

2010; Poulton et al., 2010; Reinhard et al., 2009), trace amounts of molybdenum and rhenium (Anbar et al., 2007; Wille et al., 2007), sulfur isotope fractionation associated with the presence of sulfate (Kaufman et al., 2007), and extremely ^{12}C -enriched organic carbon consistent with microbes that oxidize methane with oxidants derived from O_2 or O_2 itself (Hayes, 1994; Hayes and Waldbauer, 2006). Although uncertain and controversial, organic biomarkers for cyanobacteria and steranes derived from steroids biosynthesized with O_2 are reported up to ~ 0.3 Gy before the rise of O_2 (Eigenbrode et al., 2008; Waldbauer et al., 2009). Conical stromatolites back to 2.7 Ga also indicate cyanobacterial production of O_2 through their disrupted, curled, and contorted laminae with enmeshed millimeter-scale bubbles (Bosak et al., 2009). Because one would need to dismiss all the earlier lines of evidence, the hypothesis of Kirschvink and Kopp (2008) has failed to garner much support in the Precambrian science community.

The idea that there was a pulse of burial of organic carbon arises from excursions in the carbon isotope record. Organic matter preferentially extracts the lighter isotope, ^{12}C , from the ocean so that seawater carbon, as recorded in marine carbonates, should become more ^{12}C -depleted (or higher in $\delta^{13}\text{C}$) if organic burial rates increase. Two or three $\delta^{13}\text{C}$ excursions in carbonates occur during the period 2.4–2.06 Ga, including the global 2.2–2.06 Ga ‘Lomagundi’ excursion, named after a district in Zimbabwe (now called Makonde) where ^{13}C -rich dolomites were first studied (Bekker et al., 2006, 2008; Maheshwari et al., 2010; Melezhik and Fallick, 2010; Melezhik et al., 2007; Schidlowski et al., 1976). Karhu and Holland (1996) suggested that the Lomagundi carbonates indicated a pulse in organic carbon burial that may have caused the rise of O_2 because of associated O_2 release via eqn [9]. However, improved radiometric dating shows that the Lomagundi excursion cannot have caused the GOE because it happened ‘after’ the GOE at ~ 2.4 Ga. Instead, the excursion is probably an effect of the rise of O_2 .

The remaining possibility (on the O_2 source side) is that there was a gradual increase of organic carbon burial. Whether or not this happened depends upon an interpretation of the somewhat noisy record of $\delta^{13}\text{C}$ in carbonates and organic carbon, for which there are differing views. One pioneering study suggested a secular increase in organic carbon burial fluxes based on boxcar averaging of the $\delta^{13}\text{C}$ time series (DesMarais et al., 1992). However, the averaging started at 2.6 Ga when very negative $\delta^{13}\text{C}$ for organic carbon ($\delta^{13}\text{C}_{\text{org}}$) occur. These anomalously low $\delta^{13}\text{C}_{\text{org}}$ values were subsequently attributed to methanotrophy (Hayes, 1994; Hayes and Waldbauer, 2006; Hinrichs and Boetius, 2002). If so, the $\delta^{13}\text{C}_{\text{org}}$ represents diagenetic processing in sediments rather than an isotopic balance involving global marine seawater. Another model concerns a gradual decrease of the uptake of ^{12}C -depleted carbon into hydrothermal carbonates from the early to late Archean, which would allow the fraction of organic carbon burial to increase within the constraints of the $\delta^{13}\text{C}$ record (Bjerrum and Canfield, 2004). This model assumes a gradient in the $^{13}\text{C}/^{12}\text{C}$ ratio between the surface and deep seawater from a ‘biological pump.’ However, of $\delta^{13}\text{C}$, measurements in 3.46 Ga seafloor do not show such a gradient (Nakamura and Kato, 2004). Nonetheless, analysis of the carbon isotope data can produce a quite

variable organic burial fraction over geologic time (see Chapter 6.8).

Continental shelves are places for burying organic carbon (Knoll, 1979), while continental weathering is a source of phosphorus, so some hypotheses of increasing organic burial tie organic burial to continental growth (Godderis and Veizer, 2000). Indeed, bursts of continental growth have been inferred from zircon U–Pb ages and speculatively linked to O_2 increases (Campbell and Allen, 2008). However, such bursts are probably artifacts of crustal preservation from supercontinent formation (Hawkesworth et al., 2009). Indeed, the present continental crust volume was probably reached by ~ 2 – 3 Ga (Hawkesworth et al., 2010), which, at least on the older end of these estimates, is 0.6 billion years before the GOE. For the younger end of this age range, the question is whether support is provided for a secular increase of organic burial by the $\delta^{13}\text{C}$ record or not.

6.7.4.2 Hypotheses for a Decreasing Sink of O_2

An alternative and fairly common interpretation of carbon isotopes is that there is no clear signal in the noisy record and that since 3.5 Ga, the average $\delta^{13}\text{C}$ value of marine carbonates has remained roughly constant at $\sim 0\text{‰}$, while the average $\delta^{13}\text{C}_{\text{org}}$ has been about -25‰ (Schidlowski, 1988). In this view, the fraction of carbon buried as organic relative to marine carbonate has remained roughly constant (Holland, 1984, 2002, 2009; Kump and Barley, 2007; Kump et al., 2001).

The fraction of carbon buried as organic carbon can be estimated from mass balance. On timescales exceeding $\sim 10^5$ years, which is the residence time of carbon on the ocean, the total amount of carbon entering the atmosphere–ocean system must balance the total amount leaving. Because the carbon is buried either as carbonate or organic carbon, the burial fractions of each type of carbon, f_{carb} and f_{org} , respectively, will sum to unity:

$$f_{\text{carb}} + f_{\text{org}} = 1 \quad [20]$$

Similarly, the input and output flux must balance for the isotopic composition of carbon, however one expresses it, whether a $^{13}\text{C}/^{12}\text{C}$ ratio or $\delta^{13}\text{C}$. So, in steady state, the isotopic composition of carbon input from mantle and riverine sources, $\delta^{13}\text{C}_{\text{in}}$, will equal the output, $\delta^{13}\text{C}_{\text{out}}$. One can expand eqn [20] to include the isotopic composition of organic matter, $\delta^{13}\text{C}_{\text{org}}$, and carbonates, $\delta^{13}\text{C}_{\text{carb}}$, as follows:

$$\begin{aligned} \delta^{13}\text{C}_{\text{in}} = \delta^{13}\text{C}_{\text{out}} &= f_{\text{org}}\delta^{13}\text{C}_{\text{org}} + f_{\text{carb}}\delta^{13}\text{C}_{\text{carb}} \\ &= f_{\text{org}}\delta^{13}\text{C}_{\text{org}} + (1 - f_{\text{org}})\delta^{13}\text{C}_{\text{carb}} = \delta^{13}\text{C}_{\text{carb}} - f_{\text{org}}\Delta_{\text{B}} \end{aligned} \quad [21]$$

Here, Δ_{B} is the difference between carbonate and organic carbon isotopic composition:

$$\Delta_{\text{B}} = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}} \quad [22]$$

Consider the $\delta^{13}\text{C}$ values in the earlier equations. Today, volcanic gases show that mantle carbon has $\delta^{13}\text{C}$ around -5‰ . This input value appears to have been constant over geologic time because ancient carbon in peridotitic xenoliths has $\delta^{13}\text{C}$ of about -5‰ (see Chapter 3.5), as does carbon in mantle-derived basalts and carbonatites (Mattey, 1987). Also, the riverine source from the weathering of organic carbon and carbonates

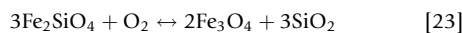
has a mean $\delta^{13}\text{C}$ value of about -5% as well (Holser et al., 1988). So, $\delta^{13}\text{C}_{\text{in}} \approx -5\%$. Marine sediments throughout geologic time have $\delta^{13}\text{C}_{\text{carb}} \approx 0\%$. While $\delta^{13}\text{C}_{\text{org}}$ has considerable scatter, it averages around -25% (Schidlowski, 1988). Thus, from eqn [22], one obtains $\Delta_B \approx 25\%$. Substituting this and other values into eqn [21], one has $-5\% = 0 - f_{\text{org}}(25\%)$. Solving for f_{org} one gets $f_{\text{org}} \sim 0.2$. Consequently, roughly 20% of incoming carbon is buried as organic carbon, while the remaining 80% fluxes out as carbonate carbon.

Given the relative constancy of average $^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ since 3.5 Ga, some have argued for relative constancy of the ratio of the burial rates of organic and carbonate carbon (Holland, 1984, 2002, 2009; Kump and Barley, 2007; Kump et al., 2001). On the other hand, others have interpreted the data to suggest a larger magnitude of Δ_B in the Archean. For example, Hayes and Waldbauer (2006) suggest that f_{org} was ~ 0.15 throughout much of Earth's history and rose to ~ 0.24 since 0.9 Ga. Canfield (2005) also favors lower f_{org} in the Archean (see also Chapter 6.8).

If there had been relative constancy of the organic burial fraction within the error bars of the data and oxygen photosynthesis arose before 2.7 Ga, then the only way that Archean O_2 could have remained a trace atmospheric gas is if there had been a large O_2 sink from a volcanic and metamorphic reductants (Catling et al., 2001; Holland, 2002; Kasting et al., 1993; Kump et al., 2001). Oxygen would have risen once the sink declined.

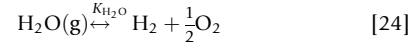
Following this line of logic, one group of hypotheses for the GOE suggests that there was a greater proportion of reducing gases in volcanic gases on the early Earth and that this fraction diminished in time. In other words, volcanic gases gradually became more oxidized (Holland, 2002; Kasting et al., 1993; Kump et al., 2001). Volcanic gases have a redox state that is controlled by the redox state of the mantle. Simply put, a more reducing mantle produces more reducing volcanic gases. So volcanic gases could have been more reducing in the Archean if the Archean mantle had been at a lower oxidation state than the Proterozoic mantle. However, analyses of redox-sensitive chromium and vanadium abundances in basalts (Canil, 2002; Delano, 2001; Li and Lee, 2004) indicate that the mantle's average oxidation state has remained roughly constant since ~ 3.5 Ga. This is somewhat surprising because it seems almost certain that the mantle has lost hydrogen to the atmosphere and then space (Catling et al., 2001; Kasting et al., 1993). However, the ability to lose reducing power and stay at the same oxidation state can be explained by the mantle's size and strong redox buffering (Lee et al., 2005).

The mantle redox state is expressed in terms of oxygen fugacity F_{O_2} . The term 'fugacity' generally represents the effective partial pressure of a gas in thermodynamic equilibrium with a particular mineral assemblage. But O_2 itself is not a gas species in rock. Instead, the dissociation of H_2O , CO_2 , and SO_2 or the reduction of Fe^{3+} supplies oxidizing power, for which F_{O_2} is a theoretical index of the redox state (Frost, 1991). Petrologists define various synthetic mineral assemblages to characterize oxygen fugacities. These assemblages do not exist in nature but are used to express an equivalent F_{O_2} for natural assemblages. A common synthetic assemblage is the quartz-fayalite-magnetite (QFM or FMQ) buffer:



The oxygen fugacity for this reaction is calculated as $F_{\text{O}_2} = 10^{-8.5}$, using a temperature- and pressure-dependent parameterization (Mueller and Saxena, 1977) with conditions appropriate for surface volcanism of 5 atm pressure and 1200 °C, or 1473.15 K (Holland, 1984).

Volcanic gases can be assumed to attain a redox state defined by the mantle oxygen fugacity. For example, the ratio of volcanic H_2 to steam will be determined by an equilibrium reaction as follows:



Here, $K_{\text{H}_2\text{O}}$ is an equilibrium constant defined through the following:

$$K_{\text{H}_2\text{O}} = \frac{F_{\text{H}_2} \times F_{\text{O}_2}^{0.5}}{F_{\text{H}_2\text{O}}} \Rightarrow r_{\text{H}_2} = \frac{F_{\text{H}_2}}{F_{\text{H}_2\text{O}}} = \frac{K_{\text{H}_2\text{O}}}{F_{\text{O}_2}^{0.5}} \quad [25]$$

In the second equality, r_{H_2} is ratio of the hydrogen and water fugacities, $F_{\text{H}_2}/F_{\text{H}_2\text{O}}$. Gibbs free energy values (available online from the US National Institute of Standards and Technology (NIST)) allow $K_{\text{H}_2\text{O}}$ to be calculated as 1.31×10^{-6} . Consequently, substituting $F_{\text{O}_2} = 10^{-8.5}$ in eqn [25], one derives a modern value of r_{H_2} as ~ 0.02 , which is similar to typical measured volcanic gas compositions (Holland, 1978). The geochemical studies mentioned earlier suggest that the average oxygen fugacity, F_{O_2} , in the Archean mantle differed from the modern mantle by no more than 0.3 \log_{10} units. If F_{O_2} were 0.3 \log_{10} units lower than $10^{-8.5}$, r_{H_2} would only increase to 0.03. Volcanic gases with $\sim 3\%$ of the hydrogen as H_2 compared to H_2O instead of $\sim 2\%$ today would make a negligible difference to the redox balance of the early atmosphere. Much larger changes in oxygen fugacity are necessary for significant effect. For example, if the Archean mantle F_{O_2} had been $10^{-11.5}$ atm, that is, 3 \log_{10} units lower than today's $10^{-8.5}$, about three-quarters of volcanic hydrogen would have been emitted as H_2 rather than water vapor, providing a huge sink for O_2 . But the geochemical data do not allow for such drastic F_{O_2} changes.

Although the mantle redox state has apparently remained roughly constant through time, it is still possible for the redox state of volcanic gases to have changed through other mechanisms. For example, consider the H_2/CO_2 flux ratio. The flux of H_2 is a sink on O_2 , whereas the flux of CO_2 is related to the O_2 source flux because O_2 derives from carbon fixation and subsequent organic burial. In terms of fugacities, one can write

$$\begin{aligned} \frac{\text{Volcanic flux of H}_2}{\text{Volcanic flux of CO}_2} &\approx \text{fugacity ratio} = \left(\frac{F_{\text{H}_2}}{F_{\text{H}_2\text{O}}} \right) \left[\frac{F_{\text{H}_2\text{O}}}{F_{\text{CO}_2}} \right] \\ &\approx r_{\text{H}_2} \left[\frac{\text{H}_2\text{O flux}}{\text{CO}_2 \text{ flux}} \right] \end{aligned} \quad [26]$$

From eqn [26], one can see that if the flux ratio of $\text{H}_2\text{O}/\text{CO}_2$ through volcanoes changed in the past, the gas flux ratio of H_2/CO_2 would change even if r_{H_2} (the ratio of fugacities $F_{\text{H}_2}/F_{\text{H}_2\text{O}}$) had remained constant. Holland (2009) has put forward the hypothesis that carbon accumulated in the surface reservoir over time from outgassing so that the $\text{H}_2\text{O}/\text{CO}_2$ flux ratio through volcanoes decreased. In that case, the proportion of H_2 relative to the carbon outgassing would have been greater in the past, providing a larger sink on O_2 . Holland also suggests

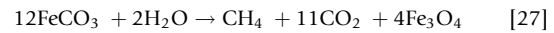
that the $\text{SO}_2/\text{H}_2\text{O}$ flux ratio increased with time because of greater geologic cycling of sulfur. Certainly, after sulfate became abundant, subduction recycling of sulfur should have increased because people know that some seawater sulfur cycles through subduction zone volcanoes today. However, increased sulfur cycling is probably a positive feedback of the GOE, rather than its cause, because marine sulfate derives from the oxidation of sulfide. The history of carbon cycling is more complex. Some carbon cycle models establish a maximum surface reservoir of carbon by about 3 Ga (Zahnle and Sleep, 2002), which is much earlier than the GOE but there are many variables in such models.

Kump and Barley (2007) provide an alternative way to effect a change in the redox properties of volcanic gases. They suggest that the predominant style of volcanism evolved from submarine to subaerial. Submarine volcanism has a large area of relatively low-temperature, off-axis emissions that are more reducing than gases from high-temperature subaerial volcanism. Also, if there were shallower mid-ocean ridges, thermodynamics predicts a larger Fe^{2+} flux from hydrothermal vents compared to today, especially when seawater is depleted in sulfate (Kump and Seyfried, 2005). Today, the subaerial volcanic sink on O_2 is twice that of the submarine volcanic gas. Together, the subaerial and submarine volcanic sinks are a factor of ~ 4 smaller than the O_2 flux released from organic burial according to inventories in Table 2 versus Table 1. So the proposal of Kump and Barley (2007) requires large changes in the balance of volcanic emissions between subaerial and submarine. Another proposal on a similar theme is that the change in degassing pressure between submarine and subaerial volcanism shifted the redox state of the gases, based on model calculations (Gaillard et al., 2011). However, gas composition is sensitive to temperature, so the effect of reequilibration with lower-temperature surroundings as gases emerge from magmas requires further investigation.

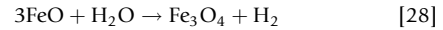
A final and similar idea for a decreasing sink on O_2 is that the proportion of reducing gases in the metamorphic gas flux decreased from the Archean to the Proterozoic (Catling et al., 2001; Claire et al., 2006). Such gases, by definition, arise from

regions in the crust that do not melt, and so, they are not constrained by the mantle redox.

A couple of chemical examples show how the crust could have lost hydrogen and become progressively oxidized. Some Archean BIFs (see Chapter 6.6) contain siderite (FeCO_3), which decomposes to magnetite during thermal metamorphism, as follows (McCollom, 2003):



In addition, serpentinization in hydrothermal systems generates hydrogen, which can be written schematically as



Methane is often released from rocks where such serpentinization occurs because microbes convert the hydrogen into methane (Chapelle et al., 2002; Sherwood Lollar et al., 2006). Serpentinization certainly occurred in Archean greenstone belts, which are elongate regions with an abundance of altered mafic to ultramafic igneous rocks. In eqns [27] and [28], ferrous iron is oxidized to ferric iron and hydrogen-bearing gas is released. In the anoxic Archean atmosphere, high levels of methane or hydrogen would have necessarily caused a significant flux of hydrogen to escape to space (see Section 6.7.2.1). Subsequent metamorphic processing of the more oxidized crust would produce less reducing metamorphic gases as a matter of Le Chatelier's principle during each geologic cycle.

The proposal that the crust oxidized as a result of hydrogen loss is supported by inventories of oxidized and reduced species in the continental crust (Figure 4). If photosynthesis were solely responsible for the oxidation state of the crust, the number of moles of excess oxygen in ferric iron, sulfate, and free oxygen should be balanced by an equal number of moles of organic carbon (see eqn [9]). The continental crust, ocean, and atmosphere contain $\sim 2.5 \times 10^{21}$ mol of excess O_2 equivalents (Catling et al., 2001), which is mostly in the form of ferric iron that started out as ferrous iron. However, the quantity of reduced carbon in the crust is much smaller,

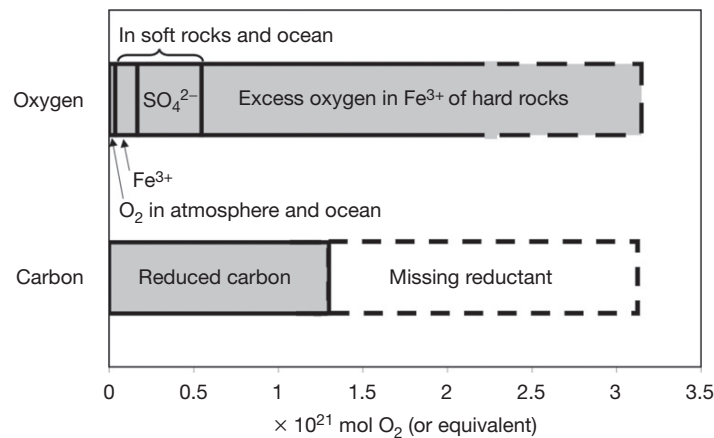


Figure 4 The inventory of oxygen in the Earth's crust. 'Hard rocks' are high-grade metamorphic rocks and igneous rocks. 'Soft rocks' are sedimentary rocks. The imbalance between oxygen and reduced carbon shows that there is a missing reductant (based on tabulated values in Catling et al., 2001 and references therein).

$<1.3 \times 10^{21}$ mol (Wedepohl, 1995). Hydrogen escape to space is a plausible explanation for the missing reductant because the expected quantity of oxidation is the correct size. If the concentration of methane in the Archean atmosphere had been $\sim 10^3$ ppmv, as calculated in photochemical models, the hydrogen escape rate would have been $\sim 7 \times 10^{12}$ mol O_2 year $^{-1}$ from the theory of Section 6.7.2.1. Over 0.4 by, the escape of hydrogen at this rate would produce an irreversible quantity of 2.8×10^{21} mol O_2 equivalents – more than enough to account for the oxidation of the crust. Extra oxidation could have been taken up by the mantle with little effect on its overall redox state.

The overall result of a decline in the proportion of reducing gases in volcanic or metamorphic gases is the same: a transition to an oxic atmosphere. Claire et al. (2006) describe results of a box model that tracks the comings and goings of redox fluxes in the Earth system. The model includes parameterized photochemistry that allows calculation of the concentrations of atmospheric O_2 and methane. In this box model, crustal fugacity controls the oxidation state of metamorphic gases and, for numerical simplicity, the model converts organic carbon to Fe^{2+} equivalents via a process of greenschist metamorphism, $6Fe_2O_3 + C \rightarrow 4Fe_3O_4 + CO_2$. The model can be run assuming either that the volcanic gas sink diminished or that the metamorphic gas sink declined. Figure 5 shows that either scenario can generate an oxic transition. Common characteristics of such models are that there is negligible oxidative weathering prior to the GOE and

that a transition to an oxic atmosphere occurs when K_{oxy} (as defined in eqn [12]) reaches unity.

6.7.5 Changes in Atmospheric Chemistry and Climate Associated with the Rise of O_2

6.7.5.1 The Collapse of Methane at the GOE

Earlier (Section 6.7.3.2), we discussed the possibility that a collapse of atmospheric methane levels was responsible for Paleoproterozoic glaciation. This would be consistent with increasing oxidation in the Earth system, particularly greater concentrations of sulfate in the ocean and diminished methane fluxes to the atmosphere as a result of methanotrophy using sulfate (Catling et al., 2007).

One can consider the biogeochemistry and associated atmospheric change in more detail. In the Archean microbial ecosystem models of Kasting et al. (2001) and Claire et al. (2006), the key redox-sensitive biogenic gases emitted to the atmosphere are O_2 and CH_4 . Once oxygenic photosynthesis arose, it was the main source of sedimentary organic matter, which could be fermented by a consortium of microbes to make methane. The net reaction can be deduced as follows:

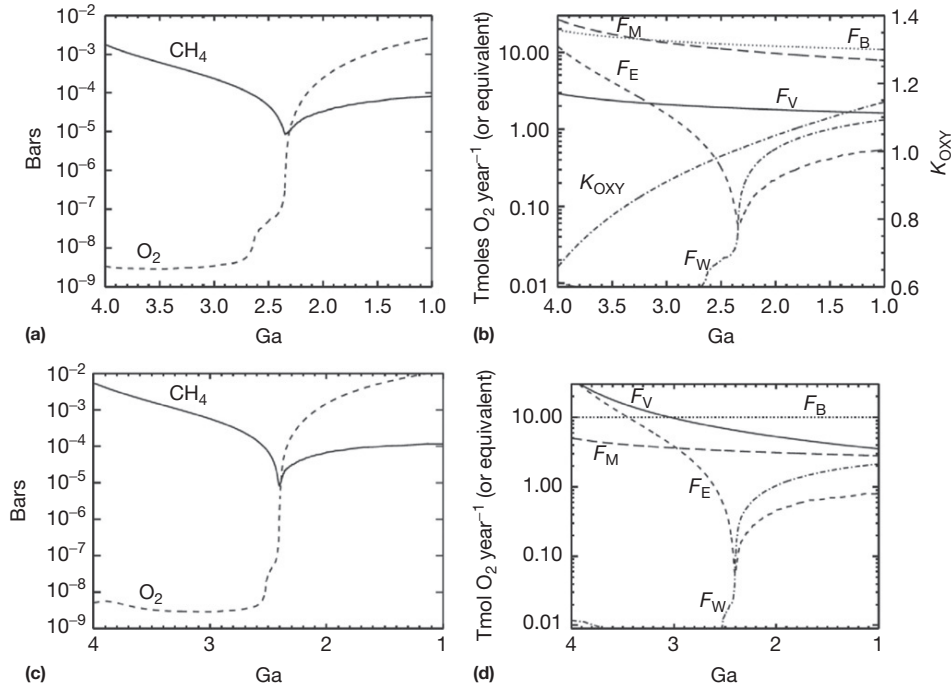
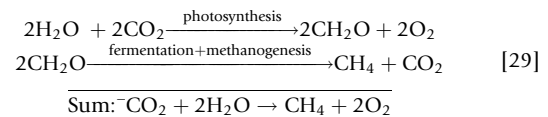


Figure 5 Results from the box model of Claire et al. (2006). (a, b) The upper row shows the results when the model assumes that metamorphic reducing gases are the primary sink on Archean O_2 . (c, d) The lower row shows results where the model assumes that volcanic gases are the main O_2 sink. Qualitatively, there is no difference to the results from either assumption. Fluxes are as follows: F_W = continental oxidative weathering, F_E = hydrogen escape to space, F_V = volcanic sink, and F_M = metamorphic sink. K_{oxy} is the oxygenation parameter defined in the text, which reaches unity when the atmosphere goes through its 'Great Oxidation Event' (GOE).

Thus, oxygenic photosynthesis followed by fermentation and methanogenesis produces fluxes of O_2 (ϕ_{O_2}) and CH_4 (ϕ_{CH_4}) in the ratio $\phi_{O_2}/\phi_{CH_4} = 2$. Of course, methane is a relatively inert molecule, whereas O_2 reacts with a plethora of gases and soluble cations, particularly on a reducing early Earth. Consequently, one would not expect a simple 2:1 mutual destruction of O_2 and CH_4 but rather an atmosphere with negligible O_2 and relatively abundant methane, as data and models suggest. However, once standing pools of oxidants, such as marine sulfate, became more available, ϕ_{CH_4} should have dropped relative to ϕ_{O_2} because of methanotrophy (Valentine, 2002).

Photochemical models show that when the ϕ_{O_2}/ϕ_{CH_4} flux ratio increases, an atmosphere can flip to a permanently oxidic state. Figure 6 shows the results of a photochemical model, which was run as a thought experiment. In this model, the ground-level methane abundance was held constant at 100 ppmv, while the ground-level O_2 mixing ratio was increased. The model calculated the fluxes of CH_4 and O_2 needed to maintain the prescribed atmosphere. This model used fixed outgassing fluxes of ~ 1 Tmol S year⁻¹ (with SO_2/H_2S in 10:1 ratio), 2.7 Tmol H_2 year⁻¹, and 0.3 Tmol CO year⁻¹. This outgassing sink on oxygen adds up to only ~ 2.15 Tmol O_2 year⁻¹, but one can think of it as a net flux that ignores the zero sum of an organic burial flux that would be of order ~ 10 Tmol O_2 year⁻¹ and a complementary ~ 10 Tmol O_2 year⁻¹ geologic gas sink. Figure 6 also shows the rainout fluxes of SO_4^{2-} and S_8 aerosols generated by the photochemistry. When the O_2 mixing ratio increases above 10^{-6} , that is, >1 ppm, one sees that the S_8 fallout flux drops off, which one interprets as related to the loss of MIF of sulfur isotopes (as described in Section 6.7.3.1). The plus symbols (+) indicate the ϕ_{O_2}/ϕ_{CH_4} flux ratio, which maps to the right-hand vertical axis. In Figure 6, shaded regions require biogenic fluxes that Zahnle et al. (2006) argue are

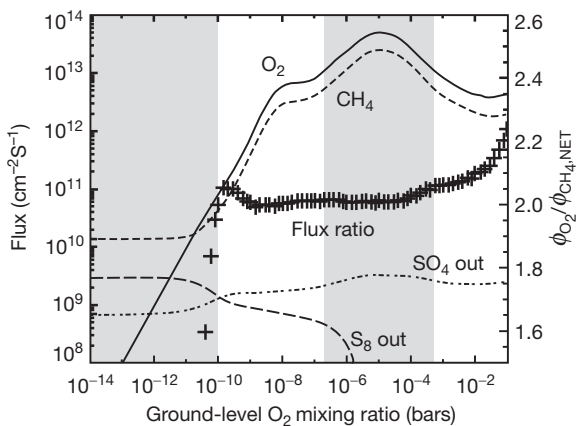
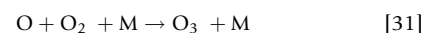
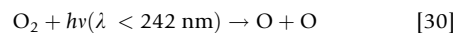


Figure 6 Atmospheric fluxes of chemical species as a function of the ground-level O_2 mixing ratio. Mixing ratio is equivalent to a partial pressure in bars for a 1 bar atmosphere. Results are shown from a photochemical ‘thought experiment’ where the ground-level CH_4 mixing ratio is fixed to 100 ppmv and volcanic outgassing fluxes of sulfur gases and reducing gases are also fixed (see text). Plus symbols (+) map to the right-hand vertical axis and show the net ratio of the biogenic O_2 flux (ϕ_{O_2}) to CH_4 flux (ϕ_{CH_4}) as a function of the ground-level O_2 mixing ratio. The shaded regions represent cases when the biogenic O_2 fluxes are either implausibly high or low (from Catling et al., 2007).

unreasonable. On the anoxic part of the graph, ϕ_{O_2}/ϕ_{CH_4} is ~ 2 but not precisely because there are fluxes of redox-sensitive rainout species, principally hydrogen peroxide and formaldehyde, which have to be tallied up to describe the atmosphere’s redox budget precisely. Nonetheless, examination of Figure 6 shows that oxidic solutions on the right have higher ϕ_{O_2}/ϕ_{CH_4} ratios than the anoxic solutions on the left. But the change is not much. An increase in the flux ratio ϕ_{O_2}/ϕ_{CH_4} of less than 3% creates a flip between an anoxic atmosphere with O_2 mixing ratio $\leq 2 \times 10^{-7}$ and an oxidic atmosphere with O_2 mixing ratio $\geq 6 \times 10^{-4}$. Effectively, the increase in ϕ_{O_2}/ϕ_{CH_4} is equivalent to creating an imbalanced O_2 source where O_2 source exceeds the outgassing flux of reductants.

6.7.5.2 The Formation of an Ozone Shield

After the GOE, the Earth was protected from shortwave ultraviolet by a stratospheric ozone layer. Stratospheric ozone (O_3) is derived from molecular oxygen. The photolysis of O_2 in the stratosphere produces oxygen atoms, which then combine with other O_2 molecules to make ozone, as follows:



In eqn [31], ‘M’ is any air molecule – usually the most abundant one, N_2 . ‘M’ removes energy liberated by the reaction, which is dissipated in molecular collisions. Ozone atoms formed in eqn [31] are able to absorb ultraviolet photons when they photolyze. Such absorption protects the Earth’s surface from the biologically harmful range of ultraviolet wavelengths of 200–300 nm.

The ozone column abundance, that is, the number of molecules above a unit area of the Earth’s surface, is related to how much UV can be absorbed. This column abundance has a nonlinear dependence on O_2 levels. Figure 7 shows the results of photochemical modeling (Kasting and Donahue, 1980). A relatively minor O_2 concentration $\geq 1\%$ of the modern atmospheric level is sufficient to generate an ozone column that protects the surface from harmful ultraviolet. Thus, the small amount of O_2 expected after the GOE was enough to give rise to significant ozone shielding. This presumably would have expanded ecological niches for land-based life.

6.7.6 Conclusions

The concentration of an atmospheric gas is controlled by a kinetic competition between its production and loss. The GOE occurred because there was an imbalance between the O_2 source flux and the O_2 sink flux, which led to an accumulation of O_2 in the atmosphere. Several lines of evidence suggest that O_2 was being produced several hundred million years before the GOE at 2.4 Ga (see Chapter 6.4). However, the Archean atmosphere would have remained anoxic if O_2 consumption fluxes exceeded the long-term source of O_2 from the flux of organic carbon burial. In an anoxic atmosphere, the loss of O_2 to continental oxidative weathering is negligible, so the dominant sinks on O_2 in the Archean must have been reactions with volcanic and metamorphic reductants, including reducing gases (H_2 , CH_4 , CO, SO_2 , and H_2S) and dissolved reducing cations (e.g., Fe^{2+}) in direct communication with the atmosphere. A ‘tipping point’

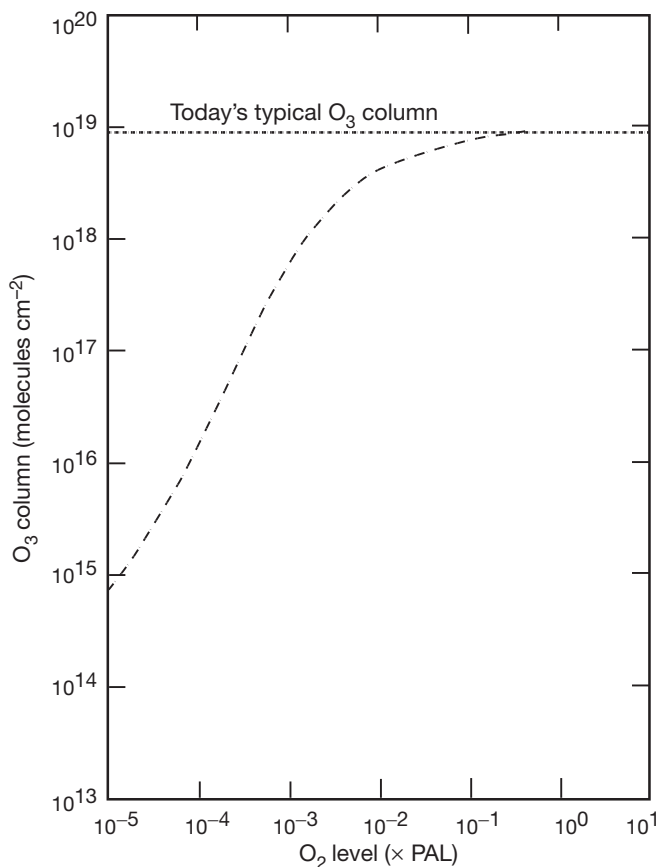


Figure 7 The ozone (O_3) column abundance shown as the dashed line as a function of the concentration of ground-level atmospheric oxygen. The O_2 level is expressed as a ratio to the present atmospheric level (PAL). Today's typical ozone column abundance is shown as a dotted line. The ozone layer's protective absorption of biologically harmful ultraviolet radiation becomes significant at $\sim 10^{-2}$ PAL.

would have been reached when the flux of O_2 from organic carbon burial exceeded the O_2 loss to volcanic and metamorphic sinks. After the GOE, oxidative weathering was a significant new sink on O_2 and helped set its new level.

In the redox chemistry of the atmosphere, hydrogen-bearing reduced gases (such as CH_4 and H_2) are the chemical adversaries of O_2 . When the concentration of one goes up, the other declines, and vice versa. Photochemical reactions cause rapid mutual annihilation between O_2 and the reducing gases. In general, people expect the redox chemistry of the pre-GOE atmosphere to have been dominated by methane and hydrogen (even though they were both probably at levels below a percent), whereas O_2 would have been a trace gas at less than 1 ppmv. It is opposite to the redox control in the modern atmosphere. Models suggest that the GOE occurred when the rate of supply of reduced gases to the atmosphere dropped below the O_2 flux to the atmosphere (Claire et al., 2006; Goldblatt et al., 2006; Holland, 2009).

The GOE appears in the rock record at the same time as global cooling. In detailed models of the GOE, there is a decline in the supply of reducing gases prior to the GOE, which means that the methane concentration in the pre-GOE atmosphere falls to low levels even before O_2 rises to a substantial concentration (Zahnle et al., 2006). The loss of

greenhouse gases such as methane and its photochemical product, ethane, is plausibly responsible for global cooling at ~ 2.4 Ga. It is possible that the global climate and atmospheric composition oscillated until conditions of permanent oxygenation were established, which would account for multiple glaciations during 2.45–2.22 Ga.

Moderate levels of O_2 established in the Proterozoic (probably somewhere between 0.2% and 2% O_2 by volume) were sufficient to establish a stratospheric ozone (O_3) layer (Kasting and Donahue, 1980) and protect the Earth's surface from harmful ultraviolet in the range 200–300 nm. A counter-intuitive effect of the ozone layer was to decrease the net reaction rate in the troposphere between methane and oxygen. Provided that methane fluxes were still relatively large from a poorly oxygenated and euxinic Proterozoic ocean, methane should have risen after the GOE to be a moderately significant greenhouse gas during middle Proterozoic.

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