

The coupled evolution of life and atmospheric oxygen

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ABSTRACT

See Plates 4 and 5

This review highlights the reciprocal influences of evolution on oxygen and of oxygen on evolution. Without life there would be very little free oxygen at the Earth's surface. Over Earth history, oxygen has risen from negligible concentrations to ~ 0.21 atm (~ 21% of the present atmosphere), in a series of steps. Atmospheric oxygen is the product of oxygenic photosynthesis, which probably evolved over 3.5 Gyr ago (billion years ago), and was definitely occurring in cyanobacteria 2.7 Gyr ago. The capacity to detoxify reactive oxygen species and the potential for aerobic respiration arose before oxygenic photosynthesis. Oxygen remained below 0.0008 atm until 2.2 Gyr ago, but probably reached significant dissolved concentrations in localized oxygen oases, including microbial mats. Localized accumulation of oxygen triggered an increase in defences against oxygen toxicity, the development of metabolic pathways utilizing oxygen, and facilitated the appearance of eukaryotic cells with mitochondria. Between 2.2 and 2.0 Gyr ago the Earth underwent a great oxidation event in which atmospheric oxygen rose above 0.002 atm and possibly above 0.03 atm.

Exhaustion of some oxygen sinks and increased organic carbon burial (a major oxygen source) both contributed. The rise of oxygen generated an ozone layer providing effective UV protection, increased the availability of nitrogen in the ocean, but reduced the availability of many bio-essential metals. Eukaryotes with chloroplasts appeared at this time, possibly as a result of increased nitrogen availability. From 2.0 to 0.8 Gyr ago oxygen concentrations remained above 0.002 atm and were sufficient for the evolutionary radiation of multi-cellular eukaryotes, but fossil evidence for this does not appear until 1.0 Gyr ago. Oxygen rose again between 0.8 and 0.57 Gyr ago, exceeding 0.03 atm. Episodes of enhanced organic carbon burial in this interval have been attributed to favourable geologic conditions and the evolution of metazoans that produced fast-sinking faecal pellets. The deep ocean may not have been oxygenated until this time. Ventilation of the ocean opened an evolutionary window for the diversification of large metazoans seen in the Cambrian explosion 0.54 Gyr ago. By 0.37 Gyr ago oxygen had exceeded 0.14 atm, and by 0.3 Gyr ago it had reached at least 0.21 atm, driven upwards by vascular plants colonizing the land surface and increasing organic carbon burial. Since then, the atmospheric fraction of oxygen has been stabilized close to 21% by feedback mechanisms involving terrestrial and marine biota. These have prevented oxygen rising to dangerously flammable concentrations for forests (~ 25%), or falling to suffocating concentrations for large animals (~ 15%). Previous estimates that oxygen reached ~ 35% of the atmosphere in the late Carboniferous (0.3 Gyr ago) need to be reconsidered.

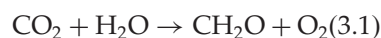
3.1 Introduction

An appreciation that air, fire and life are linked can be found throughout much of recorded history, but it was not until the Enlightenment that the connecting substance was isolated (Gilbert, 1981). Joseph Priestley, a liberal minister in England, is usually credited with the discovery of oxygen in 1774. Priestley realized that since even a small candle uses a large amount of pure air, there must be a provision in nature to replace it, and he found that a sprig of mint would revive the foul air left after combustion, such that it could support a flame once more. When heating mercury(II) oxide, Priestley discovered that it gave off large amounts of a gas in which a candle would burn with an enlarged flame, and in which mice lived longer than in a similar volume of normal air. Priestley named the gas 'dephlogisticated air' because he firmly believed the erroneous theory that combustion releases a substance called phlogiston into the air. Karl Wilhelm Scheele, a pharmacist in Sweden, independently isolated oxygen about two years before Priestley but was slower to publish his finding. He named the gas 'fire air' because it supports combustion. Antoine Lavoisier discovered the mechanism of oxidation in 1775 and was the first to appreciate the chemical significance of the action of oxygen. He repeated Priestley's experiments and by 1778 was convinced that the gas given off by heating mercury(II) oxide is the same one that is present in the air and combines with substances during combustion. Lavoisier called it 'oxygine' (from the Greek 'acid producing').

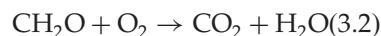
Oxygen is a colourless, odourless, gaseous element. Its common form is the diatomic oxygen molecule, O_2 (dioxygen). Oxygen reacts with most other elements to form oxides. It is the most abundant element in the Earth's crust (49.2% by weight, 58% of the atoms), and the dioxygen molecule, O_2 , comprises 20.946% of the Earth's atmosphere by volume (Duursma and Boisson, 1994).

O_2 is released during oxygenic photosynthesis. There are two principal reactions. In the light-dependent reaction, energy from sunlight

is absorbed by photosynthetic pigments (principally chlorophyll) and used for the photolysis of water. The electrons released pass along an electron transfer chain, losing their energy, some of which is used to convert ADP to ATP (photophosphorylation). Electrons and protons released in the photolysis of water are also used to reduce NADP to NADPH. The ATP and NADPH produced in the light reaction provide energy and reducing power, respectively, for the ensuing light-independent (or 'dark') reaction. In this reaction carbon dioxide is reduced to carbohydrate in a metabolic pathway known as the Calvin cycle. Oxygenic photosynthesis can be summarized by the equation:

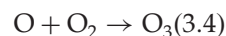
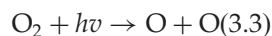


O_2 is the strongest molecular oxidant widely available to life, meaning that in oxidation reactions it gives the greatest energy yield, and hence aerobic respiration is widespread:



All eukaryotes use aerobic respiration with organic carbon as fuel. In contrast, prokaryotes show great metabolic diversity, using many different oxidants. As well as being essential to aerobes, O_2 is very toxic. Obligate anaerobes cannot use free O_2 for metabolism, and are typically killed by exposure to it. Facultative anaerobes are normally aerobic but can respire anaerobically during periods of O_2 shortage.

There is a triatomic form of oxygen, O_3 , commonly known as ozone. Ozone (O_3) is a colourless gas, produced by the action of high-energy ultraviolet radiation on O_2 :



Its presence in the stratosphere acts as a protective screen for ultraviolet radiation called the ozone layer. However, ozone is also a potent greenhouse gas and a powerful oxidant. Human and natural sources of NO_x and volatile organic carbon compounds (VOC) lead to photochemical production of O_3 in the troposphere, and can cause ozone to reach sufficient concentrations in the boundary layer to cause

oxidative damage to plants and animals (Mudd, 1996).

This chapter reviews the contemporary oxygen cycle (section 3.2), the history of atmospheric oxygen (section 3.3), its toxicity (section 3.4), its influences on evolution (section 3.5), and the mechanisms that have controlled its concentration (section 3.6).

3.2 The oxygen cycle

Figure 3.1 summarizes the global oxygen cycle, which is currently close to steady state. O_2 is

liberated in net primary production (which is the balance of oxygenic photosynthesis and aerobic respiration by the primary producers) and a corresponding amount of organic matter is generated. Almost all of this O_2 and organic carbon is consumed in aerobic respiration by heterotrophs, or in methane production (by methanogens) and its subsequent oxidation (by methanotrophs or by chemical reaction). A small remainder (currently $\sim 0.1\%$) of the O_2 produced in oxygenic photosynthesis provides a net source of O_2 to the atmosphere. This source flux corresponds to the small amount of organic carbon that is buried in new sediments,

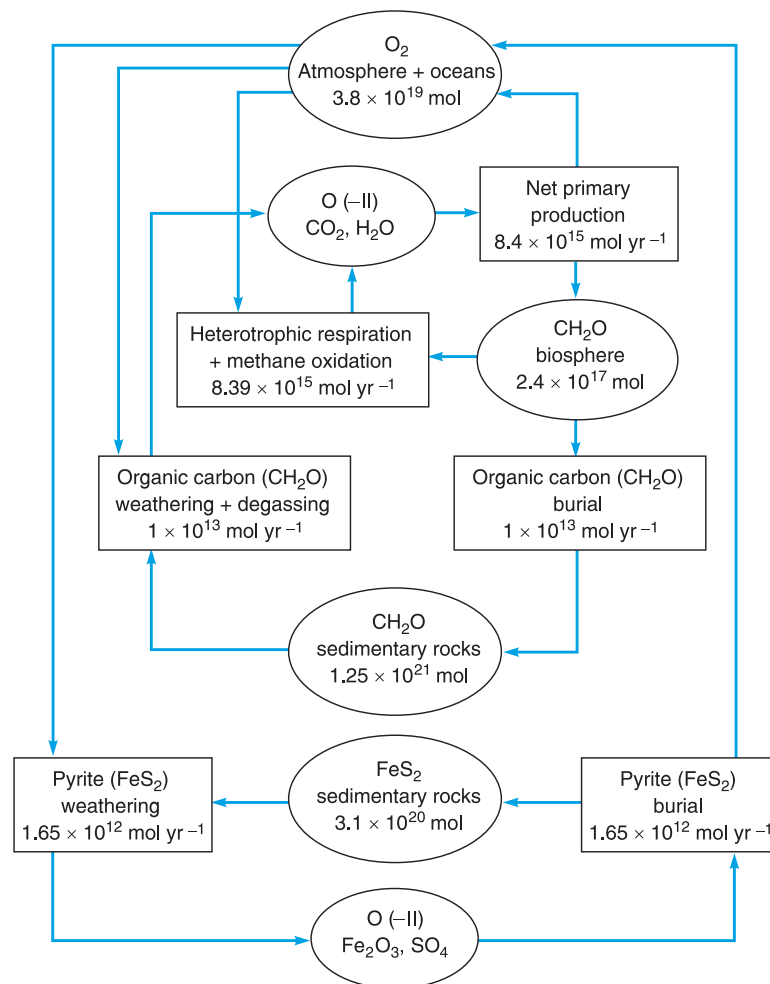
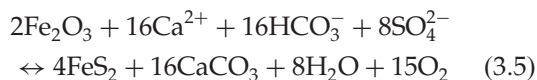


Figure 3.1 The oxygen cycle. Ovals indicate reservoirs in moles of O_2 or reducing equivalents. Boxes indicate fluxes in moles of O_2 per year. Estimated values are from Schlesinger (1997), Betts and Holland (1991), Berner and Canfield (1989) and Van Cappellen and Ingall (1996).

having escaped aerobic respiration or conversion to methane and subsequent oxidation. The effect of organic carbon burial is described by the same chemical equation as photosynthesis (3.1) (with 'CH₂O' referring to the organic carbon being buried in rocks). The corresponding sink flux of O₂ is the oxidation of organic carbon exposed in rocks on the continents (oxidative weathering) or degassed by volcanic and metamorphic activity. Oxidative weathering of organic carbon is sometimes called the 'respiration' of the rocks, because the overall chemical reaction is identical to aerobic respiration (3.2).

There are also significant burial and weathering fluxes of the other main redox elements – iron and sulphur. Iron pyrite (FeS₂), which contains both iron and sulphur in reduced form, is produced by bacteria that use sulphate and Fe(III) as oxidants. For each mole of sulphur buried 15/8 moles of O₂ are liberated. The reaction is reversed when pyrite undergoes oxidative weathering:



Currently $\sim 1.65 \times 10^{12} \text{ mol O}_2 \text{ yr}^{-1}$ are exchanged due to pyrite burial and weathering (Berner and Canfield, 1989) and $\sim 1 \times 10^{13} \text{ mol O}_2 \text{ yr}^{-1}$ due to organic carbon burial and weathering (Betts and Holland, 1991). Hydrogen escape to space provides a further source of oxygen and oxidation of reduced volcanic gases such as H₂ a further sink, but these are minor components of the current O₂ budget. $3.75 \times 10^{19} \text{ mol O}_2$ is present in the atmosphere and $3.1 \times 10^{17} \text{ mol O}_2$ is dissolved in the ocean (Duursma and Boisson, 1994). Dividing the total atmosphere/ocean oxygen reservoir by the net source (or sink) flux gives a 'residence time' for O₂ of ~ 3.25 million years. This is the average amount of time an O₂ molecule spends in the atmosphere/ocean system.

Far more O₂ has been produced since the origin of oxygenic photosynthesis than is currently present in the atmosphere and ocean. The reservoir of organic carbon in the crust is $\sim 1.25 \times 10^{21}$ moles (Berner and Canfield, 1989; Berner, 1991) and assuming that oxygenic photosynthesis has been the dominant path-

way of carbon fixation since the origin of life, a corresponding number of moles of O₂ have been produced. A further $\sim 3.1 \times 10^{20}$ moles of O₂ have been liberated due to FeS₂ burial in the crust. The atmospheric and oceanic O₂ reservoirs are $\sim 2.4\%$ and $\sim 0.02\%$ of the total, respectively. The remaining ~ 40 times as much oxygen must have formed oxidized compounds, which are incorporated in the rocks of the crust and the mantle. These include ferric oxide in the form of banded iron formations and redbeds and sulphate minerals such as gypsum.

3.3 History of atmospheric oxygen

Over the history of life on Earth, atmospheric oxygen has risen intermittently from essentially zero to its present concentration and the oxygen cycle has undergone major reorganizations. This section reviews the constraints on the oxygen trajectory that have been derived from models of atmospheric chemistry, geochemical evidence, and the O₂ requirements of past organisms. The discussion spans the four geologic eons of Earth history: Hadean, ~ 4.5 –4 Gyr ago (billion years ago); Archean, 4–2.5 Gyr ago; Proterozoic, 2.5–0.57 Gyr ago; and Phanerozoic, 0.57–0 Gyr ago. Past oxygen concentrations are generally expressed as partial pressures (pO₂) in atmospheres (1 atm = 101 325 pascals = 60 mm Hg) or as fractions or percentages of present atmospheric level (PAL), which is ~ 0.21 atm. These measures are independent of the total atmospheric pressure. However, Phanerozoic oxygen levels are often expressed as fractions or percentages of the atmosphere, because the proportion of oxygen to unreactive gas determines flammability and this in turn sets narrow constraints on O₂ variation. Usually it is assumed that the reservoir of inert gas, mostly N₂, was constant (~ 0.79 atm) over Phanerozoic time (Holland, 1978). Oxygen partial pressure and atmospheric fraction (f_{O₂}) can then be easily interconverted: $f_{\text{O}_2} = p_{\text{O}_2} / (p_{\text{O}_2} + 0.79)$, $p_{\text{O}_2} = 0.79f_{\text{O}_2} / (1 - f_{\text{O}_2})$.

After the formation of the Earth but before the origin of life, in the Hadean, there can only

have been negligible concentrations of atmospheric O₂. O₂ would have been produced by photo-dissociation of H₂O and CO₂ at high altitudes, reaching $\sim 10^{-3}$ atm at 60 km. However, there was an excess of H₂ supply from volcanoes over O₂ supply at low altitudes, and the by-products of water vapour photolysis catalyses the reaction between these two gases. This kept O₂ $< 10^{-12}$ PAL (pO₂ $< 10^{-15}$ atm) near the Earth's surface (Kasting, 1993).

There is isotopic evidence for life on Earth early in the Archean, 3.85 Gyr ago, in the oldest sedimentary rocks (Mojzsis *et al.*, 1996). Reduced carbon microparticles in rocks from >3.7 Gyr ago are of biogenic origin and may have been derived from planktonic photoautotrophs (Rosing, 1999). Oxygenic photosynthesis evolved early in the history of life, but how early is still poorly constrained. Photosystem II, which liberates oxygen, evolved after photosystem I. Hence the first photosynthesizers with just photosystem I were anaerobic and may have used H₂S as a reductant to produce free sulphur (as in green sulphur bacteria) or sulphate. These sulphur bacteria would have drained the limited supplies of H₂S in the ocean, thus inadvertently selecting for oxygenic photosynthesis using abundant H₂O as a reductant. Molecular fossils (biomarkers) provide direct evidence of cyanobacteria, the first oxygenic photosynthesizers, 2.7 Gyr ago (Brocks *et al.*, 1999) and 2.5 Gyr ago (Summons *et al.*, 1999). Indirect evidence suggests cyanobacteria may have originated long before this, probably in ancient microbial mats (DesMarais, 1991; Schopf, 1993). Bacterial microfossils from 3.5 Gyr ago bear a striking resemblance to modern cyanobacteria (Schopf, 1993). Organic nitrogen isotopes are consistent with cyanobacteria 3.4–2.7 Gyr ago (Beaumont and Robert, 1999). Cyanobacteria were almost certainly part of microbial mats that formed stromatolites in lakes 2.7 Gyr ago (Buick, 1992), and the stromatolite record extends back to 3.5 Gyr ago (DesMarais, 1991). The banded iron formations (BIFs) present from 3.5 Gyr ago may have been formed by reaction of ferrous iron with O₂ produced by oxygenic photosynthesis, but formation by anoxygenic photosynthesis is also possible (Widdel *et al.*, 1993).

Figure 3.2 summarizes the constraints on atmospheric oxygen that have been estimated for the past 3 billion years. The unlabelled points in Figure 3.2 are all paleosols (ancient soils that were exposed to the atmosphere), summarized by Rye and Holland (1998) who determined the pO₂ limits for each. In order of decreasing age: upper limit paleosols are Mt Roe (2.765 ± 0.01 Gyr), Pronto/NAN (2.46 ± 0.02 Gyr), Hokkalampi (2.32 ± 0.12 Gyr), Hekpoort (2.15 ± 0.1 Gyr); lower limit paleosols are Drakenstein (2.08 ± 0.16 Gyr), Flin Flon (1.85 ± 0.05 Gyr), Sturgeon Falls (~ 1.1 Gyr), Arisaig (~ 0.45 Gyr). Wolhaarkop (2.08 ± 0.16 Gyr) is also a paleosol, for which the pO₂ lower limit was determined by a different technique (Holland and Beukes, 1990). Uraninites upper limit is from Holland (1984). Biological lower limits on pO₂ are updated from Runnegar (1991) with earlier records of sterols (Brocks *et al.*, 1999) and *Grypania* (Han and Runnegar, 1992), and additional estimates for *Beggiatoa* (Canfield and Teske, 1996) and the Cambrian fauna (Holland, 1984). These biological constraints may reflect localized dissolved O₂ concentrations rather than the global atmospheric pO₂ concentrations suggested. The appearance of charcoal (Rowe and Jones, 2000) is the first convincing evidence for pO₂ nearing the present level.

Despite the existence of oxygenic photosynthesis, atmospheric oxygen remained at very low concentrations during the late Archean, because the source of O₂ was insufficient to overwhelm the flux of reduced gases from volcanoes and from photo-oxidation of iron and other reduced elements in the surface ocean. Late Archean pO₂ $\sim 10^{-11}$ atm has been estimated from a photochemical model (Kasting, 1991), while weathering profiles suggest higher concentrations, but still < 0.0005 atm before 2.44 Gyr ago (Rye and Holland, 1998). Methane was an important component of the late Archean atmosphere (~ 2.8 Gyr ago) that contributed significantly to the greenhouse effect (Lovelock, 1995), with pCH₄ > 0.00002 atm (Hayes, 1994; Rye and Holland, 2000) and probably pCH₄ > 0.0001 atm (Pavlov *et al.*, 2000). Local 'oxygen oases' in the surface ocean where photosyn-

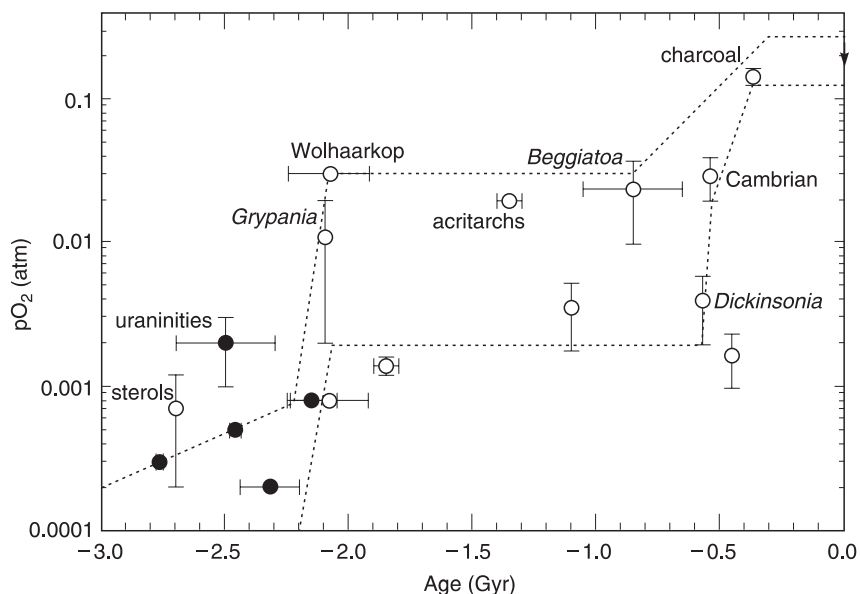


Figure 3.2 Geochemical and biological constraints on atmospheric oxygen over the past 3 billion years. Filled circles are estimated upper limits on oxygen. Empty circles are estimated lower limits on oxygen. The inverted triangle indicates the present partial pressure of oxygen. Age error bars indicate uncertainty in dating or the range of ages over which sediments were deposited. Partial pressure error bars indicate uncertainties in the estimates. The dashed lines are approximate upper and lower bounds on atmospheric oxygen. Unlabelled points are all paleosols (ancient soils that were exposed to the atmosphere) – see text for details.

thetic activity was high, could have had up to ~10% of the current dissolved oxygen concentration (Kasting, 1991), while in the active parts of cyanobacterial mats, oxygen could have reached supersaturating concentrations (L.J. Rothschild, personal communication). Evidence of oxygen demanding metabolic processes sets independent lower limits on local, dissolved oxygen concentrations. Isotopic evidence indicates that methanotrophs were globally abundant ~2.8 Gyr ago and these require $pO_2 \sim 0.0005$ atm to oxidize methane (Hayes, 1994). The production of sterols unique to eukaryote biochemistry was occurring 2.7 Gyr ago (Brocks *et al.*, 1999) and requires $pO_2 > 0.0002$ atm (0.001 PAL) (Runnegar, 1991). $pO_2 > 0.002$ atm (0.01 PAL) is required for aerobic respiration (Runnegar, 1991), and this probably also evolved in the Archean (Knoll, 1992). However, in each case it is likely that the oxygen consumers thrived in close proximity to oxygenic photosynthesi-

zers, e.g. in microbial mats (DesMarais, 1991) or ponds (Rye and Holland, 2000), while the bulk of the environment remained essentially oxygen free and chemically reducing.

Between about 2.2 and 2.0 Gyr ago in the early Proterozoic, a global oxidation event occurred in which atmospheric pO_2 rose from < 0.0008 atm to > 0.002 atm (Holland *et al.*, 1989; Rye and Holland, 1998) and possibly as high as > 0.03 atm (Holland and Beukes, 1990). This was the first major step in the oxidation of the Earth's surface environment (Holland, 1999). The bounds on O_2 are inferred from the weathering profiles of paleosols – ancient soils exposed to the atmosphere (Rye and Holland, 1998). These set limits on the O_2/C ratio of the atmosphere. When combined with an independent estimate of $pCO_2 < 0.02$ atm (Rye *et al.*, 1995) (obtained for 2.75–2.25 Gyr ago and assumed to hold 2.25–2.0 Gyr ago), a limit on the O_2 content of the atmosphere is obtained. Reduced iron is

mobile while oxidized iron is not. If Fe was mobile during weathering, as it is in paleosols older than 2.2 Gyr, this indicates that O₂ must have been below a certain concentration. If Fe was immobile, as it is in later paleosols, this indicates that O₂ must have been above a critical concentration. Red beds (oxidized layers) deposited above paleosols aged ~ 2.2 Gyr are indicative of more oxidizing conditions after this time (Rye and Holland, 1998), and the disappearance of large ore deposits of uraninite by 2.0 Gyr ago is also consistent with a major increase in O₂ (Holland, 1984). Organelle-bearing eukaryote fossils from 2.1 Gyr ago resemble the photosynthetic algae *Grypania* (Han and Runnegar, 1992). This organism respired aerobically and probably required pO₂ ~ 0.002–0.02 atm, but if it was photosynthetic it could have generated its own oxygen supply locally (Runnegar, 1991). The inference that pO₂ exceeded 0.03 atm in the interval 2.2–2.0 Gyr ago comes from a high degree of Fe retention in the Wolhaarkop paleosol (Holland and Beukes, 1990). If this reflects the global situation, O₂ may have peaked before relaxing to somewhat lower concentrations consistent with later constraints. A large positive carbon isotope shift of carbonates 2.2–2.0 Gyr ago suggests a massive increase in organic carbon burial, releasing an estimated 12–22 times the current atmospheric O₂ inventory, more than sufficient to generate the inferred rise in atmospheric O₂ (Karhu and Holland, 1996). Hypotheses for the ultimate cause of the oxidation event are discussed in section 3.6.

After the first major rise in oxygen, there was an interval of relative stability during the middle of the Proterozoic, 2.0–1.0 Gyr ago (although the precise oxygen concentrations are poorly constrained). Paleosols from 1.8–1.9 Gyr ago and ~ 1.1 Gyr indicate pO₂ > 0.002 atm. Spherical acritarch cells of 0.6 mm diameter from 1.3–1.4 Gyr ago can be used to derive higher minimum oxygen concentrations, assuming diffusion-limited respiration, but this is not robust because respiration may not have occurred in the centre of the cells (Runnegar, 1991). The last of the major banded iron formations were deposited ~ 1.8 Gyr ago

and this has usually been attributed to a rise in atmospheric oxygen ventilating the deep sea and removing ferrous iron (Holland, 1984). However, it has recently been suggested that the deep ocean remained anoxic until the late Proterozoic and that sulphide was responsible for removing iron from deep ocean water (Canfield, 1998). Simple models suggest that when atmospheric oxygen was an order of magnitude lower than now, if ocean nutrient concentrations and marine productivity were not greatly reduced, the demand for oxygen to respire sinking organic matter would have greatly exceeded the supply of oxygen (via diffusion from the surface and sinking of oxygen-rich surface waters). Hence all of the oxygen would have been removed from ocean water below the well-mixed surface layer.

Trends in the carbon isotope composition of sedimentary organic matter and carbonate through the Proterozoic suggest that the organic carbon reservoir grew in size, relative to the carbonate reservoir (DesMarais *et al.*, 1992). A second significant increase of oxygen has been postulated in the late Proterozoic. Carbon isotope studies suggest high organic carbon burial rates 1.1–0.8 Gyr ago (DesMarais *et al.*, 1992) and 0.8–0.7 Gyr ago (Knoll *et al.*, 1986). The evolution of non-photosynthetic sulphide-oxidizing bacteria (*Beggiatoa*) and an increase in sulphur-isotope fractionation suggest that oxygen increased from below to above 5–18% PAL (0.01–0.04 atm) during the interval 1.05–0.64 Gyr ago (Canfield and Teske, 1996). This appears to conflict with the estimate that pO₂ had already exceeded 0.03 atm, 2.0 Gyr ago (Holland and Beukes, 1990). Hence the suggestion above that oxygen peaked ~ 2.0 Gyr ago before relaxing to a lower concentration for most of the Proterozoic. A further increase in oxygen has been suggested in a relatively brief interval just before the Cambrian boundary 0.6–0.57 Gyr ago (Logan *et al.*, 1995).

The first large multi-cellular creatures, the Ediacara, appeared near the end of the Proterozoic, ~ 0.6 Gyr ago. They have conventionally been interpreted as metazoans adapted to low dissolved oxygen concentrations. If it was a metazoan, *Dickinsonia* would only have

required $pO_2 \sim 0.002$ atm (Runnegar, 1991). This would be consistent with parts of the ocean remaining anoxic right until the end of the Proterozoic (Canfield, 1998). However, the evolutionary scenario is counterintuitive – the first large metazoans are unlikely to evolve in the most oxygen-depleted habitats. The alternative hypothesis is that the Ediacara were phototrophs and therefore generated their own O_2 supply (McMenamin, 1998). Evidence from paleosols suggests that atmospheric oxygen had been >0.002 atm since 2.0 Gyr ago (Rye and Holland, 1998).

Concentrations of oxygen in the first 200 million years of the Phanerozoic eon (0.57–0.37 Gyr ago) are poorly constrained. The fauna appearing in the Cambrian required dissolved $[O_2] >45 \mu\text{mol kg}^{-1}$ which in turn demands atmospheric $pO_2 >0.02$ atm, but it could have been much higher (Holland, 1984). Geochemical models driven by the abundance of reduced matter in different rocks or by carbon and sulphur isotope records predict $pO_2 \sim 0.1$ – 0.2 atm (Berner, 1989; Berner *et al.*, 2000), but these should be treated with caution because the data driving them are scarce in this interval and they are probably missing key feedback mechanisms. The colonization of the land surface by plants, which began ~ 420 Myr ago (million years ago) caused large amounts of organic carbon to be buried on the continents for the first time (Berner and Canfield, 1989) and produced lignin, which is difficult to biodegrade and hence tended to be buried in continental and marine sediments. Plants also amplified the rate of rock weathering, enhancing the supply of phosphorus to the land surface and oceans, thus tending to increase productivity and organic carbon burial (Lenton and Watson, 2000). These mechanisms should have increased atmospheric O_2 .

By ~ 370 Myr ago the first fossilized charcoal appeared (Rowe and Jones, 2000) suggesting that oxygen had risen sufficiently high to sustain fires. Combustion experiments indicate that fire cannot be sustained in dry paper at 17% O_2 (Watson, 1978). Burning wood is extinguished when O_2 is reduced to 13.2–19%, depending on the orientation of the fuel (Rasbash and Langford, 1968). The charcoal

record has been continuous since 350 Myr ago, indicating that O_2 has been at least $\sim 15\%$ of the atmosphere since then (early Carboniferous). Combustion experiments also indicate that small increases in O_2 above 21% cause large decreases in the ‘ignition energy’ required to start and sustain fire (Watson, 1978). This translates into a rapid increase in fire probability with rising oxygen. However, forests have been widespread throughout the past 350 million years, indicating that fires have never been so frequent as to prevent forest regeneration. This suggests that O_2 has never risen above some critical upper limit, which has been estimated as $\sim 25\%$, using terrestrial ecosystem models (Watson, 1978; Lenton and Watson, 2000).

Data on the abundance and organic carbon and pyrite sulphur contents of different sediment types have been used to force a geochemical model which predicts that atmospheric oxygen rose to $\sim 35\%$ in the Carboniferous (~ 300 Myr ago), dropped to $\sim 15\%$ in the Triassic (~ 200 Myr ago) and rose again to $\sim 27\%$ in the Cretaceous–early Tertiary (~ 50 Myr ago) (Berner and Canfield, 1989). Early models driven by carbon and sulphur isotope records tended to predict even larger, unrealistic oxygen variations, including negative values (Berner, 1987; Berner, 1989; Lasaga, 1989). Recognition that carbon and sulphur isotope fractionation are sensitive to oxygen concentration can return oxygen variations between $\sim 35\%$ and $\sim 15\%$ (Berner *et al.*, 2000). These geochemical models lack sufficient negative feedback to further reduce the oxygen variations. Their high O_2 predictions need revision downwards because they are inconsistent with the continuous existence of forests. Stabilizing mechanisms (Lenton and Watson, 2000) that could have regulated oxygen close to 21% of the atmosphere throughout the past 350 Myr are discussed further in section 3.6.

3.4 Oxygen toxicity

Despite oxygen being one of the most abundant biological products at the Earth’s surface,

its metabolic products are extremely toxic to life. The following explanation of oxygen toxicity draws heavily on the review by Fridovich (1977). The basis of oxygen's toxicity to biology lies in its physics and chemistry. Unusually for a gas, dioxygen is paramagnetic, having two unpaired electrons with parallel spins. This presents a barrier to chemical reaction with any organic reductant that has a pair of electrons to give up to O_2 . The incoming electron pair cannot be accommodated in the partially filled orbitals on O_2 . Hence the organic donor must undergo relatively slow spin inversion before it can react. This spin restriction is eliminated in electronically excited singlet oxygen (1O_2), making it vastly more reactive than ground state oxygen. If atmospheric oxygen were as reactive as singlet oxygen life would be impossible and any accumulation of organic matter would be unlikely.

The spin restriction can be circumvented in two ways. Combining O_2 with a paramagnetic transition metal is the course followed by many oxidases containing, for example, Cu^{2+} and Fe^{2+} . Alternatively, the univalent pathway of adding electrons one at a time is quite common. This explains oxygen's toxicity, because the intermediates produced are much more reactive than O_2 itself. In the reduction of O_2 to $2H_2O$, the superoxide anion radical (O_2^-), hydrogen peroxide (H_2O_2) and the hydroxyl radical ($OH\cdot$) are all produced. Superoxide always gives rise to hydrogen peroxide in the pH range of biochemistry and together they interact to produce both $OH\cdot$ and singlet 1O_2 within cells. The hydroxyl radical ($OH\cdot$) reacts rapidly with virtually all organic compounds, giving reason enough for oxygen toxicity. In addition, singlet 1O_2 is a powerful oxidant and more discriminating, reacting rapidly at carbon/carbon double bonds, attacking polyunsaturated fatty acids and, by a free radical chain reaction, causing disproportionately great damage to cell membranes.

Given that $OH\cdot$ and singlet 1O_2 are so dangerous to living things, organisms should avoid producing them, and where their production is unavoidable the consequences must be minimized. Production can be avoided by multivalent oxygen reduction (avoiding the

univalent pathway). Enzymes to achieve this use paramagnetic transition metals, or special organic substances such as flavins, at their reactive sites. Most of the oxygen consumed by aerobes is reduced by cytochrome *c* oxidase, which contains iron (heme) and copper at its active site and reduces O_2 to water. Several copper-containing oxidases achieve the same reduction. Many flavin-containing oxidases reduce O_2 to H_2O_2 without producing intermediates.

Unfortunately some production of harmful intermediates appears to be unavoidable in respiring cells, and active defences are required against this. The accumulation of H_2O_2 is prevented by two related classes of iron-containing enzymes, the catalases and the peroxidases, which catalyse its reduction to $2H_2O$. The accumulation of O_2^- is prevented by enzymes called superoxide dismutases that catalyse an oxidation-reduction reaction in which O_2^- is both electron donor and electron acceptor and H_2O_2 is formed. Oxygen also enhances the lethality of ionizing radiation, and this deleterious effect is inhibited by superoxide dismutases and catalases.

Superoxide dismutases, catalases and peroxidases provide the 'frontline defences' against oxygen toxicity, but even in their presence a low level of oxidative attack occurs. Compounds called antioxidants act in the 'rear guard' to minimize the damage it causes. The free radical chain reaction triggered by singlet 1O_2 , which oxidizes polyunsaturated lipids, can be broken by antioxidants that react with the chain-propagating radicals. Vitamin E (α tocopherol) is one such compound, deficiency of which causes muscular dystrophy and reproductive failure in humans.

There are mechanisms to repair damage done by oxygen radicals and their reactive progeny, but some of the damage is irreversible, and can be viewed as chronic, low-level, cumulative oxygen toxicity. This is the chemical cause of ageing – the gradual wearing down of organisms. Hence it has been remarked of oxygen that 'as little as one breath is known to produce a life-long addiction to the gas ... which invariably ends in death' (Campbell, quoted by Gilbert, 1981).

3.5 Influences of oxygen on evolution

The capacity to detoxify reactive oxygen species must have evolved prior to oxygenic photosynthesis and aerobic metabolism, or the first aerobic organisms would have poisoned themselves. This poses something of a puzzle as to what drove evolution of protection from O₂ toxicity before there were significant amounts of O₂ in the environment (McKay and Hartman, 1991). Carotenoids (corrin derivatives), which protect against H₂O₂, are found in ancient anaerobic bacteria and do not require O₂ for their production, yet protect against its toxic effects (Gilbert, 1981). Cytochrome oxidase, which catalyses the reduction of oxygen to water, also arose prior to oxygenic photosynthesis (Castresana *et al.*, 1994; Castresana and Saraste, 1995). Such occurrences suggest that there was another source of reactive oxygen species on the early Earth, the nature of which is uncertain at present. Photochemical production of oxidants such as H₂O₂ in surface waters (McKay and Hartman, 1991) is now thought to be unlikely (according to modelling by J.F. Kasting, personal communication).

After the origin of oxygenic photosynthesis, localized accumulation of O₂ would have applied a common selection pressure to a varied biota, driving the evolution of a variety of oxygen defences. After the corrin derivatives, the more oxidized porphyrins including catalases and peroxidases appeared (Gilbert, 1981). These occur in most bacteria except methanogenic bacteria and anaerobic clostridia.

Superoxide dismutases (SODs) must have evolved at an early stage and are present in all organisms except some oxygen-sensitive obligate anaerobes (Fridovich, 1981). There are three main types of SODs, those containing copper and zinc, those containing manganese, and those containing iron. The manganese and iron SODs are found in prokaryotes and the mitochondria of eukaryotic cells, and may have appeared before oxygenic photosynthesis, because they are present in some ancient non-oxygenic photosynthesizers. Obligate anaerobic photosynthetic bacteria (green sulphur bac-

teria, purple sulphur bacteria) contain the iron SOD. Facultative aerobic photosynthetic bacteria (purple non-sulphur bacteria) contain the manganese SOD. This anaerobic/facultative aerobic distinction suggests the iron SOD may have evolved before manganese SOD. The cuprozinc SODs are characteristic of the cytoplasm of eukaryotic cells. The eukarya diverged from the bacteria and archaea early in the history of life (Knoll, 1992), hence the cuprozinc SOD is probably of similar antiquity to the other SODs (Runnegar, 1991). Eukaryotes later acquired mitochondria by symbiosis (Knoll, 1992), as indicated by the similarities between bacterial and mitochondrial SODs coupled with the great differences between mitochondrial and cytosolic SODs from the same species.

Figure 3.3 summarizes current evidence for the appearance of some important oxygen-producing and oxygen-consuming organisms. The potential for aerobic respiration arose before oxygenic photosynthesis, with the evolution of the key enzyme, cytochrome oxidase (Castresana *et al.*, 1994; Castresana and Saraste, 1995). However, there was essentially no O₂ in the environment to support aerobic respiration prior to the first oxygenic photosynthesizers. Their origin was discussed in section 3.3, and they probably performed aerobic respiration as the most rewarding means of utilizing the energy they had made available. Once O₂ became locally available, free-living aerobic respiring bacteria, which included the ancestors of mitochondria, could have thrived. Local accumulation of O₂ would also have triggered the evolution of further metabolic pathways utilizing its power as an oxidant. Methane oxidation is one such pathway that was widespread by ~42.8 Gyr ago (Hayes, 1994), occurring also in ponds on the land surface (Rye and Holland, 2000). Oxygenic photosynthesis provided the basis of microbial mat communities (Buick, 1992) that included a suite of organisms utilizing the oxygen and organic carbon produced.

The origin of eukaryotic cells with mitochondria (which all perform aerobic respiration) was at least facilitated by rising oxygen. Their O₂ requirement of ~0.002 atm is harder

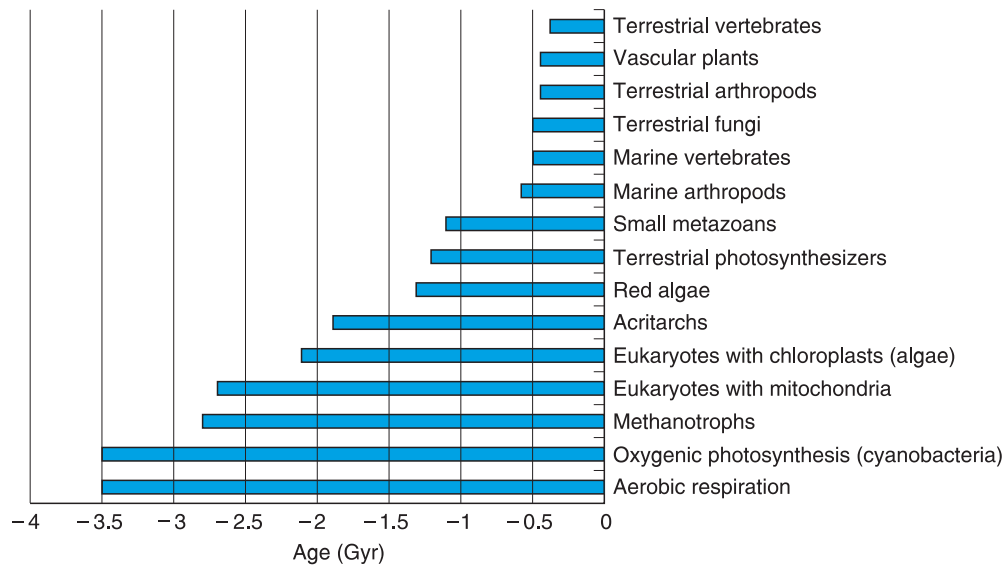


Figure 3.3 Major events in the evolution of oxygen-producing and oxygen-consuming organisms. Simplified from Raven (1997) with the addition of aerobic respiration (Castresana and Saraste, 1995), methanotrophs (Hayes, 1994; Rye and Holland, 2000), eukaryotes with mitochondria (Knoll, 1992) and small metazoans (Knoll, 1992). Acritarchs are thought to be cysts of green algae of the class Prasinophyceae. Dates of appearance are approximate and subject to revision. For example, the earliest appearance of eukaryotic algae was pushed back significantly with the discovery of 2.1-Gyr-old *Grypania* (Han and Runnegar, 1992).

to satisfy than that of free-living aerobic prokaryotes, because the mitochondria are encased within a larger cell that limits O_2 supply by diffusion (Runnegar, 1991). However, sufficiently O_2 -rich local environments likely existed in the late Archean, and the acquisition of mitochondria has been tentatively dated at 2.8–2.4 Gyr ago (Knoll, 1992). Phylogenetic trees suggest that chloroplasts were acquired after mitochondria (Knoll, 1992), despite the fact that photosynthesizing eukaryotes (those with chloroplasts) are less likely to be O_2 limited because they have their own O_2 supply. A plausible explanation is that when O_2 was at low Archean concentrations, fixed nitrogen would have been very scarce in the surface ocean (Knoll, 1992). Heterotrophs (including eukaryotes with mitochondria) could obtain nitrogen easily enough but autotrophs would have had to fix their own. Most prokaryote autotrophs can fix nitrogen but eukaryote chloroplasts do not. Rising O_2 may have lifted a barrier to their evolution by triggering wide-

spread nitrification and thus increased nitrate production. The earliest eukaryote fossils appear to be algae (Han and Runnegar, 1992) and are contemporaneous with the first major rise of atmospheric O_2 around 2.1 Gyr ago.

The rise of atmospheric O_2 2.2–2.0 Gyr ago must have disrupted obligate anaerobes at the Earth's surface, banishing them to anoxic environments, but it was probably not as catastrophic for anaerobes as previously suggested. Obligate anaerobic photosynthetic bacteria (green bacteria, purple sulphur bacteria) that could have been widespread under a reducing atmosphere and have formed the basis of many microbial mat communities would have had to migrate to deeper levels in the mats. However, if the deep ocean remained anoxic until the late Proterozoic (Canfield, 1998) obligate anaerobic heterotrophs could have continued to thrive there. Even anaerobic photosynthesizers may have been able to persist in the ocean, if the anoxic horizon was in the photic zone near the surface. The main beneficiaries of the rise

in oxygen were the aerobes. The amount of free energy available to the biota was increased and aerobic heterotrophs could now achieve global significance, no longer limited to living in close proximity to photosynthesizers.

The rise in O₂ also had indirect environmental consequences that would have exerted strong selective pressure on the biota. It triggered loss of methane from the atmosphere and its greenhouse effect, cooling the planet and perhaps causing low-latitude glaciation, which could have decimated any early land biota. The methane-rich late Archean atmosphere probably had an organic haze layer that reduced the UV flux to the surface (Lovelock, 1995; Pavlov *et al.*, 2000). As O₂ rose this atmospheric shield would have disappeared, bathing the surface in extra UV. However, both prokaryotes (Margulis *et al.*, 1976) and early eukaryotes (Rothschild, 1999) had their own UV protection mechanisms. The organic haze was soon replaced by an effective ozone shield, once O₂ exceeded ~ 0.1% PAL (~ 0.0002 atm) (Margulis *et al.*, 1976). Early ideas that a lack of UV protection delayed the origin of life on land or of eukaryotes now seem unlikely (Rothschild, 1999).

During the mid-Proterozoic (2.0–1.0 Gyr ago) both oxygen concentrations and the biota appear to have been relatively stable. The next major evolutionary development was the radiation of phenotypic diversity in eukaryotes (Knoll, 1992). Fossils suggest this occurred 1.1–1.0 Gyr ago. Small, primitive metazoans (multi-cellular animals) are thought to have first become widespread around 1.0 Gyr ago. Trace fossils and possible fossilized metazoan faecal pellets are widespread from this time onwards. Early metazoans contributed to the demise of stromatolites through grazing and burrowing activity, augmented by declining levels of atmospheric CO₂ reducing carbon fixation rates (Rothschild and Mancinelli, 1990). High continental weathering rates suggest terrestrial photosynthesizers were present ~ 1.2 Gyr ago (Horodyski and Knauth, 1994). Some multi-cellular algae certainly existed in the oceans. A multi-cellular bangiophyte red alga aged 1.26–0.95 Gyr ago is the oldest eukaryote that can be confidently assigned to an

extant phylum (Butterfield *et al.*, 1990). Multi-cellular eukaryotes typically have a higher oxygen demand than single cells. However, there is no indication of a rise in O₂ driving the observed diversification of eukaryotes. Indeed O₂ was probably sufficient by 2.0 Gyr ago. It is possible that eukaryote diversification occurred substantially earlier than 1.0 Gyr ago but the resulting organisms were not preserved. Alternatively, some other factor may have inhibited diversification, perhaps a late establishment of sexual population structures (Knoll, 1992).

A late-Proterozoic rise in oxygen is often hypothesized as a trigger for the Cambrian 'explosion', the diversification of large metazoans 0.54 Gyr ago (Knoll, 1996; Thomas, 1997; Knoll and Carroll, 1999). In order to attain a significant size, metazoans evolved a circulatory system with an oxygen carrier, haemoglobin. However, atmospheric oxygen probably rose above the concentration necessary for animal radiation (~ 0.02 atm) long before the first large metazoans evolved (Holland and Beukes, 1990; Canfield and Teske, 1996). Thus from current geochemical evidence it seems that pO₂ > 0.02 atm was a necessary but not a sufficient condition for the evolution of large, metabolically active animals. Ecological drivers were probably at least as important (Erwin, 1993; Knoll and Carroll, 1999).

Oxygen is relatively insoluble in water and its solubility decreases with increasing salinity and temperature. Hence dissolved oxygen concentration limits the maximum potential size of some aquatic metazoa (Chapelle and Peck, 1999). The propensity of metazoa to suffer extinction events has been linked to their oxygen demand – the higher the oxygen demand, the more likely they are to be victims of any oxygen variability (McAlester, 1970). During the Phanerozoic, animals evolved to breathe air and thus benefited from a greater availability of oxygen that allowed them to become more metabolically active and made them less likely to suffer oxygen starvation than their aquatic counterparts. Terrestrial arthropods appeared ~ 420 Myr ago, followed by terrestrial vertebrates ~ 370 Myr ago. The transition from water- to air-breathing increased the

potential for damage by reactive oxygen species, and vertebrates acquired unique oxygen defences, for example the antioxidant glutathione peroxidase (Gilbert, 1981).

A range of evolutionary changes among plants and animals has been tentatively linked to predicted O₂ variations over the last ~350 Myr (Robinson, 1989; Graham *et al.*, 1995; Dudley, 1998; Dudley, 2000). However, the variations in O₂ (Berner and Canfield, 1989) are probably significantly overestimated (Lenton and Watson, 2000). The postulated late-Carboniferous to early-Permian pulse of O₂ to higher than present levels broadly correlates with the diversification of insects and tetrapods, the origin of flight, insect gigantism, and size increases among aquatic invertebrates (Graham *et al.*, 1995). A postulated drop to lower than present O₂ levels at the end of the Permian broadly correlates with extinction of many tetrapod and insect lineages. It has long been noted that O₂ supply by diffusion limits body size in insects (Haldane, 1928). Increased O₂ partial pressure enhances diffusion dependent respiration, and it offers a greater energy supply for increases in metabolic rate, turnover and resource availability (Graham *et al.*, 1995; Dudley, 1998). Hence increased O₂ partial pressure has been put forward as a hypothesis to explain invertebrate gigantism in the Carboniferous, particularly giant flying insects, for example dragonflies (Protodonata) (Graham *et al.*, 1995; Dudley, 1998). A higher partial pressure of O₂ without a concomitant increase in the O₂ mixing ratio could have occurred if both atmospheric N₂ and O₂ increased during the Carboniferous. However, the burial of organic matter has a much weaker effect on N₂ than O₂, because the C/N burial ratio is >10 and the N₂ reservoir is larger than the O₂ reservoir. An alternative hypothesis (to avoid inferring highly flammable mixing ratios of O₂) is that the giant Carboniferous insects had special adaptations to concentrate oxygen.

The multiple historical origins of vertebrate flight in the late Jurassic and Cretaceous (150–100 Myr ago) have been linked to a postulated second rise in O₂ (Dudley 2000), although O₂ is not predicted to have peaked until the early Tertiary (50 Myr ago) (Berner and

Canfield, 1989). However, there has probably been sufficient O₂ for flight to occur throughout the last 350 Myr. O₂ appears not to have fallen below 15% in this interval, and 15 kPa corresponds to the oxygen partial pressure at 2.5 km altitude at present (Graham *et al.*, 1995). Bird and insect flight are observed well above this altitude (personal observations while mountaineering). As with the appearance of metazoans, sufficient O₂ opened a window of opportunity for the evolution of flight. However, evolution itself is driven by localized natural selection. For example, the evolution of flight may have been driven by its benefits as an escape from predation.

O₂-fuelled fires have shaped terrestrial ecosystems since the Carboniferous (Robinson, 1989; Scott and Jones, 1994), including triggering the evolution of fire tolerance and fire exploitation 'strategies'. Limited data on the charcoal content of coals (Robinson, 1989) and deep-sea cores (Herring, 1985) show some interesting variation in fire regimes over this time. If the mixing ratio of atmospheric oxygen has ever risen significantly above the present level this would have exerted, via increased fire frequency, stronger selective pressures on terrestrial plant ecology (Robinson, 1989). High-O₂ floras are expected to have thick bark as protection for the cambium, clonal reproduction and/or colonization through copious seeding, fire-proof seeds, investment in below-ground reproductive and storage tissues, restricted upper canopies, and dispensable leaves on low and mid-height plants (Robinson, 1989). Some of these features are observed in the fossils of Carboniferous swamp floras, and this has been taken as support for higher than present O₂ levels (Robinson, 1989). However, the dominant arborescent lycopods ('fern trees') had low reproduction rates and a morphology that looks very fire sensitive, while the climate was relatively dry, encouraging fires.

Oxygen directly affects C₃ plant growth by suppressing carbon assimilation, because O₂ and CO₂ compete for the oxygenase or carboxylase activity of the enzyme rubisco (ribulose biphosphate carboxylase/oxygenase). The effect is determined by the CO₂/O₂ ratio and

temperature. At a given O_2 and temperature, a low CO_2 compensation points exist at which net CO_2 exchange is zero. For a given CO_2 and temperature, a high O_2 compensation point also exists at which net O_2 exchange is zero (Tolbert, 1994). Atmospheric CO_2 probably dropped by an order of magnitude after plants colonized the land surface (~ 420 Myr ago) (Berner, 1998), making present levels of O_2 somewhat limiting to C_3 plants. This was a necessary condition for the much later evolution of C_4 plants (~ 13 Myr ago) that use a CO_2 concentrating mechanism, but their evolution was more likely driven by declining CO_2 than rising O_2 . C_3 plant rubisco has a high selectivity for CO_2 relative to O_2 , which probably evolved in response to declining CO_2/O_2 ratios (Raven, 1997). For the history of life prior to the Devonian (~ 400 Myr ago) low O_2 and high CO_2 concentrations would not have significantly limited rubisco activity, particularly as all extant cyanobacteria and most algae possess a CO_2 concentrating mechanism.

3.6 Oxygen regulation and the Gaia theory

Life has produced atmospheric oxygen, which is in turn one of the key environmental variables affecting life. This implies that there are feedback mechanisms between the activities of life and the oxygen content of the atmosphere. The Gaia theory posits that the Earth is a self-regulating system in which such feedback mechanisms control major environmental variables (Lovelock, 1995; Lenton, 1998). The stability of atmospheric oxygen over the past 350 Myr has often been taken as evidence for such regulation. The stepwise rise of oxygen since the origin of oxygenic photosynthesis, with periods of stability interspersed with intervals of rapid change is also consistent with oxygen being under feedback control. If so, a regulatory system has evolved, with a series of progressively higher 'set points', as oxygen was driven upwards by biotic activity.

Prior to 2.2 Gyr ago, atmospheric pO_2 was maintained below 0.0008 atm by oxygen

removal always exceeding the oxygen source. This was probably due to a combination of geochemical and biological control. The relative importance of biotic and abiotic factors has been the subject of some debate. Towe (1990) argued that a large flux of aerobic respiration was necessary to prevent the rise of oxygen, and hence aerobic respiration must have evolved early in the Archean. Kasting (1991) countered this, estimating that geochemical sources of reduced matter dominated the sink. Lovelock (1989) included the geochemical oxygen sink together with aerobic respiration and methane oxidation in a model that predicts oxygen regulation at very low concentrations during the Archean and a transition to $pO_2 > 0.001$ atm around 2.2 Gyr ago, consistent with existing constraints (Figure 3.1).

The cause of the great oxidation event 2.2–2.0 Gyr ago is unresolved. Oxygen production must have exceeded oxygen consumption for O_2 to rise, and both a gradual decline in the oxygen sink and a more rapid increase in the oxygen source appear to have contributed to tipping the redox scales. As the Archean progressed, the reservoirs of reduced iron, sulphur, etc. in the ocean would have been gradually oxidized. Volcanic and metamorphic activity also declined with time, weakening the supply of reduced matter. Hence a decline in the oxygen sink without any change in the oxygen source could have started the oxidation event, as has been simulated (Lovelock, 1989). The oxidation event is then amplified by increased organic carbon burial.

Increased organic carbon burial could equally have triggered the oxidation event, given that the two are roughly coincident in the geological record (Karhu and Holland, 1996). The evolution of the first algae (photosynthesizing eukaryotes) may have predated the oxidation event, because a large alga (*Grypania*) was already present during it (Han and Runnegar, 1992). The first algae would have occupied new niches, and were better adapted to oxygen than cyanobacteria (Gilbert, 1981). Hence their evolution could have driven increased global primary productivity and organic carbon burial. Tectonic activity may also have generated particularly

suitable geologic conditions for carbon burial at this time (DesMarais *et al.*, 1992).

An alternative hypothesis is that methanogens caused the great oxidation event (D.C. Catling, C.P. McKay and K.J. Zahnle, personal communication). By creating a methane-rich atmosphere in the late Archean they greatly increased hydrogen loss to space resulting in net oxidation of the atmosphere/ocean-sediment system. Burial of organic carbon and oxidation of reduced matter are assumed to have been in balance until the oxidation event began. As oxygen rose, methanogen communities would have been disrupted because they are obligate anaerobes. Their contribution to the recycling of organic carbon may have been reduced and any delay before aerobic respiring organisms filled the carbon-recycling niche would have resulted in a greater fraction of primary production being buried.

Between 2.0 and ~ 0.8 Gyr ago, pO_2 probably remained between ~ 0.002 atm and ~ 0.02 atm. If the deep ocean remained anoxic during this interval then simple models suggest $pO_2 < 0.006$ atm (Kasting, 1991). The question arises as to what mechanisms can stabilize oxygen at these low concentrations? The need for stabilizing mechanisms was probably even greater then than it is now because the residence time of oxygen would have been significantly shorter. It seems likely that oxidative weathering was incomplete, hence there would have been negative feedback on the sink of oxygen – increasing atmospheric oxygen concentrations would generate increased oxygen removal. This mechanism is potentially fairly sensitive, because at low pO_2 the oxygen sink increases rapidly with small increases in pO_2 until the point is reached where the majority of incoming reduced matter ($\sim 10^{13}$ mol yr $^{-1}$) is oxidized (Holland, 1984). If the deep ocean were anoxic, much oxygen would also have been consumed within the water column, in the oxidation of up-welling reduced sulphur (Logan *et al.*, 1995; Canfield, 1998). However, this sink would have to have depended on oxygen production and/or pO_2 for it to stabilize oxygen. The ‘set point’, about which oxygen was regulated, may have been determined by the limiting effects of oxy-

gen toxicity on growth (Lovelock, 1995), for example of some cyanobacteria (Gilbert, 1981) and early eukaryotes (Knoll, 1992). Higher oxygen concentrations may not have been maintainable until improved oxygen tolerance had evolved.

Postulated rises in oxygen in the late Proterozoic ~ 0.8 – 0.57 Gyr ago have been linked to tectonics generating favourable conditions for organic carbon burial (DesMarais *et al.*, 1992) and to the evolution of metazoans with muscular, unidirectional guts, which packaged organic matter into rapidly sinking faecal pellets (Logan *et al.*, 1995). Prior to this evolutionary innovation, organic matter sank slowly through the water column, as finer material, and would have been more completely oxidized. With the advent of faecal pellets more organic carbon would have reached the sediments, more oxygen would have been released from surface waters and the deep ocean would have become more fully oxygenated. ‘Oxygen happens’ as K.J. Zahnle put it (personal communication). The resulting atmospheric oxygen concentrations in the early Phanerozoic (0.57–0.37 Gyr ago) are poorly constrained, but we can be confident that oxygen had approached the present level by ~ 370 Myr ago.

The stability of atmospheric oxygen over the past ~ 350 Myr is remarkable because the oxygen residence time is only ~ 3.25 Myr. Therefore, the whole oxygen reservoir has been replaced over 100 times, while its size has hardly varied. Processes such as the uplift of continents exposing more reduced matter should have tended to force changes in size of the oxygen reservoir. The only reasonable explanation is that some negative feedback mechanisms have been stabilizing oxygen.

The oxidative weathering sink of oxygen is saturated at present – all the reduced matter that is exposed is oxidized. Hence regulation of atmospheric oxygen is thought to involve negative feedback on the source of oxygen. The first suggestion was that the burial of organic carbon is enhanced under anoxic conditions, because anaerobic consumers are less efficient than their aerobic counterparts. If so, a decline in oxygen would be counteracted by an

increase in the organic carbon burial source of oxygen. However, the observed effect is too weak to stabilize atmospheric oxygen (Betts and Holland, 1991).

The main control of the organic carbon burial flux in the ocean is the amount of marine productivity, which in turn depends on nutrient supply. A number of oxygen regulation mechanisms have been proposed involving phosphate as the control of productivity over long timescales. For example, it has been noted that the burial of phosphorus in organic matter (Van Cappellen and Ingall, 1996) and bound to iron minerals (Colman *et al.*, 1997) is less efficient under anoxic conditions. Hence, declining oxygen should cause more phosphorus to be recycled to the water column, fuelling more productivity and increased organic carbon burial. The problem with such mechanisms is that they are ineffective against rising oxygen, which readily tends to remove anoxia from the ocean, thus switching off the feedback (Lenton and Watson, 2000).

The main victims of rising oxygen would be plants on the land surface, especially forests, and it has been suggested that they play a role in oxygen regulation (Lovelock, 1995). A recent proposal (Lenton and Watson, 2000) involves the biological amplification of weathering, which is ultimately the only source of phosphorus to the land and ocean. Vascular plants amplify the rate of rock weathering by about an order of magnitude relative to primitive land biota (e.g. lichen and moss cover) and the effect is greatest for trees with their deep rooting systems (Bormann *et al.*, 1998). Increasing atmospheric oxygen tends to suppress vegetation by inhibiting photosynthetic carbon fixation. At the current CO₂ concentration, ~ 27% O₂ causes growth to cease in a crop plant (tobacco) (Tolbert *et al.*, 1995), while birch is less sensitive (Beerling *et al.*, 1998). More importantly, above about 21% oxygen, increasing fire frequency will tend to trigger ecological shifts from forest to faster regenerating ecosystems such as grassland. By these mechanisms, rising oxygen should suppress rock weathering and hence suppress the supply of phosphorus to the land and ocean, which in turn suppresses productivity and organic carbon burial.

This mechanism is extremely effective at regulating against rising oxygen because of the high sensitivity of fire frequency to rising oxygen (Lenton and Watson, 2000). Furthermore, declining oxygen is counteracted by increased plant growth, more efficient rock weathering and increased phosphorus supply fuelling organic carbon burial.

If land plants are instrumental in regulating the oxygen content of the atmosphere at present, this may help constrain oxygen concentrations before plants began to colonize the land surface. Prior to land plants, the liberation of phosphorus from rock weathering would have been greatly reduced, tending to suppress global productivity and organic carbon burial. Furthermore, there was no lignin production and minimal burial of organic carbon on the continents. A weaker oxygen source implies a lower oxygen concentration, perhaps an order of magnitude lower (O₂ ~ 0.02 atm). This is consistent with the requirements of early metazoans (Figure 3.1). However, with more anoxia in the ocean, organic carbon burial would be more efficient and phosphorus recycling would be enhanced, tending to counteract reduced phosphorus input and maintain a significant marine organic carbon burial flux. Hence O₂ ~ 0.05–0.1 atm is suggested as a best guess for the interval ~ 0.6–0.4 Gyr ago. Further work should enable tighter constraints to be put on past concentrations of atmospheric oxygen.

3.7 Conclusion

Oxygen is one of the ‘master variables’ of the Earth system. Once oxygenic photosynthesis had arisen it was destined to transform the Earth’s surface environment. The stepwise rise of atmospheric oxygen suppressed obligate anaerobes, and forced life to evolve numerous protections against oxygen toxicity. However, the great increase in the amount of free energy available to the biota more than outweighed these pitfalls. The progressive oxidation of the Earth’s surface environment paved the way for single-celled then multi-cellular eukaryotes to

dominate the biota. Metazoa were able to evolve and then become progressively larger and more metabolically active. Ultimately we owe our existence to myriad past photosynthesizers increasing the oxygen content of the atmosphere and a tight coupling between the evolution of the biota and its physical environment, which has prevented oxygen reaching dangerously flammable levels over the last ~ 350 million years. The co-evolution of the biota and the oxygen content of the atmosphere over Earth history, the increase in free energy and biotic activity, and the emergent self-regulation of the coupled system support the Gaia theory (Lovelock, 1995; Lenton, 1998).

3.7 References

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