

Reports

Mars: Retention of Ice

Abstract. *Water in the form of ice can exist on Mars as permafrost that is either in equilibrium with the water content of the atmosphere or gradually evaporating through a protective layer of soil. The latter situation is evaluated quantitatively, and the required thicknesses of the protective layers are estimated. The presence of subsurface ice may explain the higher radar reflectivity of the dark areas than of the bright areas. Observation of its seasonal variations is suggested.*

The biological, climatological, and morphological implications of the existence of water on Mars depend radically upon its amount, form, and location. The best values (1) of the triple point of water, 6.11 mb and 273°K, fall right in the middle of the range of pressures deduced from the Mariner IV occultation experiments (2), and they are bracketed by the calculated and observed surface temperatures.

The occurrence of pressures and temperatures appropriate for liquid water, however, is rarer than for ice and vapor. The only direct quantitative measurement available is that of precipitable water vapor in the atmosphere in the amount of $14 \pm 7 \mu$ (3, 4). The generally subfreezing surface temperatures (5) imply also that there may be considerable amounts of ice as subsurface permafrost (6). The polar caps now appear to be of solid CO₂ rather than ice as was previously assumed. One can be sure also that there are no open bodies of water, but the occurrence of surface

temperatures (7) as high as 340°K suggests that there may be localized temporary and periodic melting. My purpose is to look quantitatively into the stability of permafrost, and its preservation in the Martian soil.

If the mean annual temperature is low enough, permafrost can exist in equilibrium with the water content of the atmosphere. Under this condition permafrost on Mars can exist within a few meters of the surface at latitudes higher than about 45 deg (4, 6). On the other hand, when the mean temperatures are higher, the ice is gradually depleted and its lifetime is determined by the thickness of a protective particulate layer. To a certain extent this question resembles the problem of the retention of ice on Moon (8).

The Martian yellow clouds require (7, 9) particles not smaller than a couple of hundred microns, but these particles constitute probably only a small fraction of the actual surface coverage. A careful analysis (10) of the thermal

properties of the Martian surface suggests that the predominant size is from a few tenths of 1 μ up to about 20 μ . The larger particles are undoubtedly mixed in, but the effective pore size will be determined by the smaller grains. Table 1 shows the effective pore sizes m for the range of porosities ϵ and grain diameters ϕ that I consider. Porosity is here defined as the ratio of the total pore volume to the total volume of the porous layer.

If it is assumed (2) that the Martian pressure near the surface is 5 mb, one obtains in the highly diluted CO₂-H₂O mixture a mean free path of 4 to 8 μ for an H₂O molecule for temperatures varying from 160° to 300°K. The fact that these values fall in the middle of the range of pore diameters listed (Table 1) indicates that the mechanism of transport of water vapor varies from normal diffusion in large pores to Knudsen flow in small pores. In normal diffusion, the mean free path of molecules is determined by collisions between molecules, and the collision with the walls can be neglected. In the Knudsen flow, the situation is just the opposite: it is the pore size that determines the mean free path of the molecules. Under these conditions the theory of diffusion in porous media at uniform pressure (11) must be used. In the normal diffusion region in a binary gas mixture the flux of molecules A along z -axis is given by

$$J_A = -D_{AB} (\delta n_A / \delta z) + X_A J$$

where D_{AB} is the usual interdiffusion coefficient, n_A is the number of molecules A per cubic centimeter, X_A is their mole fraction, and $J = J_A + J_B$. For small X_A the second term can be omitted. In the Knudsen region, on the other hand,

$$J_A = -D_{AK} (\delta n_A / \delta z)$$

applies where D_{AK} is the Knudsen diffusion coefficient. In the intermediate region the effective diffusion coefficient is given by the Bosanquet relation:

$$(D_A)_{\text{eff}}^{-1} = (D_{AB})_{\text{eff}}^{-1} + D_{AK}^{-1}$$

and

$$J_A = -(D_A)_{\text{eff}} (\delta n_A / \delta z)$$

Using the appropriate formulas (12, 13) and numerical values for the CO₂-H₂O mixture, one obtains

$$(D_{AB})_{\text{eff}} = 20.3 (\epsilon/q) (T/T_0)^2$$

and

$$D_{AK} = 4.8 \times 10^4 (m/q) (T/T_0)^{3/2}$$

Table 1. Pore sizes (in microns) for various grain diameters and porosities.

Grain diameter (μ)	Porosity				
	.01	.1	.2	.5	.8
0.5	8×10^{-4}	0.01	0.021	0.083	0.332
10	1.7×10^{-2}	.02	.42	1.7	6.8
200	0.33	3.9	8.3	33	130
1000	1.7	20	42	169	667

Table 2. Mean effective diffusion coefficients (square centimeters per second) for various grain diameters and porosities.

Grain diameter (μ)	Porosity				
	.01	.1	.2	.5	.8
0.5	0.0004	0.004	0.008	0.07	1.3
10	.004	.06	.1	.7	9
200	.009	.08	.2	1.1	11
1000	.01	.1	.25	1.2	12

where $T = 273^\circ\text{K}$ and q is the tortuosity factor. This factor is supposed to take care of the fact that at low porosities many of the pore paths lead to sideward or even backward diffusion; it is usually determined from experimental data. For porosities in the range .2 to .5, parameter q turns out to be about 5; for lower porosities it is higher.

It appears that between 160° and 300°K the influence of temperature on the effective diffusion coefficient is negligible compared to the influence of the mean pore diameter. Table 2 shows the resulting mean effective diffusion coefficients for various porous materials; it is assumed that $q = 1$ for $\epsilon = .8$, $q = 5$ for $\epsilon = .5$, and $q = 10$ for the lower porosities.

The model consists of ice under a layer of thickness L of porous soil, and it is assumed that, in order to have appreciable permafrost or subsoil ice on Mars, a layer of ice 10 m in thickness existed for 10^9 years; thus the maximum permissible loss rate is determined. The partial vapor pressure of water above ice is given by its temperature T , and we assume that at the surface, temperature T_s , the partial pressure of water is effectively zero.

Thus one has a system in which the water vapor diffuses down a concentration gradient and along a temperature gradient. In view of the fact, mentioned above, that temperature has only a secondary effect on the diffusion coefficient, this influence can be neglected. The calculated thicknesses L of the protective layers (Table 3) have primarily relative significance because the absolute values are uncertain within a factor of at least 2 or 3. For $\epsilon = .8$, the calculated thicknesses L were greater than 10 m. I should stress that the dependence of L on T reflects the variation of the pressure of water vapor over ice, and not the variation of the diffusion rate, which, as I have mentioned, is only a slow function of temperature. The range of temperatures in Table 3 covers the range of mean annual temperatures (6) on Mars. It appears that there is a considerable range of particle sizes and porosities at which ice could be preserved during a period of the order of 10^9 years under a layer of reasonable thickness; thus it seems that ice or permafrost may exist also at latitudes lower than 45° .

The results (Table 3) are based on the assumption that the layer of ice loses water by evaporation; in fact it is possible that juvenile water is slowly out-

gassing from the Martian interior and replenishes, at least partially, the permafrost layer near the surface. If the content of juvenile water of Mars, per unit mass, is comparable to that of Earth, such a process may be quite significant. This situation, which at present cannot be evaluated even approximately, would be analogous to that which has been variously suggested for Moon (8). Consequently the thicknesses of the protective layers (Table 3) represent only their upper limits.

The behavior of ice and water on Mars is affected undoubtedly by the seasonal and diurnal variations of the surface temperature at various latitudes. At a sufficient depth below the surface these variations are negligible, but they may reach 100°K and more at the surface (7). It follows that the temperature gradient between the layer of ice and the surface is sometimes positive and sometimes negative. In the first case, the water vapor escapes in the manner discussed; in the second case, however, it may condense in the colder outside layers and form ice that exists until the temperature gradient is gradually re-

versed. In some pores ice may be very stable, since only a small fraction of its surface is exposed to the atmosphere. In this connection it should be kept in mind that the results (Tables 1-3) were obtained for a mean pore diameter m given by ϕ and ϵ ; in fact, even for a large noncapillary value of m , there is a considerable fraction of capillary pores. For instance (14), for a fixed porosity .5 and grain size decreasing from about 4 mm to less than 0.5 mm, the fraction of capillary volume increases from 20 to 93 percent of the total pore volume.

Since, in the warmer regions of Mars, temperatures well above the freezing point were observed, it follows that under favorable circumstances some water may be retained at least for a while in capillary pores; this retention may have biological consequences. The existence of ice in intergranular pores implies that ice may form also in cracks of the grains themselves; such a condition leads to gradual breakup of the grains and to comminution of the surface material, in analogy to well-known geological phenomena on Earth. Furthermore the presence of intra- and intergranular ice may alter the local effective thermal conductivity of the soil and alter interpretation of the observed (10) thermal inertia.

It is interesting to speculate whether ice or water content could affect the radar reflectivity of the soil. An analysis of this reflectivity indicates (15) that the effective dielectric constant of the bright areas is about 2.2; for the dark areas, 3.5. Typical values for sand are near 2.8, compared to dielectric constants of about 80 and 3.3 to 130 (depending on frequency and temperature) for water and ice, respectively. Thus it appears quite possible that the differences in radar reflectivity (16) could be attributed, at least partially, to ice or water retained in the subsurface layers. The thicknesses of the protective layers listed (Table 3) and those calculated from equilibrium considerations (6) are comparable to the penetration depth of the 3.8- to 70-cm radar wavelengths used in various Martian studies.

Without further knowledge of the gradients of porosity and of particle size below the surface, one cannot calculate the true distribution of ice in the soil. Nevertheless, even if the radar does not reach the permafrost itself, it will easily reach the seasonal condensation layer that I have discussed. According to various studies of the thermal prop-

Table 3. Thicknesses (centimeters) of protective layers of soil required to preserve ice for various temperatures, grain diameters, and porosities.

Temp. ($^\circ\text{K}$)	Porosity			
	.01	.1	.2	.5
<i>Grain diameter, 0.5 μ</i>				
240	1000			
230	330			
220	100	1000		
210	30	300	580	
200	6	60	120	900
190	1.5	15	30	220
170		2.5	5	36
160				6
<i>Grain diameter, 10 μ</i>				
220	1000			
210	300			
200	62	900		
190	15	220	370	
180	2.5	36	60	250
170		6	9	36
160			1	4
<i>Grain diameter, 200 μ</i>				
210	580			
200	120	900		
190	30	220	370	
180	4.8	36	60	
170		5.4	9	
160			2	
<i>Grain diameter, 1000 μ</i>				
210	730			
200	150			
190	37	370	930	
180	6	60	150	
170		9	22	
160		1	3	

erties of the Martian surface (6, 10) the amplitude of seasonal temperature variations decreases by a factor of 10 within a layer of the order of several centimeters. If this is the case, the shorter wavelengths would be more likely to reflect seasonal variation than would the longer wavelengths.

Recent radar results (16) suggest that Martian dark areas are probably lowlands rather than highlands; thus one is tempted to ascribe to them higher humidity and higher reflectivity than to the dry, bright uplands. One way to check this conclusion would be to measure seasonal and diurnal changes in radar reflectivity of bright and dark areas; any correlation between radar reflectivity and the well-known Martian "wave of darkening" would be of great interest. This task will be difficult to accomplish from Earth because of the small variation of the phase angle and the large variation of distance between Earth and Mars; an orbiter would be ideally suited for the purpose. One must remember, however, that planetary radar reflectivity is a function of many parameters; thus a seasonal variation could be accounted for by several models. Nevertheless, the ice-water mechanism seems more realistic and more attractive than an analogous mechanism based on the variable photoconductivity (17) of the soil.

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Atmospheric Particulates: Specific Surface Areas and Densities

Abstract. *Suspended particulates in Pittsburgh air were collected on glass-fiber filters. The specific surface areas of particulates brushed from the filter surface varied from 1.55 to 4.51 square meters per gram when measured by the Brunauer-Emmett-Teller (BET) method with nitrogen and krypton, after 8-hour degassing of the samples at 25°C. Specific surfaces of the same samples varied from 4.3 to 8.00 square meters per gram after 4-hour degassing at 200°C. Bulk densities and densities of samples were 0.49 to 0.64 and 2.0 to 2.6 grams per cubic centimeter, respectively. These data provide some basis for explanation of unpredictable responses reported after inhalation of mixtures of pollutant gases and particles by animals and man; they should also assist in interpretation of gas-solid phase reactions in the atmosphere.*

It has been clearly demonstrated experimentally that simple mixtures of air pollutants, when inhaled by animals during single short exposures, can cause unpredictable responses (1); two of the responses noted have been referred to as synergism and antagonism (2). The interaction of gases and vapors with particles is believed to be associated with the abnormal effects observed in the population during episodes of acute air pollution in Donora, Pennsylvania, the Meuse Valley, and London. Although such studies were followed by investigations of the particle-size distributions of potentially irritant particulates in urban atmospheres (3), little work has been done on the physical properties of suspended particulates in urban air. One of the mechanisms proposed to explain the enhanced effects observed when certain combinations of gases and particles are inhaled is that the gas is adsorbed or absorbed by the particle, with subsequent high local concentration of gas at the site of deposition of the particle in the lung (4).

We now report data on specific surface area and density for suspended particulates in Pittsburgh, Pennsylvania.

These data, the first to be reported for an urban aerosol, together with accumulating data on the dimensions and chemical natures of urban aerosols, should assist toxicologists in interpretation of effects observed during episodes of acute air pollution and during inhalation experiments with animals in the laboratory.

Samples of air were collected on the roof of the Graduate School of Public Health between November 1966 and April 1967. Particulates were collected on filter paper (5) with a high-volume sampler (6). Stations of the National Air Sampling Network normally collect samples during a 24-hour period, but this study required large samples for analysis, and sampling time was 1 to 2 weeks at flow rates of 0.87 to 1.45 m³/min. For analysis, samples of about 1 g were obtained by brushing of the top layer of removable dust from the filter; data on particulate weight concentration (micrograms per cubic meter) for this site are available (7).

The specific surface of samples was measured by the Brunauer-Emmett-Teller (BET) method (8); nitrogen and krypton were each used for four sam-

Table 1. Specific surface areas, bulk densities, and densities of suspended particulates in Pittsburgh air; adsorbates are in parentheses. Density values are averages of two determinations for each sample. Effective cross-sectional areas occupied by the adsorbates were assumed to be 16.2 and 19.5 Å² per molecule for nitrogen and krypton, respectively (8).

Sampling period	Specific surface (mg ² /g) degassed at		Density (g/cm ³)	
	25.0°C	200°C	Bulk	Specific
10-22 Nov. 1966	(N) 4.51	(N) 6.86	0.49	2.1
22-29 Nov. 1966	(Kr) 2.61	(Kr) 4.81	.62	2.1
12-26 Jan. 1967	(N) 2.83	(N) 7.27	.57	2.0
26 Jan.-10 Feb. 1967	(N) 3.35	(N) 8.00	.60	2.1
10-24 Feb. 1967	(N) 2.46	(N) 4.52	.63	2.6
3-18 Mar. 1967	(Kr) 1.55	(N) 4.61	.64	2.0
3 Mar.-7 Apr. 1967	(N) 2.86	(N) 4.49	.62	2.0
10-17 Apr. 1967	(Kr) 2.35	(N) 4.31		2.3
	<i>Arithmetic means</i>			
		5.61	0.59	2.2
	<i>Arithmetic standard deviation</i>			
	0.86	1.50	0.05	0.2