

Inconclusive evidence for nonterrestrial isoleucine enantiomeric excesses in primitive meteorites

Pizzarello et al. (1) recently described the soluble organic content of eight Antarctic Renazzo-type (CR) carbonaceous chondrites and reported large enantiomeric excesses (*ee*) of L-isoleucine and D-alloisoleucine. The reported values of *ee* decrease with inferred increases in aqueous alteration. We believe the conclusions presented in the paper are not fully justified and the data are potentially flawed.

Potential terrestrial contamination of meteoritic amino acid data must always be considered. The manuscript states that “terrestrial contamination levels... were evaluated based on the presence of proteinogenic amino acids’ L-excesses and accounted for when needed,” but this “accounting” is not described. A wide range of L-proteinogenic amino acid excesses was measured even within single meteorites (1) (0–80% in Queen Alexandra Range (QUE) 99177), and it is not clear how these data were corrected to allow reliable measurements of the proteinogenic amino acid L-isoleucine *ee*, which ranged from 3.6 to 50% in different chondrites. Previous analyses of the CR chondrites QUE 99177 and Elephant Moraine (EET) 92042 (2, 3) measured racemic proteinogenic amino acids, including aspartic and glutamic acids, serine, and alanine. The recent work reported *ee* of up to 80% for these same compounds in the same meteorites (1), indicating that the recently analyzed fragments were far from pristine. Compound-specific isotopic data are needed to establish the terrestrial contribution to the reported *ee*.

Coeluting compound interferences must also be considered (4). The entire mass fragmentation pattern of isoleucine and alloisoleucine peaks in the meteorite samples must be compared with pure standards to reduce the possibility of other coeluting compounds leading to inaccurate measurements of *ee* (there are 31 amino acids that are structural isomers of isoleucine); these data are not presented. Analysis of the other acyclic C₆ amino acid isomers, procedural blanks, and measurement errors, essential to understanding the significance of the measurements, are not discussed.

Even if the reported *ee* are both accurate and extraterrestrial in origin, aqueous processes are not necessarily responsible for the reduction of L-isoleucine and D-alloisoleucine *ee* from 60% in the most primitive chondrites to <5% in the most aqueously altered chondrites. Reducing the *ee* of L-isoleucine and of D-alloisoleucine requires converting L-isoleucine into D-isoleucine and D-alloisoleucine into L-alloisoleucine. This racemization involves simultaneous inversion of chiral centers at both the α- and β-carbons, which is highly unlikely (5). One possibility would be to convert excess L-isoleucine first to D-alloisoleucine by α-carbon epimerization, followed by epimerization at the β-carbon to convert the D-alloisoleucine to D-isoleucine. However, the β-epimerization rate has a half-life of 10⁸–10¹¹ y on the Earth’s surface (5); it is difficult to explain reduction of *ee* via aqueous alteration on meteorite parent bodies on a much shorter time scale. Additionally, if the chiral excess in the precursor aldehyde was preserved during amino acid synthesis, the *ee* in both L-isoleucine and D-alloisoleucine should be nearly the same; however, as shown by Pizzarello et al. (1), this was not the case. Finally, the predominance of α-amino acid isomers in these CR meteorites is consistent with formation through aqueous processes (2) and does not require the invocation of preaccretionary syntheses.

Jamie E. Elsila^{a,1}, Daniel P. Glavin^a, Jason P. Dworkin^a, Zita Martins^b, and Jeffrey L. Bada^c

^aSolar System Exploration Division, Goddard Space Flight Center, National Aeronautics and Space Administration, Greenbelt, MD 20771; ^bDepartment of Earth Science and Engineering, Imperial College London, London SW7 2AZ, United Kingdom; and ^cGeosciences Research Division, Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093

1. Pizzarello S, Schrader DL, Monroe AA, Lauretta DS (2012) Large enantiomeric excesses in primitive meteorites and the diverse effects of water in cosmochemical evolution. *Proc Natl Acad Sci USA* 109:11949–11954.
2. Glavin DP, Callahan MP, Dworkin JP, Elsila JE (2010) The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteorit Planet Sci* 45:1948–1972.
3. Martins Z, Alexander CMOD, Orzechowska GE, Fogel ML, Ehrenfreund P (2007) Indigenous amino acids in primitive CR meteorites. *Meteorit Planet Sci* 42:2125–2136.
4. Pizzarello S, Cronin JR (1998) Alanine enantiomers in the Murchison meteorite. *Nature* 394:236–236.
5. Bada JL, Zhao M, Steinberg S, Ruth E (1986) Isoleucine stereoisomers on the Earth. *Nature* 319:314–316.

Author contributions: J.E.E., D.P.G., J.P.D., Z.M., and J.L.B. wrote the paper.

The authors declare no conflict of interest.

¹To whom correspondence should be addressed. E-mail: jamie.elsila@nasa.gov.