Mantle data imply a decline of oxidizable volcanic gases could have triggered the Great Oxidation

Shintaro Kadoya✉1, David C. Catling1, Robert W. Nicklas2, Igor S. Puchtel3 & Ariel D. Anbar4

Aerobic lifeforms, including humans, thrive because of abundant atmospheric O2, but for much of Earth history O2 levels were low. Even after evidence for oxygenic photosynthesis appeared, the atmosphere remained anoxic for hundreds of millions of years until the ∼2.4 Ga Great Oxidation Event. The delay of atmospheric oxygenation and its timing remain poorly understood. Two recent studies reveal that the mantle gradually oxidized from the Archean onwards, leading to speculation that such oxidation enabled atmospheric oxygenation. But whether this mechanism works has not been quantitatively examined. Here, we show that these data imply that reducing Archean volcanic gases could have prevented atmospheric O2 from accumulating until ∼2.5 Ga with ≥95% probability. For two decades, mantle oxidation has been dismissed as a key driver of the evolution of O2 and aerobic life. Our findings warrant a reconsideration for Earth and Earth-like exoplanets.
The geological record of mass-independent sulfur isotope fractionation shows that O₂ first inundated the atmosphere during the Great Oxidation Event (GOE) between 2.4 and 2.1 Ga. However, redox-sensitive iron and molybdenum isotope data suggest the presence of O₂ in the 3.2–3.0 Ga marine photic zone, which implies that O₂-producing cyanobacteria existed long before the GOE. Indeed, models show that, under a globally anoxic atmosphere, cyanobacteria-derived O₂ produces photic zone oxygen oases. Geological data also indicate the presence of methanotrophy and oxidative nitrogen cycling in Neoproterozoic oceans and lakes, which suggest that O₂ was oxidizing sulfides and ammonium to make sulfate and nitrate, respectively. Such inferences are consistent with phylogenetic interpretations that oxygenic photosynthesis evolved by the mid-Archean. However, redox-sensitive iron and molybdenum isotope data suggest the presence of O₂ in the 3.2 Ga zone, which implies that O₂-producing cyanobacteria existed in the marine photic zone during the GOE.

In addition, paleoredox proxies suggest O₂ transients at 2.5 Ga, and point to the possibility of pervasive oxygenation of the oceans over continental margins. The reasons for the delay of oxygenation of the atmosphere for hundreds of millions of years after the advent of oxygenic photosynthesis remain unknown. Numerous hypotheses rely on the notion that the atmospheric O₂ level is determined by a kinetic balance between O₂ supply and consumption. If the rapid and efficient O₂ sinks are larger than the O₂ supply, there are excess reductants, and the atmosphere remains anoxic even in the presence of global oxygenic photosynthesis. Rapid sinks include net reactions of O₂ with reducing gases emanating from the solid Earth, e.g., H₂, CO, H₂S, SO₂, and CH₄.

One possibility is that an increase in O₂ fluxes overwhelmed the efficient O₂ sinks, causing the GOE. However, the available data are not particularly persuasive. Oxygenic O₂ production is accompanied by organic matter (CH₂O) in the net reaction CO₂ + H₂O = CH₂O + O₂. Because respiration or oxidative decay reverse this reaction (presently in ~50 years), the long-term net flux of O₂ occurs when organic matter is segregated from O₂ and buried.

Long-term changes in the burial rate of organic matter—and hence in the net supply of O₂—can be inferred from C isotopes in sedimentary rocks. Organic matter concentrates ¹²C relative to ¹³C, leaving marine inorganic carbonate ¹²C depleted; as such, carbon isotopes in marine carbonates and kergen tracks f org the fraction of total carbon buried as organic matter. Isotopic mass balance shows little difference between the average organic burial fraction for 3.6–2.5 Ga of f org = 0.15 ± 0.02 [2 standard deviations (SD)] and that for 1.8–1.0 Ga of f org = 0.18 ± 0.02 [2 SD] suggesting no significant increase in O₂ flux.

Of course, the inferred organic burial flux and associated O₂ flux depend on assumptions about the carbon cycle. Challenges to a conventional carbon mass balance model include organic carbon sequestered into seafloor carbonates or into authigenic carbonates, or isotopic weathering inputs that scaled with the amount of atmospheric O₂. The first two hypotheses lack supporting evidence. Seafloor carbonate is not isotopically lighter than typical marine sedimentary carbonates, and the abundance of authigenic carbonates is low before the GOE compared with afterward, and is relatively small today. The third idea is plausible: the lack of oxidative weathering in the Archean could modulate f org. However, the average organic content of Archean sedimentary rocks is indistinguishable from that of Proterozoic (3.56 wt%) and the cumulative distribution of total organic content in organic-rich Archean sedimentary rocks is identical to that of Neogene rocks.

Here we are interested in examining the potential implications of the trend in mantle redox state on the GOE. A lower Archean O₂ flux may be a possible factor, but that is not the focus of this paper. Because f org changed little with a conventional carbon cycle model, it has been proposed that a secular decline of efficient O₂ sinks, rather than an increase in f org, caused the tipping point that initiated the GOE; this point would have been reached when the efficient O₂ sink flux fell below the organic burial flux of O₂. Models show that atmospheric O₂ would then rapidly accumulate, until oxidative weathering of the continents became a significant sink, causing O₂ concentrations to level off. Proxies suggest that the O₂ level, however, was still far below today's atmospheric O₂ concentrations.

Qualitatively, the pre-GOE O₂ sink flux could have declined if the mantle's oxidation state increased over time. The proportion of reducing gases in volcanic emissions depends inversely on the oxygen fugacity (f O₂) in their magma source region. If the mantle mantle's f O₂ was low, the H₂/H₂O and CO/CO₂ ratios in Archean volcanic gases would have been high, supporting O₂ levels.

Until recently, studies suggested that the mantle's f O₂ had been similar to the modern value since at least the early Archean. The mantle f O₂ estimated by many of these studies has uncertainties that vary between ~1 log₁₀ unit and ~2 log₁₀ units. Changes in the oxygen fugacity of the mantle as small as ~0.5 log₁₀ units have been suggested to have a significant effect on atmospheric redox evolution, therefore, prior results do not preclude involvement of the GOE.

A notable study of mantle redox evolution is Li and Lee, who used the V/Sc ratios of a large database of primitive basalts to report that mantle oxidation state had not changed by more than 0.3 log₁₀ units since the Archean. The use of the V/Sc oxybarometer on large amounts of published basalt data relies upon the assumption that all of the studied basalts are the result of similar degrees of partial melting, and that they sample a spinel peridotite source with a primitive mantle V/Sc of ~5. None of these are necessarily safe assumptions. Average degree of partial melting was likely higher in the Archean due to higher mantle potential temperature. In addition, not all of the studied basalts were likely generated from melting of spinel peridotite, and residual garnet can have a potentially strong effect on V/Sc. Finally, the mantle sources of basalts vary greatly in the degree of previous melt depletion, and remelting of a previously depleted source can generate a low V/Sc melt and an erroneously reduced f O₂. For all these reasons, the conclusions and quoted uncertainties of Li and Lee must come into question.

Two new studies reveal an f O₂ trend. Aublab and Stagno carefully filtered V/Sc data to only include Archean basalts formed in a mid-ocean ridge (MOR)-like environment, while Nicklas et al. calculated the f O₂ of ultramafic lavas directly without making assumptions about their source compositions. These new data, shown in Fig. 1a, indicate that mantle f O₂ increased by ~1.3 log₁₀ units from the early Archean to Proterozoic, and likely represent the current best estimate for mantle redox evolution.

Both datasets in Fig. 1a show a similar f O₂ trend, but each dataset was determined using a different oxybarometer. The f O₂ derived from different oxybarometers shows a systematic offset, the reason for which is currently unclear, as oxybarometry performed using different methods on modern rocks gives values that vary outside of analytical uncertainty. One possible explanation involves the degassing of volatile species, such as SO₂, which have the potential to strongly reduce a lava shortly prior to eruption. Degassing may lead to an offset between these two datasets because the V-partitioning oxybarometer of Nicklas et al. measures the f O₂ of komatiites and picrites, while the V/Sc ratio oxybarometer of Aublab and Stagno infers the f O₂ of basalts and picrites. Komatiites are high-temperature, high-degree
In this study, we show that the new data imply that reducing Archean volcanic gases would prevent atmospheric O₂ from accumulating, and then the GOE would occur by or after ~2.5 Ga with ≥95% probability. Thus, we conclude that secular oxidation of the mantle have indeed triggered oxygenation of the atmosphere.

Results

Oxygenation parameter. We evaluate whether the atmosphere was prone to oxygenation at any given time using an oxygenation parameter, \( K_{\text{oxy}} \). This parameter is the ratio of O₂ source fluxes to kinetically efficient O₂ sink fluxes, which we consider here to be dominated by oxidizable volcanic gases

\[
K_{\text{oxy}} = \frac{\text{O}_2 \text{ source fluxes}}{\text{non-weathering O}_2 \text{ sink fluxes (may incl. excess reductants)}}
\] (1)

Fluxes are quantified in units of T mol O₂ yr⁻¹. When \( K_{\text{oxy}} \) < 1, gaseous volcanic O₂ sinks exceed O₂ sources, and excess H₂ builds up until balanced by escape to space. When \( K_{\text{oxy}} > 1 \), O₂ sources exceed efficient O₂ sinks, and O₂ builds up until balanced by oxidative weathering. Box modeling coupled to photochemistry shows that \( K_{\text{oxy}} = 1 \) defines the point when the atmosphere becomes oxic (see Fig. 7b of Claire et al.34). For detailed information, see the “Methods” section and the Supplementary information.

Evolution of the oxygenation parameter. As an initial, illustrative trial, we took the organic burial fraction (\( f_{\text{org}} \)) to be constant at 20%, which is a canonical value adopted by previous researchers [e.g., refs. 21,32], to isolate the effect of the secular change in mantle \( f_{\text{org}} \) shown in Fig. 1b. As shown in Fig. 2a, the results are that the oxygenation parameter (\( K_{\text{oxy}} \)) monotonically increases with time.

In Fig. 2a, \( K_{\text{oxy}} \) larger than unity occurs when the production of O₂ via organic burial and deposition of pyrite (i.e., the numerator of Eq. (20)) exceeds the consumption of O₂ from oxidizable volcanic gases (i.e., the denominator of Eq. (20)). Then atmospheric O₂ accumulates, and oxidative weathering kicks in and balances the excess O₂ production22,33,34. In contrast, when \( K_{\text{oxy}} \) is smaller than unity, the production of O₂ via organic burial and deposition of pyrite (i.e., the numerator of Eq. (20)) is smaller than the consumption of O₂ by reducing volcanic gases (i.e., the denominator of Eq. (20)). Under such a condition, atmospheric O₂ cannot accumulate, and the buildup of excess of reducing gases, such as CH₄ and H₂, is limited by their decomposition in the upper atmosphere and the escape of hydrogen to space22,33,34.

The 5% probability quantile of \( K_{\text{oxy}} \) (the lower end of gray shaded region) crosses unity (a dotted gray line) at 2.62 Ga and later, the probability that \( K_{\text{oxy}} \) > 1, allowing the point when the atmosphere becomes oxic before 2.5 Ga (Supplementary Fig. 1). Hence, even when we include temporal changes of \( f_{\text{org}} \), the atmosphere still becomes oxic at 2.48 Ga (or afterward) with 95% (or more) probability.
For comparison, we also did calculations for three hypothetical scenarios where the mantle $f_{O_2}$ was fixed at FMQ-2, FMQ-1, and FMQ (Fig. 2c). We also included temporal fluctuations in $f_{deg}$ as in Fig. 2b, which are reflected in the fluctuations of $K_{oxy}$. In these scenarios, an oxic transition for $K_{oxy}$ does not occur, although $K_{oxy}$ occasionally becomes greater than 1 in the FMQ-1 case within the gray shaded region of uncertainty in Fig. 2c. Thus, the transitions from $K_{oxy} < 1$ to $K_{oxy} > 1$ in Fig. 2a, b are mainly due to the temporal increase in mantle $f_{O_2}$ taken from the fit in Fig. 1.

**Discussion**

As shown above, an empirically-inferred increase in mantle $f_{O_2}$ causes an increase in $K_{oxy}$ resulting in the shift of the atmosphere from reducing to oxic (Fig. 2). However, this result does not exclude a role for other processes in the oxidation of the atmosphere as explained below.

The result of the standard case shows that uncertainties in the $f_{O_2}$ time series and the oxygen flux estimates from the carbon isotope record propagate through the calculations, so that the uncertainty envelope allows an oxic regime even before $\sim 2.5$ Ga (Fig. 2b). On the other hand, geological evidence, such as mass-independent sulfur isotope fractionation, indicates an anoxic atmosphere for the Archean Earth before 2.4–2.3 Ga though a recent study suggests that the GOE occurred somewhat earlier than 2.4 Ga. This discrepancy in the timing of the GOE might also be caused by not considering other processes that may delay the oxic transition.

To investigate the effect of processes proposed by previous studies, we did some sensitivity studies and obtained the same trends as previous studies. As explained in Supplementary Note 1, $K_{oxy}$ decreases if the degassing pressure is high, if the carbon and/or sulfur degassing fluxes are low, and/or if the rate of magnetite deposition via serpentinization is high, which generates oxidizable hydrogen that is a sink for $O_2$.

If $K_{oxy}$ was lower, the atmosphere in the early Archean would be more reducing, and the oxic transition time would be delayed, because of the following processes: a secular decrease in the degassing pressure due to a transition from submarine to subaerial volcanism, a secular increase in the carbon and/or sulfur degassing due to an increase in their continent and/or ocean floor reservoirs, and/or a secular decrease in the magnetite deposition flux via serpentinization, which might result from a decrease in the degree of partial melting of the mantle caused by secular cooling. The magnitude of the Archean serpentinization flux of $H_2$ is debated, since it is only significant today from slow-spreading centers where ultramafic rocks are exposed.

There is another possible process that contributed to the delay in the oxic transition along with slow mantle oxidation. Because of the lack of oxidative weathering in the Archean, the carbon isotope input into the atmosphere-ocean could have been relatively heavy compared with mantle values, and so less organic burial was needed for the mass balance.

We also investigated the uncertainty of the anchoring value of the mantle $f_{O_2}$ evolution (Supplementary Note 1). For the standard case (Fig. 2), we modeled the evolution of the mantle $f_{O_2}$ anchoring the trend to the average $f_{O_2}$ of modern MORB, i.e., $\Delta FMQ = +0.2$ [see also Eq. (4)]. However, this reference value has an uncertainty of 0.3 log$_{10}$ units. Anchoring the $f_{O_2}$ trend to a lower $\Delta FMQ$ value causes lower mantle $f_{O_2}$ in the past, resulting in a more reducing atmosphere in the Archean and delaying the oxic transition time (Supplementary Fig. 8).

Thus, all of the processes discussed in the preceding three paragraphs might affect the GOE’s timing and so are potentially complicating factors.
Observations show that erupted volcanic gas is more oxidized, i.e., has a larger $\Delta$FMQ, than its source melt\cite{54,55}. The relative oxidative state of the volcanic gas results from reactions within a closed gas mixture due to cooling\cite{54,55}. Consequently, it has been proposed that secular cooling of the mantle could have facilitated the GOE\cite{56}. Also, observations seem to indicate that it is not possible to calculate the oxidation effect, i.e., $K_{\text{oxy}}$, of the volcanic gas using the $\Delta$FMQ of its source, although we did this in this study. However, the assumptions of these previous studies\cite{54,56} need to be reconsidered, as follows.

Recent work\cite{56} discusses how cooling affects the oxidation state and the $K_{\text{oxy}}$ of a volcanic gas mixture considering two stages of degassing, i.e., the stage where volcanic gas is buffered by its source melt (melt-buffered stage), and the stage where the volcanic gas is a closed system (closed stage). For the closed stage, the same conclusion was reached as in the previous studies\cite{54,56}, i.e., cooling increases $\Delta$FMQ of a closed volcanic gas compared with that of its source melt. However, in a closed gas mixture, oxidation of a gas should be accompanied by a reduction of another gas, so any reaction in the closed gas mixture does not change the overall $O_2$ sink in the gas mixture\cite{56}. Hence, to evaluate the $K_{\text{oxy}}$ of volcanic gas, we can neglect the effect of reactions after the volcanic gas separated from its source, i.e., the observed difference in the oxidation state between erupted volcanic gas and its source melt.

For the melt-buffered stage, cooling results in reduction of a gas mixture and a decrease in $K_{\text{oxy}}$ if the $\Delta$FMQ of the source melt is buffered and constant\cite{56}. This is because cooling decreases the absolute value of $f_{O_2}$ of the FMQ buffer (Supplementary Fig. 4). A trend of smaller $K_{\text{oxy}}$ with lower mantle temperature is shown in Supplementary Fig. 3a. However, the oxic transition time is insensitive to temperature if the temperature is higher than the solidus temperature of dry peridotite (~1390 K)\cite{57}, as shown in Supplementary Fig. 3b. The mantle temperature in the Archean would be between 1600 and 1900 K [e.g., refs. 57–59]. Hence, the secular cooling of the mantle would affect less the GOE.

Note that Holland’s $f$ number [e.g., ref. 32] was used in Moussallam et al.\cite{48}, while $K_{\text{oxy}}$ was used in Kadoya et al.\cite{56}. However, the temperature dependence of Holland’s $f$ number is essentially the same as that of $K_{\text{oxy}}$. This point is explained in Supplementary Note 2.

A decrease in mantle temperature might delay the oxic transition time if the temperature was lower than the solidus temperature of dry peridotite (Supplementary Fig. 3b). Degassing would occur under such a low temperature in arc volcanism because the hydrous phase of the subducted crust can lower the melting temperature [e.g., ref. 50]. However, the island arc basalts are often more oxidized than the mid-ocean ridge basalt or oceanic island basalt\cite{61}. Hence, we cannot conclude that arc volcanism, whose degassing temperature would be low, delayed the oxic transition time.

A question might arise about our assumption that the $f_{O_2}$ of the volcanic gas was equal to that of the upper mantle. Degassing can reduce the source melt, e.g., $SO_2$ degassing\cite{48}. However, during the melt-buffer stage, i.e., when the volcanic gas mixture interacts with the ambient melt, the $f_{O_2}$ of the gas will be equal to that of the melt. In addition, during the closed stage, i.e., after the gas mixture decouples from the ambient melt, any reaction within the gas mixture does not change the oxidation effect of the gas\cite{56}. Thus, the oxidation effect of the gas should be examined using the $f_{O_2}$ of the gas when the gas decouples from the melt. Also, at that time, the $f_{O_2}$ of the gas would be equal to that of the ambient melt, which has already experienced degassing. Therefore, we can calculate $K_{\text{oxy}}$ using the $f_{O_2}$ from the Archean that is anchored today to modern MORB $f_{O_2}$.

It is also noteworthy that the similar trend of the mantle $f_{O_2}$ with time is observed by the measurement of $f_{O_2}$ of different rocks\cite{46,59}. This similarity indicates that the increase in $f_{O_2}$ of melts follows the same trend of the decreasing mantle $f_{O_2}$ with time, despite the difference in the degree of partial melting, which also supports our assumption that the $f_{O_2}$ of the volcanic gas increased with time.

The assumption of the anchoring values of $f_{O_2}$ bears consideration. In this study, we anchored the $f_{O_2}$ of the volcanic gas and the melt at the value of the modern MORB, implicitly assuming that the $f_{O_2}$ of the melt does not change after the melt decouples from the gas. However, if the $f_{O_2}$ of the melt changes after the decoupling from the gas, it also changes the timing of the GOE as indicated by the parameter study of the anchoring value of the $f_{O_2}$ (Supplementary Fig. 8).

Of course, a major question is what drove the increase in mantle $f_{O_2}$ and, hence, could have driven the GOE. One possibility is that convection-driven homogenization of an initially redox-stratified primordial mantle was responsible for this change\cite{45,46,62}. The basic idea is that in the early deep mantle, $Fe^{3+}$ is disproportionated to $Fe^{3+}$ and Fe metal due to high pressure. The latter was lost to the core, leaving a more oxidized lower mantle below a relatively reduced upper mantle. According to Andraut etc.\cite{62}, the primitive mantle contained excess of $Fe^{3+}$ corresponding to ~60% of an ocean’s worth of oxygen.

However, another possible driver of upper mantle oxidation has recently gained evidence in its favor. Ancient air dissolved in inclusions of seawater in Archean quartz shows that the nine isotope of Xe become increasingly isotopically heavy throughout the Archean and early Proterozoic until the GOE\cite{63}. The most plausible explanation is a very rapid escape of hydrogen to space that dragged along ionized Xe atoms, which would have fractionated Xe isotopes because of mass-dependent escape\cite{64}.

Substantial loss of a strong reducing agent, i.e., hydrogen, would have oxidized the Earth, with the oxidation affecting the reservoir from which the hydrogen originated. Thus, the mantle would become gradually more oxidized because the hydrogen comes from the decomposition of water in volcanic melts, schematically represented as $3FeO + H_2O \rightarrow Fe_2O_3 + H_2$. The upper mantle (down to ~660-km depth) contains the equivalent of ~20% of an ocean’s worth of oxygen as $Fe^{3+}$ [ref. 65, p. 207]. The Xe isotope data require Archean hydrogen loss from the equivalent of ~10 s of percent of an ocean\cite{64}. Thus, if the $f_{O_2}$ trend in Fig. 1b explains the GOE, as shown in Fig. 2b, the $f_{O_2}$ trend, in turn, may have been driven by hydrogen escaping to space from the Earth’s pre-GOE anoxic atmosphere [e.g., refs. 19,66].

Hydrogen escape as a mechanism for mantle oxidation\cite{36} has been proposed previously, but has been rejected over the last two decades because of reports of seemingly constant mantle $f_{O_2}$ through time\cite{39,67,68}. Our results suggest that this mechanism may need to be reconsidered.

In summary, we examined whether new data for increasing mantle oxygen fugacity ($f_{O_2}$) since the Archean could explain the GOE, when O$_2$ first accumulated in the Earth’s atmosphere. The onset of the GOE can only be properly quantified by considering sources and sinks of oxygen in a global redox balance of the surface environment. The oxygenation parameter $K_{\text{oxy}}$ used for this purpose is defined as the ratio of $O_2$ sources to kinetically rapid sinks. For an anoxic atmosphere, $K_{\text{oxy}} < 1$, while for an oxic atmosphere, $K_{\text{oxy}} > 1$; by evaluating when $K_{\text{oxy}} = 1$, we determined how mantle $f_{O_2}$ trends affected the onset of the GOE.

A more reducing mantle with low $f_{O_2}$ produces a greater proportion of reducing volcanic gases. So, we found that the data-derived trend of mantle $f_{O_2}$ likely prevented $O_2$ building up in the atmosphere with relatively high probability (~70% at 3.6 Ga) and
caused an oxic transition from $K_{\text{oxy}} < 1$ to $K_{\text{oxy}} > 1$ with $>95\%$ probability after 2.5 Ga.

Our calculated timing of the GOE is relatively insensitive to the mantle potential temperature, but depends on the assumed degassing pressure, and total outgassing fluxes of carbon and sulfur relative to total hydrogen. An additional oxidative sink of ferric iron in magnetite deposition has a minor effect, unless this flux in the Archean exceeded ten times the modern flux.

If a trend in mantle $F_{\text{oxy}}$ controlled the timing of the GOE, then the cause of mantle oxidation is ultimately important for setting the tempo of biological evolution because macroscopic, energy-intensive aerobic life was impossible when $O_2$ levels were negligible. Possible drivers of mantle redox evolution are the mixing of a redox heterogeneous mantle or the time-integrated oxidative effect of the breakdown of mantle water in volcanism, and the escape of hydrogen to space. Such processes could also apply to other Earth-like planets elsewhere, and would thus determine whether such planets could be habitable for complex aerobic life with high $O_2$ demand.

**Methods**

The redox tipping point of the atmosphere can only be quantified by considering the global redox flux balance of the early atmosphere and ocean, which is as fundamental as mass or energy conservation

\[ K_{\text{oxy}} = \frac{F_{\text{out}}}{F_{\text{in}}} \]

(2)

The fluxes, $F_{\text{in}}$ and $F_{\text{out}}$ are calculated using fluxes of volcanic gas, such as CO and SO$_2$, organic burial flux, and pyrite burial flux. In the subsequent sections, we will describe a model of each flux, and then explain models of $F_{\text{in}}$ and $F_{\text{out}}$.

**Fluxes related to source and sink of oxygen.** In this section, we explain the components, which are used to calculate the source ($O_2$) fluxes ($F_{\text{roxy}}$) and a kinetically rapid sink of $O_2$ ($F_{\text{oxy}}$). For the calculation of $F_{\text{oxy}}$ and $F_{\text{roxy}}$, see the next section.

Hydrogen is degassed to the ocean-atmosphere system as hydrogen molecules (H$_2$), water vapor (H$_2$O), methane (CH$_4$), and hydrogen sulfide (H$_2$S). Accordingly, a total flux of hydrogen ($F_{\text{hydrogen}}$) can be expressed as follows:

\[ F_{\text{hydrogen}} = F_{\text{H}_2} + F_{\text{H}_2\text{O}} + 2F_{\text{CH}_4} + F_{\text{H}_2\text{S}} \]

(3)

where $F_x$ is a flux of x. Methane contains the equivalent of two H$_2$ molecules, so $F_{\text{CH}_4}$ is weighted by a factor of 2.

Carbon is degassed to the ocean-atmosphere system as carbon dioxide (CO$_2$), carbon monoxide (CO), and methane (CH$_4$), and deposited as organic matter (org) and carbonate (carb). Since we assume that carbon is in a steady state, the total flux of carbon ($F_{\text{carbon}}$) is equal to input and output fluxes, which can be expressed as follows:

\[ F_{\text{carbon}} = F_{\text{CO}_2} + F_{\text{CO}} + F_{\text{CH}_4} = F_{\text{org}} + F_{\text{carb}} \]

(4)

where $F_x$ is a flux of x as in Eq. (3).

The ratio of the organic burial to the total carbon flux (i.e., $F_{\text{org}}/F_{\text{carbon}}$) can be evaluated using the geological record of carbon isotopes in organic and inorganic carbon [e.g., ref. 24]. Supplementary Fig. 1 shows the temporal change in the $f_{\text{org}}$ which is derived from Krissansen-Totton et al. 24.

Similarly, sulfur ($S$) is degassed to the ocean-atmosphere system as sulfur dioxide (SO$_2$) and hydrogen sulfide (H$_2$S), and deposited as pyrite (FeS$_2$) and sulfate (e.g., CaSO$_4$). However, we neglect the deposition of sulfate because we focus on the Archean eon, the surface environment was anoxic, and there was very little sulfate (2.5 μM, i.e., 0.01% of modern level) in the Archean ocean.26-27. Since we assume that sulfur is in steady state, a total flux of sulfur ($F_{\text{sulfur}}$) is equal to input and output fluxes, which can be expressed as follows:

\[ F_{\text{sulfur}} = F_{\text{SO}_2} + F_{\text{H}_2\text{S}} = \frac{1}{2} F_{\text{FeS}_2} \]

(5)

where $F_x$ is a flux of x as in Eq. (3).

**Sources and sinks of oxygen.** In this section, we explain models of the $O_2$ source ($F_{\text{roxy}}$) and a kinetically rapid sink of $O_2$ ($F_{\text{oxy}}$), which are used for the calculation of $K_{\text{oxy}}$ (Eq. (2)).
These equations have equilibrium constants that are as follows, in terms of fugacities ($f$) for each volatile species $x$:

$$
K_i = \frac{f_{{\text{H}_2}\text{O}}}{f_{{\text{H}_2}\text{O}}} \quad K_j = \frac{f_{{\text{CO}}}}{f_{{\text{CO}}}} \\
K_3 = \frac{f_{{\text{CH}_4}}}{f_{{\text{CH}_4}}} \\
K_4 = \frac{f_{{\text{SO}_2}}}{f_{{\text{SO}_2}}}
$$

We assume that gas fluxes will be in proportion to their fugacities, e.g., $f_{\text{H}_2} = f_{{\text{H}_2}}^{\text{tot}} \times f_{\text{H}_2}/f_{\text{H}_2}$. Here, $f_{{\text{H}_2}}^{\text{tot}}$ is a total pressure under which degassing occurs. $f_{{\text{H}_2}}^{\text{tot}}$ is a total degassing flux that can be written as

$$
f_{{\text{H}_2}}^{\text{tot}} = f_{{\text{H}_2}\text{O}} + f_{{\text{H}_2}} + f_{{\text{carbon}}} + f_{{\text{muller}}},
$$

where $f_{{\text{O}_2}}$ is a oxygen fugacity, which we will explain later. We calculate equilibrium constants of the above reactions using data of NIST. According to Eqs. (3)–(5), we also obtain the following equations:

$$
\begin{align*}
\text{H}_2 + \text{H}_2\text{O} + 2\text{CH}_4\text{X}_e + \text{H}_2\text{S}\text{X}_e &= 1 \\
\text{CO}_2 + \text{CO} + \text{CH}_4\text{X}_e &= 1 \\
\text{SO}_2 + \text{H}_2\text{O} &= 1 \\
\end{align*}
$$

Hence, given mantle temperature, a total pressure, and oxygen fugacity in the mantle, and solving Eqs. (26) and (27), we obtain fluxes of each molecular species. Hereafter, we explain how to solve Eqs. (26) and (27). First of all, we defined variables as follows:

$$
A = K_1 f_{{\text{O}_2}}^{\text{tot}}/f_{{\text{O}_2}} , B = K_2 f_{{\text{O}_2}}^{\text{tot}}/f_{{\text{O}_2}} , C = K_3 f_{{\text{O}_2}}^{\text{tot}}/f_{{\text{O}_2}} , D = K_4 f_{{\text{O}_2}}^{\text{tot}}/f_{{\text{O}_2}} \\
r_{\text{H}_2} + r_{{\text{H}_2}\text{O}} + 2r_{\text{CH}_4\text{X}_e} + r_{\text{H}_2\text{S}\text{X}_e} = 1 \\
r_{\text{CO}_2} + r_{\text{CO}} + r_{\text{CH}_4\text{X}_e} = 1 \\
r_{\text{SO}_2} + r_{\text{H}_2\text{O}} = 1
$$

Then, Eq. (27) can be rewritten as follows:

$$
\begin{align*}
(1 + A)r_{\text{H}_2}\text{O} + 2X_e (C_{\text{CH}_4}/C_{\text{CH}_4}) r_{\text{CO}_2} + X_e D_{\text{SO}_2}/2 &= 1 \\
r_{\text{CO}_2} + Br_{\text{CO}} + C_{\text{CH}_4}/C_{\text{CH}_4} &= 1 \\
r_{\text{SO}_2} + D_{\text{SO}_2}/2 &= 1
\end{align*}
$$

Hence,

$$
r_{\text{CO}_2} = \frac{r_{{\text{O}_2}}}{(1 + B)r_{{\text{O}_2}}^{\text{tot}} + D_{\text{SO}_2}} \\
r_{\text{SO}_2} = \frac{r_{{\text{O}_2}}}{r_{{\text{O}_2}} + D_{\text{SO}_2}}
$$

The unknown variable, $f_{\text{H}_2}\text{O}$, is obtained by solving the following equation:
8. Stüeken, E. E. & Buick, R. Environmental control on microbial diversification and methane production in the Mesoproterozoic. *Precambrian Res.* **304**, 64–72 (2018).

9. Schirrmieier, B. E., Gugger, M. & Donoghue, P. C. J. Cyanobacteria and the Great Oxidation Event: evidence from genes and fossils. *Palaeontology* **58**, 769–785 (2015).

10. Kaufman, A. J. et al. Late Archean biosphere oxygenification and atmospheric redox state. *Science* **317**, 1900–1903 (2007).

11. Anbar, A. D. et al. A whirl of oxygen before the Great Oxidation Event? *Science* **317**, 1903–1906 (2007).

12. Reinhard, C. T., Raiswell, R., Scott, C., Anbar, A. D. & Lyons, T. W. A late Archean sulfidic sea stimulated by early oxidative weathering of the continents. *Science* **326**, 713–716 (2009).

13. Duan, Y. et al. Molybdenum isotope evidence for mild environmental oxygenification before the Great Oxidation Event. *Geochim. Cosmochim. Acta* **74**, 6655–6668 (2010).

14. Kendall, B., Bremengea, G. A., Weyer, S. & Anbar, A. D. Uranium isotope fractionation suggests oxidative uranium mobilization at 2.5 Ga. *Chem. Geol.* **362**, 105–114 (2013).

15. Kendall, B., Creaser, R. A., Reinhard, C. T., Lyons, T. W. & Anbar, A. D. Transient episodes of mild environmental oxygenation and oxidative continental weathering during the late Archean. *Sci. Adv.* **1**, e1500777 (2015).

16. Stüeken, E. E., Buick, R. & Anbar, A. D. Selenium isotopes support free O2 in the latest Archean. *Geology* **43**, 259–262 (2015).

17. Kendall, B. et al. Redox oxygenation along late Archean ocean margins. *Nat. Geosci.* **3**, 647–652 (2010).

18. Ostrander, C. M. et al. Fully oxygenated water columns over continental shelves before the Great Oxidation Event. *Nat. Geosci.* **12**, 186–191 (2019).

19. Catling, D. C., Zahnle, K. J. & McKay, C. P. Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. *Science* **293**, 839–843 (2001).

20. Kump, L. R. & Barley, M. E. Increased subaerial volcanism and the rise in atmospheric oxygen. *Earth Planet. Sci. Lett.* **352**, 233–236 (2012).

21. Huber, D. E. New insights into the burial history of organic carbon on the early Earth. *Geochim. Cosmochim. Acta* **75**, 4001–4004 (2011).

22. Schrag, D. P. Authigenic carbonate and the history of the global carbon cycle. *Science* **339**, 1383–1385 (2013).

23. Dewey, L.A. Organic carbon cycling and the lithosphere, in *Treatise on Geochemistry* (Second Edition) (eds. Holland, H. D. & Turekian, K. K.) 239–249 (Elsevier, Oxford, 2014).

24. Daines, S., Mills, B. J. W. & Lenton, T. M. Atmospheric oxygen regulation at low protozoic levels by incomplete oxidative weathering of sedimentary organic carbon. *Nat. Commun.* **8**, 1437 (2017).

25. Nakamura, K. & Kato, Y. Carbonatization of ocean crust by the seafloor hydrothermal activity and its significance as a CO2 sink in the early archean. *Geochim. Cosmochim. Acta* **68**, 4595–4618 (2004).

26. Fallick, A.E., Melezghi, V.A. & Simonson, B.M. The ancient anoxic biosphere was not as we know it. in *Biophysics and Evolution of Early Earth* (eds. Dobretsov, N., Neill, H. S. & Puchtel, I. S.) 1–22 (Springer US, Boston, 2014).

27. Planavsky, N. et al. A case for low atmospheric oxygen levels during Earth’s middle history. *Energ. Top. Life Sci.* **2**, 149–159 (2018).

28. Kasting, J. F. & Yung, Y. L. Earth’s atmospheric history: Implications for the origin of life and early Mars. *Proc. Nat. Acad. Sci.* **90**, 4839–4843 (1993).

29. Lee, C.-T.A. et al. Two-step rise of atmospheric oxygen linked to the growth of continents. *Geochem. Geophys. Geosyst.* **19**, 524–527 (2018).

30. Schrag, D. P. Authigenic carbonate and the history of the global carbon cycle. *Science* **339**, 1383–1385 (2013).

31. Catling, D. C. & Claire, M. W. How Earth’s atmosphere evolved to an oxic state: a status report. *Earth Planet. Sci. Lett.* **237**, 1–20 (2005).

32. Claire, M. W., Catling, D. C. & Zahnle, K. J. Biogeochimical modelling of the rise in atmospheric oxygen. *Geobiology* **4**, 239–269 (2006).

33. Planavsky, N. J. et al. A case for low atmospheric oxygen levels during Earth’s middle history. *Energ. Top. Life Sci.* **2**, 149–159 (2018).

34. Kasting, J. F., Yung, Y. L. & Catling, D. C. Evolutionary redox evolution of the Earth’s atmosphere. *J. Geol.* **101**, 245–257 (1993).

35. Kump, L. R., Kasting, J. F. & Barley, M. E. Rise of atmospheric oxygen and the “upside-down” Archean mantle. *Geochim. Cosmochim. Acta* **2**, 2000GC001114 (2001).

36. Kasting, J. F. & Claire, M. W. How Earth’s atmosphere evolved to an oxic state: a status report. *Earth Planet. Sci. Lett.* **237**, 1–20 (2005).

37. Claire, M. W., Catling, D. C. & Zahnle, K. J. Biogeochimical modelling of the rise in atmospheric oxygen. *Geobiology* **4**, 239–269 (2006).

38. Planavsky, N. J. et al. A case for low atmospheric oxygen levels during Earth’s middle history. *Energ. Top. Life Sci.* **2**, 149–159 (2018).

39. Kasting, J. F. & Yung, Y. L. Earth’s atmospheric history: Implications for the origin of life and early Mars. *Proc. Nat. Acad. Sci.* **90**, 4839–4843 (1993).

40. Lee, C.-T.A. et al. Two-step rise of atmospheric oxygen linked to the growth of continents. *Geochem. Geophys. Geosyst.* **19**, 524–527 (2018).

41. Li, Z.-X. A. & Lee, C.-T. A. The constancy of upper mantle fO2 through time and implications for the chemical evolution of the Earth’s interior: implications for the origin of complex life on habitable planets and the concept of planetary oxygenation. *Astrobiology* **5**, 415–438 (2005).
70. Canfield, D. E., Habicht, K. S. & Thamdrup, B. The Archean sulfur cycle and the early history of atmospheric oxygen. Science 288, 658–661 (2000).
71. Crowe, S. A. et al. Sulfate was a trace constituent of Archean seawater. Science 346, 735–739 (2014).
72. Sleep, N.H. Dioxygen over geologic time. in Metal Ions in Biological Systems, Vol. 43, Biogeochemical Cycles of Elements (eds. Sigel, H. & Sigel, R.) 49–73 (Taylor & Francis, Boca Raton, FL, 2005).
73. Canfield, D. E., Rosing, M. T. & Bjerrum, C. Early anaerobic metabolisms. Philos. Trans. R. Soc. B 361, 1819–1834 (2006).
74. Chase, M.W. NIST-JANAF thermochemical tables, Fourth edition (American Institute of Physics, 1998).
75. Davis, F. A. & Cottrell, E. Experimental investigation of basalt and peridotite oxybarometers: Implications for spinel thermodynamic models and Fe\(^{3+}\) compatibility during generation of upper mantle melts. Am. Mineral. 103, 1056–1067 (2018).
76. Birner, S. K., Cottrell, E., Warren, J. M., Kelley, K. A. & Davis, F. A. Peridotites and basalts reveal broad congruence between two independent records of mantle fO\(_2\) despite local redox heterogeneity. Earth Planet. Sci. Lett. 494, 172–189 (2018).
77. Herzberg, C., Condie, K. & Korenaga, J. Thermal history of the Earth and its petrological expression. Earth Planet. Sci. Lett. 292, 79–88 (2010).
78. Holland, H.D. The Chemical Evolution of the Atmosphere and Oceans. (Princeton University Press, Princeton, 1984).

Acknowledgements
Funding support came from NSF Frontiers in Earth System Dynamics award No. 1338810.

Author contributions
D.C.C. designed the study. S.K. performed the calculation and data analysis. S.K. with D. C.C. wrote the paper with input from R.W.N., I.S.P., and A.D.A. All authors discussed the results and commented on the paper.

Competing interests
The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-16493-1.

Correspondence and requests for materials should be addressed to S.K.

Peer review information Nature Communications thanks Bruno Scaillet and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2020
Supplementary Information for
“Mantle data imply
a decline of oxidizable volcanic gases
could have triggered the Great Oxidation”

Shintaro Kadoya¹, David C. Catling¹,
Robert W. Nickal², Igor S. Puchtel³ & Ariel D. Anbar⁴

1. Department of Earth and Space Sciences/ cross-campus Astrobiology Program, University of Washington

2. Geoscience Research Division, Scripps Institution of Oceanography

3. Department of Geology, University of Maryland

4. School of Earth and Space Exploration and School of Molecular Sciences, Arizona State University
Supplementary Figures

Supplementary Figure 1: Evolution of organic burial fraction ($f_{org}$) based on Krissansen-Totton et al. [1]. This diagram corresponds to the case of the locally weighted scatterolot smoothing (LOWESS) in Fig. 3C of Krissansen-Totton et al. [1]. The black solid line and gray shaded region represents the median value and 95% confidence interval, respectively.
Supplementary Figure 2: Probability that the oxygenation parameter ($K_{\text{oxy}}$) is larger than unity ($P(K_{\text{oxy}} > 1)$) as a function of time. The black solid line represents the $P(K_{\text{oxy}} > 1)$ for the standard case (See also Fig.2b). The $P(K_{\text{oxy}} > 1)$ tends to increase with time, which corresponds to the increase in $K_{\text{oxy}}$ (See also Fig.2b). The $P(K_{\text{oxy}} > 1)$ is 95% (the gray dotted line) at 2.4 Ga, which is the oxic transition time.

Supplementary Notes

Supplementary Note 1: Sensitivity test

In the main text, we assumed that the mantle temperature, degassing pressure, and the total flux ratio of carbon and sulfur (i.e., $\chi_c$ and $\chi_s$ in Equation 15), were constant. We also neglected the deposition of magnetite and the uncertainty of the oxygen fugacity of the modern mantle. Here, we examined the sensitivity of our results to changes in these parameters.

As a consequence of the sensitivity tests, we generally obtained trends consistent with previous works. As explained below, the mantle temperature has little effect on the oxic transition time (Supplementary Figure 3). On the other hand, a degassing pressure much higher than assumed in the the standard case can affect the oxic transition time (Supplementary Figure 5). The oxic transition time may also be sensitive to other parameters: factors related to sedimentary recycling of carbon and sulfur ($\chi_c$ and $\chi_s$) as shown in Supplementary Figure 6, the deposition flux of magnetite (Supplementary Figure 7), and the oxygen fugacity that is assumed for the modern mantle (Supplementary Figure 8).
1.1 Mantle temperature

For our standard case (Fig. 2b), we assumed a mantle temperature of 1623.15 K, i.e., the modern potential temperature of the mantle [2]. In contrast, [3] estimated the modern redox proportions of volcanic gases using a temperature of 1473.15 K. However, it is likely that the potential temperature of the Archean mantle was higher today [e.g., 2, 4, 5]. On the other hand, the temperature for the gas vented from volcanic arcs would be lower than the mantle potential temperature because hydration associated with subduction would decrease the melt temperature, resulting in low degassing temperature. Hence, we calculated $K_{\text{oxy}}$ with different temperatures (Supplementary Figure 3). In each calculation, we kept the mantle temperature constant and did not consider mantle cooling.

Supplementary Figure 3a shows the evolutions of $P(K_{\text{oxy}} > 1)$ for different temperatures. As shown in Supplementary Figure 3a, higher temperature tends to result in higher $P(K_{\text{oxy}} > 1)$, i.e., larger $K_{\text{oxy}}$. This is because an absolute value of oxygen fugacity of the mantle, $f_{O_2}$, decreases with a decrease in the temperature. Here, note that the oxidation state of the mantle is represented as $\Delta \text{FMQ} \equiv \log_{10} f_{O_2} - \log_{10} f_{O_2, \text{FMQ}}$, where $f_{O_2, \text{FMQ}}$ is the oxygen fugacity of the fayalite-magnetite-quartz buffer (see also Fig. 1). Since the $f_{O_2, \text{FMQ}}$ decreases with the decrease in temperature (Supplementary Figure 4), the $f_{O_2}$ of source melt, and therefore, $f_{O_2}$ of the volcanic gas do decrease with the cooling even if $\Delta \text{FMQ}$ is constant. So, lower temperature results in more reducing volcanic gas (Supplementary Figure 3a).

Supplementary Figure 3b shows the oxic transition time for different temperatures. As explained above, cooling causes a decrease in $K_{\text{oxy}}$ (Supplementary Figure 3a), the cooling also decreases the oxic transition time (Supplementary Figure 3a). However, such temperature dependence of volcanic gas is relatively weak and not significant for a mantle temperature exceeding 1400 K (Supplementary Figure 3a).

Given that cooling of the potential temperature of the mantle from 1900 K to 1600 K [e.g., 2, 4, 5], the hot mantle in the early Archean tends to cause a relatively high possibility of $K_{\text{oxy}} > 1$, i.e., of the oxic atmosphere (Supplementary Figure 3a). However, the oxic transition time does not change so much (Supplementary Figure 3b).

On the other hand, arc volcanism seems to decrease the $K_{\text{oxy}}$ (Supplementary Figure 3a) and the oxic transition time (Supplementary Figure 3b) considering that the hydrous phases within the oceanic crust lower the melt-
Supplementary Figure 3: A sensitivity study for mantle temperature: (a) probability that the oxygenation parameter is larger than unity ($P(K_{oxy} > 1)$) as a function of time, and (b) an oxic transition time as a function of the mantle temperature. Here, the oxic transition time is the time at which $P(K_{oxy} > 1)$ is 95%. Black diamonds represent outputs of the standard case (see also Supplementary Figure 2).
Supplementary Figure 4: Oxygen fugacity of the fayalite-magnetite-quartz buffer as a function of temperature. The \( f_{O_2, FMQ} \) is calculated using a function given by [6].

ing temperature [e.g., 7]. However, we have to note that island arc basalts tends to be more oxidized than mid-ocean ridge basalt or oceanic island basalt [8]. Hence, to examine the oxidation effect of the volcanic gas vented from arc volcanoes, we also have to consider the difference in \( \Delta FMQ \) between the mantle and the volcanic arc.

**Comparison with previous study**  This trend of the oxic transition time with mantle temperature is consistent with [9] but inconsistent with [10]. The main difference of these studies is the assumption of the \( f_{O_2} \) of volcanic gas. In [9] and this study, it is assumed that the \( f_{O_2} \) of the volcanic gas is buffered by the \( f_{O_2} \) of mantle. Hence, cooling results in a decrease in the absolute value of \( f_{O_2} \) of the mantle and the volcanic gas, which makes volcanic gas more reducing.

In [10], it is assumed that the volcanic gas is a closed system, i.e., decoupled with its source melt. Under such a condition, cooling causes reduction of \( SO_2 \) to \( H_2S \), which is accompanied by oxidation of \( H_2 \) to \( H_2O \) [10, 9]. Hence, the ratio of \( H_2O \) to \( H_2 \) in the volcanic gas increases with cooling, resulting in the apparent increase in \( f_{O_2} \) of the volcanic gas relative to \( f_{O_2} \) of the source melt. However, in a closed system, reduction of one gas must be accompanied by oxidation of another gas because the reduction of \( SO_2 \) is accompanied by the oxidation of \( H_2 \). Hence, the overall \( O_2 \) sink in the gas mixture does not change [9].
1.2 Degassing pressure

Volcanic gases tend to become more reducing with increasing pressure of degassing. Thus, previous studies [e.g., 11, 12] proposed that a change in volcanic degassing from submarine settings (where the weight of the ocean can add a few 100 bar) to subaerial settings triggered the GOE, though the effect of pressure might be overestimated [13]. Here, we calculated $K_{\text{oxy}}$ with different degassing pressure (Supplementary Figure 3) and obtained a similar trend [e.g., 11, 12].

Supplementary Figure 5: A sensitivity study for degassing pressure: (a) $P(K_{\text{oxy}} > 1)$ as a function of time, and (b) an oxic transition time as a function of the pressure. See also Supplementary Figure 3. The $P(K_{\text{oxy}} > 1)$ tends to increase with the decrease in the mantle temperature (a), which is consistent with previous works [e.g. 11, 12].

Supplementary Figure 5a shows the evolutions of $P(K_{\text{oxy}} > 1)$ for differ-
ent pressures of degassing. As shown in Supplementary Figure 5a, higher degassing pressure tends to result in lower $P(K_{\text{oxy}} > 1)$, i.e., smaller $K_{\text{oxy}}$. This trend is consistent with previous works [e.g., 11, 12]. Hence, the oxic transition time becomes smaller in units of Ga (Supplementary Figure 5b).

Thus, a transition from submarine to subaerial volcanism, i.e., a decrease in the degassing pressure, might have played a role in the oxygenation of atmosphere [11], in addition to secular mantle oxidation.

### 1.3 Total flux ratio of carbon and sulfur

We assumed constant total flux ratios of carbon ($\chi_c$) and sulfur ($\chi_s$) relative to total hydrogen in Eq. (2) for the standard case (Fig. 2), but they may have changed with time. Indeed, [14] assumed that the volcanic recycling of CO$_2$ and SO$_2$ increased with time as sedimentary reservoirs of carbon and sulfur grew and suggested that the ratio of CO$_2$/H$_2$O and SO$_2$/H$_2$O increased with time, which caused the GOE. Here, we examined the effect of ($\chi_c$) and ($\chi_s$) on $K_{\text{oxy}}$ (Supplementary Figure 6) and obtained similar trend [14].

Supplementary Figure 6a and 6b show the evolution of $P(K_{\text{oxy}} > 1)$ for (a) different ratios of a total carbon flux to a total hydrogen flux ($\chi_c$) and (b) different ratios of a total sulfur flux to a total hydrogen flux ($\chi_s$). As shown in Supplementary Figure 6a and 6b, higher $\chi_c$ ($\chi_s$) tends to result in higher $P(K_{\text{oxy}} > 1)$, i.e., higher $K_{\text{oxy}}$. This is because larger $\chi_c$ ($\chi_s$) tends to increase the numerator of Eq. (2). These results are consistent with the suggestion of Holland [14] that larger $\chi_c$ ($\sim$ CO$_2$/H$_2$O) and/or $\chi_s$ ($\sim$ SO$_2$/H$_2$O) tend to favor an oxic atmosphere and could drive the GOE.

Supplementary Figure 6c and 6d show the oxic transition time as a function of (c) $\chi_c$ and (d) $\chi_s$. Note that in Supplementary Figure 6c and 6d, black diamonds, which represent the oxic transition time of the standard case, are slightly offset from the dashed lines. This is because for the standard case, we integrated the oxic transition time using the distribution of $\chi_c$ and $\chi_s$. The increase in $\chi_c$ ($\chi_s$) increases the oxic transition time (Supplementary Figure 6c and 6d) because larger $\chi_c$ ($\chi_s$) results in larger $K_{\text{oxy}}$ (Supplementary Figure 6a and 6b).

Estimating the evolution of parameters $\chi_c$ and $\chi_s$ is outside of the scope of this study but may be necessary for understanding of the evolution of Earth’s surface oxidation.
Supplementary Figure 6: A sensitivity study for the ratio of a total flux of an element (C or S) to the total flux of hydrogen: a and c are for the total carbon flux to the total hydrogen flux, $\chi_c$, and b and d are for the ratio of the total flux of sulfur to the total flux of hydrogen, $\chi_s$. The gray shaded regions represent the 95% confidence interval of modern values of $\chi_c$ (0.1 ± 0.06 [2SD]) and $\chi_s$ (0.023 ± 0.017 [2SD]), respectively. See also Supplementary Figure 3.
1.4 Magnetite deposition

The deposition of magnetite via serpentinization works as a sink of oxygen because it generates oxidizable hydrogen (simplified as $3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$), although serpentinization is a relatively minor sink today [15, 16]. However, in the Archean, serpentinization rates might have been enhanced by an oceanic crust including a larger amount of olivine. Such crust could have been produced by a higher mantle temperature because the higher mantle temperature would cause a greater degree of partial melting, resulting in an igneous product that is similar to its mantle source [17]. Hence, the deposition of magnetite might affect the redox state of the atmosphere on the Archean Earth [17]. Here, we calculated the $K_{\text{oxy}}$ by varying the magnetite deposition flux (Supplementary Figure 7) and obtained a similar conclusion to Kasting [17].

Supplementary Figure 7a shows the evolutions of $P(K_{\text{oxy}} > 1)$ for different fluxes of magnetite deposition. As shown in Supplementary Figure 7a, higher magnetite deposition flux results in lower $P(K_{\text{oxy}} > 1)$, i.e., smaller $K_{\text{oxy}}$.

Supplementary Figure 7b shows the oxic transition time for different fluxes of magnetite deposition. The modern flux of magnetite deposition is estimated to be 0.05 to $\sim 0.2$ TmolO$_2$ yr$^{-1}$ [15, 16], and the range is represented by the gray shaded region in Supplementary Figure 7a. Given the higher mantle potential temperature in the Archean, the oceanic crust would have been thicker and more olivine-rich than today [e.g., 18]. As a result, the flux of magnetite deposition may have been as much as 10 times or more higher than the modern flux ($\sim 2$ TmolO$_2$ yr$^{-1}$) as suggested by [17].

1.5 Oxygen fugacity of the modern mantle

As explained in Supplementary Note 4, we anchor the evolution of oxygen fugacity ($f_{O2}$) of the mantle so that at $t = 0$ Ga (now) the average value of $f_{O2}$ is that inferred for the mantle from mid-ocean ridge basalt (MORB). Hence, the $f_{O2}$ value chosen for the modern mantle anchors the absolute value of the trend of past $f_{O2}$, and therefore affects the calculated trend of $K_{\text{oxy}}$ in the past.

For the standard case, we apply the average oxygen fugacity of the modern mantle, which is +0.2 in the log$_{10}$ unit relative to the fayalite-magnetite-quartz (FMQ) buffer (i.e., $\Delta \text{FMQ}_0 = +0.2$) according to [19]. However,
Supplementary Figure 7: A sensitivity study for deposition flux of magnetite (Fe₃O₄): (a) $P(K_{oxy} > 1)$ as a function of time, and (b) an oxic transition time as a function of the deposition flux of magnetite. See also Supplementary Figure 3. The gray shaded region represents the range of modern flux of magnetite deposition [0.05 ~ 0.2 TmolO₂ yr⁻¹; 15, 16]. See also Supplementary Figure 3.
∆FMQ₀ has an uncertainty of σ = 0.3 in log₁₀ units [19]. Here, we investigated the effect of ∆FMQ₀ on the evolution of \( K_{\text{oxy}} \) (Supplementary Figure 8).

Supplementary Figure 8: A sensitivity study for the oxygen fugacity of modern mid-ocean ridge basalt: (a) \( P(K_{\text{oxy}} > 1) \) as a function of time, and (b) an oxic transition time as a function of the pressure (See also Supplementary Figure 3) The gray shaded region represents the 95% confidence interval of the oxygen fugacity of modern MORB (FMQ+0.2 ± 0.6 [2SD]) according to [19]. See also Supplementary Figure 3.

Anchoring the \( f_{O_2} \) trend to a large ∆FMQ₀ causes higher oxygen fugacity of the mantle throughout the past (Eq. (4)). So, this obviously results in a larger \( P(K_{\text{oxy}} > 1) \) (Supplementary Figure 8a) and earlier oxic transition time Supplementary Figure 8b.
Supplementary Note 2: Holland’s f number

2.1 Relation between Holland’s f number and oxygenation parameter

As discussed in Kadoya et al. [9], the oxygenation parameter, \( K_{\text{oxy}} \), of a closed gas mixture does not flip from \(< 1\) to \(> 1\) or vice versa if reactions occur within a closed gas mixture. Also, the same conclusion can be obtained in terms of Holland’s f number. This point can be mathematically derived by considering the relation between f and \( K_{\text{oxy}} \), as follows.

Holland’s f number is calculated as follows [e.g., 20]:

\[
f = \frac{F_{\text{H}_2} + (1 - 2f_{\text{org}})F_{\text{CO}} + (4 - 2f_{\text{org}})F_{\text{CH}_4} - 2f_{\text{org}}F_{\text{CO}_2} + 3F_{\text{H}_2}\text{S}}{3.5F_{\text{S,all}}} + \frac{1}{3.5}
\]

where \( F_x \) represents the flux of a material, \( x \). Note that total carbon flux is \( F_{\text{C,all}}(= F_{\text{CO}_2} + F_{\text{CO}} + F_{\text{CH}_4}) \), and total sulfur flux is \( F_{\text{S,all}}(= F_{\text{SO}_2} + F_{\text{H}_2}\text{S}) \). The parameter, \( f_{\text{org}} \), is the organic burial fraction, which was set at 0.2 in Holland [20]. In this formulation, we also consider methane flux, \( F_{\text{CH}_4} \), for consistency with the oxygenation parameter. Note that degassing of 1 mol \( \text{CH}_4 \) is equivalent to a source of 4 mol \( \text{H}_2 \): \( \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \).

The oxygenation parameter, \( K_{\text{oxy}} \), is calculated as follows [e.g., 21]:

\[
K_{\text{oxy}} = \frac{4f_{\text{org}} \times F_{\text{C,all}} + 5F_{\text{SO}_2}}{2F_{\text{H}_2} + 2F_{\text{CO}} + 8F_{\text{CH}_4} + F_{\text{H}_2}\text{S}}.
\]  

Using Eqs. S.1 and S.2 produces following equation:

\[
f - 1 = \frac{2f_{\text{org}}F_{\text{C,all}} + 2.5F_{\text{SO}_2}}{3.5F_{\text{S,all}}} \times \left( \frac{1}{K_{\text{oxy}}} - 1 \right).
\]  

Since \( F_{\text{C,all}}, F_{\text{S,all}}, F_{\text{SO}_2}, \) and \( f_{\text{org}} \) are not negative, the sign of \((f - 1)\) is identical with that of \((-1 + 1/K_{\text{oxy}})\); therefore,

\[
\begin{align*}
&f > 1 \iff K_{\text{oxy}} < 1 \\
&f = 1 \iff K_{\text{oxy}} = 1 \\
&f < 1 \iff K_{\text{oxy}} > 1
\end{align*}
\]  

The oxygenation parameter, \( K_{\text{oxy}} \), of a closed gas mixture does not flip from \(< 1\) to \(> 1\) or vice versa as long as reactions occur within the closed
gas mixture [9]. According to the relation between \( f \) and \( K_{\text{oxy}} \) summarized in Eq. S.4, Holland’s \( f \) number of the closed gas mixture also does not flip from \( > 1 \) to \( < 1 \) or vice versa as long as reactions occur within the closed gas mixture.

2.2 Temperature dependence of Holland’s \( f \) number and oxygenation parameter

The temperature dependence of Holland’s \( f \) number and \( K_{\text{oxy}} \) is shown in Fig. 9 and 10.

First, assume that the oxygen fugacity of a gas mixture is buffered by that of the ambient melt (i.e., the melt-buffer system in Kadoya et al. [9]). Note that the oxidation state of each case in Fig. 9 is represented by \( \Delta \text{FMQ} \) that is a difference of the logarithm of oxygen fugacity of a gas mixture from that of the fayalite-magnetite-quartz buffer level. For consistency with another case, we represent the oxidation state as \( \Delta \text{FMQ}_{2000} \) that is \( \Delta \text{FMQ} \) at 2000 K. However, we assumed that \( \Delta \text{FMQ} \) of the ambient melt, and therefore of the gas mixture, is constant.

For the melt buffer system, a decrease in temperature tends to decrease \( K_{\text{oxy}} \) (Fig. 9a). Note that Fig. 9a is the same with Fig. 1b of Kadoya et al. [9]; so for detailed information, see Kadoya et al. [9]. On the other hand, the decrease in temperature tends to increase the \( f \) number (Fig. 9b). Here, let us focus on the case of \( \Delta \text{FMQ}_{2000} = -0.5 \) (dashed lines in Fig. 9). As explained in Kadoya et al. [9], \( K_{\text{oxy}} \) of \( \Delta \text{FMQ}_{2000} = -0.5 \) shifts from \( > 1 \) to \( < 1 \) with a decrease in temperature around 1400 K (Fig. 9a). On the other hand, the \( f \) number of \( \Delta \text{FMQ}_{2000} = -0.5 \) shifts from \( < 1 \) to \( > 1 \) with a decrease in temperature around 1400 K (Fig. 9b). Both of these shifts indicate that the decrease in temperature results in a shift of atmosphere from oxic to anoxic.

Second, consider a closed gas system. For the closed gas system, a decrease in temperature changes \( K_{\text{oxy}} \), but \( K_{\text{oxy}} \) does not flip from \( < 1 \) to \( > 1 \) or vice versa (Fig. 10a) as explained in Kadoya et al. [9]. Note that Fig. 10a is the same with Fig. 2b of Kadoya et al. [9]. Similarly, the \( f \) number does not flip from \( < 1 \) to \( > 1 \) or vice versa though temperature changes (Fig. 10b). As discussed in Kadoya et al. [9], these results are because of a redox conservation within a closed system.

Thus, temperature dependence of Holland’s \( f \) number is essentially same with that of \( K_{\text{oxy}} \) in terms of redox evolution of the atmosphere.
Supplementary Figure 9: Oxygenation effect of a volcanic gas as a function of temperature: (a) oxygenation parameter \(K_{\text{oxy}}\), and (b) Holland’s \(f\) number. The melt-buffer system is assumed (see Fig. 1 of Kadoya et al. [9]). Decrease in temperature results in (a) a decrease in \(K_{\text{oxy}}\) and (b) an increase in \(f\) number. In particular, \(K_{\text{oxy}}\) of \(\Delta FMQ_{2000} = -0.5\) (dashed lines in a) flips from \(>1\) to \(<1\) around 1400 K. Similarly, the \(f\) number of \(\Delta FMQ_{2000} = -0.5\) (dashed lines in b) flips from \(<1\) to \(>1\). Both of these lines show that temperature decrease shift atmosphere from oxic to anoxic if the oxidation state of the melt, and therefore of a volcanic gas, is \(\Delta FMQ = -0.5\). For detailed information, see Kadoya et al. [9].
Supplementary Figure 10: Oxygenation effect of a volcanic gas as a function of temperature: (a) oxygenation parameter ($K_{oxy}$), and (b) Holland’s $f$ number. The closed system is assumed (see Fig. 2 of Kadoya et al. [9]). Decrease in temperature changes $K_{oxy}$; however, $K_{oxy}$ does not flip from $< 1$ to $> 1$ or vice versa. Similarly, Holland’s $f$ number does not flip from $< 1$ to $> 1$ or vice versa. For detailed information, see Kadoya et al. [9].
Supplementary Note 3: Oxygen fugacity of mantle

In this study, we model the evolution of the oxygen fugacity of mantle according to the data of Aulbach and Stagno [22] and Nicklas et al. [23]. As shown in Fig. 1a, these two datasets seem to have similar trends but are offset. In this section, we discuss the similarity and difference between the two datasets by using a linear function. Then, we derive the model of the evolution of the oxygen fugacity of mantle.

3.1 Comparison of trends of two datasets of the oxygen fugacity evolution

First of all, we compare trends of the two datasets using an F test. For a null hypothesis, we assumed that the two datasets are fitted by two linear functions whose slopes are the same but whose intercepts are different from each other: i.e., for the data of Aulbach and Stagno [22],

\[ \Delta \text{FMQ} = a_1 t + \Delta \text{FMQ}_{1,\text{AS}}, \quad (S.5) \]

and for the data of Nicklas et al. [23],

\[ \Delta \text{FMQ} = a_1 t + \Delta \text{FMQ}_{1,N}. \quad (S.6) \]

Here, \( t \) is in the unit of Ga, and the oxygen fugacity is in log_{10} units relative to the Fayalite-Magnetite-Quartz (FMQ) buffer. The parameters, \( a_1 \), \( \Delta \text{FMQ}_{1,\text{AS}} \), and \( \Delta \text{FMQ}_{1,N} \), are analytically computed to be \(-0.29 \pm 0.05 [2\sigma]\) in the unit of [/Ga], \(0.0 \pm 0.15 [2\sigma]\), and \(1.20 \pm 0.05 [2\sigma]\), respectively. Using these functions, the squared sum of residuals is 96.9.

On the other hand, as an alternative hypothesis, we assumed that the two datasets are fitted by two linear functions whose slopes and intercepts are different from each other: i.e., for the data of Aulbach and Stagno [22],

\[ \Delta \text{FMQ} = a_{2,\text{AS}} t + \Delta \text{FMQ}_{2,\text{AS}}, \quad (S.7) \]

and for the dataset of Nicklas et al. [23],

\[ \Delta \text{FMQ} = a_{2,N} t + \Delta \text{FMQ}_{2,N}. \quad (S.8) \]

Equations S.7 and S.8 are represented by dotted and dashed lines in Fig. 1a, respectively. The parameters for Aulbach and Stagno [22], \( a_{2,\text{AS}} \) and \( \Delta \text{FMQ}_{2,\text{AS}} \),
are analytically computed to be $-0.41 \pm 0.17$ [2σ] in the unit of [/Ga] and $0.14 \pm 0.24$ [2σ], respectively. Similarly, the parameters for Nicklas et al. [23], $a_{2,N}$ and $\Delta FMQ_{2,N}$, are analytically computed to be $-0.27 \pm 0.05$ [2σ] in the unit of [/Ga] and $1.2 \pm 0.1$ [2σ], respectively. Using these functions, the squared sum of residuals is 94.7.

The number of data is 12 for Aulbach and Stagno [22] and 18 for Nicklas et al. [23]. We use four parameters for the null hypothesis and three parameters for the alternative hypothesis. So, the F-value is calculated as follows:

$$F = \left(\frac{96.9 - 94.7}{12 + 18 - 3} - (12 + 18 - 4)\right) \left(\frac{94.7}{12 + 18 - 4}\right)^{-1} \sim 0.61. \quad (S.9)$$

Considering an F distribution with this F-value (0.61), the p-value is calculated to be 44%. Since the p-value is higher than a canonical rejection rate (5%), we cannot reject the null hypothesis. Hence, we consider that the slopes of the fitting functions for the two datasets are the same as each other.

### 3.2 Comparison of offsets of two datasets of the oxygen fugacity evolution

As explained above, we fit the two datasets by linear functions whose slopes are the same as each other. Then, we compare the intercepts of the linear functions using the F test.

For a null hypothesis, we assumed that the two datasets are fitted by one linear function. The fitting function for both of Aulbach and Stagno [22] and Nicklas et al. [23] is as follows:

$$\Delta FMQ = a_3 t + \Delta FMQ_3. \quad (S.10)$$

The parameters, $a_3$ and $\Delta FMQ_3$, are analytically computed to be $-0.21 \pm 0.05$ [2σ] in the unit of [/Ga] and $0.9 \pm 0.1$ [2σ], respectively. Using this function, the squared sum of residuals is 329.3.

On the other hand, for an alternative hypothesis, we assumed that the two datasets are fitted by two linear functions whose slopes are the same but intercepts are different from each other: i.e., the null hypothesis above (see Eq. S.5 and S.6, and related explanation). As explained above, using Eq. S.5 and S.6, the squared sum of residuals is 96.9.

The number of data is 12 for Aulbach and Stagno [22] and 18 for Nicklas et al. [23], and we use three parameters for the null hypothesis and 2 parameters
for the alternative hypothesis. So, the F-value is calculated as follows:

$$ F = \left( \frac{329.3 - 96.9}{(12 + 18 - 2) - (12 + 18 - 3)} \right) \left( \frac{96.9}{12 + 18 - 3} \right)^{-1} \approx 64.8. \quad (S.11) $$

Considering an F distribution with this F-value (64.8), the p-value is calculated to be $1.2 \times 10^{-6}$%. Since the p-value is lower than the canonical rejection rate (5%), we reject the null hypothesis.

### 3.3 Oxygen fugacity of the modern mantle

As explained above, the two datasets of the oxygen fugacity ($f_{O2}$) evolutions [22, 23] are fitted by linear functions whose slopes are the same but whose intercepts are different. The difference in the absolute values of $f_{O2}$ is due to the issue of the inter-calibration of different oxybarometers, or due to the difference in mantle melting process between ridge and plume [24, 23].

In this study, we anchor the evolution of the $f_{O2}$ at the value which is evaluated using the oxidation state of iron in the modern mid ocean ridge (MORB) samples [19]. According to O’Neill et al. [19], the $f_{O2}$ of the modern MORB is $0.2 \pm 0.6$ $[2\sigma]$ in log$_{10}$ units relative to the FMQ buffer. So, for a standard case of this study, we assumed that the oxygen fugacity of the modern mantle is FMQ+0.2. The variation in the modern oxygen fugacity is considered later as a parameter study.

Setting the oxygen fugacity of the modern mantle, we can regard the intercepts calculated above (i.e., $\Delta FMQ_{1,AS}$ in Eq. S.5, and $\Delta FMQ_{1,N}$ in Eq. S.6) as the offset from the evolution of the oxygen fugacity. For the standard case, the average offset is +0.2 for Aulbach and Stagno [22], and -1.00 for Nicklas et al. [23].
Supplementary References

[1] Krissansen-Totton, J., Buick, R., & Catling, D. C. A statistical analysis of the carbon isotope record from the Archean to Phanerozoic and implications for the rise of oxygen. *Am. J. Sci.* **315**, 275–316 (2015).

[2] Herzberg, C., Condie, K., & Korenaga, J. Thermal history of the Earth and its petrological expression. *Earth Planet. Sc. Lett.* **292**, 79–88 (2010).

[3] Holland, H. D. *The Chemical Evolution of the Atmosphere and Oceans*. (Princeton University Press, Princeton, 1984).

[4] Nisbet, E. G., Cheadle, M. J., Arndt, N. T., & Bickle, M. J. Constraining the potential temperature of the Archean mantle - a review of the evidence from komatiites. *Lithos* **30**, 291–307 (1993).

[5] Aulbach, S. & Arndt, N. T. Eclogites as palaeodynamic archives: Evidence for warm (not hot) and depleted (but heterogeneous) Archaean ambient mantle. *Earth Planet. Sc. Lett.* **505**, 162–172 (2019).

[6] Wones, D. R. & Gilbert, M. C. The fayalite-magnetite-quartz assemblage between 600 and 800 c. *Am. J. Sci.*, 267:480–488, 1969.

[7] Till, C. B., Grove, T. L., & Withers, A. C. The beginnings of hydrous mantle wedge melting. *Contrib. Mineral. Petr.* **163**, 669–688 (2012).

[8] Carmichael, I. S. E. The redox states of basic and silicic magmas: a reflection of their source regions? *Contrib. Mineral. Petr.* **106**, 129–141 (1991).

[9] Kadoya, S., Catling, D. C., Nicklas, R. W., Puchtel, I. S., & Anbar, A. D. Mantle cooling causes more reducing volcanic gases and gradual reduction of the atmosphere. *Geochem. Perspec. Lett.* **13**, 25–29 (2020).

[10] Moussallam, Y., Oppenheimer, C., & Scaillet, B. On the relationship between oxidation state and temperature of volcanic gas emissions. *Earth Planet. Sc. Lett.* **520**, 260–267 (2019).

[11] Kump, L. R. & Barley, M. E. Increased subaerial volcanism and the rise of atmospheric oxygen 2.5 billion years ago. *Nature* **448**, 1033–1036 (2007).
[12] Gaillard, F., Scaillet, B., & Arndt, N. T. Atmospheric oxygenation caused by a change in volcanic degassing pressure. *Nature* **478**, 229–233 (2011).

[13] Brounce, M., Stolper, E., & Eiler, J. Redox variations in mauna kea lavas, the oxygen fugacity of the hawaiian plume, and the role of volcanic gases in Earth’s oxygenation. *P. Natl. Acad. Sci. USA* **114**, 8997–9002 (2017).

[14] Holland, H. D. Why the atmosphere became oxygenated: A proposal. *Geochim. Cosmochim. Ac.* **73**, 5241–5255 (2009).

[15] Sleep, N. H. Dioxygen over geologic time. in *Metal Ions in Biological Systems, Vol. 43, Biogeochemical Cycles of Elements* (eds. Sigel, H. & Sigel, R.) 49–73 (Taylor & Francis, Boca Raton, FL 2005).

[16] Canfield, D. E., Rosing, M. T., & Bjerrum, C. Early anaerobic metabolisms. *Philos. T. R. Soc. B.* **361**, 1819–1834 (2006).

[17] Kasting, J. F. What caused the rise of atmospheric O2? *Chem. Geol.* **362**, 13–25 (2013).

[18] Sleep, N. H. Evolution of the Earth: Plate tectonics through time. in *Treatise on Geophysics (Second Edition)* (eds. Schubert, G.) 145–172 (Elsevier, Oxford, 2015).

[19] O’Neill, H. S. C., Berry, A. J., & Mallmann, G. The oxidation state of iron in mid-ocean ridge basaltic (MORB) glasses: Implications for their petrogenesis and oxygen fugacities. *Earth Planet. Sc. Lett.* **504**, 152–162 (2018).

[20] Holland, H. D. Volcanic gases, black smokers, and the Great Oxidation Event. *Geochim. Cosmochim. Ac.* **66**, 3811–3826 (2002).

[21] Catling, D. C. & Claire, M. W. How Earth’s atmosphere evolved to an oxic state: A status report. *Earth Planet. Sc. Lett.* **237**, 1–20 (2005).

[22] Aulbach, S. & Stagno, V. Evidence for a reducing Archean ambient mantle and its effects on the carbon cycle. *Geology* **44**, 751–754 (2016).
[23] Nicklas, R. W. et al. Secular mantle oxidation across the Archean-Proterozoic boundary: Evidence from V partitioning in komatiites and picrites. *Geochim. Cosmochim. Ac.* **250**, 49–75 (2019).

[24] Mallmann, G. & O’Neill, H. S. Calibration of an empirical thermometer and oxybarometer based on the partitioning of Sc, Y and V between olivine and silicate melt. *J. Petrol.* **54**, 933–949 (2013).