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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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Reply to criticism Anonymous Referee # 2

I. "That Fiebig et al., 2007 invoke hydrothermal CH4 is not in dispute, but to quote Haqq-Misra et al. 2008 here is wrong." Still, the existence of significant concentrations of methane in the atmosphere of even the late Archean is recognized by quite a few highly skilled researchers. The model of Haqq-Misra and others [Haqq-Misra et al., 2008] shows that greenhouse warming by methane and higher hydrocarbon

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gases, especially ethane (C2H6), may have helped to keep the Late Archean Earth warm. Another thing - the interpretation of this fact. Volcanic emissions, fluid seepage of hydrocarbons or hydrothermal serpentinization are possible, but the authors believe that “methanogenic bacteria, which were arguably extant at that time, may have contributed to a high concentration of atmospheric CH4”. II. The appearance of autotrophic carbon fixation, in our opinion, occurred in ancient hydrothermal systems, similar to some modern hydrothermal fields of the mid-ocean ridges. Methane, which appeared as a result of serpentinization of olivine, could also be a source of carbon for the nascent metabolism. Therefore, Etiope, 2017 and Dodd et al., 2017 are cited as examples of low-temperature hydrothermal methane formation and the detection of signs of life in Archean hydrothermal systems. This alternative scenario, apparently, needs to be changed and described in more detail. III. “methane in serpentinized peridotitesis likely produced by FTT reactions during low temperature serpentinization? (Etiope, 2017)“ We agree with this and the fact that “magmatic or mantle-derived CH4 is abiotic, but not all abiotic CH4 is mantle-derived” [Etiope, Sherwood Lollar, 2013]. In addition, the article gives us study Wang et al. 2018,which provide evidence that water-rock reactions occurring at temperatures lower than 200°C (serpentinization) do not contribute significantly to the quantities of methane venting at mid-ocean ridge hot springs. There is another unified deep high-temperature process (under redox conditions characterizing intrusive rocks derived from sub-ridge melts) of making methane for hydrothermal areas. In our opinion, degassing of hydrothermal systems and high-temperature magmatic processes in volcanic and geothermal areas are interrelated. General relations between the deep evolution of the Earth and its near-surface development represent one of the main geological problems. Hydrocarbons not only “the diffuse and spasmodic delivery from basaltic lava flows”. Hydrocarbons beginnings in the deep alkaline magmatism could be the basis of organic matter and the source of oil and gas deposits on Earth [Simoneit, 1988; Gold, 1992; Sugisaki., Mimura, 1994; Kenney et al., 2002; Glasby, 2006; Marakushev, Marakushev, 2008, 2010; Höök et al., 2010; Kolesnikov et al., 1017; Huang Fang et al., 2017]. Theoretical calculations

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and experimental data have been presented in support of a persistent assertion that petroleum originates chiefly through abiogenic processes at the high pressures and temperatures found ∼ 100 km [Kenney et al.,2002]. Methane is proved to form inorganically at mantle pressures and temperatures from any carbonate species, such as FeCO3 (siderite) or MgCO3 (magnesite), at oxygen fugacities near the wüstite-magnetite fO2 buffer. Such conditions may be widespread in the mantle and can be moderated by the presence of iron-bearing phases such as Fe2SiO4 (fayalite) or FeS (troilite, pirrotite) [Scott et al., 2004]. Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates. Episodic infiltration of reduced ïňĆuids in the ophicarbonates and methanogenesis occurred from at least 40 km depth to ∼15–20 km depth [Brovarone et al., 2017]. The best evidence of the predominant methane degassing possibility of the early Earth is the detection of significant concentrations of methane and other hydrocarbons in gas-liquid inclusions of diamond [Smit et al., 2016], in ultramafic rocks genetically related to mantle chambers [Tingle, Hochella, 1993], in alkaline igneous Archean minerals [Potter et al., 2004], and also in gas-liquid inclusions in quartz from Archean conglomerates [Schreiber et al., 2017]. IV. “But from my reading of the literature the origin of the hydrocarbons in the post Archean alkaline complexes Khibina, Lovozero and Ilímaussaq is “controversial” and probably Fischer Tropsch and probably NOT mantle-derived.” “The hydrocarbon gases are most likely the product of a series of post-magmatic abiogenic reactions related to carbonatite.” However, the presence of hydrogen, helium, and argon together with hydrocarbons in alkaline mineral inclusions [Potter et al., 2004] directly indicates their deep origin. V. “volcanically-derived atmosphere to have been relatively oxidized (Rubey, 1951; Poole, 1951; Goldschmidt, 1952).” There is the redox heterogeneity in magmatic systems, for example, the pre- and post-eruptive magmatic history has enabled to conïňĄrm the relatively oxidised nature of ocean island-type mantle compared to that of mid-ocean ridge mantle [Hartley et al., 2017]. VI. The environmental conditions of the Urey, 1952 and Miller, 1953, 1955 experiments are not related to the hydrothermal system under consideration. It is assumed a high partial pressure of

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methane, which allows to shift the equilibrium of methane oxidation or addition reactions towards the reaction products (in the presence of transition metal oxides), may be for a sufficiently long geological time. VII. “Geochemical and isotopic evidence now strongly supports the earlier geological views that the atmosphere, was relatively oxidized and has been oxidizing for the last 4.4 Ga is because the redox state of carbon in the quartz-feldspar-magnetite buffered hot upper mantle is as carbonate.” This is not entirely correct. The presented article in Figure 3 shows the equilibrium FMQ, HM and PPM oxygen buffers (dashed line) in a hydrothermal solution. The equilibrium CH4 ↔ CO2 in the whole temperature range is located in the magnetite facies, and the formal degree of oxidation of carbon in this facies can vary from +4 to -4. Metastable equilibria of dicarboxylic acids (with different degrees of carbon oxidation) separate the facies of their oxidative transformation. VIII. ‘Thus wouldn’t it be more reasonable to argue, given the early ocean was very likely carbonic (bearing several moles of CO2) and that the alkaline hydrothermal springs carried methane (<3mmol) as well as hydrogen (15mmol), that the ïňĄrst cells exploited both sources of carbon, CH4 and CO2? Would the authors consider modifying their hypothesis, keeping their original idea, but also involving CO2 to offer the carboxyl radical?” The idea that both CO2 and CH4 were equally the ultimate sources of organic carbon at the emergence of autotrophic metabolism was considered in [Russellet al., 2014]. In the MF cycle under consideration (Fig. 2), the introduction of carbon in the reaction pyruvate + CH4 = oxaloacetate is a major chemical problem. Carboxylation of pyruvate is possible to solve the problem of introduction of carbon in the form of a carboxyl group to form of intermediary metabolism intermediates - dicarboxylic acid. In this case, regeneration of fumarate as in the reductive tricarboxylic acid cycle (rTCA, Arnon-Buchanan cycle), will occur in the following sequence: pyruvate (C3H4O3) + CO2 → oxaloacetate (C4H4O5) + H2 → malate (C4H6O5) → fumarate (C4H4O4) + H2O. IX. “Fluids ejected from the liquid core were initially saturated with hydrogen, with oxygenic components being of minor importance.” This statement is at odds with the surface exhalation assumptions of most others (see appended references)”. The cores of all stratified planets in the period of

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their endogenous activity are under a giant fluid pressure of hydrogen. Therefore, fluids initially saturated with hydrogen are transformed into CH4-rich fluids (3H2 + CO = CH4 + H2O). In the deeper part of modern Earth's upper mantle, the fluid mainly composed of the mixture of H2O–CH4–H2–C2H6 [Zhang, Duan, 2009]. It is very possible to generate methane and ethane under mantle conditions. When ïňĆuid ascends across the boundary between lithosphere and asthenosphere, the reduced species may be oxidized and the fluid is mainly composed of H2O–CO2–CO [Zhang, Duan, 2009]. However, even in the modern oxidative regime of the Earth degassing, endogenous hydrocarbons are being emanated to the surface of the continental and oceanic crust. X. "Instead one could look to the depleted melts in olivine-hosted melt inclusions from the Ontong Java Plateau (Jackson et al., 2015) which indicates a range of CO2 comparable to that in the mid-Atlantic popping rocks with CO2 contents (Cartigny et al., 2008; cf Dasgupta and Hirschmann, 2008). Methane goes unmentioned." Olivine-hosted melt inclusions really have high CO2 contents. At the same time, olivine-hosted melt inclusions possess a large redox heterogeneity in magmatic systems [Frost et al., 2008; Hartley et al., 2017], which indicates the impossibility of the existence of a single formal degree of oxidation of carbon (-4). Hydrocarbons and organic matter of Archean rocks [Schreiber et al., 2017] with varying degrees of carbon oxidation are relics of the ancient degassing of the Earth. XI. "91-102 This paragraph is entirely irrelevant to the Hadean conditions at the origin of life 117 (marine sedimentary rocks, gas-hydrates, mud volcanoes, black smokers, hydrocarbon seeps)" These are all examples of modern oxygen-free environments for the study of anaerobic oxidation of methane (AOM). XII. "141 the sole source of reduced carbon for primordial metabolism (Nitschke and Russell, 2013). They presented a model of the methanotrophic acetogenesis with methane as half the carbon source" I agree. Such a model is assumed there, CH4 and CO2 are assimilated in the biomimetic reconstructed reversible WL path. XIII. "146 Consider adding Wong et al., 2017)?" Yes thank you. Indeed, the possible appearance of strong oxidizing agents in hydrothermal systems is shown. XIV. "I don't consider the phrase "whereas the pre-LUCA period proceeded in a reducing environment with a signiïňĄ-

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cant predominance of methane" has been irrefutably argued." Apparently "irrefutably argued" it is too affirmative. Not so categorical: "whereas the pre-LUCA period proceeded in a reducing environment with a signiïňĄcant predominance of methane" has been to some extent argued." The given examples of theoretical calculations, experimental modeling and data on gas-liquid inclusions in the minerals of Archean rocks show that apparently the methane atmosphere and hydrosphere are possible in some periods of the Archean and Hadean era. XV. "156 consider referencing McGlynn et al., 2018 here. 160 Smith and Morowitz, 2004; Marakushev and Belonogova, 2009, 2013; Fuchs, 2011; 179 "metabolic cycles, for example, fumarate+CH4 ! 2-methylsuccinate" Did I miss something? How were the very ïňĄrst methane molecules entrained into the cycle before the carboxyl-bearing pyruvate was generated?" Pyruvate, which is found even in carbonaceous chondrites, could be synthesized abiogenically, as, for example, in experiments in the presence of the organometallic phases [Cody et al., 2000]. The formation of succinate and acetate during the oxidation of ethane in hydrothermal systems is theoretically shown in [Marakushev, Belonogova, 2009]. XVI. "228 it is NOT "obvious that methane oxidation with nitrogen compounds is thermodynamically very favorable" because thermodynamics includes kinetics, and they are certainly extremely unfavorable." Well, this is nagging. It is also clearly written that the methane oxidation with nitrogen compounds is thermodynamically very favorable, especially in contrast to the sulfate-sulfite pair. The answer to the question about the unfavorable kinetics of methane oxidation is to solve the problem of methane C–H bond activation or oxidant activation. This problem was partially discussed when I responded to remarks of referee # 1. XVII. "265 Table 2 would beneïňĄt from displaying the free energy availability of the fumarate + CO2 reaction and CO2 + pyruvate. But the disequilibria is between CH4 (and H2) inside and CO2 (and nitrate/nitrite or Fe3+ or Mn4+) outside so how could the barely evolved and defenseless metabolizing system(s) resist the CO2?" It's a good idea to give in the table the free energies of the CO2 fixation reactions of the MF cycle components for comparison. In the table, it is interesting to consider reactions 6 and 7 of carbon fixation with pyruvate. Comparison of carbon assimilation reactions

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in the form of CH4 or CO2 indicates that under standard conditions the free energies of the reactions are almost the same, then with increasing temperature and pressure, thermodynamics becomes much more favorable when CH4 is fixed. From the some data it can be seen that the thermodynamically CH4 fixing system can resist the CO2 fixation.

Table. Free energy of reaction of CO2 and CH4 fixation (ΔG0T) at PSAT. ΔG0298 kJ/mol ΔG0473 kJ/mol Acetogenesis 1 CO2 + 2H2 = 0.5CH3COOH (Acetate) + H2O. -84.75 -57.65 2 CO2 + 4FeS + 5H2O = 0.5CH3COOH+ 2Fe2O3 + 4H2S 174.47 160.22 3 CO2 + 2Fe2O3 + 8H2S = 0.5CH3COOH + 7H2O + 4FeS2 -399.13 -275.54 4 CO2 + 2.67FeS + H2O = 0.5CH3COOH+ 0.67Fe2O3 + 1.33FeS2 -18.34 13.36 5 CO2 + 2Fe2SiO4 + H2O = 0.5CH3COOH + 2Fe2O3 + 2SiO2 -17.83 31.16 Carbon fixation 6 CH3(CO)COOH (Pyruvate) + CO2 = CH2CO(COOH)2 (Oxaloacetate) 13.11 35.03 7 CH3(CO)COOH + CH4 + 12Fe2O3= CH2CO(COOH)2 + 2H2O + 8Fe3O4 12.52 -17.84 8 CH3(CO)COOH + CH4 + 3FeS2 + Fe3O4 = CH2CO(COOH)2 + 2H2O + 6FeS 78.23 52.84 9 CH3(CO)COOH + CH4 + 4Fe3O4 + 6SiO2 = CH2CO(COOH)2 + 2H2O + 6Fe2SiO4 103.3 27.6 Free energy of formation from [Shock, 1995; Amend and Shock, 2001; Marakushev and Belonogova, 2012; Marakushev and Belonogova, (El. Suppl. Mat.), 2013]. XVIII. “This is a complicated enzyme involving large-scale electroconformational coupling (Grabarse et al., 2001; Scheller et al., 2017) – not an obvious prebiotic entity.” Sorry, it was not clear. Was meant biomimetic analogue of the enzyme active center: 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 cluster of methyl coenzyme M reductase or iron-cupper cluster of methan-monooxygenase. XIX. “327 “The high stability of the succinate-fumarate-acetate paragenesis in hydrothermal systems at 200 (473 K) was experimentally shown (Estrada et al., 2017).” This is rather high for metabolic reaction” The stability of the paragenesis of intermediates of protometabolic cycles at high temperatures confirms the possibility of their self-organization and development in high-temperature hydrothermal systems. XX. “331. Figure 3. Please add

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(HM), (PPM), (QMF) to this useful figure." HM, PPM, QMF equilibrium oxidative mineral buffers in fig. 3 marked dashed lines.

The evolution of the Earth is part of the overall evolution of the solar system, many of the planets and satellites of which have modern hydrocarbon degassing. Even Mars that has lost its endogenous activity is still showing methane exhalation. There are theoretical calculations, experimental and geological data, which are evidence of the existence of significant methane degassing in Archean. Hydrothermal systems of the ancient Earth, similar to the modern Lost Sity, under conditions of methane degassing could be widespread in the hydrosphere. Organic substances (aldehydes, carboxylic acids, etc.) synthesized in these "chemical reactors" could form prebiotic autocatalytic cycles capable of assimilating methane.

Thanks to the referee #2 for often valid criticism and valuable advice. According to one of them, we give the MF cycle in Fig. 2 with structural formulas.

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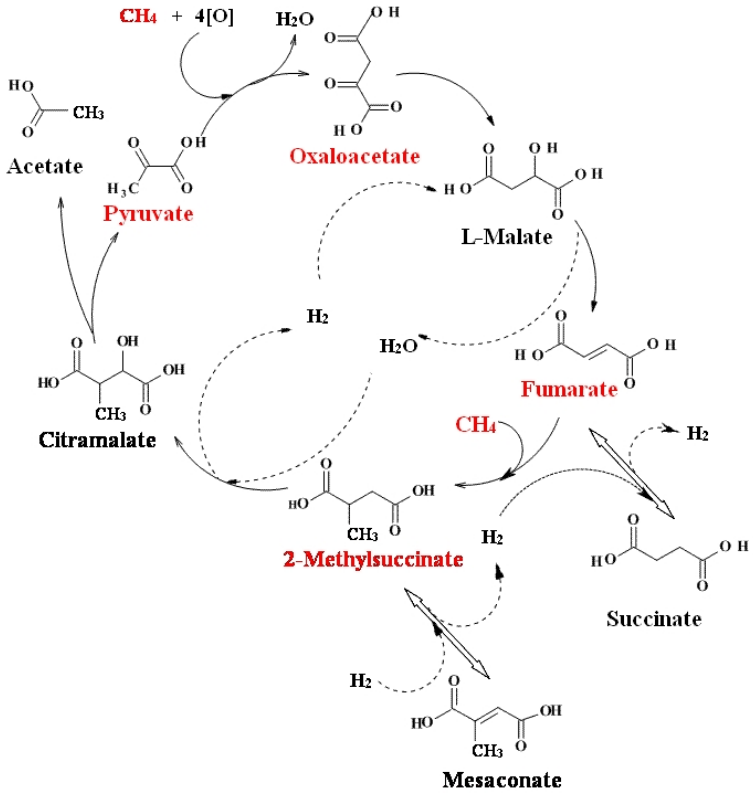

Fig. 1.

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