ABIOTIC ORGANIC SYNTHESES IN DEEP SUBMARINE, ALKALINE HYDROTHERMAL SYSTEMS CATALYSED BY Fe^0, MACKINAWITE, VIOLARITE AND GREEN RUST.

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The building blocks of life were likely generated between 25° and 150°C in the limbs, updrafts and secondarily entrained waters, of medium enthalpy alkaline Mg^{2+}-bearing submarine hydrothermal convective systems 4.4 to 4.3 Ga. Fe^0>>Ni^0 were the primary catalysts as well as the reducing agents. Carbon oxides were the feedstock. Introduced to the Fe-bearing ~10°C carbonic acid ocean at the point of exhalation, the hydrothermal OH^- and HS^- reacted with Fe^{2+} and photolytic Fe^{III}, to precipitate a mound of flocculates and films which, depending on pH, comprised ~$Fe^{II}_2Fe^{III}(OH)_7$ and FeS>>$FeNi_2S_4$. The films prevented direct neutralization while permitting restricted e^-, H^+ and small molecule flow, so 'preparing' constituents for phosphorylation, interaction and polymerization and enabling respiration. The temperature of the fluid trapped in the interior of the bubbles formed by the films was ~50°-100°C.

Mackinawite and violarite can catalyse the synthesis of activated acetate (cf. Huber and Wächtershäuser 1997) while at lower temperature, in the mound flanks, green-rust induces the generation of ribose-2,4-biphosphate at a yield of ~10% from glycolaldehyde phosphate and glyceraldehyde-2-phosphate (Krishnamurthy et al. 1999). Amidotriphosphate (AmTP) is a required reactant, perhaps synthesised in the green rust. AmTP converts glycolaldehyde to the phosphate in the presence of $MgCl_2$ (ibid). Glyceraldehyde is generated from the glycolaldehyde by reaction with formaldehyde at pH 10.5, again catalysed by a mixed valence double layer metal hydroxide (Krishnamurthy et al. 1999). And Yamagata et al. (1995) have generated AMP in 10% yield, though none of the 5'-phosphorylated product was formed. Such nucleotides may have been refluxed back into the mound.

In outline and extrapolating from this work we speculate that the phosphate of ribose-phosphate nucleotides polymerised as they registered stereospecifically, in the presence of acetate (Tessis et al. 1999), to the (001) surface of mackinawites comprising micro-channels in the membrane. Thus mackinawite acted as the template for RNA. Stacking interactions of the bases effectively offered a variety of triplet clefts to the side chains of amino acids supplied from the hydrothermal system (Mellersh 1993; Hennet et al. 1991). Also the clefts had just the right spacing and polarities to affiliate the alpha chain (Mellersh 1993). And N3 on adenine could have accepted a proton donated by the nucleophilic amino group when the pH oscillated to a low value. Thus N3 acted as an acid-base catalyst (cf. Muth et al. 2000). Alternations of pH within the membrane is to be expected as the bubbles periodically suffered invasion of the acid ocean during their fitful inflation with alkaline hydrothermal fluid. The effect of this "proton shuttling" was to polymerise the amino acid array. Thereby, freed of their bonds to the nucleic acids, the protopeptides could, depending on their sequence, react with other molecules in this milieu. Meanwhile, in a surviving bubble, the nucleic acid mould either attracted a new influx of similar amino acids to repeat the process, or as nucleic acid concentrations built up, the antisense RNA could be generated, the duplex unzipped by protons, and the information transported elsewhere for the codons to be reconstituted with fresh nucleic acid molecules. But to borrow a phrase from Ervin Laszlo, "chirality itself was probably settled in a war involving complex organisms, the progenote winning through, a progression from multiplicity and chaos to oneness and order".

The first 'useful' codons, bonded to mackinawite, may have been derived from the nucleotides guanine, cytosine and uracil (GCU) by triplet expansion and point mutation (Trifinov & Bettecken 1997). Thus, as Eck & Dayhoff suggested in 1966, the ancestral protein was derived from a repeated sequence coding for Ala (GCN), Asp (GAU), Ser (UCU) and Gly (GGU). They further suggested that Cys, Val, Pro and Gln were then incorporated to generate a polypeptide which, on doubling, sequestered $[Fe_4S_4]^{2+}$ to produce the first ferredoxin. Further doubling led to ferredoxins containing between two and twelve $[Fe_4S_4]^{2+/+}$ clusters. The ferredoxins and related iron-sulfur proteins served not only as electron transfer agents, hydrogenation enzymes and redox catalysts, but also as structural components of the first organic membrane. In this way they took over control of electron and proton transport from the iron sulfide in the films. The composition of the organic self-assembling membrane fillers which then kept the two fluids far from equilibrium may have been polymers of C-H-S-N such as $(C_8H_{16}S_5N_2)_n$. We conclude that metabolism and the genetic code emerged in tandem.

References:

See http://www.gla.ac.uk/Project/originoflife01