

# Challenges raised by the observations of Martian methane

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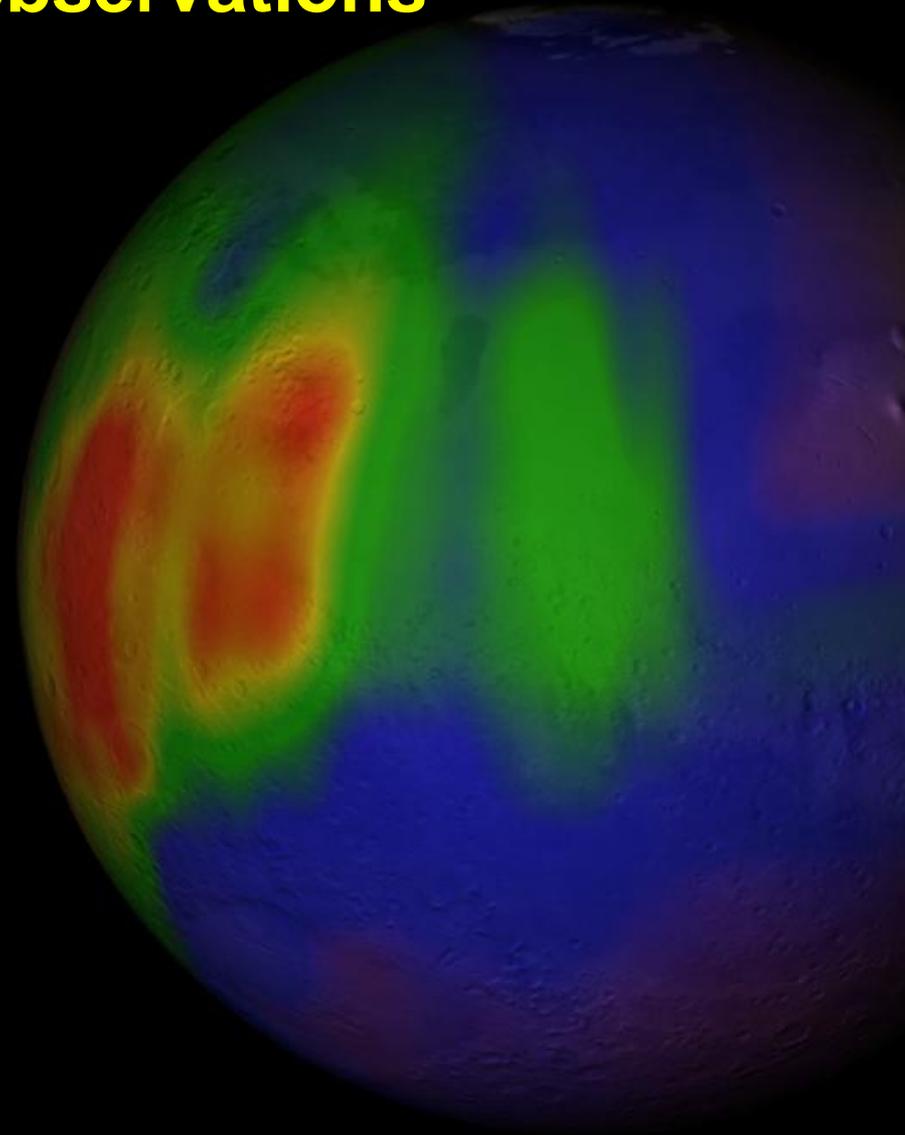
*LMD  
CNRS/Université Pierre et Marie Curie, Paris*

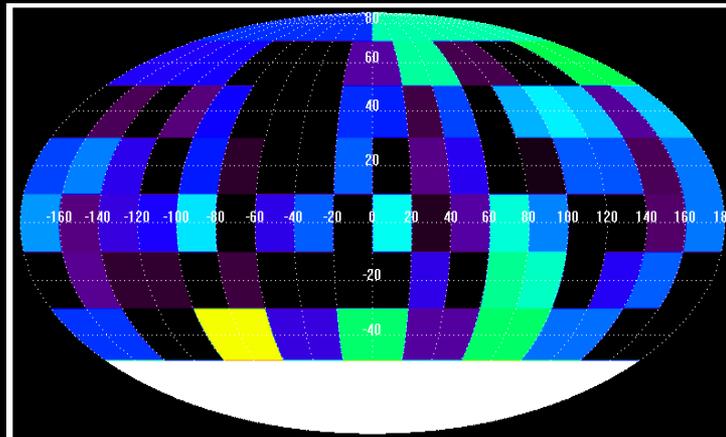
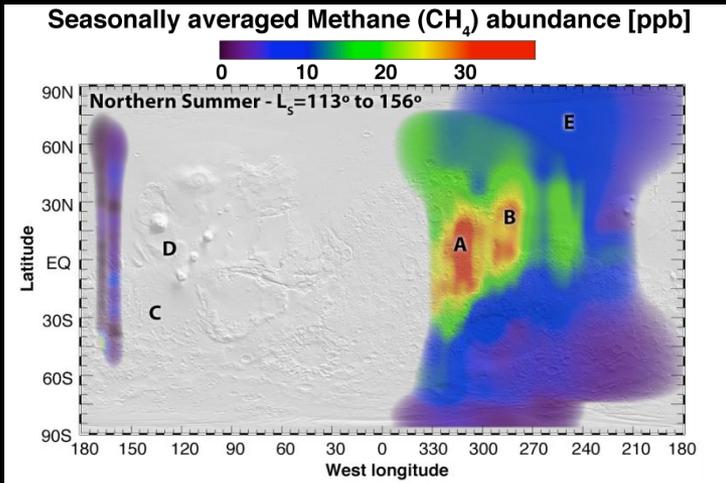
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*University of Colorado, Boulder*





$L_s = 90-180$

## CSHELL/NIRSPEC

Mumma et al.  
Science, 2009

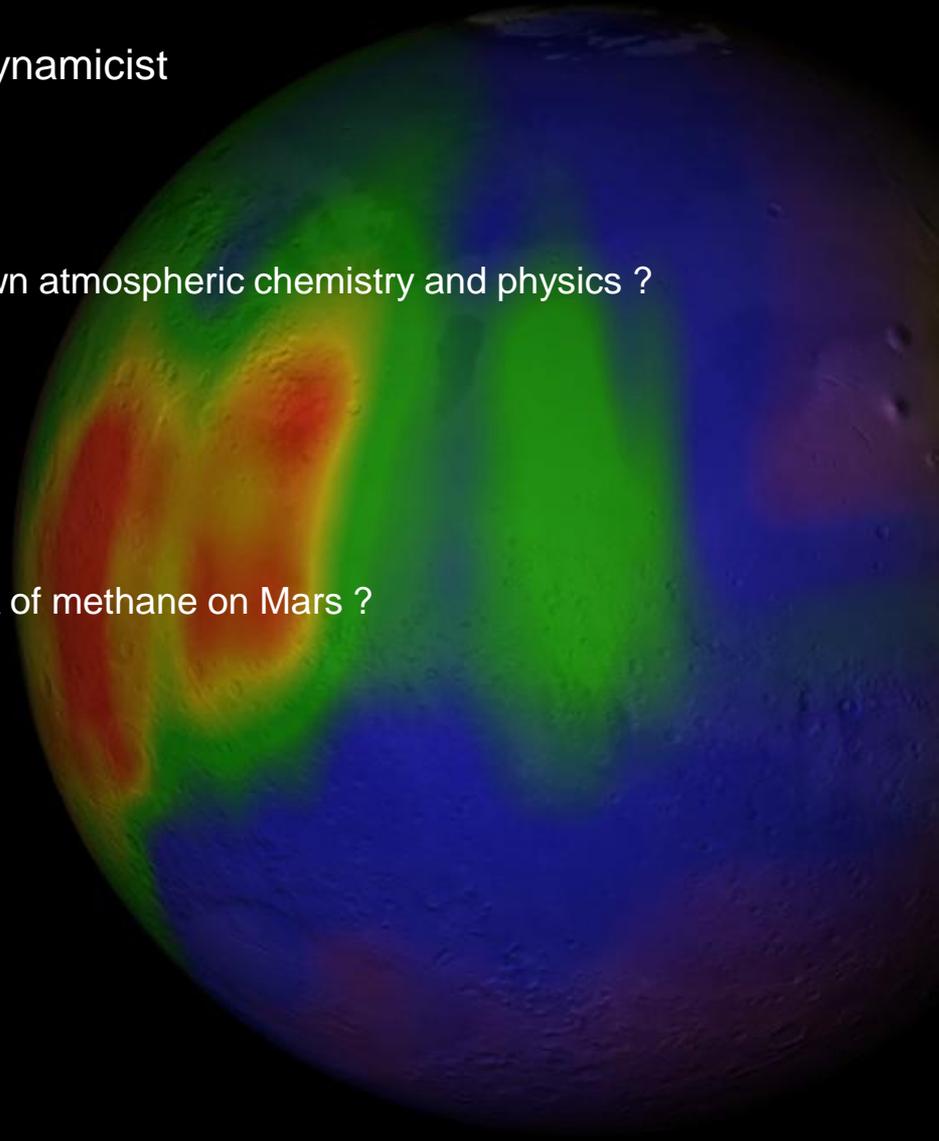
## PFS

Formisano et al.  
ESA-ASI Methane workshop, 2009



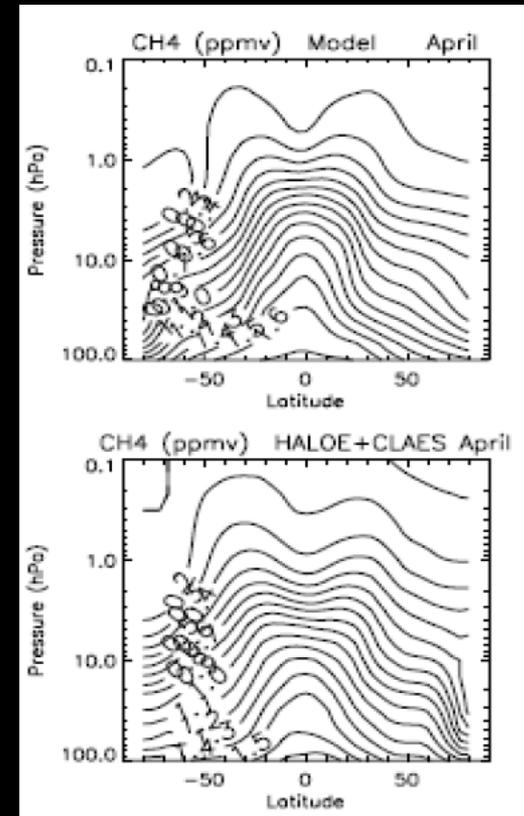
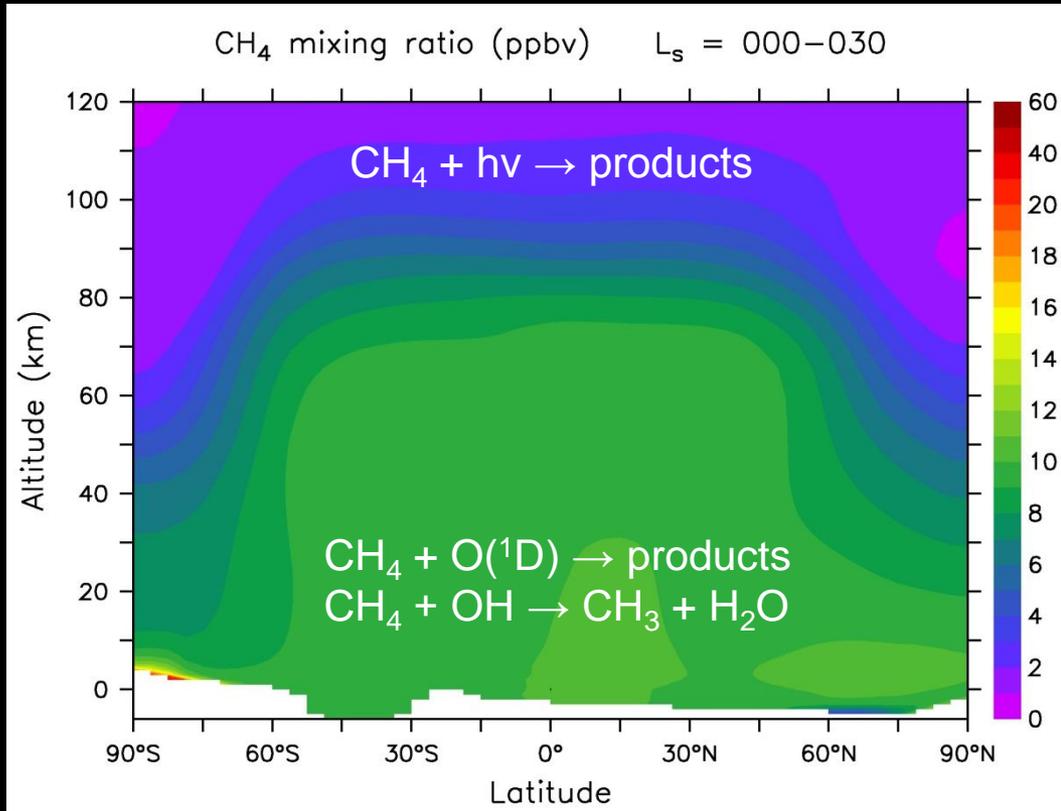
## The point of view of the atmospheric chemist & dynamicist

- Are the observed variations consistent with the known atmospheric chemistry and physics ?
- Can the Mars atmosphere create variations ?
- What happens if the source is localized ? episodic ?
- What are the implications on the lifetime/source/sink of methane on Mars ?



# The chemistry-as-we-know-it scenario

- Methane implemented in the LMD global climate model with coupled photochemistry



GCM

Earth

Observations

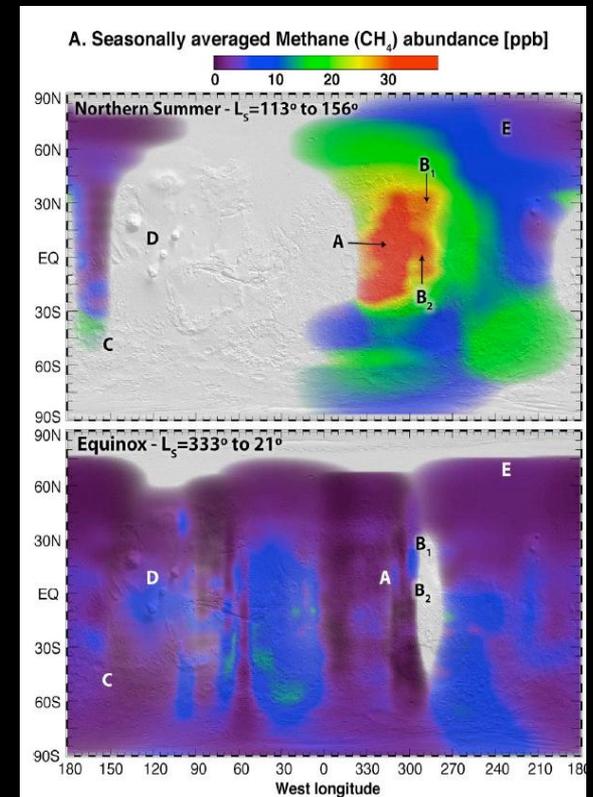
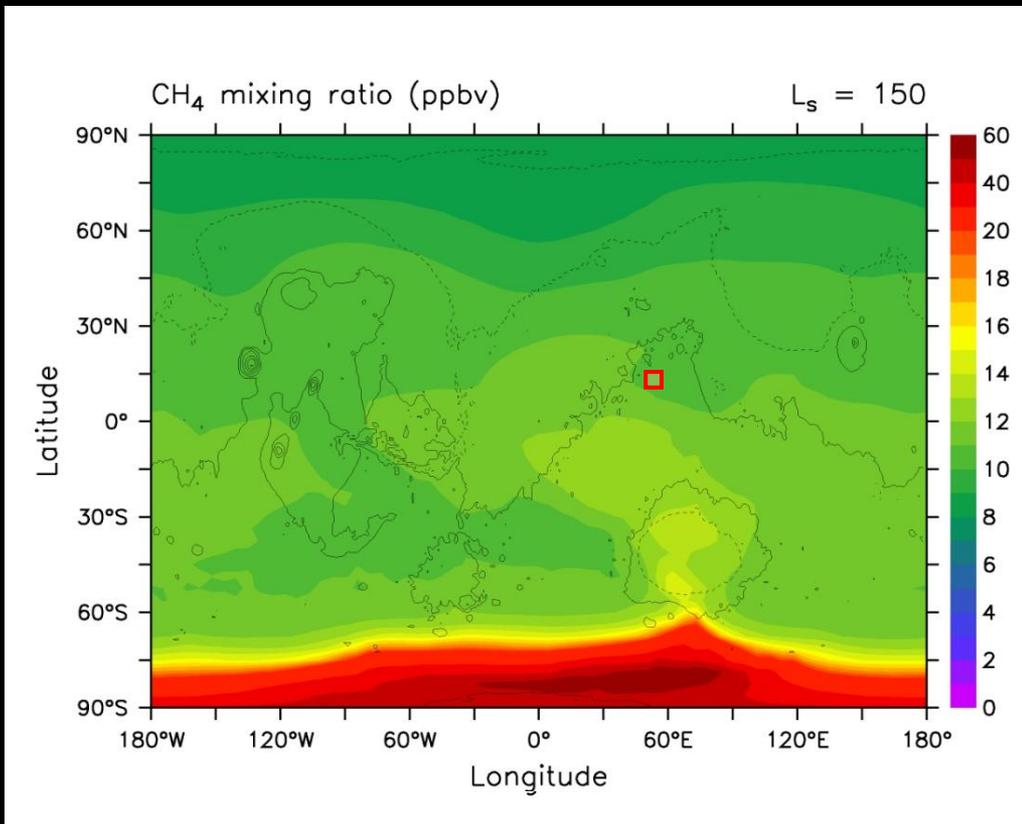
Jourdain et al., 2008

- Lifetime: 330 terrestrial years
- Source: 260 t terrestrial year<sup>-1</sup> (Earth: 582×10<sup>6</sup> t year<sup>-1</sup>)

# The chemistry-as-we-know-it scenario

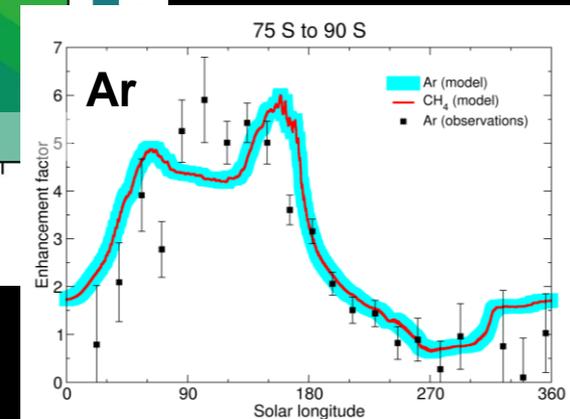
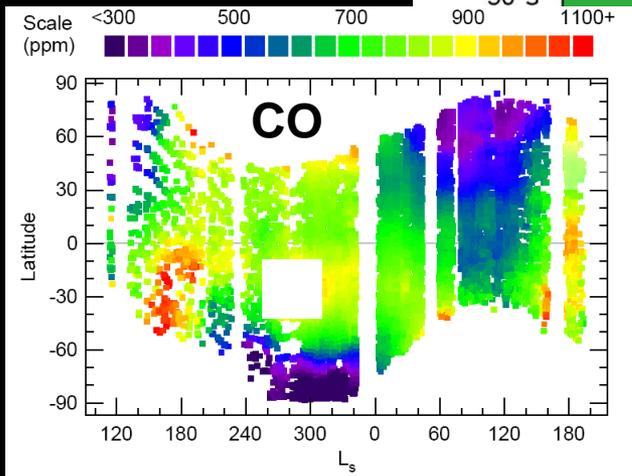
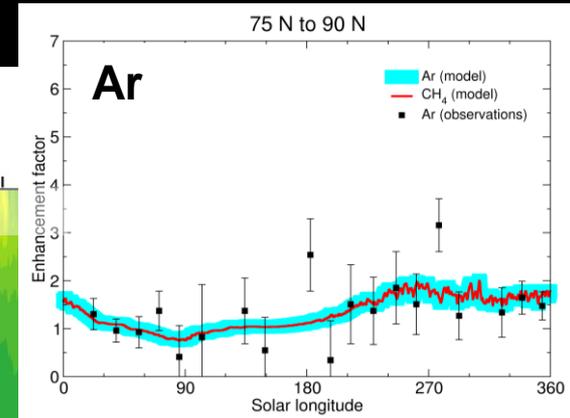
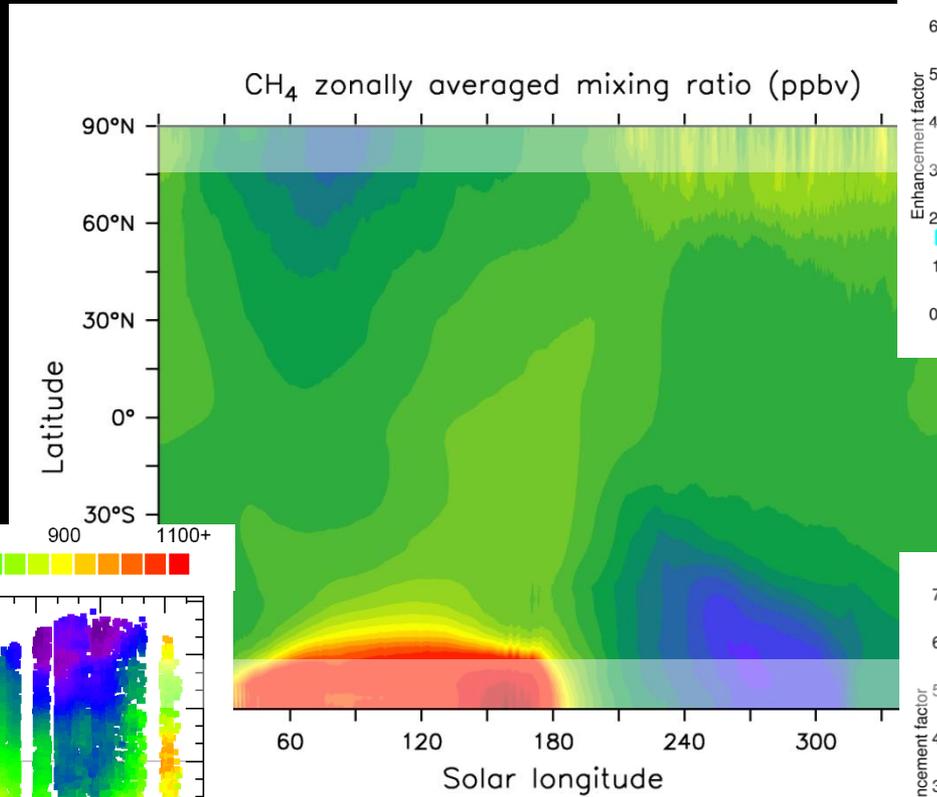
- what if the methane source is localized ? episodic ? both ?

release:  $L_s = 135-166^\circ$  (60 sols)  $\Rightarrow$  most favourable case!



Villanueva et al.  
ESA-ASI Methane workshop, 2009

# the chemistry-as-we-know-it scenario

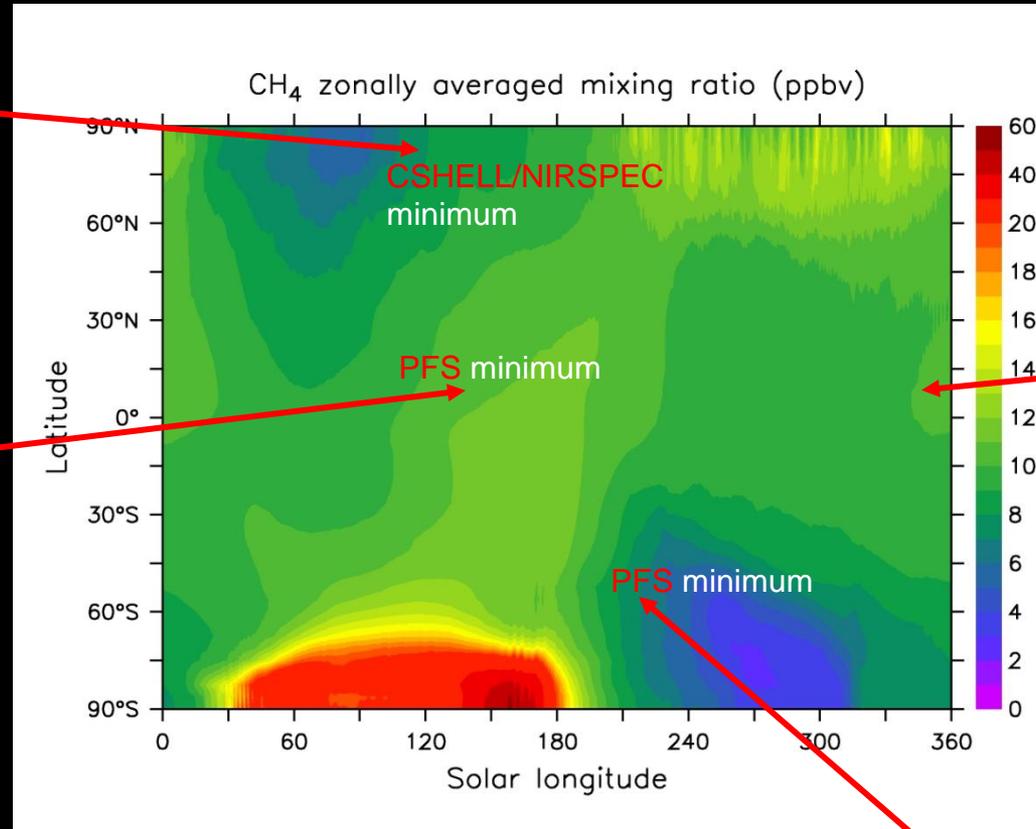


et, 2009

Smith et al., 2009

Sprague et al., 2004; 2007

# The chemistry-as-we-know-it scenario



PFS observes a maximum here

Geminale et al., 2009

CSHELL/NIRSPEC observe a maximum here

Mumma et al., 2009

CSHELL/NIRSPEC and PFS observe a minimum here

Geminale et al., 2008

Mumma et al., 2009

CSHELL observes a maximum here

Villanueva et al., 2009

➤ A (much) stronger source is needed → stronger sink → shorter lifetime

# Shorter lifetime ?

- Idealized tracers released from Syrtis Major
- Episodic source ( $L_s \sim 150^\circ$ )
- Various lifetimes (1000 years to 100 days)

Tracer mixing ratio (ppbv)

$L_s = 120-150$

Lifetime: 300 years

Tracer mixing ratio (ppbv)

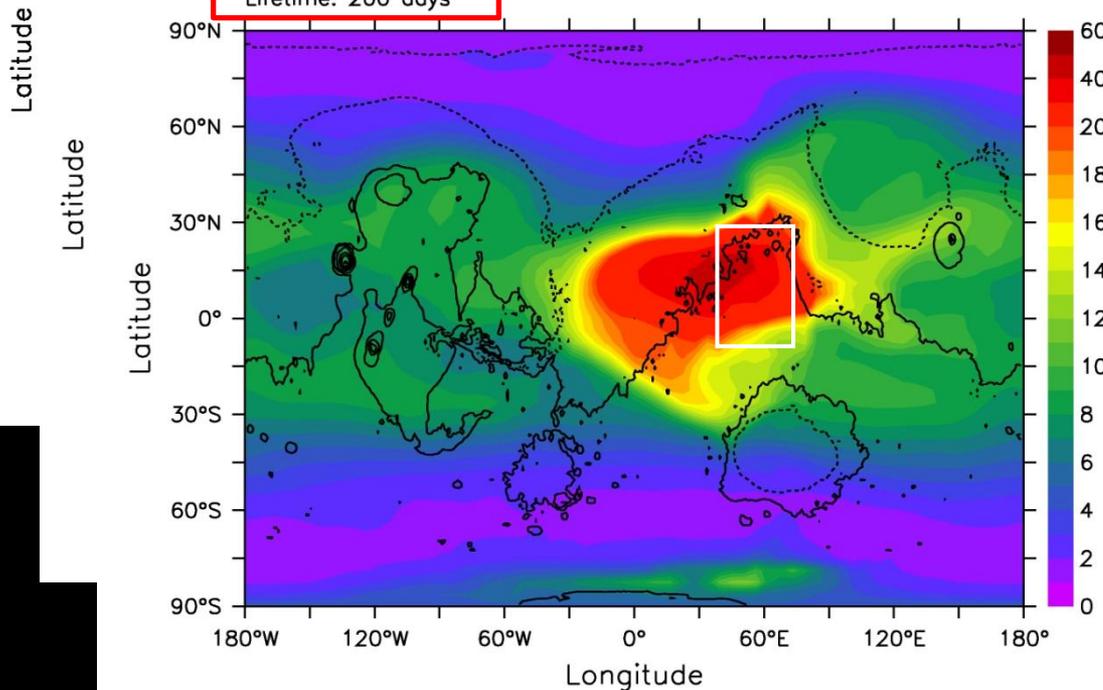
$L_s = 150$

Lifetime: 3 years

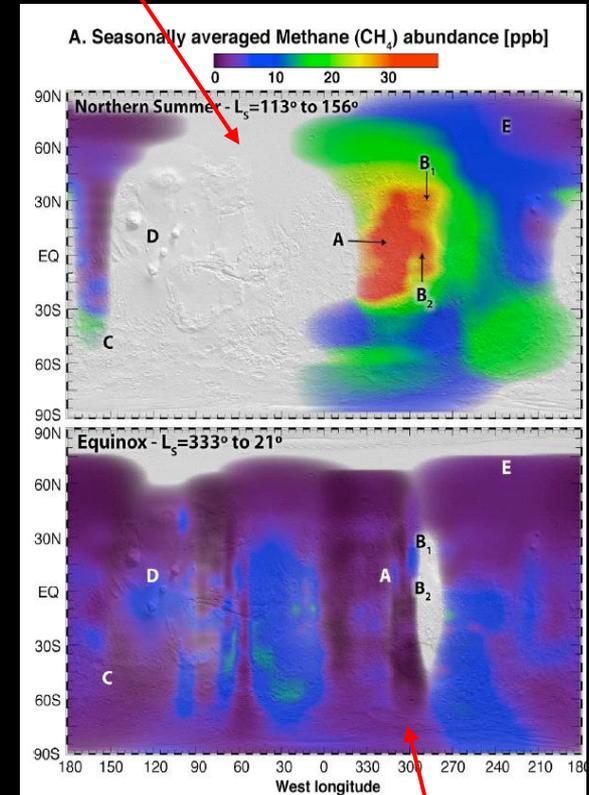
Tracer mixing ratio (ppbv)

$L_s = 150$

Lifetime: 200 days



Jan-Mar 2003 (MY26)



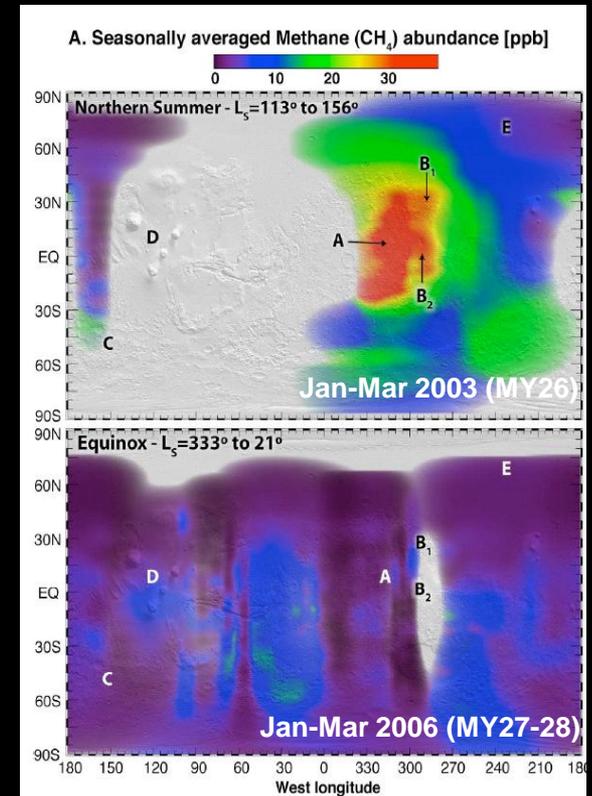
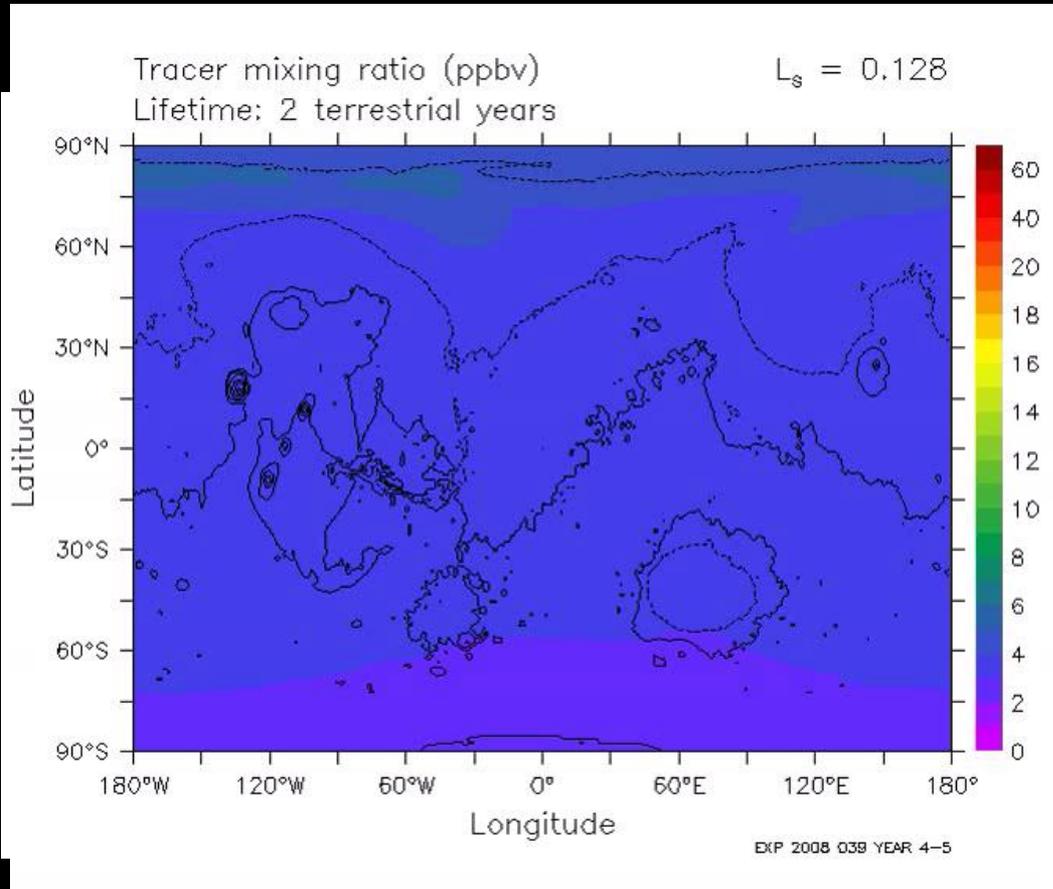
Villanueva et al., ESA-ASI methane workshop, 2009

Jan-Mar 2006 (MY27-28)

Lifetime: 200 days

# The CSHELL/NIRSPEC scenario

Lifetime in the atmosphere: 2 terrestrial years  
 release:  $L_s = 120-183^\circ$  (120 sols)



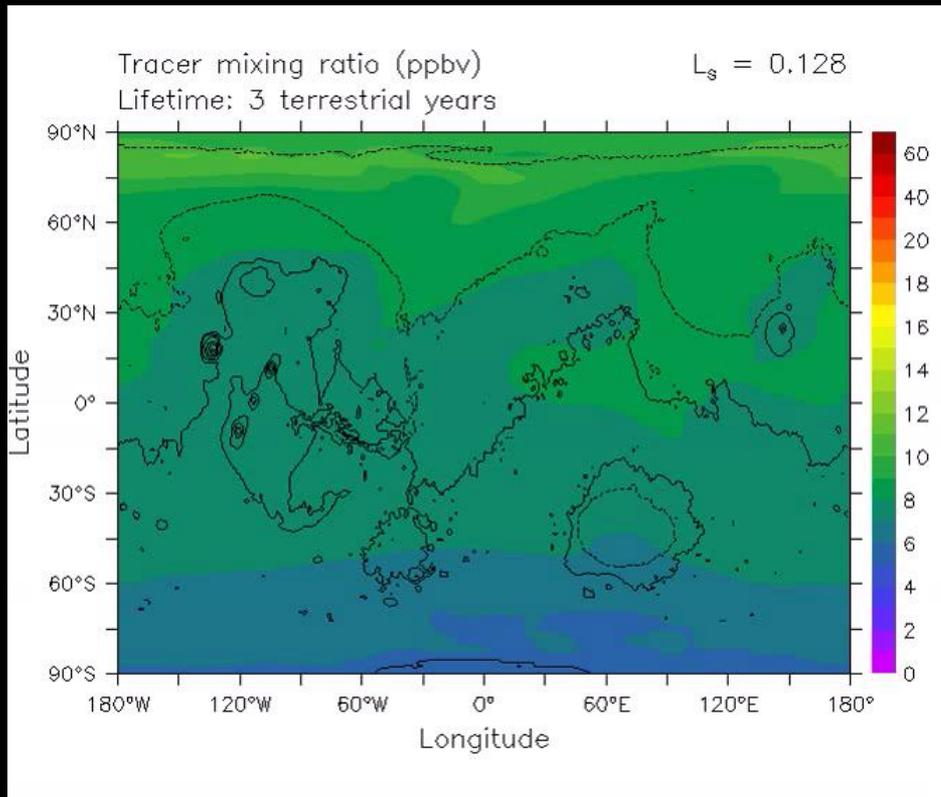
Villanueva et al., 2009

Source:  $\sim 80\,000\text{ t}$  ( $\sim 150\,000\text{ t}$  if seasonal)

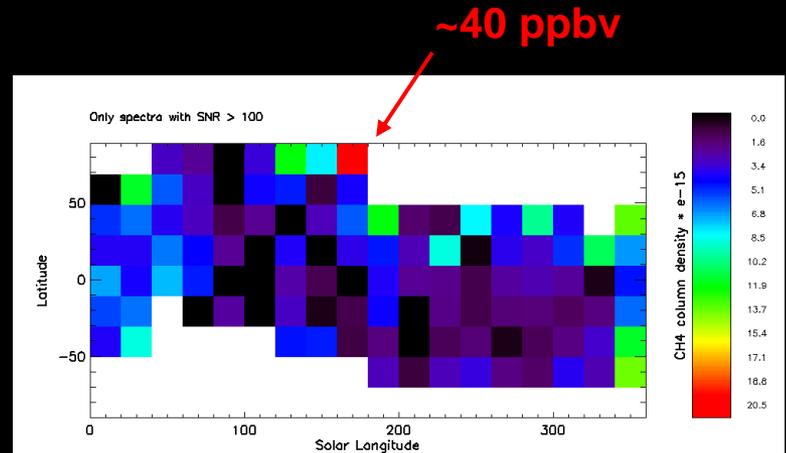
Mid-Atlantic Ridge:  $50\,000-130\,000\text{ t yr}^{-1}$   
 (Keir et al., 2005)

# The PFS scenario

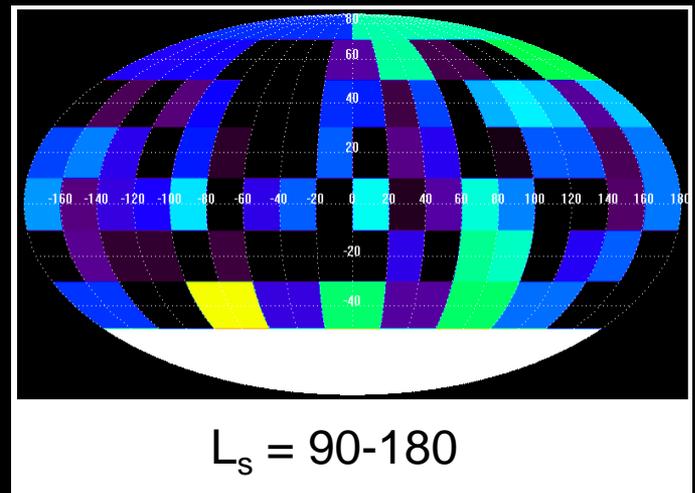
Lifetime in the atmosphere: 3 terrestrial years  
 release:  $L_s = 120-183^\circ$  (120 sols)



- methane source : between 25-30 km altitude



Geminale et al., ESA-ASI Methane workshop, 2009



Formisano et al., ESA-ASI Methane workshop, 2009

# A missing atmospheric loss of methane ?

Maybe!

but

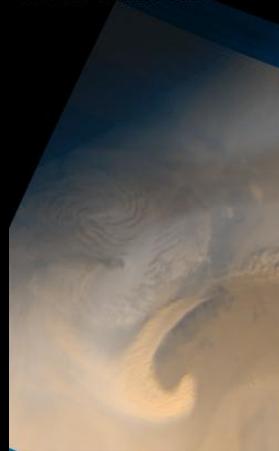
1. This process must be extremely powerful (100-500 x faster than the « conventional » methane loss)
2. It must be consistent with the observed behaviour of methane on Earth
3. It must be consistent with the observed behaviour of other species on Mars:

O <sub>3</sub>	Perrier et al., 2006; Fast et al., 2008; Lefèvre et al., 2008; Krasnopolsky, 2009
CO	Smith et al., 2009
H <sub>2</sub> O <sub>2</sub>	Clancy et al., 2004; Encrenaz et al., 2004; 2008; Lefèvre et al., 2008

- CH<sub>4</sub> loss by triboelectricity in the atmosphere
- CH<sub>4</sub> reversible adsorption in the regolith
- CH<sub>4</sub> irreversible loss in the regolith

# Methane loss by triboelectricity

6/30/1999 06:51:59 UTC



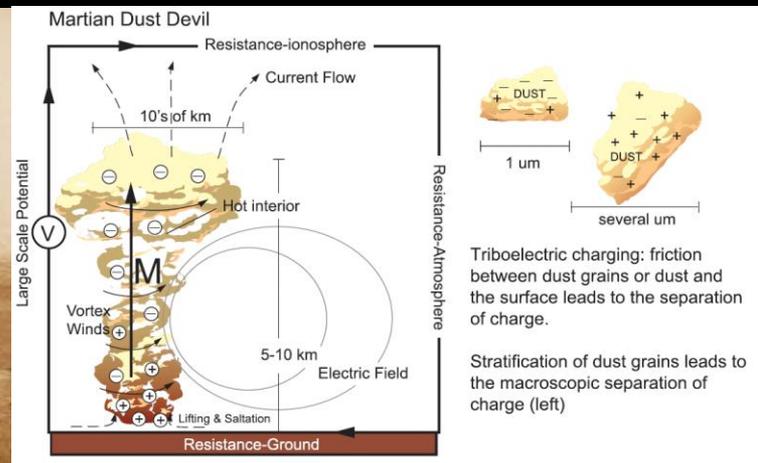
6/30/1999 08:49:34 UTC



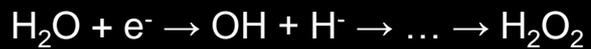
6/30/1999 10:47:11 UTC



6/30/1999 12:44:52 UTC

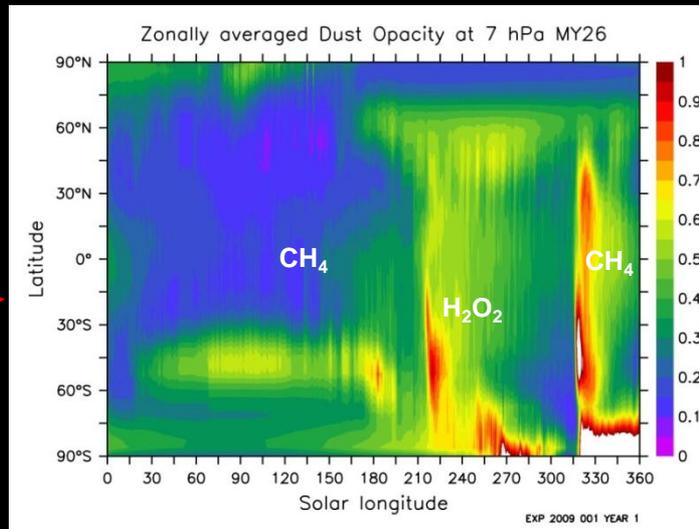


DeLory et al., *Astrobiology*, 2006; Atreya et al., *Astrobiology*, 2006; Farrell et al., *Geophys. Res. Lett.*, 2007



# Simulation with triboelectricity

$E \approx 25 \text{ kV m}^{-1}$   
for  $\tau_{\text{vis}} \geq 2$

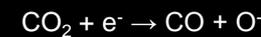
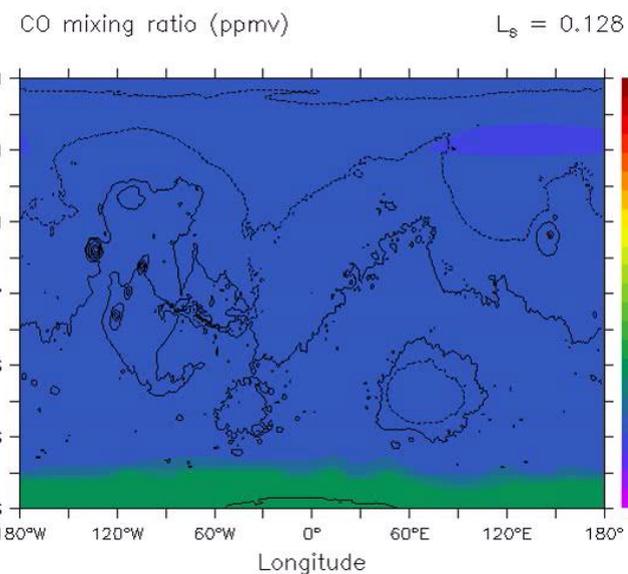
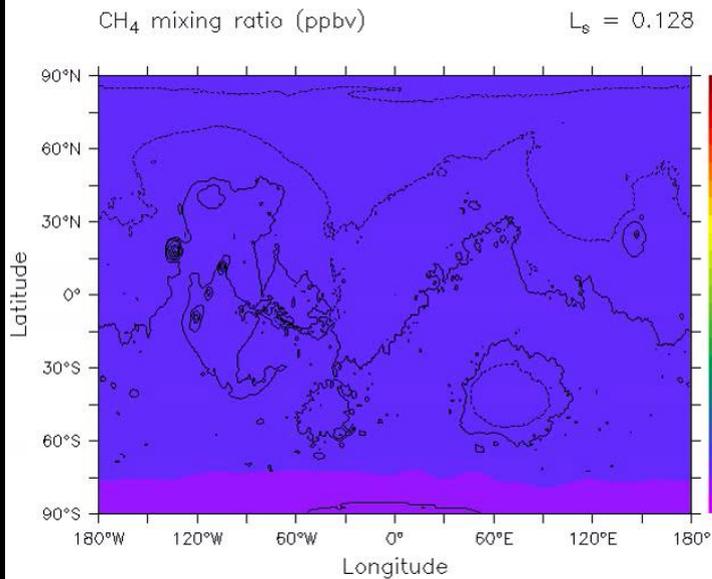


TES dust opacity  
MY26 (2002-2004)

50 times as large as the observations



**CH<sub>4</sub>**



**CO**

observations:  
~800 ppmv

# Methane loss in the regolith



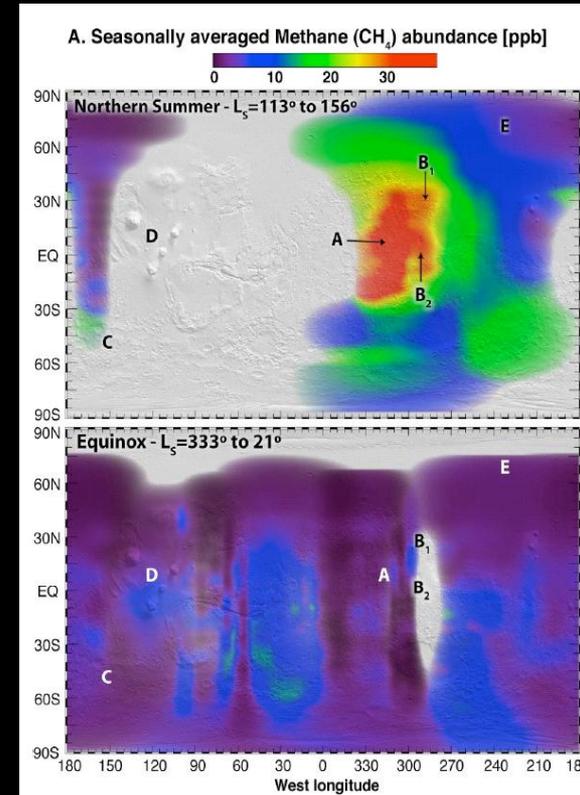
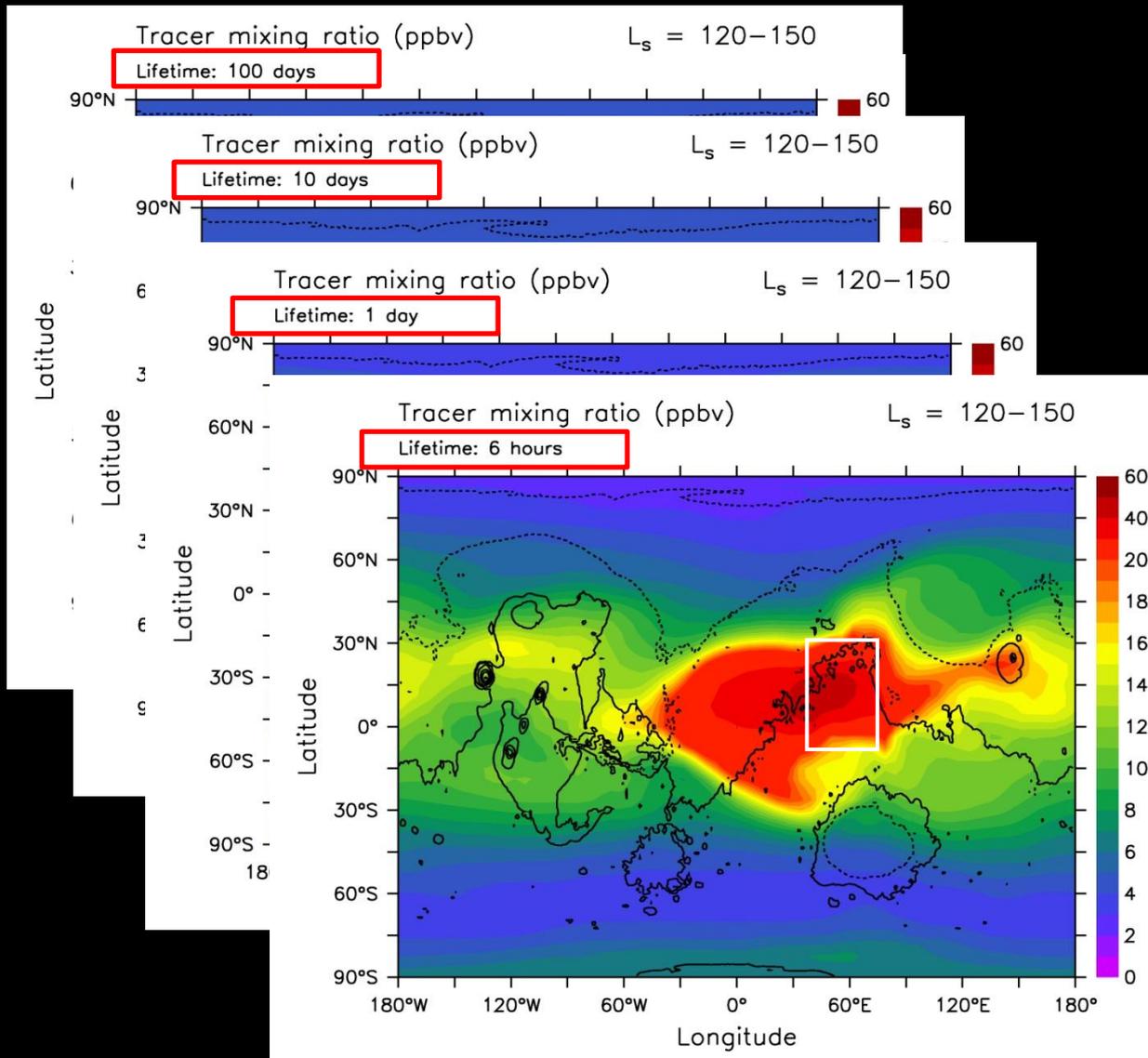
- reversible adsorption of  $\text{CH}_4$
- irreversible loss of  $\text{CH}_4$  (reaction with oxidants in the regolith)
  - triboelectric production of  $\text{H}_2\text{O}_2$
  - in situ production of  $\text{H}_2\text{O}_2$  and other oxides/superoxides

Gough et al., in press; Meslin et al., submitted

Atreya et al., 2006; 2007

Hurowitz et al., 2006; Davila et al., 2008

# methane loss in the regolith



Villanueva et al., 2009

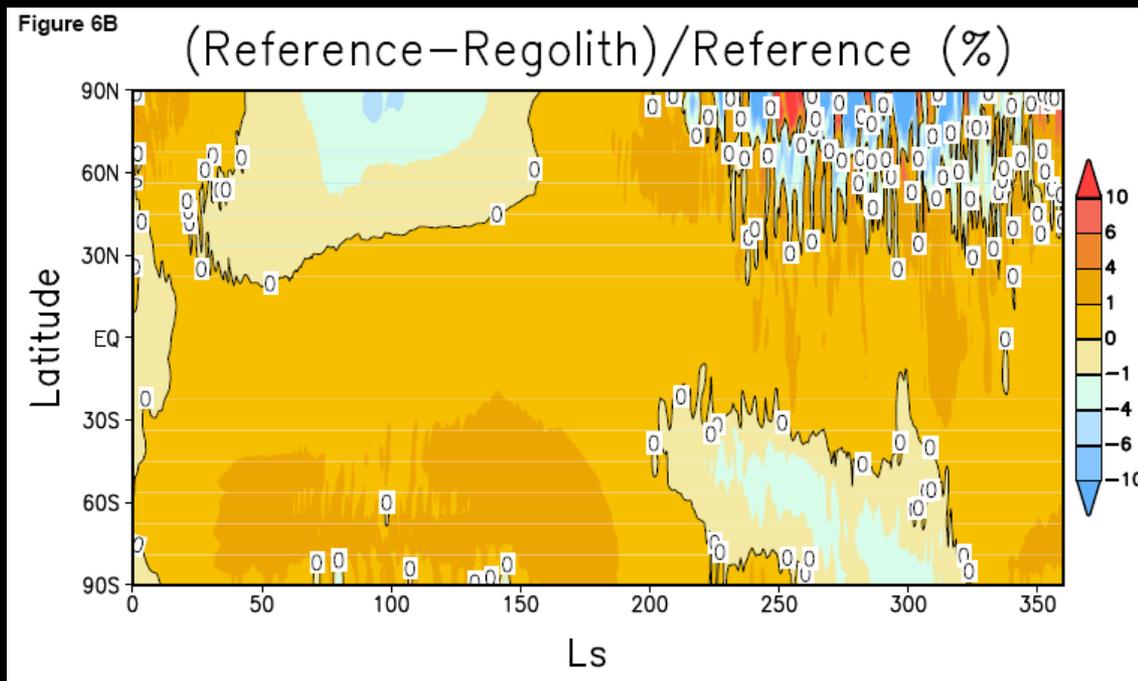
Lifetime: ~ 6 hours

# CH<sub>4</sub> adsorption in the regolith



- Uptake coefficient ( $\gamma$ ) of CH<sub>4</sub> measured experimentally on Martian soil analog (JSC Mars-I, Gough et al., in press)
- $\gamma(T)$  introduced in a full subsurface-atmosphere transport module, taking into account the thermodynamics and kinetics of the adsorption process

Impact on CH<sub>4</sub> seasonal cycle





# CH<sub>4</sub> permanent loss in the regolith

Raina Gough et al., *University of Colorado*  
*ESA-ASI Methane Workshop, Frascati, 2009*

TiO<sub>2</sub>•H<sub>2</sub>O<sub>2</sub>  
(Quinn and Zent, 1999)



JSC-Mars-1 + H<sub>2</sub>O<sub>2</sub>  
(Levin and Straat, 1981)



Na<sup>+</sup> and Mg<sup>2+</sup>  
perchlorate



- Samples in vials with N<sub>2</sub> atmosphere were kept at 2°C
- Headspace was sampled, analyzed with gas chromatography (GC)
- After initial (t=0) measurement, organics or methane were added
- GC measurements taken at 24, 48, 72 hrs
- Several controls were used to rule out contamination

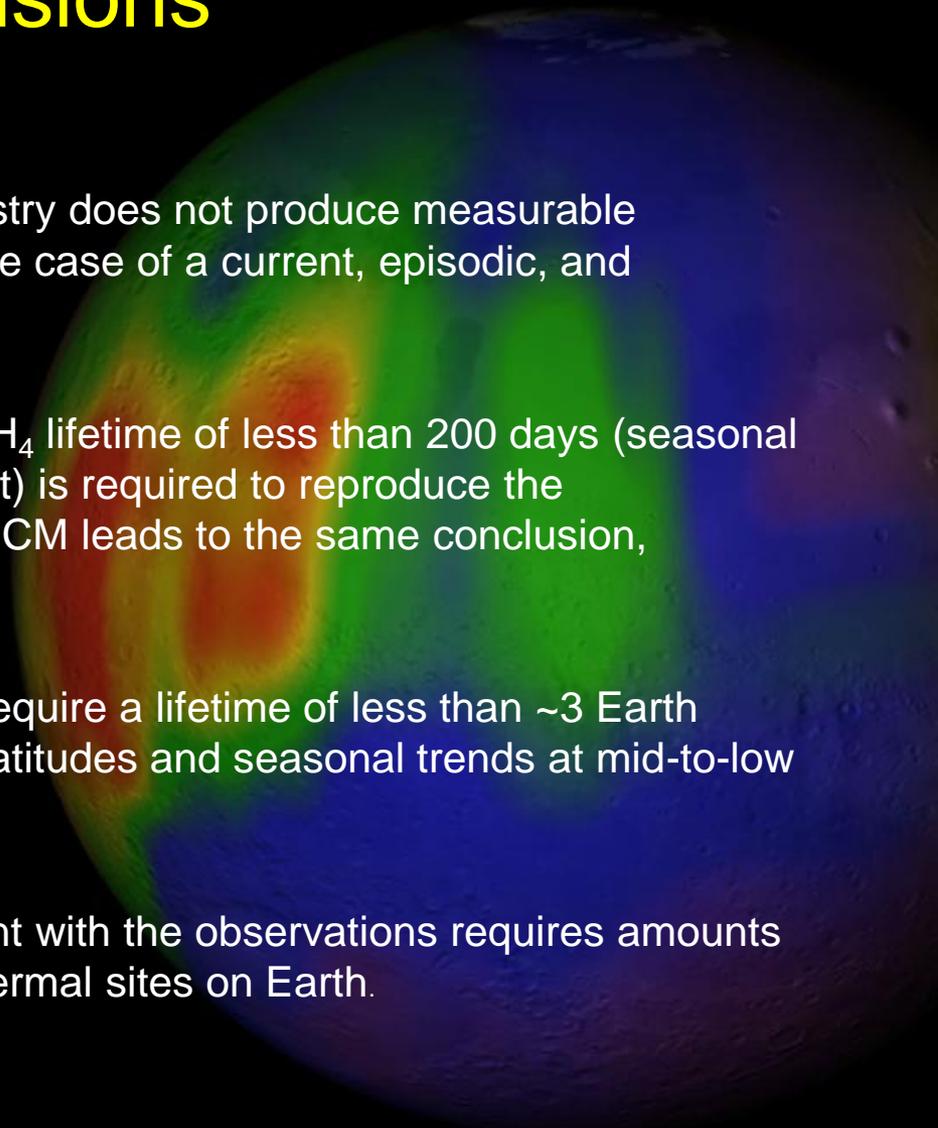
Oxidizes organics,  
but not methane

Oxidizes organics,  
but not methane

Nothing is oxidized

# Conclusions

- The "conventional" atmospheric chemistry does not produce measurable methane variations on Mars, even in the case of a current, episodic, and localized source.
- CSHELL/NIRSPEC: an atmospheric CH<sub>4</sub> lifetime of less than 200 days (seasonal release) or ~2 Earth years (single event) is required to reproduce the observations (work with NASA Ames GCM leads to the same conclusion, Malynda Chizek, 2009).
- PFS: measurements at high latitudes require a lifetime of less than ~3 Earth years. Longitudinal variations at high latitudes and seasonal trends at mid-to-low latitudes cannot be reproduced.
- The CH<sub>4</sub> source: quantitative agreement with the observations requires amounts comparable to the most active hydrothermal sites on Earth.



# Conclusions

## Solutions ?

- fast atmospheric loss of methane by electrochemistry:
  - is not supported by current observations of CO, H<sub>2</sub>O<sub>2</sub>, and O<sub>3</sub>
- fast loss of methane in the regolith:
  - must be extraordinarily rapid (< 24 h) to satisfy the observations
  - is not supported by current observations of other minor species (CO, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>), or must be highly selective
  - is not supported by on-going laboratory work

