THE POTENTIAL FOR PREBIOTIC CHEMISTRY IN BORATE-BEARING CLAYS.
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Introduction: Boron has been detected in groundwater-emplaced veins of calcium sulfate (Fig. 1) in Gale crater, Mars with the NASA *Curiosity* rover ChemCam instrument [1,2]. The detection of boron in calcium sulfate veins implies that boron was oxidized to borate and was a constituent of Gale crater groundwater. Under alkaline conditions, borates adsorb to 2:1 phyllosilicates [3]. Hence, borates may have been adsorbed by clay minerals on Mars while groundwater circulated through the bedrock.

The discovery of boron on Mars has important implications for martian and terrestrial prebiotic chemistry. Borates can react with and stabilize important prebiotic molecules, including sugars [4], and the formation of borate-sugar complexes may be an important step in the prebiotic synthesis of ribonucleic acids (RNA) which may have led to the origin of life on Earth [5]. The presence of borate in Mars groundwater opens up the possibility of prebiotic reactions on early Mars [1] and perhaps the preservation of organics in martian clay minerals by borate complexation.

As with borates, organics can be trapped within 2:1 phyllosilicates, such as montmorillonite [6]. Since both organics and borates are present, it is likely that interaction of organics and borates occurred in early Mars groundwater or while these materials were adsorbed and concentrated on clay surfaces, potentially allowing for prebiotic chemical reactions to occur on Mars. Our project focuses on studying the role of clay mineral chemistry on the reaction of sugars and borates under typical Mars and terrestrial groundwater conditions, including understanding the role of pH in borate uptake by clays [7] and borate-organic reactions.

Methods: Borate-bearing clay minerals at various pH conditions are being produced [7]. Clay mineral samples include terrestrial clay minerals, kaolinite, montmorillonite, and bentonite, and Mars analog clays, nontronite, and saponite. We will mix ribose with the borate-bearing clays suspended in water and monitor for the breakdown of ribose using an alkylsilyl derivatization gas chromatography tandem mass spectrometry (GC-MS-MS) technique [8]. The resulting half-life of ribose mixed with the borate-bearing clays will be compared to control experiments to determine the effects of clays on the reaction.

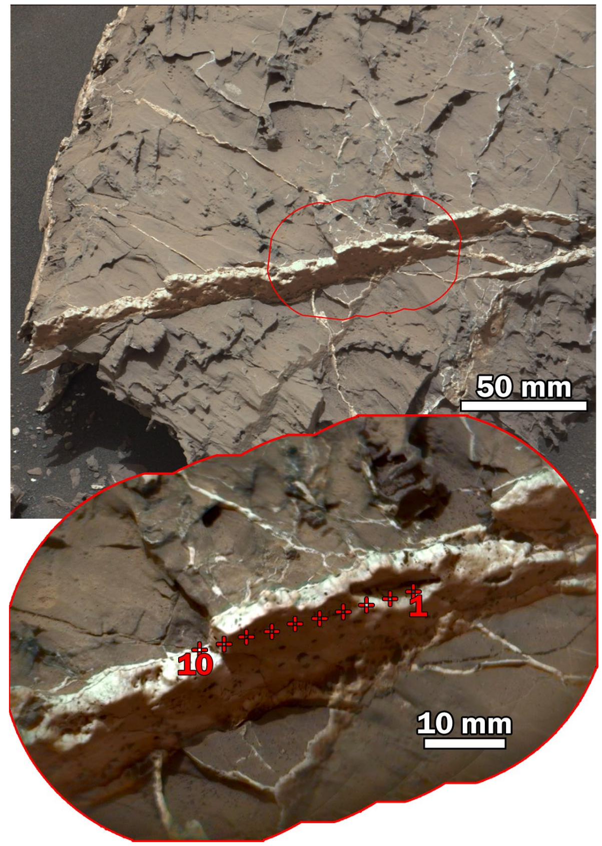

FIGURE 1: ChemCam target "Catabola" where boron has been observed in light-toned calcium sulfate filled fractures (light-toned resistant feature) within clay mineral rich lacustrine bedrock (darker-toned rock hosting calcium sulfate vein). Mastcam context image shown above with colorized ChemCam remote micro image shown below with crosshairs indicating positions of ChemCam laser observation points. Image Credit: JPL-Caltech/MSSS/LANL/CNES-IRAP.

Our preliminary experiments are based on [4], where we stir ribose in pH 11.5 water at 80°C and monitor for reaction products for 24 hours. Aliquots are taken from the reaction mixture and quickly dried using N_2 to prevent further reaction. Results from these experiments will act as a baseline for future experiments between borate-bearing clay minerals and ribose while helping us to refine our GC-MS methods.

Results: Figure 2 shows that ribose chromatogram peak area decreases rapidly with the onset of the experiment, but slows after 4 hr. Other sugars form during the reaction, glucose, fructose, as well as sugar acids gluconic acid and ribonic acid. Within 2 hr, sugar acid concentrations peak and then decrease. Glucose and fructose concentrations rapidly rise until t = 4 hr and then increase at a slower rate until the end of the experiment.

Discussion: The results from the preliminary experiment show that we can track ribose and its reaction products using high resolution GC-MS-MS and the alkylsilyl derivation technique. In addition, the results of the experiment likely show that the reaction stopped at ~4 hr. As sugar acids formed in the reaction mixture, the acids decreased the pH of the reaction solution, preventing further reaction of the remaining ribose.

Borate-sugar complexes [10] are potentially important for prebiotic chemicals. The study of sugar stability in martian clay minerals is important for determining if sugars, and other important organic biosignatures, could be preserved in the martian subsurface by reaction with clays and borate-bearing clays. Sugars are very rare in abiotic conditions due to their susceptibility to breakdown in water [4,9]; sugars have only been detected in carbonaceous meteorites in very small quantities [9]. Thus, sugars are unlikely to be found on Mars without being replenished by life. If our experiments show clay-borate-sugar complexes form stable products, then this class of molecule and their derivatives could be potentially preserved in the martian subsurface, allowing for detection by instruments on Mars, or returned samples.

Conclusions: These preliminary results show that we can differentiate between ribose and its breakdown products that include other sugars and their stereoisomers. The first goal of this project include refining our experimental techniques and GC-MS methodologies based on the results shown here. The second goal is reaction of a sugar mixture with many types of borate-bearing clays in alkaline water to determine which sugars bind to borates on clays, determine what role clay minerals chemistry and structure play during these reactions, and determine the stability and structure of any final products.

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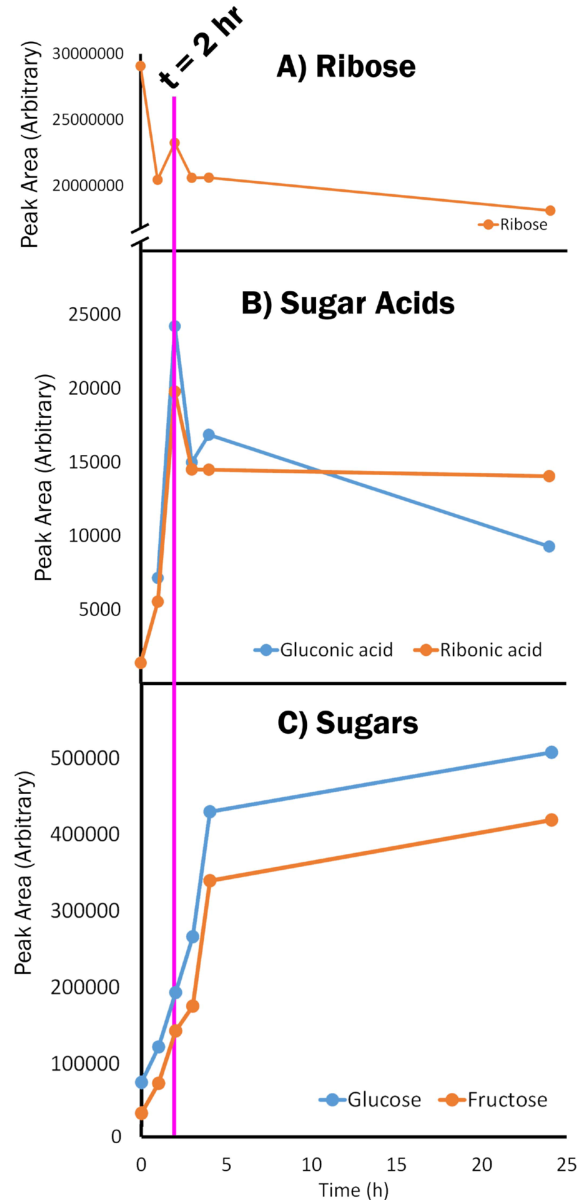

FIGURE 2: Preliminary results of the ribose reaction in alkaline water experiment over a 24 hr period. A) The concentration of ribose reactant. B) The concentration of sugar acids produced during the reaction. C) The concentration of hexose sugars produced during the reaction. Reactants and products change rapidly in the first 2 hours of the experiment (pink line).