TOWARDS A QUANTITATIVE UNDERSTANDING OF MARTIAN OZONE

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Introduction:

Ozone (O_3) is the most reactive species measured in the Martian atmosphere. Since the first modeling studies carried out in the early 1970s [e.g., *Parkinson and Hunten*, 1972] it has been known that the abundance of ozone on Mars is tightly controlled by the hydrogen radicals (HO_x) produced by the photolysis and oxidation of water vapor. Thus, ozone is a sensitive tracer of the hydrogen photochemistry that stabilizes the Mars CO_2 atmosphere. It also provides important information on the conditions of habitability of the planet, not only by determining the ultraviolet flux reaching the surface, but also as an indirect tracer of the oxidizing capacity of the atmosphere by hydrogen oxides. Quantitative understanding of Martian ozone is therefore of potentially great significance, but has often been problematic with the one-dimensional models used until now. An accurate assessment of this understanding is also a prerequisite before invoking possible chemical processes that are not included in the 'conventional' gas-phase CO_2-H_2O-HO_x-O_x scheme. This type of study can be carried out with an unprecedented level of precision using new chemical models that have now reached the same degree of sophistication as those used for Earth (three-dimensions, interactive dynamics-radiation-water cycle-chemistry, etc). The wealth of data recently obtained by the Spicam spectrometer on board Mars-Express also allows to broaden considerably the pool of available O_3 data with which to validate the photochemical models. In this paper I will use our Global Climate Model (GCM) with chemistry to analyze the O_3 data collected over the last 35 years from space, Earth, or the Space Telescope, and to try to evaluate our progress towards a quantitative understanding of the Martian photochemistry.

Model Description:

Our chemical model is an adaptation of the chemical package used in the Reprobus model developed earlier for the terrestrial stratosphere [e.g., *Lefèvre et al.*, 1994; 1998]. It provides a comprehensive description of the oxygen, hydrogen, and CO chemistries on Mars, and is implemented as a chemical subroutine into the GCM developed since the early 1990s at Laboratoire de Météorologie Dynamique (LMD), in collaboration with the University of Oxford (AOPP) and the Instituto de Astrofísica de Andalucía (IAA) [*Forget et al.*, 1999].

For each photolyzed species we employed the most recent absorption cross-sections or the data recommended by *Sander et al*. [2003] commonly used in the modeling of the Earth atmospheric chemistry. Photolysis rates are calculated off-line and are stored in a 4-dimensional lookup table as a function of the overhead CO_2 column, the overhead O_3 column, the solar zenith angle, and the temperature. For ozone studies the chemical model computes the three-dimensional distribution of 12 constituents ($O(^1D)$, O, O_2, O_3, H, OH, HO_2, H_2, H_2O, H_2O, CO, and CO_2) using 42 photolytic or chemical reactions. Most of the rates and branching ratios that we have adopted are those recommended by the Jet Propulsion Laboratory 2003 compilation [*Sander et al.*, 2003]. At each model timestep, the CO_2, H_2O, and other chemical fields are exchanged between the GCM and the chemical routine to achieve a fully interactive coupling between dynamics, radiation, water cycle, and chemistry. The coupled model is usually run on 32 vertical levels with a horizontal resolution of 64 longitudes by 48 latitudes 5.625°x3.75°).

Model Ozone climatology:

The results of our three-dimensional simulations of ozone on Mars were presented in detail in *Lefèvre et al.* [2004]. The overall behavior of the ozone seasonal evolution calculated by the model is shown in Figure 1, together with the water vapor column. Ozone is destroyed by odd hydrogen catalytic cycles that effectively control the local amount of ozone on Mars. An anticorrelation between the abundances of water vapor, which is the source of HO_x, and ozone is therefore expected in the Martian atmosphere. At first order the anticorrelation between the ozone and water vapor columns seems clearly visible. At high latitudes of both hemispheres, the ozone column is maximum in winter, when condensation on polar caps suppresses most of the atmospheric water vapor. Polar ozone is minimum in summer, indicating an efficient O_3 destruction by the HO_x radicals released from the large amounts of water vapor and sunlight. However the classical anticorrelation expected between the O_3 and H_2O columns is only spatially verified at a given solar longitude: over the Martian year, the low-latitude O_3 column shows for instance little anticorrelation with the H_2O column. This is almost entirely due to orbital (L_s) variations in the H_2O vertical distribution. Our results confirm the effectiveness of a mechanism first hypothesized by *Clancy and Nair* [1996]: over the period L_s=180-330° centered on perihelion, water vapor saturation occurs in the model at high altitude (>40 km at L_s=250°), leading to considerable HO_x production and O_x loss in the middle atmosphere. As a result, O_3 is essentially confined in a 'surface layer' below 20 km. During the rest of the year (L_s=330-180°), the altitude of water vapor saturation is lower

(~10 km at L_s=90°) which reduces the HO_x production and allows the formation of an additional O_3 layer in the model at 25-70 km altitude. The maximum O_3 densities in this layer are reached around aphelion.

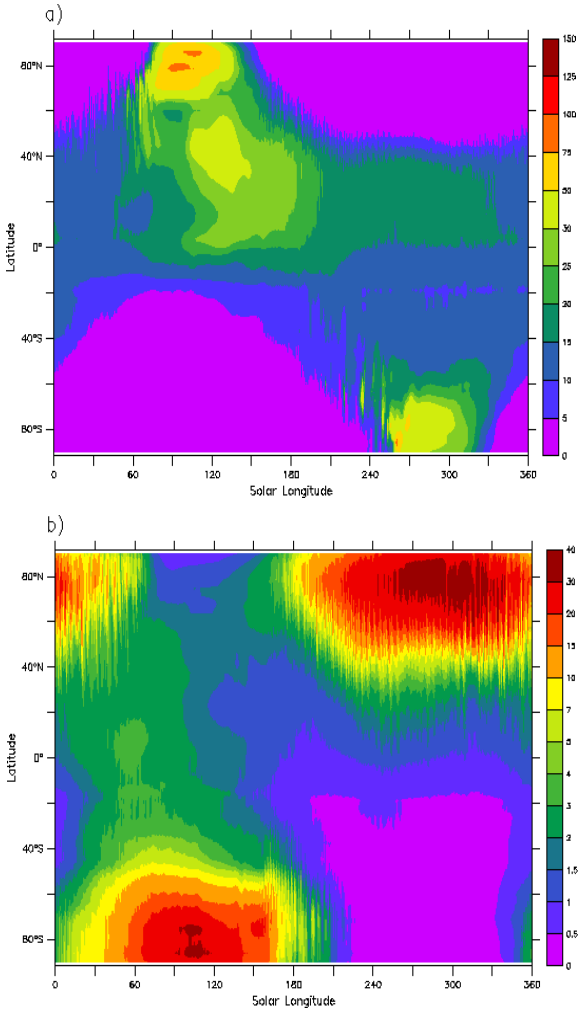

Fig 1. (a) zonally averaged water vapor column (pr-µm) (b) zonally averaged ozone column (µm-atm) calculated by the GCM as a function of solar longitude.

Comparison to observations:

Let us remind that the version of the model presented here only includes the 'conventional' CO_2-H_2O gas-phase chemistry, thus ignoring possible effects of sulfur, halogen, or methane chemistries on ozone, as well as heterogeneous processes, or electrochemistry.

Pre-Mars-Express era. Until 2004 few observational data of ozone on Mars were available and they usually covered a limited range of latitudes or solar longitudes. I will first compare the 3D model results to observations of the latitudinal distribution of ozone obtained with three different instruments: the Mariner 9 ultraviolet spectrometer, from which the first systematic measurements of ozone on Mars were performed in 1971-1972 [*Barth et al.*, 1973]; the FOS and STIS spectrometers on the HST between 1995 and 2003 [*Clancy et al.*, 1999]; and infrared heterodyne spectrometry from Earth between 1988 and 2003 [*Fast et al.*, 2006]. All these data collected in the 'pre-Mars-Express era' show a rather good coherence between them. When they are compared in a stringent way (similar to what is done for Earth stratospheric models) to our 3D model predictions, a relatively clear picture tends to emerge:

1. the O_3 amounts in the polar regions are well understood throughout the year. In winter, the quantities of ozone calculated by the model are in agreement with the observation, as well as their considerable day-to-day variability shown to be associated with dynamical disturbances of the polar vortex. In summer, the lower than 1 µm-atm O_3 columns calculated at high-latitudes are also quantitatively consistent with the observational data.
2. A good quantitative agreement is also achieved at all latitudes during half of the year centered on perihelion (corresponding to northern hemisphere autumn and winter, Ls=180°-000°). This is the period when low-to-mid latitude ozone columns are minimum in response to the increase of available water vapor and HO_x.
3. The model consistently underestimates the O_3 columns in the period L_s=40°-100° centered on aphelion. Although our simulations do reproduce the global increase in O_3 that is measured from perihelion to aphelion, the amplitude of this orbital variation is too small by about a factor of two compared to the observational data considered here.

Mars-Express data. The European mission Mars-Express arrived at Mars in January 2004, during Mars late northern winter. On board, the dual UV/IR spectrometer Spicam has been conducting the first long-term study of ozone from orbit since Mariner 9. Spicam can retrieve atmospheric ozone in its UV chanel using two different methods: in nadir geometry, the O_3 vertical column is derived from the analysis of the solar light backscattered by the surface and the atmosphere [*Perrier et al.*, 2006]; in limb geometry, UV spectra are recorded during stellar occultations to derive the O_3 nighttime vertical distribution [*Lebonnois et al.*, 2006]. The measurements obtained from Spicam now cover one entire Martian year and represent the most complete O_3 dataset ever obtained on the planet. They have been systematically compared to the GCM results in both modes (nadir and limb) of observation. Preliminary results of this analysis can be summarized as follows:

1. The quantitative analysis of the vertically-integrated O_3 column shows a very good agreement between Spicam and the GCM throughout the year (Figure 2). Interestingly, whereas Spicam observations are in line with HST and Earth-based measurements during the perihelion seasons, the O_3 columns retrieved from the instrument around aphelion are substantially smaller than those previously observed in the same season. This brings the GCM into better agreement with the observa-

tional data. Geographical variations such as the accumulation of ozone observed by Spicam in regions of low surface elevation (*i.e.* Hellas of Argyre) are also well captured by the model.

2. The first systematic observations of the O_3 vertical profile reveal a seasonal/orbital evolution that is globally consistent with the GCM predictions: the top of the 'surface layer' is visible throughout the year below 20-30 km altitude; above 30 km, ozone is highly variable with latitude and season: no ozone is identified near perihelion, whereas maximum abundances are retrieved near aphelion (6 to 8x10^9 mol.cm^{-3} at the peak altitude). The quantitative agreement between Spicam and the model is satisfactory over the L_s=40°-70° period centered on aphelion (Figure 3), when ozone reaches maximum abundances. However, the period during which the high-altitude O_3 layer forms in the model is too long. In particular, the sharp drop-off in the O_3 amount observed by Spicam shortly after aphelion is not predicted to occur before L_s=150° in the GCM.

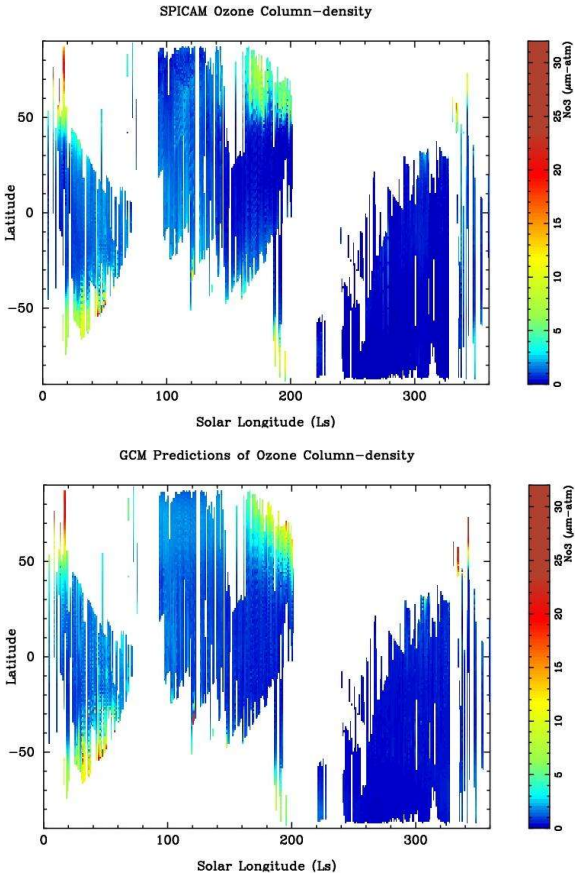

Fig. 2. Top: Ozone column latitudinal distribution (µm-atm) measured over one Martian year (2004-2005) by Spicam on board Mars-Express. Bottom: coincident calculations by the GCM.

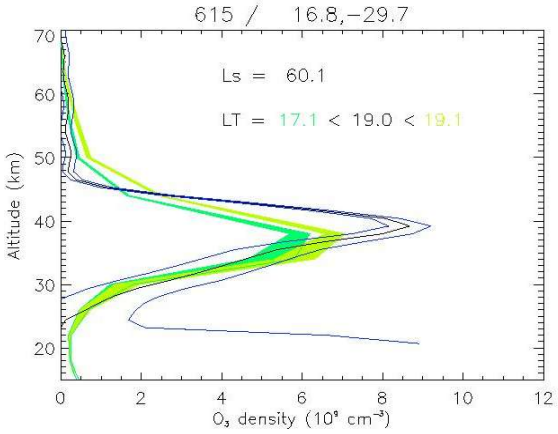

Fig. 3. Example of O_3 night-time vertical profile measured by Spicam (black curve + uncertainty) compared to coincident GCM calculations (green curves given for two different local times bracketing the observation). L_s = 60.1°, lat = 29.7S, lon = 16.8E.

Discussion:

There is a large progress in the ozone dataset on Mars, which now offers a solid basis to constrain better the chemical models and to make significant progress in our understanding of the photochemistry of the planet: measurements of the O_3 vertical column cover almost continuously the entire Martian year, and an unprecedented description of the O_3 vertical distribution is available. In general, the new ozone climatology derived from Spicam shows a good consistency with the previously existing O_3 datasets. A noticeable exception is the aphelion period, when Spicam measured O_3 columns which seem significantly smaller than those observed by other instruments at the same season. This brings our 3D model into remarkable quantitative agreement with the Spicam O_3 column data all year long, but this difference must be explained. Before concluding, the robustness of the model results must also be investigated: how can they be affected by uncertainties in kinetics data, what is the possible impact of processes not included in the model (such as heterogeneous chemistry for instance), and how do they compare with measurements of other species, such as H_2O_2. These will be among the questions addressed in the discussion.

References:

Barth et al., Science, 179, 795, 1973.
Clancy and Nair, JGR, 101, 12785, 1996.
Clancy et al., Icarus, 138, 49, 1999.
Fast et al., Icarus, in press, 2006.
Forget et al., JGR, 104, 24155, 1999.
Lebonnois et al., JGR, in press, 2006.
Lefèvre et al., JGR, 99, 8183, 1994.
Lefèvre et al., GRL, 25, 2425, 1998.
Lefèvre et al., JGR, 109, 2004.
Parkinson and Hunten, JAS, 29, 1380, 1972.
Perrier et al., JGR, submitted, 2006.
Sander et al., JPL Publ. 02-25, 2003.