

Evolution of the Atmosphere and Oceans: Evidence from Geological Records

2. Enhancement of Oxygen in the Atmosphere

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In Part 1 we described the early atmosphere which was rich in nitrogen and carbon dioxide and was oxygen deficient. In due course photosynthesis liberated free O_2 from CO_2 . The abundance of O_2 reached modern levels by the turn of the Proterozoic and triggered metazoan radiation. However tectonic activity exerted the ultimate control on the growth of atmospheric O_2 by enhanced organic carbon burial in sediments.

The Rise of Free O_2

The O_2 concentration in the prebiotic atmosphere was presumably low as its sources were meager and sinks more plentiful. The principal source of O_2 prior to the advent of photosynthesising plants was photochemical dissociation of H_2O in the upper atmosphere followed by escape of H_2 into space. As free O_2 is very reactive the liberated O_2 would have back reacted with H_2 before reaching lower atmospheric levels. Other sources of H_2 that were also abundant in the early Earth might have prohibited the accumulation of free O_2 . Kasting 1986, estimated that the O_2 abundance in the prebiotic surficial Earth would not have been greater than 1 part in 10^{12} (today it is 210000 parts in 10^6).

Unequivocal fossil evidence for earliest photosynthesis dates back to ~ 3.46 Ga¹ in the form of algal mats and stromatolites. (Grotzinger and Rothman 1996, however, proposed an abiotic origin for the stromatolite structures.) Photosynthesis at that time, however, need not have been oxygenic, as some bacteria and algae are known to follow a non-oxygenic pathway (Box 1). On biological grounds it has been argued that this was probably the first photosynthetic course followed by organisms. We are

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¹Ga means billion years (ago) and Ma, million years (ago).

Box 1. Photosynthesis: Oxygenic and Non-oxygenic.

Green plants utilise CO_2 to synthesise carbohydrates using light energy of the sun liberating O_2 : $\text{CO}_2 + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{O}_2$. J W Schopf in 1992 recorded microfossils of blue green algae (Cyanobacteria) from a 3.46 Ga old Apex chert in NW Australia. This is the oldest known fossil record of oxygenic photosynthesis. Besides, there are many bacteria that follow non-oxygenic photosynthesis. Certain sulphate bacteria, for instance, use H_2S instead of water, and CO_2 to produce carbohydrates in the presence of light energy. This reaction releases S and H_2O as byproducts and not O_2 : $\text{CO}_2 + 2\text{H}_2\text{S} = \text{CH}_2\text{O} + 2\text{S} + \text{H}_2\text{O}$.

thus left with the UV dissociation of H_2O as the principal source of molecular O_2 in the early Archaean.

Elemental O_2 is lethal to anaerobic organisms; the transition to oxygenic photosynthesis was obviously gradual. Oxygen produced by photosynthesis today is rapidly used up for the decay of organic matter, besides being consumed by living organisms for respiration; small amounts of O_2 are also lost in the oxidation of sulphides and other minerals of rocks undergoing chemical weathering and in the oxidation of reduced gases of volcanic origin. If the O_2 given out by green plants is not consumed in the above processes, its concentration in the atmosphere will shoot up and may even lead to fire hazards. Such an eventuality is believed to have occurred during the Permo-Carboniferous (340 Ma) period of coal formation and the Cretaceous-Eocene period of black shale deposition. Large-scale burial of organic matter during these periods elevated atmospheric O_2 to the level of triggering forest fires. Evidence for such a calamity exists in the rock record of those times in the form of fossil charcoal called fusinite. Molecular O_2 can thus accumulate in the atmosphere over geologically short periods of time by oxygenic photosynthesis.

The rock record tells us that free O_2 was low in the early Archaean and that the transition to oxygenic photosynthesis was well under way by about the end of Archaean. There are several occurrences of quartz-pebble conglomerates in Archaean terrains all over the world (Witwatersrand, S Africa; Blind river and Elliot lake, Canada; Dharwar and Singhbhum, India) which

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contain detrital, well-rounded grains of pyrite and uraninite. The rounded morphology is indicative of fluvial transportation. These minerals are unstable in modern oxidative weathering environments; they get oxidised to ferric oxide and uranyl ion, respectively and rarely get transported as grains. The ubiquitous presence of both minerals in 3-2.7 Ga old conglomerates but not in younger ones suggests that prior to 2.7 Ga, atmospheric O₂ was considerably low. In addition, Precambrian palaeosols older than about 2.7 Ga do not retain ferric iron oxide unlike the modern sections. Obviously Fe in the absence of O₂ was removed as soluble ferrous oxide. Based on palaeosol data Holland and Beukes 1990, arrived at the conclusion that there was a dramatic rise in O₂ concentration from ~1% present atmospheric level (PAL) in the Archaean to 15% PAL at 2.2-1.9 Ga.

Despite the antiquity of oxygenic photosynthesis it took nearly 1.5 Ga, dating back to the first appearance of blue-green algae, for significant rise in O₂. Kasting and his group pointed out in 1993 that the rise of O₂ was kept under control by the evolving oxidation state of the Earth's mantle. Fluid inclusion studies of diamond and spinel show that the mantle was reducing through most of the Archaean. Dissociation of mantle water and streaming of H₂ is considered to have kept the oxidation state of the mantle and, therefore, of the atmosphere low. Oxidation of volcanic gases accounts for ~25% of the current sink for O₂. These authors argue that a four-fold increase in reduced gas emission in the Archaean is enough to preclude the build up of O₂ even if organic C was buried at today's rate.

Very little Fe is transported today to the oceans in dissolved form as modern oxidative weathering prohibits dissolution of Fe. In the O₂-free Archaean, stupendous quantities of Fe were delivered to the seas from continental and hydrothermal sources. This Fe remained stored in the oceans as dissolved ferrous Fe for millions of years until the build up of O₂. As oxygenic photosynthesis gained momentum by late Archaean times, the continental flux of Fe to the oceans decreased (because Fe was oxidised and left behind in residual weathering profiles as ferric oxide)

and oceanic Fe^{2+} was oxidised to Fe^{3+} . The entire oceanic reservoir of Fe was thus swept away and deposited as banded iron formations (BIF), which are so prolific in early Proterozoic rock record. Thus although green plant photosynthesis yielded copious O_2 to oxidise oceanic Fe by early Proterozoic times, the supply was nevertheless insufficient to invade the atmosphere until it could first exhaust all the dissolved oceanic Fe.

Banded iron formations are not completely absent in the Archaean. Together with rare instances of oxidised margins in Archaean pillow lavas, these BIF perhaps indicate localised availability of O_2 . However, R F Dymek and C Klein 1988, concluded that the BIF of Isua (3.8 Ga) were chemically precipitated from hydrothermal solutions. The first occurrence of red beds (*Box 2*) and evaporite sulphate at about 1.8-2.0 Ga strongly supports the availability of free O_2 , though its concentration still remained low. BIF were profusely deposited between 2.2 Ga and 2.0 Ga, just prior to the appearance of red beds and sulphate evaporites in stratigraphic records. Kasting and coworkers 1992, proposed a three-stage model for the evolution of atmospheric O_2 (*Figure 1*). The stippled area in the figure represents the permissible values of O_2 in their model. Stage-I called 'reducing' had no free O_2 in the atmosphere-ocean reservoir; stage-II called 'oxidising' had limited free O_2 in the atmosphere-upper ocean reservoirs but the deep ocean remained anoxic. Stage-III is called 'aerobic' and was characterised by the presence of free O_2 in the entire atmosphere-ocean reservoir.

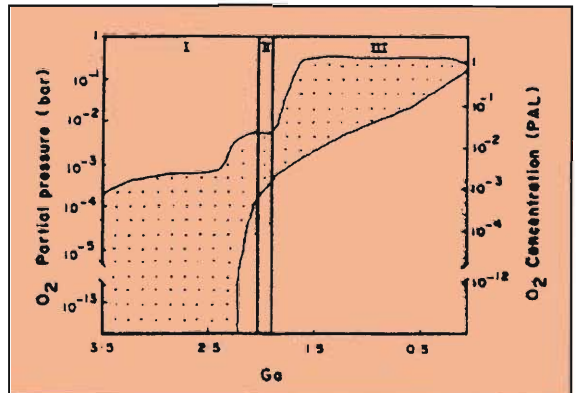
Box 2. Redbeds

Red beds are sedimentary deposits like sandstone in which the particles are coated with red ferric oxide (haematite), requiring O_2 for oxidation. They are obviously absent in the Archaean.

An Anoxic Archaean?

The Archaean environments are generally considered to be anoxic and so the O_2 produced by photosynthesis was not used up for aerobic respiration (respiration here means bio-oxidation of organic matter to CO_2). Today this process converts 99% of organic C of marine photosynthesis to CO_2 . Schidlowski 1988, reported that organic C

Figure 1. Three-stage growth of atmospheric O_2 (Simplified from Kasting and others, 1992)



Microbial communities are some of the most productive ecosystems of the world and according to Schidlowski, under favourable conditions their Archaean ancestors would have sustained formidable rates of primary productivity.

in ~3.8 Ga old Isua supracrustal sediments of Greenland exhibits a 20 % to 30 % depletion of ^{13}C , similar to that in Phanerozoic sediments. Recent work of Mojzsis and coworkers in 1996 confirms similar degrees of ^{13}C depletion in still older (~3.85 Ga) rocks of Isua. As Calvin cycle photosynthesis is the chief process entailing such a degree of ^{13}C depletion in organic matter, it implies that oxygenic photosynthesis commenced operation almost 4 Ga ago.

Assuming an average burial rate of 20% of productivity in the Archaean and an average organic C preservation rate of 0.3% of productivity as in modern sediments, Kenneth M Towe 1990, estimated that the Archaean primary productivity was of the order of $25\text{-}30 \times 10^{13}$ g C/year. Although this amounts to <1% of modern global marine productivity, it must nevertheless have released equal moles of O_2 to the ocean-atmosphere system according to the equation given in Box 1.

Several other evidences support that Archaean productivity was really not that low. The extant benthic procaryotes for instance, are very prolific primary producers with C turnover rates of 8-12 g C/cm²/day. Microbial communities are thus some of the most productive ecosystems of the world and according to Schidlowski, under favourable conditions their Archaean ancestors would have sustained equally formidable rates of primary productivity. This is consistent with the average organic C content of Archaean marine sediments differing little from those of later periods. This means that production of C and generation of molecular O_2 has remained fairly constant since the evolution of microbial communities in early Archaean. If so, it is difficult to conceive a process that recycled 80% of this unburied productivity if the Archaean was anoxic. In addition, the O_2 produced by photosynthesis as confirmed by C isotope data also has to be accounted for.

If global Archaean anoxia as indicated by detrital pyrite and uraninite is to be maintained, the bulk of the photosynthetic O_2 needs to be removed. It is believed that this O_2 was used up for



oxidising dissolved ferrous Fe in the ocean and not for C oxidation by respiration. However, the low average Fe abundance of Archaean sediments is at variance with this argument. Other possible sinks for O₂ are also not geologically viable. Towe, therefore, argued that the only process that could prevent the build up of O₂ prior to the Proterozoic, recycling organic C at the same time, is aerobic respiration. He proposed a plausible solution to the C-Fe dilemma of the Archaean by abandoning the idea of an anoxic Archaean and replacing it with one of low but stable O₂ atmosphere. He considered that if the Archaean atmosphere is assumed to have contained 1-2% PAL of O₂, it is sufficient to offer at least the minimum level of O₂ (0.2-0.4%) necessary for aerobic recycling of organic matter. This would also remove a large part of photosynthetic O₂.

Tectonism and Atmospheric O₂

Many authors have argued that though the growth of O₂ was governed primarily by biological evolution, the ultimate control was exerted by geologic processes in the form of tectonic activity. David J Des Marais and coworkers 1992, reviewed this problem as briefly summarised below.

We have seen earlier that the production of organic matter liberates O₂ while its oxidation consumes O₂ and that if organic matter is prevented from being oxidised (by quick burial) the atmospheric O₂ level will increase. Organic C burial, therefore, elevates atmospheric O₂ and the O₂ so liberated oxidises surficial environments. Accumulation of organic matter and sulphides in sediments leads to accumulation of Fe³⁺, O₂ and SO₄²⁻ in crustal environments. Therefore, oxidation of surficial environments is promoted not by biological processes alone, but by their interaction with geological processes such as sedimentation.

Studies by the above authors show that crustal C reservoir had increased in two pulses in the Proterozoic, one between 2.5 Ga and 1.8 Ga and another between 1.3 Ga and 700 Ma, roughly synchronous with two pulses of tectonic activity (*Figure 2*).





Figure 2. Carbon burial and orogenic events in the Precambrian (Adapted from Des Marais D J and others 1992).

These spasmodic events must have increased the crustal abundances of Fe^{3+} and SO_4^{2-} and atmospheric abundance of O_2 . Increased organic C burial is dependent not only on increased productivity, governed in turn by increased nutrient supply, but also by enhanced rates of preservation governed, in turn, by faster sedimentation rates

Des Marais and coworkers also observed that the $\delta^{13}\text{C}$ difference between sedimentary carbonate C and organic C (this difference is designated as Δ_{C}) declined in the Proterozoic. This is interpreted to be due to the fact that the isotopic discrimination during biological uptake of CO_2 decreased in response to declining CO_2 in the atmosphere and oceans. The greatest decline in Δ_{C} occurred during episodes of rifting and global orogeny indicating that withdrawal of CO_2 was enhanced during these periods of accelerated sedimentation.

Late Proterozoic Rise in Atmospheric O_2

Atmospheric O_2 is believed to have reached 100% PAL at the close of the Proterozoic. This period coincided with the evolution of metazoans between 800 Ma and 1.0 Ga, although the earliest metazoan remains called Ediacaran fauna appear in the rock record roughly at 590 Ma. Metazoans require free O_2 not only for respiration but also for the synthesis of the structural protein called collagen present in all metazoans. The rise of O_2 to PAL at the close of the Proterozoic is also supported by enhanced organic C burial rates between 900 Ma and 600 Ma indicated by anomalously high ^{13}C in limestones ($^{13}\text{C} = +5\%$) deposited during this period. The elevated $\delta^{13}\text{C}$ values also signal significant rise of O_2 during this period as C burial leads to atmospheric O_2 rise. Recently Ronald Confield and Andreas Teske 1996 reported stable S isotope and bacterial evidences in support of this conclusion.

Sulphide is produced in the marine environment by bacterial reduction of sea water sulphate, during which a depletion of the

heavy isotope (^{34}S) occurs to the extent of $51 \pm 10\%$. Interpretation of a large number of data pertaining to S isotopes in sedimentary rocks dating from the present to Mesoproterozoic by these researchers confirms depletion of ^{34}S by $\sim 55\%$ compared to ocean water sulphate. The depletion extends back in time to Neoproterozoic (\sim upto 860 Ma) beyond which the discriminations are of a lower degree. This, according to Conefield and Teske, indicates a fundamental change in the process controlling the isotopic composition of sedimentary sulphides between 640 Ma and 1.05 Ga. This interval coincides with the widespread initiation of the oxidative S cycle as driven by the accumulation of O_2 in the atmosphere-ocean system in the late Proterozoic. This is also contemporaneous with a significant phylogenetic radiation of marine sulphide oxidising bacteria and the liberation of O_2 during the enhanced burial of organic C at the close of Proterozoic. Although this period predates the first appearance of Ediacaran fauna, it is synchronous with the late Proterozoic metazoan radiation, as evidenced by amino acid comparison studies of Runnegar in 1991.

The O_2 content of the atmosphere had remained constant since about 350 Ma, though minor departures did occur. Chaloner and coworkers in 1990 have shown that the presence of fusinite in coals deposited since Carboniferous sets a lower limit of 13% for the atmospheric O_2 during fusinite formation. Fusinite is an indicator of forest fire that requires a minimum atmospheric O_2 of 13%. The presence of large fossil trees in coals in the opinion of these authors sets an upper limit of 30-35% O_2 in the atmosphere, as at higher levels forest fires would be frequent, prohibiting the growth of large trees. In a similar way Landis and coworkers in 1990 constrained atmospheric O_2 during the last 100 Ma by measuring O_2 in air bubble trapped in amber. Their studies show that the O_2 content of the atmosphere decreased from 35% in the Cretaceous to 22% at the base of the Tertiary and that it remained essentially constant since then.

To recapitulate, the evolution of the atmosphere and related events can be summarised as given in *Box 3*. The prebiotic

Box 3. Sr Isotopes

The ratio of radiogenic to stable isotope of Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) of shell carbonates is used to trace past fluctuations in sediment flux to the sea. While the abundance of ^{86}Sr remains constant, ^{87}Sr is continuously produced by the decay of ^{87}Rb contained in potassium feldspars of continental rocks. During times of lowered sea level, more continental areas become exposed to weathering and erosion that transport excess ^{87}Sr to the sea. Marine organisms secrete their carbonate shells in isotopic equilibrium with ocean water. Times of low sea level and orogenic uplift deliver excess sediments to the ocean and enhanced ^{87}Sr too, elevating the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of biogenic carbonates.

The CO₂ concentration could not have been too high nor too low to trigger a runaway greenhouse effect or a global glaciation, respectively.

atmosphere was essentially CH₄-NH₃-H₂-dominated and persisted for ~200 Ma (4.6 to 4.4 Ga). CH₄ and NH₃ soon dissociated and oxidised to CO₂ and H₂O. The transient primary atmosphere soon evolved to a CO₂-rich secondary atmosphere. However, the CO₂ concentration could not have been too high nor too low to trigger a runaway greenhouse effect or a global glaciation, respectively. Neither of these possibilities is consistent with the geological record. The CO₂-dominated Archaean atmosphere evolved further to oxygenic atmosphere by the release of photosynthetically produced O₂. Oxygenic photosynthesis commenced roughly 4.0 Ga ago and obviously the Archaean was not entirely anoxic but was O₂-deficient. The photosynthetically liberated O₂ first invaded the oceans and escaped into the atmosphere only after saturating the hydrosphere. The close of the Proterozoic marks the growth of atmospheric O₂ to modern levels. This phase of O₂ build up is broadly synchronous with the late Proterozoic metazoan evolution. Nevertheless, geological processes ultimately controlled the O₂ concentration by burial of organic C during episodes of accelerated tectonic activity. The O₂ level has been relatively stable since about 350 Ma, while N₂ abundance in the atmosphere remained largely unchanged since the early catastrophic degassing event.

Suggested Reading

- [1] H D Holland and others, Evolution of the atmosphere and oceans, *Nature*, 320, 27–33, 1986.
- [2] E Donald Canfield and Andreas Teske, Late Proterozoic rise in atmospheric oxygen, Concentration inferred from phylogenetic and sulphur isotope studies, *Nature*, 382, 127–132, 1996.
- [3] Rob Rye and others, Atmospheric carbon dioxide concentrations before 2.2 b.y ago, *Nature*, 378, 603–605, 1995.
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- [5] M Schidlowski, 3800 million year isotopic record of life from carbon in sedimentary rocks, *Nature*, 333, 313–318, 1988.

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