Rapid timescale for an oxic transition during the Great Oxidation Event and the instability of low atmospheric O2

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The Great Oxidation Event (GOE), arguably the most important event to occur on Earth since the origin of life, marks the time when an oxygen-rich atmosphere first appeared. However, it is not known whether the change was abrupt and permanent or fitful and drawn out over tens or hundreds of millions of years. Here, we developed a one-dimensional time-dependent photochemical model to resolve time-dependent behavior of the chemically unstable transitional atmosphere as it responded to changes in biogenic forcing. When forced with step-wise changes in biogenic fluxes, transitions between anoxic and oxic atmospheres take between only 10⁵ and 10⁶ y. Results also suggest that O₂ between ~10⁻³ and ~10⁻⁴ mixing ratio is unstable to plausible atmospheric perturbations. For example, when atmospheres with these O₂ concentrations experience fractional variations in the surface CH₄ flux comparable to those caused by modern Milankovich cycling, oxygen fluctuates between anoxic (~10⁻⁸) and oxic (~10⁻⁴) mixing ratios. Overall, our simulations are consistent with possible geologic evidence of unstable atmospheric O₂, after initial oxygenation, which could occasionally collapse from changes in biogenic or volcanic fluxes. Additionally, modeling favors mid-Proterozoic O₂ exceeding 10⁻⁴ to 10⁻³ mixing ratio; otherwise, O₂ would periodically fall below 10⁻⁷ mixing ratio, which would be inconsistent with post-GOE absence of sulfur isotope mass-independent fractionation.

Great Oxidation Event | photochemistry | oxygen

Abundant atmospheric O₂ at 21% by volume is the most distinctive and consequential feature of Earth's atmosphere. Produced by cyanobacteria, algae, and plants, O₂ is a clear sign of our biosphere that is detectable across interstellar space by telescopic spectroscopy (1). Oxygen permits aerobic respiration, the only known metabolism with sufficient energy yield to sustain complex animal life (2). However, for about the first half of Earth's 4.5-billion-year-old history, the atmosphere had negligible O₂ (e.g., ref. 3). This changed ~2.4 billion years ago.

The timing of the Great Oxidation Event (GOE) and the magnitude of atmospheric O₂ concentrations before and after the GOE can be constrained by the geologic record of sulfur isotopes in combination with photochemical models. Archean and earliest Proterozoic sedimentary minerals contain sulfur isotopes with characteristic mass-independent fractionation (MIF) which abruptly disappears 2.4 billion years ago (4). Sulfur MIF in marine sediments likely requires that atmospheric photochemistry produce elemental sulfur, S₈ (for explanation, see the introduction in ref. 5) (6, 7). Zahnle et al. (5) used a one-dimensional (1D) photochemical model to show that atmospheric S₈ production only occurs when atmospheric O₂ is below ~2 × 10⁻⁷ mixing ratio. An often cited threshold of 2 × 10⁻⁶ was from an earlier photochemical model that did not simulate atmospheres with surface O₂ mixing ratios between 2 × 10⁻⁶ and ~10⁻⁷ (6). Therefore, the disappearance of the sulfur isotope MIF signal at 2.4 Ga is strong evidence that O₂ first rose above 2 × 10⁻⁷ mixing ratio then.

Geologic evidence may suggest that the GOE was not a single monotonic rise of oxygen but characterized by oscillations. Using U-Pb dating, Gumsley et al. (8) updated the chronology of sulfur isotope MIF in the stratigraphic record, finding evidence for two oxic-to-anoxic transitions between ~2.4 and ~2.3 Ga. More recently, Poulton et al. (9) report 2.3 Ga to 2.2 Ga marine sediments with sulfur isotopes consistent with approximately five oxic-to-anoxic transitions. Fluctuating O₂ levels coincide with three to four widespread glaciations, indicating extreme climate instability (10). Overall, geochemical evidence tentatively suggests that O₂ concentrations and climate were unstable for 200 million years until 2.2 Ga, which marks the most recent estimated timing of the permanent oxygenation of the atmosphere (9). However, interpretations of oscillating O₂ have been questioned (11). While the geochemical evidence for the O₂ oscillations remains equivocal, the data have raised significant questions regarding the feasibility and timescales for Earth's great oxidation. Some have argued that the oxygen-rich

Significance

Understanding the rise of atmospheric oxygen on Earth is important for assessing precursors to complex life and for evaluating potential future detections of oxygen on exoplanets as signs of extraterrestrial biospheres. However, it is unclear whether Earth's initial rise of O₂ was monotonic or oscillatory, and geologic evidence poorly constrains O₂ afterward, during the mid-Proterozoic (1.8 billion to 0.8 billion years ago). Here, we used a time-dependent photochemical model to simulate oxygen's rise and the stability of subsequent O₂ levels to perturbations in supply and loss. Results show that large oxygen fluctuations are possible during the initial rise of O₂ and that Mesoproterozoic O₂ had to exceed 0.01% volume concentration for atmospheric stability.

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atmosphere is more stable than an oxygen-poor atmosphere (12), which favors a single rise of O$_2$ instead of O$_2$ oscillations.

Evidence for O$_2$ instability and the time-dependent behavior of O$_2$ concentrations has not been reconciled with atmospheric photochemical models. All previous models treated the GOE as successive photochemical steady states (5, 6, 13–19). A photochemical steady state occurs when no atmospheric species changes concentration over time, because their production and loss from reactions and surface sources (e.g., volcanoes or biology) are balanced. Such steady-state calculations have been crucial for understanding the GOE by contextualizing sulfur isotope MIF observations (5, 6), and establishing the relationship between atmospheric O$_2$ concentrations and the degree to which O$_3$ blocks UV photons from Earth’s surface (i.e., O$_3$ shielding) (13, 15, 16), but they do not evaluate time-dependent changes and transient imbalances, or characteristic timescales.

Several theories for the rise of O$_2$ suggest that it relied on a global redox titration over 10$^8$ y to 10$^9$ y involving oxidation of the upper mantle and/or crust, plausibly driven by hydrogen escape, which led to a tipping point where the source flux of O$_2$ exceeded a kinetically rapid O$_2$ sink from volcanic and metamorphic reductants (20–24). Beyond the tipping point, O$_2$ flooded the atmosphere, reaching a new, long-term balance limited by oxidative weathering.

Here, we developed a time-dependent 1D photochemical model capable of investigating changes of O$_2$ at the tipping point itself over timescales of 10$^8$ y to 10$^9$ y rather than the longer-term planetary changes which initiated the GOE. We simulate changing O$_2$ as a time-dependent evolution, in contrast to the steady-state approach used in previous studies (e.g., ref. 13), because O$_2$ can change on relatively rapid timescales that are not well characterized by steady states. With our model, we compute the time required for an anoxic-to-oxic atmospheric transition, and the time required for deoxygenation. Additionally, we investigate the stability of O$_2$ concentrations against perturbations to surface gas fluxes produced by biology. Finally, we use our model results to better constrain O$_2$ levels and stability during the GOE (starting at $\sim$2.4 Ga), and during the mid-Proterozoic eon (1.8 Ga to 0.8 Ga).

Results

To investigate the time-dependent behavior of O$_2$ during the GOE, we first computed grids of photochemical steady-state atmospheres. These steady states establish the context for time-dependent photochemical modeling described in subsequent sections. Fig. 1 shows the predicted steady-state surface O$_2$ mixing ratio (Fig. 1A), the surface CH$_4$ mixing ratio (Fig. 1B), and the precipitation of atmospheric S$_8$ (gray shading) as a function of surface O$_2$ flux between 3 x 10$^{10}$ and 10$^{13}$ molecules per cm$^2$ s$^{-1}$, and CH$_4$ flux/O$_2$ flux ratios between 0.27 and 0.49 where gas fluxes are those entering the atmosphere. The surface O$_2$ fluxes reported here are net emissions into the atmosphere which exclude recycling within the biosphere. For reference, a comparable model of the modern Earth requires a surface O$_2$ flux of 10$^{12}$ molecules per cm$^2$ s$^{-1}$, and a CH$_4$ flux/O$_2$ flux of 0.09 (CH$_4$ flux = $\sim$9 x 10$^{10}$ molecules per cm$^2$ s$^{-1}$) (16). We consider a CH$_4$/O$_2$ flux ratio close to 0.5 to be more realistic for the Late Archean, prior to the GOE, because this ratio is expected if oxygenic photosynthesis is balanced by methanogenesis. In net (21), where “CH$_2$O” represents organic matter,

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$$ (Oxygenic Photosynthesis)

$$2\text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2$$ (Methanogenesis)

$$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$$ (Net).  [1]

The CH$_4$ flux/O$_2$ flux ratio is smaller than 0.5 on modern Earth largely because of the microbial anerobic oxidation of methane via SO$_4^{2-}$ in ocean sediments, a process that was unimportant in the anoxic mid-Archean ocean with little sulfate (25–27). We include O$_2$ fluxes several orders of magnitude smaller than the modern value ($\sim$10$^{12}$ molecules per cm$^2$ s$^{-1}$) because of evidence for smaller primary productivity during the Proterozoic eon (28, 29).

Recall that atmospheric S$_8$ deposition is considered necessary to preserve sulfur isotope MIF in ocean sediments (6). We find that S$_8$ production is not possible above a $\sim$10$^{-7}$ O$_2$ mixing ratio (the gray-to-white shading boundary in Fig. 1), consistent with previous results (5).

Fig. 1 uses Archean outgassing surface fluxes for CO, H$_2$, H$_2$S, and O$_2$ listed in Table 1, with the CO$_2$ surface mixing ratio fixed to 1% for all model runs—a reasonable value for the Late Archean according to carbon cycle modeling (30). Additionally, over the same span of surface O$_2$ fluxes and H$_2$ flux/O$_2$ flux ratios, we compute photochemical steady states for the modern fluxes for CO, CH$_4$, H$_2$S, and O$_2$ listed in Table 1, again fixing CO$_2$ to 1%. The results are shown in SI Appendix, Fig. S1.

![Fig. 1. Colored contours show photochemical steady states of (A) log$_{10}$ surface O$_2$ mixing ratio and (B) log$_{10}$ surface CH$_4$ mixing ratio as a function of log$_{10}$ O$_2$ surface flux and CH$_4$ flux/O$_2$ flux. Gray shading indicates the magnitude of elemental S$_8$ production in the atmosphere, which is considered essential for the preservation of sulfur isotope MIF in marine sediments. Peak S$_8$ production is $\sim$10$^7$ molecules per cm$^2$ s$^{-1}$. Gray shading fades to white for S$_8$ production less than 10$^{-10}$ molecules per cm$^2$ s$^{-1}$, a negligibly small value. Arrows labeled “Figure 2a” and “Figure 2c” indicate start and end points for time-dependent photochemical models of the oxic transition shown in Fig. 2 A and C. Red, blue, and green stars are the initial conditions used in the simulations shown in Fig. 4 B, D, and E, respectively.]
Table 1. Fixed surface flux boundary conditions for SO₂, H₂S, H₂, and CO used in this study

| Model       | SO₂     | H₂S     | H₂      | CO      |
|-------------|---------|---------|---------|---------|
| Archean     | 10⁷     | 10⁷     | 3 × 10⁷ | 3 × 10⁷ |
| outgassing* |         |         |         |         |
| Modern      | 3.5 × 10⁹ | 3.5 × 10⁸ | 1.22 × 10⁸ | 2.65 × 10¹¹ |

All fluxes have units of molecules per square centimeter per second.

*The same fluxes as the “Archean High” values from Table 1 in Zahnle et al. (5).

†Surface flux values required to reproduce the concentration of each gas in modern Earth’s atmosphere. These values are also the “Case 1” fluxes described in Gregory et al. (16).

In the following sections, we calculate the time required to transition between different steady-state atmospheres shown in Fig. 1 and SI Appendix, Fig. S1.

The Timescale of Atmospheric Oxygenation. The orange arrow labeled “Figure 2A” in Fig. 1 corresponds to the approximate start and end states of the time-dependent photochemical model run shown in Fig. 2A. The model starts with an atmosphere at a steady state, then, at t = 0 y, we impose a stepwise decrease in the surface methane flux from 4.9 × 10¹⁰ to 4.7 × 10¹¹ molecules per cm²·s⁻¹ (we keep the surface O₂ flux constant at 10¹² molecules per cm²·s⁻¹). This perturbation causes O₂ to rise from 3 × 10⁻⁸ to 3 × 10⁻⁵ mixing ratio over 3,500 y, eliminating photochemical S₈ production.

The O₂ transition in Fig. 2A, i is modulated by O₃ shielding of tropospheric H₂O (13). When a stratospheric O₃ layer begins to develop, OH production from H₂O decreases (Fig. 2A, ii). Decreasing OH concentrations prevent the mutual annihilation of O₂ and CH₄ (by CH₄ + OH → CH₃ + H₂O followed by CH₃ + O₂ → products), so O₂ levels increase. The mixing ratio of CH₄ also rebounds. O₃ shielding (protecting life on the surface from harmful solar UV radiation) is just barely beginning to operate in this example compared to modern Earth. After the atmosphere reaches a new steady state, the atmospheric column has 3 × 10¹⁷ O₃ molecules per cm², some 26 times smaller than the modern value of 8 × 10¹⁸ molecules per cm². Note that the extent to which O₃ shields tropospheric H₂O can be strongly modulated by 3D dynamical effects (31), which we do not account for.

Like Fig. 2A, Fig. 2B also shows a transition between a 5 × 10⁻⁸ and 2 × 10⁻⁵ O₂ mixing ratio, but this model uses the modern outgassing fluxes for CO, H₂, H₂S, and SO₂ listed in Table 1 instead of presumptive Archean outgassing values. Also, at t = 0 y, we impose a stepwise increase of the O₂ flux from 10¹² to 1.8 × 10¹³ molecules per cm²·s⁻¹ while keeping the CH₄ flux/O₂ flux ratio at 0.45 (see SI Appendix, Fig. S1 for context). While the anoxic-to-oxic transition itself still occurs rapidly, the atmosphere simulated in Fig. 2B takes 60,000 y to reach the tipping point, which is much longer than the comparable O₂ transition shown in Fig. 2A.

The time required for O₂ to begin to rise in concentration is controlled by the reservoir of reducing gases, primarily CH₄, H₂, and CO, in the preoxygenated atmosphere. Big reservoirs of reducing gases slow the timescale of oxygenation, because reducing gases must be mostly removed before O₂ can increase. O₂ cannot increase while reducing gases are abundant, because large oxygen sinks from reactions with reducing gases prevent it. That is why 3,500 y elapse before O₂ begins to rise in Fig. 2A, and why 60,000 y elapse before O₂ rises in Fig. 2B. Fig. 2B starts with more reducing gases, which take longer to eradicate.

We can roughly estimate the time required for O₂ to begin to rise, with a back-of-the-envelope calculation of the rate at which reducing gases are eliminated from the anoxic atmosphere. The total reservoir of reducing gases in the preoxygenated atmosphere in O-equivalent units is

\[ N_\text{reducing} = \sum_j N_j \alpha_j \approx -4N_{\text{CH}_4} - N_{\text{CO}} - N_{\text{H}_2}. \]  

Here, \( N_\text{reducing} \) is the O-equivalent column abundance of reducing gases (Oequiv molecules per cm²) which is equal to the sum of all reducing gases in the atmosphere (\( N_j \)) multiplied by \( \alpha_j \), the redox state of each gas. Redox state is a relative quantity that requires defining redox-neutral reference species. Following previous models of early Earth (5), we define H₂O, SO₂, CO₂, and N₂ as redox neutral, with the oxygen redox parameter \( \alpha_O = +1 \). Therefore, \( \alpha_H = -0.5, \alpha_S = -2, \) and...

![Fig. 2. Three models of anoxic-to-oxic transitions. (A) Atmospheric oxygenation caused by a step-wise decrease in the methane flux from 4.9 × 10¹¹ to 4.7 × 10¹¹ molecules per cm²·s⁻¹ (orange arrow in Fig. 1). (i) Surface O₂ and CH₄ mixing ratios, and O₂ and SO₂ column abundance over time; (ii) OH surface mixing ratio and tropospheric H₂O photolysis rate. (B) Transition caused by step-wise increase in the O₂ flux from 10¹² to 1.8 × 10¹³ molecules per cm²·s⁻¹ and a stepwise increase in the CH₄ flux to maintain constant CH₄ flux/O₂ flux = 0.45 (SI Appendix, Fig. S1). Transition in C results from a step-wise decrease in the CH₄ flux from 4.9 × 10¹¹ to 4.5 × 10¹¹ molecules per cm²·s⁻¹ (black arrow in Fig. 1).](https://doi.org/10.1073/pnas.2205618119)
\( \alpha_C = -2 \), from redox stoichiometry of hydrogen, sulfur, and carbon, respectively. It then becomes straightforward to calculate the \( \alpha_j \) for any molecule. For example, \( \alpha_{\text{CH}_4} = \alpha_C + 4\alpha_H = -2 - 2 = -4 \). For a more in-depth explanation of atmospheric redox, see section 3 in Harman et al. (32) or chapter 8 in Catling (33). \( N_{\text{reducing}} \) is approximately equal to the weighted sum of \( \text{CH}_4 \), \( \text{H}_2 \), and \( \text{CO} \) because these are the main reducing gases in an Archean Earth-like atmosphere.

The change in column abundance of reducing gases is the difference between the redox columns at the final and initial atmospheric states.

\[
\Delta N_{\text{reducing}} = N_{\text{reducing}}^{\text{final}} - N_{\text{reducing}}^{\text{initial}}. \tag{3}
\]

In Fig. 2A and B, we initiate the rise of oxygen by changing the surface flux of \( \text{CH}_4 \) and/or \( \text{O}_2 \) flux. We can quantify this flux perturbation in units of \( \text{O}_\text{equiv} \) molecules per square centimeter per second (\( \Delta F_{\text{O}_\text{equiv}} \)).

\[
\Delta F_{\text{O}_\text{equiv}} = \sum_j F_{j}^{\text{final}} \alpha_j - \sum_j F_{j}^{\text{initial}} \alpha_j \tag{4}
\]

Therefore, the time required to oxidize the reducing gases in the atmosphere and permit oxygen to begin rising is approximately

\[
\tau_{\text{oxy}} = \frac{\Delta N_{\text{reducing}}}{\Delta F_{\text{O}_\text{equiv}}}. \tag{5}
\]

Plugging in values for the \( \text{O}_2 \) transition in Fig. 2B yields \( \tau_{\text{oxy}} \approx 2,900 \text{ yr} \); a value only slightly smaller than the 3,500 yr predicted by the time-dependent photochemical model. For Fig. 2B, \( \tau_{\text{oxy}} \approx 29,000 \text{ yr} \), which is about a factor of 2 smaller than the figure from 1D photochemistry. Our estimate is too small in this case because the reducing column and its destruction rate are not constant prior to the rise of oxygen (SI Appendix). This calculation illustrates that the time required for oxygen to begin rising, once a tipping point of fluxes is reached, mostly depends on the quantity of reducing gases in the preoxygenated atmosphere.

Fig. 2C shows a more substantial anoxic-to-toxic transition compared to simulations shown thus far (also see Movie S1). We start with the same steady-state atmosphere as in Fig. 2A, except we decrease the methane flux by twice as much at \( t = 0 \), from \( 4.9 \times 10^{11} \) molecules per \( \text{cm}^2 \cdot \text{s}^{-1} \) to \( 4.5 \times 10^{11} \) molecules per \( \text{cm}^2 \cdot \text{s}^{-1} \) instead of \( 4.7 \times 10^{11} \) molecules per \( \text{cm}^2 \cdot \text{s}^{-1} \) (we keep the surface \( \text{O}_2 \) flux constant at \( 10^{12} \) molecules per \( \text{cm}^2 \cdot \text{s}^{-1} \)). \( \text{O}_2 \) begins to rise and eliminates \( \text{S}_8 \) production after \( \sim 1,500 \text{ yr} \), but \( \text{O}_2 \) will reach higher levels because of the lower \( \text{CH}_4 \) flux. It takes \( \sim 300,000 \text{ yr} \) for \( \text{O}_2 \) to reach its final steady-state abundance of \( 4 \times 10^{-3} \) mixing ratio. While the switch from \( 10^{-8} \) to \( 10^{-5} \) \( \text{O}_2 \) mixing ratio remains as rapid as in Fig. 2A, the predicted increase in \( \text{O}_2 \) concentrations to \( 4 \times 10^{-3} \) mixing ratio requires far longer. This timescale is roughly analogous to the time required to deplete \( \text{H}_2 \) and \( \text{CH}_4 \) reservoirs to allow \( \text{O}_2 \) to initially rise in concentration.

In summary, the timescale for \( \text{O}_2 \) to rise in concentration depends on the reservoir of redox gases in the atmosphere, and the magnitude of the perturbation to redox surface fluxes. For \( \text{O}_2 \) to rise from \( 10^{-8} \) to \( 10^{-5} \), reducing gases must first be removed, which can take thousands to tens of thousands of years (Fig. 2A and B). Increasing \( \text{O}_2 \) concentrations beyond \( 10^{-5} \) to near percentage levels requires filling a large \( \text{O}_2 \) reservoir, which occurs on 10^5-yr timescales in our model run (Fig. 2C).

**The Time Required for Deoxygenation.** Here, we use our time-dependent photochemical model to address the controversy of the reversibility of the oxic transition (9, 11). Fig. 3 shows the reverse of model runs shown in Fig. 2. For each model run, we start with an atmosphere initially at a steady state at the end of the simulations shown in Fig. 2. Then we impose a stepwise change in the \( \text{O}_2 \) and \( \text{CH}_4 \) flux at \( t = 0 \text{ yr} \) to return the atmosphere to anoxia. The reversal of Fig. 2 takes \( \sim 700, 100 \), and 40,000 yr, respectively, in comparison to the 3,500, 60,000, and 300,000 yr required for oxygenation.

Like the timescale for oxygenation, the timescale for deoxygenation depends on the column abundance of redox-sensitive gases. In the previous section, we established that the timescale required for \( \text{O}_2 \) to begin to rise is merely the time required to deplete
The Stability of Post-GOE Atmospheric Oxygen. In the previous two sections, we show that reservoirs of redox gases, primarily methane and oxygen, give the atmosphere chemical inertia, controlling the timescale of O₂ changes. When reservoirs are big, for similar flux perturbations, the O₂ mixing ratio will change relatively slowly over time; however, when reservoirs are small, photochemistry permits rapid O₂ transitions. Therefore, the abudance of redox gases in an atmosphere is closely linked to the photochemical stability of oxygen.

Fig. 4A shows the steady-state inertial timescale of redox gases, τ_inertia, over the same axes as Fig. 1, which shows mixing ratios. τ_inertia is the sum of all redox gases in the atmospheric column (O-equivalent molecules per square centimeter), divided by a characteristic flux perturbation, which we take to be 10% of the O₂ flux,

\[ \tau_{\text{inertia}} = \frac{N_{\text{redox}}}{F_{\text{redox perturb}}} = \sum_i |\alpha_i| N_i / 0.1 \alpha_{O_2} F_{O_2}. \]  

We choose the characteristic flux perturbation to be 10% of the O₂ flux because it is the same order of magnitude as natural redox variations that occur on modern Earth during Milankovitch cycling (see Discussion). An upper limit for the characteristic flux perturbation would be 100% of the O₂ flux. This would decrease all τ_inertia values in Fig. 4A by a factor of 10, which would not change our interpretation. Since CH₄, CO, H₂, and O₂ are the most important redox gases, the numerator in Eq. 6 is well approximated by 4N CH₄ + N CO + N H₂ + 2N O₂. Oxygen is the most prone to change for the smallest τ_inertia values, coinciding with O₂ mixing ratios between ~10⁻⁸ and ~10⁻⁵ shown in the whitish region of Fig. 4A.

The time-dependent photochemical models shown in Fig. 4B-D illustrate the relationship between τ_inertia and O₂ instability. To produce Fig. 4B, we started with the steady-state atmosphere indicated on Fig. 4A, then imposed 17% amplitude oscillations to the CH₄ flux with a period of 10,000 y. This forcing had no perceptible effect on the 3 × 10⁻⁹ atmospheric O₂. A similar 20% CH₄ flux oscillation also did not significantly perturb an anoxic atmosphere starting with 3 × 10⁻⁴ O₂ (Fig. 4D). However, just 5% CH₄ flux oscillations cause approximately four-orders-of-magnitude oscillations in surface oxygen concentrations for an incipiently oxic atmosphere starting with 3 × 10⁻⁵ O₂ (Fig. 4C). O₂ is most unstable where the abundance of all redox gases is smallest relative to a characteristic redox surface flux (the whitish area of Fig. 4A) between ~10⁻⁸ and ~10⁻⁵ O₂ mixing ratio. Stability continually increases outside of this range of O₂ concentrations.

While O₂ was relatively stable in the Fig. 4 B and D simulations, it does not mean these atmospheres and initial oxygen concentrations are stable to all atmospheric perturbations. The stability of any O₂ mixing ratio depends on the atmospheric forcings that are likely in nature. In Discussion, we argue that the CH₄ flux oscillations used in Fig. 4 are realistic because comparable fractional changes in the methane flux have occurred over the past 650,000 y.

Flux oscillations over timescales greater than ~10 y are required to significantly affect O₂ concentrations. Imposing 100% amplitude fluctuations to the CH₄ flux with a period of 1 y, starting with the same atmosphere as Fig. 4C, did not significantly alter the atmosphere over time. Atmospheres with between ~10⁻⁸ and ~10⁻⁵ O₂ contain some CH₄ and O₂, which gives the atmosphere inertia against annual to decadal change.

**Discussion**

Recently, Gregory et al. (16) computed photochemical steady-state atmospheres for a wide range of surface O₂ and CH₄ fluxes and found bistable O₂ concentrations. Their model allows steady-state atmospheres for O₂ concentrations below 6 × 10⁻⁷ and above 2 × 10⁻⁵ mixing ratio but admits few steady-state solutions in between. They hypothesized that feedbacks between O₂ and O₃ shielding eliminate most solutions with these intermediate O₂ concentrations. In contrast, our model can yield a steady-state solution with intermediate O₂ concentrations given the right constant surface flux boundary conditions [e.g., Fig. 2B; see also Gregory et al.’s (16) figure 8]. The difference might be
caused by different steady-state convergence criteria, chemical reaction networks, boundary conditions, or a combination of these factors.

However, a photochemical steady state, for example, at $10^{-6}$ O$_2$ mixing ratio, does not mean that such an atmosphere is stable and realistic over $10^3$- to $10^7$-y timescales. Gas fluxes from Earth's surface can vary during these timescales and significantly change O$_2$ concentrations (Results).

For example, in the past 650,000 y, the biogenic methane flux has oscillated with an amplitude of 25% (6 × $10^5$ molecules per cm$^2$ · s$^{-1}$) and a 100,000-y period (34, 35). On modern Earth, methanogens in wetlands are a major source of atmospheric methane (36). Every 100,000 y, ice sheets have advanced and retreated, covering and uncovering wetlands, changing the CH$_4$ flux to the atmosphere. These ice ages and methane flux variations are in response to Milankovich cycles with characteristic periods between 20,000 and 100,000 y. This exact same methane oscillation would not have occurred in the Late Archean or Early Proterozoic because modern wetlands did not exist then, but a similar process involving microbial mats is conceivable.

Zhao et al. (37) modeled cyanobacterial mats on Proterozoic land, finding that they could have been a substantial CH$_4$ source to the atmosphere. Ice sheets covering and uncovering microbial mats could have affected global CH$_4$ fluxes. Fig. 4C illustrates the effect of 5% methane flux variations over Milankovich timescales on an atmosphere starting with $3 \times 10^{-7}$ O$_2$. O$_2$ oscillates nearly four orders of magnitude between $\sim 10^{-8}$ (anoxic) and $\sim 10^{-4}$ (oxic) (Fig. 4).

An oscillating methane flux is only one of many possible atmospheric perturbations. The Early Proterozoic geologic record preserves evidence of large igneous provinces (LIPs), or massive volcanic eruptions (8). In SI Appendix, we show that the H$_2$ and CO outgassed from a significant LIP eruption could cause the O$_2$ surface mixing ratio to drop from $2 \times 10^{-5}$ to $4 \times 10^{-9}$ in $\sim 100$ y, causing a return to sulfate isotope MIF. In this simulation, we use the maximum LIP eruption rates reported in the literature (38). In addition to LIPs, a Snowball Earth event concurrent with the GOE would have presumably affected gases produced by the biosphere (10).

Constant surface gas fluxes from biology and volcanism for millions of years in the aftermath of the initial rise of O$_2$ are unlikely. Additionally, our photochemical modeling shows that, for atmospheres with transitional O$_2$ concentrations, relatively small atmospheric perturbations (e.g., a CH$_4$ flux change of 5%) over timescales as short as hundreds of years can cause O$_2$ to change by orders of magnitude (e.g., Fig. 3B). Therefore, substantial variability of O$_2$ during the GOE appears possible.

For these reasons, our photochemical modeling results are compatible with recently published evidence of fluctuating sulfur isotope MIF (8, 9) indicating that O$_2$ was unstable between 2.4 and 2.2 Ga. We find that shutoff of S$_a$ aerosol production, which is required to produce sulfur isotope MIF, occurs at $\sim 10^{-7}$ O$_2$ mixing ratio, a region of the parameter space where O$_2$ is prone to rapid change (Fig. 4). But, oxygen surface levels between $\sim 10^{-8}$ and $\sim 10^{-4}$ mixing ratio were likely unstable. Short period changes to the biosphere, or volcanic outgassing rates, could have caused order of magnitude O$_2$ changes over 100- to 100,000-y timescales. Occasionally, big perturbations to the atmosphere, such as an LIP might have lowered O$_2$ concentrations enough for sulfur isotope MIF to reoccur. Note that the above explanation for the cause of O$_2$ oscillations prior to 2.2 Ga is complicated by S-MIF data presented in Izon et al. (11), which do not suggest the same O$_2$ variability found by Poulton et al. (9).

After 2.2 Ga, and during the mid-Proterozoic, sulfur isotope MIF never returned. Therefore, this time must have had O$_2$ concentrations large enough to prevent O$_2$ collapse. Our modeling shows that larger O$_2$ concentrations give the atmosphere chemical inertia, slowing atmospheric oxygenation (Fig. 3). It is therefore challenging to reconcile our modeling results with the interpretation of Planavsky et al. (39), who used Proterozoic chromium isotopes to argue that O$_2$ could not have been larger than $2 \times 10^{-4}$ mixing ratio. Such a small O$_2$ reservoir would have been unstable to LIP eruptions, or variations in the CH$_4$ flux from Milankovich cycles (Fig. 4), which both have evidence of occurring in the mid-Proterozoic stratigraphic record (40–42). We conclude that, for stability, mid-Proterozoic O$_2$ levels should have exceeded $\sim 10^{-4}$. This conclusion is compatible with mid-Proterozoic Fe isotopes in ironstones, which suggest O$_2$ levels between approximately $2 \times 10^{-4}$ and $2 \times 10^{-3}$ mixing ratio (43).

Our results are not sensitive to the changing solar UV photon flux between the GOE (~2.4 Ga) and the mid-Proterozoic. Recalculating Fig. 1 using the solar UV flux at 1.3 Ga (44) results in surface O$_2$ and CH$_4$ surface mixing ratios within a factor of 2 of Fig. 1.

Our work also has implications for the most likely oxygen levels before the GOE. Johnson et al. (45) analyzed molybdenum isotopes in the Archean sedimentary record for signs of continental oxidative weathering. Their work is compatible with two end-member interpretations: 1) If Archean O$_2$ was evenly distributed over the globe, then the surface O$_2$ mixing ratio was $\sim 3 \times 10^{-7}$ and $< 2 \times 10^{-7}$, or 2) if O$_2$ accumulation was geographically restricted, then the O$_2$ surface flux was greater than 0.01 Tmol · y$^{-1}$ ($3 \times 10^7$ molecules per cm$^2$ · s$^{-1}$). Our modeling suggests interpretation 1 is unlikely because we find that O$_2$ is likely unstable over geologic time for this range of oxygen levels.

In our modeling, we do not explicitly consider redox reservoirs in the oceans, sediments, crust, and mantle, for good reason. These reservoirs are coupled to the atmosphere and can modulate O$_2$ levels. However, the timescale of equilibration between the atmosphere and other redox reservoirs is often relatively long (e.g., 100 My for organic carbon in continental sediments), so we consider them to be approximately constant over the timescale of O$_2$ transitions ($< 10^3$ y).

A caveat is that the coupling between redox reservoirs in the atmosphere, crust, or sediments might depend on atmospheric composition. An example is the pyrite oxidation rate, which depends on the partial pressure of oxygen (16). We do not explicitly consider such feedbacks, which could affect the timescale of changing O$_2$ levels.

An additional, related caveat is that our model does not consider biological feedbacks. The rise of O$_2$ would limit habitats for anaerobes, and permit more widespread aerobic respiration, potentially dropping the CH$_4$ flux/O$_2$ flux ratio farther than we have modeled here. Also, a stronger ozone UV shield would make new habitats for cyanobacteria and allow the expansion of life on land, promoting chemical and oxidative weathering. All these changes, which we do not explicitly model, would modulate oxygen levels. In this article, we impose changes in the CH$_4$ and O$_2$ flux that are supposed to be representative of a changing biosphere, but a better model would determine more realistic changes in gas fluxes by directly coupling 1D photochemistry and biology.
Conclusions

Our time-dependent photochemical modeling of the GOE suggests that oxygen can rise and fall over geologically short periods of time. For an anoxic-to-oxic transition, once a tipping point of imbalanced redox fluxes is reached, the reservoir of reducing gases in the atmosphere must be eliminated before O$_2$ can begin to rise. This takes hundreds to 10 thousands of years. O$_2$ accumulation to just hundreds or tenths of percent levels requires filling a large O$_2$ reservoir, which may occur on a $10^5$-y timescale. Atmospheric deoxygenation occurs over similar periods of time, mainly controlled by the magnitude of the initial O$_2$ abundance.

We also find O$_2$ instability, especially for mixing ratios between $\sim 10^{-5}$ and $\sim 10^{-3}$. For these O$_2$ concentrations, photochemistry demands that both CH$_4$ and O$_2$ be relatively small in concentration. This small reservoir of redox-sensitive gases permits rapid changes to the atmosphere's redox state. For example, for an atmosphere starting with $3 \times 10^{-7}$ O$_2$, 5% amplitude oscillations to the methane flux with a period of 10,000 y cause oxygen to fluctuate four orders of magnitude between anoxic and oxic. Additionally, we show that a LIP eruption could cause the collapse of O$_2$ and the return of sulfur isotope MIF for an atmosphere starting with $2 \times 10^{-5}$ O$_2$ mixing ratio (SI Appendix).

We emphasize that the short-term ($10^2$ to $10^5$ y) variability in O$_2$ levels considered here occurred on the backdrop of the billion-year oxidation of the crust and mantle, and long-term organic burial, which are argued to be the ultimate causes of the rise of oxygen on Earth (e.g., ref. 20).

Overall, our modeling is compatible with, but does not prove, proposed geologic evidence for fluctuating and unstable atmospheric O$_2$ after the initial rise of oxygen 2.4 billion years ago. A single, unidirectional, oxidation event remains plausible, although it would require strong and perhaps biological feedbacks promoting permanent substantial changes in the global CH$_4$ flux/O$_2$ flux ratio. While this is evident between the Archean (CH$_4$ flux/O$_2$ flux $\approx 0.5$) and modern (CH$_4$ flux/O$_2$ flux $\approx 0.1$) biospheres, the dynamics of the Proterozoic biosphere remain largely unexplored. Also, our results suggest that a stable, post-GOE, mid-Proterozoic atmosphere would need an O$_2$ mixing ratio exceeding a value in the $10^{-4}$ to $10^{-3}$ range.

Materials and Methods

To investigate the transition between an anoxic and oxygen-rich Earth, we use a photochemical model with one spatial dimension of altitude, approximating a global average vertical profile. One-dimensional photochemical models are typically governed by a simplification of the continuity equation for molecules,

$$\frac{\partial n_i}{\partial t} = -\frac{\partial}{\partial z} \Phi_i + P_i - L_i + R_{\text{rainout}} + Q_{\text{lightning}}.$$  [7]

Table 2 defines all the variables and their units. Here, the flux $Q_i$ is given by

$$Q_i = -Kn_i \frac{\partial}{\partial z} \left( \frac{n_i}{n} \right) - D_n \frac{\partial n_i}{\partial n} + \frac{1}{T} \frac{\partial}{\partial z} \left( \frac{1 + \alpha_T}{T} \frac{\partial T}{\partial z} \right).$$

The above system of partial differential equations (PDEs) describes how the mixing ratio ($n_i$) of each chemical species $i$ changes over altitude and time.

In our photochemical model, we solve a simplified version of Eq. 7 which assumes that the total number density does not change over time ($\partial n_i/\partial t \approx 0$). This assumption is valid for atmospheric transitions which maintain approximately constant surface pressure and atmospheric temperature. The continuity equations can then be written in terms of mixing ratios ($f_i$) instead of number densities (see Appendix B.1 in ref. 33 for a derivation),

$$\frac{\partial f_i}{\partial t} = -D_n \frac{\partial f_i}{\partial n} + \frac{1}{T} \frac{\partial}{\partial z} \left( \frac{1 + \alpha_T}{T} \frac{\partial T}{\partial z} \right).$$  [8]

$$\Phi_i = -(K + D_n) n_i \frac{\partial f_i}{\partial n} - \frac{\partial}{\partial z} \left( \frac{1}{H_i} f_i \frac{\partial \zeta}{\partial z} \right).$$  [9]

$$\zeta = D_n \frac{1}{H_i} \frac{\partial}{\partial z} \left( \frac{1}{H_i} + \alpha_T \frac{\partial T}{\partial z} \right).$$  [10]

To approximate Eq. 8, the model replaces the spatial derivatives with finite difference approximations, turning the system of PDEs into a larger system of ordinary differential equations (ODEs). This is the “method of lines” approach to solving a PDE. Catling and Kasting (33), their Appendix B.2, provides a detailed description of how to do this with Eq. 8; therefore, we will omit a detailed description here, except to point out a sign error. The first two terms for the equation for $B$ in their equation B.16 should have minus signs instead of plus signs.

Table 2. Variables in Eq. 7

| Variable | Definition | Units |
|----------|------------|-------|
| $f_i$    | Mixing ratio of species $i$ | Dimensionless |
| $n_i$    | Number density of species $i$ | Molecules per cubic centimeter |
| $z$      | Altitude | Centimeters |
| $t$      | Time | Seconds |
| $n$      | Total number density | Molecules per cubic centimeter |
| $P_i$    | Total chemical production of species $i$ | Molecules per cubic centimeter per second |
| $L_i$    | Total chemical loss of species $i$ | Molecules per cubic centimeter per second |
| $R_{\text{rainout}}$ | Production and loss of species $i$ from rainout | Molecules per cubic centimeter per second |
| $Q_{\text{lightning}}$ | Production and loss of species $i$ from lightning | Molecules per square centimeter per second |
| $\Phi_i$ | Vertical flux of species $i$ | Molecules per cubic centimeter per second |
| $K$      | Eddy diffusion coefficient | Molecules per cubic centimeter per second |
| $D_n$    | Molecular diffusion coefficient | Molecules per cubic centimeter per second |
| $H_i$    | $N_a kT / \mu g$, The scale heights of species $i$ | Centimeters |
| $H_a$    | $N_a kT / mg$, The average scale height. | Centimeters |
| $N_a$    | Avogadro's number | Molecules per mole |
| $k$      | Boltzmann's constant | Grams per mole |
| $\mu$    | Molar mass. $\mu$ is mean molar mass of the atmosphere, and $\mu_i$ is the molar mass of species $i$ | Centimeters per square second |
| $g$      | Gravitational acceleration | Centimeters per square second |
| $\alpha_T$ | Thermal diffusion coefficient of species $i$. We neglect this term ($\alpha_T = 0$) | Centimeters per square second |
| $T$      | Temperature | Kelvins |

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The system of ODEs derived from finite differencing Eq. 8 can be evolved forward in time with numerical integration. However, the photochemical ODEs are “stiff,” meaning that some dependent variables (i.e., the mixing ratios) change much more quickly than others. For example, in the modern atmosphere, OH typically has a chemical lifetime of about 1 s, while CH₄ has a chemical lifetime of ~10 y. Stiff equations require special, high-stability, “implicit” integration methods. For more details on stiff equations and the implicit methods used to solve them, see ref. 46.

Often, we solve for steady states of the photochemical continuity equation ($\partial C_i/\partial t = 0$). To find steady states, we begin with some initial atmospheric composition, then integrate Eq. 8 forward in time until the atmosphere ceases to change, that is, a steady state is reached. The assumption of photochemical steady state is approximately valid for most periods of Earth’s history, because the atmosphere changes slowly enough to be in a quasi-steady state. However, the Paleoproterozoic rise of O₂ was a relatively fast atmospheric transition that is not well modeled as a photochemical steady-state process. Therefore, describing it requires accurately solving the continuity equation over time.

To model the photochemistry of the GOE, we modified the photochemical model contained within the Atmos modeling suite (described in Appendix B of ref. 33) so that it can accurately solve the time-dependent behavior of Eq. 8. We call the modified version of the model PhotochemPy. Instead of using a Backward Euler as in Atmos, we used CVODE BDF ODE solver from Sundials Computing (47). CVODE BDF is an implementation of the backward differential formulas (BDF) and is a gold standard for solving large chemical kinetics problems. For details, see SI Appendix.

PhotochemPy is open source under a Massachusetts Institute of Technology license. The version of the code (v0.2.14) used in this paper and the corresponding Python scripts to reproduce work done in this article are at https://zenodo.org/record/6824092. However, the most up-to-date version of the code can be found at the following GitHub link: https://github.com/Nicholaswogan/PhotochemPy.

Data, Materials, and Software Availability. Source code has been deposited in Zenodo (https://zenodo.org/record/6824093#.Y3CuozMKCc) (48). PhotochemPy code and the corresponding Python scripts are available at https://zenodo.org/record/6824092. The most up-to-date code is available at https://github.com/Nicholaswogan/PhotochemPy (49).

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Supplementary Information for

Rapid Timescale for an Oxic Transition During the Great Oxidation Event and the Instability of Low Atmospheric $\text{O}_2$

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This PDF file includes:
- Supplementary text
- Figs. S1 to S4 (not allowed for Brief Reports)
- Legend for Movie S1
- SI References

Other supplementary materials for this manuscript include the following:
- Movie S1
Supporting Information Text

All Great Oxidation Event (GOE) simulations use the solar spectrum at 2.4 Ga, calculated with methods described in Claire et al. (2012) (1). We also always include chemical rainout and NO production from lightning. 95% of steady state simulations conserve redox to a factor better than $10^{-6}$. 3% of models, all with $>0.1\%$ steady-state $O_2$, conserve redox to a factor of $\sim 10^{-3}$. Figure S1 shows results from steady-state photochemical simulations over the same parameter space as Figure 1 (main text), except using the “Modern Values” fluxes from Table 1 in the main text. Figure S2 shows assumed eddy diffusion and temperature profiles.

Estimating the timescale of the rise of $O_2$

In the results section of the main text, we estimated the timescale for the rise of $O_2$ using the following equation:

$$\tau_{oxy} = \left| \frac{\Delta N_{\text{reducing}}}{\Delta F_{O_{\text{equiv}}}} \right|$$

Applying this equation to the Figure 2b (main text) simulation:

$$\Delta F_{O_{\text{equiv}}} = (2F_{O_2}^{\text{final}} - 4F_{\text{CH}_4}^{\text{final}}) - (2F_{O_2}^{\text{initial}} - 4F_{\text{CH}_4}^{\text{initial}})$$

$$= (2(1.8 \times 10^{10}) - 4(8.1 \times 10^{11})) - (2(1.0 \times 10^{12}) - 4(4.5 \times 10^{11}))$$

$$= 1.6 \times 10^{11} \text{ molecules cm}^{-2} \text{s}^{-1}$$

$$\tau_{oxy} = \left| \frac{\Delta N_{\text{reducing}}}{\Delta F_{O_{\text{equiv}}}} \right| = \frac{1.47 \times 10^{21}}{1.6 \times 10^{11}} = 9.8 \times 10^{10} \text{ s} = 29,000 \text{ years}$$

This estimation is about a factor of two smaller than the $\sim 60,000$ years predicted by our time-dependent photochemical model.

Figure S3 shows the column of reducing gases and its destruction rate during the Figure 2b simulation. Our estimation for the timescale of oxygenation (Equation Eq. (3)) is off by a factor of two because the reducing column evolves over time, and our estimation of its destruction rate ($\Delta F_{O_{\text{equiv}}}$) is too large. In the photochemical model, chemistry and transport does not permit a reducing column destruction rates identical to the imposed change in redox fluxes at the surface ($1.6 \times 10^{11}$ O molecules cm$^{-2}$ s$^{-1}$).

A Large Igneous Province may have destabilized atmospheric oxygen

Here, we show that the $H_2$ and CO outgassing from large igneous provinces (LIPs), or massive volcanic eruptions, could have potentially caused the collapse of transitional $O_2$ concentrations ($\sim 10^{-8}$ to $\sim 10^{-4}$ mixing ratio).

To compute $H_2$ and CO outgassing rates from LIPs, we use the outgassing model described in (2). To briefly summarize, the model estimates the composition of gas bubbles suspended in magma just prior to release into the overlying atmosphere or ocean. Gas composition is computed by solving a system of equations including solubility relationships for $H_2O$ and $CO_2$, gas-phase equilibrium relationships, and mass conservation of hydrogen and carbon. The model has five inputs: Magma oxygen fugacity, temperature, and overburden pressure, and the $H_2O$ and $CO_2$ mass fractions ($m_{H_2O}^{\text{tot}}$ and $m_{CO_2}^{\text{tot}}$) in the magma before degassing occurs. For LIPs, we assume a magma oxygen fugacity one log-unit below the fayalite-magnetite-quartz mineral redox buffer (i.e. $\Delta F_{\text{FMQ-1}}$) following Archean proxies (3). See Chapter 7 in (4) for a description of the fayalite-magnetite-quartz redox buffer. Additionally, we use $m_{H_2O}^{\text{tot}} = 0.5$ wt% and $m_{CO_2}^{\text{tot}} = 0.05$ wt% which agrees with estimates of LIP volatile concentrations (5). Finally, we take the degassing temperature and pressure to be 1473 K and 1 bar, respectively. With these inputs, our outgassing model predicts $1.6 \times 10^{-2}$ mol $H_2$/kg magma and $1.7 \times 10^{-3}$ mol CO/kg magma.

Converting gas production rates (e.g. mol $H_2$/kg magma) into gas fluxes to the atmosphere requires estimations of magma eruption rates during LIPs. Basaltic LIPs typically last several million years and cumulatively produce $>3 \times 10^{18}$ kg magma (6). This magma is release over 10s to 100s of eruptions each lasting several years to 10s of years with eruptions rates between $3 \times 10^{13}$ to $3 \times 10^{15}$ kg magma yr$^{-1}$ (7). Multiplying these eruption rates by calculated gas production yields $H_2$ fluxes between $1.9 \times 10^9$ and $1.9 \times 10^{11}$ molecules cm$^{-2}$ s$^{-1}$ and CO fluxes between $2.0 \times 10^8$ and $2.0 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$.

The time-dependent photochemical simulation shown in Figure S4 shows how atmospheric $O_2$ responds to maximum LIP $H_2$ and CO outgassing scenario. The simulation starts with an atmosphere initially at equilibrium, then at $t = 0$ years, we increase the $H_2$ and CO outgassing fluxes by $1.9 \times 10^{11}$ and $2.0 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$, respectively. $O_2$ drops from $2 \times 10^{-5}$ to $4 \times 10^{-9}$ in 100 years. Basaltic LIP eruptions can last for 10s of years (7), so a 100 year eruption, which is required to cause $O_2$ to collapse, is within the realm of possibility. However, the period of anoxia would likely be maintained for only a few hundred years, until the eruption ceased. Several periods of anoxia, each corresponding to a significant eruption, might occur during an entire several-million-year LIP event.

It is unclear whether a 100 year period of anoxia is detectable in the geologic record of multiple sulfur isotopes. A single sample from the sedimentary record might represent a period of time greater than 100 years, thus containing sulfur from both an oxic and anoxic atmosphere, diluting the S-MIF signal. Evaluating the detectability of short-term anoxia in the sedimentary record of sulfur isotopes is an interesting target for future work coupling in-situ and bulk rock measurements (8).
LIPs may have additional effects on the atmosphere that we are not accounting for in the above calculations. For example, increased Cl outgassing could catalyze O$_3$ and CH$_4$ destruction (e.g. Cl + O$_3$ → ClO + O$_2$ and Cl + CH$_4$ → HCl + CH$_3$), which could have a non-trivial effect on the O$_2$ concentration.

**CVODE numerical integrator**

To accurately track atmospheric chemistry over time with our photochemical model, we use the CVODE BDF ODE solver. The reasons CVODE BDF can reliably solve the continuity equation over time are its method of timestep selection and local error control. At each timestep, CVODE estimates the local error that will be introduced with a given timestep size. If the local error is less than the accuracy requirement specified by the user, then the step is accepted and the integration proceeds. Otherwise, the step is rejected, and CVODE retries with a smaller timestep. This general approach is standard in production-grade ODE solvers and will guarantee that each step introduces less local error than that specified by the user (9). The time stepping approach in the older versions of the *Atmos* photochemical model does not estimate the local error introduced with each step, and thus the inaccuracies introduced with integration. This makes it very challenging to determine whether an integration is a good approximation of the true solution or not.

CVODE BDF is also several times faster, depending on the problem, than the backward Euler implementation in older versions of *Atmos*. CVODE uses implementations of the backward differential formulae that are up to 5$^{th}$ order accurate. Backward Euler is 1$^{st}$ order accurate. Higher order ODE integration methods are generally faster because they can take larger timesteps compared to lower order methods while achieving the same accuracy. CVODE also only computes a new Jacobian every few steps when a new one is needed, while the original integrator in *Atmos* computed a Jacobian every single timestep. Jacobians are expensive to compute, thus fewer Jacobian calculations means a faster program.

In addition to implementing time-accurate integration, PhotochemPy is distinct from *Atmos* in a several other ways. The list below highlights the most important differences.

- We restructured the Fortran 77 code using modern Fortran practices. Refactoring in modern Fortran allows more program bugs to be caught during compilation.
- We significantly reduced hard-coding in the model, increasing model generality. PhotochemPy can model vastly different atmospheres such as Saturn, Earth, or Mars with minimal parameter changes which are clear to the user, and not buried deep in the source code.
- We also used the Numpy F2PY tool to generate a deep Python interface to the compiled Fortran (10). This enables easy parallel photochemical integrations using Python multiprocessing tools.
- We introduced extensive call-back errors, which significantly reduces the chances of unnoticed bugs, like a reaction rate which is entered incorrectly.
Fig. S1. Identical to Figure 1 in the main text, except we use the “Modern Values” surface fluxes in Table 1 in the main text. The time-dependent photochemical simulation shown in Figure 2b (main text), is indicated with a black arrow.
Fig. S2. The temperature and eddy diffusion used for every simulation.
Fig. S3. Reducing gas column and its destruction rate for the simulation shown in Figure 2b.
Fig. S4. Modeled oxic to anoxic transition caused by H$_2$ and CO outgassing from a large igneous province eruption. The simulation begins with a photochemical equilibrium atmosphere, and then is perturbed by a stepwise increase of the H$_2$ and CO flux by $1.9 \times 10^{11}$ and $2.0 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$, respectfully. A LIP eruption should able to produce these outgassing fluxes for the 100 years required to cause O$_2$ to collapse (see text).
Movie S1. Time dependent photochemical model of the rise of oxygen. This is the same simulation that is shown in Figure 2c in the main text. Left-hand plot shows the mixing ratio of several key species as a function of altitude and time. Right-hand plot shows the photon flux at the top of the atmosphere and the surface as a function of photon wavelength and time. As oxygen rises, and an ozone layer develops, almost all photons < 300 nm are shielded from the surface.

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