Review of Marakushev Development of nascent autotrophic carbon fixation systems

The proposal made in this manuscript is that the first carbon fixation system was via a methane-fumarate cycle. This is an original and potentially highly significant hypothesis in that it might explain how, and from where, the reduced carbon was contributed to the first biomolecules. However, it is much more of a stretch to argue that even the carboxyl radical carbons were so derived. Indeed, the evidence to support the methane-only feed is misleading. The authors assertion that there were "two main regimes of degassing of Earth in the form of CO_2 or CH_4" exaggerates the likely volume of (anyway diffuse) exhalations of magmatic methane as compared to carbon dioxide. The evidence for methane exhalation is based on Touret's qualified suggestion that there was likely hydrothermal methane exhaling in the early Archean (3.8) (2003), but even this suggestion is qualified, and the possibility of it being biogenic is admitted. That Fiebig et al., 2007 invoke hydrothermal CH_4 is not in dispute, but to quote Haqq-Misra et al. 2008 here is wrong. These authors clearly state that the supposed high atmospheric methane concentrations that apply to the late Archean are the result of "biological productivity of the Archean ecosystem" (Haqq-Misra et al. 2008)! And Etiope, 2017 argues that methane is likely produced by Fischer-Tropsch Type reactions during low temperature serpentinization (typically <100°C). Also, I could find no mention of methane in Dodd et al. (2017); only that their observations "are consistent with an oxidized biomass and provide evidence for biological activity in submarine-hydrothermal environments more than 3,770 million years ago."!

So yes, there were methane emanations on the early Earth just as today, but for life to emerge required a steady and focused delivery rather than the diffuse and spasmodic delivery from basaltic lava flows. Thus, the view that (all the) ancestral carbon used in metabolism may have been derived from the generation of hydrocarbons from impulse degassing of the Fe-Ni liquid core is not persuasive on present evidence. Geologists, geochemists and mineralogists have long considered the Earth's early post-Theia impact, volcanically-derived atmosphere to have been relatively oxidized (Rubey, 1951; Poole, 1951; Goldschmidt, 1952). Indeed, at the dawn of the Hadean such volatiles would have been dominated by H_2O, CO_2, SO_2, N_2 and minor concentrations of NO_x (Yung and McElroy 1979; Dasgupta and Hirschmann 2006; Martin et al. 2007; Hirschmann et al. 2009; Wong et al. 2017).

It is true of course that these "waters" were muddied by Harold Urey's 1952 argument that metallic iron-bearing planetesimals (chondrites) impacting the young Earth would have volatilized to produce a >10,000°K early atmosphere out of which would rain native iron and silicate micro to macro spheres, so producing a highly reducing atmosphere comprising H_2, H_2O, CH_4, N_2 and NH_3 (Urey, 1952). With Urey as advisor, a direct result of these assumption were Miller's famous experiments that produced "prebiotic" molecules such as amino acids which had the effect of reinforcing Haldane's 1929 idea of a prebiotic soup (Haldane, 1929). However, the hydrides in this super-hot atmosphere would have been rapidly photo-oxidized and much of the hydrogen lost to space. Now the prejudices that derived from the Miller-Urey experiments (Miller, 1953, 1955) are finally being abandoned and, in my opinion, it would be retrograde for these dated views to be revived here.

Geochemical and isotopic evidence now strongly supports the earlier geological views that the atmosphere, was relatively oxidizing with the same gases as assumed by those pre-Urey scientists that the Hadean atmosphere and ocean 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 may seem surprising given that the Earth is largely an amalgam of metal-bearing chondrites, many of them carbonaceous. The reasoning goes that as the olivine-rich mantle is subjected to pressures beyond ~ 21 GP, it tends to metamorphose to perovskite, a mineral that requires a 3+ valence metal, normally aluminum. However, as there is negligible aluminum in the mantle, iron in the olivine disproportionates with Fe(III) deputising for Al(III) while the native iron tends to gravitate to the core (Wood et al. 1990, 2006; Shock, 1992; Wade and Wood 2005; Frost et al. 2008).

Thus wouldn't it be more reasonable to argue, given the early ocean was very likely carbonic (bearing several moles of CO_2) and that the alkaline hydrothermal springs carried methane (<3mmol) as well as hydrogen (15mmol), that the first cells exploited both sources of carbon, CH_4 *and* CO_2? CO_2 could then be reduced to CO while the methane-fumarate pathway might account for the entry of reduced carbon. Would the authors consider modifying their hypothesis, keeping their original idea, but also involving CO_2 to offer the carboxyl radical?

Detailed considerations

50 spelling: ([CO_2]/[CH_4]) (**Rainbow**, Von Damm)

51 spelling: (Lost **City**, Lucky Strike)

62 "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)

87 "With increasing alkalinity in the fluid inclusions of igneous minerals invariably appear different hydrocarbons (Potter and Konnerup-Madsen, 2003)." 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. Or they maybe late mineralizing fluids (Nivin et al., 2005 state that "The hydrocarbon gases are most likely the product of a series of post-magmatic abiogenic reactions related to carbonatite."

I interpret this to imply that they are 1) not derived the core and 2) to be irrelevant to Hadean magmatism! 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.

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**)

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,

146 Consider adding **Wong et al., 2017**)?

154 I don't consider the phrase "whereas the pre-LUCA period proceeded in a reducing environment with a significant predominance of methane" has been irrefutably argued.

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+CH_4 → 2-methylsuccinate"

Did I miss something? **How were the very first methane molecules entrained into the cycle before the carboxyl-bearing pyruvate was generated?**

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**.

265 Table 2 would benefit from displaying the free energy availability of the fumarate + CO_2 reaction and CO_2 + pyruvate.

But the disequilibria is between CH_4 (and H_2) inside and CO_2 (and nitrate/nitrite or Fe^{3+} or Mn^{4+}) outside so how could the barely evolved and defenseless metabolizing system(s) resist the CO_2?

275-287 "Therefore, different proto-metabolic cycles could be formed….. Methyl group formation by the oxidation of methane is limited by kinetics, because the dissociation energy of the C–H bond in methane (439 kJ/mol) exceeds that of the X–H bond in other organic molecules, with the exception of the O–H bond in H_2O (497 kJ/mol) and other oxygen-derived molecular species." YES!

"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 enzyme of methanogenesis, namely, methyl coenzyme M reductase."

Please explain. This is a complicated enzyme involving large-scale electroconformational coupling (Grabarse et al., 2001; Scheller et al., 2017) – not an obvious prebiotic entity.",

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

331. Figure 3. Please add (HM), (PPM), (QMF) to this useful figure.

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