

BEYOND SULPHURIC ACID – WHAT ELSE IS IN THE CLOUDS OF VENUS? C.F. Wilson¹ and the Venus Clouds Team of the International Space Sciences Institute, Berne, Switzerland. ¹Dept. of Physics, Oxford University, Parks Road, Oxford UK, wilson@atm.ox.ac.uk.

Standard cloud models for Venus, such as that found in the Venus International Reference Atmosphere [Ragent et al., *Adv. Spa. Res.*, 1985], consider that all clouds and hazes are composed of liquid droplets of sulphuric acid mixed with water, with sulphuric acid making accounting for 75% to 96% by weight of the cloud composition. However, other minor constituents may make up the cloud particles – we review here observations constraining cloud and haze particle composition and discuss measurement needs.

Upper Clouds - UV absorber

The major goal in the upper clouds is to identify the as-yet unidentified substance which absorbs sunlight at wavelengths below 400 nm. The absorption spectrum of this “UV absorber” is broad without distinct peaks, which implies that it is particulate rather than gaseous. Venera-14 descent probe profiles have been interpreted as showing that the dominant UV absorption “is by aerosols at altitudes above 57 km, and by gases below this level” [Economov et al., *Nature* 1984]. It is still not clear whether dynamical or chemical processes are responsible for the formation of UV contrasts in the upper cloud (see e.g. discussion in Esposito & Travis, *Icarus*, 1982). Candidate particles include polysulphur (S_3 , S_4 , S_x), $FeCl_3$, and dozens of other possibilities.

Upper clouds - evidence from phase functions

Analysis of polarisation phase functions obtained through decades of observations from Earth, performed by Hansen & Hovenier [*J. Atm. Sci.*, 1974], revealed that the main particulates at the cloudtops of Venus were spherical, with a narrow size distribution centred on a radius of 1.05 microns and with a refractive index consistent with a composition of approximately 75% wt H_2SO_4 : 25%wt H_2O . Observation by Pioneer Venus allowed more detailed analysis of intensity and phase functions – all observations could be matched assuming only $H_2SO_4:H_2O$ mixtures.

Observations of intensity phase functions from Venus Express / VMC find that refractive index can reach 1.49, which is too high for $H_2SO_4:H_2O$ mixtures [Petrova et al., *Plan Spa Sci*, under review 2014]. An analysis of polarization phase functions from the SPICAV instrument is currently underway [e.g. Rossi et al., *EPSC*, 2013], this will provide a constraint on refractive index independent of the VMC work.

Middle Clouds - condensation nuclei

At altitudes from 50-60 km, the convective stability of the atmosphere is close to zero, which implies that this layer experiences convective overturning and associated condensational cloud, with sulphuric acid as the

major condensing species. The critical question here is to establish which species, if any, act as cloud condensation nuclei (CCNs). Chemical models such as those by Krasnopolsky, or by Yung et al. readily form polysulfur (S_3 , S_4 , S_x) but these are not soluble in sulfuric acid so their efficiency as CCNs is low. Meteoritic dust may act as CCNs [see e.g. Gao et al, *Icarus*, 2014], as volcanic ash.

It's unknown whether there is ever rain in the condensational cloud of Venus. This can be investigated in situ, or from orbit using high-frequency radar.

Middle & lower cloud - X-ray spectrometry

Venera 13, Venera 14, Vega 1, and Vega 2 descent probes all carried X-ray fluorescence instruments. These instruments measured elemental composition of the cloud particles and found not only sulfur, but also phosphorus, chlorine and iron – notably, as much as phosphorus as sulphur in the lower clouds below 52 km [Andreichikov et al, *Sov. Astron. Lett.* 1986, 1987]. A chemical analysis by Krasnopolsky [PSS, 1985] concluded that the phosphorus could be in the form of phosphoric acid (H_3PO_4) aerosols, which would account for the particulates observed by descent probes down to 33 km altitudes, where temperatures are far too hot to allow liquid sulphuric acid.

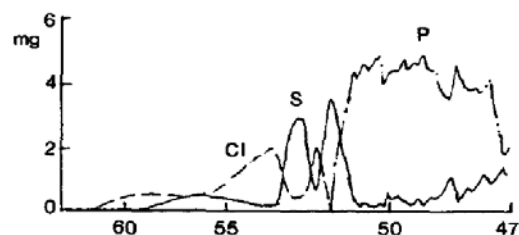


Fig. 1 – Accumulation of chlorine, sulfur, and phosphorus on the filter of the Vega 2 X-ray radiometer (Figure from Andreichikov et al. 1987).

While there have been concerns raised that some of these findings may be affected by contamination from Earth, replicating this experiment could prove valuable. We note that the Pioneer Venus descent probe LCPS appeared to show a discrete layer of large particles at 48-50 km, below the convectively unstable layer which stretched up from 50 km – this supports the hypothesis that this lower cloud may be something distinct from convective condensational sulfuric acid cloud.

Near-surface hazes?

Grieger et al. [IPPW, 2003] re-analysed photometric observations from Venera 13 and 14 landers and concluded that a discrete layer of absorbers was found at

1-2 km altitude, at both landing sites. These temperatures (around 720 K) are far too hot for sulphuric acid aerosols. Possibilities include sand/dust lifted from the surface by winds; volcanic ash; or even exotic metallic condensates such as those responsible for radar-bright deposits on high volcanoes.

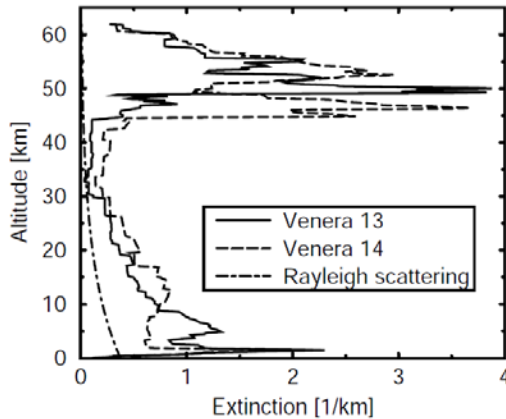


Fig. 2 - Extinction profiles as retrieved from Venera 13 & 14 spectrophotometer data at 700-710 nm. Figure from Grieger et al., IPPW 2003.

In situ mission – possible payload

Science payload for investigating cloud particles should include a **mass spectrometer with dedicated aerosol collector inlet**, similar to the Aerosol Collector / Pyrolyser (ACP) instrument on Huygens probe, to allow separate chemical analysis of aerosol and gas composition. Increased ability to distinguish between chemical species may be achieved by adding gas chromatography (GC) column to the MS inlet, but the optimal configuration of this needs to be studied for Venus conditions. An **X-ray fluorescence spectrometer** would prove very useful to verify the Venera and Vega probe's findings of phosphorus, chlorine and iron. Such an instrument, which should be mounted such that it can examine samples acquired by the aerosol collector, could prove revolutionary to our understanding of Venus clouds. Space-qualified XRF instruments are available for <200 g, see. e.g. Beagle 2 X-ray spectrometer. A **nephelometer**, i.e. a device which measures intensity (and, preferably, polarization) of scattered light as a function of angle would be a valuable addition as it measures directly the optical properties of aerosols and so ties the in situ measurements in with what is observed from orbit. A **tunable diode laser spectrometer** would improve chemical characterization of the chemistry of the cloud-level atmosphere, and would help to resolve ambiguity between species. Finally, a **camera** should not be omitted, to look at cloud morphology as well as for outreach!

For all of the above instruments, careful attention will be needed to ensure cleanliness of the mirrors /

samples inlets with respect to deposited cloud particles. This is needed in order to correctly understand the spatial distribution of aerosol composition, whether for a vertically or horizontally travelling platform. A **Venus cloud-level environment chamber**, capable of simulating different credible gas & aerosol compositions, would be valuable for these experiments.

In situ mission – mission requirements

Repeated vertical transects through the clouds, anywhere within the range of 48 – 75 km, would be ideal for understanding cloud microphysics and chemistry – with a focus of identifying UV absorber (60-75 km), CCNs and cloud processes (50-60 km), or lower cloud composition (48-52 km).

Horizontal transects would help to understand the formation of cloud contrasts, at whichever altitude they occur. If they occur in the upper cloud (60-70 km) they'd clarify the formation of UV contrasts in this convectively stable region; in the middle cloud they'd enable study of the main convective condensational cloud processes; in the lower cloud (48-51 km) they'd enable a characterization of the possibly anomalous "Mode 3" particles.

Upper cloud processes are thought to be driven largely by photochemistry, so ideally a mission should carry out **measurements around one or more full diurnal cycles**. Lower and middle cloud processes are thought to be driven largely by thermal heating from below, so investigation can be **carried out day or night or both**.

Orbital mission – possible payload

Useful cloud investigations can also be achieved from an orbital mission. Continued measurement of the spatial and temporal variation of **mesospheric SO₂ abundances** is needed to understand this most variable of mesospheric gases, and to understand how its variations are linked to cloud variations. The vertical distribution of upper clouds & hazes could be measured with an **orbital LIDAR**; having two wavelengths in this LIDAR would enable either measurement of a particular gaseous species such as SO₂ or water (for differential absorption LIDAR) or characterization of particle sizes (for more widely separated lidar frequencies). **Short wavelength radar**, e.g. X-band or shorter wavelength, would be sensitive to large precipitation-sized particles; radar instruments should be designed such that any reflections coming from the atmosphere are retained and studied rather than discarded!

Session: Atmosphere

Target: Atmosphere 0 – 100 km, but mostly altitudes of 48 – 75 km.

Science Goal(s): I.C.1, I.C.2, I.C.3, I.C.4.

Acknowledgement: We thank ISSI for supporting our team's meetings.