



# Enantiomeric excesses of chiral amines in ammonia-rich carbonaceous meteorites



Sandra Pizzarello <sup>a,\*</sup>, Christopher T. Yarnes <sup>b</sup>

<sup>a</sup> School of Molecular Sciences, Arizona State University, Tempe, AZ 85287-1604, United States

<sup>b</sup> Department of Plant Sciences, University of California–Davis, Davis, CA 95616, United States

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## ABSTRACT

Chiral homogeneity is essential to the structure and function of terrestrial biopolymers but the origin of this “homochirality” is poorly understood and remains one of the many unknowns surrounding the origins of life. Several amino acids extracted from Carbonaceous Chondrite meteorites display L-enantiomeric excesses (*ee*) and their findings have encouraged suggestions that an input of non-racemic meteoritic compounds to early Earth might have led to terrestrial homochirality. Motivated by occasional indications of possible *ee* in other classes of soluble meteoritic compounds, we have undertaken a systematic study of the chiral distribution of amines in Renazzo-type (CR) meteorites, where they are the second most abundant organic molecular species and ammonia is by far the most abundant single molecule. We report here the first time finding of L-*ee* for two chiral amines in several pristine CR meteorites from Antarctica and outline a proposal by which the compounds possibly formed from the same ketone precursors as some of the chiral amino acids. This would occur during a warm hydrous stage of the asteroidal parent body, via a reductive amination process in the presence of a large abundance of ammonia, where the precursors' adsorption upon mineral phases possessing asymmetry offered the opportunity for chiral induction. Because the precursor ketones are achiral, the proposal underscores the likelihood of diverse asymmetric influences and processes in cosmochemistry.

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## 1. Introduction

Carbonaceous chondrite (CC) meteorites are stony fragments of primitive asteroidal bodies of near solar composition that contain abundant organic carbon (e.g., Cronin and Chang, 1993; Sephton, 2002; Pizzarello et al., 2006; Pizzarello and Shock, 2010). CC falls have been relatively few and are classified in different sub-groups based on their mineralogy, chemical and isotopic compositions and inclusions, which are found sufficiently dissimilar between them to justify the assumption that their parent bodies also differed in their history and chemical environments. The most studied for their organic composition have been the CM (Mighei-type), the Murchison meteorite in particular with a fall of over 100 kg, and the CR (Renazzo-type), which are collected in the ice fields of Antarctica and are often found remarkably free of terrestrial contamination (Pizzarello et al., 2012). Seven other chondrite types are known and have been also analyzed, although not so extensively, with the exception of the Ivuna-type (CI). All have uniquely offered

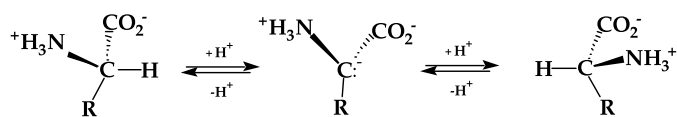
to direct analysis samples of the a-biotic chemistry that came to be in the Solar System before the onset of terrestrial life. Having meteorites showered the Earth since its accretion (Strom et al., 2005), their studies have often entered the discourse on the origin(s) of life.

Nevertheless, the search for proofs of a possible exobiology, as the idea that life's origin was aided by exogenous input of biomolecule precursors is often called, has not been easy. In fact, most of the organic carbon in CC displays structures as diverse as insoluble macromolecular materials similar to terrestrial kerosenes and soluble compounds; the latter ranging from polar species, such as amino acids, polyols and carboxylic acids, to non-polar hydrocarbons, with most of these present in complete molecular diversity. Meteoritic amino acids offer a ready example since, while including thirteen compounds also found in terrestrial proteins (Pizzarello et al., 2012), have been detected in near a hundred molecular species (Cronin and Pizzarello, 1983).

If such compositional diversity does not appear to be conducive to the specificity of life processes, its notable exception is that some CC amino acids share to some degree the trait of chiral asymmetry with biomolecules. Chirality is a general property of

\* Corresponding author.

E-mail address: pizzarello@asu.edu (S. Pizzarello).



**Scheme 1.** Racemization pathways for 2-H amino acids in water.

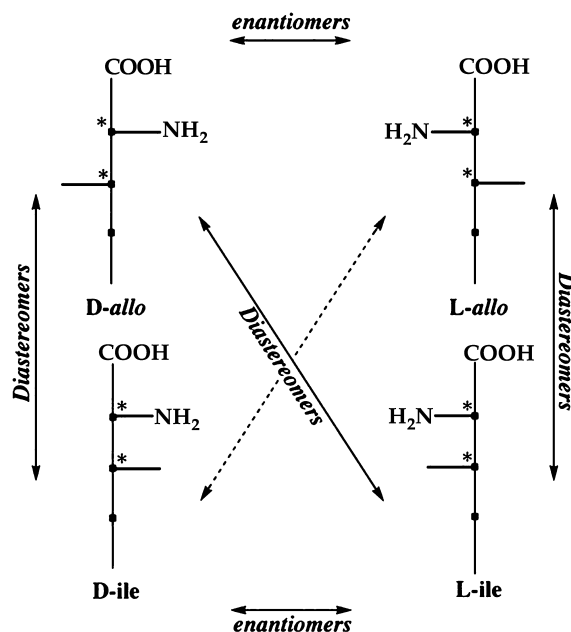
objects that can exist in two mirror image forms; it is also referred to as handedness and in fact takes the name for the Greek word for hand. It is manifested in organic molecules when a carbon atom, which has a tetrahedral distribution of its bonds, is attached to four different substituents; any molecule of this kind will then exist in two non super-imposable structures referred to as D-, and L- in the case of amino acids and (S) and (R) for other compounds, e.g., amines (e.g., Pizzarello and Groy, 2011 and references therein). Syntheses of chiral molecules, when unaided by asymmetric influences, will lead to equal amounts of the two enantiomers but in life processes biomolecules may display a strict chiral homogeneity, i.e., the whole of terrestrial proteins are made of only L-amino acid monomers while RNA and DNA use exclusively D-sugars.

The search for *ee* in meteoritic amino acids was at first controversial, because of such pervasive distribution of homochirality in the biosphere and the possibility of terrestrial contamination (Bada et al., 1983), but were ultimately detected in the Murchison meteorite for some compounds not common in terrestrial proteins and abundant in meteorites, the 2-methyl, 2-aminoacids ( $\alpha$ -methyl amino acids), and to favor the same configuration (L-) found in the biosphere (Cronin and Pizzarello, 1997).

L-*ee* have been detected for eight  $\alpha$ -methyl amino acids and one hydroxyacid in the CM Murchison and Murray meteorites (Pizzarello and Groy, 2011), one of these in the Orgueil meteorite (Ivuna-type or CI) (Glavin and Dworkin, 2009) and for one protein amino acid, aspartic acid, in the Tagish Lake meteorite (C2 ungrouped; Glavin et al., 2012). Their magnitude varies significantly, between 0–18%, and changes even within short distances in the same meteorite stone (Pizzarello et al., 2003). For the most abundant of these acids, Isovaline (2-amino, 2-methylbutanoic acid), the absence of any chiral contribution from terrestrial contaminants was validated in Murchison by isotopic analyses of the two enantiomers (Pizzarello et al., 2003; see Pizzarello and Groy, 2011, for a review).

One distinctive property of  $\alpha$ -methyl amino acids is that they do not racemize in water. Racemization is the conversion of a chiral compound from one configuration to the other and, for amino acids, it may take place in water through the stochastic loss and reacquisition of the H at C2, i.e.,  $\alpha$ - to the carboxyl, owing to electron withdrawing facility of that group (Scheme 1). Racemization will lead compounds with an  $\alpha$ -H having *ee* to be racemic with time, i.e., to a mixture with equal amounts of D- and L-enantiomers. Since protein amino acids all have a hydrogen attached to the second carbon of the alkyl chain, the same compounds in asteroids would eventually become racemic during a hydrous phase. When this H is replaced by an alkyl group, as is the case of the 2-methyl amino acids, racemization would not be possible during the same phases.

Various hypotheses have been put forward for how these *ee* could have been attained. The more pursued were the possible asymmetric decomposition of chiral compounds by UV circular polarized light (CPL) in cosmic environments (Balavoine et al., 1974; Rubenstein et al., 1983), the effect of water processes upon their syntheses in the asteroidal parent bodies (Glavin and Dworkin, 2009), and magneto chiral effects (Rikken and Raupach, 2000). So far, however, none appears to fit the data. Differential photolysis by UV CPL consists in not affecting equally the two enantiomers of a chiral molecule while, given time, eventually destroying them both; in the case of amino acids, their anisotropy factor, i.e., the



**Scheme 2.** The particular case of racemization that involves amino acids with two chiral centers and are present as two sets of enantiomers, shown for the four stereoisomers of isoleucine and alloisoleucine.

ratio between photolysis of one enantiomers versus total decomposition, is so small (Balavoine et al., 1974) that it would restrict *ee* to values much lower than those determined in meteorites. Magneto-chiral effects would produce even lower *ee* (Rikken and Raupach, 2000). As for the effect of protracted water exposure for the amino acids in meteorites, both the crystallization behavior determined for isovaline (Pizzarello and Groy, 2011) and its inability to racemize due to the lack of an  $\alpha$ -H, exclude their attaining of *ee* by the most commonly proposed processes involving phase change accompanied by racemization (Klussmann et al., 2006).

The molecular and chiral distributions determined for organic compounds in CM and CI meteorites do not apply to all CC equally and differ significantly for the Renazzo-type (CR) meteorites. These meteorites contain ammonia and amino acids in higher abundance than CMs, by at least an order of magnitude, and show a predominance of linear-chain over  $\alpha$ -methyl amino acids. This distribution is opposite to that found for CMs and differs also in that CR  $\alpha$ -methyl amino acids show few and small L-*ee*, which were detected just for isovaline, only in some stones and, when present, of ~2% (Pizzarello et al., 2008).

The novel finding for CR amino acids was their display of large *ee* for the set of diastereomers L-isoleucine (Ile) and D-allo-isoleucine (alle). These are two six-carbon amino acids that have the same general formula but differ in having different distributions of their substituents along the chain. Their C2 and C3 both have H substituents, however, only C2 can racemize while C3, too far removed from the carboxyl, cannot. As a consequence racemization of any diastereomer in the set does not lead to its enantiomer but to the diastereomer of opposite configuration (Scheme 2). This behavior and the *ee* data obtained for these amino acids in CRs, therefore, have allowed a view of the possible extent of the original chiral asymmetry to be found in meteorites. Although Ile is a protein amino acid and common terrestrial contaminant, the indigeneity of its *ee* was corroborated by isotopic analyses (Pizzarello et al., 2008).

The above findings have allowed two implications, i.e., that *ee* might have been originally present in other  $\alpha$ -H amino acids but were later lost to racemization, and that, since amino acids are believed to have formed in meteorites' parent bodies via Strecker-type syntheses from aldehydes or ketones in the pres-

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