Mantle cooling causes more reducing volcanic gases and gradual reduction of the atmosphere

S. Kadoya1*, D.C. Catling1, R.W. Nicklas2, I.S. Puchtel2, A.D. Anbar4

Abstract

The early atmosphere contained negligible O2 until the Great Oxidation Event (GOE) around 2.4 Ga, but evidence suggests that production of photosynthetic O2 began hundreds of millions of years earlier. Thus, an ongoing debate concerns the trigger of the GOE. One possibility is that volcanic gases became more oxidising over time. Secular cooling of the mantle affects thermodynamic equilibria and also changes the proportions of reduced and oxidised volcanic gases. Here, we examine the consequences of mantle cooling for the evolution of Earth’s atmospheric redox state. Contrary to some previous hypotheses, we show that as the mantle cools, volcanic emissions contain a greater proportion of reducing gases, which produces a more reducing atmosphere. However, the atmosphere became more oxic. Therefore, the redox consequences of other processes, such as secular oxidation of the mantle and/or hydrogen escape to space, must have dominated over that of mantle cooling in shaping the redox evolution of Earth’s atmosphere.

Introduction

The partial pressure of Archean atmospheric O2 was <0.2 × 10-6 bar and rose during the Great Oxidation Event (GOE), between 2.4 Ga and 2.1 Ga, as indicated by the disappearance of mass independent sulfur isotope fractionation in sedimentary rocks (Farquhar et al., 2000; Pavlov and Kasting, 2002; Zahnle et al., 2006). However, chromium, iron, and molybdenum isotope data suggest the presence of O2 in the marine photic zone (oxygen oases) as early as ~3 Ga (Planavsky et al., 2014; Saikoski et al., 2015), and evidence exists for mild oxygenation from these and other proxies at 2.5 Ga (Ostrander et al., 2019 and references therein). Evidence for free O2 before the GOE is also consistent with phylogenetic inferences that oxygenic photosynthesis evolved by the mid to late Archean (Catling et al., 2017; Moussallam et al., 2019) suggesting that a decrease in volcanic emission temperature, which they defined as that of the fumarole where gases enter the air, caused the secular cooling of the planetary interior caused a decrease in emission temperatures, oxidation of volcanic gases, and the GOE. Specifically, they considered the cooling of a parcel of gas in a volcanic vent as a closed system separated from a melt.

1. Department of Earth and Space Sciences / cross-campus Astrobiology Program, University of Washington, Box 35130, Seattle, WA 98195-1300, USA
2. Department of Geology, University of Maryland, College Park, MD 20742, USA
3. Geoscience Research Division, Scripps Institution of Oceanography, La Jolla, CA 92093, USA
4. School of Earth and Space Exploration and School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA
* Corresponding author (email: shintaro.kadoya@gmail.com)
Here, we examine how cooling affected volcanic gas buffered by a surrounding melt and gases in a subsequent closed system. We analyse the effect of inferred changes in the proportions of oxidised and reduced volcanic gases on the redox state of the atmosphere.

## Model

We begin by describing our model briefly. Supplementary Information Section S-1 contains additional details. We assume that volcanic gas consists of H$_2$O, H$_2$, CO$_2$, CO, CH$_4$, SO$_2$, and H$_2$S in thermodynamic equilibrium at a total pressure of 5 bar, assuming a subaerial volcanic eruption (Holland, 1984; p. 47). Section S-8 discusses how the redox state of volcanic gases changes outside of this nominal pressure value. Partial pressures of the gas species are calculated using mass conservation of hydrogen, carbon, and sulfur, and relevant thermodynamic equilibria (see also Section S-1).

We model two end members of the redox state of the gas mixture. This redox state corresponds to the amount of oxygen within the gas mixture, which is described in our two cases as follows. In one case, the “buffered system”, the gas interacts with surrounding melt and rocks. Oxygen exchanges with the melt such that O$_2$ fugacity is fixed at a given temperature and pressure. For the other case, the “closed system”, we assume that the gas and its reactions are isolated from the melt, and since no constituents are supplied or released, we conserve mass for oxygen, hydrogen, carbon, and sulfur (Supplementary Information Eq. S-12; see also Eq. S-6, S-7 and S-8).

We evaluate the oxygen effect of volcanic gas using an oxygenation parameter, $K_{oxy}$, introduced in previous studies (Catling and Claire, 2005; Claire et al., 2006; Kasting, 2013). This parameter is the ratio of the source flux of O$_2$ ($F_{source}$) to the kinetically rapid sink flux of O$_2$ ($F_{sink}$):

$$K_{oxy} = \frac{F_{source}}{F_{sink}}$$

Eq. 1

Here, $F_{sink}$ corresponds to degassing of reductive, i.e. oxidisable, volcanic gases, which can include an excess of reductants beyond that which reacts with O$_2$.

By construction, $F_{source}$ and $F_{sink}$ are not meant to balance each other: they omit fluxes that depend on atmospheric redox state, such as hydrogen escape to space in $F_{source}$ and oxidative weathering, e.g., oxidation of Fe$^{2+}$ to Fe$^{3+}$ in $F_{sink}$ (Catling and Claire, 2005; Kasting, 2013). When $K_{oxy} < 1$, O$_2$ sinks exceed O$_2$ sources and excess H$_2$ accumulates until balanced by escape to space. When $K_{oxy} > 1$, O$_2$ sources exceed O$_2$ sinks and O$_2$ accumulates until balanced by oxidative weathering. The evolution of $K_{oxy}$ in a box model coupled to photochemistry shows how atmospheric oxygenation occurs when $K_{oxy}$ reaches unity (Claire et al., 2006).

We assume that oxygenic photosynthesis is present because we are evaluating O$_2$ build-up. We consider H$_2$O, CO$_2$, and SO$_2$ to be redox neutral, while H$_2$, CO, CH$_4$, and H$_2$S fluxes consume O$_2$ in atmospheric photochemistry. The burial of organic matter and pyrite (FeS$_2$) are O$_2$ source fluxes. Considering the stoichiometry of O$_2$ consumption and production, we rewrite Eq. 1 as follows (derived in Section S-1):

$$K_{oxy} = \frac{4f_{org} \times (pCO_2 + pCO + pCH_4) + 5pSO_2}{2pH_2 + 2pCO + 8pCH_4 + pH_2S}$$

Eq. 2

Here, $f_{org}$ represents the fraction of carbon buried as sedimentary organic carbon. Although $f_{org}$ has changed with time, for a nominal case, we set $f_{org}$ to 20 %, which is a rough average over geologic time (Krissansen-Totton et al., 2015). Section S-7 discusses the dependence of $K_{oxy}$ on variations of $f_{org}$.

The mechanism that sets $f_{org}$ is beyond our scope. However, $f_{org}$ might be controlled by divalent cation fluxes that modulate the carbonate burial flux, which complements the organic burial flux (Sleep, 2005).

## Results and Discussion

The degassing process has two stages. Firstly, a gas bubble emerges from melt. The oxygen fugacity of this gas mixture is buffered by the surrounding melt since gases react with the melt. So, this stage corresponds to the buffered system case. Secondly, the bubble ascends within the melt, and the gas temperature adiabatically decreases with decompression (Oppenheimer et al., 2018). In this stage, gases react with each other within the closed system bubble. Hereafter, we explain the redox speciation of volcanic gases during each stage.

First, we consider the oxidation state of global volcanic gas emissions for the buffered system. We define the redox state as the difference of logarithm of $f_{O_2}$ from that of the Quartz-Fayalite-Magnetite (QFM) buffer: $\Delta QFM = \log f_{O_2} - \log f_{O_2,qfm}$. Also, we consider 4 different redox states of the surrounding melt (and rocks), and we assume that the redox state of the surroundings in each case is constant and independent of temperature. Since we consider cooling from 2000 K, we denote the oxidation state of the melt as $\Delta QFM_{2000}$. The choice of the initial temperature is arbitrary and does not affect our conclusions.

The $\Delta QFM$ of the gas is equal to the $\Delta QFM$ of the surroundings and is temperature independent (Fig. 1a) because of buffering by the surrounding melt and rocks. However, since the reference $f_{O_2}$ of the QFM buffer decreases with cooling (Fig. S-1a), the absolute $f_{O_2}$ value of gas and melt decreases with cooling even though their $\Delta QFM$ values are constant.

The corresponding $K_{oxy}$ value tells us whether atmospheric oxygenation occurs. $K_{oxy}$ depends on gas composition (Eq. 2), which depends on the equilibrium constant of each reaction in addition to $f_{O_2}$. Equilibrium constants also depend on temperature (Fig. S-1b). Consequently, cooling causes oxidative CO to CO$_2$ and reduction of SO$_2$ to H$_2$S (Fig. S-1c), even though the redox buffer relative to QFM is constant (see also Section S-2). The net effect of these opposing changes is a step-like decrease in $K_{oxy}$ with cooling, as shown in Figure 1b. In particular, for the case with $\Delta QFM = -0.5$, cooling decreases $K_{oxy}$ from $>1$ to $<1$ (dashed line, Fig. 1b), which would cause the atmosphere to flip from oxic to reducing.

Now consider a parcel of volcanic gases separated from a melt, e.g., in a volcanic vent. For this closed system gas composition, we calculate an equivalent $\Delta QFM$ using the mole ratio of gas species, such as H$_2$ / H$_2$O (Section S-4). Cooling changes the $\Delta QFM$ (Fig. 2a), unlike in the buffered system (Fig. 1a). In particular, for relatively oxidised cases (i.e. $\Delta QFM_{2000} = 0$ and -0.5), $\Delta QFM$ increases with cooling (solid and dashed lines in Fig. 2a), consistent with the results of Moussallam et al. (2019). However, for relatively reduced cases (i.e. $\Delta QFM_{2000} = -1$ and -1.5), the change in $\Delta QFM$ is moderate (dash-dot and dashed lines in Fig. 2a). The increase in $\Delta QFM$ with cooling in the closed system occurs because reduction of SO$_2$ to H$_2$S is accompanied by oxidation of H$_2$ to H$_2$O by redox conservation (Section S-3). Consequently, the ratio pH$_2$ / pH$_2$O declines, producing a relative increase in $f_{O_2}$ (see Sections S-3 and S-4).

$K_{oxy}$ also changes with cooling of the closed system gas (Fig. 2b). However, within the closed system, reduction of one gas is accompanied by oxidation of another gas. Consequently, temperature dependent reactions within a closed system gas mixture do not change the overall sink of O$_2$ in the gas mixture, contrary to the conclusions of Moussallam et al. (2019).
Geochemical Perspectives Letters  Letter

Figure 1  (a) Oxidation state ($\Delta$QFM) buffering volcanic gas composition, and (b) oxygenation parameter ($K_{\text{oxy}}$), as a function of temperature. Here, we assume a system where gases are redox buffered by the surrounding melt and rocks. $\Delta$QFM$_{2000}$ represents the oxidation state at 2000 K. By definition, $\Delta$QFM is independent of temperature and equal to $\Delta$QFM$_{2000}$ in (a) whereas cooling tends to decrease $K_{\text{oxy}}$ in (b).

For example, consider a mixture initially containing 1 mol of SO$_2$ and 3 mol of H$_2$, where all SO$_2$ is reduced, SO$_2$ + 3H$_2$ $\rightarrow$ H$_2$S + 2H$_2$O (see also Section S-3). The moles of O$_2$ that can be consumed by the gas mixture do not change. Reduction of 1 mol SO$_2$ accompanied by oxidation of 3 mol H$_2$ decreases the overall sink of O$_2$ by 0.25 mol O$_2$ but the production of 1 mol H$_2$S compensates.

A subtlety is that although the O$_2$ sink cannot change, $K_{\text{oxy}}$ shifts because $K_{\text{oxy}}$ also accounts for global O$_2$ sources from converted volcanic gases. In our ‘toy’ example, 1 mol SO$_2$ corresponds to a 1.25 mol O$_2$ source (see Section S-1.2), while 3 mol of H$_2$ and 1 mol of H$_2$S correspond to 1.5 mol O$_2$ and 0.25 mol O$_2$ sinks, respectively. Hence, the initial $K_{\text{oxy}}$ is 1.25 / 1.5 = 5 / 6, but after reactions, $K_{\text{oxy}}$ becomes 0 / 0.25 = 0. Here, the expected reduction of SO$_2$ to pyrite in the global environment (Eq. S-18) is the source of O$_2$ that changes $K_{\text{oxy}}$. The important point is that an initial $K_{\text{oxy}}$ of <1 remains less than unity.

Figure 2  (a) Oxidation state ($\Delta$QFM), and (b) oxygenation parameter ($K_{\text{oxy}}$), as a function of temperature. Here, we assume a closed system of gases, and the $\Delta$QFM of the gases at 2000 K is denoted as $\Delta$QFM$_{2000}$. Cooling changes $\Delta$QFM unlike the melt buffered case (Fig. 1a) and changes $K_{\text{oxy}}$. However, an initial $K_{\text{oxy}}$ that exceeds unity remains >1 with cooling, and an initial $K_{\text{oxy}}$ that is less than unity remains <1.

Consider again Figure 2. Temperature dependent gas reactions within a closed system do not change the overall sink of O$_2$ in the gas mixture. For relatively oxidised cases ($\Delta$QFM$_{2000}$ = 0 and -0.5), cooling increases $K_{\text{oxy}}$ (solid and dashed lines in Fig. 2b). However, for relatively reduced cases ($\Delta$QFM$_{2000}$ = -1 and -1.5), cooling decreases $K_{\text{oxy}}$ (dash-dot and dotted lines in Fig. 2b). In summary, an initial $K_{\text{oxy}}$ of >1 remains larger than unity with cooling, while an initial $K_{\text{oxy}}$ of <1 stays less than unity (Fig. 2b).

Therefore, reactions under a melt buffer system change the capacity of the gas to consume O$_2$ and affect atmospheric oxygenation while reactions within the closed system cannot. So, the oxygenation effect of volcanic degassing depends on interactions with the melt.

The Earth’s interior likely cooled with time (Bickle, 1982; Nisbet et al., 1993; Herzberg et al., 2010; Aulbach and Arndt, 2019). However, even if the upper mantle’s oxidation state was constant (e.g., $\Delta$QFM = -0.5), its cooling would decrease $K_{\text{oxy}}$. Therefore, the impact of volcanic degassing on the Earth’s atmosphere would be less with cooling.
and even reduce the atmosphere (Fig. 1b). Thus, processes that dominate over such a \( k_{\text{oxy}} \) decrease are required to explain the GOE.

The trigger for the GOE is debated (Kasting et al., 1993; Catling et al., 2001; Holland, 2002; Gaillard et al., 2011; Moussallem et al., 2019). Proposed secular oxidation of the upper mantle caused by hydrogen escape (Kasting et al., 1993) has been dismissed for about two decades because evidence appeared to show a constant oxidation state of the upper mantle (Canil, 1997; Delano, 2001; Canil, 2002; Lee et al., 2005). However, two recent studies suggest that the upper mantle \( \Delta QFM \) increased by \(-1.5 \log_{10} \) units since the early Archean (Aulbach and Stagno, 2016; Nicklas et al., 2019). Such oxidation would cause \( k_{\text{oxy}} \) to increase and so possibly triggered the GOE. Regardless, we have shown that if mantle \( \Delta QFM \) does not increase, mantle cooling actually makes the atmosphere more reducing, contrary to previous claims that mantle cooling would trigger the GOE (Moussallem et al., 2019).

## Conclusions

We examined the effects of Earth’s secular cooling and volcanic gases on oxygenation of the atmosphere using an oxygenation parameter, \( k_{\text{oxy}} \), that is less than unity for an anoxic atmosphere and exceeds unity for an oxic atmosphere (Catling and Claire, 2005; Kasting, 2013). Low temperature favours \( \text{H}_2\text{S} \) more than \( \text{SO}_2 \) because both equilibria constants and the absolute \( \text{O}_2 \) fugacity of the QFM buffer depend on temperature. Hence, for a buffered system, cooling increases the \( \text{pH}_2\text{S} / \text{pSO}_2 \) ratio in volcanic gases and decreases \( k_{\text{oxy}} \). For a closed system of gases in a vent that is not melt buffered, cooling also increases the \( \text{pH}_2\text{S} / \text{pSO}_2 \) ratio but this is counteracted by a decrease in \( \text{pH}_2\text{O} \). Hence, cooling of a closed system parcel of gas does not change the overall capacity of the volcanic gases to consume \( \text{O}_2 \).

We conclude that the long term cooling of the mantle induced changes in volcanic gas composition that reduced the atmosphere. However, other processes dominated because the atmosphere oxygenated with time. Possibilities include secular oxidation of the mantle (Aulbach and Stagno, 2016; Nicklas et al., 2019) and/or growth in the \( \text{O}_2 \) source flux due to higher rates of organic carbon burial (relative to oxidant burial) (Kris-sansen-Totton et al., 2015).

## Acknowledgements

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

Editor: Ambre Luguet

## Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article2009.

This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at http://www.geochemicalperspectivesletters.org/copyright-and-permissions.

## References


Mantle cooling causes more reducing volcanic gases and gradual reduction of the atmosphere

S. Kadoya, D.C. Catling, R.W. Nicklas, I.S. Puchtel, A.D. Anbar

Supplementary Information

The Supplementary Information includes:

- S-1 Model Description
- S-2 Temperature Dependence of the QFM Buffer and Equilibrium Constants
- S-3 Temperature Dependence of Gas Composition
- S-4 Temperature Dependence of Oxygen Fugacity
- S-5 Temperature Dependence of Oxygenation Parameter
- S-6 Another Effect of Temperature Decrease
- S-7 Sensitivity Test to the Organic Burial Fraction ($f_{\text{org}}$)
- S-8 Effect of Pressure
- Figures S-1 to S-9
- Supplementary Information References

S-1 Model Description

In this study, we calculate the volcanic gas composition, the source and sink of oxygen, and the oxygenation parameter as a function of temperature. Here, we describe each model in this order.

S-1.1 Volcanic gas composition

We assumed that a volcanic gas mixture is composed of H$_2$O, H$_2$, CO$_2$, CO, CH$_4$, SO$_2$, and H$_2$S, and is in thermodynamic equilibrium. The thermodynamic equilibrium is described as follows:

$$
\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{O}_2; \quad K_1 = \frac{p\text{H}_2}{p\text{H}_2\text{O}} \times f_{\text{H}_2}^{0.5}, \quad \text{Eq. S-1}
$$

$$
\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2; \quad K_2 = \frac{p\text{CO}}{p\text{CO}_2} \times f_{\text{CO}}^{0.5}, \quad \text{Eq. S-2}
$$
Here, we assume that all fugacities are equal to their partial pressure and introduce the oxygen fugacity \( (f_{ox}) \). We calculate the equilibrium constants of above equations using data of Chase and National Institute of Standards and Technology (U.S.) (1998).

In addition, we set the total pressure of volcanic gas at 5 bar (\( P_{\text{tot}} \)) which corresponds to release from subaerial volcanoes (Holland, 1984, p. 47): \( i.e. \)

\[
pH_{2}O + pH_{2} + pCO_{2} + pCO + pCH_{4} + pSO_{2} + pH_{S} = P_{\text{tot}} \tag{Eq. S-5}
\]

Additionally, we conserve in hydrogen, carbon, and sulfur fluxes:

\[
F_{H_{2}O} + F_{H_{2}} + 2F_{CH_{4}} + F_{H_{2}S} = F_{\text{hydrogen}} \tag{Eq. S-6}
\]

\[
F_{CO_{2}} + F_{CO} + F_{CH_{4}} = F_{\text{carbon}} \tag{Eq. S-7}
\]

\[
F_{SO_{2}} + F_{H_{2}S} = F_{\text{sulfur}} \tag{Eq. S-8}
\]

Here, for example, \( F_{H_{2}O} \) represents the flux of \( H_{2}O \). According to the modern global fluxes summarised in Catling and Kasting (2017), modern fluxes, \( F_{\text{hydrogen}}, F_{\text{carbon}}, \) and \( F_{\text{sulfur}} \), are 97 Tmol/yr, 9 Tmol/yr, and 2.2 Tmol/yr, respectively. In addition, we assumed that the relationship between partial pressure and flux of each gas species (\( e.g., H_{2}O \)) can be written as:

\[
pH_{2}O = \frac{F_{H_{2}O}}{F_{\text{tot}}} \times P_{\text{tot}} \tag{Eq. S-9}
\]

Here, \( F_{\text{tot}} \) is the total gas flux; \( i.e. \)

\[
F_{\text{tot}} = F_{H_{2}O} + F_{H_{2}} + F_{CO_{2}} + F_{CO} + F_{CH_{4}} + F_{SO_{2}} + F_{H_{2}S} \tag{Eq. S-10}
\]

In order to solve the above equations, we need one more equation. In this study, we apply two different assumptions. For one case, we assumed that gas is buffered by the surrounding melt; \( i.e. \) the oxygen fugacity of the gas phase is equal to that of the surrounding melt. This case is the “buffered system” case. In addition, we assumed that the oxygenation state of the melt (\( i.e. \) the difference in oxygen fugacity from the QFM buffer) is constant. For the consistency with another case, we represent the oxygenation state as \( \Delta QFM_{2000} \) that is the QFM at 2000 K. Hence, the oxygen fugacity is given as follows:

\[
\log_{10} f_{\text{ox}} = \log_{10} f_{\text{ox, qfm}} + \Delta QFM_{2000} \tag{Eq. S-11}
\]

The oxygen fugacity of QFM buffer \( (f_{\text{ox, qfm}}) \) is calculated by the equation given by Wones and Gilbert (1969).

For another case, we assumed that reactions between gases of a volcanic gas mixture occur in a closed system. This case is named as the “closed system” case. No constituent enters or leaves the closed system, so the mass of oxygen in terms of moles \( O_{2} \) is conserved as follows:

\[
\frac{1}{2} F_{H_{2}O} + F_{CO_{2}} + \frac{1}{2} F_{CO} + F_{SO_{2}} = F_{\text{oxygen}} \tag{Eq. S-12}
\]

Here, the constant of \( F_{\text{oxygen}} \) is a free parameter. To compare the closed and buffered systems, we set \( F_{\text{oxygen}} \) so that the oxygen fugacity of the closed system is equal to that of the buffered system at 2000 K. As explained above, the oxidation state (\( i.e. \) \( \Delta QFM \)) at 2000 K is denoted as \( \Delta QFM_{2000} \).

**S-1-2 Sources and sinks of oxygen**

It is necessary to define reference oxidation states for volatile species in order to analyze the global redox budget. We take \( H_{2}O, \)

\[
\text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_4 + 2\text{O}_2; \quad K_1 = \frac{p\text{CH}_4}{p\text{CO}_2} \left( \frac{f_{\text{ox}}}{p\text{H}_2\text{O}} \right)^2,
\]

\[
\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + \frac{3}{2} \text{O}_2; \quad K_1 = \frac{p\text{H}_2\text{S}}{p\text{SO}_2} \left( \frac{f_{\text{ox}}}{p\text{H}_2\text{O}} \right)^{1.5}.
\]
CO₂ and SO₂ to be redox neutral, which means that their entry or exit from the atmosphere does not change the redox budget. With this convention, H₂, CO, CH₄ and H₂S are sinks of atmospheric oxygen with net photochemical reactions as follows:

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}, \]
\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2, \]
\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}, \]
\[ \text{H}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}. \]

Hence, for example, 1 mol of H₂ degassing corresponds to 0.5 mol of O₂ consumption.

On the other hand, the burial of organic matter from oxygenic photosynthesis denoted as carbohydrate (CH₂O) is a source of oxygen:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2. \]

In addition, the reduction of SO₂ followed by the burial of pyrite is as a source of oxygen as follows:

\[ \text{SO}_2 + \frac{1}{2} \text{FeO} \rightarrow \frac{1}{2} \text{FeS}_2 + \frac{5}{4} \text{O}_2. \]

Also, the net reaction of H₂S can be written combining Eq. S-16 and S-18:

\[ \text{H}_2\text{S} + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{FeO} \rightarrow \frac{1}{2} \text{FeS}_2 + \text{H}_2\text{O}. \]

Hence, the net effect of the degassing of 1 mol H₂S is 0.25 mol O₂ sink.

Summarising above, the source \((F_{\text{source}})\) and sink \((F_{\text{sink}})\) of oxygen can be written as follows:

\[ F_{\text{source}} = F_{\text{org}} \times \left( \frac{F_{\text{CO}_2}}{F_{\text{CO}}^\text{source}} + \frac{F_{\text{CO}}}{F_{\text{CH}_4}} + \frac{F_{\text{CH}_4}}{F_{\text{H}_2\text{S}}^\text{source}} \right) + \frac{5}{4} F_{\text{SO}_2^\text{source}} \]
\[ F_{\text{sink}} = \frac{1}{2} F_{\text{H}_2} + \frac{1}{2} F_{\text{CO}} + 2 F_{\text{CH}_4} + \frac{1}{4} F_{\text{H}_2\text{S}}^\text{sink}. \]

For simplicity, we set the organic burial fraction \((f_{\text{org}})\) at 20 %, which is the canonical value, but test the sensitivity to this parameter in Section S-7.

**S-1.3 Oxygenation parameter**

According to Catling and Claire (2005), the oxygenation parameter \((K_{\text{oxy}})\) is defined as a ratio of the O₂ flux to the atmosphere, \(F_{\text{source}}\), to the flux of kinetically rapid sinks, \(F_{\text{sink}}\), where the latter can contain excess reductants above those needed to consume the O₂ flux, i.e.

\[ K_{\text{oxy}} = \frac{F_{\text{source}}}{F_{\text{sink}}} \quad \text{Eq. S-22} \]

In this paper, \(F_{\text{sink}}\) is considered to be dominated by oxidisable volcanic gases because we are explicitly considering the effect of volcanic gases on the oxygenation of the atmosphere. Consequently, we don’t consider processes that depend on redox state of the surface. The \(F_{\text{source}}\) term doesn’t include hydrogen escape to space because escape occurs under reducing conditions. The hydrogen escape rate depends on the concentration of H-bearing compounds, such as H₂ and CH₄ (e.g., Catling et al., 2001). Also, \(F_{\text{sink}}\) doesn’t include oxidative weathering of the crust because oxidative weathering only occurs under oxidising conditions and is negligible before the GOE (Sleep, 2004; Claire et al., 2006). Even in the marine realm, the ratio of Fe³⁺ / total Fe is far lower in Archean iron formations than in late Proterozoic ones (Klein et al., 1992), which indicates that less iron was oxidised in the Archean than in the Proterozoic.

When \(K_{\text{oxy}} < 1\), the flux of oxidisable volcanic gases exceeds the O₂ flux and the atmosphere is anoxic; excess hydrogen
accumulates until balanced by a continuous hydrogen escape flux. When \( K_{\text{oxy}} < 1 \), oxidative weathering is negligible because of the lack of atmospheric \( \text{O}_2 \). When \( K_{\text{oxy}} > 1 \), the \( \text{O}_2 \) source exceeds the flux of oxidisable volcanic gases and \( \text{O}_2 \) accumulates until balanced by oxidative weathering. In the oxic atmosphere, the hydrogen escape flux is far lower than that in the anoxic atmosphere. How various source and sink fluxes of \( \text{O}_2 \) evolve and how \( K_{\text{oxy}} \) changes with time has been demonstrated in the results of the oxygen model of Claire et al. (2006). We note that in the post-GOE world, the volcanic edifices themselves become \( \text{O}_2 \) sinks in addition to oxidisable volcanic gases (Sleep, 2005). The erosion of volcanoes, and the availability of ferrous iron in particular, would be an oxidative weathering sink for \( \text{O}_2 \). Indeed, it is possible that a feedback with oxidative weathering forced the levels of mid-Proterozoic \( \text{O}_2 \) to remain well below modern, although incomplete oxidative weathering of organic carbon has been proposed as the main contributor rather than ferrous iron (Daines et al., 2017).

\[ F_{\text{source}} \text{ and } F_{\text{sink}} \text{ are defined as Eq. S-20 and S-21, then Eq. S-22 can be written as follows:} \]

\[ K_{\text{oxy}} = \frac{4f_{\text{oxy}} \times (F_{\text{CO}_2} + F_{\text{CO}} + F_{\text{CH}_4}) + 5F_{\text{H}_2}}{2F_{\text{H}_2} + 2F_{\text{CO}_2} + 8F_{\text{CH}_4} + 5F_{\text{H}_2}} \]

\[ \text{Eq. S-23} \]

Since all fluxes can be written using their partial pressure, \( P_{\text{gas}} \) and \( F_{\text{gas}}, \text{ e.g., } F_{\text{H}_2}\text{O} = (p_{\text{H}_2}\text{O} / P_{\text{tot}}) \times F_{\text{tot}}, \text{ Eq. S-23 can be re-written as follows:} \]

\[ K_{\text{oxy}} = \frac{4f_{\text{oxy}} \times (p_{\text{CO}_2} + p_{\text{CO}} + p_{\text{CH}_4}) + 5p_{\text{SO}_2}}{2p_{\text{H}_2} + 2p_{\text{CO}_2} + 8p_{\text{CH}_4} + 5p_{\text{H}_2}}. \]

\[ \text{Eq. S-24} \]

**S-2 Temperature Dependence of QFM buffer and Equilibrium Constants**

If we assume that the mantle is buffered close to the Quartz-Fayalite-Magnetite (QFM) redox buffer, mantle cooling decreases the absolute oxygen fugacity (\( f_{\text{O}_2} \)), as shown in Figure S-1a; but the cooling also affects the equilibrium constants of the redox speciation reactions of C, S, and H gases (Fig. S-1b). These two effects must be convolved to determine the net effect of mantle cooling on the redox state of the atmosphere.

Under these conditions, a decrease in equilibrium constant favors reaction to the left. For example, cooling favors \( \text{H}_2\text{O} \) more than \( \text{H}_2 \) in the reaction \( \text{H}_2\text{O} \leftrightarrow \text{H}_2 + 0.5 \text{O}_2 \), whose equilibrium constant is shown by solid line in Figure S-1b. However, the actual ratio of partial pressures, (e.g., \( p_{\text{H}_2} / p_{\text{H}_2}\text{O} \)) can depend more on the temperature-dependence of oxygen fugacity, as we illustrate below.

Figure S-1c shows the ratio of the partial pressures of volcanic gases as a function of temperature, assuming that the \( f_{\text{O}_2} \) value follows the QFM buffer and accounting for temperature-dependent equilibria (i.e. Fig. S-1a). As shown in Figure S-1c, cooling decreases the ratio of \( p_{\text{CO}} / p_{\text{CO}_2} \) (dotted line). Cooling also decreases the ratio of \( p_{\text{H}_2} / p_{\text{H}_2}\text{O} \) (solid line), but the change is more moderate for \( p_{\text{H}_2} / p_{\text{H}_2}\text{O} \) than for \( p_{\text{CO}} / p_{\text{CO}_2} \) (Fig. S-1c). In contrast, cooling increases the ratios of \( p_{\text{H}_2}\text{S} / (p_{\text{SO}_2} p_{\text{H}_2}\text{O}) \) (dash-dot line in Fig. S-1c). The decrease in temperature also increases \( p_{\text{CH}_4} / (p_{\text{CO}_2} (p_{\text{H}_2}\text{O})^2) \) (dashed line in Fig. S-1c). However, as indicated by Figure S-1b and S-1c, the concentration of methane is essentially negligible. Hence, cooling causes the oxidation of \( \text{CO} \) to \( \text{CO}_2 \) and the reduction of \( \text{SO}_2 \) to \( \text{H}_2\text{S} \).
Figure S-1  (a) Oxygen fugacity of the Quartz-Fayalite-Magnetite (QFM) buffer, (b) equilibrium constant, and (c) ratio of the partial pressure of each volcanic gas, as a function of temperature. In (c), we assume that oxygen fugacity follows the QFM buffer (i.e. Fig. S-1a).
S-3 Temperature Dependence of Gas Composition

Long-term cooling of the planetary interior changes thermodynamic equilibrium among gases. Hence, the composition of volcanic gases should change with time even if other parameters remain constant. Figure S-2 shows the volcanic gas composition as a function of temperature. Here, the reference oxygen fugacity is set at ΔQFM\text{2000} = 0 at 2000 K. In other words, we assumed QFM buffer for the buffered system (Fig. S-2a).

For both cases of the buffered system and the closed system, cooling decreases CO and increases CO₂ (Fig. S-2). This is because cooling favors CO₂ more than CO, which is indicated by the decrease in equilibrium constant of a reaction involving carbon with the decrease in temperature (dashed line in Fig. S-3). Thus, the ratio of pCO to pCO₂ decreases (i.e. more oxidative) with cooling (Fig. S-2; see also the dotted line in Fig. S-1c).

On the other hand, cooling decreases SO₂ and increases H₂S for both cases of the buffered system and the closed system (Fig. S-2). This is because cooling favors H₂S more than SO₂, which is indicated by the increase in equilibrium constant of a reaction involving sulfur with cooling (solid line in Fig. S-3). Thus, the ratio of pH₂S to pSO₂ increases (i.e. more reductive) with cooling (Fig. S-2; see also the dash-dot line in Fig. S-1c).

The main difference between the buffered and closed systems lies in the temperature dependence of hydrogen and sulfur. So, we focus on the following reaction:

\[ \text{SO}_2 + 3\text{H}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}. \]  
Eq. S-25

As explained above, cooling increases the ratio of pH₂S to pSO₂ for both systems. However, while cooling changes the dominant species of sulfur from SO₂ to H₂S for the buffered system (Fig. S-2a), SO₂ and H₂S are comparable even at low temperature (~1000 K) for the closed system (Fig. S-2b). On the other hand, cooling decreases H₂ more for the closed system (Fig. S-2b) than for the buffered system (Fig. S-2a).

The difference in hydrogen and sulfur (Fig. S-2) results from the difference in the assumption between the buffered and closed systems. For the buffered system, the oxygen fugacity of the gas is equal to the oxygen fugacity of the melt by definition. Hence, the ratio of pH₂ to pH₂O in the buffered system is set by the following equation (see also Eq. S-1):

\[ \log_{10} \frac{\text{pH}_2}{\text{pH}_2\text{O}} = K_1 + \frac{1}{2}\log_{10} f_{\text{O}_2\text{melt}} \]  
Eq. S-26

In other words, the H₂ decrease due to reduction of SO₂ to H₂S (Eq. S-25) is buffered by reduction of H₂O to H₂ (i.e. H₂O → H₂ + 0.5 O₂) while oxygen is consumed by the melt. Therefore, the change in the ratio of pH₂O/pH₂ due to the temperature change is moderate for the buffered system (dashed line in Fig. S-4). In addition, cooling can result in the reduction of all SO₂ to H₂S (Fig. S-2a) because of the large change in the equilibrium constant (solid line in Fig. S-3).

On the other hand, for the closed system, the reduction of SO₂ to H₂S is accompanied by the oxidation of H₂O as for the buffered system, but the oxygen fugacity is not buffered. Hence, cooling results in the decrease of H₂ and SO₂, and an increase in H₂S (Fig. S-2b) following reaction Eq. S-25 and temperature dependence of the equilibrium constant (solid line in Fig. S-3). Since the amount of H₂ is limited and not buffered by the melt, the reduction of SO₂ to H₂S due to cooling is incomplete (Fig. S-2b). In addition, cooling increases the ratio of pH₂O to pH₂ much more for the closed system than for the buffered system (Fig. S-4).

![Figure S-2](image-url)  
Figure S-2  Gas composition of (a) the buffered system and (b) the closed system of volcanic gases, as a function of temperature. Here, the reference oxygen fugacity [ΔQFM\text{2000}] is set at 0. Solid lines represent neutral or oxidative gas, and dashed lines represent reductive gas. Cooling decreases H₂ and CO. On the other hand, the decrease in temperature decreases SO₂ and increases H₂S. In particular for the buffered system case (a), all of the sulfur is SO₂ under high temperature (~2000 K) and H₂S under low temperature (~1000 K). These changes due to temperature are caused by the temperature dependence of equilibrium constant (Fig. S-3).
Figure S-3 Equilibrium constant as a function of temperature. Cooling increases the ratio of $p_{H_2S} / p_{SO_2}$ (solid line). On the other hand, cooling decreases the ratio of $p_{CO}$ to $p_{CO_2}$ (dashed line).

Figure S-4 Ratio of $p_{H_2O}$ to $p_{H_2}$ as a function of temperature. Here, the reference $\Delta QFM$ ($\Delta QFM_{2000}$) is set at 0. The decrease in temperature makes the ratio of the closed system larger than the ratio of the buffered system, which corresponds to the increase in $\Delta QFM$ of the closed system (see also Eq. S-29).

**S-4 Temperature Dependence of Oxygen Fugacity**

S-4.1 Temperature dependence of the closed system of volcanic gas

As shown in Figure 1a and Moussallam et al. (2019), $\Delta QFM$ of the closed system tends to increase with cooling. This is due to the temperature dependence of the gas composition, especially the ratio of $p_{H_2O} / p_{H_2}$ as equilibrium constants change with temperature.

The oxygen fugacity of the closed system of gas can be calculated as follows:

$$\log_{10} f_{O_2\text{closed}} = 2 \log_{10} K_{eq} + \log_{10} \left( \frac{p_{H_2O}}{p_{H_2}} \right)_{\text{closed}}.$$

Eq. S-27

Similarly, the oxygen fugacity of the buffered system can be calculated as follows:

$$\log_{10} f_{O_2\text{buffered}} = \log_{10} f_{O_2\text{buffered}} + \Delta QFM_{\text{buffered}} = 2 \log_{10} K_{eq} + \log_{10} \left( \frac{p_{H_2O}}{p_{H_2}} \right)_{\text{buffered}}.$$

Eq. S-28
Therefore, $\Delta QFM$ of the closed system is calculated using Eq. S-27 and S-28 as follows:

$$\Delta QFM_{\text{closed}} = \Delta QFM_{\text{buffer}} + 2 \log_{10} \left( \frac{\text{pH}_2}{\text{pH}_2} \right)_{\text{buffer}} $$

Eq. S-29

As shown in Fig. S-4, cooling increases the ratio of $\text{pH}_2 / \text{pH}_2$ much more for the closed-system than for the buffered system. Hence, cooling results in higher $\Delta QFM$ for the closed system than for the buffered system.

S-4.2 Temperature dependence of oxygen fugacity for the case excluding sulfur

As explained, the increase in $\Delta QFM$ with cooling for the closed system results from the increase in the ratio of $\text{pH}_2 / \text{pH}_2$. Also, the increase in the ratio of $\text{pH}_2 / \text{pH}_2$ results from the consumption of $\text{H}_2$ via the reaction of Eq. S-25. Therefore, the change in $\Delta QFM$ is mainly caused by the reaction involving sulfur (Eq. S-25).

To highlight this point, Figure S-5 compares $\Delta QFM$ of two cases for the closed-system case. For one case, we include the sulfur-containing species (i.e. $\text{SO}_2$ and $\text{H}_2\text{S}$) in addition to other gas species (i.e. $\text{H}_2\text{O}$, $\text{H}_2$, $\text{CO}_2$, $\text{CO}$, and $\text{CH}_4$). For another case, we exclude the sulfur-containing species and consider only other gas species. For the sulfur-including case (solid line in Fig. S-5), cooling increases $\Delta QFM$ as explained above.

On the other hand, for the sulfur-excluding case (dashed line in Fig. S-5), cooling slightly decreases $\Delta QFM$. Such a decrease in $\Delta QFM$ (i.e. decrease in the ratio of $\text{pH}_2 / \text{pH}_2$) results from the reduction of $\text{H}_2\text{O}$ to $\text{H}_2$ via the reaction of $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$. Note that low temperature favors $\text{CO}_2$ and $\text{H}_2$, as indicated by the dashed line in Figure S-3.

![Figure S-5](image)

**Figure S-5** Oxygen fugacity represented as the difference from QFM buffer level in log$_{10}$ units (i.e. $\Delta QFM$). The closed system is assumed. Considering sulfur-containing species (i.e. $\text{SO}_2$ and $\text{H}_2\text{S}$), cooling decreases and then increases $\Delta QFM$ (solid line; see also Fig. 3a). On the other hand, if we exclude sulfur-containing species, $\Delta QFM$ monotonically decreases with cooling (dashed line).

S-5 Temperature Dependence of Oxygenation Parameter

Since the thermal evolution of planetary interior (i.e. cooling) changes the volcanic gas composition as explained above, the evolution also changes the capability of volcanic gases to act as a sink of $\text{O}_2$, i.e. affects the oxygenation parameter, $K_{\text{oxy}}$, as shown in Figures 1b and 2b.

As explained above, cooling decreases $\text{pCO}_2 / \text{pCO}$ and increases $\text{pH}_2 / \text{pSO}_2$ (Fig. S-2) following the temperature dependence of equilibrium constants (Fig. S-3). Hence, cooling decreases the oxygen source flux ($F_{\text{source}}$) owing to the decrease in the flux of $\text{SO}_2$ (Fig. S-6; see also Fig. S-2). However, the organic burial flux is assumed constant since the total carbon flux and the fraction buried as organic carbon are assumed constant. Therefore, $F_{\text{source}}$ reaches a constant value asymptotically at low temperature (Fig. S-6a and S-6b).

On the other hand, cooling decreases the oxygen sink flux ($F_{\text{sink}}$) owing to the decrease in the flux of $\text{CO}$, especially under high temperature (~1800 K) as shown in Figure S-6a and S-6b (see also Fig. S-2). However, further decrease in temperature (~1000 K) increases the flux of $\text{H}_2\text{S}$, hence the $F_{\text{sink}}$ also reaches asymptotically a constant value (Fig. S-6a and S-6b; see also Fig. S-2). Such non-linear change in $F_{\text{source}}$ and $F_{\text{sink}}$ also causes the non-linear change in $K_{\text{oxy}}$ ($= F_{\text{source}} / F_{\text{sink}}$) as shown in Figure 1b and 2b.
As shown, the non-linear change of $K_{\text{oxy}}$ results from the temperature dependence of the reaction involving sulfur (Eq. S-25). Hence, if we exclude sulfur-containing species (i.e. SO$_2$ and H$_2$S), the decrease in temperature even increases $K_{\text{oxy}}$ monotonically (dashed line in Fig. S-7). This is because the temperature decrease favors H$_2$O and CO$_2$ more than H$_2$ and CO, respectively (See Fig. S-1c).

Thus, the evolution of $K_{\text{oxy}}$ strongly depends on the redox speciation of sulfur gases.

![Figure S-6](image)

**Figure S-6**  Fluxes in the units of TmolO$_2$/yr as a function of temperature: (a) for the buffered system and (b) for the closed system. Here, the reference $\Delta$QFM ($\Delta$QFM$_{1200}$) is set at 0. Dotted lines represent the oxidative gas flux, and dashed lines represent the reductive gas flux. The ratio of the oxygen source ($F_{\text{source}}$) to kinetically rapid oxygen sink ($F_{\text{sink}}$) from reducing gases is the oxygenation parameter ($K_{\text{oxy}}$). Cooling decreases the flux of H$_2$ and CO (See also Fig. S-2). Hence, $F_{\text{sink}}$ asymptotically reaches a constant value for the closed system under low temperature (b). For the buffered system, $F_{\text{sink}}$ even increases under low temperature (a). Cooling also decreases the flux of SO$_2$. Hence, $F_{\text{source}}$ decreases with cooling (a and b). However, since the flux of organic burial is assumed constant here, $F_{\text{source}}$ asymptotically reaches a constant value with cooling (a and b). Such non-linear change in $F_{\text{source}}$ and $F_{\text{sink}}$ causes the step-like change in $K_{\text{oxy}}$ as shown in Figures 1b, 2b, and S-7. Note that $K_{\text{oxy}}$ is the ratio of $F_{\text{source}}$ to $F_{\text{sink}}$.

![Figure S-7](image)

**Figure S-7**  Oxygenation parameter ($K_{\text{oxy}}$) as a function of temperature. Here, the buffered system and QFM buffer is assumed. Including sulfur-containing species (i.e. SO$_2$ and H$_2$S), $K_{\text{oxy}}$ decreases with the decrease in temperature (solid line) as shown in Figure 2b. On the other hand, excluding sulfur-containing species, $K_{\text{oxy}}$ monotonically increases with the decrease in temperature (dashed line).

**S-6 Another Effect of Temperature Decrease**

One caveat of this study lies in the potential decrease in serpentinisation with secular cooling. As discussed in Kasting (2013), mantle cooling should have decreased the depth of partial melting. Hence, in the past, i.e. when mantle temperature was higher
than the present, the oceanic crust should have been thicker and more mafic than present. This trend for the oceanic crust would decrease the H₂ release via serpenitisation, i.e. the sink of O₂, with time. The modern H₂ flux via serpenitisation corresponds to 0.2 TmolO₂/yr. On the other hand, the sink of O₂ is in the order of ~1 TmolO₂/yr (e.g., Fig. S-6). Hence, if the H₂ flux via serpenitisation was larger by an order of magnitude or more and then decreased with time, the decrease in serpenitisation caused by temperature decrease might oxidise the Earth’s surface (Kasting, 2013). However, the extent of the change in serpenitisation remains uncertain.

### S-7 Sensitivity Test to the Organic Burial Fraction (f_{org})

The oxygenation parameter (K_{oxy}) depends on the organic burial fraction (f_{org}) as shown in Eq. S-24. Figure S-8 shows the effect of f_{org} on K_{oxy}. Here, we vary f_{org} from 10% to 30%, which roughly corresponds to the evolutionary range of f_{org} from 3.6 Ga to the present (Krissansen-Totton et al., 2015).

The larger f_{org} results in larger K_{oxy} as shown in Figure S-8 and also in the previous work (Krissansen-Totton et al., 2015). However, the difference in f_{org} does not change the overall effect of cooling on the K_{oxy}. Namely, for the buffered system, cooling decreases K_{oxy} (Fig. S-8a). On the other hand, for the closed system, an initial K_{oxy} that exceeds unity remains > 1, and an initial K_{oxy} that is less than unity remains < 1.

According to Krissansen-Totton et al. (2015), the secular increase of f_{org} indicated by geological evidence was not able to cause the Great Oxidation Event (GOE) if the other fluxes were constant and if a conventional carbon cycle model is assumed. Moreover, as explained, the secular cooling of the mantle causes the reduction of a volcanic gas mixture, and therefore, the reduction of atmosphere with time. Hence, we conclude some other mechanisms are required to explain the GOE.

**Figure S-8** Oxygenation parameter (K_{oxy}) as a function of temperature: (a) for the buffered system and (b) for the closed system. Orange lines represent the K_{oxy} of ΔQFM_{2000} = -0.5, and blue lines represent the K_{oxy} of ΔQFM_{2000} = -1. Solid lines represent the K_{oxy} of f_{org} = 30%, and dotted lines represent the K_{oxy} of f_{org} = 10%. Larger f_{org} results in larger K_{oxy} (a and b). However, difference in f_{org} does not change the conclusion. Namely, for the buffered system, cooling decreases K_{oxy} (a) as shown in Figure 1b. On the other hand, for the closed system, an initial K_{oxy} that exceeds unity remains > 1, and an initial K_{oxy} that is less than unity remains < 1 (b) as shown in Figure 2b.

### S-8 Effect of Pressure

As a nominal case, we set total pressure of volcanic gas, P_{volc}, at 5 bar, assuming an eruption of a subaerial volcano (Holland, 1984, p. 47). However, some have suggested that a higher degassing pressure, such as under submarine conditions, causes more reducing volcanic gas (Kump and Barley, 2007; Gaillard et al., 2011). Here, we investigate the effect of the total pressure of volcanic gas and show that we obtain a similar trend as in previous works.

Figure S-9 shows the mole ratios of reducing gases to their neutral or oxidative equivalent, e.g., H₂ / H₂O. A total pressure of 100 bar results in larger ratios of H₂S / SO₂ and CH₄ / CO₂ than at 5 bar while the ratios of H₂ / H₂O and CO / CO₂ are independent of the total pressure. How the redox state of volcanic gases depends on pressure is mainly affected by the equilibrium state of sulfur because the H₂S / SO₂ ratio is about a few, while CH₄ / CO₂ is much less than unity (Fig. S-9a). Hence, higher total pressure causes more reducing volcanic gas mainly because of the equilibrium state of sulfur, as suggested previously (Kump and Barley, 2007; Gaillard et al., 2011).
The more reducing volcanic gases caused by higher total pressure also produce a lower oxidation parameter, $K_{\text{ox}}$ (Fig. S-9b). Nonetheless, the temperature dependence of $K_{\text{ox}}$, i.e. the decrease in $K_{\text{ox}}$ with cooling, is similar for both pressure cases. Also, the difference caused by total pressure diminishes at temperatures less than ~1200 K (Fig. S-9b). At such low temperature, almost all of sulfur is H$_2$S for both cases of pressure. Note that at 1000 K, H$_2$S / SO$_2$ is $\approx 10^3$ for the case of 5 bar and $\approx 10^4$ for the case of 5 bar (Fig. S-9a). Similarly, the difference caused by total pressure diminishes at temperatures exceeding ~1900 K (Fig. S-9b) because almost all the sulfur becomes SO$_2$ (Fig. S-9b).

In summary, we obtained a pressure dependence of the redox state of the volcanic gas that is consistent with previous works (Kump and Barley, 2007; Gaillard et al., 2011). Nonetheless, the temperature dependence of $K_{\text{ox}}$ of the volcanic gas at 5 and 100 bar has similar behavior (Fig. S-9b). Hence, even considering a different pressure regime, the main conclusion of this study does not change.

![Figure S-9](image_url)

**Figure S-9** Effect of total pressure, $P_{\text{tot}}$, (a) volcanic gas mole ratios and (b) the oxygenation parameter ($K_{\text{ox}}$) as a function of temperature. Here, the buffered system and QFM buffer is assumed. Solid lines represent the case of $P_{\text{tot}}$ = 5 bar, and dashed lines represent the case of $P_{\text{tot}}$ = 100 bar. Higher $P_{\text{tot}}$ results in larger ratios of H$_2$S / SO$_2$ and CH$_4$ / CO$_2$, i.e., more reducing volcanic gas (a). Hence, higher $P_{\text{tot}}$ results in lower $K_{\text{ox}}$ (b).

### Supplementary Information References