

# THE ECOPOESIS MODEL: DID FREE OXYGEN FUEL THE ORIGIN OF LIFE?

Raul A. Félix de Sousa  
felixdesousa@terra.com

## ABSTRACT

A model for biopoiesis is proposed where a complex, dynamic ecosphere, characterised by steep redox potentials, precedes and conditions the gradual formation of organismal life. A flow of electrons across the Archean hydrosphere, proceeding from the reducing constituents of the lithosphere and pumped by the photolytic production of oxygen in the Earth's atmosphere is the central feature of this protobiological environment. The available range of electrochemical potentials allows for the geochemical cycling of biogenic elements. In the case of carbon, carboxylation and decarboxylation reactions are essential steps, as in today's organisms. Geochemical evidence for high levels of carbon dioxide in the Earth's early atmosphere and the biological relevance of carboxylations are the basis for a hypercarbonic conception of the primitive metabolic pathways. Conversion of prochiral chemical species into chiral molecules, inherent to hypercarbonic transformations, suggests a mechanistic method for the generation of homochirality through propagation. The solubility of oxygen in lipid materials points to an aerobic course for the evolution of cellularity.

**KEYWORDS:** origin of life, geochemical cycles, biogenic elements, oxygen, palaeoatmosphere, homochirality

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## INTRODUCTION.

Ever since the Miller-Urey experiment, in 1953, attracted the public eye to the field of the origin of life, the requirement of a reducing, or at least neutral, atmosphere has become a fundamental assumption for practically every reasoning concerning the early evolution of the biosphere. For decades, very few dissident voices, such as Melvin Calvin (1959), and more constantly, Kenneth M. Towe (1978, 1981, 1983, 1988, 1990, 1994, 1996) have stood against this certainty.

The enduring impact of Miller's work can be attributed not only to the fact that a number of biologically relevant organic compounds were synthesised from plausible atmospheric components but also to undisputed evidence that no such compounds can ever be formed or even remain stable in oxidising atmospheres (Miller and Urey, 1959).

Other sources of organics, however, have been shown to be feasible. The possibility of extraterrestrial delivery by comets and meteors (Lazcano Araujo and Oró, 1981) has been confirmed both by spectroscopic observations and by direct analysis of meteoritic material (Whittet, 1997). Conversions based on the use of geochemically derived reductants within the hydrosphere are central to the proposal of a chemoautotrophic origin for the first organisms, and are currently the object of intense research (Wächtershäuser, 1990, 1992; Blöchel et al., 1992; Morowitz et al., 2000; Cody et al., 2001; Cody, 2005). The hydrolysis of metallic derivatives of biogenic elements, such as carbides and nitrides, an old idea defended by some pioneers in the field, has been recently revisited by Cataldo (2003).

The existence of such alternative, non-atmospheric routes for the formation of biological materials ensures the possibility of novel theoretical formulations about the nature of the Earth's earliest ecosphere. Not only could a variety of new data concerning the metabolic evolution of organisms thus be addressed, but also the growing awareness of the importance of redox potentials as planetary prerequisites of life (Gaidos et al., 1999). With the possibility of an ozone layer, DNA-damaging UV radiation fluxes would not deter the development of life processes requiring shallow, illuminated areas, particularly the photochemical conversions leading to the evolution of photosynthesis.

## THE SETTING.

The standard models for the evolution of the atmospheres of the terrestrial planets postulate that Venus, the Earth and Mars initially had a very similar composition, with carbon dioxide, water and nitrogen as their main constituents (Hunten et al., 1989). The subsequent evolution, creating the distinct current makeups, involves, as major factors, massive loss of water for Venus, retention of CO<sub>2</sub> by the Earth due to the formation of carbonate deposits, and general loss of volatiles from Mars (Hunten, 1993).

Besides cosmochemical considerations concerning the abundance of volatile elements, attention was also given to the fact that, according to stellar evolution models (Newmann and Rood, 1977), our sun was about 30% fainter than today, but there is no evidence for glaciations in the Archean. The consequent requirement to explain the relatively high temperatures was tackled by climate models by postulating that the dense CO<sub>2</sub> atmosphere was needed to retain solar heat (Owen et al., 1979, Kasting and Ackermann, 1986, 1987; Kasting, 1988, Kasting and Toon, 1989, Kasting, 1993, 1995). Subsequent work on the issue has been mainly inspired by a proposal by Sagan and Chyba (1997) whereby methane, rather than carbon dioxide, would be the key to climate stabilisation and to the constitution of an organic haze as a shield against ultraviolet radiation (Pavlov et al., 2000, Kasting, 2004).

Although debate has arisen regarding the high concentrations of CO<sub>2</sub> in the Earth (Sleep and Zahnle, 2001) and even the idea of the "faint young sun" has been challenged (Graedel et al., 1991; Wuchterl and Klessen, 2001; Schilling, 2001; Sackmann and Boothroyd, 2003), the basic concepts underlying atmospheric evolution and climate regulation models remain valid. Their generic application to the early days of terrestrial or similar extrasolar planets still points to dense, wet, CO<sub>2</sub> dominated atmospheres, with relatively high temperatures.

Far more controversial and critical for the chemistry of early life is the redox state of the paleoatmosphere. The only significant net source of free oxygen available for an abiotic planet is the atmospheric photolysis of water vapour with subsequent hydrogen escape (Carver, 1981). This process is widely accepted to have happened in a large scale in Venus, to account for the loss of her oceans (Kasting, 1997; Schindler and Kasting, 2000). The remaining free oxygen would have been eroded by the solar wind, owing to the lack of a magnetic field to retain it (Lammer et al., 2006).

Much has been debated about the actual rates of water photolysis and loss of its components from the early atmospheres of the terrestrial planets (Berkner and Marshall, 1965, 1967; Brinkman, 1969; Walker, 1977; Blake and Carver, 1977; Carver, 1981; Canuto et al., 1982, 1983; Kasting et al. 1979; Kasting, 1993; Chassefière, 1996; Kasting and Catling, 2003; Tian et al., 2005). Even more crucial to the establishment and maintenance of an oxygen-rich atmosphere, however, is that the Archean environment should, as much as possible, prevent the consumption of free oxygen by the overwhelming excess of reducing components of the lithosphere and hydrosphere.

The quest for reliable biosignatures, applicable to the newly-discovered exoplanets, has once again drawn attention to the fact that, while on the Earth, oxygen and, indirectly, ozone are the by-products of biological activity, it does not follow that the presence of life is the only explanation for an atmosphere enriched with these compounds (Selsis et al., 2002; Kaltenecker and Selsis, 2009).

The action of removing processes such as the oxidation of rocks by soil weathering and the oxidation of volcanic gases is necessary to prevent the accumulation of abiotic O<sub>2</sub> produced by photodissociation of H<sub>2</sub>O (Léger et al., 2004). Since, on the Earth, such factors are usually assumed to have been always very effective, atmospheric scientists have predominantly agreed that there were no conditions for the development of an oxygen-rich atmosphere prior to the development of oxygenic photosynthesis.

The geologic record, however, has delivered an ambiguous message, giving rise to two radically divergent lines of thought.

Although the guidelines for the understanding of the nature of planetary atmospheres have been established about a century ago (Arrhenius, 1910), real dissent concerning the Earth's palaeoatmosphere only became evident some decades later. In 1955, W. W. Rubey, making ample use of geochemical evidence, criticised the idea, defended by H. C. Urey (1951, 1952), that our planet might have initially had a strongly reducing atmosphere, similar to that of the Jovian planets.

The task of reconciling Urey's proposition with the geologic record was undertaken by P. Cloud (1968, 1972, 1973) who assembled arguments for reducing environments in the early history of the Earth and put forth a rationale linking the chronology of banded iron formations, detrital pyrites and subaerial red beds with the oxygenation of the atmosphere. Cloud's formulation has found wide acceptance and was quickly raised to orthodoxy, although the robustness of his interpretation has been tenaciously questioned ever since. Besides Kenneth Towe, the dissent includes a number of geologists such as Van Valen (1971), Dimroth and Kimberley (1976), Clemmey and Badham (1982), Phillips et al., (2001) and the group led by Hiroshi Ohmoto (Ohmoto, 1996, 1997, 1999, 2004; Ohmoto et al., 2004; Lasaga and Ohmoto, 2002; Watanabe et al., 1997; Yamaguchi, 2002; Kato et al., 2009; Haoshi et al., 2009).

A new twist to the controversy was given by the discovery of mass independent fractionation (MIF) of sulphur isotopes in sedimentary rocks older than ~2.4 billion years (Farquhar et al., 2000, 2003; Bekker et al., 2004), which was proposed to result from photochemical reactions of sulphur species in a reducing atmosphere. This interpretation was challenged both by the discovery of significant MIF signatures in volcanic ashes associated with recent eruptions (Savarino et al., 2003) and by its absence in Archean sediments and shales (Ohmoto et al., 2006), suggesting that it could better explained as a result of intense volcanic activity in an oxic atmosphere. Besides, the MIF signature has also been shown to be created by non-photochemical reactions (Lasaga et al.,

2008; Watanabe et al., 2009), thereby undermining its use as a tool for the understanding of the evolution of atmospheric chemistry.

Throughout the debate about early Precambrian oxygen (for a review: see Yamaguchi, 2005), the putative incompatibility of an oxidising atmosphere with biopoiesis has weighed strongly against it, as its opponents consistently emphasised the conformity of their views with the conventional origin-of-life models.

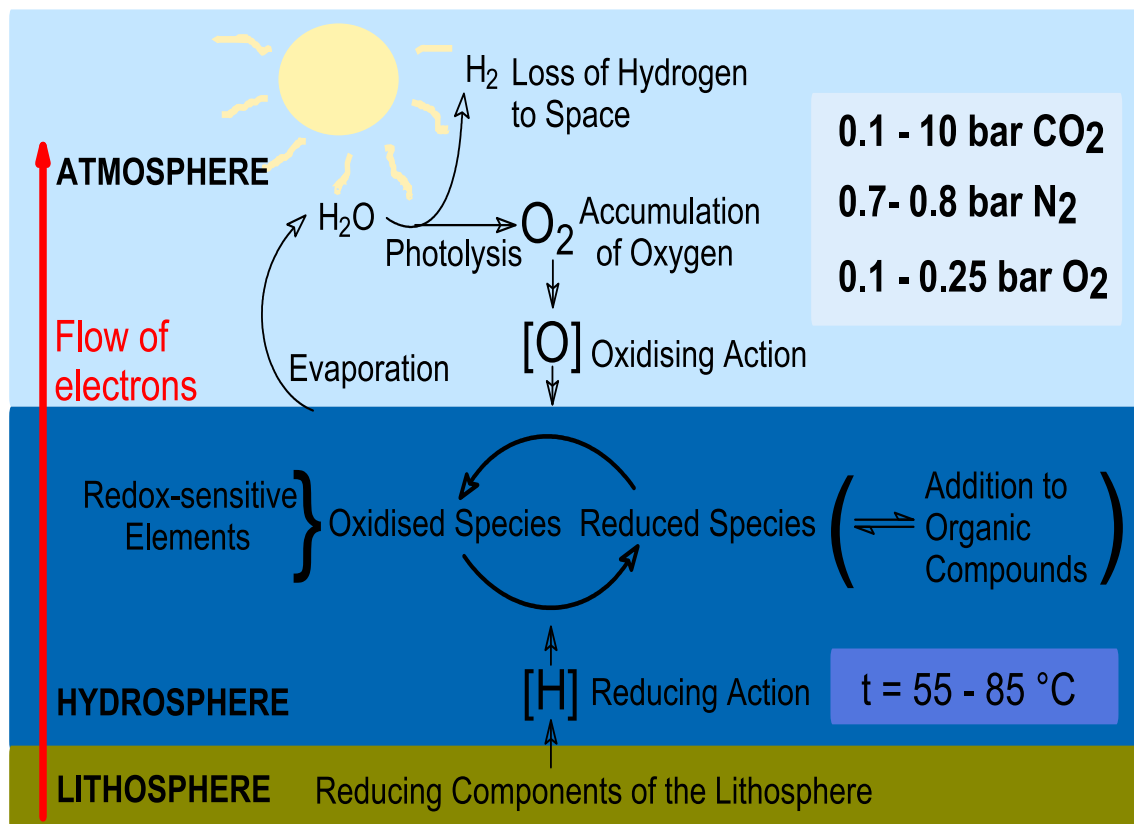
The Ecopoiesis Model (Félix de Sousa, 2000, 2006) is not an attempt to delve into the technical aspects of the discussion about the composition of the Archean atmosphere. Rather, it seeks to show that, as far as the origination of life is concerned, the previous presence of an atmosphere containing significant levels of abiotically generated oxygen can arguably be regarded as an essential feature of the Earth's earliest ecosphere and even as the most probable driving force in the development of the primordial metabolic processes.

## THE CENTRAL HYPOTHESIS.

The Ecopoesis Model offers a different perspective as compared to other formulations of biopoesis. Traditionally, the origin of life has been equalled to the fortunate appearance of very simple cellular organisms, whose metabolic evolution would thenceforth conduct the general evolution of the environment (the oxygen-rich atmosphere being a result of this process). In Ecopoesis, in contrast, the physical environment plays the leading role, and not organisms.

Besides endowing the environment with the continuous protection of an ozone layer, the early presence of free oxygen determines the onset of a flow of electrons, which leaving the reducing components of the lithosphere, cross the Archean seas, pumped by the photolytic production of oxygen in the Earth's atmosphere. This flow is mediated by, and predominantly channelled through the redox transitions of the redox-sensitive elements in the hydrosphere.

These large-scale environmental interactions cause the development of a geochemically based metabolism in a planetary protoplasm (holoplasm) setting the stage for the gradual evolution of organismal life to take place.



**Figure 1** General scheme of the redox ecosphere proposed in the Ecopoesis Model. Values for  $p[CO_2]$  are from Ohmoto (2004) and Kasting (1987), values for  $p[O_2]$  are from Ohmoto (1996, 1997, 1999). Temperatures are from Knauth and Lowe (2003) for the 3.2 – 3.5 Ga period.

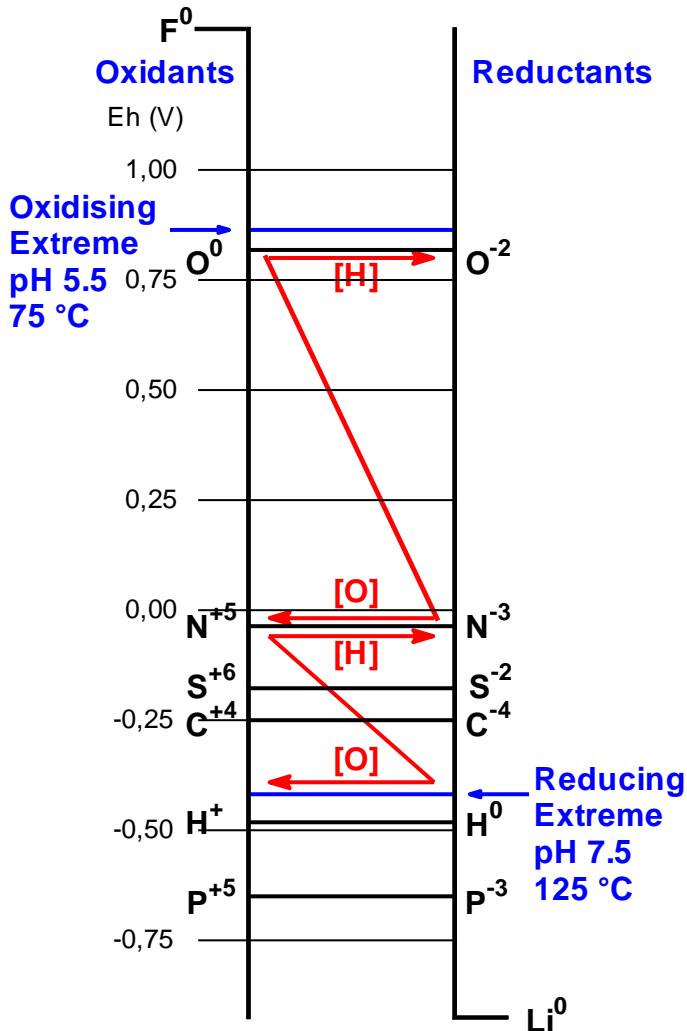
The wide difference of electrochemical potentials in the primordial environment would cause the appearance of the geochemical cycles of biogenic elements. The primitive metabolic pathways are originated by the interaction of these cycles and their products. The build-up of order in the system arises from the energetically favourable transitions, particularly in the oxidation of organic matter, and from the physicochemical properties of the compounds involved. This planetary protometabolism is essentially congruent to today's biochemistry, including carbon and nitrogen fixation, and aerobic degradation of organic compounds (full oxidation to CO<sub>2</sub>).

Biological evolution, as a rule, would proceed through the increasing functional control of such reactions, rather than through their creation. A naked geochemical metabolism would thus evolve congruently towards our modern enzymatic processes.



## GEOCHEMICAL CYCLES IN THE ARCHEAN.

The span of electrochemical potentials in the protobiological Earth would range from the values of lithospheric divalent iron to those of atmospheric oxygen. The first geochemical cycles are made up from the possible chemical species for the biogenic elements and their transitions within this interval.

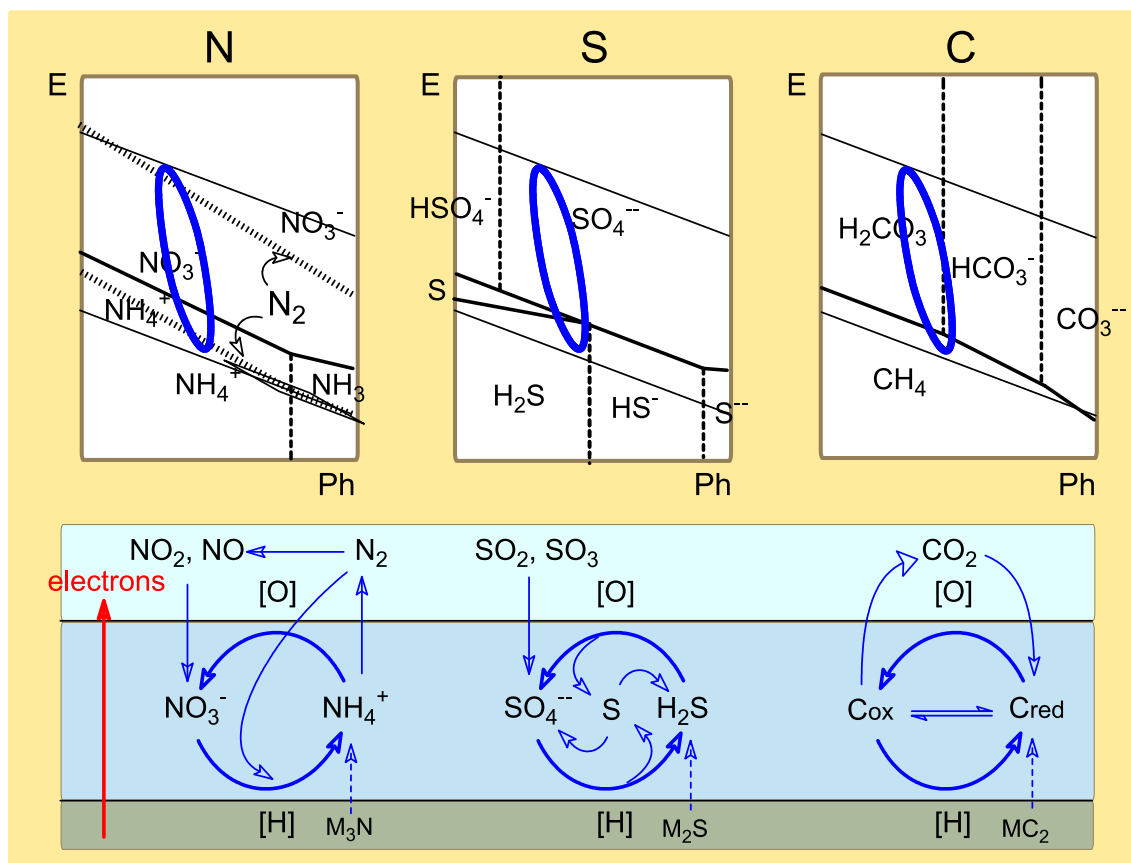


**Figure 2** Redox potentials of biogenic elements, calculated for 75 °C and pH = 6.0. As extreme environmental values, the reduction of atmospheric oxygen at pH 5.5 and T= 75 °C, and the oxidation of divalent iron  $10^{-3}$  M at pH 7.5 and T = 125 °C were chosen. This wide interval enables all redox transitions pertinent to modern biogeochemical cycles.

In the example shown with red arrows, nitrogen species are reduced from nitrate to ammonia when coupled with the oxidation of divalent iron, and conversely ammonia is oxidised to nitrate, thanks to the action of molecular oxygen.

The sparingly low solubility of oxygen in the hot primordial oceans (Knauth, 2005) would determine the maintenance of a high concentration of oxygen in the atmosphere, in order that the flow of electrons from the hydrospheric and lithospheric compartments could compensate for the loss through the photolysis of water.

Geochemical evidence from the Earth's oldest igneous rocks indicates that the redox state of the Earth's mantle has not been significantly altered over the past 3.9 Ga (Delano, 2001; Canil, 2002), ruling out the possibility that volcanism could have delivered massive amounts of reducing gases to the atmosphere. Besides, among these gases,  $\text{SO}_2$  and  $\text{H}_2\text{S}$  are extremely soluble in water and would therefore either be delivered directly to the hydrosphere or have short residence in the atmosphere. Small amounts of the less soluble methane, carbon monoxide and hydrogen could also have been produced, but they would have co-existed as minor constituents in equilibrium with the oxidising atmosphere, as today.

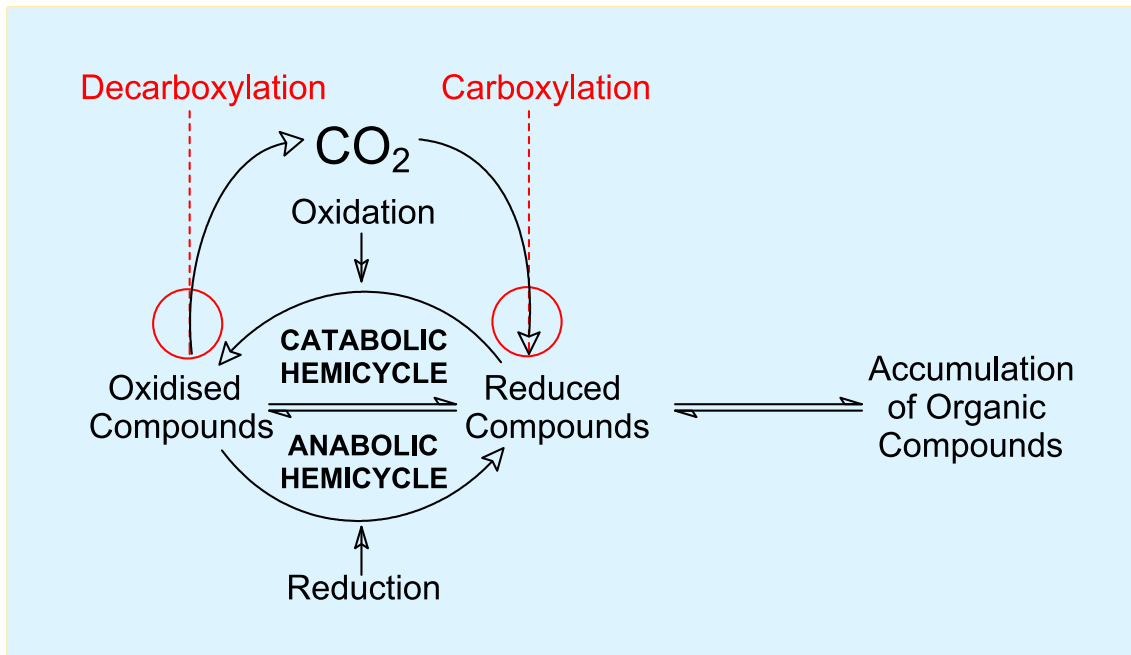


**Figure 3** The stability areas for the chemical species derived from biogenic elements are plotted in the Pourbaix diagrams. The blue circle links the extreme values of pH and electrochemical potential. It is intended to depict, in an approximate view, the possible chemical transitions in the proposed protobiological conditions.

Sulphur cycles would be further complicated by the interactions with divalent iron. The Pourbaix diagram for carbon includes just the two extremes, the most reduced species - methane, and the most oxidised, carbon dioxide (and its aqueous derivatives, carbonic acid, bicarbonate and carbonate ions), out of numerous possible compounds displaying intermediate reduction states.

Since carbon dioxide itself is remarkably stable towards reduction in aqueous solution, carbon cycling would depend on the carboxylation of pre-existing carbon compounds. Protobiological carbon cycles would run in the anabolic sense intercalating carboxylation reactions of organic compounds with reduction steps (carbon assimilation). Conversely, catabolic cycles would alternate decarboxylations and oxidation steps, as in modern metabolic cycles. The

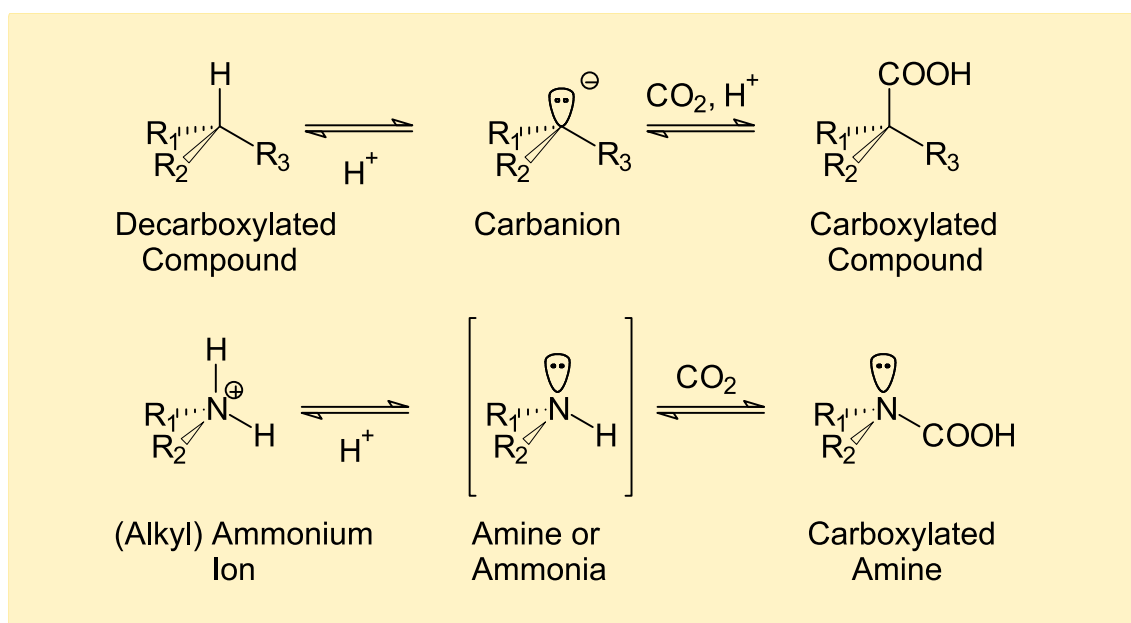
reduction-oxidation equilibrium in the protobiological ecosphere would thus be tightly bound to the carboxylation-decarboxylation processes.



**Figure 4** The redox transitions of carbon compounds, or carbon cycle, are the most important link between the energy flow across the hydrosphere and the organic reservoir, depleted and replenished by the catabolic and anabolic hemicycles, respectively. Accumulation and expenditure of organic compounds are at the basis of the economy of reducing power, the central principle guiding the evolution of metabolic processes.

## A HYPERCARBONIC WORLD.

The expression "hypercarbolic medium" describes the reactive properties of the oceanic environment of the early Earth under the presence of a heavy CO<sub>2</sub> atmosphere. Owing to the high amount of dissolved CO<sub>2</sub>, chemical species such as carbonic acid, bicarbonate and divalent ions (mainly the alkaline-earth magnesium) are present in much higher concentrations than in today's ocean, imparting carboxylating properties, which may affect amino groups and carbanions. Under the thus arising carboxylation-decarboxylation equilibrium, many organic compounds would form series of closely related "hypercarbolic analogues", whose members differ solely by the amount of CO<sub>2</sub> added to their molecules.



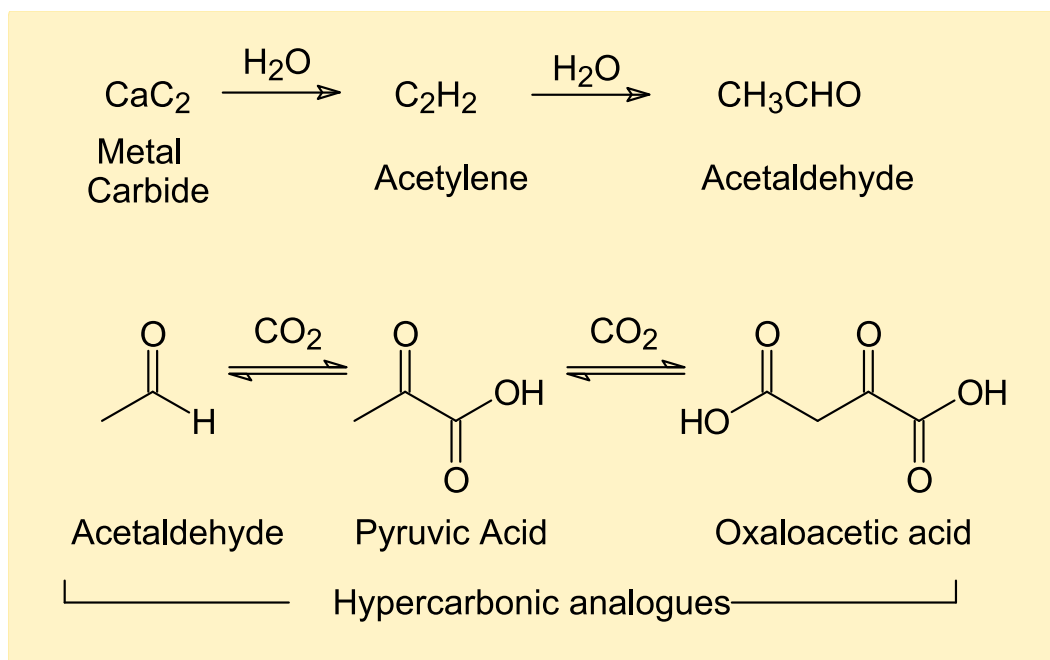
**Figure 5** Carboxylation affects carbanions derived from the dissociation of labile hydrogen atoms bound to carbon, and amino groups.

This highly ionic medium with a lowered water activity ( $A_w$ ) also influences the hydration-dehydration equilibrium. The factors determining the carboxylation-decarboxylation equilibrium and the hydration-dehydration equilibrium are termed permanent factors and are linked to very slightly fluctuating conditions whereas the reduction-oxidation equilibrium is governed by the so-called eventual (contingent) factors, which vary widely, within the redox extremes of the protobiological environment.

The chemistry of the hypercarbolic medium lies at the heart of the Ecopoiesis Model because it reconciles, as dictated by the principle of congruence, the biological relevance of carboxylation and decarboxylation reactions with the geologic and astronomic evidence of a heavy CO<sub>2</sub> paleoatmosphere.

Carbon assimilation would also require at least a modest input (primary input) of lithospheric carbide-derived hydrocarbons (Cataldo, 2003). Acetylene, in

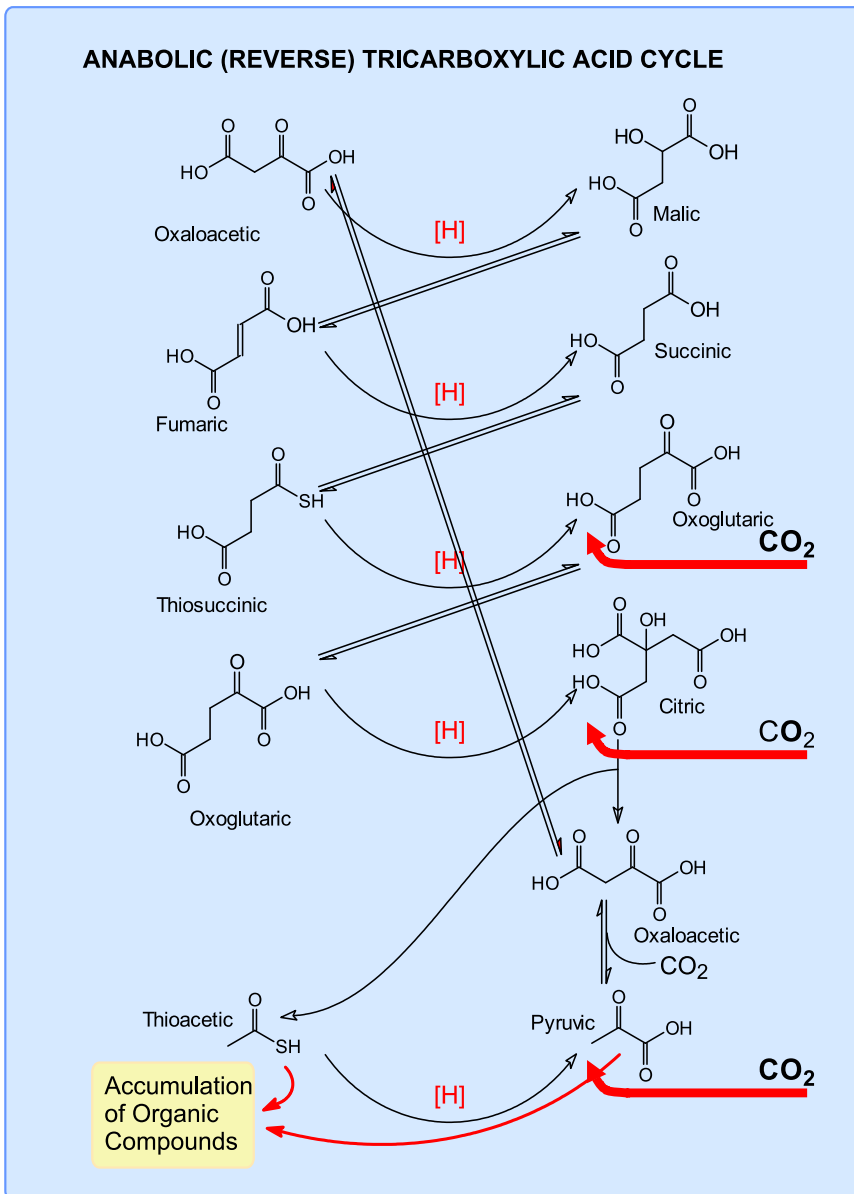
particular, originated by the action of water on divalent ionic carbides, could be directly converted, through hydration and carboxylation, into pyruvic and oxaloacetic acids, which are a part of the very core of biochemical pathways.



**Figure 6** The primary input of reduced carbon from mineral carbides represents the basis of the organic reservoir, to which carbon from  $\text{CO}_2$  is assimilated, at the expense of lithospheric reductants. Acetaldehyde can be obtained by the hydration of acetylene, a major constituent of this input. The hypercarbionic derivatives of acetaldehyde are central to all primary metabolism, interconnecting the chemistry of lipids, carbohydrates and amino acids with the main energy-yielding biochemical pathways.

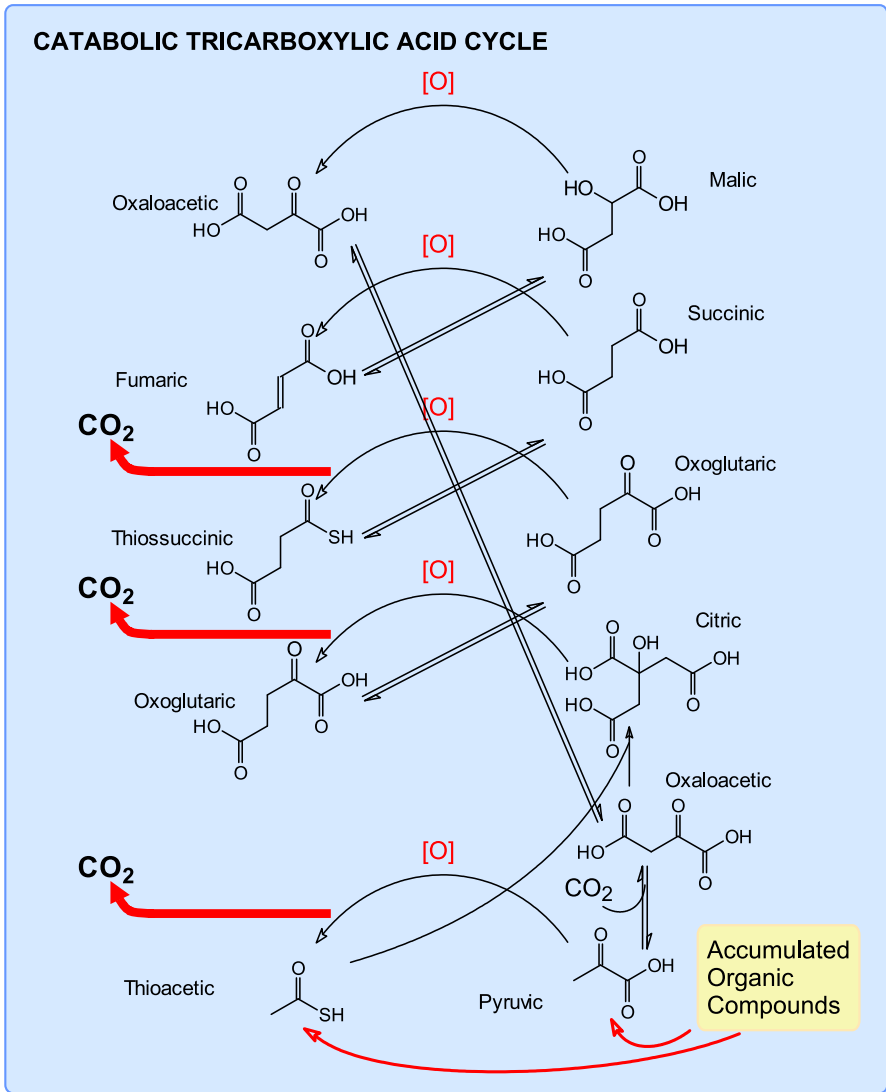
Concurrently with the ideas of a chemoautotrophic early life (Wächtershäuser, 1990), the likelihood of a protometabolism based on the reductive tricarboxylic acid (or reverse Krebs) cycle (Buchanan and Arnon, 1990) has been the focus of increasing investigation (Morowitz et al., 2000; Cody et al., 2001; Smith and Morowitz, 2004; Kalapos, 2007; Hügler et al., 2007) both on the grounds of chemical reactivity and that of phylogenetics.

Pyruvic and oxaloacetic acids would thus permit the initiation of the anabolic hemicycle reactions, in which carbon dioxide is assimilated through carboxylations and, thanks to lithospheric reductants, converted in organic carbon.



**Figure 7** Addition of  $\text{CO}_2$  and reduction steps alternate in the anabolic hemicycle, leading to the accumulation of organic compounds.

The presence of the necessary precursors and the exposure to oxidisers generated by the action of an oxidising atmosphere would allow for the inversion of this cycle, suggesting the bi-directional Krebs cycle as the main feature in the circulation of carbon in the early ecosphere.



**Figure 8** Under oxidising conditions the tricarboxylic acid cycle flows in catabolic direction with loss of  $\text{CO}_2$  and depletion of accumulated organic compounds.

The availability of reducing power for anabolic processes (deriving mainly from lithospheric divalent iron and sulphides), would, in most oceanic domains, outbalance the total amount of oxidising power brought in by the slightly soluble atmospheric oxygen, causing the accumulation of organic compounds in the hydrosphere.

Inquiry into the nature of these compounds and their formation processes may be helped by the presumption of a congruent evolution.

## **CONGRUENCE IN THE HYPERCARBONIC WORLD.**

The principle of congruence is a heuristic tool meant to guide the investigation of the history of living systems. It states simply that modern life is a highly useful and necessary reference in the study of life's previous stages. Congruence can be envisioned as complement to evolutionary theory since it represents the search for evidences of common descent at a biochemical level. The universality of metabolic processes, such as the tricarboxylic acid cycle, is the focus of this quest.

Although the biochemical similarities among existing organisms are generally held as an unambiguous proof of their common evolution, classical models for the origin of life propose a previous "prebiotic" world, where organic compounds would have accumulated through processes foreign to today's biochemistry, such as atmospheric syntheses (Lazcano and Miller, 1999).

The first theoretical propositions regarding the research of the evolutionary nature of metabolism were laid out by Granick (1950, 1957), and were later applied, mainly by De Duve (1990) and by Morowitz (1993), to the field of the origin of life. The Ecopoesis Model further extends the realm of congruence, from the evolution of organisms to that of the ecosphere as a whole.

This conception implies that geochemical cycles of biogenic elements have always been essentially the same, but also that the steep energy gradients that fuel vital processes were not created by organisms. Instead, the very existence of energy yielding processes in the primordial environment, especially the aerobic degradation of organic matter (total oxidation to CO<sub>2</sub>), would have been essential to the creation of order inherent to organismal life.

The use of the term "protobiological", implying primitive life, as opposed to "prebiotic" (before life) emphasises the kind of continuity that characterises the principle of congruence.

Congruence requires chemical analogy between these two stages of the biochemical evolution, and the action of protobiological environmental factors is proposed to parallel that of coenzymes.



**Table 1:** Protobiological environmental factors and corresponding metabolic agents.

1 - Permanent.

Environmental factors (and opposite reaction)	Origin	Corresponding metabolic Agents (coenzymes)
+ H <sub>2</sub> O - H <sub>2</sub> O	Hydro-atmosphere	(spontaneous) ATP, GTP, etc.
+ CO <sub>2</sub> - CO <sub>2</sub>	Hydro-atmosphere	Biotin (spontaneous)

2 -Eventual (contingent) primary.

[H]	Lithospheric Reducing Power (Fe <sup>2+</sup> , H <sub>2</sub> S, FeS clusters)	Ferredoxins, Reduced Transporters (NADH, FADH <sub>2</sub> , etc.)
[O]	Atmospheric Oxygen	Oxidised Transporters (NAD <sup>+</sup> , FAD, etc.)
+ H <sub>2</sub> S - H <sub>2</sub> S (+H <sub>2</sub> O)	Hydro-atmosphere (S Cycle)	CoenzymeA-SH (spontaneous)
+ NH <sub>3</sub> (NH <sub>2</sub> COOH) - NH <sub>3</sub> (+H <sub>2</sub> O)	Hydro-atmosphere (N Cycle)	Amine compounds (spontaneous)
+ H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> - H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> (+H <sub>2</sub> O)	Hydro-atmosphere	ATP, GTP, etc. (spontaneous)

3 - Eventual (contingent) secondary.

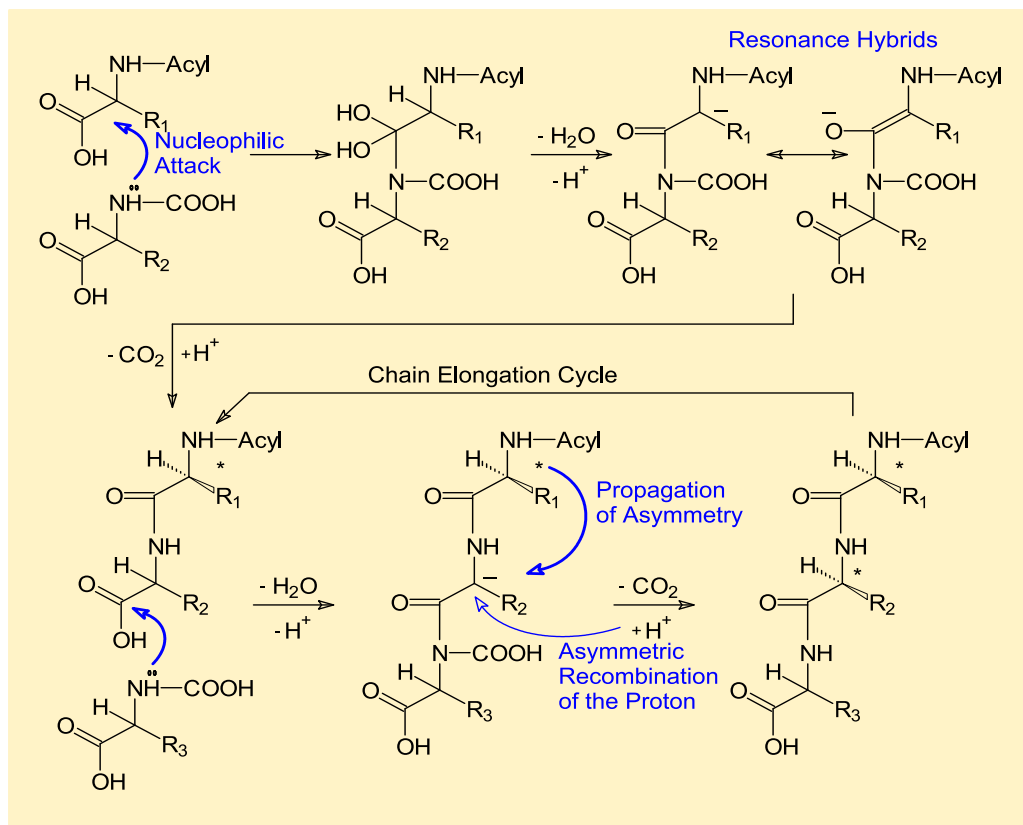
H <sub>2</sub> S <sub>2</sub>	H <sub>2</sub> S / [O]	Lipoic acid
NH <sub>2</sub> COOH / [H] (NH <sub>2</sub> COSH / [H]) Nitrogen nucleophile	NH <sub>2</sub> COOH / [H]	Pyridoxamine
CN <sup>-</sup> , etc. Carbon nucleophile	Cyanide or Formic acid derivatives (One-carbon)	Thiamine



Besides those coenzymes that have clear protobiological counterparts, a minimal system capable of all transformations inherent to the core of metabolic reactions would require two factors with functional group catalytic action, analogous to the pyridoxal-pyridoxamine pair and to thiamine (nitrogen and carbon nucleophiles respectively). A minimal 'one-carbon' chemistry, which is also needed for the synthesis of purine nucleotides, must provide a thiamine-like factor in the protobiological hypercarbonic world. Cyanide, which has been shown to catalyse analogous reactions (Breslow, 1958, 1962), might initially have been provided abiotically (primary input). A congruent route would soon be using serine as source of the 'one-carbon' required.

## HYPERCARBONIC CHIRAL PROPAGATION.

Chiral propagation (enantioselective polymerisation) would ensure the synthesis of homochiral polypeptides owing to the formation of prochiral centres in the hypercarbonic derivatives of peptidic materials.



**Figure 10** The chiral propagation mechanism here shown for racemic amino acids is a minimally stripped down version of the possible equilibrium forms in the hypercarbonic medium. Accordingly, N-carboxylation and protonation of the main-chain carboxyl are essential, but the actual reactive species may involve the addition of CO<sub>2</sub> or H<sub>2</sub>S to the peptidic material, with the use the corresponding aminodiacids and thioacid derivatives. Although modern organisms use optically active amino acids, this mechanism is otherwise fully congruent with present-day biochemistry.

In the hypercarbonic medium, amino acids are deprived of their zwitterionic properties. The nucleophilic attack of the carboxylated amino group on the protonated carboxyl proceeds easily, generating an adduct that contains a resonance stabilised carbanion. The asymmetric recombination with the proton through the Marckwald synthesis (Kenyon and Ross; 1951, 1952) is oriented by the amino acid residue added in the previous cycle. Since initiation may occur through acylation by an achiral carboxylic acid, the first amino acid of the chain can be anyone of the two enantiomers. It will determine, however, the chiral orientation of all subsequent units, giving rise to homochiral polypeptides.

Another important aspect is that the acylation of the amino group of the aminoacid residue raises the pK<sub>a</sub> of the carboxyl group thereby increasing the proportion of protonated carboxyls and favouring chain elongation rather than the attack on monomers.

## EVOLUTION OF ORGANISMALITY.

The organismal characteristics of life are only gradually acquired and cells are fairly latecomers in this model. Interaction between the biogeochemical cycles and their products would determine the first steps in the evolution of organismality.

The initial aggregation of organic matter, countering the entropic tendency to dilution, is ascribed to a combination of circumstances:

- 1) The lowered water activity ( $A_w$ ) of the hypercarbonic medium.
- 2) The coalescence of hydrophobic compounds (minimising energy due to charge-separation in the highly ionic medium).
- 3) The kinetics of formation of thioacids and their partial extraction into the lipid phase.
- 4) The stabilisation of the hydrophobic micelle through the formation of surface amphiphilic compounds.
- 5) The facile formation of peptide bonds due to the destruction of the zwitterionic character of amino acids through N-carboxylation.
- 6) The adhesion of the peptide fraction to the micellar surface amphiphilic compounds due to charge affinity, possibly involving polyvalent cations.
- 7) The adsorption of low-molecular weight organics to the peptide fraction.

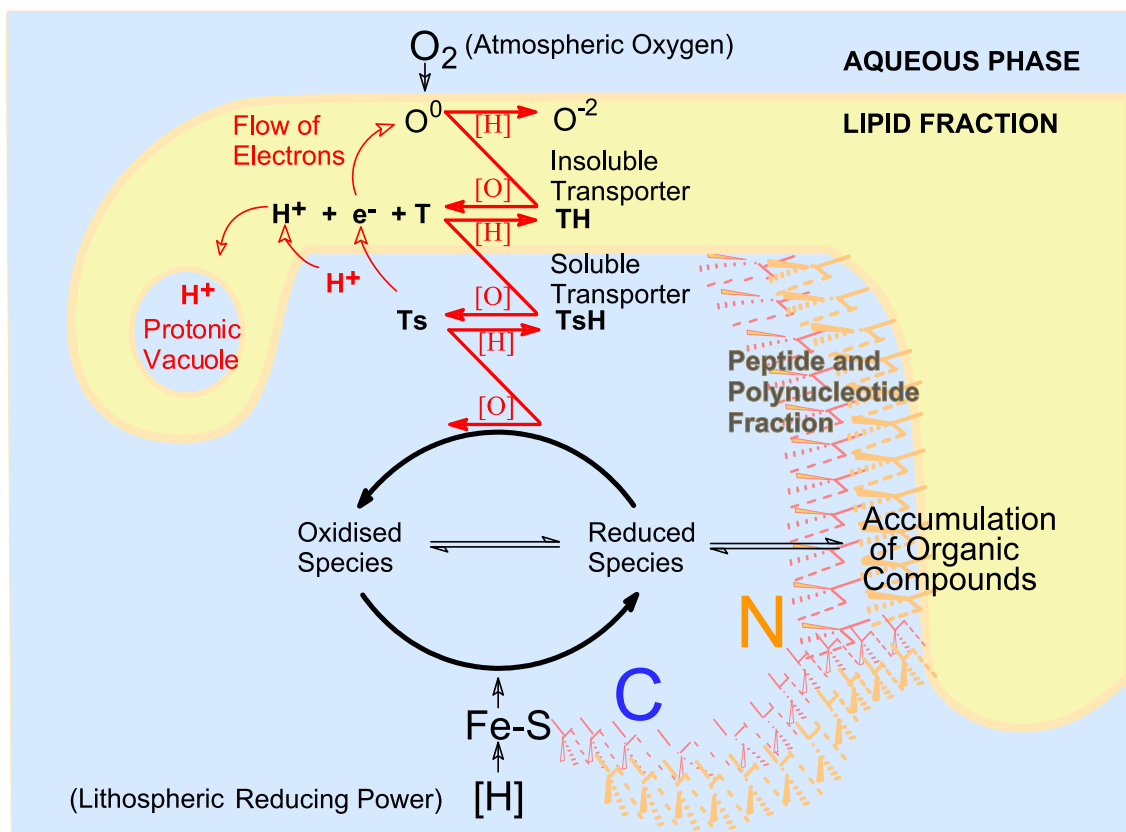
All these properties would stabilise colloidal aggregates in dilute solution. They are fully compatible with the vision of the early Earth as a "water-world", devoid of significant evaporating surfaces.

The energetic autonomy of these colloidal aggregates would develop as a consequence of their physical and chemical structure. The preferential solubility of oxygen in the lipid phase (Battino et al., 1983) favours oxidation processes next to the micelle surface. Oxidation of hydrogen sulphide to hydrogen disulphide (lipoic acid analogues), would cause the oxidation of alpha-ketoacids to thioacids, permitting the synthesis of 'high-energy' compounds, paving the way to the evolution of substrate level phosphorylation. Sulfur-containing amino acids in the peptide fraction could bind divalent iron of lithospheric origin. These primitive iron-sulphur clusters, ancestors of today's ferredoxins, would be responsible for the localisation of reducing power, concentrating redox potentials within each one of these aggregates, which would thus have both reducing and oxidising poles.

At this step translation could arise as a consequence of the improvement of an initially loose and generic interaction between polypeptides and phosphodiester polymers (primitive RNA).

Although heterogeneous phosphorylation ("respiration") requires physical barriers, like membranes, it could precede the advent of true cellularity, since protons resulting from the oxidation of lipid soluble electron transporters could segregate in protonic vacuoles. A potential between this vacuole and the external (or metabolic) compartment would thus ensue, and this would lead to the possibility of a more efficient path for the synthesis of high-energy

compounds. Besides providing a rational path for the evolution of the cellular habit, this inverted cell is consistent with evidence for an asymmetric biological membrane at this stage (Jékely, 2006).



**Figure 11** General functional organisation of a pre-cellular organic aggregate. Before specialised transporters TH and TsH were developed, oxidation of organic matter would be mainly mediated by the  $H_2S/H_2S_2$  pair alone. Iron-sulphur clusters bound to hydrophilic polymers (belonging to the lipid-anchored Peptide and Polynucleotide Fraction) make the reducing power of the lithosphere locally available. C- and N-nucleophiles are also associated with the polymeric fraction.

Cellularity would thus first arise, not as a method to protect organic compounds from dilution, but to promote and to profit from their oxidation. Emphasis on the functional energetic properties of cells rather than on their physical appearance suggests this aerobic dawn for prokaryotic cellularity. True cells would be the product of the gradual enclosure of the metabolic recess, after which the protonic vacuole would no longer be needed.

The role of competition and selection would only become meaningful as individual identity gradually evolved.

## DISCUSSION.

The construction of models articulating the largest possible amount of data about the genesis of the chemical composition and functional structure of the ecosphere has been a constant concern in the scientific questioning of the origin of life.

The need to coordinate such varied information should not lead, however, to fossilise science within doctrinarian or dogmatic viewpoints. In this sense, the idea that a neutral or reducing atmosphere is a necessary requirement for the appearance of the biological world must be questioned.

The existence of free oxygen in our primitive atmosphere is completely coherent with the Earth's position as a terrestrial planet, and is backed by robust geological evidence. The heterogeneous nature of the terrestrial environment assures that, from a strictly chemical point of view, it is no obstacle to the formation of organic compounds and that it is probably an essential factor in the richness and complexity of the protobiological world.

The whole dimension of its importance, however, can only be appreciated in a systemic approach. Besides permitting the formation of an ozone layer, protecting nascent life from the harmful action of ultraviolet rays, free atmospheric oxygen endowed the ecosphere, from its very beginnings, with a great functional axis.

Far from being an amorphous soup of organic compounds, the Earth's primitive ocean would already elicit a global dynamism, anticipating the evolution of the main biogeochemical cycles.

The flow of electrons that leaves the lithosphere and crosses the hydrospheric compartment, pumped by the gravitational loss of hydrogen after the photolysis of water vapour, is the central factor in this dynamism. This planetary environmental feature would impart to the chemistry of life a qualitative and spatial amplitude that is far greater than that which is attainable by the exploitation of small geochemical disequilibria, of local nature, or the chemical energy delivered by disproportionations.

The classical conception, which calls for an anoxic environment owing to the instability of organic compounds towards oxidation, should therefore be replaced by the notion that it is precisely with respect to this instability that the energetic processes that characterise the living world are structured.

With this perspective, it seems pointless to imagine that a phenomenon such as life might have been developed without a close association to efficient energy exchanges, which are as essential to it as its own chemical constitution.

And it is hardly conceivable, in our planet, that these exchanges could have been otherwise enabled, since only the presence of free oxygen in the atmosphere, owing to its ability to oxidise organic matter, could provide the primitive ecosphere with a great oxidising pole, a universal electron acceptor.

Before the advent of photosynthesis, the electrochemical potentials needed to fuel life were necessarily maintained by the continuous supply of abiotically generated redox pairs. Exploiting favourable energy gradients between electron donors and acceptors are a fundamental thermodynamic constraint underlying the diversity of metabolic lifestyles (Nealson and Conrad, 1999).

Within the variety of alternative electron acceptors used by microorganisms today, such as sulphate, nitrate and transition metals in their higher oxidation states, practically all of them are the product of an oxidising environment. They are only indirect forms of aerobic metabolism. The great exception is carbon dioxide, but, since CO<sub>2</sub> cannot be used to oxidise carbon compounds, its use as final electron acceptor needs necessarily to be coupled to the use of strong electron donors as reductants, and this coupling implies an organised, cellular system (actually, organic compounds are oxidised through carboxylation, but only canonically - this means that through the addition of carbon dioxide the average oxidation state of carbon in a molecule is increased, but the carbon backbones remain unaffected). That methanogenesis has rapidly become a successful form of metabolism among some earlier branches of life is hardly surprising given the abundance of environments where CO<sub>2</sub> is the only electron acceptor available. But its physical and chemical properties preclude its use in a genetically uncontrolled, pre-cellular metabolism. As in the case of the evolution of methanogenesis in Archaea (Gribaldo and Brochier-Armanet, 2006), there are no biochemical or phylogenetic grounds to classify the specialised metabolisms of anyone of those various modern microorganisms as primitive.

Indeed, the very fact that we can safely presume primitive organisms to use energy through much less efficient processes, implies, with to an even higher degree of certainty, the need for a primordial environment endowed with wide electrochemical potentials.

This judgement, based on the Darwinian concept that biological systems tend to become more efficient with time, as a result of mutation and natural selection, has been recalled by Kirschvink and Weiss (2002) as a guide to understand the evolution of biological energy exchange processes up from their very fundamental planetary prerequisites (Gaidos et al., 1999).

The perspective of a primordial ecosphere being bounded by dynamic factors is reminiscent of Vernadski's ideas (1940) opposing the then prevalent heterotrophic hypothesis, which he considered to be constructed upon a wrong question: the doubt concerning the nature of the first organisms. He argued that the independent existence of specific metabolic habits was not conceivable from a geochemical point of view, since none of them could supply all the functions inherent to life. The basic functionalities of the biosphere should therefore be established prior to the appearance of organisms. According to him, for example, the first abiotic photochemical synthesis would already constitute an incipient form of photoautotrophism. In a similar way, when the energy of the thus obtained compounds was utilised for new syntheses, a nascent heterotrophism would be present.



Following a similar track, Ycas (1955) suggested that the advent of organisms should have been preceded by the appearance of non-organismal chemical cycles, bearing analogies with the metabolic cycles.

Such opinions, despite their extremely generic nature, pointed clearly to the idea that the history of life in our planet cannot be envisaged merely as a history of the organisms, but rather that of the evolution of an integrated system of exchanges of energy and materials.

As far as materials are concerned, there has been little doubt that, from a chemical standpoint, all life forms on Earth are essentially identical. Proteins, nucleic acids, lipids and sugars have all the same function in every organism.

When it comes to energy exchanges, on the other hand, emphasis has always been attributed to the functional differences distinguishing the many metabolic habits. This approach avoided the chore of framing the problem within a more generic concept, encompassing the fundamental energy-yielding processes of the biological world. As a result, little attention was given to the fact that, regardless of whether aerobic or anaerobic respiration, fermentation, or the many kinds of photosynthesis and chemosynthesis, the energetic directives of all organisms are subject to a single principle: that of the economy of reducing power. This central principle, which determines the valuation of reduced compounds as an energetic resource, prone to accumulation or expenditure, is the common currency of all metabolic lifestyles.

And it is precisely the ample and permanent possibility of oxidation of these reduced compounds, in planetary dimension, that may have given a direction and justified the concerted evolution of all these processes.

The usefulness and scope of these concepts come to evidence as we question, for instance, the origin of the light-dependent reactions of photosynthesis, which exhibit a level of organisation implying a fully constituted organismality. Towe (1978) was the first to point out the inconsistency of the idea that an overpopulation of cyanobacteria could have been the origin of our oxidising environment. There is no reason to think that a reducing aqueous medium, which, by definition, contains better electron donors than water, could exert selective pressure demanding the use of water as an electron donor.

How could one understand the development and the persistence, for hundreds of millions of years, of a complex machinery having the sole purpose of paying high for a cheap resource? Not to mention the immense energetic lavishness represented by oxygenic photosynthesis being used by organisms that were unable to aerobically consume the reduced carbon that they were producing.

The shortage of reducing power in the photic zone seems to be the only plausible explanation, from an energetic standpoint, to justify the development of the light-dependent reactions of photosynthetic processes. The required long-standing and permanent selective pressure can only be accounted for by the pre-existence of an atmosphere containing abundant free oxygen.

The conception of a model where life is the product of the circulation of materials and energy in the ecosphere, and that these cycles precede organismal life, is frontally opposed to all classical conceptions.

Traditionally, the creation of life, or biopoesis, has been regarded as being indistinguishable from the creation of organisms, and anterior to the development of most metabolic pathways, which are thought to have come about through natural selection.

Accordingly, the great biogeochemical cycles would only have been established as a consequence of the action of organisms on the environment, after the origination of the participating metabolic lifestyles.

The heterotrophic hypothesis, founding paradigm of the classical conceptions of biopoesis, postulated a sequential approach, whereby the first organisms invented fermentative metabolism to consume the abiotically produced organics of the primordial broth, enriching the atmosphere with the carbon dioxide generated as waste. Later, upon the exhaustion of these organics, they learned how to use sunlight to synthesise their nutrients from carbon dioxide. This process generated, again as a waste product, molecular oxygen. Free oxygen would initially oxidise the excess divalent iron in the hydrosphere and, only later, after the consumption of this sink, become an important atmospheric component. Profiting from the waste of the previous step organisms would invent aerobic metabolism, entitling life to an explosive radiation.

More recent knowledge about the phylogenetic distribution of metabolic habits among organisms has completely upset this plan, but the basic concept, proposing the initial emergence of a compartmented, cellular life, that progressively conquers and modifies its environment, still pervades all scientific inquiry into the origin of life to our days. This contrasts sharply with the idea that the autonomy of organisms only arose gradually, and that life, for roughly the first third of its history (prior to the invention of the light-dependent reactions of photosynthesis) depended exclusively on geochemically generated electrochemical potentials.

Under a thermodynamic viewpoint, a simple analogy with well-known physical systems can illustrate the fundamental difference between the two conceptions. When a mass of water is heated from below, the temperature difference between the lower and upper parts result in the formation of convection cells, organised systems favouring more efficient heat conduction, and the suppression of the temperature gradient.

In nature, the formation of organised systems is always linked to the creation of structures that are able to dissipate energy (or increase entropy) in a more efficient way (Schneider and Kay, 1995).

It is therefore hard to conceive that life, an organised system, functionally defined by Chaisson (2001) as an “open, coherent structure kept far from equilibrium by a flow of energy”, might have been able to constitute itself before

the energy flows that maintain it, and to create differences of electrochemical potential before being able to use them efficiently.

The precedence of geochemical cycles, structured upon the reduction and oxidation reactions of the biogenic elements, as compared to the appearance of organisms thus represents a new formulation for the first chapters of the history of the terrestrial environment, compatible with the general principles that determine the creation of order in nature.

Although a strictly deterministic sequence does not follow from this formulation, the underlying concepts cast light upon the gradual generation of order in each step in the creation of the ecosphere, demanding from chance no more than a very modest contribution.

The creation of the ecosphere, or Ecopoiesis, comprises the appearance of the primary metabolic pathways and their environmental complements (Trophopoesis). This planetary metabolism precedes the emergence of organismal life (Ontopoesis), supplying its material substrate and informing its energetic directives.

The proposal of a metabolic and aerobic dawn for life, traced in the reconstitution of the path from the “non-living” towards what we could define as “life” would not be complete without the mention, albeit brief, of some additional angles through which the question of our origins may be focused.

In such fields, the extended and varied amount of data supplied by technical advancements in biology has brought about a vigorous questioning or even the revision of traditional concepts sedimented within scientific knowledge.

In the first place, cellular biology, where an improved knowledge about the structure, organisation and functionalities of the cell led De Duve (1990) to defend the idea of late encapsulation. Inspired by Blobel’s original proposals (1980) for the evolution of cellularity, he argued that the creation of a distinct internal medium, separated from the environment, would necessarily have been preceded by the development of metabolic abilities of a reasonable degree of complexity. Pointing out to the fact that any spontaneously formed vesicles, such as the liposomes, would be destined to immediate death through starvation, due to the lack of contact with the external medium, De Duve came up with the idea of a protobiological metabolism in an open environment, which he called the protocytosol. A functional metabolism already linked to genetic controls, was, in his view, a preliminary condition for a late encapsulation event to originate a true cell with its minimal functional requirements. Besides, he emphasised the importance of a congruent pattern for the evolution of metabolism in the early development of the enzymatic machinery.

The other great angle is that of molecular biology and genomics, where the possibility of sequencing genes and proteins has enabled science to catch a much clearer glimpse of the tree of life, inherent to the evolutionary history of organisms, inquiring the past through the convergence of traits in the course of time. The compared study of the gene sequences of organisms pertaining to the

three fundamental taxonomic domains, focused on the general mechanisms of gene transference that would determine the existing homologies and their distribution within groups, has been presenting increasing evidence that their common origin should precede cellular life (Woese, 1998, 2000, 2002; Doolittle, 1999, 2000).

But nowhere have such studies caused a deeper revision of concepts than in the understanding of the evolution of metabolism. Not only did they help deny the alleged simplicity of organisms previously thought to be representative of primitive life forms, but they were also essential in establishing the picture of a common complexity that testifies to the long evolutionary history that all living beings share.

Protein homologies have brought firm evidence that the enzymatic systems involved in respiratory chains precede the common ancestry of organisms (Saraste, 1994; Castresana et al., 1994, 1995, 1999, 2001, 2004; Schäfer et al., 1996, Brochier-Armanet et al., 2009). Although such systems could imply both aerobic and anaerobic respiration, the latter, which does not use molecular oxygen directly, also requires it to be present in the environment.

Besides, the phylogenetic tree of bacterial lineages, constructed on the basis of whole genome sequencing, has revealed that cyanobacteria were one of the last offshoots to diverge from the common bacterial stem. Accordingly, their appearance took place much after that of uncontroversial evidence for widespread oxygenation of the ecosphere, traditionally attributed to their action, or of lifestyles relying on the presence of strong oxidants (Blank, 2002, 2004). These findings are in agreement with the recent re-evaluation of evidence for early photosynthetic organisms in the form of fossilised structures (Brasier, 2002; Pinti, 2008) or in that of biomarkers (Rasmussen, 2008), which reverts the accepted timetable for the appearance of cyanobacteria to ca. 2.15 Ga (Hofmann, 1976).

While phylogenetic research provides an ever-growing consistent record of diversification and increase of biological complexity, geochemical evidence brings increasing support for the idea of an ecosphere where the cycling of biogenic elements has been operative throughout geologic time (Fenchel and Finlay, 1995 in Line, 2002; Lasaga and Ohmoto, 2002; Yamaguchi, 2005). The need to conciliate this apparent contradiction is likely to become the main challenge facing new inquiry into the evolution of the biosphere.

For that reason, innovative approaches to the comprehension of the action of environmental factors and its connections with the history of metabolism are required. Such ideas, focused on the cycling of materials and energy in the ecosphere as well as on the physical and chemical properties of the components of the primitive environment, can help us better understand the origins of chirality, of oxidative phosphorylation and enzymatic catalysis. Besides, they can prove to be a valuable guide in pointing out new directions in the investigation of the basic question of how the functionalities inherent to life – the metabolic pathways, the energetic economy, and replication - emerge and are progressively incorporated to the structural reality of organisms.

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