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Chirality of meteoritic free and IOM-derived monocarboxylic acids and implications for prebiotic organic synthesis

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Abstract

The origin of homochirality and its role in the development of life on Earth are among the most intriguing questions in science. It has been suggested that carbonaceous chondrites seeded primitive Earth with the initial organic compounds necessary for the origin of life. One of the strongest pieces of evidence supporting this theory is that certain amino acids in carbonaceous chondrites display a significant L-enantiomeric excess (*ee*), similar to those use by terrestrial life. Analyses of *ee* in meteoritic molecules other than amino acids would shed more light on the origins of homochirality. In this study we investigated the stereochemistry of two groups of compounds: (1) free monocarboxylic acids (MCAs) from CM2 meteorites LON 94101 and Murchison; and (2) the aliphatic side chains present in the insoluble organic matter (IOM) and extracted in the form of monocarboxylic acids (MCAs) from EET 87770 (CR2) and Orgueil (CI1). Contrary to the well-known *ee* observed for amino acids in meteorites, we found that meteoritic branched free and IOM-derived MCAs with 5–8 carbon atoms are essentially racemic. The racemic nature of these compounds is used to discuss the possible influence of ultraviolet circularly polarized light (UVCPL) and aqueous alterations on the parent body on chirality observed in in carbonaceous chondrites.

Abbreviations: *CP, circular polarization; UVCPL, ultraviolet circularly polarized light; IRCPL, infrared circular polarized light; MCAs, monocarboxylic acids; ee, enantiomeric excess(es); amu, atomic mass units; UV-MCD, UV-magnetic circular dichroism; GC, gas chromatography; GC-FID, GC-flame ionization detector; GC–MS, GC–mass spectrometry; GC–IRMS, GC–isotope ratio mass spectrometry; GC–MRM-MS, GC–metastable reaction monitoring-MS; ISM, interstellar medium*

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1. INTRODUCTION

The identification of diverse classes of organic compounds such as amino acids, carboxylic acids and polyhydroxylated compounds in carbonaceous chondrites, suggests a possible link between these abiotic organic compounds and the development of early life on Earth (Sephton, 2002; Pizzarello et al., 2006). The abundances, structural features and stable isotopic ratios of these molecules provide insights into primordial organic synthesis in the inter-stellar medium (ISM) and the Solar System (Cronin and Chang, 1993; Herbst, 1995). One structural aspect of meteoritic compounds is of particular significance—the excess of (L) over (D) enantiomers exhibited by certain meteoritic amino acids. Proteins in living organisms on Earth are biosynthetically assembled exclusively from L-amino acids (so-called homochirality). It is therefore possible that the selection of L- rather than D-amino acids to construct proteins in living organisms is not entirely accidental, but an inheritance from the primordial assemblage of the amino acids delivered by carbonaceous chondrites.

What is the origin of the enantiomeric excess (*ee*) of amino acids in carbonaceous chondrites? Enantiomers have identical chemical and physical properties, except for the direction in which they rotate the plane of linearly polarized light, and are synthesized in equal quantities in the absence of chiral catalysts (Peltzer et al., 1984; Lerner et al., 1993). Several studies have proposed the Strecker–cyanohydrin pathway for the synthesis of amino acids in carbonaceous chondrites during the parent body aqueous alteration (Pizzarello et al., 2003, 2008; Glavin and Dworkin, 2009; Glavin et al., 2011; Pizzarello and Groy, 2011), which is supported by the presence of the full suite of amino acids including α-iminopropionicacetic acid and its derivative N-acetyl amino acid from the same meteoritic piece (Pizzarello and Cooper, 2001; Lerner and Cooper, 2005). However, this pathway yields racemic mixtures in the absence of chiral initiators, which is in sharp contrast to the observed 14% L-isoleucine *ee* (Pizzarello et al., 2008), and 18% L-isovaline *ee* (Glavin and Dworkin, 2009), found in the Murchison meteorite. One prominent theory for the origin of L-*ee* in meteoritic amino acids is the irradiation of these organic compounds by UV circularly polarized light (UVCPL) during destructive or synthetic reactions in the interstellar medium (Flores et al., 1977; Rubenstein et al., 1983; Bonner, 1991; Cronin and Chang, 1993; Meierhenrich and Thiemann, 2004). UVCPL, which can selectively destroy or synthetically favor one enantiomer over the other (Takano et al., 2007; De Marcellus et al., 2011), and thus induce *ee* (Greenberg et al., 1994; Bailey et al., 1998), may originate from the synchrotron radiation emitted by neutron stars that form after massive supernova explosions (Rubenstein et al., 1983; Bonner, 1991), or from reflection nebulae in regions of star formation (Bailey, 2001; Meinert et al., 2011), in which circularly polarized light in the infrared range has been observed.

Aliphatic chains such as those of carboxylic acids or amino acids are thought to be formed by ion and radical reactions in the gas phase of the interstellar medium (ISM) (Cronin and Chang, 1993; Herbst, 1995). Therefore, carboxylic acids or other related compounds synthesized in interstellar molecular clouds could be similarly affected by UVCPL as amino acids. Many compounds identified in carbonaceous chondrites—especially Murchison—possess asymmetric carbon centers, e.g., branched carboxylic acids and hydroxy acids (Peltzer and Bada, 1978; Yuen et al., 1984). These compounds should also be subjected to selective degradation by UVCPL, thereby leading to enantiomeric excesses. However, so far amino acids are the only compound class that has been extensively examined for *ee* (Engel and Macko, 1997; Pizzarello and Groy, 2011). Monocarboxylic acids (MCAs) are often more abundant than amino acids in carbonaceous chondrites (Sephton, 2002; Pizzarello et al., 2006) and many branched MCAs such as 2-methylbutanoic acid, 2,3-dimethylbutanoic acid and 2-methylpentanoic acid contain a chiral center (Figs. S2 and S3). Some MCAs are essential biological components—the very existence of cells in living organisms requires lipid bilayers as cell membranes that primarily contain C_{16} and C_{18} MCAs in bacteria and eukaryotes (e.g., Deamer et al., 2002). A thorough understanding of MCA chirality thus may have major implications for our understanding of the origin of the first building blocks used to construct the first cell membranes.

A number of studies have attempted to determine the chirality of MCAs in various carbonaceous chondrites using γ-DEX™ 120 chiral GC columns (Huang and Alexandre, 2006; Pizzarello et al., 2008, 2012), but the chromatographic co-elution of different compounds presents a major challenge for accurate measurements of *ee* in the majority of MCAs. It was not possible to accurately analyze *ee* of free MCAs in Murchison sample using this approach due to co-elution of the extremely complex mixture of MCAs present (with hundreds of compounds containing virtually all possibilities of alkyl substitutions; Huang et al., 2005; Aponte et al., 2011). Instead, Huang and Alexandre (2006) focused on MCAs derived from the RuO_4 oxidation of macromolecules with less complex structural diversity. Free MCAs from a number of Antarctic meteorites have been previously reported, where they were analyzed after separation on chiral GC columns. However, this data was published as Supplementary data only and lacked any discussion of the astrobiological significance of these results (Pizzarello et al., 2008, 2012). In addition, these results are rather inconclusive: some samples and/or compounds exhibit large *ee*, whereas others do not. In the absence of hydrogen isotopic data for the individual MCAs (Pizzarello et al., 2008, 2012) it remains unclear whether these *ee* differences are due to terrestrial contamination, chromatographic co-elutions or a genuine feature of indigenous MCAs in the studied carbonaceous chondrites.

The objectives of the present study were: (1) to develop methods for the accurate analysis of *ee* in MCAs in complex matrices; (2) to examine the presence/absence of *ee* in the MCAs in carbonaceous chondrite samples; (3) to discuss the origin of *ee* in meteoritic amino acids and their synthetic similarities or differences with free and IOM-derived MCAs; and (4) present novel hypotheses based on our new data and promote more discussions on the complex problem—the origin of homochirality. We here show that