Methane on Mars

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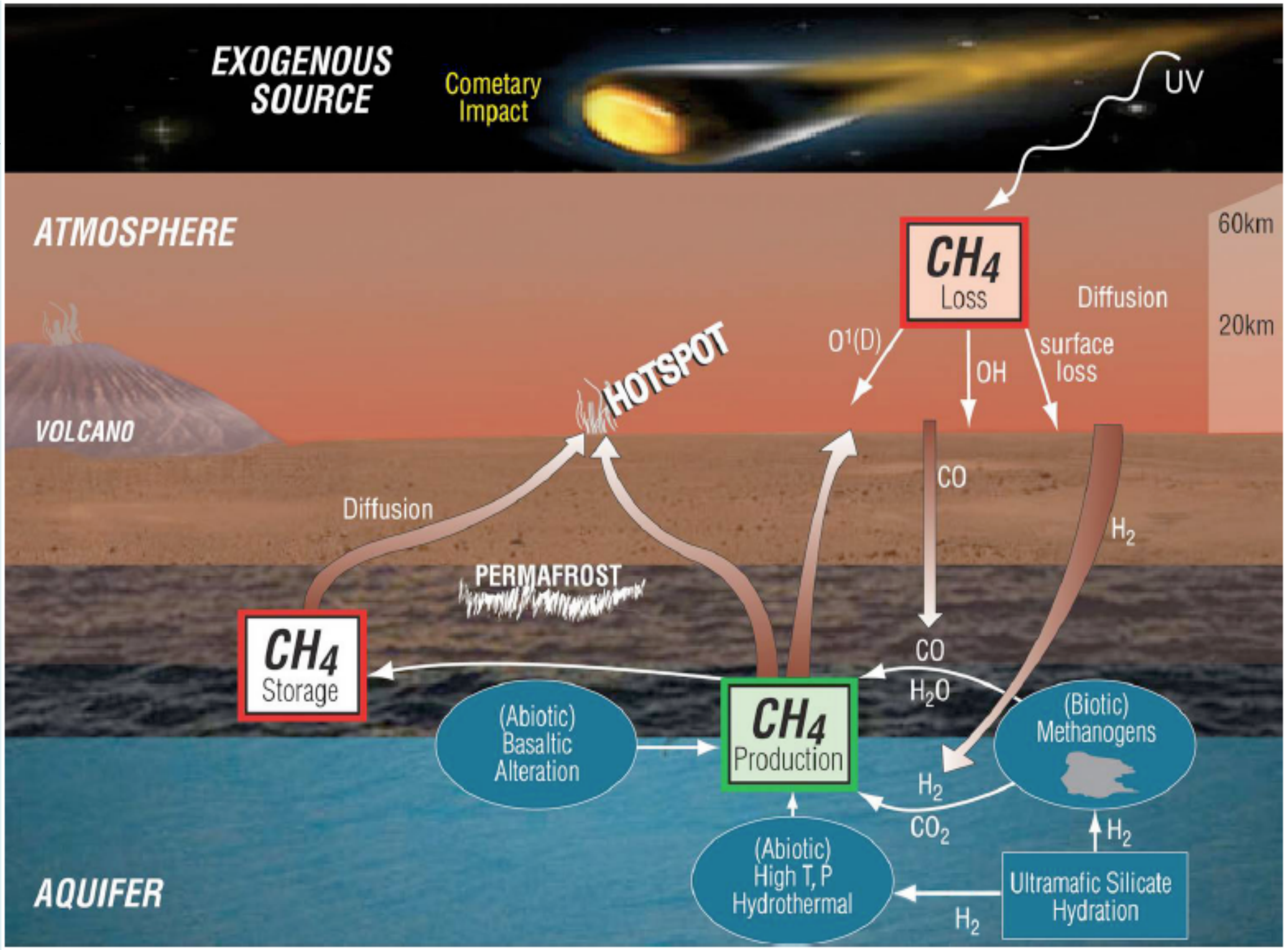
Possible origins of methane

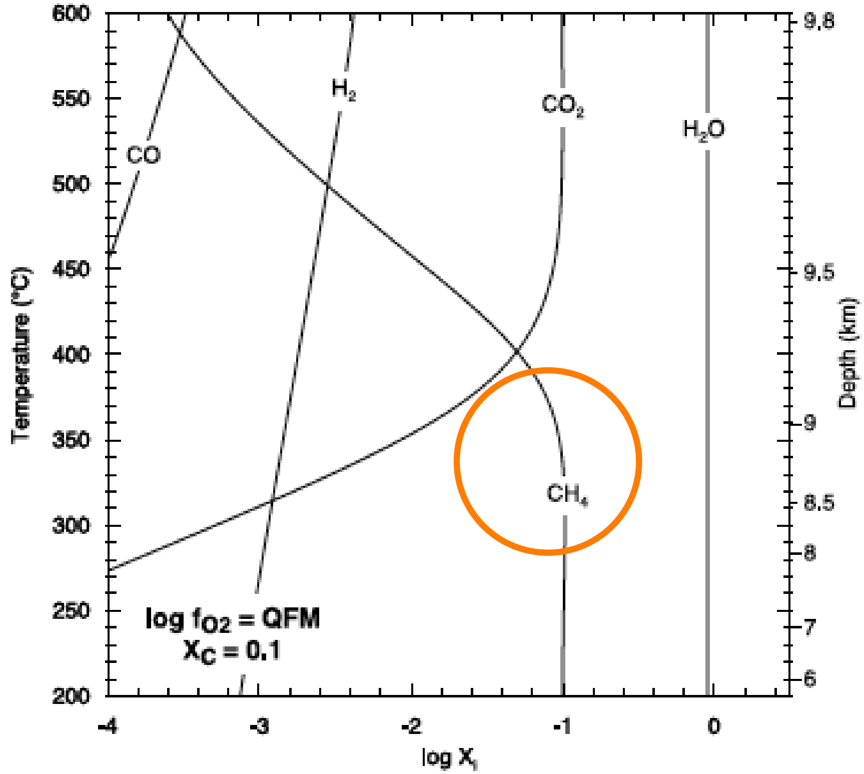
- *External sources: meteorites, comets, IDP? → small*
- Biological sources?
- Geochemical sources:
  - Volcanism
  - Hydrothermalism (serpentinization, thermodynamical equilibration?)

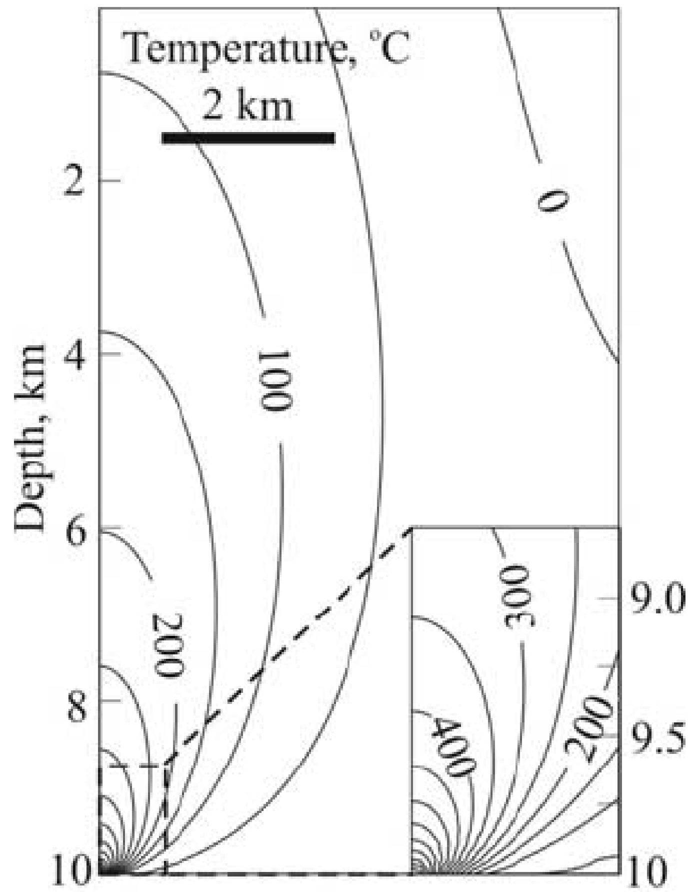


Atreya et al., 2006

Thermodynamical equilibration of C dissolved in hydrothermafluids at depth

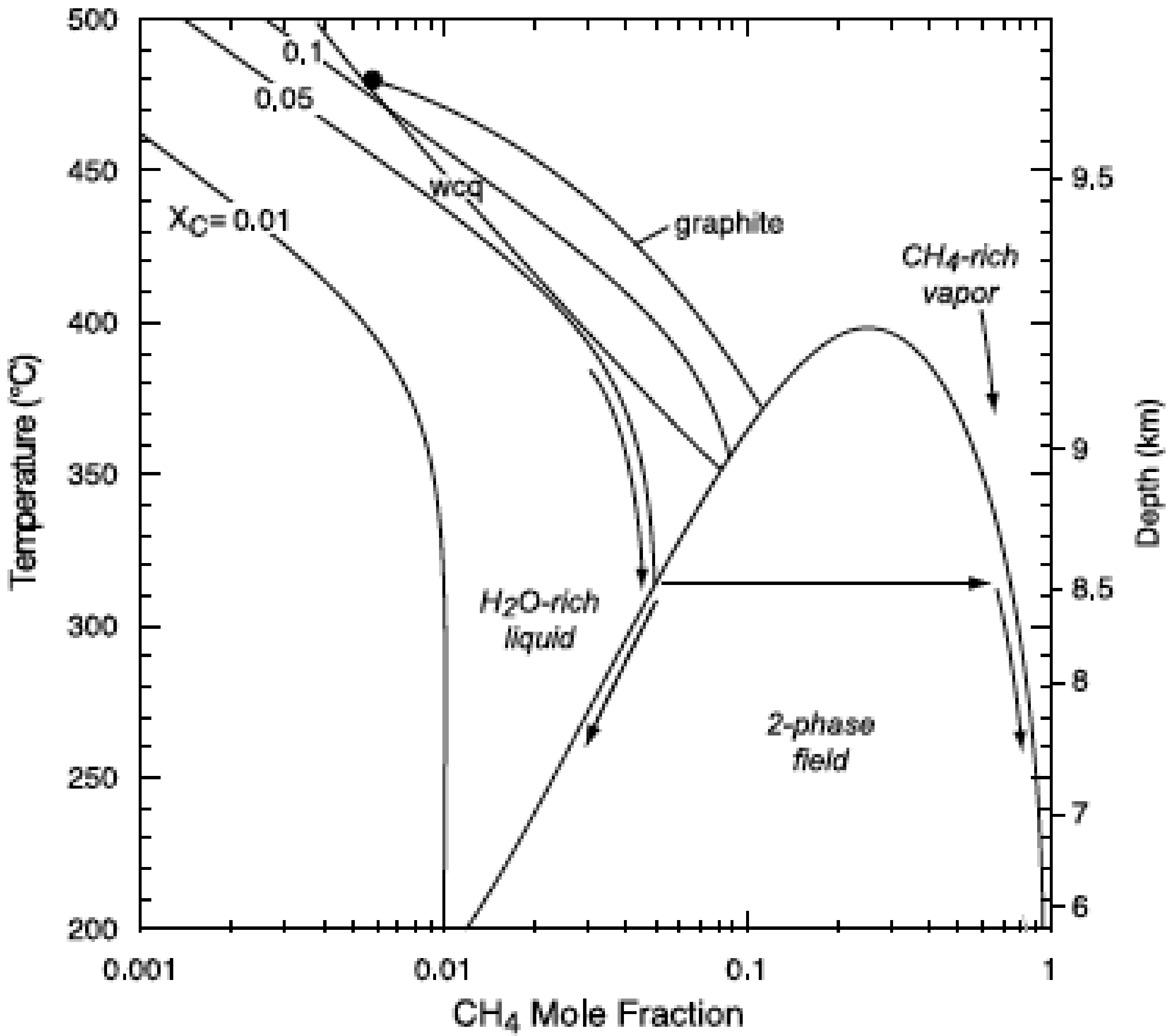
- Model of hydrothermal system(Lyons et al, 2005)





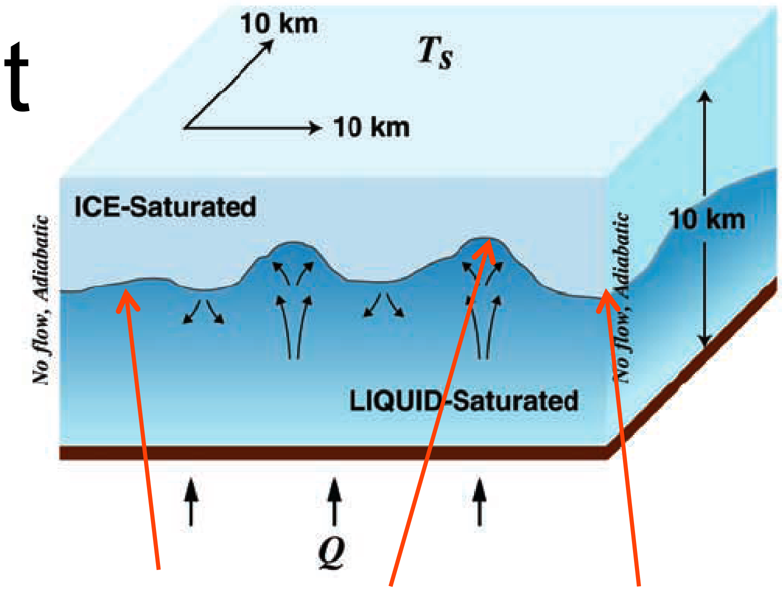
Transport and release of CH_4 to the atmosphere

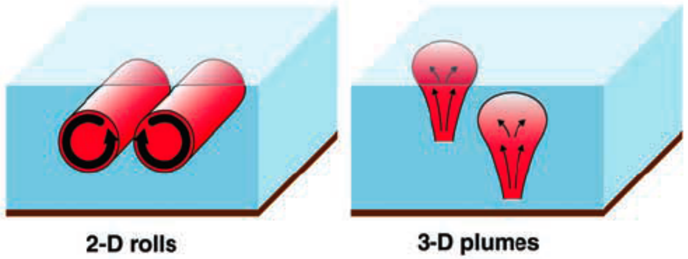
- Assuming a C molar fraction of 0.05, exsolution occurs at 8.5 km depth.
- Above 8.5 km depth, progressive enrichement of the gas phase in CH_4.
- Ultimate release to the atmosphere.
- No H_2 produced together CH_4.



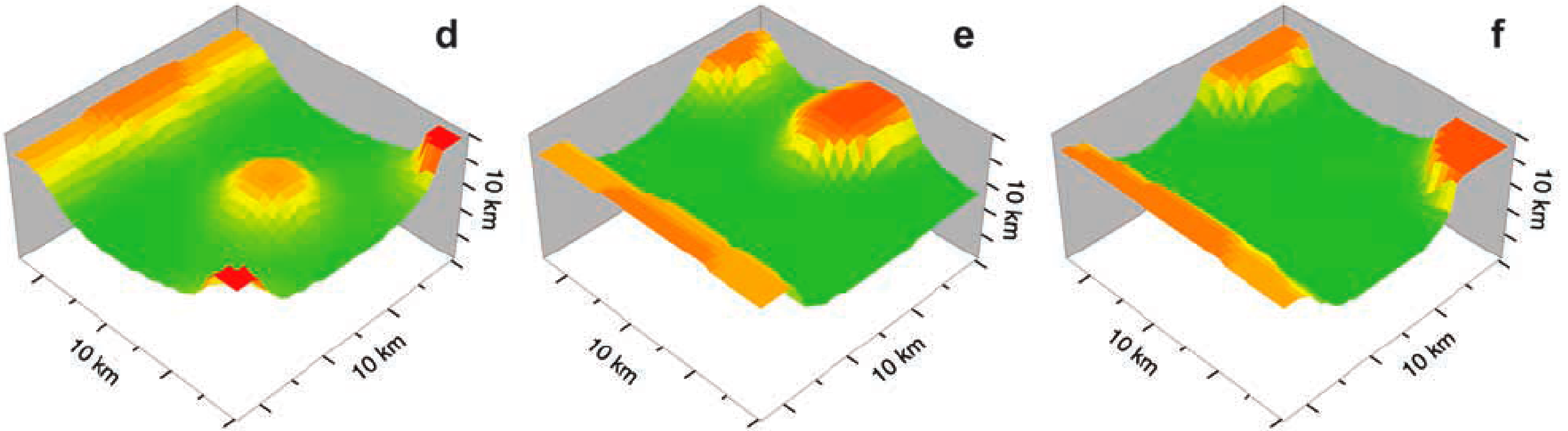
Convection and enrichment of the cryosphere in CH_4

- Water convection in Martian crust(Travis et al, 2003)

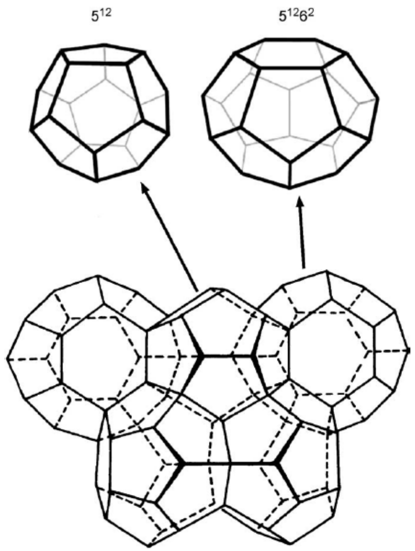




Progressive enrichment of water ice in methane clathrates at the interface?

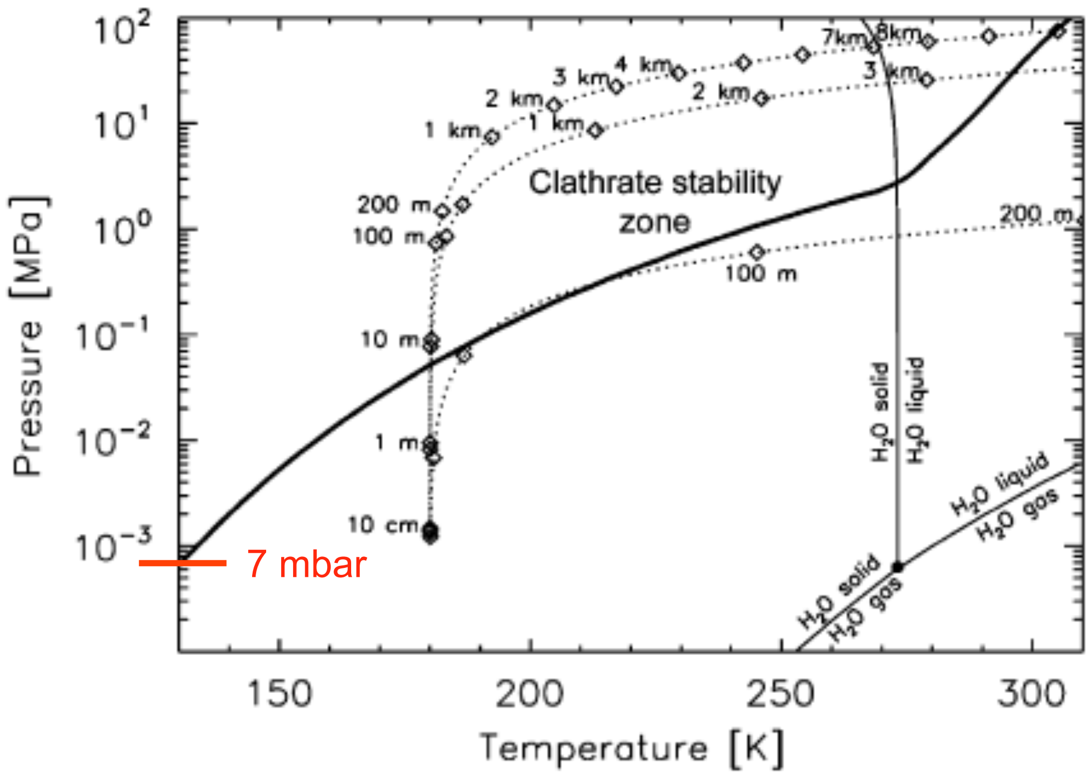


CH_4 Clathrates

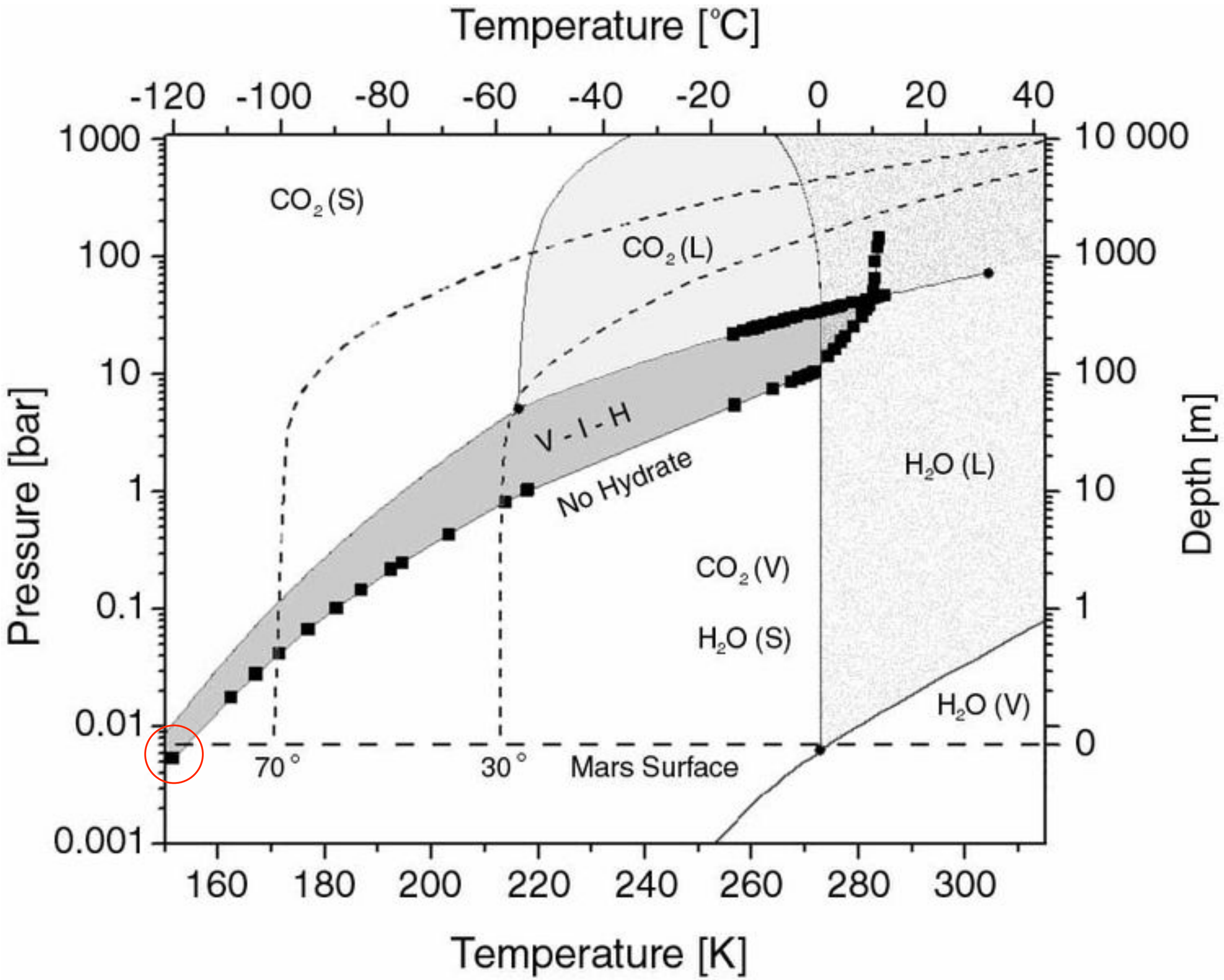


Chastain and Chevrier, 2007

- Clathrates : molecules of CH_4 trapped in cages of H_2O: CH_4-5.85 H_2O.
- Formed at high pressure(oceanic groundfloor on Earth), **but NOT in Martian atmospheric conditions**.
- May be formed in the subsurface at p>≈1 bar.



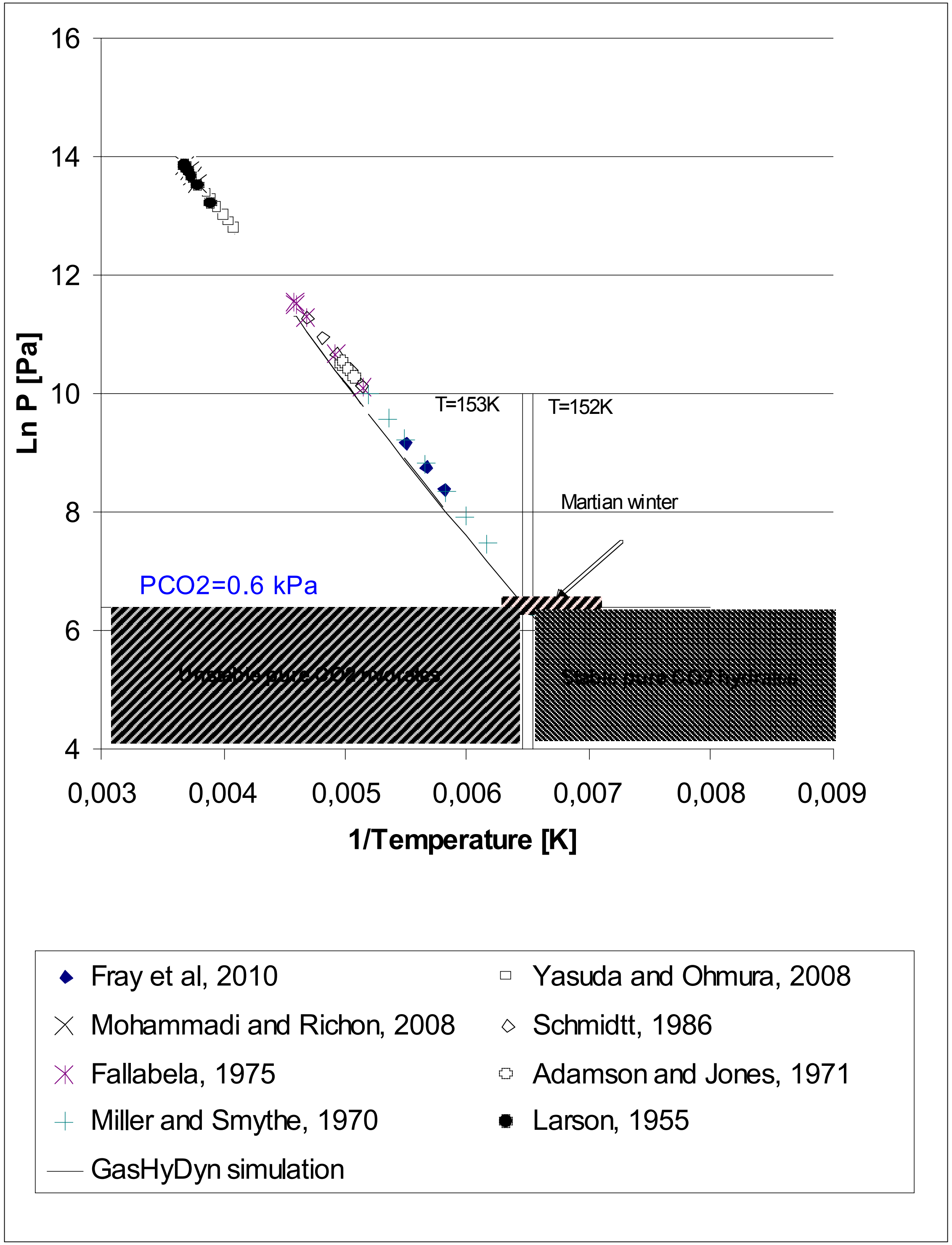
Possible formation of mixed CO_2-CH_4 clathrates on the south polar cap



Calculation/lab. measurements

- « Van der Waals » approach.
- T<150 K : formation of CO_2 clathrates.
- T(south cap) ≈145 K.

Herri et al., 2011

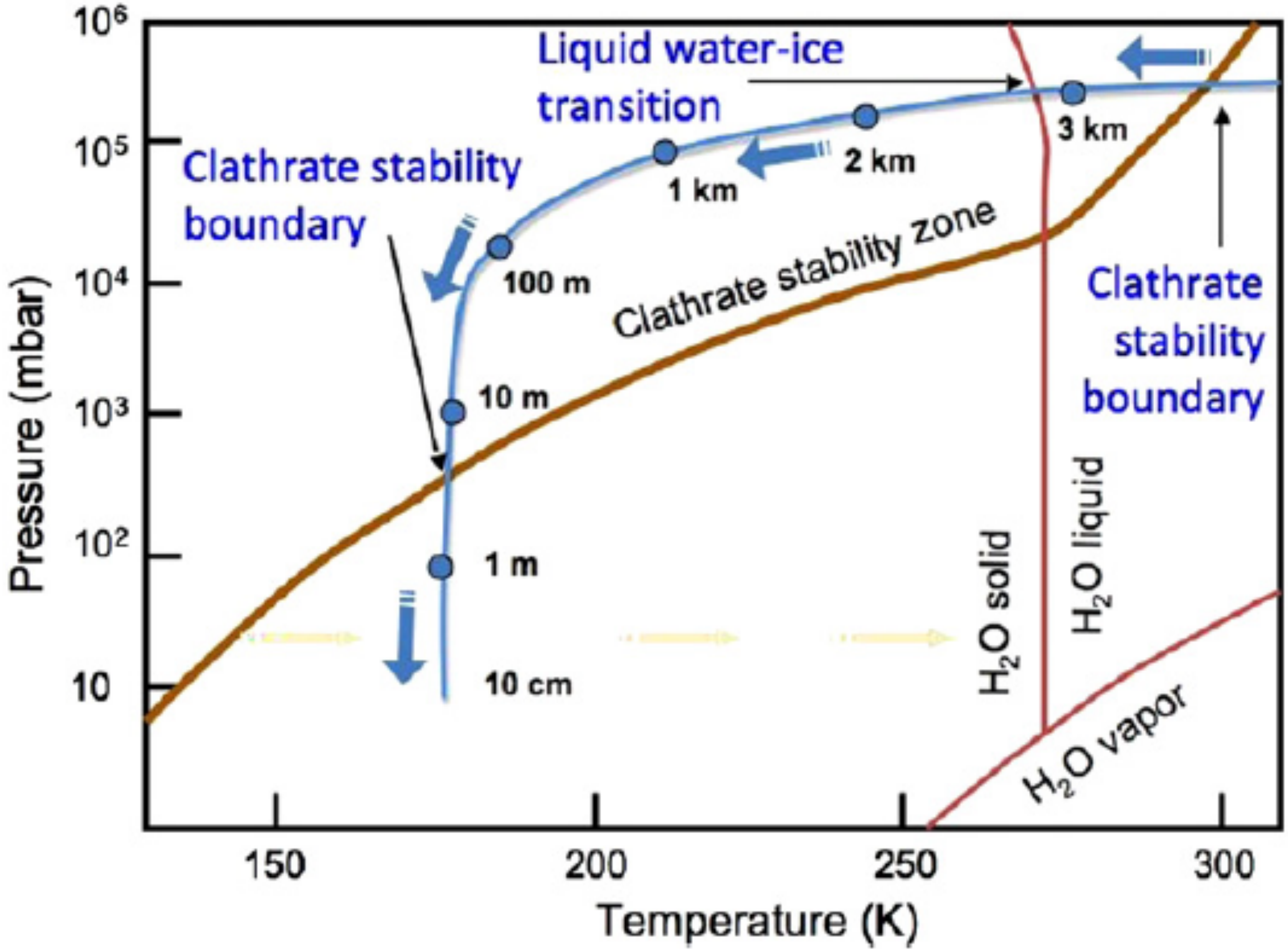


Abundance fraction of component in clathrate versus component in gas

Equilibrium condition Gas= 97,4% CO_2, 2,7%N_2, 2% Ar, 15 ppb CH_4		Abundance ration =xi/fi xi : composition of i in the hydrate fi : composition of i in the gas			
T (K)	P (kPa)	CO2	N2	Ar	CH_4
139	113,6	1,048	0,010	0,028	0,270
143	181,5	1,048	0,012	0,033	0,281
147	284,5	1,048	0,013	0,038	0,291
150	393,5	1,048	0,015	0,042	0,299
151	437,5	1,048	0,015	0,043	0,302
154	596,8	1,048	0,017	0,048	0,310
155	661,7	1,048	0,017	0,049	0,313
157	809,4	1,048	0,018	0,052	0,318
158	893,6	1,047	0,019	0,054	0,320
159	985,6	1,047	0,019	0,056	0,323
160	1086,1	1,047	0,020	0,057	0,326

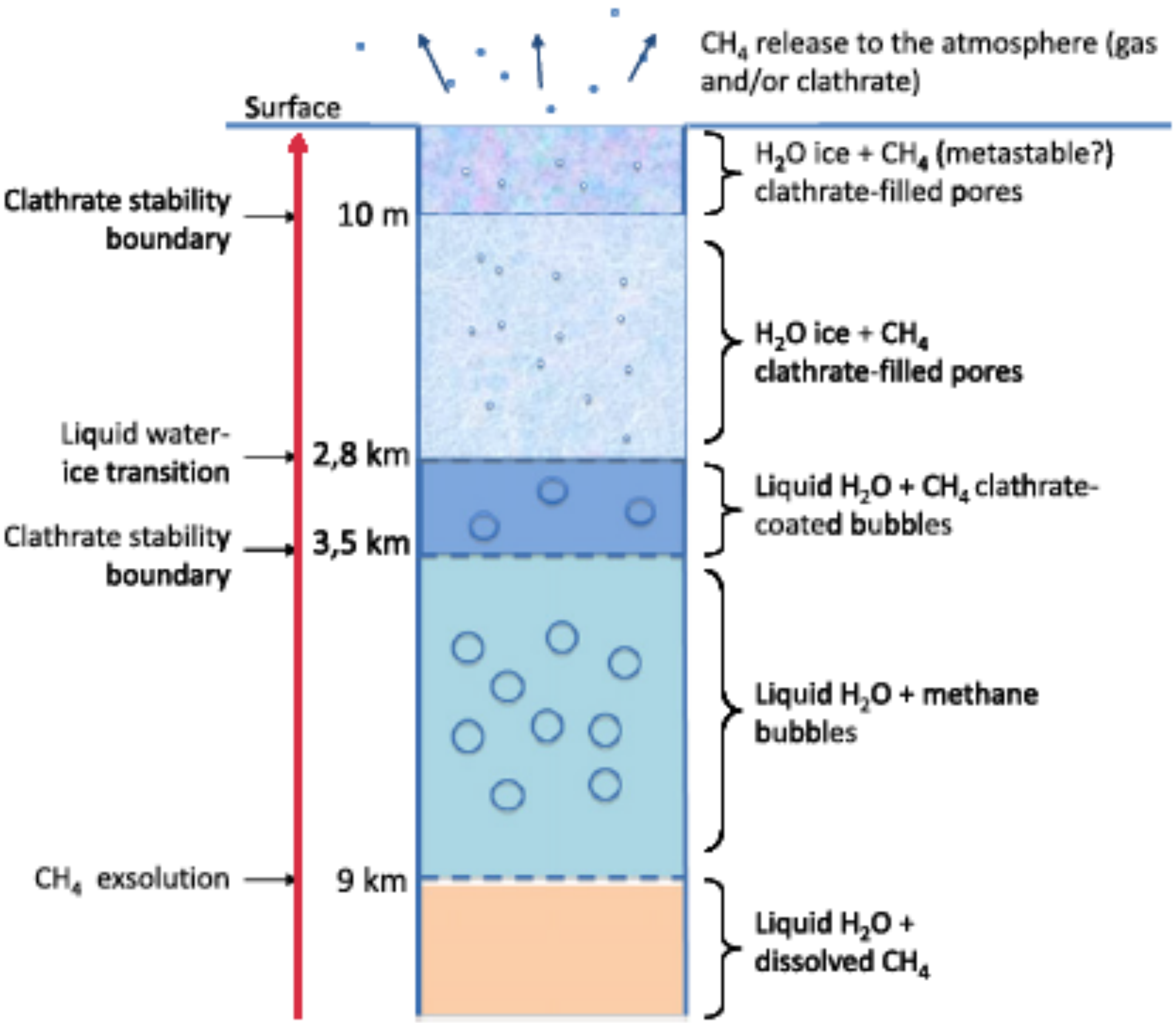
Herri et al., 2011

Path of a CH_4-rich fluid parcel in the phase diagram

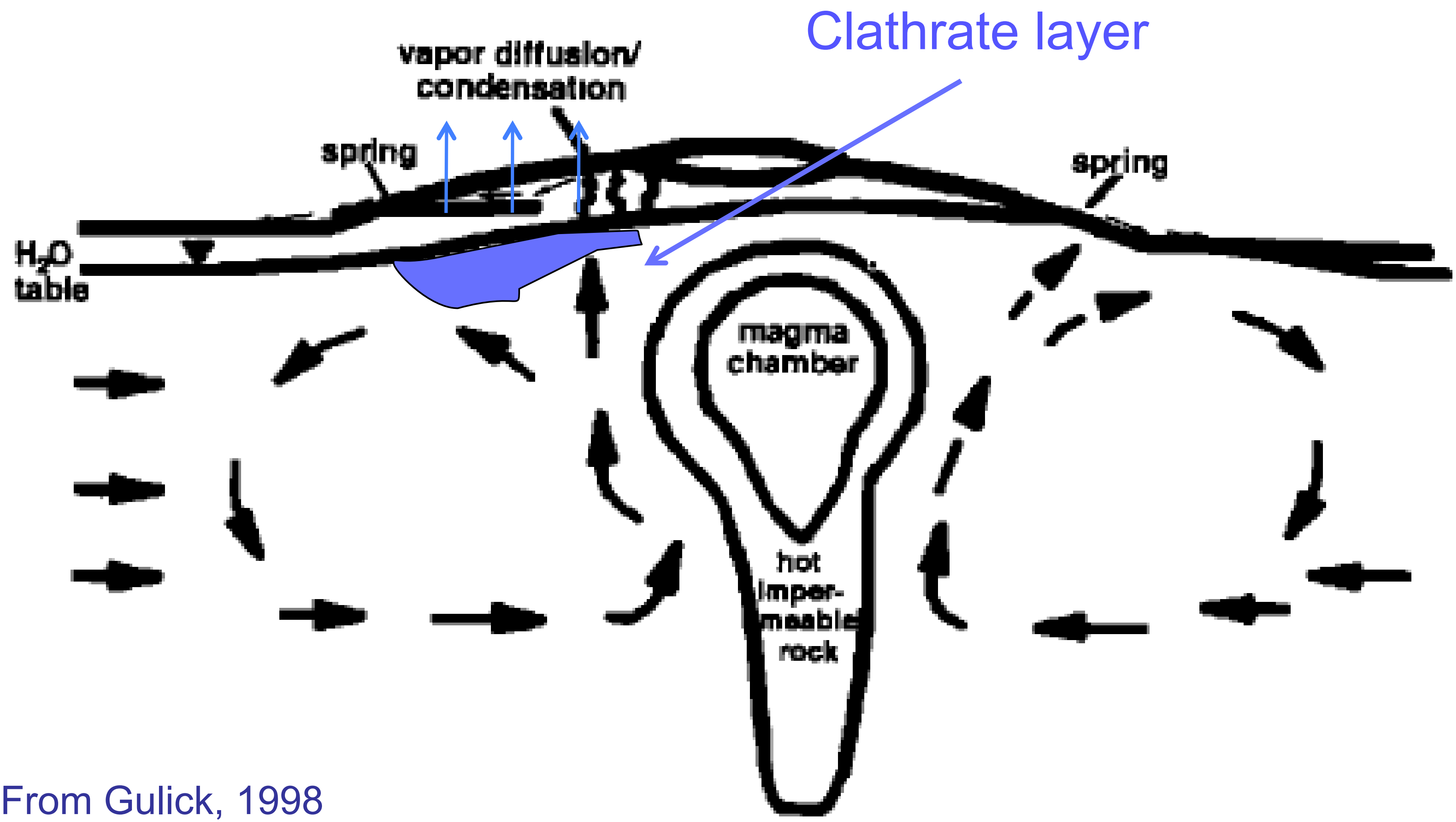


Chassefière et Leblanc, PSS, 2011

Physical states of the fluid



Release of water and methane to the surface and atmosphere



From Gulick, 1998

Another possible abiotic source of CH_4 : serpentinization

- Generic serpentinization reaction at Mars, with Mg/(Mg +Fe)=0.75 (Oze and Sharma, 2005)

$$Mg_{1.5}Fe_{0.5}SiO_4 + 1.17H_2O \rightarrow 0.5\underset{\text{Serpentine}}{Mg_3Si_2O_5(OH)_4} + 0.17\underset{\text{Magnetite}}{Fe_3O_4} + 0.17H_2$$

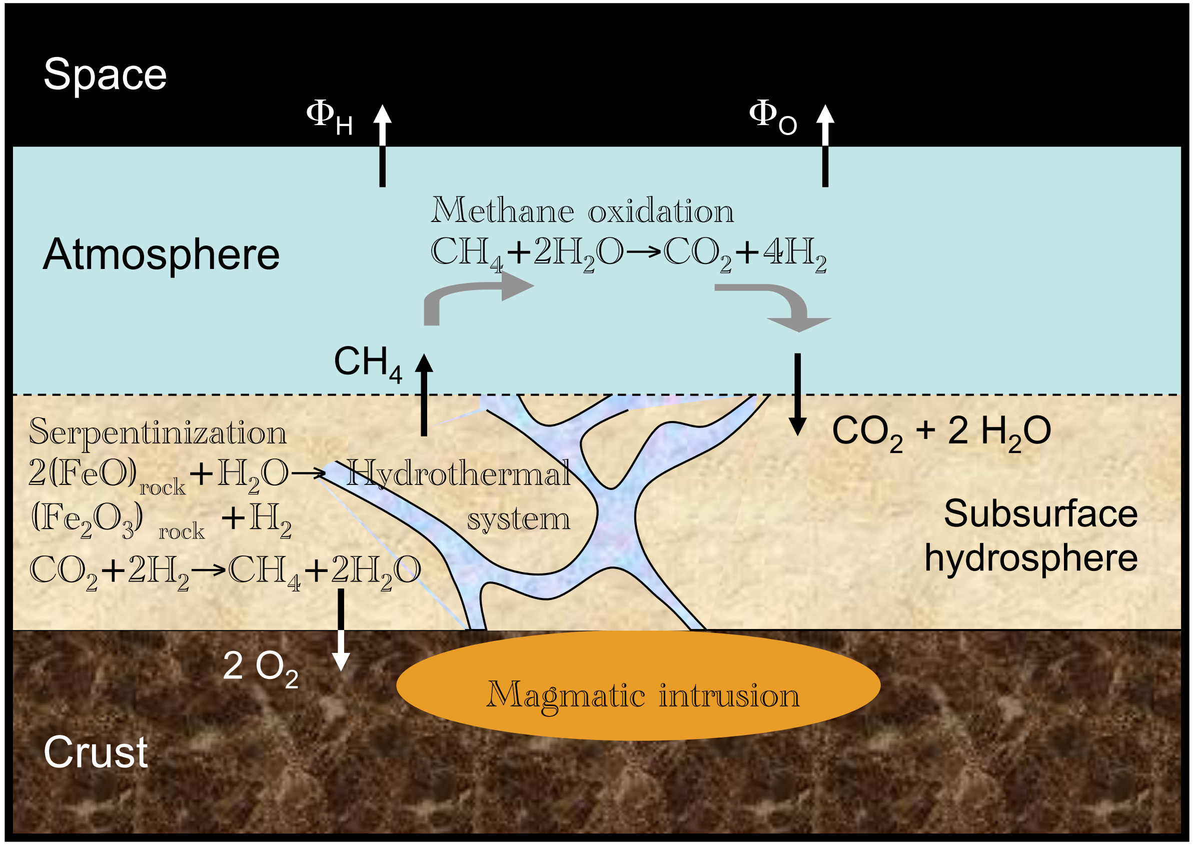
- Further oxidation of H_2 through hydrocarbon formation processes (McCollom and Bach, 2009) :

$$CO_2 + H_2 \rightarrow CH_4 + C_2H_6 + \ldots + C_nH_m + \ldots + H_2O$$

- CH_4 released to the atmosphere, then oxidized (in the subsurface?), through the net redox reaction :

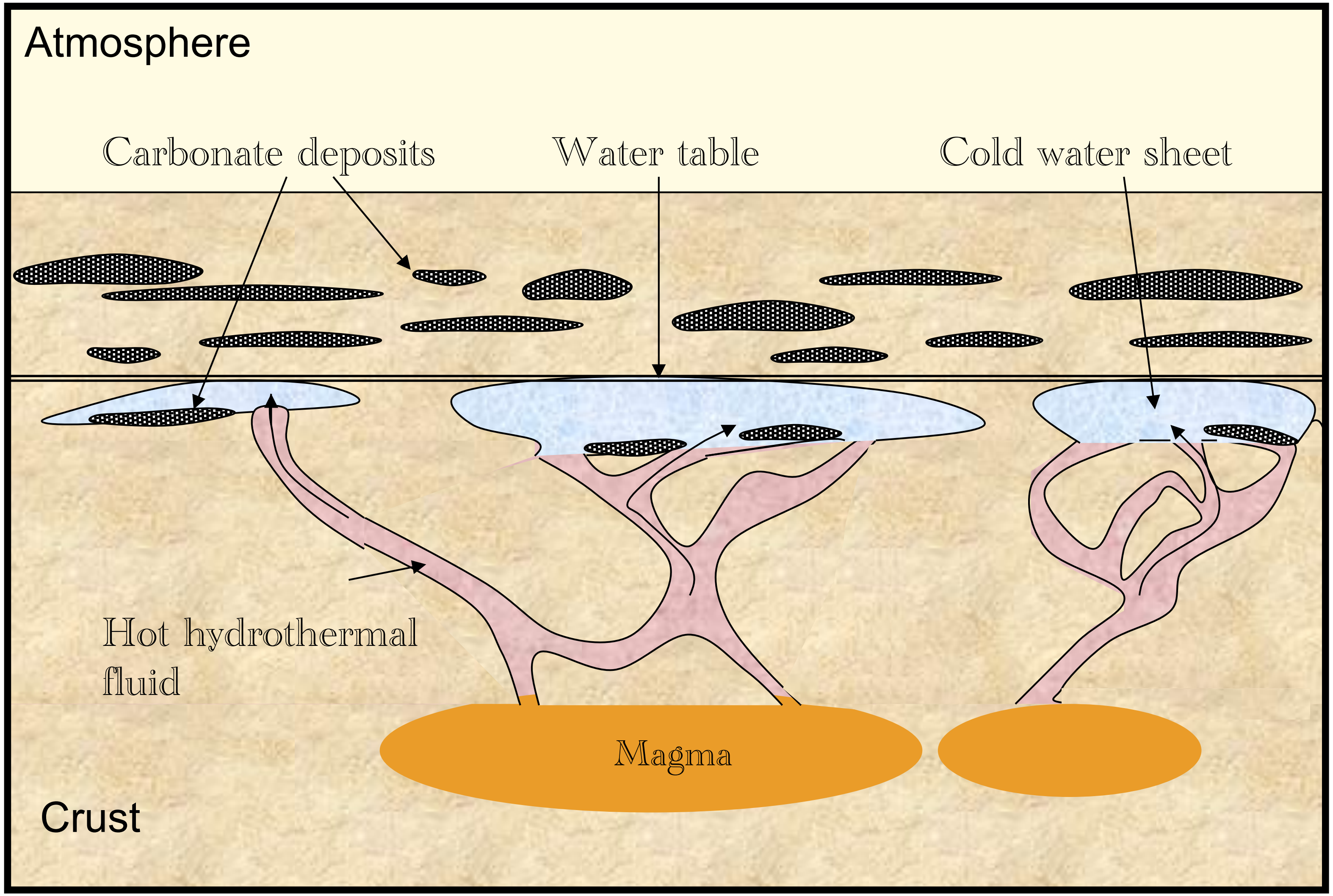
$$CH_4 + 2\,H_2O \rightarrow CO_2 + 4\,H_2$$

Possibility of a cycling of carbon through atmosphere and crust



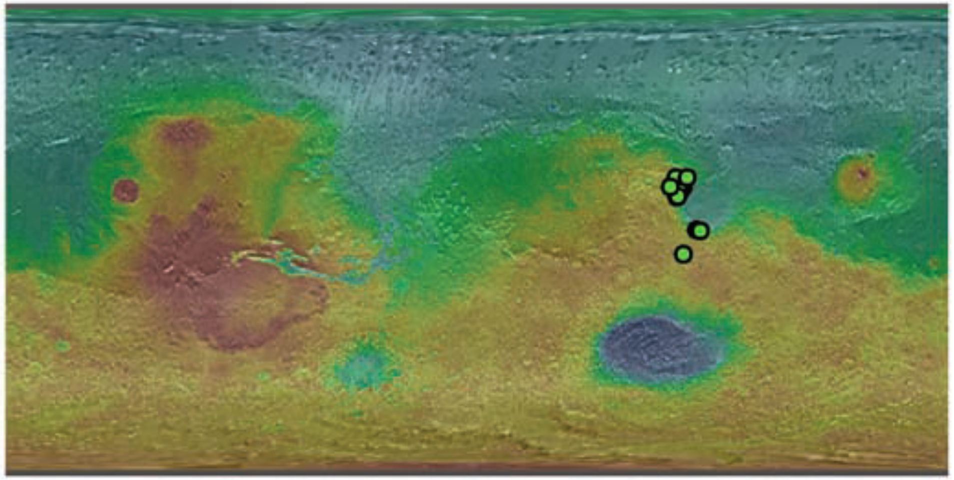
- ➢ Released to the atmosphere oxidized to CO_2
- ➢ CO_2 recycled to the crust (basal melting at the south polar cap?)
- ➢ CO_2 precipitation to carbonates in the crust
- ➢ Decomposition of carbonates and reduction by H_2

Crustal carbonates on Mars (≈1 bar equivalent or more?)

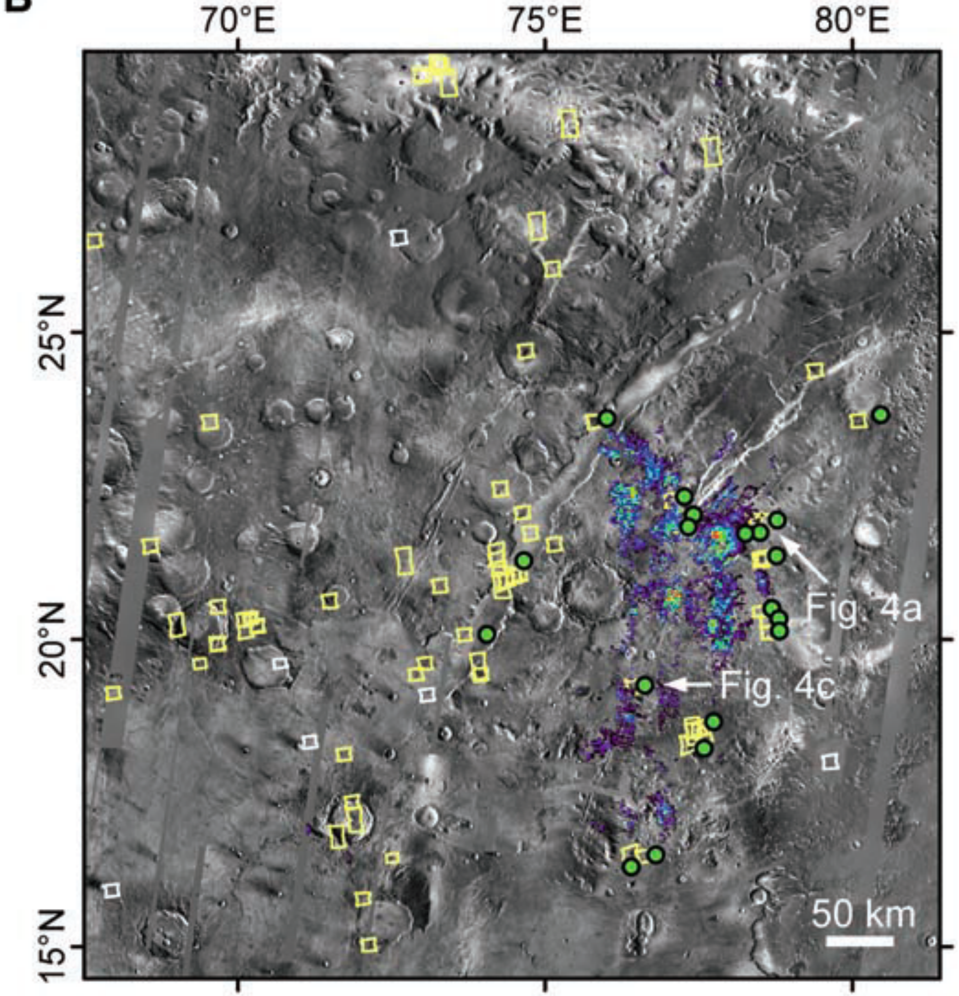


Detection of carbonates at the surface of Mars

A



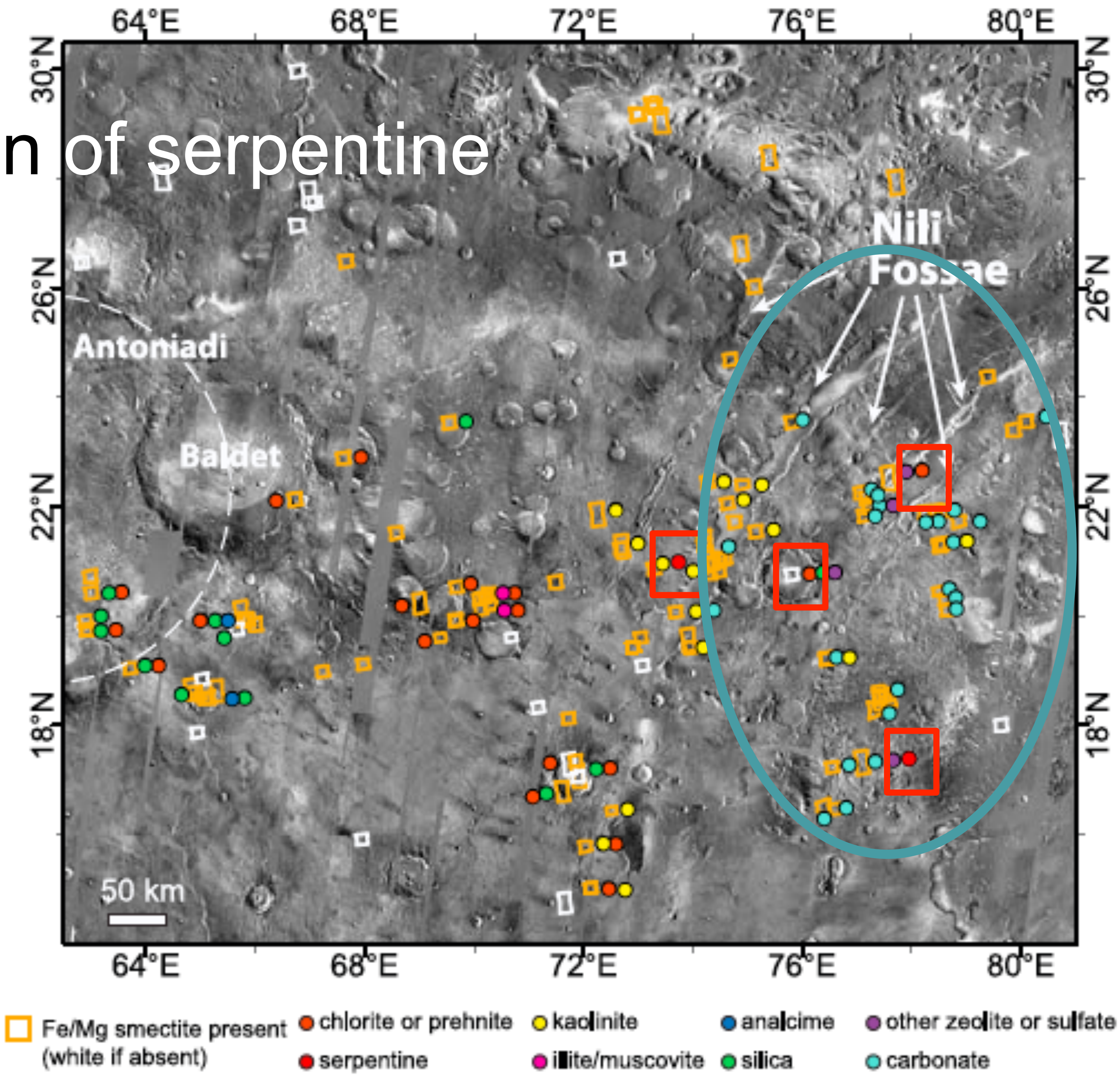
B



- Carbonates observed by CRISM/MRO in the Nili Fossae region (green circle).
- Fe-Mg phyllosilicates (zones outlined in yellow).

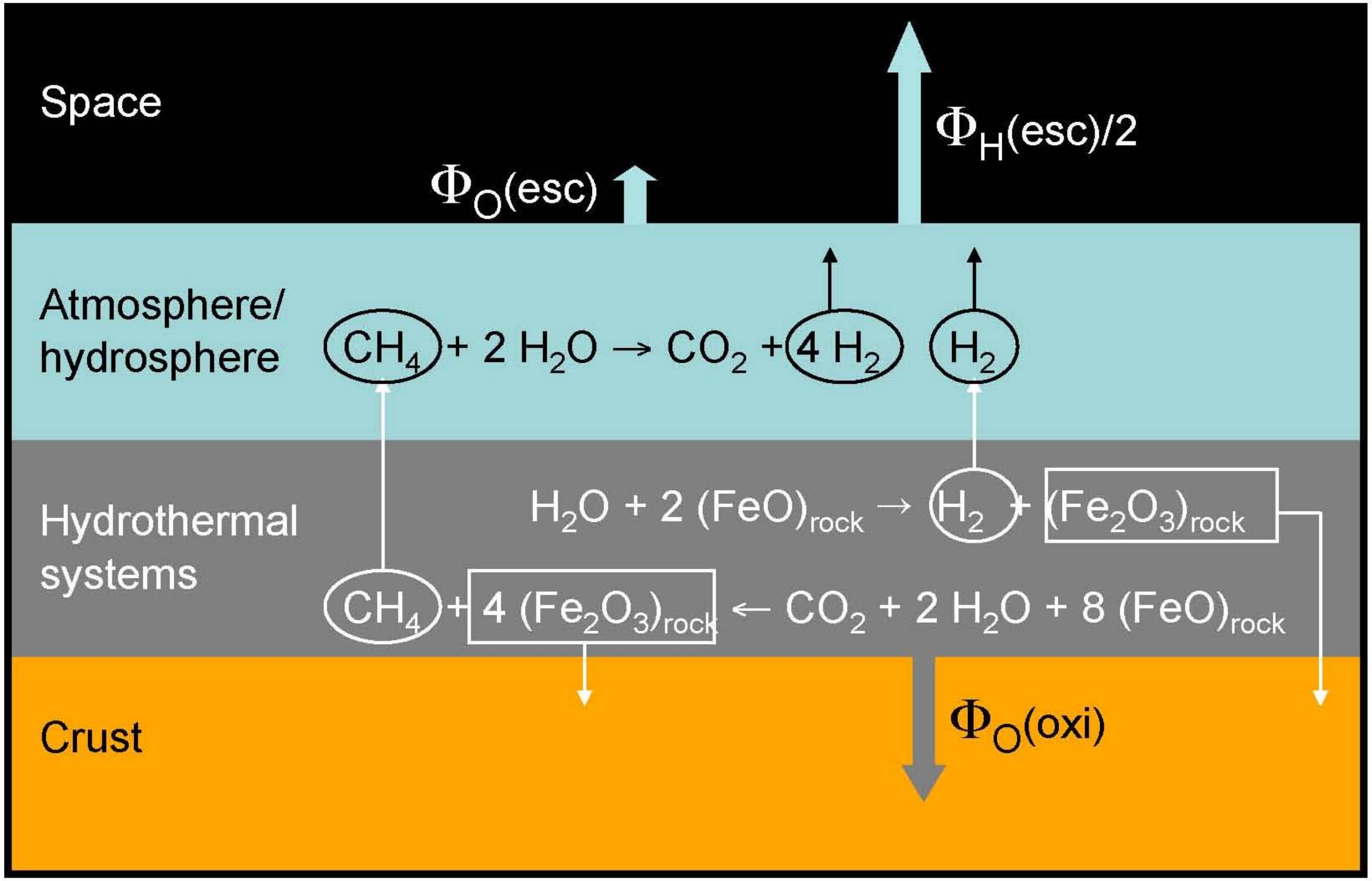
Ehlmann et al., 2009

Detection of serpentine



Ehlmann et al., 2009

Carbon hydrothermal cycle from a redox point of view



Chassefière and Leblanc, 2011

Present imbalance between H and O escape fluxes

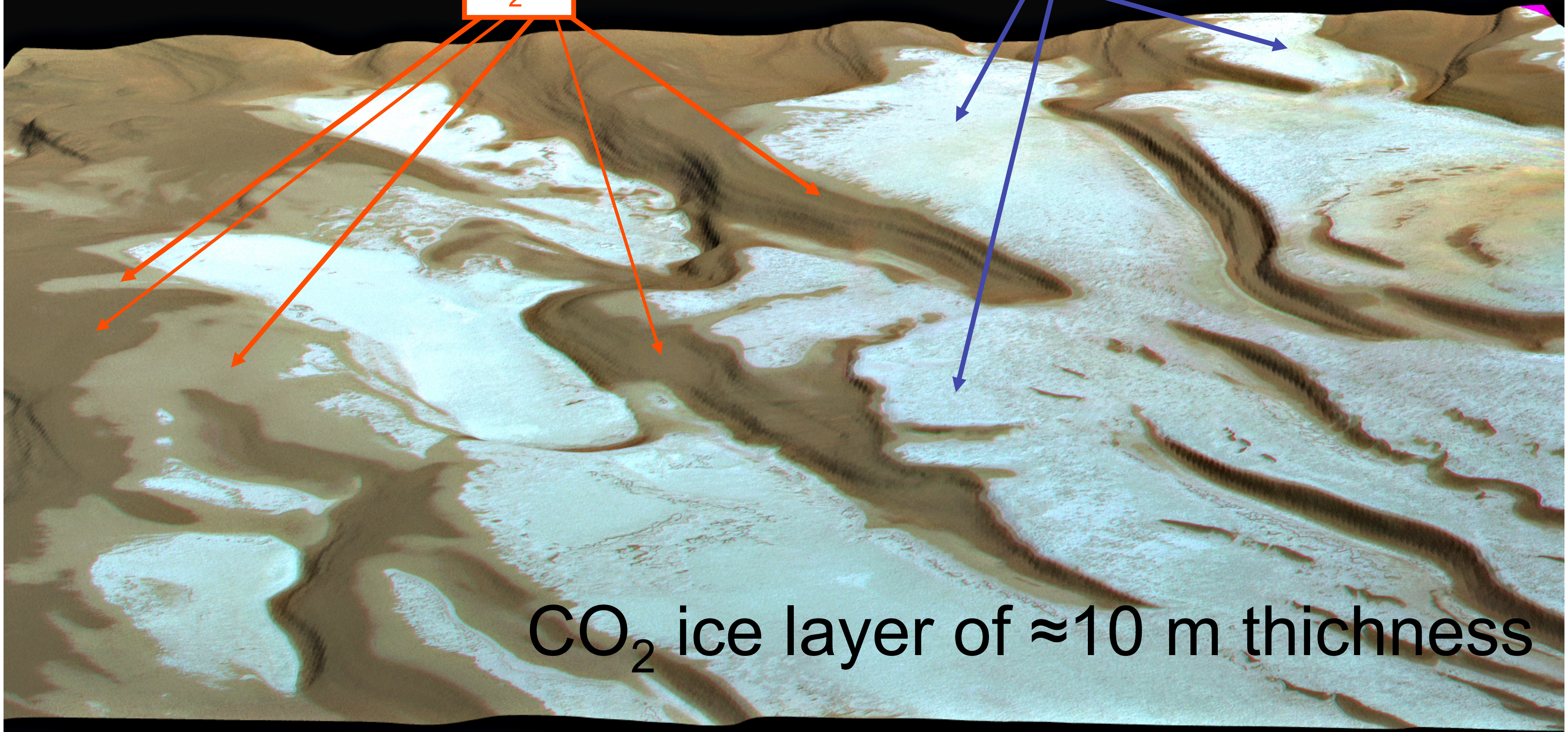
- Imbalance between H and O escape fluxes ($\Phi_O \neq 1/2\ \Phi_H$) → variation of H_2 to restore the balance (Mc Elroy and Donahue, 1972, Liu and Donahue, 1976).
- Typical damping time of imbalance = $\tau(H_2) \approx 1000$ years.
- Present escape O and H fluxes :
  - H thermal escape flux close to the limited-diffusion flux (Chaufray, 2007; Zahnle et al., 2008) : $4\ 10^8$ cm^{-2} s^{-1}
  - O non-thermal escape : 2-8 10^7 cm^{-2} s^{-1} (Valeille et al, 2009; Chassefière and Leblanc, 2010)
  - ➢ ***$\Phi_O \approx 0.05\text{-}0.2\ \Phi_H < 0.5\ \Phi_H$: small O escape/ H escape → strong redox imbalance.***
- Two possibilities (Nair et al., 1994) :
  - ➢ ***Flux of reduced gases from the interior (CH_4, H_2…)***
  - ➢ Continuous oxidation of surface rocks.

CH_4 : a potential sink for atmospheric O_2?

- A CH_4 mixing ratio of 15 ppbv and a CH_4 lifetime of ≈200 days results in **a CH_4 flux compatible with the global redox balance of H and O fluxes** (**$\Phi_H = 2 (\Phi_O + \Phi_{ox})$**).
- **The present CH_4 release flux could have been at a comparable level for at least ≈1000 yr** (H_2 lifetime)
- At the present CH_4 release rate, the CH_4 released since the last obliquity transition (**3 Myr ago**) results in a superficial CO_2 ice layer on the south polar cap similar to the observed one (**10 m thick**).
- The preferred value of the molar fraction of CH_4 in the vented gas is ≈1 (not 0.1 like on Earth), **with therefore no simultaneous H_2 release**.

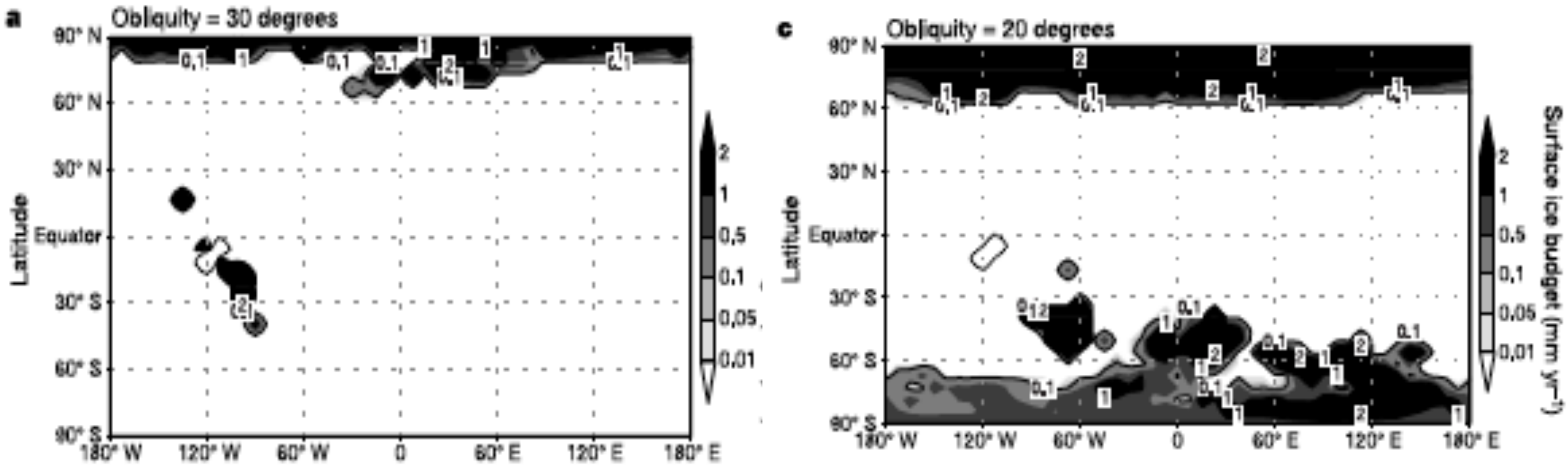
Chassefière and Leblanc, 2011

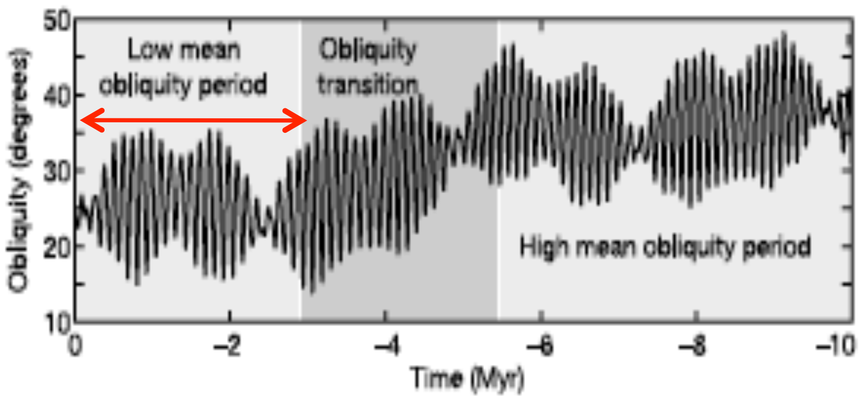
OMEGA / HRSC



J.-P. Bibring & OMEGA team

Last obliquity transition





Levrard et al. 2004

- ➢ No south polar cap at high obliquity.
- ➢ Deposition of south polar cap 3 Myr ago/
- ➢ **Subsequent deposition of ≈10 m thick layer of CO_2 ice due to CH_4 release (?).**

Why no significant H_2 release?

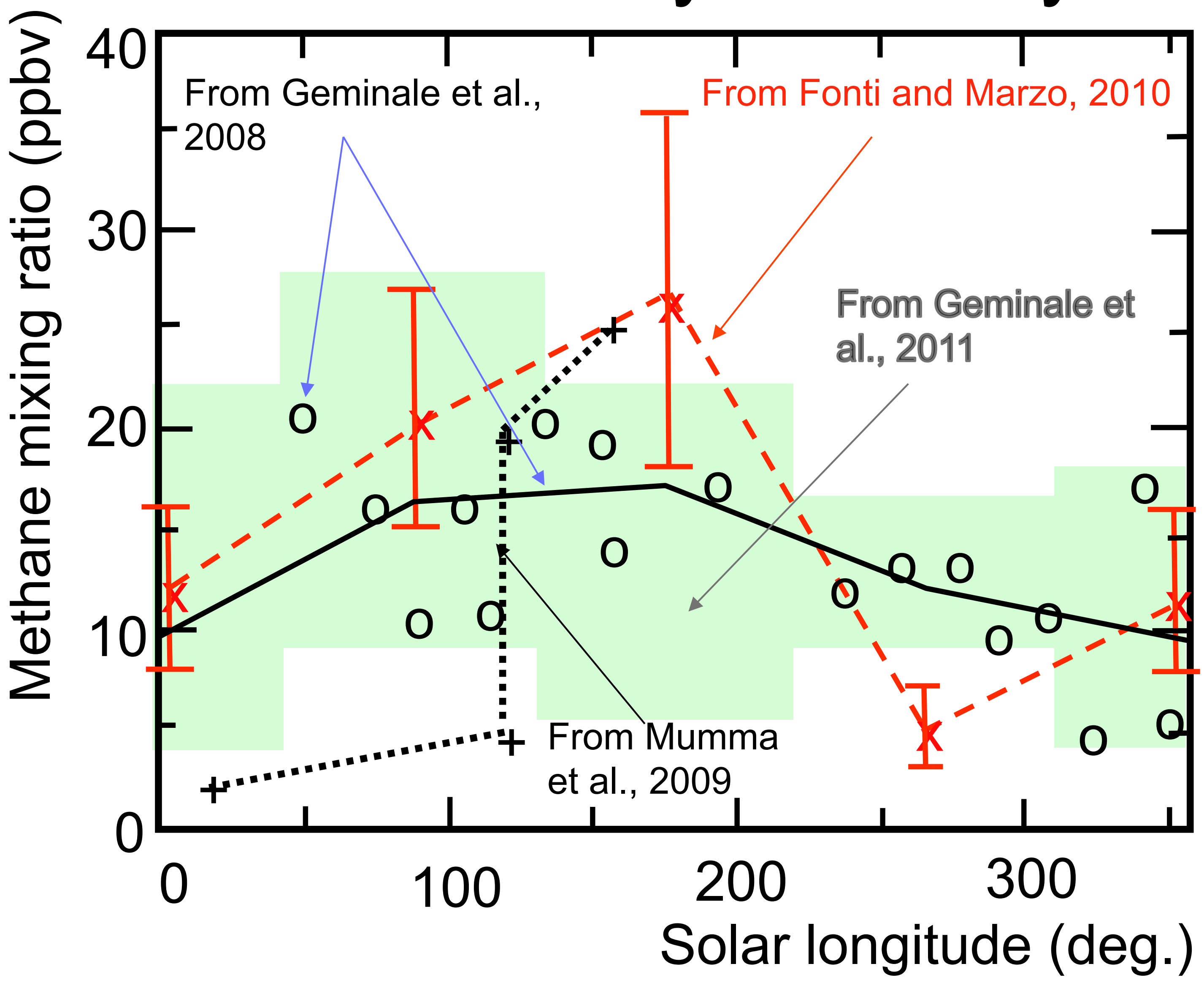
(AT LEAST) THREE POSSIBLE REASONS :

- CH_4 stored in subsurface clathrates (unlike H_2 rapidly outgassed during hydrothermal events).
- CH_4 formed by direct thermodynamical equilibration of carbon dissolved in deep hot fluids, no H_2 released (Lyons et al., 2006).
- H_2 consumed by microbes before reaching the surface (C. Muller, personal communication, 2010).

A few suggestions

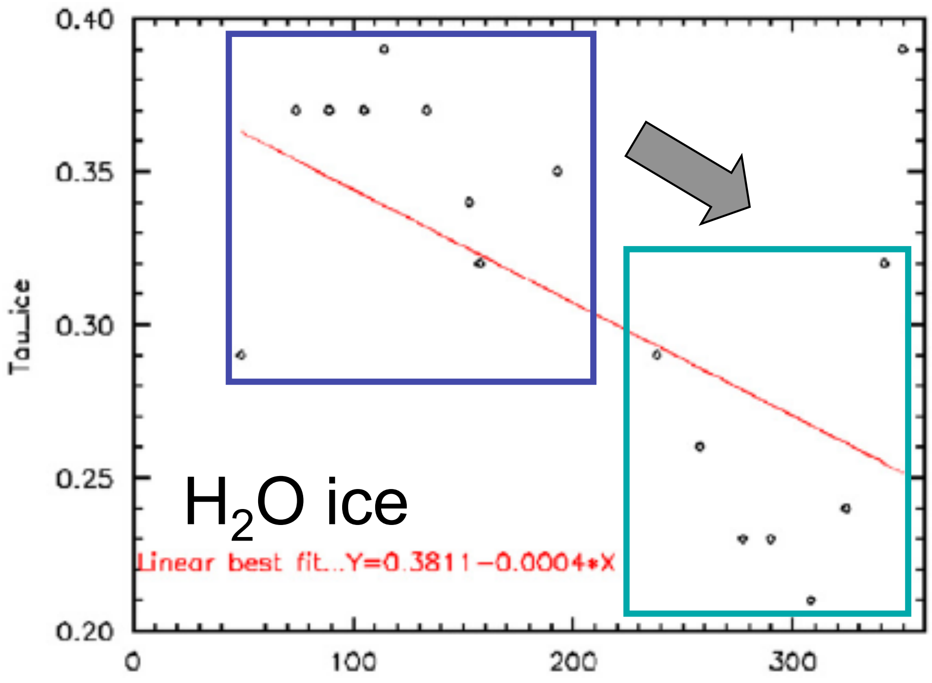
- CH_4 release at present rate since several thousand or million years.
- Subsurface CH_4 clathrate-rich cryosphere could serve as intermediate reservoir for CH_4.
- An active long-term carbon cycle, progressively decreasing with volcanic/hydrothermal activity, may occur through various reservoirs : carbonates, clathrates, atmosphere.
- The lack of present H_2 release could also sign a volcanic and/or biotic origin.

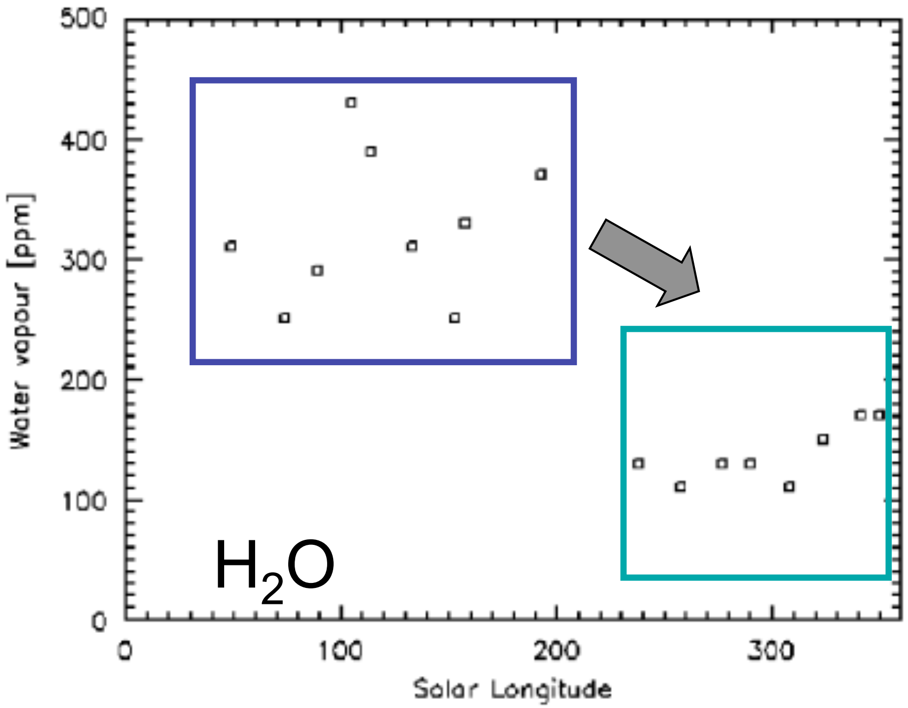
Seasonal cycle of CH_4 over the last 5 seasonal cycles : why?

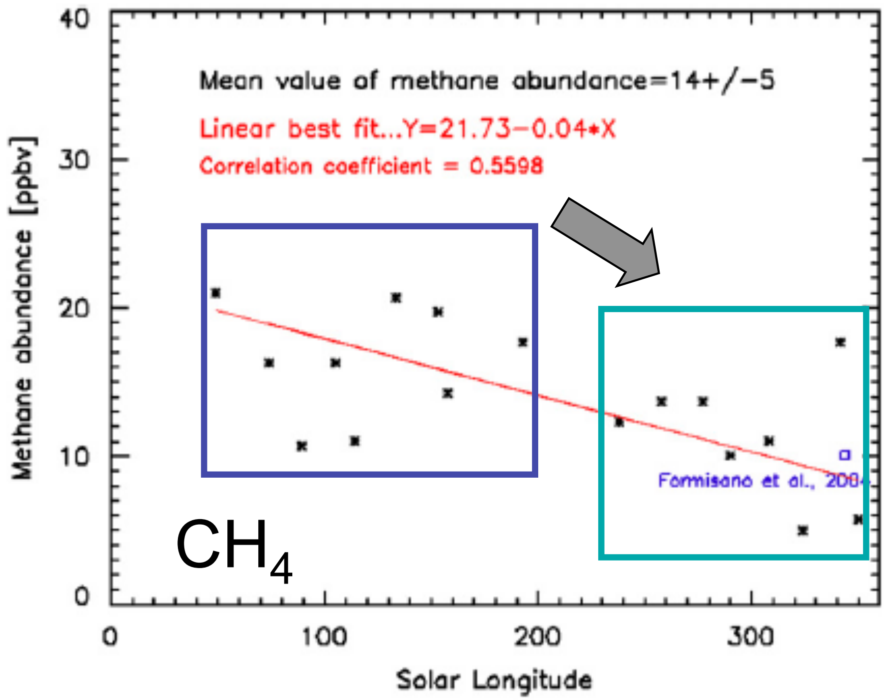


Seasonal correlation of methane with water and ice optical depth

Geminale et al, 2008

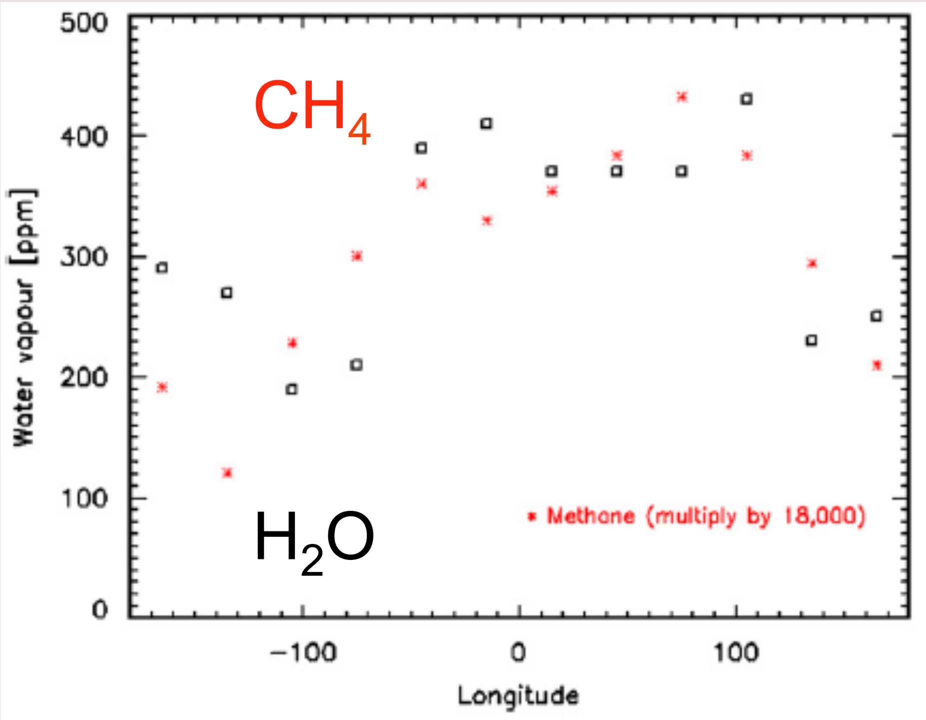


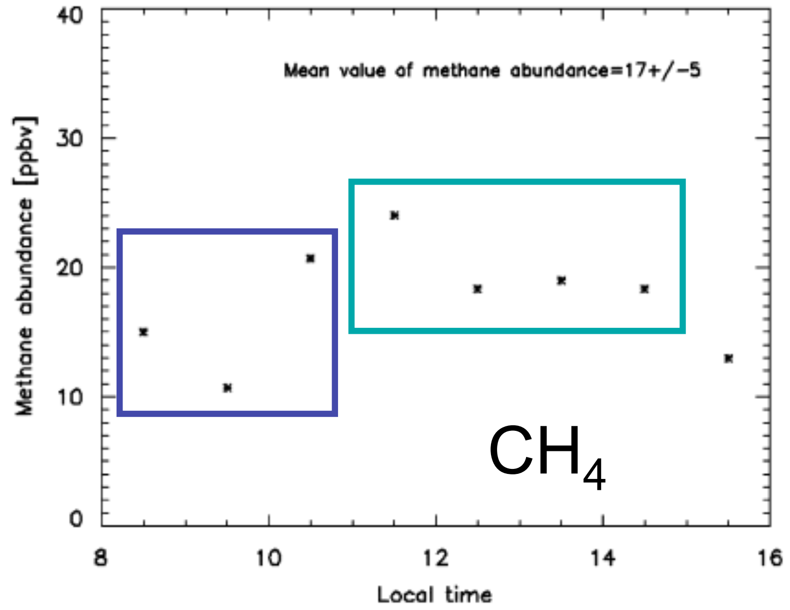


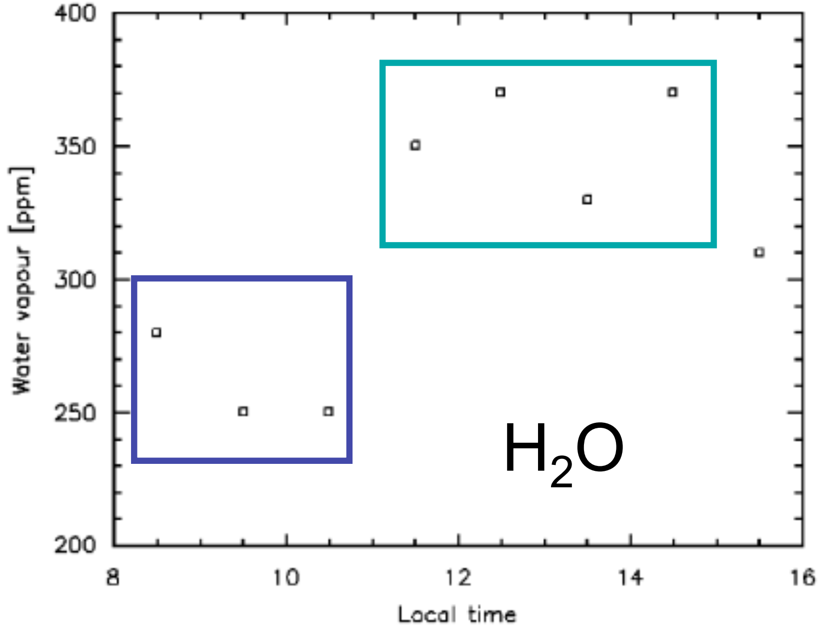


Local time variations

Longitudinal variations



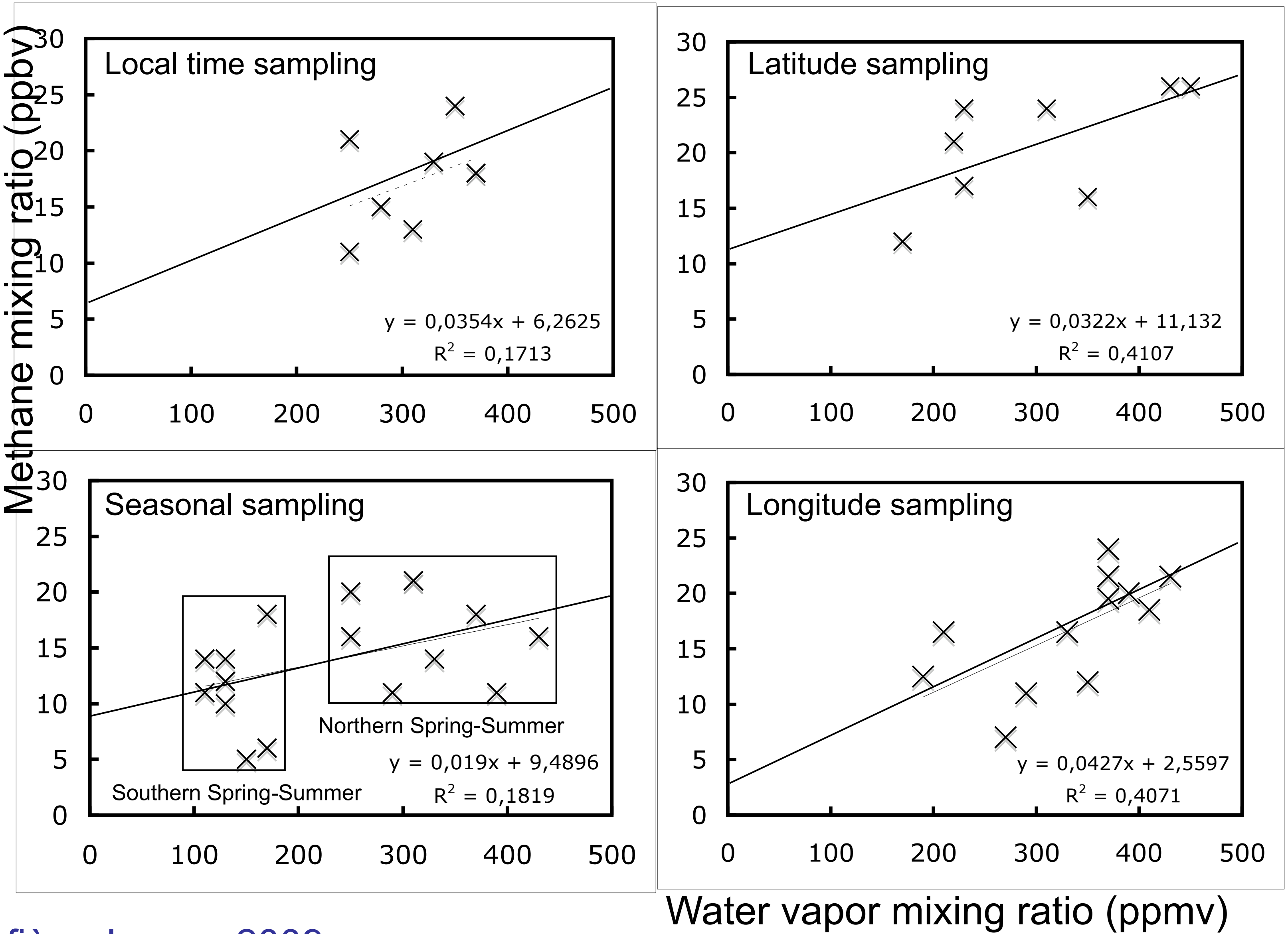




Geminale et al, 2008

Correlation coefficients

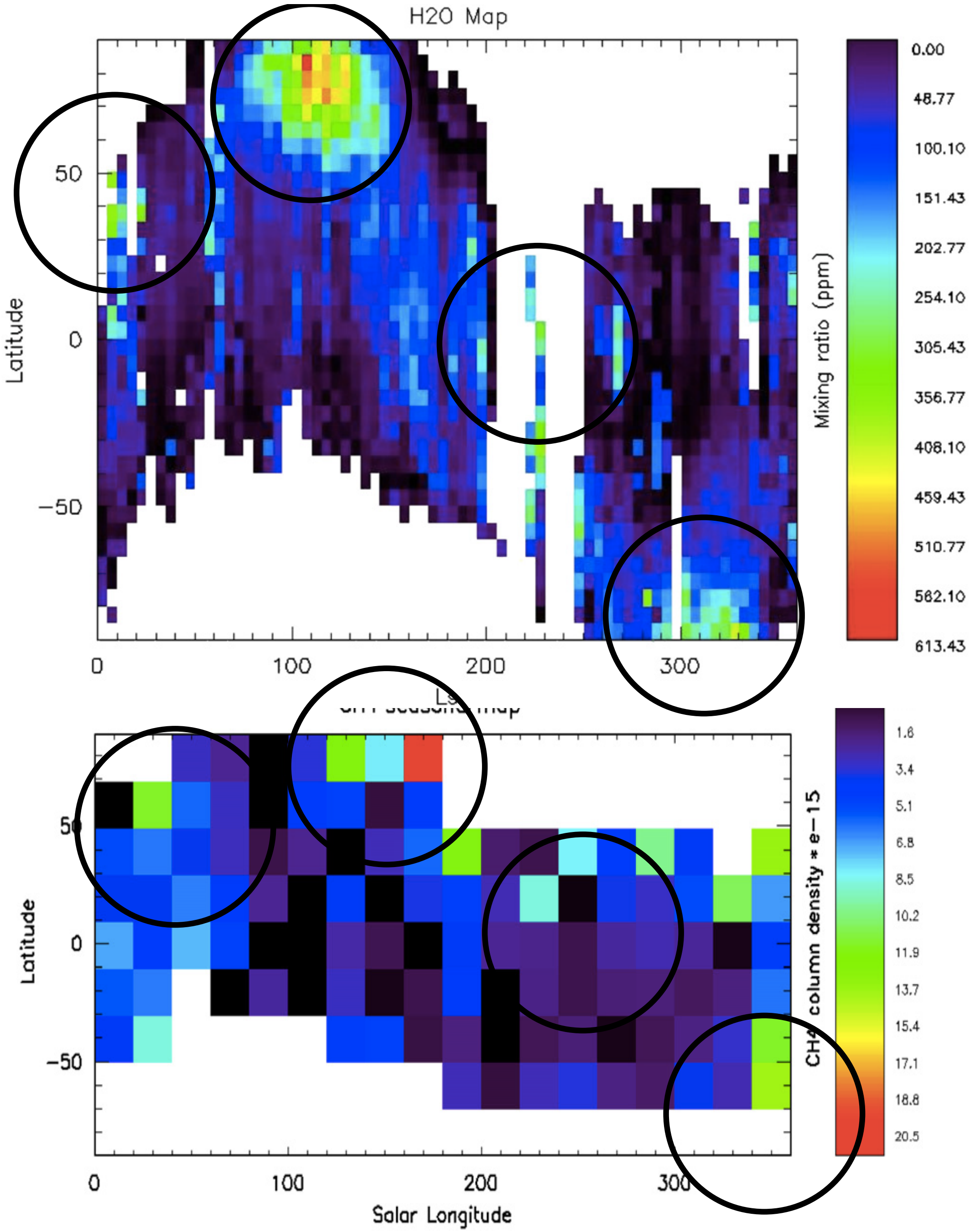
Data from Geminale et al, 2008



Chassefière, Icarus, 2009

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

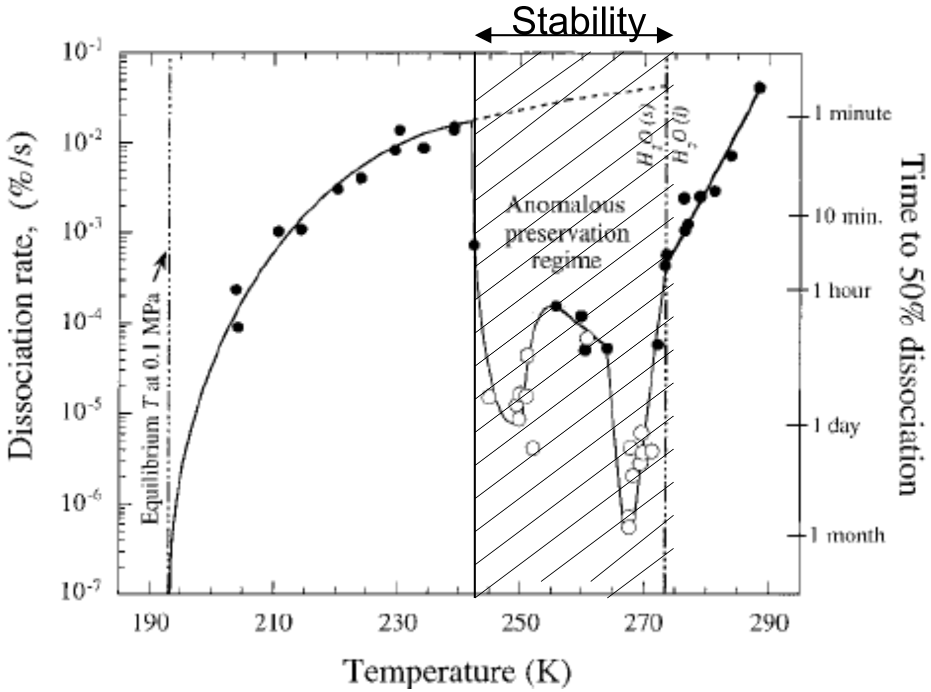
Release of methane under the form of metastable clathrate particles

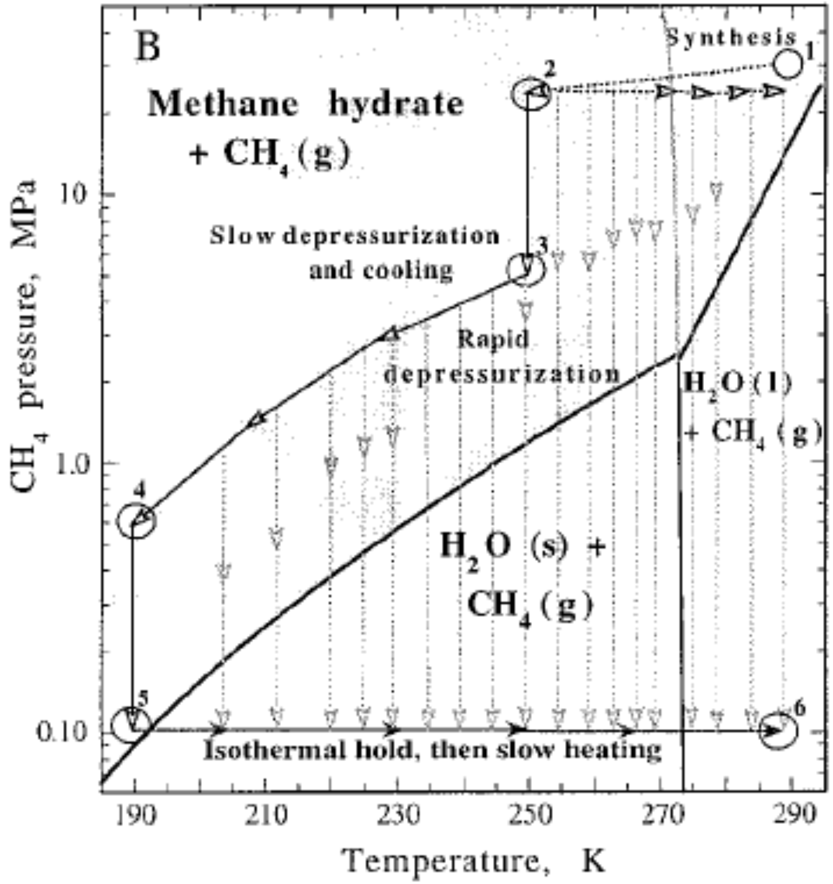
- Anomalous preservation of clathrates (Stern et al., 2001, and ref. therein). *Clathrates more difficult to dissociate than to build.*
- Ultra-stability of very pure clathrate crystals (Zhang et Rodgers, 2008): **<1% dissociation at 1 bar & 268 K in 10 days.**
- Atmospheric gaseous methane could be released from metastable clathrate particles suspended in the atmosphere.

➔ **The cause of particle decomposition could be water condensation, explaining the CH_4/H_2O global correlation** (Chassefière, 2009).

« Anomalous preservation » of clathrates

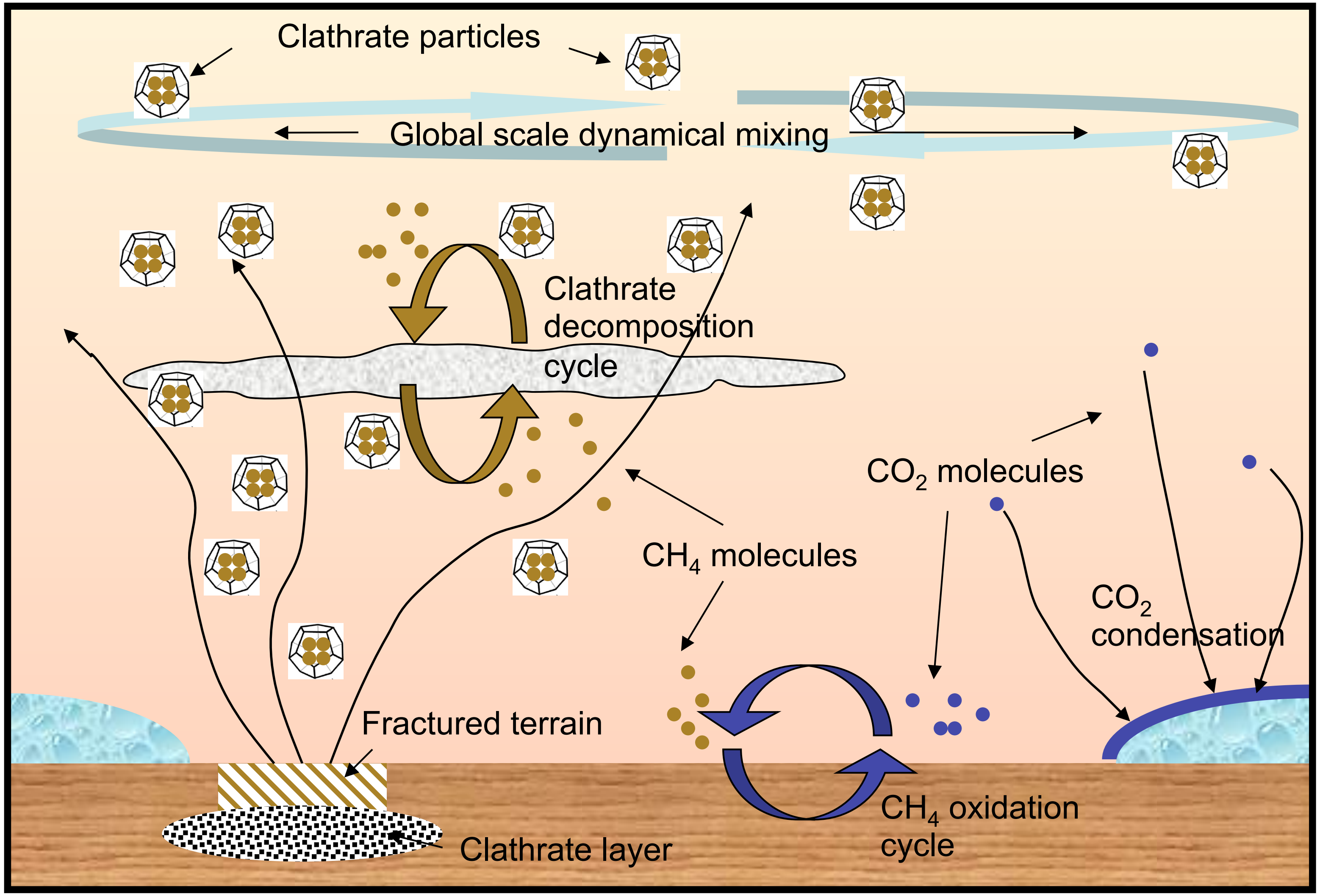
- Anomalous preservation of clathrates (Stern et al. 2001 and ref. therein)





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

Present methane cycle according to the hypothesis of clathrate particle release



Chassefière, 2009

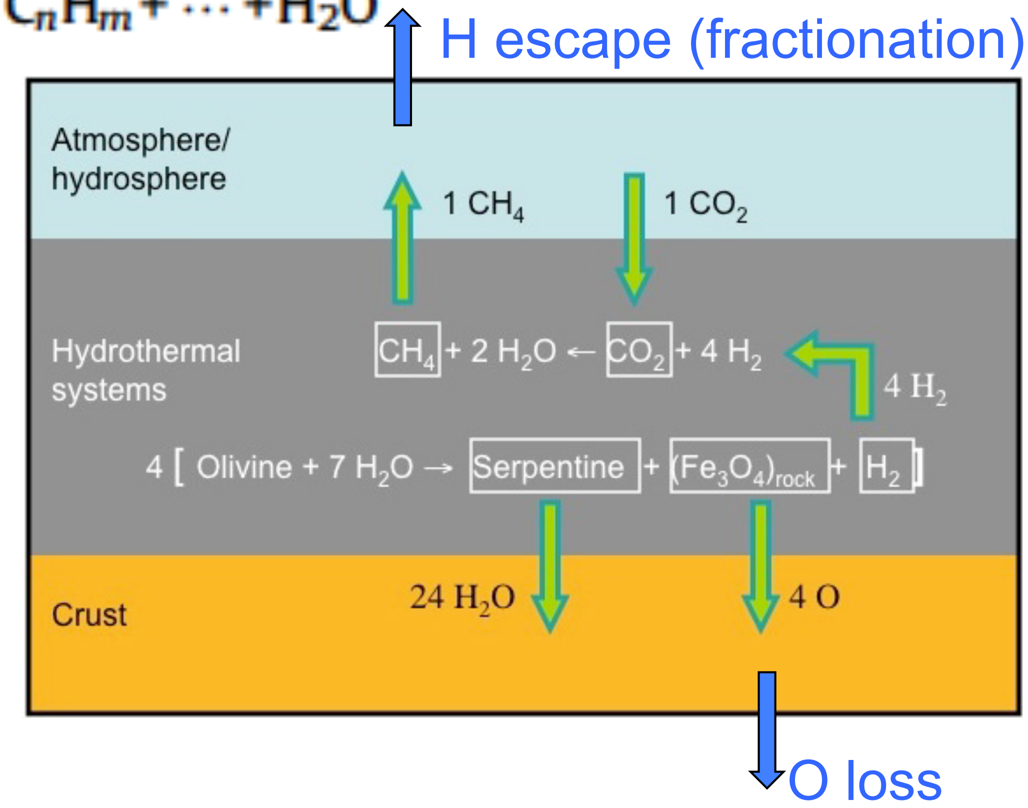
Potential role of serpentinization in storing water in the crust

- Release of CH_4 and H_2 by serpentinization → thermal escape of H atoms → **increase of the D/H ratio**.

$$Mg_{1.5}Fe_{0.5}SiO_4 + 1.17H_2O \rightarrow 0.5\underset{\text{Serpentine}}{Mg_3Si_2O_5(OH)_4} + 0.17\underset{\text{Magnetite}}{Fe_3O_4} + 0.17H_2$$

$$CO_2 + H_2 \rightarrow CH_4 + C_2H_6 + \cdots + C_nH_m + \cdots + H_2O$$

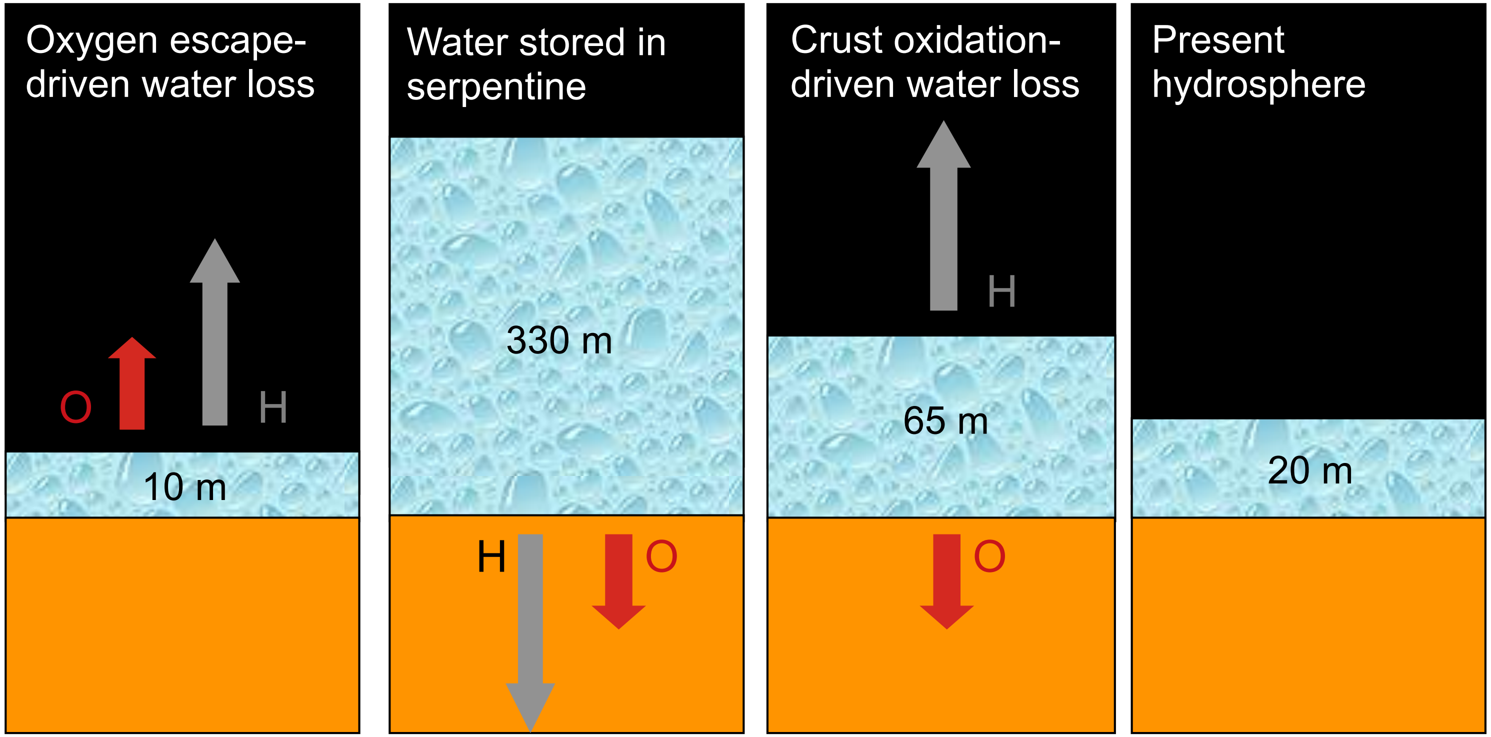
- A model calculating the D/H ratio due to serpentinizatioon since the late Noachian has been implemented.



Chassefière and Leblanc, EPSL, in press, 2011

Possible scenario of water history

- A maximum serpentinization rate resulting in the present D/H value (≈5 SMOW) can be calculated.
- A H_2O global equivalent layer of ≈400 m depth could have been removed during the last 3.8 Gyr, most of it being stored in subsurface serpentine.



Chassefière and Leblanc, EPSL, in press, 2011