

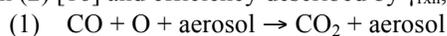
**POTENTIAL IMPACTS OF HETEROGENEOUS CHEMISTRY ON VENUS' MESOSPHERIC CHEMISTRY.** F. P. Mills<sup>1,2</sup>, M. Shunmuga Sundaram<sup>3</sup>, M. Allen<sup>4,5</sup>, and Y. L. Yung<sup>5</sup>, <sup>1</sup>Fenner School of Environment and Society, Australian National University, Canberra ACT 0200 Australia, Frank.Mills@anu.edu.au, <sup>2</sup>Space Science Institute, Boulder, CO 80301 USA, <sup>3</sup>Research School of Physics and Engineering, Australian National University, Canberra ACT 0200 Australia, <sup>4</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109 USA, <sup>5</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125 USA,.

**Introduction:** Three large-scale chemical cycles appear to dominate the chemistry in Venus' atmosphere: the carbon dioxide, sulfur oxidation, and polysulfur cycles [1]. The first maintains the chemical stability of the atmosphere's primary constituent. The second produces the global sulfuric acid cloud layers and links with the CO<sub>2</sub> cycle through the production and loss of O, as shown in Figure 1. The third may be responsible for producing the unidentified ultraviolet absorber [e.g., 1,2,3], which, along with CO<sub>2</sub> near the tops of the clouds, appears to be responsible for absorbing about half of the energy deposited in Venus' atmosphere [4].

The CO<sub>2</sub> cycle comprises photodissociation of CO<sub>2</sub> at wavelengths < 210 nm to form CO and O, production of O<sub>2</sub> from two O, and reformation of CO<sub>2</sub> from CO and O<sub>2</sub>. Fast O<sub>2</sub> production has been confirmed by observations of intense O<sub>2</sub>(a<sup>1</sup>Δ-X<sup>3</sup>Σ) airglow on the day and night sides [e.g., 5,6]. Production of CO<sub>2</sub> is believed to proceed primarily via catalytic cycles involving chlorine compounds [e.g., 1,7,8,9], but no model has yet identified process(es) for producing CO<sub>2</sub> that are sufficiently fast to generate a modeled O<sub>2</sub> abundance which is consistent with the observational upper limit (vmr) of 3×10<sup>-7</sup> [10,11,12]. Heterogeneous catalyzed CO<sub>2</sub> production is a possible fast mechanism [13].

**Methods:** The Venus photochemical model used for the initial parametric study is based on that used for [9]. It solves the 1-d continuity equation for simultaneously for all species over 58-110 km altitude with 2-km thick layers. The global-average simulations used high solar irradiance fluxes [14] at 45° latitude at local noon. The eddy diffusion coefficient profile was set based on observations, chemical data was drawn primarily from [15], and the water vapor profile was fixed to match the equilibrium vapor pressure over 75 wt% sulfuric acid. The mixing ratios for CO<sub>2</sub>, CO, HCl, OCS, and SO<sub>2</sub> at 58 km were set to 0.965, 45 ppm, 0.4 ppm, 1 ppb, and 1 ppm, respectively.

Heterogeneous oxidation of CO was simulated by Reaction (1) with reaction rate constant given by Equation (2) [16] and efficiency described by  $\gamma_{\text{rxn}}$ ,



$$(2) \quad K = \gamma_{\text{rxn}} J_i n_{\text{aer}} 4 \pi r_{\text{aer}}^2$$

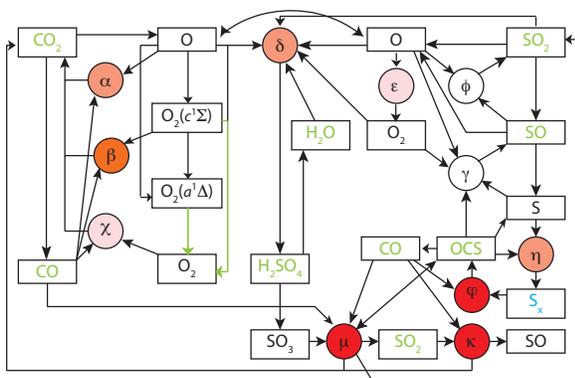
where  $J_i$  is the flux onto the aerosols and  $n_{\text{aer}}$  and  $r_{\text{aer}}$  are the aerosol particle number density and radius, respectively. No attempt has been made to identify a mechanism by which the hypothesized heterogeneous reaction might occur.

**Preliminary Results:** Initial calculated O<sub>2</sub> abundance and CO mixing ratio profiles are shown in Figures 2 and 3, respectively. For  $\gamma_{\text{rxn}} < 10^{-5}$ , the calculated O<sub>2</sub> column abundance is  $\geq 2 \times 10^{18} \text{ cm}^{-2}$ . For  $\gamma_{\text{rxn}} = 10^{-4}$ , the calculated O<sub>2</sub> column abundance is  $1.2 \times 10^{18} \text{ cm}^{-2}$ , which is smaller than the original interpretation of the most stringent upper limit,  $1.5 \times 10^{18} \text{ cm}^{-2}$  [10] but larger than the most recent interpretation,  $0.8 \times 10^{18} \text{ cm}^{-2}$  [12]. Below 75 km altitude, significant differences between the calculated and observed CO profiles are evident whenever heterogeneous oxidation of CO is important.

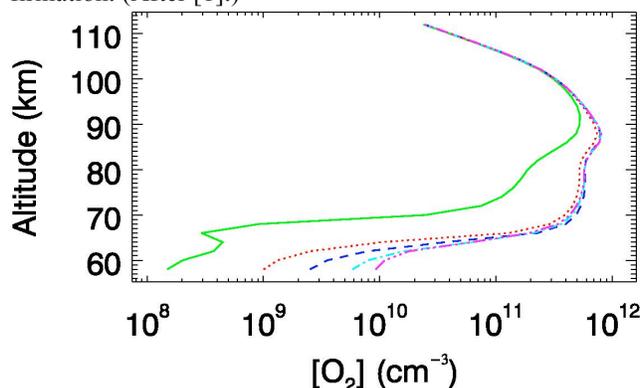
**Preliminary Conclusions:** Heterogeneous chemistry with a plausible reactive uptake coefficient can significantly increase the rate at which CO is oxidized and reduce the calculated O<sub>2</sub> abundance. However, the actual abundance of ground-state O<sub>2</sub> is not yet known and the calculated CO mixing ratios in the global-average model below 75 km are significantly smaller than has been observed. The broader impacts remain to be investigated, further study is required to assess whether conditions exist under which heterogeneous chemistry can satisfy simultaneously observational constraints on both O<sub>2</sub> and CO, and the viability of a specific mechanism needs to be established in laboratory studies.

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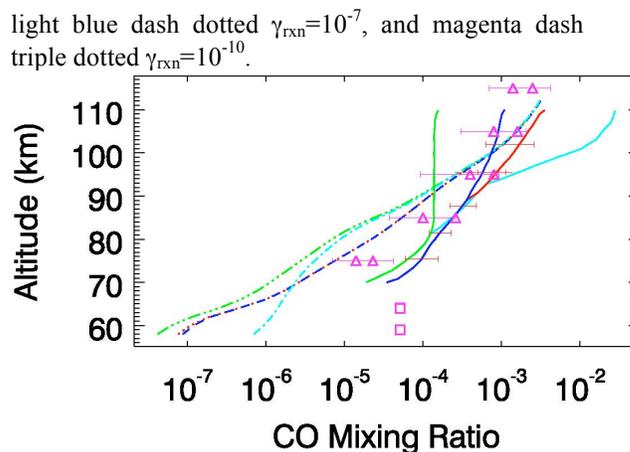
**Fig. 1.** Schematic diagram for the atmospheric chemistry on Venus. Catalytic schemes are indicated by the Greek letters in circles. The degree of laboratory confirmation is indicated by the lightness of the shade of red. The darkest red have received no confirmation. (After [1].)



**Fig. 2.** Calculated O<sub>2</sub> [17]. Green solid  $\gamma_{rxn}=10^{-4}$ , red dotted  $\gamma_{rxn}=10^{-5}$ , dark blue short dashed  $\gamma_{rxn}=10^{-6}$ ,

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**Fig. 3.** Observed and calculated CO [17]. Green dash triple dotted  $\gamma_{rxn}=10^{-5}$  with enhanced CICO stability, red dotted  $\gamma_{rxn}=10^{-5}$  without enhanced CICO stability, dark blue short dashed  $\gamma_{rxn}=10^{-5}$  without enhanced CICO stability but with increased OCS, light blue dash dotted  $\gamma_{rxn}=10^{-10}$ .