PREBIOTIC CHEMISTRY IN HIGH PRESSURE ENVIRONMENTS. K. L. Rogers[1,2], B. Burcar[2,3], M. Ackerson[1,2], E. Garbenis[4], E. B. Watson[1,2] and L. B. McGown[2,3], [1]Department of Earth and Environmental Sciences, (rogerk5@rpi.edu), [2]New York Center for Astrobiology, [3]Department of Chemistry and Chemical Biology, [4]Department of Civil and Environmental Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180.

Introduction: The pathway to life on Earth inevitably led sooner or later to the first molecules capable of self-replication, information storage and chemical evolution. Polymerization of these precursors is a necessary first step toward these capabilities and much attention has focused on the potential for RNA to polymerize abiotically into strands that eventually had sufficient length and the appropriate sequences for autocatalysis and self-replication. During abiotic RNA polymerization, hydrophobic, electrostatic, pi-pi, and hydrogen bonding interactions among nucleotide mixtures can affect reversible self-assembly or aggregation. These aggregates may play a critical role in the availability of nucleotides for incorporation into RNA polymers, therefore exerting a selective pressure on both polymer length and the sequence variability, which consequently affect the self-replication and information storage potential of the polymers.

The environmental parameters that effect RNA polymerization length and reversible self-assembly are poorly constrained, however a catalytic mineral surface and nucleobase activation are common components of RNA polymerization experiments. Additional environmental factors such as pressure, temperature, fluid chemistry, mineralogy and redox potential have not previously been investigated in detail, however these parameters can vary widely across the early Earth environments that could have given rise to prebiotic molecules essential for the emergence of life. Here we report on a suite of experiments investigating the effects of high pressure on abiotic RNA polymerization and aggregation, as well as the coupled effects of temperature and mineralogy at these conditions.

Experimental Methods: High pressure RNA polymerization experiments were conducted in a solid-media piston cylinder apparatus at 5kbar and 10kbar with samples contained in Ag capsules pressure-sealed at ambient temperature. Each triplicate experiment contained imidazole-activated mononucleotides in a buffer in the presence of a mineral catalyst. Parallel control experiments with unactivated nucleotides, or without mineral catalysts, and at ambient pressure conditions were also conducted in triplicate. Detection and analyses of RNA polymerization products were performed using Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS), by which linear and aggregation products can be characterized [1].

Effects of pressure, temperature and mineralogy on RNA polymerization: RNA polymerization experiments with imidazole-activated adenosine monophosphate and guanosine monophosphate with montmorillonite clay as the mineral catalyst at 5 and 10 kbar showed increased aggregation of short oligomers compared to ambient pressure experiments, though overall polymer length was not substantially different for variable pressure conditions. In geological systems temperature often increases concomitantly with pressure, and so the coupled effects of elevated temperature (50-100°C) and pressure on RNA polymerization were also investigated. Temperatures in excess of 75°C caused the nucleotides to dephosphorylate, thus preventing the formation of polymers in excess of 5 nucleotides in length. However, at 50°C and 5kbar imidazole-activated adenosine monophosphate formed polymers up to 10 nucleotides in length, with the addition of uncharacterized products that were not observed at ambient pressure.

To date, mineral catalysis of abiotic RNA polymerization has been demonstrated for certain montmorillonite clays in experiments that have generally been performed at ambient pressure [2]. However, early Earth environments hosted a variety of mineral assemblages and more mafic mineralogies were likely abundant in these environments, including deep-sea hydrothermal systems. To investigate the effects of both pressure and mineralogy on RNA polymerization we used nontronite, a mafic clay and common hydrothermal alteration product of basalt, in the place of montmorillonite. While nontronite did not catalyze RNA polymerization under ambient pressure conditions, oligomers up to 5 and 6 nucleotides long were observed at 5 and 10 kbar, respectively, showing for the first time a pressure-dependence of mineral catalytic function. RNA polymerization with mafic clays under high pressure conditions represents a novel geochemical environment for prebiotic chemistry.

Implications for early Earth chemistry: The results suggest that mineral catalysis of RNA polymerization could be a more common phenomenon in prebiotic chemistry than previously thought when examined under a wider range of early Earth environments.

References: [1] Burcar, B T et al. (2013) *OLEB 43*, 247-261. [2] Ferris, J P (2002). *OLEB 32*, 311-332.