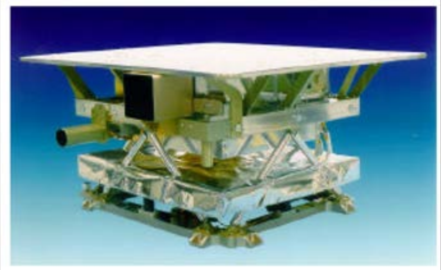

Venus's ultraviolet absorber: Cyclo-octal (S_8) and polymeric sulfur (S_x) and their latitudinal behavior.

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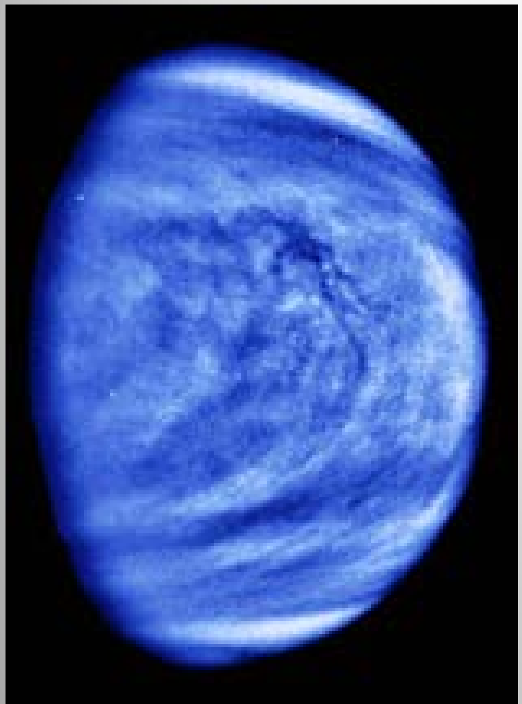
[4]*California Institute of Technology, Pasadena, California USA*



Some suggested Venus UV absorbers:

Formaldehyde CH_2O

Carbon suboxide C_3O_2

Nitrosylsulfuric acid $NOHSO_4$

Nitrogen dioxide NO_2 and nitrogen tetroxide N_2O_4

Ammonium nitrite NH_3NO_2

Ammonium sulfate $(NH_4)_2SO_4$

Ammonium pyrosulfate $(NH_4)S_2O_5$

Ammonium chloride NH_4Cl

Amides

Chlorine Cl_2

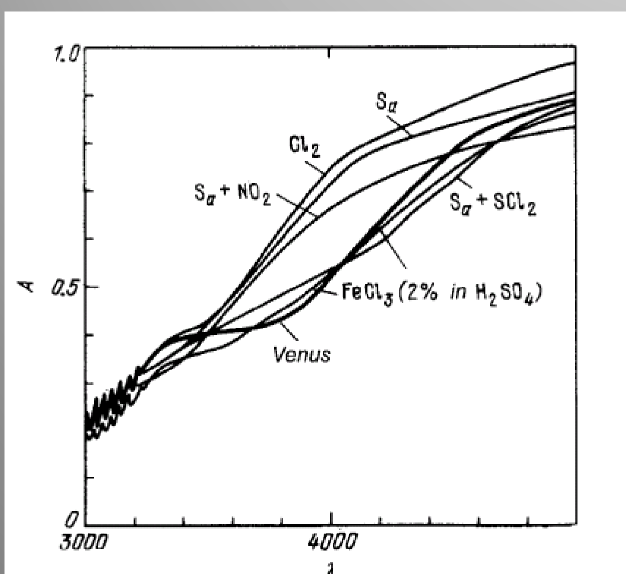
Sulfur dichloride, SCl_2

Iron chloride $FeCl_2 \bullet 2H_2O$, $FeCl_3$

Perchloric acid $HClO_4$

Disulfur monoxide S_2O

Sulfur



Ferric chloride at Venus?

$FeCl_3$

The (uncommon) mineral Molysite

Associated with terrestrial fumaroles

Considered by Kuiper (1969)

Resurrected by Zasova, Krasnopolsky, & Moroz (1981)

Computed profile matches Mode-1 particles in lower and middle clouds (Krasnopolsky, 2006)

Forms sulfuric acid cloud droplets with $FeCl_3$ in solution

↑

Ferric chloride, a salt, is deliquescent and $FeCl_3$ aerosols can act as a condensation nuclei

↑

Dimer condenses at 315 K (54 km)

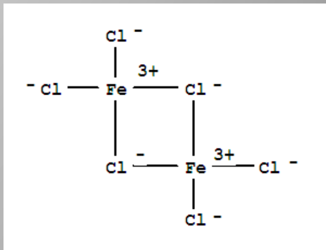
↑

$(FeCl_3)_2$ gas formed at 400 K (42 km)

↑

$FeCl_3$ gas from plume and sublimation

↑



$FeCl_3$ in plume

Molysite ($FeCl_3$) deposits

Spectroscopy of $FeCl_3$ solutions

Transmission spectra by Mark Anderson

Obtain absorption coefficient and imaginary index

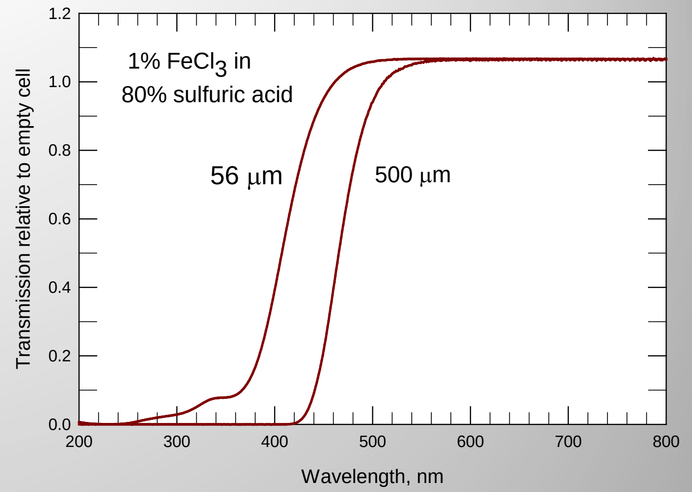
In sulfuric acid solution,

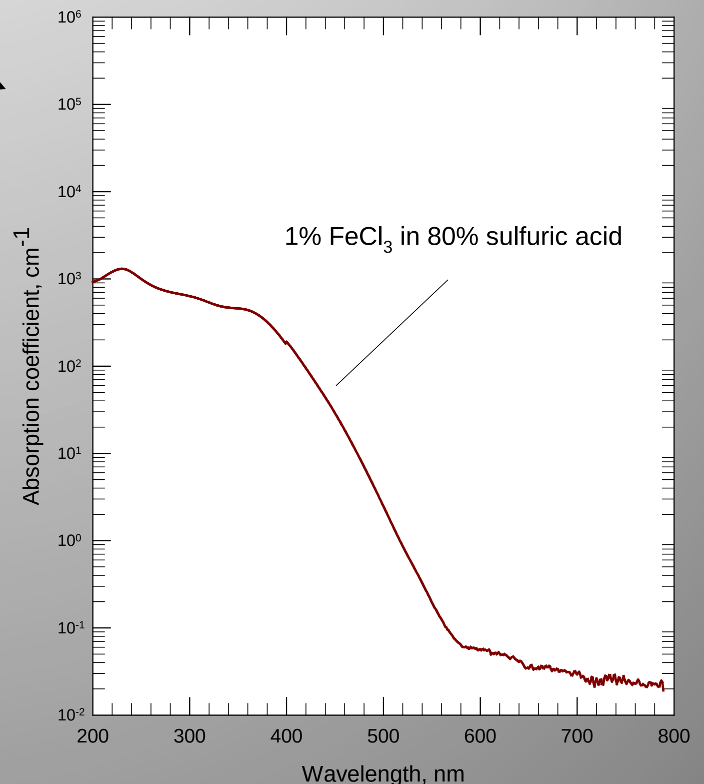
get mainly Fe^{3+}, $FeSO_4^{+}$, $FeHSO_4^{2+}$

Fe^{3+} absorption bands at 194 nm and ` 245 nm (Brown & Kester, 1980)

$FeSO_4^{+}$ and $FeHSO_4^{2+}$ bands at about 290 and 360 nm.

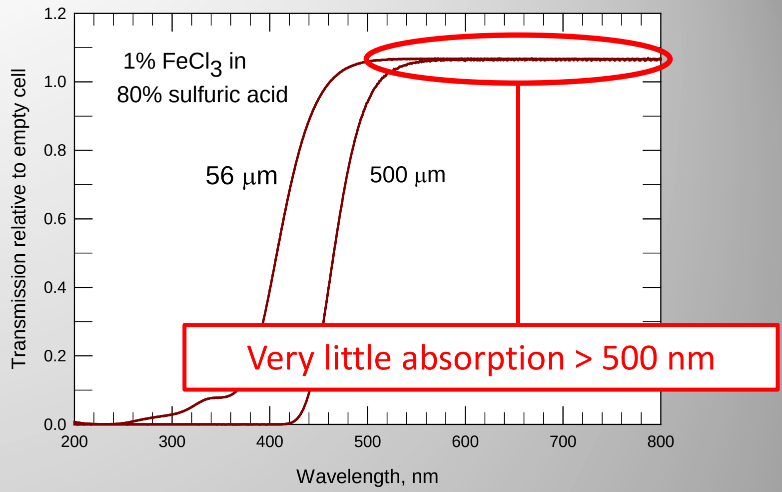
Extends into visible region



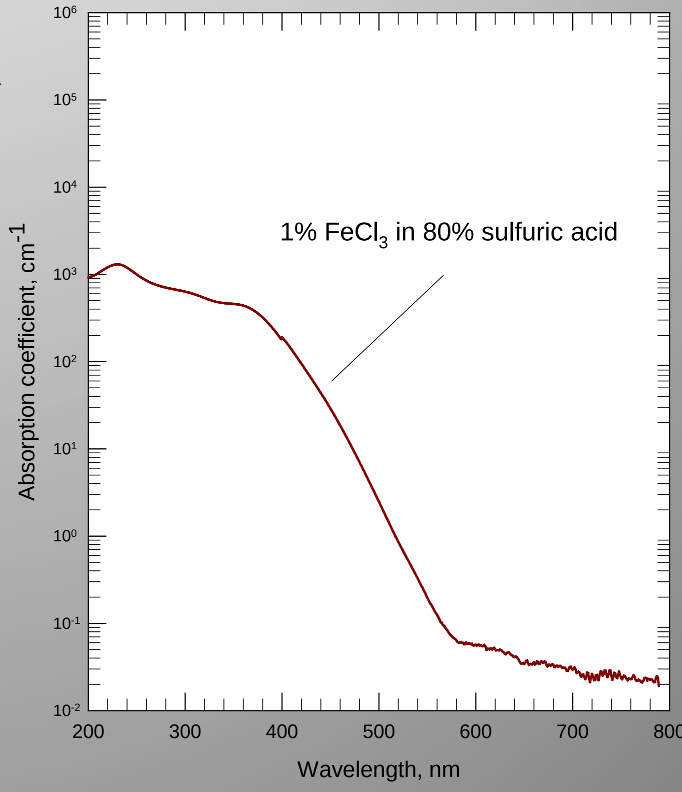


Spectroscopy of $FeCl_3$ solutions

Transmission spectra by Mark Anderson



Obtain absorption coefficient and imaginary index



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Extends into visible region

Expected $FeCl_3$ signature at Venus

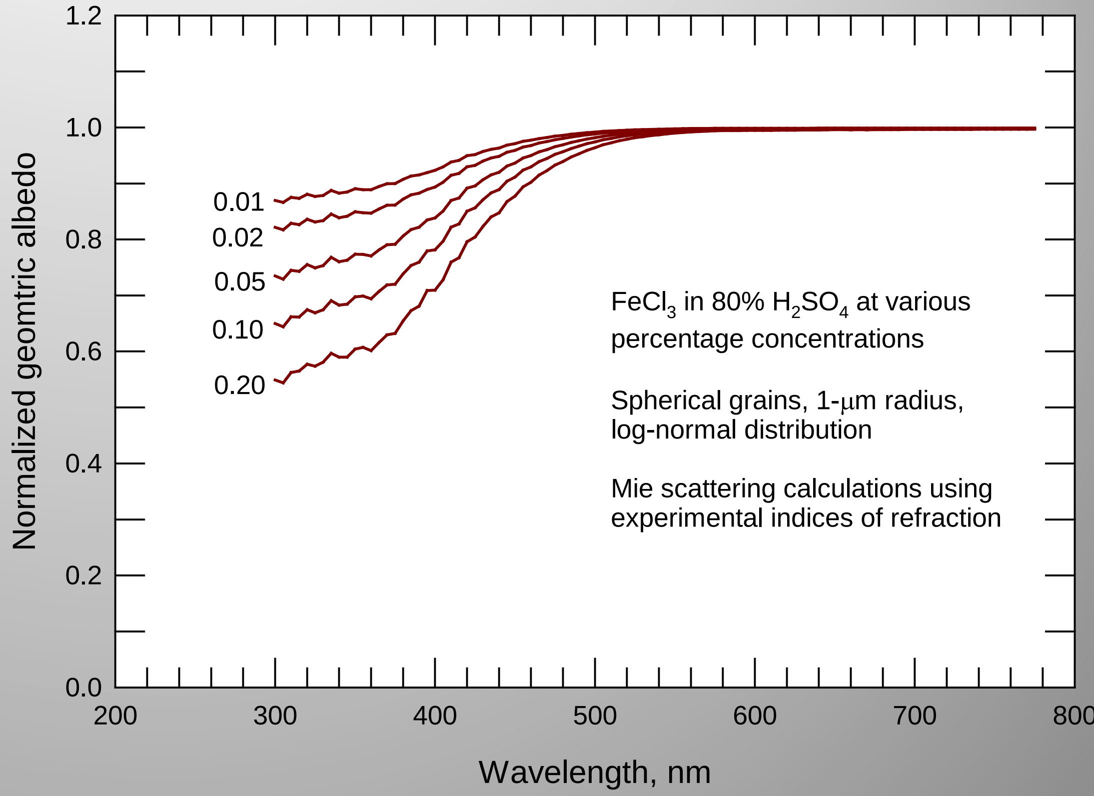
Cloud droplets of $FeCl_3$ in sulfuric acid

Mie scattering for single scattering albedo, asymmetry factor

Radiative transfer a la Hapke

Geometric albedo →

$FeCl_3$ at Venus? Normalized geometric albedo spectra for various concentrations.



Elemental sulfur

Elemental sulfur is one component of Venus's sulfur cycle

H_2SO_4, SO_2, SO, OCS, SO_3, S_x

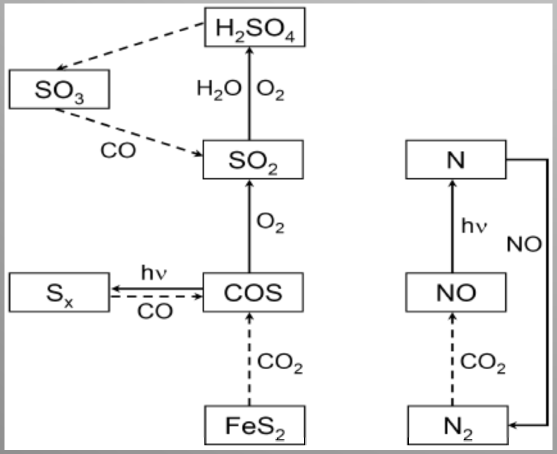
$SO_2 + h\nu \rightarrow SO + O$, $SO + h\nu \rightarrow S + O$

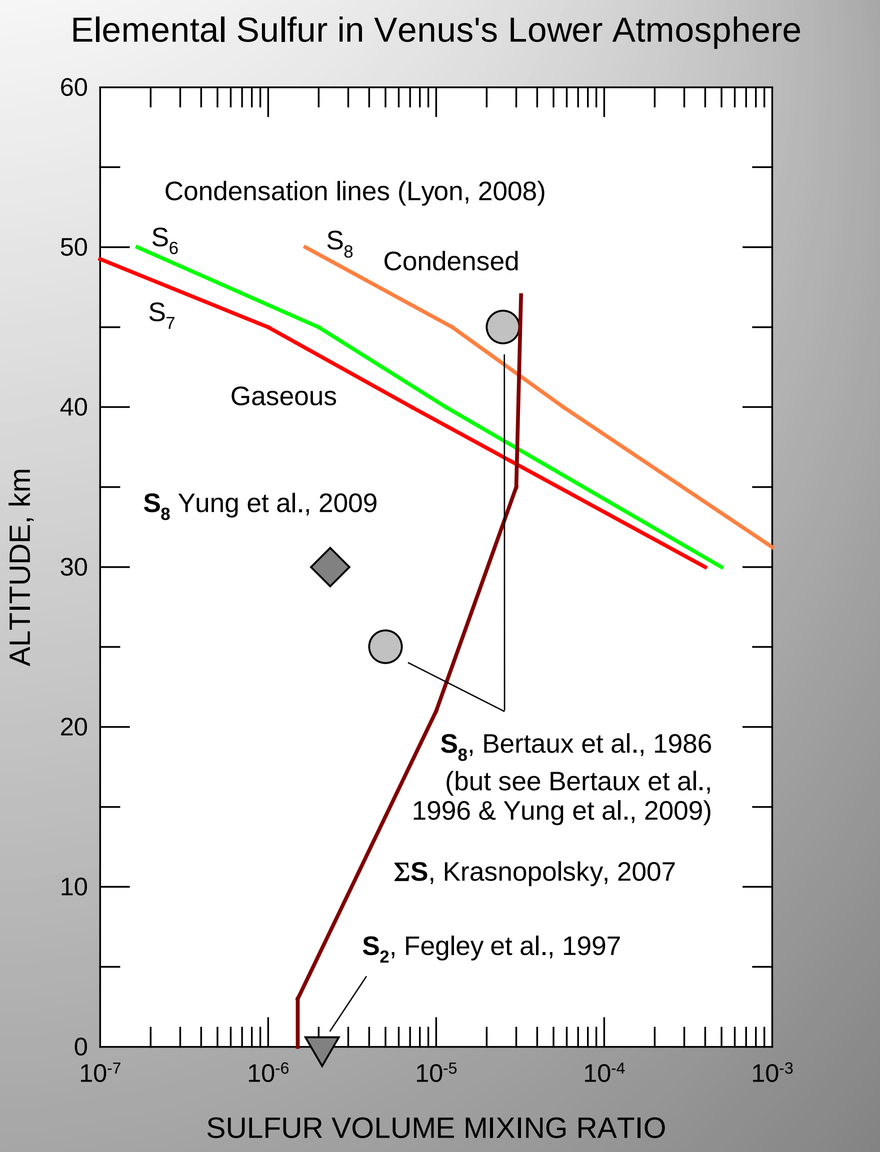
$OCS + h\nu \rightarrow CO + S$

$(SO)_2 + OCS \rightarrow CO + SO_2 + S_2$

Sublimation from surface

Mills, Esposito, & Yung 2007





Spectral properties of S_8 and S_x

The stable form of sulfur is cyclo-octal S_8

which has absorption bands at ~ 220, 260, and 280 nm,

and a gaussian tail that extends to ~450 nm.

Similar to $FeCl_3$, little absorption > 500 nm

BUT

Absorption in these bands breaks the S_8 ring.

Forms amorphous sulfur a-S

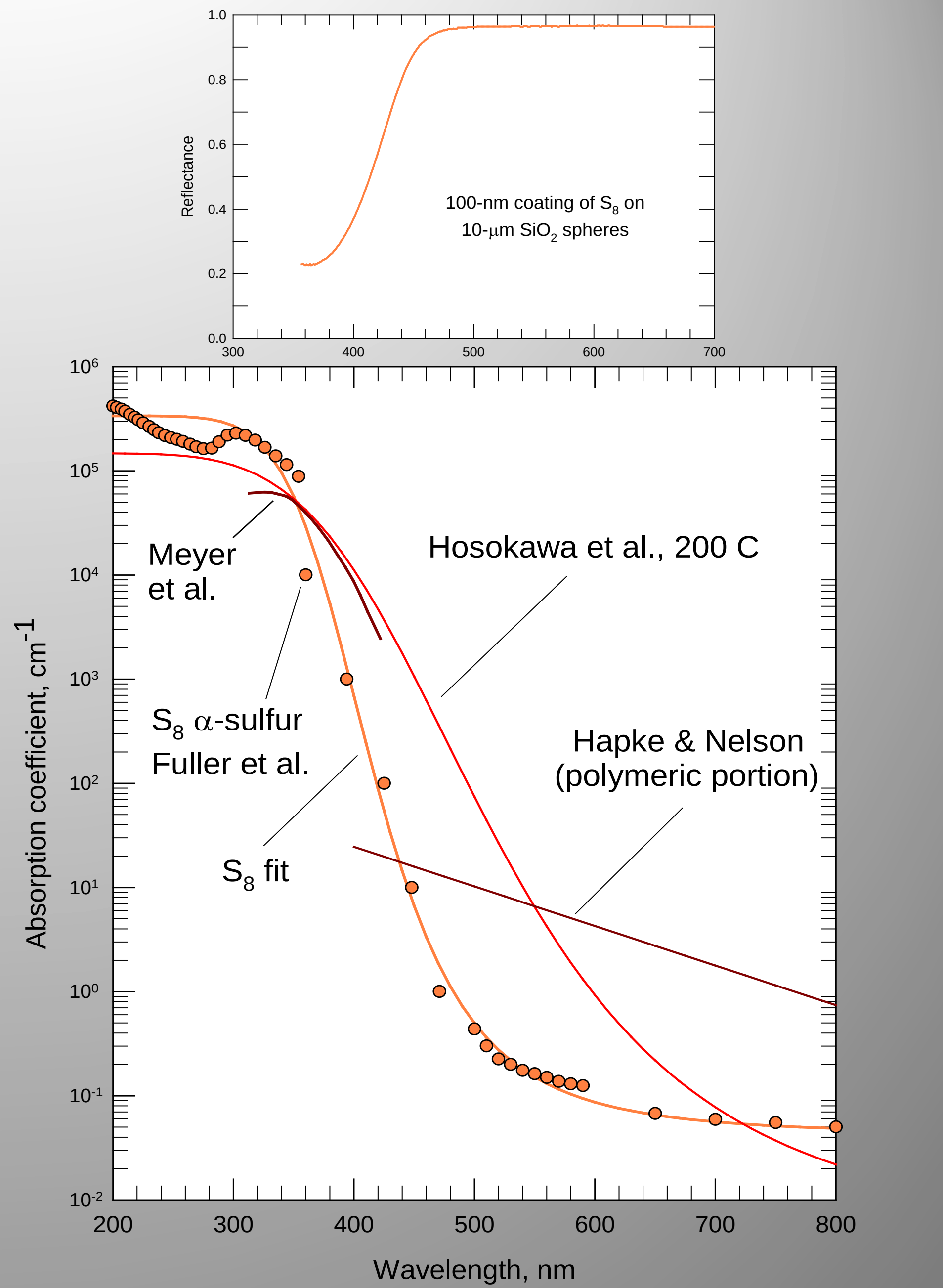
Similar structure to polymeric sulfur S_x produced in liquid sulfur (long chains, large rings)

New bands at longer wavelengths, so…

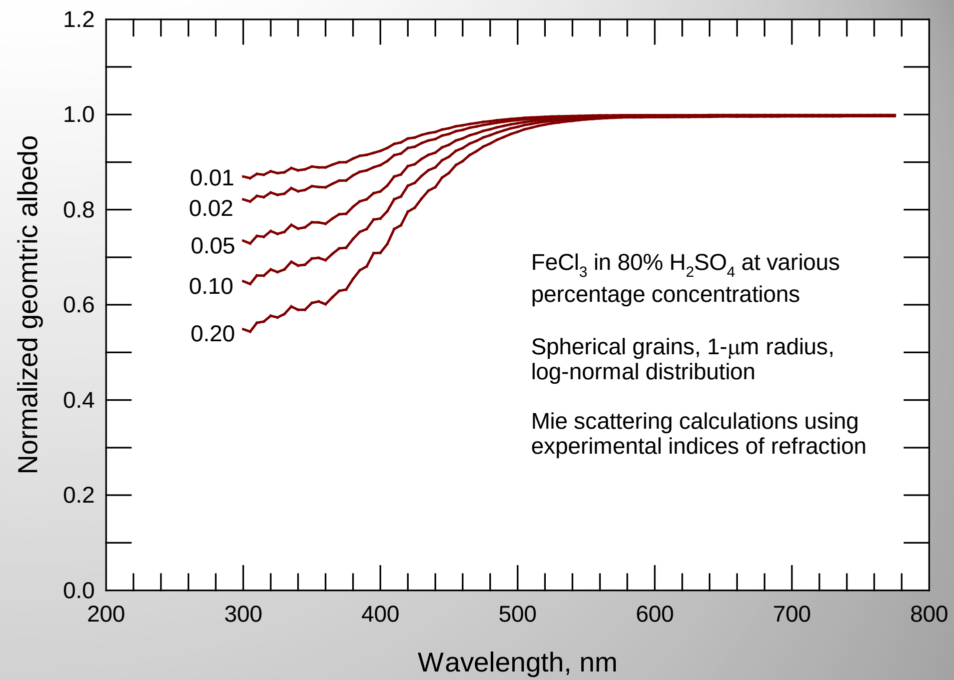
…absorption extends to longer wavelengths

Proposed for Venus by Hapke & Nelson (1975)

Spectral shape can evolve with UV exposure



FeCl$_3$

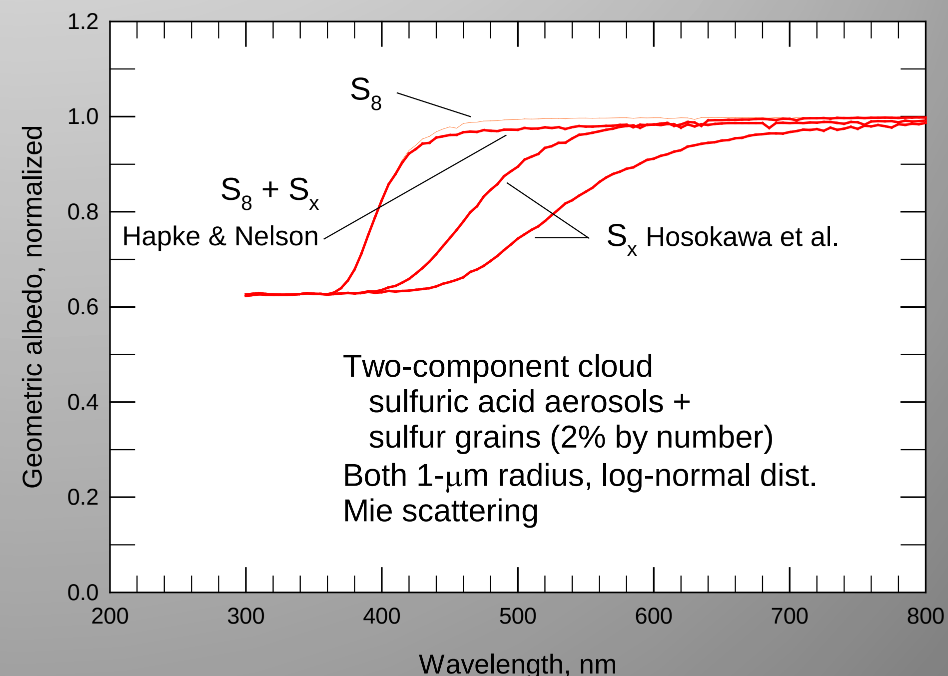


Polymeric sulfur S_x and FeCl$_3$ compared

Computed to match observed UV absorber band depth

Can discriminate using the long-wave region > 500 nm

S_8 & S_x



Venus Express VIRTIS hyperspectral image cube

VV0459_03, MTP016

Image uses 380 to 400-nm UV bands and is illumination-corrected and stretched

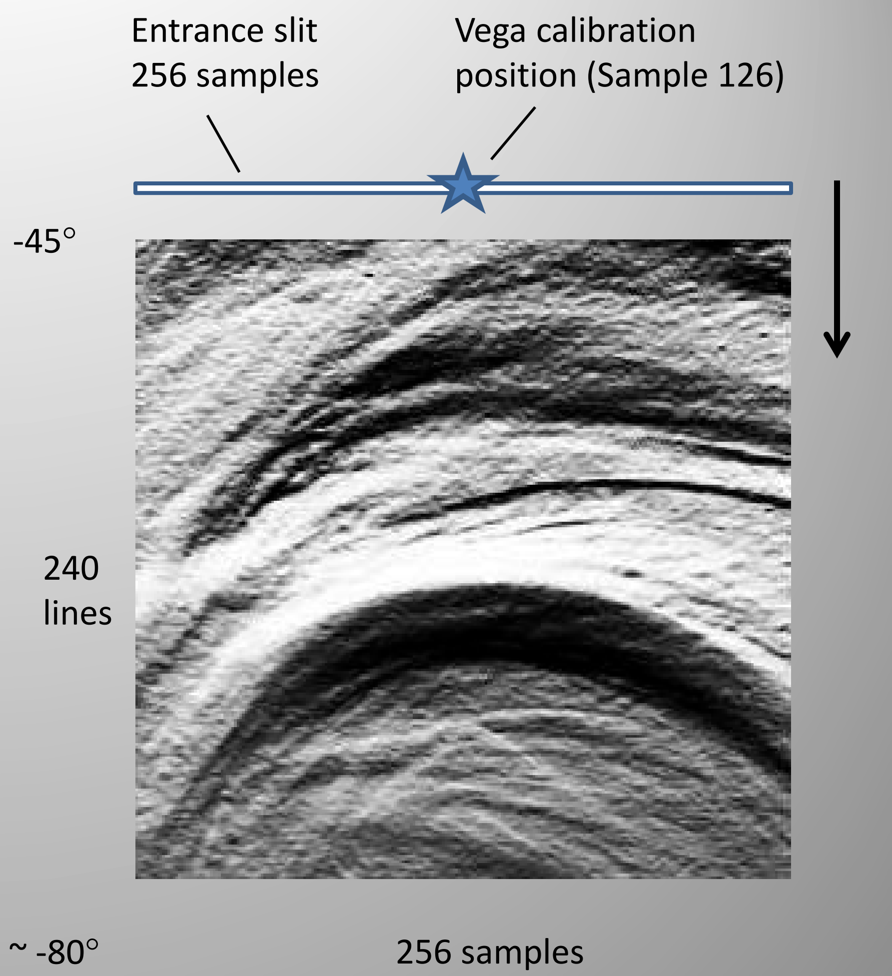
Black denotes UV absorption

Scanning mirror moves slit in ~ N - S scan

Use Vega calibrated sample (126)

60 spectra, each for 1 sample × 4 lines

Spectra normalized to "white" polar cloud



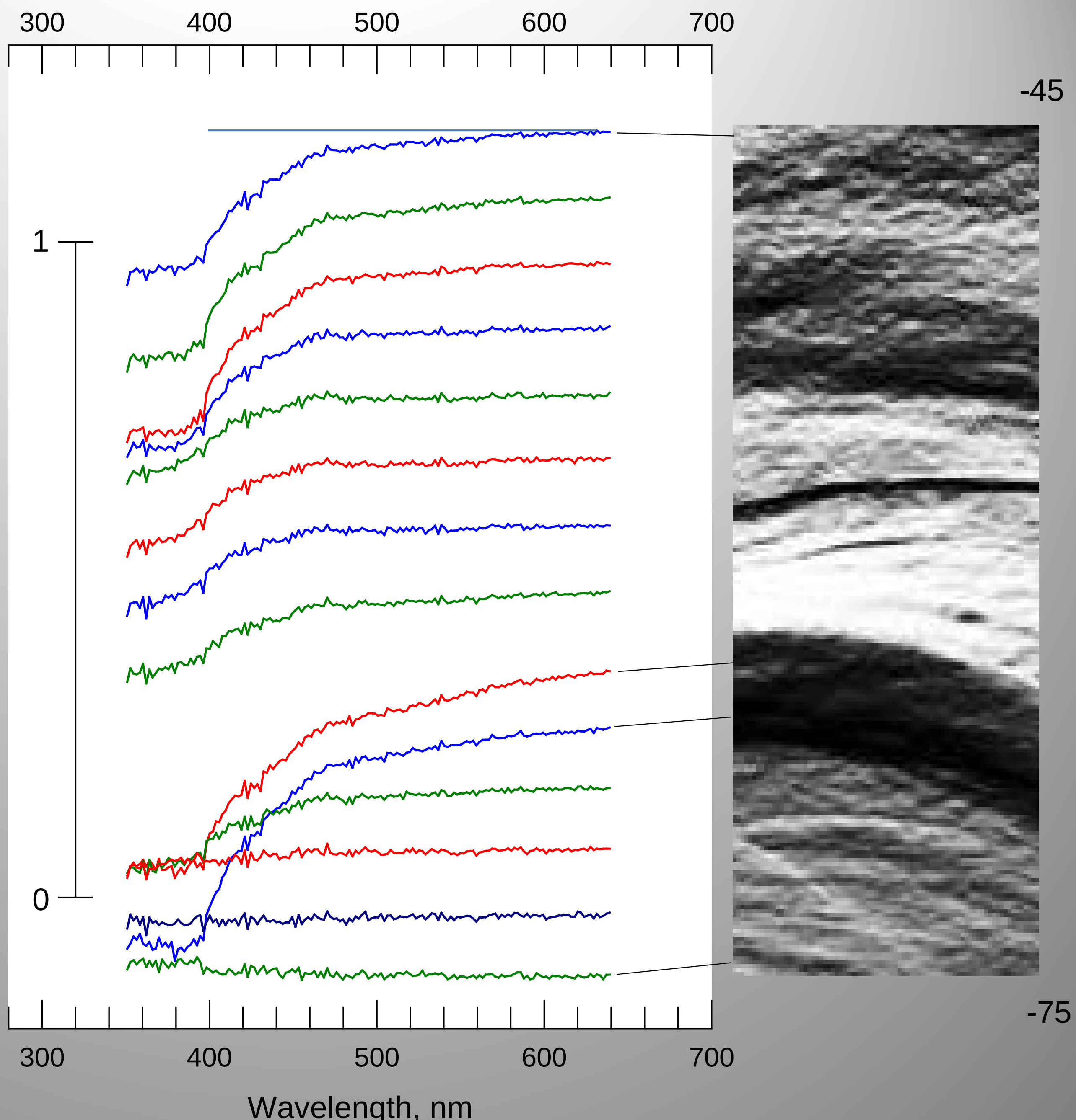
Absorption extending to 640 nm and well beyond!

So not predominately $FeCl_3$ nor pure S_8.

Polymeric sulfur implicated

(but may be consistent with Krasnopolsky's lower and middle cloud $FeCl_3/H_2SO_4$ aerosols)

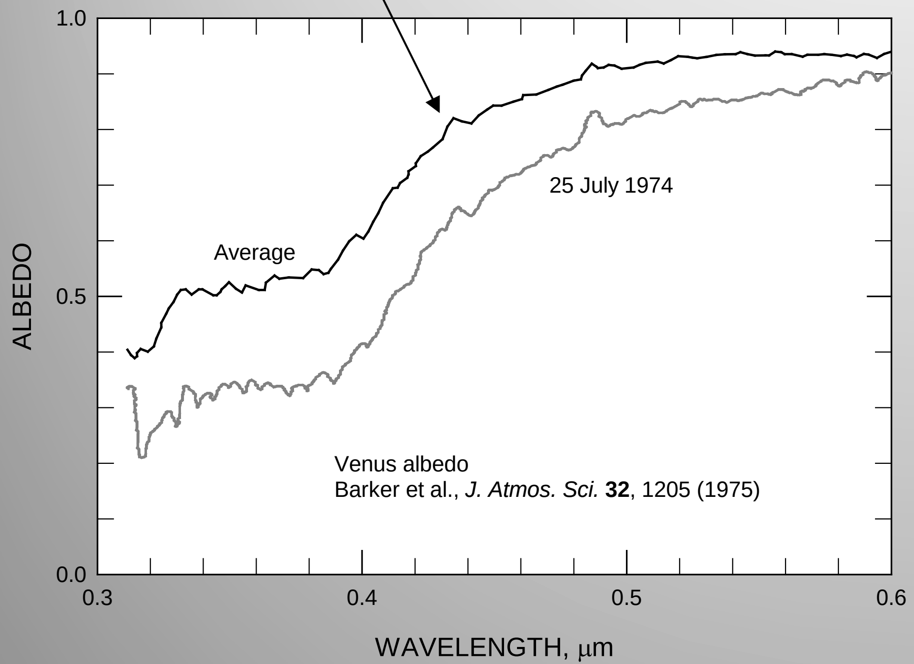
As south latitude increases, slope increases

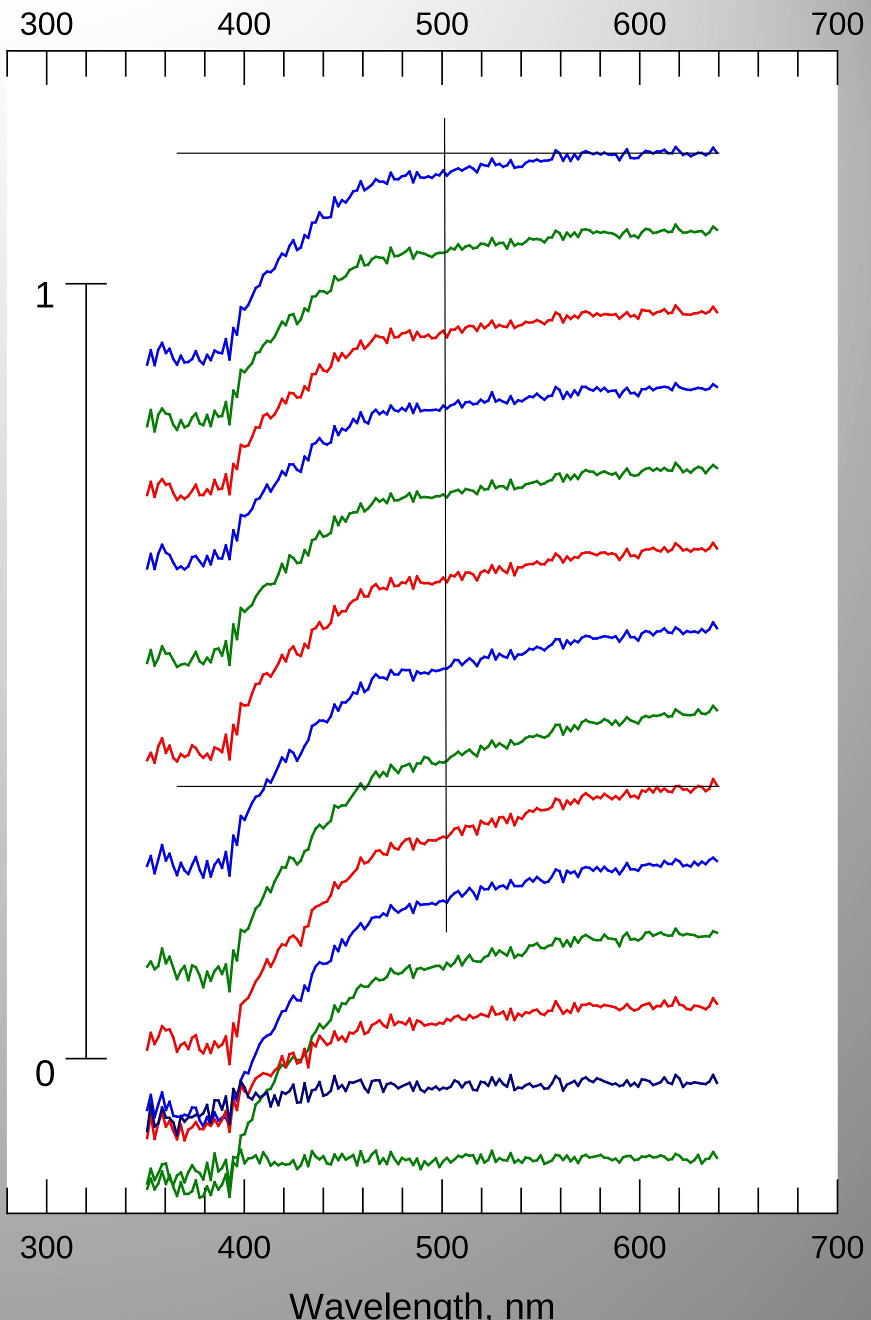


Two examples

VV0436_03:

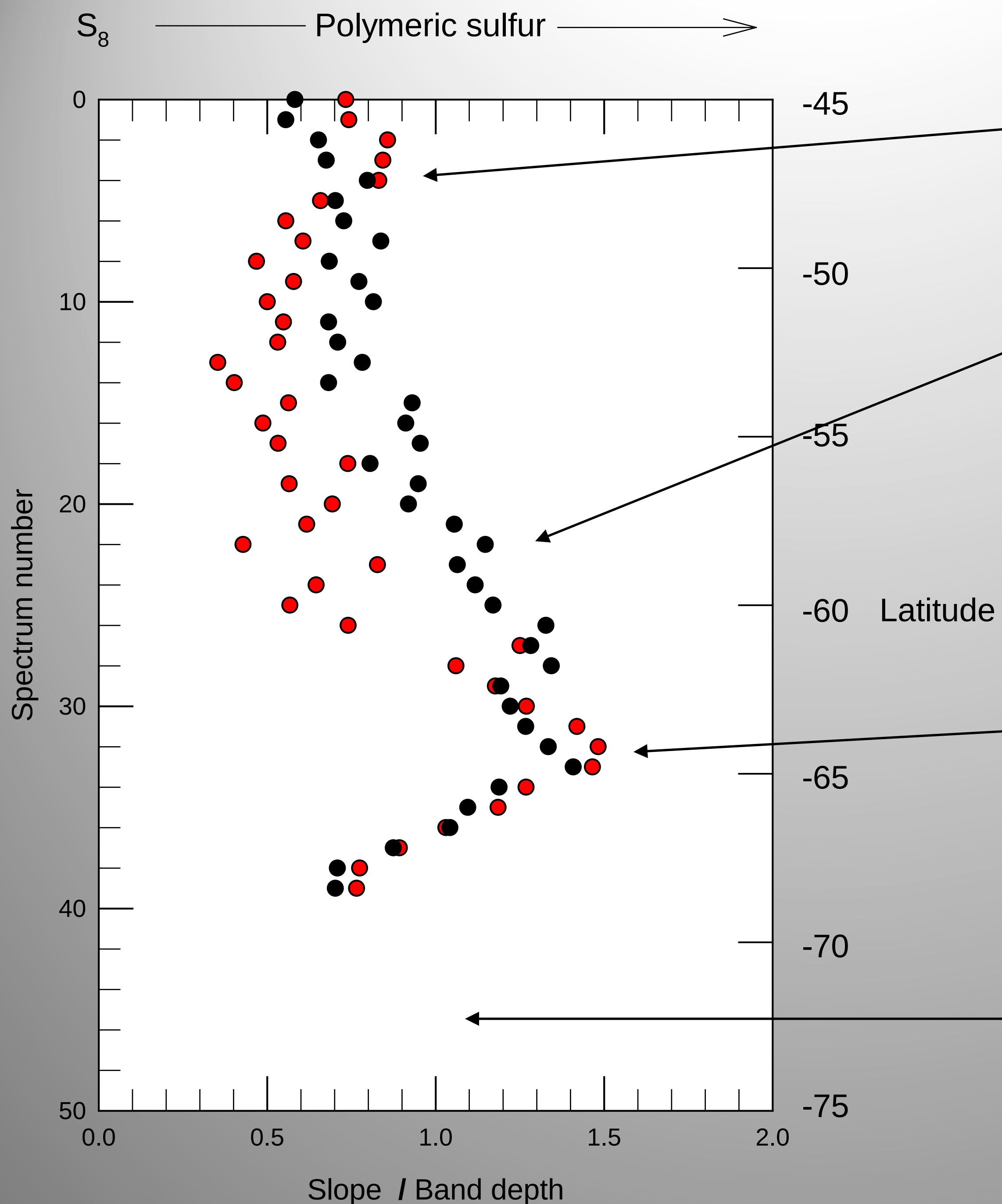
Barker's ground-based spectra





To investigate further:

Take ratio of 500 – 700 nm slope to band depth at 350 nm



Somewhat polymeric at -45°

Polymeric content increases with south latitude…

…and time in Hadley cell

Decrease in amount of sulfur and relative slope starting at ~ -65° where….

…cloud top descends in cold collar…

…and overlying hazes provide complications.

Bright white polar hazes here

Summary

Provides good evidence for polymeric sulfur as Venus's UV absorber

Supports Hapke & Nelson's 1975 suggestion

Consistent with the UV absorber brought up from depth in low latitudes as suggested by Titov et al. 2008.

Polymerization appears to proceed as sulfur aerosols move poleward

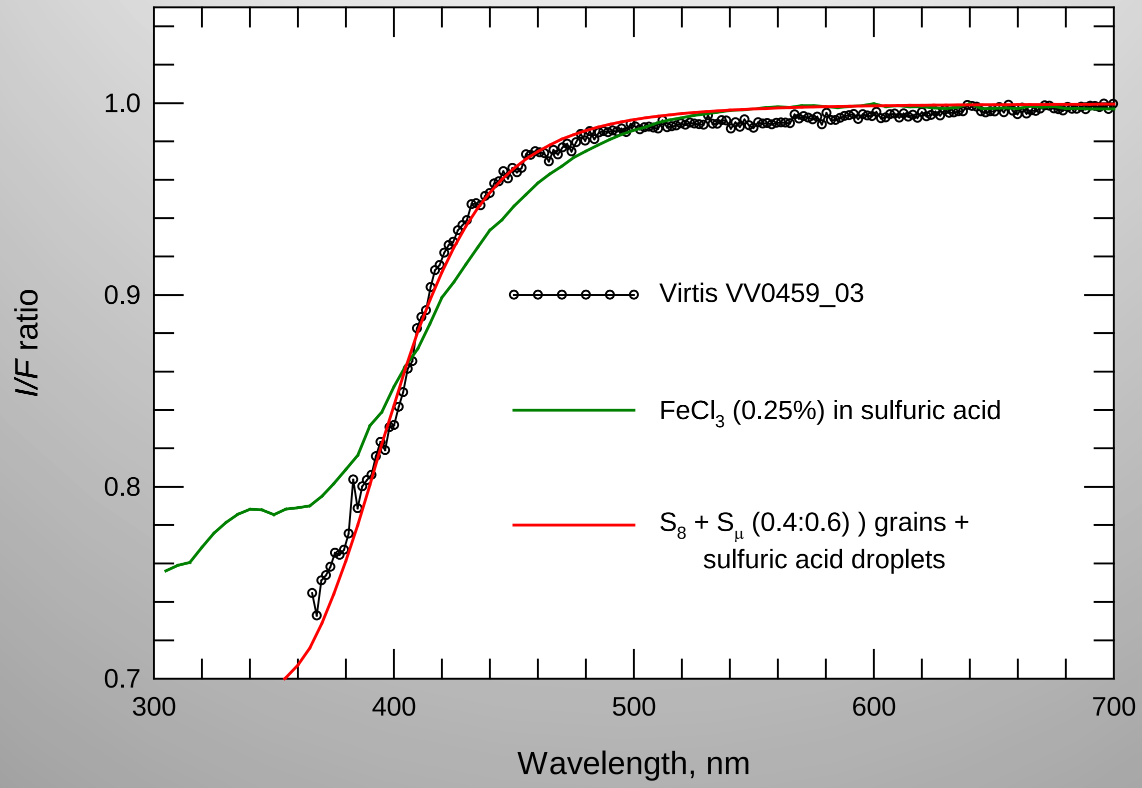
Curious and unexplained behavior at high latitudes
(annealing, mixing effect, temperature effect, stratification?)

Lots more data available for further analysis

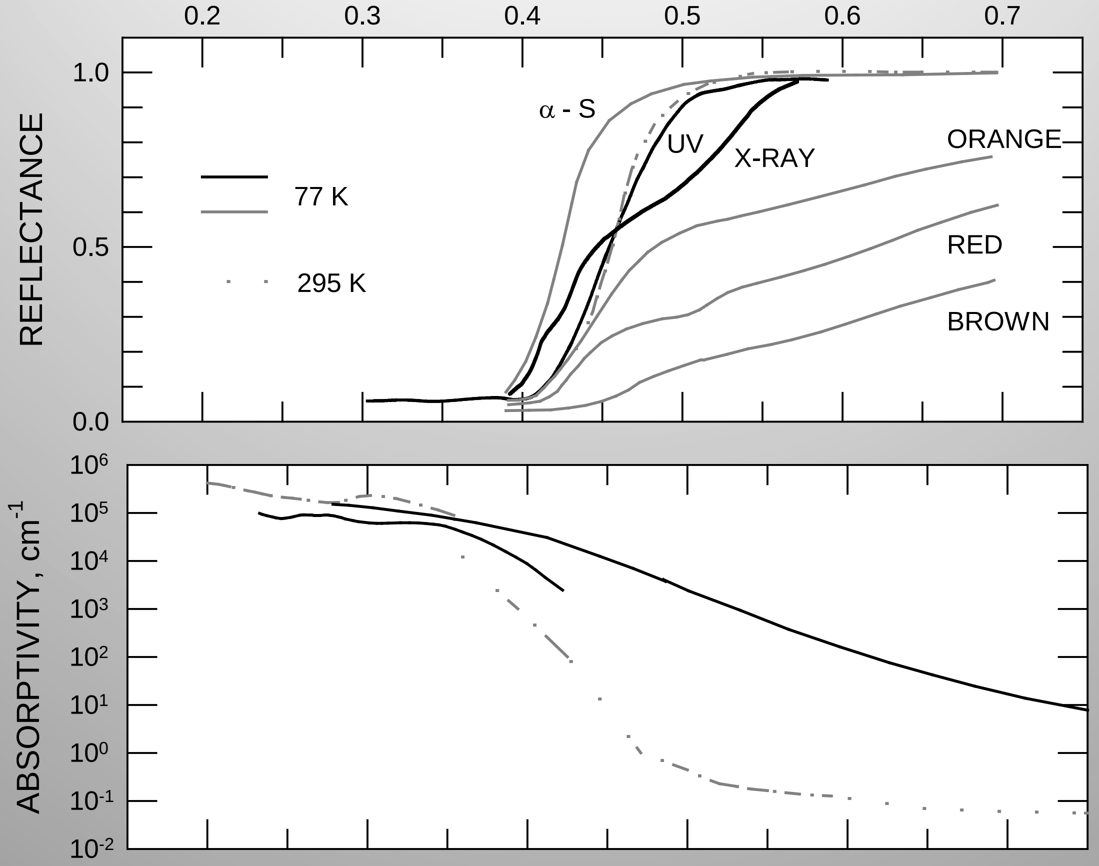
Also need photolysis measurements of micron-size S_8 grains!

- Rate of polymerization as function of excitation wavelength
- Absorption spectra changes with temperature
- Annealing rate at various temperatures

Backup Material
(Previous work and notes)

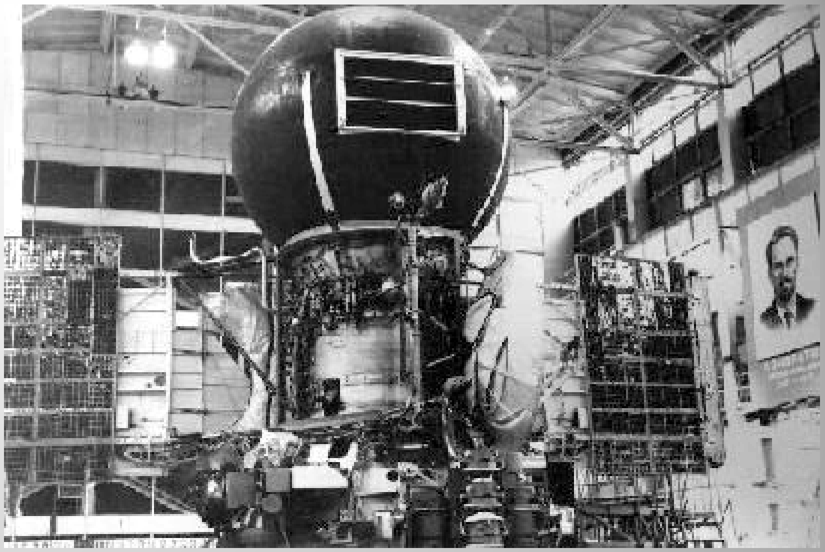


I/F ratio
1.0
0.9
0.8
0.7
300
400
500
600
700
Wavelength, nm
Virtis VV0459_03
FeCl3 (0.25%) in sulfuric acid
S8 + Sμ (0.4:0.6)) grains +
sulfuric acid droplets



0.2
0.3
0.4
0.5
0.6
0.7
1.0
0.5
0.0
REFLECTANCE
α - S
UV
X-RAY
ORANGE
RED
BROWN
77 K
295 K
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
ABSORPTIVITY, cm^-1

Venera 9



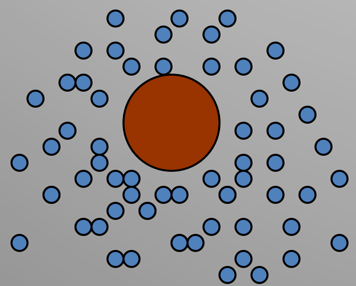
In-situ & orbital measurements inferring sulfur

S elemental	X-ray fluorescence, (Andreichikov et al. 1987; see Krasnopolsky 1989 for review of Vega cloud results)
S elemental	Gas chromatography of cloud refractory material (Porshnev et al. 1987; Surkov et al. 1987)
S_2, S_3	Descent spectra, $S_2 \sim 2 \times 10^{-8}$, $S_3 \sim 3 \times 10^{-11}$ to 10×10^{-11} (Moroz, 1979; Sanko 1980; Moshkin 1983; Krasnopolsky 1987, Malorov et al. 2004)
$S_{2\text{-}8}$, S_8	Descent active absorption spectroscopy, 25 ppm at 45 km, 5 ppm at 25 km (Bertaux et al. 1986) But see Bertaux et al., 1996.
S_{12}	Venera 15 infrared spectroscopy (Spankuch & Schuster 1990)

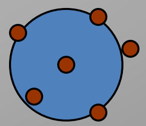
Sulfur Models and Thoughts

$S_8 + S_\mu$	Hapke & Nelson 1974, 1975	One 10-μm S_x grain per 670 H_2SO_4 droplets. (sulfur mass > H_2SO_4 mass!)
S_{2n}	Prinn 1975	Simultaneously suggested sulfur as the absorber from photochemical S_2
S_8	Young 1977	Can be S_8 if concentration increases with depth
Not S_8	Pollack et al., 1979; Tomasko et al.1979	S_8 band edge too sharp, and shifts on cooling. (but UV irradiation shifts in opposite direction)
S_8+S_3+S_4	Toon et al. 1982	Sulfur grains act as condensation nuclii, forming cores with H_2SO_4 mantles. But S_3 and S_4 are unstable.
	Young 1983	Sulfur doesn't "wet" sulfuric acid, so can't form cores. suggests "Gumdrop" Model
	James et al. 1997	H_2SO_4 cloud model seems to require soluble condensation nucleii

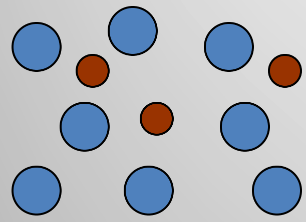
Hapke & Nelson



Young



Two-component cloud

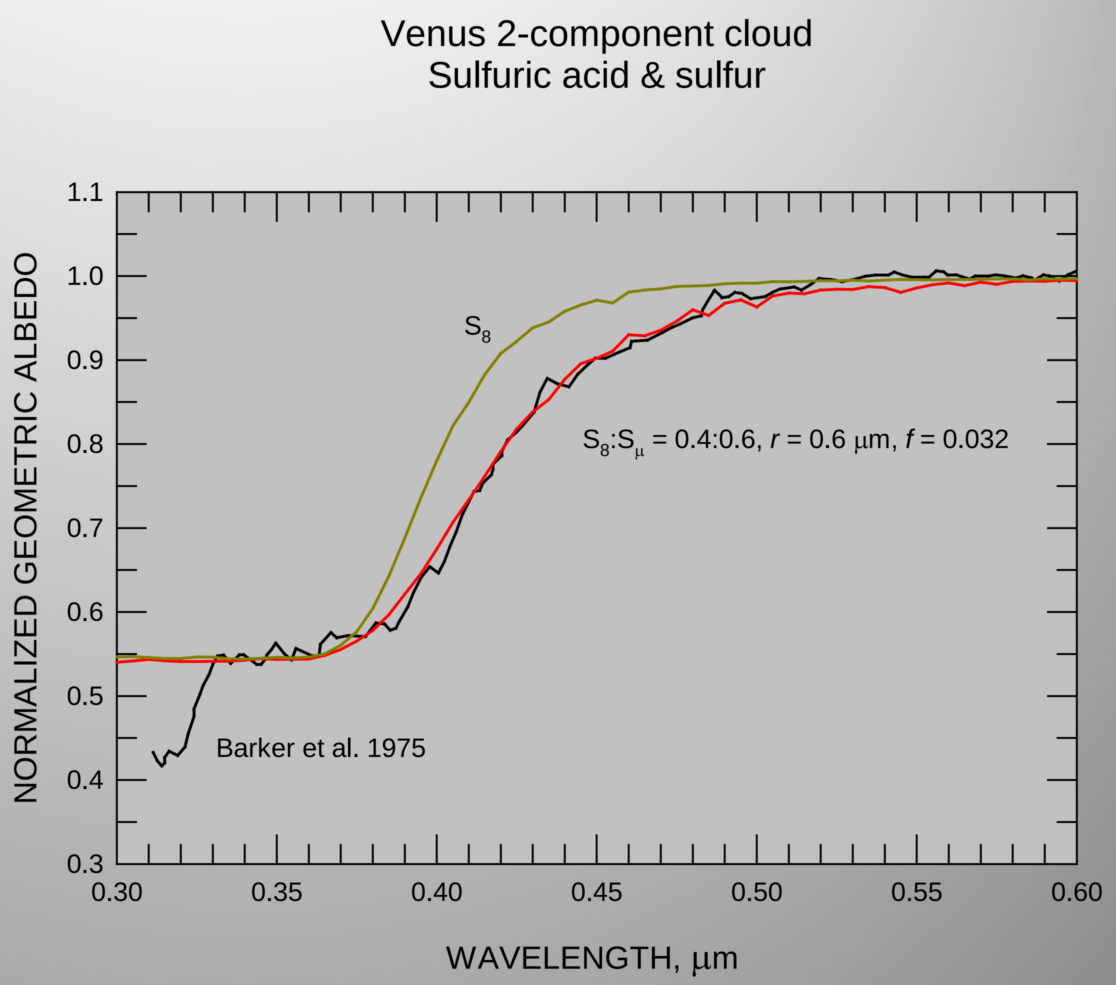


$S_8:S_\mu$ ~ 1:1

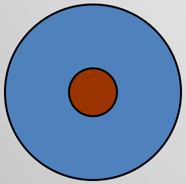
S grain sizes ~ ½ μm

Relative number ~ 3%

Elemental S/H_2SO_4 ~ 1%



Composite particle

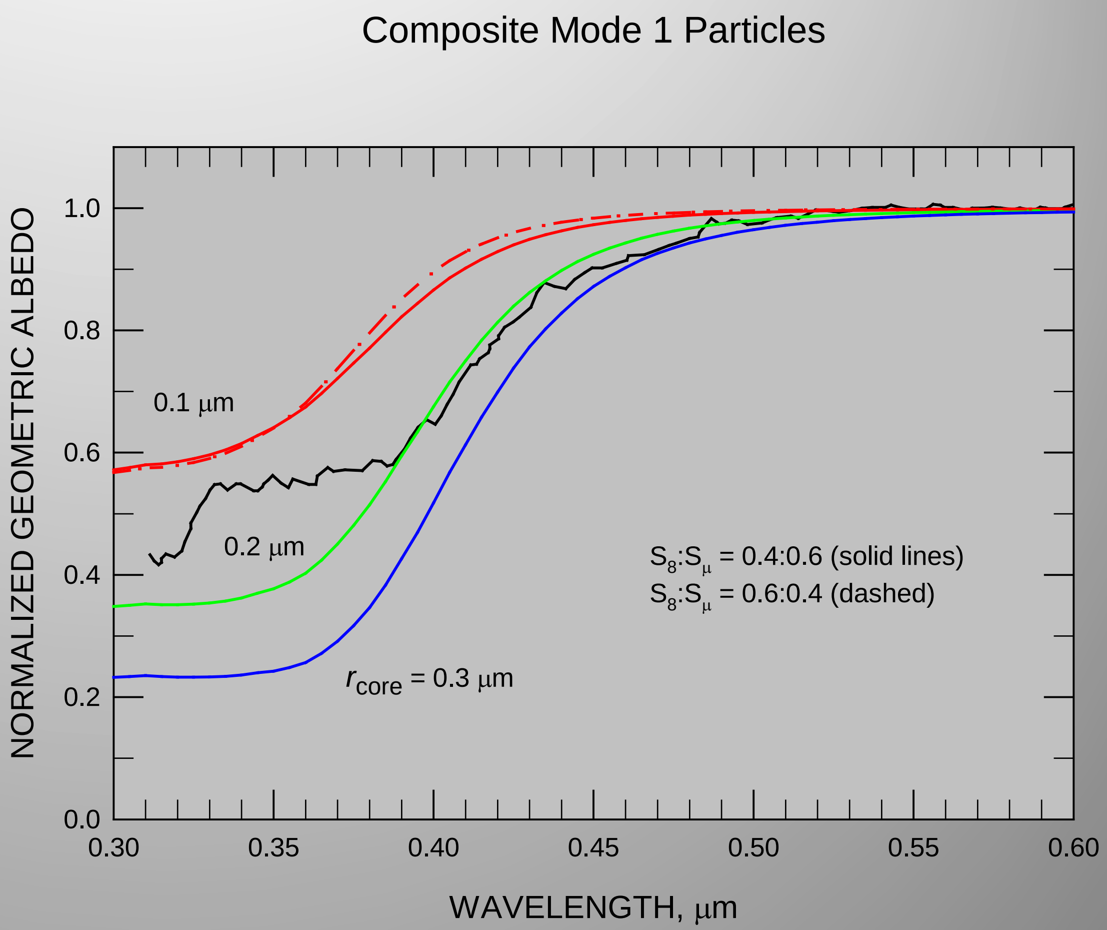


If one assumes that all cloud particles are nucleated with monodisperse soluble sulfur grains (e. g. thionates), then

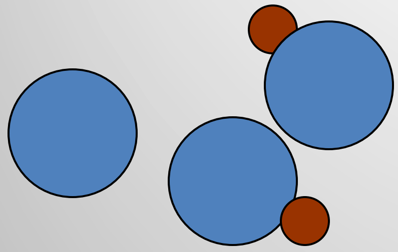
The models don't match observations!

Inclusion of smaller sulfur grains may help. Probably would require a bi-modal distribution.

Or allow the presence of non-nucleated droplets.



Gumdrop Model



Droplets “decorated” with many small sulfur grains does not work (too much absorption).

OK for low grain/droplet ratio, with some fraction “decorated” with one S grain, most not.

Elemental S/H_2SO_4 ~ 1%

Results preliminary; more work needed for very small S grains.

"Gumdrop" model for sulfur-sulfuric acid aerosols