

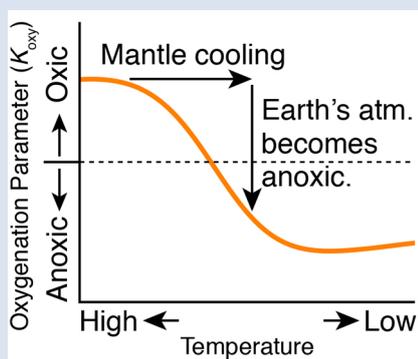
Mantle cooling causes more reducing volcanic gases and gradual reduction of the atmosphere

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Abstract



The early atmosphere contained negligible O_2 until the Great Oxidation Event (GOE) around 2.4 Ga, but evidence suggests that production of photosynthetic O_2 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.

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Introduction

The partial pressure of Archean atmospheric O_2 was $<0.2 \times 10^{-6}$ 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 O_2 in the marine photic zone (oxygen oases) as early as ~ 3 Ga (Planavsky *et al.*, 2014; Satkoski *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 O_2 before the GOE is also consistent with phylogenetic inferences that oxygenic photosynthesis evolved by the mid to late Archean (Schirmeister *et al.*, 2015; Magnabosco *et al.*, 2018); earlier, anoxygenic photosynthesis would have been present (Sleep, 2018).

The reason for the apparent time lag between the advent of oxygenic photosynthesis and the GOE is debated (Catling *et al.*, 2001; Holland, 2002; Kump and Barley, 2007; Holland, 2009; Gaillard *et al.*, 2011; Kasting, 2013; Ciborowski and Kerr, 2016; Lee *et al.*, 2016; Brounce *et al.*, 2017; Duncan and Dasgupta, 2017; Moussallam *et al.*, 2019). One possibility is that if ancient volcanic gases were sufficiently reducing, they

would have overwhelmed O_2 production fluxes, limiting O_2 to trace levels. If volcanic gases became gradually more oxidised, atmospheric O_2 would accumulate rapidly at a tipping point when the reducing volcanic gas flux fell below the O_2 production flux (Holland, 2002; Claire *et al.*, 2006).

Several hypotheses account for gradual oxidation of volcanic gases: the oxidation of the mantle as a consequence of hydrogen escape to space (Kasting *et al.*, 1993); a decrease in volcanic degassing pressure associated with an increase in subaerial volcanoes (Kump and Barley, 2007; Gaillard *et al.*, 2011) though this hypothesis is contradicted by Brounce *et al.* (2017); increasing CO_2 and/or SO_2 degassing due to increased subduction of carbonate and sulfate sediments (Holland, 2002, 2009) or plume magmatism (Ciborowski and Kerr, 2016); and/or an increase in recycling of organic material (Duncan and Dasgupta, 2017).

Recently, Moussallam *et al.* (2019) suggested that a decrease in volcanic emission temperature, which they defined as that of the fumarole where gases enter the air, caused volcanic gases to become more oxidised. They argued that 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.

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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 H₂O, H₂, CO₂, CO, CH₄, SO₂, and H₂S 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-1.1).

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 O₂ 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 oxygenation 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 O₂ (F_{source}) to the kinetically rapid sink flux of O₂ (F_{sink}):

$$K_{\text{oxy}} \equiv \frac{F_{\text{source}}}{F_{\text{sink}}} \quad \text{Eq. 1}$$

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 O₂.

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 Fe²⁺ to Fe³⁺, in F_{sink} (Catling and Claire, 2005; Kasting, 2013). When $K_{\text{oxy}} < 1$, O₂ sinks exceed O₂ sources and excess H₂ accumulates until balanced by escape to space. When $K_{\text{oxy}} > 1$, O₂ sources exceed O₂ sinks and O₂ 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 O₂ build up. We consider H₂O, CO₂, and SO₂ to be redox neutral, while H₂, CO, CH₄, and H₂S fluxes consume O₂ in atmospheric photochemistry. The burial of organic matter and pyrite (FeS₂) are O₂ source fluxes. Considering the stoichiometry of O₂ consumption and production, we rewrite Eq. 1 as follows (derived in Section S-1):

$$K_{\text{oxy}} \equiv \frac{4f_{\text{org}} \times (p\text{CO}_2 + p\text{CO} + p\text{CH}_4) + 5p\text{SO}_2}{2p\text{H}_2 + 2p\text{CO} + 8p\text{CH}_4 + p\text{H}_2\text{S}} \quad \text{Eq. 2}$$

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: $\Delta\text{QFM} = \log_{10} f_{\text{O}_2} - \log_{10} f_{\text{O}_2, \text{qfm}}$. 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 ΔQFM_{2000} . The choice of the initial temperature is arbitrary and does not affect our conclusions.

The ΔQFM of the gas is equal to the ΔQFM 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 ΔQFM 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 oxidation of CO to CO₂ and reduction of SO₂ to H₂S (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 $\Delta\text{QFM} = -0.5$, 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 ΔQFM using the mole ratio of gas species, such as H₂ / H₂O (Section S-4). Cooling changes the ΔQFM (Fig. 2a), unlike in the buffered system (Fig. 1a). In particular, for relatively oxidised cases (*i.e.* $\Delta\text{QFM}_{2000} = 0$ and -0.5), ΔQFM 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.* $\Delta\text{QFM}_{2000} = -1$ and -1.5), the change in ΔQFM is moderate (dash-dot and dashed lines in Fig. 2a). The increase in ΔQFM with cooling in the closed system occurs because reduction of SO₂ to H₂S is accompanied by oxidation of H₂ to H₂O by redox conservation (Section S-3). Consequently, the ratio $p\text{H}_2 / p\text{H}_2\text{O}$ 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 O₂ in the gas mixture, contrary to the conclusions of Moussallam *et al.* (2019).



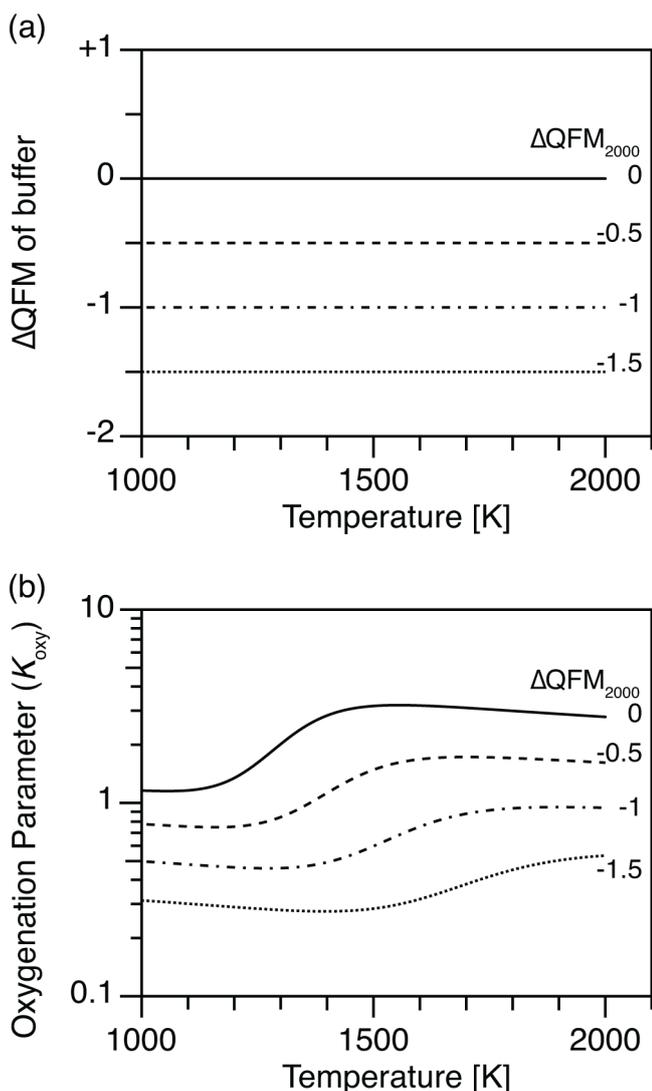


Figure 1 (a) Oxidation state (ΔQFM) buffering volcanic gas composition, and (b) oxygenation parameter (K_{oxy}), as a function of temperature. Here, we assume a system where gases are redox buffered by the surrounding melt and rocks. ΔQFM_{2000} represents the oxidation state at 2000 K. By definition, ΔQFM is independent of temperature and equal to ΔQFM_{2000} in (a) whereas cooling tends to decrease K_{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, $SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$ (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_2S compensates.

A subtlety is that although the O_2 sink cannot change, K_{oxy} shifts because K_{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_2S correspond to 1.5 mol O_2 and 0.25 mol O_2 sinks, respectively. Hence, the initial K_{oxy} is $1.25 / 1.5 = 5 / 6$, but after reactions, K_{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_{oxy} . The important point is that an initial K_{oxy} of <1 remains less than unity.

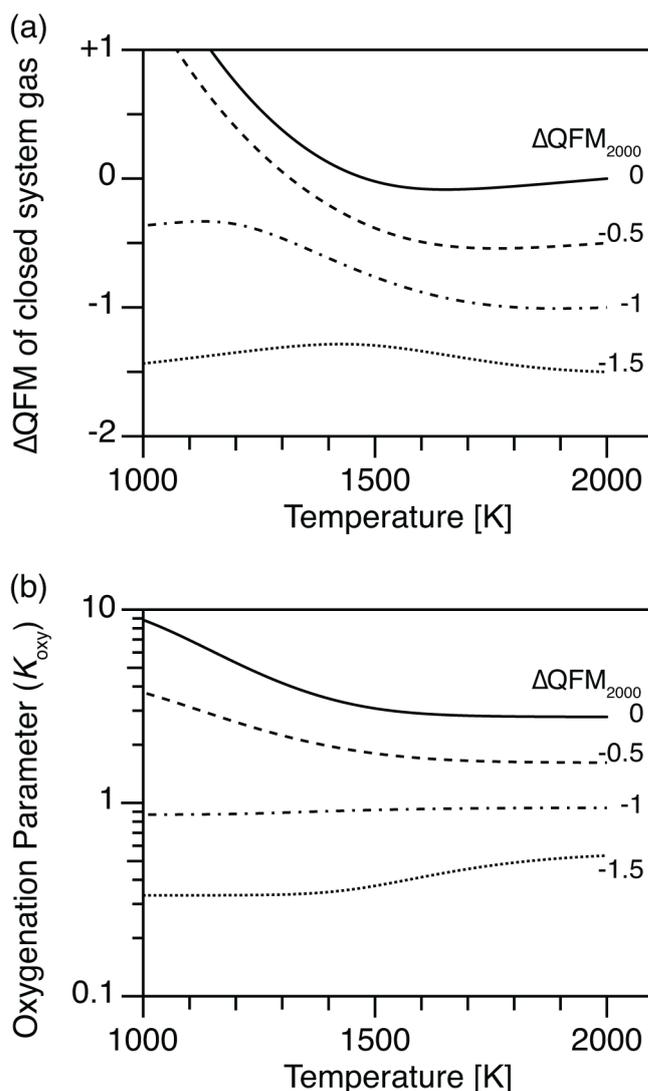


Figure 2 (a) Oxidation state (ΔQFM), and (b) oxygenation parameter (K_{oxy}), as a function of temperature. Here, we assume a closed system of gases, and the ΔQFM of the gases at 2000 K is denoted as ΔQFM_{2000} . Cooling changes ΔQFM unlike the melt buffered case (Fig. 1a) and changes K_{oxy} . However, an initial K_{oxy} that exceeds unity remains >1 with cooling, and an initial K_{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_{oxy} (solid and dashed lines in Fig. 2b). However, for relatively reduced cases ($\Delta QFM_{2000} = -1$ and -1.5), cooling decreases K_{oxy} (dash-dot and dotted lines in Fig. 2b). In summary, an initial K_{oxy} of >1 remains larger than unity with cooling, while an initial K_{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_{oxy}

and even reduce the atmosphere (Fig. 1b). Thus, processes that dominate over such a K_{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; Moussallam *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 ΔQFM increased by $\sim 1.5 \log_{10}$ units since the early Archean (Aulbach and Stagno, 2016; Nicklas *et al.*, 2019). Such oxidation would cause K_{oxy} to increase and so possibly triggered the GOE. Regardless, we have shown that if mantle ΔQFM does not increase, mantle cooling actually makes the atmosphere more reducing, contrary to previous claims that mantle cooling would trigger the GOE (Moussallam *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_{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 H_2S more than SO_2 because both equilibria constants and the absolute O_2 fugacity of the QFM buffer depend on temperature. Hence, for a buffered system, cooling increases the $p\text{H}_2\text{S} / p\text{SO}_2$ ratio in volcanic gases and decreases K_{oxy} . For a closed system of gases in a vent that is not melt buffered, cooling also increases the $p\text{H}_2\text{S} / p\text{SO}_2$ ratio but this is counteracted by a decrease in $p\text{H}_2 / p\text{H}_2\text{O}$. Hence, cooling of a closed system parcel of gas does not change the overall capacity of the volcanic gases to consume 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 O_2 source flux due to higher rates of organic carbon burial (relative to oxidant burial) (Kris-sansen-Totton *et al.*, 2015).

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Additional Information

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



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