

FINDING EVIDENCE OF A PREBIOTIC PYRUVATE REACTION NETWORK IN METEORITES. A. C. Rios^{1,2} and G.W. Cooper², ¹Blue Marble Space Institute of Science, MS 239-4, NASA-Ames Research Center, Moffett Field, CA 94035, andro.c.rios@nasa.gov. ²Exobiology Branch, NASA-Ames Research Center, MS 239-4, Moffett Field, CA 94035, george.cooper@nasa.gov

Introduction: The organic compounds of carbonaceous chondrites are structurally diverse products of the prolonged abiotic chemistry that occurred before and during the early stages of the solar system [1]. They also represent the types of prebiotic compounds that may have participated in chemical evolutionary processes that gave rise to life [2]. Pyruvic acid is a key component of primary metabolism that has recently been found in carbonaceous chondrites [3]. Its prominence in biology has inspired us to explore its chemistry and possible role in the origin of metabolism. Our laboratory investigations have found that pyruvate (the ionized form of pyruvic acid) can serve as a single-source reactant to generate what we term a pyruvate reaction network (PRN). The core of the PRN is driven by pyruvate aldol polymerization and decay reactions. These decay reactions lead to the production of stable and unstable compounds which include mono, di, and tricarboxylic acids and a variety of keto acids. Importantly, many of these reactions apparently lead back to pyruvate, establishing a feedback process.

Finding evidence of this reaction network in meteorites would establish that the chemistry of pyruvate did occur in a prebiotic environment and indeed many of the known compounds found in pyruvate reaction mixtures were detected in the Murchison and Murray meteorites [3]. However, multiple synthetic origins, not tied to pyruvate chemistry, might also explain their meteoritic presence. Thus finding compounds unique to the PRN, such as reaction intermediates, would provide stronger evidence in support of its prebiotic relevance. The identity of these intermediates can only be confirmed by acquiring chemical standards, however, as most are not available commercially, we engaged in extensive chemical synthesis. Obtaining these standards also provides the opportunity to study their subsequent chemistry and roles in the PRN.

Methods: Synthetic experiments were conducted on the 50-200 mg scale using methyl or ethyl ester precursors for ease of handling, purification and subsequent experimentation. Purifications of individual compounds were most often carried out by column chromatography using silica gel, or simply through liquid-liquid extraction depending on the nature of the isolated crude mixtures. Purified products were subjected to LC-MS, ¹H and ¹³C NMR spectroscopy for confirmation of product purity and chemical structure.

Reactions of sodium pyruvate, used to model prebiotic chemistry, were carried out under aqueous alkaline conditions (pH 10, carbonate buffer) at varying temperatures and concentrations. The progress (time course) of pyruvate reactions was monitored via liquid chromatography-mass spectrometry (LC-MS and LC-MS/MS) in order to develop a reaction map of pyruvate products. Comparison of synthesized compounds and isolated pyruvate reaction mixtures with meteoritic samples were made by derivatizing samples with tert-butyldimethylsilyl (TBDMS) reagents in order to increase volatility for GC-MS analyses as previously described [3].

Results and Discussion: Our synthetic investigations starting with the PRN intermediates at the aldol dimer stage have helped us to verify that the α - β -unsaturated keto acids shown in Figure 1 can lead to other dicarboxylic acids. Four of the shown dicarboxylic acids result from thermal or oxidative decarboxylation reactions and have long been known to occur in meteorites [4], [5]. One of the α - β -unsaturated keto acids has also been identified (Figure 1) in two meteorite samples, its two isomers have not been found. However, based on our synthetic experimentation, the one identified in meteorites (the trans configuration) dominates the equilibrium under most conditions and therefore significant portions of the others might have converted to it through facile enolization reactions.

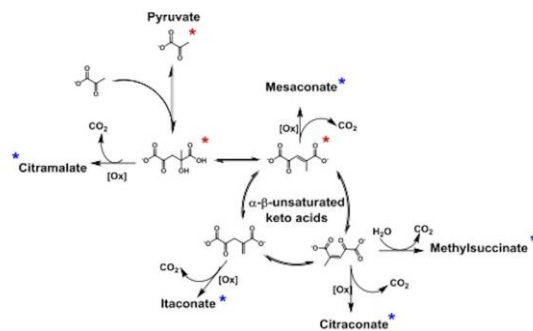


Figure 1. Relationship between keto-acids in the PRN and meteoritic dicarboxylic acids. Identification of keto acids in meteorite samples are marked with a red asterisk. Previous meteoritic identification of dicarboxylic acids are marked with a blue asterisk.

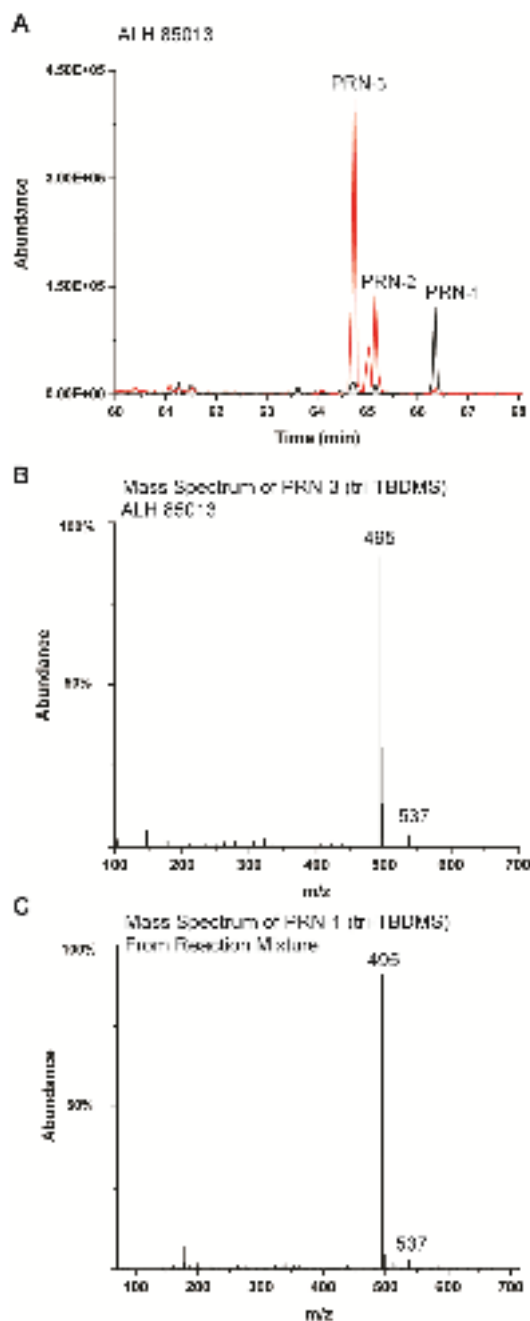


Figure 2. GC-MS identification of PRN intermediates from pyruvate reaction mixtures in meteorite samples. Suspected reaction intermediate (labeled PRN-1), and possible isomers (labeled PRN-2, PRN-3), were matched with two meteorite samples (only one is shown here). Panel A. Chromatogram trace of pyruvate reaction mixture (black) and overlay with ALH 85031 meteorite trace (red.) Panel B. Representative mass spectrum of peak PRN-2 from ALH 85013. Panel C. Matching representative mass spectrum of suspected PRN-1, from pyruvate reaction mixture.

We also report evidence of an isomeric mixture of mature PRN compounds (Figure 2) i.e., those that are suspected to result from subsequent chemistry of pyruvate aldol trimers in meteorite samples. Based on our reaction monitoring studies, the production of these intermediates appear to be part of the pathway for downstream product keto acids, including oxaloacetate and other prominent metabolic compounds. The structural verifications of these PRN species are still under way. Their role in the reaction network and other PRN compounds identified in meteorites will be presented.

References: [1] Pizzarello S. Cooper G. W. Flynn G. J. (2006) In "meteorites and the early Solar System II". D. Lauretta, L. A. Leshin, and H. Y. McSween Jr., Eds. University of Arizona Press. [2] Pizzarello, S. and Shock, E. (2010). Cold Spring Harbor Perspet. Biol. 2, doi:10.1101/cshperspect.a002105. [3] Cooper, G., Reed, C., Nguyen, D., Carter, M. Wang, Y. (2011). PNAS. 108, 14015-14020. [4] Cronin, J. R., Pizzarello, S., Epstein, S., Krishnamurthy, R.V. (1993). Geochimica et Cosmochimica. Acta 57, 4745-4752. [5] Pizzarello, S. and Huang, Y. (2002). Meteoritics & Planet. Sci 37, 687-696.