The loss of mass-independent fractionation in sulfur due to a Palaeoproterozoic collapse of atmospheric methane

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ABSTRACT
We use a 1-D numerical model to study the atmospheric photochemistry of oxygen, methane, and sulfur after the advent of oxygenic photosynthesis. We assume that mass-independent fractionation (MIF) of sulfur isotopes – characteristic of the Archean – was best preserved in sediments when insoluble elemental sulfur ($S_8$) was an important product of atmospheric photochemistry. Efficient $S_8$ production requires three things: (i) very low levels of tropospheric $O_2$; (ii) a source of sulfur gases to the atmosphere at least as large as the volcanic $SO_2$ source today; and (iii) a sufficiently high abundance of methane or other reduced gas. All three requirements must be met. We suggest that the disappearance of a strong MIF sulfur signature at the beginning of the Proterozoic is better explained by the collapse of atmospheric methane, rather than by a failure of volcanism or the rise of oxygen. The photochemical models are consistent in demanding that methane decline before $O_2$ can rise (although they are silent as to how quickly), and the collapse of a methane greenhouse effect is consistent with the onset of major ice ages immediately following the disappearance of MIF sulfur. We attribute the decline of methane to the growth of the oceanic sulfate pool as indicated by the widening envelope of mass-dependent sulfur fractionation through the Archean. We find that a given level of biological forcing can support either oxic or anoxic atmospheres, and that the transition between the anoxic state and the oxic state is inhibited by high levels of atmospheric methane. Transition from an oxygen-poor to an oxygen-rich atmosphere occurs most easily when methane levels are low, which suggests that the collapse of methane not only caused the end of MIF S and major ice ages, but it may also have enabled the rise of $O_2$. In this story the early Proterozoic ice ages were ended by the establishment of a stable oxic atmosphere, which protected a renewed methane greenhouse with an ozone shield.

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INTRODUCTION
Mass-independent fractionation (MIF, or nonzero $\Delta^{33}S$) of stable sulfur isotopes is widely recognized as a defining geological signature of the Archean Earth, even though the origin of the signal remains somewhat obscure. What is striking about the isotopic signature is that (i) it exists at all; (ii) the signal is strong through much of the Archean; and (iii) the strong signal seems to disappear abruptly ca. 2.45 Ga (Farquhar et al., 2000; Farquhar & Wing, 2003; Bekker et al., 2004; Papineau et al., 2005), just before a set of severe ice ages began, and somewhat before the classic indicators of an anoxic atmosphere disappeared and the classic indicators of an oxic atmosphere appeared (Cloud, 1968, 1988; Walker, 1977; Walker et al., 1983; Kasting, 1993; Holland, 1999, 2002; Canfield, 2005; Catling & Claire, 2005). A much weaker MIF signal lingered on for some 400 Myr (Farquhar et al., 2003; who call the middle interval Stage 2), but clearly something changed abruptly and permanently.

Leading interpretations of the end of MIF stress the rise of $O_2$ as the cause (Farquhar et al., 2000; Pavlov & Kasting, 2002; Ono et al., 2003). These arguments are based on considerations of atmospheric photochemistry that will be discussed in detail below. The earlier consensus had placed the rise of $O_2$ at 2.2 or 2.3 Ga (cf. Holland, 1999, 2002), some 200 Myr after MIF $S$ disappeared. The old chronology was strongly
influenced by a pronounced and long-lasting excursion in carbonate $\delta^{13}$C values between 2.05 and 2.25 Ga (Des Marais et al., 1992; Karhu & Holland, 1996). The isotope excursion has been widely interpreted as a major carbon burial event that in some sense caused the rise of O$_2$ (Karhu & Holland, 1996). Whether there truly was a 200 Myr delay between the end of Stage 1 and the advent of an oxic atmosphere seems debatable, because the dates are uncertain and because the sedimentary record has been compromised by the ice ages (Farquhar & Wing, 2005). Nevertheless, the apparent mismatch between the two chronologies raises questions about why MIF S stopped when it did.

Known mechanisms for generating MIF signals require gas phase photochemistry stemming from the ultraviolet (UV) photolysis of SO$_2$ (Farquhar et al., 2001). Laboratory experiments show that SO$_2$ photolysis at 193 nm generates a strong MIF signal in the photolysis products and that 248 nm does not (Farquhar et al., 2000). Farquhar et al. (2001) hypothesized that the major source of the MIF signal is the photodissociation of SO$_2$ to SO and O, a channel that cuts off at 220 nm. More recent laboratory work suggests that MIF S can occur at wavelengths somewhat longer than 220 nm through excited states of SO$_2$ (Masterson et al., 2006).

In an oxic atmosphere, photons longer than 200 nm are chiefly absorbed by ozone. However, ozone is not extremely opaque to 200 < $\lambda$ < 220 nm; this is a spectral window between much stronger absorption at shorter wavelengths by water and CO$_2$ and at longer wavelengths by ozone. Consequently, it requires a considerable column of ozone, approaching modern levels, to fully suppress MIF-generating SO$_2$ photolysis. This in turn requires a considerable amount of O$_2$, on the order of 0.01 PAL (Kasting & Donahue, 1980; PAL means Present Atmospheric Level). We therefore would expect MIF S to persist in atmospheric gases until the atmosphere became mildly aerobic (Farquhar & Wing, 2005). Even today nonzero $\Delta^{34}$S is found in some Antarctic ices, where it derives from stratospheric photochemical processing of volcanic gases and where competition from other sulfur sources is small (Savarino et al., 2003).

In the discovery paper, Farquhar et al. (2000) pointed out that the observed sedimentary signature of MIF S is best explained by separating the photochemically processed sulfur into water-soluble and water-insoluble fractions. Separate soluble and insoluble channels have the additional advantage of discouraging the sulfur from pooling in the oceans, where the various S-containing species would mix back together and the MIF signature would be diluted or lost (Pavlov & Kasting, 2002). Pavlov & Kasting (2002) suggested that the key vector was elemental sulfur (S$_8$), which is insoluble and which photochemical modelling indicates a major product of sulfur photochemistry in oxygen-poor atmospheres (Kasting et al., 1989). Pavlov & Kasting (2002) computed that O$_2$ levels as low as 10$^{-5}$ PAL (2 ppmv) would shut off S$_8$ production and thus prevent MIF S from reaching the sediments.

A potential problem with Pavlov & Kasting’s (2002) result is that their model was not capable of treating atmospheres with intermediate levels of oxygen. Instead they used separate photochemical models for high and low oxygen levels. The two models do not meet in the middle. Unfortunately it is precisely in this unexplored space in the middle that S$_8$ production shuts off. We have therefore decided to revisit the S$_8$ production threshold using a model that does not have this problem.

In this study we accept the hypothesis that MIF S records the precipitation of S$_8$ from the atmosphere. However, we will show that S$_8$ production shuts off well before the atmosphere becomes oxic. In keeping with our focus on the rise of oxygen, we restrict our discussion to Earth after the origin of oxygenic photosynthesis.

**THE PHOTOCHEMICAL MODEL**

For our numerical experiments we used an updated version of the 1-D diffusive photochemical code originally developed by Kasting et al. (1989) to study sulfur photochemistry on early Earth. The version used here includes 46 chemical species that participate in 206 chemical reactions. As we will consider only atmospheres with more CO$_2$ than CH$_4$, hazes do not form (Zahnle, 1986), and so we truncate hydrocarbon chemistry at C$_2$H$_6$. Vertical transport occurs by eddy transport. H$_2$ and H also flow upward by molecular diffusion. The equations solved are

$$\frac{dN_i}{dt} = P_i - L_i N_f - \frac{\partial\phi_i}{\partial z}$$

and

$$\phi_i = b_{ia} f_i (H_a^{-1} - H_i^{-1}) - (b_{ia} + KN) \frac{df}{dz}$$

where $N$ is the atmospheric density; $f_i$ is the mixing ratio of the (minor) species $i$; $P_i - L_i N_f$ are the chemical production and loss terms, respectively; $\phi_i$ is the upward flux of species $i$; $b_{ia}$ is the binary diffusion coefficient between $i$ and the background atmosphere $a$; $H_a$ and $H_i$ are the scale heights of the background atmosphere and of species $i$; and $K$ is the eddy diffusion coefficient.

**General model assumptions**

Steady-state solutions are obtained for an average sun angle of 50°. The surface temperature is set to 284 K, the tropopause is at $z_{tr} = 11$ km, and the stratosphere is isothermal at 186 K. Tropospheric water vapor follows the Manabe-Wetherald (1967) relative humidity profile. The eddy diffusivity is set to 10$^6$ cm$^2$ s$^{-1}$ in the troposphere and to 10$^5$ (p$_{tr}$/p($z$))$^{0.5}$ cm$^2$ s$^{-1}$ in the stratosphere. To take some account of the higher activity of the Sun ca. 2.5 Ga, UV at wavelengths longer than 175 nm is doubled over today and UV at wavelengths shorter than
175 nm is quadrupled (Ribas et al., 2005). The surface pressure is set to 1 bar of N₂. The CO₂ mixing ratio is set at 1%. The top of the model is at 80 km. Results are not very sensitive to any of these assumptions.

**Sulfur chemistry**

Sulfur is injected into the atmosphere abiogenically as volcanic gases, chiefly SO₂ and H₂S, and it enters the atmosphere biogenically chiefly as CH₃SCH₃ (dimethyl sulphide, usually written ‘DMS’), OCS, and CS₂ (Toon et al., 1987). Our model does not yet include CS₃, DMS and their photochemical products. These gases are important when the biogenic sulfur source is strong, as seems likely for the late Archean and early Proterozoic. DMS in particular is thought to be produced exclusively by eukaryotic phytoplankton (Charlson et al., 1987). A more complete accounting of the sulfur cycle that takes biogenic sources into account is clearly desirable but fell beyond the scope of this study.

In today’s oxic atmosphere, S is either rained out as SO₂ or it is oxidized to SO₃, which after prompt reaction with H₂O precipitates as sulfuric acid (H₂SO₄). In a more reduced ancient atmosphere, sulfur can take any oxidation state from −2 to +6 (Kasting et al., 1989). As today, S can exit the atmosphere as SO₂ or H₂SO₄, but there are more reduced options as well. Most S-containing species are moderately soluble (SO₂, H₂S, OCS, CS₂) and can be washed out of the atmosphere in rain. If the atmosphere is sufficiently reducing and the sulfur source big enough, elemental sulfur particles can form and precipitate (Kasting et al., 1989; Pavlov & Kasting, 2002; Ono et al., 2003).

The model includes rainout of soluble species in proportion to their presence in raindrops. The model also includes sulfuric acid aerosols and elemental sulfur particles. H₂SO₄ condenses when its saturation vapor pressure is exceeded; the H₂O/H₂SO₄ ratio of the particles is self-consistently predicted. Elemental sulfur particles can form when photochemically produced HS and S combine to form S₂. The S₂ can polymerize to form longer chains (the model uses only S₂ and S₄). Polymerization is assumed to stop at the stable ring molecule S₈, which is then assumed to immediately condense. Kasting et al. (1989), Kasting (1990), and Pavlov et al. (2001) describe in more detail how rainout, aerosol formation and deposition are implemented.

**Redox**

The model cannot explicitly conserve H or O because tropospheric water vapor is set by evaporation and precipitation of what is in effect an infinite ocean of water. However, the difference between H₂ and O – the redox – is conserved, and it is imperative that it be conserved in a model that purports to compute the redox state of the atmosphere.

It is convenient to define H₂O, N₂, CO₂, and SO₂ as the redox neutral gases. These are the most important volcanic gases for H, N, C, and S, respectively. The redox state of the atmosphere can be defined as the number of extra O atoms minus half the number of extra H atoms. For example, with this definition, H₂SO₄ has a redox state of +1 (H₂SO₄ = H₂O + SO₂ + O), and HCO has a redox state of −1.5 (HCO = CO₂ + 1/2 H₂O − 3/2 O). Minor volcanic gases, such as CO, H₂, and H₂S, are reducing. By assumption the major biogenic gases are CH₄ and O₂, the former strongly reducing and the latter strongly oxidizing. Other important terms in the atmosphere’s redox budget include precipitation of S₈ and H₂SO₄ aerosols; rainout of soluble species, especially H₂CO and H₂O₂; and hydrogen escape to space.

Redox conservation is one of the best tests of how credibly the photochemical code performs and consequently it has been the focus of a great deal of development effort. The photochemical code used here always maintains redox conservation to better than 10 ppb, and usually to better than 10 ppt, when the O₃ source is significant. This is excellent performance. The code does not perform as well when the O₂ source is negligible, as would have been the case before the advent of oxygenic photosynthesis. In this study we use the code only in regimes in which it performs extremely well.

**Hydrogen escape**

We treat hydrogen escape using diffusion-limited flux. Diffusion-limited escape makes the single assumption that escape is easy for hydrogen once it has diffused through the lower, well-mixed atmosphere. This is a good approximation for Earth today. The upper boundary condition is implemented by setting an escape velocity at the top of the computational grid. In diffusion-limited flux the effusion velocity at the top of the grid is

\[ v_e = \frac{\dot{H}_e}{N(H^{-1}_e - H^{-1}_i)}. \]  (3)

Equation 3 is readily derived from Equation 2 in the limit that \( \partial/\partial z \to 0 \) (e.g. Walker, 1977). In diffusion-limited escape with modern volcanic degassing fluxes and no biology, the H₂ mixing ratio would be on the order of 100–1000 ppmv, depending on the exuberance of the volcanic flux.

It has recently been suggested that the hydrogen escape rate might have been much lower than the diffusion-limited flux (Tian et al., 2005). The Tian et al. (2005) model makes several assumptions that suppress H escape, the most important of which is to assume that the thermosphere was cold. The motivation for their model is that the thermospheres of Venus and Mars – both of which have CO₂ atmospheres – are cool. In our opinion Tian et al. (2005) have not made a convincing case against diffusion-limited flux for Earth (Catling, 2006).

**Lower boundary conditions**

Minor gases are treated assuming deposition velocities (in many cases set to zero, but these do not matter much because
they are minor). The important lower boundary conditions are those for which the lower boundary is (or can be) an important source. In our model these species are \( \text{O}_2 \), \( \text{CH}_4 \), \( \text{H}_2 \), \( \text{CO} \), \( \text{SO}_2 \), and \( \text{H}_2\text{S} \). For most of the numerical experiments discussed in this study we have used constant mixing ratio boundary conditions for \( \text{CH}_4 \) and \( \text{O}_2 \), and constant flux boundary conditions for important volcanic gases \( \text{H}_2\text{S}, \text{H}_2, \) and \( \text{CO} \). Kasting et al. (1989) argued that dissolution of \( \text{SO}_2 \) into the ocean was a major sink for \( \text{SO}_2 \). To allow for surface deposition of \( \text{SO}_2 \), we distributed the volcanic \( \text{SO}_2 \) source over the troposphere and lower stratosphere; this is also more in keeping with the nature of volcanic eruptions. Numerical experiments using flux boundary conditions on \( \text{CH}_4 \) and \( \text{O}_2 \) provide a different perspective on the relative likelihood of different atmospheres, but as a practical matter constant mixing ratio boundary conditions are computationally more robust and better suited to generating suites of output.

We also consider two alternative sets of lower boundary conditions on \( \text{H}_2 \) and \( \text{CO} \). One set is simply to impose low mixing ratios at the surface (10 ppmv for \( \text{H}_2 \) and 1 ppmv for \( \text{CO} \) that implicitly presume voracious biological consumption. A second set is to impose deposition velocities at the surface that take into account the rate that gases can cross the air–water interface. Kharecha et al. (2005) suggest \( \nu_{\text{dep}} = 2.5 \times 10^{-4} \text{cm s}^{-1} \) for \( \text{H}_2 \) and \( \nu_{\text{dep}} = 1.2 \times 10^{-4} \text{cm s}^{-1} \) for \( \text{CO} \). To include either of these alternatives as LBCs requires distributing the volcanic source. We distribute that source in the same way that we distribute volcanic \( \text{SO}_2 \). Numerical experiments indicate that model results are insensitive to the lower boundary conditions on \( \text{H}_2 \) and \( \text{CO} \) save where the biogenic \( \text{O}_2 \) and \( \text{CH}_4 \) sources are small.

**Volcanic sources**

We consider three sets of volcanic fluxes, which we call ‘low modern’, ‘high modern’, and ‘high Archean’. We denote these cases V1, V2, and V3, respectively. These cases are summarized in Table 1. In practice the important role of volcanic gases in these simulations is that they are the source of S-containing gases to the atmosphere. The role of volcanic gases in governing the redox state of the atmosphere – crucial to dead planets – is questionable on a living world, and as a practical matter our numerical simulations are not very sensitive to \( \text{CO} \) and \( \text{H}_2 \) volcanic fluxes.

For \( \text{H}_2 \) we use a low modern flux of \( 2 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \) (\( \approx 5 \times 10^{11} \text{mol year}^{-1} \)), as recommended by Sleep & Bird (2006). This estimate includes arc volcanoes and a serpentinitization source of the same magnitude. The arc flux is based on the rate that hydrous minerals in ocean basalts are subducted and a volcanic QFM \( \text{H}_2 / \text{H}_2\text{O} \) ratio of 0.02. Pavlov & Kasting (2002) used a much higher \( \text{H}_2 \) flux of \( 2.5 \times 10^{10} \text{cm}^{-2} \text{s}^{-1} \) for the Archean, which they attribute to Holland (1984). Holland’s most recent estimate for \( \phi(\text{H}_2) \) is \( 1.8 \times 10^{10} \text{cm}^{-2} \text{s}^{-1} \) (Holland, 2002). Holland’s estimate is bigger than Sleep and Bird’s (2006) because Holland uses a bigger volcanic flux of \( \text{H}_2\text{O} \), which he obtains from the \( \text{CO}_2 \) outgassing flux using a reported \( \text{CO}_2 / \text{H}_2\text{O} \) ratio of 0.03. We have used \( 1 \times 10^{10} \text{cm}^{-2} \text{s}^{-1} \) as the high modern flux for \( \text{H}_2 \).

For \( \text{CO} \) we scale directly from the reported modern volcanic \( \text{CO}_2 \) source of \( 3 \times 10^{10} \text{cm}^{-2} \text{s}^{-1} \) (Sleep & Zahnle, 2001; Zahnle & Sleep, 2002) using a volcanic QFM \( \text{CO}/\text{CO}_2 \) ratio of 0.03. This results in a volcanic \( \text{CO} \) flux of \( 8 \times 10^8 \text{cm}^{-2} \text{s}^{-1} \). We use \( 2 \times 10^8 \text{cm}^{-2} \text{s}^{-1} \) for a low modern case and \( 1 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \) for the high modern case.

Walker & Brimblecombe (1985) presented strong arguments that oceanic sulfate in the Archean had as its main source volcanic gases, chiefly \( \text{SO}_2 \) and \( \text{H}_2\text{S} \). Estimates of the modern \( \text{SO}_2 \) range between \( 1 \times 10^9 \) and \( 3 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \) (Andres & Kasgnoc, 1998; Marty & Tolstikhin, 1998; Arthur, 2000). We use \( 1 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \) for the low modern value and \( 3.5 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \) as the high modern value, as the latter is the \( \text{SO}_2 \) outgassing rate used by Pavlov & Kasting (2002). Ono et al. (2003) consider \( 3.5 \times 10^8 \), \( 1 \times 10^9 \), and \( 3.5 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \) for their low, medium and high volcanic fluxes, respectively.

The \( \text{H}_2\text{S}/\text{SO}_2 \) ratio is more uncertain. The volcanic QFM ratio of 0.02 is lower than field measurements seem to indicate. Recent measurements imply that the ratio can be much higher in certain volcanoes (Aiuppa et al., 2005). Global estimates for \( \text{H}_2\text{S} \) flux range from \( 2 \times 10^8 \) and \( 7.7 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \). Given the uncertainty, we have arbitrarily fixed the \( \text{H}_2\text{S}/\text{SO}_2 \) at 0.1 for all three cases.

We assume that Archean volcanic fluxes were roughly three times higher than modern volcanic fluxes. Hence for V3, we use \( 3 \times 10^{10} \), \( 3 \times 10^9 \), \( 1 \times 10^{10} \), and \( 1 \times 10^9 \text{cm}^{-2} \text{s}^{-1} \) for \( \text{H}_2 \), \( \text{CO} \), \( \text{SO}_2 \), and \( \text{H}_2\text{S} \), respectively.

**Oxygen and methane**

There is compelling evidence preserved in molecular fossils that oxygenic photosynthesis originated no later than 2.75 Ga (Brocks et al., 1999, 2003; Summons et al., 2006) and therefore at least 300 Myr before the end of MIF \( \text{S} \) and 500 Myr before the rise of \( \text{O}_2 \). Early consequences of oxygenic photosynthesis are a jump in primary productivity and a jump in atmospheric methane (Walker, 1987; Catling et al., 2001; Claire et al., 2006). We expect the latter for two reasons. First, with more organic matter to ferment, more fermentation is to be expected; and second, because \( \text{O}_2 \) is a much more reactive molecule than \( \text{CH}_4 \), we expect that the geochemical sink for \( \text{O}_2 \) would have been bigger than the sink on \( \text{CH}_4 \) until the

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**Table 1 Volcanic fluxes. All quantities given in units of molecules cm\(^{-2}\) s\(^{-1}\)**

<table>
<thead>
<tr>
<th>Model title</th>
<th>( \text{SO}_2 )</th>
<th>( \text{H}_2\text{S} )</th>
<th>( \text{H}_2 )</th>
<th>( \text{CO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1 – ‘modern low’</td>
<td>( 1 \times 10^6 )</td>
<td>( 1 \times 10^8 )</td>
<td>( 2 \times 10^9 )</td>
<td>( 2 \times 10^9 )</td>
</tr>
<tr>
<td>V2 – ‘modern high’</td>
<td>( 3.5 \times 10^7 )</td>
<td>( 3.5 \times 10^8 )</td>
<td>( 1 \times 10^{10} )</td>
<td>( 1 \times 10^9 )</td>
</tr>
<tr>
<td>V3 – ‘Archean high’</td>
<td>( 1 \times 10^{10} )</td>
<td>( 1 \times 10^9 )</td>
<td>( 3 \times 10^{10} )</td>
<td>( 3 \times 10^9 )</td>
</tr>
</tbody>
</table>
crust was oxidized. By contrast Kopp et al. (2005) reject a lengthy delay between the advent of oxygenic photosynthesis and the appearance of abundant free O₂. They suggest instead that oxygenic photosynthesis was invented during the early Proterozoic ice ages ca. 2.3 Ga and promptly annihilated a pre-existing methane greenhouse.

A fundamental assumption underlying most of our numerical experiments is that the net flux of photosynthetic O₂ into the atmosphere was approximately stochiometrically balanced by the net flux of biogenic reduced gases into the atmosphere, chiefly CH₄. The justification for this is that the atmosphere is a small reservoir that quickly equilibrates with the chemical forcing. The balance is inexact because we do not force it explicitly – our explicit assumption is that an atmosphere can exist with the ground level O₂ and CH₄ mixing ratios we prescribe. The photochemical model does the accounting and computes the fluxes consistent with a photochemical steady state. Any stochiometric imbalance between CH₄ and O₂ is accounted for in several generally smaller terms in the atmospheric redox budget, including H escape, rainout of reduced and oxidized species, volcanic gases, and fallout of sulfur.

By conserving the redox budget of the atmosphere, we have in effect put a bag around the atmosphere. The redox fluxes of gases entering and exiting the bag sum to zero. So far as the atmosphere is concerned, this is correct: our possible atmospheres are self-consistent. We have not attempted to apply redox balance to the oceans, sediments, crust, and mantle that lie outside the bag. In our model there is in general a small net difference between the reducing power of volcanic gases added to the atmosphere and the reducing power lost to the atmosphere by hydrogen escape. This difference is proximally added to (or extracted from) the oceans. There are many terms in the ocean’s redox budget that are comparable to or bigger than the atmospheric term. These include burial of reduced carbon in sediments, subduction of sediments and altered oceanic crust, volcanic gases vented directly into the oceans, and reduced or oxidized sediments and altered crust accreted by or weathered from continents. These terms involve big reservoirs with long time constants (e.g. 100 Myr for reduced carbon in continental sediments) that are not plausibly held to redox balance on time scales relevant to the atmosphere.

Captive cyanobacterial mats grown and monitored in the laboratory emit O₂ in the day and H₂ at night (Hoehler et al., 2001). The mats do not emit much CH₄ because methanogens lose the competition with sulfate reducers, and in the mats sulfate is generally present in excess. A net excess of photosynthetic O₂ is balanced not by burial of organic carbon but rather by the loss, or export of, soluble organic matter to the waters beyond the mat. The exported oceanic organic matter can be oxidized with sulfate and, if the sulfate runs out, it can be biologically reduced to CH₄.

Hydrogen has similar photochemical effects to CH₄ in an anoxic atmosphere with an underlying photosynthetic source of O₂. In particular, it is comparably effective as a reducing agent to precipitate S₈. If other factors are neglected, a big biogenic H₂ source provides as good an explanation for MIF S as a big biogenic source of CH₄. In other words MIF S does not distinguish between H₂ and CH₄ as the reduced partner to photosynthetic O₂.

Of course other factors do matter. One difference is that methane is not as biologically desirable as hydrogen. Methane can be eaten aerobically or anaerobically using sulfate (Valentine, 2002). In the anoxic atmosphere aerobic oxidation would be restricted to localized oases. Sulfate would have been relatively unimportant while oceanic sulfate was scarce, as it was through much of the Archean (Canfield et al., 2000; Canfield, 2005). Anaerobic methane oxidation using sulfate provides another reason to expect that the methane source shrank as oceanic sulfate grew. On the other hand H₂ is very useful biologically for many purposes. We expect that the biological sink on atmospheric H₂ has always been significant. Some of the H₂ is converted to CH₄ by ordinary methanogenesis. A second difference is that CH₄ is an effective greenhouse gas; much of what makes methane attractive to theorists is that it is the only plausible supplement to CO₂ as a way of keeping the young Earth warm (Pavlov et al., 2000).

RESULTS

Our numerical experiments are performed over a grid of constant O₂ and CH₄ ground-level mixing ratios. For CH₄ we consider mixing ratios between 10⁻⁶ and 10⁻³. For O₂ we consider a wider range of mixing ratios, from extremely anoxic cases with less than 10⁻¹⁴ to quasi-modern atmospheres with 10⁻².

O₂ and CH₄ are photochemically consumed in the atmosphere to make CO₂ and H₂O. In the model, O₂ and CH₄ flow in through the lower boundary to maintain the assumed constant ground-level mixing ratios; this inflow we identify with the biogenic sources. When the model reaches steady state the computed O₂ and CH₄ lower boundary fluxes exactly balance the net photochemical destruction.

Long-lived CH₄ is generally well mixed, but O₂ is only well mixed when it is more abundant than methane. Examples of oxic and anoxic atmospheres are shown in Figs 1 and 2. To first approximation the less oxic atmospheres feature oxic stratospheres but extremely anoxic tropospheres. In these atmospheres, oxygen mixes up from the surface photosynthetic source and it mixes down from the stratosphere, to be consumed by the troposphere in the middle. This is a general property of reduced atmospheres.

Sulfate aerosols are produced at all heights, especially in the relatively oxidizing stratosphere. Elemental sulfur aerosols tend to form in the anoxic troposphere or near the tropopause, where descending products of SO₂ photolysis mix with ascending reduced gases from the troposphere. Figures 3 and 4 show where sulfur and sulfate aerosols form in the oxic and anoxic atmospheres of Figs 1 and 2. These are for the high
modern volcanic S fluxes (V2). The $S_8$ and $H_2SO_4$ formation regions are compared to where $SO_2$ absorbs UV shorter than 220 nm. Rainout of $SO_2$, which is not shown, is confined to the troposphere. We expect that the MIF S signal is strongest when the production regions of $S_8$ and sulfate overlap with the region where $SO_2$ absorbs $\lambda < 220$ nm. These conditions are met in all the anoxic models.

In each model with significant $S_8$ deposition, we verified that the $SO_2$ photolysis rate by the MIF-producing photons ($190 < \lambda < 220$ nm, for $SO_2 + h\nu \rightarrow SO + O$) was higher than the $S_8$ production rate at every height at which $S_8$ was produced. In addition, each model shows numerically higher $S$ production rates by the photolysis of $SO + h\nu \rightarrow S + O$, along with higher total $S$, $S_3$ and $S_4$ production rates at each model altitude with $S_8$ production. We use the above tests to identify our deposited $S_8$ as a likely carrier of the MIF signal, given that Pavlov & Kasting (2002) have shown that the MIF signature is distributed among sulfur species in an anoxic atmosphere.

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Figure 5 is a summary figure over a grid of models differing only in the prescribed ground-level O2 mixing ratio. The CH4 mixing ratio is fixed at 100 ppmv, which is near the lower limit of what would be required for methane greenhouse warming to maintain temperate conditions at Earth’s surface 2.8 Ga, given the upper limit on atmospheric CO2 inferred by Rye et al. (1995). Figure 5 treats the O2 mixing ratio as the independent variable. This gives an accurate description of how the photochemical model was implemented. The dependent variables are the O2 and CH4 fluxes required to sustain the assumed mixing ratios, and the various fluxes of chemical products leaving the atmosphere. The most important of the latter are rainout of formaldehyde (H2CO) and hydrogen peroxide (H2O2).

Perhaps the first thing one sees in Fig. 5 is that the O2 and CH4 fluxes peak at an O2 mixing ratio of 10 ppmv. The peak is caused by rising levels of ozone (also shown against the right-hand axis). At low O2 mixing ratios ozone is unimportant and the photochemical reactions between CH4 (and its products) and O2 (and its products) increase as O2 increases. But at higher O2 levels the ozone becomes abundant enough that a significant fraction of the incident UV photons are wasted shuffling oxygen atoms between O2 and O3: O2 + O → O3, O3 + hv → O2 + O. In atmospheric photochemistry the ultimate speed limit is set by the number of photons.

As a philosophical point, one thinks of the O2 and CH4 fluxes as the true independent variables, and of the O2 and CH4 mixing ratios as the consequences of photochemical reactions acting upon the fluxes. This is correct to the extent that the effect of mixing ratios upon biological activity can be ignored – a significant caveat. When Fig. 5 is viewed from the perspective of O2 as the independent variable, one sees that the solution is multiple valued. The same level of biological productivity can support either a highly anoxic or a rather oxic atmosphere. There is something to this, but recall that we have fixed CH4 at 100 ppmv; as depicted here, the demonstration of multiple solutions is rigorously valid only if there is an external control over f(CH4), as for example might be provided by a Gaian thermostat.

Another perspective on Fig. 5 is to view the increase in f(O2) as an evolution through time. This is tempting; after all, O2 did increase. Again there is something to this, but again, one must not ascribe too much import to f(O2) as an independent variable; it is not. Rather, explaining why f(O2) increases (i.e., the quest for the true independent variable) drives this whole field of research. An additional complication in viewing Fig. 5 as an evolutionary plot is that methane levels do not remain constant and are likely anticorrelated to oxygen levels in a nonlinear fashion (Claire et al., 2006).

Figure 5 also shows the three major losses for atmospheric sulfur. Fallout of sulfuric acid particles and rainout of SO2 occur at all f(O2) but fallout of S8 is restricted to anoxic atmospheres with f(O2) < 10^-6. Separate exits through sulfate or through SO2 allow for some preservation of photochemical MIF S in more oxic atmospheres, but as noted above the signal would be diluted or lost when the species dissolved together in liquid water. Today MIF S is restricted to extremely dry environments. In the early Proterozoic the MIF signal in SO2 and sulfate should have been stronger, while the ozone layer was thinner and lower; perhaps there is some explanation here for Stage II as defined by Farquhar et al. (2003).

The O2 and CH4 fluxes in Fig. 5 are large. The modern gross CH4 flux is 1.5 × 10^12 cm^-2 s^-1. About 90% of this is consumed by methanotrophs before it reaches the atmosphere; we presume that a much higher fraction reached the anoxic atmosphere.

In the modern world oxygenic photosynthesis generates O2 at a rate of ~4 × 10^13 cm^-2 s^-1 (Walker, 1977). Obviously most of this O2 is respired. Today, on geological time scales the net O2 flux into the atmosphere is balanced by oxidation of rocks, minerals, and fossil carbon at a rate on the order of ~4 × 10^10 cm^-2 s^-1 (Holland, 1984). On shorter time scales the imbalances are bigger. The annual imbalance between photosynthesis and respiration can be seen in the 6 ppmv annual variation of atmospheric CO2, which implies that on
seasonal timescales, O\textsubscript{2} production and consumption are out of balance by \(4 \times 10^{12}\) cm\(^{-2}\) s\(^{-1}\), which is on the order of 10% of the total production.

Before O\textsubscript{2} became plentiful, respiration would have been local, confined to oxygen oases in the immediate vicinity of the photosynthetic source, and probably diurnal. Thus, there is no reason to expect that respiration should so nearly cancel O\textsubscript{2} emission as it does today, and we might reasonably expect the flux of O\textsubscript{2} into the atmosphere to have been as large as the annual imbalance today.

For specificity we have set an upper bound on the O\textsubscript{2} flux into the atmosphere at \(1 \times 10^{13}\) cm\(^{-2}\) s\(^{-1}\). This is 25% of the modern total photosynthetic production, and 2.5 times bigger than today’s net production/respiration imbalance on a seasonal timescale. We have set the lower bound at \(1 \times 10^{11}\) cm\(^{-2}\) s\(^{-1}\). This is 2.5 times the modern net O\textsubscript{2} flux averaged over geological time scales. The lower bound is very conservative, given how rapidly O\textsubscript{2} would be consumed either in the environment by oxidative weathering or in the atmosphere by photochemistry (cf. Walker, 1987). For comparison Pavlov & Kasting (2002) set higher upper and lower bounds of \(6 \times 10^{11} < \phi(O_2) < 3 \times 10^{13}\) cm\(^{-2}\) s\(^{-1}\).

Figure 6 is analogous to Fig. 5 for a range of methane mixing ratios. To limit clutter only the O\textsubscript{2} flux, the H escape, and the S\textsubscript{8} fallout are shown. Methane mixing ratios range from 1 to 1000 ppmv. Not surprisingly, the more methane-rich atmospheres are more reduced and permit proportionately higher levels of hydrogen escape. At \(f(CH_4) < 10^{-3}\) only highly anoxic atmospheres (featuring \(f(O_2) < 10^{-8}\)) are accessible with \(\phi(O_2) < 10^{13}\) cm\(^{-2}\) s\(^{-1}\). The model predicts that such atmospheres generate S\textsubscript{8} abundantly. By contrast, we regard any \(f(O_2)\) level as potentially accessible for CH\textsubscript{4} mixing ratios smaller than 30 ppmv.

Ono \textit{et al.} (2003) showed that sulfur speciation depended on the methane mixing ratio, with the more strongly reduced atmospheres making more strongly reduced sulfur. One difference between our results and those reported by Ono \textit{et al.} (2003) is that our reduced models are significantly less reduced than theirs. In their most reduced atmospheres, Ono \textit{et al.} (2003) predicted that rainout or surface deposition of H\textsubscript{2}S and the radical HS represent important atmospheric exit channels. We do not see this, and we have no explanation for the different model behaviours.

Figure 7 shows that S\textsubscript{8} production is a strong function of methane mixing ratio for the high modern volcanic SO\textsubscript{2} flux (Case V2) and for a ground-level oxygen mixing ratio \(f(O_2) = 10^{-7}\). Higher \(f(O_2)\) shifts the S\textsubscript{8} cutoff to higher \(f(CH_4)\), and lower \(f(O_2)\) shifts the S\textsubscript{8} cutoff to lower \(f(CH_4)\). A similar figure was presented by Ono \textit{et al.} (2003; their Fig. 4) for extremely anoxic atmospheres with no biogenic O\textsubscript{2} source. In the absence of O\textsubscript{2} the dependence of S\textsubscript{8} production on \(f(CH_4)\) is not as strong.

Ono \textit{et al.} (2003) also showed that S\textsubscript{8} production is a strong function of the volcanic SO\textsubscript{2} source. They considered three SO\textsubscript{2} fluxes, two of which were equivalent to our V2 and V1 models, and a third with a smaller SO\textsubscript{2} flux of \(3.5 \times 10^{8}\) cm\(^{-2}\) s\(^{-1}\). They found that S\textsubscript{8} production is shut off at low SO\textsubscript{2} fluxes and low levels of CH\textsubscript{4}. We see much the same.

**Fig. 6** O\textsubscript{2} flux, H escape, and S\textsubscript{8} fallout as a function of \(f(O_2)\) for \(f(CH_4)\) between \(10^{-6}\) and \(10^{-3}\). Curves are labelled by \(f(CH_4)\). Hydrogen escape and the threshold for S\textsubscript{8} production increase directly with the amount of CH\textsubscript{4} in the atmosphere. Note that transition between low and high O\textsubscript{2} states is effectively impossible at 1000 ppmv CH\textsubscript{4}, but is relatively easy for \(f(CH_4) < 10\) ppmv. These are high volcanic SO\textsubscript{2} flux models (V3).

**Fig. 7** Sulfur fluxes as a function of CH\textsubscript{4} mixing ratio at a ground-level O\textsubscript{2} mixing ratio of \(10^{-7}\). In this particular example, with \(f(O_2)\) fixed, S\textsubscript{8} production, and by presumption MIF S, shuts off for \(f(CH_4) < 8\) ppmv. Volcanic fluxes are at the high modern levels (V2).
Atmospheres that require net O₂ fluxes greater than $1 \times 10^{13}$ cm⁻² s⁻¹ are marked with ‘×’ symbols. For reasons described in the text, we regard O₂ fluxes greater than $1 \times 10^{13}$ cm⁻² s⁻¹ as implausible. With this limitation, ground-level O₂ mixing ratios $2 \times 10^{-7} < f(O_2) < 2 \times 10^{-4}$ are inaccessible for $f(CH_4) \geq 5 \times 10^{-5}$. By net fluxes, we refer to the difference between production and respiration on timescale longer than the characteristic response time of the atmosphere. For an anoxic atmosphere with $f(O_2) < 10^{-7}$, the lifetime of atmospheric O₂ is measured in days to weeks. It seems obvious that such an atmosphere would be strongly driven by variable biogenic fluxes, so that specific steady state solutions such as those discussed here have limited value. For oxic solutions with $f(O_2) > 10^{-4}$, the O₂ lifetimes range from a decade up.

For the low SO₂ flux (Fig. 8), significant S₈ production is limited to atmospheres with ground-level $f(O_2) < 10^{-10}$. To first approximation very low $f(O_2)$ is better regarded as a proxy for $f(O_3)$ than as an actual O₃ mixing ratio. This occurs because the troposphere is both very reduced and very photochemically active. For all the models considered in this study, for very low $f(O_2) \sim 10^{-10}$ the relation between the flux and the mixing ratio is nearly linear and approximately given by $\phi(O_3) = 5 \times 10^{20} f(O_2)$ cm⁻² s⁻¹ (Fig. 6). If we take $\phi(O_3) > 10^{11}$ cm⁻² s⁻¹, we would conclude that $S_8$ and therefore strong MIF S is unlikely for SO₂ fluxes smaller than $1 \times 10^9$ cm⁻² s⁻¹.

Figure 9 addresses our high modern volcanic flux (V2) models with $\phi(SO_2) = 3.5 \times 10^9$ cm⁻² s⁻¹ and $\phi(H_2S) = 3.5 \times 10^8$ cm⁻² s⁻¹. The inaccessible regions do not change appreciably for the different volcanic fluxes. Higher S fluxes increase the stability field of $S_8$. Dependence of $S_8$ production on $f(CH_4)$ is more pronounced than for smaller volcanic fluxes.

Figure 10 addresses our high Archean volcanic flux (V3) models with $\phi(SO_2) = 1 \times 10^{10}$ cm⁻² s⁻¹ and $\phi(H_2S) = 1 \times 10^9$ cm⁻² s⁻¹.

Figures 8, 9, and 10 are contour plots that show the computed $S_8$ production as a function of $f(O_2)$ and $f(CH_4)$. These figures indicate the range of atmospheres that can give rise to substantial $S_8$ production. Production is given in units of Tmol of S per annum.

Figure 8 addresses our low modern volcanic flux (V1) models with $\phi(SO_2) = 1 \times 10^9$ cm⁻² s⁻¹ and $\phi(H_2S) = 1 \times 10^8$ cm⁻² s⁻¹.

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of interest – is as strong a function of threshold for S8 production. S8 production is always confined to atmospheres are in any event impossible. The snaking solid grey curve represents the is abrupt, especially at the higher methane levels for which oxic atmospheres are in any event impossible. The snaking solid grey curve represents the threshold for S8 production. S8 production is always confined to atmospheres that feature extremely anoxic tropospheres. It is noteworthy that the atmosphere can be very anoxic and yet not generate S8, even at, or especially at, high methane levels. The ground-level mixing ratio \( f(\text{CH}_4) \) is essentially the same result obtained by Pavlov & Kasting (2002) for the equivalent case. These computations use volcanic flux model V2.

The steadily widening envelope of mass-dependent S fractionation through the Archean implies that methanogens ate well, and that methane fluxes into the atmosphere were big.

The story told in this paper begins with the invention of oxygenic photosynthesis. A likely consequence of this invention was a general increase in global productivity. Another likely consequence was an increase in atmospheric methane, because methane is a biological end-product and it is chemically more stable than oxygen. Because methane is a potent greenhouse gas, it warmed the Earth. The warmer conditions promoted CO2-consuming weathering reactions, which suggests that atmospheric CO2 levels were probably reduced by the increased methane.

A key consequence of abundant atmospheric methane was nontrivial H escape to space. Hydrogen escape irreversibly oxidizes the Earth, especially the near surface reservoirs, and the crust in particular (Catling et al., 2001). It takes hundreds of millions of years to oxidize key crustal reservoirs of iron and sulfur. Both iron and sulfur record this history in their fractionated isotopes. With sulfur the record seems straightforward:

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available oceanic sulfate steadily increased through the Archean, as one expects of an inexorably oxidized crust.

As the oceanic sulfate pool increased, greater competition with sulfate reducers left less room for methanogens. Net methane production must have decreased and atmospheric methane levels must have decreased accordingly (the O2 flux to the atmosphere would also have decreased, although \( f(O_2) \)'s decrease may have been offset somewhat by increased emission of photochemically labile biogenic S-gases and of biogenic H2). The decline of CH4 caused sulfur MIF to stop and the climate to cool, the latter culminating in severe ice ages. This sequence of events is nicely illustrated in Fig. 12, which creates a history of MIF S by combining Claire et al.'s (2006) reference model for the histories of atmospheric O2 and CH4 with the \( S_8 \) production rates shown in Fig. 9. The order of events is general: (i) oceanic sulfate increases, (ii) atmospheric methane declines, (iii) sulfur MIF disappears and greenhouse warming collapses, (iv) oxygen rises and the methane greenhouse returns under the photochemical protection of abundant oxygen and ozone.

We speculate that it was the increasing sulfate pool and the concomitant reduction of atmospheric methane that made the transition to an oxic atmosphere possible. While CH4 and O2 fluxes remained large and methane abundant the atmosphere remained trapped in a stable anoxic state, as we showed most clearly in connection with Fig. 5. Although oxic atmospheres exist with essentially the same biogenic forcings as those driving the anoxic atmosphere, the oxic states are inaccessible when methane is abundant in the atmosphere. This is seen in Figs 5, 6, and 8–10. At lower levels of atmospheric CH4 the barrier against transition to an O2-rich atmosphere is small enough that realistic biogenic fluxes can overcome it. It is no accident that the rise of O2 took place during ice ages at a time when atmospheric CH4 levels were low.

CONCLUSIONS

- We assumed that the characteristic of the Archean sulfur MIF signal is a product of atmospheric photochemistry, and that the photochemical signature was preserved in the rock record when sulfur was able to leave the atmosphere in both soluble (e.g. \( SO_2, H_2SO_4 \)) and insoluble (\( S_8 \)) forms. We used a 1-D atmospheric photochemistry model to characterize the conditions conducive to the condensation and precipitation of particles of elemental sulfur. We assumed a volcanic source of sulfur gases. Our models presume oxygenic photosynthesis and a rough stochiometric balance between the net fluxes of O2 and CH4 into the atmosphere.

- Precipitation of \( S_8 \) depends on the \( SO_2 \) source and the mixing ratios of CH4 and O2. In particular, we showed that \( S_8 \) deposition is a strong function of CH4 for oxygen levels and \( SO_2 \) sources likely in the late Archean. The necessary conditions for forming \( S_8 \) are best understood as requiring a large sulfur source, an anoxic troposphere, and a sufficient amount of a reduced gas (either CH4 or H2 will do). All three requirements must be met to form \( S_8 \).

- Collapse of atmospheric methane in the late Archean to below 10 ppmv provides the best explanation of the disappearance of MIF in sulfur. This differs from previous work attributing the loss of MIF to the rise of O2. We suggest that the methane collapse was driven by the increasing importance of sulfate and the increasing competitive advantage of sulfate reducers over methanogens. The collapse of CH4 also explains widespread low-latitude glaciation in the early Proterozoic.

- We suggest that the growth of the oceanic sulfate pool reflects secular changes in the redox balance of the atmosphere–ocean–crust system, probably driven by hydrogen escape.

- The rise of O2 to geologically detectable levels took place after the collapse of MIF, and was facilitated by generally low levels of atmospheric methane characteristic of the ice ages.

- The ice ages were ended by the rise of O2. The Proterozoic was relatively rich in methane (at ~100 ppmv levels) because the ozone layer provided methane with protection against photochemical destruction.

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