Mars: The Case Against Permanent CO_2 Frost Caps

ANDREW P. INGERSOLL

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91109

Leighton and Murray have argued that there is a polar reservoir of solid CO_2 on Mars that lasts throughout the year and whose vapor pressure determines the mean partial pressure of CO_2 in the atmosphere. This model is discussed in the light of recent data, and several difficulties emerge. First, such a system might be unstable, owing to the tendency of poleward heat transport to increase with atmospheric pressure. Second, the annual retreat of the CO_2 frost cover would be slower according to the model than that observed. Moreover, the observations seem to indicate that the residual polar cap that lasts throughout the year is composed of water ice rather than CO_2. Finally, observations of water vapor in the atmosphere appear to be inconsistent with a permanent CO_2 cold trap in continuous existence for many years. These difficulties hold also for a CO_2 reservoir buried by water ice and for a hydrated CO_2 clathrate. If Leighton and Murray's model does not apply, several alternatives remain. First, the total accumulated CO_2 may simply be equal to that observed in the atmosphere. Second, there may be a buried reservoir of CO_2 that is not in vapor equilibrium with the atmosphere. Third, adsorption of CO_2 and water in the Mars regolith may control the amounts of these compounds observed in the atmosphere at present. Unfortunately, not one of these alternatives provides a satisfactory quantitative theory for the present CO_2 partial pressure in the atmosphere.

The principal constituent of the Martian atmosphere, and possibly also of the Martian polar caps, is CO_2. Processes affecting CO_2 are therefore the key to understanding the state of the atmosphere and its history. The prevailing view, presented 8 yr ago by *Leighton and Murray* [1966], is that the polar caps are storage reservoirs containing large amounts of CO_2 and that they determine the partial pressure of CO_2 in the atmosphere. Other possibilities are that there are no reservoirs other than the atmosphere itself or that the reservoirs are buried and are effectively isolated from the atmosphere. This paper is a critical review of Leighton and Murray's hypothesis of a CO_2 frost reservoir in the light of recent data.

Leighton and Murray's Two Hypotheses

By considering the seasonal heat balance and the expected temperatures of the polar regions, Leighton and Murray concluded that condensation and sublimation of CO_2 frost accounted for the annual advance and retreat of the Martian polar caps. The observational basis for their conclusion was the determination by *Kaplan et al.* [1964] of the atmospheric abundance of CO_2, from which it was shown that CO_2 would condense on the Martian surface at temperatures in the range $148° \pm 1°K$. Another important statistic was provided by *Kliore et al.* [1965], who showed that the Martian surface pressure is about 6 ± 1 mbar, indicating that CO_2 is the principal atmospheric constituent. This low value of the surface pressure made it plausible to neglect poleward heat transport in the atmosphere as a means of heating the polar regions.

Leighton and Murray found that the seasonal temperature changes at the poles are small, owing to buffering by the vapor pressure of CO_2 in the atmosphere. During the autumn and winter the heat lost by infrared radiation is supplied by latent heat of condensation as the cap grows, and during the spring and summer the excess solar radiation over the outgoing infrared radiation goes into latent heat again as the cap shrinks. Knowing the radiative heat fluxes and the latent heat of CO_2, the thickness and the extent of the annual frost cap can be computed. These predictions of the model are supported by detailed observations of the polar caps [*Murray et al.*, 1972; *Soderblom et al.*, 1973], by spectroscopic evidence of condensed CO_2 at the poles [*Herr and Pimentel*, 1969], and by the infrared observation that the polar temperatures are indeed around 150°K, cold enough for CO_2 to condense on the Martian surface [*Neugebauer et al.*, 1969; *Kliore et al.*, 1972; but see also *Chase et al.*, 1972].

A separate but potentially more important point made by Leighton and Murray is that there may be a reservoir of solid CO_2 at the poles that lasts throughout the year and is in vapor equilibrium with the atmosphere. If such a reservoir were to exist, its temperature would be nearly constant at the value corresponding to a CO_2 vapor pressure of about 6 ± 1 mbar. Assuming no net annual change in the mass of the reservoir and negligible heat transport by the atmosphere, we can compute the expected temperature of this reservoir by requiring that the annual rate of cooling by infrared radiation exactly balance the annual rate of heating by absorbed solar radiation. To a good approximation this temperature is

$$T = \left[\frac{(1 - A)S \sin \theta}{\epsilon\sigma\pi}\right]^{1/4} \qquad (1)$$

where A is the albedo of the reservoir for solar radiation, S is the solar heat flux at the orbit of Mars, θ is the obliquity, i.e., the angle between the orbital axis and the rotation axis of Mars, ϵ is the surface infrared emissivity, and σ is the Stefan-Boltzmann constant. If we assume $T = 148°K$, corresponding to a CO_2 partial pressure of 6.5 mbar, and $\epsilon = 0.85$, we find that the albedo A needed to satisfy (1) is 0.71. These values of ϵ and A are reasonable values for a frost-covered surface on Mars.

The question of the existence of such a reservoir is of fundamental significance for several reasons: First, a permanent CO_2 reservoir would naturally account for any excess CO_2 present on Mars as a result of outgassing from the planet's interior. The ratio of the mass of CO_2 in the atmosphere to the mass of the planet is 4×10^{-10} for the earth, 4×10^{-8} for

Mars, and 1.1 × 10^{-4} for Venus [*Ingersoll and Leovy*, 1971]. However, most of the earth's outgassed CO_2 is now in sedimentary rocks. The size of this buried reservoir indicates that the outgassing of CO_2 for the earth has been comparable to that for Venus. It is important to determine whether Mars is similar to or different from the earth and Venus with respect to CO_2 outgassing.

A large frost reservoir could also provide the mechanism for climatic changes on Mars. *Ward* [1973] has shown that the obliquity of Mars oscillates with a period of 1.2 × 10^5 yr, the amplitude of the oscillation varying on a cycle of 1.2 × 10^6 yr. At present the oscillations are of relatively small amplitude, with minimum and maximum values of 23° and 27°, respectively, but during the past these values have reached 15° and 36°, respectively. Substituting these extreme values into (1) and relating the computed temperature to the CO_2 partial pressure, we find that the atmospheric mass might have varied by a factor of 6 above and a factor of 11 below its present value.

Finally, the existence of a large CO_2 frost reservoir could lead to climatic instability on Mars, as has been pointed out by *Sagan et al.* [1973] and by *Gierasch and Toon* [1973]. Instability arises because increases of atmospheric mass due to sublimation of CO_2 frost tend to be self-augmenting. This tendency is due to the fact that atmospheric heat transport is a direct function of atmospheric mass. This effect, which is not included in (1), can lead to instability of the atmosphere-reservoir system. Sudden increases of atmospheric mass by a factor of 100 are possible provided a CO_2 reservoir of sufficient capacity exists.

To summarize, there are two fundamental points raised by Leighton and Murray in their discussion of CO_2 on Mars. The first is that the large seasonal changes in the Martian polar caps are primarily due to CO_2 condensation. The second is that there may be a reservoir of solid CO_2 at the poles that lasts throughout the year and whose mass is at least comparable to the present Martian atmospheric mass. Both points are now widely accepted, especially the first, which is supported by the observational evidence already cited. This paper focuses on the second point and reviews the evidence for and against the existence of a permanent CO_2 reservoir. The paper stresses the arguments against the reservoir because many of these arguments are new and have not yet appeared together in a single article.

THE MEAN POLAR HEAT BALANCE

The first argument in favor of a CO_2 reservoir is the apparent agreement between the radiative equilibrium temperature computed according to (1) and the 148° ± 1°K temperature of saturated CO_2 vapor at a pressure of 6 ± 1 mbar. However, uncertainties in the mean heat input to the pole make the apparent agreement less impressive. Many frosts, including CO_2 frost grown in the laboratory, have albedos in the range 0.8 to 1.0 (H. Kieffer, private communication, 1973). On the other hand, frost albedos are extremely sensitive to dark impurities, especially when the frost is subliming and leaving the impurities concentrated at the surface. On Mars, impurities such as dust would have their greatest effect on the albedo during the spring and summer, when the rate of sublimation is greatest. Since this time coincides with the time that the caps are exposed to sunlight, the effective albedo of the caps for the Martian year also might be quite low.

Figure 1 shows how the expected pressure of CO_2 on Mars

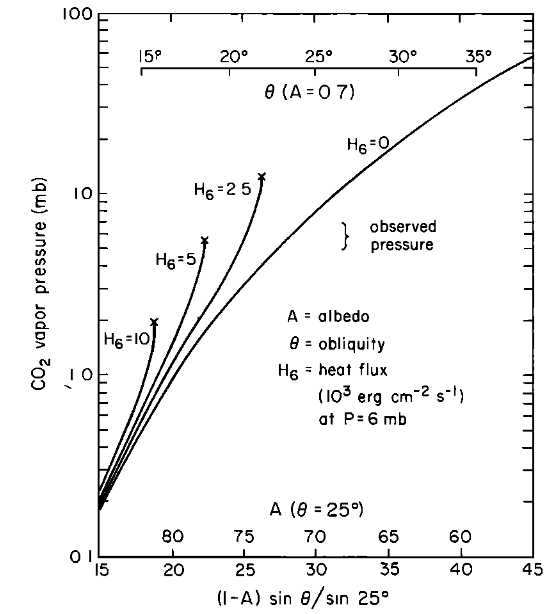

Fig. 1. Predicted CO_2 vapor pressure of the Martian polar caps as a function of heat input parameters. The mean solar heating is proportional to $(1 - A) \sin \theta$, where A is the polar cap albedo and θ is the obliquity, the angle between the rotation axis and the orbit axis of Mars. Atmospheric heating is assumed to be proportional to CO_2 vapor pressure, and H_6 is the value of the atmospheric heating at the observed pressure of 6 mbar. For each nonzero value of H_6 there is a limiting pressure above which the system is unstable.

varies with the albedo A and the obliquity θ. The curve labeled $H_6 = 0$ gives the CO_2 vapor pressure at temperatures computed according to (1). For $\theta = 25°$, which is the value of the obliquity at present, the observed 6-mbar partial pressure corresponds to an albedo $A = 0.71$. However, for $A = 0.61$ and $A = 0.81$ the computed vapor pressures are 30 mbar and 0.6 mbar, respectively. These values of albedo are within the range of uncertainty discussed in the preceding paragraph, this fact indicating that the expected vapor pressure is uncertain by a factor of 5 above and a factor of 10 below its present value. Whether this constitutes any agreement at all is largely a matter of taste. Notice that the effect of albedo uncertainty is comparable to the maximum variation of CO_2 partial pressure due to changes in obliquity.

Further uncertainties arise because of atmospheric infrared emission and atmospheric poleward heat transport. The downward infrared emission of the atmosphere lowers the surface emissivity ϵ and thereby raises the expected polar temperatures and vapor pressures. *Leovy* [1966] and *Leighton and Murray* [1966] estimate the effect of pure gaseous CO_2 in the Martian atmosphere to be about 15% of the surface infrared emission. Thus the net infrared cooling of the surface is reduced by this fraction, this reduction leading to the adopted value of the emissivity, $\epsilon = 0.85$. However, a further reduction in the emissivity may be appropriate, owing to clouds and dust in the atmosphere [*Leovy*, 1966]. During much of the dark season the pole is apparently covered by the clouds of the polar hood. This phenomenon is observed from the earth [*Slipher*, 1962] and was studied by Mariner 9 [*Leovy et al.*, 1972]. These clouds have the effect of further reducing the infrared cooling of the surface without appreciably affecting the absorption of sunlight, which occurs at a season when the polar hood is weak.

Atmospheric heat transport not only contributes an additional uncertain term in the annual polar heat budget but also leads to the possibility that the present Mars atmosphere would be unstable if there were a permanent CO_2 reservoir. The latter possibility suggests that such a reservoir does not exist. We let $\bar{H}$ be the surface heating rate at the pole, averaged over the year, due to heat transport from lower latitudes. Then (1) may be rewritten

$$\epsilon\sigma T^4 = (1 - A)S \sin \theta/\pi + \bar{H} \quad (2)$$

The value of $\bar{H}$ for the present Mars atmosphere can be estimated from the dynamical model of *Leovy and Mintz* [1969] and is related to the 'net convergence' in Figure 13 of their paper. They find values of H ranging from 0 to 1.0×10^4 erg cm^{-2} s^{-1}, depending on season. For comparison the infrared cooling rate $\epsilon\sigma T^4$ is about 2.3×10^4 erg cm^{-2} s^{-1} for $\epsilon = 0.85$ and $T = 148°K$. If the annual average of H were 5×10^3 erg cm^{-2} s^{-1}, inclusion of the second term in (2) would lead to a temperature change from 148°K to 156°K and a corresponding vapor pressure change from 6 mbar to 15 mbar.

However, the possibility of feedback exists, as has been pointed out by *Sagan et al.* [1973] and by *Gierasch and Toon* [1973]. Feedback arises because $\bar{H}$ increases as the atmospheric mass increases, owing to the increased heat capacity of the atmosphere. Here we shall assume that $\bar{H}$ is simply proportional to $P(T)$, where $P(T)$ is the CO_2 vapor pressure at the polar temperature T, computed according to (2). Thus we assume

$$\bar{H} = H_6 P(T)/6 \text{ mbar} \quad (3)$$

where H_6 is the value of the atmospheric heat flux at the present atmospheric pressure of 6 mbar. In fact, however, $\bar{H}$ should also be proportional to the mean horizontal wind speed and the mean horizontal temperature difference. In (3) we are treating these quantities as constants independent of $P(T)$. This treatment is valid provided the equator-to-pole temperature differences and the corresponding wind speeds are controlled mainly by radiation, as is assumed by Leighton and Murray.

Equations (2) and (3) together constitute an implicit relation between the polar temperature T and the quantity $(1 - A) \sin \theta$, which is proportional to the mean solar heating. This relation is plotted in Figure 1 for three assumed values of H_6, namely, 2.5, 5.0, and 10.0×10^3 erg cm^{-2} sec^{-1}. When the albedo A is high and the obliquity θ is low, the curves coalesce, this coalescence indicating that the pressure is so low that atmospheric heat transport is negligible. However, as the albedo decreases and the obliquity increases, the curves diverge and approach limiting values where the slope is infinite. The atmospheric model, based on the existence of a CO_2 reservoir whose temperature is governed by (2), is unstable beyond this point. The curves for $H_6 = 10.0$ and 5.0×10^3 erg cm^{-2} s^{-1} are unstable for values of pressure greater than 2.0 mbar and 5.5 mbar, respectively. This finding indicates that the present Mars atmosphere may be unstable according to the reservoir model. This difficulty can be avoided by assuming either that the reservoir is nonexistent or that it is somehow isolated from the atmosphere. In either of these cases there is no CO_2 to drive the instability, and the present atmosphere may be stable.

As has been explained by Sagan et al., instability leads to a runaway situation in which increasing temperatures at the poles lead to further increases in atmospheric heat transport until either the reservoir is exhausted or the polar temperature reaches some mean value characteristic of the planet as a whole when the pressure is about 1 bar. Sagan et al. have chosen a value of H_6 for which the present atmosphere is stable, but they find that a 10% increase in $(1 - A) \sin \theta$ leads to instability. Thus the atmosphere would have been unstable in the past when the obliquity was large, a large obliquity occurring every 10^5–10^6 yr. However, evidence of such events is debatable at best. Studies of crater statistics, both in the heavily cratered terrains [*Hartmann*, 1973] and in the channel areas [R. P. Sharp and M. C. Malin, unpublished manuscript, 1974; *Sagan et al.*, 1973], suggest relatively little erosion and deposition over the last 10^8–10^9 yr. The alternate possibility again is that there is no reservoir available to drive the atmospheric instability.

If there were no reservoir, only the present atmospheric mass being available for polar cap storage, the possibility still remains that permanent CO_2 caps existed in the past during epochs of low obliquity. The curves of Figure 1 indicate that atmospheric heat transport becomes negligible as the obliquity decreases. Then at some value of the obliquity, permanent CO_2 caps would form as predicted in the Leighton-Murray model. The pressure at which permanent (perennial) caps would first form is uncertain by at least a factor of 5 because of the albedo uncertainty discussed earlier in this section.

In summary, the present Mars atmosphere might be unstable if its pressure were controlled by the temperature of a polar reservoir. This possibility suggests either that such a reservoir does not exist or that the reservoir is isolated from the atmosphere and does not function as it does in Leighton and Murray's original model. In either case one must explain the apparent agreement between the expected vapor pressure of such a reservoir and the observed CO_2 partial pressure in the Martian atmosphere. However, since estimates of the expected vapor pressure differ by factors of 5 above and 10 below the observed value, this agreement could also be the result of coincidence.

POLAR CAP RECESSION DATA

We now consider observations of the rate of retreat of the Martian polar caps during the spring and summer seasons. These data provide information about the rate of heat transfer to the polar caps, since the thickness, area, and rate of retreat all depend on the polar heating. Two approaches are possible. The first approach is that of *Leighton and Murray* [1966], who assume that a permanent CO_2 reservoir exists and determine the albedo A from (1), requiring that the reservoir be in net equilibrium on an annual basis. This then leads to predictions about the seasonal advance and retreat of the polar cap boundary, which can be compared with observation. The other approach is that of *Briggs* [1974], who abandons the idea of a permanent CO_2 frost reservoir and uses the polar cap recession data to fix the albedo and other polar heat sources. The idea of a permanent reservoir can then be tested by seeing whether such a reservoir would be gaining or losing net mass on an annual basis.

Figure 2 shows some results. The mean diameters of the north and south polar caps are plotted as functions of L_s, the celestial longitude of the sun as seen from Mars ($L_s = 0°$ at northern vernal equinox). Ground-based observations are from *Fischbacher et al.* [1969] and *Dollfus* [1973]. The Mariner 7 television observation is from *Murray and Malin* [1973*a*]. The Mariner 9 television observations are from *Soderblom et al.* [1973] and from *Murray and Malin* [1973*a*]. The three Mariner 9 radio occultation observations are from

Woiceshyn [1974]. The theoretical curves are from *Leighton and Murray* [1966] and were obtained by reading points along the abscissa in Figure 3 of their paper. The theoretical point at $L_s = 175°$ for the north polar cap is special and was obtained by shifting the curve labeled N pole in Leighton and Murray's Figure 3 downward until it just touched the abscissa. The justification for this shifting is given in their paper and is related to the fact that the north polar cap lasts throughout the year in their model. Finally, several errors were noted, namely, a plotting error in Figure 1 of *Murray and Malin* [1973*a*] and a mislabeled theoretical curve in Figure 5 of *Soderblom et al.* [1973]. The former error was originally noted by P. M. Woiceshyn (private communication, 1974).

According to Leighton and Murray's model, only the north polar cap remains throughout the year. This asymmetry is an artifact of their model and is due to an approximate treatment of the orbital eccentricity of Mars. However, *Murray and Malin* [1973*a*] point out that the lower elevation of the north pole relative to the south pole would lead to the same result, everything else being equal. In his model, Briggs uses an exact treatment of the orbit and also takes into account the polar elevation differences. He finds that Leighton and Murray's curve for the north polar cap is typical of all models in which the reservoir is assumed to be in net equilibrium and that their curve for the south polar cap is typical of models in which the polar cap is losing net mass on an annual basis. Thus the curves of Figure 2 form the basis of the general discussion that follows.

The importance of Figure 2 is in the fact that neither of the theoretical curves fits the observations well. Both curves predict a rate of recession in the spring that is slower than that observed. In particular, the north polar cap curve, which is constrained to be consistent with a permanent reservoir, lags the observations by as much a 1½ Martian months ($\Delta L_s = 45°$) in the northern spring. The south polar cap curve lags the observations by less than 1 Martian month ($\Delta L_s = 30°$) in the southern spring, but it predicts that the cap should be gone during most of the southern summer.

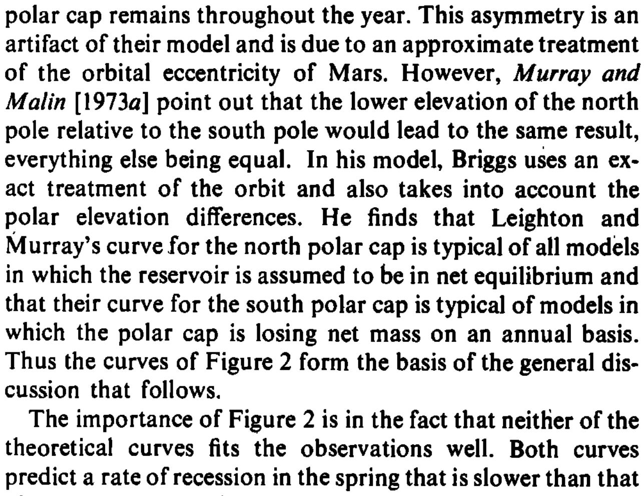

Fig. 2. Angular diameter of the north and south polar caps versus the Martian season; L_s is the celestial longitude of the sun at Mars, equal to 0° at northern vernal equinox. The spring and summer ground-based and Mariner points are obtained from the optical appearance of the cap at visible wavelengths. The autumn Mariner 9 points of *Woiceshyn* [1974] are obtained from radio occultation studies of surface temperature. The theoretical curves of *Leighton and Murray* [1966] are obtained from Figure 3 of their paper. The theoretical curve for the southern cap fits the observations better than that for the north, but it predicts that the CO_2 cap should disappear at the beginning of the summer.

Briggs' model includes atmospheric heat transport and has different albedos for the advancing and retreating caps, but his results are similar to Leighton and Murray's. He is able to model the early, rapid retreat of the caps in the spring by assuming a low albedo for the retreating cap and a relatively high value for the atmospheric heat transport. His curves resemble the south cap theoretical curve in Figure 2, but there is an even greater period in the summer during which the polar caps are absent. In other words the polar heating in his model is so large that the CO_2 deposited during autumn and winter is gone by the beginning of summer. H. Kieffer (private communication, 1973) and *Cuzzi and Muhleman* [1972] find the same difficulty in fitting the polar cap recession data with a model in which there are permanent CO_2 frost caps. The models that fit the data are not consistent with a permanent CO_2 frost reservoir.

The fact remains, however, that a residual white frost remains at each pole throughout the summer. One possibility is that these residual caps are made of a less volatile substance, such as water ice, that is capable of remaining in net equlibrium during the year. This possibility was originally proposed by *Murray et al.* [1972]; further supporting evidence was provided by *Soderblom et al.* [1973] and by *Murray and Malin* [1973*a*]. Other possibilities are that the residual cap is CO_2 but that the polar heat sources are much smaller during the summer than during the spring. At present, there is no theoretical reason or observational evidence to justify such an assumption. Briggs raises the possibility that CO_2 frost may be blown from the edge of the cap to the center during the Martian dark seasons. The rapid retreat of the cap during the spring then does not necessarily imply that the residual cap is out of equilibrium. Again, there is little basis for assuming that such a process is actually taking place.

If the residual caps were CO_2, they would be losing mass at a certain annual rate. We shall now use the polar cap recession data to estimate this rate. Since most of the seasonal CO_2 cap, which forms during the dark seasons, is lost during the first half of the bright season, we may assume that an equal amount is lost during the second half of the bright season. The latter amount is not replaced and represents the net mass lost during the Martian year. According to Leighton and Murray, about 1 or 2 m of CO_2 is deposited during the dark seasons; therefore the net decrease of thickness of a residual CO_2 cap would be about 1 m yr^{-1}. According to this result, if a residual CO_2 cap were suddenly to exist, it would either become depleted in a few years, or else the atmospheric mass would increase until a new equilibrium was established. This process would be accelerated by the associated increase of atmospheric heat transport, as is discussed in the last section.

The results of this section can also be compared with observations of atmospheric pressure changes reported by *Woiceshyn* [1974]. Leighton and Murray's model predicts semiannual pressure changes of about ±0.8 mbar due to storage of CO_2 in the seasonal polar caps. Minimum atmospheric pressures are expected at the equinoxes, when either the northern or southern cap is at its maximum, according to Leighton and Murray's Figure 4. However, according to our Figure 2, the actual retreat of the caps may occur as much as 1½ Martian months earlier than that predicted by Leighton and Murray. Thus the minimum atmospheric pressures might occur 1½ Martian months before the equinoxes, in the middle of the winter/summer seasons. This expectation is consistent with the results of Woiceshyn's analysis of Mariner 9 radio occultation data. Measurements were made during three periods of observation: the standard mission (northern winter/southern summer: $L_s = 292°$ to $L_s = 316°$), the first extended mission (northern spring/southern autumn: $L_s = 25°$ to $L_s = 48°$), and the second extended mission (northern summer/southern winter: $L_s = 89°$ to $L_s = 102°$). Pressures for the standard mission and the second extended mission are systematically about 0.8 mbar lower than those for the first extended mission, these lower values suggesting that minimum pressures do occur in the middle of the winter/summer seasons. If the residual polar caps were CO_2 and if they continued to lose mass during the summer season, minimum atmospheric pressures would occur at the equinoxes, as they do in Figure 4 of Leighton and Murray.

To summarize, it is difficult to reconcile the observed rapid retreat of the transient cap during the spring and the observed atmospheric pressure changes with the existence of a permanent residual CO_2 cap in equilibrium with the atmosphere. The obvious conclusion, in view of the fact that permanent residual caps exist at both poles, is that the residual caps are composed of water ice. In the next section we consider models in which water ice or another substance overlies a permanent CO_2 frost reservoir. Following that section, we abandon the idea of a permanent CO_2 reservoir and examine the expected seasonal behavior of water and compare it with observation.

BURIED CO_2 RESERVOIRS

The arguments of the preceding sections suggest that an exposed CO_2 reservoir, one in good thermal and mechanical contact with the atmosphere, would probably lose net mass under present Martian conditions. Thus if there is excess CO_2 on Mars in addition to that observed in the atmosphere and in the transient polar caps, it must be bound more tightly to the solid planet than it would be in an exposed reservoir. In this section we consider three kinds of buried reservoirs: CO_2 frost that is thermally isolated from the atmosphere, CO_2 frost that is both thermally and mechanically isolated from the atmosphere, and CO_2 that is adsorbed on crystal surfaces in the Mars regolith.

Murray and Malin [1973*a*] propose that a CO_2 frost reservoir is buried under a relatively thin water ice cover within the area of the north polar cap. Their model is similar in most respects to the original Leighton-Murray model; the effect of the water ice cover is simply to reduce the seasonal flow of heat into and out of the buried reservoir. This would explain why changes in the residual cap during the summer are small in spite of the presumed existence of a CO_2 frost reservoir at the pole. The reservoir is assumed to be in vapor contact with the atmosphere via breaks in the water ice cover. The mean polar heat balance is assumed to be essentially as described in the original Leighton-Murray model, i.e., (1) and (2) of this paper. By considering the degree of filling-in of underlying topography by the residual frost cap, Murray and Malin conclude that the total capacity of the CO_2 reservoir is no more than 2–5 times the present Martian atmospheric mass. This is a small amount in comparison with the amount associated with uncertainties in the mean polar heat balance, as discussed earlier.

However, there is a serious inconsistency in the idea of a buried reservoir in vapor contact with the atmosphere. According to Figure 2, the seasonal CO_2 frost cover disappears from the pole around the summer solstice. The temperature of the residual water frost is then no longer buffered by latent heat of CO_2 sublimation and will rise until radiative losses can balance solar heating. During much of the Martian summer the water frost temperature will be above the CO_2 saturation temperature. During the rest of the year, when the water surface is covered by CO_2 frost, the temperature will be equal to the CO_2 saturation temperature. The annual average temperature at the top of the water frost will therefore be above the CO_2 saturation temperature, and so there will be an annual average temperature difference between the top of the water layer and the bottom, which is assumed to be in contact with CO_2 at the saturation temperature. This will lead to a net heat flow to the buried CO_2 reservoir and an accompanying net mass loss due to sublimation.

The inconsistency also appears if one compares the stability of two adjacent CO_2 reservoirs, one of which is exposed and one of which is covered by water ice. According to the preceding argument, the annual average temperature of the water ice will be higher than the CO_2 saturation temperature. The CO_2 in the covered reservoir will therefore have a higher vapor pressure than that in the uncovered reservoir, and so the covered reservoir will tend to lose mass to the uncovered reservoir. Thus if there is a permanent CO_2 frost reservoir in vapor contact with the atmosphere, it will probably be exposed on the Martian surface. Burial decreases the stability of a CO_2 reservoir.

Reasoning of this sort was presented by Murray and Malin as an argument against CO_2 reservoirs covered by dust. However, it applies for any nonvolatile cover unless the albedo of the cover is so high that the solar heating during summer is less than radiational cooling at the CO_2 saturation temperature. Such a cover would have to have a value of $1 - A$ from one-fourth to one-half the value for CO_2 frost in order to protect the CO_2 reservoir over geologic time. This point was missed both by Murray and Malin and by the present author, who read a preliminary version of their paper.

It is possible to estimate the mean daily and annual temperatures of a water frost surface at the pole by using the polar cap recession data to estimate the polar heat sources. In *Briggs'* [1974] model, the value for the albedo of the retreating CO_2 cap that gives a best fit to the data is about 0.6. If the albedo A of the residual water cap is also 0.6, the maximum summertime temperatures of the north and south polar caps are about 195° and 207°K, respectively, according to Briggs. Raising or lowering A by 0.1 changes these temperatures by about 10°–12°K. Summer temperatures of the polar caps quoted by the Mariner 9 radiometer and radio occultation experimenters are in the range 180°–200°K [H. Kieffer, private communication, 1973; *Woiceshyn,* 1974], but these do not necessarily represent actual temperatures of the frost surface.

From Briggs' curves we can also compute the mean annual temperature difference between the water ice surface and a CO_2 frost reservoir in vapor equilibrium with the atmosphere. This temperature difference is the same for both poles in spite of the elevation differences and orbital effects. For $A = 0.5$, 0.6, and 0.7 the value of this temperature difference is about 11.3°, 9.4°, and 7.5°, respectively. The fact that the water ice is warmer than the CO_2 reservoir indicates that such a reservoir is unstable and will lose net mass.

On the other hand, *Miller and Smythe* [1970] point out that the clathrate $CO_2 \cdot 6H_2O$ is more stable at Martian temperatures than pure CO_2 frost. At the same partial pressure of CO_2 the temperature at which the clathrate will be in equilibrium is about 5°K greater than that at which pure CO_2 frost will be in equilibrium. According to the numbers in the preceding paragraph this temperature difference is about one-half the value needed if the clathrate were to be stable. Thus clathrate formation is a potentially important process, although it appears to be unstable according to present models. Moreover, postulating that the CO_2 reservoir is in the form of clathrate does not prevent it from acting as a cold trap for water vapor, a problem discussed in the next section. Finally, since the clathrate composition is only 15% CO_2, the capacity of the reservoir is quite small if we accept *Murray and Malin*'s [1973*a*] estimate that the total mass of the residual cap is no more than 2–5 times the atmospheric mass. Thus it appears that the residual caps are pure water ice with no clathrate, although the question deserves further study.

The above arguments apply to buried CO_2 reservoirs that remain in vapor contact with the atmosphere. One can also imagine a completely sealed reservoir for which the CO_2 vapor pressure is not necessarily equal to the atmospheric partial pressure. The cover for such a reservoir must be very thick and solid, since CO_2 is the major atmospheric constituent and is therefore exchanged by hydrodynamic flow rather than diffusion. A completely sealed reservoir would play no role in surface processes, although it could provide a sink for large amounts of outgassed CO_2. One would then face the problem of explaining the present atmospheric abundance of CO_2. This problem is a feature of all models that abandon Leighton and Murray's original hypothesis of a CO_2 frost reservoir in vapor equilibrium with the atmosphere.

The question now arises, How could a completely sealed reservoir have formed in the first place? As is pointed out by G. A. Briggs (private communication, 1974), such a reservoir might have been deposited on the surface during a colder climate when the exposed CO_2 reservoir was in equilibrium with the atmosphere. The present 6-mbar atmospheric pressure might therefore reflect the equilibrium vapor pressure at the time when burial occurred. Such a hypothesis seems plausible, but it is difficult to test, and the details have yet to be worked out.

Similar arguments apply to adsorbed CO_2 in the Mars regolith. *Fanale and Cannon* [1971, 1974] point out that the total mass of adsorbed volatiles in 1 km of Mars regolith is potentially many times the mass of overlying atmosphere. The role of this reservoir in affecting surface processes depends on the depth of the regolith and the rates of heat and mass exchange with the overlying atmosphere. If both exchange rates are small, the reservoir is completely sealed and has little effect on surface processes. If the transfer of heat is slow but the transfer of mass (i.e., CO_2 vapor) is rapid, the reservoir functions as a 'passive isothermal buffer,' according to Fanale and Cannon. In that case, the effect of the regolith is to reduce the amplitude of any atmospheric pressure changes associated with CO_2 transfer between the atmosphere and the polar caps. However, *Woiceshyn*'s [1974] data suggest that seasonal pressure changes are not significantly reduced by such a mechanism. Finally, if there is rapid heat and mass exchange between the reservoir and the surface, the regolith temperature, together with the polar cap temperature, might determine the atmospheric partial pressure. *Fanale and Cannon* [1974] favor the last possibility, based on the existence of seasonal pressure changes reported by Woiceshyn. Some combination of the above processes, combined with a different climate in the past, can probably explain the present 6-mbar pressure, but the details have yet to be worked out.

In summary, only certain types of CO_2 reservoirs could exist under present Martian conditions. A buried frost reservoir in vapor contact with the atmosphere is less stable in the long run than an exposed reservoir. On the other hand, a clathrate of CO_2 and water ice is somewhat more stable than pure CO_2. A sealed frost reservoir not in vapor contact with the atmosphere could exist as a remnant of a colder past climate. A reservoir of adsorbed CO_2 whose vapor pressure is less than that of CO_2 frost could also be significant provided the depth of regolith is sufficiently great. For a sealed frost reservoir or a reservoir of adsorbed CO_2, one is forced to abandon Leighton and Murray's simple explanation for the present 6-mbar partial pressure of CO_2 in the Martian atmosphere.

WATER RELATIONSHIPS

Water vapor observations provide further evidence against the existence of a permanent CO_2 frost reservoir in vapor contact with the atmosphere. If such a reservoir were to exist, it would act as a cold trap and would eventually remove all but an undetectable amount of water from the atmosphere. Thus present Martian atmospheric water vapor cannot be in equilibrium with a permanent CO_2 cold trap. This fact was appreciated by Leighton and Murray; its significance depends on the rate at which equilibrium would be established. If this rate is slow on a geologic time scale, the present water vapor excess may not be significant. If this rate is fast, the water vapor excess implies that there is no CO_2 cold trap.

The observed column density of water vapor varies with time and place on the Martian surface. Maximum values of $\sim$50 μm precipitable water are observed, usually in the summer. Upper limits of 10 μm are reported in the spring and fall. Thus most of the atmospheric water vapor is removed semiannually. Estimates vary on what fraction would find its way to the CO_2 cold trap if such a cold trap were to exist. If this fraction were unity and if the cold trap covered a fraction of 5×10^{-4} of the Martian surface, as is suggested by *Murray and Malin* [1973*a*], the rate of deposition would be about 10 cm yr^{-1} of precipitable water. On the other hand, if water, along with CO_2, were deposited in the same proportion as their atmospheric abundances, the annual water deposit would be about 10^{-4} of the annual CO_2 deposit, or approximately 10^{-2} cm yr^{-1} of precipitable water. These estimates, which differ by 3 orders of magnitude, cover most of the possibilities that have been envisioned.

Leighton and Murray [1966] and *Leovy* [1973*a*] argue that most of the water condenses out on the periphery of the growing CO_2 cap and that very little water reaches the inner permanent cap. Their models differ in other respects, but both estimate the growth rate on the permanent cap to be about 0.5×10^{-2} cm yr^{-1}, which is slightly below the low estimate given in the last paragraph. However, if most of the atmospheric water were condensing out on the periphery of the growing CO_2 cap, it should reappear in the spring, when the CO_2 cap is retreating. Instead, water vapor seems to appear in the summer, when only the residual cap remains. This led *Leovy* [1973*b*] to suggest that much of the atmospheric water condenses close to the residual cap and is then released when the residual cap is exposed. If the CO_2 reservoir were a significant fraction of the residual cap area, that fraction of the total atmospheric water vapor might be trapped each season. This possibility is the basis for the high estimate given in the last paragraph.

Leighton and Murray invoke the 50,000-yr precessional cycle to reconcile the existence of a permanent CO_2 cold trap with the relatively large amounts of water vapor observed in the Martian atmosphere. Their argument was based on an in-exact treatment of the orbital eccentricity and was modified by *Murray et al.* [1973] and by *Murray and Malin* [1973*a*, *b*]. In essence, these authors argue that the polar caps of Mars have wandered in such a way that the position of the residual polar cap shifts by approximately its own radius every 10^7 yr. Water vapor, because of its low mobility on Mars, gets left behind, and so the present water vapor abundance represents a balance between trapping at the present CO_2 reservoir and outgassing at the sites of past reservoirs. In 10^7 yr at a deposition rate of 0.5×10^{-2} cm yr^{-1}, about 500 m of ice would accumulate in the reservoir. This is comparable to the maximum observed thickness of the residual north polar cap, according to *Murray and Malin* [1973*a*]. If the deposition rate were 10 times larger, say, 5×10^{-2} cm yr^{-1}, the accumulated thickness of water ice at the permanent CO_2 reservoir would be about 5 km in 10^7 yr, which is unacceptably large, according to Murray and Malin. To resolve this difficulty, one would have to assume either that the CO_2 reservoir changes its location rapidly, say, every 10^6 yr, or else that such a reservoir does not exist.

The difficulty in explaining the disequilibrium between atmospheric water and the presumed CO_2 cold trap is independent of whatever other sources or buffer mechanisms exist for water on Mars. Water may be outgassing at the sites of past polar reservoirs as is discussed above, it may be outgassing from volcanoes and hot springs, or it may be outgassing from the regolith, as is proposed by *Pollack et al.* [1970*a*, *b*] and by *Fanale and Cannon* [1971, 1974]. However, in all cases, one has the problem of unacceptably large accumulations of water at the CO_2 cold trap if such a cold trap is in continuous existence for more than 10^7 yr.

The problem is mitigated if the CO_2 cold trap is allowed to disappear periodically at intervals short in comparison with 10^7 yr. Then the summer temperatures at the poles will rise to 200°K for a water-covered surface [*Briggs,* 1974] and to higher temperatures for a soil-covered surface. At these temperatures the vapor pressure of water may be greater than the atmospheric partial pressure of water, and the poles will no longer function as a cold trap. For instance, if water were saturated at the surface and mixed uniformly with CO_2 above, the atmospheric column density would be

$$\int_0^\infty \rho_w \, dz \approx \rho_w(0) H_c \quad (4)$$

where ρ_w is the water vapor density, $\rho_w(0)$ is the saturation density at the surface, and H_c is the scale height for CO_2, about 10 km. Dividing by the density of liquid water, we obtain column densities of about 20 μm and 80 μm precipitable water for surface temperatures of 200° and 210°K, respectively. These column densities are comparable to the maximum values observed in the Martian atmosphere.

Furthermore, the net rate of evaporation for water at these temperatures is comparable to the net deposition rate discussed at the beginning of this section. In the turbulent boundary layer of the earth's atmosphere, evaporation takes place at the rate [*Priestley,* 1959]

$$E \approx 0.002 \rho_w(0) U \quad (5)$$

Here E is the vertical mass flux of water, U is the wind velocity 1 m above the surface, and $\rho_w(0)$ is the saturation vapor density at the surface, as it is in (4). The fact that similar empirical formulas hold for turbulent transfer in other fluids suggests that the above formula may be appropriate also to Mars. We assume that appreciable evaporation takes place only during the season when the polar temperatures are at their maximum. Thus the average annual evaporation rate is approximately one-fifth the value given by (5), $\rho_w(0)$ being evaluated at the maximum temperature of the residual water cap. Taking U = 10 m/s and dividing by the density of liquid water, we obtain evaporation rates of 0.025 and 0.1 cm yr^{-1} precipitable water for temperatures of 200° and 210°K, respectively. These annual evaporation rates are in the range of possible deposition rates given earlier, this fact indicating that the poles might lose net water if the CO_2 cold trap were to disappear periodically.

The obvious way that the CO_2 cold trap might disappear every 10^5–10^6 yr is a result of obliquity increases and climatic instability, as was discussed earlier. According to this hypothesis, water is periodically liberated at the poles, from which it migrates to other reservoirs such as the deep regolith, where it is adsorbed onto crystal surfaces. During periods of low and intermediate values of the obliquity, such as the present, water outgasses from the regolith and accumulates at the poles until the cycle repeats itself. According to this hypothesis the present abundance of water in the regolith reflects a warmer, wetter climate in the past. However, according to *Ward* [1973], the obliquity has increased slightly during the past 50,000 yr, this increase indicating slightly cooler climates during the recent geologic past. Whether any of these arguments is relevant to the present water vapor abundance is unresolved.

The other way to resolve the difficulty of the water vapor abundance is to assume that there is no permanent CO_2 cold trap at present. Then the poles might be in net equilibrium with the atmosphere and the regolith: water deposited during the autumn and winter is liberated during the spring and summer when the polar temperatures rise to 200°K or higher. This possibility was proposed by *Murray and Malin* [1973*a*] in connection with their model of a permanent CO_2 reservoir buried by water ice. However, in the last section, we pointed out that a permanent CO_2 reservoir is not likely to remain buried but will tend to redeposit itself on the surface. In other words, the difficulties of the water vapor abundance remain as long as there is a permanent CO_2 cold trap at a temperature of about 148°K throughout the year. These difficulties appear to be resolved if one assumes that there is no permanent CO_2 reservoir. In this case the annual rates of deposition and evaporation of water at the poles might be equal, although these rates are not well known at present.

SUMMARY AND CONCLUSIONS

There are several arguments against the existence of a permanent CO_2 frost reservoir in vapor equilibrium with the atmosphere. First, the atmospheric heat transport may be so large that the atmosphere would be unstable if a permanent reservoir were to exist. Second, the rapid retreat of the transient CO_2 cap implies a sizable depletion of any permanent CO_2 cap during the summer. Third, the observed atmospheric water abundance implies a gross imbalance between atmospheric water and any permanent CO_2 cold trap. The tendency to lose net mass is even greater for a buried reservoir than it is for an exposed reservoir provided the buried reservoir is in vapor equilibrium with the atmosphere. On the other hand, the tendency is somewhat less for a clathrate of CO_2 and water.

The above arguments do not apply to a sealed frost reservoir that is not in vapor equilibrium with the atmosphere or to an adsorbed CO_2 reservoir whose vapor pressure is lower than that of solid CO_2. Such a buried reservoir could account for a large amount of outgassed CO_2, many times the present atmospheric mass, provided the regolith is deep enough. However, if we adopt the idea of a deep reservoir, we cannot claim to understand the processes that determine atmospheric pressure. Thus it appears that Leighton and Murray's original hypothesis, that the CO_2 polar caps determine the atmospheric pressure, is faced with severe difficulties in the light of recent data.

If Leighton and Murray's original hypothesis is correct, then at least part of the residual caps must be CO_2, and this CO_2 must be bare during the summer, when the seasonal frost cover is absent. This CO_2 reservoir is also more likely to be in the north than in the south as a result of elevation differences. This likelihood narrows the possibilities and makes detection much easier. In particular, it should be possible to detect a CO_2 frost reservoir by remote sensing during the summer season. If polar summer temperatures are always well above 150°K and if no spectroscopic evidence of solid CO_2 is found, then one may conclude that there is no permanent CO_2 frost reservoir controlling the atmospheric pressure.

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