

RACEMIC MONOCARBOXYLIC ACIDS IN CARBONACEOUS CHONDRITES QUESTION UVCPL AS THE SOURCE OF MOLECULAR ASYMMETRY OBSERVED IN METEORITIC AMINO ACIDS. Y. Huang and M.R. Alexandre, Department of Geological Sciences, Brown University, RI02912 (Yongsong_huang@brown.edu)

Introduction: The organic matter in carbonaceous chondrites offer a unique glimpse into the organic chemistry occurred in the interstellar molecular clouds and subsequent reactions happened during asteroidal processes. Over the past several decades, a spectacular array of polar and nonpolar organic compounds have been found in carbonaceous chondrites [see 1-3 for reviews and references therein]. Many of the meteoritic organic compounds, such as amino acids, carbohydrates and carboxylic acids, are structurally identical or similar to biomolecules that have been found and serve essential functions in terrestrial life. It has been hypothesized that meteorite organic compounds could have seeded early Earth with a critical inventory of prebiotic organic compounds that then lead to the origin of life on Earth [4]. One prominent support for this external delivery hypothesis by carbonaceous chondrites is that enantiomeric excess (ee) has been unambiguously detected in meteorite amino acids [5,6,7], whereas no other proposed abiotic organic synthetic pathways (e.g., Fischer Tropsch reactions, Miller-Urey reactions, hydrothermal synthesis, impact synthesis etc.) have been shown to be capable of yielding chiral organic compounds in the absence of initial chiral agents. The prominence of chirality in the biochemistry of extant life requires that any proposed theories for the origin of life be capable of rationalizing the emergence of molecular asymmetry.

Despite the overwhelming importance of chirality in understanding the role that meteorites may have played in the origin of life on Earth, the only type of organic compounds that undergone extensive examination for their chiral asymmetry in carbonaceous chondrites is amino acids. One recent study [8] show the existence of chiral asymmetry in the insoluble organic matter (IOM) by using an ultra-sensitive asymmetry amplification reaction [9]. However, the study [8] does not provide information on the quantity of original ee present in the samples, nor does it attribute chirality to any specific structural moieties in the IOM.

The origin of enantiomeric excess of amino acids in carbonaceous chondrites has been a focus of much speculation. A prominent hypothesis is the selective destruction of the D- α -amino acid relative to L-form by the UV circularly polarized starlight [10,11]. If this hypothesis is true, however, other organic compounds present simultaneously with amino acids in the interstellar medium must also be similarly affected, as long as they also possess chiral center in their molecular structures. The goal of current study is to explore the molecular asymmetry in the monocarboxylic acids (notably the most abundant soluble compounds in carbonaceous chondrites) from both the water soluble fraction and those

derived from IOM aliphatic side chains in carbonaceous chondrites in order to further test the the UVCPL hypothesis.

Procedures: The powdered Murchison and Orgueil meteorite samples were first extracted with double-distilled water for 24h at 110°C under vacuum. After extraction, the solution were adjusted to pH >10 using NaOH solution and subjected to rotary evaporation. The volume-reduced solution is then transferred to a 2 mL vial and acidified just prior to analyses using SPME coupled with GC and GC-MS analyses [12]. The solvent extraction residues were treated with HCl 4 mol L⁻¹ and then demineralized using a mixed CsF-HF solution [13,14]. Basically, the CsF-HF solution attacks the silicate minerals by producing HCl soluble fluoride salts and liberating the IOM. The IOM samples were subsequently treated with ruthenium tetroxide [15] to oxidize the aromatic cores and convert the aliphatic side chains into monocarboxylic acids (MCAs) [16]. The monocarboxylic acids in water soluble fractions and IOM derived fractions were analyzed quantitatively using solid phase micro extraction (SPME) coupled with GC-FID, followed by GC-MS for identification. SPME provides excellent recovery for monoacids [12]. Subsequently a chiral GC column (γ -DEXTM 120, 30m \times 0.25mm \times 0.25 μ m) installed on a GC-FID is used for separation of monoacid enantiomers in order to determine the possible enantiomeric excesses.

Results and discussion: In this report we will pay particular attention to the monocarboxylic acids derived from RuO₄ oxidation of the IOM residues, because: 1) there is little chance for terrestrial contamination of IOM, and 2) due to insoluble nature, the chiral centers on aliphatic side chains of the IOM cannot be racimized during aqueous alteration, hence will preserve their interstellar molecular asymmetry (if present). We will focus on two enantiomeric pairs of compounds: 2-methyl hexanoic acid and 2-ethyl hexanoic acid, in this discussion because they are completely resolved by the chiral GC column and careful GC-MS examination showed no coeluting compounds (Fig.1). Based on GC-FID quantification, the peak areas of the well-separated enantiomers for both compounds are identical within analytical error. The water soluble monocarboxylic acids also show identical peak areas for the enantiomers of the above two compounds. We therefore conclude these two monoacids do not contain enantiomeric excess.

Our results have important implications for understanding the origin of chirality in carbonaceous chondrites. Hydrogen isotopic ratios of individual branched amino acids and monocarboxylic acids are the highest among all compound classes in carbonaceous chondrites (amino acids, 500 to 3500 ‰, branched monoacids, 800 to 2000 ‰) [3, 12], indicating that both classes of compounds are initially

formed in the cold interstellar environments via similar radical and ion reactions. If UVCPL lead to selective destruction of D-amino acids and enrichment of the L-amino acids, it should also have induced similar ee for the monocarboxylic acids. The fact that aliphatic side chains “frozen” onto the meteorite IOM (the high D/H ratios of IOM of carbonaceous chondrites also attest to their interstellar sources) are racemic mixtures argue against UVCPL as the source of chiral asymmetry observed in amino acids of carbonaceous chondrites. In fact, the UVCPL theory is already having difficulty explaining 15 % ee observed in isovaline in Murchison [3], as the theoretical limit for ee induced by UVCPL has been shown to be 9 % at most [17]. The significance of our results are further augmented when one considers that monocarboxylic acids are the most abundant soluble organic compounds in carbonaceous chondrites, about 6 times higher in abundance than amino acids [18]. Our results suggest that both amino acids and monocarboxylic acids may have arrived at asteroidal stage as racemic interstellar molecules: it is the late stage synthesis or modification on the surface of or within the asteroidal parent bodies that ultimately lead to enantiomeric excess in these compounds. Such reactions can be catalyzed by asymmetric catalysts residing in either organic or mineral phases [3]. In the case of amino acids, ee could also be formed by Strecker synthesis involving asymmetric catalysts [19].

Conclusion: Our results dispute UVCPL as the source for chiral asymmetry in carbonaceous chondrites. Instead, reactions involving asymmetric catalysts on the asteroidal bodies may have been more important in giving rise to enan-

tiometric excess observed in amino acids and other organic compounds of carbonaceous chondrites.

References: [1] Cronin J.R. and Chang S. (1993) In *Chemistry of Life's Origins* (J.M. Greenberg et al., eds.), pp. 209-258. Kluwer, Dordrecht. [2] Sephton M.A. (2002) *Nat. Prod. Rep.*, **19**, 292-311. [3] Pizzarello S. (2006) *Acc. Chem. Res.* **39**, 231-237. [4] Chyba C.F. and Sagan C. (1992) *Nature*, **355**, 125. [5] Engel M.H. and Macko S.A. (1997) *Nature*, **389**, 265-268. [6] Pizzarello S. et al. (2003) *GCA*, **67**, 1589-1595. [7] Pizzarello S. and Huang Y. (2005) *GCA* **69**, 599-605. [8] Kawasaki et al. (2006) *GCA* **70**, 5395-5402. [9] Sato et al. (2003) *Angew. Chem. Int. Ed.* **41**, 1614-1616. [10] Rubenstein E. et al. (1983) *Nature* **306**, 118. [11] Bailey J. (2001) *OLEB* **31**, 167. [12] Huang Y. et al. (2005) *GCA*, **69**, pp.1073-1084. [13] Cody G.D. and Alexander M.O'D. (2002) *GCA* **66**, 1851-1865. [14] Wang, Y. et al (2005) *GCA* **69**, 3711-3721. [15] Remusat L et al (2005) *GCA*, **69**, pp.4377-4386. [16] Huang et al. (2006), LPSC. [17] Balavoine G. et al. (1974) *J. Am. Chem. Soc.* **96**, 5152-5158. [18] Cronin et al., (1988) In *Meteorites and the Early Solar Systems* (J.F. Kerridge and M.S. Matthews eds.), pp. 817-857, Univ. Of Arizona, Tucson. [19] Cronin J.R. and Reisse J. (2005) In *Lectures in Astrobiology 1* (M. Gargaud, ed.), pp.473-514, Springer-Verlag, Berlin.

Acknowledgements: This study is funded by NASA Exobiology grant NNG04GJ34G to Y. Huang.

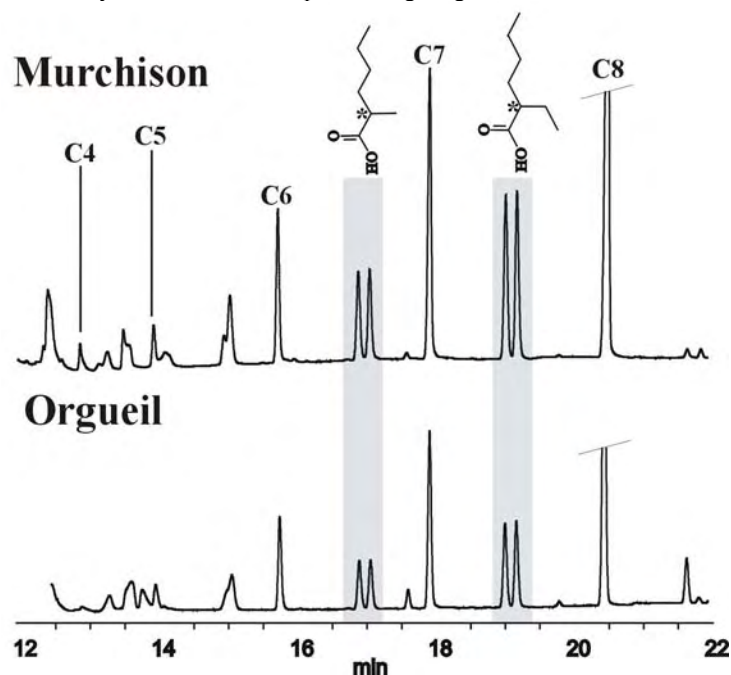


Figure 1 – Partial gas chromatograms showing the distribution of monocarboxylic acids in Murchison and Orgueil IOM samples following RuO_4 oxidation of insoluble organic matter (IOM). The shade peaks are enantiomers of monocarboxylic acids. The chiral carbons in the acids are marked with *.