BRIEF COMMUNICATIONS ARISING

# Atmospheric oxygenation and volcanism

Around 2.5 billion years ago, Earth's atmosphere turned from anoxic to oxic in what is known as the Great Oxidation Event. Gaillard *et al.*[1] suggest that this oxygenation was caused by the emergence of the continents and a shift in volcanism from predominantly submarine to primarily subaerial conditions. Because the ratio of volcanic SO_2 to H_2S in their model increases with this shift, they argue that the atmosphere became more oxidized. But their model also predicts that outgassing of CO_2 decreases at the lower pressure of continental volcanism, and that this should act against atmospheric oxygenation because CO_2 is the substrate for the production of oxygen from photosynthesis. Hence, their mechanism may not trigger a rise in atmospheric O_2.

There are three problems to consider. First, Gaillard *et al.*[1] argue that the release of SO_2 comes at the expense of H_2S, according to:

$$H_2S + 2H_2O \rightarrow SO_2 + 3H_2 \qquad (1)$$
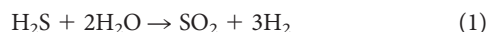
But the extra H_2 released by this reaction exactly compensates for the switch from H_2S to SO_2. The mixture of SO_2 and H_2 has the same redox potential as H_2S and water[2]. Fortunately, what happens in their model is different. The H_2S to SO_2 ratio is buffered by magma, which has a fixed oxidation state, described in terms of a fixed oxygen fugacity. The relevant reaction is:

$$H_2S + {}^\prime O_2{}^\prime \rightarrow SO_2 + H_2 \qquad (2)$$
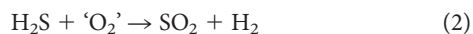
where 'O_2' represents oxidants (mostly ferric iron) in the melt. Reaction (2) produces SO_2 and H_2 in equimolar proportions, in agreement with results shown in figure 2 of ref. 1. When SO_2 is reduced to pyrite, FeS_2, it consumes hydrogen as follows:

$$4\,SO_2 + 10\,H_2 + 2\,FeO \rightarrow 2\,FeS_2 + 10\,H_2O \qquad (3)$$
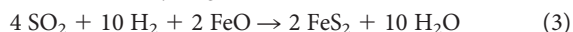
Because reaction (3) consumes more hydrogen per mole of SO_2 than is produced by reaction (2), the net effect is to oxidize the atmosphere. Thus, this part of their proposed atmospheric oxidation mechanism appears to work, but not for the reasons they stated.

The second issue is that sulphur-containing gas fluxes are not the only ones that control O_2. CO_2 is crucial because some CO_2 is reduced to organic carbon, CH_2O, which is then buried. A mole of photosynthetic O_2 is released for every mole of buried CH_2O. However, O_2 can be lost in atmospheric reaction with H_2, so the net effect is:

$$CO_2 + 2H_2 \rightarrow CH_2O + H_2O \qquad (4)$$
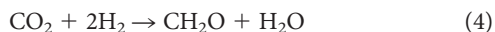
The carbon isotope record suggests that ~20% of outgassed CO_2 is reduced and buried in this manner[3,4]. Holland[4] quantified the effect of volcanic gases on the hydrogen budget by defining a parameter denoted f. Gases for which $f > 1$ can reduce 20% of the CO_2 to organic matter and all of the SO_2 to pyrite, leaving excess hydrogen to support an anoxic atmosphere; gases with $f < 1$ contain too little hydrogen to do this. Atmospheric O_2 'wins' over hydrogen when f drops below unity. This analysis neglects other sources of hydrogen that might have been important (for example, serpentinization of ultramafic rocks on the continents and seafloor, or precipitation of ferric iron in banded iron formations), but it is useful for analysing the volcanic gases of ref. 1.

In the model of Gaillard *et al.*[1], the proportion of CO_2 in released volcanic gases decreases by a factor of ~3 when volcanoes switch

from submarine to subaerial conditions because the pressure decreases from 100 bar to 1 bar. This change should tend to oppose atmospheric oxygenation, as less organic matter is buried (given a constant burial fraction), and thus less H_2 is consumed. To estimate the net effect on atmospheric redox balance, we calculated f values for cases listed in the Supplementary Information of ref. 1. Gaillard *et al.*[1] include S_2 as a species, which requires us to modify Holland's f parameter, as follows:

$$f = \frac{m(H_2) + 0.6m(CO) - 0.4m(CO_2) + 3m(H_2S) + 4m(S_2)}{3.5[m(SO_2) + m(H_2S) + 2m(S_2)]} + \frac{1}{3.5}$$

Here, $m(i)$ is the mole fraction of species i in the released gases. As shown in Table 1, f is less than unity in the cases shown in Supplementary Tables 1 and 2 of Gaillard *et al.*[1], and so would not allow a reduced atmosphere before 2.4 Gyr ago. This means that no rise of O_2 is possible because the initial atmosphere is already oxidized. This could be because other hydrogen sources are neglected, as mentioned above, or because model parameters—for example, the outgassing temperature—are incorrect. In any case, the model, as presented in ref. 1, appears incapable of triggering a rise in atmospheric oxygen if Holland's method of analysis is correct.

Last, Gaillard *et al.*[1] assume that gases released from a submarine magma at 1,300 °C do not re-equilibrate with the surrounding basalts at lower temperatures as they emerge from depth; this assumption is at odds with previous work[5,6]. Such re-equilibration might have allowed Archaean volcanic gases to be more reduced; hence, a switch to subaerial volcanism around 2.5 Gyr ago might then result in atmospheric oxidation. But this would be a different oxidation mechanism from the one described in ref. 1. There is also a broader caveat. The reduced oxidation state of volcanic gases comes at the expense of oxidizing the source rocks; thus, erosion and subsequent reduction of the source rocks may cancel out surficial redox change in the long term.

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Table 1 | f values for different cases from ref. 1

Case	Pressure (bar)	
	1	100
Supplementary Table 1	0.60	0.62
Supplementary Table 2	0.73	0.88

Gaillard *et al.* reply

Kasting *et al.*[1] question the model of ref. 2, in which we suggest that the oxygenation of the atmosphere, around 2.45 Gyr ago, was promoted by the emergence of subaerial volcanism, producing volcanic gases with much more elevated SO_2/H_2S ratios than submarine volcanism.

Kasting *et al.*[1] claim that the enhanced SO_2/H_2S ratio in subaerial volcanic gases was accompanied by enhanced H_2 production, which may limit the oxidative capacity of emitted gases. This is only partly correct, because enhanced SO_2 also derives from the reaction[2,3]:

$$S^{2-} \text{(melt)} + 3Fe_2O_3 \text{(melt)} \rightarrow SO_2 + 6FeO \text{(melt)} + O^{2-} \text{(melt)}$$

which implies that subaerial degassing extracts more oxygen from the melt than submarine degassing. The oxygen reservoir of the melt, a fundamental aspect of our model[3] that has so far not been taken into account, implies that more oxygen was therefore degassed as subaerial volcanism became abundant at about 2.7 Gyr ago.

Also, Kasting *et al.*[1] argue that the amount of outgassed CO_2 decreases by a factor of 3 as venting pressure decreases from 100 bar to 1 bar, which should limit production of organic carbon (CH_2O) and thereby limit the associated consumption[4] of atmospheric H_2. However, although the molar fraction of CO_2 in the gas decreases, the flux of CO_2 into the atmosphere is unchanged between 100 and 1 bar venting pressures[2], owing to the exceedingly low solubility of CO_2 in silicate melt in this pressure range (unlike the case for sulphur).

The *f* parameter of Holland[4] is used by Kasting *et al.*[1] to evaluate how much H_2 is consumed to reduce volcanic CO_2 into organic matter and SO_2 to pyrite. According to Kasting *et al.*[1], as pressure decreases, the *f* values of our calculated gas compositions indeed decrease (that is, their reducing power decreases, as required), but do not reach low enough values to drive the atmosphere to oxidizing conditions. However, the calculation of *f* is based on the way H_2S is produced or consumed in volcanic gases: Holland[4] first considered decomposition of H_2S during cooling, which is equivalent to production of H_2 (hence the $+3m(H_2S)$ term in the *f* equation). The more recent analysis[5] by Holland considers instead that H_2S is the product of reaction between SO_2 and H_2 during cooling, a H_2-consuming reaction ($-3m(H_2S)$ in the *f* equation).

Conventionally, about 20% of volcanic CO_2 is consumed to produce organic matter[4]. Any variation of the amount severely affects the results of calculations made using the *f* equation, highlighting the difficulties in using it as to determine the oxidative capacity of volcanic gases. Holland's more recent analysis[5] of the causes of oxygenation suggests that oxidation was due to an increase in CO_2 and SO_2 volcanic fluxes, which is what our model predicts as volcanism changed from quasi-exclusively-submarine to partially subaerial. At this point, we stress that our model[2] not only describes an increase in the oxidative capacity of volcanic gas but also a chain reaction likely to facilitate atmospheric oxygenation. Of prime importance are the sulphate reduction processes, which should have been exacerbated by elevated volcanic SO_2 emissions. Biological sulphate reduction transforms sedimentary organic carbon into CO_2, which results in oxygen production[6]. In parallel, hydrothermal sulphate reduction, which decreases the reducing potential of

hydrothermal fluids and fixes hydrothermal ferrous iron as pyrite, also contributed to atmospheric oxygenation[4]. All these reaction paths are not included in Holland's *f* factor, whereas they were certainly involved in the Great Oxidation Event.

We agree with the final recommendation of Kasting *et al.*[1] that both volcanic gases and hydrothermal fluids should be considered in models of the Great Oxidation Event. However, whereas we accept that thick Archaean oceanic crust was on average more mafic than younger crust, the uppermost layers—those most susceptible to hydrothermal alteration—would have consisted of olivine-poor basalt. In both modern oceanic plateaus and presumably in Archaean oceanic crust, parental picritic magma differentiates, leaving olivine cumulates at the Moho and erupting relatively evolved lava[7]. Basalt with little to no olivine is the dominant component of the upper parts of both modern oceanic plateaus and Archaean greenstone belts[7,8]. These rocks are not susceptible to serpentinization; therefore little H_2 would have been produced during their hydrothermal alteration, and its impact on the atmospheric oxygenation should not have been as important as claimed by Kasting *et al.*[1].

Last, Kasting *et al.*[1] expressed concern about low-temperature re-equilibration processes between volcanic gases and basalts that were not considered by us[2]. We answer that this comment seems to re-introduce confusion between volcanic gas inputs (from mantle to exosphere) and hydrothermal recycling (seawater that reacts with basalts) that may arise from a misinterpretation of ref. 9. Volcanic degassing and hydrothermal emissions are two fundamentally distinct processes, which not only differ in temperature, but chiefly differ in their source (igneous input versus surficial recyling).

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