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CO_2 Snow on Mars and Early Earth: Experimental Constraints

David L. Glandorf[1], Anthony Colaprete[2], Margaret A. Tolbert[1], and Owen B. Toon[3]

[1]Department of Chemistry and Biochemistry and CIRES
Campus Box 216
University of Colorado, Boulder CO 80309-0216

[2]NASA Ames Research Center
Moffett Field, MS 245-3
Mountain View, CA 94035-1000

[3]Laboratory for Atmospheric and Space Physics
and
Department of Atmospheric and Oceanic Sciences
University of Colorado, Boulder CO 80309-0392

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Abstract. Greenhouse warming due to carbon dioxide atmospheres may be responsible for maintaining the early Earth's surface temperature above freezing and may even have allowed for liquid water on early Mars. However, the high levels of CO_2 required for such warming should have also resulted in the formation of CO_2 clouds. These clouds, depending on their particle size, could lead to either warming or cooling. The particle size in turn is determined by the nucleation and growth conditions. Here we present laboratory studies of the nucleation and growth of carbon dioxide on water ice under Martian atmospheric conditions. We find that a critical saturation, $S = 1.34$, is required for nucleation, corresponding to a contact parameter between solid water and solid carbon dioxide of $m = 0.95$. We also find that after nucleation occurs, growth of CO_2 is very rapid and proceeds without a surface kinetic barrier. Because growth would be expected to continue until the CO_2 pressure is lowered to its vapor pressure, we expect particles larger than those being currently suggested for the present and past Martian atmospheres. Using this information in a microphysical model described in a companion paper, we find that CO_2 clouds are best described as "snow", having a relatively small number of large particles.

Keywords: Mars, atmosphere; ices; experimental techniques

suggested fairly recent liquid water runoff on the Martian surface (Malin and Edgett 2000). Greenhouse warming by carbon dioxide gas has been suggested to account for the higher temperatures of the early Martian climate such that liquid water could exist (Pollack *et al.* 1987). While carbon dioxide is an effective greenhouse gas, current pressures are too low to effectively warm the surface. Early Mars may have had a significantly denser CO_2 atmosphere and thus a stronger greenhouse. However, the abundance of CO_2 needed to warm the planet above freezing yields portions of the atmosphere with pressures significantly higher than the CO_2 vapor pressure, so that clouds might form and potentially offset the warming by scattering sunlight (Kasting 1991). Forget and Pierrehumbert (1997) suggested recently that infrared scattering by carbon dioxide clouds might instead yield a significant warming effect. This suggestion refocused the early atmospheres debate on the role of carbon dioxide, but the effectiveness of the clouds as a "scattering greenhouse" is not yet fully understood. The warming potential of the clouds depends on the percent cloud cover, the total optical depth of the cloud, the size of the particles, and the altitude of cloud formation, just as it does for terrestrial cirrus clouds. The size of the CO_2 particles formed and thus their ability to warm through IR scattering will depend on the nucleation mechanism.

Despite the many interesting roles that carbon dioxide clouds might play in early and current atmospheres, little is known about their formation mechanism. Analogous to ice nucleation in the Earth's atmosphere, it is unlikely that carbon dioxide would nucleate homogeneously in the Martian atmosphere due to the very high supersaturations required to overcome the energy barrier to form a critical germ. Heterogeneous nucleation begins with a seed particle that allows the germ to reach the critical size with a smaller number of condensate molecules, thus requiring a lower supersaturation. Possible nucleation substrates for carbon

During a typical experiment, the silicon surface was cooled to temperatures near those of the Martian winter poles. Water vapor was introduced into the chamber and the growth of the ice film on the silicon surface monitored by FTIR transmission spectroscopy. The surface temperature for water growth was varied between 110 and 160 K. At these temperatures, water ice is stable against evaporation, and no changes in the water spectra occurred over the course of the experiments. The water ice thickness was calculated from optical constants measured in the same chamber (Toon *et al.* 1994). The experiments can be divided into two thickness regimes. The "thick" water ice films were on the order of 0.5 to 1 μm thick. The "thin" films were between 30 and 100 nm thick, which is near the detection limit of the FTIR. When the ice film reached the desired thickness, the water supply was shut off.

After preparation and characterization of the water ice film, carbon dioxide vapor was introduced into the chamber at pressures below the saturation pressure. The carbon dioxide pressure was then increased incrementally to the point where CO_2 had clearly nucleated onto the water ice surface according to the infrared spectrum, as described below. After nucleation, the carbon dioxide pressure was adjusted to perform the frost point calibration. During the frost point calibration, the CO_2 pressure was varied until the infrared spectrum revealed no growth or evaporation within the detection limits. The pressure at this point is used with the literature CO_2 vapor pressure (Brown and Ziegler 1979) to calibrate the surface temperature. The pressure and temperature were then varied to further grow or desorb carbon dioxide, and the frost point calibration repeated. Between two and five calibrations were performed for each experiment. The mean deviation for our calibrated temperature sensors was 0.2° C. Data collected during the frost point calibration was also used to determine the condensational growth rate of CO_2.

reached this range. In some experiments the CO_2 pressure was brought quickly to a saturation ratio of 1, then the pressure was allowed to increase more slowly. In other cases, the pressure rise was slow throughout the entire experiment. Occasionally the CO_2 pressure was sustained for a longer time (over 20 minutes) at a value above one to be sure that the nucleation was not kinetically limited. However, our repeatability suggests we are near the actual value. In all cases, a slower approach is expected to give a more accurate critical value, as overshooting would also result in nucleation.

We have not seen any evidence for the formation of a water carbon dioxide clathrate. As shown in Fig. 2, the infrared spectra appear simply as the addition of separate carbon dioxide and water condensed phase spectra. The $CO_2{\bullet}6H_2O$ (or $CO_2{\bullet}5.75H_2O$) clathrate has been shown to have a higher CO_2 equilibrium vapor pressure than does pure CO_2 (Miller and Smythe 1970). It may be tempting to explain our critical saturation ratio as nucleation at $S=1$ with respect to the clathrate equilibrium pressure. However, even within our small temperature range (130-140 K), the ratio of equilibrium pressures of the clathrate to pure carbon dioxide varies from 1.24 to 1.56. This variation would be easily identifiable with our precision, but our results (Table 1) indicate a critical supersaturation around 1.34 without temperature dependence. In addition, no observable difference was recorded between experiments with thick or thin ice layers. In all cases, the amount of carbon dioxide was in substantial excess of the water such that clathrate formation could not be extensive. This is the case in the Martian atmosphere as well.

After nucleation, the pressure in the chamber could be varied slightly above or below the equilibrium vapor pressure, and the film responded by growing or evaporating, respectively. To quantify the growth, the infrared absorbance of the 3700 cm^{-1} band in condensed CO_2 was used along with the optical constants for condensed CO_2 (Warren 1986) and an optical model (Toon *et*

We were unable to find an experimentally determined surface free energy of solid CO_2 with respect to the vapor. However, an approximate value can be obtained through the use of Antonoff's rule (Pruppacher and Klett 1997) where *s*, *l* and *v* denote the solid, liquid and vapor phases, respectively:

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \tag{2}$$

Given $\sigma_{sl} = 32.3$ erg/cm^2 calculated from the heat of fusion (Turnbull 1950) and $\sigma_{lv} = 34.7$ erg/cm^2 (Van der Waals 1894), the surface free energy can be estimated as $\sigma_{sv} = 67$ erg/cm^2. This value is in reasonable agreement with that calculated by Wood (1998) of $\sigma_{sv} = 80$ erg/cm^2 based on the crystal structure and heat of vaporization of CO_2.

The critical germ radius is related to the free energy of germ formation, ΔF, through:

$$\Delta F = \tfrac{4}{3}\pi\, r_c^2\, \sigma_{sv}\, f \tag{3}$$

where *f*, the matching function, is related to the matching parameter for a flat surface by:

$$f_{flat} = \frac{(2+m)(1-m)^2}{4} \tag{4}$$

Finally, the nucleation rate, *J*, is exponentially related to the free energy of germ formation:

$$J(\mathrm{cm^{-2}sec^{-1}}) = K(\mathrm{cm^{-2}sec^{-1}})\ e^{-\Delta F/kT} \tag{5}$$

For our studies, we visually observed that several sites nucleated on our 1 cm^2 surface over the course of several seconds. We thus approximate the nucleation rate as as J = 1 cm^{-2} sec^{-1}, an approximation that is evaluated below. The prefactor K was estimated based on germ growth occurring via surface diffusion of adsorbed molecules as described in Pruppacher and Klett (1997). At a CO_2 pressure of 1 Torr, a temperature of 140 K, and assuming monolayer coverage of CO_2 on the ice, we calculate K= 10^{27} cm^{-2} sec^{-1}. Equations 1, and 3 - 5 are then solved to parameter is not very sensitive to these estimates. Figure 5 shows the magnitude of the nucleation rate according to supersaturation. The nucleation rate changes several orders of magnitude for a small change in supersaturation. This is consistent with our laboratory observations, as nucleation and growth begin dramatically once the critical S is reached. Raising and lowering the ratio of the nucleation rate to the kinetic factor, J/K, by three orders of magnitude leads to average contact parameters of 0.955 and 0.950, respectively.

Implications for Martian Clouds

For spherical nuclei of radius r_N,

$$J_{sphere} = 4\,\pi\, r_N^2\ K \exp(-\Delta F_{curved}/kt) \qquad (6)$$

where the free energy of germ formation is given by Eq. 3 with f_{flat} replaced by f_{curved} (Pruppacher and Klett 1997). Equation 6 is then used with Eqs. 1 and 3 to determine the supersaturation at which a particular nucleation rate, J_{sphere}, is achieved according to particular radii. The results of the calculation are shown in Fig. 5. It can be seen that smaller nuclei require higher supersaturations (lower temperatures) to achieve the same nucleation rate. It has been speculated that CO_2 clouds may form at the coldest temps measured in the Pathfinder data set near 80 km. If large nucleating particles were present (0.5 μm or bigger), our measurements would indicate a supersaturation of 0.35 would be required for a significant nucleation rate. If 0.1 μm particles were instead present, a supersaturation of 0.45 would be required, as can be seen in Fig. 5. At Martian pressures at these altitudes, that supersaturation represents a cooling of about 1.25 K below the frost point of CO_2. Particles below about 0.05 μm would require extremely high supersaturations.

Our results thus suggest that large CO_2 particles may form in the current Martian atmosphere and may play a role in depositing CO_2 to the planet's surface. The sizes suggested by our results are significantly higher than proposed, if CO_2 particles are to explain the observed clouds of Clancy and Sandor (1998). Additionally, very large CO_2 crystals would be expected to have formed in early Earth and Mars atmospheres. For example, for a near-surface dust loading of 50 particles/cm^3, our results suggest that CO_2 cloud particles would have a radius of greater than 200 μm for a 2 bar Martian CO_2 atmosphere. While such particles would have an IR scattering greenhouse, the clouds would likely be ephemeral and patchy, more like a CO_2 "snow". Colaprete and Toon (this issue) show that CO_2 clouds with extremely large particle sizes and low optical depths contribute only faintly to warming the surface on a planetary scale. Our results then call into question the ability of CO_2 to warm Early Earth or Mars to above the freezing temperature of water.

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Temp (K)	Water ice	S	m
140.0	thick	1.34	0.949
136.1	thick	1.33	0.954
135.9	thin	1.34	0.951
133.2	thin	1.38	0.947
133.2	thin	1.34	0.952
132.7	thin	1.35	0.951
132.5	thin	1.30	0.958
132.3	thick	1.32	0.955
131.7	thick	1.34	0.953
130.2	thick	1.35	0.952

Table 1. Critical saturation ratio (S) and contact parameter (m) of carbon dioxide on water ice. Average values are 1.34 for S and 0.952 for m.

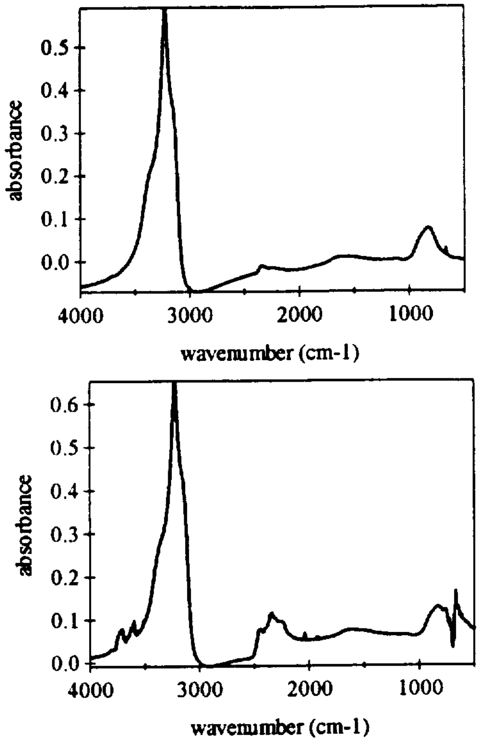

Figure 2. FTIR transmission spectra of water ice (2a) and carbon dioxide condensed onto water ice (2b). Note the broad absorbance features in 1b at 2350 cm^{-1} (asymmetric stretch) and 667 cm^{-1} (bend), indicative of condensed CO_2.

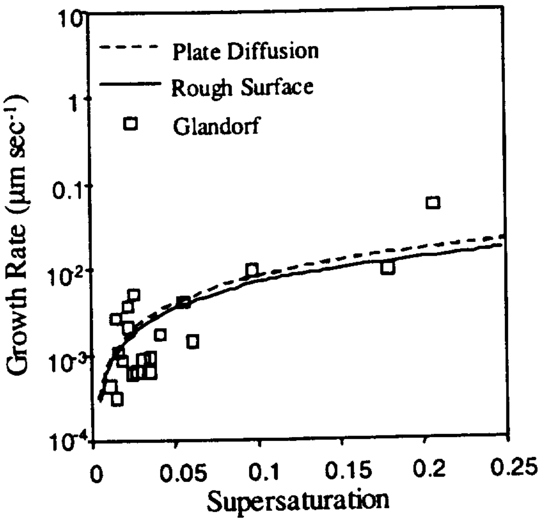

Figure 4. The growth rate of CO_2 ice as a function of supersaturation derived from absorption measurements (circles). The two curves in this figure are growth rates according to the two theories discussed in the text.