THE QUESTIONABLE PROSPECT OF DEEP SEA ALKALINE VENTS AS ORIGIN SITES David S. Ross SRI International (Retired) dsross3@yhoo.com

Introduction and Background: With presumed parallels to present-day bioenergy management, accounts over the past two decades have presented deep sea alkaline vents as sites for the start of life [1]. They posit that pH gradients of 6-10 across inorganic membranes provoke the conversion of phosphate to pyrophosphate, which then through its subsequent exergonic reversion to phosphate activates endergonic oligomerizations of neighboring nucleotides and amino acids.

Discussion: It is argued here that the flawed application of a number of kinetic and thermochemical factors challenge the viability of the proposition. The shortcomings include the absence of evidence supporting the existence of such membranes [2] and the apparent disregard of the prohibitive hydrolytic instability of oligonucleotides [3] which at vent temperatures and pHs should undergo full and exhaustive hydrolysis over characteristic times of hours. The accounts moreover describe the application of software tools that employ aqueous data bases and are designed unambiguously for aqueous geochemical modeling to support the notion of a hydrophobic and ostensibly nonaqueous membrane medium. Perhaps the most significant failure of the proposition is its violation of the second law of thermodynamics. The breakdown derives from the fact that while exergonic, pyrophosphate hydrolysis is anti-entropic at vent pHs. Its pairing with the negative reaction entropy of nucleotide oligomerization then dictates that the summed enthalpic yield of the pair boost the entropy of the medium sufficiently to effect second law noncompliance. The assigned intricate and multifarious catalytic features of the proposed medium, however, including phosphate confinement and peristaltic activity along narrow channels, are far too highly anti-entropic to be balanced by the modest enthalpic yields of assisted oligomerization, and compliance with the second law becomes unattainable.

Conclusion: Vent environments are highly corrosive and obstruct the spontaneous formation of both pyrophosphate and oligonucleotides; they are both kinetically and thermodynamically excluded from a role in life's beginnings. Fundamental perspectives dictate that an origins site include both an acidic rather than an alkaline medium and a means of shifting the Gibbs energies of the oligomerization reactions from end- to exergonic values while concurrently avoiding second law noncompliance. Those requirements are met in the evaporating pools within naturally occurring hydrothermal fields; that setting both shifts the oligomerization Gibbs energies through a swing in the properties of the aqueous medium from near ideal to highly crowded and nonideal [4], and provides a suitable second law offset arising from the highly entropy-positive evaporation of water.

References: [1] Russell MJ et al. (2014) *Astrobiology* 14:308–343. [2] Jackson JB (2016) *Journal of Molecular Evolution* 83:1–11. [3] Wächtershäuser G (2016) *Journal of Molecular Evolution* 82:75-80. [4] Ross DS and Deamer D (2016) *Life (Basel)* 6:28–34.