

VENUS CLOUD COMPOSITION SUGGESTED FROM THE PIONEER VENUS LARGE PROBE NEUTRAL MASS SPECTROMETER DATA. M. Yu. Zolotov¹, R. Mogul², S. S. Limaye³, M. J. Way^{4,5} and J. B. Garvin⁶, ¹School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, e-mail: zolotov@asu.edu. ²Chemistry & Biochemistry Department, California State Polytechnic University, Pomona, CA. ³Space Science & Engineering Center, University of Wisconsin, Madison, WI. ⁴NASA Goddard Institute for Space Studies, 2880 Broadway, New York, NY. ⁵Theoretica Astrophysics, Department of Physics and Astronomy, Uppsala University, Uppsala, SE-75120, Sweden. ⁶NASA Goddard Space Flight Center, Greenbelt, Maryland 20771.

Hypothesis: We propose that a non-pure H₂SO₄ cloud composition is suggested by mass spectra obtained by the Pioneer Venus Large Probe Neutral Mass Spectrometer (LNMS) below clouds. The LNMS data show spikes, or temporary increases, in the ion counts at several mass positions from the cloud deck to the surface. We posit that these spikes represent chemical species that arise from captured particles that were degraded throughout the descent through thermal sublimation, decomposition, and reactivity.

Rationale: Liquid sulfuric acid is the only firmly detected aerosol component in the main cloud layer (~47–65 km) of Venus [1-3]. It is unclear if non-S solutes are present in the H₂SO₄-rich aerosol droplets and if grains are present within the H₂SO₄ aerosols or as individual particles. Polysulfur (S_x) grains could compose 7–10 wt% of the aerosol based on the Vega gas nephelometry, particle size spectrometry and chromatography [2,3], but have yet to be confirmed. The presence of Cl-bearing species in captured aerosols is inferred from Venera 12 and Vega 1/2 mass and X-ray fluorescent spectrometry, while reported bulk Fe and P contents are questionable [2,3]. Nevertheless, both dissolved and granular non-H₂SO₄ species are expected in the clouds that could contain materials from above and below. Here we discuss sources, composition, and fate of non-H₂SO₄ species in and below clouds in the context of the LNMS data.

The Large Probe Descent: The atmosphere was sampled by the LNMS through an inlet assembly that protruded outside the supposed Probe's boundary gas layer (~1 cm). Particles could have been captured within the inlet openings and on the inlet surfaces. The LNMS inlet assembly included a heating element to prevent the condensation of volatile species such as H₂SO₄ near the inlet surfaces (per review of archived PV documentation at NASA ARC by M. Way). Nevertheless, the LNMS inlets became clogged by cloud particles at ~50 km – as evidenced by the significant though temporary decrease in atmospheric CO₂ intake at ~50–25 km [4,5]. These observations suggest a presence of cloud-sourced particles, which are less volatile than liquid H₂SO₄ and could not be removed by heating of the LNMS inlet. Accordingly, we are focused on correlating the mass spikes at <47 km with the thermal and chemical stabilities of candidate non-H₂SO₄ compounds.

PVLP Mass Spectra: Our review of the LNMS spectra reveals spikes during the main clog (~50–25 km) and at <22 km (Fig 1). At ~40–30 km, spikes are seen for SO₂⁺ (*m/z* 64), SO⁺ (*m/z* 48), S⁺ (*m/z* 32), and H₂O⁺ (*m/z* 18). In [5], these observations were interpreted as signatures for H₂SO₄ aerosols that clogged the inlets and thermally degraded. Below ~20 km, we reveal additional spikes at several mass positions. We observe no spikes for internal standards in the data (at *m/z* 1, 15, 16, 28, 40, and 136), nor any anomalous behaviors in

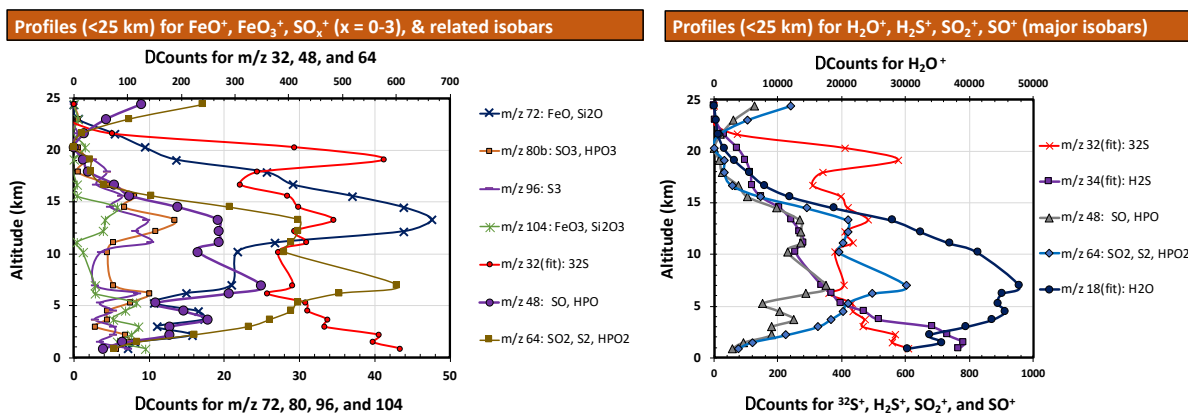


Fig. 1. Altitude profiles for mass positions of potential H, C, O, Si, S, P, and Fe species (Δ counts were calculated using counts at 24.4 km as the reference; 20.3 km was used for SO₂⁺ and SO⁺).

the peak shapes, ionization yields, and/or fragmentation patterns. Hence, the observed data spikes may not be due to noise or failures in the mass analyzer. Rather, the data spikes could represent an influx of compounds arising from the degradation of captured particles.

Sources of Non-H₂SO₄ Cloud Materials: The flux of interplanetary material on Earth and Venus ($\sim 3 \times 10^4$ kg/day) mainly consists of dust from Jupiter Family comets (JFC) and Halley Type/Oort cloud comets [6,7]. This implies the dominance of C > Si, Mg, Fe, and S followed by Na, Ca, Al, and Ni (H, N, and O are not listed) [8,9]. Cometary dust is dominated by Mg silicates, FeS, Fe-Ni metal, and organic matter (~ 30 – 60 wt%) [8,9], though some JFCs contain C-less chondritic solids thermally processed in the inner solar system [10]. Delivery of air-born sub- μ m surface grains [e.g., 11,12] via the global [13] circulation is less certain but not excluded. Endogenic grains could consist of basaltic glass, Ca-Mg-Fe pyroxene, Ca-rich plagioclase, Mg-Fe pyroxene, Mg-Fe olivine, Fe sulfides, and magnetite. Granular products of chemical weathering could include silica, Ca sulfate, Mg pyroxene, magnetite, hematite, pyrite, Na-rich plagioclase, and Al-rich silicates [14].

Fate of Cloud Materials: Mass flux [6] into Venus' atmosphere reaches the H₂SO₄ aerosol mass ($\sim 3.3 \times 10^{13}$ kg [15]) in ~ 3 Ma. The geologically short residence times of space materials implies their net sink toward the surface in the present epoch since the global volcanic resurfacing ~ 0.3 – 1 Ga. Although many cosmic compounds (silicates, Fe-Ni, sulfides) dissolve in the acidic aerosol, alteration products could include temporarily suspended grains of S₈ [16,17], silica, Fe(III) sulfate [c.f., 2,7,16], Fe(III) chloride [e.g., 2,17], Al chloride [2], and insoluble organic matter (IOM). At the cloud deck, grains of opal, metal (Fe(III) [17], Mg, Ca, Na, Al, and Ni) sulfates and chlorides, and a silica alumina gel (and/or Al-rich opal) could form via evaporation of the H₂SO₄ aerosol droplets. The particle flux towards the surface could yield sub-cloud (47–30 km) and deep (<20 km) hazes and affect surface composition [18]. Sunk particles are subjected to dehydration (salts, opal, Al-rich opal), decomposition (Fe(III) sulfate \rightarrow Fe₂O₃ + SO₃; IOM \rightarrow C-H-O-N-S gases + graphite), and reactions with air gases [14, 18].

Particles could have entered the LNMS inlet in the clouds, dense hazes at 47–30 km, and low-density hazes below 20 km. Some solids could have entered the MS after evaporation of liquid sulfuric acid in the inlet.

Candidate Cloud Species Based on the PVLV Data: Interpretation of mass count profiles (Fig. 1) will require experimental and numerical models for thermal and chemical degradation of candidate particles. Here are our initial suggestions about origins of inferred

profiles. H₂O (m/z 18) is the likely product of dehydration and fragmentation of salts (mostly sulfates and chlorides of Fe and Mg), opal, and less abundant Al-rich opal. Mass counts (m/z 72, 104) could be fragmentation products of SiO₂-rich (opal, Al-rich opal) and ferric (sulfates, oxides, and chlorides) grains. The mass counts (m/z 32, 34, 48, 64, 80, 96) suggest the presence of S, H₂S, SO, S₂, SO₂, SO₃, and S₃. These counts could reflect decomposition and fragmentation of captured particles of S₈, sulfates, and IOM. A correlation of mass counts 80, 72 and 104 (SO₃, FeO, FeO₃) suggests decomposition of Fe(III) sulfate that is chemically [18] and thermally unstable. A correlation of mass counts 48 (SO) and 64 (SO₂, S₂) suggests a common S source. SO and S are likely fragmentation products of S-bearing species. S₃ could be dissociation and fragmentation product of higher S allotropes. H₂S is the known product of IOM pyrolysis [19] and could form via reduction of S-bearing species by C-H (e.g., CH₄) and/or H₂ gases released from heated IOM.

Summary: The PVLV mass spectra suggest a presence of Si-, Fe-, and S-bearing particles in clouds and hazes, consistent with a geologically short residence time of cometary dust in the clouds. Cloud aerosols could be saturated with respect to space materials that are dissolved in the H₂SO₄ aerosol and altered to SiO₂-rich, sulfate, chloride, insoluble organic, and Si-Al-O-rich particles that are suspended in clouds/hazes and sink toward the surface. This work will help preparation of the DAVINCI mission [20] because cloud grains could affect planned mass spectrometric measurements.

References: [1] Esposito L. W. et al. (1997) In *Venus II*, ed. by S. W. Bougher et al., Univ. of Arizona Press, Tucson, 415–458. [2] Krasnopolsky V. A. (1989) *Icarus*, 80, 202–210. [3] Titov D. V. et al. (2018) *Space Sci. Rev.*, 214, 126. [4] Mogul R. et al. (2023) *Icarus*, 392, 115374. [5] Hoffman J. H. et al. (1980) *JGR*, 85, 7882–7890. [6] Carrillo-Sánchez J. D. et al. (2020) *Icarus*, 335, 113395. [7] Frankland V. L. et al. (2017) *Icarus*, 296, 150–162. [8] Jessberger E. K. et al. (1988) *Nature*, 332, 691–695. [9] Bardyn A. et al. (2017) *MNRAS*, 469, S717–S722. [10] Zolensky M. E. et al. (2006) *Science*, 314, 1735–1739. [11] Kreslavsky M. and Bonderenko N. (2017) *Aeolian Res.*, 26, 29–46. [12] Lefévre M. (2022) *Icarus*, 387, 115167. [13] Lee C. et al. (2010) *Icarus*, 206, 662–668. [14] Zolotov M. Yu. (2018) *Rev. Miner. Geochem.*, 81, 351–392. [15] Dai L. et al. (2022) *JGR Planets*, 127, e2021JE007060. [16] Young A. T. (1983) *Icarus*, 56, [17] Krasnopolsky V. A. (1985) *Planet. Space Sci.*, 33, 109–117. [18] Zolotov M. Yu. (2021) *LPS LII*, Abstract #2615. [19] Mimura K. et al. (2020) *Geochem. J.*, 54, 255–265. [20] Garvin J. B. et al. (2022) *Planet. Sci. J.*, 3, 117.