

SUBLIMATION KINETICS OF CO₂ ICE ON THE SURFACE OF MARS V. F. Chevrier¹, L. A. Roe¹, K. F. White², K. Bryson¹ and D. G. Blackburn¹, ¹Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR 72701, USA, ²Department of Physics & Astronomy, Ball State University, Muncie, IN 47306, USA <vchevrie@uark.edu>.

Introduction: The martian polar caps are in majority composed of CO₂ ice [1-3]. Early modeling of the polar caps suggested that they were in equilibrium with the ~6 mbar CO₂ atmosphere [2], and various observations have shown a cyclicity of growth and retreat, following martian seasons [4]. However, other studies show that CO₂ ice constitutes only a thin veneer on the surface of a probably much thicker ice layer [5]. This veneer is too small for the caps to be in equilibrium with the atmosphere [6,7]. This would also suggest that the polar caps are very young [8]. Therefore, there must be a much larger unidentified CO₂ reservoir in the martian subsurface, possibly adsorbed CO₂ in the regolith [9,10], to buffer the much larger atmosphere, or it means the total budget of CO₂ is present in the atmosphere, and that Mars has today much less CO₂ than other telluric planets.

However, the majority of dynamic models of the polar caps are based on CO₂ ice sublimation, lacking laboratory confirmation. Most studies use thermal modeling [2] or geomorphic observations [7] to study sublimating CO₂, but the details of CO₂ sublimation in a CO₂ atmosphere remain unknown, and could have deep implications for the dynamics of the polar caps on the martian surface. We report here the experimentally measured sublimation rate of pure CO₂ ice under simulated martian conditions, as done previously for H₂O [11,12].

Methods: Dry ice was packed into a beaker with a thermocouple above surface of the dry ice and, in later experiments, a second thermocouple placed inside the dry ice. Our planetary environmental chamber was evacuated to less than 0.09 mbar, filled with dry gaseous CO₂ (g) to atmospheric pressure, and cooled to between 0 and -10°C. Once stable, the chamber was opened and the sample was placed on a top loading analytical balance inside the chamber. The platform supporting the balance and the sample was then lowered into the chamber. The chamber was then evacuated to 7 mbar. Experiments lasted ~1 hour and mass, pressure, and temperature were recorded every minute. Pressure and atmospheric temperature were maintained between 6.5 and 7.5 mbar and -11 to -1°C, respectively. Before and after each experiment the height and diameter of the dry ice was measured.

Results: The mass loss of CO₂ is extremely linear, with R² coefficients systematically above 0.99 (Fig. 1). The mass loss in g min⁻¹ is converted into sublimation rate E_s in mm h⁻¹ using the density and the surface area of the sample. Results are summarized in Table 1 and show remarkably constant values, validating the

reproducibility of our experiments. The average value for CO₂ ice is 1.20 ± 0.27 mm h⁻¹. These results are less than one order of magnitude higher than *in situ* measurements of polar caps retreat showing 0.13-0.19 mm h⁻¹ [4] and 0.36 mm h⁻¹ [6]. This suggests a common process for the sublimation mechanism on Mars and in our chamber.

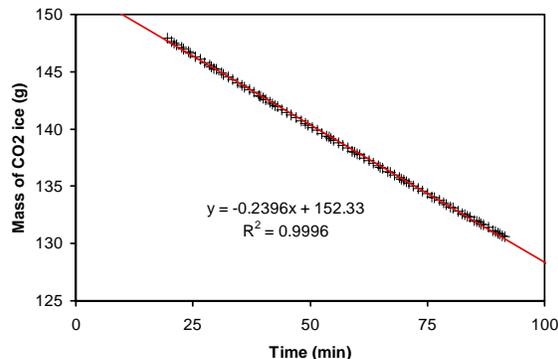


Figure 1. Mass of CO₂ ice as a function of time (sample #3 in Table 1).

Table 1. Sublimation rates E_s for the 10 samples studied in our chamber.

#	Texture	Mass loss (g min ⁻¹)	E _s (mm h ⁻¹)
1	Gravel	0.46	1.06
2	Solid block	0.24	1.01
3	Solid block	0.24	0.99
4	Powder	0.34	1.36
5	Powder	0.37	1.63
6	Powder	0.34	1.68
7	Loose powder	0.47	1.22
8	Loose powder	0.43	1.09
9	Packed powder	0.33	0.91
10	Packed powder	0.36	1.04

Discussion: It has been shown previously that surface temperature controls the sublimation rate of water ice [11,13]. We measured the temperature profiles inside the sample, a about 3 mm above the surface and 20 cm above the sample (Fig. 2). The temperature of the atmosphere remains very constant during the experiments, as well as the sample temperature at 148–153K, which corresponds to the equilibrium temperature of CO₂ at 7 mbar. This is exactly what is observed on the surface of Mars, where the polar caps are usually at the temperature 150K, thus in thermal equilibrium with the atmospheric pressure. The temperature a few mm above the surface is higher, 30 to 60K, as a result of the strong gradient between the

surface and the atmosphere. The sudden increase in the sample temperature at $t = 18$ min (Fig. 2) results from the fact that the thermocouple reaches the surface when the ice is recessing due to sublimation. The temperature then converges towards the temperature a few mm above the surface.

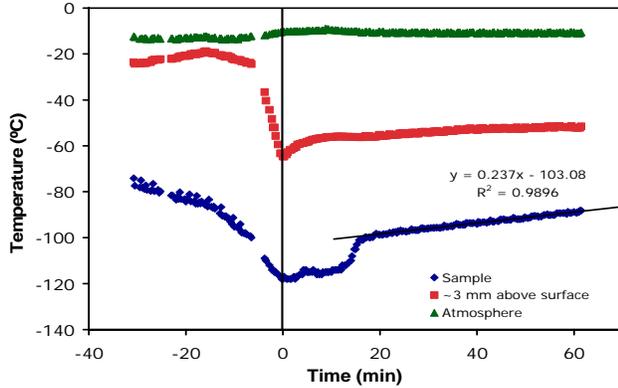


Figure 2. Thermal profiles of the atmosphere, 20 cm above the sample (green), 20 mm above the surface (red) and inside the sample (blue), obtained during sublimation of CO₂ ice at 7 mbar.

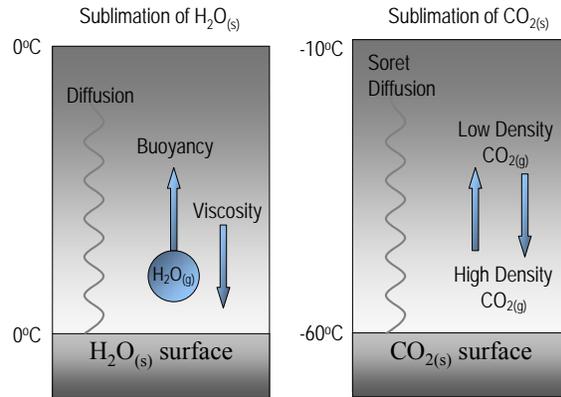
The CO₂ sublimation process is governed by heat transfer between the chamber and the ice, and by diffusion of the sublimated molecules from the surface. There are three possible heat transfer processes: conduction from the ice surface into the ice interior, heat transfer from the warmer atmosphere to the cooler ice surface, and radiation from the chamber walls to the ice surface.

At the beginning of the experiment, the thermocouple below the ice surface reads ~150K, indicating that conduction has caused the ice to reach internal thermal equilibrium during the approximately 30 min pump-down. As a result, the surface and interior of the ice are at the same temperature, eliminating conduction into the ice as a heat transfer model. At this point, the ice surface has reached the solid - vapor equilibrium temperature associated with chamber pressure (7 mbar, 150K, Fig. 2). Therefore sublimation occurs because the atmosphere is too warm compared to the cold ice surface (263K against 150K, Fig. 2).

Thermal conduction in the CO₂ atmosphere is too low to be an efficient process in the chamber. Since the ice surface is considerably colder than the atmosphere, there are no buoyancy effects creating free convection, and there is no wind to create forced convection. Therefore, sublimation of CO₂ ice is controlled by radiation from the walls. We therefore use the following equation to describe CO₂ ice sublimation:

$$E_S = \frac{\Delta E_{rad}}{\rho_{ice} \Delta H_{298K, 1bar}^{sub}} \quad (1)$$

where ΔE_{rad} is the energy absorbed by the surface ($W m^{-2}$), ρ_{ice} is the CO₂ ice density ($1562 kg m^{-3}$) and $\Delta H_{298K, 1bar}^{sub}$ is the latent heat of sublimation ($571.3 \times 10^3 J kg^{-1}$). Our calculations show that radiative energy from the walls at 263K is about $220 W m^{-2}$, giving a sublimation rate of $0.89 mm hr^{-1}$, a value close to experimental results ($1.2 mm hr^{-1}$). Including the conduction from the atmosphere ($\sim 20 W m^{-2}$) raises the sublimation rate to $0.97 mm hr^{-1}$.



$$E = \{D (C_{surf} - C_{\infty}) / L\} G_f \quad E = \{D (C_{surf} - C_{\infty}) / L\} \chi_f$$

Figure 3. Comparison between sublimation processes of H₂O and CO₂ ice on Mars. Water ice sublimation is mostly driven by diffusion and buoyancy into the heavier CO₂ atmosphere [13]. In the case of CO₂, the density gradient is reversed since the atmosphere is less dense than the surface. This situation simplifies the heat transfer to radiation from the walls only (no possible convection, and very low conduction from the gas phase).

Conclusions: Our experimental results suggest that radiative transfer is controlling sublimation. Interestingly, our radiative energy value is very close to the highest values calculated for martian polar caps (about $250 W m^{-2}$ at $85^\circ N$). This explains the strong similarity between our measured sublimation rate and values measured from polar caps recession [4,6].

References : [1] Langevin Y. et al. (2005) *Science* 307, 1581-1584. [2] Leighton R. B., B. C. Murray (1966) *Science* 153, 136-144. [3] Murray B. C., M. C. Malin (1973) *Science* 182, 437-443. [4] Smith D. E. et al. (2001) *Science* 294, 2141-2146. [5] Bibring J. P. et al. (2004) *Nature* 428, 627-630. [6] Malin M. C. et al. (2001) *Science* 294, 2146-2148. [7] Byrne S., A. P. Ingersoll (2003) *Science* 299, 1051-1053. [8] Fishbaugh K. E., J. W. Head III (2001) *Icarus* 154, 145-161. [9] Fanale F. P. et al. (1982) *J. Geophys. Res.* 87, 10215-10225. [10] Fanale F. P., W. A. Cannon (1971) *Nature* 230, 502-504. [11] Chevrier V. et al. (2007) *Geophys. Res. Lett.* 34. [12] Sears D. W. G., S. R. Moore (2005) *Geophys. Res. Lett.* 32. [13] Ingersoll A. P. (1970) *Science* 168, 972-973.