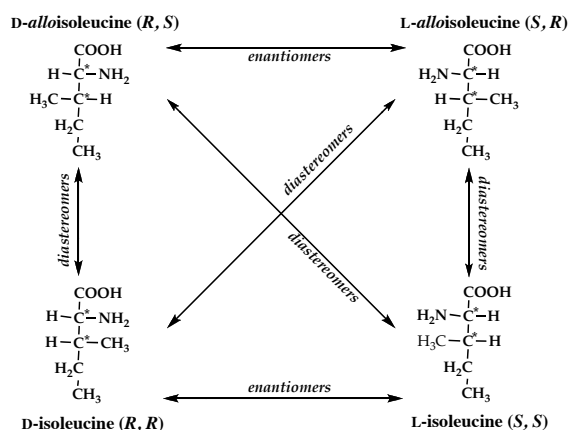


**METEORITIC AMINO ACIDS: THE PRODUCTS OF STILL UNKNOWN COSMIC AND SOLAR PROCESSES.** G. M. Chaban<sup>1</sup> and S. Pizzarello<sup>2</sup>, <sup>1</sup>NASA Ames Research Center, Moffet Field CA 94035; galina.m.chaban@nasa.gov. <sup>2</sup>Arizona State University, Dpt. of Chemistry & Biochemistry, Tempe AZ 85287-1604; pizzar@asu.edu.

The CM, CI [1] and CR [2] type Carbonaceous Chondrites (CC) contain abundant and complex suites of soluble organic compounds. So far, their studies have offered the only detailed analyses of the extraterrestrial chemistry that preceded terrestrial life. Amino acids carry a particular significance in this regard, as they have identical counterparts in terrestrial proteins. We know that their formation might have involved solar as well as presolar cosmic regimes [1]; however, we have not as yet reached a satisfactory understanding of the synthetic sequence that lead to their diverse suite in meteorites. This knowledge would tell us of the processes and locales responsible for the abiotic syntheses of molecule essential to life as well as allow assessment of their possible extent outside the Earth and the solar system.

One intriguing property of meteoritic amino acids is the distribution of diastereomer species within longer chain compounds. Diastereomers are molecules that have two chiral centers (C\*), i.e., two carbons with four different substituents. Amino acids of this type are present as two distinct compounds, depending on the spatial arrangement of substituent about these C\*, and two sets of D- and L-enantiomers (called diastereomers). The most known example is that of the isoleucine (Ile) and *allo* isoleucine (*Allo*) pairs described below.



In general, Murchison extracts found that amino acid abundances decline with increasing chain

length (e.g., [1]) and, within subgroups, favors the branched species at any given carbon number (e.g.,  $\alpha$ -amino isobutyric acid >  $\alpha$ -amino-*n*-butyric acid;  $\beta$ -amino-2,2-dimethylpropanoic acid >  $\beta$ -pentanoic acid, etc.).

In the case of *Allo*-Ile diastereomers, however, the *Allo* enantiomers are significantly more abundant than those of *Ile* (*Allo*/*Ile*  $\approx$  2-1.5) in spite of their similarity in C number and branching. The same was found true in a CR2 meteorite that has shown a different relative distribution of soluble organics [2]. Analyses of the distribution of the Murchison sixteen 7C  $\alpha$ -amino acids [3] further showed that abundances follow the extent and position of the branching in the alkyl chain; e.g., 2-amino-2,3-methylpentanoic acid is twice as abundant as 2-amino-2-methylhexanoic acid and three times as 2-amino-3,3-methylpentanoic acid. In two diastereomer sets (the 2-amino-3-methylhexanoic and 2-amino-3,4-methylpentanoic acid pairs), the *allo* forms were also more abundant than the others while those of the third set, 2-amino-2,3-methylpentanoic acid, are of about equal amounts.

These analytical results and the large diastereomeric abundance ratios in meteorites were unexpected; in fact, compounds of similar composition such as those of diastereomer pairs should have comparable energies of formation (as, for example, was found for the 6C isomers leucine and isoleucine [4]) and are expected to have synthetic ratios close to unity under equilibrium conditions.

In general terms, these distribution data seem to suggest that the synthetic conditions for these meteoritic amino acids, or their precursors, were far from thermodynamic equilibrium. Because such distributions may be related to the compounds' synthetic processes, we have initiated computer-aided *ab initio* calculation of selected 6 & 7C amino acid diastereomer species. The aim is to compare amino acids' expected distributions based on their energies of formation with the abundances in meteorites, in the hope the study would help constrain the conditions/likely locals that affected their syntheses.

We report here our first assessment, which was obtained with calculations done at the MP2/DZP level of theory. This is not the highest level possible but should offer reasonable accuracy. The data for 6C *Allo/Ile* (Table 1) confirmed previous reports on 6C amino acid isomers and that little difference in energies of formation exist between the two diastereomers. For the 7C amino acids analyzed, the lower energy structure is that of *Allo*2-amino-2,3-methylpentanoic acid followed closely by its diastereomer acid. These data would agree with the findings in Murchison of approximately equal amounts of the diastereomers. However, the other diastereomer species, which are about 3-5 Kcal/mol higher, do not seem to show large enough differences between diastereomer pairs to justify the 2:1 amount ratios observed in the meteorite.

TABLE 1. Energies of formation of some diastereomer amino acids.

Amino acid (a)	Total energies (Atomic units)	Rel. energies (Kcal/mol)
Isoleucine	-440.4442015	0.0
<i>Allo</i> isoleucine	-440.4435339	0.4
2amino3methylhexanoic a.	-479.6294615	3.0
<i>Allo</i> " "	-479.6288505	3.4
2amino4methylhexanoic a.	-479.6265454	4.8
<i>Allo</i> " "	-479.6293236	3.1
2amino2,3methylpentanoic a.	-479.6335644	0.4
<i>Allo</i> " "	-479.6342675	0.0

These preliminary data are somewhat puzzling and lead to several questions. Do they indicate amino acid syntheses that involved processes far from conditions of thermodynamic equilibrium, possibly through radical precursors? Or do the observed ratios represent instead formation at or near equilibrium at very low temperatures, as it would be consistent with the high deuterium content of these amino acids in meteorites?

All meteoritic  $\alpha$ -amino acids have shown marked D-enrichment, albeit with unique isotopic trends for each of the structural subgroups [1]. This deuterium enrichment has been interpreted to suggest a formative relationship between the compounds and the cold (5-10K) dense clouds of the interstellar medium (ISM), where syntheses are driven by ion-molecule reactions and are known to yield highly deuterated molecules. Models of ISM reactions have also predicted a possible one-step growth of carbon chains on the surface of

growth of carbon chains on the surface of grains [5] as well as a complex cloud chemistry with time leading to large D-enrichments in pre-stellar core regions [6].

We could speculate that similar processes may have accounted for the formation of the more highly deuterated amino acids of meteorites, e.g., the precursor radicals of these long-chain branched compounds could have built up with high D-content on the surface of icy grains of the ISM dense clouds and did so following still unknown energetic pathways that favored certain elongation branching. Subsequent warmer stages of star formation may have allowed their desorption, further mixing, reactions, and the addition of functional groups (e.g., [7, 8]).

What analyses of these amino acids in meteorites do suggest with more certainty is that it is unlikely that much epimerization between diastereomers [4] took place during an asteroidal aqueous phase, i.e., they seem to point to either short periods of warming or cold aqueous environments for at least CM2 and CR2 parent bodies.

Computations will be repeated to obtain thermodynamic properties of the amino acids at temperatures relevant to cold cosmic conditions and, to this purpose, Columbia supercomputer time at NASA Ames has recently been awarded. Should these new data give energies of formation for diastereoisomeric amino acids that still imply abundances markedly different from those determined in meteorites, the findings will be one more analytical feature that any model aimed to explain the formative chemistry of meteoritic amino acid precursors, in the ISM or elsewhere, will have to reconcile with.

**References:** [1] Pizzarello S. et al. (2006) In: *Meteorites and the Early Solar System II*, D. S. Lauretta and H.Y. McSween Jr., Ed.s, University of Arizona Press, Tucson, pp. 625-651. [2] Pizzarello S. et al. (2008) *PNAS in press*. [3] Cronin J. R. and Pizzarello S. (1986) *Geochim. Cosmochim. Acta* **50**, 2419-2427. [4] Smith G. G. et al. (1978) *J. Org. Chem.* **43**, 1-5. [5] Charnley S. B. et al. (2004) *Mont. Not. R. Astron. Soc.* **347**, 157-162. [6] Vestel C. et al. (2004) *A.J.* **606**, L127-130. [7] Greenberg J. M. (1982) In: *Comets*, L. L. Wilkening Ed. University of Arizona Press, Tucson, pp. 131-163. [8] Bottinelli S. et al. (2005) *Ap J.* **615**, 354-358.