Laboratory investigation of the role of heterogeneous processes in Martian methane variability

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Workshop on Methane on Mars, Frascati, Italy

25 November, 2009

CIRES
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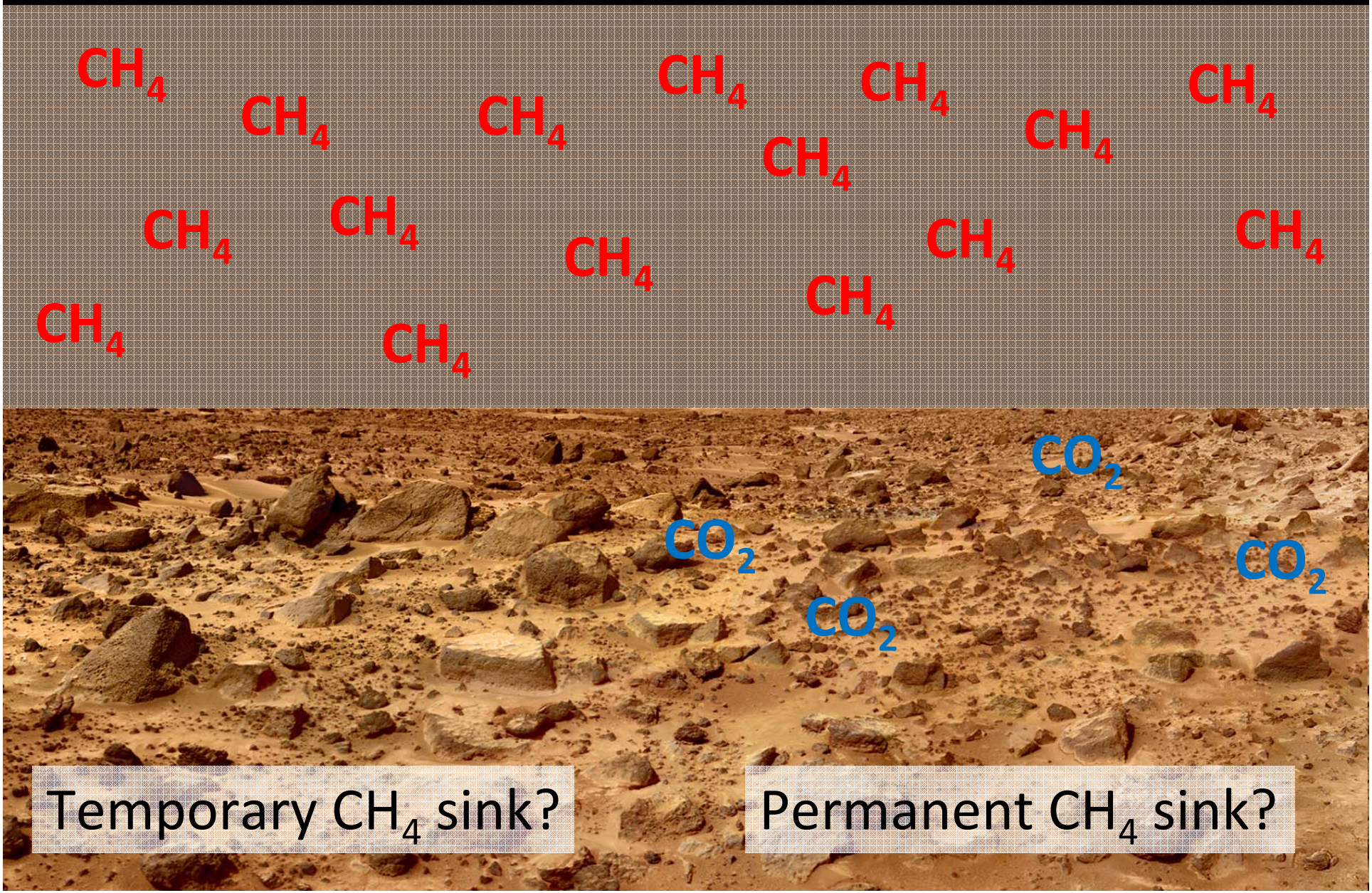
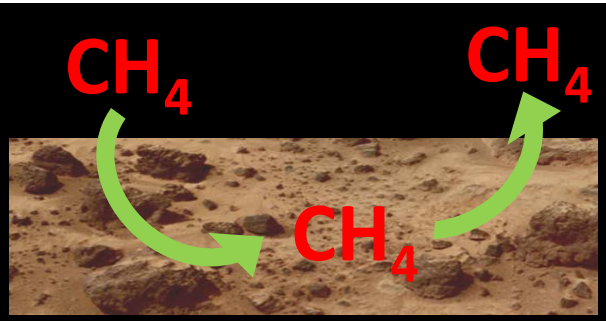
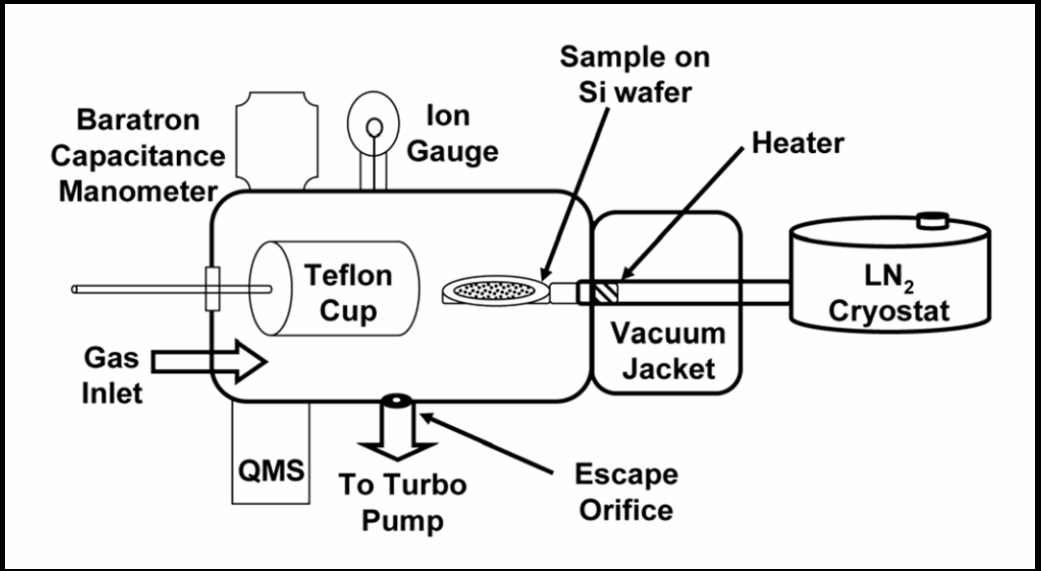
Possible heterogeneous chemistry on Mars?





Temporary CH_4 sink?

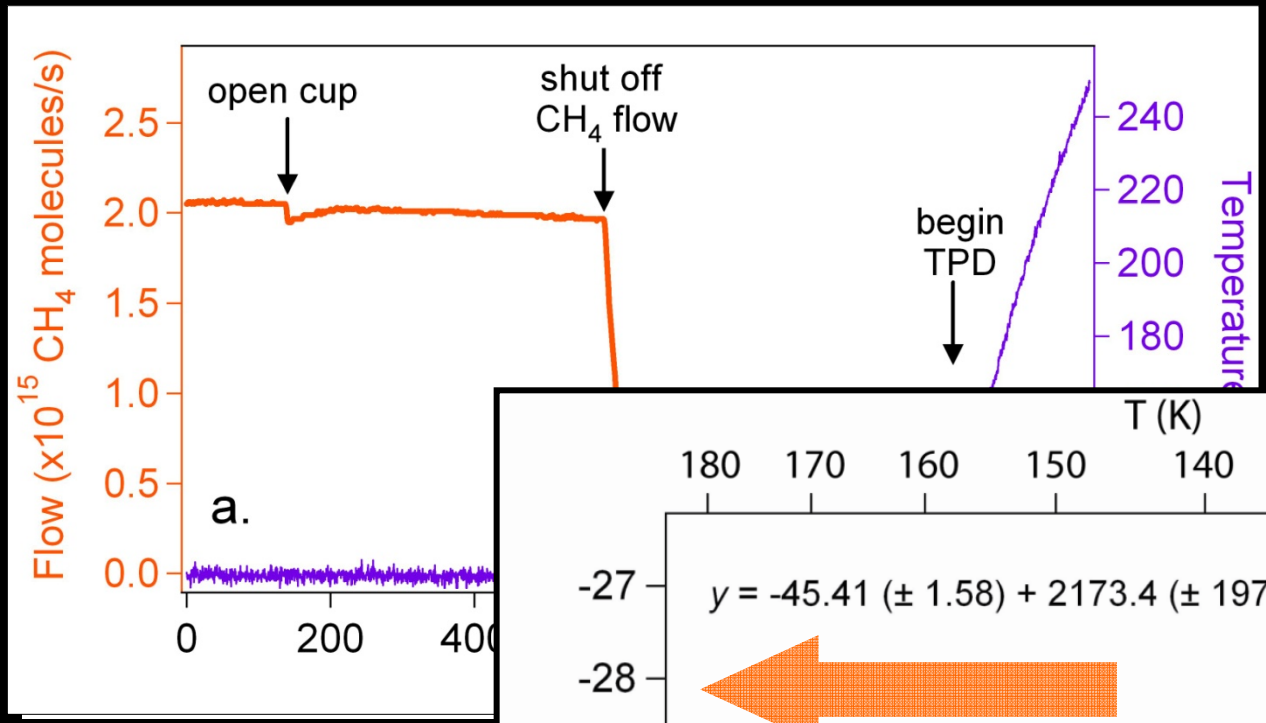
- Physisorption of CH_4 on JSC-Mars-1 was studied using a high-vacuum chamber (Knudsen cell)

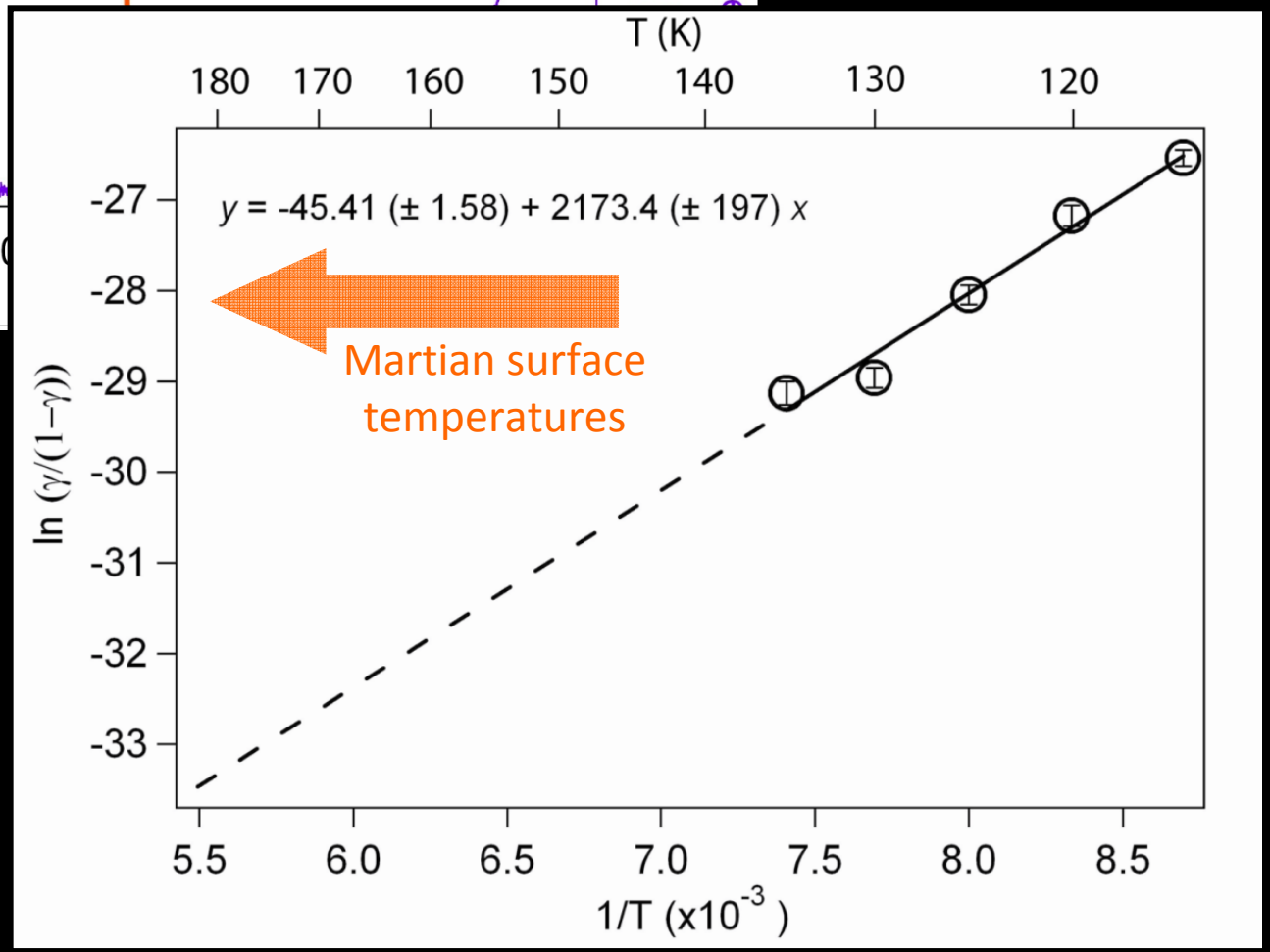


- Uptake coefficient (γ) values were determined as a f(T).

$$\gamma = \frac{\#\text{ of molecules that stick}}{\#\text{of collisions with the surface}}$$

Gough, R.V., *et al*. Icarus, *in press*

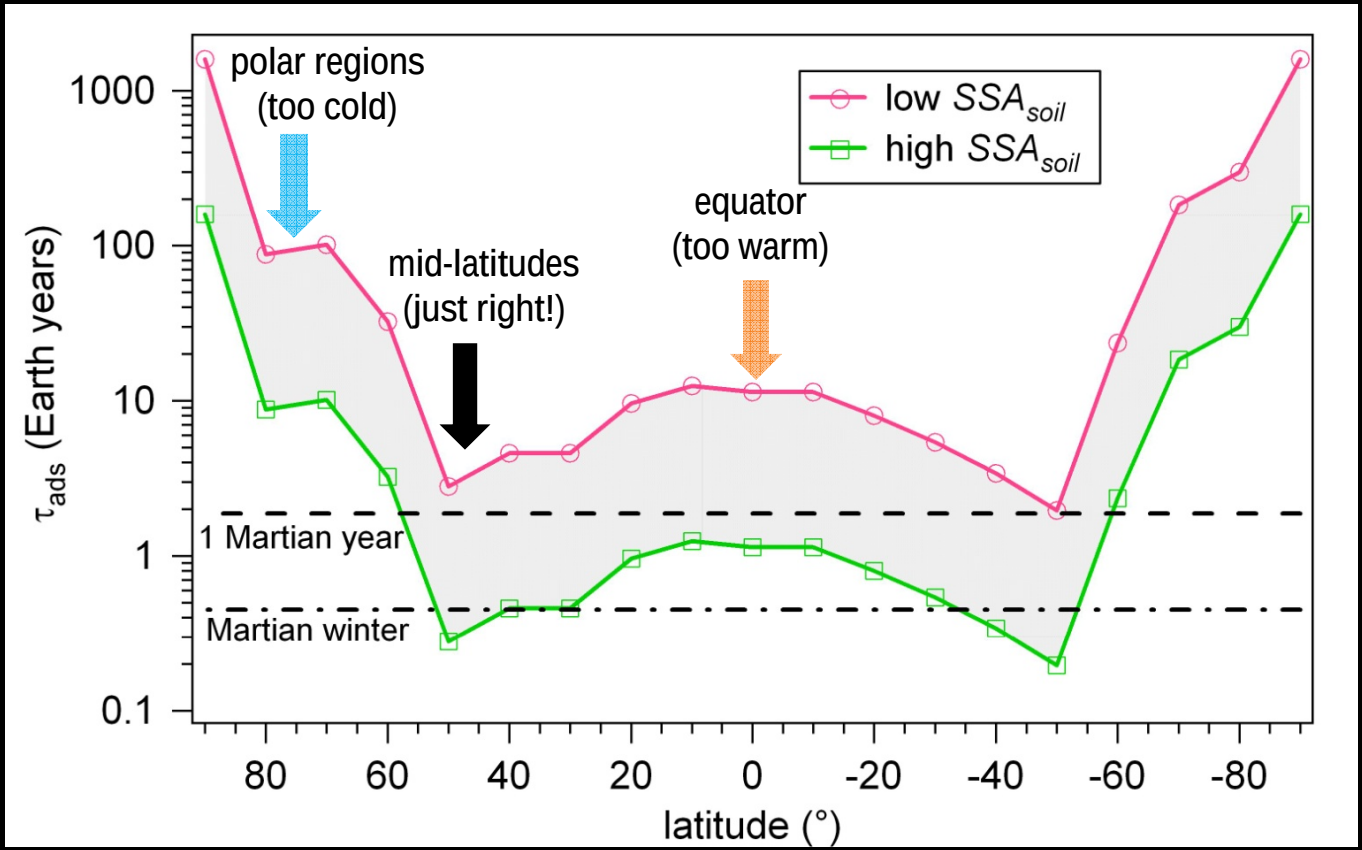




- γ values are very small
- $\gamma \downarrow$ as T $\uparrow$
- Adsorption enthalpy is weak (~5 kcal/mol)

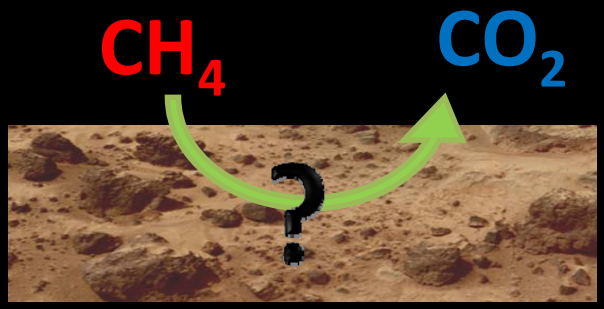
Gough, R.V., *et al*. Icarus, *in press*

Implications for Mars?



(Using annual mean and min. subsurface T's from Tokano et al.; ice table depths from Mellon et al. 2004)

- **Mid-latitudes** are most likely to be a temporary CH_4 sink/source
- More extensive simulations accounting for subsurface variability and atmospheric transport are warranted (Meslin et al., this meeting)



Permanent CH_4 sink?

$TiO_2 \bullet H_2O_2$
(Quinn and Zent, 1999)

$TiCl_4 + H_2O \rightarrow TiO_2$
$TiO_2 + H_2O_2 \rightarrow \mathbf{TiO_2 \bullet H_2O_2}$

JSC-Mars-1 + H_2O_2
(Levin and Straat, 1981)

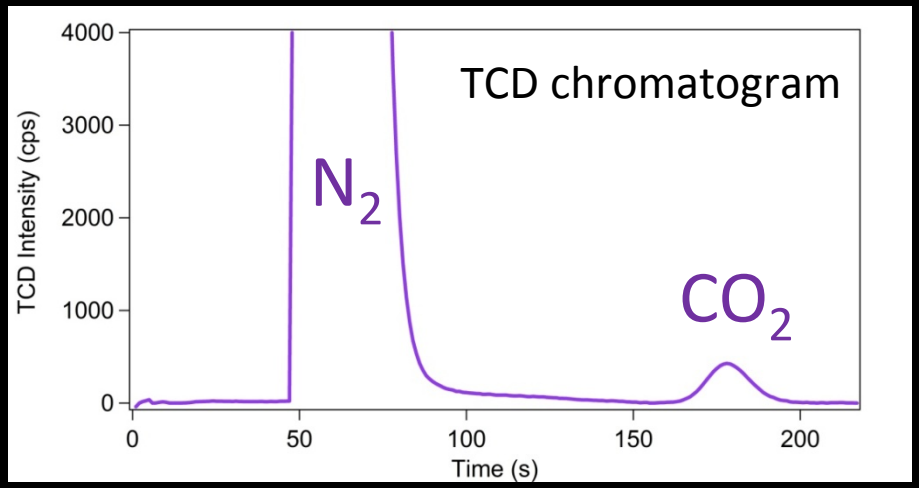
Na^+ and Mg^{2+} perchlorate

1. $NaClO_4$
2. $Mg(ClO_4)_2 \bullet 6H_2O$

- For all samples, we determined the reactivity toward the **"Viking organics"** as well as **CH_4**

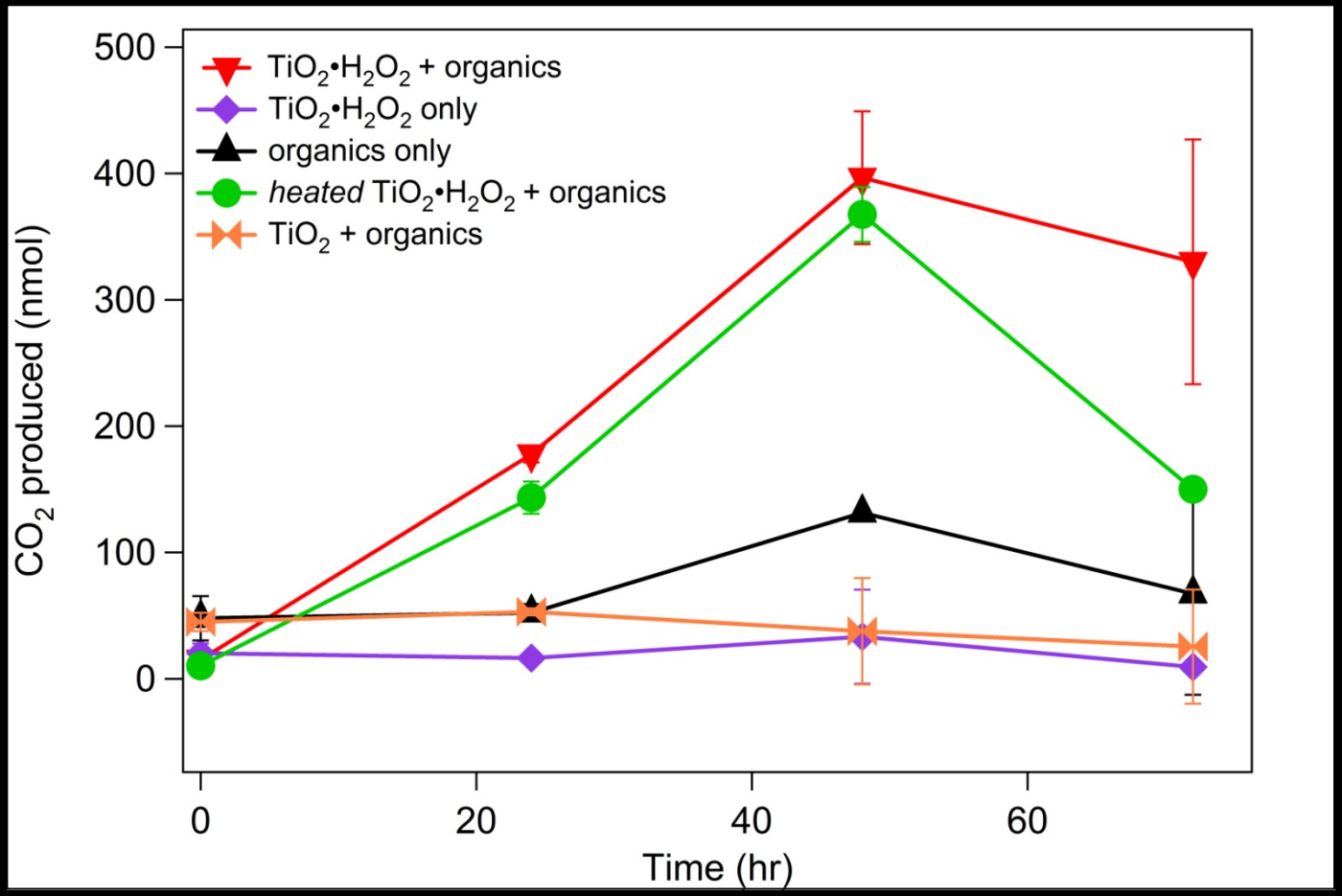
Experimental technique

- Samples in vials with N_2 atmosphere were kept at 2°C
- Headspace was sampled, analyzed with gas chromatography (GC)



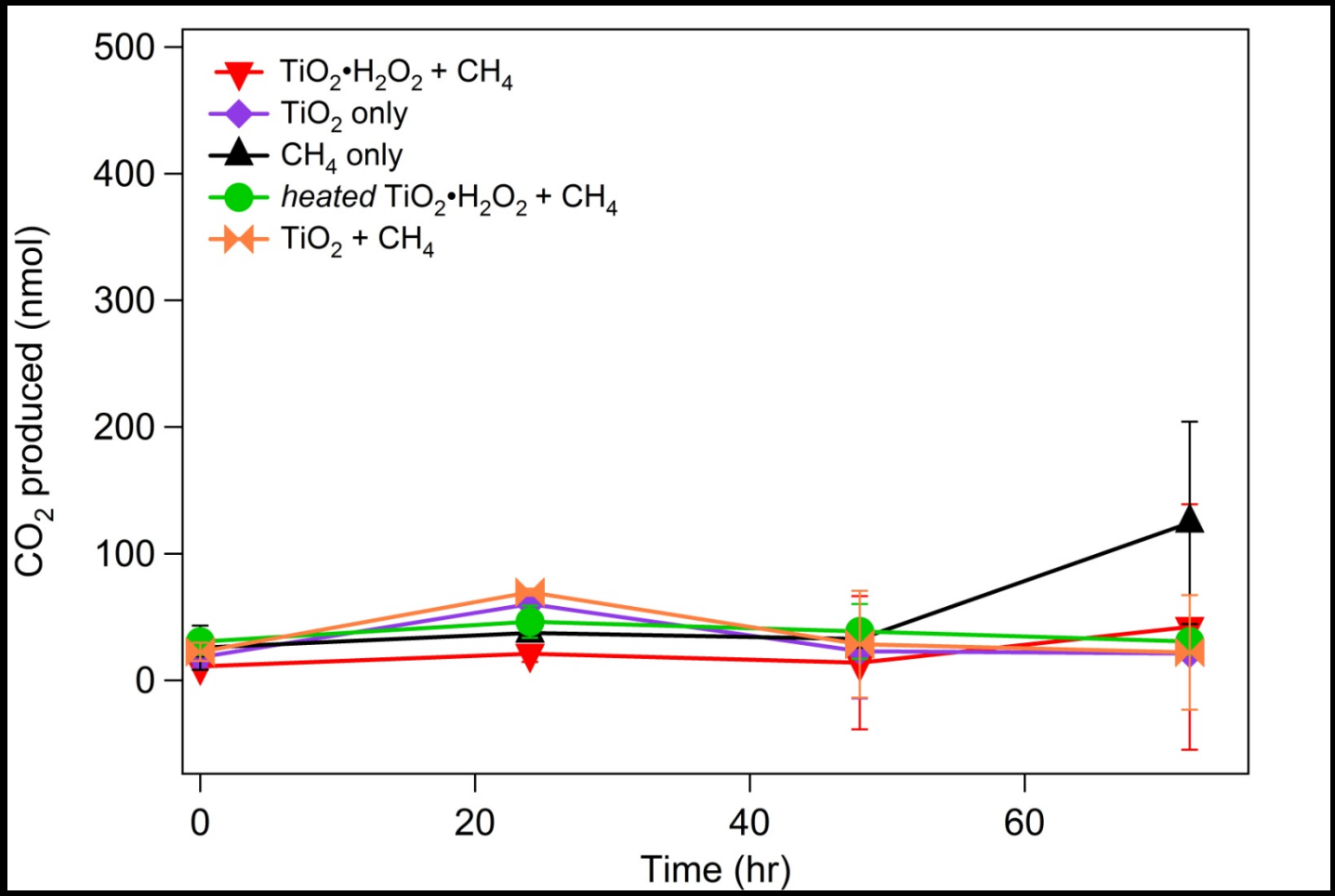
- After initial (t=0) measurement, **organics *or* methane** were added
- GC measurements taken at 24, 48, 72 hrs
- Several controls were used to rule out contamination

Results: $TiO_2 \bullet H_2O_2$ + organics



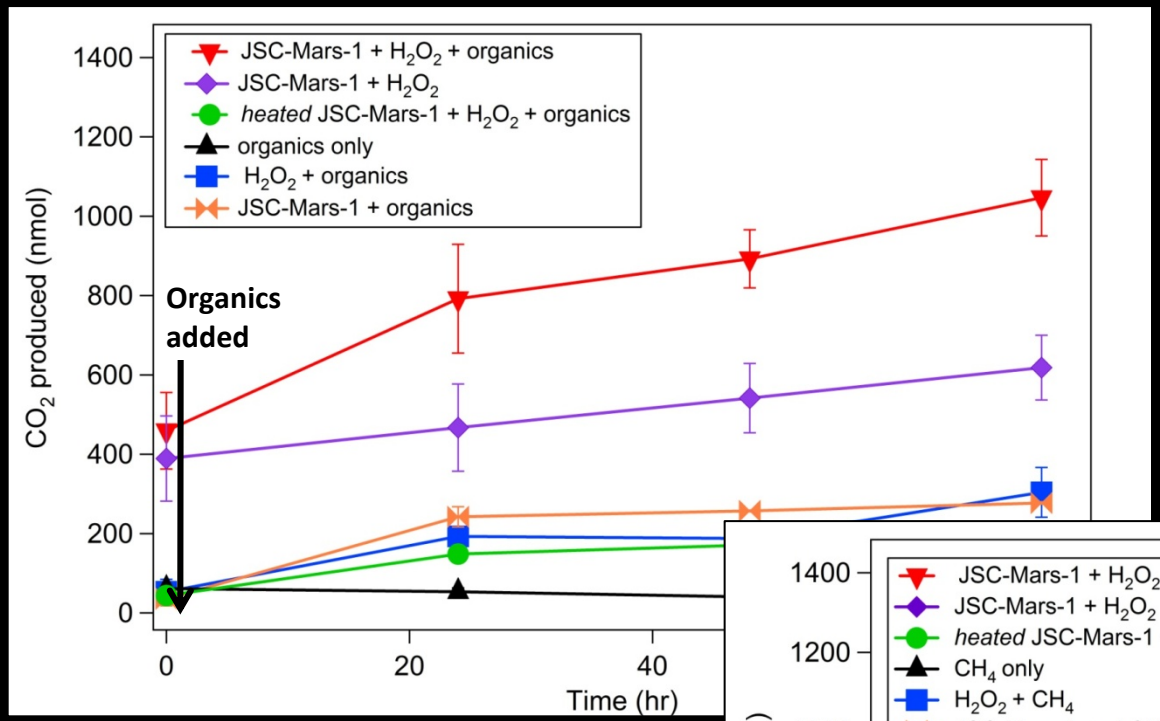
- Material is able to oxidize **organics**
- Results similar to Quinn & Zent (1999) (and Viking LR exp)

Results: $TiO_2 \bullet H_2O_2$ + CH_4



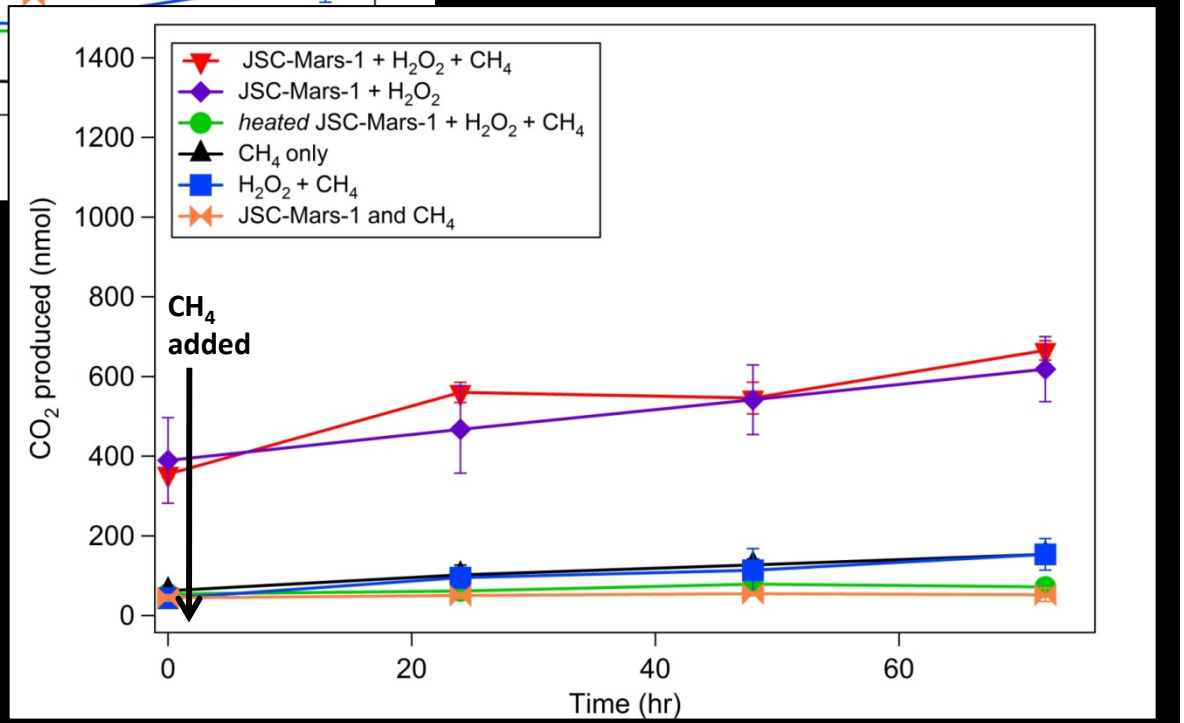
- No formation of CO_2 from **CH_4**

JSC-Mars-1 + H_2O_2 + **organics**



- Organics are oxidized into CO_2…

JSC-Mars-1 + H_2O_2 + **CH_4**



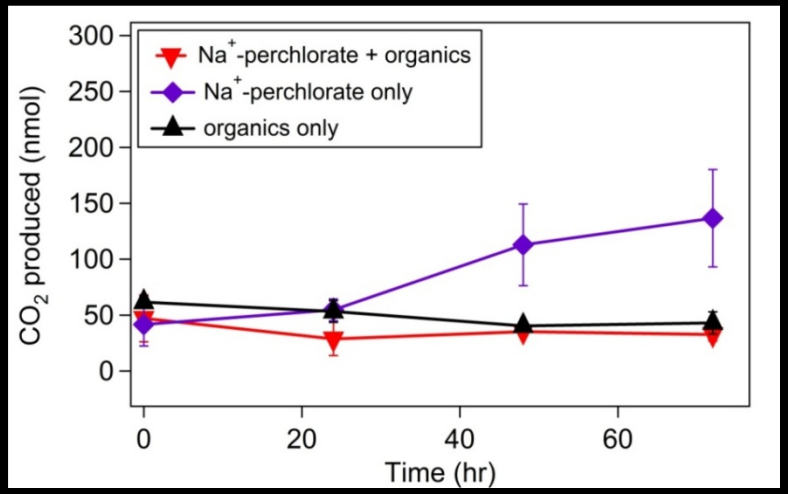
…but not CH_4!

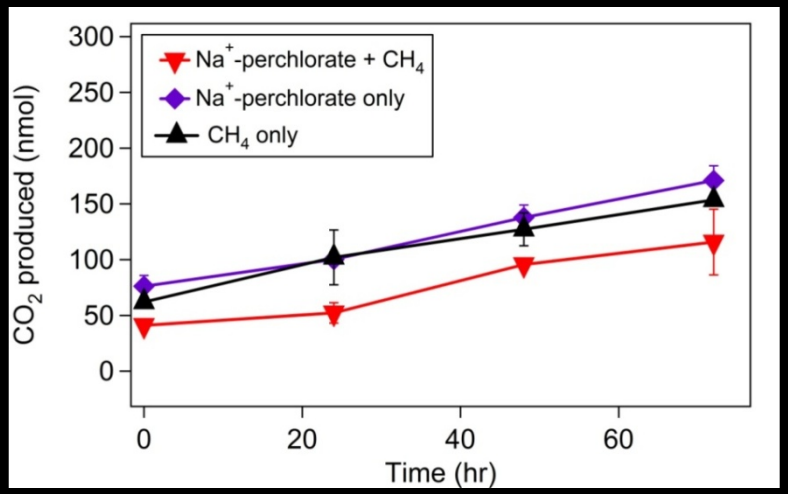
Na^+ and Mg^{2+} perchlorate salts

organics

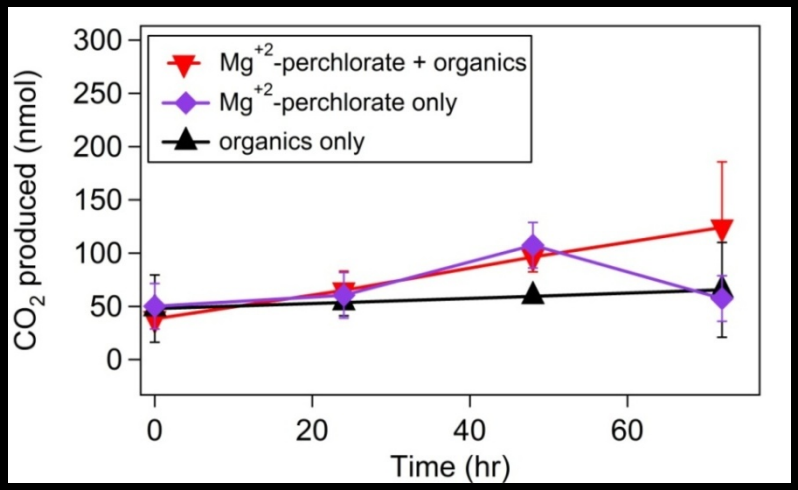
CH_4

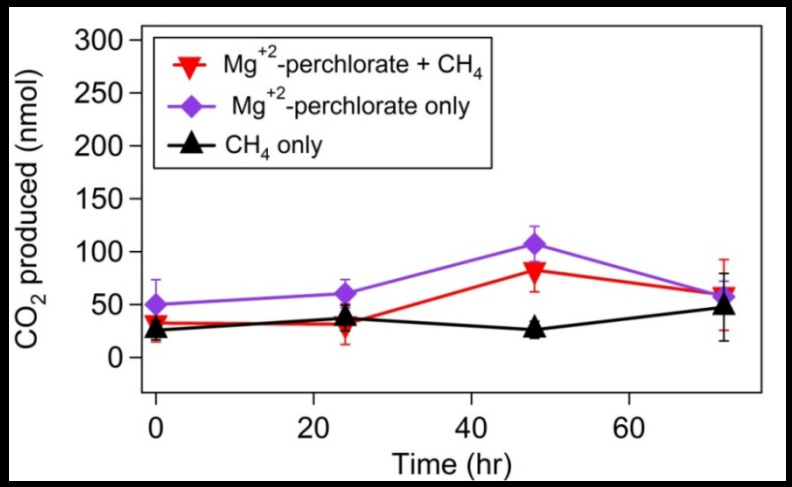
Na^+





Mg^{+2}





- Nothing is oxidized by perchlorate salts!

Martian implications

$$CH_{4(g)} \xrightarrow{k_{ox}} CO_{2(g)}$$

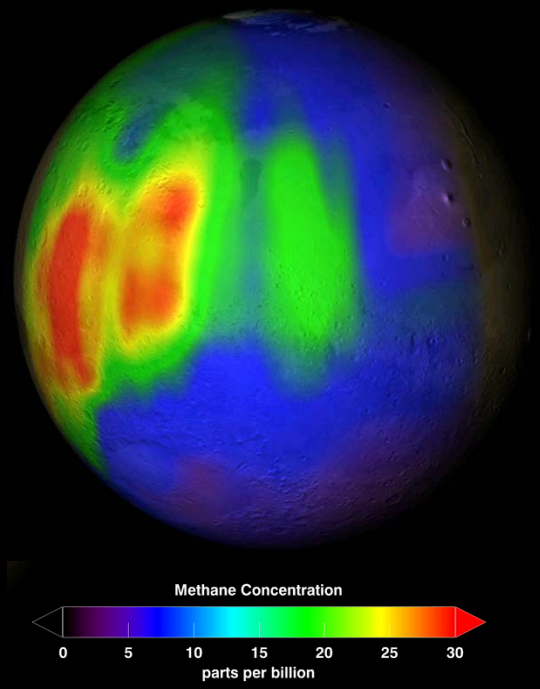
$$\frac{-d[CH_4]}{dt} = k_{ox}[CH_4]$$

- Detected **no CH_4 oxidation** by any of the 3 sample types studied

- Can determine **upper limit rate constant (k_{ox})** as we know CH_4 conc. in vials, $[CH_4]$, as well as upper limit of oxidation rate, $d[CH_4]/dt$.

- For all 3 "oxidizing surfaces", **k_{ox} < 4.94e-10 s^{-1}**.

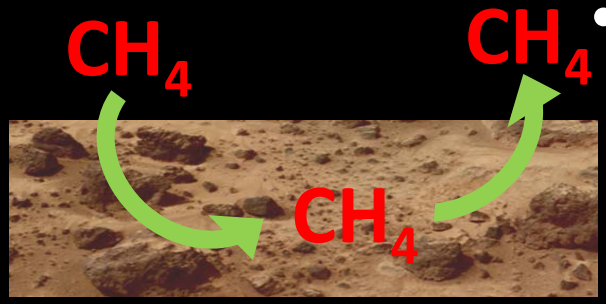
Martian implications



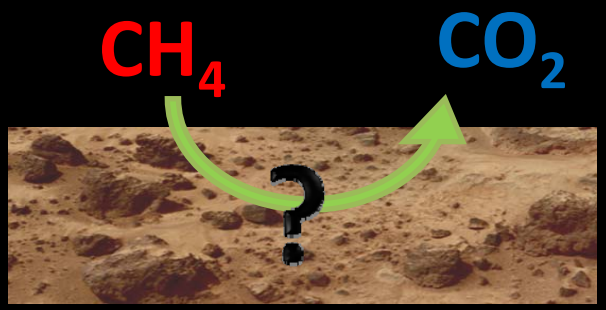
(Mumma et al., 2009)

- What size k_{ox} would be needed to explain recent CH_4 observations? (Mumma et al., 2009)?
  - Global average **6 ppbv in 2003** → **3 ppbv in 2006**
- If loss caused by oxidation, rate constant (k_{ox}) must be at least ~3e-9 s^{-1}
- Compare to experimental upper limit value: **k_{ox} < 4.94e-10 s^{-1}**
- Levevre & Forget (2009): surface loss must be very fast (3-6 hr) to explain observations!
- Heterogeneous loss of CH_4 probably not important on the 3 surfaces studied

Conclusions



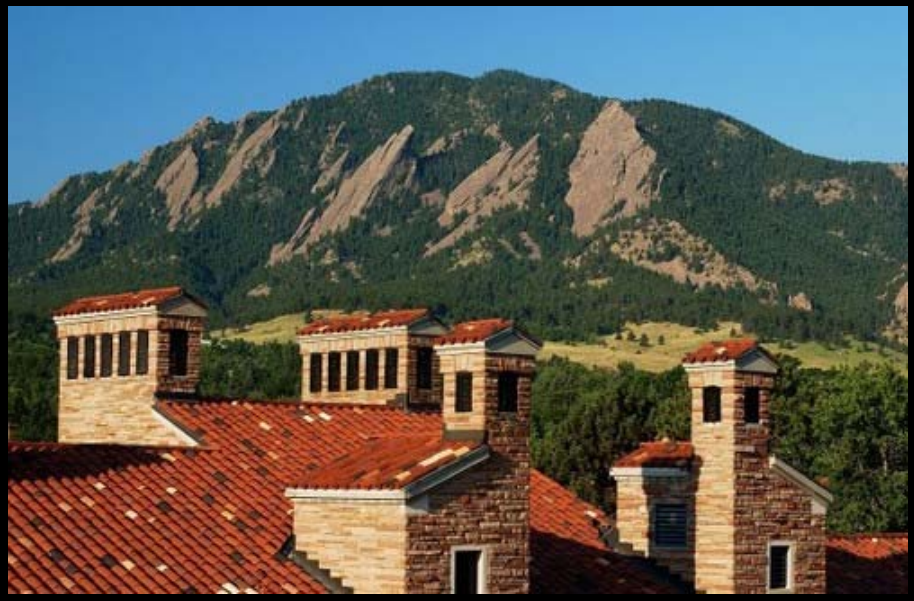
- **Temporary CH_4 sinks:**
  - Temperature-dependent adsorption of CH_4 in the regolith could play a role.
  - Could explain several recent observations



- **Permanent CH_4 sinks:**
  - Several proposed oxidative surfaces were studied
    - $TiO_2 \bullet H_2O_2$, JSC-Mars-1 + H_2O_2, perchlorate
  - No CH_4 oxidation was detected; rxn on similar surfaces on Mars is likely very slow
  - Observed atmospheric loss possibly to other processes.

Acknowledgements

- Jake Turley
- Stephanie Wood
- Grant Ferrell
- Kyle Cordova



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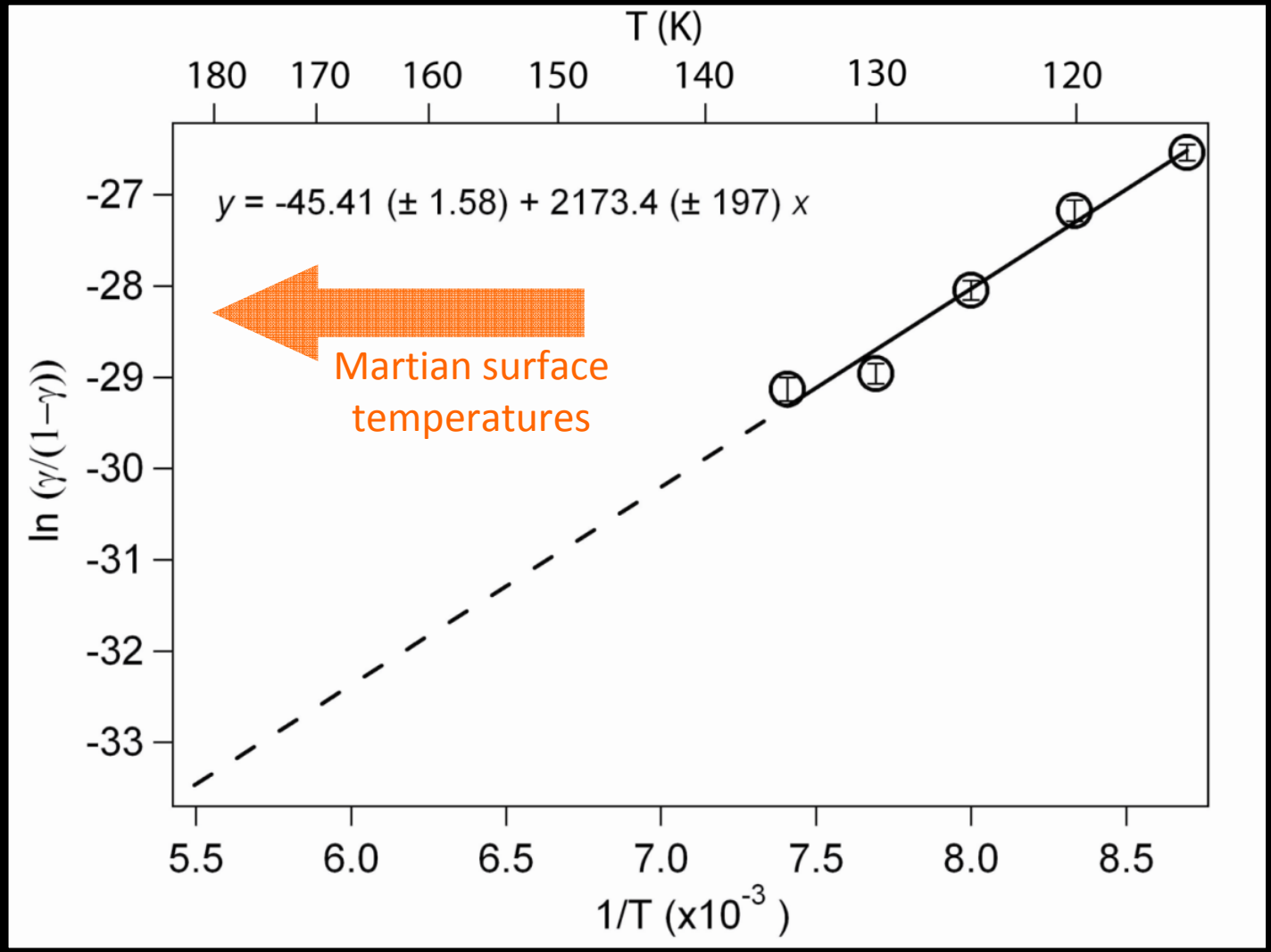
– ($) NASA grants 05-MFRP05-0066 and NNX08AG93G


T (K)
180
170
160
150
140
130
120
-27
-28
-29
-30
-31
-32
-33
y = -45.41 (± 1.58) + 2173.4 (± 197) x
Martian surface temperatures
ln (γ/(1−γ))
5.5
6.0
6.5
7.0
7.5
8.0
8.5
1/T (x10-3)