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 prior to about 3.7 billion years ago. Before and around this time, the erosion of valley networks by liquid water suggests a past climate that was warmer. But exactly how the early atmosphere produced warmer conditions and the extent to which it did so remain open questions. Suggestions include an ancient greenhouse effect enhanced by various gases, impacts that created temporary wet climates by turning ice to vapor and rainfall, and periodic melting of ice under moderately thicker atmospheres as Mars’ orbit and axial tilt changed. For the last 3.7 billion years, it is likely that Mars has been predominantly cold and dry so that outflow channels that appeared later were probably formed by fluid release mechanisms that did not depend on a warm climate. Very recent gullies and narrow, summertime dark lineae that form on steep slopes are features that form in the current cold climate. In addition, wind erosion, dust transport, and dust deposition have been modulated by changes in Mars’ orbital elements over time, which complicates the interpretation of climate and volatile history. In the past, surface modification by winds in a denser atmosphere may have been significant.

1. INTRODUCTION

The most interesting and controversial questions about Mars revolve around the history of liquid water. Because temperatures are low, the current, thin Martian atmosphere only contains trace amounts of water as vapor or ice clouds. In larger quantities, water is present as ice and hydrated minerals near the surface. Some geological structures resemble dust-covered glaciers or rock glaciers, while others strongly suggest the flow of liquid water 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. Temperatures above freezing occur only under highly desiccating conditions in a thin layer at the interface between the soil and atmosphere. Also, the surface air pressure over much of the planet is below the triple point of water (611 Pa or 6.11 mbar); under these conditions, at temperatures above freezing, liquid water would boil away. If liquid water is present near the surface of Mars today, it is confined to thin adsorbed layers on soil particles or highly saline solutions. No standing or flow
Conditions appear to have been more favorable for liquid water in the ancient past. The landscape has a number of fluvial (stream-related) features, of which the most important for climate are the valley networks, which are dried-up riverlike depressions fed by treelike branches of tributaries. Deltas exist at the end of a small fraction of valleys. Fluvial features that occurred later than the valleys are giant outflow channels. The valley networks indicate wetter past climates, while the outflow channels are commonly interpreted as massive release of liquid water from subsurface aquifers or the melting of underground ice (although a minority opinion argues in favor of runny lavas as the primary erosive agent). In addition to fluvial features, the soil and sedimentary rocks incorporate hydrous (water-containing) minerals that are interpreted to have formed in the presence of liquid water. 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 and so could have influenced the past climate and the occurrence of liquid water. Here we review the current understanding of volatile reservoirs, the sources and sinks of volatiles, the current climate, and evidence for different climates in the past. We consider 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. The possible relevance of very large orbital variations (Milankovitch cycles) for Mars’ climate history is also examined.

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. Consequently, we also discuss evidence for how the surface has been changed 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 (CO₂), and in addition to the major gaseous components listed in Table 16.1, the atmosphere contains a variable amount of water vapor (H₂O) up to 0.1%, minor concentrations of photochemical products of carbon dioxide and water vapor (e.g. CO, O₂, H₂O₂, and O₃), and trace amounts of the noble gases neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe). Methane (CH₄), averaging about 10 parts per billion by volume (ppbv), has been reported based on spectra from ground-based telescopes (which are complicated by having to remove the effect of viewing Mars through the Earth’s atmosphere) and relatively low resolution spectra obtained by European Space Agency’s (ESA’s) Mars Express orbiter. However, in situ measurements by National Aeronautics and Space Administration’s (NASA’s) Mars Science Lab rover have found no methane with an upper limit of about 1 ppbv, which must be taken as more definitive.

Volatiles that can play important roles in climate are also stored in the regolith and near-surface sediments. The regolith is a geologic unit that includes fine dust, sand, and rocky fragments comprising the Martian soil together with loose rocks, but excluding bedrock. Approximate estimates of the inventories of water, carbon dioxide, and sulfur are given in Table 16.2.

Water is stored as ice in the permanent north polar cap and its surrounding layered terrains, in layered terrains around the South Pole, and as ice, hydrated minerals, or adsorbed water in the regolith. The 5-km-deep residual northern polar cap consists of a mixture of ≥95% water ice and fine soil or dust, while layered south polar terrains contain water ice and about 15% dust. Taking account of their volumes and ice fractions, each cap and associated layered terrain contains water ice equivalent to a global ocean about 10 m deep.

Measurements of the energy of neutrons emanating from Mars into space by NASA’s Mars Odyssey orbiter has also 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 (Figure 16.1). 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

<table>
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<tr>
<th>TABLE 16.1 Basic Properties of the Present Atmosphere</th>
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<tr>
<td>Average surface pressure</td>
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<td>Surface temperature</td>
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<td>Major gases</td>
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<td>Significant atmospheric isotopic ratios relative to the terrestrial values</td>
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distribution. Abundant hydrogen serves as a proxy for water and/or hydrated minerals. In 2008, the robotic arm and thrusters on NASA’s Phoenix Lander exposed ice at 68°N some 5–10 cm below the surface, verifying the inferences from Mars Odyssey’s neutron measurements. However, water ice probably extends to no more than ~20–30 m depth in the mid- to high-latitude regolith based on radar and the morphology of small craters. Consequently, the total water inventory appears to be dominated by hydrated minerals rather than ice and has a depth of 200–1000 m of a global equivalent ocean.

The inventory of CO₂ mainly depends on how much is locked up in carbonates hidden in the subsurface. Weathering of dust has occurred over billions of years even in the prevailing cold dry climate, and as a consequence some CO₂ appears to have been irreversibly transferred from the atmosphere to carbonate minerals in dust particles. The total amount depends on the global average depth of dust. Some CO₂ is likely to be adsorbed in the soil also, but the quantity is limited by competition for adsorption sites with water. From orbital spectra, some carbonate sedimentary rock outcrops have been identified but with an area of only 10⁷ km² assuming a subsurface extent underneath associated geologic units. Taking an average thickness of 100 m, the CO₂ inventory in these outcrops is only 3 mbar. However, the carbonate inventory in the subsurface remains unknown. Also, carbonate outcrops that are smaller than orbital resolution can detect are likely present. Indeed, instruments on NASA’s Spirit Rover identified a small carbonate outcrop in the Columbia Hills region of Gusev Crater.

Table 16.2 also lists sulfates. Although there are presently no detectable sulfur-containing gases in the atmosphere, sulfur gases should have existed in the atmosphere in the past when Mars was volcanically active. Measurements by NASA’s landers and rovers show that sulfur is a substantial component in soil dust (~7–8% by mass) and surface rocks. Hydrated sulfate salt deposits have been identified in numerous layered deposits from near-infrared spectral data collected by Mars Express and NASA’s Mars Reconnaissance Orbiter (MRO). About two-thirds of these deposits are within 10° latitude of the equator. Several sulfate minerals have been detected and the total sulfur abundance can be estimated. Notable sulfate minerals include kieserite (MgSO₄·H₂O) and gypsum (CaSO₄·2H₂O). Jarosite (XFe₃(SO₄)₂(OH)₆, where “X” is a singly charged species such as Na⁺, K⁺ or hydronium (H₃O⁺)) has been identified by the Opportunity rover in Meridiani Planum. Additional sulfate as gypsum is present in northern circum-polar dunes. Anhydrous sulfates, such as anhydrite (CaSO₄), are probably present but would give no signature in near-infrared spectra.

The total sulfur in visible deposits on Mars is around 10¹⁹ kg SO₃, which is within an order of magnitude of Earth’s oceanic sulfate of 3.2 × 10¹⁷ kg SO₃ but well below Earth’s sulfur inventory of 2.4 × 10¹⁹ kg SO₃ that includes sedimentary sulfur in the form of pyrite and sulfates. Thus, even accounting for its lower surface area, Mars’ surface apparently has a smaller sulfur inventory than the Earth, which is presumably because of less extensive volcanic outgassing.

Evidence of volatile abundances also comes from Martian meteorites [See Meteorites]. These meteorites are known to be from Mars because of their igneous composition, unique oxygen isotope ratios, spread of ages, 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 4.4 to 0.15 billion years, which implies a parent body with active volcanism during this entire interval. Many of the Martian meteorites contain salt minerals, up to 1% by volume,
which can include halite (NaCl), gypsum, anhydrite, and carbonates of magnesium, calcium and iron. The bulk meteorite compositions are generally dry, 0.05–0.3 wt% water, compared to terrestrial H₂O contents from 0.1 wt% in midocean ridge basalts to 2 wt% in basaltic magmas from subduction zones. There is debate about the extent to which Martian magmas may have degassed on eruption and lost their water. Consequently, estimates for the preeruptive volatile contents of Martian magmas vary from nearly anhydrous to about 2 wt% H₂O, which is a range from lunarlike to Earth-like. On the other hand, the Martian mantle is generally inferred to be sulfur rich, with 0.06–0.09 wt% S compared to 0.025 in Earth’s mantle.

One important Martian meteorite, ALH84001, is a sample of 4.1 billion-year-old crust and 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 associated with the carbonates were considered of possible biological origin: the carbonates themselves, traces of organic compounds, 0.1 μm-scale structures identified as microfossils, and crystals of the mineral magnetite (Fe₃O₄) (McKay et al., 1996). However, the biological nature of all these features has been strongly disputed and alternative abiotic origins have been proposed.

2.2. Sources and Losses of Volatiles

Volatile acquisition began during the formation of Mars. Planetary formation 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, and noble gases. Nonetheless, formation of Jupiter and the outer planets would have gravitationally deflected volatile-rich asteroids from the outer asteroid belt and Kuiper Belt comets into the inner solar system. Analyses of the compositions of the Martian 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 in Mars’ atmosphere and surface 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 erosion, must have removed much of any early Martian atmosphere. Hydrodynamic escape is pressure-driven escape that occurs when a planet’s upper atmosphere is sufficiently warm to expand, accelerate through the speed of sound, and attain escape velocity en masse. Because this process is easiest for hydrogen-rich atmospheres, the general conception of hydrodynamic escape on Mars is of an early hydrogen-rich atmosphere flowing outward in a planetary wind (analogous to the “solar wind”) that entrains and removes other gases. Heavy atoms are carried upward by collisions with hydrogen faster than they diffuse down under gravity, and the downward diffusion gives only weak selectivity to atomic mass. Nonetheless, the high 38Ar/36Ar ratio (Table 16.2) could be a sign of early hydrodynamic escape, although later escape processes can also drive this ratio high (see below).

Intense solar ultraviolet radiation and soft X-rays provide the energy needed to drive hydrodynamic escape. These fluxes would have been at least two orders of magnitude larger than at present during the first 10⁷ years after the solar system formed as the evolving sun moved toward the

![FIGURE 16.1 Water-equivalent hydrogen content of subsurface water-bearing soils derived from the Mars Odyssey Neutron Spectrometer. From Feldman et al. (2004).]
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 10 times faster than present, which would have caused more magnetic activity, associated with over a 100 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 chemical reaction of iron and water during accretion and the segregation of the core and mantle. If water brought in by impactors could mix with free iron during 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 Martian meteorites indicates that Mars’ mantle is rich in iron oxides relative to the 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 much of the atmospheric volatiles in the current inventory.

Early Mars was also potentially vulnerable to impact erosion—the process where atmospheric gases are expelled as a result of the large-body impacts. Big impacts release enough energy to accelerate atmospheric molecules surrounding the impact site to speeds above the escape velocity. A large fraction of these fast molecules escape. Since escape is easier with a smaller gravitational acceleration of the planet, impact erosion 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, and most models suggest net atmospheric erosion for early Mars rather than accumulation of volatiles. Based on dating of lunar rocks and impact features, bombardment by massive objects is known to have declined rapidly with time after planet formation. The interval from 4.1 to 3.7 billion years ago is the Noachian eon in Martian geologic time, so that massive bombardment effectively ceased around the end of the Noachian. The base of the Noachian is defined by the time of formation of the Hellas impact basin around 4.1 billion years ago, before which is the Pre-Noachian. Interestingly, the lunar record suggests a spike in the impact flux 4.0–3.8 billion years ago, called the Late Heavy Bombardment, when most impact melt rocks formed. Thus, the late Noachian was probably a time of particularly intense impacts.

Bombardment by massive bodies during the Noachian has left an imprint in the form of large impact craters that are obvious features of the southern hemisphere (Figure 16.2). 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 erosion should have removed all but ~1% of an early CO2-rich atmosphere (e.g. see Carr, 1996, p.141). Water in ice and carbon in carbonates would have been relatively protected, however, and the exact efficiency of the removal of volatiles by impact erosion is unknown.

What was the size of Mars’ volatile reservoirs after Late Heavy Bombardment, some 3.7 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 16.1).

Another approach to estimating the CO2 abundance at the end of the Noachian 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 massive impact bombardment, its current abundance probably corresponds closely to the abundance at the end of the Noachian. Impact erosion would have effectively removed all gases independent of atomic mass, so the ratio of $^{85}$Kr abundance to C in plausible impactors (Kuiper Belt comets or outer solar system asteroids) can then yield estimates of the total available CO2 reservoir at the end of the Noachian. The corresponding atmospheric pressure, if all CO2 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 $^{15}$N/$^{14}$N ratio (Table 16.1).

If ~0.1 bar was left at the end of the Noachian, besides nonthermal escape, slow carbonate weathering of atmospheric dust could also have removed CO2 from the atmosphere (as mentioned previously). This irreversible mechanism may account for the fate of a large fraction of the CO2 that was available in the late Noachian, along with adsorbed CO2 in the porous regolith (Table 16.2). It has long been speculated that much of the CO2 that was in the
Noachian atmosphere got tied up as carbonate sedimentary deposits beneath ancient water bodies. However, so far only small outcrops and no significant quantities of carbonate sedimentary rocks have been found (see further discussion below).

Escape of water in the form of its dissociation products H and O takes place now, and must have removed significant amounts of water since the Noachian. Isotopic ratios of D/H and $^{18}$O/$^{16}$O in the atmosphere and in Martian 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 are 30–50 m of equivalent global ocean. These amounts are roughly comparable to estimates of the water currently stored as ice in the polar caps and regolith (Table 16.2).

Sulfur is not stable in the current Martian atmosphere as either sulfur dioxide (SO$_2$) or hydrogen sulfide (H$_2$S) because both gases oxidize and ultimately produce sulfate aerosols that fall to the surface; however, significant sulfur gases must have been introduced into the atmosphere by volcanism. Estimated ages of volcanic surfaces on Mars indicate that rates of volcanism declined and became more intermittent after about 3.5 billion years ago. Formation of the Tharsis ridge volcanic structure, believed to have occurred in the late Noachian eon, must have corresponded with outgassing of large amounts of sulfur as well as water from the mantle and crust. The probable quantity of sulfur released is consistent with the relatively high mass fraction of sulfur in the soil and the presence of large deposits of sedimentary sulfates. Martian meteorites are ~5 times as rich in sulfur as in water and 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 the sulfates found in Martian meteorites is that sulfur and oxygen isotopes 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 when ultraviolet radiation interacts with certain atmospheric gases in photochemistry. 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 Martian meteorites suggests that a similar process produced these sulfates on Mars, and implies that the sulfur cycled through the atmosphere at some ancient time.

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 5—8 K above the 210 K 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 residual CO₂ polar cap at the South Pole, which persists all year round in the current epoch; it represents a potential increase in the CO₂ pressure of 4–5 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 daily. Water vapor exchanges with the polar caps over the course of the Martian year, especially with the North Polar cap. After sublimation of the winter CO₂ polar cap, the summertime central portion of the cap surface is water ice. Water vapor sublimes 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 dust as well as icy particles that form clouds. 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 μm, 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 ice ice clouds occur at times over the polar caps, and they occur rarely as high-altitude cirrus clouds of CO₂ ice particles.

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 the Earth (23.5°), and a Martian year 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 that of the 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 the Earth. Mars’ rotation rate is similar to that of the Earth’s, and like the 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, which is similar on Mars and Earth. Both planetary atmospheres are dominated by a single meandering mid-latitude jet stream, strongest during winter, and a 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 shielded on Earth by the ozone layer and oxygen, can reach the lower atmosphere and surface on Mars. This allows water vapor dissociation close to the Martian surface (H₂O + 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 HO₂) are produced in near-surface air. These conditions as well as the lack of liquid water probably preclude life at the very surface on present-day Mars.

Although liquid water may not be completely absent from the surface, even in the present climate, it is surely 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 for 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.

### 3.2. Past Climates

Several types of features suggest that fluids have shaped the surface during all eons—the Noachian (4.1—3.7 billion years ago), Hesperian (3.7 to 3.5—3.0 billion years ago), and Amazonian (from 3.5 to 3.0 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 (Figure 16.3). The morphology of valley networks is very diverse, but most consist of dendritic networks of small valleys, often with V-shaped profiles in their upper reaches becoming more U-shaped downstream. Their origin is
attributed to surface water flows or groundwater sapping. The latter is when underground water causes erosion and collapse of overlying ground. Although often much less well developed than valley network systems produced by fluvial erosion on Earth, Martian valley networks are suggestive of widespread precipitation and/or 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 (~3.7 billion years ago). In Figure 16.3, we show two examples of valley network features. Figure 16.3(a) 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 16.3(b) shows fairly typical valley networks that are incised on Noachian terrain. A relatively small number of valleys on Mars terminate in deltas, which provides strong evidence of liquid water. However, the deltas are undissected, which implies an abrupt end to the era of valley formation. Some deltaic deposits also contain clay minerals such as the one in Jezero crater (18.4° N, 282.4° W) (Figure 16.4), which is fed by a valley network northwest of Isidis.

Valley networks are incised on top of a Noachian landscape of craters with heavily degraded rims and infilling or erosion (Figure 16.3(b)). Such crater morphologies indicate relatively high erosion rates. Some models suggest that erosion and deposition was caused by fluvial activity, at least in part. However, the interpretation is 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.

Besides valley networks, a second class of geomorphic features suggesting liquid flow is a system of immense

**FIGURE 16.3** (a) An image of Nanedi Vallis (5.5° N, 48.4° W) from the Mars Orbiter Camera (MOC) on NASA's Mars Global Surveyor (MGS) 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.)* (b) Valley networks that illustrate dissected Noachian terrain (14° S, 61° E). Part of the rim of Huygens Crater is shown on the left of the image. Note that the valley networks incise a Noachian landscape with large craters that were that were degraded by some process prior to the formation of the valleys. *HRSC image from orbit 532, ESA/DLR/FUB.*

**FIGURE 16.4** A deltaic deposit in western Jezero Crater. The delta feature is in positive relief, which shows that the material in the deposit was more resistant to erosion than surroundings. Yellow and blue colors indicate basaltic minerals, while clay minerals are green. Purple-brown surfaces have no distinctive spectral features. *NASA/JPL/JHUAPL/MSSS/Brown University.*
channels that formed during the late Hesperian (Figure 16.5). 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 occur mainly in low latitudes (between 20° north and south) around the periphery of major volcanic provinces such as Tharsis and Elysium, where they debouch 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 a few hundred meters 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 outflow channels is unknown, but the dominant hypothesis is that they were generated by catastrophic release of water from subsurface aquifers or rapidly melting subsurface ice. Alternatively, volcanic or impact heating caused catastrophic dehydration of massive hydrated sulfate deposits and resulting high-volume flows of liquid water. 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. A minority view is that the outflow channels were not carved by water but runny lavas. Some outflow channels (e.g. Mangala Valles, Athabasca Valles) have lava flows on their floors (Figure 16.6) and the source of some outflow channels are also sources of lava, e.g. Cerberus Fossae for Athabasca Valles or Memnonia Fossae for Mangala Valles. However, water and lava are not mutually exclusive. Magmatic intrusions could have melted subsurface ice, triggering floods of water in association with lava flows.

Unlike the valleys and channels, gullies are very recent features that have been interpreted to imply fluvial flow, but evidence from MRO images suggests that gullies can form today in association with carbon dioxide ice rather than liquid water. Gullies are incisions of tens to hundreds of meters length commonly found on poleward facing sloping walls of craters, plateaus, and canyons, mainly at southern midlatitudes (~30°–55°S) (Figure 16.7). The gullies typically have well-defined alcoves above straight or meandering channels that terminate in debris aprons. Their setting and morphology has led to comparisons with debris flows in terrestrial alpine regions that are produced by rapid release of meltwater and consist typically of ~75% rock and silt carried by ~25% water.

High-resolution images from MRO show that gullies are forming on Mars today when carbon dioxide frost turns to vapor at the end of winter (Figure 16.7). Sublimation of CO₂ frost presumably causes a fluidlike, dry flow of rock and soil with the CO₂ gas providing lubrication. This mechanism explains the predominant location of gullies in the southern hemisphere where there is a greater seasonal accumulation and distribution of carbon dioxide frost than in the north because of prolonged southern winters. Consequently, gullies do not require a warm climate or low-latitude reservoirs of subsurface water or ice. In fact, gullies...
induced by CO₂ sublimation illustrate how features that look very similar to fluvially eroded analogs on Earth can actually have other causes.

Other curious features that develop on Mars today are Recurring Slope Lineae (RSL), which may be associated with seasonal melting of water ice. RSL are dark, narrow (0.5—5 m) lineaments that develop during warm seasons on steep rocky slopes that are equator facing in equatorial or mid latitude regions (Figure 16.8). The RSL fade and disappear during the cold season. Their formation is not understood, but an association with peak surface temperatures ranging from 250 to 300 K supports the idea that melting of water ice is probably involved. Salts dissolved in the water would also allow flow below 273 K.

Minerals on very ancient surfaces provide evidence for a wetter early Mars that bolsters the inference of liquid water from valley networks and outflow channels (if water eroded). Much of the surface on Mars is basalt, a dark-colored igneous rock rich in iron and magnesium silicate minerals. When basalt reacts with water, “alteration minerals” are produced, such as clays. So alteration minerals can be diagnostic of the past presence of liquid water and sometimes they suggest its pH. For example, clay minerals tend to be produced when alkaline water reacts with basaltic minerals. Notably, clay minerals have been detected in mudstone by NASA’s Curiosity Rover in an area interpreted as an ancient dried-up lake bed in Gale Crater.

Alteration minerals on Mars have a broad trend in their distribution in geologic time. Orbital spectroscopy suggests that hydrous alteration minerals cover about 3% of Noachian surfaces in the form of clays and some carbonates. Sulfate minerals tend to be found on late Noachian or Hesperian surfaces, while younger Amazonian surfaces have reddish, dry iron oxides. To some, this broad pattern suggests three environmental epochs, starting in Noachian when alkaline or neutral pH waters made clay minerals from basalt. In the second epoch, sulfates were presumably derived from sulfur-rich volcanic gases. The third epoch is the cold, dry environment with rust-colored surfaces that continues today.

3.3. Mechanisms for Producing Past Wetter Environments

Despite extensive investigation, the causes of early warm climates in the Noachian or Hesperian remain to be identified. Here we review several possibilities.

3.3.1. Carbon Dioxide Greenhouse

A suggestion put forward after the Mariner 9 orbiter mission in 1972 is that the early atmosphere contained much more CO₂ than it does now. The idea is that substantial CO₂ caused an enhanced greenhouse effect through
its direct infrared radiative effect and the additional greenhouse effect of increased water vapor that 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 3.7 billion years ago (about 75% of the present flux), and consequent large amount of CO2 required to produce an adequate CO2−H2O greenhouse effect. At least several bars of CO2 would have been required to produce widespread surface temperatures above freezing. However, such thick atmospheres are not physically possible because CO2 condenses into clouds at ~1 bar and also into permanent ice caps at pressures exceeding ~3 bar. CO2 ice clouds can have some greenhouse effect because they scatter infrared radiation, but three-dimensional climate models show that the clouds are never opaque enough in the infrared to warm the surface to a mean temperature above freezing anywhere on the planet.

Apart from the difficulties with climate simulations, if a massive CO2 atmosphere ever existed at the same time as abundant liquid water, it would have eventually collapsed due to removal of the CO2 by dissolving in the water and subsequently forming carbonate sediments. However, despite extensive efforts, few outcrops of carbonate sediments have been found and their equivalent global pressure of CO2 is insubstantial (Table 16.2). Carbonates are absent even in areas in which water is interpreted to have flowed, such as valley networks, and in areas of extensive erosion where we would expect exposures of carbonate sediments buried beneath regolith. In contrast, sulfate sedimentary deposits are widespread at low latitudes, 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 CO2 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 seems doubtful, and the amount of CO2 available seems inadequate to have produced a warm enough climate to account by itself for the valley networks by surface in the late Noachian.

### 3.3.2. 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 and that the drop off in impact flux explains why valley formation declines after the early Hesperian. 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. The effect of water clouds on the postimpact climate also needs further study. However, impact heating of ice must have released water to the atmosphere and caused subsequent precipitation at some times during the Noachian.

#### 3.3.3. 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. In the atmosphere in the presence of water vapor, reduced sulfur would rapidly oxidize to SO2 and then form aerosols of sulfate and, in more reducing atmospheres, elemental sulfur also. Sulfur dioxide is a powerful greenhouse gas, but in the presence of liquid water, it dissolves and is removed from the atmosphere by precipitation very rapidly. More importantly, the sulfate and sulfur aerosols that form reflect sunlight so that the net effect of sulfur gases would be to cool Mars. Such cooling has been measured as an effect of volcanic eruptions on Earth that inject SO2 into the stratosphere where the resulting sulfate aerosols increase the albedo of the Earth.

#### 3.3.4. Methane-Aided Greenhouse

Methane is also a greenhouse gas, but because of its long-term instability in the atmosphere resulting from photolysis and oxidation, it is not an attractive option for contributing to an early warm climate. To have a role of any significance, early Mars would require a global methane flux similar to that produced by the present-day biosphere on Earth. Even so, calculations suggest that the net warming would be limited and inadequate to solve the early climate problem.

#### 3.3.5. Hydrogen-Aided Greenhouse

In an atmosphere that is thick and hydrogen-rich, hydrogen behaves as a greenhouse gas and this might have relevance for early Mars. Although hydrogen (H2) is a nonpolar molecule, collisions with other molecules can cause it to acquire a temporary dipole or absorb infrared photons in
transitions that are normally forbidden; the effect is “collision-induced absorption” (CIA). Indeed, hydrogen is an important greenhouse gas in all the giant planet atmospheres because of CIA. If a thick atmosphere of early Mars had five to tens of percent H₂, the greenhouse warming might be significant. However, hydrogen easily escapes from Mars into space and so very large volcanic fluxes of H₂ would be required. Furthermore, such a solution to the early Mars climate problem, if true, would disfavor life on the early planet because hydrogen is a food for primitive microbes and so its high abundance in the early air would imply an absence of biological consumption.

3.3.6. Mechanisms for Producing Fluvial Features in Cold Climates

Although some precipitation must have occurred due to impacts and short-lived greenhouse warming is plausible, other factors may have been conducive to widespread fluvial features. One proposal concerns seasonal snowmelt under atmospheres that have surface pressures of a few hundred millibars. A second idea is that many of the fluids were low-temperature brines that can exist at temperatures far below 0°C.

On Mars today, at a particular latitude with the same solar heating, there is a little variation of temperature with altitude, but when the pressure exceeds a few hundred millibars, vertical convection maintains a temperature gradient in the atmosphere that influences the temperature of topography, so that the tops of mountains become much colder than low altitudes. As a result, the southern highlands can become ice or snow covered and periodic melting from changes in orbital characteristics (see below) might be sufficient to erode valleys. If salty fluids rather than pure water were prevalent on early Mars, melting could have occurred at temperatures many tens of degrees below 0°C. For example, the eutectic temperature (at which a salty solution freezes into ice and solid salt) is −50°C for calcium chloride (CaCl₂), −75°C for calcium perchlorate (Ca(ClO₄)₂), and −57°C for magnesium perchlorate (Mg(ClO₄)₂). In addition, laboratory experiments show that brines of some salts (such as the aforementioned perchlorates) can supercool tens of degrees Celsius below the eutectic temperature for periods exceeding a Martian day.

The outflow channels remain enigmatic because of the large flows of water that are required relatively late in geologic time, in the late Hesperian, when the atmosphere was probably thin. The idea that very fluid lava flows might have responsible for channel erosion is the only concept that has no need of a warmer climate to allow flows to persist for hundreds of kilometers. Extensive outflow channels, some of which strongly resemble Martian outflow channel features, are found on Venus and are explained by low-viscosity lava flows. The spatial relationship between the Martian outflow channels and the major volcanic constructs is suggestive of the idea that very fluid lavas 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 (Figure 16.9). 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-driven changes of insolation force variations of annual average surface temperature, they can cause exchanges of volatiles between various surface reservoirs and the atmosphere. Water vapor can migrate 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 complex layered structure in both the north polar water ice cap and terrains surrounding the south polar residual carbon dioxide ice cap. Also, rhythmic variations in the layering of some sedimentary deposits in low latitudes have been interpreted as a probable sign of influence from orbital cycles, perhaps because such cycles shifted ice to the tropic in times of high obliquity that were followed by periods of melting.

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.

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.
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 below.

Today, dunes, ripples, and other 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 exert stress on the surface that can initiate saltation (hopping motion) of fine sand grains (diameter $\sim 100$–1000 $\mu$m) and creep of larger particles. Saltating grains can dislodge and suspend finer dust particles (diameters $\sim 1$–10 $\mu$m) in the atmosphere, thereby initiating dust storms. Minimum wind speeds required to initiate saltation are typically $\sim 30$ m/s at the level 2 m above the surface, but this saltation threshold wind speed decreases with increasing surface pressure.

Strong winds needed for saltation are rare. Wind observations at the Viking Lander sites and computer simulations 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 low-elevation regions than uplands because the relatively high surface pressure in 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 planetwide 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 dust devils, which are small-scale quasivertical 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 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 past 4 billion years, 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 inferences. 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 4 billion years, so it is difficult to fully comprehend the modifying effect of Martian winds over such a long time. However, it is clear from the surface imagery that in some areas repeated burial and exhumation events 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 above 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. Model results indicate 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, a major outstanding problem is that we still do not know the exact conditions responsible for releasing liquid water on early Mars or what controlled the early ancient climate (see Figure 16.10 for a timeline). As the sophistication of climate models for early Mars have grown, it has perhaps become increasingly difficult (rather than easier) to explain how Mars could have had a sustained, warm, and wet climate during the Noachian or Hesperian. The basic problem is that the early Martian surface needs about 80 °C of greenhouse warming to raise its mean global temperature above freezing, which is more than double the greenhouse warming of 33 °C of the modern Earth. The discovery of only a few outcrops of sedimentary carbonates provides little support for the idea that a large CO2 reservoir exists on Mars today and was derived from an earlier thick atmosphere; in any case, three-dimensional climate models are unable to raise global mean surface temperatures above freezing for any CO2–H2O atmosphere. More generally, no widely accepted solution to the climate of early Mars has been found despite numerous modeling permutations of an enhanced greenhouse effect with various gases on early Mars.

In view of the new data and theoretical constraints, other candidate mechanisms for the release of fluids at the surface to form valley networks and outflow channels need to be considered. During the Noachian, large impacts
would have provided sufficient heat to vaporize subsurface volatiles, such as water and CO₂ 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 might explain why valley networks appear to peak in occurrence around the era of the Late Heavy Bombardment (the late Noachian, early Hesperian) and why there is subsequently an apparently large drop in erosion rates. The periodic release of meltwater from high-altitude ice and snow that occurs under moderately thicker atmospheres is another mechanism that seems likely to have produced fluvial erosion on early Mars. Also, the potential of thicker Noachian atmospheres to cause wind erosion requires further consideration.

Geochemical data and models suggest that most of Mars’ original volatile inventory was lost early by hydrodynamic escape and impact erosion (Figure 16.10). However, we still do not know the degree to which some volatiles were sequestered into the subsurface as minerals and protected. Future landed and orbital missions can refine our understanding of the distribution and properties of hydrated minerals and subsurface ices. However, determining the amount of sulfate and carbonate that has been sequestered into the subsurface will require drilling into the subsurface. Further study of the geology of Mars from orbit and the surface will also help establish the amount of fluvial erosion, its duration, or episodicity. Finally, resolving questions of timing ultimately requires absolute (radiometric) dating of Martian surfaces.

**BIBLIOGRAPHY**


