THE MARS ATMOSPHERE TWO-DIMENSIONAL MODEL
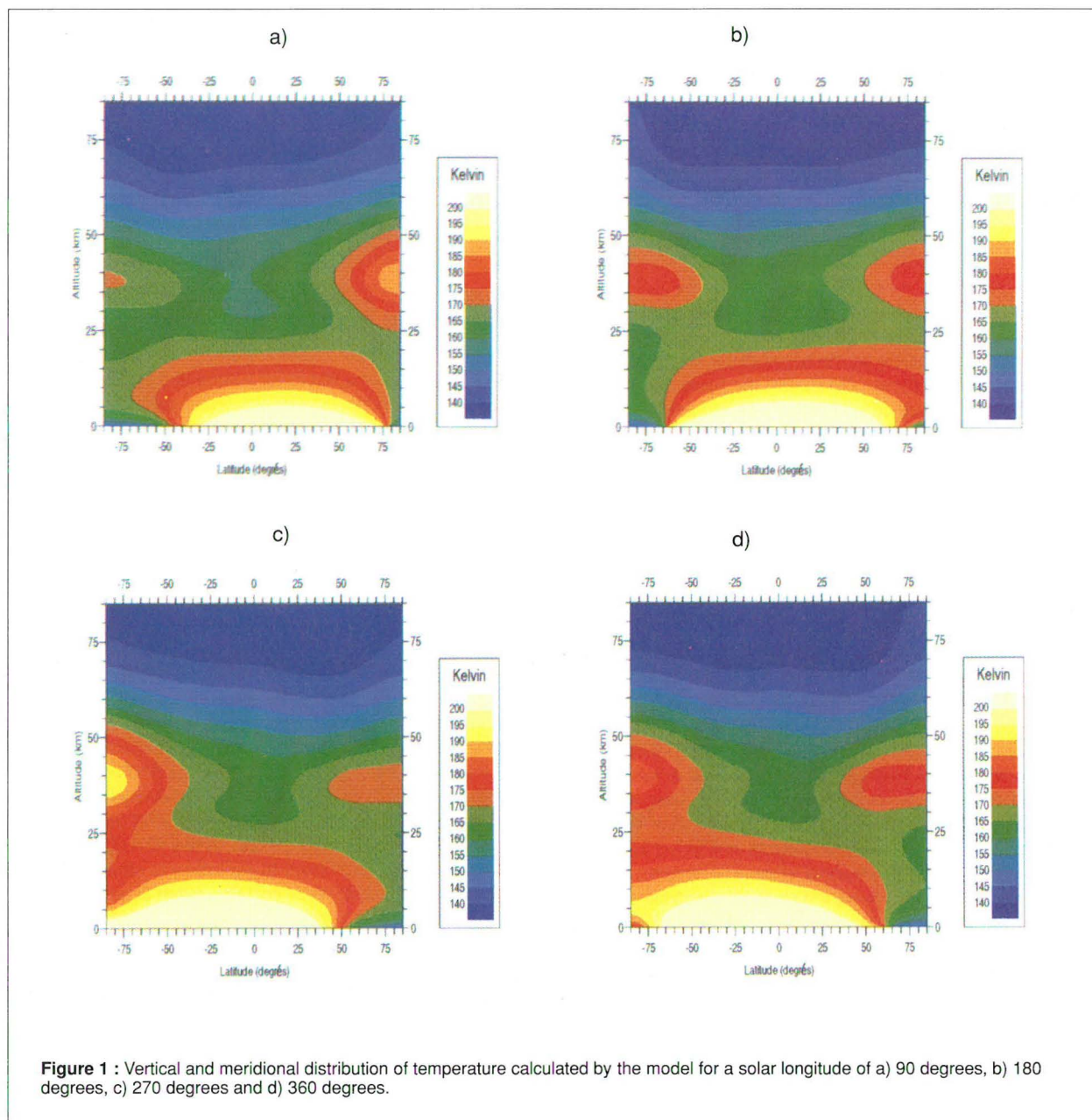
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During the last 30 years, our knowledge of the chemical composition of the Martian atmosphere greatly increased mainly as the result of the development of spectroscopic technic. Observations have been first acquired from ground based observatories and after by spacecraft orbiting around the planet. The Martian atmosphere consist mainly of carbon dioxide with trace quantities of N_2, Ar, O_2, CO and less abundant species. Up to now, seven molecules have been effectively detected in the martian atmosphere and signature of organic molecule has been highlighted. Carbon dioxide was first detected by Kuiper (1947, 1952), carbon monoxide by Kaplan et al. (1969) and Connes et al. (1969), molecular oxygen by Carleton and Traub (1972) and Barker (1972), and water by Schorn et al., (1969) and Tull (1970). Ozone has been detected during Mariner 7 mission by Barth and Hord (1971). Argon and nitrogen were observed more recently by the mass spectrometer on board Viking 1 (Nier et al., 1976; Owen and Bieman, 1976). The last molecule which has been probably detected in the martian atmosphere is formaldehyde (CH_2O) during PHOBOS mission (Korablev et al., 1993). The mean mixing ratios derived from these observations are listed in table 1. In the past, one-dimensional chemical models have been developed to determine the expected vertical profile of atmospheric trace compounds in the Martian atmosphere (*Hunten and McElroy*, 1970; *Yung et al.*, 1977; *Lindner*, 1988). These models have provided an estimate of the mean concentration of these gases as a function of height. They do not however account for the effects of meridional transport nor for the latitudinal and seasonal variation of solar insolation. Two-dimensional models provide a better description of these processes and include a more detailed formulation of mass, momentum and energy transport.

Tableau 1 : Chemical composition of Martian atmosphere

CO_2	95.32	%
N_2	2.70	%
Ar	1.50	%
O_2	0.13	%
CO	0.07	%
O_3	10^{-4}	%
H_2O	0.01	%
CH_2O	$<10^{-5}$	%

Description of the model

The model developped is an interactive radiative, dynamical and chemical two-dimensional model of the Martian atmosphere which calculates meridional and vertical distributions of 31 chemical species from 5 chemical families. As this model is well described in Moreau et al. (1991), we will briefly outline the model characteristics. The model is an adaptation for Martian conditions of the two-dimensional model of the Earth's middle atmosphere developed by Brasseur et al. (1990). It extends from pole to pole with a meridional resolution of 5 degrees and from the surface up to 85 km altitude with a vertical resolution of 1 km. Net atmospheric heating/cooling rate is computed in the model using the NCAR CCM1 radiative scheme (Khiel et al., 1987) adapted for Martian conditions. The radiative transfer equations are solved for two large spectral regions: 0-0.9 µm and 0.9-4.0 µm, respectively. Above 40 kilometres of altitude where conditions depart significantly from local thermodynamical equilibrium, the cooling rate of the atmosphere is computed using a Newtonian cooling formulation. Thus, in this part of the atmosphere, radiative exchange is assumed to occur between a given atmospheric layer and the upper boundary of the atmosphere. In the model, potential temperature and chemical species are advected by a residual mean meridional circulation which is forced by gravity waves (*Lindzen*, 1982) and Rossby waves (Hitchmann and Brasseur, 1985). The chemical model of the Martian atmosphere is developed to study a CO_2-H_2O-N_2-SO_x-Cl_x atmosphere. it includes the calculation of the meridional distributions of CO_2, O_2, CO, O, $O(^1D)$, O_3, H_2, H, OH, HO_2, H_2O_2, N, NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, N_2O, Cl, ClO, HCl, SO_2, SO, S, CH_2O, CH_3O, CH_3O_2, CH_3OH, CH_4, HCO, CH_3OOH .The distribution of long-lived species (CO_2, CO, O_2, H_2, N_2O) or chemical families (HO_x, O_x, NO_y, SO_x, Cl_x) is derived by solving for each of them a continuity/transport equation. For the fast reacting species, photochemical equilibrium conditions are assumed. Surface temperature is calculated in the model using an energy balance equation applied at the surface (Moreau et al., 1991). All simulations presented in the paper have been conducted for several seasonal cycles in order to eliminate any effects due to initial conditions with a global surface pressure of 6.1 mb.

Figure 1 : Vertical and meridional distribution of temperature calculated by the model for a solar longitude of a) 90 degrees, b) 180 degrees, c) 270 degrees and d) 360 degrees.

Despite the fact that total amount of atmospheric water vapour changes from year to year (Clancy et al., 1992), we used for our simulations the total column of water derived from Viking data (Jakosky and Farmer, 1985) and the scale height for vertical distribution (4.9 km) derived from Phobos data (Krasnopolsky, 1991). Solar fluxes (Brasseur and Simon, 1981) have been adjusted for high solar activity.

Model results and discussion

Thermal structure of the atmosphere

Temperature data for the lower Martian atmosphere have been provided by the Mariner 9 Iris (e.g., Conrath, 1981) and Viking IRTM (Kieffer, 1977) experiments. Using ground-based laser heterodyne spectroscopy, Deming et al. (1986) have shown that at high latitude, both in summer and in winter, the middle atmosphere temperature exceeds the radiative equilibrium temperature by more

than 40 K. In the Martian atmosphere, temperature distribution varies mainly with season, latitude, solar activity and atmospheric dust content. For a clear atmosphere, the radiative heating is mainly produced by radiative action of carbon dioxide and ozone. The meridional distribution of temperature derived by the model by solving the thermodynamic equation in which radiative transfer and transport of heat are explicitly included, is shown in figure 1. For the different seasons, the basic features of the observed thermal field are well reproduced by the model. The temperature minimum observed between southern and northern midlatitude in the middle atmosphere is well reproduced and is mainly due to the adiabatic decompression produced by the ascending branch of the Hadley cell. Simulation shown that the polar middle atmosphere heating reproduced by our model is purely dynamical by essence and results from momentum drag by internal gravity waves as well as by air compression induced by the downward branch of the Hadley cell.
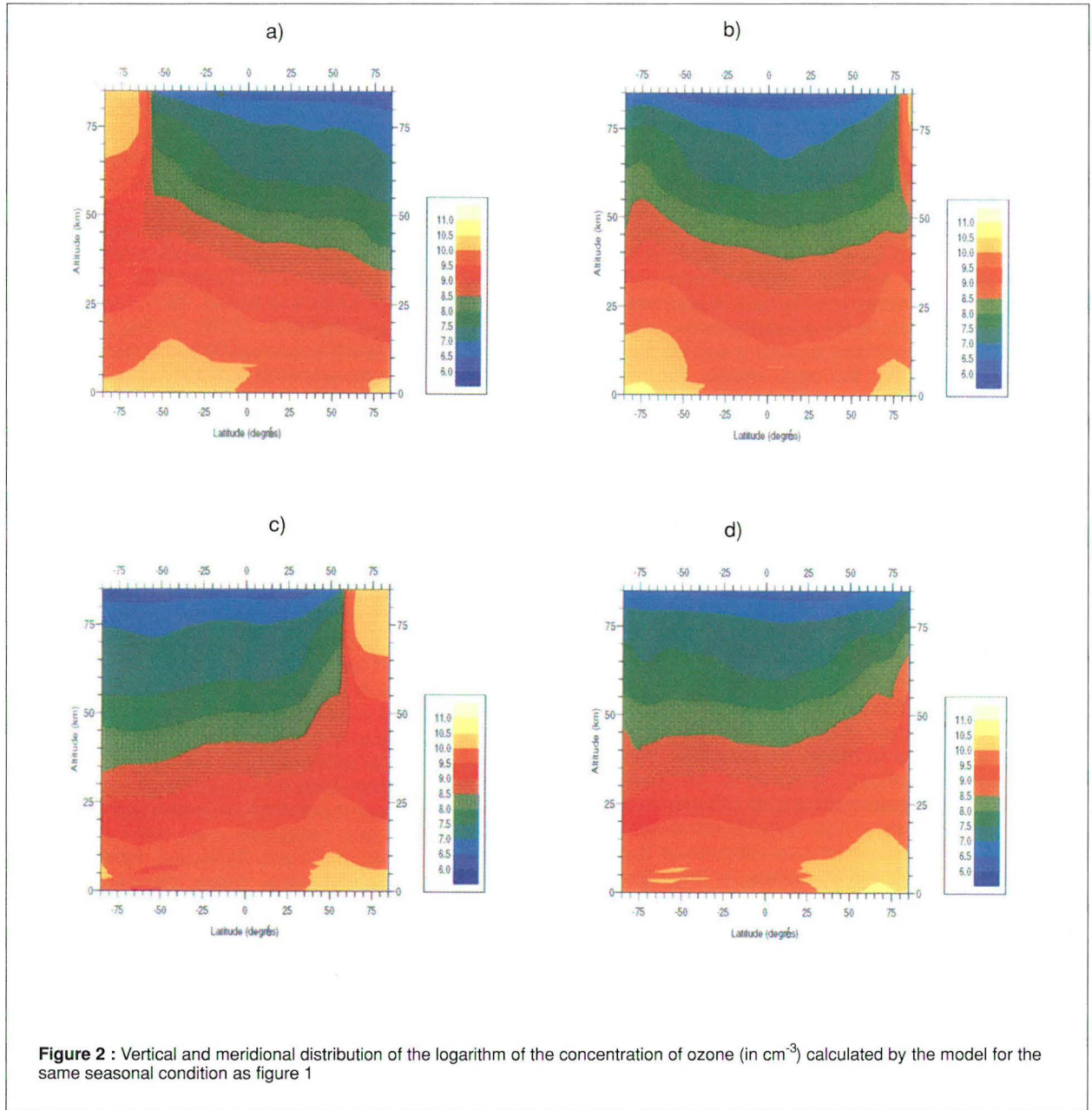
Ozone distribution

The formation of odd oxygen compounds in the Martian atmosphere results from the photolysis of CO_2; its destruction results from the recombination of O and O_3 which is catalysed by the presence of hydrogen and nitrogen radicals. In 1971, during almost half of Martian year and two complete seasons for each hemisphere, the Mariner 9 ultraviolet spectrometer provided data on the latitudinal and seasonal variation of the ozone amount (e.g., Barth et al., 1973). Figure 2 shows the calculated meridional distribution of ozone for the different seasons. The model predicts an ozone meridional distribution which is consistent with the very low abundance detected by Mariner 9. Near the surface, the ozone concentration reach a maximum at 60 degrees of latitude in winter for each hemisphere and shows a poor meridional variation in the middle and high atmosphere. The model shown that, in the lower atmosphere, the latitudinal variation of ozone is determined by spatial variations in the distribution of water which is controlled by condensation processes at winter polar latitude. The behaviour of ozone near the pole in winter is also sensitive to transport by the meridional circulation and to eddy mixing. The decrease of concentration of ozone at low and middle latitude results from the high water vapour densities in these regions and, consequently, to the efficient destruction of ozone by the odd hydrogen catalytic cycles.

Organic processes in the current martian atmosphere

Comprehension of the origin and evolution of organic processes has been and remains a fundamental issue for the scientific community. An evident approach to define this origin is, obviously, to search signature of such processes in environments where physical, hydrological and geochemical characteristics authorize or authorized such development, but also to search in environments easy to observe with current technic of observation. In this framework, like the Earth, Mars is a planet of the solar system witch has an atmosphere and surface conditions compatible with the stability of a wide range of complex organic molecules. The first tentative to measure in situ organic processes in the Martian environment was conducted during Viking missions. Viking landers contained several experiments to detect biological activity (Klein et al., 1976; Oyama et al., 1976; Horowitz et al., 1977; Levin and Straat, 1977; Oyama et al., 1977; Banin and Rishpon, 1979). At the time of this mission, even if the Martian regolith was chemically reactive, no organic molecules in sufficient amount were detected. At the present time, an interpretation for these results is that the chemical activity was stimulated by abiotic reactions involving oxidizing minerals like hematite. Nevertheless, a small uncertainty remains, this being comforted by the lake of knowledge on the physical and chemical information on the martian environment available at the moment of the mission. Since Viking mission, abundant data (telescopic and Phobos data) have been added to the previous data sets and authorised now to reexamine the problem starting on more concrete basis. The key point is to identify the potential atmospheric witness permitting to accredit the reality of such phenomena on Mars. It is legitimate to consider that the first warrant of such processes will come from the discovery of simple reduced carbon species in the current Martian atmosphere. During the last 20 years, various theoretical and experimental works on production of organic molecules in abiotic and prebiotic environments have been accomplished (e.g., Hubbard et al., 1971; Tseng and Chang, 1974; Bar-Nun and Hartmann, 1978; Bar-Nun and Chang, 1983; Wen et al., 1989). The principal result of these studies is that gas phase photolysis of CO_2 - H_2O - CO - O_2 mixtures in presence of silicates and/or ferrous catalyst could lead to the production of simple organic molecules. Today, Martian atmosphere consist mainly of a low pressure mixture of CO_2-H_2O-CO-O_2, CO_2 being the most abundant constituent (95.32%). Consequently, comparable photo-induced mechanisms of production of organic molecules could also be effective in the present Martian atmosphere. Additionally, fresh solar occultation observations of the Martian atmosphere by August experiment on board of Phobos spacecraft provided new spectra in UV, visible and infrared ranges which shown new absorption features (Korablev et al., 1993) not detected previously. After a careful analysis of these spectra, the best candidate today to explain these absorption features is formaldehyde (Korablev et al., 1993). We will now present meridional and vertical distributions of formaldehyde computed by our two-dimensional model and will describe the catalytical cycle permitting to organic molecule to exist in the current Martian atmosphere.
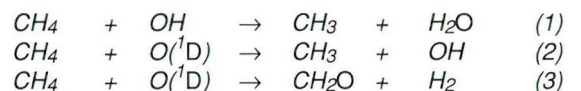
Figure 2 : Vertical and meridional distribution of the logarithm of the concentration of ozone (in cm^{-3}) calculated by the model for the same seasonal condition as figure 1
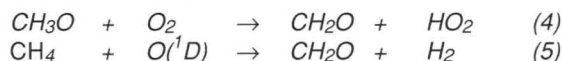
Photochemical scheme of organic compounds

Methane is the most theoretically stable organic molecule in the present martian atmosphere but has not yet been detected. This deficiency of observation is primary justified by the fact that ground-based observations of Martian methane are difficult to achieve due to terrestrial CH_4 perturbations of spectra and because methane is not a microwave absorber. The first published attempt of ground-based observations of methane in the Martian atmosphere permitted to determine an upper limit for concentration of 20 ppbv. However, under present atmospheric conditions, methane is not photochemically produced in the atmosphere because its complexity and the amount of energy required for its formation are prohibitive.
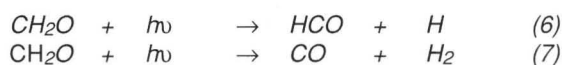
In our model, methane is mainly destroyed by reaction with hydroxyl radical $O(^1D)$:

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (1)$$
$$CH_4 + O(^1D) \rightarrow CH_3 + OH \qquad (2)$$
$$CH_4 + O(^1D) \rightarrow CH_2O + H_2 \qquad (3)$$

Due to its very long lifetime, CH_4 is in diffusive equilibrium and exhibits a nearly constant mixing ratio with altitude and latitude. Simulations by our two-dimensional model also revealed that formaldehyde is the second most abundant reduced carbon specie. In the present martian atmosphere, formaldehyde is mainly formed through reactions of methyl oxide and methane with molecular oxygen and excited atomic oxygen respectively :

$$CH_3O \quad + \quad O_2 \quad \rightarrow \quad CH_2O \quad + \quad HO_2 \qquad (4)$$
$$CH_4 \quad + \quad O(^1D) \quad \rightarrow \quad CH_2O \quad + \quad H_2 \qquad (5)$$

Formaldehyde is mainly destroyed by photolysis processes :

$$CH_2O \quad + \quad h\upsilon \quad \rightarrow \quad HCO \quad + \quad H \qquad (6)$$
$$CH_2O \quad + \quad h\upsilon \quad \rightarrow \quad CO \quad + \quad H_2 \qquad (7)$$

and by reactions with odd hydrogen compounds

$$CH_2O \quad + \quad H \quad \rightarrow \quad CH_3O \qquad (8)$$
$$CH_2O \quad + \quad OH \quad \rightarrow \quad HCO \quad + \quad H_2O \qquad (9)$$
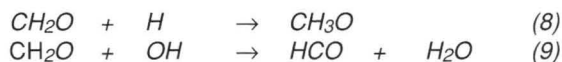
In fact, in our model and as modeled for the Earth's environment, formaldehyde is a product of the catalytical oxidation of methane and photochemical production of CH_2O is governed by rapid catalytical reactions involving other organic species and trace gases present in the atmosphere (odd hydrogen, odd oxygen and odd nitrogen compounds). The major catalytical cycle of production of CH_2O is complex and proceeds through three principal mechanisms. The catalytical cycle is initiated by the production of methyl radicals principally by reaction of methane with excited atomic oxygen :
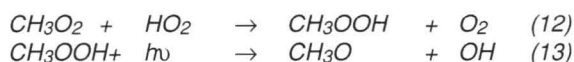
$$CH_4 \quad + \quad O(^1D) \quad \rightarrow \quad CH_3 \quad + \quad OH \qquad (10)$$

This chemical process is followed by a fast termolecular reaction of methyl radical with molecular oxygen to form CH_3O_2 :

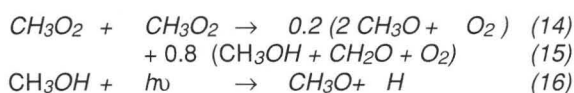$$CH_3 \quad + \quad O_2 + M \rightarrow \quad CH_3O_2 + \quad M \qquad (11)$$

When CH_3O_2 is produced, the catalytical cycle progress through three principal ways to form methyl oxide :

branch 1 :

$$CH_3O_2 + \quad HO_2 \quad \rightarrow \quad CH_3OOH \quad + \quad O_2 \qquad (12)$$
$$CH_3OOH+ \quad h\upsilon \quad \rightarrow \quad CH_3O \quad + \quad OH \qquad (13)$$

branch 2 :

$$CH_3O_2 + \quad CH_3O_2 \rightarrow \quad 0.2 \, (2 \, CH_3O + \quad O_2\,) \qquad (14)$$
$$+ \, 0.8 \, (CH_3OH + CH_2O + O_2) \qquad (15)$$
$$CH_3OH + \quad h\upsilon \quad \rightarrow \quad CH_3O+ \quad H \qquad (16)$$

branch 3 :

$$CH_3O_2 \quad + \quad NO \quad \rightarrow \quad CH_3O + \quad NO_2 \qquad (17)$$

When CH_3O is produced, it reacts with molecular oxygen to form formaldehyde :

$$CH_3O \quad + \quad O_2 \quad \rightarrow \quad CH_2O + \quad HO_2 \qquad (18)$$

The third branch of the catalytical cycle above described could be particularly efficient during dusty conditions when photodissociation rates of species are lowered. Vertical and meridional distribution of formaldehyde calculated by the model for the two solstices and equinoxes and for an upper limit for methane concentration of 20 ppbv is displayed in figure 3. Formaldehyde distribution of concentration results mainly from an equilibrium between photochemical production and loss mechanisms specified above. The model computes different regions of maxima : around 65 kilometres of altitude in the summer hemisphere, around 40 kilometres of altitude and near the surface in the winter polar atmosphere and around 10 kilometres in the equatorial region. These maxima originate from different photochemical mechanisms. In the polar winter region, maxima of concentration of formaldehyde in the middle atmosphere and near the ground primary originates from an increase of photochemical lifetime of formaldehyde due to a reduction of its photodissociation rate due to larger zenith angles (winter hemisphere). Moreover, in the winter middle atmosphere, associated with larger zenith angles is an increase of $O(^1D)$ concentration due to the maximum ozone concentration present in this latitudinal range at this time (figure 2) which consequently increases the efficiency of indirect photolysis of methane (reactions 2 and 3). Increasing the indirect photolysis of methane provides methyl radicals needed by the catalytical cycle just described above. Decreasing the principal loss of formaldehyde, and increasing the chemical production, equilibrium concentration of CH_2O will growth. Close to the ground larger pressures, higher concentration of nitrous oxide and low temperatures increase the efficiency of the catalytical cycle described above. In the summer upper atmosphere, maximum of concentration results mainly from an augmentation of photolysis rates CO_2, O_3 and O_2 increasing the production of $O(^1D)$ which react with methane to form directly methyl radicals. In this region of the atmosphere, it is indirect photolysis of methane which induces the maximum in formaldehyde concentration. Maximum of formaldehyde in equatorial regions is a combination of the two mechanisms just described with also a non negligible contribution of the second branch of the catalytical cycle described above. In the organic family, other compounds react rapidly and locally and are in the state of photochemical equilibrium. Consequently these compounds have a low equilibrium concentration. As we mentioned, new data have been provided by August experiment on board of Phobos spacecraft. During this mission, solar longitude was between 1.5 and 18 degrees, and seven observations were conducted with success, primarily in the equatorial region
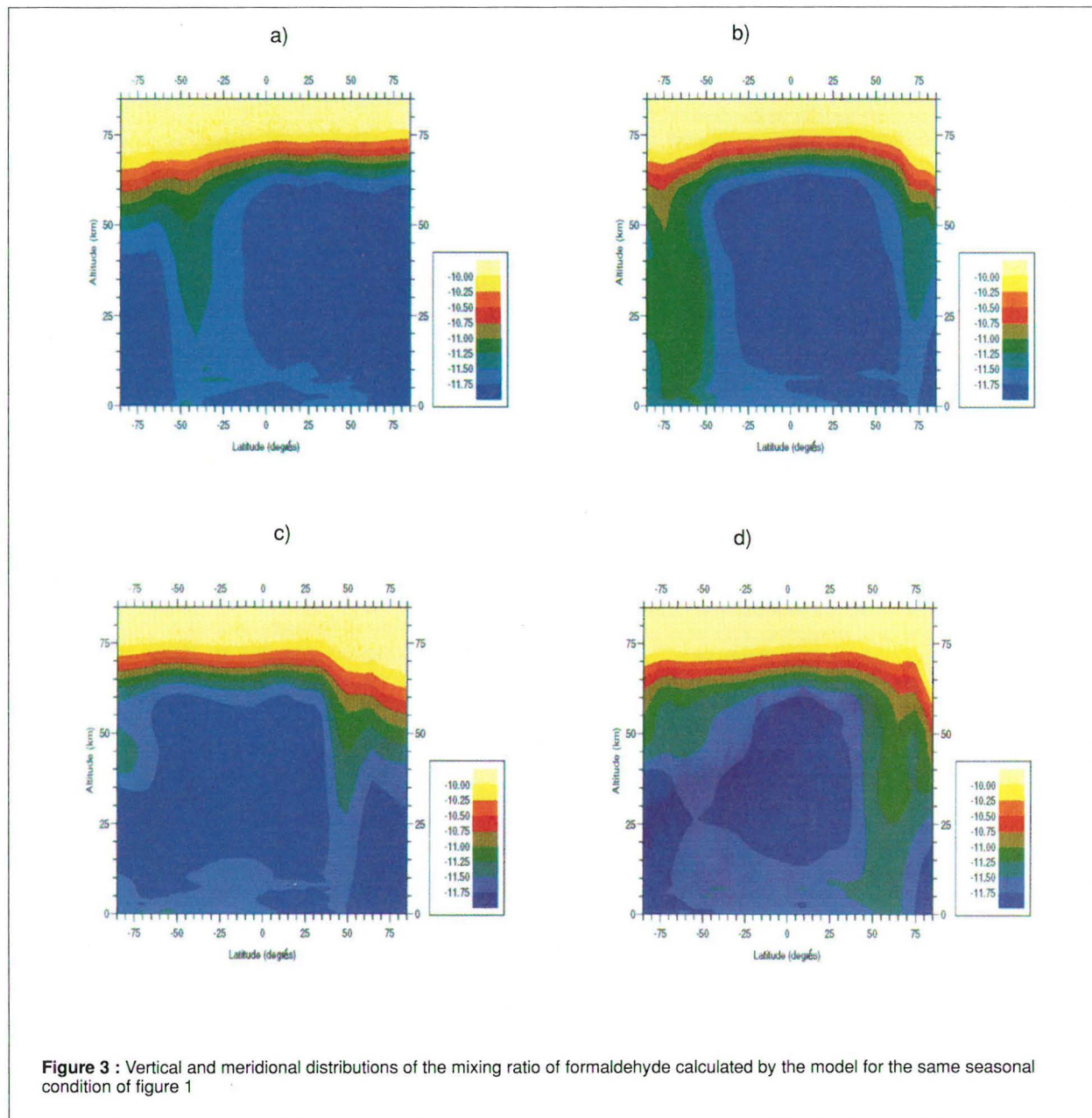
Figure 3 : Vertical and meridional distributions of the mixing ratio of formaldehyde calculated by the model for the same seasonal condition of figure 1

above 10 km altitude (Korablev et al., 1993). The analysis of the first-order spectrum obtained after a set of corrections described in Korablev et al. (1993) permitted to derive concentration of formaldehyde of the order of several ppmv. Figure 4 shows a comparison between the envelop curve of lower and upper limits derived from these data and results obtained by our model for the same spatial and temporal conditions and an upper limit for methane of 3 ppmv. Clearly it exist a good agreement between theoretical and experimental results which seems to validate the photochemical scheme introduced in our model. However, such concentration of methane used has never been detected in the current Martian atmosphere.
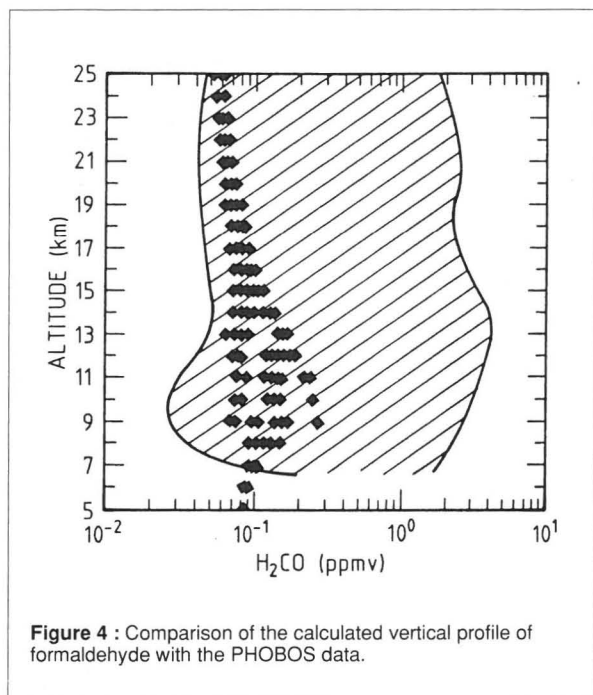
Figure 4 : Comparison of the calculated vertical profile of formaldehyde with the PHOBOS data.

Discussion

The primary result obtained by the simulations with our model is that elementary organic molecules are stable in the present atmosphere. Equilibrium concentration of formaldehyde, one of the most abundant organic specie, results mainly from a competition between photolysis processes, chemical reactions with odd hydrogen compounds and fast catalytical reactions occurring inside the organic family. By analogy with Earth environment, we introduced in our model a photochemical scheme simply based on methane catalytical chain of oxidation. This photochemical scheme shown its capabilities to reproduce qualitatively and quantitatively Phobos observations using an upper limit for methane concentration of 3. ppm. Since chemical production of a methane molecule in the current atmosphere is a very inefficiency process, the two most probable sources of these compounds comparatively with works done in the frame of Earth's environment studies are the heterogeneous catalytical production and the volcanic outgassing. Production by heterogeneous catalytical production is difficult to investigate now due to the lake of knowledge in this field of research. However, as a possible guarantee of efficiency of this process, their exist some observations of organic molecules bands absorption in dust cloud (Abadi et al., 1978). Moreover, there exists today some geomorphological, geochemical and atmospheric evidences that geothermal activity could be still active on Mars (Boston et al., 1992). If this is really the case, reduced carbon species could also be leaked in the atmosphere during such events. Surprisingly, methane hypothesis cannot offer full explanation for all observations made of organic species. Indeed, tentative of confirmation of the detection of formaldehyde performed in the microwave spectral range (Moreau et al., 1992) lead us to conclude that methane is certainly not the precursor of formaldehyde. For the moment, our conclusion is that, we can affirm that August experiment on board of Phobos spacecraft detected the spectral signature of one molecule or of a mixing of molecules which could be un combination of formaldehyde and acetic acid with a ratio depending of the variation of the oxidising capacity of the atmosphere due to the year to year variability of global atmospheric water vapour amount (Moreau et al., 1994). Reality is certainly much complicated that this simple scenario but it as the advantage today to explain the different sets of observations. Today, it would be perilous to say which source is dominant, our knowledge of the chemical and mineralogical of the regolith, of the geological processes of the planet and on the heterogeneous catalytical processes on silicate aerosols are to scarce to conclude. Nevertheless, the only way to distinguish between the two potential sources could be the analysis of the isotopic ratio of carbon contained in organic molecules. In situ measurements of the value of this isotopic ratio could be a major objective of the MARS96 SPICAM experiment and could offer a response on this important problem.

Conclusion

We have developed the first two-dimensional model of the Martian atmosphere including a interactive treatment of dynamical, chemical and radiative processes. This model shown its capabilities to reproduce the main features observed by previous ground-based observations and spacecraft missions (Mars, Mariner, Viking, Phobos) and is now used to prepare the future ground-based and spacecraft campaigns of observations of the planet Mars. In the frame of the planetary program of the Belgian Institute for Space Aeronomy, we installed at the Nasmyth cabin of the alt-azimuthal 6m-telescope of the Special Astronomy Observatory of Zelenchuk (Caucasus/Russia) a classical rapid scanning Michelson interferometer. This experiment will be used during the next opposition of the planet in february 1995 to confirm the presence of organic molecules in the Martian atmosphere as well as to study the meridional variation in the chemical composition of the polar cap and the polar hood.

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