The Fingerprints of Volcanism: Modelling Secondary Atmospheres on Rocky Planets P. Liggins[1], S. Jordan[2], P. B. Rimmer[1,3,4] and O. Shorttle[1,2], [1]University of Cambridge, Department of Earth Sciences (pkl28@cam.ac.uk), [2]University of Cambridge, Institute of Astronomy, [3]University of Cambridge, Cavandish Astrophysics, [4]MRC Laboratory of Molecular Biology, Cambridge.

Introduction: To understand the geology of rocky planets, we must learn to use observations of their atmospheres to infer the properties of their interiors. Here, we focus on volcanism as a key window into planetary geochemistry. On Earth, volcanic gases are indicative of the redox state (fO_2) and volatile content of the parent magmas and mantle they originated from. However, a key question remains as to what extent low pressure, low(er) temperature atmospheres preserve information about the higher temperature and pressure environment volcanic gases are initially supplied from.

A commonly used approximation for modelling exoplanet atmospheres is to assume they will exist in thermochemical equilibrium [1,2,3]. However the extent to which high temperature volcanic gases erupted into a cooler background atmosphere will relax and re-equilibrate to a new, low temperature equilibrium is unclear. If the high-temperature volcanic gases cannot re-equilibrate, they will instead 'quench', where the gas-phase speciation is locked in at the temperature at which chemical reactions become slow enough that the speciation is effectively constant even over geological time periods.

Here, we model how volcanic secondary atmospheres will grow and evolve over time. 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, while identifying the temperature limit beyond which thermochemical equilibrium within the atmosphere cannot be assumed.

Previous work has looked at the effect of increasing atmospheric pressure on the composition of a volcanic atmosphere [4], on the composition of very early atmospheres [5], on those in equilibrium with magma oceans [6,7,8,9], and of stagnant-lid planets [10,11] using models of mantle convection. Our modelling builds on previous work by expanding the number of species being considered to include sulfur and nitrogen species, and by re-calculating the gas chemistry of the atmosphere upon 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) [12] which calculates the eruption path to the surface of a COHSN volatile system; and 3) an atmosphere component, comprising of the FastChem [13,14] equilibrium chemistry model and a calculation of the bulk atmospheric chemistry. An overview of the model components and how they relate to each other is shown in Fig 1.

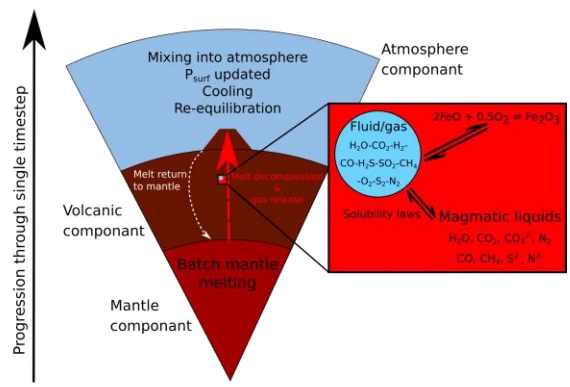

Figure 1: An overview of the EVolve model used.

To test whether a volcanic atmosphere will maintain thermochemical equilibrium at a given temperature, a chemical-kinetics code for planetary atmospheres was used, consisting of a solver, ARGO, and a chemical network, STAND2020 [15]. A 0D, surface pressure atmosphere after 1 Gyr of volcanic activity and at 1473K was assumed to be instantaneously cooled/heated, and ARGO was used to calculate the speciation of the gas as a function of time as it moved towards equilibrium. Where ARGO could not reach equilibrium, and a time to equilibrium could therefore not be established, instantaneous chemical timescales were calculated.

Results: In Fig. 2 we show how the composition of a 1D volcanic atmosphere will vary according to the mantle fO_2 of the planet, after 1 Gyr of volcanic activity, at surface pressure and 800 K. We find that at Venus-like surface temperatures, volcanic atmospheres can be split into classes according to their chemical speciation. These classes are directly linked to the fO_2 of the planet's mantle, and can therefore be used as geological indicators. These classes are identified using sets of (often minor) species:

Class O: Representing an oxidized mantle, and containing SO_2 and sulfur allotropes

Class I: Intermediate mantle fO_2 between IW-1.5 and IW+2.5, containing CO_2, CO and CH_4 all above 0.1%

Class R: Reduced mantles, containing H_2, NH_3 and CH_4.

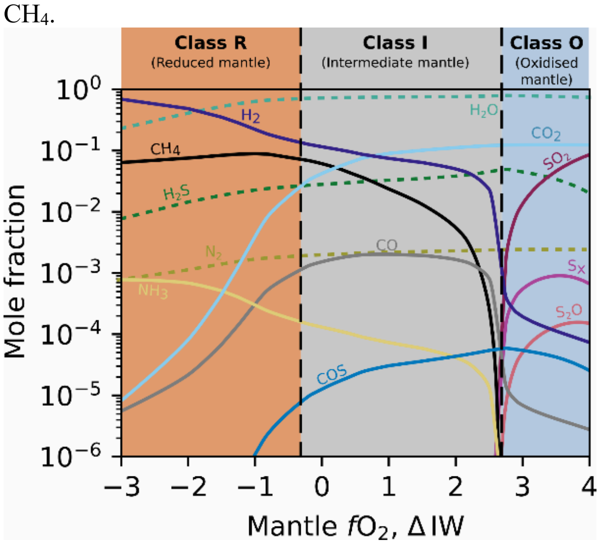

Figure 2: Chemical composition of a volcanic atmospheres according to their mantle fO_2 at surface pressure and a temperature of 800 K, after 1 Gyr of activity. The three compositional classes identified are indicated.

The equilibrium abundances of 3 species, CO, CH4 and NH3, are key for creating the class transitions shown above in Fig. 2. However, the CO to CH_4 and N_2 to NH_3 conversions are known to be strongly inhibited at low temperatures [2,5]. The timescales to equilibrium for different atmospheric temperatures for these three species were calculated (Fig. 3).

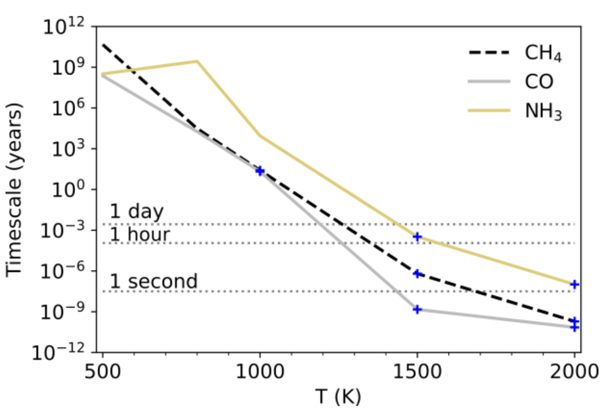

Figure 3: Timescale to equilibrium for species in an atmosphere instantaneously cooled/heated from 1473K to the new temperature, at 25 bar pressure. Blue crosses indicate thermochemical equilibrium was reached by ARGO; otherwise, instantaneous chemical timescales were calculated to estimate time to equilibrium.

At temperatures of 1100K and above, thermochemical re-equilibration of all species occurs within 100 years, a geological blink of an eye. However, below 700K, all three species take over 1 Myr to reach their new equilibrium abundances. At 500 K, assuming no reaction catalysis is occurring, it takes longer than the age of the universe for CH_4 to reach its equilibrium abundance. As a timescale to equilibrium of 1 Myr is 1000X shorter than the age of the atmospheres used in our calculations, we consider this to be the cutoff point for assuming thermochemical equilibrium, where longer timescales (in cooler atmospheres) indicate that the abundance of species in the atmosphere will start to diverge from the equilibrium abundance.

Conclusions: Rocky planets with Venus-like surface temperatures show three atmospheric classes which are dictated by the fO_2 of the mantle. Distinct sets of indicator species mean these atmospheric classes may be distinguishable with JWST. However, cooler atmospheres will not show these classes as the timescale to equilibrium is so long for several key species that the composition of the atmosphere will quench with speciations reflecting higher temperature origins. Models which assume thermochemical equilibrium on planets with atmospheric temperatures much below 700K may need to invoke alternative processes, such as catalysis, for their results to be valid.

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