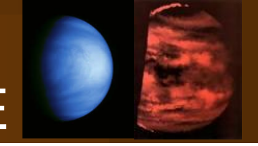
AN AEROSOL INSTRUMENT PACKAGE FOR CHARACTERIZING THE VENUS CLOUD HABITABILITY ZONE



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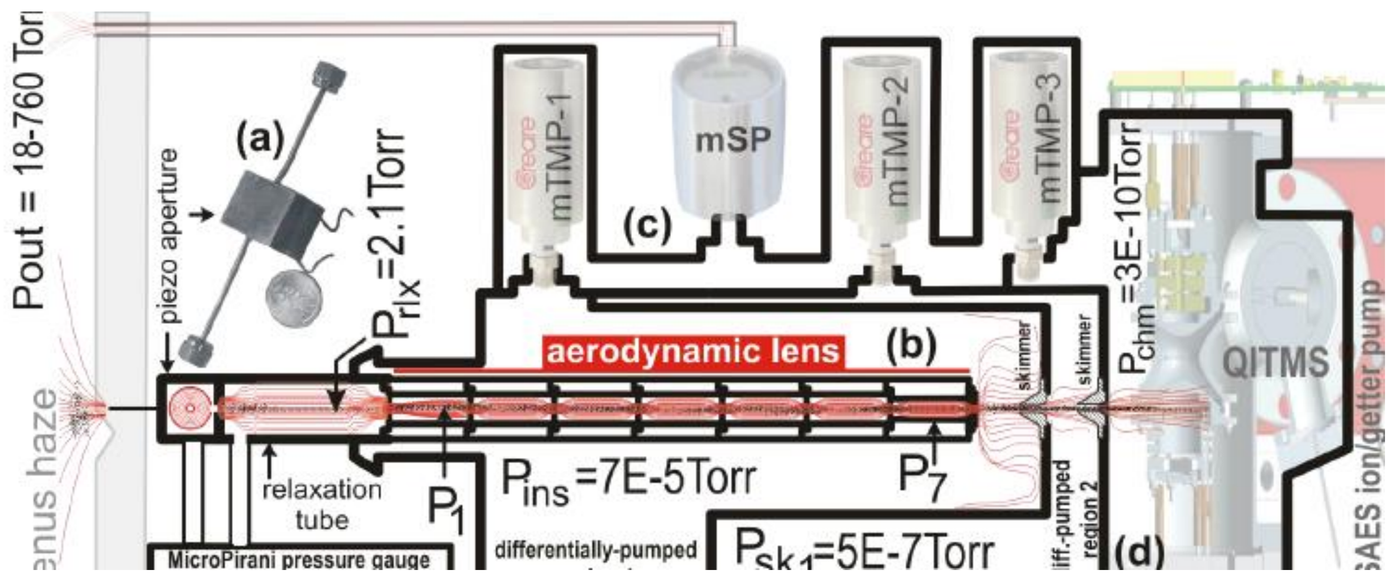
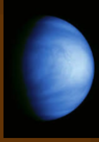
[4] Space Science and Engineering Center, U. of Wisconsin- Madison



The Venera-D Landing Sites and Cloud Habitability Workshop,
The Space Research Institute (IKI), Moscow, October 5, 2019

AN AEROSOL INSTRUMENT PACKAGE FOR CHARACTERIZING THE VENUS CLOUD HABITABILITY ZONE



Agenda-

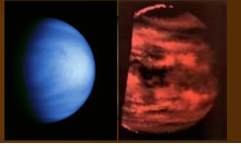
- Motivation: Cloud/Aerosol Characterization
  - Composition – Including particle interiors
  - Particle Size/Distribution/Concentration
  - Particle Type Characterization (Refractory vs Condensates; Spherical vs Fractal)

- Current Instrument Design/Capabilities
  - 2 Components, in integrated single-pathway system
    - The same particles are measured by both components
    - Proximal (few cm away) gas-only sample measured as well

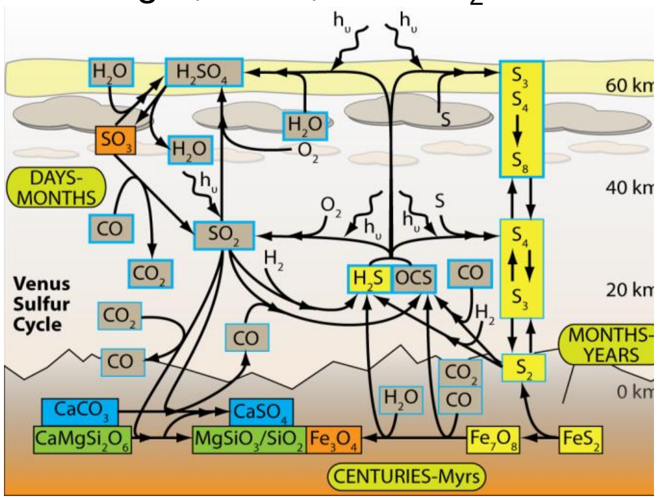
  - Component A: JPL Venus Aerosol Mass Spectrometer (**VAMS**): Composition, including isotopic distributions

  - Component B: CNES-CNRS/LPC2E **LONSCAPE** Nephelometer: Particle size, distribution, scattering phase function; Particle type

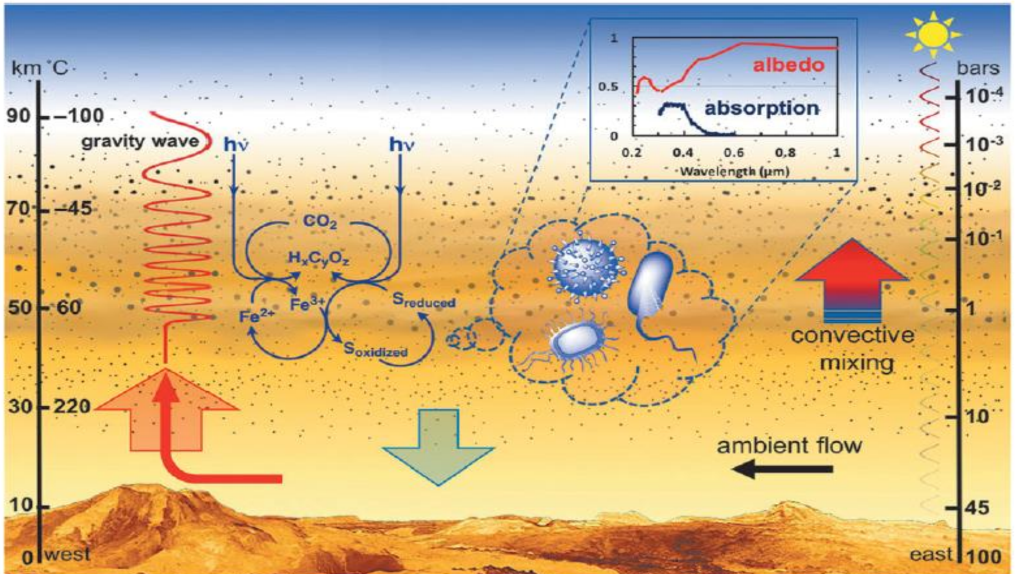
Understanding Venusian Aerosols: Sulfur Cycle, Radiative Balance, Meteorology, and Potentially, Life



- **H_2SO_4 Aerosols: Key to Venus's Clouds, Radiative Balance, Meteorology, and Circulation**
- **<u>Sulfur-Cycle</u>** H_2SO_4 clouds highly variable: Depend on amounts of UV light, water, and SO_2 .
  - $H_2O + SO_3$ (from SO_2, UV photolysis) => H_2SO_4
  - UV light depends on time of day
  - Variable water at cloud base (Tsang *et al*, 2010)
  - SO_2 : Expected to vary by > 200% over a few km of altitude
  - Variable H_2SO_4-H_2O acidity predicted with altitude/temperature
  - Additional variations due to vertical dynamics and advection
  - Sink and source of sulfuric species



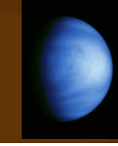
- **<u>UV-Absorbing Patchy Haze Layer of Particular Interest:</u>**
  - **Unknown Composition => Perhaps complex chemistry, Life?**
  - Significant Effect on Radiative Balance and Thermal Structure



<u>Life in the Clouds</u>? (Limaye et al, 2017):
<u>Micro-organism Survival mechanisms</u>:
- Energy: iron/sulfur oxidation via fixated CO_2
- Gravity waves, convection locally counter precipitation

Limaye et al., 2017, *Astrobiology* 18, DOI 10.1089/ast.2017.1783

In-Situ Platforms: Atmospheric Instruments and Measurement Objectives

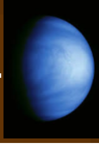



Instruments	Abbreviation	Measurement Type/Objectives
ATMOSPHERIC GAS COMPOSITION		
Mass Spectrometer	MS or GCMS	Atmospheric species including noble gases and their isotopes. Survey instrument
Tunable Diode Laser Spectrometer	TDL	Trace species including isotopic abundances. Targeted on a few species
UV/IR Spectrometer	UVS, IRS	Atmospheric species from their spectal signatures. Survey instrument
Chemical Sensors (MEMS based)	ChemSens	Chemical species. Small low power instrument targeted on a few species
CLOUD AND HAZE PARTICLES		
Nephelometer	Neph	Size, scattering properties and abundance of cloud and haze particles in bulk
Light Optical Amospheric Counter	LOAC	Size, scattering properties and abundance of cloud and haze particles individual
Imaging Microscope	Mic	Images larger cloud particles captured on a filter.
Aerosol Mass Spectrometer	AMS	Chemical composition or biological nature of aerosols (individual or bulk)
ATMOSPHERIC STRUCTURE		
Atmospheric Structure Instrument	ASI	Temperature, pressure and vertical wind speed.
Net Flux Radiometer	NFR	Upward and downward flux of radiation in multiple spectral bands
Ultra Stable Oscillator	USO	Wind velocity from Doppler signatures from DSN and orbit

Instrument Package covers

From “Aerial Platforms for the Scientific Exploration of Venus”, October, 2018

THE JPL VENUS AEROSOL MASS SPECTROMETER (VAMS) CONCEPT



VAMS Measurement Objectives:

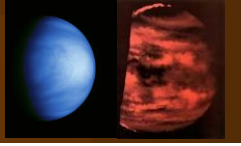
I. Composition of UV/blue-absorbing aerosols, currently thought to be present throughout the clouds from ~ 70 to 48 km altitude (Krasnopolsky, 2017 ; Limaye et al., 2018)

- S_3, S_4, S_8 perhaps from OCS photochemistry at ~55-60 km altitude (Toon et al, 1982; Krasnopolsky, 2016)
- Iron Chloride ($FeCl_3$; Zasova et al., 1981; Krasnopolsky, 2017)
- Hydrobromic acid (HBr; Sill, 1975; Kasnopolsky, 2017).
- Daughter products of HCl, HF, HBr-H_2SO_4 aqueous chemistry (Baines and Delitsky, 2013; Delitsky and Baines, 2015, 2018)
- Croconic Acid ($C_5O_5H_2$; Hartley et al., 1989)
- Biological Sources (e.g., Morowitz and Sagan, 1967; Schulze-Makuch and Irwin, 2006; Limaye et al., 2018)

II. Composition of Major Cloud

- H_2SO_4-H_2O weight percent over altitude
- H_2SO_4, with admixtures of HCl, HF, HBr, etc: ~2 ppb HCl/H_2SO_4 at 55 km altitude
- Other contaminants
- Biological Sources

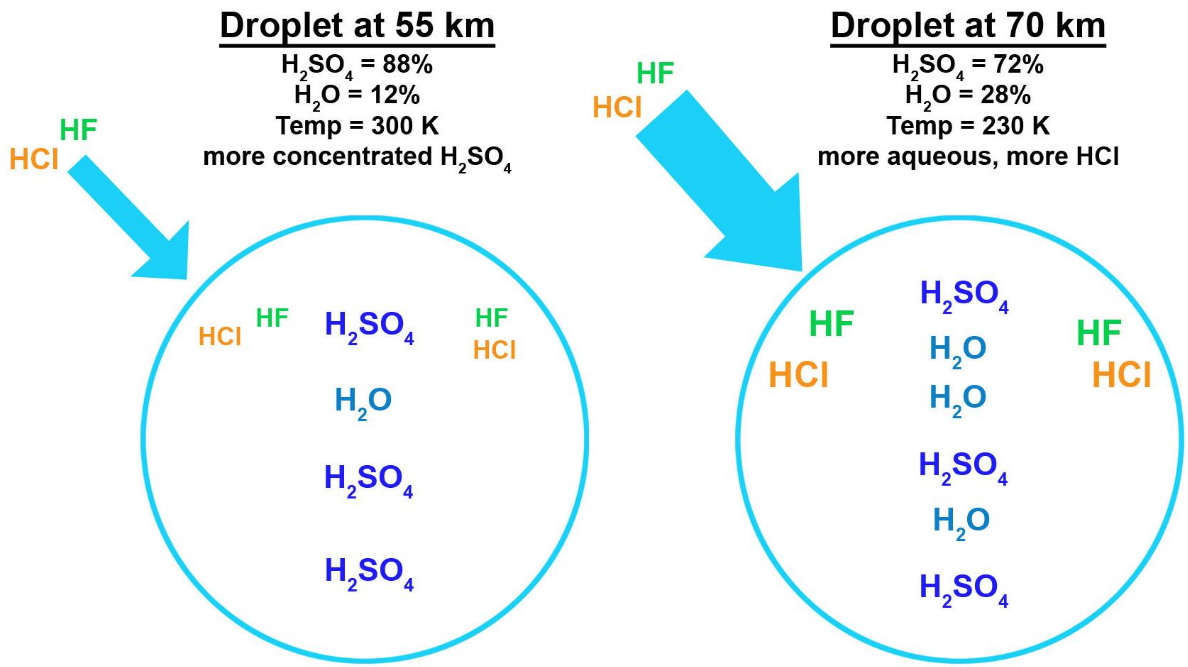
Aqueous Chemistry in Sulfuric Acid Clouds



Three + Steps:

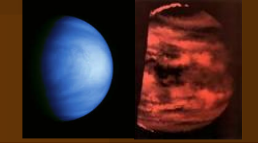
1. Uptake of HF, HCl (and HBr) molecules into H_2SO_4-nH_2O particles
2. Buildup toward the Henry's Law saturation amount
3. Chemical conversion of trace gases into complex molecules
   - Continued buildup toward saturation, continued chemical conversion

Uptake:



Delitsky and Baines, 2018

Formation of Sulfonic Acids and Daughter Products in Sulfuric Acid Clouds



Formation of Sulfonic Acids

H_2SO_4 + HCl $ClSO_3H$

H_2SO_4 + HF FSO_3H

H_2SO_4 + HBr $BrSO_3H$

$H_2O + CO_2$ H_2CO_3

$H_2SO_4 + SO_3$ $H_2S_2O_7$

$H_2SO_4 + H_2O$ $H_2SO_4 .nH_2O$

Formation of Daughter Products of Sulfonic Acids

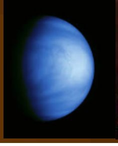
$ClSO_3H \rightarrow SO_2Cl_2 + SOCl_2$

$FSO_3H \rightarrow SO_2F_2 + SOF_4$

Chemical reactions involving HCl, HF and Br with H_2SO_4 in aerosol particles create more complex molecules.

Additional complex chemistry occurs Within H_2SO_4 aerosols once sulfonic acids are formed

Delitsky and Baines, 2018




Predicted Saturated Abundance of HCl/H_2SO_4 inside H_2SO_4 Aerosol Particles in Venus

Altitude (km)	C (wt%)	T (K)	Pressure (mbar)	HCl/H_2SO_4 Abundance (ppb)	Required Measurement Capability for 20% Accuracy (ppb)	H_2SO_4 Aerosol Mass (mg/cm3)
70	72.8	216	25.1	87217.8	17443.6	7.94E-07
69	73.7	221	30.2	37738.0	7547.6	8.91E-07
68	74.1	224	36.3	26153.5	5230.7	1.00E-06
67	74.6	227	42.7	18000.2	3600.0	1.12E-06
66	75.0	232	52.5	10644.6	2128.9	1.26E-06
65	75.3	238	66.1	6207.4	1241.5	1.41E-06
64	76.1	243	79.4	3176.7	635.33	1.58E-06
63	76.9	245	95.5	2194.5	438.89	1.78E-06
62	78.4	247	120.2	1152.1	230.42	2.00E-06
61	79.0	249	151.36	919.33	183.87	2.24E-06
60	**79.7**	**251**	**177.83**	**655.80**	**131.16**	**3.16E-06**
59	79.0	254	220	870.17	174.03	2.51E-06
58	81.0	265	250	164.50	32.901	1.58E-06
57	83.2	272	300	43.250	8.6499	2.51E-06
56	85.5	280	340	9.9342	1.9868	3.16E-06
55	**88.0**	**290**	**410**	**2.0517**	**0.4103**	**2.00E-05**
54	90.0	300	490	0.5619	0.1124	2.00E-05
53	92.0	312	580	0.1464	0.0293	2.00E-05
52	94.0	325	690	0.0393	0.0079	2.00E-05
51	96.0	334	800	0.0127	0.0025	1.58E-06
50	**97.0**	**342**	**970**	**0.0047**	**0.0009**	**1.00E-05**

Measurement Goal: 2 ppb in 300 second integration

Estimated Abundances of Other Potential Species in H_2SO_4 Particles to Explain UV Absorption:

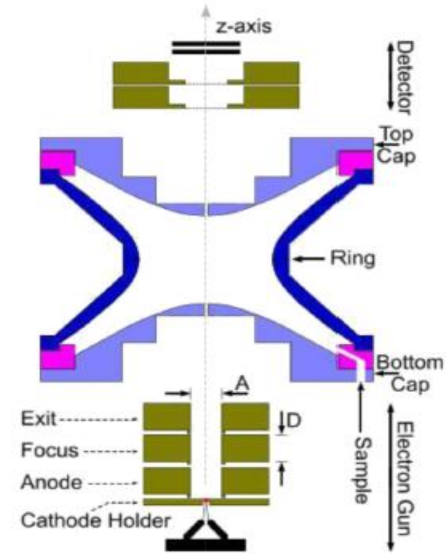
$FeCl_3/H_2SO_4$: ~1% (Zasova et al, 1981; Krasnopolsky, 2017)

HBr/H_2SO_4: ~ 3 x HCl/H_2SO_4 (1.2 ppb in atmosphere vs 400 ppb for HCl, Krasnopolsky, 2017, with H* ~ 10^3 greater)

Delitsky and Baines, 2018

JPL AMS Measurement Technique

QITMS – Quadrupole Ion Trap Mass Spectrometer (Madzunkov and Nikolić, 2014) - fed by aerosols injected through an Aerodynamic Lens system that separates aerosols from atmospheric gases.



- Atmospheric sample is sequentially expanded through orifices from high-pressure segments of aerodynamic lens into progressively lower pressure segments.
- Gases expanded away, while much heavier aerosols remain collimated on the jet axis
- Jet of aerosols mixed with rarified gas phase is introduced into the QITMS, striking heated electrodes (~ 350 C) and vaporizing upon impact.
- Aerosol-produced vapor is analyzed to determine aerosol composition

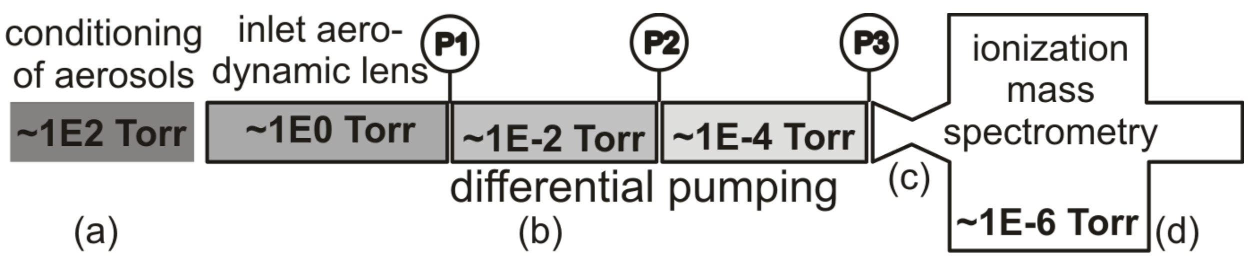
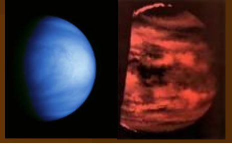


Diagram of aerosol mass spectrometer (AMS) with typical downstream operating pressures. Three turbomolecular pumps (P1-P3) evacuate the particle inlet and three chambers, where P1 can be either a turbomolecular or a mechanical pump.

JPL VAMS Measurement Capabilities



QITMS – Quadrupole Ion Trap Mass Spectrometer - fed by aerosols injected through an Aerodynamic Lens system that separates aerosols from atmospheric gases.

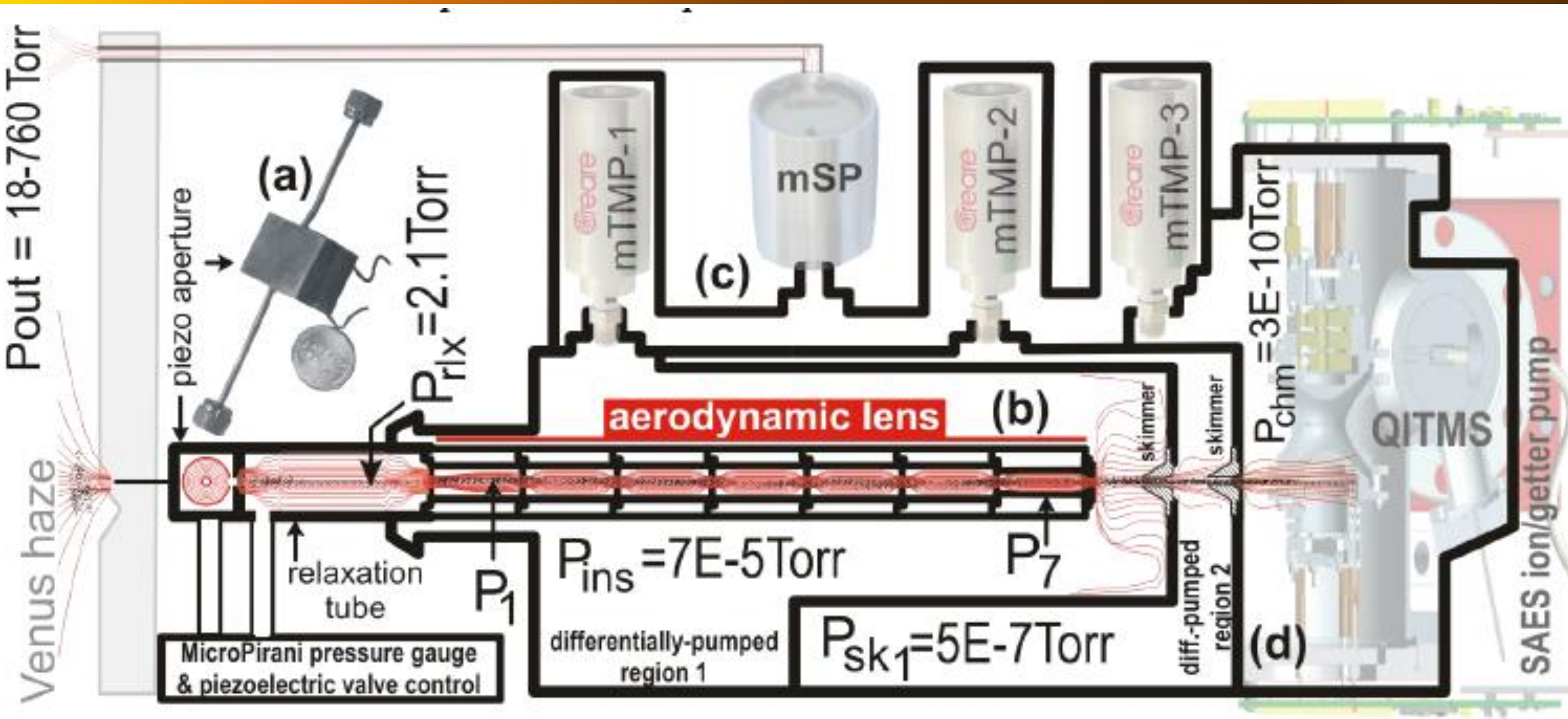
Goal: HCl/H_2SO_4 abundances: 2 ppb measured to 10% accuracy in 300s at 55 km with H_2SO_4 atmospheric aerosol mass density of 20 mg/m^3 (per Knollenberg and Hunten, 1980)

1-150 amu: Covers 48% of S_8 fragments, 97% of amino acid fragments (With 1 MHz RF frequency, amplitude 1.5 kV; Possible to extend to 300 amu with 4 times higher voltage)

Multiplexing Mass Spectrometer: 16,385 channels measured simultaneously => 0.01 amu resolution in high-amu-sensitivity mode (e.g. for isotopes) in 50 ms samples (20 complete spectra per second)

- Channels can be binned to 16 for improved S/N for bulk constituent measurements: ~0.15 amu resolution

THE JPL VENUS AEROSOL MASS SPECTROMETER CONCEPT

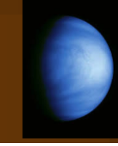


<u>Schematic diagram</u>: Proposed lightweight Aerosol Separator (thick line envelope) in tandem with the QITMS aerosol chemical composition analyzer. Red flow lines and black dots represent, respectively, gas streamlines and suspended aerosol particles. Adjustable piezoelectric aperture ensures relaxation tube is kept at P_{rlx}=2.1 Torr over Venusian pressures of 19 to 760 torr, corresponding to a Venus altitude range of 70-50-km.

<u>Aerodynamic Lens</u>: Based on nanojet technology; Presently Schreiner type; 7 step-down sections; 10.7-cm long; Collaboration with Integrated Deposition Solutions, Inc (IDS).

Goal: Entire VAMS Component < 9 kg; < 40 W peak power (with heater, 30 W nominal). Adding on reactive gas and noble gas modes: Additional ~2 kg,Total: < 11kg))

THE LONSCAPE/LOAC CONCEPT



Potential for combining with CNES-CNRS/LPC2E LONSCAPE Nephelometer/ LOAC Aerosol Counter Concept

- LONSCAPE: Light Optical Nephelometer Sizer and Counter for Aerosols in Planetary Environments

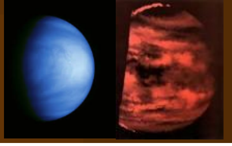
  Next Generation Version of LOAC: Light Optical Aerosol Counter

Combined with the JPL Aerosol Mass Spectrometer Concept, would create essentially a complete Aerosol Instrument Package that measures:

- Particle size distribution/concentration, scattering properties
- Particle phase functions
- Particle composition (via both direct sampling and particle phase function information)

LONSCAPE presented in paper under review at Space Science Reviews:

Renard, J.-B., Mousis, O., Rannou, P., Levasseur-Regourd, A.-C., Berthet, G., Geffrin, J.-M., Hadamcik, E., Verdier, N., and Millet, A.-L., Daugeron, D. (2020). Counting and phase function measurements to determine the physical properties of the aerosols in the ice giant atmospheres (LONSCAPE instrument). *Space Sci. Rev.,* Submitted.



LONSCAPE Nephelometer
- Measures 11 angles
- 20 – 170° phase angle every 15°
- Should be able to measure
  - ~ 300 particles/cm³ for small (~0.2 µm) particles
  - 0.2 – 10 µm particles

Use Laser and 11 photodiodes
~ 10.0 x 5.5 x 3.0 cm³

- Would be positioned in front of the VAMS Aerosol Separator in the airflow.
  - LONSCAPE first measures particles size/shape and cattering characteristic
  - VAMS then directly samples their composition, up to 150 AMU, including isotopic information

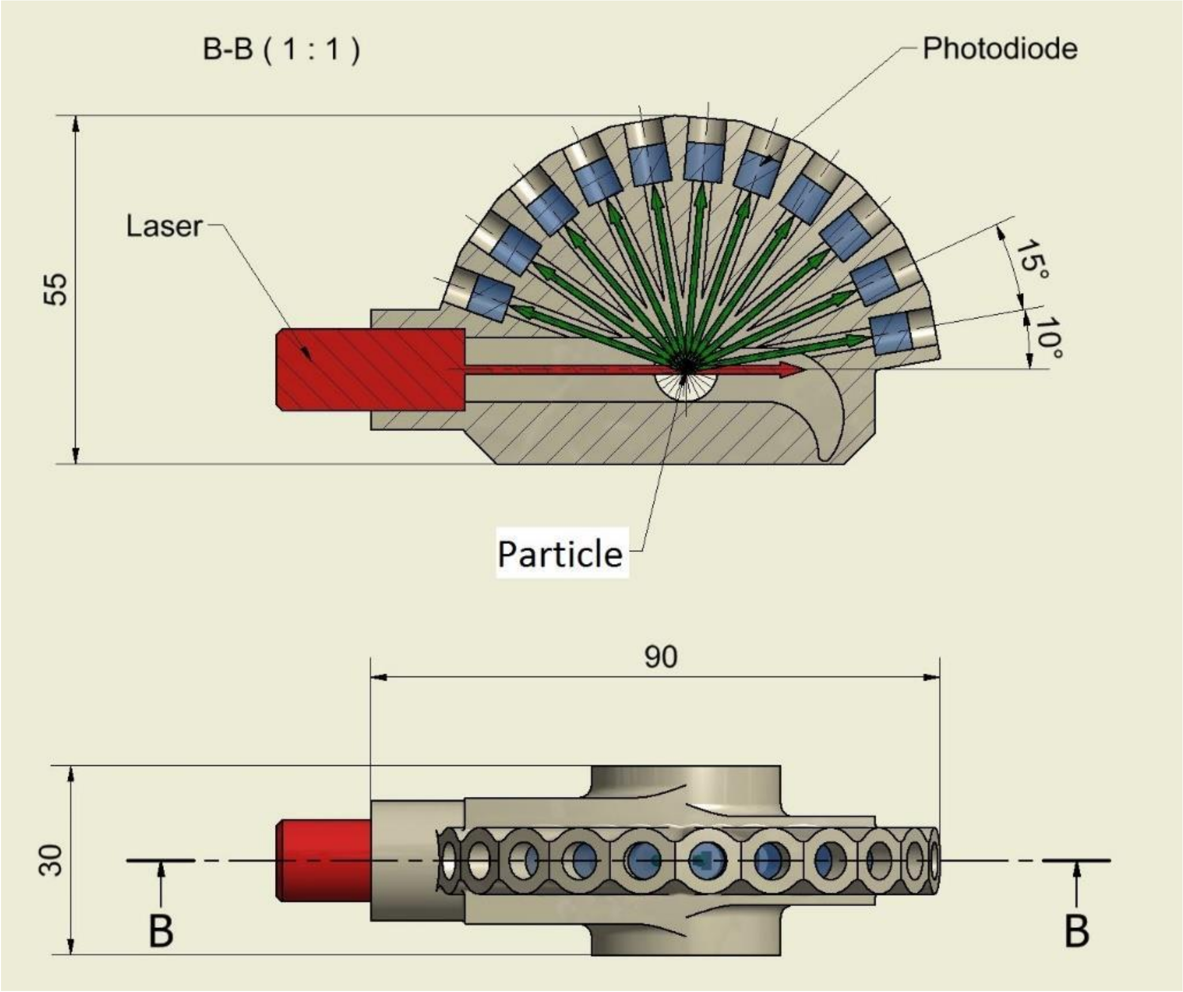
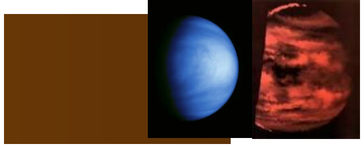


Fig.3 Possible design of the optical chamber for the LONSCAPE instrument (sizes are in mm)

From: Renard et al.,2020. *Space Sci. Rev.*, Submitted



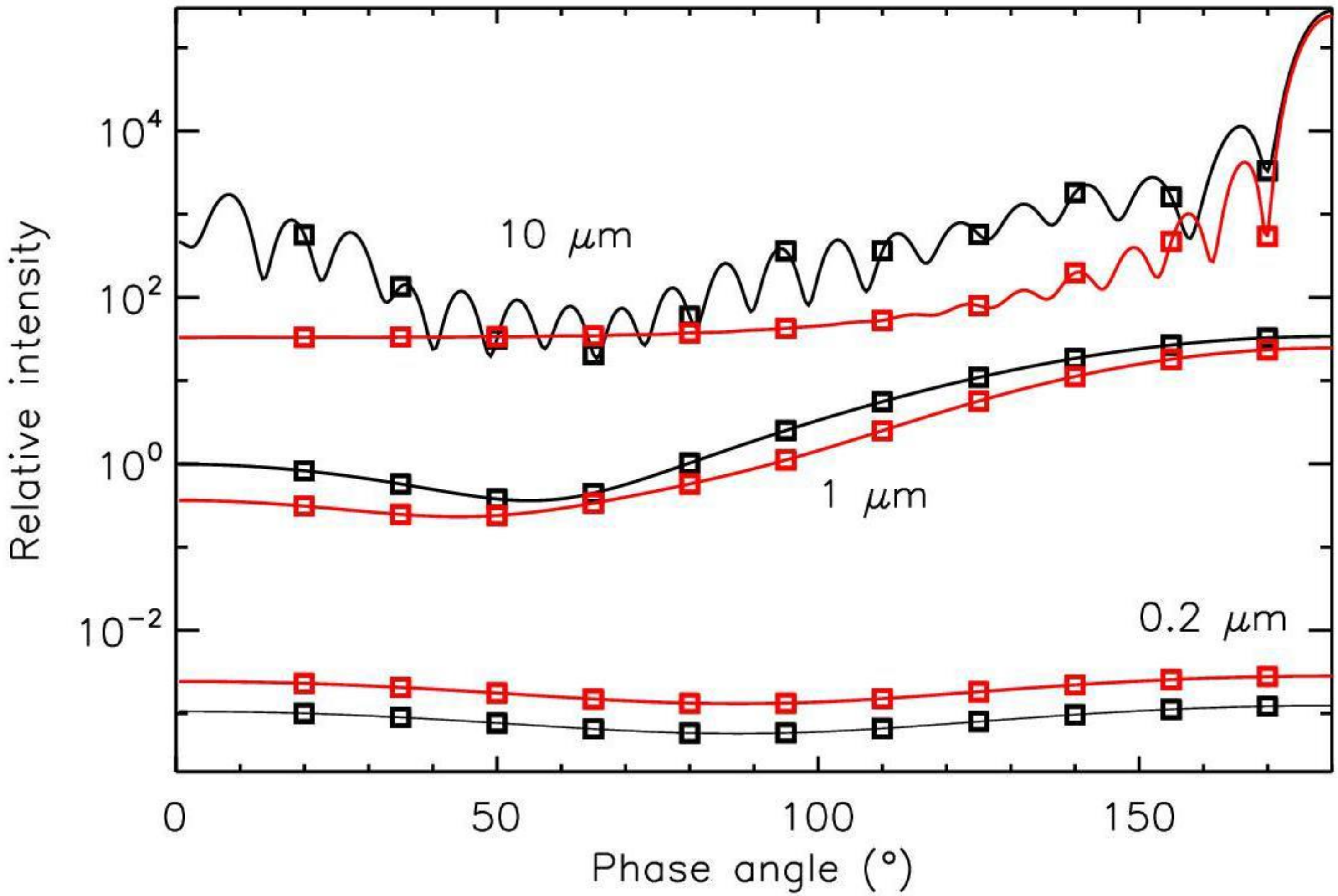
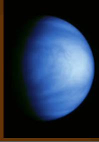


Fig.4 Mie scattering calculations for transparent (black lines) and strongly absorbing droplets (red lines) at l = 650 nm, for 3 sizes of monodisperse particles; the chosen complex refractive indexes are 1.45 and 1.5 + 0.5i, respectively, for illustration purpose. The squares represent the values of the phase function for the 11 angle positions proposed for LONSCAPE.

From: Renard et al.,2020. *Space Sci. Rev.,* Submitted



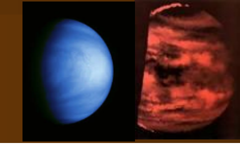
Potential Applications AIP for Venus Cloud Habitability Studies on In-Situ Missions

- Probes: Profile of composition with depth
  - ~ 100 m/s descent rate => 1 km sampling every 10 s:
    => 12 ppb to 10% accuracy

- Aerial platforms: Aerobots (e.g., Variable Altitude Balloons; See Rabinovitch et al. talk)
  - Linger for hours over small range of altitudes
  - Can traverse to different altitudes
  - Measure 2 ppb to 10% accuracy in 300 s,
  - Measure Aerosol Composition/Size/Type Over:
    - Aerobot altitude
    - Time (e.g. dynamical effects, day/night cycle)
    - Latitude and longitude (low, mid, high lats)

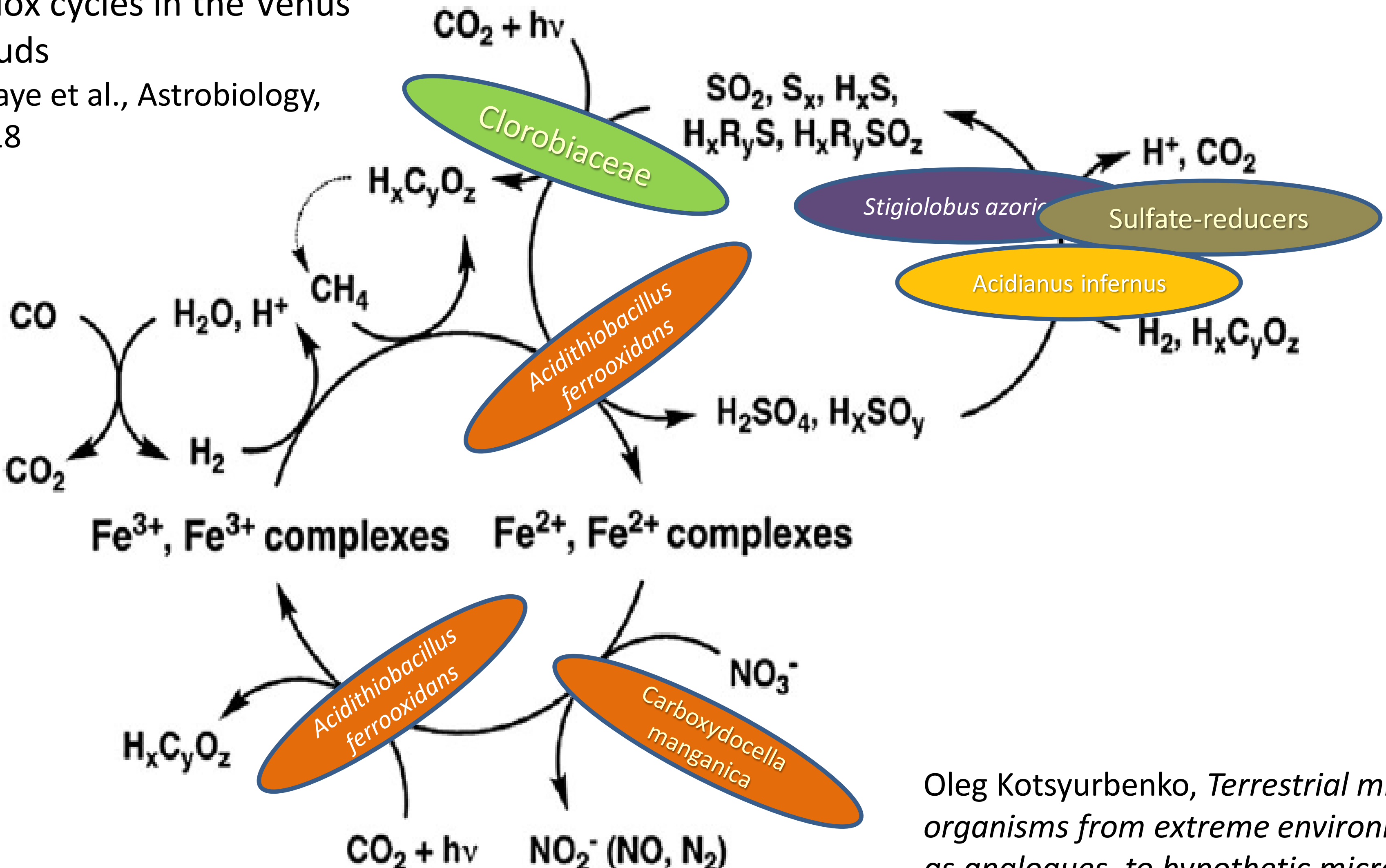
- Compare aerosol composition against attendant gases
  - Measure Isotopic differences ($^{13}C/^{12}C$; $^{17}O/^{16}O$, $^{15}N/^{14}N$, $^{33}S/^{34}S$, D/H, etc)
  - Hydrocarbons, $H_xC_yN_z$, Phosphorus compounds e.g., H_3PO_4 (Phosphoric acid: ~98 amu)

Extremophile Microorganisms Able to Withstand Venus Cloud Conditions



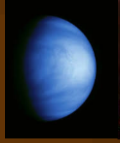
Possible Iron-Sulfide Chemical Redox cycles in the Venus Clouds

Limaye et al., Astrobiology, 2018



Oleg Kotsyurbenko, *Terrestrial micro-organisms from extreme environments as analogues to hypothetic microbial forms inhabiting Venus Clouds*, This Workshop

The Importance of Phosphorus Detection for Venus Cloud Habitability

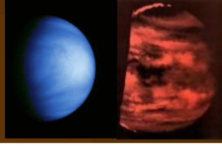


- Prior Venus measurements have revealed that five of the six common **elements** found in **living** organisms the CHNOPS elements carbon, hydrogen, nitrogen, oxygen, phosphorus and sulfur are present in the cloud habitability layer

- Phosphorus has never been detected anywhere on Venus, If present in the cloud layer it is most likely present in aerosols. Phosphine (PH_3), unstable in the Venus atmosphere, is the only likely volatile phosphorus compound

- A key contribution of the proposed experiment with an aerosol mass spectrometer is to search for phosphorus in the Venus cloud layer.
  - If phosphorus is **present,** then all of the elements necessary for life as we know it are present in the Venus cloud habitability layer
  - If phosphorus is **absent**, it means a key element necessary for life is missing and the possibility that microbial life would be detected there is drastically reduced

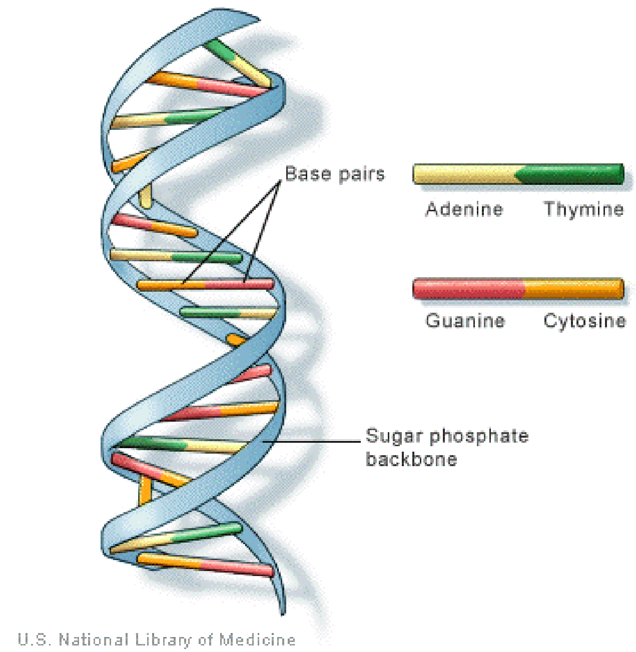
Why is Phosphorus Critical for Life?*



- Phosphoric acid is specially adapted for its role in nucleic acids because it can link two nucleotides and still ionize. The resulting negative charge
  - Stabilizes the di-esters against hydrolysis
  - Helps retain the molecules within a lipid membrane

- A similar explanation for stability and retention also holds for phosphates that serve as intermediate metabolites or energy sources

- No other elements or combination of elements appears to be able to fulfil the unique role of phosphorus in biochemistry

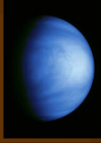


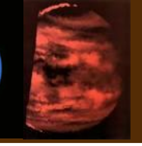
Phosphates form the backbone of the DNA double helix

Confirming the presence of phosphorus in aerosols of the Venus cloud habitability layer would provides critical information on the potential for supporting life

Reference: **Why Nature Chose Phosphates by F.H. Westheimer, Science Vol. 235, 1173-1178, 1987*

Venus Cloud Habitability: Desired Measurements





Cloud Habitability: Desired Measurements

Objective	Cloud Property	Desired Altitude Range	Desired Time-of-Day Range	Desired Latitudes and/or Terrains	Desired Sensitivity
Bulk Cloud Properties	Aerosol Number Density	~65 - 45 km	0 -24 hours	Temporate to Polar Lats	
	Aerosol Size distribution	~65 - 45 km	0 -24 hours	and over high-elevation	
	Aerosol bulk composition	~65 - 45 km	0 -24 hours	features (Gravity wave	
	(H_2SO_4 acidity)			effects)	
Cloud Dynamics	Pressure, Temperatures				
	Vertical winds				
	Waves (gravity,planetary)				
Cloud Particle Trace Species Composition	HCl, HF, HBr and daughter species				
	Hydrocarbons				
	H_2O				
	Phosphorus				
	Light isotopes:				
	$^{13}C/^{12}C$				
	$^{15}N/^{14}N$				
	D/H				
Composition of Attendant Cloud Gases	HCl, HF, HBr				
	Hydrocarbons				
	H_2O				
	Phosphorus				
	Light isotopes:				
	$^{13}C/^{12}C$				
	$^{15}N/^{14}N$				
	D/H				

Astrobiologists: Please Help to Fill Out and Expand Such a Table!