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 (I, p. 362; J, 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 CO₂ as the dominant substance comprising the Martian polar caps.

Further, we are led to suggest that (i) the total amount of CO₂ on Mars may exceed the amount present in the atmosphere by a considerable factor, the excess being present as solid CO₂ and CO₂ permafrost in and under the permanent north polar cap; (ii) the partial pressure of CO₂ 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 CO₂ 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 CO₂ (and H₂O) in the solid phase may help explain the anomalously high concentration of CO₂ (and probably H₂O) 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 T₁, which absorbs a fraction F of the incident solar radiation, emits blackbody radiation at temperature T₁ 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 CO₂ and H₂O.

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 H₂O or CO₂ 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 3000 centimeter-atmosphere of CO₂ at pressure of 5 milibars (based on the tables of calculated CO₂ 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 × 10⁻⁴ watt cm⁻¹ (K⁻¹); C = 3.3 j g⁻¹ (K⁻¹); ρ = 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, x₁ = 0; (ii) nine equal layers 1.5 cm thick, centered at x₀ = 0.75, . . . x₉ = 12.75 cm; and (iii) ten equal layers 30 cm thick, centered at x₁₀ = 15, . . . x₀ = 2.85 cm. The boundary conditions on the temperature at a given latitude were as follows.

1) The surface temperature T₁ was taken as a linear extrapolation to the surface of the values for the upper two layers: T₁ = (3T₀/2) − (T₀/2).
2) The net heat gain or loss, $Q_2$, for the top layer was taken as
\[ Q_2 = (-E_\lambda T_\lambda + S_\lambda \cos \lambda Z + K(T_\lambda - T_\beta)/\Delta \lambda) \Delta t \]
where $S_\lambda$ ($= 0.06$ W cm$^{-2}$) is the solar constant at Mars; $\sigma$ is the Stefan-Boltzmann constant; $\cos Z$ is the cosine of the zenith angle of the sun; $\Delta \lambda = 3600$ seconds, and $\Delta \lambda = 1.5$ 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$_2$O, 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 $(T_{10} - T_{11})/\Delta \lambda$, and with the lower layers in proportion to the gradient $(T_{12} - T_{11})/\Delta \lambda'$, with $\Delta \lambda' = 30$ 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 $\Delta T_i$ at the end of each annual calculation according to the equation
\[ \Delta T_i = (T_{11} - T_{10}) (2x_i/x_{10} - x_i/x_{10}) \]
where $T_{10}$ 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 $T_\mu$ throughout the year. Therefore, the rate $R_\mu$ at which heat is radiated throughout the year is constant and is
\[ R_\mu = E_\mu T_\mu^\delta \]
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 $I_\mu$ at the north pole is fixed by the size and eccentricity of Mars's orbit and the inclination of the rotation axis. Thus,
\[ I_\mu = \int_{-\pi/2}^{\pi/2} \sin \delta \cos \phi (1 - 2e \cos \phi) \times (1 - \beta) \cos \epsilon \ d\phi \]
where $S_\mu$ is the mean intensity of solar radiation at Mars's orbit; $\delta$ is the inclination of Mars's equator with respect to its orbital plane; $\phi$ is the longitude of the sun, measured from the north summer solstice; $e$ 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 CO₂ or H₂O condensation. \( K = 6 \times 10^{-4} \text{ cal cm}^{-2} \text{ sec}^{-1} \text{ °K}^{-1} \); \( E = 0.85 \). The condensation temperature of CO₂ at pressure of 4 millibars is indicated by the dashed line. Fig. 3 (bottom left). Amount of precipitated CO₂ 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 CO₂ partial pressure, due to seasonal condensation and evaporation. The Martian date for the measurement of CO₂ 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 see $Z (= 1/\sin \delta_0 \cos \phi)$ is the secant of the zenith angle of the sun. Numerically, $S_0 = 0.060 \text{ watt cm}^{-2}$, $\sin \delta_0 = 0.407$; $\epsilon = 0.096$; and $\beta \approx 0.02$ (as a rough estimate). These values yield

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

Now, if $R_r > I_{sv} (1 - A)$, the polar cap will gain CO$_2$ at an average rate

$$\dot{M} = (R_r - I_{sv}) / \nu$$

where $\nu (= 450 \text{ J g}^{-1})$ is the latent heat of vaporization of CO$_2$ at temperature $T_r$. 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 $R_r$. Of the other hand, if $R_r < I_{sv} (1 - A)$, 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

$$R_r = I_{sv} (1 - A)$$

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

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

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 $I_{sv}$), $P_0$ 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 $P = P_0 e^{r^2 - r_0}$ for $T$ near $T_0$. Then, if $T = T_0 + \Delta T$, a linear approximation to $\Delta R$, and $\Delta P$ yields a time constant

$$\tau = T R_e / \nu R_g$$

$$\approx 0.6 \times 10^6 \text{ sec (= 200 yr)}$$

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

$$I_{sv} (\lambda) = I_{sv} (90^\circ) [1 + (5 \times 10^{-4}) (90 - \lambda)^2]$$

At latitude $80^\circ$, 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 $80^\circ$ would be about $7 \text{ g cm}^{-2} \text{ yr}^{-1}$.

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

$$M = I_{sv} (1 - A) t_r / 2$$

$$\approx 140 \text{ g cm}^{-2}$$

where $t_r (= 687 \times 86,400)$ 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.

**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
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 CO₃ model and (curve 2) a model having lower (and variable) infrared emissivity adjusted so as to prevent the precipitation of CO₂ but permit the condensation of H₂O. Fig. 8 (bottom left). Dependence of partial pressure P of CO₂ in the Martian atmosphere upon visual reflectivity $\alpha$ and effective infrared emissivity $E$ of CO₂ frost. Fig. 9 (bottom right). Mean annual temperature as a function of latitude (CO₂ 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 CO₂ 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 H₂O and CO₂ 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 CO₂ frost. There is at present no evidence, from polarization studies of Mars, which would enable one to distinguish between a frost cap of H₂O and one of CO₂.

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 ± 7 × 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 H₂O absorption lines originating in the earth's atmosphere might complicate the interpretation of H₂O 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, CO₂, in several ways.

First, the basic problem of the transfer of H₂O 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 CO₂, since, at the minimum, 10⁴ times as much CO₂ as H₂O must be transferred by the wind system. If all the H₂O 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 would 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 CO₂, the atmosphere near the surface can become depleted in H₂O 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 radiation, 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 H₂O and if they always remain warm enough so that solid CO₂ 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 might 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 CO₂ near 15 microns, all wavelengths longer than 19 microns were blocked. This led to an effective emissivity relative to tempera-
ture which ranged from 0.1 at 140°K to 0.5 at 270°K. Although this procedure
drove the desired result—a negligible quantity of CO2 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
NH3, CH4, or H2O 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 consis
tent with, the radio data, as shown
in Fig. 7. We are thus reluctant to ac
ccept the view that atmospheric molecu
lar blanketing effects are present in
sufficient strength to invalidate our
thermal model.

In addition to blanketing by atmos
pheric molecular constituents, there is
the possibility of blanketing by clouds
of condensed H2O or CO2. An autumnal
polar-haze cap is regularly observed
(21), and some of the recent atmo
sphere models of Mars seem to suggest
that solid particles of CO2 might be
commonly present in the atmosphere at
all latitudes (22). We recognize that
clouds of CO2 or H2O ice crystals
could seriously retard thermal emission
from the surface and thus reduce the
accumulation of CO2, but of course
such clouds might also contribute ad
ditional frozen CO2 to the surface by
“snowfall.” Theoretical analyses of var
dious hypothetical haze and cloud condi
tions that might prevail in the Martian
atmosphere may provide insight into
the actual importance of such possi
bilities.

We have also examined the case in
which both CO2 and H2O are present,
with CO2 dominant both in the atmo
sphere and in the polar cap. If the
north polar cap is CO2, its winter tem
perature of 145°K is so low that water,
were it in equilibrium at this tempera
ture, 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 CO2 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 va
por 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-
dergree step.

Because of the precession of Mars’s
obliquility 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, 1/2π, of
the effective precession period of about
5 × 10⁴ years (23). This would amount
to about 40 g of ice per square centi
meter—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 cen
timeter with the presence of large
amounts of frozen CO2, 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 × 10⁻³ 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 rec
onciling our model with the polar cap
observations previously cited, it is of
interest to note that, although the
amount of H2O condensed is very
small compared with the amount of
CO2, the H2O will remain in the cap
until all the CO2 has disappeared.
Furthermore, as the CO2 evaporates,
the H2O may well become concentrated
in a thin film at the top surface of the
receding cap and may alter the reflec
tive properties of the cap enough to
make it appear to be composed of wa
ter ice.

If we accept the possibility that, on
the average, 10⁻³ g of water vapor is
present per square centimeter, we are
interested to some further conclusions of in
terest. First, if this water vapor can
entrate 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 observa
tions, it may reach a region where the
temperature is perpetually below the
190°K condensation temperature at the
corresponding surface-level vapor pres
sure 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

...
course of the $5 \times 10^4$-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°C—far below the melting temperature of ice, (273°K). Furthermore, even if the temperature were to rise above 273°C, 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 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.

![Fig. 10. Depth of top surface of H$_2$O 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 $5 \times 10^4$-year precessional period.](image)

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.

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°C estimated by Gross et al. (19) or the 85°C 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$_2$O 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°C. Thus it would seem that organic substances significantly more volatile than H$_2$O 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 remnant southern polar cap.

4) Variations of reflectivity with angle of incidence of the sunlight were 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$_2$O.

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$_2$O 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.

References and Notes


2. G. J. Stoney, Astrophys. J. 7, 75 (1918); this paper refers to an even earlier suggestion by the same author.


11. We neglect here the small but important variation of temperature with elevation due to (i) decrease of barometric pressure with altitude and (ii) adiabatic cooling of surface air as it flows from the edge to the middle of the polar cap.


23. The period for the procession of the perihelion is about 72,000 years (see D. Brouwer and G. M. Clemencx, Planets and Satellites (Univ. of Chicago Press, Chicago, 1961), p. 50) while that due to solar tidal precession of the rotation axis may be estimated as about 180,000 years, a value obtained by correcting the solar part of the total earth's precession, (7.5/2.4) by the appropriate factors for distance and moment of inertia. We are indebted to Professor W. M. Kaula for helpful discussions on this point.


25. C. Apen, general communication (1965).


27. J. J. Heyden, ibid., p. 1003.


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