

CO₂ fixation on metal oxides

Svatopluk Civiš

Chemie CO₂ a TiO₂

aneb

Od dýchajících minerálů k životu na Marsu

Obsah přednášky

Studium TiO₂ nanomateriálů a představení jejich unikátních vlastností

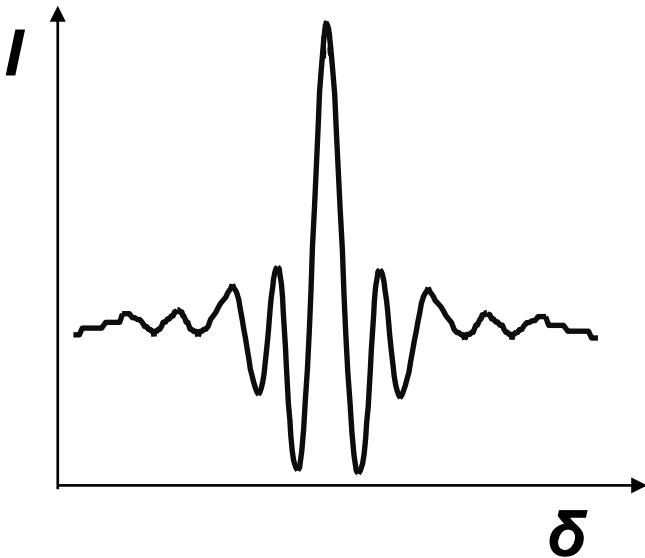
1. Výměna kyslíků mezi CO₂ a kyslíkatými minerály
2. Fotokatalytická redukce **CO₂** na povrchu minerálu (katalyzátoru)
$$\text{CO}_2 + \text{TiO}_2/\text{montmorillonite} + \text{UV} + [\text{H}^+] \rightarrow \text{CH}_4$$
3. Vznik **CH₄** na **Marsu**
4. Tvorba vody na povrchu TiO₂ (sluneční vítr)



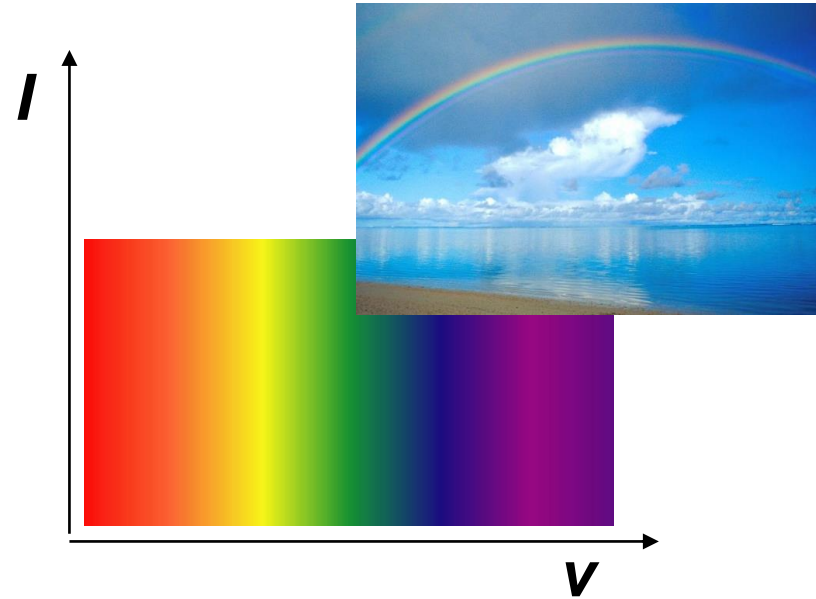
IFS 125HR

Fourier transformation

Interferogram



Spectrum

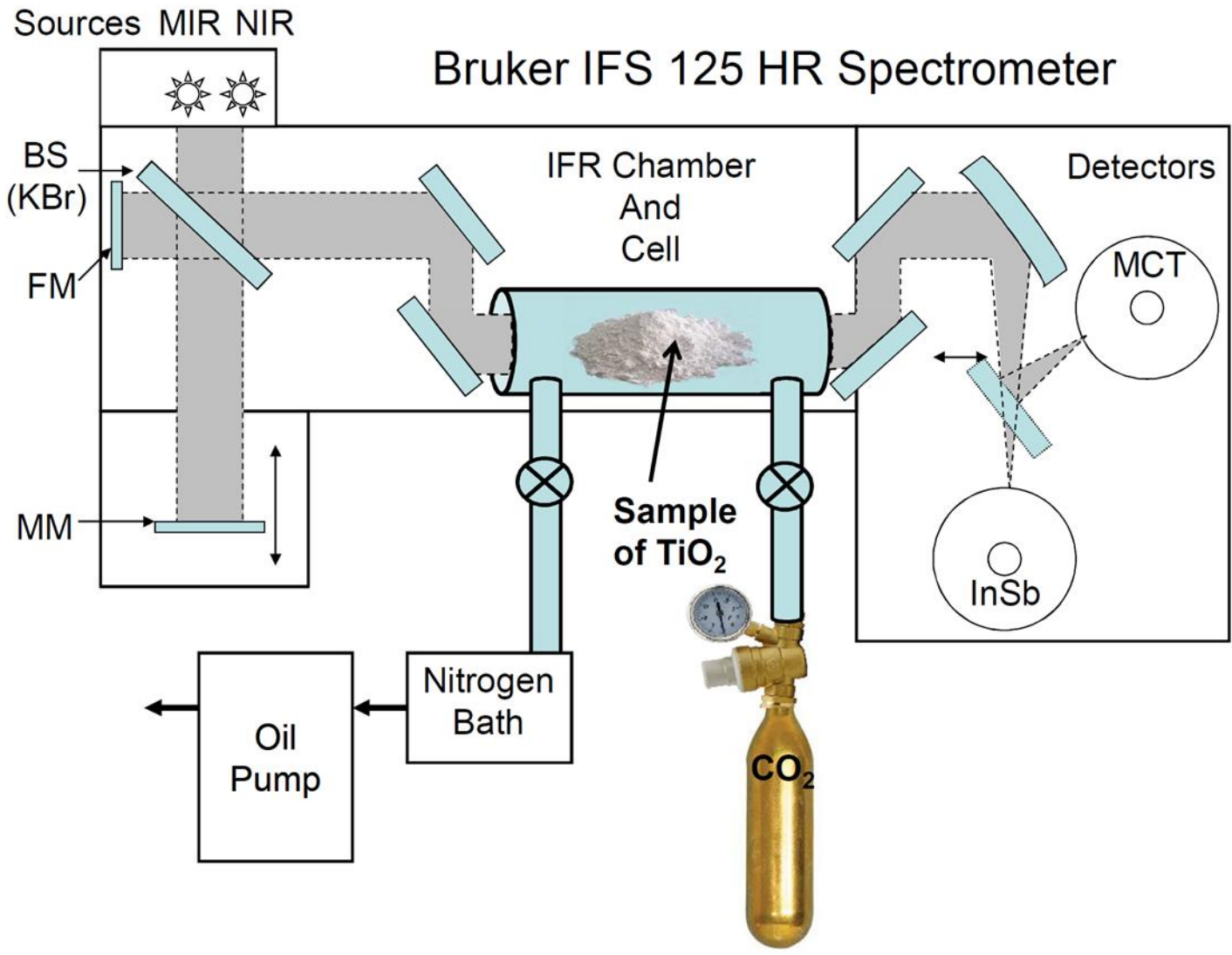


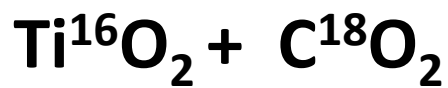
$$I(\delta) = \int_{-\infty}^{\infty} B(\nu) \cos(2\pi\nu\delta) d\nu$$



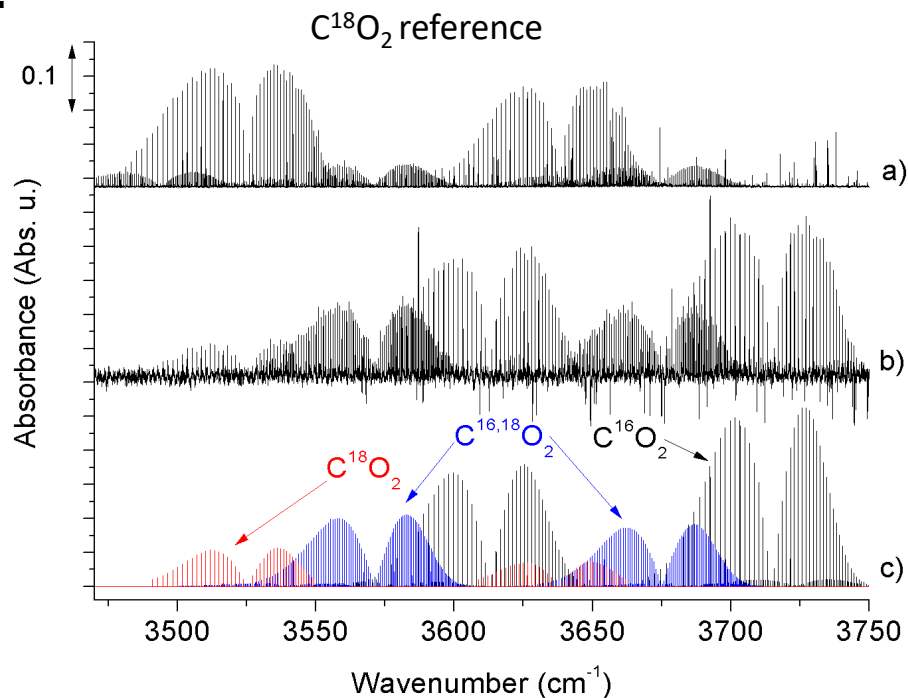
$$B(\nu) = \int_{-\infty}^{\infty} I(\delta) \cos(2\pi\nu\delta) d\delta$$

S3.





3.

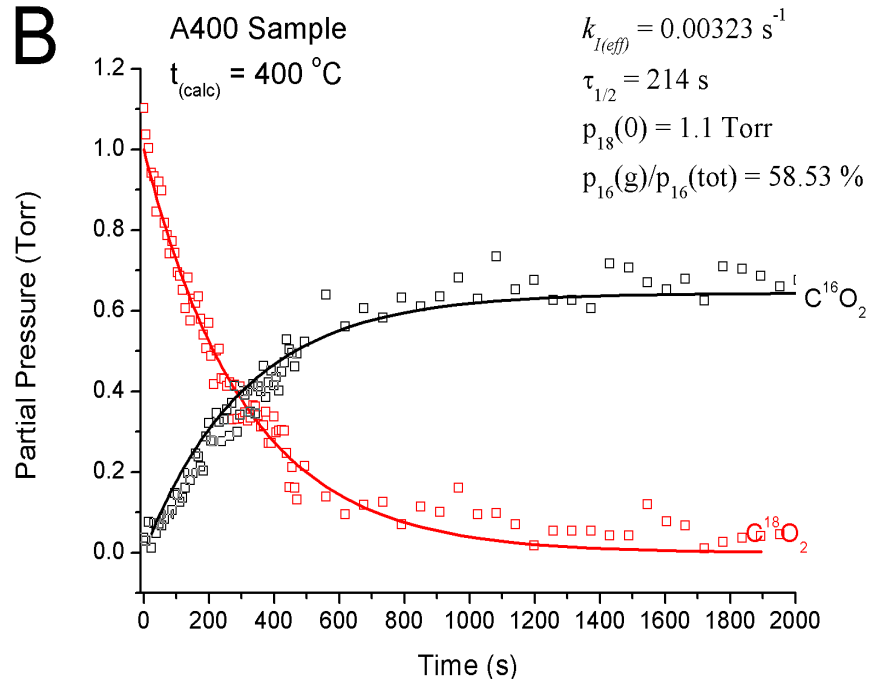


HR-FTIR spectra of the $\nu_1+\nu_3$ and $2\nu_2+\nu_3$ combination bands of CO_2 near 3600 cm^{-1} following oxygen isotope exchange between A450 Ti^{16}O_2 and C^{18}O_2 .

- The reference spectrum of C^{18}O_2 .
- The experimental spectrum measured after 300 s of contact together with C^{18}O_2 with A450.
- Simulated spectrum using the Winproof program for HIRTRAN database

Fast measurement –
1 scan only, speed of scanning mirror
80 kHz

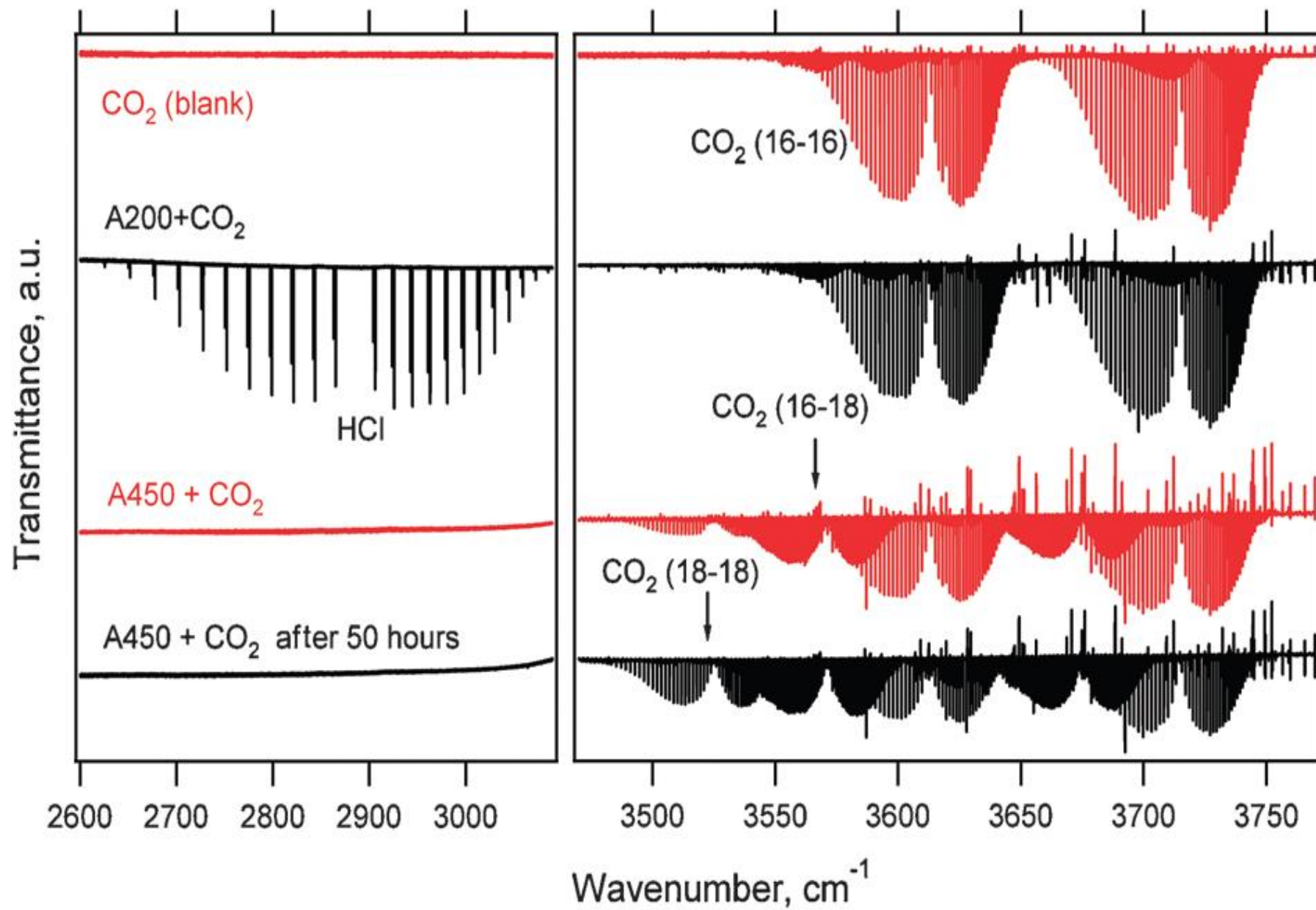
B

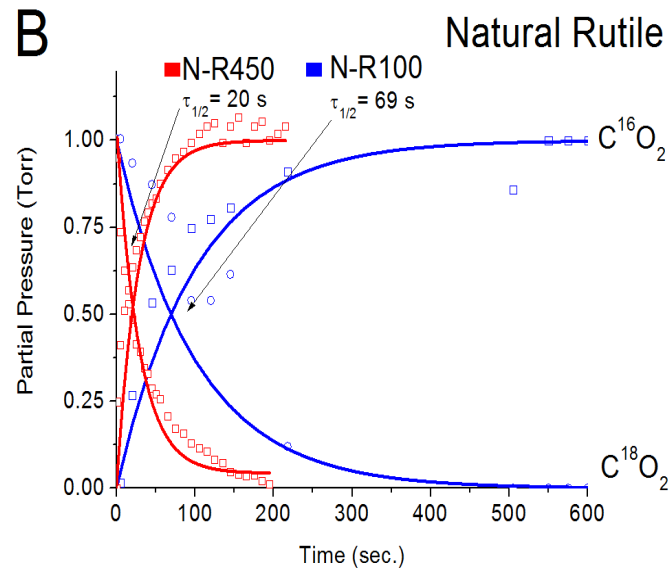
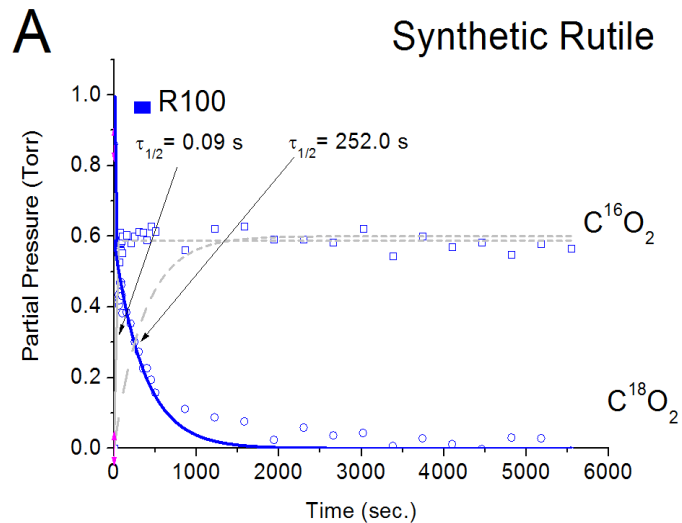


S1.

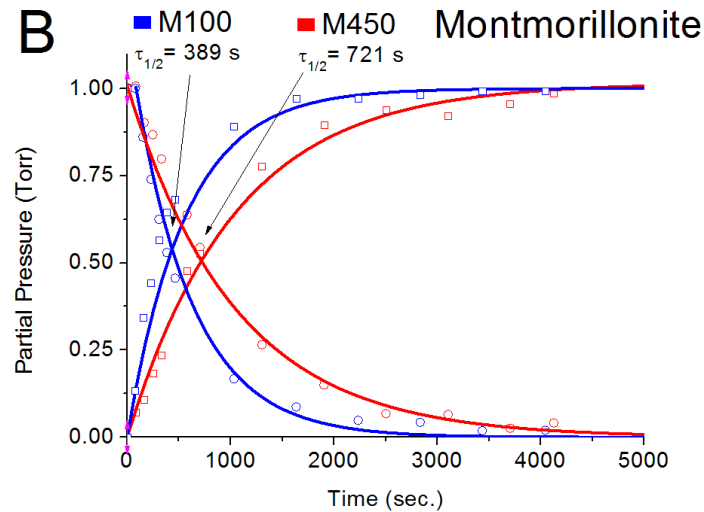
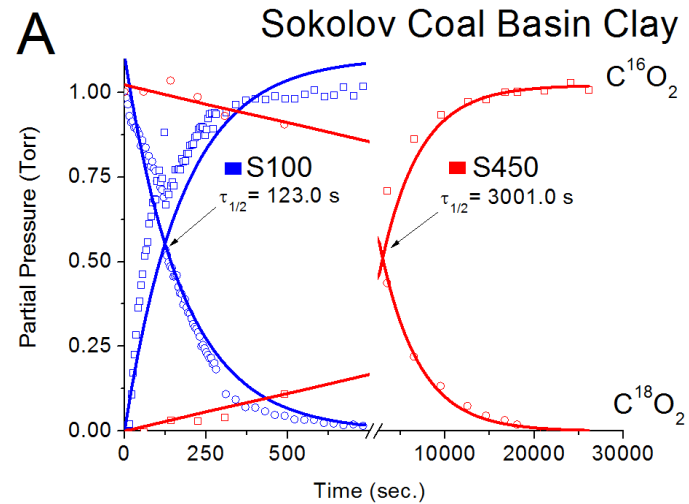
Ti^{18}O_2

C^{16}O_2



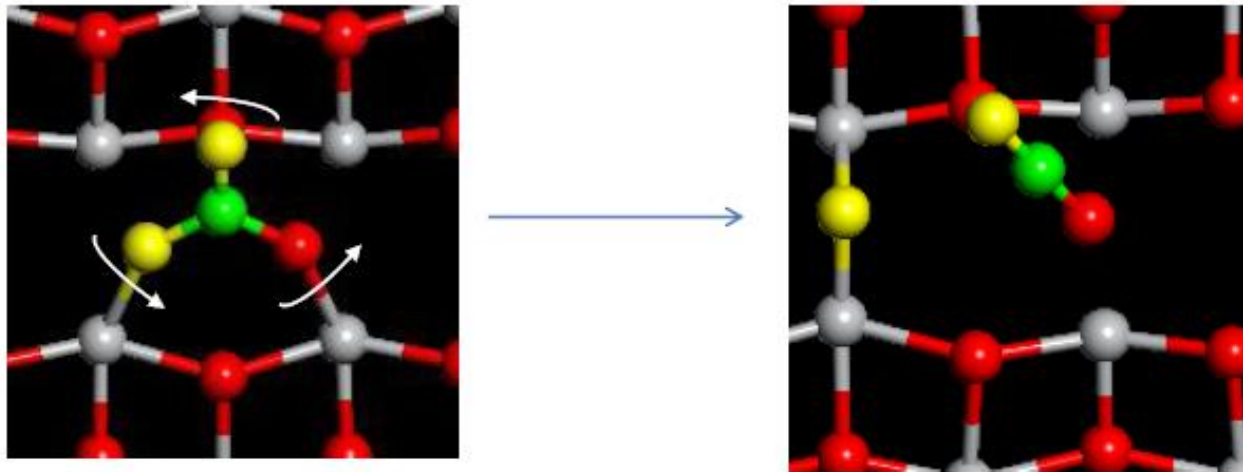


Comparison of the C^{18}O_2 oxygen exchange activities of non-calcined nanoscale samples of Ti^{16}O_2 with synthetic rutile in panel A and natural rutile in panel B.

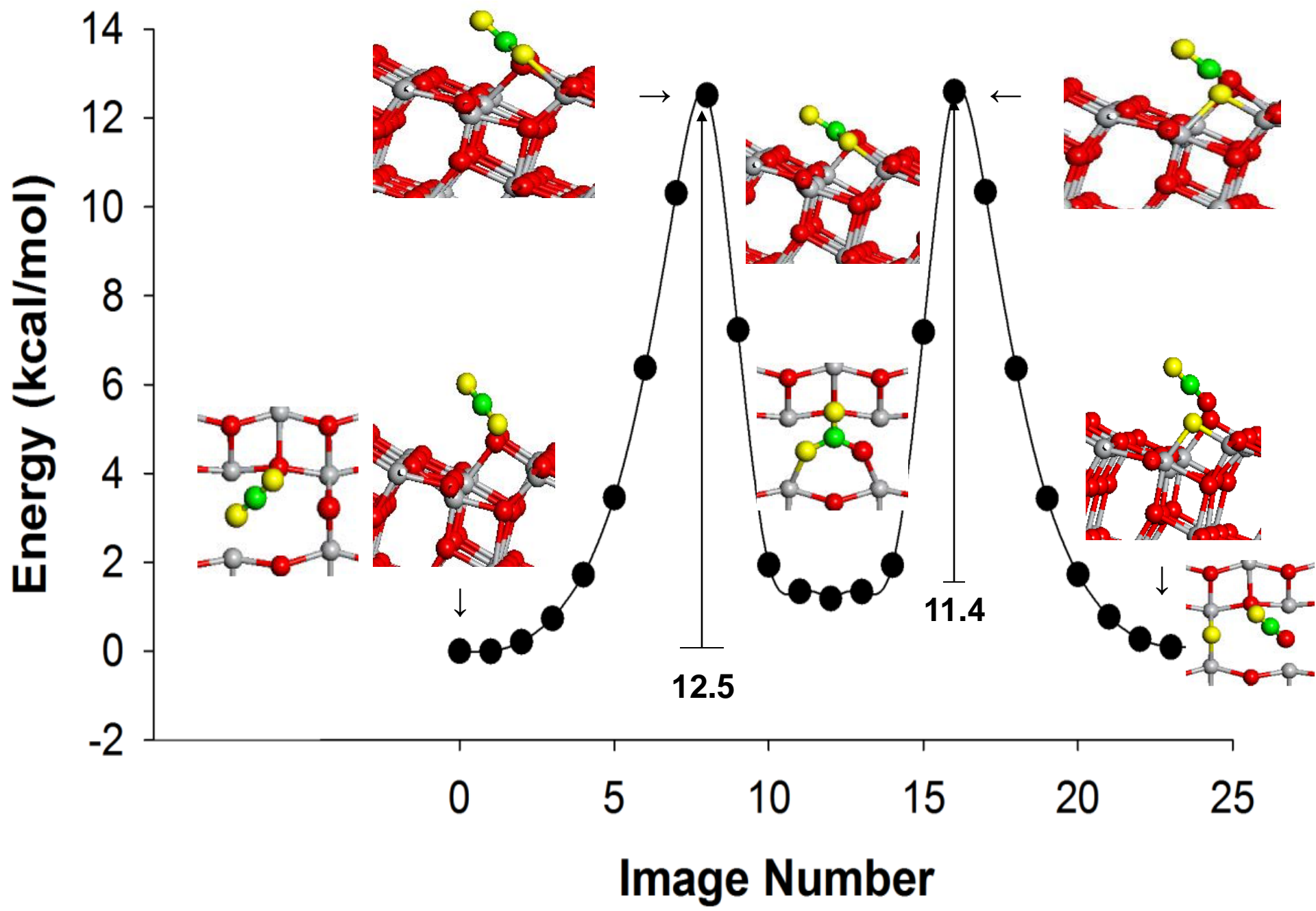


Comparison of the C^{18}O_2 oxygen exchange activities between non-calcined and calcined samples of the Sokolov Coal Basin clay (Sample 1) (**A**) and montmorillonite (Sigma Aldrich) (**B**).

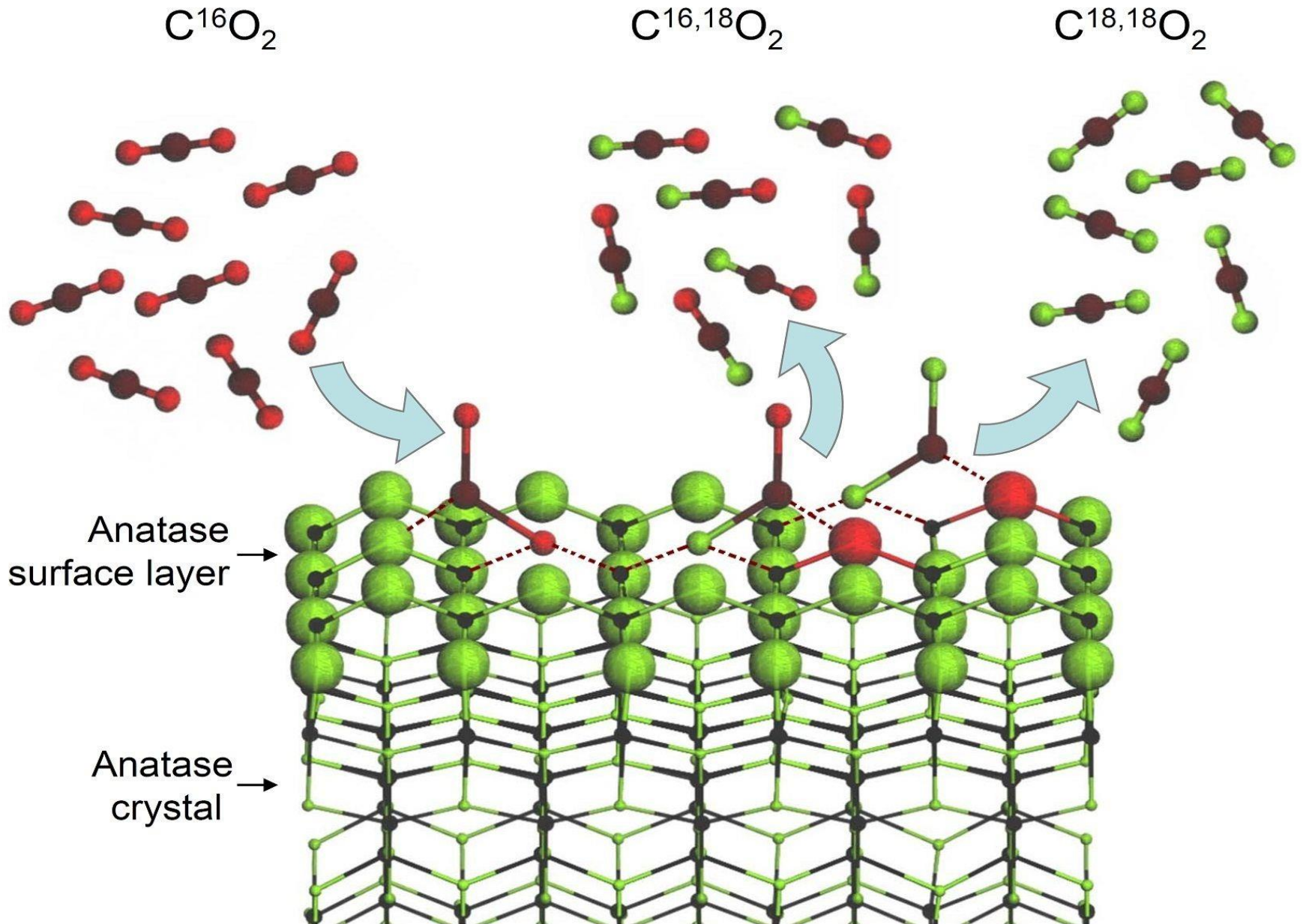
Mechanism II: Thermal rotation of CO_3 followed by O- CO_2 bond rupture and CO_2 desorption



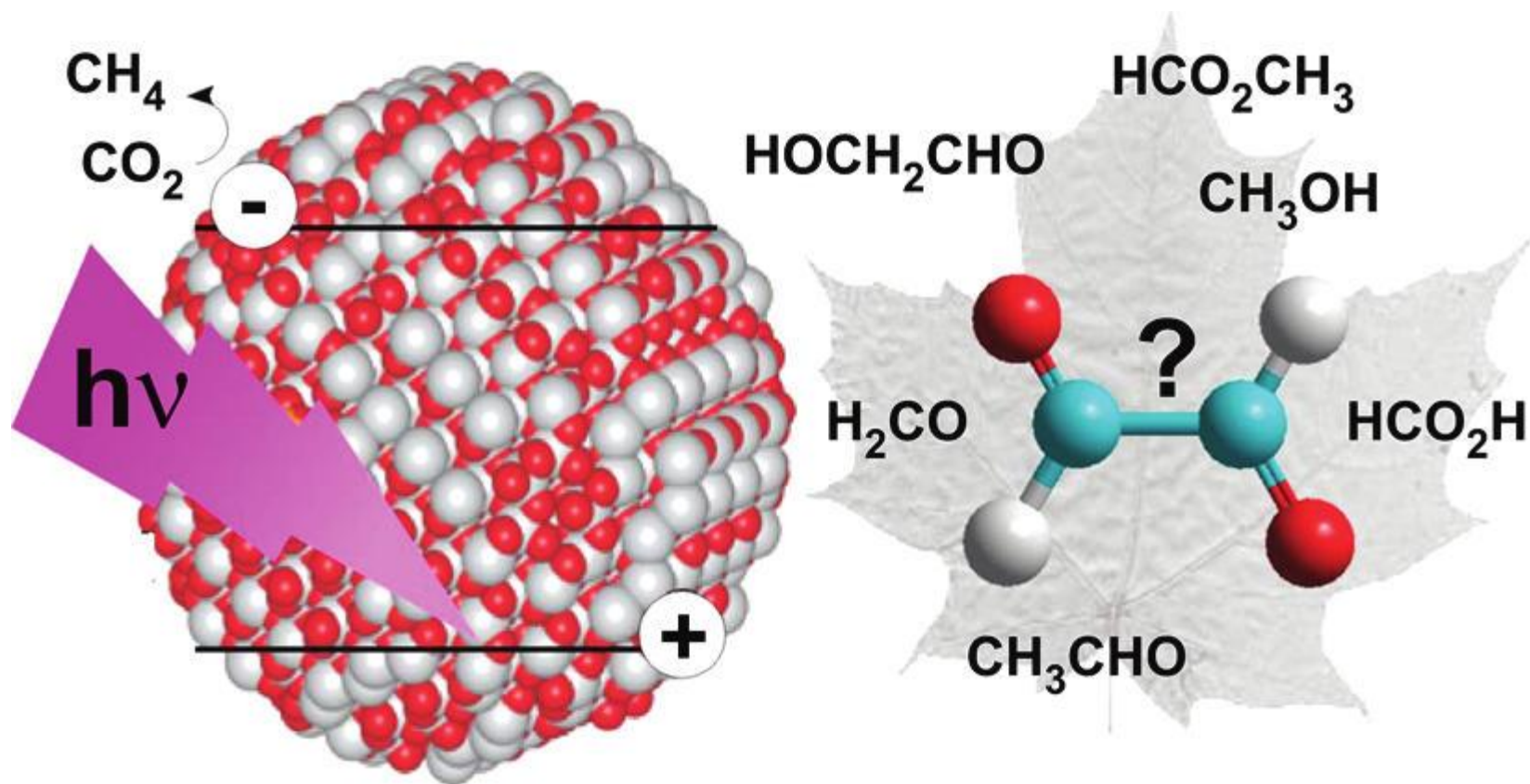
The barrier for such a process needs to be evaluated.



Oxygen Reduced TiO_2 Anatase: in dark, room temperature self operating convertor of CO_2



Fotokatalytická redukce

$$\text{Ti}^{16}\text{O}_2 + \text{CO}_2 + \text{H}_2\text{O} + [\text{H}^+]$$


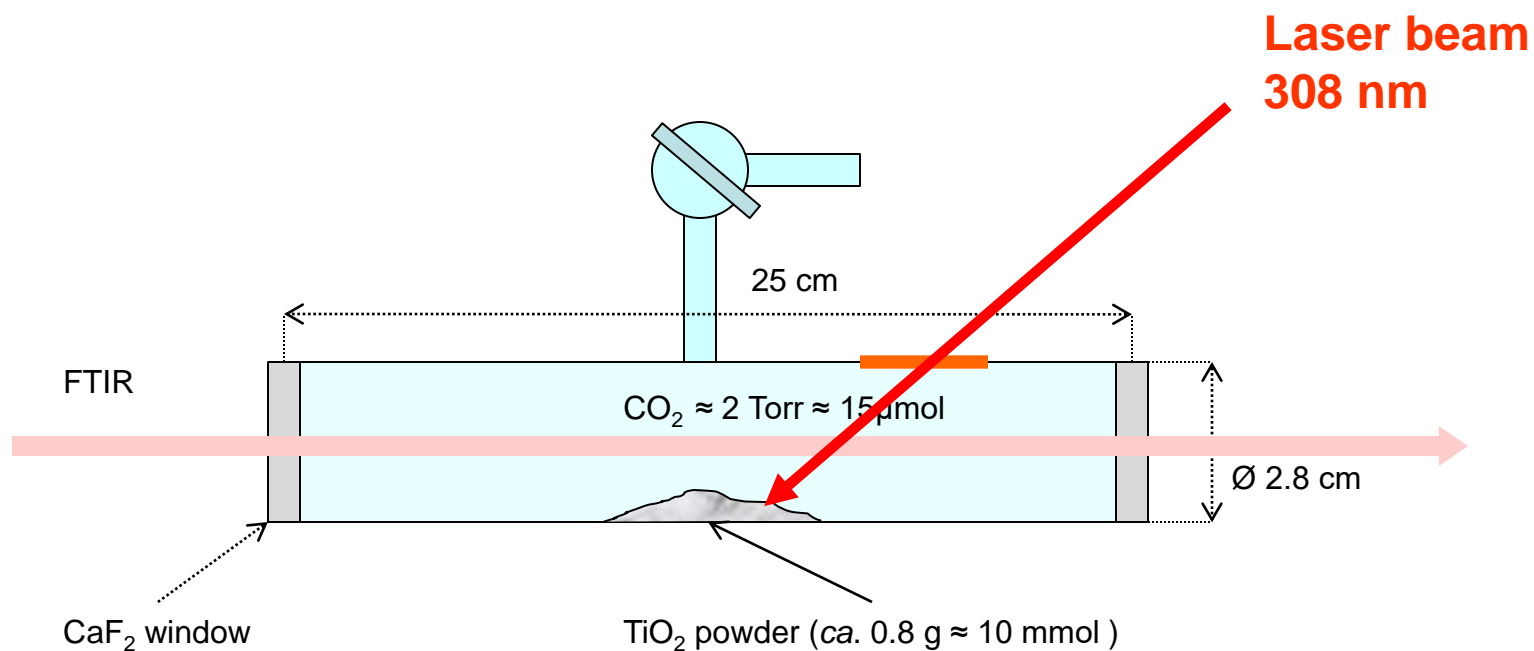
CO₂ fixation on metal oxides

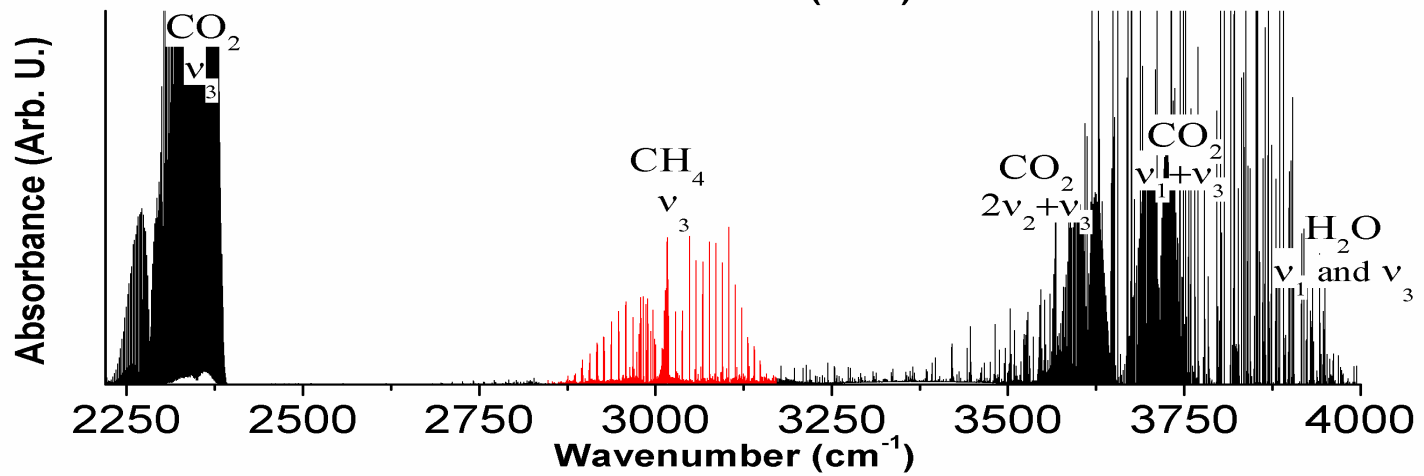
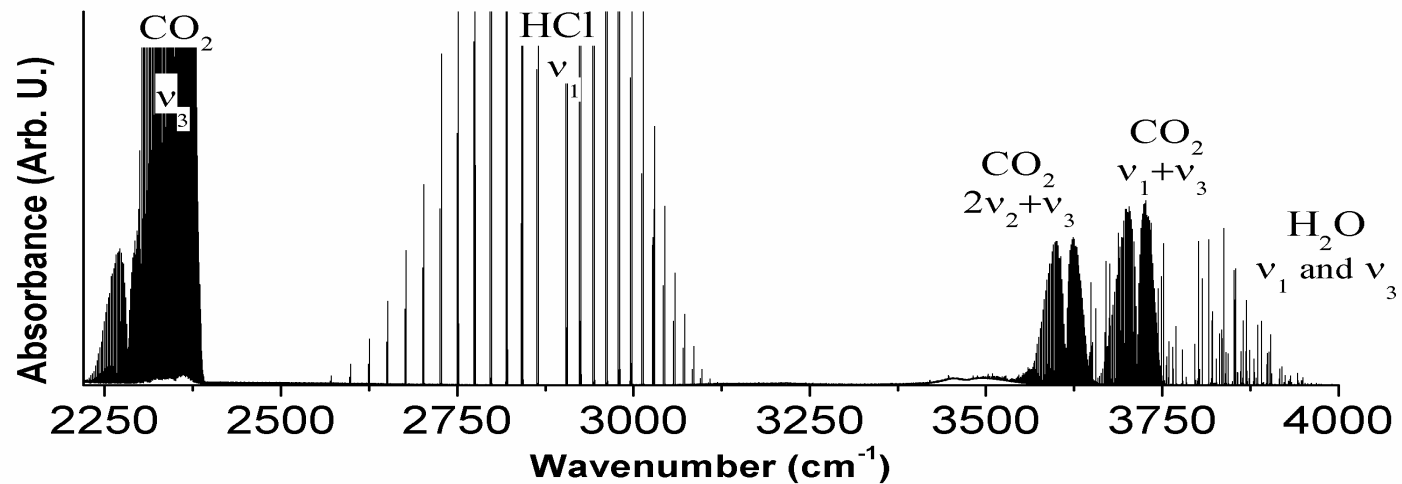
Fotokatalytická redukce

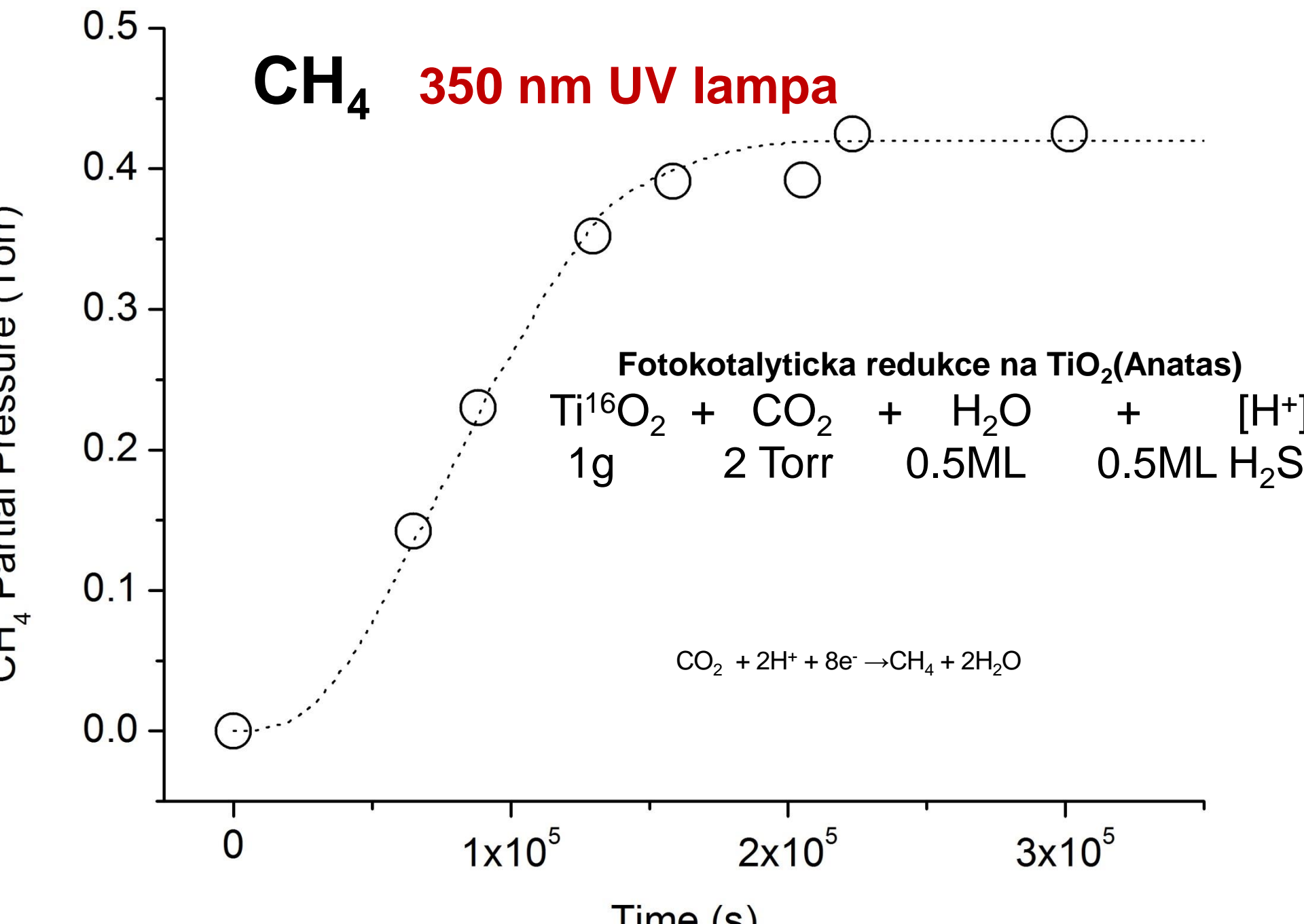


0.8 g 2 Torr

0.5ML + 0.5ML HCl







CO₂ is stepwise reduced to the formyl radical in reactions 1 to 3;

(b) two formyl radicals recombine to yield glyoxal

(c) glyoxal is reduced to glycolaldehyde

(d) glycolaldehyde is reduced to acetaldehyde

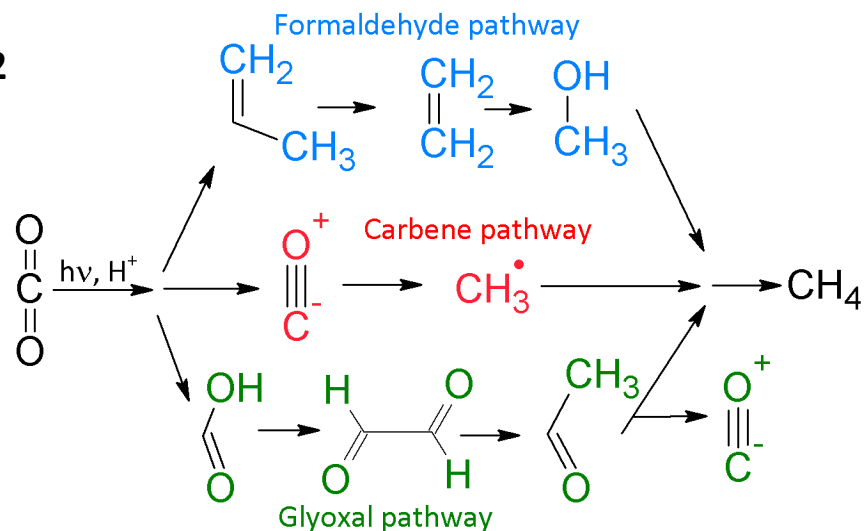
(e) acetaldehyde is oxidized to the methyl radical

(f) the organic intermediates generated in these reactions (including formate, methanol, and formaldehyde) serve as sacrificial hole scavengers;

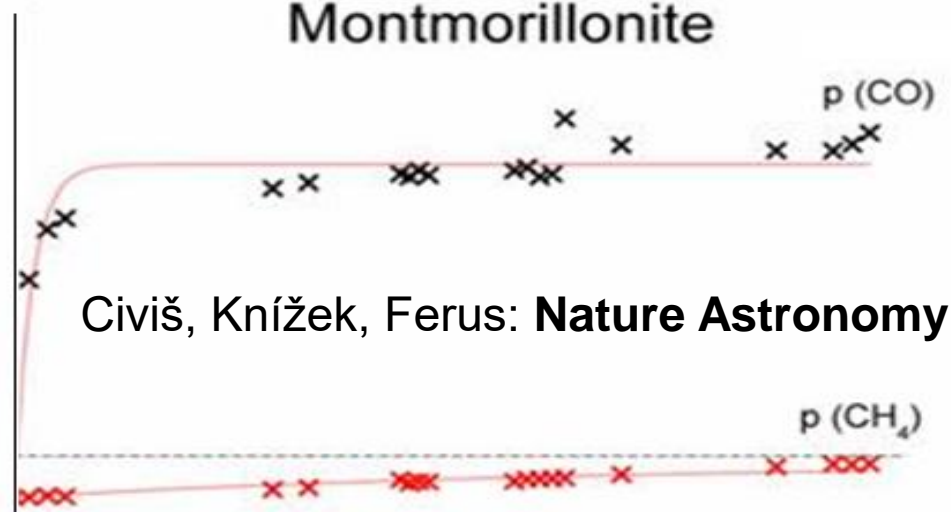
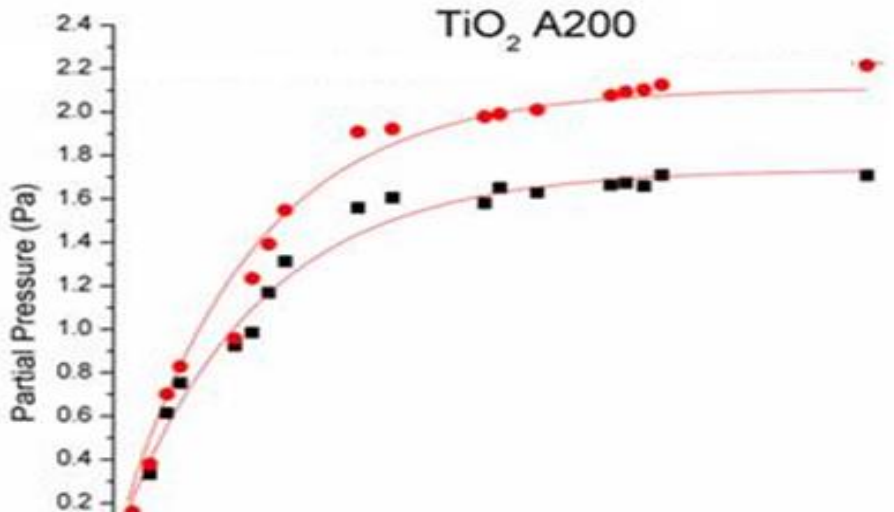
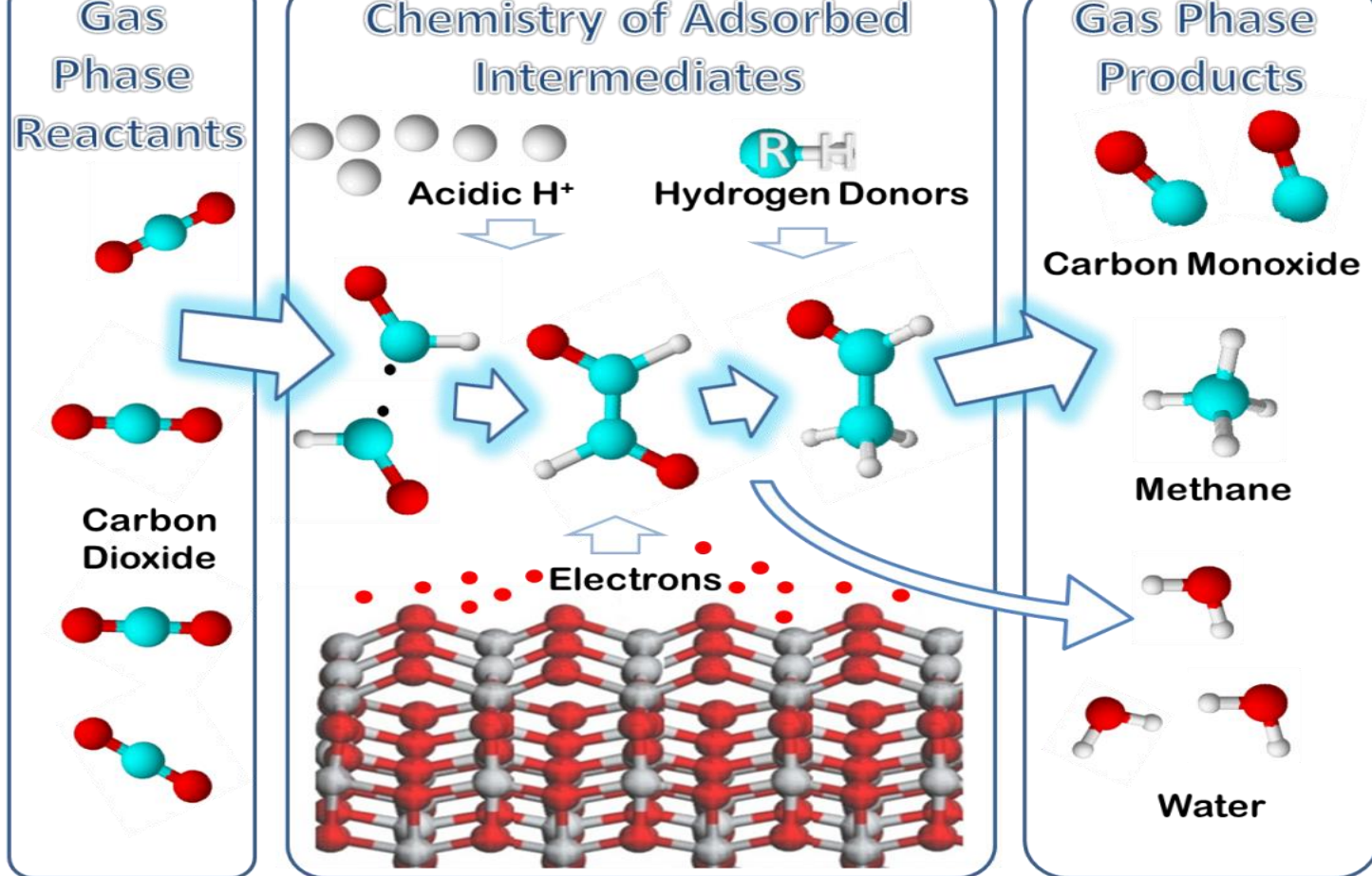
(g) the hydroxymethyl radicals recombine, yielding ethylene glycol, which is oxidized to the vinoxyl radical

Navrhované reakce redukce CO₂ na metan

- 'glyoxal pathway'



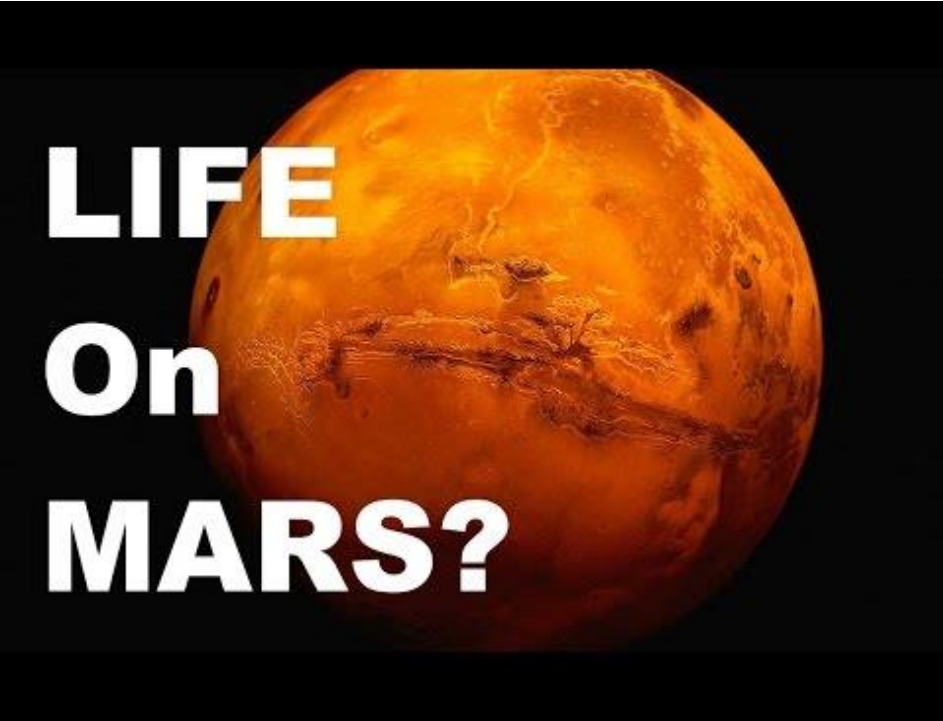
P. Zapol et al., *J. Phys. Chem. C* 2012, 116, 9450–9460,



Civiš, Knížek, Ferus: **Nature Astronomy**

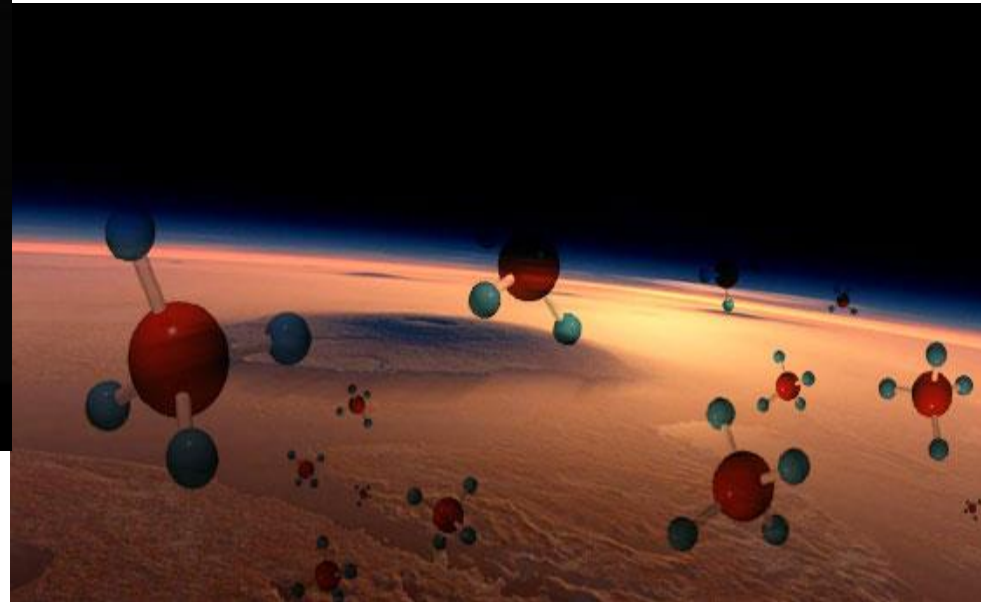
Planetární chemie na Marsu

- Povrch Marsu: Fe^{3+} oxidy - regolith (1% TiO_2)
- Atmosféra hlavně CO_2
- Stopové množství metanu v atmosféře
- Koncentrace metanu je proměnlivá

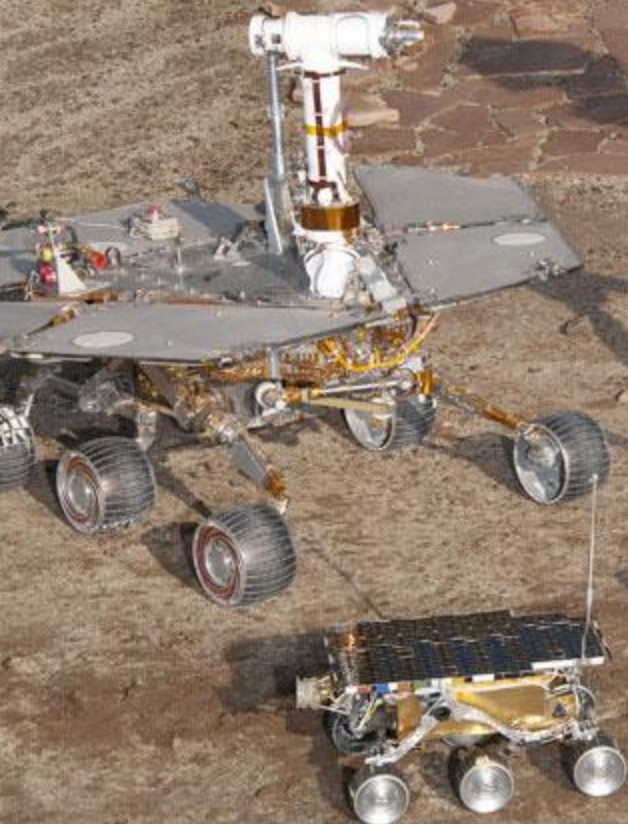


**LIFE
On
MARS?**

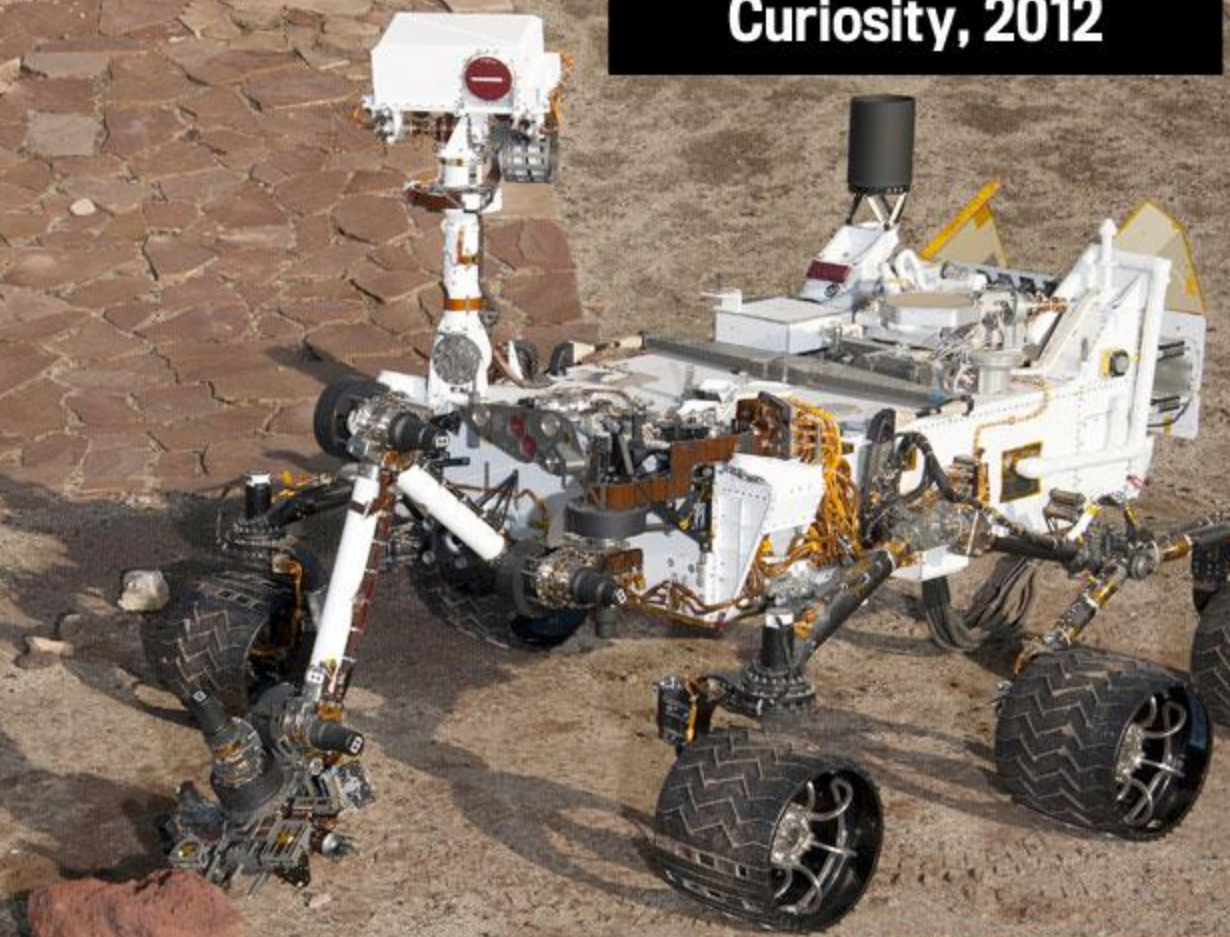
Metan na Marsu- život?



Spirit/Opportunity, 2004



Curiosity, 2012

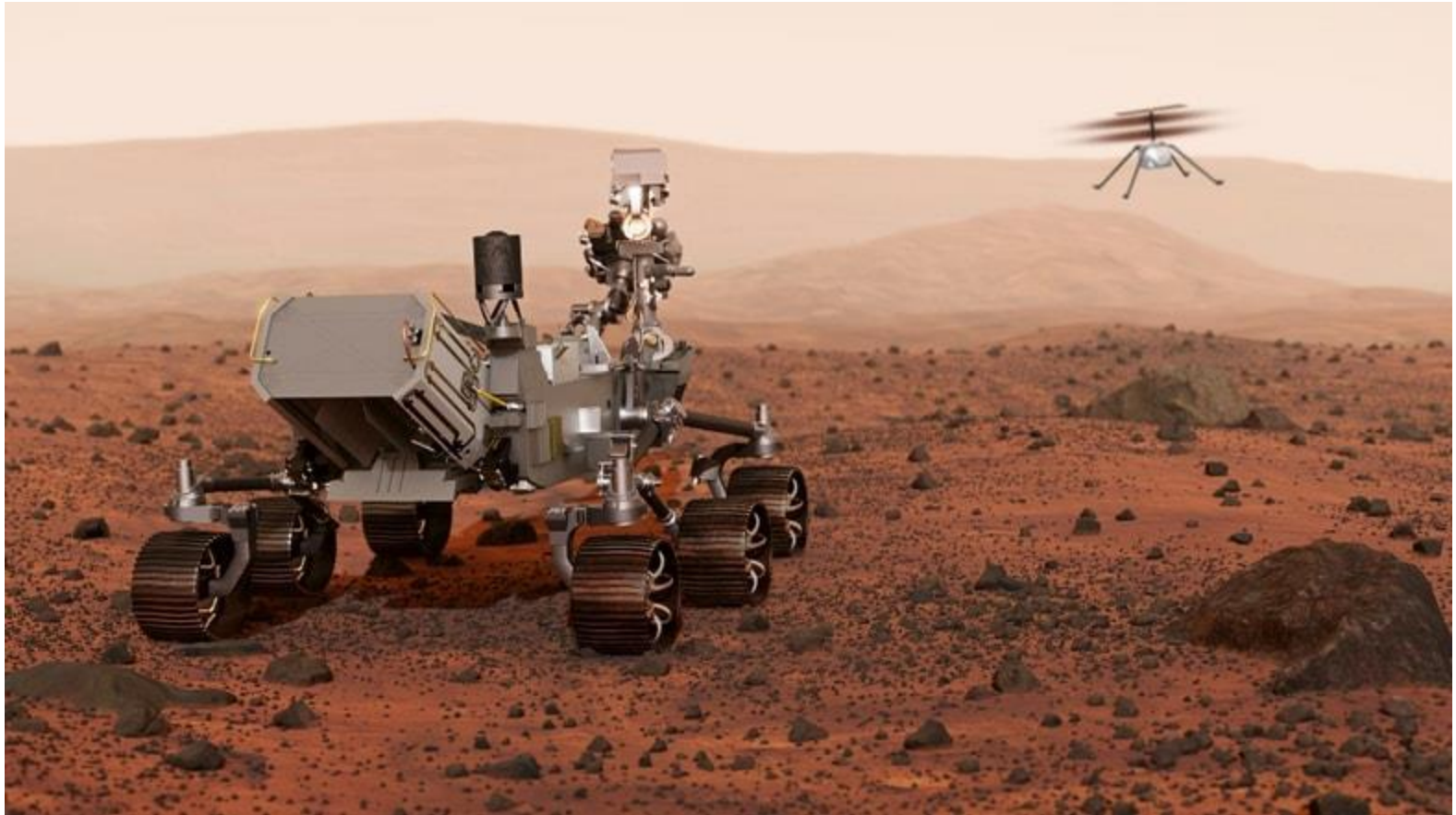


Sojourner, 1997





NASA's Perseverance Rover slaví více jak rok na Marsu



Mars Curiosity Rover Mission



**Marsovská vozítka“
Curiosity“, ‘selfie‘
Aeolis Mons foothill
6/10/2015**

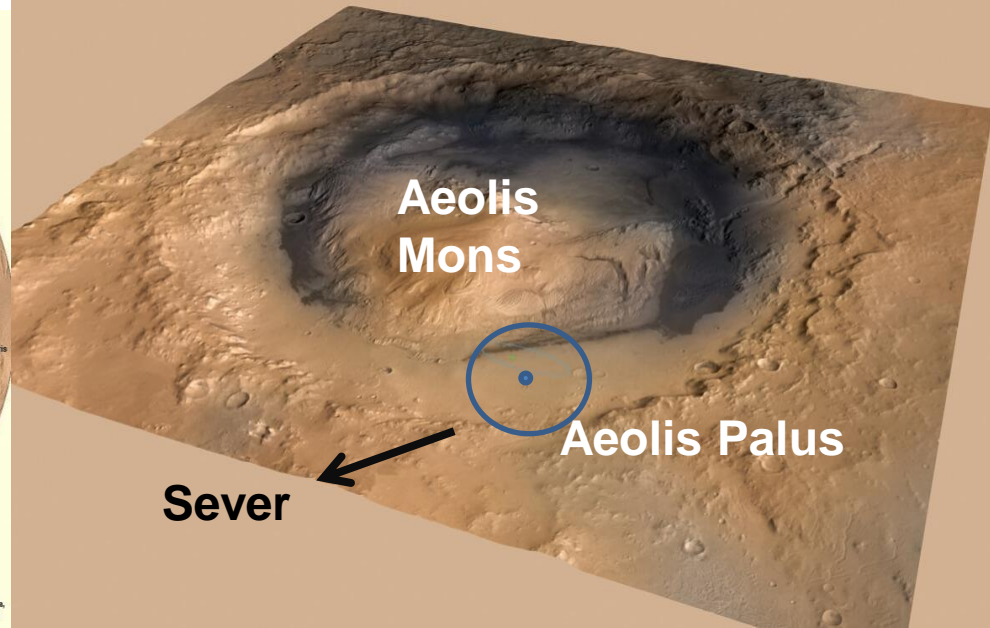
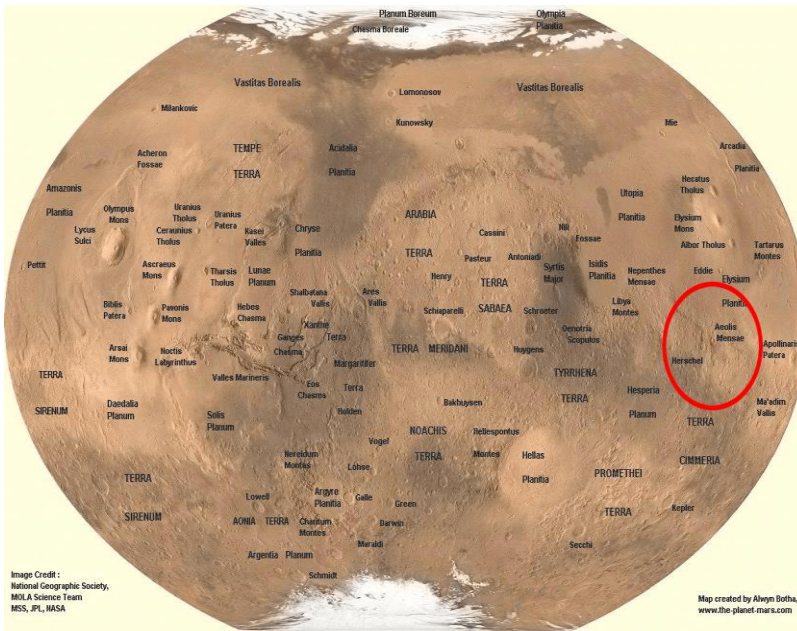
**vypuštěno: 26 November 2011 15:02 UTC,
Cape Canaveral, Florida, USA**

**přistání: 6 August 2012 05:17 UTC, Aeolis
Palus, Gale Crater, Mars**

cíle:

- **Část NASA marsovská vědecká laboratorní mise**
- **Výzkum klimatu a geologie**
- **Výzkum podmínek pro život v kráteru Gale v průběhu historického vývoje Marsu**
- **Role vody na Marsu**
- **Průzkum obyvatelnosti planety**
- **Určení koncentrace metanu v průběhu roku**

Gale kráter



- Severozápadní strana Aeolis quadrangle, těsně pod rovníkem
- 5.4°S , 137.8°E
- Aeolis Mons (Mount Sharp) uprostřed
- Aeolis Palus – planina na severní straně – místo přistání Curiosity

Data z Curiosity

- **Analýza vzorků na Marsu –laser diodový laditelný spektrometer**
- **0.7 ppb CH₄ v atmosféře**
- **Výkyvy až 7 ppb CH₄**
- **atmosférická voda od 10 ppm do 60 ppm v Gale kráteru**
- **Atmosférický tlak od 7 mbar do 9.5 mbar (95.2% atmosféry je CO₂)**



Curiosity's view of Aeolis Mons (20/9/2012)

Navržené scénáře sezóního kolísání metanu

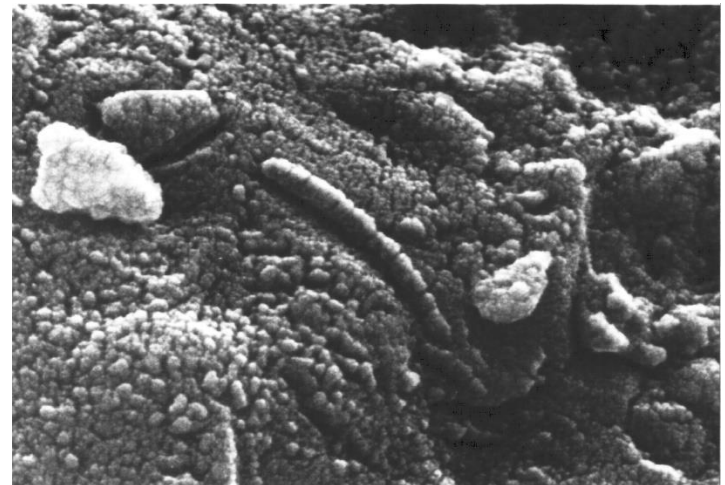
Scenář #1

- Regolit v Gale kráteru adsorbuje metan (suché období), uvolňování metanu dochází za vlhka
- Regolit obvykle adsorbuje metan CH_4 (sucho)
- Při odpařování povrchu, chloristany které jsou na povrchu regolitu deaktivují adsorpční místa a dochází následně k uvolňování CH_4

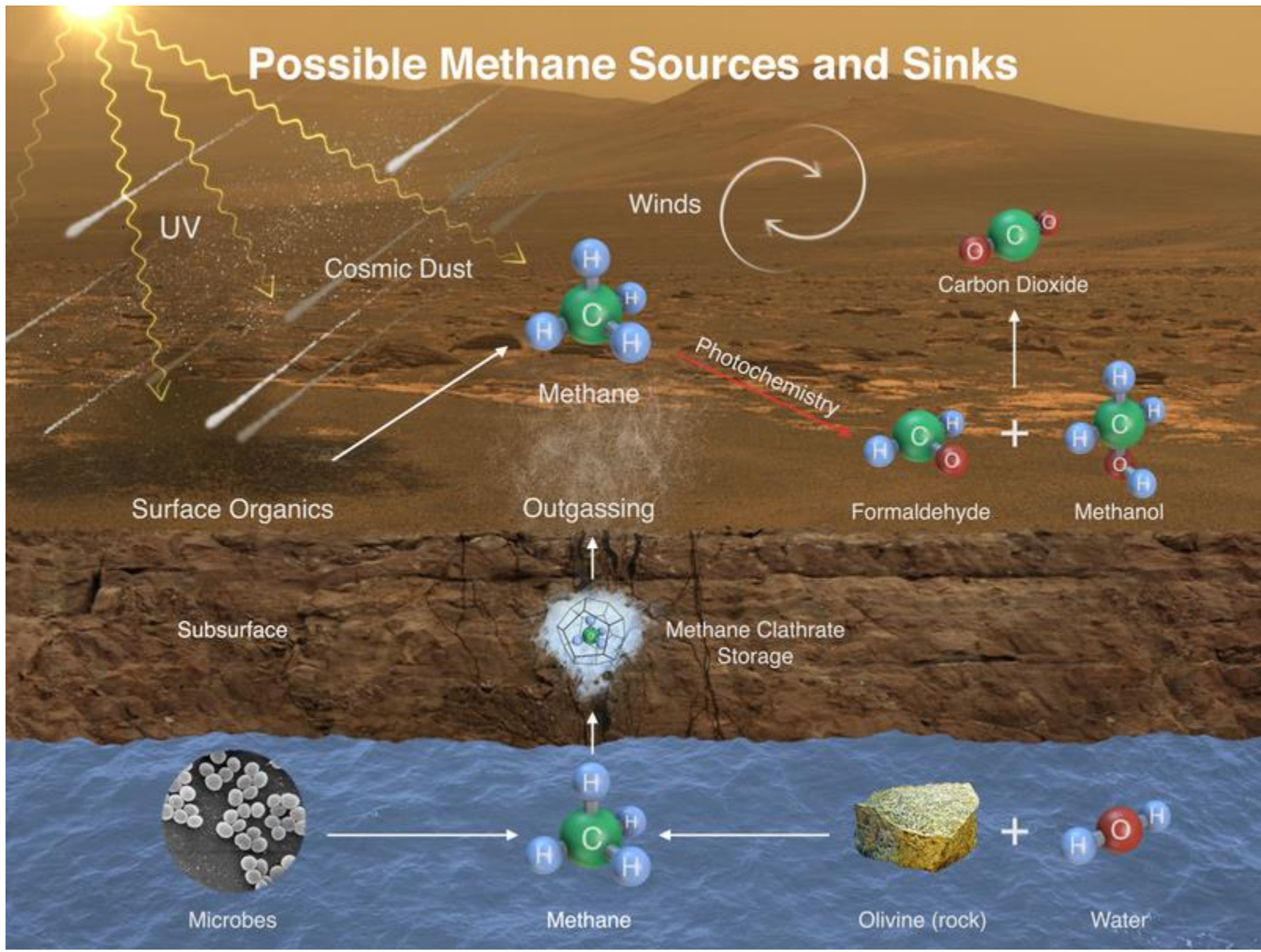


Scenář #2

- Mikroorganismy konvertují v kapalném stavu organickou hmotu na metan
- Předpoklad existence života na Marsu
- Motivací pro tuto hypotézu bylo objevení chlorobenzenu a dichloroalkanů v Yellowknife Bay (oblast kráteru Gale)
- Mikroorganismy na Zemi jsou přímo schopny hydrogenace. (e.g. *Hydrogenobacter thermophilus*, *Helicobacter pylori*)

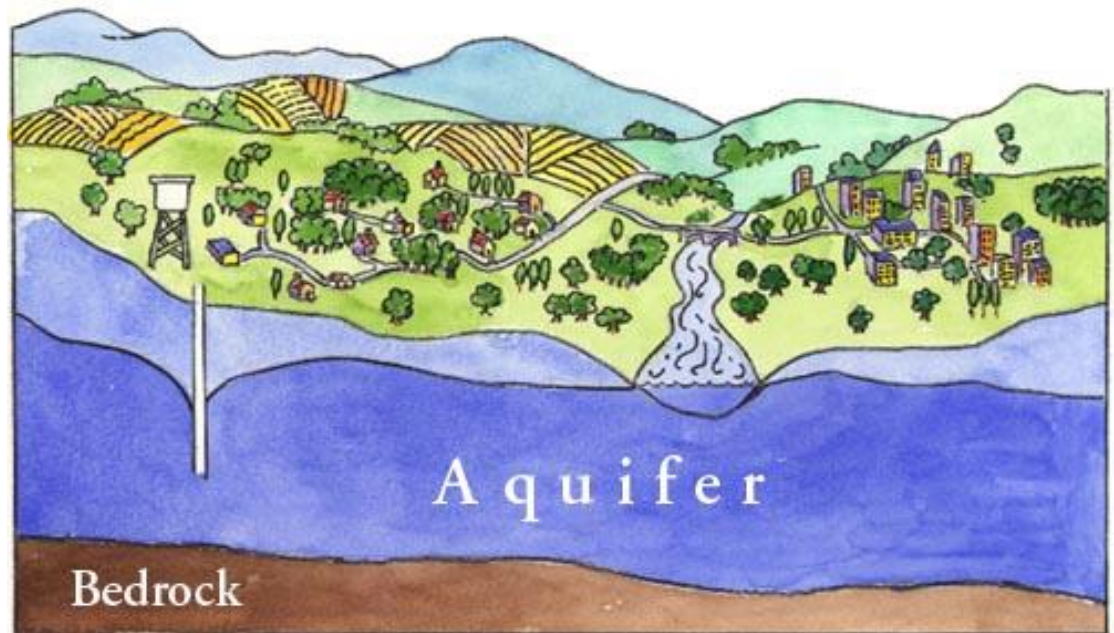


Possible Methane Sources and Sinks



Scénář #3

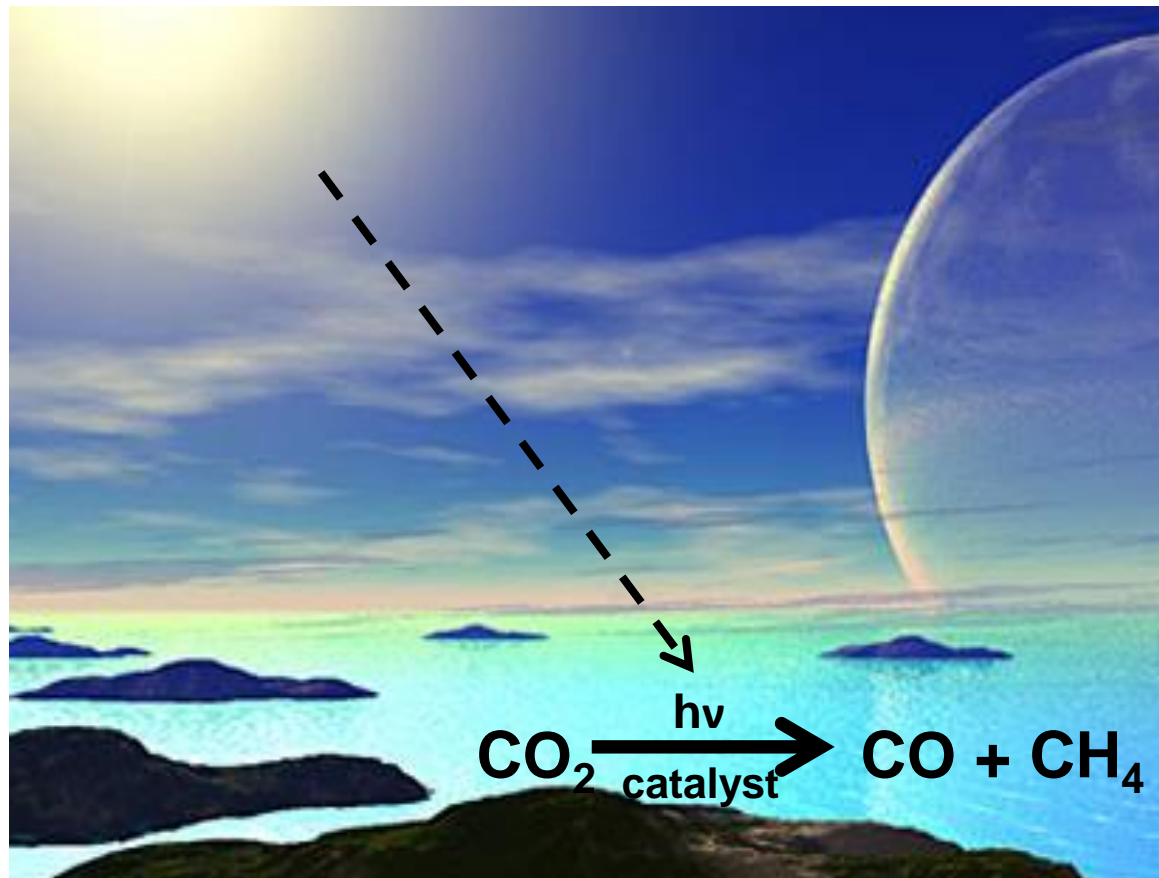
- Vzřídla metanu z podzemí- permanentní zdroje výroby plynu
- Může být vázáno na podpovrchovou chemii: plyn- voda – hornina
- Důležité: doba života metanu na Marsu je zhruba 300 let
- Podobně jako v arktické tundře na Zemi (jeden z největších zdrojů metanu v zemské atmosféře)



Hu, R et al., Astrobiology
2016

Scenář #4 Náš scénář

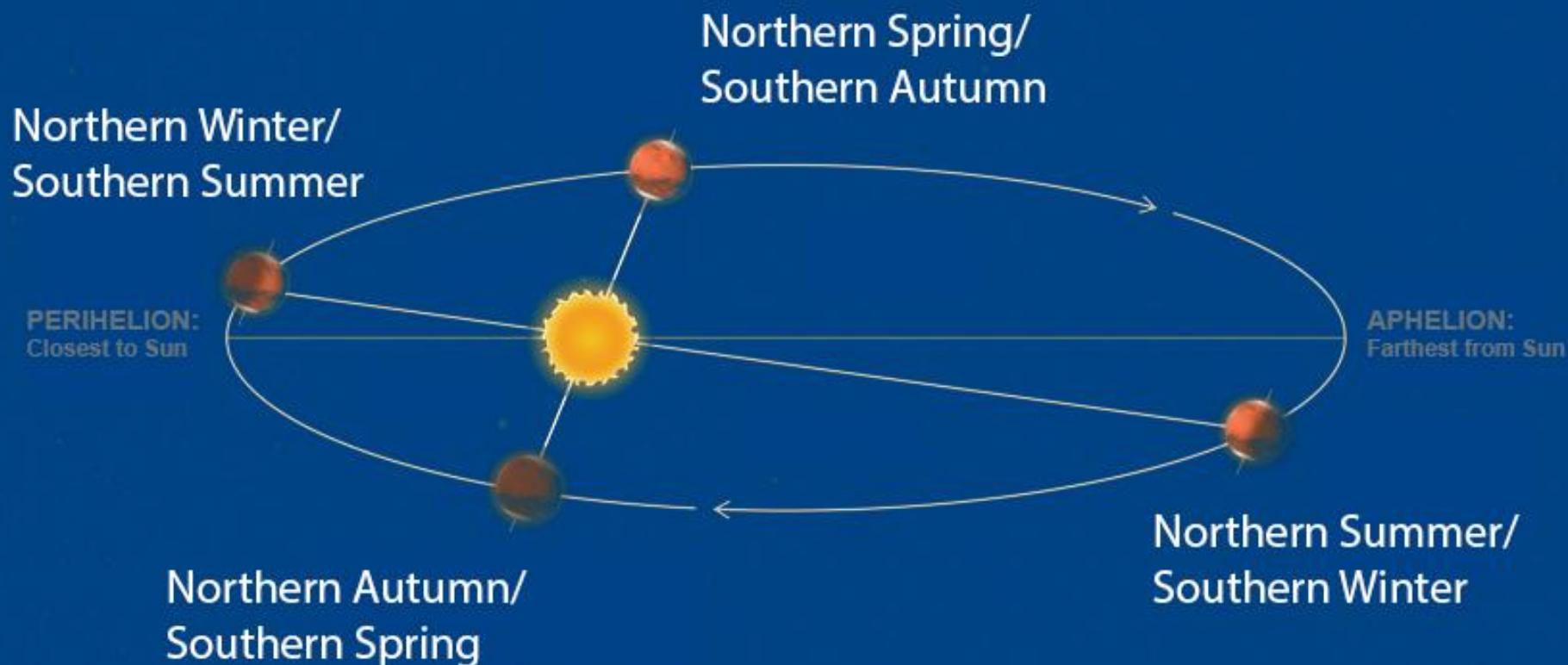
- Metan vzniká působením UV záření na povrch Marsu (regolit, voda, CO₂ a proton vodíku)



Mars během roku

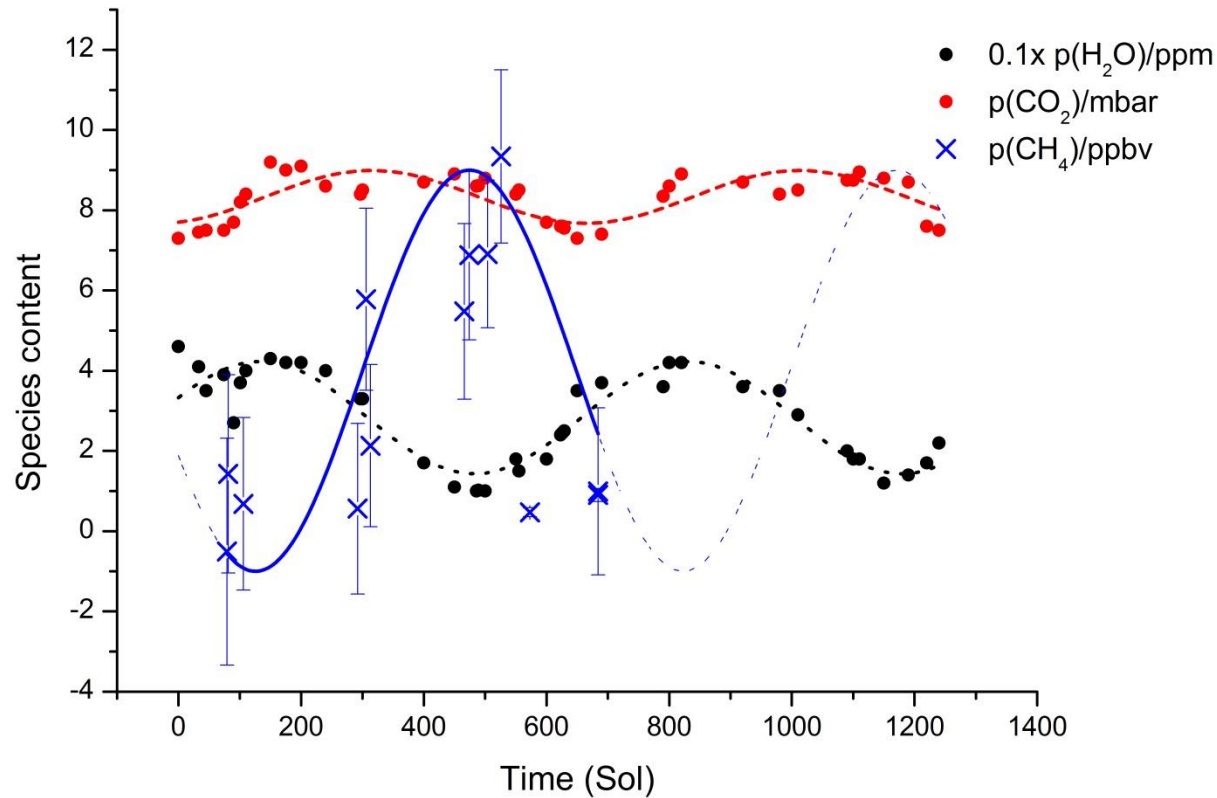
Sezónní změny klimatu podobně jako na Zemi:

- Perihelion = northern winter
- Aphelion = northern summer



Doplněná sezonní variace metanu, vodní páry a CO₂ na Marsu

Obrázek byl vytvořen na základě všech dostupných dat publikovaných Websterem et al., Curiosity and Mars Express publikovaných NASA, a Martín-Torres et al.

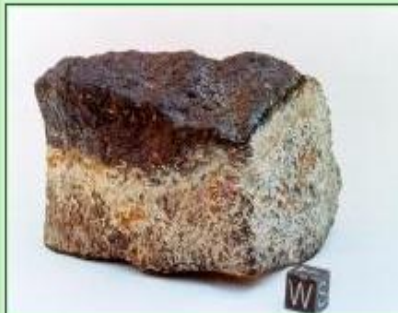




Mars Meteorites

Jet Propulsion Laboratory
California Institute of Technology

The Los Angeles Meteorite



A Mars meteorite stone (shergottite) weighing 452.6 grams.



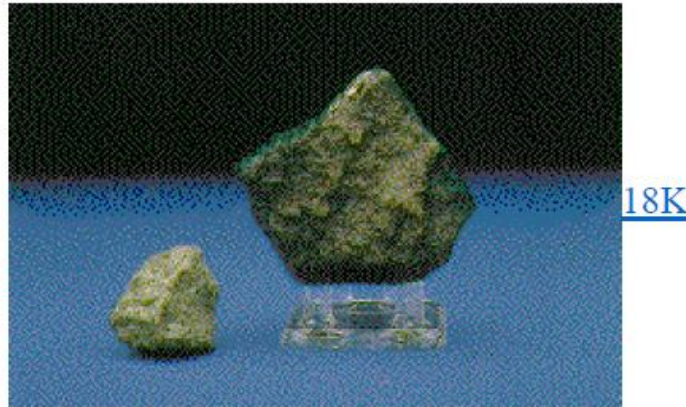
A Mars meteorite stone (shergottite) weighing 245.4 grams.

Of the 60,000 or so meteorites that have been discovered on Earth, only **124** have been identified as originating from the planet Mars. These rare meteorites create a trail throughout the world when [NASA announced in August 1996](#) that evidence of microfossils may be present in one of these Mars meteorites.

The meteorites in the table below are grouped by their pairings and listed roughly in the order that they were found.

Meteorite Name	Location Found	Date Found	Mass (g)	Type
Chassigny	France, Haute-Marne province, village of Chassigny	October 3, 1815	~4,000	dunite (chassignite)
Shergotty	India, Bihar State, town of Shergahti	August 25, 1865	~5,000	basaltic shergottite
Nakhla	Egypt, El-Baharnya, village of El-Nakhla	June 28, 1911	~10,000	clinopyroxenite (nakhlite)

The Nakhla Meteorite



The Nakhla Meteorite
Copyright 1996 Fotosmith

Meteorite: Nakhla

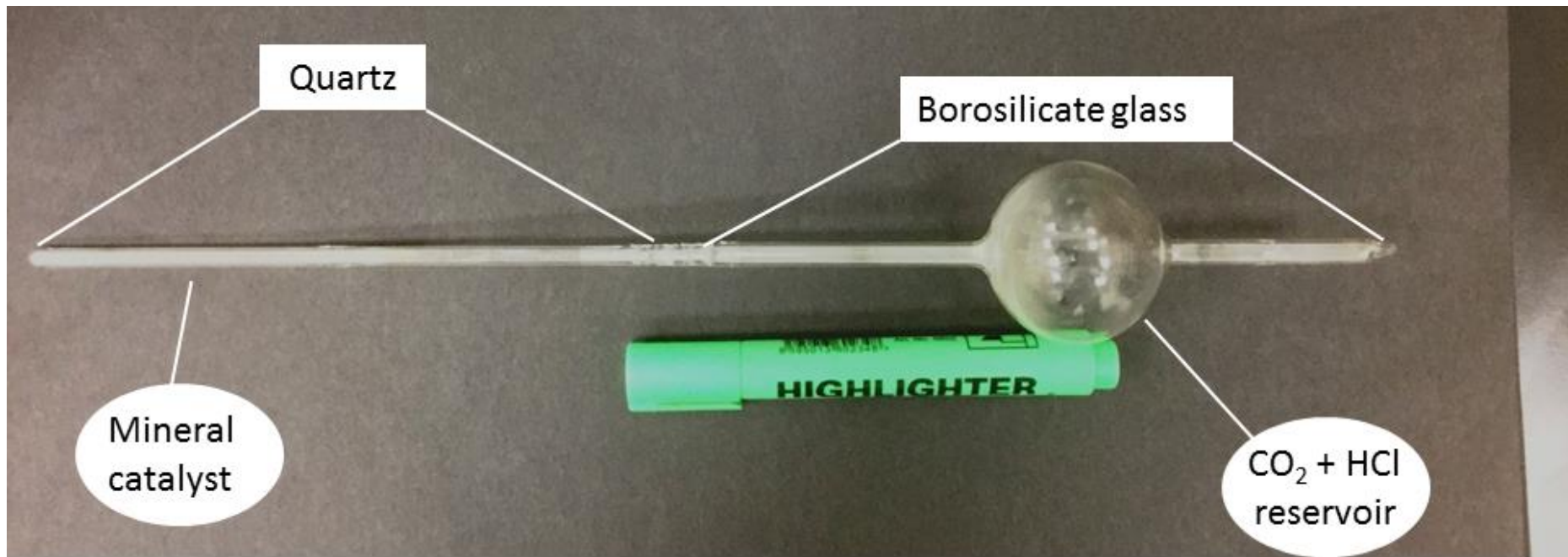
Location: Nakhla, Abu Hommos, Alexandria, Egypt

Fell: June 28, 1911, 09:00

Type: Nakhlite (SNC)

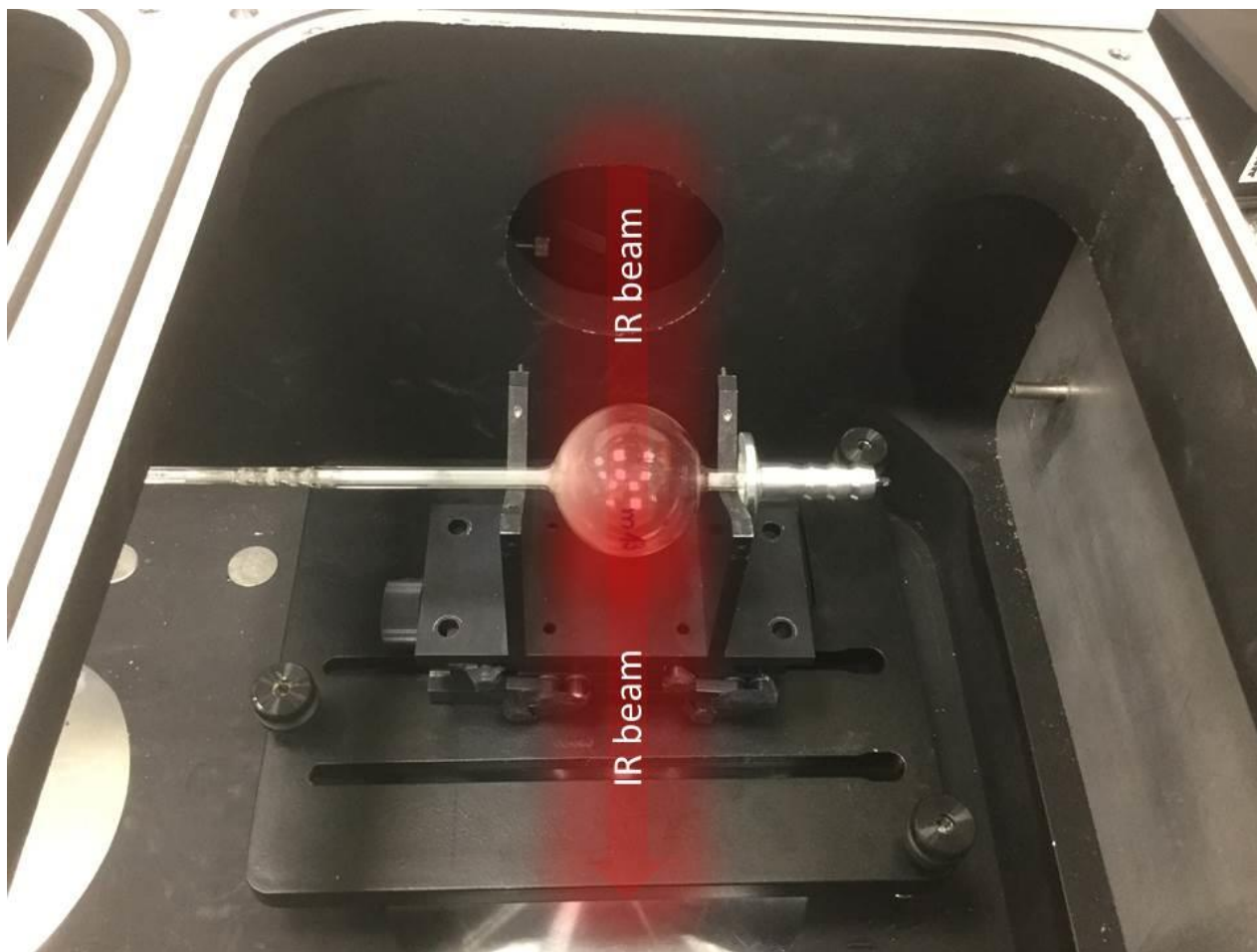
A rain of 40 stones fell from the sky in 1911 near Nakhla in Egypt. The falls were preceded by an appearance of a cloud and detonations, frightening local residents. This is an eye witness account that provided accurate descriptions of the Nakhla fall - including detonations and smoke trails along a mention that one of pieces hit a dog. This dog story did lead directly to the recovery of several fragments of the Nakhla meteorite. The meteorites are very real, so there's no reason to doubt the dog story. The stones from this meteorite fall ranged in size from 20g to 1813g, and it is estimated a total weight of 10kg (22 pounds) had fallen.

Experimentální zařízení vytvořené k detekci metanu pomocí fotochemické redukce CO_2 na povrchu Nakhla meteoritu



Experimentální uspořádání uvnitř spektrometru:

Paprsek spektrometru prochází sférickým rezervoárem a monitoruje vznik metanu po fotochemickém ozařování

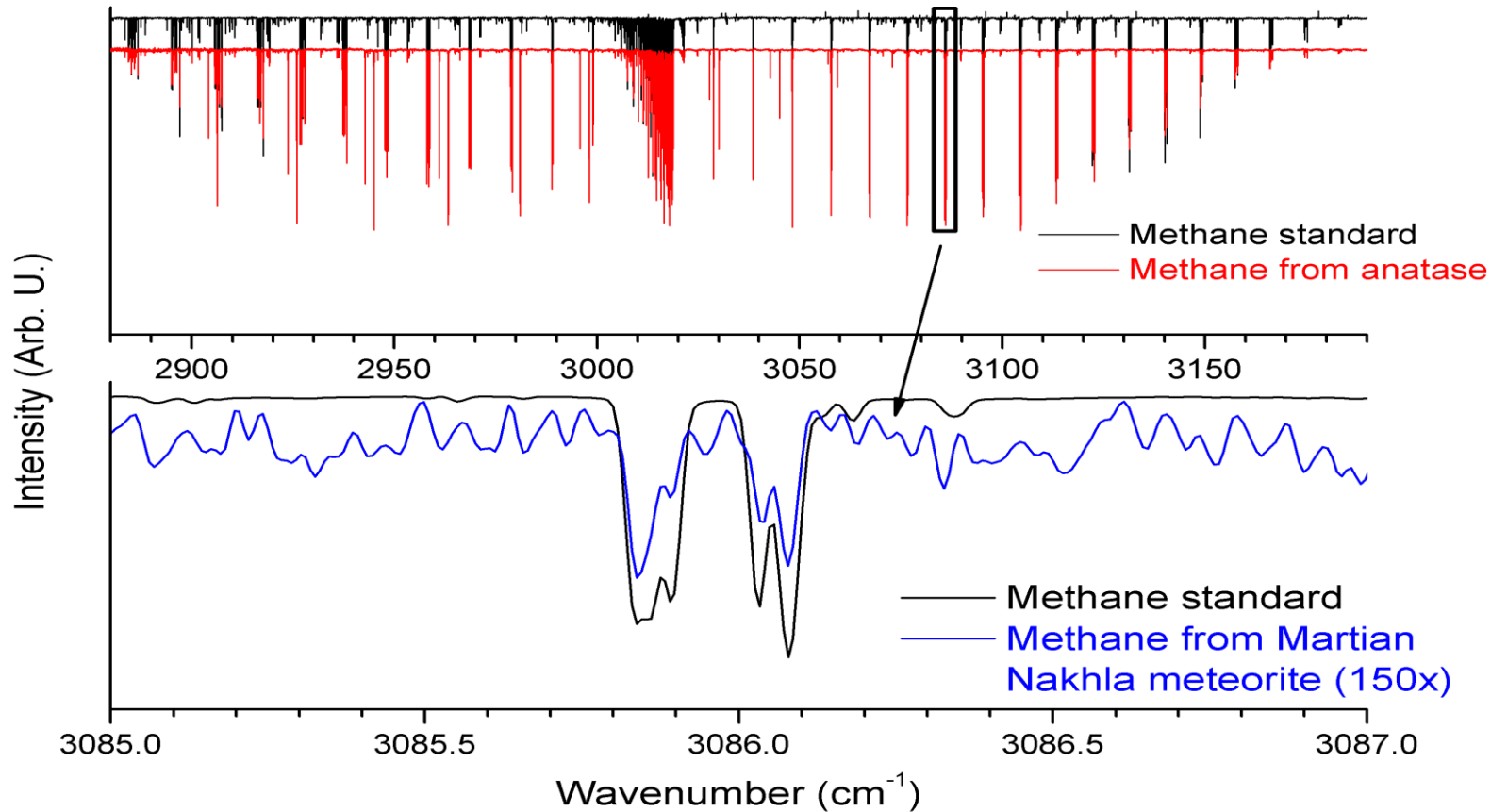


UV ozařování 72 hodin pomocí 160 W UV lampy Nakhla meteoritu.

Horní spektrum (černé) ukazuje referenční spektrum metanu 3085.7 cm^{-1} měřený jako standard při 0.69 Torr

Methanogeneze na povrchu anatasu (červeně) po 1,000 hod. UV ozařování

Spodní spektrum ukazuje linii metanu po ozařování vzorku Nakhla meteoritu (modře) pomocí Hg lampy (350 nm 72 hodin)



Metan a chlorečnany, chloristany detekce a pevná část vzorku

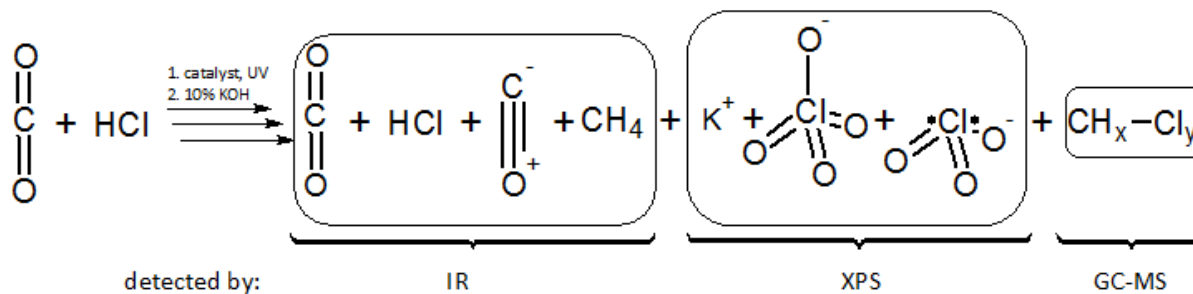
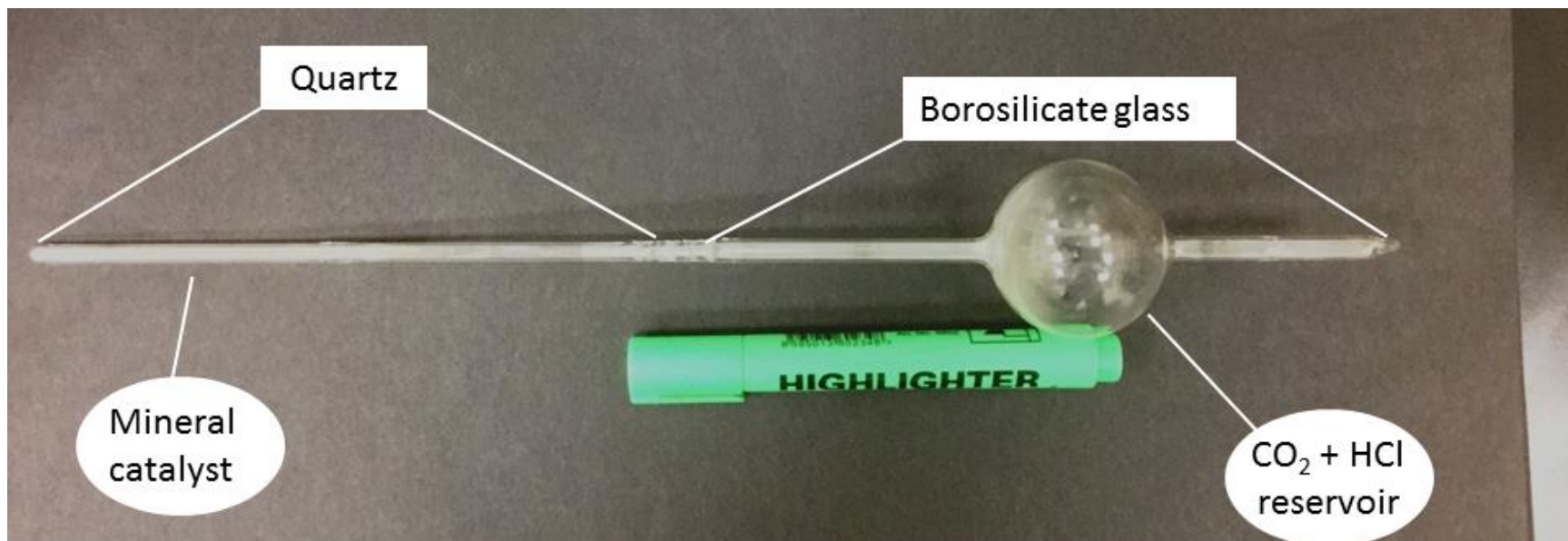


Table 1 Minerals detected on Mars from landed and orbital data sets^a

	Class	Group/mineral/phase	Formula
Primary	Framework silicates	Olivines	(Mg, Fe) ₂ SiO ₄
		Orthopyroxenes	((Mg, Fe) _{0.95+x} , Ca _{0.05-x})Si ₂ O ₆
		Clinopyroxenes	(Ca, Mg, Fe)Si ₂ O ₆
		Plagioclase feldspars	(Ca, Na)(Al, Si)AlSi ₂ O ₈
		Alkali feldspars	(K, Na)AlSi ₃ O ₈
	Sulfides	Pyrrhotite ^b	Fe _{1-x} S
		Pyrite/marcasite ^c	FeS ₂
	Oxides	Magnetite ^d	Fe _{3-x} Ti _x O ₄
Ilmenite ^d		FeTiO ₃	
Secondary	Oxides	Hematite	Fe ₂ O ₃
		Goethite ^d	FeO(OH)
		Akagancite ^b	Fe(O, OH, Cl)
	Phyllosilicates (clay minerals)	Fe/Mg smectites (e.g., nontronite, saponite)	(Ca, Na) _{0.3-0.5} (Fe, Mg, Al) ₂₋₃ (Al, Si) ₄ O ₁₀ (OH) ₂ · <i>n</i> H ₂ O
		Al smectites (e.g., montmorillonite, beidellite)	(Na, Ca) _{0.3-0.5} (Al, Mg) ₂ (Al, Si) ₄ O ₁₀ (OH) ₂ · <i>n</i> H ₂ O
		Kaolin group minerals (e.g., kaolinite, halloysite)	Al ₂ Si ₂ O ₅ (OH) ₄
		Chlorite	(Mg, Fe ²⁺) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈
		Serpentine ^c	(Mg, Fe) ₃ Si ₂ O ₅ (OH) ₄
		High-charge Al/K phyllosilicates (e.g., muscovite, illite)	(K, H ₃ O)(Al, Mg, Fe) ₂ Al _x Si _{4-x} O ₁₀ (OH) ₂
	Other hydrated silicates	Prehnite	Ca ₂ Al(AlSi ₃ O ₁₀)(OH) ₂
		Analcime	NaAlSi ₂ O ₆ ·H ₂ O
		Opaline silica (<i>n</i> > 0), quartz (<i>n</i> = 0)	SiO ₂ · <i>n</i> H ₂ O
	Carbonates	Mg/Ca/Fe carbonates	(Mg, Fe, Ca)CO ₃
	Sulfates	Kieserite (MgSO ₄ ·H ₂ O); szomolnokite (FeSO ₄ ·H ₂ O); Fe(II)-, Fe(III)-, and Mg-polyhydrated sulfates	(Fe, Mg)SO ₄ · <i>n</i> H ₂ O
		Gypsum (<i>n</i> = 2), bassanite (<i>n</i> = 0.5), anhydrite ^b (<i>n</i> = 0)	CaSO ₄ · <i>n</i> H ₂ O
		Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆
		Jarosite	KFe ₃ (OH) ₆ (SO ₄) ₂
		Not a named mineral	Fe ³⁺ SO ₄ (OH)
	Chlorides	Chlorides	e.g., NaCl, MgCl ₂
	Perchlorates	Perchlorates ^f	e.g., (Mg, Ca)(ClO ₄) ₂

Mineralogy of the Martian Surface

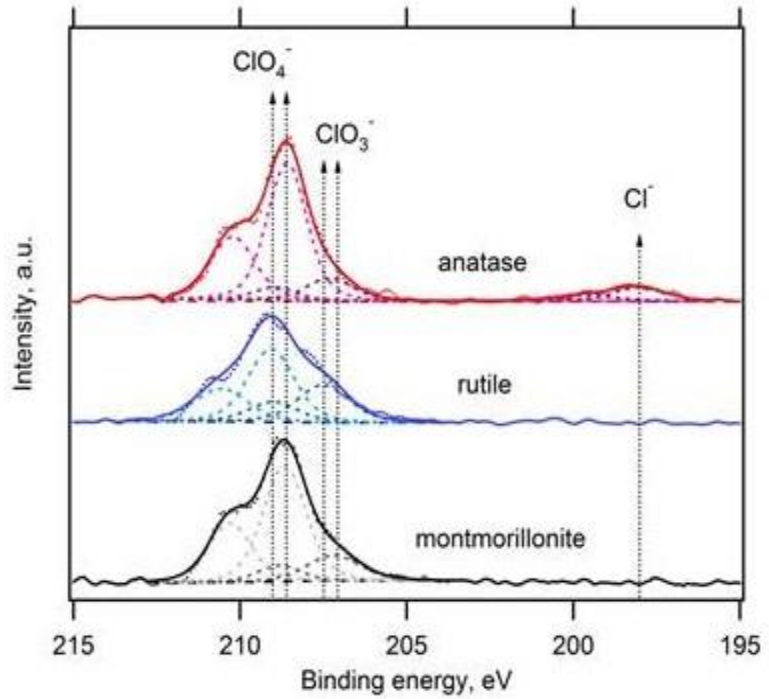
Bethany L. Ehlmann and Christopher S. Edwards, *Annu. Rev. Earth Planet. Sci.* 2014. 42:291–315

XPS spektra v oblasti elektronických přechodů v atomech Cl 2p katalyzátoru po 1000 hod. ozařování.

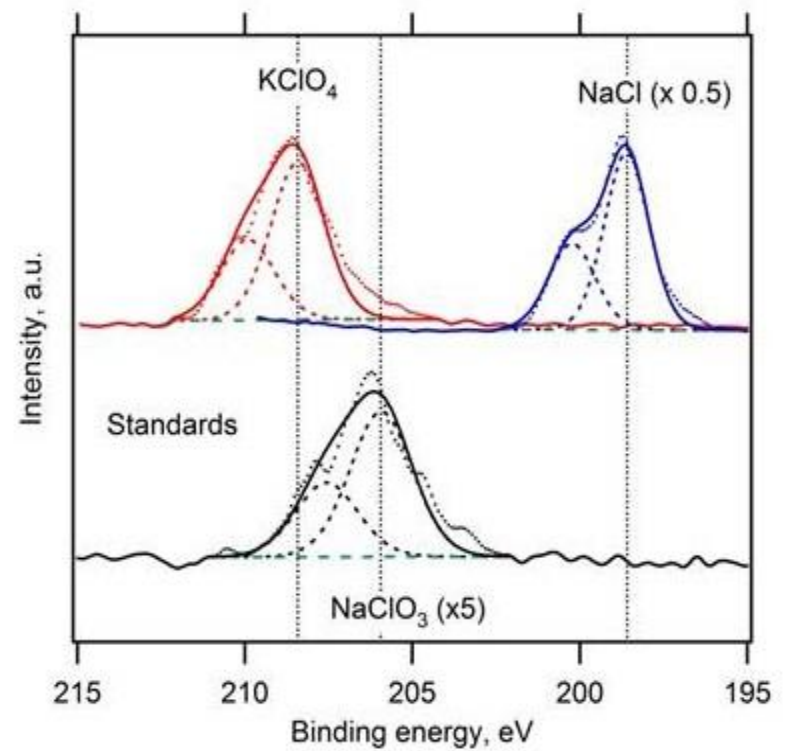
Anatas, rutile a montmorillonite prášky byly UV ozářeny v přítomnosti par HCl, H₂O a CO₂, a byly neutralizovány KOH.

Oblasti fotoemisních linií Cl 2p_{3/2} ClO₄⁻, ClO₃⁻ a Cl⁻, jsou označeny šipkami

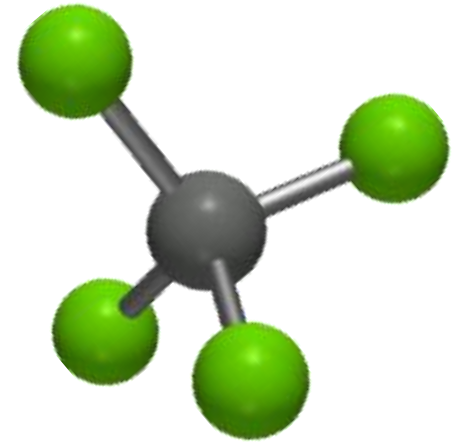
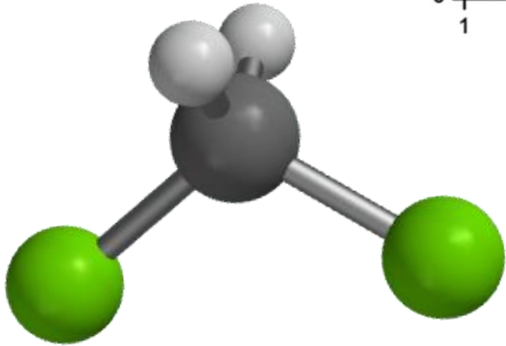
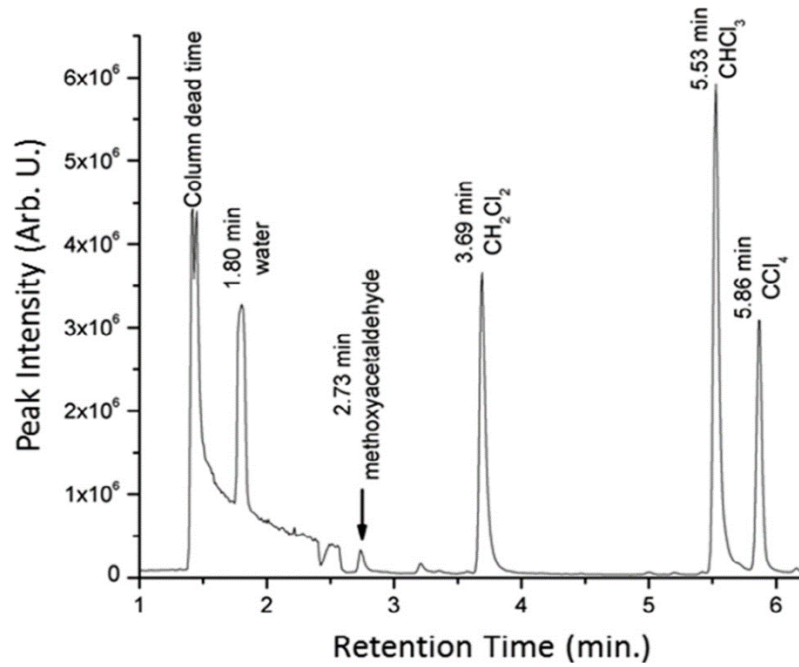
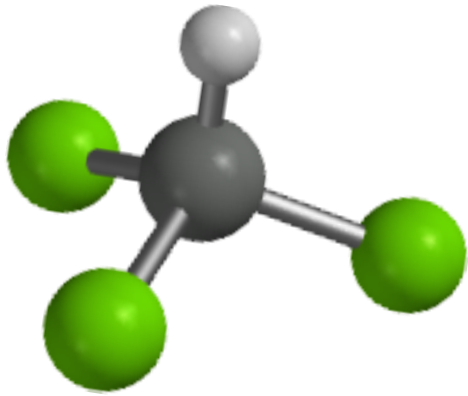
XPS spectra of the solid phase of our samples



XPS standards of perchlorate, chlorate and chloride



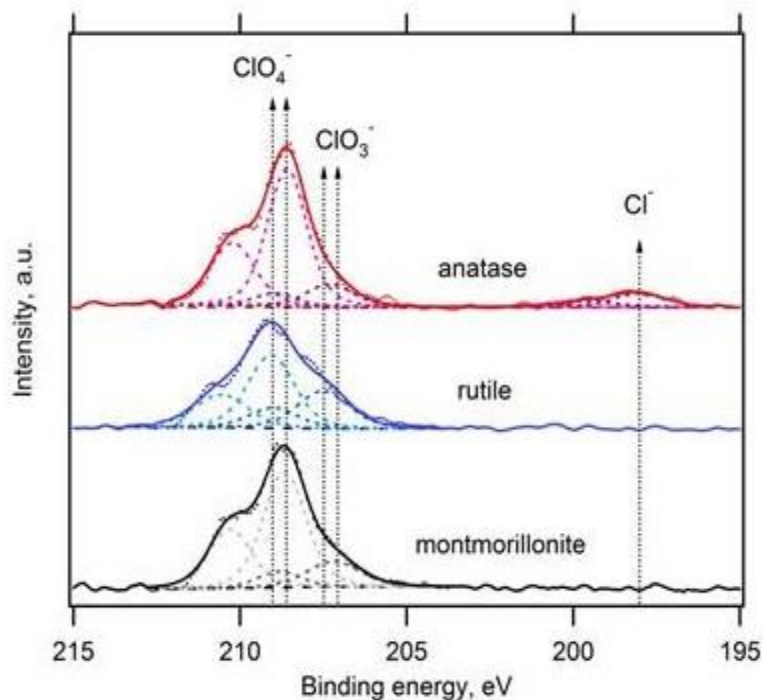
GC-MS detection of methylchlorides



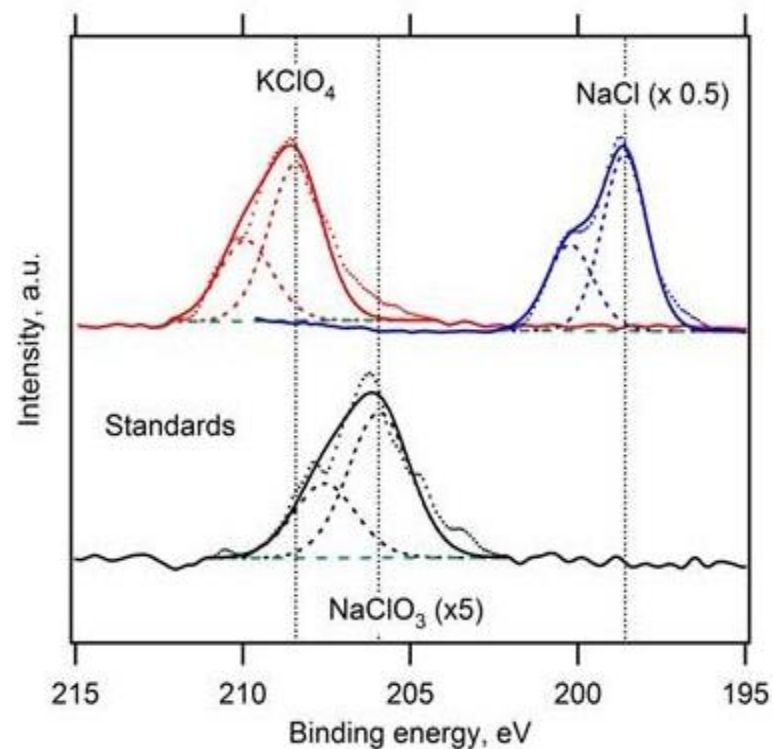
Photoelectron (XPS) spectra in the region of Cl 2p of the catalysts after 1000 hours of irradiation.

The anatase, rutile and montmorillonite powders were UV-irradiated in the presence of HCl vapour, H₂O and CO₂, and were neutralized by CO₂⁻ free KOH immediately after removal from the photoreactor. The regions of the Cl 2p_{3/2} photoemission lines of ClO₄⁻, ClO₃⁻ and Cl⁻, respectively are labelled by arrows.

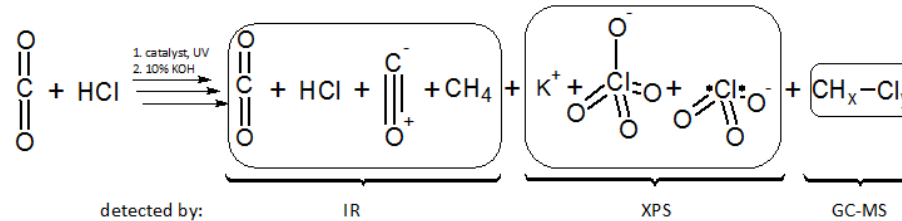
XPS spectra of the solid phase of our samples



XPS standards of perchlorate, chlorate and chloride



Perchlorate content on Mars



$$d = \frac{NM}{N_A w \rho S}$$

N - total of produced molecules of ClO_4^- (3×10^{37} over the past 1 Ga)

M - the molar mass of ClO_4^- ($99.4 \text{ g}\cdot\text{mol}^{-1}$)

N_A - the Avogadro constant

w - the mass fraction of perchlorates in the Martian soil (0.005)

ρ - the average density of Martian surface rocks ($1.5 \text{ g}\cdot\text{cm}^{-3}$)

S - the surface area of Mars ($1.44 \times 10^{18} \text{ cm}^2$)

Cloristany na Marsu

0.5 wt% Chloristany v marsovském povrchu

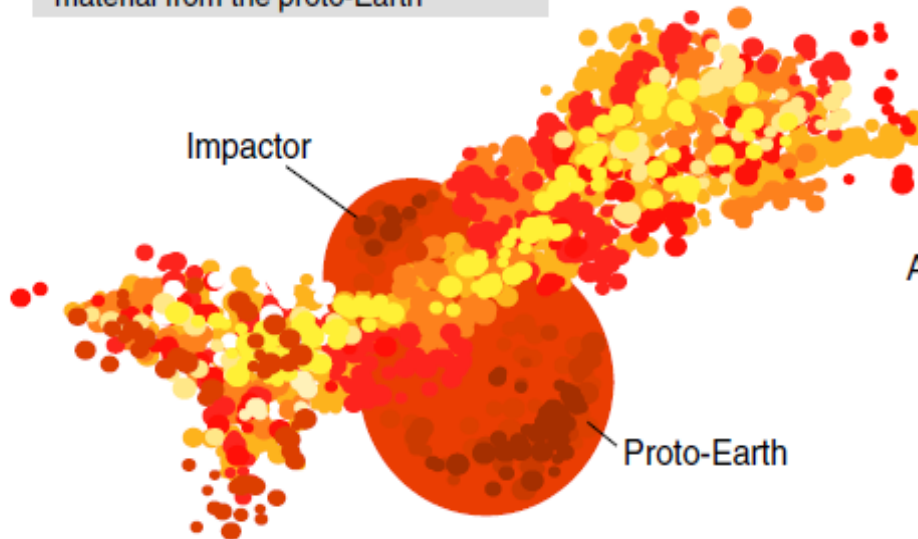
5 - 50 cm hluboko

Predikce k budoucímu ověření

Původ vody vázané na povrchu oxidických minerálů

a

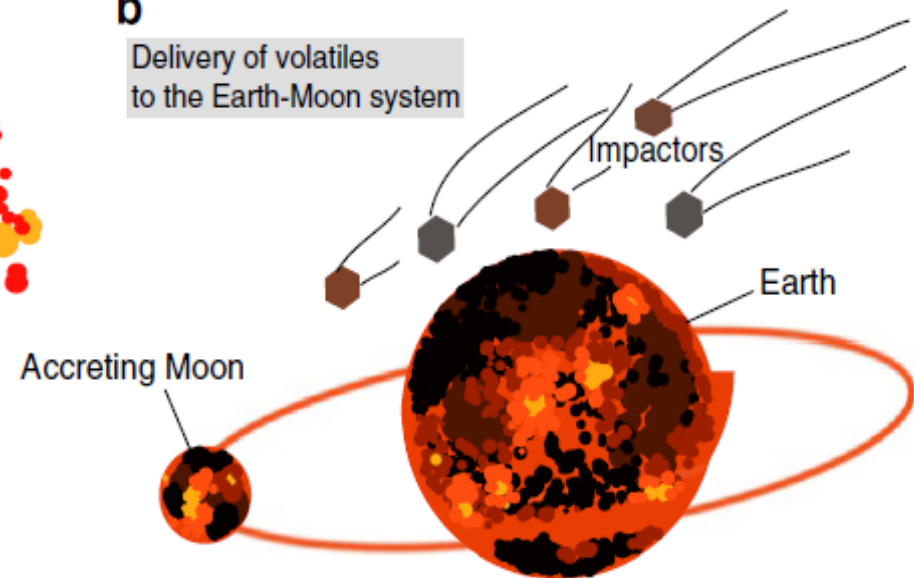
Volatiles accreted with Moon-forming material from the proto-Earth



Water survives Moon-forming event and does not escape proto-lunar disk

b

Delivery of volatiles to the Earth-Moon system



Earth and Moon receive delivery of volatiles by asteroids and comets during the initial stages of planetary differentiation

Planets may either **be born with water** or have their water **delivered by collisions** with water bearing planetary objects like **asteroids**.

Izotopické složení vody:

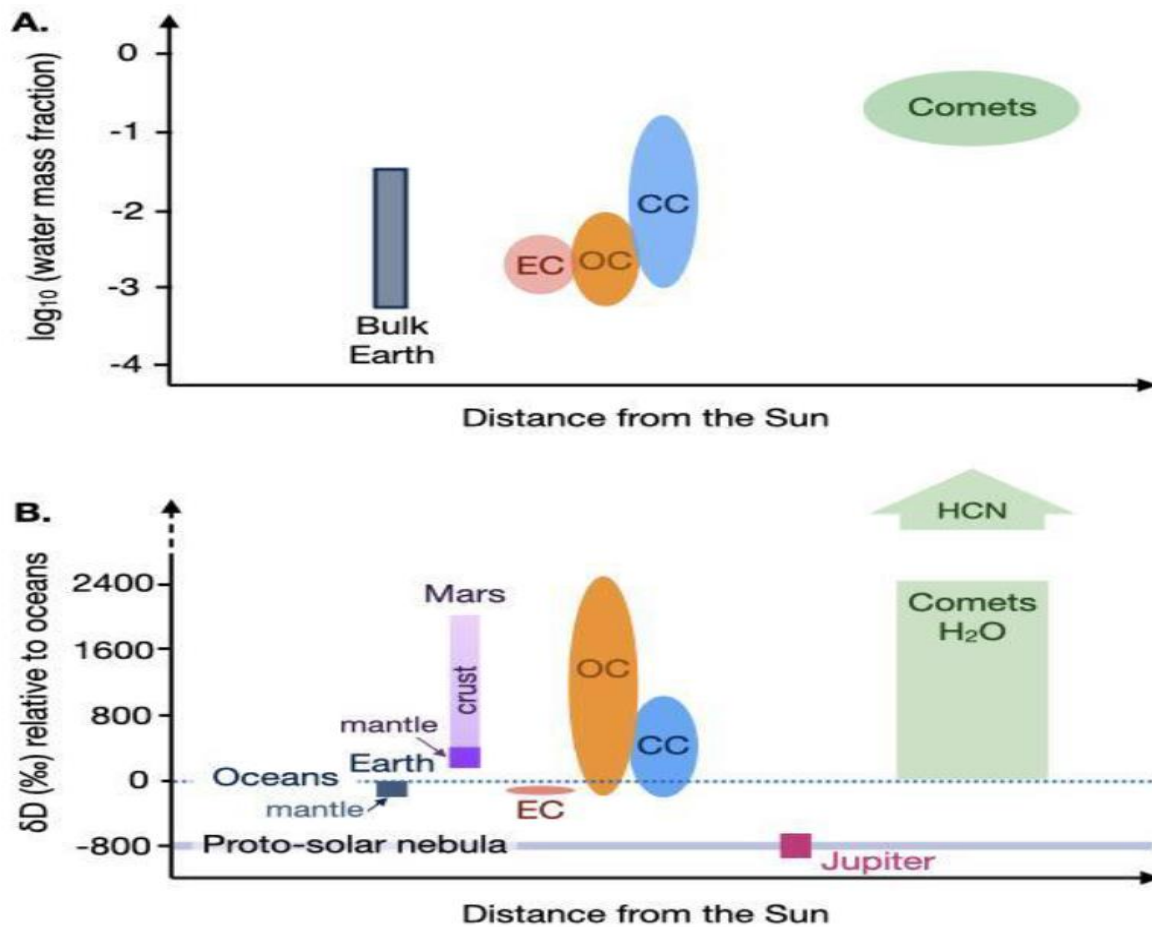
(vyjádřené jako D/H poměr nebo jako δ relativně k pozemskému poměru oceánská voda)

Země **D/H poměr $\approx 156 \times 10^{-6}$ (or $\delta D \approx 0\text{‰}$)**

The Sun's natal gas disk and Jupiter's gaseous envelope show very low D/H ratios of $\approx 21 \times 10^{-6}$ (or $\delta D \approx -800\text{‰}$) which is a factor of 7x nižší

Outer Solar System objects, such as the comet **67P/Churyumov Gerasimenko** generally show much higher D/H ratios in the sublimated water molecules, with values up to 530×10^{-6} (or $\delta D \approx 2400\text{‰}$)

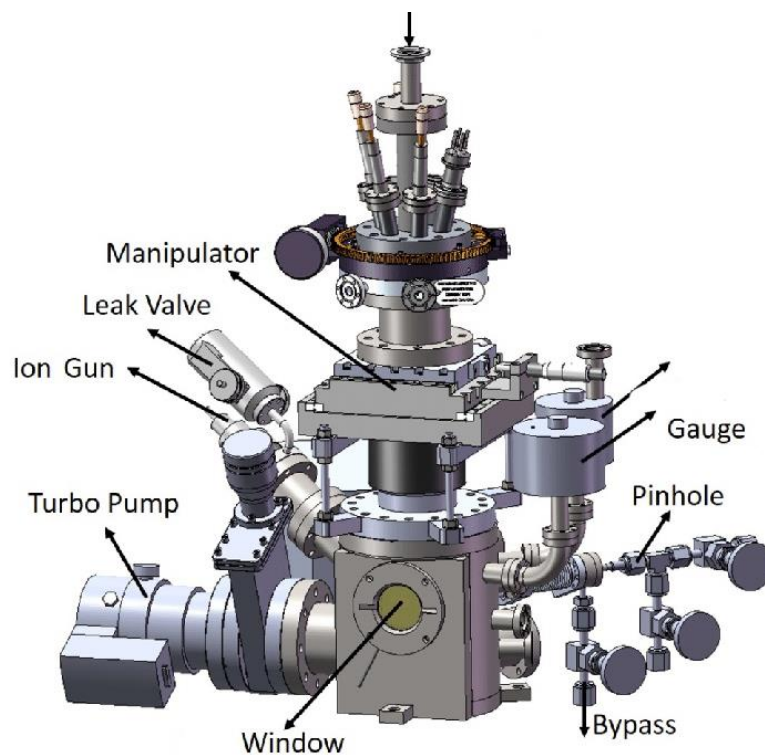
CCs (uhlík obsahující chondritické and OCs kyslíkaté minerály D/H poměr podobný oceánské vodě



(A) Obsah vody (B) izotopický poměr různých planetárních materiálů
 Koncentrace vody je vyjádřena v hmotnostních frakcích jednotek H₂O

1. (A) vzrůst obsahu vody s rostoucí vzdáleností od slunce. Celkový obsah vody na Zemi je určen 3900 ppm weight H₂O (grey rectangle) (Peslier and De Sanctis 2022 this issue).
2. (B) ukazuje variabilitu D/H poměrů pro různé minerály (bulk chondrites) (Vacher and Fujiya 2022 this issue) a komet (Bockelée-Morvan et al. 2015) ve srovnání D/H složením pozemských a marsovských hornin a minerálů (Peslier and De Sanctis 2022).

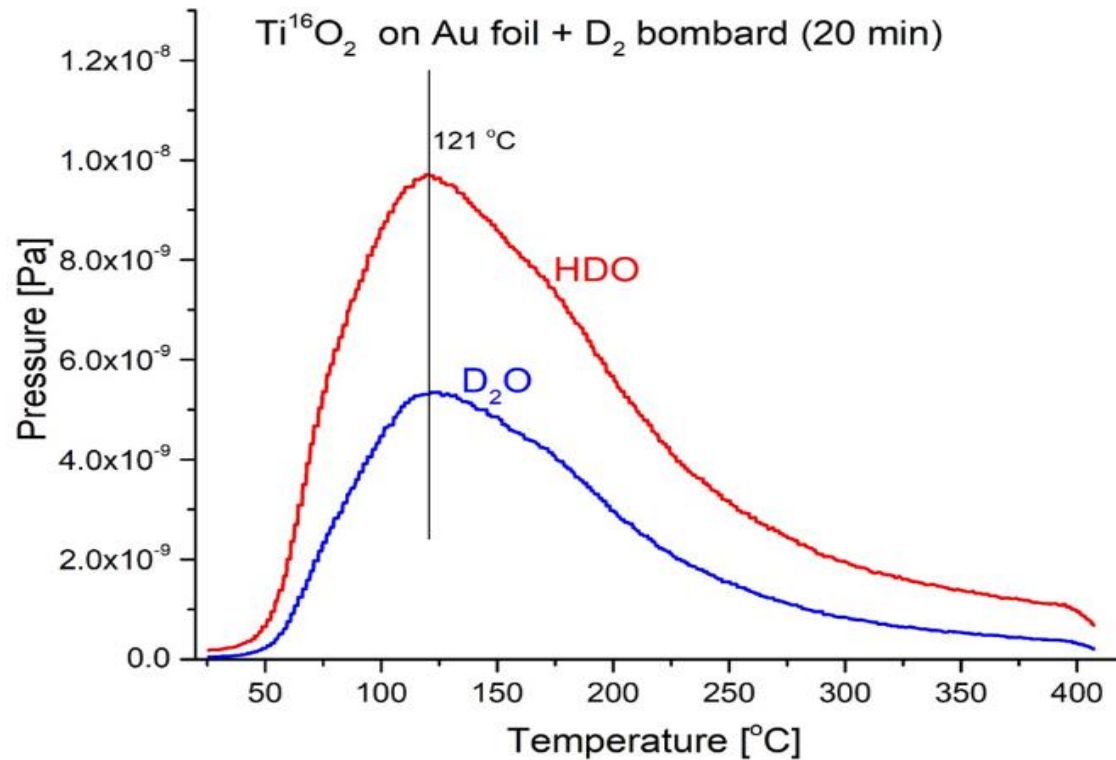
Původ vody vázané na povrch TiO_2



Teplotní programovaná desorpce vody s hmotnostní detekcí (TPD-MS)

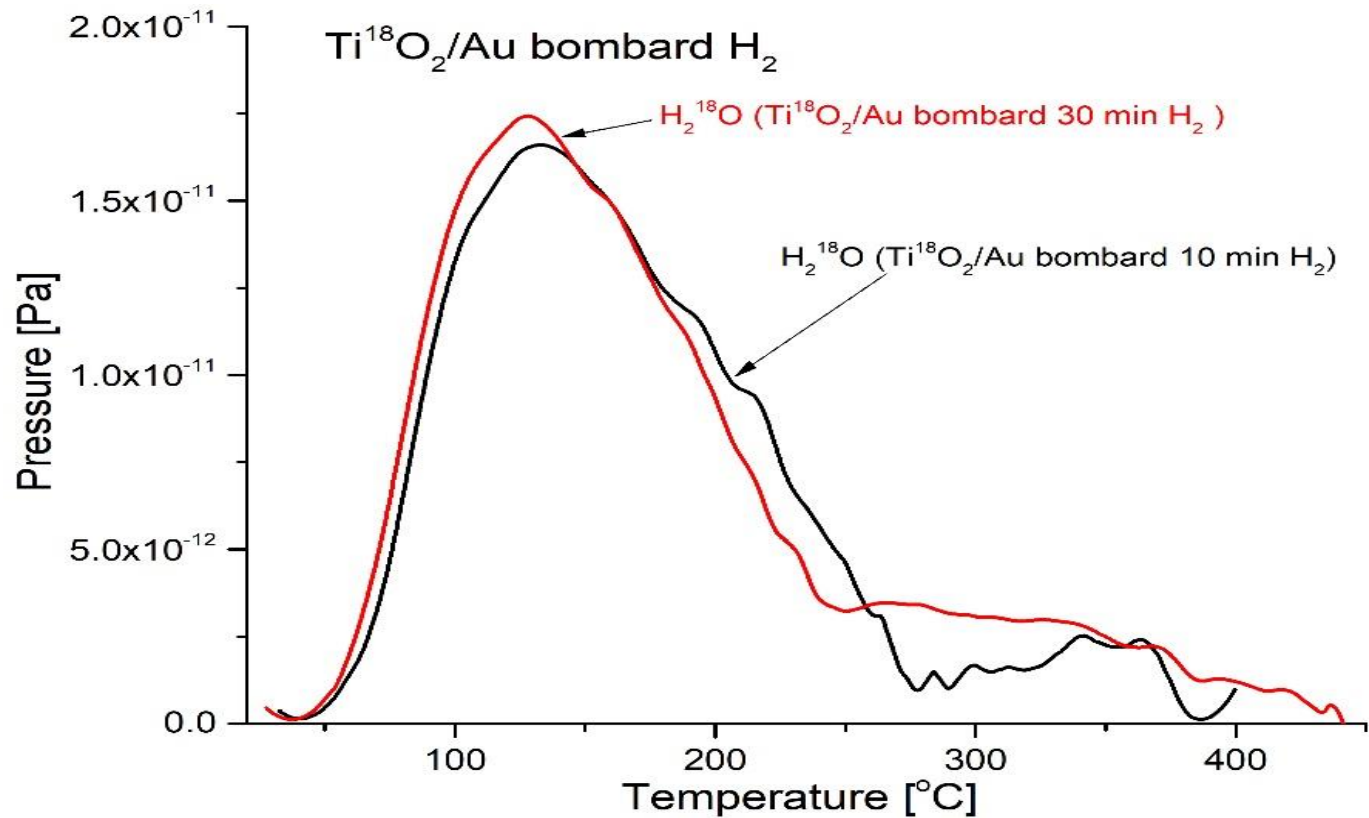
Thermal programmable desorption with mass spectroscopy (TPD-MS)

TiO₂ - TPD experiment



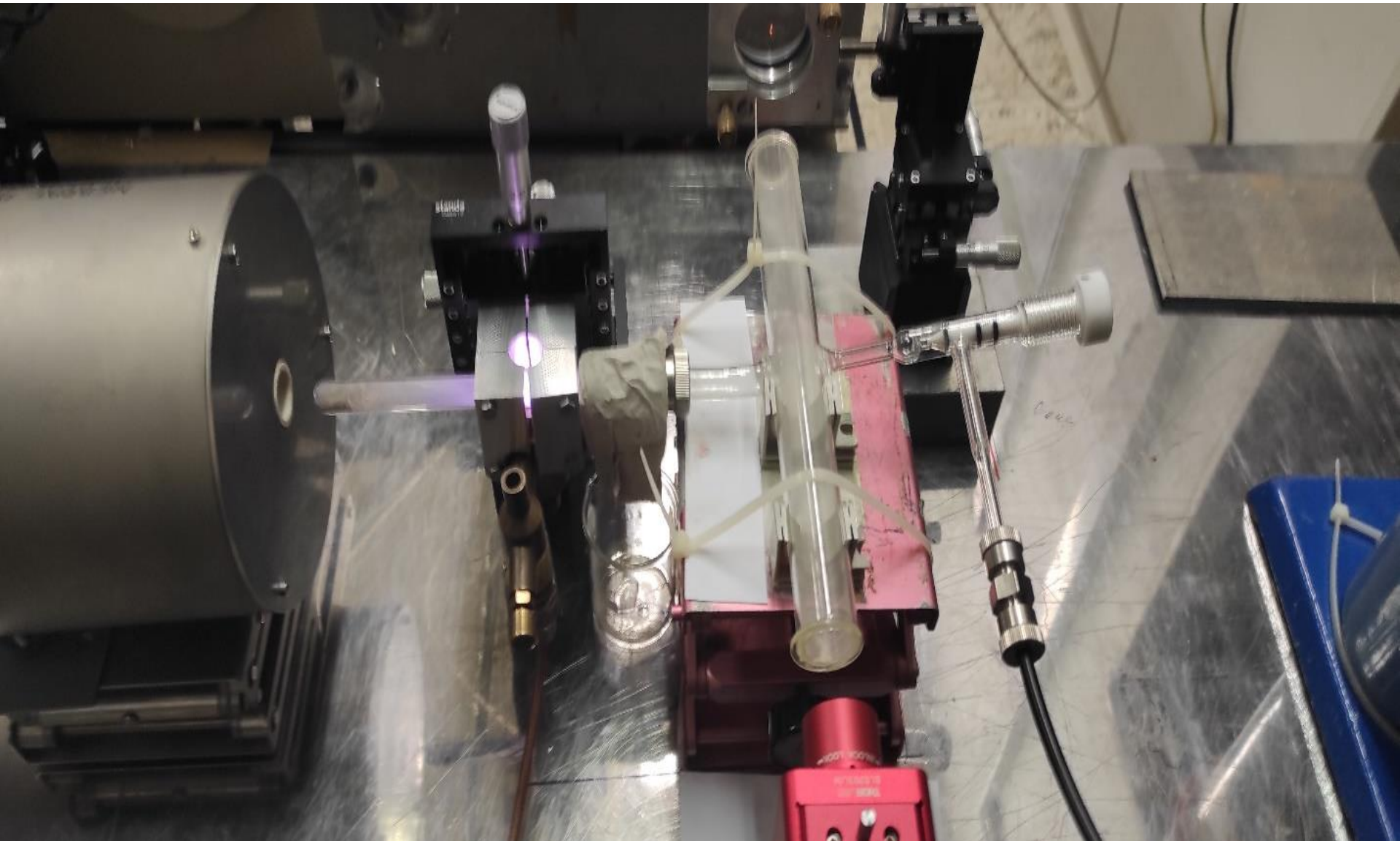
Teplotně programovaná desorpce spektra of D₂O molekul z povrchu Ti¹⁶O₂ , vzorek na Au podložce, bombardování molekulami D₂ , 20 min. (modře)
HDO (19 m/z) and D₂O (20 m/z) molekuly

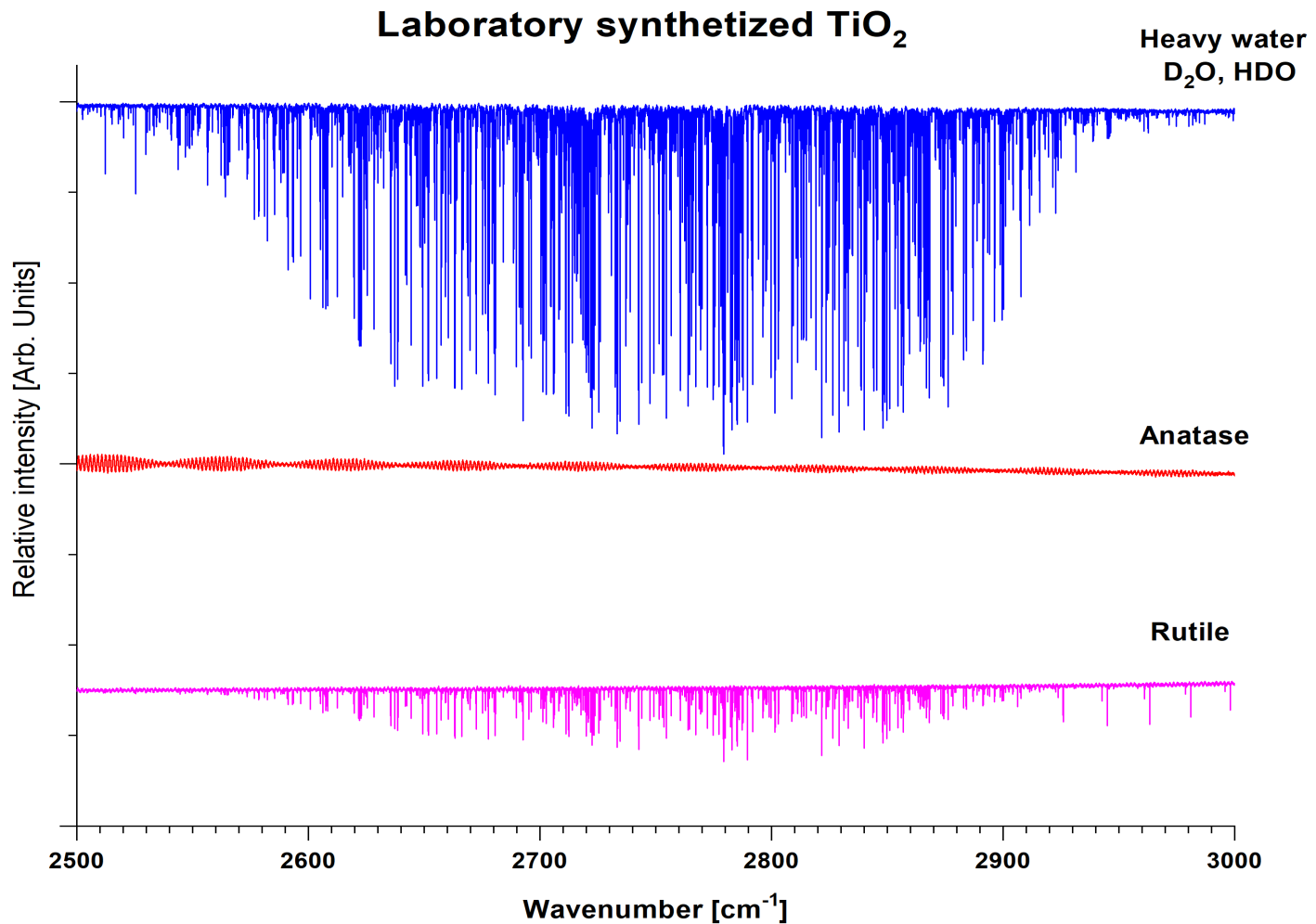
TPD



Teplotně programovaná desorpce spektra H_2^{18}O molekul Ti^{18}O_2 vzorek na Au podložce, bombardovaná molekulami H_2 (10 min. (černě) a 30 min. (červeně), tlak H_2 8.5×10^{-5} mbar.

Vysoce rozlišitelná infračervená spektroskopie s Fourierovou transformací (FTIR)

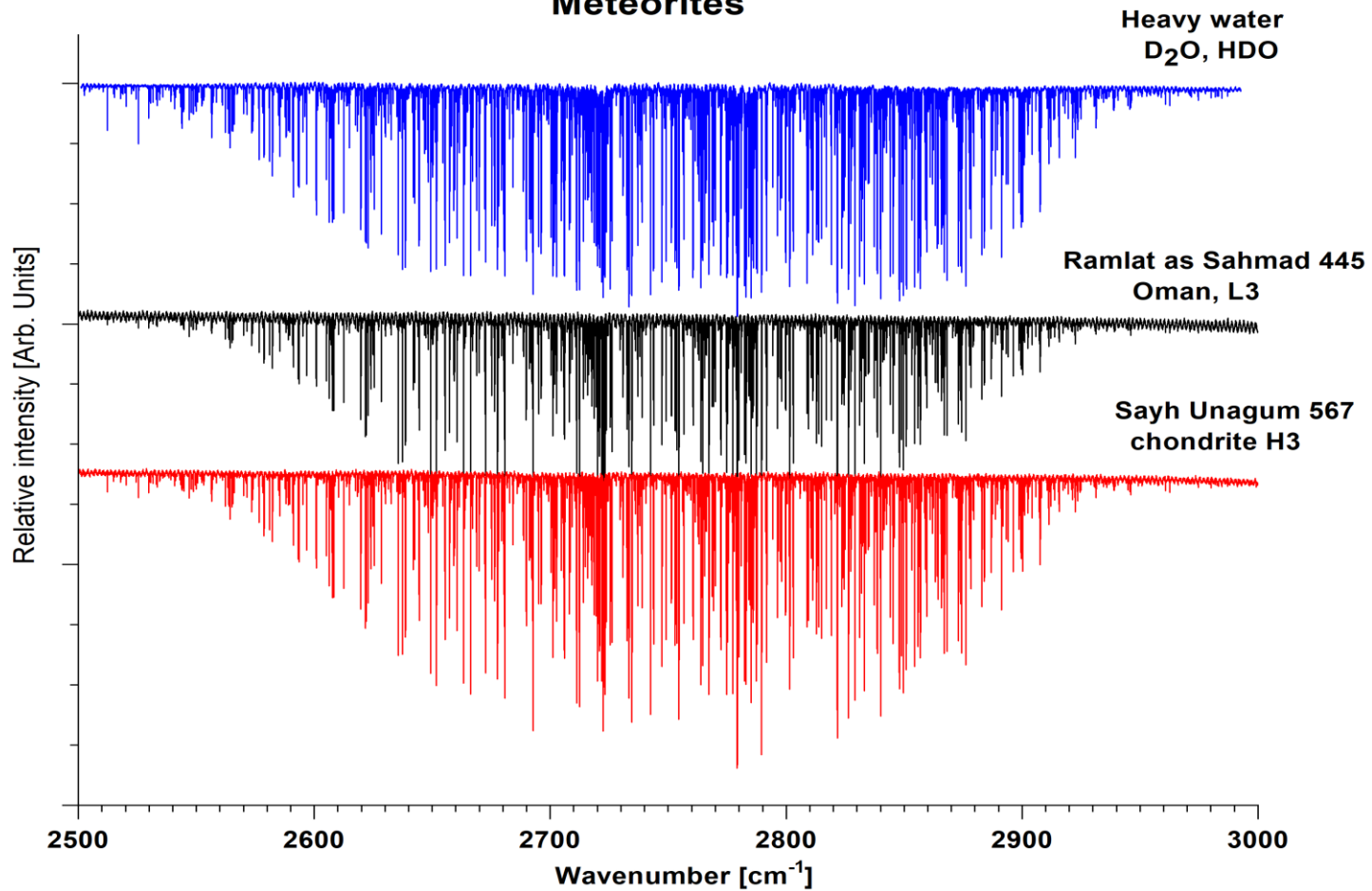




Voda (D₂O) generovaná bombardováním TiO₂ ionty deuteria na povrch {101} anatasu je následně rozložena na vodík a kyslík UV zářením generovaným MW výbojem

{101} orientovaný povrch představuje primární místo pro fotokatalytickou redukci vody na vodík a kyslík redukci. ***The {101} orientation is the only one that forms hydrogen upon illumination.***

Meteorites



SPRINGER BRIEFS IN MOLECULAR SCIENCE

Svatopluk Civiš
Martin Ferus
Antonín Knížek

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The origin of methane and biomolecules from a CO₂ cycle on terrestrial planets

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Understanding the chemical evolution of newly formed terrestrial planets involves uncertainties in atmospheric chemical composition and assessing the plausibility of biomolecule synthesis. In this study, an original scenario for the origin of methane on Mars and terrestrial planets is suggested. Carbon dioxide in Martian and other planetary atmospheres can be abiotically converted into a mixture of methane and carbon monoxide by ‘methanogenesis’ on porous mineral photoactive surfaces under soft ultraviolet irradiation. On young planets exposed to heavy bombardment by interplanetary matter, this process can be followed by biomolecule synthesis through the reprocessing of reactive reducing atmospheres by impact-induced shock waves. The proposed mechanism of methanogenesis may help to answer the question concerning the formation of methane and carbon monoxide by photochemical processes, the formation of biomolecules on early Earth and other terrestrial planets, and the source and seasonal variation of methane concentrations on Mars.

Historically, many arguments have been presented for both neutral (i.e. rich in CO₂, N₂ or H₂O (ref. ¹), supported by several modern geochemical findings² and reducing (CH₄, NH₃, H₂, HCN, CO and so on)³ atmospheric compositions of early Earth. Recent results comprehensively mapping terrestrial isotopic ratios of hydrogen and nitrogen show a difference from interplanetary gaseous or cometary material. Rather, they are in the range of values characterizing primitive meteorites⁴. These findings suggest exogenous delivery of terrestrial H₂O and atmosphere to early Earth (for a broad review see ref. ⁵). It has been demonstrated that Earth lost its nebula-based proto-atmosphere during the first 100–500 Myr after its creation⁶. Nevertheless, a hydrogen envelope of a moderate mass around early Earth may have acted during the first 100 Myr as a shield against the deterioration of the atmosphere by the solar wind⁷. Compromise scenarios incline towards a weakly reducing atmospheric mixture consisting of volcanic gases such as CO₂, N₂, CO and H₂O, with lesser amounts of H₂, SO₂, CH₄ and H₂S. However, as mentioned above, the effects of exogenous delivery⁸ of reducing compounds or Fischer-Tropsch processes⁹ could have significantly contributed to even more reducing conditions (CO₂/N₂ atmosphere with significant amounts of CH₄, NH₃, H₂S and H₂)¹⁰. Such a reducing state of the early terrestrial atmosphere is documented in indigenous zircons³. In accordance with several theories inclining towards a neutral gas composition for early Earth’s atmosphere, Mars can serve as a prototype of a photochemically driven planet. The Martian atmosphere represents a CO₂-rich environment that might have been similar to early Earth’s. Recent in situ measurements of CH₄ on Mars by the Curiosity rover reported significant variations in its concentration¹⁰. Across the Gale Crater, where the measurements were taken, CH₄ was detected at a background concentration of ~0.7 parts per billion (ppb) with tenfold spikes detected on four occasions across a period of two months. The

possible abiotic synthesis of CH₄ as a reducing gas in a natural CO₂-rich atmosphere is also highly relevant to studies of Earth’s and Mars’s early stages of atmospheric evolution. Both planets contained H₂O as a source of hydrogen, and they were exposed to a significant ultraviolet flux¹¹. Even though its levels are debated, according to a comprehensive study by Chyba and Sagan¹², energy dissipation from ultraviolet irradiation on early Earth might have been two orders of magnitude more powerful (not effective) as an energy source compared with impact shock waves^{12–15} and four orders of magnitude more powerful than electric discharges.

Based on photochemical models and on the current understanding of the composition of the Martian atmosphere, CH₄ exhibits a chemical lifetime of 300–600 years, which is, on the geological scale, a very short period¹⁶. This implies that there must be an active source of CH₄ on Mars. Hu et al.¹⁷ formulated three hypotheses for the origin of CH₄ on Mars:

- The regolith in the Gale Crater adsorbs CH₄ when dry and releases CH₄ on deliquescence during winter.
- Microorganisms convert organic matter in the soil to CH₄. However, this scenario supposes the existence of extant life on Mars. Other explanations concerning life on Mars are summarized in ref. ¹⁸.
- Deep subsurface aquifers generate bursts of CH₄.

A fourth hypothesis has been formulated by Shkrob et al.¹⁹ and this is further developed in our study. The idea is that a complex, ultraviolet-governed carbon chemistry could exist:

- Mars could simultaneously be a planetary-sized ‘photoreactor’ that decomposes carboxylated feedstock molecules producing CH₄ (ref. ¹⁹) and a ‘photosynthetic’ planet, where CH₄ is generated from CO₂ over catalytic surfaces^{20,21}.

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Formation of Methane and (Per)Chlorates on Mars

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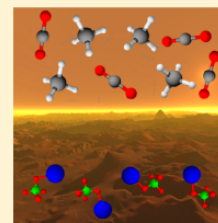
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Supporting Information

ABSTRACT: Methane, perchlorates, chlorates, and methyl chlorides have all been detected on Mars. The origin of these species has never been adequately explained. In this paper, we irradiated mixtures of CO₂, HCl, and a mineral catalyst—anatase, rutile, montmorillonite, and the Nakhla meteorite—with soft UV radiation for up to 3500 h and observed the formation of perchlorates, chlorates, methyl chlorides, and methane in a single experiment. Additionally, the methanogenesis for anatase was observed at −196 °C. Further, we propose that while methane is decomposed relatively quickly and therefore attains a steady-state concentration (0.41 ± 0.16 ppbv), the chlorinated compounds are much more stable and therefore would have accumulated throughout the Martian history. We estimate that this mechanism would be sufficient in the course of Martian history to accumulate perchlorate in the soil in 0.5 wt % in 5–50 cm depth, which is in accordance with the observed perchlorate content on Mars. This predicted perchlorate gradient may be observed with the Insight rover. Further, if microbes are present on Mars, they will likely inhabit depths below the perchlorate (i.e., 5–50 cm). This chemistry likely still continues on Mars to a certain extent, and any future exploration by rovers or planetary models should account for this process during their analyses.

KEYWORDS: methane on Mars, photocatalytic reduction, perchlorates, infrared spectroscopy, X-ray photoelectron spectroscopy



1. INTRODUCTION

Methane and perchlorates are two chemical species that are directly relevant to life on Earth. Up to 95% of methane on present day Earth is of biogenic origin,¹ and for this reason, it is often used as a biomarker gas for exoplanetary atmosphere detections.² Perchlorates, on the other hand, have bacteriocidal effects, which are enhanced by the presence of iron oxides, peroxides and UV radiation, as has been shown on the viability of *Bacillus subtilis* in simulated Martian conditions.³ Detection of both these species on Mars^{4–10} has therefore direct relevance to the study of potential life on Mars. Indeed, the discovery of methane (CH₄) on Mars initiated a debate concerning, among others, the possible chemical evidence of ongoing microbial metabolism on the Red planet.^{11,12} Also, the presence of perchlorates does not ultimately rule out the presence of life on the Red Planet,¹³ but the chances of survival in perchlorate-rich soil are significantly lower than on Earth. In this paper, we present an abiotic scenario of the creation of both species through photochemical reactions on the Martian surface.

1.1. Chlorinated Compounds on Mars. Several chlorine-containing species were detected on Mars, but their origin has not been explained yet. Up to this day, the detected chlorinated molecules on Mars are perchlorates, chlorates, and chloroalkanes such as dichloroethane, dichloropropane, chloromethanes (CH_xCl_y, where $x, y = \{1, 2, 3, 4\}$), and dichlorobutane.^{4,5} Chlorobenzene and chlorinated organics were also detected by the rovers Viking and Curiosity, but they are likely to have formed in the instrument oven during analysis.

Perchloric acid is highly reactive and readily forms perchlorate salts, which accumulate on the surface and whose content in Martian soil reaches 0.5 to 1 wt %.¹⁴ The presence of perchlorates has been observed by the Thermal and Evolved Gas Analyzer (TEGA) and the Microscopy,

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