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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

Sergey A. Marakushev and Ol'ga V. Belonogova

shukaram@yandex.ru

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Dear editor!

I. Serious comments of reviewers and interesting proposal reviewer 2 forced us to reconsider the proposed MF cycle with the inclusion of CO2 fixation stage This forced us to reconsider the thermodynamic and kinetic possibilities of the functioning of the cycle in hydrothermal conditions with a significant presence of methane. Firstly, the stoichiometry of the cycle reactions began to coincide with the assimilation of CO2 and

CH4 in many cases of methanotrophic acetogenesis and, secondly, the cycle became truly autocatalytic, for example, doubling malate in a cycle using CH4 and CO2 as substrates: C4H6O5 (malate) + 1,5CH4+2,5CO2 = 2C4H6O5. Despite the comments of reviewer 3, the methane reaction with fumarate still satisfies the "minimal energy requirements" for autotrophic growth [Beasley, Nunny, 2012]. II. This change in the functioning of the cycle makes it necessary to change the structure of the article and the thermodynamic table of the cycle reactions, and this, taking into account the substantial comments of the reviewers (especially reviewer 3), will take some time. III. I appeal to the editors of the journal about the possibility of resubmission of the article, with replies to the reviewers comments, after a while. denial of the existence IV. A very powerful argument from reviewers is the denial of the possibility of the existence of significant methane degassing on the early Earth. However, despite a developing consensus that the Hadean mantle and surface environments were relatively oxidizing [e.g., Kasting, 2014], some geological evidence points to more reducing conditions [e.g., Yang et al., 2014]. The major species in the gas phase under oxidizing magmatic conditions will be CO2 and SO2, as in modern basalts. The major species in the gas phase under reducing conditions will be CO, CH4 and H2S [Iacono-Marziano et al., 2012; Yang et al., 2014]. There are also good reasons to believe that methane was a significant gas in the Archean and Haden atmosphere and hydrosphere [Pavlov et al., 2000; Touret, 2003; Schaefer, Fegley, 2007; Shibuya et al., 2016; Large et al., 2018], in which case it could also be the source of nascent autotrophic paleometabolism. Fluid methane degassing of the Earth (i.e., the existence of significant concentrations of methane in the Archean and Hadean lithosphere) is confirmed by the existence of hydrocarbon gas-liquid inclusions in ancient minerals [Schreiber et al., 2017]. In addition, high-temperature deep synthesis of methane, rather than low-temperature process of serpeninization (about 100°C), is the main source of methane in seeps and hydrothermal vents even now [e.g., Scott et al., 2004; Huang et al., 2017; Brovarone et al; 2017: Wang et al., 2018]. This conception will also be further additionally reviewed.

With respect Sergey Marakushev

Beasley K.K, Nunny M.A. Potential Energy Surface for Anaerobic Oxidation of Methane via Fumarate Addition, Environ. Sci. Technol. (2012) 46(15), 8244–8252. doi: 10.1021/es3009503. Brovarone, A. V., Martinez I., Elmaleh A., Compagnoni R., Chaduteau C., Ferraris C., Esteve I. Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates from the Italian Alps. Nat. Commun. (2017) 8, 14134. doi: 10.1038/ncomms14134. Huang F., Isabelle D., Cardon H′., Montagnac G., Sverjensky D.A. Immiscible hydrocarbon ïňĆuids in the deep carbon cycle, NAT. COMM. (2017) 8:15798, doi: 10.1038/ncomms15798. Large R.R., Mukherjee I., Zhukova I., Corkrey R., Stepanov A., Danyushevsky L.V. Role of uppermost crustal composition in the evolution of the Precambrian ocean–atmosphere system, Earth and Planetary Science Letters (2018) 487, 44–53. Iacono-Marziano, G. et al. (2012). Extremely reducing conditions reached during basaltic intrusion in organic matter-bearing sediments. Earth Planet. Sci. Lett. 357, 319–326. Pavlov A.A., Kasting J.F., Brown L.L., Rages K.A., and Freedman R. (2000) Greenhouse warming by CH4 in the atmosphere of early Earth. J Geophys Res 105:11981–11990. Schaefer L., and Fegley J.B. Outgassing of ordinary chondritic material and some of its implications for the chemistry of asteroids, planets, and satellites: Icarus (2007) v. 186, p. 462–483, doi:10.1016/j.icarus.2006.09.002. Schreiber U, Mayer C, Schmitz OJ, Rosendahl P, Bronja A, GreuleM, et al. Organic compounds in fluid inclusions of Archean quartzâĂŠAnalogues of prebiotic chemistry on early Earth. PLoS ONE (2017) 12(6): e0177570. doi: 10.1371/journal.pone.0177570. Scott H.P., Hemley R.J., Mao H., Herschbach D.R., Fried L.E., Howard W.M., Bastea S. Generation of methane in the Earth's mantle: In situ high pressure–temperature measurements of carbonate reduction. Proc Natl Acad Sci USA (2004) 101: 14023–14026. doi: 10.1073/pnas.0405930101. Shibuya T., Russell M.J., Takai K. Free energy distribution and hydrothermal mineral precipitation in Hadean submarine alkaline vent systems: Importance of iron redox reactions under anoxic conditions. Geochim Cosmochim Acta (2016) 175: 1-19. doi: 10.1016/j.gca.2015.11.021. Wang, D.T., Reeves, E.P., McDermott, J.M., Seewald, J.S., and Ono, S. Clumped isotopologue constraints

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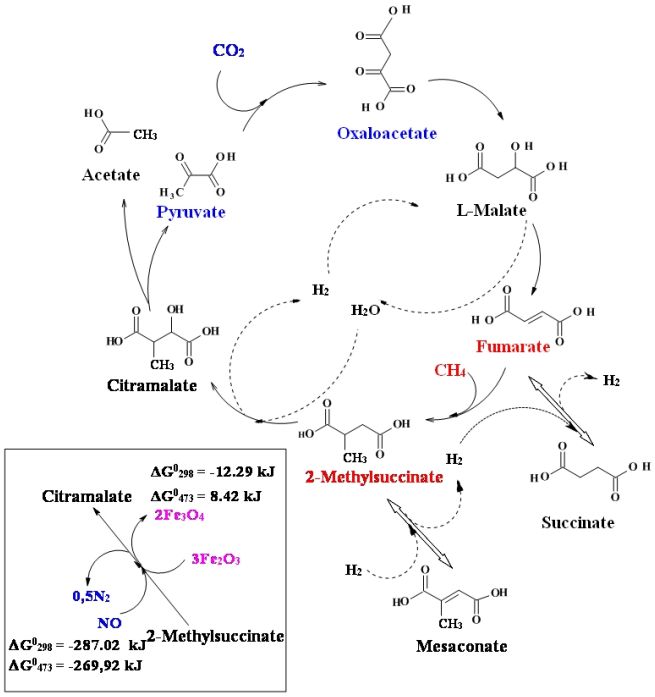
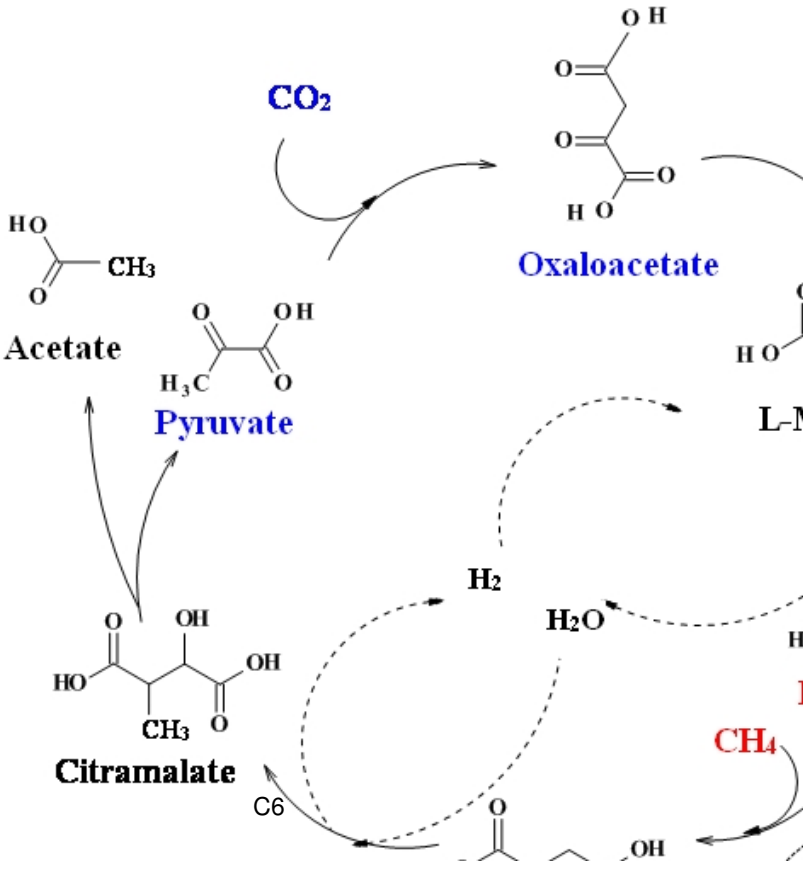


Fig. 1. The scheme of the proposed methane-fumarate (MF) cycle



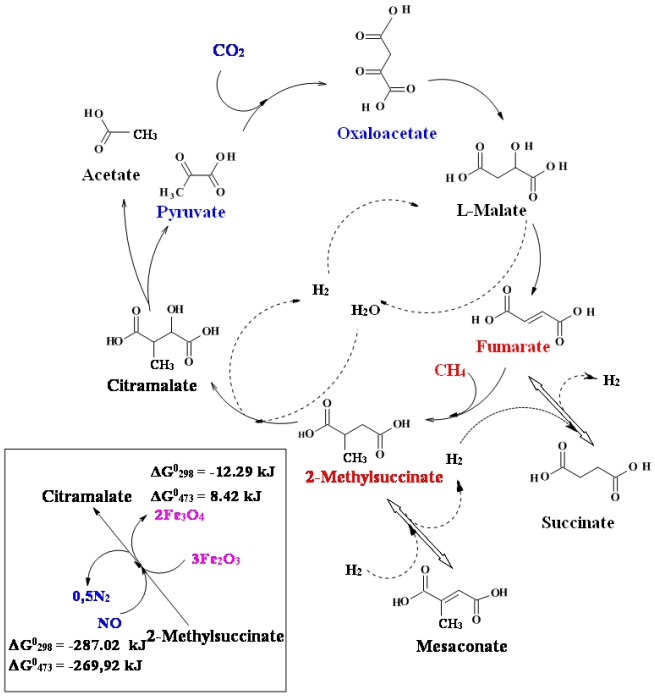

CO2
Oxaloacetate
Acetate
Pyruvate
L-Malate
H2
H2O
Fumarate
Citramalate
CH4
H2
2-Methylsuccinate
Succinate
H2
Mesaconate
ΔG0298 = -12.29 kJ
ΔG0473 = 8.42 kJ
Citramalate
2Fe3O4
3Fe2O3
0,5N2
NO
2-Methylsuccinate
ΔG0298 = -287.02 kJ
ΔG0473 = -269,92 kJ

Fig. 3.