

CITRIC ACID, PYRUVIC ACID, HOMOLOGS, AND RELATED COMPOUNDS IN CARBONACEOUS METEORITES. G. Cooper¹, C. Reed¹, D. Nguyen¹, M. Carter¹, Y. Wang². ¹Space Science Division NASA-Ames Research Center, Moffett Field, CA, 94035 USA. Email: george.cooper@nasa.gov. ²DPRA/ZymaX Forensics Isotope, 600 S. Andreasen Drive, suite B, Escondido, CA 92029. Email: yi.wang@zymaxusa.com

Introduction: Carbonaceous meteorites deliver a variety of organic compounds to Earth. We report three new classes of meteoritic organic compounds: keto acids, hydroxy tricarboxylic acids and tricarboxylic acids. Each exhibits the properties of abiotic mixtures, namely a general decrease in concentration with increasing carbon number and the presence of many structural isomers. Some of the compounds, such as pyruvic acid and citric acid, are at the core of intermediary metabolism. Laboratory syntheses using ¹³C-labeled reactants indicate that pyruvate alone can produce several potentially important pre-biotic compounds including oxalacetic acid. The isotopic composition of some of the meteoritic keto acids points to (at least partial) interstellar or pre-solar origins, indicating that such compounds might also exist in other planetary systems.

Materials and Methods: Initial meteorite extraction and GC-MS preparation procedures, including separation of compounds into fractions by ion exchange resins are similar to those used previously [1]. For GC-MS identifications compounds were converted to tert-butyldimethylsilyl (tBDMS) derivatives and, with similar derivatization procedures and solvents, trimethylsilyl (TMS) derivatives. Compounds in some extracts were derivatized to isopropyl esters (ISP) by published methods [2]. Two GC-MS units were used: An Agilent 6890N GC interfaced to an Agilent 5975B inert mass-selective detector (Agilent Technologies) or a Finnigan ion trap GCQ (Thermoquest Corporation). Typical parameters: column, DB-17 (30 or 60 m x 0.25 mm) fused silica capillary (J & W Scientific.); carrier gas, helium at 1ml/min; injector temp., 230 °C with splitless injection; oven temperature program: 45 °C initially - 4 °C/min to 240 °C - hold for 120 min; oven for TMS keto acids, 35 °C initially - 2.5 °C/min to 240 °C - hold for 120 min.

For isotope measurements target compounds were injected into an Agilent 6890 gas chromatograph (GC) linked to an oxidation furnace (for ¹³C/¹²C) or a pyrolysis furnace (for D/H) and a Micromass IsoPrime Isotope Ratio Mass Spectrometer (IRMS) [3].

RESULTS: Using gas chromatography-mass spectrometry (GC-MS) to analyze extracts of Murchison, Murray and Allan Hills (ALH) 83102 (also a CM2 meteorite) we have observed homologous series of several keto acids, tricarboxylic acids, and hydroxy tricarboxylic acids (Fig. 1). The vast majority of the

compounds have been identified in several extracts and as multiple volatile derivatives: tBDMS, TMS, and ISP. In all but one extract, citric acid is the dominant member of the hydroxy tricarboxylic acid series. Depending on the extract, some citric acid homologs are not seen at all. Overall, this group of compounds is relatively low in abundance: the concentration of citric acid in one sample of Murchison is approximately 55 pmole/gram.

Identified keto mono-acids are the straight-chained three-carbon (3C) pyruvic acid through the eight-carbon (8C) 7-oxooctanoic acid. Several additional tentatively identified keto acids also appear to be terminal-acetyl acids, based on the similarity of their mass spectra. The keto dicarboxylic acid (and dimer of pyruvic acid), 4-hydroxy-4methyl-2-ketoglutaric acid (parapyruvic acid), readily forms in solutions of pyruvate [4, 5]. Pyruvic acid recovered from ALH83102 corresponds to approximately 15 nmole/gram. Levulinic acid recovered from Murchison and ALH83102 is approximately 5.4 and 45 nmol/gram, respectively. In order to perform isotope measurements on some keto acids, a Murchison keto acid fraction was further purified by ion chromatography to isolate individual compounds. We measured the ¹³C/¹²C values of levulinic acid, 5-oxo-hexanoic acid, and 6-oxo-heptanoic acid and the D/H ratio of levulinic acid; all were from Murchison and were measured as their TMS derivatives. The resulting $\delta^{13}\text{C}$ values (‰) were +17.04, +15.24, and +12.94, respectively; the δD of levulinic acid was +425 ‰. All of these values are more positive than the range of terrestrial isotopic values and point to low temperature extraterrestrial synthesis.

Definitively identified tricarboxylic acids are (Fig. 1) 1, 2, 3-Propanetricarboxylic acid (tricarballic acid) at approximately 2 nmole/gram in ALH83102 and 371 pmole/gram in Murchison is the dominant member of the series but less abundant than succinic acid, a relatively abundant meteoritic dicarboxylic acid [6]. The tricarboxylic acids consist of several isomers and extend to at least C-10.

DETERMINING ORIGINS: To determine if reactions of the described keto acids could be partly responsible for the presence of other known meteoritic compounds we began a series of reactions of keto acids under conditions thought to be related to those of the

meteorite parent-body or comets. Extracts of carbonaceous meteorites are often in the pH 7-9 range: likely due in part to the abundance of carbonates. Most estimates of aqueous alteration temperatures for carbonaceous meteorites are in the range of ~ 0 to 25 °C [7]. HCN is ubiquitous and abundant in comets: one estimate of the total abundance of HCN, before polymerization, is 4% relative to water [8]. An oxidant, hydrogen peroxide, was also included in some of the experiments: carbonaceous meteorites show various degrees of oxidation [8] and a relatively mild oxidant such as hydrogen peroxide is also effective at converting nitriles (produced from HCN and keto acids) to carboxamides and carboxylic acids.

In the experiments a reactant, most often pyruvate, was placed in a solution of carbonate buffer or sodium bicarbonate with or without the addition of KCN and/or peroxide and allowed to react at 2 °C or 22 °C. To verify products of the reactions and elucidate reaction mechanisms ^{13}C -labeled reactants were also used.

Labeled reactants were K^{13}CN , $^{13}\text{C}_1$ -pyruvate, $^{13}\text{C}_2$ -pyruvate, $^{13}\text{C}_{2,3}$ -pyruvate or fully labeled ^{13}C -pyruvate (U- ^{13}C).

In the case of pyruvate a variety of products were produced: all were found to be ^{13}C labeled to various degrees when starting with labeled reactants. Many are also found in carbonaceous meteorites. Pyruvate reaction products and mechanisms of formation will also be presented.

References: [1] Cooper G. W. and Cronin J. R. (1995) *Geochim. Acta* 59, 1001-1015. [2] Cooper G., Sant M. and Asiyó C. (2009) *J. Chrom. A*, 1216, 6838–6843. [3] Wang Y., Huang Y., Alexander C. M. O'D, Fogel M. and Cody G. (2005) *Geochim. Cosmochim. Acta*, 69, 3711-3721. [4] Wolff L. (1899) *Liebig's Ann.* 305 (2), 154-165. [5] Margolis S. A. and Coxon B. (1986) *Anal. Chem.*, 58, 2504-2510. [6] Pizzarello S., Cooper G.W. and Flynn G. J. (2006) In *Meteorites and the Early Solar System II*, D.S. Lauretta, H.Y. McSween Jr., Eds, (Univ. of Arizona Press, Tucson), pp. 625-651. [7] Brearley A.J. (2006) In *Meteorites and the Early Solar System II*, D.S. Lauretta, H.Y. McSween Jr., Eds, (Univ. of Arizona Press, Tucson), pp. 587–624. [8] Rettig T.W., Tegler S. C., Pasto D. J. and Mumma M. J. (1992) *Ap. J.* 398, 293–298.

