Methane formation in the Martian atmosphere by water photolysis in the presence of CO

Akiva Bar-Nun and Vasili Dimitrov

Department of Geophysics and Planetary Sciences, Tel-Aviv University, Tel-Aviv, Israel

Methane Sources

- Was it a release of 19,000 tons of CH_4 during the spring and summer [Mumma et al.]?
- How does the amount released change if the lifetime of methane in the atmosphere is reduced to a few hours [Lefevre and Forget, 2009] due to interaction with the perchlorates detected in the soil by the Phoenix Mars Lander and suggested by the Viking landers bases on the absence of organics on the surface?

Serpentinization

$3Fe_2SiO_4+2H_2O \rightarrow 2Fe_3O_4+3SiO_2+2H_2$

$(Fe, Mg)_2SiO_4+nH_2O+CO_2 \rightarrow$
$Mg_3Si_2O_5(OH)_4+FeO_4+CH_4$

Namely, hydrogenation of CO_2 by hydrogen to form CH_4

Photolysis of H_2O in the presence of CO

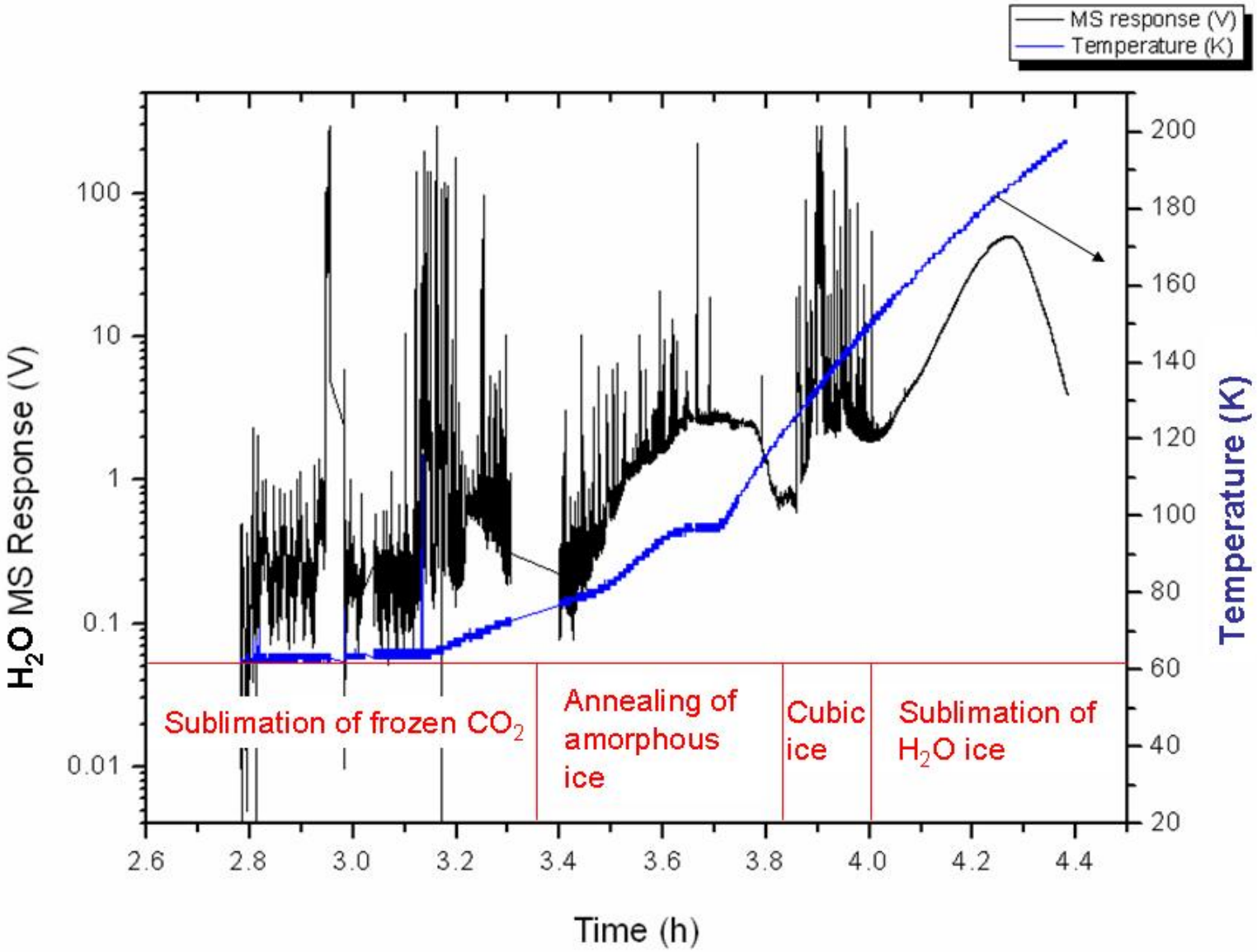
$$H_2O \xrightarrow{UV} OH + H$$

$$OH + CO \rightarrow CO_2 + H$$

$nH+CO \dashrightarrow CH_2O, CH_3OH, CH_4$

Correlation with spring-summer:

Release of ice grains to the atmosphere when the CO_2 ice sublimates in spring-summer.


MS response (V)
Temperature (K)
H_2O MS Response (V)
Temperature (K)
Time (h)
100
10
1
0.1
0.01
200
180
160
140
120
100
80
60
40
20
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
Sublimation of frozen CO_2
Annealing of amorphous ice
Cubic ice
Sublimation of H_2O ice

The water gas reaction

Is there a correlation between H_2O and CH_4 in the Martian atmosphere?!

$CO+H_2O \rightarrow CO_2+H_2+10.44$ kcal mole^{-1} (exothermic)

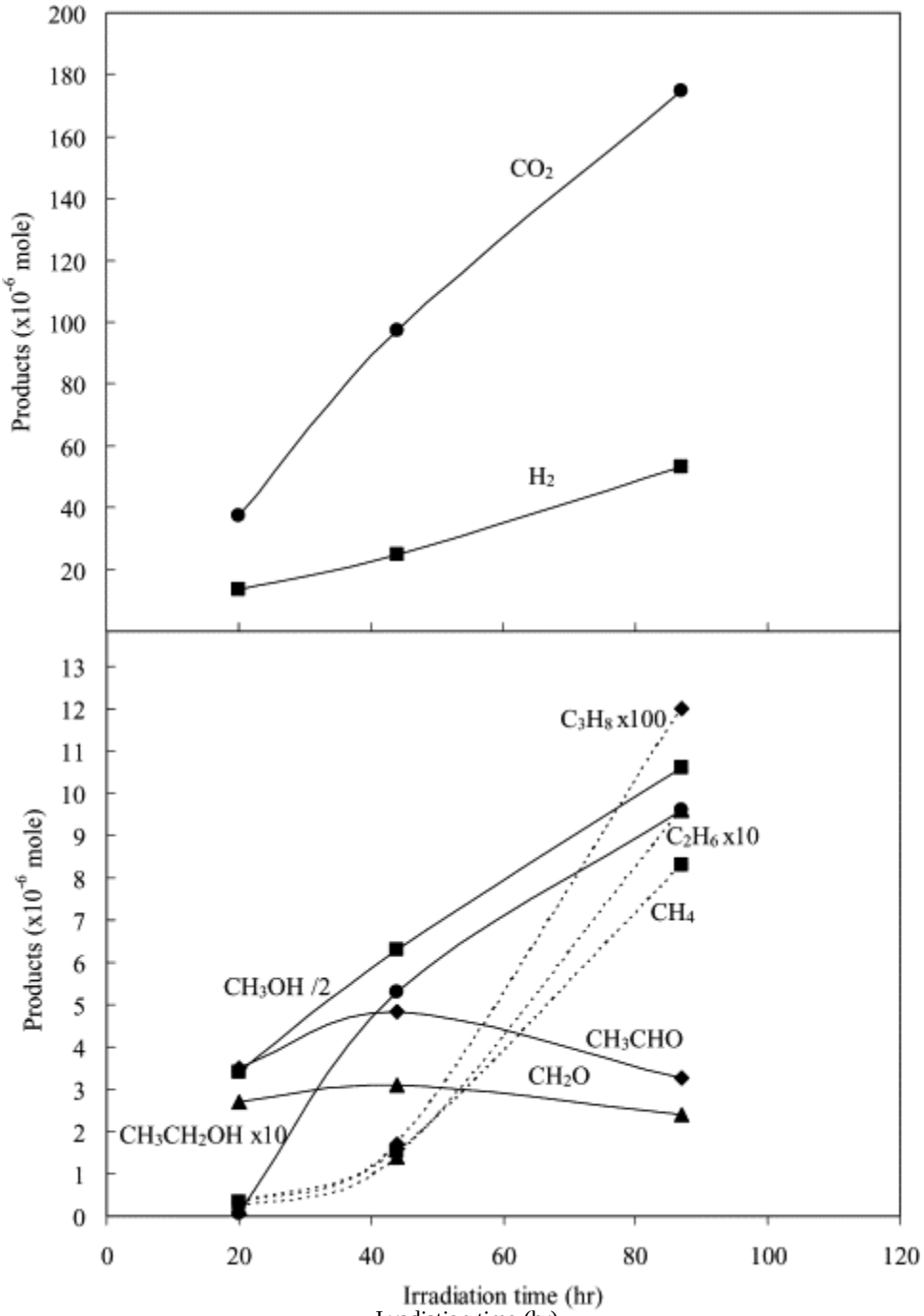
$CO+3H_2 \rightarrow CH_4{}^{+}H_2O+49.25$ kcal mole^{-1} (exothermic)

The equilibrium constant

$$Kp=\frac{P_{CH_4}P_{H_2O}}{P_{CO}P^{3}_{H_2}} \quad =3.7\times10^{24} \text{ strongly in favor of } CH_4$$

An experimental study of conversion of CO to CH_4 by H_2O photolysis [Bar-Nun and Chang, JGR, 88, 6662-6672 (1983)]

Photochemical reactions of water and carbon monoxide in Earth' primitive atmosphere



Irradiation time (hr)

	P(mbar)	T(K)	Initial composition (mixing ratios)				Products (mixing ratios)			
			N_2	**CO**	**H_2O**	**CO_2**	**H_2**	**CO_2**	**CO**	**CH_4**
Exp. #15 of BC[a]	390	329	9.8(-1)	1.0(-2)	1.0(-3)	0.0	4.0(-3)	5.0(-3)	- [b]	1.6(-4)
Equil. of Exp. #15	390	300	9.8(-1)	1.0(-2)	1.0(-3)	0.0	4.7(-4)	6.0(-4)	6.8(-5)	8.6(-5)
Mars Equil.[c]	7	300	2.7(-2)	9.7(-5)	1.0(-4)	9.5(-1)	5.3(-4)	9.5(-1)	9.7(-5)	2.8(-5)

a- Bar-Nun and Chang (1983)
b- Not measured
c- Composition after Encrenaz et al. (2004)