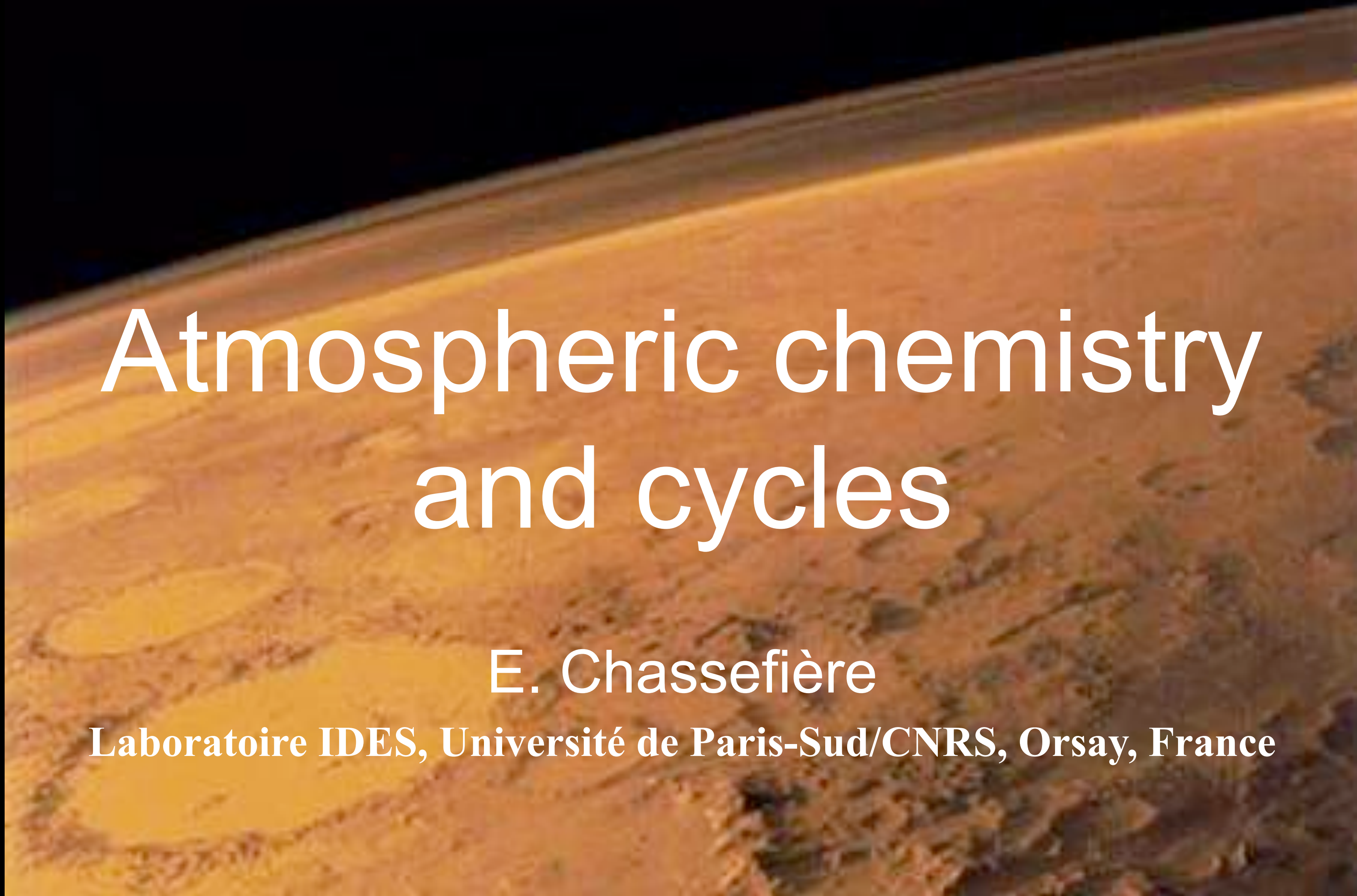


Atmospheric chemistry and cycles

E. Chassefière

Laboratoire IDES, Université de Paris-Sud/CNRS, Orsay, France

Second ESA-CAS Mars Advanced School in China, 12-22 September 2011, Weihai, Shandong, China

Chemical composition of the atmosphere

Constituent	Mixing ratio
(a) Composition of the Martian atmosphere	
CO_2	0.9532[a]
N_2	2.7×10^{-2} [a]
^{40}Ar	1.6×10^{-2} [a]
O_2	1.3×10^{-3} [a]
CO	7×10^{-4} [a]
H_2O	2×10^{-4} [b]
H_2O_2	4×10^{-8} [c]
O_3	$(1\text{–}80) \times 10^{-8}$ [d]
CH_4	$(1 \pm 0.5) \times 10^{-8}$ [e]
CH_2O	$\leqslant 5 \times 10^{-7}$ (tentative)[f]
	$< 3 \times 10^{-9}$ [g]
$^{36+38}Ar$	5.3×10^{-6} [a]
Ne	2.5×10^{-6} [a]
He	$(1.1 \pm 0.4) \times 10^{-6}$ [h]
Kr	3×10^{-7} [a]
Xe	8×10^{-8} [a]
H_2	$(1.5 \pm 0.5) \times 10^{-5}$ [i]

Atreya et al, 2007

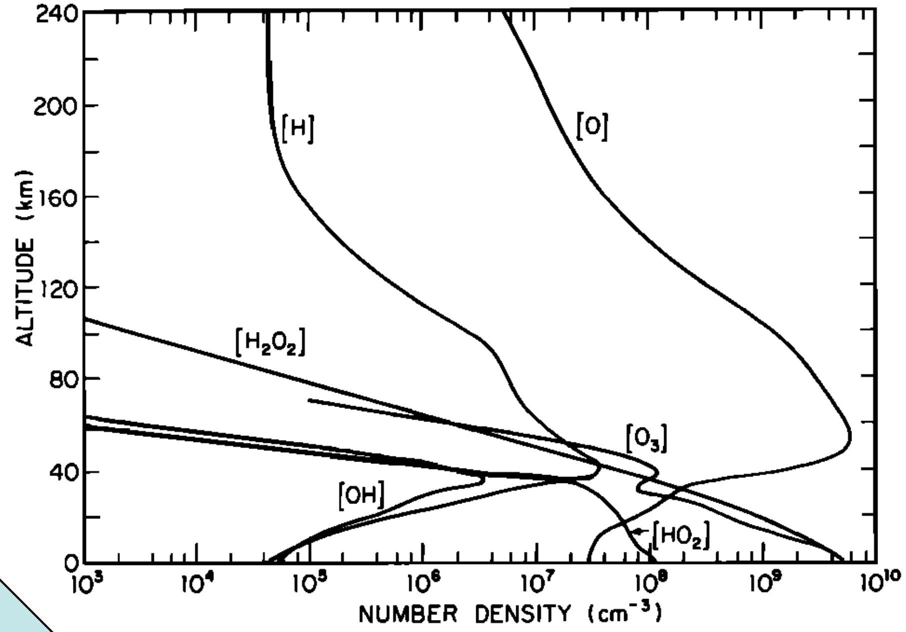
Atmospheric photochemistry

Reaction No.	Reaction	Rate Expression
(1)	$h\nu + CO_2 \rightarrow CO + O$	
(2)	$CO + O(^3P) + CO_2 \rightarrow CO_2 + CO_2$	2×10^{-37}
(3)	$CO + OH \rightarrow CO_2 + H$	$9 \times 10^{-13} \exp(-500/T)$
(4)	$H + O_2 + CO_2 \rightarrow HO_2 + CO_2$	$2 \times 10^{-31}(T/273)^{-1.3}$
(5)	$O + HO_2 \rightarrow OH + O_2$	7×10^{-11}
(6)	$O + O + CO_2 \rightarrow O_2 + CO_2$	$3 \times 10^{-33}(T/300)^{-2.9}$
(7)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	5.5×10^{-12}
(8)	$h\nu + H_2O_2 \rightarrow OH + OH$	
(9)	$O + OH \rightarrow O_2 + H$	5×10^{-11}
(10)	$h\nu + H_2O \rightarrow OH + H$	
(11)	$O(^1D) + H_2O \rightarrow OH + OH$	3×10^{-10}
(12)	$O(^1D) + H_2 \rightarrow OH + H$	1.9×10^{-10}
(13*a*)	$h\nu + O_3 \rightarrow O_2(^1\Delta_g) + O(^1D)$	
(13*b*)	$h\nu + O_3 \rightarrow O_2 + O(^3P)$	
(14)	$OH + HO_2 \rightarrow H_2O + O_2$	$8.24 \times 10^{-11} \exp(-150/T)$
(15)	$H + HO_2 \rightarrow H_2 + O_2$	$9 \times 10^{-12} \exp(-333/T)$
(16)	$h\nu + O_2 \rightarrow O + O$	
(17)	$O + O_2 + CO_2 \rightarrow O_3 + CO_2$	$1.4 \times 10^{-33}(T/300)^{-2.5}$
(18)	$O + O_3 \rightarrow O_2 + O_2$	$1.32 \times 10^{-11} \exp(-2140/T)$
(19)	$H + O_3 \rightarrow OH + O_2$	2.6×10^{-11}
(20)	$O(^1D) + CO_2 \rightarrow O(^3P) + CO_2$	1.8×10^{-10}
(21)	$O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-) + h\nu$	2.6×10^{-4}
(22)	$O_2(^1\Delta_g) + CO_2 \rightarrow O_2(^3\Sigma_g^-) + CO_2$	$\left\{ 4 \times 10^{-18};\ \leq 8 \times 10^{-20};\ \leq 1.5 \times 10^{-20} \right\}$

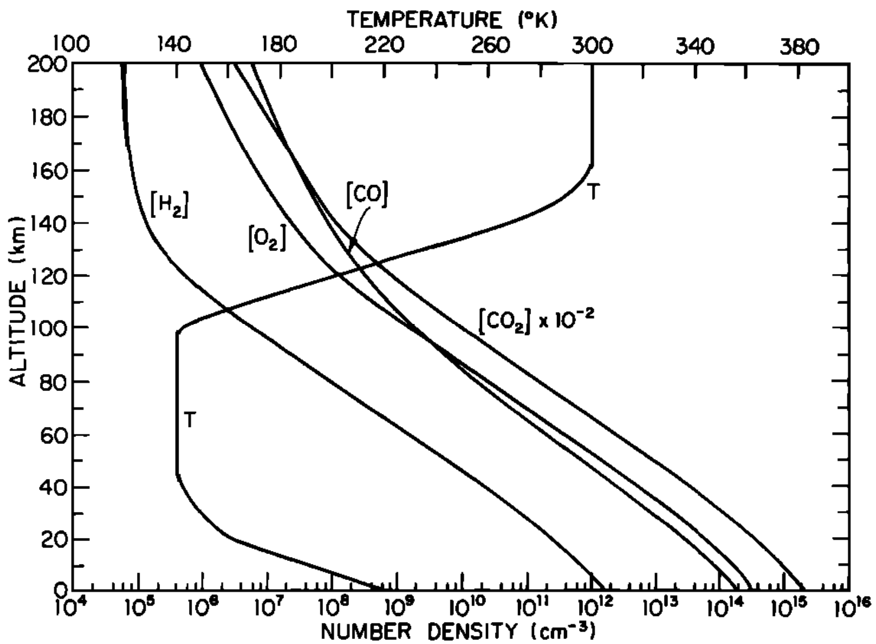
McElroy et al. (1977)

1-D models

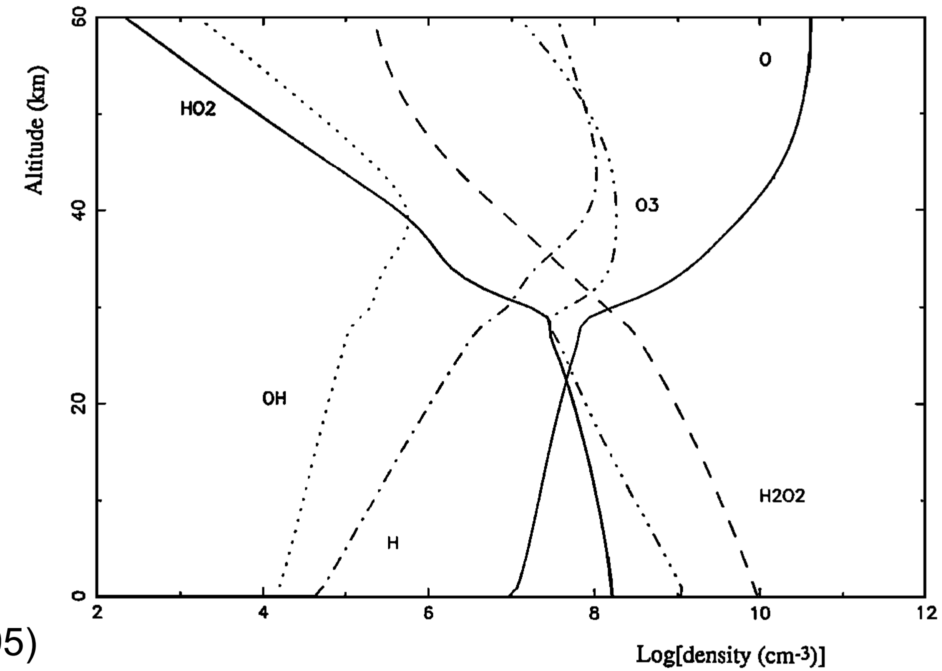
Vertical transport represented by an « eddy diffusion coefficient »



McElroy et al. (1977)



Background atmosphere



Rosenqvist and Chassefière (1995)

Photochemical stability of the Martian atmosphere

$2\times \quad CO_2 + h\nu \rightarrow CO + O$

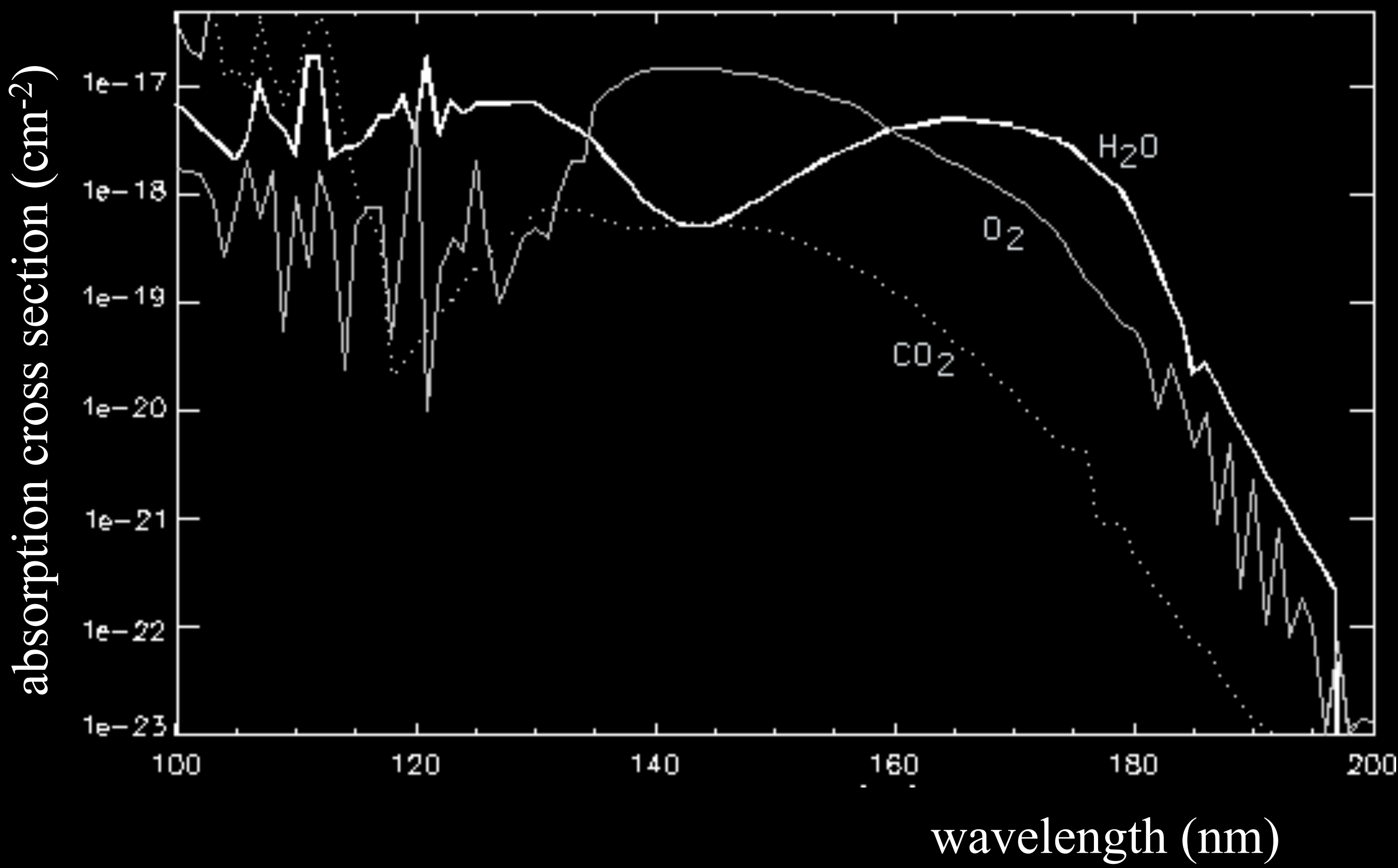
$O + O + M \rightarrow O_2 + M$ (k_1) $k_1/k_2 > 10^5$

$(CO + O + M \rightarrow CO_2 + M)$ (k_2) So reaction 2 can be neglected

$\mathbf{2CO_2 + 2\,h\nu \rightarrow O_2 + 2CO}$

McElroy and Donahue (1972), Parkinson and Hunten (1972), Atreya and Gu (1994): CO_2 is unstable - the Martian atmosphere should be changed into CO and O_2 in about 6000 yrs…

UV absorption cross sections of H_2O, CO_2 et O_2



When the level of O_2 increases, photons previously used to photolyse CO_2 and thus to produce O_2 are now used to destroy O_2

This overlap of the absorption cross-sections limits the build up of O_2 (*Nair et al. 1994*)

$O_2/CO_2 < 5\%$

But on Mars $O_2/CO_2 = 0.1\ \%$

Photolysis of water vapor

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

$\rightarrow HO_X$: H, OH, HO_2, H_2O_2

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

$O + HO_2 \rightarrow O_2 + OH$

$CO + OH \rightarrow CO_2 + H$

~~**$CO + O \rightarrow CO_2$**~~

Ozone photochemistry

Mars' case :

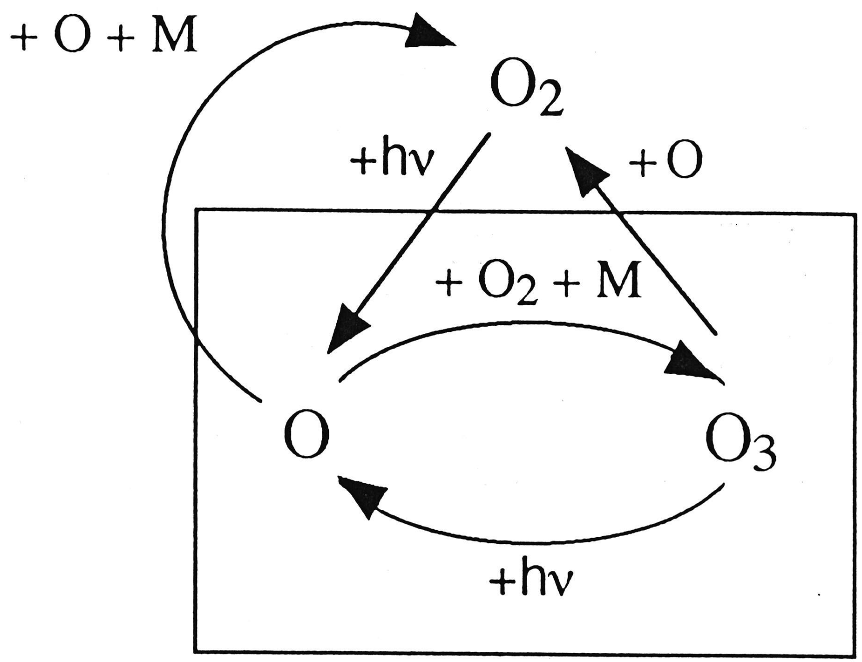
$H_2O + h\nu \rightarrow O + OH$

$OH + O_3 \rightarrow HO_2 + O_2$

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

→ H_2O/O_3 anticorrelation expected

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



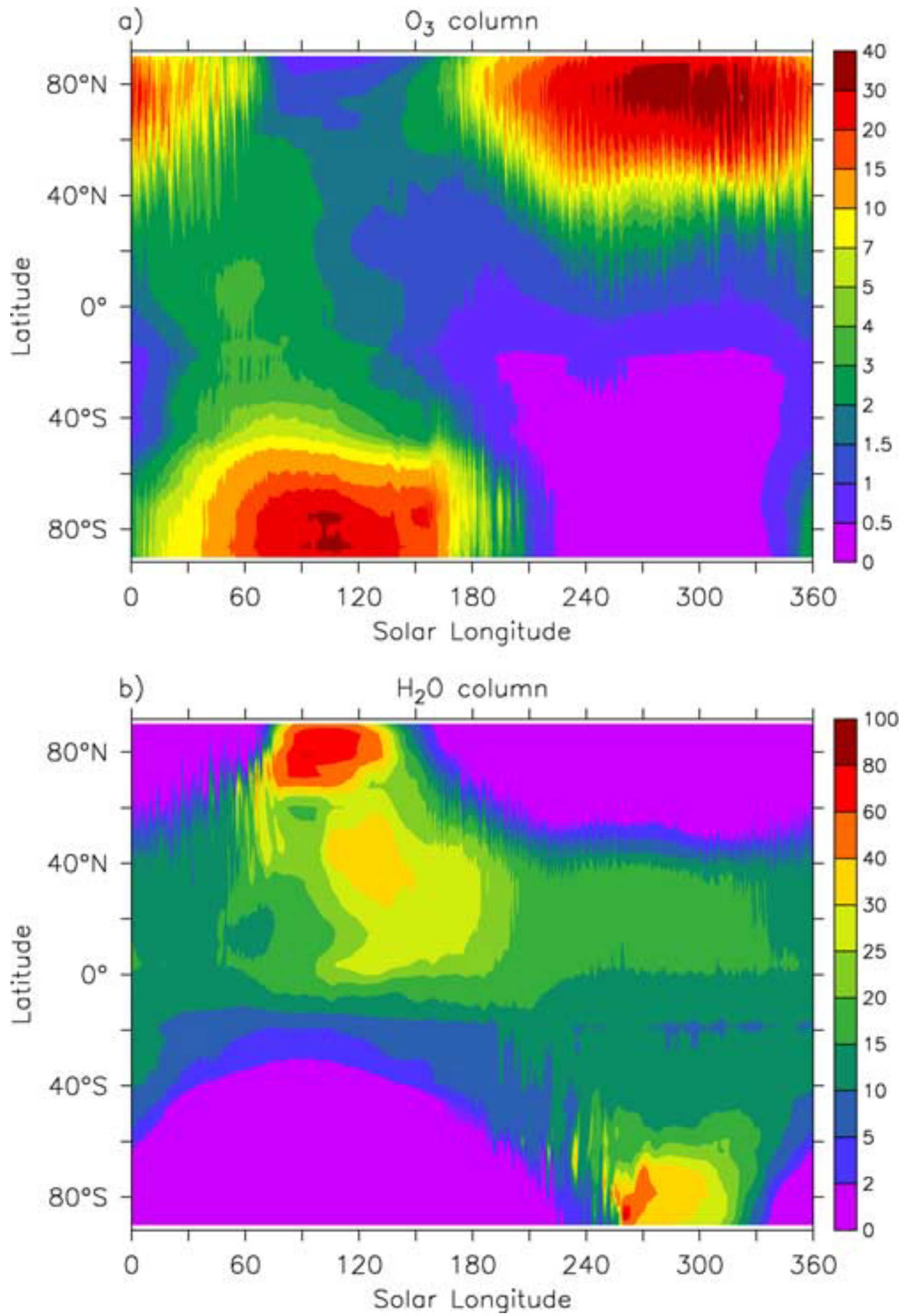
Chapman cycle on Earth

3-D models

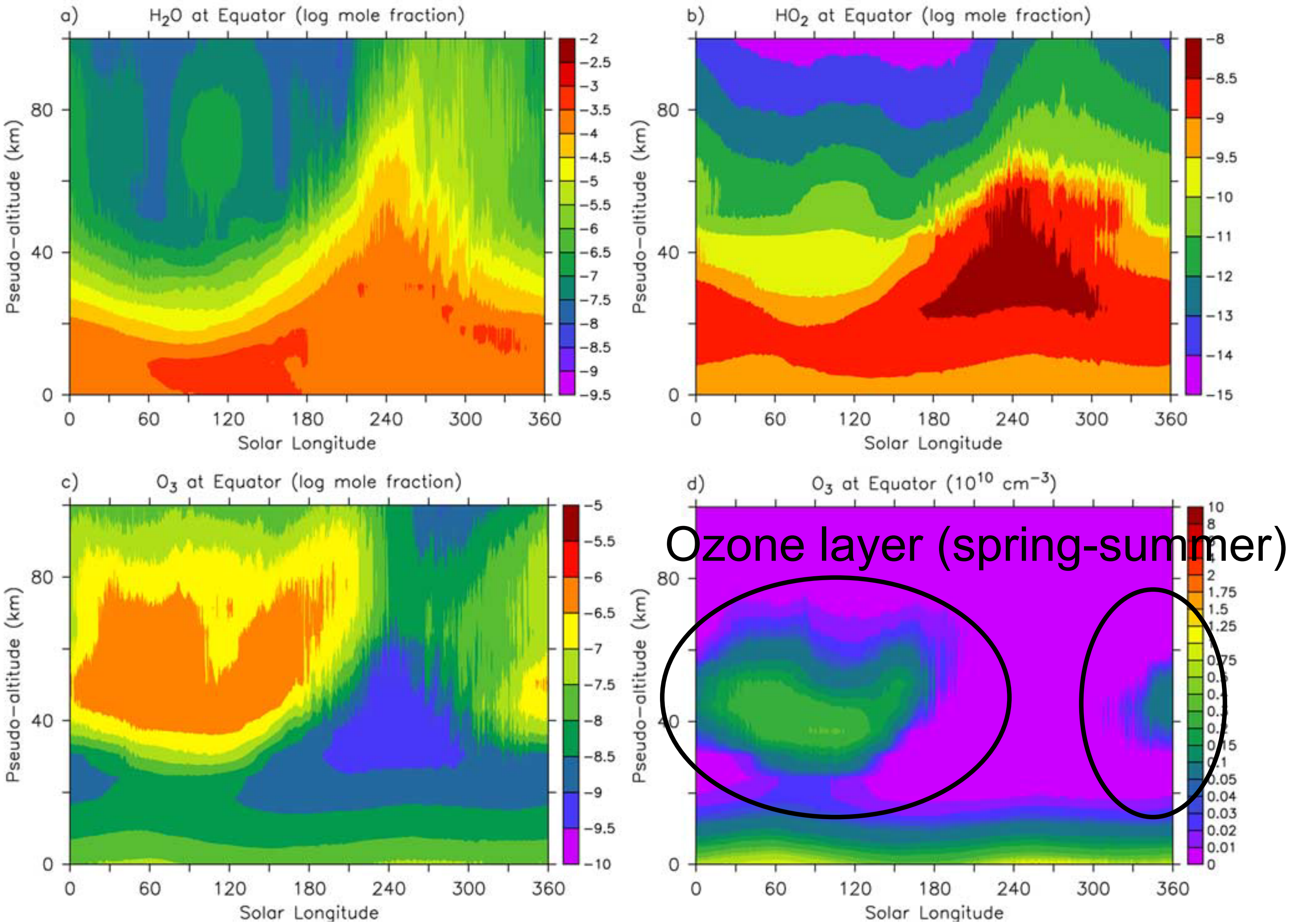
- Coupling between « General Circulation Models » and photochemical models

H_2O/O_3 anticorrelation observed on model results

(a) Zonally averaged ozone column (mm-atm) and (b) zonally averaged water vapor column (precipitable microns, pr-mm) as a function of solar longitude (Lefèvre et al., 2004)

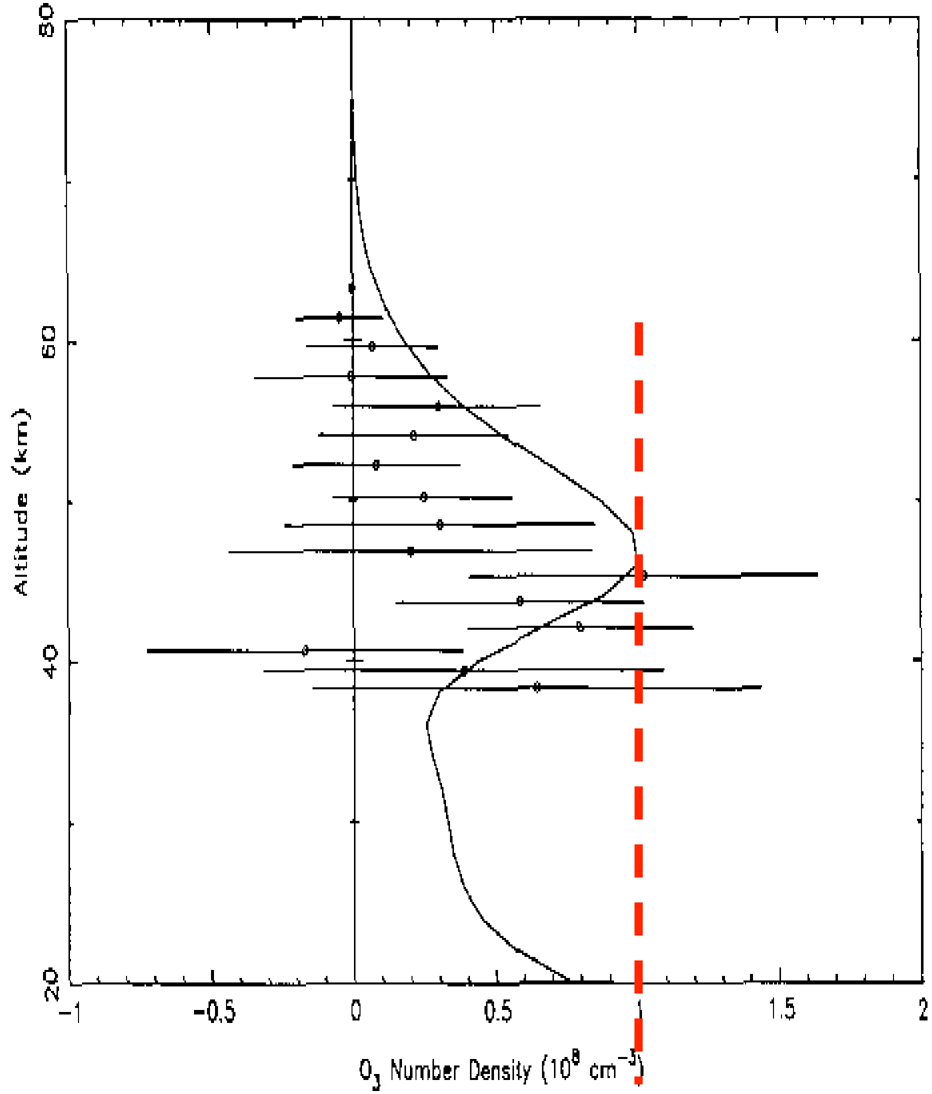


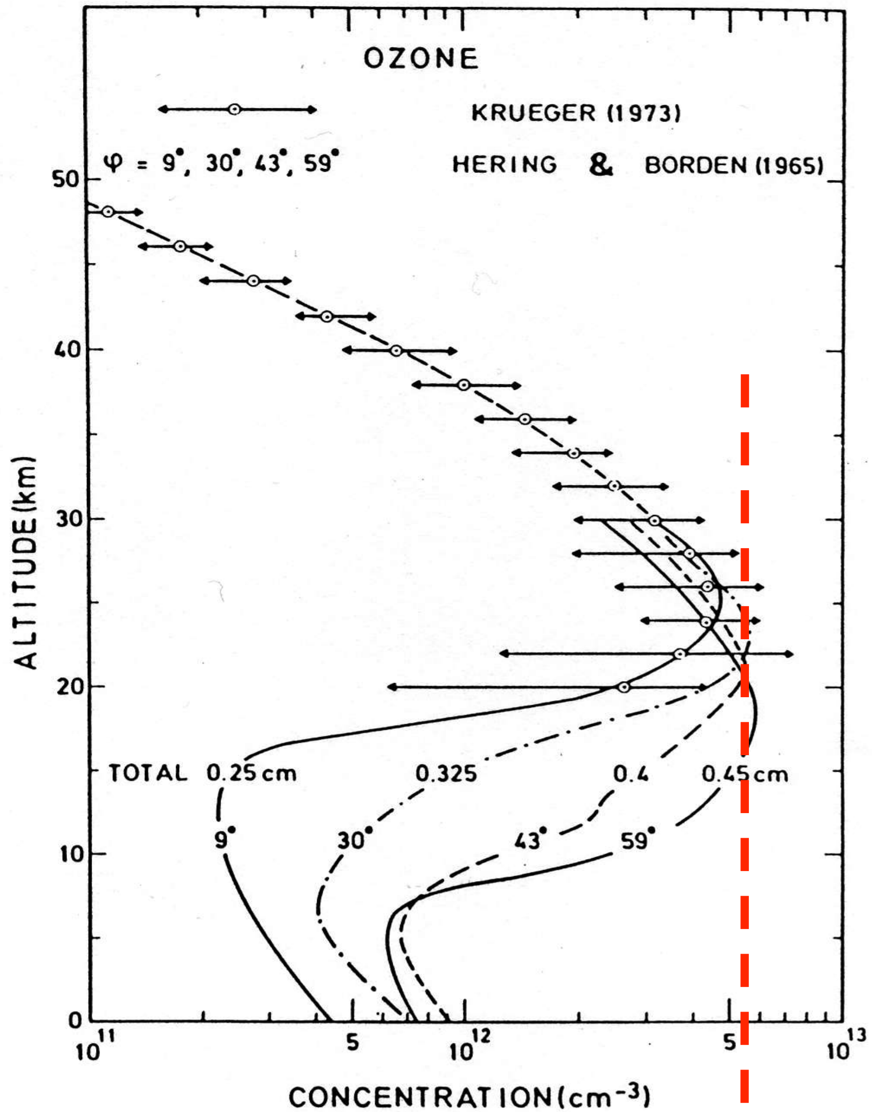
Lefèvre et al., 2004



Lefèvre et al., 2004

Ozone layers on Mars and Earth





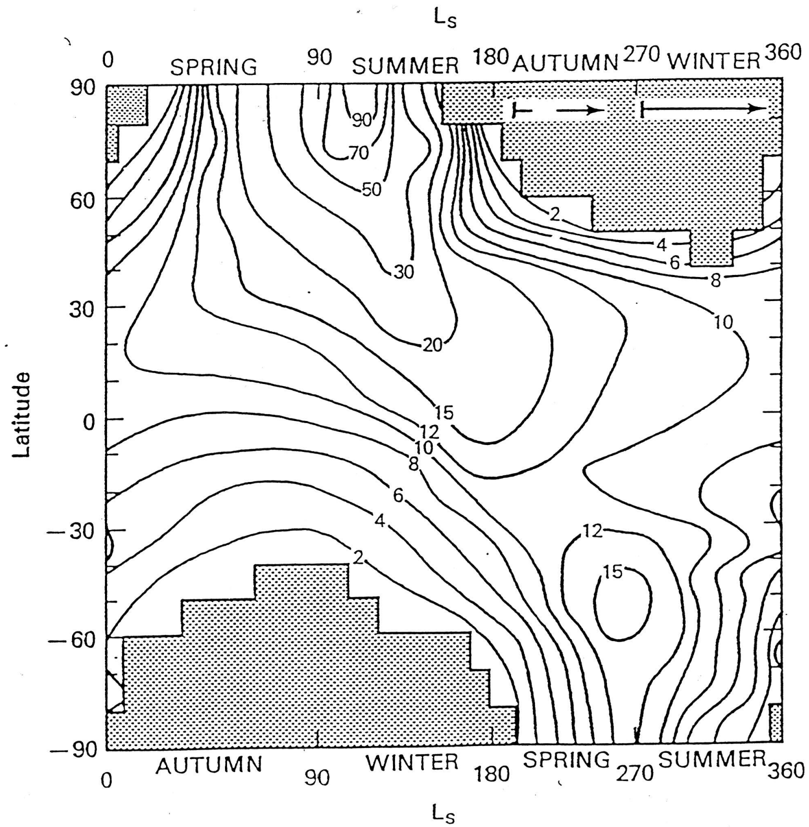
Nair et al., 1994

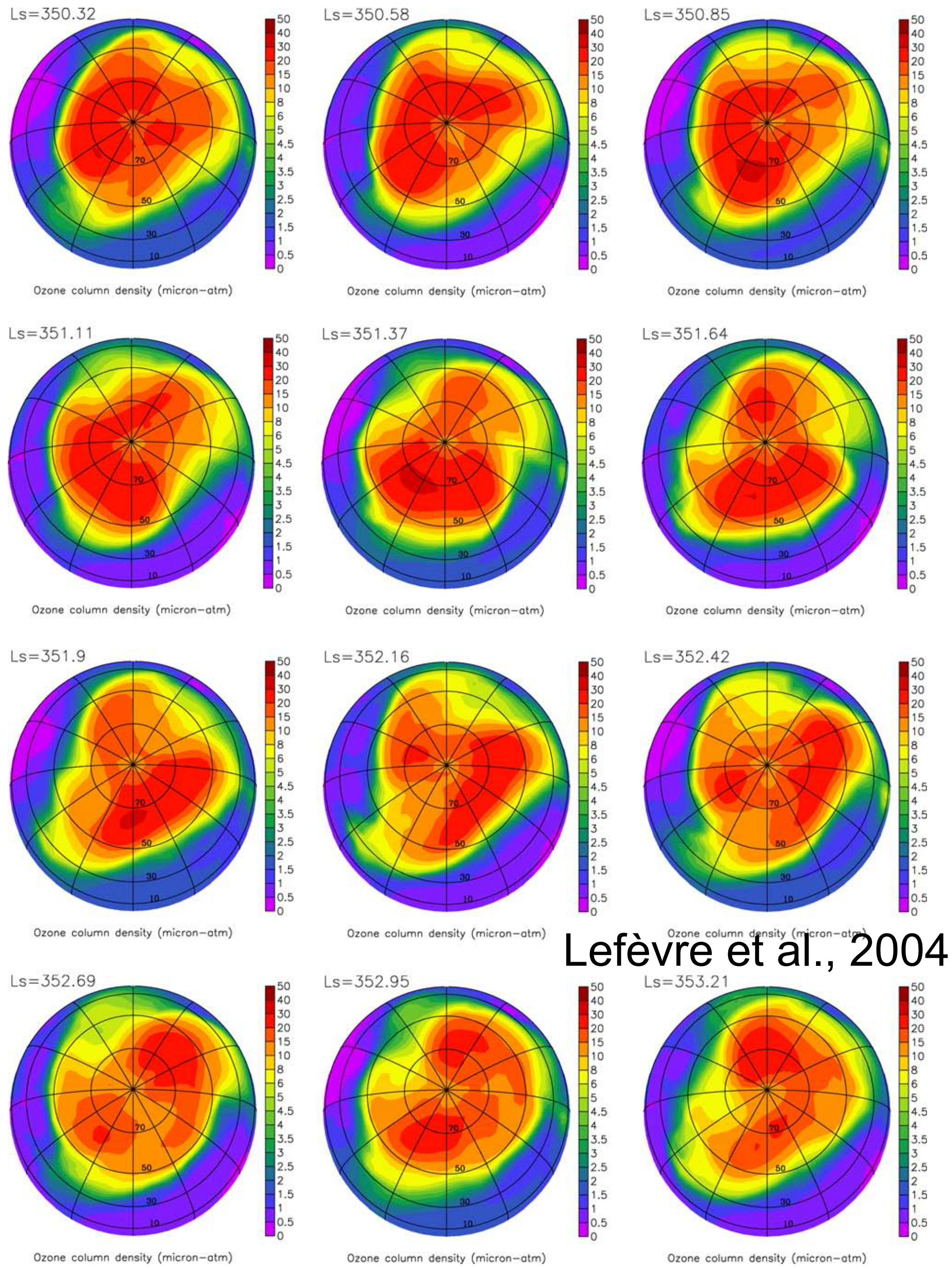
10^8 cm^{-3}

$5\ 10^{12}$ cm^{-3}

Polar ozone on Mars

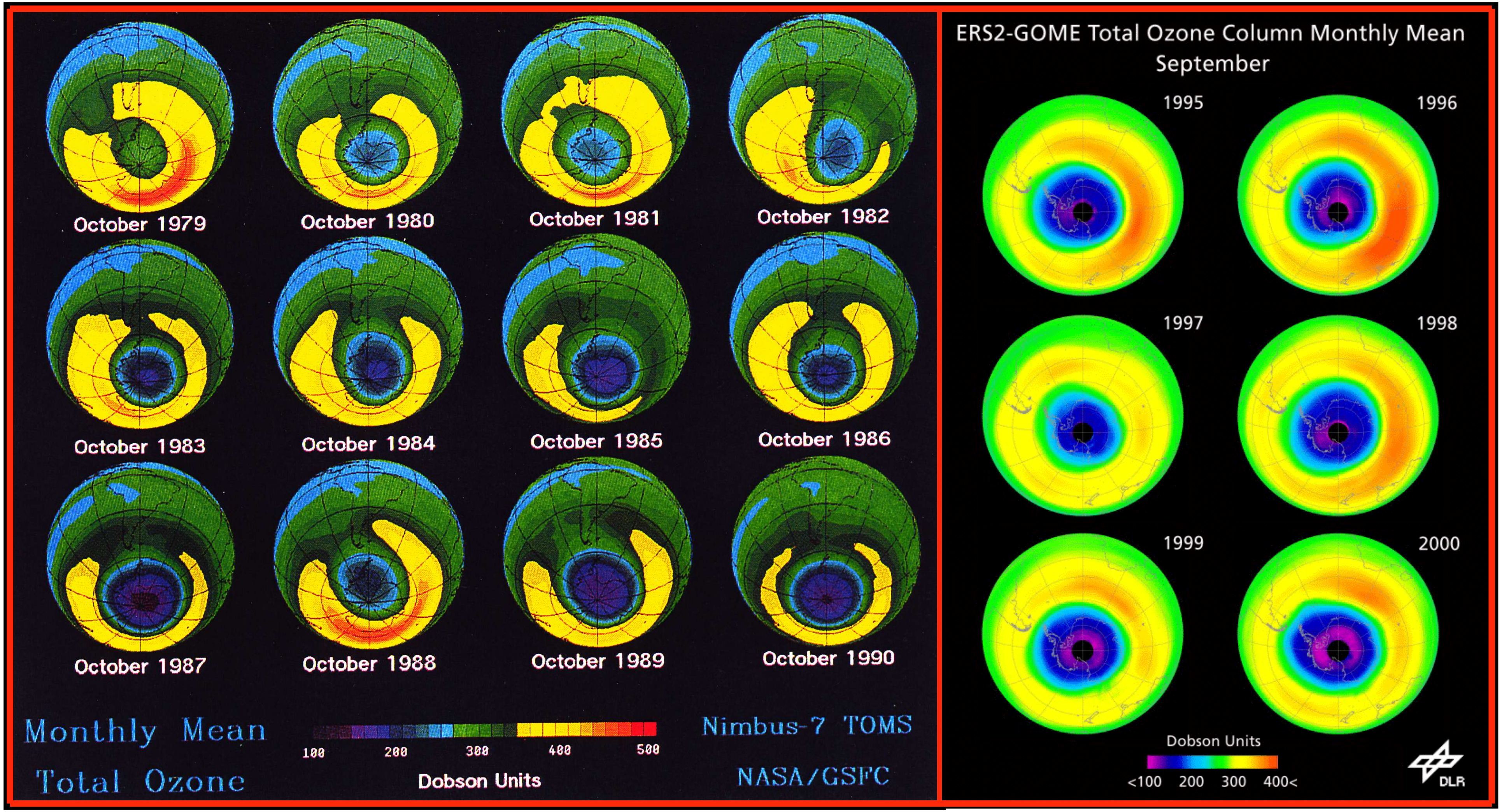
- Decrease of polar ozone at the end of Northern winter.





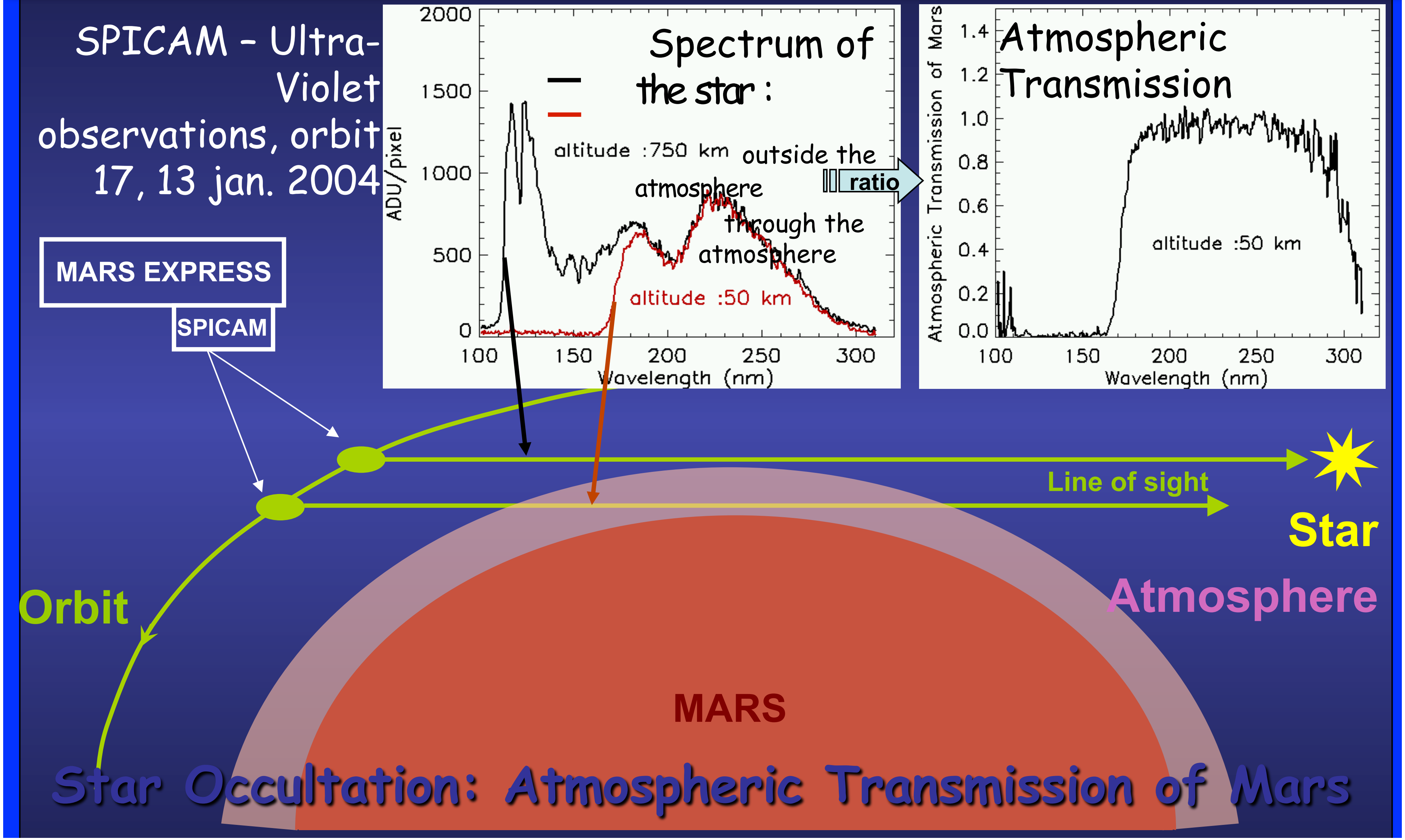
Lefèvre et al., 2004

Decrease of polar ozone on Earth



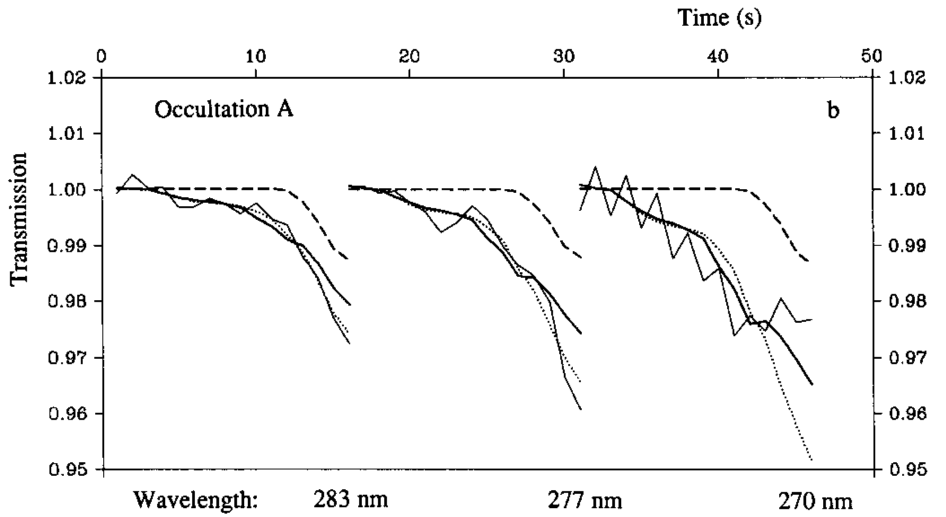
Measurement of ozone by solar and stellar occultation

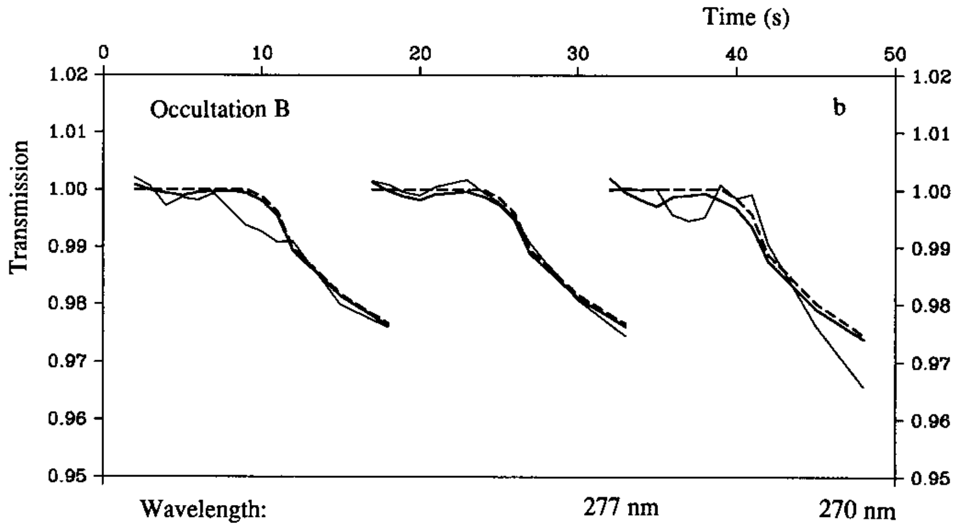
SPICAM – Ultra-Violet observations, orbit 17, 13 jan. 2004

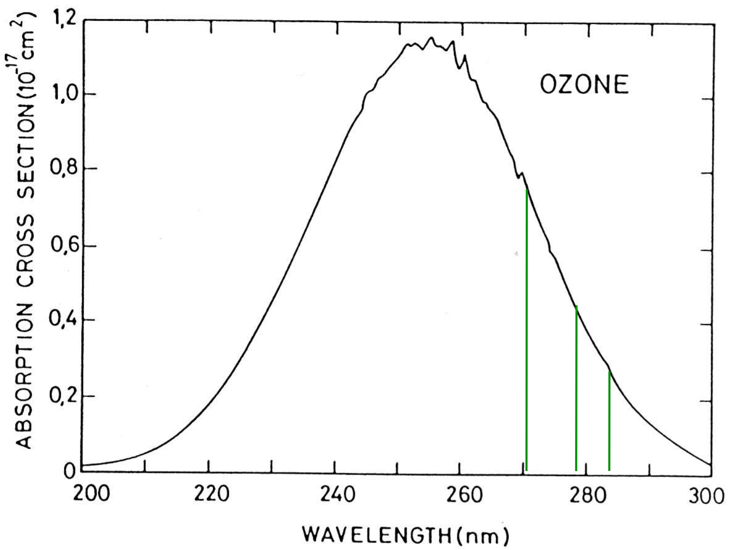


Discovery of ozone layer by solar occultation on Phobos 2 (1989)

Optical transmission :
T = exp(-τ)
at 3 wavelength : 270 nm, 277 nm and 283 nm.





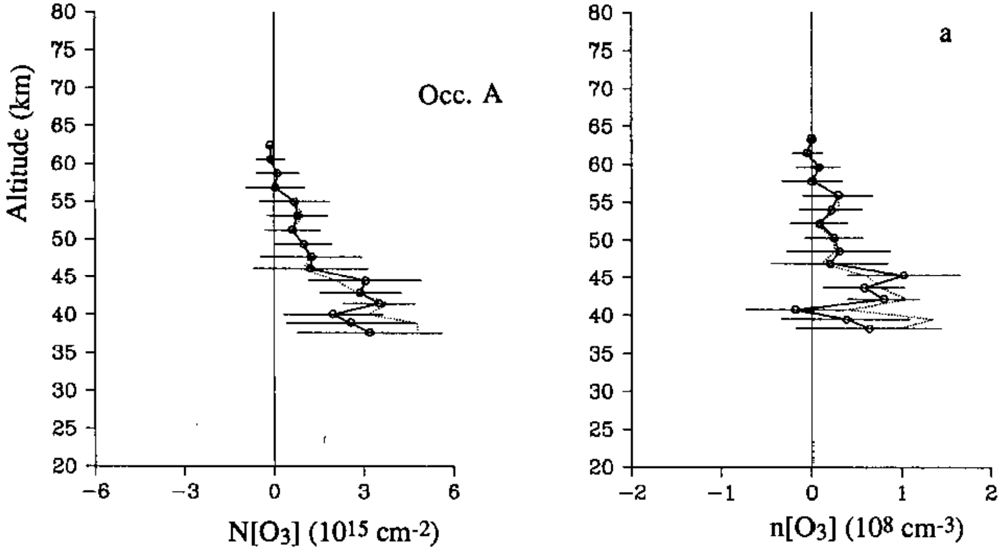


O_3 absorption cross-section in the 200-300 nm range

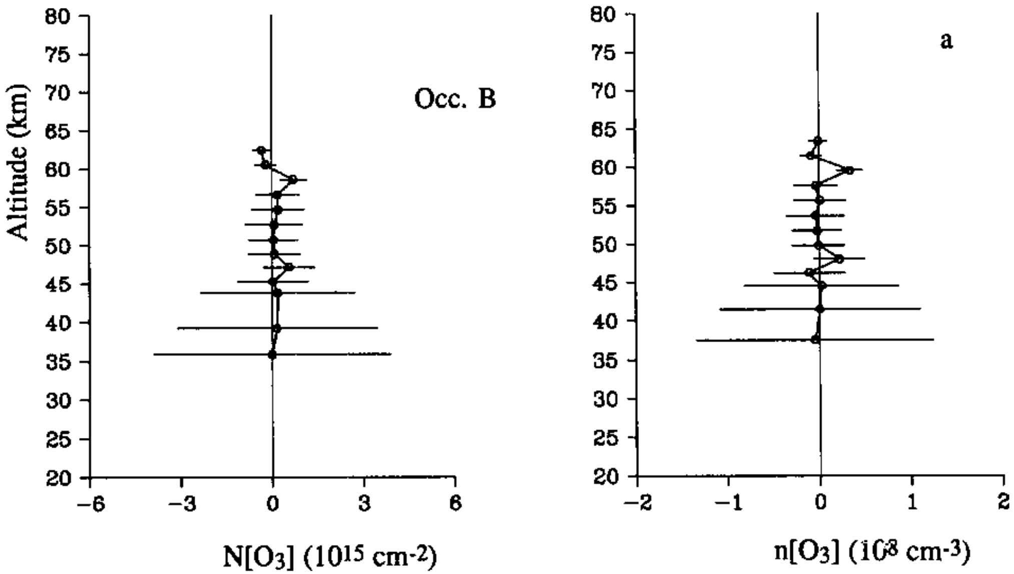
Blamont and Chassefière, 1993

Ozone vertical profiles in 2 cases

Occultation A

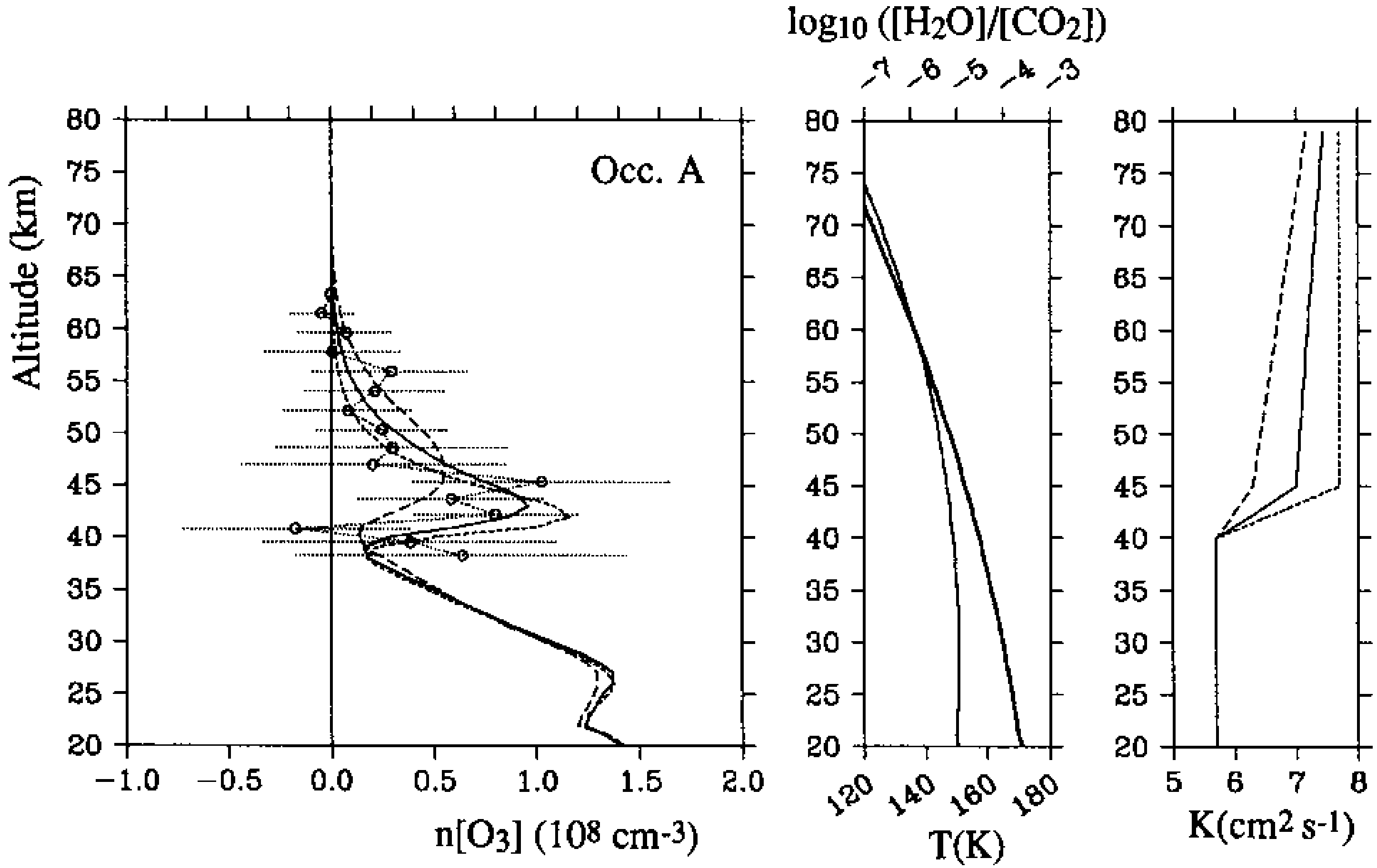


Occultation B



Blamont and Chassefière, 1993

Comparison between 1-D model and PHOBOS 2 observations

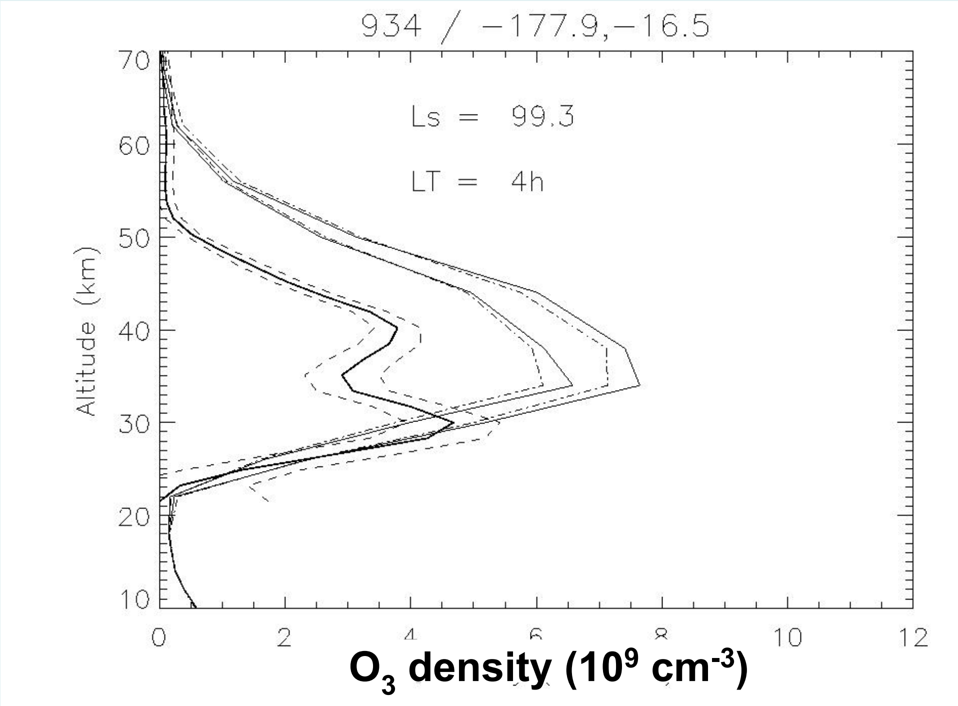


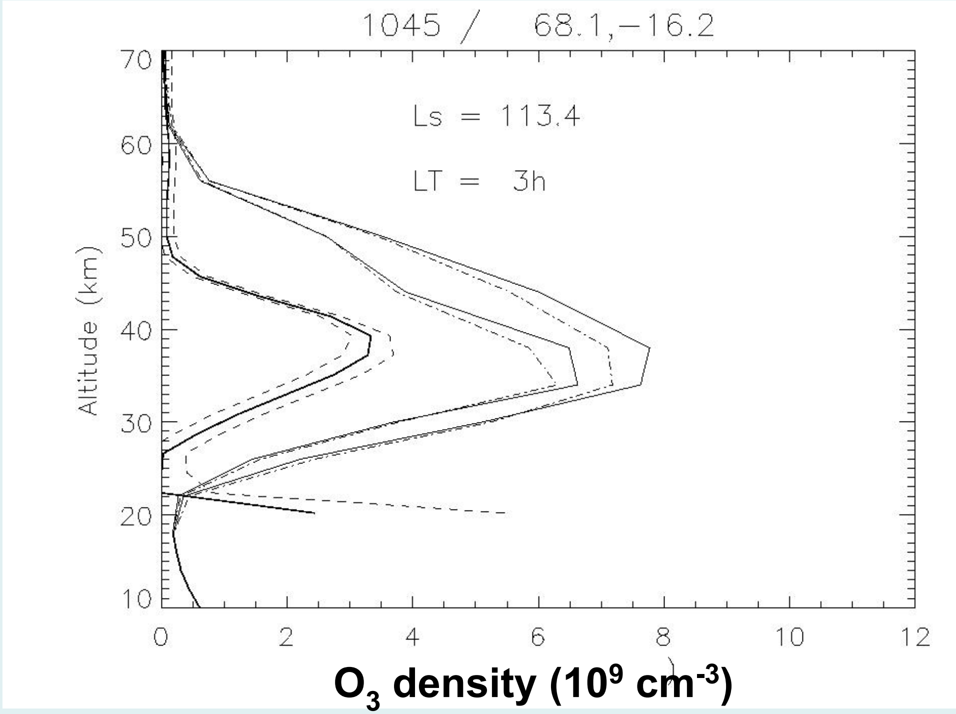
Blamont and Chassefière, 1993

Comparison between 3-D models and SPICAM observations (MEX)

Ls = 90-115°: Early Winter / 0-30° S

Comparison to LMD MGCM :



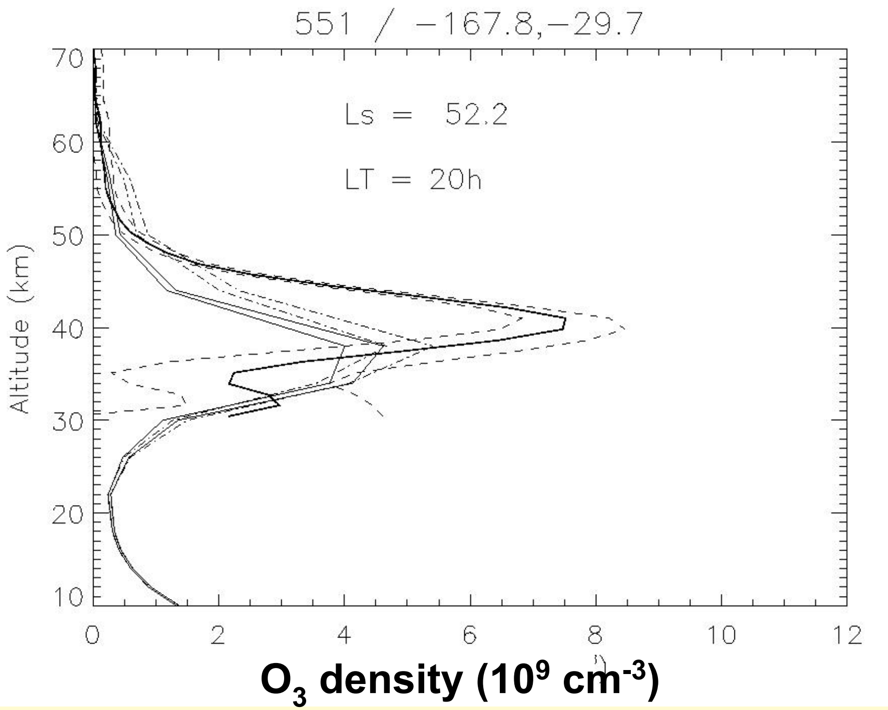


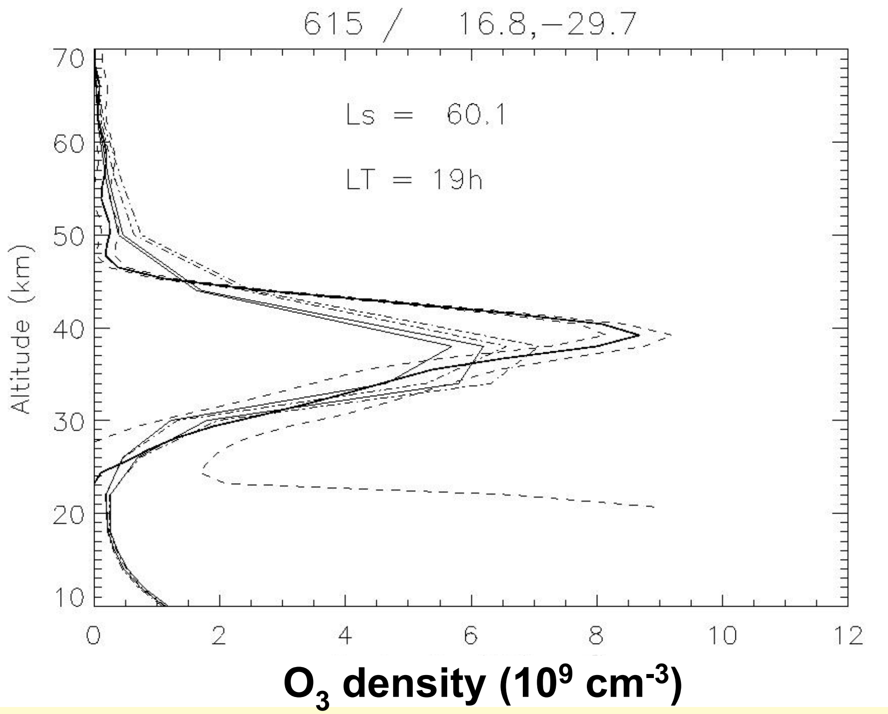
S. Lebonnois & SPICAM team

Another example

Ls = 50-80°: Late Fall / 0-30° S

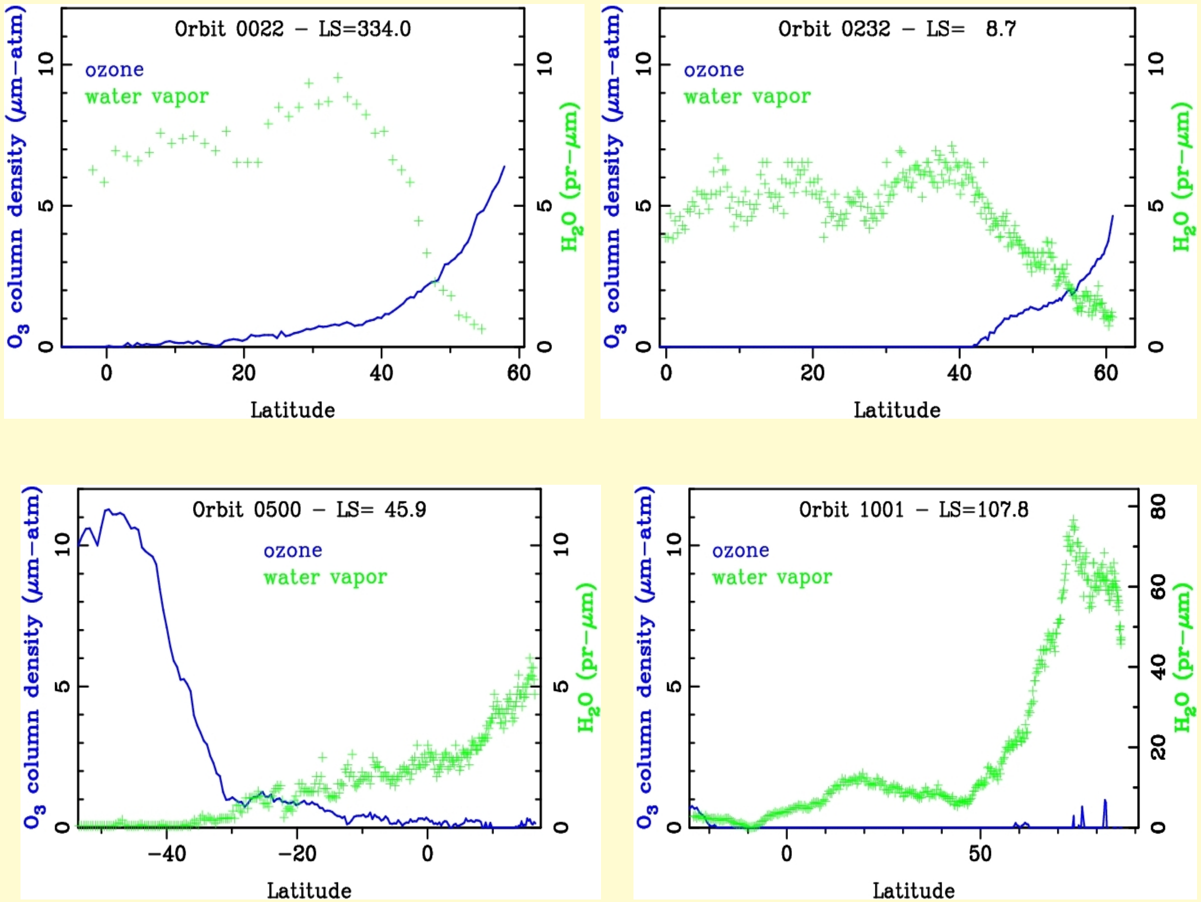
Comparison to LMD MGCM :





S. Lebonnois & SPICAM team

H_2O/O_3 anticorrelation measured by solar occultation



$$X + O_3 \longrightarrow XO + O_2$$

$$O_3 + h\nu \longrightarrow O + O_2$$

$$O + XO \longrightarrow X + O_2$$

$$2\,O_3 + h\nu \longrightarrow 3\,O_2$$

X = OH

X = O (Chapman cycle)

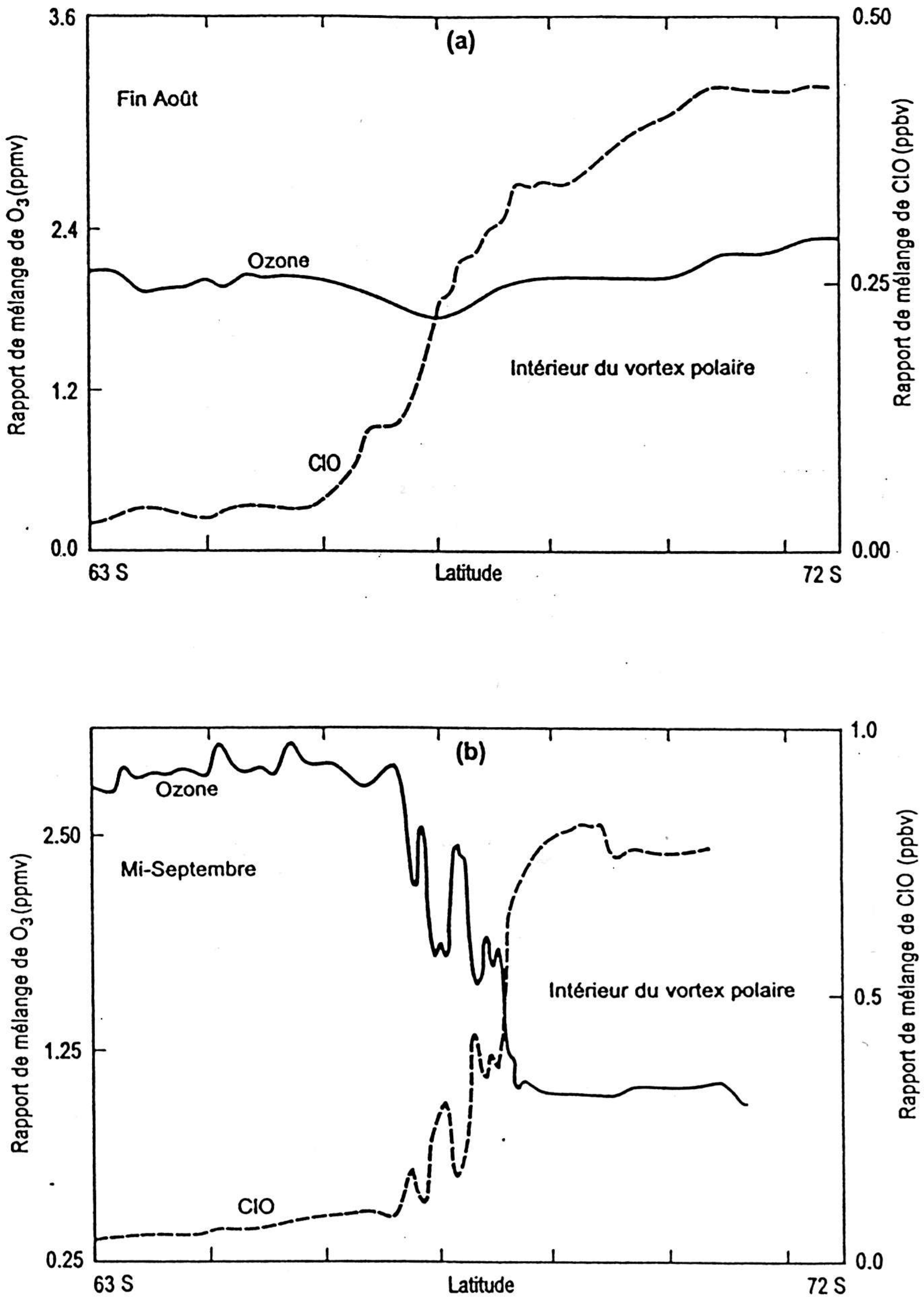
In Earth's stratosphere:

X = Cl

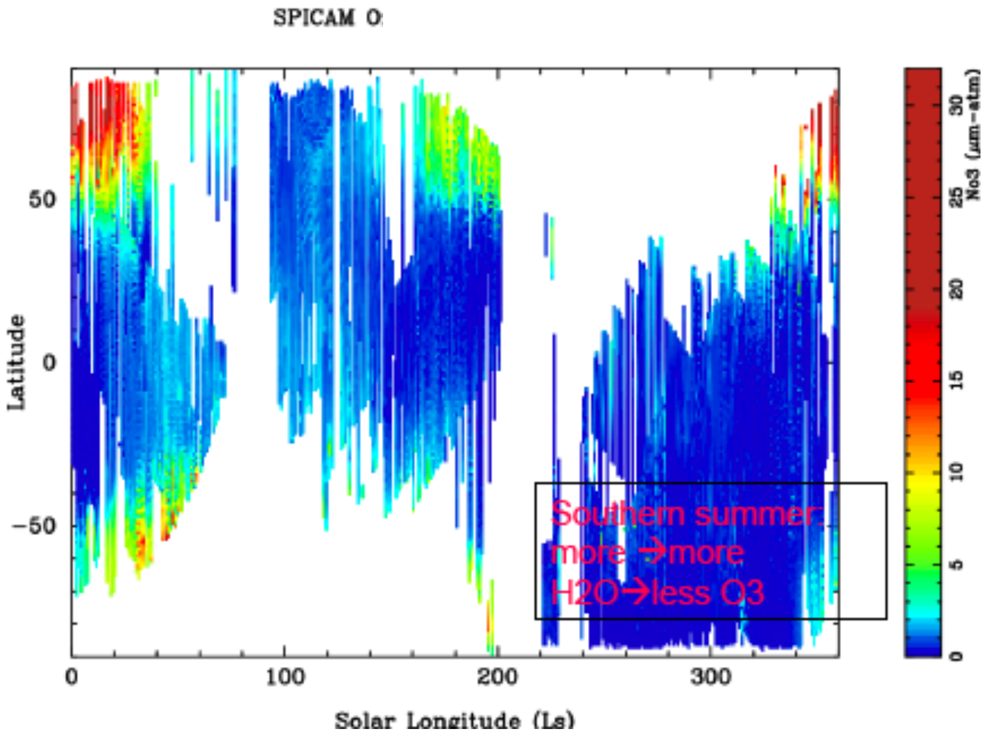
X = NO

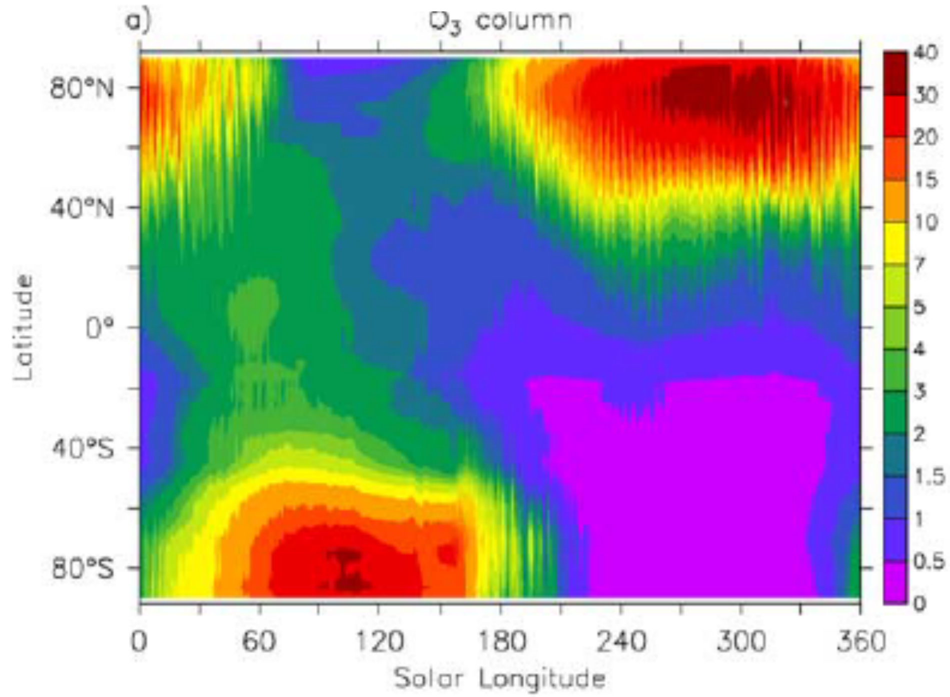
S. Perrier & SPICAM team

ClO/O_3 anticorrelation in Earth's polar stratosphere



3-D field of ozone





Perrier et al, 2006

OBSERVATION **GCM MODELLING**

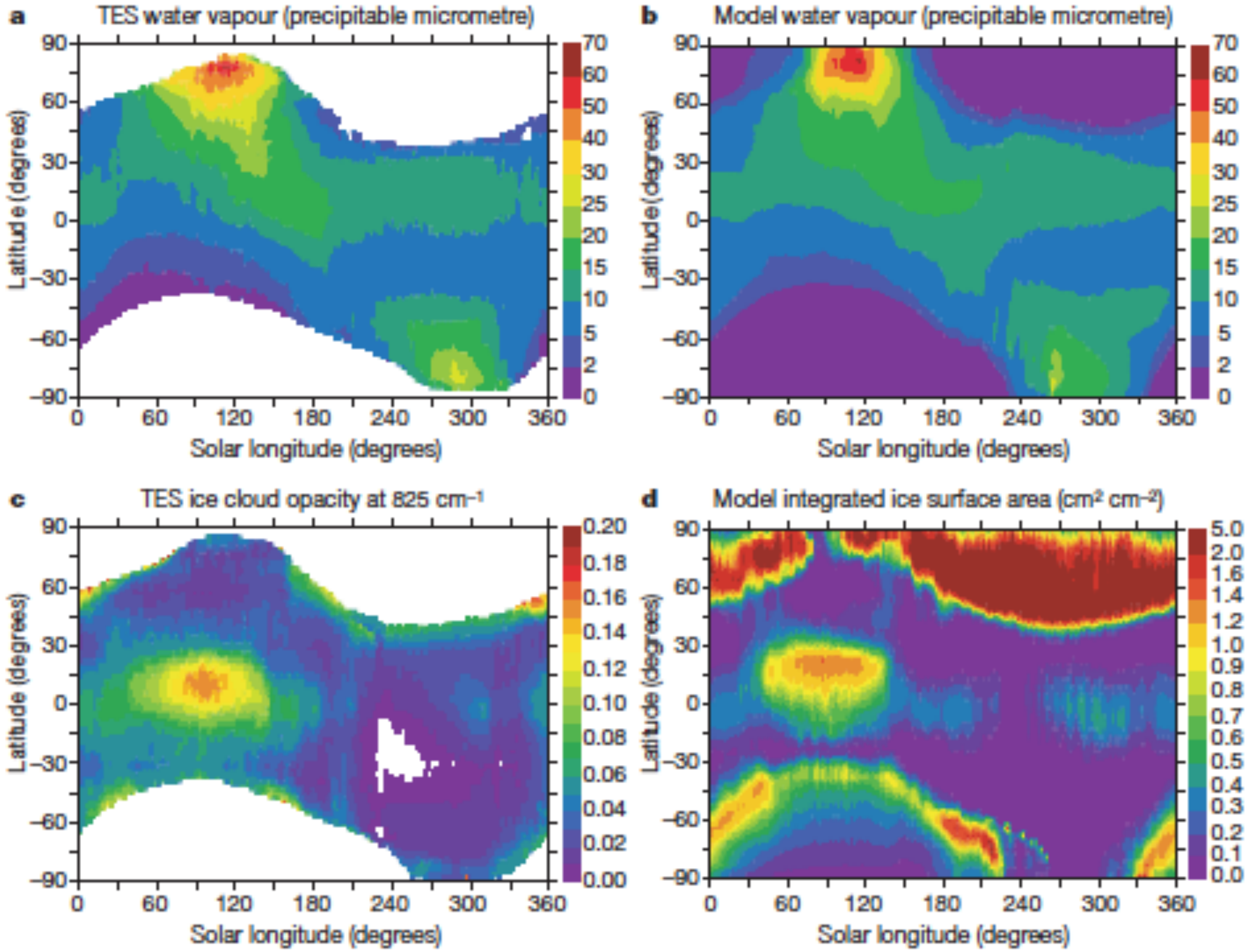
Lefèvre et al, 2004

Potential role of heterogeneous chemistry in Mars' H_2O ice clouds

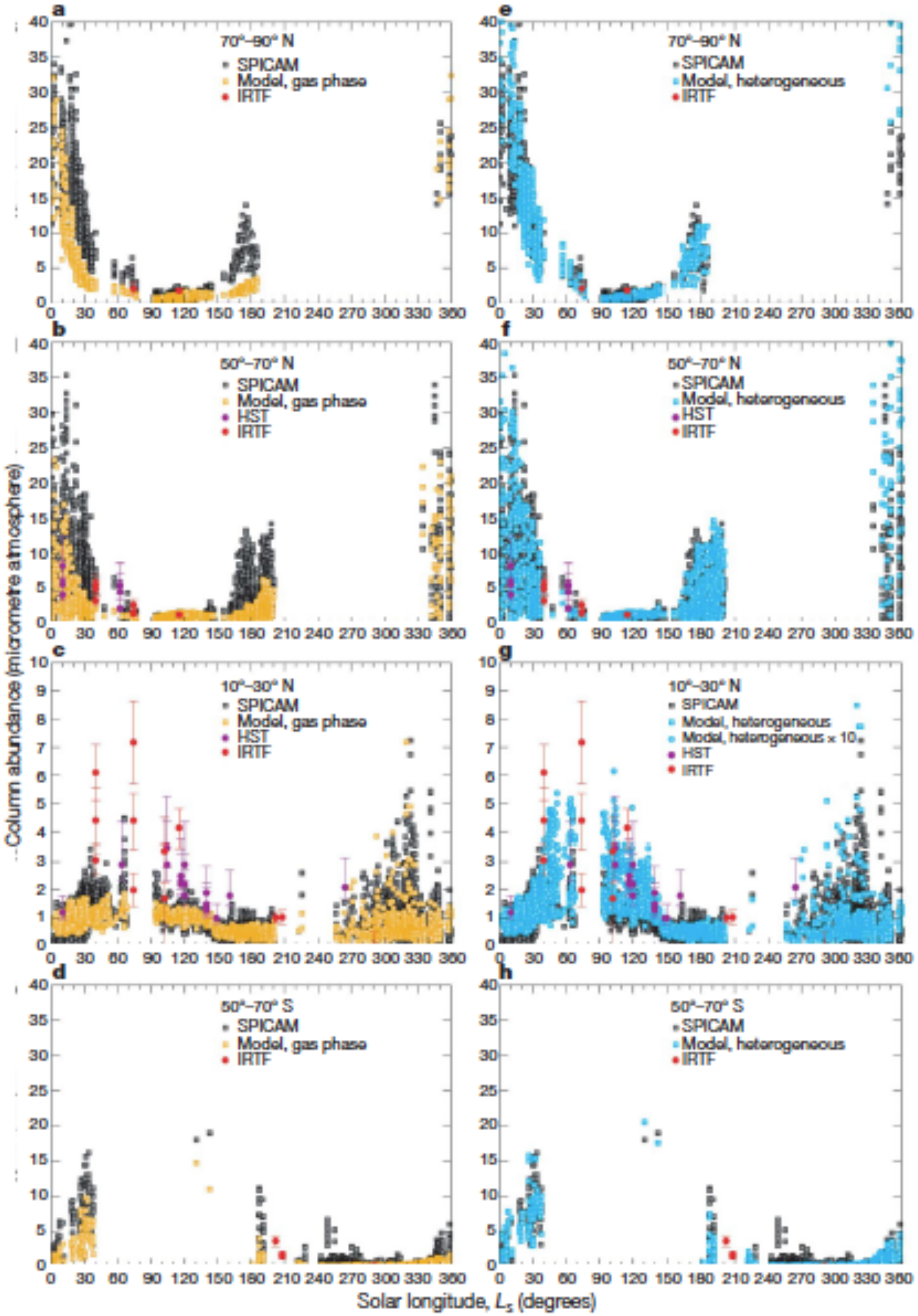
- On Earth, Polar Stratospheric Clouds form at T<195 K.

- Heterogenous chemistry involving N and Cl compounds responsible for ozone hole.

- Potential role of of Martian clouds in chemistry.



Lefèvre et al, 2008



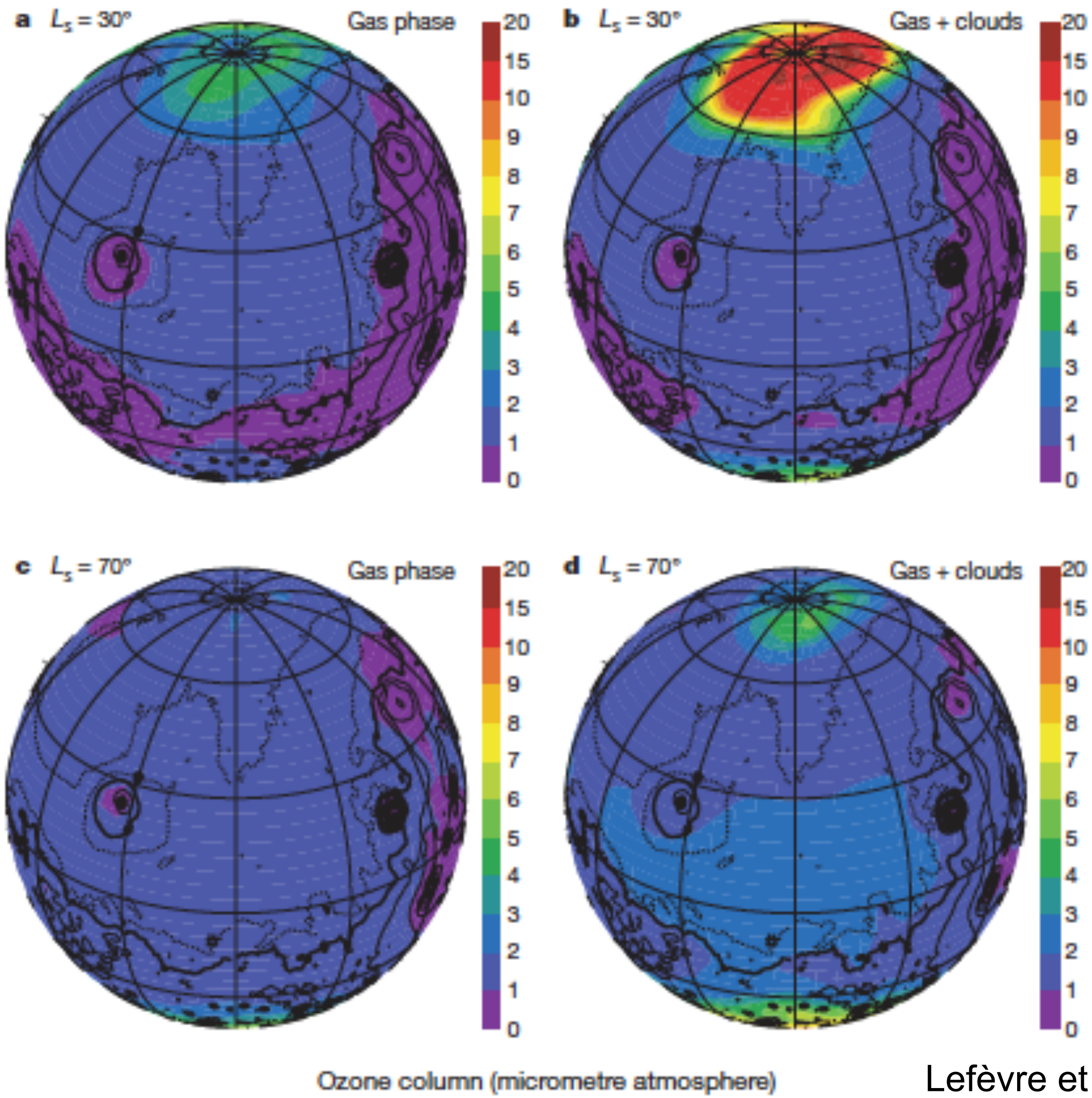
Enhancement of O_3 level through heterogeneous chemistry

- More ozone than observed in gas phase models.
- Introducing heterogeneous chemistry of HO_2 and OH on ice particles, more ozone simulated.

Lefèvre et al, 2008

Distribution of O_3 column without and with heterogeneous chemistry

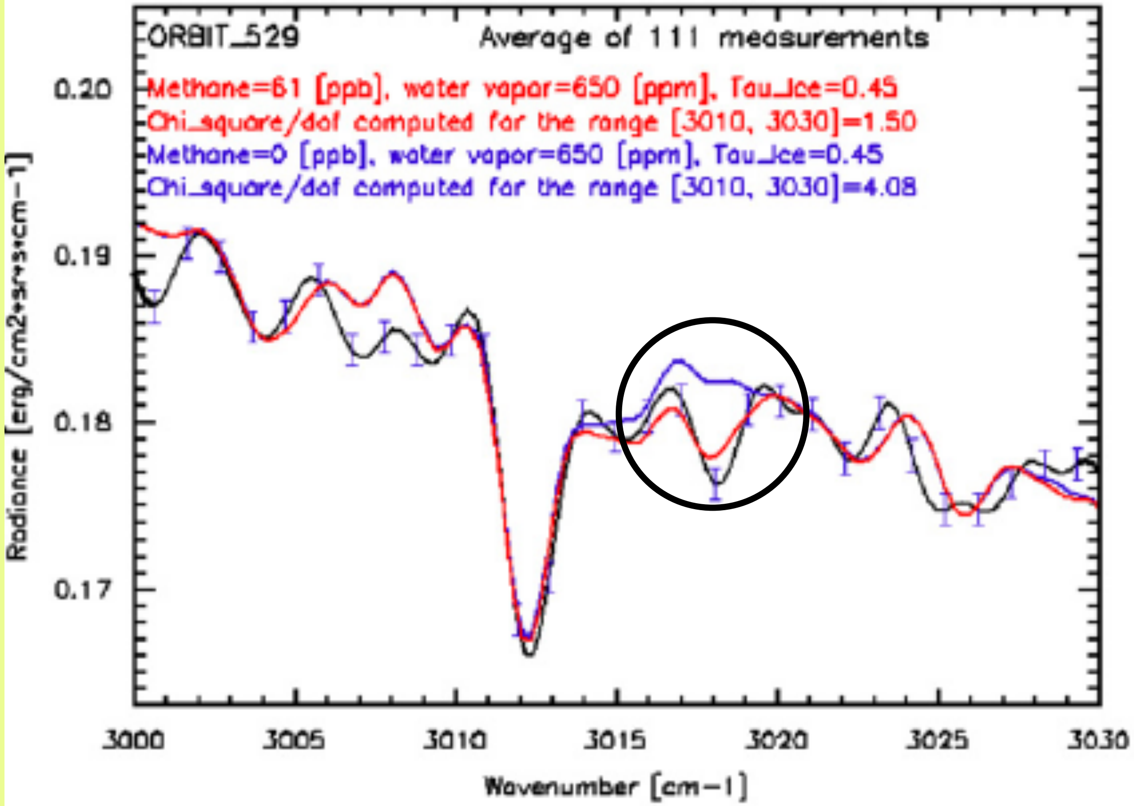
- Unit : micron-atm.
- Northern spring and aphelion



Lefèvre et al, 2008

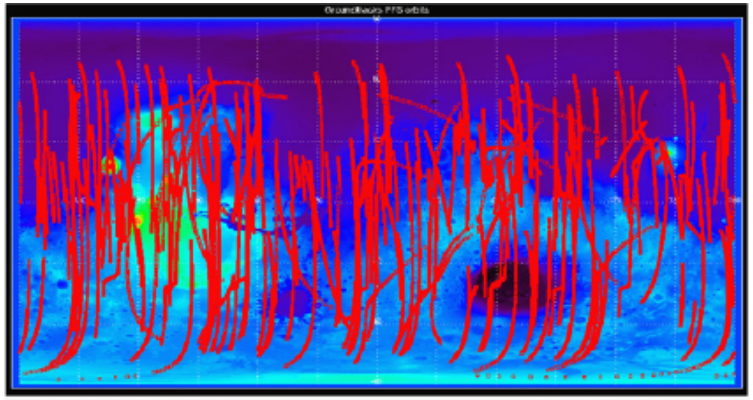
Detection of methane by PFS (Mars Express)

- Methane detected in its Q-branch at 3018 cm^{-1} (Formisano et al, 2004).
- Relatively low SNR ratio & spectral resolution, requiring averaging spectra.
- Data spanning all seasons, latitudes, longitudes, local times (except night time).

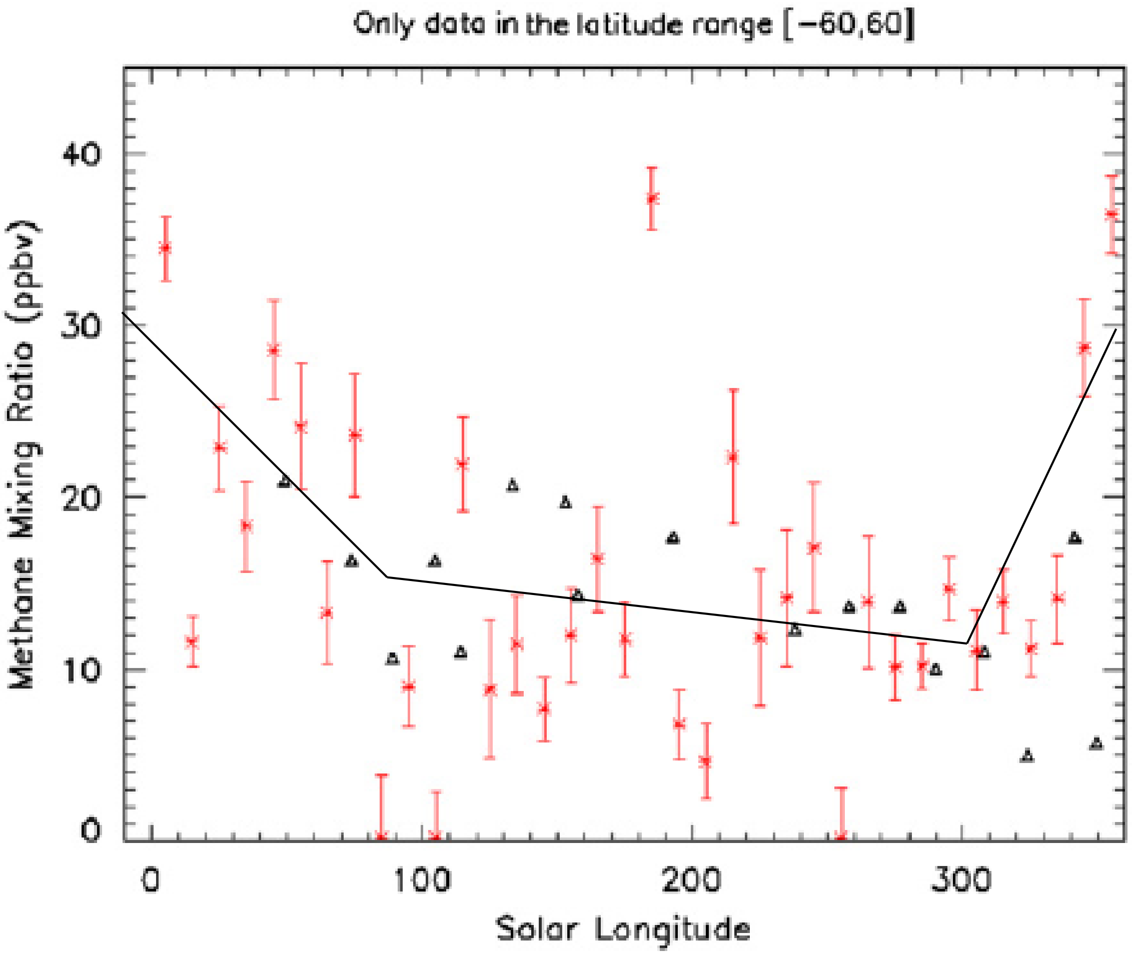


PFS spectrum average of 111 measurements in orbit 529 (Geminale et al, 2008)

Seasonal cycle of methane



Seasonal variations of the abundance of methane over 3 seasonal cycles

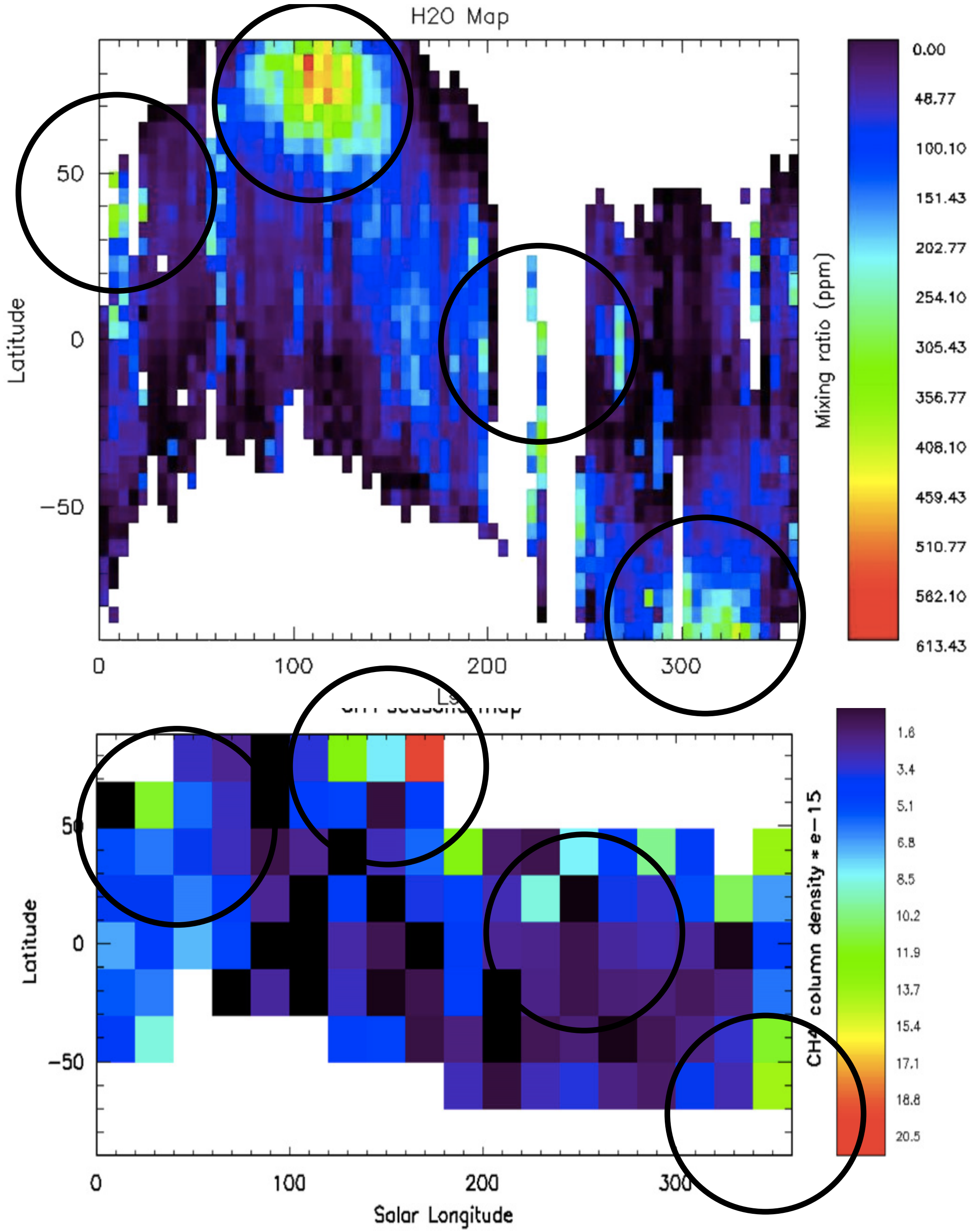


Formisano et al, 2004

Geminale et al, 2011

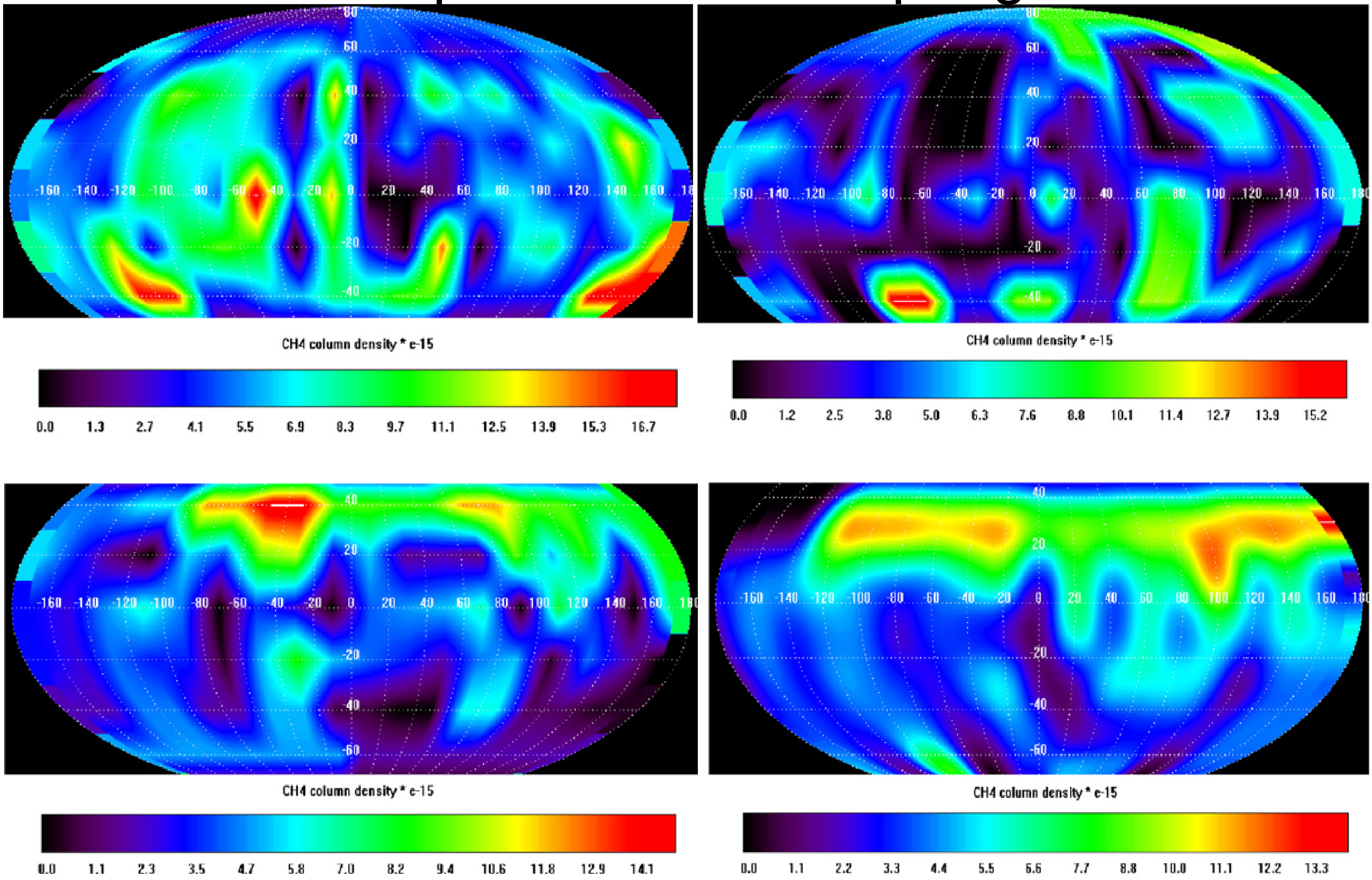
Recent reanalysis of PFS data

Seasonal/latitudinal maps of CH_4 and H_2O observed by the same instrument (PFS/ Marx Express).



Geminale et al., 2011

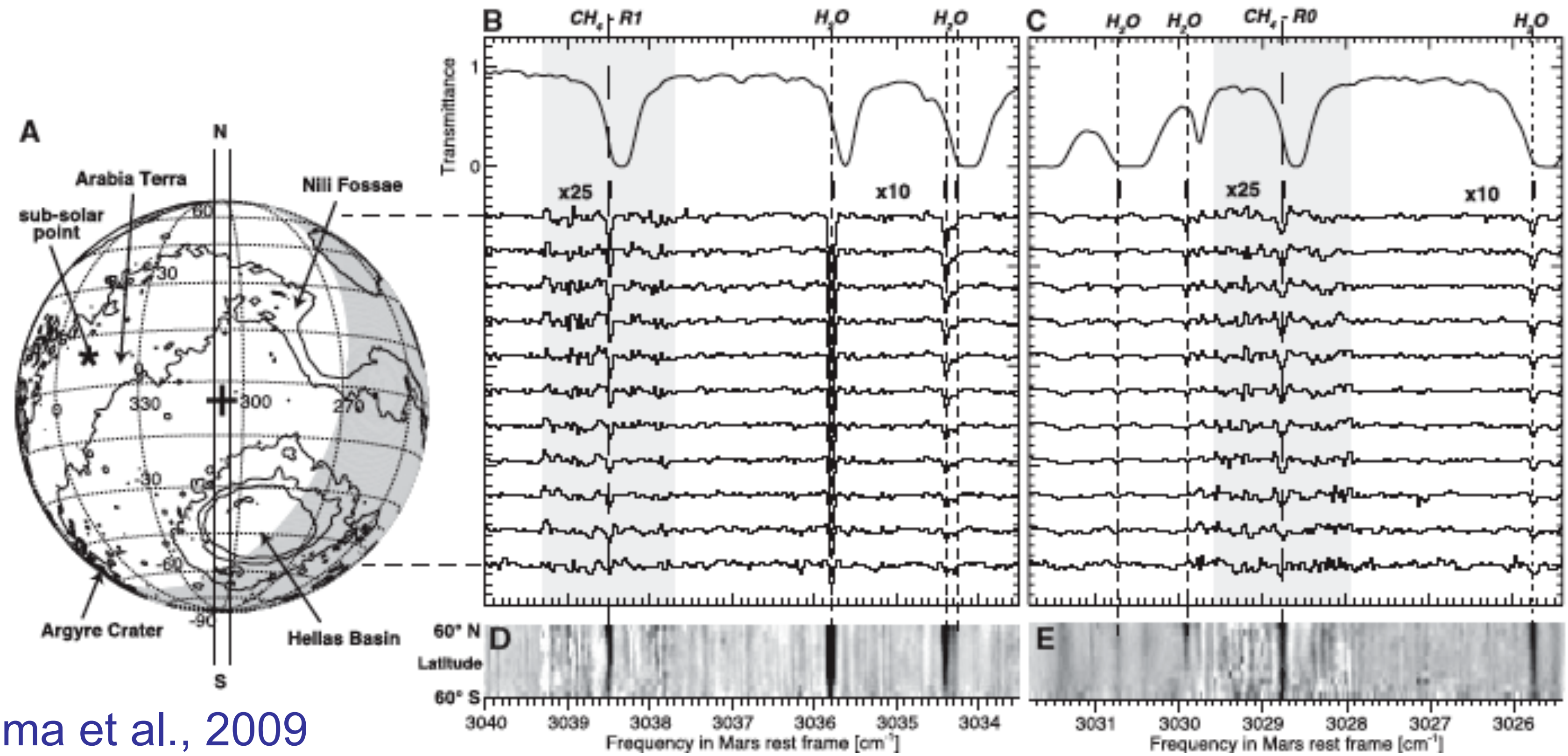
Seasonal maps of methane: Spring → Winter



Geminale et al, 2011

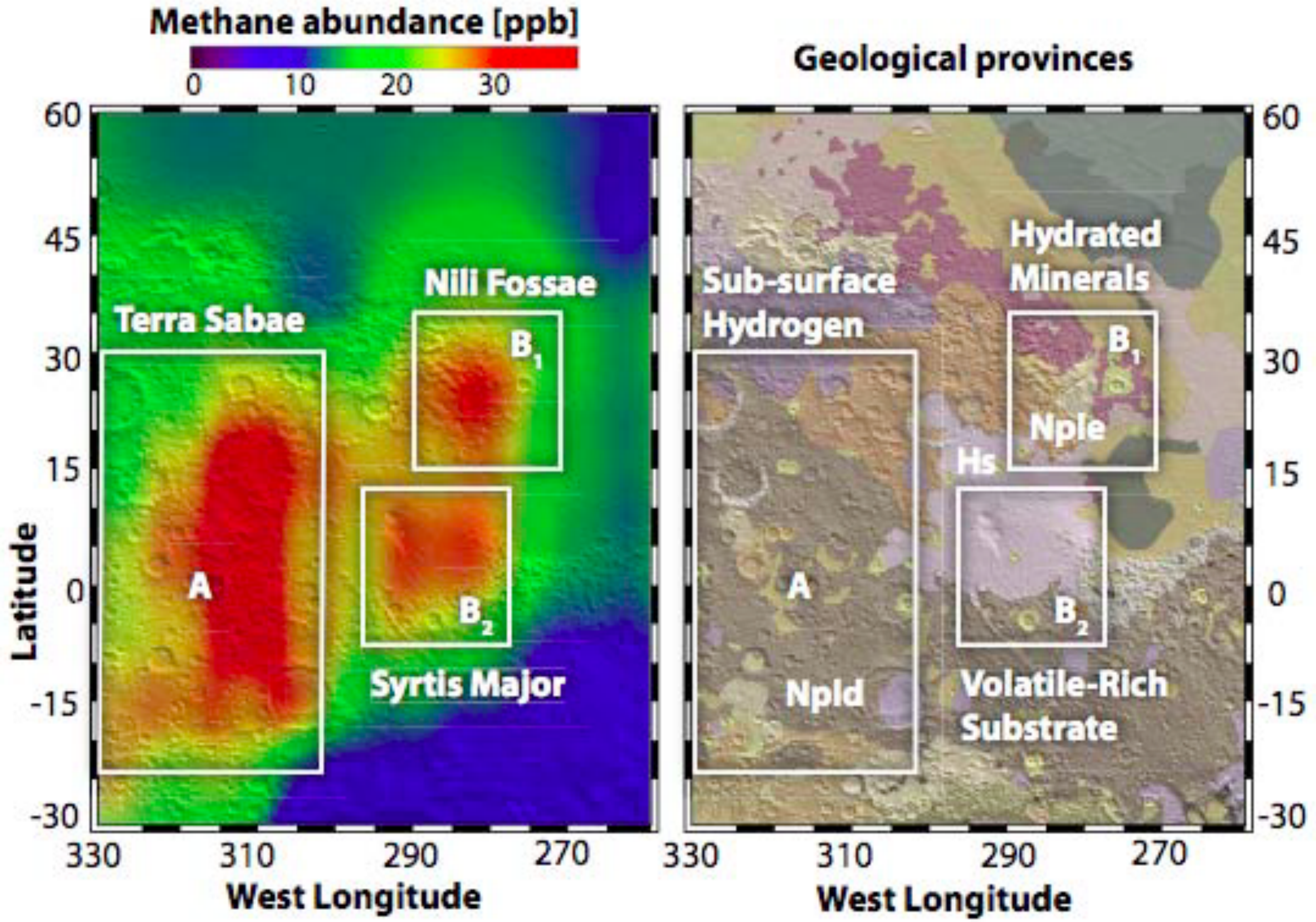
Recent detection of methane from Hawaï

- CSHELL/IRTF, NIRSPEC/Keck-2
- Two lines detected simultaneously at 3029 and 3038 cm^{-1}.
- Correction by telluric extinction required.
- More precise than PFS data, but no seasonal/geographical coverage.



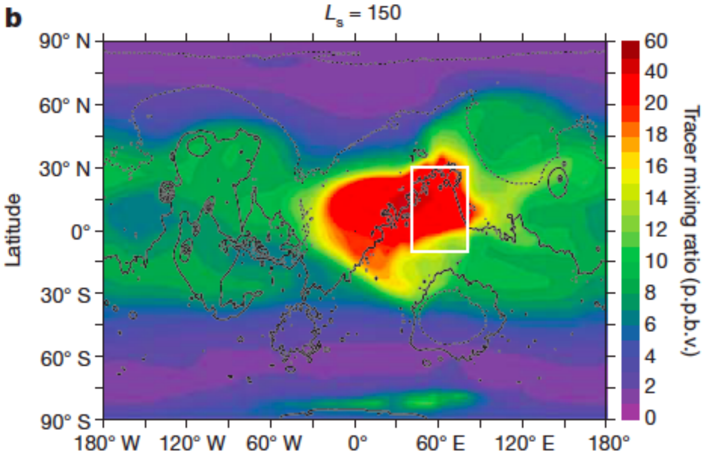
Mumma et al., 2009

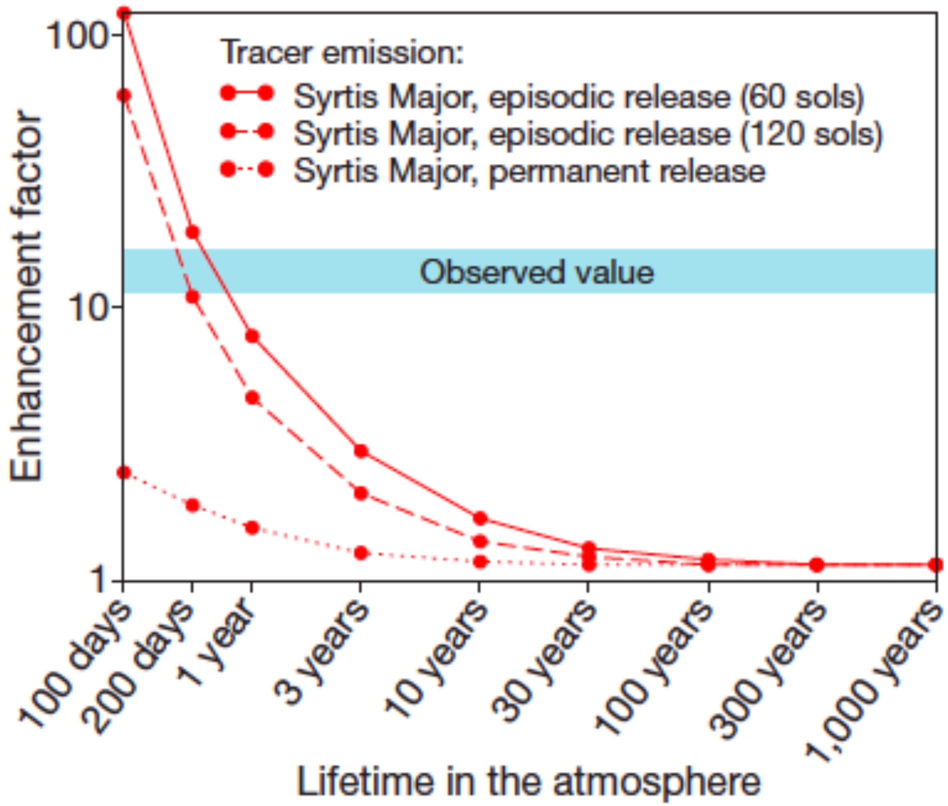
Geographic distribution of observed CH_4



Mumma et al., 2009

The puzzling question of the lifetime of methane





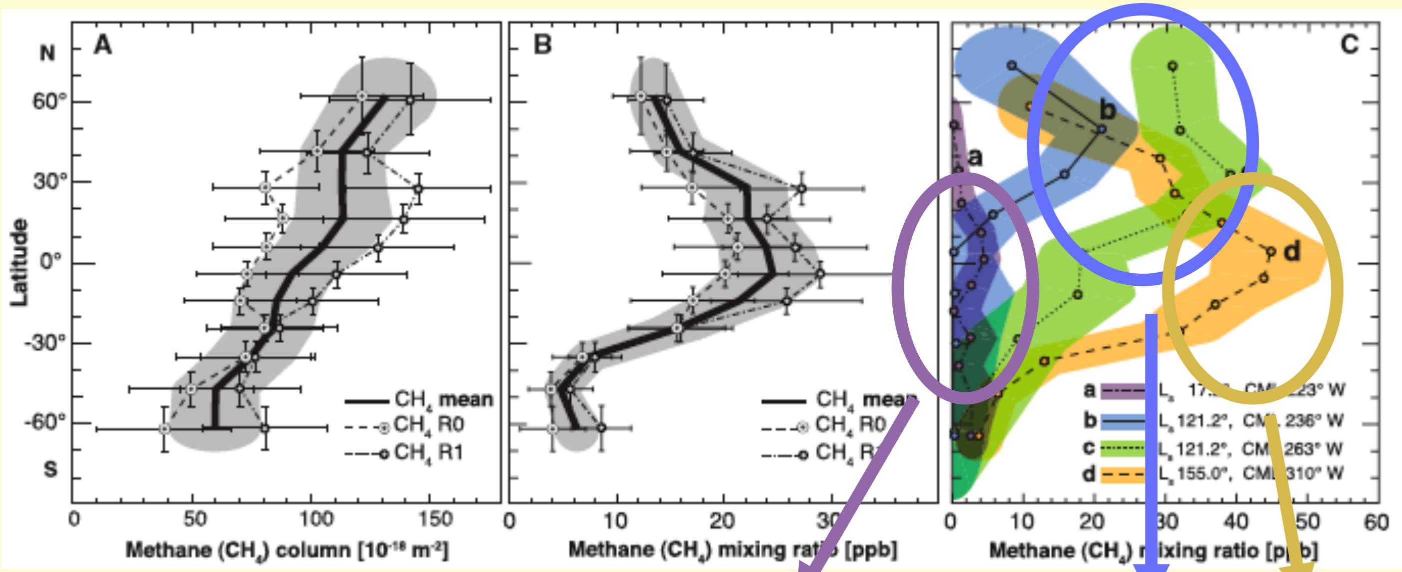
Photochemical lifetime(CH_4+OH) : 300 years.

According to GCM calculations : 3 months!

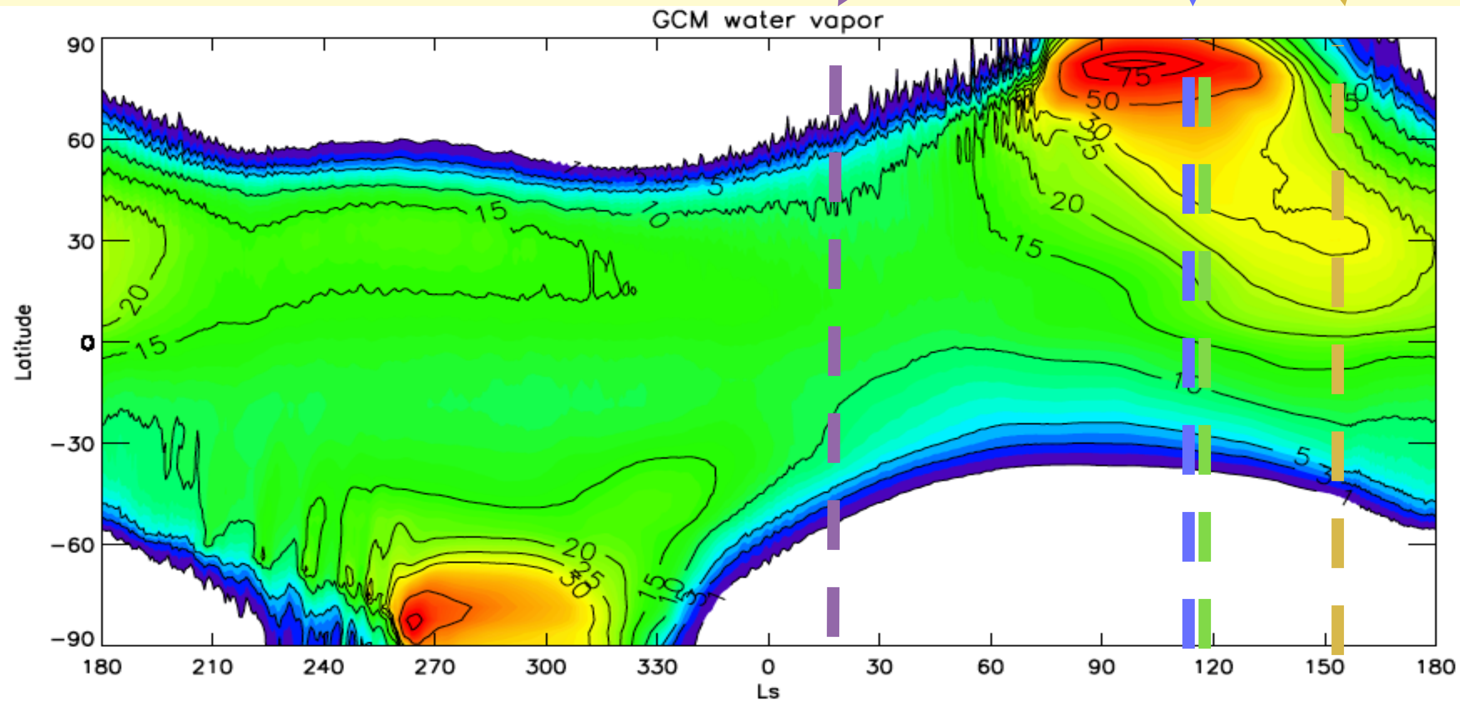
Lefèvre et Forget, 2009

➢ ***Heterogeneous oxidation of CH_4 in the regolith : H_2O_2, Fe^{3+}, …?***

Latitudinal profiles and correlation with H_2O



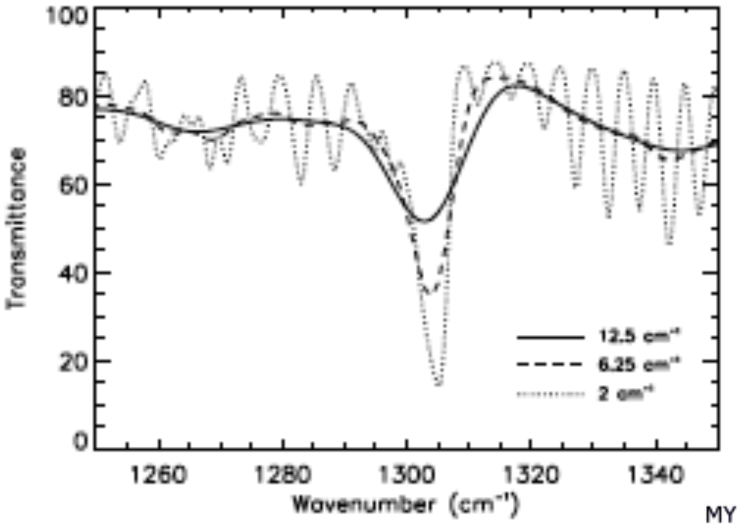
Mumma et al., 2009



Montmessin et al., 2004

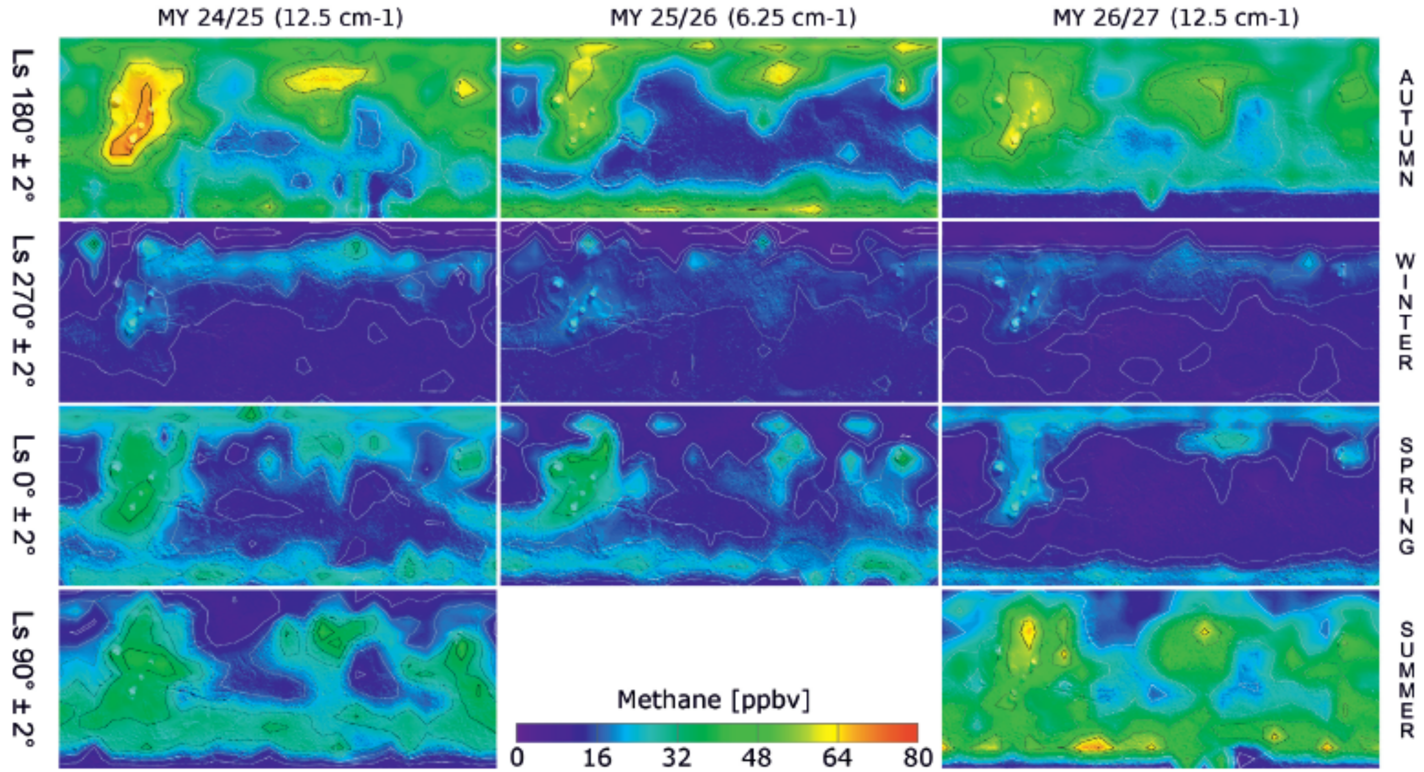
Data agree with a global CH_4-H_2O correlation

Mapping of methane from TES/MGS



3 000 000 TES spectra used in the 1260-1340 cm^{-1} range (thermal IR)

Fonti and Marzo, 2010



Seasonal cycle of CH_4 over the last 5 seasonal cycles