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

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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

\[ 3\text{Fe}_2\text{SiO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 + 2\text{H}_2 \]

\((\text{Fe, Mg})_2\text{SiO}_4 + n\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{FeO}_4 + \text{CH}_4\)

Namely, hydrogenation of CO\textsubscript{2} by hydrogen to form CH\textsubscript{4}
Photolysis of $\text{H}_2\text{O}$ in the presence of CO

\[ \text{H}_2\text{O} \xrightarrow{\text{uv}} \text{OH} + \text{H} \]

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]
nH+CO $\rightarrow$ CH$_2$O, CH$_3$OH, CH$_4$

Correlation with spring-summer:
Release of ice grains to the atmosphere when the CO$_2$ ice sublimates in spring-summer.
The water gas reaction

Is there a correlation between H$_2$O and CH$_4$ in the Martian atmosphere?!

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 + 10.44 \text{ kcal mole}^{-1} \text{ (exothermic)} \\
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} + 49.25 \text{ kcal mole}^{-1} \text{ (exothermic)}
\]

The equilibrium constant

\[
K_p = \frac{P_{\text{CH}_4}P_{\text{H}_2\text{O}}}{P_{\text{CO}}P^3_{\text{H}_2}} = 3.7 \times 10^{24} \text{ strongly in favor of CH}_4
\]
An experimental study of conversion of CO to CH₄ by H₂O photolysis [Bar-Nun and Chang, JGR, 88, 6662-6672 (1983)]

Photochemical reactions of water and carbon monoxide in Earth’s primitive atmosphere
Products (x10^-6 mole) vs. Irradiation time (hr)

- CH2O
- CH3CHO
- CH4
- C2H6 x10
- C3H8 x100
- CH3OH /2
- CH3CH2OH x10
- CO2
- H2
<table>
<thead>
<tr>
<th>P(mbar)</th>
<th>T(K)</th>
<th>Initial composition ( mixing ratios)</th>
<th>Products ( mixing ratios)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>N₂</td>
<td>CO</td>
</tr>
<tr>
<td>Exp. #15 of BC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>390</td>
<td>329</td>
<td>9.8(-1)</td>
</tr>
<tr>
<td>Equil. of Exp. #15</td>
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<td>300</td>
<td>9.8(-1)</td>
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<tr>
<td>Mars Equil.&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7</td>
<td>300</td>
<td>2.7(-2)</td>
</tr>
</tbody>
</table>

<sup>a</sup>- Bar-Nun and Chang (1983)

<sup>b</sup>- Not measured

<sup>c</sup>- Composition after Encrenaz et al. (2004)