

# Prebiotic petroleum

MEKKI-BERRADA ALI 2014  
Paris, France  
mekali@pre.fr

## Postulate

- My research on an open system consisting of a simple network of chemical reactions catalyzed by a group of some amino acids and coenzyme found themselves quickly at an impasse.
- The way of the liposomes appeared to me very quickly especially promising by delimiting an interior where order can progress, and the possibility of abiogenic synthesis of their fatty acids. Only this synthesis confronts controversy of abiogenic oil.
- So I set as basis postulate for the investigation of the origins of life, the following one:
- "The class of more complex molecules of life that may have geochemical and abiogenic origin is the class of fatty acids with long aliphatic chains".

## State of research on the pocket of abiogenic oil: *In the field*

### On mid-ocean ridges

- They spread over 64 000 km.
- Production of large quantities of gas in vents at extreme conditions: 300°C, 400 bars.
- **Geochemical processes**: serpentinization and reactions of Fischer-Tropsch type.
- Produced hydrocarbons are **abiogenic**. (Proskurowski 2008).

Table 1: the gases produced on mid-atlantic ridges.

Gas (mmol/kg)	Number of sites	intervalle	Sea water
CO2	6	5.2-28	2.30
N2	6	0.9-3.0	0.59
H2S	7	0.5-11	0
CH4	7	0.023-2.63	0.0003
H2	7	0.020-16	0.0004

Synthetic table extracted from data of:  
**Charlou J.L.**, *Geochemistry of high H2 and CH4 vent fluids, issuing from hydrothermal rocks at the Mid-Atlantic Ridge*. *Chemical Geology*, vol. 191, 2002, p. 345-350.

### Hypothesis of gas hydrates on the slopes of ridges

Are there a frozen gas hydrates on the slopes sedimented of the slow ridges, as already found on continental margins sedimented? Possible. Because of the conditions of pressure and temperature, the presence of a hydrothermal convection resulting water flow through the fractured crust associated with intense methane production by serpentinization, the hypothesis of deposit formation gas hydrates solid trapped in the sediment on the slopes of ridges can be given now.  
(translation Mekki-Berrada) J.L. Charlou 2007

### On subduction zones

- They are the Pacific Ring of Fire, 40 000 km long.
- **H2 production** by serpentinization at 50-300 °C (temperature and 0.1-10 kbar pressure, which corresponds to geological facies blueschist up to 18 km depth).  
According to the synthesis of the serpentine subduction zones:  
B.W. Evans 2004.
- **Geochemical processes**: serpentinization and ascent of hydrothermal fluids of magmatic origin.
- **Mud volcanoes** produce large amounts of methane and are associated with subduction zones. The abiogenic origin of this methane has not been demonstrated.
- **Many hydrates submarine gas sites** were identified at subduction zones but not yet exploited.

### Hypothesis of gas hydrates of subduction zones

Hypothetical prebiotic hydrates gas of the subduction zones have a different constitution and an **different evolution** from those of mid-ocean ridges. Including hydrates ridges should be subjected to diagenesis to transform their N2 to NH4+ in the presence of H2.

### Elements N P S

- **H2S** is present in large quantities in the vents and hydrothermal fluids of magmatic origin.
- The Earth's crust contains 700 molar ppm of **phosphorus**. But it is usually in the form of insoluble apatite.
- **Polyphosphates** are present in **magmatic hydrothermal solutions** at micromolar concentrations.  
Yamagata et al. 1991
- In **seawater** phosphate leaching from land surface precipitate as **hydrogen-phosphates** and can provide oligo-phosphates under conditions of contact metamorphism or those of hydrothermal vents surface.  
Arrhenius et al. 1997
- The Earth's crust contains 35 molar ppm of nitrogen as **NH4+** replacing K+. The majority of sedimentary origin but some is of magmatic origin. It is incorporated by **hydrothermal alteration**.  
Hall 1999
- **Seawater** contains 11 molar ppm N2 (0.59 mmol/L) and dissolved nitrates, of biogenic origin, at 0.6 molar ppm.  
Broecker & Peng 1982

## State of research on the pocket of abiogenic oil: *In laboratory*

Table 2: Abiotic processes

### Serpentinization

(Mg, Fe)SiO4 + H2O => Mg3Si2O5(OH)4 + Mg(OH)2 + Fe3O4 + H2  
olivine + water = serpentine + brucite + magnetite + hydrogen  
2(FeO)rock + H2O = (Fe2O3)rock + H2

### Fischer-Tropsch process

(2n+1) H2 + nCO => CnH(2n+1)X + nH2O  
X: H OH CO2H CHO CH=CH2

The gas is produced by steam reforming of CH4.

CH4 + H2O => 3H2 + CO ΔH = 191.7 kJ/mol  
H2O + CO => H2 + CO2 ΔH = -40.4 kJ/mol

The gas derived from the formic acid present in the hydrothermal fluid.  
CO + H2O <=> HCOOH <=> H2 + CO2

### Haber-Bosch Process

N2 + 3H2 => 2NH3 ΔH = -92.2 kJ/mol

### Oligo-phosphates

Mg(OHPO3)3.H2O => H-(HPO3)n-OH

To complete the research path from the liposome, in this article "prebiotic petroleum", I established the state of research on the **synthesis of hydrophilic heads** that require glycerol and/or serine, ethanolamine, choline. And I finish this article with the **formation of liposomes**. The initialization of the metabolism, writing at the end, is a summary of items "chemo-osmosis prebiotic" and "prebiotic chirality".

- [http://en.wikiversity.org/wiki/Prebiotic\\_chirality](http://en.wikiversity.org/wiki/Prebiotic_chirality)
- [http://en.wikiversity.org/wiki/Prebiotic\\_chemo-osmosis](http://en.wikiversity.org/wiki/Prebiotic_chemo-osmosis)
- [http://en.wikiversity.org/wiki/Prebiotic\\_Petroleum](http://en.wikiversity.org/wiki/Prebiotic_Petroleum)

- T.M. McCollom et al. 2009: Modélisation
- Bernard W. Evans 2010: Experimentation, T= 50-300°C, P= 0.1-10 kbar
- Industrial process, gas phase: T.G. Kreutz et al. 2008
- T= 220-350°C, P= 25-45 bars; catalyst: Fe, mineral surfaces.
- Hydrothermal conditions: T.M. McCollom et al. 1999 T= 175 °C, P= 325 bars; catalyst: montmorillonite + alumine.

- Industrial process, gas phase: T= 500-600°C, P= 200-300 bars, catalyst Fe, mineral surfaces.
- Hydrothermal conditions: A. Smirnov 2008: T= 200 °C, P= 55 bars, catalysts from *serpentinization of hydrothermal sites*: Fe, Ni, Fe, Ni.
- G. Arrhenius et al. 1997: heating under 1 bar at 100 to 550°C. Same with Ca(OHPO3)2.H2O and HMGCa9(PO4)7

## Formation of pocket of abiogenic oil

### Currently there is no deposition of abiogenic oil proved on Earth

- By cons there is an abundant production of H2
- **On ridges**: There are very few abiogenic hydrocarbons produced, other than CH4, and aliphatic chains are very short. The H2/CH4 ratio can be very high. This is due to the very short run at high temperature of CO2 and H2 gases in the vents necessary for the realization of the Fischer-Tropsch process. They are part of gas hydrates.
- **On subduction zones**: The run of gases at high pressure and high temperature can be very long up to 18 km depth, limits of the formation of H2 by serpentinization. These conditions correspond to industrial gas phase processes. But the slopes of plunging plates are very strong and hydrothermal fluids back quickly. It is therefore expected that gas hydrates detected in these areas are comprised primarily of CH4 and few H2.  
Mud volcanoes, rich in CH4 can eject hydrocarbons with long aliphatic chains and are often associated with low hydrocarbon deposits. But the abiogenic nature of these hydrocarbons has not been demonstrated.

### Hypothesis diagenesis clathrates

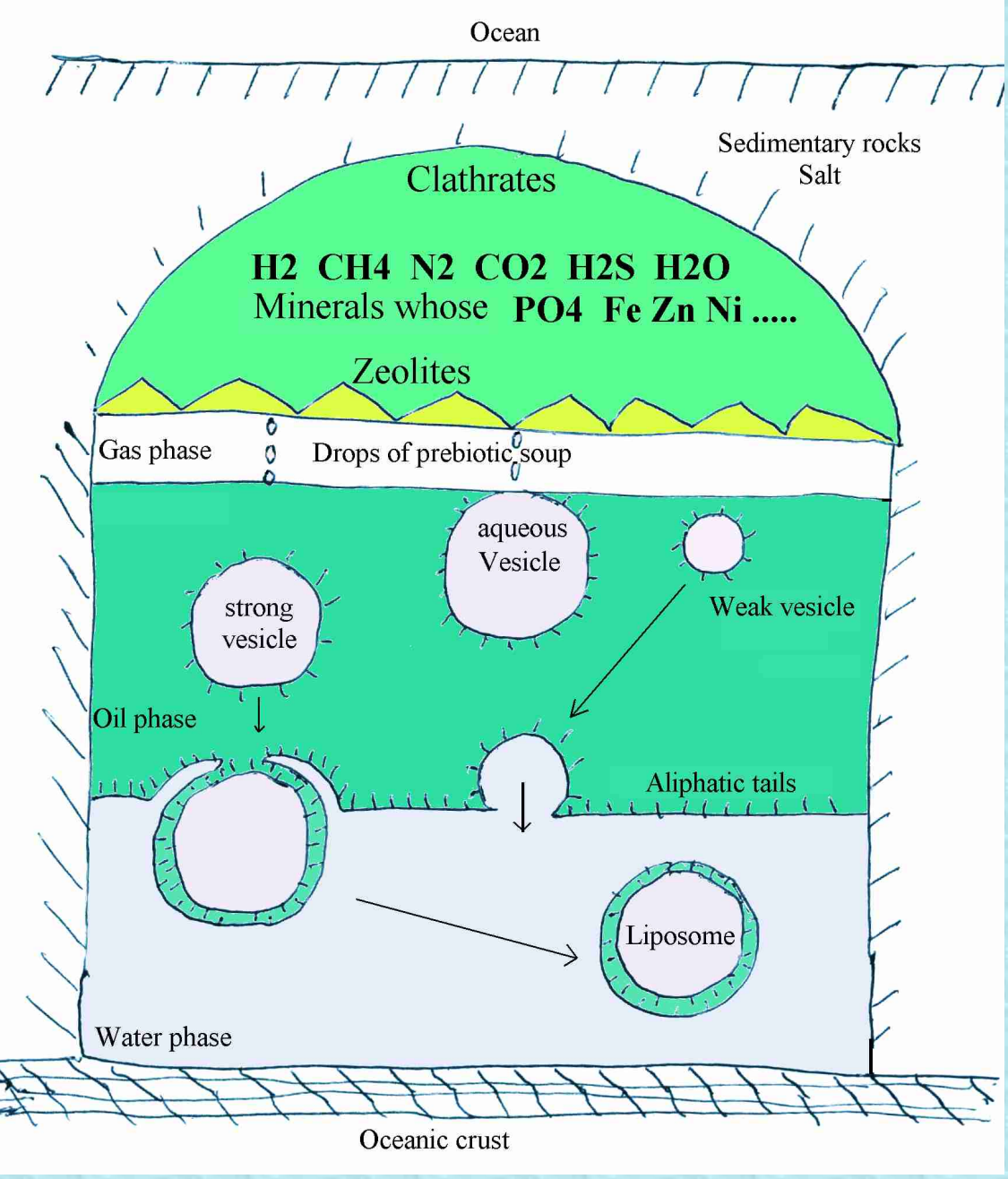
- It is based on the abundance of H2 produced by ridges and slopes and H2 is accompanied in equal proportions of CO2, H2S and N2.
- This hypothesis states that the clathrates formed on these slopes will undergo diagenesis under the weight of sediment to reach the P and T conditions that will trigger the Fischer-Tropsch process to produce hydrocarbons and hydrogenation process to produce NH3 from N2.

### The main arguments in favor of the hypothesis of diagenesis clathrates

- **Abiotic formic acid**: clathrates originally contain abiogenic formic acid that required for equilibrium with CO in Fischer-Tropsch process which in turn will produce formic acid: CO + H2O <=> HCOOH <=> H2 + CO2.
- **Temperatures near hydrothermal experiments**: Clathrates are produced at a depth of about 3 000 m (see Charlou 2002). This gives us about T = 2 °C and P = 300 bars.  
They give a prebiotic petroleum field equivalent to Tupi structure field in Brazil, for example, with 2000 m of water, 3000 m of rock and 2000 m of salt. This gives approximately :  
T=150°C et P=1.5 kbar versus T=175°C et P=325 bars for hydrothermal hydrocarbons experience of McCollom 1999 ; and T=200°C et P=55 bars for hydrothermal ammonia experience of Smirnov 2008.
- **High pressures 5 to 30 times those of hydrothermal experiments**.  
Shifting equilibria  
1 - **Geological periods**: the example of the Tupi field represents the final phase, the process had to start at lower temperatures but with slower speeds of reactions. Geological periods are needed to reach the final stage observed in this example.  
2 - **The continuous production of gas** on the slopes over long periods. See hypothesis Charlou 2007. This moves the thermodynamic equilibrium towards the products.  
3 - **The principle of Le Chatelier** for the high pressures: Thermodynamic equilibria move to an exothermic reaction products with increasing hydrostatic pressure.  
4H2+CO2=CH4+2H2O ΔH=-151.3 kJ/mol ; 3H2+N2=2NH3 ΔH=-92.2 kJ/mol  
For hydrocarbons, methane is trapped in longer and longer aliphatic chains. For the ammonia, nitrogen is not trapped in long chains but in very simple and various products whose amino acids.
- **Removal of products**: This is what industrial processes do. In the case of prebiotic pocket reactions are performed in a porous rock containing clathrates and the products fall in the oil through the gas layer.

### Catalysis by mineral surfaces

- **Clathrates**: Sediments that will cover the clathrates can be inserted and be a very porous rock increasing the catalyst mineral power.
  - **Zeolites**: Zeolites sedimentary facies is at a depth of 1-5 km with a temperature of 50-150°C and a pressure of 200-1200 bars. Roughly as gas clathrates. They can also be formed on the seafloor due to hydrothermal flows that pull up salts. Zeolites are microporous aluminosilicates, structured cage containing alkali and alkaline earth cations such as clathrates whose cages contain the gas. They are used in the synthesis of synthetic oil and petrocchemicals as catalysts for many reactions of organic chemistry.  
In the hypothesis of diagenesis clathrates, zeolites underlying these clathrates or intimately mixed with each other, substantially enrich the prebiotic soup with organic molecules.
- Convergence of the fields of investigation on the prebiotic oil**
- **Temperature 150°C, Pressure 1.5 kbar**: It is remarkable that all fields of investigation on the origin of life often revolve around these values:
    - ✓ Diagenesis clathrates we saw here,
    - ✓ Geological facies of zeolites we saw here,
    - ✓ The adaptation of bacteria to extreme conditions we see below in the parallel between the pocket of fossil and prebiotic petroleum.
    - ✓ Organic chemistry at high hydrostatic pressures to perform improbable reactions to standard conditions (R.V. Eldik 2006).
    - ✓ Hydrocarbons and ammonia on Titan that would be produced in the depths of its seas.



### Synthesis of prebiotic soup by diagenesis clathrates, and liposome formation

**Clathrates et zeolites**  
Clathrates and zeolites have cell structures. They can be intimately mixed.  
Here zeolites are drawn apart to show that they come from the oceanic crust.

**Synthesis of prebiotic soup**  
The clathrates are converted to prebiotic soup under the action of diagenesis and catalysis by minerals and optionally by zeolites.  
The remaining minerals and zeolites form a salt layer after disappearance of clathrates.

**Liposome formation**  
Liposomes are formed, after migration of the vesicles to the water under the action of gravity, by invagination of the water/oil interface containing phospholipids and fatty acids of vesicles which have aborted.

### The main problems posed by the hypothesis of diagenesis clathrates

- **From the point of view of the detection on the field**: It would be difficult to differentiate diagenesis clathrates from diagenesis of organic matter that are found in the sediments overlying these clathrates.
- **From a theoretical point of view**: Is evolution of clathrates to prebiotic petroleum would not be inhibited by certain processes such as H2S and other sulfur species prevalent in the synthesis of synthetic oil?

	fossil	prebiotic
<b>Pressure, kbar</b>	0.4-0.8	0.4-1.5
<b>Temperature, °C</b>	50-80	2-150
<b>pH</b>	4-9	NA
<b>Salinity, g/L</b>	0.1-300	Salt layer
<b>Anoxia</b>	+	+

**Comparison with a pocket of fossil petroleum**

As in prebiotic petroleum, there are: CO2, CH4, H2O, H2S, N2, H2, CH3COOH  
missing: PO4H3, NH3  
being spare: NO3-, sugars (CH2O)n

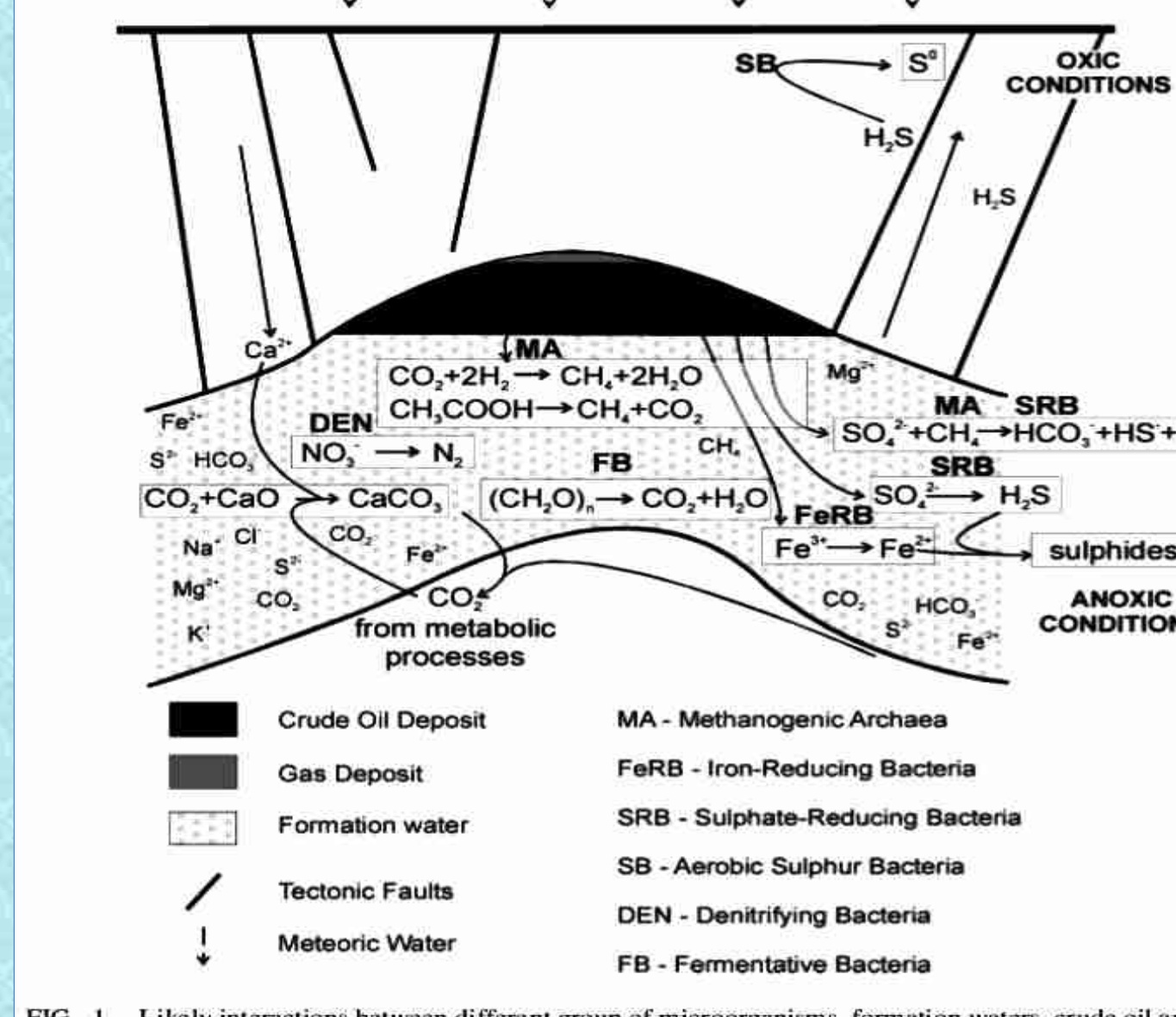


FIG. 1. Likely interactions between different group of microorganisms, formation waters, crude oil and gas deposit.  
Extract from article:  
**D. Wolicka et al.**, Interactions between Microorganisms, Crude Oil and Formation Waters. *Geomicrobiology Journal*, 27:43-52, 2010

## Prebiotic chemo-osmosis

- After establishing the first draft of initialization metabolism in the "prebiotic petroleum," we can ask that the way of the liposome, as it is now, can initiate molecular evolution? Because if you can not make communication between inside and outside of the liposome, no further development is possible. So before making elaborations on the synthesis of hydrophilic heads, I did a search on the possibility of creating simple exchange channels through the liposome.  
On bibliographic research on liposomes quickly led the process of **chemo-osmosis Peter Mitchell (1961)** which involves membrane proteins and ion channels themselves protein. This process is subtended by the electrical potential which is created between the inside and outside.
- It is evident, then, that if we can synthesize a liposome as the current one, but without the proteins, this potential also exists. This potential I called "prebiotic electric potential" and it subtends a prebiotic chemo-osmosis that has nothing to do with the power of current chemo-osmosis.  
I make then the hypothesis that prebiotic chemo-osmosis, even if it proved very weak, promote the incorporation of amino acids in the bilayer because they have the ability to cling to the outer face of the liposome having zwitterionic heads conformation very close to that of phospholipid.  
The example of simple exchange channels, so that I'm looking for would be like ionophores which are peptides of a few amino acids and alpha-acid hydroxides, both D or L, and allow the exchange of monoatomic ions whose proton.
- The article outlines the evolution to other membrane proteins, but the most important are the conceptual implications for molecular evolution:
  - Here we have a **network of electrons and protons** across the membrane instead of a network of chemical reactions in an open system.
  - Alkali metal cations **Na+** and **K+** are also important elements that N, P and S.
  - The 1st all stages of molecular evolution increase **differentiation between inside and outside** and including sorting between amino acids to the inner leaflet.
  - The **cohesion of the sheets** through the zwitterionic structure and length of the hydrophilic head should require conformation of amino acids and in particular their chirality, and that of glycerol of the phospholipids.
  - The **phosphate ion** must be treated separately, because it is the backbone of sheets and its size and electric charge do not allow him to pass by diffusion as mono-atomic ions. I suggested that the process of flip-flop, without enzymes, should explain its entry into the liposome. Its incorporation into the central metabolism and nucleic acids is what I call sequestration phosphate.
  - The membrane is not only a container. It determines in space **5 zones to different chemical reactivities**:  
1-**The external medium**, at the beginning of molecular evolution is prebiotic soup; 2-**The external face** of the liposome with the hydrophilic head in contact with the outside; 3-**The hydrophobic membrane region** consisting of aliphatic chains only; 4-**The inner face** of the liposome with the hydrophilic head in contact with the interior; 5-**The internal medium** is the central metabolism.

- 2 - **The external face of the liposome with the hydrophilic head in contact with the outside**
  - 2 - **Evolution of the outer surface of the liposome**:
    - The liposome surface, made of about 10 million zwitterionic heads, promote the penetration of amino acids and alpha-hydroxy acids in the membrane and their combination on the surface.
    - **Cohesion of the liposome**: However, the steric hindrance of the hydrophilic heads imposed by putting closer aliphatic chains, opposed a strong constraint to penetration. And this is reinforced by the length of the mobile arms, for example ethanolamine, which ties up a phospholipid to its neighbor. This is also what makes the strength and consistency of the liposome. Methylamine instead of ethanolamine not allow storage and propylamine would make too loose.
    - **Amino acid configuration**: The cohesion of the liposome should impose steric configuration amino acids and alpha-hydroxy acids which enter the membrane. This configuration concerns their length and chirality.
    - **Synergy structure-chemo-osmosis**: Thus we see that the outer face as well as the inner face, the liposome occurs by its very structure, regardless of chemo-osmotic process which it is added. Prebiotic chemo-osmotic process, although its action may seem much lower than that of biotic process, it nevertheless operates in a reactional medium structured by and with the liposome, mutually reinforcing.

- 3 - **The hydrophobic membrane region consisting of aliphatic chains only**
  - 3 - **Evolution of the hydrophobic region of the membrane**:
    - It will inherit the molecules and the chemical reactivity of the external medium which, in the prebiotic pocket network, is the prebiotic soup.
    - **Integration of amino acids**: The integration of small polar molecules or even ionized by the hydrophilic heads in the membrane will force them to take spatial configurations specific of aliphatic environments. The amino acid and alpha-hydroxy acids groups, optionally together with chelated minerals catalysts, can become catalytic centers or ion channels.
    - **Hydrophobic molecules**: These molecules, such as heme, hydroquinones and nucleic bases easily intercalate into the membrane and may have, on either side of the membrane, the chemical functions which are chemically modified by the inner and outer medium, or serve as a coenzyme in the integrated membrane amino acid groups.
    - **Transduction of electrical potential**: Hydrophobic molecules which extend over the entire thickness of the membrane can serve as the electrical potential transducer.

- 4 - **The inner face of the liposome with the hydrophilic head in contact with the interior**
  - 4 - **Evolution of the inner surface of the liposome**:
    - It has the same structure as the zwitterionic outer face but a portion of the hydrophilic heads may be partly serine responsible for the electrical potential between the two faces.
    - It will inherit molecules sorted by the previous 2 areas. Amino acids may be more uniform, especially as regards the chirality.
    - It will get into the membrane molecules specific to indoor environments, including trioses and small amino acids we have seen in the part of the poster dedicated to the initialization of metabolism in the pocket of prebiotic petroleum which are Gly Ala Ser Glu Asp and amino acids derived from the latter by the nascent metabolism.
    - In contact with the internal medium, it will undergo its chemical reactivity and organization.

- 5 - **The internal medium is the central metabolism**
  - 5 - **The inner medium**:
    - A **closed medium**: It is closed and small, limiting diffusion and promoting the organization.
    - **Limited chemical reactions during initialization of metabolism**: In pocket of prebiotic petroleum hypothesis, prebiotic soup contains small molecules that easily diffuse through the membrane. These are H2, formaldehyde, formic acid, acetaldehyde, NH3 and CO2, and are the source of the formose reaction which produces trioses, and the source of reactions which produce small amino acids (see above).
    - **Ionization**: The electrical potential should change the ionization of weak acids and bases.
    - **Sequestration phosphate**: Inside, the phosphate will be integrated into the emerging metabolism and later in nucleic acids. This is what I call sequestration phosphate. Phosphate is poly-atomic, big, ionized at biological pHs and can carry 1-3 negative charges. It should become much more difficult as mono-atomic ions. However its diffusion rate through the membrane is similar to that of K+ and Na+. Hydrolysis of the hydrophilic heads, unbalancing phospholipids, makes possible the passage of the sheet of these phospholipids to the other, by the known process called flip-flop. This would explain its rate of diffusion.

### The problems posed by prebiotic chemo-osmosis

- Article prebiotic chemo-osmosis leaves open discrimination between Na+/K+ and processes the electrical potential improperly is the material point of classical physics including actions at a distance between the inside and outside as suggests the notion of electrical potential. These two aspects were treated after writing prebiotic chemo-osmosis and prebiotic chirality in "continuity between molecular evolution and darwinian evolution" (in preparation in Wikipedia: [http://en.wikiversity.org/wiki/Continuity\\_between\\_molecular\\_evolution\\_and\\_darwinian\\_evolution](http://en.wikiversity.org/wiki/Continuity_between_molecular_evolution_and_darwinian_evolution)).
- The article does not clearly express the chirality of the glycerol-P, much less homochirality of amino acids especially as ionophores feature 2 chirality of their monomers. A hypothesis that I scaffolded in the article concludes that the two chirality of glycerol and serine should be complementary (and by extension to all amino acids). It is based on the representation of the head of the phosphatidyl glycerol, where two glycerol are attached to the same phosphate-glycerol-P-glycerol. The steric hindrance is the same for the two glycerols, their position relative to phosphate seemed to make them with complementary chirality. But in archaea glycerol (or serine) of the cation of the hydrophilic head does not change its chirality, as the glycerol linked to 2 fatty acids, changes it. Article prebiotic chirality addresses this problem (see poster of prebiotic chirality).