# CLIMATIC AND CHEMICAL CONSEQUENCES OF EPISODIC ERUPTIONS ON EARLY MARS

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## Introduction

An abundance of geomorphological, mineralogical and geochemical evidence suggests relatively widespread aqueous conditions on the surface or early Mars [1-3]. However, recent studies of Mars' early climate, using sophisticated three-dimensional climate models, have concluded that in the absence of warming agents other than CO<sub>2</sub> (gas and clouds) and H<sub>2</sub>O, average surface temperatures do not become high enough to explain the observations [4,5]. A possible conclusion drawn on the basis of these studies is that the early climate was, on average, comparably cold and dry to today. An implication of the dry surface is that winds easily lifted fine-grained particles and that the atmosphere was dusty, much like the present atmosphere in which the average visible dust optical depth is approximately 0.5 [6].

Volcanic sulfur-bearing gases, especially SO<sub>2</sub>, have been suggested as a possible solution to the early climate problem [7,8]. Because it is a strong greenhouse gas, ~250 ppm of SO<sub>2</sub> warm the surface on average by ~50 K, and locally by up to ~80 K [8]. However, scattering of incoming solar radiation by sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) aerosols has been suggested to result in net cooling as SO<sub>2</sub> levels increase [9]. In addition, we argue here that even in the absence of H<sub>2</sub>SO<sub>4</sub> aerosols, reasonable long-term average volcanic outgassing rates are unable to sustain climatically important atmospheric concentrations of SO<sub>2</sub>. This is a consequence of the reactivity of SO<sub>2</sub> and its sensitivity to ultraviolet photodissociation [9,10].

Here, on the basis of morphological similarity to terrestrial flood basalt provinces, we suggest that early martian eruptions were highly episodic, and characterized by exceptionally rapid emission rates during short bursts of activity, separated by long quiescent periods. We show that the background climatic state was cold and dry, and that climate models aiming to understand early martian climate must account for the effect of atmospheric dust particles. Additionally, we show that volcanic emission rates during brief and strong ("punctuated") eruptions were enough to sustain climatically important  $SO_2$  levels, and that the net effect of injection of  $SO_2$ into a dusty atmosphere is warming, despite the formation of H<sub>2</sub>SO<sub>4</sub>-bearing aerosols. Finally, we discuss probable climate feedbacks associated with the above scenario, the possible existence of multiple climate states, and the chemical consequences of punctuated volcanic eruptions on early Mars.

## Methods

A flood basalt analog to plains volcanism. A long maximum in volcanic activity during the transition between the Noachian and Hesperian [11] appears coeval with widespread evidence for aqueous activity on the surface of Mars. This includes geomorphological evidence for the formation of the majority of valley networks and open-basin lakes [1-3], and the deposition of massive sulfate deposits [12]. The Hesperian Ridged Plains (Hr) on Mars appear to have effused rapidly from wide fissures, rather than central cones or calderas [13,14]. This, in addition to their occurrence as laterally extensive plains, suggests an analogy with terrestrial flood basalts.

Individual flows in the Columbia River Flood Basalts and the Deccan Traps reach volumes as high as 1,300-10,000 km<sup>3</sup> and have estimated eruption durations of 1-10 years [15,16]. With typical terrestrial volatile content, the implied outgassing rate of sulfur during the emplacement of these flows is up to several hundred times the total global rate. Considering the likely higher sulfur content of martian magmas [17], the sulfur outgassing rate during similar eruptions on Mars could perhaps be three orders of magnitude higher than the terrestrial rate. Finally, plains basalts on Mars are larger in volume and area than any known terrestrial flood basalt province (Figure 1), suggesting that emplacement of the Hr involved a greater number of eruptions and lasted for a longer time than is typical on Earth.



Figure 1: Background: Flat topography associated with Hr. Foreground: Volumes (colored spheres) and areas (gray circles) of terrestrial flood basalt provinces and Hr.

A coupled aerosol microphysics-radiative transfer model. To explore the effects of punctuated eruptions on early Mars' climate, we developed a model of aerosol microphysics. The single-column model dynamically treats the formation, growth and transport of pure H2SO4 and mixed dust-H2SO4 aerosols. Model inputs are a size distribution of newly lofted dust, constrained by present-day observations [6], and a volcanic emission rate. The lofting rate of new dust is chosen to result in a steady-state optical depth of 0.5 during quiescent periods. The conversion rate of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> is parameterized using the results of full photochemical models [9,10]. Model output is a time-dependent size distribution of atmospheric aerosols composed of a dust core and a H<sub>2</sub>SO<sub>4</sub> coating of variable thickness (Figure 2). We use this output in a line-by-line radiative transfer model [18] to calculate radiation fluxes in atmospheres with a range of surface temperatures and fixed atmospheric pressure-temperature profiles. We find the approximate equilibrium surface temperature, at which the top-of-the-atmosphere upwelling radiation exactly equals the incoming solar radiation (~110 W m<sup>-2</sup> globally or ~140 W m<sup>-2</sup> in the equatorial regions with 75% present solar luminosity).



Figure 2: The steady-state size distribution of coated particle cores (**a**) and the thickness of  $H_2SO_4$  coatings in the different size bins (**b**). The crosses outside of the size distribution are pure  $H_2SO_4$  aerosols.

#### **Results and Discussion**

If early martian climate was indeed cold and dry, as recently suggested in sophisticated global climate models, then studies aimed at understanding the conditions that allowed wetter conditions despite a less luminous early Sun, must account for the presence of atmospheric dust.

The background climate state. We calculated a global mean annual surface temperature (MAST) of 207 and 206 K, with a solar constant 75% its present value and a vapor-saturated clear-sky atmosphere containing 0.5 and 1 bar of CO<sub>2</sub>, respectively (shown in Figure 3 for the 1 bar case). The lower global MAST in the 1 bar case arises from more efficient scattering by the CO<sub>2</sub> and only a modestly more effective greenhouse effect, which results because the planet emits so little infrared radiation at such low surface temperatures. Addition of dust results in a decrease in the MAST of approximately 10 and 12 K, respectively in these cases. The tropical MAST is only ~240 K with 1 bar of CO<sub>2</sub>, too low for the existence of liquid water (Figure 3). This demonstrates the difficulty in warming early Mars caused by the presence of atmospheric dust, which should be considered in paleoclimate studies.

The effect of punctuated eruptions. The background climate state described above cannot explain the geomorphological evidence for surface water. However, both at the atmospheric steady state and during episodes of strong volcanic eruption, we find that



Figure 3: Global and tropical MAST as a function of the volcanic outgassing rate in vapor-saturated atmospheres with 1 bar CO<sub>2</sub>. Lines show the steady-state MAST, and markers show the MAST during a lengthy punctuated eruption. Without sulfur species, the steady-state global MAST with a dusty atmosphere (gray lines) is ~12 K cooler than in the clear-sky case (black lines). Adding only SO<sub>2</sub> causes strong warming (red lines), but even with the effect of H<sub>2</sub>SO<sub>4</sub>-bearing aerosols included, volcanic emission of SO<sub>2</sub> results in relatively strong net warming (orange lines). For the punctuated eruption calculations, backround and active emission rates were  $1 \times 10^{10}$  and  $1 \times 10^{12}$  molec cm<sup>-2</sup> s<sup>-1</sup>, respectively.

injection of SO<sub>2</sub> into a dusty martian atmosphere causes net warming, even when scattering by  $H_2SO_4$ bearing aerosols is included. The reason is mostly that the atmosphere already scatters an appreciable fraction of the incident solar radiation due to the presence of dust aerosols. The increase in the fraction of scattered radiation as SO<sub>2</sub> is photochemically converted to  $H_2SO_4$  is minor. The major greenhouse effect by SO<sub>2</sub> then results in net warming.

The global average MAST does not exceed 220 K even for long-term average volcanic emission rates more than 300 times the global terrestrial rate (Figure 3). However, the tropical MAST exceeds 273 K for long-term average volcanic emission rates ~200 times the terrestrial rate. Such rates are unlikely over long periods, even given the higher sulfur content of the martian mantle. However, on the basis of the analogy between martian plains volcanism and terrestrial flood basalts, rates such as these and even higher are sustainable for years to a few decades.

Although during punctuated eruptions the atmosphere doesn't reach  $SO_2$  concentrations in steady state with the high volcanic emission rate, the tropical MAST significantly increases (Figure 3). It is likely that in the summer months during the day surface temperatures exceed 273 K. These conditions last well after the eruption ceases due to the relatively slow destruction of atmospheric  $SO_2$ , which has a lifetime of centuries if its atmospheric mixing ratios exceed 10 ppb [10]. Warm summer conditions may thus last a few centuries after exceptionally strong volcanic eruptions.

The finding that tropical MAST may exceed 273 K only during the summer months and only decades to centuries after large eruptions is consistent with growing evidence for transient rather than sustained wet conditions on the surface of early Mars [e.g., 1,2]. Furthermore, warm temperatures occur only at low latitudes, consistent with the low-latitude bias in the spatial distribution of valley networks and openbasin lakes [2,3]. An upper estimate on the duration required to carve the valley networks is  $\sim 10^7$  years [19]. If the total average duration of warm and wet conditions as a result of a single 10-year-long eruptive event is  $\sim 1$  year ( $\sim 10\%$  of 10 years), then  $10^6$ such events are required to form the valley networks. If each of the events emplaced a volume of ~2,000 km<sup>3</sup> and the Hr covers one third of the surface of Mars, then the thickness of Hr required to form the valley networks is only ~15 m instead of the hundreds of meters observed [13]. However, given that most eruptions would last less than 10 years and would not inject enough SO<sub>2</sub> to reach climatically important levels (~1 ppm), the actual thickness required is probably at least a factor of 10 higher than that of the eruptions strong enough to cause warming, consistent with the observed thicknesses.

*Climate feedbacks?* In addition to explaining the low-latitude distribution of valley networks and

open-basin lakes, the mechanism we propose for causing warm and wet conditions on early Mars suggests the existence of possible climate feedbacks.

The first of these is a positive feedback involving the scavenging of atmospheric particles as warmer conditions invigorate the hydrological cycle. We show that the dustier atmosphere results in colder surface temperatures (Figure 3) and, by inference, a drier climate. When conditions become warm enough to melt ice in tropical regions, hydrological activity increases both on the surface and in the atmosphere. An increase in precipitation rates results in more rapid scavenging of atmospheric particles, irrespective of their composition. In addition, a moister surface results in less efficient lofting of new dust aerosols by wind. Unless the surface reservoir of water becomes large, the more vigorous hydrological activity does not result in appreciable removal of  $SO_2$  from the atmosphere (see below). The decreasing optical depth of atmospheric aerosols results in less scattering of solar radiation, while greenhouse warming by SO<sub>2</sub> continues. This leads to further warming and invigoration of the hydrological cycle.

The return to a dusty atmosphere can only occur once  $SO_2$  levels decrease to a threshold value below which the climate becomes too cold and dry to prevent efficient lofting of dust. Due to the cleanliness of the atmosphere, this threshold value is lower than the value that  $SO_2$  levels needed to reach in order to trigger warmer and wetter conditions in a preeruption dusty atmosphere (Figure 4).

A second feedback involves the influence of the liquid hydrosphere volume on atmospheric  $SO_2$  levels. In this negative feedback, as the climate warms due to increasing atmospheric  $SO_2$  concentrations, the volume of aqueous solutions on the surface increases. As  $SO_2$  is highly soluble, an increasing size of the aqueous reservoir makes it harder to saturate



Figure 4: Hysteresis between a dusty and clean state of the early martian atmosphere. Punctuated eruptions push a dusty atmosphere to the clean branch by invigorating the hydrological cycle and causing the scavenging of atmospheric particles. Climate deterioration after the cessation of eruptions pushes the atmosphere back to the dusty branch.



Figure 5: The concentration of total dissolved sulfite species as a function of the  $SO_2$  mixing ratio in a 1-bar atmosphere and the pH.

the surface of the planet with  $SO_2$ . Consequently, rather than rapidly reaching equilibrium with atmospheric levels of  $SO_2$  [7], the surface acts as a sink for depositing  $SO_2$ . The resulting decrease in atmospheric  $SO_2$  concentrations causes cooling, which leads to a decrease in the size of the aqueous reservoir and releases dissolved  $SO_2$  back into the atmosphere.

Aqueous speciation of sulfite species (dissolved SO<sub>2</sub>) is pH-dependent [7]. Thus, the lower the pH, the lower the concentration of total dissolved sulfite (Figure 5). Consequently, the strength of the aqueous sink for SO<sub>2</sub> depends on the pH of the surface aqueous reservoir and, therefore, on the partial pressure of atmospheric CO<sub>2</sub>. At  $pCO_2$  of 1 bar, dilute solutions would initially have a pH value of ~4 and hold little total sulfite. As the pH of these solutions increases by reaction with rocks and soils, their capacity to hold sulfite would also increase, resulting in an increase in this sink magnitude with time.

*Chemical consequences.* As mentioned above, depending on the duration of punctuated eruption, conditions conducive to the existence of liquid water could last several decades. As the climate cooled after the cessation of active volcanic emission, the water at the surface would eventually refreeze. The sulfur that accumulated in solution, along with additional solutes derived from the dissolution of preexisting salts and from weathering of silicate rocks, would precipitate to form sulfate and sulfite minerals [7,20]. It is expected that these sulfates and sulfites accumulate in topographic lows where water ponded.

However, subsequent wet episodes, perhaps millions of years later than the first salt-forming events, would remobilize the salts precipitated during earlier aqueous episodes. For example, a 10-year-long eruptive event at 1000 times the terrestrial average sulfur outgassing rate, would inject approximately 25 Gt of sulfur into the atmosphere. Most of this sulfur would be scavenged in the tropics, where the hydrological cycle is most active and would end up making sulfate minerals when the planet refroze. If the sulfates had a cation composition similar to martian crust, then precipitation rates of less than 10 mm/y would be enough to redissolve these minerals during the next warm episode. With time, the salts would get deposited on increasingly young surfaces, and be ultimately preserved where they formed during some of the last aqueous episodes. This may explain the apparent Hesperian age of most sulfate deposits, broadly contemporaneous with the waning stages of Hr emplacement.

#### Conclusions

Despite the apparent inability of climate models to maintain near-melting surface temperatures on early Mars, widespread evidence exists for warmer and wetter conditions. We suggest that these conditions were possible due to emission of  $SO_2$  into the martian atmosphere during punctuated volcanic eruptions in which the outgassing rate may have reached hundreds to thousands of times the terrestrial global average rate. The cooling effect by  $H_2SO_4$ -bearing aerosols is minor when these aerosols form in an already dusty atmosphere, such as the one expected on early Mars.

While global MAST never approaches 273 K, tropical MAST exceeds 250 K during punctuated eruptions, and summertime temperatures during the day probably reached and even exceeded 273 K at low-latitudes. This result is consistent with the low-latitude distribution of most known valley networks, open-basin lakes and sedimentary rock deposits. Warming is expected to have lasted decades to a maximum of one or two centuries and only during the summer months. The integrated duration of aqueous conditions is consistent with estimates of the time required for formation of the valley networks.

When eruption ceased and SO<sub>2</sub> levels declined, water on the planet's surface refroze and solutes precipitated as sulfate and sulfite salts, only to be remobilized during subsequent wet episodes. The salts were ultimately preserved when volcanic activity on Mars slowed in the Hesperian, explaining their mostly Hesperian ages.

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