

## ***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 #1**

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This paper makes the case for a hypothetical methane-fumarate metabolism on the basis of thermodynamic considerations and provides a rough geochemical scenario for how it might be driven. The idea is interesting but I have some serious concerns with the proposal on the basis that it ignores recent advances in phylogenetics but more importantly on the basis that several of the proposed chemical reactions are highly kinetically unlikely.

The authors state “Lateral gene transfer and subsequent phylogenetic divergence erased most evolutionary information recorded in ancestral prokaryotic genomes. Cur-

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rently, it remains unclear which, among the existing genomes, are ancient and sourced from the last universal common ancestor (LUCA) (Martin et al., 2012).” This statement is a bit out of date. In 2016, Martin and co-workers developed reconstruction techniques that attempt to distinguish between genes that might be widespread by virtue of LGT versus those that are indeed ancient (10.1038/nmicrobiol.2016.116). This study points to a small collection of genes that are likely to have been present in LUCA. In fact, such genes indicate the presence of enzymes that code for enzymes used in the Wood-Ljungdahl pathway of CO<sub>2</sub> fixation.

The authors may want to refer to a recent report of abiotic chemistry that parallels the Wood-Ljungdahl pathway (10.1038/s41559-018-0542-2).

I think it would be highly useful for some readers if the proposed methane-fumarate cycle were drawn out showing the chemical structures of the intermediates.

The present paper considers only the thermodynamic feasibility of the proposed reaction network. In agreement with the authors proposal, it would be good to mention that the proposed reactions oxaloacetate → malate → fumarate → succinate have been abiotically demonstrated (10.1038/s41559-017-0311-7). However, several of the reactions in the proposed cycle are highly kinetically unfavorable. If the proposal is indeed that they would have occurred abiotically this would pose a serious problem. The C-H bond of methane is highly kinetically stable and the activation of methane is a longstanding challenge for chemistry. Reports of methane activation in the chemical literature do exist, but they usually involve very strong oxidants such as persulfates under highly acidic conditions or the use of highly reactive radicals or cations to abstract a C-H bond. It is difficult to imagine abiotic chemical conditions to allow for the methane oxidation that would not also destroy the other intermediates proposed here, such as the ketoacids. Accordingly, it has been demonstrated that the reaction sequence described above is driven in reverse under oxidizing conditions such as those required to enable C-H activation of methane (10.1038/s41559-017-0083). This poses a chemical problem for this proposal.

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