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# The parageneses thermodynamic analysis of chemoautotrophic CO<sub>2</sub> fixation archaic cycle components, their stability and self-organization in hydrothermal systems

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#### ABSTRACT

The parageneses physico-chemical analysis based on a method of thermodynamic potentials has been used to study the system of C-H-O organic compounds, which are, in particular, components of biomimetically built primordial cycles of carbon dioxide chemoautotrophic fixation. Thermodynamic data for aqueous organic compounds allowed one to construct the chemical potential diagrams and establish the areas of thermodynamic stability (facies) of components of CO<sub>2</sub> fixation pathways in hydrothermal systems, in particular, a reductive citric cycle (RCC), 3-hydroxypropionate cycle (3-HPC) and acetyl-CoA pathway. An alternative deep source of carbon (hydrocarbons) proved by the data on endogenous emission of hydrocarbons in hydrothermal fields of oceanic ridges was suggested. The system was determined, which combines hydrocarbons, CO2 and components of RCC, 3-HPC and acetyl-CoA pathway with characteristic parageneses of methane and ethylene with acetate in two-component  $CH_4-CO_2$  and  $C_2H_4-O_2$  subsystems, respectively. The thermodynamic analysis of a redox mode at various pressures and temperatures allowed one to uniquely determine hydrocarbon-organic system able to independently generate acetate and succinate at oxidation of deep hydrothermal hydrocarbon fluids emerging on sea surface. The limits for thermodynamic stability of CO<sub>2</sub> archaic fixation (CAF) components responsible for generation and self-organization in hydrothermal environment was identified. The tentative integrated system of CAF was developed as a combined acetyl-CoA pathway, 3-HPC and RCC containing a succinate-fumarate core, capable of switching electron flow in forward or reverse direction depending on redox potential of geochemical environment that is governed by the  $(CH)_2(COOH)_2+H_2=(CH_2)_2(COOH)_2$  reaction. This core is a "redox switch", which is sensitive to certain conditions of hydrothermal environment and defines electron flow direction. The redox geochemical mode caused by temperature, pressure, composition of a hydrothermal fluid and a mineralogical setting defines stability of CAF cycle components in paragenesis with hydrocarbons and possibility of cycle self-organization.

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#### 1. Introduction

One of the most striking geothermal phenomena on the Earth are hydrothermal hot spring vent fluids at mid-oceanic ridges, which since their discovery are in the center of many hypotheses related to the origin of life on the ancient Earth. The main idea of these hypotheses consists in that organic compounds could be synthesized as a source of prebiotic self-organizing network on the early Earth inside hydrothermal systems including vent complexes associated with ocean ridges, deep aquifers and other subsurface aqueous environments. Several experiments were

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performed to simulate synthesis of organic substances in hydrothermal systems (Cody et al., 2001, 2004; McCollom and Seewald, 2007; Seewald, 1994, 2001). Thermodynamics was used to suggest a possible mechanism of organic synthesis during hydrothermal fluid mixing with sea water, in particular, the formation of thermodynamically stable associations of organic acids (Shock, 1990, 1992; Shock and Schulte, 1998).

The problem of origin, self-organization and evolution of prebiotic chemical systems is basic in the development of the general theory of origin of life in scenario of primary molecular genetics ("replication first") (Delaye and Lazcano, 2005; Joyce, 2002; Lazcano and Miller, 1999; Orgel, 2004; Robertson et al., 2000) and in scenario of primary metabolism ("metabolism first") (Eschenmoser, 2007; Fernando and Rowe, 2007; Kaufman, 1993; Lindahl, 2004; Smith and Morowitz, 2004; Wächtershäuser, 1988a, 1992, 1997).

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It is reasonable to assume that primordial self-organized chemical systems and primitive archaic forms of life arose in the vicinity of mineral-rich hydrothermal systems produced by submarine reduced volcanic vents (Corliss, 1990; Cody et al., 2001; Di Gulio, 2000; Holm and Anderson, 1998; Nisbet and Sleep, 2001; Shock, 1990; Wächtershäuser, 1988a, b, 1997). Long lifetime of hydrothermal systems, chemical nonequilibrium state together with slow kinetic reactions and compact localization of chemical energy sources predetermine them to be ideal site for organic synthesis and origin of primary archaic metabolic systems.

At a modern level of developing chemoautotrophic models of life origin, the major problem is to determine physical and chemical conditions thermodynamically and kinetically favorable for the formation of self-organizing system components of primary archaic metabolism. All extant forms of life directly or indirectly depend on autotrophic CO<sub>2</sub> fixation, i.e. an autocatalytic process that results in the reductive transformation of inorganic carbon (CO<sub>2</sub>) to low-molecular-weight building blocks for biosynthesis. Biomimetic models of archaic CO<sub>2</sub> fixation are based on biochemical reactions of reductive citric acid cycle (RCC) (the Krebs reverse cycle, reductive tricarboxylic acid cycle) (Cody et al., 2001; Lindahl, 2004; Morowitz et al., 2000; Smith and Morowitz, 2004; Wächtershäuser, 1990) and acetyl-CoA pathway (Pereto et al., 1999; Russell and Martin, 2004) in hydrothermal systems. The RCC reactions are specified by kinetic advantage as compared with numerous possible reactions due to autocatalytic nature of a cycle, when reaction products accelerate the reaction and reactions of other cycle components, and a number of CO<sub>2</sub> acceptors is doubled in each turn. Small amounts of cycle components formed from inorganic substance are needed to initiate cycle functioning. Once arisen, the cycle becomes autocatalytic (Lindahl, 2004; Wächtershäuser, 1990). The reaction sequence of RCC is a networkautocatalytic cycle along the relaxation pathway for redox couples in nonequilibrium reducing environments, which provides starting organic components for the synthesis of all major classes of biomolecules (Smith and Morowitz, 2004).

Considering conventional universality of forward and reverse, full or incomplete Krebs cycle in chemoautotrophic bacteria and archaea, which have ancient phylogenetic roots (Atomi, 2002; Meléndez-Hevia et al., 1996; Wächtershäuser, 1990; Wood et al., 2004), and, in particular, live in deep-sea hydrothermal environments (Campbell and Cary, 2004), it should be noted that a lot of their species, for example, thermoacidophilic archaeabacteria *Acidianus brierleyi, Metallosphaera sedula, Sulfolobus metallicus* and others use another type of chemoautotrophic CO<sub>2</sub> fixation, namely, 3-hydroxypropionate cycle (3-HPC) (Alber et al., 2006; Berg et al., 2007; Hügler et al., 2003a; Ishii et al., 1997, 2004; Klatt et al., 2007), which is a widely presented metabolic cycle as well as RCC and acetyl-CoA pathway. 3-HPC is a unidirectional pathway, where acetate reductively transforms via 3-hydroxypropionate to succinate.

The present work reports on the problem of origination and self-organization of components of primordial metabolic networks of chemoautotrophic  $CO_2$  fixation in hydrothermal geochemical systems, in particular, the determination of carbon source for their synthesis and their environmental stability conditions using a biomimetic approach and a thermodynamic method of parageneses physico-chemical analysis.

#### 2. Methodical approach

Paragenesis is an association (assemblage) of thermodynamic stable phases united by general origin in certain physical and chemical conditions. Physical and chemical analysis of parageneses is widely used in geochemical research (Korzhinskii, 1959) of mineral systems. It is based on generalization of thermodynamic and physical properties of minerals observed in rocks and ores for the determination of their parageneses formation conditions. The thermodynamic potential method (Gibbs, 1948; Korzhinskii, 1959) is used, which allows one to develop the system of geochemical mineral facies (thermodynamic stability areas) (Marakushev and Perchuk, 1966; Marakushev, 2000).

Our preliminary calculations showed that paragenetic analysis can be extended to organic compounds, which form systems listed below in a sequence of complication of their chemical composition and structure: C–H–O, C–H–O–N, C–H–O–N–P and C–H–O–N–P–S. The paragenetic analysis developed in the present work is limited to the C–H–O system, which is a basis for more complicated systems listed above. The fundamental concept is "independently existing phases as carriers of individual properties and a physical manifestation of an ideal complex of atoms or corresponding parts assumed by us in compounds" (Kurnakov, 1940). Phase equilibrium in a system is stipulated by equal chemical potential of any component in all phases and described by phase diagrams defining number, composition and ratio of masses of the equilibrium phases.

The paragenetic analysis is based on the Gibbs phase rule, according to which a number of degrees of freedom for equilibrium thermodynamic system is equal to a number of system independent components plus two minus a number of phases. In this case the number of independent components is the least one of chemical components, whose combination provides compositions of all possible phases. The phase rule is not limited to considering extensive parameters of a system and, hence, is completely applicable to the open systems with chemical potential as an independent parameter (Korzhinskii, 1966). Determination of all independent parameters (intensive and extensive) of a system and use together with the Gibbs phases rule provides a way to the study of thermodynamic systems properties.

The system state depending on external conditions was calculated using values of free partial energy formation ( $\Delta G_{f,T}^0$ ) of organic substance. The state diagrams, which reflect the areas of organic compound thermodynamic stability (facies) and their assemblages (parageneses), are graphically presented. When considering organic compounds in fluid and hydrothermal systems, the chemical composition-paragenesis (at constant values of pressure (*P*), temperature (*T*) and chemical potential ( $\mu_i$ )) diagrams, chemical potential-temperature (at constant *P*) diagrams, and chemical potential of components diagrams, for example,  $\mu_{H_2O} - \mu_{CO_2}$ ,  $\mu_{H_2} - \mu_{O_2}$  and etc. (at constant *P* and *T*) are most important ones.

The most known are temperature-pressure diagrams. In a kcomponent system, each association composed of k+2 phases is nonvariant according to the Gibbs phases rule and the certain point corresponds to it in the P-T diagram. If one of phases disappears, the association of k+1 phases becomes monovariant and, hence, it should correspond to a curve starting from a nonvariant point in the P-T diagram. Thus, in the general case, there are *k*+1 phases involved in each monovariant reaction and *k*+2 monovariant curves should start from a nonvariant point to form a so-called Schreinemakers beam (Korzhinskii, 1959). Each field between two curves of a beam corresponds to temperature and pressure conditions, in which no more than k phases simultaneously are in stable association in the given system. These fields are called facies of these phases. The Schreinemakers method is a geometric approach used to determine the relationships of reaction curves, which intersect at an nonvariant point in multicomponent systems. It was used in the present work.

The major equilibrium factors in the parageneses physicochemical analysis are chemical potentials ( $\mu_i$ ) of components representing its partial energy, the value  $\mu_i$  is expressed through activity  $\alpha_i$  and fugacity  $f_i$  as follows:  $\mu_i = (\mu_i^0)_{T,P} + RT \ln \alpha_i = (\mu_i^0)_{T,P} + RT \ln f_i$ . Here numerical values depend on conventional standard states. For activity, the state of pure crystalline substance or unit molal concentration is usually considered as a standard state at given temperature and pressure. In this state  $\alpha_i = 1$  and, hence,  $\mu_i = (\mu_i^0)_{T,P}$ . For fugacity, ideal gas state is considered as a standard condition at P = 1 bar, hence,  $f_i = 1$  and  $\mu_i = (\mu_i^0)_{T,P}$ . The fundamental thermodynamic equations for systems with chemical reactions are given here (Alberty, 2001).

Carbon dioxide (CO<sub>2</sub>) and monoxide (CO), ethane (C<sub>2</sub>H<sub>6</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>) in an ideal gas state should be considered as an elementary example of diagrams of chemical potential and composition of the C–H–O system. A triangular diagram (Fig. 1) defines positions of composition of the compounds in this system with characteristic paragenesis of C<sub>2</sub>H<sub>6</sub> with CO at unstable association (the absence of paragenesis) of C<sub>2</sub>H<sub>4</sub> with CO<sub>2</sub>. In many cases it is possible to consider the three-component system studied by us, as that built by one inert component, namely, carbon and two mobile components, namely, oxygen and hydrogen. As a result, oxygen and hydrogen turn from extensive parameters to intensive ones and the system can be considered as a single-component one. Such system state, which is dependent of chemical potentials of oxygen and hydrogen (Fig. 2), can be simulated using the composition–paragenesis diagram (Fig. 1).

Really, in a single-component system, the association of three compounds is nonvariant (0 = 1+2-3) at constant temperature (T) and pressure (P), according to the Gibbs phases rule (n = k+2-F), where *n* is a number of degrees of freedom, *k* is a number of independent components. *F* is a number of phases). and certain values of chemical potentials, in particular,  $\mu_{\rm O_2}$  and  $\mu_{\rm H_2}$ , i.e. a certain point in the diagram (Fig. 2) corresponds to it. There are two points in our diagram for triple associations:  $C_2H_4+CO+C_2H_6$  and  $C_2H_6+CO+CO_2$ . Three straight lines, which correspond to stability of two-component association, start from each triple points. The lines are monovariant at constant T and P according to phases rule. The direction of these monovariant lines can be obtained if one draws up reactions of conversion of one compound of the given system to another ones and calculates free energy  $(\Delta G_r^0)$  of the reactions using standard free energy of formations for these substances (here, according to Stull et al., 1969). For example,  $C_2H_4+O_2 = 2CO+2H_2$ ,  $\Delta G^0_{C_2H_4} + \mu_{O_2} = 2\Delta G^0_{CO} +$ 



**Fig. 1.** Triangular phase diagram for composition—paragenesis of C–H–O systems with carbon dioxide (CO<sub>2</sub>), monoxide (CO), ethane ( $C_2H_6$ ), ethylene ( $C_2H_4$ ) and parageneses between them.



**Fig. 2.** Diagram of oxygen and hydrogen chemical potentials  $(\mu_{O_2} - \mu_{H_2})$  of a single-component system (C) at P = 1 bar and T = 298 K corresponding to the diagram (Fig. 1). Nonvariant three-phase equilibrium is denoted with points, monovariant two-phase equilibrium is denoted with lines, which divide single-phase divariant areas of stability (the facies) CO<sub>2</sub>, CO, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>. Free energies of gaseous substances formation (Stull et al., 1969) were used in calculations.

 $2\mu_{H_2}$ ,  $\Delta G_p^0 = 2\Delta G_{CO}^0 - \Delta G_{C_2H_4}^0 = -342$ , 46 kJ/mol and  $\mu_{O_2} = \Delta G_p^0 + 2\mu_{H_2}$ . Similarly, we used the conversion reactions of investigated substances to obtain other monovariant lines in the diagram, which start from nonvariant points (Fig. 2). The diagram clearly shows the dependence of conversion of oxidized and reduced carbon compounds on oxygen and hydrogen mode, the existence of C<sub>2</sub>H<sub>6</sub>-CO paragenesis, and the absence of C<sub>2</sub>H<sub>4</sub>-CO<sub>2</sub> paragenesis that corresponds to the composition–paragenesis diagram (Fig. 1).

The investigation of substances of the C-H-O system in aqueous solutions is of great importance for various chemical, biochemical and geochemical processes. Recently, thermodynamics of hydrothermal processes has been developed, particularly, thermodynamic behavior of aqueous components of the C-H-O and C-H-O-N systems at different temperatures and pressures. In thermodynamic calculations the constants were derived using the method of electrostatic models, according to which at higher temperatures the essential role is played by a solvate constituent of chemical potential of a substance, which reflects the contribution of electrostatic interaction between substance and solvent (H<sub>2</sub>O). The standard state accepted in the present study for aqueous substances corresponds to unit activity of a species in a hypothetical one molal solution attributed to infinite dilution at any pressure and temperature. The activity of liquid H<sub>2</sub>O was taken to be 1. The values of Gibbs standard free energy for aqueous chemical substances at higher temperatures and pressures are considered in expressions for apparent standard partial molal free energy of formation:

$$\Delta G_{T,P}^{0} = \Delta G_{f}^{0} - S_{Tr,Pr}^{0}(T - T_{r}) + \int_{Tr}^{T} C_{P}^{0} dT$$
$$- T \int_{Tr}^{T} C_{P}^{0} d \ln T + \int_{Pr}^{P} V^{0} dP,$$

where  $\Delta G_f^0$  is standard partial molal energy of formation from elements at standard temperature ( $T_r = 298,15$  K) and pressure ( $P_r = 1$  bar) and  $S^0$ ,  $C_P^0$  and  $V^0$  relate to standard molal entropy, heat capacity and volume, respectively. Fully integrated form corresponding to the equation and the calculations of necessary coefficients are reported in (Amend and Shock, 2001; Helgeson et al., 1993; Oelkers et al., 1995; Shock, 1992).

A series of papers by Shock with coauthors reports on thermodynamic analysis of transformation of some organic substances in various conditions of hydrothermal system development, which is based on the data on thermodynamic properties of aqueous organic substances at high temperatures and pressures. Thermodynamic calculations of the Gibbs standard free energy and the analysis of geochemical constraints showed that abiotic synthesis of organic compounds in hydrothermal systems occurs in a metastable state due to kinetic barriers, which prohibit achievement of stable equilibrium in the C-H-O-N system (Helgeson et al., 1993; Shock, 1990; Shock and Schulte, 1998). Most of organic substances in condensed phase are in metastable state, i.e. they do not correspond to the minimal Gibbs free energy for the given composition of elements (Desiraju, 2002). Thus, they are "kinetic" or "metastable" phases (Brazhkin, 2006). The term "metastable phase" is applied to a nonequilibrium state of a substance, whose properties change reversibly in experiment or observation. In the present work the diagrams construction is based on the postulated existence of a kinetic barrier preventing the attainment of general thermodynamic equilibrium in hydrothermal systems (Helgeson et al., 1993; Seewald, 2001; Shock et al., 1995). For example, the lowest temperature, at which CH<sub>4</sub> and CO<sub>2</sub> attain isotopic equilibrium, is higher than 500 °C. Organic acids are conventionally considered in protonic form, which dominates in hydrothermal solution at pH < pK, i.e. the conditions for a number of deep-sea hydrothermal sources (Reysenbach et al., 2006). With the temperature increase, water disproportionation quickly attains thermodynamic equilibrium (Seewald, 2001). Thus, oxygen activity directly correlates with hydrogen activity according to the equation:  $H_2O(lq) = H_2(aq)+0.5O_2(aq)$  that implies the increase in oxygen activity at decreasing hydrogen activity and vice versa.

# 3. Hydrothermal transformation of hydrocarbons in components of archaic metabolic cycles

Let us consider compounds of metabolic pathways of a RCC, 3-HPC and acetyl-CoA pathway of CO<sub>2</sub> chemoautotrophic fixation (Alber et al., 2006; Atomi, 2002; House et al., 2003; Hügler et al., 2003a; Ishii et al., 1997, 2004; Meléndez-Hevia et al., 1996) shown in the composition-paragenesis phase diagram in a threecomponent C-H-O system (Fig. 3). The extreme position is occupied by acetate and 3-hydroxypropionate (7), which are on the intersection of H<sub>2</sub>-CO, CH<sub>4</sub>-CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>-O<sub>2</sub>, H<sub>2</sub>O-C connodes, i.e. they belong to these two-component subsystems. The arrangement of compositions of most of compounds (ten) shown in the diagram along H<sub>2</sub>-CO connode allows one to suggest the relationship between their formation and the most reduced high-temperature fluids. Acetate (7), 3-hydroxypropionate (7) and propionate (8) can be formed as products of simple oxidation of  $C_2H_4$ , whereas fumarate (1), aconitate (1), oxaloacetate (13) and glyoxylate (12) are products of acetylene  $(C_2H_2)$  oxidation. Typical natural hydrocarbons (alkanes, alkenes) are in the range of compositions limited by CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. This line segment is a base of the C<sub>2</sub>H<sub>4</sub>-CO<sub>2</sub>-CH<sub>4</sub> triangle, in which all components of considered pathways of the CO<sub>2</sub> fixation are located. Thus, the system is determined, which combines hydrocarbons, and RCC, 3-HPC and acetyl-CoA-pathway components with CO<sub>2</sub>. The system includes characteristic parageneses of methane and C2H4 with acetate (7) in the two-component  $CH_4-CO_2$  and  $C_2H_4-O_2$ subsystems, respectively.

The  $CH_4-C_2H_4$  range (Fig. 3) covers compositions of hydrocarbons generated in hydrothermal vents at oceanic ridges, which abundantly enter on an sea-floor along a global system of world ocean rift zones. For example, higher alkanes  $C_{16}H_{34}-C_{29}H_{60}$ 



**Fig. 3.** Phase diagram of composition of RCC, 3-HPC and acetyl-CoA pathway components in three-component C-H-O system. I—simple substances: H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CO, C; II—hydrocarbons: CH<sub>4</sub>—methane, C<sub>2</sub>H<sub>6</sub>—ethane, C<sub>2</sub>H<sub>4</sub>—ethylene; III—components of RCC; IV—components of 3-HPC. 1—fumarate, aconitate, 2—oxoglutarate, 3—malonate–semialdehyde, pyruvate, 4—succinate, methylmalonate, 5—methylmalate, 6—acrylate, 7—acetate, 3-hydroxypropionate, 8—propionate, 9—malate, 10—citrate, isocitrate, 11—malonate, 12—glyoxylate and 13—oxaloacetate.

(CH<sub>2,125</sub>–CH<sub>2,069</sub>) within the Rainbow hydrothermal field of the Mid-Atlantic Ridge are described in works (Charlou et al., 2002; Holm and Charlou, 2001). According to (Cruse and Seewald, 2006), hydrocarbons in paragenesis with methane presented by gaseous alkanes, namely, C<sub>2</sub>H<sub>6</sub>, propane (C<sub>3</sub>H<sub>8</sub>), butane (C<sub>4</sub>H<sub>10</sub>), alkenes, namely, C<sub>2</sub>H<sub>4</sub>, propylene (C<sub>3</sub>H<sub>8</sub>), and benzene (C<sub>6</sub>H<sub>6</sub>) and toluene (C<sub>7</sub>H<sub>8</sub>) were found in the northern Juan de Fuca Ridge hydrothermal fluids in the Pacific Ocean. Ascending migration of hydrocarbons is traced in hydrogen rich alkaline fluids, for example, ultramafic-hosted Lost City hydrothermal fields of mid-Atlantic Ridge (Proskurowski et al., 2008). Hydrocarbons prevailing in these sources are methane, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> and C<sub>2</sub>H<sub>4</sub>, whose endogenous nature is proved by high enough content of heavy carbon isotope ( $\delta^{13}C \approx -10$  to -15%).

Hydrothermal systems of oceanic ridges develop in a wide range of oxidation–reduction conditions, and the relationship between temperature and hydrothermal fluid redox state is a primary factor governing organic synthesis in deep-sea hydrothermal fields. Therefore, the best research method is parageneses facies analysis of hydrocarbons and some components of CO<sub>2</sub> fixation cycles in the temperature-oxygen chemical potential diagram ( $T - \mu_{O_2}$ ). Such phase diagrams are built for aqueous solutions at saturated vapor pressure ( $P_{sat}$ ) and 500 bars, and 273–900 K using free energy formation values ( $\Delta G_{T,P}^0$ ) of aqueous hydrocarbons, organic acids and minerals (Amend and Shock, 2001; Oelkers et al., 1995).

The diagram shown in Fig. 4 is considered at  $P_{sat}$ , i.e. at temperatures and pressures lower than critical ones (373.9 °C, 220.4 bar (pure water) and 407 °C, 298.5 bar (sea water)). It represents a two-component system (C–H are extensive parameters) since oxygen presented by either chemical potential or activity of O<sub>2</sub> in solution ( $\mu_{O_2}^p = RT \ln a_{O_2}$ , where  $a_{O_2}$  is oxygen chemical activity in hydrothermal solutions) passes to intensive parameters together with temperature and pressure. Thus, at arbitrary pressure nonvariant equilibrium in the diagram (points) consists of four phases, and three-phase equilibria (lines) divide



**Fig. 4.** The parageneses facies of aqueous hydrocarbons and compounds of RCC and 3-HPC in the  $T - (\mu_{O_2} = RT \ln a_{O_2})$  diagram at saturated vapor pressure ( $P_{sat}$ ). The parageneses for every facies are presented by linear diagrams. The equilibria of hematite (Fe<sub>2</sub>O<sub>3</sub>)-magnetite (Fe<sub>3</sub>O<sub>4</sub>), pyrite (FeS<sub>2</sub>)-pyrrhotite (FeS<sub>3</sub>O<sub>4</sub>) and quartz (SiO<sub>2</sub>)-magnetite (Fe<sub>3</sub>O<sub>4</sub>)-fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) mineral buffers are shown. Temperatures for four-phase nonvariant equilibrium are presented.

divariant stability fields (facies) of two-phase equilibria. Corresponding parageneses of hydrocarbons and organic acids are presented in linear schemes. They define the facies characteristics.

Nonvariant four-phase equilibrium at T = 614 K characterized by the reaction:  $C_2H_4+2CH_3COOH$  (acetate)= $C_2H_6+(CH_2)_2$ (COOH)<sub>2</sub> (succinate) is on the intersection of two lines of threephase monovariant equilibria and one line of two-phase equilibrium ( $C_2H_4+O_2=CH_3COOH$ ), which define the appearance of high-temperature paragenesis of acetate with C<sub>2</sub>H<sub>6</sub>. However, oxidation of C<sub>2</sub>H<sub>4</sub> results in the appearance of succinate (component of RCC and 3-HPC) in paragenesis with C<sub>2</sub>H<sub>6</sub> at extremely low chemical potential of oxygen in almost all temperature range of the considered system. Two of four monovariant equilibria, crossing nonvariant equilibria at 457 K define the occurrence of high-temperature and low-temperature paragenesis of acetate and succinate with ethane and methane, respectively. The next two equilibria stipulate the formation of paragenesis between these organic acids. Integrally, they appear as a hydrocarbon-organic system able to independently generate acetate and succinate at oxidation of abyssal hydrothermal hydrocarbon fluids venting on a surface of the oceanic crust.

The paragenesis of CH<sub>4</sub>-CH<sub>3</sub>COOH-(CH<sub>2</sub>)<sub>2</sub>(COOH)<sub>2</sub> should especially be stable in numerous methane-rich hydrothermal fluids in a corresponding redox mineral environment, for example, in the hydrogen-methane ultramafic-hosted hydrothermal system of Rainbow (Charlou et al., 2002; Holm and Charlou, 2001). It is seen from the diagram (Fig. 4) that the stability area (facies) with its paragenesis is located between equilibria of two mineral buffers, namely, quartz-magnetite-fayalite (SiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>SiO<sub>4</sub>) and hematite-magnetite (Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>) and corresponds to the magnetite facies in almost all considered temperature range at Psat. The pyrite-pyrrhotite-magnetite mineral equilibrium  $(FeS_2-FeS-Fe_3O_4)$  is located within the area of this facies. The analysis (Shock, 1990; Shock et al., 1995; Shock and Schulte, 1998) shows that stable "kinetic" or "metastable" phases of organic acids exist in methane facies and are limited by the quartz-magnetite-fayalite equilibrium. The increase in oxygen potential to hematite-magnetite equilibrium is accompanied by methane

oxidation and the formation of acetate—water paragenesis. In these conditions, paragenesis of acetate–succinate remains. With the further increase in oxygen potential, the succinate– $H_2O$  paragenesis forms below 307 K, and then the acetate–malonate (a component 3-HPC) paragenesis forms above 307 K. The further increase in oxygen potential results in the formation of the malonate facies and the malonate–formate paragenesis.

In deep-sea hydrothermal volcanic systems, pressure and temperature can attain several hundred bar and 900 °C, respectively, (Holm and Anderson, 1998; Shock, 1992). A similar diagram at 500 bar pressure (Fig. 5) allows one to expand noticeably a temperature range for the development of hydrothermal hydrocarbon-organic system, which provides a higher number of nonvariant equilibria and the facies formed. The increase in pressure in the system results in the shift of nonvariant equilibrium (614 K), which define the occurrence of acetate and succinate facies, to higher temperature (644 K). At higher temperatures and potentials of oxygen (fixed the oxygen isoplets) a new four-phase nonvariant equilibria appear at 663 K (2CH<sub>4</sub>+  $4HCOOH = 3CH_3COOH + 2H_2O$ ), at 755 K (CH<sub>3</sub>COOH + CH<sub>2</sub>(COOH)<sub>2</sub>) = HCOOH+(CH<sub>2</sub>)<sub>2</sub>(COOH)<sub>2</sub>) and at 821 K (C<sub>2</sub>H<sub>4</sub>+2HCOOH=2CH<sub>3</sub>-COOH), which define the occurrence of formate facies. Similarly to the analysis in Fig. 4, we shall consider the magnetite facies located between equilibria of quartz-magnetite-favalite and hematite-magnetite mineral buffers (Fig. 5). Eight facies of organic acids are located in this range (numerated with Roman figures). The facies with paragenesis of CH<sub>4</sub>-CH<sub>3</sub>COOH-(CH<sub>2</sub>)<sub>2</sub>  $(COOH)_2$  (the shaded area-facies III) at P = 500 bar extends up to temperature  $\sim$ 700 K and is limited by three curves of three-phase monovariant equilibria of organic acids and by two curves of equilibria of mineral buffers. This area is considered by us to be the most ideal simulation of the hydrothermal system to provide the generation and self-organization of components of archaic CO<sub>2</sub> fixation pathways. Thus, certain facies of some key components of metabolic systems of CO<sub>2</sub> fixation and its parageneses with a number of hydrocarbons have been determined.

Transformation of organic acids is defined by both temperature and redox conditions, and acid–alkaline potential (pH) of a

S.A. Marakushev, O.V. Belonogova / Journal of Theoretical Biology 257 (2009) 588-597



**Fig. 5.** The parageneses facies of aqueous hydrocarbons and compounds of RCC and 3-HPC in the  $T - \mu_{0_2}$  diagram at 0.5 kbar pressure. Facies of organic acids in the field of magnetite stability are denoted with Roman numerals. The shaded area in facia III is a space of  $T - \mu_{0_2}$  stability of self-organizing cycles of CO<sub>2</sub> fixation. Isopletes of oxygen activity are presented. Other notations correspond to Fig. 4.



**Fig. 6.** The *T*-pH diagram at *P*<sub>sat</sub> for reactions of formate, acetate, malonate and succinate dissociation (on the constants according to Amend and Shock, 2001). Neutral pH values are denoted by dashed line. The point of  $(CH_2)_2(COOH)_2 = H^-(CH_2)_2(COO)^-+H^+$  equilibrium curve intersection with a curve of pH neutrality corresponds to 531 K, the temperature of nonionized succinate transition from acid to alkaline hydrothermal conditions.

hydrothermal system. It is seen from the diagram (Fig. 6) that  $pK_a$  of organic acids increases with temperature, but for all that, the curve of neutral pH values goes down with rising temperature. Thus, the paragenesis CH<sub>3</sub>COOH–(CH<sub>2</sub>)<sub>2</sub>(COOH)<sub>2</sub> of nonionized acids is stable in acid hydrothermal environment up to 531 K and is stabile in alkaline one above this temperature.

The fundamental mechanism of hydrothermal synthesis accepted now is the Fischer–Tropsch process, based on the reduction of oxidized compounds of carbon (CO, CO<sub>2</sub>) by molecular hydrogen (see review McCollom and Seewald, 2007). Some of paragensis presented in Figs. 4 and 5 were found in natural hydrothermal systems ( $C_2H_6-C_2H_4$  (Cruse and Seewald, 2006; Proskurowski et al., 2008)) and were received in a number of experimental works ( $C_2H_6$ –methane– $C_2H_4$ –acetate (McCollom and Seewald, 2001, 2006; Seewald, 2001) on simulating hydrothermal conditions. Hydrothermal synthesis suggested by us is based on using of reduction compounds (hydrocarbons) as a source of carbon. Physico-chemical conditions of this process shown in diagrams 4 and 5 can be used as a theoretical fundamental for future experiments.

## 4. Self-organization of archaic carbon metabolic systems components in autocatalytic cycles

When considering chemoautotrophic CO<sub>2</sub> fixation of RCC and 3-HPC systems, it should be noted that electron flows in these cycles are differently directed. RCC and 3-HPC have the same succinate-fumarate-malate chain link, which consists of cycle components, and the sequence of the reactions is oppositely directed:  $(CH_2)_2(COOH)_2 \leftrightarrow (CH)_2(COOH)_2 \leftrightarrow CH_2CH(OH)(COOH)_2$ . Hence, a superposition these cycles based on this general sequence of components allows one to enhance considerably stability of the system on the whole to changes in redox conditions of the environment. We tried to present the full general system of CO2 archaic fixation (CAF) as combined acetyl-CoA-path, 3-HPC and RCC (Fig. 7) that is proved by the detection of a relic constructional mosaic of all three autotrophic pathways in archeabacteria (Hügler et al., 2003b). Moreover, the carbon isotopes fractionation is realized by these three ways with almost similar values of  $\delta^{13}$ C between 0 and -12% (House et al., 2003)



**Fig. 7.** The scheme of chemoautotrophic CO<sub>2</sub> archaic fixation (CAF). 3-HPC is 3-hydroxypropionate cycle, RCC is reductive citric cycle, ACAP—acetyl-CoA pathway (empty arrows). CH<sub>3</sub>COOH—acetate, HOOC-CH<sub>2</sub>-COOH—malonate, OCH-CH<sub>2</sub>-COOH—malonate-semialdehyde, HOCH<sub>2</sub>-CH<sub>2</sub>-COOH—3-hydroxypropionate, CH<sub>2</sub>=CH-COOH—acrylate, CH<sub>3</sub>-CH<sub>2</sub>-COOH—propionate, HOOC-CH(CH<sub>3</sub>)-COOH—methylmalonate, HOOC-CH<sub>2</sub>-CH<sub>2</sub>-COOH—succinate, HOOC-CH=CH-COOH—fumarate, HOOC-CH(OH)-CH<sub>2</sub>-COOH—malonate, OCH-COOH—methylmalate, CH<sub>3</sub>-CO-COOH—pyruvate, HOOC-CH=CH-COOH—oxaloacetate, HOOC-CH<sub>2</sub>-C(OH)-CH<sub>2</sub>-COOH—glyoxylate, HOOC-CH(CH<sub>3</sub>)-CH(OH)-COOH—methylmalate, CH<sub>3</sub>-CO-COOH—pyruvate, HOOC-CO-CH<sub>2</sub>-COOH—oxaloacetate, HOOC-CH<sub>2</sub>-C(OH)(COOH)-CH<sub>2</sub>-COOH—citrate, HOOC-CH<sub>2</sub>-C(COOH)=CH-COOH—aconitate, HOOC-CH<sub>2</sub>-CH(COOH)-CH(OH)-COOH—isocitrate and HOOC-CH<sub>2</sub>-CH<sub>2</sub>-COOH—coxaloacetate.

(unlike photoautotrophic pathways of CO<sub>2</sub> fixation). This indicates essentially similar molecular mechanisms of the process.

In the presented biomimetically built system, the reduction potential is provided by reactions with molecular hydrogen. In contemporary metabolic systems hydrogen is transferred by hydride carriers, similarly to NADH, and at the first stages of origin of life hydrogen could by transferred either directly or by such hydride carriers as thiols and quinones. Independently of hydrogen transfer way, its energy and direction are defined by twoelectron reduction potential of CAF pair components (reactions 1–10, Fig. 7).  $CO_2$  fixation is realized in four reactions of a bicycle (RCC+3-HPC), namely transformation of acetate to malonate (enzyme, catalyzing this reaction is acetyl-CoA carboxylase), propionate to methylmalonate (propionyl-CoA carboxylase), succinate to 2-oxoglutarate (2-oxoglutarate: ferredoxin oxidoreductase), 2-oxoglutarate to isocitrate (isocitrate dehydrogenase) and in four reactions of combining acetyl-CoA-path and RCC: the transformation of CO<sub>2</sub> to CO (CO-dehydrogenase), CO<sub>2</sub>+CO to acetate (acetyl CoA-synthase), acetate to pyruvate (pyruvate carboxylase) and pyruvate to oxaloacetate (pyruvate: ferredoxin oxidoreductase). In hydrothermal systems the absence of enzymes in the CAF cycle is compensated by catalytic parageneses of minerals (Cody et al., 2001, 2004; Russell and Martin, 2004), which in some cases are biomimetically similar to iron-sulfur clusters of some enzymes of CO<sub>2</sub> fixation contemporary pathways (for example, succinate dehydrogenase, fumarate reductase, CO-dehydrogenase, etc.) and the replacement of coenzyme A by methylthiols and thiocarboxylates in reactions. In the magnetite facies (methane-acetate-succinate), at both  $P_{sat}$  and  $T = \sim 400$ -600 K (Fig. 4), and P = 500 bar and  $T = \sim 400-700$  K (Fig. 5) paragenesis of pyrite-pyrrhotite is stable. Therefore, the possibility of Fe<sub>3</sub>O<sub>4</sub>, FeS and FeS<sub>2</sub> participation in catalytic reactions

of CAF cycle is justified. Moreover, in the magnetite facies, both pure greigite ( $Fe_3S_4$ ) and its nickel form ( $Fe_5NiS_8$ ) (Russell and Martin, 2004; Russell, 2007) are stable, being the analogue of a CO–dehydrogenase catalytic cluster ( $Fe_4NiS_5$ ), which effectively binds and reductively activates CO<sub>2</sub> (Jeoung and Dobbek, 2007).

For self-organization and function of autocatalytic systems a certain degree of their stability is required, which is defined as "robustness", produced by competition of branched autocatalytic ways (Goldstein, 2006) in conditions of their component stability (Figs. 4 and 5). In steady-state system its tendency to a stable state is coordinated with formation of a lower-entropy product (Galimov, 2004). Stability to changes in kinetic parameters and concentration is traced in all existing biochemical networks of cellular metabolism (Morohashi et al., 2002) and should be present in any model of self-organization and chemical natural selection. A combinatory cycle of CAF contains a succinatefumarate core (Fig. 7) capable of switching an electron flow in a forward and reverse direction depending on redox potential of geochemical environment that is governed by the (CH)<sub>2</sub>(COOH)<sub>2</sub>+  $H_2 = (CH_2)_2(COOH)_2$  reaction. This core is a "redox switch", which corresponds to certain conditions of a hydrothermal environment and defines an electron flow direction. Fig. 8 shows the threephase nonvariant equilibrium of succinate-fumarate-malate in aqueous solution in standard conditions. Depending on the value of hydrogen chemical potential, the reactions in the CAF cycle will shift the electron flow to a direction of 3-HPC or RCC, and the competition between these cycles provides robustness of the CAF cycle to the changes in redox conditions in a hydrothermal system. "switches" of such type play an essential role in self-organization, selection and evolution of chemical systems (Abel and Trevors, 2006). It is essential that reaction systems

involving the succinate–fumarate conjugated pair were conserved during organism evolution since enzymes (reversible succinate– dehydrogeneses) catalyzing their interconversion are present in



**Fig. 8.** Phase ratio in the area of  $\mu_{\text{H}_2} - \mu_{0_2}$  chemical potentials for aqueous succinate–fumarate–malate system at P = 1 bar and T = 298 K. The point corresponds to three-phase nonvariant equilibrium, lines correspond to two-phase monovariant equilibria, which divide single-phase succinate, fumarate and malate facies.

all three domains of life (Shaefer et al., 1999). Moreover, the succinate–fumarate core is conservative in almost all variants of evolution of a direct oxidizing citrate cycle, which is an evolutionary heir to RCC (Meléndez-Hevia et al., 1996).

The most essential feature of the Wächtershäuser theory of primary metabolism is the dependence of RCC reactions on iron sulfides, which provide initial stages of cycle development with energy and links geochemistry with biochemistry, in general (Blöchl et al., 1992; Wächtershäuser, 1988b, 1992). The work (Kalapos, 2007) suggests a variant of the RCC autocatalytic cycle with a lower number of its components and quantitative estimation of reactions energy. Based on these works, generalized reactions of the CAF double cycle are presented in Fig. 9. In the top part of the cycle CO<sub>2</sub> is fixed to form acetate according to the overall reaction: I. 2CO<sub>2</sub>+4FeS+4H<sub>2</sub>S=4FeS<sub>2</sub>+2H<sub>2</sub>O+CH<sub>3</sub>COOH,  $\Delta G_{298}^0 = -183,33 \text{ kJ mol}^{-1}$ , whereas in the bottom part glyoxylate forms through the following reaction: II.  $2CO_2+2FeS+2H_2S=$ 2FeS<sub>2</sub>+H<sub>2</sub>O+OCHCOOH,  $\Delta G_{298}^0$  =+11,45 kJ mol<sup>-1</sup>. It is obvious that the oxaloacetate-citrate cycle (I) is energetically more favorable than the acetate-malate one, which should "switch on" as a result of lack of pyrrhotite and hydrogen sulfide substrates near the equilibrium condition defined by reaction II.

Stability of the CAF cycle components in paragenesis with hydrocarbons and the use of FeS/H<sub>2</sub>S system as a primordial source of redox energy provide wide possibilities of the formation of amphiphilic molecules from hydrocarbons and their selforganization, and a subsequent formation of protometabolic systems of CO<sub>2</sub> fixation inside membrane vesicles. It was shown (Dörr et al., 2007), that reactive metal sulfides incorporating into



Fig. 9. Combined oxaloacetate-citrate and malate-acetate cycles (CAF cycle) are based on pyrite-pyrrhotite paragenesis. The equilibrium of succinate fumarate "switcher" of electron flow is set off in boldface. Free energy values (kJ/mol) for pyrite-pyrrhotite dependent reactions in standard conditions are shown.

liposomes might result a source of different catalytic reactions important for the reaction networks of protocellular systems. Pyrite particles also catalyze membrane assembly and could presumably become encapsulated within vesicles, raising the possibility of mineral catalyzed metabolic transformations within vesicles (Hanczyc et al., 2007).

#### 5. Conclusion

Our model is based on the theory of volcanic hydrothermal origin of self-organized autocatalytic cycles of chemoautotrophic metabolism (Wächtershäuser, 1990, 2006). In this theory, oxidized compounds of carbon (mainly CO<sub>2</sub>) carried out by deep-sea fluids of abyssal mantle plumes, serve as a source of carbon for metabolic systems. Moreover, it is supposed that reactions of prebiotic fixation of CO<sub>2</sub> are initiated by CO, which is a source of carbon for metabolic systems as well (Ferry and House, 2006; Russell, 2007; Huber and Wächtershäuser, 1997). An alternative deep-sea source of carbon (hydrocarbons) proved by works on endogenous origin of hydrocarbons and oil pools formed by them (Kenney et al., 2002; Marakushev and Marakushev, 2006, 2007; Sugisaki and Mimura, 1994) is a constant source of substance (and probably energy-hydrocarbon potential) for irreversible reactions of steady-state archaic metabolic systems. The works (Holm et al., 2006; Marakushev and Marakushev, 2008; Russell, 2007) report on a relationship between alkaline ultramafic magmatism and alkaline fluids in the processes of prebiological organic synthesis, occurrence and evolution of a life. There are data on that compositions of hydrothermal fluids are primarily determined by their interactions with mantle-derived rocks, whose oxidation state has not changed significantly in the last four billion years (Delano, 2001). Redox transformation of hydrocarbons to components of archaic metabolic systems was realized namely in alkaline fluids rich in hydrogen and light hydrocarbons, as, for example, in ultramafic rocks of the mid-Atlantic Ridge Lost City hydrothermal fields (Proskurowski et al., 2008).

The suggested CAF cycle based on evolutionary conservatism principle is a biomimetic chemical system able to function in nonequilibrium conditions near a steady-state limit (guasi-steadystate system (Lindahl, 2004)) at steady-state inflow of its components from a hydrothermal pool. The redox geochemical mode stipulated by temperature, composition of a hydrothermal fluid and a mineral environment defines stability of the CAF cycle components in paragenesis with hydrocarbons (Figs. 4 and 5), capability of self-organization of a cycle and its further development. Organic acids formed from hydrocarbons form an autocatalytic network of CO<sub>2</sub> fixation, which is able to reproduce itself. The hydrocarbon-aqueous environment provides an opportunity of compartmentation by the formation of lipid micelles and liposomal membranes (Furuuchi et al., 2005; Macia and Solé, 2007; Segre et al., 2001; Tomas and Rana, 2007), while the conjugation of autocatalytic cycles inside membrane vesicles and their self-development and propagation can result in the development of life-like systems (stable to external fluctuations) with supramolecular functional properties (Ganti, 1997, 2002; Fernando and Rowe, 2007; Goldstein, 2006; Kauffman et al., 2008; Smith and Morowitz, 2004).

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