Space Sci Rev (2008) 139: 399–436
DOI 10.1007/s11214-008-9413-5

Atmospheric Escape and Evolution of Terrestrial Planets and Satellites

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Received: 14 December 2007 / Accepted: 1 July 2008 / Published online: 12 August 2008

Abstract The origin and evolution of Venus', Earth's, Mars' and Titan's atmospheres are discussed from the time when the active young Sun arrived at the Zero-Age-Main-Sequence. We show that the high EUV flux of the young Sun, depending on the thermospheric composition, the amount of IR-coolers and the mass and size of the planet, could have been responsible that hydrostatic equilibrium was not always maintained and hydrodynamic flow and expansion of the upper atmosphere resulting in adiabatic cooling of the exobase temperature could develop. Furthermore, thermal and various nonthermal atmospheric escape processes influenced the evolution and isotope fractionation of the atmospheres and water inventories of the terrestrial planets and Saturn's large satellite Titan efficiently.

Keywords Atmosphere evolution · Young Sun/stars · Isotope anomalies · Escape · Magnetic protection · Terrestrial planets

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1 Introduction

In order to understand the evolution of the planetary atmospheres of Venus, Earth, Mars and Saturn's satellite Titan and the principles that generated Earth's present atmosphere and those of the other terrestrial bodies in the Solar System and possible Earth-type exoplanets, one has to understand the evolutionary influence of the solar/stellar radiation and particle environment on planetary atmospheres. Besides these effects which can modify and fractionate planetary atmospheres over long time spans, surface-atmosphere interaction processes such as the carbon-silicate cycle that controls the CO_2 partial pressure, oxidation processes on the soil, the generation of magnetic dynamos and the influence of life forms and the modification of atmospheres by them, have also taken into account.

The eight major Sections of this Chapter cover a wide range of topics that are connected to the evolution of the atmospheres of terrestrial planetary bodies. In Sect. 2 we discuss the observed isotope anomalies in the atmospheres of Venus, Earth, Mars and Titan and their relevance for atmospheric evolution. In Sect. 3 we focus on the present knowledge of the radiation and particle environment of the young Sun inferred from solar proxies with different ages. After discussing the initial solar and atmospheric conditions we focus in Sect. 4 on questions related to the loss of the initial water inventory from early Venus. In this section we discuss and review in detail the runaway greenhouse effect, and thermal and non-thermal atmospheric escape of Venus' initial H_2O inventory. Section 5 focuses on the evolution of Earth's atmosphere, from its formation, loss processes, magnetospheric protection, to its modification after the origin of primitive life forms. In Sect. 6 we review and discuss the formation, evolution and loss of the initial Martian atmosphere and its water inventory. Finally, in Sect. 7 the evolution of Titan's dense nitrogen atmosphere and its alteration by atmospheric loss processes, the contribution of sputtering, and its relevance to the escape from other satellite atmospheres is reviewed and discussed.

2 Isotope Anomalies in the Atmospheres of Venus, Earth, Mars, and Titan

After the establishment of atmospheric and internal volatile reservoirs during the accretionary and early post-accretionary phases of planet formation, further modifications of isotopic ratios might still occur over long periods of time as a result of thermal and non-thermal escape processes (e.g., Pepin 1991; Becker et al. 2003; Lammer and Bauer 2003). For example, Hutchins and Jakosky (1996) estimated that about $90 \pm 5\%$ of ^{36}Ar and about $80 \pm 10\%$ of ^{40}Ar have been lost by atmospheric sputtering from the martian atmosphere after the intrinsic magnetic field vanished about 4 Gyr ago (Acuña et al. 1998). In this context isotopic fractionation in planetary atmospheres may result from the diffusive separation by mass of isotopic and elemental species and occurs between the homopause, the level above which diffusion rather than turbulent mixing is the controlling process, and the exobase, above which collisions are rare. The lighter particles are more abundant at the exobase and exosphere than the heavier species.

When particles are removed from a planetary exosphere by atmospheric loss processes, the lighter isotopes are preferentially lost and the heavier ones become enriched in the residual gas. The diffusive separation effect leads to enrichment of the lighter isotope in the exosphere, depending on the homopause altitude (Lammer and Bauer 2003). This effect enhances the importance of all atmospheric escape processes that occur at the exobase level. Atmospheric escape mechanisms that can lead to isotope fractionation in a planetary atmosphere are high Jeans escape rates, dissociative recombination, impact

Table 1 Hydrogen, oxygen, carbon and nitrogen Isotope ratios observed in the atmospheres of the three terrestrial planets (Kallenbach et al. 2003; Lammer and Bauer 2003 and references therein) and Titan (Niemann et al. 2005)

Isotope ratios	Venus	Earth	Mars	Titan
D/H	$1.6–2.2 \times 10^{-2}$	1.5×10^{-4}	$8.1 \pm 0.3 \times 10^{-4}$	$2.3 \pm 0.3 \times 10^{-4}$
$^{18}O/^{16}O$	$\sim 2 \times 10^{-3}$	2.04×10^{-3}	$1.89 \pm 0.2 \times 10^{-3}$	
$^{13}C/^{12}C$	$1.14 \pm 0.02 \times 10^{-2}$	1.12×10^{-2}	$1.18 \pm 0.12 \times 10^{-2}$	1.21×10^{-2}
$^{15}N/^{14}N$	$\sim 3.5 \times 10^{-3}$	3.7×10^{-3}	$6.4–5.0 \times 10^{-3}$	$5.46 \pm 0.2 \times 10^{-3}$

dissociation of molecules by energetic electrons, charge exchange, atmospheric sputtering, and ion pick up by the solar wind (Chamberlain and Hunten 1987; Johnson 1990; Lammer and Bauer 1993).

The volatile isotopic compositions in planetary environments were initially established at the time of the formation. For Earth, we have abundant samples of crustal and upper mantle rocks to study, and a well-determined atmosphere. For example from $^{40}Ar/^{36}Ar$ isotope fractionation in the present Earth mantle and the ^{40}Ar degassing rate from the crust it is found that only an early catastrophic degassing model is compatible with the atmospheric $^{40}Ar/^{36}Ar$ ratio (e.g., Hamano and Ozima 1978). The Earth was formed from large planetesimals, therefore, the most likely cause for catastrophic degassing is linked to impacts (e.g., Lange and Ahrens 1982; Matsui and Abe 1986a, 1986b).

Isotopic composition reflects the various reservoirs that went into making up the planets. It is expected that the primary reservoir for oxygen, nitrogen, and probably carbon would have been solid objects, representatives of which may still exist in the various meteorite populations (e.g., Clayton 2003; Grady and Wright 2003). In the case of noble gases and hydrogen the initial reservoirs (Kallenbach et al. 2003; and references therein) were most likely dominated by nebular gases of solar composition, very cold condensates, and solar wind implantation. One does not know how much of any specific reservoir was incorporated in any specific planet and by how much the initial planetary composition was then fractionated by addition of further material or by removal of material from the planet. In addition to infall of micrometeoritic or cometary material, fractionation processes may have occurred during the early stages of the Solar System, caused by high thermal escape rates or rapid non-thermal loss processes from more expanded upper atmospheres which were heated by intense EUV flux from the young Sun.

What we know about the present-day isotopic composition of the planets is limited by observations that have thus far been carried out. Table 1 shows the hydrogen, nitrogen, oxygen and carbon isotope ratios in terrestrial-like planetary atmospheres. For Venus, we have atmospheric data only, with significant uncertainties for many of the isotopic ratios. Interpretations of the mass spectrometry data of Pioneer Venus regarding the D/H ratio suggest that Venus once may have had more water, corresponding to at least 0.3% of an Earth-like ocean. Unfortunately, the D/H ratio on Venus of about $1.6–2.2 \times 10^{-2}$ can be explained two ways: impacts by H_2O-rich planetesimals with similar water abundance as Earth and Mars (Dayhoff et al. 1967; Walker et al. 1970; Donahue and Pollack 1983; Kasting and Pollack 1983; Morbidelli et al. 2000; Raymond et al. 2004), or Venus was formed from condensates in the solar nebula that contained little or no water (Lewis 1970, 1974). The supply of water to the Venus' atmosphere by comets was studied by Lewis (1974), Grinspoon and Lewis (1988) and more recently by Chyba et al. (1990).

However, Grinspoon and Lewis (1988) have also argued that present Venus' water content may be in a steady state where the loss of hydrogen to space is balanced by a continuous input of water from comets or from delayed juvenile outgassing. In case the external water delivery occurs, then no increase of Venus' past water inventory is required to explain the observed D/H ratio. However, recent models of solar system formation (e.g., Morbidelli et al. 2000; Raymond et al. 2004) suggest a wet early Venus (e.g., Dayhoff et al. 1967; Walker et al. 1970; Donahue and Pollack 1983; Kasting and Pollack 1983) because the suggest that most of Earth's water came from the asteroid belt region, not from 1 AU. If so, then Venus must have been hit with H_2O-rich planetesimals as well. The process is stochastic, as it involves large planetesimal impacts, but still it is highly unlikely that Venus ended up with $\leq 10\%$ of Earth's water inventory. This is in agreement with earlier suggestions that the initial water content on early Venus should have been larger (e.g., Shimazu and Urabe 1968; Rasool and DeBergh 1970; Donahue et al. 1982, 1997; Kasting and Pollack 1983; Chassefière 1996a, 1996b).

If Venus was wet, the planet must have lost most of its water during its history. As can be seen in Table 1, besides the enrichment of D in Venus' atmosphere compared to Earth, mass spectrometer measurements of the isotope ratios of $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{13}C/^{12}C$ show that these ratios are close to that on Earth (Lammer and Bauer 2003; Kallenbach et al. 2003; and references therein).

Venus' high noble gas abundances and solar-like elemental ratios, except for Ne/Ar, suggest that at least the heavier noble gases in the Venusian atmosphere are not greatly evolved from their primordial states (e.g. Cameron 1983; Pepin 1991, 1997). Neon and Ar isotope ratios also appear to be biased toward solar values compared to their terrestrial counterparts. Venus, therefore, seems to be in a unique position in that its atmosphere may have been altered from its initial composition by a planet specific fractionating loss mechanism to a much smaller extent than the highly processed atmospheres of Earth and Mars. Sekiya et al. (1980, 1981) and Pepin (1997) suggested that hydrodynamic escape from early Venus could have generated Ne and Ar isotope ratios close to the observed values in its present time atmosphere and noble gas ratios similar to those derived for Earth's initial atmosphere.

For Mars, as for Earth, we have data for the atmosphere as well as for some mantle-derived rocks in the form of the martian meteorites. The D/H isotope ratio in the present martian atmospheric H_2O vapor is $8.1 \pm 0.3 \times 10^{-4}$ which is greater than the terrestrial value by a factor of 5.2 ± 0.2 (e.g. Owen et al. 1988; Yung et al. 1988; Krasnopolsky et al. 1997). Modeling the atmospheric D/H ratio by using different methods results in a total H_2O loss of a 3.6–50 m global layer of H_2O from Mars during the past 3.5 Ga (e.g. Yung et al. 1988; Lammer et al. 1996, 2003a; Kass and Yung 1999; Krasnopolsky and Feldman 2001; Bertaux and Montmessin 2001). One should also note that the amplitude and the chronology of water exchange between the atmosphere and the polar caps may also influence the atmospheric D/H ratio. At the present total hydrogen (neutrals and ions) escape rate of about $1.5–2 \times 10^{26}$ s^{-1} (e.g., Anderson and Hord 1971; Krasnopolsky and Feldman 2001; Lammer et al. 2003a), the atmospheric water vapor (10 μm pr.) is completely lost in about 10,000 years. This is a short time; therefore, one cannot exclude that atmosphere-polar caps exchanges, driven by orbital parameter variations and other mechanisms, have an impact on the atmospheric D/H ratio, in addition to escape. Thus, one can see from the wide range of model results and the possible influence of atmosphere-polar cap interactions, that constraining water loss from D/H ratios can result in large uncertainties.

From the mass spectrometer measurements on board of Viking an anomalous $^{15}N/^{14}N$ ratio equal to 1.62 ± 0.16 times the Earth value was observed (Nier 1976; Nier et al. 1976). The $^{15}N/^{14}N$ anomaly on Mars is an important indicator for escape related fractionation processes during the evolution of the Martian atmosphere (Fox and Hać 1997; Manning et al. 2007). In contrast to the nitrogen isotopes, the relative abundances of O and C isotopes on Mars appear to be similar to the observed values on Earth and seem, therefore, to be buffered by surface reservoirs. The atmospheric evolution on Mars can be separated into an early and late period. The early evolutionary epoch can be characterized by a higher CO_2 surface pressure and a possible greenhouse effect, while the second later epoch is related to a low surface pressure and a polar-cap regolith buffered system initiated by polar CO_2 condensation after the late heavy bombardment period about 3.8 Ga ago (Pepin 1994).

During the early evolution period heavy noble gasses were most likely fractionated to their present value by the interplay between solar EUV-driven diffusion-limited hydrogen escape from a steam atmosphere toward the end of accretion (Zahnle et al. 1990) and atmospheric escape and fractionation due to large impacts (Pepin 1997). During this early extreme period in Mars' history, the isotope fractionation the CO_2 surface pressure, and the isotopic history were dictated by an interplay of losses to erosion, sputtering, and carbonate precipitation, additions by outgassing and carbonate recycling, and perhaps also by feedback stabilization under greenhouse conditions.

The atmospheric collapse after the late heavy bombardment period led to an abrupt increase in the mixing ratios of pre-existing Ar, Ne, and N_2 at the exobase and their fast escape by sputtering and pick up loss. Current abundances and isotopic compositions of these species are therefore entirely determined by the action of sputtering and photochemical escape on gases supplied by outgassing during the late evolutionary epoch (Jakosky et al. 1994; Becker et al. 2003; Kallenbach et al. 2003). The present atmospheric Kr inventory on Mars derives almost completely from solar-like Kr degassed during this period (Pepin 1994). Consequently, among current observables, only the Xe and ^{13}C isotopes survive as isotopic tracers of atmospheric history prior to its transition to low surface CO_2 pressure values. The values of the $^{40}Ar/^{36}Ar$ ratio and Ar abundance in the martian atmosphere measured by Viking lead to the conclusion that the martian atmosphere was also generated by secondary degassing from the martian interior (e.g., Hamano and Ozima 1978).

For Titan, recent observations by the Cassini Ion Neutral Mass Spectrometer (INMS) measured in situ at 1250 km altitude an enrichment of ^{15}N of about 1.27 ± 1.58 compared to the terrestrial ratio (Waite et al. 2005). Furthermore, the Huygens probe measured during its decent with the Gas Chromatograph and Mass Spectrometer (GCMS) a similar enrichment of ^{15}N compared to ^{14}N of about 1.47. As on Mars, this enrichment of $^{15}N/^{14}N$ compared to Earth indicates that Titan's atmosphere experienced high escape rates and associated isotope fractionation during its early evolution.

A recent study by Nixon et al. (2008) investigated the $^{12}C/^{13}C$ isotopic ratio in Titan hydrocarbons using Cassini/CIRS infrared spectra. They found that Titan's $^{12}C/^{13}C$ ratio (80.8 ± 2.0) is about 8% lower on Titan than at the Earth and lower than the typical value for outer planets (88.0 ± 7.0; Sada et al. 1996). Because Titan's enrichment in ^{13}C is anomalous in the outer solar system, they suggested that preferential escape of the lighter isotope and isotope dependent chemical reaction rates may have favored the gradual partitioning of ^{12}C into heavier hydrocarbons, so that ^{13}C was left behind in CH_4.

3 Activity of the Young Sun and Stars and Its Relevance to Planetary Atmosphere Evolution

3.1 Evolution of the Solar Radiation Environment

One can only understand the evolution of planetary atmospheres and their water inventories if the evolution of the radiation and particle environment of the Sun is known. Solar luminosity has increased from the time when the young Sun arrived at the Zero-Age-Main-Sequence

Table 2 Wavelength range $\Delta\lambda$ and corresponding flux values in units of erg s^{-1} cm^{-2} normalized to a distance of 1 AU and to the radius of the Sun (Ribas et al. 2005)

$\Delta\lambda$ [nm]	EK Dra	π^1 UMa	κ^1 Cet	β Com	Sun
	[0.1 Gyr]	[0.3 Gyr]	[0.65 Gyr]	[1.6 Gyr]	[4.56 Gyr]
0.1–2	180.2	21.5	7.76	0.97	0.15
2–10	82.4	15.8	10.7	2.8	0.7
10–36	187.2	69.4	22.7	7.7	2.05
36–92	45.6	15.2	7.0	2.85	1.0
92–118	18.1	8.38	2.9	1.7	0.74

(ZAMS) ~ 4.6 Gyr ago up to the present, and its effect on Earth's climate evolution has been studied by various researchers (e.g., Sagan and Mullen 1972; Owen 1979; Guinan and Ribas 2002). The total radiation of the young Sun was about 30% less than today. Solar evolution models show that the luminosity of the Sun will increase in the future and will be 10% about 1 Gyr from now. At that time the Earth's oceans may start to evaporate (e.g., Caldeira and Kasting 1992; Guinan and Ribas 2002), unless negative cloud feedback—not included in the published models—delays the expected surface warming.

Although the total radiation flux of the young Sun was lower than today, observations of young solar-like stars (solar proxies) indicate that the early Sun was a much more active source of energetic particles and electromagnetic radiation in the X-ray and EUV spectral range ($\lambda < 100$ nm) (Newkirk 1980; Skumanich and Eddy 1981; Zahnle and Walker 1982; Ayres et al. 2000; Guinan and Ribas 2002; Ribas et al. 2005). The short wavelength radiation is of particular interest because it can ionize and dissociate atmospheric species, thereby initiating photochemistry that can change atmospheric composition. Additionally, the soft X-rays and EUV radiation is absorbed in a planetary thermosphere, whereby it can heat and expand it significantly (e.g., Lammer et al. 2006a, 2007; Kulikov et al. 2006, 2007; Tian et al. 2008). This results in high predicted atmospheric escape rates from primitive atmospheres (e.g., Sekiya et al. 1980, 1981; Watson et al. 1981; Zahnle et al. 1990; Kulikov et al. 2007; Zahnle et al. 2007).

The active phase of the young Sun lasted about 0.5–1.0 Gyr and included continuous flare events. The period where the particle and radiation environment was up to 100 times, or even more intense than today lasted about 0.15 Gyr after the Sun arrived at the ZAMS (Keppens et al. 1995; Guinan and Ribas 2002; Ribas et al. 2005). This is comparable to, but slightly longer than, the expected time scale for terrestrial planet accretion, 10–100 million years (see, e.g., Morbidelli et al. 2000). The "Sun in Time" observational program was established by Dorren and Guinan (1994) 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.

Observations at various wavelength ranges were carried out by the following satellites: ASCA ($\Delta\lambda = 0.1$–2 nm), ROSAT ($\Delta\lambda = 2$–10 nm), EUVE ($\Delta\lambda = 10$–36 nm), FUSE ($\Delta\lambda = 92$–118 nm). The data gap between 36–92 nm is caused by strong interstellar medium absorption. To overcome this problem Ribas et al. (2005) inferred the total integrated flux in that interval by comparison with the flux evolution in the other wavelength ranges. Details of the data sets and the flux calibration procedure employed are provided in Ribas et al. (2005). Table 1 shows a sample of solar proxies that contains stars with ages from 0.1 Gyr up to the age of the Sun. These authors estimated the total irradiance in the wavelength range between 0.1–120 nm and obtained a power law fit for the flux $\Phi(t) = 29.7 \times t^{-1.23}$ in units of [erg s^{-1} cm^{-2}] as a function of stellar age t in units of Gyr (Ribas et al. 2005). From this relation it follows that the fluxes normalized to the present time solar value as a function of time are: ~ 6 times [$t = 3.5$ Gyr ago], ~ 10 times [$t = 3.8$ Gyr ago], ~ 20 times [$t = 4.13$ Gyr ago], ~ 30 times [$t = 4.24$ Gyr ago], ~ 50 times [$t = 4.33$ Gyr ago], ~ 70 times [$t = 4.37$ Gyr ago], and ~ 100 times 4.467 Gyr ago. One should note that during the first 0.1 Gyr the soft X-ray and EUV flux were saturated to these high values and hard X-ray fluxes were even higher (Ribas et al. 2005). It is reasonable to suggest that much stronger high-energy radiation flux of the young Sun should have had a critical impact on ionization, photochemistry, and evolution of the early atmospheres of the terrestrial planets.

3.2 The Solar Wind of the Young Sun

Besides the much higher radiation, which was related to frequent flaring of the young Sun, one should also expect a more powerful stellar wind. HST high-resolution spectroscopic observations of the hydrogen Lyman-α feature of several nearby main-sequence G and K stars by Wood et al. (2002, 2005) have revealed the absorption of neutral hydrogen associated with the interaction between the stars' fully ionized coronal winds with the partially ionized local interstellar medium. These absorption features formed in the astrospheres of the observed stars provided the first empirically-estimated coronal mass loss rates for solar-like G and K main sequence stars.

Wood et al. (2002, 2005) estimated the mass loss rates from the system geometry and hydrodynamics and found from their small sample of stars, where astrospheres can be observed, that mass loss rates increase with stellar activity. The correlation between the mass loss rate and X-ray surface flux follows a power law relationship, which indicates a total plasma density in the early solar wind and Coronal Mass Ejections (CMEs) of about ≥ 100–1000 times higher than today during the first 100 Myr after the Sun reached the ZAMS. The total ejected plasma density decreases as the solar activity subsides and may have been ≥ 30–100 times higher than today at 3.5 Ga ago (e.g., Lundin et al. 2007). However, the present stellar sample analyzed by Wood et al. (2002, 2005), Lundin et al. (2007) is not large enough; therefore, many uncertainties regarding the early solar wind remain, and more observations of young solar-like G and K stars are needed to enhance our knowledge of stellar winds during periods of high coronal activity.

4 Loss of Water from Early Venus

4.1 The Runaway Greenhouse

Venus presents an especially interesting problem for the field of planetary aeronomy. As mentioned in the Introduction, Venus shows clear evidence of having lost substantial amounts of water during its history. The process by which this occurred is typically referred to as a runaway greenhouse, although as we shall see, this term can be defined in different ways that have different physical implications for Venus' history.

The basic concept of the runaway greenhouse has been understood for many years (Ingersoll 1969; Rasool and DeBergh 1970; Walker et al. 1970). Venus' mean orbital distance is 0.72 AU, and so it receives roughly 1.9 times as much sunlight as does Earth. Suppose, following Rasool and DeBergh (1970), that Venus started off with no atmosphere whatsoever, and that it outgassed a mixture of CO_2 and H_2O from volcanoes. If we neglect the

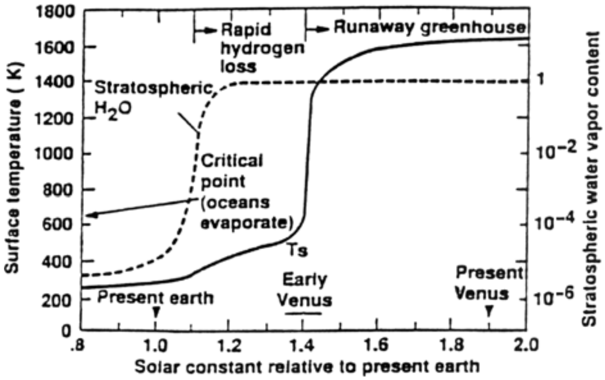


Fig. 1 Diagram illustrating what would happen to Earth if it were slowly pushed inwards towards the Sun. The *horizontal scale* is the solar flux relative to its value at 1 AU. The *solid curve* represents mean global surface temperature (*left-hand scale*). The *dashed curve* represents stratospheric H_2O mixing ratio (*right-hand scale*). The solar flux at Venus today and at 4.5 billion years ago is indicated (adapted from Kasting 1988)

change in solar luminosity over time, as they did, Venus' initial mean surface temperature would have been about 320 K. As its atmosphere grew thicker, however, the surface temperature would have increased as a consequence of the greenhouse effect of CO_2 and H_2O. If one tracks the subsequent evolution, one finds that the surface is always too hot for liquid water to condense, and so all of the outgassed H_2O ends up in the atmosphere as steam. Importantly, even the upper atmosphere would have been H_2O-rich. At these levels, H_2O could have been photodissociated by solar ultraviolet radiation. The hydrogen would have escaped to space by processes described below; the oxygen could either have been dragged along with it, if the escape was fast enough, or it could have reacted with reduced gases (e.g., CO) in the atmosphere and with reduced materials (e.g., ferrous iron) in the planet's crust. Eventually, all of the water would have been lost, and Venus would have been left with the dense CO_2 atmosphere that we observe today.

Although this story sounded satisfactory at the time when it was first proposed, later advances in our understanding of how planets form created problems for this model. The final stages of terrestrial planet accretion are now thought to involve impacts of planetesimals that were Moon-sized or larger. Some of these planetesimals should have originated from the asteroid belt region or beyond (see, e.g., Raymond et al. 2004), and so they would have been rich in H_2O and other volatiles. When they collided with a growing planet, either Venus or Earth, most of these volatiles should have been injected directly into its atmosphere in a process termed impact degassing (Lange and Ahrens 1982). Hence, the atmosphere and ocean, if it was stable, should have formed as the planet itself formed. This process has been simulated using numerical models that include both the atmosphere and the growing solid planet (Matsui and Abe 1986a, 1986b; Zahnle et al. 1988). These calculations indicate that the planet's entire surface should have been molten during the main part of the accretion period, creating a magma ocean, and that it should have been overlain by a dense (~ 100 bar), steam atmosphere that was in quasi-equilibrium with the magma. For Venus, it is uncertain whether this steam atmosphere would have condensed out when the accretion process ended or whether it would have remained as vapor. In any case, as we will see, its fate should have been similar to that predicted by the earlier models: loss by photodissociation, followed by escape of hydrogen to space.

It is easier to understand how this process works by examining a somewhat simpler calculation described by Kasting (1988), the results of which are summarized in Fig. 1. In this numerical simulation, a planet resembling modern Earth was "pushed" closer to the Sun by gradually increasing the incident solar flux. (The horizontal axis, S_{eff}, represents the solar flux relative to its value at modern Earth, ~ 1365 W/m^2.) The solid curve in the figure shows the evolution of the planet's mean surface temperature, T_s. T_s increases slowly at first, then "runs away" to extremely high values when S_{eff} reaches ~ 1.4. At this point, all remaining water vaporizes, leaving the Earth with a dense, 270 bar steam atmosphere that is in every sense a true runaway greenhouse.

Figure 1 also shows something else, however: the dashed curve, which goes with the scale on the right, represents the mixing ratio of H_2O in the planet's stratosphere, $f(H_2O)$. At low surface temperatures (corresponding to low S_{eff}), $f(H_2O)$ is very low—only a few times 10^{-6}, i.e., a few parts per million by volume (ppmv). This corresponds to the situation on modern Earth, for which $f(H_2O)$ is about 3–5 ppmv. But for surface temperatures exceeding $\sim$340 K, or 70°C, $f(H_2O)$ rises quickly to values near unity, and the stratosphere becomes water-dominated. In this model, this phenomenon occurs at $S_{eff} \geq 1.1$. This should lead to photodissociation of H_2O and escape of H to space, as before, with the difference being that liquid water remains present on the planet's surface until the very last part of the escape process.

The model calculation described here is heuristic and may not apply directly to early Venus because its atmosphere and initial water inventory were almost certainly different from modern Earth. The results of the calculation nevertheless suggest what may have happened on Venus. The Sun was about 30 percent less luminous when it formed (Gough 1981), so the solar flux on early Venus was approximately 1.34 times the value for modern Earth, or ~ 1825 W/m^2. This value is right near the "runaway greenhouse" threshold in this model, when the oceans actually vaporize, and it is well above the critical solar flux for water loss. If clouds—which were not explicitly included in the model shown here—act to cool the surface, and if Venus' initial water endowment was a substantial fraction of Earth's, then early Venus could well have had liquid oceans on its surface. This hypothesis may be testable at some time in the future when we have the technology to sample Venus' surface and subsurface.

4.2 Thermal Escape of Light Species

The theory of thermal escape from an atmosphere was developed in the 1960s (Chamberlain 1961; Öpik and Singer 1963). Because the density of the atmosphere decreases with altitude the atmosphere becomes collisionless above a certain level, called the exobase. The exobase distance, where the atmospheric scale height is equal to the collisional mean free path, is ≈ 200 km on present Venus. Present thermal escape, or "Jeans" escape, consists of the (small) upward flux of atoms whose velocity is larger than the escape velocity (10.4 km s^{-1}) at the exobase. Because of the low exospheric temperature of Venus (≈ 275 K), which is caused by the large abundance of CO_2, a strong infrared emitter, present thermal escape of hydrogen on Venus is almost negligible. But at epochs in the past when the water abundance in Venus' atmosphere was higher and when the Sun was a more powerful EUV emitter, the exospheric temperature was probably much higher and thermal escape could have taken the form of a "hydrodynamic" escape. Hydrodynamic escape is a global, cometary-like, expansion of the atmosphere. It requires the deposition of a large flux of EUV energy into the atmosphere to allow species to overcome gravity. Such conditions may have been reached in H- or He-rich thermospheres heated by the strong EUV flux of the young Sun (Sekiya et al. 1980, 1981; Watson et al. 1981; Zahnle and Walker 1982; Yelle 2004, 2006; Tian et al. 2005; Munoz 2007; Penz et al. 2008), e.g. in the following cases:

(i) primordial H_2/He atmospheres;
(ii) an outgassed H_2O-rich atmosphere during an episode of runaway and/or wet greenhouse.

The theory of hydrodynamic escape was developed by Parker (1963) for the solar wind plasma and was first applied to study hydrodynamic escape of hydrogen-rich early atmospheres of terrestrial planets by Sekiya et al. (1980, 1981), Watson et al. (1981), Kasting and Pollack (1983), and later by many other authors. Öpik and Singer (1963) defined the state of an expanding atmosphere when its outflow velocity, $v_{\rm exo}$, at the exobase is equal to or exceeds the escape velocity, $v_{\rm esc}$, from a planet at that altitude ($v_{\rm exo} \geq v_{\rm esc}$) as blow-off. This corresponds to a Jeans escape parameter, $\lambda (= GMm/r_{\rm exo}kT_{\rm exo})$, of < 1.5. This condition may occur if an atmosphere is sufficiently heated and if the flow of the main escaping species is not diffusion limited.

Hydrodynamic models were also applied to mass fractionation of planetary atmospheres (Zahnle and Kasting 1986; Hunten et al. 1987; Chassefière and Leblanc 2004). However, the models of hydrodynamic escape of atomic hydrogen from water-rich early atmospheres of terrestrial type planets were not quite satisfactory (e.g. Chassefière 1996a). The main reason for this is the fact that these models did not take into account the transition from the fluid regime to the collisionless regime in the upper planetary corona. Once collisions become infrequent, solar EUV energy cannot be readily converted into bulk translational kinetic energy (Chassefière 1996a).

Sekiya et al. (1980, 1981) and Watson et al. (1981) in their pioneering work studied hydrodynamic escape of an atomic hydrogen rich atmosphere from a terrestrial planet due to solar EUV heating by applying idealized hydrodynamic equations. From their thermospheric model of the Earth Watson et al. (1981) obtained supersonic flow solutions for which the sonic point was reached at a distance of about 2×10^5 km or some 30 planetary radii, r_0. These authors argued that supersonic hydrodynamic escape of atomic hydrogen was possible from hydrogen dominated Earth's atmosphere even if it were exposed to the present time solar EUV flux. However, as pointed out above, these authors assumed that the fluid equations applied above the exobase, which is not internally self-consistent. So, there is some question as to whether their supersonic solutions could really be achieved. Indeed, the flow at the exobase ($r_{\rm exo} \approx 7.5r_0$) in their model is subsonic, and its velocity of ~ 100 m s^{-1} is an order of magnitude lower than the escape velocity of 1.5 km s^{-1}. As the conversion of internal thermal energy of the neutral gas into kinetic energy of the flow is retarded by the lack of collisions above the exobase, the flow of neutral particles cannot be accelerated anymore and it is not clear that either the sonic or even the escape velocity can be reached.

These negative considerations should be tempered by the realization that H_2- or H-dominated upper atmospheres on rocky planets are not likely to remain hydrostatic if some appreciable stellar EUV heating is present. As pointed out by Kasting and Pollack (1983), their more H_2O-rich early Venus atmospheres would remain collisional out to all distances if the hydrostatic assumption was adopted. Application of the barometric law would then imply that the atmospheric mass was infinite a result that cannot be physically correct (Chamberlain and Hunten 1987; Walker 1977). Hence, such atmospheres must be expanding hydrodynamically into space, albeit perhaps at somewhat less than the escape rate that corresponds to transonic outflow. Accurately calculating the escape rate in such cases could in principle be accomplished by using a hybrid approach similar to that employed by Chassefière (1996a), in which a fluid dynamical solution was joined to a modified Jeans' solution at the exobase (see below for more details). Alternatively, a "moment" type of approach (e.g., Schunk and Watkins 1979), in which the particle velocity distribution is calculated self-consistently, could be applied at all altitudes. In carrying out such modeling efforts it should be borne in mind that the real escape problem is inherently 2- or 3-dimensional as a consequence of interactions of the escaping gas with the impinging stellar wind. Hence, any 1-D approximation, regardless of its level of sophistication, is just that—an approximation.

If we ignore these complications for the moment, and simply acknowledge that the published hydrodynamic solutions represent upper limits on the hydrogen escape rate, we can see that thermal escape rates from hydrogen-rich terrestrial planets could have been large in the past, especially during the earliest epochs when the solar EUV radiation was much more intense than today (Ribas et al. 2005).

In a recent study Tian et al. (2008), like Chassefière (1996a), matched subsonic outflow solutions to Jeans escape boundary conditions at the exobase. They showed that heavier species like C, O or N atoms can be incorporated in the hydrodynamic flow if the heating is strong enough. Adiabatic cooling associated with the hydrodynamic flow results in reduced exobase temperatures and thus controls the escape rates.

It is thought that the thermosphere of Venus was rich in water vapor at the time when a runaway greenhouse occurred (Fig. 1), theoretically allowing hydrodynamic escape to develop, although there is no clear evidence that such an episode of intense hydrodynamic escape ever occurred on terrestrial planets.

Kasting and Pollack (1983), following Watson et al. (1981), developed a coupled photochemical-dynamic model of hydrodynamic escape on Venus. In their model, the vertical thermal structure of the thermosphere up to the exosphere and its chemical composition were calculated self-consistently. The temperature at the cold trap, that is the bottom of the thermosphere, was assumed to be 170 K. The altitude of the cold trap, which controls the mixing ratio of water vapor in the thermosphere, is presently 90 km but was probably larger at primitive epochs, when the atmosphere was hotter. Accordingly, several cases with H_2O mass mixing ratios at the cold trap in the range from $\approx 10^{-3}$ up to ≈ 0.5 were studied.

Hydrodynamic expansion, starting at a level of about 200 km altitude, results in a flow where the bulk velocity increases with altitude (up to ≈ 1 km s^{-1} at ≈ 10 planetary radii), and the temperature moderately increases up to the distance ≈ 1 planetary radius (≈ 500 K), and decreases above this height due to adiabatic cooling. A hydrogen escape flux up to $\approx 3\times10^{11}$ cm^{-2} s^{-1} was found for a large H_2O mixing ratio and present solar EUV conditions. This value has to be multiplied by 10 or even higher values for relevant primitive solar EUV conditions. At this rate, the hydrogen of an Earth-type ocean could be removed in a few hundred million years.

As mentioned above, the Kasting and Pollack calculation assumed collisional flow up to infinity, although the exobase level was reached at an altitude of ≈ 1 planetary radius. Because the temperature of the flow at the exobase level is only a few hundred Kelvins, the transition from the collisional to the non-collisional regime is expected to inhibit expansion. But the expansion cannot be stopped entirely; otherwise, the atmosphere would again be collisional at all altitudes.

In order to study the possible effect of this transition, Chassefière (1996a) proposed a hybrid formulation, using both a dynamic model for the inner fluid region and a Jeans approach for the upper, collisionless region. The conservation equations were solved from the base of the expanding flow up to the exobase using a complete scheme of solar EUV energy deposition. An additional source of energy was introduced at the top of the dynamic model (exobase level), representing the collisional deposition of the kinetic energy of energetic neutral atoms (ENAs) created by charge exchange between escaping H atoms and solar wind protons. This energy diffuses inward, throughout the (subsonic) expanding flow, and heats the expanding medium in addition to solar EUV. The solar wind energy deposition controls the temperature gradient below the exobase, which is taken as a boundary condition of the model. The upward flux at the exobase was calculated using the classical Jeans theory and compared to the flux below the exobase, as provided by the dynamic model. Self-consistent solutions, for which the upward flux was continuous across the exobase,

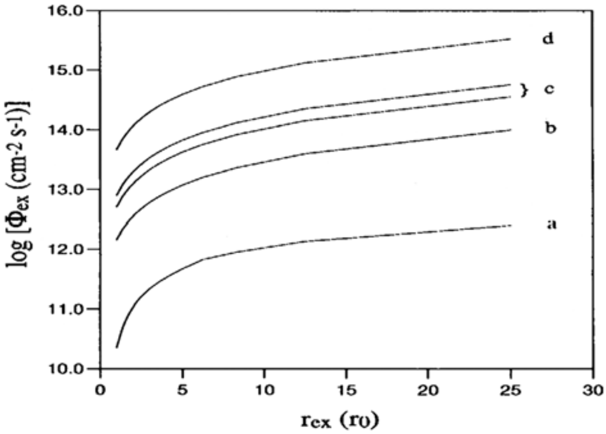


Fig. 2 Escape flux as a function of the planetocentric altitude of the exobase (in units of planetary radius r_0) for a solar wind enhancement factor with respect to present of: (**a**) 1, (**b**) 30, (**c**) 500–2000 and (**d**) 100,000 (from Chassefière (1997)

were exhibited. Calculations done for present solar EUV conditions are in agreement with the values found by Kasting and Pollack and showed that the additional contribution of energy from particle heating by solar wind-produced ENAs may be quite substantial. It was noted that for an exobase altitude of one planetary radius, any planetary magnetic field pushing away the obstacle up to an altitude larger than ≈ 3 planetary radii inhibits the solar wind energy source.

In a follow-up paper, Chassefière (1997) used a simplified approach to quantify the effect of an enhanced solar wind on the hydrodynamic escape flux from a hydrogen-rich upper Venus' atmosphere. Numerical simulations using the hybrid model showed that at high solar EUV flux the altitude of the exobase might reach ≈ 10 planetary radii, although numerical instabilities did not allow him to obtain firm, self-consistent solutions. The goal of the simplified approach presented in the 1997 paper was to calculate the Jeans escape flux as a function of the exobase altitude, assuming energy balance between incoming energetic neutrals and outgoing escaping atoms. The results are displayed in Fig. 2.

Assuming that the exobase was at 10 planetary radii altitude and that the solar wind density was larger by one order of magnitude at primitive epochs, an escape flux of 10^{13} cm^{-2} s^{-1} or more was derived, sufficient to remove all the hydrogen contained in an Earth-type ocean in less than ten million years. It was emphasized that the escape rate in this case might be limited by diffusion at the cold trap and be possibly below the energetically possible value.

This would necessarily have become true once the bulk of Venus' water had been lost and water vapor became a minor constituent of the lower atmosphere. Interestingly, energetic neutrals are formed at ≈ 20 planetary radii from the planet (assuming the exobase is at ≈ 10 radii altitude), and this mechanism would work even in the presence of a magnetosphere of the size of the terrestrial magnetosphere.

Although the EUV-powered hydrodynamic escape is of thermal nature, the interaction with the solar wind may result in an additional source of energy. The process described above is only one possible mechanism, although energetically representative of the maximum possible contribution of the solar wind, as all the kinetic energy carried by the solar wind beam intercepted by the exobase is assumed to be deposited. However, one should note that recent studies and observations of present Venus and Mars indicate that the main production region of these ENAs occurs at solar zenith angles > 30 degrees and, because the ENAs carry the energy and momentum of the solar wind protons, they essentially follow the streamlines of the flow past the planet (e.g., Kallio et al. 1997; Holmström et al. 2002;

Lichtenegger et al. 2002; Futaana et al. 2006; Galli et al. 2007). Therefore, only a smaller fraction of these ENAs may contribute to the heating of the upper thermosphere. Other interactions, like sputtering, where ions originate in the atmosphere itself (Luhmann and Kozyra 1991), are examined in a following section.

Because of the lack of observational constraints, it is difficult to assess the reliability of the existing approaches, but depending on the young Sun radiation and particle conditions it appears plausible that hydrodynamic escape was able to remove all the hydrogen contained in an Earth-sized ocean from the primitive Venus' atmosphere within a few tens to a hundred million years. A (still missing) precise measurement of the noble gas isotopic ratios in the Venus' atmosphere and a detailed comparative study in reference to the Earth case are necessary to better understand the evolution of the primitive atmospheres of the two planets and would provide a diagnostic tool for estimating the role of hydrodynamic escape.

4.3 Thermal Loss of Oxygen from an H_2O-Rich Early Venus

The absence of molecular oxygen at a substantial level in the atmosphere of Venus is still poorly understood. If all the hydrogen contained in the initial water of Venus has been removed by hydrodynamic escape, as previously described, what was the fate of the oxygen atoms contained in water molecules and released by photodissociation in the high atmosphere? If oxygen has remained in the atmosphere, this process would provide a way for a planet to form a massive abiotic oxygen atmosphere (Zahnle and Kasting 1986). This possibility, as pointed out by Kasting (1997), deserves to be seriously studied in order to interpret future observations of the chemical composition of extrasolar planets from space (DARWIN, TPF). Studying Venus offers an opportunity to understand what is the fate of oxygen on a planet that loses its water by early massive hydrogen escape.

A first possibility is oxidation of the crust. Assuming FeO represents 5% in mass of the mantle, it may be calculated that an extrusion rate of $\approx 20\ \mathrm{km^3\ yr^{-1}}$, similar to the present terrestrial rate, averaged over 4.5 Ga is required to provide the chemical reservoir able to absorb the amount of oxygen contained in an Earth-type ocean (Lewis and Prinn 1984). Independent estimates of the present volcanic activity on Venus, based on geophysical, geological, and geochemical data, generally suggest maximum extrusion rates of approximately $0.4\ \mathrm{km^3\ yr^{-1}}$ (Bullock and Grinspoon 1993).

Considering that extrusions are assumed to account for only 5–10% of the total crust production, the upper limit of the crustal growth rate including extrusions may be about 4 $\mathrm{km^3\ yr^{-1}}$ (D. Breuer, personal communication, 2007), too small to account for the removal of the oxygen content of a full Earth-type ocean. Similar conclusions were reached by Lewis and Prinn (1984, p. 190). However, crustal overturn on Venus may be highly episodic (Turcotte 1993), and so the oxygen consumption rate averaged over time could be larger than estimated here.

Escape to space provides an alternative, and/or complementary, potential sink for oxygen (Zahnle and Kasting 1986; Chassefière 1996a, 1996b). We will examine in this section the hypothesis of thermal (hydrodynamic) escape, whereas possible non-thermal mechanisms are described later. Indeed, in the case of an intense hydrodynamic escape of atomic hydrogen, the theory predicts that heavy atoms can be dragged off along with escaping H atoms (Hunten et al. 1987). A heavy constituent "2", of mass m_2 and mixing ratio X_2, is dragged off along with a light escaping constituent "1" (H or H_2), of mass m_1 and mixing ratio X_1, according to the following law:

$$F_2 = \frac{X_2}{X_1} F_1 \left[\frac{(m_c - m_2)}{(m_c - m_1)} \right], \tag{1}$$

where F_i are the fluxes and

$$m_c = m_1 + \left(\frac{kTF_1}{bgX_1}\right), \tag{2}$$

is the "crossover mass" (b is the product of the density by the diffusion coefficient of "2" in "1"). If $m_2 < m_c$, "2" can escape with "1" (the flux F_2 is proportional to the difference $m_c - m_2$).

The possibility that oxygen atoms produced by H_2O photodissociation could be dragged off along with hydrogen atoms may be assessed by using Hunten's theory, with $m_1 = 1$ uma (H) and $m_2 = 16$ uma (O). The crossover mass m_c may be estimated for Venus, assuming present solar EUV conditions. Assuming escape is limited by energy (EUV only), with a typical efficiency factor of 0.25 (the fraction of incident EUV energy converted into escape energy), and taking into account the geometrical amplification of the intercepted EUV flux due to the enhanced altitude of the exobase, m_c is in the range from 1.4 uma to 7.2 uma for present EUV conditions (Chassefière 1996b), with a most likely value of 2.8 uma. Since m_c is (nearly) proportional to the amplitude of the EUV flux, and assuming that this flux varies with time t as $(t_0/t)^{5/6}$, where t_0 is the present time (4.6 Gyr), m_c falls below 16 at ≈ 600 Myr, with a large uncertainty (between 200 Myr and 1.8 Gyr). This means that, theoretically, oxygen could escape together with hydrogen during the first hundreds million years. But, if oxygen was massively dragged off with hydrogen (and therefore is not a minor species like in the theory of Hunten), the EUV energy required for removing a 2:1 stoichiometric mixture of H and O (2 H atoms for 1 O atom) is 9 times larger than for hydrogen alone (ratio of 18 for H_2O to 2 for H_2). Thus, if Venus' atmosphere lost most of its oxygen with the hydrogen, the "effective" crossover mass would have been $2.8 \times 9 = 25$ uma, pushing the end of the hydrodynamic escape phase of oxygen back to 40 Myr (between 30 Myr and 130 Myr). Through an analytical rigorous theory derived from Hunten's theory, Chassefière (1996b) has shown that no more than 30% of the oxygen content of a Venusian Earth-sized ocean might have been lost by EUV-driven hydrodynamic escape over the period from 100 Myr to 1 Gyr.

Finally, assuming that the solar wind was more intense at primitive epochs, and applying the simplified treatment previously described to estimate the energy deposited at the exobase by energetic neutrals formed through charge exchange between escaping atoms and solar wind protons (Chassefière 1997), it has been found that, if the solar wind was enhanced by three orders of magnitude at primitive stages, it is theoretically possible to remove most of the oxygen of an Earth-sized ocean in ten million years by hydrodynamic escape. However, early planetary intrinsic or induced magnetic fields could have reduced this heating process and the resulting loss rates. The fate of oxygen originating from water released by impacting bodies at a later stage could be high thermal and non-thermal loss rates and/or oxidation of the crust.

As a conclusion, in the case of a purely EUV-driven hydrodynamic escape, the removal of all (or most of) the oxygen contained in an Earth-sized ocean was possible only at very early times (t < 30–40 Myr). Such a removal could have occurred later (t > 100 Myr) only if there was a substantial additional source of energy such as the (possibly) enhanced primitive solar wind. An enhancement factor of $\approx 10^3$ with respect to the present value is theoretically able to remove the oxygen in ≈ 10 Myr. Another possible loss mechanism caused by solar wind interaction with an upper atmosphere is non-thermal escape, which is described in the following section. It may be concluded that an extended period of water delivery by impacting bodies, until ≈ 300 Myr (Weissman 1989) or even later, resulting in the progressive building of an ocean, would be difficult to reconcile with the hypothesis of massive hydrodynamic oxygen escape, except if a very strong solar wind (three orders of magnitude above the present value) survived for a few hundred million years after the formation of the Sun. On the other hand, if most of the water was delivered to Venus at the very beginning, during accretion, EUV-SW-powered hydrodynamic escape was potentially able to remove large amounts of water from a primitive atmosphere.

4.4 Non-Thermal Oxygen Loss During Venus History

The flow of the solar wind around non-magnetized planets like Venus and Mars has been studied extensively by using gas dynamic and convection magnetic field models (e.g., Spreiter et al. 1966; Spreiter and Stahara 1980), semi-analytical magnetohydrodynamic (MHD) flow models (e.g. Shinagawa et al. 1991; Biernat et al. 2001), and by hybrid models (e.g., Terada et al. 2002; Kallio et al. 2006). The solar X-ray and EUV radiation produces an ionized region in the upper atmosphere where large concentrations of ions and free electrons can exist. This region, where the solar wind generates a magnetic field and interacts with the ionospheric plasma of a non-magnetized planet, builds up an atmospheric obstacle, over which the stellar wind plasma is deflected. For the non-thermal loss processes, like ion pick-up from un-magnetized or weakly magnetized planets, the solar activity dependence of the ionopause altitude becomes a controlling factor. The atmosphere below the ionopause is protected against erosion by the solar wind, while neutral gas above can be ionized and picked up by it. As a result, the ion escape rate during a planet's history would have depended on the early solar X-ray, EUV, and solar particle flux conditions.

If early Venus had no intrinsic planetary magnetic field that was strong enough to shield the solar wind of the young Sun, the solar plasma flow should have been blocked like today by the ionospheric plasma pressure. This pressure balance occurs in the collision-free regime above the exobase level because the Interplanetary Magnetic Field (IMF) is enhanced above the ionosphere by the ionospheric induction current (e.g., Alfvén and Fälthammar 1963), by which the shocked solar wind is deflected.

Neutral atoms and molecules above the ionopause can be transformed to ions by charge exchange with solar or stellar-wind particles, EUV radiation or electron impact. These newly generated planetary ions are accelerated to higher altitudes and energies by the interplanetary electric field and are guided by the solar- or stellar wind plasma flow around the planetary obstacle to space, where they are lost from the planet (e.g., Spreiter and Stahara 1980; Lundin et al. 1989, 1990; 2007; Lichtenegger and Dubinin 1998; Biernat et al. 2001; Lammer et al. 2006b; Terada et al. 2002).

Another important effect of the ions pick up process is that a part of neutral atoms above the ionopause can be directed back to the upper atmosphere of the planet where they collide with the background gas so that the collision partners can be accelerated by sputtering to energies above the escape energy. As can be seen in Fig. 3, atmospheric sputtering refers to a mechanism by which incident energetic particles (mostly charged particles) interact with a planetary atmosphere or surface and produce the ejection of planetary material.

Sputtering has been recognized as an important source of atmospheric non-thermal loss in the case of Mars, but of less importance for larger planets like Venus (Luhmann and Kozyra 1991). For planets with the mass of Venus or Earth, sputtering accelerates atmospheric particles to high altitudes from where they can also be lost by ionization and stellar wind via the pick up process. On present Venus, sputtering yields O loss rates of the order of 5×10^{24} s^{-1} which is about 2 times lower than the ion pick up rate. However, it is difficult to say how efficient sputtering by an enhanced solar wind from an extended upper atmosphere compared with ion pick up is. As mentioned before, the extreme plasma interaction with early Venus might have induced a strong magnetic field which could have a reverse

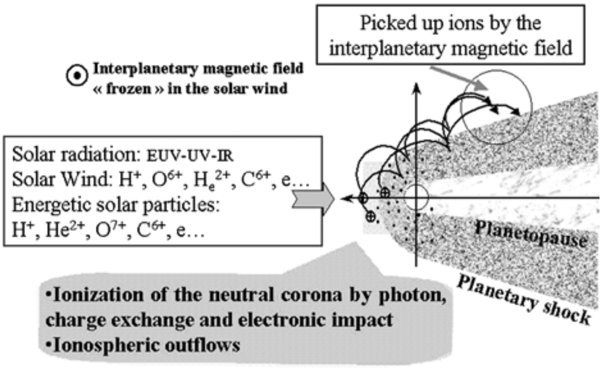


Fig. 3 Illustration of picked up planetary ions, directed backwards to a planetary atmosphere, which is not protected by a strong magnetic field. These ions can act together with solar wind particles as sputter agents (courtesy of F. Leblanc)

effect on the sputter loss between 4–4.5 Gyr ago. But to be sure how efficient sputtering is compared with other non-thermal loss processes, model calculations under extreme early Venus conditions have to be carried out in the future.

Barabash et al. (2007) find from the analysis of direct measurements by the Venus Express plasma instrument package that the dominant escaping ions from Venus are O^+, He^+, and H^+, which leave Venus through the plasma sheet, a central portion of the wake, and a boundary layer of the induced magnetosphere. They reported that the cool O^+ ion outflow triggered by the solar wind interaction through the plasma tail is of the order of $\leq 10^{26}$ s^{-1}.

In addition to ion pick up and cool ion escape, plasma clouds are observed above the ionopause, primarily near the terminator and further downstream. The detailed analysis of several detached plasma clouds has shown that the ions within the clouds themselves are ionosphere-like in electron temperature and density (Brace et al. 1982; Russell et al. 1982). In the magnetic barrier, plasma is accelerated by a strong magnetic tension directed perpendicular to the magnetic field lines. This magnetic tension forms specific types of plasma flow stream lines near the ionopause, which are orthogonal to the magnetic field lines. This process favors the appearance of Kelvin-Helmholtz and interchange instabilities that can detach ionospheric plasma in the form of detached ion clouds from a planet. One can model the Kelvin-Helmholtz instability at a planetary obstacle by applying the one-fluid, incompressible magnetohydrodynamic (MHD) equations.

For studying the ion loss due to the Kelvin Helmholtz instability, Terada et al. (2002) applied a global hybrid model to present Venus. They found that the dynamic ion removal process associated with this plasma instability plays a significant role additionally to other ion loss processes. Terada et al. (2002) obtained a loss rate for O^+ ions of the order of $\sim 5 \times 10^{25}$ s^{-1}. Table 3 summarize the present time escape rates from Venus. One can see that thermal escape of hydrogen is negligible at present Venus.

Kulikov et al. (2006) studied the expected O^+ ion pick up loss rates over Venus' history by using the X-ray and EUV satellite data discussed in Sect. 3.1, as well as a range of solar wind plasma densities and velocities expected for the young active Sun and discussed in Sect. 3. For modeling the Venusian thermosphere over the planetary history, Kulikov et al. (2006) used a diffusive-gravitational equilibrium and thermal balance model which was applied for a study of the heating of the early thermosphere by photodissociation and ionization processes, exothermic chemical reactions, and cooling by CO_2 IR emission in the 15 μm band. As can be seen in Fig. 4, their model simulations resulted in expanded thermospheres with exobase altitudes between about 200 km for present EUV flux values and about 1700 km for 100 times higher EUV fluxes after the Sun arrived at the Zero-Age-Main Sequence.

Table 3 Thermal and non-thermal loss rates of oxygen and hydrogen from present Venus

Escape process	Loss [s^{-1}] 1 EUV
Jeans: H	2.5×10^{16} (1)
Photochemical reactions: H	3.8×10^{25} (1)
Electric field force: H^+	$\leq 7 \times 10^{25}$ (2)
Solar wind ion pick up: H^+	1×10^{25} (1)
Solar wind ion pick up: H_2^+	$< 10^{25}$ (1)
Solar wind ion pick up: O^+	1.5×10^{25} (1)
Detached plasma clouds: O^+	5×10^{24}–10^{25} (1, 3)
Sputtering: O	6×10^{24} (4)
Cool plasma outflow: O^+	$\leq 10^{26}$ (5)

(1) Lammer et al. (2006a); (2) Hartle and Grebowsky (1993); (3) Terada et al. (2002); (4) Luhmann and Kozyra (1991); (5) Barabash et al. (2007)

Kulikov et al. found that exospheric temperatures during the active phase of the young Sun could have reached about 8000 K if the atmosphere had a similar composition as that observed on present Venus after the Sun arrived at the ZAMS (see Fig. 3). Kulikov et al. (2006) applied a numerical test particle model for the simulation of the O^+ pick up ion loss from non-magnetized Venus over its history and found a total loss of about 180–280 bar ($\sim$ 70–110% TO: Terrestrial Ocean) for the maximum solar wind estimated by Wood et al. (2002), about 40–60 bar ($\sim$15–25% TO) for the average solar wind, and about 10–15 bar (4–6% TO) for the minimum solar wind.

From our knowledge of Earth, Venus, Mars and Titan, Yamauchi and Wahlund (2007) point out that the ionopause builds up above the exobase no matter what the solar wind conditions are. In that case the lower range of ion pick up loss rates modeled by Kulikov et al. (2006), corresponding to the planetary obstacle boundaries located near the exobase, may be more realistic. They obtain O^+ pick up loss rates at 4 Gyr ago (15 EUV) of about 1.5–5 $\times$ 10^{27} s^{-1} for minimum and average early solar wind flux conditions as estimated by Wood et al. (2002). These O^+ pick up loss rates for a 100 EUV CO_2 atmosphere (4.5–4.6 Gyr ago) correspond to loss rates of about 0.35-1.5 $\times$ 10^{30} s^{-1} for minimum and average solar wind conditions expected for the young Sun.

Thus, if one considers uncertainties in observations of stellar mass loss from young active solar-like stars (Wood et al. 2005), early Venus may have lost during its history an amount of oxygen, via the ion pick up process, equivalent to an atmosphere loss of about 5–50 bar. One should also note that the ion pick up loss rates would be different if Venus' early atmosphere had a different composition than today. This was most likely the case during the evaporation of the Venusian water ocean, as discussed in Sect. 4.3. Furthermore, the expected shift in exobase altitude shown in Fig. 4 will affect the D/H fractionation estimates of Donahue et al. (1997) and, the homopause-exobase distance will increase enhancing isotope fractionation.

In a hydrogen-rich thermosphere the exobase moves too a much larger distance compared with that calculated for the CO_2-rich thermosphere by Kulikov et al. (2006). In such a case it may be possible that oxygen and heavier species may be protected by the dense hydrogen corona until the hydrogen inventory is lost by thermal and non-thermal escape processes.

Even though the cool ion outflow and Kelvin-Helmholtz instability induced plasma clouds are more efficient ion escape processes from present Venus compared with ion pick up, it is difficult to estimate their contribution to atmospheric loss over Venus' past. While conservative $\mathbf{O^+}$ pick up estimates indicate that the planet could have lost the oxygen from

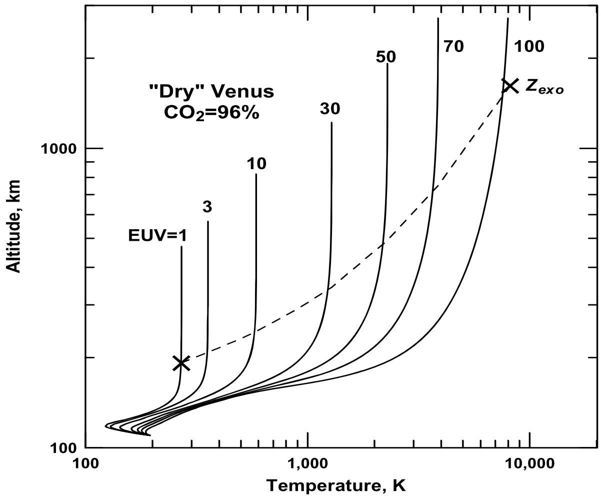


Fig. 4 Temperature profile of a "dry" CO_2-rich Venus atmosphere as a function of solar EUV flux. The *dashed line* corresponds to the exobase distance where the mean free path equals the scale height

an evaporated ocean equivalent to about 5–50 bar over Venus' history, it is possible that cool ion outflow and plasma clouds may enhance this loss up to a factor of 2–5. Hence, it is important to estimate contribution of these ion loss processes to the total loss over the solar cycle by analyzing spacecraft data (PVO, VEX, etc.), so that MHD and hybrid models could be adjusted for higher solar activity and atmospheric conditions expected during Venus' early history.

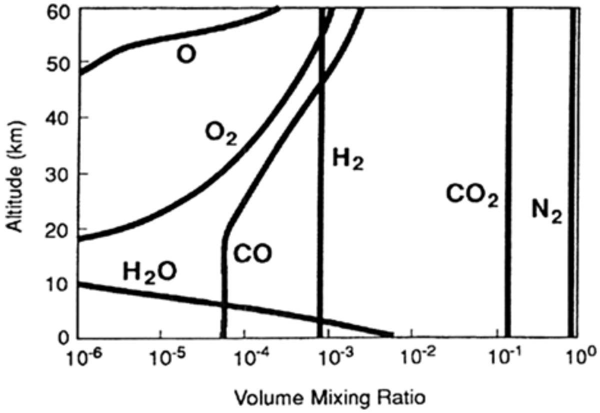
5 Early Evolution of Earth's Atmosphere

5.1 Formation of the Atmosphere

Earth's atmosphere is thought to have formed in much the same way as did Venus' atmosphere, by impact degassing of large, volatile-rich planetesimals. So, the first part of the discussion in the previous section applies here as well. The big difference, of course, is that Earth is farther from the Sun than is Venus; hence, once the main phase of accretion had stopped and the molten surface had solidified ($\sim$ 100 million years), liquid oceans should have definitely formed. This prediction has now been spectacularly confirmed by studies of oxygen isotopes in zirconium silicate minerals, or zircons, with ages as old as 4.4 Gyr (Valley et al. 2002). The $^{18}O/^{16}O$ ratio in these zircons, which is different from that in Earth's mantle, can only be explained if these minerals crystallized from magmas formed from high-^{18}O rocks that had interacted with liquid water at or near Earth's surface. The actual upper limit on surface temperature from these measurements is 200°C, which is still quite warm, but is well below the expected 1500°C temperature of a steam atmosphere (Zahnle et al. 1988).

What happened next is highly uncertain. It depends, in part, on how rapidly Earth formed relative to the lifetime of the solar nebula. If the nebula was entirely gone by the time Earth's formation was complete, then the early atmosphere may have been a weakly reduced mixture of CO_2 and N_2 (Rubey 1951; Walker 1977). If, however, the nebula was still present during the latter stages of accretion, as planetary scientists from the Japanese school have long argued (Hayashi et al. 1985), then Earth's earliest atmosphere may have been rich in

Fig. 5 An example of a typical, weakly reduced atmosphere, as simulated using a 1-D photochemical model. A surface pressure of 1 bar has been assumed. The CO_2 partial pressure, 0.2 bars, is approximately the amount needed to offset 30 percent reduced solar luminosity. The O_2 in the middle atmosphere is produced from CO_2 photolysis (from Kasting 1993)



H_2 and/or CH_4. Alternatively, an atmosphere rich in these highly reduced gases could have been produced by impacts, especially those that occurred during the earlier stages of accretion when elemental iron-rich impactors were still abundant (Schaefer and Fegley 2007; Hashimoto et al. 2007). Hence, the nature of Earth's earliest atmosphere should be viewed as an unresolved question.

Regardless of which planetary formation model is correct, the early atmosphere should have contained a substantial amount of H_2—enough to make the upper atmosphere hydrogen-rich. As can be seen in Fig. 5, even a weakly reduced lower atmosphere should have had an H_2 mixing ratio of the order of 10^{-3} (1000 ppmv) or greater (Kasting 1993; Holland 2002). This estimate is obtained by balancing the outgassing of reduced species from volcanoes with escape of hydrogen to space, assuming that the escape takes place at the diffusion-limited rate. If the escape rate was slower, as some researchers have suggested (Tian et al. 2005), then the atmospheric H_2 mixing ratio should have been even higher.

The concerns about the rapidity of hydrodynamic escape, expressed in earlier sections, could conceivably raise estimated H_2 concentrations still more. Much of the interest in this question results from its relevance to the origin of life (Chyba 2005). If the atmosphere was more reduced, then Miller-Urey type synthesis (from lightning) of prebiotic organic compounds is much more efficient (Miller and Schlesinger 1984). This is one motivation for the discussion of hydrogen escape that follows.

Once life had evolved, the composition of Earth's atmosphere would almost certainly have changed. One of the first things to happen may have been the conversion of much of the existing H_2 into CH_4 (Walker 1977; Kharecha et al. 2005). This reaction is carried out by methanogenic bacteria, or methanogens, which are thought to be amongst the earliest organism to have evolved (Woese and Fox 1977). Methanogens are anaerobic bacteria that are poisoned by free O_2 and that therefore live today in restricted habitats such as the intestines of cows and other ruminants and in the mud beneath rice paddies. On the early Earth, with its lack of atmospheric O_2, methanogens should have been ubiquitous.

Methanogens can produce methane by a number of different pathways, the most direct being the reaction

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O. \tag{3}$$

But they can also start from organic compounds, e.g. acetate (CH_3COOH), produced by the fermentation of more complex forms of organic matter. This process would have continued within the oceans and in sediments even after the origin of oxygenic photosynthesis sometime before 2.7 Gyr (Brocks et al. 1999). Indeed, methane is generated at depth within marine sediments today; however, nearly all of it is consumed by other, methanotrophic bacteria before it can make its way into the atmosphere. CO should also have been consumed by such an ecosystem, either by direct uptake by acetogens (Kharecha et al. 2005) or by the photochemically catalyzed water-gas reaction: $CO + H_2O \rightarrow CO_2 + H_2$.

A weakly reduced atmosphere is believed to have persisted until about 2.4 Ga, at which time it was replaced by one rich in O_2, like today's atmosphere (Holland 1994; Farquhar et al. 2000). So, hydrogen escape to space was probably extremely important for at least the first half of Earth's history. Indeed, the escape of hydrogen to space may have played a critical role in causing the rise of O_2 (Kasting et al. 1993; Catling et al. 2001; Claire et al. 2006). Because most of the hydrogen arrived initially in the form of H_2O, its escape left large amounts of oxygen behind. In the Kasting et al. (1993) model, this O_2 was mostly taken up by Earth's mantle, where it could conceivably have caused a change in mantle redox state. Although mantle redox change now appears unlikely, based on various petrologic indicators (Li and Lee 2004), the mantle may indeed have absorbed much of this O_2. Some of it, though, appears to have been taken up by oxidation of rocks on the continents, and this may have helped set up the O_2 rise at 2.4 Ga (Catling et al. 2001; Clair et al. Claire et al.).

Surprisingly, hydrogen may have continued to escape rapidly even following the rise of atmospheric O_2. Pavlov et al. (2003) have suggested that CH_4 concentrations may have remained relatively high, 50–100 ppmv, during the early- to mid-Proterozoic Eon, 2.5–0.8 Ga. Their argument assumes that atmospheric O_2 concentrations remained somewhat lower than today and that the deep oceans remained largely anoxic, as others have suggested previously (Canfield 1998). The recent modeling study by Goldblatt et al. (2006) supports this hypothesis. In their model, CH_4 decreased dramatically just prior to the rise of O_2, but then it increased again soon afterwards.

Indeed, high Proterozoic CH_4 levels and rapid hydrogen escape may have been required in order to balance Earth's redox budget at that time. According to this argument, hydrogen was escaping rapidly prior to the rise of O_2; hence, it must have continued to escape rapidly following the rise of O_2; otherwise, an equivalent amount of reducing power would have had to be lost as organic matter in sediments. But the relative constancy of the carbon isotope record, averaged over long time periods, indicates that no such change in organic carbon burial took place (Goldblatt et al. 2006). This last argument is speculative, but it suggests that hydrogen escape could have played a fundamental role in Earth's atmospheric evolution throughout a large fraction of the planet's history.

5.2 Thermal and Non-thermal Escape from Present and Early Earth's Atmosphere

The main problem for modeling atmospheric escape from early Earth is that there are many unknown parameters on which it depends. Besides the uncertainties in the solar wind conditions, atmospheric composition, internal, and surface heating and outgassing sources, such as volcanic activity, we do not know if early Earth was magnetized or non-magnetized at the time when life emerged. There is no magnetic record in the Earth's crust before 3.5 Gyr ago (e.g., Hale and Dunlop 1984; Sumita et al. 2001; Yoshihara and Hamano 2004; Ozima et al. 2005). A palaeointensity measurement on the Komati formation which has an age of about 3.5 Gyr may imply that the Earth's dynamo might not be very strong before the solid-state inner core was formed (Hale and Dunlop 1984). On the other hand, new paleomagnetic data (Tarduno et al. 2007) suggest that the Earth's magnetic field at about 3.2 Ga could be as strong as that of today, implying that the differentiation of the Earth's inner core began no later than 3.2 Gyr.

Depending on atmospheric composition and the exobase temperature, the observed non-thermal loss rate from the Earth-mass and size planets is much faster than Jeans escape, except for light species like H, H_2 and He (e.g., Lundin and Dubinin 1992; Cully et al. 2003; Wahlund et al. 2005 and references therein; Yamauchi and Wahlund 2007). The observed non-thermal loss rate of hydrogen from the Earth's upper atmosphere/ionosphere from non-thermal ion heating processes is of the order of about 1–10 $\mathrm{kg\,s^{-1}}$ (6×10^{26}–$\sim10^{27}$ $\mathrm{s^{-1}}$) (e.g., Moore et al. 1999; Cully et al. 2003; Yamauchi and Wahlund 2007). One should note that these ion loss rates can even be higher than the diffusion limited escape rate of neutral hydrogen. The amount of up-welling ions is connected to the solar wind pressure and activity. When for instance a magnetic cloud or a CME collide, it squeezes Earth's magnetic field, squirting particles stored in the magnetotail up the field lines towards the poles. Jeans escape of neutral H atoms is estimated to be larger at solar maximum but smaller than the non-thermal escape rate of protons during solar minimum. The upper limit of the loss rate of H atoms, which is diffusion limited, is about 10^{27} $\mathrm{s^{-1}}$ (Vidal-Madjar 1978; Kasting and Catling 2003, and references therein).

For present Earth the main escaping ion is O^+ which originates in the ionosphere, and the O^+ loss rate is larger than the H^+ loss rate, even during the solar maximum. The escape rate related to non-thermal ion heating strongly depends on the magnetospheric activity, with the largest source located in the dayside polar region (e.g., Kondo et al. 1990; Norqvist et al. 1998; Yamauchi and Wahlund 2007), where the solar wind can directly penetrate to the ionosphere through the magnetosphere. What is important for early Earth is that the escape rate of heavy ions like O^+ and N^+ increases to higher values compared with that for H^+ during high solar activity periods and major magnetic storms (Chappell et al. 1982; Cully et al. 2003). For instance, the non-thermal O^+ loss rate from the ionosphere increases by a factor of 100, while the non-thermal H^+ loss rate increases only by a factor of 2–3 when the solar $F_{10.7}$ flux increases by a factor of about 3 (Cully et al. 2003; Yamauchi and Wahlund 2007).

In a recent study Tian et al. (2008) investigated the response of the Earth's atmosphere to extreme solar EUV conditions and found that the upper atmosphere of an Earth-mass planet with the present Earth's atmospheric composition would start to rapidly expand if thermospheric temperatures exceeded 7000–8000 K.

In such a case the thermosphere is cooled adiabatically due to the outflow of the dominant species (O, N, etc.). From Fig. 6 it is seen that exobase moves upward as a consequence of the outflow. It can in fact exceed the present subsolar average magnetopause stand-off distance of about 10 Earth-radii. Kulikov et al. (2006) showed that even a "dry Venus" with the present 96% CO_2 could have reached temperature values around 8000 K during the first 100 Myr after the Sun arrived at the ZAMS. Of course, the very early Venus' atmosphere had a very different composition which would result in a different thermal structure than that modeled by Kulikov et al. (2006).

Depending on the solar EUV flux and planetary and atmospheric parameters, one can see from Fig. 6 that the exosphere could expand beyond the magnetopause. Therefore, the constituents beyond the magnetopause could be ionized and picked up by the solar wind plasma. Furthermore, other ion loss processes similar than at Venus and discussed in Sect. 4.4 would have contributed to the loss of the early water inventory. The expanded thermosphere-exosphere region, therefore, will result in high non-thermal atmospheric loss rates (Lundin et al. 2007).

It is also seen in Fig. 6 is that high amounts of CO_2, like on present Venus and Mars, can cool the thermosphere much better than Earth-like nitrogen/oxygen atmospheres, so that the exobase level remains much closer to the planetary surface. In such a case the atmosphere would be protected against erosion by the solar wind. Therefore, one can expect,

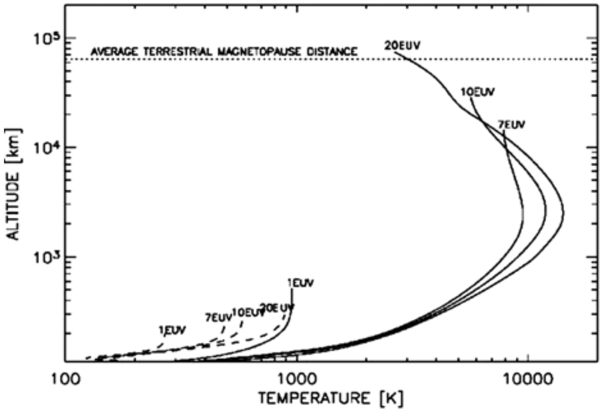


Fig. 6 Thermospheric temperature profiles between 100 km and the corresponding exobase levels for present (=1), 7, 10 and 20 times higher EUV solar fluxes than today, applied to Venus (Kulikov et al. 2006) and Earth (Tian et al. 2008) with the present time atmospheric composition. The efficient IR-cooling due to large amount (96%) of CO_2 in the hydrostatic thermosphere of Venus yields much lower exobase temperatures and atmospheric expansion compared with an Earth-like atmospheric composition

in agreement with Kulikov et al. (2007) that the atmosphere of the early Earth may have had during its first 500 Myr a higher amount of CO_2 in its thermosphere, which resulted in a less expanded upper atmosphere and exobase levels below the magnetopause. Otherwise early Earth's atmosphere would have been hot and unstable. By contrast an early CO_2-poor Earth's atmosphere may have experienced high nonthermal loss rates. In case that the early Earth's upper atmosphere was hydrogen-rich, as suggested by Tian et al. (2005), most of the expanded hydrogen exosphere would be ionized and lost from the planet by nonthermal loss processes like ion pick up, even if the thermal loss rate was lower due to a cooler exosphere as suggested by these authors. To investigate if early Earth could have kept its atmosphere, ion-loss test particle and MHD models have to be applied to extended atmospheres.

6 Evolution of Mars' Atmosphere

6.1 Early Mars' Climate: Was There a Dense CO_2 Atmosphere?

Mars, as one of the terrestrial planets, probably formed in much the same way as did Venus and Earth. So, volatiles should have been delivered to its surface by impact degassing of planetesimals originating from the asteroid belt or beyond. Mars, however, is different from Earth and Venus in one important respect: its mass is just slightly over 1/10th of Earth's mass. Mars' small mass has likely had a huge impact on its initial retention of volatiles and on its subsequent evolution.

Consider the retention issue first. As discussed earlier, impact degassing of incoming planetesimals is widely accepted as a source of planetary volatiles. However, impact erosion has also been widely discussed as a loss mechanism for volatiles (see, e.g., Walker 1986; Melosh and Vickery 1989). It should be noted that there is no generally accepted theory that describes how this process works, and so the two references given differ widely in their predictions. The efficiency of impact erosion is, not surprisingly, highly dependent on the mass of the growing planet. Large planets are better able to hold onto their atmospheres because their escape velocities are higher relative to the expected impact velocities of incoming planetesimals. In a pioneering study, Melosh and Vickery (1989) concluded that if Mars had simply been given a 1-bar CO_2 atmosphere initially at 4.5 Ga, it could have lost nearly all of it by 3.8 Gyr as a consequence of impacts that occurred during the heavy bombardment period of Solar System history. This process could conceivably explain why Mars has such a thin atmosphere ($\sim$ 6 mbar surface pressure) today.

This hypothesis raises several issues that require further discussion. First, how could Mars first accumulate an atmosphere and then lose it by essentially the same process, i.e., impacts? A possible answer is that the presumed impact velocities of the incident planetesimals were different at different times in Mars' history. During the early phases of accretion, planetesimals were small, and they should also have been on nearly circular orbits because collisions with other small bodies were relatively frequent. Hence, the relative velocity between the planetesimals and the growing protoplanet should have been smaller. By contrast, the bodies that arrived several hundred million years later are assumed to have been perturbed (by Jupiter) from initial orbits in the asteroid belt. They would have had higher eccentricities and would thus have hit Mars at higher relative velocities. Hence, the planetesimals that arrived early added to Mars' atmosphere, while those that arrived later may have removed it. That said, it seems unlikely that Mars could have lost its entire initial atmosphere in this way, as the impact of even one large, slow-moving body during the latter stages of accretion would have left an appreciable amount of volatiles behind. Such an explanation has been offered to account for the thick atmosphere on Saturn's moon, Titan (Griffith and Zahnle 1995).

The heavy bombardment period is itself a matter of contention. The idea that the inner solar system was subjected to an intense bombardment by late-arriving planetesimals grew out of the analysis of Moon rocks brought back by the Apollo missions between 1969 and 1973 (see, e.g., Hartmann 1973; Neukum and Wise 1976). These rocks had radiometric age dates that clustered near 3.8–3.9 Gyr. Although some researchers interpreted this as a "pulse" of impacts at about this time (Ryder 2003, and references therein), others suggested that the impacts that formed these rocks represented the tail end of an extended period of heavy bombardment. The latter view has prevailed until just recently. However, a new dynamical model for Solar System formation (Tsiganis et al. 2005; Gomes et al. 2005) suggests that the "pulse" hypothesis may indeed have been correct. In this model—which has been termed the "Nice model" because several of its authors are from the vicinity of the city of Nice in southern France—Jupiter and Saturn began their lives closer to each other than they are now. Jupiter migrated inward and Saturn migrated outward as a result of interactions with planetesimals in the disk. After some elapsed time ($\sim$ 700 million years if one chooses parameters properly), they crossed the 2:1 mean motion resonance, where Saturn's orbital period was exactly twice that of Jupiter.

At this point, all hell broke loose from a dynamical standpoint. Uranus and Neptune, which were formed close to Saturn in this model, were thrown into the outer Solar System where they perturbed the remaining population of planetesimals. These icy planetesimals from the outer Solar System were then responsible for causing a great pulse of bombardment on both the Moon and the terrestrial planets. Because they would have arrived with high relative velocities, these impacts would almost certainly have caused extensive atmospheric erosion.

Returning now to the question of Mars' early atmospheric evolution, we can see that from a theoretical standpoint it is highly uncertain. The Nice model is just that—a model—and it may or may not be correct. Hence, we cannot be sure at this time whether Mars (or Earth) was subjected to an extended heavy bombardment, and we should therefore have little confidence in our ability to predict how its atmosphere should have formed and evolved.

What we do have for Mars is lots of observations of its surface, both from spacecraft that have orbited the planet and from landers and rovers that have sampled the surface directly. The heavily cratered southern highlands of Mars are covered by fluvial features, such as the ones seen in Fig. 7. So, a flowing liquid—almost certainly water—was present on Mars' surface at some time prior to 3.8 Gyr ago. By contrast, the less heavily cratered northern plains are essentially devoid of such features, suggesting that the planet dried up and became much colder soon after this time. This last conclusion is reinforced by geochemical data from instruments such as TES (the Thermal Emission Spectrometer) that flew aboard the Mars Global Surveyor spacecraft. Such studies have revealed the widespread presence of minerals such as olivine that react readily with liquid water (Hoefen et al. 2003). So, Mars' surface has evidently been dry throughout most of its history.

Adding further to our confusion about Mars' early history is the fact that we do not understand how the fluvial features were formed. Some researchers (e.g., Segura et al. 2002) have suggested that they could have been created in the aftermath of large impacts, even if the early Martian climate was quite cold. Others (Pollack et al. 1987) have argued for a warm, almost Earth-like, early Mars. But the warm early Mars theory has problems because climate models (Kasting 1991) suggest that it is difficult to bring Mars' average global surface temperature above freezing using the greenhouse effect of a dense CO_2 atmosphere. At high CO_2 partial pressures, the increase in albedo caused by Rayleigh scattering outweighs the increased greenhouse effect from infrared absorption. CO_2 ice clouds may have helped to warm the surface (Forget and Pierrehumbert 1997), but this mechanism only works well for nearly 100 percent cloud cover. Furthermore, despite intensive spectroscopic searches from a series of orbiting spacecraft, no outcrops of carbonate rocks have ever been found [although carbonate minerals have been identified in Martian dust (Bandfield et al. 2003)].

If CO_2 was abundant, and if liquid water was present, why didn't they form? One suggestion is that the surface was too acidic, and that the CO_2 was lost from the upper atmosphere (Fairen et al. 2004). If so, it is obviously important to understand how this processes work. So, our theories about how Mars' atmosphere has evolved are strongly shaped by our knowledge of atmospheric escape processes.

6.2 Loss of Water and Other Volatiles from Early Mars

The evolution of the martian atmosphere and the evidence of the existence of an early hydrosphere are of great interest for studies regarding the evolution of the planet's water inventory and the search for life by current and future Mars missions. As shown in Fig. 7 the history of the martian atmosphere can be divided into early and late evolutionary periods (e.g., Carr 1987; Zahnle et al. 1990; Carr 1996; Pepin 1994; Hutchins and Jakosky 1996; Chassefière and Leblanc 2004; Donahue 2004; Chassefière and Leblanc 2004). Although the martian climate is at present too cold and the atmosphere too thin to allow liquid water to be stable on the surface, there are many indications that the situation was different during the Noachian epoch.

Besides geological evidence of outflow channels, river beds, possible shorelines (e.g., Head III et al. 1999; Clifford and Parker 2001) and evidence of standing bodies of water, an observed large deuterium (D) enrichment in the atmospheric water vapor (e.g., Zahnle et al. 1990; Owen et al. 1988) indicates that significant amount of water has been lost from the surface by atmospheric escape processes over the planet's history.

After the young Sun arrived at the ZAMS, heavy noble gases, including nonradiogenic Xe isotopes, may have been hydrodynamically fractionated during the accretion phase of the planet, with corresponding depletions and fractionations of lighter primordial atmospheric

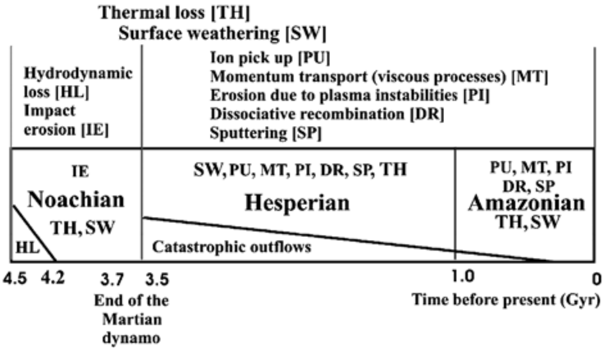


Fig. 7 Schematic illustration of various atmospheric escape processes and their expected relevance during the martian history from the early Noachian to the Hesperian and Amazonian epochs

species like deuterium (D) or H atoms (Hunten et al. 1987; Zahnle et al. 1990; Pepin 1994; Donahue 2004). Subsequently the CO_2 pressure history and the isotopic evolution of atmospheric species during this early period were determined by the interplay between impact erosion (Melosh and Vickery 1989; Chyba et al. 1990; Brain and Jakosky 1998) and impact delivery, carbonate precipitation and oxidation, by outgassing and carbonate recycling, and perhaps also by feedback stabilization under greenhouse conditions (Carr 1987, 1996; Pepin 1994). This period was also influenced by thermal and non-thermal atmospheric loss processes (e.g. Zahnle et al. 1990; Donahue 2004; Kulikov et al. 2007, and references therein). This in turn depended partly on the time of the onset of the martian magnetic dynamo, the field strength and the decrease-time of the magnetic moment, and the radiation and particle environment of the young Sun.

Carr and Head (2003) estimated the potential early martian water reservoirs from geomorphological analysis of possible shorelines of the post-Noachian epoch with the help of Mars Global Surveyor (MGS) images and altimeter data. They suggested that an amount of water equivalent to a global martian ocean with the depth of about 150–200 m could explain the observed geological surface features. However, early Mars could have had more water than this because erosional processes may have obscured and erased the geological signatures of hydrological activity during the Noachian epoch.

The second period of martian atmospheric evolution, from the Hesperian to the present Amazonian epoch, is characterized by uniform atmospheric loss enhanced by the vanished intrinsic magnetic field and various non-thermal atmospheric escape processes that have resulted in the present surface pressure of about 7–10 mbar (e.g., Jakosky et al. 1994; Lammer et al. 2003a, 2003b, and references therein).

Table 4 summarizes the most reasonable results of atmospheric escape rate models for three level of solar EUV flux: 1 EUV (present moderate martian solar activity), 2 EUV and 6 EUV (roughly corresponding to the flux about 3.5 Gyr ago (Zahnle and Walker 1982; Ribas et al. 2005) at the beginning of the Hesperian epoch). More results can be found in the literature, but many escape rates were revised after more accurate atmospheric data and plasma data of the martian environment became available. The question marks in Table 4 correspond to species and escape processes for which no escape rates have been modeled.

Carlsson et al. (2006) and Barabash et al. (2007) estimated the present loss rates for molecular O_2^+ and CO_2^+ ions from the analysis of the Mars Express (MEX) Ion Mass Analyzer (IMA) sensor of the ASPERA-3 instrument. Loss rates for moderate solar activity for O_2^+ and CO_2^+ and O^+ related ion loss rates are about 1.8×10^{24}–3.6×10^{24} (O_2^+) and 8.0×10^{23}–2.0×10^{24} (CO_2^+), respectively. Recently Ma and Nagy (2007) reproduced the observed O^+, O_2^+ and CO_2^+ ion escape rates for low solar activity Mars Express mission conditions with a 3D multi-species non-ideal magnetohydrodynamic model. Recent hybrid model results by Chaufray et al. (2007) yield similar ion loss rates.

The ASPERA instrument on board the Phobos 2 spacecraft observed strong interaction between the solar wind plasma and the cold ionospheric plasma in the Martian topside ionosphere. The solar plasma appears to transfer momentum directly to the Martian ionosphere from the dayside transition region to the deep plasma tail (Lundin et al. 1989, 1990). This is in agreement with reported the detection of cold electrons above the Martian ionopause, indicating the presence of detached plasma clouds (Acuña et al. 1998; Cloutier et al. 1999).

Pérez-de-Tejada (1992), Lundin and Dubinin (1992), Pérez-de-Tejada (1998), and Lammer et al. (2003b) found that this momentum transport process is capable of accelerating ionospheric O^+ to velocities $> 5\ \mathrm{km\,s^{-1}}$ resulting in energies larger than the martian escape energy. Analytic models (Pérez-de-Tejada 1992; Lammer et al. 2003b) give estimates which are in rough agreement with the observations. As shown in Table 4, cool ion escape from the martian plasma tail can yield O^+ loss rates for moderate solar activity of about $10^{25}\ \mathrm{s^{-1}}$.

Assuming the oxygen which was lost from Mars during the Amazonian and Hesperian period originated from H_2O these authors estimated that Mars may have lost the equivalent of a global ocean with a depth of ≤ 15 m over 3.5 Gyr. This is smaller than the $\sim$30–80 m reported in earlier studies (Luhmann et al. 1992; Jakosky et al. 1994; Kass and Yung 1995, 1996, 1999; Krasnopolsky and Feldman 2001), but larger than the estimates of 3 to 5 m obtained by Yung et al. (1988) and Lammer et al. (1996). The models of Leblanc and Johnson (2002), Lammer et al. (2003a, 2003b) and Penz et al. (2004) used atmospheric input parameters for higher the EUV flux obtained form Zhang et al. (1993).

Finally, the results in Table 4 should only be considered rough estimates until accurate thermosphere-ionosphere-hot particle-exosphere models related to the evolution of the solar EUV flux are obtained based on MHD and hybrid simulations.

While there are agreements between different model results and ion escape observations, the dissociative recombination O atoms loss rates for 1 EUV (Luhmann 1997) shown in Table 4 may be larger. A recent study of the martian coronae and related escape by a complex 3 D Monte Carlo model give escape rates of $\sim 10^{25}\ \mathrm{s^{-1}}$ and $4 \times 10^{25}\ \mathrm{s^{-1}}$ for low and high solar activity conditions respectively (Chaufray et al. 2007). However, we show in Table 4 the values of the Luhmann (1997) model because this author applied the model also to higher EUV values. We note that dissociative recombination related escape of atomic O is important for present Mars, but it is suggested to be less important during earlier periods (Johnson and Luhmann 1998; Lillis et al. 2006).

Lammer et al. (2006a) and Kulikov et al. (2007) applied a thermospheric model to the CO_2 atmosphere of Mars for high EUV radiation levels (10, 50, and 100 times the average present solar value). They found that the average dayside exobase temperature grows on Mars in a 95% CO_2 atmosphere by approximately a factor of 3 from about 355 K to about 1230 K for the EUV flux increasing from 10 to 100 times that of the present Sun. As shown by Zahnle et al. (1990) a H_2-rich early martian atmosphere may have developed hydrodynamic conditions.

It appears that the early evaporation of the martian CO_2 atmosphere by thermal loss processes was very unlikely, and if early Mars had a strong magnetic dynamo, it is unlikely that the planet lost several bars of CO_2, C, nitrogen and oxygen due to non-thermal loss processes (Kulikov et al. 2007). If early Mars lost its main atmosphere and water inventory during the first hundred Myr after the planet's origin, the model results would be in agreement with the observations by the OMEGA instrument on board of Mars Express which found no definite evidence that CO_2 sustained a long-term greenhouse effect enabling liquid water to remain stable for geological time periods on the surface of Mars in

Table 4 Modeled thermal and non-thermal loss rates of atomic and molecular hydrogen, oxygen, nitrogen and carbon species (neutrals and ions) from Mars at present time moderate solar activity conditions (1 EUV), at 2 EUV periods and for 6 EUV ($\sim$ 3.5 Gyr ago)

Species	EUV	Jeans	Photochem.	Sputtering	Pick up	Plasma clouds	Cool ion outflow
H	1	1.5×10^{26} [1]	?	?			
H_2	1	3.3×10^{24} [2]	?	?			
H^+	1				1.2×10^{25} [3]	?	?
H_2^+	1				$\sim 10^{25}$ [3]	?	?
	1		2.8×10^{24} [4]	3.5×10^{23} [5(3)]			
O	2		$3.0\times^{25}$ [4]	1.3×10^{23} [5(3)]			
	6		8.0×10^{25} [4]	1.5×10^{27} [5(3)]			
	1				$3.0\times^{24}$ [3]	$1.0\times^{24}$ [6]	$\sim 10^{25}$ [7]
O^+	2				4.0×10^{25} [3]	$8.0\times^{24}$ [7]	$5.0\times^{2}$ [7]
	6				8.3×10^{25} [3]	2.0×10^{26} [6]	3.0×10^{27} [7]
N	1		4.5×10^{23} [8]	?	?	?	?
O_2^+	1				1.8×10^{24}–3.6×10^{24} [9]		
C	1		3.0×10^{24} [10]	?	?	?	?
	1		8.0×10^{23} [11]	3.7×10^{22} [5(3)]	?	?	?
CO	2			$2.0\times^{24}$ [5(3)]	?	?	?
	6			2.5×10^{23} [5(3)]	?	?	?
	1			$5.0\times^{22}$ [5(3)]			
CO_2	2			2.3×10^{24} [5(3)]			
	6			4.0×10^{25} [5(3)]			
CO_2^+	1				8.0×10^{23}–2.0×10^{24} [9]		

[1] Anderson and Hord (1971), [2] Krasnopolsky and Feldman (2001), [3] Lammer et al. (2003a), [4] Luhmann (1997) for 1 EUV, 2 EUV, 6 EUV also in agreement with Kim et al. (1998) for 1 EUV, [5] Leblanc and Johnson (2002), [6] Penz et al. (2004), [7] Lammer et al. (2003b), [8] Fox and Dalgarno (1983), [9] molecular ion outflow is estimated (Carlsson et al. 2006), [10] Nagy et al. (2001), [11] Fox and Bakalian (2001)

the post-Noachian terrains (Bibring et al. 2005). Bibring et al. (2005) concluded that the OMEGA observations are consistent with early strong escape of the most of the martian CO_2 atmosphere.

The simulated loss rates discussed in this section are highly model dependent and have to be compared with future observational data and measurements by some martian aeronomy and environmental orbiter. However, the missing data which may help us to understand the evolution of the early martian magnetic dynamo, the atmospheric surface pressure, atmospheric sputtering and photochemical loss processes, etc. over the planet's history can only be procured by using a comprehensive package of instruments during a high solar activity period, such as proposed for the low altitude Mars Magnetic and Environmental Orbiter (MEMO) (Leblanc et al. 2007).

7 Evolution of Titan's Atmosphere

7.1 Origin of Titan's Atmosphere and the Relevance of the $^{15}N/^{14}N$ Isotope Fractionation to Its Evolution

The origin of Titan's atmosphere which contains mainly N_2 and CH_4 was not well understood before the arrival and observations of Cassini/Huygens although thermodynamic models of the solar nebula predicted that C and N_2 were mainly available in the form of CO and N_2. Two possible sources of volatiles have been suggested: comets that condensed outside the Saturnian nebula (e.g. Prinn and Fegley 1989), and b) planetesimals that condensed within a Saturnian subnebula (Griffith and Zahnle 1995). Carbon within cometary matter is mainly concentrated in the form of heavy organics like CO and CO_2, with a small fraction of CH_4. But CO is much less abundant than Titan's CH_4 (e.g., Gautier and Raulin 1997).

One can overcome this problem if Titan was generated in Saturn's subnebula which was warmer than the surrounding solar nebula so that the temperature-pressure conditions favored the conversion of CO to CH_4 as well as the conversion of N_2 into NH_3, respectively. Based on this scenario Lunine and Stevenson (1987) suggested that CH_4 and NH_3 were trapped in the planetesimals which formed Titan as hydrate and clathrate hydrates from where they were outgassed as NH_3 and CH_4 (Atreya et al. 1978; McKay et al. 1988).

Mousis et al. (2002) investigated this hypothesis in more depth and modeled for the first time the formation of clathrate hydrates of CH_4 and of hydrates of NH_3 in an evolutionary solar nebula and found that Titan formed from planetesimals that were relics of those embedded in the feeding zone of Saturn and contained NH_3 hydrate and CH_4 clathrate hydrates. They also found that for plausible abundances of CH_4 and NH_3 in the solar nebula at 10 AU the masses of CH_4 and NH_3 trapped in Titan could even be higher than the estimate of these compounds in Titan's primitive atmosphere.

Data obtained by the Cassini/Huygens spacecraft contributed to the understanding of Titan's atmosphere evolution. Measurements with the Gas Chromatograph Mass Spectrometer (GCMS) aboard the Huygens probe confirmed the low abundance of CO. The abundance of noble gasses like Ar was also found to be very low and Kr and Xe were even below the detection threshold (Niemann et al. 2005). The detected low noble gas abundances are not in agreement with the thermo dynamical calculations which predict solar abundances or even over-solar in Titan (Prinn and Fegley 1989; Mousis et al. 2002).

In a more recent study Alibert and Mousis (2007) calculated Saturn's subnebula consistent with the end phase of Saturn's formation by avoiding the limitations in Mousis et al. (2002) such as "equilibrium of Saturn's subnebula during its cooling phase" and neglecting the fact that Saturn accreted gas and gas coupled material during a substantial fraction of the subnebula lifetime (Lubow et al. 1999; Magni and Coradini 2004). Alibert and Mousis (2007)

Two scenarios were studied, one where Titan is formed in the late cold subnebula from preserved planetesimals produced in Saturn's feeding zone and Titan is formed in an early subnebula. They found that in the first scenario the CO/CH_4 molar mixing ratio would be orders of magnitude larger than that observed in Titan's atmosphere, but the second scenario predicted abundances similar to the observed ones. However, in addition to these scenarios, volatiles delivered by comets could have, modified the initial atmospheric inventory (Griffith and Zahnle 1995).

Recent in situ measurements by the Cassini Ion Neutral Mass Spectrometer (INMS) at 1250 km altitude found an enrichment of ^{15}N that is only about 1.27–1.58 the terrestrial value (Waite et al. 2005). Furthermore, the Huygens probe measured during its decent with the Gas Chromatograph and Mass Spectrometer (GCMS) a similar enrichment of ^{15}N compared to ^{14}N of about 1.47 (Niemann et al. 2005). These $^{15}N/^{14}N$ isotopic ratio observations are an indication that Titan experienced considerable nitrogen escape. Waite et al. (2005) compared the INMS measurements with the model results of Lunine et al. (1999), by assuming that the initial nitrogen ratio was similar to the present terrestrial value and that the temperature between the exosphere and the homopause remained unchanged over the course of atmospheric evolution. By considering these assumptions they found that Titan may have lost 1.7 ± 0.05 to 10 ± 5 times its present atmosphere. The large uncertainty in their estimate is due to the unknown efficiency for dissociative fractionation of the isotopes. Further, Waite et al. (2005) mention that these values correspond to the upper-end of the INMS-measured range. If they use the lower end of the INMS-measured range, the range of atmospheric loss over Titan's history becomes 2.8 ± 0.2 to 100 ± 75.

If one considers the present solar activity and nitrogen loss rates caused by sputtering in the order of about 10^{25}–10^{26} s^{-1} (e.g. Shematovich et al. 2003; Michael et al. 2005) or loss of CH_5^+, $C_2H_5^+$, H_2CN^+, $C_xH_y{}^+$ ions due to ionospheric outflow of about 5×10^{24}–10^{25} s^{-1} (Hartle et al. 1982; Lammer and Bauer 1991; Keller et al. 1994; Keller and Cravens 1994; Keller et al. 1998; Nagy et al. 2001; Sillanpää et al. 2006; Ma et al. 2007) its difficult to understand how Titan could have lost several times the present atmosphere mass (see also Johnson et al. 2008). Even if CH_4 escapes from present Titan in the order of about 4–5×10^{10} amu cm^{-2} s^{-1} (Yelle et al. 2008; Johnson et al. 2008) one can not explain the ^{15}N enrichment.

In a recent study Penz et al. (2005) used astrophysical observations on radiative fluxes and stellar winds of solar-like stars with different ages and lunar and meteorite fossil records (Newkirk 1980). These data indicate that the early Sun underwent indeed a highly active phase resulting in up to about 100 times higher X-ray and EUV radiation fluxes (Zahnle and Walker 1982; Ribas et al. 2005) and much higher solar wind mass fluxes (Wood et al. 2002) 100–500 Myr after it arrived to the Zero-Age-Main-Sequence. The results of Penz et al. (2005) indicate, in agreement with Johnson (2004), that atmospheric sputtering even with a strong early solar wind cannot be responsible for the observed enrichment in ^{15}N isotopes in Titan's atmosphere. The estimated non-thermal nitrogen loss rates during the young Sun epoch after Titan's origin are 100–1000 times higher ($\leq 10^{28}$ s^{-1}) than that of today but the time period was too short to have lost several bar of atmosphere (Penz et al. 2005).

But they suggest that Titan's early atmosphere may have been in a state of nitrogen blow-off due to EUV enhanced heating and exobase expansion of the upper atmosphere. These authors suggested that, because of Titan's low gravity and an expanded exobase level the dynamically driven nitrogen flow could overcome the escape velocity at the exobase level, so that more than 30 times of its present atmospheric mass may have escaped (Penz et al. 2005). Such an expected rise in exobase altitude would result in a larger homopause-exobase distance Δz and, hence, in a strong effect of mass-driven diffusive separation (Lunine et al. 1999; Lammer et al. 2000), where the diffusive separation factor

$$f = \mathrm{EXP}\left(\frac{\Delta z}{H_d}\right) - 1, \tag{4}$$

with

$$H_d = \frac{kT(r)}{(m_2 - m_1)\, g(r)}, \tag{5}$$

where H_d is the diffusive scale height, k the Boltzmann's constant, m_2 and m_1 is the mass of the heavier ^{15}N and lighter ^{14}N isotope, respectively. T and g are the temperature and gravitational acceleration halfway between the homopause and the exobase levels.

By assuming that nitrogen was the main species, as it is today, and the mass fractionation during escape is the Rayleigh process, the original atmospheric mass relative to the present one can be written as (Lunine et al. 1999)

$$\frac{n_1^0}{n_1} = \left(\frac{n_2}{n_1} \Big/ \frac{n_2^0}{n_1^0}\right)^{\frac{(1+f)}{f}}. \tag{6}$$

The ratio n_2/n_1 is the measured isotope fractionation and n_2^0/n_1^0 is the initial value prior to atmospheric enrichment and can be assumed to be the terrestrial value.

Figure 8 shows the initial nitrogen reservoir of Titan needed to reproduce the measured average ^{15}N isotope enrichment of about 1.47 (Waite et al. 2005; Niemann et al. 2005) as a function of exobase levels above the surface and different temperatures in (5) and resulting different diffusive scale heights. The homopause position in Fig. 8 corresponds to the observed altitude of 1195 km (Waite et al. 2005). Because, of enhanced thermosphere heating by the young Sun, and concomitant exobase expansion the temperature between the homopause and exobase might rise rather than remain close to 150 K as assumed by Lunine et al. (1999) and Waite et al. (2005). As a result, the diffusive scale height in (5) would be larger, resulting in a decrease of the diffusive separation factor f in (4).

As one can see from Fig. 8, it is hard to constrain the amount of atmospheric loss over Titan's history. The uncertainties are largely due to our imprecise knowledge of the position of the homopause and exobase levels as well as due to the unknown temperature value between the homopause and exobase levels. Correspondingly the measured nitrogen isotope anomaly is an indication that Titan's atmosphere was at least several times denser than today.

If one considers reasonable temperatures of $\sim$150–500 K between the homopause and exobase one can see from Fig. 8 that for exobase levels at altitudes $\geq$ 3000 km above Titan's surface the satellite may have lost 2–10 times of its present atmospheric mass. Whereas the nitrogen isotope measurements suggest considerable atmospheric loss, the carbon isotope ratios, remarkably, do not. Prior to the Cassini observations it had been suggested that photo-absorption by methane and its photoproducts played an important role in heating the atmosphere. However, if the supply of methane to the atmosphere is episodic, then, the due to the depleted hydrocarbons, the nitrogen atmosphere might cool and could become thin or collapse prior to the next outgassing event (Lorenz et al. 1997; Lunine et al. 1998).

This would clearly affect the estimates of nitrogen loss over time. The carbon isotope ratios from the Cassini measurement confirm that there must be a subsurface source

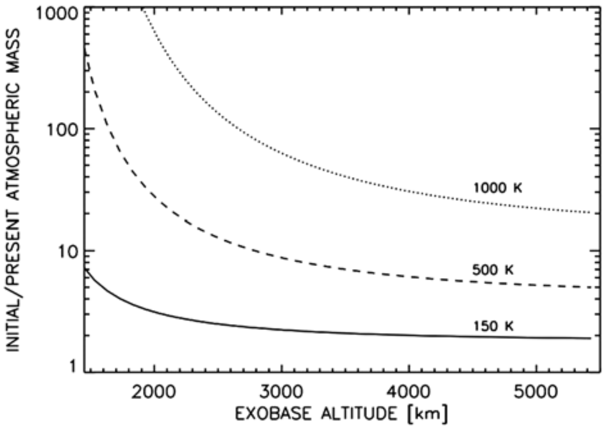


Fig. 8 Titan's initial nitrogen reservoir, normalized to the present nitrogen atmospheric mass as a function of exobase altitude from Titan's surface and average temperature between the homopause and exobase levels

of methane. Cryovolcanic outgassing of methane stored as clathrate hydrates within an icy shell above an ammonia-enriched water ocean has been proposed (Tobie et al. 2006; Atreya et al. 2006). Whether such a source is steady or episodic is not clear. Therefore, in future atmospheric evolution studies, the effect of cryovolcanism on the atmosphere structure needs to be considered.

In addition self consistent hydrodynamic models of the thermosphere are needed which examine adiabatic cooling due to dynamic expansion caused by a rise in thermospheric temperature as well as cooling as a function of the change in mixing ratios of minor atmospheric species like HCN. Such studies are important for finding out, to which altitude the exobase level could expand due to EUV heating by the young Sun and if Titan's exosphere could reach hydrodynamic blow off conditions, and, if so, over which time periods such conditions may have been active. An explanation of the nitrogen isotope anomaly is important for enabling us to estimate the nitrogen reservoir required to produce the present Titan atmosphere. It is also of importance for understanding the formation, evolution, and escape of atmospheres around other satellites like Callisto, Ganymede, Europa, Triton and small planetary bodies like Pluto because their early atmosphere environments should have also experienced an enhanced EUV flux. Below we consider one aspect of this, the role of the incident plasma in driving escape.

7.2 Contribution of Atmospheric Sputtering to Titan's Isotope Fractionation

Estimates of the magnetospheric ion and the pick-up ion flux onto Titan's exobase were made using a hybrid calculation based on the ambient ion fluxes from Voyager (see Bretch et al.; Ledvina Chapter). These fluxes were used in a number of Monte Carlo simulations of Titan's exobase region in order to describe the plasma heating (Michael and Johnson 2005) and sputtering of Titan's atmosphere (Shematovich et al. 2003; Michael et al. 2005). Such simulations showed that, using present atmospheric sputtering rates, the fraction of Titan's atmosphere that would be lost over its lifetime is only about 0.5% of the present atmospheric molecular nitrogen inventory. If the exobase region was populated by NH_3 instead of N_2 over a significant fraction of its history, then the net loss would be, very roughly, about twice that, which is still too small to affect the isotope ratios.

Lammer, Bauer, and co-workers (Lammer et al. 2000; Lammer and Bauer 2003) obtained similar results, but also considered the fact that an early more robust solar wind would have compressed Saturn's magnetosphere and, possibly, sputtered the atmosphere more efficiently. Early estimates of the net loss assuming a T-tauri phase suggested that such a process might explain the isotope ratios. That was subsequently re-examined (Penz et al. 2005), as described above.

With the large number of passes of Cassini through Titan's exobase region, we are now in a position to re-examine this process in more detail. That is, rather than use model fluxes, the corona structure and escape rates can be linked to actual plasma fluxes. For instance, Cassini INMS measurements show that the structure of Titan's corona above the nominal exobase differs from that produced thermally (De La Haye et al. 2007a) and this structure and exobase temperature appear to vary spatially and/or with local time. The non-thermal component, however, cannot be re-produced by detailed models of the photon and electron induced chemistry in Titan's exobase region (De La Haye et al. 2007b). Therefore, it is suggested that the observation might be explained by atmospheric sputtering. Since the energetic particle flux onto Titan's exobase is not much different from that assumed in earlier simulations (Ledvina et al. 2004), it is suggested to be due to an enhanced flux of low-energy pick-up ions or "hot" out-flowing ionospheric particles associated with fields which penetrate below the exobase (De La Haye et al. 2007a). In addition, estimates made using INMS data suggest that the loss rates for hydrogen and methane may be larger than earlier estimates (Yelle et al. 2008; Strobel 2007). Therefore, present Titan's loss rates are not easy to explain, although they are not likely to be large enough to account for the observed isotope ratios.

7.3 Relevance of Sputter-Loss from Titan to Loss from Other Satellite Atmospheres

Although it has a very thick atmosphere, Titan is similar in size to the other large moon's of the giant planets that do not have thick atmosphere's. For example, Triton is sufficiently far from the Sun, so that much of its atmosphere could be frozen out on the surface. This is not the case for the large Jovian moons, suggesting that they possibly lost their dense gravitationally bound atmospheres by some atmospheric erosion process. Whereas Io's relatively thin atmosphere is produced by present volcanism, there is no evidence for volatiles associated with nitrogen or carbon. In addition, Europa, Ganymede, and Callisto have thin atmospheres which appear to be formed by sublimation and radiation-induced decomposition of water ice containing some trapped volatiles and, possibly, trace minerals (Johnson et al. 2004; McGrath et al. 2004).

Scaled by the parent planet radius, Callisto is farther from Jupiter, in Jupiter radii, than Titan is from Saturn, in Saturn radii, but Titan has retained a large atmosphere and Callisto has not. This has been attributed to differences in solar driven escape rates and impact erosion rates (Griffith and Zahnle 1995). However, we also note that all three icy Galilean satellites orbit much deeper in Jupiter's magnetosphere than Titan does in Saturn's magnetosphere. That is, they reside a considerable distance from the magnetopause, in a region of much higher field strength. At present, they also experience plasma pressures that are, going from Callisto to Io, 10 to 10^4 times that experienced by Titan when it is in Saturn's magnetosphere. Although the calculation of accurate atmospheric loss rates requires detailed consideration of the molecular physics, this pressure is a measure of the ability to remove an atmosphere and to retain the ions formed, allowing plasma to build up. Therefore, estimates of present atmospheric sputtering rates were used to show that Io and Europa would have rapidly lost a Titan-like atmosphere, whereas Ganymede and Callisto would have lost $\sim$30% and 3% respectively of a Titan-like atmosphere at present plasma bombardment rates. Assuming a more dense plasma torus when Io and Europa were being stripped, atmospheric sputtering alone might be able to account for the lack of a primordial atmosphere on the Jovian satellites, although Callisto with its more copious CO_2 inventory may be an interesting intermediate case.

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8 Conclusion

The origin and evolution of the atmospheres of the terrestrial planets in the solar system and Saturn's large satellite Titan were discussed. Due to the extreme radiation (X-ray, soft X-ray and EUV) and plasma (solar wind mass flux) environment of the young Sun we expect that the atmospheres and planetary water inventories were strongly affected by thermal and various nonthermal escape processes mainly during the first Gyr after the Sun arrived at the Zero-Age-Main-Sequence. Due to the heating of the much higher solar EUV flux the thermosphere and exobase levels extended to higher altitudes than at present time, which resulted in larger solar wind—atmosphere interaction areas and higher nonthermal loss rates. The extended exobase levels and resulting larger homopause-exobase distances were also responsible for the enrichment of heavy isotopes in the present atmospheres. Under certain activity conditions of the young Sun hydrostatic equilibrium could not kept resulting in large thermal escape rates.

Acknowledgements Helmut Lammer, James F. Kasting, Eric Chassefière and Yuri N. Kulikov thank the Helmholtz-Gemeinschaft as this research has been supported by the Helmholtz Association through the research alliance "Planetary Evolution and Life". Yu. Kulikov and H. Lammer acknowledge also support by the Austrian Academy of Sciences, "Verwaltungsstelle für Auslandsbeziehungen", by the Russian Academy of Sciences (RAS), for supporting working visits to the PGI/RAS in Murmansk, Russian Federation. H. Lammer and Yu. N. Kulikov also acknowledge the International Space Science Institute (ISSI; Bern, Switzerland) and the ISSI team "Evolution of Exoplanet Atmospheres and their Characterization". R.E Johnson acknowledges the support of NASA's Planetary Atmospheres Program.

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