LONGEVITY OF ATMOSPHERIC SO$_2$ ON EARLY MARS.

S. S. Johnson[1], A. A. Pavlov[2], and M. A Mischna[3], [1]Dept. of Earth, Atmospheric and Planetary Sciences, MIT, 77 Mass. Ave., 54-810, Cambridge, MA 02139, ssj@mit.edu, [2]University of Arizona, Lunar and Planetary Lab, Tucson, AZ 85721, pavlov@lpl.arizona.edu, [3]Jet Propulsion Lab, M/S 183-401, 4800 Oak Grove Dr., Pasadena, CA 91109, michael.a.mischna@jpl.nasa.gov

Introduction: Recent work suggests that the radiative properties of sulfur volatiles degassed into the Martian atmosphere may have caused a greenhouse effect early in the planet's history [1]. It remains unclear, however, over what timescales these warming pulses would have persisted, and consequently how significant these pulses may have been. While photochemistry research to date has concentrated on current Martian conditions [2], the ancient Martian atmosphere was thicker, warmer, and more reducing than the current regime.

Photochemical Model: We use a globally averaged one-dimensional model adapted from a previous study of sulfur in the terrestrial Archean atmosphere [3]. For our simulations of Mars, the model atmosphere is divided into 100 2-km vertical layers. At each layer, the continuity equation is solved for long-lived species, including transport by eddy and molecular diffusion. The combined equations are cast in centered, finite difference form. Reactions and rate constants are adopted from [3]. Boundary conditions are applied at the top and bottom of the atmosphere for each chemical species as in [3]. At the upper boundary, zero flux is assumed for most species, and escape of H and H$_2$ is simulated by assuming a diffusion-limited upward flux [4, 5]. As in [2] and [6], a fixed flux of atomic oxygen of 10^8 cm^{-2} s^{-1} is assumed for the upper boundary to balance hydrogen loss. For CO, we employ a fixed deposition velocity of 10^{-9} cm s^{-1}, in accordance the abiotic rate determined by [7]. We assign the gravity for Mars at 373 cm s^{-2}, the albedo at 0.215, and the altitude of the tropopause at 15 km. Due to the increased distance from the Sun, we assign the solar flux scaling for Mars as 0.43 of that incident upon Earth. The resulting set of coupled ordinary differential equations is integrated to steady state (where sources and sinks for all chemical species are in balance and all major atmospheric species have converged) using the reverse Euler method.

Ancient Mars: Following validation of our model under current Martian conditions (generating results that are highly consistent with [2] and [6]), we set the atmospheric pressure of CO$_2$ and N$_2$ to 500 mb and 100 mb, respectively. We specify water vapor at the saturation vapor pressure throughout the atmosphere, and scale the solar flux up by a factor of five to account for higher Lyman-α UV fluxes in the Late Noachian [8]. Our base vertical temperature profile spans from 258 K at the surface to 168 K in the upper atmosphere [1]. Our precipitation scheme is designed to mimic the hyperarid core of the Atacama Desert, as recent studies suggest that the geomorphology of Late Noachian basins on Mars are dominated by equal or greater aridity [9] (precipitation as calculated by the terrestrial parameterization of [10] is reduced by a factor of 500). We employ a terrestrial eddy diffusion profile scaled by the square root of density for the Martian atmosphere.

We begin from a steady state atmosphere containing very little SO$_2$ (f(SO)$_2$)<10^{-10}) and assign a new SO$_2$ mixing ratio between 10^{-8} and 10^{-6}) to the lower 20 km of the atmosphere, simulating a Plinian eruption [see 11]. Snapshots of the atmosphere are taken after specified time steps (e.g. 1, 10, 100, 1000 model years, etc.) as the atmosphere slowly returns to steady state. We assume that excess water vapor released with the eruption condenses quickly in the lower atmosphere, well before significant amounts of SO$_2$ (having a relatively low Henry constant) can be converted to H$_2$SO$_4$ (having a higher Henry constant) and entrained. To test this, we simulated three days of rainout following the eruption at rates characteristic of the terrestrial tropics (an overestimate, in part because much of the initial water vapor would have formed ice crystals). Nevertheless, an initial f(SO$_2$) of 10^{-6} falls only by 16% during this time.

We have also completed a number of sensitivity studies on our simulations involving an initial SO$_2$ mixing ratio of 10^{-6}. We consider a higher temperature regime, consistent with a 25 K greenhouse warming effect from a pulse of SO$_2$ in the atmosphere [1]. This vertical temperature profile, spanning from 283 K at the surface to 180 K in the upper atmosphere, is taken from radiative transfer steady state simulation results for a "wet" 500 mb CO$_2$ ancient Martian atmosphere within three years of a 1.2×10^{13} kg pulse of SO$_2$ (giving rise to a SO$_2$ mixing ratio of 6.14×10^{-6}) [1].

We also explore the effects of a different hydrologic scheme. One set of simulations with a higher rate of precipitation is designed to mimic the rainout regime under conditions an order of magnitude more moist by reducing the parameterization of [10] by a factor of 50 (consistent with a few cm of precipitation per year). Another set considers even more arid conditions, reducing the parameterization by a factor of 1000 (see Figure 1).

Discussion: Sulfur leaves the early Martian atmosphere via three paths: as S$_8$ aerosols, as SO$_4$ aerosols, and as SO$_2$ rainout. The efficiency of these processes ultimately determines the lifetime of SO$_2$ in the atmosphere. While the SO$_2$ photolysis rate
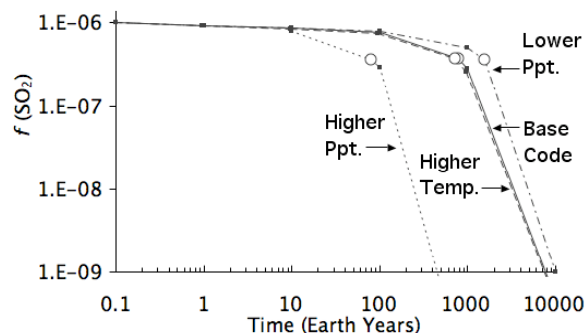
Figure 1. SO$_2$ longevity and sensitivity factors. *e*-folding times are marked by circles.

decreases linearly with decreasing altitude in the current Martian atmosphere, in the ancient Martian regime, the rate drops dramatically in the lower atmosphere at moderate mixing ratios of SO$_2$. Furthermore, SO$_2$ photolysis alone cannot be considered as a loss of sulfur from the atmosphere, as recycling reactions may convert sulfur atoms back to SO$_2$.

The deposition of reduced sulfur is impeded by inefficient photolysis (see Figure 2), which limits effective conversion of SO$_2$ to elemental S and on to S$_8$ aerosols. Simultaneously, near-surface SO$_2$ becomes a significant sink for oxidants and, although mixing ratios of H$_2$O reach 10^{-2} near the bottom of the atmosphere in many simulations, a lack of oxidants precludes effective conversion of SO$_2$ to sulfate aerosols. Thus, the abundance of aerosols, which tend to cool the atmosphere by reflecting incoming sunlight back to space, remains limited in the model atmosphere.
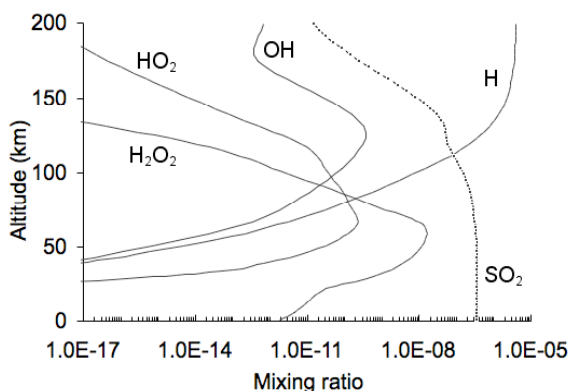

Figure 2. Profiles of radicals in ancient Martian regime at the *e*-folding time (for reference, a profile of SO$_2$ is also shown). Under these conditions, oxidants become scavenged near the surface.

The major remaining loss process for sulfur is SO$_2$ rainout, and when rainout is small, SO$_2$ remains in the atmosphere. However, even at small rainout rates, SO$_2$ rainout is the dominant mechanism for removal, and over time most of the initial influx in our simulations is lost as dissolved SO$_2$.

A long lifetime for SO$_2$, the result of the reduced efficiency of the processes that destroy atmospheric SO$_2$, has important implications for understanding the ancient Martian atmosphere given recent studies assessing the potential for sulfur-induced greenhouse warming. For instance, [1] reports significant greenhouse warming at high SO$_2$ mixing ratios, in the range of 10^{-6} to 10^{-4}, and [12] describes the possibility of an SO$_2$ climate feedback. Although simulations at high SO$_2$ mixing ratios impose too large an initial discontinuity in the system for model convergence, *e*-folding times for SO$_2$ will only increase as additional sulfur is loaded into the atmosphere. Our results therefore suggest that transient greenhouse warming, arising from the degassing of SO$_2$ volatiles, likely persisted for at least hundreds of years, allowing for the stability of liquid water in the form of near-surface groundwater, lakes, and streams.

Not only would sulfur in the form of SO$_2$ have had strong atmospheric effects, the deposition of SO$_2$ (eventually oxidized to sulfate at the surface-atmosphere interface) would have generated potent acidity on the ancient Martian terrain. Indeed, extremely low pH levels are recorded in the mineral jarosite, recently discovered in Martian outcrop that dates to the Late Noachian [13]. Sulfuric acid can drastically depress the freezing point of water; for instance, a eutectic aqueous solution of 39% H$_2$SO$_4$ does not freeze until 200 K [14]. It is thus likely that sulfur played a dual role in the early history of the Mars: primarily as a potent greenhouse gas, and secondarily as an agent allowing sulfate-charged waters to remain in liquid form even after surface temperatures dropped below 273 K.

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