Atmospheric chemistry and aerosols (I)

Composition of planetary atmospheres

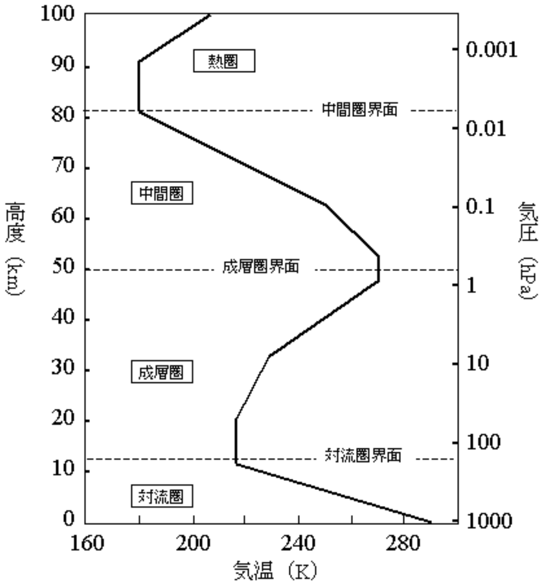
Object	Mass (kilograms)	Carbon Dioxide	Nitrogen	Oxygen	Argon	Methane	Sodium	Hydrogen	Helium	Other
Sun	$3.0\text{x}10^{30}$							71%	26%	3%
Mercury	1000			42%			22%	22%	6%	8%
Venus	$4.8\text{x}10^{20}$	96%	4%							
Earth	$1.4\text{x}10^{21}$		78%	21%	1%					<1%
Moon	100,000				70%		1%		29%	
Mars	$2.5\text{x}10^{16}$	95%	2.7%		1.6%					0.7%
Jupiter	$1.9\text{x}10^{27}$							89.8%	10.2%	
Saturn	$5.4\text{x}10^{26}$							96.3%	3.2%	0.5%
Titan	$9.1\text{x}10^{18}$		97%			2%				1%
Uranus	$8.6\text{x}10^{25}$					2.3%		82.5%	15.2%	
Neptune	$1.0\text{x}10^{26}$					1.0%		80%	19%	
Pluto	$1.3\text{x}10^{14}$	8%	90%			2%				

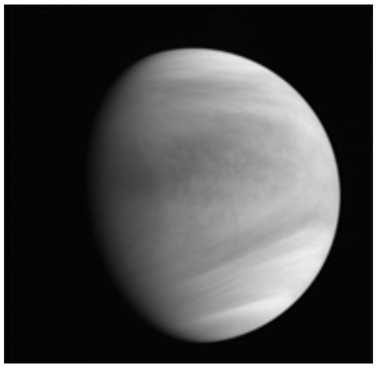
from NASA HP

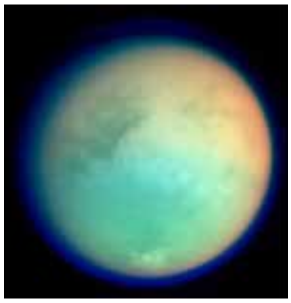
photosynthesis

$$6\ CO_2 + 6H_2O + \text{energy} \longrightarrow C_6H_{12}O_6 + 6\ O_2$$

Need for understanding chemistry







Chemical kinetics

A reaction between reactants A and B to form product C:

A + B → C reaction rate = k [A] [B]

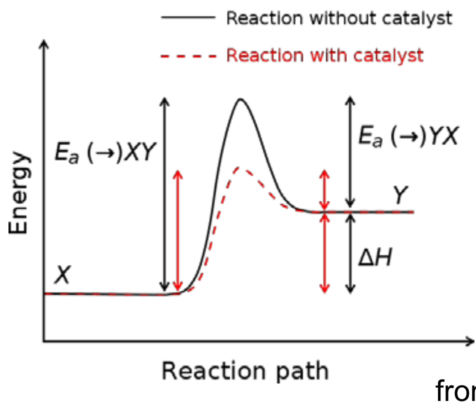
A + B + M → C + M reaction rate = k [A] [B] [M]

M is any inert molecule that can remove the excess energy.

k is the reaction rate constant that usually depends on the temperature as (Arrhenius equation):

$$k = A \exp\left(-\frac{E_a}{k_B T}\right)$$

where E_a is the activation energy.



from Wikipedia

Production and destruction of ozone

Chapman theory

$O_2 + h\nu \rightarrow 2O$
$O + O_2 + M \rightarrow O_3 + M$

$3O_2 \rightarrow 2O_3$

$O_3 + h\nu \rightarrow O + O_2$
$O + O_3 \rightarrow 2O_2$

$2O_3 \rightarrow 3O_2$

- Chapman theory predicts an ozone amount of several times larger than the observations.
- Other loss mechanisms are required.

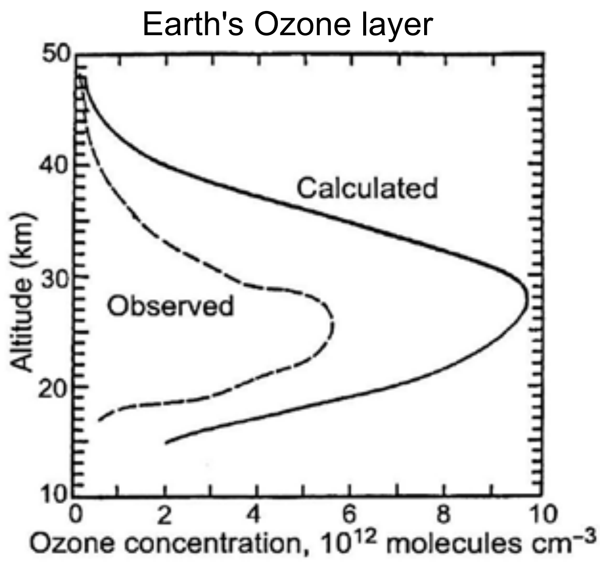


Figure 3.1 An ozone profile calculated with the Chapman reactions at the equator overestimates the ozone compared with observations over Panama at 9° N on November 13, 1970. The reason is that natural catalysts that destroy ozone are omitted from the oxygen-only Chapman reactions. (Adapted from Seinfeld and Pandis (1998). Reproduced with permission. Copyright 1998, John Wiley and Sons.)

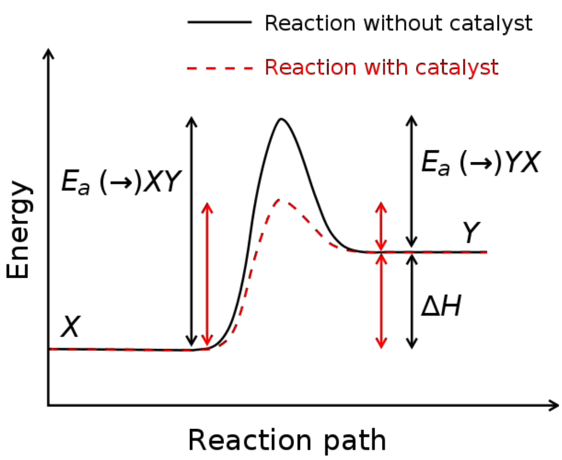
Catling & Kasting (2017)

Catalytic cycles

$X + O_3 \rightarrow XO + O_2$
$XO + O \rightarrow X + O_2$

$O + O_3 \rightarrow 2O_2$

X : Free radical such as OH, NO, Cl, Br



The net result of the catalytic cycle is to remove O and O_3 rapidly.

Stability of CO_2 atmosphere

$$
\begin{array}{l}
2(CO_2 + h\nu \rightarrow CO + O) \\
O + O + M \rightarrow O_2 + M \\
\hline
\text{Net: } 2CO_2 \rightarrow 2CO + O_2
\end{array}
$$

The reaction $CO + O \rightarrow CO_2$ is very slow (spin forbidden).

Mars and Venus atmospheres are expected to be converted to CO and O_2 in 6000 years.

Catalytic cycle on Mars ?

On Mars, OH radicals are thought to play crucial roles.

$$H_2O + h\nu \rightarrow OH + H$$

McElroy and Donahue [1972]

Production of OH

$$H + O_2 + M \rightarrow \boxed{HO_2} + M$$
$$\boxed{HO_2} + O \rightarrow \boxed{OH} + O_2$$

Production of CO_2

$$CO + \boxed{OH} \rightarrow CO_2 + H,$$

Net reaction

$$CO + O + M \rightarrow CO_2 + M.$$

Parkinson and Hunten [1972]

Production of OH

$$2(H + O_2 + M \rightarrow \boxed{HO_2} + M)$$
$$\boxed{HO_2} + \boxed{HO_2} \rightarrow \boxed{H_2O_2} + O_2$$
$$\boxed{H_2O_2} + h\nu \rightarrow \boxed{OH} + OH$$

Production of CO_2

$$2(CO + \boxed{OH} \rightarrow CO_2 + H),$$

Net reaction

$$2CO + O_2 \rightarrow 2CO_2.$$

Atreya and Gu (1994)

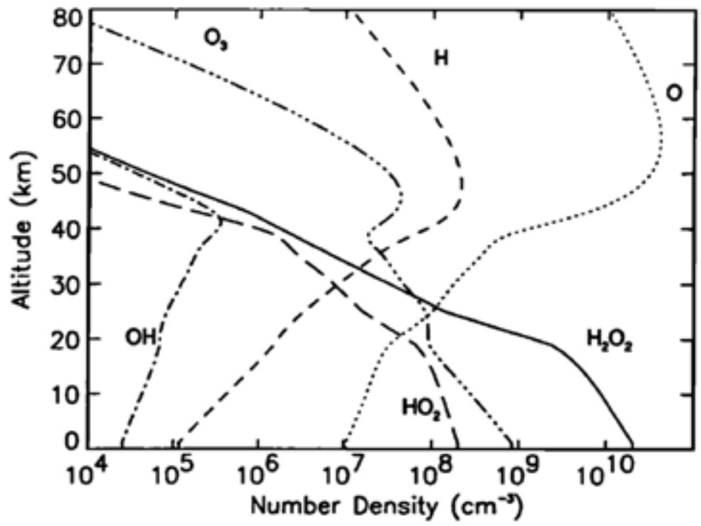


Figure 8. Distribution of key constituents based on the nominal model ($H_2O = 150$ ppm, $K = 10^6\ cm^2 s^{-1}$, $\tau_d = 0.4$; see text).

Photochemistry is effective even near the surface on Mars because of the thin atmosphere.

Catalytic cycle on Venus?

Cl radicals are thought to play crucial roles.

$$
\begin{array}{lr}
Cl + CO + M \rightarrow \boxed{ClCO} + M & (27) \\
\boxed{ClCO} + O \rightarrow CO_2 + Cl & (28) \\
\hline
\text{Net: } CO + O \rightarrow CO_2 & (E)
\end{array}
$$

$$
\begin{array}{lr}
\boxed{Cl} + CO + M \rightarrow \boxed{ClCO} + M & (27) \\
\boxed{ClCO} + O_2 + M \rightarrow \boxed{ClC(O)OO} + M & (29) \\
\boxed{ClC(O)OO} + \boxed{Cl} \rightarrow CO_2 + ClO + \boxed{Cl} & (30) \\
ClO + O \rightarrow \boxed{Cl} + O_2 & (26) \\
\hline
\text{Net: } CO + O \rightarrow CO_2 & (G1)
\end{array}
$$

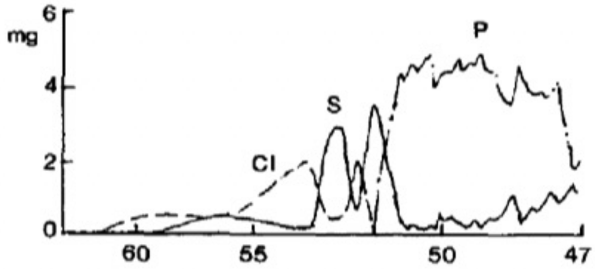
$$
\begin{array}{lr}
\boxed{Cl} + CO + M \rightarrow \boxed{ClCO} + M & (27) \\
\boxed{ClCO} + O_2 + M \rightarrow \boxed{ClC(O)OO} + M & (29) \\
\boxed{ClC(O)OO} + O \rightarrow CO_2 + O_2 + \boxed{Cl} & (31) \\
\hline
\text{Net: } CO + O \rightarrow CO_2 & (G2)
\end{array}
$$

$$
\begin{array}{lr}
\boxed{Cl} + CO + M \rightarrow \boxed{ClCO} + M & (27) \\
\boxed{ClCO} + O_2 + M \rightarrow \boxed{ClC(O)OO} + M & (29) \\
\boxed{ClC(O)OO} + h\upsilon \rightarrow CO_2 + ClO & (32) \\
ClO + O \rightarrow \boxed{Cl} + O_2 & (26) \\
\hline
\text{Net: } CO + O \rightarrow CO_2 & (G3)
\end{array}
$$

Mills et al. (2007)

Mills et al. (2007)

Vega-2 X-ray spectrometer result (Andreychikov et al. 1987)



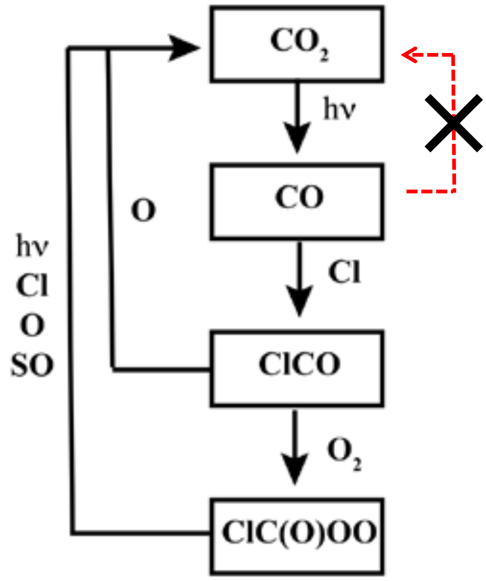
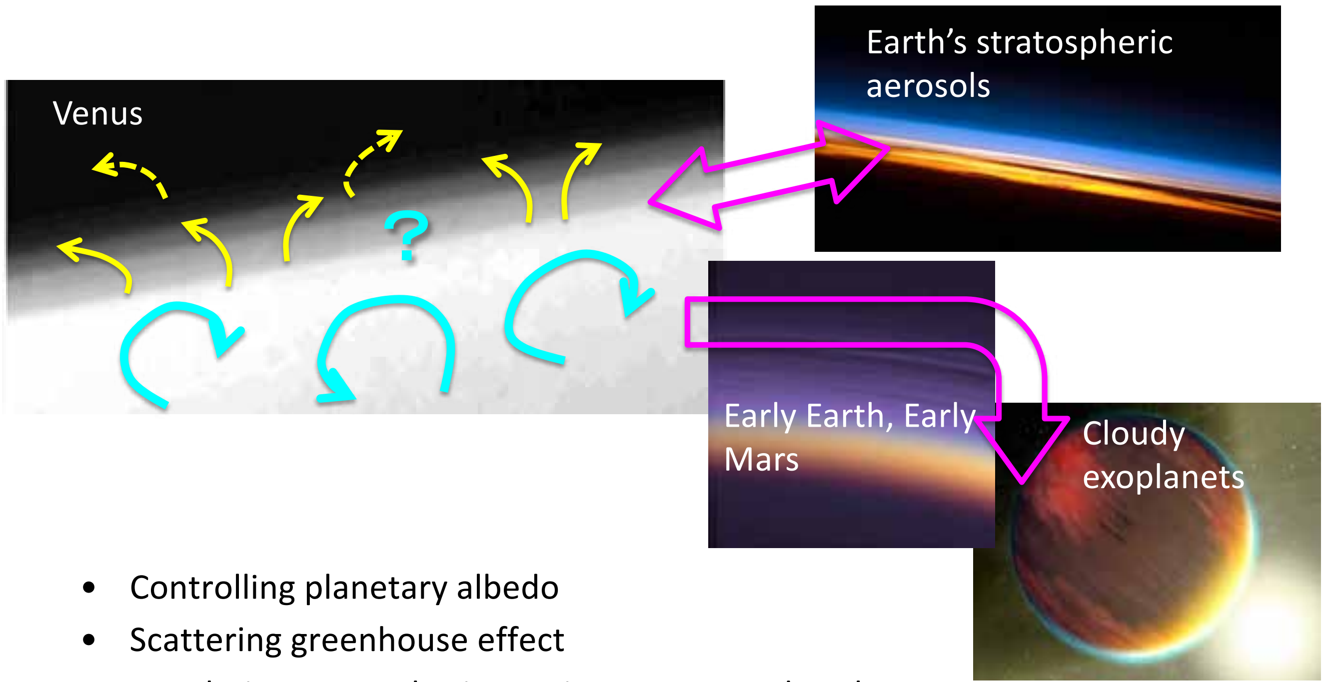


Figure 3. Schematic showing primary pathways for production of CO_2 via chlorine chemistry. The reaction $ClCO + O \rightarrow CO_2 + Cl$ accounts for 15 and 20% of the column total CO_2 production in the $+0.5\sigma$ and $+2.0\sigma$ models from Table 5, respectively.

ClCO, $ClCO_3$ and other key species have never been observed.

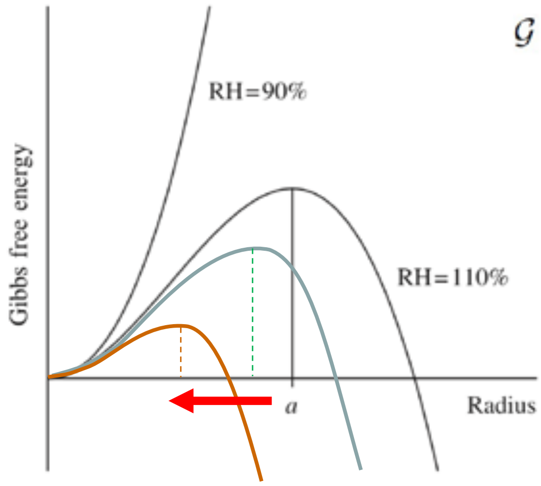
Clouds/aerosols



- Controlling planetary albedo
- Scattering greenhouse effect
- Regulating atmospheric species transported to the upper atmosphere

Cloud formation

Andrews (2010)



Gibbs free energy

$$\mathcal{G} - \mathcal{G}_0 = -\frac{4}{3}\pi a^3 \rho_l R_v T \ln\left(\frac{e}{e_s(T)}\right) + 4\pi a^2 \gamma$$

a : radius of droplet
e : partial vapor pressure
e_s : saturation vapor pressure
γ : surface tension
ρ_l : liquid density
R_v : gas constant
T : temperature

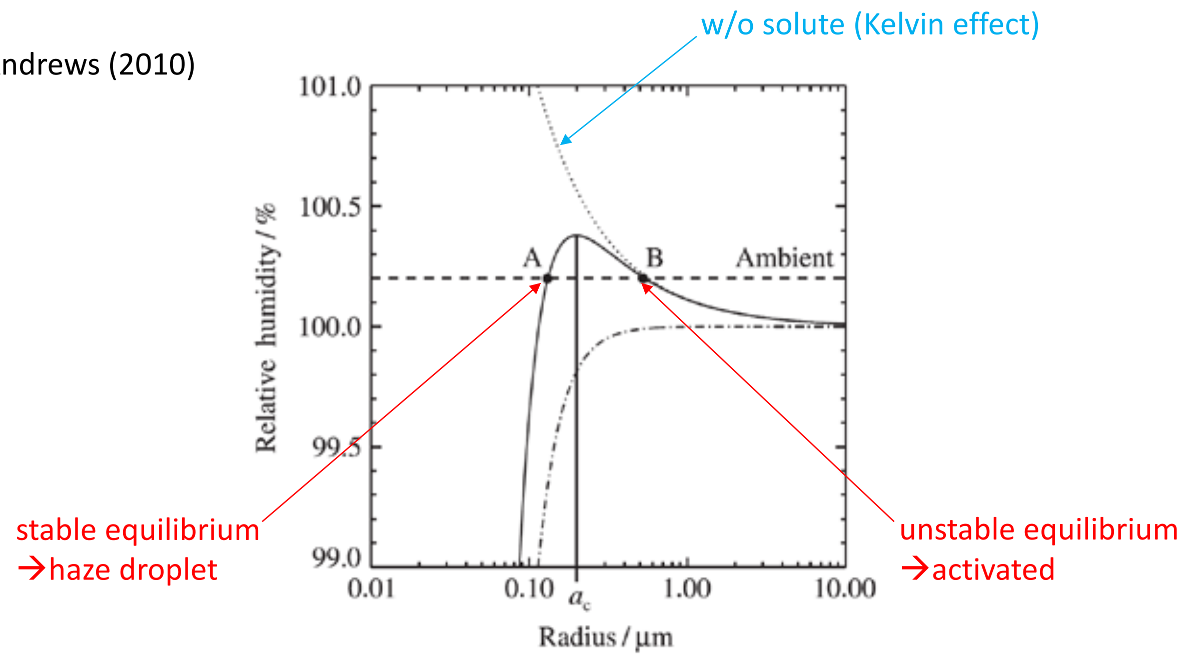
Pure water:

equilibrium radius	relative humidity(RH)
0.01 µm	→ 112%
0.1 µm	→ 101%
flat surface	→ 100%

If a cloud droplet is to survive, it must somehow attain a radius greater than the equilibrium radius a corresponding to the ambient relative humidity
→ Need for condensation nucleus

Role of soluble cloud condensation nuclei (CCN)

Andrews (2010)



The Köhler curve (solid) for the relative humidity RH = e/e_s over a spherical droplet of water containing solute, as a function of droplet radius a, at 5 °C. The solute is taken to be 10^{-19} kg of NaCl. The Kelvin factor is given by the dotted curve and the Raoult factor is given by the dash-dotted curve. The thick horizontal dashed line and points A and B are discussed in the text.

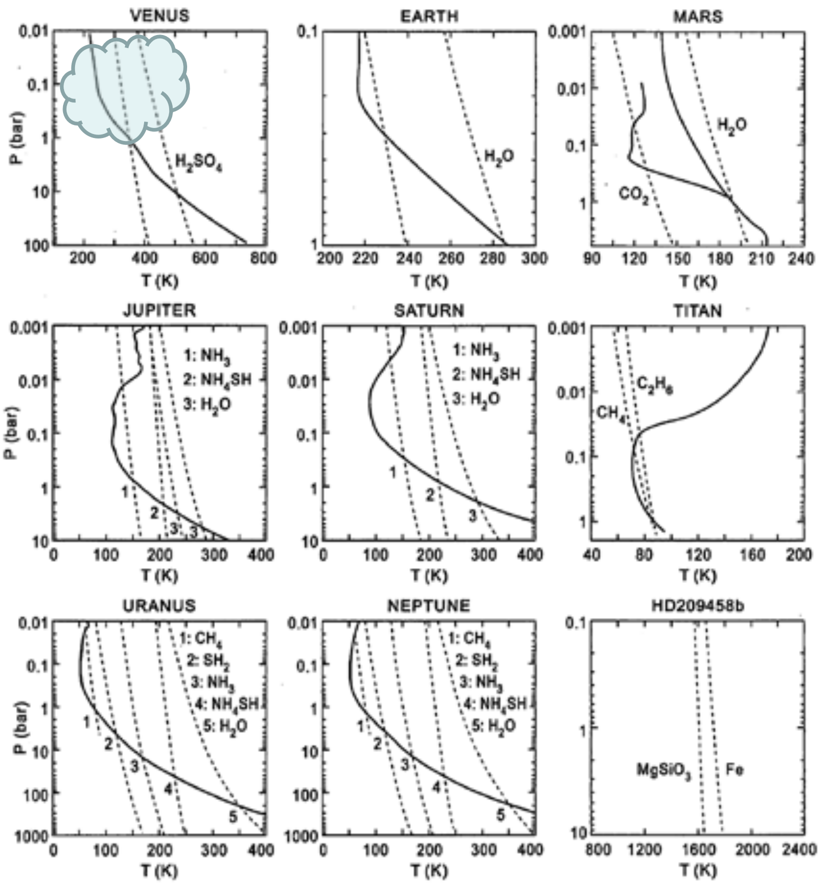
Composition of CCN

Example of the composition of ice forming nuclei in Earth's troposphere (Pruppacher & Klett 1997)

TABLE 9.6
Composition of ice forming nuclei derived from aerosolized soil in Montana (from Rosinski *et al.*, 1981).

Chemical composition	Aerosol particles number	Aerosol particles %	Ice-forming nuclei active at temperature −12°C number	−12°C %	−15°C number	−15°C %	−20°C number	−20°C %
Clay minerals:								
montmorillonite	194	24	28	18	17	13	41	28
feldspar	287	36	74	48	41	32	54	38
illite	163	20	37	24	39	31	28	19
miscellaneous	27	3	8	5	19	15	10	7
Organic particles	139	17	7	5	12	9	11	8
Number of particles: analyzed	810		154		128		144	
Mixed particles containing:								
NaCl	7		14	9	28	22	21	15
CuX	2		1		0		1	
$FeO_x.nH_2O$	-		7	5	12	9	11	8
Total	9		22	14	40	31	33	23

- The characteristics of CCN on other planets are totally unknown.
- Dust particles will serve as CCN on Mars.
- Galactic cosmic rays may also work. Cosmic rays increase small ions (charged molecules or charged small clusters of molecules) in the atmosphere, leading to increase in the nucleation rate of aerosol particles.



Catling & Kasting (2017)

The solid curves are the typical vertical profiles of pressure versus temperature. Dashed curves are the saturation vapor pressure curves for various condensables.

Particles condense when the partial pressure reaches the saturation vapor pressure.

H_2SO_4 clouds of Venus

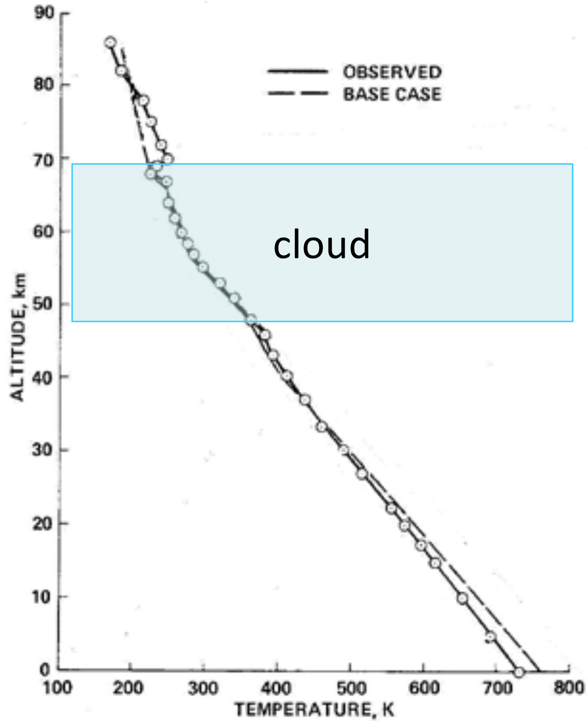
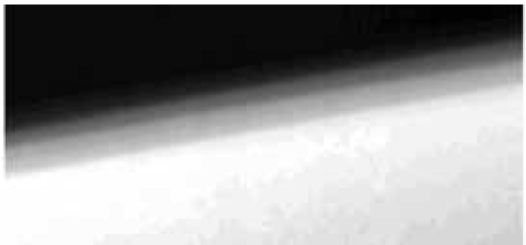


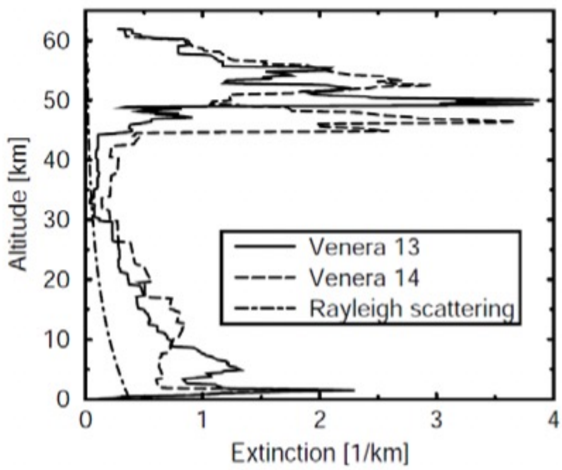
Fig. 2. Comparison between the observed temperature structure of Venus' lower atmosphere and that of several models, which are described in the main text.



- Solar energy flux reaching the Venus surface ($17 W/m^2$) is much less than that of the Earth ($168 W/m^2$).
- Greenhouse effect of massive CO_2 and small amount of H_2O explains the high temperature.

Pollack et al. (1980)

Extinction profiles as retrieved from Venera 13 & 14 spectrophotometer data at 700-710 nm (Grieger et al. 2003)



Tomasko et al. (1980)

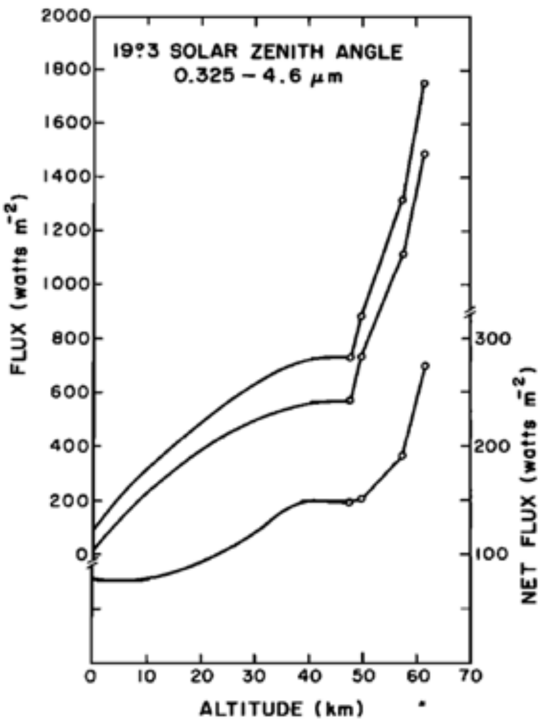
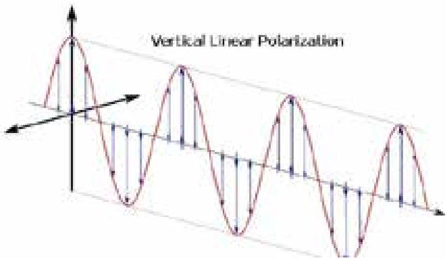


Fig. 19. The total (0.325–4.6 μm) upward, downward, and net flux profiles near the Venera 11 and 12 entry sites ($\theta_S = 19.3°$).

Polarization of sunlight reflected by Venus



Hansen & Hovenier (1974)

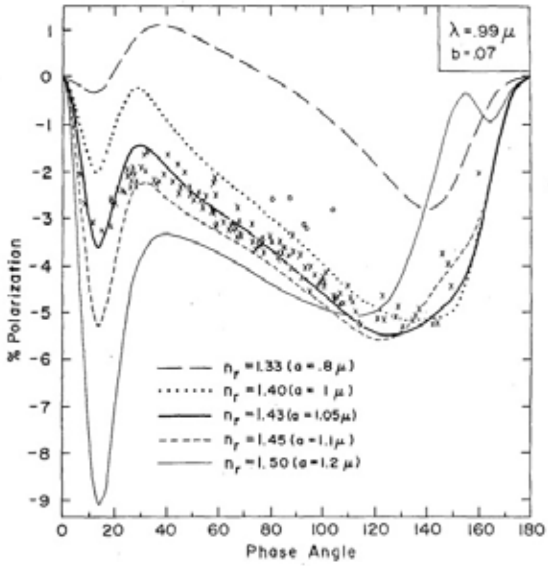


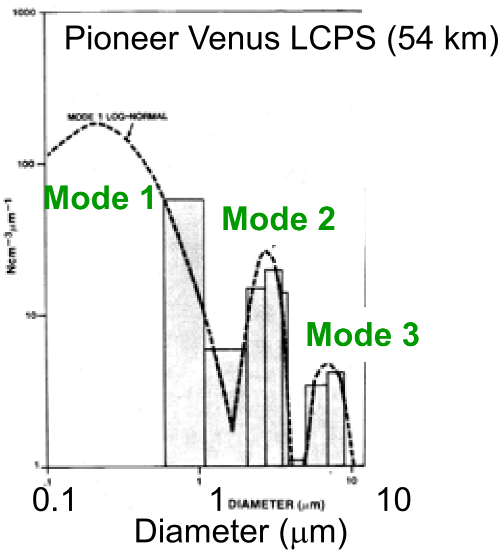
FIG. 7. Observations and theoretical computations of the polarization of sunlight reflected by Venus at λ = 0.99 μm. The observations were made with an intermediate bandwidth filter, the ×'s being obtained by Coffeen and Gehrels (1969) in 1959–67 and by Coffeen (cf. Dollfus and Coffeen, 1970) from 1967 to March 1969, and the ○'s being obtained by Coffeen (cf. Dollfus and Coffeen, 1970) in May–July, 1969. The theoretical curves are for spherical particles having the size distribution (8) with b = 0.07. The different theoretical curves are for various refractive indices, the effective particle radius being selected in each case to yield closest agreement with the observations for all wavelengths.

Refractive index = 1.44
→consistent with H_2SO_4-H_2O solution

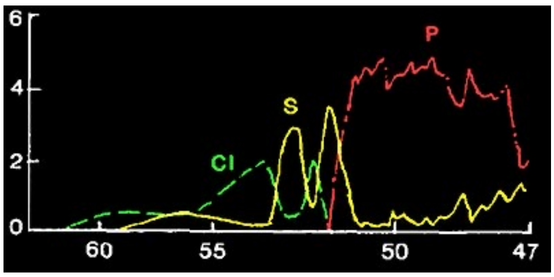
Effective radius ~ 1 μm

Microphysical properties of Venus clouds

- H_2SO_4-H_2O droplets with radii r < 5 μm
- Smallest mode (including sub-cloud haze) might be condensation nuclei whose composition is unknown.
- Size distribution is variable.

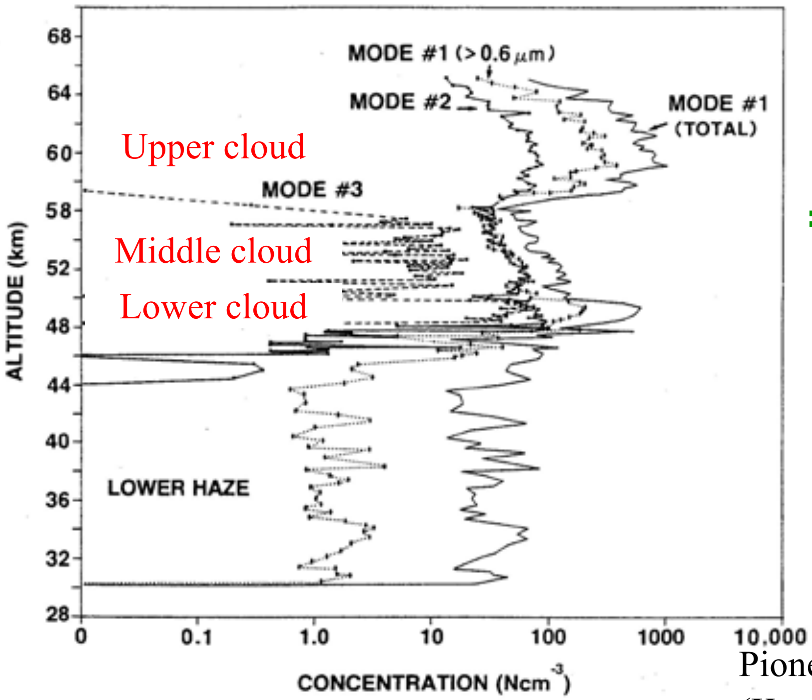


Venera-13 Lander



Cl ? S ? P ?

Three-layered structure of Venusian clouds

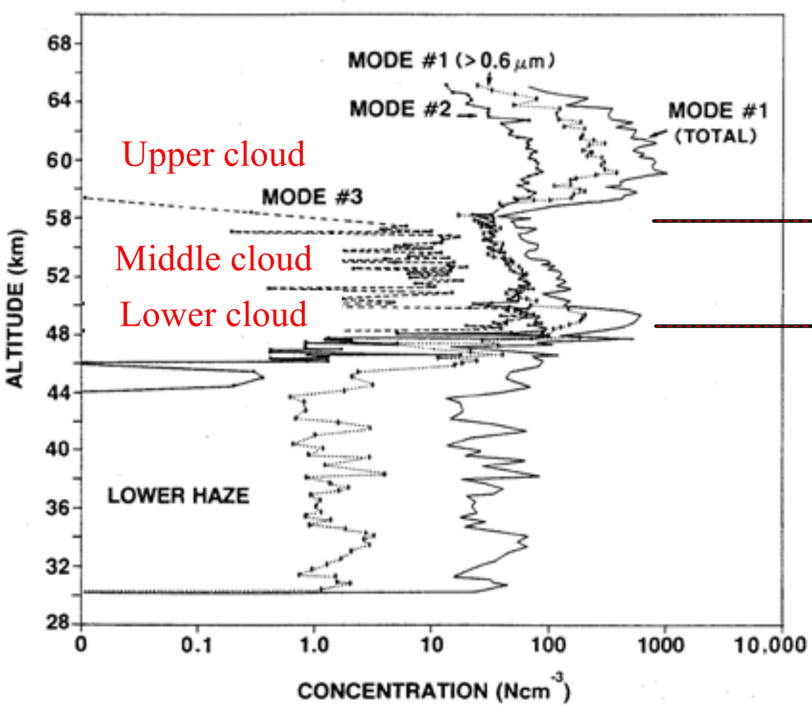


The bulk of the mass exists in Mode 2 (r ~ 1 μm)

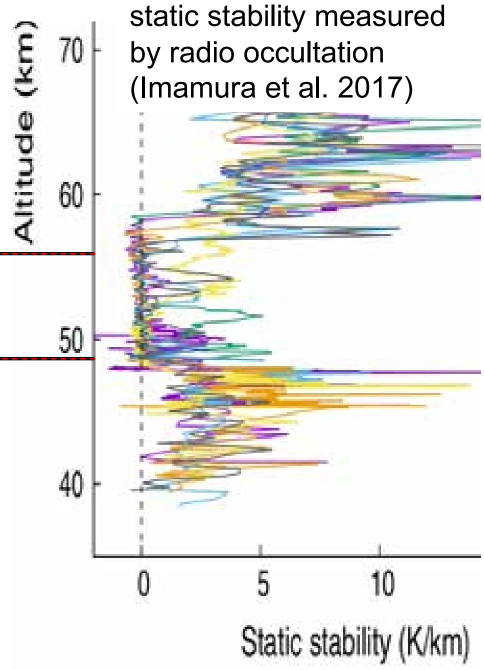
The bulk of the mass exists in Mode 2 and 3 (r = 1-5 μm)

Pioneer Venus LCPS
(Knollenberg and Hunten, 1980)

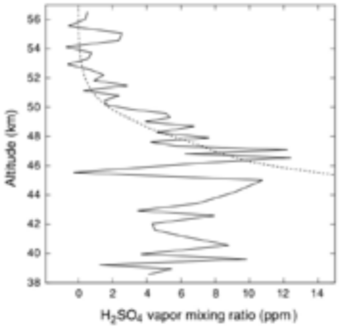
Three-layered structure of Venusian clouds



static stability measured by radio occultation (Imamura et al. 2017)



H_2SO_4 vapor in Venusian atmosphere



Imamura et al. (2017)

Measurement by radio occultation

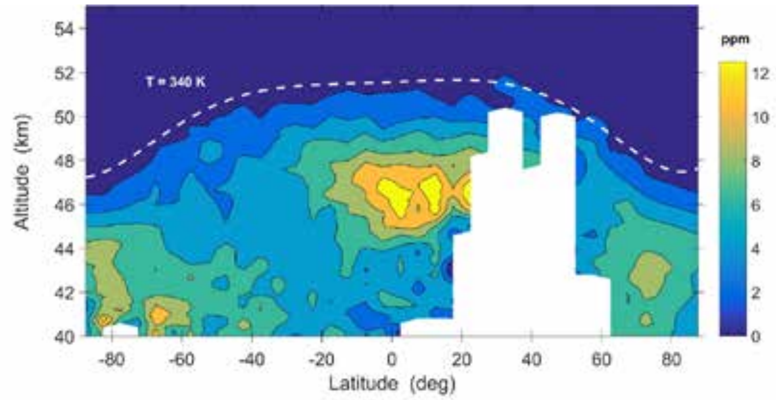


Fig. 9. Zonally and time-averaged sulfuric acid vapor distribution in the Venus lower atmosphere at all latitudes between the years 2006 and 2014 (lower panel). The hemispheres were subdivided into equal latitudinal bins of 5° each and $H_2SO_4(g)$ profiles located within each bin were averaged to one mean profile. The number of data samples used for averaging is shown in the upper panel. The white dashed line in the lower panel shows the isotherm at $T = 340$ K derived from VeRa X-band radio occultation data from the same period. The $H_2SO_4(g)$ values above this isotherm are generally as high as their uncertainties. Below the isotherm the values are higher than their uncertainties. The lack of measurements at northern mid-latitudes between 20° and 60° is a consequence of the VEX orbit geometry.

Oschlisniok et al. (2021)

Sulfur-rich atmosphere: origin of H_2SO_4

SO_2 measurements by Vega landers

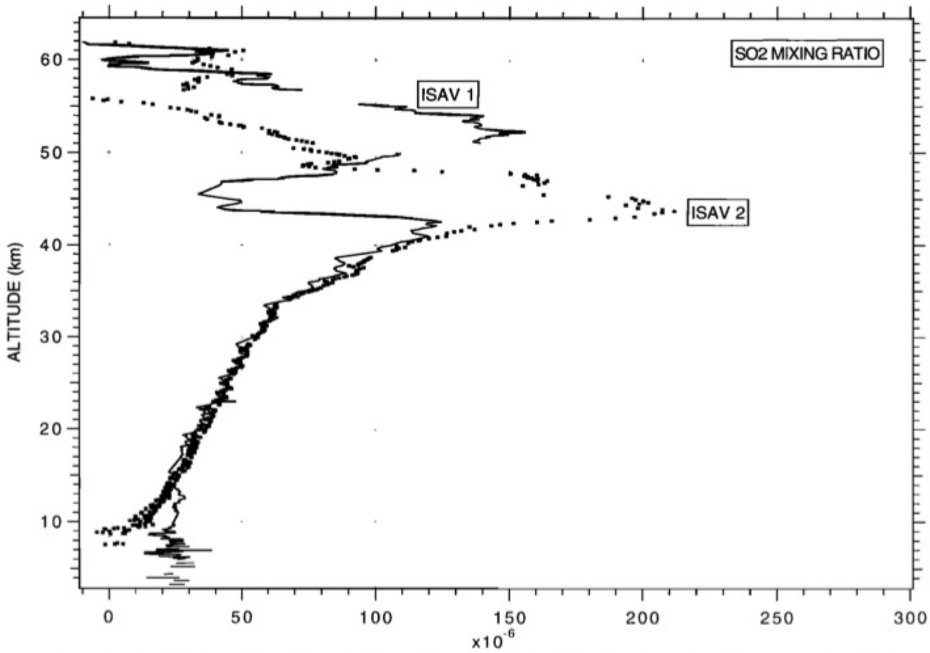


Figure 24. The SO_2 mixing ratio vertical profile retrieved for ISAV 2 (data points) is compared to that determined for ISAV 1. There is a large difference of structure above 40 km, while the profiles are nearly identical below 40 km. A peak of 210 ppm is observed at 43 km in the ISAV 2 data.

Bertaux et al. (1996)

Origin of clouds

Photochemistry above clouds

Scenario #1 (Net reaction driven by catalytic cycles including ClOx, HOx, NOx)

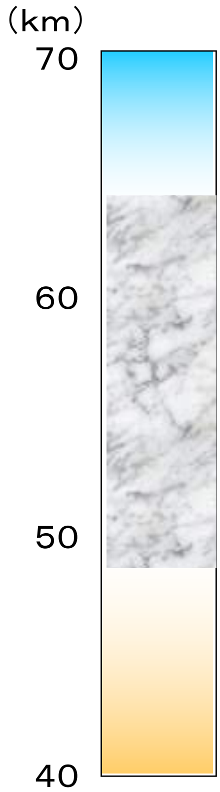
$$2CO_2 + h\nu \rightarrow 2CO + O_2$$
$$CO + SO_2 + O_2 + h\nu \rightarrow CO_2 + SO_3$$
$$\overline{CO_2 + SO_2 + h\nu \rightarrow CO + SO_3}$$

Scenario #2

$$SO_2 + h\nu \rightarrow SO + O$$
$$SO + h\nu \rightarrow S + O$$
$$SO_2 + O \rightarrow SO_3 \quad (\times 2)$$
$$\overline{3\,SO_2 + h\nu \rightarrow S + 2SO_3}$$

- SO_3 rapidly reacts with H_2O: $\boxed{SO_3 + H_2O \rightarrow H_2SO_4}$
- Elemental sulfur (S) can serve as condensation nuclei.

Origin of clouds



H_2SO_4 vapor and H_2O vapor condenses onto condensation nuclei.

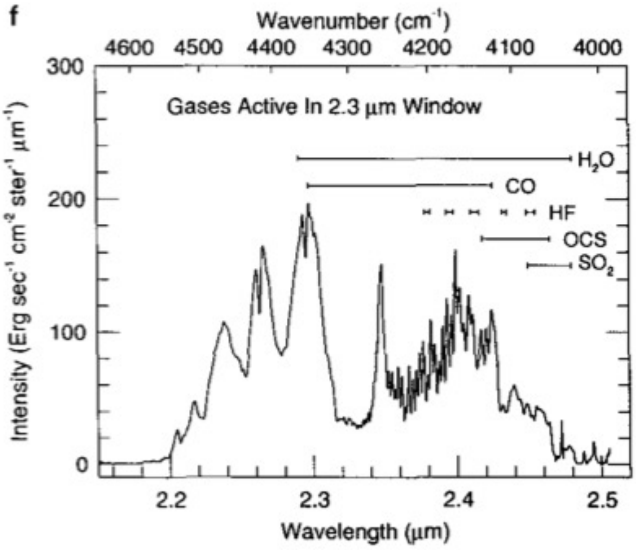
Growth of particles via collision during gravitational sedimentation

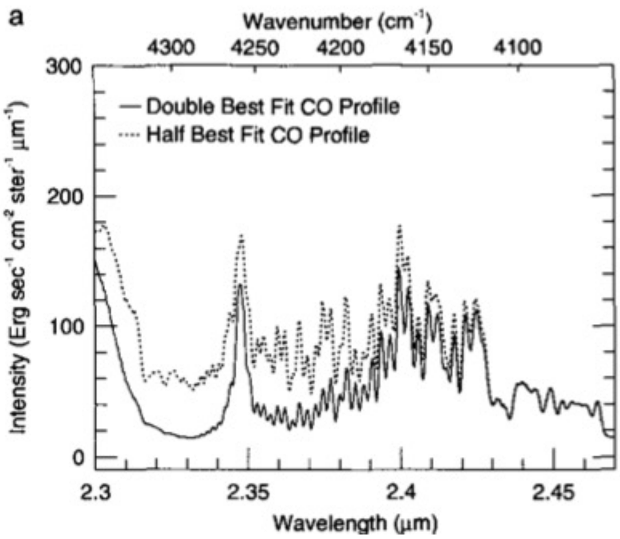
Evaporation around 50 km altitude due to high temperature

Thermochemistry below clouds (Net reaction driven by catalytic cycles

$$H_2SO_4 \rightarrow H_2O + SO_3$$
$$SO_3 + CO \rightarrow CO_2 + SO_2$$
$$SO_3 + OCS \rightarrow CO_2 + (SO)_2 \qquad \text{etc}$$
$$\overline{H_2SO_4 + 4CO \rightarrow H_2O + 3CO_2 + OCS}$$

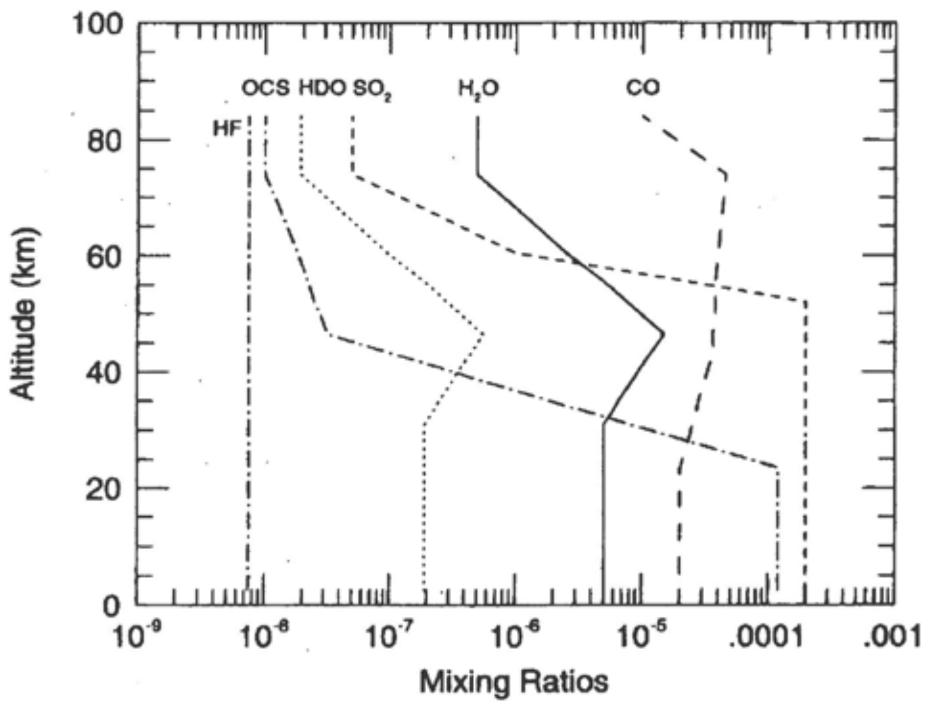
Ground-based observations of cloud-related gaseous species





Pollack et al., Icarus 103, 1, 1993

Retrieved vertical profiles



Pollack et al., Icarus 103, 1, 1993

Sedimentation of particles

Stokes velocity for a spherical particle

$$w_{\mathrm{sed}} = \frac{g\rho d^2}{18\eta}$$

g : gravitational acceleration
ρ : mass density of particle
d : diameter of particle
η : viscosity coefficient of air

comparable

Time constant of Hadley circulation
τ ~ 100 Earth days (from energy budget)
→ Vertical flow velocity ~ H/τ ~ 1 mm/s

Sedimentation velocity of droplets in Venusian atmosphere
(Imamura & Hashimoto 1998)

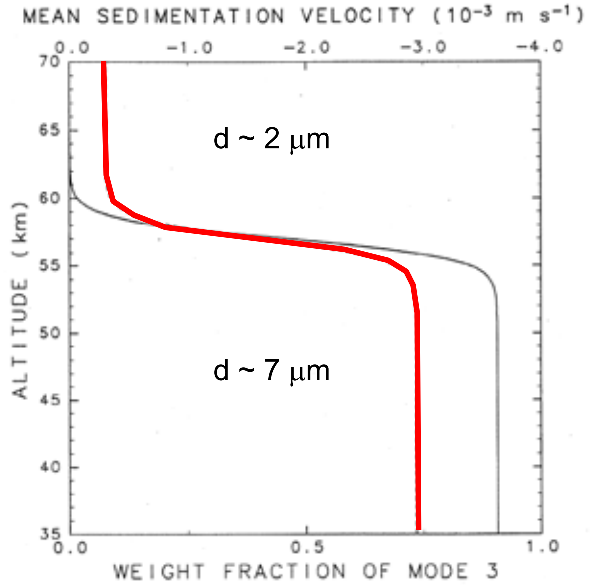
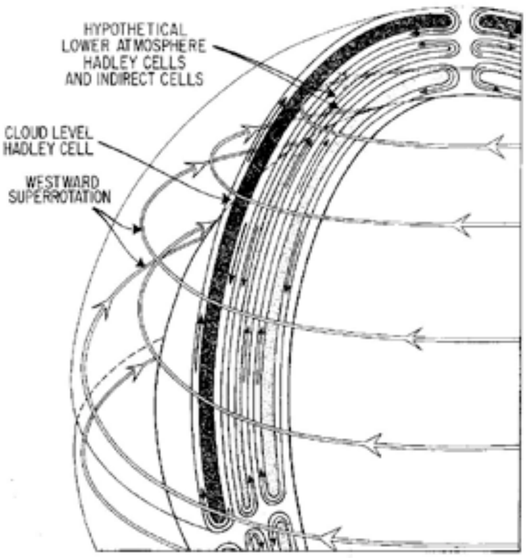
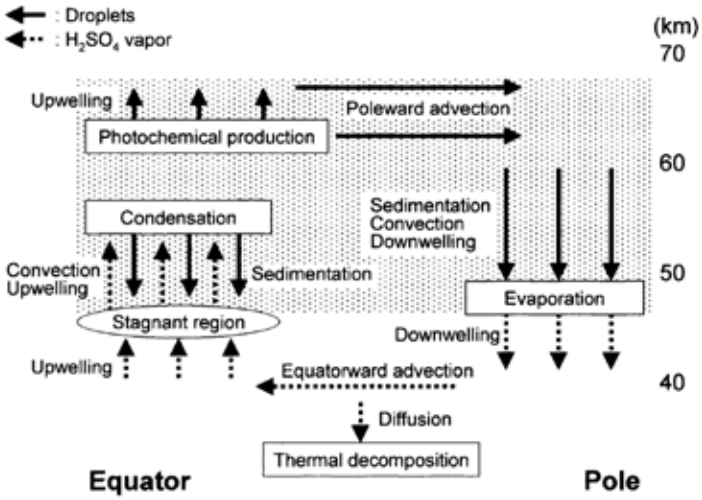


Figure 2. Fraction of Mode 3 particles by weight in the cloud (solid curve) adopted in the model after the observation by the Pioneer Venus particle size spectrometer, and the calculated mean sedimentation velocity W_{sed} (dashed curve). The cloud mass is assumed to be composed of particles of fixed radii, Mode 2 ($r = 1.15$ μm) and Mode 3 ($r = 3.65$ μm).

Possible role of planetary-scale meridional circulation

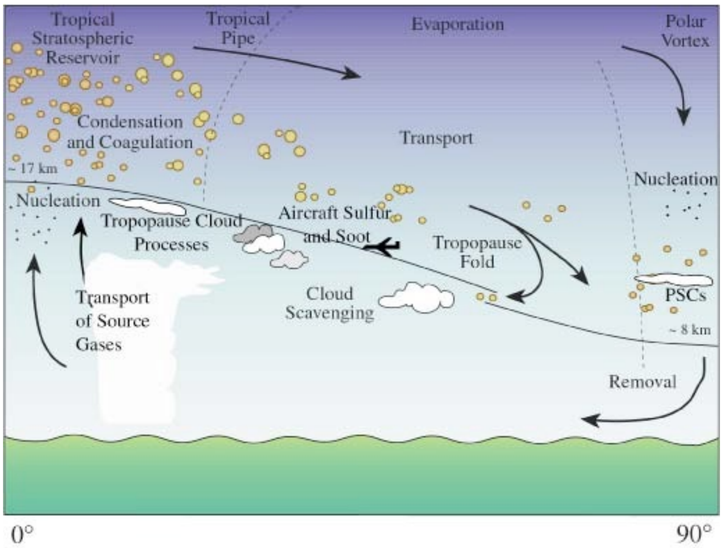


Schubert (1983)



Imamura & Hashimoto (2001)

Lifecycle of Earth's stratospheric aerosols



Hamill et al. (1997)

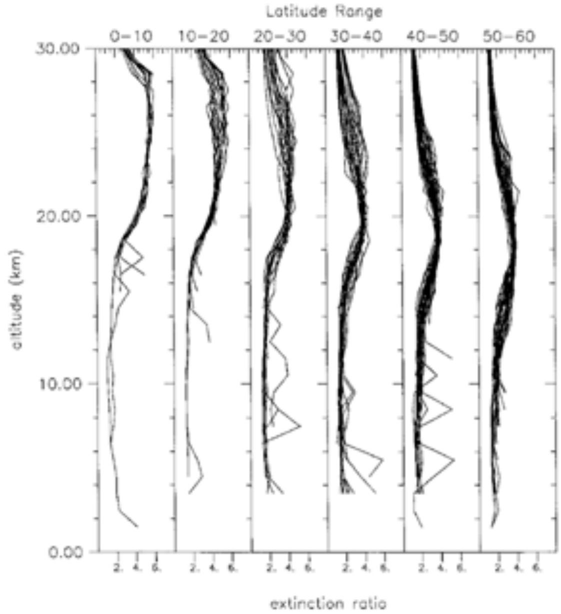
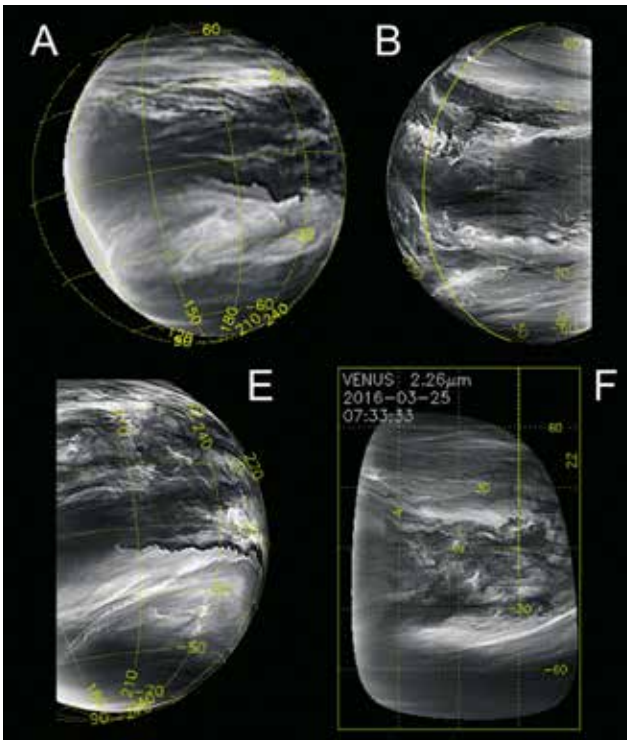


FIG. 9. Extinction ratios from the SAGE II satellite system in various latitude ranges. The extinction values were measured in April 1989 in the Southern Hemisphere. We have removed extinction ratios greater than 7 at lower altitudes for these are indications of tropospheric clouds.

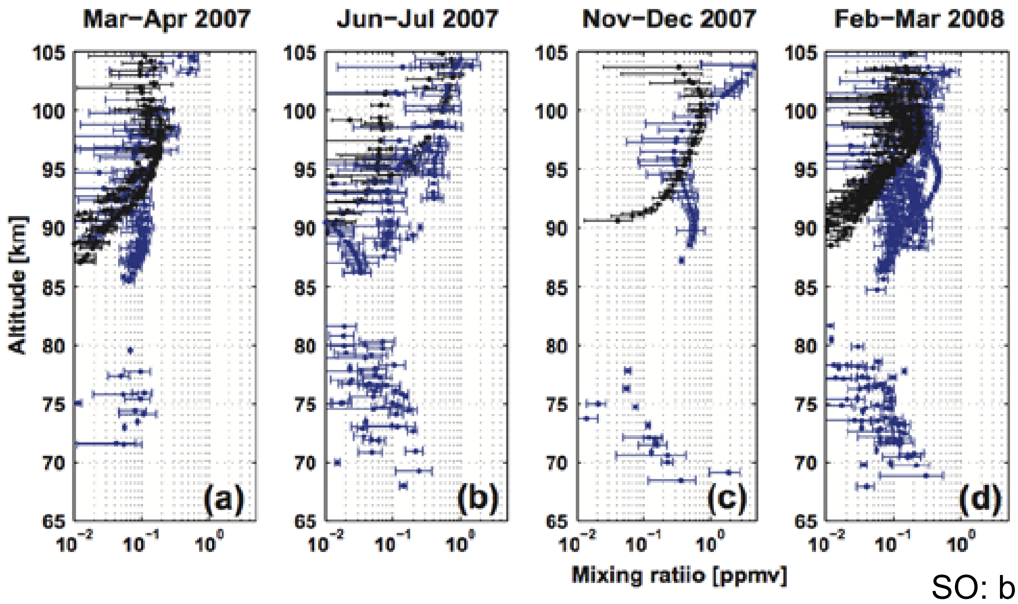
Observed cloud morphology



Peralta et al. (2018)

Equatorial dark clouds might be produced by large-scale upwelling near the cloud base

SO, SO_2 profiles above cloud observed by Venus Express solar occultations (Belyaev et al. 2011)



SO: black
SO_2: blue

- Enhancement at high altitudes cannot be explained by traditional photochemical models.

Chemical model of Venusian stratosphere (Zhang et al. 2012)

Artificial H_2SO_4 source added above 90 km:

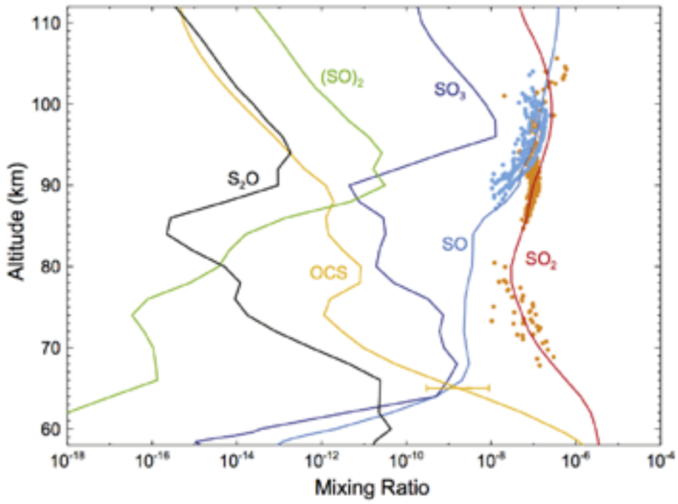
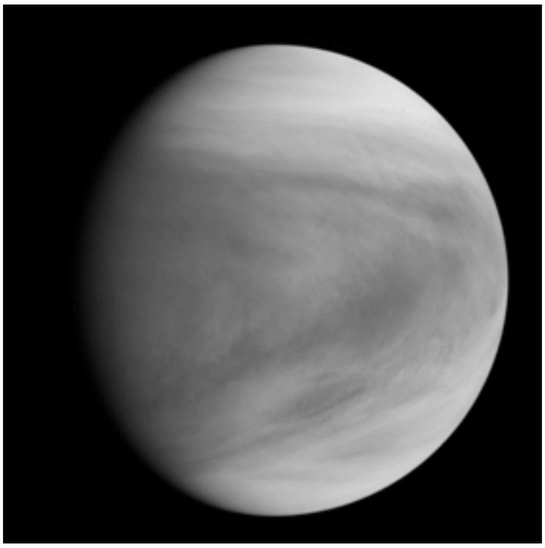


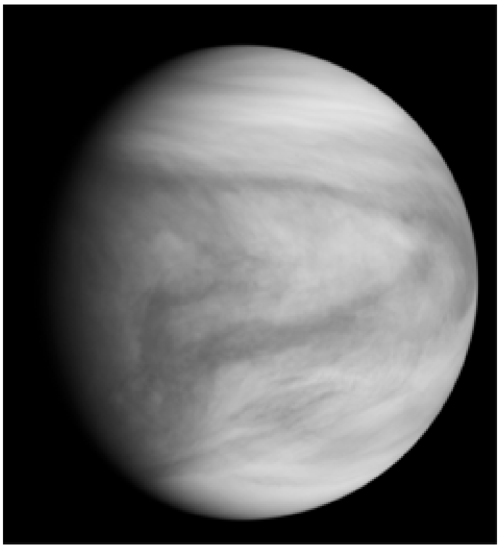
Fig. 8. Same as Fig. 2, for the sulfur oxides. The SO_2 and SO observations with errorbars are from the Belyaev et al. (2012). The temperature at 100 km is 165–170 K for the observations. The OCS measurement (0.3–9 ppb with the mean value of 3 ppb) is from Krasnopolsky (2010).

Transport of cloud particles to the upper atmosphere by winds ?
→ Open question

SO_2 (283 nm)



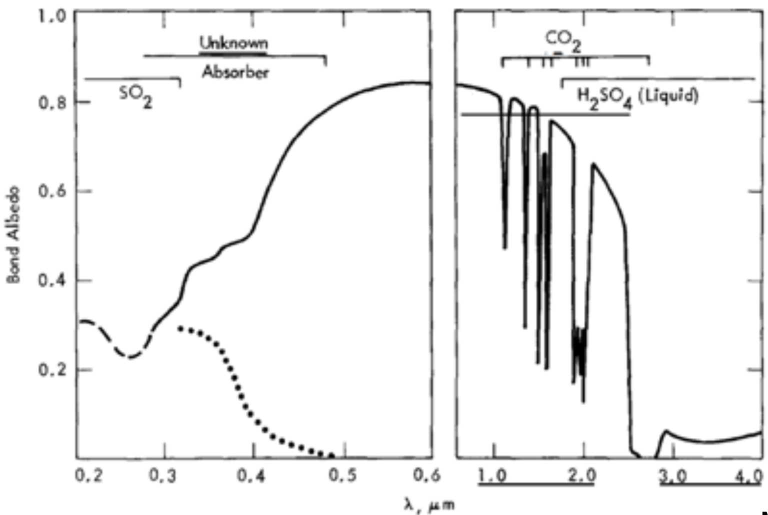
Unknown absorber (365 nm)



Venus is completely covered by clouds that are featureless in the visible but exhibit variable ultraviolet features.

Origin of visible-UV absorption

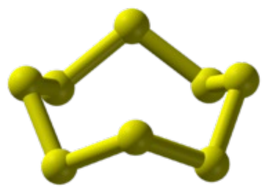
- Absorbing material at far UV (<320nm) is mostly SO_2
- Absorption at near UV (>320nm) is a mystery. Candidate species are S, S_2O_2, S_2O, $FeCl_2$, etc.



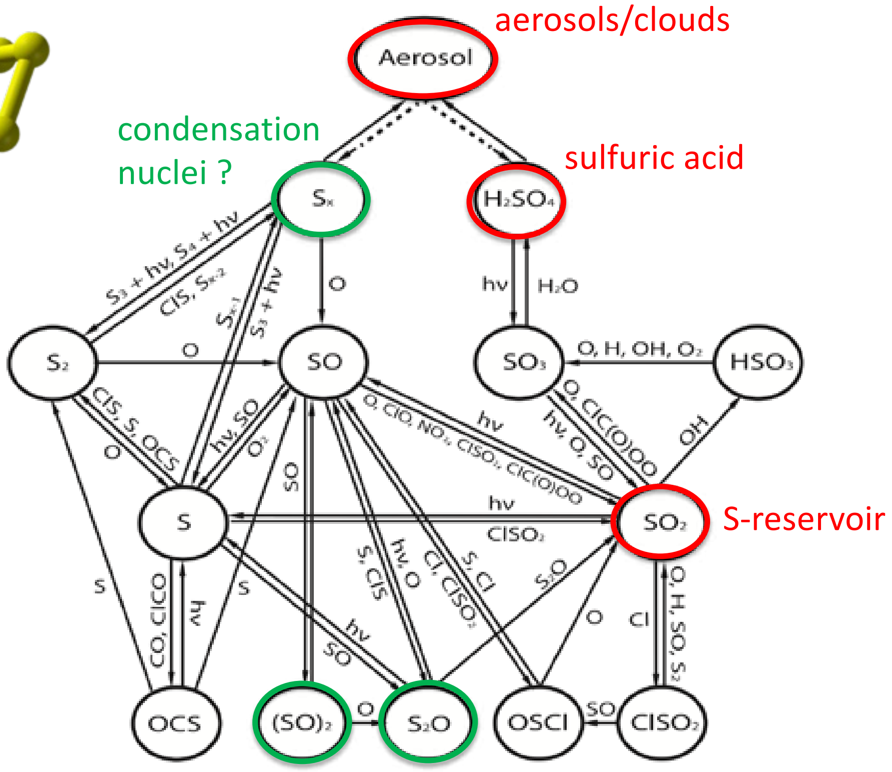
Moroz et al. (1985)

Figure 6-1. The Monochromatic Bond Albedo of Venus as a Function of Wavelength (Moroz, 1983 - Normalized to the Integrated Albedo A = 0.76). The points show the wavelength dependence of the maximum contrast between dark and light UV features (Coffeen, 1977).

Sulfur cycle in Venus's atmosphere

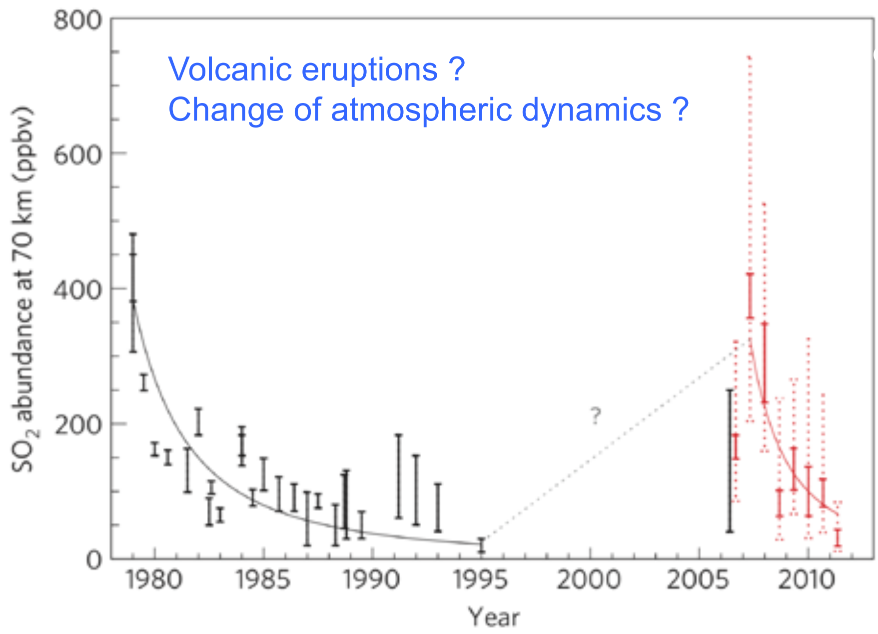


S_8



Zhang et al. (2012)

Variability of SO_2 above clouds



Marcq et al. (2013)

Figure 3 | More than thirty years of SO_2 measurements at Venus's cloud top. Black stands for previously published measurements[26]. Red stands for the 8-month moving average of the retrievals also shown in Fig. 1. Solid red error bars represent 1σ random uncertainty, and dotted red error bars represent measurement dispersion in each temporal bin.