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# „Photochemically Induced Formation of Mars-Relevant Oxygenates and Methane from Carbon Dioxide and Water“

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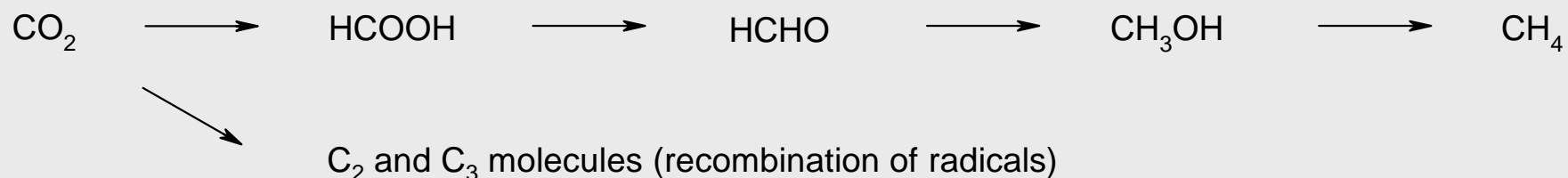
# (Photo)Chemistry – a Source for Methane?

→ by reduction of oxygenates (CO<sub>2</sub>, HCHO, and other)

Reduction (non-radical)



A probably way is a reaction via radicals formed by UV-radiation or photocatalysis.



## Reaction Conditions and Equipment

Reaction cell with quartz window, volume: 53 ml

UV-radiation: HBO 100 (mercury short arc light source, 100 watt)

Radiation time: up to 5 hours

Temperature: room temperature (25 °C) or 70 °C

Solid / Catalyst: hematite, synthetic  $\text{Fe}_2\text{O}_3$  as nanomaterial,  $\text{TiO}_2$

Atmosphere:  $\text{CO}_2$ ; 2%  $\text{CO}_2$  in He

Pressure: 1013 mbar

Water: 0 ... 70  $\mu\text{l}$  per cell volume (as moistened hematite)  
~3  $\mu\text{l}$  results in a saturated atmosphere at  
room temperature



# Measurement Set-up

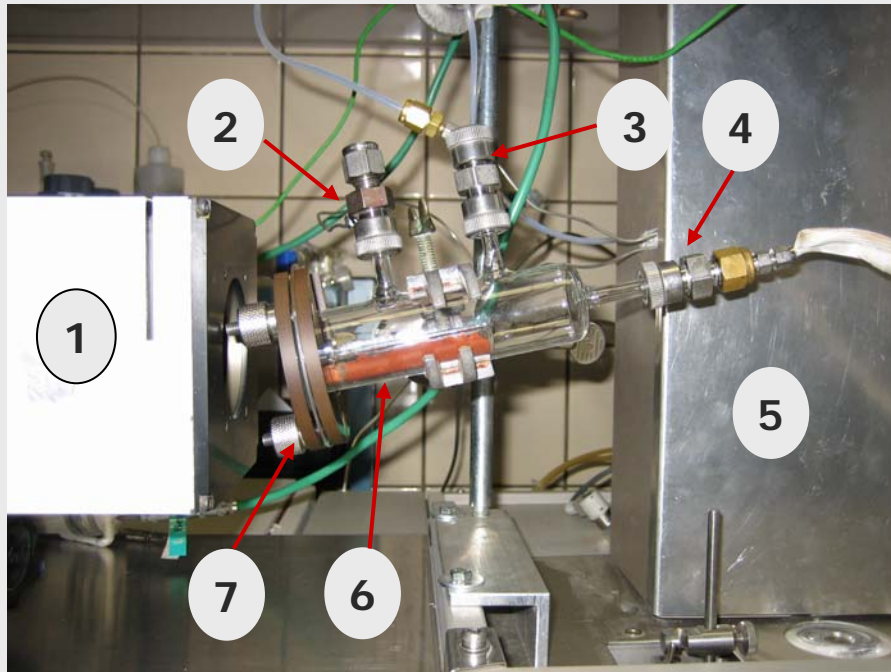
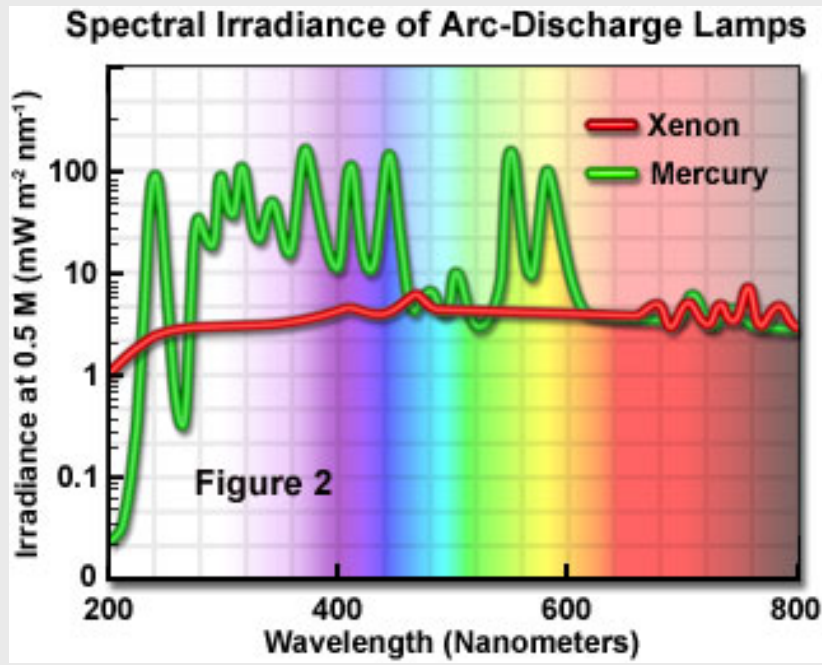


Photo of measurement set-up including analytic system

- (1) Mercury short arc lamp
- (2) Helium-inlet for flushing or injection
- (3) Septa for injection
- (4) Cell outlet (to analyzing system)
- (5) Valves for injection to analytic system
- (6) Reaction cell with Hematite sample
- (7) Quartz window

# Equipment



Spectral irradiance of a mercury short arc lamp

Quartz shell with hematite



# Analysis

## Gas chromatography with mass spectroscopy

Simultaneous qualitative determination of all components

Quantitative determination of methanol, formaldehyde, carbon dioxide and further oxygenates ( $C_2$  and  $C_3$  components)

Quantitative determination of methane by modification of analytical system

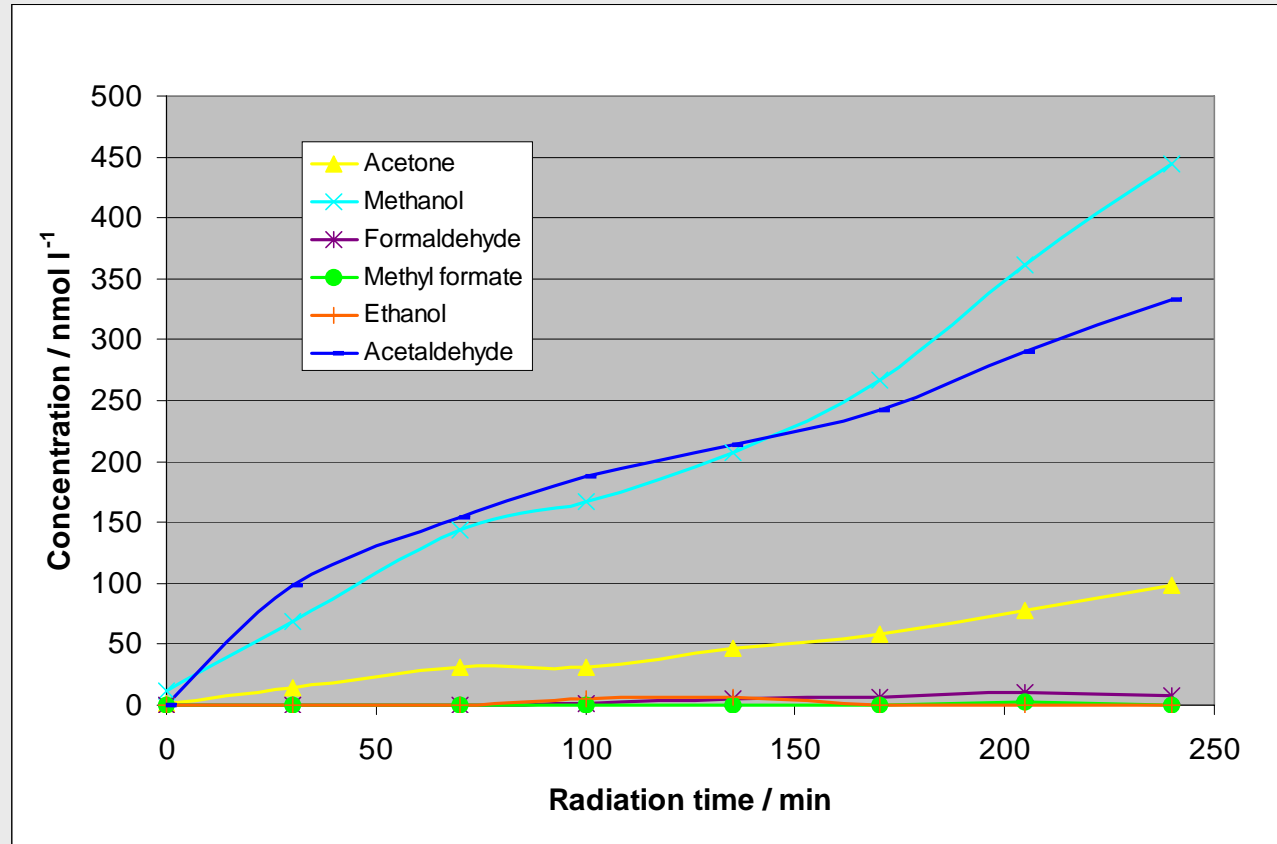
Analysis of gas phase:

- at reaction temperature (on-line),
- gas phase after thermal desorption at 70 °C  
("adsorbed" molecules at surface of solids)



# Influence of Radiation Time

Reaction conditions: CO<sub>2</sub> atmosphere, Hematite with 70 μl H<sub>2</sub>O

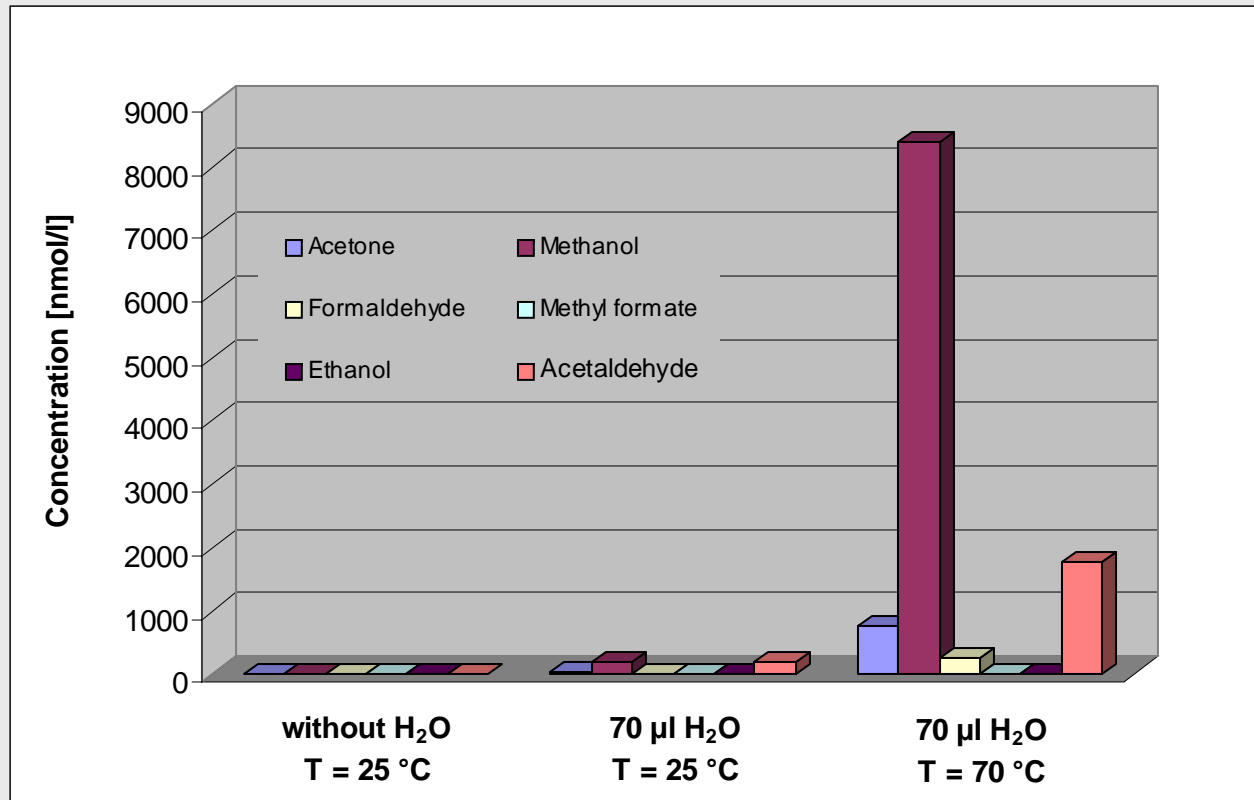


→ Same products with similar distribution



# Influence of Reaction Temperature

Reaction conditions: CO<sub>2</sub> atmosphere, Hematite, 2 h radiation time



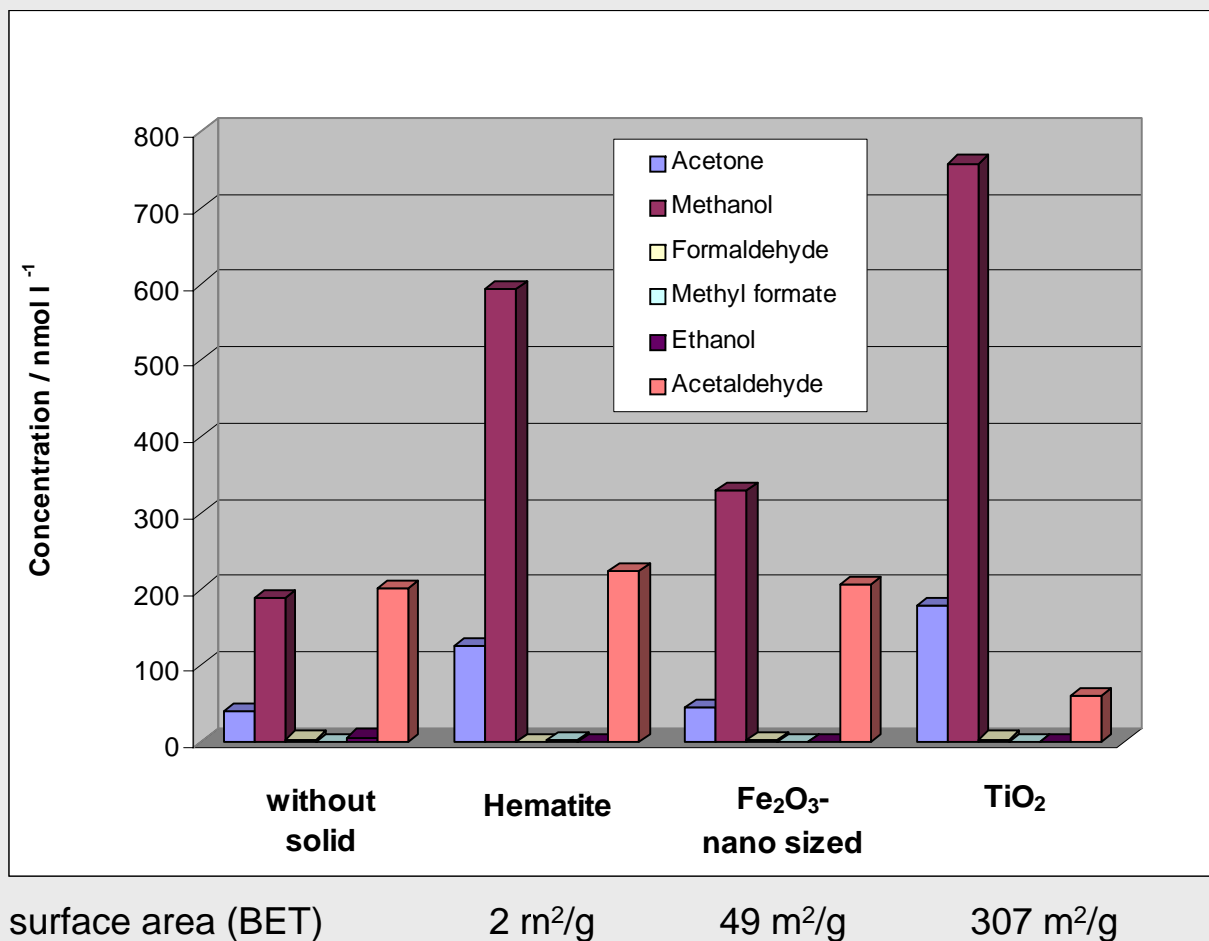
→ Same products with similar distribution





# Influence of Solid / Catalyst

Reaction conditions: CO<sub>2</sub> atmosphere, 70 µl water, 2 h radiation time



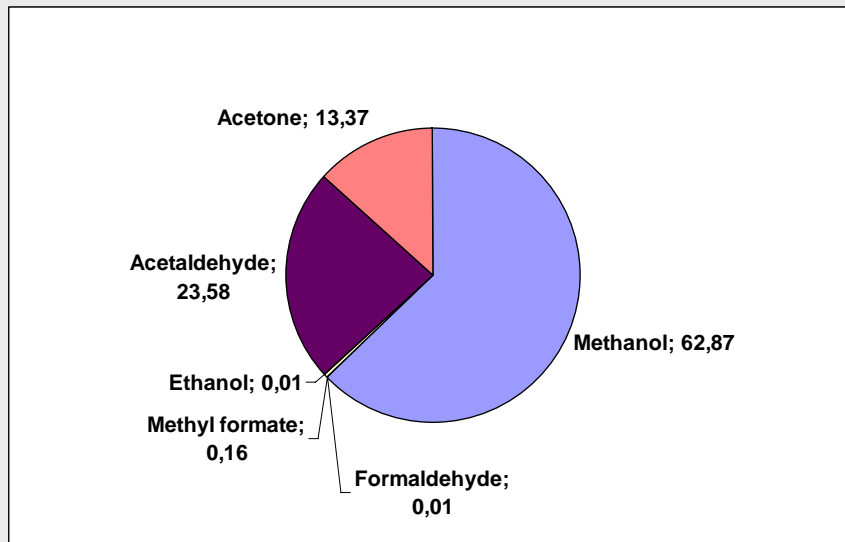
- Formation of products by gas phase reaction
- No influence of inner surfaces
- Solid as a possible catalyst



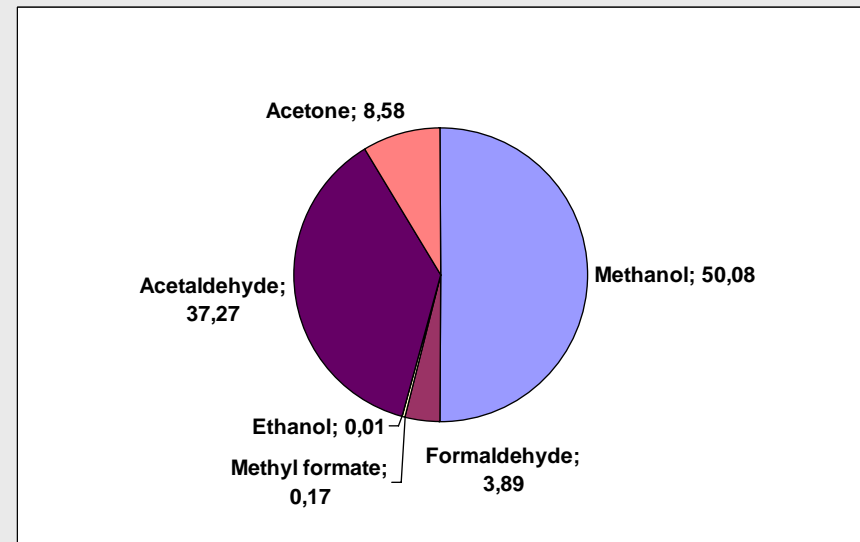
# Influence of CO<sub>2</sub> Concentration

Reaction conditions: Hematite with 70 µl H<sub>2</sub>O, 2 h radiation time

**Pure CO<sub>2</sub>-atmosphere**



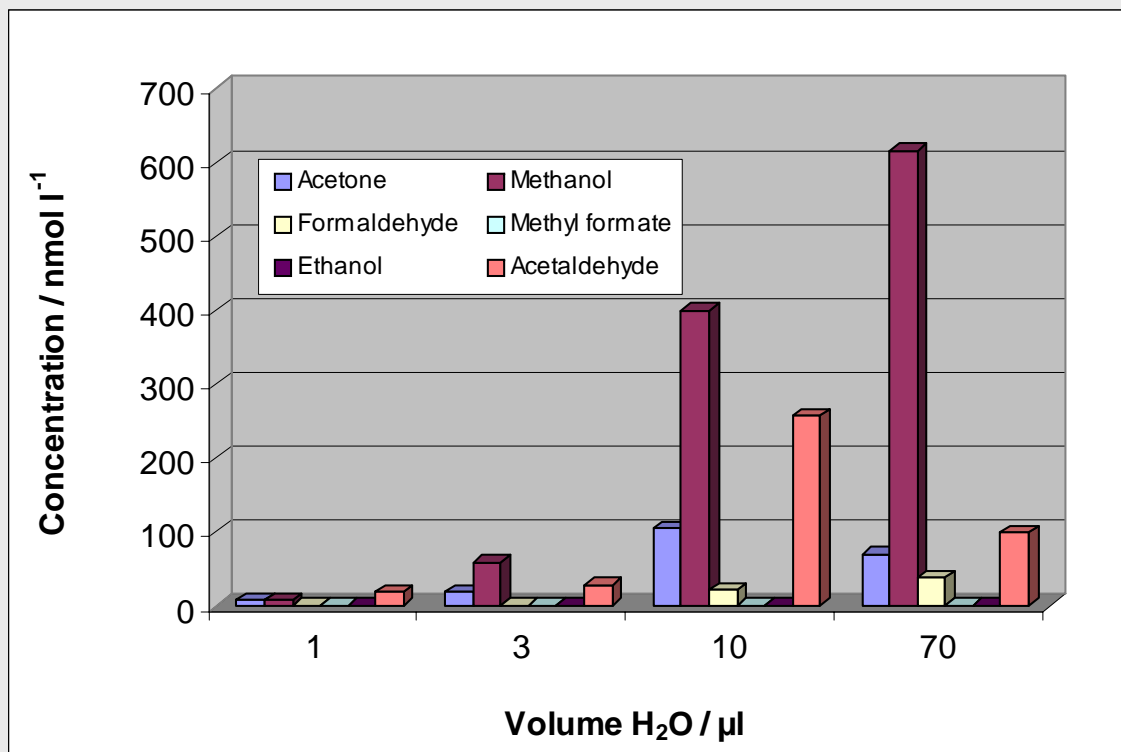
**2 % CO<sub>2</sub> in He**



→ Same products with similar concentrations

## Influence of Water Content

Reaction conditions: 2 % CO<sub>2</sub> in helium, Hematite, 2 h radiation time

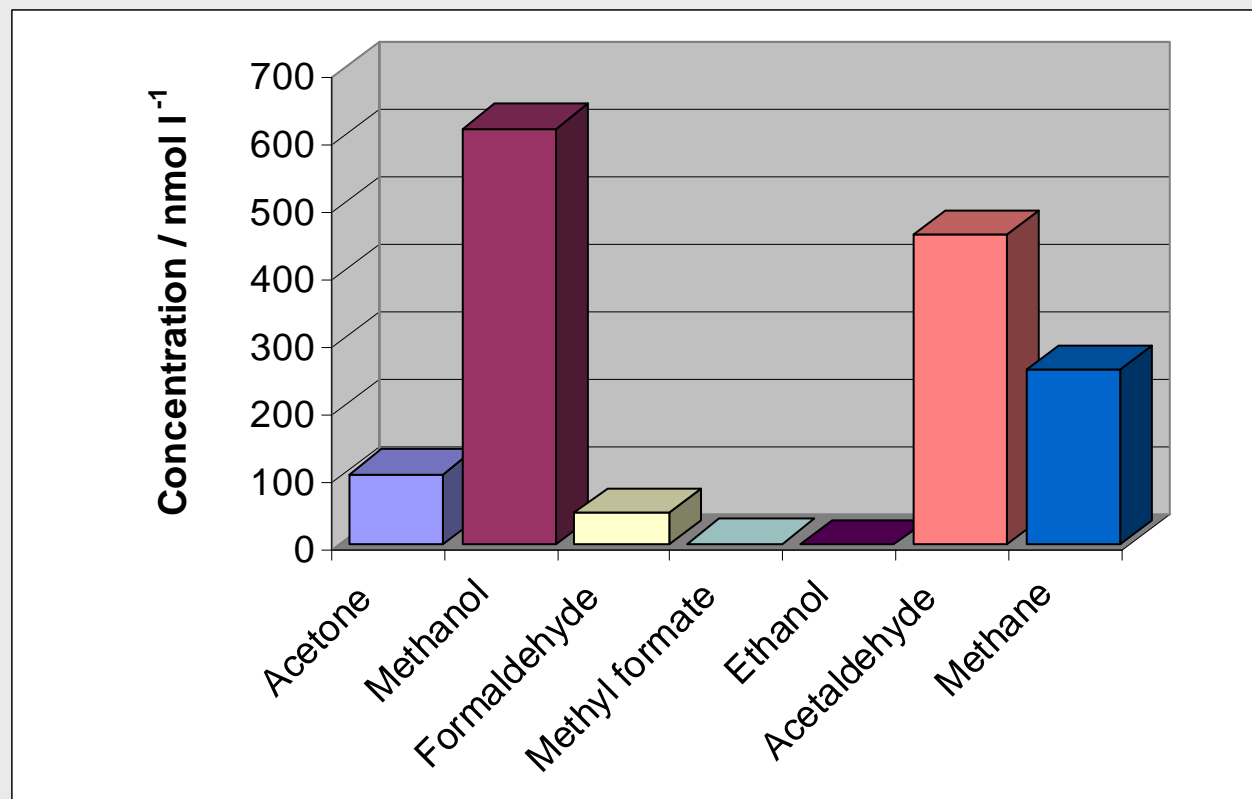


→ Without water no reaction, with 1 μl water favored formation of acetaldehyde, with 3 – 70 μl water formation of same products with similar distribution



# Quantitative Determination of Methane

Reaction conditions: 2 % CO<sub>2</sub> in helium, 70 µl water, 2 h radiation time



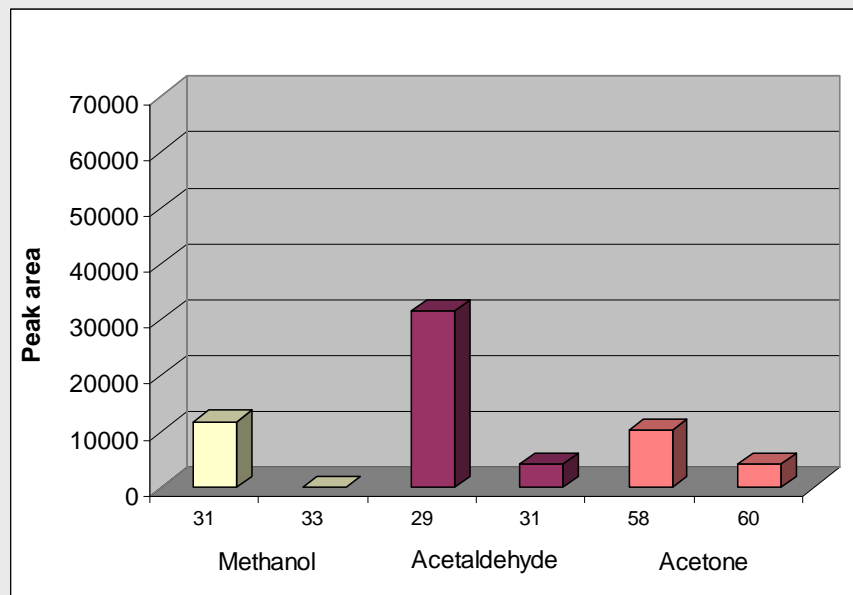
→ Formation of 260 nmol/l methane, conversion of CO<sub>2</sub>: 0.16 %



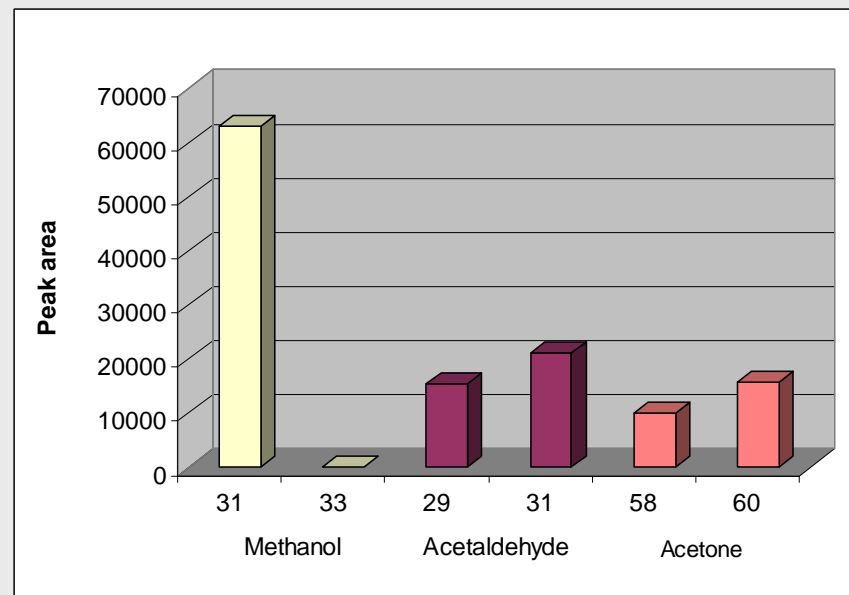
# Isotope Investigations

Reaction conditions: 2 % CO<sub>2</sub> in helium, H<sub>2</sub><sup>18</sup>O water, 2 h radiation time

1 μl H<sub>2</sub><sup>18</sup>O



3 μl H<sub>2</sub><sup>18</sup>O



- No water saturated atmosphere → molecules are formed with oxygen (<sup>16</sup>O) from CO<sub>2</sub>

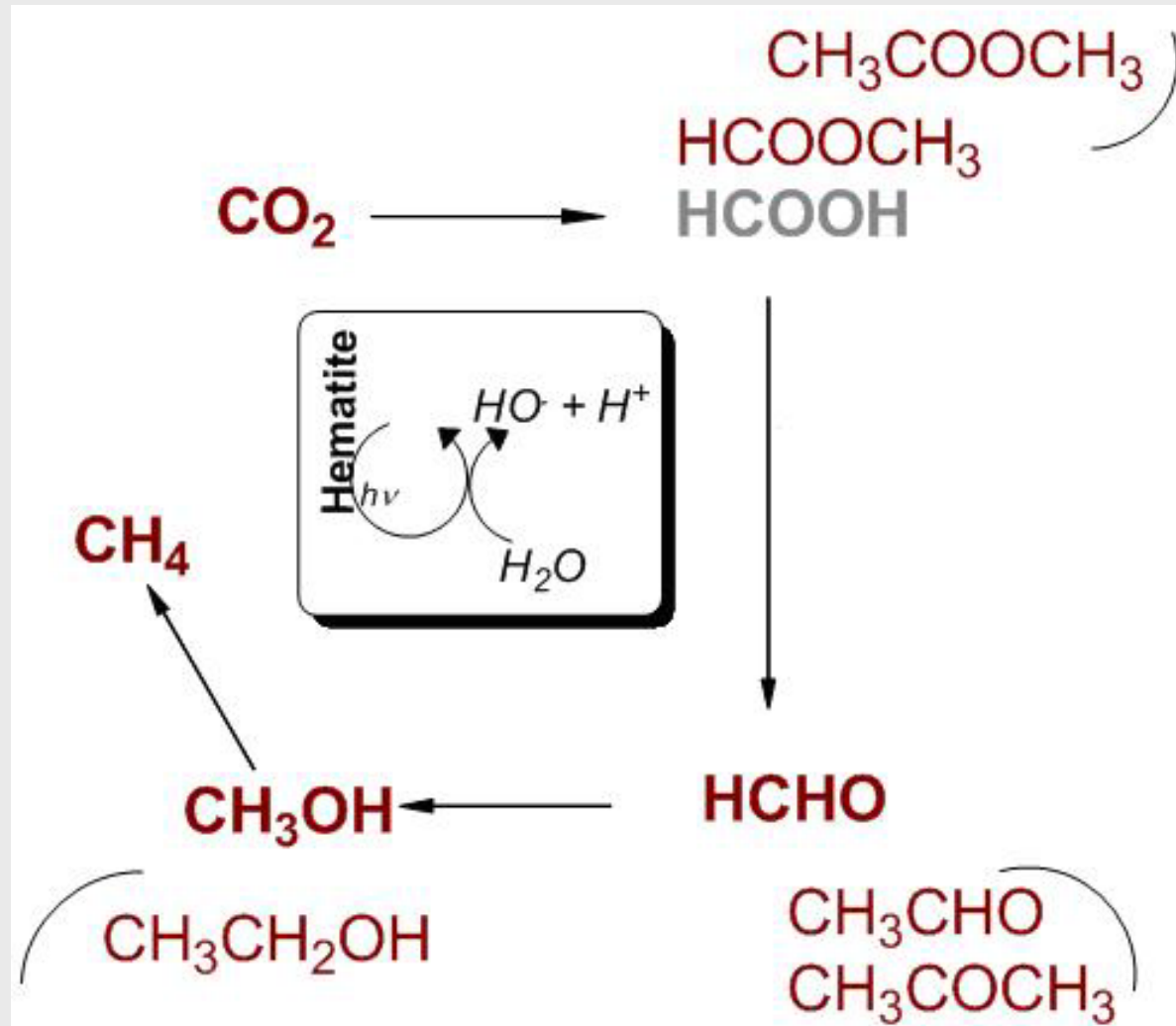
- Water saturated atmosphere → molecules are formed also with oxygen (<sup>18</sup>O) from water



**Indication of different reaction pathways and mechanisms**



# Results



## Results - 2

CO<sub>2</sub> + water + UV-radiation are necessary requirement for chemical reactions

→ Formation of organic molecules including methane and further C<sub>2</sub> and C<sub>3</sub> components

Gas phase reactions and also reactions at surfaces

Influence of water content on concentration of reaction products

→ indication of different reaction pathways and mechanisms

Experiments in lab with high UV density

→ high proportion of gas phase reaction → low selectivity

In lab experiments conversion of 0.16 % CO<sub>2</sub>

→ **Formation of methane under Martian conditions should be possible by (photo)chemistry.**



## Next Steps

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- Long-time experiments (starting from CO<sub>2</sub> or CH<sub>4</sub> and mixtures of them)
- Kinetic studies (determination of reaction rates)
- Investigation of further solids / minerals (as catalysts)
- Reaction under Martian conditions (low pressure, lower temperature)
- Xenon light source for a continuous UV spectrum (imitation of sun light)
- Further experiments with gases with a special stable isotope ratio for determination of reaction channels





# Acknowledgement

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