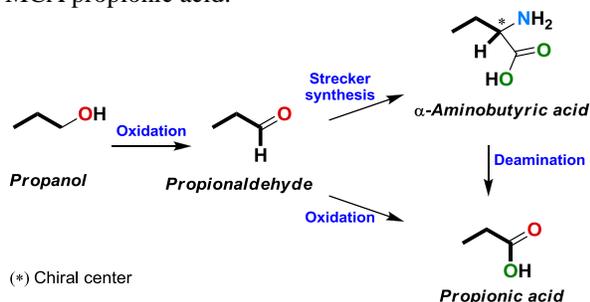


**METHOD DEVELOPMENT TOWARDS THE SIMULTANEOUS ENANTIOMERIC QUANTIFICATION AND  $\delta^{13}\text{C}$  ISOTOPIC ANALYSES OF METEORITIC MONOCARBOXYLIC ACIDS.** H. K. Woodward<sup>1,2,3</sup>, J. C. Aponte<sup>2,3</sup>, J. E. Elsila<sup>3</sup>, D. P. Glavin<sup>3</sup>, J. P. Dworkin<sup>3</sup>, <sup>1</sup>Department of Chemistry, University of Reading, Reading RG6 6UA, UK, e-mail: jp010820@reading.ac.uk. <sup>2</sup>Catholic University of America, Washington, DC 20064, USA, e-mail: jose.c.aponte@nasa.gov. <sup>3</sup>Solar System Exploration Division, Code 691, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA.

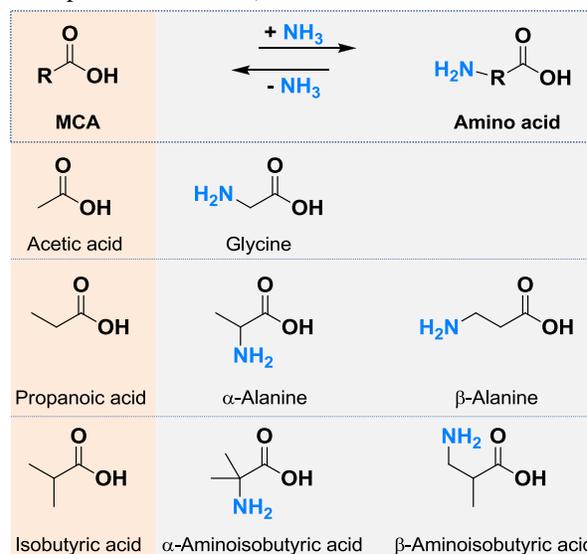
**Introduction:** Carbonaceous chondrites are among the oldest and most primitive materials in the Solar System. Their organic content can be used to decipher the history of prebiotic organic chemistry and how it may have resulted in the development of life. Several types of organic compounds have been identified in carbonaceous chondrites, including monocarboxylic acids (MCAs) and other structurally related aliphatic molecules [1]. Meteoritic MCAs may form from the oxidation of alcohols and aldehydes and from the deamination of amino acids (Scheme 1), with both mechanisms potentially occurring under aqueous and thermal processing inside the asteroid parent body.

**Scheme 1.** Potential formation mechanisms of the MCA propionic acid.



MCAs constitute the most abundant class of water-soluble organic compounds in the CM2 Murchison meteorite [2]. MCAs are of potential astrobiological importance as long-chain MCAs are found in biological membranes and may therefore be important for the origins of life on Earth. MCAs and amino acids may be related through the addition or loss of ammonia (Scheme 2); MCAs, like some amino acids, may also be chiral. The delivery of enantiomerically enriched amino acids inside meteorites and comets to the early Earth may have contributed to the development of homochirality [3]; understanding the relationship between amino acids and their structurally analogous MCAs may shed light on their prebiotic break in symmetry. Additionally, water-soluble organic meteoritic compounds often show distinctive isotopic compositions (D/H,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ) compared to those of their terrestrial analogs. Thus, the study of meteoritic MCAs can provide information about the prebiotic synthesis of amino acids and other carbonyl compounds present in meteorites, and about the processes that occurred inside their asteroid parent bodies.

**Scheme 2.** MCAs and amino acids are structurally related through the loss or addition of ammonia (three examples shown below).



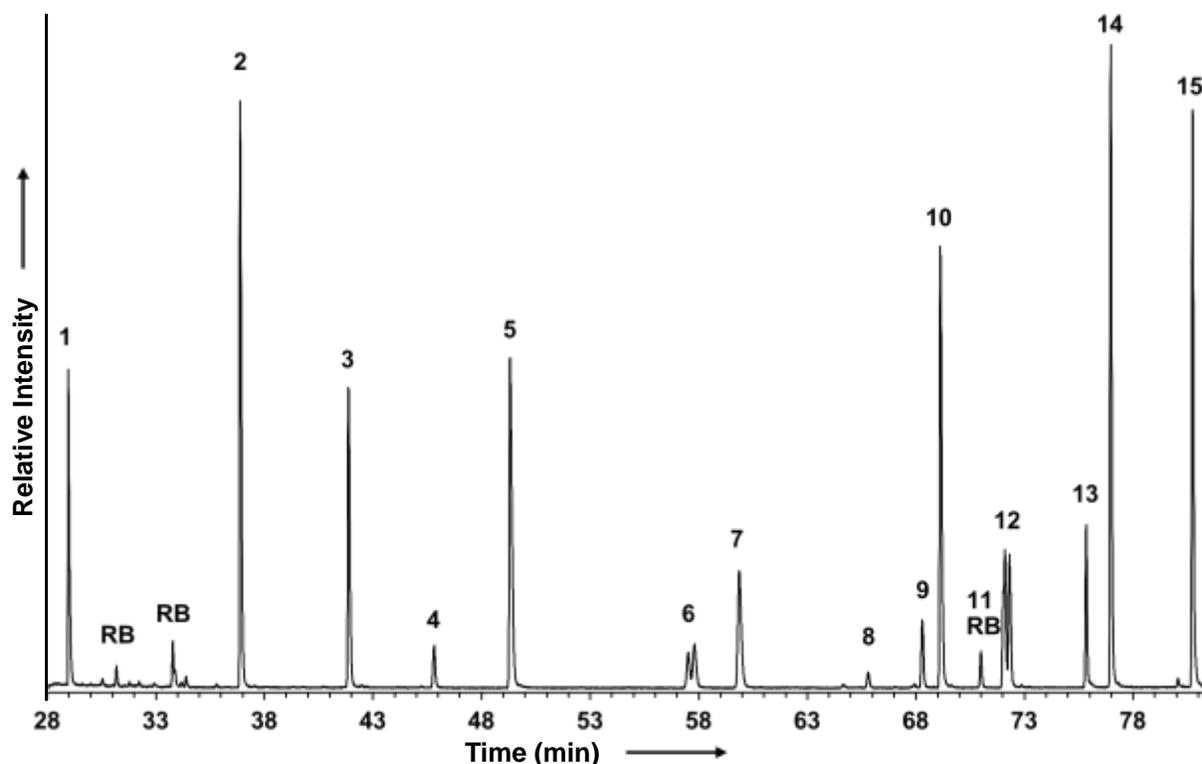
The molecular distributions and abundances of MCAs have been previously evaluated from various carbonaceous chondrites in their underivatized form using liquid chromatography [4] and gas chromatography (GC) coupled to varying detectors such as flame ionization and mass spectrometry (MS) [5]. Given the high volatility of MCAs, however, some degree of isotopic fractionation using these methods may be unavoidable [6]; thus, analyses of these compounds in their underivatized form may result in biased data. In this light, the derivatization of MCAs is desirable for the analyses of their molecular distribution and abundance, including enantiomeric compositions. MCAs have previously been evaluated after derivatization using GC-MS either alone or coupled with multiple reaction monitoring (MRM) [7,8]. Potential difficulties for derivatization are the high volatility of derivatized MCAs [7] and the formation of a large suite of derivatization byproducts that may alter the measured isotopic composition of meteoritic MCAs [8]. Indeed, the use of MRM as a detector after GC was needed because of the large levels of byproducts generated during the derivatization step [8]. Therefore, a single method capable of yielding MCA-derivatives with low levels of volatility and byproduct formation for the simultaneous quantification of abundance, enantiomeric composi-

tion, and isotopic distribution of meteoritic MCAs is needed.

We will present advances towards the development of a novel method for the simultaneous chiral and isotopic analyses of meteoritic MCAs. In this study, we separated sixteen branched and unbranched short chained MCAs (Figure 2). After optimization of the method using laboratory standards, the method will be rigorously tested with terrestrial soils and mineral meteorite analogs before meteorite samples are analyzed. This is a laborious process to optimize as the tests must be shown to produce reproducible results on the nanomole scale before applying it to meteoritic materials.

Our innovative method for the analysis of meteoritic MCAs will allow the measurement of a clear abundance of the least-hindered short-chained ( $\leq 6$  carbons) MCAs, including chiral MCAs. Finally, we hope that the methods developed here can be rigorously tested enough for analysis of samples returned by missions such as OSIRIS-REx. Analysis of a returned sample with a known parent body will put into perspective the results of the organic content analysis of analyzed meteorites and will contribute towards further progress of understanding the origins of the organic matter in the Solar System.

**Figure 2.** Initial separation of the 16 listed MCA's seen using a GC-MS triple quad; derived from the refined laboratory method. Different abundances are seen mostly due to variation in steric hindrance. Chiral MCA's have been successfully separated into S and R forms. Compounds in chromatogram: [1] acetic acid; [2] propanoic acid; [3] isobutyric acid; [4] 2,2-dimethylpropanoic acid; [5] butyric acid; [6] (*R,S*)-2-methylbutyric acid; [7] isopentanoic acid; [8] 2,2-dimethylbutyric acid; [9] 3,3-dimethylbutyric acid; [10] pentanoic acid; [11] 2-ethylbutyric acid; [12] (*R,S*)-2-methylpentanoic acid; [13] (*R,S*)-3-methylpentanoic acid; [14] 4-methylpentanoic acid; [15] hexanoic acid; [16] benzoic acid (not shown in chromatogram); [RB] reaction byproduct.



**References:** [1] Pizzarello S., et al. (2006) In *Meteorites and the Early Solar System II*, pp 625-651. University of Arizona Press: Tucson, AZ. [2] Huang Y., et al. (2005) *Geochim. Cosmochim. Acta*, 69, 1073-1084. [3] Engel M. H. and Macko S. A. (1997) *Nature*, 389, 265-268. [4] Yuen G. U. and Kvenvolden K. A. (1973) *Nature*, 246, 301-303. [5] Aponte J. C., et al. (2011) *Geochim. Cosmochim. Acta*, 75, 2309-2323. [6] Dias

R. F. and Freeman K. H. (1997) *Anal. Chem.*, 69, 944-950. [7] Pizzarello S., et al. (2008) *Proc. Natl. Acad. Sci. U.S.A.*, 105, 3700-3704. [8] Aponte J. C., et al. (2014) *Geochim. Cosmochim. Acta*, 131, 1-12.