

NOTE

CO₂ Greenhouse in the Early Martian Atmosphere: SO₂ Inhibits Condensation

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Many investigators of the early martian climate have suggested that a dense carbon dioxide atmosphere was present and warmed the surface above the melting point of water (J. B. Pollack, J. F. Kasting, S. M. Richardson, and K. Poliakoff 1987. *Icarus* 71, 203–224). However, J. F. Kasting (1991. *Icarus* 94, 1–13) pointed out that previous thermal models of the primitive martian atmosphere had not considered the condensation of CO₂. When this effect was incorporated, Kasting found that CO₂ by itself is inadequate to warm the surface.

SO₂ absorbs strongly in the near UV region of the solar spectrum. While a small amount of SO₂ may have a negligible effect by itself on the surface temperature, it may have significantly warmed the middle atmosphere of early Mars, much as ozone warms the terrestrial stratosphere today. If this region is kept warm enough to inhibit the condensation of CO₂, then CO₂ remains a viable greenhouse gas. Our preliminary radiative modeling shows that the addition of 0.1 ppmv of SO₂ in a 2 bar CO₂ atmosphere raises the temperature of the middle atmosphere by approximately 10 degrees, so that the upper atmosphere in a 1D model remains above the condensation temperature of CO₂. In addition, this amount of SO₂ in the atmosphere provides an effective UV shield for a hypothetical biosphere on the martian surface. © 1997 Academic Press

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Introduction. The surface of Mars exhibits many ancient fluvially generated channels, strongly suggesting the existence of a warmer climate that could sustain flow of water (see, e.g., the review by Baker *et al.* 1992). But the current atmosphere of Mars is cold and arid; the greenhouse effect due to CO₂ is only about 6 K. To sustain a warm climate with fluid flow on the surface a greenhouse effect of 30 K is needed. Modeling by Cess *et al.* (1980) and Pollack *et al.* (1987) showed that a CO₂ atmosphere on the order of a bar would provide a sufficient greenhouse for the early Mars. However, Kasting (1991) pointed out that all previous thermal models of the primitive martian atmosphere had neglected the condensation of CO₂. When this effect was incorporated, Kasting found that a CO₂ greenhouse was inadequate to warm the surface, especially when the solar luminosity was about 25–30% lower than today.

Early work on the martian greenhouse has raised the possibility of greenhouse molecules other than CO₂. For instance, Sagan and Mullen (1972) considered reducing gases such as H₂S, CH₄, and NH₃. However, due to the short photolytic lifetimes of these species in the atmosphere, it is difficult to suggest martian chemical sources that are large enough to maintain high concentrations of these gases in the atmosphere. Sulfur dioxide has been suggested as an additional greenhouse gas (Postawko and Kuhn 1986, Postawko and Fanale 1992). The possibility of a high concentration of SO₂ in the early martian atmosphere has recently gained support among geochemists. Shergottites, Nakhilites, and Chassigny (SNC) meteorites are very dry rocks, especially the Shergottites. SNC meteorites are generally believed to have originated from Mars. They contain very little carbon, while the concentrations of sulfur (and chlorine) are higher than those in terrestrial rocks. Wanke and Dreibus (1994) argued that SO₂ should be the most abundant compound in martian volcanic gases. The 0.1 ppmv SO₂ we shall postulate might be a conservative estimate of early martian SO₂, considering that the majority of martian volcanic material seems to come from the Hesperian era (Mouginis-Mark *et al.* 1992). The Hesperian era may have been as short as 250 Ma (Neukum and Wise 1976).

Quantitative modeling by Postawko and Kuhn (1986) showed that the presence of 1000 ppmv of SO₂ in a 3 bar CO₂ atmosphere could increase the greenhouse effect by as much as 10°C, primarily via its absorption in the strong infrared bands. The principal difficulty with this much SO₂ in the atmosphere is to envision a scenario which could keep the SO₂ abundance high in view of its short photochemical life. We suggest, instead, that SO₂ plays a different role. SO₂ absorbs strongly in the near UV region of the solar spectrum. While a small amount of SO₂ may have a negligible effect by itself on the surface temperature, it may have significantly warmed the middle atmosphere of early Mars, much as ozone warms the terrestrial stratosphere today. If this region is, in the latitudinal average, above the condensation temperature of CO₂, then at least some areas should be cloud-free and the CO₂ greenhouse would not be so effectively offset by the formation of clouds. As we shall show in this paper, the addition of small amounts of SO₂, on the order of 0.1 ppmv (10⁻⁷ by volume), in a 2 bar CO₂ atmosphere could raise the temperature of the middle atmosphere by approximately 10 degrees.

Radiative model. We have developed a one-dimensional numerical model to simulate the effects of radiation, convection, conduction, and condensation in a planetary atmosphere. The time dependent energy balance equation is

$$\rho c_p \frac{\partial T}{\partial t} = Q_R + \frac{1}{\lambda} \frac{\partial}{\partial z} \left(\lambda \rho c_p K \left(\frac{\partial T}{\partial z} + \frac{g}{c_p} \right) \right) + \frac{1}{\lambda} \frac{\partial}{\partial z} \left(\lambda \kappa \frac{\partial T}{\partial z} \right) + Q_L.$$

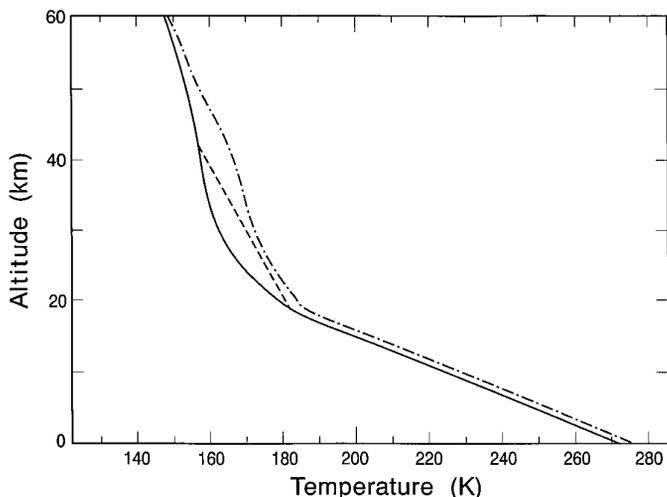


FIG. 1. Vertical temperature profile (solid line) computed in the standard model of the early martian atmosphere with 2 bar CO_2 . The dash-dot line represents results of calculation performed with 0.1 ppmv of SO_2 . The dashed line is the condensation temperature of CO_2 as a function of altitude.

where T is temperature, t is time, ρ is the mass density of the atmosphere, c_p is the specific heat, Q_R is the net radiative heating term, λ is a geometric term to account for the sphericity of the atmosphere, z is altitude, K is the eddy diffusion coefficient (for which we will use values similar to those employed in our photochemical model), g/c_p is the dry adiabatic lapse rate, κ is the thermal conductivity, and Q_L is the heating rate due to condensation, given by

$$Q_L = \alpha AL(\rho - \rho_s)\sqrt{RT/2\pi},$$

where α is a sticking coefficient, A is the aerosol area per unit volume, L is the latent heat of sublimation, ρ_s is the density at the saturation vapor pressure, and R is the gas constant. For the value of the sticking coefficient, we used 10^{-3} . Most of these terms are described more fully in Yelle *et al.* (1991).

Since we are investigating a hypothetical situation in which significant amounts of liquid water were present on the martian surface, we have used values of A that are similar to modern terrestrial values. The dry, dusty Mars of today is not the object of comparison. However, it might be argued that the intense volcanic activity we have already mentioned would call for a larger value of A . An experiment in which the A value was tripled showed a one degree increase in the most crucial region around 20 km.

We approximate the differential equation by finite differences and use the Newton-Raphson method to solve for the thermal profile. The numerical method is analogous to the method employed in the Caltech/JPL one-dimensional photochemical model (Allen *et al.* 1981). To achieve energy balance we used an iterative technique from Ramanathan (1976).

The absorption line parameters for gases at infrared wavelenths were taken from the 1992 edition of the HITRAN database (Rothman *et al.* 1992). The gas absorption cross sections at ultraviolet and visible wavelenths were taken from DeMore *et al.* (1992).

Crisp (1986, 1989, 1990) has developed fast, accurate methods for finding radiative fluxes and heating rates in scattering and absorbing planetary atmospheres. For a description of later modifications, see Gerstell *et al.* (1995). The Voigt quasi-random model (Crisp 1989, 1990) is used to find the broadband gas transmission functions in spectral inter-

vals 2 cm^{-1} wide in the thermal infrared. The solution to the equation of transfer is identical to that described in Crisp (1989, Eqs. (5)–(9)), except that we have added the surface boundary condition given in Crisp (1990, Eq. (14)). The solar spectrum (0.125 to $6.00 \mu\text{m}$) was divided into several hundred spectral intervals to resolve the wavelength dependence of the solar flux and of absorption features. The solar fluxes and heating rates were evaluated at four solar zenith angles, and these results were integrated over the solar day to obtain the diurnally averaged solar heating rates. Thermal radiances were obtained for two streams (one up, one down). Finally, the net heating rates at each altitude were obtained by differencing the solar heating rates and thermal cooling rates.

Results and discussion. The results of our model calculations for the vertical temperature profile of early Mars are summarized in Fig. 1. The standard case (solid line) is a pure CO_2 atmosphere with no SO_2 . The results are similar to those obtained by Kasting (1991). The temperature of the martian atmosphere was computed by assuming an eddy diffusion coefficient (K) of $10^8 \text{ cm}^2 \text{ sec}^{-1}$ in the troposphere, decreasing to smaller values in the upper atmosphere. The choice was somewhat arbitrary and was motivated by this value on Mars today and the need to maintain the lapse rate in the lower atmosphere close to that of the adiabatic lapse rate of $-10^\circ\text{C km}^{-1}$.

Referring to the standard case in Fig. 1, we note that near and above the tropopause region, the temperature is cold enough for CO_2 to condense (see dashed curve). Additional runs were carried out with small concentrations of SO_2 added to the atmosphere. The dash-dot curve gives the new temperature for including a uniform mixing ratio of 0.1 ppmv of SO_2 in the atmosphere. The net result is an increase in the temperature of the upper atmosphere by several degrees. The additional heating (broken lines) keeps the average temperature at each altitude above the condensation temperature of CO_2 . The heating rates computed in the models are shown in Fig. 2. The principal absorption of solar energy in the atmosphere is by CO_2 , as shown by the solid curve. It is clear that most of the additional heating is derived from the addition of SO_2 , which plays a role in the early martian atmosphere that is similar to that of ozone in the terrestrial atmosphere today.

Our model is too simple, for the small excess of our predicted temperatures above saturation temperatures would not inhibit the formation of clouds in regions of upwelling. However, the proposal of greenhouse warming by CO_2 only (Pollack *et al.* 1987) was subsequently shown to

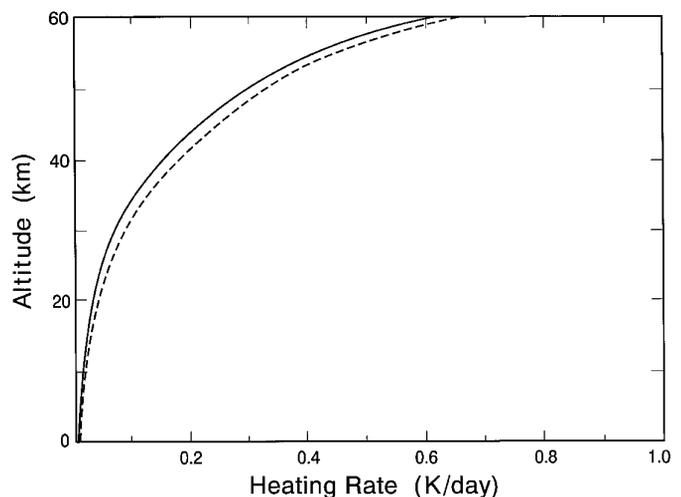


FIG. 2. Heating and cooling rates in the standard model (solid line) and the model with 0.1 ppmv of SO_2 .

fail a minimal test of plausibility, because it implied supersaturated conditions in the lower stratosphere (Kasting 1991). The large SO₂ concentration tested by Postawko and Kuhn (1986) seemed even to them to be unsustainable. Yet the view that martian channels were cut by liquid water, or at least a brine, is still widely held. To determine whether the small amount of SO₂ we have proposed is large enough, when dynamical effects are included, would require 3-dimensional modeling. Our position is that the present proposal overcomes what Kasting (1991) called the “unphysical” outcome of the pure CO₂ model, and thus merits the attention of 3D modelers. The question as to what determines the amount of clouds in the Earth’s atmosphere has not been answered from first principles. However, a recent empirical study derived a simple relation between cloud water/ice content versus cloud temperature (Lemus *et al.* 1997). The cloud amounts can be fitted to an exponential function with an exponent very similar to that for the saturation water vapor pressure. This suggests that thermodynamics (temperature) plays a role that is as fundamental as 3D motion. We do not know how clouds would be formed in a CO₂ atmosphere where the major constituent becomes the condensate. But if the clouds in the terrestrial atmosphere were a good analog of martian clouds, this 1D study would provide a useful guideline.

Conclusions. The ancient climate of Mars is an outstanding problem. The need for another radiatively active component in the atmosphere in addition to CO₂ has been demonstrated in recent work. We have proposed in this article the possibility that a small amount of SO₂ served as a powerful source of heating in the upper atmosphere of Mars, near the tropopause region where condensation of CO₂ would occur in the absence of additional heating. In this preliminary work we have not investigated the photochemistry of SO₂ in the martian atmosphere. By analogy with Venus, we expect that SO₂ would be destroyed by photolysis, recycled back to SO₂, and there would be a net production of H₂SO₄ (Yung and DeMore 1982). In the absence of a quantitative model, we may use the present atmosphere of Venus as a guide to the loss rate of SO₂. The loss rate is estimated to be 10¹² molecules cm⁻² sec⁻¹, or about 1000 Tg S/year. (Here S is sulfur.) For comparison, the present terrestrial volcanoes emit about 10 Tg S year⁻¹. The heating rates obtained in this paper may have to be reduced somewhat if the cooling by H₂SO₄ aerosols is taken into account. However, the heating rates may be increased if there is a possibility for the formation of absorbers such as polysulfur. The presence of this quantity of SO₂ in the early atmosphere of Mars could provide an effective UV shield for the surface of Mars, a condition that is conducive to the origin of life.

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