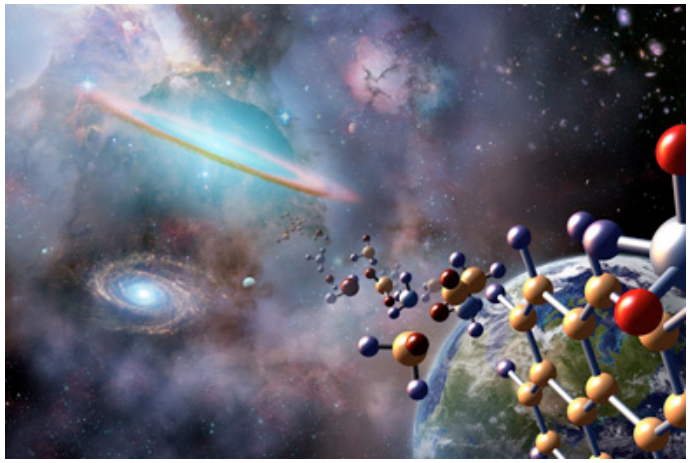
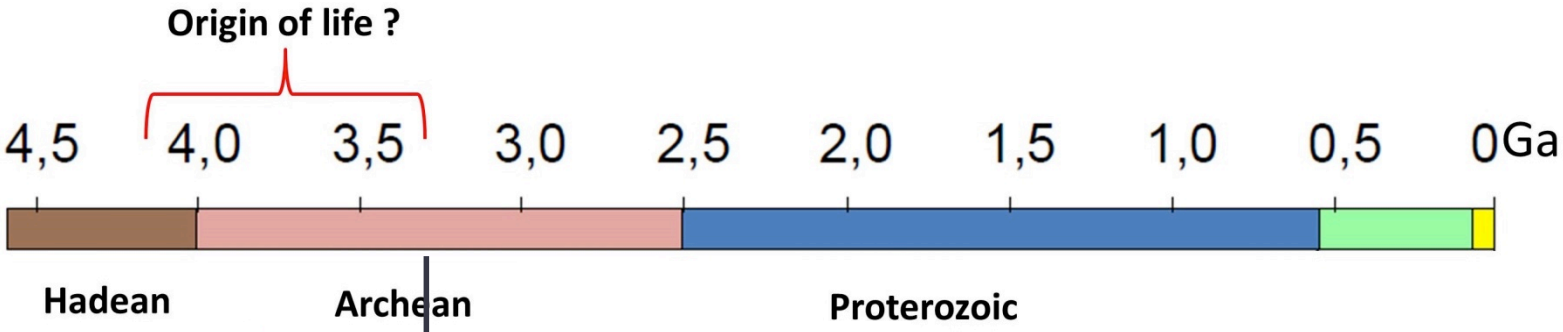
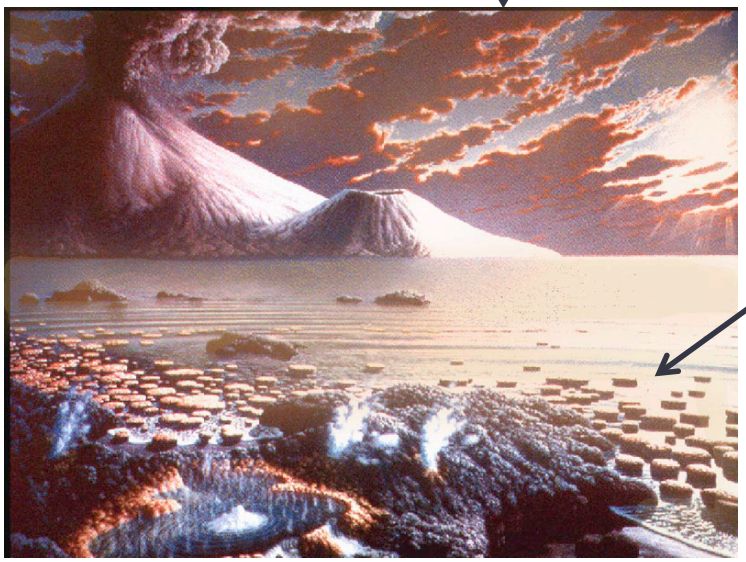
ORGANIC CHEMISTRY IN THE ATMOSPHERE OF THE EARLY EARTH

Prebiotic molecules in Space and Origins of Life on Earth
664. Wilhelm und Else Heraus-Seminar. Bad Honnef



When life appears on Earth
Key for success: ocean + organic molecules





Oldest fossiles discovered date from 3,4 Ga
Found in Australia
Stromatolites: column structures produced by cyanobacteria

When life appears on Earth
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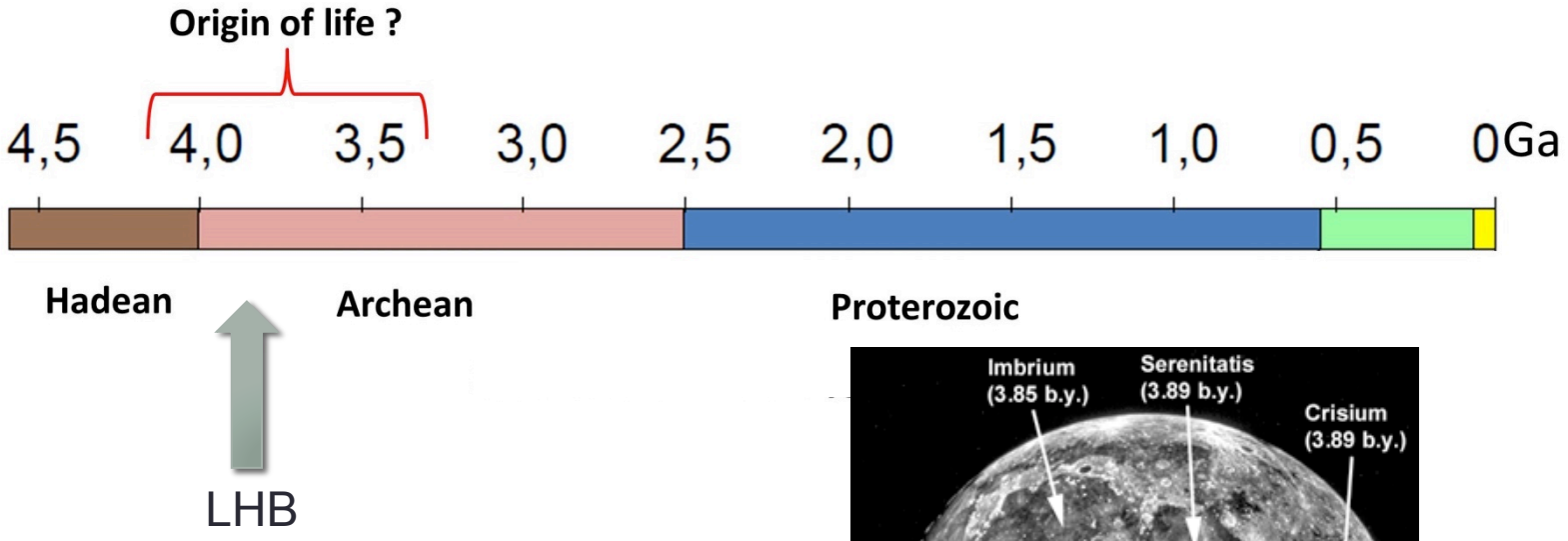

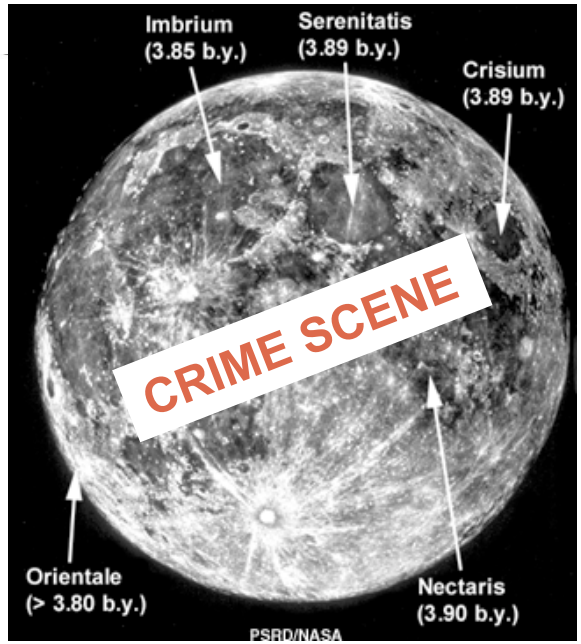

Late Heavy Bombardment
→Late Veneer?
Volatiles are possibly added during this period

When life appears on Earth
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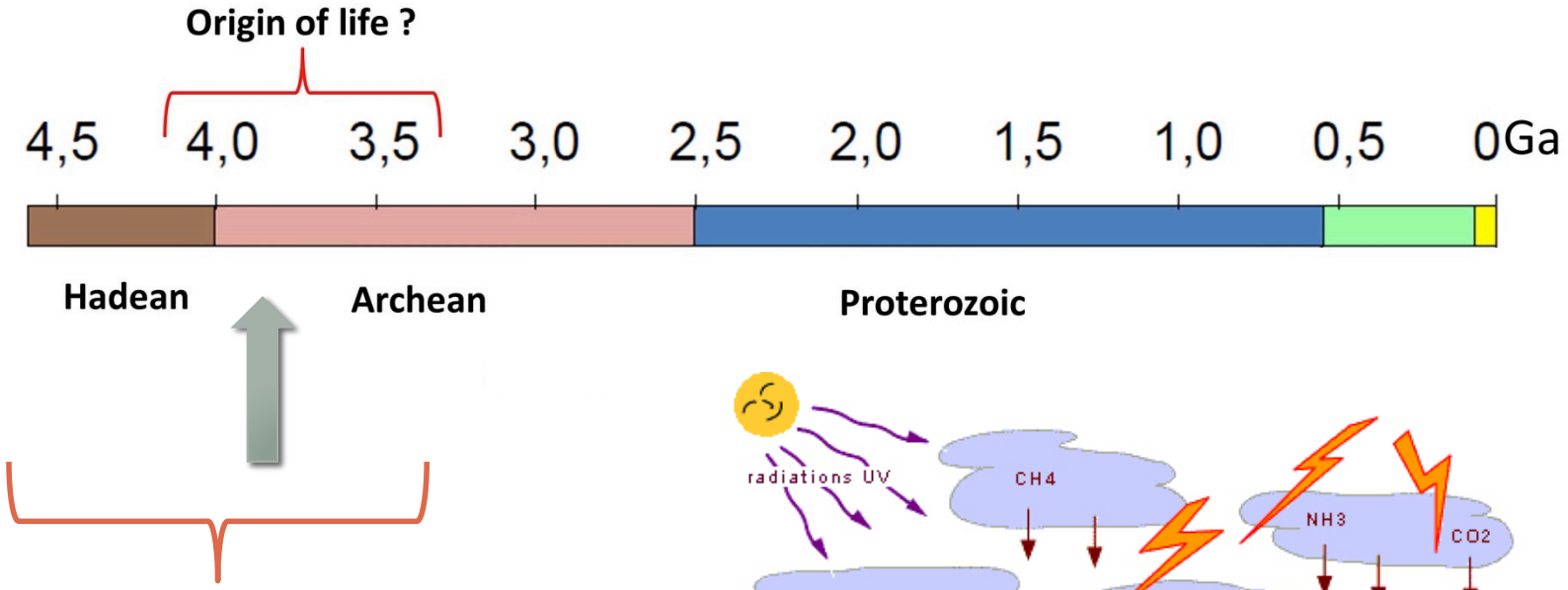
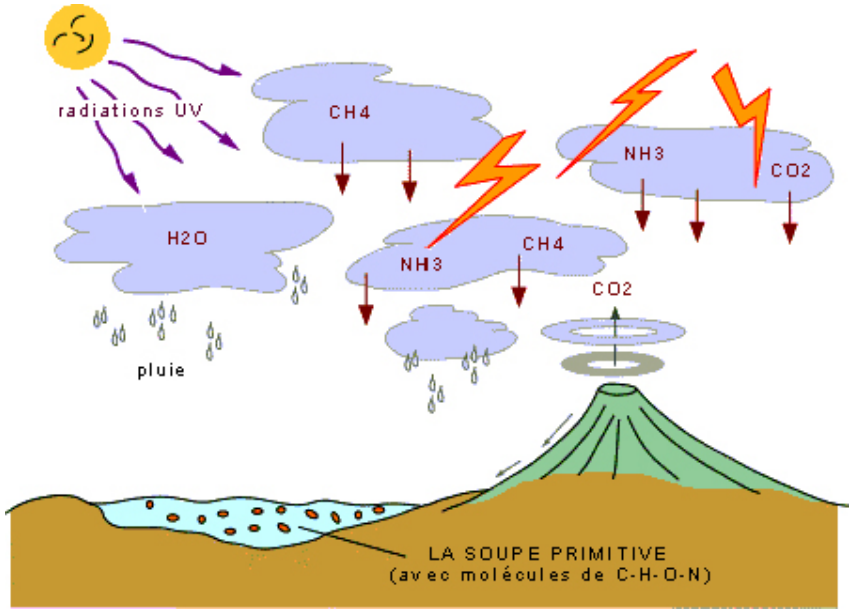


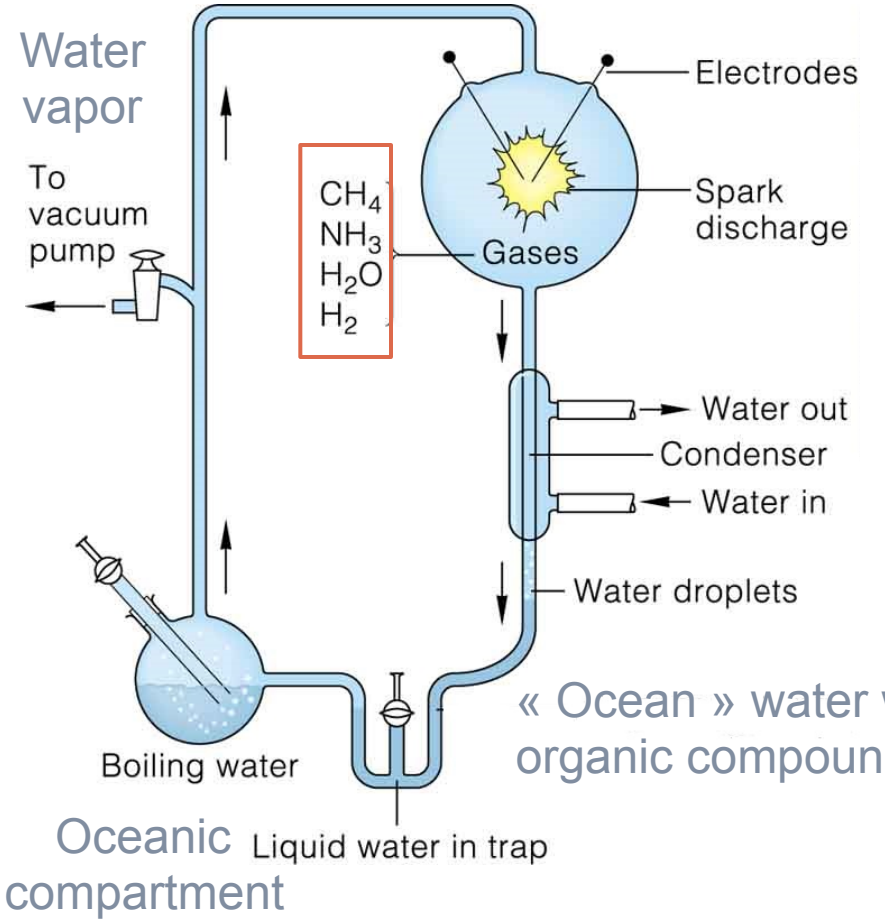
- Environmental conditions at this epoch?
- Role of the atmospheric chemistry & the primitive soup theory?



Oparin, 1924

Experimental simulation of the early Earth atmosphere

- Experiment by Miller&Urey (1953)



Primitive atmosphere expected to be made of CH_4, NH_3, H_2O, H_2

=Analogy with giant planets @time before H_2 excape

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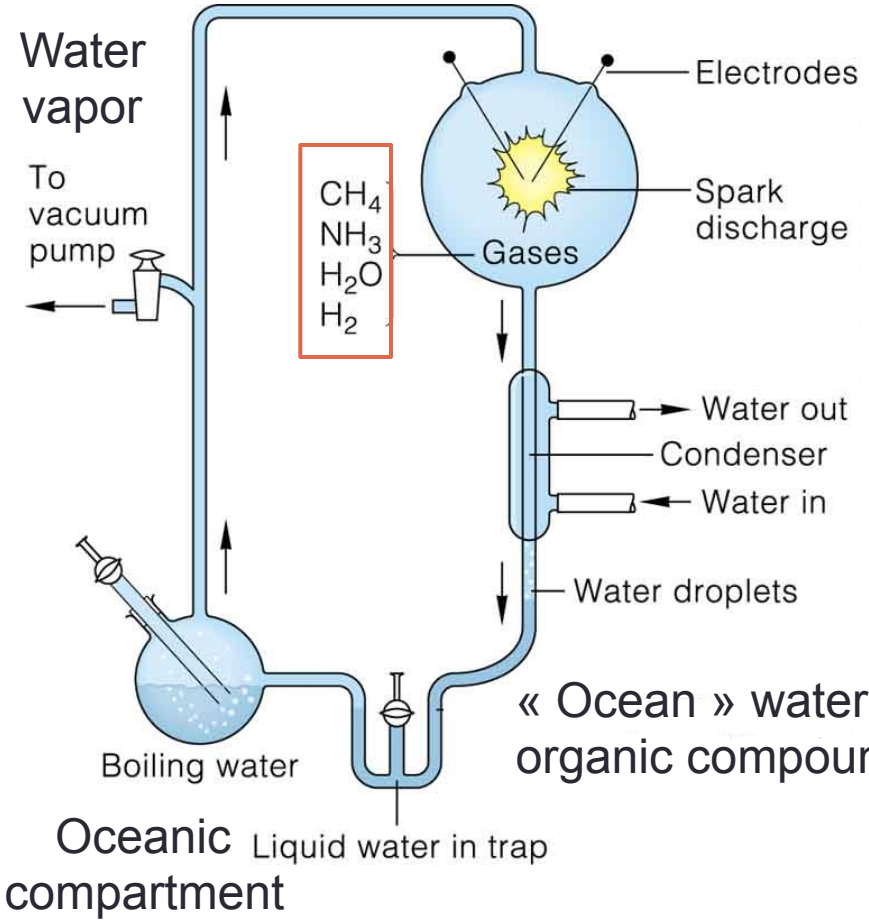

« Ocean » water with dissolved organic compounds for analysis

Tens of amino-acids!

Strong theory
→OK until the 2000's

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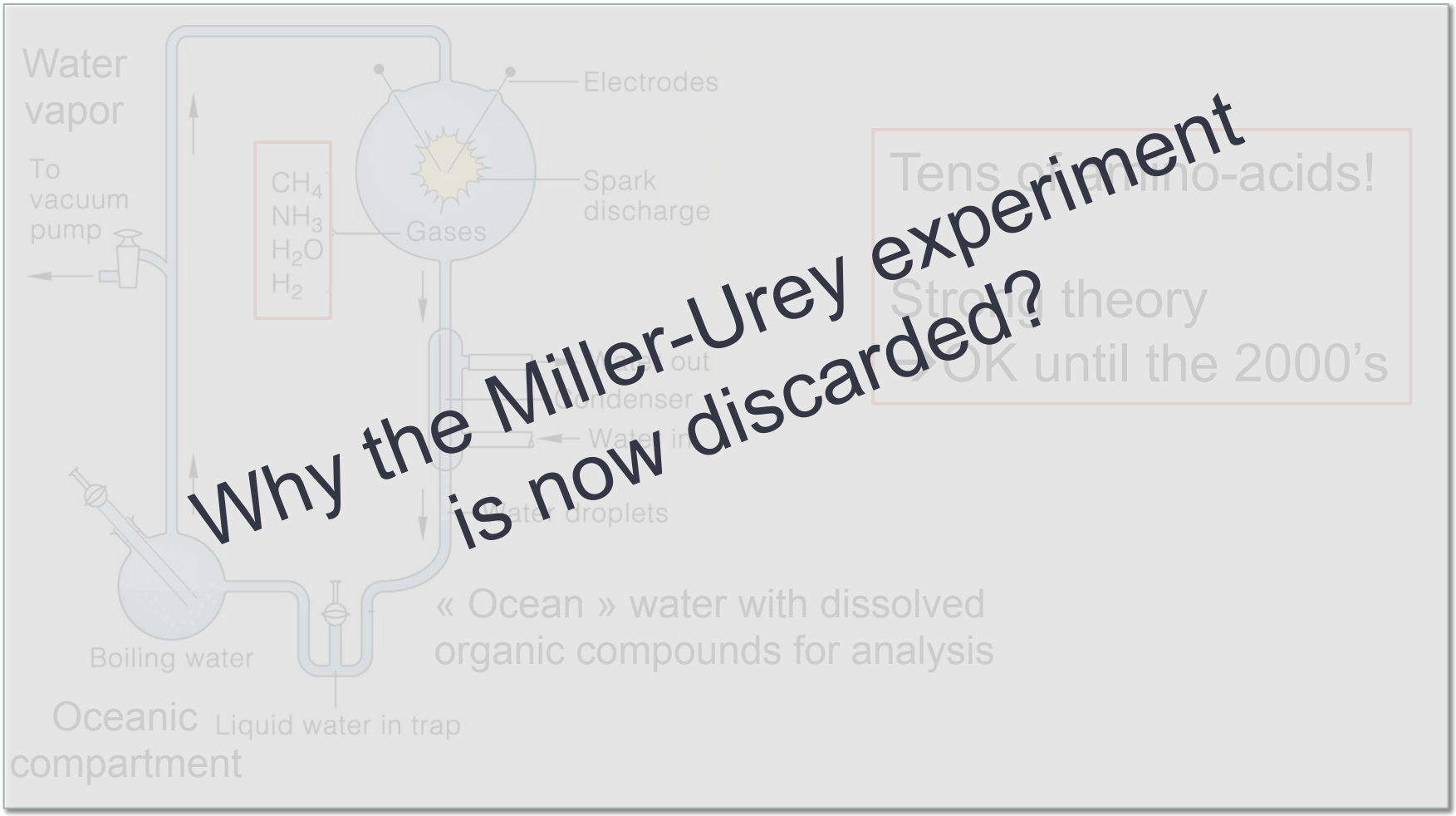
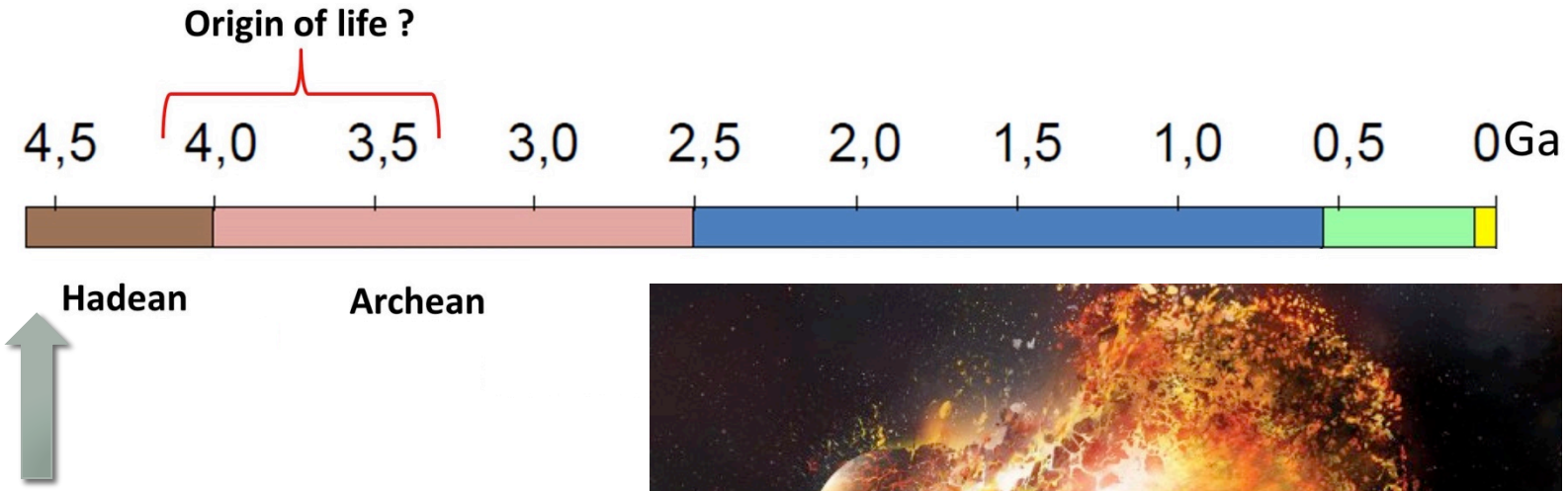


Massive escape of the proto-atmosphere



Large impacts
Degassed steam

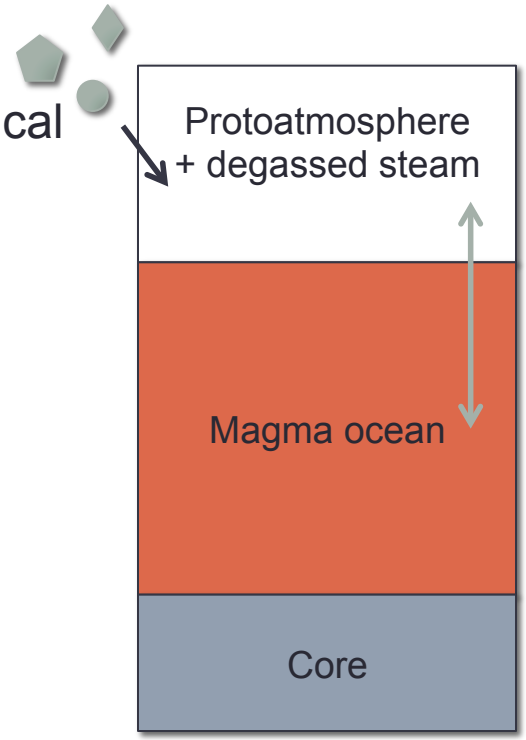
→No more primitive reduced atmosphere

Artist view of the cataclysmic impact that formed the Moon

Reconstruction of a 2^{ndary} atmosphere

1. Magma ocean:
   Ingassing process through gas-solubility equilibrium
   →capture of a small portion of the primitive atmosphere

Constant meteoritical inputs (CC)



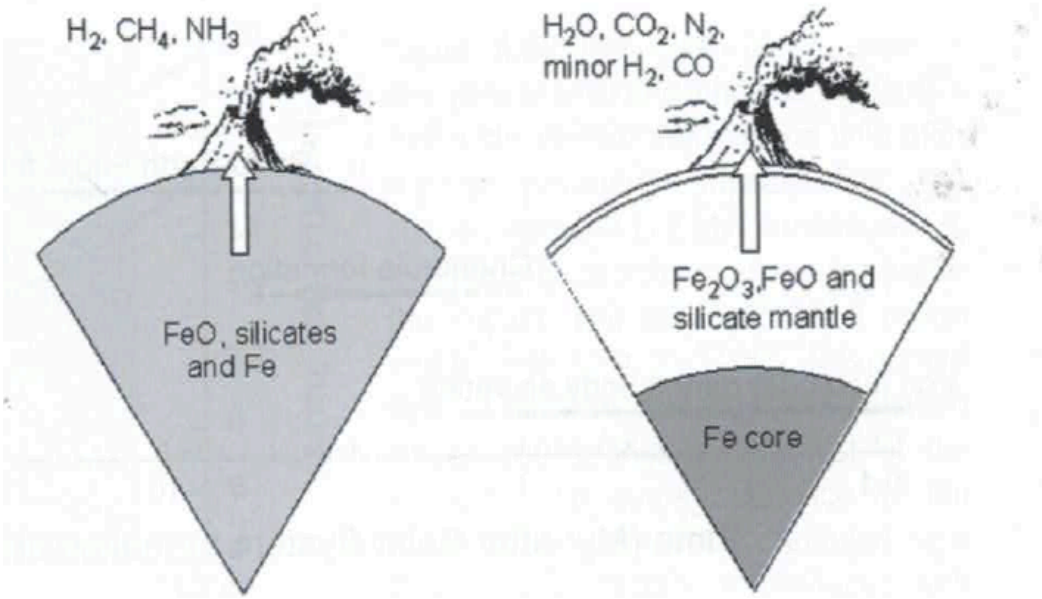
Gas solubility equilibrium
Ingassing / outgassing

Carbon storage

Jacobsen+ 2008
Dasgupta 2013

Reconstruction of a 2ndary atmosphere

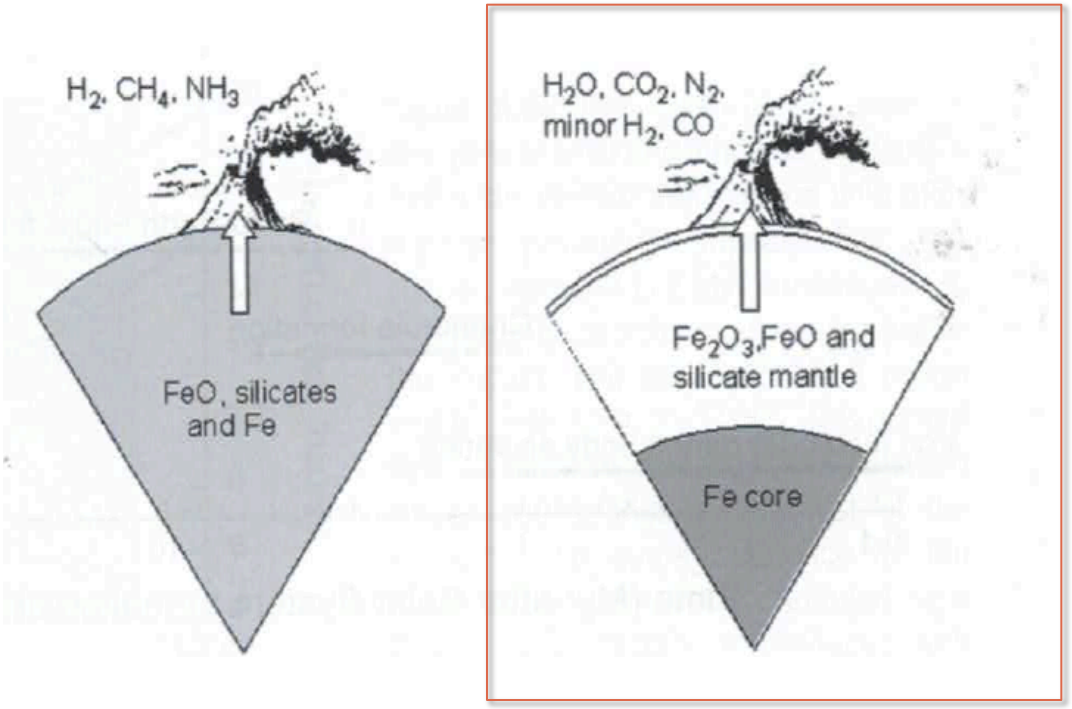
2. Outgassing during Hadean eon: formation of the ocean and the atmosphere



Depending on the oxydation state of the mantle,
the degassed atmosphere can be either reduced or oxydized

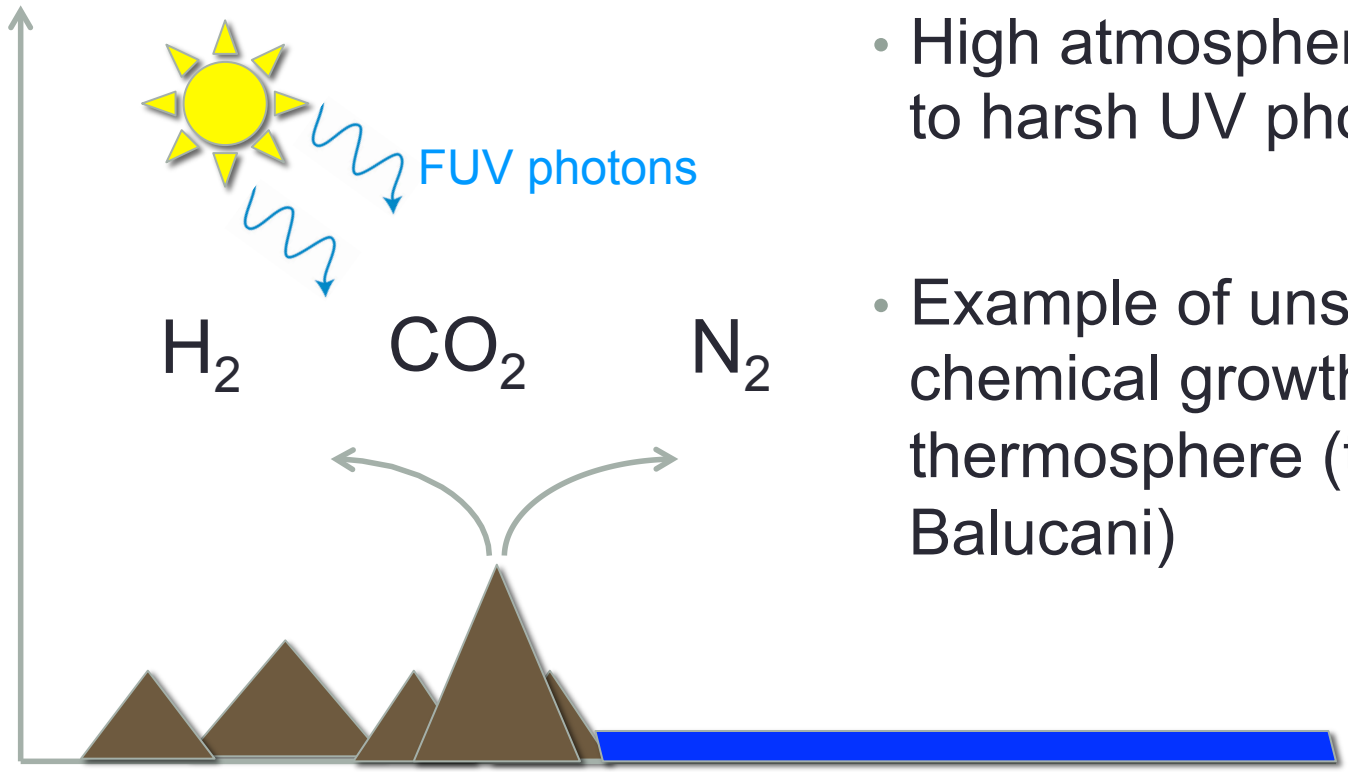
Reconstruction of a 2ndary atmosphere

2. Outgassing during Hadean eon: formation of the ocean and the atmosphere



Hadean oxygen fugacity similar as in present day mantle (Tail et al. 2011)

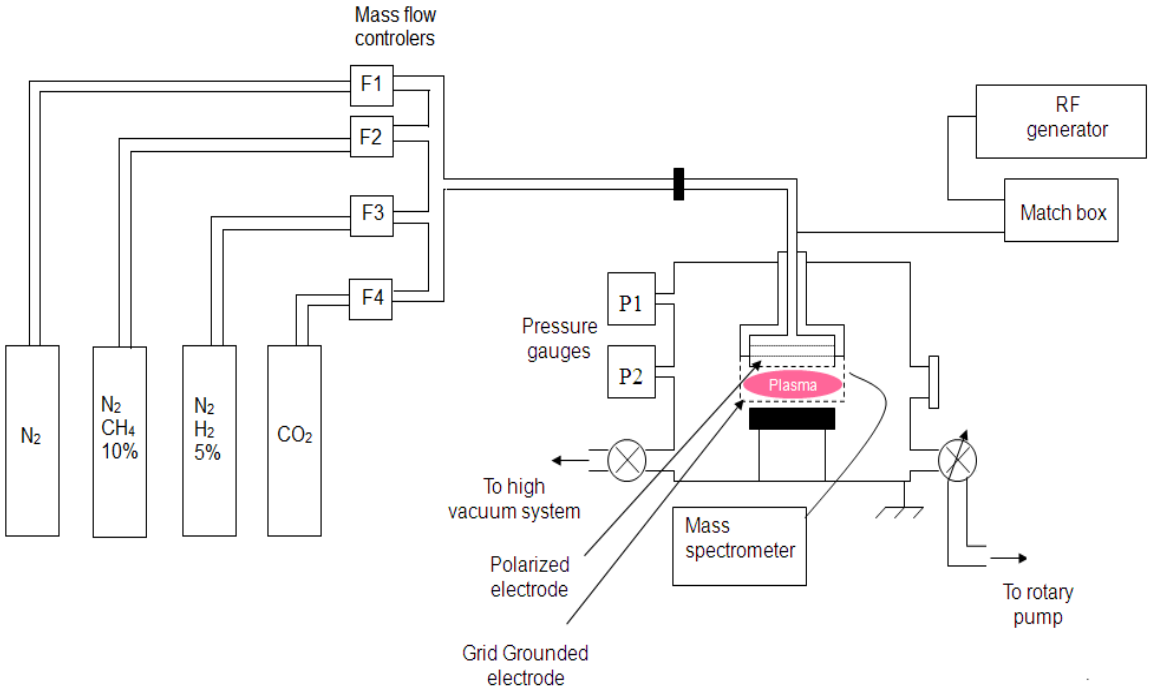
Organic chemistry in an oxydized atmosphere in the Hadean eon?



- High atmosphere submitted to harsh UV photons
- Example of unsuspected chemical growth in Titan thermosphere (talk by N. Balucani)

Experimental simulation of the chemistry in the early Earth high atmosphere

Benjamin Fleury, PhD thesis, 2015



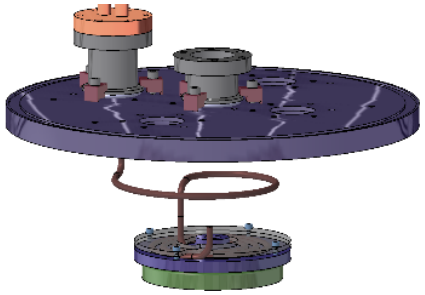
RF Plasma discharge: e- as proxys for FUV photons

Gas mixture: **N_2 – CO_2 – H_2** 91 - 5 - 4%

P=1 mbar, neutrals and ions at room temperature

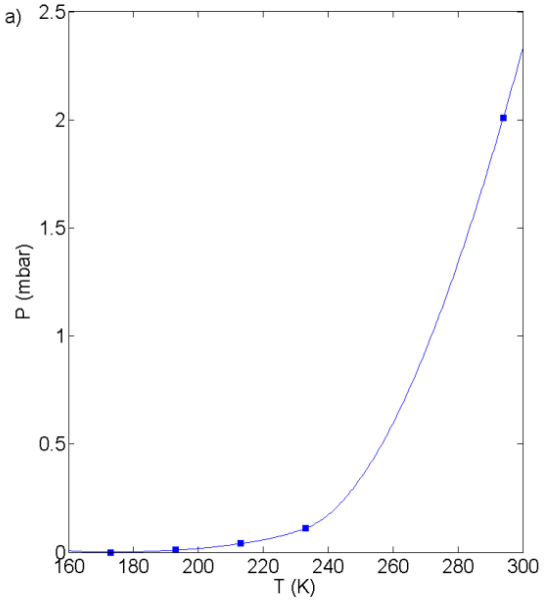
Cryogenic trapping of the gas products

- Cooling of the electodes by a regulated LN_2 circulation: T=173K



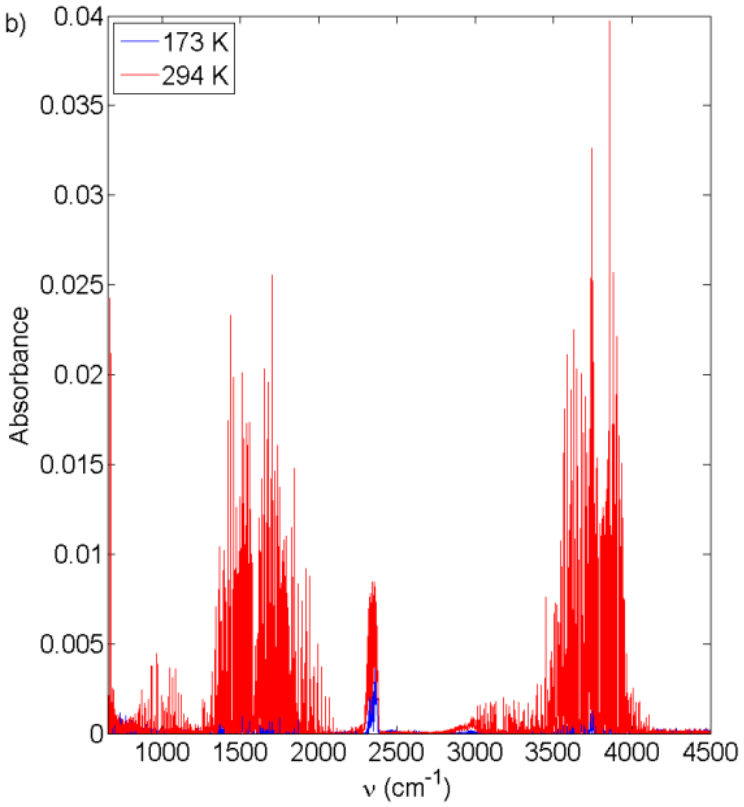
- Accumulation of gas products
- After 2 hrs of running experiment
  - Vacuum pumping
  - isolation of the reactor
  - Slow warming

→ 2 mbar of products



Main product : Water !

- Analysis by mid-IR spectroscopy



- Formation of O(1D) from CO_2

$CO_2 + e^- \rightarrow CO + \mathbf{O(^1D)} + e^-$

$CO_2 + e^- \rightarrow CO_2^+ + 2\ e^-$

$CO_2^+ + e^- \rightarrow CO + \mathbf{O(1D)}$

- Formation of OH radicals

$H_2 + O(^1D) \rightarrow \mathbf{OH} + H$

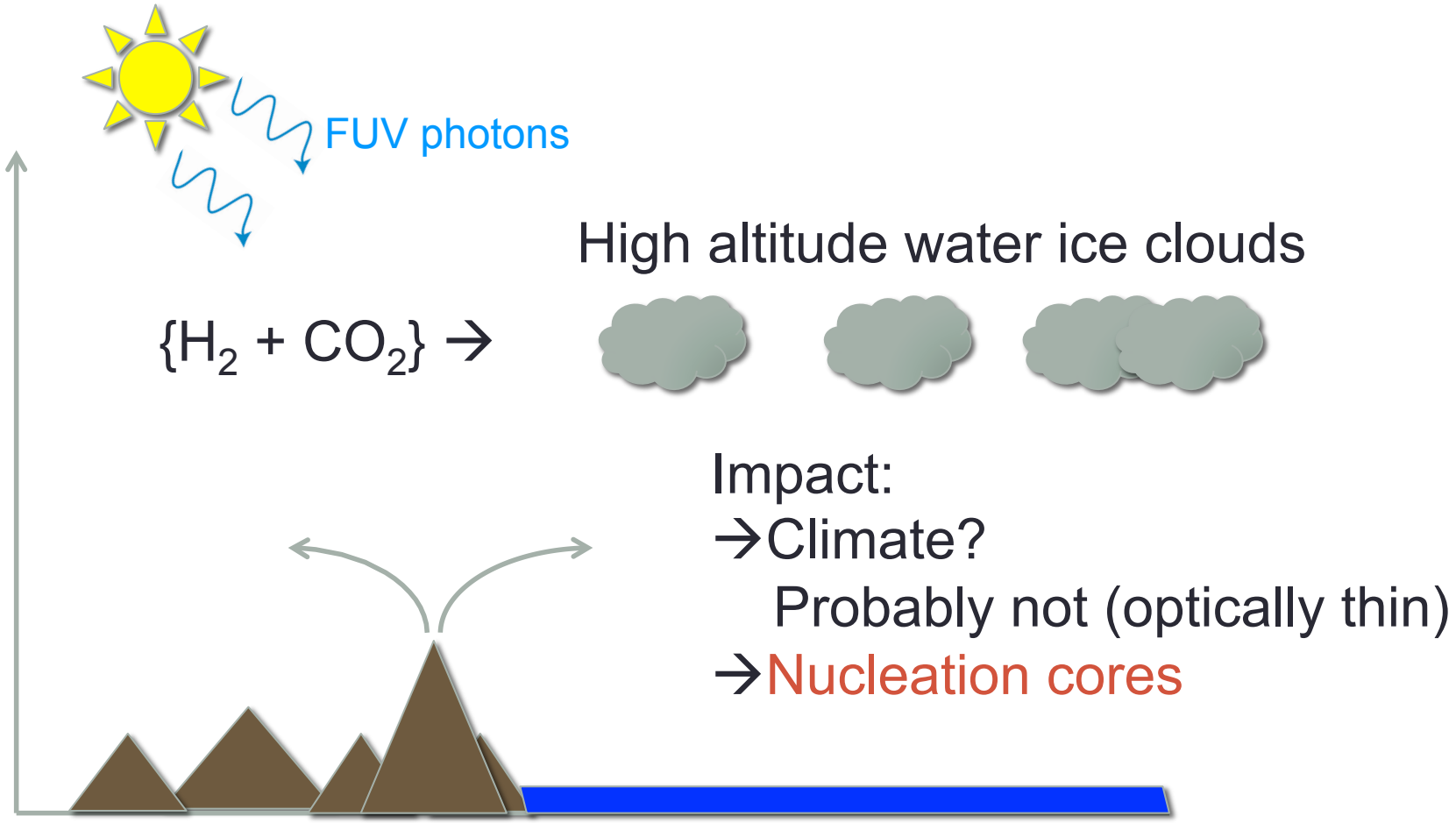
- Production of water

$H_2 + OH \rightarrow \mathbf{H_2O} + H$

$2\ OH \rightarrow \mathbf{H_2O} + O$

Fleury, Carrasco et al., ApJL, 2015

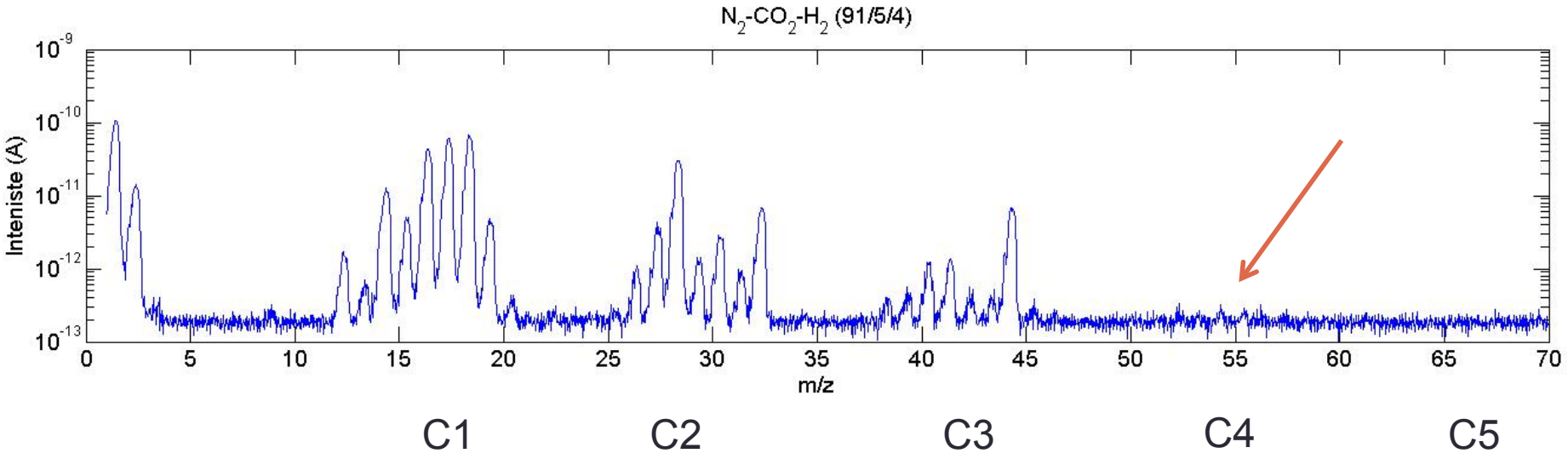
Unsuspected water formation at high altitude



Impact:
→Climate?
Probably not (optically thin)
→Nucleation cores

Fleury, Carrasco et al., ApJL, 2015

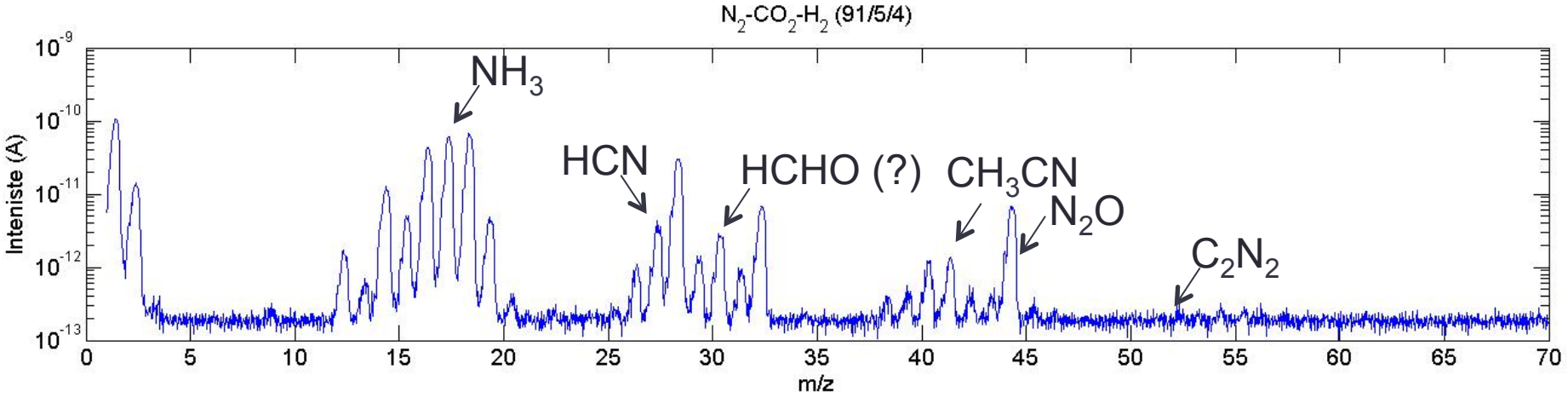
Analysis by *in situ* mass spectrometry



Detection of gas phase products up to C4
→CO_2 enables organic growth

Fleury, Carrasco et al., EPSL 2017

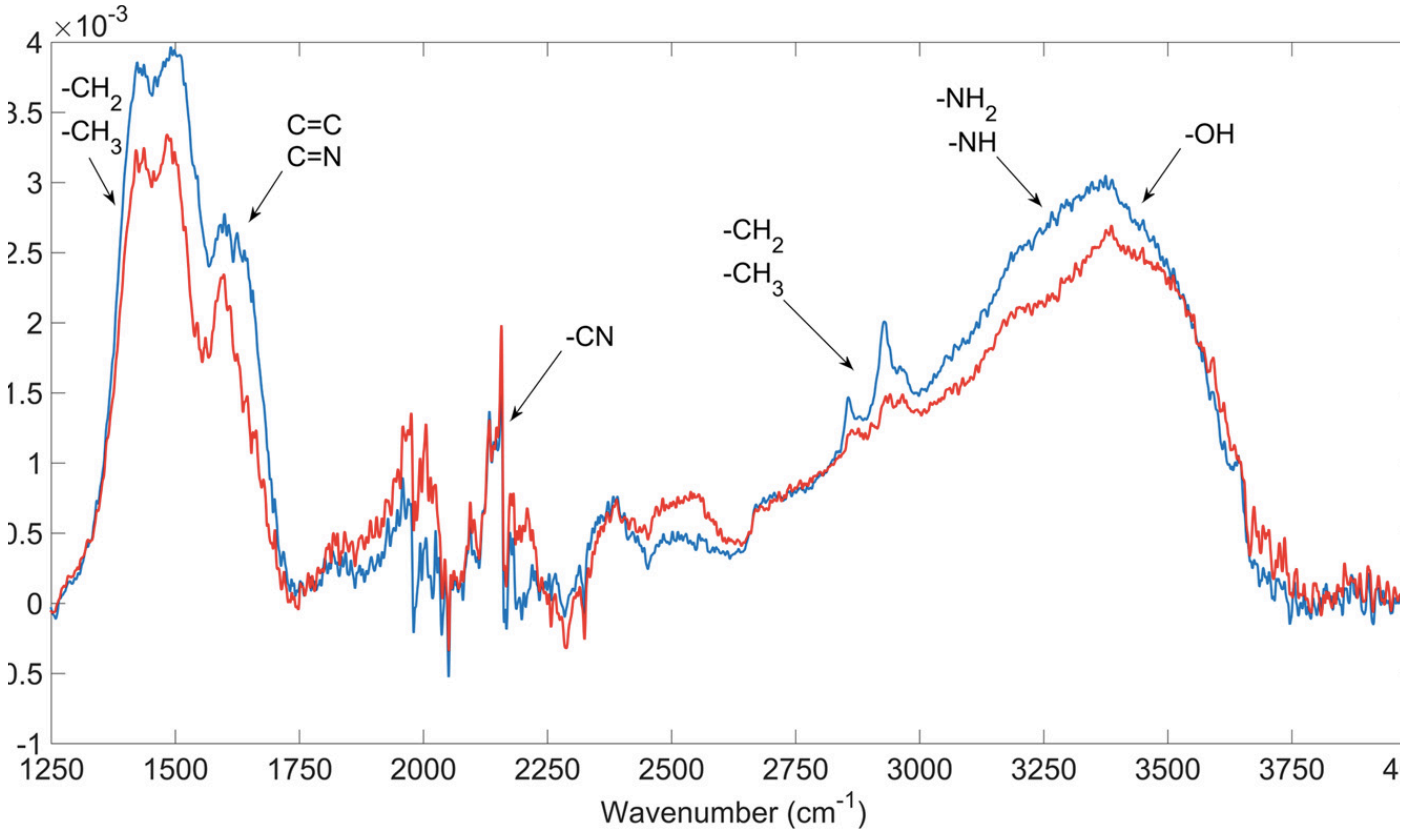
Analysis by *in situ* mass spectrometry



- Identifications by mid-IR spectroscopy & GCMS
- Importance for prebiotic chemistry
  - Strecker synthesis (amino acids): NH_3, HCN, HCHO
  - Formation of adenine (nucleic basis): HCN

Fleury, Carrasco et al., EPSL 2017

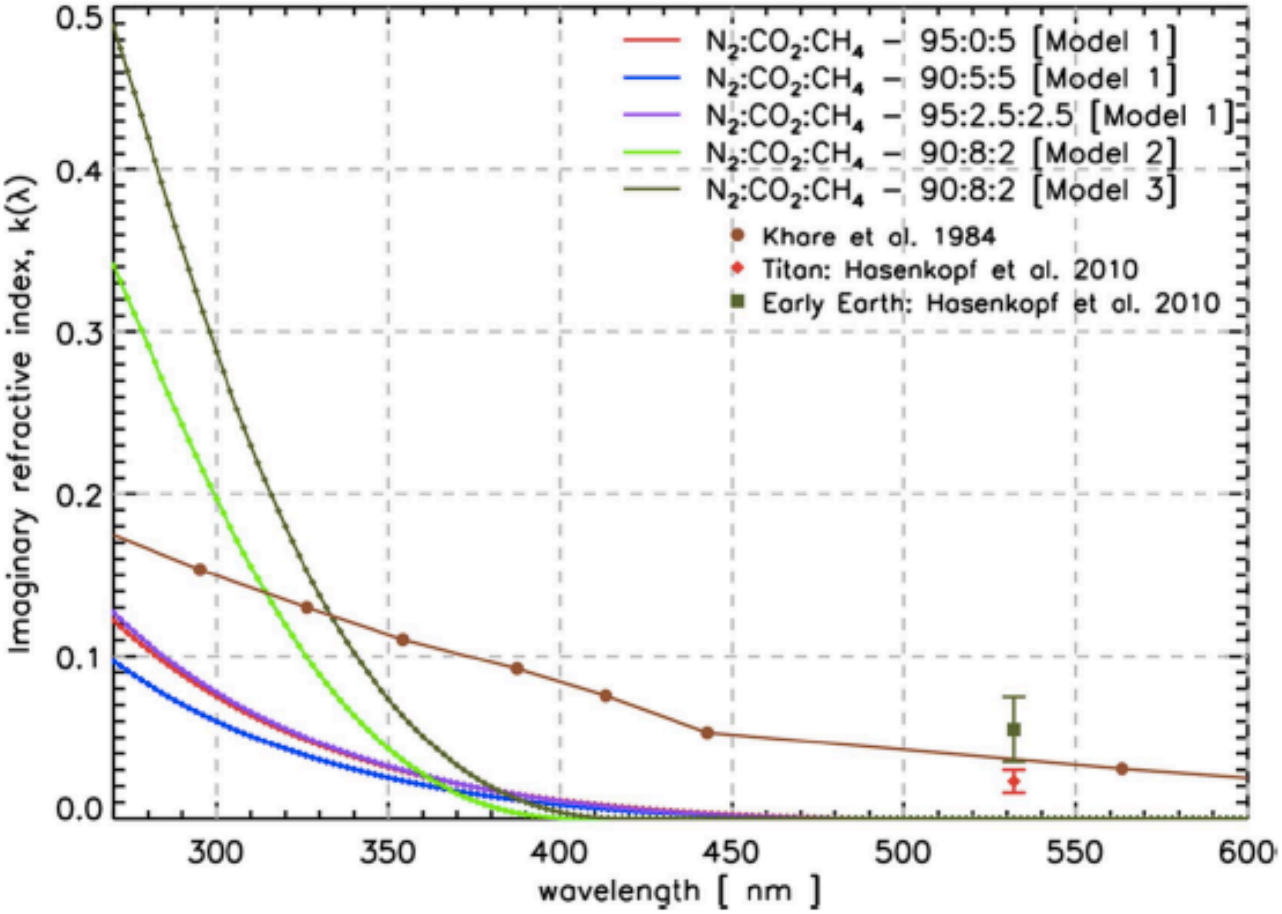
Production of solid organic material!



IR absorption spectra of the films deposited on 2 substrates in a N_2 / CO_2 / H_2 plasma (86 / 10 / 4%). Plasma duration = 40h

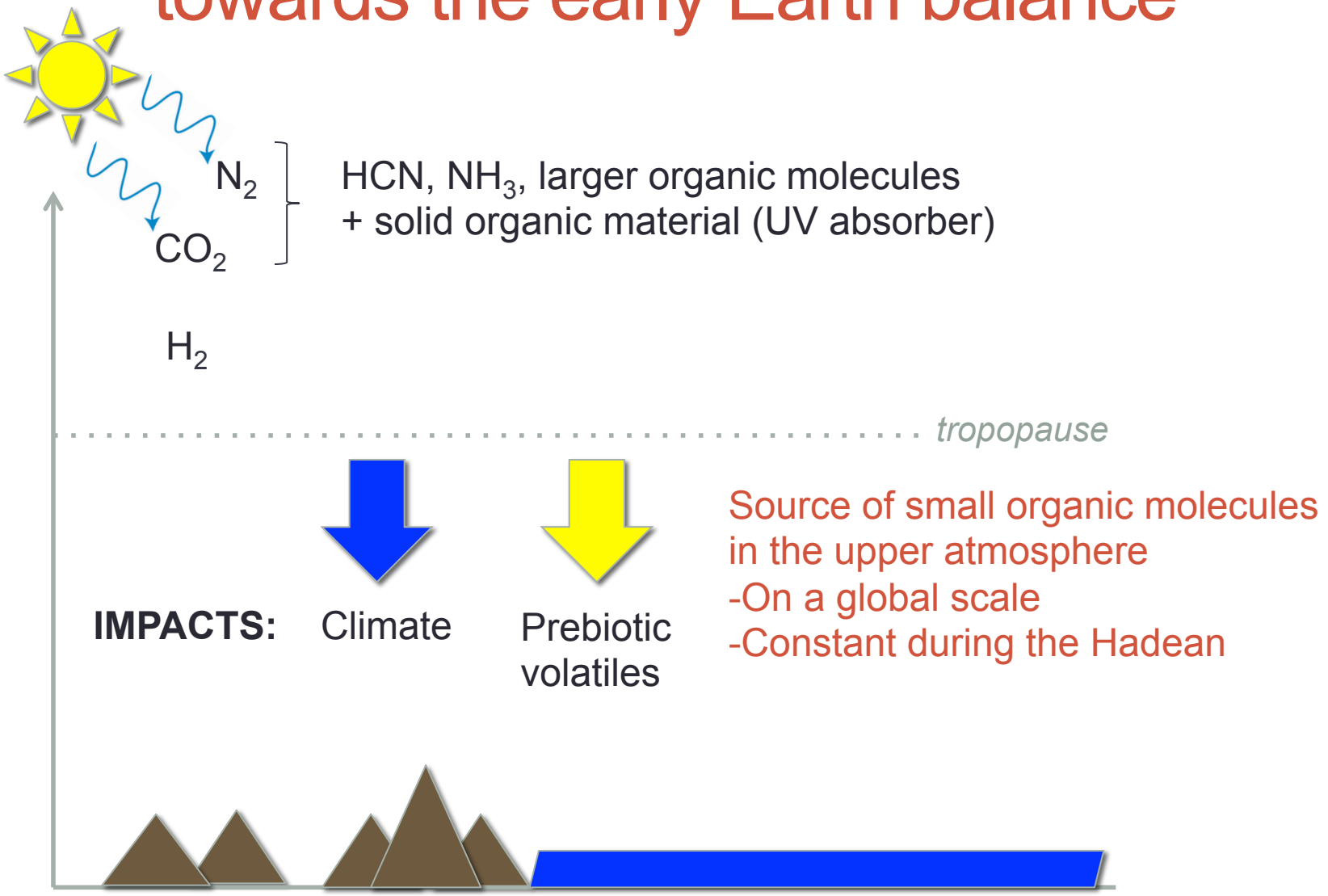
Fleury, Carrasco et al., EPSL 2017

Oxydized organic films: UV aborbers

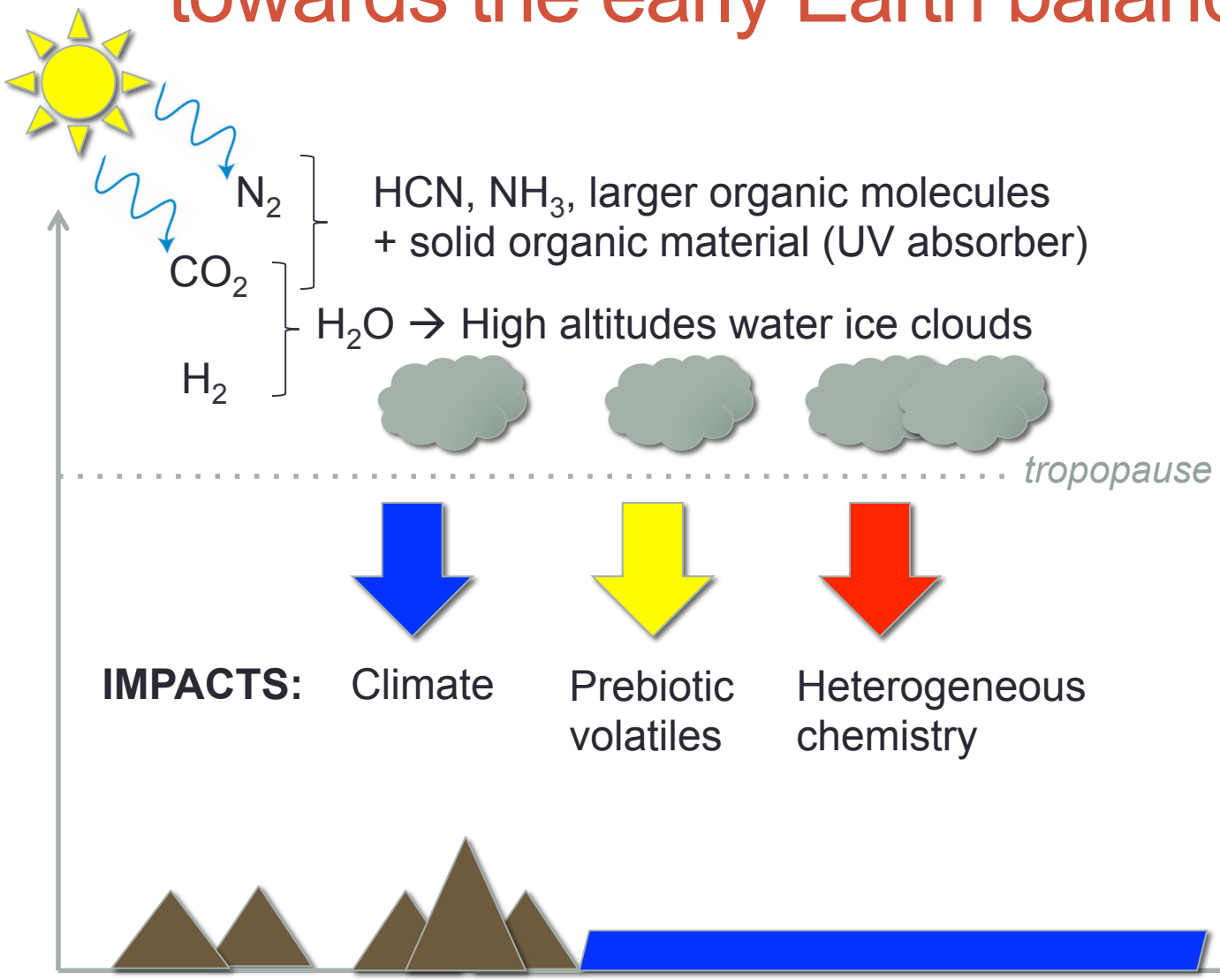


Gavilan, Broch, Carrasco et al. ApJL, 2017

Impacts of a CO_2-rich atmosphere towards the early Earth balance

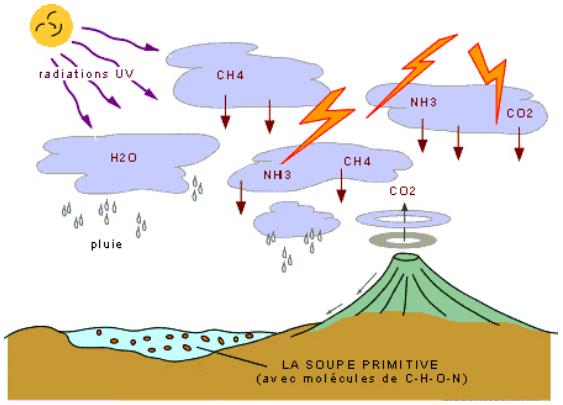


Impacts of a CO_2-rich atmosphere towards the early Earth balance



Conclusion :
The upper atmosphere of the CO_2-rich early Earth as an unsuspected source for water ice and organic molecules

- Small molecules in the gas phase: NH_3, HCN
- Ubiquitous and permanent during the Hadean eon
- Not to be neglected compared to exogeneous sources



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