

**THE RACEMIC NATURE OF THE FREE AND IOM-DERIVED MONOCARBOXYLIC ACIDS IN CARBONACEOUS CHONDRITES SUGGESTS THE ORIGIN OF CHIRALITY DURING PARENT BODY MODIFICATION PROCESSES.** J. C. Aponte<sup>1</sup>, R. Tarozo<sup>1</sup>, C. Hallmann,<sup>2</sup> R. E. Summons<sup>2</sup> and Y. Huang<sup>1</sup>. <sup>1</sup>Department of Geological Sciences, Brown University, RI 02912. E-mail: jc\_aponte@brown.edu. <sup>2</sup>Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, MA, 02139.

One striking feature observed in extraterrestrial amino acids (AAs) found in carbonaceous chondrites is their enantiomeric excess (*ee*). No abiotic synthetic route capable of yielding *ee* without the use of certain chiral initiators is known to humankind. To date, only eight AAs (most prominently isovaline and leucine isomers) and one hydroxyl acid (lactic acid) have been found as non-racemic mixtures in CCs, showing *ee* ratios ranging from 2.5 to 19.6% in Murchison [1]. However, AAs are of relatively low abundance in the CCs to monocarboxylic acids, with concentrations of the former being 60 ppm and the later 332 ppm in the Murchison CC [2]. Many monocarboxylic acids also possess chiral centers, but so far these compounds have not been examined for their chirality.

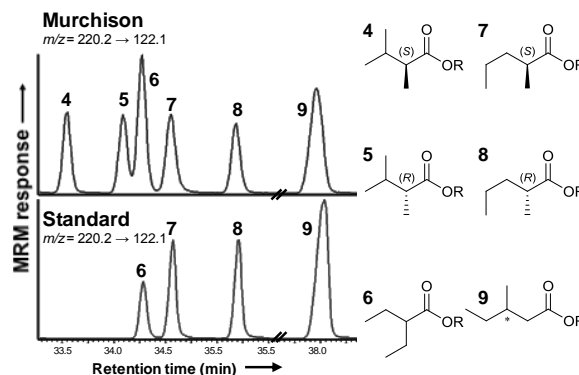
Inside CCs, monocarboxylic acids (MCAs) can be found as free water-soluble organics, or can be generated by the chemical oxidation of IOM using ruthenium tetroxide (RuO<sub>4</sub>) as a mild and selective oxidating reagent [3]. Despite free-MCAs are often the most abundant compounds present in CCs (especially on CM2 type), and that the insoluble organic matter (IOM) constitutes 70 to 80% of their total organic content, the chirality of these organics have not been reported before. For these reasons, the analysis and quantification of *ee* in meteoritic MCAs would provide important insights to better understand the homochirality that defines life on Earth today [4].

In this study, we investigated the chirality of the aliphatic chains (containing five and six carbons, C5 and C6) on free MCAs extracted from Lonewolf Nunataks (LON) 94101 (CM2) and Murchison (CM2) CCs, and the IOM-derived MCAs from Elephant Moraine (EET) 87770 (CR2). Because IOM is least likely to suffer from terrestrial contamination, it is important to probe the possibility of asymmetry in IOM. Also, the IOM-aliphatic side chain are likely more resistant to secondary thermal and aqueous alterations on the parent bodies, hence; they may be a more reliable representation of their primordial synthesis in the presolar cloud than soluble compounds [5]. In addition, the abundance, molecular distribution and isotopic ratios of free and IOM-derived MCAs extracted from six CCs belonging to different petrologic types showed similar general trends such as: a) a complete suite of structural diversity; b) an overall abundance of branched MCAs over straight-chain MCAs; c) a decrease on the abundance with the increase of the aliphatic chain size and; d) a general dominance of highly

positive  $\delta D$  isotopic ratios; in these two compound classes. These similarities suggested a genetic relationship between the synthetic pathways of free and IOM-derived MCAs [5].

In order to determine the *ee* of the free and IOM-derived MCAs, we transformed these acids to diastereomeric-esters by esterifying them with optically pure (S)-1-phenethyl alcohol. The diastereomeric-esters were subsequently analyzed by gas chromatography (GC) and GC-multiple reaction monitoring (MRM) to determine the enantiomeric ratios of selected MCAs (Figure 1). We found C5 and C6 branched MCAs are racemic. Our results may suggest the free-MCAs and the aliphatic side-chains of the IOM may have been synthesized as racemic presolar molecules during the gas phase ion-radical reactions. If the aliphatic chain on the amino acid precursors were produced in similar pathways as the IOM-derived aliphatic chains [6], our results would indicate the *ee* in AAs might have been a product of their late synthesis/destruction or modification on the surface of the asteroidal parent body.

**Figure 1.** Partial GC-MRM chromatogram showing the separation of diastereomeric-esters of chiral C6 MCAs present in the Murchison.



**References:** [1] Pizzarello S. and Groy, T. L. 2011. *Geochim. Cosmochim. Acta* 75:645-656. [2] Sephton M. A. 2002. *Nat. Prod. Rep.* 19:292-311. [3] Huang Y., Alexandre M. R., Wang Y. 2007 *Earth Planet. Sci. Lett.* 259:517-525. [4] Cronin J. R. and Carleton B. M. 1971. *Science* 172:1327-1329. [5] Aponte J. C., Alexandre M. R., Wang Y., Brearley A. J., Alexander C. O'D., Huang Y. 2011. *Geochim. Cosmochim. Acta* 75:2309-2323. [6] Kerridge J. F. 1999. *Space Sci. Rev.* 90:275-288.