EPSC Abstracts
Vol. 5, EPSC2010-17, 2010
European Planetary Science Congress 2010

Competition and evolution of archaic autocatalytic CO_2 fixation cycles

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There are essential foundation to consider, that the last common universal ancestor (LUCA) on the ancient Earth was a chemoautotrophic microorganism. Modern models for the origin of autotrophic metabolism biochemistry has been developed on the general scheme of formation of complex systems from simple, including system of chemoautotrophic CO_2 fixation, as a basis of the central intermediary metabolism evolution [3,4,5.8,9]. The autocatalytic system of CO_2 archaic fixation (CAF) was submitted as a combined 3-hydroxypropionate (3-HP) and reductive citrate (RC) cycles (fig. 1). This bicycle contain a succinate – fumarate core, capable of switching electron flow in forward or reverse direction depending on redox potential of geochemical environment.

It is postulated, that the competition between autocatalytic cycles in structure of CAF bicycle in conditions of the ancient Earth led to physicochemical selection, major factors of which were temperature, redox potential and mineral composition of the surrounding hydrothermal environment. Adequacy of cycles to these conditions was criterion of the selection. The hydrocarbons of geochemical hydrothermal systems fill up a pool of central intermediates of CAF bicycle with formation of acetate at higher temperatures and succinate at lower ones (fig. 2). Temperature dependence of free energy change ($\Delta G^0_{298} \rightarrow \Delta G^0_{473}$) of cycles turnover shows, that high-temperature alkaline conditions of the hydrothermal environment are more favorable for archaic 3-HP cycle in comparison with RC cycle. The redox potential for the succinate – fumarate pair (in standard conditions μ_{H2} =-84,43 kJ/mol or E_{0r} = -0,438 V) determines the stability of RC cycle at higher potentials and 3-HP cycle at lower ones, that allows to present divergence of CAF bicycle in two directions (the scheme on fig. 2). The redox equilibrium corresponding potential E_{0r} = -0,438 V ($a_{O2} = 10^{-54}$ M), divides the diagram in two parts - phase space at the left and at the right of isopotential line favorable for development of RC and 3 HP cycles, respectively. Thus, the competition of archaic cycles led to their selection defined by physicochemical conditions of the hydrothermal environment and has created primary metabolic division between groups of arising archaic protocells.

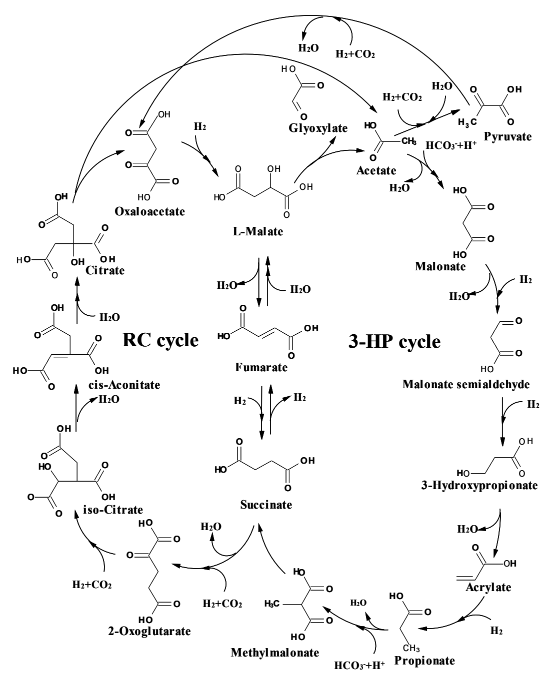

Figure 1: The scheme of proposed LUCA central intermediary metabolism (CAF bicycle) in the form of coupled autocatalytic loops of RC and 3-HP cycles.

Coevolution of this metabolic network and lipid membrane, enzymatization by ribozymes or by polypeptides of CAF bicycle reactions and development of the primitive genetic device (replication and translation) has led to emergence of population LUCA cells, containing RC and 3-HP chemoautotrophic metabolic systems as constituents of CAF bicycle. Thus, the CAF bicycle became a basis of intermediary metabolism of LUCA located in the root of bacterial phylogenetic tree of life, opening the way for the evolution of this first autonomous protocells on the Earth.

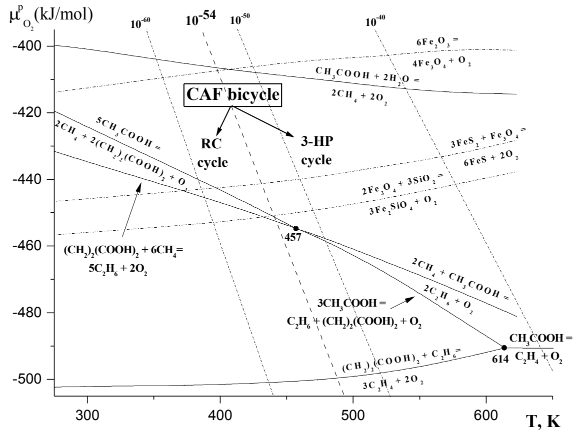

Figure 2: Aqueous hydrocarbons and compounds of RC and 3-HP cycles in the T - (μ_{O2} = RTlna_{O2}) diagram at saturated vapor pressure. a_{O2} – designates chemical activity of oxygen in hydrothermal solutions. The equilibria of hematite (Fe_2O_3) – magnetite (Fe_3O_4), pyrite (FeS_2) – pyrrhotite (FeS) – magnetite (Fe_3O_4), and quartz (SiO_2)- magnetite (Fe_3O_4), - fayalite (Fe_2SiO_4) mineral buffers are shown. Isopotential lines corresponding of activity O_2 (10^{-n}) are presented.

The natural selection under influence of ancient hydrothermal environment resulted in the divergence of LUCA cells with formation of ancestral phyla Aquificae and Chloroflexi, which extant species function on the basis of RC and 3-HP cycles respectively. This earliest bifurcation follows from researches of prokaryotes membrane topology and analysis of insertion and deletion found within paralogous gene sets [1,2]. This phenotypic diversification was controlled by main factors of selection, temperature, redox potential and mineral components of environments. Mainly, redox conditions of surrounding hydrothermal environment have defined ecological niches favorable for development of ancestral taxons Chloroflexi and Aquificae. So ancestral *Aquifex* was located in reductive conditions deep-water hydroterm, and ancestral *Chloroflexus* was extended in more oxidizing high-temperature areas at geodynamic shift a hydroterms in the photic zone. Extant species of filamentous green non sulfur anoxygenic phototrophic *Chloroflexus*, phylogenetically distant from any other photosynthetic group, widely distributed throughout alkaline hot springs and formed yellow-orange-greenish mats with cyanobacteria. On the basis of data on stable carbon isotopes fractionating it is shown, that these mats are modern analogues of ancient Archaean stromatolite formations [6], which have been generated or by filamentous *Chloroflexus* or by more simple ancestral branch of this bacteria which could exist 3 - 3,5 billion years ago [7].

Acknowledgements

This work was supported by Presidium of Russian Academy of Sciences (program fundamental researches No 24 "Origin of biosphere and evolution of geo-biological systems").

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