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Fabrice Gaillard, Bruno Scaillet, Nicholas Arndt

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Gaillard *et al.* reply

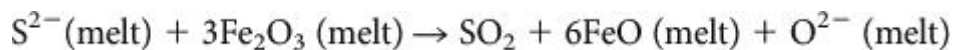
Fabrice Gaillard,¹ Bruno Scaillet¹ & Nicholas T. Arndt²

REPLYING TO J. F. Kasting, D. C. Catling & K. Zahnle *Nature* 487,

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 SO₂/H₂S ratios than submarine volcanism.

Subject terms: Geology ; Geophysics ; Earth sciences

Kasting *et al.*¹ claim that the enhanced SO₂/H₂S ratio in subaerial volcanic gases was accompanied by enhanced H₂ production, which may limit the oxidative capacity of emitted gases. This is only partly correct, because enhanced SO₂ also derives from the reaction^{2,3}:



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 model³ 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 CO₂ decreases by a factor of 3 as venting pressure decreases from 100 bar to 1 bar, which should limit production of organic carbon (CH₂O) and thereby limit the associated consumption⁴ of atmospheric H₂. However, although the molar fraction of CO₂ in the gas decreases, the flux of CO₂ into the atmosphere is unchanged between 100 and 1 bar venting pressures², owing to the exceedingly low solubility of CO₂ in silicate melt in this pressure range (unlike the case for sulphur).

The *f* parameter of Holland⁴ is used by Kasting *et al.*¹ to evaluate how much H₂ is consumed to reduce volcanic CO₂ into organic matter and SO₂ 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 H₂S is produced or consumed in volcanic gases: Holland⁴ first considered decomposition of H₂S during cooling, which is equivalent to production of H₂ (hence the +3*m*(H₂S) term in the *f*

equation). The more recent analysis⁵ by Holland considers instead that H₂S is the product of reaction between SO₂ and H₂ during cooling, a H₂-consuming reaction ($-3m(\text{H}_2\text{S})$ in the f equation).

Conventionally, about 20% of volcanic CO₂ is consumed to produce organic matter⁴. 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 analysis⁵ of the causes of oxygenation suggests that oxidation was due to an increase in CO₂ and SO₂ 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 model² 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 SO₂ emissions. Biological sulphate reduction transforms sedimentary organic carbon into CO₂, which results in oxygen production⁶. In parallel, hydrothermal sulphate reduction, which decreases the reducing potential of hydrothermal fluids and fixes hydrothermal ferrous iron as pyrite, also contributed to atmospheric oxygenation⁴. 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 lava⁷. 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 H₂ 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 us². 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 recycling).

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