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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

Anonymous Referee #3

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The paper by Marakushev and Belonogova provides a hypothesis for an early metabolism based on anaerobic oxidation of methane. In biology today, two unique routes of methane oxidation are known: 1 archaeal which makes use of enzymes known from methanogens, and one found in bacteria which makes use of a separate set of enzymes and is oxygen dependent. Unique to this proposal, two methane molecules are used per cycle. This proposal is highly creative, but it also seems highly unlikely, since methane is notoriously difficult to oxidize and doing this twice in one cycle would be doubly kinetically challenging. The manuscript in its current form will

be difficult to be understood by many readers, and it contains a number of statements which preclude publication in the current form. I recommend the authors try to better explain their diagrams in particular, since they use a vocabulary which may be foreign to many biochemists and chemists. Below are minor comments that need clarification: Why isn't Korzhinskii, D.S., 1959 cited? Didn't that author develop the paragenesis idea? This book is not known in my field, therefor some introduction and development of this idea is important here. Line 42 and 55: The process described as "impulse degassing" does not clarify the nature of this process and a description of it cannot be found in the reference (Touret, 2003). Line 43: (Touret, 2003) points towards a metamorphic origin of the methane inclusions or most likely a hydrothermal vent system, but originating from mid-crustal depth at best, therefore not from the earth's core. Line 47: Significant concentrations of CH_4 should be substituted by estimated values. The upper limit of concentrations of abiogenic CH_4 has been given by Fiebig et al. 2007 as 50-80Mt/year, derived from serpentinization reactions in the ultramafic crust. These authors calculated that abiotic methane emissions would be around 1% of those today which are biologically driven. The above citations describe serpentinization reactions as the source of H_2 and none deal with H_2 degassing from the Fe-Ni core. How can the authors explain this? Line 51: Lost City Line 62: what is the meaning of silicate shells? What is the meaning of this statement and what are the references. Line 64: what is the meaning of "Oscilliatory nature of the geomagnetic field"? what references support this idea? Line 86: what does "determine the alkaline slope in the development of magmatism" mean? What are the references and why is it relevant to this paper? Line 94: What have you demonstrated? I don't see any demonstration. Line 97 – 101: This section is not clear and needs revision. How could it be that "different regimes of fluid degassing determined the emergence and development of various systems of ancient metabolism"? Line 120-122: This is incorrect, M. oxyfera was not shown to generate nitrite, but rather to consume it. Please read Haroon et al 2013 Nature. Line 147. Citations are needed with reference to the acetogeneic pathway possibly being in the LUCA. Gunter Wachtershauser? Mike Russell? Eric Smith? Bill Martin? Line 155:

There is no evidence that I know of about this “predominance of methane” – how can the authors make this claim? What are the citations? Line 176. Is there ANY evidence that methane can react with fumarate in this way? According to Beasley and Nanny 2012, the reaction is extremely difficult DOI: 10.1021/es3009503. Line 185-189: The autocatalytic nature of intermediates of the citric acid cycle has never been shown and the notion that they are versatile (in terms of functions, assembly or as reaction intermediates?) requires references. Line 188: Which oxidants and where would they come from? Line 203: Please indicate that the subscript numbers correspond to degrees K. Line 219-220: Not clear what this sentence means. Line 229: Why is sulfate/Sulfite considered? No organisms are known that only do this, they may reduce all the way to sulfide, or sulfite to sulfide, but this is not a reasonable redox couple. Table 1: the authors state that the reactions are more energetic in the “ionized form” which I interpret to mean making acetate where the carboxy group is deprotonated. However, the reaction energies all seem fairly comparable except for that involving 4HNO2. What is the pKa of protonating NO2? Line 245: It is not possible to oxidize sulfate. Line 251: Paraphrase to make the meaning clear Line 254: verb missing at the end of the subordinate clauses Line 258: example or reasoning behind the large energy barrier Line 284: In prebiotic hypotheses of Russell and Wächtershäuser the reacting minerals, namely Mackinawite and Greigite, resemble the structure of the FeS-cluster catalyzing the reaction whereas here none of the mineral catalysts resemble the nitrogen coordinated Ni-centers in F430. Line 288: Why is it highly possible? I’m not convinced. Line 307: What is “nonvariant equilibria” Line 382: What is the reasoning behind this statement? It could be that early life was all heterotrophic and that autotrophy was late, so I’m not sure we need to believe in a greater variety of early carbon fixation schemes. Figure 1: The composition ratio of the H-C-O compounds does not contribute to a deeper understanding of the underlying properties of the geodynamic regimes/ reaction conditions/ catalysts that perform these reactions. Figure 2: Is an enzymatic reaction known that can insert a hydroxyl group into the C2 position? Mechanistically this seems too difficult. Figure 3: axis labeled in Russian. Please clarify this depiction of chemical potential. Does it mean that above the line, the reaction proceeds right to left, and below the line, the reaction proceeds left to right? What does the vertical line with fumerate, succinate, and acetate correspond to?

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