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The Origin of Bioenergetics on Earth: The Emergence of Phosphoric Metabolism in Ancient Hydrothermal Systems

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The origin of phosphorus metabolism is one of the central problems in the context of the emergence of life on Earth. In our article, it has been shown that the C–H–O primitive metabolic system can be transformed into a four-component C–H–O–P system with the formation of a gluconeogenesis path in a possible Achaean hydrothermal condition under the influence of a phosphorus chemical potential. This system became the energy supply basis for protometabolism, and facilitated the formation of a new CO_2 fixation cycle (the reductive pentose phosphate pathway).

The modular design of central metabolism in the C–H–O–P system is derived from the parageneses (associations) of certain substances, and the emerging modules in turn associate with each other in certain physical and chemical hydrothermal conditions. The assembly of malate, oxaloacetate, pyruvate, and phosphoenolpyruvate is a reversible 'turnstile-like' mechanism with a switching of reaction direction that determines the trend of specific metabolic systems development. Thus, there is a natural selection of emerging metabolic systems.

Keywords: origin of metabolism energetic, Achaean eon, ancient hydrothermal systems, autocatalytic cycles, gluconeogenesis, CO_2 fixation, chemical potentials.

Introduction

One of the most important concepts in the theories of the chemolithoautotrophic origin of life in the Archean volcanic hydrothermal environment is autocatalytic CO_2 fixation *[Wächtershäuser 1988, 1990; Morowitz et al. 2000; Smith, Morowitz 2004; Lindahl 2004; Marakushev, Belonogova 2009; Zachar, Szathmary 2010; Pereto 2012; Braakman, Smith 2012]*. It has also been suggested that the last universal common ancestor (LUCA) of all extant cell lineages was a chemolithoautotrophic thermophilic anaerobe *[Wächtershäuser 1988; Srinivasan, Morowitz 2009; Hugler, Sievert 2011; Fuchs 2011; Stüeken et al. 2013]* capable of synthesizing organic 'building blocks' from the inorganic carbon. Thus, these microorganisms can serve as a model for studying primordial metabolism. However, CO_2 fixation requires energy, which was provided by energy from high-energy intermediates, organic phosphates in particular, that are presently involved in the primary biochemical pathways.

In previous works we have considered the thermodynamic factors of natural selection in the coupled autocatalytic cycles of CO_2 fixation (redundant modular constructions) in the three-component C-H-O system *[Marakushev, Belonogova 2009, 2010]*. It is rationalized that these systems are the primordial metabolic autocatalytic reductive citrate (RC) cycle (reductive tricarboxylic acid, Arnon-Buchanan cycles) and 3-hydroxipropionate (3-HP) cycle. An important factor in the stability and subsequent evolution of these coupled cycles is the reversibility of some key chemical reactions such as succinate ↔ fumarate, malate ↔ fumarate and others *[Marakushev, Belonogova 2013]*. The further development of this system with negative feedback involves increasing the number of independent components by maintaining additional supply of phosphorus, nitrogen, and sulfur. Adding phosphorus (forming a four-component C–H–O–P system) leads to the development of the gluconeogenesis system, which produces phosphorylated sugars, a basic source of energy for different biosynthetic pathways. The nodal intermediates and proposed autocatalysts in this process are malate, pyruvate, and oxaloacetate, the transformation of which into phosphoenolpyruvate permits the formation of phosphorylated sugars–trioses, pentoses, and hexoses.

The fundamental role of phosphorylated carbohydrates and the universality of the few modern metabolic interconversions suggest their origin at the earliest evolutionary stage. The possibility of gluconeogenesis first originating as a precursor to phosphorus metabolism in hyperthermophilic microorganisms was considered in *[Ronimus, Morgan 2003]*. Gluconeogenesis starting with phosphoenolpyruvate uses the unusual ancient enzyme fructose 1,6-bisphosphate aldolase/phosphatase, which converts triose phosphates to fructose 1,6-bisphosphate *[Say, Fuchs 2010; Fuchs 2011]*. The ancient origin of gluconeogenesis with the consequent origin of the ancestral Aquificae, Chloroflexi, and Thermotogae taxa is postulated. Reactions converting triose phosphate into fructose 1,6-bisphosphate are generally reversible, but the reaction of fructose 1,6-bisphosphate into stable fructose 6-phosphate is irreversible and substantially determines the unidirectionality of gluconeogenesis, which precedes the emergence of glycolysis evolutionarily *[Ronimus, Morgan 2003]*.

The early origin of gluconeogenesis is indirectly supported by data from the non-enzymatic metal-catalyzed formation of phosphorylated three-carbon sugars and pyruvate *[Pitsch et al. 1995; Cody 2000]*, and the widespread role of non-enzymatic catalysis in phosphate metabolism is considered in *[Keller et al. 2015]*. It should be noted that both non-enzymatic and enzymatic reactions are based on the same fundamental thermodynamic laws. Experimental analysis of the conditions required for phosphorylated intermediate formation and stability in the pentose phosphate pathway is given in *[Keller et al. 2014]*. The reactions underlying the interconversion of phosphorylated carbohydrates were examined under the conditions found in a putative Archean ocean, which were determined based on the chemical composition of sedimentary rocks in this time period. It was shown that the simple inorganic ions (Fe (II), Co (II), Ni (II), Mo (IV)) found in rocks from the Archean period could catalyze the reactions observed in the extant metabolic pathways. It was also concluded that iron (at concentrations of 20 μM to 5 mM) was the most effective catalyst of metabolic reactions requiring substrate phosphorylation in early anoxygenic Archean ocean. It is assumed that the ancient ocean was enriched not only by ferro-ions but also phosphates *[Keller et al. 2014; Van Cappellen, Ingall 1996; Pasek et al. 2013]* that emanated from high-temperature alkaline hydrothermal fluids to the surface of the Earth *[Shibuya et al. 2010]*. Nevertheless, it requires some thermodynamic analysis of the possibility of phosphorylated carbohydrates formation.

A simplified biomimetic image of primordial anaerobic central carbon metabolism in the form of branching metabolic reactions with the formation of gluconeogenesis and the reductive pentose phosphate (RPP) CO_2 fixation cycle (Calvin-Benson cycle) is presented in **Fig. 1**, which shows the development of coupled autocatalytic systems (archaic RC and 3-HP cycles *[Marakushev, Belonogova 2011]*) in the direction of phosphorus metabolites — triose phosphates and phosphorylated sugars. It is assumed that these metabolic changes took place during of the origin of life energetics aspect.

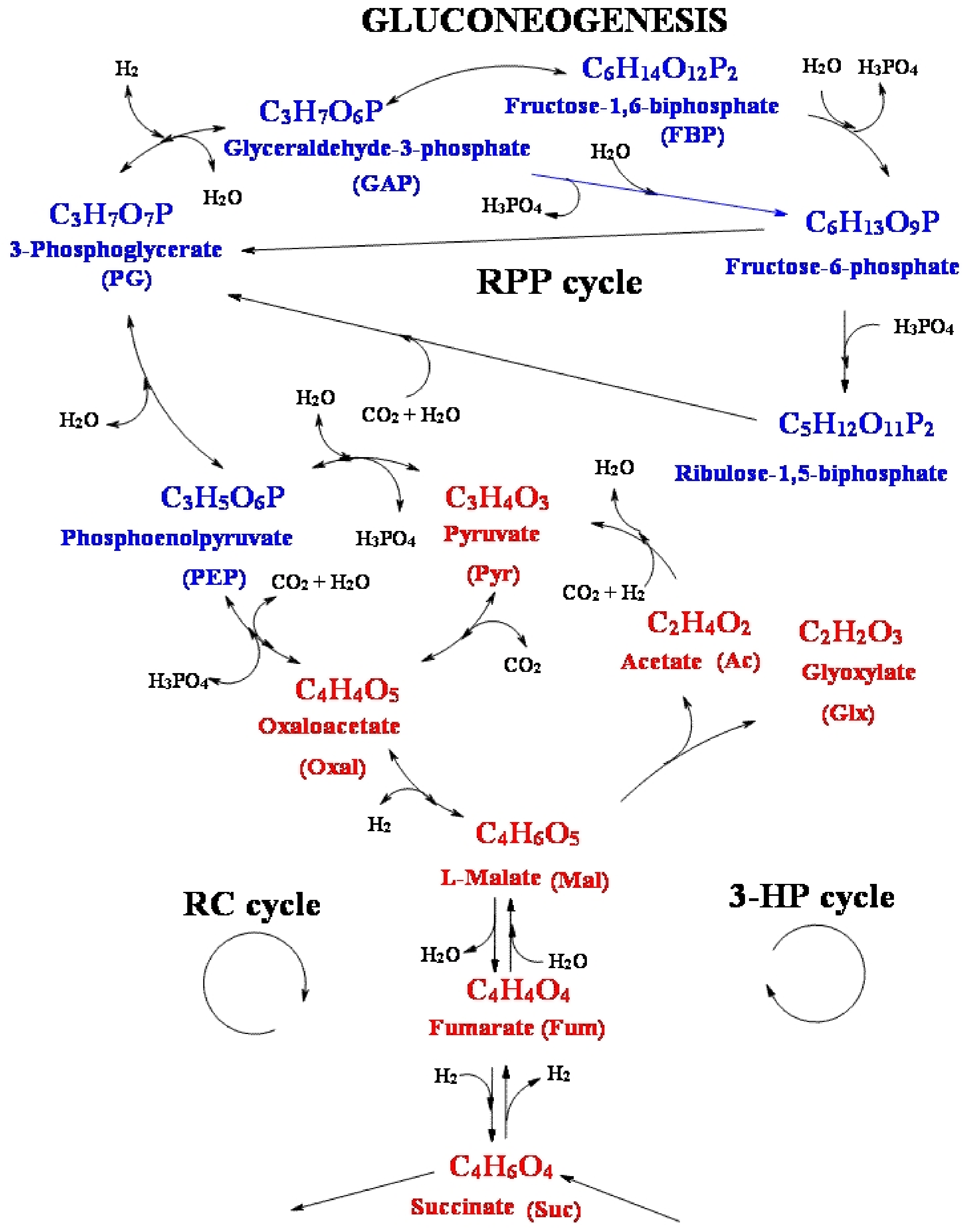

Figure 1. Inferred coupling of the autocatalytic loops of the archaic reductive citrate (RC) and 3-hydroxipropionate (3-HP) cycles (**red formulas**) with the further development of phosphorus metabolism (**blue formulas**) in the archaic systems of gluconeogenesis and the reductive pentose phosphate (RPP) pathway of CO_2 fixation. The arrows show the direction of reactions. The circular arrows show the direction of reactions in the coupled RC and 3-HP cycles. In the RPP cycle, three molecules of fructose-6-phosphate regenerate three molecules of ribulose-1,5-bisphosphate and one molecule of 3-phosphoglycerate.

Methodical Approach

The physicochemical analysis of parageneses (associations, assemblages) is widely used in geochemical researches of mineral systems *[Korzhinsky 1959]*. This approach is based on a generalization of the thermodynamic and physical properties of minerals in order to detect the conditions responsible for the formation of the parageneses observed in rocks and ores. In this case, the thermodynamic potential method *[Gibbs 1878; Korzhinsky 1959]*, which allows one to develop a system of geochemical mineral facies (thermodynamic stability areas) is used. Our preliminary calculations indicated that paragenetic analysis can be extended to organic substances, which form the systems listed below (the systems are listed in increasing complexity of chemical composition and structure): C–H–O, C–H–O–N, C–H–O–N–P, and C–H–O–N–P–S *[Marakushev, Marakushev 2006; Marakushev, Belonogova 2009; Marakushev, Belonogova 2010]*.

The studies of organic substances assemblages (parageneses) and areas of their thermodynamic stability (facies) is based on the Gibbs phase rule, according to which the number of degrees of freedom for a thermodynamic system in equilibrium is equal to the number of system independent components plus two minus the number of phases. In this case, the number of independent components is the smallest number of chemical components; the compositions of all possible phases of the system can be obtained by their combination. The phase rule is not limited to consideration of the extensive parameters of the system and, hence, is completely applicable to open systems with chemical potential as an independent parameter *[Korzhinsky 1966; Marakushev, Belonogova 2013]*. Determining the total number of system independent parameters (intensive and extensive), and using this number together with the Gibbs phase rule provides a way to study the thermodynamic properties of organic systems.

The system state was calculated using free partial energy values for organic substance formation ($\Delta G^{o}_{f,T}$), depending on external conditions. The state diagrams, which reflect the facies of organic compounds and their parageneses, are graphically presented. When considering these organic compounds in fluid and aqueous hydrothermal systems, the points of major importance are shown with diagrams: a) chemical composition-paragenesis (at constant pressure (P), temperature (T), and chemical potential (μ_i)), b) chemical potential-temperature (at constant P), c) the relationship between chemical potentials of the components: μ_{H2O}-μ_{CO2}, μ_{H2}-μ_{O2}, etc. (at constant P and T).

The major equilibrium factors in the physicochemical analysis of parageneses are the chemical potential (μ_i) of each component (representing its partial energy). The value μ_i is expressed through activity, $a_{i,}$ and fugacity, $f_{i,}$ as follows:

$$\mu_i = (\mu^0{}_i)_{\mathrm{T,p}} + RT\ln a_i = (\mu^0{}_i)_{\mathrm{T,p}} + RT\ln f_i \,.$$

The aqueous constants used were derived using the electrostatic model method, according to which the solvate constituent of a substance plays an essential role in the chemical potential at different temperatures, reflecting the contribution from electrostatic interactions between the substance and solvent (H_2O) *[Shock 1992; Helgeson et al. 1993; Oelkers et al. 1995 Amend, Shock 2001]*. Thermodynamic calculations of the Gibbs standard free energy and analysis of the geochemical constraints showed that the abiotic synthesis of organic compounds in hydrothermal systems is limited by the metastable equilibrium that results from kinetic barriers, which prevent the achievement of stable equilibrium *[Helgeson et al. 1993; Shock 1990; Shock et al. 1995; Shock, Schulte 1998]*. Most of the organic substances in condensed and dissolved phases are in a metastable state, i.e., these substances do not reach the minimum Gibbs free energy for the given composition of elements, and thus are 'kinetic' or 'metastable' phases *[Desiraju (2002; Brazhkin 2006]*.

Previously, we calculated a diagram of composition-paragenesis for the ternary C–H–O system (e.g., *[Marakushev, Belonogova 2009]*). The addition of phosphorus to the C–H–O system forms the quaternary system C–H–O–P, in which the independent components — carbon, hydrogen, oxygen, and phosphorus — are extensive parameters (f_{ex}). **Figure 2** presents the phase diagram of compositions for the compounds shown in **Fig. 1**. In this ternary C–H–O diagram, the phases of the phosphorylated compounds are represented by the subtracting of orthophosphoric acid (H_3PO_4). If, in thermodynamic calculations, the chemical potential is determined for H_3PO_4 (μ_{H3PO4}), and phosphorus becomes an intensive parameter (f_{in}), then the quaternary system becomes ternary (C–H–O). If the chemical potential is calculated for hydrogen or methane (μ_{CH4}, μ_{H2}), and hydrogen becomes intense parameter (f_{in}), then the ternary system becomes a binary system, C–O (**Fig. 2 a, b**).

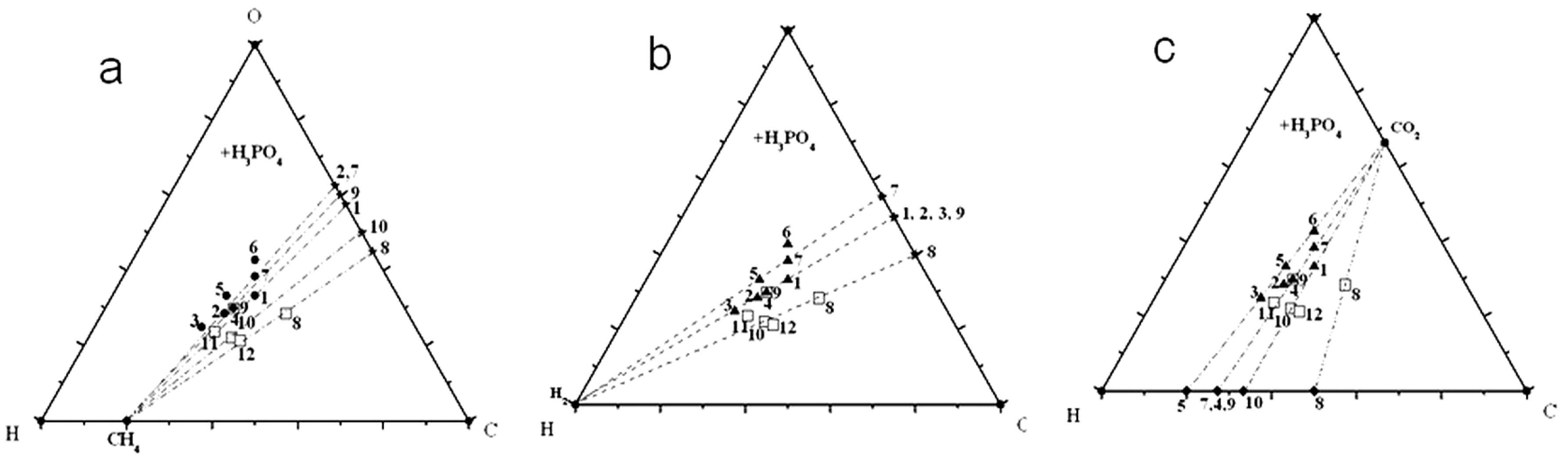

Figure 2. C–H–O phase diagram representing the compositions of the compounds shown in the modular scheme (**Fig. 1**). The two-component C–O system is generated when the chemical potentials of CH_4 and H_2 (**a** and **b**) are used. The two-component C–H system (**c**) is generated when the chemical potential of CO_2 is used. Phosphorylated compounds are represented by the subtracting of orthophosphoric acid (H_3PO_4) composition. Substances in the C–H–O system are indicated with filled triangles and substances in the C–H–O–P system are indicated with empty boxes. Designations of the substances: **1** — fumarate (Fum), **2** — succinate (Suc), **3** — acetate (Acet), **4** — pyruvate (Pyr), **5** — malate (Mal), **6** — glyoxylate (Glx), **7** — oxaloacetate (Oxal), **8** — phosphoenolpyruvate (PEP), **9** — 3-phosphoglycerate (PG), **10** — glyceraldehyde -3-phosphate (GAP), **11** — fructose 6-phosphate, **12** — ribulose 1,5 bisphosphate, **13** — fructose 1,6-bisphosphate (FBP).

The dashed conodes connect CH_4 and H_2 with substances phases, which are represented by stars on the triangle side. The composition diagram (**Fig. 2c**) shows that, if the chemical potential is calculated for CO_2 (μ_{CO2}), and CO_2 becomes an intensive parameter (f_{in}), then the ternary system becomes a binary system, C–H (dashed conodes connect the CO_2 point, and substance phases represented by rhombs on the triangle base). The free energies of aqueous ionized phosphorus substance formation were taken from *[Mavrovouniotis 1991]* and were designed for non-ionized forms using the method described in *[Mavrovouniotis 1991; Alberty 2001]*. The constants for substances in the C–H–O system were taken from *[Marakushev, Belonogova 2013]*.

Certainly, the hydrothermal systems are generally characterized by a more high-pressure and high-temperature conditions. However, these conditions cannot fundamentally change the character the diagrams of chemical potentials — as a rule, the equilibrium shifts in a direction of its higher values.

It is assumed that the anoxygenic Archean ocean saturated with siliceous compounds and Fe (II) contained a higher level of dissolved orthophosphate than the modern ocean *[Van Cappellen, Ingall 1996; Konhauser 2007; Li et al. 2013]*. These conditions have primarily been determined with the use of the orthophosphate chemical potential in thermodynamic calculations of the origin and the evolution of protometabolic pathways related to the four component C–H–O–P system.

The Chemical Potentials of Methane, Molecular Hydrogen, and Carbon Dioxide

The most important energy factors in the generation of organic compounds, which are intermediates of protometabolic pathways in hydrothermal systems, are the chemical potentials of molecular hydrogen and hydrocarbons. The predominant widespread hydrocarbon is an abyssal methane, the concentration of which (e.g., in volcanic oceanic emissions) is usually more than two orders of magnitude higher than the concentration of other hydrocarbons *[Shock et al. 2013]*. At the present time, the abiotic synthesis of organic compounds in the hydrothermal systems of mid-ocean ridges has been confirmed in a number of publications (e.g. *[Fu et al. 2015; McDermott et al. 2015]*). Alkanes and carboxylic acids represent some of the most abundant organic substances found in natural marine and terrestrial hydrothermal systems.

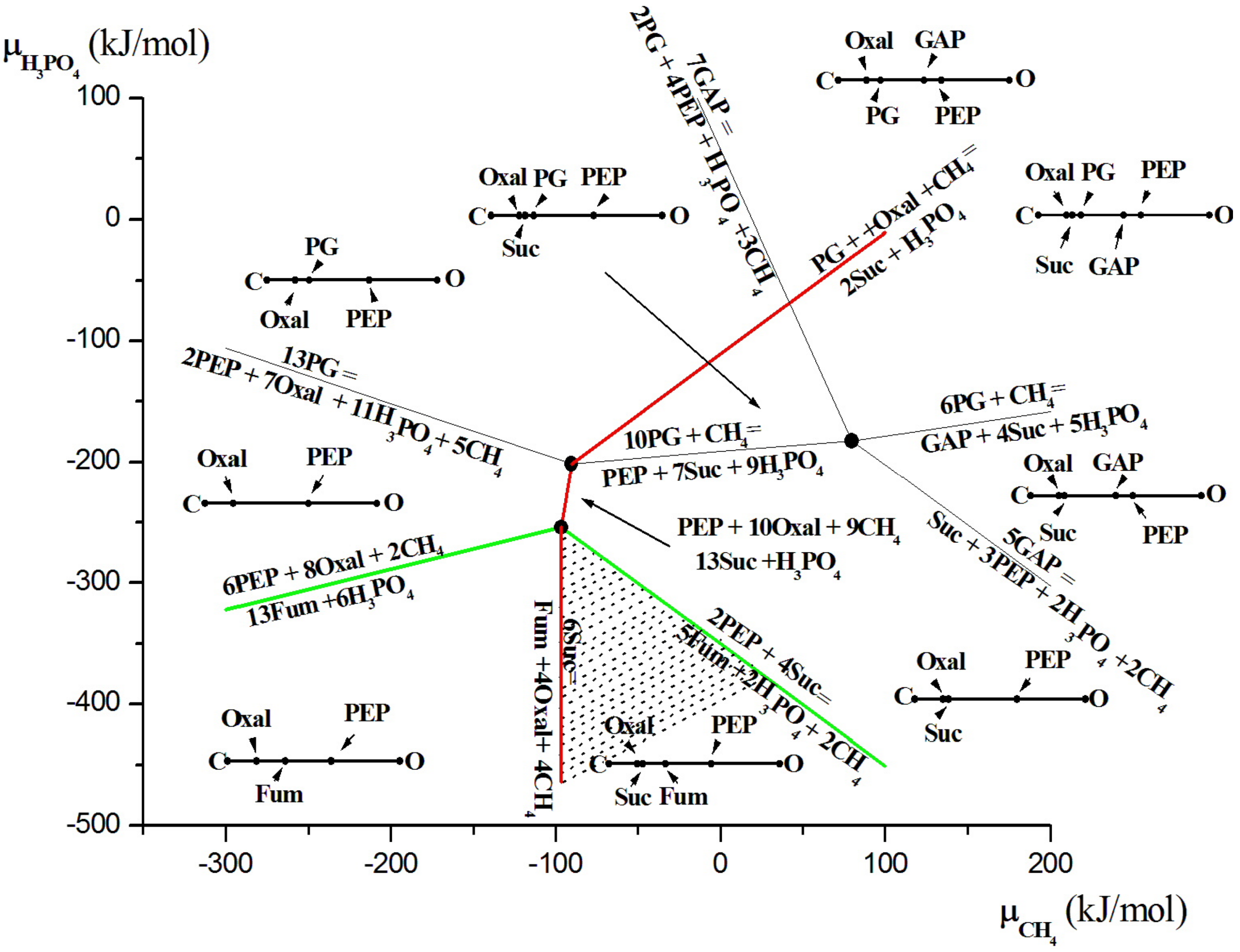

Figure 3. Diagram of the chemical potentials of CH_4 and H_3PO_4 (μ_{CH4} = RTlnαCH_4, μ_{H3PO4} = RTlnαH_3PO_4, where α represents the activities of the corresponding respective substances in aqueous solution at standard conditions). The free energy of aqueous substance formation values (ΔG^0_{298}) are given in the table (values are at standard conditions). The shaded field indicates the partially overlapping facies of fumarate (delineated by **green lines**) and succinate (delineated by **red lines**). The parageneses of substances for each facies are shown in the linear diagram of the C–O system. 3-HP and RC are the archaic 3-hydroxipropionate and reductive citrate cycles. The substance designations correspond to the designations in **Fig. 2**.

The diagram in figure 3 is based on aqueous constants at standard conditions and shows the formation and development of coupled C–H–O–P metabolic systems, **Fig. 1**, under the influence of the chemical potentials of methane (μ_{CH4}) and phosphoric acid (μ_{H3PO4}).

According to the Gibbs phase rule, the diagram represents the four-phase nonvariant equilibria in this two-component C–O system (see **Fig. 2a**), whereas the monovariant equilibriums are three-phase, separating divariant fields of phase stability and their parageneses and are identified by linear diagrams in the system facies. Increasing the H_3PO_4 chemical potential results in the stable paragenesis phosphoenolpyruvate-oxaloacetate at a relatively low chemical potential of methane (< -100 kJ/mol).

Further development of the system leads to the facies formation of 3-phosphoglycerate and glyceraldehyde phosphate, permitting the development of the ancient pathway of substrate phosphorylation-gluconeogenesis and the reductive pentose phosphate (RPP) cycle of CO_2 fixation. Attention should be drawn to the overlapping facies (shaded field) of succinate (RC-cycle) and fumarate (3-HP cycle) with oxaloacetate-succinate-fumarate-phosphoenolpyruvate paragenesis. This field is an area of thermodynamic stability of coupled RC + 3-HP bicycle *[Marakushev, Belonogova 2009]* and the new metabolic pathways apparently originated at the beginning of these redundant autocatalytic metabolic systems.

Fig. 4 shows a diagram of the chemical potentials of hydrogen and H_3PO_4. In general, this diagram is similar to **Fig. 3** (also see **Fig. 2a** and **2b**), and the monovariant equilibriums are three-phase or degenerate two-phase. As we have shown previously *[Marakushev, Belonogova 2010; Marakushev, Belonogova 2011]*, the association of succinate with fumarate acts as a redox switch, turning electron flow in the direction of archaic chemoautotrophic 3-HP and RC cycles in the wide temperature range.

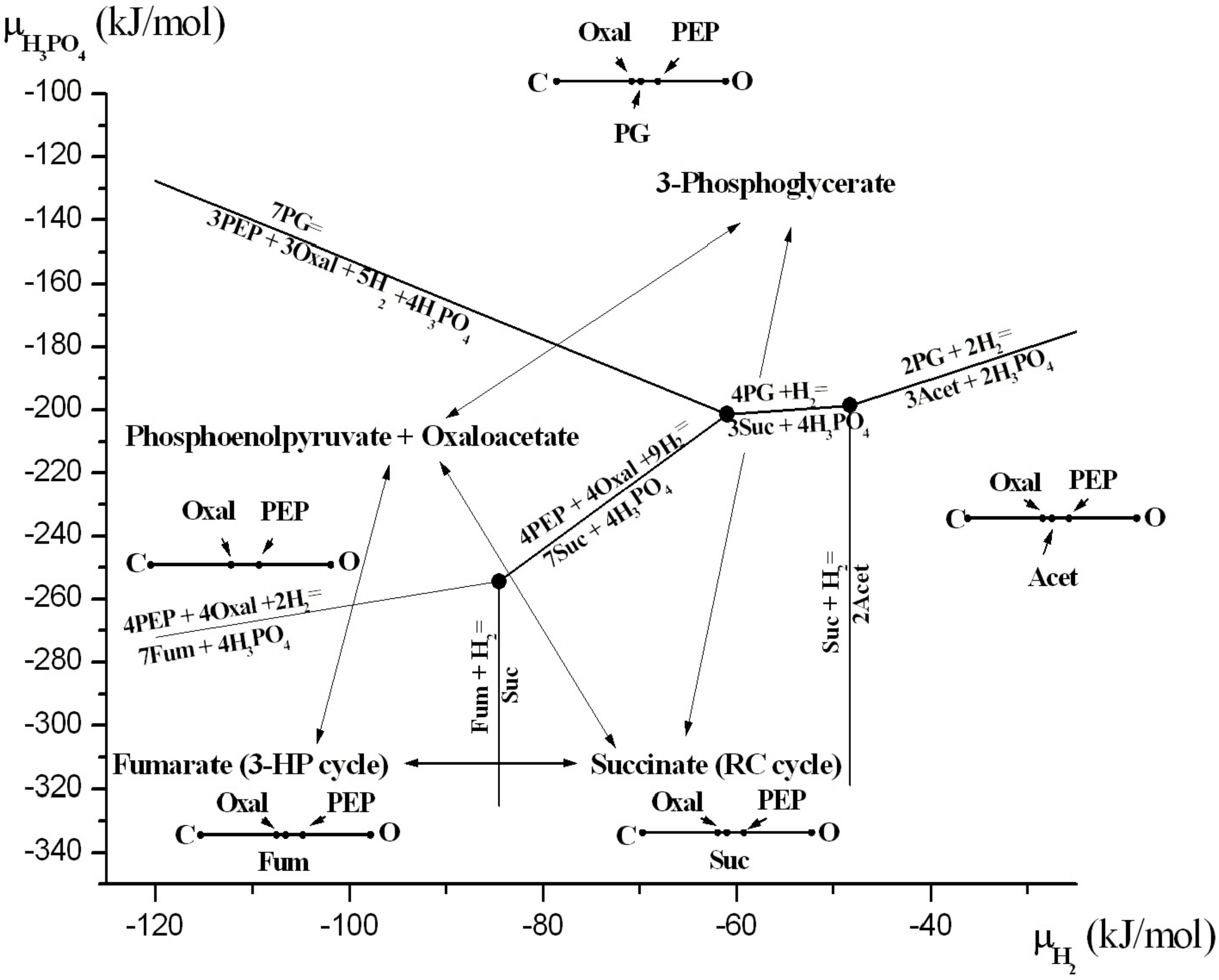

Figure 4. Diagram of the chemical potentials of H_2 and H_3PO_4 (μ_{H2} = RTlnαH_2, where α represents the activity of molecular hydrogen in solution) at P = 1 bar and T = 298 K. The substance designations correspond to the designations in **Fig. 2**. The arrows show the reversible reactions

The chemical potential of H_2 divides the lower region of the diagram (**Fig. 4**) on the facies of the dicarboxylic acids (succinate ↔ fumarate) and thus fixes the phase areas of stability of the archaic autotrophic 3-HP and RC cycles of CO_2 assimilation. With an increase in the chemical potential of H_3PO_4, facies of fumarate (3-HP cycle initiation) transform into facies of phosphoenolpyruvate-oxaloacetate, and a further increase in the chemical potentials of H_2 and H_3PO_4 leads to the decomposition of the metastable paragenesis with the formation of facies of 3-phosphoglycerate, which is a central metabolite (and autocatalyst *[Kun et al., 2008]*) in both gluconeogenesis and the RPP autocatalytic CO_2 fixation cycle (see **Fig. 1**). Similarly, increasing the H_3PO_4 chemical potential in facies of succinate (RC cycle initiation) also leads to the formation of facies with phosphoenolpyruvate-oxaloacetate paragenesis and further to facies of 3-phosphoglycerate.

According to *[Fuchs 2011]*, phosphoenolpyruvate and oxaloacetate are nodal molecules of all anabolic networks (in addition to acetate, pyruvate, and 2-oxoglutarate). From the diagrams in **Fig. 3** and **4**, it is clear that facies with phosphoenolpyruvate-oxaloacetate paragenesis are an area of bifurcation (network node) that determines the development of the primordial 3-HP (fumarate) and RC cycles (succinate), system of gluconeogenesis (3-phosphoglycerate ↔ fructose 1,6-bisphosphate →fructose 6-phosphate) and the RPP cycle (3-phosphoglycerate → ribulose-1,5-bisphosphate → 3-phosphoglycerate). It is obvious that 3-phosphoglycerate must be added to the five nodal molecules of autotrophic anabolic networks mentioned above. Thus, the diagram in **Fig. 3** and **4** represents a thermodynamic basis of 'encrustation' of the C-H-O system by a chemical 'shell' of phosphorus under the influence of a chemical potential of methane and/or hydrogen and phosphorus. However, the autotrophic nature of the parageneses formation of carboxylic acids and triose phosphates is manifested the best with consideration of the chemical potential of carbon dioxide.

On the diagram of CO_2 and H_3PO_4 chemical potentials (**Fig. 5**), a phosphoenolpyruvate-malate paragenesis is located in a sufficiently limited range of the considered chemical potentials (center diagrams) and develops in the direction of the discussed metabolic systems (**Fig. 1**) at varying chemical potentials. Thus, increasing the chemical potential of phosphorus leads to the emergence of phases of 3-phosphoglycerate and glyceraldehyde phosphate (emerging at a low chemical potential of CO_2), and these compounds (phosphorylated acid and aldehyde) are the initiators of gluconeogenesis and the RPP cycle. It should be noted that glyceraldehyde phosphate is also one of the main centers of the ancient evolutionary development of the non-oxidative branch of the pentose phosphate pathway, which leads to the formation of a series of phosphorylated sugars *[Stincone et al. 2015]*.

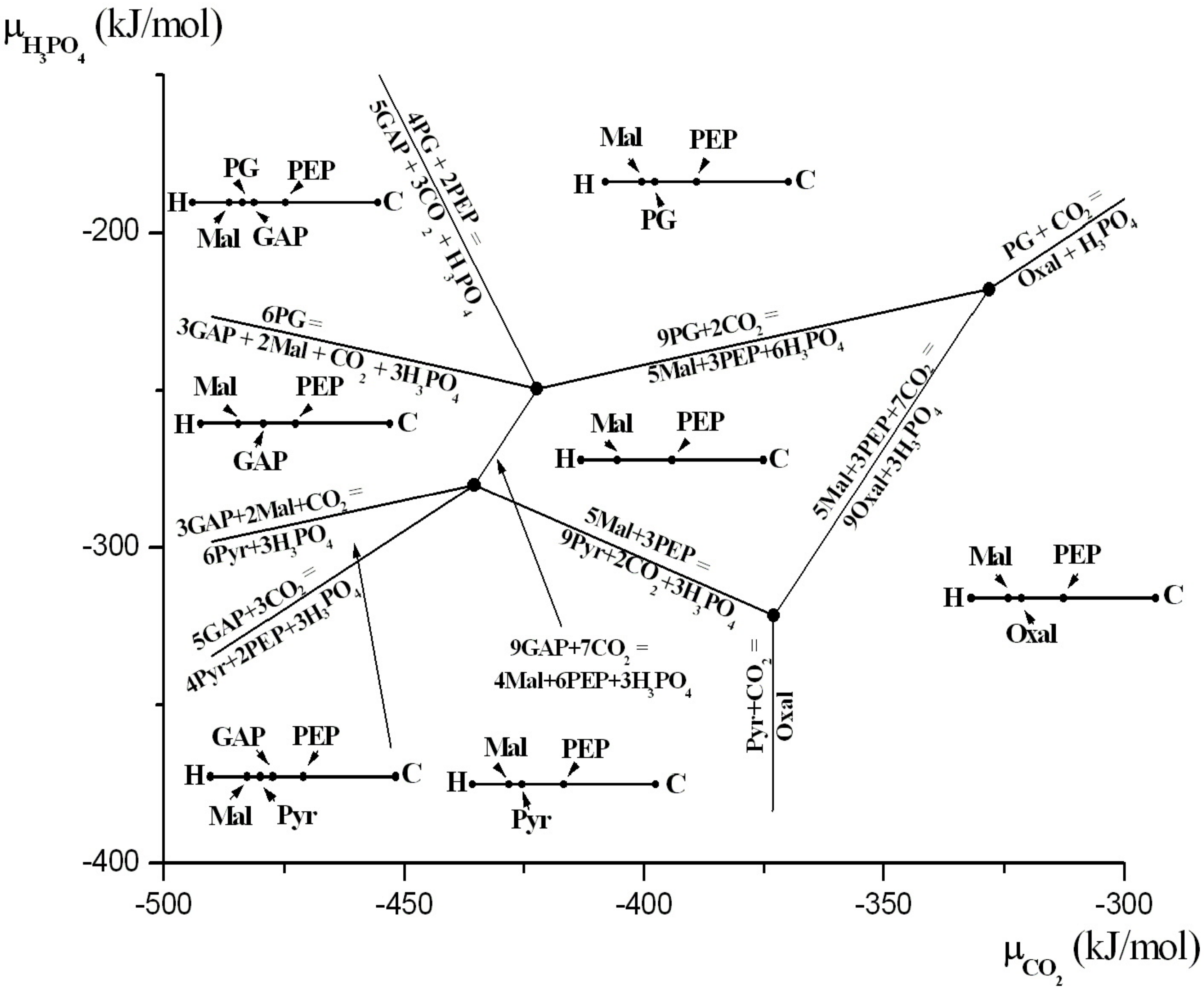

Figure 5. Diagram of the chemical potentials of CO_2 and H_3PO_4 (μ_{CO2} = RTlnαCO_2, where α represents the activity of CO_2 in aqueous solution at standard conditions). The parageneses of substances for each facies are shown in the linear diagram of the C–H system. Abbreviations as above.

Decreasing the chemical potential of phosphorus leads to the disappearance of the phosphoenolpyruvate-malate paragenesis and the appearance of phosphoenolpyruvate-pyruvate (with decreasing μ_{CO2}) and phosphoenolpyruvate-oxaloacetate (with increasing μ_{CO2}) parageneses. In general, increasing the CO_2 chemical potential leads to the carboxylation of compounds and their association with the formation of nodal facies — the center of phosphorus metabolism (malate-oxaloacetate-phosphoenolpyruvate). In this facies, as depicted in the diagram (**Fig. 3**, **4**), the autocatalytic oxaloacetate-phosphoenolpyruvate paragenesis is also a 'paragenesis bifurcation', meaning that this paragenesis determines the direction of natural selection of the primitive gluconeogenesis and CO_2 fixation metabolic pathways. According to **Fig. 1**, phosphoenolpyruvate, oxaloacetate, and pyruvate assemblage are 'turnstile-like' chemical mechanisms, allowing the direction of development of metabolic systems to change.

Conclusion

The energy processes within the living cells are chiefly determined by an element such as phosphorus, and phosphates play a crucial role in the activation of organic molecules through phosphorylation. Therefore, it is reasonable to assume that some types of phosphorylated compounds also played a major role in the formation of the first protometabolic systems on the early Earth. Early evolution likely ensured the storage and consumption of energy in the substrate phosphorylation process (e. g. *[Ferry, House 2006]*), which was the main driving force behind the development of both other metabolic systems and replication, and allowed the further development of energy pathways in aerobic and anaerobic organisms in all three domains of life.

Unlike other designs, the modular systems of metabolism are much more capable of evolutionary development *[Braakman, Smith 2013; Clune et al., 2013]*. The modules of the core metabolic pathways are derived from the parageneses of certain substances (micromodules-associations of chemical compounds, which ultimately function together), and the resulting modules are in turn in paragenesis with each other in certain physical and chemical conditions. Malate, oxaloacetate, pyruvate, and phosphoenolpyruvate (**Fig. 1**) form the reversible 'turnstile-like' mechanism capable of switching reaction directions. A change in the external conditions shifts the coupled modular autocatalytic system toward developing in the direction that is most favorable to the formation of specific metabolic systems. The chemical C–H–O system acquired new 'layers' from phosphorus, nitrogen, and sulfur. The present work investigated only the phosphorus 'layer', which led to the development of new protometabolic energy systems. Thus, in early chemical protometabolic reactions of the CO_2 fixation energetics, which primordially was provided by the partial energy of environmental chemical potentials (mainly due to the endogenous flow of hydrogen and hydrocarbons), was then replaced with energy from high-energy organic phosphates.

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ПРОИСХОЖДЕНИЕ БИОЭНЕРГЕТИКИ НА ЗЕМЛЕ:
ЗАРОЖДЕНИЕ ФОСФОРНОГО МЕТАБОЛИЗМА В ДРЕВНИХ ГИДРОТЕРМАЛЬНЫХ СИСТЕМАХ

Работа выполнена при финансовой поддержке Президиума РАН (программа фундаментальных исследований «Эволюция органического мира и планетарных процессов»).

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Зарождение фосфорного метаболизма является одной из центральных проблем возникновения жизни на Земле. Показано, что в гидротермальных условиях Архея под воздействием химического потенциала фосфора примитивная метаболическая система C-H-O преобразовывалась в четырехкомпонентную систему C-H-O-P с формированием системы глюконеогенеза, ставшей основой снабжения протометаболизма энергией, и образования нового цикла фиксации CO_2 (восстановительного пентозофосфатного пути). Модулярные конструкции центрального метаболизма системы C-H-O-P формируются из парагенезисов (ассоциаций) определенных веществ, а формирующиеся модули в свою очередь находятся в парагенезисе друг с другом в определенных физико-химических гидротермальных условиях. Малат, оксалоацетат, пируват и фосфоенолпируват представляют собой обратимый «турникет–подобный» механизм переключения направления реакций, определяющий тренд развития конкретных метаболических систем. Таким образом, происходит естественный отбор зарождающихся метаболических систем.

Ключевые слова: зарождение энергетики метаболизма, автокаталитические циклы, фосфорный метаболизм, глюконеогенез, фиксация CO_2, эра Архея, древние гидротермальные системы.

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