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Estimation of the past and present Martian water-ice reservoirs by isotopic constraints on exchange between the atmosphere and the surface

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Abstract: The discovery of high concentrations of water-ice just below the Martian surface polar areas made by Mars Odyssey has strengthened the debate about the search for life on Mars. Generally it is believed that life on Earth emerged in liquid water from the processing of organic molecules. Thus, the possible origin of life on early Mars should have been related to the evolution of the planetary water inventory, consequently it is important to know the amount of water-ice stored below the planetary surface. The search and mapping of the present subsurface water and ice reservoirs will be carried out experimentally by Mars Express with its Mars Advanced Radar for Subsurface and Ionospheric Sounding (MARSIS) ground-penetrating radar in the near future. We estimate the present and past water-ice reservoirs, which are and were in exchange with the atmosphere by using the observed D/H ratio in the atmospheric water vapour, measured D/H ratios in Martian SNC meteorites and D/H isotope ratios based on a study by Lunine *et al.* (2003) regarding asteroid and cometary water delivery to early Mars. Using the results of this study with initial D/H ratios of about 1.2–1.6 times the terrestrial sea water (TSW) ratio and the assumption that these ratios were not fractionated by XUV-driven hydrodynamic escape due to a more active young Sun prior to 3.5 Ga, one finds a present water-ice reservoir, which can exchange with the Martian atmosphere, equivalent to a global ocean layer with a thickness of about 3.3–15 m. By assuming that hydrodynamic escape fractionated the D/H ratio to a value that is stored in the old Martian SNC meteorites with a measured average enrichment of about 2.3 times the TSW ratio we estimate a present water-ice reservoir equivalent to a global layer with a thickness of about 11–27 m. From the obtained range of the estimated present water-ice deposit, we estimate a water-ice reservoir exchangeable with the atmosphere on Mars 3.5 Ga equivalent to a global ocean with a thickness of between 17 and 61 m. All the estimated reservoirs depend on the escape of water from Mars since 3.5 Ga equivalent to a global ocean with a thickness of about 14 m (minimum) to 34 m (maximum). The main uncertainties in the estimate of the minimal and maximal water-ice reservoir is related to the present uncertainties in the efficiency of atmospheric escape rates triggered by plasma instabilities and momentum transfer effects between the solar wind and the ionosphere. However, these uncertainties will be reduced in the near future, since both loss processes will be studied in detail by the Automatic Space Plasma Experiment with a Rotating Analyzer (ASPERA-3) on-board Mars Express. The obtained results combined with the discovery of the present water-ice subsurface reservoirs by the MARSIS radar and isotope studies as presented in this work, will also give us an idea of how enriched the atmosphere was in D compared with H after the heavy bombardment corresponding to a better understanding of the efficiency of the hydrodynamic escape process due to the young Sun.

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Introduction

High-resolution altimetric data from the Mars Orbiter Laser Altimeter (MOLA) instrument on-board the Mars Global Surveyor (MGS) has defined a detailed topography of the northern Martian lowlands (Head *et al.* 1999). A wide range of data are now consistent with the hypothesis that a lowland-encircling geological contact represents the ancient shoreline of a large standing body of water in the Martian past. The MOLA data support this hypothesis since the flatness and smoothness of these features have shown that they were part of a large watershed (e.g. Head *et al.* 1999), where outflow channels empty into the northern lowlands (Carr 1987; Baker 2001). Some gullies on the Martian surface have been attributed to recent H_2O seepage and runoff, suggesting water or ice close to the surface. Actual observations by the High Energy Neutron Detector (HEND) on-board Mars Odyssey give strong evidence that water-ice is concentrated in the subsurface of the northern and southern hemispheres (Mitrofanov *et al.* 2002).

The Martian atmosphere has currently little detectable water with an average of 10 precipitable microns (1 pr μm water is equivalent to a 1 μm deep layer over the entire planetary surface) (Jakosky & Framer 1982; Kieffer *et al.* 1992; Carr 1996). The main indication that Mars once had a larger water reservoir is the evidence owing to an observed large deuterium (D) enrichment in the atmospheric water vapour (e.g. Owen *et al.* 1988), which is an indication that significant amounts of water have been lost from the surface by atmospheric escape processes over the history of the planet.

Previous studies have estimated present water-ice reservoirs, which are in isotopic exchange with the Martian atmosphere equivalent to a global ocean with a thickness of about 0.2 m (Yung *et al.* 1988), 0.5 m (Donahue 1992), 8 m (Kass & Yung 1999) and 5 m (Krasnopolsky 2000). These studies used different fractionation factors between D and H escape rates as well as different estimated total water loss rates from the present to 3.5 Ga. Furthermore, all of the previous studies used the terrestrial sea water (TSW) value as the initial D/H ratio.

In this work, we estimate the water loss to space since the end of the heavy bombardment phase using new results for thermal escape rates of H, H_2, ion pick up of H^+, H_2^+, O^+, dissociative recombination of O, sputtering of O, CO and CO_2 of Lammer *et al.* (2003) and additional loss of O^+ ions triggered by plasma instabilities, studied in detail by Penz (2003) and Penz *et al.* (2003) and cold O^+ ion outflow triggered by momentum transport of the solar wind (Lundin *et al.* 1991; Perez-de-Tejada 1992, 1998; Amerstorfer 2003; Erkaev *et al.* 2003). To estimate the water loss from Mars the studies of Lammer *et al.* (2003), Penz (2003) and Amerstorfer (2003) used, for the first time, data on the solar wind density from the present to 3.5 Ga from stellar wind observations of solar-like young stars (Wood *et al.* 2002). Furthermore, to estimate the present and past water-ice reservoirs we use initial D/H ratios obtained from a recent asteroid and cometary impact model of Lunine *et al.* (2003) and low fractionation factors between D and H (Krasnopolsky 2000; Bertaux & Montmessin 2001), which are in agreement with Hubble Space Telescope (HST) observations of D depletion in the upper Martian atmosphere.

The source of the Martian water

There is significant chemical and dynamical evidence that the source for the terrestrial crustal and surface water originated from planetary embryos, which have their origin in the asteroid belt (Morbidelli *et al.* 2000). This source is consistent with the isotopic record of the water content of the asteroid belt, from the chondrite record (Robert 2001) and in the role of gas giants in clearing the asteroid belt (Petit *et al.* 2000). The observed terrestrial D/H ratio is also consistent with the isotopic record of the D/H ratio in carbonaceous chondrites and terrestrial ocean water, for which the principal source is from the asteroid belt.

The D/H ratio of the water vapour in the current Martian atmosphere is about five times the TSW value of about 8×10^{-4} (Owen *et al.* 1988), where the cause for this difference is commonly assumed to be due to isotopic fractionation during atmospheric escape of water which can exchange with water sources in the Martian crust and the surface (Yung *et al.* 1988; Owen 1992; Donahue 1995). Although, the original D/H ratio in the Martian water, obtained from planetesimals is not well known, there are three main possibilities for the delivery of water to growing terrestrial planets: planetary embryos from beyond 2.5 AU, small asteroids from beyond 2.5 AU and comets from the Jovian orbital distance and beyond.

The orbit of Mars is close to that of the asteroid belt. Thus, frequent collisions with asteroids and comets have occurred. A recent study determined how much water Mars could have acquired from asteroid and comet populations (Lunine *et al.* 2003). By estimating the cumulative collision probability between asteroids and comets with Mars and by assuming that comets consist of about 50% water-ice with a D/H ratio of about 3.2×10^{-4} (Bockelée-Morvan & Gautier 1988; Meier *et al.* 1988; Eberhardt *et al.* 1995), which is about twice the TSW ratio of about 1.56×10^{-4} and that asteroids have about 10% water by mass (with D/H values comparable to the TSW value based on carbonaceous chondrites), it was found that Mars has acquired an amount of water equivalent to 0.06–0.27 times that of the Earth's oceans with a D/H isotope ratio of about 1.6 times the TSW ratio for 0.06 and 1.2 times the TSW ratio for 0.27 Earth-oceans (Lunine *et al.* 2003).

The study by Lunine *et al.* (2003) indicates that Mars actually received more water from small comets and asteroids with semi-major axes larger than 2.5 AU than Earth, while Earth may have received the bulk of its water from large embryos. Using this result, one finds that the estimated values of about 0.06–0.27 times Earth's oceans on Mars corresponds to about 600–2700 m worth of water equivalent on the Martian crustal regolith and surface, which is in agreement with previous studies by Carr (1996) and Baker (2001), because out-gassed water of about 500 m depth on the Martian surface corresponds to about 1000 m equivalent total accreted (Lunine *et al.* 2003).

The D/H ratio of about 1.2–1.6 times the TSW value is below or closer to the average value of about 2.3 times the TSW ratio, measured in Martian SNC meteorites and comets (Leshin *et al.* 1996; Leshin 2000). An enrichment of about 1.6 times the TSW value is in agreement with the D/H ratio measured in the 3.9 Gyr old Martian meteorite ALH84001. The difference between the D/H ratio in the Shergottites and the asteroid–comet collision study of Lunine *et al.* (2003) can be interpreted as the D/H ratio in these Martian SNC meteorites being derived from magmatic water, which represents either a primordial Martian value obtained from accretion of a mixture of asteroidal and cometary water, or was enhanced from the primordial value due to hydrodynamic escape caused by a more active young Sun (Donahue 1995; Leshin 2000; Lunine *et al.* 2003).

There is evidence that liquid water could exist on Mars up to the end of the erosion of the atmosphere due to hydrodynamic escape (e.g. Donahue 1995; Krasnopolsky *et al.* 1998) and large-scale asteroid impacts (Melosh 1989; Melosh & Vickery 1989). It is commonly believed that both processes are very efficient and do not cause much fractionation of the isotopes. We consider two cases for the estimation of the present water-ice reservoir on Mars: (1) we assume that the initial D/H isotope ratio obtained by Lunine *et al.* (2003) has not changed much since the end of the heavy bombardment 3.5 Ga and (2) we assume that the initial D/H ratio obtained by Lunine *et al.* (2003) was enriched in D by a ratio of about 2.3 times the TSW value as measured in Shergottites (Leshin *et al.* 1996) due to hydrodynamic escape.

Table 1. *Overview of the D/H ratio in the Martian atmosphere, in the TSW, in comets and in Martian SNC meteorites. The crystallization ages and ejection ages for most meteorites are taken from Nyquist* et al. (*2001*). *The crystallization age for ALH 84001 is taken from Turner* et al. (*1997*) *and the measured D/H values are taken from Leshin* et al. (*1996*). *The ejection age refers to the time of ejection from the Martian surface* (*space exposure and terrestrial age*)

Name	D/H (1×10^{-4})	Crystallization (Myr)	Ejection (Myr)
Martian atmosphere	8		
Terrestrial sea water	1.56		
Comets	3.2		
Shergottites (*basalts*)			
Elephant Moraine 79001	3.86	173 ± 3	0.73 ± 0.15
Shergotty	3.39	165 ± 4	2.73 ± 0.20
Zagami	3.28	177 ± 3	2.92 ± 0.15
Nakhlites (*clinopyroxenites*)			
Governador Valadares	1.97	1330 ± 10	10.0 ± 2.1
Lafayette	2.47–2.8	1320 ± 20	11.9 ± 2.2
Nakhla	2.24–2.73	1270 ± 10	10.75 ± 0.40
Others			
Chassigny (dunite)	1.49–1.6	1340 ± 50	11.3 ± 0.6
Allan Hills 84001 (orthopyroxenite)	2.45	3920 ± 40	15.0 ± 0.8

Evolution of the Martian water-ice reservoir

The deuterium in the Martian atmosphere has been detected by resolution of several Doppler-shifted lines of HDO vapour near 3.7 μm in the planetary spectrum and revealed an enrichment compared to the D/H ratio of the TSW value by a factor of 5 (e.g. Owen *et al.* 1988; Owen 1992; Donahue 1995). Given the large size of water reservoirs on Earth, one can assume that the TSW D/H ratio has not changed much during the past billion years. As discussed before, the initial D/H ratio in the Martian water reservoir has its origin from impacts of asteroids and comets and may have been of the order of about 1.2–1.6 times that of the TSW ratio. One can see from Table 1 that measurements in Martian SNC meteorites also have D/H ratios of around 1.47, 2.5 and 3.5 times the TSW value (Leshin *et al.* 1996). The measured D/H ratio of the 3.9 Gyr old ALH 84001 is about 2.5 times the TSW.

The simplest interpretation of the D enrichment in the Martian atmosphere is that an appreciable amount of H associated with the original water or water-ice reservoir has escaped to space. Since the Martian obliquity changes over time periods of about 10^5 to 10^7 years between zero and 60 degrees we can expect dramatic climate change and effective isotope exchange between ice deposits and the atmosphere (Pollack 1979). One can assume that there are two water reservoirs on Mars, which can interact together, one in the subsurface $s(t)$ and one in the atmosphere $a(t)$. Generally $s(t)$ is much larger compared with $a(t)$ (Donahue 1995). We assume that the two water reservoirs exchange together and part of the atmospheric D and H are lost to space with different efficiencies by various atmospheric escape processes and R increases with time. The isotope ratio R at time t_2 to that of an earlier time t_1 is independent of the escape fluxes but depends on the ratio $r(t)$,

$$r(t)=\left[\frac{R(t_2)}{R(t_1)}\right]^{1/(1-f)}, \tag{1}$$

with the fractionation factor f,

$$f=\frac{\phi_2}{\phi_1}R=\frac{d[\mathrm{D}]/\mathrm{D}}{d[\mathrm{H}]/\mathrm{H}}, \tag{2}$$

where $r(t)$ is the factor of how many times the present exchangeable water-ice reservoir was larger in the past, while ϕ_1 and ϕ_2 are the H and D escape fluxes and [H] and [D] are the abundances of H and D in the combined reservoirs in atoms per cm^2 (Donahue 1995; Bing-Ming *et al.* 1999; Kass & Yung 1999; Krasnopolsky 2000). A fractionation factor $f=1$ indicates that D escapes as easily as H atoms. If $f=0$ no D isotopes can escape and only H atoms are lost. A study by Yung *et al.* (1988) estimates f as about 0.32, but observations with the Goddard high-resolution spectrograph on-board the HST indicate a much smaller f of between 0.016 and 0.02 in the lower Martian atmosphere (Krasnopolsky *et al.* 1998; Krasnopolsky 2000).

Bertraux & Montmessin (2001) found from recent Lyman α HST observations of D atoms that the D/H ratio in the upper Martian atmosphere is about 11 times smaller than the D/H ratio in the lower atmosphere (Krasnopolsky *et al.* 1998). These authors propose a photo-induced fractionation effect, due to a lower absorption cross section of solar UV of HDO compared with H_2O. To explain this D depletion in the upper Martian atmosphere, Bertraux & Montmessin (2001) suggest further that this effect is enhanced by a preferred

Table 2. *Factor* r(t) *of how many times the water-ice reservoir, which is in isotopic exchange with the present Martian atmosphere, was larger in the past as a function of various fractionation factors* f *of Yung* (*1988*, f = *0.32*), *Krasnopolsky* (*2000*, f = *0.016*), *Bertraux & Montmessin* (*2001*, f = *0*) *and initial D/H isotope ratios like the TSW ratio, the two initial D/H ratios from the asteroid–comet collision study of Lunine* et al. (*2003*) *and the D/H isotope ratio of about 2.3 times the TSW value measured in Martian Shergottite meteorites and comets. We use the underlined values in our study resulting from a fractionation factor* f ≈ *0.016* (*Krasnopolsky 2000*) *close to zero*

	$r(t)$			
f	$R(t_1)=\mathrm{TSW}$	$R(t_1)=1.2\times\mathrm{TSW}$	$R(t_1)=1.6\times\mathrm{TSW}$	$R(t_1)=2.5\times\mathrm{TSW}$
0.32	11.04	8.45	5.53	3.25
0.016	<u>5.26</u>	<u>4.36</u>	<u>3.26</u>	<u>2.25</u>
0	5.12	4.27	3.2	2.23

condensation of HDO in rising air. Both, the photo-induced and the condensation/evaporation fractionation effects can explain the observed paucity of D atoms in the upper Martian atmosphere and indicate that f is close to 0, implying a very low escape rate for D isotopes compared with H atoms at present and over the history of the planet. Table 2 shows values of $r(t)$ by using in Eq. (1), $f=0$ (Bertraux & Montmessin 2001), $f=0.016$ (Krasnopolsky 2000), and as a comparison the value of $f=0.32$ used in previous studies by Yung *et al.* (1988) as function of the TSW ratio: 1.2 and 1.6 times the TSW ratio (Lunine *et al.* 2003) and 2.3 times the TSW ratio for $R(t_1)$ as possible initial D/H ratios (3.5 Ga).

A fractionation factor f of about 0.32 overestimates the early water reservoir on Mars by up to a factor of about 2. Because the HST observations imply a low f, one can see in Table 2 that there was about 2–4.2 times more hydrogen and thus water in the early Martian crust and atmosphere than there is today. One can see that the difference between $f=0.016$ and 0 is very small, therefore, in our study we use $f=0.016$ (Krasnopolsky 2000).

By knowing the total amount of water lost to space over Martian history, one obtains a constraint of the thickness $s(t)$ equivalent to a global water layer (e.g. Donahue 1995; Kass & Yung 1999)

$$s(t)=\frac{L_{\mathrm{H_2O}}}{\left\{[R(t_2)/R(t_1)]^{1/(1-f)}\right\}-1}, \tag{3}$$

where $L_{\mathrm{H_2O}}$ is the total water lost from Mars equivalent to a global ocean depth in units of metres. The evolution of the Martian water inventory is influenced by thermal escape of H, H_2 and non-thermal atmospheric loss processes of H^+, H_2^+, O, O^+, CO_2 and O_2^+ into space, as well as by chemical weathering due to oxygen incorporation in the surface soil (Lammer *et al.* 2003). The efficiency of these escape processes depends on the history of the intensity of the solar XUV radiation (Guinan & Ribas 2002) and the solar wind density (Wood *et al.* 2002).

For the estimation of $L_{\mathrm{H_2O}}$ we use the results of Lammer *et al.* (2003), whose study includes actual stellar data from the observation of solar proxies with different ages (Guinan & Ribas 2002) for reconstructing the Sun's radiation and particle environment from the present to the end of the heavy bombardment period (3.5 Ga). The total loss of water from Mars caused by ion pick up, atmospheric sputtering and dissociative recombination over the last 3.5 Gyr was estimated to be equivalent to a global Martian water ocean with a layer thickness of about $L_{\mathrm{H_2O}}\approx 12$ m, which is smaller than the values reported by previous estimates of between 30 and 80 m (Luhmann *et al.* 1992; Jakosky *et al.* 1995; Kass & Yung 1995, 1996, 1999; Krasnopolsky & Feldman 2001), but larger than the estimates of between 3 and 5 m of Yung *et al.* (1988) and Lammer *et al.* (1996).

The main reason for the different result of Lammer *et al.* (2003) compared with the previous studies is a result of the use of different solar wind density values by all previous studies for the three XUV (2 Gyr) and six XUV (3.5 Gyr) epochs. Furthermore, for the calculation of the atmospheric sputter escape rates, Lammer *et al.* (2003) employed the sputter yields from Table 1 of a new study by Leblanc & Johnson (2002) together with their newly modelled incident O^+ ion pick-up fluxes. Because, of the fact that the upper atmospheric composition and the solar wind interaction of Mars and Venus are similar, other atmospheric loss processes observed on Venus but not considered by Lammer *et al.* (2003) should also occur.

Measurements of the Pioneer Venus Orbiter revealed a number of characteristic ionospheric structures that may be signatures of solar wind–ionosphere interaction processes in the Venus plasma environment (Brace *et al.* 1982; Russell *et al.* 1982). Among them are wave-like plasma irregularities observed at the top of the dayside ionosphere and plasma clouds observed above the ionopause, primarily near the terminator and further downstream. The analysis of several clouds has shown that the plasma within the clouds themselves is ionospheric in electron temperature and density (Brace *et al.* 1982).

When such plasma clouds were seen far above the ionosphere, they were clearly separated by an intervening region of ionosheath plasma. This large separation in a direction perpendicular to the ionosheath flow suggests that the ionospheric plasma in the clouds must have originated in the ionosphere upstream on the dayside, indicating that magnetohydrodynamic (MHD) instabilities may occur at the Venusian ionopause. Therefore, Elphic & Ershkovich (1984) analysed the stability of the Venusian ionopause by using one-fluid MHD equations for a perfectly conducting, incompressible, inviscid fluid, and concluded that the Kelvin–Helmholtz instability may be the dominant instability over most of the dayside Venusian ionopause.

The magnetometer of Mars Global Surveyor has clearly demonstrated that, like Venus, Mars does not have a significant, global, intrinsic magnetic field (Acuña *et al.* 1998; Connerney *et al.* 2001). Acuña *et al.* (1998) reported the detection of cold electrons above the Martian ionopause, indicating the presence of plasma clouds and correspondingly an additional loss process for water in the magnetosheath of Mars. Since this loss process was not studied in detail before, in this study we use the model results of Penz (2003) and Penz *et al.* (2003) and estimate the amount of water that may escape from the Martian ionosphere by ionospheric clouds over Martian history by taking into account for the early solar wind the observationally based stellar wind data from Wood *et al.* (2002) and Lammer *et al.* (2003) and for the early Martian ionopause particle densities, profiles modelled by Zhang *et al.* (1993). We find that these additional loss process may raise the total water loss equivalent to a global Martian ocean with a thickness of about 12 up to at least 14 m.

The ASPERA instrument on-board the Phobos 2 spacecraft observed a strong interaction between the solar wind plasma and the cold ionospheric plasma in the Martian topside ionosphere in such a way that the solar wind plasma transfers momentum directly to the Martian ionosphere in a dayside transition region to the deep plasma tail (Lundin *et al.* 1991) is

$$v_i = v_{sw} k \left[1 - \left(\frac{n'_{sw} v'^2_{sw}}{n_{sw} v^2_{sw}}\right)\right]^{1/2}, \quad (4)$$

with

$$k = \left(\frac{n_{sw} m_{sw} \delta_{sw}}{n_i m_i \delta_i}\right)^{1/2}, \quad (5)$$

where n_{sw} and n_i are the number density of the solar wind and ionospheric plasmas, respectively, n'_{sw} is the density of the solar wind at the boundary of the planetary obstacle, m_{sw} and m_i are the mass of the solar wind protons and the dominant ionospheric O^+ ions, v'_{sw} and v_{sw} are the velocities of the solar wind at the boundary of the planetary obstacle and outside the velocity shear, and δ_i and δ_{sw} correspond to the effective momentum flux thickness of the ionospheric flow and the velocity shear in the shocked solar wind (Perez-de-Tejada 1992). Perez-de-Tejada (1992, 1998) and Amerstorfer (2003) found that this momentum transport seems to be capable of accelerating ionospheric O^+ ions to velocities $v_i \geqslant 5$ km s^{-1}, resulting in energies greater than the Martian escape energy $\geqslant 2$ eV.

In a previous study, Perez-de-Tejada (1992) showed that cool ion escape due to momentum transport effects may have removed water from Mars equivalent to a global ocean with a thickness of about 10–30 m, depending on the uncertainties of solar wind parameters and the Martian plasma environment in the past. Amerstorfer (2003) studied this loss process using the observed average stellar wind data of young solar-like stars by Wood *et al.* (2002) and Lammer *et al.* (2003) and the ionospheric density profiles modelled by Zhang *et al.* (1993) over Martin history and found an additional loss of water over 3.5 Gyr equivalent to a global ocean with a thickness of about 20 m.

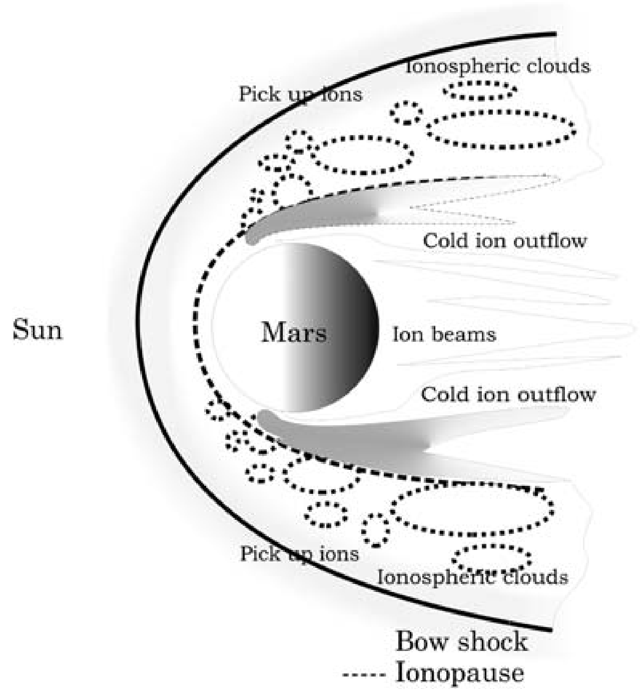

Fig. 1. Illustration of the atmospheric and water loss from Mars. The main loss processes over the Martian history are ion pick up of atmospheric neutral gas between the ionopause (dashed line) and the bow shock (solid line), ionospheric clouds or bubbles (closed dotted lines), which are triggered by plasma instabilities at the ionopause and outflow of cold ions caused by momentum transfer between the solar wind and the ionosphere (shaded areas), where δ_i and δ_{sw} correspond to the effective momentum flux thickness of the ionospheric flow and the velocity shear in the shocked solar wind (Perez-de-Tejada 1992; Amerstorfer 2003). Phobos 2 also observed ion beams in the Martian nightside, the additional contribution of which to atmospheric/water loss is uncertain at present. However, the efficiency of loss processes caused by ionospheric clouds, momentum transfer and ion beams will be studied in detail by the ASPERA-3 instrument on-board Mars Express.

Thus, the total atmospheric escape on Mars may have removed an amount of water equivalent to a global ocean with a thickness of up to 34 m. Fig. 1 illustrates the solar wind interaction and related atmospheric loss processes on Mars. Table 3 shows all atmospheric escape rates of hydrogen and oxygen, i.e. water, estimated from the different atmospheric loss processes at the present time, 2 and 3.5 Ga. One can see from this table that atmospheric/water loss caused by the momentum transfer process between the solar wind and the ionosphere seems to be the most relevant atmospheric escape process on Mars. The present uncertainties in the estimation of the atmospheric escape rates caused by plasma instabilities and momentum transfer effects should be minimized after the analysis of Mars Express' ASPERA-3 data.

The obtained upper value of about 34 m is lower than previous estimates by Luhmann *et al.* (1992), Jakosky *et al.* (1994) and Kass & Yung (1995, 1996, 1999) of between 50 and 80 m, but agree well with the estimation of about 30 m by Krasnopolsky & Feldman (2001). It should be noted that all

Table 3. *Loss rates corresponding to various processes for oxygen and the related H_2O escape rates from the Martian atmosphere and ionosphere at the present time, 2 and 3.5 Ga. The loss rates depending on various different processes are estimated by* [*1*] *Lammer* et al. (*2003*), [*2*] *Luhmann* (*1997*), [*3*] *Penz 2003*, [*4*] *Perez-de-Tejada* (*1992*) *and* [*5*] *Amerstorfer* (*2003*). *Here PU is the solar wind pick up, DR is the dissociative recombination, SP is sputtering, BU are bubbles* (*ionospheric clouds*) *caused by plasma instabilities and MT is the loss of ions due to momentum transfer between the solar wind and the ionosphere*

	Age (Gyr)		
	Present (s^{-1})	2 Ga (s^{-1})	3.5 Ga (s^{-1})
PU: O^+ [1]	3×10^{24}	3.8×10^{25}	8×10^{26}
DR: O [1, 2]	2.8×10^{24}	3×10^{25}	8×10^{25}
SP: O [1]	2.2×10^{23}	7×10^{25}	1.3×10^{27}
SP: CO [1]	3.5×10^{22}	2.3×10^{24}	4×10^{25}
SP: CO_2 [1]	5×10^{22}	2×10^{24}	2.5×10^{25}
BU: O^+ [3]	1×10^{24}	8×10^{24}	2×10^{26}
MT: O^+ [4, 5]	1×10^{25}	5×10^{26}	3×10^{27}
Total O loss	1.7×10^{25}	6.5×10^{26}	5.4×10^{27}
Total H_2O loss	8.5×10^{25}	6.5×10^{26}	5.4×10^{27}

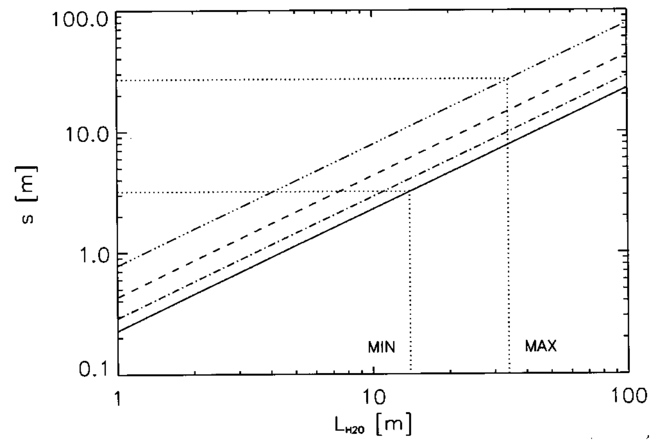

Fig. 2. Estimated minimal (Min) and maximal (Max) present Martian surface water-ice reservoir equivalent to a global ocean with a layer thickness *s* (dotted lines), which is in isotopic exchange with the atmosphere as a function of total water loss from Mars over the past 3.5 Gyr with various initial D/H isotope ratios. The solid line has an initial D/H ratio equal to the TSW value. The dashed-dotted and dashed lines have D/H ratios of 1.2 times and 1.6 times the TSW value (Lunine *et al.* 2003) and the dashed-dotted-dotted lines correspond to the average D/H value measured in Martian SNC meteorites of about 2.5 times the TSW value, which is comparable to the D/H ratio in comets.

of these studies have not considered ionospheric clouds triggered by plasma instabilities and momentum transfer effects, but used overestimated atmospheric sputtering and ion pick up loss rates.

Fig. 2 shows the present water-ice reservoir, which is in isotopic exchange with the Martian atmosphere corresponding to a global ocean with a thickness *s* as a function of the equivalent global water layer with thickness L_{H_2O} lost from the planet over 3.5 Gyr. The solid line corresponds to the TSW ratio, the dashed-dotted line to a D enrichment of 1.2 times the TSW ratio, the dashed line to an enrichment in D of 1.6 times the TSW ratio (Lunine *et al.* 2003) and the dashed-dotted-dotted line of about 2.3 times the corresponding TSW ratio as measured in Martian Shergottite meteorites and comets (Leshin *et al.* 1996).

Discussion

One can see from our estimates in Fig. 2 that Mars should have at present a water-ice reservoir that can exchange with its atmosphere equivalent to a global layer with a thickness of about 3.3–27 m, depending on the initial isotope D/H ratio and water loss rates. If the Martian water was enriched in D, to 2.3 times the TSW ratio, the present layer thickness could reach about 11–27 m. The lower thickness values of our study agree with the model results of Krasnopolsky *et al.* (1998), Lammer *et al.* (1996) and Krasnopolsky (2000) that a global water-ice layer with a thickness of about 5 m is exchangeable with the atmosphere. Our estimated upper thickness values are larger than the estimated thickness of about 8 m obtained by Kass & Yung (1999), although their estimate is inside our range. One should note that the comparable values of previous studies inside our estimated minimum and maximum range are a coincident because Krasnopolsky *et al.* (1998) and Krasnopolsky (2000) used loss rates of about 30 m and Kass & Yung (1999) of about 50 m and a fractionation factor *f* of about 0.02 and the TSW value as the initial D/H ratio.

By using *r*(*t*) from Table 2, we obtain a water-ice reservoir exchangeable with the Martian atmosphere 3.5 Ga shown in Table 4, which is equivalent to a global ocean with a thickness of about 17–44 m if the initial D/H ratio was close to the TSW value or 1.2 times the TSW ratio of about 20–49 m if the initial D/H ratio was 1.6 times the TSW value and 25–61 m if the initial D/H ratio was enriched to the Shergottite on cometary ratios before 3.5 Gyr.

Zuber *et al.* (1998) estimated from MOLA data a volume of the Martian north polar ice cap of about $1.2\pm0.2\times10^6$ km^3 over an area of 1.04×10^6 km^2 with an average thickness of about 1030 m. This estimated ice volume corresponds to an equivalent global layer of water with a thickness of about 9 m. One can see from Fig. 2 that this value agrees with our estimation if the initial D/H ratio was close to the TSW value or 1.2 times the TSW ratio and an equivalent global water layer with a depth of about 34 m was lost to space. On the other hand, if the initial D/H isotope ratio was 1.6 times the TSW ratio, an equivalent ocean with a thickness of about 24 m should have been lost to space over 3.5 Gyr. If the initial D/H ratio was about 2.5 times the TSW value, the lower escape value equivalent to an ocean with a layer thickness of about 14 m would also have been higher than the amount of water-ice stored in the northern polar cap.

Although there are uncertainties in our estimation, our study shows that the water-ice reservoir which is in isotopic exchange with the atmosphere can be similar but also three

Table 4. *Estimated present and past Martian water-ice reservoirs equivalent to a global ocean with a layer thickness given in the table in units of meter, as a function of various initial D/H isotope ratios 3.5 Ga, a fractionation factor* f *of 0.016* (*Krasnopolsky 2000*) *and minimum* (*Min*) *and maximum* (*Max*) *loss rates for hydrogen and oxygen to space of about 14 m* (*Lammer* et al. *2003*; *Penz 2003*) *and the resulting additional water loss of about 20 m due to momentum transport between the solar wind and the ionosphere result to layer a thickness of about 34 m* (*Perez-de-Tejada 1992*; *Perez-de-Tejada 1998*; *Amerstorfer 2003*)

	$R(t_1)=$TSW	$R(t_1)=$ $1.2\times$TSW	$R(t_1)=$ $1.6\times$TSW	$R(t_1)=$ $2\times$TSW
	Present atmospheric exchangeable H_2O-ice reservoir			
Min	3.3 m	4.3 m	6.2 m	11.2 m
Max	8 m	10.1 m	15 m	27.2 m
	Atmospheric exchangeable H_2O-ice reservoir 3.5 Ga			
Min	17.36 m	18.75 m	20.2 m	25.2 m
Max	42.1 m	44 m	49 m	61.2 m

times greater than the estimated water-ice available in the Martian polar cap. If the water-ice stored in the polar cap melts, it would fill approximately the 4680 m contour and cover a region of about 4.5×10^6 km^2 with an average depth of about 270 m (Zuber *et al.* 1998), where the extent of the melted cap would be the Chryse Basin area (45° N, 340° E), which coincides with areas into which most outflow channels emptied (Carr 1996). By assuming that the amount of water-ice stored in the northern polar cap is equivalent to the present reservoir, which is in isotopic exchange with the Martian atmosphere, the melted ancient reservoir would have filled the surface area in the Chryse Basin to an average depth of about 750–1260 m. The obtained maximum ancient water-ice reservoir in Table 4 of an equivalent global ocean thickness of about 61 m could have filled the same region with a thickness up to about 1836 m.

However, much better estimates of the Martian water-ice reservoir, which was in isotopic exchange over the planetary history, should be possible after exact ion outflow measurements are made on Mars by the ASPERA-3 instrument on-board Mars Express, which will reduce the uncertainty in the current estimations of atmospheric loss caused by solar wind plasma interactions with the ionospheric environment (ionospheric clouds and momentum transfer effects) and the *in situ* determination of the D/H ratio in the Martian surface by future studies planned with instruments such as the proposed Search for Life Indicators on Mars (SLIM) experiment on the Pasteur instrument payload on ESA's EXOMARS mission. SLIM can perform atmospheric, ground and underground *in situ* measurements by gas chromatography associated to mass spectrometry.

If there is also a non-atmospheric exchangeable bulk water-ice subsurface reservoir remaining from the delivered 0.06–0.27 × Earth-oceans as modelled by Lunine *et al.* (2003), it can only be determined by radar sounding and should be discovered by the MARSIS instrument on-board Mars Express. If MARSIS does not detect such an additional reservoir, this may have been lost due to hydrodynamic escape and impact erosion prior to 3.5 Ga. Studies on XUV-driven hydrodynamic escape due to the young Sun predict escape rates of hydrogen in the order of 10^{28}–10^{29} s^{-1} from Mars (Kasting & Pollack 1983; Hunten 1993; Donahue 1995). These escape rates are large enough to remove the hydrogen from an equivalent terrestrial ocean in about 300 Myr. Chasseféire (1996) showed, that hydrodynamic escape of oxygen from early Mars could have removed a primitive ocean equivalent to 0.2–0.45 present terrestrial ocean values.

By using the estimated water reservoirs 3.5 Ga from Table 4 related to the value of 2.3 times the TSW ratio, we can estimate the minimum and maximum reservoirs, where the D/H isotope ratio was enriched from 1.2 or 1.6 times the TSW ratio due to hydrodynamic escape. One finds water reservoirs affected by isotopic fractionation equivalent to a global ocean with a depth of between 97 and 115 m if 1.2 times the TSW ratio and 35–86 m if 1.6 times the TSW ratio were the initial isotope ratios in Martian water 4.5 Ga. The difference with respect to the out-gassed volume of the modelled 0.06–0.27 Earth-oceans may have escaped unfractionated to space between 3.5 and 4.5 Ga. Thus, if hydrodynamic escape was active on early Mars, we suggest that MARSIS may find a maximal amount of water-ice equivalent to a global layer with a thickness of about 27 m, which is about three times the amount of water-ice currently stored in the northern polar cap.

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