

IS HELICOIDAL GREEN RUST THE MISSING LINK BETWEEN HYDROTHERMAL CHEMISTRY AND BIOCHEMISTRY? M. J. Russell, P. Beckett, NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109 (mrussell@jpl.nasa.gov)

Arrhenius [1] was first to consider double layer hydroxides (DLHs, e.g., variable valence green rust, GR, $\sim\text{Fe}^{2+}_4\text{Fe}^{3+}_2\{\text{OH}\}_{12}\text{SO}_4^{2-}\cdot 8\text{H}_2\text{O}$) as exhibiting ‘primitive cellular metabolic function’, further suggesting ‘that it may be possible to synthesize the tape on which the information for life could be recorded, if we only knew how.’ One hundred years earlier, and troubled by similar thoughts, Barclay [2] had turned to the Jacquard loom – a semi-automated weaving machine introduced 100 years before that – for mechanical inspiration as to how life might have been first guided. Jacquard had demonstrated how a stored program comprising a series of perforated cards strung together could produce a patterned textile. Drexler, in his 1990 book *Engines of Creation*, placed the idea in a modern framework, reminding us that “...over three billion years before Jacquard, cells had developed the machinery of the ribosome”. That green rust can act like a multifunctional enzyme is demonstrated by the rapid reduction of $\text{NO}^-_{3/2}$ to ammonium [3], and thence the amination of carboxylic acids to amino acids [4]. At the same time, could aggregates of green rust comprising initially inorganic membranes at a submarine alkaline vent act as a digitally informed multi-functional engine with the potential to evolve partway toward LUCA – Fe^{2+} and Fe^{3+} acting effectively as mobile zeros and ones in the brucite layers [5]? After all, Génin and Ruby [6] have demonstrated that for GR_{sulfate} with ratio $2\text{Fe}^{2+}:\text{Fe}^{3+}$ the dianion distribution in the interlayers is propagatable across layers, resulting in significant long-range order of both cations and anions. Thus, information on the charge distribution from one sheet is transferred to adjacent sheets. However, as the Jin group [7] have demonstrated, the crystal growth of DLHs are driven by screw dislocations. Thus, the adjacent sheets actually comprise just one single dislocated layer. In these circumstances, dissipation of redox and pH disequilibria is likely to be quickened through feedback and -forward autocatalysis [8].

Equipped with these capabilities, a screw-dislocated helicoidal GR presents itself as a programmable proto-enzyme suite at the emergence of life to act as a general oxidoreductase, aminase, and polymerase. Encouraging such a view is the fact that the bilateral internal walls of the green rust interlayers are somewhat flexible, and respond both to charge and the size of the intercalating molecules [1,5,9]. Electrons released from hydrothermal hydrogen at a Ni-Fe site could hop along the *semiconducting* cationic layers in the green rust to the high potential acceptors $\text{NO}^-_{3/2}$ in the Hadean Ocean [8,9,10]. Synchronous charge hop-

ping will generate peristaltic motions on the brucite-like walls, i.e., doing ‘metabolic’ work along the way to reducing $\text{NO}^-_{3/2}$ to aminogen [8]. At the same time these oxidants provided high potential electron acceptors to drive endergonic steps, probably involving electron bifurcation, producing a methyl group from hydrothermal methane with the concomitant reduction of CO_2 to CO [8]. These findings lead us to propose that helicoidal green rusts were *the* multifunctional proto-enzymes that had the potential to act as the first guided metabolizing systems or vehicles to launch from the alkaline vent on the way to the first cells. In this hypothetical sketch we suggest that within these screw dislocated microcrystals, an expanding series of more specialized and discriminatory proto-enzymes were differentiated – a division of labor typical of bounded self-organizing systems. A rotational twinning screw dislocation and lattice twist gives the optimal arrangement for packing and a triangulated path length for the improvising metabolic system while maximizing product and assemblies thereof at low H_2O activity. It wasn’t until the emergence of the eukaryotes that life managed to construct a similar parking-garage structure of its own; the Golgi apparatus and associated helicoidally stacked endoplasmic reticulum sheets [11].

Reaction-diffusion processes within the interlayers would lead to improvised self-organizing flows of interacting molecules in an evolving metabolism [12]. Delamination or exfoliation through the accumulation of amyloid peptide at intervals in the galleries could be the initial cause of cell division [13]. Thus, the free energy extracted by such GR engines could be used to self-propagate, so reproducing *and* replicating with variation, ever-evolving metabolizing cellular nanoengines [14].

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