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The present-day atmosphere of Mars: Where does it come from?

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ABSTRACT

Recent observations and missions to Mars have provided us with new insight into the past habitability of Mars and its history. At the same time they have raised many questions on the planet evolution. We show that even with the few data available we can propose a scenario for the evolution of the Martian atmosphere in the last three billion years. Our model is obtained with a back integration of the Martian atmosphere, and takes into account the effects of volcanic degassing, which constitutes an input of volatiles, and atmospheric escape into space. We focus on CO_2, the predominant Martian atmospheric gas.

Volcanic CO_2 degassing rates are obtained for different models of numerical model crust production rates [Breuer, D., Spohn, T. 2003. Early plate tectonics versus single-plate tectonics on Mars: Evidence from magnetic field history and crust evolution. J. Geophys. Res. - Planets, 108, E7, 5072, Breuer, D., Spohn, T., 2006. Viscosity of the Martian mantle and its initial temperature: Constraints from crust formation history and the evolution of the magnetic field. Planet. Space Sci. 54 (2006) 153–169; Manga, M., Wenzel, M., Zaranek, S.E., 2006. Mantle Plumes and Long-lived Volcanism on Mars as Result of a Layered Mantle. American Geophysical Union Fall Meeting 2006, Abstract #P31C-0149.] and constrained on observation. By estimating the volatile contents of the lavas, the amount of volatiles released in the atmosphere is estimated for different scenarios. Both non-thermal processes (related to the solar activity) and thermal processes are studied and non-thermal processes are incorporated in our modelling of the escape [Chassefière, E., Leblanc, F., Langlais, B., 2006, The combined effects of escape and magnetic field history at Mars. Planet. Space Sci. Volume 55, Issue 3, Pages 343–357.]. We used measurements from ASPERA and Mars Express and these models to estimate the amount of lost atmosphere.

An evolution of the CO_2 pressure consistent with its present state is then obtained. A crustal production rate of at least 0.01 km^3/year is needed for the atmosphere to be at steady state. Moreover, we show that for most of the scenarios a rapid loss of the primary (and primordial) atmosphere due to atmospheric escape is required in the first 2 Gyr in order to obtain the present-day atmosphere. When CO_2 concentration in the mantle is high enough (i.e. more than 800 ppm), our results imply that present-day atmosphere would have a volcanic origin and would have been created between 1 Gyr and 2 Gyr ago even for models with low volcanic activity. If the volcanic activity and the degassing are intense enough, then the atmosphere can even be entirely secondary and as young as 1 Gyr. However, with low activity and low CO_2 concentration (less than 600 ppm), the present-day atmosphere is likely to be for the major part primordial.

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1. Introduction

The present state and composition of the Martian atmosphere are usually assumed to be rather well known (Encrenaz, 2001; Hanel et al., 1972; Seiff and Kirk, 1977; Zurek, 1992; Owen et al., 1977; Smith et al., 1997). They have been constrained, in the last decades, by several missions and Earth based observations. The space missions have shown that the Martian atmosphere has dramatically changed in the last few billion years, and that a much denser and possibly wet atmosphere existed 3–4 billion years ago.

Most scenarios constrained by geomorphological observations (Masson et al., 2001; Head et al., 2001) assume that water was stable in earliest times of Mars (Zuber et al., 2000) due to an atmosphere much warmer, wetter and thicker than at present times. This is supported by studies on early hydrous melting and degassing of the Martian interior, leading to the formation of an atmosphere during the early Noachian (Médard and Grove, 2006), and by observations from the OMEGA spectrometer showing phyllosilicates and sulphates associated with Noachian outcrops (Poulet et al., 2005; Gendrin et al., 2005). The processes leading to the loss of the water are however still subject of discussion, but two of these, the early hydrodynamic escape and the late heavy bombardment, may be responsible for most of the escape (Brain and Jakosky, 1994).The

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amount of water lost is not known exactly and studies tend to point at rough values of 50–90% of the atmosphere (Brain and Jakosky, 1994).

In this paper, we adopt a different approach for estimating the pressure of the past atmosphere of Mars and propose to study it by modelling both the atmospheric loss and production in the last few billion years.

The present-day atmosphere on Mars is thin and mostly composed of CO_2 (95% of a 7 mbars atmosphere). Very little water vapour is present today in the atmosphere of Mars (around 0.03%).

It has been suggested that a large amount of CO_2 (equivalent to 1 to 2 times the present atmospheric CO_2) could be adsorbed in the Martian regolith (Zent et al., 1987). But this hypothesis is nowadays deemed as unrealistic since observation suggests that most of the subsurface at high latitudes contains water ice (Boynton et al., 2002) which prevents CO_2 to be stored in any relevant amount.

Recent observations from the Spirit and Opportunity rovers and the OMEGA team failed to uncover any sign of carbonates, confirming the negative detection of past studies (Pollack et al., 1990; Clark et al., 1990; Lellouch et al., 2000), even if buried carbonates or a very low abundance, below the present detection level, cannot be excluded. The most simple and realistic explanation would be that there might be no carbonates on Mars (Bibring et al., 2005), which will be our assumption.

The last possible reservoir of CO_2 (except from the mantle) is the ice caps. However, it has been observed that both Martian ice caps are mostly composed of water ice with only a thin CO_2 ice layer on top (Byrne and Ingersoll, 2003; Bibring et al., 2004, 2005). The pressure of CO_2 released by the sublimation of the south polar cap would only amount to a fraction of the present CO_2 atmospheric pressure (for a 10 m CO_2 layer in the polar caps, the pressure would be around 0.36 mbar).

For water, things are a little bit more complex. The polar caps are one of the reservoirs but we also know (Boynton et al., 2002) that extensive areas of Mars might contain subsurface water–ice deposits. It is however still difficult to obtain an accurate estimate of the amount of water available in these reservoirs and to find out how they interact with the atmosphere over geological timescales.

It is also crucial to have a good understanding of the different processes acting on the atmosphere. On one hand, it can be replenished by volcanic activity and the degassing of the mantle. On the other hand, the Martian atmosphere loses molecules to space due to atmospheric escape.

The history of degassing is uncertain due to the lack of measurements. However its importance is undeniable as stated by Phillips et al. (2001). Numerical models have yielded some estimates for crust production rates over time, but there is little data to constrain these results. Observations are limited to surface production and their relative ages obtained by crater counting (Hartmann and Neukum, 2001), but we require volumes to be able to determine the amount of gas production as well as the efficiency of degassing and some idea on the magma's volatile content.

Production rates are directly dependent on the activity of Mars and the observation of volcanic features can provide some constraints. The late activity in particular can be constrained by observation since recent volcanism on Mars is relatively easy to study (e.g. Neukum et al., 2004). However, the estimation of volatile contents and degassing rates still lacks reliable measurement data due in part to the difficulty of acquiring samples.

Much uncertainty also exists about how much gas has been lost to space. For sputtering (ions reimpacting the neutral atmosphere leading to the ejection of neutral particles) only, loss of CO_2 has been estimated to range from 60 mbar (Leblanc and Johnson, 2001, 2002) to 800 mbar (Kass and Yung, 1995, 1996). Part of this uncertainty is attributed to the poorly known date of the Martian dynamo extinction (Acuña et al., 1998; Lillis et al., 2005) and our study will therefore be focussed on the last 3 Gyr, after the extinction of the dynamo (Breuer and Spohn, 2003, 2006).

We have now identified the main processes for the evolution of CO_2 in the atmosphere (with the absence of other extensive reservoirs for the atmosphere to exchange carbon). These processes are discussed in more detail in the second section.

2. Model and data

Even with the few available data that exist, it is possible to obtain significant insight in the way an atmosphere evolves as a result of its loss of volatiles into space and replenishment from the tectonic activity. Complex models would be impossible to constrain efficiently but the trend can be obtained by simple models of the physical interactions and mechanisms. These results seem sufficient to draw a general scenario of the evolution of the Martian atmosphere.

A simple model is used to compute the evolution of volatiles over time in the atmosphere of Mars during the last 3 Gyr. We focus on CO_2. As a first step we consider degassing and escape as the two main processes controlling the history of the atmosphere. Water is more complex to model, with many new parameters, and will be considered in the future. The results obtained for CO_2 (expressed as a pressure) correspond to the total amount of CO_2 present in the surface reservoirs.

The atmospheric escape model is constrained by data and relevant for the whole planet. The model is described in detail by Chassefière et al. (2006) and data are used from the ASPERA experiment on Mars Express (Carlssona et al., 2006).

Degassing is taken from published numerical models (dealing with internal dynamics) obtained by several teams working on the evolution of the Martian mantle (Breuer and Spohn, 2006; Manga et al., 2006; O'Neill et al., 2007). They supply us with the crustal production rate evolutions over time, which allow us to compute an approximation of the degassing by using chosen efficiencies and compositions. The degassing model is heavily dependent on the choice of degassing efficiency and mantle composition as demonstrated below.

Our approach starts from the present and goes step by step back in the past by using the source of CO_2 and atmospheric escape to update the Martian atmospheric pressure. In terms of equation, this means:

$$Q_{CO_2}(t-\delta t) = Q_{CO_2}(t) - \delta t \times D + \delta t \times E,$$

where Q_{CO_2} 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.

We take CO_2 as the major atmospheric constituent over the last 3 Gyr (Manning et al., 2006). Known escape or trapping processes do not seem to have been able to remove other gasses efficiently enough to allow us to take them into account.

We also calculate the evolution of the ratio between late atmosphere (created by volcanism degassing) and early atmosphere (what remains after the first 1.5 to 2 billion years of evolution of Mars). We assume that the atmospheric escape does not discriminate between the two origins of the atmosphere and that the total amount of “early” (or primordial) atmosphere is given by the pressure at the minimum seen around 2.5 Gyr ago in the CO_2 pressure evolution (see Figs. 4–8). When no minimum is observed, we use an arbitrary time of 2.5 Gyr for the transition. This allows us to compute the fraction of atmosphere older than 2.5 Gyr and the younger fraction. The early atmosphere (i.e. older than 2.5 Gyr) is not the primordial one, as a fraction of it can still be secondary. This however provides us with a first estimate of the mean age of the atmosphere.

2.1. Volcanic degassing

Volcanism is the major input of CO_2 for the atmosphere of Mars, considering the absence of any other major reservoir such as carbonates or CO_2-rich polar ice caps (our hypothesis in this study).

Geophysical modelling of the activity of Mars provides us with estimations of the amount of lava produced (km^3/yr). Geological data obtained through the observation of the volcanic provinces of Mars and the dating of lava flows can be a means to constrain this volumetric lava production rate. This allows us to deduce the massic production per year assuming a basaltic density and then the amount of volatiles released into the atmosphere.

As an input for the amount of volatiles released into the atmosphere, we mainly use data from numerical studies (Fig. 1) from Breuer and Spohn (2006) and Manga et al. (2006) but also consider other sources such as O'Neill et al. (2007). Breuer and Spohn compute the amount of crust produced during the evolution of the Martian mantle. They used a parameterized model of stagnant lid convection with core cooling, mantle melting and crust production, constrained by a given crustal thickness and the magnetic field history. This model enables us to test different scenarios for several mantle temperatures but also an evolution including the presence of primordial crust. This last scenario gives estimates of crust production that are much lower than when no primordial crust is considered and tend to agree more with values cited by O'Neill et al. (2007) or measured by Greeley and Schneid (1991).

To broaden our study by other possible realistic evolutions, we use a slightly different model adapted from data by Manga et al. (2006) who obtain stable plumes and long term volcanism over most of the evolution of Mars which might be necessary both for the formation of the Tharis province and the recent volcanic events observed by Hartmann and Neukum, 2001. Their estimate of the evolving crust production rate is somewhat lower than in the model by Breuer and Spohn but shows production rates of the same order (see Fig. 2).

We also compared these results with other data from Hartmann and Neukum (2001), obtained by observation of the surface of the planet. However, comparisons are difficult because observations only provide us with estimates on the area of produced volcanic rock. Observations seem to indicate activity weaker than for numerical models, even with estimates such as those by Greeley (1987), who found an average flow thickness of 1 km. This result has later been lowered to 200 m (Greeley and Schneid, 1991), which is probably more realistic. On the other hand, these observations are not taking into account intrusive processes that may occur.

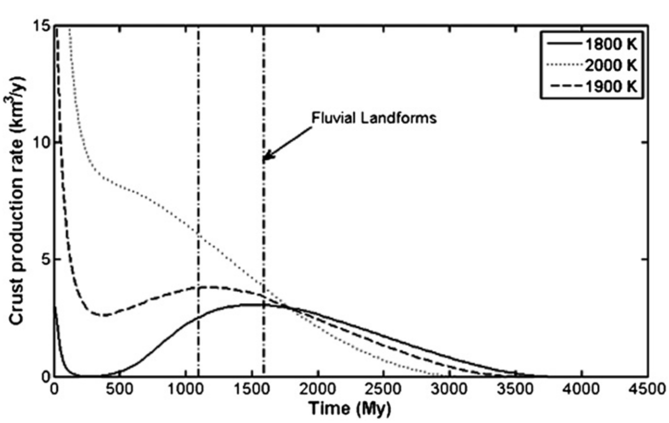

Fig. 1. Evolution of crust production rates, for two different mantle temperatures, adapted from the results of a numerical model for Martian internal dynamics by Breuer and Spohn (2006). The solid line corresponds to the main model considered here, with a 1800 K mantle. The dashed line corresponds to a slightly hotter 1900 K mantle and the dotted line to a 2000 K mantle.

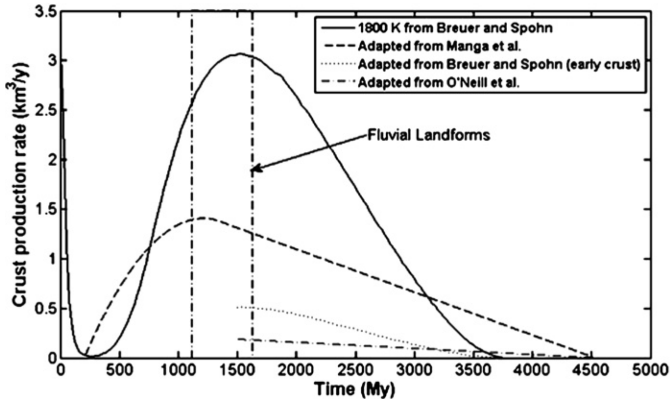

Fig. 2. Evolution of crust production rates, for two different numerical models. The solid line corresponds to the cool mantle case in Fig. 1, adapted from Breuer and Spohn, 2006. The dashed line is adapted from a numerical model by Manga et al. (2006).

Therefore, we also included the model of O'Neill et al. (2007) essentially an extension of Greeley and Schneid (1991) as a lower bound. These crust production rates are even lower than those from Manga et al. or Breuer and Spohn (even with primordial crust) and fit better with the observation of the surface of Mars. They propose volcanic rates ranging from over 0.17 km^3/yr for the Hesperian to around 10^{-4} km^3/yr at present, in agreement with the value of 0.02 km^3/yr for average post Noachian extrusion rates proposed by Greeley and Schneid. In this case, we apply a linearly decreasing profile with lower production rates, comparable to those proposed by O'Neill et al. These values are based on observation from Greeley and Schneid (1991) and fit with studies from Hartmann and Neukum (2001).

Our models are therefore chosen in order to include the wide range of possible evolutions as featured in the recent literature. The evolution of crust production rates show mainly decreasing profiles over the time period studied here but feature several small differences (Manga et al.'s is mainly linear whereas Breuer and Spohn's decreases faster in the early period). The values here are also chosen to take into account both the high end of the estimations of the Martian activity and the lower values used by O'Neill et al. or Greeley and Schneid (1991).

As it has been stated above, results might depend heavily on compositional data. Few well constrained and dependable data exist on the CO_2 content due to the lack of samples, limited to the Martian meteorites. We compared different sources that gave insight in this problem. Fig. 3 shows a small compilation of results (considered as post eruptive contents) that have been obtained from Martian meteorites and also some results for Earth for comparison. Our values (between 200 ppm and 2000 ppm) are within the range of published estimates. Several results on Martian meteorites lead to the assumption that either CO_2 is quite rare in the Martian mantle or that the degassing is quite effective, maybe due to low surface pressure. However, some data support larger CO_2 contents, as some SNC measurements show much higher concentration than the average value. Moreover, if Mars is not much different from the Earth, its mantle might contain much more CO_2 than Martian meteorites seem to suggest and the degassing is quite efficient. Another hypothesis (Kuramoto, 1997) even hints at larger CO_2 concentrations due to higher silicon content in the core. It has however been suggested that concentrations much higher than 3000 ppm would not be consistent with today's data as they appear in Fig. 3. With this in mind, we did not use very high concentrations such as those proposed by Phillips et al. (2001), with a 0.65 wt.% CO_2 (6500 ppm) in the lavas of Tharsis.

However, all samples used above to estimate CO_2 contents are degassed samples, depleted with regard to their initial state. The efficiency of the degassing is missing for obtaining the atmospheric production.

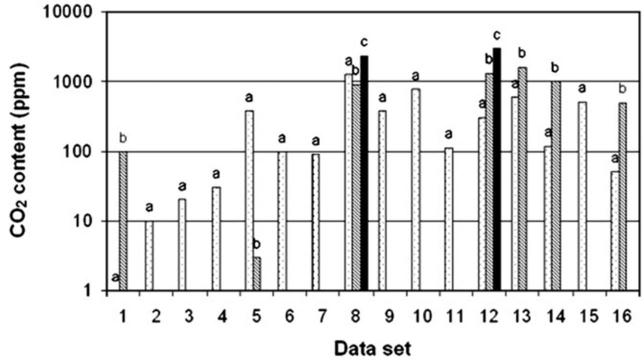

Fig. 3. Compilation of estimates from the literature of the CO_2 contents of degassed lavas on Mars. Each data set is composed of one, two or three values, being either different results or extreme values as indicated below. 1. M.M. Grady et al., 2004, Martian meteorites. 2. ALHA77005, a) Wright et al. (1986), b) Gooding et al. (1990) is zero. 3. EETA79001A, Wright et al. (1986). 4. EETA79001B, a) Wright et al. (1986), b) Gooding et al. (1990) is zero. 5. EETA79001C, a) Gooding et al. (1990), b) Wright et al. (1986), c) Gooding et al. (1990) is zero. 6. Shergotty, Wright et al. (1986). 7. Chassigny, Wright (1990). 8. EETA79001A Gooding et al. (1990). 9. EETA79001C, Gooding et al. (1990). 10. Nakhla, Gooding et al. (1990). 11. Nakhla, Carret al., (1985). 12. Terrestrial MORBs, Jambon (1994), a) Minimum value, b) mean value, c) maximum value. 13. Terrestrial mean abundance, Jambon, a) Minimum value, b) Maximum value. 14) CO_2 content of Martian lavas used in this study, a) minimum value, b) maximum value. 15) Estimate for Iceland volcanism used in O'Neill et al., 2007. 16) Earth upper mantle content by Trull et al., 1993.

This parameter depends on many other conditions such as the surface temperature, the volatile content of the lavas, the state of the hydrosphere and so on. Even on Earth, studies are not categorical; in many ways we do not know what fraction of the volatiles contained in the molten material is released into the atmosphere (Eric Hummler, private communication, 2007). No existing method or experiment has been able to yield reliable results. And even so, it is doubtful that they could directly be applied to Mars.

In our model the releasing of 30% of a given CO_2 concentration would lead to results that would be the same as with a releasing of 90% and three times less CO_2 or of 3% and ten times more CO_2, since the total amount of degassed volatiles is the same in the three cases. Therefore we assume that all the volatiles contained in the melted material can be released into gaseous form due to low atmospheric pressure (thus explaining the low CO_2 contents of the Martian meteorites). What could help us to distinguish between these possibilities would be measurements of the composition CO_2 in the basalt after a lava flow has cooled. But even then, in order to obtain definite results, we would have to establish a clear estimate of the initial CO_2 content of the lava in a non-degassed sample.

In our model the efficiency parameter takes into account the fact that not all the released volatiles can reach the atmosphere (for example if the melted material does not reach the surface); thus the efficiency measures the fraction of volatiles that enter the atmosphere relative to the amount of volatile present in the lava. We arbitrarily chose an efficiency of 15% because all produced melted material is not reaching the surface. Since we are not able to calculate the fraction of lava reaching the surface (some studies with self sufficient internal dynamics modelling have calculated this parameter as in O'Neill et al., 2007), our value of 15% is not precise. However, it seems reasonable as it falls between the boundaries estimated by Greeley and Schneid (1991) for the efficiency factor, namely 5 to 20%. We will not vary this parameter because its effects are the same as varying the CO_2 content. It is best to keep a common value and leave just one free parameter.

2.2. Atmospheric escape

Atmospheric escape is the main way of efficiently removing volatiles from the atmosphere. Other interactions are minor since we cannot find any other significant CO_2 reservoirs and a single plate stagnant lid convection mechanism is thought not to allow mantle regassing (Hauck and Phillips, 2002).

Atmospheric escape can occur either through thermal or through non-thermal processes.

We use data from Chassefière et al. (2006) to quantify the amount of gases (H_2O and CO_2) lost to space during the last 3 Gyr through non-thermal processes such as sputtering, dissociative recombination, ionospheric outflow and ion pick-up (see their Fig. 4). This Fig. shows the loss rates of CO_2 and H_2O on Mars for the different processes detailed here. These processes correspond to the different ways radiation from the Sun interacts with the atmosphere and contributes to driving away part of it:

Sputtering corresponds to a mechanism where ions produced in the corona or in the ionosphere can reimpact the neutral atmosphere with enough energy to lead to the ejection of an important quantity of neutral atmospheric particles (see Luhmann and Kozyra, 1991).

During dissociative recombination, ions produced in the ionosphere by UV photo-ionization recombine with electrons and form in some cases energetic neutrals with enough energy to escape Mars.

Ion pick-up is another escape process: ions produced by photo-ionization, electron impacts and charge exchanges in the Martian exosphere are dragged along by the moving solar magnetic field lines wrapping around the planet.

Ionospheric outflow is the last considered process: ions are produced within the ionosphere (below the exobase) and can in some cases flow up to the ionopause where they are also dragged away by the solar wind.

It is thought that those processes are strongly dependent on the solar EUV flux. Solar UV emission is supposed to have been higher in the past than at present time, thus explaining the higher values before 2 Gyr (Chassefière et al., 2006). To account for this dependence, the time scale has been divided into three different eras, each corresponding to a given EUV flux, 1 EUV (1 time the present minimum EUV flux), 3 EUV and 6 EUV.

From observation of other solar-type stars, it is possible to obtain rough estimates of the time periods corresponding to these eras and a possible parameterization for the solar EUV flux (Ribas et al., 2005):

$$\text{Flux} = \text{Flux}(\text{present average cycle conditions}) \times [\text{Age(Sun)}/\text{Age}]^{1.23\pm0.1}$$

where Flux is the EUV flux and 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.

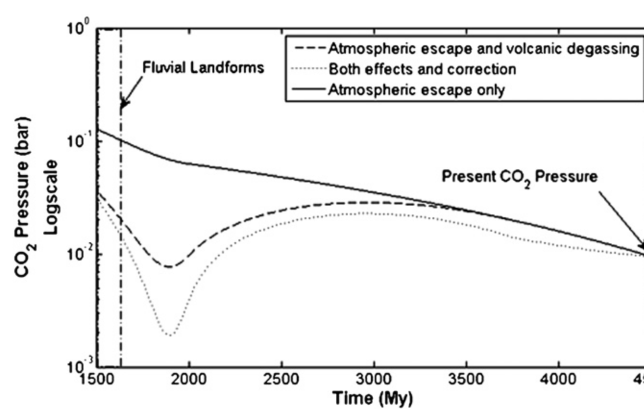

Fig. 4. Evolution of maximum CO_2 pressure in the atmosphere of Mars over the last three billion years. The vertical axis is a logscale. Efficiency of degassing is set to 15%. The CO_2 content is set to 240 ppm. The interior dynamics model used here is adapted from Breuer and Spohn (2006) as shown in Fig. 1 with a 1800 K mantle. The solid line shows the effect of atmospheric escape only. The dashed line shows the effects of atmospheric escape and degassing. The dotted line shows the effects of atmospheric escape and degassing with a correction for recent times. The box shows times when fluvial landforms were formed (Mangold et al., 2004).

This explains the evolution of the different curves shown by Chassefière et al. (2006) in their Fig. 4. The change of slope in the same figure is attributed to the non-linearity of the processes. We assume that one oxygen atom escapes with two hydrogen atoms and that one Carbon atom is associated with two oxygen atoms. The H_2O loss rate is at least one order of magnitude higher than CO_2 loss rate. So here, we use the CO_2 loss rate as the limiting parameter.

In the model we use, the escape rate of CO_2 is calculated for the different epochs (1EUV, 3 EUV and 6 EUV) by using the calculations from Zhang et al. (1993) on the structure of the upper Martian atmosphere at those times and then with different methods depending on the escape mechanism. The CO_2 loss through dissociative recombination is found using studies from Fox (2004) who calculated the carbon escape for solar minimum and maximum conditions. A simple exponential law is used to interpolate the escape flux for earlier periods. The loss associated with ionospheric outflow is also extrapolated (assuming an exponential dependency) from escape rates for solar minimum and maximum calculated by Ma et al. (2004). The effect of sputtering is calculated from studies by Leblanc and Johnson (2002). Finally, ion escape rates depend from sputtering and dissociative recombination as the amin mechanism producing carbon neutral particles in the Martian corona.

As new data have become available from space missions, we included those in our models. The latest ASPERA measurements for the present-day atmospheric escape (Carlssona et al., 2006) have been included. The values are somewhat lower than what was previously found (and is used Chassefière et al., 2006): 0.29 kg/s for the CO_2 loss rate.

The main thermal processes are hydrodynamic escape and Jeans escape. They are not major mechanisms of escape in the late history of Mars. Hydrodynamic escape consists of a complete expansion of the whole upper atmosphere due to the high energy of solar emissions (Chassefière, 1996a,b). It is a critical case of Jeans escape. Jeans escape occurs (only for light species such as H, and sometimes H_2 and He; others are too heavy) in the exosphere, that is to say in the absence of collision, when the radial speed of a species is higher than the escape velocity. The atmosphere is not gravitationally linked to the planet anymore and it is globally blown off, entraining heavier species.

Hydrodynamic escape occurs only when a high quantity of EUV (Extreme UV) radiation enters the system in the high atmosphere; moreover it requires a H-rich thermosphere. It thus needs, for example, a primordial H_2/He atmosphere. Moreover, hydrodynamic processes only take place during the first hundreds of million years. Jeans escape still occurs but only depletes slightly the tail of the

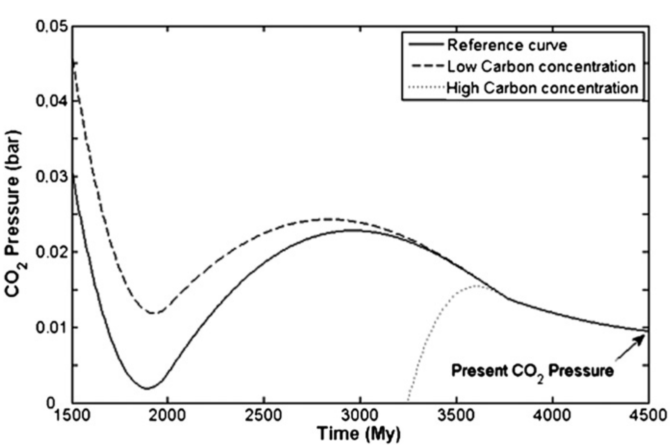

Fig. 5. Evolution of maximum CO_2 pressure over time for several CO_2 contents of the lavas. The model is adapted fromBreuer and Spohn (2006) with a cool mantle. Efficiency is set to 15%. The solid line shows the evolution with low CO_2 content (240 ppm, reference model). The dashed line is for lower CO_2 content (200 ppm). The dotted line is for a higher CO_2 content (1200 ppm).

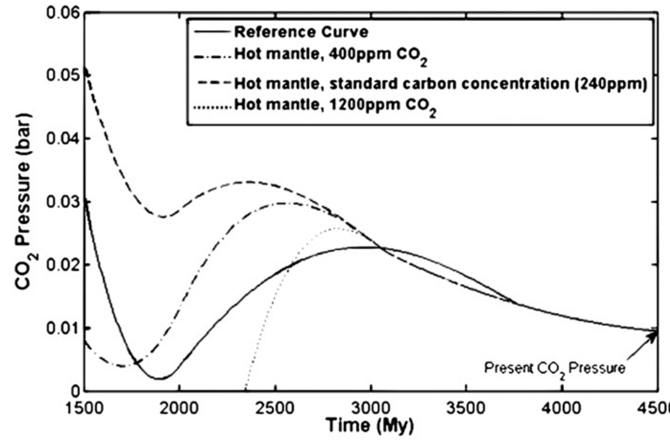

Fig. 6. Evolution of the maximum CO_2 pressure for different interior dynamics and crust production models adapted from Breuer and Spohn (2006). Three CO_2 contents are used. Efficiency is set to 15%. The cool mantle model is included for comparison (solid line). All other models use the hot mantle model. The dashed line shows results for 240 ppm CO_2. The dotted line is for 1200 ppm. The dashed and dotted line is for 400 ppm.

molecule distribution for hydrogen atoms which are not our main subject here. Since our model focuses on the last 3 Gyr, we can neglect the effect of the heavy bombardment.

3. Results

Our results are presented in Figs. 4–8. They show the evolution of maximum CO_2 pressure given fixed present-day conditions, that is to say the amount of CO_2 in the atmosphere at a given time in order to obtain the present state.

Fig. 4 demonstrates the three components of the model: evolution of maximum CO_2 pressure when only atmospheric escape is considered, when we take the degassing of the mantle into account, and when we correct for the late crust production model to fit the present atmospheric escape. Here we use crust production rates from Breuer and Spohn (2006) with a large CO_2 input.

The first result, when considering only atmospheric loss of CO_2 to space, is a steady decrease of the atmosphere's CO_2 pressure over the past 3 billion years. Moreover, 3 Gyr ago the maximum CO_2 pressure barely reached 0.12 bar. This means that even 3 Gyr ago, a thick CO_2 atmosphere was unlikely on Mars. This is consistent with studies implying that thick CO_2 atmospheres would first condensate then

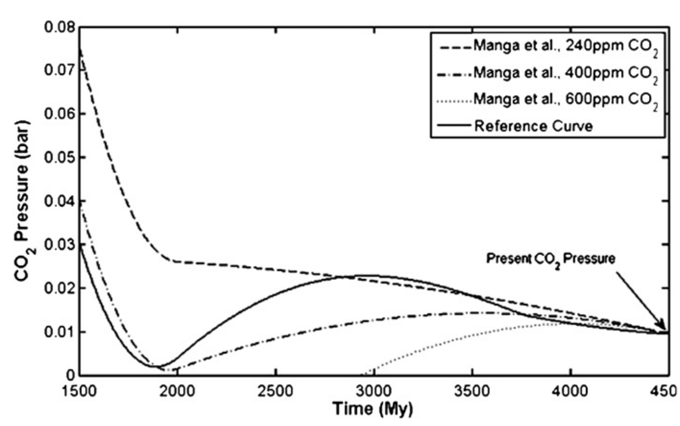

Fig. 7. Evolution of maximum CO_2 pressure; comparison of two models. Three CO_2 contents are used here (240, 400 and 600 ppm). Efficiency is set to 15%. The Breuer and Spohn (2006) model with low (1800 K) mantle temperature is indicated by the solid line (240 ppm CO_2). The dashed line (240 ppm), the dashed and dotted line (400 ppm) and the dotted line (600 ppm) indicate the Manga et al. (2006) model.

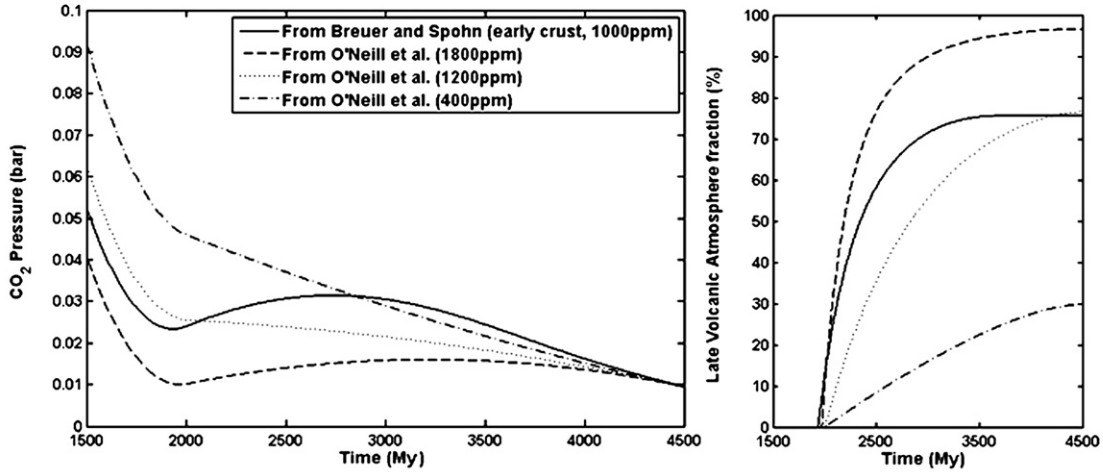

Fig. 8. Evolution of the maximum CO_2 pressure (left) and fraction (%) of the late volcanic part of the atmosphere (right). Efficiency is 15%. Solid line shows the evolution of the CO_2 pressure for a degassing adapted from Breuer and Spohn (2006) with primordial crust (1000 ppm), the dashed line shows the evolution for a model adapted from O'Neill et al. (2007) with 1800 ppm, the dotted line for O'Neill et al. (2007) with 1200 ppm and the dotted and dashed line for O'Neill et al. (2007) with 400 ppm. The legend is the same for the right-hand panel.

precipitate at ~1 bar. (Catling and Leovy, 2007). This result could be tested in the future with a better measurement and modelling of the mean eolian erosion rate in the last 3 Gyr.

The second curve of Fig. 4 shows the cumulative effects of atmospheric escape and degassing based on crustal production rates from Breuer and Spohn (2006). Values for the maximum CO_2 pressure are significantly lower and stay on the order of several to several tens of millibars. It shows a period around 2.7 Gyr ago when CO_2 pressure was minimal. This means that the later atmosphere's main constituent is CO_2 of volcanic origin and that Mars has lost a significant part of its primordial atmosphere.

The last curve includes a correction used to represent the fact that today Mars is still active (Neukum et al., 2004, show that volcanic events occurred less than 100 Myr ago with phases of activity as young as 2 Myr). The amount of present-day volcanism was chosen to balance present atmospheric escape.

This is linked to a problem that retained our attention; the question of the equilibrium of CO_2 cycles on Mars and the Earth, which depends directly on their activities. Contrary to Earth, atmospheric escape is occurring at the present day on Mars. Since there is still some CO_2 ice left on the Martian South Pole, it can be hypothesised that CO_2 ice sublimation compensates for this atmospheric escape. This case, however, seems quite surprising, since we would be witnessing the "last days" of CO_2 ice on Mars. Given the relatively small amounts of CO_2 ice at present time (assuming the ice caps are mostly water ice), the process cannot last long. Maybe there are other processes that could replenish the CO_2 lost into space.

We tried to compare the efficiencies of atmospheric replenishment. On Mars, at present time, it takes around 800 Myr for 10 mbar of atmosphere to escape. Earth is not subject to atmospheric escape but another mechanism exists: CO_2 precipitates and is extracted from the atmosphere when carbonates are trapped in subducting oceanic crust (Javoy et al., 1982). This process extracts around 1 bar every 50 Myr. A quick calculation gives us the ratio of the speeds of extraction: 1/1600. If we assume the atmosphere of Mars and the Earth are near steady state, the integrated activity of Mars should be around 1600 times less that of the Earth. Considering Earth's crust production to be around 20 km^3/year, we find that Mars' crust production should be around 0.0125 km^3/year. This number is really small but seems to be in agreement with numerical studies such as those from Breuer and Spohn (2003, 2006) that indicate low mean crustal production over the last 500 Myr. If the CO_2 contents on Mars is comparable to the Earth one, present Martian crust production rates of around 0.01 km^3/year are sufficient to obtain a balance between atmospheric escape and volcanic degassing. The much lower estimates of Greeley and Schneid (10^{-4} km^3/yr) will imply a degassing efficiency two orders of magnitude better to lead to a steady regime.

Interestingly, we also find in this case the minimum around 2 Gyr. Most of our examples suggest that we can obtain today's Martian atmosphere without needing much, or even without, primordial atmosphere. In fact most of it is a product of volcanic activity and thus a secondary (and quite recent) atmosphere, instead of the remnant of a primordial atmosphere as often thought.

Mangold et al. (2004) have recently proposed that episodic fluvial periods have existed on Mars in the Late Hesperian. They illustrate this hypothesis with several valley networks near the equator. As this period seems to coincide with both the maximum in crust production rates from models we use (Breuer and Spohn, 2006; Manga et al., 2006) and the high pressure of 20–30 mbar observed in the first 500 Myr of our reference time (i.e. 3–2.5 Gyr before present), we perform an estimation of the water content associated with such an atmosphere. Moreover, around 1.5 Gyr ago, we observe a similar CO_2 pressure indicating that the atmosphere might have been able to sustain liquid water to some extent.

To explore this hypothesis, we can make a simple calculation. Assuming the relative proportions of CO_2 and H_2O are roughly the same in Martian lavas as in those from Earth (Phillips et al., 2001, use 0.65 wt.% CO_2 and 2 wt.% H_2O on Earth for Hawaiian basaltic lavas), and that the only source of water and CO_2 is volcanism, we can calculate an approximate H_2O partial pressure.

$$P(H_2O) = P(CO_2) \times n(H_2O)/n(CO_2)$$

where $P(i)$ is the partial pressure of component I and $n(I)$ is its molar fraction.

Thus we find that the partial pressure for H_2O would roughly be 7.5 times higher than the partial pressure for CO_2. With our results, this amounts to more than 150 mbar around 1.5 Gyr ago. H_2O, however, is lost around ten times faster than CO_2 so it stays in the atmosphere for a much shorter time. Thus we can realistically divide the previous result by 10, leading to an estimation of more than 15 mbar H_2O at these times. This is well above the triple point (around 6 mbar) in a water phase diagram and, provided the surface temperature is high enough, liquid water could have been present at least during brief episodes. Volcanic emissions would also release large quantities of SO_2 in the atmosphere, thus leading to short term warming. The high loss rate of H_2O might also explain why fluvial landforms are found by Mangold et al. (2004) only between 3.6 and 2.9 billion years ago.

Before that, water was not able to accumulate as it was efficiently removed from the atmosphere. The amount of water in the atmosphere thus depends on the production rate rather than on a constant build up during the first billion year. It follows that it is only when degassing is at its peak (this period corresponds with the maximum in both models from Breuer and Spohn, 2006 and Manga et al., 2006), that the amount of water in the atmosphere might be high enough to create fluvial landforms.

We considered several models to test the influence of CO_2 content in the molten material used for the degassing (see Fig. 5). We assumed that 15% of the volatiles was released into the atmosphere in this model. CO_2 contents vary from 120 ppm to 1000 ppm.

We observe that for low CO_2 content, most of the late atmosphere is of volcanic origin and that 2.7 Gyr ago we observe a period where CO_2 pressure was very low.

In the models where the amount of CO_2 available is higher, the maximum CO_2 pressure drops. In order to obtain the present-day atmosphere, given the higher CO_2 inputs forced by volcanism, the atmosphere must have been lost around 1.5 Gyr ago. We can calculate the mean age for these atmospheres and it ranges from 2.2 to 1.9 Gyr. It should also be noted that the atmosphere is created very rapidly. 20 mb are produced in 500 Myr only.

However, this evolution requires an efficient mechanism for the removal of the atmospheric CO_2 in order to compensate the rather high CO_2 emissions due to degassing and to explain the near absence of CO_2 before 1.5 Gyr ago. The impact erosion is too small and no widespread carbonate layer has ever been discovered, which suggests that it might never have formed. At the present state of our studies, we cannot propose a likely mechanism for such an important atmospheric loss. Hence it might be that, considering the employed model, higher CO_2 compositions of the lavas may not be compatible with the present-day situation.

Other models were used to study the influence of global activity on the evolution of maximum CO_2 pressure. Those are presented in Fig. 6. Breuer and Spohn (2006) give the curves for several crust production rates, depending on the initial temperature of the mantle. We compare results for a 2000 K hot and a 1800 K mantle (used in the previous model).

The solid line corresponds to the cases above and is shown for comparison. It still exhibits the minimum CO_2 pressure around 2.7 Gyr ago.

We see that for low CO_2 content (240 ppm), “higher” pressures can be obtained (of the order of 50 mbar compared to 30 mbar previously). In this case, the present-day atmosphere is mostly a remnant of an older one (prior to 3 Gyr ago) whose loss to space has been the main factor in its evolution. However, as soon as we use higher CO_2 contents, the same pattern as for the “cold mantle” model occurs and it appears that the present-day atmosphere is a volcanism-produced one.

The atmospheres obtained with these scenarios are a little older than in the previous case due to the late period of lower volcanic activity (the last 1.5 Gyr instead of the last 750 Myr). Here, the Martian atmosphere is roughly 2.0 Gyr old.

We also used an alternative model for the crust production rate, adapted from a study by Manga et al. (2006) as discussed above.

Fig. 7 shows a comparison between the results obtained with this model and those based on Breuer and Spohn (2006) for two different CO_2 contents of the mantle. Results with this new evolution of crust production differ to some degree from what we found before.

For the low end value of our range of mantle compositions (240 ppm CO_2), the evolution of maximum CO_2 pressure does not show any minimum in the early period (around 2.7 Gyr). The model allows up to 70 mbar CO_2 in the atmosphere 3 Gyr ago.

The other curves show the evolution with twice as much CO_2 in the mantle. In this case, we observe again the minimum and an atmosphere without much CO_2 before 2 Gyr ago.

We also compare two different possibilities for atmospheric escape models: one adapted from Chassefière et al. (2006), the other from ASPERA present-day data (Carlssona et al., 2006). The latter presents a structure that is similar to our other results. In this model, the lower present-day escape implies that the planet could have lost less CO_2 to space during the past few tens of million years than in the other (with higher escape). It thus means that the past atmosphere was even less dense with this low escape rate model. This would favour the young present-day atmosphere hypothesis.

However, new (and still unpublished) developments seem to imply that the low escape rates used here might underestimate the total atmospheric escape on Mars since ASPERA didn't take into account low energy ion flux that seem to be the main means of atmospheric loss. To this day no definitive answer has been found and results vary depending on the method used to calculate the escape rate. The new values should be higher than what is shown here, but we don't know how much higher due to the lack of data and constraints. Therefore our high escape rate model might be more realistic than the other one.

O'Neill et al. (2007) propose a different range of values for the volcanic CO_2 input flux based on Greeley and Schneid. Their volcanic rate is lower (around 0.17 km^3/yr for the Hesperian and 10^{-4} km^3/yr at present) and is constrained by the observation. These, along with results of calculations using results from Breuer and Spohn's model with primordial crust, are shown on Fig. 8. We use a constant decrease during the past 3 Gyr as O'Neill et al. do not show any precise evolution profile. We ran the model with their values, using both low (≈200 ppm) and high (from >500 ppm, i.e. what O'Neill et al. use in their calculations, to 2000 ppm) CO_2 concentrations and a 15% efficiency as for our other calculations. Results for high CO_2 contents that still correspond to Earth-like conditions (1600 ppm and above) are similar to what we obtained in our previous models and they exhibit the same features (secondary atmosphere, pressure drop 2.5 billion years ago, higher pressure 3 billion years ago) with the same range of pressure values. In this case the late evolution, between 2 billion years ago and present time, does not exhibit large variations. Instead, after the strong decrease in pressure ending 2.5 Gyr ago, the minimum is not as marked as with crust production rates from Breuer and Spohn, even if values reached are of the same order. With CO2 concentrations higher than 1400 ppm (and using crust production rates from O'Neill et al.), the present day atmosphere is always composed of more than 90% of volcanic gazes. Moreover, an estimate the mean age of the present-day atmosphere gives values of around 1.25 Gyr.

However, with lower volatile contents, the atmospheric escape is dominant. These lower CO_2 concentrations range from 240 ppm to roughly 800 ppm and are compatible with data we have on Martian conditions (and Earth-like conditions). In this case the present-day atmosphere is definitely a remnant of the primordial atmosphere. These concentrations lead to present-day atmospheres containing less than 55% volcanic gazes and that are older than 1.8 to 2 Gyr. Between the two behaviours mentioned above, we obtain a range of intermediate CO_2 concentrations that produce a situation where part of the atmosphere is clearly produced by the volcanism but where no minimum is visible on the figure. In these cases however volcanic gazes are a major component of the present-day atmosphere as it is made of between 55% (for 800 ppm) to 76% (for 1200 ppm) late degassed volatiles. The estimated mean age of the atmosphere in these intermediary cases is around 1.6 Gyr.

The results of the calculations using the model from Breuer and Spohn including primordial crust are similar to those detailed above. We tested different CO_2 concentrations ranging from 200 ppm to 2000 ppm. Just like in the previous case, when the amount of degassed CO_2 was sufficient to counter the atmospheric loss, we see the same minimum around 2.5 Gyr ago then atmospheric growth due to volcanism and finally decrease toward the present-day situation. To obtain this evolution and a secondary atmosphere, we need more than

800 ppm CO_2 (and less than 1500 ppm). Unlike what happened in the previous case, with this crust production rate model, the late maximum due to volcanism is well marked. We calculated in this case with a CO2 concentration of 1000 ppm, that the present-day atmosphere would be composed of 75% of volcanic gases and be 2 Gyr old. For higher concentrations such as 1200 ppm, we obtain 88% of late atmosphere but the age of the atmosphere stays roughly the same.

Lower CO_2 concentrations (<600 ppm) in the mantle, however, will lead to the atmosphere not being supplied with enough volatiles to create a secondary atmosphere, therefore removing the late maximum and the possibility for present-day atmosphere to be of volcanic origin. In this case the atmospheric escape is the most visible process. 800 ppm corresponds to roughly 60% late atmosphere and 600 ppm to 45%.

We finally calculated the same ratio between late and early atmosphere for the Breuer and Spohn crust production model that did not include any primordial crust and obtained for 200 ppm a value of 88% late volcanic gazes in the present-day atmosphere. However, its mean age is still 1.9 Gyr.

The different pressures we obtain in these cases are compatible with the existence of fluvial landforms around 3 billion years ago as found by Mangold et al. (2004). Moreover when we use the crust production rates from Breuer and Spohn with primordial crust, the CO_2 pressure at the late maximum leads us to calculate a water partial pressure of 22 mbar following the method detailed above. This pressure would be high enough for sustained liquid water in a warm atmosphere, possibly due to volatiles (maybe sulphur) released by the volcanic activity. With the values cited by O'Neill et al., the same calculation gives similar results but with a lower value (11 mbar), much closer to the triple point pressure: this makes liquid water less likely.

4. Discussion and outlook

Let us summarize our results. Depending on the volcanic production rate and the loss rate several scenarios can be proposed.

For a low volcanic activity, comparable to O'Neill et al., i.e. ~10^{-4} km^3/yr at present, we find that about half of the present atmosphere was produced in the last 2.5 Gyr, with a mean age of about 1.8–2 Gyr. The evolution of the atmospheric pressure is mainly a steady decrease with time.

For a higher volcanic activity of about 10^{-2} km^3/yr at present, corresponding to the models from Breuer and Spohn or Manga et al., or for more efficient degassing of CO2 rich lava of the O'Neill et al. model (more than 1000 ppm), we have a completely different result with more than 75% of the present atmosphere produced during the last 2 Gyr. In this case, the age of the present atmosphere ranges between 1.25 and 1.6 billion years. The evolution of the atmosphere occurs in two phases. First a steady decrease between 3 Gyr ago and 2.5 Gyr ago, leading to a minimum with a tenuous atmosphere. Then an atmospheric regrowth occurs due to volcanism, leading to the present atmosphere.

Following our study, results support the idea that the present-day atmosphere could be a young atmosphere created mainly by volcanic degassing. Our models show that as long as volatiles reach the atmosphere in sufficient amounts, which seems possible even with models presenting a low activity (such as ones from O'Neill et al.), volcanism can play a distinct role in the evolution of the atmosphere. In this case, the present atmosphere would be composed from CO_2 of volcanic origin. Thus, the present-day atmosphere only needs 800 ppm CO_2 in the mantle to be composed of 55% volatiles of volcanic origin, which is reasonable. However, a primordial origin for the present-day Martian atmosphere seems to be possible. It could indeed be that the CO_2 content of the mantle is low enough, or that few volatiles reach the surface. It seems likely that the volcanic activity is low (corresponding with the lower estimations used in this study) but that parameter only does not precludes the possibility of a young atmosphere.

However, if several factors are present (strong atmospheric escape, low volcanic activity and especially low CO_2 contents) then atmospheric escape becomes the dominant mechanism and the effect of volcanism becomes negligible, leading to a present atmosphere being mostly the remnants of an old eroded one. For the atmosphere to be young, the CO_2 content of the Mantle needs to be quite high, with values depending on the crust production rate evolution. In the case of the models from Breuer and Spohn (2006) without primordial crust, or Manga et al. (2006), we need roughly 400 ppm CO_2 in the upper mantle. However with more realistic assumptions as the model with primordial crust from Breuer and Spohn or the values found by Greeley and Schneid (supported by observation and compatible with studies by O'Neill et al.) will require values higher than 800 ppm to create a substantially young atmosphere. While these concentrations are conceivable and could occur on Mars, they are quite important. This implies that to find out more about the CO_2 concentration in the Martian mantle might allow us to discriminate between the different evolution proposed in this study and decide if the present atmosphere is quite recent or not.

We can also look at these results from another point of view by studying how much CO_2 was left after the first billion years. With our model (and regardless of the crust production rates or CO_2 contents we assumed), we can account for CO_2 pressure ranging from 0 to several tenths of a bar 3 billion years ago. Without any important hidden reservoir or loss, a larger amount than that in the past atmosphere does not appear possible unless the atmospheric escape was much higher that what is assumed here (which is possible but has not been proved or quantified yet). This would imply that either Mars might not have had a thick atmosphere in the first place or the mechanisms that depleted it were very effective (Impact erosion i.e.). This does not preclude out of hand the possibility of liquid surface water. It seems that even with quite low partial pressures, given the right temperature conditions, the triple point can be reached. Fluvial landforms found by Mangold et al. (2004) seem to be such an occurrence.

Moreover, it seems that if there were more than around 100 mbar CO_2 left three billion years ago, the present-day atmosphere should still either be composed of a fair amount of primordial gasses or be thicker. Since we can observe its present state, we obtain a rough upper boundary on the thickness of the past atmosphere of Mars for the past 3 Gyr. This also requires a small CO_2 concentration in the mantle or low volcanic activity, as higher CO_2 concentrations lead to cases that have no physical explanation. Low volcanic activities however rarely lead to any incoherency as large CO_2 concentrations are required to obtain a secondary atmosphere. Thus it seems probable that our cases where crust production is low are more realistic and more coherent with present-day atmospheric conditions.

If, on the other hand, there was less CO_2 left three billion years ago (around 30 mbar typically), our models lead to the conclusion that the present-day atmosphere is much younger (maybe as young as 1 Gyr, as our calculations show) and has been created essentially by the volcanic degassing occurring in the late period of the planet activity.

It must be noted that when a model with lower volcanic rates is used, such as the one from O'Neill et al. (2007), high Earth-like CO_2 concentrations (~1000 ppm) are viable and yield essentially similar results than what is obtained with low crust production rates. However, in this case, if low CO_2 concentrations are used (typically 400–800 ppm), the atmospheric escape becomes the dominant process and the effect of volcanic activity is not obvious, although it can still compose up to 60% of the present-day atmosphere.

It would be interesting to have constraints on the age of the present-day atmosphere in order to discriminate between the possible evolutions that have been discussed above.

One means to obtain these constraints would be to study the fractionation of isotopes such as $^{14}N/^{15}N$ and $^{12}C/^{13}C$. Considering the rate of escape of these species, it would be possible to estimate, independently from the model used here, a rough value for the age of the Martian atmosphere.

The setting of the model do not allow us to make any calculation about the evolution of the D/H ratio with time due to the numerous possible exchange mechanisms that we do not study here and that have a strong influence on the evolution of hydrogen and water. Hidden reservoirs are not taken into account here and would need to be studied to propose any realistic theory about the D/H ratio. However the loss of water that is associated with this ratio is still compatible with our models since we need a massive early loss of volatiles to reach the present situation from the dense primordial atmosphere.

However, our results seem to fit with data available on Argon. Most of the Argon in the Martian atmosphere is radiogenic which is compatible with the hypothesis of a young atmosphere mainly created by volcanism, as it implies the primordial Argon is a minor component.

Another means to improve the accuracy of the models would be to obtain a history of recent Martian volcanic activity which should be possible, given the quality of today's pictures of the planet. The last tens to hundreds of million years are accessible as direct data instead of just raw numerical estimations. This could be used to constrain the late volcanic volatile production. Even if the estimation of lava flow thicknesses is still a challenge, one interesting hypothesis it would be to test whether the present-day Martian atmosphere is at steady state or if it is still slowly escaping without being replenished.

It would finally be interesting to model the evolution of the Martian water in the history of Mars, for two reasons. Firstly, the presence of (liquid) water is most certainly a major question because it is one of the main conditions for habitability of a terrestrial planet (e.g. Van Thienen et al., 2007; Lognonné et al., 2007). Secondly some features seen on the planet are thought to require liquid water to be created at least for (relatively) short periods of time. We would also need good estimates of water history to be able to have insight in pH-related problems such as the successive formation of phyllosilicates (neutral to slightly basic pH) and sulphates ($pH<2$) that have been inferred from OMEGA spectrometer observations (Bibring et al., 2005).

Currently, we are able to estimate the amount of water that could have been lost to space during the last 3 Gyr. It amounts to roughly half a bar of total water pressure in the atmosphere. However, it is doubtful that so much water could enter the atmosphere without some being condensed in the polar ice caps, thus limiting water vapour in the system. This part would not be difficult to model.

The main difficulty would be to obtain realistic estimates of the evolution of the water pressure. For that we will need more accurate estimates on the amount of water present in the different accessible reservoirs on Mars, such as water trapped in the subsurface. Once this data set is available, it would be possible to obtain valuable results.

The key would be to estimate the surface temperature from the state of the atmosphere (water, CO_2 and other components) using a simple atmosphere (e.g. radiative convective) model which would allow us to obtain the amount of condensed water. The main problem is that, for now, we have pressure variations ranging from 10 mb to 60 mb. When we translate these pressure variations to temperature variations (Forget et al., 1999), we obtain a 6 K temperature increase when pressure increases from 5 mb to 60 mb if only the greenhouse effect is taken into account. However we obtain a larger decrease in temperature of about 20 K when the effect of dust is taken into account, as a thicker atmosphere contains more particles (Forget, personal communication, 2007). It is still hard to define the clear influence of the evolution of the atmosphere on the climate without taking into account all other green house volcanic gases, as well as the differences in their relative escape rates (and precipitation rates, for SO_2), which have a strong influence on their life time in the atmosphere.

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