

**POSSIBLE MECHANISM(S) IN THE PHOTO-MAGNETIC PRODUCTION OF ENANTIOMER EXCESSES.** G. Cooper<sup>1</sup>, W. Jackson<sup>2</sup>, M. Thompson<sup>3</sup>, A. C. Rios<sup>3</sup>, K. Yeung<sup>3</sup>, and C. Dateo<sup>1</sup>, <sup>1</sup>Exobiology Branch, NASA-Ames Research Center, MS 239-4, Moffett Field, CA 94035, george.cooper@nasa.gov, <sup>2</sup>Department of Chemistry, Univ. of California Davis, Blue Marble Space Institute of Science, NASA-Ames, <sup>3</sup>Blue Marble Space Institute of Science, Exobiology Branch, NASA-Ames.

**Introduction:** Among the multitude of organic compounds identified in carbonaceous chondrites [1, 2] are sugar acids ((HO-R)<sub>x</sub>COOH), i.e., oxidized counterparts of the common aldehyde sugars (e.g., glyceraldehyde, erythrose, ribose, glucose, etc.). In the historical study of extraterrestrial compounds chiral analyses are particularly significant in origins-of-life studies. Chiral compounds 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 chiral monomers usually consist of only one of the two enantiomers. 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) amounts [3]. The latter results may argue for, at least, significant enantiomer excesses in organic compounds before the origin of nucleic acids and life. Therefore, the finding that amino acids [4, 5] and sugar acids [6] in carbonaceous chondrites possess enantiomeric excesses may aid in understanding one source of precursors to homochirality.

There is a scarcity of prebiotically plausible mechanisms that can induce enantiomer excesses [7]. Two laboratory-accessible mechanisms have stood out for creating net enantiomer excesses in organic compounds: (1) the slight relative destruction of one enantiomer by circularly polarized UV light [8, 9]. (2) photo-magnetic effects [10]: 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 due to a greater dissociation of one enantiomer over the other. Powerful magnetic fields (up to  $\sim 15$ T) were required, however, natural physical forces such as magnetism and radiation were likely significant in shaping the early Solar System [11].

Formaldehyde and glycolaldehyde are generally regarded as likely sources of sugar derivatives in the early solar system due to their reactions in alkaline aqueous solution [12, 13]. Both compounds are ubiquitous in interstellar environments and were also likely delivered throughout Earth's history: they are found in comets [14] and carbonaceous chondrites [15, 16].

Our project involves the laboratory synthesis of sugars and their derivatives with aqueous formaldehyde

and/or glycolaldehyde under the influence of magnetic fields and radiation. As in early results (17), this work continues to determine if the interaction between these compounds and the above physical forces, in relevant prebiotic conditions, could have led to the synthesis of enantiomer excesses in prebiotic organic compounds.

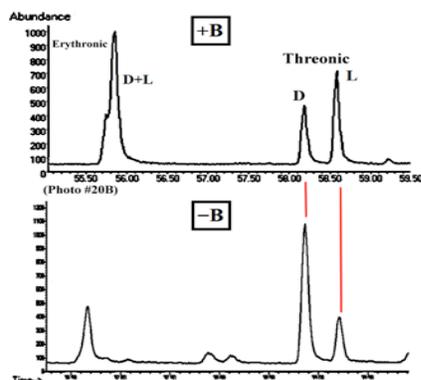
**Methods:** Most reaction conditions, analytical methods (including gas chromatography-mass spectrometry (GC-MS) and materials were described previously [17]. Briefly, reaction mixtures are typically placed in magnetic fields of varying strengths: up to  $\sim 0.5$ T with concurrent irradiation. These fields are reversed in attempts to produce opposite enantiomer excesses as shown previously (e.g., Figure 1). The GC-MS is an Agilent 6890 GC-5975 quadrupole MS. Compounds were separated as their isopropyl-trifluoroacetyl derivatives using an Agilent (Chrompack) Chirasil Dex-CB column (25m x 0.25). Absorption measurements were made with a SpectraMax M5 spectrometer (Molecular Devices).

**Results:** For reference, Figure 1 shows a previous result [17] of just one experiment aimed at the creation of reversible photo-magnetic enantiomer excess (ee). One question is what effects (if any) cation-sugar complexation have on the formation of ee. Is there evidence of such complexes in our reaction mixtures? In Figure 2 we modified a presentation of absorption measurements from Khomenko and Krylov, 1974 [18]. That work and others demonstrated formation of the enediol form of sugars (glucose, in Figure 2) in alkaline solution: this species absorbs at 310 nm: addition of calcium shifts absorption to  $\sim 330$ -340 nm. However, all such work (that we are aware of) report that such species only occur in highly alkaline solutions (e.g., employing NaOH or Ca(OH)<sub>2</sub>). We are not aware of reports of such absorptions ( $\sim 330$  nm) using glycolaldehyde. We attempted to determine if glycolaldehyde would also form such a calcium complex, Figure 3 shows the results. A substantial complex, in a solution of glycolaldehyde and NaOH, can be seen in the range of  $\sim 320$ -340 nm.

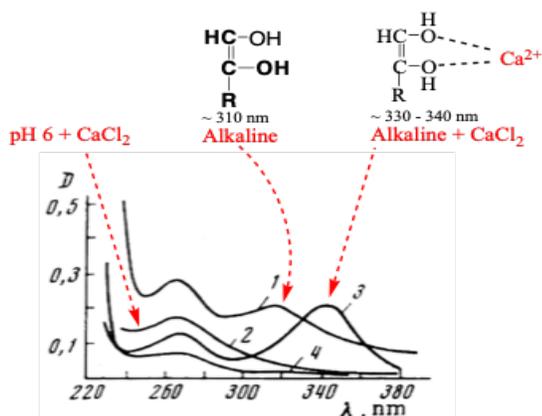
However, from a plausible prebiotic point of view, and relevant to our reaction mixtures, can such complexes form under pH-neutral or slightly alkaline conditions? Reference 18 states that such complexes are not formed in neutral solution, e.g., Figure 2, Trace 2. However, we show in Figure 4 that at least the calcium-gly-

colaldehyde complex is likely present in neutral solution. Also (not shown), is a complex in carbonate solution. Calcium complexes with larger sugars almost certainly occur in our neutral and/or alkaline reactions as synthesis of larger sugars gradually proceeds during the progress of reactions: Angyal [19] and others have demonstrated the relative stability of certain five- and six-carbon sugar-calcium complexes in aqueous solution. We will present further evidence that we are seeing calcium complexation and discuss other possible mechanisms that contribute to the formation of enantiomer excesses.

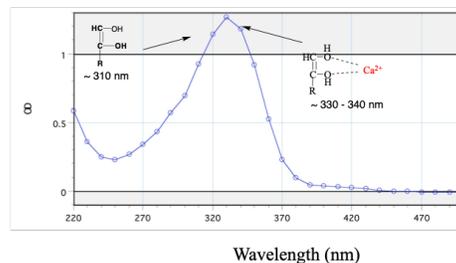
**Figure 1. Previous result [17]: reversible enantiomer excesses in photo-magnetic fields. +B and -B refer to opposite magnetic field direction.**



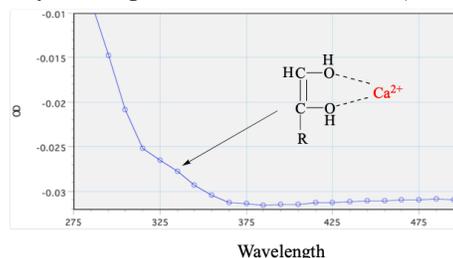
**Figure 2. Modified from Khomenko et al. [18]: absorption shift upon calcium addition. UV spectra of 0.5M glucose solutions. Trace 1: In alkaline solution (pH 12.4); Trace 2: Solution (1) acidified to pH 6; Trace 3: Alkaline solution of 0.5 M CaCl<sub>2</sub> + 0.1 M Ca(OH)<sub>2</sub>; Trace 4: solution (3) acidified (with HCl) to pH 2. Sugars may also be in the enolate (negative charge) form in highly alkaline solution.**



**Figure 3. Formation of a Ca<sup>2+</sup>-glycolaldehyde complex under highly alkaline (NaOH) conditions (this work). The neutral (shown) and enolate forms of glycolaldehyde are likely present.**



**Figure 4. Formation of an enediol and Ca<sup>2+</sup>-glycolaldehyde complex in neutral solution (this work).**



**References:** [1] Botta O. and Bada J. L. (2002) *Surveys in Geophysics*, 23, 411-465. [2] Pizzarello S. Cooper G. W. Flynn G. J. (2006) In "meteorites and the early Solar System II". D. Lauretta, L. A. Leshin, and H. Y. McSween Jr., Eds. University of Arizona Press. [3] Joyce G. F. et al. (1984) *Nature*, 310, 602-604. [4] Cronin, J.R. and Pizzarello, S. (1997) *Science*, 275, 951-955. [5] Glavin D. P. and Dworkin J. P. (2009) *Proc. Natl. Acad. Sci. USA*, 106, 5487-5492. [6] Cooper G. and Rios A. C. (2016) *P. Natl. Acad. Sci. USA*, 113, E3322-E3331. [7] Barron L. D. (2013) *Rend. Lincei*, 24, 179-189. [8] Flores J. Bonner W. A. Massey G. A. (1977) *JChS*, 99, 3622-3625. [9] Modica et al. (2014) *ApJ*, 788, 79-90. [10] Rikken G. and Raupach E. (2000) *Nature*, 405, 932-935. [11] Fu R. R. et al. (2004) *Science*, 306, 1089-1092. [12] Butlerow A. M. (1861) *Compt. Rendus Acad. Sci.*, 53, 145-147. [13] Delidovich I. V. Simonov A. N. Taran O. P. Parmon V.N. (2014) *ChemSusChem*, 7(7), 1833-46. [14] Milam S. N. et al. (2006) *Astrophys. J.*, 649, 1169-1177. [15] Pizzarello S. Schrader D. L., Monroe A. A. (2012) *Proc. Nat. Acad. Sci. USA*, 109, 1949-1954. [16] Lerner N. R. and Cooper G. W. (2005) *Geochim. Cosmochim. Acta* 69, 2901-2906. [17] Cooper G and Rios A. C. (2018) *LPS XLIX Abstract #2726*. [18] Khomenko T.I. and Krylov O.V., (1974) *Kinet. Katal.*, 15, 625-630. [19] S. J. Angyal S. J. (1973) *Pure Appl. Chem.*, 35, 131-146.