

Title of the white paper: Atmospheric chemistry on Venus – New observations and laboratory studies to progress significant unresolved issues

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Atmospheric chemistry on Venus – New observations and laboratory studies to progress significant unresolved issues. F. P. Mills^{1,2,3}, K. L. Jessup⁴, and A. S. Brecht⁵, ¹Space Science Institute (4765 Walnut St, Suite B, Boulder, CO 80301, USA, fmills@spacescience.org), ²University of Texas at Austin, ³Australian National University, ⁴Southwest Research Institute (1050 Walnut St, Suite 300, Boulder, CO, 80302, USA, jessup@boulder.swri.edu), ⁵NASA Ames Research Center (MSC 245-3, Moffett Field, CA, 94035, USA, amanda.s.brecht@nasa.gov).

Introduction: The *Venus Express-Akatsuki* era has brought major advances in understanding Venus’ atmosphere, but first-order unknowns remain. New observations and lab studies are needed to support and enhance recent progress in our theoretical understanding. Geographic and local time variations in composition provide important information on chemical, dynamical, and climate processes. The recent development of much more capable and accurate 2D and 3D atmospheric general circulation models (AGCMs) and chemical transport models (CTMs), including data assimilation schemes, provide the tools needed to interpret high resolution 3D data sets. Systematic observations to identify both long-term climatological abundances and short-term variability are needed. Further ab initio and lab studies (e.g., spectroscopy, chemical kinetics, and state-specific probing) are needed as well to confirm the validity of postulated chemical mechanisms, clarify unknown or poorly constrained photochemical parameters, and assist with quantitative interpretation of observations. These advances will enable increased integration of multi-dimensional dynamics and chemistry and enhanced understanding of their interactions.

Venus is not only our nearest neighbor. It is also our nearest laboratory for understanding the diversity of atmospheric chemistry that will be found on exoplanets and a key comparative benchmark for understanding the divergent evolutionary paths of terrestrial-like planets.

Scientific Issues and Challenges: Venus’ bulk atmospheric composition (96.5% CO₂, 3.5% N₂) and the identity of many of its most abundant reservoir species (SO₂, H₂SO₄, HCl, H₂O) have been known for decades (Marcq et al., 2018). Its major chemical processes are even believed known – CO₂ photolysis and CO oxidation; sulfur oxidation, condensation to form H₂SO₄ clouds, and evaporation; and polymerization of sulfur to form polysulfur (Marcq et al., 2018). Yet beneath this veneer of top-level “knowledge” lie significant and important uncertainties and unknowns (Marcq et al., 2018):

- What chemical mechanisms quantitatively maintain the photochemical stability of CO₂?
- What chemical/aerosol species absorb sufficient UV-blue light to account for around 50% of the solar radiation absorbed by Venus’ atmosphere?
- How, how much, and where do the atmosphere and surface interact?
- What are the implications for and consequences of active volcanism on Venus?

New, systematically planned and acquired observations are critical for answering these questions. Integration of increasingly complex chemical mechanisms with circulation models that are increasing markedly in sophistication, resolution, and accuracy is also critical because observed species distributions reflect the complex interactions of dynamics, chemistry, and radiation. Underpinning the advances from new observations and integrated models are lab studies identifying and validating postulated chemical mechanisms. Advances in all of these areas are needed to further not only our understanding of Venus’ atmospheric chemistry, but also to interpret observations of terrestrial-like exoplanets, including exo-Venuses, and to advance comparative studies of Mars, Earth, and Venus and understand their apparent evolutionary divergence.

Atmospheric chemistry is complex because of both its interaction with transport and its sensitivity to species whose relative abundances may be a few parts per billion (ppb) or parts per

trillion (ppt). Trace radicals, in particular, regenerate many times in catalytic cycles that drive atmospheric composition away from the disequilibrium created by absorption of solar radiation (DeMore and Yung, 1982). Absorption of solar radiation, in turn, alters the atmosphere's thermal structure which drives large- and small-scale circulation (e.g., Sanchez-Lavega et al., 2017; Limaye et al., 2018).

The Photochemical Stability of CO₂ on Venus: Irradiation at wavelengths $\sim < 200$ nm photolyzes CO₂ to produce CO and O. The direct reaction of CO with O is a slow, spin-forbidden reaction, so long-term chemical stability of CO₂ on Venus requires catalytic processes that are sufficiently fast to balance photolysis of CO₂ (e.g., Mills et al., 2007). The abundance of ground-state O₂ is a sensitive indicator of whether we plausibly understand the chemical mechanisms that stabilize CO₂ on Venus, and simulations that include the known catalytic processes (e.g., CO+OH→CO₂+H, CO+Cl+O→CO₂+Cl, and CO+2Cl+O₂→CO₂+Cl+ClO) all find a global steady-state O₂ column abundance that is at least a factor of 10 larger than the observational upper limit on ground-state O₂ (e.g., Marcq et al., 2018; and references therein).

Determining the (column) abundance of ground-state O₂ in Venus' atmosphere is critical for providing a known target against which to measure the accuracy of atmospheric models. The lowest observational upper limit on mesospheric ground-state O₂ was obtained from several hours of integration with a Fabry-Perot spectrometer, $R = \lambda/\delta\lambda = 240,000$, on the 2.5-m Mt Wilson telescope (Trauger and Lunine, 1983). **Observational requirements and options** are:

- 1) Collect all scattered light from Venus' dayside on a 4-m or larger telescope with spectral resolving power, R , $\sim 100,000$ -400,000. Continue observations to determine whether the global abundance of O₂ varies on decadal timescales, as has been observed for cloud-top SO₂. (e.g., Marcq et al., 2013)
- 2) Spacecraft-borne instruments could detect ground-state O₂ and also determine its vertical profile and geographic and local-time variations. Potential techniques are a mass spectrometer or spectrometer on a balloon, limb-sounding from orbit with a submillimeter spectrometer, and solar occultation from orbit with a visible-near infrared spectrometer.

Significant gaps exist in our laboratory-based understanding of the chlorine-catalyzed oxidation of CO believed to predominate on Venus. The thermal stability of the chloroformyl radical (ClCO) is a critical parameter in the primary CO oxidation pathways in Venus models (Mills and Allen, 2007). Assuming greater thermal stability (but within the experimental uncertainty) greatly reduces the calculated O₂ column abundance (Zhang et al., 2012) but causes the calculated CO mixing ratio to deviate significantly from observations near the cloud top (Mills and Allen, 2007). More accurate laboratory measurements of the ClCO equilibrium constant are needed. The next step in the CO oxidation process is formation of peroxychloroformyl radical (ClC(O)O₂). Photolysis of ClC(O)O₂ in a matrix has been shown to produce CO₂ (Pernice et al., 2004), but none of the hypothesized kinetic reactions for destruction of ClC(O)O₂ has been studied in the laboratory.

Improving our understanding of chlorine and oxygen chemistry through lab studies, observations, and chemical transport modeling is critical for understanding Venus' current state and its recent evolution. Chlorine chemistry will also be important for some exoplanets and has not been included in any exoplanet chemistry models (e.g., Harman et al., 2018).

The Spatial and Temporal Distributions of Sulfur Oxides on Venus: Sulfur species on Venus play major roles in Venus' climate through its energy budget and thermal structure. The large single scattering albedo of sulfuric acid in the global clouds causes Venus to have a bond albedo of ~ 0.76 -0.8 (Titov et al., 2007), Fig. 1, while the clouds are sufficiently opaque to thermal

radiation to contribute about 20% of Venus' atmospheric greenhouse effect (Titov et al., 2007). The largest gas-phase sulfur reservoir is SO₂ in the troposphere and known significant sinks are production of condensed sulfuric acid in the clouds and photolysis within and above the upper cloud. Consistent with this, the SO₂ mixing ratio decreases with increasing altitude from ~ 30 km

to ~ 80 km but above ~ 80-85 km altitude, the SO₂ mixing ratio increases with increasing altitude, forming an inversion layer in the upper mesosphere. **Conversion of SO₂ to H₂SO₄ cannot be the sole loss for SO₂ through the cloud layers.** The SO₂ mixing ratio, which is a factor of four larger than the H₂O mixing ratio in the troposphere, decreases by a factor of 1000 through the cloud layers while the H₂O mixing ratio decreases by a factor of 30 (Vandaele et al., 2017;). No model has accurately simulated this decrease in SO₂ (Vandaele et al., 2017; Marcq et al., 2018). Likewise, no model has yet provided a fully satisfactory explanation for the

upper mesosphere inversion layer (e.g., Sandor and Clancy, 2012). The inversion implies an additional significant sulfur reservoir (besides SO₂ and SO) must exist in Venus' mesosphere (~70-100 km), as do observations of spatial variability of SO₂ and SO at ~ 70 km with HST (Jessup et al., 2015) and temporal variability at ~ 85-100 km with JCMT (Sandor et al., 2010). **At present, the identity of the reservoir(s) and how it is linked to other chemical processes in Venus' atmosphere are unknown.** The large spatial variations in SO₂ observed within the upper cloud are potentially linked to observed variations in H₂O (e.g., Encrenaz et al., 2020) via bifurcation within the SO₂-H₂O-H₂SO₄ ternary system (Parkinson et al., 2015). Large spatial variations in SO₂ and SO are also observed above 80 km altitude (Sandor et al., 2010; Encrenaz et al., 2015). Because sulfur photochemistry drives formation of the aerosol and cloud layers, existing significant uncertainties in Venus' sulfur chemistry translate into significant unanswered questions about Venus' overall energy and radiation budgets. Key questions that need to be answered are:

- 1) What chemical, microphysical, and dynamical processes occur within the cloud layers to produce the observed gaseous and condensed-phase species distributions?
- 2) What chemical, microphysical, and/or dynamical processes produce the observed upper mesosphere SO₂ and SO inversion layer?

Answering the first question requires in situ measurements of species and cloud particle abundances within the cloud layers as a function of altitude, latitude, longitude, and local solar time. Complementary nadir-viewing imaging spectroscopy from orbit with sufficient spectral resolution to quantify SO₂ and SO abundances and apparent temperatures is needed to provide contextual information, particularly for large-scale features such as the observed mountain lee waves (Fukuhara et al., 2017; Kitahara et al., 2019). Regular and continuous monitoring with an appropriate sampling is needed to discriminate among chemical and dynamical processes.

Progress on the second question requires detailed maps of the distributions of SO₂, SO, and possibly other species relative to altitude, latitude, and local time with sufficient spatial and temporal resolution to properly sample the known/anticipated chemical/dynamical timescales and sufficient spectral resolution to quantify SO₂ and SO abundances. Although Venus' SO profile was estimated based on residuals secondary to the SO₂ fit based on SPICAV occultation observations (Belyaev et al., 2012), unambiguous SO retrievals could not be derived from the

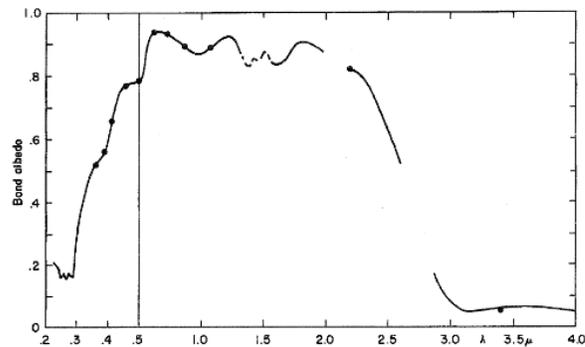


Fig. 2 Bond albedo vs. wavelength 0.2-4.0 μ . Sources described in text. Details near 1.5 μ somewhat uncertain.

Fig 1. Venus bond albedo as a function of wavelength (Kuiper et al., 1969).

nadir-viewing data which limited the range of local time and latitudes at which SO gas abundance was documented (e.g., Marcq et al., 2020).

Improved laboratory data on the condensate and chemical reaction properties of species

Number	Absorber	Absorption Range (nm)
1	SO ₂	240 - 330
2	SO	UV
3	COS	240
4	CS ₂	
4	Disulfur Oxide and disulfur dioxide (OSSO)	320 - 400
5	S ₂ O	310-470, 650 - 740
6	S ₈	320-500
7	Amorphous sulfur (S ₃ , S ₄)	UV
8	SCL ₂	270 - 450
9	Ammonium pyrosulfite. (NH ₄) ₂ S ₂ O ₅	320 - 500
10	Nitrosylsulfuric acid (NOHSO ₄)	250 - 500
11	Carbon suboxide polymer	215
12	Cl ₂	190 - 500
13	Croconic acid - C ₅ H ₅ O ₂	220 - 420
14	NO	215, 226.5
15	N ₂ O	170 - 220
16	H ₂ S	180 - 230
17	HNO ₃	2000, 300
18	FeCl ₃	300-450
19	FeCl ₂	UV
20	Perchloric acid (HClO ₄)	UV
21	Anhydrous silicate	2700 - 4000
22	Fe-S based microorganisms	
23	Photosynthetic microorganisms	
	Hypothetical	

Table 1. Proposed candidates for the unidentified UV-Blue absorber(s) (Limaye et al., 2020).

involved in the sulfur chemical cycle – e.g., rate coefficients for kinetic reactions, cross sections and branching ratios for photo-absorption/dissociation, and spectroscopic information (e.g., Huestis et al., 2008) – will be needed to support these detailed observations and ongoing theoretical modelling efforts.

Venus is a key end member for climate studies and for assessment of climate and habitability on exoplanets. Consequently, advancing our understanding of the sulfur chemical cycles that drive Venus' cloud formation and climate is a high priority.

The Unidentified UV-Blue Absorber(s):

Venus' very high albedo at 500-2000 nm, Fig. 1, means solar radiation absorbed at wavelengths < 500 nm drives the atmospheric energy budget. Absorption at 200-320 nm is largely explained by SO₂ and SO gas within and above the upper cloud. A long-standing mystery is what is responsible for the absorption at 320-500 nm, the wavelengths at which Venus' distinctive UV markings are seen. In addition, an underlying continuum absorption has been identified in recent higher precision photometry at wavelengths < 300 nm that is not due to SO₂ or SO but may be linked to the longer-wavelength absorption (Krasnopolsky, 2012; Jessup et al., 2020). Radiative transfer simulations indicate the unidentified UV-Blue absorber(s) is/are responsible for almost half of the solar energy deposited in Venus' atmosphere (Crisp, 1986), so its production and distribution play important roles in Venus' climate, thermal structure, and circulation patterns. A large number of candidates have been proposed of a-biogenic and biogenic origin, Table 1 (Limaye et al., 2020).

Remote observations have provided valuable clues about the characteristics of the unidentified UV-Blue absorber(s). **Only in situ measurements can provide definitive identification.** Tracing the absorber(s)' distribution as a function of altitude, latitude, and local time is critical input for understanding the drivers of Venus' distinctive but enigmatic superrotation and potential feedbacks

among chemistry, microphysics, and dynamics. **Several types of platforms can contribute**

including: dropsondes/probes, aerial platforms such as solar planes and balloons, and kite-like atmospheric gliders.

Ongoing laboratory studies will be needed to determine the spectra of candidate absorber(s) so they may be assessed in numerical models.

Tropospheric Chemistry and Atmosphere-Surface Interaction: At the high pressures and temperatures below the Venus clouds, the atmosphere may be in or close to thermochemical equilibrium. Consequently, to zeroth order, one does not expect detectable spatial variability in trace gases, although modern thermochemical calculations suggest gas-phase thermochemical equilibrium may be reached only in the lowest few kms (Fegley et al., 1997). Observations, however, have found significant latitudinal variations in trace gas abundances, such as large increases in gaseous sulfuric acid (H_2SO_4) toward the poles, increases in CO from the equator to mid-latitudes and an opposite trend in OCS (e.g., Marcq et al., 2018). Meridional transport, with vertical upwelling at the equator and subsidence at higher latitudes, has been offered as the explanation based on simulations with CO and OCS treated as passive tracers with specified loss rates. More detailed simulations have found good agreement with observations (Yung et al., 2009; Krasnopolsky, 2013; Stolzenbach, 2016), but only a few of the reactions used in those studies have had their viability assessed and rate coefficients measured in laboratory studies (Marcq et al., 2018). Furthermore, **the two most detailed studies of tropospheric chemistry on Venus reached very different conclusions about surface-atmosphere interactions** – Krasnopolsky (2013) found no requirement for a significant surface source of OCS while Yung et al. (2009) found a significant surface source was required at equatorial latitudes.

Observational improvements have yielded great insight into the distribution of some species below Venus' clouds. **Required observations:** Continued ground-based observations are needed to elucidate or clarify spatial variations in tropospheric abundances and vertical gradients of species and to detect changes that may indicate volcanic activity or changes in circulation. Combining *in situ* observations of species abundances, more detailed observations of spectrally-resolved UV-visible irradiance as a function of altitude, latitude, and local time in Venus' troposphere, and data assimilation will enable the next jump in understanding chemistry, dynamics, and climate on Venus.

Laboratory studies are desperately needed. Very few UV photons, the usual source of disequilibrium energy, reach the troposphere, yet species distributions indicate chemical reactions are occurring there. Some hypotheses are photosensitized dissociation reactions, photochemistry driven by visible-wavelength light, and heterogeneous reactions on aerosol particles. **All proposed hypotheses require laboratory work** to assess their viability and importance (Yung et al., 2009).

Connecting Laboratory Studies, Observations and Numerical Simulations: Current approaches to studying chemical cycles in Venus' atmosphere – primarily 1D chemical models and 2D transport models with passive tracers – are where terrestrial studies were 20+ years ago, before the introduction of 2D and 3D CTMs. Until recently, observational data were insufficient and 3D AGCMs were unable to accurately reproduce observed large-scale circulation patterns, so multi-dimensional chemistry models were not warranted. Observational advances during the *Venus Express-Akatsuki* era identifying or confirming vertical, meridional, and temporal variations in key species (e.g., OCS, CO, and SO_2) and significant improvements in the quality of AGCM simulations, particularly as a result of introducing more realistic radiative forcing, however, have brought 2D and 3D CTMs to the fore. Suites of 1D model simulations can provide significant insight into chemical processes but 2D or 3D chemical transport simulations are needed to understand how meridional transport and chemistry interact. Just as with terrestrial climate studies,

drawing precise conclusions from a single AGCM (or CTM) is difficult (Lebonnois et al., 2013), so support for a diversity of AGCM and CTM models and modeling approaches is needed. **Funded sensitivity studies with AGCMs and CTMs should be included in the design and planning of future flagship missions to ensure the instrument suites and operating modes are able to address key uncertainties in understanding Venus' atmosphere.**

Funding for lab studies to support interpretation of observations, numerical modeling, and mission design is also critically needed. Lab spectroscopy provides the means to detect new species and quantify abundances; chemical kinetics identifies and quantifies postulated or previously untested reaction pathways; and ab initio studies extend insight to conditions that are difficult or impossible to study in the lab. There are commonalities across the terrestrial planets, exemplified by early studies of chlorine destruction of ozone on Venus and Earth (DeMore and Yung, 1982), and Venus is our most accessible “laboratory” for exo-Venuses. However, Venus is unique in our solar system and will continue to require lab studies relevant to its unique conditions.

Significance of Venus Research: Atmospheric chemistry, dynamics, and climate are very closely linked on Venus (Limaye et al., 2018). Venus' atmospheric structure is strongly dependent on the sulfur chemistry cycle and the interaction of sulfur species with oxygen bearing gases (CO_x , O_x) and chlorine and hydrogen compounds (e.g., Mills et al., 2007). Venus is the only terrestrial-like planet in our solar system whose atmospheric chemistry encompasses photochemical and thermochemical processes operating across a range of oxidation states (Marcq et al., 2018). This makes Venus invaluable for interpreting observations of exoplanets.

Due to its comparatively easy accessibility, Venus is an important resource for exploring the diversity of evolution of terrestrial exoplanets (Kane et al., 2019; Dong et al., 2020), including the evolution of habitability. Venus can uniquely guide us on what differentials drive variations in Earth-sized planetary climate conditions relative to the evolution of a host star. For example, Venus' slow rotation fosters thick H_2SO_4 cloud formation, via long solar days, low Coriolis forces and strong subsolar convection., Venus is unique in the solar system, in that its dense H_2SO_4 clouds host an absorbing source that drives solar heating, fostering rather than buffering, climate change (Lee et al., 2019; Yang et al., 2014). For these reasons Venus is an important and intriguing end-member in the study of planet climate and habitability evolution.

Conclusions: Significant, unresolved questions on Venus' atmospheric chemistry include:

- What processes maintain the photochemical stability of CO_2 ?
- What chemical/aerosol species absorbs ~ 50% of the sunlight absorbed by Venus?
- How do the surface and atmosphere interact?
- What chemical, microphysical, and dynamical processes dominate in the cloud layers?

Answering these questions requires systematic, targeted observations from Earth, Venus orbit, and in situ. Key species to target are SO_2 , SO , OCS , ground-state O_2 , CO , and the unidentified UV-Blue absorber(s). Increased integration of multidimensional chemistry, microphysical, and dynamical models will also be required. Supporting laboratory studies are critical to the success of both new observations and modelling.

Answering these questions will provide great insight into the comparative evolution of Mars, Earth, and Venus; greater understanding of the fundamental couplings among atmospheric chemistry, microphysics, and dynamics by comparing with Earth's past and present climates; and ideas for identifying and characterizing potentially habitable environments on exoplanets.

All work advocated here addresses Essential and Important Investigations in the VEXAG 2020 [GOI](#) – goal II, “Understand atmospheric Dynamics and Chemistry on Venus.”

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