On the scattering-greenhouse effect of CO_2 ice clouds

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Abstract

We offer some remarks on the greenhouse effect due to high clouds which reflect thermal infrared radiation, but do not absorb or emit it. Such clouds are an idealization of the CO_2-ice clouds which are thought to have existed early in the history of Mars. Clouds of this type enter also in the ability of the Earth to recover from a globally glaciated "cold start," and in the determination of habitable zones of planetary systems. A simplified model of cloud optical effects is used to estimate the effect of high CO_2-ice clouds on the planetary radiation budget in the solar and infrared spectrum. It is argued that the scattering greenhouse effect certainly cancels out a large part of the cooling effect due to the cloud's visible albedo, and in some circumstances may even lead to a net warming as compared to the no-cloud case. Speculative implications for the climate of Early Mars are discussed.

Indications that young Mars was warm enough to support flowing water present a continuing enigma (Squyres and Kasting 1994). Kasting (1991) showed that, owing to the effects of CO_2 condensation on temperature lapse rate, the phenomenon cannot be accounted for on the basis of a CO_2 greenhouse effect. Kasting did not model the optical effects of CO_2-ice clouds, but remarked that because CO_2-ice (unlike water-ice) has very low infrared absorbance, CO_2-ice clouds should cool the planet through reflection of solar radiation uncompensated by infrared trapping. The formation of CO_2-ice clouds also affects the prospects of recovery of the early Earth from a "cold start" (Caldeira and Kasting 1992), and the extent of the habitable zone around stars (Kasting *et al* 1993). Kasting (1991) also noted that infrared scattering is important in CO_2-ice clouds. The purpose of this Note is to point out the existence of an infrared-scattering greenhouse effect due to high CO_2 clouds, which is strong enough to have major climatic effects under Early Mars conditions. We can argue with some confidence that the effect is strong enough to cancel out a substantial portion of the cooling that would ordinarily result from the visible albedo of the CO_2 clouds. However, our calculations are too idealized to provide a definitive answer to the question of whether the scattering greenhouse effect is potent enough to lead to a net cloud-induced warming of the planet.

An early discussion of the scattering greenhouse effect in the context of Venus can be found in Samuelsen (1967,1969). Infrared scattering by clouds has been extensively studied as a means of accounting for the observed infrared spectrum of Mars (Forget 1995) and Venus (Pollack *et al* 1993; Crisp *et al* 1991). The scattering greenhouse effect has some impact on the polar climate of the present Mars (Forget and Pollack 1996). McKay *et al.* (1989) considered the impact of the scattering greenhouse effect of methane clouds on the climate of Titan, though the effect there turned out to be inconsequential for cloud parameters consistent with spectroscopic observations of the satellite. We will argue in the following that, in contrast, the scattering greenhouse effect of CO_2 clouds could have had a highly significant effect on the climate of Early Mars. Since the scattering greenhouse effect is not widely appreciated, and since it operates rather differently from the conventional absorption/emission greenhouse effect, it is useful to see how it works in a highly idealized setting. Our calculation also serves this didactic purpose.

Consider an atmosphere-clad planet with net albedo α_o in the solar spectrum. If it is illuminated by a solar flux S_o and radiates infrared to space at a rate I_o, it is in equilibrium when $(1-\alpha_o)S_o = I_o$. Now introduce a high CO_2-ice cloud with albedo α_c in the visible and α_c' in the infrared, but which absorbs neither solar nor infrared radiation.

This perturbs both the solar and infrared terms in the radiation budget, as shown in Fig. 1. Let the cloud be high enough that it is above virtually all of the infrared-radiating mass of the atmosphere, and suppose that the subcloud atmosphere-surface system is a perfect infrared absorber. Taking into account the effects of multiple scattering between the high cloud and the subcloud regions, the cloud changes the planetary solar albedo to

$$\alpha = \alpha_c + \alpha_o \{ (1-\alpha_c)^2/(1-\alpha_c\alpha_o) \}. \qquad (1.)$$

If I_1 is the upward infrared flux from the subcloud atmosphere, the flux escaping to space is $(1-\alpha_c')I_1$. To restore equilibrium with the insolation S_o, the temperature must change so as to make $I_1 = \{ (1 - \alpha)/(1-\alpha_c') \} S_o$.

The I_1 required to balance the absorbed solar radiation becomes infinite if $\alpha_c' \rightarrow 1$ with $\alpha<1$, in which case the planetary temperature also becomes infinite. In this limit, the cloud acts like a one-way mirror which lets solar radiation in, but does not let any planetary radiation out. This state of affairs would violate the Second Law of Thermodynamics, as the planetary temperature would exceed the solar blackbody temperature. In fact, the temperature limits itself because, once the surface warms to solar temperatures, it radiates at solar wavelengths and the albedo for solar and planetary radiation become identical. This limit nevertheless shows the potency of the cloud-mirror effect. In contrast, the conventional greenhouse effect for a single-layer IR-absorbing cloud could increase the unperturbed temperature by no more than a factor of $2^{1/4}$. Unlike the conventional greenhouse effect, the scattering greenhouse effect blocks IR emission to space without the clouds having to absorb any IR themselves. The clouds therefore do not have to heat up in response to the absorbed radiation, which removes a limit to warming inherent in the conventional single-layer case.

Instead of determining the cloud-induced temperature change using a radiative-convective model, we instead ask the question of how we must change the incident solar flux so as to restore equilibrium at the original temperature. The assumption of unchanged temperature implies $I_1 = I_o = (1-\alpha_o)S_o$, and if the new solar constant needed to maintain equilibrium is called S_1 we then have

$$S_o = \{(1 - \alpha)/((1-\alpha_c')(1-\alpha_o)) \} S_1 \equiv \gamma S_1. \qquad (2.)$$

The high clouds make the planet act as if the sun were brighter by a factor γ. The warming factor has two especially significant limiting behaviors which can be inferred from (1). When $\alpha_o = 0$, $\gamma = (1-\alpha_c)/(1-\alpha_c')$, which is the solar/infrared coalbedo ratio for the cloud, and which will henceforth be referred to by the notation γ_c. Regardless of α_o, on the other hand, when $\alpha_c \to 1$ then $\gamma \to \gamma_c/(1-\alpha_o)$, which is the coalbedo ratio amplified by $1/(1-\alpha_o)$.

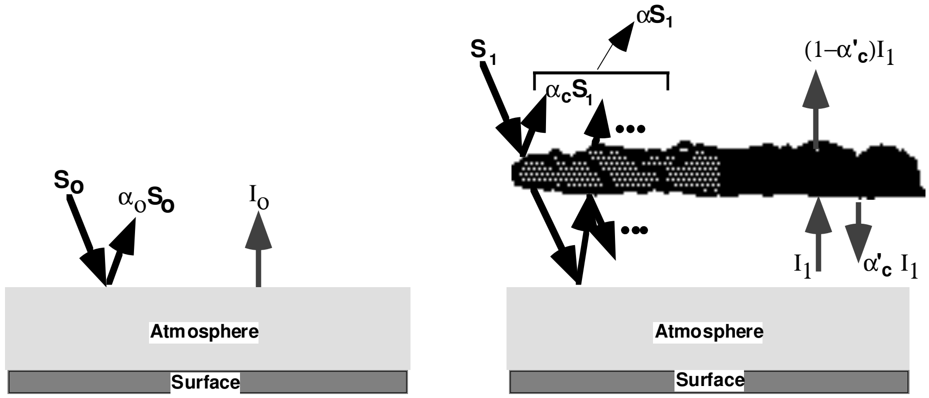

Figure 1 Left panel: Balance between absorbed solar and outgoing infrared radiation for the unperturbed planet-atmosphere system. Right panel: Perturbation of the radiation balance by a high cloud that reflects both solar and infrared radiation.

In water clouds, one is accustomed to ignoring IR scattering because the absorption is so strong that the light is absorbed before it has much opportunity to scatter. Without infrared absorption, Mie scattering theory (e.g. Bohren and Huffman 1983) would suggest higher infrared than solar albedo when the cloud particle size is comparable to the infrared wavelength. For a homogeneous cloud layer, the cloud albedo can be obtained for any of the two-stream approximations using the analytic solutions summarized in Toon *et al.* (1989, eqn 19-24), once the particle single-scattering properties are known. Results below were calculated for the δ-Eddington approximation. Single-scattering properties were obtained using Mie theory for equivalent spheres, and the real index of refraction was held fixed at 1.4, which is approximately the mean of the (slightly fluctuating) measured value for CO_2 ice in the .5 - 10 μ wavelength range (Warren 1986). To bring out the salient aspects of the scattering greenhouse effect more starkly, absorption was set to zero for the purposes of the present calculation. Also, gaseous absorption and scattering within the cloud was neglected. The solar albedos presented below were computed at .75 μm wavelength and infrared albedos were computed at 10 μm wavelength. Solar albedos were computed with a zenith angle of 60°, which is the value typically taken as representative of the planetary average. Infrared radiation is diffuse, and so the infrared albedos were computed as a flux-weighted isotropic average over all angles, save that zenith angles greater than 75° were excluded because the two-stream approximations can become unreliable at glancing incidence.

Figure 2 shows the infrared and solar albedo as a function of ice path, for a cloud composed of particles with a 20 micron radius. Both albedos asymptote to unity in the limit of thick clouds, and except for very thin clouds which are strongly influenced by the incidence angle effects, the IR albedo is large than the solar albedo. This is mostly because the IR albedo for this particle size benefits from enhanced Mie scattering, whereas the visible scattering is more in the geometric optics limit. The most interesting possibilities for substantial warming occur in the thick-cloud limit, and we will argue shortly that this is in any event the most likely regime for Early Mars. In this case, it is most informative to look at the coalbedo ratio, which also has the virtue of being closely allied to the warming factor.

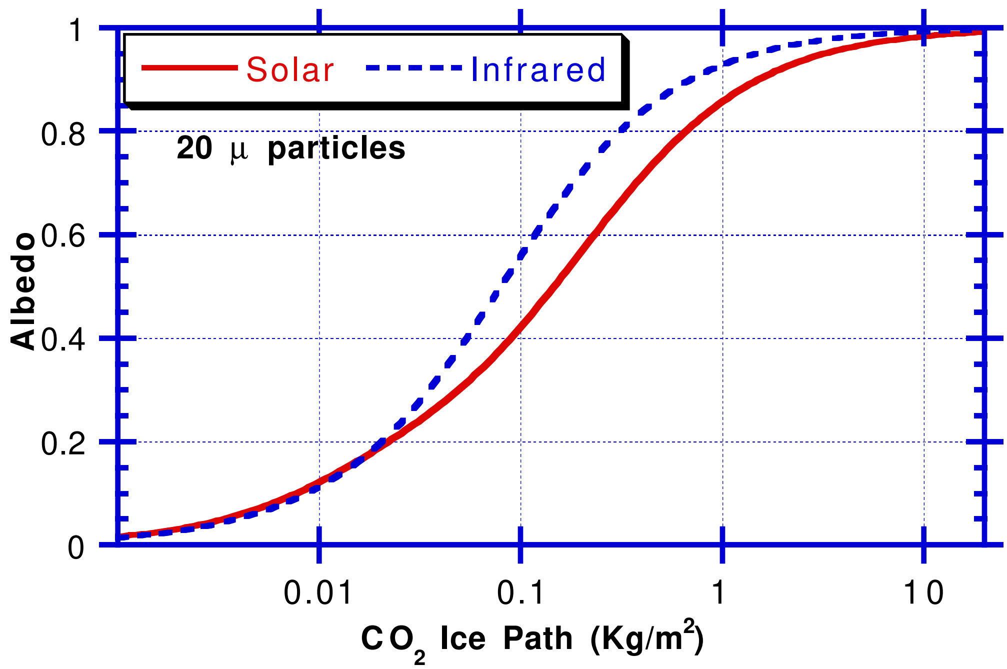

Figure 2 Infrared (10µ) and solar (.75µ) albedo as a function of condensed CO_2 path (Kg/m^2), for a cloud composed of spherical particles with a 20µ radius.

Figure 3 shows γ_c as a function of ice path and particle radius. At large ice paths where both albedos approach unity, γ_c asymptotes to a path-independent value. For 1µ particles, solar scattering overwhelmingly dominates infrared scattering, because the particles are much smaller than the infrared wavelength. However, infrared trapping substantially dominates solar reflection for 5-20 µm particles. The effect becomes less pronounced for larger particles because the geometric optics limit then becomes valid for both infrared and solar wavelengths, yielding identical albedos (apart from a weak zenith angle effect). The expression for the coalbedo ratio attains a particularly simple form for optically thick clouds, and helps reveal quantitatively how the single-scattering coefficients influence the ratio. For a nonabsorbing cloud in the limit of large optical thickness, the coalbedo is

$$1 - \alpha_c(\lambda,\mu) = \{\mu + \frac{2 + 3g_\lambda\mu}{3(1\text{-}g_\lambda)}\}\,\frac{1}{\tau_\lambda} \tag{3}$$

where λ is the wavelength, μ is the cosine of the zenith angle of the radiation, g_λ is the asymmetry factor at wavelength λ, and τ_λ is the optical thickness of the cloud. Doing the angle average for the infrared wavelength, and taking the ratio between the solar and infrared values, we find

$$\gamma_c = \frac{\{\mu + \frac{2 + 3g\mu}{3(1\text{-}g)}\}}{\{\mu' + \frac{2 + 3g'\mu'}{3(1\text{-}g')}\}}\,\frac{Q'_{ext}}{Q_{ext}} \tag{4}$$

where g, Q_{ext} and μ are the solar asymmetry factor, extinction coefficient and zenith angle cosine. Correspondingly, g' and Q'_{ext} are the infrared asymmetry factor and extinction coefficient, and μ' is the angle averaged mean of the cosine of the IR incidence angle (2/3 for the flux-weighted average over the whole hemisphere, or 1.05·2/3 if the angle average is cut off at 75^o) . In the geometric optic limit prevailing for very large particles, $Q_{ext} = Q'_{ext} = 2$, and (for the present index of refraction) g = g' = .86. In this case, $\gamma_c = .94$, which is slightly less than unity by virtue of the incidence angle effects. It takes only a small enhancement of the IR scattering to make $\gamma_c > 1$. From eqn. (4) we not also that the coalbedo ratio becomes larger if g' < g, i.e. if the IR scattering is more symmetrical than the forward-peaked visible scattering. This effect is especially important for particles between 10 and 20 microns, in which case the drop in g' for 15 micron particles offsets the dip in Q'_{ext} for such particles.

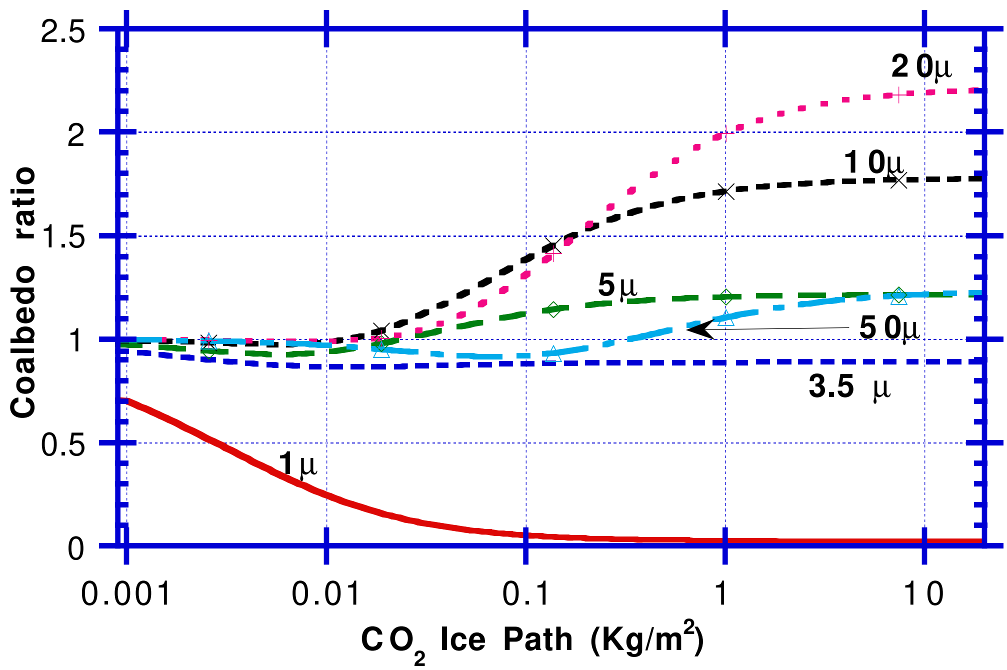

Figure 3 Ratio of infrared to solar coalbedo for the cloud alone, as a function of CO_2 ice path and cloud particle size. Numbers on curves indicate particle radius in microns.

The greatest warming is expected when γ_c significantly exceeds unity, but recall that when the clear-sky planetary albedo α_o is nonzero, one finds warming even in the large particle limit where γ_c is close to unity. This is not to say that, all other things being equal, a planet with higher clear-sky albedo will be warmer; it is only a statement about the impact of clouds on a given planet's temperature. A no-cloud planet with high α_o will generally be colder than one with low α_o, but clouds have a greater warming effect on the former than on the latter. To better quantify the effect, we show the behavior of the warming factor γ in Figure 4, computed with $\alpha_o = .2$. This is a very conservative choice of no-cloud albedo, since it takes into account the surface albedo, but neglects the Rayleigh scattering of the dense CO_2 atmosphere, which could bring the planetary albedo up to .35 for a 2bar atmosphere (Kasting 1991). From this figure we conclude that as long as the particles are not much smaller than about 3 microns in radius, the idealized cloud exerts a warming influence, in the sense that, in the presence of clouds, a given surface temperature can be maintained with a fainter Sun. Particles in the 10-20 micron range are especially effective at warming the planet.

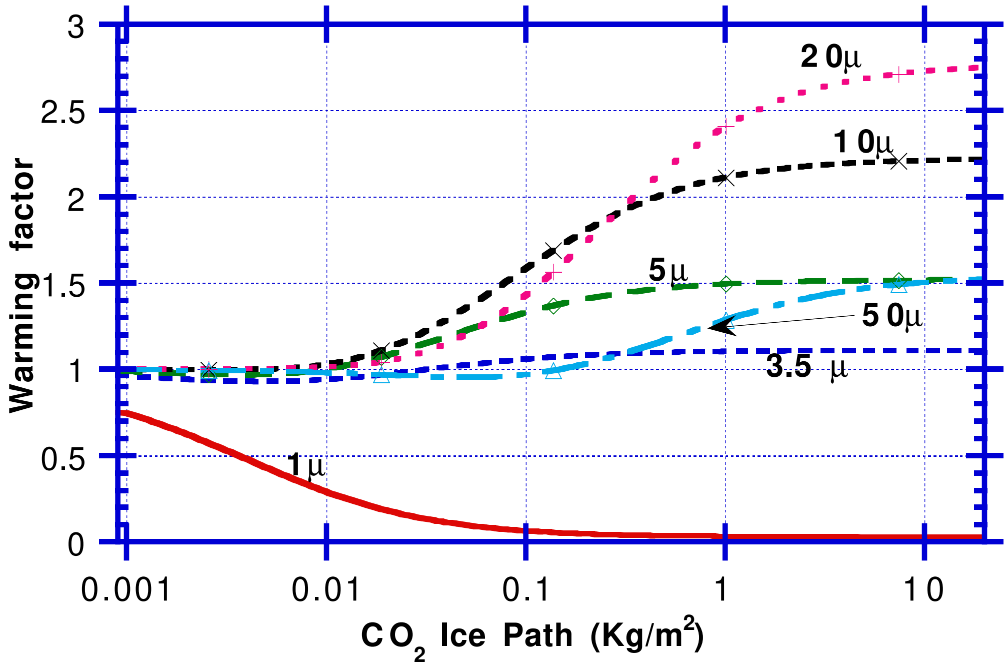

Figure 4 The warming factor γ as a function of condensed CO_2 path (Kg/m^2) and particle size.

We need at this point to make some reasonable guesses as to the values of condensate mass and particle size for Early Mars, so as to see whether the effect under discussion could be significant. The condensate burden is determined by a balance between upward flux of saturated air and loss of condensed particles through sedimentation. In high cirrus clouds on Earth, this yields water ice concentrations that reach 50% or more of the mass of water vapor in the saturated layer (Jensen *et al* 1994; Stephens *et al* . 1990; Jensen *et al* 1994; Heinzentberg *et al* 1996). On Mars, it is the primary atmospheric constituent that is condensing, and the supply of potential condensate is accordingly much greater. For the 5-bar surface pressure case in Figure 9 of Kasting (1991), the saturated CO_2 content in the midst of the cloud layer is about .75 Kg/m^3, so that a 10 Kg/m^2 condensate path in a 1 km thick cloud can be obtained by tapping a mere 1.3% of the available condensate. This is more than enough to make the visible and IR albedos close to unity, and could be achieved even if the convective mass transport were far more sluggish on Early Mars than on the current Earth. Higher concentrations of CO_2 ice do no damage to our argument, because of the asymptotic properties of γ.

Crystal size is determined by the time required for crystal growth vs. the time it takes for the particle to fall out of a super-saturated layer. Earth cirrus presents a useful analogy for the Martian clouds. Though particles 80 μm or larger are often observed in Earth's cirrus, there is now direct evidence that particles of size 20μm or less contribute significantly to, or even dominate, the ice water content of high cold clouds (Heintzenberg *et al* 1996). Further, the observed reflective properties of Earth cirrus can best be fit assuming equivalent spheres with a radius of only 16μm (Stephens *et al* 1990; Jensen *et al* 1994). As far as fall speed goes, the Early Mars clouds are in the same regime as Earth cirrus: Martian gravity is weaker than Earth's, but CO_2 ice is denser than water ice and the viscosity of CO_2 gas at the cloud temperatures is lower than for the air in Earth's cirrus. On the basis of viscosity and density data from Lide (1995), and the Stokes expression for fall speed, (Landau and Lifshitz 1959), a Mars cloud particle falls as fast as an Earth particle which is only .45% larger, using viscosities computed at 200K. This estimate is not too sensitive to the temperature ratio of the Earth vs. Mars clouds, since the equivalent radius varies like the square root of the viscosity ratio, and the viscosity is not that strongly dependent on temperature over the relevant range. Comparison of the crystal growth time presents a greater challenge. Growth of water cloud particles on Earth is limited by both the diffusion of water vapor through air and the thermal diffusion of latent heat of condensation away from the particle; it is the former effect that primarily controls the growth time on Earth (Rossow 1973). As noted by Rossow (1973), CO_2 crystals growing in a CO_2 atmosphere present a totally different regime, because the mass diffusion effect is entirely absent. Instead, when CO_2 vapor condenses on the surface of the particle, a pressure drop is created, which presumably leads to a nearly instantaneous mass flux to feed the condensation. A detailed treatment of the microphysics of this regime is far beyond the scope of our paper, but a reasonable assumption in this case is that the primary limitation on crystal growth rate is the thermal diffusion effect, which can be estimated as a special case of the standard physics outlined by Rossow. Equation (12) of Rossow (1973) can be re-cast in the form

$$\frac{d}{dt} r^2 = 6\,(\rho_{sat}/\rho_{ice})\,\Gamma\,D \qquad (5)$$

where r is the particle radius, ρ_{sat} is the saturation vapor density at the ambient temperature, ρ_{ice} is the ice density, Γ is the fractional supersaturation, and D is the "effective diffusivity," taking into account the latent heat effect. To provide a crude estimate of the Martian regime, we send the vapor diffusivity in Rossow's equation (13) to infinity, and obtain

$$D = \frac{\kappa T}{\rho_{sat} L (L\, m_v/kT - 1)} \qquad (6)$$

where κ is the thermal conductivity, m_v is the mass of a vapor molecule, L is the latent heat of condensation and k is the Boltzman constant. Using T=200K and ρ_{sat} = .75 Kg/m^3, then D = 2.8 10^{-7} m^2/sec and $(\rho_{sat}/\rho_{ice})D$ = 1.3 10^{-10} m^2/sec, based on values given in Lide (1995). In contrast for water on Earth D is approximately the binary diffusion constant for water in air (5. 10^{-5} at 230K and 300mb) but (ρ_{sat}/ρ_{ice}) is only 3.3 10^{-7}, water being a trace constituent at the Earth cloud level; hence $(\rho_{sat}/\rho_{ice})D = 1.7 * 10^{-11}$. Thus, for equal supersaturations, Mars cloud particles grow faster than the corresponding Earth particles; a Mars particle takes .13 as long as an Earth particle to reach a given size. We do not know how to estimate the supersaturation for Martian conditions, but if we take Γ = .01 based on typical Earth conditions, (Rogers, 1976), then a Mars particle takes only 12.8 seconds to grow to a size of 10 microns, during which it falls only .08 meters. It takes 1280 seconds to reach 100 microns, during which time it falls 841 meters. In the extreme case where the particle fell through a 30km deep layer at 1% supersaturation (roughly the full depth of the potentially condensing layer in a radiative-convective model at 5bars surface pressure), then it reaches a radius of 250 microns.

Based on these estimates, dominance by the very small particles that pose the biggest threat to the scattering greenhouse warming seems unlikely, but particles in the size range of 10-100 microns are plausible. The presumed paucity of small particles is supported by the analysis of present Mars by Forget and Pollack (1995), who concluded that the small particles are inconsistent with IRIS spectral observations, and that particles in the size range of 10-20 microns were most likely. Cloud particles on Early Mars are likely to have been somewhat larger, because they were forming in conditions of higher ambient CO_2 density.

Under these admittedly arguable assumptions about particle size and condensate path, the scattering greenhouse effect is strong enough to permit the existence of liquid water on Early Mars. Let S_p be the present mean solar flux at the orbit of Mars. Without incorporating the optical effects of CO_2 clouds, Kasting (2) reports that liquid water can plausibly exist only for $S > .86S_p$, which was not achieved until 1.9 billion years ago. With $S = .7S_p$ as obtained 4.5 billion years ago, CO_2 clouds would then permit liquid surface water provided $\gamma > 1.23$. For thick clouds composed of large particles in the geometric optics limit, $\gamma = 1.18$ for $\alpha_o = .2$. This just misses the required threshold, but based on Figure 4, the threshold is met for 50 micron particles provided the condensate path is .65 Kg/m^2 or more. Based on eqn. (4), the warming threshold in the thick cloud limit is met for particles between 3 and 150 microns in radius. The warming effect is strongest for particles in the 11-17 micron range, for which above-freezing conditions are maintained as long as $S > .36\ S_p$.

The above estimates are illustrative, but cannot be considered definitive. First, one ought to consider the detailed wavelength dependence of all quantities (notably the thermal emission from the subcloud layer), if one is to obtain quantitatively accurate results. There are many aspects of the problem that have been neglected in our simplified model, which could adversely affect the warming. For example, crystal shape significantly influences scattering properties for water-ice — notably the asymmetry factor — allowing observed clouds to be somewhat more reflective than those composed of equivalent-volume spheres (Stephens *et al* 1990; Jensen *et al* . 1994; Heintzentberg *et al* 1996). It is significant that the results of Figure 3 and 4 are nearly as strongly influenced by the contrast between IR and visible asymmetry factors as they are by variations in the extinction coefficient. Because CO_2 is a linear molecule without the complex intermolecular forces of the bent water molecule, one might expect simpler crystal growth habits that would be more accurately approximated by equivalent spheres,but laboratory evidence bearing this out would be reassuring.

In our simplification, the cloud is non-absorbing, and hence also, by Kirchoff's Law, non-emissive. There are two neglected factors which could give the cloud some emissivity and alter the radiation balance. First, our neglect of the IR absorption of the CO_2 ice is an over-simplification of the true picture (Warren 1986). In certain bands the absorption can be quite strong, and even where it is weak it could add up to an appreciable net absorption when the cloud is thick. Second, gaseous absorption and emission by CO_2 gas within the cloud would also act to increase the cloud emissivity. If the cloud becomes emissive, part of the scattering greenhouse effect is replaced by a conventional absorption/emission greenhouse effect; to the extent that the conventional greenhouse effect is less potent than the scattering greenhouse effect that it replaces, the warming effect would be reduced. If the cloud top is cold, the maximum threat from this effect is modest. For a cloud at 160K with 20% emissivity, for example, the thermal emission from the cloud would add only 7.68 W/m^2 to the emission to space, much of which woud be offset by increased absorption of upwelling IR from below. Further, it is important to note that the gaseous or solid emissivity is sharply limited when the radiative transfer is dominated by conservative scattering by the cloud particles: From eqns. (19-24) of Toon *et al* (1989), it can be inferred that the emissivity of a thick isothermal layer composed of scatterers with a mean single-scatter albedo ω goes to zero proportionately with $(1-\omega)^{1/2}$ as $\omega \rightarrow 1$ (see also Samuelson 1969). This is the very same effect that causes fluffy new-fallen CO_2 snow on present Mars to have lower emissivity than the older compacted form (Forget and Pollack 1995).

Finally, we have neglected the effect of downwelling infrared from the above-cloud atmosphere. However, because thermodynamics constrains the CO_2 clouds to form at high altitudes, and because the stratosphere above the cloud is cold and dry, the downwelling radiation is expected to be weak; indeed an explicit calculation (using the radiation model described in Kiehl and Briegleb (1992)) for the conditions of Fig. 6 of Kasting (1991) indicates an infrared flux of at most 8 W/m^2 impinging on the top of the CO_2-saturated layer. Certainly, the emission to space in certain bands is dominated by the stratosphere, but it is only the net emission that counts in the radiation budget. The weakness of this flux is entirely consistent with Kasting's conclusion that the stratospheric structure has little effect on the tropospheric climate. However, if the cloud tops are located significantly below the top of the saturated layer yielded by Kasting's model (as a result of subsidence, for example), then the IR reflected back upwards by the clouds is more significant and the detailed response of the above-cloud layer becomes highly significant. In this case one faces the additional complication of determining how the cloud radiative effects alter the convective heat transport. In all, the warming mechanism we have proposed becomes much more uncertain if the cloud tops are significantly lower than the values suggested by the top of the saturated layer appearing in radiative-convective models.

High tropical cirrus clouds on Earth would have a substantial cooling effect were it not for their compensating infrared-trapping effect (Ramanathan *et al* 1989); the infrared mirror effect of CO_2 clouds replaces the conventional greenhouse effect of water clouds, and potentially shifts the balance in favor of a net warming. The new view of CO_2 clouds broadens the range of planetary conditions which could support a terrestrial biosphere, and narrows the possibilities for irreversible glaciation early in a planet's history. Although we cannot conclude that the clouds induce a net warming, it seems certain that the situation for CO_2 clouds resembles that for water clouds, in that the greenhouse effect of high clouds at least can be expected to cancel out a large part of the cloud cooling effect.

If the CO_2 levels are as high on Early Mars is is often supposed, our estimates lead to a picture of the planet as a rather dark place, swathed in thick clouds. The surface temperature would be determined by a balance between the trickle of solar radiation leaking in, and the trickle of infrared radiation leaking out. Recently, Sagan and Chyba

(1997) have proposed that organic hazes on Early Mars could have shielded methane and ammonia from photochemical destruction, allowing them to build up to a level producing an important greenhouse warming. Even if the CO_2 clouds in our theory had a negligable net warming effect in themselves, they could have assisted the methane/ammonia mechanism by massively reducing the solar radiation reaching the lower atmosphere. On the other hand, high clouds would act against the methane albedo effect proposed by Kasting (1997), by inhibiting the absorption of solar radiation by tropospheric methane.

The strong optical effect of the CO_2 clouds suggests an important role for dynamics in determining their global impact. Although radiative-convective models predict a deep CO_2-saturated layer, strong subsidence could inhibit cloud formation by compressionally heating the layer to the point that it became unsaturated. In the face of the resulting cloud patchiness, the solar and infrared radiation budgets could well be dominated by the effects of the clear-sky regions.

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