Inventory of CO₂ available for terraforming Mars

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We revisit the idea of 'terraforming' Mars — changing its environment to be more Earth-like in a way that would allow terrestrial life (possibly including humans) to survive without the need for life-support systems — in the context of what we know about Mars today. We want to answer the question of whether it is possible to mobilize gases present on Mars today in non-atmospheric reservoirs by emplacing them into the atmosphere, and increase the pressure and temperature so that plants or humans could survive at the surface. We ask whether this can be achieved considering realistic estimates of available volatiles, without the use of new technology that is well beyond today's capability. Recent observations have been made of the loss of Mars's atmosphere to space by the Mars Atmosphere and Volatile Evolution Mission probe and the Mars Express spacecraft, along with analyses of the abundance of carbon-bearing minerals and the occurrence of CO₂ in polar ice from the Mars Reconnaissance Orbiter and the Mars Odyssey spacecraft. These results suggest that there is not enough CO₂ remaining on Mars to provide significant greenhouse warming were the gas to be emplaced into the atmosphere; in addition, most of the CO₂ gas in these reservoirs is not accessible and thus cannot be readily mobilized. As a result, we conclude that terraforming Mars is not possible using present-day technology.

he concept of terraforming Mars has been a mainstay of science fiction for a long time, but it also has been discussed from a scientific perspective, initially by Sagan¹ and more recently by, for example, McKay et al.2. The idea has resurfaced lately in public discussions of possible human missions to Mars and long-term human colonization3. Here we take 'terraforming' to mean changing the Martian environment into one that could be more suitable for the existence of terrestrial life. Following McKay et al.2, this has two possible approaches. First, we can consider increasing the pressure enough to allow humans to work without the use of pressure suits; this approach does not necessarily require an oxygen atmosphere that can be breathed directly. Second, we can increase the abundance of an atmospheric greenhouse gas enough such that the temperature will increase to the point at which liquid water can be stable or persist. Having warmer temperatures and stable liquid water could greatly simplify all aspects of operations in the Martian environment. Both aspects require the addition of significant quantities of gas to the present atmosphere.

CO₂ and H₂O are the only greenhouse gases that are likely to be present on Mars today in sufficient abundance to provide any significant greenhouse warming. While other gases such as introduced chlorofluorocarbons have been proposed as ways to raise the atmospheric temperature^{2,4-6}, these are short-lived and without a feasible source using current technologies; they are therefore not considered further here. Previous models of atmospheric warming have demonstrated that water cannot provide significant warming by itself; temperatures do not allow enough water to persist as vapour without first having significant warming by CO₂ (ref. ⁷). CH₄ and H₂ have been proposed as possible greenhouse gases that contributed to warming early Mars⁷, but these are not expected to be present in an accessible location on Mars today. Thus, we focus on determining the inventory of CO₂ on present-day Mars, and whether the CO₂ that is present in non-atmospheric reservoirs can be put back into the atmosphere.

To understand the availability and impact of CO_2 gas on atmospheric warming, we address the following questions. Where has the CO_2 from an ancient, thicker greenhouse atmosphere gone?

Could the remaining planetary inventories of CO_2 be mobilized and emplaced into the atmosphere via current or plausible near-future technologies? Would the amount of CO_2 that could be emplaced into the atmosphere provide any significant greenhouse warming?

Our analysis follows that of ref. ², but benefits from 20 years of additional spacecraft observations of Mars. These data have provided substantial new information on the volatile history of the planet, the abundance of volatiles locked up on and below the surface, and the loss of gas from the atmosphere to space.

Reservoirs and sinks for CO₂

Non-atmospheric CO₂ reservoirs or sinks that we examine here include: polar CO₂ ice or water-ice clathrate, CO₂ adsorbed onto mineral grains in the regolith, carbon-bearing minerals (in carbon-ate-bearing rocks), and the permanent loss of CO₂ from the atmosphere to space. Below we will discuss the amount of CO₂ necessary to raise temperatures sufficiently to allow liquid water; for now, however, take a nominal requirement as being about 1 bar of CO₂, which is equivalent to about 2,500 g CO₂ cm⁻² in the atmosphere. For comparison, the present-day atmosphere has an average pressure of about 6 mbar — equivalent to about 15 g CO₂ cm⁻² at the surface.

Polar CO₂ ice and clathrate. The Martian polar caps contain a seasonal covering of CO_2 ice that deposits in winter when the surface drops below the condensation temperature of atmospheric CO_2 , and disappears in summer when sunlight causes it to sublimate back into the atmosphere. This seasonal covering can contain as much as perhaps a third of the atmosphere at any given time, or the equivalent of about 2 mbar (ref. 8).

The Martian north polar cap loses its entire covering of CO₂ ice during summer, exposing a residual polar cap. This cap consists broadly of water ice with intermixed dust in various proportions to form layers in a stack up to several kilometres thick. The ice cap is surrounded by layered deposits that are thought to contain little to no water ice, down to a latitude of about 80° (ref. ⁹).

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The south polar cap retains a thin and spatially discontinuous cover of CO_2 ice after the seasonal frost has disappeared during summer. This ice is not thought to be substantial, containing only the equivalent of a fraction of the present-day atmospheric CO_2 abundance⁸. Water ice is observed to be present beneath that CO_2 , and much of the volume of the polar deposits is thought to be water ice with intermixed dust. Within the volume of the polar deposits, however, radar measurements show what appears to be a substantial volume of clean CO_2 ice buried at depth¹⁰. This volume of ice, if emplaced into the atmosphere, would provide enough CO_2 to double the atmospheric pressure, to an estimated 12 mbar (ref. ¹¹).

H₂O and CO₂ can also occur in a clathrate structure, in which the H₂O molecules form a 'cage' that can hold CO₂ (ref. ¹²). The H₂O shell contains six molecules for every CO₂ molecule trapped inside. Clathrates can be stable in the Martian polar regions¹³, although there's no evidence to suggest that they are actually present. If the full volume of the polar ice deposits consisted of H₂O-CO₂ clathrate, they could contain up to the equivalent of about 150 mbar of CO₂. Even if clathrate is present, however, it's unlikely that the entire polar deposit could have formed in a way that allowed them to be fully populated with CO₂. Such a deposit would require high CO₂ pressures to have been present throughout the formation process¹⁴. Although it's not possible to obtain a more realistic estimate of the possible CO₂ content of the polar deposit, 150 mbar should be considered as an extreme upper limit, and it's possible that there is no clathrate present at all.

Furthermore, liquid CO_2 is not considered to be a viable reservoir for polar-region CO_2 . The pressure is above the triple-point pressure for liquid CO_2 at a depth of only a few kilometres in the polar regions¹⁵. However, temperatures are too low to allow liquid CO_2 until a depth that would be well below the ice and deep within the crust.

 ${\rm CO_2}$ clathrate or liquid ${\rm CO_2}$ can exist within the crust in nonpolar regions, based solely on their stability phase diagram¹⁴. However, for either to be present in significant quantities, the ${\rm CO_2}$ pressure in pore spaces in the crust would have to be equal to the lithostatic pressure from the overlying materials; this is not likely and, were the pores sealed in a way that allowed this, the ${\rm CO_2}$ would be effectively sequestered in the subsurface and thus rendered inaccessible¹⁴.

Adsorbed CO₂. Both CO₂ and H₂O can be adsorbed onto individual grains in the regolith and megaregolith 16,17 . This process involves a physical (as opposed to chemical) bonding at the level of the individual molecule. The amount of gas that can adsorb onto a grain depends on the specific surface area of the grain, which in turn depends on the composition and size/shape of the grain at the molecular level. Typical amounts of adsorbed CO₂ are shown in Fig. 1. Typically, 0.002 g of CO₂ can adsorb per gram of basalt, 0.005 g CO₂ per gram of nontronite (a representative clay that may form under Martian conditions), and 0.015 g CO₂ per gram of palagonite (a high-surface-area clay that represents the extreme weathering product of basalt in a water- and CO₂-rich environment).

If we take a high estimate of 0.01 g CO₂ per gram of weathered regolith, and an estimated total regolith equivalent thickness of 100 m, there could be as much as 100 g CO₂ cm⁻² adsorbed within the subsurface. This is a high estimate because not all of the weathered material would convert to something analogous to palagonite; other intermediate weathering products would be produced, and some of the original basalt would remain relatively unweathered. The regolith thickness estimate of 100 m is based on a combination of factors. First, imaging of the surface indicates that younger surfaces can have no more than a few metres to ten metres of physically or chemically altered material at the surface without masking the underlying morphological features¹⁸. Older surfaces may have a thicker regolith and there may be weathering that occurs in the subsurface, in

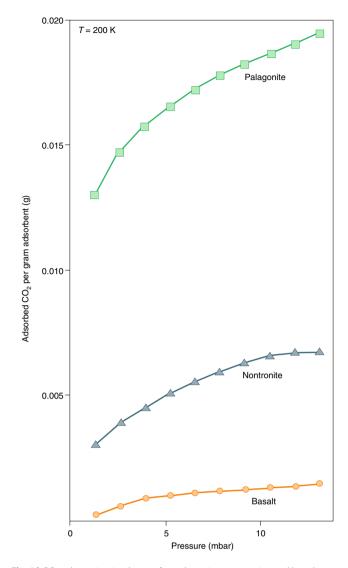


Fig. 1 \mid CO $_2$ adsorption isotherms for palagonite, nontronite and basalt. Credit: adapted from ref. 16 , Elsevier

some instances to depths of 8 km (ref. ¹⁹). However, observations where deeper layers have been exposed, such as in the walls of Valles Marineris, indicate that clay minerals formed through ground water interactions or carbonate weathering are relatively minimal and incomplete²⁰. Thus, we take 100 m as a realistic estimate of the total equivalent global thickness of weathered material.

If the full 100 g $\rm CO_2~cm^{-2}$ could be emplaced into the atmosphere, it would provide the equivalent pressure of about 40 mbar. The mobilization potential of this reservoir will be discussed below.

Carbon-bearing minerals. CO_2 can be locked up in carbon-bearing minerals. Carbonate minerals were believed for a long time to be the repository of an ancient, thick CO_2 atmosphere that is thought to have provided greenhouse warming on early Mars^{21,22}. However, no widespread global deposits of carbonates have been identified; to hold the equivalent of 1 bar of CO_2 , carbonate minerals would have to contain the equivalent of a global layer ~15 m thick, and this has not been seen. Localized deposits of carbonates have been identified^{23–25}, and carbonates have been detected in low abundances in airborne dust²⁶.

The Nili Fossae carbonate plains (Fig. 2) are the largest contiguous exposed outcrop of carbonate-bearing materials on Mars²⁴.

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These carbonates are exclusively associated with olivine-bearing materials, and the formation of carbonate (up to ~20%) is indicative of low-temperature in situ carbonation, in which the groundwater was atmospherically connected. This atmospherically connected process can only operate in the upper hundreds of metres of the surface, as the $\rm CO_2$ that diffuses in from the atmosphere would be readily exhausted²⁴. As such, several scenarios for the amount of $\rm CO_2$ that can be sequestered can be considered when assessing the size of this reservoir.

In the first scenario, the extent of the carbonate unit matches the observed extent (6,800 km²) and contains roughly 20 wt% carbonate to a depth of 0.2 km. The amount of CO_2 sequestered in this deposit would be equivalent to about 0.25 mbar if emplaced into the atmosphere.

In the second scenario, the extent of the carbonate unit is extrapolated to the observed extent of olivine-bearing rocks in the region (\sim 44 times larger in size, \sim 300,000 km²) and is altered to \sim 20 wt% carbonate to a depth of 0.5 km. In this scenario, the CO₂ locked up as carbonate would be equivalent to about 12 mbar. This scenario is fairly unlikely, however, as reliable spectral data is available over the region and few additional carbonate outcrops have been observed.

In the third scenario, the extent of the carbonate unit is extrapolated to include the complete Isidis melt sheet (~270 times larger in size, ~1.8 \times 10^6 km²) and is altered to ~20 wt% carbonate to a depth of 1 km. In this case, the CO2 would be equivalent to ~150 mbar. This scenario is even more unlikely, and is primarily useful for showing that one must invoke extreme circumstances — without considering well-established observational constraints — to even approach an amount of CO2 sequestration that could provide a significant sink for ancient atmospheric gas or source for gas to emplace into the atmosphere.

The Nili Fossae carbonates were deposited before or contemporaneously with valley network formation. Given the abundance and identification of other alteration minerals (for example, phyllosilicates and sulfates) globally in remote sensing data¹⁹, late-formed carbonate-rock units are essentially non-existent on Mars²⁴. Other carbonate outcrops²⁵ are typically small and isolated exposures, commonly thought to have formed deeper in the crust and are thus more ancient materials (that is, prior to valley network formation) that have been exhumed by impact processes²⁷. Furthermore, these 'deep' carbonates are commonly associated with phyllosilicate materials, which indicates they are again weakly altered basaltic materials (that is, not massive carbonate rock), thus limiting their ultimate reservoir potential. While 'deep' carbonate-bearing materials may sequester significant amounts of CO₂ (potentially >1 bar), they are considered only part of a largely unknowable reservoir when the limited distribution²⁷ and poor formation constraints are considered. Unlike the Nili Fossae carbonate plains, the deeper crustal carbonates are unlikely to be able to be mobilized into the atmosphere and, despite their potential sequestration quantities, are not considered a legitimate source for replenishing the Martian atmosphere.

In short, given the current ability to see and identify carbonate outcrops in the remote sensing data, it is difficult to see how more than the equivalent of about 50 mbar of CO₂ could be sequestered globally²⁴. While there is no formal upper limit on the amount of carbonate deposits — one could always argue that they are preferentially sequestered in locations that we have not or cannot observe — such deposits are both geologically implausible and difficult or impossible to access for terraforming.

Loss to space. Atmospheric gas can be removed from the upper atmosphere to space by a combination of processes driven by extreme ultraviolet light and solar wind from the Sun. These processes are observed to be operating today^{28,29} and are inferred to have also operated in the past^{30,31}. The ongoing Mars Atmosphere and Volatile Evolution Mission (MAVEN) and the Mars Express



Fig. 2 | A high-resolution image from the HiRISE (High-Resolution Imaging Science Experiment), with a false-colour compositional image from the CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) superimposed on it. The Nili Fossae carbonate plains are the typical example for the sequestration of atmospheric CO2 in rocks on Mars. The false-colour CRISM image (red, 2.38 μm; green; 1.80 μm; and blue, 1.15 μm) highlights olivine- or carbonate-bearing rocks in green, olivine-bearing sands in yellow-brown, and dark-toned basalticolivine bedrock in purple. This image is overlain over a HiRISE image for morphologic context. In general the olivine-/carbonate-bearing units (green) are lighter-toned, highly fractured and commonly have olivine non-carbonate-bearing olivine sands, which are probably derived from the units themselves riding on top. The olivine-bearing but carbonate-poor units (purple) generally have a rougher texture and may in fact be the upper, unaltered unit of the carbonate-bearing rocks²⁰. Credit: NASA/JPL-Caltech/JHUAPL/Univ. of Arizona

spacecraft orbiting Mars have been exploring the processes operating in today's upper atmosphere and extrapolating this loss backwards through time.

Both $\rm H_2O$ and $\rm CO_2$ can be removed from the Mars atmosphere to space. Once photodissociated and ionized, O from either molecule can be removed by solar wind pick-up, sputtering by precipitating O ions, or energization by dissociative recombination. C can be lost by these same mechanisms, and H can be lost by thermal (Jeans') escape. The present O loss rate from all of these processes

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is about 1.5 kg O s⁻¹, as a global average²⁹. The loss rate earlier in history would have been greater, owing to the greater intensity of solar extreme ultraviolet radiation and solar wind. Based on the history of the Sun as derived from Sun-like stars, the integrated loss through time can be estimated based on observations from Mars Express and MAVEN. The amount of O lost could come from the equivalent of either a few tens of metres (global equivalent layer) of water, close to a bar of CO_2 , or a combination of both²⁹.

It is not possible to determine observationally whether the lost O comes from CO_2 or $\mathrm{H}_2\mathrm{O}$. However, we can estimate the amount of C lost to space independently by using the ratio of its isotopes. The ratio of $^{13}\mathrm{C}/^{12}\mathrm{C}$ in atmospheric CO_2 is enriched by about 65% relative to its magmatic source 32,33 . This fractionation occurs when loss to space preferentially removes the lighter isotope and leaves the remaining gas enriched in the heavier isotope. This degree of enrichment requires that a minimum of $\sim\!50\%$ of the C has been lost to space. Replenishment of CO_2 from outgassing associated with volcanism 34 would have put unfractionated gas into the atmosphere and diluted the atmospheric fractionation; this means that the loss early in history would have been greater and could have been as much as 90% of the atmospheric C.

Although these loss estimates are uncertain due to the difficulty in extrapolating back in time and the uncertainties in the composition of the early atmosphere, the observations and extrapolations indicate that the majority of the early atmosphere has been lost to space and that loss to space was the dominant process for removing the ancient CO_2 greenhouse atmosphere^{29,35}. Obviously, once gas has been lost to space, it is no longer available to be mobilized back into the atmosphere.

Can the CO₂ be mobilized back into the atmosphere?

Terraforming Mars would require mobilizing the CO_2 remaining on the planet and present in non-atmospheric reservoirs today, moving it from its current location back into the atmosphere.

The most accessible CO_2 reservoir is in the polar caps. The CO_2 ice there could be readily mobilized by heating of the deposits. This could be done by, for example, using explosives to raise dust into the atmosphere so that it would deposit on the polar caps, effectively decreasing their surface albedo and increasing the amount of absorbed solar energy³⁶. This could also be done by utilizing explosives to heat the polar ice directly, thus triggering sublimation (as suggested by Elon Musk³⁷). However, if the whole volume of polar-cap CO_2 were emplaced into the atmosphere, it would increase the pressure to less than 15 mbar total and, while about twice the current Martian atmospheric pressure, this is well below the needed ~1 bar.

Carbonate-bearing mineral deposits could be heated to release their CO₂. The typical decrepitation temperature for carbonates is around ~300 °C. This is high enough that it could not be achieved by solar heating from greenhouse warming, and would thus require some form of deposit processing. If we limited such processing to the Nili Fossae deposits, large-scale strip-mining would put probably less than 15 mbar and certainly no more than 150 mbar of CO₂ into the atmosphere, assuming a complete mobilization process. Although other deposits that hold more CO2 exist or could possibly be identified, processing those would be more difficult due to either their diffuse distribution or their currently unknown location and, therefore, their deep burial beneath the surface. There is no plausible scenario that is feasible today or in the near future by which sufficient volumes of carbonate-bearing material could be processed to release substantial quantities of CO2. Here, we take 12 mbar as the maximum plausible amount of CO₂ that could be released from carbonates.

Adsorbed gas could be readily mobilized by heating, including through incremental increases in temperature, but this process suffers from three significant problems. First, adsorbed gas constitutes

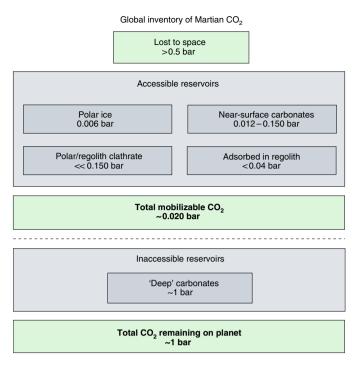


Fig. 3 | Summary of the remaining non-atmospheric reservoirs of CO_2 on Mars, including both those that can be readily mobilized and those that cannot be emplaced back into the atmosphere.

a diffuse, widespread distribution of CO₂. Thus, any processing to heat the regolith and release the gas would have to be carried out over a very widespread area. Releasing the full 40 mbar of CO₂ estimated to be in the regolith would require processing material over the entire planet to a depth of at least 100 m, again assuming a complete release of the CO₂. Second, although CO₂ could be released by even modest heating, the heating merely creates a new steady-state equilibrium between the adsorbed CO₂ and the CO₂ gas. This new balance would occur when only a small fraction of the CO2 had been put into gaseous form, due to the large fraction of gas that is present as adsorbed gas and the small fraction that is present as interstitial or atmospheric gas2. Third, the heating could be carried into the subsurface by thermal conduction, but this would take a time period as long as the thermal conduction time. For a 100-m-thick regolith, for example, it would take roughly 104 years for any increase in temperature to penetrate through the full volume. Thus, although possible, it is exceedingly difficult (and, in practice, impossible) to mobilize adsorbed CO₂ in significant quantities.

Regarding loss to space, once gas is lost it will very quickly become ionized and carried away by the solar wind. Once lost, it is gone and unable to come back.

Finally, we can look at the effects of outgassing of juvenile gas to the atmosphere. In theory, this can increase the atmospheric density. It has been suggested that a thick atmosphere could be built up if, for example, an artificial magnetic field created upstream of Mars could protect the planet from the solar wind stripping of gas, thereby allowing outgassing to build up the atmospheric thickness. Unfortunately, the rate of outgassing today is extremely low. As an example, today's volcanism rate is probably less than 0.1 km³ year $^{-1}$ (refs $^{39-41}$). For a nominal magmatic volatile abundance, this would result in a planet-wide outgassing rate of only 3×10^{-6} g cm $^{-2}$ year $^{-1}$. Even if loss to space could be cut to zero, the outgassed atmospheric volatiles would not match the current atmospheric mass for roughly 10 million years; most of this outgassed material would be $\rm H_2O$, which would condense into the polar regions and not increase atmospheric mass. Alternatively, impact-induced atmospheres 42

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may release some CO₂, although these events are transient and even at impact rates that are too high for the present epoch could only contribute a small fraction of the needed 1 bar. One could imagine redirecting asteroids to hit Mars and release volatiles, but the global distribution of the gas that is present would require covering Mars with impact craters; again, this is not feasible in practice.

Can the newly mobilized CO₂ produce significant warming?

Given the relatively small amounts of CO_2 that can be readily mobilized (Fig. 3), what is the resulting atmospheric pressure and how much warming would it produce? Although there is considerable uncertainty in an exact CO_2 pressure that could be produced, we will use 20 mbar as a representative maximum atmospheric pressure that could be achieved; while higher pressures are theoretically possible, there is no evidence to suggest that these larger amounts of CO_2 are available. While it may be straightforward to raise the pressure to 15 mbar (by mobilizing the CO_2 in the polar deposits), it would be extremely difficult to raise pressures above 20 mbar. Doing this would take exceedingly long timescales or substantial processing techniques that are beyond our current technology.

Models of greenhouse warming by CO_2 have not yet been able to explain the early warm temperatures that are thought to have been necessary to produce liquid water in ancient times. However, such models are much more straightforward at lower pressures and for the current solar output. For an atmosphere of 20 mbar, as an example, they predict a warming of less than 10 K. This is only a small fraction of the ~60 K warming necessary to allow liquid water to be stable. It would take a CO_2 pressure of about 1 bar to produce greenhouse warming that would bring temperatures close to the melting point of ice^{7,43}. This is well beyond what could be mobilized into the Mars atmosphere.

It is appropriate to discuss the significance of having pressures above the triple-point pressure of water, 6.11 mbar, as releasing even just the polar CO₂ could accomplish this. Achieving a pressure above this value is often given as the requirement that would allow the presence of liquid water. In fact, having a pressure above the triple-point pressure means only that liquid water at the surface would not boil at the coldest liquid temperature of 273 K; boiling occurs when the vapour pressure in equilibrium with the liquid at its extant temperature is greater than the atmospheric pressure. Liquid water still would evaporate, and would do so quickly into the dry Martian atmosphere. Pressure is only one of several requirements that must be met to achieve stable liquid water at the surface; temperatures above 273 K are also required. Even with 10 K of greenhouse warming, this would occur over a very small fraction of the surface and only during peak-temperature times of day. More importantly, liquid water would not be stable against evaporation, and the unsaturated Martian atmosphere would not allow significant precipitation to replenish surface liquid water (as occurs on Earth). Thus, liquid water will not be stable on the surface even if the pressure were to double or triple over present-day values.

Conclusions

There is not enough CO₂ left on Mars in any known, readily accessible reservoir, if mobilized and emplaced into the atmosphere, to produce any significant increase in temperature or pressure. Even if enough CO₂ were to be available, it would not be feasible to mobilize it; doing so would require processing a major fraction of the surface (analogous to regional- or planet-scale strip mining) to release it into the atmosphere, which is beyond present-day technology. Terraforming Mars is therefore not possible in the foreseeable future by utilizing CO₂ resources available on the planet. We anticipate being able to update the Martian CO₂ and H₂O inventories using data from the European Space Agency Trace Gas Orbiter (starting observations in orbit now), ExoMars rover (scheduled for launch in 2020) and the NASA Mars 2020 rover (also to be launched in 2020).

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Author contributions

B.M.J. carried out the atmospheric analyses and C.S.E. carried out the surface/subsurface analyses. Both authors contributed to the volatile inventory, integration and writing.

Competing interests

The authors declare no competing interests.

Additional information

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