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Astrobiological Potential of Venus Atmosphere Chemical Anomalies and Other Unexplained Cloud Properties

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Abstract: Long-standing unexplained Venus atmosphere observations and chemical anomalies point to unknown chemistry but also leave room for the possibility of life. The unexplained observations include several gases out of thermodynamic equilibrium (e.g. tens of ppm O_2, the possible presence of PH_3 and NH_3, SO_2 and H_2O vertical abundance profiles), an unknown composition of large, lower cloud particles, and the "unknown absorber(s)". Here we first review relevant properties of the Venus atmosphere and then describe the atmospheric chemical anomalies and how they motivate future astrobiology missions to Venus.

Keywords: Venus clouds; atmospheric chemistry; acidity; habitability; atmospheric gases

1. Introduction

Scientists have been speculating on Venus as a habitable world for over half a century (e.g. (Bains et al., 2023b, 2021a; Cockell, 1999; Dartnell et al., 2015; Grinspoon and Bullock, 2007; Izenberg et al., 2021; Kotsyurbenko et al., 2021; Limaye et al., 2021b, 2018; Mogul et al., 2021a; Morowitz and Sagan, 1967; Patel et al., 2021; Schulze-Makuch et al., 2004; Seager et al., 2021)), based on the Earth-like temperature and pressure in Venus' clouds at 48–60 km above the surface. The hypothesis that Venusian clouds may be inhabited by an aerial biosphere has recently been bolstered by a tentative detection of the gas phosphine (PH_3) in the atmosphere of Venus (Bains et al., 2021c; Greaves et al., 2021b). Phosphine's presence at ppb levels is not explained by any known chemistry (Bains et al., 2021c, 2022c, 2022d, 2022a, 2023a). PH_3, however, is not the only Venus' atmospheric constituent that suggests unknown chemical processes in the clouds and leaves room for the possibility of life. The presence of such unexplained chemicals came to the forefront due to recent efforts to re-analyze and reinterpret the legacy data collected by both the Pioneer Venus and Venera probes (Bains et al., 2021a; Mogul et al., 2021b, 2021a).

The former Soviet Union has sent thirteen successful in situ Venus probe missions (between 1967 and 1984). Eleven of them (Venera 4–14) were atmospheric probes and landers, two were balloons, as well as atmospheric probes and landers (VeGa 1–2). The United States launched three flyby missions and a single large mission, Pioneer Venus, in 1978, with orbiter and four in situ atmospheric probes (Fimmel, 1983).

In this paper, we review and summarize Venus' long-lasting, unexplained atmospheric observations, which have been acquired over the span of the last half century. We focus on detections and observations that have been previously dismissed as artifactual, forgotten, or otherwise remained unexplained for decades. Such unexplained observations include, for example, the "unknown absorber(s)" and the chemical composition and shape of Mode 3 cloud particles. The tentative, dismissed, unexplored, or forgotten chemical atmospheric constituents include tens of ppm O_2, the possible presence of organics, PH_3 and NH_3, to name a few. We also discuss the anomalous vertical abundance profiles of SO_2 and H_2O and summarize the model that could explain them, emphasizing the model's astrobiological implications. We discuss the original observations and methods used and the validity of the original discoveries. Such unexplained, unexplored, and chemically anomalous properties motivate and justify a dedicated Venus mission to confirm previous measurements with modern instrumentation and test for possible mechanisms behind the legacy observations, including the presence of life.

2. Motivation for a Venus Astrobiology Mission

There are many scientific reasons to explore the atmosphere, surface, and clouds of Venus, and many possible mission architectures and instrumented platforms to make measurements (Limaye and Garvin, 2023). The basic motivation to confirm and study unexplored, unexplained, and anomalous measurements in the Venusian atmosphere is that it is through detailed studies of such anomalies and their context that they can be validated and their explanation discovered, potentially including the presence of life (Cleland, 2019a, 2019b). This broad approach has been illustrated by the Galileo experiment, that is, the attempt to detect evidence of life on Earth solely from remote observations from Galileo during its flyby of Earth (Sagan et al., 1993). Sagan et al. (1993) concluded that the results of the Galileo flyby were consistent with the existence of life on Earth, based on the identification of atmospheric anomalies (e.g., the coexistence of significant CH_4 and O_2) that were challenging to explain with known abiotic mechanisms and understanding of planetary physical properties but were possible to explain with biotic mechanisms. Life has been postulated as a potential source or contributor to observed, yet poorly constrained, Venus cloud properties (e.g., the source of the strong UV absorption, mode 3 particles, etc.), yet Venus is much less well understood than Earth. Executing a similar procedure for Venus will require resolving current mysteries or unknowns regarding its atmosphere, identifying anomalies that persist despite improved understanding of the general atmospheric state, and seeking and testing explanations for these anomalies and other unexplained observations. Upon detailed study of possible missions focused on astrobiology and, in particular, on life detection, it has become clear that only a focused in situ mission and/or a sample return mission carries the likelihood of providing definitive answers to the crucial questions posed with regard to atmospheric chemistry, habitability of the clouds, and possible presence of life (Seager et al., 2022b).

This point is well illustrated by the fact that the two most recent Venus missions, both orbiters, have merely confirmed and deepened many of the outstanding mysteries of the Venus cloud region. Both Venus Express (ESA) (Svedhem et al., 2009) and Akatsuki (JAXA) (Nakamura et al., 2011) have been successful orbital spacecraft, which returned valuable data on the cloud composition and structure and on atmospheric dynamics and composition. These missions have continued to monitor the "unknown absorber(s)," which absorb a large fraction of the incident solar radiation, but have not succeeded in identifying the substance(s) responsible for this enormous unexplained absorption. Likewise, Venus Express and Akatsuki have generally confirmed the overall picture of the Venus clouds and cloud-level atmosphere provided by earlier American and Soviet entry probes (Pioneer Venus, the Venera and VeGa missions) and decades of ground-based observations. As a result, ESA and JAXA missions have filled in many details of cloud structure and dynamics, but they have not resolved the persistent mysteries that involve possible trace cloud components, unusual particle shapes, and trace atmospheric gases. These unexplained observations, both individually and taken together, are significant motivators to return to Venus for in situ observations.

The ill-defined Venus cloud properties and unexplored chemical observations fuel speculation about possible biological activity. Detailed characterization of cloud particle properties has proven particularly impervious to remote investigation and would require direct sampling of the clouds. Likewise, detection of biological activity or even life itself would require high-fidelity, novel in situ analytical methods or atmospheric sample return missions and cannot be accomplished using remote sensing techniques (Seager et al., 2022b). For an illustrative analogy, consider trying to make a definitive determination of the presence of life in a terrestrial location such as the Atacama Desert where microbial life is present but sparsely and at low abundance. Satellite remote sensing might hint at some of the right conditions, such as moisture and temperature range, but a definitive positive detection of life would likely require a platform that could directly sample the upper layers of the desert surface or even bring samples back to specialized laboratories for further study (see, e.g., Cabrol et al., 2007; Parro et al., 2011; Vítek et al., 2012). Such difficulties illustrate the limitations of remote sensing for biology by orbital missions. What is missing and the logical next step is direct sampling of the environment by an entry probe equipped with modern instrumentation (see, e.g., Limaye et al., 2021b; Schulze-Makuch and Irwin, 2002; Seager et al., 2022b, 2022a).

In this context, it is striking to consider that there has never been an in situ investigation of the atmosphere and clouds of Venus employing 21st century scientific instrumentation. The most recent American entry probes were the Pioneer Venus probes that flew in 1978. The Soviet VeGa balloons flew in 1985. It has been 38 years since any instrument from Earth was flown to directly investigate the atmosphere and the clouds of Venus. The entire scientific field of Astrobiology has matured in the interim. We now know questions to ask that we could not have formulated in the 1980s, but even more important is the progress in scientific instrumentation and miniaturization of electronics during these decades.

3. Venus' Unexplained Observations and Understudied Cloud Properties

Many intriguing in situ observations of Venus have never been fully explored (Figure 1). Nearly all of these observations could be the result of biological activity, though life may not be required to explain any of them.

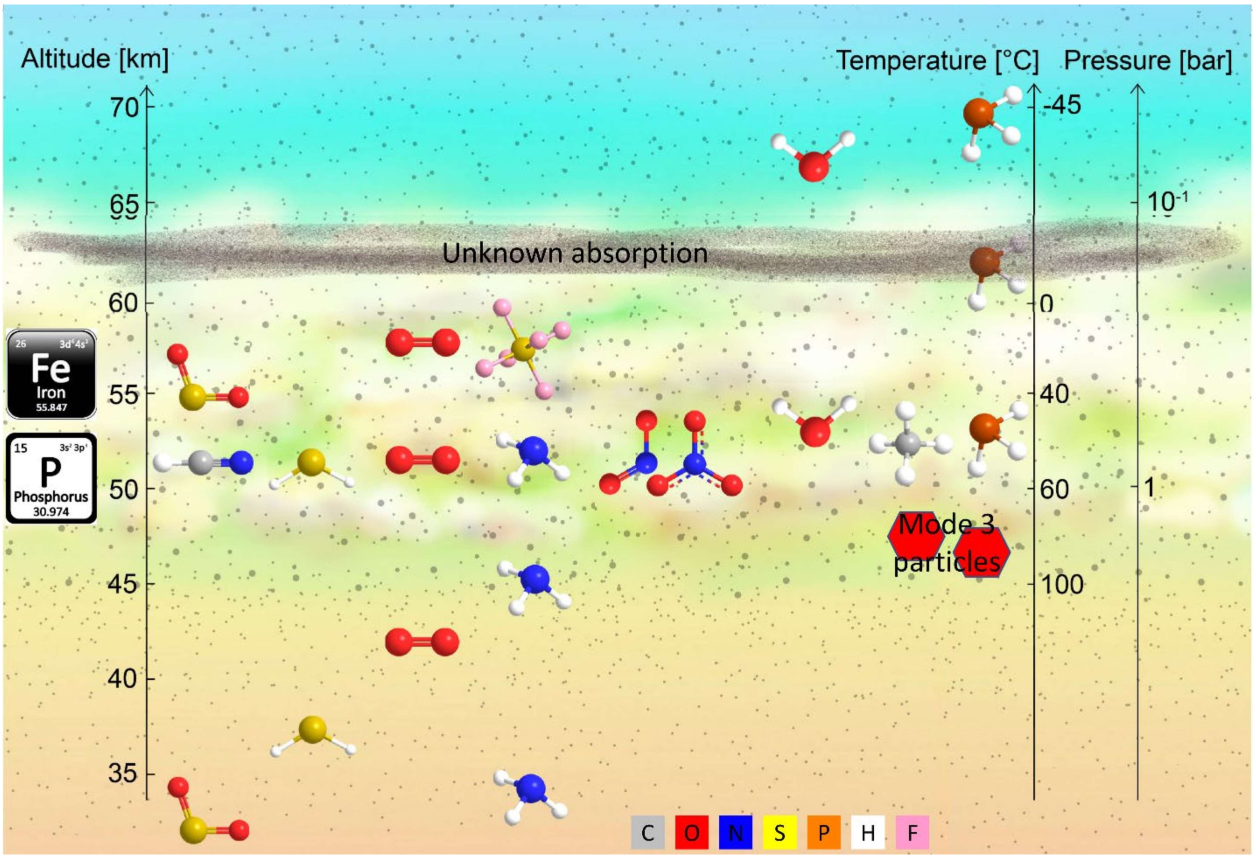

Figure 1. Unexplained and unexplored Venus' atmospheric observations. The molecule models show individual detections and altitudes for the atmospheric observations (e.g. NH_3 has been tentatively observed three times, twice, at two different altitudes by Venera 8, at ~32 and ~45 km, and once by Pioneer Venus at ~51 km, see also Table 3). If the observation has been made at the altitude range the molecule model is placed at the highest altitude of the range (e.g. SF_6 has been tentatively detected between 35 and 58 km). The SO_2 and H_2O molecule models do not represent every individual observation but rather denote the anomalous abundance profiles for SO_2 and H_2O in the atmosphere (see (Bains et al., 2021a; Rimmer et al., 2021) and Section 3.5). Most of the unexplained atmospheric observations have been recorded within the clouds (48-70 km) and in the stagnant haze layer below the clouds (31-47 km).

3.1. The Unknown Absorber(s)

While Venus appears relatively bland and featureless at visible wavelengths, observers starting in the 1920s noticed unusual high-contrast features in the ultraviolet (Ross, 1928). These features move with the ~4-day super-rotation of Venus' upper cloud deck, yet also display great variability on a wide range of temporal and spatial scales. Much effort has gone into attempting to identify the substance(s) responsible for the absorption between 320–400 nm, but no proposed candidate satisfies all of the observational constraints, leading to the oft-used descriptive term "unknown UV absorber." We note, however, that the absorption of radiation that is associated with the "unknown UV absorber" is not restricted exclusively to UV but also extends into longer wavelengths (Limaye et al., 2018; Pérez-Hoyos et al., 2018). Hence, throughout this article we use the term "unknown absorber" when referring to this unexplained phenomenon, knowing that multiple chemical species (*i.e.*, "unknown absorbers") could contribute to this phenomenon.

The current consensus, based, for example, on Venus photometric measurements, is that the unknown absorption occurs predominantly right below the cloud tops, at 60 km, and is associated with cloud particles (possibly with the smallest micron sized cloud particles referred to as Mode 1) rather than gaseous species (Ekonomov et al., 1984; Titov et al., 2012; Tomasko et al., 1980, 1979) (reviewed by Titov et al., 2018)).

After the upper clouds were identified as being composed primarily of sulfuric acid droplets (Hansen and Hovenier, 1974; Knollenberg and Hunten, 1980; Young, 1973), efforts to identify the absorber largely focused on sulfur compounds, including SO_2, S_2O, S_2O_2, and various allotropes of elemental sulfur (S_3, S_4 and S_8) (Table 1). Other proposals have focused on elemental chlorine (Cl_2), which has been identified in the upper atmosphere and shows absorption features in roughly the right spectral range. A summary of proposed candidates is given in the works of Limaye et al (2021a), Mills et al. (20070, and Pérez-Hoyos et al. (2018) and in Table 1 below.

Despite decades of effort and observations by two orbiting spacecraft in the 21st century (Venus Express by ESA and Akatsuki by JAXA), none of the proposed candidate molecules have been found to entirely fit the observational data. The candidate molecules either have too low abundance (S_2O_2) (Krasnopolsky, 2018; Titov et al., 2018) or do not entirely fit the spectral absorption profile ($FeCl_3$) (Pérez-Hoyos et al., 2018; Rustad and Gregory, 1977) (Table 1). In principle, one can overcome the problem that the narrow spectral absorption of some candidate molecules does not match the broad absorption of the unknown absorber by postulating that the absorber is a mix of materials and not a single chemical species. However, most of the proposed UV-absorbing species are unstable to UV photochemistry or predicted to be present at extremely low abundances in the absence of biological activity. Therefore, the mystery of the Venusian absorber persists. The unknown absorber is remarkably efficient, capturing more than 50% of the solar energy reaching Venus, with consequent effects on atmospheric structure and dynamics.

Several researchers have suggested that qualities of the unknown absorber could be a signature of biological activity in the clouds (Limaye et al., 2018; Schulze-Makuch et al., 2004). The spectral characteristics of the Venus clouds, including the strong UV absorption, are consistent with the spectrum of certain types of terrestrial bacteria (Limaye et al., 2018). The spatial and temporal patterns of the unknown absorber are somewhat reminiscent of terrestrial algal blooms (Grinspoon and Bullock, 2007; Limaye et al., 2018). The great efficiency of absorption, if utilized as a photosynthetic pigment, could provide a large amount of metabolic energy (Grinspoon, 1997). The consistency between the UV absorption spectrum of the unknown Venus absorber and those of bacterial cells is perhaps not surprising as many pigments and various aromatic compounds and proteins (especially in combination) present in bacterial cells have broad and diverse UV absorption properties. A selection of the spectra of UV-absorbing biomolecules would reproduce the absorber spectrum, but in the absence of any evidence that any of the components are present this would be an arbitrary fit and not evidence for the presence of those compounds.

Attempts have been made to tie the possible abundance of the unknown absorber to the expected biomass of the hypothetical aerial biosphere in Venus' clouds (Jordan et al., 2022). However, as also noted by Jordan et al. (2022), there is no reliable way to estimate and correlate the biomass abundance to the possible abundance of the unknown absorber, in a strict gram per gram fashion. This is because some biological pigments have extraordinarily strong absorption, much stronger than, for example, simple salts. Therefore, a strongly absorbing species is not inconsistent with a very low abundance biomass.

Recently, Benner and Spacek (2021), Spacek (2021), Spacek et al. (2023), and Spacek and Benner (2021) speculated on organic molecules inside the Venus cloud particles as the unknown absorber. The proposal comes from laboratory experiments that started with simple organic molecules, including formaldehyde, dissolved in concentrated sulfuric acid. A chain of chemical reactions led to a rich variety of yellow-, red-, and brown-colored organic molecules. The hypothesis is that the simple organic molecules that are precursors to the organics responsible for the unknown absorber originate from meteoritic delivery, photochemistry, or even possibly life itself (Benner and Spacek, 2021; Spacek, 2021; Spacek et al., 2023; Spacek and Benner, 2021).

Indeed, the petrochemical industry uses concentrated sulfuric acid as a catalyst during octane production from isobutane and butene and finds a rich chemistry in concentrated sulfuric acid from the reactivity of hydrocarbon molecules (Albright et al., 1972; Huang et al., 2015; Miron and Lee, 1963). While the resulting compounds called "red oil" are an undesirable side product, this chemistry substantiates the idea that the Venus cloud sulfuric acid particles can support diverse organic chemistry independent of the presence of life.

The direct detection of organic chemicals has never been attempted and should be a priority for future in situ missions to Venus. Neither Venera/VeGa probes nor Pioneer Venus directly searched for organic chemistry in the clouds. We will get more information on the possible composition of the unknown absorber(s) via NASA's DAVINCI orbiter's Compact Ultraviolet to Visible Imaging Spectrometer (CUVIS) instrument (Garvin et al., 2022), but a direct detection and identification of organic chemicals in the clouds of Venus is not a target of the selected NASA and ESA missions. The detection of organic chemicals within the cloud particles is, however, one of the science objectives of the Rocket Lab mission to Venus (French et al., 2022) and its science instrument, the autofluorescence nephelometer (AFN) (Baumgardner et al., 2022).

Table 1. List of candidates for the "unknown absorber(s)".

Proposed candidate absorber molecule	Proposed absorber explanation	Cons
sulfur dioxide SO_2	SO_2 gas is the main absorber at wavelengths from 200 to 320 nm (Ekonomov et al., 1983; Pollack et al., 1980, 1979).	The absorption at wavelengths longer than 320 nm cannot be accounted for by SO_2 (Blackie et al., 2011; Pérez-Hoyos et al., 2018).
elemental sulfur allotropes S_3, S_4, S_8	Various forms of gaseous and aerosol forms of elemental sulfur have been postulated to contribute to the absorber spectra as well as to the pale yellow color of Venus: S_3 and S_4 (Toon et al., 1982) S_8 (Hapke and Nelson, 1975; Schulze-Makuch and Irwin, 2006).	Sulfur aerosols (S_8) alone cannot account for the unknown absorber, as their abundance is too low at the cloud tops and its absorption profile does not agree with the absorber profile (Krasnopolsky, 2016, 2013); S_3 and S_4 absorption is centered at longer wavelengths, >360 nm (Pérez-Hoyos et al., 2018).
disulfur monoxide S_2O	An irradiated version of S_2O could contribute to the 350 nm core absorption feature and some absorption in the range of 400–500 nm (Hapke and Graham, 1989). Both gaseous and condensed phase S_2O have been proposed to contribute to the unknown absorber spectra.	Spectral characteristics of *cyc*-S_2O do not adequately match the unknown absorber spectra (Frandsen et al., 2020). Other S_2O isomers are too unstable (Frandsen et al., 2020).
disulfur dioxide S_2O_2	The *cis*- and *trans*- isomers of S_2O_2 (OSSO) are a good fit to the unknown absorber spectra (Frandsen et al., 2020, 2016; Wu et al., 2018).	Very short photochemical lifetime (seconds) of the OSSO species precludes its existence on the day side of the planet (Titov et al., 2018). Photochemical modeling of the atmosphere does not support S_2O_2 as major absorber (Krasnopolsky, 2018).
ammonia pyrosulfite $(NH_4)_2S_2O_5$	Ammonia pyrosulfite aerosols may contribute to the near UV absorption if $(NH_4)_2S_2O_5$ forms in the cold top cloud regions (Titov, 1983).	Inconsistent with Pioneer Venus spectroscopic observations at 365 nm (Krasnopolsky, 1986). Venus clouds should have been brighter in UV at low altitudes (Krasnopolsky, 1985).
sulfur dichloride SCl_2	Proposed to account for the core absorption around 350 nm (Krasnopolsky, 1986).	Too narrow absorption to account for the entire unknown absorber (Pérez-Hoyos et al., 2018). Photochemical abundance estimates are too low to account for the unknown absorption (Krasnopolsky, 1986). Other postulated chlorine-sulfur species (e.g. SO_2Cl, $SOCl_2$, SO_2Cl_2, SO_4Cl) (Baines and Delitsky, 2013) have not been observed or have very short photochemical lifetime (Krasnopolsky, 2013, 2007).
perchloric acid $HClO_4$	Suggested as a component of aerosols contributing to the unknown absorber (Von Zahn et al., 1983). Recent re-analysis of the Pioneer Venus LNMS data shows evidence of oxychlorine species, e.g. chlorous acid ($HClO_2$), in the atmosphere, their abundance however is uncertain (Mogul et al., 2021b).	Not good fit to the Venus spectra. The production rate of $HClO_4$ should be negligible, not enough to account for the observed unknown absorber (Krasnopolsky, 1986).
hydrobromic acid HBr	Proposed to account for the core absorption around 350 nm (Sill, 1975).	Not good fit to the Venus spectra. No confirmed detection; upper limits of ~1 ppb at the cloud tops give abundances too low for HBr to be a major contributor to the unknown absorber (Krasnopolsky and Belyaev, 2017).
chlorine Cl_2	Proposed to account for the core absorption around 350 nm (Pollack et al., 1980).	Too narrow absorption to account for the entire unknown absorber (Pérez-Hoyos et al., 2018). Photochemical abundance estimates are too low to account for the unknown absorption (Krasnopolsky, 1986).

iron chloride $FeCl_3$ in aerosols	Proposed to account for the core absorption around 350 nm (Krasnopolsky, 2017, 1985; Zasova et al., 1981).	Too narrow absorption to account for the entire unknown absorber (Pérez-Hoyos et al., 2018; Rustad and Gregory, 1977).
nitrosylsulfuric acid $NOHSO_4$	Together with other species proposed to qualitatively explain Venus' UV albedo (Krasnopolsky, 1986; Watson et al., 1979).	Not good fit to the Venus spectra. The predicted abundance of $NOHSO_4$ is insufficient to account for the observed unknown absorber (Krasnopolsky, 1986).
nitric oxide NO and other NO_x species	Postulated to contribute to the unknown absorber (Shaya and Caldwell, 1976).	Cannot fully explain the unknown absorber. Photochemical abundance estimates are too low to account for the unknown absorption (Krasnopolsky, 1986). See also early ground-based observations upper limits on NO_x abundance above the clouds (see (Moroz, 1981), their Table VI) and the newest upper limits on NO_x in the Venus lower-mesosphere using SOIR on board Venus Express (Mahieux et al., 2023).
carbon disulfide CS_2	Absorbs strongest at wavelengths <360 nm, but not between 330 and 600 nm (Keller-Rudek et al., 2013).	UV absorption at wavelengths longer than 330 nm cannot be accounted for by CS_2.
carbonyl sulfide OCS	Absorbs strongest at wavelengths <300 nm, but not between 330 and 600 nm (Keller-Rudek et al., 2013).	UV absorption at wavelengths longer than 330 nm cannot be accounted for by OCS.
fine graphite grains	Carbon suboxide polymer (which has a yellow color) and fine graphite grains have absorption bands in the UV (Shimizu, 1977).	Not good fit to the Venus spectra.
croconic acid	Sulfuric acid aerosols mixed with croconic acid; (Hartley et al., 1989) have been first to propose organic molecules as an unknown absorber candidate.	Not good fit to the Venus spectra (Bertaux et al., 1996). No evidence of croconic acid in Venus atmosphere (Mills et al., 2007).
complex organic chemicals	A mixture of diverse colored species of complex organic chemicals dissolved in sulfuric acid provides good fit to the absorber spectra and explains the pale yellow color of Venus (Spacek, 2021).	No direct evidence for sufficient amounts of organic chemicals in the top clouds, although the possibility that the absorber is brought to the upper clouds from lower atmospheric layers remains (Titov et al., 2018).
biomolecules and life itself	Some mixtures of UV absorbing biomolecules could reproduce the unknown absorber spectrum (Limaye et al., 2018).	Requires biological activity to explain the observed features of the unknown absorber.

3.2. Mode 3 Particle Composition

The composition of a subset of Venus cloud particles, large particles (>7 μm in diameter) in the lower clouds called "Mode 3," is unknown (see Table 2 for a summary of Venus cloud particle properties vs. altitude, a summary discussion on the Mode 3 particles in (Bains et al., 2021a) and (Mills et al., 2007)). Adding to the mystery is the fact that the Mode 3 particles as measured by the Large Cloud Particle Size Spectrometer (LCPS) onboard the Pioneer Venus Large Probe appear to be non-spherical (Knollenberg and Hunten, 1980, 1979). Data from the Pioneer Venus Optical Array Spectrometer (OAS) (Esposito et al., 1983) also support non-spherical particles. The OAS instrument had three photodiode arrays that measured the shadows of passing particles, which makes the particle size measurement independent of particle composition. "Non-spherical" means the Mode 3 particles cannot be liquid droplets.

The nature and composition of the Mode 3 particles is debated with data presently in hand. The key derived parameter is refractive index, which comes from the Pioneer Venus nephelometer, which measured backscattered light in a range of angles. The refractive index of the particles in the lower clouds at 49 km is reported at 1.32 ± 0.03 assuming spherical droplets (Knollenberg et al., 1980; Ragent and Blamont, 1979). This value is lower than any plausible value for sulfuric acid, and therefore, it implies that the cloud particles located at these altitudes are not composed of pure concentrated liquid sulfuric acid. This result could indicate unknown chemistry and is intriguing with regard to the possible presence of "life as we know it," which cannot withstand a concentrated sulfuric acid environment. A possible explanation is non-spherical particles (Knollenberg and Hunten, 1980; Ragent and Blamont, 1979), which again imply non-liquid particles.

Several studies have questioned the existence of the large Mode 3 particles altogether and claimed, for example, that Mode 3 could be a large "tail" of the liquid Mode 2 particle distribution, once calibration errors were taken into account (James et al., 1997; Toon et al., 1984; Zasova et al., 1996). The possibility also remains that the OAS instrument could have, on occasion, measured overlapping shadows of two or more particles as they passed in front of the photodiode arrays. The subsequent re-examination of the evidence for the large solid Mode 3 particles in the clouds reaffirms the existence of the third large mode of particles (Knollenberg, 1984). However, their putative non-spherical, crystalline nature remains uncertain and can only be resolved with new in situ measurements (Knollenberg, 1984). See also an excellent summary of the Mode 3 particle debate in the work of Mills et al. (2007).

The unknown composition of the Mode 3 particles leaves room, albeit speculative, for unknown chemistry or life. Microbial cells within the droplets would cause an index of refraction discrepancy (analogously to bacteria in water (Waltham et al., 1994)). Alternatively, salt formation in a droplet, as a result of acid neutralization either through biological activity (Bains et al., 2021a) (see Section 4) or through incorporation of mineral dust lofted from the surface (Rimmer et al., 2021) would alter droplet composition away from pure concentrated H_2SO_4 to a more clement chemical environment with a different refractive index (Bains et al., 2021a; Mogul et al., 2021a).

Such decades-long lingering questions on the true nature of the Venus cloud particles should motivate new missions to focus on characterizing the Mode 3 cloud particles and the composition of the clouds and cloud aerosols in general.

Table 2. Characteristics of the Venusian cloud particles. Data from (Knollenberg et al., 1980; Knollenberg, 1982). (1) – Mode 1 particles; (2) – Mode 2 particles; (3) – Mode 3 particles. Mode 1 particles have mean diameter around 0.4 µm, Mode 2 have diameter of few µm, Mode 3 particles are larger than Mode 1 and Mode 2 and have diameters >7 µm.

Region	**Altitude (km)**	**Temperature (K)**	**Pressure (atm)**	**Cloud Particle Properties**		
				Average Num. Density (n cm^{-3})	**Mean Diameter (µm)**	**Consensus Particle Composition**
Layers above upper haze	100–110					N/A
Upper haze	70–90	225–190	0.04–0.0004	500	0.4; Bimodal (Venus Express)	70% H_2SO_4 30% H_2O (if present); Unknown
Upper cloud	56.5–70	286–225	0.5–0.04	(1)–1500 (2)–50	Bimodal 0.4 and 2.0	liquid 80% H_2SO_4 20% H_2O
Middle cloud	50.5–56.5	345–286	1.0–0.5	(1)–300 (2)–50 (3)–10	Trimodal 0.3, 2.5 and 7.0	liquid 90% H_2SO_4 10% H_2O
Lower cloud	47.5–50.5	367–345	1.5–1.0	(1)–1200 (2)–50 (3)–50	Trimodal 0.4, 2.0 and 8.0	liquid 98% H_2SO_4 2% H_2O (or fuming acid; H_2SO_4 + SO_3))
Lower haze	31–47.5	482–367	9.5–1.5	2–20	0.2	Unknown
Sub-cloud layers	46 and 47.5	378 and 367	1.8–1.5	50 and 150	Bimodal 0.3 and 2.0	Unknown

3.3. *Presence of Non-Volatile Elements in the Cloud Particles*

Both the VeGa balloons' and Venera probes' in situ measurements of the elemental composition of the cloud particles suggest that non-volatile elements relevant for habitability are present. Venera 13 and Venera 14 analysis of cloud particles indicates the presence of sulfur, chlorine, and iron (Petrianov et al., 1981). VeGa 1 and 2 measurements of the cloud material by X-ray fluorescence spectrometer (XRF) suggest the significant presence of chlorine, sulfur (Surkov et al., 1986), and phosphorus (P) in the lower cloud (Andreichikov, 1987b), but little iron (in contrast to the Venera probe measurements). Other elements suspected to exist are I, Br, Al, Se, Te, Hg, Pb, Al, Sb, and As (Marov and Grinspoon, 1998). Indeed, recent preliminary re-analysis of Pioneer Venus LNMS data shows evidence of a non-homogenous composition of cloud and haze particles (Zolotov et al., 2023). The particles could contain many chemicals dissolved in concentrated sulfuric acid, for example, various metal ions, salts, silica and even "insoluble organics" (Zolotov et al., 2023).

Life as we know it requires metals, for example transition metals such as iron (Fe), and other non-volatile species for catalysis. Even for some of the most ancient enzymes, the protein's primary role appears to be to hold catalytic metals in place to facilitate a reaction. Detection of metals and other non-volatile species as components of cloud particles would support the potential for habitability of the Venus clouds. In other words, the presence of metals and other non-volatile elements is not a biosignature but is an indicator of habitability.

In the altitude range of 52 to 47 km, the abundance of phosphorus appears to be on the same order as the abundance of sulfur (Andreichikov, 1987a, 1987b). Phosphorus is most plausibly in the form of P(V) acids or oxides, such as H_3PO_4, $H_4P_2O_7$, etc. (Bains et al., 2021c; Krasnopolsky, 1989). If the Venera descent probe data are correct and some cloud particles indeed contain > 50% phosphorus species by mass, then by definition the concentration of sulfuric acid in those droplets must be < 50% (see Section 4 for further discussion of the composition of cloud particles). Above 52 km, no phosphorus was detected. It is, therefore, plausible that phosphorus is present in a condensed liquid or solid phase predominantly in the lower cloud layer (Bains et al., 2021c).

In summary, numerous early measurements by the VeGa balloons and the Venera probes suggest the cloud particles are not pure sulfuric acid and the particles likely contain a plethora of other dissolved species (e.g., molecules containing Fe, Cl, P, and others). The exact composition and the concentration of the dissolved species is unknown.

Establishing the presence of non-volatile elements or compounds in the cloud particles should be one of the main science objectives of any Venus mission focusing on cloud habitability and composition. The minimal objective for such missions should be to establish the elemental composition of cloud aerosols to ppb abundance levels, focusing on confirmation of the early measurements of Fe and P by the Venera and VeGa probes, and lighter metals and non-metal elements C, N, and O, including Si, which would have been a great tracer of silica-containing dust[1]. The identification of the parent compounds of the detected non-volatile elements should follow. In particular, the search for a large fraction of liquid or solid phase of phosphoric acid(s) or phosphate salts in the lower clouds is paramount. Such analysis would also address a range of non-biological issues with understanding the trace chemistry of the atmosphere, such as whether phosphorus species are really present (Krasnopolsky, 1989) and the possible presence of $FeCl_3$ and other metal-containing chemicals (Krasnopolsky, 2017).

3.4. *Unexpected Atmospheric Gases and Gas Vertical Abundances*

A number of trace gases with unexplained abundance profiles have been observed to exist in the atmosphere of Venus (Table 3). Some of them (*e.g.*, O_2 or NH_3), aside from being relevant as potential signs of life in their own right, indicate chemical disequilibrium when considered together with the main atmosphere constituents. Earth's atmospheric disequilibrium is a result of life's activity, as exemplified by the coexistence of N_2 and O_2 (Krissansen-Totton et al., 2016). Although Venus' atmosphere is not as far from equilibrium as Earth's atmosphere is, the trace gas species detected at Venus indicate chemical disequilibrium in the clouds. Those gases include CO, SO_2, H_2O, S_x, OCS, and H_2 (Von Zahn and Moroz, 1985), as well as additional trace gas species detected in situ by the Venera and Pioneer probes (including those identified

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[1] VeGa X-ray fluorescence system could not measure elements lighter than phosphorus, $Z < 15$, (it was designed to do so, but instrumental issues affected the reliability of the measurement). Therefore, for example, even if there were high loadings of organics, ammonium salts or silica-containing dust in the cloud particles, VeGa would not have detected them. See also (Krasnopolsky, 1989) for the detailed discussion of the VeGa mission results.

in the recent reanalysis of the Pioneer Venus LNMS data) such as O_2, HNO_2, PH_3, H_2S, NH_3, HCN (Table 3).

We note that a number of anomalous, unexplained findings of gases or gas distributions in Venus' atmosphere have been discounted because no explanation for their presence could be found (*e.g.*, for O_2 (Von Zahn et al., 1983)). We consider this argument weak; the measurements should be critically evaluated on instrumental and repeatability grounds, and explanations for robust measurements should then follow, not the other way around. For this reason, we next discuss some trace gas detections in detail.

Table 3. Measured abundances of trace gas species of interest in the Venus clouds and below-the-cloud atmosphere layers. Taken together, the gases demonstrate chemical disequilibrium in the Venus atmosphere. LNMS is the Pioneer Venus Large Probe Neutral Gas Mass Spectrometer. GC is the gas chromatograph on either Pioneer Venus or the Venera Probes. JCMT is James Clerk Maxwell Telescope, ALMA is Atacama Large Millimeter/submillimeter Array, SOFIA is Stratospheric Observatory for Infrared Astronomy.

Gas	Observation	Altitude	Amount	Comments	Ref.
PH_3	JCMT	>60 km	~7 ppb	Tentative detection with Earth-based telescopes.	(Greaves et al., 2021b, 2021c, 2021a)
	ALMA	>60 km	~7 ppb	Tentative detection with Earth-based telescopes.	(Greaves et al., 2021b, 2021a, 2021c)
	SOFIA	~75 km	~1 ppb	Tentative detection with Earth-based SOFIA telescope (Greaves et al., 2022a), compare with work by (Cordiner et al., 2022).	
	Pioneer Venus	51 km	~2 ppm	Identification in the reanalyzed Pioneer Venus LNMS data.	(Mogul et al., 2021b)
NH_3	Venera 8	45 km	0.01 %	Tentative detection by Venera 8 chemical probe at ~2 bar altitude.	(Surkov et al., 1973)
	Venera 8	32 km	0.1 %	Tentative detection by Venera 8 chemical probe at ~8 bar altitude.	(Surkov et al., 1973)
	Pioneer Venus	51 km	N/A	Tentative detection in the re-analyzed Pioneer Venus LNMS data.	(Mogul et al., 2021b)
O_2	Venera 14	35–58 km	18 ± 4 ppm	Detection by Venera 14 GC.	(Mukhin et al., 1982)
	Pioneer Venus	52 km	44 ± 25 ppm	Detection by Pioneer Venus GC.	(Oyama et al., 1980b)
	Pioneer Venus	42 km	16 ± 7 ppm	Detection by Pioneer Venus GC.	(Oyama et al., 1980b)
H_2S	Venera 14	29–37 km	80 ± 40 ppm	Detection by Venera 14 GC.	(Mukhin et al., 1982)
	Pioneer Venus	51 km	N/A	Identification in the original, as well as re-analyzed Pioneer LNMS data.	(Mogul et al., 2021b)
	Pioneer Venus	<24 km	3 ± 2 ppm	Identification in the original Pioneer LNMS data.	(Hoffman et al., 1980a)
HCN	Pioneer Venus	51 km	N/A	Identification in the reanalyzed Pioneer LNMS data.	(Mogul et al., 2021b)

HNO_2	Pioneer Venus	51 km	N/A	Identification in the re-analyzed Pioneer LNMS data.	(Mogul et al., 2021b)
HNO_3	Pioneer Venus	51 km	N/A	Identification in the re-analyzed Pioneer LNMS data.	(Mogul et al., 2021b)
CH_4	Pioneer Venus	51 km	~1000 ppm	Identified in the original and the re-analyzed Pioneer LNMS data; Possible contaminant.	(Donahue and Hodges Jr, 1993; Mogul et al., 2021b)
C_2H_4, C_2H_6, C_6H_6	Pioneer Venus	51 km	N/A	Identified in the re-analyzed Pioneer LNMS data; Possible contaminant.	(Mogul et al., 2021b)
SF_6	Venera 14	35–58 km	0.2 ± 0.1 ppm	Tentative detection by Venera 14 GC.	(Mukhin et al., 1982)

Oxygen (O_2). In situ detections of O_2 in the Venusian lower clouds and below the clouds have been reported by at least two probes at the 10s of ppm level: Pioneer Venus (Oyama et al., 1980b) and Venera 13/14 (Mukhin et al., 1982) (Table 3). The Pioneer Venus Gas Chromatography (PVGC) (Oyama et al., 1980c) reported 43.6 ppm molecular oxygen (O_2) in the clouds at 51.6 km, 16 ppm below the clouds at 41.7 km, and no detection of O_2 at 21.6 km (Oyama et al., 1980b). Note that the PVGC preliminary gas measurements and O_2 abundance estimations of approximately 70 ppm (Oyama et al., 1979b) were revised on several occasions (Oyama et al., 1980a, 1979a) before the final PVGC gas abundances were published (Oyama et al., 1980b). The Venera 14 Gas Chromatograph (VGC) detected 18 ppm O_2 average between 35 and 58 km (Mukhin et al., 1982). The Venera 14 VGC O_2 abundance agrees with previously established Venera 12 VGC upper limits (<20 ppm) for O_2 below 42 km (Gelman et al., 1979a) and the final revised abundance recorded by the PVGC (16 ppm at 41.7 km) (Oyama et al., 1980b)[2].

The Neutral Mass Spectrometer (LNMS) on Pioneer Venus showed a signal of 32 amu, but this signal has been attributed to O_2 ions formed in the mass spectrometer from the reaction of CO_2 (Hoffman et al., 1980a) and, therefore, is considered unreliable as an indicator of the presence of O_2 in the atmosphere. The Venera 11 and Venera 12 mass spectrometers (VMS) detected an excess signal of 32 amu at altitudes of below 23 km (Istomin et al., 1980, 1979a, 1979b). As with LNMS, the reliability of this VMS measurement is uncertain. Venera 13 and Venera 14 mass spectra also show a mass peak assigned to O_2, which could result from the dissociation of CO_2 in the ion source of the instrument (Istomin et al., 1983). We emphasize that the uncertainty on the source of O_2 is specific to mass spectrometry (Newton, 1952).

The O_2 in situ detections have been dismissed as artifactual either because of the difficulties in reconciliation with the ground-based observations (Mills, 1999; Trauger and Lunine, 1983) or lack of known physical or chemical processes that could maintain 10s of ppm O_2 levels in the hot, reactive lower atmosphere of Venus (Krasnopolsky, 2006; Von Zahn et al., 1983). However, the multiple, consistent in situ detections would suggest that O_2 is indeed present at ~10s ppm.

The source of O_2 in the clouds of Venus is unknown and has been extensively discussed elsewhere (Bains et al., 2021a). One potential source of O_2 that was not considered by Bains et al. (2021a) is generation of O_2 during the chemical transformation of organics in the sulfuric acid cloud droplets, analogous to the speculative process first proposed by Hartley et al. (1989). Recently, the idea that there are organics in the clouds of Venus gained more traction with the proposed non-biological organic carbon cycle in the clouds (Spacek, 2021), opening the possibility for this chemistry to contribute to the in-cloud O_2 reservoir. However, the

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[2] We note that the early high estimations of the abundance of O_2 in and below the clouds of Venus by Venera 4, Venera 5 and Venera 6 are likely erroneous due to the cross-reactivity of the chemical sensors with sulfuric acid. Recall that at the time of the early missions to Venus the composition of the clouds was completely unknown and the sensors have not been designed to account for high concentrations of sulfuric acid in the atmosphere (Florensky et al., 1978). Venera 11 and Venera 12 probes optical spectrometers have also provided upper limits of 50 ppm to the abundance of O_2 at altitudes below 60 km (Moroz, 1981).

generation of O_2 from organic material reacting with concentrated sulfuric acid, if it happens at all, is thermodynamically unfavorable, requires many poly-carbonyls as intermediates (which are reactive and unstable in concentrated sulfuric acid (Bains et al., 2021b, 2021d)), and is likely too inefficient to account for all of the observed PVGC and VGC abundances of O_2.

Addressing the discrepancies between the measurements should be the main objective of future missions to Venus. Currently, it is difficult to reconcile the strong upper limits on the abundance of O_2 above 58 km (<3 ppm) imposed by ground-based observations with the in-cloud O_2 abundances detected by both Pioneer Venus and Venera probes (see, *e.g.*, Mills 1999). One expects to observe a gradient of O_2 from above to below the clouds if the presence of O_2 in the clouds is not spatially or temporally varied (which it might be as other atmospheric observations, for example unknown absorber, are spatially and temporally variable (see, *e.g.*, Lee et al., 2019 and Yamazaki et al., 2018). Such discrepancies can only ultimately be resolved by new in situ measurements of O_2 in the clouds of Venus.

Phosphine (PH_3). The recent tentative detection of ppb levels of PH_3 in the atmosphere of Venus through millimeter-wavelength astronomical observations (Greaves et al., 2021b) is surprising as there is no known process capable of producing even a few ppb of PH_3 on Venus (Bains et al., 2022a, 2021c). Volcanically extruded phosphide minerals from the deep mantle have been recently proposed as a potential source of PH_3 (Truong and Lunine, 2021). However, phosphide-containing minerals, including those from deep mantle plume volcanic eruptions and meteoritic delivery, are an extremely unlikely source of ppb PH_3 on Venus (Bains et al., 2021c, 2022c, 2022d). For the former, a brand new mechanism for explosive volcanism would be required in addition to the fact that phosphide minerals easily oxidize during their transport to the surface (Bains et al., 2022c, 2022d). For the latter, Bains et al. (2021c) argued that the amounts of phosphides delivered by meteorites are too small to explain the observed abundance of PH_3, although Omran et al. (2021) provided a counter argument on the abundance of meteoritic delivery as a source of PH_3. Work of Bains et al. (2023a) showed that, regardless of the assumed value of $\Delta G^{o}_{(g)}$ for P_4O_6, the formation of PH_3 from P_4O_6 in the Venusian atmosphere is thermodynamically unfavorable. A recent assessment of the photochemical production of PH_3 from P_4O_6 suggests a PH_3 upper limit of 2 ppb between 50 and 60 km (Wunderlich et al., 2023). The existence of P_4O_6 itself in the atmosphere of Venus, however, is uncertain (Bains et al., 2023a).

Since the initial PH_3 discovery was announced, several papers have questioned the detection, either on the grounds of data analysis (Akins et al., 2021; Snellen et al., 2020; Thompson, 2021; Villanueva et al., 2021) or an assignment of the observed millimeter wavelength absorption to mesospheric SO_2 rather than cloud-level PH_3 (Lincowski et al., 2021; Villanueva et al., 2021).

The authors of the original discovery have provided a response to the critiques, both on data processing and data interpretation (Greaves et al., 2021c, 2021a) and on arguing against SO_2 contamination (Greaves et al., 2022b). Although sulfur dioxide variability is significant even on day-to-day timescales in the mesosphere, SO_2 would need to have increased 10-fold planet-wide over only a few days for SO_2 to have mimicked PH_3 in the discovery data (Greaves et al., 2022b).

The in-cloud location of the PH_3 signal has also been debated. Lincowski et al. (2021) reported that the PH_3 must reside above the clouds to produce the 1.1 mm absorption, and independent re-analyses has confirmed this finding (Greaves et al., 2022b; Villanueva et al., 2021). If mesospheric, a phosphine interpretation of the 1.1 mm feature is challenging given the expected short lifetime (Bains et al., 2021c). Simultaneously, the near-contemporaneous SO_2 measurements by Greaves et al. (2022b) render SO_2 a challenging interpretation as well. Other possibilities include a yet unknown mesospheric replenishment mechanism for PH_3 (as SO_2 is replenished in the high atmosphere (Zhang et al., 2012)), or previously unknown absorption from another molecule, or the presence of a completely novel absorber altogether (Greaves et al., 2022b).

Several groups have used IR observations to provide strong upper limits above the clouds (in the low ppb to sub-ppb range) on the abundance of PH_3 (Cordiner et al., 2022; Encrenaz et al., 2020; Trompet et al., 2020). However, recent preliminary results suggest that the IR observational upper limits are not inconsistent with tentative phosphine detections if there is a difference in abundance between day and night (Greaves et al., 2022a).

See the work of Bains et al. (2022a) and more recently Cleland and Rimmer (2022) and Clements (2023) for a summary for the phosphine debate so far.

An independent re-analysis of the Pioneer Venus Neutral Gas Mass Spectrometer (LNMS) data (Mogul et al., 2021b) shows evidence of PH_3 in the clouds of Venus, via detection of unique PH_3 fragmentation ions. The re-analysis was for the in-cloud altitude of 51.3 km, and yields a PH_3 abundance of ~2 ppm.

The debate on the presence of PH_3 in the clouds of Venus continues and will likely only be resolved by in situ measurements of PH_3 gas in the Venus atmosphere. At the time of writing, PH_3 is being considered as one of the additional target gases for the upcoming DAVINCI mission (Queen et al., 2022).

Methane (CH_4). The low-mass volatile hydrocarbons methane (CH_4), ethane (C_2H_6), and benzene (C_6H_6) were detected in situ in the atmosphere of Venus by the LNMS on the Pioneer Venus Large Probe (Donahue and Hodges Jr, 1993; Mogul et al., 2021b). CH_4 in particular was measured to be present with an unexpectedly high abundance (1000–6000 ppm) in the lower atmosphere altitudes (Donahue and Hodges Jr, 1993). In contrast to other gases discussed in this section, the detection of CH_4 and other volatile hydrocarbons by the Pioneer Venus Large probe are likely an artifactual result due to an instrumental contamination and not a genuine atmospheric gas detection (Donahue and Hodges Jr, 1993). This interpretation has been recently bolstered by results of the reanalysis of the LNMS data (Mogul et al., 2022). The high abundance (1000–6000 ppm) of methane (as well as detection of benzene and other volatile hydrocarbons) below the clouds is likely a contamination from the spacecraft itself. It is not known whether the in-cloud detection of methane by LNMS is a contamination as well (Mogul et al., 2022). The PVGC did not detect CH_4, which placed upper calculated limits of atmospheric CH_4 at <10 ppm, <3 ppm, and <0.6 ppm at 51.6 km, 41.7 km, and 21.6 km, respectively (Oyama et al., 1980b). The Venera 14 Gas Chromatograph (VGC) did not detect methane and put an abundance upper limit at 0.5 ppm below 58 km (Mukhin et al., 1982). Remote observations with Earth-based telescopes put upper limits for CH_4 abundance in the lower atmosphere at < 0.1 ppm (Pollack et al., 1993). As with any unexplained detections, the presence of CH_4 in the clouds of Venus remains to be confirmed and reconciled with the established abundance upper limits.

Early ground-based observations also established abundance upper limits, above the clouds, for several volatile organics, including simple hydrocarbons, halocarbons, formaldehyde, other volatile carbonyls, and HCN (see (Moroz, 1981), their Table VI). Recently new upper limits on HCN and formaldehyde in the Venus lower-mesosphere have also been established using SOIR instrument on board Venus Express (Mahieux et al., 2023).

We note that the Venera 13 and Venera 14 mass spectrometers also detected peaks belonging to methane, as well as hydrocarbons. Those signals, however, have been interpreted as contamination (*i.e.*, "background peaks") and are not considered valid detections of Venusian atmospheric gases (Istomin et al., 1983).

Ammonia (NH_3). NH_3 is unexpected in an oxidized atmosphere. NH_3 has been tentatively detected by two separate probes. In 1972, the Venera 8 descent probe reported the presence of NH_3 in the lower atmosphere of Venus using bromphenol blue as an indicator of a basic atmospheric component (Surkov et al., 1973)[3]. The NH_3 measurement has been challenged as erroneous, due to the indicator's potential reactivity with sulfuric acid (Young, 1977). The Venera 8 detection of NH_3 was also discounted shortly after the measurement; Goettel and Lewis (1974) discarded it on the grounds of its unlikelihood in an atmosphere at thermodynamic equilibrium. The argument by Goettel and Lewis is now weakened as a growing list of gases in the atmosphere of Venus indicates thermodynamic disequilibrium (Esposito et al., 1997; Johnson and de Oliveira, 2019; Mogul et al., 2021b).

The recent re-assessment of the Pioneer Venus Large Probe Neutral Mass Spectrometer (LNMS) has also provided suggestive, although not conclusive, evidence for the presence of NH_3 in the Venus cloud layers (Mogul et al., 2021b).

While the chemical processes that may generate NH_3 in the Venusian clouds are unknown, assuming the tentative detections of the Venera probes and Pioneer Venus are correct, the possibility that NH_3 is a biological product remains (Bains et al., 2021a). NH_3 should be a prime target for measuring with new in situ probes due to its critical role in the potential habitability of the clouds (Bains et al., 2021a; Mogul et al., 2021a) (see Section 4). At the time of writing, NH_3 is being considered as one of the additional target gases for the upcoming DAVINCI mission (Queen et al., 2022).

Similarly to O_2, the ground-based observations impose an upper limit of 6 ppb on the NH_3 abundance above the clouds (Krasnopolsky, 2012a). Even stricter upper limits of 28.4 ppt on the abundance of NH_3 in the Venus lower-mesosphere have been established using SOIR instrument on board Venus Express (Mahieux et al., 2023). These upper limits for abundance above the clouds are difficult to reconcile with the

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[3] Venera 9 and Venera 10 descent module mass spectrometers reported in situ upper limits for NH_3 of <0.05% for altitude range of 37-45 km that are consistent with tentative Venera 8 detection (Surkov, 1977).

tentative in situ observations, unless the NH_3 loss in the upper atmosphere is balanced by a constant production that is localized to the clouds and the stagnant haze layer below (Bains et al., 2021a).

Sulfur hexafluoride (SF_6). SF_6 has been tentatively detected between 35 and 58 km altitude by Venera 14 GC, in an abundance of 0.2 ± 0.1 ppm (Mukhin et al., 1982).

SF_6 has the same GC retention time as N_2O, but N_2O has been ruled out based on the unrealistically high abundance (~1%) required to explain the observed signal (Mukhin et al., 1982), such high abundance is also inconsistent with PVGC upper limits for N_2O in the atmosphere of Venus, <200 ppm, <70 ppm, and <10 ppm at 51.6 km, 41.7 km, and 21.6 km, respectively (Oyama et al., 1980b).

It is also unlikely that the tentative detection of SF_6 resulted from the contamination from the spacecraft. SF_6 is a commercial electrical insulator in high-voltage switches and transformers used in electrical gear operating at tens of kilovolts (Simmonds et al., 2020), and it is very unlikely that this engineering solution would be used in a spacecraft.

On Earth, trace amounts of natural SF_6 exist in volcanic rocks in rift zones, faults, igneous intrusions, geothermic areas, and diagenetic fluids (Busenberg and Plummer, 2000). SF_6 is predominantly present in fluorites and some granites, while basalts, for example, do not contain detectable SF_6 (Busenberg and Plummer, 2000; Harnisch and Eisenhauer, 1998). The exact process of production of natural SF_6 on Earth is unknown. It is also unclear whether SF_6 is directly made by volcanic processes on Earth or is SF_6 only released in association with volcanic activity. The work of Harnisch and Eisenhauer studied the gases from several volcanic fumaroles, for example, from Sicilian (Vulcano Island and Etna) and Japanese (Satsuma Iwojima and Kuju) volcanoes, and found that they are not significant sources of SF_6 (Harnisch and Eisenhauer, 1998). However, the underlying rocks of these volcanoes are not granitic and as a result might lack the source for SF_6 (Harnisch and Eisenhauer, 1998). The pre-industrial atmospheric equilibrium concentration of SF_6 on Earth is estimated to be <0.06 ppt (Busenberg and Plummer, 2000). See also the recent work of (Seager et al., 2023a) for detailed discussion of the possible planetary sources of SF_6.

Since Venus is significantly H-depleted, one would expect that it would have a different profile of F-containing volatiles erupted by volcanoes than that of Earth. On Earth, HF is the main source of volcanic F (see, *e.g.*, Cheng, 2018). On Venus, HF is also volcanic, but it is likely that the majority of F is erupted as other compounds, for example SSF_2, COF_2, FClCO, and SOF_2, etc. (Zolotov and Matsui, 2002). Therefore, it is not unexpected that, in an H-depleted environment of Venus, with abundant sulfur, SF_6 could also be a volcanic product released in significantly higher abundance than on Earth. SF_6 could also be the result of weathering of fluorite minerals abundance of which on Venus is poorly constrained.

3.5. Unexplained Gas Vertical Abundance Profiles of SO_2 and H_2O

The atmospheric vertical abundance profiles of sulfur dioxide (SO_2) in the Venus cloud layers and H_2O in and above the clouds remain unexplained. The presence of SO_2 is expected in the atmosphere of Venus and in the clouds. SO_2 is a common volcanically produced gas. However, the observed abundance of SO_2 ascending through the Venus cloud layers drops from an average of ~150 ppm below the clouds to sub-ppm levels above the clouds. This depletion cannot be currently explained by known atmospheric chemistry (see Rimmer et al., 2021)). There is, therefore, missing atmospheric chemistry of some kind, a fact that has been recognized by Venus researchers for decades (see, *e.g.*, Bierson and Zhang, 2019; Marcq et al., (2018); Mills et al. (2007); and Vandaele et al. (2017)).

The SO_2 depletion in the clouds is unlikely to be solely caused biologically by the three sulfur-energy metabolic strategies postulated previously (Schulze-Makuch et al., 2004; Schulze-Makuch and Irwin, 2006), which have been recently investigated by Jordan et al. (2022). Sulfur energy metabolisms investigated by these authors require reduced species as input, either hydrogen-containing compounds (H_2S or H_2) or carbon monoxide (CO). Reduced compounds are expected to be rare in Venus' oxidized atmosphere (see, *e.g.*, Marcq et al., 2018), and so it is not surprising that these metabolic strategies could not solely explain the SO_2 depletion. Therefore, either other sulfur metabolic strategies are at play or the SO_2-depletion in the clouds has another explanation altogether, including the possibility of multiple contributing processes acting at once.

The observed abundance of water vapor (H_2O) above the clouds also does not match the H_2O abundance profile predicted by atmospheric photochemistry models (Bierson and Zhang, 2019; Greaves et al., 2021b; Winick and Stewart, 1980). As in the SO_2 case, additional unknown atmospheric chemistry is needed to explain the observations of H_2O. We discuss the possible explanation for the SO_2 and H_2O abundance profiles in Section 4.

We would be remiss not to emphasize the extreme aridity of the Venus cloud environment as a significant challenge to life as we know it. In extremely dry environments, terrestrial life can survive as spores or other inactive forms but would not be actively growing and, therefore, unable to support a sustainable biosphere. Even under the assumption that life resides inside cloud particles, the water activity is extremely low, because any water molecules inside the particle will be tightly bound to sulfuric acid.

The extreme dryness of Venus' atmosphere has been considered a well-known fact for decades (see, *e.g.*, Donahue and Hodges Jr, 1992), having been described on many occasions (see, *e.g.*, Bains et al., (2021c); Bains et al., (2021d); and Seager et al., 2021)). However, there appears to be a great variability in observed water vapor abundance values. Repeated measurements by in situ probes vary from 5 ppm to 0.2% (reviewed by Rimmer et al. (2021) (see also Table 4). In situ measurements of water from the 1970s and 1980s Soviet VeGa and Venera probes and NASA Pioneer Venus give average abundances of 200–2000 ppm in the middle/lower clouds (58–48 km) and 5000 ppm just below the clouds (41.7 km) (Table 4). These values are considerably higher than the global average of around 30 ppm, which comes from water vapor abundances derived from the spectrometric measurements by Venera probes (Ignatiev et al., 1997), the Galileo spacecraft (Drossart et al., 1993), Venus Express orbiter (Bézard et al., 2009), and supported by ground-based near IR spectroscopy (De Bergh et al., 1995) (with a notable exception of the tentative 200 ppm value measured by Bell et al. (1991) near 2.3 μm). Ignatiev et al. (1997) dismissed the observations based on "contact methods" (CM) in favor of spectroscopic methods. They discarded the values without being able to "point to specific shortcomings of contact methods," because the values are so much higher than spectroscopic observations (Ignatiev et al., 1997). Recently, Mogul et al. (2021a) suggested that the higher values of the "contact methods" are due to water from the cloud particles. If such an interpretation is true, it would mean the cloud particles have more water than our current understanding of the cloud particles allows.

Nevertheless, the highest values, if confirmed, indicate the presence of local "habitable" regions with higher-than-average humidity. While all global Venus atmosphere models may, therefore, represent an average of extremely arid "desert" regions, there may exist some localized, more humid regions (albeit still far drier than any environment on Earth) future Venus mission planners would endeavor to remeasure H_2O content of the clouds in multiple locations.

The very low water activity is not a definitive refutation of the possibility of life in the clouds of Venus (Bains et al., 2023b). Life may have a completely different biochemistry to that of Earth, for example one based on concentrated sulfuric acid instead of water as a solvent (Bains et al., 2021d; Seager et al., 2023b). Or life on Venus, if it exists, may have evolutionary adaptations without precedent here on Earth to actively extract water from the dry atmosphere or from water tightly bonded to sulfuric acid inside the Venus cloud particles.

Table 4. Summary of controversial atmospheric observations and unexplained cloud property measurements. VGC is Venera Gas Chromatograph; CM is Contact Methods; PVGC is Pioneer Venus Gas Chromatograph; LNMS is Pioneer Venus Large Probe Neutral Gas Mass Spectrometer; VMS is Venera Mass Spectrometer; XRF is X-ray Fluorescence Spectrometer; LCPS is Pioneer Venus Large Cloud Particle Size Spectrometer.

Venus Atmospheric Observable	In Situ Method	Controversy	Comments
H_2O	VGC; CM	Highly variable measurements that are inconsistent with each other and the spectroscopic methods. "Contact methods" (CM) give generally much higher H_2O abundances than other in situ methods.	CM methods give H_2O abundances in a range of thousands of ppm. For example, VeGa estimates 1000 ppm H_2O at 50-60 km, decreasing to 150 ppm at 25-30 km (Surkov et al., 1987). Venera 14 humidity sensor gave the value of 2000 ppm at 46-50 km (Surkov et al., 1983, 1982) while Venera 14 GC gave 700 ppm at 49-58 km (Mukhin et al., 1982). PVGC also suggested high H_2O water mixing ratios <600 ppm at 51.6 km, ~5000 ppm at 41.7 km and 1350 ppm at 21.6 km (Oyama et al., 1980b). Venera 12 GC does not agree with such a high H_2O abundances and provides upper limits of 200 ppm below 42 km (Gelman et al., 1979b). Ultimately such discrepancies can only be resolved by new in situ measurements of water abundance at multiple locations in the atmosphere and inside the cloud particles.
O_2	PVGC; VGC	Ground-based observations provide upper limits for the abundance of O_2 above the clouds (Mills, 1999; Trauger and Lunine, 1983) that are inconsistent with the abundance reported by Venera and Pioneer probes.	There is no apparent reason to consider ppm levels of O_2 detected by PVGC and VGC as erroneous. Lab studies with PVGC confirm that O_2 is not the product of thermal decomposition of the SO_3 gas or H_2SO_4 and that the detection is robust (Oyama et al., 1979a).
	LNMS; VMS	The detections of O_2 by MS are considered unreliable. O_2 ions could originate from reaction of CO_2 in the mass spectrometer itself.	MS detections of O_2 are uncertain due to overlapping mass (isobaric species) and the potential formation of O_2 in the instrument itself.
NH_3	Chemical Sensor	Ground-based observations (Krasnopolsky, 2012a) and Venus Express upper limits (Mahieux et al., 2023) are difficult to reconcile with the in situ measurements.	The bromophenol blue chemical sensor was used as an indicator of a basic atmospheric component (Surkov et al., 1977). The change of color was registered by photoresistors. The results of the measurement are tentative (Surkov et al., 1974, 1973) and could be a result of a false positive detection due to cross-reactivity with sulfuric acid vapor (see also discussion in (Bains et al., 2021a)).
	LNMS	The detection of NH_3 is tentative due to possible isobaric species.	NH_3 identification the re-analyzed LNMS data remains tentative.
PH_3	LNMS	P^+ ion identified in the LNMS data is sufficiently separated and appears to be real (Mogul et al., 2021b). The identity of the parent gaseous compound of the P^+ ion is unknown.	The detection of P^+ ion is robust. PH_3 is the simplest gas that fits the data (Mogul et al., 2021b). Other known volatile P-species at the cloud level temperatures do not provide a good fit to the LNMS data.
H_2S	VGC	The abundance of H_2S is uncertain. Ground-based observations put upper limits of <23 ppb above the cloud tops (Krasnopolsky, 2008). The VGC detection appears to be inconsistent with PVGC upper limits: <40 ppm at 51.6 km, <10 ppm at 41.7 km and <2 ppm at 21.6 km (Oyama et al., 1980b).	H_2S has been first tentatively detected by Venera 11 and Venera 12 GC although without a firm constrain on the abundance. Venera 14 GC detection remains much more robust than earlier measurements but significant uncertainty on the abundance of H_2S remains (Mukhin et al., 1982). Possible discrepancy between Venera 14 GC measurement at 29-37 km attitude and PVGC upper limits remains.
	LNMS	Tentative identification of H_2S in the reanalyzed LNMS data confirms the original LNMS detection; significant overlap of isobaric species (Mogul et al., 2021b). Abundance of H_2S is uncertain.	The reanalyzed data from LNMS indicate the presence of H_2S at 51 km (Mogul et al., 2021b). Earlier LNMS inference of H_2S abundance (from ratio to ^{36}Ar) suggest 3 ppm ± 2 ppm below 24 km (Hoffman et al., 1980a).
HCN	LNMS	Only tentative detection in re-analyzed LNMS data (Mogul et al., 2021b). The early ground-based observations propose	HCN is thermodynamically disfavored in the atmosphere of Venus and is reactive to conc.

		1 ppm as the upper limits on HCN abundance above the clouds (see (Moroz, 1981), their Table VI). See also new upper limits on HCN in the Venus lower-mesosphere from Venus Express (Mahieux et al., 2023).	sulfuric acid. If confirmed HCN could be an important element of the Venusian nitrogen cycle.
NO_x	LNMS	Tentative identification of NO_x in the reanalyzed LNMS data (Mogul et al., 2021b). See also early ground-based observations upper limits on NO_x abundance above the clouds (see (Moroz, 1981), their Table VI) and the new upper limits on NO_x in the Venus lower-mesosphere from Venus Express (Mahieux et al., 2023).	LNMS is the only in situ instrument that detected NO_x. PVGC provided upper limits for N_2O in the atmosphere of Venus (see (Oyama et al., 1980b), their Table 3) but in situ upper limits for other nitrogen oxide species are unknown.
CH_4	LNMS; VMS	CH_4 detected by LNMS is likely an artefact arising from the outgassing within the spacecraft itself (Donahue and Hodges Jr, 1993; Mogul et al., 2022).	LMNS detection of CH_4 is considered artefactual (Donahue and Hodges Jr, 1993; Mogul et al., 2022), VMS detection is a background detection (Istomin et al., 1983). PVGC measurements provided strong upper limits to CH_4, C_2H_4, C_2H_6 and C_3H_8 abundance (see (Oyama et al., 1980b), their Table 3).
complex organic molecules	Never attempted	No uncontested evidence of organic molecules in the atmosphere of Venus.	The direct in situ detection of organic chemicals in the atmosphere of Venus has never been attempted. The potential for organic carbon cycle in the atmosphere of Venus exists (Spacek, 2021). Future Venus missions should aim to identify organic molecules in the cloud particles.
non-volatiles (e.g. P and Fe)	XRF	No reliable estimates on abundances of non-volatile species, in particular P, can be derived from VeGa 1 and VeGa 2 detections (Krasnopolsky, 1989).	The detection of P-bearing species was confirmed by the Pioneer Venus LNMS re-analysis (Mogul et al., 2021b). The debate on the possibility of the phosphoric acid as a significant component of the cloud aerosols continues and is an intriguing area for future investigation (Milojevic et al., 2021). The detection of P in the clouds is unexpected and should be confirmed by future missions. The detection of Fe (Petrianov et al., 1981) by Venera 13 and Venera 14 XRF is less controversial and generally accepted as valid (e.g. (Krasnopolsky, 1989)).
mode 3 particles	LCPS	The existence of the Mode 3 particles has been questioned (e.g. (Toon et al., 1984)) and is not supported by Venera nephelometer measurements although Venera measurements provided less conclusive data on the modality of particles than Pioneer Venus.	The reanalysis of the LCPS data reaffirmed the existence of the Mode 3 particles although their solid, crystalline nature is uncertain and can only be confirmed with new in situ measurements (Knollenberg, 1984).

4. Challenging the General Consensus of Venus Cloud Composition and Acidity

The Venus clouds' main constituent is particles composed of concentrated sulfuric acid droplets (see, *e.g.*, Knollenberg et al., 1980; Moshkin et al., 1986) (Table 2). This paradigm is supported by several findings.

1] Photochemical models of the atmosphere are consistent with H_2SO_4 clouds. The models predict H_2O, SO_3, and H_2SO_4 to be present throughout the atmosphere (see, *e.g.*, Bierson and Zhang, 2019) and gaseous H_2SO_4 (Oschlisniok et al., 2021, 2012), as well as gaseous H_2O and SO_2 (reviewed by Rimmer et al., (2021) are measured throughout. Simple, condensation models for the H_2SO_4-H_2O gas-cloud system on Venus also track the fate of liquid Mode 2 particles and confirm that they are mostly composed of H_2SO_4 (Dai et al. 2022).

The consensus model is that formation of clouds on Venus is photochemically driven (see, e.g., Krasnopolsky (2012b, 2007). Sulfuric acid vapor is first made at > 70 km.

$CO_2 + h\nu \rightarrow CO + O$

$SO_2 + O + M \rightarrow SO_3 + M$

$SO_3 + 2\,H_2O \rightarrow H_2SO_4 + H_2O$

The H_2SO_4 vapor condenses out, creates the droplets, and as the droplets rain down, sulfuric acid thermally dissociates in the lower atmosphere (below 40 km) (Krasnopolsky, 2013, 2007). A fraction of H_2SO_4 also likely reforms from the H_2O and SO_3 near the bottom of the clouds (Krasnopolsky, 2007). The measured

and modeled levels of H_2O, which together with SO_3 will efficiently form H_2SO_4, support the theory that the clouds of Venus contain sulfuric acid (Krasnopolsky, 2007; Oyama et al., 1980b; Vinogradov et al., 1970).
2] Gaseous H_2SO_4 has been detected and measured by microwave spectrometry, supporting the photochemical concept of H_2SO_4 cloud formation (Oschlisniok et al., 2021, 2012).
3] The proposed interpretation of the inferred refractive index of the cloud droplets is that the clouds are made of at least 70% w/w sulfuric acid and less than 30% w/w water (Palmer and Williams, 1975; Young, 1973). The concentration of sulfuric acid in droplets is derived through modeling (e.g., James et al., 1997) of light scattering to match in situ data. The concentration of H_2SO_4 is lower in the top clouds and increases towards the bottom of the clouds as the temperature increases (summarized in Table 2; following information from the work of Titov et al. (2018) Table 1). Furthermore, the concentrated solution of sulfuric acid (H_2SO_4-H_2O) has been found to be in good agreement with ground-based polarization data (Hansen and Hovenier, 1974) before the in situ probes.
4] The VeGa chromatographic measurements of the cloud aerosols are the only dedicated in situ estimates of the sulfuric acid concentration in the cloud particles[4]. The Vega measurements confirmed that the clouds are primarily composed of concentrated sulfuric acid and water (Gelman et al., 1986; Porshnev et al., 1988, 1987). VeGa chromatograph collected cloud aerosols on the carbon fibers between the altitudes of 63 km to 48 km. Gases—SO_2, H_2O, and CO_2—evolved upon heating of the collected sample on a carbon substrate are consistent with sulfuric acid droplets (Gelman et al., 1986)[5]. We note, however, that Gelman et al. (1986) also suggested that the cloud layers may consist of particles of more complex composition than a pure aqueous sulfuric acid solution (Gelman et al., 1986). This suggestion was later supported by the preliminary calibration experiments of the VeGa gas chromatograph (Mukhin et al., 1987). The experiments results show that the pyrolyzed sulfuric acid aerosols evolved significant amounts of H_2S, which suggests other unknown condensed or dissolved constituents of the aerosols beyond the sulfuric acid and water (Mukhin et al., 1987).

The "average concentration" of sulfuric acid in the cloud droplets is ~85% w/w H_2SO_4 (Titov et al., 2018). However, the concentration of sulfuric acid across the cloud deck likely varies significantly (Krasnopolsky, 2015). The concentration reaches ~70% in the top clouds, while in the lower clouds the concentration could reach >100%, that is, "fuming" sulfuric acid or oleum ($H_2S_2O_7$, or a solution of SO_3 in H_2SO_4) (Titov et al., 2018). The measured cloud particle refractive index suggests that the chemical composition of the clouds may include a number of chemicals that may be mixed with concentrated H_2SO_4 or be completely different from H_2SO_4 (Knollenberg et al., 1980; Ragent and Blamont, 1979). For example, the droplet sulfuric acid concentration could be highly variable, between 30% and >100% (Section 3.3).

Recently, Rimmer et al. (2021) proposed a photochemical model of the atmosphere of Venus that also includes a new view of the cloud chemistry. The model postulates that the cloud droplets are not homogenous in composition and a fraction of the cloud particles are neutralized solid or semi-solid salt particles, instead of liquid concentrated sulfuric acid droplets.

A base is needed to neutralize (convert to salts) all the sulfuric acid in a cloud particle, so that the pH of the particle reaches >0. When pH of the liquid in the droplet is >0, the equilibrium between SO_2 and sulfite (HSO_3^-) is pulled towards the sulfite, thus removing SO_2 from gas phase, that is, trapping SO_2 in the droplet as sulfite salts, providing a mechanism that could explain the mysterious depletion of SO_2 in the atmospheric cloud layers, and the vertical abundance profile of H_2O in and above the clouds (see, *e.g.*, Rimmer et al. 2021) for details on the model).

The identity of the putative acid-neutralizing base is unknown. Bains et al. (2021a) postulated that biologically produced NH_3 could be a neutralizing base for the Venusian cloud droplets.

The Bains et al. (2021a) model calculates the amount of NH_3 needed to neutralize all the sulfuric acid in the droplet and the amount needed to trap SO_2 as ammonium sulfite, therefore explaining the unusual SO_2 abundance profile (Bains et al., 2021a). In the model, all the sulfuric acid in the Mode 3 particles is reacted with NH_3 to form ammonium sulfate salts. The particles are, therefore, either solid or a slurry of solid and fluid. For the particles to absorb SO_2 they must have a pH>0 if fluid is present. Whether fluid is present, and its exact pH, will depend on the water activity in the clouds, which is poorly constrained (Section 3.5).

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[4] The Pioneer Venus LNMS was not designed to sample aerosols, however the gases evolved after the gas inlet blockade was lifted are consistent with droplets composed of 85% w/w H_2SO_4 and 15% w/w H_2O (Hoffman et al., 1980b).

[5] Note that if organic carbon compounds were present in the droplets, these would not have been identified over the background of CO_2 evolved from the carbon fibre filters.

We note that the neutralization of the sulfuric acid droplets by NH_3 in Venus' atmosphere could proceed analogously to the neutralization of sulfuric acid aerosols by NH_3 in Earth's stratosphere (see, *e.g.*, Huntzicker et al., 1980), including neutralization of particles of up to 80% acid.

The removal of concentrated sulfuric acid in the droplet by reacting it with NH_3 has a crucial outcome for the overall habitability of the clouds. The model postulates that some of the cloud particles are much less acidic than previously thought, with a pH between -1 and 1 (Rimmer et al., 2021), instead of an acidity of approximately -11 (on the Hammett acidity scale), which is uninhabitable for terrestrial life (Seager et al., 2021).

The amount of NH_3 base modeled by Bains et al. (2021a) explains many of the Venus' lingering atmospheric chemical anomalies (Table 5). The model agrees with the tentative detections of NH_3 in the clouds and below the clouds. In agreement with observations, the model predicts that both SO_2 and H_2O will be present in and above the clouds but at substantially lower abundance than they are below the clouds. The model also provides the explanation for the in-cloud abundance of O_2 and the presence of NO_x and H_2S in the atmosphere. Finally, independent of atmospheric chemistry, the predictions of Bains et al. (2021a) on the Mode 3 cloud particle composition have been supported by the re-analysis of the Pioneer Venus legacy data on the refractive index of the Venusian cloud droplets (Mogul et al., 2021a). The re-analyzed data on the refractive index of cloud particles also suggest ammonium hydrogen sulfate (NH_4HSO_4) salts as components of Mode 3 particles (Mogul et al., 2021a).

We note that one base that was not considered by Bains et al. (2021a) is hydroxylamine (NH_2OH). We find that formation of hydroxylamine as an H_2SO_4 neutralizing agent is thermodynamically less costly (requires less energy) than formation of NH_3. As in the case of NH_3, production of NH_2OH from N_2 requires a release of an oxidized product, and, as in the case of NH_3, the most energy- and water-efficient oxidized product is O_2 (see Supplementary Information, Table S1 and Table S2). However, hydroxylamine reacts readily with aldehydes and ketones and cleaves some peptide bonds (Bornstein and Balian, 1977), which means it is unlikely to be tolerated in high concentration by organisms with an Earth-like biochemistry. Interestingly, hydroxylamine itself reacts with sulfur dioxide to form sulfamic acid (Greenwood and Earnshaw, 2012), hinting at another potential chemical route to removing SO_2 from the clouds through biological action.

In situ Venus atmosphere measurements (Table 6) can verify the acidity and composition of the Venusian particles (Kaasik et al., 2022). A dedicated mission could confirm the non-spherical, semisolid nature of Mode 3 cloud particles, identify them as ammonia salts, and measure the acidity of the cloud particles, especially Mode 3 cloud particles. The confirmation of the decades-long anomalous gas abundances should also be a priority of any astrobiology-focused mission, as well as any Venus mission that focuses on the chemistry of the clouds and the atmosphere (see, *e.g.*, Agrawal et al., 2022; Buchanan et al., 2022; Seager et al., 2022a). Such measurements should include confirmation of the existence of O_2 and NH_3 as well as other nitrogen species, NO_x for example, that could be indicators of an active nitrogen cycle in the atmosphere (see Figure S1 and the Supplementary Information).

We emphasize that, while our interest in Venus is motivated by astrobiology, all of the above measurements will have value regardless of what they find. As discussed, there are many unexplained aspects of Venus' atmospheric and cloud chemistry and resolving them will be of value regardless of whether the resolution involves the discovery of life. For example, the model of Bains et al. (2021a) postulated that atmospheric abundance of O_2 and NH_3 reported by in situ measurements are real and the result of biological neutralization of the Mode 3 droplets. If accurate measurements show that Mode 3 particles have a pH of around 0, but that there is no NH_3 or O_2 present in the atmosphere, that would rule out Bains et al.'s mechanism and suggest that the abiotic mineral-based mechanism for SO_2 removal suggested by Rimmer et al. (2021) could be at play. Even if none of the unexplained observations reported here are confirmed by accurate measurement, that in itself would resolve over forty years' of uncertainty and confirm the "null hypothesis" that the consensus model of Venus' atmosphere is correct. Thus, while Table 6 is cast in terms of its astrobiological significance, the measurements suggested in Table 6 will be of value regardless of the outcome.

Table 5. Venusian atmospheric characteristics explained by the presence of NH_3 base in the atmosphere of Venus (Bains et al., 2021a).

Observable	Model Challenge[a]	Model Prediction[b]
NH_3	High fidelity altitude abundance profile measurements do not confirm tentative detections. Detailed assessment of possible sources and sinks for NH_3 to confirm that the expected abundance of NH_3 is sufficient to act as a neutralizing agent.	The presence of NH_3 in the clouds and below the clouds is consistent with tentative detections of NH_3 (Table 3). Presence of NH_3 in clouds would foster production of salts and result in non-spherical Mode 3 particles.
SO_2	Models that only include H from H_2O and low HCl abundances in clouds do not explain vertical depletion above the clouds (>70 km).	NH_3 provides a mechanism that explains the depletion of SO_2 in the atmospheric cloud layers. NH_3 provides additional H budget that impacts SO_2 budget, replicating observed SO_2 depletion.
H_2O	Models that only include H from H_2O and low HCl abundances in clouds do not explain vertical depletion above the clouds (>70 km).	NH_3 explains the vertical abundance profile of H_2O in and above the clouds. NH_3 provides additional H budget that impacts H_2O budget, replicating observed levels.
O_2	High fidelity altitude abundance profile measurements exclude the possibility of the coexistence of NH_3 and O_2 in the cloud layers.	If the chemistry of NH_3 production is the source of O_2, then the model predicts an order of 1 ppm O_2 in the cloud level of 50—60 km.
H_2S	High fidelity altitude abundance profile measurements do not confirm H_2S in the haze layer below the clouds.	If NH_3 is present in the Venus atmosphere, H_2S is a result of disproportionation of NH_4HSO_3 that yields NH_3, H_2S, and H_2O to the atmosphere below the clouds, and hence is a unique output of the Bains et al. model (Bains et al., 2021a).
NO_x	No NO_x detected within or below the clouds, insufficient data on oxidizing processes at Venus formation and in present day atmosphere to assess the expected abundance of NH_3.	If NH_3 is present in the atmosphere then it is oxidized to NO_x within and below the clouds.
mode 3 particles	The search for NH_4^+ salt ions within the cloud particles gives negative result, meaning no neutralization of acid happens, or other salt ions are detected that could neutralize the acid and act as a base instead of NH_4^+ (e.g. Ca^{2+} coming from hydroxide minerals from the surface (Rimmer et al., 2021)).	If NH_3 is the main neutralizing agent of the sulfuric acid cloud droplets, then the Mode 3 cloud particles in the lower clouds must be solid supersaturated in ammonium salts, with a small liquid phase, and therefore are not liquid, spherical droplets of concentrated sulfuric acid. This view is supported by both (Bains et al., 2021a) and (Mogul et al., 2021a).
stagnant haze layer (31—47 km)	The chemical composition of the stagnant haze layer does not match the model's predictions (small dry salt particles and coexistence of gases like NH_3, H_2S, O_2, SO_2, NO_x, N_2).	Thermal disproportionation of the salts generates gas that shatters the particles at the cloud base, the fragmented particles form the haze.

[a] Model Challenge: what potential future observations, measurements and results would falsify or challenge the Bains et al. model (Bains et al., 2021a).

[b] Model Prediction: predictions of the Bains et al. model (Bains et al., 2021a).

5. Summary and Conclusions

We have described a number of observed Venus atmosphere and cloud properties that have not been previously explained or explored by Venus chemical or planetary evolution models. These shortcomings of the available models are direct evidence of our gaps in understanding of Venus due to insufficient data (both in situ at Venus and lab-based), which has led to many open questions about the mechanics of Venus's atmosphere (Gillmann et al., 2022; Marcq et al., 2018; Mills et al., 2007; Way and Del Genio, 2020).

Significant uncertainties remain embedded into the emergent consensus model of Venusian photochemistry. For example, at high altitudes (>80 km), measurements report the presence of much higher concentrations of SO_2 than predicted by models beforehand, termed the "SO_2 inversion layer" (Belyaev et al., 2012; Sandor et al., 2010; Zhang et al., 2012). This inversion layer is unexpected because SO_2 should be readily photo destroyed at such high altitudes (Mills, 1998; Yung and Demore, 1982; Zhang et al., 2010). Photolysis of supersaturated sulfuric acid or S_8 aerosols is a possible explanation for the inversion layer and is accessible to empirical test via laboratory experiment and observational confirmation (Zhang et al., 2012). However, confirmation has not yet been obtained such that the upper-atmosphere SO_2 cycle remains in doubt.

We conclude this paper with a call for repeated observations of the Venusian atmosphere mysteries with modern instrumentation and for further re-analysis of the legacy data. It is clear that there are a lot of unknowns about Venus. Repeated, high-fidelity, in-situ observation of atmosphere and cloud properties should be a paramount objective of future missions to Venus, as the presence of unexplained chemicals in the atmosphere might be tied to the habitability of the clouds, biological activity, or unknown chemistry.

New NASA missions to Venus such as DAVINCI (Garvin et al., 2022) and VERITAS (Freeman et al., 2016) and ESA missions to Venus such as EnVision (de Oliveira et al., 2018)) will add data to resolve some of the lingering questions about the planet, but none of the planned missions are equipped to directly sample and analyze the chemical composition of cloud particles. Further, additional measurements are needed to characterize atmospheric gases. Therefore, there remains a critical opportunity to directly sample and analyze the essential properties of the Venusian clouds. Unexplained chemical anomalies, including the possible presence of NH_3, tens of ppm O_2, the SO_2 and H_2O vertical abundance profiles, and the unknown composition of Mode 3 particles, have lingered for decades, and their resolution might reveal unknown chemistry that is, in itself, worth exploring even in the absence of life.

The habitability of the Venusian clouds should also be explored by new in situ missions (Seager et al., 2022a). The acidity of the Venus cloud droplets has not been measured directly and could be key to cloud particle habitability. Similarly, no previous mission has directly searched for organic chemistry in the cloud particles. Rocket Lab Mission to Venus is planned for launch in January 2025 (French et al., 2022). The Rocket Lab mission will carry a probe containing the Autofluorescence Nephelometer (AFN) to search for autofluorescence indicative of organic molecules in cloud particles (Baumgardner et al., 2022). Detection of organic molecules, if found predominantly in the larger particles, would be an indicator of life.

New missions should aim to address each of the above objectives and continue where the pioneering missions from nearly four decades ago left off.

In the meantime, a public release of original data from the Soviet Venera and VeGa missions, as has been done recently for Pioneer Venus LNMS data (Mogul et al., 2021b), could enable further support or refutation of current models and predictions and would provide needed context for future mission results.

Table 6. Venusian atmospheric observations, their astrobiological context, required future measurements and possible mission science outcomes. See also (Seager et al., 2022a) for the detailed discussion of the atmospheric observables in the context of the science objectives and mission outcomes of the planned missions to Venus. Table modified from (Seager et al., 2022a) under CC BY 4.0 license.

Observable	Astrobiological Motivation or Hypothesis	Required Measurements	Mission Science Outcomes
NH_3	Indicator of habitability of the clouds (potential "neutralizing agent" of cloud droplets). Indicates an unknown chemical process contributing to the planetary nitrogen cycle. Challenges the notion that the clouds are solely composed of liquid droplets of concentrated sulfuric acid.	Measure altitude-dependent abundance profile of gaseous NH_3 within the clouds and below to 1 ppb precision combined with the search for NH_4^+ salt ions within the cloud particles. Measurements done at several latitudes, day vs night, by several probes would distinguish between localized vs global distribution of NH_3 and inform sources and sinks.	*Detection*: The abundance vs altitude profile constraints the source of NH_3 and tests the validity of the models and their implications. *Non-detection*: The NO_x species (if confirmed) could not be the result of oxidation of NH_3; Reconciles the upper limits provided by the remote observations with the tentative in situ detections; Puts clear constraints on the chemistry of the cloud droplets and on the chemical processes in the atmosphere.
SO_2	Variable profile, including in-cloud depletion, indicative of unknown chemistry in the atmosphere.	Measure altitude-dependent abundance profile of gaseous SO_2 measured from above the clouds to below the clouds to 1 ppb precision to characterize the degree of depletion of SO_2 within the clouds.	*Detection*: The abundance vs altitude profile constraints the source of SO_2 and other SO_x gases and tests the validity of the models and their implications; Puts clear constraints on the chemical processes in the cloud droplets and the atmosphere.
H_2O	The amount of water in the clouds is not uniform and is	Measure altitude-dependent abundance profile of water	*Detection of anomalously high abundance values*:

	locally variable. High abundance of H_2O is an indicator of relatively greater habitability of local regions within the clouds.	vapor to 1 ppb precision together with the measurement of the water content of the cloud particles. Measurements done at several latitudes, day vs night, by several probes would distinguish between localized vs global distribution of H_2O and inform sources and sinks.	Confirmation that the amount of water in the clouds is not uniform and is locally variable. Variable profile would be indicative of unknown cloud particle chemistry. *No anomalously high values detected*: Reconciles the values and upper limits provided by the remote and in situ spectroscopic observations with the tentative in situ detections.
O_2	Potential sign of life or unknown abiotic chemical processes in the clouds.	Measure altitude-dependent abundance profile of O_2 to 1 ppb precision especially in the clouds and below. Measurements done at several latitudes, by several probes would distinguish between localized vs global distribution of O_2 and inform sources and sinks. Establishing the co-existence of NH_3 and O_2 in the cloud layers tests the hypothesis of biological production of both gases.	*Detection*: The abundance vs altitude profile constraints the source of O_2 and tests the validity of the models and their implications. *Non-detection*: Reconciles the upper limits provided by the remote observations with the in situ detections; Puts clear constraints on the chemical processes in the atmosphere.
H_2S	Important component of the sulfur cycle and (in addition to H_2O) an important source of hydrogen (a limiting nutrient) for putative aerial biosphere.	Measure altitude-dependent abundance profile of H_2S to 1 ppb precision especially in the clouds and below. Measurements done at several latitudes, by several probes would distinguish between localized vs global distribution of H_2S and inform sources and sinks.	*Detection*: The abundance vs altitude profile constrains the source of H_2S and tests the validity of the models and their implications on the planetary sulfur cycle and overall reservoir of the H-containing species. *Non-detection*: Reconciles the upper limits provided by the remote observations with the tentative in situ detections; Puts clear constraints on the chemical processes in the atmosphere.
NO_x	Important components of the planetary nitrogen cycle.	Measure altitude-dependent abundance profile of gaseous NO_x to 1 ppb precision combined with the search for NO_x salt ions within the cloud particles.	*Detection*: The abundance vs altitude profile constraints the source of NO_x and tests the validity of the models and their implications. *Non-detection*: Puts clear constraints on the chemical processes in the cloud droplets and the atmosphere, including on the presence and intensity of lightning strikes.
PH_3	Indicator of an unknown chemical processes in the atmosphere and an important member of the planetary phosphorus cycle.	Measure altitude-dependent abundance profile to sub-ppb precision combined with a day and night measurements to inform chemistry sources and sinks. Measurements done at several latitudes, by several probes would distinguish between localized vs global distribution of PH_3 and further inform sources and sinks.	*Detection*: The abundance vs altitude profile constraints the source of PH_3 and tests the validity of the models and their implications. *Non-detection*: Reconciles the remote and in situ observations with the upper limits; Puts clear constraints on the chemical processes in the atmosphere, including the availability of volatile P species.

HCN	Indicator of unknown chemical processes in the clouds. Important precursor for prebiotic chemistry and planetary nitrogen cycle.	Measure altitude-dependent abundance profile of gaseous HCN to 1 ppb precision.	*Detection*: The abundance vs altitude profile constraints the source of HCN and tests the validity of the models and their implications on the planetary nitrogen cycle. *Non-detection*: Reconciles the observational upper limits with the tentative in situ detections.
CH_4	Potential sign of life or a result of an unknown abiotic chemical processes on the planet.	Measure altitude-dependent abundance profile, from the top of the clouds down to the surface, of gaseous CH_4 to 1 ppb precision. The dedicated instrumentation should be designed to specifically avoid any potential contamination with hydrocarbons brought from Earth or evolved from the instrument itself.	*Detection*: The abundance vs altitude profile constraints the source of CH_4 and tests the validity of the models and their implications; Provides a potential source for organic chemistry in the clouds. *Non-detection*: Reconciles the upper limits provided by the remote and in-situ observations with the tentative detection by Pioneer Venus LNMS.
Organic molecules	Shows that cloud particles are not chemically simple environment and could contain complex organic molecules that could be precursors to life or even be signs of life itself.	The in-situ search for organic molecules within cloud particles both through detection of fluorescence at multiple wavelengths (e.g. (Baumgardner et al., 2022)), as well as direct identification of organic species to 1 fmol precision from collected cloud particles (in situ (e.g. (Ligterink et al., 2022)) or atmospheric sample return (Seager et al., 2022b)).	*Complex and diverse organics identified*: Potential for life in the cloud particles increases with the diversity and complexity of detected organics. *Only simple and uniform organics identified*: Abiotic processes are most likely responsible for organics formation. *No organics identified*: The prospects of the clouds of Venus as a habitable environment diminish as we assume that all life, no matter its chemical makeup, requires organic chemistry.
non-volatiles (e.g. P and Fe)	Cloud particles could contain dissolved metal ions (e.g., Fe) and other ions of non-volatile elements (e.g., P) suggesting that the clouds are not homogenous. Presence of metals could be indicative of efficient interactions between the surface and the clouds.	Qualitative and quantitative elemental analysis and characterization (to 1 ppb precision) of the collected cloud particle material (in situ (e.g. (Ligterink et al., 2022)) or atmospheric sample return (Seager et al., 2022b)). Study interactions between the surface and the atmosphere that might support reservoirs of metals in the clouds.	*Metal ions detected*: The composition of the cloud particles is chemically complex; Suggests efficient exchange of material between the surface (the presumed source of the non-volatile elements) and the clouds. *No metal ions detected*: The material exchange between the surface (the presumed source of the non-volatile elements) and the clouds is not efficient limiting the habitability of the clouds.
mode 3 particles	Clouds are not homogenous and are composed of a mixture of particles which may contain different chemistries, including liquid concentrated sulfuric acid and/or solid salt particles. Acidity of cloud particles could be variable and may reach habitable levels.	Chemical analysis of the collected cloud particle material (in situ (e.g. (Ligterink et al., 2022)) or atmospheric sample return (Seager et al., 2022b)). In-situ analysis of particle shape and size distribution (Baumgardner et al., 2022), including direct imaging of particle shapes, direct in-situ determination of the acidity of single cloud particles covering the acidity range from diluted to concentrated sulfuric acid (Kaasik et al., 2022).	*Solid Mode 3 particles composed of salts detected*: Confirms the existence of the Mode 3 particles; the salt composition puts clear constraints on the chemical processes in the cloud droplets and the atmosphere; confirms that the clouds are not uniformly made of liquid concentrated sulfuric acid particles. *No solid particles detected*: Supports the model that the clouds of Venus are made of liquid droplets of concentrated sulfuric acid.

			Detection of variable acidity of cloud particles: The altitude profile of cloud acidity tests the validity of atmospheric and cloud models and model implications for the habitability of the clouds. *Acidity of cloud particles is uniform and consistent with concentrated sulfuric acid*: Puts clear constraints on the chemical processes in the atmosphere; confirms, for the first time by direct measurement, that the clouds are uniformly made of concentrated sulfuric acid particles.
unknown absorber	The chemistry of the substance, or substances, absorbing in Venus' clouds is unknown. The unknown absorber could be a sign of biological activity in the clouds.	Global monitoring of the dynamics of the unknown absorber including its spatial and temporal variability (Garvin et al., 2022). Measure the in-situ altitude-dependent UV absorption profile of the clouds. Laboratory and theoretical studies on the absorber candidates, including sulfur species (Francés-Monerris et al., 2022) and organic materials (Spacek, 2021).	*Spatial and temporal variability and quasi-seasonal changes confirmed*: Provide new spectral clues to the nature of the unknown absorption in the upper clouds. *The unknown absorber shows uniform/variable abundance throughout the clouds*: The altitude profile of UV absorption tests the validity of atmospheric and cloud models, including hypotheses on the chemical identity of the unknown absorber.

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Author contributions

Conceptualization: J.J.P., W.B., S.S., S.R., P.B.R.; methodology: J.J.P., W.B.; analysis W.B., J.J.P.; writing—original draft preparation, J.J.P., S.S. D.H.G.; writing—review and editing: J.J.P., W.B., S.S., S.R., P.B.R., D.H.G., W.P.B., R.A., R.M., C.E.C. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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Supplementary Information

Table S1. Free energy per mole for H_2SO_4/NH_3 - neutralizing reactions under Venus cloud conditions. Table values revised and updated from (Bains et al., 2021a).

Reaction	Free energy of reaction (kJ/mol)	Free energy required per mole of H_2SO_4 neutralized (kJ/mol)	Water consumed per H_2SO_4 neutralized
1a $4N_{2(aq)} + 9H_2O_{(l)} + 2H_2SO_{4(l)} \rightarrow 3NH_4^+NO_3^-{}_{(aq)} + 2NH_4^+HSO_4^-{}_{(aq)}$	1420 – 1473	710 – 736	4.5
2a $4N_{2(aq)} + 6H_2O_{(l)} + 2H_2SO_{4(l)} \rightarrow 2NH_4^+HSO_4^- + 3H_2O_{2(aq)}$	826 – 852	413 – 426	3
3a $2N_{2(aq)} + 6H_2O_{(l)} + 4H_2SO_{4(l)} \rightarrow 4NH_4^+HSO_4^- + 3O_{2(aq)}$	**701– 752**	**175 – 188**	**1.5**
4a $4N_{2(aq)} + 12H_2O_{(l)} + 3HCl_{(aq)} + 4H_2SO_{4(l)} \rightarrow 5NH_4^+HSO_4^-{}_{(aq)} + 3NH_4^+ClO_4^-{}_{(aq)}$	1045 – 1141	209 – 228	3

Table S2. Free energy per mole for H_2SO_4/NH_2OH - neutralizing reactions under Venus cloud conditions.

Reaction	Free energy of reaction (kJ/mol)	Free energy required per mole of H_2SO_4 neutralized (kJ/mol)	Water consumed per H_2SO_4 neutralized
1b $4N_{2(aq)} + 9H_2O_{(l)} + 2H_2SO_{4(l)} \rightarrow 3NOH_4^+NO_3^-{}_{(aq)} + 2NOH_4^+HSO_4^-{}_{(aq)}$	1161 – 1257	290 –314	4.5
2b $4N_{2(aq)} + 6H_2O_{(l)} + 2H_2SO_{4(l)} \rightarrow 2NOH_4^+HSO_4^- + 3H_2O_{2(aq)}$	599 – 582	280 – 291	3
3b $2N_{2(aq)} + 6H_2O_{(l)} + 4H_2SO_{4(l)} \rightarrow 4NOH_4^+HSO_4^- + 3O_{2(aq)}$	**569 – 617**	**142 – 154**	**1.5**
4b $4N_{2(aq)} + 12H_2O_{(l)} + 3HCl_{(aq)} + 4H_2SO_{4(l)} \rightarrow 5NH_4^+HSO_4^-{}_{(aq)} + 3NH_4^+ClO_4^-{}_{(aq)}$	724 – 888	145 – 178	3

Results shown in Table S1 and Table S2 are derived for the same conditions as in (Bains et al., 2021a). Free energy of formation of acid solvated NH_2OH derived from gas phase free energy (Bains et al., 2022b), predicted Henry's Constant, and the pKa of hydroxylamine from (Card et al., 2017; Krishna et al., 2003). Note that hydroxylamine nitrate readily decomposes above about 80 °C, in an autocatalytic process (Rafeev and Rubtsov, 1993), and in concentrated or pure form is unstable and liable to explosion (Wei et al., 2006), so it is unlikely to be formed in significant amounts. Hydrolylamine itself is directly dissociated by UV light (Thisuwan et al., 2020). However in the gas phase hydroxylamine absorbs at wavelengths <220 nm (Betts and Back, 1965), and so is likely to be shielded from photolysis in the middle and lower clouds, if it exists there.

Evidence for a Nitrogen Cycle in the Clouds of Venus

The recent re-analysis of the Pioneer Venus LNMS data shows evidence of nitrogen chemicals at different oxidation states (from -3 to +5): NH_3 (-3), HCN (-3), N_2 (0), NO_2^- (+3), NO_3^- (+5).

The potential presence of nitrogen chemicals at different oxidation states implies the existence of an active nitrogen cycle in the clouds of Venus (Figure S1). Such nitrogen compounds could be key electron donors for anoxygenic photosynthesis (nitrite) or a critical redox pair (nitrate and nitrite) for a postulated hypothetical iron-sulfur cycle in Venus' clouds (Limaye et al., 2018). Nitrogen species identified in the re-analyzed data from Pioneer Venus (Mogul et al., 2021b) are also major constituents of the biological nitrogen cycle on Earth (nitrate, nitrite, ammonia, and N_2) (Galloway, 2003). The potential identification of NH_3, and other N-species from the terrestrial nitrogen cycle is therefore consistent with potential biological activity in the clouds of Venus. We note however that just like on Earth any hypothetical biological production of NH_3 (e.g. through fixation of atmospheric N_2) would be an energy intensive process, and in the Venusian cloud conditions probably reliant on sunlight (Bains et al., 2021a).

Confirmation of the presence of the multitude of nitrogen species at different oxidation states in the clouds of Venus could establish the existence of an active nitrogen cycle on Venus. The existence of such a cycle will be an important insight into the cloud chemistry, either biotic or abiotic.

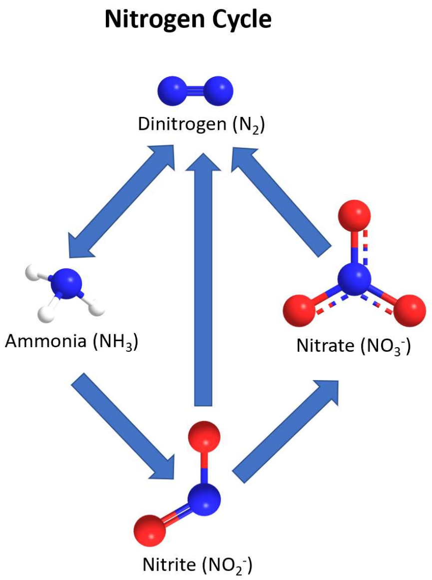

Figure S1. The potential nitrogen cycle in the Venusian clouds based on nitrogen species (nitrate, nitrite, ammonia, and N_2) tentatively identified in the reanalyzed LNMS data from the Pioneer Venus probe (Mogul et al., 2021b). The identified nitrogen species are also major constituents of the biological nitrogen cycle on Earth.

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