



Sulfuric acid aerosols in the atmospheres of the terrestrial planets

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ABSTRACT

Clouds and hazes composed of sulfuric acid are observed to exist or postulated to have once existed on each of the terrestrial planets with atmospheres in our solar system. Venus today maintains a global cover of clouds composed of a sulfuric acid/water solution that extends in altitude from roughly 50 km to roughly 80 km. Terrestrial polar stratospheric clouds (PSCs) form on stratospheric sulfuric acid aerosols, and both PSCs and stratospheric aerosols play a critical role in the formation of the ozone hole. Stratospheric aerosols can modify the climate when they are enhanced following volcanic eruptions, and are a current focus for geoengineering studies. Rain is made more acidic by sulfuric acid originating from sulfur dioxide generated by industry on Earth. Analysis of the sulfur content of Martian rocks has led to the hypothesis that an early Martian atmosphere, rich in SO₂ and H₂O, could support a sulfur-infused hydrological cycle. Here we consider the plausibility of frozen sulfuric acid in the upper clouds of Venus, which could lead to lightning generation, with implications for observations by the European Space Agency's *Venus Express* and the Japan Aerospace Exploration Agency's *Venus Climate Orbiter* (also known as *Akatsuki*). We also present simulations of a sulfur-rich early Martian atmosphere. We find that about 40 cm/yr of precipitation having a pH of about 2.0 could fall in an early Martian atmosphere, assuming a surface temperature of 273 K, and SO₂ generation rates consistent with the formation of Tharsis. This modeled acid rain is a powerful sink for SO₂, quickly removing it and preventing it from having a significant greenhouse effect.

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1. Introduction

Liquid water, and an energy source such as sunlight, volcanism, or lightning, are vital to the genesis of life (McKay, 1991). Geologic and isotopic evidence suggests that liquid water was present at some point on each of the terrestrial planets of the Solar System (Kasting, 1988; Mojzsis et al., 2001; Squyres et al., 2004). Furthermore, geological evidence suggests that all of the terrestrial planets of the solar system were volcanically active in their early history. A typical component of volcanic outgassing, sulfur dioxide (SO₂) is soluble in water, and can be oxidized to form sulfuric acid (H₂SO₄). Sulfuric acid is often formed from SO₂, however, by photochemical reactions in the gas phase. In order to understand the evolution of terrestrial planet atmospheres, we need to understand the effects that this acidification might have on the clouds and the liquids of those planets. In this paper, we discuss the consequences of sulfuric acid in the clouds of present-day Venus, present-day Earth, and early Mars. We present a brief overview of the role of sulfuric acid aerosols and clouds in planetary atmospheres, including present day Venus, and the

puzzle of the missing carbonates on Mars. We then describe the model we have used previously to study the present-day condensational clouds of Venus, and how we have adapted that model to describe the clouds of the late Noachian Martian atmosphere. Finally, we show that rainfall would be a powerful sink for SO₂ on Mars, making it unlikely that an SO₂ greenhouse atmosphere could have warmed the surface of Mars for very long.

2. Sulfuric acid clouds on Earth

Today, sulfuric acid aerosols and clouds are known to form in the atmospheres of two planets in our solar system: Earth and Venus. On Earth, sulfuric acid droplets play an important role in the microphysics and chemistry of polar stratospheric clouds (PSCs) (Tolbert and Toon, 2001). These PSCs play a key role in the destruction of ozone in the polar winter stratosphere (Solomon, 1999). Sulfuric acid aerosols are also capable of causing ozone loss, especially after large volcanic injections of SO₂ (Tabazadeh et al., 2002). The aerosols are also observed to cause short-term climate changes by scattering and absorbing sunlight. After the Toba eruption 70,000 years ago these climate changes may have been so large that humans nearly became extinct (Robock et al., 2009a). Currently, research is focused on possibly artificially

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enhancing stratospheric sulfates to geoengineer the Earth out of the potential CO₂ greenhouse crisis (Robock et al., 2009b). Sulfuric acid aerosols are also a principle component of global and local air pollution, and are an important contributor to the formation of acid rain. In the Industrial Era, rainfall was found to have become more acidic (with a pH of about 4, as compared with a typical value of about 5.2 from dissolution of carbon dioxide) (Seinfeld and Pandis, 1998). Large concentrations of SO₂ were introduced into the atmosphere, primarily due to coal-burning in industrial regions. This SO₂ then dissolved in cloud water and rain water and was oxidized to generate highly acidic precipitation downwind of these industrial regions (Galloway et al., 1987). In 1990, Title IV of the Clean Air Act severely restricted the permitted level of SO₂ emissions. As a consequence, the incidence of acid rain in the western world has been significantly reduced, but low pH levels are still commonly detected.

Since water is usually more abundant than sulfuric acid in the vapor phase, solutions of sulfuric acid and water rapidly come into an equilibrium whereby the concentration of the acid is often determined by the environmental water vapor concentration. In the Earth's stratosphere, where water vapor relative humidities are typically a few percent (Steele and Hamill, 1981), solutions around 60–75% by mass of sulfuric acid are formed. Thus, in the terrestrial case, the solution has a relatively low freezing temperature of about 230 K, well below that of pure water (273 K) or pure sulfuric acid (283 K) (Gable et al., 1950). However, this temperature is still warmer than the 220 K that is typical of the stratosphere (see Fig. 1). Furthermore, sulfuric acid exhibits a strong tendency to supercool before freezing (Ohtake, 1993; Zhang et al., 1993; Carleton et al., 1997). Hence, in the terrestrial stratosphere, where ambient temperatures tend to be about 10–40 K below the freezing point of the equilibrium sulfuric acid concentrations at those altitudes, sulfuric acid still tends not to freeze, except possibly in the cold polar night when temperatures can fall below 190 K.

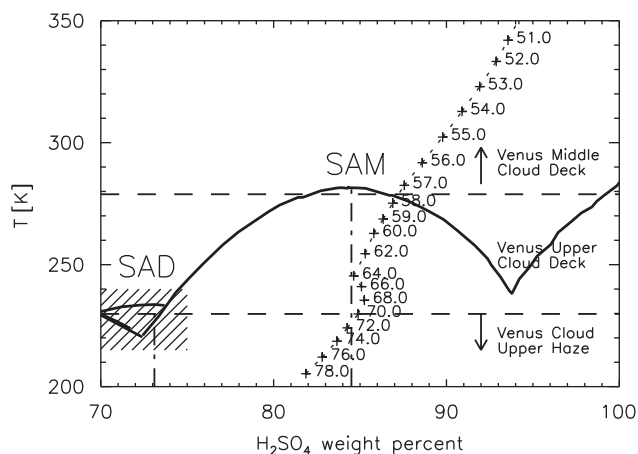


Fig. 1. The sulfuric acid freezing/melting phase diagram. The solid line represents the freezing temperature of sulfuric acid as a function of weight percent (by mass), from Gable et al. (1950). Sulfuric acid above the line is liquid, below is either frozen or supercooled liquid. The weight percents of the monohydrate (SAM) and dihydrate (SAD) are indicated by the dash-dot vertical lines. Typical Earth Stratospheric conditions are indicated by the diagonal hatching on the lower left of the diagram. The approximate locations of the Venus middle and upper cloud decks and upper hazes are indicated with text and horizontal dashed lines. The boundary between the middle and lower clouds is beyond the upper edge of the diagram. Note that since temperature increases vertically, altitude increases downwards in this diagram. Finally, also plotted, with a dotted line, is the “cooling curve” of a typical Venus sulfuric acid aerosol, assuming temperature profile from the Venus International Reference Atmosphere (Kliore et al., 1986), and water vapor mixing ratios from Pollack et al. (1993); individual Venus altitudes are indicated with symbols (+).

The physical nature of the frozen species of sulfuric acid is a matter of some disagreement in the literature. Rather than nucleating to form crystalline sulfuric acid monohydrate (SAM), supercooled sulfuric acid has been observed to become extremely viscous (Ohtake, 1993). Hence the cold sulfuric acid might be amorphous, or even a glass, rather than crystalline like SAM (Sill, 1972). On the other hand, Pinkley and Williams (1976) noted that white crystals began to form when a 87.5% sulfuric acid/water solution was cooled below 280 K, near the freezing point of SAM. Thus, it is not obvious what form or shape condensed particles of frozen sulfuric acid would take in the upper clouds of Venus. An extensive laboratory program has studied the freezing of sulfuric acid on Earth, but it concentrated on relatively dilute sulfuric acid, compared with the particles that form on Venus. The Venusian particles are more likely to freeze because their freezing points are higher (see Fig. 1).

3. Sulfuric acid clouds on present day Venus and the possibility of lightning

The Venusian cloud system is a three-layered cloud deck with areas of diminished particle concentration (traditionally referred to as upper and lower hazes on Venus) both above and below. The upper cloud, found between about 57 and 70 km, forms photochemically from SO₂ and H₂O. The SO₂ may be the product of volcanism, or may be the result of other sulfur gases in thermochemical equilibrium with surface rocks. SO₂ is likely recycled from the deep atmosphere below about 40 km where thermal chemistry dissociates the sulfuric acid back into its components (H₂O and SO₂). Because sulfuric acid has such a low vapor pressure at the temperatures of the upper cloud, the upper cloud should be thought of as a relatively involatile haze. As such, it is relatively insensitive to the air temperature, and hence to dynamical motions that can change the air temperature. Therefore, the upper cloud forms a fairly homogeneous but diffuse cloud layer, similar in terms of global coverage to that exhibited by the photochemical hydrocarbon haze on Titan. Below about 57 km, the vapor pressure of sulfuric acid and water over the cloud particles is relatively high, and therefore sulfuric acid clouds can evaporate in a relatively short period of time. As a consequence, the lower and middle cloud decks contain condensational clouds that are highly variable. The middle and lower cloud decks of Venus form by the condensation of sulfuric acid vapor transported up from beneath the clouds. The lower haze, which likely serves as condensation nuclei for the lower and middle cloud particles, extends from the cloud base down to about 40 km, and is likely a collection of involatile particles, possibly sulfur allotropes. The upper haze, on the other hand, extends from the tops of the upper cloud up to about 90 km and is likely composed of sub-micron sulfuric acid particles.

The Venus cloud particles require a multi-modal description. In this paper, we adopt the definitions of Knollenberg and Hunten (1980). Mode 1 has an effective radius of about 0.6 μm, and is found throughout the three main cloud decks. However, as noted above, its composition is unlikely to be the same at all altitudes. Mode 2 particles are spherical particles of sulfuric acid with effective radii between about 1.0 and 1.5 μm. These are the classic upper cloud particles first characterized by Hansen and Hovenier (1974). Finally, Mode 3 is a controversial class of particle that Knollenberg and Hunten concluded must be large particles of unknown composition, and possibly crystalline. However, subsequent analysis showed that the particles could possibly represent a large particle tail to the Mode 2 distribution that was mis-measured (Toon et al., 1984). This so-called “Mode 3 controversy” remains unresolved. Numerous workers have

referred to a Mode 3 of larger sulfuric acid particles, which is inconsistent with the measurements of Knollenberg and Hunten.

The lower and middle cloud particles then absorb infrared radiation from the warmer deep atmosphere and surface of Venus. This heating of the cloud base produces an unstable lapse rate within the cloud region (Pollack et al., 1980), which sustains the cloud by continually introducing fresh vapor from the subcloud region between about 40 and 48 km (James et al., 1997; McGouldrick and Toon, 2007). An optically thick cloud becomes self-supporting because radiative cooling from its top or heating from below sustains a moist adiabatic lapse rate. The middle cloud deck also cools radiatively from its top, which adds to the instability driving convection within the middle and lower cloud decks. This is similar to the formation of marine stratocumulus on Earth, which are also often driven radiatively (Fig. 2). In each case, the cloud is capped by a stable region, which results from upper-level subsidence on the Earth and by a combination of subsidence of the air in the upper cloud over portions of Venus and near-radiative equilibrium conditions in the upper cloud.

In Fig. 1, the freezing temperature of sulfuric acid is plotted as a function of weight percent of acid, over a range of weight percents that are reasonably expected in the clouds of Venus. Also shown in Fig. 1 is the “cooling curve” that an equilibrium sulfuric acid particle will experience as it descends through the Venusian atmosphere. Sulfuric acid at its equilibrium weight percent is maintained below its freezing point at all altitudes above about 57 km, an altitude that coincides with the observed transition between the middle and upper cloud regions, as shown in Fig. 3 (Knollenberg and Hunten, 1980). Thus, if the sulfuric acid freezes in the upper clouds, it will remain frozen until it melts near 57 km as it enters the middle cloud.

On Venus the ubiquitous sulfuric acid cloud particles equilibrate to an acid mass fraction that is more highly concentrated than in the Earth's stratosphere, due to the relatively high temperatures and the relatively lower concentration of water vapor. The atmosphere of Venus is similar to the stratosphere of Earth in terms of water vapor mixing ratio. The water vapor concentration in the region of the clouds is about 1 ppmv in the upper cloud region, while in the Earth's stratosphere it is about 3–5 ppmv. In the lower clouds of Venus the mixing ratio may increase to 30 ppmv at cloud base, but it is very warm so that the relative humidity is quite low relative to the Earth (Pollack et al., 1993; de Bergh et al., 1995; Bézard et al., 2009). These conditions correspond to relative humidities as low as 0.01%! Under such conditions, the concentration of sulfuric acid is in the range of about 80% to about 98% by mass (see Fig. 1). Consequently, the freezing point approaches the value for the monohydrate or pure sulfuric acid near 283 K (Gable et al., 1950). Under these

conditions sulfuric acid can be supercooled up to 60 K, making it likely that it may freeze.

The detection by Hansen and Hovenier (1974) of the signature of the primary rainbow scattering phenomenon in polarization data indicated that the upper cloud particles of Venus were predominantly spherical. However, as pointed out by Hansen and Hovenier, this observation does not completely rule out the possible existence of a small admixture of crystalline particles. Alternatively, the highly concentrated, supercooled, sulfuric acid may become an amorphous, highly viscous glasslike substance with a water to sulfuric acid molecular ratio between 1:1 and 2:1 (i.e., acid weight percent between about 85% and 73%) (Couling

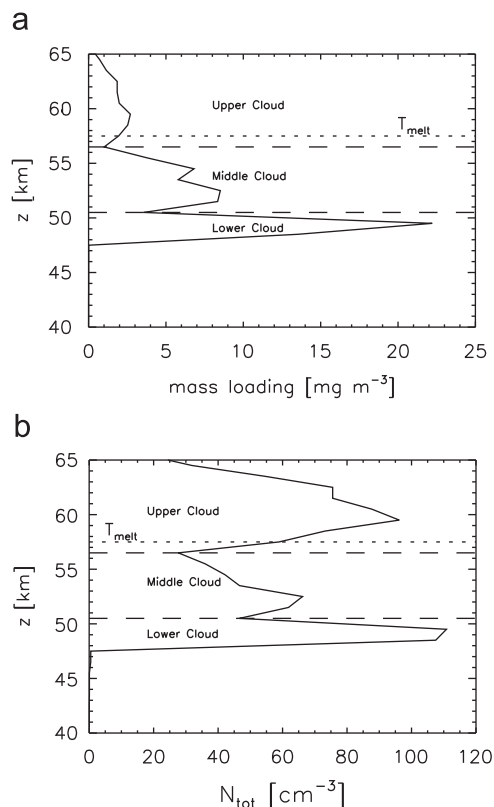


Fig. 3. (a) Mass loading and (b) particle number density of the Venus cloud system, as observed by the LCPS on Pioneer Venus. The number density includes only particles larger than $0.6\mu\text{m}$. In each panel, the dashed lines indicate the traditional divisions between the three cloud decks; and the dotted line represents the altitude of the melting temperature of sulfuric acid monohydrate (assuming the VIRA atmospheric structure, not necessarily that experienced by the LCPS probe).

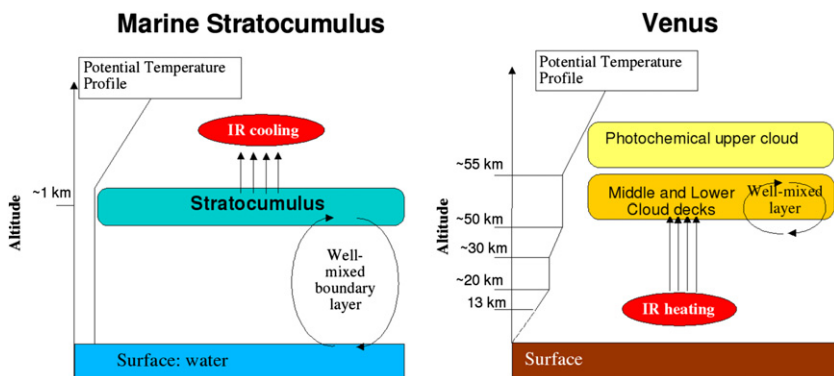


Fig. 2. A schematic comparison of the similarities and differences between the Venus cloud system and terrestrial marine stratocumulus clouds.

et al., 2003). A cloud of such amorphous sulfuric acid particles would consist of nearly spherical particles, and so might still produce the rainbow phenomenon seen in the polarimetry data.

If sulfuric acid ices can form in the upper clouds or hazes of Venus, they will grow quickly to large sizes because of the saturation vapor pressure difference between the liquids and the solid (this will not occur if the sulfuric acid becomes a glass, since the latent heat of the glass will be the same as the supercooled liquid). From the Clausius–Clapyron equation:

$$\frac{\partial \ln P_{\text{vap}}}{\partial T} = -\frac{\Delta H}{RT^2}, \quad (1)$$

it can be shown that the additional latent heat of melting present in the frozen phase significantly reduces the vapor pressure (P_{vap}) by increasing the value of the enthalpy change (ΔH). The same is true of frozen and liquid water in terrestrial clouds. The appearance of ice within a liquid cloud results in a rapid uptake of vapor by the ice particles in a cloud, at the expense of the liquid particles. On Earth, this Bergeron Process represents a key step in the process of transforming cloud droplets into rain.

Early, ground-based, observations indicated that the clouds of Venus consist of 1 μm , spherical particles (Hansen and Hovenier, 1974), composed of concentrated sulfuric acid (Sill, 1972; Young, 1973). By comparison, terrestrial water cloud particles are at least 10 times larger, and precipitation droplets are about a thousand times larger (Houze, 1993). While the possibility of frozen particles in the clouds of Venus has been mentioned in the literature (e.g., Sill, 1972; Young, 1973), it generally has been dismissed because of the strong evidence for spherical particles. The existence of non-spherical particles in the lower and middle clouds was suggested by Knollenberg and Hunten (1980), but the temperatures there are far too warm for ices of sulfuric acid to be stable (Gable et al., 1950), and the evidence in support of non-sphericity is disputed (Toon et al., 1984). Thus, if the controversial Mode 3 particles are crystalline, they cannot also be composed of sulfuric acid; another cloud constituent must be considered.

Occultation observations indicate that the sulfuric acid vapor concentration follows the saturation vapor pressure curve through the lower and middle cloud decks of the Venus atmosphere (Jenkins et al., 1994). However, this means that the atmosphere will be strongly supersaturated with respect to the ices. Consequently, it may be possible to form large (tens of microns) ice particles just above the melting layer in the clouds of Venus. The much less massive Venus cloud (as compared with terrestrial clouds) means that the particle sizes achieved will be smaller than typical terrestrial precipitation particles (which have sizes greater than 100 μm). However, the particle fall velocity depends on the square of the radius for the likely particle sizes, while the mass flux depends on the fifth power of the radius. Hence, the Venesian ice particles (or the melted remnants of them in the middle and lower clouds) could achieve sedimentation velocities and mass fluxes much higher than particles which have always been liquid.

If these same ice, or melted ice particles are able to pick up a significant amount of charge during the freezing/melting process, then this sedimentation may provide the physical charge separation necessary for a lightning discharge within the clouds, just as it does on Earth. If such charging of Venus cloud particles can be shown to have a simple microphysical origin, as we suggest is possible, then credence will be lent toward the controversial reported detections of lightning in the atmosphere of Venus, for example most recently by Russell et al. (2007). However, Michael et al. (2009) recently determined that the Venus atmospheric conductivity, though reduced by the presence of the clouds, was still too high to support the existence of lightning discharges brought about by cloud particle charging by galactic cosmic rays.

On the other hand, since the characteristics of the lightning that are reported to have been observed at Venus are similar to the characteristics of lightning on Earth (Russell et al., 2010), it seems reasonable to expect that it will be brought about by similar methods. Frozen particles in a supercooled environment can also grow by riming, which is a coagulative growth process whereby supercooled liquid droplets coagulate with and freeze directly upon a previously frozen particle. This process rarely results in 100% of the supercooled droplet mass freezing onto the frozen particle. One consequence of this is a net transfer of electrical charge (Saunders, 2008). It is currently believed that the most dominant charging processes in the generation of terrestrial lightning require collisions between particles involving a frozen phase (Saunders, 2008). Further investigation into these mechanisms can suggest times and places where it will be most favorable to observe lightning on Venus, for example with JAXA's *Akatsuki* mission (Nakamura et al., 2007).

4. Sulfuric acid clouds on early Mars

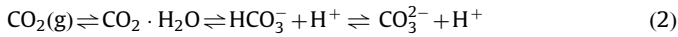
In 1971, the *Mariner 9* spacecraft discovered abundant river valley networks on Mars. The pressure of the present atmosphere of Mars is too low and the temperature too cold to sustain liquid water at the surface. The fact that the river valleys are located on the oldest terrains of Mars indicates that these features are geologically quite old (Carr and Clow, 1981). Recent dating (Fassett and Head, 2008) suggests that water last flowed through the river valley networks about 3.72 Ga ago, depending on the age dating scheme. It was once thought that a thicker CO_2 atmosphere than is currently present at Mars could sustain a greenhouse effect substantial enough to warm early Mars to the point of supporting liquid water at its surface, despite the fainter early Sun (Pollack et al., 1987; Squyres and Kasting, 1994). However, it has recently been shown that a CO_2 atmosphere would quickly escape from Mars prior to 4 Ga ago, so such an atmosphere would have to have been outgassed later than that time (Tian et al., 2009). It has also been shown that CO_2 is such a poor greenhouse gas that the quantities of CO_2 in the atmosphere of early Mars needed to achieve temperatures above freezing were so large that the CO_2 would become supersaturated, leading to the condensation of the CO_2 into clouds (Kasting, 1991). Thus, the mass of atmosphere needed to sustain warm enough temperatures at the surface could not be maintained if CO_2 alone were the source of the greenhouse warming (Forget and Pierrehumbert, 1997; Colaprete and Toon, 2003). Furthermore, such vast quantities of CO_2 would have had to have been removed from the atmosphere at some time before the present, either by loss processes or by sequestration in carbonate rocks. Loss by escape may have occurred. However, in the vision of Mars as being like contemporary Earth, continually flowing rivers (which contradicts studies of the geomorphology of the rivers which instead appear to have resulted from intermittent flow (Som et al., 2009)) should have led to significant carbonate deposits.

Despite a focused and aggressive search, such widespread carbonates have not yet been observed on the surface of Mars. Enough carbonate may be present in the Martian regolith to provide significant atmospheric abundance (Bandfield et al., 2003). However, regional geologic formations of carbonates, as would be expected from long-lasting water reservoirs, have only been detected in limited areas (Ehlmann et al., 2008).

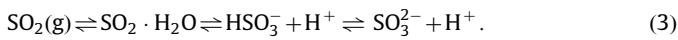
The discovery of jarosite minerals on the surface is consistent with a past wet environment rich in sulfur (Squyres et al., 2004). Such an environment may have been subsurface, and it is also possible that the jarosite originates from volcanic deposition. Widespread detection of sulfates from orbit suggests that these

sulfur-rich environments were common over large areas of Mars (Hynek et al., 2002). It has also been suggested that the production of sulfur dioxide from the volcanic production of Tharsis during the Late Noachian might have resulted in the acidification of an ancient Martian ocean (Bullock and Moore, 2007; Halevy et al., 2007). However, age dating shows that in the Late Noachian, when the river valley networks formed, clays were being deposited, while the sulfate deposits date from the late Hesperian, after the formation of the river valley networks (Fassett and Head, 2008).

The large abundance of sulfur dioxide in the lower atmosphere of Mars could have resulted in the formation of an acid rain. This decrease in pH, as a result of the greater abundance of sulfuric acid, a stronger acid than carbonic acid, would tend to inhibit the formation of carbonates:



and favor the formation of sulfates:



Bullock and Moore (2007) and Halevy et al. (2007) point out that the introduction of even small amounts of sulfuric acid to a water supply inhibits the formation of carbonate rocks to the favor of sulfite or sulfate rocks. Halevy et al. (2007) suggest that an atmosphere rich in SO_2 would result in the dissolution of that SO_2 in surface water, leading to acidic pH conditions that are expected to inhibit the carbonate formation. However, these ideas still fail to explain where the carbonate was deposited.

Recently, Halevy et al. (2007) and Johnson et al. (2008) suggested that an SO_2 greenhouse effect could potentially solve the puzzle of the ancient Martian valley networks. Bullock and Moore (2007) suggested that the presence of large quantities of SO_2 in the early Martian atmosphere would lead to the production of a photochemical haze of sulfuric acid, not unlike that seen in the upper clouds of Venus today. However, Tian et al. (2010) show that cooling by these sulfate aerosols will more than counter any greenhouse effect due to SO_2 , so that in fact a planetary cooling will occur.

In addition, there are many open problems with SO_2 greenhouses. For instance, the SO_2 greenhouse is needed to support liquid water on the surface of early Mars; yet the presence of the liquid water will rapidly destroy the SO_2 , assuming oxidants such as OH , O_3 , or H_2O_2 are present. Below, we explore the microphysical consequences of a buildup of volcanically produced sulfur dioxide for potential clouds and hazes in the late Noachian Martian atmosphere. Our goal with these simulations is to see whether the Late Noachian volcanic SO_2 production rate estimated by Halevy et al. (2007), based on the emplacement of Tharsis, is capable of making the rainfall from the clouds sufficiently acidic to inhibit carbonate formation at the surface.

4.1. Model description

We use the University of Colorado/NASA Ames Community Aerosol and Radiation Model for Atmospheres (CARMA) (Toon et al., 1988, 1989) to simulate the clouds in the simulations presented in this paper. We previously have used this code to analyse the microphysics and radiative-dynamical feedback in the middle and lower clouds of Venus (McGouldrick and Toon, 2007; McGouldrick and Toon, 2008a, b). The microphysics portion of the model activates sulfuric acid/water vapor solution droplets from involatile Cloud Condensation Nuclei (CCN). These CCN are assumed to be soluble in the solution. Growth of particles due to coagulation and coalescence, and via condensational growth, is considered, as well as droplet evaporation. Vertical transport of particles and gases occurs via particle sedimentation, prescribed

winds, and eddy diffusion. The changes due to the heating rates (if radiative transfer calculations are being performed) and the changes due to transport are applied during the dynamical timestep, which is then subdivided to handle the faster microphysical calculations.

4.2. Wet deposition of sulfate on early Mars

Settle (1979) estimated the photolytic lifetime of SO_2 in the early Martian atmosphere to be about 10 years. We assume this loss rate of SO_2 to estimate the photochemical production rate of H_2SO_4 vapors in the early Martian atmosphere. A rigorous treatment of the production rate of sulfuric acid vapor in the early Martian atmosphere would require a full model of atmospheric chemistry, similar to what has been done for Venus (Krasnopolsky, 2007).

In our simulations of early Mars, we will consider the effects of wet deposition, whereby SO_2 is scavenged from the atmosphere by the cloud water. The growth rate of the mass of SO_2 dissolved in the droplets is determined using a simple vapor scavenging calculation (Seinfeld and Pandis, 1998):

$$\frac{\partial m}{\partial t} = 4\pi r_p^2 \frac{D_g}{r_p} \left[1 + 0.3 \left(\frac{\rho_a v_{sed} r_p}{2\mu_a} \right)^{1/2} \left(\frac{\mu_a}{\rho_a D_g} \right)^{1/3} \right] (C_g - C_{eq}), \quad (4)$$

where the equilibrium aqueous concentration of SO_2 in water (C_{eq}) is determined via Henry's law calculations. In this equation, r_p is the droplet radius, D_g is the diffusivity of SO_2 gas through a CO_2 atmosphere, ρ_a and μ_a are the density and viscosity of air, v_{sed} is the sedimentation velocity of the particles, and C_g is the atmospheric concentration of gaseous SO_2 .

We assume that this mass of dissolved SO_2 represents the aqueous concentration of SO_2 , as indicated in (3). According to Henry's law considerations for aqueous phase chemical equilibria, we can determine the equilibrium total hydrogen ion concentration $[\text{H}^+]$ in the clouds droplets by calculating and incorporating the equilibrium reaction rate constants for the ionic dissociation of $\text{SO}_2 \cdot \text{H}_2\text{O}$ into bisulfite and sulfite. Note that if sufficient oxidants are also present in the atmosphere and are dissolved in the droplets, then the pH will likely drop even lower, due to the formation of sulfuric acid, which is stronger than sulfurous acid.

At this time, we do not incorporate radiative-dynamical feedback in these simulations of the early Mars atmosphere, nor do we perform radiative transfer calculations. We assume standing water at the surface, represented by a lower boundary condition on the water vapor concentration of 100% relative humidity, a surface temperature of 273 K, and a surface pressure of 1 bar of CO_2 . We calculate an atmospheric scale height ($H=g/\text{RT}$) of about 14 km; and an adiabatic lapse rate (g/C_p) of about 4.5 K/km, using 83 J/kg/K as the specific heat of CO_2 at 273 K. We also provide a flux of involatile cloud condensation nuclei (CCN) into the model at the surface. We assume a surface boundary condition of a distribution of CCN having an effective radius of 0.2 μm , and concentration of 200 cm^{-3} . The clouds form via diffusion of water vapor upward from the surface reservoir, and condensation onto the CCN. The nominal model includes a constant eddy diffusion coefficient (K_{diff}) of 10 m^2/s to ensure vertical mixing.

In this preliminary attempt at simulating the early Mars clouds, we assume that the impurities in the water (i.e., the sulfuric acid) lower the freezing point of the solution sufficiently so that it will not freeze in the Martian atmosphere. In future simulations, it will be important to consider the possibility of freezing, as the uptake of SO_2 by dissolving in the cloud droplets will obviously be curtailed, if the droplets are frozen. If the SO_2 cannot be dissolved in the cloud droplets, then the only sinks for

the SO_2 will be dissolution in possible standing surface water, or by chemical processes, including photochemistry.

4.3. Sulfuric acid clouds on early Mars limit the SO_2 lifetime

In contrast with Settle's 10 year timescale for photochemical removal of SO_2 , our simulations show that the removal of SO_2 from the atmosphere due to the dissolution in cloud droplets and wet deposition occurs significantly more rapidly, leading to a roughly steady state atmospheric concentration of about 0.02 ppmv SO_2 after a time of only a few months (see Fig. 4). Our nominal model results in a precipitation rate of about 40 cm/yr (see Table 1), comparable to but slightly less than Earth's global average precipitation rate (~ 100 cm/yr) (Köppen, 1923). This is perhaps not surprising, since we have assumed Earth-like temperatures and an ocean-covered surface.

The typical mass loading of the cloud in the nominal model is around 50 mg/m^3 , comparable to terrestrial fogs (Houze, 1993). The pH of the droplets in the cloud produced in the nominal simulation tend to be very acidic, having pH of 2.0 or less, for the most part, significantly more acidic than the threshold of 6.2, below which, sulfate formation is preferred over carbonate formation given a 1 bar CO_2 atmosphere (Halevy et al., 2007; Bullock and Moore, 2007).

The nature of our simulated early Martian cloud is significantly affected by parameters such as the eddy diffusion coefficient and the CCN boundary condition (see Table 1), but the pH of the simulated cloud is not very sensitive to the model assumptions. In Table 1, cloud mass indicates the peak mass loading within the cloud at steady state, and cloud altitude is the altitude at which the peak in cloud mass occurs. The mixing ratio of sulfur dioxide, q_{SO_2} , indicates the atmospheric SO_2 remaining in the gaseous state after the bulk of the mass has been dissolved into the cloud droplets.

We performed several test cases, results of which are shown in Table 1, to investigate the effects of some of the free parameters that are in our model. While somewhat unrealistically high, the test case in which we assume an eddy diffusion coefficient of $100 \text{ m}^2/\text{s}$ indicates the effects of a more vigorous overturning of the lower level of the atmosphere. The cloud mass and rainfall rates both increase significantly in this test case, exceeding that of a terrestrial tropical rain forest (~ 260 cm/yr).

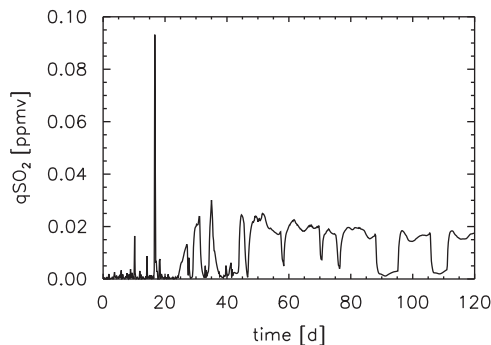


Fig. 4. The mixing ratio of SO_2 as a function of time in our nominal model.

Table 1
Early Mars acid rain sensitivity tests.

Parameter: units	Rain (cm/yr)	q_{SO_2} (ppbv)	pH	Cloud Mass (mg/m^3)	Cloud altitude (km)
Nominal	40	20	1.5–2.0	50	1.0
$K_{\text{diff}} = 100 \text{ m}^2/\text{s}$	300	4	1.5	200	2.0
CCN: 1000 cc^{-1}	40	15	1.5	50	1.0
rCCN $\sim 1 \mu\text{m}$	40	40	2.0	100	2.0
rh = 70%	2	~ 600	1.0	30	3.0

The CCN population can have a large effect on the resultant cloud. For example, a larger number of CCN will spread the condensing water vapor across a larger number of cloud droplets. Unless coagulation leads to larger particles, these smaller droplets, according to (4), will take up SO_2 at a slower rate (but will have longer residence times in the cloud, due to their smaller sedimentation velocities). This will likely have some effect on the pH of the cloud droplets. Similarly, a population of larger CCN will result in larger cloud droplets, and a more rapid uptake of SO_2 . However, these larger particles will rain out faster. These changes in the characteristics of the CCN might be related to differences in the makeup of the volcanic ash, for example.

Increasing the number of available CCN by a factor of five appears to have very little effect on the cloud. Increasing the typical size of the CCN by a factor of 10 in radius results in cloud droplets having slightly higher pH (but still very acidic), a doubling of cloud mass relative to the nominal case, and an increase in cloud altitude.

We also consider the effects on our nominal model of a decrease in the overall relative humidity. A decrease to 70% is probably more realistic, from a global average perspective, than the 100% assumed in our nominal model, for an early Mars that is only partly covered by water. In this case, the cloud base is about 3 km above the surface, and has a fairly small mass loading, comparable to the present-day Venus clouds (about 30 mg/m^3). The acidity of the clouds in this case is even stronger (pH around 1.0), but the rainfall rate is much lower (only 2 cm/yr). Perhaps most importantly, although the amount of SO_2 remaining in the atmosphere at steady state is slightly higher at about 600 ppbv, it is still significantly less abundant than the concentrations necessary to sustain an early Mars SO_2 greenhouse (Johnson et al., 2008; Tian et al., 2010).

5. Conclusions and implications

There has been much investigation into terrestrial sulfate aerosols, and various types of terrestrial clouds that interact with sulfites including PSC and acid rain. These past and continuing investigations can shed light on these analogous processes on Venus, Mars, and Titan.

We have previously shown that the Venus condensational clouds can be simulated using a radiative dynamical feedback and sulfuric acid condensation (McGouldrick and Toon, 2007). Here we have demonstrated the plausibility of the existence of frozen sulfuric acid monohydrate in the vicinity of the transition region between the upper and middle cloud decks of Venus. The temperatures at the tops of the Venus clouds will not support stable liquid sulfuric acid solutions. The particles must either be crystalline or supercooled liquids; the latter possibly glassy. Environmental conditions can support the existence of solid particles, and previous conclusions that the cloud particles are spherical, based on polarimetry observations cannot rule out either a small population of crystalline particles or a larger population of glassy particles.

The possible existence of frozen species of sulfuric acid in the atmosphere of Venus could have implications for lightning generation in the clouds of Venus. Terrestrial investigations of cloud particle charging indicate that a cloud with a mixture of both frozen and liquid species seems to be necessary for the generation of lightning. Should frozen sulfuric acid persist in the upper atmosphere of Venus, it might provide the mechanism for the generation of the controversial Venusian lightning. The frozen sulfuric acid particles should have a lower vapor pressure than the liquids as a consequence of the latent heat of fusion, so they will grow more quickly than, and at the expense of, the liquid sulfuric acid particles. They may also grow by riming, coalescence with smaller liquid particles. Such rimed particles might grow large enough to produce the spatial charge separation needed for a lightning discharge. Further research into the microphysical plausibility and implications of frozen sulfuric acid in the clouds of Venus are needed to address this question.

The formation of sulfuric acid aerosols has been shown to have been likely to have played a role in the climate evolution of Venus (Bullock and Grinspoon, 2001), and of Mars (this paper, and Tian et al., 2010). As discussed above, sulfuric acid aerosols also play a role in two of the most significant anthropogenically magnified atmospheric processes, ozone depletion and acid rain; and have been suggested as a solution for a third, global warming. However, there is still much research to be done in order to understand the nature of sulfuric acid in all of its potential phases, and its net effects on a planetary atmosphere. Since the conditions for the formation of sulfuric acid aerosols are likely to be common among active terrestrial planets, a better understanding of the nature of sulfuric acid aerosols and their role in planetary atmospheres seems vital to the study of terrestrial exoplanets and astrobiology, especially as a tool in comparative planetology.

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