How could life have mounted those first steep endergonic steps?

MICHAEL JOHN RUSSELL

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, USA: mrussell@jpl.nasa.gov

Life is not an improvement upon sluggish chemical or geochemical reactions – it really is different. Life is the carbon fixation engine, made up of a host of support engines or enzymes, that overcome thermodynamic barriers to the reduction of CO_2 – in Bernal's words, 'to produce a small but ever-renewed stock of organic molecules' [1]. Indeed, the hydrogenation of carbon dioxide is life's raison d'être, as it must have been from the very beginning. Yet autotrophic metabolic pathways face steeply endergonic barriers, so how are, and how were, they overcome? The answer is counter intuitive. Those barriers, for example, the reduction of CO_2 to CO and the putative oxidation of CH_4 on two likely paths to activated acetate and pyruvate, are mounted through Brownian impacts [2]. The supposed exergonic driving reactions, although necessarily greater than the driven ones, aren't drivers at all, but are reactions that merely prevent the reverse reaction, as a myriad of recent papers attest [2-4]. However, to enable the necessary coupling of endergonic with exergonic reactions does require enzymes, i.e., free energy converters or turnstiles [2-4].

So how could the protoenzymes or nanoengines required to get life going in the first place come about? Were there 'minéral trouvé' available in life's original hatchery to effect these roles? Arrhenius [5] considered green rust (e.g., $\sim[Fe^{II} > Mg >> Ni]_4Fe^{III}_2[OH]_{12}Cl_2.3H_2O$), with its brucite-like interlayers, the most likely candidate to have exhibited 'primitive cellular metabolic function'. Green rust rust would have comprisised portions of the alkaline submarine mound growing in the Hadean carbonic ocean [6]. That this mineral has been shown to reduce nitrate to the ammonium ion within ~200 minutes supports this view [7]. Beyond that, ferrous hydroxide 'catalyzes' the amination of pyruvate to alanine, which itself can be condensed to polyalanine on carbonates [9]. Futhermore it is likely that polyalanine could sequester the transition metal sulfides and oxides at the hydrothermal mound. If so, this would have opened up a ligand-accelerated autocatalytic cycle to seek out ways to ever increase the overall entropic output of the system [6].

[1] Russell & Hall (1997) *J Geol Soc Lond* **154**, 377-402. [2]

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