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Photochemical and climate consequences of sulfur outgassing on early Mars

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ABSTRACT

Ancient Mars might have been warm and wet compared to today, but climate models have trouble reproducing this warmth, partly because of the faintness of the young Sun and partly because of inherent limitations to CO_2–H_2O greenhouse warming. In particular, Rayleigh scattering of incoming sunlight by a dense, CO_2-rich atmosphere leads to a high planetary albedo, thereby reducing the amount of sunlight absorbed by the planet. It has been recently suggested that the presence of 1–100 ppmv SO_2 in Mars' early atmosphere might have provided enough additional greenhouse warming to maintain a warm, wet early Mars. We show, however, that this warming should have been more than offset by cooling from sulfate and sulfur aerosols in early martian atmosphere. Hence, the paradox of Mars' early climate remains unresolved.

1. Introduction

Ever since 1971, when detailed pictures of fluvial features on the martian surface were returned by Mariner 9, researchers have debated their implications for early martian climate. Advocates of a warm early Mars (Pollack et al., 1987) pointed out that volcanic CO_2 should have accumulated in Mars' atmosphere, just as it is thought to have done on early Earth (Walker et al., 1981). Subsequent climate calculations showed, however, that the greenhouse effect of gaseous CO_2 and H_2O was not sufficient to produce a warm early martian climate (Kasting, 1991). Instead, CO_2 would freeze. In principle, CO_2 ice clouds could have provided significant greenhouse warming (Forget and Pierrehumbert, 1997), but only if fractional cloud cover was close to 100%, which is unlikely (Colaprete and Toon, 2003). The apparent lack of carbonate rock outcrops on the surface, except in restricted areas (Ehlmann et al., 2008), appears to cast further doubt on the concept of a dense CO_2-rich paleoatmosphere. Alternatively, it has been argued that the fluvial features were formed by saline liquid water activity under temperature much lower than 273 °C (Fairen et al., 2009), or by rainout of steam atmospheres, along with mobilization of surface or underground ice during and shortly after large impacts (Segura et al., 2002, 2008).

Recent studies (Fairen et al., 2004; Bullock and Moore, 2007; Halevy et al., 2007) have emphasized the possible importance of sulfur gases for both weathering and climate on early Mars. Carbonate formation could have been inhibited by acidic rainwater caused by the presence of either sulfate (Fairen et al., 2004; Bullock and Moore, 2007) or sulfite (Halevy et al., 2007). Halevy et al. further suggested that the greenhouse effect was augmented by the addition of 1–100 ppmv (parts per million by volume) of SO_2. The greenhouse effect of SO_2 on early Mars has been investigated previously. Postawko and Kuhn (1986) used a latitude-dependent energy-balance climate model to study a range of different atmospheric compositions, including the contribution of SO_2 to surface warming. More recently, Johnson et al. (2008) used a 3-D general circulation model to simulate a 500-mbar martian paleoatmosphere, assuming a solar luminosity equal to 75% of its present value and two different SO_2 mixing ratios: 6.14 ppmv and 245 ppmv, for which they obtained global average surface temperatures of 283 and 315 K, respectively. In the high-SO_2 simulations, their calculated annual average temperature was ~50 °C near the equator (see their Fig. 5). However, their climate model did not include either aerosols formed from SO_2 photolysis or Rayleigh scattering, the latter of which is one key reason why CO_2–H_2O greenhouse warming is inadequate for early Mars (Kasting, 1991). Thus, it is necessary to reconsider the climate effect of SO_2 on early Mars.

On modern Earth, SO_2 produced by volcanic eruptions cools the surface by creating highly reflective sulfate aerosols that persist for months to years in the stratosphere (Turco et al., 1982; Robock, 2000). Models for the anoxic early Earth atmosphere also predict that a

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significant fraction of outgassed SO_2 would still have been converted to sulfate aerosols (Pavlov and Kasting, 2002; Zahnle et al., 2006). Plescia (1993) estimated the volatile release from Elysium volcanism on Mars and suggested that the short-term effect of SO_2 volcanic outgassing would have been to warm the climate but the long term effect would have been surface cooling, because of the formation of sulfate aerosols. As the sulfate aerosols settled from the atmosphere, the climate could have returned to its pre-eruption equilibrium.

In a recent study, Johnson et al. (2009) used a full 1-D atmospheric photochemical model to investigated the lifetime of low to moderate levels of SO_2 (10 ppbv to 1 ppmv) in Mars' early atmosphere and derived an e-folding timescale of 10^2–10^3 years. They argued that repeated transient warming periods, each lasting hundreds of years after volcanic activity, might help explain valley formation on early Mars. However, the SO_2 concentration range in Johnson et al. (2009) does not coincide with that in Johnson et al. (2008), and could not have raised surface temperature above 230 K based on our climate calculations (discussed below). Here, we consider the formation of sulfate and sulfur aerosols under higher SO_2 concentration cases and determine the combined climatic effect of SO_2 and aerosols in Mars' early atmosphere.

2. Model descriptions

2.1. Climate model

To test the effects of SO_2 and aerosols on martian paleoclimate, we expanded the 1-D radiative–convective climate model of Haqq-Misra et al. (2008) to include both sulfate and elemental sulfur aerosols. This model treats absorption of solar energy using a δ 2-stream approximation of multiple scattering (Toon et al., 1989) and uses correlated-k coefficients to parameterize absorption by gaseous species at solar and thermal-infrared wavelengths. The same 2-stream method is used in both wavelength regimes; however, the source function is scattering of the direct solar beam in the visible and LTE thermal emission in the infrared. The thermal-IR k-coefficients for CO_2 and H_2O were originally incorporated into the model by Mischna et al. (2000) and are described in detail there. Continuum absorption by H_2O from 8 to 13 µm and collision-induced absorption by CO_2 near 7 µm and longward of 20 µm were treated as in Kasting et al. (1984). This method parameterizes CO_2 absorption most strongly (Halevy et al., 2009). The latter parameterizations are shared with the model of Kasting (1991), but the k-coefficient method is different from the band model approach used in the earlier paper. Moist CO_2 and H_2O adiabats, corrected for non-ideal behavior of CO_2, were assumed in the convective troposphere in regions where CO_2 and H_2O were condensing (Kasting, 1991).

To adapt the model to early Mars, the vertical resolution was increased from 25 to 100 levels, and the (variable) vertical grid spacing was adjusted to make the levels 4 times narrower in log-pressure space at the bottom of the grid than at the top, thereby providing higher resolution in the convective troposphere. The higher resolution produced an increase of roughly 10 K in the amount of greenhouse warming at high CO_2 pressures, in comparison with the model in Kasting (1991), by decreasing emission to space from regions where the temperature gradient is steep. Further increases in vertical resolution had little effect on the results. New thermal-IR absorption coefficients for SO_2 were derived for this study. SO_2 absorption data were obtained from the PNNL (Pacific Northwest National Lab) database. 6-term k-coefficients were derived in 14 different broadband intervals near 4–5 µm, 7–10 µm, and 16–23 µm. These coefficients were derived for a pressure of 1 bar and a temperature of 25 °C. Because most of the absorption in the model atmospheres occurs at pressures <1 bar, our coefficients should provide an upper limit on greenhouse warming by SO_2 (see the Results section).

Absorption and scattering of visible/near-UV light by elemental sulfur particles were also included in the climate model. Elemental sulfur has been suggested as the source of UV absorption in the Venus clouds (Toon et al., 1982). The absorption there is attributed mostly to allotropes of amorphous sulfur, *i.e.*, sulfur chains of various lengths, ranging from S_3 to S_8. Particulate S_8 is also a strong absorber of UV radiation (Bass, 1953). A description of the optical properties of S_8 and sulfate aerosols is in the Supplemental materials. We assumed crystalline S_8 particles in these calculations.

2.2. Photochemical model

The vertical profiles of SO_2 and aerosol particles were calculated with a 1-D photochemical model derived from that of Pavlov et al. (2001) and Domagal-Goldman et al. (2008). To adapt this model to early Mars, we eliminated all hydrocarbon species with more than one carbon atom, with the exception of ethane, C_2H_6. We also eliminated hydrocarbon aerosols, leaving elemental sulfur and sulfate aerosols as the only particulate species. For photolysis of H_2SO_4, the previous model (Pavlov et al., 2001) assumed similar UV cross sections as those of HCl, following the treatment in Turco et al. (1979). Newer studies suggested much lower UV cross sections (Burkholder et al., 2000; Hintze et al., 2003) and emphasized the significance of H_2SO_4 photolysis by visible and near-IR photons in present Earth stratosphere (Vaida et al., 2003; Mills et al., 2005). In this work we use the new UV, visible, and near-IR absorption coefficients for H_2SO_4 photolysis (Mills et al., 2005; Lane and Kjaergaard, 2008; Kjaergaard et al., 2008). We also included SO_3 photolysis (through the $SO_2 + O$ pathway) based on the cross section data in Buckholder and McKeen (1997). The modified photochemical model contains 45 species (27 long-lived ones and 18 short-lived ones), linked by 219 chemical reactions. Long-lived species undergo transport by molecular and eddy diffusion in our model, whereas short-lived ones are assumed to be in photochemical equilibrium. The following reaction rate constant was updated: $N(^4S) + NO \rightarrow N_2 + O$, $k = 2.1\times^{-11}\exp(100/T)$ (Smithtro and Sojka, 2005).

The range of surface pressures considered for the photochemical calculations was 0.5–3 bar, the assumed surface temperature was 235 K, and the dominant atmospheric constituent was taken to be CO_2. The vertical grid extended from the surface to 128 km in 2-km increments. Vertical transport rates were estimated as follows: We took the eddy diffusion profile (Massie and Hunten, 1981) from our 1-bar Earth model and assumed that the same values applied at equivalent pressures on Mars. At pressures above 1 bar, our climate model predicts that the atmosphere would be convective; hence, we used an eddy diffusion coefficient of $10^5\ cm^2\ s^{-1}$, which is appropriate for an Earth-like troposphere. Note that these values are much lower than those that are typically assumed for the present, low-pressure martian atmosphere (Zahnle et al., 2008). Sensitivity experiments were performed with other eddy diffusivity profiles, but no significant change in model behavior was observed.

Sulfur gases were injected into the model at various rates, simulating volcanic outgassing. An H_2S/SO_2 ratio of 1 was assumed in the base cases, following Halevy et al. (2007), who argued that the released sulfur gases should be at least half H_2S because the martian mantle is more reduced than that of Earth. Recent work on magma degassing on early Mars suggests that SO_2 should have been the dominant sulfur species during the emplacement of the Tharsis system (Gaillard and Scaillet, 2009). Nevertheless, sensitivity runs show that our conclusion does not change significantly with enhanced or decreased H_2S/SO_2 ratios. In all models, H_2 was injected into the atmosphere at a flux $1\times10\ cm^{-2}\ s^{-1}$ (5×10^{11} mol/yr), a value close to that assumed in early Earth models (Pavlov et al., 2001). At the top boundary, hydrogen was assumed to escape at the diffusion-limited rate (Zahnle et al., 2008), and downward diffusive fluxes of CO and O were included to account for the photodissociation of CO_2 above the top boundary. The total hydrogen concentration in the model is balanced by the volcanic outgassing of hydrogen and the atmosphere escape.

Sulfate and elemental sulfur aerosol concentrations were calculated using the method of Toon and Farlow (1981) and Pavlov et al. (2001). In this method, a monodisperse particle size distribution is assumed (one average size at each altitude); the size is estimated by comparing the relative lifetimes for coagulation, diffusion, and sedimentation. The calculated particle number density and radius and the optical properties of sulfate and sulfur aerosols are inputs for our 2-stream radiative transfer model (Toon et al., 1989), which is used to compute photolysis rates.

The parameterization of rainout rates in our model assumes that the removal rate of each gas depends nonlinearly on its solubility (Giorgi and Chameides, 1985). Hence, highly soluble gases such as SO_2 and H_2SO_4 are removed much faster than weakly soluble gases such as H_2S, although all gases could have been removed slowly on a cold early Mars (see below). Sulfate and sulfur aerosols are also rained out rapidly when the climate is warm. Besides rainout, species can be lost from the atmosphere through wet or dry deposition. Surface deposition velocities for these gases were estimated (1 cm/s for SO_2 and H_2SO_4) following Lee and Schwartz (1981) and Kasting and Ackerman (1985). These velocities are appropriate for air–sea mass transfer.

The above treatments may or may not apply to early Mars because there is uncertainty on how the rainout and deposition processes would work there. If early Mars' surface was cold, the rainout rates of all gases could have been much lower than typical terrestrial values. Therefore we explored a wide range of rainout and deposition rates in the model to test the robustness of our results. In sensitivity tests corresponding to cold early Mars scenarios, both the rainout and surface deposition rates for gases were multiplied by a specified reduction factor. The rainout of aerosol particles was reduced accordingly, but their dry deposition was not reduced. If a putative martian ocean was saturated with SO_2 and dissolved S(IV) species, as assumed by Halevy et al. (2007) and in some early Earth models (Kasting et al., 1989), both SO_2 rainout and deposition should have been balanced by an equivalent return flux of SO_2 into the atmosphere. Intuitively, both the atmospheric SO_2 content and its greenhouse effect are maximized when both rainout and surface deposition are turned off. On the other hand, the aerosol loading in the atmosphere and its anti-greenhouse effect should also be maximized when rainout is slow. And this is indeed what the photochemical model calculations show. The following table summarizes the rainout and deposition conditions explored in our model:

	SO_2		Other gases		Aerosols	
	Rainout	Deposition	Rainout	Deposition	Rainout	Deposition
Normal rainout	Zero	Zero	N	N	N	N
Low rainout	Zero	Zero	R	R	R	N

N = normal (terrestrial) rates, following the parameterization in Giorgi and Chameides (1985), Lee and Schwartz (1981), and Kasting and Ackerman (1985).

R = rates reduced by a specified reduction factor (10, 100, 1000, etc.) from the normal parameterization.

3. Results

We began by repeating the climate calculations from Fig. 7 of Kasting (1991), which showed global mean surface temperature as a function of surface pressure and solar flux for cases with no SO_2. The relative solar luminosity, S/S_0, was 0.75 or lower (Gough, 1981) prior to 3.8 b.y. ago, when the martian valleys are thought to have formed. All calculations assume cloud-free conditions, a fully saturated troposphere, and a surface albedo of 0.22. This value is close to the observed albedo of present Mars (Kieffer et al., 1977) and also allows the model to reproduce the present mean martian surface temperature, 218 K, given present atmospheric composition and solar insolation. Our new results are shown in Fig. 1. The solid curves show global mean surface temperature, T_s, for a fully saturated CO_2–H_2O atmosphere. The previous calculations show that for a relative solar luminosity of 0.7, T_s reaches a maximum value of 214 K at a surface pressure of 1.5 bar (Kasting, 1991). Our new calculation shows that the maximum T_s is ~220 K at a surface pressure of 2 bar. The maximum T_s for relative solar luminosity of 0.8 in Kasting, 1991 is ~240 K at 3–4 bars, and in our new results it is 260 K at ~4 bars. These differences are caused primarily by the increased vertical resolution in our new model. At still higher surface pressures, the new model behaves similarly to the old one: the increase in planetary albedo caused by Rayleigh scattering outweighs the increase of the greenhouse effect, so the surface cools.

According to these calculations, the maximum surface temperature that could have been supported by a 3-bar, CO_2–H_2O atmosphere at 3.8 b.y. ago was about −40 °C. To determine whether and how SO_2 could have warmed the climate, we recalculated T_s as a function of surface pressure for $S/S_0 = 0.75$ and for various SO_2 mixing ratios ranging from 0 to 10^{-2} (Fig. 2). In these calculations, SO_2 was assumed to be well mixed vertically, and aerosols were neglected. Fig. 2 shows that mean surface temperatures above the freezing point of water can be achieved in a 4-bar CO_2 atmosphere with 10 ppmv SO_2 (although recall that this may be an overestimate because the SO_2 absorption coefficients were derived at 1 bar pressure). For zero SO_2 and a 3-bar CO_2 atmosphere, and for a solar luminosity of 0.75 times present, the calculated mean global surface temperature in Postawko and Kuhn (1986) was 241 K, which is 10 K warmer than what we find under these same conditions (Fig. 2). For zero SO_2 and a 0.5-bar CO_2 atmosphere, Johnson et al. (2008) found annual average temperatures above freezing near the equator. By comparison, we calculate a global mean surface temperature of ~215 K for this case (Fig. 2). The neglect of Rayleigh scattering in both these calculations could be the cause of the differences from our results. Adding 1000 ppmv of SO_2 to the atmosphere increased T_s by 27 K in Postawko and Kuhn (1986). By comparison, we get 70 K of additional warming in this case (Fig. 2).

To investigate the radiative effect of sulfate and sulfur aerosols (which were ignored in Fig. 2), we used our photochemical model to calculate the vertical distributions of sulfate and sulfur aerosols in CO_2-dominated early Mars atmospheres for different SO_2 concentrations. The calculated altitude-dependent profiles of aerosol particles and SO_2 were then incorporated into the 1-D climate model to compute surface temperatures. All rainout rates were explored in our calculations, but only those with normal rain out rates, which minimize aerosol concentrations and thus should provide optimum net surface warming, are described here. The climate and photochemical calculation results for a 3-bar CO_2 atmosphere are shown as solid curves in Fig. 3. Corresponding calculations in which aerosols were neglected are shown

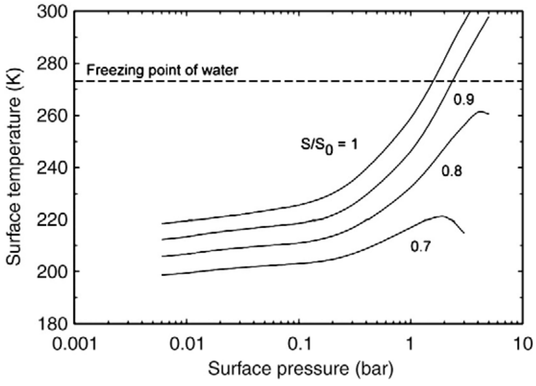

Fig. 1. Mean surface temperature as a function of surface pressure for a CO_2–H_2O atmosphere. S/S_0 represents the solar luminosity relative to today's value.

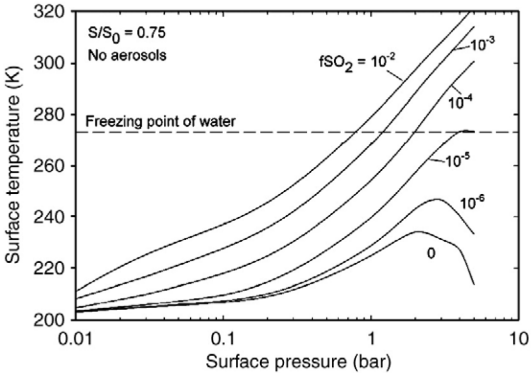

Fig. 2. Mean surface temperature as a function of surface pressure for a CO_2–H_2O–SO_2 atmosphere with $S/S_0 = 0.75$. The effect of sulfate aerosols has been ignored in these calculations.

as dotted curves. As the computed SO_2 mixing ratios increase from 1 ppbv to 10 ppmv, the sulfate aerosol extinction optical depth at 550 nm increases from 0 to ~2 (panel A), and the planetary albedo increases from ~0.42 to more than 0.5 (panel B). As a result, whereas the surface warms by as much as 40 degrees in the "non-aerosol" calculations, the surface cools by 30 degrees over this same range of SO_2 mixing ratios when aerosols are included (panel C). Thus, the net effect of volcanic sulfur outgassing is surface cooling, instead of warming. At SO_2 mixing ratios <1 ppmv, the SO_2 warming and the aerosol cooling compete against each other, although the combined effect of the two is small (less than 3 degrees). But once the SO_2 mixing ratio rises above ppmv level, the aerosol optical depth approaches ~1, the planetary albedo increases sharply, and dramatic net surface cooling occurs.

Panel D shows that sulfur outgassing fluxes 2 or 3 times greater than the maximum annual flux proposed for early Mars, 8×10^{9} cm^{-2} s^{-1} (4×10^{11} mol/yr) according to Halevy et al. (2007), would have been needed to maintain 10 ppmv SO_2 in the normal rainout case. Results of the low rainout cases are shown in panels A and D as crosses and stars. Much smaller volcanic sulfur outgassing fluxes are needed to maintain the same level of SO_2 in these cases. But this benefit is more than offset by the enhanced aerosol optical depths in the atmosphere under the same level of SO_2 (panel A). Thus, the net surface cooling caused by volcanic outgassing of sulfur would have been even more severe if the rainout rate was low on early Mars.

The diamond symbols in panel 1A represent S_8 aerosol extinction optical depth under terrestrial rainout conditions. Calculated optical depths are of the order of a few tenths to as high as 1, so these particles are not negligible. However, they do little to change our basic conclusions from these calculations. Although small S_8 aerosols ($r<0.01$ μm) have a low single scattering albedo (representing high absorption capability) at wavelengths shorter than 400 nm, the S_8 aerosols produced in the photochemical model are ~0.2 μm in size at altitudes below 50 km for SO_2 concentration ≥3 ppmv (Supplemental materials). Because of this, the calculated single scattering albedos of S_8 aerosols are relatively high, and so S_8 aerosols also contribute to the surface cooling (by as much as 20 K in the 3 ppmv SO_2 case). When the H_2S/SO_2 ratio in the outgassing flux was increased, the sulfate aerosol

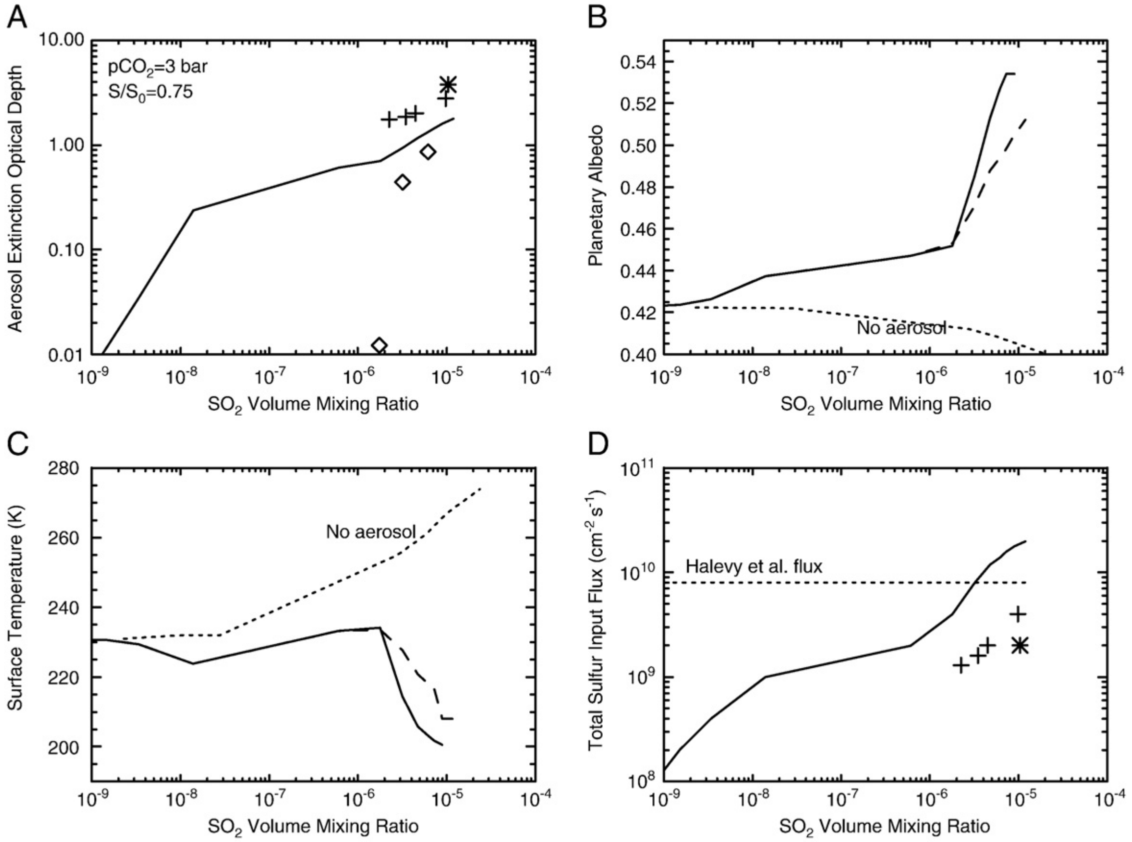

Fig. 3. Coupled photochemical and climate model calculations including both SO_2 and aerosols. Panel 'A'—aerosol extinction optical depth at 5500 Å. The solid curve is for sulfate aerosols under normal (terrestrial) rainout conditions. The diamond symbols are for S_8 aerosols under normal rainout condition. The crosses are for sulfate aerosols for rainout reduced by a factor of 100. The star is for sulfate aerosols for rainout reduced by a factor of 1000. Panel 'B'—planetary albedo. Panel 'C'—surface temperature. Panel 'D'—combined (SO_2+H_2S) fluxes, with the same symbols as those in panel A. These calculations are for a 3-bar atmosphere with $S/S_0 = 0.75$. Dotted curves in panels B and C show similar calculations in which sulfate aerosols are neglected.

optical depth decreased, the S_8 aerosol optical depth increased, and the surface temperature decreased even further. Thus, adjusting the sulfur outgassing species does not help to warm the surface in our models.

4. Discussion

4.1. Absorption capability of elemental sulfur aerosols

The particles in our model are assumed to be entirely crystalline (orthorhombic) S_8. Elemental sulfur has been suggested as the source of UV absorption in the Venus clouds (Toon et al., 1982) and the absorption there is attributed mostly to allotropes of amorphous sulfur, *i.e.*, sulfur chains of various lengths, ranging from S_3 to S_8. The optical properties of amorphous sulfur particles in the visible wavelength range are close to those of crystalline sulfur particles and thus would not have changed our conclusion. As discussed by Bass (1953) and by Toon et al. (1982), the addition of shorter-length sulfur allotropes could shift the absorption to longer wavelengths, thereby making sulfur particles more important for climate. In addition we have assumed that all S_8 particles have the same size at any altitude. This mono-size distribution assumption may underestimate the presence of small S_8 particles, which have stronger absorption capability than do large ones (Supplemental material). Both small S_8]particles and sulfur allotropes might cause greater absorption of solar radiation, thereby lowering the planetary albedo and raising the surface temperature. But any warming caused by such particles would have to overwhelm the predicted cooling from sulfate aerosols.

To test how significantly small S_8 aerosols might have influenced our climate calculations, we artificially redistributed the mass of sulfur particles obtained in our photochemical model evenly into 5 different size bins (centered at sizes at 0.002, 0.007, 0.02, 0.07, and 0.2 µm, respectively) and carried out the climate calculations with the manipulated S_8 particle population. The results are shown as dashed curves in panel B and C of Fig. 3. Using the new size distribution reduced the cooling effect of S_8 particles from -20 K to -7 K, and thus helps to raise the surface temperature. Because the uniform mass distribution overestimates particle densities in the nucleation mode (~0.01 µm) and underestimates those in the accumulation mode (~0.1 µm), a realistic scenario should lie between the dashed and the solid curves in panels B and C of Fig. 3. We further tested a wide range of particle radii, densities, and distribution parameters for 0.5 and 3.0 bar CO_2 atmospheres, and in no case did we find significant warming above the background temperature. Crystalline S_8 particles always introduce a net cooling effect.

Fig. 3 in the main text shows a critical transition in planetary albedo and surface temperature at an SO_2 mixing ratio near 2 ppmv. This is partially caused by the increased sulfate aerosol optical depth, but it is also related to the rapid increase in S8 aerosols in our model at this SO_2 concentration (optical depth shown as diamond symbols in Fig. 3A). A series of sensitivity runs in which SO_2 was the sole outgassed volcanic sulfur species were carried out, and the highest surface temperature obtained was 231 K. So, once again, volcanic SO_2 was not able to warm early Mars.

4.2. Source of sulfate aerosols

SO_2 injected into the present Earth stratosphere reacts with OH and H_2O to form H_2SO_4 within weeks after volcanic eruptions (Robock, 2000). On early Mars the availability of H_2O and OH might have been limited by cold surface temperature and the lack of UV photons. Our calculations (Supplemental material) show that the oxidation of SO_2 occurs primarily through the 3-body reaction $SO_2+O+M \rightarrow SO_3+M$, in which atomic oxygen is the product of CO_2 and SO_2 photolysis. This is similar to the sulfur photochemistry in Venus' atmosphere, where the extra source of oxygen from CO_2 photolysis favors the oxidation of SO_2 into SO_3 over the disproportionation of SO_2 to SO_3 and elemental sulfur (Mills et al., 2007).

4.3. Temporal variability

Our photochemical model seeks a steady state solution, and we did not investigate the temporal variability associated with the injection of SO_2 into the atmosphere and the subsequent formation process of the aerosols after volcanic eruption. On a time scale of decades, the release of SO_2 into the Earth's present atmosphere is dominated by non-violent volcanic fuming (Bluth et al., 1993) and not by large scale violent eruptions, such as Pinatubo. This partially justifies the steady state solution.

Suppose that a large amount of SO_2 was injected into the atmosphere by violent volcanic eruptions on early Mars. Then, additional greenhouse warming could conceivably occur before aerosols began to form in the atmosphere (Plescia, 1993; Johnson et al., 2009). Our climate calculations predict that at least 10 ppmv SO_2 would have been required to raise surface temperature above the freezing point without considering the aerosol effect (Fig. 2). In the presence of sulfate aerosols, the calculations also show that a sulfate aerosol optical depth of 0.1 at 550 nm would have been adequate to reduce the surface temperature by 10 K. Using a mass scattering efficiency of 3×10^4 cm^2 g^{-1} (Seinfeld and Pandis, 1998), an optical depth of 0.1 corresponds to a column mass of 3×10^{-6} g cm^{-2}, or a column density of 2×10^{16} cm^{-2}. The limiting step to form H_2SO_4 from SO_2 is $SO_3+H_2O \rightarrow H_2SO_4$, which has a column-integrated reaction rate of 3×10^9 cm^{-2} s^{-1} in the 10 ppmv SO_2 case. Thus, the aerosol formation time scale in our model is of the order of 10^7 s, or a few months. In comparison, SO_2 injected into the Earth's stratosphere after volcanic eruptions forms H_2SO_4 on a time scale of weeks (Robock, 2000). Thus, although the e-folding time for the reduction of atmospheric SO_2 was hundreds of years (Johnson et al., 2009, our model predicts essentially the same e-folding time), the transient warming period following a volcanic eruption should only last for months, followed by years of surface cooling.

To elevate the SO_2 concentration from negligible values to 10 ppmv in a 4-bar, CO_2-dominated, early Mars atmosphere would require the addition of 1×10^{17} g of SO_2 into the atmosphere. Mount Pinatubo emitted 2×10^{13} g of SO_2, while the annual flux of SO_2 from explosive volcanoes on the Earth is on the order of 4×10^{12} g/yr, and non-explosive volcanoes account for 10^{13} g/yr (Bluth et al., 1993). Thus, transient warming on early Mars could only have occurred after volcanic eruptions 10^4 times more powerful than Mount Pinatubo. If the estimate of total maximum sulfur outgassing during the Tharsis emplacement, 10^{21} g of sulfur (Halevy et al., 2007), is correct, then up to ~10^4 such short (monthly) transient warming events could have occurred in the mid- to late-Noachian. Another possible way to release SO_2 into early Mars atmosphere would have been through impacts into large surface sulfate deposits. This mechanism could have increased the frequency of SO_2 injection into early Mars atmosphere, especially during the late heavy bombardment period — another interesting link between impacts and early Mars climate. Whether the early martian valley networks could have been formed in such a scenario remains an open question.

4.4. Other model variables

Additional photochemical simulations were carried out with different surface temperatures, CO_2 partial pressures, and eddy diffusivity profiles. At higher surface temperatures water vapor becomes more readily available, which enhances H_2SO_4 formation. In the meantime, more water vapor makes the rainout of sulfate aerosols faster and thus could reduce the sulfate aerosol content in the atmosphere. At lower CO_2 partial pressures, Rayleigh scattering becomes less significant, which results in a lowered planetary albedo. Also, more UV photons can reach lower altitudes, thereby enabling additional photochemistry. But the CO_2 greenhouse effect is also reduced at lower CO_2 pressures. The eddy diffusion coefficient of 10^5 cm^2 s^{-1} used in the photochemical model is lower than those in present martian atmosphere (Zahnle et al., 2008). Using a higher eddy diffusion coefficient makes the vertical mixing of the atmosphere more efficient and could enhance the oxidation state of the middle atmosphere. Although the model behaviors are complex in these cases, all of our simulations generate average surface temperature at least 30 degrees below the freezing point.

One inherent shortcoming of using 1-D climate models is that the hydrological cycle can only be approximated by the global mean, time-averaged surface temperature, which ignores possible spatial variability. The closer the global mean surface temperature is to 273 K, the more likely it is that an active hydrological cycle could operate at the warmer locations on early Mars. The behavior of water vapor in the atmosphere and at the warm spots on early Mars deserves special attention in future studies.

We have used fixed surface temperature at 235 K in the photochemical calculations. This is roughly consistent with the surface temperature calculated by the climate model for early Mars (Fig. 3C). Because the main conclusion of this work is that the combined effect of SO_2 and sulfur aerosols would have been inadequate to warm up early Mars, carrying out model simulations with a lower surface temperature would not change our conclusion. A surface temperature significantly higher than 235 K is not consistent with the climate calculations. More importantly, the main effect of a higher surface and atmosphere temperature profile in the troposphere would have been more abundant water vapor in the atmosphere, which would have enhanced the formation of sulfate aerosols. Thus, using a surface temperature of 235 K provides a conservative estimate on the sulfate aerosol formation efficiency and an underestimate of the aerosol cooling effect. Our conclusion would therefore stand if the climate and the photochemical models were fully coupled.

We focused on simulations with Earth-like rainout rates for non-SO_2 species and zero dry deposition and rainout rate for SO_2. If the rainout rates for non-SO_2 species were lower than the terrestrial value, which is likely if early Mars surface temperature was below freezing, the aerosols should have built up in the atmosphere and induced a strong anti-greenhouse effect. This, in turn, is self-consistent with the low rainout rates. Rainout rates higher than the terrestrial value should only have been possible if the surface temperature was higher than the global mean temperature of Earth today (288 K). Such temperatures were not obtained in any early Mars climate model. Nevertheless, high rainout rate (3× and 10× the terrestrial rate) simulations were carried out with combined sulfur volcanic outgassing rates between $2\times10^{9}\ \mathrm{cm}^{-2}\ \mathrm{s}^{-1}$ and $1.2\times10^{10}\ \mathrm{cm}^{-2}\ \mathrm{s}^{-1}$, and the calculated surface temperature never exceeded ~230 K. Thus, the conclusions in the paper should be robust.

5. Conclusion

We conclude that the greenhouse effect of SO_2 injection into the atmosphere would have been ineffective in warming early Mars for timescales longer than a few months because it would have been outweighed by surface cooling from the inevitable formation of sulfate and large S_8 aerosols. If repeated short (monthly) warm periods were not responsible for the formation of martian valleys, early Mars must have been kept warm by other mechanisms, or else the martian valleys must have formed under a cold climate.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2010.04.016.

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