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MODELLING THE SULPHUR CYCLE ON EARLY MARS. A. S. Braude¹, L. Kerber¹, F. Lefèvre², A. Y. Jaziri², S. S. Hamid³, E. Millour⁴ and F. Forget⁴, ¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (ashwin.s.braude@jpl.nasa.gov), ²Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), CNRS, Paris, France, ³School of Earth and Space Exploration, Arizona State University, Tempe, AZ, ⁴Laboratoire de Météorologie Dynamique (LMD), CNRS, Paris, France.

Introduction: Multiple pieces of evidence show that Mars was both volcanically active and sustained liquid water on its surface episodically during the Noachian geological era (4.1-3.7 Gya), with volcanic outgassing becoming increasingly sulphurous during the later Hesperian geological era (3.7-3.0 Gya) [1]. Initial studies [2] indicated that volcanic emission of sulphur dioxide (SO_2) and hydrogen sulphide (H_2S) could have induced the necessary greenhouse warming to melt liquid water that could not be produced by increased atmospheric pressure of CO_2 alone. However, later studies [3,4,5] showed that SO_2 and H_2S would both react in the atmosphere to form sulphuric acid (H_2SO_4) and elemental polysulphur (S_8) clouds, that would produce a net cooling effect on the climate. All of these studies relied on either 1-D photochemical models, which do not accurately model the global radiation budget due to spatial variations in cloud cover, or 3-D Global Climate Models (GCMs) with very simple parametrisations of sulphur compounds in the atmosphere. In addition, the timescales of aerosol formation are finite and a short period of greenhouse warming from SO_2 and H_2S could occur before the anti-greenhouse effect from H_2SO_4 and S_8 cloud has time to counteract it.

We therefore wish to model the sulphur cycle on early Mars in order to assess whether volcanic events could have induced short periods of relative warming or cooling, and how long those periods would have lasted before the atmosphere returned to equilibrium. We also wish to test whether any induced warming would be sufficient to raise temperatures above the melting point of water. We then wish to map the relative distribution of S_8 to H_2SO_4 deposited to the ground, which would hence help us constrain the conditions of the early Martian climate from the present-day geological record.

Method: We have, for the first time, integrated a photochemical model of the sulphur cycle on early Mars into a 3-D Global Climate Model (the Generic Planetary Climate Model, hereon referred to as the Generic PCM [6]), in order to track the presence of sulphur in the Martian atmosphere from volcanic emission of SO_2 , H_2S and S_2 , to its formation of H_2SO_4 and S_8 in the atmosphere and its condensation and deposition to the surface. We assume a background atmosphere initially consisting solely of 95% CO_2 and

condensation-limited water vapour, and implement a source of surface flux of the major species predicted to be emitted from Martian volcanoes (water vapour, SO_2 , H_2S , S_2 , HCl , CO and H_2) according to [1]. The major processes we have included in the model, including the major photochemical pathways for H_2SO_4 and S_8 production, are shown in Figure 1.

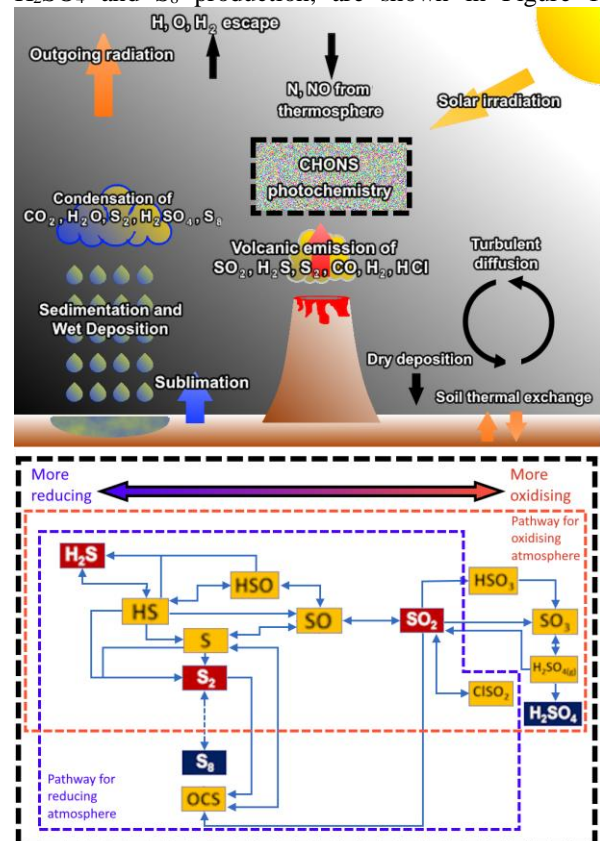


Figure 1. An overview of the main atmospheric processes that have been included in our model of the sulphur cycle, with the main photochemical pathways shown for both reducing and oxidising atmospheric conditions.

Our photochemical model consists of ~200 reactions that simulate odd-hydrogen, sulphur, nitrogen and chlorine chemistry [3,7,8,9,10]. We simulate binary H_2SO_4 - H_2O condensation according to diffusion-limited growth [11], and assuming a constant cloud particle size of $1 \mu\text{m}$ and a constant 75% weighting of H_2SO_4 per cloud droplet. The main sinks of sulphur are sedimentation of H_2SO_4 and S_8 , as well

as wet and dry deposition of H_2S and SO_2 [12,13] into the surface. All simulations are run at 32×32 spatial resolution (11.25° longitude by 5.6° latitude) with the atmosphere divided into 21 vertical layers from the surface up to 100 km altitude.

Results: Our results show that the timescales of H_2SO_4 formation are short enough that, in a 0.5 bar atmosphere, any volcanically-induced warming episodes would last for a few days at most. Increasing the atmospheric pressure increases the timescales of aerosol formation, leading to a delay in the anti-greenhouse effect (Figure 2), but also increases the timescales over which greenhouse warming by SO_2 and H_2S in the atmosphere can be induced. These results are robust to changes in the outgassing composition resulting from the uncertainty of the oxygen fugacity and water content of the Martian mantle at this time. It is therefore very difficult to create the temperatures necessary to melt liquid water using this method. Particularly large eruptions even had the potential to create a negative feedback loop where the increased cooling over time eventually led to atmospheric collapse.

We find that increasing the atmospheric pressure results in a greater amount of S_8 deposition to the Martian surface due to the higher stability of H_2S to

photolysis. Although S_8 has not been directly measured in Martian soils to date, future measurements of S_8 in Martian samples could therefore provide additional constraints on the atmospheric pressure at the time of the Noachian-Hesperian transition.

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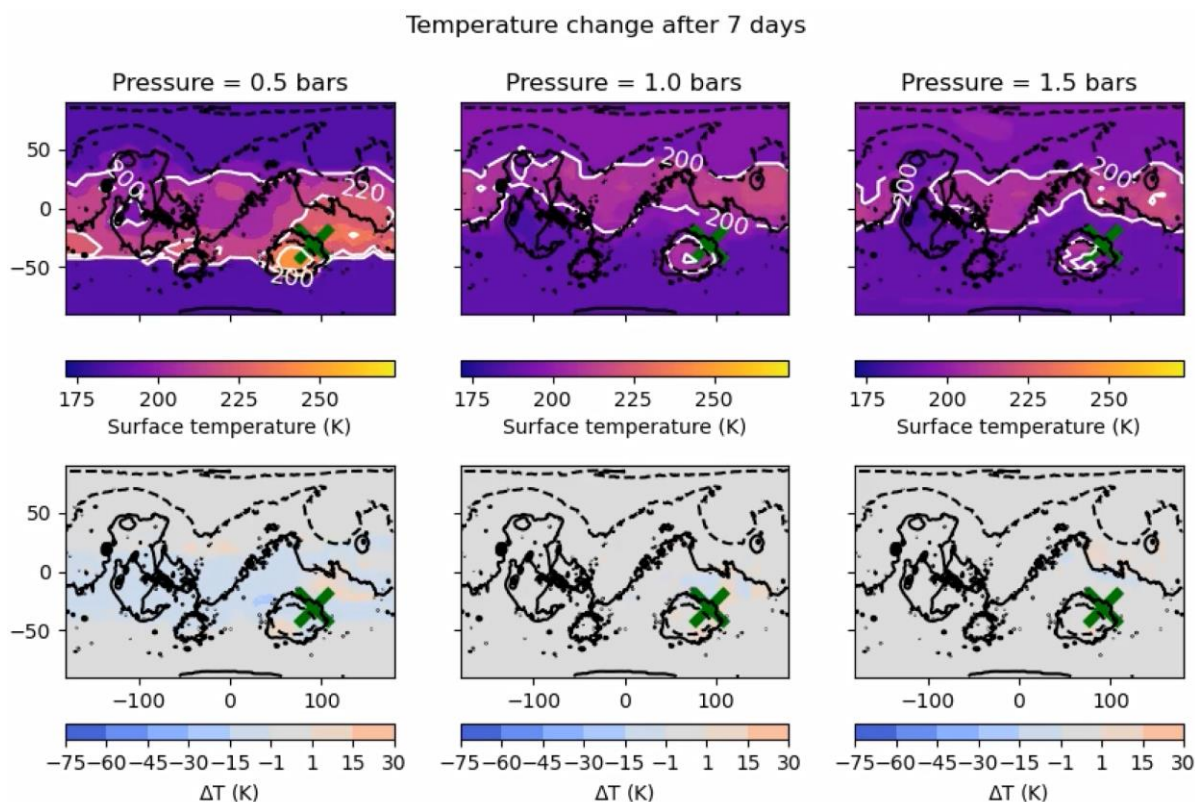


Figure 2. Relative change in temperature 7 days following a volcanic outgassing event (located at the green cross), as a function of surface pressure. Blue areas in the bottom diagrams indicate cooling. Even at these short timescales, the anti-greenhouse effect from H_2SO_4 cloud formation dominates.