The Case for a Wet, Warm Climate on Early Mars

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Theoretical arguments are presented in support of the idea that Mars possessed a dense CO_2 atmosphere and a wet, warm climate early in its history. Calculations with a one-dimensional radiative-convective climate model indicate that CO_2 pressures between 1 and 5 bars would have been required to keep the surface temperature above the freezing point of water early in the planet's history. The higher value corresponds to globally and orbitally averaged conditions and a 30% reduction in solar luminosity; the lower value corresponds to conditions at the equator during perihelion at times of high orbital eccentricity and the same reduced solar luminosity.

The plausibility of such a CO_2 greenhouse is tested by formulating a simple model of the CO_2 geochemical cycle on early Mars. By appropriately scaling the rate of silicate weathering on present Earth, we estimate a weathering time constant of the order of several times 10^7 years for early Mars. Thus, a dense atmosphere could have persisted for a geologically significant time period ($\sim 10^9$ years) only if atmospheric CO_2 was being continuously resupplied. The most likely mechanism by which this might have been accomplished is the thermal decomposition of carbonate rocks induced directly and indirectly (through burial) by intense, global-scale volcanism. For plausible values of the early heat flux, the recycling time constant is also of the order of several times 10^7 years. The amount of CO_2 dissolved in standing bodies of water was probably small; thus, the total surficial CO_2 inventory required to maintain these conditions was approximately 2 to 10 bars. The amount of CO_2 in Mars' atmosphere would eventually have dwindled, and the climate cooled, as the planet's internal heat engine ran down. A test for this theory will be provided by spectroscopic searches for carbonates in Mars' crust. © 1987 Academic Press, Inc.

1. INTRODUCTION

Today, Mars is a desert world. The globally averaged atmospheric pressure at the surface is only about 7 mbar. Hence, the dominant carbon dioxide atmosphere produces only about a 5°K warming of the surface above the temperature at which the planet radiates to space, about 212°K (Pollack 1979). Although temperatures at the surface rise above the freezing point of water near the equator during the warmest part of the day, water ice is evaporated so efficiently that its temperature at the sur-

face, except perhaps for some very special circumstances, cannot reach 273°K (Ingersoll 1970).

However, the climate of Mars may not have always been as severe as it is today. Geomorphic evidence and theoretical arguments suggest that the atmosphere of Mars may have been significantly denser early in the planet's history (Walker 1978, Pollack 1979, Pollack and Yung 1980, Cess et al. 1980, Toon et al. 1980, Kahn 1985, Schultz 1985). The resulting greenhouse warming may have been much larger than that at present, perhaps large enough to permit the common occurrence of liquid water at the surface (Pollack 1979). This possibility was first indicated by the discovery of fluvially produced channels on images obtained by the Mariner 9 orbiting spacecraft (Masursky 1973). However, it was soon realized that the large outflow channels might be generated under current climate conditions. Large amounts of liquid water, rapidly released from a near-surface reservoir, could flow large distances before totally freezing by forming a top, insulating layer of ice (Peale et al. 1975, Baker 1978). This mechanism may be appropriate to explain isolated, local channels, but it is harder to make such an argument for the fluvial gullies or valley networks. Such features are ubiquitous on the old terrain of the southern highlands. Some corresponding widespread process is needed to generate the liquid water that produced them.

Careful analyses of Mariner 9 and Viking images of valley networks indicate that they were formed chiefly by sapping, rather than by rainfall (Sharp and Malin 1975, Pieri 1980). This deduction does not provide hard evidence that Mars was warmer in its early history. On the other hand, there is still a requirement that thermal conditions close to the surface permitted the occurrence of liquid water over some finite interval of time at many locations in the old cratered terrain. A warm climate would represent one such mechanism (Pollack 1979). Alternative possibilities include widespread volcanism or greenhouse warming within an exposed ice deposit (Cloy 1984).

Geomorphic studies of large impact basins on Mars indicate that such features and their associated secondary craters and ejecta were much more heavily eroded in the planet's early history—more specifically, prior to the formation of the Argyre basin—than at later times (Schultz 1985). If this interpretation is correct, it implies the existence of a much denser atmosphere at these early times. Furthermore, there appears to have been a dramatic decrease in the density of valley networks and a change in drainage style after the Argyre impact (Schultz 1985). These correlations are consistent with the existence of a dense atmosphere in Mars' early history, one capable of raising the surface temperature above the freezing point of water for an extended period of time ($\sim 10^9$ years).

The most promising gas for creating a large greenhouse effect on early Mars is carbon dioxide. It is likely that much more of it was released into the atmosphere over the planet's history—especially at early times—than resides there today. Furthermore, carbon dioxide is relatively stable against UV photolysis (Pollack 1979, Pollack and Yung 1980, Cess et al. 1980). Alternative greenhouse gases, such as ammonia, methane, and sulfur dioxide, are rapidly photolyzed into gases and/or particles that either are poor greenhouse gases (e.g., nitrogen) or have short residence times in the atmosphere (e.g., sulfuric acid aerosols) (Pollack and Yung 1980, Cess et al. 1980). Greenhouse calculations indicate that CO_2 partial pressures in excess of about 1 bar are required to raise the surface temperature on Mars above the freezing point of water (Pollack 1979, Cess et al. 1980, Toon et al. 1980). Such quantities of carbon dioxide are consistent with estimates of the planet's total CO_2 inventory, as discussed in Section 6 of this paper.

For the time being, we assume that

enough carbon dioxide was present in the early atmosphere of Mars to raise the surface temperature above the freezing point of water, at least at low latitudes. We first perform greenhouse calculations with improved opacities for carbon dioxide and water vapor to define more precisely the amount of carbon dioxide needed to maintain these conditions. Then, we consider the stability of this dense carbon dioxide atmosphere against the formation of carbonate rocks via the weathering of silicate rocks. On Earth, in the presence of liquid water, chemical weathering proceeds at such a rate that all the atmospheric carbon dioxide would be eliminated on a time scale of 10,000 years in the absence of CO_2 sources (e.g., volcanic outgassing) (Holland 1978). We use what is known about the CO_2 geochemical cycle on Earth to estimate the time scale for CO_2 loss on Mars. Next, we evaluate the time scale on which the atmosphere can be resupplied with gas by juvenile outgassing and volcanically driven recycling of carbonate rocks. Finally, we determine the total volatile inventory of near-surface carbon dioxide required to maintain a dense carbon dioxide atmosphere over a billion years by a quasi-steady-state carbon dioxide cycle that involves a balance between production and loss. Through such analyses we hope to understand better the plausibility of a warm, wet climate on Mars in its early history. In the final sections of the paper we make such an assessment and propose a possible observational test of our scenario.

It is perhaps useful to summarize here the major theses of this paper as a guide to the following sections. Atmospheres containing several bars of CO_2 are required to permit the common occurrence of liquid water on early Mars. The chemical weathering of surface silicate rocks converts even these amounts of atmospheric CO_2 into carbonate rocks on time scales much less than a billion years when liquid water is present at the surface. However, on early Mars, carbonate rocks can be thermally

decomposed by processes associated with global-scale volcanism on time scales comparable to the weathering time scales. This decomposition returns gaseous CO_2 to the atmosphere. Hence, dense CO_2 atmospheres can be maintained on early Mars with plausible volatile inventories. However, at later times, recycling carbonate rocks becomes inefficient and so liquid water occurs on the surface far less frequently.

2. GREENHOUSE MODELS

In this section of the paper, we present estimates of the amount of atmospheric carbon dioxide needed to raise the surface temperature on early Mars above the freezing point of water. The greenhouse warming is produced by the infrared opacity of both gaseous carbon dioxide and water vapor. However, the amount of atmospheric water vapor is controlled by its vapor pressure curve, as is the case for the present atmosphere of the Earth.

2.1. Procedure

A one-dimensional radiative-convective model was used to determine the steady-state vertical temperature profile in the atmosphere and the temperature at the surface. Details of the model have been published elsewhere (Kasting and Ackerman 1986) and will not be repeated here. We assume that the lapse rate in the troposphere follows a moist adiabat and that the tropospheric relative humidity decreases linearly with pressure, starting from a value of 0.77 at the surface (Manabe and Wetherald 1967). This latter formula is appropriate for Earth, hence its use seems reasonable for modeling an Earth-like early Mars. By contrast, Pollack (1979) and Cess et al. (1980) assumed a constant relative humidity. Clouds are neglected in our calculations; the effect of this assumption is described in Section 2.2.

A key aspect of these new greenhouse calculations is the inclusion of improved

values for the opacity of gaseous CO_2 and H_2O in the thermal and solar regions of the spectrum. For most of this wavelength interval, these values were derived from line-by-line calculations based on the data given on the AFGL tape (McClatchey et al. 1971). In addition, allowance was made for the pressure-induced transitions of CO_2, the 8- to 12-μm continuum of water vapor, and the weak lines of both gases in the visible and near-infrared spectral regions (Roberts et al. 1976, Kasting et al. 1984b, Moore et al. 1966, Herzberg and Herzberg 1953, Kasting 1986).

The computed values of surface temperature, T, depend on the carbon dioxide pressure, P, the surface albedo, A_s, and the diurnally averaged amount of sunlight, S. Here, we define S as the ratio of the actual amount of sunlight at the top of the Martian atmosphere to the globally and orbitally averaged value for present-day Mars. For a given choice of values for A_s and S, T is computed for a wide range of values of P to determine the value of P at which T equals the freezing point of liquid water.

A nominal value of 0.215 was selected for the surface albedo, since this yielded a planetary albedo of 0.212 for the present Martian atmosphere with $P = 6$ mbar, in good agreement with the value determined by the Viking IRTM experiment at a time of low dust loading (Kieffer et al. 1977). However, we also performed calculations with $A = 0.1$ to simulate conditions for a hypothetical early Martian surface covered with unoxidized minerals (Toon et al. 1980).

The value of S depends on the epoch, latitude, and orbital position (Pollack and Yung 1980, Cess et al. 1980). When Mars first formed, about 4.5 billion years ago, the solar luminosity was about 25 to 30% less than its current value (Newman and Rood 1977, Gough 1981). It increased by about 5% during the first billion years of the planet's history. Mars' orbit is highly eccentric at the present epoch (eccentricity $= 0.093$). At perihelion, the incident solar flux is 22% larger than the orbitally

averaged value. Furthermore, the orbital eccentricity undergoes quasi-periodic variations on time scales of 0.1 to 1 million years, with the eccentricity varying between 0 and 0.14 (Ward 1974). At maximum eccentricity, the insolation at perihelion would be 35% larger than its orbitally averaged value. In addition, the equatorial regions receive 40% more sunlight than the planet as a whole (Toon et al. 1980). Thus, the values of S of interest range from about 0.7, corresponding to the orbitally and globally averaged value 4.5 billion years ago, to about 1.3, corresponding to the value at the equator and at perihelion at maximum eccentricity for the same epoch.

The above discussion contains the implicit assumptions that the thermal response time of the atmosphere is significantly shorter than an orbital period and that atmospheric heat transport is relatively inefficient in equalizing temperature differences between low and high latitudes. We now show that these assumptions are reasonable approximations for the atmospheric pressures of most interest (1 to 5 bars).

Consider first the thermal response time of the atmosphere. It is given by

$$t_r = \frac{c_p P \delta T}{g \sigma T_e^4}, \tag{1}$$

where c_p is specific heat at constant pressure, δT is the change of temperature over an orbital period, g, is the acceleration of gravity, σ is the Steffan–Boltzmann constant, and T_e is the effective temperature of emission to space. For $P = 1$ bar and $S = 1$, our calculations yield $T_e = 204.2°K$. For $\delta T = 30°K$, the response time of the atmosphere is 6×10^6 sec or about a factor of 10 times smaller than the orbital period. Therefore, for the range of parameters of interest, the atmosphere should respond relatively rapidly to changes in insolation over its orbit.

It is more difficult to evaluate the efficiency of the atmospheric heat transport by the paleoatmospheres of interest. Hoffert et

al. (1981) have presented a parameterization for heat transport by baroclinic eddies that provides an estimate of the temperature difference between midlatitudes and the poles. Using this parameterization for a 1-bar atmosphere, we find a temperature difference of about 30°K between midlatitudes and the poles or about 50°K between the equator and poles. These differences scale as the inverse of the square root of the atmospheric pressure. Thus, atmospheric heat transport will not erase much of the temperature variation with latitude for the atmospheres of primary interest here.

2.2. Results

Figures 1a and 1b illustrate the variation of surface temperature (standard model) and planetary albedo with surface pressure for $A_s = 0.215$ and $S = 1$. Both quantities increase slowly at first as P is increased from its present value to several tenths of a bar, and then more rapidly as P is increased further. The rapid increase in planetary albedo at the higher pressures is due to the increasing prominence of Rayleigh scattering, while the corresponding rapid increase in surface temperature at the higher pressures, in spite of the increase in albedo, is a result of the atmosphere becoming optically thick at almost all infrared wavelengths. For the standard model, a surface pressure of 2.2 bars is needed to raise the surface temperature to the melting point of water ice.

Figure 1a also shows the predicted dependence of surface temperature on CO_2 partial pressure obtained in the earlier calculations of Pollack (1979) and Cess *et al.* (1980). The results of this paper are in surprisingly good agreement with those of Pollack (1979), who simply performed an energy balance calculation at the top of the atmosphere, neglecting the change of planetary albedo with P, and using much cruder opacity coefficients. This agreement is probably the result of partially compensating effects. On the one hand, Pollack (1979) obtained somewhat higher temperatures for a fixed surface pressure by not allowing for the influence of Rayleigh scattering on the planetary albedo and by using a constant relative humidity throughout the troposphere. On the other hand, he underestimated the temperature by not including the pressure-induced transitions of CO_2.

Our predicted surface temperatures are significantly lower than those obtained by Cess *et al.* (1980), who did a full radiative-convective calculation, computed the planetary albedo, and used apparently better opacity coefficients than Pollack
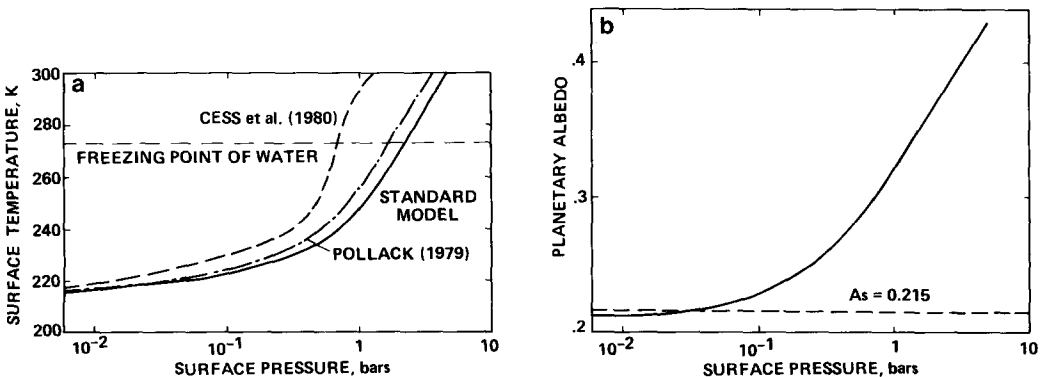

FIG. 1. (a) Surface temperature, T_s, and (b) planetary albedo, A_p, of Mars as the function of the surface pressure of CO_2 for the present surface albedo and globally and orbitally averaged solar flux. In (a), the solid curve presents results from this paper, while the other two curves represent results from two earlier calculations.

(1979). Unfortunately, there appears to have been a serious coding error in the calculations of Cess *et al.* (1980) that caused them to overestimate the surface temperature (V. Ramanathan, private communication). Hoffert *et al.* (1981) performed a calculation of the CO_2 greenhouse effect based on flux balances and found surface temperatures even higher than those of Cess *et al.* (1980) for $P \le 1$ bar. The reason that their model predicted high temperatures is not readily apparent, but it may be caused by their neglect of convection. More recently, Postawko and Kuhn (1986) performed a series of Martian surface temperature calculations for $P = 1$ and 3 bars; their results are roughly comparable to ours. They further suggested that the greenhouse effect on early Mars may have been augmented by SO_2. But, by analogy to conditions in the Earth's troposphere and stratosphere, SO_2 in an early Martian atmosphere would have been rapidly oxidized and sedimented out of the atmosphere as sulfate.

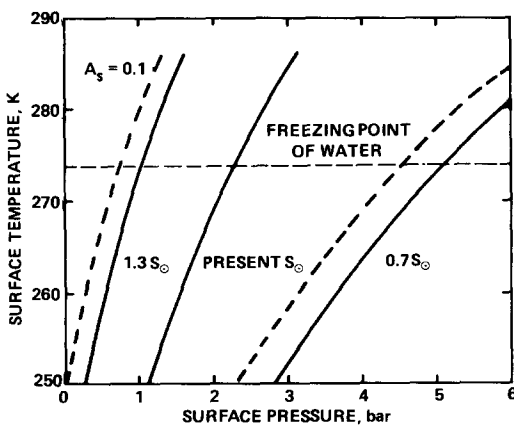Figure 2 shows the influence of the assumed values of A_s and S on the computed surface temperature. According to these results, surface pressures ranging from about 0.75 to 5 bars are needed to raise the surface temperature to the melting point of water ice. This critical pressure depends most sensitively on the value of S.

The greatest uncertainty in the above calculations is undoubtedly caused by our neglect of water clouds. Introducing a cloud layer into the model would not greatly reduce this uncertainty because one could not be sure how its height, fractional area, and optical properties varied with surface temperature. Despite these potential problems it is probable that the temperature feedbacks caused by clouds would be relatively small. The effects of clouds on the infrared and solar radiation budgets are to some extent compensating: clouds tend to lower T by reflecting incident sunlight back to space, but they also raise T by enhancing the greenhouse effect (Pollack 1979, Toon *et al.* 1980). With this in mind it is interesting to note that this same model requires only a slight adjustment in surface albedo (from 0.215 to 0.22) to reproduce the observed mean global surface temperature for a cloud-free Earth. Thus, to the extent that a warm early Mars resembled present-day Earth in terms of surface reflectivity and cloud properties, our model may do a surprisingly good job of predicting its surface temperature.

3. LOSS RATES FOR ATMOSPHERIC CO_2

On Earth, CO_2 is removed from the atmosphere/ocean system by the chemical weathering of continental silicate rocks, followed by the deposition of carbonate rocks on the ocean floors (Holland 1978). In detail, carbon dioxide dissolves in rainwater and surface water to form a weak acid. This mildly acidic water dissolves silicate rocks, releasing Ca^{2+}, Mg^{2+}, and HCO_3^- into solution. These dissolved ions are transported to the seas by rivers and eventually are precipitated as calcium and magnesium carbonates on the ocean floors. Thus, running water, exposed silicate rocks, and ocean basins are necessary ingredients in this type of chemical wea-

FIG. 2. Surface temperature as a function of surface pressure for several values of the surface albedo and incident solar flux, S. Solid lines refer to results for the current globally averaged albedo of 0.215. $S = 1$ for the present globally and orbitally averaged solar flux at Mars.

thering. In the following, we scale the weathering rates for Earth to estimate those that might apply on an early Mars with a dense carbon dioxide atmosphere and temperatures above the melting point of water ice. The object of these calculations is to estimate the time for the removal of carbon dioxide by chemical weathering in the absence of sources of new atmospheric CO_2.

3.1. Procedure

The rate of chemical weathering by atmospheric CO_2 is a function of the partial pressure of CO_2 at the surface, P, the surface temperature, T, the cation content of the exposed rocks, and the fraction of the planet occupied by open bodies of water, a. On the basis of our present understanding of the silicate weathering rate on Earth, we may formally write the mass loss rate of atmospheric CO_2 per unit surface area of the planet in terms of the product of a number of scaling factors, g_i, and the present silicate weathering rate for Earth:

$$\frac{dM}{dt} = g_1 g_2 g_3 g_4 g_5 \frac{dM_e}{dt}. \qquad (2)$$

Here g_1 incorporates the dependence of the weathering rate on pressure, g_2 expresses its dependence on the variation of runoff with temperature, g_3 gives its dependence on the variation of the weathering reaction with temperature, g_4 is its dependence on the cation content of the rocks, g_5 provides its dependence on the fraction of open bodies of water (the ultimate source of the runoff), and dM_e/dt is the present weathering rate of continental silicate rocks on Earth.

Results from laboratory experiments (Lagache 1965, 1976) indicate that the pressure-dependent factor is given by (Walker et al. 1981)

$$g_1 = \left(\frac{P}{P_e}\right)^{0.3}, \qquad (3)$$

where P_e is the partial pressure of carbon dioxide in the Earth's atmosphere (3.3 × 10^{-4} bars). This expression assumes that the high-pressure (2 to 20 bars) laboratory data can be extrapolated to the relatively low CO_2 partial pressure in Earth's atmosphere. As a consequence of this relatively weak dependence of the weathering rate on pressure, the weathering time scale increases as the pressure increases (see below).

As the temperature increases, water is evaporated at a faster rate from standing bodies of water; hence, the precipitation rate and the amount of runoff also increase. Numerical experiments with general circulation models indicate that this dependence can be expressed as (Manabe and Stouffer 1980, Berner et al. 1983)

$$g_2 = \exp(c_2 \delta T), \qquad (4)$$

where $\delta T = T - T_e$. T_e is the Earth's present mean temperature of 288°K. The constant $c_2 = 0.038$. Here, we use a somewhat different functional form for g_2 than used by Berner et al. (1983) to cover a wider range of temperature conditions. This exponential increase of the rate of precipitation with temperature is ultimately limited by the amount of sunlight available to heat the open bodies of water. Accordingly, we demand that g_2 be limited by

$$g_2 \leq c_{max} S, \qquad (5)$$

where c_{max} is a constant and S is the amount of sunlight, normalized to a value of 1 for the globally and orbitally averaged situation for present-day Mars. About half the sunlight absorbed by Earth's oceans is used to supply the latent heat of vaporization (Holland 1978). This suggests that g_2 could not be any larger than 2 for the present Earth. Note that since the oceans lose heat to the atmosphere by thermal radiative exchange and boundary layer convective processes, consideration of these other processes will not result in an increase in this upper limit, unless the atmosphere developed an inversion near the surface. Since $S \cong 2$ for

the Earth, we select 1 as a nominal value for c_{max}.

Measurements of the latitudinal dependence of the weathering rate on Earth (Harmon et al. 1975) in conjunction with the above expression for g_2 suggest the following dependence of the chemical reaction rate on temperature (Berner et al. 1983):

$$g_3 = \exp(c_3\delta T). \qquad (6)$$

The coefficient $c_3 = 0.049$. It should be noted that the expressions for g_2 and g_3 were derived for Earth-like conditions, i.e., for surface temperatures above the freezing point of water. At temperatures below the freezing point, chemical weathering rates would presumably be much smaller than assumed here; hence, Eq. (2) represents a strong upper limit on the actual weathering rates under such conditions. This equation leads to somewhat larger rates than actually occurred when temperatures were above the freezing point at only some locations or times of the year.

On Earth, Ca^{2+} and Mg^{2+} are the principal cations that are available to form carbonates. Fe^{2+} is also capable of forming carbonates, but it is very quickly oxidized to insoluble ferric iron. Presuming that early Mars, like early Earth, had little free atmospheric oxygen, Fe^{2+} would also have been available for forming carbonates. Therefore, the parameter g_4 is obtained by estimating the ratio of the Ca, Mg, and Fe content of rocks on early Mars to the Ca and Mg content of continental silicate rocks on Earth. Comparison of Viking elemental abundance measurements (Clark et al. 1977) with the extensive data set for Earth (Holland 1978) implies that this ratio is about 4 for the present surface of Mars. However, since the abundances of Fe and Mg on Mars' surface may have been significantly enhanced subsequent to the early epochs of interest here (Clark and Baird 1979), we select a nominal value of 2 for g_4.

Perhaps the hardest parameter to define is g_5, which is the dependence of the wea-thering rate on the fraction of the planet covered by open bodies of water. Since this parameter should be 0 when a equals either 0 (no water available to evaporate) or 1 (no land available to weather), we have chosen the functional form

$$g_5 = a(1 - a). \qquad (7)$$

We select a nominal value of 0.05 for a, since there is no evidence for the occurrence of large oceans on early Mars.

The chemical weathering rate, if sufficiently large, is ultimately limited by the rate of physical weathering, i.e., the rate at which fresh material is exposed at the surface. For Earth, the average physical weathering rate is only about 6 times larger than the average chemical weathering rate (Holland 1978). Furthermore, not all elements of rocks can be chemically weathered; thus, if this chemical weathering rate was only a factor of several times larger, physical weathering would act to limit it. We express this limitation formally as an upper bound on the product of scaling factors:

$$g_1g_2g_3a \leq 0.71g_{max}. \qquad (8)$$

This limit does not include the g_4 factor since the fraction of rock that is not chemically weathered is not directly related to the fraction of cations that causes a net removal of CO_2 from the atmosphere. It also does not contain the $(1 - a)$ factor of g_5 since the constraints involve a comparison of chemical and physical weathering rates per unit area of land. The factor of 0.71 on the right-hand side of the equation is the fraction of Earth's surface area occupied by oceans. The present average physical weathering rate on Earth is 30 m/10^6 years (Holland 1978). It is determined primarily by the uplift rate for continents. On early Mars, the physical weathering rate would probably have been related to the rate of volcanic resurfacing, which should have been about a factor of 10 higher than the present physical weathering rate for Earth (see below). We therefore select 30 as a nominal value for g_{max} since this parameter

has a value of about 3 for the present Earth. This latter value is crudely obtained by taking the product of the ratio of the average physical to chemical weathering rates (6) and an assumed factor of 0.5 for the soluble component of rock, as discussed above.

Finally, we derived the value for dM_e/dt from estimates of the current rates of chemical weathering of continental silicate rocks (Berner et al. 1983) and the fraction of continental surfaces occupied by these rocks. This fraction equals 0.47 (Ehlers and Blatt 1982, Ronov and Yaroshevsky 1969). The remainder of the continental area is occupied by carbonates, organic deposits, and evaporites, the weathering of which has no effect on atmospheric CO_2. Thus, we find that

$$\frac{dM_e}{dt} = 5.1 \times 10^{-4} \text{ g/cm}^2/\text{year.} \quad (9)$$

On early Mars, we assume that silicates occupy all the land area. This will lead to a slight underestimate of the weathering removal time scale.

The time scale τ_w for eliminating atmospheric CO_2 by chemical weathering is obtained from

$$\tau_w = \frac{M}{dM/dt}, \quad (10)$$

where M is the mass of atmospheric CO_2 per unit area. It is given by

$$M = 2.69 \times 10^3 P. \quad (11)$$

P has units of bars in this equation.

In the above discussion, we have tried to identify the key chemical and physical processes that determine the rate of chemical weathering on a planet having liquid water on its surface. In so doing, we have made use of the very extensive studies of the Earth's CO_2 geochemical cycle. Nevertheless, a number of the numerical constants in the above expressions are known only to an accuracy of several tens of percent. Thus, the weathering time scales estimated below are good only to a factor of about two for given values of the relevant parameters. In addition, these parameters can assume a range of plausible values for early Mars. For this reason, we performed sensitivity studies to elucidate the impact of these ranges on the values of the weathering time scales.

3.2. Results

Using the equations given in Section 3.1, we computed the weathering time scale τ_w as a function of P for the nominal parameter choices as well as for plausible alternative values. Figure 3a shows this relationship for the nominal surface temperature of 273°K, along with two higher values. For the nominal temperature, τ_w ranges from 1.5×10^7 years for a 0.75-bar atmosphere to 6×10^7 years for a 5-bar atmosphere. As the temperature is increased by 30°K above the freezing point, the weathering time scale drops by about a factor of 10. Thus, in the absence of a source of fresh CO_2, surface temperatures on a warm early Mars would have fallen rapidly towards the freezing point, as much of the atmosphere was quickly lost by chemical weathering. The time scale for this decay is short compared to the geological time scales of interest ($\cong 10^9$ years).

The sensitivity of the weathering time scale to our choice of g_{max} is explored in Fig. 3b. Only if the physical weathering rate was more than 100 times smaller than our nominal choice would it provide a significant limitation on the chemical weathering rate. Thus, it seems to be very unlikely that significantly larger chemical weathering time scales could be obtained for alternative choices of g_{max}.

Figure 3c shows the dependence of τ_w on a. As the fraction of area occupied by standing bodies of water increases, τ_w decreases in roughly the same proportion. Values of τ_w on the order of 10^9 years could be achieved by selecting a value for a on the order of 0.001. Such a low value for a seems highly unlikely for a warm, wet Mars for which the amount of outgassed CO_2 is
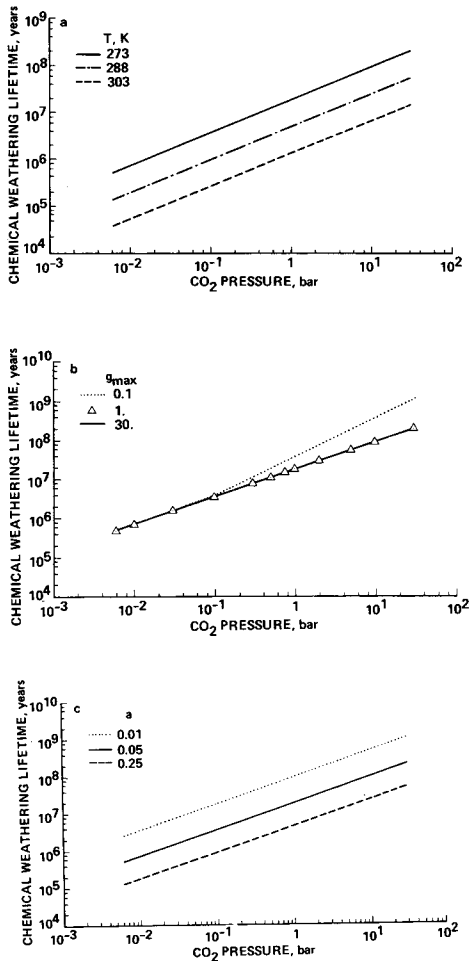
FIG. 3. Chemical weathering time scale as a function of the surface pressure of CO_2. Results are shown for three different choices of (a) surface temperature, T; (b) upper bound on the chemical weathering rate imposed by the physical weathering rate, g_{max}; and (c) fraction of the surface occupied by open bodies of water, a.

not greatly different from that expected for an Earth analog (and hence a nontrivial amount of water would have also been outgassed).

Plausible variations in any of the parameters other than the ones already discussed do not alter the computed values of τ_w by more than a factor of several. For example, the cation factor g_4 and hence τ_w might plausibly vary by a factor of 2 or so

from their nominal values. Sample calculations also show that τ_w changes very little as the solar flux parameter S varies from 0.7 to 1.3 and that it increases by no more than a factor of several as c_{max} is decreased by a factor of several below our nominal value of 1 (see Eq. (5)).

The above discussion indicates that τ_w is of the order of 10^7 years for CO_2 pressures near 1 bar and that plausible changes in parameter choices could not increase τ_w to near 10^9 years. Thus, if a wet, warm climate occurred on early Mars for a lengthy period of time and if it were produced by a CO_2 greenhouse, then the loss of CO_2 by chemical weathering of surface silicate rocks must have been balanced by a sufficiently vigorous CO_2 source. In Section 4 we consider two such possible sources.

4. SOURCES OF ATMOSPHERIC CO_2

The most obvious sources of CO_2 are the outgassing of juvenile CO_2 from the planet's interior and the recycling of carbonate rocks by intense, global-scale volcanism. In the latter case, carbonate rocks could have been thermally decomposed by contact with hot lava near the surface or by burial to a depth sufficient to reach temperatures above their decomposition point. We formulate both problems in terms of characteristic time scales for comparison with the weathering time scales of the last section.

4.1. Procedure

Since the Moon experienced extensive global-scale volcanism during the first several hundred million years of its history (Wasserburg et al. 1977), it is reasonable to suppose that such a situation also prevailed on early Mars. Early intense volcanism could have played a key role in the CO_2 cycle by providing an effective mechanism for releasing juvenile CO_2 stored in the planet's mantle and by bringing lava to the surface to recycle carbonate rocks. Here, we present a simple calculation of the time

required for each of these sources to re-plenish the CO_2 in Mars' atmosphere.

The surface heat flux, F_t, on early Mars would have been determined by the combination of heat delivered to the surface by thermal conduction, F_c, and heat generated by the cooling of lava at the surface, F_l. Let α represent the fraction of F_t carried by heat conduction. The conductive heat flux is given by

$$F_c = \alpha F_t = k \frac{dT}{dz}, \qquad (12)$$

where k is the thermal conductivity and dT/dz is the rate of increase of temperature with depth. Heat conduction results from a combination of lattice conductivity, k_l, and radiation transport, k_r. For basaltic rock (a reasonable analog for the surfaces of interest) these components of the thermal conductivity may be written in terms of the subsurface temperature, T_i, according to (Basaltic Volcanism Study Project 1981)

$$k_l = \frac{10^7}{7.4 + 0.05T_i}, \qquad (13)$$

with k_l having units of ergs/cm/sec/°K. The radiative conductivity is

$$k_r = 2.3(T_i - 500) \times 10^2 \qquad (14)$$

when T_i is greater than 500°K and is otherwise zero.

The component of the surface heat flux due to extruded lavas may be written as

$$F_l = (1 - \alpha)F_t = (L + C_p\delta T) \frac{dm}{dt}, \qquad (15)$$

where L is the latent heat released by the lava freezing, C_p is its specific heat, dm/dt is the mass of lava extruded per unit area per unit time, and δT is given by

$$\delta T = T_m - T, \qquad (16)$$

with T_m being the initial temperature of the lava when it reaches the surface and T is its final temperature after cooling. We assume that T_m equals the melt temperature and T equals the unperturbed surface tempera-ture. In our calculations we use representative values for basaltic lavas of 4×10^9 ergs/g for L, 1.2×10^7 ergs/g/°K for C_p, and 1550°K for T_m (Basaltic Volcanism Study Project 1981). We use Eq. (15) to determine the value of dm/dt for specified values of F_t and α.

Given a knowledge of dm/dt, we can readily calculate the rate at which the surface is covered over by lava extrusions:

$$\frac{dz}{dt} = \frac{1}{\rho} \frac{dm}{dt}, \qquad (17)$$

where ρ is the density of lava, here taken to be 3 g/cc. This equation is used to determine the time scales for resupplying the atmosphere with CO_2 by both juvenile out-gassing, τ_j, and recycling of carbonate rocks, τ_r.

Time scale τ_j is related to dz/dt by

$$\tau_j = \frac{P}{P_m} D_m \left(\frac{dz}{dt}\right)^{-1}, \qquad (18)$$

where D_m is the depth of the mantle that is participating in the outgassing and P_m is the amount of CO_2 contained in this region of the mantle, expressed in terms of an equivalent atmospheric pressure. We take a value of 500 km for D_m, based on thermal history models of Mars (Basaltic Volcanism Study Project 1981).

Time scale τ_r is obtained from

$$\tau_r = D_d \left(\frac{dz}{dt}\right)^{-1}, \qquad (19)$$

where D_d is the depth to which carbonate rocks need to be buried to thermally decompose into silicates and CO_2 gas. This depth can be calculated from the finite difference form of Eq. (12) and a knowledge of the minimum temperature needed for decomposition, T_d:

$$D_d = \frac{k(T_d - T)}{\alpha F_t}. \qquad (20)$$

Equation (19) for τ_r neglects thermal decomposition that occurs when hot lava comes in contact with carbonate rocks.

Thus, our computed values for τ_r will be somewhat larger than what they would actually be for the scenario under discussion. At the depths where decomposition takes place (5–20 km), a nominal value of 950°K is appropriate for T_d (Harker and Tuttle 1956). The parameter k in Eq. (20) is evaluated at a depth halfway between the surface and the depth of decomposition.

For interpreting the results presented below, it is useful to write Eq. (19) in a form that displays more explicitly the dependence of τ_r on α and F_t. Combining Eqs. (15), (17), (19), and (20), we obtain

$$\tau_r = \frac{k\rho(T_d - T)(L + C_p\delta T)}{\alpha(1 - \alpha)F_t^2}. \quad (21)$$

4.2. Results

In this section, we present estimates of the time scales, τ_j and τ_r, for resupplying the atmosphere with CO_2 by juvenile outgassing and by volcanic recycling of carbonate rocks. The results depend primarily upon the surface heat flux, F_t. F_t is useful in this role since it, in effect, provides an energy constraint on both processes and since one can place good constraints on its value during the early history of Mars. Thermal history models for Mars predict that F_t for the present epoch equals 30

mW/m^2 (Davies and Arvidson 1981), which may be compared with a value of about 100 mW/m^2 for the average heat flux from the Earth's ocean basins. During the early history of Mars, F_t was probably larger than its current value by a factor of 3 to 10 because of a larger release of heat by long-lived radioactive elements, the formation of the Martian core, and a larger residual heat from planetary accretion (Davies and Arvidson 1981, Stacey 1980).

Figure 4a presents our estimate of τ_j as a function of F_t for three alternative values of P/P_m, the ratio of the amount of CO_2 in the atmosphere to that contained in the portion of the mantle undergoing outgassing. Note that this time scale does not depend on the value of P by itself, but merely upon this ratio. According to Fig. 4a, small values of the pressure ratio are required for τ_j to be comparable to the weathering time scales, τ_w, presented in the previous section. For example, τ_w equals approximately 3×10^7 years for $P = 2$ bars and our nominal parameter choices. For τ_j to match this value at reasonable heat fluxes, the ratio P/P_m must be less than 0.07. This requires a total CO_2 inventory in excess of 30 bars. While such a large value cannot be totally excluded, it is higher than seems likely, as discussed more fully in a later section of
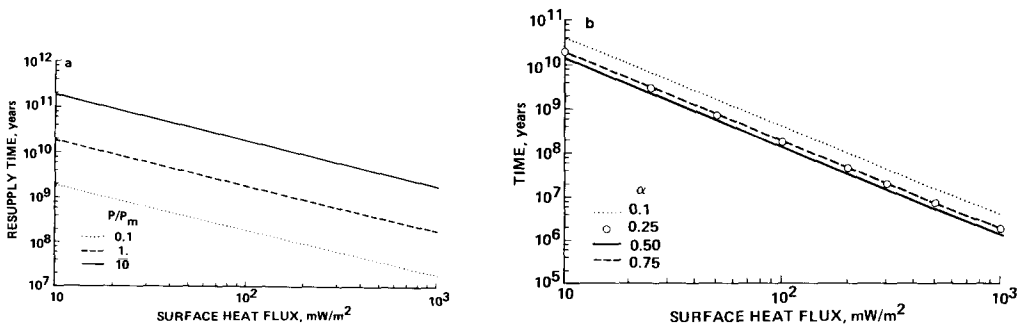

FIG. 4. Time scale for resupplying the atmosphere with CO_2 as a function of the surface heat flux from the interior. Results are shown for (a) outgassing of juvenile CO_2 from the planet's interior (the three curves correspond to alternative choices for the ratio of CO_2 in the atmosphere to that in the interior) and (b) a recycling mechanism, for which carbonate rocks formed by weathering are thermally decomposed after being buried by lava to a sufficient depth. The curves differ in the choice of the fraction of the heat flux carried by thermal conduction, α.

this paper. Such a large requirement on the volatile inventory is an almost inevitable consequence of requiring that the atmosphere be resupplied with juvenile CO_2 every few times 10^7 years for an extended period on the order of 10^9 years.

Figure 4b illustrates the dependence of the volcanic recycling time scale, τ_r, on surface heat flux for several choices of α, the fraction of the heat flux carried by conduction. τ_r does not vary very much as α changes over the range used for this figure; in fact, it has almost the same value for $\alpha = 0.25, 0.5$, and 0.75. This is because of two compensating effects: On the one hand, increasing α decreases the amount of extruded lava, but on the other hand it decreases the depth at which the subsurface temperature equals the decomposition temperature of carbonates. Both these effects operate in the same direction as F_t is varied; thus, τ_r depends quadratically on F_t, as shown in Eq. (21).

For $F_t = 100$ mW/m^2, τ_r ranges between 1 and 3×10^8 years, while for $F_t = 300$ mW/m^2, it lies between 1 and 3×10^7 years. Furthermore, as mentioned above, these values for τ_r represent slight underestimates in that thermal decomposition of carbonates by contact with hot surface lavas has been neglected. Thus, the recycling time scales are comparable to the weathering time scales and offer a plausible means for maintaining a dense CO_2 atmosphere on the planet over an extended period of time in its early history.

5. PARTITIONING OF CO_2 BETWEEN THE ATMOSPHERE AND HYDROSPHERE

In the previous two sections we have argued that a dense CO_2 atmosphere could have existed on early Mars for about a billion years, provided that recycling of carbonate rocks was sufficiently rapid to balance weathering of silicates. To this point, however, we have neglected the fact that some CO_2 should have been dissolved in the early oceans (or lakes) as carbonic acid and as carbonate and bicarbonate ions.

On Earth the amount of CO_2 dissolved in the oceans exceeds the amount in the atmosphere by a factor of $\simeq 60$ (Holland 1978). Were this same ratio to apply to early Mars, this would place unrealistic demands on Mars' total CO_2 inventory; e.g., a 1-bar CO_2 atmosphere would require a total CO_2 endowment in excess of 60 bars.

The partitioning of CO_2 between atmosphere and hydrosphere depends on the temperature, size, pH, and cation content of the hypothesized early ocean. While we cannot hope to estimate these quantities with great precision for early Mars, it is possible to make a simple model to bracket some of the uncertainties. Here, we assume that the Martian ocean was isothermal (5°C) and had a salinity of 35 parts per thousand, like Earth's oceans. We further assume that the ocean was saturated with respect to calcite ($CaCO_3$) and that the dissolved Ca^{2+} concentration was 1.03×10^{-2} M (moles/liter), the same as for Earth. The relevant carbonate equilibria can be written as

$$[H_2CO_3] = HP \qquad (22)$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad (23)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad (24)$$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}]. \qquad (25)$$

Equations (22)–(25) represent, respectively, CO_2 solubility equilibrium (Henry's law), the first and second dissociations of carbonic acid, and dissolution of calcite. The relevant constants at the specified temperature and salinity are (Broecker and Peng 1982, pp. 63, 151): $H = 5.21 \times 10^{-2}$ M atm^{-1}, $K_1 = 7.17 \times 10^{-7}$ M, $K_2 = 4.04 \times 10^{-10}$ M, and $K_{sp} = 4.8 \times 10^{-7}$ M^2.

Given the CO_2 pressure in the atmosphere and the Ca^{2+} content of the ocean, the hydrogen ion concentration can be derived by combining all four equations to yield

$$[H^+]^2 = \frac{HK_1K_2P[Ca^{2+}]}{K_{sp}}. \qquad (26)$$

Once [H$^+$] is known, the total dissolved carbon concentration in the ocean (ΣCO_2 = [H$_2$CO$_3$] + [HCO$_3^-$] + [CO$_3^{2+}$]) may be obtained from Eqs. (22)–(24):

$$\Sigma CO_2 = HP\left(1 + \frac{K_1}{[H^+]}\left(1 + \frac{K_2}{[H^+]}\right)\right).$$
(27)

The CO$_2$ content of the atmosphere in moles cm^{-2} is given by

$$M_{\text{atm}} = 1.013 \times 10^6 P/44g,$$
(28)

where P is the pressure in atmospheres and g is the surface gravity (=373 cm sec^{-2} for Mars). The total CO$_2$ content of the oceans is given by

$$M_{\text{oc}} = 10^2 \Sigma CO_2 D,$$
(29)

where D is the ocean depth in km. As a reasonable upper limit on ocean depth we use the value of 0.5 km estimated by Carr (1987 this volume).

Using the above equations and parameter choices, we have calculated several parameters characterizing the hypothetical Martian oceans for different atmospheric CO$_2$ pressures. These results are summarized in Table I. The result of direct interest here is the ratio of atmospheric to dissolved CO$_2$, which is given in the last column. For an Earth-like CO$_2$ pressure of 3.4×10^{-4} atm, the model predicts an ocean pH of 8.0 (compared to 8.3 for Earth's oceans) and a ratio $M_{\text{atm}}/M_{\text{oc}} = 0.33$. This ratio is smaller than that for Earth by a factor of about 20.

The reasons are that Earth's oceans are 6 times deeper than the (generous) Martian paleoocean considered here and Earth's gravity is 3 times stronger. For climatically reasonable CO$_2$ pressures of 1 to 5 bars (see Section 2), the model predicts that Mars' atmospheric CO$_2$ reservoir is larger than the oceanic reservoir by a factor of 10 to 15. This estimate is, of course, subject to considerable uncertainty because one does not really know the Ca^{2+} concentration in Mars' early oceans. If [Ca^{2+}] was 10 times lower than assumed, the CO$_2$ carrying capacity of the oceans would increase by about a factor of 3. The bulk of the available CO$_2$ would, however, still remain in the atmosphere. If the amount of water on early Mars was smaller than Carr's estimate, the oceanic CO$_2$ reservoir would be correspondingly less important.

Thus, despite the uncertainties in the actual physical conditions on early Mars, we feel confident in asserting that most of the CO$_2$ that was not bound up in carbonate rocks was indeed present in the atmosphere.

6. DISCUSSION

In this section, we assess the potential likelihood and longevity of a wet, warm period in Mars' early history, consider the possible time evolution of Mars' climate, compare our treatment of the CO$_2$ cycle with that of earlier papers, and present observational tests of the concepts put forward in this paper.

TABLE I

PARTITIONING OF CO$_2$ BETWEEN THE ATMOSPHERE AND HYDROSPHERE FOR A 0.5-km-DEEP OCEAN

pCO$_2$ (atm)	[H$^+$] (M)	pH	ΣCO_2 (M)	M_{atm} (moles cm^{-2})	M_{oc} (moles cm^{-2})	$M_{\text{atm}}/M_{\text{oc}}$
3.4($-$4)	1.05($-$8)	7.98	1.27($-$3)	2.10($-$2)	6.35($-$2)	0.331
0.1	1.80($-$7)	6.74	2.60($-$2)	6.17	1.30	4.75
1	5.69($-$7)	6.24	0.118	61.7	5.90	10.5
2	8.05($-$7)	6.09	0.197	123.4	9.85	12.5
5	1.27($-$6)	5.90	0.408	308.6	20.4	15.1

6.1. Mars' Volatile Inventory

In this section, we first define our current knowledge about the amount of CO_2 that was available for forming and maintaining a dense CO_2 atmosphere in the early history of Mars and then compare these estimates with the requirements obtained in earlier sections of this paper for sustaining a wet, warm climate. Unfortunately, the total inventory of volatile elements on Mars is not well constrained. A straightforward, but possibly naive, estimate can be obtained by scaling the Earth's and Venus' inventories, which are much better determined. Approximately 60 and 90 bars of CO_2 have been outgassed over the lifetimes of Earth and Venus, respectively (Holland 1978, Pollack and Yung 1980). Much of the outgassing is likely to have occurred during these planets' very early history. If we assume that Mars had the same volatile content per unit mass of planet as did Earth and Venus and that it outgassed the same fraction in its early history as did its neighbors, then the amount of CO_2 present at Mars' surface would have been about an order of magnitude smaller than for its bigger neighbors. When we account for differences among the three planets in surface area and gravity, we infer that the pressure equivalent of outgassed CO_2 for early Mars would have been on the order of 10 bars. A similar value for the inventory is obtained if one assumes that impacts with volatile-rich comets and asteroids served as the primary source of CO_2 for the terrestrial planets (Pollack and Black 1982).

There have been a number of attempts to define the volatile inventory of outgassed CO_2 for Mars by scaling the observed amount of rare gases in its atmosphere by the amounts in the atmospheres of Venus and Earth. (For a summary, see Pollack and Yung 1980.) Typical results are in the range from 0.1 to several bars. Unfortunately, the assumptions or unknowns in all these estimates can be called into question.

For example, the amount of outgassed CO_2 for Venus and Earth are very similar, yet the abundance of several rare gases in their atmospheres differs by two orders of magnitude. Such differences may result from fractionation of rare gases during an early episode of hydrodynamic escape (Hunten *et al.* 1987). It is also possible to try to reconstruct early abundances by using the observed enhancement of the ^{15}N to ^{14}N ratio for Mars' present atmosphere (McElroy *et al.* 1977), but such reconstructions depend on identifying and quantifying all relevant atmospheric loss processes, including the formation of minerals through surface weathering processes.

Mars' outgassed CO_2 inventory can also be estimated in other, indirect ways. If one knew the amount of outgassed water and assumed a terrrestrial ratio for the relative proportions of outgassed CO_2 and H_2O, then one could readily obtain the desired value. Carr (1986) has estimated that the water equivalent of at least a 0.5–1-km-deep ocean has been outgassed on the basis of geomorphic arguments. If his estimate is accepted, then the corresponding amount of outgassed CO_2 is about 3–6 bars.

Comparisons of the abundances of elements detected by the Viking X-ray experiment and the weight of the analyzed samples showed that 6 to 8% of their constituents were not detected. This deficit can be accounted for in part, although not uniquely, by presuming that all the detected Ca (5% by weight) was in the form of carbonates (Toulmin *et al.* 1977). If one grants this and assumes that the Viking results are representative of the top 1 km of the soil, then the equivalent of 1.2 bars of CO_2 would be present in this reservoir (Toon *et al.* 1980). Presumably, even more carbonate would be present at greater depths.

In summary, the outgassed CO_2 volatile inventory for early Mars is not well defined, but values of about several to 10 bars seem to be consistent with present knowledge. Below, we compare these values with the

abundances needed to sustain a warm, wet climate on early Mars.

According to the results of Section 2, CO_2 partial pressures of 0.75 to 5 bars are needed in the early Martian atmosphere to raise the surface temperature to the melting point of water ice. The lower value corresponds to conditions at the equator and at perihelion for the maximum orbital eccentricity and a surface albedo of 0.1. The higher value corresponds to a globally and orbitally averaged situation with a surface albedo of 0.215. Consider first a partial pressure of 0.75 bar. As argued in Section 5, a much smaller amount of CO_2 was dissolved in the paleooceans and so consideration of this second reservoir does not significantly enhance the amount of CO_2 present in the combined reservoirs. For our nominal parameter choices, the weathering time scale equals 1.5×10^7 years, according to Section 3. If a juvenile mantle source of CO_2 is required to replenish the atmospheric CO_2 over the first 10^9 years, then a total inventory of 50 bars is implied. Such a requirement seems to be too demanding. A juvenile source could, however, have sustained the required atmosphere for perhaps one to two hundred million years. Essentially identical results are obtained when a 5-bar atmosphere is considered.

Next consider the requirements placed on the volatile inventory by the volcanic recycling mechanism. For the nominal parameter choices of Section 4, recycling times of about 2×10^7 and 2×10^8 years are obtained for internal heat fluxes of 300 and 100 mW/m^2, respectively. Comparing these values with the weathering time scale for a 0.75-bar CO_2 atmosphere, we infer total inventories of about 2 and 11 bars, for the higher and lower heat flux values, respectively. The corresponding inventories for a 5-bar atmosphere are about 7 and 23 bars. Thus, the requirements on the outgassed CO_2 volatile inventory placed by the volcanic recycling mechanism do not seem to be excessive and it is possible that a warm,

wet climate on early Mars could have been sustained by the volcanic recycling mechanism for an extended period of time. Furthermore, it should be remembered that our recycling time scales are overestimates in that they neglect the thermal decomposition of carbonates by hot lavas, and our weathering time scales are underestimates when the temperature is above the freezing point of water in only some places or only at some times of the year. Both these effects make it even easier to sustain a wet, warm climate.

6.2. CO_2 Geochemical Cycle: Other Studies

The possible occurrence of carbonate rocks and their relevance for buffering the atmospheric abundance of CO_2 on Mars was first pointed out in Harold Urey's classical book on planets (Urey 1952). In his discussion of this problem, Urey considered only the thermodynamic equilibrium situation, whereas we now suspect that exchange of gases between surface rocks and the atmosphere is dominated by kinetics at the low temperatures of interest (Walker 1977, Holland 1978). Walker (1978) presented a discussion of the geochemical cycle of volcanism, weathering, and burial that controls the abundance of volatiles at the surface of a planet and considered the application of this cycle to Venus, Earth, and Mars. He emphasized the role of tectonism in controlling the abundance of surface volatiles, such as carbon dioxide, and suggested that they were much more abundant at earlier times on Mars than today as a result of a hotter interior in the past.

Pollack and Yung (1980) discussed the modern geochemical cycle of terrestrial CO_2 and considered its possible application to Mars. They, as well as Toon et al. (1980), suggested that a dense CO_2 atmosphere may have existed in Mars' early history due to a much higher outgassing rate then, but that the dense atmosphere would have been gradually eroded away by the formation of

carbonate rocks. Pollack and Yung (1980) also pointed out that significant additional outgassing may have taken place at later times in association with major volcanic events. However, both Pollack and Yung (1980) and Toon et al. (1980) tended to consider carbonate rock formation as an irreversible process for Mars, although Toon et al. (1980) pointed out the possibility of extensive volcanic reprocessing of surface materials.

Fanale et al. (1982) were the first to estimate the time scale for the elimination of a CO_2 atmosphere of 1–2 bars by the weathering of surface rocks. Using a simple scaling argument based strictly on the mass of CO_2 in the atmosphere (equivalent to setting our various g factors equal to 1), Fanale et al. (1982) obtained a weathering time scale of about 10^7 years, in surprisingly good agreement with the results of this paper. They concluded that a dense CO_2 atmosphere would not have survived for an extended period of time. However, as shown here, there may have been effective means of resupplying the atmospheric CO_2 during Mars' early history.

Kahn (1985) proposed that the formation of carbonate rocks over much of the lifetime of the planet may have led to a progressive thinning of the atmosphere with time and that this process may have acted as the ultimate determiner of the current partial pressure of atmospheric CO_2. He invokes transitory pockets of liquid water to effect the continual chemical weathering of surface rocks, after the period when the atmospheric pressure of CO_2 was high enough to create an effective greenhouse warming of the surface. Rates of chemical weathering for later times on Mars warrant further scrutiny and quantification.

Kahn (1985) also discussed the CO_2 geochemical cycle on Mars and suggested that recycling of carbonate rocks might be possible. Unfortunately, he emphasized the weathering of carbonate rocks as a means of accomplishing the recycling. On Earth,

and presumably on early Mars, chemically weathered carbonates simply serve as sources of new carbonate rocks, with no net production of atmospheric CO_2 (Walker 1977, Holland 1978). He also pointed out the possible importance of episodic outgassing events at later times on Mars for temporally increasing the partial pressure of CO_2.

The calculations reported in this paper represent a further step in defining the CO_2 geochemical cycle on Mars by providing quantitative estimates of the time scales associated with major sources and sinks of atmospheric CO_2. Thus, it is possible to assess the longevity of a dense CO_2 atmosphere in the early history of Mars.

6.3. Climate Evolution

Let us assume that enough CO_2 was outgassed into the early atmosphere to raise the surface temperature above the melting point of water ice over large portions of the planet and that this amount of outgassed CO_2 was large enough to sustain the greenhouse warming by a volcanic recycling of carbonate rocks, despite whatever losses of atmospheric gases occurred during early times. Accepting these assumptions for the time being, we wish to discuss the possible long-term evolution of the planet's climate.

As suggested by Walker (1978), the key drive for the evolution of the climate from the hypothesized early wet, warm climate to the dry, cold conditions of today would have been the thermal evolution of the planet's interior. A combination of the decay of long-lived radioactive isotopes, an initial hot interior due to accretion, and possibly early core formation could have sustained a value for the surface heat flux, F_t, above 100 mW/m^2 for a time scale on the order of 10^9 years after the formation of Mars (Davies and Arvidson 1981). During this epoch the recycling time scale may not have been much longer than the weathering time scale and hence a warm, wet climate

may have been maintained, as discussed above.

Ultimately, the decline of F_t with time would have caused the recycling process to become progressively less effective, because of an increasing recycling time scale (which varies inversely as F_t^2 in our model) and because of the increasing local character of the volcanism. The latter consideration implies that carbonate rocks formed at some locales would not be recycled effectively. Thus, at very early times, temperatures in excess of 273°K may have occurred over much or all of the planet during most or all seasons of the year. At somewhat later times, this benign climate may have prevailed over more restricted spatial and temporal locations, as a greater fraction of the volatile inventory was tied up in carbonate rocks. These locations would have included lower-latitude regions, at first during all seasons and later only near perihelion when the orbital eccentricity was large. It might have also included polar regions during summer solstice, especially at times of high orbital obliquity (Toon et al. 1980). Still later, these favored locations would have disappeared almost entirely, as even more atmospheric CO_2 was removed to the rock reservoir. At this point there would have been a balance between a very sluggish rate of carbonate decomposition and an equally sluggish rate of formation of new carbonate rocks, because of the very restricted conditions under which temperatures above the melting point of water ice were achieved. Essentially no carbonate rocks should have been formed when the temperature fell below 273°K. Finally, other atmospheric CO_2 removal mechanisms would have caused enough of a decline of the atmospheric reservoir to entirely eliminate the circumstances under which temperatures above the melting point of water ice could be achieved. These include the incorporation of adsorbed CO_2 into a growing regolith (Fanale et al. 1982), continued formation of carbonates in transitory liquid

water environments (Kahn 1985), and the loss of carbon and oxygen atoms to space.

Although the climate of Mars probably became progressively drier and colder with time, there may have been some short-lived episodes of a warmer climate. These transient warming epochs could have occurred in association with times of intense tectonism, volcanism, and outgassing. Large amounts of CO_2 may have been temporally introduced into the atmosphere from both mantle sources and the thermal decomposition of carbonate rocks that were present in the active regions of the planet. Quite modest amounts of atmospheric CO_2—several tens to several hundreds of millibars—could have sufficed to raise the temperature in local regions, especially the polar regions, above the freezing point of water ice (Pollack 1979, Toon et al. 1980). The requirement on the amount of atmospheric CO_2 at these later times is eased by the higher solar luminosity then as compared to its value at the early times of primary interest for this paper. Carbonate rock formation as well as other removal processes would have depleted the atmospheric CO_2, ultimately eliminating the benign climate conditions. At these later times, recycling of CO_2 was improbable because the geophysically active regions encompassed only limited areas, in contrast to their more global extent during the planet's early history.

If the above scenario is correct, it has important implications for the possible occurrence of life on Mars. It is almost universally accepted that the exobiology experiments on Viking provided strong, perhaps conclusive evidence against the habitation of living organisms on Mars at the present epoch. We suggest that much more favorable climate conditions for life may have existed for an extended period of time during the planet's early history. If so, it seems premature to abandon the exobiological investigation of Mars and particularly premature to assume that life never existed on this planet.

6.4. Observational Tests

Geomorphic studies and mineralogical determinations offer two potential means for assessing whether or not early Mars ever had a wet, warm climate, as proposed in this paper. Schultz's (1985) analyses of large impact basins have provided support for the occurrence of a much denser atmosphere on early Mars (see Section 1). Further work on the erosional history of the Martian surface would be most useful for testing our proposal, as would searches for ancient lake and ocean deposits and boundaries.

A number of minerals would be produced by chemical weathering processes on a wet, warm Mars. These include clays, evaporites (e.g., gypsum), and, of course, carbonates. Kahn (1985) has previously suggested that the search for the presence of carbonate rocks would provide a means of testing his scenario for the evolution of atmospheric CO_2 on Mars. Strong support for our hypothesis could be provided by the unambiguous detection of the above minerals and by the demonstration that they could not be produced by alterative mechanisms. Firm mineralogical identifications and the association of the minerals with specific landforms, such as the old cratered terrain, may provide a basis for making this judgment. The association of carbonates with terrain of intermediate or young age would indicate that carbonates continued to be formed at later times on Mars, in accord with Kahn's suggestions and the discussion of the previous subsection. We note that there is already limited evidence for the occurrence of all three classes of minerals (e.g., Toulmin *et al.* 1977).

In addition to calcite ($CaCO_3$) and dolomite ($MgCa(CO_3)_2$), the chief carbonate minerals present in the Earth's geological record, we would also expect that abundant quantities of siderite ($FeCO_3$) and perhaps magnesite ($MgCO_3$) would be produced when Mars had a wet, warm climate.

Siderite is not present in large amounts in the Earth's geological record, chiefly because the Fe^{2+} that is leached from silicate rocks by chemical weathering is quickly converted to insoluble ferric iron by atmospheric oxygen.

Near- and mid-infrared reflection spectroscopy offers a promising means for detecting carbonate minerals on the surface of Mars. Carbonates have a relatively weak absorption band near 2.3-μm wavelength and a much stronger signature near 4 and 7 μm (T. Roush, private communication). Searches for these features could be conducted during the 1988 opposition with Mars from the ground at coarse spatial resolution and at much better spatial resolution by the VIMS and TES instruments that will be part of the payload of the forthcoming Mars Observer spacecraft mission.

7. CONCLUSIONS

In this paper, we have attempted to define the conditions under which a wet, warm climate could have existed for an extended period of time during the early history of Mars. Using improved opacity coefficients in a one-dimensional radiative-convective model, we find that CO_2 partial pressures ranging from 0.75 to 5 bars would have been needed to raise the surface temperature to the melting point of water ice. This range of pressures reflects different choices of surface albedo, latitude, and orbital position. In all cases, a 30% lower solar luminosity, appropriate for early Mars, is used. Low values of the required pressure correspond to equatorial latitudes, perihelion for large values of orbital eccentricity, and low surface albedo. The chief uncertainty in these calculations is caused by the neglect of the radiative effects of water condensation clouds.

Atmospheric carbon dioxide would have been removed relatively quickly by the formation of carbonate rocks. Allowing for the dependence of the weathering rate on temperature, pressure, rock cation

abundance, and the fraction of surface area occupied by standing bodies of water, we estimate that the weathering time scale for the elimination of a dense (several-bar) CO_2 atmosphere is several times 10^7 years for a surface temperature of 273°K. This time scale could have varied by about an order of magnitude for plausible changes in pressure, temperature, and areal coverage by water. Thus, in the absence of CO_2 sources, it would have been very difficult to sustain a wet, warm climate for a period on the order of 10^9 years.

Outgassing of juvenile CO_2 from the interior and thermal decomposition of carbonate minerals represent two possible sources of atmospheric CO_2 on early Mars. The recycling mechanism is more promising because it imposes less of a demand on Mars' outgassed CO_2 volatile inventory. Global-scale volcanism could have acted as the driver for such recycling by directly decomposing carbonates through contact with hot lava or by burying carbonate sediments to a depth where they could have been thermally decomposed. The time scale for this latter process can be estimated by relating the rate of volcanism to the surface heat flux from the interior. This time scale is insensitive to the partitioning of the surface heat flux between conductive and volcanic transport, but varies inversely as the square of the total heat flux. For values of the heat flux lying between 100 and 300 mW/m^2, values typical of early Mars, the recycling time scale lies between about 1×10^7 and 3×10^8 years. Under such circumstances, recycling could have maintained a dense CO_2 atmosphere if the available volatile inventory was between 2 and 20 bars.

Continued studies of the geomorphology of the old cratered terrain and spectroscopic searches for carbonate minerals offer means of testing the hypotheses of this paper. If Mars did have a wet, warm climate during the first billion or so years, the possibility that life arose during this time needs to be seriously considered.

Note added in proof. J. Gooding has apparently detected trace amounts of calcium carbonate in SNC meteorites, which are believed to have originated on Mars. (This result was reported at the 1987 Lunar and Planetary Science Conference.)

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