

ENANTIOMER EXCESSES IN METEORITIC ORGANIC COMPOUNDS: A ROLE FOR RADIATION-MAGNETISM? ¹G. Cooper and ²A. C. Rios ¹Exobiology Branch, NASA-Ames Research Center, MS 239-4, Moffett Field, CA 94035, george.cooper@nasa.gov, ²Blue Marble Space Institute of Science, Exobiology Branch, NASA-Ames Research Center, MS 239-4, Moffett Field, CA 94035, andro.c.rios@nasa.gov

Introduction: Carbonaceous chondrites contain an insoluble "macromolecular" carbon phase (1–3) as well as discrete soluble organic compounds including amino acids (3, 4) and sugar derivatives (5). Both the macromolecular carbon and the sugar derivatives are thought to have formed through aqueous formaldehyde chemistry (2, 5). Formaldehyde is a ubiquitous molecule in interstellar space environments and therefore its chemistry was likely important during the formation of the Earth and other planets. It was also likely delivered throughout Earth's history: it is found in comets (6) and (asteroidal) meteorites (7, 8). Among the reactions of formaldehyde, those in water are thought to be an important part of the primordial route to today's nucleic acids, DNA and RNA. A plausible pre-biotic path to these biopolymers would begin with the "formose" reaction, the self-reaction of formaldehyde in an alkaline aqueous medium (9, 10). Formaldehyde's inclusion in the young solar system's planets would have provided a relatively fast route to a variety of hydroxylated compounds related to nucleic acids and metabolism, including sugars, sugar acids, sugar alcohols, and formaldehyde polymers.

This project involves the utilization of formaldehyde reactions to produce chiral compounds, i.e., compounds that are composed of two non-superposable mirror images or "enantiomers", analogous to a left and right hand. Such molecules are important in contemporary life because biological polymers (proteins, nucleic acids, etc.) are homochiral, i.e., their monomers consist of only one of the two enantiomers. In contrast, it has been shown, at least in one lab setting, that abiotic syntheses of significantly sized RNA polymers do not proceed if the monomers are present in racemic (50:50) mixtures due to "enantiomeric cross-inhibition" (11). In general, there is a scarcity of prebiotically plausible mechanisms that are capable of inducing enantiomer excesses (12). Therefore, there is a need to uncover plausible abiotic mechanisms (if any) that could have led to net enantiomer enrichments. Here, "net" refers to an excess of one enantiomer in the total environment, as compared to processes such as the differential melting or sublimation of enantiomers, where excesses are only present in the immediate environment of the process (i.e., the total environment is still racemic).

Two laboratory accessible mechanisms have stood out for creating actual net enantiomer excesses in organic compounds: (1) the slight preferential destruction of one enantiomer by circularly polarized UV light

(13). At low temperatures such methods might also synthesize compounds containing enantiomer excesses (14) and (2) photo-magnetic effects: so far applied only to pre-made inorganic (metal) complexes. In the latter case, although the resulting enantiomer excesses are very small ($\sim 10^{-4}$), the authors demonstrate reversible excesses with opposite magnetic direction (15). Powerful magnetic fields (up to ~ 15 T) were required. Natural physical forces such as magnetism and radiation were likely significant in shaping the early Solar System (16)

We are also attempting to synthesize compounds under the influence of magnetic fields and radiation. However, in contrast to the above photo-magnetic experiments, we are attempting to create enantiomer excesses (1) during the actual synthesis of the target compounds (2) in prebiotically plausible and relevant compounds (sugars and their derivatives) and (3) under much milder prebiotic conditions. This work may determine if the early interaction between organic precursor compounds and radiation and magnetism could have led to (at least) a portion of the enantiomer excesses observed in carbonaceous chondrites (3, 4, 5, 7).

Methods: Reaction mixtures are typically placed in magnetic fields of varying strengths: up to ~ 0.5 T with concurrent irradiation. These fields are reversed in attempts to produce opposite enantiomer excesses (e.g., Fig. 1). Irradiations, so far, have varied from ~ 254 nm to 600 nm. Reactions consist of formaldehyde in mixtures of only salts known to be present in carbonaceous chondrites (Ca^{2+} , Na^+ , SO_4^{2-} , CO_3^{2-} , etc.). Afterwards, reaction mixtures are desalted and prepared for analysis by gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS). So far, the majority of analyses have been done by derivatization/GC-MS. Carboxylic groups were derivatized to their isopropyl (ISP) or ethyl (Et) ester. Hydroxyl groups were derivatized to O-trifluoroacetyl (TFA) esters with trifluoroacetic anhydride (17). The GC-MS consisted of an Agilent 6890 GC interfaced to a model 5975 quadrupole mass spectrometer. In many applications the GC was fitted with a Varian (Chrompack) Chirasil Dex-CB column (25m x 0.25) for enantiomer separations. Typical GC injector temperatures are near 200°C and the helium flow rate varies between 1-1.7 ml/min. Typical MS detector conditions: injector - 200°C; quadrupole MS temp., 150°C; carrier gas, helium; transfer line, 200°C; electron voltage, 70eV. Typical GC conditions: initial oven temp., 45°C; heat at 3°C/min to 70°C, hold for

30 min - heat at 3°C/min. to 200°C.

Results: Figure 1 shows the result of just one preliminary experiment aimed at the creation of reversible photo-magnetic enantiomer excess. Although other experiments also appear to show the achievement of reversible excesses, we are attempting to determine if random contamination could also give such results. For example, it is known that the addition of a catalytic compound - containing an enantiomer excess - to a formose-like reaction will direct an enantiomer preference in some of the resulting sugars [18]. Therefore, could random contamination account for results such as those in Fig. 1? This and other aspects and results of experiments will be presented.

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Figure 1. Results of one photo-formose experiment showing the apparent creation of reversible enantiomer excesses. +B and -B refer to opposite magnetic field direction: otherwise, the two runs were performed under nearly identical conditions. Each of the reaction mixtures were subjected to post-reaction oxidation (H_2O_2) to convert a portion of the (several) produced sugars to sugar acids, e.g., erythronic acid and threonic acid. Several other compounds (not shown) are also present.

