

# Climate variability leads to multiple oxygenation episodes across the great oxidation event

Daniel Garduno Ruiz, Colin Goldblatt, and Anne-Sofie Ahm

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## RESEARCH LETTER

10.1029/2023GL106694

# Climate Variability Leads to Multiple Oxygenation Episodes Across the Great Oxidation Event



### Key Points:

- Across the Great Oxidation Event (GOE), extreme climate change linked to global glaciations can drive oscillations in atmospheric O<sub>2</sub> levels and mass-independent fractionation of sulfur isotopes (MIF-S) production
- Glacial climates and hot-moist greenhouse climates were likely characterized by pre-GOE and post-GOE O<sub>2</sub> levels respectively
- Temperature changes associated with global glaciations can help explain the MIF-S record across the GOE

### Supporting Information:

Supporting Information may be found in the online version of this article.

### Correspondence to:

D. G. Ruiz,  
[danielgardunorui@uvic.ca](mailto:danielgardunorui@uvic.ca)

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### Author Contributions:

**Conceptualization:** Colin Goldblatt  
**Funding acquisition:** Colin Goldblatt, Anne-Sofie Ahm  
**Investigation:** Daniel Garduno Ruiz, Colin Goldblatt  
**Methodology:** Daniel Garduno Ruiz, Colin Goldblatt, Anne-Sofie Ahm  
**Software:** Daniel Garduno Ruiz  
**Supervision:** Colin Goldblatt, Anne-Sofie Ahm  
**Visualization:** Daniel Garduno Ruiz  
**Writing – original draft:** Daniel Garduno Ruiz  
**Writing – review & editing:** Colin Goldblatt, Anne-Sofie Ahm

Daniel Garduno Ruiz<sup>1</sup> , Colin Goldblatt<sup>1</sup> , and Anne-Sofie Ahm<sup>1</sup> 

<sup>1</sup>School of Earth and Ocean Sciences, University of Victoria, Victoria, BC, Canada

**Abstract** The temporal relationship between global glaciations and the Great Oxidation Event (GOE) suggests that climate change played an important role in Earth's oxygenation. The potential role of temperature is captured by the stratigraphic proximity between glacial deposits and sediments containing mass-independent fractionation of sulfur isotopes (MIF-S). We use a time-dependent one-dimensional photochemical model to investigate whether temperature changes associated with global glaciations can drive oscillations in atmospheric O<sub>2</sub> levels and MIF-S production across the GOE. We find that extreme climate change can cause atmospheric O<sub>2</sub> to oscillate between pre (<10<sup>-6</sup> times the present atmospheric level, PAL) and post-GOE (>10<sup>-5</sup> PAL) levels. Post-glacial hot-moist greenhouse climates lead to post-GOE O<sub>2</sub> levels because the abundant H<sub>2</sub>O vapor and oxidizing radicals drive the depletion of reduced species. This pattern is generally consistent with the MIF-S signal observed in the sedimentary record, suggesting a link between global glaciations and O<sub>2</sub> oscillations across the GOE.

**Plain Language Summary** The Great Oxidation Event was the most significant environmental and chemical transformation in Earth's history, marking the first time oxygen accumulated in the atmosphere around 2.4 billion years ago. Oxygen increased from below one millionth (low) to at least one-thousandth of a percent (intermediate) of the present oxygen concentration during this event. However, measurements of geochemical oxygen proxies suggest that oxygen levels oscillated between low and intermediate levels before stabilizing after this event. The first rise of atmospheric oxygen occurred during a period of extreme climate variability indicated by the presence of glacial rock deposits around this time. In this study, we use a time-dependent photochemical model to show that extreme temperature changes caused by global glaciations can drive oscillations in atmospheric oxygen levels across the Great Oxidation Event (GOE). Our results can help explain why atmospheric oxygen shows drastic changes across the GOE in a way that is consistent with the geochemical record.

## 1. Introduction

One of the most fundamental changes to Earth's atmosphere occurred ~2.4 billion years ago during the Great Oxidation Event (GOE) when oxygen first rose to levels >10<sup>-6</sup> times the present atmospheric level, and the ozone layer finally formed (D. C. Catling & Zahnle, 2020; Zahnle et al., 2006). During the same period, Earth's climate underwent dramatic changes with multiple global scale glaciations, so-called snowball Earth events (Rasmussen et al., 2013). The geological record demonstrates that these changes in climate and oxygen were closely related, as recorded by the stratigraphic proximity between glacial deposits and swings in the record of mass-independent fractionation of sulfur isotopes (MIF-S, Gumsley et al. (2017); Poulton et al. (2021)). In this paper, we will explore whether the effect of extreme climate change on photochemical reactions can cause oxygen fluctuations across the GOE.

The GOE is expressed globally through various geological and geochemical indicators, but the main line of evidence for an O<sub>2</sub> increase during the GOE comes from the MIF-S record. The MIF-S signal forms under anoxic photochemistry in the atmosphere and is transferred to rocks through deposition of S<sub>8</sub> aerosols and sulfate particles (Farquhar et al., 2000, 2001; Pavlov & Kasting, 2002). The geological record shows that MIF-S deposition stopped between 2.5 and 2.3 billion years ago (Ga), suggesting that atmospheric O<sub>2</sub> levels increased above 10<sup>-6</sup> times the present atmospheric level (PAL) around this time (D. C. Catling & Zahnle, 2020; Zahnle et al., 2006).

The GOE is correlated with extreme climate changes. Up to four glacial deposits surround the transition to an oxygenated atmosphere in South Africa, North America, and Australia (Tang & Chen, 2013). Correlation

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between the glacial deposits and low paleo-latitude evidence suggests three of these glaciations may represent global snowball Earth events (Evans et al., 1997; Rasmussen et al., 2013; Williams & Schmidt, 1997). The global glaciations reached surface temperatures below 250K (Abbot et al., 2013) and were likely followed by hot-moist greenhouse climates characterized by temperatures above 320K (Kirschvink, 1992; Popp et al., 2016). Photochemical models suggest that this extreme climate variability affected the evolution of atmospheric O<sub>2</sub> across the GOE through changes in water vapor and the production of oxidizing radicals, leading to variations in O<sub>2</sub> and O<sub>3</sub> levels of up to three orders of magnitude after the GOE (Garduno Ruiz et al., 2023). Consequently, climate variability could be important in explaining MIF-S swings across the GOE.

The appearance and disappearance of the MIF-S signal in the South African Kapvaal craton suggest that atmospheric O<sub>2</sub> oscillated between pre and post-GOE levels across the transition to an oxygenated atmosphere. These MIF-S swings have been explained as a consequence of the dynamic interplay between changes in weathering, the input flux of nutrients to the oceans, and methane oxidation (Gumsley et al., 2017; Poulton et al., 2021).

Here, we use a time-dependent one-dimensional photochemical model (Wogan et al., 2022) to investigate if temperature change associated with the Paleoproterozoic Huronian glaciations can trigger oscillations in atmospheric O<sub>2</sub> levels across the GOE. We find that extreme climate change could explain some of the MIF-S swings present in the rock record. This paper builds on results from a previous study (Garduno Ruiz et al., 2023), which considered photochemical steady-state atmospheres to investigate the effect of temperature on O<sub>2</sub> levels. In this paper, we specifically investigate the transient evolution, and explore how temperature changes over time affect O<sub>2</sub> levels surrounding the GOE.

## 2. Methods

We use a time-dependent one-dimensional photochemical model (Archean template, Wogan et al. (2022)) to explore if temperature changes caused by global glaciations can cause oscillations in oxygen levels and MIF-S production across the GOE. Our modeling considers the effect of temperature change in atmospheric photochemistry without considering the effect on climate.

We use our simulations to evaluate the production of MIF-S across glacial and hot-moist greenhouse periods. We assume that MIF-S can be transferred to sediments when S<sub>8</sub> aerosols are an important product of atmospheric photochemistry. This condition is satisfied when O<sub>2</sub> mixing ratios are lower than 10<sup>-7</sup> (Wogan et al., 2022; Zahnle et al., 2006). For higher O<sub>2</sub> levels, the S<sub>8</sub> column goes to zero and we assume that MIF-S production stops.

### 2.1. Atmospheric Structure

We represent the temperature profile using a moist-adiabatic troposphere merged with a 215K isothermal stratosphere. At different surface temperatures we adjust the surface pressure and the height of the tropopause to account for the change in water vapor content (Garduno Ruiz et al., 2023). We use a constant relative humidity profile of 0.35 in the troposphere. We chose this profile because it is the simplest profile that approximates the observed globally averaged relative humidity profile (Abraham & Goldblatt, 2023), and because using a more complex and realistic relative humidity profile with a strong humidity gradient at the boundary layer results in numerical problems in the photochemical model. In all our simulations we keep a constant CH<sub>4</sub> to O<sub>2</sub> flux ratio of 0.49 because this ratio is considered representative of the Archean (D. Catling et al., 2007).

### 2.2. Steady States Parameter Space

To explore how the model reacts to temperature and O<sub>2</sub> flux changes, we first define a parameter space of steady state O<sub>2</sub> levels at different prescribed surface O<sub>2</sub> fluxes and temperatures. To construct this parameter space, we run the model to steady state at surface temperatures ranging from 250 to 350K (with an initial value of 290K), and O<sub>2</sub> surface fluxes ranging from 10<sup>12</sup> to 10<sup>13</sup> molecules/cm<sup>2</sup>/s (henceforth /cm<sup>2</sup>/s). The results are described in Section 3.1.

### 2.3. Time-Dependent Simulations

We subsequently prescribe a surface temperature evolution that simulates the effect of global glaciations on temperature. We characterize temperate climates with a temperature of 290K that drops to 250K during the

glaciations (Abbot et al., 2013), assuming that the glacial events spanned 10 million years (My). We use the glacial deposits age constraints compiled in Gumsley et al. (2017) and Bekker et al. (2020). After the glaciations, we increase the surface temperature to 320K to simulate a glacial exit to a hot-moist greenhouse climate (Popp et al., 2016). Finally, we simulate the return to temperate 290K conditions following a sigmoid-like decline in 10 My because some modeling studies suggest that the post-glacial moist-greenhouse state likely spanned a few million years (Hir et al., 2009), if not tens of millions of years (Mills et al., 2011).

We integrate the photochemical model over time as an initial value problem with the CVODE integration method (Wogan et al., 2022). We run the model in  $10^5$  year intervals, assuming that temperature remains constant across each  $10^5$  year window. At each  $10^5$  year interval, we update the temperature and eddy diffusivity profiles, and surface pressure, according to our prescribed surface temperature evolution.

We consider three scenarios in which we prescribe different  $O_2$  and reductant input fluxes over time. Our results are not very sensitive to the specific fluxes we choose in these scenarios. The goal of this manuscript is not to constrain absolute flux values.

### 2.3.1. Time Dependent Temperature Forcing With a Constant $O_2$ Flux

To isolate the effect of temperature changes on  $O_2$  levels, we run the model with constant  $O_2$  input fluxes of  $1.8 \times 10^{12}/\text{cm}^2/\text{s}$  and  $2.2 \times 10^{12}/\text{cm}^2/\text{s}$ . We choose these fluxes to illustrate different model responses to temperature changes depending on the  $O_2$  flux. We keep the reductant input flux at a constant value of  $3.3 \times 10^{10}/\text{cm}^2/\text{s}$  (Zahnle et al., 2006).

### 2.3.2. Time Dependent Temperature Forcing With a Linear Increase in $O_2$ Flux

We consider two cases. First, we prescribe a linear  $O_2$  flux increase with a rate of  $8.88 \times 10^9/\text{cm}^2/\text{s}$  per million years. We arbitrarily choose this rate because it matches some of the available MIF-S constraints across the GOE. Second, we superimpose a decrease of 60% in the  $O_2$  input flux during the glacial periods to simulate a decrease in productivity due to harsh conditions for primary producers, and we add a 60% increase in the  $O_2$  input flux during the hot-moist greenhouse periods to simulate an increase in productivity due to increased nutrient flux to the oceans during deglaciations (Harada et al., 2015). We choose a 60% scale factor to match the MIF-S observations during glacial periods.

### 2.3.3. Time Dependent Temperature Forcing With a Linear Decrease in Reductant Input Flux

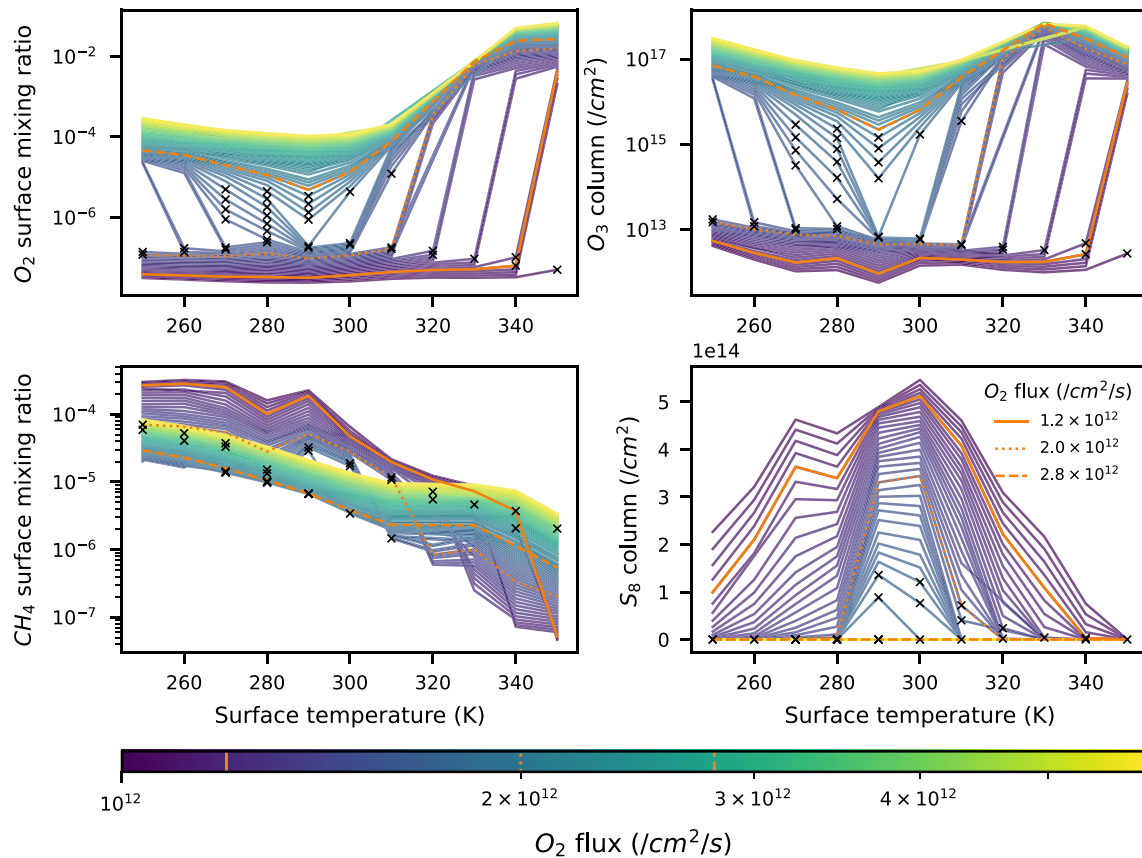
We decrease the reductant input flux from an initial value of  $2.2 \times 10^{10}/\text{cm}^2/\text{s}$  to a final value of  $1 \times 10^{10}/\text{cm}^2/\text{s}$  throughout 190 My, keeping a constant CO to  $H_2$  ratio of 0.1 (Zahnle et al., 2006). This decrease in reductant input flux is broadly consistent with previous estimates (Kadoya et al., 2020). Similarly to our  $O_2$  flux increase case (Section 2.3.2), we consider two scenarios for the  $O_2$  input flux evolution. First, we keep a constant  $2.2 \times 10^{12}/\text{cm}^2/\text{s}$   $O_2$  input flux. Second, we superimpose a 60% decrease in  $O_2$  input flux during glaciations and a 60% increase during hot-moist greenhouse periods.

## 3. Results

### 3.1. Steady States Parameter Space

The steady state parameter space shows three different scenarios where a temperature change will have dramatic effects on the  $O_2$  surface mixing ratio (Figure 1). First, for  $O_2$  fluxes below  $2 \times 10^{12}/\text{cm}^2/\text{s}$ , increasing temperature from 290K to above 310K leads to post-GOE oxygen levels. At lower  $O_2$  flux values, a bigger increase in temperature is needed to cause oxygenation. Second, for  $O_2$  fluxes between  $2 \times 10^{12}$  and  $2.8 \times 10^{12}/\text{cm}^2/\text{s}$ , a decrease in temperature from 290K to below 260K also results in oxygenation. While some of the steady states between this flux range display intermediate  $O_2$  levels, these states are very sensitive to small (5%)  $O_2$  flux perturbations and are likely to be unstable. These results suggest that it is unlikely that the atmosphere will remain in those states for long periods. Oxygen fluxes higher than  $2.8 \times 10^{12}/\text{cm}^2/\text{s}$  result in post-GOE oxygen levels for all temperatures.

The temperature sensitivity of  $O_3$ ,  $CH_4$ , and  $S_8$  aerosols follow the steady state concentration of  $O_2$  (Figure 1). High  $O_2$  concentrations lead to more oxidation and lower  $CH_4$  concentrations. In contrast, since  $O_3$  is a



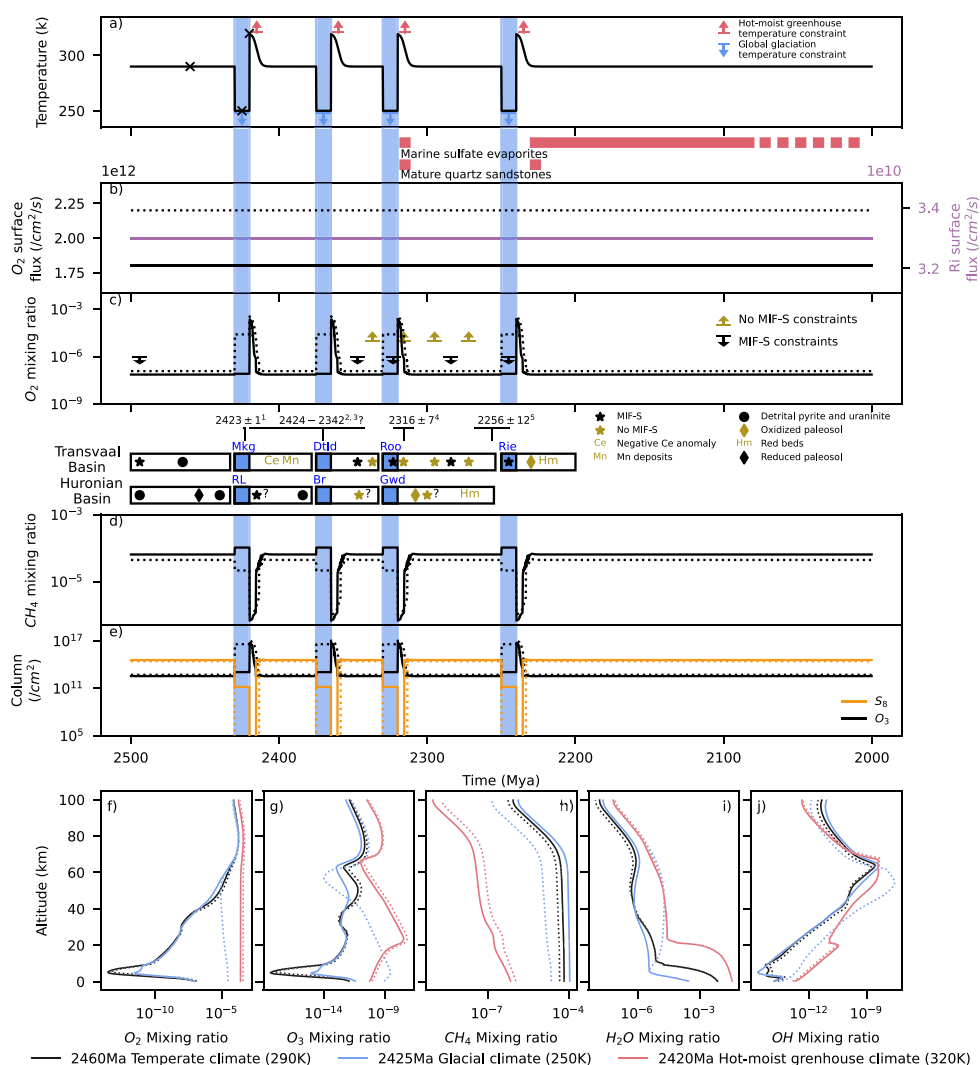
**Figure 1.** Model defined parameter space of atmospheric steady state  $O_2$  and  $CH_4$  surface mixing ratios, and  $O_3$  and  $S_8$  columns across different prescribed surface  $O_2$  fluxes and temperatures. Three characteristic model scenarios are highlighted with orange lines. The “x” symbols represent steady states that change more than a factor of two with a 5%  $O_2$  flux perturbation. These states are very sensitive to small  $O_2$  flux perturbations and are likely to be unstable.

photochemical product of  $O_2$ , the  $O_3$  concentration measured through an integrated column shows the same trends as  $O_2$ . The presence of an  $O_3$  layer inhibits the formation of  $S_8$  aerosols, so  $S_8$  aerosols are only present at low  $O_2$  fluxes.

### 3.2. Time Dependent Temperature Forcing With a Constant $O_2$ Flux

The time-dependent model simulations demonstrate that temperature changes associated with the Huronian glaciations can drive oscillations in  $O_2$  levels and MIF-S across the GOE. In the first simulation (Figure 2), these oscillations are driven by change in temperature only, as  $O_2$  and reductant input fluxes are kept constant (Section 2.3.1). While these  $O_2$  oscillations are solely driven by the changes in atmospheric chemistry caused by temperature, the specific value of the  $O_2$  input flux controls the time evolution of atmospheric  $O_2$ .

The glacial periods are characterized by low or high  $O_2$  levels depending on the  $O_2$  input flux. At an  $O_2$  input flux of  $1.8 \times 10^{12} \text{ cm}^2/\text{s}$ , the drop in temperature leads to a slight increase in surface  $O_2$  (Figure 2c continuous line). However, at an  $O_2$  input flux of  $2.2 \times 10^{12} \text{ cm}^2/\text{s}$ , the glaciations cause  $O_2$  to increase from a mixing ratio of  $10^{-7}$  to  $10^{-5}$ , leading to an oxygenated atmosphere, and suppressing the production of MIF-S through  $S_8$  aerosols (Figures 2c and 2e dotted). This behavior results from the decrease in tropospheric and stratospheric water vapor during the glacial periods. Less water vapor results in lower production of oxidizing radicals like OH, leading to lower oxidation rates and less  $O_2$  loss. At an  $O_2$  flux of  $1.8 \times 10^{12} \text{ cm}^2/\text{s}$  the lower rates of oxidation lead to a small  $O_2$  and  $O_3$  increase in the troposphere (Figures 2f and 2g). While this increase in  $O_3$  concentration also drives a decrease in  $S_8$  aerosol production, it is not enough to eliminate MIF-S across the glacial periods (Figure 2e). In contrast, at an  $O_2$  input flux of  $2.2 \times 10^{12} \text{ cm}^2/\text{s}$ , the decrease in  $O_2$  loss combined with the higher  $O_2$  input flux cause the establishment of an  $O_3$  layer and oxygenated conditions during glacial periods, terminating MIF-S signals (Figure 2g).



**Figure 2.** This figure shows two different model scenarios using a similar temperature evolution (a) but with two different constant  $O_2$  input flux values (b). Depending on the initial  $O_2$  input flux value, the  $O_2$  surface mixing ratio (c),  $CH_4$  surface mixing ratio (d), and  $O_3$  and  $S_8$  columns (e) show distinct trends. The four blue vertical bars represent glaciations (Bekker & Holland, 2012; Gumsley et al., 2017; Poulton et al., 2021). The red and blue arrows in panel (a) represent modeling temperature constraints during glacial (Abbot et al., 2013) and hot-moist greenhouse (Popp et al., 2016) periods. The “x” symbols show the points in time where we plot species profiles in panels (f–j). The red horizontal bars show times when evidence of hot climates from marine sulfate evaporites and mature quartz sandstones can be found (Bekker & Holland, 2012; Bekker et al., 2005). In panel (c) the black and gold arrows represent  $O_2$  constraints from MIF-S measurements in the Transvaal basins (Farquhar et al., 2000; Guo et al., 2009; Luo et al., 2016; Poulton et al., 2021). Note that the absolute time of these constraints is not well known. We put these constraints on a time-scale consistent with their position relative to glacial deposits. Redox proxies and their relative position to the glaciations in the Transvaal and Huronian basins are shown below panel (c) (Gumsley et al., 2017). Chronological constraints and their uncertainty near the glacial deposits come from 1. Senger et al. (2023), 2. Schröder et al. (2016), 3. Zeh et al. (2020), 4. Hannah et al. (2004), 5. Rasmussen et al. (2013). The formation name abbreviations are: Mkg (Makganyene), Dtd (Duitschland), Roo (Rooihoogete), Rie (Rietfontein), RL (Ramsay Lake), Br (Bruce), Gwd (Gowganda). In panels (f–j) we show species profiles at points in time shown in “x” symbols in panel (a) during temperate (black), glacial (blue), and hot-moist greenhouse (red) conditions. The profiles line style corresponds to the line style of the  $O_2$  fluxes in panel (b).

The exit of the glaciations to a hot-moist greenhouse climate is characterized by high  $O_2$  mixing ratios of  $\sim 5 \times 10^{-4}$  independent of the  $O_2$  input flux values (Figures 2c and 2f). The increase in water vapor during the hot-moist greenhouse conditions boosts the production of oxidizing radicals, leading to the depletion of reduced species like  $CH_4$  and increasing  $O_2$  levels (Figures 2d–2j).

Finally, the return to temperate climates results in the restoration of low O<sub>2</sub> levels. This model result suggests that although temperature changes can drive O<sub>2</sub> oscillations by themselves, an increase in the O<sub>2</sub> input flux or a decrease in reductant input flux over time is necessary to maintain post-GOE O<sub>2</sub> levels at temperate climates.

### 3.2.1. Atmospheric Chemical Profiles

The temperate, glacial, and hot-moist greenhouse climates have characteristic species profiles that are shaped by the water vapor content of the atmosphere and the O<sub>2</sub> input flux (Figures 2f–2j). First, temperate climates are characterized by low O<sub>2</sub> and O<sub>3</sub> concentrations that reach a minimum near 10 km (Figures 2f and 2g). Second, glacial climates are characterized by decreased water vapor in the troposphere and the stratosphere (Figure 2i). With less water vapor, there is less production of oxidizing radicals and less O<sub>2</sub> consumption. Thus, the O<sub>2</sub> and O<sub>3</sub> profiles show an increase in concentration compared to the temperate climate profiles, resulting in oxygenation and formation of an O<sub>3</sub> layer for the  $2.2 \times 10^{12}/\text{cm}^2/\text{s}$  O<sub>2</sub> flux case. In this case, after O<sub>2</sub> builds up, the O<sub>3</sub> layer shields H<sub>2</sub>O against photochemical destruction, causing an increase in H<sub>2</sub>O vapor above the troposphere. The abundant O<sub>2</sub> and H<sub>2</sub>O lead to higher OH production via water vapor photolysis and the reaction  $\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{OH}$ , increasing CH<sub>4</sub> oxidation and decreasing the CH<sub>4</sub> concentration at all altitudes. Third, the hot-moist greenhouse climates are characterized by high water vapor concentrations, leading to abundant oxidizing radicals (Figures 2i and 2j). These radicals react with and deplete CH<sub>4</sub>, leading to the oxygenation of the atmosphere and the formation of an O<sub>3</sub> layer.

### 3.3. Time Dependent Temperature Forcing With a Linear Increase in O<sub>2</sub> Flux

The second time-dependent model simulation (Figure 3) investigates the effect of temperature by using a linear increase in O<sub>2</sub> flux (see Section 2.3.2). Superimposing a 60% decrease during glacial periods results in pre-GOE O<sub>2</sub> levels (Figure 3c continuous). The low O<sub>2</sub> levels during glaciations lead to abundant S<sub>8</sub> production (Figure 3e continuous orange line). In contrast, if these superimposed O<sub>2</sub> flux changes are not included some glacial periods show post-GOE O<sub>2</sub> levels and no S<sub>8</sub> production (Figures 3c and 3e dotted).

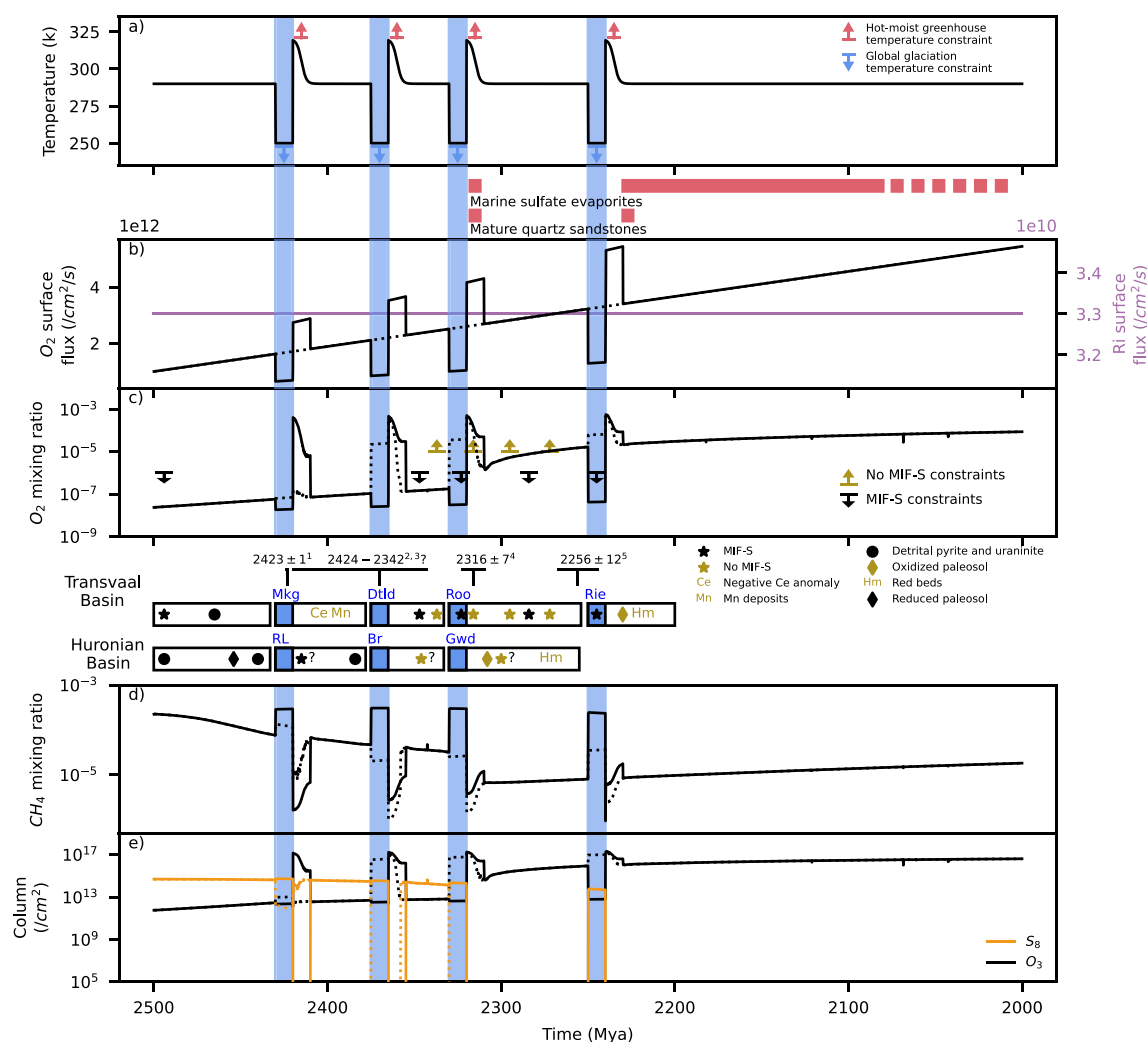
### 3.4. Time Dependent Temperature Forcing With a Linear Decrease in Reductant Input Flux

Driving a gradual increase in O<sub>2</sub> levels with a decrease in reductant input flux (Section 2.3.3) leads to similar results than driving the increase in O<sub>2</sub> levels with an increase in O<sub>2</sub> input flux (Figure 4). In this case, when the O<sub>2</sub> flux is constant, O<sub>2</sub> shows post-GOE levels during glacial and hot moist greenhouse periods (Figure 4c dotted) and the S<sub>8</sub> production stops during the first glaciation (Figure 4e dotted orange line). In contrast, superimposing a 60% decrease in O<sub>2</sub> flux during glacial periods and a 60% increase during hot-moist greenhouse periods leads to pre-GOE O<sub>2</sub> levels during glaciations, and post-GOE O<sub>2</sub> levels after glaciations (Figure 4c continuous). The low O<sub>2</sub> levels facilitate the production of MIF-S through S<sub>8</sub> aerosols during glacial periods, but the decrease in reductant input flux makes the S<sub>8</sub> production decrease over time (Figure 4e continuous orange line). This pattern occurs because S<sub>8</sub> photochemical production requires three conditions: low O<sub>2</sub> levels, enough abundance of reduced gases, and input of sulfur gases to the atmosphere (Zahnle et al., 2006).

## 4. Discussion

The MIF-S record across the GOE shows a complex pattern. There are positive MIF-S values between the second and third glaciations that disappear before the onset of the third glaciation (Guo et al., 2009). The signal comes back in the glacial deposits and surrounding breccias and conglomerates of the third glaciation and is lost again afterward (Izon et al., 2022; Luo et al., 2016; Poulton et al., 2021). Finally, sparse MIF-S signals occur between the third and fourth glaciations, with some non-zero MIF-S values in the glacial deposits of the fourth glaciation (Poulton et al., 2021).

Our results show that some of the MIF-S swings observed in the rock record can be explained by temperature changes associated with global glaciations. Provided that the O<sub>2</sub> input flux is low (e.g.,  $<2 \times 10^{12}/\text{cm}^2/\text{s}$ ) during glacial periods, our results are consistent with the presence of MIF-S signals in glacial deposits and the disappearance of the signal after the glaciations. Low O<sub>2</sub> fluxes during glacial periods are a reasonable assumption due to the difficult conditions for primary producers. In contrast, the aftermath of the glaciations leads to the loss of the MIF-S signal because the hot-moist greenhouse conditions cause oxygenation. This pattern is observed in the sedimentary record associated with the third (Izon et al., 2022; Luo et al., 2016) and fourth glaciations (Poulton

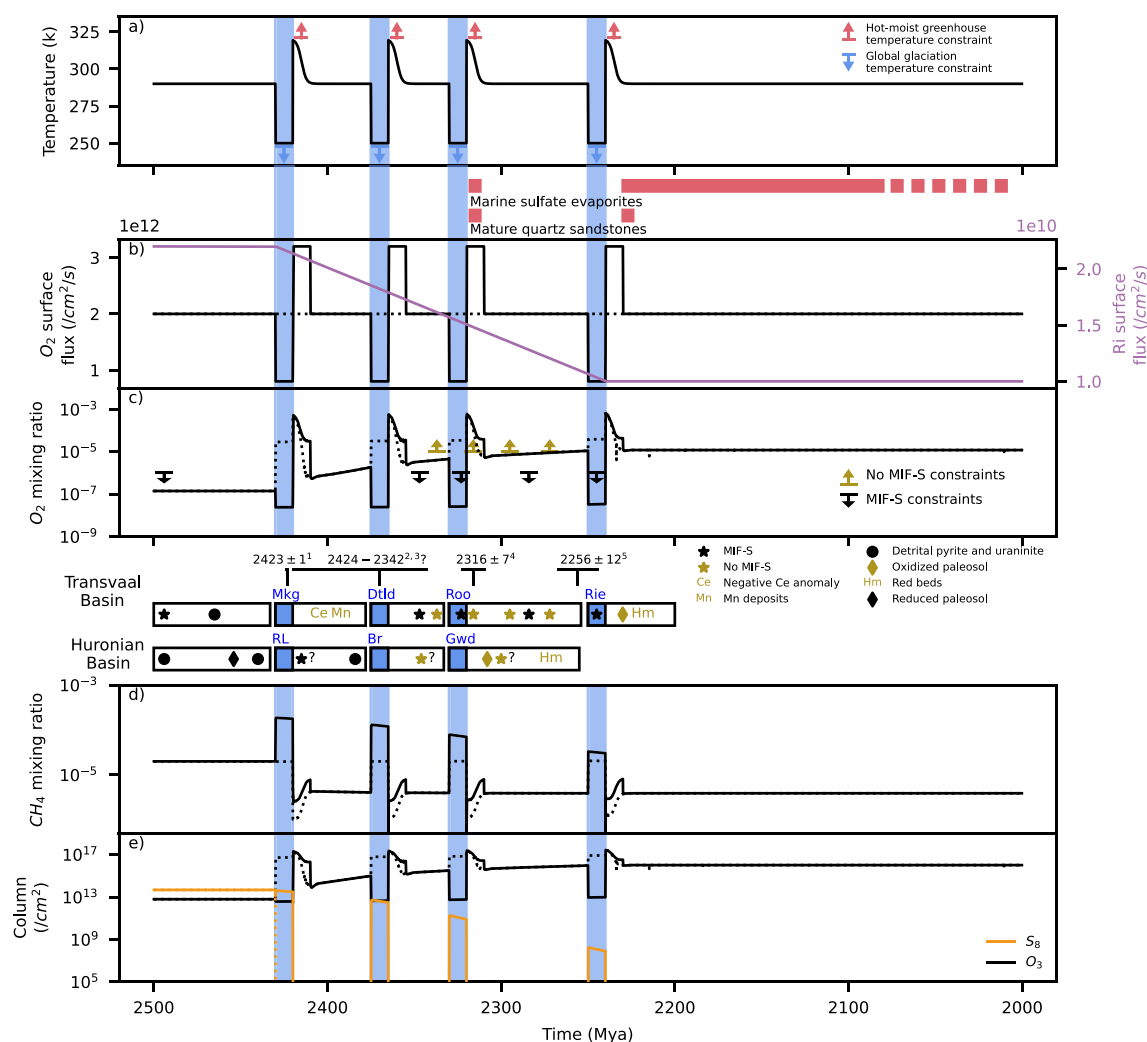


**Figure 3.** This figure shows two different model scenarios, prescribed with the same temperature evolution (a) but two different  $O_2$  input flux histories (b). First, a linear increase in  $O_2$  input flux over time (dotted line). In this case, as the  $O_2$  input flux increases, the  $O_2$  mixing ratio (c) shows a gradual increase perturbed by temperature changes. The  $O_2$  mixing ratio increases above  $10^{-5}$ , and the  $S_8$  production stops during glaciations and hot-moist greenhouse periods when the flux is  $>2.1 \times 10^{12} \text{ cm}^2/\text{s}$ . Second, a linear increase in  $O_2$  input flux that drops 60% during glaciations and increases 60% during hot-moist greenhouse climates. In this case, the decrease in  $O_2$  flux during glaciations leads to low  $O_2$  levels during glacial periods, whereas the increase in temperature and  $O_2$  input flux during hot-moist greenhouse periods lead to high  $O_2$  levels.

et al., 2021). However, there are some MIF-S constraints that we can not explain with temperature changes. For example, the disappearance of the MIF-S signal before the third glaciation and the MIF-S swings between the third and fourth glaciations are difficult to explain with temperature changes alone.

The GOE was a complex event where multiple forcings could have affected the evolution of atmospheric  $O_2$  levels. Changes in biogenic fluxes, massive volcanic eruptions, or changes in the composition of volcanic gases could have altered the concentration of  $O_2$  across the GOE (Kasting, 2013; Wogan et al., 2022). The MIF-S oscillations that are not associated with periods of climate change could represent alterations to the redox budget of the atmosphere from one of these other perturbations.

On the time scales considered in this study (500 My), changes in other redox reservoirs could have affected the evolution of atmospheric  $O_2$ . For example, changes in the rate of reduced mineral oxidation in the crust or changes in the rate of volcanic input to the atmosphere could have altered  $O_2$  concentrations. Our modeling implicitly includes external effects on atmospheric redox state by imposing changes in  $O_2$  and reductant input fluxes, but we do not explicitly include interactions between redox reservoirs. Also, our modeling does not explicitly consider the interactions and feedback mechanisms between atmospheric chemistry and climate. For example, our results



**Figure 4.** This figure shows a model scenario in which we drive a gradual increase in  $O_2$  levels with a decrease in reductant input flux (purple line in panel b, see Section 2.3.3), considering two  $O_2$  flux histories. First, we keep a constant  $2 \times 10^{12}/\text{cm}^2/\text{s}$   $O_2$  flux (dotted lines). This case shows  $O_2$  mixing ratios  $>10^{-5}$ , and no  $S_8$  production during glaciations and hot-moist greenhouse periods. Second, we superimpose a 60% decrease in  $O_2$  flux during glaciations and a 60% increase during hot-moist greenhouse climates (continuous black line in panel b). This case shows low  $O_2$  levels during glacial periods and high  $O_2$  levels during hot-moist greenhouse periods.

show that during hot-moist greenhouse periods, the increase in temperature leads to a decrease of  $CH_4$  mixing ratios from  $\sim 10^{-4}$  to  $\sim 10^{-6}$  (Figures 2d and 3e). This  $CH_4$  decrease would impact climate, decreasing temperature and going against the effect of the initial temperature increase. Also, the high  $CO_2$  concentration during hot-moist greenhouse periods could enhance the photochemical production of CO, increasing the concentration of reduced species and counteracting the  $O_2$  increase caused by high temperatures. We leave investigation of these feedback mechanisms to a future study.

Our results contrast with recent studies that suggest that the MIF-S swings in the rock record are a product of the recycling of previously produced MIF-S signals (Killingsworth et al., 2019; Philippot et al., 2018; Reinhard et al., 2013). See the Supporting Information S1 for discussion on this topic.

### 5. Conclusions

We used a time-dependent photochemical model to show that temperature changes associated with the Paleoproterozoic glaciations are a plausible cause of oxygen concentration and MIF-S oscillations across the GOE. The model results demonstrate that the glacial periods associated with the GOE are likely characterized by low  $O_2$

levels due to low O<sub>2</sub> input fluxes. The exit of the glaciations to hot-moist greenhouse climates is characterized by post-GOE O<sub>2</sub> levels, and this increase in atmospheric O<sub>2</sub> can be driven by increasing temperatures alone. These results are consistent with the sedimentary record of MIF-S signals associated with the Paleoproterozoic glacial deposits and support a primary origin for MIF-S generation.

## Data Availability Statement

The complete model output can be downloaded at Garduno Ruiz et al. (2024a). All instructions, scripts, and model output necessary to reproduce our results are available at Garduno Ruiz et al. (2024b).

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