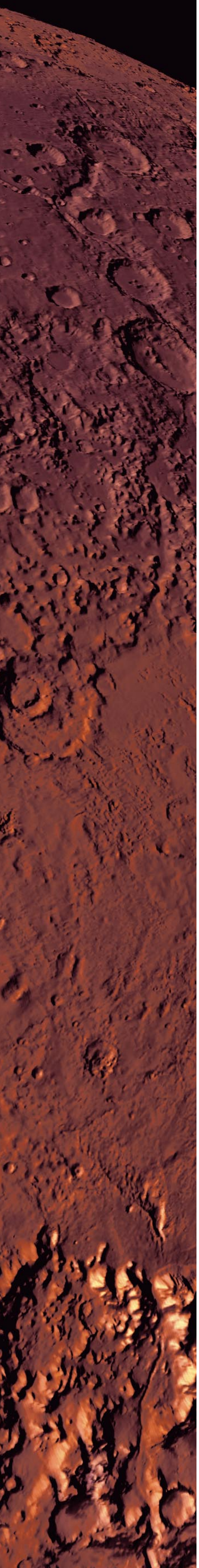

Mars' volatile and climate history

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There is substantial evidence that the martian volatile inventory and climate have changed markedly throughout the planet's history. Clues come from areas as disparate as the history and properties of the deep interior, the composition of the crust and regolith, the morphology of the surface, composition of the present-day atmosphere, and the nature of the interactions between the upper atmosphere and the solar wind. We piece together the relevant observations into a coherent view of the evolution of the martian climate, focusing in particular on the observations that provide the strongest constraints.

Unravelling its climate history is one of the main challenges in understanding the evolution of Mars. There is substantial evidence for change in the climate and the inventory of volatiles through time. This evidence points to an early environment in which water was either more stable or more abundant at the surface than it is today, and to processes of supply of volatiles to the atmosphere and their removal from it that are able to explain this shift in climate. Determining the forces behind the changing climate, particularly the relationship between the atmosphere, water at the surface, and water in the crust, is important for understanding the planet as a whole. Additionally, the potential for life to have existed in the past, or even today, is strongly governed by the occurrence of liquid water and its history over time.

The climate system of Mars is inherently complex, involving physical and chemical processes within the deep interior, the crust, the surface, the atmosphere, the upper atmosphere, and interactions with the solar wind (Fig. 1). Our goal is to integrate observations and measurements pertinent to each of these areas into a coherent view of martian climate and its evolution. We will focus on recent results from the Mars Global Surveyor mission and from ongoing analyses of the martian meteorites, and will emphasize observations that provide the strongest constraints rather than describing what is merely plausible.

The present-day atmosphere and climate

The martian atmosphere consists predominantly of CO_2, with a total atmospheric pressure averaging about 6 mbar (6 hPa), about 0.6% of the Earth's atmospheric pressure. The atmosphere also contains N_2 and Ar at a level of 1–3%, lesser amounts of H_2O, CO and O_2, and additional gases in trace amounts[1].

Water vapour is present in the atmosphere, with a typical partial pressure of 10^{-3} mbar. This corresponds to about 10^{-3} g H_2O residing above each square centimetre, equivalent to a condensed layer about 10 μm thick if it all precipitated onto the surface; the water content of the Earth's atmosphere, in contrast, is about 10^4 times greater. The atmospheric water content varies in a manner that is consistent with seasonal supply and removal from the polar caps, exchange with water adsorbed in the near-surface regolith, and global transport by means of winds[2].

Temperatures average about 220 K globally, well below the melting temperature of ice and lower than the eutectic freezing temperature of most salt-rich brines[3]. Even though surface temperatures rise above 273 K over large regions near the equator and near noon, liquid water still would not be stable. It could exist as a transient phase, but would quickly evaporate into the relatively dry atmosphere and eventually freeze out at the colder high latitudes[2,3].

Mars' north polar region is covered with CO_2 ice during winter, which sublimes away and leaves a residual summertime deposit of water ice. The south cap is covered year-round by CO_2 frost, but almost certainly has water ice mixed in or beneath it[2]. The axial obliquity, the tilt of the polar axis with respect to the normal to the orbital plane (currently 25.2°), varies on timescales of 10^5–10^6 years (refs 4, 5). On longer timescales, it is chaotic, and may have been as low as 0° or as high as 60° in the past few million years (ref. 6). At high obliquity, polar summertime temperatures may increase markedly, and substantial amounts of water ice may sublimate into the atmosphere. Exchange of this water between the north and south polar caps, modulated by the changing eccentricity and season of perihelion, is probably responsible for the formation and evolution of layered deposits in the polar regions[2,4,7].

Nature of the earliest atmosphere and climate

The observable surface record of Mars' geological history spans 4 billion years (Gyr). The oldest, most heavily cratered surfaces are thought to be about 4.0 Gyr old, and the youngest are possibly less than 100 million years (Myr) old[8–11]. Evidence pertaining to the ancient climate is inferred from processes that shaped the surface during the Noachian epoch, which ended when the cratering rate declined dramatically between 3.8 and 3.5 Gyr ago[9,11]. (Fig. 2 summarizes the history and timing of processes involved in martian climate evolution.) Although atmospheric gas undoubtedly was present before 4.0 Gyr, and was removed in part from the atmosphere by various processes[12], we focus here on processes that post-dated the onset of the visible geological record.

The ancient martian surfaces contain geological features that indicate that the early climate was different. Dendritic networks of valleys seem similar to those formed by runoff of surface water on the Earth, although the areal density of tributaries is typically lower[13]. There is debate about the relative roles of surface runoff, sapping by release of subsurface water, and discharge of water from hydrothermal systems in forming the valleys[14–16]. However, there is general agreement that water must have flowed at the surface in order to form these features and that their dendritic character and typically V-shaped cross-section requires a gradual rather than catastrophic formation process (ref. 17, and see review in this issue by Baker, pages 228–236).

Erosion rates in general were substantially greater during the Noachian. This can be seen easily on ancient impact craters. The largest craters and basins are severely degraded; ejecta deposits, crater rims and central peaks have all been removed, and a paucity of craters smaller than about 15-km diameter suggests that they have been removed in their entirety[18,19]. Some partially degraded craters have fluting and scalloping along the interior rim that suggests erosion by flowing surface water[19,20]. Estimated erosion rates were more than 1,000 times larger than in subsequent epochs, and approach values appropriate for drier regions on Earth[17,21].

Additional evidence for a shift to a colder, drier climate at the end of the Noachian is provided by the initiation of U-shaped valley forms at the downstream ends of V-shaped valleys, suggesting an evolution of valley-forming erosional mechanisms from water-related to ice-related[22]. This period of U-shaped valley formation, and valley network evolution in general, ended rapidly at the end of the Noachian or early in the Hesperian[16,22].

Together, these features strongly suggest that liquid water was present during the Noachian and flowed over the surface, and that the climate must have been such that water was either more stable or more abundant at the surface than it is at present. Such a climate is thought to have required warmer surface temperatures produced by substantial greenhouse warming[23]. Although the climate must have been 'warmer' and 'wetter', there is no consensus as to what temperatures would have been required, what the greenhouse gas would have been, or how much water would have to have been at the surface or in the atmosphere[24]. If CO_2 were the greenhouse gas, up to several bars pressure would have been required to produce the necessary warming[25–27]. A warmer climate is indicated even if valley network formation involved subsurface hydrothermal processes, as flow at the surface and gradual erosion requires a warmer climate independent of the original source of the liquid water.

Connections between ancient climate and early geology

Other events also were taking place during the Noachian period that would have affected climate. The planet was being bombarded by impacting asteroids or planetesimals, it was creating its main division into a southern highlands and a northern lowlands (which is reflected today as the ancient and younger terrains, respectively), and volcanism was forming the major Tharsis province on which sits many of the large volcanoes.

The formation of Tharsis was recognized only recently as occurring largely in the Noachian[28,29]. The heavy loading of the lithosphere, due to the dominantly magmatic formation of the Tharsis rise, resulted in a global warping of the surface[28]. Many of the ancient valley networks are seen to preferentially follow the slopes that resulted from the formation of Tharsis or, in at least one location (Margaritifer Sinus), are of the same age as those that do. This indicates that emplacement of Tharsis must have been nearly complete while the largely Noachian valley networks were still forming. Although much of the surface in Tharsis is sparsely cratered and therefore relatively young, indicating that resurfacing of Tharsis continued throughout martian history, the bulk of the volume of Tharsis must be old[28].

The volcanic magma from which Tharsis formed probably contained substantial quantities of both water and CO_2 that would have been released, providing input of gases to the atmosphere and possibly contributing to an early, thicker atmosphere. Geochemical analysis of the martian meteorites, for example, suggests a water content of as much as 1.8% by weight[30]. Thus, the timing of valley network formation may be more than coincidental. Tharsis volcanism may have supplied gases that helped maintain a climate conducive to weathering and erosion, and the cessation of volcanism may have allowed other processes to begin removal of much of the atmosphere (see below)[28].

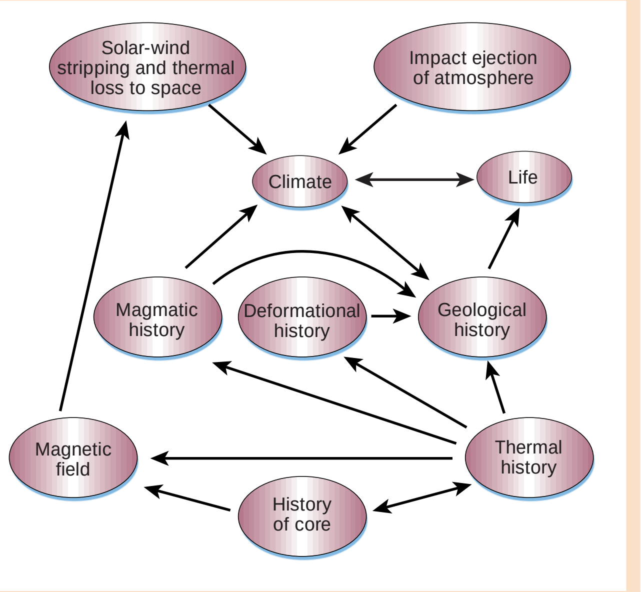

Figure 1 Schematic diagram showing the interconnected nature of the martian climate system and the relationship between climate and various processes from the deep interior to the upper atmosphere. Arrows indicate how one region affects another, with the arrow pointing towards the processes or area being affected; two-headed arrows indicate mutual interactions.

There is another compelling connection between Tharsis and the history of water. The lithospheric deformation due to the weight of Tharsis created a depression or trough encircling it at a radius of about 5,000 km (Fig. 3a). Most of the large-scale geological features related to surface water are concentrated in this trough[28]. This includes the large-scale drainages that flow northward from the Argyre basin (at 50° S latitude) and the catastrophic flood channels that emanate from the eastern end of Valles Marineris and flow north into the Chryse basin and into the northern lowlands. Argyre, for example, seems to have been filled with water, which subsequently overflowed the rim and flowed northward[31]. Although the catastrophic flooding occurred episodically throughout martian history[32], the source and flow regions concentrate in the Tharsis trough. This relationship suggests a long-lasting connection between the geological and geophysical history of Mars and the release, availability and geological effects of liquid water. But some anomalies exist, such as the paucity of similar features in the western branch of the circum-Tharsis trough and the ill-defined nature of processes, other than simple structural control of water pathways, that would provide a causal connection between the trough and the release of crustal water.

Finally, we note an apparent correlation between the regions on which crustal remanent magnetic fields are imprinted and areas on which valley networks are identified (Fig. 4)[33]. The magnetic anomalies presumably retain an imprint of a global-scale intrinsic magnetic field from an early time in martian history (see below, ref. 34, and the review in this issue by Stevenson, pages 214–219). Exceptions to the correlation include the large-scale magnetic anomalies occurring in discrete bands in the high southern latitudes[35], where valley networks may have never formed because of climate constraints, and Margaritifer Sinus, where stripping of the surface may have removed the valleys without removing enough material to eliminate the magnetic anomalies[36]. If genuine, this correlation may reflect a coincidence in timing of the formation of both the valleys and the magnetic anomalies or in the geographic location of subsequent alteration processes. Alternatively, it may involve a cause-and-effect relationship, in which valleys could represent the surface manifestation of hydrothermal systems driven by subsurface volcanism that thermally induced the creation of the localized remanent fields[37].

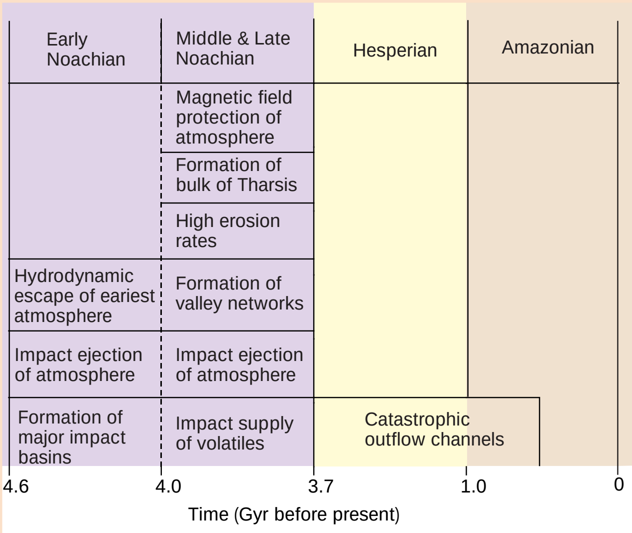

Figure 2 Schematic diagram showing the time history of the martian volatile system. The 4.6-Gyr history of Mars is divided up into the major geological epochs that have been identified, and processes that occur within each epoch are indicated. Note that the timeline is not a linear scale. Some climate-related processes are not shown (including recent polar-cap behaviour and the occurrence of possible crater lakes). Absolute ages marking the boundary between epochs are estimated based on the recent revision of cratering chronology[11].

However, as neither the mechanism of formation of the magnetic anomalies nor of their removal (if they ever were distributed globally) is understood, such connections are speculative at best.

Evolution of the Noachian atmosphere

What processes might have caused the inferred changes in Noachian climate, what sinks were available for atmospheric gases during this epoch, and can we infer the degree to which each process acted? These are especially important issues, as the output of the Sun was some 30% less 4 Gyr ago than it is today[38], making the maintenance of an early warmer climate more difficult[39,40].

Impact of large asteroids through the Noachian epoch would have ejected gas in the atmosphere to space[41]. Although inherently capable of removing large amounts of atmosphere, only those impacts occurring since the time of the onset of the geological record would have resulted in climate change that can be inferred from that record[42]. We know how many impacts occurred, based on the number of large craters and impact basins seen on the ancient terrain, and can readily extrapolate to impacts on areas subsequently buried[43]. Combined, impacts are likely to have ejected about 50–90% of the atmosphere present in the early epoch[42]. This fraction probably is an upper limit, as some volatiles (such as water) might not have resided exclusively in the atmosphere at this time or might have been outgassed late in the epoch.

Recent measurements of surface elevation have allowed identification of previously unknown impact basins buried below a relatively thin veneer in both the southern highlands and the northern plains[43]. The buried craters in the northern plains have similar abundance to the craters in the southern highlands, and justify the extrapolation of southern-hemisphere craters to a global inventory. The buried southern-highlands craters predate the geological evidence pertaining to the early climate, so those impacts would not have contributed to the changes in climate and should not be counted in summing up atmospheric loss.

Impacts of volatile-rich objects can supply new volatiles to Mars as well as remove them from the atmosphere[44]. In particular, the analysis of isotope ratios of heavy noble gases in the atmospheres of Earth and Mars suggests that much of the planets' volatiles could have been supplied by comets[45]. But the relative roles of supply and removal of volatiles by impacts is unknown.

The impingement of the solar wind can strip gases directly from the upper atmosphere. Both atom-on-atom collisions that eject individual molecules (pick-up-ion sputtering) and hydrodynamic collisions that could strip off large volumes of gas *en masse* would have been important[46,47]. But theoretical models of these processes are exceedingly uncertain even at the present epoch, and extrapolating to past epochs when the solar wind and solar ultraviolet radiation were more intense[48] compounds the uncertainties. However, two observations of the present-day atmosphere indicate that these processes were significant. First, *in situ* measurements of the energy spectrum of ionospheric electrons distinguish between ionization of gases in the upper atmosphere and those from the incoming solar wind. The morphology of discrete regions of solar-wind versus planetary electrons requires that large masses of upper atmosphere are being stripped off *en masse*[47]. Second, isotopic measurements indicate that such stripping has occurred and has been significant. The lighter isotopes of each atom are enriched relative to the heavier ones at the top of the atmosphere by diffusive separation (for example, ^{12}C relative to ^{13}C, ^{14}N to ^{15}N, or ^{36}Ar to ^{38}Ar), and will be preferentially removed to space. Consequently, the gas remaining in the atmosphere becomes enriched in the heavier isotope[49]. This enrichment pattern is observed consistently in the modern atmosphere. For example, the ratio ^{38}Ar/^{36}Ar is 30% greater on Mars than elsewhere in the Solar System, and nitrogen and carbon also show enrichments (Table 1). This enrichment indicates loss of between about 50 and 90% of the atmospheric species to space, with the actual loss probably tending towards the higher values[50,51].

In addition, compared to terrestrial values, martian water shows a fivefold enrichment of D relative to H (refs 52–54, and see Table 1). The lighter H atom can escape thermally to space more readily than D, so the considerable enrichment of observed D requires the loss of substantial quantities of hydrogen to space. The hydrogen comes from water, with the oxygen from water probably also being lost to space[55]. The inferred water loss depends on the relative supply rates of H and D to the upper atmosphere, their relative escape rates, and the initial D/H ratio on Mars[56]. Recent analysis of martian meteorites suggests that the initial D/H value on Mars was twice the terrestrial value[57]; in addition, there has been a spectroscopic detection of upper-atmospheric D and a revision of atmospheric reaction rates[54,58]. Although the initial interpretation was that about 90% of martian water had been lost to space[56], the current understanding suggests loss of about two-thirds of the water[59].

The observed isotopic enrichments indicate the fraction of each species that has been lost, but not the total amount lost. Atmospheric gases exchange with the regolith and polar caps, so it actually represents the fraction lost from the combined atmospheric plus non-atmospheric reservoir. Additionally, different portions of the polar ice, for example, may exchange with the atmosphere on different timescales[7], and outgassing of juvenile gas at later times will affect the isotope ratios[51]. The absolute loss rates to space are uncertain today and may have varied through time[60], so although we can be confident that loss of substantial volatiles to space has occurred, we are uncertain as to how much has been lost, where it came from, or exactly how much has been left behind. (Although the losses of H and O are related, and one would expect the isotopic fractionation of D/H to be related to that of ^{18}O/^{16}O, oxygen has an additional reservoir with which it can exchange — minerals in the crust — so that the connection is likely to be complex.)

Whereas stripping by the solar wind of upper-atmospheric gases will change the isotope ratios, removal by impact will not. Impacts remove the gas from the entire atmospheric column, and thereby remove all isotopes with equal efficiency. Thus, the fractions of gas lost by these two processes add together. For example, if each indicates loss of 90%, these represent a different 90% and they sum up to a net loss of 99% of the atmospheric gas. Additionally, the two loss processes probably operated at different times, with impact erosion probably being most important early in the Noachian when impact rates were highest, and solar-wind stripping occurring late in the Noachian or into the Hesperian.

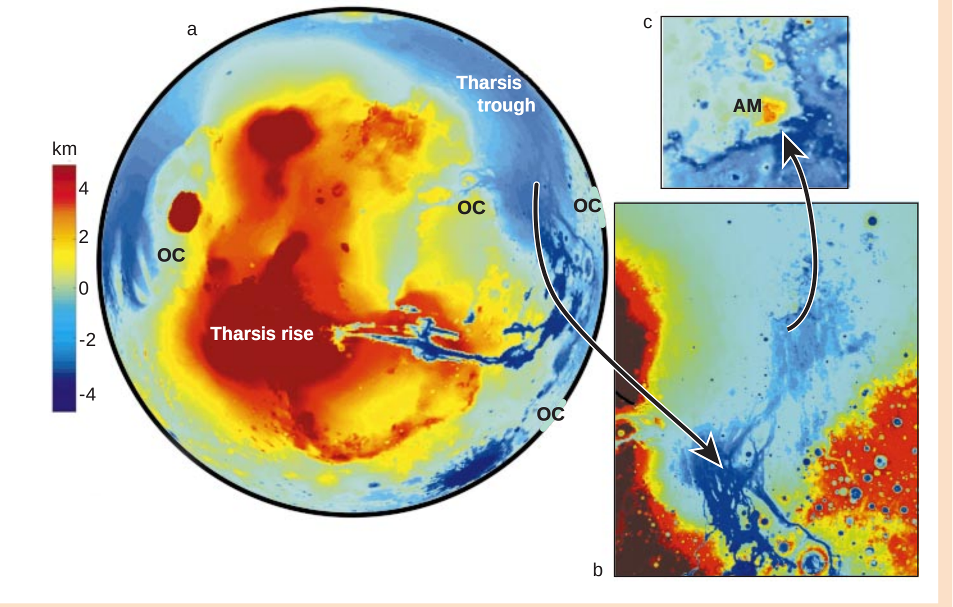

Figure 3 Topography[98] of Tharsis rise and Tharsis trough[28]. **a**, Topography, which has been saturated at ±5 km, with pole-to-pole slope[98] removed. Image is centred on 260° E longitude and view is from 10° north of equator. Outflow channel locations are marked by 'OC'. **b**, Channel detail in Chryse and Acidalia Planitiae (0°–60° N, 300°–0° E, Mercator projection; elevation range is –3.9 km to 0 km). **c**, The inlier Acidalia Mensa ('AM'), whose southern and eastern boundaries are channels (Mercator projection; elevation range is –3.0 km to –1.5 km). Eastern channel extends northwards of 50° N.

CO_2 can be removed from the atmosphere in the presence of liquid water to form carbonate minerals on the surface or in the subsurface[23]. This process occurs on Earth, where gaseous CO_2 dissolves in the oceans, combines with calcium ions weathered from the continents, and forms deposits of calcite in limestone. If SO_2 was an early greenhouse gas, it might have formed crustal sulphate minerals. Carbonates have been found in the martian meteorites and have been shown to be indigenous to Mars[61–63]. However, carbonate and sulphate minerals have not been detected in sufficient quantities that, if released in gaseous form, they could provide enough greenhouse warming to explain the early environment[64,65]. The CO_2 from a several-bar atmosphere would form a global equivalent layer of carbonates perhaps a hundred metres thick; were this distributed throughout the entire volume of the crust, perhaps carried there by circulating groundwater, it might not be detectable at the surface. Thus, the extent to which carbonate minerals could be a sink for gases from an early atmosphere remains uncertain.

But processes do exist that together can account for loss of an early thicker atmosphere. Theoretical models of the timing of volatile loss suggest that these processes can account quantitatively for the inferred change in climate, but they are not unique[42]. Two measurements, however, provide supporting evidence.

First, gas trapped in the martian meteorite ALH84001 may represent a direct sample of the ancient atmosphere[66]. Measurements of nitrogen and argon isotopes indicate that this gas is essentially unfractionated, meaning that most of the isotope-fractionating loss to space through solar-wind stripping had not yet occurred[66,67]. Isotopic measurements of the gas Xe indicate that it was trapped into the rock 3.9 Gyr ago[68]. If the Xe and lighter gases were incorporated into the rock at the same time and represent a sample of the martian atmosphere from that epoch, they provide a key time constraint on atmospheric loss (the bulk of the loss to space must have post-dated 3.9 Gyr). However, although the gases most plausibly came from the atmosphere and were incorporated into the rock at that time, there are concerns related to their uncertain carrier within the meteorite and to the presumed non-juvenile nature of the gases, such that the interpretation is not unique.

Second, measurements of localized remanent magnetic anomalies detected on Mars today[34] provide information on the timing of the shut-off of an intrinsic magnetic field. A substantial global magnetic field would cause the solar wind to stand off from the planet, limiting its ability to strip off the atmosphere[69]. In addition, local magnetic anomalies each have the ability to protect the local atmosphere, such that the atmosphere of a planet covered entirely by such anomalies also would be relatively well protected[47]. Thus, the shut-off of an intrinsic magnetic field and the 'erasure' of local remanent magnetic anomalies in the crust, if they ever were distributed globally, would have allowed the turn-on of the stripping of the atmosphere by the solar wind.

The history of the magnetic field and the timing of its shut-off is extremely uncertain (see the contrasting views of refs 34, 70, and the review in this issue by Stevenson, pages 214–219). Most of the remanent magnetic anomalies occur in the ancient terrain, indicating that Mars had a substantial intrinsic magnetic field and that it turned off relatively early in martian history[34]. Suggestion of a late turn-on of the global magnetic field[70] is at odds with magnetization found in carbonate globules in ALH84001, which indicates that a martian geodynamo was active 4 Gyr ago or earlier[71]. A few younger areas also have remanent fields, although there is a general absence of magnetic anomalies associated with Hesperian and Amazonian volcanics, adding to the confusion. It is clear, however, that an intrinsic magnetic field was most strongly connected to the Noachian epoch, and very much less so to later epochs. It may not be possible to resolve the timing issues more clearly, as it is uncertain what the carrier of the remanent magnetic fields is, whether remanent anomalies were originally distributed globally, and, if they were, what process would have erased them.

If the turn-off of the magnetic field and the erasure of localized magnetic anomalies allowed the solar wind to begin to strip species out of the atmosphere, then this atmospheric loss would have begun during the Noachian or early Hesperian. The turn-on of atmospheric loss would have been complete only when a substantial fraction of local anomalies had been destroyed. This may not have happened prior to the substantial volcanism associated with Tharsis and the subsequent Hesperian era.

Together, the isotopic and magnetic-field evidence indicate, but do not prove, that the bulk of solar-wind stripping to space occurred subsequent to 3.9 Gyr, and that the turn-on of loss occurred sometime between the Middle Noachian and the Early Hesperian. Loss by solar-wind stripping seems to have been roughly contemporaneous with the change in climate inferred from geology, with the main changes in climate coinciding with the end of the Noachian.

Evidence for liquid water in later epochs

There is substantial evidence that liquid water has been present within the martian crust up to the present. Evidence comes from geological features seen on the surface as well as from geochemical analyses.

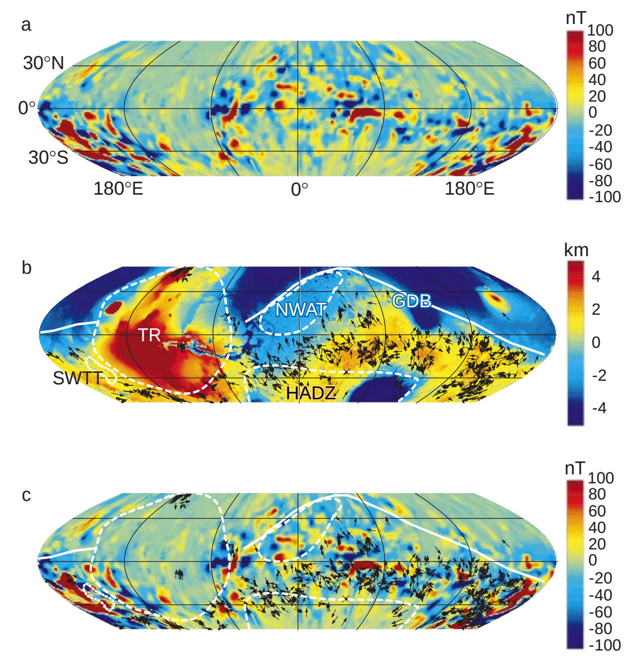

Figure 4 Comparison of martian magnetic field, topography and valley network locations. **a**, Radial component of the martian magnetic field at an altitude of 200 km (after ref. 106). Values saturated at ± 100 nanotesla (nT). Sinusoidal projection to $\pm 47.5°$ latitude. **b**, Topographic map of Mars (after ref. 98), saturated at ± 5 km elevation, and locations of valley network systems[13]. Database is limited to latitudes less than $\pm 47.5°$, which is the approximate limit of valley network distribution. Features indicated are the Tharsis rise (TR), global dichotomy boundary (GDB), northwestern Arabia Terra (NWAT), southwestern Tharsis trough (SWTT) and Hellas-Argyre disruption zone (HADZ). TR, NWAT, SWTT and the area north of GDB are regions of valley network exclusion by erosion and/or deposition and cannot be judged for the level of correlation of valley networks with anomalies in the remanent magnetic field. Likewise, TR, HADZ and the area north of GDB are regions of magnetic field exclusion by the presence of post-main-field crustal ages or crustal disruption[34]. **c**, Valley networks and features in **b** superposed on magnetic anomaly map.

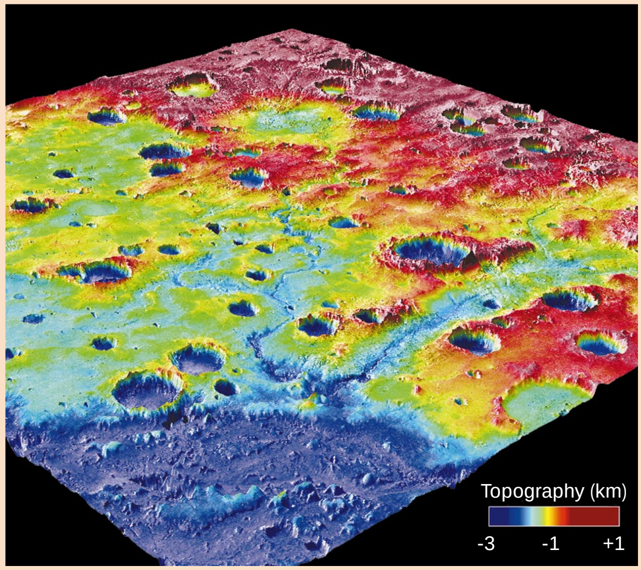

Figure 5 View of topography (from ref. 98) looking towards the southeast in Margaritifer Sinus region. Area is $30° \times 30°$ in size and there is $\times 12$ vertical exaggeration in topography. Pole-to-pole slope has been removed in topography to emphasize regional variations. The prominent depression in the centre of the image is Parana basin, a possible site of lake sediments[107]; it is drained by a prominent channel (Loire Vallis) that descends northwesterly into the Tharsis trough (foreground). Higher elevations (red shades) are Early- and Middle-Noachian plateau materials. Yellow, green and blue/grey shades of lower elevations represent widespread erosion events in the Late Noachian that removed ~1.5×10^6 km^3 of Early/Middle-Noachian material from this region[36]. Erosional remnants of older material occur in isolated mesas. (Image courtesy of B. Hynek.)

Catastrophic outflow channels provide compelling evidence that liquid water was released from within the crust, flowed over the surface, and drained into the northern lowlands (see refs 17, 72, and the review in this issue by Baker, pages 228–236). As these floods involved large quantities of water released catastrophically, with water able to flow substantial distances before freezing, they could occur even in the present cold climate[17]. They do indicate, though, that liquid water must have been present within the crust. Other eroding agents have been suggested, including liquid CO_2, SO_2, volcanic lava, ice, debris flows and the wind[73–75]. In particular, the similarity of some of the martian channels to volcanic channels, and the ability of the wind to weather and erode substantial amounts of material, have recently been highlighted (C. B. Leovy and J. C. Armstrong, manuscript in preparation), along with the difficulty of reaching unique conclusions about the eroding fluid from morphology alone (see review by Baker). However, water or water-filled debris flows[75] remain the most plausible candidates and require the fewest extrapolations (see review by Baker). Although the observed floods seem to have drained only about 10% of the surface, connected largely to the Tharsis trough, there is no reason to think that crustal water was not distributed globally[76].

The martian meteorites contain weathering products, produced when liquid water was present, filling cracks and voids in the rock. These include carbonate deposits at levels of several per cent in ALH84001, as well as trace amounts of carbonates and the mineral iddingsite (which forms from weathering of basalt in the presence of liquid water) in several of the other meteorites[61–63]. Detailed micro-stratigraphy shows that the deposits were present before the rocks were ejected from the martian subsurface, providing direct evidence that liquid water circulated through the martian crust[61,62].

Indirect geochemical evidence for liquid water in the crust comes from measurements of various isotope ratios within these weathering products. They contain enhanced D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{38}Ar/^{36}Ar$ ratios[62]. Enhancement of each of these ratios is best explained as having resulted from atmospheric processes involving preferential escape of the lighter isotopes to space (as discussed earlier). This requires that these gases once resided in the atmosphere, were left behind as a residuum of loss to space, and were subsequently incorporated into the crust. Circulation of groundwater between the surface and the crust provides the best means for exchange of these gases, again suggesting the presence of liquid water[62,77,78].

While the carbonates in ALH84001 were probably precipitated from liquid water about 3.9 Gyr ago, water also must have been present much more recently. The other martian meteorites are all much younger rocks, having crystallized between about 170 Myr and 1.3 Gyr, and also contain weathering deposits[79,80]. Thus, crustal water must have been present within the past billion years. Radiogenic dates for the weathering products in the Lafayette meteorite indicate deposition around 650 Myr ago or even more recently[81].

Several locations on the surface show spectroscopic evidence for the presence of coarse-grained haematite, probably formed in association with liquid water[82]. The haematite may have been deposited from water released from volcanic intrusions or driven by subsurface hydrothermal or aqueous systems[82], although some could have formed by volcanic processes not requiring water[83]. One of the occurrences is in Aram Chaos, a feature attributed to the release of subsurface water and not connected to volcanism. A second, larger location is in Western Terra Meridiani, located at about 0° latitude and 0° longitude, and is thought to have formed at depth and been exposed subsequently by erosion[82].

Liquid water also may have been present within the near-surface crust very recently, based on the presence of pristine gullies on the exposed walls of impact craters and valleys[84]. These are identical in size, shape and appearance to gullies on Earth carved by liquid water seeping from aquifers on exposed scarps. Liquid CO_2 has been suggested as a possible eroding agent, based on the similarity of the depth of seeping to that at which the overburden pressure equals the CO_2 liquefaction pressure[85]. However, the absence of a viable charge or recharge mechanism for liquid CO_2 and the inability of CO_2 to discharge as a liquid under martian conditions preclude its role as a significant erosive agent[86]. Rather, liquid water is much more plausible geologically (ref. 84, and see review by Baker, pages 228–236). Recent calculations of the stability of liquid water in the crust, and of the ability of cyclical oscillations in temperature to freeze and release water, suggest that this is a viable mechanism[87]. There is no means to uniquely determine the age of the features, but they are unweathered and gully debris overlies features such as sand dunes that are themselves thought to be extremely young. If these interpretations are correct, liquid water has been present within a few hundred meters of the surface within the past few million years, and may reside there today[84].

There also is geological evidence for liquid water at the surface, possibly during the later epochs of martian history. Most intriguing is the evidence for standing lakes within impact craters[88] and the Valles Marineris canyon system[17]. Potential crater lakes are identified by the presence of channels flowing into and/or out of the craters, providing a source or sink for water. Some deposits within craters have an appearance similar to deltas, sedimentary terraces and shorelines, as might be formed by flowing water. Although most of the craters themselves are relatively old, the age of the lakebed deposits is uncertain. There are few craters on the lakebed deposits, which indicates either that they are very young[88] or that they were buried for long periods and were exhumed very recently[89]; stratigraphic relationships of layered sedimentary deposits within Valles Marineris suggest an old age despite the absence of craters[89]. Well-defined layering within these deposits supports the idea of standing water, although layered lakebed deposits cannot be distinguished uniquely from windblown sediments[89]. But even if these sediments were windblown, they would have required either liquid water at least in trace amounts or water ice that might be stable at other epochs in order to cement the grains together to form coherent layers.

The catastrophic outflow channels all drain into the northern lowlands[17]. Possible shoreline features have been identified, suggesting that the water may have accumulated in the lowlands to form a large, long-lived body of water (that is, an ocean)[90,91]. The crudely constant elevation of the innermost of the two main proposed shorelines[92] and the extreme smoothness of the lowlands are held to be consistent with the presence of an ocean[93]. However, the proposed shoreline features are not visible in recent high-resolution images[94] and thus cannot be ascribed with certainty to wave action at an ocean boundary. Features described originally as 'high stands' or shorelines created by a retreating ocean[92] are now recognized as being wrinkle ridges of tectonic derivation[95]. These ridges underlie the Vastitas Borealis formation, a deposit that may in part be sedimentary in origin[96].

The smoothness of the lowlands[97,98] may have resulted from fluvially transported sediments associated with channel emplacement during the Hesperian[99]; such a process allows but does not require the presence of an ocean. Erosion of material in the Margaritifer Sinus region and an adjacent area in northwestern Arabia Terra may have provided a significant source of sediments[36]. About a kilometre of material seems to have been stripped away during the Late Noachian, and geological evidence points to erosion by liquid water (Fig. 5). The resulting debris could have filled the northern plains to a depth of about 100 m north of 30° N (ref. 36). The corresponding equivalent depth of water necessary to transport this sediment would have been several times the sediment volume[100]. Whether or not this resulted in a Late Noachian ocean would have depended on the relative rates of erosion and of water removal by ground infiltration, evaporation and so on. Linear gravity anomalies trending northward from Chryse Planitia may be indicative of early channels buried in the northern plains, analogous to the main catastrophic flood channels seen to the east of Valles Marineris[101]. These could be Noachian-era pathways that moved water and sediment from the southern highlands to the northern lowlands.

Table 1 Martian isotope ratios and atmospheric loss*

Isotope ratio	Measured value†	Amount lost to space (%)‡
D/H	5	~60–74
$^{38}Ar/^{36}Ar$	1.3	~50–90
$^{13}C/^{12}C$	1.05–1.07	~50–90
$^{15}N/^{14}N$	1.7	~90
$^{18}O/^{16}O$	1.025	~25–50

*Values taken from refs 57–59, 62, 77 and 78, and references therein.
†Value estimated, observed or derived for martian atmosphere relative to terrestrial.
‡Calculated assuming Rayleigh fractionation. D/H range includes uncertainty in escape processes. Other ranges are based on uncertain timing of outgassing relative to escape.

In addition, the Hesperian outflow flood channels can be traced northward into Acidalia Planitia. There, they converge into a basin (not presently closed) with an area $\sim 6\times10^5$ km^2, south of the high-standing Noachian inlier Acidalia Mensa at 45° N latitude (Fig. 3b). Acidalia Mensa itself has erosional boundaries on the south and east that are channels (Fig. 3c), and may at one time have formed a natural barrier to water flow. This region of channel convergence coincides closely with one of two main occurrences of kilometre-scale polygonally fractured terrain[102]. The origin of polygonally fractured terrain is controversial[103,104], but many of the processes proposed involve water. Thus, it is likely that water (and thus sediments) were carried far into the northern lowlands during the Hesperian, perhaps forming lakes. The region of channel convergence in Acidalia Planitia may mark the largest possible extent of any standing bodies of surface water. If there ever was a Hesperian northern 'ocean', it may have been more of a large lake about the size of the Caspian Sea ($\sim 4\times10^5$ km^2).

Synthesis of the observations and interpretations

It is clear that there are a number of strong constraints on the history of water on Mars. They tell us that water was present at the surface early in the planet's history, and within the crust throughout time. They also allow us to construct a self-consistent scenario of the history of martian volatiles and climate, although such a scenario is not unique.

The history of martian volatiles involved the following (see Fig. 2).

1. Most of the earliest atmosphere of Mars was lost during the Early Noachian by impact erosion and hydrodynamic escape.
2. A secondary atmosphere was created by water and CO_2 released to the atmosphere as a direct result of Tharsis volcanism, and this may have had a strong influence on climate. It is likely that volatiles were also released by non-Tharsis Noachian volcanism presumed to have been responsible for forming the ancient highland crust.
3. Water and CO_2 were lost from the surface and atmosphere system to space, to the polar caps and to carbonate deposits within the crust. There is compelling evidence for the existence of each of these sinks, as described above, although it is not possible at this time to determine uniquely the relative or absolute importance of each.
4. There is a coincidence in the timing of major events in martian history. The decrease in the impact rate at the end of heavy bombardment, the formation of the bulk of the Tharsis construct by magmatism, the decline in the intensity or existence of an intrinsic magnetic field, the change in climate inferred from the morphological characteristics of the surface, and the loss of substantial volatiles to space all occurred at nearly the same time and marked the end of the Noachian epoch about 3.7 Gyr ago. Many of these events are likely to have been causally connected to each other, although some of the similarity in timing may be coincidental. However, the loss of atmospheric protection by the shutdown of the global magnetic field

and the decline in the rate of Tharsis volcanism at the end of the Noachian probably both were instrumental in the major shift in climate as inferred from the geological record.

5. There has been a reservoir of crustal liquid water throughout martian history, continuing possibly to the present. This reservoir has exchanged, at various times and to various degrees, with water at the surface and in the atmosphere. We have little information as to how much water is contained in this reservoir today, but it is likely to be both substantial, globally distributed, and readily accessible to the surface in some places.

New measurements from both planned and potential missions will allow us both to test the above hypotheses and to further constrain the processes that have taken place (see the article in this issue by Carr and Garvin, pages 250–253). Although the list of relevant observations is long[105], some measurements will be key to improving our understanding. These include determining the present-day isotope ratios of the climate-related species (H, C, O and N) and the noble gases; sampling rocks over a broad age spectrum and determining the abundance of weathering products and the isotope ratios of gases contained within them; continuing the search for evidence for trapped carbonate or sulphate minerals within the crust, especially in rocks previously underground and now exposed at the surface; and continuing to explore the morphology of the surface for evidence of climate-related processes.

Discoveries made in the past decade have had a tremendous impact on our understanding of the history of martian water, volatiles and climate. Analysis of the martian meteorites and the measurements made from the Mars Global Surveyor spacecraft in particular have been key to progress in this area. Unravelling the history of martian volatiles and climate will be central to addressing in a meaningful way the potential for martian life and to interpreting results obtained specifically to look for evidence of present or past life. □

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