CONDITIONS FOR A THICK OZONE LAYER IN MARS' PAST

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Introduction: When modeling the past Martian atmosphere, it is often assumed that the atmospheric composition was similar to that observed today. Studies which do examine the photochemistry of CO2 atmospheres typically assume a fixed, simplified temperature profile [1, 2] following the method of Kasting [3]. However, it has been found by Selsis et al. [4] that under a Martian atmosphere of 1 bar CO2 it is possible to photochemically produce a thick ozone layer, comparable to that of modern Earth. This results in strong heating of the middle atmosphere, producing a stratosphere similar to that of Earth. This raises the question of what range of conditions in Mars' past could have produced an ozone layer thick enough to strongly modify the temperature profile.

Model: The model developed for this study is a 1D line-by-line radiative-convective model using the plane-parallel approximation coupled with a simple photochemical model. The line-by-line calculation utilizes the HITRAN 2008 spectral database [5] and an optimized wavenumber grid with variable bin size to resolve spectral lines at a minimum of 1 halfwidth throughout the atmosphere. For absorption cross-sections of photochemical species, the MT_CKD continuum model [6], MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules [7], and JPL evaluated data [8] have been used. Shortwave radiation transfer is treated according to the method of Crisp [9]. Photochemical equilibrium is found using the Kinetic Pre-Processor [10] and involves a set of reactions similar to those used by Krasnopolsky [11] for studying modern Mars (see Table 1). Loss of H2 to space is treated by a diffusion limited model.

Goals: Applying the model described above and a parameter space relevant to the evolution of Mars' climate over the past few billion years are explored to determine their effect on the characteristics of a Martian ozone layer. These parameters include surface pressure, atmospheric humidity, solar intensity, and solar spectrum. The effects of different oxidation sink models are also examined. By varying these parameters the conditions necessary for a thick ozone layer to have existed in Mars' past are identified.

References: [1] Segura, A., et al., A&A, 472, 2, 2007, [2] Zahnle, K.J., et al., JGR, 113, E11004, 2008, [3] Kasting, J.F., Icarus, 94, 1, 1991, [4] Selsis, F., et al., A&A, 388, 3, 2002, [5] Rothman, L.S., et al., JQSRT, 110, 9-10, 2009, [6] Clough, S.A., et al., JQSRT, 91, 2, 2005, [7] http://www.atmosphere.mpg.de/spectral-atlas-mainz, [8] Sander, S.R., et al., JPL Evalulation 16, 2009, [9] Crisp, D., Icarus, 67, 3, 1986, [10] Damian, V., Comp. and Chem. Eng., 26, 11, 2002, [11] Krasnopolsky, Icarus, 185, 1, 2006

Reactions
$CO_2 + h\nu \rightarrow CO + O$
$CO_2 + h\nu \rightarrow CO + O(^1D)$
$O_2 + h\nu \rightarrow O + O$
$O_2 + h\nu \rightarrow O + O(^1D)$
$O_3 + h\nu \rightarrow O_2 + O$
$O_3 + h\nu \rightarrow O_2 + O(^1D)$
$H_2O + h\nu \rightarrow OH + H$
$HO_2 + h\nu \rightarrow OH + O$
$H_2O_2 + h\nu \rightarrow OH + OH$
$CO_2 + O(^1D) \rightarrow O + CO_2$
$H_2O + O(^1D) \rightarrow OH + OH$
$H_2 + O(^1D) \rightarrow OH + H$
$CO + O + M \rightarrow CO_2 + M$
$O + O + M \rightarrow O_2 + M$
$O + O_2 + M \rightarrow O_3 + M$
$O + O_3 \rightarrow O_2 + O_2$
$H + O_2 + M \rightarrow HO_2 + M$
$O + HO_2 \rightarrow O_2 + OH$
$CO + OH \rightarrow CO_2 + H$
$O + OH \rightarrow O_2 + H$
$O_3 + OH \rightarrow O_2 + HO_2$
$O_3 + HO_2 \rightarrow O_2 + O_2 + OH$
$H_2 + OH \rightarrow H_2O + H$
$H + O_3 \rightarrow OH + O_2$
$H + HO_2 \rightarrow OH + OH$
$H + HO_2 \rightarrow H_2O + O$
$H + HO_2 \rightarrow H_2 + O_2$
$OH + HO_2 \rightarrow H_2O + O_2$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$OH + H_2O_2 \rightarrow H_2O + HO_2$
$O + H_2O_2 \rightarrow OH + HO_2$

Table 1: List of Photochemical Reactions