METASTABLE METHANE CLATHRATE PARTICLES AS A SOURCE OF METHANE TO THE MARTIAN ATMOSPHERE

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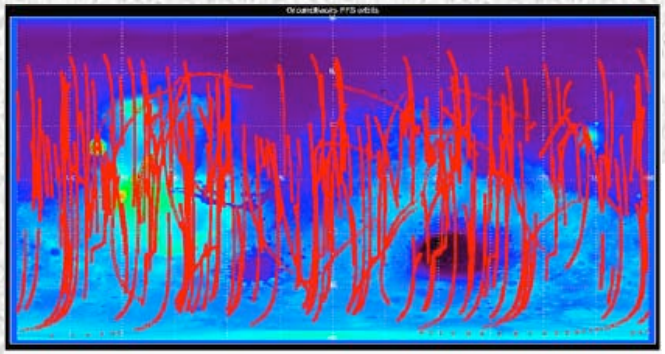
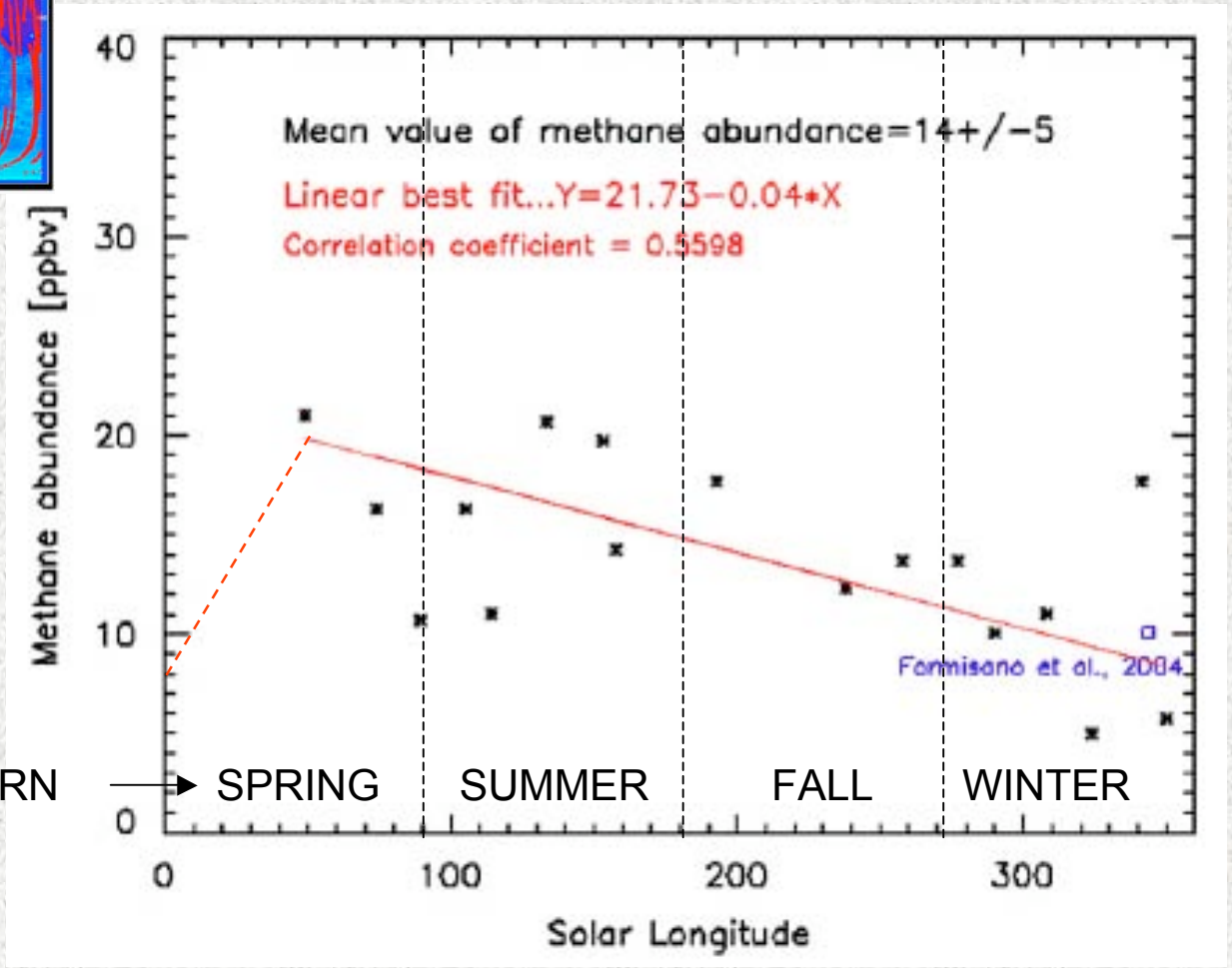
Why a seasonal cycle of methane?



Seasonal variation of methane abundance according to PFS

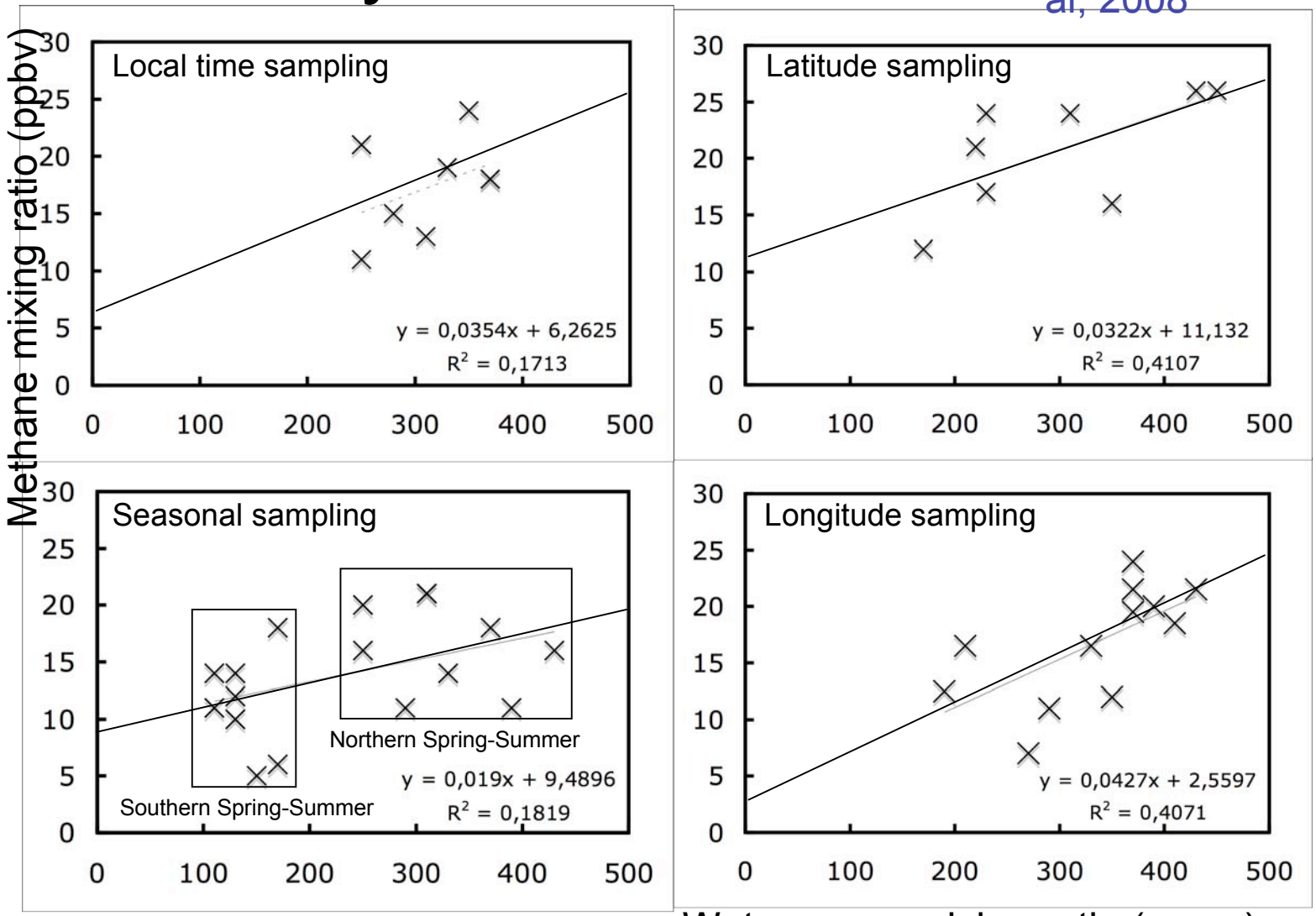


Formisano et al, 2004

Geminale et al, 2008

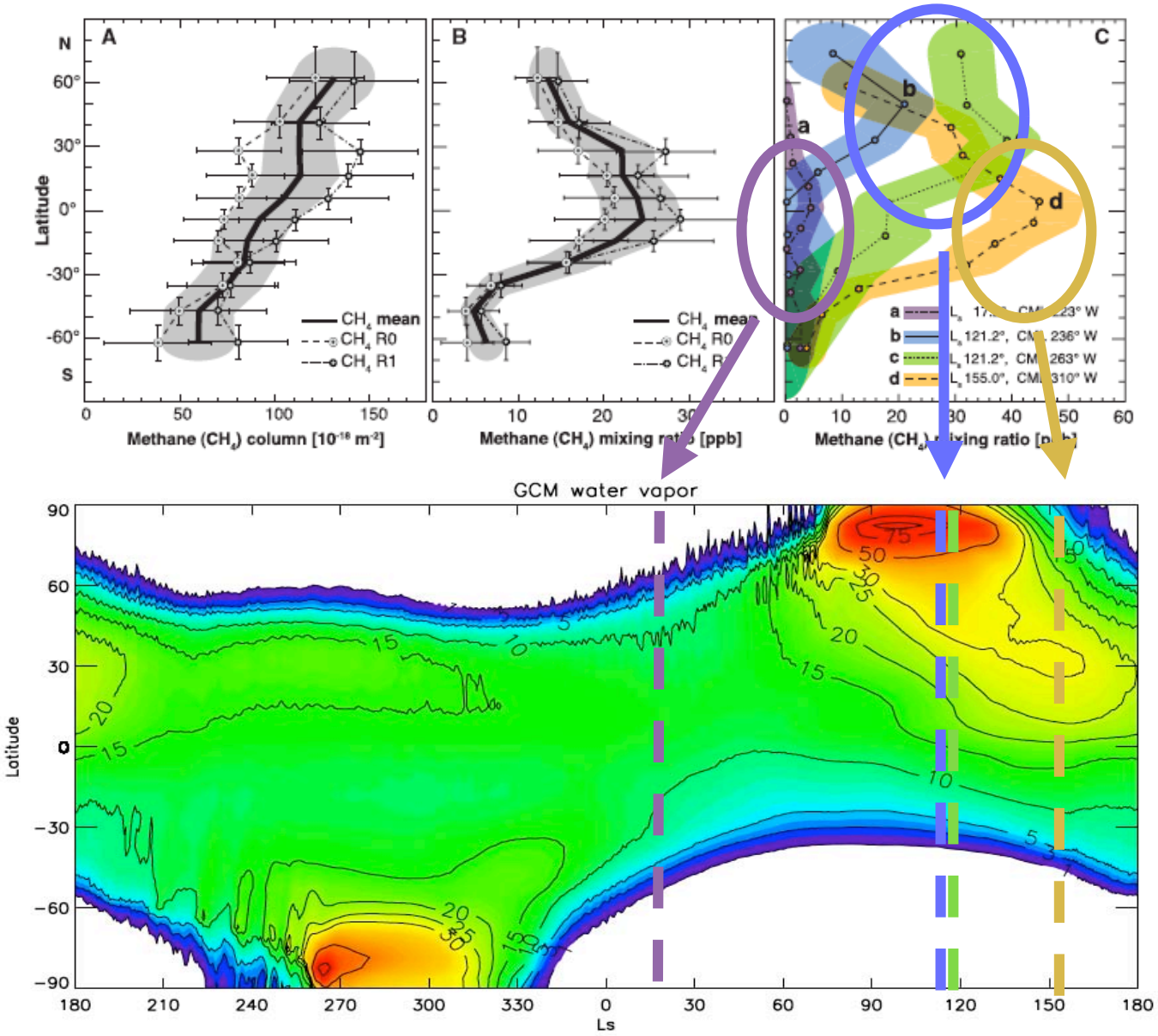
Why a general H_2O/CH_4 correlation, as seen by PFS from orbit…

Data from Geminale et al, 2008



Chassefière, 2009

… and not contradicted by recent Earth-based measurements?



Mumma et al., 2009

Montmessin et al., 2004

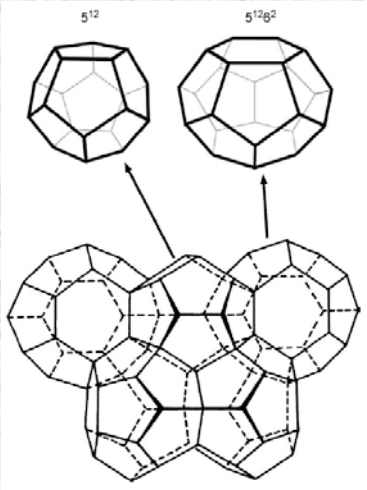
Our hypothesis to solve the mystery

- **How can the atmospheric H_2O distribution, controled by meteorology, be correlated with the CH_4 distribution if CH_4 is produced by fixed sources at the surface?**

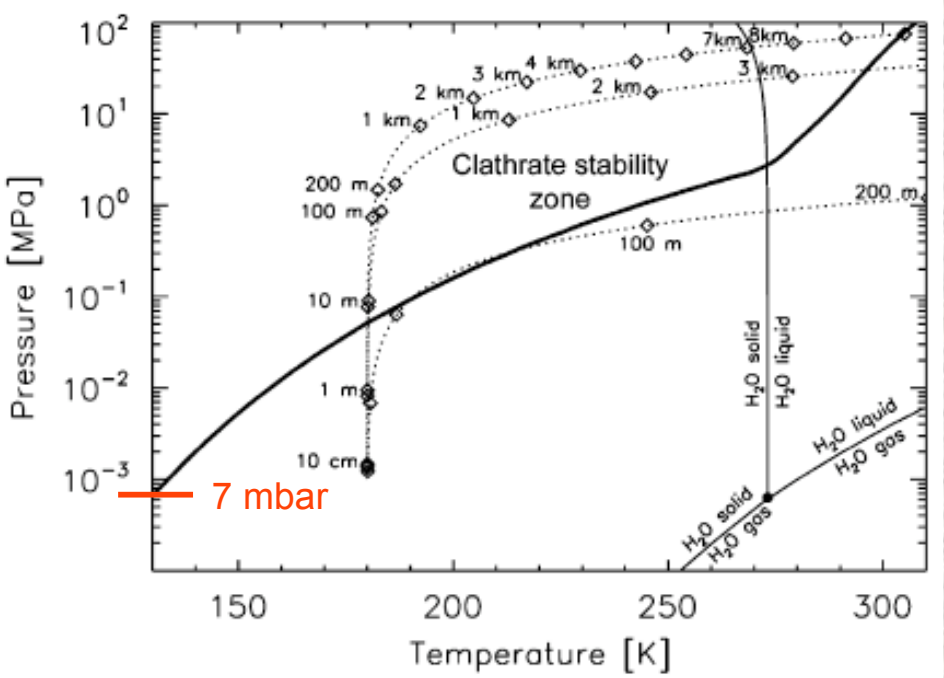
- **One possible solution : gaseous CH_4 is produced in the atmosphere by a process involving H_2O.**
- If so, the source is necessarily solid :
  - Methane ice? NO
  - Adsorbed methane? NO
  - Clathrates? POSSIBLE IF STABLE

Methane clathrate hydrate

- CH_4 molecules trapped in water molecules cavities : CH_4-5.85 H_2O.
- Form at high pressure (e.g. ocean groundfloor on Earth), but NOT in Mars atmosphere.
- May form at depth in Mars crust, at p>1 bar.

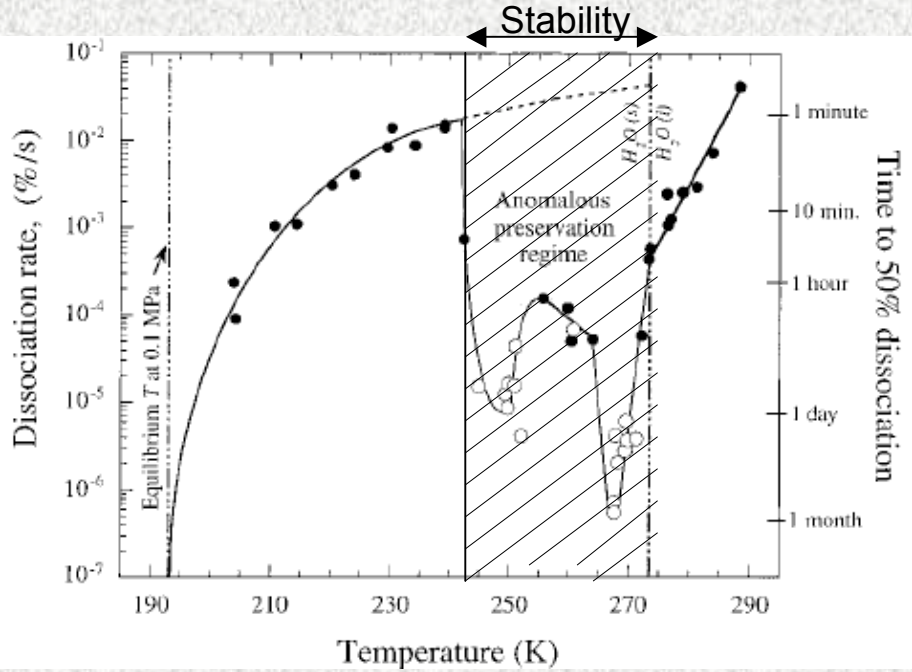


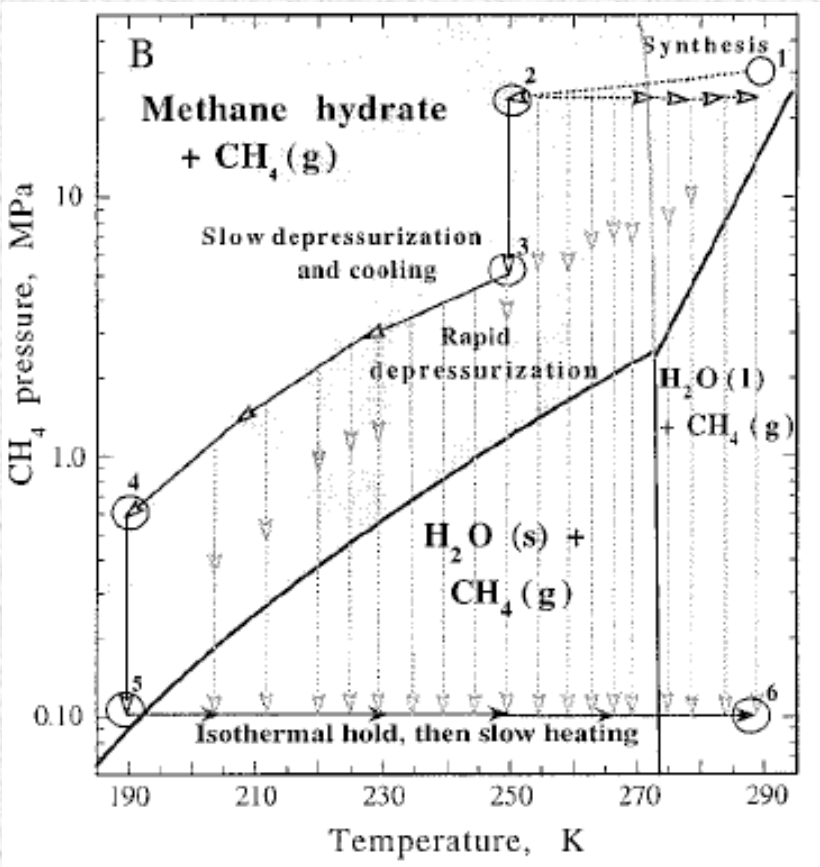
Chastain and Chevrier, 2007



« Anomalous preservation » of clathrates

- Anomalous preservation of clathrates (Stern et al. 2001 and ref. therein)





- Ultra-stability of very pure clathrate crystal agregates (Zhang and Rodgers, 2008): **<1% dissociation at 1 bar/ 268 K during 10 days.**

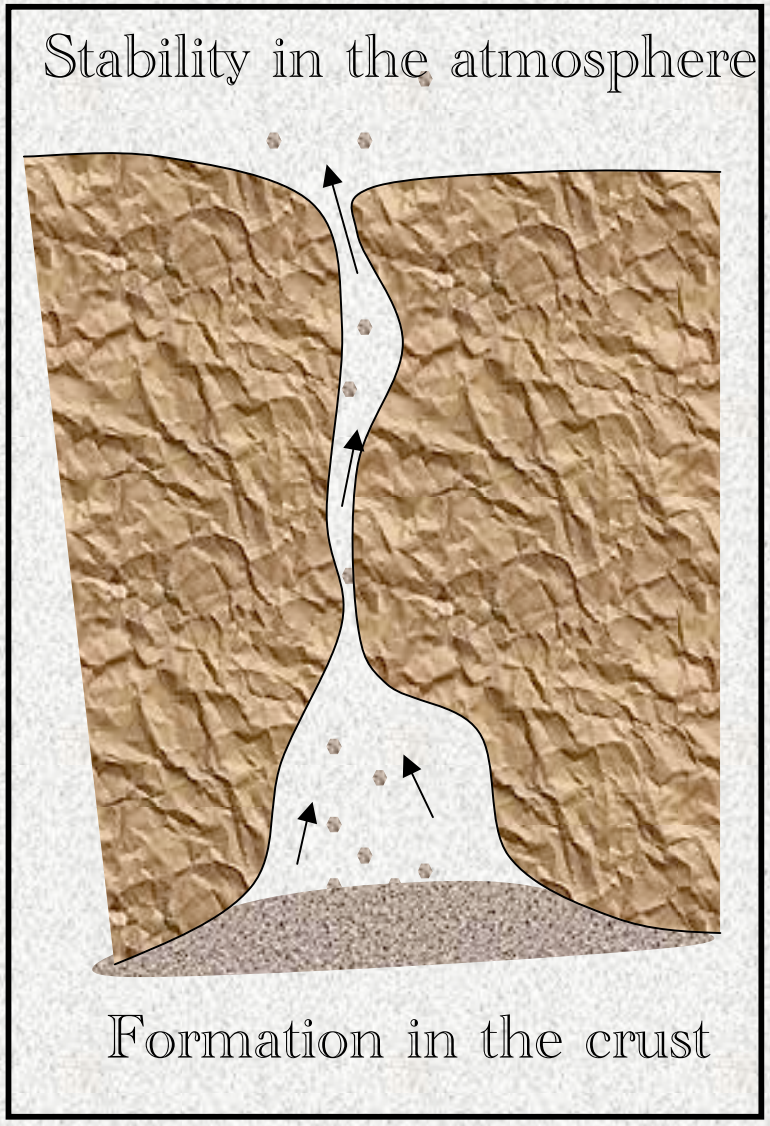
Release of methane clathrate particles

1- Formation of clathrate in the crust at high (lithostatic) pressure.

2- Fracturation of subsurface by tectonics, yielding local macroporosity.

3- Erosion of (friable) clathrate host framework and uplift of particles.

4- Release to the atmosphere of (ultra-stable) clathrate particles.

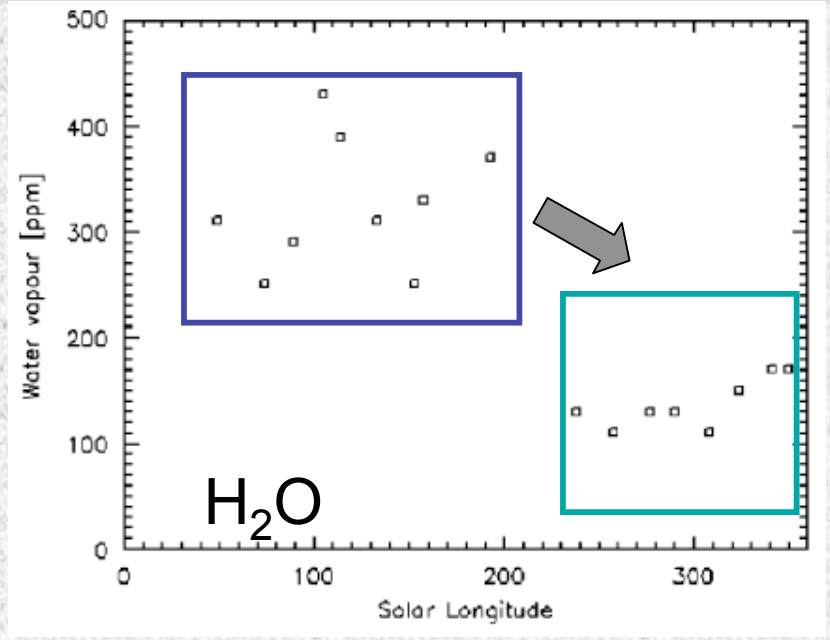


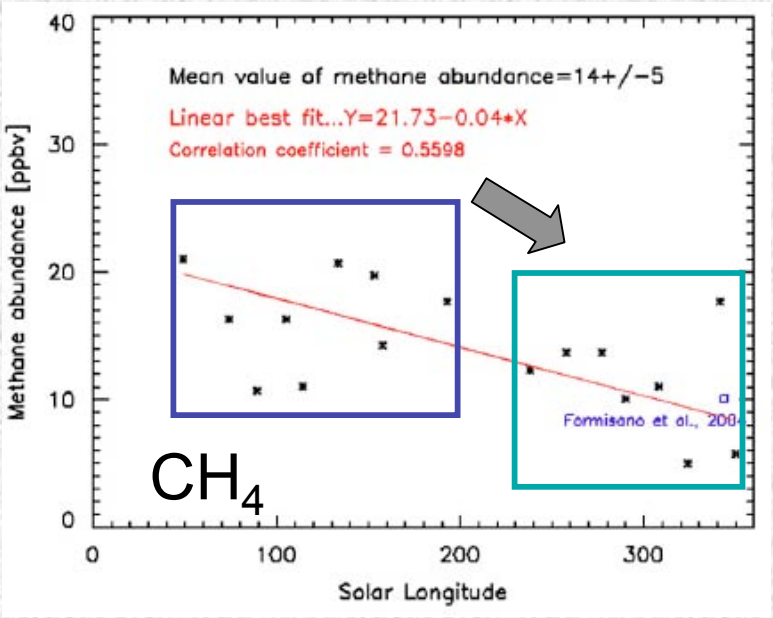
Possible destabilizing effect of water condensation

- Small clathrate particles (<1 μm), lifted up to ≈50 km, may serve as condensation nuclei *(second mode observed on Viking images by Montmessin et al, 2002?)*
- **Hypothesis : Condensation of H_2O on clathrate particles above the hygropause (z> 20 km) → destabilization of clathrate to gas phase** (by which mechanism : latent heat release, disruption of crystalline structure?)
- Needs to be studied and validated by experimental works in Martian conditions (never done).

What would our hypothesis explain?

- The seasonal cycle of methane (low level during fall/winter, followed by sharp increase at spring)
- The general H_2O/CH_4 correlation
- A mesospheric source for gaseous methane (as suggested by limb PFS results)





What would our hypothesis imply?

- First observational evidence of clathrates on Mars.
- Some correlation between gaseous CH_4 (*controled by dynamics*) and mesospheric H_2O (*controled by both dynamics and condensation*). Not straightforward (Help, GCM!)
- A partial or total loss of the memory of the (clathrate) source distribution at the surface due to atmospheric redistribution of clathrates.

Sink of gaseous methane

- Strongly inhomogeneous CH_4 : Lifetime < 200 days (Lefèvre and Forget, 2009).
- The oxidant could be H_2O_2 (or grains oxidized by H_2O_2) in the subsurface.
- Example of Haber-Weiss iron-catalyzed reaction, able to produce OH (but does it work in the absence of liquid water?)

The decomposition of H_2O_2 in soils may proceed through a number of mechanisms, the first of which can be most simply described by reactions 2–5:

$$-Fe^{3+} + H_2O_2 \rightarrow -Fe^{2+} + O_2^- + 2H^+ \quad (2)$$

$$O_2^- + -Fe^{3+} \rightarrow -Fe^{2+} + O_2 \quad (3)$$

$$O_2^- + -Fe^{2+} + 2H^+ \rightarrow -Fe^{3+} + H_2O_2 \quad (4)$$

$$-Fe^{2+} + H_2O_2 \rightarrow -Fe^{3+} + OH + OH^- \quad (5)$$

Here, $-Fe^{3+}$ represents iron in a liganded form or occupying a site at an oxide surface.[8–10] The sum of reactions 2–5 represents the Fe-catalyzed Haber-Weiss reaction

$$O_2^- + H_2O_2 \rightarrow O_2 + OH + OH^- \quad (6)$$

If the OH generated in reaction 6 reacts exclusively with H_2O_2

$$OH + H_2O_2 \rightarrow H_2O + O_2^- + H^+ \quad (7)$$

the net reaction becomes

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (8)$$

Petigara et al, 2002

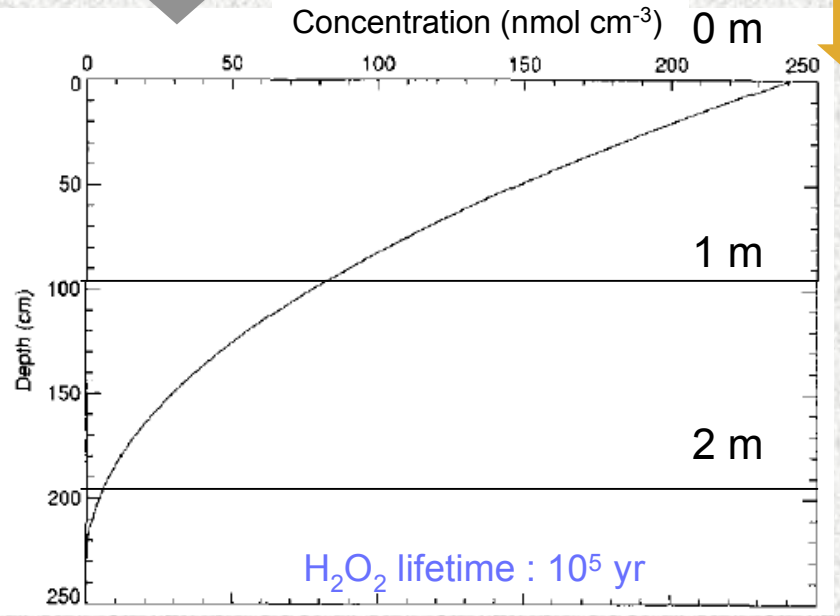
Thickness of the regolith oxidation layer

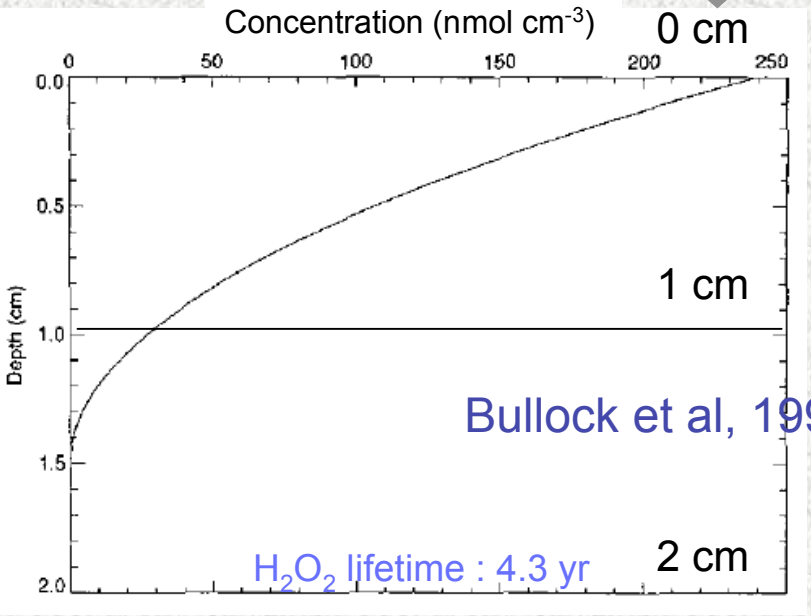
0.1 nmol H_2O_2 cm^{-2} yr^{-1}

≈10 ppb CH_4/200 days

≈5 nmol CH_4 cm^{-2} yr^{-1}

10 nmol H_2O_2 cm^{-2} yr^{-1}





Bullock et al, 1994

- Oxidation budget : $CH_4 + 4H_2O_2 \rightarrow CO_2 + 6\ H_2O$
- 1 CH_4 removes 4 H_2O_2 : ≈20 nmol H_2O_2 cm^{-2} yr^{-1} → 2 yr lifetime for H_2O_2, less than 1 cm depth.
- Centimetric (**not metric**) oxidation layer

What could be done in the future?

⇒ Laboratory measurements :

- Check and characterize clathrate metastability in Martian conditions.
- Study the decomposition of clathrates in presence of condensing H_2O.
- Study the kinetics of methane oxidation by adsorbed H_2O_2 in presence of iron-rich minerals (Haber-Weiss-type reaction)

⇒ Modelling :

- Decomposition of clathrate particles in presence of condensing water.
- GCM simulations of methane cycle (coupled with water cycle).

⇒ Space observation :

- Search for and characterize from future orbiters the second mode particle population (<1 µm) in Martian atmosphere.
- Characterize from future landers the oxidation state of the superficial regolith, with a sub-centimetric vertical sampling capability