# Degassing of volatiles in the geological history of Mars

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#### RESUMEN

Obtuve una estimación de la masa total de volátiles desgasificados en Marte y la distribución de esta desgasificación en el tiempo. La cantidad de volátiles desgasificados en toda la historia de Marte es del orden de  $3.73 \times 10^{20}$  kg, es decir, 16 000 veces la atmósfera actual marciana. El grueso del desgasamiento ocurrió en todo el periodo Noachiano y en el Hesperiano temprano. En las ultimas cinco épocas, del Hesperiano temprano al Amazoniano tardío, el desgasamiento ha sido monótonamente decreciente. La cantidad de agua líquida en la superficie en el pasado ha sido pequeña o inexistente, por lo tanto la existencia de vida en Marte es dudosa.

PALABRAS CLAVE: Atmósfera marciana, desgasamiento, vulcanismo.

#### ABSTRACT

I obtain an estimate of the total mass of degassed volatiles on Mars and the distribution of degassing in time. The amount of volatiles degassed in all the history of Mars is of the order of  $3.73 \times 10^{20}$  kg, i.e. 16 000 times the current Martian atmosphere. The bulk of the degassing occurred in Early, Middle, and Late Noachian, and in Early Hesperian. Degassing was monotonically decreasing in the last five epochs, from Early Hesperian to Late Amazonian. The amount of liquid water at the surface in the past was very little or none, thus the existence of life is doubtful.

KEY WORDS: Mars atmosphere, degassing, volcanism.

#### INTRODUCTION

"The question of changes in the planetary atmospheres in the geological past is part of the more general problem of studying the planets evolution. The publications devoted to the atmospheres history are much fewer than those on the history of the lithospheres. This is due to the absence of easily interpreted empirical materials in the geological record" (Budyko *et al.*, 1985).

The origin of atmospheres is related to degassing of the planetary mantle, and degassing history is intimately related to volcanic history. "Volcanic eruptions are a source of volatiles in the atmospheres of the terrestrial planets. The flux of volatiles to an atmosphere is dependent on the rate of volcanism, the concentrations of volatiles in the magmas, and the efficiencies of loss from magmas to atmosphere" (Schubert *et al.*, 1989).

In this work I estimate the total mass of volatiles degassed on Mars. I use the results of a two-component model for the accretion of the terrestrial planets (Ringwood, 1977, 1979; Wänke, 1981; Dreibus and Wänke, 1987, 1989). I also obtain the degassing history based on the volcanic history after Tanaka *et al.* (1987). The principal results are as follows:

- (1) The amount of volatiles degassed in the history of Mars is on the order of  $3.73 \times 10^{20}$  kg.
- (2) The bulk of degassing occurred in the early four epochs, i.e. in the first Ga of Mars's history if we accept the Hartmann-Tanaka chronology.
- (3) Degassing was monotonically decreasing over the last five epochs.
- (4) The amount of liquid water at the surface in the past was very little or nonexistent; therefore the existence of life is doubtful.

## TOTAL MASS DEGASSED FROM MARS IN ITS GEOLOGICAL HISTORY

I express the mass of volatiles in terms of terrestrial atmospheric masses (TAM), where 1 TAM =  $5.28 \times 10^{18}$  kg, the current mass of the Earth's atmosphere.

The model proposed by Ringwood (1977, 1979), Wänke (1981), and Dreibus and Wänke (1987, 1989) assumes that the earthlike planets were formed by two components, a highly reduced volatile-free component A and an oxidized volatile-containing component B. One of the conclusions of

the model is that the mixing ratio of component A with component B for Mars is 60:40 and for Earth 85:15 (Dreibus and Wänke, 1989). Thus if Mars had the same volume and mass of Earth its amount of volatiles would be 40/15=2.666 times the volatiles on Earth. As the mass of Mars is 0.10744 times that of Earth (Tholen *et al.*, 2000), its amount of volatiles should be 2.666 x 0.107 = 0.28. This is the total amount of volatiles in Mars; let us calculate the fraction that was degassed from the mantle. If the amount of volcanic materials produced on Mars was the same as on Earth the amount of degassed volatiles in Mars should be 0.28 times the amount of volatiles degassed on Earth.

The rate of degassing is proportional to the rate of volcanism. We may assume that it is proportional to the mean thermal flux F in each planet. The mean thermal flux is

$$F = \frac{E}{S} = \frac{e \rho V}{S} = \frac{e \rho r}{3}, \qquad (1)$$

where E is the energy per second generated in the planet, e is the average thermal energy per unit mass and time produced in the planetary interior,  $\rho$  is the mean density of the planet, V is its volume, S is its surface, and r is its radius.

Comparing the flux  $F_m$  on Mars with the flux  $F_e$  on Earth and assuming that e is equal in both planets we obtain

$$\frac{F_{\rm m}}{F_{\rm e}} = \frac{\rho_{\rm m} r_{\rm m}}{\rho_{\rm e} r_{\rm e}} = \frac{3950 \text{ kg/m}^3 \text{ } 3393.5 \text{ km}}{5520 \text{ kg/m}^3 \text{ } 6378 \text{ km}} = 0.381.$$
(2)

Using this factor we may correct the early calculation as follows:  $0.28 \ge 0.381 = 0.107$ . This is the fraction of Earth volatiles degassed on Mars in all its geological history. The assumption that e is equal in both planets is plausible as the two planets were formed in the same region of the solar nebula. Thus the proportion of radiogenic elements is possibly the same.

The current volatile inventory of Earth is 0.77 TAM  $(4.065 \times 10^{18} \text{ kg})$  of N<sub>2</sub>, 0.21 TAM  $(1.1088 \times 10^{18} \text{ kg})$  of O<sub>2</sub>, 60 TAM  $(3.168 \times 10^{20} \text{ kg})$  of CO<sub>2</sub> (mostly in carbonate rocks), and 600 TAM  $(3.168 \times 10^{21} \text{ kg})$  of H<sub>2</sub>O of which 261 TAM  $(1.378 \times 10^{21} \text{ kg})$  are in the oceans and the rest in the rocks (Pollack, 1981). Altogether we have 661 TAM  $(3.49 \times 10^{21} \text{ kg})$  in total. On Earth the volatiles of the atmosphere escape mainly by Jeans escape, but this is very inefficient. Hunten *et al.* (1989) estimate a loss of atomic H of  $6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ ; for all the Earth this is 0.5 kg/s. If the total flux has been the same over the history of the Earth, the total quantity is 0.014 TAM; a small fraction of the current inventory.

On the other hand the Earth's atmosphere has retained the full inventory of nonradiogenic rare gases corresponding to a chondritic composition (Fanale, 1976), which argues strongly in favor of the permanence of volatiles degassed on Earth. Thus we may assume that all the volatiles degassed in the Earth history are still present today.

We conclude that the amount of volatiles degassed in the geological history of Mars was 661 TAM x 0.107 = 70.7TAM ( $3.73 \times 10^{20}$  kg).

### DISTRIBUTION OF DEGASSING WITH TIME

We may assume that the amount of degassed volatiles during an epoch is proportional to the surface (strictly speaking the volume) of volcanic deposits produced in the epoch (Schubert et al., 1989), Tanaka et al. (1987) quantifies the exposed surface of volcanic origin on Mars by geologic epochs (Table 1). As the figure obtained by Tanaka et al. (1987) for each epoch is the exposed surface and not the total surface generated in that epoch, part of the surface may be buried under layers of later epochs. An estimate of the total surface, exposed and buried, may be obtained by dividing the exposed surface of volcanic origin of each epoch by the total exposed surface of layers of the epoch and of previous epochs. If we assume that the proportion of volcanic surface of an epoch is the same in the buried regions as in the exposed regions it is easy to obtain the total surface by multiplying the early quotient by the surface of the planet. Thus I obtain the total surface generated by volcanic activity for each epoch (Table 1). Tanaka et al. (1987) made a similar estimate but they did not include the Early Noachian. Comparing my values with that of Tanaka we may see that both are of the same order of magnitude.

To estimate the thickness of the layers we recall that when fluid materials, like lava or pyroclastic flows, reach static equilibrium their slopes are independent of volume. If the extended surface of the material increases, the thickness also increases. A linear source of volcanic material of length L (see Figure 1), the surface of the volcanic material may be expressed as

$$S = 2Lr + \pi r^2, \qquad (3)$$

where r is the distance that goes over the front of the flow. The thickness of the flow at the source is proportional to r if the slope is constant.

If  $L \approx 0$ , i.e. for a point source,  $r = (S/\pi)^{1/2}$  and the thickness varies as the square root of the surface. If L >> r, i.e. for a linear source,  $r \approx S/2L$  and the thickness varies linearly with the surface. In Table 1 we find that the smallest surface of volcanic origin in all Martian epochs is in Late

Table 1
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Epochs	Volcanic surface exposed (km²) (Tanaka <i>et al.</i> , 1987)	Total volcanic surface (km <sup>2</sup> ) (Exposed and buried)	Volume (km <sup>2</sup> x au) Linear source	Volume (km²x au) Point source
EN	2.07E+06	4.98E+07	7.53E+08	1.94E+08
MN	2.00E+07	7.14E+07	1.55E+09	3.32E+08
LN	7.70E+06	1.94E+07	1.14E+08	4.71E+07
EH	1.93E+07	3.48E+07	3.68E+08	1.13E+08
LH	1.15E+07	1.56E+07	7.36E+07	3.39E+07
EA	1.27E+07	1.50E+07	6.81E+07	3.19E+07
MA	7.27E+06	7.87E+06	1.88E+07	1.22E+07
LA	3.28E+06	3.30E+06	3.30E+06	3.30E+06

Table 2

Epochs	Mass degassed (kg) (Linear sources)	Mass degassed (kg) (Punctual sources)	Integral Mass degassed (kg) (Linear sources)	Integral Mass degassed (kg) (Point sources)
EN	9.54E+19	9.42E+19	9.54E+19	9.4211E+19
MN	1.96E+20	1.62E+20	2.9142E+20	2.5581E+20
LN	1.45E+19	2.29E+19	3.0591E+20	2.7872E+20
EH	4.66E+19	5.50E+19	3.5254E+20	3.3377E+20
LH	9.33E+18	1.65E+19	3.6186E+20	3.5024E+20
EA	8.63E+18	1.55E+19	3.705E+20	3.6578E+20
MA	2.38E+18	5.92E+18	3.7288E+20	3.7169E+20
LA	4.18E+17	1.60E+18	3.733E+20	3.733E+20



Fig. 1. Diagrammatic representation of a volcanic source. The volcanic source is the thick straight line of length L. The gray area is the area of volcanic material expelled by the source. The maximum distance that the material moves away from the source is r. If  $L\approx0$  the source is a point source.

Amazonian  $S_{LA}$ . Using an arbitrary unit to designate the thickness in this epoch, the thickness h of the other epochs is proportional to r and to  $(S/S_{LA})^{1/2}$ , if all sources are punctual, or proportional to  $S/S_{LA}$  if all sources are linear. In a planet there naturally exists both linear and punctual sources. Multiplying these values of h by the surface S in each epoch I estimate the volume of volcanic material (Table I).



Degassed Mass by Epochs

Fig. 2. Mass (in TAM) of degassed volatiles in each Martian epoch. Solid line represents the values if all the volcanic sources in Mars were point sources, and dotted line if all the sources were linear. The true situation is intermediate.



Fig. 3. Integrated mass degassed in time. Solid and dotted lines mean the same as in Figure 2.

The amount of volatiles A degassed by unit volume was obtained by dividing the amount of total degassed volatiles  $(3.73 \times 10^{20} \text{ kg})$  by total volcanic volume for all epochs. The mass M of volatiles degassed in an epoch is the total (exposed and buried) volcanic volume V produced in that epoch, times A (Table 2 and Figure 2). It was possible to obtain the integrated degassed mass by adding for every epoch the mass degassed in that epoch and in all previous epochs (Figure 3).

All these estimates were made with a relative chronology. If we want to know the data in time it is necessary to establish an absolute chronology. Lacking radiometric determinations from Mars we have no absolute chronology. However, some authors estimate this chronology from the relationship between crater densities and absolute ages for the Martian surfaces, based on the lunar experience (Neukum and Wise, 1976; Hartmann *et al.*, 1981; Tanaka, 1986). Using the Hartmann chronology as corrected by Tanaka (1986), known as the Hartmann-Tanaka chronology, I obtain Figure 4.

The estimated amount of mass degassed on Mars is showed in Table 2 and in Figures 2 through 4.

The bulk of the degassing occurred in early times, mainly in the Middle Noachian (between 30.6 and 37.1 TAM) as shown in Figures 2 and 4. A major decline in degassing of 2.7 to 4.3 TAM occurred in Late Noachian and a partial recovery of 8.8 to 10.4 TAM took place in Early Hesperian. From Early Hesperian to Late Amazonian the degassing was monotonically decreasing.

At the end of Middle Noachian, 68.5 % to 78% of all volatiles were degassed, and 93.8 % to 96.9% were degassed

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Degassed Mass by Epochs (Hartmann-Tanaka chronology)



Fig. 4. As in Figure 2 but using the Hartmann-Tanaka chronology.

by the end of the Late Hesperian (see Table 2). In the last 3.6 Ga (Amazonian) the amount of mass degassed was between 2.16 and 4.37 TAM.

#### DISCUSSION

On Earth the proportion [H<sub>2</sub>O]/[CO<sub>2</sub>] is 10 (Pollack, 1981). If the proportion is the same on Mars and if the amount of volatiles was a mixture of these two volatiles only, the amount of water degassed from Mars was 64.27 TAM and the amount of CO<sub>2</sub> was 6.43 TAM. This assumption is reasonable because the two planets were formed in the same region of the solar nebula and the proportion of compounds is possibly the same. One TAM of water on Mars is equivalent to an ocean 36.5 m deep, so 64.27 TAM is equivalent to an ocean of 2345.9 m depth. Of course this amount of water is not all in oceans: a large amount will be in the minerals as crystallization water. The actual water in oceans, rivers, lakes, and groundwater, will be called "free water". In Earth the free water is 0.435 times the total amount of water (Pollack, 1981). If the conditions on Mars are similar to those on Earth, we may expect 27.96 TAM of free water, i.e., an ocean 1020.5 m deep.

The bulk of the degassing occurred in the first two epochs (0.38 Ga) of Martian history (Figure 4 and Table 2), the epoch of heavy bombardment. Thus a large amount, if not all, the volatiles degassed at that time may have been expelled to space by the impacts. After heavy bombardment the degassing occurred at a slower rate (Figure 4 and Table 2).

In the last five epochs (see Table 2) the amount of volatiles degassed was only 12.77 TAM to 17.9 TAM  $(6.74 \times 10^{19} \text{ to } 9.45 \times 10^{19} \text{ kg})$ ; thus the amount of water de-

gassed in these epochs was between 11.61 TAM and 16.27 TAM ( $6.13 \times 10^{19}$  to  $8.6 \times 10^{19}$  kg), an ocean of 424 m to 594 m depth. The free water was between 5.05 TAM and 7.08 TAM ( $2.67 \times 10^{19}$  to  $3.74 \times 10^{19}$  kg).

On Earth, aquifers contain as much as  $6x10^7$  km<sup>3</sup> (11.36 TAM) of water (Hudak, 2000; Price, 1996). If the capacity of aquifers on Mars is similar to that of Earth all the free water was in aquifers and not in seas or lakes. This is easy to see as the volume V of aquifers of a planet is

$$V = Spf, (4)$$

where S is the surface of the planet, p is the depth at which the lithostatic pressure is sufficiently high to close the porosity and fractures of the rocks, and f is the fraction of free spaces in the rock in which the water may penetrate (porosity). The depth p is inversely proportional to the rock weight which is proportional to g the acceleration of gravity. If the rocks on Mars are similar to those on Earth, we may assume that f is the same in both planets. Then:

$$\frac{V_{\rm m}}{V_{\rm e}} = \frac{S_{\rm m}g_{\rm e}}{S_{\rm e}g_{\rm m}} = 0.75, \qquad (5)$$

where m is Mars and e is Earth.

If the aquifers on Earth are saturated, their capacity is  $6x10^7$  km<sup>3</sup> and thus the capacity of the Martian aquifers should be 0.75 x  $6x10^7$  km<sup>3</sup> =  $4.5x10^7$  km<sup>3</sup>, enough to absorb an amount of 8.52 TAM of water. If the aquifers on Earth are not saturated their capacity is >  $6x10^7$  km<sup>3</sup> and the capacity of the Martian aquifers is also larger. In the earlier result the amount of free water degassed on Mars in the last five epochs is between 5.05 TAM and 7.08 TAM; thus it seems unlikely that there ever existed a large amount of liquid water on the surface. Assuming that life first appears in oceans, the existence of life on Mars in the past, and thus in the present, is doubtful.

In conclusion:

- The amount of volatiles degassed in all the history of Mars is on the order of 70.7 TAM (3.73x10<sup>20</sup> kg), 15,940 times the current Martian atmosphere.
- (2) The bulk of the degassing occurred in the early four epochs, i.e. in the first Ga of Mars's history if we accept the Hartmann-Tanaka chronology.
- (3) Degassing was monotonically decreasing in the last five epochs.
- (4) The amount of liquid water in surface in the past was very small or nonexistent. Thus the existence of life is doubtful.

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