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**Modeling the effect of volcanic outgassing of sulfur on early Martian climate and geology.** A. S. Braude<sup>1</sup>, L. Kerber<sup>1</sup>, F. Lefèvre<sup>2</sup>, A. Y. Jaziri<sup>2</sup>, S. S. Hamid<sup>3</sup>, E. Millour<sup>4</sup> and F. Forget<sup>4</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA ([ashwin.s.braude@jpl.nasa.gov](mailto:ashwin.s.braude@jpl.nasa.gov)), <sup>2</sup>Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), CNRS, Paris, France, <sup>3</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ, <sup>4</sup>Laboratoire de Météorologie Dynamique (LMD), CNRS, Paris, France.

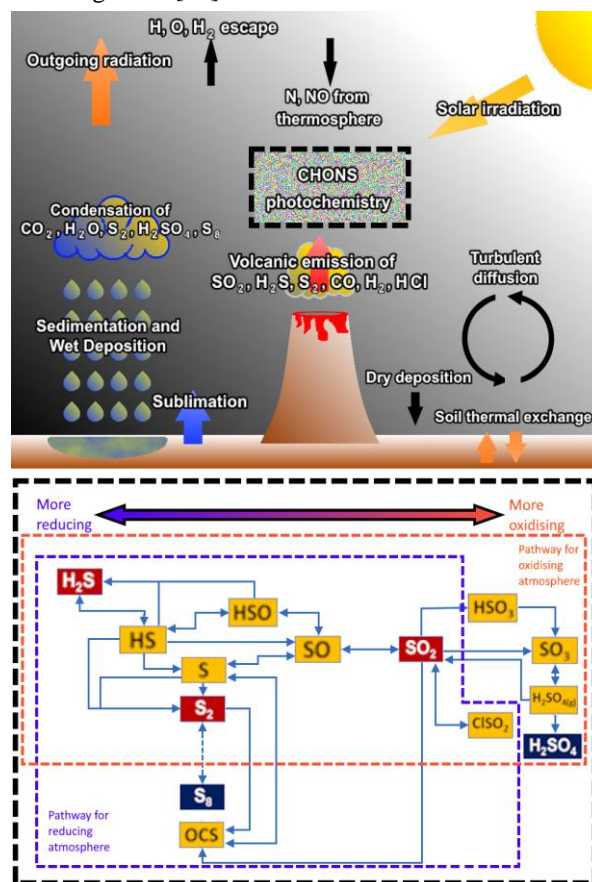
**Introduction:** The geological record strongly indicates that Mars was volcanically active for most of its history. At the transition between the Noachian (4.1-3.7 Gya) and the Hesperian (3.7-3.0 Gya) geological eras, an unknown change in the nature of volcanic activity on Mars resulted in an increase of sulfur emission into the atmosphere [1]. This transition coincided with a climactic shift from an environment in which ample liquid water flowed on its surface, to a drier and more acidic one, evident in widespread sulfates in Hesperian soils, covering approximately 5-10% of the Martian surface [2].

Volcanoes mostly emit sulfur in the form of sulfur dioxide ( $\text{SO}_2$ ) and hydrogen sulfide ( $\text{H}_2\text{S}$ ), both of which are greenhouse gases which would have had a warming effect on the Martian climate (e.g. [3]). However, they would also have reacted in the atmosphere to form a combination of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and elemental polysulfur ( $\text{S}_8$ ) condensate clouds according to the redox state of the atmosphere [4,5]. These clouds would have had a net cooling effect that would have partly neutralized  $\text{SO}_2$  and  $\text{H}_2\text{S}$  greenhouse warming [6,7,8]. Eventually, these clouds would have precipitated out of the atmosphere to form the sulfur deposits we observe today.

We have, for the first time, integrated the sulfur cycle into a 3-D Global Climate Model (GCM) of early Mars, including sulfur photochemistry and condensation of aqueous  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  cloud particles. Building on prior work [4], we explore how the balance between the warming effect of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  and the cooling effect of  $\text{S}_8$  and  $\text{H}_2\text{SO}_4$  can determine a) whether volcanic outgassing could have maintained a climate sufficiently warm for surface liquid water during the Noachian, solving the Faint Young Sun problem [9], and b) whether the change in outgassing composition in the Hesperian era could have ended this warm period. In addition, spatial differences in the deposition of  $\text{H}_2\text{SO}_4$  and  $\text{S}_8$  can be compared with the present-day geological record, in order to shed light on the redox state of the early Martian atmosphere and its potential to sustain life.

**Method:** We make use of the Generic Planetary Climate Model (PCM) [10] – a 3-D GCM generalizable to a range of exoplanetary and paleoclimate atmospheres. The model makes use of a

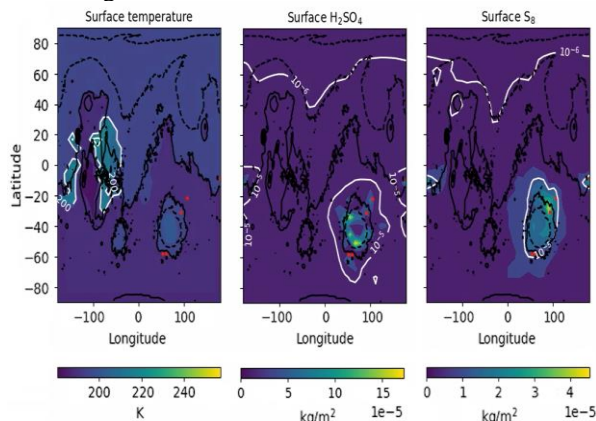
generalized radiative transfer scheme with radiatively active gases and aerosols. We integrate a photochemical scheme (**Figure 1**) [11] into this model, consisting of ~190 individual reactions involving 44 different gaseous tracers, covering odd-hydrogen, nitrogen, sulfur and chlorine chemistry [4,5,12]. The background atmospheric composition is set to 95%  $\text{CO}_2$  and 4%  $\text{N}_2$ , reflecting highly oxidizing conditions, with other gas profiles initialized using the Mars Climate Database [13]. We assume an  $\text{H}_2\text{SO}_4$  to  $\text{H}_2\text{O}$  ratio of 0.75 in sulfuric acid cloud particles and parametrize condensation rates according to diffusion-limited growth [14].



**Figure 1.** (top) Diagram of major processes in the GCM, (bottom) major reaction pathways of the sulfur species in the GCM, for oxidizing and reducing conditions. Red species are directly outgassed in the model, while blue species are condensable.

We run simulations at 32x32x21 grid resolution, corresponding to a spatial resolution of approximately 11.25° longitude by 5.6° latitude, and with the top of the atmosphere located just above 100 km. To compensate for a lack of a thermosphere in the model, we take into account downward fluxes of nitrogen species from the top of the atmosphere [15]. We parameterize volcanic outgassing from discrete point sources on Mars as a function of surface pressure according to [1], where we assume a surface pressure of 1 bar for ancient Mars as compared to a surface pressure of 0.01 bar for present-day Mars, and with HCl outgassing rates parametrized according to [16].

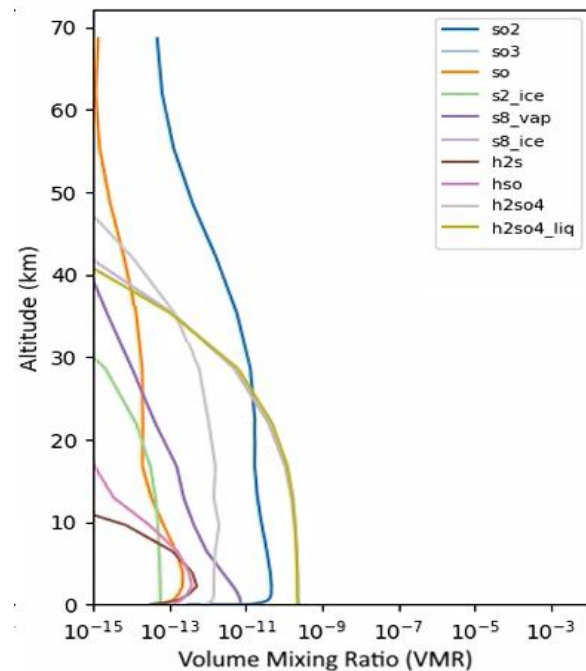
**Preliminary results:** The contribution of SO<sub>2</sub> to greenhouse warming is mostly negligible for values of SO<sub>2</sub> below 100 ppm, while H<sub>2</sub>SO<sub>4</sub> condenses out of the atmosphere almost instantaneously. It is therefore very difficult to produce even sufficient localized warming to melt liquid water for surface pressures of 1 bar (**Figure 2**). We plan further investigations to observe if obliquity variations, or changes in the microphysical properties of H<sub>2</sub>SO<sub>4</sub> cloud particles, would minimize the anti-greenhouse effect of H<sub>2</sub>SO<sub>4</sub> clouds further.



**Figure 2. Surface temperature at spring equinox, and surface H<sub>2</sub>SO<sub>4</sub> and S<sub>8</sub> deposition fluxes after 2 years. Red dots correspond to sources of volcanic emission.**

We find that the ratio of S<sub>8</sub> to H<sub>2</sub>SO<sub>4</sub> formation in the atmosphere is highly dependent on surface pressure, with higher surface pressures resulting in proportionally greater S<sub>8</sub> formation. For a surface pressure of 1 bar, the proportion of S<sub>8</sub> produced from the volcanic emission of SO<sub>2</sub> and H<sub>2</sub>S is of similar magnitude to that of H<sub>2</sub>SO<sub>4</sub>, even in highly oxidizing atmospheric conditions (**Figure 3**). As of writing, elemental polysulfur has not been detected on the Martian surface [5]. However, we show here that measurements of elemental polysulfur on the surface

of Mars (**Figure 3**) could provide useful constraints on both the redox state and the atmospheric pressure of Hesperian Mars. This would therefore also shed light on historical rates of atmospheric loss to space.



**Figure 3. Vertical, globally-averaged profiles of the major sulfur species in the model, including both gaseous species and aerosols.**

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