

**THE CARBON ISOTOPIC DISTRIBUTION OF MURCHISON AMINO ACIDS.** S. Pizzarello<sup>1</sup>, Y. Huang<sup>2</sup> and M. Fuller<sup>2</sup>. <sup>1</sup>Dept. of Chemistry & Biochemistry, Arizona State University, Tempe, AZ 85287. pizzar@asu.edu. <sup>2</sup> Dept. of Geological Sciences, Brown University, Providence, RI 02912.

The origin of amino acids in meteorites is not yet well understood, in spite of extensive molecular, isotopic, and chiral analyses of the last thirty years that have elucidated many of these compounds' features and distribution. The present general view of meteoritic amino acid formation is that of an interstellar/planetary sequence of Strecker-like reactions between aldehydes/ketones, HCN, water, and ammonia [1]. This type of reaction, however, is non-stereospecific and cannot account for the enantiomeric excesses found in some Murchison and Murray amino acids, at least not directly. Since there are indications that the reaction was, indeed, involved in the formation of amino acids in meteorites [2], the questions arise whether we should consider a concomitant intervention of asymmetric catalyst(s) [3], and that we may now detect enantiomeric excesses only in amino acids that did not racemize during parent body water alteration, or we should consider a different formation all together for amino acids displaying asymmetry. In fact, recent analyses of the Tagish Lake meteorite have suggested that the synthetic pathways for organics in meteorites, including amino acids, may have been multiple and distinct [4]. Isotopic analyses of meteoritic amino acids, which could help identify their synthetic history(ies), so far have been limited to either very few individual compounds, as in the pioneer study by Engel et al. [5], or groups of amino acids [6], and thus insufficient for detailed comparisons.

In the attempt to further our understanding of amino acid formation in meteorites and of the possible differences between their varied subgroups, we have analyzed the carbon isotopic composition of individual Murchison amino acids by gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS). Prior to isotopic analyses, the amino acids were obtained in an hydrolyzed water extract of the meteorite (~ 11.0 g interior fragments) and separated from other meteoritic components following previously tested procedures [7]. In brief, groups of amino acids of similar chain length were isolated by reverse phase HPLC and then derivatized to their O-isopropyl N-TFA derivatives for GC-MS separation and identification. With an approach somewhat different from that used in previous molecular analyses, the HPLC separation aimed to collect the compounds of interest fully in one fraction, to avoid isotopic fractionation which trials with standards have shown to occur (in small extent, ~ 3‰) along the eluting HPLC peaks.

Results are summarized in the following Table and Figure. The figure compares graphically the  $\delta^{13}\text{C}$  of the three homologous series of linear 2-amino 2-H and 2-amino 2-methyl amino acids (both referred to as  $\alpha$ -amino acids), and for the series of linear non- $\alpha$  isomers, i.e., those with the amino group in 3-,4-, 5-, etc. posi-

tion. It can be seen that all amino acids have high  $^{13}\text{C}$  content, as expected [5]. This abundance differs for the two subgroups of  $\alpha$ -amino acids and decreases for both with increasing chain length. This trend appears to be reversed for non- $\alpha$  amino acids, where the lowest value is found in  $\beta$ -alanine while amino acids of longer chain, some of which are still unknown for lack of standards but are identifiable by their mass spectra, reach higher values. An independence between isotopic values and chain length has been observed for dicarboxylic acids [4] and appears to be true also for dicarboxylic amino acids. The  $\delta^{13}\text{C}$  value measured for 2-methyl glutamic acid, a dicarboxylic six-carbon amino acid, was found not significantly lower than that of five-carbon glutamic acid. Both these sets of values are higher than those of the 5-C and 6-C monocarboxylic  $\alpha$ -amino acid measured. The N-substituted amino acid sarcosine gave the highest  $\delta^{13}\text{C}$  value determined in this study but other compounds of the N-substituted series could not be determined to establish any of the trends observed for the other  $\alpha$ -amino acids.

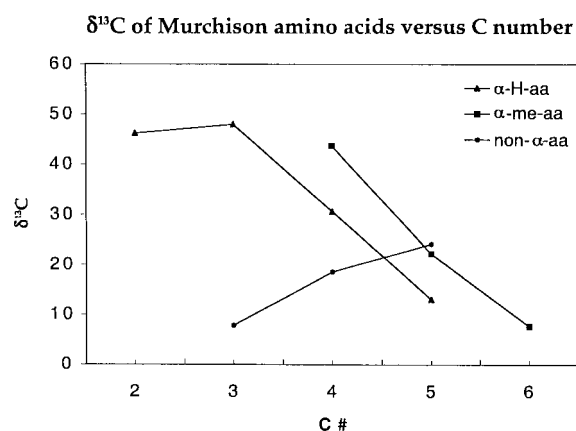
#### $\delta^{13}\text{C}$ (‰) of individual Murchison amino acids

glycine	+46.2	± 3.4
D alanine	+48.0	± 0.5
L alanine	+36.6	± 3.4
D 2-amino butyric acid	+29.6	± 0.9
L 2-amino butyric "	+30.5	± 2.8
D norvaline	+15.2	av. 2
2-amino isobutyric acid	+43.7	± 0.8
DL* isovaline	+22.1	± 1.3
DL 2-methyl norvaline	+ 7.6	± 1.2
DL 2-amino2-ethyl butyric acid	+22.1	± 1.7
$\beta$ -alanine	+ 4.9	± 0.5
4-amino butyric acid	+18.5	± 2.8
5-amino valeric "	+24.1	av. 2
3-amino 2,2-methyl propionic	+25.1	± 0.7
DL 3-amino 2-ethyl propionic	+31.6	± 3.6
4-amino valeric	+19.1	± 3.5
unknown 3-amino 6-carbon	+28.3	av. 2
" " "	+29.4	"
" " "	+35.5	"
" DL 4-amino "	+17.2	"
sarcosine	+52.8	± 3.2
nicotinic acid	+19.4	"
D glutamic acid	+28.9	± 2.1
L glutamic acid	+ 6.8	av.2
DL 2-methyl glutamic acid	+26.8	av. 2

\*DL values given combined when GC-peaks baseline resolution was lacking or the order of elution of the two enantiomers was unknown.

$\delta^{13}\text{C}$  of Murchison amino acids. Pizzarello et al.

The decreasing  $\delta^{13}\text{C}$  values with carbon number of  $\alpha$ -amino acids in Murchison resembles a similar decline observed by Yuen et al. [8] for the lower molecular weight aliphatic hydrocarbons and monocarboxylic acids of the same meteorite. They attributed this isotopic trend to two possibilities: either a kinetically governed augmentation of hydrocarbon chains by single carbon units or, in the case of carboxylic acids, a higher intramolecular  $^{13}\text{C}$  content of the carboxyl function than that of the hydrocarbon chain. Later in his work G. Yuen measured such a difference in Murchison acetic acid, where he observed [9] a higher  $\delta^{13}\text{C}$  for the carboxyl carbon (by  $\sim 20\%$ ). The same explanations could be invoked for the  $\alpha$ -amino acid  $^{13}\text{C}$  values observed in this study, e.g., a Strecker syntheses of  $\alpha$ -amino acids where reactant HCN was more  $^{13}\text{C}$  enriched than the aldehydes/ketones would be consistent with the isotopic data and further analyses are needed to ascertain the intramolecular isotopic composition of meteoritic amino acids. It should be noted that outside the homologous series charted in the figure, isotopic values of  $\alpha$ -methyl amino acids appear to vary, as the higher  $\delta^{13}\text{C}$  of 2-amino 2-ethyl butyric acid than 2-methyl norvaline seem to indicate. The difference observed between the two homologous series of  $\alpha$ -H and  $\alpha$ -alkyl amino acids is intriguing, since the latter group is the only one that displays enantiomeric excesses, however, the similarity of the isotopic trends appears to point to similar processes of formation.



Not so for the non- $\alpha$  amino acids, whose values suggest an unexpected reverse trend of increasing  $\delta^{13}\text{C}$  with chain length. It is difficult to know whether these values represent a true linear relation, i.e., are indication of a common origin, or simply represent different pathways of formation for the various amino-position isomers. For example, it has been proposed that  $\beta$ -amino acids could be the result of the addition of ammonia to unsaturated nitriles [10], a synthetic route that would leave unexplained the formation of the more abundant  $\gamma$ -amino isomers. About these we know that they become abundant in the extracts only following acid hydrolysis and

some of their precursors have been identified in Murchison as a series of lactams [11]. The isotopic values observed for  $\gamma$ -amino acids would seem to favor the idea of possible separate pathways of formation for different non- $\alpha$  position isomers, since the three  $\gamma$ -amino acids of different chain lengths we analyzed do not differ significantly in  $^{13}\text{C}$  content. It should also be kept in mind that the  $\delta^{13}\text{C}$  value for  $\beta$ -alanine could appear artificially low due to contamination.  $\beta$ -alanine is a common terrestrial amino acid which is not chiral and does not offer the possibility to assess a likely contamination, as for compounds having two enantiomers one of which is found in the biosphere. In this sample, this is seen for alanine and glutamic acid, where the L- (also terrestrial) enantiomers had excesses of 8.6 and 29%, respectively, and showed correspondingly lower  $\delta^{13}\text{C}$  values.

The high deuterium and  $^{13}\text{C}$  content of meteorite organics has been attributed to a relationship with interstellar processes, where such large enrichments have been observed. Based on the isotopic data available, therefore, we should conclude that the precursors to non- $\alpha$  amino acids, as well as those to dicarboxylic and  $\alpha$ -amino dicarboxylic acids, had reached higher chain complexity in meteorites than those of  $\alpha$ -amino acids before undergoing planetary/nebular processes. Possibly, these were mild enough to leave unaltered hydrolyzable precursors. Finally, the idea of formation of non- $\alpha$  amino acids in meteorites via the degradation of a  $^{13}\text{C}$ -rich polymer, that would account for the observed isotopic trend, cannot be excluded and could be tested with model experiments.

The isotopic data obtained in this study allow the following conclusions. Murchison indigenous amino acids, while all enriched in  $^{13}\text{C}$ , display a statistically significant variability of  $\delta^{13}\text{C}$  values from +8 to +53‰, approximately. Linear relations are seen for homologous series of some amino acids, which are suggestive of formation affinities. These relations, or lack of them, are observed for more amino acids than expected (as a possible difference between the  $\alpha$ - and non  $\alpha$ -species, since only the first group could form via a Strecker synthesis) and appear to indicate that the synthetic histories of soluble organics in meteorites may have been diverse even within groups of compounds with very similar functional composition.

**References.** [1] Peltzer E.T. and Bada J. *Nature* **272**, 443 (1978). [2] Pizzarello S. and Cooper. G.W. *MAPS* **36**, 897 (2001). [3] Pizzarello S. et al. *GCA in press*. [4] Pizzarello S. et al. *Science* **293**, 2236 (2001). [5] Engel M. et al. *Nature* **348**,47 (1990). [6] Pizzarello S. et al. *GCA* **55**, 905 (1991). [7] Pizzarello S. and Cronin J.R. *GCA* **64**, 329 (2000). [8] Yuen G. et al. *Nature* **307**, 252 (1984). [9] *ASU records and personal communication*. [10] Miller S.L. *Biochim.Biophys.Acta* **23**, 480 (1957). [11] Cooper G.W. and Cronin J.R. *GCA* **59**, 1003 (1995).