BEHAVIOR OF SOLID CO_2 ON MARS: A REAL ZOO. Hugh H. Kieffer, *U. S. Geological Survey [Emeritus], Flagstaff, AZ 86001, USA, (hkieffer@uneedspeed.net).*

Observations of the martian polar caps by TES, THEMIS and MOC have revealed several unexpected things: now informally known as cryptic material, Dalmatian spots, black spiders, oriented fans and fried eggs. These result from the characteristics and behavior of solid CO_2 on Mars, which is unlike anything on Earth. I will attempt to explain this zoo qualitatively in terms of the interaction of CO_2 and dust with the solar and thermal radiation fields on Mars. Some of these concepts have been published [11, 10, 14].

1 CO_2 Surface Condensation Modes

The condensation of the predominant gas in an atmosphere by radiative cooling yields the prominent seasonal polar caps on Mars. This process has no terrestrial analogy, which limits our intuition. This process is difficult to impossible to simulate in the laboratory because the natural force that allows condensation at a location other than at the coldest boundary (which sets the radiation balance) is gravitation, yielding a characteristic scale-height on Mars of 7 km. A practical laboratory scale would require a physical barrier that is completely transparent to thermal radiation,

The altitude at which CO_2 condenses in the martian winter has been largely clarified by TES observations. This problem was studied by Forget et al.[2]. They found that significant condensation occurs in the atmosphere initially with small grain sizes, which then rapidly grow to the order of 100 μm. However, the large grain sizes implied by the TES observations in many areas in the polar night indicate that most of the condensation occurs at the Martian surface. TES spectra in the 25 μm region indicate that the "**cryptic**" regions of cold-dark polar material consist of a CO_2 non-scattering slab composed of indeterminately large grains.

For condensation of a nearly pure gas by radiative loss there can be two end-member solutions for the form of the solid. If the abundance of non-condensing gases is negligible, so that a diffusion gradient of the condensing material is not involved, then a thick slab can form. This is particularly true when the amount of gas between the condensation site and the low-radiation background (space) is large enough that significant path lengths in the solid are needed to generate appreciable emissivities outside the bands in which the gas absorbs. In this case, which holds for Mars, the dominant radiative loss of the condensate is from inside the bulk material. Growth perturbations outward from a planar solid interface, such as a crystal spike growing upward, have a poor conductive path to the bulk solid which, in turn, can radiate away the latent heat of condensation. Lacking a diffusion gradient at the tip of such a spike, the condensation rate is limited by conductive heat loss, not by abundance of molecules in the gas phase, and this tip is at a disadvantage for condensation relative to the bulk solid. Thus these perturbations do not grow, and the expected steady state form is a thick slab with a smooth surface. Such slabs are observed to grow in laboratory conditions of pure condensing gases [8], although in those cases the thermal gradient internal to the slab results from conduction to a cold substrate rather than by radiative cooling.

In the presence of some amount of non-condensing gas, e.g., the 5% of N_2 plus Ar on Mars, at the micro-physical level there will be some diffusion gradient of the condensing gas toward the condensation sites. If one assumes that both the temperature gradient and the concentration gradient of the condensate are linear across this layer, as would be expected for steady state conditions, then, because of the nonlinear dependence of saturation pressure upon temperature, the partial pressure will be above the saturation pressure throughout this layer. Under this condition, if there is adequate heat conduction down the spike into the substrate (from which radiation is efficient), then spikes sticking up into this diffusion gradient become the favored site of condensation and they will grow more rapidly than locations deeper into the diffusion gradient. The steady state solution for the form of such a growing deposit is long columnar crystals oriented along the diffusion gradient. Such deposits also are observed to form in laboratory conditions of substrate cooling when small amounts of non-condensing gas are introduced into the chamber [8, 9]. This process of growth in a diffusion gradient gives rise to the beautiful H_2O hoar frost crystals which can be seen on calm terrestrial winter mornings.

Although it has been shown that enriched layers of the non-condensing Martian gases (nitrogen and argon) would be dynamically unstable [5], this process likely occurs at the micro-physical level, e.g., at the scale of frost grains. The requirement to address this process is a model of the stability of a gravitationally unstable diffusion gradient at the scale of millimeters or less when the primary gas is condensing with net flow downward toward the surface.

TES observations indicate that both the slab growth and deposition of fine-grain CO_2 condensates occur in the polar night and that different condensation processes are dominant in different locations. Also, fine-grained CO_2 condensates (frost) can undergo rapid metamorphism into a nonporous (and hence non-scattering for a non-birefringent material such as solid CO_2) polycrystalline layer[1]. The reason for the geographic distribution of the cryptic material is unknown.

2 Radiation Balance in a Pure Solid CO_2 Slab

During the polar night, the radiative balance of surface CO_2 will be negative (barring an extraordinarily warm atmosphere). With the Sun above the horizon, solar radiation penetrates deeply into pure CO_2 . The relative absorption lengths for solar and thermal energy become important.

Using the optical properties of solid carbon dioxide [4], the penetration of solar energy into a slab of CO_2 can be calculated as

$$\int_0^\infty S_\lambda e^{-p/l_\lambda} d\lambda \quad (1)$$

where $S_\lambda = S_\odot(1 - R_\lambda)\cos i/U^2$ is the sunlight that is refracted into the slab surface, R_λ is the Fresnel reflection coefficient, i is the incidence angle (measured from zenith), U the heliocentric distance in Astronomical Units, p is the path length from the surface along the refracted path and $l_\lambda = \lambda/(4\pi n_i/n_r)$ is the absorption length; n_r and n_i are the real and imaginary parths of the comples index of refraction.

A similar calculation at thermal wavelengths replacing $S_\odot/U^2$ with the Planck function (with $i = 60°$ to represent the upper hemisphere) yields the effective visibility of space to thermal energy within the slab.

For typical polar summer conditions (incidence angle of $65°, U = 1.5$), 2/3 of the solar energy penetrates 1m into pure solid CO_2 , whereas thermal flux is reduced to 50% in 3.7 mm. The top 2 mm of the slab are in net radiative loss; below that absorption of insolation results in net heating.

3 Dirty CO_2 Ice

Mars atmosphere is generally dusty with particles of radius on the order of 2 μm[7, 15]. During the CO_2 condensation season, atmospheric dust grains probably act as condensation nuclei; perhaps first for H_2O and then for CO_2. The proportion of dust in the CO_2 cap has not been measured, but is reasonably assumed to be near the average abundance of dust in the atmosphere. Using an average visual opacity of the atmosphere of 0.5 yields a dust abundance of about 1.5×10^{-3} kg m^{-3} or roughly 2×10^{-5} by mass. Because the particle size is smaller than thermal wavelengths, the presence of embedded dust will make little change to the thermal radiation environment, but will shorten substantially the solar absorption lengths, narrowing or removing entirely the surficial layer with net radiation loss.

Using the above values, and densities of dust grains and solid CO_2 of 2300 and 1600 kg m^{-3}, respectively, corresponds to a mean dust grain separation of ~130 μm. If a seasonal cap budget of 1000 kg m^{-2} is adopted [11], the mass of dust in the cap is 0.02 kg m^{-2} and the geometric opacity of the dust in the cap is ~1.6. The visual opacity of dust in the slab at sunrise will be roughly the average opacity of the southern atmosphere during the condensation season times the ratio of slab to atmospheric mass, or ~3.3, in agreement with the geometric opacity if the scattering efficiency is taken as 2.0, as expected from Mie theory.

4 CO_2 Self Cleaning by Entrained Dust Movement

A first approximation is that for a dirty CO_2 slab, all of the solar energy is absorbed by the dust grains. However, because the surrounding CO_2 is isothermal, this radiation absorbed by the grains must go into sublimation of solid CO_2 . If the local material is impermeable, a high-pressure pocket of gas will form around the grain and local elastic deformation will increase the pressure in the solid CO_2 , allowing some heat to be absorbed without sublimation; no quantitative calculations of this process have been done. The warmer grain cannot be in direct contact with the CO_2 , but must rest on a microscopic layer of gas at the bottom of its vapor prison. If the local gas bubble does not rupture, there will be a downward migration of the bubble through the solid as vapor re-condenses on the roof of the bubble, the location most distant from the grain and hence coolest, and the grain will "burrow" downward as sublimation continues under the grain. Thus, a sealed finite vertical columnar hole will travel downward with the grain. When the grain reaches the bottom of the impermeable layer, it will be ejected downward. This self-cleaning, self-annealing process will tend to reduce the amount of dust in the ice through the spring. Because the net solar flux is greater toward the top of the slab, the uppermost particles will move most rapidly, resulting in concentration of dust as a descending "curtain" in the slab, leaving clean ice above.

A quantitative model of the vertical migration velocity of a grain and its sealed gas envelope is wanting.

If the environment is permeable, or if the bubble fractures, the grain may be carried along in the streaming gas. The gas velocity in a tube must be higher than the regional sublimation wind; that net vertical gas velocity is related directly to the regional albedo and is easily computed ([11]section 12.2). Bright ($A = 0.8$) and dark ($A = 0.25$) regions can loft grains smaller than ~2 and ~7 μm radius, respectively. Thus, dust grains which entered the seasonal cap from the atmospher can be carried out of a CO_2 slab.

5 Development of Pathways and Vents

The net positive radiation divergence near the surface of pure CO_2 , as described above, will tend to seal small holes in the surface layer. Porosity will generally be sealed in a region that grows downward from the surface. Thus, the gas formed by springtime sublimation generally cannot diffuse upward through the CO_2 deposit. The gas resulting from net sublimation below the surface must escape somewhere and will hold open some set of larger holes. Because the gases in these vents will have some entrained dust, they can continue to absorb solar radiation, transfer energy to the vent walls, and remain open and grow. Also, gas under an impermeable CO_2 slab could reach pressures several times the atmospheric surface pressure. The saturation temperature under a 1000 kg m^{-2} slab would be 162K, enhancing the ability of venting gas to enlarge the pathways. Because higher velocities are possible and because of the r^2 heat flow versus the r^1 circumference, larger holes/paths will grow at the expense of smaller ones.

To the extent that solar energy penetrates to the bottom of the seasonal CO_2 slab, gas will be released beneath the slab and must find some path to the open atmosphere. It may travel laterally underneath the slab to vents, cracks, or even to the edge of the seasonal deposit. It is difficult to predict the spacing of such vents, but they collectively must carry the total sublimation gas flux of about 10 kg m^{-2} /day. It seems likely that the spacing between major pathways would be no more than a couple orders of magnitude greater than the thickness of the slab, or a few hundred meters. This is what is actually observed.

As the effective vents are separated by substantially more than the slab thickness, gas velocities will become far greater than required to suspend dust particles, and any sub-slab lateral transport may begin erosion of underlying loose material. Once the velocity exceeds the fluid threshold [3], erosion will begin, although the details of saltation versus suspension may be quite different in a thin layer confined both below and above than for the normal condition of a free upper boundary.

The sub-slab lateral gas velocity will depend upon the geometry of the flow; the average velocity must initially decreases away from the vent. It seems likely that the circularly symmetric case of gas radially converging to a vent is not stable and that channels will develop. Because the soil thermal inertia of the Cryptic region is low, it is likely that the surface material is incohesive and that channelized flow will develop by scouring, beginning near the vents and radiating outward. Although velocities on the order of 10 m/s are required to initiate transport of fine material by saltation [16, 3], injection of dust released from the CO_2 into the lateral flow may initiate motion and scouring at lower velocities; 2 mm/s vertical velocity is adequate to maintain atmospheric dust in suspension. Also, the initial gas flow is likely to be diffuse flow through the soil (versus stream flow above the soil in classic saltation), and small soil grains may begin to move well before saltation threshold velocities.

Dark radially converging dendritic patterns are visible in MOC images of some portions of the spring polar cap, these have been termed "**black spiders**" by the MOC team [6]. In this model, these patterns represent channels formed by sub-slab channelized flow of the sublimation gas toward the vents. Increasingly large particles could become entrained closer to the vent.

The velocity in the vents will be approximately $.005X^2$ m/s, where X is the ratio of vent separation to vent diameter. For example, for vents 1 m in diameter spaced by 100 m, the gas velocity would be 50 m/s. When the jets exhaust into the atmosphere and velocities decrease, the coarser entrained material will fall out in the prevailing downwind direction. In this model, the oriented dark **fans** seen in the MOC images are caused by this process. This is an exotic model that agrees with observations thus far. It predicts that the dark fans will be oriented into the prevailing wind, that they are seasonal and will disappear with, or shortly after, the CO_2 is gone, and that the "black spiders" will be found only in the Cryptic region.

Once a vent has grown to a radius larger than the slab thickness, wall erosion by warm venting gases becomes relatively less important, and the growth of the dark (hence warmer) spot by local re-radiation and by warming of the atmosphere immediately over the bare ground, which can waft over the neighboring frosts, will cause the defrosted areas to grow, much as terrestrial spring snow cover recedes by the growth and combination of many small defrosted spots.

Darks vents are generally, but not exclusively, associated with dunes. Vents can progress into dark spots (**Dalmatian spots**) which grow monotonically until they coalesce. Dark halos commonly develop around the Dalmatian spots; these have been termed ("**fried-eggs**" based on their symmetry and proportions. Many MOC images of the seasonal cap in summer-time show great variegation of reflectance, interpreted to be incomplete solid CO_2 cover [13]. Sequences of images show the development of evenly-distributed circular darks spots, which may represent the evolution of vents, commonly spaced by order 100 m, that gradually expand to consume the seasonal cap.

This model has been supported by a survey of the location of "spiders" in MOC imaging which shows that they are largely confined to the Cryptic region and their centers generally correlate with the location of fans[12]. Spiders commonly persist as low relief features through the summer[12].

Most of this story has been developed from observations of the south polar cap. The north and south caps seem to be somewhat different in terms of the abundance of these features; e.g., spiders have not yet been identified in the north.

6 Summary

Deep in the martian polar night, there is some CO_2 snowfall, but most of the solid CO_2 takes the form of a uniform, continuous, non-scattering slab with embedded dust (and H_2O ice) grains. Following seasonal sunrise, in some areas the ice brightens due to fracture or surficial frosting, but in other areas the slab persists to form the **cryptic** regions. The solar energy is largely absorbed by the dust grains, which either burrow downward or escape upward, cleaning the CO_2 slab which anneals small holes near its surface. Sunlight then penetrates to the bottom of the slab, warming the soil and subliming ice from the bottom. Widely spaced vents develop that allow the gas to escape. As the sub-slab gas converges toward the vents, it scours the soil surface along ragged channels (**spiders**). Dust entrained in the jetting gas falls out downwind to form **fans**. The vents enlarge to become **Dalmatian spots**, some of which form **fried-egg** halos; these enlarge to consume the seasonal cap. Only the topographic ghosts of the spiders persist through the summer.

Here is a short list of remaining known puzzles, it seems sure to grow!:
- The basis for the geographic distribution of cryptic terrain.
- Why do cryptic regions repeat year to year?
- The basis for the location and spacing of the fans and spiders.
- The causal process for the dark halo "fried eggs".
- Quantitative theory of the formation and velocities of dust bubbles.

THEMIS thermal images of the evolution of this menagerie are expected to be quite helpful in elucidating the processes.

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