Atmospheric Chemistry on Venus, Earth, and Mars: Main Features and Comparison

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- Why are the atmospheres of Venus, Earth, and Mars so different?

- Inner Solar nebula was mixed, and the planets were made of similar planetesimals and had similar volatiles

Initial and present abundances of volatiles

Planet	CO_2 (bar)	N_2 (bar)	H_2O (km)
Venus	**90** (90)	**2** (2)	3.6 (1.3 cm)
Earth	108 (3×10^{-4})	2.4 (0.8)	**4.0** (4.0)
Mars	15 (6 mbar)	0.35 (0.1 mbar)	1.5 (15 m)

- Venus: Hydrodynamic and nonthermal escape of H_2O
- Earth: (1) CO_2 was dissolved in the ocean and formed carbonates

  (2) Impact of life and formation of O_2
- Mars: (1) Loss of water in

  $$H_2O + Fe \rightarrow FeO + H_2$$

  and hydrodynamic escape of H_2

  (2) Loss of more than 90% of CO_2 and N_2 by intense meteorite impacts in the first 0.8 Ga

Upper Amospheres: Why

T_∞ = 900 K (Earth), 270 K (Venus), 250 K (Mars)

- Earth: N_2 and O_2 do not have dipole moments, and their rovibrational transitions are forbidden. Much of the absorbed EUV heats the Earth's thermosphere
- EUV Venus/Mars = $(1.52/0.72)^2$ = 4.5.
- g(Venus) = 880 cm/s^2, g(Mars) = 370 cm/s^2
- CO and O Venus/Mars ≈ 4.5x880/370 ≈ 10
- More effective cooling of Venus by

$$CO_2 + O \rightarrow CO_2(15\mu m) + O$$

- $T_\infty^{S+1} \approx a*EUV*H$, S = 1.3 for CO_2 (0.75 for N_2, O_2)

$$H(\text{Venus/Mars}) \approx 370/880 = 0.42$$

- S is smaller and variations with solar activity are stronger on Earth
- 3D modeling of thermospheres by Bougher et al. (1999, 2000)

Mars’ Chemical Composition

- CO_2 and its products

  (CO, O, O_2, $O_2(^1\Delta)$, O_3)
- H_2O and its products

  (H, OH, HO_2, H_2O_2, H_2)
- N_2 and noble gases

Mars' Photochemistry: Stability of CO_2

- $CO + O + M \rightarrow CO_2 + M$ is spin forbidden, and predictions of dry models were far above the observed CO and O_2

- McElroy and Donahue (1972):

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + O \rightarrow OH + O_2$$

$$CO + OH \rightarrow CO_2 + H$$

$$\text{Net } CO + O \rightarrow CO_2$$

- Parkinson and Hunten (1972):

$$H + O_2 + M \rightarrow HO_2 + M$$

$$½(HO_2 + HO_2 \rightarrow H_2O_2 + O_2)$$

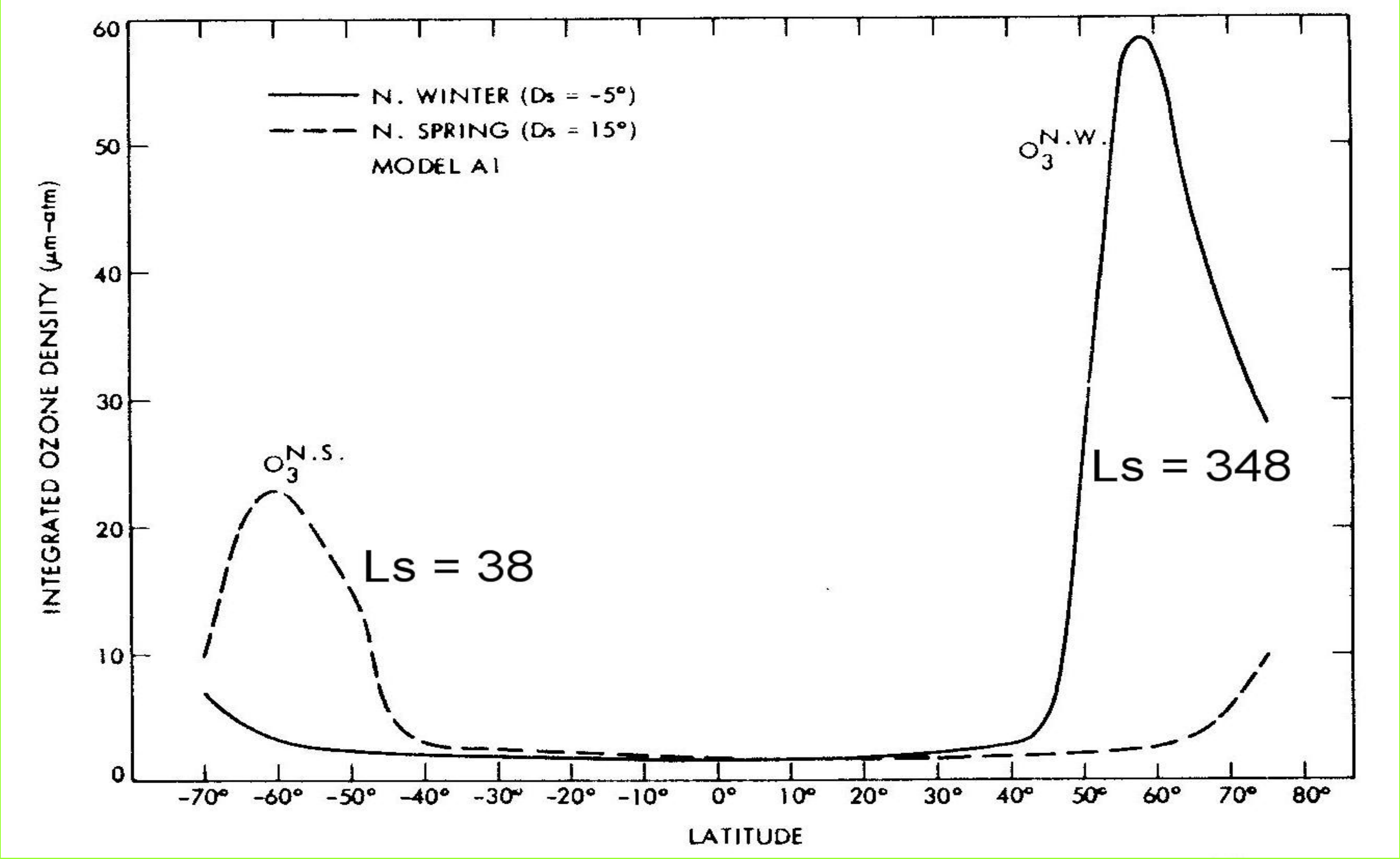
$$½(H_2O_2 + h\nu \rightarrow OH + OH)$$

$$CO + OH \rightarrow CO_2 + H$$

$$\text{Net } CO + ½O_2 \rightarrow CO_2$$

- Efficiency of these cycles is so high that CO in the models exceeds the observed values by a factor of ~3. This problem remains unsolved.

Mariner 9 observations of ozone in polar regions with O_{3max}= 60 µm were explained by freezing out of H_2O and then H_2O_2 (Kong & McElroy 1977)



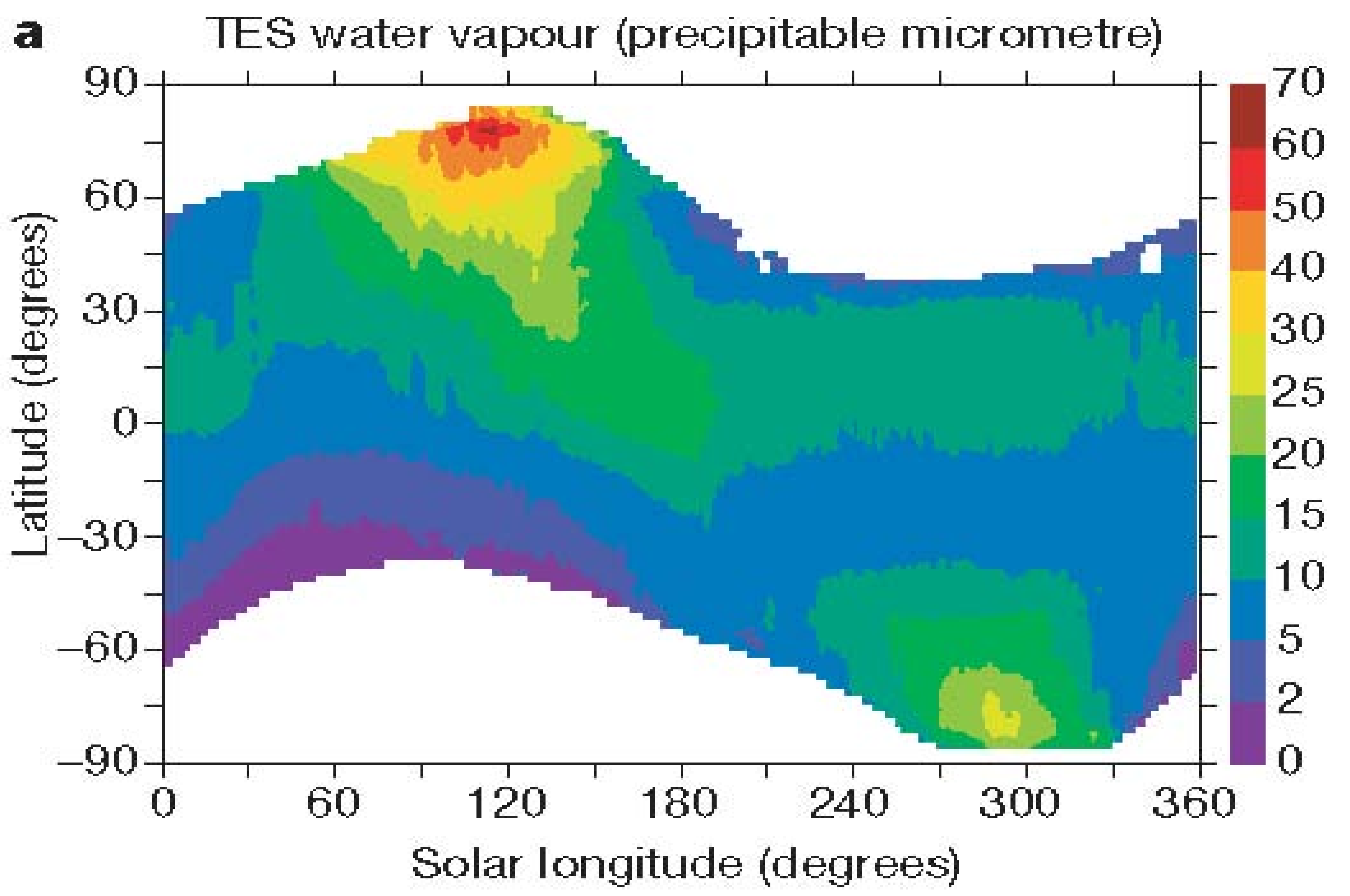
Seasonal and latitudinal variations

- Both H_2O column and altitude of condensation determine local photochemistry (Clancy and Nair 1996)
- Due to elliptic orbit of Mars, solar radiation at perihelion (L_S = 251°) exceeds that at aphelion (L_S = 71°) by a factor of 1.46
- Mars' atmosphere is cold and dust-free near aphelion and comparatively warm and dusty near perihelion
- Condensation level is ~10 km near aphelion and ~40 km near perihelion

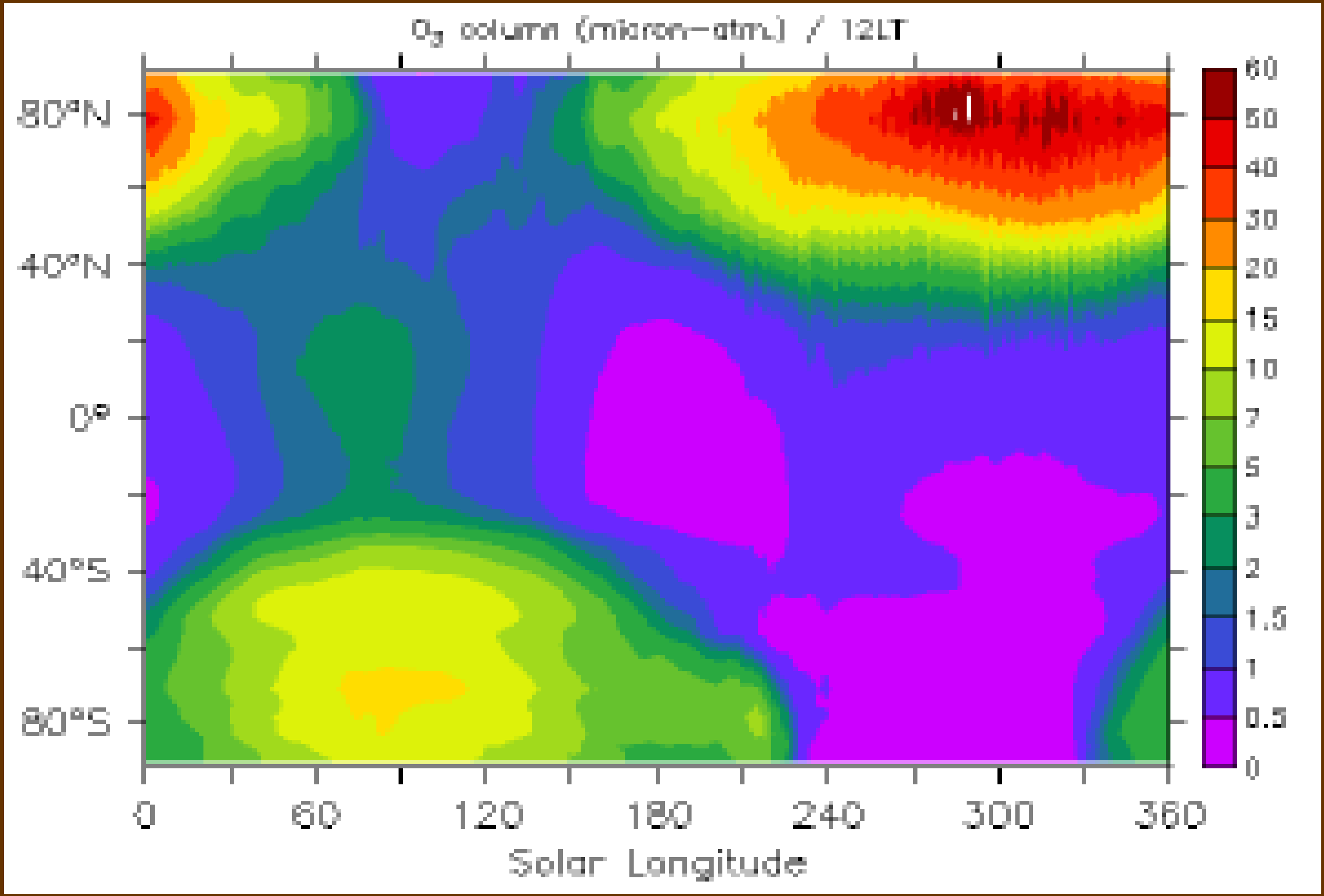
There have been a few important achievements in the studies of Mars' photochemistry in the current decade

- Long-term (7 years) monitoring of T-profiles, H_2O, dust and ice by MGS/TES (Smith 2004, continued by MEX)
- Ground-based (Fast et al. 2006), HST (Clancy et al. 1999), and MEX (Perrier et al. 2006) observations of ozone
- Ground-based (Krasnopolsky 2007) and MEX (Fedorova et al. 2006) observations of the O_2 dayglow at 1.27 μm
- Observations of H_2O_2 (Encrenaz et al. 2008, Clancy et al. 2004)
- Photochemical GCMs (Lefevre et al. 2004, 2008; Moudden and McConnell 2007)
- Using the TES data, 1D models were applied to study seasonal and latitudinal variations of Mars' photochemistry (Krasnopolsky 2006, 2009)
- MEX ozone columns are systematically smaller than the ground-based and HST data, and this presents a problem

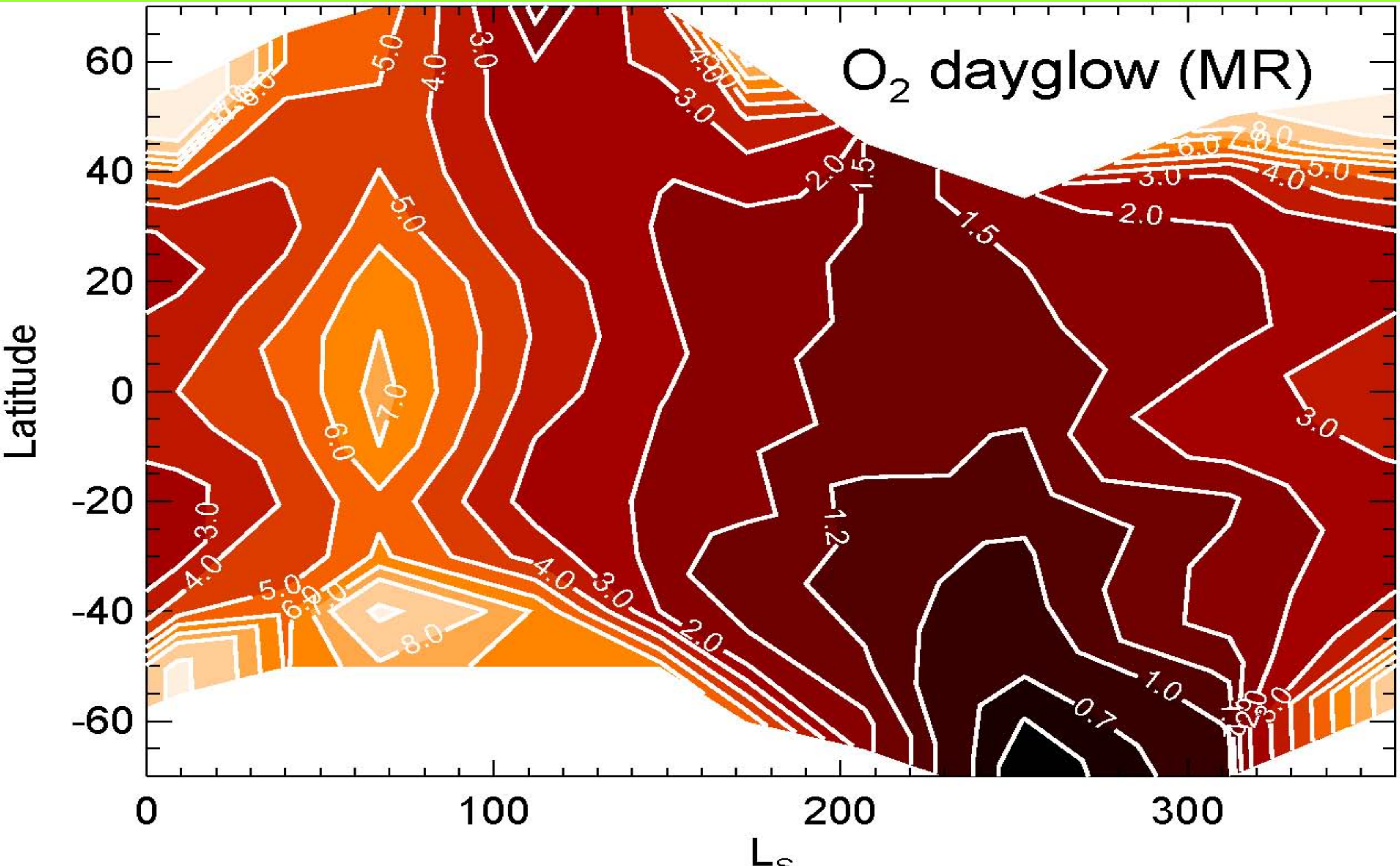
Mean seasonal-latitudinal map of H_2O observed for 7 years by MGS/TES (Smith 2004)



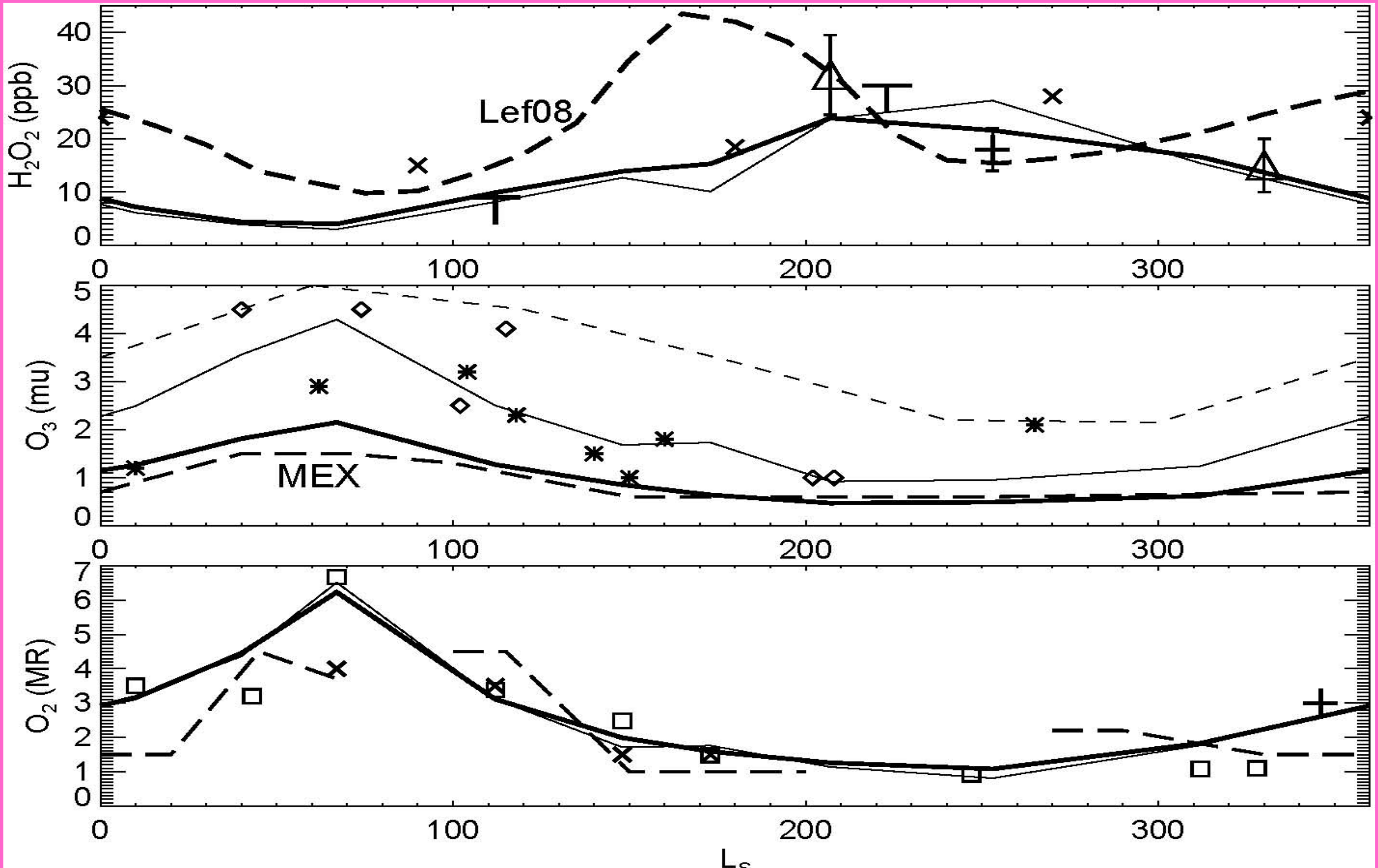
Seasonal and latitudinal variations of ozone in photochemical GCM by Lefevre et al. (2004)



Seasonal-latitudinal map of the O_2 dayglow at 1.27 μm (Kr09)



Comparison of observations and models at low latitudes



- THEMIS has not detected warm spots, and this rules out significant gas vents
- If dust devils can generate high electric field near the breakdown limit, then dissociative attachment of $H_2O + e \rightarrow OH + H^-$ may significantly exceed photolysis of H_2O. However, global effect of dust devils is $\sim 10^{-4}$ of the standard photochemistry
- Steady-state models are inapplicable to transient and localized phenomena like vents and dust devils
- $CH_4 \approx 15$ ppb (Kr. et al. 2004, Formisano et al. 2004, Mumma et al. 2009). Its atmospheric chemistry is simple and cannot disturb the basic photochemistry
- The same refers to SO_2 (< 1 ppb, Kr. 2005) and HCl (< 2 ppb, Kr. et al. 1997)

Venus

Venera 9 panorama (1975)

Middle Atmosphere (58-110 km)

- H_2O is scarce above the clouds of H_2SO_4 (85%)
- HCl, SO_2, and OCS drive photochemistry
- Prinn (1971) suggested ClO_x chemistry on Venus before it was understood in the Earth's atmosphere
- Krasnopolsky & Parshev (1980) made a model with ClCO that initiates the major cycle on Venus:

$$Cl + CO + M \rightarrow ClCO + M$$

$$ClCO + O_2 + M \rightarrow ClCO_3 + M$$

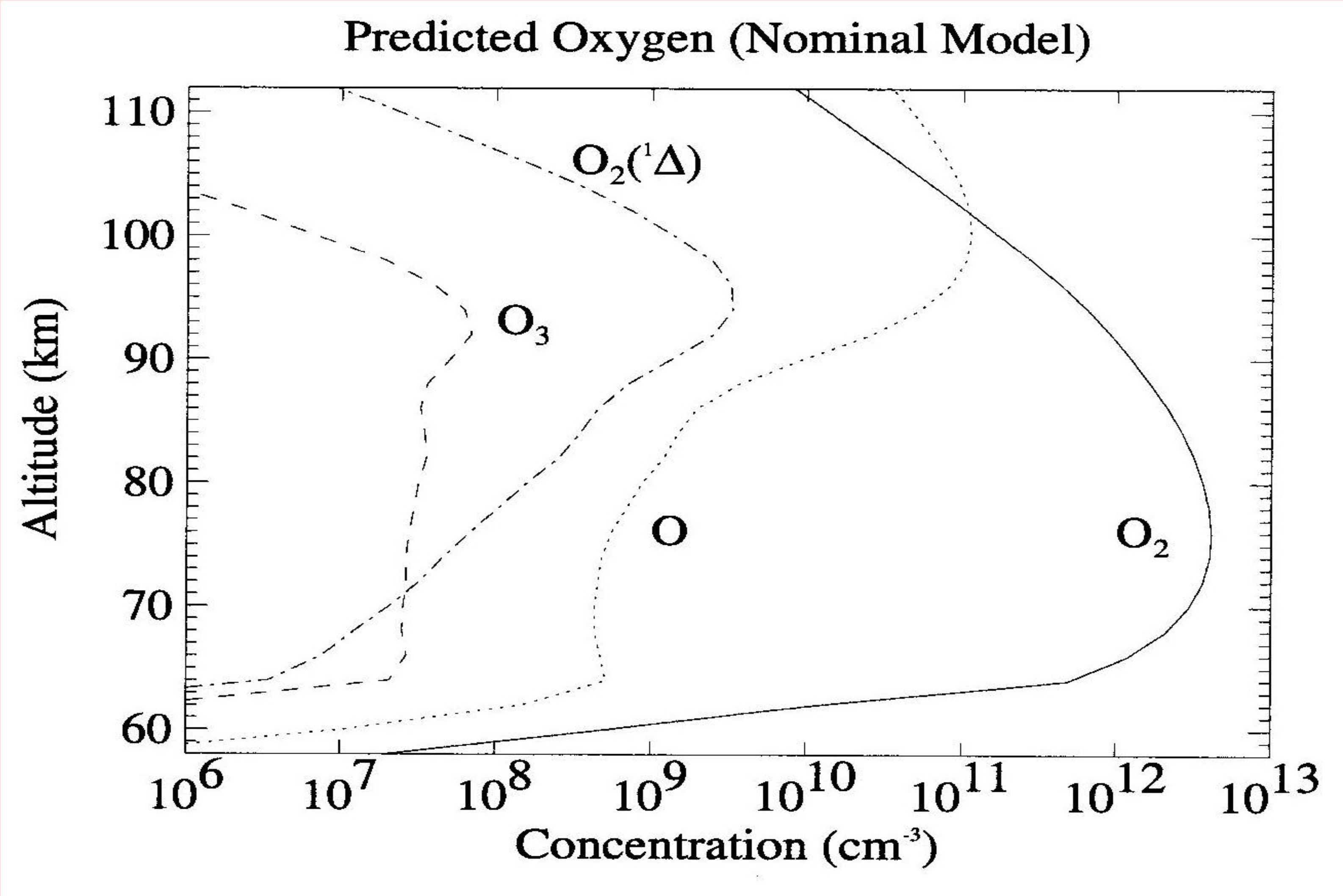
$$ClCO_3 + Cl \rightarrow CO_2 + ClO + Cl$$

$$ClO + O \rightarrow O_2 + Cl$$

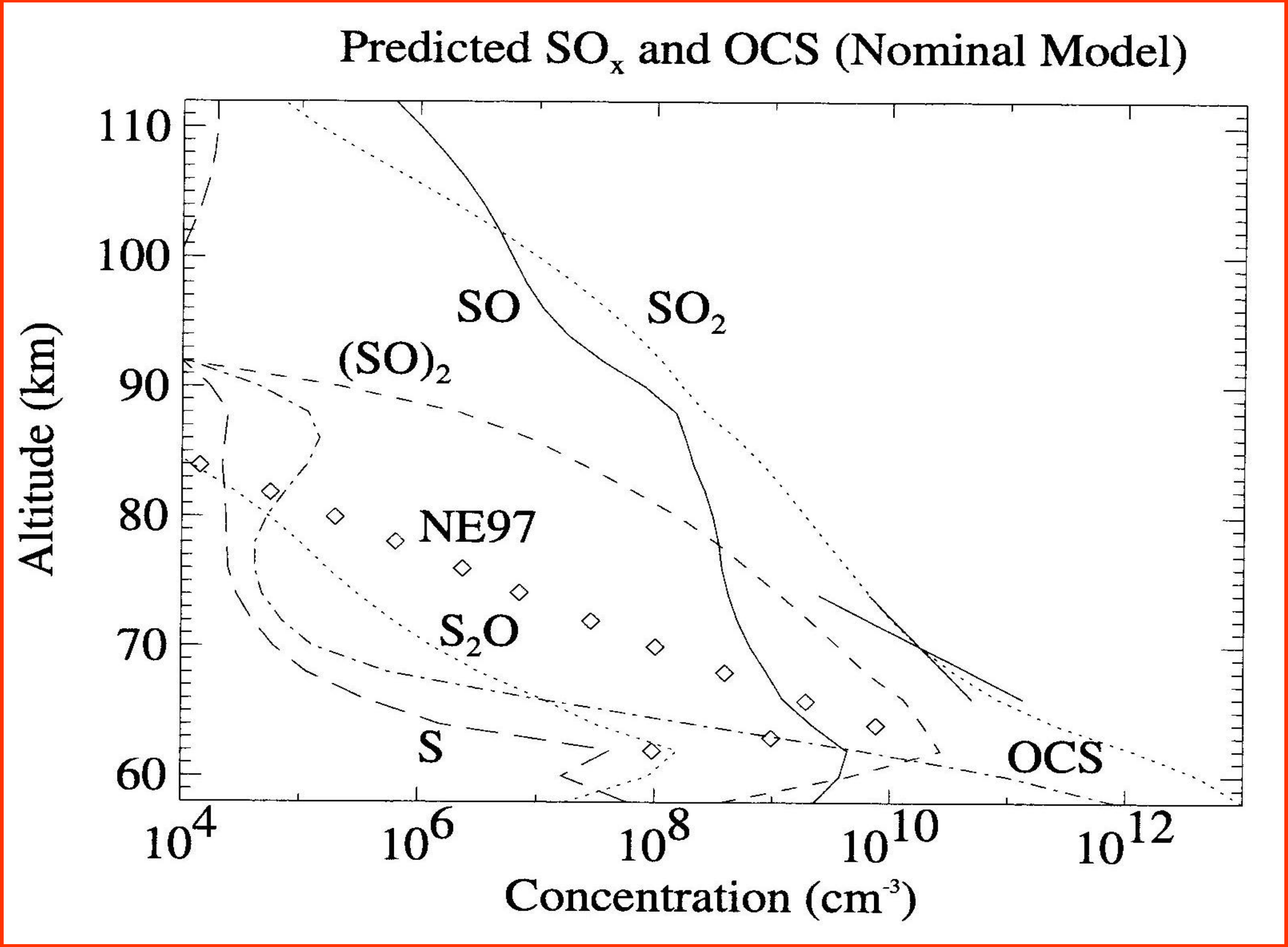
$$\text{Net} \quad CO + O \rightarrow CO_2$$

- Yung and DeMore (1982):
  - Model A, odd H chemistry, H_2 = 20 ppm (too much, 5 ppb in Kr. (2007))
  - Model B, NO chemistry, NO = 30 ppb from lightning
  - Model C, ClCO chemistry improved relative Kr. & Parshev (1980)
- Mills (1998): further improvement of the model with ClCO chemistry. There were a few later publications by Mills with some minor changes to Mills (1998). However, they were given without detail, and Mills (1998) currently remains the basic reference to Venus' photochemistry

Oxygen species in Mills (1998)



Sulfur species in Mills (1998)



- The basic effect of Venus' photochemistry:

  $CO_2 + SO_2 + H_2O \rightarrow CO + H_2SO_4 + S_x$

- Major problems:

  All models do not fit the upper limit to
  $O_2 < 8x10^{17}$ cm^{-2} above 67 km (Trauger & Lunine 1983)

  The models do not involve the recently detected NO = 5.5 ppb (Krasnopolsky 2006)

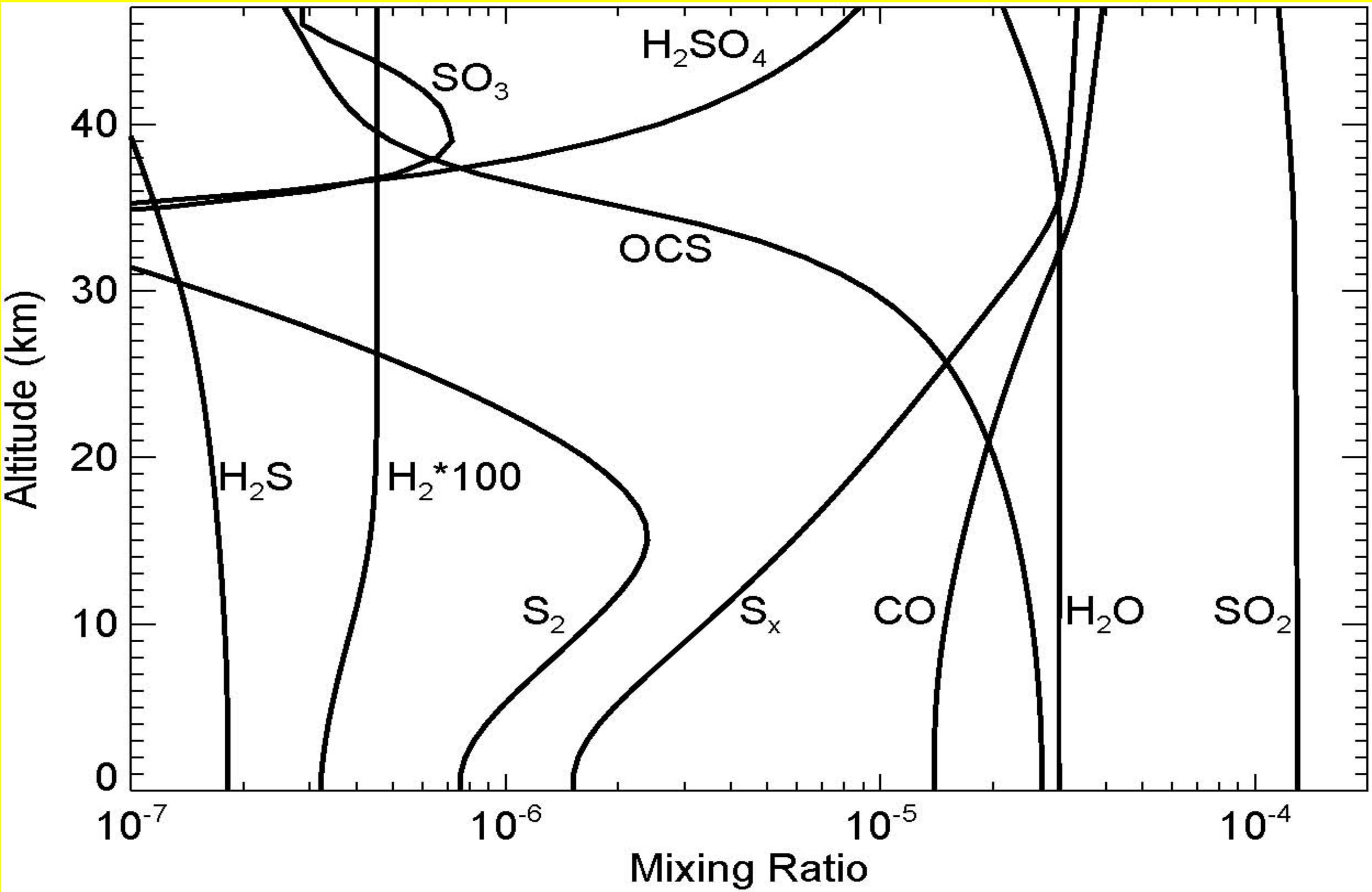
  The models are incompatible with the recently discovered OH airglow (Piccioni et al. 2008)

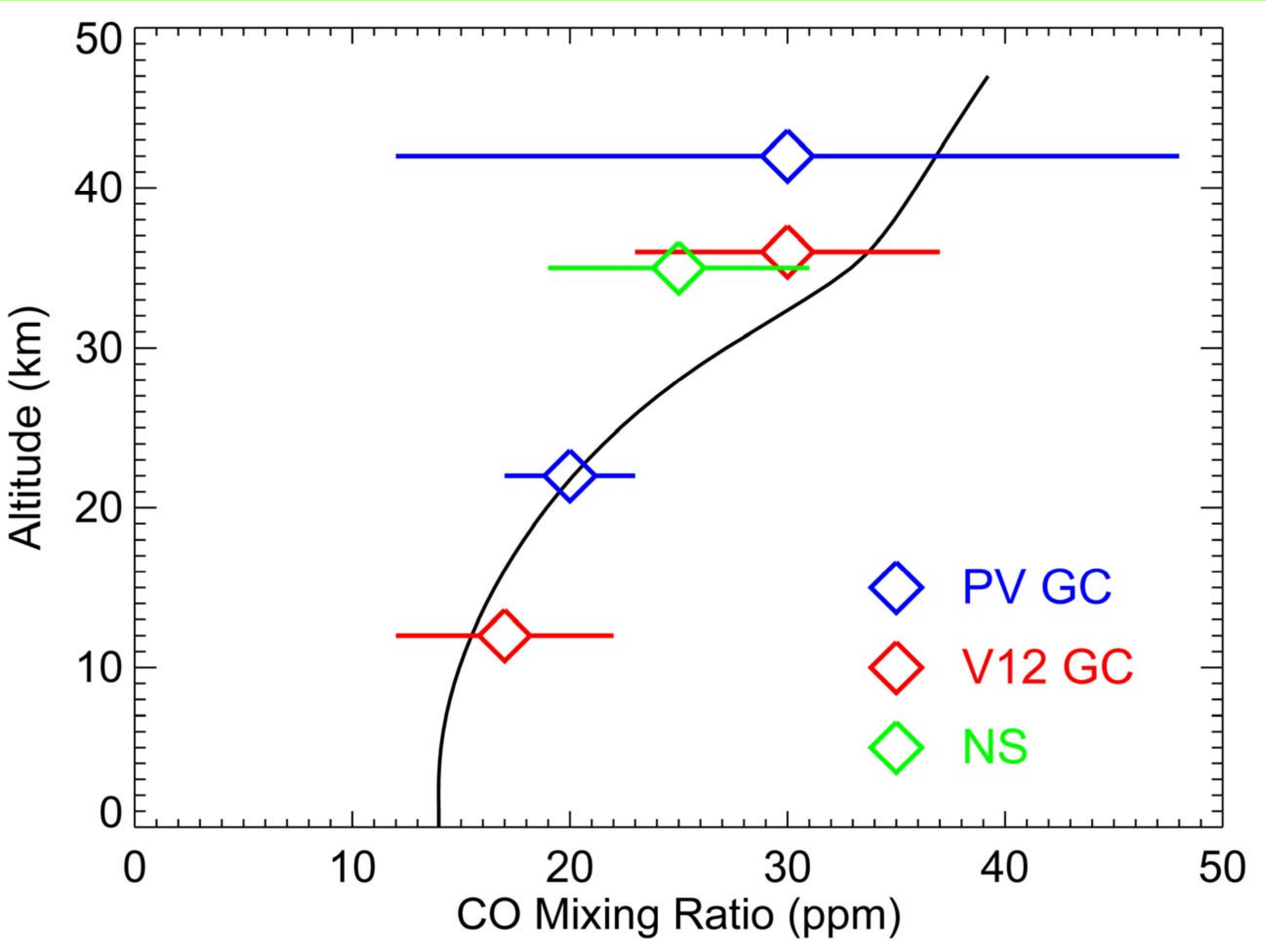
  Some other updating to cover the VEX observations is required

Venus Lower Atmosphere

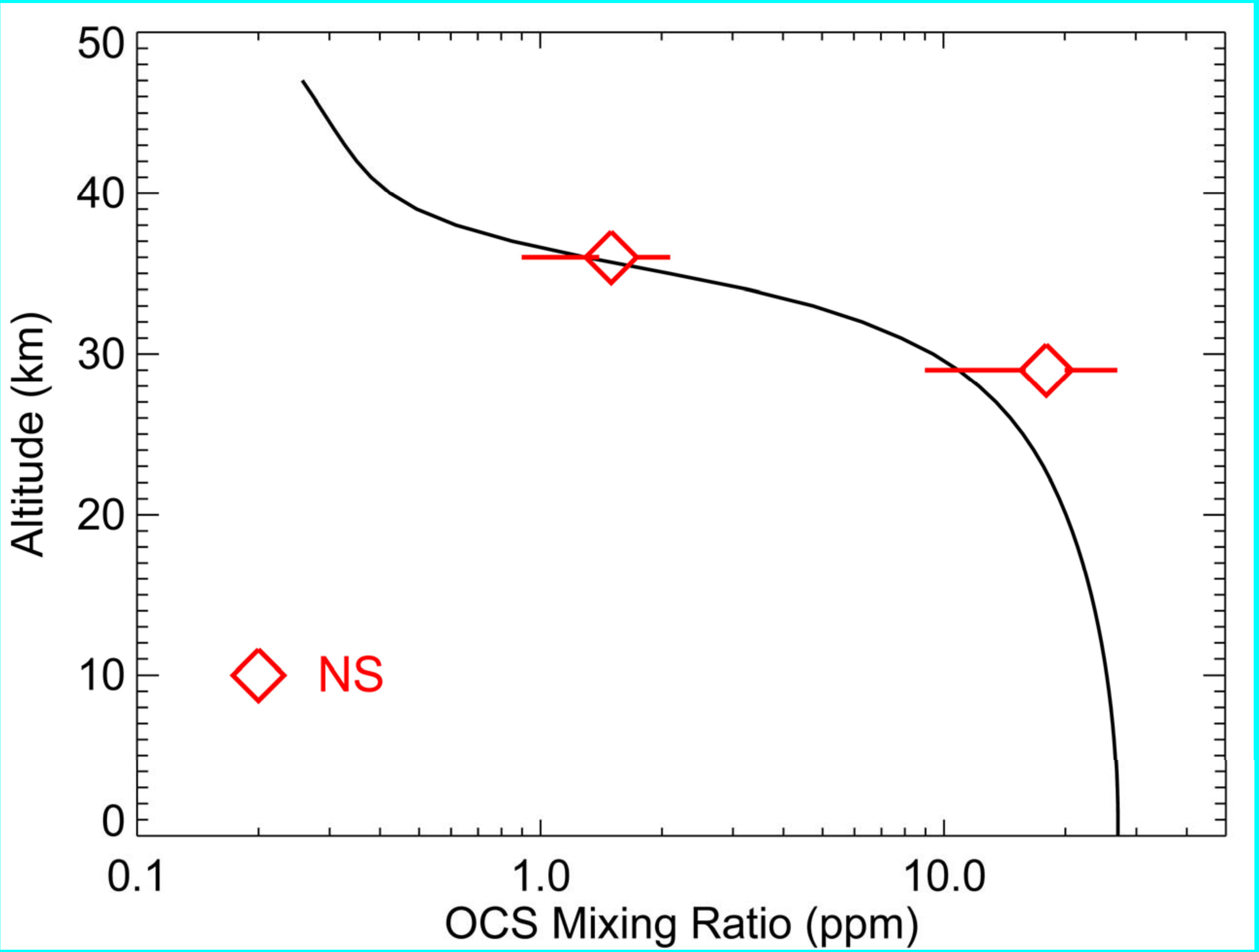
- Along with the entry probes, detection (Allen & Crawford 1984), observations, and analyses (Pollack et al. 1993) of the nightside NIR emission are currently the basic source of data on the lower atmosphere of Venus
- Both ground-based and VEX observations are available now (Marcq et al. 2006, 2008)
- Venus' atmosphere is near thermochemical equilibrium at the surface, and some useful estimates were made by Kr. & Parshev (1979) and Fegley et al. (1997) using this assumption
- Chemical kinetic model for the lower atmosphere was recently made by Krasnopolsky (2007)

Major species in the model





Altitude (km)
CO Mixing Ratio (ppm)
0
10
20
30
40
50
PV GC
V12 GC
NS



50
40
30
20
10
0
Altitude (km)
NS
0.1
1.0
10.0
OCS Mixing Ratio (ppm)

- Two basic reactions in Krasnopolsky (2007) have not been studied in laboratory:

  $OCS + SO_3 \rightarrow CO_2 + (SO)_2$

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

- Yung et al. (2009) suggest a cycle

  $S_2 + S_2 + M \rightarrow S_4 + M$

  $S_4 + h\nu \rightarrow S_3 + S$

  $S_3 + h\nu \rightarrow S_2 + S$

  $2(S + OCS \rightarrow CO + S_2)$

  Net $2\ OCS \rightarrow 2\ CO + S_2$

- However, S_4 is very minor in S_x, and

  either $S_2 + S_2 + M \rightarrow S_4 + M$ is very slow

  or $S_4 + M \rightarrow S_2 + S_2 + M$ is fast

- Overall, Venus' chemistry suggests many challenging tasks in both observations and modeling