

Probing Mantle Redox with Planetary Atmospheres. P. Liggins¹, O. Shorttle^{1,2} and P. B. Rimmer^{1,3,4},
¹University of Cambridge, Department of Earth Sciences (plk128@cam.ac.uk), ²University of Cambridge, Institute of Astronomy, ³University of Cambridge, Cavendish Astrophysics, ⁴MRC Laboratory of Molecular Biology, Cambridge.

Introduction: The geology of Earth and super-Earth sized planets will, in many cases, only be observable through their atmospheres. Therefore, to investigate the surface and interior conditions on these planets we must investigate their atmospheric fingerprints; here we focus on volcanism as a key window into planetary geophysics. On Earth, volcanic gases are indicative of the redox state and volatile content of the parent magmas and mantle they originated from, but it remains unclear whether, after allowing these gases to cool, re-equilibrate and mix into an atmosphere, the same constraints will be obtainable for exoplanets.

Here, we model how secondary atmospheres will grow and evolve over time under the influence of volcanic activity. We use these models to determine what information about the planet's geochemical state can be determined after cooling and mixing of volcanic gases into an existing atmosphere.

Previous work has looked at the effect of increasing atmospheric pressure on the composition of a volcanic atmosphere [1], on the composition of very early atmospheres [2], on those in equilibrium with magma oceans [3, 4, 5], and of stagnant-lid planets [6, 7] using models of mantle convection. However in most cases, these models focus only on H₂O and CO₂, and/or do not account for subsequent atmospheric chemistry occurring once the gases have been emitted [8]. Our modelling differs from previous work, by using a full COHSN degassing model, allowing the *f*O₂ of the equilibrated gas and melt to evolve throughout eruptions, and re-calculating the gas chemistry upon eruption and cooling to ambient environmental conditions.

Methods: We combine 3 model components to simulate the growth of a secondary atmosphere: 1) a mantle component, which undergoes melting to calculate the volatile content of a melt at each timestep, based on the total volatile budget of the mantle; 2) a volcanic component, comprising a thermodynamic magma degassing model (EVo) which calculates the eruption path to the surface of a COHSN volatile system; and 3) an atmosphere component, comprising of the FastChem [9] equilibrium chemistry model and a calculation of the bulk atmospheric chemistry. The movement of volatiles from mantle to atmosphere is demonstrated in Fig 1.

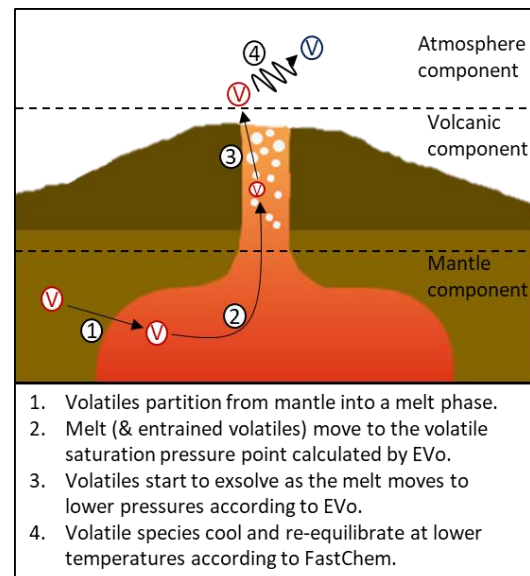


Figure 1: The path volatiles follow through our model.

At each timestep, the degassing model is instantiated by melting a fraction of the mantle, creating a melt with an appropriate volatile content. This melt packet is then degassed through the volcanic component from the point of volatile saturation, up to the dynamically updated surface pressure. The gas phase is then fed into FastChem, where the gas cools to surface temperature and re-equilibrates, and is then mixed into the existing atmosphere, updating the bulk composition and surface pressure. The model thereby tracks how a secondary atmosphere is formed (or an existing atmosphere is modified) over time under the influence of volcanism. Crucially, the inclusion of FastChem accounts for the change in gas phase speciation as the volcanic emissions cool.

Initial results:

In Fig 2, we show our initial results comparing two sets of volcanically sourced secondary atmospheres; one which has remained at eruption temperature (1473 K) and has not been passed through the FastChem network, and one which upon eruption, has cooled the volcanic gas to 400 K and re-equilibrated before being mixed into the existing atmosphere from previous steps. The 'hot' atmosphere which has not undergone any post-eruption chemistry shows the standard trends, i.e., gases produced by a reduced (low *f*O₂) mantle have higher fractions of molecules such as H₂, CO and CH₄, which decrease in prevalence as the mantle becomes

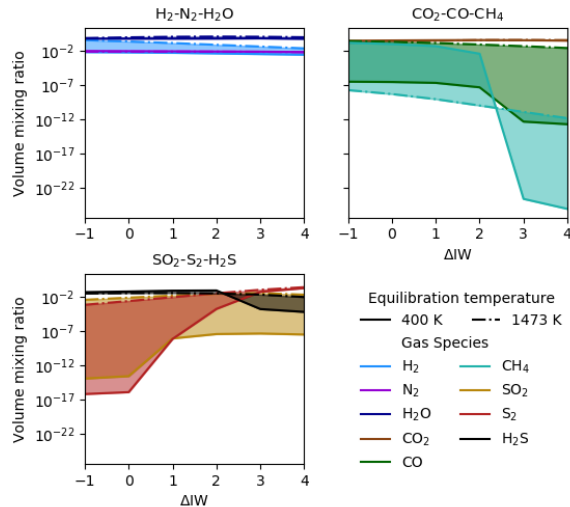


Figure 2: Comparing the composition of a cooled (to 400 K) and re-equilibrated atmosphere to one left at the eruptive temperature (1473 K) across a range of mantle fO_2 values, compared to the Iron-Wüstite (IW) rock buffer. The solid line for each species reflects the atmospheric mixing ratio when cooled and re-equilibrated at 400 K after each timestep, vs not (dash-dot line). The atmospheres are those formed after 10 Ma of degassing, with an initial atmosphere of 0.01 bar H_2 and a mantle volatile content of 160 ppm H_2O , 140 ppm CO_2 , 150 ppm S and 2 ppm N.

more oxidized (mantle fO_2 increases). However, allowing the gases to cool and re-equilibrate in the atmosphere significantly perturbs some of these mantle fO_2 -based trends, either by 1) decreasing the effect of mantle fO_2 on the species abundance, flattening the rate of change with changing mantle redox (e.g. H_2), or 2) amplifying the abundance trend with mantle fO_2 (particularly for CH_4 , S_2 and H_2S).

Initial results indicate that the formation of H_2 -rich volcanic atmospheres may have a much greater temperature dependence than previously thought [10]: producing cool H_2 -rich atmospheres will require a lower mantle fO_2 compared to a planet with a hotter surface temperature. Equally observations of abundant methane, which is often cited as a possible biosignature [e.g., 11], should be treated with caution on cool planets as this may be an artifact caused by cooling and re-equilibration of reduced volcanic gases rather than biology.

Our initial results indicate that on temperate, volcanically active exoplanets, atmospheric temperature may have an equal impact on atmospheric composition as the planet's mantle redox, adding a further level of complication to efforts attempting to deduce the geology of these planets.

Future Work:

We will expand our initial study by running similar comparisons over a variety of starting atmospheric

conditions (temperature, pressure and atmospheric composition) and mantle volatile contents, and with a range in the rate of volcanic eruption, to develop a greater understanding of how secondary atmospheres develop over time under a wide range of initial conditions. Results where the input gases are allowed to cool and re-equilibrate will be compared to cases where the volcanic input remains at eruptive temperature, as in Fig 2, to understand how this cooling may affect the results of previous models. Estimations of how the temperature change affects the atmospheric redox state will also be undertaken.

We will also expand our model to include atmospheric escape of hydrogen. Allowing hydrogen escape to occur will affect the oxidation state and size of the atmosphere, pushing the system towards a more oxidizing regime, and impacting how the pressure-composition evolution of an atmosphere proceeds through time.

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