



# STERILISATION PROPERTIES OF THE MARS SURFACE AND ATMOSPHERIC ENVIRONMENT

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## ABSTRACT

The radiative and chemical conditions at the surface and in the lower Martian atmosphere are computed at various latitudes and seasons combining a 2D photochemical model and radiation simulations. In most situations, the solar UV B and C radiations reach the surface however, suspended dust and, in polar cases, ozone can constitute an effective UV shield. The daytime and night time concentrations of the sterilizing oxidants:  $OH$ ,  $H_2O_2$  and  $O_3$  are determined, as well as the concentration of the substances which could influence the metabolism of microorganisms. The possible habitats of a remaining Mars's life as well as the possibilities of contamination by resistant earth life forms will be described. © 2002 COSPAR. Published by Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

The Martian atmosphere consists mainly of carbon dioxide (95.32 %) with trace quantities of  $N_2$  (2.7 %),  $Ar$  (1.5 %),  $O_2$  (0.13 %),  $CO$  (0.07 %) and less abundant species. The low density of the  $CO_2$  Martian atmosphere, partially transparent to the solar ultraviolet radiation, results in an intense photochemical activity, possibly including photo-catalytic processes at surface level or on the aerosols. Understanding the Martian atmospheric chemistry is of fundamental interest to characterize the history of Mars (escape of species to space, atmosphere/surface interactions like oxidation), as well as for a purpose of comparison with Earth (chemistry/dynamics coupling, possible role of heterogeneous chemistry, extreme aeronomical effects of  $CO_2$ , development of biological processes during planetary history).

## PHOTOCHEMICAL CALCULATIONS

Twenty years ago, the Viking Mission's life detection experiments proved that the Martian soil is extraordinarily oxidizing and the evolution of  $CO_2$  from the Labelled Release experiment was found to be consistent with the presence of a thermally labile oxidant. (Levin and Straat, 1981). Detection and

characterization of the chemical and physical nature of this powerful oxidant is therefore of great interest not only in the exobiology point of view but also to understand exchanges between the atmosphere and the regolith on Mars. In the thin cold Martian atmosphere, photochemical reactions occurring between traces of water and the ultraviolet radiation from the Sun lead to the production of  $H_2O_2$ , which in turn can condense onto soil grain and airborne dust. Hydrogen peroxide is a key chemical component in the lower atmosphere oxygen-hydrogen chemistry. In the classical photochemical scheme, hydrogen peroxide is almost entirely produced by  $HO_2$  "self reaction" and destroyed during the day through photolysis. An other significant sink of atmospheric  $H_2O_2$  is its condensation in the cold regions of the atmosphere. This condensation process is naturally crucial in the Martian lower atmosphere since it restrains the quantity of atmospheric odd hydrogen by playing the role of reservoir and, therefore, it controls the oxidation capacity of the atmosphere. This molecule, in fact, is be the key constituent for the chemical regulation of  $H_2$ ,  $O_2$  and  $CO$  in the today Martian atmosphere. Additional trace species are also important in understanding the behaviour of atmospheric and surface oxidants. One of these trace gases is ozone. Ozone is a good indicator for the water vapour abundance (Barth *et al.*, 1973). It is photo-chemically produced by the third body reaction of atomic oxygen, molecular oxygen and carbon dioxide and destroyed by photolysis and reactions with odd hydrogen species ( $H$ ,  $OH$ ,  $HO_2$ ).

### **BISA (Belgian Institute for Space Aeronomy) 2D MARS MODEL**

The BISA MARS-2D photochemical model (e.g. Moreau *et al.*, 1991, Moreau 1995, Moreau and Fonteyn, 1999) is a model treating interactively radiative, dynamical and chemical processes in two dimensions. Domain of application of the model extends from South Pole to North Pole and from the ground to 120-km altitude, with a horizontal resolution of 5 degrees and a vertical resolution of 1 km. The present chemical code has been developed to study a  $CO_2$ — $H_2O$ — $N_2$ — $SO_x$ — $Cl_x$  atmosphere. It includes the calculation of the meridional distributions of 36 chemical species pertaining to 6 chemical families:  $O_x$ ,  $HO_x$ ,  $NO_x$ ,  $SO_x$ ,  $Cl_x$ ,  $C_x$ . Solving for each of them a continuity/transport equation derives the distribution of all species (e.g.,  $CO_2$ ,  $CO$ ,  $O_2$ ,  $H_2$ , and  $N_2O$ ). Our model used the total column of water derived from MAWD/Viking (Mars aerosol and water detector) data (Farmer *et al.*, 1977) and for vertical distribution a scale height of 7 kilometres. In the model, the surface temperature is calculated by resolving a simple energy balance equation applied to the surface. Mariner 9 has mapped ozone thirty years ago (Barth *et al.*, 1973) and the latest reinterpretation of the data is the one by Lindner (1995), an other observation data set has been obtained from the space telescope (Clancy *et al.*, 1999). Both sets show temporal and spatial variations, with which the model has, a broad agreement. It is clear that a high quality mapping using instrument derived from the present earth ozone monitors is necessary on Mars to solve the numerous remaining uncertainties on this subject. The mechanisms of surface-atmosphere interactions are present in the model including  $H_2O_2$  condensation. This last question has been treated in detail by Bullock *et al.* (1994) but the fundamental problem of the depth to which sterilizing  $H_2O_2$  could condense in the Martian soil will only be solved after repeated samplings of the surface and a complete analysis of the adsorbed ices and their biological action.

## SPECTRAL SIMULATIONS

For spectral simulation purposes, we used the MODTRAN 3.7 model (Moderate Resolution Transmission model) modified for the Martian atmosphere and representing multiple scattering by an eight streams DISORT (discrete ordinate radiative transfer) routine. Advantages of this model are that it is standard, fast, well suited to the spectral resolution of a Martian feasible instrument. The model possesses built in representations of multiple scattering and the results are expressed in physical units that can be used as inputs to instrument mathematical models. However, disadvantages of the model is that the band models do not allow modifying isotopic ratios versus earth values and resolution of better than  $1 \text{ cm}^{-1}$  cannot be represented. Specific Martian aerosol models are still to be tested with MODTRAN. MODTRAN has been developed as the successor of LOWTRAN and is continuously maintained by the Air Force Geophysical Laboratory in Hanscom Field (Massachusetts) (Berk et al., 1998).

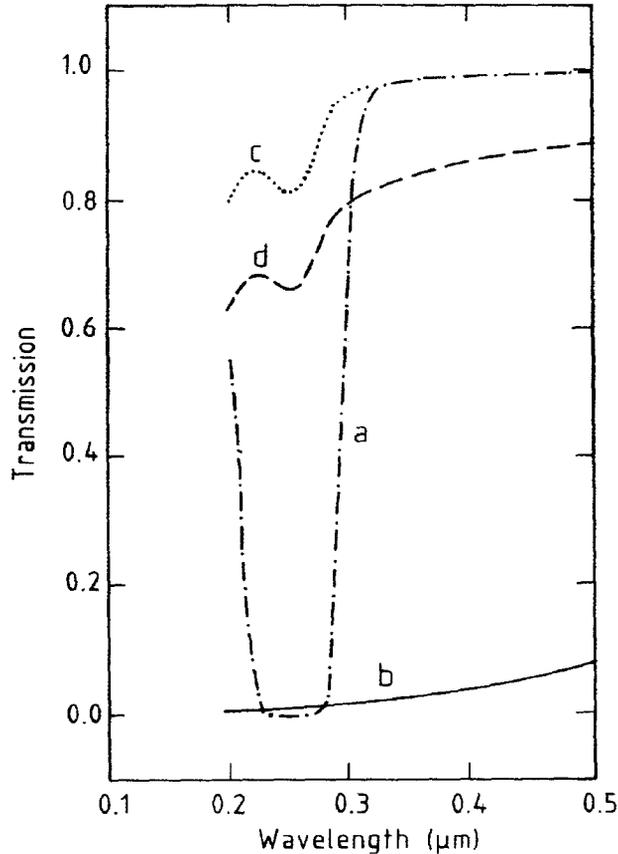
## MODTRAN AEROSOL MODEL

The MODTRAN desert aerosol model has been chosen for its simplicity, the simulation is made for two optical depths: 0.1/km and 0.01/km at the surface and a visibility increasing with altitude. Its composition of 90% quartz particles and 10% hematite represents an optical lower limit for Martian dust. The spectral dependence of Martian dust absorption has been discussed in detail by Ockert-Bell et al (1997) using the available telescopic and space observations as well as the properties of Martian well known analogues (palagonite, montmorillonite). These authors produce a reference model of the Mie scattering properties of Martian dust between 0.3 and  $4.3 \mu\text{m}$ , they also extend this model to  $0.2 \mu\text{m}$  but they note themselves that it is in contradiction with the Hubble telescope observation of a "darker dust" in the  $0.26 \mu\text{m}$  region (Wolff et al, 1997). An iron oxide, present in grains in the dust as it is in the MODTRAN desert aerosol can be an acceptable model, the quartz grains of the MODTRAN desert aerosol are however weaker absorbers in the visible and infrared than the analogues considered by Ockert-Bell et al (1997). The dust considered by Cockell et al (2000) is also a weaker absorbent in the UV but these authors did not consider insoluble iron oxides grains in their computation model. Thus, when the spectral dependence of the actual Mars dust will be known through in situ measurements, it will result certainly in much higher optical depths in the U.V. than the Ockert-Bell model as well as much higher optical depths in the visible than in the Modtran desert aerosol, as the Martian analogues are more absorbent than quartz. Unfortunately, the measurements conducted from the PATHFINDER cameras (Thomas et al, 1999) did not present sufficient spectral resolution to resolve these parameters. Presently, all models would agree that dust storms are effective U.V. screens; the remaining question is the filter effectiveness of background aerosols in quiet conditions. Figure 1 presents simulations of the transfer of direct solar radiation at the Martian surface for different conditions using the MODTRAN desert aerosol.

## SHOULD HEMATITE GRAINS BE PRESENT IN MARTIAN ANALOGUES?

Most of the substances that have been detected on Martian soils have spectra below 300 nm, which have absorptions comparable with hematite, itself, an important Martian component (Soderblom, 1992, Christensen *et al*, 2000). The granulometry of Martian dust is still to be determined, as a correct interpretation of the asymmetry parameter  $g$  requires the knowledge of the composition. The values of  $g$  indicated by Kahn et al (1992) range between 0.55 and 0.8, which are fairly independent of the size parameter. A Mie computation shows these values to be compatible with particles of a minimum size of 0.1

$\mu\text{m}$  radius, an upper limit cannot be put easily in the case of a polydispersion as  $g$  stays constant and the high  $g$  value would still be compatible with a one  $\mu\text{m}$  haze as observed by Smith *et al.*, (1997). This Pathfinder value was refined by Markiewicz *et al.* (1999) to an average  $1.71 \mu\text{m}$  effective radius. The large  $10 \mu\text{m}$  crystalline hematite surface layer recently discovered by TES (Thermal Emission Spectrometer) (Christensen, 2000) in the Sinus Meridiani region would fractionate before reaching the airborne phase. The UV properties of the other iron oxides are close in terms of refractive index (Clark *et al.*, 1993) and the conclusions drawn using hematite, as an analogue would not differ if magnetite were substituted.



**Fig. 1.** : Transmission of the solar spectrum at the surface. Case (a) represents an ozone value 100 time higher than the equatorial minimum, case (c) represents a clear atmosphere with equatorial ozone conditions. Case (b) is a case of extreme dust absorption, the visible optical depth being 0.1 for a path of 1 km; it corresponds to a dust storm and while 20 percent of the visible radiation at 550 nm is transmitted, the UV is entirely absorbed. Case (d) corresponds to a total optical depth for dust of 0.2 at 550 nm for a  $60^\circ$  zenith angle; case (b) corresponds to an optical depth of 1.6 in the same conditions. Case (d) represents the clean Martian condition outside of local dust storm events and does not provide an adequate UV shield.

## CONCLUSION

Knowledge of the ultraviolet flux incident on the Martian surface is important in the photochemical and exobiology point of view. This radiation flux depends on factor such as cloud cover, atmospheric dust loading, season, local time, and altitude. In the current Martian environment, the total integrated UV flux over 200-400 nm is comparable to the Earth's but the shorter wavelengths (UVC and UVB) contribute a greater proportion of this UV flux and, consequently are more biologically damaging. For a clear Martian atmosphere, the dominant attenuation process of the UV flux reaching the surface is  $CO_2$  Rayleigh scattering, except for high latitude in winter where ozone absorption may become significant.  $CO_2$  absorption is significant at wavelengths  $< 204$  nm and effectively provides a shield below 190 nm. For a moderate dusty atmosphere, aerosols can be effective if the aerosol contains a UV absorbing component. During dust storm conditions, atmosphere is certainly UV opaque. Additionally to this UVC-induced lethality for organic material, the UV-induced photolysis of water greatly affects the surface and atmospheric oxidizing conditions.  $H_2O_2$  tropospheric concentrations at the level of ppmv as well as presence of  $H_2O_2$  frost at the surface induce a very effective sterilizing environment. The current conditions on Mars seem to mimic the best energy efficient sterilization procedures today accepted. However, a very thin (100  $\mu$ m) layer of loose hematite sub micron spheres would be an effective protective coating and biological niches could exist near the surface under this isolating coating.

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