

## ON THE LONG TERM SURVIVAL OF METABOLIC COMPOUNDS DETECTED IN CARBONACEOUS METEORITES.

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**Introduction:** Carbonaceous meteorites provide evidence of organic compounds that were present in the Solar System before the origin of life. Amino acids, purines, pyrimidines and short monocarboxylic acids are some of the classes of prebiotically relevant compounds that have been detected in meteorites [1]. The survival of these compound classes in meteorite parent bodies and presumably in the prebiotic Earth environment is generally expected based on their known and slow aqueous degradation rates [2]. Molecules of central carbon metabolism, such as the alpha and beta keto acids, are also relevant to prebiotic chemistry but they often present a conundrum. The utility of these compounds in biological metabolism is attributed to their higher chemical reactivity and fast degradation rates [3,4]. But these chemical properties would appear to limit the survival of keto acids in uncontrolled prebiotic environments and their availability for chemical evolution.

Recently, a report has been made on the meteoritic detection of alpha and beta keto acids that may provide clues to their sustained persistence in abiotic environments [5]. Cold temperatures and perhaps minimal exposure to aqueous alteration on meteorite parent bodies might offer an explanation that aided in the survival of these labile compounds. However we have been pursuing an alternative hypothesis that can explain the persistence of these compounds in meteorites and provide a general solution to their long term survival in warmer, aqueous abiotic settings. This scenario takes advantage of the natural chemistry of pyruvic acid, the smallest and most abundant alpha keto acid that was detected in those meteoritic samples [5].

**Experimentation:** Reactions of sodium pyruvate and isotopically labeled analogues were carried out under aqueous alkaline conditions (pH 10) at varying temperatures and concentrations. Time course progress of pyruvate reactions were monitored via liquid chromatography-mass spectrometry (LC-MS and LC-MS/MS) in order to develop a reaction map of pyruvate products. Independent chemical syntheses and/or isolation of pyruvate reaction products have also been pursued to better understand how intermediates contribute to the diversity of the product mixture. From these studies some reaction products of pyruvate have been identified as candidates to search for in meteoritic samples.

**Results and Discussion:** We have found that pyruvate can serve as a single source reactant to continuously generate labile organics such as oxaloacetic acid and other compounds. The production of these metabolic intermediates appear to result from the isomerization, hydration and decarboxylation reactions of subsequent pyruvate aldol condensation products. Importantly, compounds such as oxaloacetic acid and other products replenish the starting material as they readily degrade to pyruvate. We have begun to search for larger reaction products in meteorite samples to support this scenario of pyruvate chemistry being the source of metabolic compounds detected in meteorites. Thus the chemical instability of alpha and beta keto acids does not limit their persistence in abiotic environments as long as a pyruvate source is maintained. Additional results from these studies, proposed mechanistic pathways, and implications for prebiotic chemistry will be presented.

**References:** [1] Pizzarello S. and Shock E. 2010. *Cold Spring Harbor Perspectives in Biology*. 2: a002105. [2] Wolfenden R. 2011. *Annual Review of Biochemistry*. 80:645–667. [3] Weber A.L. 2004. *Origins of Life and Evolution of the Biosphere*. 34:473–495. [4] Hanson R.W. 1987. *Journal of Chemical Education* 64:591–595. [5] Cooper G. et al. 2011. *Proceedings of the National Academy of Sciences of the United States of America*. 108:14015–14020.