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# Sulfur in the Early Martian Atmosphere Revisited: Experiments with a 3-D Global Climate Model

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## 1. Introduction

Data returned from the surface of Mars during the 1970s revealed intriguing geological evidence for a warmer and wetter early martian climate. Dendritic valley networks were discovered by Mariner 9 on ancient Noachian terrain [1], indicating that liquid water had flowed across the surface in the distant past. Since this time, geological investigations into early Martian history have attempted to ascertain the nature and level of activity of the early Martian hydrological cycle [e.g. 2-5] while atmospheric modeling efforts have focused on how the atmosphere could be warmed to temperatures great enough to sustain such activity [see 6-7 for reviews].

Geological and spectroscopic investigations have refined the history and chronology of Noachian Mars over time, and circulation of liquid water has been invoked to explain several spatially and temporally distinct morphological and chemical signatures found in the geological record. Detections of iron and magnesium-rich clays are widespread in the oldest Martian terrains, suggesting a period of pH-neutral aqueous alteration [e.g., 8]. Valley network incision also took place during the Noachian period [9]. Some chains of river valleys and craters lakes extend for thousands of kilometers, suggesting temperatures at least clement enough for sustained ice-covered flow [3, 10]. The commencement of valley network incision is not well constrained, but the period of Mg/Fe clay formation appears to have ended before the termination of valley network formation, as the visible fluvial systems appear to have remobilized existing clays rather than forming them [5,8]. There is also evidence that the cessation of valley network formation was abrupt [11]. Towards the end of the Noachian, erosion rates appear to have been significantly higher than during subsequent periods, a process that has also been attributed to aqueous processes [12]. A period of sulfate formation followed, likely characterized by acidic, evaporitic playa environments [8].

A successful working model for the early Martian atmosphere and hydrosphere must be able not only to produce conditions suitable for liquid water at the surface, but also to explain how the nature of this aqueous activity changed over time and eventually diminished. There are two major end-member hypotheses: first, that early Mars was wet and warm, with a sustained greenhouse that made it possible for liquid water to be stable on the surface for extended periods [e.g., 2, 12-14], and second, that early Mars was generally cold, and that most of the aqueous alteration took place underground [3,5] or during transient warm periods tied to impact cratering [15], or volcanism [16]. In both of these scenarios it is generally agreed that in order to make valley networks and sulfate deposits, a hydrological cycle is needed which is able to recycle water from the lowlands back to the highlands (i.e., the one-time emptying of a regional aquifer would not be sufficient to create the observed features) [4,17]. This would require some precipitation to fall on the southern highlands, either flowing overland or filtering into groundwater aquifers.

In both cases, volcanic gases (especially $SO_2$) have been suggested as a possible way of creating either a sustained or transient greenhouse. Several researchers have tested the addition of $SO_2$ to climate models in order to assess whether it would provide an adequate amount of greenhouse warming to allow liquid water to flow across the surface [18-21], with differing results. Postawko and Kuhn [18] found a warming effect of 14 K in a 0.1 bar atmosphere with an $SO_2$ abundance of 1000 ppm. Johnson et al. [20] used a 3-D global circulation model and found a warming of 15-25 K for 245 ppm of $SO_2$ in a dry 0.5 bar atmosphere. Tian et al. [21] used a 1-D model to explore a wide range of $SO_2$ mixing values and $CO_2$ partial pressures, finding a warming of around ~25 K for 100 ppm in a 0.5 bar atmosphere with a fully saturated troposphere (~40 K for a 1 bar atmosphere). These authors also included the effect of sulfate aerosol particles, which caused a dramatic cooling effect which more than canceled the warming caused by the $SO_2$ gas [21].

Here we reconsider the efficacy of a sulfur-induced greenhouse in early Noachian history using the LMD (Laboratoire de Météorologie Dynamique) 3-D Generic Climate Model (LMD-GCM), exploring the effects of $SO_2$, $H_2S$, and sulfate and $S_8$ aerosols on the surface temperature, and the expected photochemical lifetime of $SO_2$ in the atmosphere.

## 2. Methods

The GCM used in this study was developed for general planetary applications, and includes generalized radiative transfer and cloud physics [e.g., 22]. The model was adapted specifically to early Mars conditions and used by Forget et al. [7] to explore the effects of a $CO_2$ atmosphere from 0.1 to 7 bars, including the effects of different obliquities, orbital parameters, cloud microphysical parameters, atmospheric dust loading, and surface properties. A companion paper exploring the effects of a full water cycle including surface-atmosphere interactions and water ice clouds [23] concluded that even with the greenhouse warming provided by water vapor and water-ice clouds, above-freezing conditions were not met for sustained periods. However, this study found that over the long term, ice tended to be transported from the lowlands to the highlands, providing a pathway for the recharge of water. If $SO_2$ warming was responsible for valley network formation, we might expect to find high temperatures where valley networks are found, to cause preferential melting in these areas. If $SO_2$ warming was responsible for allowing ground-water-fed playa lakes to exist in a liquid form long enough to evaporate [4], we might expect higher temperatures in areas where sulfates were observed (e.g., Arabia Terra).

Simulations were run at 0.5 bars with a 32x32x15 grid, corresponding to a resolution of 11.25º longitude by 5.625º latitude in the horizontal with 15 vertical levels from the surface to ~50 km. Other resolutions and pressures were also explored to test sensitivity. The correlated-k method was used to produce a database of coefficients for use by the radiative transfer code, using 80 spectral bands in the longwave and 36 in the shortwave. Real and imaginary indices for $H_2SO_4$ were taken from the HITRAN database, using the values from [24] for wavelengths between 0.2 and 0.337 µm and between 25 µm and 50 µm, while results from [25] were used for wavelengths between 0.360 µm and 25 µm (following [21] to allow for comparison). Simulations with $H_2O$ were run with a relative humidity profile derived from the full, self-consistent water cycle (including $CO_2$ and water ice clouds) used in [23]. The relative humidity in this profile is 45% near the surface with the hygropause near 8 km.

## 3. Results

Simulations were run in a dry $CO_2$ atmosphere with various $SO_2$ and $H_2S$ mixing ratios: 0 ppm, 10 ppm, 100 ppm, 1000 ppm, and 10000 ppm. Even in the case where a large amount of $SO_2$ is added to the atmosphere, the annual average surface temperature does not rise above freezing anywhere on the planet (local maximum temperatures do exceed freezing). $H_2S$ provides significantly less warming than $SO_2$. Additional simulations were run in dry $CO_2$ atmospheres with well-mixed $H_2SO_4$ 0.5 µm particles with opacities from $\tau$= 0.2 to 10, producing cooling from a few degrees to ~23 K for $\tau$= 10. Areas of greatest warming did not coincide with valley network or sulfate occurrences.

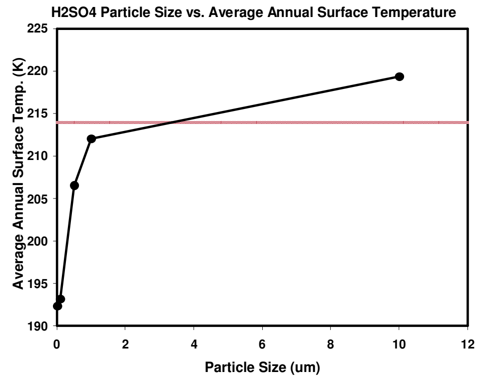


**Figure 1.**

A single layer of $H_2SO_4$ aerosols of the same opacity produced similar results. Larger particles produced less cooling with large particles (10 µm) producing mild warming (**Fig. 1**). The greenhouse warming produced by our model is therefore significantly less than that produced by that of Johnson et al. [20], but slightly greater (5-10 K) than that of Tian et al. [21]. The cooling produced by sulfate particles is significantly less than that of Tian et al. [21]. While a sustained greenhouse is not created, local and seasonal melting would be facilitated provided that the $SO_2$ lifetime was sufficient. The photochemical lifetime of $SO_2$ and $H_2S$, and the effects of $S_8$ aerosols are thus critical parameters.

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