

**ATMOSPHERIC CHEMISTRY ON PRESENT-DAY VENUS AND EARTH: UNRESOLVED ISSUES AND IMPLICATIONS FOR EXTRASOLAR PLANETS.** F. P. Mills<sup>1,2,3</sup>, C. D. Parkinson<sup>2</sup>, K. L. Jessup<sup>4</sup>, Y. L. Yung<sup>5</sup>, E. Marcq<sup>6</sup>, and A. C. Vandaele<sup>7</sup>, <sup>1</sup>Fenner School of Environment and Society, Australian National University, Canberra, ACT, Australia, <sup>2</sup>Space Science Institute, Boulder CO, USA, <sup>3</sup>McDonald Observatory, University of Texas Austin, Austin, TX, USA, <sup>4</sup>Southwest Research Institute, Boulder CO, USA, <sup>5</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA, <sup>6</sup>Laboratoire Atmosphères, Milieux, Observations Spatiales, Université de Versailles, Guyancourt, France, <sup>7</sup>Royal Belgian Institute for Space Aeronomy, Brussels, Belgium.

**Introduction:** The major foci for studies to date of atmospheric chemistry on potential/actual terrestrial-like extrasolar planets has been identification of biosignatures and habitability assessment [e.g., 1-7]. While major portions of atmospheric composition parameter space remain unexplored, there is an extremely large degree of overlap between abiotic and biotic atmospheric signatures. Given this high degree of overlap, even if a portion of atmospheric composition parameter space is found that is uniquely biotic, then one must also determine whether that uniquely biotic portion of atmospheric composition parameter space is common to all habitable or inhabited planets.

Significantly less attention has been given to assessing the atmospheric chemistry implications of atmospheric composition observations on extrasolar planets. This is an area in which solar system studies can provide extremely valuable insight. For terrestrial-like exoplanets, the atmospheric chemistry on Earth and Venus is particularly relevant and important.

Venus' atmosphere is 96.5% CO<sub>2</sub> and 3.5% N<sub>2</sub> with trace abundances of SO<sub>2</sub>, OCS, H<sub>2</sub>O, HCl, HF, and HBr, as well as their photochemical and lightning-induced products. The global clouds are composed at least partly of concentrated sulfuric acid. The surface pressure is 90 bar and surface temperatures exceed 700 K. Atmospheric chemistry transitions from ion chemistry through photochemistry to thermal equilibrium chemistry with heterogeneous chemistry likely throughout the atmosphere.

Earth's atmosphere is 78% N<sub>2</sub> and 21% O<sub>2</sub> with trace abundances of SO<sub>2</sub>, OCS, H<sub>2</sub>O, HCl, HF, HBr, and N<sub>2</sub>O, as well as their photochemical and lightning-induced products. Clouds are patchy and have compositions that vary from liquid and solid water in the troposphere to sulfur, hydrogen, and nitrogen ternary compounds in the stratosphere and mesosphere. Ion and photochemistry occur throughout the atmosphere, as does heterogeneous chemistry.

**Current understanding of Venusian atmospheric chemistry:** Three major chemical cycles have been identified: the carbon dioxide, sulfur oxidation, and polysulfur cycles [e.g., 8,9], Fig. 1. The carbon dioxide cycle includes CO<sub>2</sub> photolysis, transport of a

significant fraction of CO and O to the night side, production of O<sub>2</sub>, and conversion of CO and O<sub>2</sub> to CO<sub>2</sub>, mostly via chlorine catalyzed pathways. The sulfur oxidation cycle comprises transport upward of OCS, SO<sub>2</sub>, and H<sub>2</sub>O, oxidation to H<sub>2</sub>SO<sub>4</sub>, condensation to form the global 30-km thick cloud layers, and sulfuric acid rain. The polysulfur cycle involves the upward transport of OCS and SO<sub>2</sub>, disproportionation and production of S<sub>x</sub> (x=2-8), and downward transport of S<sub>x</sub> to react with CO and SO<sub>3</sub>. There is solid evidence for the carbon dioxide and sulfur oxidation cycles; the polysulfur cycle is more speculative but plausible. Alternatively, sulfur chemistry on Venus has been conceptually divided into fast and slow atmospheric cycles and a geological cycle [e.g., 10-12]. Recent work suggests the ternary SO<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> system may bifurcate depending on the relative abundances of H<sub>2</sub>O and SO<sub>2</sub> [13].

**Key outstanding issues in Venusian atmospheric chemistry:** Despite this general understanding, five decades of spacecraft observations, and 200 years of Earth-based observations, numerous significant unresolved issues remain. One is the means by which CO<sub>2</sub> is stabilized over geologic time - models predict abundances a factor of 10 larger than the observational upper limit [e.g., 14,15]. Another is the lack of consistency among models of the chemistry and microphysics in different regions, especially in the cloud layers, where the mixing ratios of many important trace species change by orders of magnitude within several vertical scale heights, and at the surface [10]. A third is the mechanism(s) creating an inversion layer in SO<sub>2</sub> abundances in the mesosphere, Fig. 2 [16,17,18].

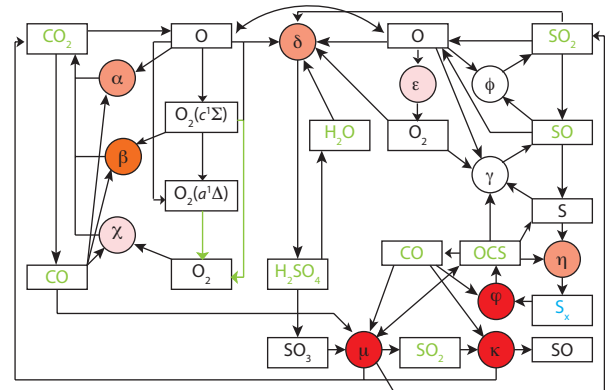
**Earth atmospheric chemistry:** Chemical cycles on Earth, as elsewhere, predominantly involve trace (radical) species whose abundances may be at the ppm to ppt level. The chemistry occurring in each portion of the Earth's atmosphere is strongly influenced by the energy of available photons and the reservoir species present.

The primary radical species are typically grouped into families based on the relatively short lifetimes for conversions between members of a family and rela-

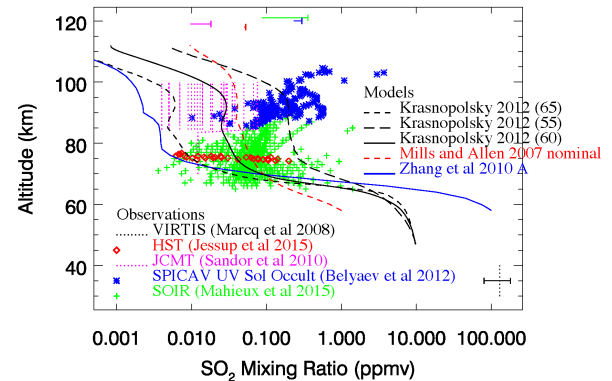
tively long lifetimes for loss from a family: odd oxygen ( $O_x = O(^3P) + O(^1D) + O_3$ ), odd hydrogen ( $HO_x = H + OH + HO_2$ ), odd chlorine ( $Cl_x = Cl + ClO + HOCl$  and  $Cl_y = Cl_x + HCl + ClONO_2 =$  reactive chlorine), and odd nitrogen ( $NO_x = N + NO + NO_2 + NO_3 + 2 * N_2O_5 + HO_2NO_2$  and  $NO_y = NO_x + HNO_3 + PAN + HONO +$  organic nitrates, etc, = reactive nitrogen), with similar definitions for  $SO_x$ ,  $Br_x$ ,  $Br_y$ , etc [19].

Species that are reasonably diagnostic of the importance of each of these families in the middle atmospheres on Earth and/or Venus, which are also potentially detectable on extrasolar terrestrial-like planets, are  $CO_2$  or  $O_2$ ,  $O_3$ ,  $H_2O$ ,  $HCl$ ,  $N_2O$ , and  $SO_2$ . Adding DCl would provide a D/H measure that is less directly affected by condensation fractionation and variable cloud cover than HDO. In addition to their potential utility for extrasolar planetary atmosphere simulations, monitoring the abundances of most of these species on hemispheric spatial scales on Earth and Venus would be diagnostic of decadal scale atmospheric changes.

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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. [16]



**Fig. 2.** Observed and modeled  $SO_2$ . Only models using standard chemistry are shown. [20]