

L-AMINO ACID ENRICHMENTS IN CARBONACEOUS METEORITES: IMPLICATIONS FOR THE ORIGIN OF BIOLOGICAL HOMOCHIRALITY. D. P. Glavin¹, M. P. Callahan¹, and J. P. Dworkin¹, ¹Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, daniel.p.glavin@nasa.gov

Introduction: Meteorites provide a record of the chemical processes that occurred in the early solar system before life began on Earth. The delivery of organic compounds by carbonaceous meteorites to the early Earth and other planetary bodies could have been an important source of prebiotic compounds required for the emergence of life as we know it [1]. The finding of slight to significant enantiomeric excess for several indigenous amino acids in the Murchison and Murray CM-type carbonaceous meteorites [2-4] could point toward a possible prebiotic contribution to the origin of biological homochirality by the delivery of extraterrestrial organic material from asteroids and comets to the early Earth.

It has been proposed that the L-enantiomeric excesses found in Murchison and Murray could be the result of asymmetric photolytic decomposition by UV circularly polarized light (UV-CPL) in the presolar cloud [5]. However, in order to produce the largest ~15% left handed excess previously reported for isovaline in Murchison [4], more than 99% of this amino acid would have to be destroyed by UV-CPL [6]. Therefore, UV-CPL as the sole mechanism for enantiomeric enrichment seems unlikely given the high concentrations of isovaline found in Murchison and Murray and evidence that isovaline and other α -amino acids formed by Strecker-cyanohydrin synthesis during aqueous alteration on the parent body [7], thus shielded from CPL. Other possible mechanisms for initial amino acid symmetry breaking include physical processes, such as crystallization [8]. It is also possible that a small initial chiral imbalance was amplified under aqueous conditions in the meteorite parent body [9,10].

To investigate the role of aqueous alteration in amino acid asymmetry in carbonaceous meteorites, we focused on the distribution and enantiomeric composition of the five-carbon (C_5) amino acids found in the most aqueous altered type 1 meteorites Orgueil (ORG, CI1), SCO 06043 (SCO, CM1), MET 01070 (MET, CM1) and GRO 95577 (GRO, CR1), the less altered type 2 meteorites Murchison (MUR, CM2), LEW 90500 (LEW, CM2) and LON 94102 (LON, CM2), and the most pristine unaltered type 2 and 3 meteorites EET 92042 (EET, CR2) and QUE 99177 (QUE, CR3). Amino acid abundances and enantiomeric ratios were determined using a highly sensitive liquid chromatography fluorescence detection and time of flight mass spectrometry (LC-FD/ToF-MS) technique coupled with OPA/NAC derivatization [11].

Results and Discussion: Large L-enantiomeric excesses of the amino acid isovaline were measured in the aqueous altered type 1 meteorites Orgueil, SCO, MET, and GRO using LC-FD/ToF-MS with values from 15% up to 29% (Fig. 1). The L-isovaline excess found in the CM1 meteorite SCO ($L_{ee} = 29 \pm 5\%$) is the largest reported for any meteorite to date. We also measured a large L-excess of $18.5 \pm 2.6\%$ for isovaline in Murchison that was higher than previous L_{ee} measurements ranging from 0 to 15.2% using gas chromatography mass spectrometry [4]. Interference from all other possible five carbon amino acid isomers, analytical biases, and terrestrial amino acid contamination were ruled out as a possible source of the L-excesses in these meteorites [11]. In contrast, we observed no L-isovaline enrichment for the most primitive unaltered type 2 and 3 CR meteorites EET and QUE. The magnitude of the L-isovaline enrichments in these meteorites is consistent with the degree of aqueous alteration as inferred from the relative abundances of the amino acids β -alanine and glycine (Fig. 1). Furthermore, the correlation between asymmetry-carrying isovaline and hydrous silicate abundances in some Murchison fragments [4] provides additional evidence that the formation of meteoritic L-excesses may have been a secondary process due to aqueous interaction with the lithic environment.

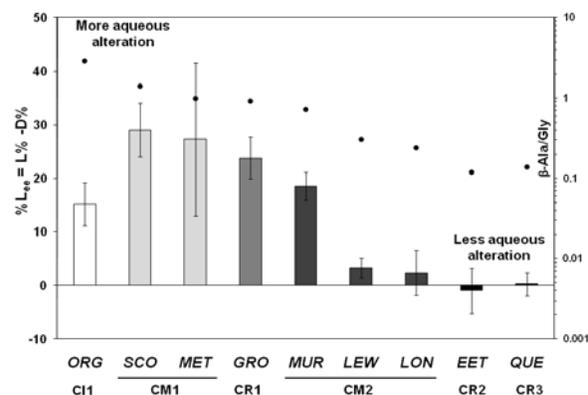


Figure 1. A comparison of isovaline enantiomeric excesses found in several meteorites compared with the degree of aqueous alteration as inferred from the relative abundances of β -alanine and glycine. The percent L-enantiomeric excess is defined as $\%L_{ee} = [(L - D) / (L + D)] \times 100$. The errors are based on the standard deviation of the average value of between 8 and 23 separate measurements.

Conclusion: The large enantiomeric excesses in isovaline that have previously been detected in Murchison have now been independently confirmed by using a different analytical technique. In addition, the discovery that the more aqueous altered CM and CR type 1 meteorites SCO, MET, and GRO have higher enrichments of L-isovaline than the less altered type 2 CM and type 2 and 3 CR meteorites, provides strong evidence that aqueous alteration played an important role in the amplification of amino acid asymmetry on the parent bodies of these meteorites. Although α -methyl amino acids such as isovaline are not common in the terrestrial biosphere, these amino acids are highly resistant to racemization and therefore may have been very well suited as catalysts for transferring their asymmetry to the α -hydrogen protein amino acids or other prebiotic compounds, such as sugars [12], important in life today. The impact of extraterrestrial input versus local abiotic synthesis of asymmetric amino acids on the origin of homochirality in life on Earth is unknown. However, the fact that only L-amino acid excesses have been found in meteorites analyzed so far (no D-excesses) may indicate that the origin of life on Earth and possibly elsewhere in our solar system was biased toward L-amino acid homochirality from the very beginning.

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