Behavior of Carbon Dioxide and Other Volatiles on Mars

A thermal model of the Martian surface suggests that Mars's polar caps are solid carbon dioxide.

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The nature of the Martian polar caps has been a subject of speculation for many decades. They have been variously conjectured to be composed of frozen water, carbon dioxide, or oxides of nitrogen (*1*, p. 362; *2*, *3*). The weight of scientific opinion, based upon a variety of evidence, currently favors water ice as the dominant substance comprising the polar caps. However, much of the relevant observational evidence has undergone significant change and improvement in recent years, so that it seems appropriate to reexamine the question in the light of the more complete and reliable measurements now available.

The purpose of this article is to report results of a new study of the problem based on a consideration of the heat balance of the planet. We believe that this study points strongly toward frozen CO_2 as the dominant substance comprising the Martian polar caps.

Further, we are led to suggest that (i) the total amount of CO_2 on Mars may exceed the amount present in the atmosphere by a considerable factor, the excess being present as solid CO_2 and CO_2 permafrost in and under the permanent north polar cap; (ii) the partial pressure of CO_2 in Mars's atmosphere may be regulated by the north polar cap; and (iii) the total pressure of the Martian atmosphere may change semiannually by a significant amount because of the freezing out of much of the atmospheric CO_2 at either pole. Considerable quantities of water-ice permafrost may also be present in the subsurface of the polar regions and perhaps of more temperate regions as well. Many organic compounds of biological interest, however, are more volatile than water at low temperatures and might be easily evaporated from permeable soil and become trapped as minor constituents of the permanent polar cap.

We propose that selective trapping of CO_2 (and H_2O) in the solid phase may help explain the anomalously high concentration of CO_2 (and probably H_2O) on Mars relative to nitrogen.

Surface and Soil Temperatures

In order to understand the behavior of volatiles on Mars more fully, we have investigated the expected diurnal and annual temperature variations at various latitudes, using a thermal model of the Martian surface in which each surface element is treated as a horizontal plane, at some instantaneous temperature T_1, which absorbs a fraction F of the incident solar radiation, emits blackbody radiation at temperature T_1 with an emissivity E, exchanges heat with underlying layers by thermal conduction (with constant conductivity), and absorbs or releases latent heat if a condensed volatile is present. Radiative thermal exchange with the atmosphere is assumed negligible except insofar as the atmosphere may affect E by blocking certain wavelengths emitted by the surface. Horizontal heat transport by wind is also neglected, although some form of planetary circulation is presumed to replenish condensed CO_2 and H_2O.

The latter two assumptions may constitute a significant oversimplification of the actual situation on Mars. In particular, Sinton has suggested the possibility of some horizontal heat transport, on the basis of temperature measurements derived from infrared brightness (*3a*). It is also possible that condensed H_2O or CO_2 particles in the atmosphere, particularly at the poles during the autumn and winter, may provide a significant local blanketing effect. We recognize that both effects may be important, but we have purposely confined our attention to a simple model in order to determine how well such a model can account for the observed properties of Mars. We find, in fact, surprisingly good agreement between the observed properties and the properties predicted on the basis of this model.

Typical values adopted for the various numerical parameters were as follows: $F = 0.85$, corresponding to an average Bond albedo $A = 0.15$; $E = 0.85$, a value which allows for the blocking effect of 5000 centimeter-atmosphere of CO_2 at pressure of 5 millibars [based on the tables of calculated CO_2 transparency of Stull, Wyatt, and Plass (*4*)] and an intrinsic emissivity of 0.95 to 1.00 (characteristic of powdered silicate minerals in the 10- to 50-micron wavelength range observed under natural conditions); $K = 2.5 \times 10^{-4}$ watt cm^{-1} $(°K)^{-1}$; $C = 3.3$ j g^{-1} $(°K)^{-1}$; $\rho = 1.6$ g cm^{-3}. The above values for soil conductivity (K), specific heat (C), and density (ρ) are similar to those derived by Leovy (*5*) from analysis of the infrared observations of Sinton and Strong (*6*).

The thermal history of such a surface was followed for 2 to 5 Martian years at 19 latitudes from $-90°$ to $+90°$, the equations of radiative and thermal exchange being evaluated (by a 7094 computer) for each 1-hour period during every 5th day to a depth of 3 meters, well below the thermal "skin depth" for annual temperature changes. The depth coordinate x was treated in three parts: (i) the top surface, $x_1 = O$; (ii) nine equal layers 1.5 cm thick, centered at $x_2 = 0.75, \ldots x_{10} = 12.75$ cm; and (iii) ten equal layers 30 cm thick, centered at $x_{11} = 15, \ldots x_{20} = 2.85$ cm. The boundary conditions on the temperature at a given latitude were as follows.

1) The surface temperature T_1 was taken as a linear extrapolation to the surface of the values for the upper two layers: $T_1 = (3T_2/2) - (T_3/2)$.

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2) The net heat gain or loss, Q_2, for the top layer was taken as

$$Q_2 = (-E_\sigma T_1^4 + S_o \cos Z + K(T_3 - T_2)/\Delta x)\,\Delta t$$

where S_0 (= 0.06 W cm^{-2}) is the solar constant at Mars; σ is the Stefan-Boltzmann constant; cos Z is the cosine of the zenith angle of the sun; Δt = 3600 seconds, and Δx = 1.5 cm.

3) The quantity Q_2 was used either to change the temperature of the top layer or (as latent heat) to condense or evaporate CO_2 or H_2O, as required by the ambient conditions.

4) The layer x_{10} was assumed to exchange heat with the upper layers in proportion to the temperature gradient $(T_{10} - T_9)/\Delta x$, and with the lower layers in proportion to the gradient $(T_{12} - T_{11})/\Delta x'$, with $\Delta x' = 30$ cm.

5) The temperature T_{11} was set equal to T_{10}, as described below.

6) The layer x_{20} was assumed to exchange heat only with overlying layers.

The initial temperatures at each latitude were constant with depth and equal to the mean annual temperatures found in pilot calculations. In order to speed the convergence to a steady state, the temperatures T_i of all layers were adjusted by amounts ΔT_i at the end of each annual calculation according to the equation

$$\Delta T_i = (T_{\mathrm{av}} - T_{20})\,(2x_i/x_{20} - x_i^2/x_{20}^2)$$

where T_{av} is the calculated yearly average surface temperature at the corresponding latitude.

For each diurnal calculation, made on an hourly basis, only the temperatures of the upper nine layers were changed; at the end of this calculation five successive iterations on the lower ten layers were made, T_{11} being held constant and equal to the final value of T_{10}.

Representative curves for the daily temperature variations at the equator are shown in Fig. 1 for three different thermal conductivities; these are in adequate agreement with the measurements of Sinton and Strong (*6*). At first, the possibility of condensation of CO_2 was ignored. The annual variation of daily minimum temperature found for this moonlike case are plotted in Fig. 2, which shows that the minimum night-time temperatures would remain above 145°K at all seasons at the equator and at low temperate latitudes, but would drop considerably below 145°K in winter time at subpolar and polar latitudes. Since the condensation temperature of CO_2 at the currently accepted pressure of about 4 millibars is 145°K, it is immediately clear from Fig. 2 that CO_2 should precipitate out and accumulate at the higher latitudes during local winter.

Carbon Dioxide Relationships

A number of calculations which permitted the condensation of CO_2 were made. These were made progressively more complete and realistic until ultimately even the effects of orbital eccentricity and depletion of CO_2 by freezing were included. Various albedos for solid CO_2 were used, ranging from 0.60 to 0.75, and different initial amounts of atmospheric CO_2 were assumed. All these calculations are in agreement with respect to the following major effects.

1) Large amounts of CO_2 were always found to precipitate near each pole during the Martian winter, as shown in Fig. 3. Typical maximum amounts were 100 to 150 g cm^{-2}.

2) Carbon-dioxide precipitation occurred above latitude + 50° and below − 45°; this is about the range observed for the actual Martian polar caps.

3) At latitudes near the boundary of a polar cap, the calculations indicated, CO_2 would precipitate at night and evaporate during the day; the "frost" would usually disappear before noon, unless the cap was growing rapidly.

4) The amount of CO_2 precipitated in the polar regions was so great as to appreciably affect the total atmospheric pressure. In a typical case, the atmospheric pressure varied semiannually by almost ± 1 millibar from the mean (Fig. 4).

In addition, the calculated rate of disappearance of a CO_2 frost cap agrees rather well with the observed rate, as illustrated in Fig. 5.

The total radio (thermal) emission from Mars has been measured at various wavelengths (*7–9*) and constitutes an important constraint upon the soil temperature derived from a model. Of course, only the very surface of the soil undergoes diurnal and annual temperature variations as great as those shown in Figs. 1 and 2. Within a few centimeters' depth the diurnal variation is damped out, and within a depth of a few tens of centimeters the annual variation is no longer significant. The average temperature over the planetary disk as seen from the direction of the sun was calculated for each depth below the surface for a number of models. Representative results for the CO_2 model are shown in Fig. 6. Since dry silicates are good insulators and therefore somewhat transparent to radio waves, radio brightness temperatures refer effectively to emission from some region within the soil at, perhaps, a depth of three to ten wavelengths. The curve of Fig. 6 for a depth of 15 centimeters can therefore be taken as an approximate guide to the radio emission of 3- to 4-centimeter wavelength. In Fig. 7, the temperature at this depth is compared with recent radio observations (*8*) for two models.

The calculations brought out another expected consequence of CO_2 solid-vapor equilibrium: if the total abundance of CO_2 is greater than about 15 g cm^{-2}, the north polar cap will not disappear during the summer, as is in fact the case on Mars. The equilibrium partial pressure of CO_2 for this (or any greater) abundance is 3 to 5 millibars. Thus, the observed partial pressure of CO_2 is itself strong evidence for the existence of a permanent CO_2 ice cap and, probably, CO_2-saturated permafrost in the north polar region. This important point merits elaboration.

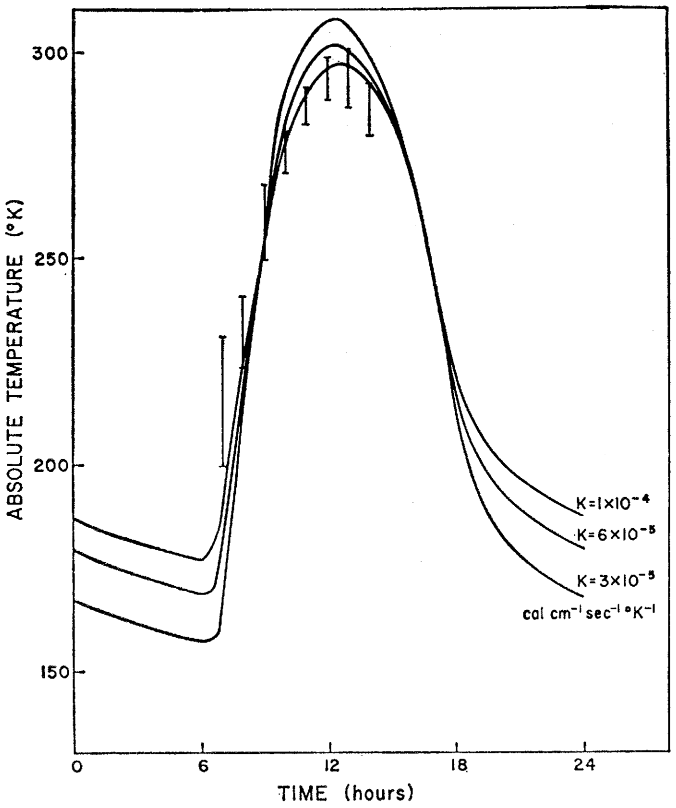
Let us assume an initial amount of atmospheric CO_2 sufficient to allow some CO_2 to remain condensed in the north polar region throughout the summer. In this case the permanent cap is, on the average, the coldest place on the planet, and, furthermore, it is of nearly constant temperature T_0 throughout the year. Therefore, the rate R_r at which heat is radiated throughout the year is constant and is

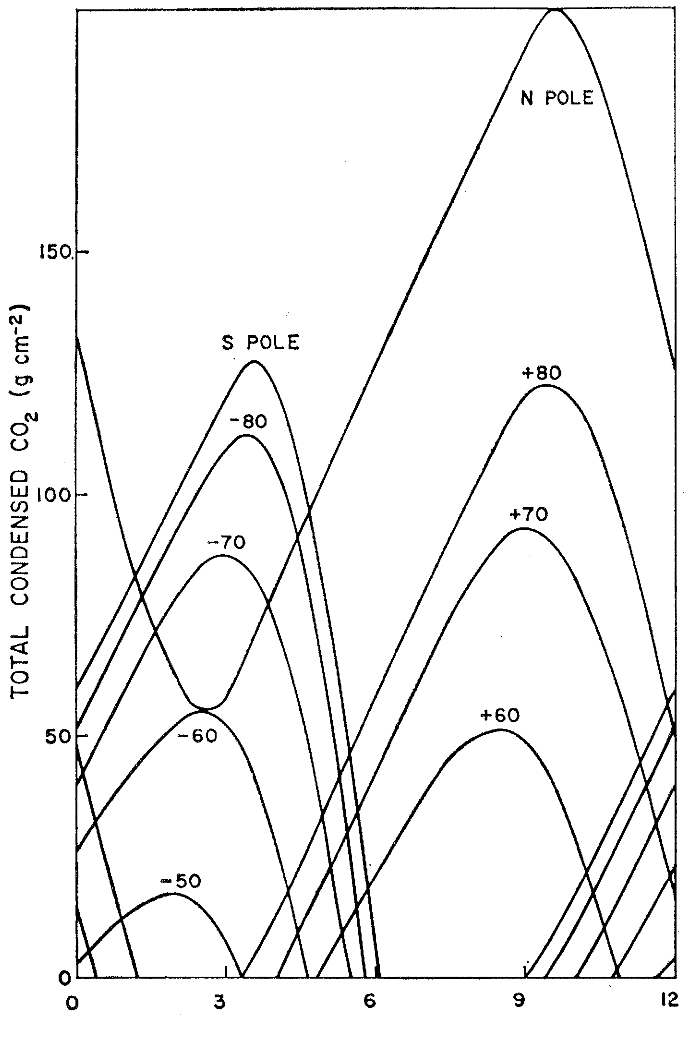
$$R_r = E\sigma T_0^4$$

where E is the infrared emissivity of solid CO_2, corrected for the effects of atmospheric blanketing. On the other hand, the yearly average insolation rate I_{av} at the north pole is fixed by the size and eccentricity of Mars's orbit and the inclination of the rotation axis. Thus,

$$I_{\mathrm{av}} = \frac{1}{2\pi}\int_{-\pi/2}^{\pi/2} S_0 \sin\delta_0 \cos\Phi\,(1 - 2\epsilon\cos\Phi) \times (1-\beta)^{\sec Z}\,d\Phi$$

where S_0 is the mean intensity of solar radiation at Mars's orbit; δ_0 is the inclination of Mars's equator with respect to its orbital plane; Φ is the longitude of the sun, measured from the north summer solstice; ϵ is the orbital eccentricity





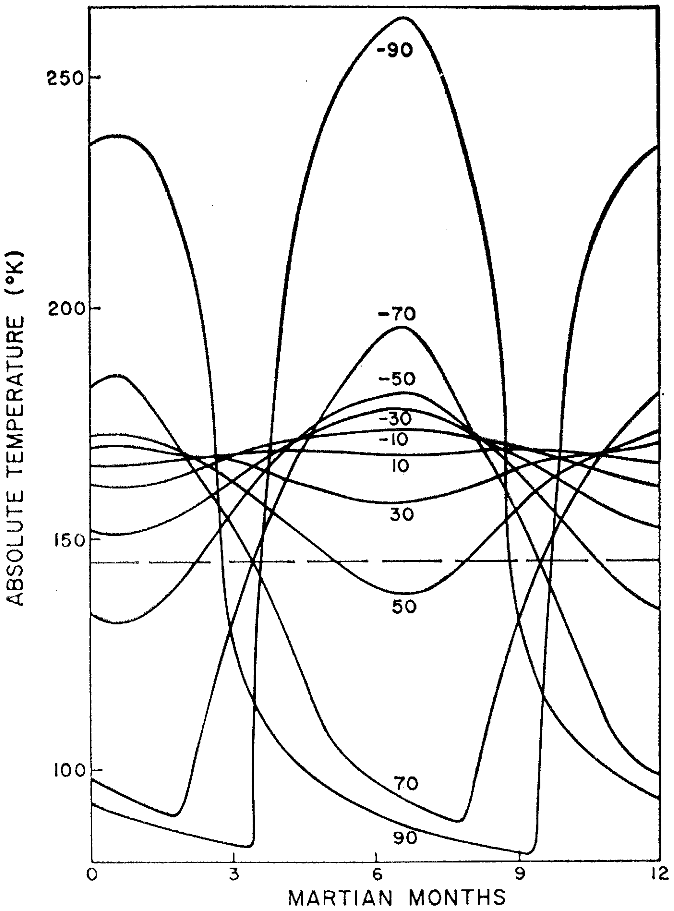
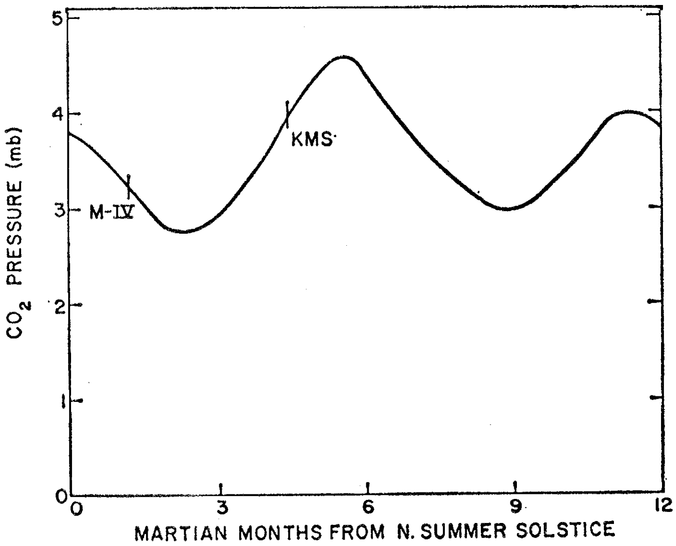


Fig. 1 (top left). Diurnal variation of surface temperature for three values of thermal conductivity of the soil (time = 3 months). Experimental values found by Sinton and Strong (*6*) are also shown (vertical bars). The soil conductivity of the middle curve was used throughout this study. Fig. 2 (top right). Annual variation of minimum diurnal temperature for various latitudes (numbers adjoining the curves) without CO_2 or H_2O condensation. $K = 6 \times 10^{-5}$ cal cm^{-1} sec^{-1} $(°K)^{-1}$; $E = 0.85$. The condensation temperature of CO_2 at pressure of 4 millibars is indicated by the dashed line. Fig. 3 (bottom left). Amount of precipitated CO_2 as a function of latitude (numbers adjoining the curves) and time. *K* as in Fig. 2. Conditions were such that a permanent north polar cap was present, so an arbitrary amount may be added to the indicated north polar curve. Fig. 4 (bottom right). Variation in CO_2 partial pressure, due to seasonal condensation and evaporation. The Martian date for the measurement of CO_2 pressure and total pressure by Kaplan, Münch, and Spinrad (KMS) (*12*) and of total pressure by Mariner IV (M-IV) (*18*) are indicated.



(aphelion is assumed to coincide with the north summer solstice); $(1 - \beta)$ is the fraction of incident solar radiation which is assumed to reach the surface when the sun is at the zenith; and sec Z $(= 1/\sin \delta_0 \cos \Phi)$ is the secant of the zenith angle of the sun. Numerically, $S_0 = 0.060$ watt cm^{-2}, $\sin \delta_0 = 0.407$; $\epsilon = 0.096$; and $\beta \approx 0.02$ (as a rough estimate). These values yield

$$I_{\text{av}} \approx 0.0060 \text{ watt cm}^{-2}$$

Now, if $R_r > I_{\text{av}} (1 - A)$, the polar cap will gain CO_2 at an average rate

$$\bar{\dot{M}} = (R_r - I_{\text{av}})/L$$

where L ($\approx$ 450 j g^{-1}) is the latent heat of vaporization of CO_2 at temperature T_0. This removal of CO_2 from the atmosphere will then reduce the partial pressure of CO_2, thereby decreasing the condensation temperature T_0 and R_r. On the other hand, if $R_r < I_{\text{av}} (1 - A)$, the polar cap will lose CO_2 at an equivalent rate, a loss resulting in an increase in T_0 and R_r. An equilibrium will therefore exist such that

$$R_r = I_{\text{av}} (I - A)$$

This condition fixes T_0, which in turn fixes the mean CO_2 partial pressure P_0 through the relation of vapor pressure to temperature. If $A = 0.65$ and $E = 0.85$, we find

$$T_0 = (I_{\text{av}} (1 - A)/\sigma E)^{1/4} = 145°\text{K}$$

At this temperature, $P_0 = 4.0$ millibars, in good agreement with current experimental values. If A and E differ from the above values (or if we have incorrectly estimated I_{av}), P_0 will, of course, differ also. The dependence of P_0 upon A and E is shown in Fig. 8.

The *rate* at which the above-described equilibrium will be approached may be estimated. Let the minimum radius of the polar cap be r radians of Martian latitude, and let $P = P_0 e^{\alpha(T - T_0)}$ for T near T_0. Then, if $T = T_0 + \Delta T$, a linear approximation to ΔR_r and ΔP yields a time constant

$$\tau = T_0 P_0 \, \alpha L / r^2 R_r g$$
$$\approx 0.6 \times 10^{10} \text{ sec } (= 200 \text{ yr})$$

In spite of its small radius of only 3 degrees, the cap should thus be quite effective in maintaining a constant partial pressure of CO_2.

Several unsuccessful attempts were made to simulate the very small residual north polar cap in the model before it was recognized that the observed behavior of the cap (it regularly shrinks to a diameter of a few hundred kilometers but always resists complete evaporation) does not imply that the cap is on the verge of disappearing when it is at minimum size. In fact, a permanent polar cap will tend to become smaller in diameter and correspondingly thicker because of the variation in insolation near the pole. Calculation shows that the insolation varies approximately according to the formula

$$I_{\text{av}} (\lambda) = I_{\text{av}} (90°) \, [1 + (5 \times 10^{-4}) (90 - \lambda)^2]$$

At latitude 80°, for example, the mean insolation is 5 percent greater than it is at the pole. However, all parts of the cap are at the same temperature, since the cap is in equilibrium with the CO_2 partial pressure, and thus radiates equally everywhere (*10*). The differential insolation therefore leads to a differential rate of growth or loss of CO_2 at the two latitudes in question until the permanent CO_2 all resides at the pole. This transfer rate is relatively rapid. In the example cited, the differential rate of loss at latitude 80° would be about 7 g cm^{-2} yr^{-1}.

The approximate annual "snowfall" of CO_2 at the north pole may also be estimated to be about half the amount that would be gained during the Martian year at the steady rate R_r/L. This amounts to

$$M = I_{\text{av}}(1 - A) t_y / 2$$
$$\approx 140 \text{ g cm}^{-2}$$

where t_y $(= 687 \times 86{,}400)$ is the length of the Martian year, in seconds. This is in good agreement with the results of the more precise calculations shown in Fig. 3.

In summary, on a rather general basis, CO_2 can be expected to be the major constituent of the polar caps on Mars, and this conclusion is consistent with (i) the size and rate of disappearance of the observed caps, (ii) the observed permanence of the north polar cap, (iii) the observed partial pressure of CO_2 on the planet, and (iv) the disk brightness temperature at radio wavelengths.

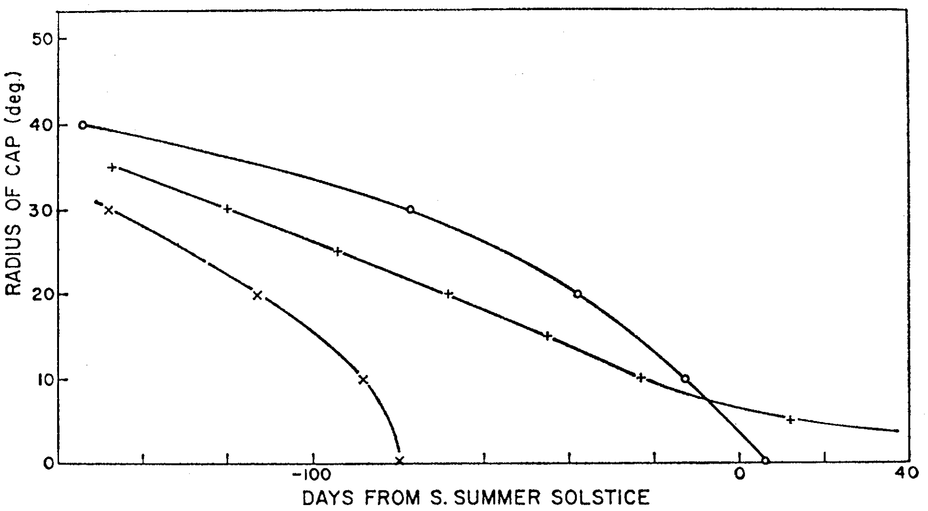


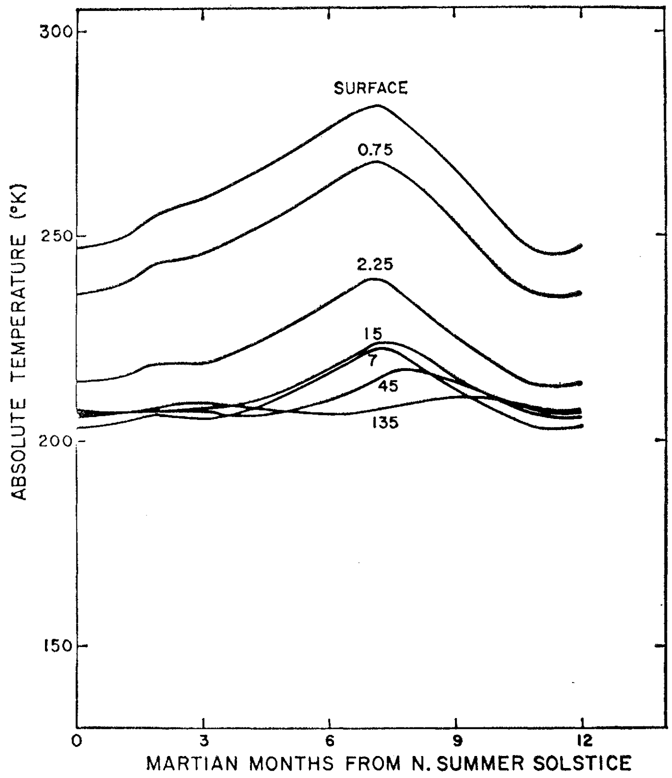
Fig. 5. Observed radius of south polar cap as a function of time (*21*) compared with predictions of models in which the caps are composed of CO_2 alone or H_2O alone. (+) Observed radius; (○) model with cap of CO_2 alone; (×) model with cap of H_2O alone. Local topographic irregularities are probably responsible for the slow recession of the cap after summer solstice, since the remanent southern cap is situated 6.5° from the pole. The recession of the cap in the H_2O model is closely in step with the solar declination because of the negligible mass of H_2O precipitated.

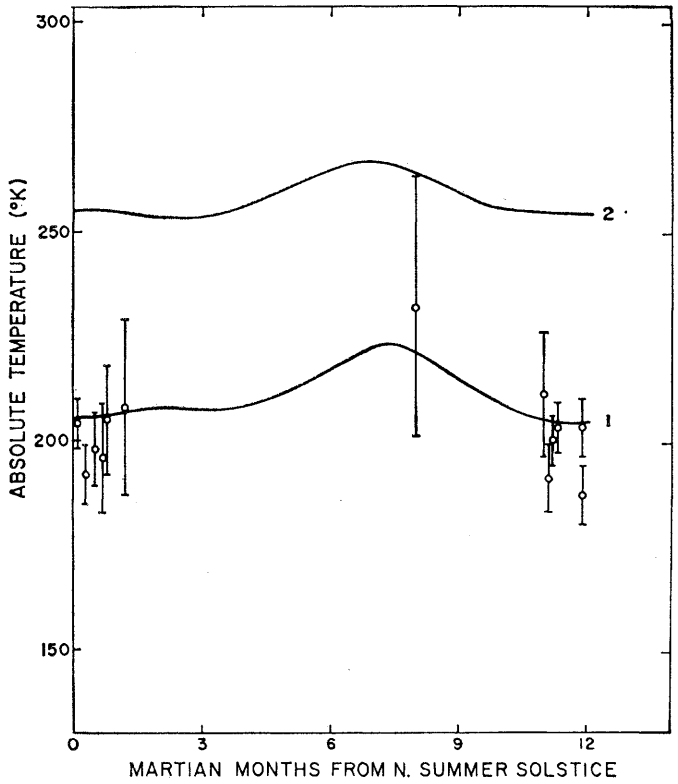
Water Relationships

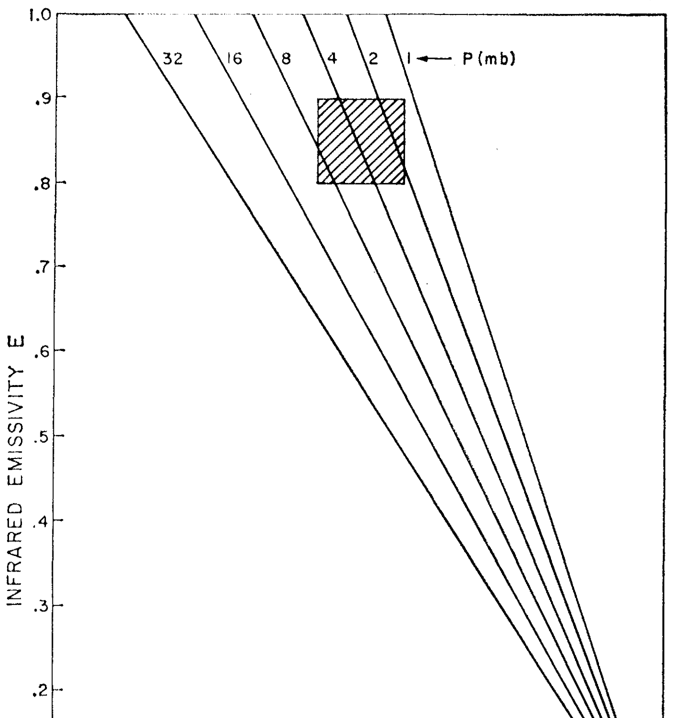
We have found, in the preceding section, that the properties of a rather simple thermal model of the Martian surface are in good agreement with many of the observed properties of Mars and suggest that the Martian polar caps consist largely of frozen CO_2. However, this result is in conflict with observations which seem to indicate that water ice, and not CO_2, is the substance comprising the polar caps. We have sought to understand the extent of this conflict and to find ways of resolving it. We see three possibilities.

1) The observations which indicate the presence of water ice, or the conclusions derived therefrom, may be in error.

2) Effects not taken into account in







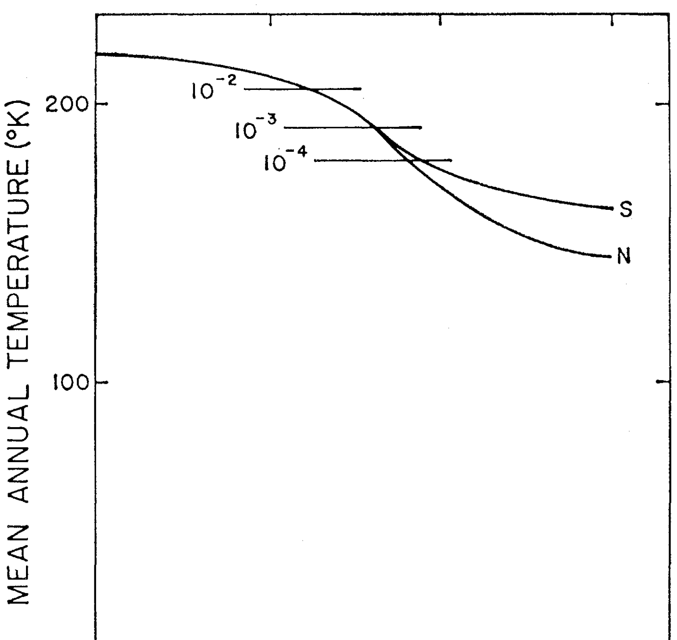


Fig. 6 (top left). Annual variation of average temperature of the disk as viewed from the sun for various depths, in centimeters (numbers adjoining curves), for the CO_2 model. The damping out of the diurnal and annual variations with depth are well shown in these curves. Fig. 7 (top right). Comparison of average disk temperature at depth of 15 centimeters for two thermal models with radio observations (vertical bars), at wavelength of 3 to 4 centimeters. The radio brightness temperatures have been multiplied by a factor 1.1 to correct approximately for an observed reflectivity of about 0.10 (*24*). The two models are (curve 1) the CO_2 model and (curve 2) a model having lower (and variable) infrared emissivity adjusted so as to prevent the precipitation of CO_2 but permit the condensation of H_2O. Fig. 8 (bottom left). Dependence of partial pressure *P* of CO_2 in the Martian atmosphere upon visual reflectivity *A* and effective infrared emissivity *E* of CO_2 frost. Fig. 9 (bottom right). Mean annual temperature as a function of latitude (CO_2 model). Saturation temperatures corresponding to three values for precipitable water vapor (in grams per square centimeter) are indicated.

the study discussed here may render our conclusions invalid.

3) A small amount of water ice may be present together with a large amount of frozen CO_2 and in some way affect the observational results, giving a magnified estimate of the abundance of water.

Water in solid form on the frost caps of Mars has been reported by Kuiper (*1*) and Dollfus (*11*), and water vapor has been reported by Kaplan, Münch, and Spinrad (*12*) and by Dollfus (*13*). Kuiper compared the infrared spectral reflectivity of the polar cap with similar laboratory spectra of ice and dry ice, while Dollfus made a study of the polarization of the polar cap. Moroz (*14*) has recently confirmed the existence of the near-infrared spectral feature and, like Kuiper, attributes it to the presence of water ice. However, we are not aware of a sufficiently thorough published study of the reflection spectrum of *both* solid H_2O and CO_2 deposited under simulated Martian conditions to justify the identification.

Dollfus' discussion of his polarization measurements was restricted to a consideration of the physical state of the condensed material and not its composition. He found difficulty in producing a form of water ice that would exhibit the very small amount of polarization that was observed, and he did not study the properties of CO_2 frost. There is at present no evidence, from polarization studies of Mars, which would enable one to distinguish between a frost cap of H_2O and one of CO_2.

There are also difficulties in reconciling the optical properties and seasonal behavior of supposed water ice polar caps with the extremely minute quantities of water that spectroscopic studies have revealed. The Kaplan, Münch, and Spinrad observation was sensitive enough to permit an estimate of the total precipitable water above the Martian surface: $14 \pm 7 \times 10^{-4}$ g cm^{-2}. Comparable measurements of water vapor have also been obtained independently by Spinrad over a number of years (*15*). Although Heyden *et al.* (*16*) have recently pointed out that heretofore unrecognized weak H_2O absorption lines originating in the earth's atmosphere might complicate the interpretation of H_2O absorption features of the Mars spectrum, it seems unlikely that all observations would be similarly affected because of the variable Doppler displacements of the Martian lines. A further consideration regarding Martian water vapor has been raised by Johnson (*17*). He argues that very low atmospheric temperatures are indicated by the Mariner IV occultation experiment (*18*) and that these would be incompatible with a water-vapor concentration of as much as 10^{-3} g cm^{-2}, because ice-crystal cloud formation should set in at a concentration lower by perhaps an order of magnitude. On the other hand, Gross, McGovern, and Rasool (*19*) believe that higher atmospheric temperatures are more likely, in which case there is not necessarily a contradiction. Any such discrepancy between theory and observation evidently will not be resolved until more is known about the details of Martian meteorology, so it seems reasonable to conclude for the present that there may well be 10^{-3} g of water vapor per square centimeter commonly present in the Martian atmosphere but that an upper limit can perhaps be set around 3×10^{-3} g cm^{-2}. Thus we see that water constitutes at most 0.03 percent, by weight, of the Martian atmosphere, and probably less than 0.01 percent. It is, therefore, a minor constituent, and its condensation and evaporation will differ markedly from that of the major constituent, CO_2, in several ways.

First, the basic problem of the transfer of H_2O in an evaporation-condensation cycle from a solid state at one place on the planet to a solid state at another is vastly more difficult than the corresponding problem for CO_2, since, at the minimum, 10^4 times as much CO_2 as H_2O must be transferred by the wind system. If all the H_2O is not removed during a single cycle (because of insufficient vertical mixing, for example) the ratio becomes correspondingly larger, and an unreasonably strong wind system would be required for the effective transport of water vapor. For example, one might assume, as an extreme upper limit, that during the disappearance of one cap and the growth of the other the entire 10^{-3} g of water vapor above each square centimeter of the disappearing cap is transported to the growing cap and deposited there *daily* as frost. (Such a process would require net north-south winds of about 500 kilometers per hour blowing steadily for perhaps 100 days, combined with complete vertical mixing daily at each end.) Even in such an extreme case only about 0.1 g cm^{-2} woud be transferred from one cap to the other—a thickness of a few millimeters at most. Since the Martian surface undoubtedly has some microrelief, this tiny coating of frost would probably accumulate only in the shadowed areas, such as on the colder, poleward slopes of topographic features and on the poleward sides of individual rock fragments. A frost cap only a few millimeters thick very probably would not be observable at all from the direction of the sun, yet this is the direction from which the planetary frost caps are observed from Earth at opposition.

A second, and equally serious, difficulty with the hypothesis that water ice is the dominant constituent of the Martian caps is the fact that, unlike the case for CO_2, the atmosphere near the surface can become depleted in H_2O and the depletion causes the condensation rate to become extremely small and dependent upon the vagaries of the vertical and horizontal circulation system of the planet. Inasmuch as that circulation system is governed by the planetary heating and reradiation, and perhaps by rotation, and, unlike the case for Earth, is not significantly influenced by the atmospheric content of water vapor, such redistribution of water as does take place is the result of purely accidental effects.

These considerations make us doubt that water could be the dominant constituent of the Martian polar caps. To place the analysis in more quantitative form, however, we have investigated two specific hypothetical cases which have also led us into some interesting considerations concerning the possible occurrence of permafrost on Mars.

First, we have studied what is required if the frost caps are in fact H_2O and if they always remain warm enough so that solid CO_2 does not accumulate on the surface at either pole at any time during the year. This is equivalent to requiring that the mean daily temperature not fall below about 145°K anywhere on the planet. Since it appears, from terrestrial experience, that supplementary sources of heat (for example, radioactivity) of adequate magnitude are most unlikely, it is only through introducing, in the model, a decrease in radiative heat loss from the planet by atmospheric blanketing that such a result may reasonably be achieved. In order to retard the radiative heat loss at low temperatures and yet avoid unduly high daytime temperatures, a far-infrared absorption was introduced such that, in addition to the expected absorption of CO_2 near 15 microns, all wavelengths longer than 19 microns were blocked. This led to an effective emissivity relative to temperature which ranged from 0.1 at 140°K to 0.5 at 270°K. Although this procedure gave the desired result—a negligible quantity of CO_2 was found to condense—it led to other results that are in serious conflict with observation. Not only would the assumed absorption require the presence of substantial amounts of molecular species such as NH_3, CH_4, or H_2O in the atmosphere which have escaped detection in the visible (*20*), near-infrared (*1*, p. 351), or far-infrared (*4*) regions, but, in addition, the infrared photometry of Low (*9*) indicates that the integral brightnesses of Mars at wavelengths of 10 microns and 20 microns are similar, and consistent with the absence of any such greenhouse effect. Furthermore, the average disk temperature was found to be much higher than, and not consistent with, the radio data, as shown in Fig. 7. We are thus reluctant to accept the view that atmospheric molecular blanketing effects are present in sufficient strength to invalidate our thermal model.

In addition to blanketing by atmospheric molecular constituents, there is the possibility of blanketing by clouds of condensed H_2O or CO_2. An autumnal polar-haze cap is regularly observed (*21*), and some of the recent atmospheric models of Mars seem to suggest that solid particles of CO_2 might be commonly present in the atmosphere at all latitudes (*22*). We recognize that clouds of CO_2 or H_2O ice crystals could seriously retard thermal emission from the surface and thus reduce the accumulation of CO_2, but of course such clouds might also contribute additional frozen CO_2 to the surface by "snowfall." Theoretical analyses of various hypothetical haze and cloud conditions that might prevail in the Martian atmosphere may provide insight into the actual importance of such possibilities.

We have also examined the case in which both CO_2 and H_2O are present, with CO_2 dominant both in the atmosphere and in the polar cap. If the north polar cap is CO_2, its winter temperature of 145°K is so low that water, were it in equilibrium at this temperature, would be quite undetectable in the atmosphere. On the other hand, the *rate* at which any temporary excess of water would accumulate on the polar cap is likely to be quite low. For instance, calculations based on the CO_2 model and four additional assumptions show that the polar cap might accumulate ice only at the rate of 0.005 g cm^{-2} yr^{-1} if the mean annual content of water vapor at the equator were 10^{-3} g cm^{-2}. The four assumptions are that (*i*) water can be removed from the atmosphere only at a rate proportional to the water vapor content and with a time constant of 5 days, to empty a vertical column above the surface; (ii) water condenses out at this rate wherever the surface temperature falls below the local frost point; (iii) the water can be returned to the atmosphere as rapidly as the sun can evaporate it; and (iv) water vapor is transported in latitude in a "random walk" at the rate of 5 days for a 10-degree step.

Because of the precession of Mars's perihelion and rotation axis, which will periodically reverse the roles of the north and south poles as the sites of a permanent cap, we need only consider how much water would be accumulated at this rate during a fraction, $1/2\pi$, of the effective precession period of about 5×10^4 years (*23*). This would amount to about 40 g of ice per square centimeter—a quite negligible amount. We therefore conclude that it is possible to reconcile the observed presence of 10^{-3} g of water vapor per square centimeter with the presence of large amounts of frozen CO_2, including a semipermanent polar cap.

The calculation just described also showed that the amount of water vapor above each pole varied by a factor of 2 to 3 throughout the year, being about 6×10^{-4} g cm^{-2} in the winter and about 15 to 20×10^{-4} g cm^{-2} following the disappearance of the polar cap in the summer. About 20 to 30×10^{-4} g of ice per square centimeter was found to be deposited annually on the transient polar caps.

Concerning a possible means of reconciling our model with the polar cap observations previously cited, it is of interest to note that, although the amount of H_2O condensed is very small compared with the amount of CO_2, the H_2O will remain in the cap until all the CO_2 has disappeared. Furthermore, as the CO_2 evaporates, the H_2O may well become concentrated in a thin film at the top surface of the receding cap and may alter the reflective properties of the cap enough to make it appear to be composed of water ice.

If we accept the possibility that, on the average, 10^{-3} g of water vapor is present per square centimeter, we are led to some further conclusions of interest. First, if this water vapor can penetrate into the soil to a depth of at least a few meters, as should be the case for porous surface material such as is indicated by the infrared observations, it may reach a region where the temperature is perpetually below the 190°K condensation temperature at the corresponding surface-level vapor pressure of 3.7×10^{-4} millibar. The water would tend to migrate to such regions and condense as permafrost. The mean annual temperature as a function of latitude is shown in Fig. 9, together with the condensation temperatures corresponding to amounts of water vapor equal to 10^{-2}, 10^{-3}, and 10^{-4} g cm^{-2}. It may be seen that, in both hemispheres, the regions poleward of latitudes 40° to 50° will tend to trap water as permafrost.

It is difficult to estimate the quantity of water likely to be present as permafrost because we can only speculate on the depth of loose, permeable material, and on whether such loose material is saturated. Since we are here concerned with geological time scales of tens or hundreds of millions of years, it seems likely that the trapping layers are saturated with ice. However, internal heat sources may impose a downward thermal gradient which at some unknown depth will raise the temperature above the condensation temperature. It would be most surprising if the saturated trapping layer did not extend to depths of at least several tens of meters, so it seems quite possible that several hundred grams of water per square centimeter could be present in the pores of the soil.

While we cannot specify the depth to which the permafrost layer extends, we are able to estimate at what depth below the surface its top is situated. At a given latitude this level will be that at which the vapor pressure of water, averaged throughout the year, is equal to the atmospheric average vapor pressure, for then the net annual exchange of water with the atmosphere will be zero. This depth is plotted as a function of latitude in Fig. 10.

Figure 10 shows that the top of the permafrost layer should be only a few centimeters below the surface except near the boundaries of the layer, and that the layer should be some 30 centimeters nearer the surface at a given latitude in the northern hemisphere than in the southern. This depth difference, multiplied by the fractional porosity of the soil and integrated over a hemisphere, represents the amount of water potentially available for transfer between the two hemispheres in the course of the 5×10^4-year precessional cycle. We have not investigated this transfer process in detail.

Although local irregularities in the surface and subsurface conditions will introduce corresponding fluctuations in the depth to the top of the permafrost, we do not expect to find gross departures from the results obtained with the model insofar as the distribution and physical state of near-surface water are concerned. In particular, we would not expect to find large amounts of water (or ice) at any depth in the equatorial regions unless the area was extremely well isolated from the atmosphere.

The possible occurrence of liquid water is a question of some concern. An attractive idea is the possibility that soil moisture sometimes exists in the Elysium region, where relatively strong radar reflections (*24*) and persistent morning clouds (*25*) were observed during the 1965 opposition period. However, nothing in our study points toward the occurrence of liquid water at any place or time during the daily, annual, or precession cycle. The maximum temperature attained in the permafrost layer was about 200°K—far below the melting temperature of ice, (273°K). Furthermore, even if the temperature were to rise above 273°K, it is not certain that the ice would melt rather than sublime, since the total atmospheric pressure, 5 to 10 millibars, could be less than the 6.9-millibar vapor pressure of water at its triple point.

Of course, we cannot exclude the possibility that very small amounts of liquid water might form for brief periods in connection with the evaporation of the residual water ice of a polar cap after the CO_2 has disappeared if, for example, the ice frost were partially trapped in the upper few millimeters of the surface under conditions where solar heating was intense but evaporation was retarded by the limited porosity of the soil. Again, strongly deliquescent salts situated near the surface might, under some circumstances, lead to the presence of moisture in the soil.

Other Volatiles

There are no confirmed reports of other volatiles on Mars. Kiess *et al.* (*3*) have reported nitrogen oxides; more recently that subject has been discussed by Sagan, Hanst, and Young (*26*) and by Heyden (*27*). Perhaps more surprising than the possibility that nitrogen oxides are present is the apparent dearth of nitrogen itself. An upper limit of a few millibars for the partial pressure of nitrogen in the Martian atmosphere is implied by the Mariner IV occultation results. Such a low abundance would seem anomalous, on the basis of geochemical considerations, if the atmosphere of Mars was formed in a manner at all similar to the formation of the earth's atmosphere.

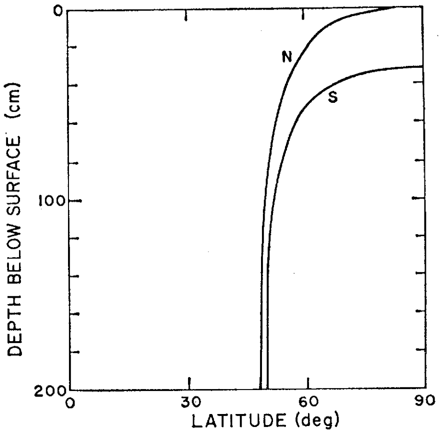


Fig. 10. Depth of top surface of H_2O permafrost, as a function of latitude. The difference in depth between the two hemispheres defines an amount of water that should be exchanged between the hemispheres or during the 5×10^4-year precessional period.

Carbon dioxide can be expected to be lost from Mars, by various dissociation and ionization processes, at a much higher rate than that at which nitrogen is lost. Gravitational escape will not be significant in either case if the exospheric temperatures are as low as the 550 ± 150°K estimated by Gross *et al.* (*19*) or the 85°K estimate of Johnson (*17*). Accordingly, it is difficult to understand how an enormous CO_2 enrichment relative to nitrogen could take place if both gases were present either in a primordial atmosphere or in continuing volatile emissions from the interior of Mars. One possible clue to the apparent anomaly is the suggestion that CO_2 might have been preferentially trapped upon and beneath the surface in a solid state while the entire mass of nitrogen was always in the gas phase at the surface and thus able to escape much more effectively. It is possible that on Mars, as on the moon (*28*), the presence of a low-vapor-pressure solid phase of a volatile molecular or atomic species may be of more significance in retention of the volatile than is the species' resistance to escape from the vapor phase. Another fractionation mechanism for selective retention on Mars of a heavier, condensable gas relative to a lighter, noncondensable one was discussed by Stoney (*2*) prior to 1898.

The other class of Martian volatiles about which there has been much speculation is that of organic compounds, particularly those related to possible biological activity. While our analysis is too restricted to form the basis of any discussion of the *a priori* likelihood of biogenic compounds being formed now, or having been formed in the past, on the surface of Mars, it may offer some insight into the probable redistribution of such compounds should they be present on Mars. In particular, our analysis for the evaporation and redistribution of H_2O should be roughly applicable to any volatile minor constituent. If solid (or liquid) organic compounds are present near the surface anywhere in the temperate or in the equatorial regions of the planet, they should be evaporating also, and condensing in the polar regions. If the circulation is sufficiently rapid, the mass transferred would be roughly in proportion to the ratio of the evaporation rate of the substance to the evaporation rate of water in the temperature range around 170° to 200°K. Thus it would seem that organic substances significantly more volatile than H_2O in the low-temperature range should be depleted from the soil over most of the planet and transferred to the polar areas well within a single 8000-year portion of the precessional cycle.

Summary and Conclusions

We have found that a rather simple thermal model of the Martian surface, in combination with current observations of the atmospheric composition, points strongly toward the conclusion that the polar caps of Mars consist almost entirely of frozen CO_2. This study was based upon the following principal assumptions.

1) Carbon dioxide is a major constituent of the Martian atmosphere.

2) The blanketing effect of the atmosphere is small, and due principally to the absorption band of CO_2 near 15 microns.

3) Lateral and convective heat transfer by the atmosphere is negligible.

4) The far-infrared emissivity of the Martian soil and of solid CO_2 are near unity.

5) The reflectivities of the soil and of solid CO_2 in the visible part of the

spectrum are about 0.15 and 0.65, respectively.

6) Values for soil conductivity, density, and specific heat are those characteristic of powdered minerals at low gas pressure.

7) Water is a minor constituent of the Martian atmosphere, the maximum total amount in the atmosphere being 10 to 30 $\times 10^{-4}$ g cm^{-2}.

In addition, several simplifications were made, which might have significant effects but should not alter our principal conclusions. Among these are the following.

1) Local blanketing or snowfall effects due to clouds or polar haze were ignored.

2) Dark and light areas were not differentiated in this study, although Sinton and Strong *(6)* have observed temperature differences between such areas.

3) The effects of local topography and microrelief were neglected. We believe that these must have quite significant effects at the higher latitudes, especially in connection with the evaporation of the remanent south polar cap.

4) Variation of reflectivity with angle of incidence of the sunlight was neglected.

5) Temperature dependence of soil conductivity and specific heat was ignored.

6) Effects of saturation of the soil by ice upon the thermal properties of the soil were neglected.

Although in our main investigation we used certain specific values for the various relevant parameters, we also tested the effects of moderate changes in these quantities. Specifically, the soil conductivity was varied by a factor of 3, the albedo and emissivity of the surface were changed by 15 to 20 percent, and the effects of a gross amount of atmospheric blanketing were studied, as described. Only the last of these variations had any significant effect on the model, and other results of the atmospheric blanketing were in disagreement with other physical observations of the planet. Consequently, we find it difficult to avoid the conclusion that CO_2 must condense in large amounts relative to H_2O.

The main conclusions indicated by this study are the following.

1) The atmosphere and frost caps of Mars represent a single system with CO_2 as the only active phase.

2) The appearance and disappearance of the polar caps are adequately explained on the presumption that they are composed almost entirely of solid CO_2 with perhaps an occasional thin coating of water ice.

3) If the currently reported water-vapor observations are correct, water-ice permafrost probably exists under large regions of the planet at polar and temperate latitudes.

4) The geochemically anomalous enrichment of CO_2 relative to N_2 in the present Martian atmosphere may be a result of selective trapping of CO_2 in the solid phase at and under the surface.

5) If the basic evaporation and condensation mechanisms for CO_2 and H_2O discussed in this article are correct, the possible migration of volatile organic compounds away from the warm temperate regions of the planet and their possible accumulation in the polar regions need to be carefully considered.

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