concentration of hydrogen-bearing reducing gases. At high altitude, the decomposition of such gases causes hydrogen to escape to space at a rate that is significant on geologic timescales, which oxidizes the whole Earth and diminishes further release of reductants. In particular, in an anoxic atmosphere, methane reaches concentrations hundreds of times greater than today's 1.8 ppmv. Most methane is ultimately produced microbially from fermentation of photosynthesized organic matter. Ultraviolet light decomposes methane in the upper atmosphere, causing it to lose hydrogen. When hydrogen escapes from the planet, oxygen is gained irreversibly through a schematic reaction as follows:



Evidence for this hypothesis is found in the redox components of the crust. If photosynthesis were the only process responsible for segregating redox components, the number of moles of equivalent O₂ in the Earth's crust should be balanced by equimolar reduced carbon (Eq. 1). But instead there is excess oxygen in the crust by a factor of 1.5–2.2 (Catling and Claire 2005; Sleep 2005). The excess can be quantitatively reconciled with time-integrated hydrogen escape and net oxidation expected from a methane-rich Archean atmosphere.

Various geological and biological causes have been suggested for the Neoproterozoic second rise of oxygen, but the problem remains unsolved. Geological proposals include the enhanced production of clays that adsorbed and buried organic matter, or the assembly of a supercontinent whose weathering added nutrients to the sea and stimulated organic carbon burial. Also, it has been suggested that moderately high levels of methane



throughout the Proterozoic could have promoted hydrogen escape and oxidized the Earth. Biological proposals include continental weathering accelerated by lichen, and the evolution of zooplankton with fecal pellets that enhanced organic burial. However, presently, all of these ideas for the cause of the second rise of O₂ are, at best, just qualitative proposals.

Conclusion and Future Directions

The atmosphere evolved from an anoxic to oxygenated state. There are multiple lines of geochemical evidence for a rise of O₂ or *Great Oxidation Event* (GOE) at 2.45–2.32 Ga. However, oxygenic photosynthesis appears to have existed at least 0.3 billion years beforehand. A self-consistent explanation for the delay between the origin of oxygenic photosynthesis and oxygenation of the atmosphere is that excess volatile reductants efficiently scavenged O₂. This sink on O₂ diminished until the GOE occurred. Following the GOE, sulfate levels increased in the ocean as a result of a greater role for oxidative weathering in balancing O₂ production from the burial of organic carbon and pyrite. In the late Precambrian, around 750–580 Ma, a second rise of O₂ occurred, along with a further increase in marine sulfate. This second rise appears to have been a precursor to the appearance of macroscopic animals.

Considerable further research will no doubt further constrain the levels of O₂ through geologic time and our understanding of the past biogeochemical cycles of various elements – such as carbon, sulfur, and nitrogen. Measurements of new isotopic systems, such as those of trace metals, will no doubt bring advances. Biomarkers also have the potential to reveal what microorganisms and microbial processes were present in the Precambrian biosphere. So it is likely that further study of biomarkers will help us better understand the role of microbial ecology in shaping the oxidation state of Earth's ancient atmosphere.

See also

- ▶ Archean Environmental Conditions
- ▶ Archean Traces of Life
- ▶ Banded Iron Formation
- ▶ Biomarkers
- ▶ Carbon Isotopes as a Geochemical Tracer
- ▶ Earth, Formation and Early Evolution
- ▶ Earth's Atmosphere, Origin and Evolution of
- ▶ Great Oxygenation Event
- ▶ Hematite
- ▶ Iron Oxyhydroxides
- ▶ Isotope Biosignatures
- ▶ Nitrogen Isotopes
- ▶ Oceans, Origin of
- ▶ Oxidizing Atmosphere
- ▶ Oxygenic Photosynthesis
- ▶ Photosynthesis
- ▶ Pilbara Craton
- ▶ Redox Zonation
- ▶ Siderite
- ▶ Sulfidic Oceans
- ▶ Sulfur Cycle
- ▶ Sulfur Isotopes
- ▶ Transition Metals and Their Isotopes
- ▶ Transvaal Supergroup, South Africa

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