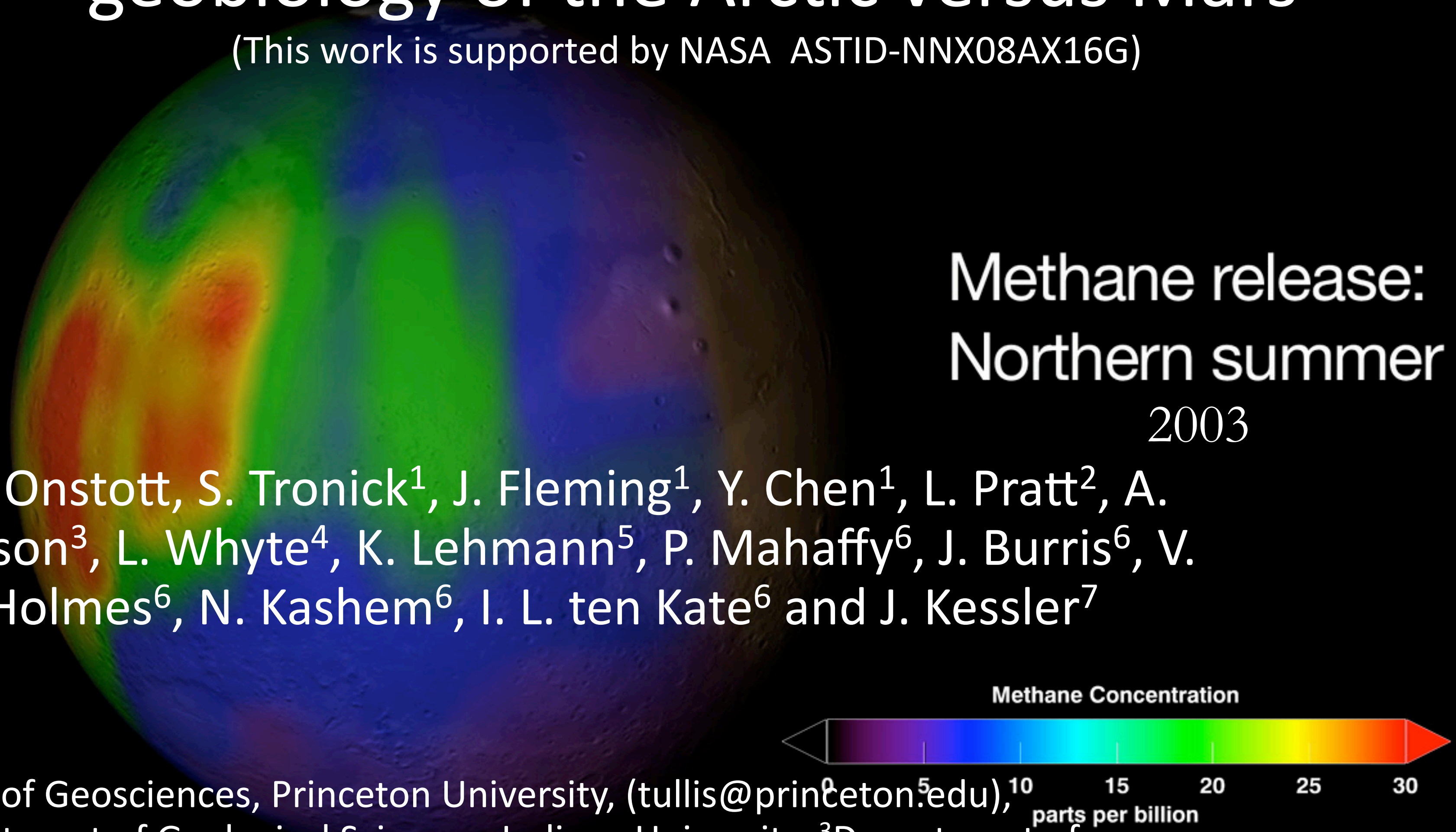
Methane Sources and Sinks: The geobiology of the Arctic versus Mars

(This work is supported by NASA ASTID-NNX08AX16G)



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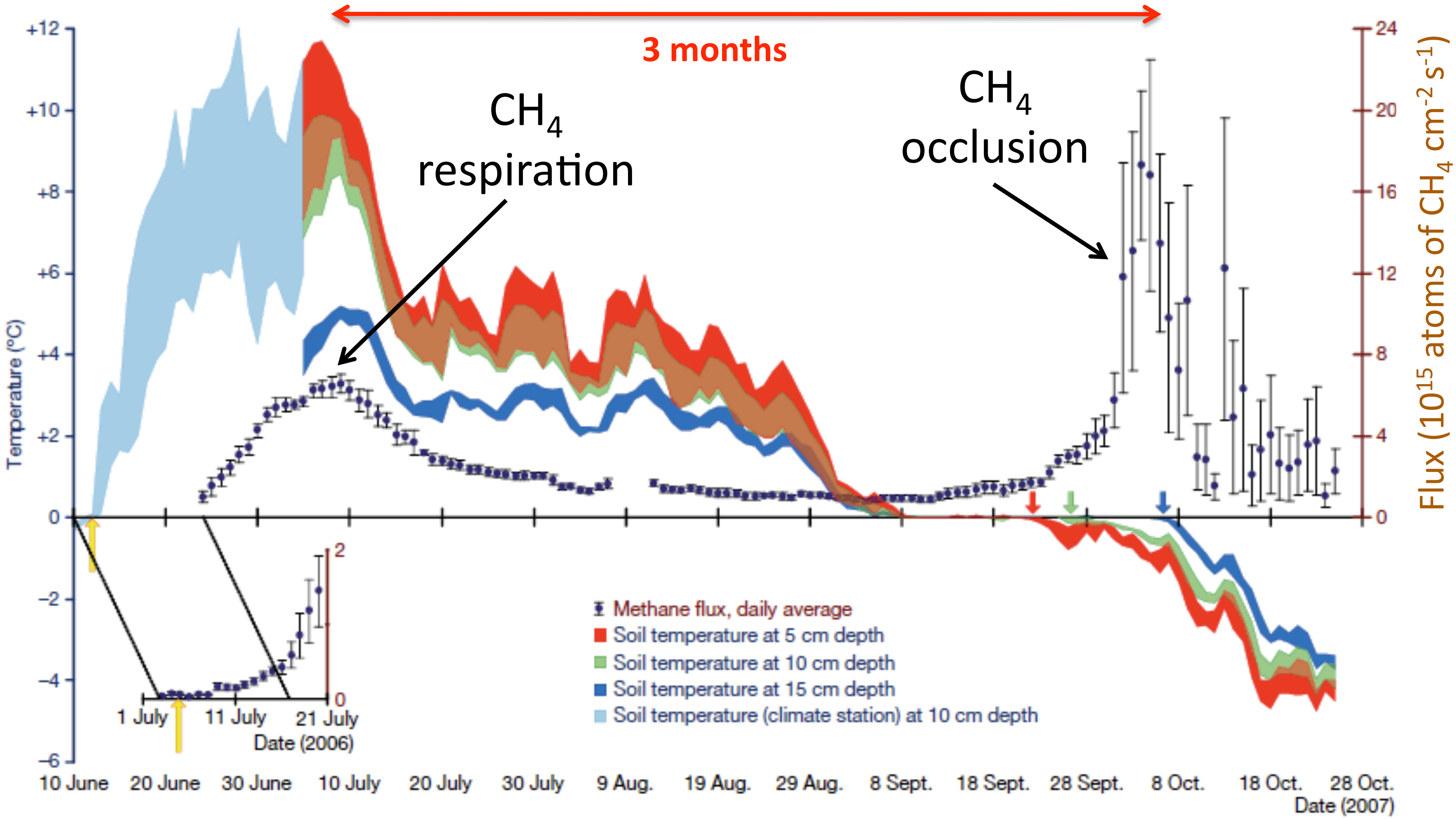
What does CH_4 release look like in the Arctic?

Source:International Permafrost Association, 1998.
Circumpolar Active-Layer Permafrost System (CAPS), version 1.0.

Zackenberg Research Station, Greenland

Philippe Rekacewicz, 2005

Arctic Sources

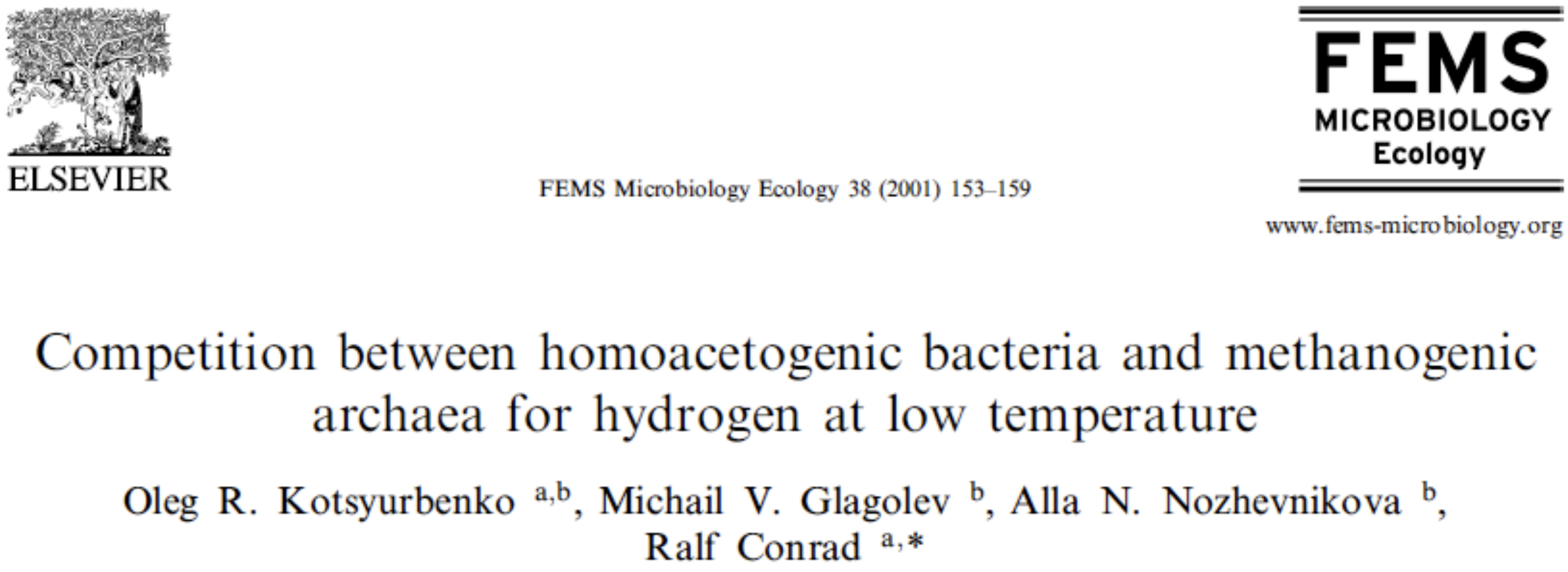


3 months

CH_4 respiration

CH_4 occlusion

74ºN Greenland tundra/permafrost – Mastepanov et al. 2008



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FEMS Microbiology Ecology 38 (2001) 153–159

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Competition between homoacetogenic bacteria and methanogenic archaea for hydrogen at low temperature

Oleg R. Kotsyurbenko [a,b], Michail V. Glagolev [b], Alla N. Nozhevnikova [b], Ralf Conrad [a,*]

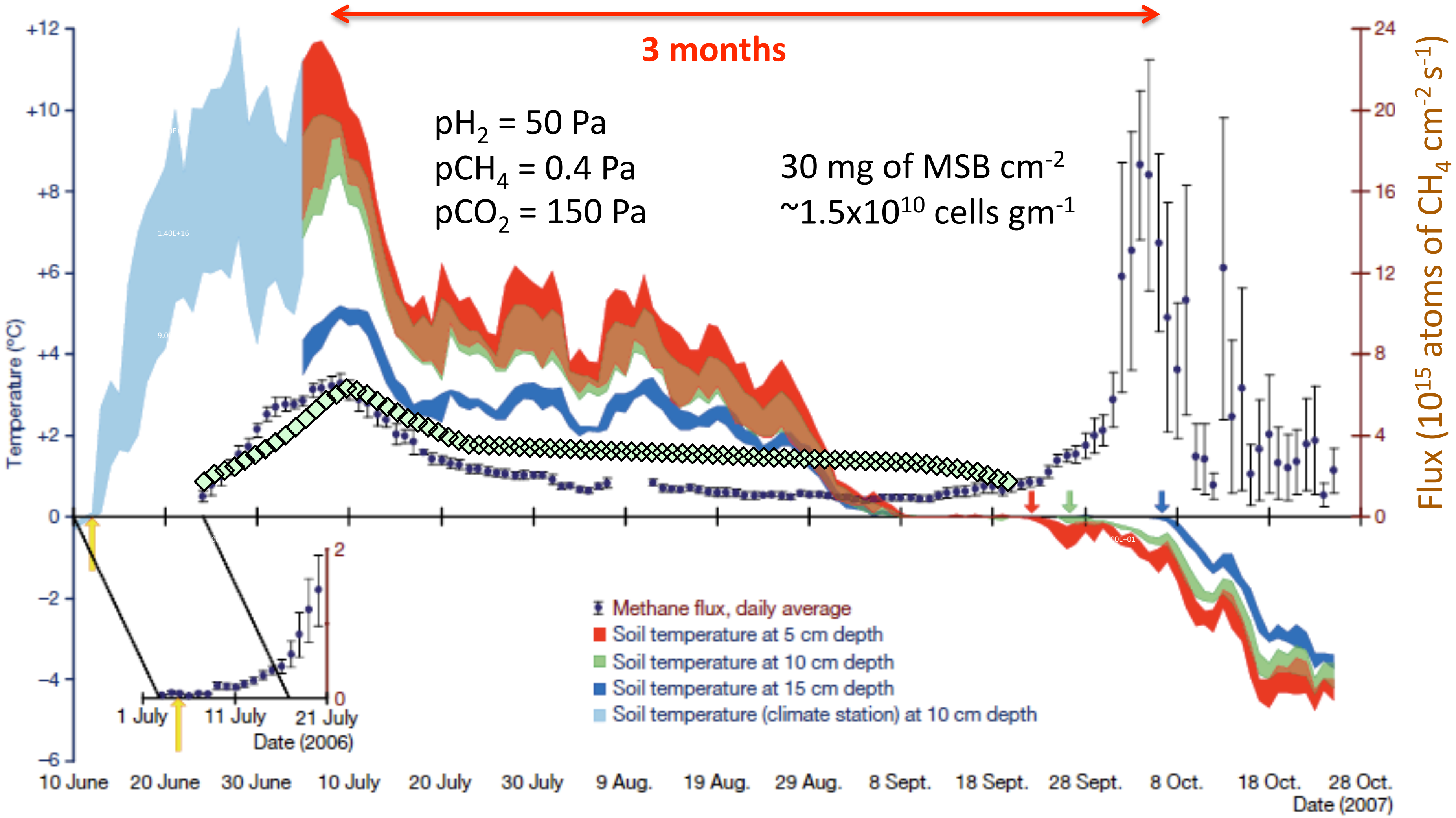
For permafrost autotrophic methanogen strain MSB

V_{max} (mols CH_4 mg^{-1} s^{-1}) = $3x10^7$ exp[-88,813/(8.3143xT(°K)]

CH_4 rate (mols CH_4 mg^{-1} s^{-1}) = V_{max} $[pH_2/(190 + pH_2)][1- e^{-[(\Delta G+\Delta G_t)/RT]}]$

where pH_2 is in Pa and ΔG_t is the threshold Gibbs free energy for metabolism.

Arctic Sources



3 months

pH_2 = 50 Pa
pCH_4 = 0.4 Pa
pCO_2 = 150 Pa

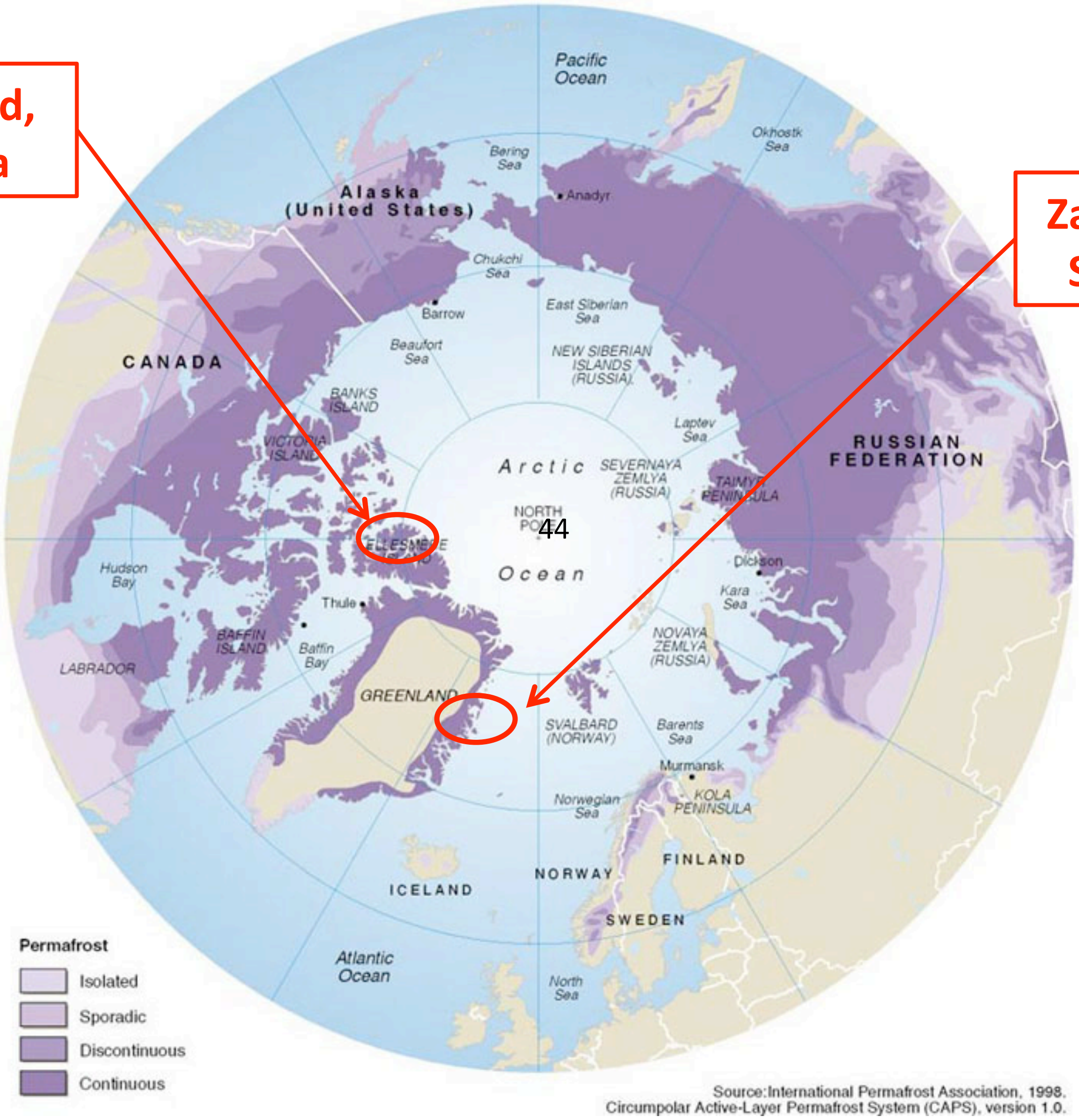
30 mg of MSB cm^{-2}
~1.5×10^{10} cells gm^{-1}

74°N Greenland tundra/permafrost – Mastepanov et al. 2008

What does CH_4 release look like during winter?

Axel Heiberg Island, Nunavut, Canada

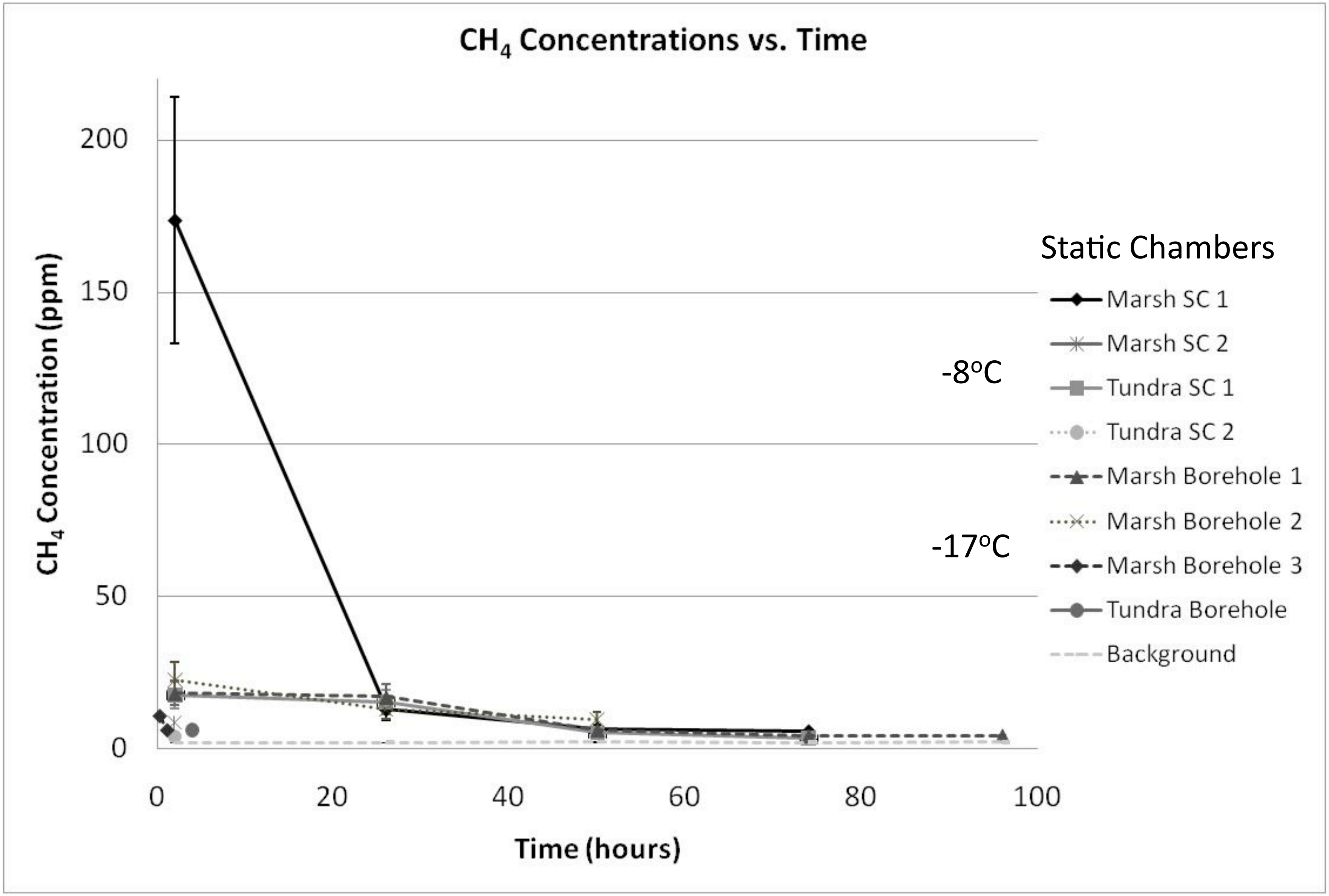
Zackenberg Research Station, Greenland



Source: International Permafrost Association, 1998. Circumpolar Active-Layer Permafrost System (CAPS), version 1.0.

Philippe Rekacewicz, 2005

Permafrost CH_4 flux in April (by CRDS)

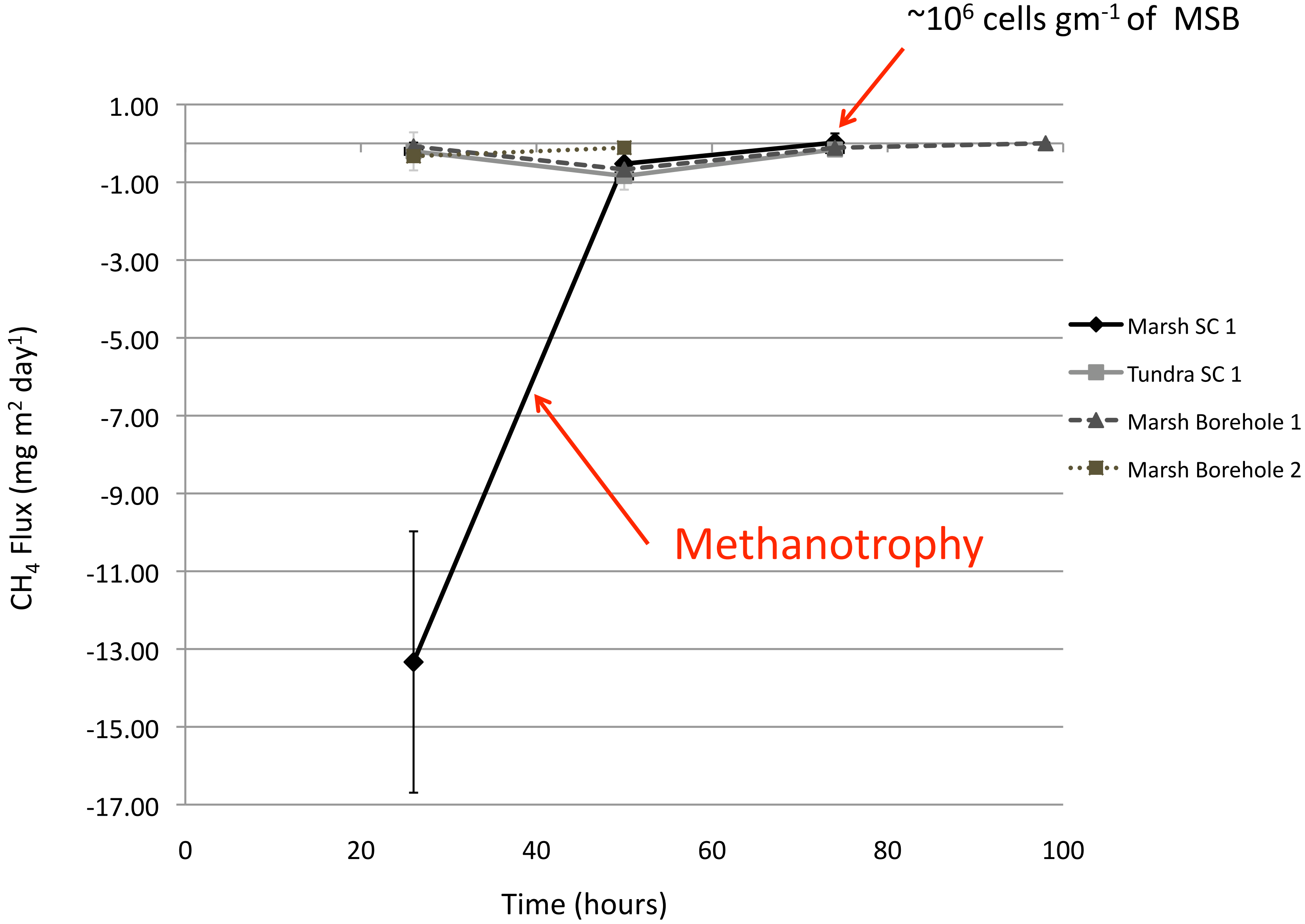


Static Chambers

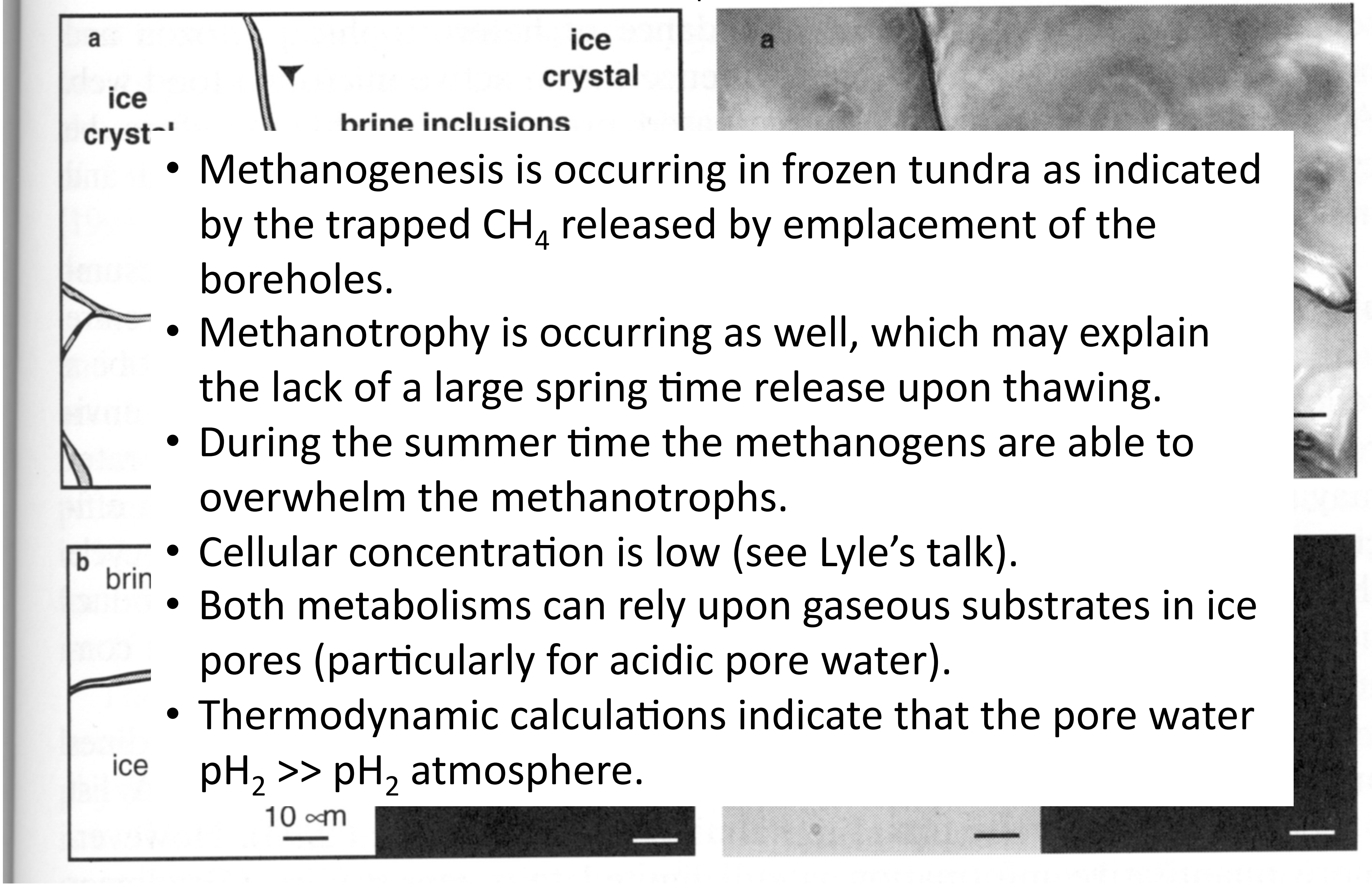
-8°C

-17°C

CH_4 Flux vs. Time



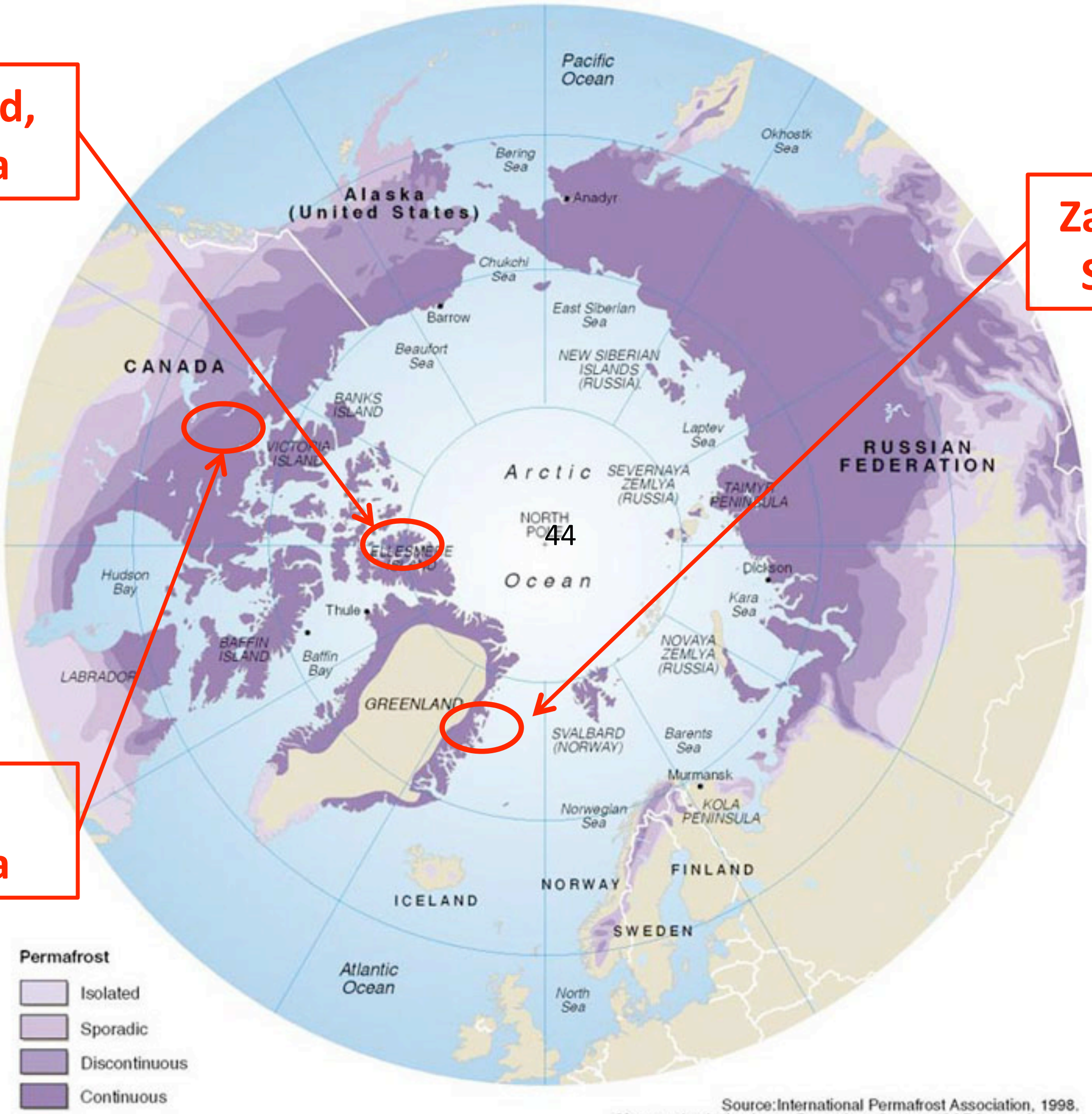
Controls on winter permafrost CH_4 flux



- Methanogenesis is occurring in frozen tundra as indicated by the trapped CH_4 released by emplacement of the boreholes.
- Methanotrophy is occurring as well, which may explain the lack of a large spring time release upon thawing.
- During the summer time the methanogens are able to overwhelm the methanotrophs.
- Cellular concentration is low (see Lyle's talk).
- Both metabolisms can rely upon gaseous substrates in ice pores (particularly for acidic pore water).
- Thermodynamic calculations indicate that the pore water $pH_2 >> pH_2$ atmosphere.

Tung et al. 2006

What does subpermafrost CH_4 look like?



Axel Heiberg Island, Nunavut, Canada

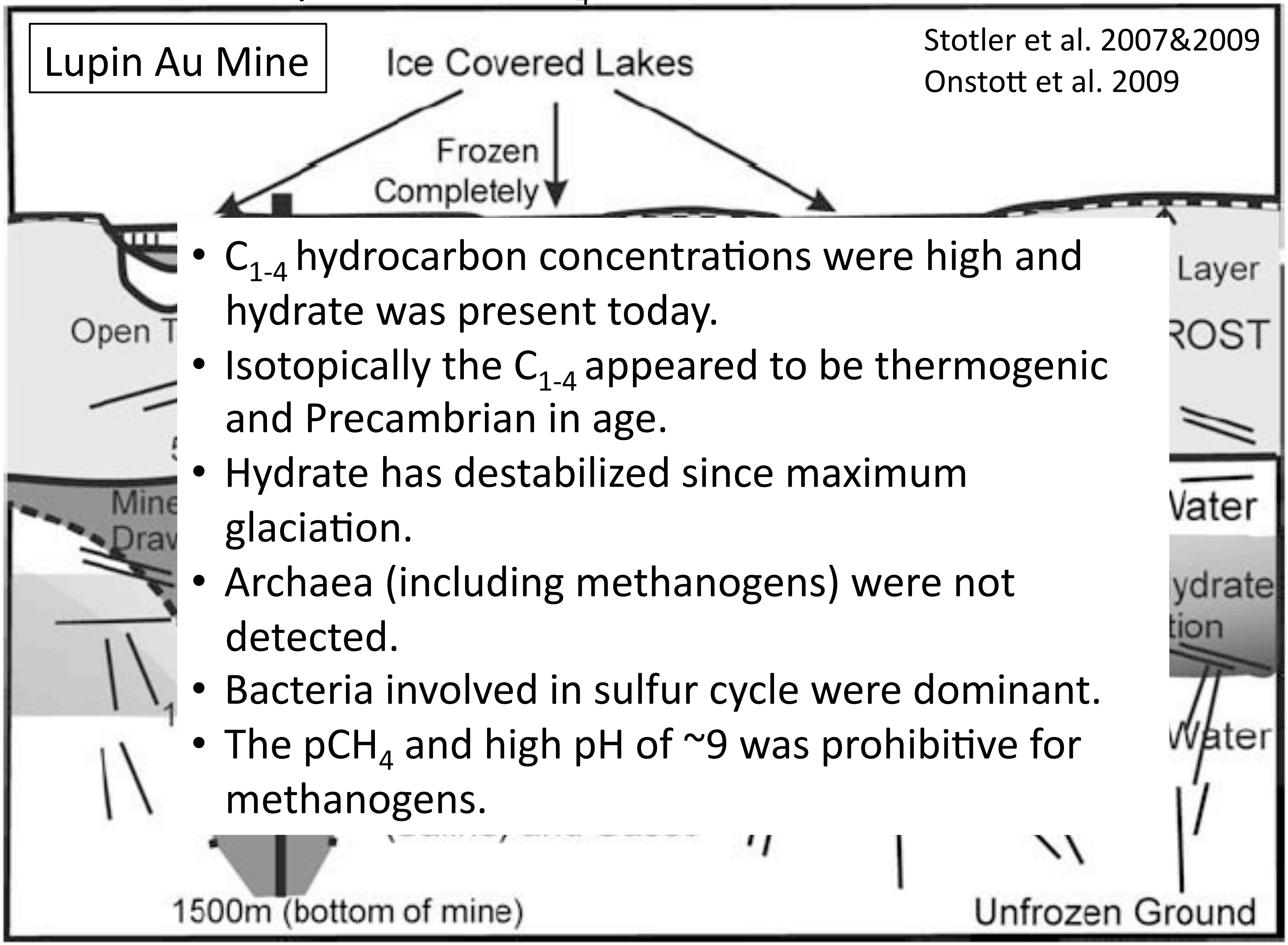
Zackenberg Research Station, Greenland

Lupin Au mine, Nunavut, Canada

Source: International Permafrost Association, 1998. Circumpolar Active-Layer Permafrost System (CAPS), version 1.0.

Philippe Rekacewicz, 2005

Controls on sub-permafrost CH_4 flux

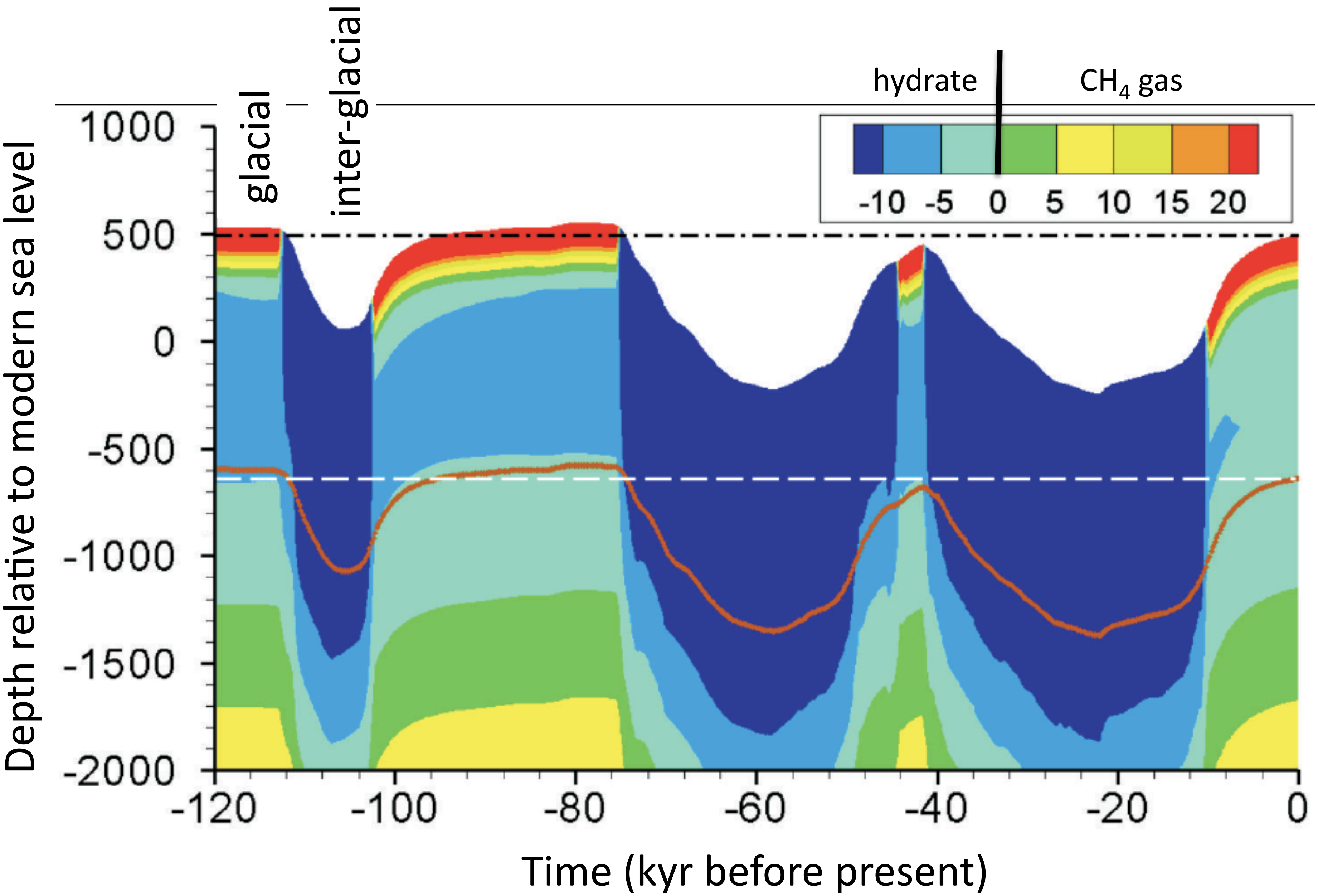


Lupin Au Mine

Stotler et al. 2007&2009
Onstott et al. 2009

- $C_{1\text{-}4}$ hydrocarbon concentrations were high and hydrate was present today.
- Isotopically the $C_{1\text{-}4}$ appeared to be thermogenic and Precambrian in age.
- Hydrate has destabilized since maximum glaciation.
- Archaea (including methanogens) were not detected.
- Bacteria involved in sulfur cycle were dominant.
- The pCH_4 and high pH of ~9 was prohibitive for methanogens.

Fig. 12. Hydrogeologic conceptual model of the Lupin area.


glacial
inter-glacial
hydrate
CH_4 gas
-10
-5
0
5
10
15
20
Depth relative to modern sea level
1000
500
0
-500
-1000
-1500
-2000
-120
-100
-80
-60
-40
-20
0
Time (kyr before present)

Controls on sub-permafrost CH_4 flux

Lupin Au Mine

Stotler et al. 2007&2009
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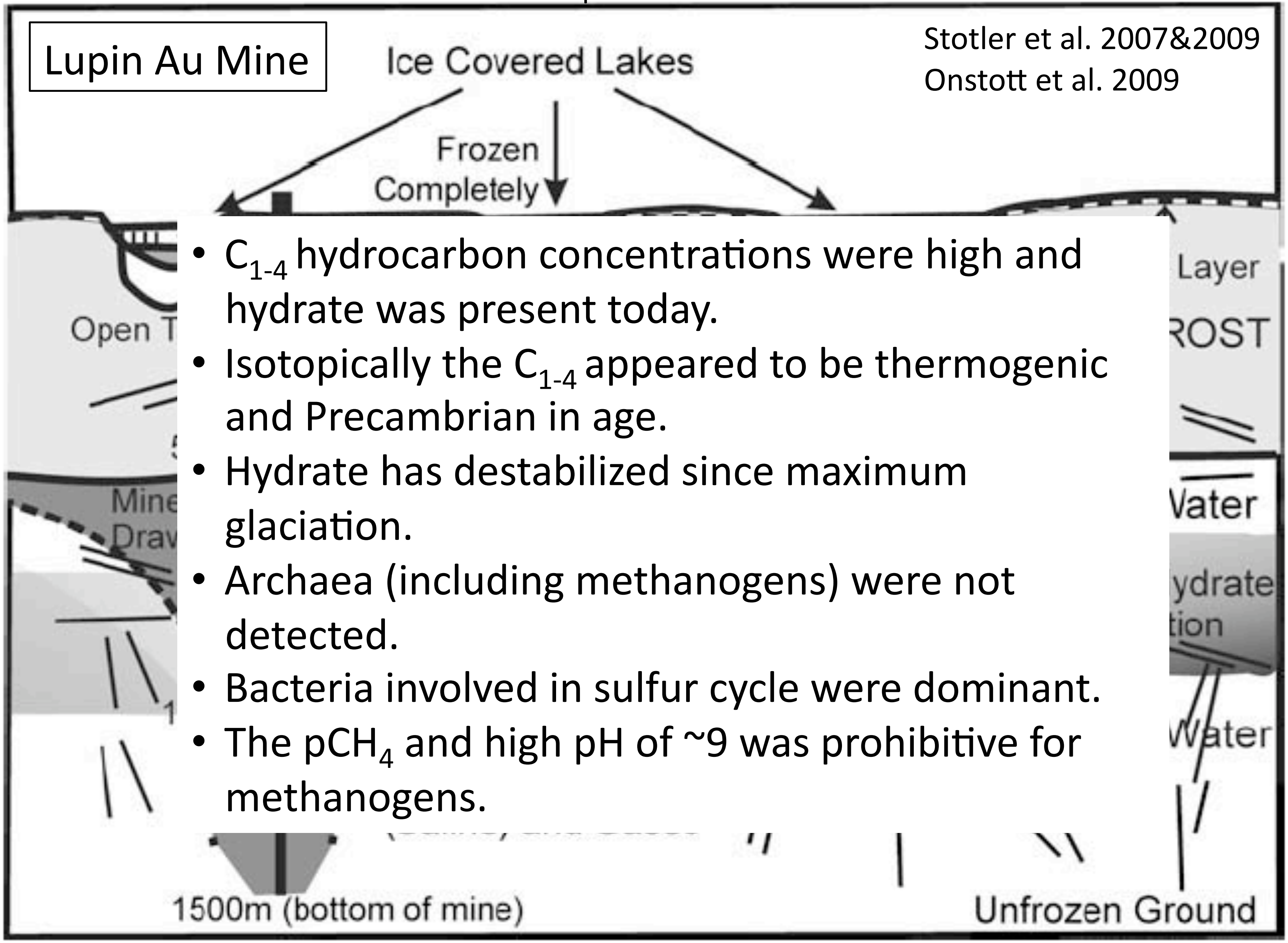

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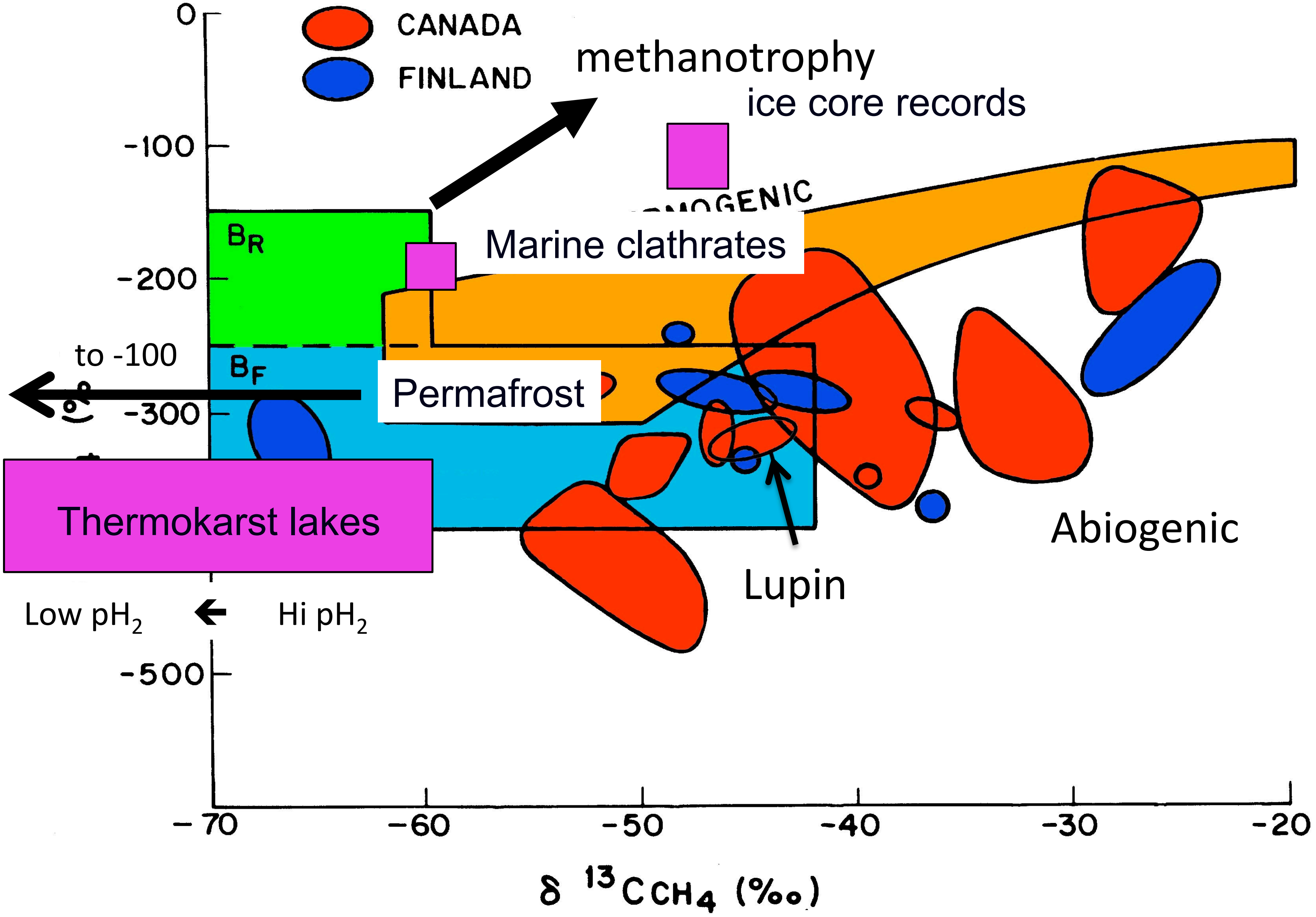
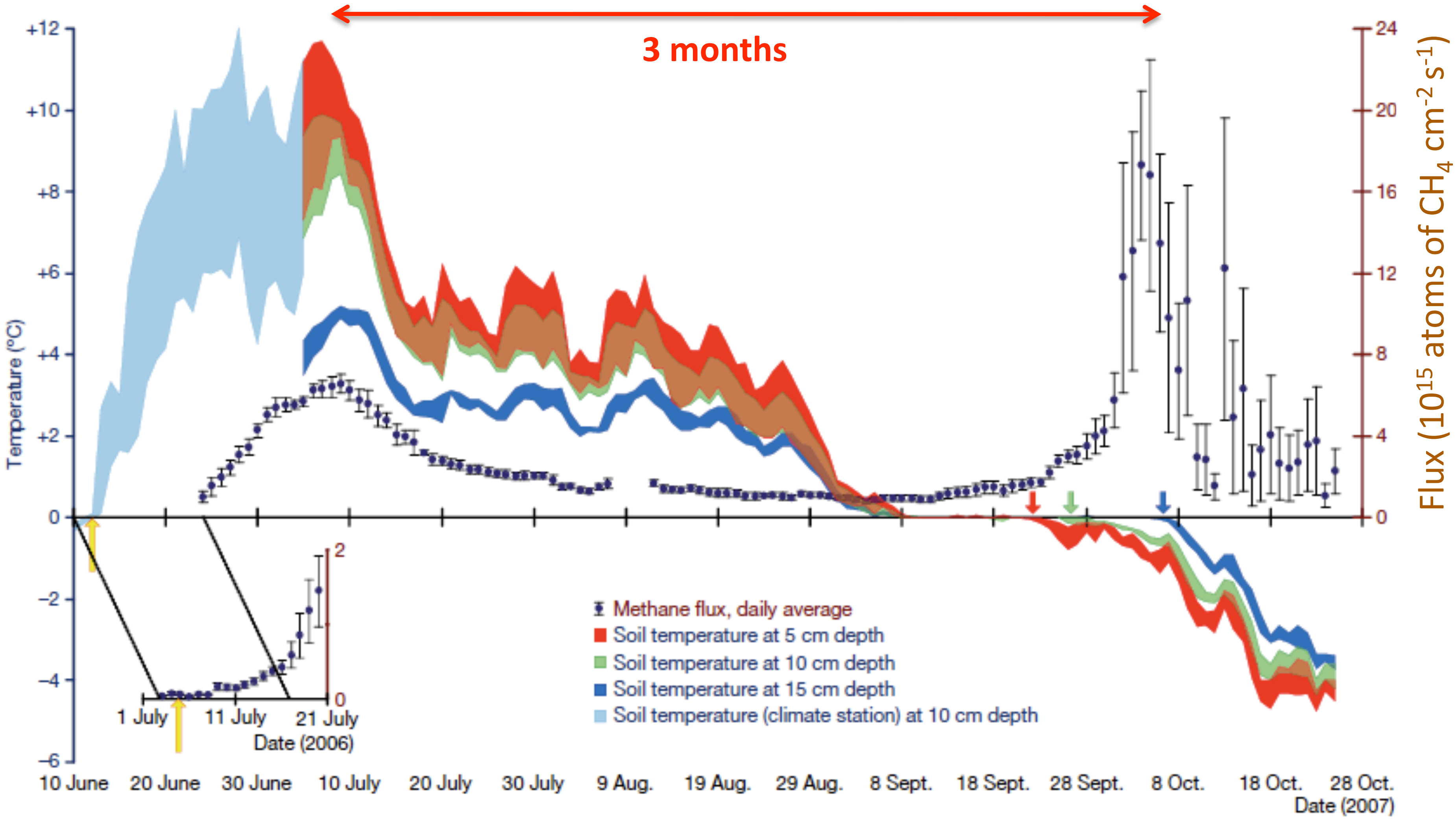
Stable Isotopes distinguish CH_4 sources

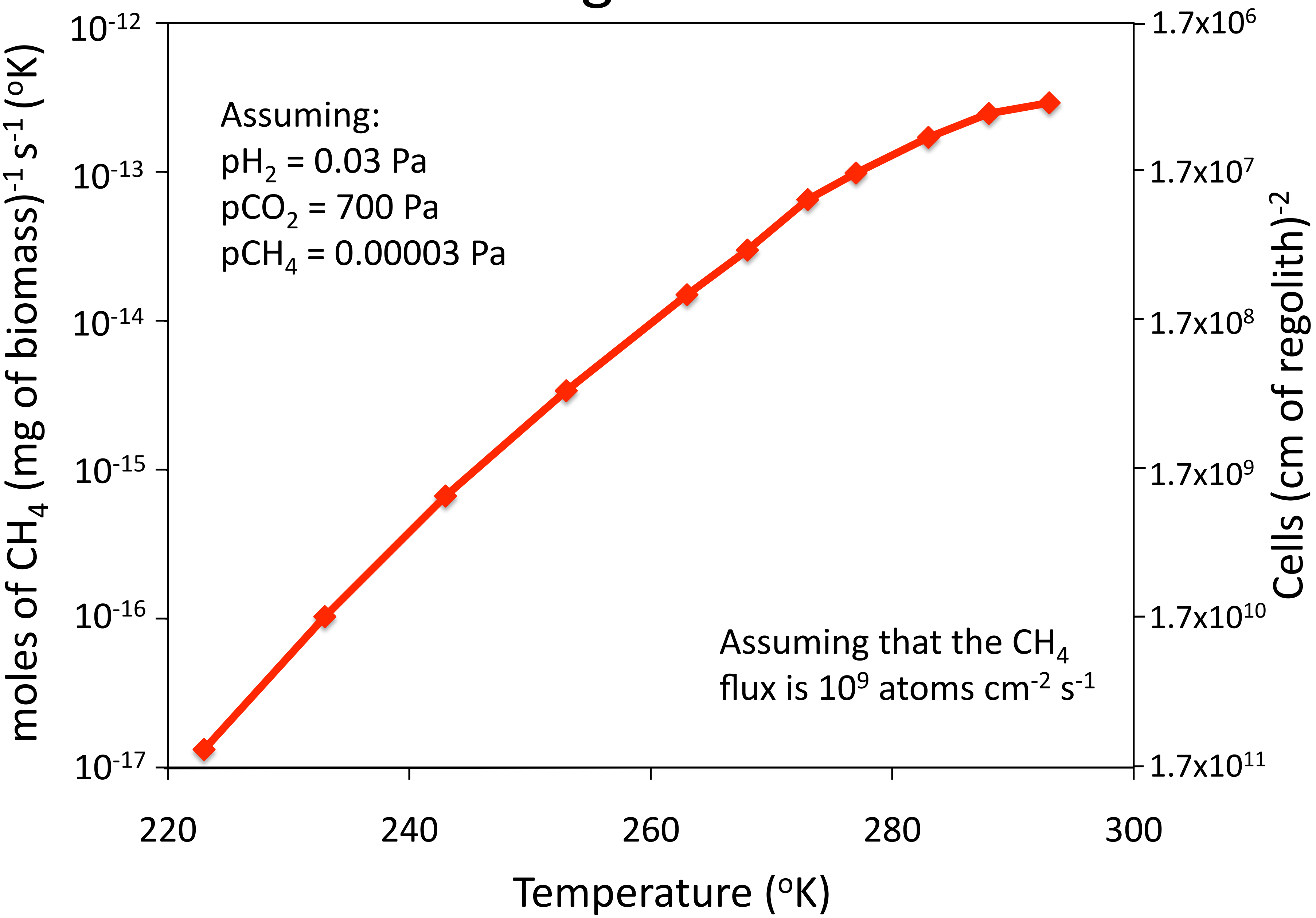


Does is the stable isotope composition of CH_4 change temporally?



74°N Greenland tundra/permafrost – Mastepanov et al. 2008

Methanogen MSB on Mars



Assuming:
$pH_2 = 0.03$ Pa
$pCO_2 = 700$ Pa
$pCH_4 = 0.00003$ Pa

Assuming that the CH_4 flux is 10^9 atoms cm^{-2} s^{-1}

Kinetic, not thermodynamic constraints

- Methanogen MSB is not thermodynamically constrained from utilizing atmospheric sources. This is because the K_D for H_2 uptake rate is 190 Pa whereas the threshold H_2 is ~ 0.1 Pa. Further isolation of methanogens from low organic, cold, yet anaerobic environments may yield hydrogenases with lower K_D values.
- Methanotrophs are not thermodynamically constrained in a Martian environment, but the K_D values for CH_4 for MMO are sufficiently high that 10 ppb of CH_4 makes them slower than methanogen MSB. So they are kinetically constrained. But more should be done to isolate type I methanotrophs from cold, organic-poor environments.

The Martian source

- Seasonal – on and off? 60-120 days during summer
  - Temperature control => near surface – below limit of diurnal temperature variations, but above the seasonal temperature fluctation.
  - If clathrate - must be capped by a few meters regolith with equivalent lithostatic pressure of 2 to 15 meters.
  - If deeper then requires fluid seeps with icy caps?

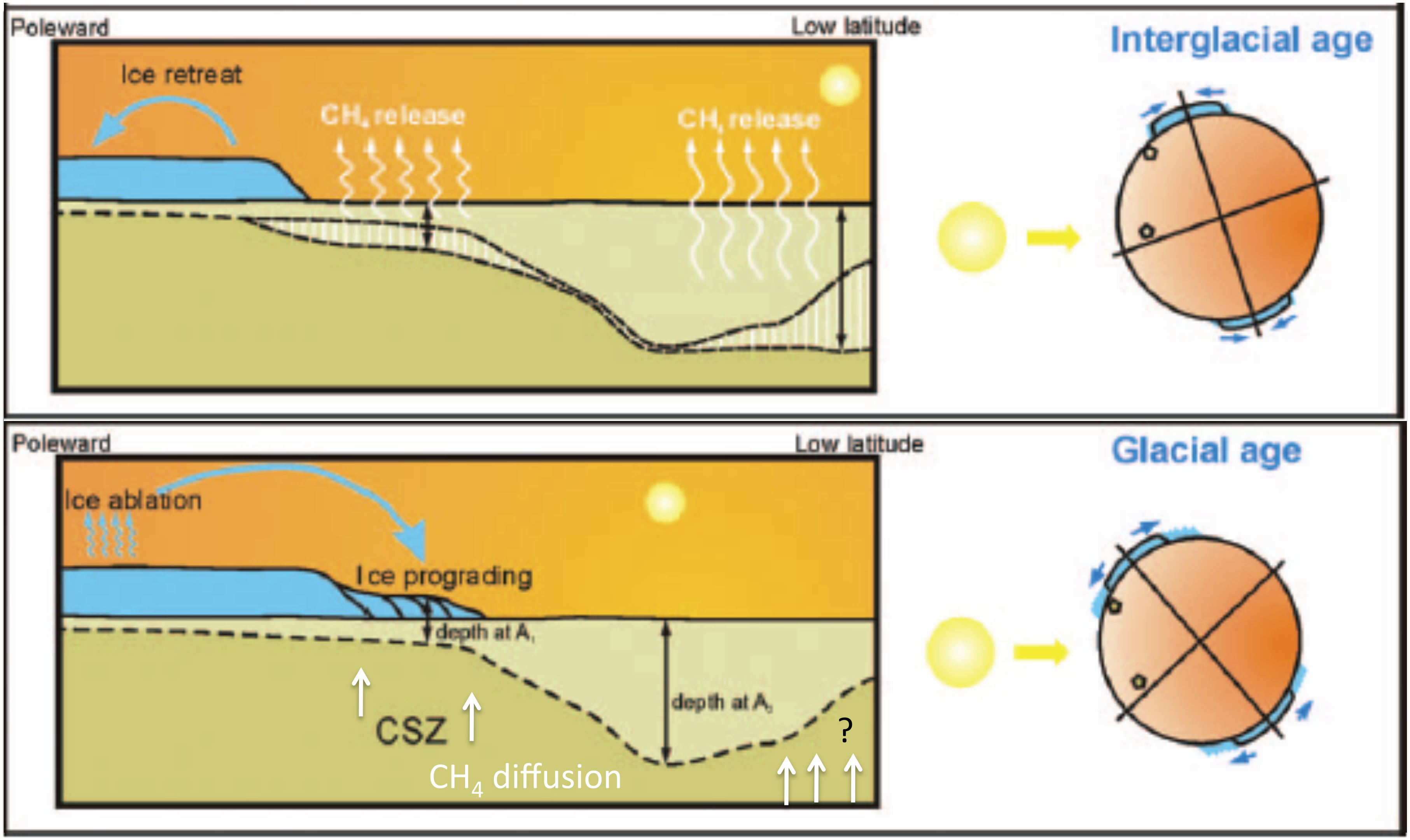
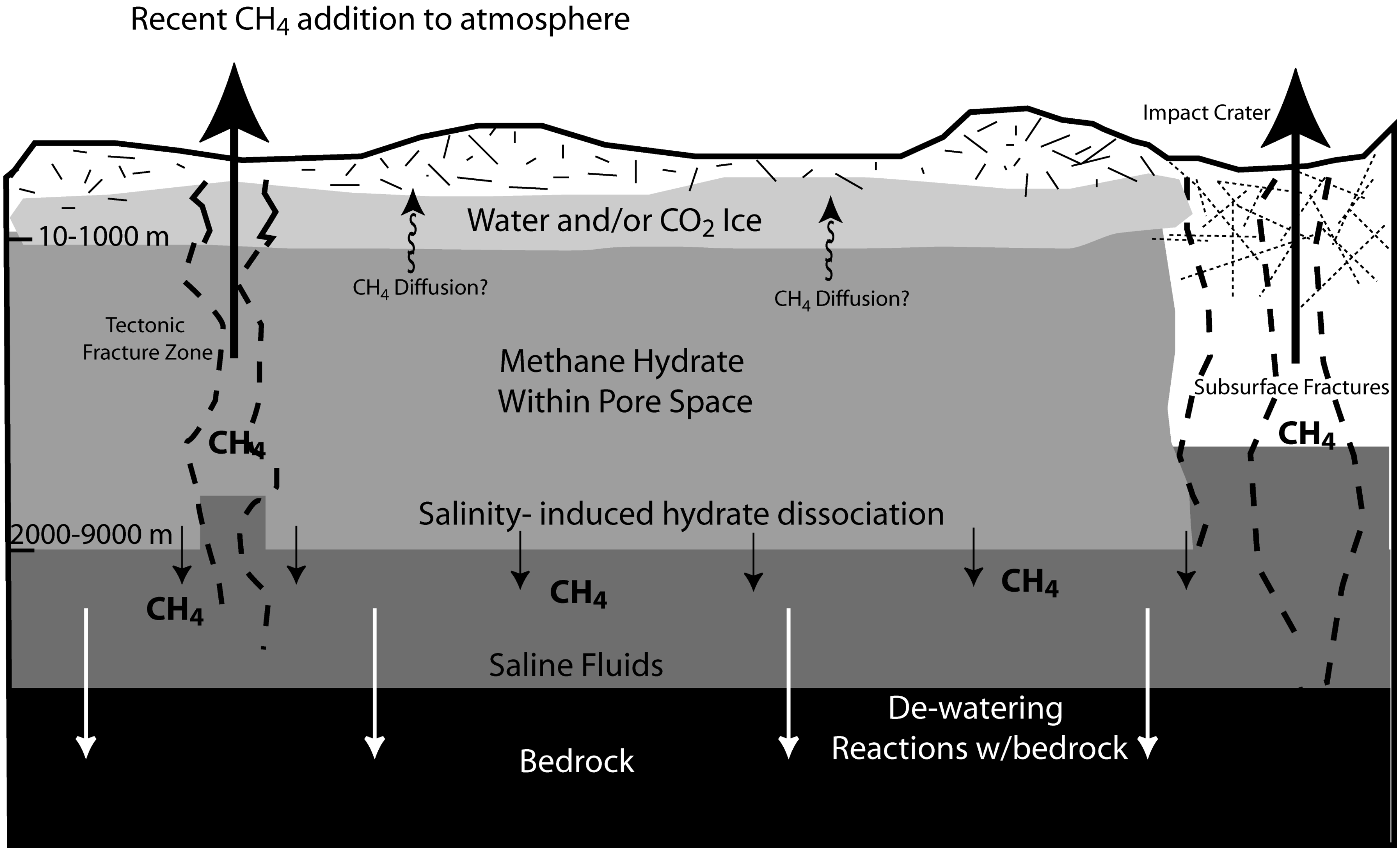


Figure 2. Destabilization of clathrate hydrates as a consequence of glacial deposit retreat at middle latitudes. Methane clathrate stability zone (CSZ) profile is a consequence of different local surface temperature [$T(A_1) < T(A_2)$], heat flow, and lithostatic pressure of overlying materials. Lower panel: during interglacial periods, CSZ is re-allocated, producing dissociation of clathrates and releasing methane.

Prieto-Ballesteros et al. 06

Elwood Madden et al. 2007



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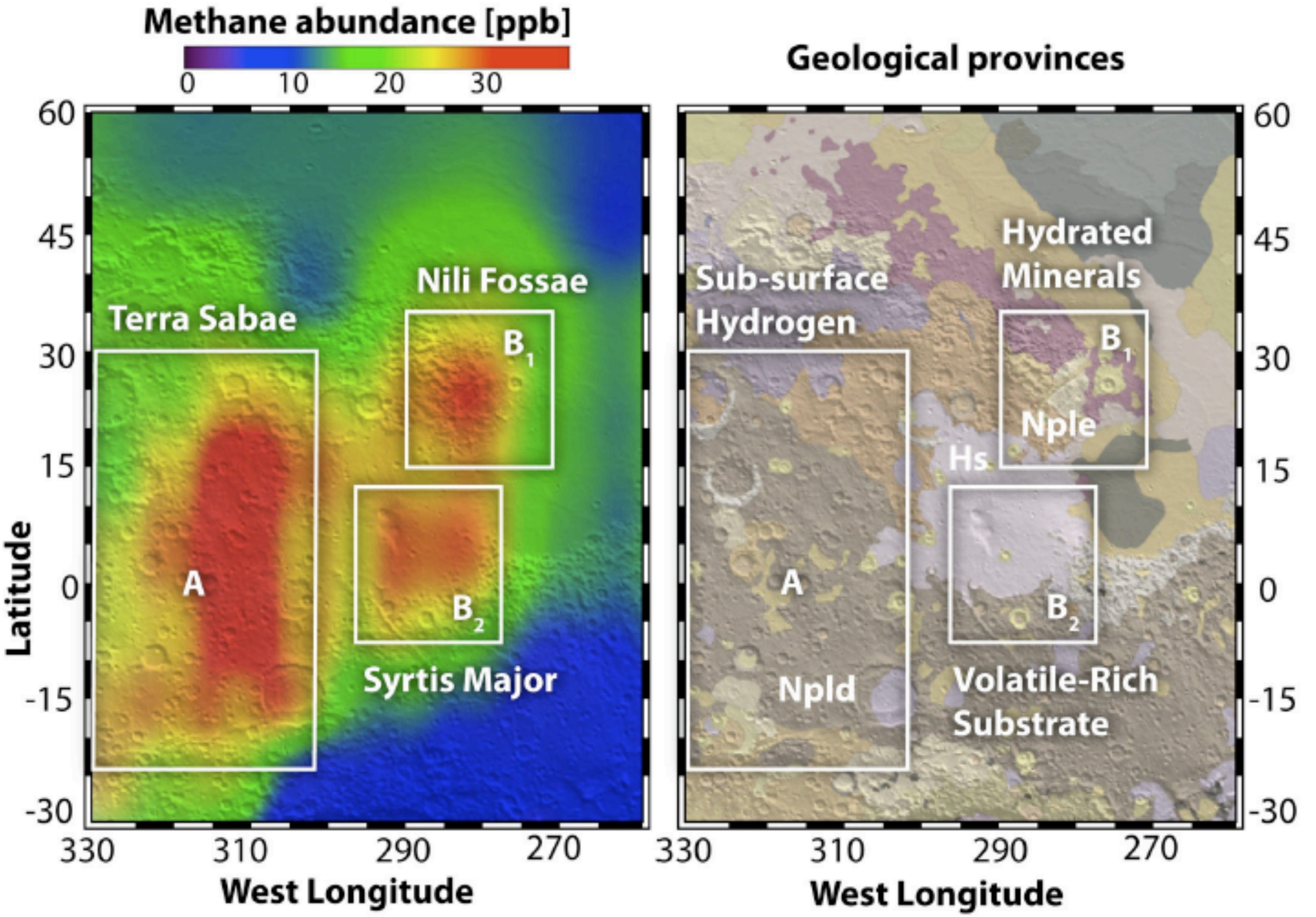
- Spatially localized –
  - Noachian age crust => ancient clathrate reservoir, not globally distributed near the surface now
  - Structural control, aka. Fractures or seeps => deep methane source
  - Mineralogical control => mineral/water interaction providing H_2 source and perhaps carbonate.

Mumma et al. 2009



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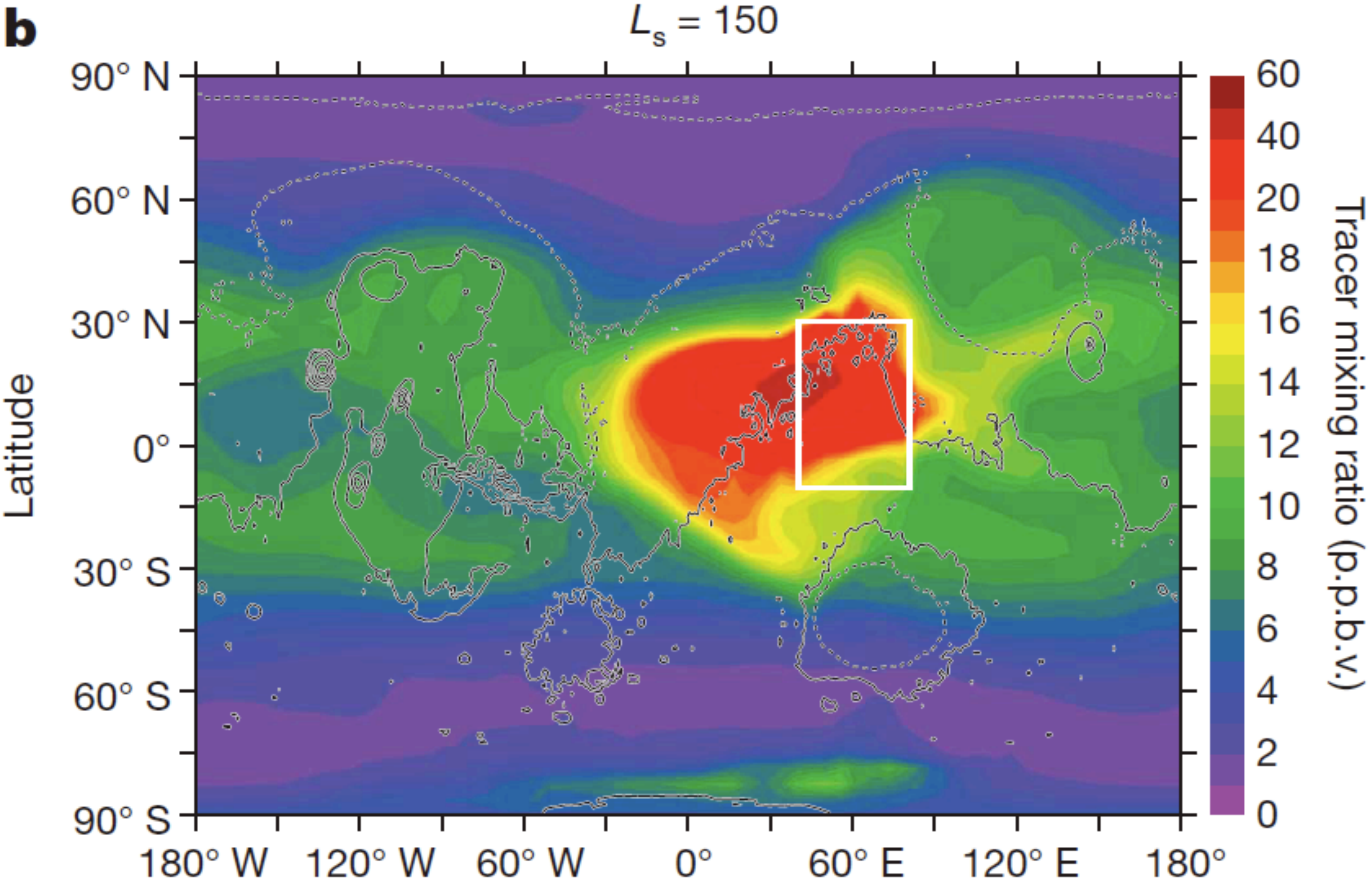
- Strong - ~10^9 (Mumma) to 10^{10} atoms/cm^2-s (Lefévre&Forget) or ~10^9 (Mumma) to 10^{10} (Lefévre&Forget) moles of CH_4 released each season (every 2 Earth years).
  - If active => more likely biological than abiogenic.
  - If not active, like a clathrate reservoir => how long does it last?

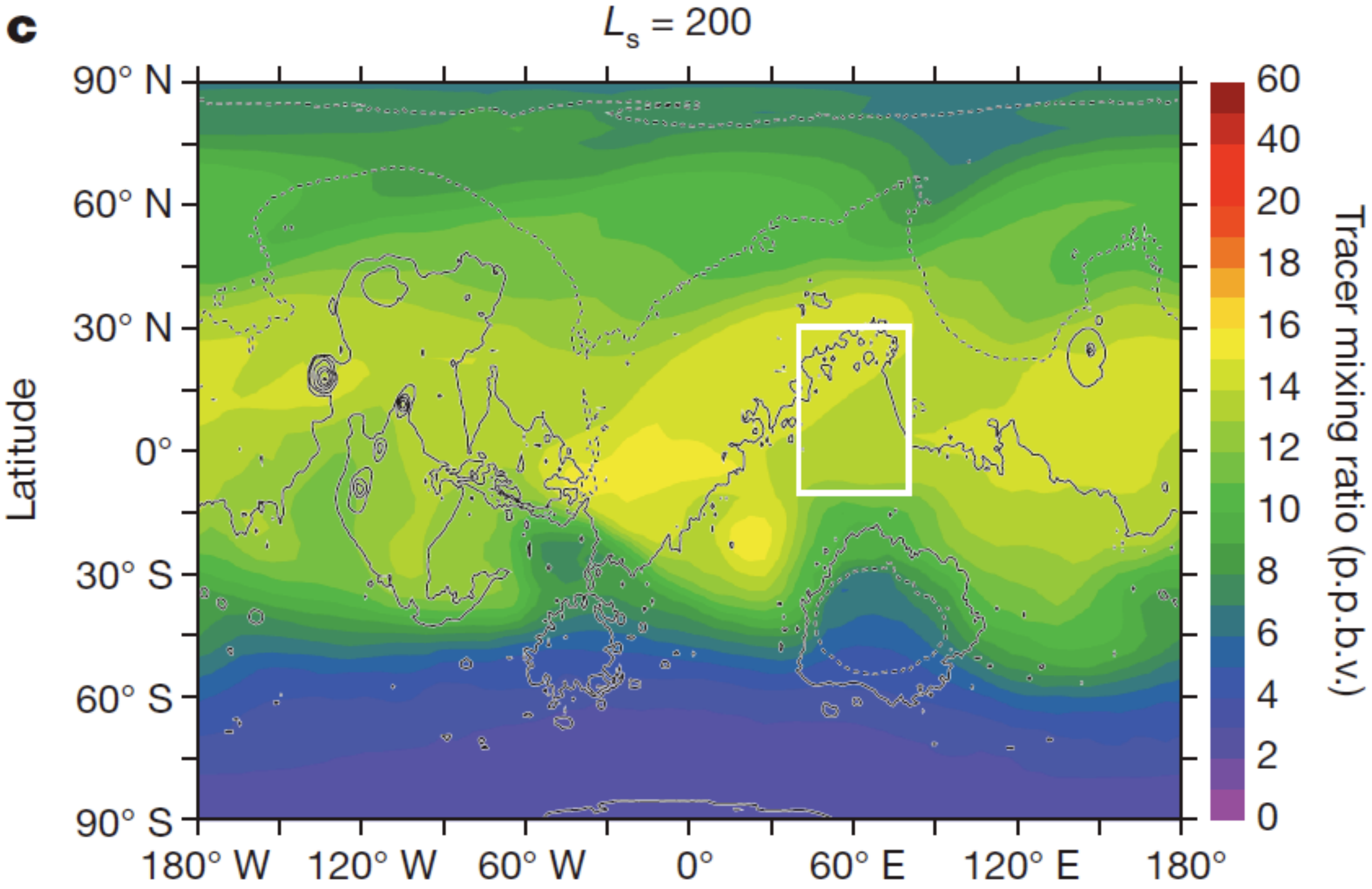
Lefévre and Forget 2009

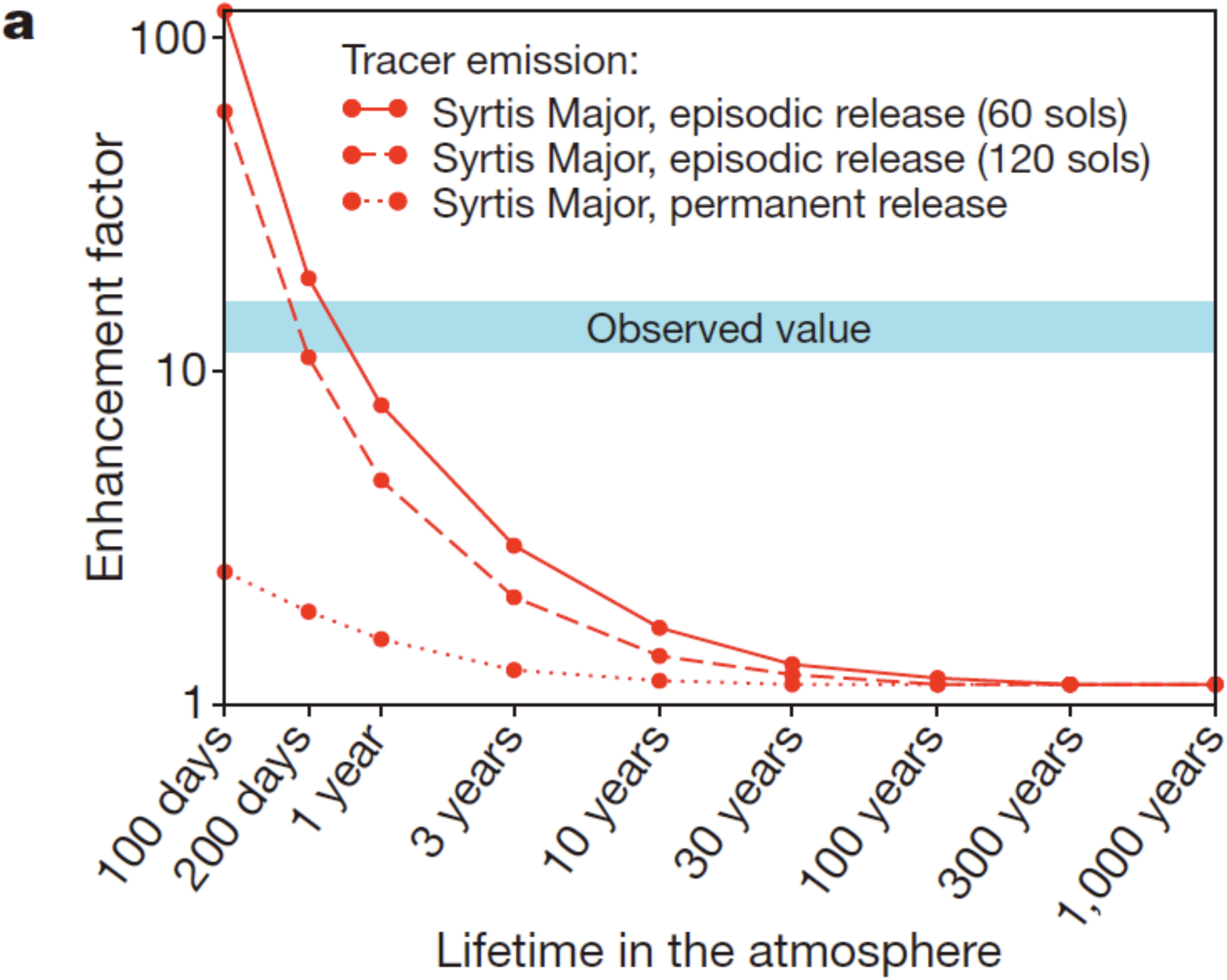


Syrtis Major region source

- 10^{10} (Lefévre&Forget) moles of CH_4 released each season (every 2 Earth years) = $1.3x10^6$ m^3 of CH_4 hydrate.
- If distributed uniformly over a $60x60^o$ spatial source (unlikely) then this only requires 0.1 μm of CH_4 hydrate per martian years (compared to 10 mm for H_2O ice sublimation).
- But for 4 billion Earth years, ~30 meters of CH_4 hydrate would be required. This should be detectable in surface morphology.
- If a residue of billion year old CH_4 hydrate, then what is so special about this region in terms of either preserving it through so many obliquity oscillations or actively excavating it versus other locations?
- If not a billion year old CH_4 hydrate (more likely), then a mechanism for recharging the CH_4 hydrate reservoir at a million year time-scale is still required.

Lefévre and Forget 2009



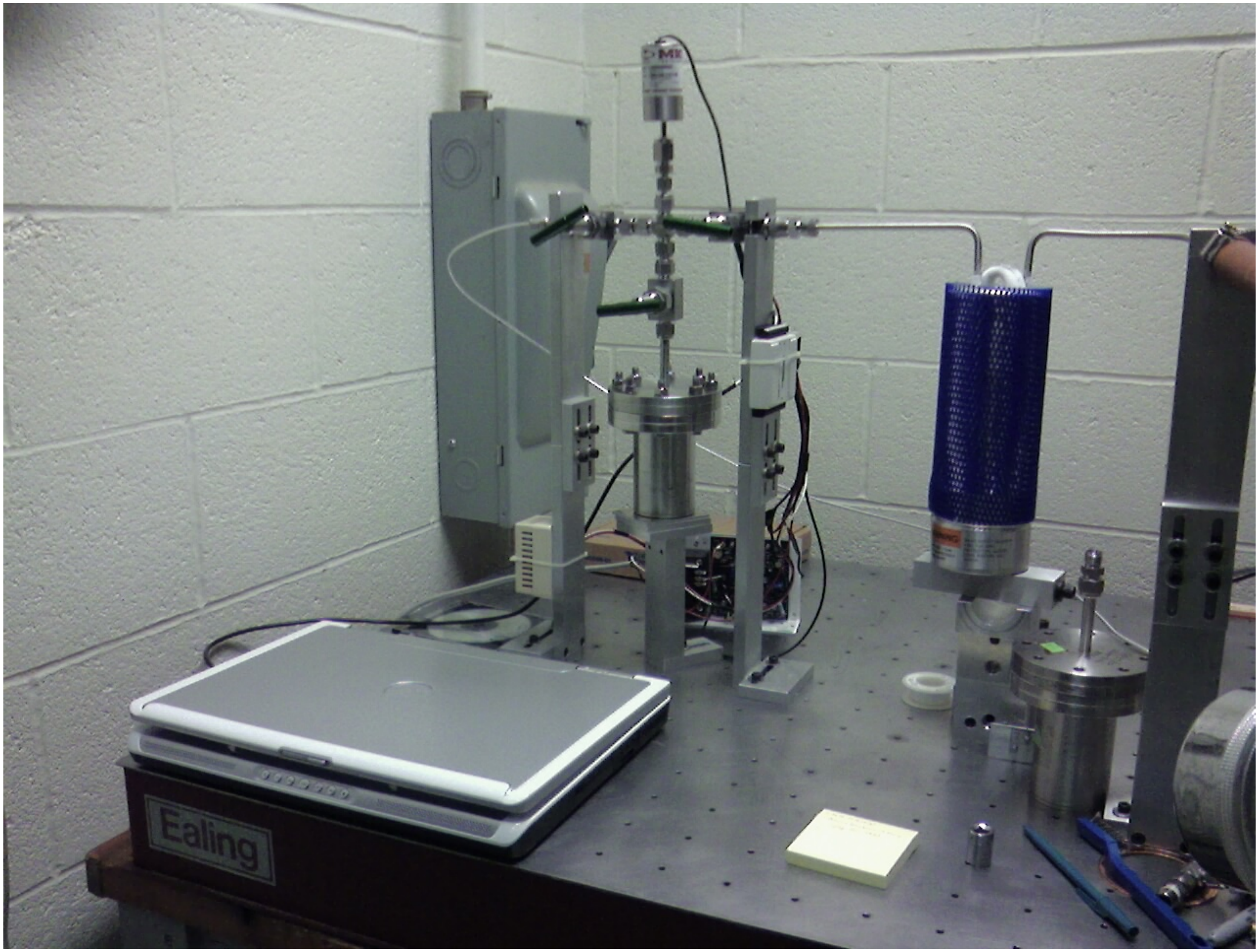

a
Tracer emission:
Syrtis Major, episodic release (60 sols)
Syrtis Major, episodic release (120 sols)
Syrtis Major, permanent release
Observed value
Enhancement factor
100
10
1
100 days
200 days
1 year
3 years
10 years
30 years
100 years
300 years
1,000 years
Lifetime in the atmosphere

Methane sink

- Presumed oxidation to CO_2 (no trapping).
- Strength (spatially and temporally unconstrained?)
  - Atmospheric loss - if uniform - 10^8 atoms/cm^2-s in atmospheric column above surface (Lefévre&Forget) .
  - Regolith loss – if uniform across planet - >>10^8 atoms/cm^2-s (Lefévre&Forget)?
  - If the source is destabilization of near surface CH_4 hydrate you still need to recharge the hydrate which means that the oxidation process has to be very surficial. You do not want H_2O_2 oxidizing CH_4 in the subsurface in this case.
  - Are the CH_4 plumes located where the surficial oxidation process is absent?
- The strength of the destruction rate calibrated by the Syrtis Major plume suggests that if this is a global phenomena, then other CH_4 sources could exist, but are hidden because the CH_4 surface oxidation is so intense. If by H_2O_2 or O_2 then it is constrained by H_2O_2 or O_2 photolytic production. Could you detect this? Is there an intermediate, like CO that might be detectable?

Extra Slides

Experiments on methanogens under Mars atmospheric conditions



Strain	**1**	**2**	**3**	**4**
Formal name	*Methanosarcina mazei* JL01	*Methanobacterium arcticum* M2	*Methanobacterium veterum* MK4	*Methanogenium frigidum*
Media	Rivkina et al., 2007 + casaminic acid (1 g L-1)	Media 141	Medium 506	MSH (or Media 141)
Media source	Rivkina et al., 2007 from Balch et al., 1979	DSMZ	DSMZ	Ni and Boone, 1991 (or DSMZ)
Cysteine-HCl or Na_2S	Cysteine-HCl in media	Cysteine-HCl and Na_2S in media	Cysteine-HCl and Na_2S in media	Neither in MSH media
Final pH of media	6.8 – 7.0	7.0 – 7.2	7.2 – 7.4	7.3 (7.2)
Carbon source	Acetate	H_2/CO_2	H_2/CO_2	H_2/CO_2
Topt	24 – 28°C	37°C	28°C	15°C
pHopt	6.8 -7.3	7.0 – 7.2	7.2 – 7.4	7.2 – 7.4
Cells		Nonmotile Slightly bent rods 0.45 – 0.5 μm Diam 3.0 – 6.0 μm length	Nonmotile Crooked rods 0.3 – 0.4 μm Diam 4 – 6 μm length	Nonmotile Irregular coccoids 1.2 – 2.5 μm Diam
Grouping with other cells?	Small aggregates	Chains, sometimes over 30 μm long		
Gram- positive or negative	Gram-positive	Gram-negative	Gram-negative	Gram-negative
Age of sediment	Holocene	Holocene	Pliocene	Ice covered lake
Reference for Strain	Rivkina et al., 2007	Rivkina et al., 2007	Rivkina et al., 2007	Franzmann et al., 2007

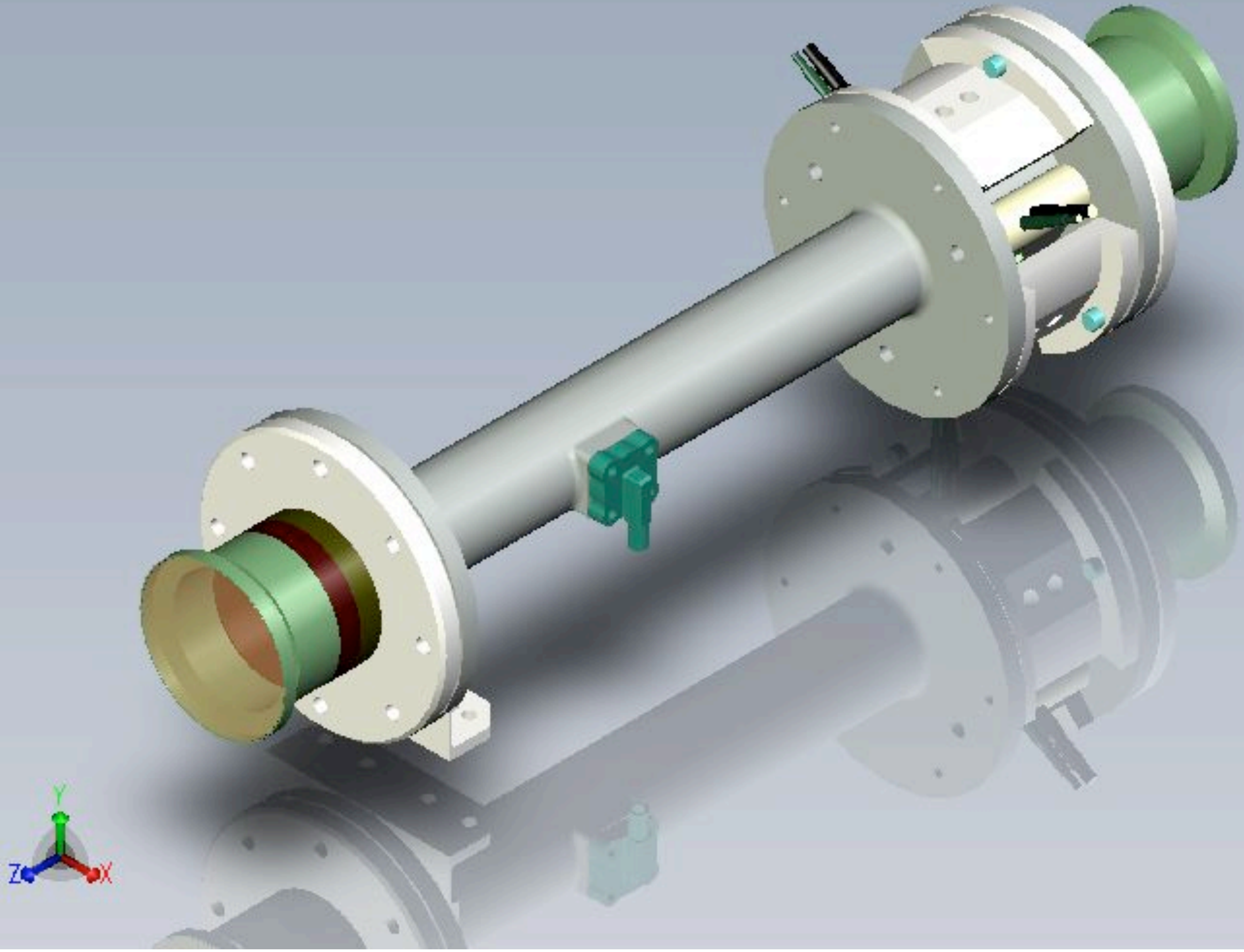
Preliminary Results

- 10^9 cells of MK4 mixed with 10 grams of regolith simulant prepared by Adam Johnson at Indiana University.
- Mars atmospheric composition with 20 mbars and 100 ppm H_2.
- Incubated at room temperature for 6 weeks.
- CH_4 measured in headspace by CRDS.
- ~2 ppm of CH_4 observed relative to control.
- Methanotrophs have not survived dessication yet.

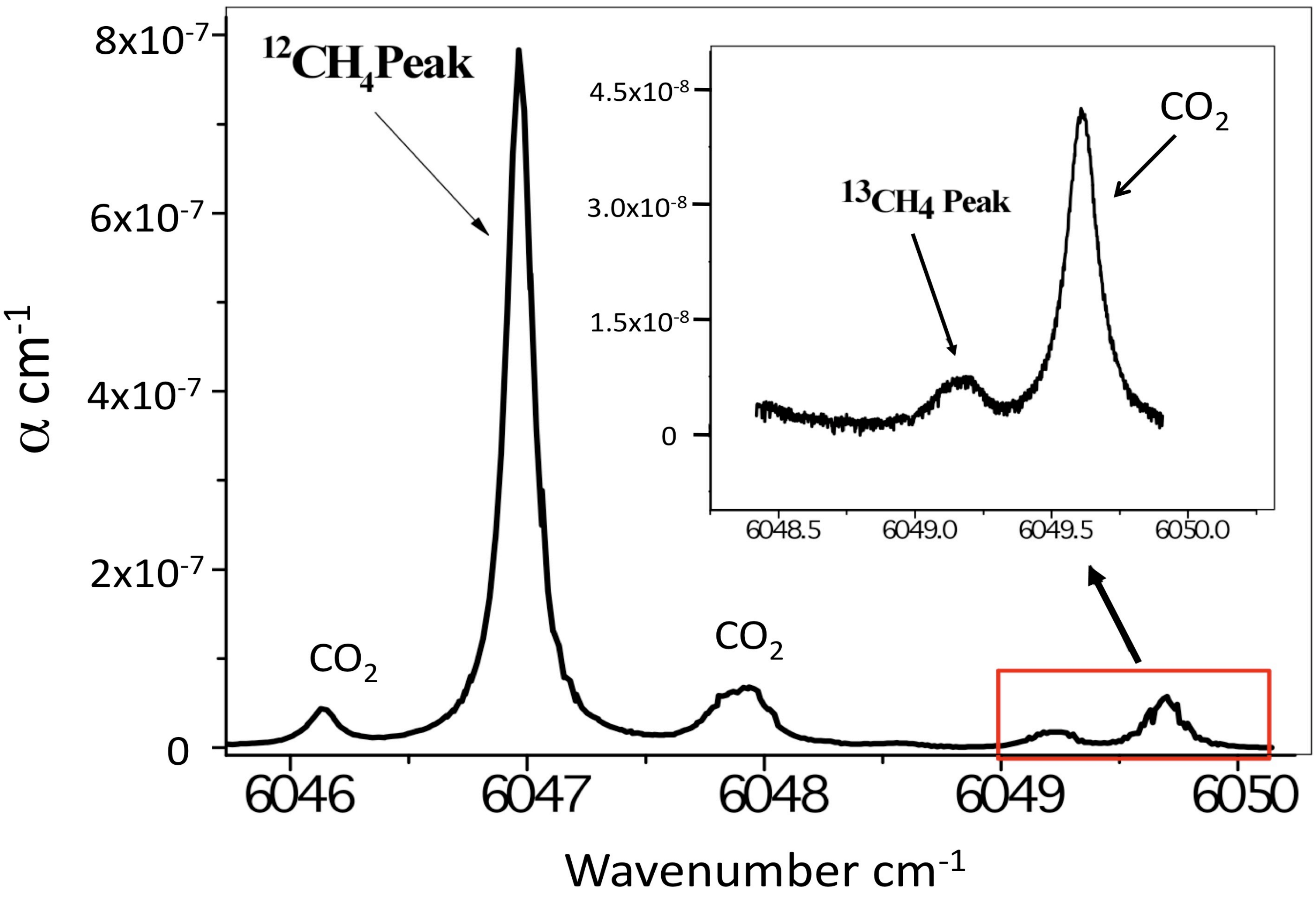
Conclusions

- Physical sources and sinks – to explain the temporal variation requires a renewable source that resides close to the surface (perhaps hydrate), but then why is it spatially restricted? Need to identify cold oxidant in lab and test isotopic fractionation.
- Biological source and sink – easier to explain temporal variation due to kinetics (autotroph), but then why are they spatially restricted.

Development of TRL6 CRDS for CH_4 isotopes



Atmospheric CH_4 Isotopes by CRDS



Future Plans

- Completion of prototype CRDS and testing with isotope standards.
- Field testing of prototype CRDS in Arctic this winter for *in situ* isotope measurements.
- Assembly and testing of TRL6 CRDS.
- Further experiments on permafrost methanogens at Mars ambient conditions to isotopic fractionation using the CRDS.

*This work is being supported by ASTID-NNX08AX16G