Production of ammonia makes Venusian clouds habitable and explains observed cloud-level chemical anomalies

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The atmosphere of Venus remains mysterious, with many outstanding chemical conundrums. These include the unexpected presence of ~10 ppm O2 in the cloud layers, an unknown composition of large particles in the lower cloud layers, and hard to explain measured vertical abundance profiles of SO2 and H2O. We propose a hypothesis for the chemistry in the clouds that largely addresses all of the above anomalies. We include ammonia (NH3), a key component that has been tentatively detected both by the Venera 8 and Pioneer Venus probes. NH3 dissolves in some of the sulfuric acid cloud droplets, effectively neutralizing the acid and trapping dissolved SO2 as ammonium sulfite salts. This trapping of SO2 in the clouds, together with the release of SO2 below the clouds as the droplets settle out to higher temperatures, explains the vertical SO2 abundance anomaly. A consequence of the presence of NH3 is that some Venus cloud droplets must be semi-solid ammonium salt slurries, with a pH of ~1, which matches Earth acidophile environments, rather than concentrated sulfuric acid. The source of NH3 is unknown but could involve biological production; if so, then the most energy-efficient NH3-producing reaction also creates O2, explaining the detection of O2 in the cloud layers. Our model therefore predicts that the clouds are more habitable than previously thought, and may be inhabited. Unlike prior atmospheric models, ours does not require forced chemical constraints to match the data. Our hypothesis, guided by existing observations, can be tested by new Venus in situ measurements.

Venus is often called Earth’s sister planet because of its similar mass and size to Earth. Yet, owing, in part, to the greenhouse effect from its massive CO2 atmosphere, Venus’s surface temperature is higher than 700 K—too hot for life of any kind. The Venusian surface is therefore a complete contrast to Earth’s temperate surface and rich surface biosphere. Nonetheless, scientists have been speculating on Venus as a habitat for extraterrestrial life. Life could be making its own environment on Venus. The model predictions for the abundance of gases in Venus’ atmosphere match observation better than any previous model, and are readily testable.

Significance

This research provides a transformative hypothesis for the chemistry of the atmospheric cloud layers of Venus while reconciling decades-long atmosphere anomalies. Our model predicts that the clouds are not entirely made of sulfuric acid, but are partially composed of ammonium salt slurries, which may be the result of biological production of ammonia in cloud droplets. As a result, the clouds are no more acidic than some extreme terrestrial environments that harbor life. Life could be making its own environment on Venus. The model’s predictions for the abundance of gases in Venus’ atmosphere match observation better than any previous model, and are readily testable.

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Previous consensus models explained the SO₂ profile by suggesting that SO₂ is photochemically oxidized to SO₃, which then reacts with water to form sulfuric acid in the clouds:

\[
\begin{align*}
\text{CO}_2 + h\nu &\rightarrow \text{CO} + \text{O} \\
\text{SO}_2 + \text{O} + \text{M} &\rightarrow \text{SO}_3 + \text{M} \\
\text{SO}_1 + \text{2H}_2\text{O} &\rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \\
\text{SO}_2 + \text{H}_2\text{O} + \text{CO}_2 &\rightarrow \text{H}_2\text{SO}_4 + \text{CO}.
\end{align*}
\]

However, as there is 5x more SO₂ than H₂O, this chemistry should strip all the water out of the cloud layer, and additionally react with and prevent water from reaching and accumulating above the clouds as well, while only reducing SO₂ by 20%, not the 99.9% observed (20). Previous models provide a numerical fix to match the observations, arbitrarily removing SO₂ or artificially keeping the water abundance constant (21, 22).

Another mystery is the presence of O₂ in the clouds (23, 24), as there is no known process for O₂ formation in the cloud layers (discussed further below). Finally, the SO₂, O₂, and H₂O anomalies, together with other trace atmospheric gas abundances, form a chemical disequilibrium in the clouds of Venus (25–27).

A more tentative but intriguing anomaly is that of the detection of NH₃ in and below the cloud layers. NH₃ was tentatively detected both by the Venera 8 chemical probe (28) and in reanalyzed Pioneer Venus (Pioneer 13) data (27). The reanalysis of Pioneer Venus data showed additional N species (NOₓ), suggesting further chemical disequilibrium in the cloud layers. The cloud particles themselves also contain many unknowns. The largest particles, predominant in the lower cloud decks [called Mode 3 particles (29)], may have a substantial solid component, implying that they cannot be exclusively made of liquid concentrated sulfuric acid (30).

Some additional anomalies that are not directly relevant to this work, such as the “unknown UV absorber” (31) and the possible presence of methane (32) or phosphine (33, 34), have all been suggested as signs of life in the clouds.

How the Rimmer et al. Model Resolves the SO₂ and H₂O Abundance Conundrum

Recently, Rimmer et al. (20) proposed a mechanism to explain the depletion of SO₂ in the atmospheric cloud layers, as well as the vertical abundance profile of H₂O in and above the clouds. If a base is present inside the cloud sulfuric acid droplets, SO₂ will dissolve in the liquid droplets (by reaction with OH⁻) to form sulfite. The base (B), therefore traps the SO₂ inside the cloud droplet as sulfite (HSO₃⁻).

\[
\text{SO}_2 + \text{H}_2\text{O} + \text{B} \rightarrow \text{SO}_2 + \text{BH}^+ + \text{OH}^- \rightarrow \text{BH}^+ + \text{HSO}_3^-.
\]

In summary, the equilibrium of the reaction

\[
\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_3
\]

is pulled to the right of the above equation, and S(IV) species are trapped as sulfite salts through reaction with the base. Thus, SO₂ is depleted in the cloud layer, compared to the model with no bases. Eventually, the cloud droplets rain down to lower atmosphere layers, and the salts dissociate due to higher temperatures, releasing SO₂.

Water is consumed in the sulfite-forming reaction, but is recycled into the lower atmosphere on breakdown of the sulfites, which provides a mechanism to explain the water vapor abundance profile through the clouds. Some water is removed from the cloud layer, but, because it is replenished by recycling from below the clouds, the water removal is not absolute, and so some water remains at the cloud top and in the atmosphere above the clouds. Thus the Rimmer et al. (20) model predicts that both SO₂ and H₂O will be present above the clouds but at substantially lower abundance than they are below the clouds, in agreement with observation.

The formation of the sulfite salt within a droplet effectively neutralizes the acid in the droplet, with the very important outcome that some of the cloud droplets are much less acidic than previously thought, with a pH between 1 and 1 (20), instead of an acidity of approximately −11 (on the Hammett acidity scale). If correct, the revised pH range of some droplets has a significance for the habitability of the clouds of Venus that cannot be overstated. Such a pH range is habitable by terrestrial extremophiles (35), as compared to the acidity of concentrated sulfuric acid in which all terrestrial life, and most terrestrial biochemicals, would be destroyed (14).

We argue that the identity of any droplet-neutralizing base is unknown. Rimmer et al. (20) adopted NaOH as a model base for their calculations, but noted that iron oxides are a more physically realistic possibility. In principle, minerals that can absorb SO₂ could be delivered to the clouds from Venusian volcanic eruption, from wind lofting of dust, or from meteoritic infall. However, it has not been demonstrated that such mechanisms could deliver the very high amount of ∼20 tonnes per second flux of mineral salts (specifically iron oxides) required (20).

We are motivated to extend ref. 20’s analysis with the hypothesis that the neutralizing base that is capturing SO₂ is locally generated in the clouds. We postulate that NH₃ is the neutralizing agent for the Venusian cloud droplets, trapping SO₂ and thus explaining the drop in SO₂ abundance across the clouds. We are additionally motivated by the tentative in situ observations of NH₃ in the Venus cloud layers, from both Venera 8 chemical assay (28) and Pioneer Venus probe mass spectrometry (27). If present, NH₃ observations cannot yet be readily explained through any known abiotic planetary processes (36). We therefore also explore the possibility that the NH₃ is biologically produced.

Results

Ammonia as a Neutralizing Agent in the Venustian Cloud Droplets.

We propose NH₃ as the only plausible neutralizing base that can be generated in situ in the clouds from gas-phase components (see SI Appendix, section 1 for further details on potential neutralizing agents in the cloud layers). The presence of NH₃, as with any neutralizing base, leads to chemistry that results in the SO₂ depletion in the clouds and the observed H₂O abundance profile, and is consistent with a subset of Mode 3 particles being nonspherical (i.e., not liquid) and not composed of pure concentrated sulfuric acid. The presence of NH₃ may also solve the otherwise unexplained presence of O₂ in the clouds, especially if the source of NH₃ is biological.

To support our hypothesis that NH₃ could explain the presence of O₂ within the clouds, we first explore the limited number of possible chemical reactions that could lead to the formation of NH₃ in the Venustian atmosphere cloud layer conditions (Table 1).

The most abundant source of nitrogen atoms in the atmosphere of Venus is N₂ gas, so, to make NH₃, N₂ must be reduced to NH₃. The reduction of N₂ to form NH₃ requires a source of hydrogen atoms, and a source of electrons (reducing equivalents). Hydrogen atoms are rare in the atmosphere of Venus. The most abundant gas-phase source of hydrogen atoms in the atmosphere of Venus is H₂O, followed by HCl. In order to generate reducing equivalents, some species must be oxidized. Species available to be oxidized include CO, OCS, SO₂, N₂, H₂O, and HCl. Phosphorus, if present, will be overwhelmingly present as H₃PO₄ (34); neither H₃PO₄ or CO₂ can be further oxidized.
but which would also produce O2 on breakdown, and at the
clouds (Table 1), whose detection is one of the anomalies
∼ 3O2(aq), as the basis for our model for two reasons. Firstly, par-
sequester SO2, and only NH3 sequesters SO2. If other species
consistent, to within an order of magnitude, with the mass loss at the
This flux is calculated assuming that NH3 is only produced to
organisms in the clouds of Venus are making NH3. All of the
production rate on the rate at which SO2 would be
equilibrium values in the atmospheric cloud layers. We
expected sulfuric acid has not been explored. Volcanic sources of
nano- and perchlorate, respectively) clouds also alternatively explain the presence of O2. Nitrate and perchlorate would
reactive) leads us to prefer a reaction that uses the smallest
energy and its use to water. We note that reaction 4 could produce hypochlorite, chlorite, or chlorate as an oxidized product, but, as perchlorate is
relatively stable and is the weakest oxidizing agent, we have shown this reaction for illustration only. Reaction 5 generates more acid than it consumes, and
so cannot be a source of the base which neutralizes H2SO3. We also note that reaction 1 and reaction 4 (reactions making nitrate and perchlorate,
respectively) clouds also alternatively explain the presence of O2. Nitrate and perchlorate would “rain out” and decompose to N2 and O2 or HCl, Cl2, and
O2, respectively, below the clouds. In situ measurements of NOx and ClO4 abundance in the clouds could rule out these reactions as a potential source of indirect formation of O2.

The most energy- and water-efficient NH3-producing reaction (reaction 3 in Table 1) also produces molecular oxygen. We
choose reaction 3, 2N2(aq) + 10H2O(l) → 4NH4OH +
3O2(aq), as the basis for our model for two reasons. Firstly, par-
simony leads us to prefer a reaction that uses the smallest
amount of rare materials (H2O and energy). Secondly, reaction
3 is the only NH1-forming reaction that directly produces O2 in the
clouds (Table 1), whose detection is one of the anomalies we wish to explain (discussed below); the other reactions pro-
duce different oxidized species which would not be observed but which would also produce O2 on breakdown, and at the
cost of greater energy consumption.

A key question is what NH3 production rate (by reaction 3) is
needed for maintaining the low SO2 abundance, as compared to
expected equilibrium values in the atmospheric cloud layers. We
base the SO2 production rate on the rate at which SO2 would be
replenished into the clouds by mixing from below, and hence the
rate at which it must be removed from the clouds. The flux is
∼1011 tonnes per year NH3, which is on the order of photosyn-
thetic production of O2 on Earth (see Materials and Methods).
This flux is calculated assuming that NH3 is only produced to
sequester SO2, and that only NH1 sequesters SO2. If other species
contribute to removing SO2, whether hydroxide salts, iron oxides,
or other species, the NH3 production will be accordingly lower.
Any byproduct of SO2 sequestration must have a flux of ∼1011
tones per year at the bottom of the clouds, based on the SO2
depletion within the clouds. A flux of 1011 tonnes per year is con-
sistent, to within an order of magnitude, with the mass loss at the
bottom of the clouds from rainout of Mode 3 particles from our
calculations (SI Appendix, section 2).

All of the NH1-producing reactions in the Venusian atmo-
sphere conditions are highly endergonic (Table 1), and so must
be coupled to an energy source if the reactions are to produce net, “surplus” NH3. There are several energy sources that
could, in principle, drive the production of NH3. Lighting falls
short by many orders of magnitude of the necessary rate of pro-
duction of NH3 (SI Appendix, section 7.1 and Table S3), and is
very unlikely to produce both NH3 and O2 simultaneously. Sim-
ilarly, UV photochemistry is unlikely to produce NH3 in more
than trace amounts (SI Appendix, section 7.2), although we
note that the photochemistry of nitrogen species in concent-
trated sulfuric acid has not been explored. Volcanic sources of
NH3 on Earth are closely associated with organic deposits,
including coal, and also are quantitatively insufficient, even
based on terrestrial rates of volcanic NH3 production, which
are likely to be much higher than any plausible NH3 production on Venus (SI Appendix, section 7.3 and Fig. S4).

The ability to couple chemical energy to drive endergonic reactions is a universal characteristic of life, and, specifically,
the use of energy to drive the reduction of N2 to NH3 in an oxi-
dizing environment is widely found in terrestrial organisms (37,38). We should therefore consider the possibility that living
organisms in the clouds of Venus are making NH3. All of the
NH3-producing reactions presented in Table 1 consume water,
which is a rare resource in the clouds of Venus. The energy
expended and water molecules consumed in the process of
making NH3 must be balanced by an equally powerful benefit
to the organism for this apparently wasteful chemistry. Neutral-
izing the acid to make the droplets habitable is a clear benefit.

We discuss the other, possibly insuperable barriers to the
concept of life in the Venusian clouds below. Here we only
note that the presence of life could explain the observed pres-
ence of NH3 and O2, and later show that it could explain the
observed vertical abundances of H2O and SO2 within and
above the atmospheric cloud layers, and the semisolid nature of
Mode 3 particles. An additional consequence of the NH3 cloud
droplet chemistry is that the pH of cloud particles with dis-
solved NH3 must have a pH between −1 and 1, as first shown by Rimmer et al. (20) for NaOH (Fig. 1).

The Flux of NH3 is Within the Plausible Biomass Production. The
flux of NH3 needed to achieve the neutralization effect is not
prohibitive for a realistic biomass within the cloud droplets. We
calculate the biomass required by this model as follows. The

### Table 1. Free energy per mole for NH3-generating reactions under Venus cloud conditions

| Reaction | Free energy of reaction (kJ/mol) | Free energy required per mole of surplus NH3 (kJ/mol) | Water consumed per surplus NH3 |
|----------|----------------------------------|-----------------------------------------------------|-------------------------------|
| 1        | 4N2(aq) + 11H2O(l) → 2NH4OH − 8H2O | 1,730 to 2,024 | 865 to 1,012 | 6.5 |
| 2        | N2(aq) + 8H2O(l) → 2NH4OH + 3H2O | 1,203 to 1,471 | 602 to 736 | 4 |
| 3        | 2N2(aq) + 10H2O(l) → 4NH4OH + 3O2 | 1,000 to 1,306 | 262 to 343 | 2.5 |
| 4        | 4N2(aq) + 17H2O(l) + 3NH4OH + 3H2O | 1,364 to 1,634 | 273 to 323 | 3.4 |
| 5        | N2(aq) + 6H2O(l) + 3O2 → (NH4)2SO4 + 2H2O | 1,193 to 1,313 | N/A | N/A |

Free energies of NH3-producing reactions are calculated from refs. 83–85. Ranges are minimum to maximum over a range of pH = −3 to pH = +4 and
temperature from 2°C to 115°C. Concentrations of SO2 and H2O are as described in ref. 34. O2 fractional abundance is assumed to be 10−6. Table columns are as
follows. First column: reaction number. Second column: possible chemical reaction that produces NH3. Third column: free energy of reaction
assuming that NH3 is accumulated to 2 molar concentration. For the fourth and fifth columns, values were calculated in terms of “surplus NH3,” which is
the amount of NH3 synthesized as NH4OH. Fourth column: free energy per mole of “surplus NH3” produced. Fifth column: number of water molecules
consumed per “surplus” NH3. Reaction 3 (bold type), which produces molecular oxygen as an oxidized byproduct, is the most efficient, in both its use of
energy and its use to water. We note that reaction 4 could produce hypochlorite, chlorite, or chlorate as an oxidized product, but, as perchlorate is
relatively stable and is the weakest oxidizing agent, we have shown this reaction for illustration only. Reaction 5 generates more acid than it consumes,
and so cannot be a source of the base which neutralizes H2SO3. We also note that reaction 1 and reaction 4 (reactions making nitrate and perchlorate,
respectively) clouds also alternatively explain the presence of O2. Nitrate and perchlorate would “rain out” and decompose to N2 and O2 or HCl, Cl2, and
O2, respectively, below the clouds. In situ measurements of NOx and ClO4 abundance in the clouds could rule out these reactions as a potential source of indirect formation of O2.
production of $10^{11}$ tonnes per year is equivalent to $3 \times 10^{9}$ g NH$_3$ per second. Several species of cyanobacteria fix nitrogen at an average rate of $\sim 4 \times 10^{-4}$ g per g wet weight biomass per second (39–41). If life is present in the clouds of Venus, it will not be terrestrial life; however, if we take these terrestrial organisms as precedent, $10^{11}$ tonnes per year would be produced by $\sim 8 \times 10^{15}$ g wet weight of organism. While this mass might appear significantly high, it is $\sim 1/2,000$ (0.05%) the biomass of the Earth (42). This mass translates to $\sim 1.5$% of the mass of cloud particles in the lower 5 km of the cloud deck (25).

Our model for the production of NH$_3$ by life is summarized in Fig. 2.

**Toward a Resolution of Venus Atmospheric Anomalies**. The incorporation of NH$_3$ in our photochemistry model of the Venussian atmosphere produces profiles of atmospheric gases that match the observed abundances of some atmospheric gases better than existing models of Venus’s atmosphere. Although NH$_3$ is an input to our model, no existing Venus photochemical models include NH$_3$ (e.g., refs. 22 and 43). In Figs. 3 and 4, we show a summary of the output of the modeling with NH$_3$ included, compared to the same model run without NH$_3$ and O$_2$ input, the latter as reported in ref. 20. The atmospheric photochemistry of the clouds was modeled as described in refs. 20 and 34, and is summarized in Materials and Methods. Specifically, our model better explains, compared to previous models, 1) the observed disequilibria in the clouds of Venus; 2) the measured, but subsequently ignored, abundances of O$_2$ in the clouds; 3) the abundance profile of water vapor; 4) the tentative detections of NH$_3$ by Venera 8 and Pioneer Venus probes; and 5) the abundance profile of SO$_2$ through the cloud layers. To demonstrate how well our model with NH$_3$ fits the measured data, we show three model results in Figs. 3 and 4: one model with NH$_3$, one model without NH$_3$ but with an unphysical arbitrary depletion rate of SO$_2$ (a fix common among other models in order to fit the data), and one model without NH$_3$ and without any artificial chemical constraints.

We now turn to each relevant atmosphere anomaly, first reviewing the data, and then how the presence of NH$_3$ helps resolve the anomaly.

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O$_2$ in the clouds is a natural outcome of NH$_3$ production. Our model provides an explanation for the presence of O$_2$ in the Venus cloud layers. O$_2$ has been measured via in situ measurements (44, 45). The Pioneer Venus gas chromatography (GC) 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 oxygen at 21.6 km (23). The Venera 14 GC detected 18 ppm O$_2$ average between 35 and 58 km (24). [The Large Neutral Mass Spectrometer (LNMS) on Pioneer Venus showed a signal of 32 amu, but this was attributed to O$_2$ ions formed from reaction of CO$_2$ in the mass spectrometer (46), and therefore was considered unreliable. However, we emphasize that this uncertainty about the source of O$_2$ is specific to mass spectrometry (47).]

We also note that several ground-based observations attempted to provide upper limits for the abundance of O$_2$ above the clouds (48, 49). The spectroscopic searches for O$_2$ have been subjected to varying interpretations (16, 17) and are claimed to be difficult to reconcile with the in-cloud O$_2$ abundance detected by both Pioneer Venus and Venera probes, because one expects to observe a gradient of O$_2$ from above to below the clouds. Such discrepancies can only ultimately be resolved by new in situ measurements of O$_2$ in the clouds of Venus.

In the past, the validity of O$_2$ has been challenged based on thermodynamics. Initial studies of the atmosphere of Venus in the 1970s and 1980s assumed the atmosphere was at thermodynamic equilibrium. One author discounted O$_2$ as follows (44): “We therefore conclude, that either we have to accept a strong disequilibrium state among CO, SO$_2$, O$_2$ and H$_2$O in the lower atmosphere of Venus, or discard at least one of the measurements in order to save the assumption of thermodynamic equilibrium. The latter course is our preferred one.” Some subsequent studies followed this argument (17, 23, 36), although not all (50), and the author himself modified his opinion in a subsequent paper (45). By now, it has been accepted for over two decades that the atmosphere of Venus is not at thermodynamic equilibrium (25, 26, 51, 52), although Venus’s atmosphere is not as far from disequilibrium as Earth’s atmosphere is (51, 52). Recently, the reanalysis of the Pioneer Venus data showed the atmosphere was farther from equilibrium than previously thought, due the presence of a range of reduced gases (27). Still, the cause of the Venus atmosphere thermodynamic disequilibrium is one of the unsolved problems in Venus science (17).

If the chemistry of NH$_3$ production is the source of O$_2$, then our model predicts on order 1 ppm O$_2$ in the cloud level between about 50 and 60 km; 1 ppm is 20-fold lower than the measured values (23, 24). However, the value of 1 ppm at lower altitudes is far greater (15 orders of magnitude) than predicted by our and other photochemistry models that exclude NH$_3$. While there are no known nonbiological processes that could produce O$_2$ locally in the clouds of Venus, we note, for future work, that other biological processes such as oxygenic photosynthesis could also be contributing to the overall O$_2$ budget in the clouds.

It has been suggested that O$_2$ could also be produced by lightning, which is consistent with O$_2$’s presence in and below but not above the clouds (53). Lightning and coronal discharge can produce O$_2$ in a CO$_2$ + N$_2$ atmosphere (54). A thermodynamic-based calculation suggests that the amount of O$_2$ possibly produced by lightning is four to five orders of magnitude too low to explain the observations (SI Appendix, section 8.1 and Table S4). However, the efficiency of the production of O$_2$ by lightning could be tested experimentally on Earth. It is possible that all the O$_2$ detections summarized above were made as spacecraft fell through high-intensity storm regions (55), but it seems an unlikely coincidence for two or three separate probes to experience storms. In addition, any NH$_3$ present in the clouds would be destroyed by the lightning, and only...
trace amounts would reform (SI Appendix, section 7.1). The thermal decomposition of H$_2$SO$_4$ to O$_2$ and SO$_2$ has been suggested as an industrial process (56), but it is unlikely under Venus conditions (SI Appendix, section 8.2 and Fig. S5).

At altitudes above the cloud level (~62 km), no O$_2$ has been detected, strongly suggesting a fractional abundance of less than 10$^{-7}$ (48). Yet, all existing photochemical models predict significant molecular oxygen above the clouds (e.g., ref. 22) due to the instability of CO$_2$ to photolysis. CO$_2$ is dissociated into CO and O, which cannot rapidly recombine because the recombination reaction is spin forbidden. Some alternative pathway, involving, for example, OH chemistry, sulfur chemistry, or chlorine chemistry, is required to restore CO$_2$ (see ref. 18), but none of these pathways are sufficient to draw above-cloud O$_2$ below 1 ppm (22). This mismatch between the extremely low observed O$_2$ levels above the clouds and the higher predicted levels is a well-known conundrum of Venus’s cloud layer chemistry. Our model provides a partial solution by predicting a reduced O$_2$ level above the clouds compared to the same model without NH$_3$ (Figs. 3 and 4).

**Model output H$_2$O and SO$_2$ abundance profiles are consistent with observations.** Our photochemistry model with NH$_3$ production is, together with the model it is based on (20), consistent with the observed H$_2$O and SO$_2$ abundance profiles in and above the clouds.

SO$_2$ and H$_2$O have been observed on many occasions by remote campaigns, orbiters, and in situ probes (reviewed in refs. 20 and 26). For example, the Visible and Infrared Thermal Imaging Spectrometer instrument on board Venus Express observed a mean abundance of H$_2$O and SO$_2$ below the clouds at 30 km to 40 km, to be ~30 ppm and ~150 ppm, respectively (57). The observed abundances of H$_2$O and SO$_2$ just below the clouds are consistent between remote, orbiter, and in situ observations (20). Recall, that the 5x excess SO$_2$ over H$_2$O should strip all the water out of the cloud layer, and hence remove all water above the clouds as well, a solution that is not consistent with observations. The Rimmer et al. (20) model uses cloud chemistry (NH$_3$ or mineral bases) to strip the SO$_2$ in the clouds. As a result, water remains in the clouds and above the clouds, which agrees with the remote, orbiter, and in situ observations of a few parts per million of H$_2$O above the cloud layers (reviewed in ref. 20).

Within the Venus cloud layers, there is substantial difference among measurements of water abundance in the clouds as summarized by ref. 20, which may represent varied local conditions.
Below the clouds, our photochemical model with NH₃ predicts the same H₂O abundance as models without NH₃, including previous models (e.g., ref. 43).

**NH₃ in the clouds and below the cloud layers is consistent with tentative observations.** NH₃ is a necessary input for our photochemistry model; indeed, the input of NH₃ is the core assumption of our hypothesis. We therefore discuss the tentative observations of NH₃ on Venus.

The Venera 8 descent probe reported the presence of NH₃ in the lower atmosphere of Venus. The estimated amounts from the signal are large and varied from 0.01 to 0.1%. (For further discussion on the validity of the Venera 8 NH₃ detection, see SI Appendix, section 6.) A recent reassessment of the Pioneer Venus LNMS has also provided suggestive evidence for the presence of NH₃ and its oxidation products in gas phase in the cloud decks of Venus (27).

The Venera 8 observations were largely discounted at the time because NH₃ is not likely to be present if Venus's atmosphere is in thermodynamic equilibrium (36). At least one author supported the plausibility of the presence of NH₃ in the cloud layers: Florensky et al. (50), in the late 1970s, argued that the upper parts of the Venus troposphere do not necessarily have to be in chemical equilibrium and could contain a number of minor chemical species, including NH₃ (45).

An additional argument against the plausibility of NH₃ is that an atmosphere containing sulfuric acid droplets cannot contain a significant amount of a free base; all of the base, in this case NH₃, would be sequestered in the droplets as ammonium ions. However, if the clouds have a pH of >10 and contain significant ammonium salts, then partial pressures of >1 ppm of free ammonia gas are expected over those droplets in the lower clouds (Materials and Methods and SI Appendix, section 5).

Our model provides a mechanism for the release of NH₃ below the clouds. As the droplets gravitationally settle out of the atmosphere to higher temperatures, the droplet evaporates, and NH₃ is released through the thermal decomposition of ammonium sulfate and ammonium sulfite. NH₃ is subsequently oxidized to NOₓ and N₂ (Fig. 2). We note that a NOₓ signal has been identified in the Pioneer Venus LNMS reanalyzed data (27).

**Mode 3 cloud particles.** Measurements by the Pioneer Venus and Venera Probes indicate that the Mode 3 particles might not be spherical, and that their composition differs from pure concentrated sulfuric acid. (See SI Appendix, section 3 for a brief discussion of the observational support for nonspherical particles.)

If NH₃ is the main neutralizing agent of the sulfuric acid cloud droplets, then the Mode 3 cloud particles in the lower clouds must be supersaturated in ammonium salts, with a small liquid phase, and therefore are not liquid droplets of concentrated sulfuric acid. Thus, the mechanism proposed here predicts that the Mode 3 particles in the lower cloud are solid or semisolid, and hence likely to be nonspherical.

Specifically, the Mode 3 (largest) cloud particles in the lower cloud must be 9.3 molar to 18.1 molar in ammonium salts in order to provide sufficient downward transport of SO₂ to produce the observed drop in SO₂ concentration across the clouds (Materials and Methods and SI Appendix, section 5). Such concentrations are not implausible if the Mode 3 particles in the cloud are actually a semisolid slurry of ammonium salts and sulfuric acid.

We note that presence of NH₃ creating nonspherical Mode 3 particles is consistent with the Mode 1 and/or Mode 2 particles being of quite different composition than the Mode 3 particles. If NH₃ production were the result of biological activity, then...
life could be confined to the larger Mode 3 particles, which have more volume. If NH$_3$ was produced by a nonbiological process, then it would be expected to apply to particles of all sizes, and not discriminate in favor of Mode 3 particles. However, the data on particle size and shape is consistent with Mode 1 and 2 particles being spherical (29).

Our model also explains the presence of the so-called stagnant haze layer below the cloud decks (30 km to 47 km altitude) (9). If the large Mode 3 particles are made of mostly solid ammonium sulfite and ammonium sulfate, then evaporation of any residual H$_2$SO$_4$ at the cloud base leaves dry solid particles. The subsequent thermal disproportionation of the remaining salts generates gas that shatters the particles at the cloud base (~100°C at ~47 km), and the fragmented particles form the haze. The haze that settles down and is not mixed back up into the clouds decomposes at ~200°C at the bottom of the stagnant haze layer at ~30 km (Fig. 2). The layered structure and the altitudes of the boundaries between the layers is therefore a natural consequence of the ammonia-based cloud chemistry. See also ref. 7 for a discussion of the composition of the haze layer.

H$_2$S below the clouds. We also note that our model predicts the presence of H$_2$S below the clouds (Figs. 2 and 3). The presence of H$_2$S is consistent with the tentative detection of H$_2$S below the clouds by the Venera 14 GC (24), which is the only in situ measured abundance value for H$_2$S. If NH$_3$ is present in the Venus atmosphere, H$_2$S is a result of disproportionation of NH$_4$HSO$_3$ that yields NH$_3$, H$_2$S, and H$_2$O to the atmosphere below the clouds, and hence is a unique output of our model. H$_2$S was also tentatively identified in the recent reanalysis of the Pioneer Venus LNMS data (27). H$_2$S, however, is a known volcanic gas on Earth so it is likely produced by volcanoes on Venus as well.

Discussion

Our model provides a view of the habitability of Venusian clouds. Concentrated sulfuric acid would make the Venusian cloud environment both chemically aggressive and extremely dry (7, 14). Our model removes the issue of extreme acidity for a subset of cloud particles from consideration.

Our model implies that the Mode 3 cloud particles cannot be all composed of concentrated H$_2$SO$_4$. Instead, there has to be a population of cloud particles that are less acidic and have a higher pH (between ~1 and 1) than concentrated sulfuric acid. Specifically, our model predicts that the Mode 3 cloud particles are semisolid ammonium sulfites and sulfates (Fig. 2) with a pH as high as one (Fig. 1). We emphasize that not all droplets need to contain semisolid ammonium sulfate and (if the NH$_3$ is made by life) ammonia-producing microorganisms.

Relevant to the Mode 3 cloud particles is a recent, independent finding that the Mode 3 cloud particle composition is not primarily sulfuric acid, but instead is consistent with some particles being ammonium hydrogen sulfate (NH$_4$HSO$_4$), as also model in refs. 20 and 34). Gray points with error bars are data from observations tabulated in ref. 20. (Top) O$_2$. Our model with NH$_3$ chemistry improves upon both the long-standing problem of presence and overabundance of O$_2$ in the upper atmosphere and the presence of O$_2$ in the cloud layers. (Middle) H$_2$O. Our model with NH$_3$ chemistry supports the presence of water vapor above the cloud layer (>80 km). (Bottom) SO$_2$. Our models with NH$_3$ chemistry (solid line) and without NH$_3$ chemistry but with arbitrary constraints on SO$_2$ (dashed line) both provide a fit to observed values throughout the atmosphere except for the top (>85 km). Key is that the model without NH$_3$ and without the SO$_2$ arbitrary removal rate (dotted line) fits the cloud layer data very poorly, whereas the model with NH$_3$ (with no arbitrary constraints; solid line) fits the data much better.
predicted in our analysis. Mogul et al. (58) base this finding on a reanalysis of the Pioneer Venus legacy data on the refractive index of the Venusian cloud droplets, independent of atmospheric chemistry. Also, independently from our work presented here, Mogul et al. (58) have described the potential for phototrophic synthesis of NH\textsubscript{3} to neutralize sulfuric acid cloud droplets, leading to the Mode 3 particle possibly containing NH\textsubscript{4}HSO\textsubscript{4}.

A pH of zero to one is within the range of environments known from Earth to be habitable and, in fact, to be inhabited. Life can grow in acid (pH = 0) aqueous environments (35), and microbial growth in solutions as acidic as a pH of -0.5 has been claimed (59). Furthermore, most of the Mode 3 particles have been detected at altitudes in the temperature range (60\textdegree C to 80\textdegree C), a range that overlaps with environments known to harbor thermophilic acidophiles on Earth (with life that can grow in temperatures up to 100\textdegree C; e.g., refs. 60–63).

Remarkably, examples of life on Earth secreting NH\textsubscript{3} to neutralize a droplet-sized acidic environment exist. Pathogens such as Mycobacterium tuberculosis and Candida albicans can neutralize the interior of phagosomes (acid-containing vesicles inside cells used for digestion of captured organic material) by secreting ammonia, thus evading destruction (64–66). Some plant pathogens also secrete ammonia to neutralize local pH in their target plant cells (67). By contrast, pond-dwelling acidophilic microorganisms adapt to low pH in other ways, because it is implausible for them to neutralize an entire river or pond.

Challenges to life in the Venus atmosphere remain. The extreme aridity of the Venus cloud environment has been well known for decades (e.g., ref. 68), having been often described (e.g., refs. 7, 14, and 34), and most recently reviewed in ref. 69, and remains a significant challenge to life as we know it. Our model predicts a water vapor abundance mixing ratio of 10\textsuperscript{-5} in the lower clouds, that is, a relative humidity of 0.02\% (depending on temperature). This is ~50-fold lower than the lowest water activity known to support life on Earth. (We note that terrestrial life can survive extremely hot and dry environments as spores or other inactive forms, as summarized in the legend to Fig. 2 and SI Appendix, section 10, but these are not actively growing, and to survive an ecosystem requires at least some cells or organisms to be actively growing.) The range of in-cloud water vapor abundance mixing ratios reported in the literature is very large (5 ppm to 0.2\%), as summarized by ref. 20, which may represent the presence of more element local conditions. All global models may therefore represent an average of extremely arid “desert” regions and much more humid “habitable” regions.

The extreme aridity is a reflection of the very low number density of hydrogen atoms in the Venusian atmosphere. The scarcity of H atoms argues against the presence of life. Terrestrial biochemicals are typically ~50% hydrogen by atom number (as illustrated by the database of natural products compiled by ref. 70; SI Appendix, section 9 and Table S5). However, much of the water in a bacterial cell is derived from reactions of the metabolites within the cell (71–73). For example, under active growth of Escherichia coli, up to 70% of the intracellular water is generated during metabolism and not transported across the membrane from the outside environment (71). If there is life on Venus, it is therefore likely to have substantially different biochemistry from Earth’s, and, if it is based on water as a solvent, it is likely to have very different strategies for water accumulation and retention to combat extreme aridity of the clouds. We note, however, that the lack of hydrogen is not just a challenge for the habitability of Venus’s clouds but also a challenge for making detectable amounts of any hydrogen-saturated gas-phase species, such as NH\textsubscript{3}, by any mechanism, abiotic or biological.

We note that additional challenges such as nutrient scarcity or high energy requirements are comparatively less limiting than aridity; for an in-depth discussion of the challenges to life in the Venusian clouds, see ref. 7.

An origin for life on Venus is an open question. If life exists in the Venus clouds, it may have originated on the Venus surface and migrated into the clouds. One model of Venus’s evolution to its modern state suggests that Venus had element surface conditions after formation, only to have entered the current greenhouse runaway after up to 3.5 billion years (74, 75). This model is dependent on a range of specific conditions but, if correct, suggests that Venus in the past had similar conditions to those under which life originated on Earth. If life emerged on the surface, terrestrial precedent suggests that some organisms would adapt to living some of the time in the clouds (reviewed in ref. 7). The microbial acid-neutralizing strategy provides a facile evolutionary path to Venusian cloud life. As the Venus surface became increasingly hot and uninhabitable, cloud dwelling would become a permanent lifestyle.

As the atmospheric chemistry changed to high acidity, the cloud-dwelling organisms would adapt by neutralizing their droplet habitats. A plausible evolutionary path is therefore suggested by the unique role of a droplet environment in the acid-neutralizing strategy, and the proposed history of Venus. We note, however, that, if life is the source of NH\textsubscript{3} on Venus, it very likely does not resemble the elemental ratios of life on Earth and likely has a different biochemistry than life on our planet, specifically adapted to the unique challenges of the Venusian cloud environment.

The Venus low D/H ratio (76) and the possible existence of felsic rocks which form in the presence of water (77–80) imply the presence of past Venus oceans, yet the debate on whether or not Venus ever had oceans continues. Recently, Turbet et al. (81) demonstrated, with a three-dimensional (3D) global climate model, that Venus may have been too hot early on for water oceans to form. Their climate model shows that the steam atmosphere of early Venus never condensed on the planet’s surface to form liquid water oceans. Instead, according to the model, water vapor condensed on the nightside of the planet to form clouds that warmed the surface by absorbing and reemitting the planet’s outgoing infrared radiation (81). However, Turbet et al. (81) do state that a comprehensive sensitivity study is needed to quantitatively confirm their result, as cloud and atmospheric circulation feedbacks can vary nonlinearly and nonmonotonically with rotation period. The newly selected VERITAS and EnVision missions, as well as DAVINCI’s instruments, should solidify or rule out the possibility of the past water-rich era of Venus, by a combination of D/H measurements and multispectral imaging of the tesserae regions for mineral compositions.

**Summary and Critical Future Measurements**

Our hypothesis of locally produced NH\textsubscript{3} in the Venus clouds explains a number of anomalies in the atmosphere and clouds of Venus. Our photochemical model of the consequences of NH\textsubscript{3} production explains the SO\textsubscript{2} depletion in the clouds and vertical abundance profile of H\textsubscript{2}O, building on the work of ref. 20, explains the presence of O\textsubscript{3} in the clouds, supports the in situ detection of H\textsubscript{2}S below the clouds, and explains the nonspherical nature of Mode 3 particles. While the presence of other mineral bases could contribute, none of them can explain the parts per million levels of O\textsubscript{3} in the clouds or the tentative presence of NH\textsubscript{3}. No definitive source for NH\textsubscript{3} has been identified; in chemical terms, biological production is the most plausible, but the concept of life in the clouds of Venus remains controversial. Many of the in situ observations should be repeated...
for confirmation, and more model work is needed to fully resolve the vertical abundance profiles of relevant gases.

We must be careful not to fall for a conjunction fallacy. While life may explain the combined anomalies with some external assumptions, there may yet be a chemical explanation for each individual anomaly.

An in situ Venus probe can support or refute our proposed view of Venus as an inhabited planet with the following measurements.

Gases.

- Establish the existence of NH\textsubscript{3} and O\textsubscript{2} in the cloud layers.
- Measure the amounts of NO\textsubscript{x} to establish which NH\textsubscript{3}-destruction pathway dominates.
- Determine the specific altitude-dependent abundance profiles of H\textsubscript{2}O, SO\textsubscript{2}, and H\textsubscript{2}S, ideally with day and night measurements to inform chemistry sources and sinks.

Cloud Particles.

- Confirm the nonspherical, semisolid nature of Mode 3 cloud particles and identify them as ammonia salts.
- Measure the pH of cloud particles, especially Mode 3 cloud particles.
- Detect organic molecules in cloud particles; if found exclusively in the larger particles, this would be an indicator of life.

Search for Life.

- Analyze a large number of individual cloud particles, especially Mode 3, for morphological and chemical signs of life.

In the meantime, a public release of original data from the Russian Venera and Vega missions could enable further support or refutation of current models and predictions, and would provide needed context for future mission results.

We have presented an initial analysis of several sources for the NH\textsubscript{3} on Venus. We have argued that biological production may be a potential source of both NH\textsubscript{3} and O\textsubscript{2} that we have identified that meets the quantitative requirements for NH\textsubscript{3} production. Although the biomass required to make NH\textsubscript{3} and O\textsubscript{2} at the required rate is not unrealistic, at 0.05% of the total biomass on Earth and ~1.5% of the total Venusian cloud mass, life in the clouds of Venus has been considered implausible because of very high acidity, very low water activity, and scarcity of hydrogen atoms. By predicting a Mode 3 particle pH of -1 to 1 due to neutralizing NH\textsubscript{3}, our work implies both that Venus clouds are more habitable than previously thought and, by the requirement of locally produced NH\textsubscript{3}, that clouds may be inhabited. We hope our work will encourage further studies into habitability and astrobiological potential of Venusian clouds.

Materials and Methods

Photochemical Model. The details of the model are provided in SI Appendix, section 4. In summary, we employ a 1D Lagrangian photochemistry/diffusion code that follows a single parcel as it moves from the bottom to the top of the atmosphere. The temperature, pressure, and actinic UV flux are prescribed at each altitude in the atmosphere (20).

Calculation of Flux of Ammonia. We calculate the flux of ammonia necessary to maintain the observed gradient of SO\textsubscript{2} through the clouds following the method of Rimmer et al. (20). The goal is to explain the removal of nearly all of 3.5 \times 10^{15} m\textsuperscript{-2} of SO\textsubscript{2} (1.5 \times 10\textsuperscript{-4} bar at 300-K level of the atmosphere) that should be present from upward mixing from volcanic sources and recycled SO\textsubscript{2}. The time taken for SO\textsubscript{2} to mix through the region 45 km to 65 km is calculated using Lee et al.’s (82) equation 7,

\[
\text{Time} = \frac{2 H^2 \Delta h}{K_{zz}} \approx 2.6 \times 10^8 \text{ s} \approx 8.25 \text{ Earth years.}
\]

In other words, SO\textsubscript{2} will be replenished in the atmospheric cloud layers in 8.25 Earth years, and this is the timescale that the presence of NH\textsubscript{3} needs to remove SO\textsubscript{2}. The atmospheric scale height H = 6.5 \times 10\textsuperscript{3} cm is the average scale height in the atmospheric cloud layers, \(\Delta h = 2 \times 10\textsuperscript{3} \text{ cm}\) is the distance between 45 and 65 km, and \(K_{zz} = 10^8 \text{ cm}^2 \text{s}^{-1}\) is the eddy diffusion coefficient throughout the atmospheric cloud layers. The flux (per square centimeter per second) of SO\textsubscript{2} into the clouds is therefore given by

\[
\phi = \frac{\text{Amount} \cdot \text{Distance}}{\text{Time} \cdot \text{Area}} = \frac{3 \times 10^{-5} \text{ cm}^2}{2 \times 10^{-8} \text{ s}} = 270 \text{ cm s}^{-1}.
\]

Recall that there is a one-to-one molar ratio for NH\textsubscript{3} to remove SO\textsubscript{2}. Given the mass of NH\textsubscript{3}, the flux rate above is equivalent of 1.1 \times 10\textsuperscript{11} tonnes per year of NH\textsubscript{3}.

Calculation of Concentration of NH\textsubscript{3} in Particles. The concentration of salts in the cloud droplets can be estimated from the concentration necessary to provide the flux of NH\textsubscript{3} as calculated above. The necessary flux of NH\textsubscript{3} is dependent on the size of the particles, and hence the particles’ rate of fall. For a given particle size, we can calculate the rate of fall, and hence the volume of cloud material removed per second, and, from this, the concentration of salts in that volume needed to provide the flux calculated above. See SI Appendix, section 2 for the details on the calculation of the concentration of ammonium salts in the lower cloud particles.

Calculation of Concentration of Gaseous NH\textsubscript{3} over Droplets. The concentration of gaseous NH\textsubscript{3} over an acid droplet containing dissolved NH\textsubscript{4}\textsuperscript{+} is calculated as follows. The fraction of total N species that is present as NH\textsubscript{3} and as NH\textsubscript{4}\textsuperscript{+} is calculated using Lee et al. (82) equation 7, and the eddy diffusion coefficient throughout the atmospheric cloud layers. The flux (per square centimeter per second) of SO\textsubscript{2} into the clouds is therefore given by

\[
\phi = \frac{\text{Amount} \cdot \text{Distance}}{\text{Time} \cdot \text{Area}} = \frac{3 \times 10^{-5} \text{ cm}^2}{2 \times 10^{-8} \text{ s}} = 270 \text{ cm s}^{-1}.
\]

Recall that there is a one-to-one molar ratio for NH\textsubscript{3} to remove SO\textsubscript{2}. Given the mass of NH\textsubscript{3}, the flux rate above is equivalent of 1.1 \times 10\textsuperscript{11} tonnes per year of NH\textsubscript{3}.

Data Availability. Previously published data were used for this work (20). All other study data are included in the article and/or SI Appendix.

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