Loss of water from Mars: Implications for the oxidation of the soil

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Abstract

The evolution of the martian atmosphere with regard to its H2O inventory is influenced by thermal loss processes of H, H2, nonthermal atmospheric loss processes of H+, H2+, O, O+, CO2, and O2+ into space, as well as by chemical weathering of the surface soil. The evolution of thermal and nonthermal escape processes depend on the history of the intensity of the solar XUV radiation and the solar wind density. Thus, we use actual data from the observation of solar proxies with different ages from the Sun in Time program for reconstructing the Sun’s radiation and particle environment from the present to 3.5 Gyr ago. The correlation between mass loss and X-ray surface flux of solar proxies follows a power law relationship, which indicates a solar wind density up to 1000 times higher at the beginning of the Sun’s main sequence lifetime. For the study of various atmospheric escape processes we used a gas dynamic test particle model for the estimation of the pick up ion loss rates and considered pick up ion sputtering, as well as dissociative recombination. The loss of H2O from Mars over the last 3.5 Gyr was estimated to be equivalent to a global martian H2O ocean with a depth of about 12 m, which is smaller than the values reported by previous studies. If ion momentum transport, a process studied in detail by Mars Express is significant on Mars, the water loss may be enhanced by a factor of about 2. In our investigation we found that the sum of thermal and nonthermal atmospheric loss rates of H and all nonthermal escape processes of O to space are not compatible with a ratio of 2:1, and is currently close to about 20:1. Escape to space cannot therefore be the only sink for oxygen on Mars. Our results suggest that the missing oxygen (needed for the validation of the 2:1 ratio between H and O) can be explained by the incorporation into the martian surface by chemical weathering processes since the onset of intense oxidation about 2 Gyr ago. Based on the evolution of the atmosphere-surface-interaction on Mars, an overall global surface sink of about 2 × 10^{12} oxygen particles in the regolith can be expected. Because of the intense oxidation of inorganic matter, this process may have led to the formation of considerable amounts of sulfates and ferric oxides on Mars. To model this effect we consider several factors: (1) the amount of incorporated oxygen, (2) the inorganic composition of the martian soil and (3) meteoritic gardening. We show that the oxygen incorporation has also implications for the oxidant extinction depth, which is an important parameter to determine required sampling depths on Mars aimed at finding putative organic material. We found that the oxidant extinction depth is expected to lie in a range between 2 and 5 m for global mean values.

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1. Introduction

High resolution altimetric data from the Mars Orbiter Laser Altimeter (MOLA) instrument on board of the Mars Global Surveyor (MGS) spacecraft has measured the detailed topography of the northern martian lowlands (Head III et al., 1999). A wide range of data are now consistent with the hypothesis that a lowland-encircling geologic contact may represent an ancient shoreline of a large-standing body of H2O in the martian past, where large outflow channels empty into the northern lowlands (Baker, 2001). These an-
cient fluvial networks on the martian surface (Carr, 1987) and recent studies on the early solar luminosity (Sackmann and Boothroyd, 2002) suggest that the atmosphere was warmer, denser and wetter at least 3.5 Gyr ago. Actual observations by the High Energy Neutron Detector (HEND) on board of Mars Odyssey give further evidence that H2O-ice is concentrated in the subsurface in the northern and southern hemisphere (Mitrofanov et al., 2002).

To investigate the fate of water on Mars over the past 3.5 Gyr we consider escape of atmospheric hydrogen and oxygen into space and planetary surface sinks for oxygen. Since all escape processes depend on the level of solar activity, we consider in Section 2 the effects of higher solar XUV fluxes as obtained by the Sun in Time program and solar wind density estimations of solar-like stars (Wood et al., 2002).

In Section 3 we study the thermal and nonthermal escape of H and H2. In Section 4 we investigate the loss of oxygen, which can only be removed through nonthermal escape processes. Escape of O include dissociative recombination, atmospheric sputtering, ion pick up and solar wind erosion.

Because the escape rates for oxygen depend on the model assumptions of different authors, the estimated current O fluxes found in the literature cover a wide range between 3.0 × 10^6 cm^{-2} s^{-1} (2.5 × 10^24 s^{-1}) and 1.2 × 10^6 cm^{-2} s^{-1} (1 × 10^{26} s^{-1}) (Fox and Bakalian, 2001). However, some of the values still cited in the literature are about 30 years old and based on simple assumptions. Thus, we discuss in Section 5 all loss rates available in the literature and use new particle simulations to derive a more realistic estimation for the loss of H2O during martian history.

In the concluding sections it is shown that the stoichiometrically desirable ratio of 2:1 of H to O escape to space is at present not observed. Hence, to account for the missing oxygen, additional sinks such as chemical surface weathering are necessary. The general aim of our work is to achieve a better understanding of the evolution of the martian water inventory.

2. Time evolution of the solar XUV and particle flux

Because solar radiation plays a major role in all atmospheric processes, the evolution of planetary atmospheres must be understood within the context of the evolving solar energy and particle fluxes. The escape of atmospheric constituents in the martian atmosphere depends on the evolution of the solar XUV radiation (λ < 1000 Å), which affects the exosphere temperature as well as the photoionization and escape rates. Observations and studies on isotope anomalies in planetary atmospheres (Bauer, 1983; Lammer et al. 2000a, 2000b; Lammer et al., 2002; Lammer and Bauer, 2003), radiative fluxes, stellar magnetic fields, stellar winds of solar-type stars with different ages (Zahnle and Walker, 1982; Ayres, 1997; Guinan and Ribas, 2002; Wood et al., 2002) and lunar and meteorite fossil records (Newkirk, 1980) indicate that our early Sun underwent a highly active phase after its formation.

This active phase of the Sun, which lasted about 0.5–1.0 Gyr, included continuous flare events where the particle and radiation environment was several hundred times more intense than today. The high radiation levels of the young Sun were triggered by strong magnetic activity. The magnetic activity of the Sun is expected to have greatly decreased with time (Skumanich, 1972; Simon et al., 1985; Guinan and Ribas, 2002) as the solar rotation slowed down through angular momentum loss. Observational evidence and theoretical models suggest that the young Sun rotated about 10 times faster than today and had significantly enhanced magnetically generated coronal and chromospheric activity (Keppens et al., 1995; Guinan and Ribas, 2002).

The Sun in Time program (Dorren and Guinan, 1994) was established to study the magnetic evolution of the Sun using a homogeneous sample of single nearby G0-V main sequence stars which have known rotation periods and well-determined physical properties, including temperatures, luminosities, metal abundances and ages. As can be seen in Table 1, the sample of solar proxies contains stars that cover the entire main sequence lifetime from 130 Myr to 8.5 Gyr. One of the primary goals of the Sun in Time program is to reconstruct the spectral irradiance evolution of the Sun.

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The parameters of the solar proxies are: type, luminosity, effective temperature, mass, distance, rotation period, and age.
To this end, a large amount of multiwavelength (X-ray, EUV, FUV, UV, optical) data have already been collected. The observations, obtained with the ASCA, ROSAT, EUVE, FUSE, and IUE satellites, cover a range between 1 and 3300 Å, except for a gap between 360 and 920 Å, which is a region of very strong interstellar medium absorption. Details of the data sets and the flux calibration procedure employed are provided in (Guinan and Ribas, 2002). Full spectral irradiance tables have already been completed for five of the stars in the Sun in Time sample (EK Dra (130 Myr), π¹ UMa (300 Myr), κ¹ Cet (750 Myr), β Com (1.6 Gyr), β Hyi (6.7 Gyr)) and show an excellent correlation between the emitted flux and stellar age.

The coronal XUV emissions of the young main-sequence Sun were about 1000 times stronger than those of the present Sun. Similarly, the transition region and chromospheric FUV-EUV emissions of the young Sun are expected to be 10 to 100 and 5 to 10 times stronger, respectively, than present and the flux variation over age is therefore a steep wavelength function. As discussed above, for the present work we have focused on the spectral range with λ < 1000 Å, which includes X-rays and EUV. We have computed integrated fluxes for the stars with complete irradiance and scaled the resulting values to a distance of 1 AU.

The resultant relative fluxes are plotted in Fig. 1 and show a striking power law behavior. A fit to the observations yields the following expression with very high correlation

$$\frac{\text{flux}}{\text{flux}_{\text{current}}} = 6.13 \cdot \text{(age (Gyr))}^{-1.19}, \quad 1 < \lambda < 1000 \text{ Å}. \quad (1)$$

This relationship indicates that the solar XUV flux 2.5 and 3.5 Gyr ago was about 3 and 6 times higher, respectively, than today and that the high-energy flux of the Zero-Age Main Sequence Sun was stronger up to a factor of hundred. These results are in general agreement with former studies by Iben (1965), Cohen and Kuhı (1979), Gough (1977), Zahnle and Walker (1992), and Ayres (1997), although their studies focused on stars that are not necessarily true solar proxies.

Upper planetary atmospheres are mainly controlled by absorption of XUV radiation. Thus, we used a scaling relation for the exospheric temperature ($T_\infty$) based on the assumption of an equilibrium between XUV heat input calculated from Eq. (1) and heat transport by conduction in the thermosphere (Bauer, 1971; Bauer and Hantsch, 1989). From this relation we estimate the evolution of $T_\infty$ with time. We find values for $T_\infty$ of ~350 and ~600 K, 2.5 Gyr (3 EUV) and 3.5 Gyr ago (6 EUV), respectively. These results are in good agreement with the values used by Zhang et al. (1993a).

For past solar wind ion pick up calculations, we estimated the solar wind density and velocity over the history. Hubble Space Telescope high-resolution spectroscopic observations of the H Lyman-α feature of several nearby main-sequence stars carried out by Wood et al. (2002) have revealed neutral hydrogen absorption associated with the interaction between the stars’ fully ionized coronal winds with the partially ionized local interstellar medium. Wood et al. (2002) modelled the absorption features formed in the atmospheres of these stars and provided the first empirically-estimated coronal mass loss rates for G-K main sequence stars.

They estimated the mass loss rates from the system geometry and hydrodynamics and found from their small sample of G-type stars where astrospheres can be observed, that mass loss rates increase with stellar activity. This study suggests that the early Sun had a much denser solar wind than today. The correlation between mass loss and X-ray surface flux follows a power law relationship, which indicates an average solar wind density up to 1000 times higher than today during the first 100 Myr after the Sun reached the Zero-Age Main Sequence.

Mass loss rates of cool main sequence stars depend on their rotation periods, which are in turn correlated with the star’s ages. A dense early solar wind has important implications for planetary atmospheric evolution studies. From the results in Wood et al. (2002), we derived the following power law relationship for the mass loss rate as function of rotation period $P_{\text{rot}}$

$$\frac{dM}{dt} = 1.0 \times 10^{-9} P_{\text{rot}}^{-3.3} \cdot [d]\left[\frac{M_\odot}{\text{yr}}\right]. \quad (2)$$

By using the rotation period data listed in Table 1 we estimated an empirical relation for the evolution of the solar mass loss and the solar wind density with time. We used these relations for the calculation of the martian ion pick up processes over time. In doing this, the solar wind density was scaled to an average martian distance of 1.5 AU (Selsis et al., 2002b) and the evolving solar wind velocity was taken from Newkirk (1980). The corresponding evolution of the average solar wind density and velocity at the martian orbit is illustrated in Fig. 2.

![Fig. 1. Relative solar XUV flux as function of solar age calculated by using data for 5 solar proxies in the Sun in Time program.](image-url)
3. Thermal and nonthermal escape of hydrogen

3.1. Hydrogen production on Mars

When H$_2$O evaporates from the martian surface and subsurface ice reservoirs, the H$_2$O vapor reaches the upper atmosphere, where solar UV radiation can break up the molecules into H, H$_2$, and O (e.g., Hunten and McElroy, 1970).

The production of reactive radical atmospheric HO$_x$ species is initiated through the following chemical reaction

\[ \text{H}_2\text{O} + \text{O}^1D \rightarrow \text{OH} + \text{OH} \]  

where the excited oxygen atom is produced by the photolysis of ozone. The HO$_x$ radicals participate in catalytic cycles for the oxidation of CO to CO$_2$ molecules. Further, the HO$_x$ species are destroyed by the reaction

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  

which transforms them back to H$_2$O. This reaction limits the abundance of HO$_x$ radicals in the martian atmosphere. Another less effective reaction removes HO$_x$ via

\[ \text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2 \]  

resulting in the formation of H$_2$ and O$_2$ molecules. The majority of H$_2$ produced via reaction (5) is removed by

\[ \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \]  

(6)

\[ \text{H}_2 + \text{O}^1D \rightarrow \text{OH} + \text{H} \]  

(7)

But a small fraction of the H$_2$ produced in Eq. (5) escapes the chemical destruction by HO$_x$ radicals in the lower martian atmosphere and is transported to the upper atmosphere. At higher altitudes H$_2$ molecules can participate in the following ionospheric reactions with molecular CO$_2^+$ ions

\[ \text{H}_2 + \text{CO}_2^+ \rightarrow \text{CO}_2\text{H}^+ + \text{H} \]  

(8)

\[ \text{CO}_2\text{H}^+ \rightarrow \text{CO}_2 + \text{H} \]  

(9)

where the molecular hydrogen is transformed into atomic hydrogen which can escape to space. H atoms produced in the lower martian atmosphere have a short chemical lifetime and cannot diffuse to the upper atmosphere where they would be lost by Jeans escape mechanism (e.g., Hunten and McElroy, 1970).

3.2. Thermal escape

The Jeans escape rate of hydrogen from Mars was estimated by Anderson and Hord (1971) by fitting $T_\infty$ needed to reproduce the Mariner 6 and 7 H Lyman $\alpha$ dayglow observations. A best fit of their data revealed a value for $T_\infty$ of about 350 ± 100 K and a number density $n_c$ for H atoms at the exobase level at some 240 km altitude of about $3.0 \times 10^6$ cm$^{-3}$. By means of the Jeans escape flux equation

\[ \Phi_{\text{Jeans}} = \frac{v_0}{2 \sqrt{\pi}} n_c (1 + x_c) e^{-x_c} \]  

(10)

with the escape parameter $x_c$

\[ x_c = \frac{G M m}{r k T_\infty} = \frac{v_\infty^2}{v_0^2} \]  

(11)

one obtains an escape flux for H atoms of about $1.8 \times 10^8$ cm$^{-2}$ s$^{-1}$ ($1.5 \times 10^{26}$ s$^{-1}$). Here $G$ and $k$ are the gravitational and Boltzmann constants, respectively, $m$ and $M$ the particle and planetary masses, respectively, $v_\infty$ the escape velocity, $v_0 = (2 k T_\infty / m)^{1/2}$ the most probable velocity of a Maxwellian distribution at the exobase, and $r$ is the planetocentric distance. Equation (10) clearly indicates that $T_\infty$ is an important parameter for the calculation of the thermal H and H$_2$ escape rates.

Recently, Krasnopolsky and Feldman (2001) observed four H$_2$ lines in a spectrum of Mars with the Far Ultraviolet Spectroscopic Explorer (FUSE) satellite. The line intensities correspond to a column abundance of molecular hydrogen of $1.17 \pm 0.03 \times 10^{13}$ cm$^{-2}$, 140 km above the martian surface, resulting in an H$_2$ mixing ratio of 15 ± 5 parts per million in the lower martian atmosphere. Using this value we calculate from Eq. (10) a thermal H$_2$ escape flux of about $4 \times 10^6$ cm$^{-2}$ s$^{-1}$ (3.3 × 10$^{24}$ s$^{-1}$). The thermal H$_2$ loss rate is thus negligibly small when compared to the atomic H loss rate. Therefore, we derive a total thermal escape flux of H atoms of about $1.8 \times 10^8$ cm$^{-2}$ s$^{-1}$ ($1.5 \times 10^{26}$ s$^{-1}$).

Shizgal and Blackmore (1986) used a kinetic model for studying the transition region between the collision-dominated and the collisionless upper atmosphere regions on Earth and Mars. They determined a steady state velocity distribution function from the Boltzmann equation by including collisions by incoming particles, effects of curvature and gravitational force. Their results showed that the escape flux obtained by the Jeans formula may overestimate the escape flux from the martian exosphere and may be reduced to about $1.2 \times 10^8$ cm$^{-2}$ s$^{-1}$ ($1 \times 10^{26}$ s$^{-1}$).

Significant progress in the measurement of the martian exosphere temperature of the thermal background gas and an

3.3. Nonthermal escape of hydrogen

Measurements carried out aboard the Phobos 2 spacecraft have shown that the plasma tail of Mars consists mainly of ions coming from the martian atmosphere (Lundin et al., 1989, 1990; Rosenbauer et al., 1989). Cold H\textsuperscript{+} ions of planetary origin with densities of about 1–2 cm\textsuperscript{-3} were observed by the ASPERA (Automatic Space Plasma Experiment with a Rotating Analyzer) instrument inside the martian magnetic boundary.

Rosenbauer et al. (1989) recorded two proton populations that could clearly be distinguished from the energy spectra. The flux of cold H\textsuperscript{+} ions, which was attributed to a planetary source, increased abruptly at the bow shock, while in the magnetosheath a gradual thermalization of both components provided their mixing and a separation of both populations became less evident.

For studying the nonthermal hydrogen escape rates from Mars we used a test particle model that involves the motion in the environmental electric and magnetic fields based on the Spreiter–Stahara model (Spreiter and Stahara, 1980; Lichtenegger and Dubinin, 1998; Lichtenegger et al., 2002). This test particle model was successfully used to explain several characteristic features obtained by the Pioneer Venus Orbiter for Venus (Luhmann, 1993) and by the Phobos 2 plasma measurements on Mars (Lichtenegger et al., 1995; Lichtenegger and Dubinin, 1998).

For the present paper we consider only the magnetosheath flow obtained by the gasdynamic model and neglect the field and flow inside the wake. Although the ions produced inside the obstacle are not taken into account, this will have little effect on our results, since the ion flow inside the obstacle is quite low compared to the flow in the magnetosheath. The total production rate of planetary H\textsuperscript{+} and H\textsubscript{2}\textsuperscript{+} ions is the sum of the rates of the main ionization processes, i.e., photoionization, electron impact and charge exchange. For the reaction of solar wind protons with planetary H, H\textsubscript{2}, and O, energy dependent charge exchange cross sections have been employed (Kallio et al., 1997).

To calculate the impact ionization frequency, which involves both the electron temperature and density, we assume that the solar wind electrons behave like the ideal gas of the gasdynamic model and we approximate the electron temperature by the gasdynamic temperature (Zhang et al., 1993b). For atomic hydrogen, the ionization frequency per incident electron as a function of electron temperature is taken from Cravens et al. (1987). For molecular hydrogen electron impact cross sections are taken from Kim and Rudd (1994). Further, upon determination of the photoionization frequency, we assume that the exosphere is optically thin, i.e., we ignore any attenuation of the photon flux. Finally, neutral densities of H and H\textsubscript{2} for present solar mean conditions are taken from Krasnopolsky and Gladstone (1996).

The simulation of the particle fluxes is initialized by dividing the space around Mars into a number of volume elements ΔV. Production rates of planetary ions are then obtained by first calculating the absorption of the solar wind flow along streamlines due to charge exchange with atmospheric neutral H, H\textsubscript{2}, and O. The solar wind flux \(\Phi_{SW}(r_i)\) in an element ΔVi at position \(r_i\) with respect to the planetary center is given by

\[
\Phi_{SW}(r_i) = \phi_{SW}^{(0)}(r_i) e^{-\int_{s_i}^{s_f} \sigma_n \sigma_a ds},
\]

where the integration is performed from the upstream solar wind to the corresponding point \(s_i\) at position \(r_i\) on the streamline. Here, \(\phi_{SW}^{(0)}\) is the unperturbed solar wind flux, \(n_\alpha\) the density of neutral species \(\alpha\) as a function of altitude, \(\sigma_a\) is the energy dependent charge exchange charge cross section between a proton and the neutral constituent \(\alpha\) and \(ds\) is the line element along the streamline. The loss rates of solar wind protons \(L_{SW}\) (cm\textsuperscript{-3} s\textsuperscript{-1}) due to the interaction with atmospheric H and H\textsubscript{2} thus becomes

\[
L_{SW}^H = \Phi_{SW} n_{H\alpha} \sigma_{alpha}, \quad L_{SW}^{H_2} = \Phi_{SW} n_{H_2\alpha} \sigma_{alpha},
\]

and the corresponding planetary ion production rates \(p\) due to charge exchange are simply equal to the corresponding loss rates of the solar wind, i.e., \(p_{SW}^\alpha = L_{SW}^\alpha\) with \(\alpha\) denoting the ion species. The rate of ions produced by electron impact is given by \(p_{ei}^\alpha = \nu n_e n_{\alpha}\), where \(\nu\) is the (temperature dependent) ionization rate coefficient and \(n_e\) the electron density. Hence, the total planetary ion production rate of species \(\alpha\) in each volume element is the sum \(p_{\alpha}^\text{tot} = p_{\alpha}^{ei} + p_{\alpha}^{ce} + p_{\alpha}^{\gamma}\), with \(p_{\alpha}^{\gamma}\) being the rate due to photoionization.

To determine the flux of H\textsuperscript{+} and H\textsubscript{2}\textsuperscript{+} ions from each volume element, a test particle, which is considered to represent all particles in the volume, is launched and its trajectory followed by integrating the equation of motion

\[
\frac{d^2x}{dt^2} = -\frac{q}{m}(E + v \times B),
\]

where \(q\) is the particle charge, \(m\) is the particle mass, \(v\) is the particle velocity, \(B\) is the magnetic field and \(E = -\vec{v}_{SW} \times \vec{B}\) is the motional electric field, i.e., we assume that the magnetic field is frozen into the flow. The total ion flux associated with one particle of species \(\alpha\) through an area \(\Delta A\) which is born inside the element \(\Delta V^{(i)}\) finally becomes

\[
\phi_{\alpha}^{(i)} = \frac{p_{\alpha}^{\text{tot}} \Delta V^{(i)}}{\Delta A},
\]

where \(p_{\alpha}^{\text{tot}}\) has to be taken at the creation point of the particle.

Table 2 summarizes the parameters of the solar wind as well as the photoionization rates used in the simulation. The calculation of the ion fluxes has been performed for present medium solar wind conditions. The subsolar and the terminator height of the obstacle were assumed to be constant and taken as 300 and 1200 km, respectively (e.g., Cravens, 1991). Further, the simulated total planetary ion escape rates
of $H^+$, $H_2^+$, and $O^+$ for present conditions are also given in Table 2. By adding the $H^+$ and $H_2^+$ escape fluxes we obtain a present total nonthermal loss rate for hydrogen of about $3.5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ ($3.0 \times 10^{25} \text{ s}^{-1}$) for medium solar wind conditions.

4. Nonthermal escape of oxygen

The thermal and nonthermal escape of hydrogen from the martian atmosphere has important implications for the atmospheric chemistry. By assuming that hydrogen has its origin from $H_2O$, each loss of one $H_2$ molecule leaves behind one O atom. This implies that, if there were no permanent sinks for oxygen, its concentration in the martian atmosphere would be highly enriched. By assuming that the martian atmosphere has reached a steady state, there should be sinks for oxygen comparable in magnitude to the total thermal and nonthermal escape flux of hydrogen to space according to

$$\Phi_O = \frac{1}{2} \Phi_H,$$

where $\Phi_O$ and $\Phi_H$ are the total escape fluxes of oxygen and hydrogen, respectively, in any form. Because oxygen is too heavy to escape from Mars thermally, nonthermal atmospheric loss processes must be at work. Since Mars lacks an appreciable intrinsic magnetic field at present (Acuña et al., 1998), the atmosphere can be eroded by particle sputtering and solar wind pick up, thereby transporting oxygen away from the planet. Dissociative recombination of molecular oxygen ions is also known to lead to a loss of atomic constituents because the gravitational potential at Mars is easily overcome by the energy imparted in the production of hot atoms. Other sinks of oxygen are the possible oxidation reactions with the martian surface.

4.1. Dissociative recombination

Based on the first measurements obtained by Mariner 4 and then current atmosphere models, McElroy (1972) estimated an average escape flux into space for hot O atoms produced via dissociative recombination, i.e.,

$$O_2^+ + e \rightarrow O^* + O^* + \Delta E,$$

where $\Delta E$ is the energy of the hot oxygen atoms. A value of about $6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ ($5.0 \times 10^{25} \text{ s}^{-1}$) was obtained through the simplifying assumption that atoms are emitted with equal probability in the upward and downward hemispheres and a factor 2 was adapted to account for the absence of escaping atoms on the martian night side. This value was and is still used in many papers, since the estimated escape rate of O could balance to some extent the thermal escape rate of neutral H atoms as interpreted by Anderson and Hord (1971).

Lammer and Bauer (1991) used a Monte Carlo model that followed the hot O atoms by including collisions and energy loss on their way up to the exosphere. They found a reduction in the average escape flux of hot O atoms with respect to the values of McElroy (1972) by about one order of magnitude, i.e., $6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ ($5 \times 10^{24} \text{ s}^{-1}$). Fox (1993) used newly measured rate coefficients for the dissociative recombination of $O_2^+$ ions and obtained an average escape flux of hot O atoms of about $3 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ ($2.5 \times 10^{24} \text{ s}^{-1}$). This is somewhat lower than the value derived by Lammer and Bauer (1991) but in general agreement with their result and over one order of magnitude lower than the simple estimation by McElroy (1972).

In a study of the ancient oxygen exosphere of Mars, Luhmann et al. (1992) and Zhang et al. (1993a) obtained erroneous values for the hot O escape flux of about $9.6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ ($8 \times 10^{25} \text{ s}^{-1}$) which seemed again to be in agreement with the simple estimation by McElroy (1972) and could also balance the H loss rate obtained by Anderson and Hord (1971). However, in a correction to the papers, Luhmann (1997) noted that the escape flux values are lower, and for present Mars are about $7 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ ($6 \times 10^{24} \text{ s}^{-1}$). Kim et al. (1998) examined the solar cycle variability of hot O atoms at Mars and estimated similar escape rates than Lammer and Bauer (1991).

It may be concluded that the majority of model simulations give escape fluxes and loss rates that are at least one order of magnitude lower than the simple estimations by McElroy (1972).

4.2. Atmospheric sputtering

Luhmann et al. (1992) studied atmospheric sputtering loss rates for O atoms and CO$_2$ molecules and derived values of about $3.6 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ ($3 \times 10^{23} \text{ s}^{-1}$) both for O atoms and for CO$_2$ molecules.

Kass and Yung (1995) used a 1D Monte Carlo type atmospheric sputtering model, anisotropic scattering func-
tions and energy-dependent cross sections and found sputtering fluxes for O and CO$_2$ of about $5.6 \times 10^6$ cm$^{-2}$ s$^{-1}$ (4.7 $\times$ 10$^{24}$ s$^{-1}$) and $2.9 \times 10^6$ cm$^{-2}$ s$^{-1}$ (2.4 $\times$ 10$^{24}$ s$^{-1}$). These results are about one order of magnitude higher than Luhmann et al. (1992).

In a recent study, Leblanc and Johnson (2001) modelled the sputtered population inside the hot corona and described escaping particles by using a sophisticated 3D test particle model, whereas the heating effect due to the incident particle flux is described by using a 2D direct Monte Carlo simulation. Their results for the present martian average sputtering escape flux of O atoms of about 5

ion loss rates for O$^+$, indicating that Mars is characterized by a strong loss of plasma from the topside ionosphere during solar maximum conditions (e.g., Lundin et al., 1989, 1990, 1991). These loss rates result mainly from ion pick up due to mass loading of the solar wind in the martian boundary layer and were estimated to be about $3.6 \times 10^7$ cm$^{-2}$ s$^{-1}$ (3 $\times$ 10$^{25}$ s$^{-1}$) during the Phobos 2 encounter.

The ASPERA instrument was also able to measure the distribution of different ion species. Lundin et al. (1990) and Norberg et al. (1993) showed that the inner environment of Mars is filled not only with H$^+$, H$_2^+$, and O$^+$ ions but contains also a substantial mixture of molecular ions like O$_2^+$ and CO$_2^+$. Barabash and Norberg (1994) reported also the detection of He$^+$ ions. Lammer and Bauer (1991) and Luhmann et al. (1992) modelled the ion loss processes and obtained escape fluxes for O$^+$ ions in medium solar wind conditions of about $1.2 \times 10^7$ cm$^{-2}$ s$^{-1}$ (1 $\times$ 10$^{25}$ s$^{-1}$) and $7.2 \times 10^6$ cm$^{-2}$ s$^{-1}$ (6 $\times$ 10$^{24}$ s$^{-1}$), respectively.

Liu et al. (1999) and Ma et al. (2002) carried out a 3D multi-fluid MHD study of the solar wind interaction with Mars and obtained a total oxygen ion escape flux of approximately $3.3 \times 10^7$ cm$^{-2}$ s$^{-1}$ (2.7 $\times$ 10$^{25}$ s$^{-1}$). This result is also comparable with Phobos 2 observations (corresponding to high solar wind conditions).

To estimate the average pick up O$^+$ ion loss rates for present medium solar wind conditions (1 EUV), we used the test particle model described in Section 3.3 and found a total escape flux of O$^+$ ions of about $3.6 \times 10^6$ cm$^{-2}$ s$^{-1}$ (3 $\times$ 10$^{24}$ s$^{-1}$), as shown in Table 2.

4.4. Ionospheric erosion

Ionospheric profiles observed by the Viking 1 and 2 landers indicate that the solar wind may erode the martian ionosphere (Kar et al., 1996). Ionospheric bubbles or clouds triggered by plasma instabilities at the solar wind-ionopause transition region were observed on Venus and may also contribute as an additional escape process to the loss of heavy ions from the martian ionosphere (Wolff et al., 1980; Arshukova et al., 2002; Terada et al., 2002; Pérez-de-Tejada, 1992, 1998).

Fox (1997) considered the upper limits of the outflow of oxygen ions produced above the photochemical equilibrium region for the case that all of them could be lost and obtained a maximum escape flux of about $1.2 \times 10^8$ cm$^{-2}$ s$^{-1}$ (1 $\times$ 10$^{26}$ s$^{-1}$). It is important to note that only this high flux value is sufficient for establishing the present martian stoichiometrically desirable ratio of 2:1 of H and O loss rates to space.

Because the solar wind ionosphere-erosion processes depend strongly on the solar activity, these processes may have played an important role in the past but at present it is unlikely that the martian atmosphere has such a high average atmospheric oxygen escape flux. A detailed study of plasma ionosphere-erosion processes triggered by instabilities is beyond the scope of this paper and may have to await the measurements and observations obtained during the Nozomi and Mars Express missions in 2004–2005.

It should also be noted that Hodges Jr. (2000) estimated very high oxygen escape rates of about $3.6 \times 10^7$ cm$^{-2}$ s$^{-1}$ (3.5 $\times$ 10$^{25}$ s$^{-1}$) to $8.4 \times 10^8$ cm$^{-2}$ s$^{-1}$ (7.0 $\times$ 10$^{26}$ s$^{-1}$). However, such high escape rates do not agree with observational and photochemical considerations.

4.5. Total oxygen escape rates

Adding O escape fluxes from dissociative recombination of about $6 \times 10^6$ cm$^{-2}$ s$^{-1}$ (5.0 $\times$ 10$^{24}$ s$^{-1}$) (Lammer and Bauer, 1991; Fox, 1993; Luhmann, 1997; Kim et al., 1998), the 3D-sputter model results for atmospheric sputtering of atomic oxygen of about $5.2 \times 10^5$ cm$^{-2}$ s$^{-1}$ (4.3 $\times$ 10$^{23}$ s$^{-1}$) (Leblanc and Johnson, 2002) and our obtained ion pick up escape during medium solar wind conditions of about $3.6 \times 10^6$ cm$^{-2}$ s$^{-1}$ (3 $\times$ 10$^{24}$ s$^{-1}$) yields a total average O escape flux to space for present Mars of about $1 \times 10^7$ cm$^{-2}$ s$^{-1}$ (8.4 $\times$ 10$^{24}$ s$^{-1}$). This result fails by far to balance the total thermal and nonthermal escape flux of hydrogen of about $2.2 \times 10^6$ cm$^{-2}$ s$^{-1}$ (1.8 $\times$ 10$^{26}$ s$^{-1}$). Table 3 contains a summary of observed and modelled loss rates for hydrogen and oxygen for the present Mars and for various solar wind conditions.

5. Loss of water during the martian history

Based on numerical studies, McElroy (1972), McElroy and Donahue (1972), and Liu and Donahue (1976) found
that a change in O loss can stabilize the H escape flux at twice the O escape flux. For modest changes, the atmosphere readily adjusts to a new equilibrium state with a different CO/O₂ mixing ratio and is known as self-regulation. The production rate of H₂ is proportional to H and HO₂, which is the most abundant HO₂ radical in the martian atmosphere. Its concentration is larger than both OH and H and determines the number density of H atoms in the martian atmosphere.

The CO concentration changes inversely with the H₂O concentration: A decrease in the H₂O concentration by a factor of 2 increases the CO concentration by a similar factor, while the O₂ concentration decreases by about 50%.

An increase of the O escape, associated for example with an increase of solar XUV flux in the martian past, will result in an increased amount of atmospheric CO (McElroy, 1972; Liu and Donahue, 1976, McElroy and Donahue, 1972). By assuming a fixed H₂O concentration, the amount of HO₂ will increase as well and the production of H₂ and the subsequent escape of H changes accordingly.

Further, the O₂ concentration will decrease due to the higher O loss rate, resulting in an increase in the production of H₂ and in a greater H escape flux. A new steady state would be reached, again satisfying the stoichiometric ratio of 2:1 for H and O again.

At high O₂ concentrations, H and the production of H₂ are small and vice versa. If $\Phi_O < \Phi_H/2$, O₂ will build up and the rate of the production of H₂ would fall as a result of the increase of O₂. A new steady state may be established in which the escape flux $\Phi_H$ would be smaller so that $\Phi_H = \Phi_H/2$ is satisfied again.

According to the present escape rate of hydrogen, photolysis of H₂O will produce the observed oxygen concentration in the martian atmosphere in just $10^5$ years. This points to a large surface oxygen sink rather than escape to space as the dominant process. Accordingly, it appears that the missing oxygen needed for validating the total 2:1 ratio between H and O is incorporated into the surface by chemical weathering processes which should oxidize the martian soil.

To determine the loss of H₂O from ancient Mars we must estimate the time when the escape of O to space became more efficient than the loss to the surface. By using the enhanced XUV flux values obtained by the Sun in Time program and the corresponding $T_{\infty}$ of about 350 K (3 EUV) and 600 K (6 EUV), it turns out that the critical temperature $T_c = 2mMG/(3kr)$ of about 1000 K, $(m$: particle mass, $r$: planetocentric distance, $M$: planetary mass) which would lead to exospheric blow off conditions (e.g., Öpik, 1963) for H atoms will not be achieved. $G$ is the gravitational constant and $k$ is the Boltzmann constant. Therefore, the O to H coupling should also be maintained also 3.5 Gyr ago.

Lammer et al. (1996) estimated the upper limit of the H₂ escape flux from the saturation vapor pressure, the resulting
H$_2$O density profile and the H$_2$O/CO$_2$ mixing ratio 2 Gyr ago. These assumptions lead to an overestimate by a factor of four of the present escape flux. The average escape flux between the upper limit and the present flux is about \(1.6 \times 10^{10}\,\text{cm}^{-2}\,\text{s}^{-1}\) (1.3 \(\times 10^{26}\,\text{s}^{-1}\)). By using this hydrogen escape flux value, one finds that the O loss into the surface may have dominated over the escape to space during the past 2 Gyr. As pointed out previously, the increase of O escape to space before about 2 Gyr ago should also result in an increase of the production of H$_2$, thus producing a greater loss of H, so that the ratio 2:1 for H and O remains the same.

As discussed previously, the observational results for the evolution of the solar XUV flux with time obtained by solar proxies within the *Sun in Time* program agree well with the values obtained by Zahnle and Walker (1982). Thus, the exospheric O escape fluxes estimated by Luhmann (1997) (using Zahnle and Walker (1982) fluxes) of about \(3.6 \times 10^7\,\text{cm}^{-2}\,\text{s}^{-1}\) (\(3 \times 10^{25}\,\text{s}^{-1}\)) 2 Gyr ago and about \(9.7 \times 10^7\,\text{cm}^{-2}\,\text{s}^{-1}\) (\(8 \times 10^{25}\,\text{s}^{-1}\)) 3.5 Gyr ago should be accurate and represent realistic values.

In a recent study, Johnson and Luhmann (1998) investigated pick up induced ion sputtering and found that the addition of sputtered atoms to the martian corona initiates feedback processes which can enhance the atmospheric present sputtering rate but could have limited it in the past.

Leblanc and Johnson (2001, 2002) found with their 3D models an O escape flux for sputtering of about \(1.5 \times 10^7\,\text{cm}^{-2}\,\text{s}^{-1}\) (\(1.3 \times 10^{26}\,\text{s}^{-1}\)) 2 Gyr ago and of about \(1.8 \times 10^9\,\text{cm}^{-2}\,\text{s}^{-1}\) (\(1.5 \times 10^{27}\,\text{s}^{-1}\)) 3.5 Gyr ago. These values are significantly lower than the former model values of Luhmann et al. (1992) and Kass and Yung (1995).

For the calculation of past pick up ion escape rates and pick up ion sputtering one must be able to estimate the hot oxygen corona density during the martian past. Zhang et al. (1993a) used the National Center for Atmospheric Research (NCAR) non-LTE (NLTE) one-dimensional (1D) code as a modeling tool for the estimation of the average properties of the ancient martian thermosphere and ionosphere for the calculation of hot particle coronae. Luhmann and Johnson (1998) and Leblanc and Johnson (2002) deduced the corona profiles from Zhang et al. (1993a) to study the role of molecular species in pick up ion sputtering of the ancient martian atmosphere. In the present work we also used the profiles of Zhang et al. (1993a) for the pick up O$^+$ ion loss estimations of the 3 and 6 XUV cases.

We note that our result of the escape flux of O$^+$ ions for the present Mars of about \(3.6 \times 10^6\,\text{cm}^{-2}\,\text{s}^{-1}\) (\(3 \times 10^{24}\,\text{s}^{-1}\)) closely agrees with the value of about \(4.8 \times 10^6\,\text{cm}^{-2}\,\text{s}^{-1}\) (\(4 \times 10^{24}\,\text{s}^{-1}\)) found by Zhang et al. (1993a). However, the values for the 3 and 6 XUV cases obtained by Zhang et al. (1993a) for O ion pick up loss rates are about 10 and 2 times larger, respectively, than those found in our calculations.

The main reason for these discrepancies is because of their use of different solar wind density values for the 3 and 6 XUV epochs, for which we used observation-based stellar wind data of Wood et al. (2002). Further, for the calculation of the atmospheric sputter escape rates we employed the sputter yields from Table 1 of Leblanc and Johnson (2002) together with our modelled incident O$^+$ ion pick up fluxes.

Table 4 shows the escape rates of H$_2$O and of the various nonthermal loss processes at present and 2.0 and 3.5 Gyr ago. The current dissociative recombination based O loss rate is taken from Lammer and Bauer (1991) and Kim et al. (1998) while the 3 and 6 XUV are taken from Luhmann (1997). As indicated in Table 4 there is a lower total O escape rate to space compared to H$_2$ escape during the last 2.0 Gyr. Because the ratio of 2:1 between H to O loss should be fulfilled, our result imply that during this time oxygen may have reacted very efficiently with the surface material by chemical weathering.

The integration of the water loss rate from the planet by using the total H$_2$O loss rate results in a mass \(\Delta M\) of about \(2.5 \times 10^{18}\,\text{kg}\) of H$_2$O lost from Mars during the past 35 Gyr.

By using

\[
d = \frac{\Delta M}{4\pi R_M^2 \rho_{H_2O}},
\]

with \(R_M\) the planetary radius of 3400 km and \(\rho_{H_2O}\) the density of water, one finds that Mars had lost a global H$_2$O ocean with a depth \(d\) of about 12 m. Interestingly, our estimation lies between former estimations by Lammer et al. (1996) of about 5 m and Krasnopolsky and Feldman (2001) of about 30 m, but is significantly lower than the estimations based on the high loss rate models of Kass and Yung (1995, 1996, 1999). However, due to a denser ionosphere and solar wind mass flux, ion erosion due to momentum transport processes may have been a relevant process as suggested by Pérez-de-Tojada (1992, 1998) and could have enhanced the water loss rates by a factor of about 2. Note also that the estimated 12-m depth is based on a full active self regulation coupling mechanism between O and H.
6. Oxidation processes of the martian soil

As outlined above, an oxygen surface sink may explain the observations and model calculations for the escape of hydrogen and oxygen from Mars. Such an irreversible process can only be explained by means of chemical weathering. Two main-groups of weathering materials are known to be present on Mars: ferric oxides (Murchie et al., 1993; Mustard and Bell III, 1994; Morris et al., 2000) and sulfates (Toulmin et al., 1977; Rieder et al., 1997).

The primary precursor materials for soil formation are magmatic rocks and/or meteoritic matter, both containing iron and sulfur at comparatively low oxidation states. In the following section we try to quantify the effects of oxygen removal from the atmosphere by oxidation of iron- and sulfur-bearing primary materials on the martian surface. The estimated regolith depth is used as a monitor parameter to evaluate the results.

In our model we assume that oxygen removal from the atmosphere is dominated by the oxidation of impact ejecta and by diffusion of oxidants into the soil. Meteoritic gardening is thought to be responsible for burying of oxidized soil and releasing fresh material on the surface. A similar approach was taken by Zent (1998) who estimated the degree of oxidation of the martian regolith with depth. We partly use the results of Zent (1998) and combine them with our estimation of the size of the oxygen surface sink and with geochemical models.

6.1. The oxygen surface sink and oxidation sources

The overall, irreversible oxygen surface sink is based on atmospheric evidence as shown in Table 4. Assuming a linear relationship between the recent and ancient loss-rates to space of H2O and total oxygen given in Table 4 results in a net-loss of oxygen atoms \( n_O \) of about \( 2 \times 10^{42} \), which must have been incorporated into the martian surface since the onset of significant oxidation around 2.0 Gyr ago. Obviously, the oxygen flux into the surface may be higher at present than in the past. This suggestion is consistent with existing models of UV-induced oxidation. Such process has been extensively discussed in the past by Huguenin (1973a, 1973b) and Morris and Lauer (1980). Recent experimental studies confirm that solar UV induced oxidation of metallic iron may well occur under martian conditions and probably involves adsorbed superoxide ions (Yen, 1999; Yen et al., 2000).

It was shown by Selsis et al. (2002a, 2002b), Lammer et al. (2000b), and Rontó et al. (2003) that a super ozone layer at an altitude of about 50 km (Fig. 5 in Selsis et al., 2002a), with a higher or at least comparable concentration to Earth’s, can be photochemically produced in a humid 1 bar CO2 atmosphere. This study shows that photochemically-produced ozone could have reduced the surface reactions in the martian past. Further, the record along the entire martian geologic history suggests that volcanic activity could have ejected considerable amounts of dust and gases such as SO2 especially in the martian past (Tanaka et al., 1992). Yung et al. (1997) showed that even small amounts of SO2 could have shielded the martian surface against solar UV radiation. In addition to an enhanced ozone concentration this may have led to extensive radiative protection in eras prior 2 Gyr ago. It remains, however, to be explored whether or not a fully inorganic process, driven by photochemical reactions, is sufficient to explain the global oxygen surface sink.

Impact-driven processes should also be considered as an additional source for the oxidation of the martian soil (Bell III et al., 2000). The thermal energy liberated by the kinetic energy of the impact could be transferred to the ejected material. The temperature may reach the melting point of target and impactor materials and may surpass the threshold for thermal oxidation in an oxidizing atmosphere. Because of the lack of intense plate tectonics on Mars, the accumulated matter remains in the regolith layer and is not consumed into the planet’s interior by subduction. Thus, the meteoritic influx may be generally important for the soil formation process.

6.2. Formation of ferric oxy-hydroxides and sulfates

The oxidation of iron may schematically be described in terms of the transformation of the ferrous component of iron-bearing precursor phases into a ferric oxide (oxidation states are indicated by roman numerals as superscripts)

\[
2\text{Fe}^{II}O^{-II} + 0.5\text{SO}_2^0 \rightarrow \text{Fe}^{III}O_3^{-II},
\]

with the following particle number equation:

\[
n_{\text{Fe}}^{\text{Fe}} = \frac{1}{2}n_{\text{Fe}}.
\]

The ferric oxide on Mars may be hematite and/or maghemite, which are chemically identical. The fact that each ferrous iron atom may extract 4 O atoms from the atmosphere can be expressed by Eq. (19). The oxidation process itself is independent of the transformation of ferric oxides into oxy-hydroxides

\[
\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{FeOOH}.
\]

Reaction (19) only considers the oxidation of ferrous iron which is, by far, the dominant oxidation state of iron in magmatic and meteoritic Mg–Fe silicates such as olivine, pyroxene and amphibole and which is also the most common oxidation state in magmatic and meteoritic sulfides. Meteorites may also contain metallic iron, the oxidation of which would be even more efficient in removing oxygen from the atmosphere with the particle number equation

\[
\frac{n_{\text{Fe}}^{\text{Fe}}}{2} = \frac{3}{2}n_{\text{Fe}}.
\]

The amount of metallic iron introduced to the martian surface by meteoritic infall is, however, not known at any accuracy, therefore, the metallic iron component was neglected in our calculations.
The formation of sulfates may be as important as rusting. The positive correlation of magnesium with sulfur may indicate that magnesium-sulfate should be common on Mars (Clark and Van Hart, 1981; McSween and Keil, 2000). However, for the oxidation process itself, the kind of sulfate is unimportant. Under the oxidizing conditions on the martian surface, any sulfur in the soil should be bound in sulfatic weathering phases.

The formation of kieserite from brucite with volcanic gases that migrate through the upper soil-horizons is shown in the following equation:

\[
\text{Mg(OH)}_2 + S^{IV} \text{O}_2^{II} + 0.5 \text{O}_2^{0} \rightarrow \text{MgS}^{VI} \text{O}_4^{II} \cdot \text{H}_2 \text{O}. \quad (23)
\]

with the particle number equation

\[
\nu_O^S = n_S. \quad (24)
\]

The number of sulfur atoms and additional oxygen atoms is the same. Brucite could be formed by hydrothermal decomposition of magnesium-bearing silicatic materials. Because magnesium-sulfate is a strong hygroscopic phase, it should occur at least as kieserite even under martian conditions.

Another possible reaction is the generation of sulfates (amarantite) from the oxidation of meteoritic and magmatic sulfides (troilite/pyrrhotite)

\[
2\text{Fe}^{II} \text{S}^{III} \cdot \text{II} + 4.5 \text{O}_2^{0} + 7\text{H}_2 \text{O} \rightarrow 2\text{Fe}^{III} \cdot [\text{S}^{VI} \text{O}_4^{II} / \text{O}^{III} \text{H}] \cdot 3\text{H}_2 \text{O}. \quad (25)
\]

The capacity for oxygen removed from the atmosphere is expected by

\[
\nu_O^{Fe} = \frac{1}{2} n_{Fe} \quad (26)
\]

and

\[
\nu_O^{S} = 4n_S. \quad (27)
\]

For the formation of sulfates only Eq. (27) is of importance. Magmatic sulfides are represented mainly by FeS2 (pyrite). The oxidation number of sulfur in the di-sulfidic ion of pyrite equals I so that the use of pyrite in Eq. (25) would represent a more moderate approach of oxygen incorporation upon sulfatification. We used in our model FeS as a sulfidic precursor material.

A further potential loss of oxygen into the surface is the reaction of reduced gases emanating from volcanos and vents. Oxidation of hydrogen sulfide (H2S) involves formation of both sulfate species and water, which may escape from the subsurface to the atmosphere and experience photochemical reactions. The result is the same as given in Eq. (27), diminished by one equivalent of H2S because of the access of hydrogen escaping to space, which was not originally derived from H2O. This moderate approach was neglected because of the expected small absolute amount of sulfuric hydrogen compared to the mass of weatherable magmatic sulfides.

In the presence of brucite, amaranite could react to form magnesium-sulfate and ferric oxide:

\[
2\text{Fe}[\text{SO}_4 / \text{OH}] \cdot 3\text{H}_2 \text{O} + 2\text{Mg(OH)}_2 \rightarrow 2\text{Mg}[\text{SO}_4] \cdot \text{H}_2 \text{O} + \text{Fe}_2 \text{O}_3 + 7\text{H}_2 \text{O}. \quad (28)
\]

Combination of Eqs. (25) and (28) yields the following water conserving reaction:

\[
2\text{FeS} + 4.5\text{SO}_2 + 2\text{Mg(OH)}_2 \rightarrow 2\text{Mg}[\text{SO}_4] \cdot \text{H}_2 \text{O} + \text{Fe}_2 \text{O}_3, \quad (29)
\]

which may account for the presence of hydrous magnesium sulfate and ferric oxides and, if enough water is available, ferric oxy-hydroxides.

6.3. Soil properties

We used in our calculation the composition of Mars Pathfinder (MPF) soils (A-8, A-10, A-15) given in Rieder et al. (1997) and averaged the results for soil analysis which gave totals close to 100%. Of particular importance is the iron and sulfur content of the soils. The averaged iron and sulfur contents considered in our model are \( k_{Fe} = 12.4 \text{ wt}\% \) and \( k_S = 2.2 \text{ wt}\% \), respectively. To simplify, we assume that these values are globally valid mean values. The density of the soil \( d \) was adopted from Hviid et al. (1997), who found 1.5 g cm\(^{-3}\).

Another important input for our model regards the initial and final oxidation states of iron in the soil. For MPF-soils and -rocks the oxidation state was determined by means of reflectance spectroscopy. The ratio of ferric to ferrous iron was found to be within the range of 3–20 for the soils and within 0.7–3 and for the rocks (Morris et al., 2000). This indicates that 41 to 75% of the total amount of iron is in the ferric state within the rocks and 75 to 95% within the soils.

The estimation of the ferric/ferrous ratio by means of VIS-NIR reflectance band investigation is possibly subject to large systematic errors. Satisfactory results are only expected if grain-size-distributions of the ferrous and ferric phases are equal. But this seems not to be valid for the martian soils, since overall spectra indicate nano-phased ferric oxides in the presence of detrital ferrous phases (Morris et al., 2000). Thus, the fine ferric dust could mask the spectral behavior of the bulk system. This could be the case for the soils and for the rocks because of coating effects and weathering rims.

The observations of the Mars Global Surveyor Thermal Emission Spectrometer (TES) yield evidence that most of the soil consists of basaltic/andesitic detritus (Hamilton et al., 2001). An amount of up to 95% of ferric iron is not consistent with abundant basaltic/andesitic components comprising mainly ferrous phases. The same accounts for 41 to 75% of ferric iron in martian rocks. In comparison, martian basaltic meteorites seem to exhibit a range of 0 to 53% of ferric iron (Dyar et al., 2001). Therefore, we used the final
oxidation state as a free variable $X_{\text{Fe}^{3+},f}$, rather than as a fixed parameter.

Due to the oxygen fugacity in the differentiated magma, martian magmatic precursor rocks (basalts, andesites) exhibit a certain amount of initial ferric iron $X_{\text{Fe}^{3+},i}$. The values for martian meteorites and lunar mare basalts are obtained by the investigation of magmatic feldspar (Dyar et al., 2001):

$$
\frac{n_{\text{Fe}^{3+}}}{n_{\text{Fe}^{3+}} + n_{\text{Fe}^{2+}}} = X_{\text{Fe}^{3+},i} = 0.0/0.23/0.53, \quad (30)
$$

where 0.0 is from SNC QUE 94201, 0.23 corresponds to Lunar mare basalt 15555 and 0.53 to SNC Zagami. $n_{\text{Fe}^{2+}}$ and $n_{\text{Fe}^{3+}}$ correspond to iron particle numbers. Iron is a common trace element in feldspar, and because of its small amount the influence of crystallographic site tolerances on ferric/ferrous iron distribution is thought to be negligible (Dyar et al., 2001). Martian meteorites underwent two impact processes, so it cannot be ruled out that the ferric/ferrous ratio was shifted since the origin of these rocks.

Only two values for martian basaltic meteorites are available, and the range within them is very large. Moreover, because the oxygen fugacity in the basaltic rocks on the Moon is unaffected by any atmospheric process at all, lunar values should represent reasonable values also for Mars. They are believed to give the best proxies also for Mars and must be used until Mössbauer spectroscopy data from the martian surface become available.

Therefore, the lunar value in Eq. (30) was used for our calculation of the regolith depth. The true value of initial ferric iron for martian precursor soils might be shifted downward because of meteoritic material, which comprise mainly ferrous and metallic iron.

### 6.4. Depth of oxidized soil

Based on the parameters given above, a hypothetical sediment-cover of a homogenous oxidized soil can be calculated by using the following equations:

$$
V_{\text{Fe\_soil}} = \frac{n_{\text{Fe\_tot}} \cdot M_{\text{Fe}} \cdot 100}{N_A \cdot k_{\text{Fe}} \cdot d}, \quad (31)
$$

$$
V_{\text{S\_soil}} = \frac{n_S \cdot M_S \cdot 100}{N_A \cdot k_S \cdot d}, \quad (32)
$$

$$
n_{\text{Fe\_tot}} = \frac{2n_O}{X_{\text{Fe}^{3+},f} - X_{\text{Fe}^{3+},i}}, \quad (33)
$$

$$
n_O = n_O^S + n_O^F, \quad (34)
$$

$$
n_S = 0 \quad \text{without sulfates}, \quad (35)
$$

$$
n_S = n_O^S \quad \text{with sulfates from sulfitic gases}, \quad (36)
$$

$$
n_S = \frac{n_O^S}{4} \quad \text{with sulfates from sulfides}, \quad (37)
$$

$$
V_{\text{S\_soil}} = V_{\text{Fe\_soil}} \rightarrow D_{\text{soil}}. \quad (38)
$$

Additional parameters in Eqs. (31) and (32) are the Avogadro number $N_A$ and the molecular weight of iron and sulfur $M_{\text{Fe}}$ and $M_S$, respectively. $V_{\text{soil}}$ is the volume of the oxidized soil layer.

Figure 3 shows the results in terms of the depth of oxidized soil versus the final oxidation state of iron in the soil. It becomes clear that sulfates are probably more important for the surface sink than oxidation of ferrous iron. This can be seen by comparison of depths obtained with and without the formation of sulfates at the same initial oxidation state.

The results shown in Fig. 3 are based on the assumption that the layer of oxidized soil is homogeneous. It has however been argued by Zent (1998) that the degree of oxidation may decrease with depth within the regolith. To obtain a more realistic estimate of the minimum regolith depth, the oxidant extinction depth and the effects of meteoritic gardening must be introduced.

![Fig. 3](image-url)
7. Oxidant extinction depth and meteoritic gardening

An important parameter for the evaluation of the oxidation of inorganic and organic material is the oxidant extinction depth, at which the concentrations of the oxidizing agents approach zero due to its chemical interaction with the subsurface environment (Bullock et al., 1994; Zent, 1998). This implies that the oxidants are produced by the interaction with the atmospheric and radiation environment.

The extinction depth is the result of all physico-chemical properties of the oxidants and the interaction with their surroundings:

1. concentration at the base of the martian atmosphere,
2. resistance and use-up in their surroundings including different kinds of oxidants and reductants and thermodynamic and kinetic conditions, and
3. constraints on oxidant diffusion.

To calculate the oxygen incorporation into the soil, the effect of meteoritic gardening must be considered. Fresh material will be brought up to the surface and oxidized material will be buried during this process (Zent, 1998). Meteoritic production populations represent the frequency distribution of impacts and are responsible for meteoritic gardening. Size-frequency distribution functions can be established from crater counting studies (e.g., Carr, 1981; Neukum and Ivanov, 1994; Hartmann and Neukum, 2001).

In Fig. 4 several distribution functions are given in terms of crater abundance and crater diameter. Due to effects of erosion and deposition, size-frequency distribution functions and production populations are not equal. However, the meteoritic size-frequency distribution functions given by Neukum and Ivanov (1994) and Carr (1981) were assumed to represent meteoritic production populations in the work of Zent (1998) and in our calculation model. Zent (1998) calculated the degree of oxidation of the martian surface with depth on the basis of different oxidant extinction depths and meteoritic gardening models.

New results from crater counting are shown in Fig. 4 (Hartmann and Neukum, 2001; Ivanov, 2001). The crater isochrone of 1.5 Gyr, which is consistent with the onset of oxidation between 1.5 and 2 Gyr, is located well within the old curves for Neukum and Carr data used in the work of Zent (1998). This is especially the case of larger impacts, which are more important with regard to effective meteoritic gardening and oxygen incorporation.

Figure 5 shows the degree of oxidation versus depth. The soil is assumed to be fully oxidized above the level of the extinction depth. Two meters and an extrapolated value of five meters is used in our study for the oxidant extinction depth, together with the production populations of Neukum and Carr. Meteoritic ejecta are assumed to become oxidized during impact.

8. Regolith depths

For the estimation of the regolith depth, the concept of a homogenous oxidized soil has to be combined with the extinction depth and meteoritic gardening models. An explicit expression for regolith depth $D_{\text{soil}}(D_{\text{rego}})$ is derived from integration of the curves in Fig. 5:

$$
D_{\text{soil}}(D_{\text{rego}}) = \int_{0}^{D_{\text{rego}}} X(D) dD \to D_{\text{rego}}(D_{\text{soil}}). \quad (39)
$$

Because the regolith consists also of a certain amount of rock, we assigned 10 vol% of regolith to martian rocks. Figures 6 and 7 show our results in terms of the martian regolith depth versus the final ferric/ferrous oxidation state.

The estimation of the regolith depth based on impact geometry by means of Mars Orbital Camera (MOC) data on board of Mars Global Surveyor amounts to a range between 20 to 113 m (Gilmore, 1999). If this range is regarded as globally valid mean values, this can be used for evaluation of the theoretical depths obtained by our model. Neukum production functions combined with a two-meter oxidant extinction depth result even with sulfatic production from
sulfides in several hundred meters of regolith. Using the Carr production function and two-meter extinction depth gives a regolith depth of about 20 m (Fig. 6). Roughly the same depth can be obtained by combination of Neukum production populations and five-meter extinction depth—although an entire production of sulfates from sulfides is not theoretically possible in this case (Fig. 7).

Since these new models of meteoritic size-frequency distribution functions indicate populations within the Carr and Neukum range, our calculation shows that an oxidant extinction depth of about two meters may represent a minimum value. This also means that the value should be certainly below five meters. Interesting in this context is the work of Bullock et al. (1994). They calculated an upper limit for the extinction depth of about 2.7 m for the thermal decomposition lifetime of $10^5$ years of the oxidant in the Viking Labeled Release (LR) experiment (Chyba et al., 1989).

9. Conclusions

The results of our investigation imply a total loss of $\text{H}_2\text{O}$ equivalent to a depth of about 12 m over the past 3.5 Gyr from Mars if we assume the self-regulation mechanism between the loss of O and H as postulated by McElroy (1972). This amount is lower than previous estimates by Kass and Yung (1995, 1996, 1999) of about 50 to 80 m. However, ionospheric erosion processes as discussed in Section 4.4 may enhance the loss rates up to a factor of two.

By assuming that all hydrogen lost to space has its origin from water, our study suggests that the stoichiometrically $\text{H}:\text{O}$ escape ratio of 2:1 to space cannot be maintained at present. This result implies an oxygen surface sink and a strong atmosphere-surface-interaction. The oxygen surface sink, which is needed for establishing the 2:1 ratio between the H and O loss over the past 2 Gyr, may be responsible for an enhanced soil/surface oxidation process. We estimate
a sink of about $2 \times 10^{42}$ O particles which is equivalent to a global water layer of about 40 cm in depth.

We found that it is possible to incorporate this amount of oxygen into the regolith by oxidation of inorganic soil-precursors. Depending on different models of meteoritic gardening, the expected range for the oxidant extinction depth should be between 2 and 5 m. These constraints on the oxidant extinction depth are important for the search of organic material since in-situ excavation of samples from the subsurface with penetrating moles or drills should therefore be capable of reaching depths of at least 5 m to have a chance of finding non-oxidized samples. However, since this range refers to global mean values, appropriate landing sites could exhibit smaller oxidant extinction depths. The location of these sites will strongly depend on spatial and seasonal solar UV radiation conditions and water adsorption (Patel et al., 2003).

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References


Hydrogen and oxygen loss from Mars


