Enantiomer Ratios of Meteoritic Sugar Derivatives

George Cooper
NASA-Ames Research Center, MS 239-4, Moffett Field, CA 94035
george.cooper@nasa.gov

Carbonaceous meteorites contain a diverse suite of soluble organic compounds. Studies of these compounds reveal the Solar System's earliest organic chemistry. Among the classes of organic compounds found in meteorites are keto acids (pyruvic acid, etc.), hydroxy tricarboxylic acids (1), amino acids, amides, purines and pyrimidines [2-3]. The Murchison and Murray meteorites are the most studied for soluble and insoluble organic compounds and organic carbon phases. The majority of (indigenous) meteoritic compounds are racemic, (i.e., their D/L enantiomer ratios are 50:50). However, some of the more unusual (non-protein) amino acids contain slightly more of one enantiomer (usually the L) than the other [4, 5]. This presentation focuses on the enantiomer analyses of three to six-carbon (3C to 6C) meteoritic sugar acids. The molecular and enantiomer analysis of corresponding sugar alcohols will also be discussed. Detailed analytical procedures for sugar-acid enantiomers have been described [6].

Results of several meteorite analyses show that glyceric acid is consistently racemic (or nearly so) as expected of non-biological mechanisms of synthesis. Also racemic are 4-C deoxy sugar acids: 2-methyl glyceric acid; 2,4-dihydroxybutyric acid; 2,3-dihydroxybutyric acid (two diastereomers); and 3,4-dihydroxybutyric acid. However, a 4C acid, threonic acid, has never been observed as racemic, i.e., it possesses a large D excess. In several samples of Murchison and one of GRA 95229 (possibly the most pristine carbonaceous meteorite yet analyzed) threonic acid has nearly the same D enrichment. In Murchison, preliminary isotopic measurements of individual threonic acid enantiomers point towards extraterrestrial sources of the D enrichment.

Enantiomer analyses of the 5C mono-sugar acids, ribonic, arabinonic, xylonic, and lyxonic also show large D excesses. It is worth noting that all four of these acids (all of the possible straight-chained 5C sugar acids) are present in meteorites, including the rare lyxonic acid, and their relative abundances are in equilibrium proportions [7]. In addition (in contrast to the above D-only excesses), some of the above acids are found in biology as the L enantiomer. Whether rare are common, all of the 6C sugar acids that are present in sufficient amounts to allow enantiomer analysis (Mannonic, gluconic, altronic, talonic, idonic, gulonic, and galactonic) also, apparently, possess significant D excesses.

References:

[1] Cooper G, Reed C, Nguyen D, Carter M and Wang Y (2011) Detection and formation scenario of citric acid, pyruvic acid, and other possible metabolism precursors in carbonaceous meteorites. PNAS 108, 14015-14020.

[2] Pizzarello S, Cooper G W and Flynn G J (2006) The Nature and Distribution of the Organic Material in Carbonaceous Chondrites and Interplanetary Dust Particles in Meteorites and the Early Solar System II. D. Lauretta, L. A. Leshin, and H. Y. McSween Jr., Eds. University of Arizona Press.

[3] Callahan M P, Smith K E, Cleaves H J, Ruzicka J, Stern J C, Glavin D P, House C H and Dworkin J P (2011) Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases. Proceedings of the National Academy of Sciences of the United States of America. 108 (34): 13995-13998.

[4] Pizzarello S and Groy T L (2011) Molecular asymmetry in extraterrestrial organic chemistry: An analytical perspective Geochimica et Cosmochimica Acta 75, 645–656.

[5] Glavin D P and Dworkin J P (2009) Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies. Proc. Natl. Acad. Sci. USA 106, 5487-5492.

[6] Cooper G, Sant M and Asiyo C (2009) Gas Chromatography-Mass Spectrometry Resolution of Sugar Acid Enantiomers on a Permethylated β-Cyclodextrin Stationary Phase. J. Chrom. A, 1216, 6838–6843.

[7] Kalman M, Sokolowski J, Szafranek J and Lönnberg H (1987) Kinetics and Mechanism for the Epimerization of Aldopentonic Acid Potassium Salts in Aqueous Alkali. J. Carbohydr. Chem., 6, 587-592.