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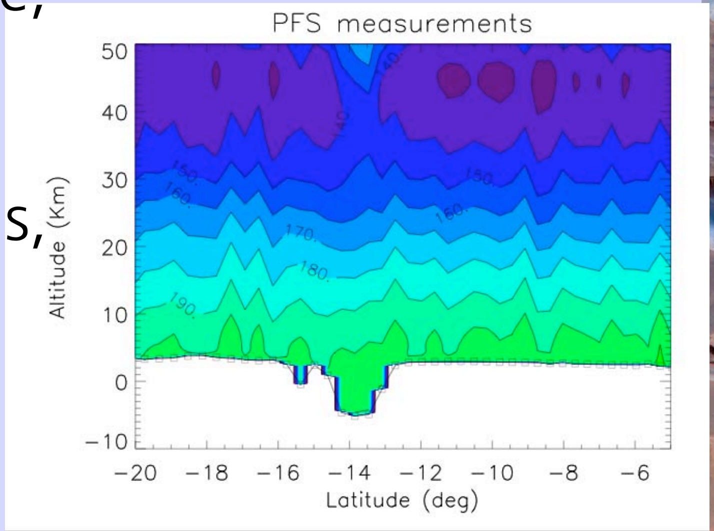
21-25 February 2005, ESA/ESTEC
Noordwijk, The Netherlands

Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

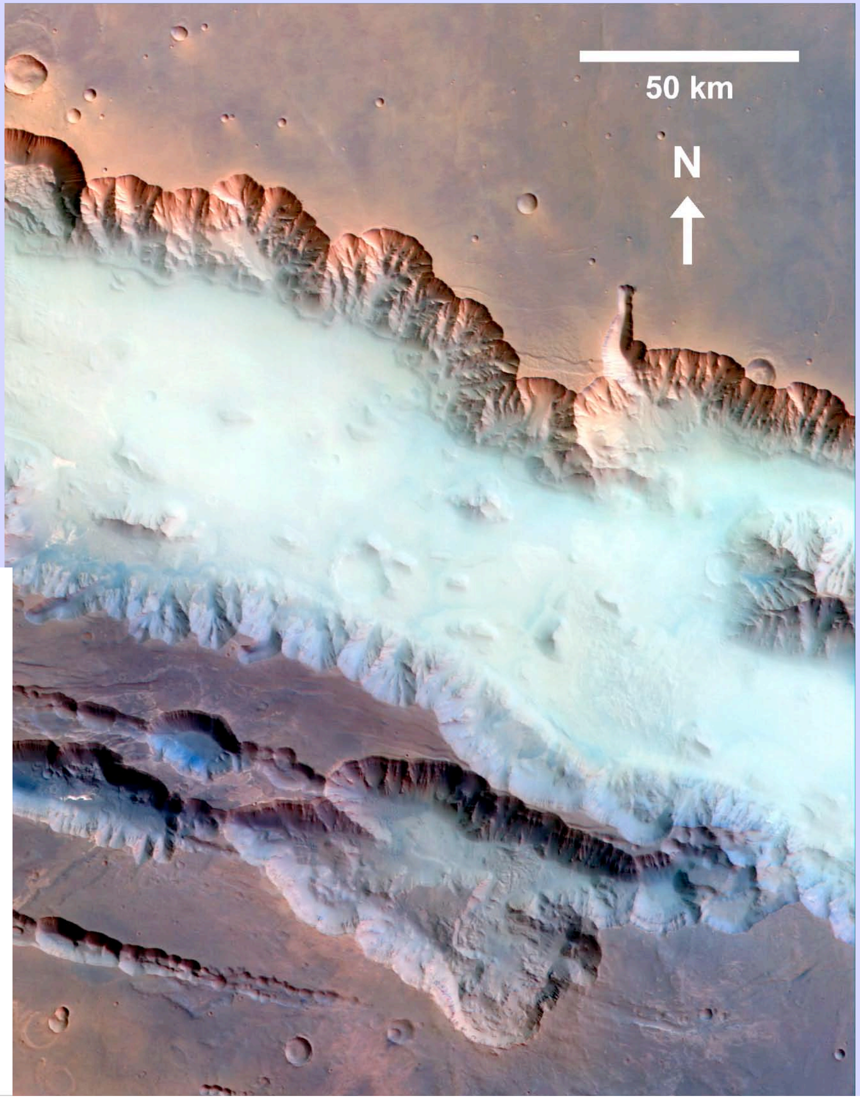
Viking: There is water vapor in the martian atmosphere with contents of several 10 pr µm (equivalent to 10 g per square meter)

Modeling teaches that adsorption and condensation of water are characteristic for the interaction between atmosphere and the uppermost soil layers (mm - cm). Adsorption water behaves liquid-like, it is expected to support there chemical reactions, also at present.

MEX-PFS temperatures
(Formisano, Grassi, 2004)



(C) ESA/DLR/FU Berlin (G.Neukum)
Bildmitte bei -14.17° Breite und 57.52°W Länge. Aufnahmezeitpunkt 25.05.2004



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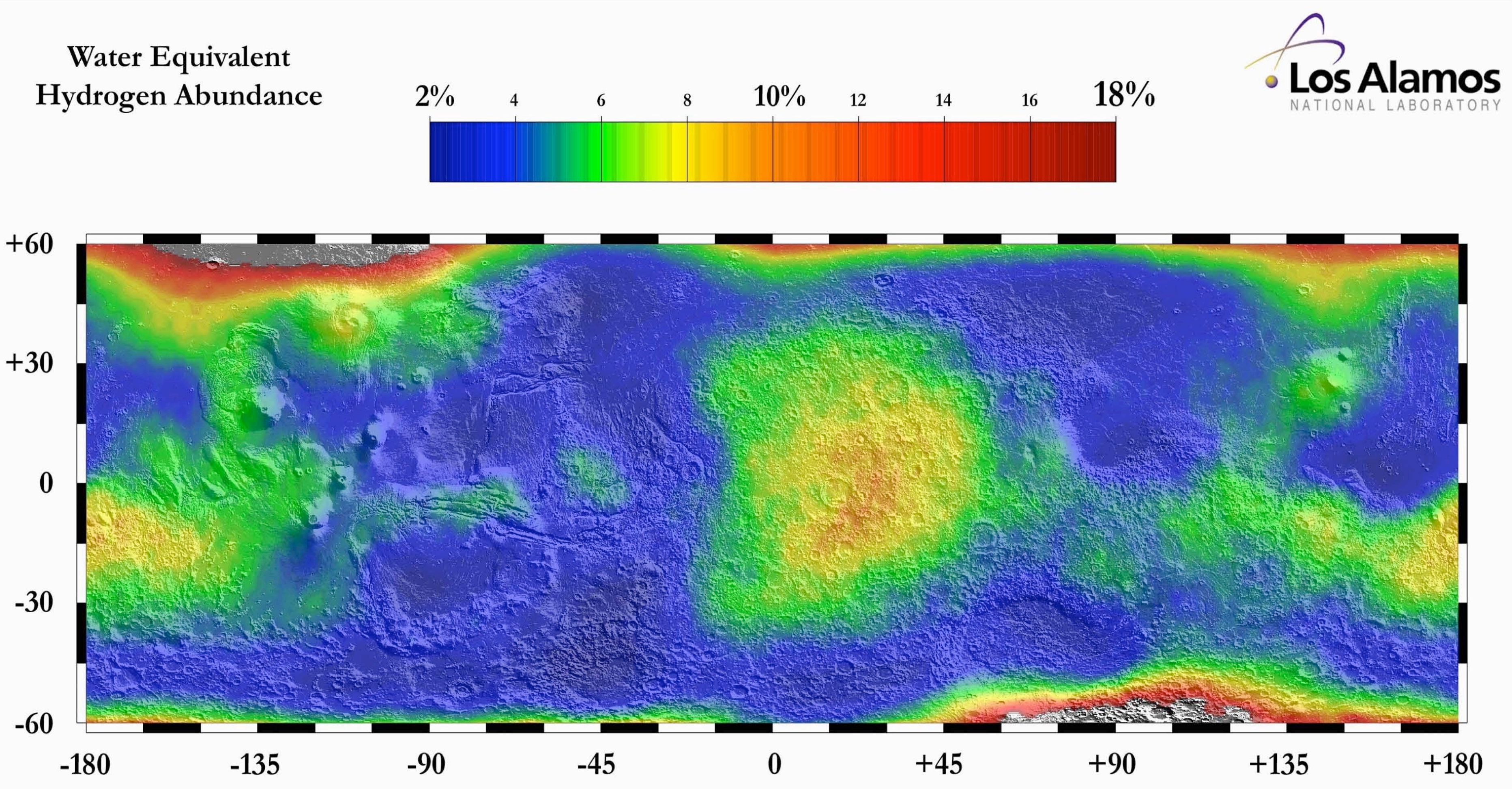
Feldman, W.C., T.H. Prettyman, W.V. Boynton, S.W. Squyres, D.L.Bish, R.C. Elphic, H.O. Funsten, D.J. Lawrence, S.Maurice, K.R. Moore, R.L. Tokar, D.T. Vaniman, 'The global distribution of near-surface hydrogen on Mars, Sixth International Conference on Mars, [CD-ROM], Abstract 3218, 2003.:



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Sublimation of water ice (Sonntag, 1990) :

$$p[\mathrm{Pa}] = 611.2\, e^{\frac{22.46\,(T[K] - 273.15)}{T[K] - 0.53}} \qquad (-65°\,C < T[°C] < 0.01°\,C)$$

$$T[K] \gg 0.53 \Rightarrow p[\mathrm{Pa}] = 611.2\, e^{22.46\left(1 - \frac{273.15}{T[K]}\right)} = 3.47\; 10^{12}\, e^{-\frac{6134.949}{T[K]}} =$$

$$= 3.47\; 10^{12}\, e^{\frac{8.4662\; 10^{-20}\,\mathrm{Ws}}{kT}} = 3.47\; 10^{12}\, e^{-\frac{0.528\,\mathrm{eV}}{k\,T[K]}}$$

This corresponds with a molecular weigth of water of 18.015

to a "Sublimation Enthalpy" of $\Delta H_{ice} = 50.622$ kJ mol^{-1}

The evaporation enthalpy of water is of $\Delta H_{water} = 45.054$ kJ mol^{-1} (at 0° C)

Hydration enthalpies of minerals are reported to have values up to

$\Delta H_{mineral} \approx 100$ kJ mol^{-1}, and more.

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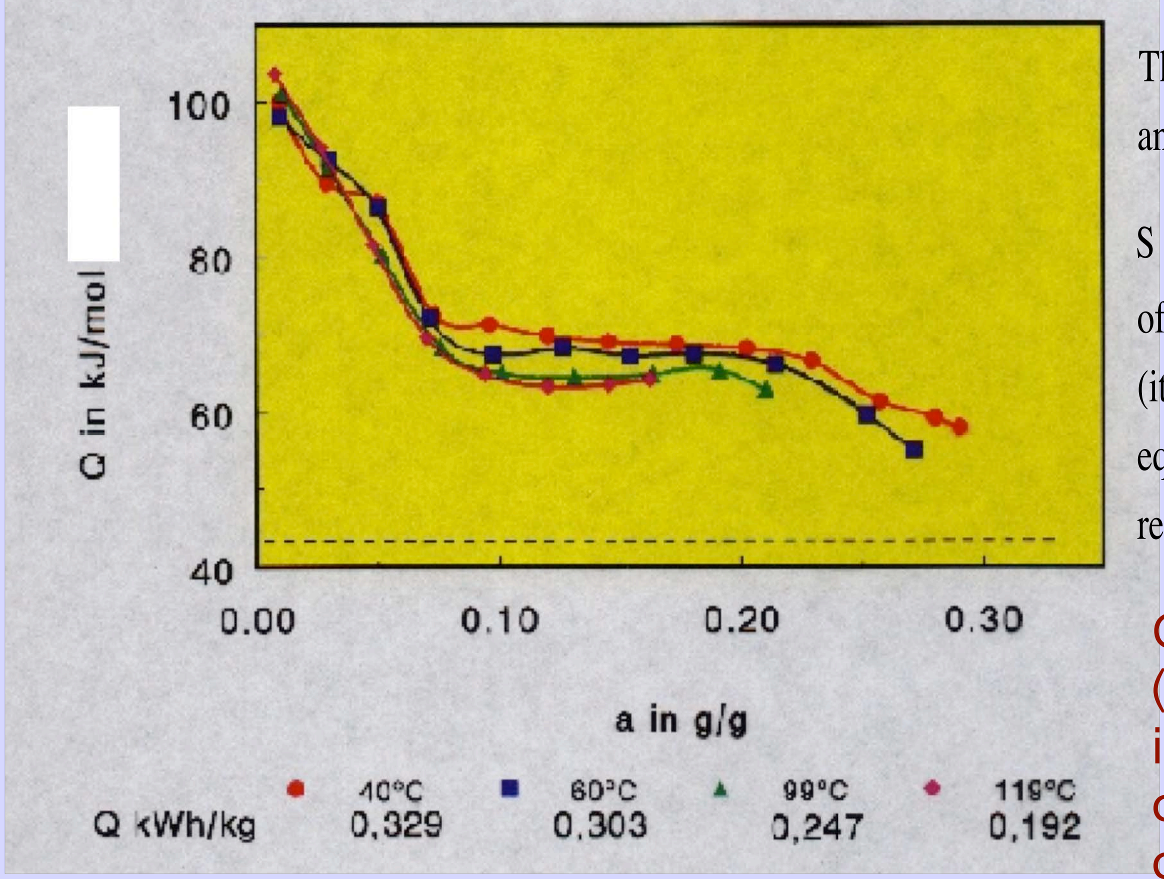
Bulk water: 45 kJ/mol, Water ice: 50 kJ/mol.
Adsorption water is stronger bond.
Strongest bonds (surface forces) start at about 0.07 g/g.



The ratio S = E/Z of the evaporation rate E of adsorption water and the sublimation rate Z is the proportional to

$S = e^{-\frac{(\varepsilon_{ads} - \varepsilon_{ice})}{kT}}$. This is for adsorption bond energies of $\varepsilon \approx$ 0.8 eV of about $S^{-1} \approx 7.3510^{6}$. Thus, adsorption water can survive ice (it evaporates million times slowlier than ice sublimates under equal conditions). Adsorption water is expected to exist in Martian regions which are completely free of ice (dried out).

Conclusion: Adsorption water must (at least temporarily) exist also at present in the upper martian surface as a consequence of the atmospheric water content and the soil - atmosphere interaction.

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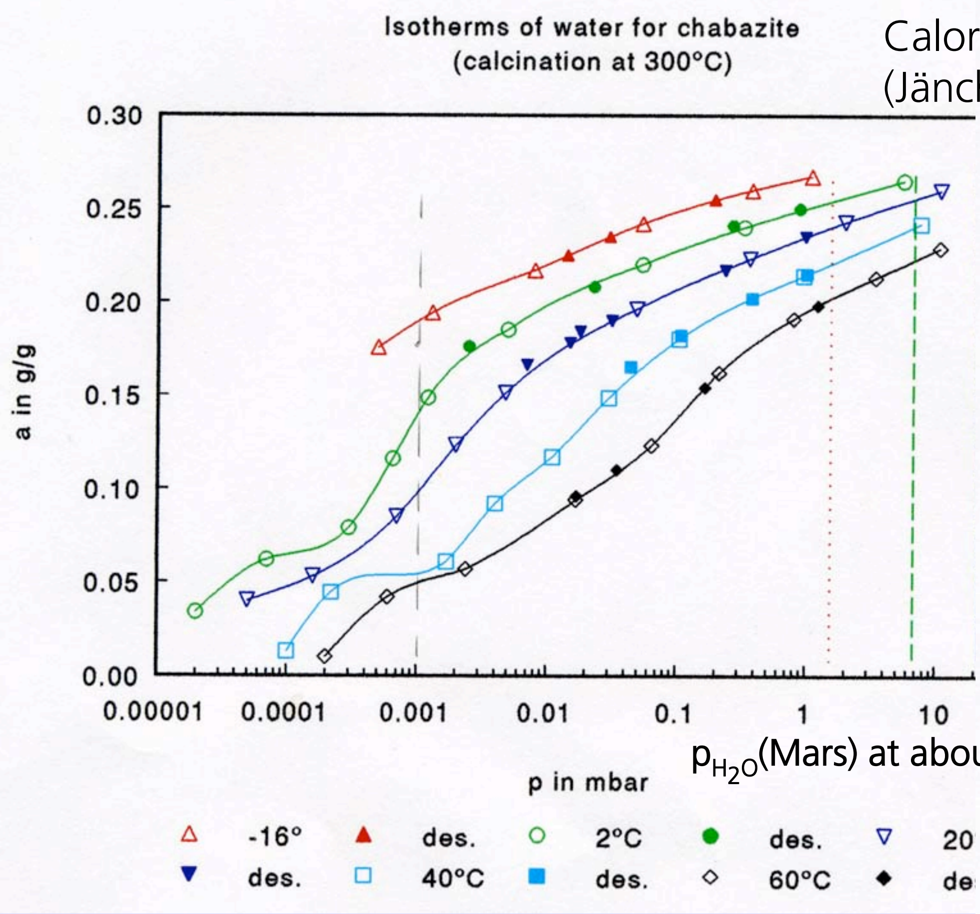
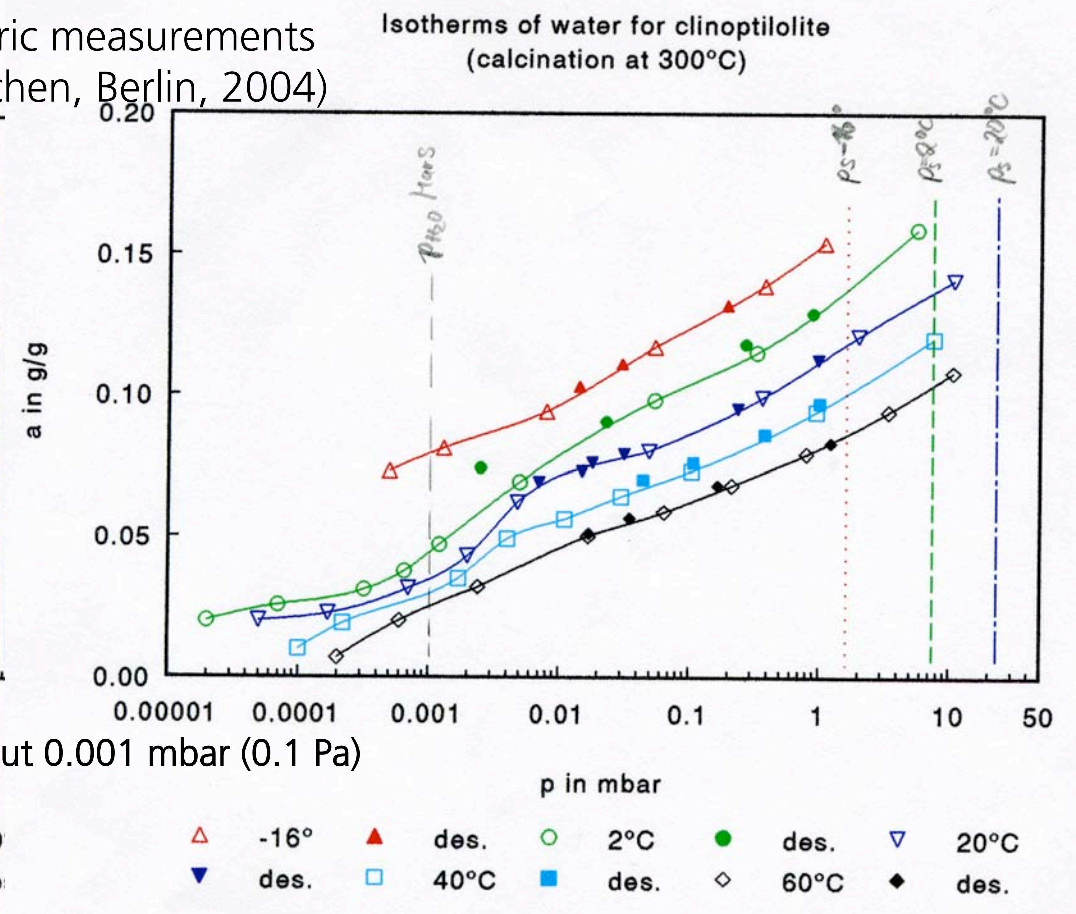


Caloric measurements
(Jänchen, Berlin, 2004)



p_{H_2O}(Mars) at about 0.001 mbar (0.1 Pa)

Terrestrial model substances (minerals) can explain the observed water content of the upper martian surface by adsorption water. But, chemisorbed water is expected to be present too. Relative abundance ratios (physisorbed/chemisorbed) are yet unknown.

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Mass ratio of adsorption water (mass m) and dry soil (mass M)

$$m/M = n\,\Sigma\,S$$

(n - number of monolayers, Σ = surface mass density of one layer of adsorption water ($\Sigma = 3\ 10^{-7}$ kg m^{-2}), S - specific surface of the soil material (Ballou et al. 1978 - $S = 1.7\ 10^{4}$ m^{2} kg^{-1}).

$$\Rightarrow \frac{m}{F} = \frac{n\Sigma SM}{F} = \frac{n\Sigma SV\rho}{F} = n\Sigma S\rho h, \quad \Rightarrow h = \frac{m/F}{n\Sigma S\rho}$$

The amount of 10 pr m of water can be adsorbed (at one monolayer) within an uppermost layer of 1.31 mm depth (in case of $S = 1.7\ 10^{4}$ m^{2} kg^{-1})

A value of m/M = 1% corresponds to $n = (m/M)/(SS) = 1.96$.

A relative content of 1 % (by weight or mass) of adsorption water in soil corresponds to the presence of about 2 monolayers (in case of S according to Ballou et al., 1978).

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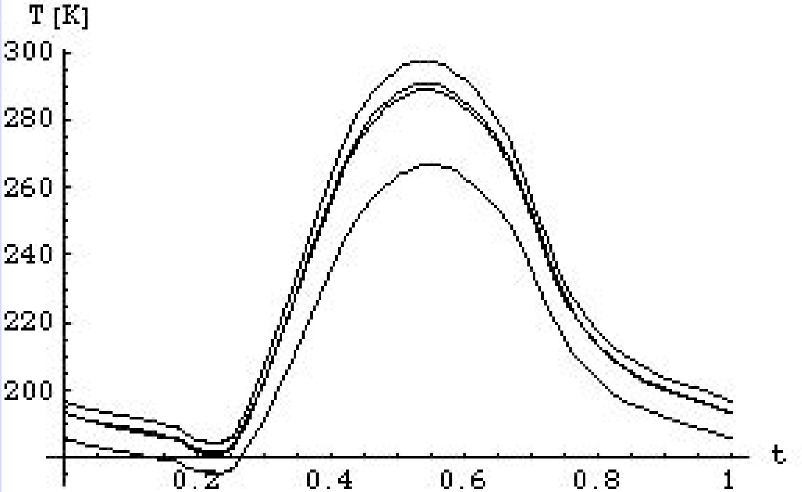
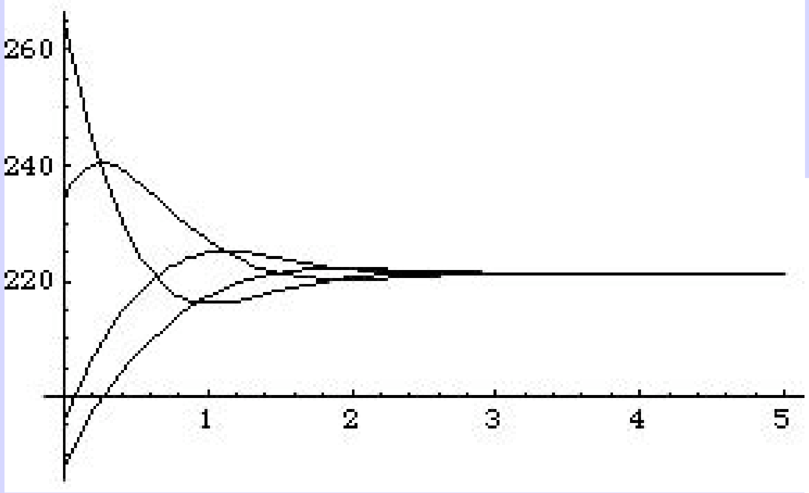




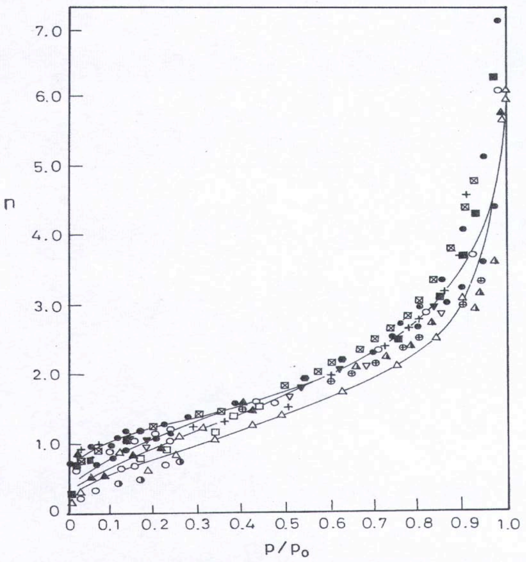
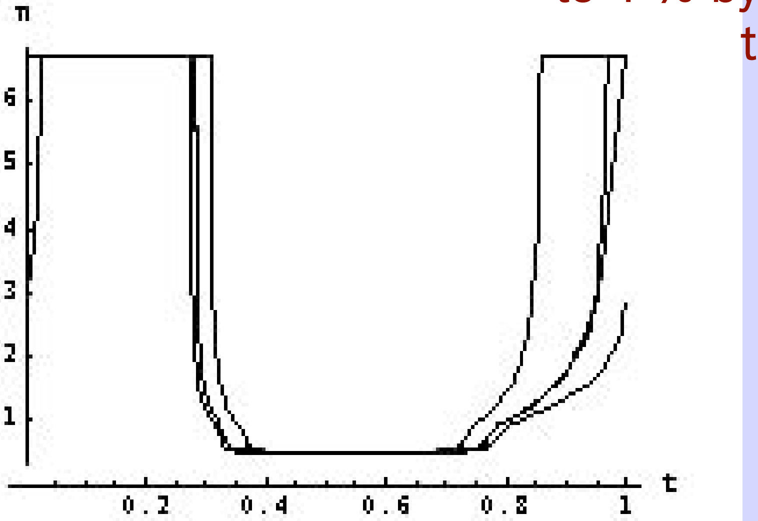


Fig. 2.31 *t*-Curves for pore structure analysis by water vapour adsorption[92]. The following symbols are used for the experimental points: zirconium silicate ($C = 4.2$) ◑ ◑; rutile ($C = 5.2$) △ △; silica ($C = 7$) ○ ○; silica gel, Davidson 81 ($C = 10$) □ □; zirconium silicate ($C = 14.5$) ▲ ▲; silica gel, Davidson 59 ($C = 23$) ▽ ▽; quartz ($C = 23$) ● ●; anatase (C about 50) ■ ■; anatase (C about 60) ⊕ ⊕; calcite (C about 70) ⊠ ⊠; barium sulphate (C about 120) ▼ ▼; barium sulphate (C about 160) ● ●; quartz (C about 200) + +

The presence of adsorption water is expected to have an influence on physical (mechanical, electrical, optical, thermal) properties of the upper martian soil.

Adsorption water is expected to exist (at least temporarily) in the upper martian surface with a content of about 3% to 4 % by weight (or temporarily more).



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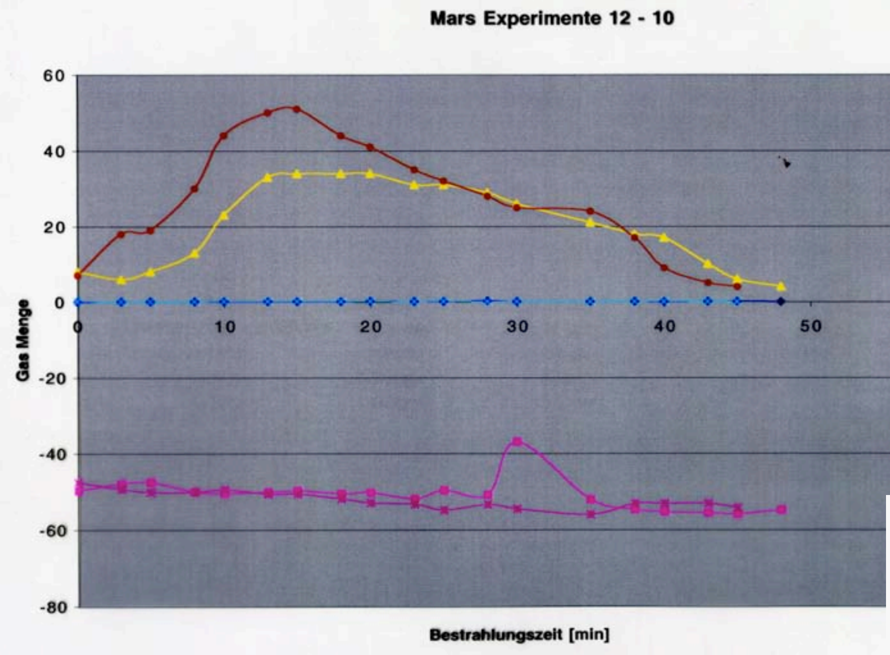

Experiments to study adsorption water supported and UV-driven chemistry on haematite (Jung, Sattler, Möhlmann, DLR- TT,RS - Cologne, 2003)

Result: Chemistry works with adsorption water,
oxidizing OH-radicals are produced and act oxidizing.

$$\mathrm{Fe_2O_3} + 3\,\mathrm{H_2O} \rightarrow 2\,\mathrm{Fe^{3+}} + 6\,\mathrm{H^-}$$

$$\mathrm{Fe^{3+}_{aq.}} + \mathrm{H_2O} \overset{\underbrace{h\,\nu}}{\rightarrow} \mathrm{OH^{\bullet}} + \mathrm{Fe^{2+}_{aq.}} + \mathrm{H^+}$$

Production of OH-radicals measured by Production of CO_2 (oxidation product of Isopropanol, which was added)

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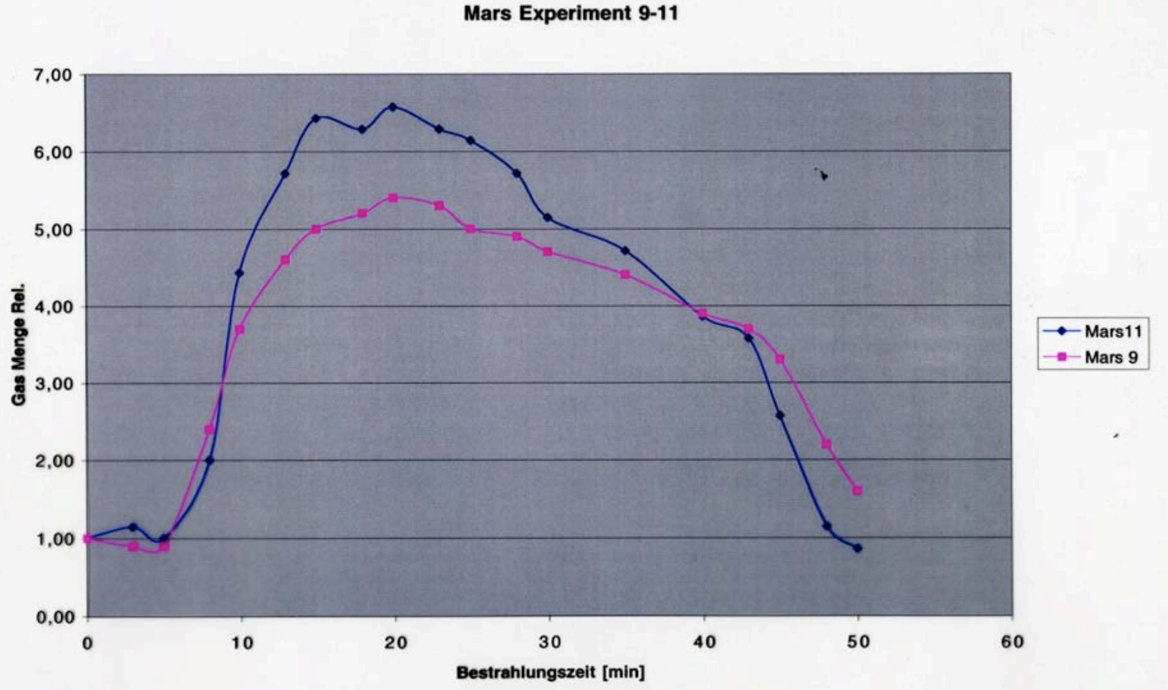

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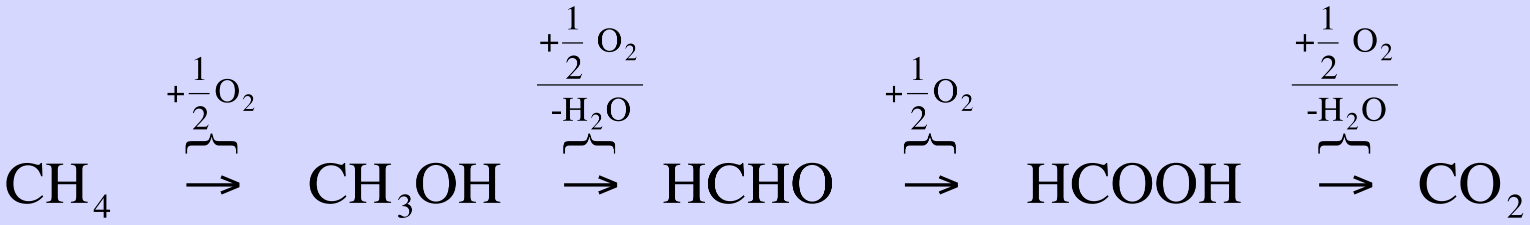
Oxidation of Methane :



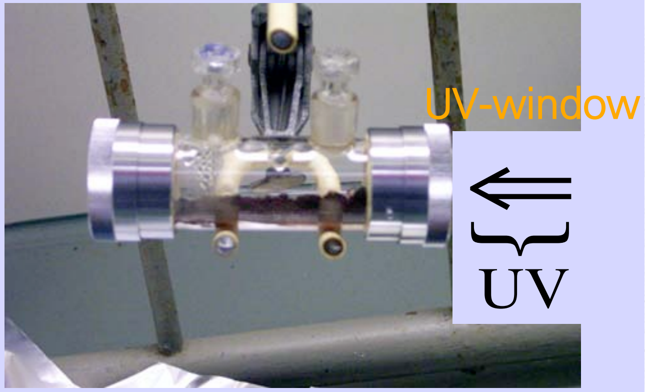
$$\mathrm{CH_4} \overset{\underbrace{+\frac{1}{2}\mathrm{O_2}}}{\longrightarrow} \mathrm{CH_3OH} \overset{\underbrace{\frac{+\frac{1}{2}\mathrm{O_2}}{-\mathrm{H_2O}}}}{\longrightarrow} \mathrm{HCHO} \overset{\underbrace{+\frac{1}{2}\mathrm{O_2}}}{\longrightarrow} \mathrm{HCOOH} \overset{\underbrace{\frac{+\frac{1}{2}\mathrm{O_2}}{-\mathrm{H_2O}}}}{\longrightarrow} \mathrm{CO_2}$$

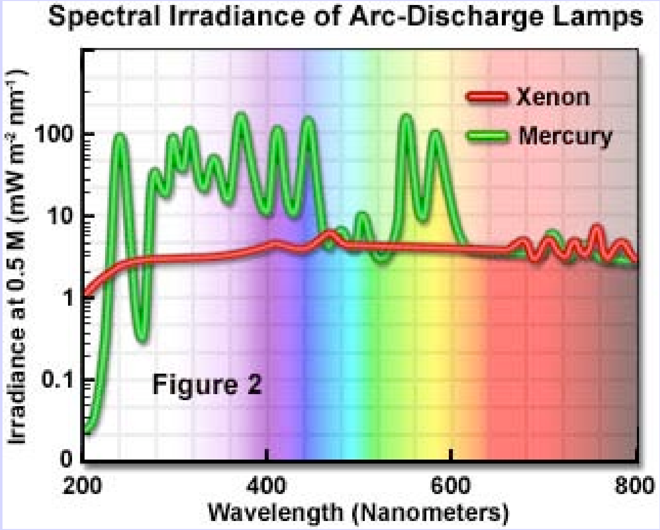
Methane Methanol Formaldehyde Formic acid

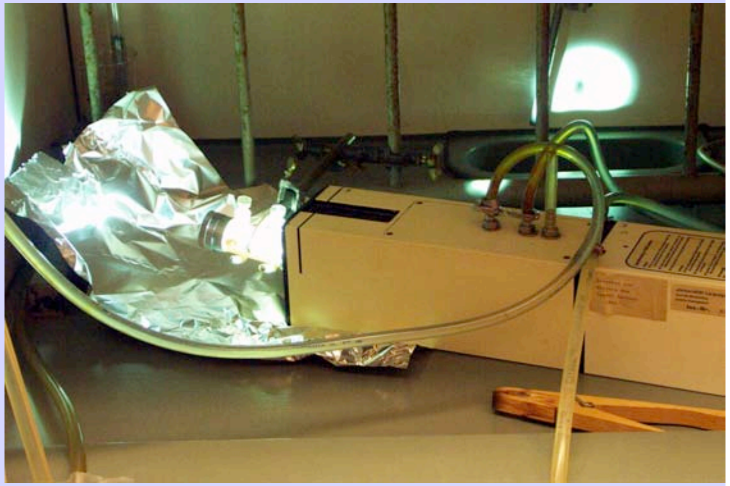
Mars-relevant experiment set-up: Inst. of Nonclassical Chemistry, University of Leipzig (Staudt, Wecks) and DLR Inst. of Planetary Research, Berlin (Möhlmann):

10 g wetted haematite (water:5% by weight) UV-source (HBO 100)
Atmosphere of 100% methane (25° C, 1013 bar) (no heating, IR is filtered out) experiment set-up

50 ml cuvette (reaction volume)







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Haematite and (adsorption-) water:

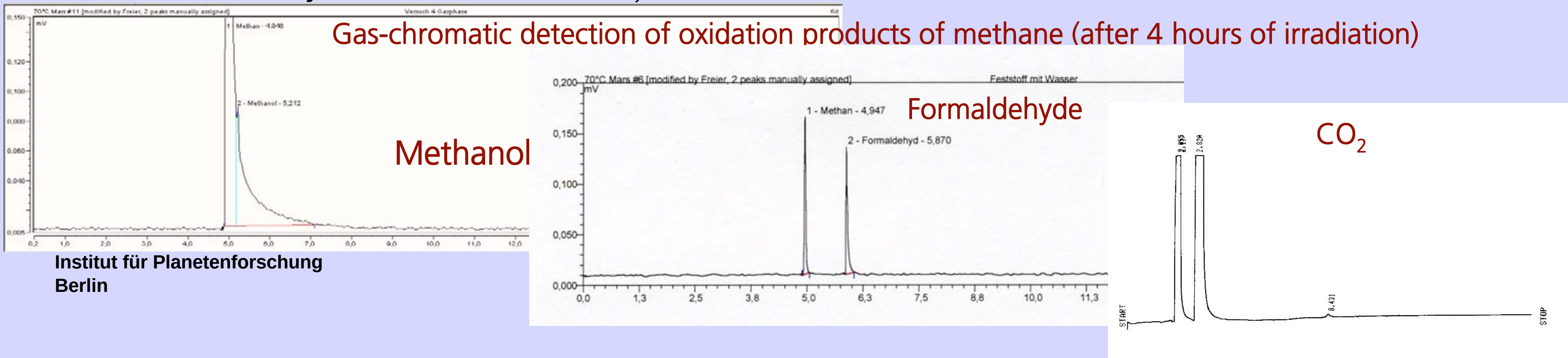
$$\mathrm{Fe_2O_3} + 3\,\mathrm{H_2O} \rightarrow 2\,\mathrm{Fe}^{3+} + 6\,\mathrm{H}^{-}$$

Photo-Fenton-reaction (UV-triggered reduction of iron):

$$\mathrm{Fe}^{3+}_{aq.} + \mathrm{H_2O} \overbrace{\rightarrow}^{h\nu} \mathrm{OH}^{\bullet} + \mathrm{Fe}^{2+}_{aq.} + \mathrm{H}^{+}$$

The resulting OH-radicals act extremely oxidizing. OH-radicals have a high oxidation potential.

Application to Mars: Haematite, UV and adsorption water are (at least locally and temporarily) present. Oxidizing OH-radicals are expected to be effective.
Methane is present on Mars with about 10 $\mathrm{ppb_V}$. (Formisano, 2004).
Oxidation of methane is expected. Proof by detecting resulting oxidation products (methanol, formaldehyde, formic acid, CO_2).



Gas-chromatic detection of oxidation products of methane (after 4 hours of irradiation)

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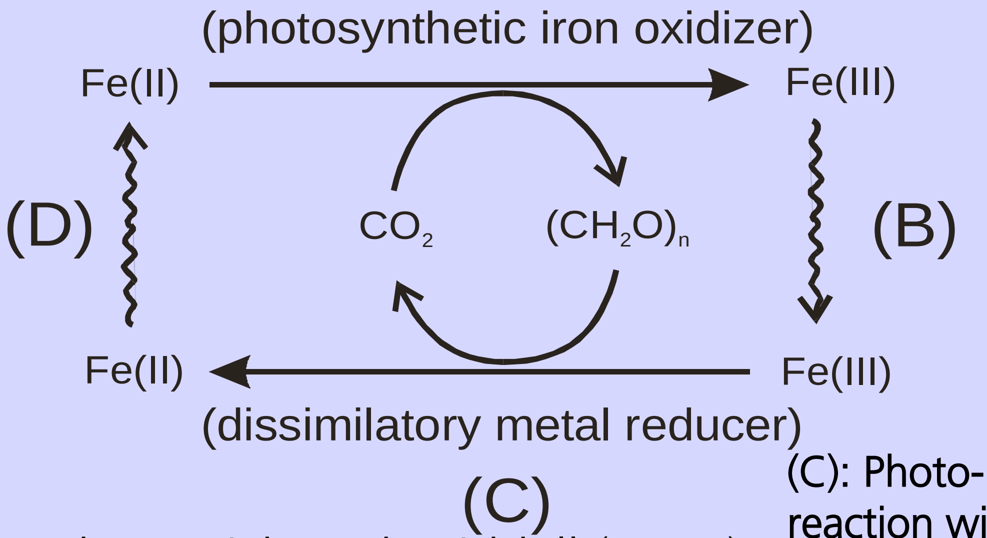
Reference: http://ntmf.mf.wau.nl/aquaporin/images/mechan._aqpl.jpg

Suggested by Nealson & Stahl (1997)
“to stimulate thought ...”(A)



(photosynthetic iron oxidizer)

$Fe(II)$ → $Fe(III)$

(D) CO_2 $(CH_2O)_n$ (B)

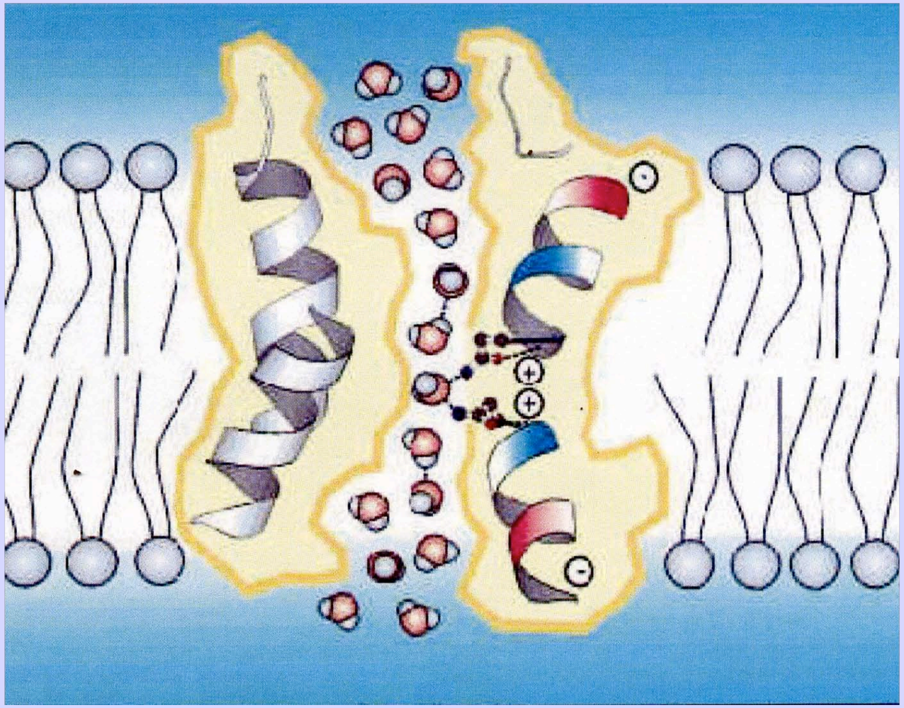
$Fe(II)$ ← $Fe(III)$

(dissimilatory metal reducer)

(C)

Ehrenreich and Widdell (1994) have isolated photosynthetic bacteria, which use the energy of sunlight to drive the fixation of CO_2 to „organic carbon“ in $(CH_2O)_n$: (A) $Fe(II) + CO_2 + H_2O \overset{\text{UV, sunlight}}{\rightarrow} Fe(III) + (CH_2O)_n$

(C): Photo-Fenton reaction with Haematite (FeIII-oxide), UV, and adsorption water



Can microbes (and other organisms ?) regulate their water balance by using adsorption water from their surfaces (via aquaporines, e.g.)?

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Adsorption water in the upper martian surface is an actual challenge to martian surface chemistry and possibly also to exobiology:

* Adsorption water makes possible and/or supports a martian surface chemistry, also at present: These processes are energetically driven by photons (UV). Current martian surface chemistry is mainly (non-thermal) photo-chemistry.

* Existing iron oxides (as haematite), UV and adsorption water are a cause for the production of oxidizing OH-radicals, which are expected to contribute to the oxidation of organics (Methane, carbonaceous meteorites).

* Adsorption water mobilizes acids (as sulfuric acid), which can modify earlier formed carbonates (surface cover by sulfates, e.g.).

* **Adsorption water covered catalytic surfaces** of minerals are expected to be essential agents in **non-thermal photo-chemical** processes. Photon driven non-thermal **redox-processes** on catalytic surfaces might together with atmospheric CO_2 cause a non-biogenic production of organics (?). Related experiments are in preparation.

* Adsorption water deposits also on the surfaces (cell walls) of microbes etc. There, it can be a source of water for the microbial metabolism. Physico-chemical processes can be supported by adsorption water. To study the relevance of adsorption water for life-processes is a current challenge to exobiology. Related experiments are in preparation.

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