

SUBLIMATION KINETICS OF CO₂ ICE ON THE SURFACE OF MARS. K. White^{1,2}, V. Chevrier¹, L. Roe¹ and K. Bryson¹, 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 <kfwhite@bsu.edu, 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 H₂O ice layer [5]. This veneer is too small for the caps to be in equilibrium with the atmosphere [6,7]. This would also confirm the fact that polar caps are apparently 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, that completely lack any 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 present here the results of experiments measuring the sublimation rate of pure CO₂ ice under simulated martian conditions, as we have previously done for H₂O [11,12].

Methods: Dry ice was packed into a beaker. For the initial experiments a thermocouple was placed on the surface, while for later experiments a thermocouple was placed below the surface and another on the surface to understand the temperature profile. Our planetary environmental chamber was evacuated to less than 0.09 mbar, filled with dry gaseous CO₂ (g) to approximately 1000 mbar, 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 at $-10 \pm 1^\circ\text{C}$, respectively. Before and after each experiment the height and diameter of the dry ice were measured.

Results: All measurements show that the mass loss of CO₂ is extremely linear, with R² coefficients systematically above 0.99 (Fig. 1). From the mass loss in g min⁻¹, we determine the 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 sublimation mechanism on Mars and in our chamber.

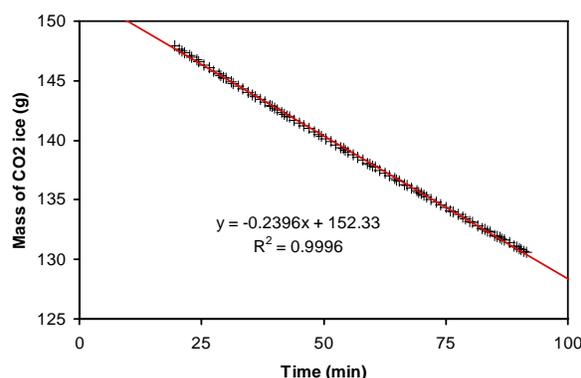


Figure 1. Mass of CO₂ ice as a function of time (sample #3 in Table 1).

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

#	Type	E _s (mm h ⁻¹)
1	Gravel	1.06
2	Solid block	1.01
3	Solid block	0.99
4	Powder	1.36
5	Powder	1.63
6	Powder	1.68
7	Loose powder	1.22
8	Loose powder	1.09
9	Packed powder	0.91
10	Packed powder	1.04

It has been shown previously that surface temperature is a major parameter controlling the sublimation rate of water ice [11,13]. We measured the temperature profiles inside the sample, a few mm above the surface and in the atmosphere, 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 150

± 2 K which corresponds to the equilibrium temperature of CO_2 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 thermodynamic equilibrium with the atmosphere. The temperature a few mm above the surface is logically higher of 30 to 60 K, as a result of the strong gradient between the surface and the atmosphere. This thermodynamic disequilibrium between the environment and the CO_2 ice surface is the cause of the sublimation (the environment = chamber + atmosphere is too warm).

The jump on the inside temperature profiles (Fig. 2) results from the fact that the thermocouple reaches the surface when the ice is recessing due to sublimation. This therefore records the thermal boundary layer during sublimation. Then, straight lines indicate that thermal transfer is principally achieved through conduction. Using the slope of the lines (Fig. 2), we can extract the average temperature gradient in the atmosphere, in our case about 0.85 K mm^{-1} .

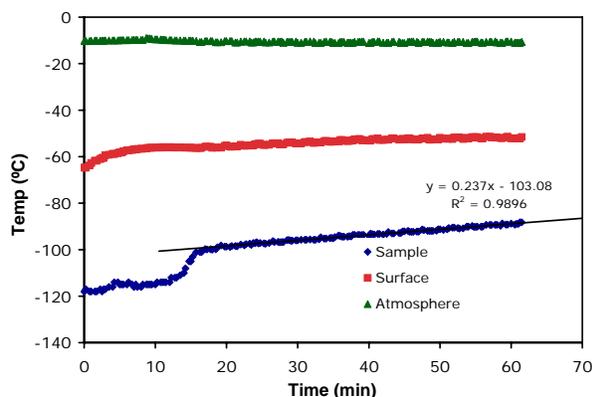
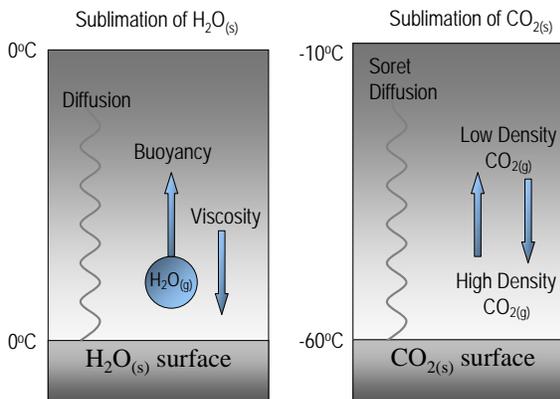


Figure 2. Thermal profiles of the atmosphere, 20 cm above the sample (green), 20 mm above the surface (red) and inside the sample (blue), obtained during sublimation of CO_2 ice at 7 mbar.

Discussion: The CO_2 sublimation process is governed by heat transfer between the chamber and the ice, and by transfer of the sublimated molecules away from the surface. There are three potential heat transfer processes in effect: conduction / convection from the warmer atmosphere to the cooler ice surface, conduction from the ice surface into the ice interior, and radiation from the chamber walls to the ice surface. It is found that radiation from the chamber walls at 263 K to the ice surface at 150 K is the dominant heat transfer mechanism.

During the initial 1 hour pump-down period, the temperature of the ice surface rapidly reaches the solid-vapor saturation temperature associated with chamber pressure (7 mbar, 150K, Fig. 2). At the beginning of the experiment, an embedded thermocouple, approximately 1 cm below the ice

surface, also reads 150 K, indicating that conduction has caused the ice to reach internal thermal equilibrium. As a result, the surface and interior of the ice are at the same temperature, eliminating conduction into the ice as a heat transfer mode, for our conditions.



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

Figure 3. Comparison between the sublimation processes of H_2O and CO_2 ice on Mars. Water ice sublimation is mostly driven by diffusion and buoyancy into the heavier CO_2 atmosphere [13]. In the case of CO_2 , the density gradient is reversed since the atmosphere is warmer than the surface, and the diffusing gas has the same molecular weight as the atmosphere.

Conclusions: Radiative transfer appears to be the dominant heat transfer process in our case. The situation is similar on the martian surface where the chamber walls are replaced by the sun. Therefore the difference between our experimentally measured rates and those observed on Mars probably results from differences in radiation flux. Alternatively, in our case the mass transfer from the surface to the atmosphere may be affected by density gradients resulting from temperature gradients between the very cold surface and the warm atmosphere.

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.