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

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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; 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 O₂ before the GOE is also consistent with phylogenetic inferences that oxygenic photosynthesis evolved by the mid to late Archean (Schirrmeister 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 Dagaruma, 2017; Moussallam et al., 2019). One possibility is that if ancient volcanic gases were sufficiently reducing, they would have overwhelmed O₂ production fluxes, limiting O₂ to trace levels. If volcanic gases became gradually more oxidised, atmospheric O₂ would accumulate rapidly at a tipping point when the reducing volcanic gas flux fell below the O₂ 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 CO₂ and/or SO₂ 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 Dagaruma, 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.
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 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 O₂ (F_{source}) to the kinetically rapid sink flux of O₂ (F_{sink}).

\[
K_{ oxy} = \frac{F_{source}}{F_{sink}} \tag{1}
\]

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 Fe^{2+} to Fe^{3+}, in F_{sink} (Catling and Claire, 2005; Kasting, 2013). When K_{oxy} < 1, O₂ sinks exceed O₂ sources and excess H₂ accumulates until balanced by escape to space. When K_{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):

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

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_{o2} from that of the Quartz-Fayalite-Magnetite (QFM) buffer: ΔQFM = log_{10} f_{o2} – log_{10} f_{o2,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 ΔQ_{Fm}. 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_{o2} of the QFM buffer decreases with cooling (Fig. S-1a), the absolute f_{o2} 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_{o2}. 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 ΔQFM = -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. ΔQFM_{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. ΔQFM_{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 pH₂ / pH₂O declines, producing a relative increase in f_{o2} (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 (Koxy), 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 Koxy in (b).

Figure 2 (a) Oxidation state (ΔQFM), and (b) oxygenation parameter (Koxy), 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 Koxy. However, an initial Koxy that exceeds unity remains >1 with cooling, and an initial Koxy that is less than unity remains <1.

For example, consider a mixture initially containing 1 mol of SO₂ and 3 mol of H₂, where all SO₂ is reduced, SO₂ + 3H₂ → H₂S + 2H₂O (see also Section S-3). The moles of O₂ that can be consumed by the gas mixture do not change. Reduction of 1 mol SO₂ accompanied by oxidation of 3 mol H₂ decreases the overall sink of O₂ by 0.25 mol O₂ but the production of 1 mol H₂S compensates.

A subtlety is that although the O₂ sink cannot change, Koxy shifts because Koxy also accounts for global O₂ sources from converted volcanic gases. In our ‘toy’ example, 1 mol SO₂ corresponds to a 1.25 mol O₂ source (see Section S-1.2), while 3 mol of H₂ and 1 mol of H₂S correspond to 1.5 mol O₂ and 0.25 mol O₂ sinks, respectively. Hence, the initial Koxy is 1.25 / 1.5 = 5 / 6, but after reactions, Koxy becomes 0 / 0.25 = 0. Here, the expected reduction of SO₂ to pyrite in the global environment (Eq. S-18) is the source of O₂ that changes Koxy. The important point is that an initial Koxy of <1 remains less than unity.

Consider again Figure 2. Temperature dependent gas reactions within a closed system do not change the overall sink of O₂ in the gas mixture. For relatively oxidised cases (ΔQFM_{2000} = 0 and -0.5), cooling increases Koxy (solid and dashed lines in Fig. 2b). However, for relatively reduced cases (ΔQFM_{2000} = -1 and -1.5), cooling decreases Koxy (dash-dot and dotted lines in Fig. 2b). In summary, an initial Koxy of >1 remains larger than unity with cooling, while an initial Koxy of <1 stays less than unity (Fig. 2b).

Therefore, reactions under a melt buffer system change the capacity of the gas to consume O₂ 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., ΔQFM = -0.5), its cooling would decrease Koxy.
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; 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 $\Delta$QFM increased by $\sim 1.5 \log_{10}$ units since the early Archean (Aulbach and Stagno, 2016; Nicklas et al., 2019). Such oxidation would cause $K_{\text{oxy}}$ 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 (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, $K_{\text{oxy}}$, 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 $O_2$ 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 $K_{\text{oxy}}$. For a closed system of gases in a vent that is not well buffered, cooling also increases the $p\text{H}_2\text{S}/p\text{SO}_2$ ratio but this is counteracted by a decrease in $p\text{H}_2\text{O}/p\text{H}_2O$. 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

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### References


