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ChemPhys

Ferromagnesian rocks in association with carbonates as a signature for life

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Rocks to prebiotic molecules

Chemical evolution

World of rocks → World of Life

Which signs produced by rocks may be signatures of life ?

* Cavities inside rocks are media for concentration of molecules
* Some rocks evolve in water and carbon dioxide with production of heat
* Some rocks are sources of heat and excitation through radioactive decay

Serpentinization

Reactions are usually written :

olivine + pyroxene ⇔ serpentine

$(FeMg)_2SiO_4 + (FeMg)SiO_3 + H_2O + CO_2 \Leftrightarrow (Fe^{2+}Fe^{3+}Mg)_3Si_2O_5(OH)_4$

+ talc + brucite + magnetite + quartz + siderite

$(FeMg)_3Si_4O_{10}(OH)_2 + (FeMg)(OH)_2 + Fe_3O_4 + SiO_2 + FeCO_3$

+ magnesite

$+ MgCO_3 + \mathbf{H_2}$ (1)

Hydrolysis of olivine (fayalite, forsterite)

* $3\ Fe_2SiO_4 + 2H_2O = 2\ Fe_3O_4 + 3SiO_2 + 2\ H_2$ (2)

ΔH° = +42.7 kJ.mol^{-1} **ΔG° = +17.2 kJ.mol^{-1}**

* $2Mg_2SiO_4 + 3H_2O = Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$ (3)

ΔH° = -81,1 kJ.mol-1 **ΔG° = -47,4 kJ.mol-1**

Carbonation of olivine

* $Fe_2SiO_4 + 2CO_2 = 2FeCO_3 + SiO_2$ (4)

ΔH° = -157,3 kJ.mol^{-1} **ΔG° = -55,8 kJ.mol^{-1}**

* $Mg_2SiO_4 + 2CO_2 = 2MgCO_3 + SiO_2$ (5)

ΔH° = -177,3 kJ.mol-1 **ΔG° = -72,9 kJ.mol-1**

(Individual values from Robie and Hemmingway 1995)

Laboratory experiment

Denmark, *I. Aaberg et al. Goldschmidt'2013 Conference*

***Forsterite** was exposed to pure deionised water*
and supercritical $\boldsymbol{CO_2}$
***120°C**, 80 bars, 7 days of reaction*

"After reaction, synthetic forsterite, Mg_2SiO_4*, had transformed to well defined crystals, up to 25 µm in size, of **magnesite*** $\boldsymbol{MgCO_3}$ *and to spherical particles consisting dominantly of* $\boldsymbol{SiO_2}$*."*

CO_2 sc : (31.1°C, 73 bars)

Hydrolysis of pyroxene (ferrosilite, enstatite)

* $3FeSiO_3 + H_2O = Fe_3O_4 + 3SiO_2 + H_2$

ΔH° = +23,6 kJ.mol^{-1} ΔG° = +9,5 kJ.mol^{-1}

* $3MgSiO_3 + 2H_2O = Mg_3Si_2O_5(OH)_4 + SiO_2$

ΔH° = -62.3 kJ.mol^{-1} ΔG° = -39,6 kJ.mol^{-1}

Carbonation of pyroxene

* $FeSiO_3 + CO_2 = FeCO_3 + SiO_2$

ΔH° = -77,9 kJ.mol-1 ΔG° = -26,7 kJ.mol-1

* $MgSiO_3 + CO_2 = MgCO_3 + SiO_2$ in dry or wet conditions (zz)

ΔH° = -84,9 kJ.mol-1 ΔG° = -33,1 kJ.mol-1

(Individual values from Robie and Hemmingway 1995)

Production of talc

* $Mg_3Si_2O_5(OH)_4$ (serp) + 2 SiO_2 = $Mg_3Si_4O_{10}(OH)_2$ (talc) + H_2O

$\Delta H°$ = **- 4,4 kJ.mol-1** $\Delta G°$ = -12,6 kJ.mol-1

First conclusion :

Exothermic reactions of carbonations of Fe/Mg olivine and pyroxene and of hydrolyses of Mg-olivine and pyroxene might **locally** produce **heat** and induce the endothermic hydrolyses of Fe-olivine and pyroxene with release of **H_2 , even in a cold environment.**

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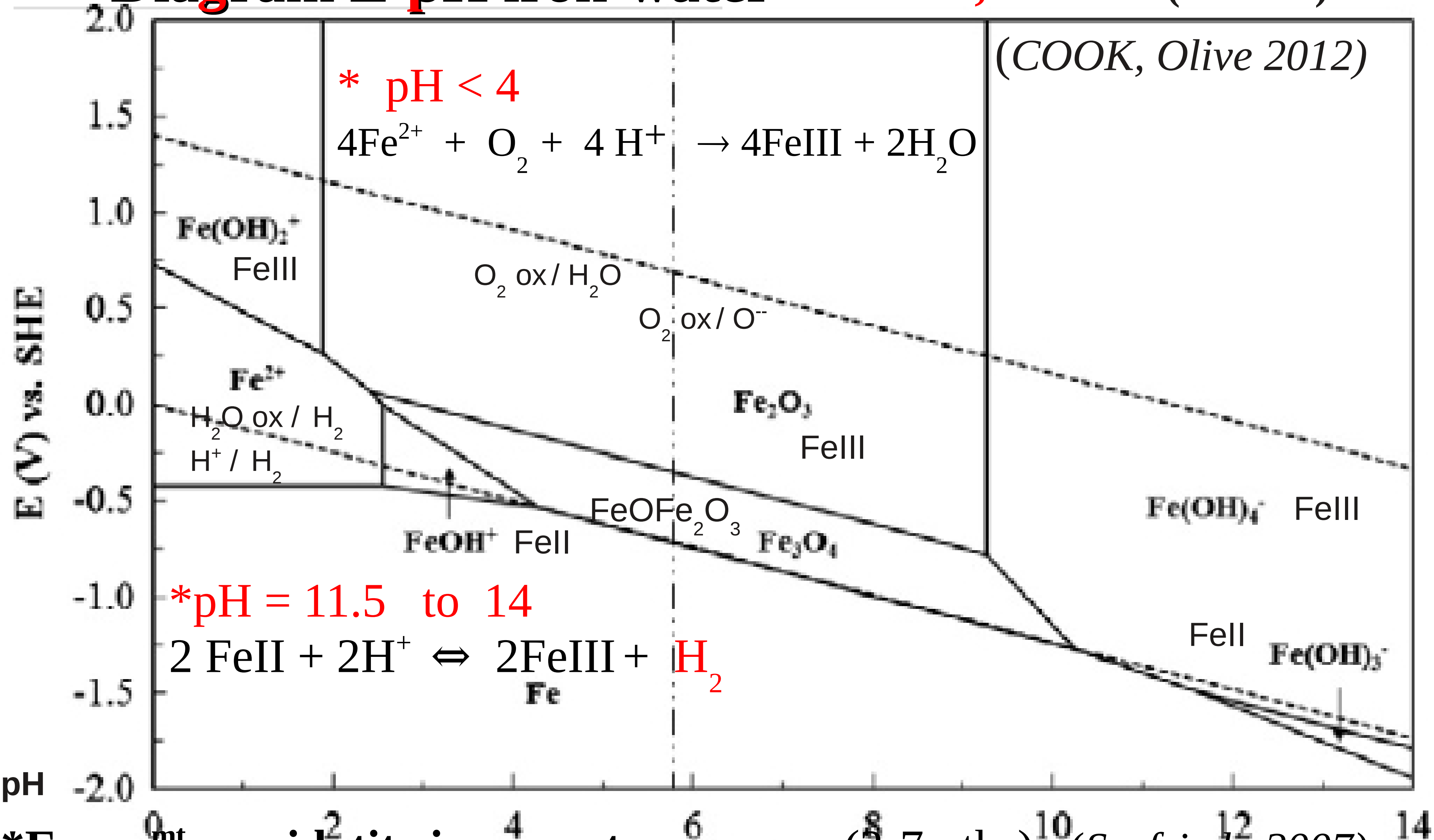
* SiO_2 + H_2O = $Si(OH)_4$

$\Delta H°$ = kJ.mol-1 $\Delta G°$ = kJ.mol-1

* 3 Fe_2SiO_4 + 8H_2O = 2 Fe_3O_4 + 3$Si(OH)_4$ + 2 H_2

$\Delta H°$ = +109.6 kJ.mol^{-1} **$\Delta G°$ = +85.3 kJ.mol^{-1}**

Diagram E-pH iron-water at 350 °C, 250 bar (25 MPa)



***Exper**[mt] **: peridotite in seawater** (3-7mths) *(Seyfried...2007)*

200°C, 500 bar pH 9.7-12.2 ; [H2] ↑up to 76 mmol/kg

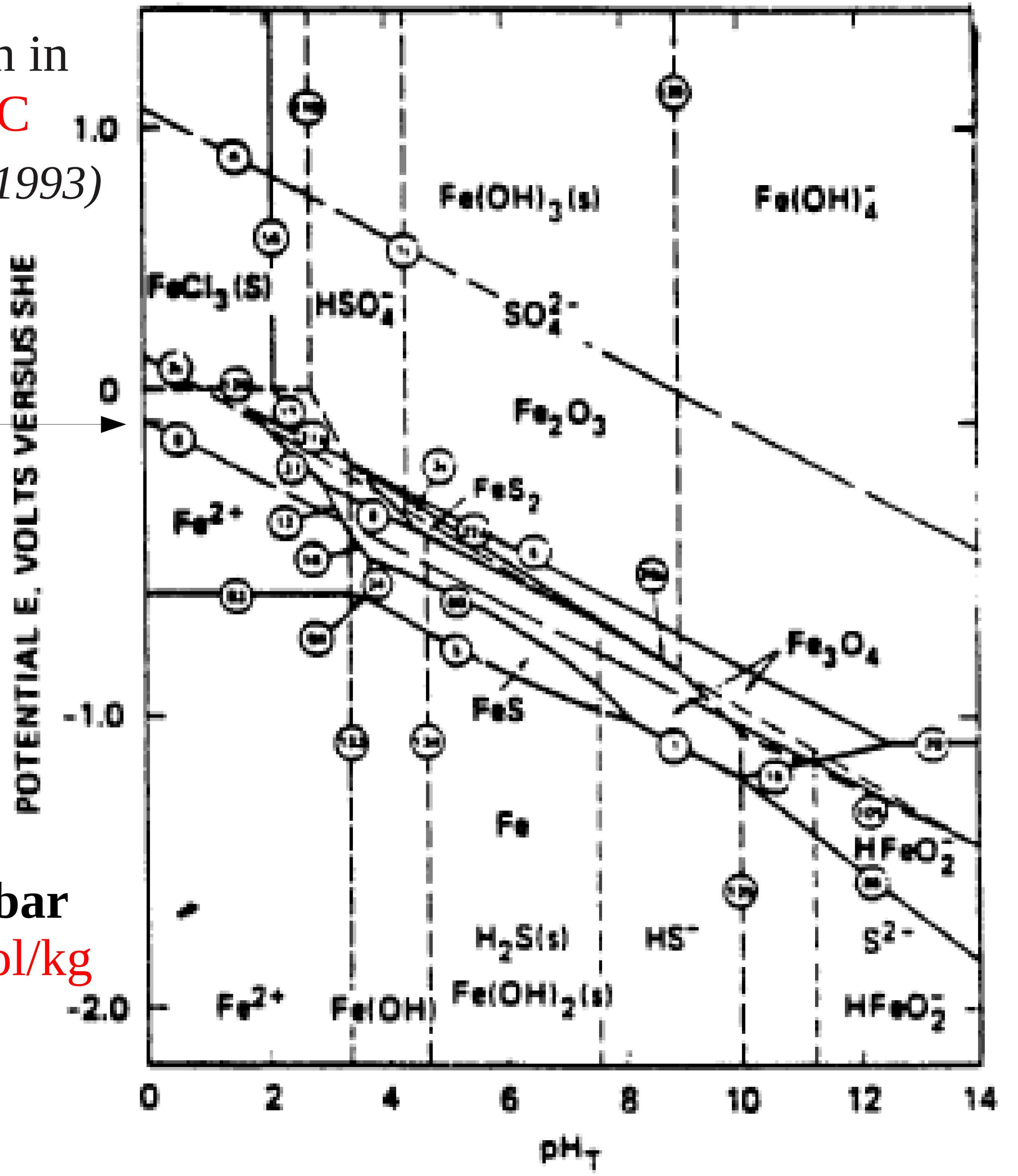
***Lost City** → 90°C, rocks highly serpentinized, chimneys in carbonates

pH9-11,[H2]↑15mmol/kg, *(Kelley Sci.307, 2005, Proskurowski Sci. 319, 2008)*

Diagram E-pH for iron in high-salinity brine at 250°C

Digby Macdonald (1981, 1993)

Equilibrium line of redox system H^+ / H_2 →



pH=3.5 to 8 ;↓when T↑

3FeS + 4H2O = Fe3O4 + 3SH2 + H2

no O_2 required for Fe_3O_4

*** Rainbow 365°C, 235 bar**

pH=2.8 $[H_2]$=16 mmol/kg

(Charlou...2002)

Laboratory synthesis of peptide like molecules

* $(\mathbf{CO}+N_2(NH_3)+H_2O)_g$ + protons, He ions, e-, soft X-rays, γ rays,

→ peptide-like → **amino acids** (N_2 not UV, NH_3 yes UV)

CO not CO_2 *(Kensei KOBAYASHI...OLEB1990..2008....)*

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* $CO_2 + \mathbf{H_2} \rightarrow \mathbf{CO} + H_2O$ P_{atm}, H_2 flow - **500°C** / 5h *(Chen...2000)*
* $CO_{2\ \mathbf{hydrothermal}}$ + 4 $\mathbf{H_2}$ → $\mathbf{CH_4}$ + 2 H_2O

390°C, 400 bars *(Foustoukos...Science 304, 2004)*

250°C, 325 bars *(McCollom... Earth Planet Sci. Lett. 243, 2006)*

FTT : $\mathbf{CO_{gaz} + H_2}$ → CH_4 + hydrocarbons *(Anderson 1984)*

Hydrogenation of CO_2 within the **locally heated** ferromagnesian rocks should lead to CO.

Origin of H_2 ?

* **Endothermic hydrolysis of Fe olivine and pyroxene at high pH : 11.5-14**

* **Water radiolysis**
  * Gamma rays induce water radiolysis :
    H^+, $H^\bullet$, $OH^\bullet$, e^-_{hyd} also : O_2 , H_2O_2 and mainly **H_2**
  * Radiolysis of supercritical water → exponential production of H_2
  * High [H_2] found at 700 to 3300m, in Witwatersrand Basin, Sth Africa, where FeIIsilicates are absent.
    [H_2] : consistent with production through radioactive decay of ^{238}U, ^{232}Th and ^{40}K. *(Lin L.H. 2005, G3)*

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cosmic radiation and/or radionuclides might participate to formation of H_2 and excitation.

(M.P. BASSEZ C.R. Chimie 2008)

Second conclusion

Geological sites with serpentine (a proof of production of heat through exothermic hydrolyses of Mg olivine and pyroxene)

and/or talc (product of slightly exothermic reaction of SiO_2 on serpentine)

associated with Fe/Mg carbonates (a proof of high heat production and of CO production when Fe-carbonates are present)

might **locally** be favorable for peptide like molecules.

Cosmic radiation and/or
Short-lived radionuclides from **Early Earth** or **LHB**, and **long-lived radionuclides** might have contributed to $\mathbf{H_2}$ formation and also to **excitation** of the N_2, CO, H_2O reacting mixture.

Geological sites with rocks biosignatures

* In Archean times on Earth

* P_{atm} (**CO_2**) several times higher
* P_{atm} (**N_2**) < 1.1 bar ; =0.5 bar ? *(Marty 2013)* ; actual $P_{atm}(N_2)$=0.8 bar

* The **Earth magnetic field** was much **lower** :
  ~17 % of present day value *(Hale 1987, Yoshihara and Hamano 2002)*
  ~ 50-70 % of present day (*Tarduno 2010*)
* Paleoarchean Sun is still under debate :
  little is known about coronal mass ejection
* **Cosmic radiation** : gamma rays, protons, electrons...
  → surface of the Earth

* ~3.8 Ga ago : Late Heavy Bombardment : LHB
  now extinct **radionuclides**

(Marie-Paule BASSEZ 2008, 2009, 2010, 2012, 2014)

*** the Archean Isua Supracrustal Belt, ISB,**

* Mafic to ultramafic rocks, rich in **Fe** and **Mg**.

* Intra-oceanic **subduction** zone operating ~3.8 Ga *(Polat...2002, Furnes... 2009).*

* **Serpentinites** : ~Archean analogs of the modern serpentinite mud volcanoes of the Mariana and Izu Bonin arc,
with fluids T **100-300°C** and **high pH values, 9 to 12.6** *(Pons 2011).*

* **Associations of carbonates and phyllosilicates** are observed.
There is *"a spatial correlation between metacarbonates (*alternating layers of silicates and carbonates) *and ultramafic rocks* " *(Rose 1996)*
Veining : "*a result of fluid movement across the ultramafic-host-rock"*

* ISB dated 3.8 Ga with **U**-Pb analyses of zircons *(Michard-Vitrac 1977).*

Radionuclides were present : from Uranium and LHB

In the subducted zone, water was apolar and concentrated CO_2 and N_2 *(Bassez 2003)*

Some collected samples contain talc and Fe carbonate *(Albarede 2014)*

*** on Mars** on the Mars Reconnaissance Orbiter (MRO) with the Compact Reconnaissance Imaging Spectrometer (CRISM)

* in and near **Nili Fossae**, west of the Isidis basin, in Noachian-aged rocks (~3.8 Ga) olivine, **serpentine** and **carbonates** *(Ehlmann 2010).*

* On the floor of **McLaughlin Crater** at Mawrth Vallis, in Noachian terrain : **Fe/Mg-rich phyllosilicates** and **Mg-carbonates** *(Michalski 2013)*

* Nili Fossae : carbonates related to magnesite (MgCO3),
* McLaughlin : Fe/Mg-carbonates and Fe-dolomite *(Bishop 2013).*

* OMEGA instrument on ESA Mars Express, showed **phylloslicates** only within the oldest Noachian terrains *(Bibring...2006).*

* Curiosity: **phyllosilicates** in John Klein and Cumberland *(Vaniman 2014)*

Mars

* Cosmic radiation and radionuclides from LHB

* N_2 on early Mars : if $P(N_2)=0.5$ bar, T still < 0°C *(von Paris, 2013)*

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* Radionuclides from LHB, in **Noachian** terrains
might have induce **local formation of water in liquid state**,
which triggered the **exothermic reactions** of ferromagnesian rocks

* Hydrolysis and carbonation of olivine
→ **H_2** , **Fe/Mg-carbonates, local heat** , and **CO**.

Nili Fossae and McLaughlin as other Noachian terrains might contain **peptide-like molecules** which have been dried or aggregated in the form of water insoluble macromolecules.

Favorable sites for a search for biological molecules,
(Bassez Nature Precedings 2011)

* Meteorites

* **Murchison** carbonaceous chondrite, CC
  CI1 chondrites **Orgueil** and **Ivuna**, and **Tagisk Lake** :
  osnium labelled **organic matter** associated with **serpentines**
  (Pearson 2007).
* Murchison : magnetite is not associated with organic material.
  (Pearson 2007).

* **Uranium** present inside Murchison *(Goldmann 2014).*

Cosmic radiation encountered by Murchison along the path between the asteroid belt and Earth, or radionuclides might induce reactions described.

* Enceladus - satellite of Saturn

Cassini :

* icy surface above a hot ocean and a **high density core** *(Iess 2014)* composed of **olivine** *(Sekine 2011).*
* *water-rich plumes erupting from warm fractures near the south pole (Sekine 2011)* .
* Gases in the plumes : CO_2, CH_4, NH_3, HCN, CO or N_2, H_2

Na,K-carbonates, nano-sized silicate icy grains, **radiogenic ^{40}Ar** *(Waite 2009, zolotov 2011, Postberg 2011, sekine 2011, Morooka 2011,).*

Hypothesis : Radioactive decay might have trigger the melting of ice and set some water in the liquid state. Then exothermic reactions contributed to the formation of the liquid ocean and of organic molecules.

Conclusion

In cold terrains, **radionuclides** might trigger formation of water out of ice.

Consecutively, the suite of exothermic carbonations of Fe/Mg olivine and pyroxene, and hydrolyses of Mg olivine and pyroxene, maintain water in the liquid state and produce serpentine and/or talc associated with Fe/Mg carbonates.

Which signs produced by rocks may be signatures of life ?

serpentine and/or talc in association with Fe/Mg carbonates in an environment of cosmic radiation and/or radionuclides

(Marie-Paule BASSEZ 2008, 2009...2012, 2014 just submitted)

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Empedocle of Agrigento

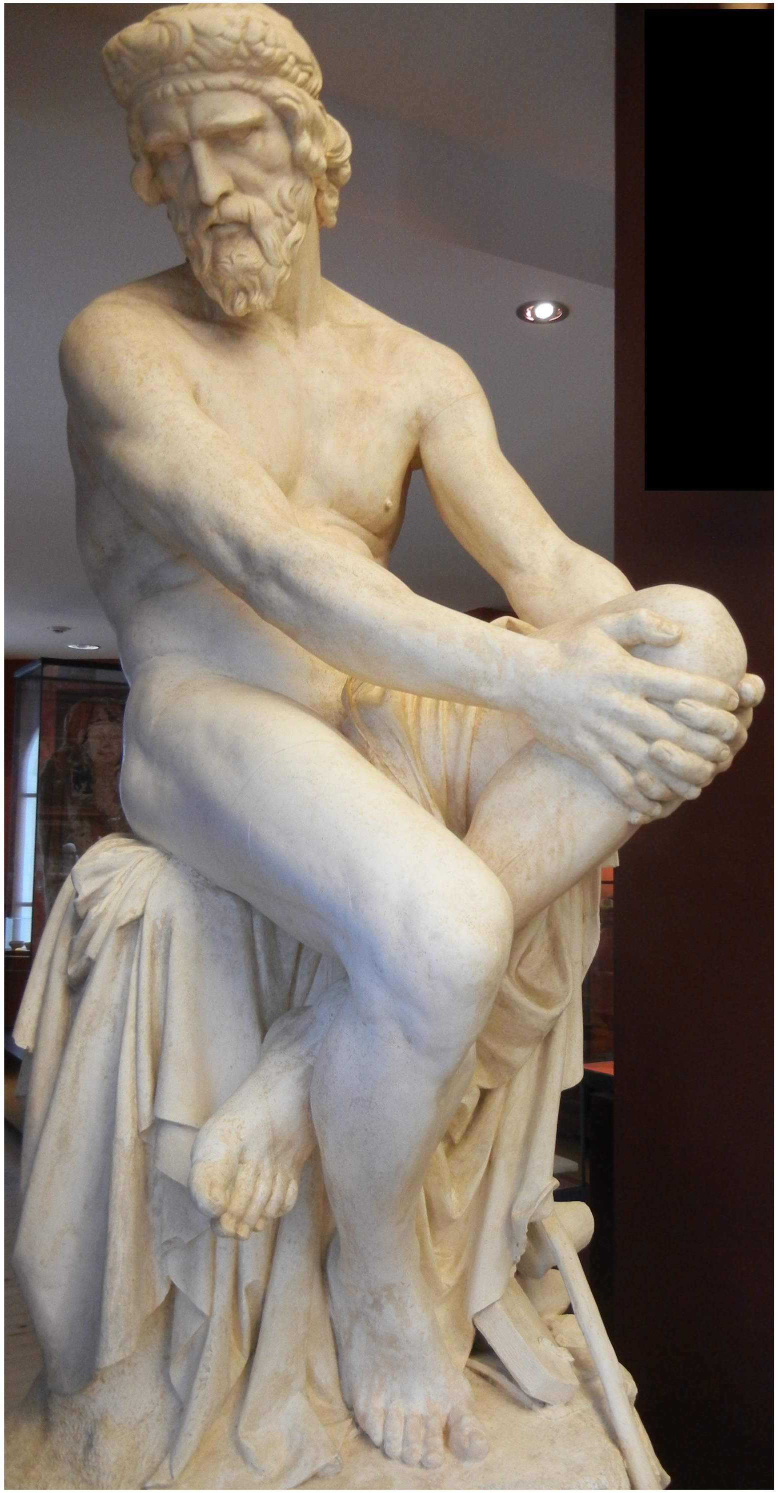
490 - 430 bC

water, air, earth and fire

ferromagnesian rocks and/or radioactive rocks are the **pantakouspermes** for life

παντακοῦ τῆς Γῆς
καὶ τοῦ κοσμοῦ

Signatures of life are the products of their evolution :
serpentine and/or talc and Fe/Mg carbonates



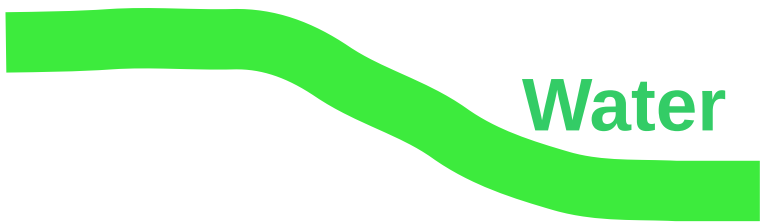
Ferdinand Taluet 1875
collection musée Joseph Denais
Beaufort-en-vallée - France
photo : *Marie-Paule Bassez*

Synthesis of prebiotic molecules

Air : N_2 CO_2

Cosmic radiation

γ,UV, protons, X,



experiment

N_2 + **CO → amino acids**

(Kensei KOBAYASHI et al. 1990...)

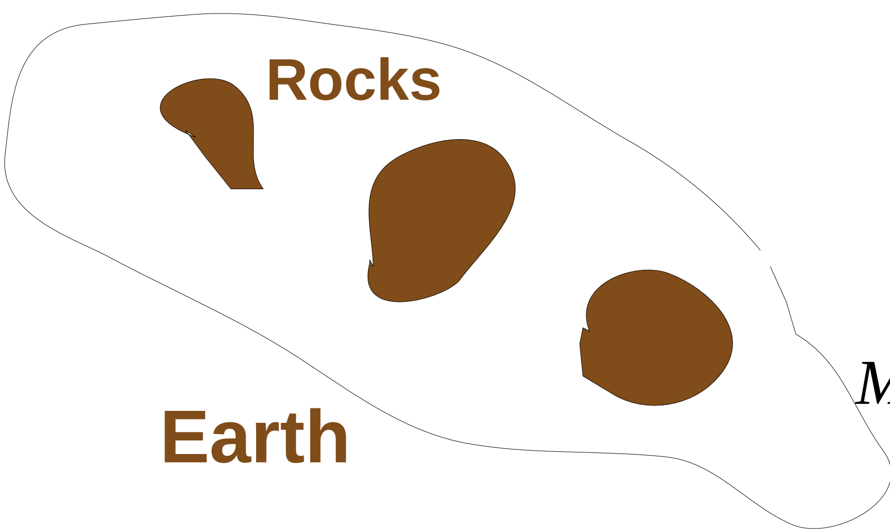
physico-chemical model

rocks + water → H_2 + heat

H_2 + water highT + CO_2 → CO

N_2 + CO + **γ** → amino acids

Marie-Paule BASSEZ 2008...Vienna 2013



Mineral World ***chemical evolution*** → **Prebiotic world**

* **Supporting Experiment : aqueous dissolution of biotite**

100°C pH=4.7 Fe(II)/Fe(III) : 9/1

Anoxic water : Fe(II)-rich vermiculite or smectite ↓

Oxic water : Fe(III)- and Al-(hydr) oxides were observed

(MURAKAMI et al. 2004)

* **^{40}K (half-life 1.277 x10^{9}a), ^{238}U (half-life 4.51 x10^{9}a), ^{232}Th (half-life 1.4 x10^{10}a) and ^{235}U (half-life 7.1 x10^{8}a).**