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Development of nascent autotrophic carbon fixation systems in various redox conditions of the fluid degassing in early Earth

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Abstract. Strategies for the origin and development of primary metabolism on early Earth were determined by the two main regimes of degassing of Earth in the form of CO_2 or CH_4 fluid impulses. Among the existing theories of the autotrophic origin of the life, CO_2 is usually considered the carbon source for nascent autotrophic metabolism. However, the ancestral carbon used in metabolism may have been derived from CH_4 if the outflow of magma fluid to the surface of the Earth consisted mainly of methane. Primary biochemical systems are present in methane degassing regimes developed in an environment of high partial pressure of methane, which is a source of carbon for nascent metabolic systems. Due to the absence of molecular oxygen in the Archaean conditions, this metabolism would have been anaerobic, i.e., oxidation of methane must be realized by inorganic high-potential electron acceptors. In light of the primacy and predominance of CH_4-dependent metabolism in hydrothermal systems of the ancient Earth, we propose a model of carbon fixation, which is a sequence of reactions in a hypothetical methane-fumarate (MF) cycle. Thermodynamics calculations showed a high efficiency of oxidation of methane to acetate (methanotrophic acetogenesis) by oxidized nitrogen compounds in hydrothermal systems. Thermodynamically favorable were also reactions involving the introduction of carbon methane into the intermediates of the proposed MF cycle. The methane oxidation reactions with the use of oxygen of iron mineral buffers are closer to the equilibrium state, which apparently determines the possibilities of primordial cycle flow in the forward or reverse directions.

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1 Introduction

The degassing of seismically active planets and satellites manifests in the form of volcanism and fluid flows, allowing us to observe the regime of hydrocarbon degassing of the liquid cores. For example, there is a preponderance of methane on Titan and Enceladus (the satellites of Saturn) (Tobie et al., 2006; Bouquet et al., 2015) and on Europa (the satellite of Jupiter) (Russellet al., 2017). Additionally, high concentrations of methane are assumed to be present on early Mars (Oehler and Etiope, 2017).

On Earth, the generation of hydrocarbons from impulse degassing of the Fe-Ni liquid core can be traced since the ancient times. This has been observed in the quartz–methane amygdaline inclusions that occur in the form of relics present even in metamorphic-basaltic rocks of Greenland that are aged at 3.8 billion years (Touret, 2003). Multiple lines of evidence indicate significant concentrations of abiogenic CH_4 in the Archaean atmosphere and hydrosphere (Fiebig et al., 2007; Haqq-Misra et al., 2008; Etiope, 2017; Dodd et al., 2017). Modern volcanism, including hydrothermal emissions at mid-oceanic ridges, is characterized by a primary regime of degassing, with a high carbon dioxide to methane concentration ratio ($[CO_2]/[CH_4]$) (Reinbow, Von Damm) and also by a secondary regime, with low $[CO_2]/[CH_4]$ (Lost Sity, Lucky Strike) (Sephton and Hazen, 2013; Konnet al., 2015). We believe these dominant degassing regimes resulted from various types of magmatism and explosive methane venting tectonics (Marakushev and Marakushev, 2008, 2010; Morner, 2017). There is convincing evidence indicating the presence of at least two main geodynamic regimes of fluid impulse degassing of the hydrogen-rich nickel-iron liquid core in the history of Earth's development (Alldredge, 1984; Milanovsky, 2004; Valet and Herrero-Bervera, 2007; Aubert et al., 2010). These two regimes are believed to have led to the formation of a C–H–O chemical system (Marakushev and Marakushev, 2006, 2010). It is important to note that the core is the most significant reservoir of carbon (Dasgupta and Walker, 2008; Nakajima et al., 2009).

Fluids ejected from the liquid core were initially saturated with hydrogen, with oxygenic components being of minor importance. However, when the permeability of silicate shells across the Earth increased (during the expansion of silicate shells of the Earth due to the oscillatory nature of the geomagnetic field), there began a selective migration of hydrogen, the most mobile component, out of the fluid. This process is responsible for hydrogen losing its leading position in ejected fluids and being fundamental to the evolution of low and normal alkalinity magmatism (Marakushev and Marakushev, 2008). In this scenario, the

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fractionation of chemical components in fluid would result in rich CO_2 solutions (for example, $H_2+2CO = H_2O+0.5CO_2+1.5C$ and $H_2O+CO_2 = H_2CO_3$). These solutions are widely observed in the composition of fluid inclusions in minerals of all igneous rocks of low and normal alkalinity. In Fig. 1, this region of thermodynamic stability (facies) representing the paragenetic association of $H_2O–C–CO_2$ is denoted by (**I**).

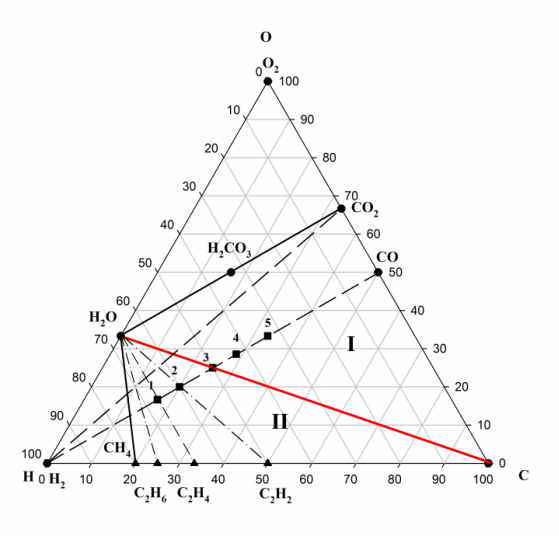

Figure 1. Two regimes of evolution of the C–H–O system on the diagram of its compositions. Roman numerals denote various regimes of hydrogen fluid evolution: (**I**) water-carbonic and (**II**) water-hydrocarbon solutions, separated by $H_2O–C$ equilibrium (red). Parageneses (assemblages) of the initial substances (H_2, CO, CO_2) are denoted by dashed sub-lines, while dash-dotted lines indicate the parageneses ($C_2H_6–H_2O$, $C_2H_4–H_2O$, etc) of hydrocarbons (black triangles) with water. Black squares denote organic substances within the two component ($H_2–CO$) system: methanol (1), ethylene glycol (2), acetate (3), succinate (4), and fumarate (5).

The transition to compression of silicate shells prevents hydrogen migration from fluids and stimulates the production of hydrocarbons within them; for example, consider the reactions: $3H_2+CO = H_2O+CH_4$, $5H_2+2CO = 2H_2O+C_2H_6$ (Fig.1, facies **II**, reducing conditions). The hydrogen in the reaction like $4H_2+H_2CO_3 = 3H_2O+CH_4$ destroys the acid components in fluids, and this determines the alkaline slope in the development of magmatism. With increasing alkalinity in the fluid inclusions of igneous minerals invariably appear different hydrocarbons (Potter and Konnerup-Madsen, 2003; Nivin et al., 2005). This

is a two-stage model of the development of the C–H–O system (**I** ↔ **II**), which depends on the composition of Earth's core fluids, and their transformations in magma chambers.

The existing theories on the origin of autotrophic life identify carbon dioxide as the unique carbon source for metabolism. This should have occurred at a high partial pressure of CO_2 in the environment (paragenesis CO_2 + H_2O, Fig. 1, facies **I**). However, in geodynamic regime **II,** we demonstrated that the carbon of ancestral metabolism could be hydrocarbonic (paragenesis CH_4+H_2O) if the flow of free energy from the geochemical environment was conjugated to formation reactions of the biomass. Perhaps, these different regimes of fluid degassing determined the emergence and development of various systems of ancient metabolism. In regime **II** (Fig. 1), carbon fixation could occur in the form of methane or other hydrocarbons. For example, in aerobic acetogenesis (CH_4+O_2 = 0,5CH_3COOH+H_2O), more free energy is released in the methane fixation reaction (ΔG^0_{298} = -417.35 kJ/mol under standard conditions; aqueous constants from (Amend and Shock, 2001)) than in the process of CO_2 fixation (CO_2+2H_2= 0,5CH_3COOH+H_2O; ΔG^0_{298} = -84.75 kJ/mol).

Geochemical evidence strongly indicates highly disparate redox conditions between modern Earth and those in the early Archaean. We consider that the anaerobic geochemical conditions of the Archaean played a decisive role in the origin and development of carbon and energy metabolism, which are vastly different from those observed in the tops of the branches of the modern phylogenetic tree of prokaryotes. Most metabolically-anaerobic chemoautotrophic organisms are either extinct or strongly limited to narrow anoxic ecological niches. Lateral gene transfer and subsequent phylogenetic divergence erased most evolutionary information recorded in ancestral prokaryotic genomes. Currently, it remains unclear which, among the existing genomes, are ancient and sourced from the last universal common ancestor (LUCA) (Martin et al., 2012).

2 Anaerobic oxidation of methane

The study of anaerobic oxidation of methane (AOM) in modern oxygen-free environments (marine sedimentary rocks, gas-hydrates, mud volcanoes, black smokers, hydrocarbon sipes) has increased in recent years. This direction was sparked by the discovery of anaerobic methanotrophic archaea (Hinrichs et al., 1999) and, subsequently, their structural consortia with sulfate-reducing bacteria (Knittel and Boetius, 2009). A similar relationship was later discovered in archaea species that functions in chemical conjunction with the bacterium *Candidatus* Methylomirabilis oxyfera, which generates nitrite – a terminal electron acceptor

in the methane oxidation pathway (Ettwig et al., 2010). Furthermore, the microbiological AOM was recently shown to be directly associated with the reduction of iron and manganese compounds and minerals (Beal, 2009; Ettwig et al., 2016; Oniand Friedrich, 2017; He et al., 2018), as in the reaction $CH_4 + 8Fe^{3+} + 2H_2O \rightarrow CO_2 + 8Fe^{2+} + 8H^+$ ($\Delta G^{0'}$ = -454 kJ mol^{-1} CH_4).

Recent studies have suggested that both archaea (ANME-2d) (Haroon et al., 2013) and bacteria (Methylobacter) (Martinez-Cruz et al., 2017), without partners, may themselves be versatile methanotrophs capable of using different oxidants as electron acceptors under different environmental conditions. AOM is proposed to occur by reversal of the canonical methanogenesis pathway. For example, nickel enzyme purified from methanogenic archaea can catalyze the oxidation of methane to methyl coenzyme M (CH_4 + CoM–S–S–CoB → CH_3–S–CoM + HS–CoB; $\Delta G^{o'}$=30±10 $kJmol^{-1}$) (Scheller et al., 2010). Methano- and methylotrophs use different but often interrelated pathways of carbon fixation (Smejkalová et al., 2010). Newly described methanotrophic anaerobic prokaryotes are frequently discovered in various extreme environmental conditions (Semrau et al., 2008), underscoring the functional and phylogenetic diversity of this group. The search for relict forms of anaerobic methanotrophic metabolism continues.

In 2013, Wolfgang Nitschke and Michael Russell described the possibility of methane as the sole source of carbon for primordial metabolism (Nitschke and Russell, 2013). They presented a model of the methanotrophic acetogenesis with methane as the carbon source, distinguished by the direction of the reactions from the modern acetyl-CoA pathway. The proposed methane oxidant in this pathway of CH_4 fixation was activated nitric oxide (NO), formed via nitrate/nitrite transformation (‘denitrifying methanotrophic acetogenesis’) (Russell and Nitschke, 2017). It is assumed that this reverse acetyl-CoA acetogenic pathway was the metabolic foundation for early hydrothermal ecosystems and emergence of LUCA. The authors consider the process of harzburgite (ophiolites) hydrothermal serpentinization in the presence of carbon oxides served as the main source of methane. Nevertheless, Wang et al. (2018) suggest that there is another unified deep high-temperature process (under redox conditions characterizing intrusive rocks derived from sub-ridge melts) of making methane for these hydrothermal areas.

The LUCA era apparently proceeded in an environment with high CO_2 partial pressure, whereas the pre-LUCA period proceeded in a reducing environment with a significant predominance of methane. The question thus arises: was this ancestral reverse acetyl-CoA

relic pathway the only metabolic CH_4 fixation system, or were there other proto-biochemical mechanisms for the assimilation of carbon?

In addition to the acetyl-CoA pathway, autocatalytic CO_2 fixation cycles have been suggested as the first metabolic autocatalytic systems on early Earth (Wächtershäuser, 1990; Smith and Morowitz, 2004; Marakushev and Belonogova, 2009, 2013; Futch, 2011; Braakman and Smith, 2012, 2013). These include a reductive citrate cycle (reverse cycle of tricarboxylic acids, the Arnon cycle), a 3-hydroxypropionate cycle, a 3-hydroxypropionate/4-hydroxybutyrate cycle, a reductive dicarboxylate/4-hydroxybutyrate cycle, and a reducing pentose phosphate (Calvin–Benson–Bassham) cycle. The defined conservative sequences of intermediates of these cycles are modules such that their combination can create a variety of metabolic systems, including the specific pathways of carbon fixation (Lorenz et al., 2011; Marakushev and Belonogova, 2010, 2015; Braakman and Smith, 2012, 2013). To be considered a possible metabolic alternative, assimilating methane through autocatalytic cycle intermediates must satisfy the fundamental requirements of thermodynamics.

3 The proposed methane-fumarate (MF) cycle

Based on the hypothesis of primordial anaerobic methanotrophic metabolism origin, we assume that some components and modules of the metabolic cycles (carboxylic and keto acids, and their parageneses) may also be relicts of ancient methanotrophic acetogenesis. One of the few known reactions of CH_4 fixation is the formation of 2-methylsuccinate as a result of the reaction: fumarate+CH_4 → 2-methylsuccinate (Thauer and Shima, 2008; Austin and Groves, 2011; Haynes and Gonzalez, 2014). Regeneration of fumarate can occur in various metabolic cycles, for example, fumarate+CH_4 → 2-methylsuccinate → mesaconate+2H → citramalate → citramalyl-CoA → pyruvate+acetyl-CoA →→→ oxaloacetate → citrate → isocitrate → 2-oxoglutarate+CO_2+2H → succinyl-CoA+CO_2+2H → succinate → fumarate+2H or fumarate+CH_4 → 2-methylsuccinate → 2-methylsuccinyl-CoA → 2-ethylmalonyl-CoA → butyryl-CoA+CO_2 → crotonyl-CoA+2H → 3-hydroxybutyryl-CoA → 4-hydroxybutyryl-CoA → 4-hydroxybutyrate → succinate semialdehyde+2H → succinyl-CoA+2H →succinate → fumarate+2H (Thauer and Shima, 2008). In hydrothermal early-Archaean reducing conditions, the most versatile and widely-used carboxylic and keto acids could form autocatalytic cycles of methane fixation and release both carbon dioxide and acetate. In the presence of high-potential inorganic oxidants, conditions became possible for the oxidative introduction of methane into the intermediates of putative cycles, seen, for

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example, in the hypothetical reactions of pyruvate → oxaloacetate and acetate → oxaloacetate.

We propose a simplified model of the methane-fumarate (MF) cycle, Fig. 2, that is initiated by the reaction of fumarate + methane → 2-methylsuccinate at a high partial pressure of endogenous methane (facies II, Figure 1), as in Archaean reductive hydrothermal systems (Dodd et al., 2017). In the hydration and dehydrogenation reactions, 2-methylsuccinate is converted to citramalate, which is disproportionate to acetate and pyruvate with cleavage of carbon-carbon bond. The resulting keto acid pyruvate, binding methane, is converted into keto acid oxaloacetate with the participation of inorganic oxidants (oxidized forms of nitrogen and transition metals such as iron, manganese, and nickel). Oxaloacetate is transformed into fumarate in the reactions of the citrate cycle intermediates (Fig. 2). The resulting fumarate assimilates methane and begins another autocatalytic MF cycle. Without the regeneration of acetate → pyruvate, the MF cycle would be a synthetic pathway for pyruvate ($C_3H_4O_3$) + $2CH_4$ + $12Fe_2O_3$ → acetate ($C_2H_4O_2$) + pyruvate + $8Fe_3O_4$ + $2H_2O$ (ΔG^0_{298} = 11.84, ΔG^0_{473} = -6.49 kJ/mol CH_4), by using pyruvate as a network catalyst. Acetate → pyruvate synthesis enables positive feedback in the cycle: $5CH_4$ + $30Fe_2O_3$ + 2-methylsuccinate ($C_5H_8O_4$) → $6H_2O$ + $20Fe_3O_4$ + 2 2-methylsuccinate (ΔG^0_{298} = 14.7, ΔG^0_{473} = 0.25 kJ/mol CH_4), or, with another oxidant, $3CH_4$+$14HNO_2$+pyruvate = 2 pyruvate ($C_3H_4O_3$)+14NO+$11H_2O$ (ΔG^0_{298} = -283.3, ΔG^0_{473} = -347.32 kJ/mol CH_4), creating network autocatalysis. This model of AOM is an autocatalytic system of oxidative assimilation of carbon.

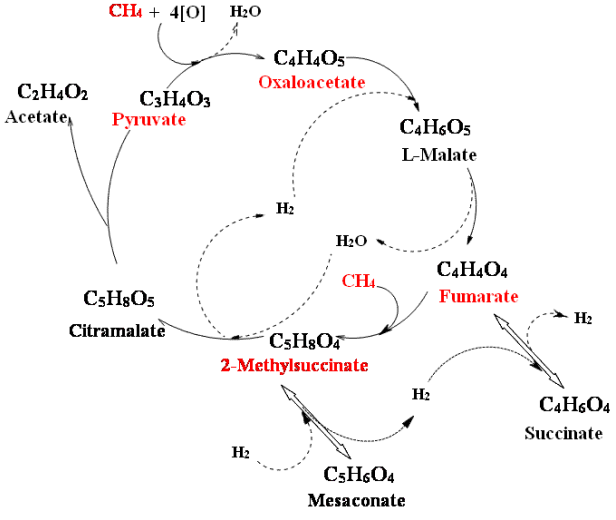

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Figure 2. The scheme of the proposed methane-fumarate (MF) cycle. [O], which is the oxidant of methane, denotes the oxygen of an inorganic redox pair (HNO_3/HNO_2, HNO_2/NO, H_2SO_4/H_2SO_3, Fe_2O_3/Fe_3O_4, etc.). Carbon from methane is introduced into the cycle components (indicated in red) with the formation of a C–C bond, and the oxygen atoms of the oxidant are assimilated in the cycle intermediates and in water. The chemical potential of hydrogen in the environment determines the equilibrium shift in the reactions succinate ↔ fumarate and 2-methyl succinate ↔ mesaconate.

AOM implies the availability of an oxidant that corresponds to the thermodynamic and kinetic limitations of this process. In the absence of oxygen, electron acceptors with high redox potential (such as nitrate, manganese (IV), iron (III), and sulfate) are required. Thermodynamic calculations of anaerobic methanotrophic acetogenesis reactions in aqueous hydrothermal conditions that require oxidized compounds such as sulfur, nitrogen, and iron are considered in Table 1. For example, the free energy of the reaction $CH_4+6Fe_2O_3 = 0.5CH_3COOH+H_2O+4Fe_3O_4$ at 473 K is equal to the sum of the free energy of products formation minus the sum of free energy of the reactants formation at the same temperature ($\Delta G_{473}^0 = (0{,}5\Delta G^0_{CH3COOH}+\Delta G^0_{H2O}+4\Delta G^0_{Fe3O4})-(\Delta G^0_{CH4}+6\Delta G^0_{Fe2O3}) = -6.49$ kJ/mol). It is obvious that methane oxidation with nitrogen compounds is thermodynamically very favorable, especially in contrast to the sulfate-sulfite pair.

Table 1. Free Gibbs energy of aqueous reactions (ΔG^0_T) of anaerobic methanotrophic acetogenesis as a function of the oxidant (oxidized forms of nitrogen, sulfur, and iron). The oxidation of methane to fully ionized and non-ionized forms of acetate is presented at temperatures of 298 and 473 K at the saturated vapor pressure (P_{SAT}). TR – represents the temperature regime of the reactions from low (L) to high-temperatures (H). Free energies of aqueous substances formation at P_{SAT} (Amend and Shock, 2001; Marakushev and Belonogova, 2012) were used in calculations.

Redox pair of nitrogen	ΔG^0_{298} kJ/mol CH_4	ΔG^0_{473} kJ/mol CH_4	TR
$CH_4 + 2NO = 0.5CH_3COOH + H_2O + N_2$	-586.78	-563.18	L
$CH_4 + 2NO = 0.5CH_3COO^- + 0{,}5\ H^+ + H_2O + N_2$	-573.39	-538.33	
$CH_4 + 4NO = 0.5CH_3COOH + H_2O + 2N_2O$	-582.32	-535.87	L
$CH_4 + 4NO = 0.5CH_3COO^- + 0{,}5\ H^+ + H_2O + 2N_2O$	-568.93	-511.02	
$CH_4 + 4HNO_2 = 0.5CH_3COOH + 3H_2O + 4NO$	-264.46	-320.79	H
$CH_4 + 4NO_2^- + 3.5H^+ = 0.5CH_3COO^- + 4NO + 3H_2O$	-324.71	-398.7	
Redox pair of iron (mineral buffers)			
$CH_4 + 6Fe_2O_3 = 0.5CH_3COOH + H_2O + 4Fe_3O_4$	11.84	-6.49	H
$CH_4 + 6Fe_2O_3 = 0.5CH_3COO^- + 0{,}5\ H^+ + H_2O + 4Fe_3O_4$	25.23	18.36	

$CH_4 + 1.5FeS_2 + 0.5Fe_3O_4 = 0.5CH_3COOH + H_2O + 3FeS$	44.65	28.85	H
$CH_4 + 1.5FeS_2 + 0.5Fe_3O_4 = 0.5CH_3COO^- + 0{,}5\ H^+ + H_2O + 3FeS$	58.04	53.7	
$CH_4 + 2Fe_3O_4 + 3SiO_2 = 0.5CH_3COOH + H_2O + 3Fe_2SiO_4$	57.23	16.19	H
$CH_4 + 2Fe_3O_4 + 3SiO_2 = 0.5CH_3COO^- + 0{,}5\ H^+ + H_2O + 3Fe_2SiO_4$	70.62	41.04	
Sulphate – sulphite redox pair			
$CH_4 + 2H_2SO_4 = 0.5CH_3COOH + H_2O + 2H_2SO_3$	114.88	124.09	L
$CH_4 + 2SO_4^{-2} = 0.5CH_3COO^- + 0{,}5\ H^+ + H_2O + 2SO_3^{-2}$	128.27	148.94	

Methanotrophic acetogenesis reactions are energetically more preferable under alkaline hydrothermal conditions (ionized compound forms). The change in the free energy with temperature change indicates whether the reaction displays a thermodynamic preference for low-temperature (L) or high-temperature (H) conditions (Table 1). For example, the sulfate-oxidase reaction is the most thermodynamically favorable at low-temperature (increasing ΔG^0_r with increasing T), whereas the nitrite-oxidase reaction is very favorable at high-temperature (decreasing ΔG^0_r with increasing T). Sulfate oxidation is most favorable in its non-ionized form (acidic conditions) and nitrite oxidation in its ionized form (alkaline conditions).

Table 2 shows the free energy of the carbon fixation reactions by intermediates in the MF cycle (Fig. 2). The nitrite-nitric oxide (HNO_2-NO), nitrogen oxide-nitrous oxide (NO-N_2O), and nitrogen oxide-molecular nitrogen (NO-N_2) redox pairs were the most thermodynamically favorable "anaerobic" oxidants. Free energy values calculated at low and high temperatures (ΔG^0_{298} and ΔG^0_{473}) informed the estimated temperature regime of these reactions. The redox nitrogen pairs were clearly the most thermodynamically favorable for methane assimilation through MF cycle intermediates, but the oxidation reaction with the HNO_2/NO pair is high-temperature, while that with the 2NO/N_2O and NO/0.5N_2 pairs is low-temperature.

The free energy of the CH_4 fixation by MF cycle intermediates strongly favors nitrogen pairs over mineral buffers pairs, but can be limited by the availability of the oxidant and kinetically blocked by a large energy barrier. On the other hand reactions with iron mineral buffers are closer to the equilibrium state, which ultimately determines the possibilities of primordial cycle flow in the forward or reverse directions (development of methanogenesis or methanotrophic acetogenesis). An analysis of the oldest known association of microfossils suggests that methane-cycling methanogen−methanotroph communities were a significant component of Earth's early biosphere (Schopf et al., 2017).

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Table 2. Free energy of the proposed MF cycle reactions at 298 and 473 K at P_{SAT} with various oxidants (Fe_2O_3, Fe_3O_4, NO, HNO_2) in hydrothermal conditions. For comparison, the reactions of methane oxidation with molecular oxygen are considered. Free energies of aqueous substances formation at P_{SAT} (Amend and Shock, 2001; Marakushev and Belonogova, (El. Suppl. Mat.), 2013) were used in calculations.

Reactions of MF cycle	ΔG^0_{298} kJ/mol	ΔG^0_{473} kJ/mol
$(CH)_2(COOH)_2$ (**Fumarate**) + CH_4 = $(CH_2)(CH_3CH)(COOH)_2$ (**2-Methylsuccinate**)	-44.95	-29.97
$(CH_2)(CH_3CH)(COOH)_2 + H_2O = (CH_3CH)CH(OH)(COOH)_2$ (**Citramalate**) + H_2	96.57	94.14
$(CH_3CH)CH(OH)(COOH)_2 = CH_3COOH$(Acetate) + $CH_3(CO)COOH$ (**Pyruvate**)	19.35	1.73
$CH_3(CO)COOH + CH_4 + 2O_2 = CH_2CO(COOH)_2$ (**Oxaloacetate**) + $2H_2O$	-845.86	-803.44
$CH_3(CO)COOH + CH_4 + 12Fe_2O_3 = CH_2CO(COOH)_2 + 2H_2O + 8Fe_3O_4$	12.52	-17.84
$CH_3(CO)COOH + CH_4 + 3FeS_2 + Fe_3O_4 = CH_2CO(COOH)_2 + 2H_2O + 6FeS$	78.23	52.84
$CH_3(CO)COOH + CH_4 + 4Fe_3O_4 + 6SiO_2 = CH_2CO(COOH)_2 + 2H_2O + 6Fe_2SiO_4$	103.3	27.6
$CH_3(CO)COOH + CH_4 + 8NO = CH_2CO(COOH)_2 + 2H_2O + 4N_2O$	-1175.72	-1076.6
$CH_3(CO)COOH + CH_4 + 8HNO_2 = CH_2CO(COOH)_2 + 6H_2O + 8NO$	-540.08	-646.44
$CH_3(CO)COOH + CH_4 + 4NO = CH_2CO(COOH)_2 + 2H_2O + 2N_2$	-1184.72	-1131.22
$CH_2CO(COOH)_2 + H_2 = CH_2CH(OH)(COOH)_2$ (**L-Malate**)	-65.49	-55.78
$CH_2CH(OH)(COOH)_2 = (CH)_2(COOH)_2 + H_2O$	5.68	-5.26
$(CH)_2(COOH)_2 + H_2 = (CH_2)_2(COOH)_2$ (**Succinate**)	-102.24	-88.88
$(CH_3C{=}CH)(COOH)_2$ (**Mesaconate**) + H_2 = $(CH_2)(CH_3CH)(COOH)_2$	-66.53	-54.85

The reversibility of the reactions in the citrate cycle is mainly determined by the equilibrium of fumarate+H_2 = succinate (ΔG^0_{298} = -102.24, ΔG^0_{473} = -88.88 kJ/mol). The change in the direction of electron flow therein is determined by the chemical potential of hydrogen (Marakushev and Belonogova, 2009). Therefore, different proto-metabolic cycles could be formed, for example, the oxidative citrate and reductive 3-hydroxipropionate cycles (succinate → fumarate), the reductive cycle of CO_2 fixation (fumarate → succinate), or the proposed CH_4 fixation cycle (succinate → fumarate → 2-methylsuccinate). Assimilation of CH_4 in the MF cycle (pyruvate → oxaloacetate, Fig. 2) demonstrates highly favorable thermodynamics with all redox pairs of nitrogen. The same reaction with hematite (Fe_2O_3)-magnetite (Fe_3O_4) redox pair is unfavorable at 298 K and becomes favorable at 473 K. Methyl group formation by the oxidation of methane is limited by kinetics, because the dissociation energy of the C–H bond in methane (439 kJ/mol) exceeds that of the *X*–H bond in other organic molecules, with the exception of the O–H bond in H_2O (497 kJ/mol) and other oxygen-derived molecular species. Nevertheless, these limitations are overcome in conditions of high methane and its oxidants concentration and in the presence of metallocatalysts similar

to the active center of metalloenzymes, as the key iron-nickel enzyme of methanogenesis, namely, methyl coenzyme M reductase.

It is highly possible that the MF cycle existed in a geodynamic regime of high endogenous methane flow in ancient Earth. The thermodynamics of carbon fixation from methane through the archaic MF cycle with its various redox associations of Fe-buffers demonstrate the proximity of these reactions to equilibrium. This proximity enabled multiple possibilities for metabolic reactions to develop in various directions, governed by environmental conditions (temperature, pressure, and chemical potentials of substances). We expect future biochemical studies of AOM to reveal new insights into reaction mechanisms and into energetic and kinetic principles of overall nascent metabolism.

4 Anaerobic methane oxidation in a hydrothermal system

Under hydrothermal conditions, and in the fluid evolution of the Earth in general (Fig. 1), there is a distinct separation the areas of thermodynamic stability (facies) of CO_2 and CH_4. We represent the hydrothermal system in the form of a phase diagram which displays the chemical potential of oxygen vs. temperature at saturated vapor pressure (P_{SAT}), where temperatures and pressures are below critical thresholds (647,3 K and 22,1 МПа) (Fig. 3). It is a two-component system (extensive parameters: C and H), since oxygen become intensive parameters, as the temperature, and pressure. Oxygen is represented by the chemical potential of O_2 in hydrothermal solution ($\mu^{P}_{O2} = RT\ln a_{O2}$, where a_{O2} denotes the chemical activity of oxygen). Accordingly, at arbitrary pressure, the nonvariant equilibria in the diagram (points) consist of four phases, and the three-phase equilibria (lines) divide the divariant stability fields (facies) of the two-phase equilibria.

The equilibrium $CH_4+2O_2 = CO_2+2H_2O$ (bold line) divides the diagram into the facies of CO_2 **(I)** and CH_4 **(II)** and illustrates the two main possibilities for the development of the C–H–O system in the facies carbon dioxide or methane. The CO_2/CH_4 equilibrium determines the oxic and anoxic conditions of the hydrothermal system. Intermediates of the MF cycle are acetate, succinate, and fumarate, and we considered their metastable equilibria and parageneses. In all phase space under consideration, there are fumarate facies. The equilibrium of $5Fum+4CH_4+2O_2 = 6Suc$ at low-temperature (Fig. 3), is located in the region of very low partial pressures of oxygen, whereas the equilibrium of $Fum+2CH_4+O_2 = 3Acet$ at high-temperature occurs in facies of high pressures. Acetate and succinate facies (contoured with a red and blue lines, respectively) completely encompass the equilibrium of $CH_4+O_2 =$

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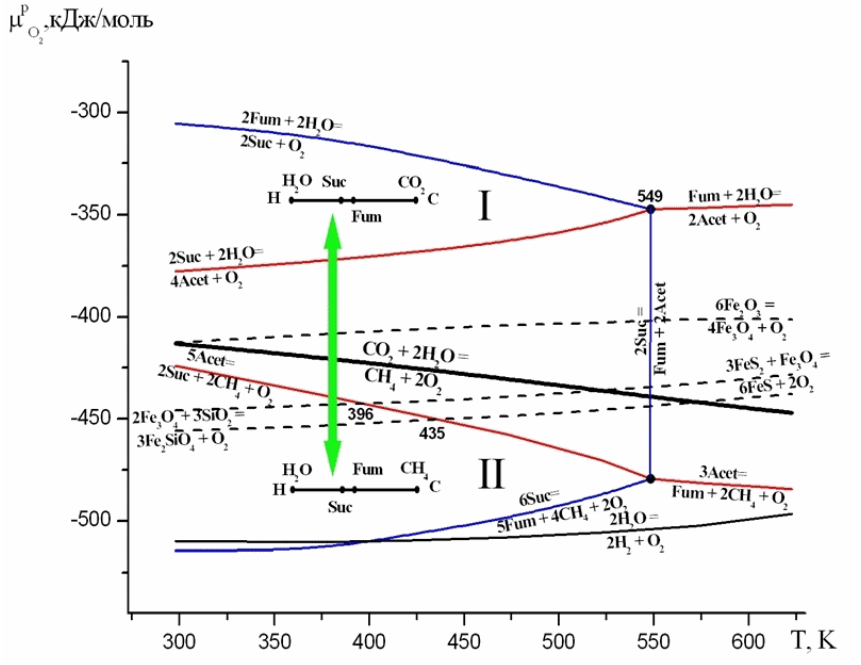
320 CO_2+H_2O. That is, in hydrothermal solution, the parageneses of some components within the
321 MF cycle are stable in both the CO_2 and the CH_4 facies. The whole system can develop in
322 either of two directions as the chemical potential of oxygen changes: 1. the formation of low-
323 temperature (Suc-H_2O) and high-temperature (Fum-H_2O) paragenesis in CO_2 facies (I) and 2.
324 the formation of low-temperature (Suc-CH_4) and high-temperature (Fum-CH_4) paragenesis in
325 CH_4 facies (II). Thus, within these facies, protobiochemical systems supporting carbon
326 fixation in the form of CO_2 or CH_4 can develop, and methane facies (II) represent a broad area
327 of CH_4 assimilation by carboxylic acids and keto acids in an aqueous environment. The high
328 stability of the succinate-fumarate-acetate paragenesis in hydrothermal systems at 200° C
329 (473 K) was experimentally shown (Estrada et al., 2017).



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331 **Figure 3.** Diagram of the chemical potential of oxygen (μ^P_{O2}) - temperature (T, K) at
332 saturated vapor pressure (P_{SAT}). The areas of thermodynamic stability of substances and their
333 parageneses were calculated according to the method described in Marakushev & Belonogova
334 [2009]. Points (indicated by temperature values) and lines represent four-phase and three-
335 phase equilibria, separating the two-phase divariant fields of substance stabilities. The bold
336 line represents the equilibrium of CO_2↔CH_4 and separates their areas of thermodynamic
337 stability (I and II). The dashed lines are equilibria of mineral buffers: hematite-magnetite,
338 Fe_2O_3/Fe_3O_4 (HM), pyrite-pyrrhotite-magnetite, FeS_2+Fe_3O_4/FeS (PPM), and quartz-

magnetite-fayalite, SiO_2+Fe_3O_4/Fe_2SiO_4 (QMF). We provide linear diagrams of the two-component C–H system in the CO_2 and CH_4 facies. The transition between the facies when the chemical potential of oxygen changes is indicated by a green arrow. Abbreviation: Succinate – Suc, Fumarate – Fum, Acetate –Acet.

Mineral buffers up to 549 K are located in the facies of succinate, but the equilibrium of HM remains in the area of thermodynamic CO_2 stability (facies I). PPM and QMF equilibria occur in methane facies II and intersect the fundamental equilibrium of $2Suc+2CH_4+O_2 = 5Acet$, the clear basis of methanotrophic acetogenesis. Magnetite (Fe_3O_4) facies (between HM and QMF equilibria) encompass CH_4/CO_2 equilibrium in nearly the entire temperature range of the hydrothermal system under consideration, and hematite (Fe_2O_3) becomes an effective methane oxidant over the entire temperature range. This determines the P/T conditions for the development of methanotrophic systems with the participation of hematite as an oxidant, e.g. reaction pyruvate ($C_3H_4O_3$)+CH_4+$12Fe_2O_3$ = oxaloacetate ($C_4H_4O_5$)+$2H_2O$+$8Fe_3O_4$ is favorable at high temperature, Table 2. The formation of magnetite also occurs above 396 K for the PPM buffer and above 435 K for the QMF buffer. Thus, the redox conditions of magnetite stability correspond to the formation conditions of CH_4 assimilating systems. The presence of magnetite in the early Archaean ocean was shown by (Li et al., 2017]. The functional importance of the keto group for chemical transformation of the C–C bond was experimentally demonstrated under hydrothermal conditions by Yang et al., (2018), where magnetite and hematite minerals catalyzed the C–C and C–H fragmentation of ketones.

Prior to the great oxidative event of 2.2-2.4 billion years ago on the Earth's surface, the oxidation potential of the hematite-magnetite redox buffer apparently determined the chemical potential of environmental oxygen. Shibuya et al. (2016) demonstrated the necessity of iron compound redox reactions for the process of relict methanogenesis and methanotrophic acetogenesis to function, as in the most ancient forms of metabolism.

5 Conclusion

In general, cyclic planetary fluid flows drive Earth's chemical evolution, leading to the formation of geobiochemical systems of carbon fixation. Impulses of CO_2 and CH_4 degassing on our planet must have contributed to the development of various types of carbon metabolism. It is generally accepted that autotrophic metabolism is the fixation (assimilation) of inorganic carbon solely in the form of CO_2, but CH_4 is also deep and inorganic; therefore,

carbon fixation from methane is also a manifestation of autotrophic metabolism. The variety of modern autotrophic carbon fixation seems to be due to the association of the different metabolic modules created by a diverse assemblage of ancestral metabolic modules presented in the LUCA. Lateral gene transfer and subsequent phylogenetic divergence erased much of the evolutionary information in the genomes; thus, it is not clear which genes among the sequenced genomes are truly ancient (i.e., traced to LUCA) (Martin et al., 2016). When a CO_2 degassing regime began to dominate on our planet, relict systems of methanotrophy were forced to die out or to be thrown back into uncommon and extreme ecological niches. If we consider LUCA as a relatively recent player in the evolution of life (Cornish-Bowden and Cárdenas, 2017), then the number of carbon-fixing metabolic systems in putative pre-LUCA organisms should be incommensurably greater than the present numbers.

In the process of development of CO_2 fixation systems on Earth, the main problem was the presence of electron donors (therefore, evolution created selective reducing agents: NADH, NADPH, FADH), whereas the fixation of CH_4 essentially depended on the presence of electron acceptors. In the hydrothermal systems, oxygen-containing nitrogen compounds are the best oxidants, but we believe that the redox pairs of hematite-magnetite and quartz-magnetite-fayalite create a specific area of chemical potential of oxygen that satisfies the thermodynamic requirements of oxidation and assimilation of methane by protometabolic pathways. Hydrothermal systems of ancient Earth may have been very similar to those that currently exist on some extraterrestrial cosmic bodies, such as Europa or Enceladus. The degassing of these cosmic bodies can currently support methane metabolism, but the problem is to know if there are electron acceptors there (Russell et al., 2017).

Author Disclosure Statement

No competing financial interests exist.

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