Volatiles in the atmosphere of Mars: The effects of volcanism and escape constrained by isotopic data

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ABSTRACT

We study the long term evolution of the conditions on the surface of Mars through the modeling of the effects of volcanic degassing and atmospheric non-thermal escape during the last four billion yr. We propose to use the recent advances due to observation and modeling to constrain possible evolutions of the atmosphere of Mars with the help of isotopic data from carbon, nitrogen and argon. The history of argon is studied through direct calculation of its degassing and escape, whereas, for other species, the analysis is an integration backwards in time from present-day situation. In our calculation, we do not consider early impact erosion, hydrodynamic escape or carbonate formation.

Volcanic degassing is obtained from crust production models, observation of the surface, and realistic volatile contents of the lavas. ASPERA (Analyzer of Space Plasma and EneRgetic Atoms) measurements and modeling of the escape rates produced by ionic escape, sputtering and dissociative recombination constitute the sink of volatiles. We constrain the maximum escape flux of CO_2 with the evolution of argon and the $^{40}Ar/^{36}Ar$ ratio in the atmosphere and measurements of the present-day situation. This imposes restricted escape flux, consistent with the recent lowering of the expected escape efficiency on Mars. Our model is able to reproduce present day ^{36}Ar abundance and $^{40}Ar/^{36}Ar$ ratio. We also show that the present-day atmosphere of Mars is likely to be constituted by a large part of volcanic gases. With a low CO_2 concentration in the magma (150 ppm), present atmosphere is constructed of 50% of volcanic gases emitted since 3.7 billion yr ago. We oppose this "late" volcanic atmosphere to the "early" atmosphere, in place during Noachian and composed of primitive volatile brought during accretion, magma ocean phase and pre 3.7 Ga volcanism. Likewise, the mean age of the atmosphere is estimated to be no more than 1.9 to 2.3 billion yr. Atmospheric pressures and variations on Mars are predicted to be low (50 mbar), as the result of degassing and non-thermal escape. This seems in line with the assumption of a big loss of volatiles during the first 500 Myr. Isotopic ratios lead us to propose that nitrogen is probably old in the Martian atmosphere and has been subjected to the fractionation of atmospheric escape. The $^{12}C/^{13}C$, on the other hand is more stable and indicates that carbon is younger. Water could have existed on Mars through the last 4 billion yr evolution within a factor of 1.6 times greater to 3 times less than the present-day inventory including polar caps, depending on the volcanic degassing. It is however unlikely to reside in the atmosphere or in liquid form unless large scale perturbations occur (changes in obliquity and large input of greenhouse gases due to a short burst of volcanism).

1. Introduction

With the progress of the observation of terrestrial planets in the solar system, we possess increasing amounts of data on their present and past state. Mars, in particular, has been visited by many probes and stays a main target of scientific investigation, as a possible place where liquid water could have existed in the past. Centre piece among this research is the knowledge of surface conditions of the planet and their evolution over time.

Indeed, in recent years there has been further evidence that it might once have sported free running water on its surface for significant periods of time, especially early in its history when it could have been stable (Zuber et al., 2000) due to the thick primitive atmosphere. Moreover, large deposits of ancient phyllosilicates have been observed by the OMEGA spectrometer (Bibring et al., 2005; Gendrin et al., 2005; Poulet et al., 2005) that require the presence of neutral water on the surface of Mars.

The later state of the surface conditions on Mars also shows that water has existed on the surface of the planet in a liquid form. Outflow channels and valley networks, for example (Bouley et al., 2009; Head

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et al., 2001; Mangold and Ansan, 2006; Mangold et al., 2004), are evidence that water flowed on the surface of Mars when they formed (from 3.6 to 3.1 Ga), although some recent work has suggested an alternative model where low viscosity lavas carved some of the outflow channels (Jaeger et al., 2010; Leverington, 2007).

In the present state of the planet, however, water doesn't exist in a liquid form due to low atmospheric pressure and temperature. It can however be found in a solid state in the polar caps (Bibring et al., 2004) or in the regolith (Boynton et al., 2002; Phillips et al., 2008).

The essential question is how and why the atmosphere of Mars evolved from a point where it could sustain stable liquid water for long periods of time to the situation we know rather well today (Encrenaz, 2001; Smith et al., 1997; Zurek, 1992). It is likely that the past atmosphere of Mars would have required the accumulation of large amounts of greenhouse gases to reach a state where liquid water is stable. The most straightforward way to accomplish this is with a very thick CO_2 atmosphere (Jakosky and Phillips, 2001; Pollack et al., 1987). However, this situation is by no means certain. Models have tried to investigate the evolution of the CO_2 pressure with time through the estimation of the different fluxes and reservoirs (Haberle et al., 1994) and sometimes obliquity (Manning et al., 2006). Others have focused on the water reservoirs (Donahue, 1995).

Here we expand upon our earlier attempts at defining possible states of the atmosphere of Mars during the last three billion yr (Gillmann et al., 2009), by refining the volatile fluxes we use and by constraining them with better data and isotopic constraints. We propose to study the effects of atmospheric escape and volcanic degassing of CO_2, which are the most straightforward sources and sinks of CO_2 during the last 4 billion yr and the two mechanisms that can be quantified with reasonable amounts of assumptions.

2. Modeling

2.1. Reservoirs and fluxes

It is important to identify the different sources and sink of CO_2. The first source of volatiles for the atmosphere is degassing by volcanism. Some approximation of the way volcanism evolves can be obtained by numerical modeling (Breuer and Spohn, 2006; Manga et al., 2006; O'Neill et al., 2007) and by observation of the surface (Craddock and Greeley, 2009; Greeley and Schneid, 1991; Hartmann and Neukum, 2001). The actual volume of gases released in the atmosphere is difficult to estimate because of the lack of volcanic samples from Mars (other than meteorites) and uncertainties over the true contents of the lavas.

The main sink of volatile we study here is the atmospheric escape through non-thermal mechanisms. It has long been considered as the major sink of gases on Mars for the last 4 billion yr (Chassefière et al., 2007; Leblanc and Johnson, 2001). Recent observation (Barabash et al., 2007; Lundin et al., 2009) and modeling (Chaufray et al., 2007) tend to suggest that this sink is not as important as previously thought. Several mechanisms can account for non-thermal escape. Dissociative recombination of ions produces energetic neutrals from the combination of ions and electrons. Ion escape of particles that form in the upper atmosphere and diffuse to higher altitudes is based on the pick up of ions by solar wind. Some hot neutral atoms produced by charge exchange can also escape due to the solar wind. Finally, with sputtering, part of the pick up ions impacts the atmosphere and brings additional energy to neutral species that can escape.

Other possible reservoirs and sinks of volatiles exist. The other important atmospheric escape processes are two types of thermal escape. Jeans escape occurs in the present-day situation but only concerns very light species such as H and D. The second mechanism, hydrodynamic escape, consists in a fluid-like outward flow that occurs if enough energy is brought to the atmosphere. The situations arise

during the first few tens of millions of years of the history when extreme UV flux is high.

Another possible escape mechanism is impact induced escape. Early in its history, Mars would have been impacted by large bodies such as asteroids and comets, which could have blown a part of the atmosphere away to space (Hamano and Abe, 2005; Melosh and Vickery, 1989; Svetsov, 2007).

Other reservoirs include the solid state CO_2, which can be found in low quantities in the polar caps. These are however mainly composed of water ice (Bibring et al., 2004, 2005; Byrne and Ingersoll, 2003). CO_2 in the regolith has also been proposed (Zent et al., 1987) but this hypothesis is nowadays deemed unrealistic since observation suggests that most of the subsurface at high latitudes contains water ice (Boynton et al., 2002). A last reservoir of CO_2 on Mars would be subsurface carbonates. Observation from the spirit and opportunity rovers or the OMEGA team could not detect any carbonates (Bibring et al., 2006). However some magnesium carbonates have been found by the CRISM spectro-imager on MRO (Ehlmann et al., 2008) and in situ measurements by the Phoenix lander revealed 3–5 wt.% calcium carbonate (Boynton et al., 2009).

2.2. Volcanic degassing

To estimate the effect of degassing during the last few billion years of the evolution of Mars we model it through different profiles of volcanic activity obtained by published works on internal dynamics for the mantle of the planet and compared to observation of the Martian surface. These models compute melt production. From this value we extrapolate to the amount of material reaching the surface. Finally, estimates of the volatile contents of the lavas are necessary to propose a realistic profile of the degassing.

We compare the results from numerical studies by Breuer and Spohn (2006), Manga et al. (2006) and O'Neill et al. (2007) (summarized on Fig. 2 of Gillmann et al., 2009) to data from observation of the surface (Craddock and Greeley, 2009; Greeley and Schneid, 1991; Hartmann and Neukum, 2001). Numerical studies provide a wide range of values for the crust production rates that we approximate to the total volcanic production (intrusive and extrusive). Both Breuer and Spohn (2006) and Manga et al. (2006) propose models which produce large amounts of crustal material, with a two phase evolution. Other models, on the other hand, such as Breuer and Spohn (2006) with primordial crust or O'Neill et al. (2007), do not show this behavior. Observational data shows that expected volcanic productions correspond with the lower values predicted by these models. Indeed, photogeologic methods used by Greeley and Schneid (1991) appear to point towards a mean melt production rate of 0.17 km^3/yr over the last 3.8 billion yr on Mars. Recent estimates would indicate values of around 10^{-4} km^3/yr for present (Kiefer, 2003). With this in mind we choose models with low late activity and a clear decrease of the melt production over the last past 3.8 billion yr. Those are based on the results by Breuer and Spohn (2006) and scaled down to fit observation (Fig. 1). Our preferred profile for volcanic activity fits with most reports of post 4.0 Ga activity with a relatively large Late Noachian/Early Hesperian rate and a slowing, but still present, geological activity after 3 Ga (Carr and Head, 2010). Our estimates fit with results reported by Greeley and Schneid (1991) and should be taken as a reasonable minimum. Despite the age of this work, it remains a good estimation of volcanic activity at least over the last 4 billion yr, as lava thickness determination and surface dating techniques have not changed significantly since then. A study by Phillips et al. (2001) constitutes the only significant challenge to this estimate of past volcanic activity, mainly due to their conclusion of a pre Noachian emplacement of Tharsis. Craddock and Greeley (2009) have presented arguments against it, related to the dating of the surface of Tharsis by very large impacts and subjectivity of the mapping of valley networks from imagery data alone, which were not
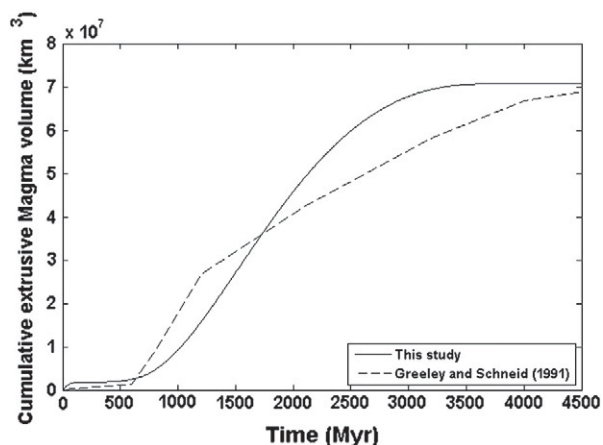
Fig. 1. Cumulative extrusive magma volume in km³ over the history of Mars for our preferred activity model and results from photogeologic mapping as shown by Greeley and Schneid (1991). Ages for the Greeley and Schneid curve are from Tanaka et al. (1992).

addressed by Phillips et al. (2001). In any case, this discrepancy only affects us marginally, as most of our model concentrates upon the last 4 billion yr and does not usually deal with the early emplacement of Tharis, and the later activity in our model is comparable to what is currently viewed as a consistent picture of the late Martian volcanism (Carr and Head, 2010; Neukum et al., 2010; Werner, 2009). Moreover we do not consider very recent volcanic events as they are unlikely to bring significant amount of volatiles to the atmosphere on the scales we are studying in this work (Vaucher et al., 2009). Finally, due to the timescales we used, we have considered averaged volcanic production rates rather than modeling the volatile releases in more focused events. Although perhaps less realistic, without precise data on the long term volcanic activity and timing of said episodic events, the solution we used is deemed more conservative and reliable.

We set an efficiency parameter for the degassing corresponding to the part of the lava that actually reaches the surface. In this model only material that is actually erupted is able to release volatiles into the atmosphere. The ratio between intrusive and extrusive magma varies between 12:1 and 5:1 in favor of intrusive, in the case of Earth (Crisp, 1984). Here we use a fixed value for this parameter and so 15% of produced lavas are erupted.

The last parameter that influences the volcanic degassing is clearly the concentration of volatiles. We suppose the composition of the lavas does not vary with time in this study. Martian volcanic material is likely to be mainly basaltic (Greeley, 1987). SNC analysis can give some insight on the abundance of C but the concentrations found are usually very low (Gooding et al., 1990; Wright et al., 1986), from 0 up to several tens of ppm. However, this indicates mainly that degassing of subaerial basalts is very efficient (Dixon et al., 1997). The other source of data is the comparison with Earth and Hawaiian or Iceland volcanoes. This leads to estimations of 0.023 to 0.65 wt.% (Craddock and Greeley, 1995; Manning et al., 2006; Phillips et al., 2001). Mars, however, as a single plate planet, might have a much more depleted mantle than Earth. A last approach is used by Hirschmann and Withers (2008). They try to estimate the CO_2 concentration in Martian magmas by considering the thermodynamic equilibrium between dissolved C species and carbon-bearing phases in the mantle, based on the assumption that the Martian mantle is reduced and that carbon resides in graphite (Karner et al., 2007; Shearer et al., 2006; Wadhwa, 2001). They conclude that graphite limits the liberation of CO_2 and yields magmas with between 50 and 500 ppm CO_2. We will use this latter range of values in this study, as they take into account the specificities of the Martian mantle and are consistent with data derived from SNC, rather than being simple Earth-like values.

In the case of water, on Earth, basaltic material contains roughly between 1000 and 6000 ppm H_2O with Hawaiian lavas in the upper

range (Byers et al., 1986; Jambon and Zimmermann, 1987). These Earth-like values might overestimate the content of Martian lavas because Mars could have lost large amounts of volatiles early in its degassing (Franck and Bounama, 1995; Médard and Grove, 2006; Senshu et al., 2002). Geomorphologic studies of the lava flows on Mars however suggest that they are compatible with andesitic basalts that would contain up to 0.5% (wt.) water (Zimbelman, 1985). Furthermore, recent geochemical studies provide us another estimate of the water contents of the SNC and their parental magma (in the case of McCubbins et al., 2010). They measured the water content of the kaersutite at 0.41–0.74 wt.% (roughly four times higher than previous studies; Watson et al., 1994). This might translate into a minimum water content of the parental melt to the Chassigny melt inclusions ranging from 0.43 to 0.84 wt.% H_2O. All these studies point at a roughly terrestrial water content. When dealing with nitrogen, due to the lack of precise Martian measurements, it is best to use Earth-like contents between 2 and 40 ppm (Goldblatt et al., 2009; Mather et al., 2004), favoring lower end values, as found in terrestrial samples (Li et al., 2007).

Isotopic data suffer from the same uncertainties as composition. Here we consider ^{12}C, ^{13}C, ^{14}N and ^{15}N. Degassing does not create any isotopic fractionation. We suppose the mantle ratios are constant with time. In the case of carbon, SNC data allow us to have an estimate of the ratio in the lavas ($^{12}C/^{13}C = 91.3$; Wright et al., 1990). For nitrogen we use an Earth-like value for the isotopic ratio in the lavas due to the lack of reliable Martian values ($^{14}N/^{15}N$ around 277.8; Marty and Dauphas, 2002). Likewise, atmospheric isotopic ratios are 85–95 for $^{12}C/^{13}C$ and 155–185 for $^{14}N/^{15}N$ (Krasnopolsky et al., 1996; Swindle, 1995).

2.3. Non-thermal escape

In this study we focus on the atmospheric escape non-thermal processes. Gillmann et al. (2009), following Chassefière et al. (2007), proposed an evolution of the efficiency of this escape. Their estimations, consistent with the state of observations (Carlsson et al., 2006), resulted in an important overall escape. More recent modeling and observation tend to favor lower present-day atmospheric escape (Barabash et al., 2007; Lundin et al., 2009).

Non-thermal escape efficiency depends mainly on the Extreme UV flux (EUV) which decreases with time during the evolution of the sun, unlike luminosity. The actual EUV solar flux can be approximated with the following law (Ribas et al., 2005):

$$\text{Flux} = \text{Flux(present average cycle conditions)} \times [\text{Age(Sun)} / \text{Age}]^{1.23 \pm 0.1}$$

(1)

where Age(Sun) is set to 4.7 Gyr. This implies that roughly 2.8 Gyr ago, the sun's average flux was three times greater than its present value.

The history of the solar emission is often divided into different periods depending on the EUV flux: 1 EUV (present situation), 3 EUV (three times the present emission) and 6 EUV. Solar maximum at present-day roughly corresponds to twice the EUV flux at solar minimum, and that is also the solar minimum two billion yr ago. In this study we use the mean solar emission as the base for the computation. Changes in the slope of the evolution of atmospheric escape are attributed to the non linearity of the mechanisms. Data from solar minimum and maximum allow us to interpolate likely profiles for the history of atmospheric escape between present-day and two billion yr ago. We then extrapolate for more ancient times, following Chassefière et al. (2007). We also use the yield efficiency calculated by Leblanc and Johnson (2002).

Lundin et al. (2009) report escape rates from the ASPERA instrument of $3.5 \, 10^{23} \, \text{s}^{-1}$ at solar minimum for ion escape of CO_2^+, while O^+ escapes at a rate of $2.1 \, 10^{24} \, \text{s}^{-1}$ and O_2^+ at $1.4 \, 10^{24} \, \text{s}^{-1}$. Sputtering has been studied by Cipriani et al. (2007) (taking into account collisions between neutral particles only), who suggest that, at solar maximum

and high EUV flux, it is the most efficient escape mechanism with rates of $1.4\,10^{23}$ to $9.0\,10^{24}$ C/s for carbon at solar minimum and maximum, respectively. It has been suggested by Chaufray et al. (2007) that pick-up ions reimpacting the atmosphere might generate lower escape flux than previously thought in the case of oxygen, and possibly for carbon also. Fox (2004), with a very complete model with detailed background atmosphere and major and minor photodissociation reactions, propose a photodissociation escape rate of $7.5\,10^{23}$ to $4.4\,10^{24}$ C/s for low and high solar activity, respectively. Recent ion escape models from Fox (2009), based and improved on previous work, yield escape rates of 2.6 to $3.9\,10^{24}$ CO_2^+ s^{-1}, much higher than observation for solar minimum. Ma and Nagy (2007) use a 3D non-ideal magneto-hydro-dynamic model, taking into account recent results on the ion chemistry and neutral atmosphere model (Bougher et al., 2006). They propose escape flux in the range of 10^{23} CO_2^+ s^{-1}. For oxygen escape we follow ASPERA observations and consistent results from modeling. Chaufray et al. (2007), using a 3D hybrid model propose a robust modeling of the escape processes of oxygen species and take into account the crucial importance of the modeling of the Martian corona and interaction with the solar wind. In the case of nitrogen, measurements and studies are less common and the different escape mechanisms have been covered by works from Jakosky et al. (1994), who paved the way and proposed most of the basic assumption for nitrogen escape, and Bakalian and Hartle (2006), who use more advanced modeling and recent advances in our understanding of the planetary atmosphere composition, structure and interaction with solar emission. Fig. 2 summarizes the escape fluxes.

To estimate the fractionation of Ar, C and N, due to atmospheric escape, we follow Chasseffère and Leblanc (2004) who propose a simplified calculation of the effects of non-thermal escape for sputtering and dissociative recombination. Sputtering fractionation is gravitational. It occurs at the exobase. The energy of pick-up ion is much higher than the escape energy, so no fractionation occurs due to the escape itself. Dissociative recombination usually occurs below the exobase so we can ignore the gravitational fractionation. Fractionation occurs only due to the escape itself.

2.4. Main model

We chose to build upon our previous work on the subject by improving the constraints on the degassing and escape flux (Gillmann et al., 2009). To do so, we model the evolution of two relevant fluxes for the atmosphere, volcanic degassing and non-thermal escape, over the late history of Mars (the last 3 to 4 billion yr). The main species we

study is CO_2, as the major atmospheric constituent during this period (Manning et al., 2006). We also have an interest in argon, nitrogen and water. Our first goal is to monitor the evolution of the atmospheric pressure, water contents and isotopic ratios for C, N and Ar.

We start with the calibration of the past escape of CO_2. This part of the study of atmosphere history consists in a direct evolution from the start of the escape to the present-day situation. Scenarios for this escape are used to estimate the isotopic ratios of Ar. It is indeed possible to relate the sputtering escape of C to that of Ar through estimates of the relative efficiency of sputtering applied to multi-species atmosphere (Jakosky et al., 1994; Johnson et al., 2000). We use the following approximation to scale the Ar sputtering escape to that of C (Johnson et al., 2000):

$$Y_{Ar} / Y_C = C_{Ar} / C_C x Ues_C / Ues_{Ar} \qquad (2)$$

where Y is the yield of the sputtering for the described species (Ar or C), C is the concentration of the species at the exobase and Ues is the gravitational escape energy of the species. We suppose that the concentration of Ar in the Martian atmosphere in the past is proportional to the amount of argon degassed by volcanism. At present-day this concentration is 1.6% (Owen et al., 1977).

We then combine these Ar escape fluxes with the history of volcanic degassing and models for the abundance in argon and potassium. Radioactive potassium is the source of ^{40}Ar and so it decays into ^{40}Ar and ^{40}Ca. Models for initial abundance of potassium on Mars give us a range of values from 300 to 900 ppm K (Lodders and Fegley, 1997; Wänke and Dreibus, 1994). Anders and Owen (1977) give us an estimate of the primitive abundance of ^{36}Ar in the atmosphere of Mars: $1.6\,10^{-10}$ cm^3/g and we assume there was a negligible amount of ^{40}Ar at that time in the atmosphere. Degassing of ^{40}Ar is solved by using the following mass balance equations:

$$d / dt \left[^{40}K\right]_{man} = -\lambda_T \left[^{40}K\right]_{man} \qquad (3)$$

$$d / dt \left[^{40}Ar\right]_{man} = \lambda_e \left[^{40}K\right]_{man} - K_D \left[^{40}Ar\right]_{man} \qquad (4)$$

$$d / dt \left[^{40}Ar\right]_{atm} = K_D \left[^{40}Ar\right]_{man} \qquad (5)$$

where $[^{40}Ar]$ is the amount of Ar, $[^{40}K]$ the amount of potassium, the subscripts "man" and "atm" relate to the mantle and the atmosphere respectively, λ_T is the total decay constant of 40 K, λ_e is the decay
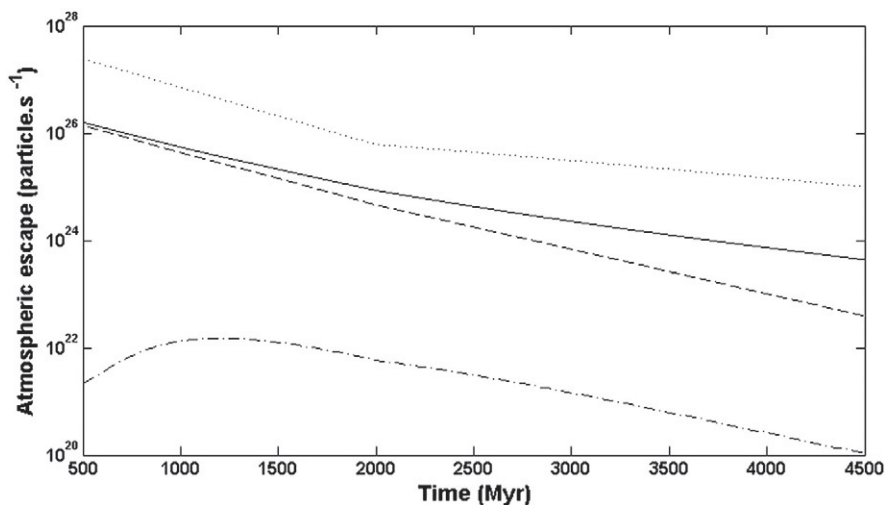

Fig. 2. Evolution of the atmospheric escape rates due to non-thermal mechanisms as calculated in this work for mean solar conditions (in terms of atoms). The solid line corresponds to the total C escape rate; the dashed line corresponds to the sputtering escape of C; the dotted line corresponds to the total escape of O and the dashed and dotted line corresponds to the escape of Ar.

constant of the reaction producing ^{40}Ar from ^{40}K, and K_D is a coefficient of the degassing rate.

From the scenarios of degassing and atmospheric escape of argon, we obtain a possible evolution of the amount of ^{36}Ar and $^{40}Ar/^{36}Ar$ isotopic ratio in the atmosphere. Escape scenarios that lead to acceptable results are validated and used further for the evolution of the bulk of the atmosphere.

In a second part of the work, in order to study the evolution of the main species, we then proceed with a step by step integration backwards in time of the earlier eras, starting with the present-day situation, as in Gillmann et al. (2009),. We can translate our procedure into the following equation for CO_2:

$$Q_{CO2}(t-\delta t) = Q_{CO2}(t)-\delta t \times D + \delta t \times E, \qquad (6)$$

where Q_{CO2} is the amount of CO_2 present in the atmosphere at a given time (t), D is the CO_2 production rate due to degassing, E is the carbon loss rate due to atmospheric escape and δt is the time step. Other gases are treated in the same way. In other words, we know at what pressure we need to end and the amount of volatiles that is lost or brought to the atmosphere. We use these assumptions to find out at what pressure we need to start.

We first model the evolution of the pressure and volatile abundance during the last four billion yr. During that time, the model is able to compute the evolution of the isotopic ratio for carbon and nitrogen from the volcanic source and the isotopic fractionation due to the atmospheric escape processes. We differentiate between non-thermal mechanisms. Present day isotopic data from Viking is being used (Krasnopolsky et al., 1998; Owen, 1992; Swindle, 1995). We finally monitor the evolution of the ratio of late (post 4 Ga) volcanic CO_2 to primitive (pre 4 Ga) CO_2. We assume that atmospheric escape does not discriminate between early and volcanic CO_2. Early CO_2 is not attributed to a precise origin but is likely to be part remnants of the primitive volatiles brought during accretion, part early degassing of the hot mantle or magma ocean and part late veneer of volatiles brought during the late heavy bombardment. We deduce an approximate age for the present-day atmosphere from the relative sources of the CO_2.

3. Results

Results of our model are presented below. They show the history of some volatile species (Ar, CO_2, N and H_2O) over time. We first study the case of argon and how it can be used to better understand the evolution of Mars.

Fig. 3 shows the evolution of isotopic ratio $^{40}Ar/^{36}Ar$ for maximal atmospheric escape. It takes into account both atmospheric escape and volcanic degassing and compares this situation with what would happen if escape didn't occur. With this case, present-day isotopic ratio as predicted by the model reaches the upper boundary of the observational data, even if the difference with the "no-escape" case is quite small at present-day. As atmospheric escape causes fractionation, the isotopic ratio is larger than in the basic case. Corresponding escape rates for carbon sputtering are in the range of values obtained by modeling and ASPERA observations for present-day Mars. They also fit estimated ancient times escape rates and limit them to lower to medium range values, which is useful as that period is difficult to constrain with data. With higher early escape rates, the fractionation differs even more from observed isotopic ratios as primitive ^{36}Ar is increasingly depleted up to the point when all the primitive argon is lost to space during the first 500 Myr. We therefore use lower and more realistic estimates for atmospheric escape as detailed in the previous sections.

On Fig. 4 we present a typical evolution of the argon over the history of Mars with moderate escape rates. The volatile input uses a basaltic lava melting rate and a 15% degassing efficiency. Initial Ar composition of the mantle is 600 ppm. The influence of atmospheric escape is moderate, with a present day difference between the two cases of roughly 100 for $^{40}Ar/^{36}Ar$ and 4% for present day ^{36}Ar abundance in the atmosphere. The influence of the escape is mainly seen during the first few hundred million years of the evolution. At that time most of the early argon is efficiently removed from the atmosphere. At later times, atmospheric escape of argon does not produce much fractionation. Degassing is the main mechanism for the evolution of the isotopic ratio and the argon contents of the atmosphere. It follows that parameters governing the release have the most influence on the predicted evolution of argon. In particular, the initial distribution of K is important, as is the melting rate and the efficiency of the degassing. These parameters are all difficult to constrain efficiently. However, initial K concentrations much larger than 600 ppm are unlikely to lead to predictions consistent with present-day observation. Likewise, the efficiency parameter is unlikely to be higher than 15%. It is however possible that the early conditions on Mars were largely different from what we estimate and the melting rate, could differ from our assumptions. It is also possible that we underestimate the degassing by not considering ^{40}Ar (and other volatiles) trapped in the crust.
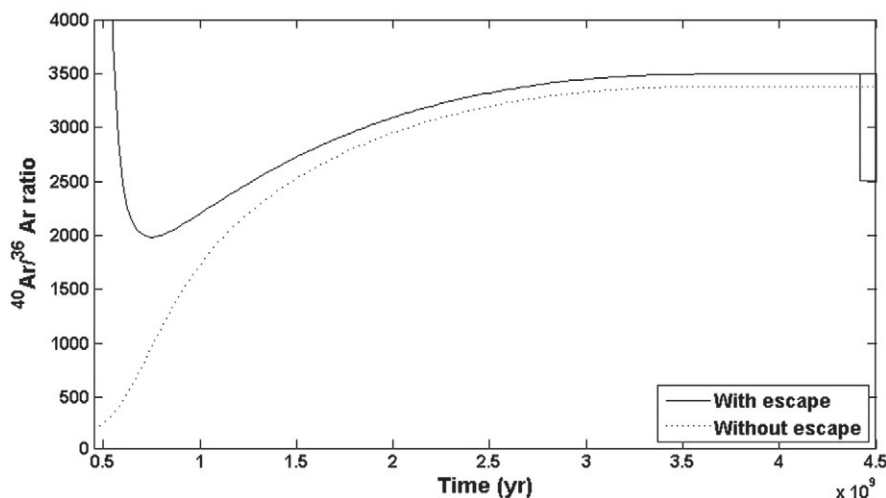

Fig. 3. Evolution of the $^{40}Ar/^{36}Ar$ isotopic ratio through the effects of degassing and non-thermal escape (solid line) and degassing only (dashed line). Volcanic production corresponds to our preferred model, K initial in the mantle abundance is 650 ppm, melting rate is considered to be basaltic, and efficiency parameter is 15%. Atmospheric escape, when used, is maximum (higher escape would generate too much fractionation and remove too much ^{36}Ar). The rectangular box at present state corresponds to the range of available isotopic data.
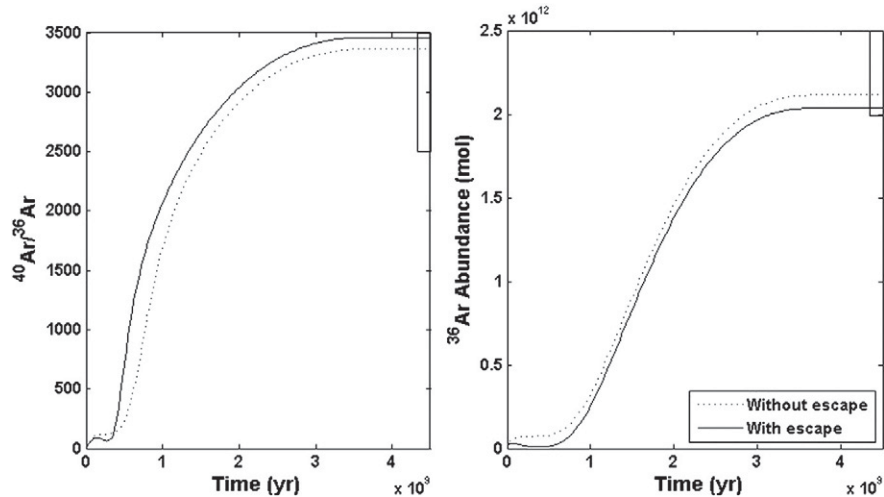
Fig. 4. Example of the evolution of isotopic ratio of Ar (left hand panel) and ^{36}Ar abundance (right hand panel) with time. Curves for the case without escape are shown too. Parameters are the same as used before but with a somewhat lower atmospheric escape. Rectangular boxes show present-day data ranges.

Fig. 5 shows the evolution of CO_2 pressure over the last past four billions yr. The CO_2 pressure shown here is the pressure needed to obtain the present-day situation. The general behavior of the CO_2 pressure is comparable to what Gillmann et al. (2009) presented. It must be kept in mind that, on Fig. 5, CO_2 pressure is indicative of the amount of carbon dioxide leading to the present situation, given degassing and escape fluxes. Here the escape flux is fixed and several values for the CO_2 concentration of the lavas are shown. Higher concentrations correspond to lower past pressures. Indeed, higher concentrations mean that the overall degassing is larger, so the atmosphere is brought more volatiles over the considered period of time. As a result, with the present-day situation taken as a fixed point, past pressures are found to be lower in order to accommodate the surplus CO_2 without exceeding present-day pressure. In other words, since we force more volatiles in the atmosphere with the final state fixed, we need to start with a lower pressure.

Despite the similar profile of the results from Fig. 5, lower fluxes due to lower atmospheric escape and lower concentrations in the lavas lead to several differences with results from Gillmann et al. (2009). We find three phases in this evolution. The first is an early period (500–1500 Myr) when escape is dominant and pressure decreases from higher pressure to a minimum. Secondly, we observe between 1500 and 3500 Myr an increase of the CO_2 pressure to a local

maximum, as volcanic degassing is the dominant process. Finally, this period of activity dwindles and atmospheric escape is strong enough to remove more volatiles than volcanism can release. The variations of the CO_2 pressure are not as extreme as what is featured in the work by Gillmann et al. (2009), with values ranging from a minimum of around 2 mbar to 10 mbar during the last 3 billion yr and only 40 mbar four billion yr ago. Models with less degassing (300 ppm and less) present a monotonous decrease of CO_2 pressure over the last four billion yr. In this case, however the effect of degassing is still seen in the resulting present-day atmosphere.

We also present the ratio between volcanic atmosphere and "early" atmosphere. We find that with lower escape rates it seems even more likely that the present-day atmosphere has been created by volcanism after 3.5 Ga. For lower degassing, the present-day atmosphere exhibits a larger part of primitive volatiles (50% for 150 ppm and more than 75% for 300 ppm). The mean age of the present day CO_2 revolves around 2 billion yr. It doesn't change much with the composition of lavas and stays between 2.3 and 1.9 Ga. That value is higher than what was proposed in Gillmann et al. (2009). Our present model exhibits very low volcanic degassing during the last 1–1.5 billion yr, which precludes any chance to obtain a young atmosphere by increasing the late degassing. If Mars has known some young volcanism, the atmosphere would appear younger.
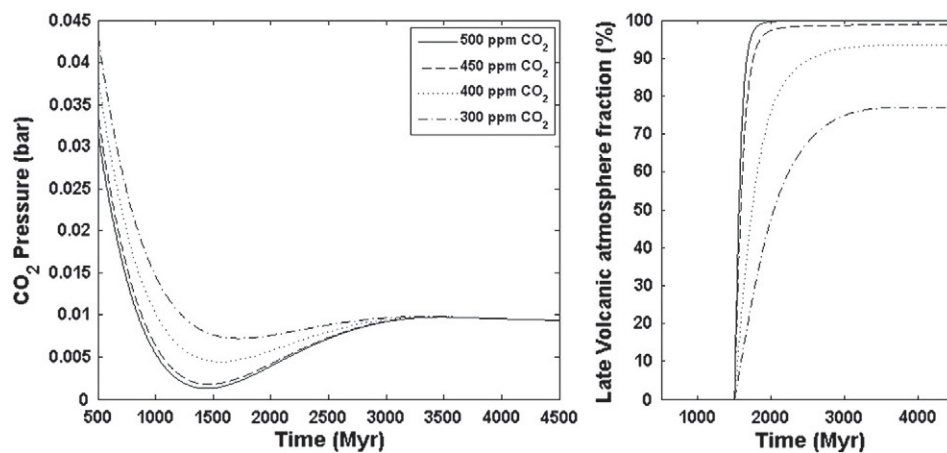

Fig. 5. Evolution of the CO_2 pressure with time (left hand panel) and the ratio of volcanic atmosphere over early atmosphere with time (right hand panel). CO_2 pressure over time corresponds to the amount of carbon dioxide needed at any time in order to obtain the present situation given a precise degassing and escape flux. As a rule, higher CO_2 concentrations in the lava equal to higher release over time and thus to lower past pressures, as higher past pressures would not be compatible with present-day situation. CO_2 contents of the degassing lavas (that is the total content of the melted material prior to the release of volatiles in the atmosphere) are shown on the picture. Volcanic activity model is our preferred model. Degassing efficiency is 15%.

Observation of the surface of Mars however shows that even if the planet is still active, the production rates at present-day should be very low.

Fig. 6 summarizes the results we obtain for isotopic ratio evolution of $^{14}N/^{15}N$ and $^{12}C/^{13}C$. The effect of atmospheric escape is to reduce the ratio during the course of the history of the planet. The effect of degassing is to move it back to the volcanic value (roughly 278 for N and 91 for C). For both N and C, the present day value is lower than the assumed value for the main source of volatile. This could be explained by the low recent degassing rates implying atmospheric escape is the dominant process for recent evolution. The evolution of the $^{14}N/^{15}N$ ratio doesn't vary much with different lava compositions due to the low concentration of N in them. The ratio slowly decreases from values in the range of the volcanic source three to four billion yr ago to the present lower value.

In the case of C, the situation is a little bit different due to the competition between degassing and atmospheric escape. Massive atmospheric escape leads to a sharp decrease of the ratio from high early values. More moderate values for the output of C allow degassing to play a role in the evolution of the ratio. Low degassing only mitigates the effects of late evolution and produces a two phase profile with an early period (500–1500 Myr) of decrease from high values (between 180 and 250) followed by a late period when the ratio is somewhat stable around 90. For higher CO_2 contents of the lavas (above 450 ppm) the degassing counterbalances the escape and the ratio can stay below the volcanic source value during most of the history of the planet. Values around 95–100 four billion yr ago are followed by a minimum due to the action of escape when degassing is low. Later, volcanic activity increases and the isotopic ratio increases. In a late period, it stabilizes around the present-day value and evolves slowly.

4. Discussion

4.1. What about water

It is possible to use the same model to study the evolution of water on the Martian surface. The background atmosphere is provided by CO_2. We study the evolution of the total water content of the atmosphere plus the content of the polar ice. We do not however take into account the water that can be stored in the subsurface of Mars nor

in the regolith as it is difficult to quantify accurately and uncertain if it can interact freely with the atmosphere. Ice caps on Mars represent between 1 and 3 million km^3 of ice water (Mouginot, 2008; Smith et al., 1999).

On Fig. 7 the total equivalent water pressure evolution in the atmosphere follows the same type of profile as that of CO_2. However pressures are much higher, due to the large amount of water contained in the ice (up to 450 mbar) and the higher total escape of oxygen. Very early, the combined effects of escape and degassing yield a H_2O pressure of up to 700 mbar in some cases. With higher water concentrations in the magma (6000 ppm to 9000 ppm), the picture is different as present-day water abundance becomes a maximum: three to four billion yr ago the surface (including both water from the atmosphere and found under solid or liquid states) are found to have harbored only about half the present water abundance. The present day water would have been mainly degassed by volcanism. On the contrary, with lower water concentrations (1000 ppm) there is no minimum in the water pressure profile despite the fact that a part of the present day water is brought by volcanism.

Whatever the case, surface water contents is high. It is likely that this amount is enough to produce the fluvial features observed on the surface of Mars (Bouley et al., 2009; Mangold et al., 2004). The main problem is to explain how this water could reside in the atmosphere rather than in solid state. Actual partial pressure of water in the atmosphere depends on the surface temperature and pressure. It is possible to calculate the surface temperature corresponding with the greenhouse effect due to CO_2 (with a model by Forget et al., 1999), allowing us to find the corresponding partial pressure of water. If we only take into account the greenhouse effect, we find that, when the atmosphere reaches 50 mbar from a present-day pressure of around 10 mbar, temperature only increases from 208.7 K to 213 K. Such a small rise of temperature is unlikely to be enough to allow the formation of fluvial landforms by itself, as it only corresponds to a rise of water partial pressure of 1.8 to 2.5 mbar. Worse, it is highly likely that the rise of CO_2 pressure would be accompanied by an increase in the amount of dust and aerosols in the atmosphere. With the same parameterization, we calculate that this would reduce the temperature to 195 K for the same CO_2 pressure variation, translating into a partial pressure much lower than 1 mbar of water.

According to these results, even if water is available, it is unable to reside in the atmosphere and would freeze. It is unlikely that inputs of
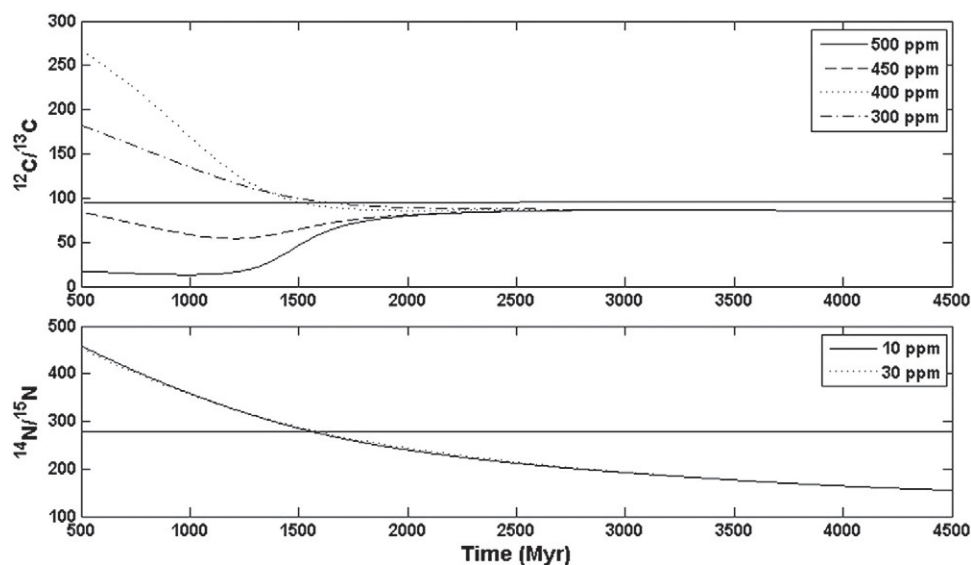

Fig. 6. Evolution of $^{12}C/^{13}C$ isotopic ratio with time (upper panel) and $^{14}N/^{15}N$ isotopic ratio with time (lower panel). Parameters are the same as before. Several CO_2 and N concentrations in the degassing lavas are used and indicated in each case (C or N) on the picture. Present day isotopic ratio for N and C corresponds to data we possess. Horizontal lines (on both panels) correspond to the isotopic ratio for the volcanic source.
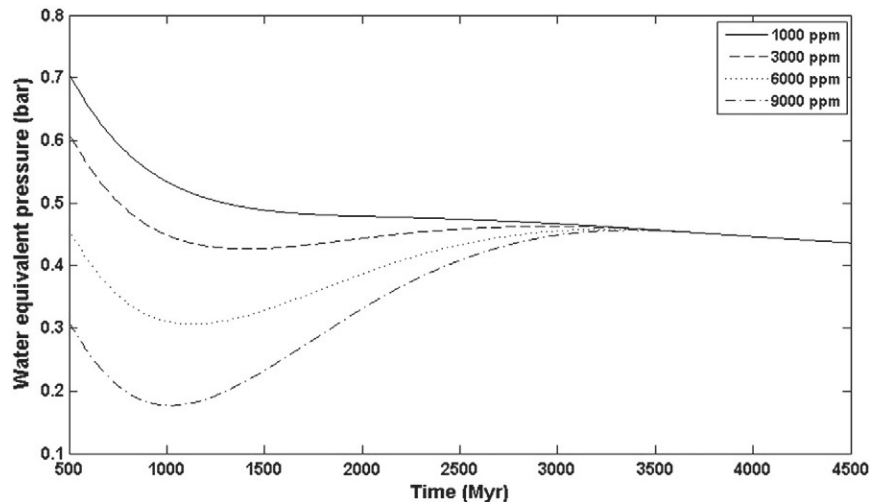
Fig. 7. Evolution of the equivalent water pressure at the surface of Mars with time. This corresponds to the available water, including ice caps and not to an actual pressure, which would be much lower. The same parameters as before are used and we test several water contents for the degassing lavas as indicated on the picture. Present day situation includes water from the ice caps and fits recent estimations.

water or CO_2 can lead to a situation where liquid water exists on the surface. Two solutions exist that could allow for the formation of fluvial landforms. The first possibility is the variation of orbital parameters. A change in obliquity (Laskar and Robutel, 1993) could destabilize the ice cap, leading to the activation of fluid cycles (Forget et al., 2006). It has also been suggested that the influence of other greenhouse gases such as SO_2 could locally or for relatively short periods raise the temperature (of about 10 K, Postawko et al., 1987) despite SO_2's short lifetime (Settle, 1979). However, recent studies with more precise models have shown that it is likely that the opposite effect occurs and that SO_2 actually reduces atmospheric temperatures through the formation of sulfate aerosols (Tian et al., 2010). It might nevertheless be relevant to observe that fluvial landforms have roughly the same age as the major period of volcanic activity (considering Greeley and Schneid, 1991).

4.2. The origin of the atmosphere

When looking at the results presented in the previous section, it is clear that volcanic degassing has an important role to play in the evolution of the Martian atmosphere. It is possible to compare these results to older estimates for degassing and atmospheric escape, such as those presented in Gillmann et al. (2009). CO_2 contents of the lavas have been reduced (from 800–1800 to 100–500 ppm), partly due to modeling of the effect of oxygen fugacity on the oxidation state of the Martian mantle by Hirschmann and Withers (2008). The amount of degassing we suggest is therefore much lower than what is often used (that is Earth-like values up to 6500 ppm) and also represents the fact that unlike on Earth, the Martian mantle can hardly recycle volatiles from the surface with its single plate tectonics. It remains however clear that during the last past four billion yr, a large amount of volatiles have been released into the atmosphere. Moreover, even for moderate volatile compositions of the lavas, it seems the present-day atmosphere is mainly composed of gases of volcanic origin (usually above 75%). This situation occurs due to the relatively strong volcanism that occurs between 3.7 and 2.5 billion yr ago, which is intense enough to replenish the atmosphere in most cases (even with our conservative values for volcanic activity). This late maximum in activity has been modeled in several studies (Breuer and Spohn, 2006; Manga et al., 2006) and is confirmed by observation of the surface (Carr and Head, 2010; Greeley and Schneid, 1991; Head et al., 2002, 2006). To the present knowledge of Martian volcanic history, our results are reliable. It is however possible that future research bring data that change our understanding of the evolution of degassing, in

particular about the early (Noachian) period or the details of the production rates profiles. Among the most likely features that were not included in our model, we can underline several possibilities. First, recent work has highlighted many occurrences of (Amazonian) post 1 Ga volcanism on Mars (Vaucher et al., 2009). These late volcanic eruptions have been found to bring only small amount of material to the surface and should contribute only marginally to the atmospheric volatile balance. Were they found to be more abundant than previously thought, however, they would only reinforce the conclusions of our study and emphasize the importance of recent volcanism. The second possibility has already been mentioned by Phillips et al. (2001) with the early emplacement of Tharsis, which does not reflect on our model (Fig. 1). As we detailed in Section 2, it is unlikely that large volcanic rates would only be found in the early Noachian. It is however possible we underestimated them. This would not have any bearings on our results for water, CO_2 and nitrogen, as we study mainly the post 3.7 Ga period and use an integration backwards in time starting with the present-day situation. The pressures we obtain through this study do not depend at all from what occurs during the early Noachian. In our model early degassing only has any bearings on Ar. It however takes place at a time when atmospheric losses are large (all the mechanisms are not taken into account in our model, but those that already remove most of the early argon from the Martian atmosphere). Moreover, during Noachian, the radiogenic isotope of Ar has not been produced in large amounts yet. To efficiently investigate the Noachian evolution of volatiles, we would not only need precise estimation of the volcanic production but also (and maybe even more importantly) estimates about the atmospheric escape through hydrodynamic process, non thermal processes and impact erosion, as volcanism only would not be enough to obtain a reliable picture of that era. Finally, the last main possibility is that the volcanic eruptions actually occur in episodic pulses. This has not been tested here and could have had some effect on the surface temperatures in the past of Mars. Precise data on the timing and intensity of those pulses are however limited to Amazonian features.

The situation is reinforced by the recent estimations of atmospheric non-thermal escape, now believed to be much less efficient than previously thought. Both recent modeling and observation (ASPERA; Lundin et al., 2009) point in this direction, explaining high volcanic/primitive ratios we suggest. It follows that present-day atmosphere is not the remnants of an early atmosphere steadily lost to space but has known several phases including a replenishing by volcanism after the intense early escape. In the same way, mean age of the atmosphere of 2 Gyr is not as young as estimates from Gillmann

et al. (2009) but clearly puts the origin of the atmosphere at a time when volcanic activity was high. An age of 2.5 Gyr is likely to be a maximum, as our model already uses a moderate degassing and we consider that the entire early atmosphere (what is left after the first phase of escape leading to the minimum in pressure) has its source before 500 Myr. Moreover, our degassing profile presents very low volatile release in the recent times, which has the effect of pushing back the age of the atmosphere. Higher degassing, the introduction of a secondary source of volatiles between 500 and 1500 Myr or a late phase of activity would all result in a younger atmosphere.

Recent history, however, is characterized by very low degassing (crustal production is estimated to be in the order of only 10^{-4} km^3/yr at present-day), which is unable to compensate for the non-thermal escape measured by ASPERA, even with lower estimates. The present day atmosphere seems to be progressively (if slowly) lost to space and, consequently, without replenishment, and the thin CO_2 ice layer observed at the poles should be on the way to disappearing. Given the small amount of CO_2 in the polar caps, such a process cannot last long (the CO_2 contents of the caps are only a fraction of what resides in the atmosphere). It has therefore been proposed that a hidden reservoir in contact with the atmosphere could exist. Some have suggested the oxidation of methane into CO_2 (Chassefière, 2009). According to their calculations, the south polar cap layer of CO_2 could be created in several million years. Other studies have however underlined the many problems this hypothesis created (discrepancies between common models of Martian atmosphere chemistry and the life-time of methane in the atmosphere of Mars required with these hypothesis, huge sink of O_2, and unknown sources for CH_4; Zahnle et al., 2010).

Even if it is unlikely that degassing and escape are the only important processes, these are beyond the scope of our present study, as we focus on the estimation of the effects of those two mechanisms. These effects tell us that during the last past four billion yr, they cannot account for high CO_2 pressures. CO_2 pressure has evolved slowly and could have remained in the order of 10 mbar for most of the evolution. Only when degassing is at its lowest and escape still strong, before 2.5 Ga, does the model predict large changes. We obtain at most several tens of millibars, with 50 mbar being a reasonable upper limit under the conditions detailed in this work. These low pressures are mainly due to the lower estimate of atmospheric escape in the post 4 Ga period. Non-thermal processes simply cannot remove enough volatiles from the atmosphere to allow for higher past pressures. A thick atmosphere during this period is then unlikely to be due to degassing and atmospheric escape. This low maximum pressure at 4 Ga would imply that even with a large initial inventory of volatiles, Mars would have lost most of it during the first 500 Myr. This can be explained by early hydrodynamic thermal escape rates as calculated by Tian et al. (2009), who propose that even a thick early atmosphere could be lost in several tens of millions of years (hydrodynamic escape would only require 1–10 Myr to remove 1 bar CO_2 before 4.1 Ga). A dense Martian atmosphere (and consequently a wet Mars) could only have formed after that period.

Low pressures are also consistent with studies implying that thick CO_2 atmosphere would condensate into clouds (Catling and Leovy, 2007). Our results are also in line with what is called "thin models" (Manning et al., 2006), with a low initial CO_2 inventory (with pressures lower than 5 bar). In this case the early history of Mars would be characterized by intense loss of volatiles, removing most of the available CO_2 by the end of Noachian and producing a minimum in pressure at that period, in the same way as we propose. This would also fit with the thin CO_2 ice caps. In the case of "thick models", Manning et al. suggest a surplus of several hundreds of millibars of CO_2, which cannot be accounted for by atmospheric escape and would lead, among other things to thick CO_2 ice caps (of nearly 100 mbar). Such a thick atmosphere would require the formation of significant amounts of carbonates to fit present day observation.

When using our moderate CO_2 composition models (around 450 ppm) our results (Fig. 6) are consistent with isotopic data from SNC, and in particular with old meteorites like ALH84001 (with carbonates dated from 3.9 Ga) that indicates $^{12}C/^{13}C$ of 83 to 86 and an enrichment of ^{13}C due, it seems, to early atmospheric processes (Jakosky, 1999). This would point at a scenario where early atmosphere is efficiently removed and enriched in ^{13}C. Afterwards, volcanism is dominant and can produce a secondary moderately thick atmosphere while atmospheric escape diminishes steadily, which allows wet conditions to occur. During that period a higher $^{12}C/^{13}C$ ratio is progressively restored through atmospheric degassing and potentially carbonate formation. This implies that volcanism has been an important process during the late evolution of Mars while atmospheric escape became less important (Niles et al., 2010). Therefore moderate CO_2 compositions (around 450 ppm) seem more likely, as higher concentrations would lead to cases with no CO_2 atmospheres during some periods in the past of Mars (between 3.5 and 1.5 Ga), which would be difficult to explain. Such high degassing rates could only be realistic if comparatively strong sinks of CO_2 existed. For example large deposits of carbonates could have formed continuously during the evolution of the planet. They have however not been detected yet and it is still unknown if they could have survived possible acidic phases of the early evolution of Mars and how much could have formed. It is also unknown if these carbonates could have interactions with the atmosphere later in the history of Mars. Lower compositions are also unlikely as they lead to high $^{12}C/^{13}C$ ratios early in the history of the planet, which would be in contradiction with the effects of early atmospheric escape (that removes the light species). It could be argued that during the end of the Noachian, the Late Heavy Bombardment could have played a role in the evolution of the atmosphere. It is indeed possible that around 3.9 Ga, a brief period of violent bombardment occurred (Ryder, 2002; Ryder et al., 2000). It could have removed massive amounts of the primitive atmosphere or/and brought an external supply of volatiles, in particular with impacts by comets (Levison et al., 2001). We still don't know which one would be dominant and under what conditions. However, it has been speculated that intense bombardment could remove 50–90% of the early atmosphere (Brain and Jakosky, 1994) and it can be calculated (from data by Levison et al., 2001) that up to 200 mbar CO_2 could be released into the atmosphere by comets. Such effects could mean that primitive volatiles could be mainly lost before 3.8 Ga and that a secondary atmosphere could be in place by that time. At this point we can compare our results for the isotopic ratios of C and N to what is known about comets. Most of the comets present an isotopic ratio for $^{12}C/^{13}C$ of around 92 ± 7 (Jehin et al., 2008), with some higher values (Hale-Bopp, LINEAR, Kohoutek, Tago-Sato-Kosaka): 165 ± 40 et 115 ± 20 (Arpigny et al., 2003), 135 ± 65 (Danks et al., 1974), 100 ± 20 (Owen, 1973). Although this is no definite proof, such values roughly correspond to the ratio we predict around 3.8–4 Ga. In the case of nitrogen the values do not fit. The cometary ratio 14 N/15 N is around 151 ± 21 (Arpigny et al., 2003; Jehin et al., 2008). Primitive solar nebula values, however, are estimated to be around 424.4 ± 4 (Meibom et al., 2007), which corresponds to what we predict. In that case, carbon could have been first lost to space, then an external supply would have been brought by comets and finally, the interplay of degassing and non-thermal escape would have led to the present state. For nitrogen, an early supply of N would have been steadily lost to space over the last past four billion yr.

Acknowledgements

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