

Making Mars habitable

Christopher P. McKay, Owen B. Toon & James F. Kasting

Mars is believed to be lifeless, but it may be possible to transform it into a planet suitable for habitation by plants, and conceivably humans. The success of such an enterprise would depend on the abundance, distribution and form of materials on the planet that could provide carbon dioxide, water and nitrogen.

It is becoming increasingly clear that humans can alter the environment on a planetary scale. Our introduction of greenhouse gases into Earth's atmosphere at rates sufficient to modify the climate has led to suggestions that we should take active global measures to counteract the predicted warming^{1,2}—in effect, 'terraforming' the Earth. Renewed interest in human exploration and settlement of Mars by using indigenous martian resources and ecological life-support systems^{3,4} has led to the question of the impact of human activities on Mars and the possibility that Mars could be intentionally altered to make it more habitable.

Although there seems to be no life on Mars today, there is considerable evidence that early in the planet's history, liquid water habitats existed, and conditions may have been suitable for the origin of indigenous life, now long since extinct⁵. If Mars did have an early clement, possibly life-supporting, environment, then it is important to our understanding of planetary evolution to develop models for the fate of the early atmosphere^{6,7} and to consider under what conditions, artificial or natural, this environment could return.

Here we consider the possibility that the atmosphere and climate of Mars could be altered to allow terrestrial life forms, and possibly human beings, to survive on the surface (we assume that Mars is lifeless). Several papers have been published on the technical aspects of planetary-scale alteration of Mars⁸⁻¹⁴. The philosophical and ethical aspects of the problem have also been considered^{15,16}. Our analysis differs from previous discussions of terraforming Mars in two ways. First, although our analysis is based on simplified models, we have attempted a comprehensive treatment, thus exposing substantial problems that were not obvious from studies that considered limited portions of the problem. We hope our analysis will form an initial step towards organizing studies of terraforming Mars so that a quantitative understanding can be developed. Second, we have limited our consideration to technologies that are not far beyond the current art.

We do not, therefore, consider the fundamental physical parameters of a planet to be susceptible to alteration¹². Thus the orbit, rotation rate, mass and volatile inventory are not, at present, plausible targets for anthropogenic change. It may seem surprising that we cannot import atmospheric volatiles, but this can easily be demonstrated by considering the mass of gas required to produce an atmospheric pressure of just 1 bar on Mars, $\sim 4 \times 10^{15}$ tons. The Space Shuttle can lift a mere 40 tons into low Earth orbit, and even heavy lift launchers under consideration have a proposed capacity of only 140 tons. The possibility of obtaining volatiles by moving large asteroids and comets into collision courses with Mars may not be completely unrealistic, but we do not consider this approach here. It would require more than one million comets of 1 km radius to provide the mass equivalent of a 1-bar atmosphere on Mars. We cannot realistically expect to alter the physical properties of Mars by planetary engineering, but we could change the environmental parameters of the planet¹²: the distribution of volatiles, the surface temperature and pressure, atmospheric composition and opacity, planetary albedo, precipitation and humidity.

Habitability

Mars has a rotation rate similar to that of the Earth, and we assume that its surface gravity (0.38g) would be adequate for long-term biological adaptation. As Mars is 1.52 times as far from the sun as the Earth, the amount of sunlight incident on the planet is only 43% of the terrestrial value. This amount of sunlight is much more than is needed for photosynthesis, so we assume that light will not in itself be a limiting factor.

A key parameter of a habitable planet is its average surface temperature. For Earth, this is 15 °C at present; for Mars it is -60 °C. A habitable planet must have liquid water on the surface, so we assume that the average surface temperature must be 0-30 °C. The lower limit is set by the freezing point of water; the upper limit is arbitrarily chosen but is not relevant to terraforming Mars. Accurate determination of the limits on the mean temperature at which the equatorial regions would be too cold or, alternatively, the polar regions too warm would require a detailed three-dimensional model. The range of temperatures specified here is identical to that used by Dole¹⁷ in an early discussion of habitability.

Plants. We consider first a world suitable for plants and anaerobic microorganisms. The carbon dioxide pressure on Earth today (~ 0.35 mbar) is low enough that certain plants (particularly C-3 plants) are often limited in their ability to obtain CO₂ for photosynthesis. C-3 plants lose the ability for net production at concentrations of 35-45 p.p.m. (ref. 18), whereas C-4 plants continue net photosynthesis down to vanishingly small concentrations. In general, net photosynthesis is depressed as the concentration decreases to less than ~ 0.25 mbar (refs 19, 20). We therefore take 0.15 mbar as the lower limit for CO₂. The same value was used by Lovelock and Whitfield²¹. There is no clear upper limit on CO₂ for plants²²; although concentrations over 1 mbar can have adverse effects on certain species²³, Seckback *et al.*²⁴ reported on photosynthetic algae that thrive under pure CO₂.

Oxygen is not required for anaerobic microorganisms, but some is required by plants for aerobic mitochondrial respiration. Plants actually prefer oxygen levels well below the current value. The requirements vary depending on the plant but, in general, net primary production increases as O₂ is reduced from the ambient level of 210 mbar until a point is reached where the concentration is low enough (~ 20 mbar) to cause metabolic complications²⁰. It may be possible to adapt plants to accept even lower concentrations (~ 1 mbar), because the mitochondrial enzyme that requires oxygen has such a strong affinity for it that it can function with oxygen partial pressures of 0.1 mbar (refs 20, 25). Nitrogen is required for all organisms, and the amount of atmospheric nitrogen must be high enough to allow biological nitrogen fixation. Recent work indicates that bacteria can fix nitrogen at pressures of 10 mbar and less²⁶.

Plants and anaerobic microbes can tolerate total pressures much lower than 1 bar. In addition to a few millibars of N₂ and O₂ and 0.15 mbar of CO₂, the atmosphere need only support the vapour pressure of water at ambient temperatures (6.1 mbar at 0 °C). Thus, pressures as low as 10 mbar may be permissible for a planet suitable for plants and anaerobic microorganisms.

Humans. The minimal tolerable partial pressure of oxygen for humans is ~130 mbar over a wide range of oxygen mixing ratios and total pressures²⁷. At oxygen partial pressures above those normal at sea level (210 mbar), effects of oxygen toxicity appear²⁷⁻²⁹. At partial pressures only slightly above normal there are demonstrable symptoms after exposure for 200 hours. Oxygen partial pressures of 500 mbar generate symptoms within 24 hours. Dole¹⁷ also suggested an upper limit of 500 mbar. These data suggest that the upper limit to the oxygen partial pressure is close to the present sea-level value. Long-term exposure to pure oxygen at 345 mbar, as was used during the Apollo missions, seems to be tolerated. But there is a problem with flammability of natural materials at high partial pressures of O₂ (ref. 30), suggesting that we should set the limit at ~50% above the present partial pressure. We therefore take 300 mbar as the upper limit for oxygen. For humans, and presumably other animals, CO₂ becomes toxic to the blood buffer system at ~10 mbar (refs 27, 31), which is roughly the partial pressure of CO₂ on Mars today.

An atmosphere suitable for humans to breathe on a long-term basis will probably require a buffer gas to prevent oxygen toxicity and spontaneous combustion. On Earth, of course, the buffer gas is nitrogen, N₂. The Solar System abundances of the elements suitable for use as buffer gases, normalized to silicon, are: He, 3 × 10⁹; Ne, 4 × 10⁶; N, 2 × 10⁶; Ar, 1 × 10⁵; Kr, 45; Xe, 4 (ref. 32). On Mars the atmospheric concentrations of the noble/gases (He, Ne, Ar, Kr and Xe) presumably represent the entire available inventory and are negligible³³. Other light elemental gases (H₂, F₂ and Cl₂) that could be manufactured on Mars are either explosive or toxic. Carbon dioxide is not suitable, as it is toxic above 10 mbar. We have been unable to identify any more complex gas (such as CH₄, H₂O, CO, HCN, halogen compounds or SF₆) that would be a suitable buffer gas and that could exist in quantities large enough to provide a partial pressure of several hundred millibars. We therefore think that N₂ is the only candidate. Atmospheric N₂ on Mars is also much too scarce to provide a breathable atmosphere; however, nitrogen may exist in solid reservoirs such as nitrate.

At the temperature of the human body, 37 °C, the vapour pressure of water is ~60 mbar, which corresponds to the partial pressure of water vapour in the lungs²⁷. Combined with the normal lung partial pressure of CO₂ (50 mbar) and O₂ (130 mbar), this pressure puts a firm lower limit on the total ambient pressure of a pure O₂ atmosphere of ~250 mbar (ref. 27). At pressures below this, humans, and presumably other animals with warm body temperatures, would need pressure

suits to survive. For air-like mixtures, an estimate of the lower limit on pressure can be obtained by considering humans fully adapted to life at high elevations. Billings²⁷ states that long-term habitation at 15,000–20,000 ft (500 mbar) is possible, and below 10,000 ft (700 mbar) there is no significant physiological effect. A minimum atmospheric column mass may, however, be required to provide adequate shielding against cosmic and solar radiation. Because of the lower gravity on Mars, an atmosphere with only 390 mbar total pressure would have the same column mass as the terrestrial atmosphere. In Table 1, we suggest 500 mbar as the lower limit for pressure with an air-like gas. Of this, ~300 mbar must be buffer gas, as the upper limit on oxygen is near 200 mbar. The upper limit of total pressure for an atmosphere breathable by humans is determined by the narcotic and toxic effects of inert gases at pressures exceeding ~5 bar²⁷.

As summarized in Table 1, we have considered two fundamentally different biospheres on Mars. The first is a world suitable only for plants and anaerobic microorganisms, with an atmosphere composed of almost pure CO₂ along with the small amounts of N₂ and O₂ required for plant metabolism. The second is an atmosphere that would be breathable by humans and other terrestrial animals.

Do suitable climate states exist for Mars?

Having specified the environmental requirements that must be met simultaneously for a planet to be habitable, we now consider whether suitable climate states exist on Mars that meet these requirements.

Plant life. We first consider a CO₂-dominated atmosphere suitable for supporting plant life. The amount of CO₂ needed is determined by the temperature requirements, not by plant physiology. The temperature that would result from a CO₂-dominated atmosphere can be estimated from the climate-modelling calculations of Pollack *et al.*⁶. Their results indicate that the pressure of CO₂ needs to be slightly above 2 bar for the mean surface temperature to be above freezing. Other studies have found similar values³³⁻³⁷. Of course, on Mars today the temperature can rise above freezing during the day in the equatorial regions³⁸. It is the need to keep the daily averaged temperature high that requires such large amounts of CO₂.

In the current martian atmosphere, the mixing ratio of O₂ is 0.13% (ref. 33) and is set by photochemistry³⁹. A thick CO₂ atmosphere (2 bar) on Mars might be similar to some model atmospheres proposed for the early Earth^{40,41}. There, vanishingly low O₂ concentrations are predicted because of the reaction of O₂ with reduced volcanic gases or with reduced minerals at the surface. The interior of Mars is relatively quiescent, however, so the volcanic outgassing rate is probably low. Furthermore, the surface is highly oxidizing and might act as a source for O₂ rather than a sink⁴². Ambient O₂ concentrations could therefore be relatively high, even in the absence of biological production. If the surface pressure were 2 bar and the O₂ mixing ratio were the same as at present, the partial pressure of O₂ would be 2.5 mbar, possibly enough for plant respiration, as discussed above. Much higher O₂ partial pressures could be produced by introducing photosynthetic plants.

Perhaps more critical than the supply of O₂ is the supply of N₂. To provide enough N₂ for nitrogen fixation and for biomass production, the present atmospheric concentration (0.3 mbar) must be raised to several millibars. The possible, but unconfirmed, source is soil nitrogen. Assuming a few millibars of nitrogen stored as nitrites and nitrates that might be released by soil microorganisms, we conclude that a CO₂ atmosphere on Mars with a pressure of 1–3 bar could provide a habitable environment for plants only.

Human environment. To investigate the question of human habitability, we considered a case in which an Earth-like atmosphere was present on Mars: 200 mbar O₂ and 790 mbar N₂, with CO₂ set to the upper limit for breathable air (10 mbar) and with water vapour present. Such an atmosphere on Earth would result

TABLE 1 Limits for habitability

| Parameter | Limits | Note |
|---------------------|------------|--|
| Global temperature | 0–30 °C | Earth temperature 15 °C |
| Plants only: | | |
| Total pressure | >10 mbar | Water vapour pressure plus O ₂ , N ₂ and CO ₂ |
| CO ₂ | >0.15 mbar | Lower limit set by photosynthesis No clear upper limit |
| N ₂ | >1–10 mbar | Nitrogen fixation |
| O ₂ | >1 mbar | Plant respiration |
| Human breathable: | | |
| Total pressure | | |
| Pure O ₂ | >250 mbar | Lung water vapour, CO ₂ and O ₂ |
| Air mixture | >500 mbar | Based on high elevation |
| | <5000 mbar | Buffer gas narcosis |
| CO ₂ | <10 mbar | Set by toxicity |
| N ₂ | >300 mbar | Buffer gas |
| O ₂ | >130 mbar | Lower limit set by hypoxia |
| | <300 mbar | Upper limit set by flammability |

in temperatures considerably warmer than at present, as it includes 30 times the present terrestrial CO₂ partial pressure.

Figure 1 shows the thermal infrared energy that would be lost to space from Mars if the surface temperature were arbitrarily set to 15 °C with the nitrogen–oxygen atmosphere described above. To perform these calculations we used the one-dimensional radiative convective model described by Kasting and Ackerman⁴³. The energy emitted from the top of the martian atmosphere is compared in Fig. 1 with the black-body emission at temperatures of 288 K and 212 K. As Mars's effective temperature (set by its distance to the sun) is 212 K, the energy emitted to space must be equal to the total energy of the lower black-body curve to balance the planet's energy budget. As the energy emitted by the surface follows the upper black-body curve, the greenhouse effect of the atmosphere would have to lower the outgoing emission accordingly. The reduction in outgoing radiation provided by this Earth-like atmosphere is insufficient (Fig. 1). To balance the radiation budget the opacity of the atmosphere must be greatly increased, particularly in the window region between 800 and 1,200 cm⁻¹.

If we allow the model to adjust the surface temperature until the atmosphere is in equilibrium, we find that the resulting surface temperature is surprisingly cold, -55 °C (see Fig. 2). This can be understood by considering the greenhouse effect on Mars today which amounts to an increase of ~6 K. Adding N₂ and O₂, which have no infrared absorption, broadens the CO₂ lines and increases the greenhouse effect, but only slightly. By contrast, the greenhouse effect on Earth is ~33 K, despite the lower CO₂ concentration. The larger greenhouse effect on Earth is due to the higher concentration of water vapour in the atmosphere. If Mars could be made warmer, the concentration of water vapour would increase, and the greenhouse effect would be more effective. We conclude that an Earth-like atmosphere on Mars would be far too cold to be habitable.

As one possible way to provide an increased greenhouse effect on Mars, Lovelock and Allaby¹³ suggested the introduction of trace amounts of chlorofluorocarbons (CFCs) into the martian atmosphere. These compounds absorb radiation in the window region where CO₂ and H₂O have little absorption.

Gases of particular interest as greenhouse gases are CF₃Br, C₂F₆, CF₃Cl and CF₂Cl₂. We choose these gases because they are composed of elements that could be found on Mars and have relatively long lifetimes against destruction by solar ultraviolet radiation. Mixing ratios of ~1 part in 10⁹ (1 p.p.b.) of these gases can cause a surface temperature increase of ~0.1 K (ref. 44). This combination of gases does a good job of filling in the window region between 800 and 1,200 cm⁻¹. The first of these, CF₃Br, is used as a refrigerant and as a fire inhibitor. In the Earth's atmosphere CF₃Br has a half-life of over 100 years and is only destroyed in the stratosphere. C₂F₆, CF₃Cl and CF₂Cl₂ are even more stable with lifetimes of >500, 400 and 110 years, respectively⁴⁴. Another possible greenhouse gas considered by Ramanathan *et al.*⁴⁵ is SF₆. This has a long lifetime (>500 years), and is a 'strong' absorber, but we do not have enough detailed information to assess its potential as an artificial greenhouse gas on Mars. None of these gases are toxic at concentrations of parts per million⁴⁵.

The required warming on Mars is ~60 °C, or a factor of 700 larger than the changes considered by Ramanathan *et al.*⁴⁴. It is therefore likely that these CFCs would be needed in concentrations of parts per million or more (1,000 times the concentration considered by Ramanathan *et al.*) to provide the additional greenhouse warming needed to warm the nitrogen–oxygen atmosphere on Mars to a habitable temperature. The radiative transfer methods and band models used by Ramanathan *et al.* cannot be applied with confidence to these greatly increased concentrations. For the purposes of illustration we assume that 10 p.p.m. (0.01 mbar) of these gases would need to be introduced into the martian atmosphere. The total weight of this material would be ~4 × 10¹⁰ metric tons, too much to carry from Earth

as was suggested by Lovelock and Allaby¹³. But if we imagine a continuous production of gases on the surface of Mars at a rate that would offset loss by ultraviolet photolysis, the required production rate of material would be ~10⁸ tons yr⁻¹, if the lifetime of this mix of four CFC gases on Mars is taken to be ~400 years. An upper limit on the required production rate of CFCs can be obtained by noting that such gases would probably destroy any ozone layer on Mars and would therefore be photolysed themselves by photons of wavelength 200–300 nm. If we assume that each of these photons destroys a single CFC molecule, of mean relative molecular mass 200, then ~3 × 10¹² tons of CFCs must be produced each year to offset the loss. Current production of CF₃Cl (CFC-11) and CF₂Cl₂ (CFC-12) on Earth total ~10⁶ tons yr⁻¹ (ref. 46). As discussed later, the concentrations of Cl, F and Br on Mars are probably adequate to provide these quantities of gases.

To assess more quantitatively the effect of adding greenhouse gases to a nitrogen–oxygen atmosphere on Mars, we have modified the radiative–convective model of Kasting and Ackerman⁴³ to include an arbitrarily specified absorber. Lacking adequate information on the optical properties of these CFCs at high column densities, we have considered two cases with a uniformly mixed absorber in our calculations. In one case, the absorption occurs in the window region (800–1,200 cm⁻¹) of the thermal infrared spectrum only. In the other, the absorption covers the entire thermal infrared spectrum with the same opacity at all wavelengths (grey absorption). The surface temperature is plotted in Fig. 2 as a function of the grey opacity added to the model. As can be seen, the first case (absorption in the window region only) does not produce enough warming to raise the planetary average temperature above freezing even when the opacity is high; radiation loss becomes dominated by other spectral regions. In the second case, the temperature rises steeply with absorber amount once the opacity becomes close to unity. Temperatures above freezing are reached when the absorber concentration corresponds to an optical depth in the thermal infrared of ~10. Also shown in Fig. 2 is the effect of adding the absorber active in the window region to the present martian atmosphere rather than the 1-bar nitrogen–oxygen atmosphere.

It therefore seems possible, in principle, to produce a warm oxygen-rich martian atmosphere, given an adequate supply of N₂, O₂ and the appropriate trace greenhouse gases. One of the chief problems is the possibility that the trace gases would prevent the formation of an ozone layer. Then, as discussed

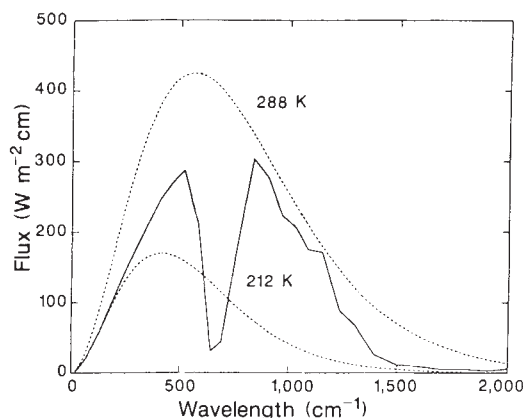


FIG. 1 Thermal balance of a 1-bar nitrogen–oxygen atmosphere on Mars with 10 mbar of CO₂ in equilibrium with water, and a surface temperature set to 15 °C. Shown as the solid line is the thermal infrared radiation emitted from the top of the atmosphere for $T_s = 288$ K. Also shown are the black-body curves at 15 °C and -60 °C (dotted lines). To be in equilibrium, the area under the curve of outgoing infrared flux must equal the area under the curve for the -60 °C black body. The surface is too warm (by ~70 °C) to be in equilibrium.

above, production of these trace gases would have to be at a high enough rate to compensate for their loss by ultraviolet destruction, although they would effectively shield the surface. The possibility of producing a plant-habitable martian atmosphere is higher because of the CO₂ greenhouse effect. We describe next how such a CO₂ greenhouse might be accomplished.

The runaway CO₂ greenhouse effect

Early discussions of warming Mars focused on the possible 'runaway' greenhouse effect of a CO₂ atmosphere in contact with a presumed polar reservoir of CO₂ ice. An initial warming is amplified by sublimation of CO₂, adding to the warming and subliming more CO₂ (refs 8, 47, 48). Carbon dioxide adsorbed into the regolith is another reservoir on Mars that may be susceptible to a runaway effect.

Polar caps. Gierasch and Toon⁴⁷ found that advection of heat from mid-latitudes on Mars becomes an important source for warming the poles when the surface pressure is increased to ~100 mbar. This resulted in a runaway condition, subliming the polar ice caps, if atmospheric pressure were raised above a critical value. These calculations neglected the greenhouse effect entirely. The positive feedback between CO₂ pressure and temperature is much stronger when the greenhouse effect is included. We have extended their model by treating the latitudinal temperature difference as a simple exponential in pressure and by allowing the mean surface temperature to vary with atmospheric CO₂ (ref. 6). We can then express the polar temperature as

$$T_{\text{pole}} = T_{\text{mean}}(\text{CO}_2) - \Delta T e^{-P/P_0} \quad (1)$$

where $T_{\text{mean}}(\text{CO}_2)$ is the mean planetary temperature (Fig. 4a), ΔT is the difference between the mean planetary temperature and polar cap temperature with no advective transport of heat, and $P_0 = 200$ mbar, determined from a fit to the middle curve in Fig. 1 of ref. 47. This expression gives results that are significantly different from the earlier analysis⁴⁸ (Fig. 3). A low-pressure stable state exists, but as the surface pressure increases a transition point is reached (an unstable equilibrium) above which there is no stable state and the polar cap sublims completely. The final temperature and pressure are set by the available CO₂.

This analysis presumes that there is a large permanent reservoir of CO₂ at the martian poles. But the existence of a permanent

CO₂ cap can be ruled out for the north pole⁴⁹, although there is evidence for a year-round CO₂ reservoir at the south pole⁴⁹. The size of this reservoir is not known, but the residual cap is small, only ~350 km in diameter, and basal melting should limit the thickness of CO₂ it could contain. A 1-km-thick cap of this diameter could provide ~100 mbar of CO₂, and hence a more detailed assessment of the existence and stability of a permanent CO₂ cap at the south pole on Mars would be of interest.

Regolith. Another possible positive feedback results from CO₂ adsorbed into the martian regolith, estimated to be as much as 300 mbar of CO₂ (refs 50-52). To model the desorption of the regolith CO₂ on heating we use the following expression⁵³

$$M_a = C \exp(-T/T_d) P^\gamma \quad (2)$$

where T and P are the surface temperature and pressure, M_a is the total column amount of CO₂ adsorbed and C is a normalization constant that depends on the specific surface area of the adsorbent and the depth of the regolith. C determines the total mass of adsorbed gas. T_d and γ are constants that determine the response of adsorption to temperature and pressure, respectively. Physically, T_d is the temperature change required to outgas a fraction 1/e of the regolith CO₂; small values of T_d indicate that the CO₂ is only weakly bound. As we are interested in the effects of warming the regolith, γ is of secondary interest and we use the value of 0.275 from Toon *et al.*⁵³, which is between the two recommended values from Zent *et al.*⁵⁴. In our calculations, we have let T_d vary from 10 K to 60 K. Estimates from materials analogous to Mars soil suggest $T_d \approx 60$ K (refs 50, 53), but Toon⁵³ noted that this overestimates the mass of adsorbed gas at higher temperatures. Data for adsorption at higher temperatures and pressures are not available for Mars analogue materials, but for activated carbon at a partial pressure of 0.5 bar, $T_d \approx 35$ K (ref. 55). Although the amount of CO₂ indicated for the regolith corresponds to only 300 mbar, we have set it to 1 bar to illustrate a maximal temperature-driven desorption response.

In Fig. 4, we have plotted the partial pressure of CO₂ that would result from heating the regolith for two limiting cases. In the first case, the regolith containing the CO₂ is spread over the entire planet and we treat it as being at the average planetary temperature. In the second case, we assume that only the polar regolith holds any appreciable CO₂. The latter case may be more reasonable, as cold regions will preferentially collect the CO₂. In this case the temperature that governs the release of regolith CO₂ is T_{pole} from equation (1). In all cases the coefficient C is determined by the total amount of CO₂ assumed to be in the atmosphere-regolith systems. The implied depth and specific surface area of the regolith corresponding to the coefficient C depend on the current surface temperature (either the mean surface temperature of 217 K or the polar temperature of 150 K) and on the current CO₂ pressure (6 mbar). For our calculations the total amount of CO₂ is the important quantity because as $T \rightarrow \infty$, all the CO₂ goes into the atmosphere. Figure 4a shows the results for the case of the global regolith, Fig. 4b for the polar regolith. Similar curves are obtained when the total amount of CO₂ is varied except that the pressure asymptote shifts. The results are relatively insensitive to the pressure exponent (γ) over the range 0.2-0.35.

Stable states exist where the desorption curves cross the atmospheric (or polar) temperature curve, and where the slope of the atmospheric curve is less steep than the slope of the desorption curve. For all values of T_d , the current condition is stable in both cases; all curves cross at this point by construction. For the global regolith, the only curve that is of interest is the top one ($T_d = 10$ K). In this case, the desorption curve crosses the atmosphere curve thrice and two stable states exist: one has most of the CO₂ adsorbed into the regolith and the other has most of it in the atmosphere. Unfortunately, a value of $T_d = 10$ K is not easily justifiable. For the polar case the results are more promising: multiple stable states exist for $T_d < 40$ K.

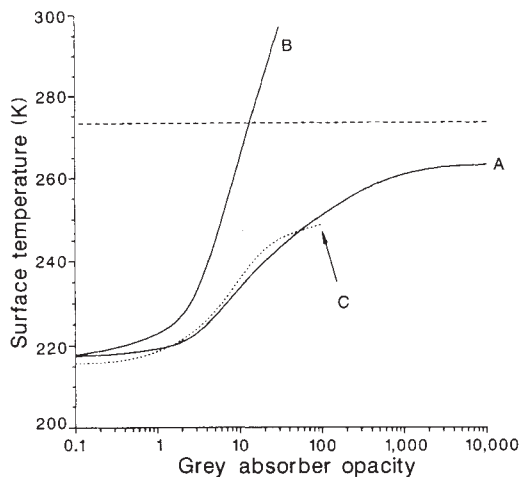


FIG. 2 The effect of adding an absorber on the surface temperature of Mars. For the 1-bar nitrogen-oxygen atmosphere (see Fig. 1), two types of absorbers were considered: curve A is for an absorber that is active in the 'window' region of the thermal infrared spectrum (800-1,200 cm⁻¹) only, curve B for an absorber that is active over the entire spectrum. Curve C shows the effect of adding an absorber active only in the window region to the present 6-mbar CO₂ atmosphere. The dashed line indicates the freezing point of water.

TABLE 2 Total volatile inventory for Mars

| | CO ₂ (mbar) | N ₂ (mbar) | H ₂ O (m) | Note |
|--------------------------------------|---------------------------|--------------------------|-------------------------|---|
| Required for terraforming | ≥2,000 | ≥300 | ≥500 | |
| Present Mars atmosphere | ~10 | 0.2 | ~7 × 10 ⁻⁶ | Atmosphere only |
| Earth scaling† | 27,000 | 300 | 1,200 | Equal volatiles (g per g) |
| Rasool and Le Sargeant ⁵⁸ | 198 | 3.1 | 5.9 | ³⁶ Ar, ordinary chondrites |
| Anders and Owen ⁵⁷ | 140–525 | 2–8 | 9.4 | K, ⁴⁰ Ar, ³⁶ Ar/ ⁴⁰ Ar |
| McElroy <i>et al.</i> ⁶⁰ | 1,760 | 21.5 | 133 | ¹⁴ N/ ¹⁵ N |
| Clark and Baird ⁵⁹ | 187–410 | 8.6 | 88 | ⁴⁰ Ar, 'excess volatiles' |
| Pollack and Black ⁶¹ | 1,000–3,000 | 6.6–66 | 80–160 | N, noble gases, Venus data |
| Carr ⁶⁷ | 10,000–20,000 | 100–300 | 500–1,000 | Geomorphology |
| Dreibus and Wänke ⁶² | (3,000)‡ | (33)‡ | 130 | SNC meteorites, martian CI |
| Greeley ⁶⁶ | (>1,000)‡ | (>11)‡ | >45 | Volcanism only |

This compilation is adapted from McKay and Stoker⁵.

† Determined by assuming that the martian ratio of volatiles per gram of planet is the same as the Earth's. Earth volatiles⁶³: CO₂, 190 bar, N₂, 2 bar, H₂O, 3,200 m.

‡ These values are not from the referenced source but were determined assuming that the ratios of volatiles are the same as the Earth scaling result.

Thus, an interesting possibility seems to exist: in the case of the polar regolith and $T_d = 20$ K, if the surface temperature could be raised (for example, by adding of greenhouse gases) by ~25 K, raising the surface pressure above the unstable equilibrium point at 30 mbar, the system would switch to the new stable state at a surface pressure of ~800 mbar and a surface temperature of 250 K. For the global regolith ($T_d = 10$ K) a similar transition occurs at 100 mbar, with the final state having essentially totally outgassed the regolith CO₂. Clearly, the existence of stable states which result from the desorption of CO₂ depends on the total amount of CO₂ in the atmosphere-regolith system, the latitudinal distribution of the regolith and, very sensitively, on the parameter T_d . The final temperature of the steady state depends only on the total CO₂ outgassed, and can be determined by the observation that most of the CO₂ is desorbed. Thus, a 2-bar regolith reservoir would have a stable state at ~273 K; a 3-bar reservoir would produce a temperature >280 K.

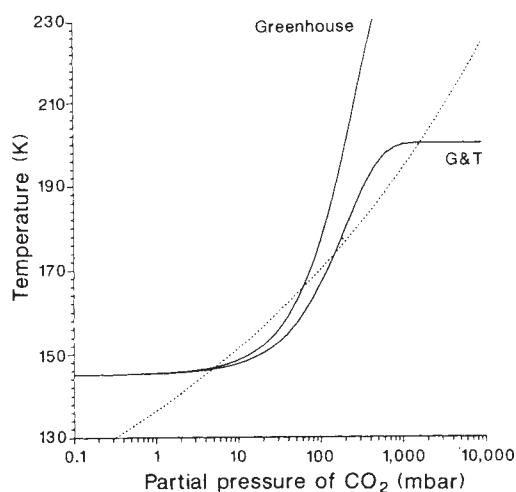


FIG. 3 Equilibrium temperature of a polar CO₂ cap on Mars as a function of surface pressure. The dotted line is the vapour pressure of condensed CO₂. The solid lines are models of the dependence of the polar-cap temperature on the total atmospheric pressure. The curve labelled G&T is a typical result from the work of Gierasch and Toon⁴⁷ who considered only advective transport of heat from mid-latitudes to the poles. For the case represented by this curve, stable states exist at a few millibars and at several hundred millibars total pressure. The other solid curve includes the greenhouse effect, and the polar-cap temperature is now given by equation (1). In this case there is no high-pressure stable state with a persistent polar cap; the cap totally sublimates in a 'runaway' effect.

Here we have assumed large, weakly bound, reservoirs of CO₂ in the martian regolith. The CO₂ released is useful for constructing a plant-habitable atmosphere but may be undesirable in a human-habitable atmosphere. Unfortunately, there are insufficient data to determine the definite role of regolith desorption in warming Mars, but our results suggest that it is an area worth further investigation.

Mars volatile inventory

We now consider whether the volatile inventory on Mars is sufficient to provide the gaseous constituents of a habitable atmosphere. Table 2 shows our estimate of the total inventories of CO₂, N₂ and H₂O that would be needed to construct habitable environments on Mars. The amount of CO₂ is that required to raise the mean temperature to near the freezing point. The amount of N₂ is that required to provide a buffer gas for a breathable atmosphere (see Table 1). The required amount of water is somewhat arbitrary but, as will be discussed below, large bodies of water are probably needed to sequester carbon-bearing sediments, thus liberating O₂. In addition, a habitable planet probably requires an active hydrological cycle. Also listed in Table 2 are various published estimates for the volatile endowment of Mars^{5,7}.

Early theoretical models of Solar System volatiles⁵⁶ predicted that Mars should be more volatile-rich than Earth, as it formed further from the sun. A second geochemical approach^{57–59} is to scale the volatile inventory by the observed argon concentrations, both nonradiogenic ³⁶Ar and radiogenic ⁴⁰Ar. McElroy *et al.*⁶⁰ used the preferential loss of ¹⁵N compared with ¹⁴N to estimate the total nitrogen inventory and then scaled this by Earth's ratios to obtain CO₂ and H₂O. Pollack and Black's method⁶¹ used both the argon and nitrogen values. All of these geochemical models suggest that Mars is volatile-poor compared with the Earth. Dreibus and Wänke⁶² based their estimate of water abundance on an analysis of the SNC meteorites, which are thought to have come from Mars^{63–65}. Greeley⁶⁶ calculated a lower limit by considering only the amount of water that should have been released by the observed volcanic features, assuming 1% as the water content of martian magma.

An alternative method of estimating the amount of water present on early Mars is to use geomorphological evidence. For example, Carr⁶⁷ determined the amount of water that must have flowed through the Valles Marineris system to create the observed channel features. He obtained a lower limit by assuming maximal efficiency for erosion by the flowing water. By extrapolating these results to the rest of the planet, he inferred that Mars has outgassed water equivalent to a depth of 0.5–1 km; this implies that Mars is volatile-rich, with a volatile endowment comparable to the Earth scaling result (Table 2).

All estimates of the initial complement of volatiles are greater than the abundance of water, CO₂ and nitrogen currently residing in the atmosphere of Mars (Table 2). The present loss rate of volatiles due to atmospheric escape is insufficient to deplete the initial endowment of water and other volatiles, so most of the volatiles may still be on the planet in subsurface reservoirs. If the rate of atmospheric escape has remained constant for water (as 2H and O) at $6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ (refs 60, 68) and for N₂ at $5.6 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ (ref. 69), the total loss over the past 4.5 Gyr would be 2.5 m of water and 1.4 mbar of N₂. That the current D/H ratio on Mars is 6 times as large as on Earth^{70,71} may only reflect fractionation processes in the current atmospheric reservoir⁷². It is also possible that Mars lost a considerable fraction of its early atmosphere as a result of erosion by high-velocity impacts⁷³.

The total complement of volatiles on Mars and their fate over geological time is therefore highly uncertain. If the upper range of estimates is correct, then Mars has the volatiles needed to achieve both habitable states discussed above. If the lower range is correct, or if Mars has lost its initial volatiles to space, then it is unlikely that any habitable state can be produced. This is an important area in which we need better information to evaluate the possibility of terraforming Mars.

If large volatile reservoirs do exist on Mars, they could take several forms. The polar caps may hold large amounts of water ice, perhaps as much as 5,000 km³ (ref. 74), corresponding to a layer of water 4 cm thick covering the entire planet (probably not enough to provide for a green planet). Much larger amounts of water may be tied up as permafrost in the regions poleward of 30° (ref. 75). If there is indeed water equivalent to a depth of hundreds of metres on Mars, this must be where it is located.

As discussed earlier, CO₂ could be stored in the south polar cap (<100 mbar) and in the regolith (~300 mbar). Another, possibly much larger, reservoir for CO₂ is carbonate rocks. Carbonates could have been formed early in Mars's history by reactions of CO₂ with silicate minerals in the presence of liquid water⁶. The existence of a carbonate reservoir on Mars is uncertain, although there is some recent spectral evidence for it⁷⁶. Releasing the CO₂ from carbonate materials would be much more difficult than release from the polar cap or regolith¹⁴.

The most serious potential shortfall of material is N₂ (Table 2). If the present amount of nitrogen in the atmosphere represents the available amount, then this will severely limit the biological possibilities for Mars. Even under the assumption that the C/N ratio of biomass can be stretched to values near 100 (by reduced requirements in nitrogen-limited ecosystems and preferential recycling of N compared with C in sediments), the current N₂ inventory of 0.2 mbar would only allow for the production of 60 g cm⁻² of sediment biomass. This amount of carbon fixation would release only 40 mbar of O₂. Clearly the question of non-atmospheric reservoirs of nitrogen on Mars is a critical, if not the most critical, question that must be answered to assess the feasibility of terraforming Mars. It has been suggested^{5,7} that nitrogen would have been tied up as nitrate on an early wet Mars, and it is possible that considerable nitrogen reservoirs exist in the soil.

In addition to C, H, N and O, the elements S and P are required for life. Sulphur is available on Mars with concentrations reported at the Viking landing sites 10 to 100 times those in terrestrial rocks and soils⁷⁷. Phosphorus was not measured by Viking because its X-ray fluorescence signal was masked by S and Si. Nevertheless it is thought to be present⁷⁸. Thus all the

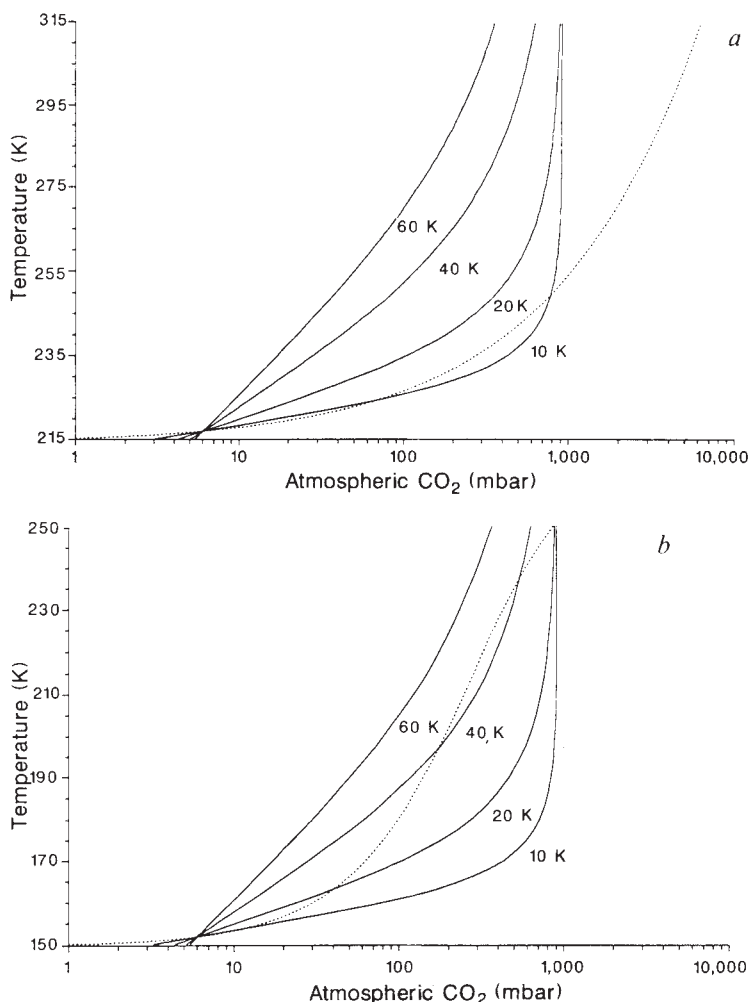


FIG. 4 Desorption of CO₂ from *a*, a global regolith and *b*, a polar regolith for assumed total CO₂ equivalent to a partial pressure of 1 bar. The four solid curves correspond to values of T_d of 10 K, 20 K, 40 K and 60 K (see equation (2)). The dotted line shows the average temperature on Mars from climate model calculations⁶. In *b*, the dotted line is the polar-cap temperature as a function of pressure, from equation (1). Where a solid line intersects the dotted line, there is a potential steady state.

TABLE 3 Energy requirements for terraforming Mars

| Initial state | Final state | Amount (g cm ⁻²) | Energy (J cm ⁻²) | Energy/solar power* (years) |
|--|--|----------------------------------|------------------------------|--------------------------------|
| CO ₂ (s) at 150 K | CO ₂ (g) at 288 K | 2 bar; 5,400 g cm ⁻² | 3.7 × 10 ⁶ | 7.9 |
| Dirt at 215 K | Dirt at 288 K | ~10 m; 2,000 g cm ⁻² | 1.2 × 10 ⁵ | 0.3 |
| H ₂ O(s) at 215 K | H ₂ O(l) at 288 K | 10 m; 1,000 g cm ⁻² | 5.5 × 10 ⁵ | 1.2 |
| H ₂ O(s) at 215 K | H ₂ O(g) at 288 K | 20 mbar; 54 g cm ⁻² | 1.6 × 10 ⁵ | 0.33 |
| H ₂ O(s) at 215 K | H ₂ O(l) at 288 K | 500 m; 50,000 g cm ⁻² | 2.8 × 10 ⁷ | 56 |
| CO ₂ (g) + H ₂ O | CH ₂ O + O ₂ (g) | 200 mbar; 540 g cm ⁻² | 8 × 10 ⁶ | 17 |

* The global averaged solar energy on Mars is $4.68 \times 10^5 \text{ J cm}^{-2} \text{ yr}^{-1}$.

major elements of life (C, H, N, O, P and S) are present on the surface of Mars, and most of the trace elements required, such as Fe, Mg and Al, have also been directly detected. To construct the four CFC gases we suggested as greenhouse gases, Cl, F and Br would be required. Chloride has been observed on Mars (0.007 ± 0.003 by mass in the soil⁷⁸). The Solar System ratio of Cl to F (which was not detectable by the Viking landers) based on meteorites³² is 6.2, implying considerable F on Mars ($\sim 0.1\%$ by mass⁷⁹). The F concentration is only ~ 40 p.p.m. in the SNC meteorites thought to represent martian materials⁸⁰, but these also contain only 108 p.p.m. of Cl, well below the Viking value. The availability of F therefore remains uncertain. Bromine was detected in two or three spectra on the Viking X-ray instrument⁸¹ and is estimated to be 20–30 p.p.m. (B. Clark, personal communication). The Solar System abundance of Br³² would imply a concentration in the martian soil of ~ 2 p.p.m. by mass if scaled to Si, and 16 p.p.m. if scaled to Cl, compared with 0.15 p.p.m. determined from the SNC meteorites⁶².

Timescales for terraforming Mars

We next consider how a suitable steady state might be achieved, assuming that the volatile inventory is adequate to achieve it. From energy considerations, terraforming Mars breaks down naturally into two steps: warming the planet, and altering its chemical state. In Table 3 we have listed the initial and final states associated with this process and the energy required to achieve the change in state. The energy requirements are also listed in terms of the equivalent number of years of sunlight, assuming 100% could be used. This provides a strong lower limit to the time required to achieve the desired transition.

Warming the planet. A plant-habitable environment could be established by exploiting the positive feedback of a CO₂ atmosphere, as discussed above. If the temperature of the martian surface were increased, say, by warming the poles with giant mirrors, or by spreading black soot over the polar caps, or by introducing greenhouse gases, then the amount of CO₂ and water vapour in the atmosphere would also increase. This would have the effect of warming the atmosphere still further and so on. As discussed above, it is possible that above a certain CO₂ pressure the process would accelerate until a high-pressure stable state was reached or until all the CO₂ was outgassed. Regardless of the mechanism, the energy required to complete this step would be $\sim 10^6 \text{ J cm}^{-2}$, equivalent to 10 years of Mars solar energy. This amount of energy corresponds to subliming and warming 2 bar of CO₂, warming a layer of martian regolith 10 m thick, melting a layer of water 10 m thick and evaporating moisture into the atmosphere. Assuming that the process could be sustained and could use 10% of the solar energy on Mars, it would require ~ 100 years. On a much longer timescale, the deep layers of permafrost ice would melt. To melt a layer of water 500 m deep over the entire planet requires 55 years of solar energy. But the process would probably be limited by the rate of diffusion of heat into the regolith, which might require $\sim 10^5$ years. If the 2 bar of CO₂ were distributed over a 500-m depth of regolith, it could require ~ 100 years to diffuse out of the soil if driven by a pressure gradient, but 10^5 years for the soil to be warmed enough at depth to degas it⁵³.

Chemical modification of the atmosphere. The only mechanism that seems capable of changing the bulk composition of a planetary atmosphere is planetary-scale biology, producing O₂ from CO₂. The energy required for O₂ production is larger than that required for the initial warming step. Furthermore, current biological ecosystems have very low efficiencies for conversion of incident solar energy into biomass energy. Net primary production in terrestrial ecosystems ranges from 0.001 to 0.1 g cm⁻² yr⁻¹, with a global average of 0.033 g cm⁻² yr⁻¹ (ref. 82). These numbers correspond to energy efficiencies of 1.5×10^{-5} , 1.5×10^{-3} and 5×10^{-4} , respectively. For a typical average efficiency of ($\sim 10^{-4}$), the production of a breathable atmosphere would require over 100,000 years. Specially developed organisms could yield much higher efficiencies⁸. The limiting step in the production of any net O₂ on Mars may not be the efficiency of photosynthesis, however, but the necessity of sequestering the organic material in places (presumably deep sediments) where it is not reoxidized. This, in turn, probably requires an active hydrological cycle and deep stable basins. Unless vast amounts of water could be liberated, this step could prove to be difficult. This is yet another reason why a human-habitable environment is much more difficult to construct than a plant-habitable one.

The timescales discussed above can be compared with the timescale for the decay of a thick atmosphere on Mars. In the case of a 2-bar CO₂ atmosphere, the dominant loss mechanism would presumably be the formation of carbonate rocks. Pollack *et al.*⁶ have estimated that the lifetime of a thick CO₂ atmosphere on early Mars is $\sim 10^7$ years in the absence of any recycling mechanisms. Maintaining the atmosphere for longer than 10^7 yr would require some mechanism, either biological or mechanical, for recycling carbonate materials into the atmosphere¹⁴. Nonetheless, it seems that the processes acting to remove the atmosphere of a habitable Mars may be significantly slower than the processes that could create such an atmosphere, so that the resulting system could persist for tens of millions of years.

Conclusions

The complexity of the problem of terraforming a planet does not allow us to draw detailed conclusions. The problem is similar in scope to understanding the Earth's biosphere and biogeochemical cycles. Our work has been a preliminary attempt to identify the important issues and to quantify the problem. Our main deduction is that on Mars a CO₂-rich, plant-habitable atmosphere would seem feasible to construct, given adequate reservoirs of CO₂ and H₂O, whereas an O₂ rich, human-habitable, atmosphere would be very difficult to construct and possibly impractical to warm.

From our analysis, one could propose the following sequence of events: production of CFCs (or other greenhouse gases) starts on Mars and the surface temperature warms up by ~ 20 K. The regolith and polar caps release their CO₂ and the pressure rises to 100 mbar. One of two things could then happen. If there were large regolith and polar CO₂ reservoirs the pressure would continue to rise on its own. If these were absent, the CO₂ pressure would stabilize, and additional CO₂ would have to be released from carbonate minerals. At this point (perhaps between 100

and 10⁵ years) Mars may be suitable for plants. If there was a mechanism for sequestering the reduced carbon, these plants could slowly transform the CO₂ to produce an O₂-rich atmosphere in perhaps 100,000 years. If sufficient N₂ could also be released from putative soil deposits, and the CO₂ level kept low enough, then a human-breathable atmosphere would be produced. Continued production of CFCs that absorb radiation across the whole spectrum would be required to maintain the warm temperature. Destruction of ozone by these CFCs would probably require these gases be made in sufficient amount (considerably in excess of current terrestrial production rates) to constitute an ultraviolet shield. This proposed process for terraforming Mars relies only on processes that have been demonstrated, and in fact are current, on Earth.

Our analysis is incomplete for several reasons. Most important, our knowledge of Mars is insufficient to determine many key quantities. In addition, we have used only simple models or estimates of many key processes. But our results do suggest that further investigation would be fruitful and that terraforming studies can be made quantitative. We have identified several areas that warrant further investigation: (1) the availability of N₂ and other volatiles on Mars; (2) more detailed models of the processes for warming Mars from its present state with 'runaway' effects involving both the polar caps and regolith; (3)

chemical and biological methods for releasing CO₂ from carbonates; (4) the effects of artificial heating mechanisms, such as albedo changes, greenhouse gases and solar mirrors, on the present martian climate; (5) the photochemistry and O₂ mixing ratio of a 2-bar CO₂ atmosphere on Mars; (6) photochemistry of O₃ in a 1-bar nitrogen-oxygen atmosphere on Mars with parts per million of halogenated gases; (7) climate of a thick atmosphere on Mars, including latitudinal effects and large bodies of water; and (8) the long-term stability of a thick atmosphere on Mars in the absence of tectonic recycling of sediments. Many of these questions can be studied with numerical models, but some require the further exploration of Mars.

If such investigations indicate that it is feasible to make Mars habitable, the motivation to do so may depend on the potential for life (human and non-human) on Mars, the economic payoff, and the nature of other large-scale efforts that provide habitats in space. We suggest that a key goal for future exploration of Mars should be to determine the feasibility of terraforming that planet. □

Christopher P. McKay is at the Space Science Division and Owen B. Toon at the Earth System Science Division, NASA Ames Research Center, Moffett Field, California 94035, USA. James F. Kasting is at the Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, USA.

1. Maddox, J. *Nature* **346**, 311 (1990).
2. Joos, F., Sarmiento, J. L. & Siegenthaler, U. *Nature* **349**, 772-775 (1991).
3. McKay, C. P. (ed.) *The Case for Mars II*, Am. Astronaut. Soc. Sci. Technol. Ser. Vol. 62 (Univelt, San Diego, 1985).
4. Stoker, C. R. (ed.) *The Case for Mars III*, Am. Astronaut. Soc. Sci. Technol. Ser. Vol. 74, 75 (Univelt, San Diego, 1985).
5. McKay, C. P. & Stoker, C. R. *Rev. Geophys.* **27**, 189-214 (1989).
6. Pollack, J. B., Kasting, J. F., Richardson, S. M. & Poliakoff, K. *Icarus* **71**, 203-224 (1987).
7. McKay, C. P. *Adv. Space Res.* **6**, 269-285 (1986).
8. Avner, M. M. & MacElroy, R. D. (eds) *On the Habitability of Mars*, NASA SP-414 (US Government Printing Office, Washington DC, 1976).
9. Burns, J. A. & Harwit, M. *Icarus* **19**, 126-130 (1973).
10. Sagan, C. *Icarus* **20**, 513-514 (1973).
11. Oberg, J. E. *New Earths* (Stackpole, Harrisburg, Pennsylvania, 1981).
12. McKay, C. P. *J. Brit. Interplanet. Soc.* **35**, 427-433 (1982).
13. Lovelock, J. E. & Allaby, M. *The Greening of Mars* (Warner, New York, 1984).
14. Fogg, M. J. *J. Brit. Interplanet. Soc.* **42**, 577-582 (1989).
15. Haynes, R. H. in *Moral Expertise* (ed. MacNiven, D.) 161-183 (Routledge, London, 1990).
16. McKay, C. P. in *Moral Expertise* (ed. MacNiven, D.) 184-197 (Routledge, London, 1990).
17. Dole, S. H. *Habitable Planets for Man*, 2nd edn (Elsevier, New York, 1970).
18. Bauer, J. A. & Martha, P. Z. *Pflanzenphysiol.* **103**, 445-450 (1981).
19. Lloyd, N. D. H., Canvin, D. T. & Culver, D. A. *Plant Physiol.* **59**, 936-940 (1977).
20. Salisbury, F. B. & Ross, C. W. *Plant Physiology* (Wadsworth, Belmont, California, 1985).
21. Lovelock, J. E. & Whitfield, M. *Nature* **296**, 561-563 (1982).
22. Rogers, H. H., Thomas, J. F. & Bingham, G. E. *Science* **220**, 428-429 (1983).
23. Hickleton, P. R. & Jolliffe, P. A. *Can. J. Bot.* **58**, 2181-2189 (1980).
24. Seckbach, J., Baker, F. A. & Shugarman, P. M. *Nature* **227**, 744-745 (1970).
25. Drew, M. C. *Curr. Adv. Plant Sci.* **36**, 1-14 (1979).
26. Klingler, J. M., Mancinelli, R. L. & White, M. R. *Adv. Space Res.* **9**, 173-176 (1989).
27. Billings, C. E. in *Bioastronautics Data Book* (eds Parker, J. F. Jr & West, V. R.) NASA SP-3006, 1-34; 35-64 (Washington DC, 1973).
28. Welch, B. E., Morgan, T. E. Jr & Clamann, H. G. *Federation Proc.* **22**, 1053-1056 (1963).
29. MacEwen, J. D. in *Bioastronautics Data Book* (eds Parker, J. F. Jr & West, V. R.) NASA SP-3006, 455-488 (Washington DC, 1973).
30. Lovelock, J. E. *Gaia* (Oxford University Press, Oxford, 1979).
31. Roth, E. M. in *Atmosphere in Space Cabins and Closed Environments* (ed. Kemmermeyer, K.), 13-31 (Merideth, New York, 1964).
32. Anders, E. & Grevesse, N. *Geochim. cosmochim. Acta* **53**, 197-214 (1989).
33. Owen, T. et al. *J. geophys. Res.* **82**, 4635-4639 (1977).
34. Pollack, J. B. *Icarus* **37**, 479-533 (1979).
35. Cess, R. D., Ramanathan, V. & Owen, T. *Icarus* **41**, 159-165 (1980).
36. Hoffert, M. I., Callegari, A. J., Hsieh, C. T. & Ziegler, W. *Icarus* **47**, 112-129 (1981).
37. Postawko, S. E. & Kuhn, W. R. *Proc. 16th Lunar Planet. Sci. Conf., J. geophys. Res.* **91**, D431-D438 (1986).
38. Kieffer, H. H. et al. *J. geophys. Res.* **82**, 4249-4292 (1977).
39. Kong, T. Y. & McElroy, M. B. *Icarus* **32**, 168-189 (1977).
40. Kasting, J. F. & Walker, J. C. G. *J. geophys. Res.* **86**, 1147-1158 (1981).
41. Kasting, J. F., Pollack, J. B. & Crisp, D. J. *atmos. Chem.* **1**, 403-428 (1984).
42. Oyama, V. I. & Berdahl, B. J. *J. geophys. Res.* **82**, 4669-4676 (1977).
43. Kasting, J. F. & Ackerman, T. P. *Science* **234**, 1383-1385 (1986).
44. Ramanathan, V., Cicerone, R. J., Singh, H. B. & Kiehl, J. T. *J. geophys. Res.* **90**, 5547-5566 (1985).
45. Weast, R. C. *CRC Handbook of Chemistry and Physics* (CRC, West Palm Beach, Florida, 1978).
46. Hammit, J. K. *Nature* **330**, 711-716 (1987).
47. Gierasch, P. J. & Toon, O. B. *J. Atmos. Sci.* **30**, 1502-1508 (1973).
48. Sagan, C., Toon, O. B. & Gierasch, P. J. *Science* **181**, 1045-1049 (1973).
49. Paige, D. A., Herkenhoff, K. E. & Murray, B. C. *J. geophys. Res.* **95**, 1319-1335 (1990).
50. Fanale, F. P. & Cannon, W. A. *J. geophys. Res.* **84**, 8404-8414 (1979); **79**, 3397-3402 (1974).
51. Fanale, F. P., Salvail, J. R., Banerdt, W. B. & Saunders, R. S. *Icarus* **50**, 381-407 (1982).
52. Zent, A. P. & Fanale, F. P. *J. geophys. Res.* **91**, D439-D445 (1986).
53. Toon, O. B., Pollack, J. B., Ward, W., Burns, J. A. & Bilski, K. *Icarus* **44**, 552-607 (1980).
54. Zent, A. P., Fanale, F. P. & Postawko, S. E. *Icarus* **71**, 241-249 (1987).
55. Valenzuela, D. P. & Meyers, A. L. *Adsorption Equilibrium Data Handbook* (Prentice Hall, Englewood Cliffs, New Jersey, 1989).
56. Lewis, J. S. *Earth planet. Sci. Lett.* **15**, 286-290 (1972).
57. Anders, E. & Owen, T. *Science* **198**, 453-465 (1977).
58. Rasool, S. I. & LeSergeant, L. *Nature* **266**, 822-823 (1977).
59. Clark, B. C. & Baird, A. K. *Geophys. Res. Lett.* **6**, 811-814 (1979).
60. McElroy, M. B., Kong, T. Y. & Yung, Y. L. *J. geophys. Res.* **82**, 4379-4388 (1977).
61. Pollack, J. B. & Black, D. C. *Science* **205**, 56-59 (1979); *Icarus* **51**, 169-198 (1982).
62. Dreibus, G. & Wänke, H. *Icarus* **71**, 225-240 (1987).
63. Becker, R. H. & Pepin, R. O. *Earth planet. Sci. Lett.* **69**, 225-242 (1984).
64. Pepin, R. O. *Rev. Geophys.* **25**, 293-296 (1987).
65. Bogard, D. D. & Johnson, P. *Science* **221**, 651-654 (1983).
66. Greeley, R. *Science* **236**, 1653-1654 (1987).
67. Carr, M. H. *Icarus* **68**, 187-216 (1986).
68. Liu, S. & Donahue, T. M. *Icarus* **28**, 231-246 (1976).
69. Fox, J. L. & Dalgarno, A. *J. geophys. Res.* **88**, 9027-9032 (1983).
70. Owen, T., Maillard, J. P., de Bergh, C. & Lutz, B. L. *Science* **240**, 1767-1770 (1988).
71. Yung, Y. L. et al. *Icarus* **76**, 146-159 (1988).
72. Carr, M. H. *Icarus* **87**, 210-227 (1990).
73. Melosh, H. J. & Vickery, A. M. *Nature* **338**, 487-489 (1989).
74. Meyer, T. R. & McKay, C. P. *J. Brit. Interplanet. Soc.* **42**, 147-160 (1989).
75. Squyres, S. W. & Carr, M. H. *Science* **231**, 249-252 (1986).
76. Pollack, J. B. et al. *J. geophys. Res.* **95**, 14595-14628 (1990).
77. Toulmin, P. III, Baird, A. K., Clark, B. C., Keil, K. & Rose, H. J. *Jr Science* **194**, 81-84 (1976).
78. Toulmin, P. et al. *J. geophys. Res.* **82**, 4625-4634 (1977).
79. Prinn, R. G. & Fegley, B. Jr. *Ann. Rev. Earth planet. Sci.* **15**, 171-212 (1987).
80. Dreibus, G. & Wänke, H. *Meteoritics* **20**, 367-381 (1985).
81. Clark, B. in *Mars* (University of Arizona Press, Tucson, 1991).
82. Whittaker, R. H. *Communities and Ecosystems* 2nd edn (Macmillan, New York, 1975).
83. Turekian, K. K. & Clark, S. P. Jr. *J. Atmos. Sci.* **32**, 1257-1261 (1975).