

RIBOSE STABILITY IN SOLUTIONS WITH BORATE AND BORATE-BEARING CLAYS: IMPLICATIONS FOR ORIGINS OF LIFE ON EARTH AND MARS. S. A. Legett¹, C. M. Yeager¹, P. J. Gasda¹, M. A. Nellesen², L. J. Crossey², E. J. Peterson², N. L. Lanza¹, A. L. Reyes-Newell¹, D. M. Delapp¹, A. Labouriau¹, R. C. Wiens¹, S. M. Clegg¹, and D. Das³, ¹Los Alamos National Laboratory, Bikini Atoll Road, Los Alamos, NM ²University of New Mexico, Department of Earth & Planetary Sciences, Albuquerque, NM 87131, ³McGill University, Department of Earth & Planetary Sciences, Montreal, Quebec, Canada.

Introduction: One possible pathway for the origins of life is called the “RNA World” hypothesis, which hypothesizes that RNA is capable of spontaneously forming and enduring under prebiotic conditions and was likely the first means of transferring genetic information [1]. For RNA to form, ribose – which makes up the backbone of RNA – must first be present. Ribose can be formed from glycoaldehyde and formaldehyde, which have been found in interstellar materials and were likely present on Early Earth and Mars [2].

While ribose can be formed in alkaline solutions containing glycoaldehyde and formaldehyde, under these conditions, it has a very short (minutes- to hours-long) half-life and quickly transforms into a “brown tar” – the result of a caramelization reaction – before it can accumulate in any meaningful amount [2]. This study focuses on determining how ribose may have been stabilized under prebiotic conditions on Earth and Mars.

Background: Laboratory experiments have shown that borate in solution will preferentially complex with ribose. This complexation inhibits the caramelization reaction and stabilizes ribose in solution while also promoting phosphorylation, which is necessary to form the backbone of RNA [1, 2, 3]. Therefore, if borates were present in prebiotic environments on Early Earth and Mars, ribose could have been stable enough to accumulate and feed the chemical reactions needed for RNA synthesis.

As borate, boron is highly mobile and quickly goes into solution during weathering. However, borate in solution can be concentrated by sorbing to clays. On Early Earth, trace amounts of borates likely weathered out of major minerals before sorbing to available clay minerals in groundwater [2, 3]. On Mars, the ChemCam instrument on board the Curiosity rover recently found borate in Ca-sulfate veins within a clay-rich, lacustrine environment in Gale Crater, suggesting that similar processes may have happened there [4, 6]. Additionally, research associated with this project has shown that, under alkaline conditions, Mars-relevant clays can sorb 100s of ppm borate, while their Earth-relevant counterparts can sorb even higher concentrations of borate [5]. Because of this evidence for borate concentration on and association with clays on both Earth and Mars, we hypothesize that clays could function as a concentrating scaffold for ribose-borate complexes, eventually leading to the phosphorylation of ribose and RNA formation.

Methods: *Ribose degradation experiments.* We produced ribose-borate-clay solutions by dissolving a D-ribose standard along with sodium tetraborate decahydrate (AKA borax) in ultrapure water containing various Earth- and Mars-relevant clay minerals at various temperatures and pH levels representing potential prebiotic conditions on Earth and Mars. The ribose concentration (1 g / 100 mL water) was held constant for all tests, and experimental variables included: boron concentrations (0 ppm, 10 ppm, or 100 ppm), temperature (room temperature or 60 °C), pH (7–11), and clay compositions (Ca-montmorillonite, kaolinite, nontronite, saponite, and unknown clay from the Rio Tinto Borax Mine [5]). The clays either were left untreated prior to these assays or were pre-treated through boron sorption experiments [5]. The ribose solution pH was maintained throughout the experiments by monitoring with a pH probe attached to an autotitrator. Following initiation of the reactions, 100- μ l samples were taken at 1, 2, and 4 hours and immediately diluted with 400 μ l cold (≤ 4 °C) ethanol to stop the ribose degradation reaction prior to analysis via GC-HRMS.

GC-HRMS analysis. We used a LECO Pegasus GC-HRT+ 4D with a time-of-flight mass spectrometer in high-resolution mode to determine the extent of ribose degradation and discover what molecules form in the solution as a result of the ribose-borate-clay reactions. This analysis method allows us to differentiate the various pentoses (including ribose) present in solution despite all pentoses having the same mass. Prior to analysis, samples were dried and derivatized via methoximation and silylation in order to increase the stability and volatility of sugars during GC-MS analysis. After analysis, the data were processed using LECO’s ChromaTOF software to detect and identify chromatographic peaks.

Results and Discussion: In the reactions with ribose only, we noticed a dramatic change in the color of the solution throughout the experiment, while there was no change in color when borate was added to the ribose solution (Fig. 1). The color change in the ribose only solution is likely the result of ribose caramelization to the tar-like material mentioned previously, while the lack of color change in the solutions containing borate suggests that the transformation of ribose has been slowed in these experiments.

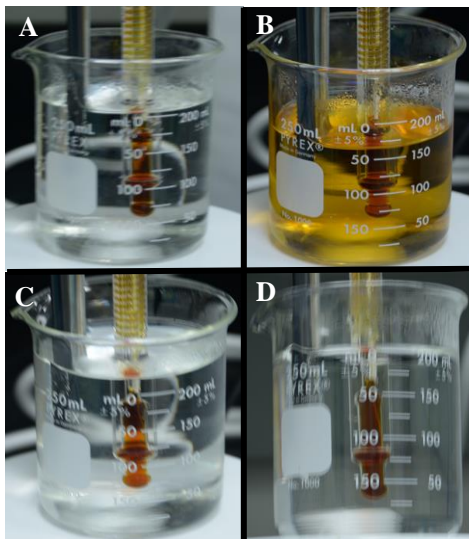


Fig. 1. Color change from initial solutions (A and C) to solutions after 4 hours (B and D). A and B = ribose only; C and D = ribose + 10 ppm B. This is consistent with the findings of [2].

Similarly, when we added clays to the ribose mixtures, we saw comparable color changes (Fig. 2). The unaltered Ca-montmorillonite (Mont A) began as white (Munsell 10YR 8/1) and became more yellow as it interacted with the ribose solutions, turning to light gray (10YR 7/2) when pretreated with boron sorption and very pale brown (10YR 7/3) when left untreated prior to the reaction with ribose. Again, this browning of the clays is likely the result of caramelization, which is more pronounced in the untreated clay compared to the B-sorbed clay.

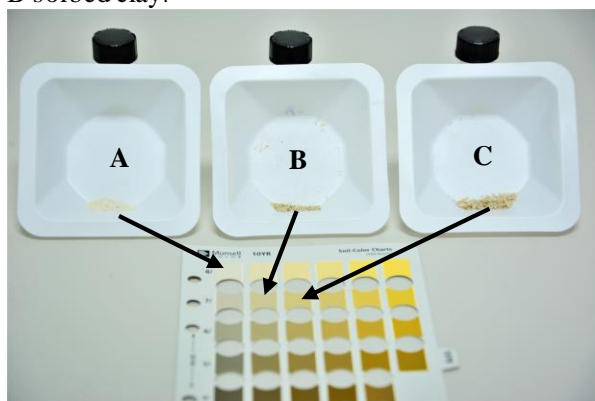


Fig. 2. Color change in clays. A is completely untreated, B is post-experiment pretreated w/ borate, and C is post-experiment untreated Mont A.

To track the degradation of ribose, we analyzed the difference in ribose peak areas throughout the experiments identified via GC-MS (Fig. 3). We found that at pH 10 and room temperature, 20% of the initial ribose disappeared after 1 hour in ribose only and ribose + 10 ppm B reactions, while the ribose concentration decreased by ~5% and remained stable throughout the rest

of the experiment when we added 100 ppm B to the solution, confirming that borate slows the degradation of ribose in alkaline solutions. At pH 10 and 60 °C, the ribose only and ribose + untreated Mont A reactions exhibited similar degradation trends. Again, we saw relatively early stabilization of ribose concentration in the ribose + 100 ppm B solution. Most noticeably, a rapid decrease in ribose concentration was observed in solution after 2 hours when mixed with the B-sorbed Mont A, suggesting that a different mechanism for ribose removal from solution is at work here.

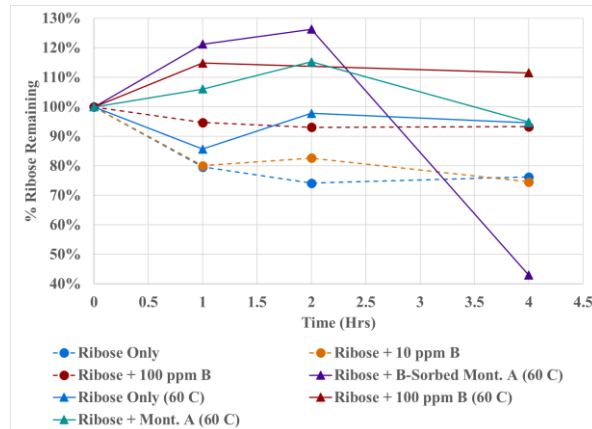


Fig. 3. Ribose remaining throughout experiments.

Conclusions & Future Work: Based on the work completed thus far, we conclude that: 1) the addition of borate to a ribose solution significantly slows the degradation of ribose consistent with [2], 2) the presence of untreated Mont A does not appear to affect ribose degradation in solution, and 3) borate sorbed to Mont A may be sufficient to remove ribose from solution to concentrate on the clay mineral surfaces. Alternatively, the presence of B-sorbed Mont A may cause and/or accelerate the breakdown of ribose and the production of other sugars and/or sugar alcohols.

Future work on this project includes extending the reaction periods to 12-24 hours, adding experiments with Mars-relevant clays, varying the experimental atmosphere to include nitrogen-only as well as air, incorporating different salinities into the solutions to assess the effect of competing ions representative of Early Earth- and/or Mars-relevant compositions, and performing Nuclear Magnetic Resonance and X-ray Diffraction analyses of the post-ribose experiment clays.

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