ATMOSPHERIC EVOLUTION OF MARS

Introduction

Today, Mars is a cold, dry global desert. However, there is considerable evidence that Mars’ climate and its inventory of volatiles (substances that tend to form gases or vapor) have changed greatly during the planet’s history. The evidence comes from a variety of sources, including the geomorphology and mineralogy of the surface, the atmospheric composition, and the nature of subsurface materials inferred from the analysis of Martian meteorites (reviewed by Kieffer et al., 1992). In general, geochemical observations suggest that a once much greater volatile inventory was mostly lost very early in Martian history. We discuss below how isotopic data, in particular, suggests that as much as 99% of the original nitrogen and carbon atmospheric inventory of Mars was lost before about 3.8 Ga, ~0.9% has been lost since, and perhaps only ~0.1% remains. The geomorphology suggests a period of early Martian history when liquid water was present on the surface, although perhaps only sporadically. This period is largely coincident with the time before ~3.8 Ga when Mars was undergoing heavy bombardment from asteroid and comet impacts. Taken as a whole, the evidence suggests that Mars has likely been cold and dry for much of the last 4 Gyr. During this time, the surface of Mars has been altered by the effect of atmospheric sedimentation of dust and ice, and wind erosion. The climatic effects of quasi-periodic “ice ages” driven by changes in orbital parameters have probably been an important influence. During such times, polar ice, including both carbon dioxide and water ice, has extended down to much lower latitudes than today.

In discussing how the atmosphere has evolved, we use the geologic timescale for Mars. This timescale is divided up into three periods of increasing age: the Amazonian, the Hesperian, and the Noachian. Surfaces on Mars are categorized into these periods according to the density of superimposed impact craters. Older surfaces are those that have accumulated more impact craters. A Noachian surface is defined as one where an area of $10^6$ km$^2$ has accumulated at least 200 impact craters with diameters larger than 5 km and 25 craters larger than 16 km. Over the same area, a Hesperian surface will have accumulated at least 67 larger impact craters larger than 5 km and 400 craters larger than 2 km, but not enough craters to be classified as Noachian. Amazonian surfaces have insufficient craters to be Hesperian. The absolute ages corresponding to these cratering intensities are poorly constrained. However, the impact cratering record of the Moon has been radiometrically dated using samples returned by the Apollo missions, and lunar cratering rates have been extrapolated to Mars via models to estimate absolute ages of cratered Martian surfaces. In this way, the Noachian is determined to be older than 3.5 Ga, while the Hesperian-Amazonian boundary is estimated to be around 2.9-3.3 Ga (Hartmann and Neukum, 2001).

The Present-Day Atmosphere And Surface Environment

The thin, present-day atmosphere of Mars exerts a spatial and annual average surface pressure of only ~600 Pa compared to Earth’s sea-level pressure of $10^5$ Pa. According to mass spectrometry measurements made by the Viking probes in the 1970s, the atmosphere is well mixed up to 120 km altitude and is principally composed of carbon dioxide (95.3% by volume), with minor components of nitrogen (2.7%), argon (1.6%) and trace gases (Table 1). Mars is about 50% farther from the sun than Earth, so on average the solar flux is 43% less. Were the atmosphere to be absent, the mean global temperature on Mars would be 210 K. However, the thin, dry Martian atmosphere provides a modest greenhouse warming of ~5-8 K, which raises the mean global temperature to around 215-218 K. Temperatures and pressures are too low for liquid water to be in equilibrium with the atmosphere, and water persists at the surface only as vapor or ice. Water vapor is seasonally and geographically
variable but typically exerts a partial pressure of only ~0.1 Pa. Consequently, the absolute abundance of water vapor is ~$10^{-2}$-$10^4$ times less than in the Earth’s atmosphere. Mars is also cold enough that the main constituent of the atmosphere condenses at the poles each winter, forming 1-2 m thick CO₂ ice deposits. During northern summer, CO₂ ice completely sublimes away from the north polar cap to reveal underlying water ice. The southern cap is partially covered year round with CO₂ ice, although water ice is known to lie beneath. Measurements of the energy spectrum of neutrons emanating from Mars into space suggest that water ice also exists in the shallow subsurface in certain areas. Cosmic rays enter the subsurface and cause neutrons to be ejected with a variety of energies that can be related to the distribution of elements in the subsurface to a depth of ~1 meter. Hydrogen serves as a proxy for water and hydrated minerals. At latitudes greater than about 55° in each hemisphere, water ice is inferred to exist within 1 m of the surface at an average mass abundance of 50%. Hydrogen is also found to be relatively abundant (2-10% by mass) in certain low-latitude locations, such as Valles Marineris and Arabia Terra (Feldman et al., 2004). This may indicate either buried relic ice from ancient climate regimes or, more probably, hydrated minerals.

**Table 1** Basic planetary parameters for Mars and current atmospheric composition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value on Mars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean surface pressure (bar)</td>
<td>0.006</td>
</tr>
<tr>
<td>Mean global surface temperature (K)</td>
<td>215-218</td>
</tr>
<tr>
<td>Mass relative to Earth’s mass of 5.97 × 10^{24} kg</td>
<td>0.107 = 1/9</td>
</tr>
<tr>
<td>Mean radius relative to Earth’s mean radius of 6371 km.</td>
<td>0.532 = 1/2</td>
</tr>
<tr>
<td>Composition of the atmosphere (by volume) below 120 km</td>
<td>CO₂ 95.32%</td>
</tr>
<tr>
<td></td>
<td>N₂ 2.7%</td>
</tr>
<tr>
<td></td>
<td>Ar 1.6%</td>
</tr>
<tr>
<td></td>
<td>O₂ 0.13%</td>
</tr>
<tr>
<td></td>
<td>CO 0.08%</td>
</tr>
<tr>
<td></td>
<td>H₂O 0.03% (varies)</td>
</tr>
<tr>
<td></td>
<td>NO ~100 ppm</td>
</tr>
<tr>
<td></td>
<td>Ne 2.5 ppm</td>
</tr>
<tr>
<td></td>
<td>Kr 0.3 ppm</td>
</tr>
<tr>
<td></td>
<td>Xe 0.08 ppm</td>
</tr>
<tr>
<td></td>
<td>O₃ 0.04-0.2 ppm (varies)</td>
</tr>
<tr>
<td>Column dust content of the atmosphere</td>
<td>0.3-5 visible optical depth</td>
</tr>
</tbody>
</table>

There is much interest in the possibility of life on Mars but the contemporary surface environment that we just described is hostile to life for several reasons. First, there is a lack of liquid water, which is thermodynamically unstable. Second, Mars has no ozone layer. Thus, ultraviolet (UV) light with wavelengths down to about 200 nm (below which CO₂ absorbs) reaches the surface and sterilizes the soil. Third, photochemistry in the lower atmosphere produces peroxides, such as hydrogen peroxide (H₂O₂), that oxidize and destroy organic material in the soil. As a result, most hopes for extant life on Mars reside in the possibility that a primitive biota exists in the deep subsurface where geothermal heat might support aquifiers. There is also much speculation about past life on early Mars when the ancient surface environment may have been less hostile.

Recently, methane (CH₄) has been spectroscopically detected in the Martian atmosphere at an average abundance of ~10 ppb (e.g., Formisano et al., 2004). Currently, a range of methane values have been reported and differences have yet to be reconciled. Methane only has a lifetime in the atmosphere of a few hundred years because photochemistry converts it to carbon dioxide and water. To maintain 10 ppb
requires significant sources to replenish it, which at present are a matter of speculation. On Earth, methane production is dominated by biology. Biogenic methane production from subsurface life cannot be ruled out for Mars, but abiotic production from geothermal activity and photochemical reactions must be considered more probable at present.

Geological and Geochemical Inferences of Past Climates

Fig. 1 Nanedi Vallis (5.5° N, 48.4° W) imaged by the Mars Orbiter Camera (MOC) on NASA’s Mars Global Surveyor (MGS) spacecraft. At the top of the image, the sinuous path of this valley is suggestive of meanders. In the upper third of the image, a central channel is observed and large benches also indicate earlier floor levels. These features suggest that this valley was formed by sustained fluid flow. (The inset in the figure shows the a lower-resolution Viking Orbiter image for regional context) (Portion of image MOC-8704, NASA/Malin Space Science Systems).

Evidence for Past Liquid Water from Geomorphology

The present Martian climate contrasts sharply with a warmer, wetter ancient climate that has been commonly inferred from several types of eroded geological features seen on the Martian surface (1996).

Dendritic valley networks are observed in the Noachian highlands (Figure 1). Valleys are typically a few kilometers wide, 100-200 m deep, with flat floors and steep walls. They often have some tributaries but generally with a much lower areal density than terrestrial river valleys. How the valleys were formed is debatable, but majority opinion holds that the process was gradual and required liquid water to flow at or near the surface. Various erosive valley formation mechanisms have been suggested, including runoff from rainfall, groundwater sapping (i.e., subsurface flow of water accompanied by collapse of overlying ground), and discharge from hot springs. Low drainage densities, rounded alcove-like termini, and relatively rectangular U-shaped cross-sections (unlike V-shaped valleys commonly on Earth) generally favor a sapping origin. However, valley networks are not uniform. Some
valley morphologies are more consistent with formation from surface runoff and some valleys that originate at crater rim crests are incompatible with formation from sapping. Certain valleys also are associated with distributary fans. Figure 2 shows such a fan-like feature where the general pattern of the channels and low topographic slopes provide strong circumstantial evidence for a delta, i.e., a deposit made when a river or stream enters a body of water.

Figure 2 A 14 km by 13.3 km mosaic of high-resolution images taken by the camera on NASA’s MGS spacecraft. North is up and the scene is illuminated by sunlight from the left. The picture shows a remnant distributary fan in a 64 km diameter crater northeast of Holden Crater. Only the floors of channels in the fan have remained, and these have been elevated by erosion so that the floors of former channels now stand as ridges. Presumably the material deposited in valley floors was more resistant to the forces of erosion than surrounding material. (Image MOC2-543a, NASA/Malin Space Science Systems).

Noachian craters often has degraded rims and and infilling, which suggests a more erosive Noachian climate. Rates of Noachian erosion, however, are still only comparable to those in drier regions on Earth. On post-Noachian surfaces, estimated erosion rates drop by a factor of about $10^3$. This strongly suggests a causal link between the heavy bombardment and the relatively higher ancient erosion rates. Some crater degradation models suggest that the erosion was in part caused by fluvial activity. However, the image data suggests that craters were also degraded or obscured by impacts, eolian transport, and mass wasting.

Outflow channels are a further type of feature generally thought to have a fluvial origin (Baker, 2001). Such channels are 20-100 km wide and can extend for thousands of kilometers (Figure 3). The outflow channel interiors are generally not heavily cratered, and so the channels are inferred to be less ancient than the valley networks. Because the source of outflow channels often originates in chaotic terrain (areas where the ground is collapsed and broken), the expulsion of groundwater in floods is widely held to have been responsible for channel genesis. Such floods could conceivably have occurred in a cold environment similar to today’s, initiated by geothermal heating of subsurface ice. Other workers have emphasized that wind and ice may have widened outflow channels over geologic time (Cutts and Blasius, 1981). Liquid CO$_2$ has also been suggested as a possible agent of erosion. However, CO$_2$ is unable to discharge as a liquid under present Martian conditions and also
there is no well-defined mechanism for recharging CO₂ “aquifers”. Outflow channels drain into the northern lowlands on Mars, where possible shoreline features have been identified, which some interpret as the boundaries of a past ocean (Carr and Head, 2003). The shoreline features remain controversial because high-resolution images do not reveal distinctive geomorphology (Malin and Edgett, 1999) and “shorelines” have also been interpreted as tectonically-derived wrinkle ridges (Withers and Neumann, 2001).

**Figure 3** A mosaic of Viking Orbiter images showing the 300 km-long head of the channel Ravi Vallis. The source region for the channel can be seen on the left: An area of chaotic terrain. Ravi Vallis feeds into a system of channels that flow northward into Chryse Basin in the northern lowlands of Mars. (NASA/Lunar and Planetary Institute)

**Figure 4** Gully-like features on the sidewall of a crater near 33.3°S, 267.1°W. The arrow indicates a light-toned material, probably rich in ice. This layer appears to be genetically associated with the gullies, given that the tops of the gullies originate from the same level as the top of the light-toned layer. The picture is about 2.8 km by 5.8 km, a portion of MOC image M09-02875. (NASA/JPL/Malin Space Science Systems).

Other intriguing geological features on Mars include gullies on the sidewalls of impact craters and valleys (Figure 4). These features are geologically recent because they lack superimposed small craters and sometimes have debris that
overlies sand dunes. Such gullies are found preferentially on poleward-facing slopes at latitudes higher than 30° in both hemispheres. Longevity of ice is favored on such poleward-facing slopes. Consequently, it is possible that snowpack or ice formed in past orbital-driven climate regimes melted at its base, causing the formation of the gullies (Figure 4) (Christensen, 2003). However, the exact formation mechanism for gullies is currently uncertain.

Evidence for Past Liquid Water from Surface Geochemistry and Sedimentology

Although the surface of Mars is dominated by igneous rock (Christensen et al., 2001), infrared spectroscopy from NASA’s Mars Global Surveyor orbiter indicates spectral absorption features consistent with the presence of coarse-grained crystalline hematite (Fe₂O₃) in a few unique locations on Mars where it outcrops from exhumed layered terrain. In 2004, NASA’s Mars Exploration Rover B, or “Opportunity” rover, landed in Meridiani Planum to examine the hematite there (Squyres et al., 2006). The hematite is found in small spheres (with >50% Fe₂O₃ as hematite) uniformly distributed in laminated sulfate-rich sandstones. The sandstone is crumbling away due to wind erosion, and the hematite spherules, which are more resistant to erosion, are falling out. Hematite spherules or their broken fragments litter the plains of Meridiani and represent leftovers of several hundred thousand square kilometers of erosion. The spherules are concretions that form when water carries dissolved minerals through soft sediments or porous rock and minerals precipitate around a nucleus, incorporating or replacing surrounding sediment. Although the Meridiani rocks are mostly wind-deposited sandstones, some upper sandstone beds show sinuous-crested ripples of a few centimeters height characteristic of sand that was subject to flow in shallow water. Overall, the geologic history in Meridiani Planum is inferred to have gone through three stages: 1) Basalt was altered by acid sulfate to produce sand grains consisting of sulfates and a residue of aluminum-rich amorphous silica. 2) Grains were eroded and re-deposited as sandstone by the wind. 3) Subsequently, groundwater penetrated the sandstone and even pooled at the surface in some areas. The groundwater produced hematite concretions and dissolved some soluble components in the rock. Because only wind has subsequently modified the sandstone, water has likely been scarce at Meridiani for the past several billion years.

Sulfates are an important component of the Martian surface according to many spacecraft observations. A companion rover to Opportunity, named Spirit, found sulfate-rich rocks in Gusev crater, while measurements by NASA’s Mars Pathfinder and Viking landers showed that sulfur is a substantial component of soil (7-8% by mass) and surface rocks. Hydrated sulfate deposits have also been identified in numerous deposits, some the size of mountains, in the Martian tropics from near-infrared spectra obtained by the European Space Agency’s Mars Express spacecraft. Observed sulfate minerals include gypsum (CaSO₄·2H₂O) and kieserite (MgSO₄·H₂O), while jarosite has been found by Opportunity. (Jarosite is XFe₃(SO₄)₂(OH)₆, where “X” is a singly charged species such as Na⁺, K⁺, or hydronium (H₃O⁺)). Anhydrous sulfates, such as anhydrite (CaSO₄), may also be present but would give no signature in the spectral region studied by Mars Express. In general, the sulfates are thought to have formed from alteration of basaltic rocks by sulfuric acid.

Mars Express has also discovered clays in a few locations in exhumed Noachian terrain (Poulet et al., 2005). These clays incorporate Fe³⁺ and Fe²⁺. Such clays generally form when basaltic rocks are altered by water. Given that clays often deposit in alkaline or near-neutral conditions, it has been proposed that they formed in a different environment from the acid sulfates found elsewhere.
Climate Implications

Because liquid water is widely thought to have been the erosive agent that sculpted the ancient valley networks and produced the various hydrated minerals described above, it is often assumed that Mars must have had a persistently warmer and wetter climate in the Noachian than it does today. However, there are several problems with this hypothesis. First, the solar luminosity was about 30% lower 4 Gyr ago compared to today, which requires a very thick CO$_2$ atmosphere (up to ~5 bar surface pressure) to generate enough greenhouse warming to maintain a warm, wet climate at that time (Pollack et al., 1987). Such thick atmospheres are not physically plausible because at ~1 bar, CO$_2$ condenses into clouds and the CO$_2$ ice particles rain out (Kasting, 1991).

Although there has been speculation that CO$_2$ ice clouds themselves could act as a greenhouse blanket, recent models suggest that they could not warm the surface above freezing because such warming is self-limiting: by heating the air, the clouds cause themselves to dissipate (Colaprete and Toon, 2003). Other significant greenhouse gases such as CH$_4$ and SO$_2$ are problematic. Enough CH$_4$ could only be sustained if there were a global microbial biosphere comparable to Earth’s. Volcanic SO$_2$ would quickly dissolve and rain out if Mars had been warm enough for a hydrological cycle. Instead, 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 asteroid impacts to produce above-freezing conditions. There is no geochemical evidence that a thicker CO$_2$ atmosphere persisted long because under warm, wet conditions atmospheric CO$_2$ would weather rocks and make abundant carbonate sediments. No carbonate outcrops have been observed spectroscopically at the 100 m scale, despite a global search from spacecraft. Atmospheric dust particles contain a few percent carbonate but carbonate weathering of dust may have occurred in the prevailing cold dry climate and the total amount of carbonate may be small, depending on the global average depth of dust. Upon reflection, it is not surprising that carbonate outcrops are absent whereas sulfate deposits are relatively widespread. In the presence of abundant sulfuric acid, carbonate would be converted to sulfate with release of CO$_2$ to the atmosphere where CO$_2$ would be subject to various loss processes discussed below.

Atmospheric Origin

Atmospheric origin

Volatiles important to the origin of Mars’ atmosphere include water, carbon and nitrogen. The depletion of noble gases on Mars relative to solar abundance indicate that when Mars formed it did not accrete gases directly from the solar nebula. Instead, volatiles must have been acquired as solids. For example, water would have been acquired as water ice or the water of hydration bound in silicate minerals, and carbon would have been acquired as solid hydrocarbons or perhaps carbonates. Mars acquired volatiles either during planetary accretion or during subsequent bombardment by impacting asteroids or comets. Computer simulations of the formation of planets suggest that Earth acquired much of its crustal and surface water from large “planetary embryos” that grew in the asteroid belt between the orbits of Mars and Jupiter before they were ejected by the gravitational influence of Jupiter towards Earth or outward from the Sun. Comets are ruled out as the source of Earth’s oceans on isotopic and dynamical grounds (Zahnle, 1998). In contrast, to explain the smallness of Mars requires that it suffered essentially no giant collisions from planetary embryos and that it grew through smaller asteroidal bodies that accreted later. This means that Mars could have started out with a much smaller fraction of the volatiles than the Earth (Lunine et al., 2003). However, an alternative school of
thought argues that Mars and Earth acquired volatiles from local planetesimals in a cold nebula, which would argue for a similar volatile fraction on Earth and Mars (Drake and Righter, 2002).

**Atmospheric Loss: Impact Erosion, Hydrodynamic Escape, Sputtering, and Surface Sinks.**

Today, the Martian atmosphere has little carbon and nitrogen, which suggests considerable atmospheric loss. The Earth is estimated to have the equivalent of 60-90 bars of CO$_2$ locked up in carbonate rocks, such that if it were all released, Earth’s atmosphere would be similar to that of Venus. Mars, scaling by its relative mass, presumably had an original inventory of no more than 10 bars of CO$_2$, if we conservatively assume that Mars’ volatile fraction had been similar to Earth’s. However, there is no evidence for a large CO$_2$ inventory today. With an area of 88 km$^2$ and a thickness between 1 and 100 m thick, the residual southern cap contains no more than 0.6-60% as much CO$_2$ as the atmosphere. The regolith on Mars contains an unknown amount of adsorbed CO$_2$, but probably < 0.04 bar (Kieffer and Zent, 1992). Martian meteorites contain < 0.5% carbonate salts by volume, which scaled to the crust provide < 0.25 bar CO$_2$ equivalent per kilometer depth. Thus, the current CO$_2$ inventory of Mars is perhaps a few times 0.1 bar, which, to the nearest order of magnitude, is ~0.1% of the original estimated inventory. This depletion is consistent with isotopic constraints discussed below. Similarly, the current atmospheric N$_2$ inventory is merely $1.6 \times 10^{-4}$ bar, compared to 0.78 bar and 3.3 bar N$_2$ in the atmospheres of Earth and Venus, respectively. Nitrogen could perhaps exist on Mars as nitrate minerals, but the lack of nitrates in Martian meteorites and the absence of spectral evidence for nitrates on the surface do not support such speculation.

**Impact erosion**

![Figure 5](image.png)

Figure 5 The effect of impact erosion on the surface atmospheric pressure $P(t)$ as a function of time, normalized to present surface pressure, $P_0$. (From Melosh and Vickery, 1989).

One efficient mechanism for atmospheric loss is impact erosion. Impact erosion occurs when the hot vapor plume from a large asteroid or comet impact imparts sufficient kinetic energy as heat for atmospheric molecules to escape en masse. The impact velocity must be large enough to create a plume that expands faster than the planet’s escape velocity. Consequently, Mars, with its small escape...
velocity, is much more prone to atmospheric impact erosion than Earth or Venus. Modeling based on the estimated cratering rate on early Mars suggests that the early atmosphere was reduced in mass by a factor of ~100 (Figure 5) (Melosh and Vickery, 1989). Thus, if Mars started with a 5 bar atmosphere after accretion, it would have had a 0.05 bar atmosphere by ~3.8-3.5 Ga, when bombardment had subsided, assuming that the CO$_2$ was in the atmosphere and subject to escape rather than locked up as carbonates in the surface.

Hydrodynamic Escape

Another atmospheric loss process that is thought to have operated very early in Martian history is hydrodynamic escape. This escape mechanism applies to a hydrogen-rich primitive atmosphere, which may have existed from 4.5 Ga to roughly about 4.2 Ga. The source of hydrogen would have been volcanism generated by a much more radioactive mantle than today. During this early time, the upper atmosphere was heated by high fluxes of extreme ultraviolet radiation (EUV) from the young sun. (Although the young sun was fainter than today overall, astronomical observations and theory show that young stars have much greater output of EUV). Hydrodynamic escape occurs when the typical thermal energy of hydrogen in the upper atmosphere becomes comparable to the gravitational binding energy. As a result, the atmosphere expands into the surrounding vacuum of space. The same process currently happens to the solar atmosphere and results in the solar wind. By analogy, hydrodynamic escape of a planetary atmosphere is termed a planetary wind. The escape rate is so rapid that the outward speed of the atmosphere at high altitudes reaches and then exceeds the speed of sound. Heavy atoms get dragged along when collisions with hydrogen push the heavy atoms upward faster than gravity can pull them back. This leads to loss of heavy gases and mass fractionation between different isotopes of the same element. The noble gases on Mars display isotopic patterns consistent with fractionation by early hydrodynamic hydrogen escape (see below). Consequently, bulk gases, such as CO$_2$ and N$_2$, should have also been lost through hydrodynamic escape.

Sputtering and Nonthermal Escape

A further atmospheric loss mechanism is sputtering, also known as solar wind stripping of the atmosphere. Ions in the upper atmosphere are “picked up” by magnetic fields generated by the flow of the solar wind around the planet. The ions undergo charge exchange, which is the process where a fast ion passes its charge to a neutral atom through collision and becomes a fast neutral atom. The large energy is then imparted to surrounding particles through further collisions. Fast, upward-directed particles generated in this process can escape. Today Mars has no global dipole field, but solar wind stripping would have been prevented by the presence of a substantial global magnetic field on early Mars, which would have forced the solar wind to flow around the planet at a greater distance, without significant atmospheric interaction. Mars is known to have once had a global field because the planet has regions of large remnant magnetization, where new volcanic rocks crystallized in the presence of a magnetic field. Thus, sputtering would have only been important after Mars lost its magnetic field. The timing of the shut-off of the global magnetic field is uncertain. However, there are clues. Unlike much of the other ancient terrain, the Hellas impact basin and surrounding areas lack any magnetic signature. This is most easily explained if the Hellas impact, which is at least 4 Gyr old (based on its size), occurred when Mars no longer possessed a global magnetic field. Thus stripping of the atmosphere by the solar wind would have occurred since about ~4 Ga, but not before. Models suggest that solar wind stripping may have removed up to 90% of the post-4 Ga atmosphere. Such atmospheric losses are cumulative. For example, if
impacts and hydrodynamic escape removed 99% of the earliest atmosphere and sputtering removed a further 90% of the remainder, the total loss would be 99.9%. Atmospheric escape is happening today by sputtering and other means. Escape occurs from the base of the Martian exosphere, which is at about 230 km altitude. In the exosphere, the probability of collisions is so small that particles with sufficient upward velocities escape from the planet. The most important species that escape today are hydrogen, oxygen, nitrogen, and carbon. Hydrogen and oxygen loss are coupled. Water vapor photolysis in the lower atmosphere produces H\(_2\). Above \(~120\) km altitude, hydrogen diffuses upwards and gets converted to atomic hydrogen by photochemical reactions. Atomic hydrogen possesses enough thermal energy to escape to space, so the rate of escape is limited by slow diffusion through the upper atmosphere, and, in turn, by supply of hydrogen-bearing species from the lower atmosphere. Although oxygen produced from water vapor photolysis is too heavy to escape to space through its thermal motion alone, another mechanism exists for oxygen loss. Ionized oxygen molecules (O\(_2^+\)) in the ionosphere combine with electrons in "dissociative recombination". Recombination dissociates the molecules into O atoms with enough kinetic energy to escape (O\(_2^+\) + e\(^-\) \rightarrow O + O). On Mars, it has been hypothesized that the oxygen escape flux adjusts itself so that it balances the hydrogen escape flux in 2:1 ratio, i.e., effectively, water escapes (McElroy and Donahue, 1972). However, recent estimates of O escape suggest that the H:O escape ratio is \(~20:1\), implying a surface sink for oxygen (Lammer et al., 2003).

Isotopic ratios of D/H and \(^{18}\)O/\(^{16}\)O in the atmosphere and in Martian meteorites provide weak constraints on the amount of water that has escaped over Martian history. Upper bounds on the estimates of water loss range up to 30-50 m of equivalent global ocean (Krasnopolsky, 2002). These amounts are roughly comparable to estimates of the inventory in the current polar caps and regolith. Nitrogen and carbon are also able to escape via dissociative recombination. Such loss mechanisms have probably been important for the last 4 Gyr of Martian history and can account for observed C and N isotopic ratios on Mars (see below).

Surface Sinks

A final possible atmospheric loss mechanism is to the surface. In the presence of liquid water, CO\(_2\) will dissolve to form carbonic acid and react with the surface through chemical weathering. Carbonic acid reacts with silicate minerals in igneous rocks to release cations (such as Mg\(^{2+}\), Ca\(^{2+}\), Fe\(^{2+}\), K\(^+\), and Na\(^+\)), bicarbonate (HCO\(_3^-\)) and other anions, and silica. The ions so released would be expected to precipitate in sediments producing abundant carbonates such as siderite (FeCO\(_3\)), calcite (CaCO\(_3\)) and magnesite (MgCO\(_3\)). Weathering and deposition thus produce overall reaction of the type CO\(_2\) + CaSiO\(_3\) = CaCO\(_3\) + SiO\(_2\). The weathering lifetime of a massive CO\(_2\) atmosphere is geologically so short (~1.5 \times 10\(^7\) years) that a recycling mechanism such as thermal decomposition by volcanism must be hypothesized to maintain the CO\(_2\) (Pollack et al. 1987). A 1 bar CO\(_2\) atmosphere, if it were all eventually converted to calcite, would generate a global layer of calcite about 200 m thick. But there is no evidence from remote spectroscopy for even a single carbonate outcrop. If Mars started out with abundant CO\(_2\), the most likely loss appears to have been to space and not to the surface. Noble gas constraints strongly support this idea.

**Inferences from noble gases and the isotopic composition of the atmosphere**

The isotopic composition of the atmosphere of Mars was measured directly on the surface of Mars by mass spectrometers on two Viking lander spacecraft in the 1970s. For noble gases, more precise measurements have become available from gases trapped within Martian meteorites (Table 2). Atmospheric gases were incorporated into these meteorites when they were melted under the shock of impact that ejected
them from Mars. The compositional and isotopic similarity of such meteorite gases to the Viking measurements is convincing evidence that such meteorites come from Mars. Isotopic measurements of gases in the shergottite meteorite sub-class of Martian meteorites have proved particularly valuable because the shergottites originated from shallow depths on Mars so that they are not generally contaminated with gases that have emanated from the Martian interior.

The isotopic composition of volatiles on Mars points to loss of the early atmosphere. Both $^{40}$Ar/$^{36}$Ar and $^{129}$Xe/$^{132}$Xe noble gas ratios are considerably larger than terrestrial values (Table 2). The “radiogenic isotopes”, $^{40}$Ar and $^{129}$Xe, result from the decay of radioactive $^{40}$K and $^{129}$I, respectively. In contrast, the “primordial isotopes”, $^{36}$Ar and $^{132}$Xe, are not radioactive decay products and were assimilated when Mars formed. The relative enrichment of the radiogenic isotopes suggests that the primordial isotopes were lost. $^{40}$K has a ~1.28 Gyr half-life, while $^{129}$I has a half-life of only ~16 Myr, which suggests that most of the $^{132}$Xe was lost from Mars very early. A plausible loss mechanism for the primordial isotopes is intense impact erosion in the early Noachian.

Isotopic measurements also indicate that hydrogen, argon, carbon, nitrogen and oxygen have escaped from Mars by gradual processes that continue to operate today. As a result, the light isotopes are depleted relative to the heavy ones; for example, $^{14}$N relative to $^{15}$N (Table 2). This isotopic fractionation arises because above 120 km altitude, gases separate diffusively according to mass and the heavier isotopes decrease in abundance more rapidly than light isotopes. Consequently, more light isotopes are available for removal at the base of the exosphere. Thus, the atmosphere below becomes enriched in heavy isotopes. This enrichment indicates a loss of 50-90% of the atmospheric species to space (Jakosky and Jones, 1997; Jakosky, 2001).

Table 2 The isotopic composition of the atmosphere of Mars as measured by the Viking lander spacecraft and in trapped gas bubbles in Martian shergottite meteorites (Owen 1992; Bogard et al., 2001).

<table>
<thead>
<tr>
<th>Isotopic Ratio</th>
<th>Martian atmosphere (Viking)</th>
<th>Martian atmosphere (Shergottites)</th>
<th>Earth’s atmosphere</th>
<th>Martian isotope ratio relative to terrestrial</th>
</tr>
</thead>
<tbody>
<tr>
<td>D/H</td>
<td>(9±4) × 10^4</td>
<td>6.9 × 10^4</td>
<td>1.56 × 10^4</td>
<td>~4.4-5</td>
</tr>
<tr>
<td>$^{12}$C/$^{13}$C</td>
<td>90±5</td>
<td>not reported</td>
<td>89</td>
<td>~1</td>
</tr>
<tr>
<td>$^{14}$N/$^{15}$N</td>
<td>170±15</td>
<td>&gt;181</td>
<td>272</td>
<td>&gt;0.6</td>
</tr>
<tr>
<td>$^{20}$Ne/$^{22}$Ne</td>
<td>not measured</td>
<td>~10</td>
<td>9.8</td>
<td>~1</td>
</tr>
<tr>
<td>$^{16}$O/$^{18}$O</td>
<td>490±25</td>
<td>~490</td>
<td>489</td>
<td>~1</td>
</tr>
<tr>
<td>$^{40}$Ar/$^{36}$Ar</td>
<td>3000±500</td>
<td>1800±100</td>
<td>296</td>
<td>~6</td>
</tr>
<tr>
<td>$^{36}$Ar/$^{38}$Ar</td>
<td>5.5±1.5</td>
<td>≤3.9</td>
<td>5.3</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>$^{129}$Xe/$^{132}$Xe</td>
<td>2.5^{+2}_{-1}</td>
<td>2.4-2.6</td>
<td>0.97</td>
<td>~2.5</td>
</tr>
</tbody>
</table>

Hydrodynamic escape can reasonably account for the isotopic fractionation of some of the noble gases found in the Martian atmosphere: argon, neon and xenon. Hydrodynamic escape has been invoked to explain the Martian $^{36}$Ar/$^{38}$Ar ratio of <3.9, which is isotopically heavy compared with a terrestrial ratio of 5.32 and the average carbonaceous chondrite value of ~5.3 (thought to be representative of the material from which Mars formed). However, if argon escapes and fractionates, neon must also fractionate because it is lighter. Martian atmospheric $^{20}$Ne/$^{22}$Ne appears to be ~10, similar to the terrestrial atmospheric ratio but smaller than a chondritic value ~13.7. If the original Martian ratios of $^{36}$Ar/$^{38}$Ar and $^{20}$Ne/$^{22}$Ne were 5.35 and 13.7, respectively, hydrodynamic escape models produce a $^{20}$Ne/$^{22}$Ne ratio
no greater than $9.5 \pm 1.3$, similar to our observation. Interpretation of xenon isotopes is complicated by virtue of its nine stable isotopes, several of which have been affected by the decay of extinct radionuclides. However, fractionation of non-radiogenic xenon isotopes can plausibly be explained by mass fractionation during hydrodynamic escape of hydrogen (Pepin, 1991). Xenon, in particular, is too heavy to escape by means such as sputtering or thermal escape, so early hydrodynamic escape would seem to be required.

Atmospheric loss has also left an imprint on the overall abundance of volatiles. The stable and most abundant isotope of krypton, $^{84}{\text{Kr}}$, is probably the best volatile tracer of atmospheric loss because it should not be subject to fractionation by gradual atmospheric escape of the kind that occurs today for hydrogen, nitrogen, carbon and oxygen. Thus krypton has probably been retained ever since the end of heavy bombardment around 3.8 Ga. The ratio $C/^{84}{\text{Kr}}$ is $\approx 4 \times 10^7$ for Earth and Venus but $= (4.4-6) \times 10^6$ on Mars. This suggests that the amount of CO$_2$ that Mars had when heavy bombardment and impact erosion ended was 10 times greater (i.e., a 90% loss, consistent with isotopic fractionation of nitrogen). Given that Mars has ~6 mbar CO$_2$ now, the atmosphere may have had ~60 mbar CO$_2$ at around 3.8 Ga. In addition, $^{21}{\text{Kr}}$ per kg on Mars is only about 1% of that on Earth. This implies a factor of ~100 depletion (of both krypton and carbon) due to early impact erosion before 3.8 Ga, which is consistent with the predictions of impact erosion models. A primordial inventory of $\geq 6$ bar CO$_2$ would be inferred, consistent with inferences about Mars’ original endowment of volatiles.

Taken together, we see that the isotopic and abundance evidence suggests that Mars may have lost ~99% of its atmospheric volatiles by the end of heavy bombardment and has perhaps since lost a further ~90% of what remained at that time. This conclusion is tempered by the knowledge that some volatiles, like water, readily form solids in the subsurface, which affords protection against loss to space.

**Martian Milankovitch Cycles, Chaotic Obliquity Fluctuations, And Quasi-Periodic Climate Change**

**Table 3** The orbital elements of Mars and the Earth and their variability.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Present Mars</th>
<th>Martian Variability: Range</th>
<th>Cycle (years)</th>
<th>Present Earth</th>
<th>Terrestrial variability: Range</th>
<th>Cycle (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obliquity (°)</td>
<td>25.19</td>
<td>~12-47*</td>
<td>120,000**</td>
<td>23.45</td>
<td>22-24</td>
<td>41,000</td>
</tr>
<tr>
<td>Eccentricity</td>
<td>0.093</td>
<td>0-0.12</td>
<td>120,000***</td>
<td>0.017</td>
<td>0.01-0.04</td>
<td>100,000</td>
</tr>
<tr>
<td>Longitude of perihelion (°)</td>
<td>250</td>
<td>0-360</td>
<td>51,000</td>
<td>285</td>
<td>0-360</td>
<td>21,000</td>
</tr>
</tbody>
</table>

*For times older than about 10 Ma, obliquity variations are chaotic and would have varied between 0 and 60° (Touma and Wisdom, 1993).

**The amplitude of obliquity oscillation is modulated with a ~1.2 Myr period envelope.

***The amplitude of eccentricity oscillation is modulated with a ~2.4 Myr period envelope.

$^3$Eccentricity, $e$, is defined by $e = (1-(b/a)^2)^{0.5}$ where $a$ is the semi-major axis and $b$ is the semi-minor axis of the ellipse traced by the planet’s orbit around the sun.

Mars has very large variations in its orbital elements compared to the Earth (Table 3; Figure 6). Today, the eccentricity of the Martian orbit is 0.093, about 5 times greater than for the Earth, which means that Mars receives about 40% more insolation at perihelion than aphelion. Mars’ rotation rate and obliquity (the angle between its spin axis and the normal to the orbital plane) are similar to Earth’s. Consequently, daily
and seasonal changes are analogous. Today, the obliquity of Mars, 25.2°, is close to its mean value over the last 10 Myr but obliquity has varied considerably during that time. Moreover, the spin dynamics is chaotic with an exponential divergence timescale of 3 to 4 million years, so that for timescales longer than 10^7 years, the obliquity could have varied between 0° and 60°. The average obliquity for Mars over geologic time was ∼40°, and sometimes the obliquity may have reached as high as ∼80° (Laskar, 2004). In recent history, eccentricity and obliquity have oscillated with a primary period of ∼10^5 years, modulated on timescales of 2.4 Myr and 1.2 Myr respectively (Figure 6). In addition, the spin axis orientation (which determines the season of perihelion) has precessed with a 51,000-year period.

Figure 6 simulated variations of Martian orbital elements over the last 10 Myr. (Data courtesy of J. Armstrong).
Of the three parameters (season of perihelion, eccentricity and obliquity), obliquity exerts the largest influence on the climate because changes in obliquity alter the latitudinal distribution of sunlight. Indeed, above 54° obliquity, the poles receive more annual average insolation than the equator. However, the global annual mean surface temperature is calculated to drop at high obliquity because of the increased extent of the bright seasonal CO₂ ice caps. The larger caps would also cause the mean annual surface pressure to be somewhat lower at high obliquity, assuming that the amount of exchangeable CO₂ desorbed from polar regolith is small. If the obliquity were 45° (with other orbital parameters the same as today’s), the southern winter cap would reach the equator of Mars during southern winter (Haberle et al., 2003). Consequently, polar ice may have reached the equator even in the last 10 Myr.

Probable evidence for orbital-driven climate change can be found in geologic features on Mars. Both polar regions have extensive layered terrain, which is ~10 Myr old based on the lack of craters. The polar layered terrain consists of multiple layers, each meters to tens of meters thick, with variable brightness. One possible explanation for the origin of layered terrains is that quasi-periodic oscillations in Mars’ orbital parameters cause the climate to oscillate. In particular, the shuffling of the climate regimes causes cyclic changes in ice and dust deposition over time. For example, higher (or lower) eccentricity will mean more (or less) dust transport, modulated with ~10⁶ year cyclicity. The short period obliquity and precession cycles will also modulate deposition and erosion over 10⁵ years. The two spatial frequencies observed in the polar layered terrain may be related to these two temporal frequencies (Figure 7).

Figure 7 Polar layered deposits. Top inset shows a picture of the north polar cap. Left is a blow-up of the edge of the permanent north polar cap in a Viking Orbiter image (VO 560B60). This image shows a box, which is magnified further in the right-hand MOC image from the MGS spacecraft (Portion of image number SP2-46103 near 79.1°N, 340°W). The high-resolution image shows that the polar cap is made up of many layers with thicknesses tens of meters in scale or less. Layers that are ~100 m thick have many discrete layers within them. (Images MOC2-70A–70B, NASA/JPL/Malin Space Science Systems).

A thin, patchy mantle of material, apparently consisting of cemented dust, has also been observed within a 30-60° latitude band in each hemisphere (Figure 8). The material is interpreted to be an atmospherically deposited ice-dust mixture from
which the ice has sublimated, leaving behind a loosely cemented material. Such residue would be susceptible to wind erosion, which would account for its patchy nature. Today, near-surface ground ice is stable poleward of \( \pm 60^\circ \) latitude (Feldman et al., 2004), whereas the two latitude bands where the mantling material is observed correspond to places where the stability of near-surface ice has occurred over the last few million years due to orbital changes. Viscous flow features and gullies, which are probably associated with ice from past climate regimes, are also found within these same latitude bands (Milliken et al. 2003). In addition, some geologic features at low latitudes resemble dust-covered glaciers or rock glaciers (Head et al., 2005).

**Figure 8** Ice-dust mantling material located at 43.7° S, 239.6° W. The material is being removed, typically on equator-facing slopes. In areas where the material is completely removed, the surface is rough and dissected at this scale. (Portion of MOC image FHA01450 NASA/JPL/Malin Space Science Systems).

**Long-Term Atmospheric Evolution: A Synthesis Of Evidence And Theory**

The history of the Martian atmosphere is clearly subject to different interpretations because of uncertainty about the climate conditions under which various geological features were formed. However, certain geochemical indicators, such as inferences from the isotopic composition of the atmosphere, are less ambiguous.

Taken together, geochemical data and models support the view that most of the original \( \text{CO}_2 \) and nitrogen volatile inventory was lost very early by impact erosion and hydrodynamic escape. Models of impact erosion and the absolute abundance of volatiles like nitrogen and krypton suggest that as much as 99% of the original inventory may have been lost by 3.8 Ga. Before this time, however, large impacts would have provided sufficient heat to decompose carbonates and vaporize subsurface volatiles, such as water and \( \text{CO}_2 \) ice. Consequently, impacts would have generated temporary (~10^2-10^3 years) warm, wet climates (Segura et al. 2002). During such episodes, rainwater would erode valley networks or recharge aquifers, producing conditions that allowed groundwater flow and sapping. Such a scenario would explain the apparent coincidence between the end of heavy bombardment and the large drop in erosion rates. It would also explain why valley networks are largely confined to heavily cratered Noachian terrains. During quiescent periods, and after heavy bombardment, water and carbon dioxide would be lost from the atmosphere to
polar caps, to the subsurface, and to space. The disappearance of the global dipole field some time before 4.0 Ga allowed the solar wind to strip the upper atmosphere of Mars. As a result of solar wind stripping, as well as thermal and other nonthermal escape processes, another 50-90% of the Mars’ volatile inventory of carbon and nitrogen was probably lost after 3.8 Ga. This is most clearly reflected today in the ratios of the stable isotopes of nitrogen and argon. Also the ratio of $^{13}C/^{84}Kr$, when compared to Earth and Venus, indicates loss of carbon that is consistent with calculations of escape to space. Outflow channels presumably formed as a result of geothermal activity that melted ground ice (perhaps accumulated near the equator during high obliquity or an ancient time when the pole was a different location (Schultz 1985)). However, the huge size of outflow channels remains enigmatic. In recent epochs, the variation of the orbital elements of Mars in Milankovitch-type cycles has almost certainly caused ice to be stable at lower latitudes than today. As the ice has retreated, it has left behind a variety of telltale features including remnant loess from desiccated dust-ice mixtures, gullies, and perhaps remnant polar terrain at low latitudes. However, none of these features require an atmosphere that is substantially different from today (Figure 9).

![Figure 9](image-url) A schematic overview of the history of Mars, showing three periods: the Noachian, Hesperian and Amazonian. The igneous crystallization ages of Martian meteorites are shown, which indicate that Mars has been volcanically active throughout its history (N = nakhliites, C = Chassigny, S = shergottites). The oldest meteorite, ALH84001, has a crystallization age of about 4.5 Ga, but contains carbonate salts of 3.9 Ga age. In the Noachian, the planet had a magnetic field and suffered heavy impact bombardment. Valley networks formed mainly in the Noachian. Later, the large outflow channels formed. As Mars aged, the Sun’s brightness increased. Also the Martian atmosphere grew thinner, mostly in the Noachian.

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Cross-references

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Atmospheric evolution, Earth
Atmospheric evolution, Venus