Mars Atmosphere History and Surface Interactions

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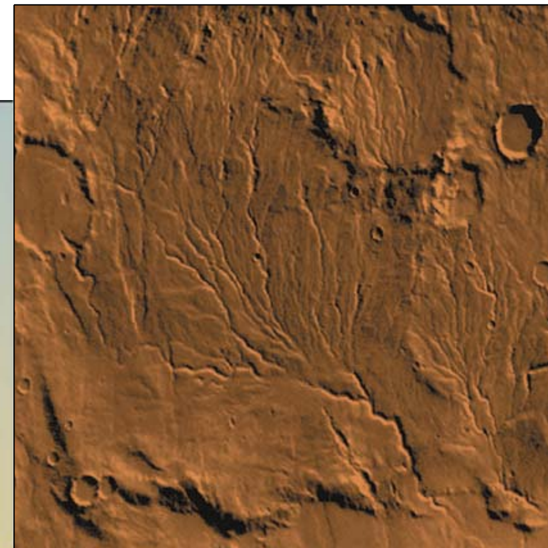


CHAPTER 15

A fundamental question about the surface of Mars is whether it was ever conducive to life in the past, which is related to the broader questions of how the planet's atmosphere evolved over time and whether past climates supported widespread liquid water. Taken together, geochemical data and models support the view that much of the original atmospheric inventory was lost to space before about 3.5 billion years ago. It is widely believed that before this time the climate would have needed to be warmer in order to produce certain geological features, particularly valley networks, but exactly how the early atmosphere produced warmer conditions is still an open question. For the last 3.5 billion years, it is likely that Mars has been cold and dry so that geologically recent outflow channels and gullies were probably formed by fluid release mechanisms that have not depended upon a warm climate.

1. Introduction

The most interesting and controversial questions about Mars revolve around the history of water. Because temperatures are low, the very thin Martian atmosphere can contain only trace amounts of water as vapor or ice clouds, but water is present as ice and hydrated minerals near the surface. Some geological structures resemble dust-covered glaciers or rock glaciers. Others strongly suggest surface water flows relatively recently as well as in the distant past. But the present climate does not favor liquid water near the surface. Surface temperatures range from about 140 to 310° K. Above freezing temperatures occur only under highly desiccating conditions in a thin layer at the interface between soil and atmosphere, and surface pressure over much of the planet is below the triple point of water [611 Pascals or 6.11 millibars (mbar)]. If liquid water is present near the surface of Mars today, it must be confined to thin adsorbed layers on soil particles or highly saline solutions. No standing or flowing liquid water, saline or otherwise, has been found.

Conditions on Mars may have been different in the past. Widespread geomorphic evidence for liquid flowing across the surface may indicate warmer and wetter past climates and massive releases of liquid water from subsurface aquifers. Hydrated minerals and sedimentary features interpreted to indicate liquid flow found by one of NASA's twin Mars Exploration Rovers (MERs), named *Opportunity*, in Terra Meridiani support the hypothesis that water once flowed at or near the surface, but the timing and circumstances of flow remain unknown. On the opposite side of Mars from *Opportunity*, instruments on the *Spirit Rover* have identified hydrated minerals in rocks in an apparent ancient volcanic setting in the Columbia Hills region of Gusev Crater. NASA's *Mars Odyssey* orbiter has also detected subsurface ice, mainly in high latitudes, while the *Mars Express* orbiter of the European Space Agency (ESA) has detected hydrated minerals in locations ranging from the northern circumpolar dunes to layered deposits in the equatorial regions. The extent and timing of the presence of liquid water are central to the question of whether microbial life ever arose and evolved on Mars.

Atmospheric volatiles are substances that tend to form gases or vapors at the temperature of a planet's surface. Consequently, such volatiles can influence climate. Here we review the current understanding of volatile reservoirs, the sources and sinks of volatiles, the current climate, and the evidence for different climates in the past. We focus on the hypothesis that there have been one or more extended warm and wet climate regimes in the past, the problems with that hypothesis, and the alternative possibility that Mars has had a cold, dry climate similar to the present climate over nearly all of its history, while still allowing for some fluid flow features to occur on the surface. Mars undergoes very large orbital variations (Milankovitch cycles), and the possible relevance of these differences to climate history will be discussed. Whether or not extended periods of warm, wet climates have occurred in the past, wind is certainly an active agent of surface modification at present and has probably been even more important in the past. We discuss the evidence for modification of the surface by wind erosion, burial, and exhumation and the resulting complications for interpreting Mars' surface history. We conclude with a brief overview of open questions.

2. Volatile Inventories and their History

2.1. Volatile Abundances

Mars' thin atmosphere is dominated by carbon dioxide (Table 1). In addition to the major gaseous components listed, the atmosphere contains a variable amount of water vapor (H_2O) up to 0.1%, minor concentrations of photodissociation products of carbon dioxide (CO_2) and water vapor (e.g., CO, O_2, H_2O_2, and O_3), and trace amounts of noble gases neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe). Recently, trace amounts of methane (CH_4) have also been identified, averaging ~10 parts per billion by volume, although currently a wide range of methane values have been reported, and these differences have yet to be reconciled. The differences may represent measurement errors or variability in the source of methane and its transport.

Volatiles that can play important roles in climate are stored in the regolith and near-surface sediments. Crude estimates of some of these are given in Table 2. Water is stored in the permanent north polar cap, north polar cap layered terrains, and layered terrains surrounding the South Pole, and as ice, hydrated salts, or adsorbed water in the regolith. The regolith is a geologic unit that includes fine dust, sand, and rocky fragments made up of the Martian soil together with loose rocks, but excluding bedrock. Although the surface of the residual northern polar cap is water ice, the ~5 km deep cap itself consists of a mixture of ice and fine soil with an unknown proportion of each. Layered south polar terrains may also contain an amount of water ice equivalent to a global ocean 20 m deep. Measurements of the energy of neutrons emanating from Mars into space have provided evidence for abundant water ice, adsorbed water, and/or hydrated minerals in the upper 1–2 m of regolith at high latitudes and in some low-latitude regions (Fig. 1). Cosmic rays enter the surface of Mars and cause neutrons to be ejected with a variety of energies depending on the elements in the subsurface and their distribution. Abundant hydrogen serves as a proxy for water and/or hydrated minerals. If water ice extends deep into the regolith, it could correspond to tens of meters of equivalent global ocean. It is also possible that Mars has liquid water aquifers beyond the depth where the temperature exceeds the freezing point (the so-called melting isotherm), but direct evidence is currently lacking.

Carbonate weathering of dust has occurred over billions of years in the prevailing cold dry climate, and as a consequence some CO_2 appears to have been irreversibly transferred from the atmosphere to carbonate weathered dust particles. The total amount depends on the global average

TABLE 1 Basic Properties of the Present Atmosphere

Average surface pressure	~6.1millibars (mbar), varying seasonally by ~30%
Surface temperature	Average 215 K, range: 140–310 K
Major gases	CO_2 95.3%, $^{14}N_2$ 2.6%, ^{40}Ar 1.6%
Significant atmospheric isotopic ratios relative to the terrestrial values	D/H = 5
	$^{15}N/^{14}N = 1.7$
	$^{38}Ar/^{36}Ar = 1.3$
	$^{13}C/^{12}C = 1.07$

TABLE 2 **Volatile Reservoirs**

Water (H_2O) Reservoir	*Equivalent Global Ocean Depth*
Atmosphere	10^{-5} m
Polar caps and layered terrains	5–30 m
Ice, adsorbed water, and/or hydrated salts stored in the regolith	0.1–100 m
Deep aquifers	Unknown
Carbon Dioxide (CO_2) Reservoir	*Equivalent Surface Pressure*
Atmosphere	~6 mbar
Carbonate in weathered dust	~200 mbar per 100 m global average layer of weathered dust
Adsorbed in regolith	<200 mbar
Carbonate sedimentary rock	~0 (at surface)
Sulfur Dioxide (SO_2) Reservoir	*Equivalent Global Layer Depth*
Atmosphere	0
Sulfate in weathered dust	~8 m per 100 m global average layer of weathered dust
Sulfate sedimentary rock reservoirs	Extensive, but not yet quantifiable

depth of dust. Some CO_2 is likely to be adsorbed in the soil also, but the amount is limited by competition for **adsorption** sites with water. Despite an extensive search from orbit, no carbonate sedimentary rock outcrops have been identified down to a spatial resolution of about 100 m.

Table 2 also lists sulfates. Although there are no detectable sulfur-containing gases in the atmosphere at present, sulfur is an important volatile for climate because it may have briefly resided in the atmosphere in the past. Measurements by NASA's *Mars Pathfinder* and *Viking* landers showed that sulfur is a substantial component of soil dust (~7–8% by mass) and surface rocks. Hydrated sulfate salt deposits have also been recently identified in numerous deposits in the Martian tropics from near-infrared spectral data on the European Space Agency's *Mars Express* spacecraft. Observed sulfate minerals include gypsum ($CaSO_4{\cdot}2H_2O$) and kieserite ($MgSO_4{\cdot}H_2O$), while jarosite has been found by the *Opportunity* rover. [Jarosite is $XFe_3(SO_4)_2(OH)_6$, where X is a singly charged species such as Na^+, K^+, or hydronium (H_3O^+).] Anhydrous sul-

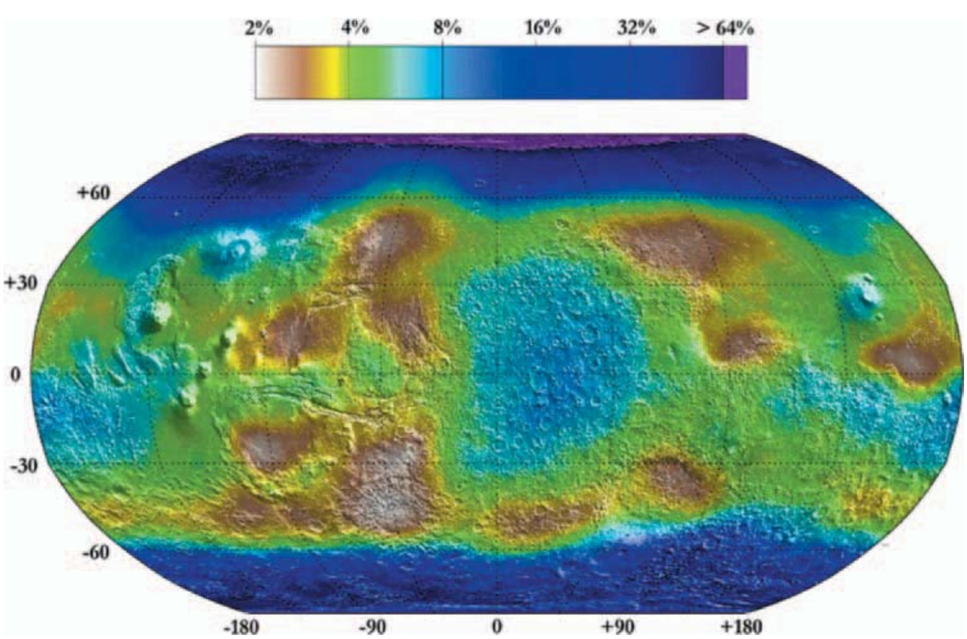


FIGURE 1 Water-equivalent hydrogen content of subsurface water-bearing soils derived from the *Mars Odyssey* neutron spectrometer. (From Feldman et al., 2004, *J. Geophys. Res.* **109**, E09006, doi:10.1029/2003JE002160.)

fates, such as anhydrite ($CaSO_4$), are also likely to be present but would give no signature in the spectral region studied by *Mars Express*.

Evidence of volatile abundances also comes from analysis of a certain class of meteorites, the Shergotite, Nahkla, and Chassigny or SNC meteorites. [*See* METEORITES.] These meteorites are known to be of Martian origin from their relatively young ages, igneous composition, unique oxygen isotope ratios, and gaseous inclusions whose elemental and isotopic compositions closely match the present Martian atmosphere. Ages of crystallization of these basaltic rocks (i.e., the times when the rocks solidified from melts) range from ∼1.35 billion years to ∼0.16 million years. Many of the SNC meteorites contain salt minerals, up to 1% by volume, which include halite (NaCl), gypsum, anhydrite, and carbonates of calcium, magnesium, and iron. The bulk meteorite compositions are generally dry, 0.04–0.4 weight percent water. This is consistent with a relatively dry Martian mantle (<1.8 weight percent water for preeruptive magmas). On the other hand, the Martian mantle is inferred to be sulfur-rich compared with Earth (estimated as ∼0.025 wt% sulfur). Another type of Martian meteorite, identified as ALH84001, is a unique sample of very early crust, ∼4.5 billion years old, which contains about 1% by volume of distributed, 3.9-billion-year-old carbonate. ALH84001 has been heavily studied because of a controversial investigation in which four features of the meteorite were argued to be of possible biological origin: the carbonates, traces of organic compounds, 0.1-micrometer-scale structures identified as microfossils, and crystals of the mineral magnetite (Fe_3O_4) (McKay et al; see Bibliography). However, the biological nature of all of these features has been strongly disputed, and many scientists have suggested that they were formed by abiological processes.

2.2. Sources and Losses of Volatiles

Volatile delivery began during formation of the planet. Planetary evolution models indicate that impacting bodies that condensed from the evolving solar nebula near Mars' orbit were highly depleted relative to solar composition in the atmospheric volatiles—carbon, nitrogen, hydrogen, and noble gases. Nonetheless, formation of Jupiter and the outer planets would have gravitationally deflected volatile-rich asteroids from the outer solar system and **Kuiper Belt** comets to the inner solar system. Analyses of the compositions of the SNC meteorites indicate that Mars acquired a rich supply of the relatively volatile elements during its formation. However, carbon, nitrogen, and noble gases are severely depleted compared with Earth and Venus, apparently because loss processes efficiently removed these elements from Mars, as they did for hydrogen.

Two processes, **hydrodynamic escape** and impact escape, must have removed much of any early Martian atmosphere. Hydrodynamic escape blowoff occurs when hydrogen flowing outward in a planetary wind (analogous to the solar wind) entrains and removes other gases. Since all atmospheric species can be entrained in this process, it is not very sensitive to atomic mass. Intense solar ultraviolet radiation and solar wind particle fluxes provide the energy needed to drive hydrodynamic escape. These fluxes would have been several orders of magnitude larger than at present during the first $\sim 10^7$ years after planet formation as the evolving Sun moved toward the **main sequence**. Although the early Sun was 25–30% less luminous overall, studies of early stars suggest that the early Sun was rotating more than ten times faster than at present, which would have caused more magnetic activity, associated with over a hundred times more emission in the extreme ultraviolet portion of the spectrum than today. Consequently, hydrodynamic escape would have been a very efficient atmospheric removal mechanism if hydrogen had been a major atmospheric constituent during this period.

The amount of hydrogen in the early atmosphere of a terrestrial planet depends on the interactions between iron and water during accretion and separation of the core and mantle. If water brought in by impacting bolides could mix with free iron in this period, it would oxidize free iron, releasing large amounts of hydrogen to the atmosphere and fostering hydrodynamic escape. Interior modeling constrained by Mars' gravitational field and surface composition together with analyses of the composition of the SNC meteorites indicates that the mantle is rich in iron oxides relative to Earth, consistent with the hypothesis that a thick hydrogen-rich atmosphere formed at this early stage. It has been suggested that hydrodynamic escape removed the equivalent of an ocean at least 1 km deep together with most other atmospheric volatiles from Mars, although this estimate is based on extrapolation from the current value of the deuterium–hydrogen ratio (D/H), which is uncertain because D/H may reflect geologically recent volatile exchange rather than preferential loss of hydrogen compared to deuterium over the full history of Mars. Comets arriving after the completion of hydrodynamic escape may have brought in most of the atmospheric volatiles in the current inventory.

Mars is also vulnerable to impact-induced escape. Large impacting bodies release enough energy to accelerate all atmospheric molecules surrounding the impact site to speeds above the escape velocity. A large fraction of these fast molecules would escape. Since this mechanism is very sensitive to the gravitational acceleration, impact-induced escape would have been far more efficient on Mars than on Earth. The early history of the inner solar system is characterized by a massive flux of large asteroids and comets, many of which would have been capable of causing impact-induced escape at Mars. Based on dating of lunar rocks and impact features, this "massive early bombardment" is known to have declined rapidly after planet formation, and it terminated in the interval 4.0–3.5 Ga. The period on Mars

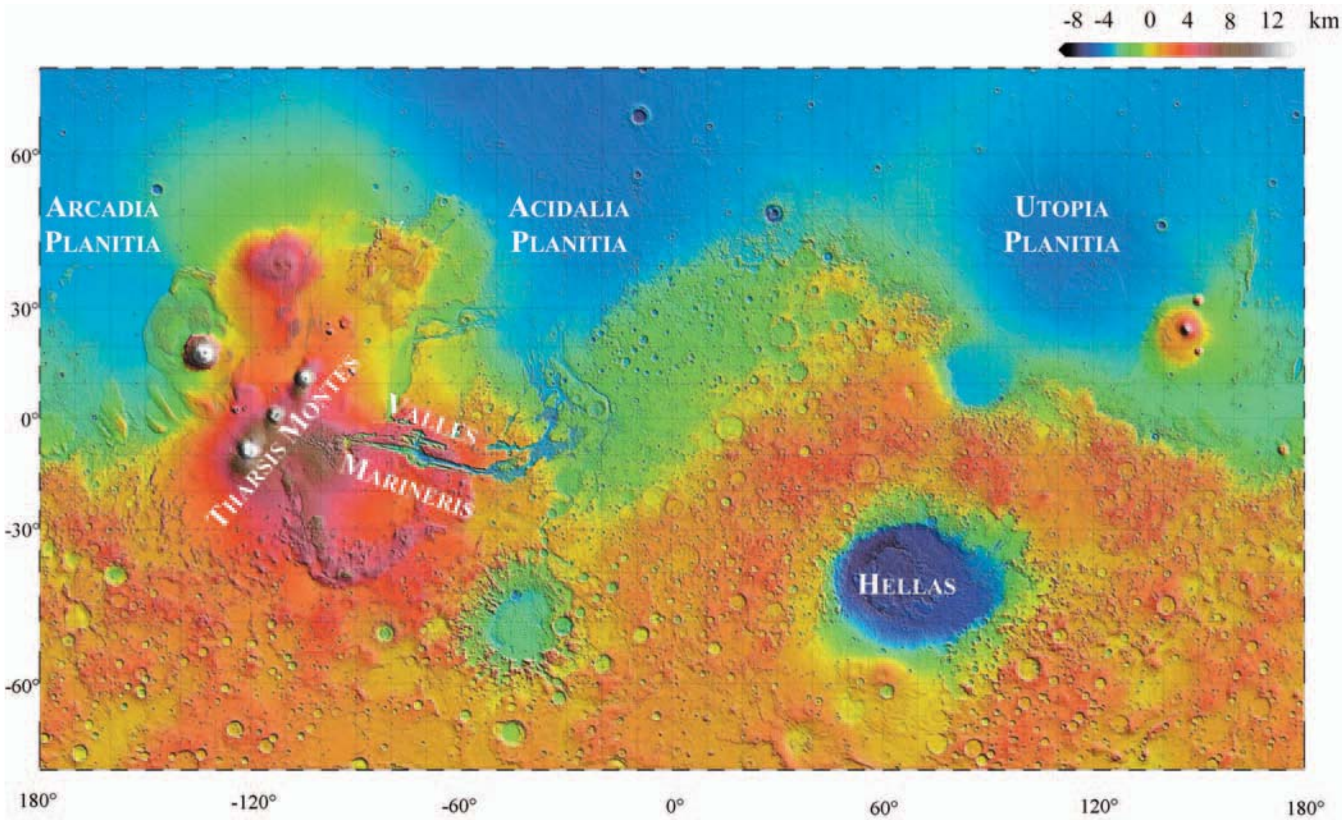


FIGURE 2 Elevation map of Mars derived from the Mars Orbiter Laser Altimeter (MOLA) on NASA's *Mars Global Surveyor*, with some major features labeled. (NASA/MOLA Science Team.)

prior to about 3.5 Ga is known as the Noachian epoch, so that massive bombardment effectively ceased around the end of the Noachian.

The late stage of massive early bombardment has left an obvious imprint in the form of impact basins (e.g., Hellas) and large impact craters that are still obvious features of roughly half of the surface (Fig. 2). More subtle "ghost" craters and basins that have been largely erased by erosion and/or filling in the relatively smooth northern plains provide further evidence of Noachian impact bombardment. Calculations suggest that impact escape should have removed all but ~1% of an early CO_2 rich atmosphere (Carr, 1996, p. 141; see Bibliography). Water in an ocean or in ice would have been relatively protected, however, and the efficiency of its removal by massive early bombardment is unknown.

What was the size of Mars' volatile reservoirs at the end of the massive impact bombardment period ~3.5 billion years ago? The isotopic ratios $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{38}Ar/^{36}Ar$, and $^{15}N/^{14}N$ are heavy compared with the terrestrial ratios (see Table 2). This has been interpreted to indicate that 50–90% of the initial reservoirs of CO_2, N_2, and cosmogenic argon may have been lost over the past 3.5 billion years by mass-selective **nonthermal escape** from the upper atmosphere (mainly **sputtering** produced by the impact of the solar wind on the upper atmosphere). Considering the possible current reservoirs of CO_2 in Table 1, the resulting CO_2 available 3.5 billion years ago could have been as much as ~1 bar and as little as a few tens of millibars.

Another approach to estimating the CO_2 abundance at the end of massive impact bombardment is based on the abundance of ^{85}Kr in the present atmosphere. Since this gas is chemically inert and too heavy to escape after the end of the period of massive impact bombardment, its current abundance probably corresponds closely to the abundance at the end of massive impact bombardment. Since impact escape would have effectively removed all gases independent of atomic mass, the ratio of ^{85}Kr abundance to C in plausible impacting bodies (Kuiper Belt comets or outer solar system asteroids) can then yield estimates of the total available CO_2 reservoir at the end of the Noachian. The corresponding atmospheric pressure, if all CO_2 were in the atmosphere, would be only ~0.1 bar, in the lower range of estimates from the isotopic and escape flux analysis. This low estimate is consistent with the low modern nitrogen abundance after allowing for mass selective escape as indicated by the high ratio $^{15}N/^{14}N$ (Table 2). But early nitrogen abundance estimates are sensitive to uncertainties in modeling escape.

As mentioned previously, slow carbonate weathering of atmospheric dust has also removed CO_2 from the atmosphere. This irreversible mechanism may account for the fate of a large fraction of the CO_2 that was available in the late Noachian. Some CO_2 may also reside as adsorbed CO_2 in the porous regolith (Table 2). It has long been speculated that much of the CO_2 that was in the early atmosphere got tied up as carbonate sedimentary deposits beneath ancient water bodies. However, the failure to find carbonate sediments, in contrast to discovery of widespread sulfate sedimentary deposits, makes the existence of a large sedimentary carbonate reservoir doubtful (see further discussion later).

Escape of water in the form of its dissociation products H and O takes place now and must have removed significant amounts of water over the past 3.5 billion years. Isotopic ratios of D/H and $^{18}O/^{16}O$ in the atmosphere and in SNC meteorites and escape flux calculations provide rather weak constraints on the amount that has escaped over that period. Upper bounds on the estimates of water loss range up to 30–50 m of equivalent global ocean. These amounts are roughly comparable to estimates of the amounts currently stored in the polar caps and regolith.

Sulfur is not stable in the Martian atmosphere in either oxidized or reduced form, but significant amounts must have been introduced into the atmosphere by volcanism. Formation of the Tharsis ridge volcanic structure, believed to have been in the late Noachian period, must have corresponded with outgassing of large amounts of sulfur as well as water from the mantle and crust. Martian soils contain up to 7–8% by weight of sulfur in the form of sulfates, and Martian rocks are also rich in sulfates. SNC meteorites are ~5 times as rich in sulfur as in water. It is likely that the regolith contains more sulfur than water. The volatile elements chlorine and bromine are also abundant in rocks and soils, but more than an order of magnitude less so than sulfur.

An important observation in SNC meteorites is that sulfur and oxygen isotopes in sulfates are found in relative concentrations that are mass-independently fractionated. Most kinetic processes fractionate isotopes in a mass-dependent way. For example, the mass difference between ^{34}S and ^{32}S means that twice as much fractionation between these isotopes is produced as between ^{33}S and ^{32}S in a mass-dependent isotopic discrimination process such as diffusive separation. Mass-independent fractionation (MIF) is a deviation from such proportionality. MIF is found to arise due to the interaction of ultraviolet radiation with atmospheric gases in certain photochemical processes. On Earth, the MIF of oxygen in sulfates in the extraordinarily dry Atacama Desert is taken to prove that these sulfates were deposited by photochemical conversion of atmospheric SO_2 to submicron particles and subsequent dry deposition. The MIF signature in sulfates in SNC meteorites suggests that a similar process may have produced these sulfates on Mars.

Recent discovery of methane in the atmosphere is a major surprise. Methane is removed from the atmosphere by photochemical processes that ultimately convert it to carbon dioxide and water, with a lifetime in the atmosphere of only a few hundred years. The maintenance of significant amounts of methane in the atmosphere therefore requires significant sources to replenish it. At present, sources of methane remain a matter of speculation. On Earth, methane production is almost entirely dominated by biological sources. Biogenic methane production cannot be ruled out for Mars, but abiotic production from geothermal processes (known as thermogenic methane) must be considered less speculative at this stage.

3. Present and Past Climates

3.1. Present Climate

The thin, predominantly carbon dioxide atmosphere produces a small greenhouse effect, raising the average surface temperature of Mars only about 5°C above the temperature that would occur in the absence of an atmosphere. Carbon dioxide condenses out during winter in the polar caps, causing a seasonal range in the surface pressure of about 30%. There is a small seasonal residual CO_2 polar cap at the South Pole but this cap is quite thin, and it probably represents a potential increase in carbon dioxide pressure of <2 mbar if it were entirely sublimated into the atmosphere. The atmospheric concentration of water vapor is controlled by saturation and condensation and so varies seasonally and probably daily as well. Water vapor exchanges with the polar caps over the course of the Martian year, especially with the north polar cap. During summer, the central portion of the cap surface is water ice, a residual left after sublimation of the winter CO_2 polar cap. Water vapor sublimates from this surface in northern spring to early summer, and is transported southward, but most of it is precipitated or adsorbed at the surface before it reaches southern high latitudes.

In addition to gases, the atmosphere contains a variable amount of icy particles that form clouds and dust. Dust loading can become quite substantial, especially during northern winter. Transport of dust from regions where the surface is being eroded by wind to regions of dust deposition occurs in the present climate. Acting over billions of years, wind erosion, dust transport, and dust deposition strongly modify the surface (see Section 3.5). Visible optical depths can reach ~5 in global average and even more in local dust storms. A visible optical depth of 5 means that direct visible sunlight is attenuated by a factor of $1/e^5$, which is roughly 1/150. Much of the sunlight that is directly attenuated by dust reaches the surface as scattered diffuse sunlight. Median dust particle diameters are ~1 micrometer, so this optical depth corresponds to a column dust mass

~3 mg/m^2. Water ice clouds occur in a "polar hood" around the winter polar caps and over low latitudes during northern summer, especially over uplands. Convective carbon dioxide clouds occur at times over the polar caps, and they occur rarely as high-altitude carbon dioxide cirrus clouds.

Orbital parameters cause the cold, dry climate of Mars to vary seasonally in somewhat the same way as intensely continental climates on Earth. The present tilt of Mars' axis (25.2°) is similar to that of Earth (23.5°), and the annual cycle is 687 Earth days long or about 1.9 Earth years. Consequently, seasonality bears some similarity to that of the Earth, but Martian seasons last about twice as long on average. However, the **eccentricity** of Mars' orbit is much larger than Earth's (0.09 compared with 0.015), and perihelion (the closest approach to the Sun) currently occurs near northern winter solstice. As a consequence, asymmetries between northern and southern seasons are much more pronounced than on Earth. Mars' rotation rate is similar to Earth's, and like Earth, the atmosphere is largely transparent to sunlight so that heat is transferred upward from the solid surface into the atmosphere. These are the major factors that control the forces and motions in the atmosphere (i.e., atmospheric dynamics). Consequently, atmospheric dynamics of Mars and Earth are similar. Both are dominated by a single meandering midlatitude jet stream, strongest during winter, and a thermally driven **Hadley circulation** in lower latitudes. The Hadley circulation is strongest near the solstices, especially northern winter solstice, which is near perihelion, when strong rising motion takes place in the summer (southern) hemisphere and strong sinking motion occurs in the winter (northern) hemisphere.

Mars lacks an ozone layer, and the thin, dry atmosphere allows very short wavelength ultraviolet radiation to penetrate to the surface. In particular, solar ultraviolet radiation in the range 190–300 nm, which is largely shielded on Earth by the ozone layer, can reach the lower atmosphere and surface on Mars. This allows water vapor dissociation close to the Martian surface (H_2O + ultraviolet photon → H + OH). As a consequence of photochemical reactions, oxidizing free radicals (highly reactive species with at least one unpaired electron, such as OH or HO_2) are produced in near-surface air. In turn, any organic material near the surface rapidly decomposes, and the soil near the surface oxidizes. These conditions as well as the lack of liquid water probably preclude life at the surface on present-day Mars.

Although liquid water may not be completely absent from the surface, even in the present climate it is certainly very rare. This is primarily because of the low temperatures. Even though temperatures of the immediate surface rise above freezing at low latitudes near midday, above freezing temperatures occur only within a few centimeters or millimeters on either side of the surface in locales where the relatively high temperatures would be desiccating. A second factor is the relatively low pressure. Over large regions of Mars, the pressure is below the triple point at which exposed liquid water would rapidly boil away.

Because the present atmosphere and climate of Mars appear unsuitable for the development and survival of life, at least near the surface, there is great interest in the possibility that Mars had a thicker, warmer, and wetter atmosphere in the past. These possibilities are constrained by the volatile abundances, estimates of which are provided in Table 2.

3.2. Past Climates

Three types of features strongly suggest that fluids have shaped the surface during all epochs—Noachian (prior to about 3.5 billion years ago), Hesperian (roughly 3.5 to 2.5–2.0 billion years ago), and Amazonian (from roughly 2.5 to 2.0 billion years ago to the present). In terrains whose ages are estimated on the basis of crater distributions and morphology to be Noachian to early Hesperian, "valley network" features are abundant (Fig. 3). The morphology of

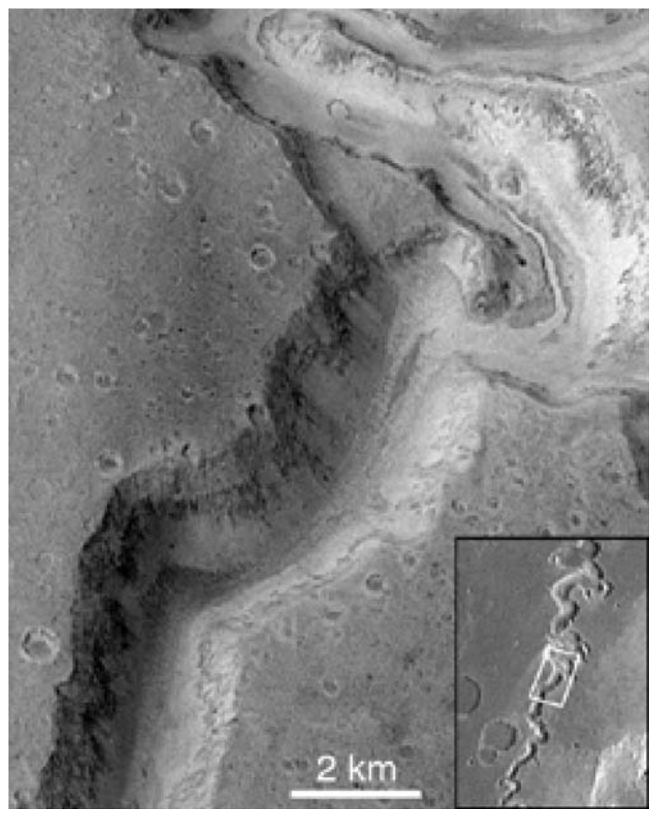


FIGURE 3a An image of Nanedi Vallis (5.5°N, 48.4°W) from the Mars Orbiter Camera (MOC) on NASA's *Mars Global Surveyor* spacecraft. The sinuous path of this valley at the top of the image is suggestive of meanders. In the upper third of the image, a central channel is observed and large benches indicate earlier floor levels. These features suggest that the valley was incised by fluid flow. (The inset shows a lower-resolution *Viking Orbiter* image for context.) (From image MOC-8704, NASA/Malin Space Science Systems.)

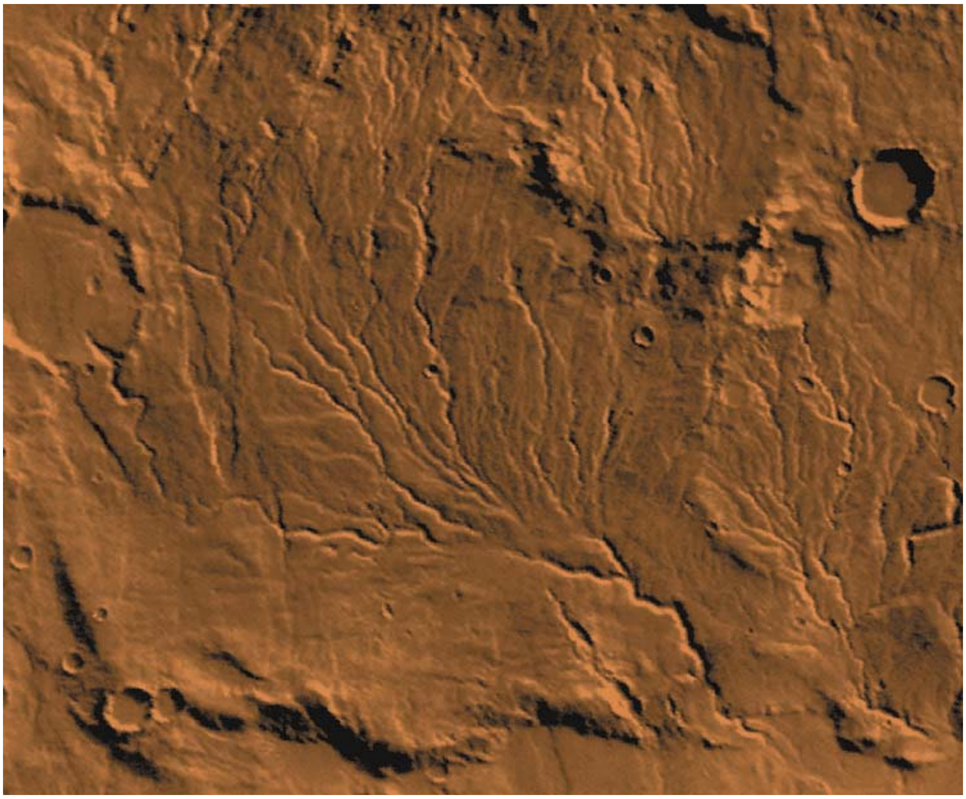


FIGURE 3b A valley network, centered near 42°S, 92°W. The image is about 200 km across. This false color mosaic was constructed from the *Viking* Mars Digital Image Map. (From NASA/Lunar and Planetary Institute Contribution No. 1130.)

valley networks is very diverse, but most consist of dendritic networks of small valleys, often with V-shaped profiles that have been attributed to surface water flows or groundwater sapping. Although generally much less well developed than valley network systems produced by fluvial erosion on Earth, they are suggestive of widespread precipitation and/or subsurface water release (groundwater sapping) that would have required a much warmer climate, mainly but not entirely, contemporaneous with termination of massive impact events at the end of the Noachian (~3.5 billion years ago). In Fig. 3, we show two very different examples of valley network features. Fig. 3a is a high-resolution image that shows a valley without tributaries in this portion of its reach (although some tributary channels are found farther upstream), but its morphology strongly suggests repeated flow events. Figure 3b shows a fairly typical valley network at comparatively low resolution. Such images, from the *Viking* spacecraft, suggested a resemblance to drainage systems on Earth. However, at high resolution, morphology of the individual valleys in this system does not strongly suggest liquid flow, possibly due to subsequent modification of the surface.

A second class of features suggesting liquid flow is a system of immense channels apparently produced by fluid activity during the Hesperian to early Amazonian epochs (Figs. 4, 5). These features, referred to as outflow channels (or catastrophic outflow channels), are sometimes more than 100 km in width, up to ~1000 km in length, and as much as several kilometers deep. They are found mainly in low latitudes (between 20° north and south) around the periphery of major volcanic provinces such as Tharsis and Elysium, where they debauch northward toward the low-lying northern plains. The geomorphology of these channels has been compared with the scablands produced by outwash floods in eastern Washington State from ice age Lake Missoula, but if formed by flowing water, flow volumes must have been larger by an order of magnitude or more. It has been estimated that the amount of water required to produce them is equivalent to a global ocean at least 50 m deep. Many of these channels originate in large canyons or jumbled chaotic terrain that was evidently produced by collapse of portions of the plateau surrounding Tharsis. The origin of these features is unknown, but the dominant hypothesis is that the outflow channels were generated by catastrophic release of water from subsurface aquifers or rapidly melting subsurface ice. If water was released by these flows, its fate is unknown, although a number of researchers have proposed that water pooled in the northern plains and may still exist as ice beneath a dust-covered surface.

Gullies are a third piece of evidence and suggest that water has flowed in the very recent geologic past across the surface. Such features are commonly found on poleward-facing sloping walls of craters, plateaus, and canyons, mainly at southern midlatitudes (~35–55°S) (Fig. 6). These gullies typically have well-defined alcoves above straight or

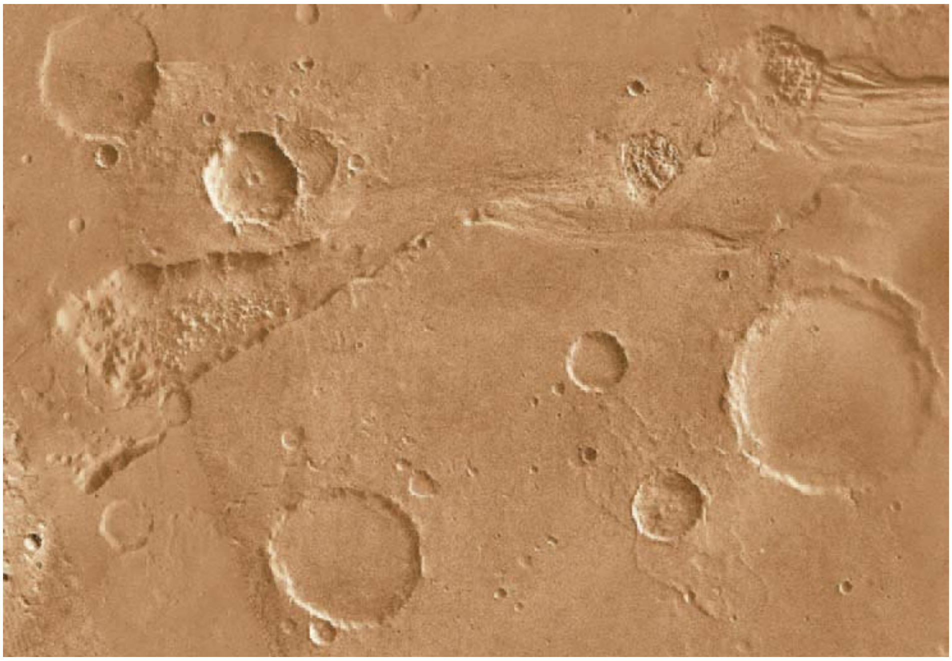


FIGURE 4 The head of the channel Ravi Vallis, about 300 km long. An area of chaotic terrain on the left of the image is the apparent source region for Ravi Vallis, which feeds into a system of channels that flow into Chryse Basin in the northern lowlands of Mars. Two further such regions of chaotic collapsed material are seen in this image, connected by a channel. The flow in this channel was from west to east (left to right). This false color mosaic was constructed from the *Viking* Mars Digital Image Map. (From NASA/Lunar and Planetary Institute Contribution No. 1130.)

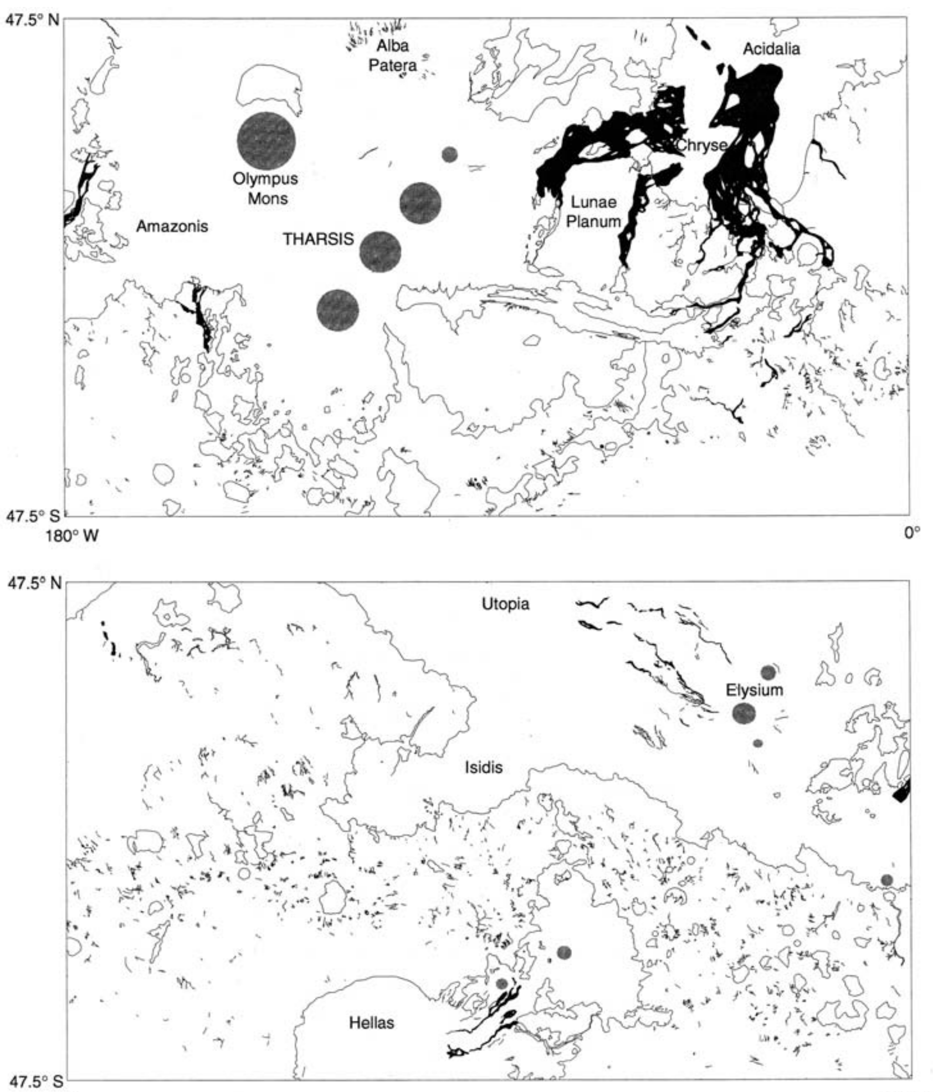


FIGURE 5 The distribution of outflow channels and valleys over ±47.5° latitude. The upper panel shows the western hemisphere and the lower panel the eastern hemisphere. Outflow channels are marked in black and drain into four regions: Amazonis and Arcadia, Chryse and Acidalia, Hellas, and Utopia; valley networks are marked as finer features. Volcanoes are shaded gray except for Alba Patera so that valleys on its flanks are not obscured. A thin line marks the boundary between Noachian and Hesperian units. (From Carr, 1996.)

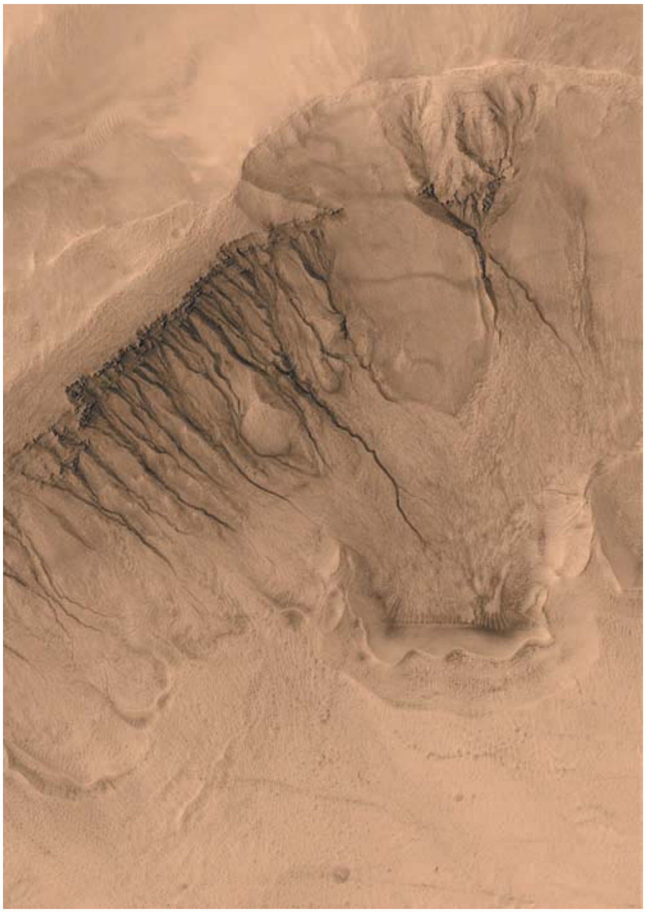


FIGURE 6 Gullies in the northern wall of an impact crater in Terra Sirenum at 39.1°S, 166.1°W. The image is approximately 3 km across. (Synthetic color portion of Mars Orbiter Camera image E11-04033; NASA/Malin Space Science Systems.)

meandering channels that terminate in debris aprons. Their setting on steep slopes and their morphology suggest that they were produced in the same way as debris flows in terrestrial alpine regions. These flows are typically produced by rapid release of water from snow or ice barriers and consist typically of ∼75% rock and silt carried by ∼25% water. Several possible mechanisms have been suggested to generate local release of water or brines in debris flows from ice-rich layers on Mars (including slow heating variations due to Milankovitch cycles—see discussion later). Evidence for the active influence of Milankovitch-type cycles includes a thin, patchy mantle of material, apparently consisting of cemented dust, that has been observed within a 30–60° latitude band in each hemisphere, corresponding to places where near-surface ice has been stable in the last few million years due to orbital changes. The material is interpreted to be an atmospherically deposited ice–dust mixture from which the ice has sublimated. Gullies, which are probably associated with ice from past climate regimes, are found within these same latitude bands. Consequently, gullies do not require an early warm climate or enormous low-latitude reservoirs of subsurface water or ice, so we will not discuss gullies further.

The three geomorphic features listed previously (valleys, channels, and gullies) provide for a reasonably direct attribution for the cause of erosion. For completeness, we mention that relatively high erosion rates are evident in the Noachian from craters with heavily degraded rims and infilling or erosion. Some models of the degradation of craters suggest that the erosion and deposition was caused by fluvial activity, at least in part. However, the interpretation is necessarily complex because the image data suggests that craters were also degraded or obscured by impacts, eolian transport, mass wasting, and, in some places, airfall deposits such as volcanic ash or impact ejecta.

3.3. Mechanisms for Producing Warm Climates

Despite extensive investigation, the causes of early warm climates, if indeed they have existed since the late Noachian, remain to be identified. Here we review several possibilities.

1. Carbon dioxide greenhouse. An appealing suggestion put forward after the *Mariner 9* orbiter mission in 1972 is that the early atmosphere contained much more CO_2 than it does now. The idea is that substantial CO_2 caused an enhanced greenhouse effect through its direct infrared radiative effect and the additional greenhouse effect of increased water vapor, which the atmosphere would have held at higher temperatures. Applied to the late Noachian period of valley network formation, this theory runs into difficulty because of the lower solar output at ∼3.5 billion years ago (∼75% of present output), and consequent large amount of CO_2 required to produce an adequate CO_2–H_2O greenhouse effect. At least several bars of CO_2 would have been required to produce widespread surface temperatures above freezing. However, such thick atmospheres are not physically possible because CO_2 condenses into clouds at ∼1 bar. It has been suggested that such CO_2 ice clouds could have contributed to the greenhouse effect to the degree that made up for the loss of CO_2 total pressure. However, recent studies indicate that CO_2 ice clouds could not warm the surface above freezing because CO_2 particles would grow rapidly and precipitate, leading to rapid cloud dissipation. Warming may also be self-limiting: by heating the air, the clouds could cause themselves to dissipate.

If a massive CO_2 atmosphere ever existed, it could have persisted for tens of millions of years, but it would have eventually collapsed due to removal of the CO_2 by solution in liquid water and subsequent formation of carbonate sediments. However, despite extensive efforts, not a single outcrop of carbonate sediments has been found*. The absence occurs even in areas in which water is interpreted to have flowed (the *Opportunity* rover site) and in which extensive erosion would be expected to have exposed carbonate

*Since writing, small ~10 km^2 outcrops of (possibly hydrothermal) Mg-carbonate were identified in Nili Fossae (Ehlmann et al., 2008. *Science* 322, 1828).

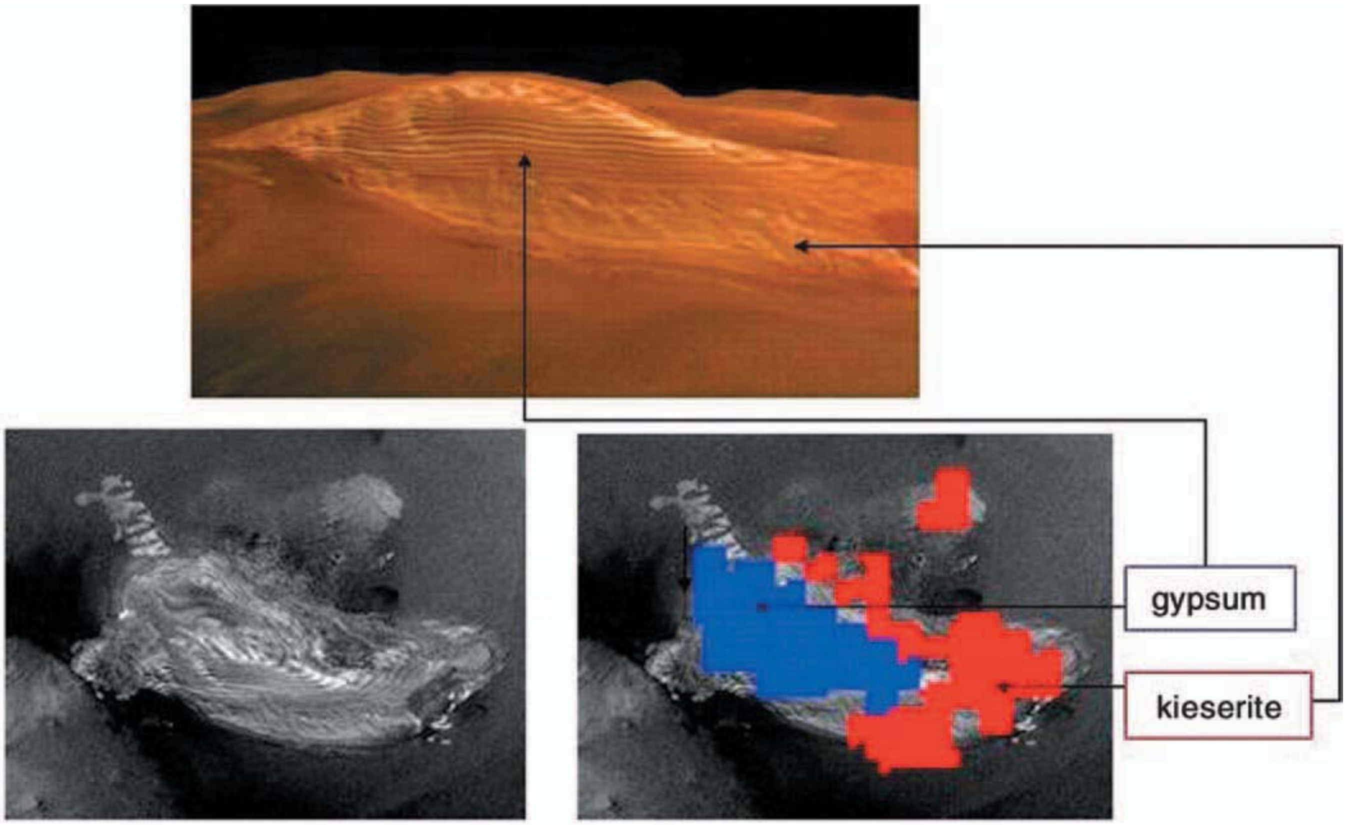


FIGURE 7 The upper three-dimensional view shows a 2.8-km-tall and 40-km-long sulfate-rich layered deposit that lies within Juventae Chasma, a deep chasm some 500 km north of Valles Marineris. Below are maps of sulfates on the deposit obtained by a near-infrared spectrometer, OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité), on the Mars Express spacecraft. Gypsum (blue) dominates in the layered bench-cliff topography, while kieserite (red) lies around and below. (Reprinted with permission from Bibring et al., 2005, *Science* **307,** 1576–1581. Copyright AAAS.)*

sediments buried beneath regolith. In contrast, sulfate sedimentary deposits are widespread in the tropics (Fig. 7), some in terrains that have been exhumed by wind erosion. In retrospect, it is not surprising that carbonate reservoirs have not been found. In the presence of abundant sulfuric acid, carbonate would be quickly converted to sulfate with release of CO_2 to the atmosphere, where it would be subject to various loss processes discussed earlier.

Although a future discovery of a large carbonate sediment reservoir cannot be ruled out, it now seems doubtful, and the amount of CO_2 available seems inadequate to have produced a warm enough climate to account by itself for the valley networks by surface runoff and/or groundwater sapping in the late Noachian.

2. Impact heating. The largest asteroid or comet impacts would vaporize large quantities of rock. Vaporized rock would immediately spread around the planet, condense, and, upon reentry into the atmosphere, would flash heat the surface to very high temperature. This would quickly release water from surface ice into the atmosphere. Upon precipitation, this water could produce flooding and rapid runoff over large areas. Water would be recycled into the atmosphere as long as the surface remained hot, anywhere from a few weeks to thousands of years depending on impact size. It has been proposed that this is an adequate mechanism for producing most of the observed valley networks. Although a very extended period of warm climate would not be produced this way, repeated short-term warm climate events could have occurred during the late Noachian to early Hesperian. Detailed questions of timing of large impact events and formation of the valley network features needed to test this hypothesis remain to be resolved, but impact heating must have released ice to the atmosphere and caused subsequent precipitation at some times during the Noachian.

3. Sulfur dioxide greenhouse. The high abundance of sulfur in surface rocks and dust as well as in the Martian meteorites suggests that Martian volcanism may have been very sulfur-rich. In contrast to Earth, Martian volcanoes may have released sulfur in amounts equal to or exceeding water vapor releases. In the atmosphere in the presence of water vapor, reduced sulfur would rapidly oxidize to SO_2

*Since writing, it has been argued that the spectra should be interpretated as showing indeterminate polyhydrated sulfates and not gypsum. (Kuzmin et al., Planet. Space Sci. 2009. doi:10.1016/j.pss.2008.12.008.)

and perhaps some carbonyl sulfide, COS. Sulfur dioxide is a powerful greenhouse gas, but it would dissolve in liquid water and be removed from the atmosphere by precipitation very rapidly. SO_2 could only have been a significant greenhouse gas if it raised the average temperature to near freezing, making it easier for perturbations such as impacts to warm the climate. In this way, with a sufficient SO_2 volcanic flux, the amount of SO_2 would perhaps have been self-limiting. Detailed constraints on possible early SO_2 greenhouse conditions, including persistence and timing have yet to be worked out.

4. Methane-aided greenhouse. Methane is also a powerful greenhouse gas, but because of its instability in the atmosphere, it has not seemed an attractive option for contributing to an early warm climate until very recently. With the apparent detection of methane in the current atmosphere and the lack of definitive identification of its sources, the possibility of an early methane-aided greenhouse warrants further investigation. However, the required amount of methane to warm early Mars would require a global methane flux from the surface of Mars similar to that produced by the present-day biosphere on Earth.

5. Mechanisms for producing large flow features in cold climates. Although some precipitation must have occurred due to impacts and short-lived greenhouse warming is plausible, other factors may have produced valley network and outflow channel features. Hydrated sulfates are widespread at the surface today and must have been widespread on early Mars as well. Volcanic or impact heating could have caused rapid dehydration of sulfates and flow of the resulting brines across the surface. Under some circumstances, catastrophic dehydration of massive hydrated sulfate deposits could have occurred, and resulting high volume flows could have produced outflow channel features. It is also possible that fluids other than water or brine produced the outflow channels. For example, the abundance of sulfur indicated in mantle and crustal rocks suggests that Martian volcanism may have produced very fluid sulfur-rich magmas. Indeed, extensive fluid lava flows have been identified in high-resolution images of the Martian surface. Extensive outflow channels, some of which strongly resemble Martian outflow channel features, are found on Venus. These unexpected features were apparently formed by highly fluid magma flows. The spatial relationship between the Martian outflow channels and the major volcanic constructs is consistent with the hypothesis that very fluid magmas may have played some role in the formation of outflow channels.

3.4. Milankovitch Cycles

As on Earth, Mars' orbital elements (**obliquity,** eccentricity, argument of perihelion) exhibit oscillations known as Milankovitch cycles at periods varying from 50,000 to several million years. The obliquity and eccentricity oscillations are much larger in amplitude on Mars than on Earth (Fig. 8). Milankovitch cycles cause climate variations in two ways. First, they control the distribution of incoming solar radiation (insolation) on both an annual average and seasonal basis as functions of latitude. Second, because Milankovitch cycle variations of insolation force variations of annual average surface temperature, they can drive exchanges of volatiles between various surface reservoirs and between surface reservoirs and the atmosphere. Water vapor can move between polar cap ice deposits, and ice and adsorbed water in the regolith. Carbon dioxide can move between the atmosphere, seasonal residual polar caps, and the surface adsorption reservoir. Milankovitch variations are believed to be responsible for the complex layered structures in both the north polar water ice cap and terrains surrounding the south polar residual carbon dioxide ice cap.

In general, annual average polar cap temperatures increase relative to equatorial temperatures as obliquity increases. At very low obliquity ($<$10–20° depending on the precise values of polar cap **albedo** and thermal **emissivity**), the carbon dioxide atmosphere collapses onto permanent carbon dioxide ice polar caps. Orbital calculations indicate that this collapse could occur ~1–2% of the time. At high obliquity, atmospheric pressure may increase due to warming and release of adsorbed carbon dioxide from high-latitude regolith. Calculations indicate, however, that the maximum possible pressure increase is likely to be small, only a few millibars, so Milankovitch cycles are unlikely to have been responsible for significant climate warming.

3.5. Wind Modification of the Surface

Orbital and landed images of the surface show ubiquitous evidence of active wind modification of the surface, which complicates the interpretation of climate and volatile history. The action of wind erosion, dust transport, and dust deposition is modulated by Milankovitch cycles and must have strongly changed the surface over the last few billions of years and during the Noachian, as we discuss later.

Today, dunes, ripples, and other aeolian bedforms are widespread. Wind-modified objects, known as ventifacts, are very evident in the grooves, facets, and hollows produced by the wind in rocks at the surface. Yardangs are also common, which are positive relief features in coherent materials sculpted by wind on scales from tens of meters to kilometers. Strong winds that exert stress on the surface can initiate saltation (hopping motion) of fine sand grains (diameter ~100–1000 micrometers) and creep of larger particles. Saltating grains can dislodge and suspend finer dust particles (diameters ~1–10 micrometers) in the atmosphere, thereby initiating dust storms. Minimum wind speeds required to initiate saltation are typically ~30 m s^{-1} at the level 2 m above the surface, but this saltation threshold wind speed decreases with increasing surface pressure.

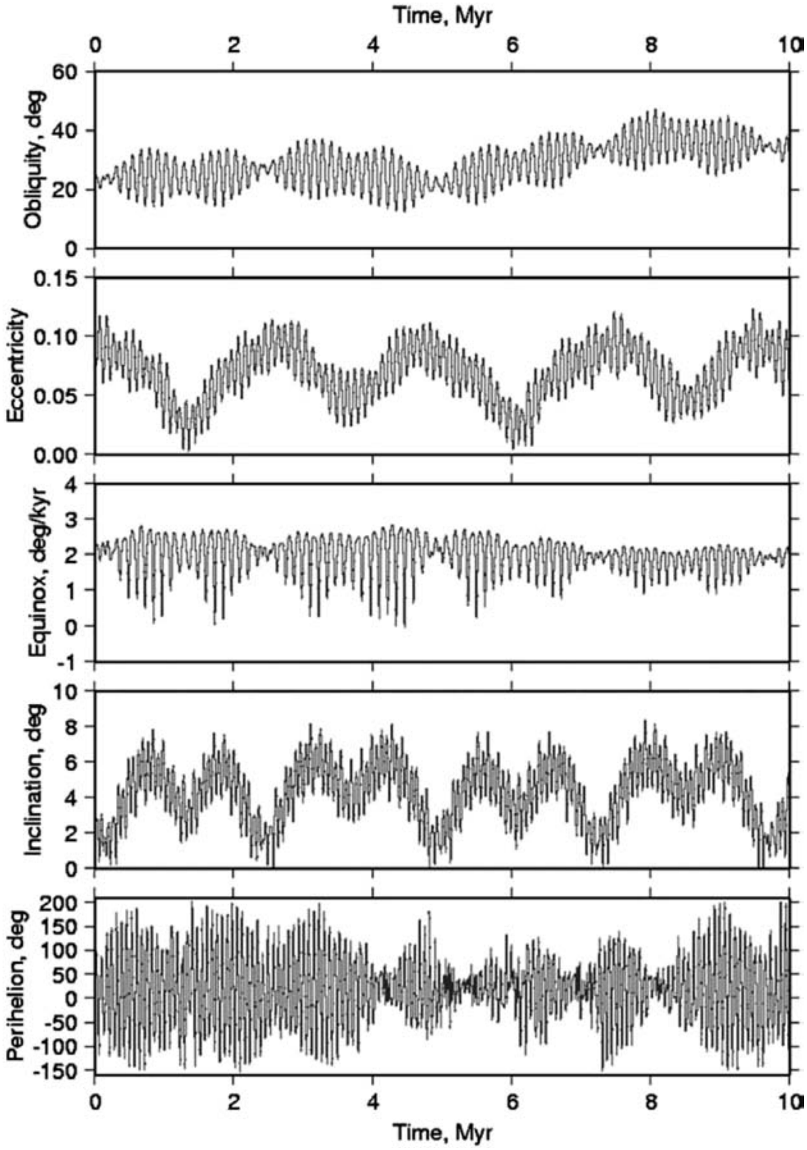
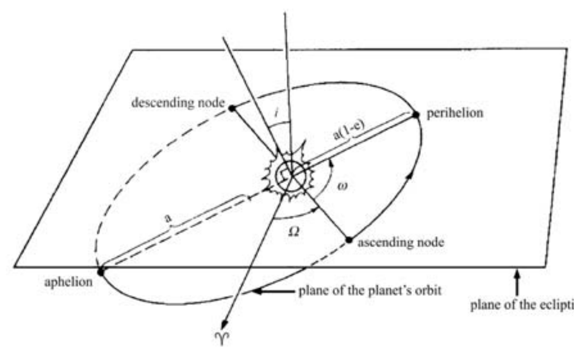


FIGURE 8 (a) Orbital elements. Mars, like other planets, moves in an elliptical orbit with a semimajor axis a. The eccentricity e defines how much the ellipse is elongated. The plane of the orbit is inclined by angle i to the ecliptic, which is the geometrical plane that contains the Earth's orbit. The ascending node is the point where the planet moves up across the ecliptic plane and the descending node is where the planet moves below it. The vernal equinox, marked ⊥, represents a reference direction that defines the longitude of the ascending node, Ω. Angle ω is the argument of perihelion. (b) Calculated variations in Martian orbital parameters over the last 10 million years. (Reprinted from Armstrong et al., 2004, *Icarus* **171**, 255–271, with permission from Elsevier.)



Such strong winds are rare on Mars. In the *Viking* lander, both wind observations and computer simulation models of the atmospheric circulation suggest that they occur at most sites <0.01% of the time. Nevertheless, over the planet as a whole, dust storms initiated by saltation are common; they tend to occur with greater frequency in the lower elevation regions rather than in the uplands because relatively high surface pressure in the lowlands lowers the saltation threshold wind speed. They are favored by topographic variations, including large- and small-scale slopes and are common over ice-free surfaces near the edges of the seasonally varying polar caps and in "storm track" regions where the equator-to-pole gradient of atmospheric temperature is strong. Dust storms generated by strong winds and saltation are common in some tropical lowland regions, especially close to the season of perihelion passage when the Hadley circulation is strong (near the southern summer solstice at the current phase of the Milankovitch cycle). During some years, these perihelion season storms expand and combine to such an extent that high dust opacity spreads across almost the entire planet. These planet-wide dust events are fostered by positive feedbacks between dust-induced heating of the atmosphere, which contributes to driving wind systems, and the action of the wind in picking up dust.

Dust can also be raised at much lower wind speeds in small-scale quasi-vertical convective vortices called dust devils. Because the atmosphere is so thin, convective heating per unit mass of atmosphere is much greater on Mars than anywhere on Earth, and Martian dust devils correspondingly tend to be much larger sizes (diameters up to several hundred meters and depths up to several kilometers). Since the winds required to raise dust in the vortical dust devils are lower than saltation threshold winds, dust devils are common in some regions of Mars during the early afternoon and summer when convective heating is strongest. They are often associated with irregular dark tracks produced by the removal of a fine dust layer from an underlying darker stratum. The relative importance of large saltation-induced dust storms and dust devils to the overall dust balance is unclear, but modeling studies suggest that the former are substantially more important.

Over the four billion–year history of the observable surface of Mars, there must have been substantial systematic wind transport of fine soil particles from regions in which erosion is consistently favored to regions of net deposition. Models of Martian atmospheric circulation and the saltation process suggest that net erosion must have taken place in lowland regions, particularly in the northern lowlands, the Hellas basin, and some tropical lowlands (e.g., Isidis Planitia and Chryse Planitia), with net deposition in upland regions and in some moderate elevation regions where the regional slope is small and westward facing, such as portions of Arabia Terra and southern portions of Amazonis Planitia. The distribution of surface **thermal inertia** inferred from the measured surface diurnal temperature variation supports these distributions. Regions of high thermal inertia, corresponding to consolidated or coarse-grained soils, exposed surface rocks, and bedrock patches are found where the circulation–saltation models predict net erosion over Milankovitch cycles, and regions of very low thermal inertia corresponding to fine dust are found where net deposition is predicted by the models.

There are no terrestrial analogs of surfaces modified by wind erosion and deposition over four billion years, so it is difficult to comprehend fully the modifying effect of Martian winds extending over such a long time. However, it is clear from the surface imagery that wind has played a large role in modifying the surface. In some areas, repeated burial and exhumation events must have taken place. Based on the heights of erosionally resistant mesas, the Meridiani Planum site of the *Opportunity* rover activities appears to have been exhumed from beneath at least several hundred meters and perhaps as much as several kilometers of soil. Many of the sulfate layer deposits described earlier appear to be undergoing exhumation. Since surface features can be repeatedly buried, exposed, and reburied over time, inferences of event sequences and surface ages from crater size distributions are rendered complex.

Because the saltation process operates on the extreme high-velocity tail of the wind speed distribution, it is very sensitive to surface density or pressure changes. Some model results have indicated that an increase in surface pressure up to only 40 mbar would increase potential surface erosion rates by up to two orders of magnitude. If, as is likely, Mars had a surface pressure ~100 mbar or higher during the late Noachian, rates of surface modification by wind should have been orders of magnitude greater than today. Indeed, it has long been observed that late Noachian surfaces were undergoing much more rapid modification than during later periods. This has generally been attributed to precipitation and runoff under a warmer climate regime, as discussed earlier. But surface modification by winds under a denser atmosphere should also have contributed to the observed rapid modification of late Noachian age surfaces.

4. Concluding Remarks

Although ice is now known to be widespread near the surface and there is considerable evidence that liquid water once flowed across the surface in dendritic valley networks and immense outflow channels, we still do not know the exact conditions responsible for releasing water (or other fluids) at the surface. New observations point to the importance of sulfur compounds, particularly sulfates, in Martian surface and atmosphere evolution, and the high ratio of sulfur to water in Martian meteorites suggests that sulfates may have exerted an important control on the availability of water rather than conversely as on Earth. Recent spectroscopic identification of methane is a surprise because of its relatively short lifetime in the atmosphere, which requires a continuous source. Future measurements should aim to confirm this result and define the distribution of methane. If significant amounts of methane are indeed found to be present in the atmosphere, then the methane source and potential past climatic impact need to be understood.

It has always been difficult to understand how Mars could have had a sufficiently dense carbon dioxide atmosphere to produce a warm wet climate at any time from the late Noachian onward. The severity of the problem is that the early Martian atmosphere has to provide ~80°C of greenhouse warming to raise the mean global temperature above freezing, which is more than double the greenhouse warming of 33°C of the modern Earth. So, despite new spectral data from orbit, the failure to find sedimentary carbonate rocks showing that exhumed sulfate deposits are widespread is noteworthy, though in retrospect it should not be surprising. If a large sedimentary carbonate reservoir is indeed absent, it is far less likely than previously thought that Mars has had extended episodes of warm wet climate due to a carbon dioxide greenhouse at any time from the late Noachian onward. In view of these new results, other candidate mechanisms for the release of fluids at the surface to form valley networks and outflow channels should be considered. During the Noachian, large impacts would have provided sufficient heat to vaporize subsurface volatiles, such as water and CO_2 ice. Consequently, impacts may have generated many temporary warm, wet climates, which would be accompanied by erosion from rainfall or the recharge of aquifers sufficient to allow groundwater flow and sapping. Such a scenario would explain why the end of massive impact bombardment is accompanied by an apparently large drop in erosion rates, as well as why valley networks are found predominantly on Noachian terrain.

Geochemical data and models suggest that most of Mars' original volatile inventory was lost early by hydrodynamic escape and impact erosion. However, we do not know the degree to which volatiles were sequestered into the subsurface as minerals or ices and protected. Future landed and orbital missions can refine our understanding of the distribution and properties of subsurface ices and hydrated minerals. Radar measurements could show the depth of water ice deposits and possibly the presence of any subsurface liquid water or brine aquifers, if subsurface ice extends deep enough to allow these. But determining the amount of sulfate and carbonate that has been sequestered into the subsurface will require drilling into the deep subsurface and extensive further exploration of Mars.

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