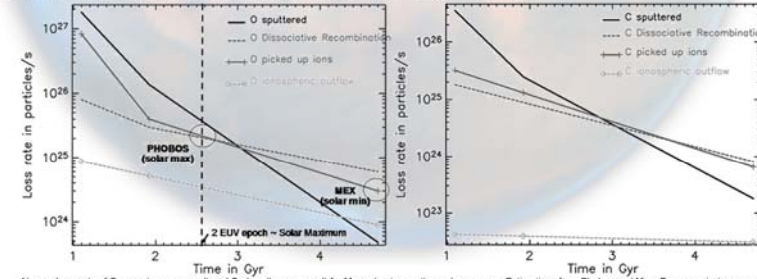


Abstract.
 Past evolution of terrestrial planets is difficult to study due to the lack of data and in situ measurements. However, it is necessary in order to explain some of the features that are observed by recent missions. This work is meant to show that even with the few data we have and by using simple straightforward models, it is possible to have some answers about the evolution of Mars during the last 3 Gy. We study possible states of the past Martian atmosphere consistent with present observations through a simple evolution model based on realistic outgassing scenarios and atmospheric loss. We focus on CO₂ as the most likely main gas present in the atmosphere at that time and involved in large scale and long term processes. Volcanic degassing is obtained through the use of results from numerical model analysis that yielded the evolutions of crust production rates (Breuer et al., 2003 and 2006, Manga et al., 2006). By evaluating the contents of the lavas, the amount of volatiles that are released can be estimated through different scenarios. The mechanisms leading to the loss of the Martian atmosphere are all thought to be part of the atmospheric escape rather than some surface reservoirs such as carbonate formation as no carbonate has been found on Mars to this day. Atmospheric escape is due to non thermal processes (involving solar emissions) as opposed to thermal processes (such as hydrodynamic escape). We used measurements from ASPERA and Mars Express and models from Chassefère et al. (2006) to estimate the amount of lost atmosphere. Thus we obtain evolutions of the CO₂ pressure that are consistent with the present state of the atmosphere. It first appears that a present-day crustal production of at least 0.01 to 0.1 km³/year is needed for the atmosphere to be at steady state. Moreover our models provide us with a rough constraint on the CO₂ contents of the Martian mantle. It seems it should be lower than 200ppm in order to fit with present-day conditions. Higher concentrations would lead to thicker atmospheres due to intense release of gases by late volcanism. We also witness around 3 Gy ago a rapid loss of the primary (and primordial) atmosphere due to atmospheric escape. It is finally found that for most of the scenarios (we investigate a wide range of mantle compositions and atmospheric escape models) the present atmosphere is of volcanic origin and has been created between 1 Gy and 1.5 Gy ago. If the volcanic activity and the degassing are intense enough then the atmosphere can even be entirely secondary and as young as 500 Myr, meaning that the present Martian atmosphere can be very young.

A simple model is used to compute the evolution of different volatiles over time in the atmosphere of Mars during the last 3 Gy. We focus on Water and CO₂. On the first order we consider degassing (input of gases) and escape (which removes the gases from the atmosphere) as the two main processes which control the history of the atmosphere.

Atmospheric Escape.
 Since our model focuses on the last 3 Gy, the main processes for atmospheric escape are non-thermal. We use data from Chassefère, Leblanc and Langlais (2006) for sputtering, dissociative recombination, ionospheric outflow and ion pick-up to estimate the amount of CO₂ and H₂O lost to space.
 -Sputtering: ions produced in the corona or in the ionosphere reimpact the neutral atmosphere and lead to the ejection of neutral particles.
 -Dissociative recombination: ions from the ionosphere recombine with electrons and form energetic neutrals with enough energy to escape.
 -Ion pick-up: ions produced in the exosphere are dragged along by the solar magnetic field lines wrapping the planet.
 -Ionospheric outflow: ions are produced within the ionosphere and can flow up to the ionopause where they are dragged by the solar wind.

The change of slope in the same figure is attributed to the non-linearity of the processes. We suppose that one oxygen atom escapes with two hydrogen atoms and that one carbon atom is associated with two oxygen atoms. This enables us to have an estimate of the amount of CO₂ and H₂O lost to space. The H₂O loss rate is at least one order of magnitude higher than CO₂ loss rate. So here, we use CO₂ loss rate as the limiting parameter. As new data become available thanks to missions, we adapt our models. Latest ASPERA measurements for the present-day atmospheric escape might give insight in the evolution of the atmosphere and so have been included (Carlson et al., 2006). The values are somewhat lower than what was found previously (and is used Chassefère et al., 2006) since Carlsson et al. give 0.29kg/s for the CO₂ loss rate, which probably corresponds to the solar minimum. Our other sources (mainly the results from modelling as presented by Chassefère et al., 2006) tend to suggest values around 2 to 5 times higher. Since our model focuses on the last 3 Gy, we can neglect the effect of heavy bombardment, which is thought to have efficiently removed up to 99% of the Martian atmosphere and which occurred early in the history of the planet (before 3.9Gy, the approximate age of the end of the late heavy bombardment).



Above: Loss rate of Oxygen (upper panel) and Carbon (lower panel) for Mars, due to non-thermal processes. Estimations from Phobos and Mars Express missions are also shown (reproduced Chassefère et al., 2006).

Evolution of the Martian Atmosphere: Results.

First results are shown to the right on the upper panel. We wanted to have an estimation of the state of the atmosphere at any given time with the main constraint that we obtain the real situation at the present time. For CO₂, that means we enforce present pressure to be just below 10mbar. We did not go back further than 3 Gy due to earlier events such as bombardment, and hydrodynamic escape.

Here we can first see CO₂ maximum pressure when only atmospheric escape is considered. This means that even 3 Gy ago it was unlikely for Mars to have a thick CO₂ atmosphere. The two other curves take into account degassing based on crustal production rates from Breuer et al. (2006). Values for the maximum CO₂ pressure are significantly lower and stay in the order of several to several tens of millibars. What is really interesting is the minimum around 2Gy. It shows we can obtain today's atmosphere for Mars without needing much primordial atmosphere. In fact most of what we see nowadays might well be a produce of volcanic activity (thus a secondary (and quite recent) atmosphere) instead of the remnant of a primordial atmosphere.

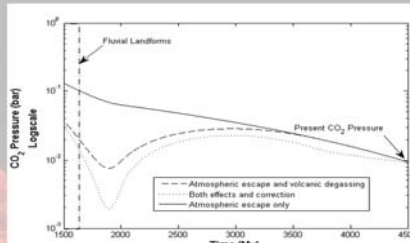
Before the significant drop in pressure occurring 2.6 Gy ago, the CO₂ pressure was at its highest for the period of time we study here. This relatively dense atmosphere happens to coincide with the occurrence of fluvial landforms as proposed by Mangold et al. (2004). Since the pressure is not that much higher than the one we observe during the late period of activity (around 1.5 Gy ago), it might be possible that liquid water existed at this time on the surface.

Assuming the proportions between CO₂ and H₂O are roughly the same in Martian lavas as in those from Earth (Phillips et al., 2001), use 0.65 wt % CO₂ and 2 wt % H₂O on Earth for Hawaiian basaltic lavas, and that the only source of water and CO₂ is volcanism, we can calculate an approximate H₂O partial pressure.

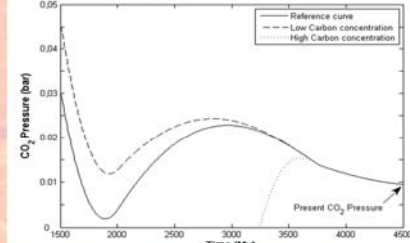
$$P(H_2O) = P(CO_2) \times n(H_2O) / n(CO_2)$$

where P(i) is the partial pressure of component i and n(i) is its molar fraction. We find that the partial pressure for H₂O would roughly amount to some 150 mbar around 1.5 Gy ago. This is well above the triple point in a water phase diagram and thus, provided the surface temperature is high enough, liquid water could have been present at least during brief episodes, such as volcanic ones that would release large quantities of SO₂ in the atmosphere, thus leading to short term warming.

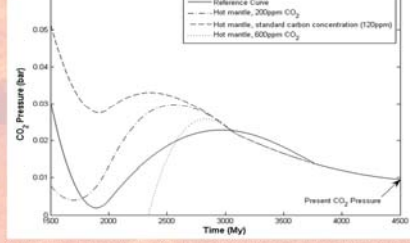
We considered several models to test the influence of CO₂ content in the melted material used for the degassing. We observe that for very low CO₂ degassing, a part of the primordial atmosphere remains. However, as soon as the amount of CO₂ available gets higher, the maximum CO₂ pressure drops. This means that with these models, the whole present atmosphere is secondary and originates only from recent volcanism. We can estimate an age for these atmospheres and it can be as young as 1.5 Gy. Other models where used to study the influence of global activity on the evolution of maximal CO₂ pressure. Breuer et al (2006) give several curves for crust production rates depending on the initial temperature of the mantle. We compared results for a 200K mantle and a 1800K one. (Figure to the right, lower panel). They tend to show the same kind of behaviour.



Above: Evolution of maximum CO₂ pressure in the atmosphere of Mars over the last three billion years. Vertical axis is a logscale. Efficiency of Degassing is set to 30%. CO₂ content is set to 120ppm. Interior dynamics model used here is adapted from Breuer et al. (2006) with a 1800K 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 occurred (Mangold et al., 2004).



Above: Evolution of maximum CO₂ pressure over time for several CO₂ contents of the lavas. Model is adapted from Breuer et al. (2006). Three CO₂ contents are used. Efficiency is set to 30%. The solid line shows the evolution with low CO₂ content (120ppm). The dashed line is for lower CO₂ content (100ppm). The dotted line is for a higher CO₂ content (600ppm).



Above: Evolution of the maximum CO₂ pressure for different interior dynamics and crust production models adapted from Breuer et al. (2006). Three CO₂ contents are used. Efficiency is set to 30%. The cool mantle model is included for comparison (solid line). All other models use the hot mantle model. The dashed line shows results for 120ppm CO₂. The dotted line for 600ppm. The dashed and dotted line for 200ppm.

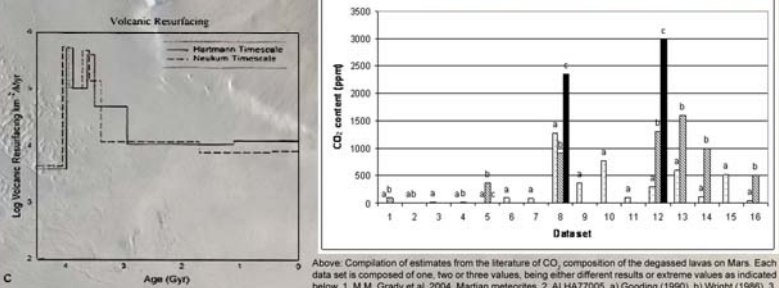
Degassing.
 Volcanism is the major input of CO₂ that can be found for the atmosphere of Mars, considering the absence of any other major reservoir such as carbonates or CO₂-rich polar ice caps. Geophysical modelling of the activity of Mars provides us with estimations of the amount of lavas produced that will allow us to deduce the amount of volatiles that are released into the atmosphere. As an input for the amount of volatiles released into the atmosphere, we mainly use data from numerical studies from Breuer and Spohn, (2006) and Manga et al. (2006) but also consider other sources such as O'Neill et al. (2007). Breuer et al. employed a parameterized model of stagnant lid convection with crust production, core cooling and mantle melting. The model is constrained by both crustal thickness and magnetic field history, applying data from Mars Pathfinder, Mars Global Surveyor and Mars Express.

We compared these results with other data from Hartmann and Neukum (2001), obtained by observation of the surface of the planet. Observations seem to show that activity is not as strong as the numerical results seem to imply. On the other hand, these observations are not taking into account intrusive processes that may occur. The estimates from O'Neill et al. (2007) are even lower than those from Manga et al. and fit better with the observation of the surface of Mars. They propose volcanic rates ranging from over 0.17 km³/yr for the Hesperian to around 10⁻⁶ km³/yr at present.

Few well constrained and dependable data exist about CO₂ content, instead, information given by the study of Martian meteorites is often used.

We show some data we used in this study. Several results on Martian meteorites lead to the assumption that CO₂ is quite rare in the Martian mantle, but data exist that would imply rather larger CO₂ contents. If Mars is not much different from the Earth, its mantle might contain a lot more CO₂ than Martian meteorites seem to suggest. Another hypothesis (Kuramoto, 1997) even hints at larger CO₂ concentrations due to higher silicon content in the core. It has however been suggested that concentrations much higher than 1000 ppm would not be consistent with today's data.

However, all samples used above to estimate CO₂ contents are degassed samples, depleted with regard to their initial state. One important parameter is not known and can not be constrained. It is not known how efficient the degassing is on Mars.



Above: Evolution of volcanic resurfacing over time. Note that we are only interested in the last 3 Gy here and that the scale shows a surface per Myr which tends to complicate evaluations of melt volume. (Reproduced from Hartmann and Neukum (2001)).
 Below: Compilation of estimates from the literature of CO₂ composition of the 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) Gooding (1990), b) Wright (1996), 3. EETA79001A, Wright (1986), 4. EETA79001B, a) Gooding (1990), b) Wright (1986), 5. EETA79001C, a) Gooding (1990), b) Gooding (1990), c) Wright (1986), 6. Shergotty, Wright (1986), 7. Chassigny, Wright (1990), 8. EETA79001A Gooding (1990), 9. EETA79001C, Gooding (1990), 10. Nakhlite, Gooding (1990), 11. Nakhlite, Carr (1995), 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) CO₂ content of Martian lavas used in this study, a) minimum value, b) maximum value, 15) Estimate for Iceland volcanism (Galason et al., 2002) used in O'Neill et al., 2007, 16) Earth upper mantle content by Trull et al., 1993.

We also used an alternative model for the crust production rate, adapted from a study by Manga et al. (2006) as discussed above. The upper right hand panel shows a comparison of results obtained with this new model to those based on Breuer and Spohn (2006). For the low end value of our range of mantle compositions (120 ppm CO₂), the evolution of maximum CO₂ pressure does not show any minimum in the early period (around 2.7 Gy). Instead we observe a change in the slope that corresponds to the transition from the 3 EUV to the 1 EUV era. That is the only striking feature apart from the relatively high CO₂ pressures (compared to the other model) 3 Gy ago. The model allows up to 70mbar CO₂ in the atmosphere at that time.

O'Neill et al. (2007) propose a different range of values for the volcanic CO₂ input flux. We ran the model with their values, using both low (100 ppm) and high (<500 ppm, i.e. what O'Neill et al. use in their calculations), CO₂ concentrations and a 100% efficiency. Results for high CO₂ contents (that correspond to Earth-like conditions) are similar to what we obtained with lower concentration in our previous models and exhibit the same features with the same range of values for the pressure at any given time. However with low volatile contents, the atmospheric escape is dominant.

On the middle right hand panel we compare two different possibilities for atmospheric escape models: one adapted from Chassefère et al. (2006), the other from ASPERA present-day data (Carlsson et al., 2006). The one where new ASPERA measurements are used presents a structure that is similar to other results. The latter present-day escape implies that the planet could have lost less CO₂ to space during the past few tens of million years in this new model than in the other (with higher escape). It thus means that past atmosphere was even less dense with this low escape model. Indeed, in this case, the Martian atmosphere seems to be quite stable for the past two billion years with a pressure staying around present-day values (never exceeding 0.02 bars). Again this atmosphere is a secondary atmosphere. Between 2.5 Gy and 2 Gy ago it would have been building up due to volcanism and prior to this, nearly no atmosphere existed for a while and it can be said that the primary atmosphere had been lost.

The lower right hand panel shows a possible origin for the higher CO₂ pressures that occur around 3Gy ago in our models. Late heavy bombardment could be intense enough to contribute to the volatile inventory on Mars without blowing off the atmosphere and lead to the several tenths of bar our model shows. Our future investigations will incorporate this possibility and the next developments of the model will see this input of volatiles added in order to have better estimates of the atmospheric pressure during the older periods.

Conclusions and perspectives.
 Our results suggest that the present-day atmosphere seems to be a secondary atmosphere almost entirely or entirely created by volcanic degassing, with low CO₂ contents in the lavas. 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 3Gy. This also requires a very small CO₂ concentration in the mantle as higher CO₂ concentrations lead to cases that have no physical explanation. These cases can however be thought of as constraints on the CO₂ contents of the lavas. Thus it seems that CO₂ content can only be less than 200ppm else we still would observe an atmosphere thicker than what is seen at present time. If, on the contrary, there was less CO₂ left three billion years ago (around 30mb typically), our models lead to the conclusion that the present-day atmosphere is much younger (maybe as young as 1 Gy) 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), Earth-like CO₂ concentrations (<500ppm) are viable and yield essentially similar results than what is obtained with low crust production rates. However, in this case, if low CO₂ concentrations are used (typically 100-200ppm), the atmospheric escape becomes the dominant process. One means to obtain these constraints would be to study the fractionation of isotopes such as ¹⁵N/¹⁴N and ¹³C/¹²C. It would be possible to estimate, independently from the model used here, a rough value for the age of the Martian atmosphere. It would finally be interesting to model the evolution of the Martian water in the history of Mars as it plays a major role both for habitability and in terms of species formation (the need to have a neutral pH environment for photosynthesis formation for example). The main obstacle we encounter for now is our need for a climate model to compute the surface temperature that is required to estimate the state and amount of water on the surface.