

RNA Oligomerization in Laboratory Analogues of Alkaline Hydrothermal Vent Systems. B. T. Burcar^{1,2}, L. M. Barge^{3,4}, D. Trail^{1,5,6}, E. B. Watson^{1,5}, M. J. Russell^{3,4}, and L. B. McGown^{1,2}, ¹New York Center of Astrobiology, Rensselaer Polytechnic Institute, 120 Cogswell, 110 8th Street, Troy, NY 12180 USA, ²Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 120 Cogswell, 110 8th Street, Troy, NY 12180 USA, ³NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109 USA, ⁴NASA Astrobiology Institute, Icy Worlds, ⁵Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute School of Science, 110 8th Street, Troy, NY 12180 USA, ⁶Department of Earth and Environmental Sciences, University of Rochester, 227 Hutchison Hall, Rochester, NY 14627 USA

Introduction: Determining pathways which could promote long-chain RNA formation under feasible prebiotic conditions has long been an important process in demonstrating the viability of the RNA World hypothesis. Intensive research efforts have provided evidence of RNA oligomerization using circular ribonucleotides [1], imidazole-activated ribonucleotides with montmorillonite catalyst [2], ribonucleotides in the presence of lipids [3], and ribonucleotides subject to wet-dry cycles [4]. Additionally, mineral surfaces such as borates, apatite, and calcite have been shown to catalyze the formation of small organic compounds from inorganic precursors, pointing to possible geologic sites for the origins of life [5]. The catalytic properties of these particular minerals provide compelling evidence for alkaline hydrothermal vents as a potential site for the origins of life since, at these vents, large metal-rich chimney structures can form that have been shown to be energetically favorable to diverse forms of life. Our research tests the ability of iron- and sulfur-rich chimneys to support RNA oligomerization reactions using imidazole-activated and non-activated ribonucleotides.

Experimental Methods: Synthetic hydrothermal chimney systems were created by injecting an anoxic solution of sodium sulfide and sodium silicate into an anoxic solution of ferrous chloride, contained within a modified weaton glass serum bottle. This method created iron-sulfide-silicate based precipitates which have been shown to have a significant degree of compartmentalization, sequester small organic molecules, and create an electrochemical gradient [6,7]. Imidazole-activated ribonucleotides (ImpX – where X is the nucleobase) and non-activated ribonucleotides were either simultaneously or sequentially injected into the chimneys. The effects of elemental composition, pH, inclusion of catalytic montmorillonite clay, doping of chimneys with small organic compounds, and *in situ* ribonucleotide activation on RNA polymerization reactions were investigated. The solutions were analyzed via Matrix Assisted Laser Desorption Ionization Time-Of-Flight Mass Spectrometry (MALDI-TOF MS) for oligomerization products, while the chimneys were elementally characterized using Laser Ablation Induc-

tively Coupled MS (LA-ICP MS) and electron microprobe analysis.

Oligomerization at Synthetic Chimney Systems:

Our initial experiments have shown, under certain conditions, successful dimerization using unmodified ribonucleotides, with the generation of RNA oligomers up to 4 units in length when imidazole-activated ribonucleotides were used instead. These results are significant since they demonstrate for the first time that nucleotide oligomerization can occur in synthetic alkaline hydrothermal chimney systems, and further, that oligomerization can occur for both the activated and unactivated nucleotide. A particularly exciting result is the detection of AMP dimers (and possibly, trimers) for oligomerization reactions of unactivated AMP in the chimney-forming systems with an untreated montmorillonite floor. This was not observed in the controls, nor has it been previously reported for montmorillonite-catalyzed oligomerization reactions in aqueous solution. The introduction of untreated montmorillonite into the chimney-forming system appears to improve overall oligomerization for both ImpA and AMP relative to that of the chimney alone. Oligomer length for ImpA reactions were increased to 4-mers when UMP was incorporated into a pre-formed chimney that subsequently had a solution of ImpA and sodium sulfide injected through it. We also observed that the addition of imidazole as a dopant led to a minor increase in oligomerization for ImpA-based reactions. In addition, elemental analysis of the chimney precipitates and the reaction solutions showed that most of the metal cations that were quantified were preferentially partitioned into the chimneys.

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