

# **The Loss of the Martian Atmosphere**

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**Abstract**

It is widely accepted that Mars had an atmosphere at least 4 Gyr ago. The processes that led to the loss of the Martian atmosphere are still debated. Solar-wind-induced sputtering, impact erosion, weathering, sequestration into the regolith and polar caps, and photodissociative reactions are the mechanisms believed to be responsible for removing the atmosphere. No one process has been shown to be capable of removing the entire Martian atmosphere, so it appears that several processes worked cooperatively to bring about the present atmosphere.

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**1. Introduction**

There are two reasons why people think Mars' climate was different than the present one: (1) the display of valley networks suggest that liquid water was once existent and (2) erosion rates 3.5-4 Gyr ago (1 Gyr = 1 billion years) are much higher than they are today (Haberle, 1994). Since liquid water is not stable on the present Mars, the early climate must have been warmer and wetter due to the greenhouse effect of CO<sub>2</sub> (Haberle, 1994). The current atmospheric reservoir of CO<sub>2</sub> is about 7 mbar, but 1-5 bar CO<sub>2</sub> are needed in order to raise the surface temperature to the melting point of water (Haberle, 1998).

The sudden decline in erosion rates 3.5-4 Gyr ago indicates that the Martian climate changed abruptly (Haberle, 1994). Haberle (1994) estimates that the global mean temperature around this period was about 250K (-23°C) and that the surface pressure was at least 30 mbar. 30 mbar is the minimum pressure at which water leaves the surface at the same rate as water diffusing into the atmosphere (Haberle, 1994). At a lesser pressure, water in the form of ice sublimates before it even gets the chance to melt (Haberle, 1994).

1-5 bar constitutes a massive atmosphere, and one must wonder how it was lost. Brain and Jakosky (1998) discuss what they consider the main processes involved in the removal of the atmosphere: ejection of atmospheric gas by impacts, loss to space due to pick-up-ion sputtering,

and sequestration into regolith or polar caps. In addition, photochemical reactions play a significant role in the elimination of nitrogen (Jakosky et al., 1994).

## **2. Mechanisms of Atmosphere Removal**

### **2.1 Impact Erosion**

According to Brain and Jakosky (1998), the amount of atmospheric gas lost due to ejection by impacts is dependent on the properties of the impactor and the planet's atmosphere. Hunten (1993) also mentions that impact erosion efficiency depends on planet mass (which explains why impact erosion is inefficient on Earth and Venus). Brain and Jakosky (1998) discuss two scenarios: small impacts and large impacts.

In the first scenario, a small impactor can remove a mass of the atmosphere roughly equal to the mass intercepted by the impactor as it travels through the atmosphere (Brain and Jakosky, 1998). In the second scenario, a large impactor can do much more damage and eject more than merely the mass of atmosphere it intercepts (Brain and Jakosky, 1998). A large impact is capable of removing part of the atmosphere by creating an outwardly expanding plume (Haberle, 1998). Melosh and Vickery (1989) concluded that a minimum impact velocity of 11-14 km/s is needed in order to create a plume exceeding the escape velocity of Mars. Moreover, the expanding vapor cloud can remove the surrounding atmosphere at speeds greater than the escape velocity (Brain and Jakosky, 1998). It has been suggested that the amount of atmosphere ejected could equal the mass of the atmosphere above the plane tangent to the point of impact (Brain and Jakosky, 1998). For the current atmosphere, a silicate impactor with a diameter of 3 km travelling faster than 14 km/s could accomplish this "tangent-plane mass" removal of the atmosphere (Brain and Jakosky, 1998). Brain and Jakosky. (1998) use Mars' geology to argue

that impacts alone are not capable of removing the required amount of atmosphere to produce the present conditions and, thus, estimate that large impacts account for 50-90% of atmospheric loss.

## 2.2 Sputtering

All the planets are hit by solar winds—streams of protons and helium ions expelled from the sun (Samuel, 2001; Jakosky et al., 1994). Earth has a magnetic field that deflects the solar wind around and past the planet (Samuel, 2001). Mars no longer has a magnetic field, but studies show that it did at one time (Samuel, 2001). The surface terrain is magnetized, showing the remnants of an ancient magnetic field (Samuel 2001). However, the terrain inside many Martian craters is not magnetized, indicating that the magnetic field was lost before the time of impacts—roughly 4 Gyr ago (Samuel, 2001). A former magnetic field is also suggested by the slight magnetism detected in the SNC meteorite ALH84001 (Brain et al., 1998). The absence of a magnetic field is due to the planet's lack of plate tectonics (Samuel, 2001). Plate tectonics, the circulation of molten iron within a planet's core, give rise to a magnetic field (Samuel, 2001). As Mars' magnetic field disappeared, the planet grew susceptible to sputtering.

Sputtering is a photochemical process in which neutral atoms in the upper atmosphere are ionized by the solar wind and are then accelerated by the magnetic field of the solar wind (Brain and Jakosky, 1998). These high velocity ions can collide elastically with other upper atmosphere atoms or molecules and eject them into space (Jakosky et al., 1994). It was previously thought that sputtering by solar wind protons and He ions alone removed atmospheric gases, but this type of sputtering has very small effects (Jakosky et al., 1994).

### 2.3 Weathering

Weathering can deplete CO<sub>2</sub> by converting CO<sub>2</sub> into carbonate rock (Haberle, 1998). On Earth, CO<sub>2</sub> dissolves in rain, forming weakly acidic carbonic acid (Haberle, 1998). This rainwater then interacts with silicate and carbonate rocks, producing cations (e.g. Ca<sup>+2</sup>, Mg<sup>+2</sup>) and anions (e.g. HCO<sub>3</sub><sup>-</sup>) (Haberle, 1998). These ions then accumulate in the oceans, where marine organisms convert them back into carbonates for their shells (Haberle, 1998). When these organisms die, their shells sink to the ocean floor, and the carbonate from them is eventually buried in the crust (Haberle, 1998). Haberle (1998) points out, however, that carbonate formation can still occur in the absence of shell-forming biota. The cation and anion concentration would increase until carbonate began forming abiotically (Haberle, 1998). The rate of carbonate formation would ultimately be independent of whatever process was occurring; at equilibrium, the loss of cations and anions must equal the gain from runoff rainwater (Haberle, 1998). Through such an abiotic process, Martian CO<sub>2</sub> could have easily been converted into carbonates.

### 2.4 Incorporation into the Regolith and the Polar Caps

The regolith and polar caps are also possible storehouses for atmospheric gases, especially C and O. It is estimated that the regolith can hold approximately 300 mbar CO<sub>2</sub> (Haberle, 1994). Some assert that it could hold up to 1 bar, although this is highly unlikely given that a 1 km deep uniformly spread regolith of nontronite clay in a near polar thermal environment would be required (Haberle, 1994). Jakosky et al. (1994) argue that a basaltic regolith is capable of adsorbing as much as 120 mbar CO<sub>2</sub>. The polar caps could hold about 5 mbar CO<sub>2</sub> (Haberle, 1994).

According to Jakosky et al. (1994), O can be stored in the form of either CO<sub>2</sub> or H<sub>2</sub>O. However, H<sub>2</sub>O would most likely be the preferred form (Jakosky et al., 1994). If O were to be stored as CO<sub>2</sub>, the regolith would be required to hold 0.5-1 bar, which it is not capable of containing (Jakosky et al., 1994). O stored in the form of H<sub>2</sub>O could be held easily in the polar caps (Jakosky et al., 1994). It is quite possible for O to be stored as both CO<sub>2</sub> and H<sub>2</sub>O. Another possible reservoir for O is silicate minerals within the crust (Jakosky, 1999).

## 2.5 Photochemical Processes

Most of the Martian atmospheric gases are removed via the mechanisms discussed above. Nitrogen, however, is an exception in that it is subject to photochemical reactions as well (Jakosky et al., 1994). These photochemical mechanisms include photodissociation, photodissociative ionization, electron impact dissociative ionization, ion-molecule reactions and dissociative recombination (Table 1) (Jakosky et al., 1994).

## 3. Discussion

Each of the processes described above does not have the capability of singly removing the atmosphere. For instance, Jakosky et al. (1994) showed that sputtering could not have been the sole means of atmospheric loss even though it would have been able to eject most of the CO<sub>2</sub> required for a greenhouse. The resulting fractionation of N would have been too large to have resulted in the present N isotopic ratio (Jakosky et al., 1994). Models of how the different atmospheric removal processes interact have been put forth.

### 3.1 A Model of Atmospheric Loss

The Brain and Jakosky model (1998) emphasize sputtering and impact erosion as the two main sources of atmospheric loss. It was mentioned earlier that impact erosion was capable of removing 50-90% of Mars' atmosphere (Brain and Jakosky, 1998). If impacts alone produced the current atmospheric conditions on Mars, the early Martian atmosphere would not have been sufficient to sustain the climate necessary for the formation of fluvial features (Brain and Jakosky, 1998). Brain and Jakosky (1998) consider sputtering to be another important phenomenon for removal of the atmosphere.

Sputtering removes lighter atmospheric isotopes, which weigh less and are therefore found higher in the atmosphere (Brain and Jakosky, 1998). Because of this preferential removal of lighter isotopes, one can measure isotopic ratios to estimate the amount of atmosphere lost by sputtering. Brain and Jakosky (1998), using the isotope ratios of Ar, C, H, and N, calculate that 85-95% of each gas has been lost. There are, however, several uncertainties with this value (Brain and Jakosky, 1998). For instance, Mars was very likely to have had a magnetic field at one point (Brain and Jakosky, 1998). This magnetic field would have greatly reduced the effects of sputtering. Another uncertainty is the absolute amount of gas lost to space; so much of it has disappeared that it is hard to quantify (Brain and Jakosky, 1998). Because isotopic analysis can only yield the fraction—not the absolute quantity—of gas lost, Brain and Jakosky (1998) assume that the absolute amount of gas lost is sufficient to account for much of the atmospheric loss. They establish 90% as the value for bulk atmospheric loss by sputtering (Brain and Jakosky, 1998).

Sputtering and impact erosion work independently: atmospheric loss by impacts does not preferentially remove light isotopes, and sputtering does not affect the fraction of atmosphere

lost by impact erosion (Brain and Jakosky, 1998). Therefore, the losses by each process multiply rather than add to yield the net loss (Brain and Jakosky, 1998). It was mentioned before that impact erosion was not a significant occurrence until 500 Myr after the formation of Mars. Sputtering would seemingly be the first means of removing atmospheric gases. Beginning with the initial surface pressure, sputtering would remove 90% of the atmosphere, while impact erosion would remove 50-90% of the remaining atmosphere, leaving 1-5% of the original atmosphere (Brain and Jakosky, 1998). The assumption here is that sputtering began immediately, which poses a few problems (Brain and Jakosky, 1998). The presence of a magnetic field and even impact delivery of volatiles could decrease the net loss of atmospheric species (Brain and Jakosky, 1998). The existence of a magnetic field would imply that sputtering occurred after the bulk of loss by impacts (Brain and Jakosky, 1998). However, if the multiplicative behavior proposed by Brain and Jakosky is valid, whether sputtering occurred before or after the time of heavy bombardment makes no difference and still gives their estimate of 95-99% total atmospheric loss (Brain and Jakosky, 1998).

Brain and Jakosky (1998) conclude that impact erosion and sputtering together are not sufficient to remove an atmosphere large enough to have sustained liquid water. Excluding other processes, the present 6 mbar pressure (Brain and Jakosky, 1998) indicates that the Martian surface pressure was 120-600 mbar at the onset of the geologic record. This is not enough pressure for liquid water to exist (Brain and Jakosky, 1998). However, if the atmosphere was assumed to be as thick as 3 bar, the loss of 95-99% of the atmosphere by sputtering and impact erosion would leave behind 30-150 mbar (Brain and Jakosky, 1998). The regolith and polar caps could adsorb most of this remaining gas: 30-40 mbar of CO<sub>2</sub> could be held in the regolith,

and 100-200 mbar CO<sub>2</sub> could be sequestered into the ice or clathrate at the poles<sup>1</sup> (Brain and Jakosky, 1998). However, a more probable estimate for the poles is a few tens of mbar (Brain and Jakosky, 1998).

The remaining non-adsorbed CO<sub>2</sub> (0-100 mbar), if any, could be present in the form of carbonates (Brain and Jakosky, 1998). Given such a small quantity of CO<sub>2</sub>, a substantial carbonate reservoir would not be necessary (Brain and Jakosky, 1998). Thus, impact erosion, sputtering, and sequestration into the surface provide a plausible means for the removal of several bars of the early Martian atmosphere (Brain and Jakosky, 1998). Because Brain and Jakosky (1998) conclude that their model does not require a large quantity of carbonates containing the CO<sub>2</sub> from the early atmosphere, the absence of observed carbonate features does not present a significant problem (Brain and Jakosky, 1998).

### 3.2 Implications for a Reduced Early Atmosphere

The Martian atmosphere is enriched with <sup>13</sup>C (Galimov, 2000). The simplest explanation is isotopic fractionation, in which the lighter isotope <sup>12</sup>C has been removed over time (Galimov, 2000). But it is unlikely that this process was effective in the case of C (Galimov, 2000). According to Galimov (2000), the photochemically induced loss of CO<sub>2</sub> to space can be no more than 10 mbar. This is comparable with the present atmospheric pressure but does not suggest 3 bar of an early atmosphere (Galimov, 2000). Sputtering could remove anywhere from 120 mbar to 1 bar (Galimov, 2000) and could explain the present isotopic ratios as found in Jakosky et al. (1994). Galimov (2000), however, argues that isotopic fractionation by sputtering is far from proven and that, even if it does work, it does not entirely explain the measured isotope

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<sup>1</sup> Clathrates are compounds with inclusion complexes in which molecules of one substance are completely enclosed within the crystal structure of another (Hoffman, 1999).

fractionation of C. Furthermore, it has been shown that CO<sub>2</sub> condensation can reduce the greenhouse effect and make it impossible to achieve temperatures greater than 230 K (Kasting, 1991). He thus proposes that C was present in a reduced form—as CH<sub>4</sub> or CO but not CO<sub>2</sub> (Galimov, 2000).

The idea of a reduced atmosphere on Earth (made popular by Urey's experiment which demonstrated that organic compounds could be synthesized in a reduced environment) was abandoned because the oxidation state of Earth's mantle does not suit a reduced atmosphere (Galimov, 2000). Since Mars' evolution is believed to have been similar to that of Earth, the reduced atmosphere concept was debunked (Galimov, 2000). In addition, CH<sub>4</sub> can be dissociated by solar radiation quite rapidly (Galimov, 2000). Sagan and Chyba (1997) proposed that photochemical reactions in a CH<sub>4</sub> atmosphere could have created a high-altitude aerosol that absorbed UV radiation and allowed reduced gases to remain for a longer period of time. Galimov also questions the possibility of Earth's mantle changing from a reduced state to the present oxidized state (Galimov, 2000). Thus, C could have been in its reduced form in the early atmosphere.

When water was present and the climate was warmer, atmospheric CO<sub>2</sub> must have migrated into the crust, where it is converted into carbonate (Galimov, 2000). However, as pointed out earlier, no carbonate features have been found on the surface of Mars. Galimov (2000) argues that CH<sub>4</sub> could have been the primary atmospheric component because it would have been able to provide a warm climate, but would not have been stored as carbonate. It is proposed that CO<sub>2</sub>, being a minor atmospheric species, became enriched with <sup>13</sup>C through isotopic exchange with CH<sub>4</sub> (Galimov, 2000). This isotopically heavy CO<sub>2</sub> was then converted into carbonate, which survived atmospheric loss by sputtering and impact erosion as described

by Brain and Jakosky (1998) and became the eventual source of atmospheric CO<sub>2</sub> (Fig. 1) (Galimov, 2000). These processes would have been about the same if CO was the primary form of C (Galimov, 2000). According to Galimov, the model of atmospheric loss put forth by Brain and Jakosky (1998) works for a reduced atmosphere as well.

#### **4. Summary**

The discovery of fluvial features on the Martian surface in images by Mariner 9 has suggested that climatic conditions on early Mars were warmer and wetter than they are today (Haberle, 1998). It has been speculated that the atmosphere could have been as thick as 5 bar, although 3 bar is a more reasonable estimate. Many models have consequently been proposed as to how such a massive atmosphere could have been lost. Solar-wind-induced sputtering, impact erosion, weathering, incorporation into the crust, and photochemical reactions are all significant processes in atmospheric removal.

Most models tend to focus on how a single process could remove the atmospheric species and produce the conditions seen today. Brain and Jakosky (1998), however, combine the roles of impact erosion, sputtering, and sequestration into the regolith or polar caps to create a model that seems quite convincing. They estimate the loss of 50-90% of the early Martian atmosphere through impact erosion (Brain and Jakosky, 1998). When combined with sputtering, 95-99% of the early atmosphere was lost, leaving behind only 30-150 mbar. CO<sub>2</sub>, constituting most of this remaining atmosphere, could have easily been stored in a small quantity of carbonate (Brain and Jakosky, 1998). Thus, the scarcity of carbonate rocks does not pose a problem (Brain and Jakosky, 1998). Galimov (2000), although he proposes a reduced initial atmosphere, also utilizes Brain and Jakosky's model of atmospheric removal (1998). It appears that the Brain and

Jakosky model can apply to either an oxidized early atmosphere or a reduced early atmosphere.

The enormous loss of atmospheric species to space does not permit us to know the absolute amount of gas lost and, thus, presents a major problem to models of atmospheric loss (Brain and Jakosky, 1998). The future use of SPICAM Light (Spectroscopy for the Investigation of the Characteristics of the Atmosphere of Mars) on Mars Express will hopefully provide data that can facilitate our understanding of atmospheric escape (J.-L. Bertaux et al., 2000).

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## Appendix

Table 1

Photochemical reactions involved in the fractionation of N

Photochemical process	Mechanism	
Photodissociation	$N_2 + h$	$N + N$
Photodissociative ionization	$N_2 + h$	$N^+ + N + e^-$
Electron impact dissociative ionization	$N_2 + e^-$	$N^+ + N + 2e^-$
Ion-molecule reactions	$N_2^+ + O$	$NO^+ + N$
	$O^{+2} + N_2$	$N^+ + N + O^+$
Dissociative recombination	$N_2^+ + e^-$	$N + N$

Fig.1

Evolution of a Reduced Atmosphere