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Biogeosciences Discussions

Interactive comment on "Development of nascent autotrophic carbon fixation systems in various redox conditions of the fluid degassing in early Earth" *by* Sergey A. Marakushev and Ol'ga V. Belonogova

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Response

Within the framework of the "metabolism first" theory, the hypothesis of primacy of the Wood-Lundgal (WL) chemoautotrophic pathway (acetyl-CoA pathway) has been developed by William Martin and Michael Russell for nearly three decades. The definite finale of this hypothesis development is the phylogenetic acceptance of the WL pathway as the basis of the chemoautotrophic metabolism of LUCA [Weiss et al., 2016,

10.1038/NMICROBIOL.2016.116]. The WL pathway is a road for the synthesis of the metabolic systems intermediates starting with acetate and pyruvate. Pyruvate can subsequently be carboxylated to form the dicarboxylic acids, creating a chemical space of the intermediates of the carbon fixation autocatalytic cycles. In our opinion, this protometabolic network is able to evolve with changing of the environmental conditions and with the formation of new cycles of the carbon fixation. In addition, according to a number of the phylogenetic analysis data of Bacteria, the most ancient were the specimens of Aquificeae taxon, functioning on the basis of the rTCA cycle [e.g., Barion et al., 2007; doi: 10.1016/j.biosystems.2006.02.011; Valas, Bourne, 2009, doi: 10.1186/1745-6150-4-30] and even Chloroflexi with the autotrophic 3-hydroxypropionate cycle of CO2 fixation [Boussau et al. 2008, doi: 10.1186/1471-2148-8-272]. The chemical experimental modeling of the pre-enzymatic CO2 fixation also shows the reality of the inorganic catalysts functioning both in the reactions of the WL pathway and in the reactions of the intermediates of CO2-assimilating cycles of carboxylic acids in the proposed hydrothermal conditions [He et al., 2010, doi: 10.1021/ol9025414; Zubarev et al., 2015, doi: 10.1038/srep08009; Roldan et al., 2015, doi: 10.1039/c5cc02078f; Muchowska et al., 2017; doi: 10.1038/s41559-017-0311-7; Keller et al., 2017, doi: 10.1038/s41559-017-0083]. In a recent paper [Varma et al., 2018, doi: 10.1038/s41559-018-0542-2], the reactions of the WL pathway in an aqueous medium, at the physiological temperatures (30-100 ° C) and high pressures of CO2 (up to 40 bar) with the participation of native iron, as a catalyst, were experimentally performed. Previously they also showed selective Fe0-promoted non-enzymatic transformations 7 of the 11 reactions of the rTCA cycle intermediates. It is probable parallel between plausible prebiotic chemistry and the ancient CO2-assimilating pathways. The network of chemical reactions of autotrophic metabolism is universal [Morowitz et al., 2000; doi: 10.1073ypnas.110153997; Bar-Even et al., 2010, doi: 10.1073/pnas.0907176107; Meringer, Cleaves, 2017, doi: 10.1038/s41598-017-17345-7] and therefore, in our opinion, cycle intermediates could be involved in the process of methane assimilation. The WL pathway as the basis of the autotrophic metabolism of LUCA could function in the reducing

(CO2 → CH4 or CH3COOH) and oxidative (CH4 → CO2 or CH3COOH) directions, creating and breaking C-H bonds in the methane molecules. But the energy of C-H bond cleavage is very high and, of course, the activation of methane in "physiological conditions" is a longstanding challenge for chemistry. The biomimetic approach makes it possible to reveal the basic chemical features of the oxidation of this very stable substance. The main successes in this direction were achieved in the study of aerobic methane oxidation (e.g. in methane monooxygenase), where the activation of the oxidant (molecular oxygen), rather than the C-H bond, is the most important factor in the fixation mechanism. Perhaps, in anaerobic conditions, the activation of oxidants, such as oxides of sulfur, nitrogen and transition metals (not very strong oxidants) contributed to the overcoming of the activation barrier of unreactive C-H bonds cleavage and played a decisive role in the emergence of anaerobic methanotrophic metabolism. Reverse WL pathway from anaerobic methanogenic microorganisms participates in AOM and the enzyme responsible for the first step and activation of C-H bond conversion of methane to methyl-tetrahydromethanopterin is a homolog of the methyl-coenzyme M reductase. The enzymatic mechanism of this enzyme with Ni-porphinoid F430 tetrapyrrole macrocycle [Ragsdale et al., 2017, doi: 10.1039/9781788010580-00149] is the basis for biomimetic modeling of the C-H bond activation by complexes of transition metals. The introduction of methane carbon into the pyruvate molecule, Fig. 2, with the breaking and making of a covalent bond leads to the formation of oxaloacetate as a possible autocatalyst of the methane-fumarate (MF) cycle. Developing metal-catalyzed C-H activation/functionalization chemistry allows the original construction of C-C bond starting from hydrocarbons in the mild conditions [Roudesly et al., 2017, doi: 10.1016/j.molcata.2016.06.020]. We assume a possible participation of complexes of transition metals and their minerals as homogeneous or heterogeneous catalysts of the C-H bond activation in the methane molecule. In the field of alkane oxidation enzymatic metal-oxo species promote C-H activation through a metallo-radical pathway. This involves hydrogen radical abstraction from the alkane by the oxo species, followed by rapid rebound of the radical species onto the metal hydroxo - intermediate

[Roudesly et al., 2017, doi: 10.1016/j.molcata.2016.06.020]. The reaction mechanism of fumarate + CH4 → 2-methyl succinate, Fig. 2 seems to be similar a radical mechanism breaking the C-H bonds and the formation of C-C bond at microbiological toluene fixation by fumarate (benzylsuccinate synthase reaction) [Buckel, Golding, 2006, doi: 10.1146/annurev.micro.60.080805.142216].

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 (HNO3/HNO2, HNO2/NO, H2SO4/H2SO3, Fe2O3/Fe3O4, and others).

Figure X. Proposed scheme of the methane activation by a Gly-Gly radical. Radicals of amino acids and dipeptides (such as Tyr, Trp, Gly-Gly, Cys, and, in particular, Gly.) are possible catalysts of methane activation with the formation of methyl radical as an attacking agent, Fig. X. In carbonaceous chondrites, amino acids and dipeptides are widely represented, and this shows their abiogenic origin. It is interesting that in the presence of sulfate radicals generated from peroxydisulfate (typical components of Archaean sediments), the intermediates of TCA cycle underwent a large number of non-enzymatic interconversion reactions [Keller et al., 2017, doi: 10.1038/s41559-017-0083]. According to [Weiss et al., 2016, 10.1038/NMICROBIOL.2016.116], LUCA's biochemistry was replete with radical reaction mechanisms, which may have functioned in the MF cycle reactions, overcoming kinetically unfavorable reactionary steps. In addition the favorable thermodynamics of reactions, possible autocatalysis and high partial pressure of methane in the atmosphere and the hydrosphere of the early Archaean contributed to the formation of anaerobic pathways of CH4 fixation. The sequence of reactions oxaloacetate → malate → fumarate → succinate, Fig.2, was experimentally demonstrated under reducing conditions [Varma et al., 2018, doi: 10.1038/s41559-018-0542-2] and, naturally, it could be carried out under the reducing conditions of the ancient Earth (H2 and CH4 degassing). The problem is the presence of electron acceptors under similar conditions, which is the subject of discussions, for example [Russell et al., 2017, 10.1089/ast.2016.1600, 2017].

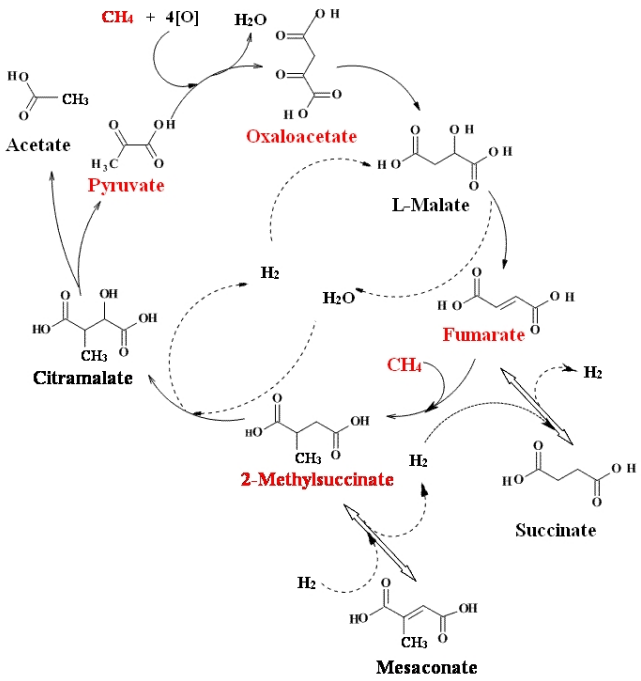
CH4 + 4[O]
H2O
Acetate
Pyruvate
Oxaloacetate
L-Malate
Fumarate
H2O
H2
Citramalate
CH4
H2
2-Methylsuccinate
H2
Succinate
H2
Mesaconate

Fig. 1.

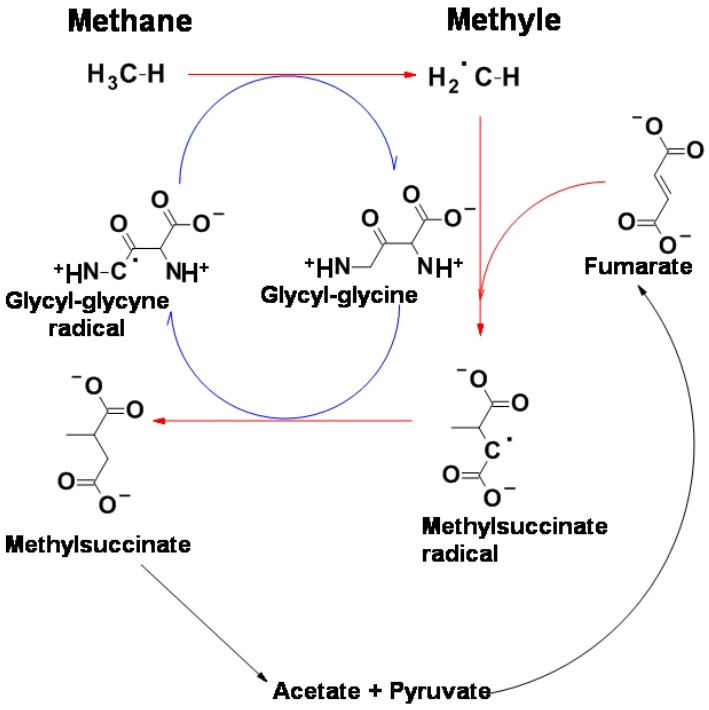
Methane
Methyle
H3C-H
H2˙C-H
Glycyl-glycyne radical
Glycyl-glycine
Fumarate
Methylsuccinate
Methylsuccinate radical
Acetate + Pyruvate

Fig. 2.