Compound-specific isotopic ratios of amino acids in CM and CR chondrites. J. E. Elsila[1], S. B. Charnley[1], A. S. Burton[2], D. P. Glavin[1], and J. P. Dworkin[1], [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, email: Jamie.Elsila@nasa.gov, [2]Catholic University of America, 8800 Greenbelt Rd., Greenbelt MD 20771.

Introduction: Carbonaceous chondrites contain a wealth of organic compounds, including a variety of amino acids. The abundance, isotopic composition and structural distributions of these compounds reflect their synthesis and evolution, providing information on the original composition and processing of the molecular cloud and solar nebula from which the solar system formed and on subsequent processing of meteorite parent bodies.

Many formation mechanisms have been proposed for the amino acids detected in carbonaceous chondrites. These include the Strecker-cyanohydrin synthesis, which postulates the formation of α-amino acids from the reaction of ketones or aldehydes with hydrogen cyanide, ammonia, and water [1], as well as Michael addition, in which β-amino acids are formed from addition of ammonia to an α,β-unsaturated nitrile [2]. Other proposed mechanisms include addition of carbon dioxide to amines [3] or the reductive amination of keto acids [4].

As each of these proposed mechanisms utilizes different precursor molecules, the stable carbon, nitrogen, and hydrogen isotopic ratios ($\delta^{13}C$, $\delta^{15}N$, and δD) of the resulting individual amino acids may point toward the most likely of these proposed pathways. Here we report on the compound-specific stable isotopic ratios of amino acids from four CM and three CR carbonaceous chondrites. This data both confirms previous measurements and greatly extends the available set of compound-specific meteoritic amino acid isotopic data. We compare the trends observed in these ratios with predictions of expected isotopic enrichments from potential formation pathways and environments.

Analytical techniques and samples: The following carbonaceous chondrites were analyzed: ALH 83100 (CM1/2), Murchison (CM2), LEW 90500 (CM2), LON 94101 (CM2), GRA 95229 (CR2), EET 92042 (CR2), and QUE 99177 (CR3). Sample sizes from 0.5 to 8.2 g were crushed, extracted in water, hydrolyzed with HCl acid vapor, and desalted with cation-exchange resin. Amino acid abundances and distributions were analyzed via ultra-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry (UPLC-FD/ToF-MS); measurements were made on ~1% of each extract following derivatization with *o*-phthaldialdehyde/N-acetyl-L-cysteine (OPA/NAC). Compound-specific isotopic measurements were performed on the bulk of the extract, with ~10% used for carbon measurements,

~30% for nitrogen, and ~60% for hydrogen. Extracts were derivatized with trifluoroacetic anhydride (TFAA) and isopropanol prior to analysis via gas chromatography and combustion coupled with mass spectrometry and isotope ratio mass spectrometry (GC-MS/IRMS). Experimental details have been provided elsewhere [5].

Results and Discussion: Complete isotopic data for the individual amino acids detected in the seven carbonaceous chondrites is presented elsewhere [5]. Figure 1 shows the isotopic relationships (δD versus $\delta^{13}C$, $\delta^{15}N$ versus $\delta^{13}C$, and δD versus $\delta^{15}N$) for amino acids when more than one isotope was measured in a single amino acid in a given meteorite. Areas of the plots in which structurally similar amino acids grouped together are outlined.

We compared the isotopic data with predictions for four formation mechanisms (details provided in [5]). The Strecker-cyanohydrin synthesis should produce α-amino acids, with a decrease in ^{13}C enrichment as chain length increases and a corresponding increase in D enrichment. Our measurements of the two-to-five carbon α-amino, α-H amino acids in five of the carbonaceous chondrites followed these trends and thus support a Strecker origin; similar measurements were not possible due to low abundances of these amino acids in the other two meteorites (ALH 83100 and LEW 90500).

We investigated the effects of amine position, and observed a lower $\delta^{13}C$ value for β-alanine than for its corresponding α-amino acids (D- and L-alanine) in the six meteorites with measurable levels of these amino acids. This observation could reflect formation of β-alanine via Michael addition, because the precursor nitriles involved in this reaction are expected to be less enriched in ^{13}C than the carbonyl-containing precursors that form α-amino acids through Strecker synthesis.

We observed a correlation of isotopic enrichment with alpha-subsituent. Amino acids with an α-methyl group were consistently more enriched in D than the corresponding α-hydrogen amino acids. No consistent $\delta^{13}C$ correlation was observed. The α-methyl amino acid isovaline was less enriched in ^{15}N than other amino acids. The δD and $\delta^{15}N$ trends may be caused by the formation of precursor molecules in cold interstellar or presolar environments where the spin-state of hydrogen molecules was important in fractionation chemistry.
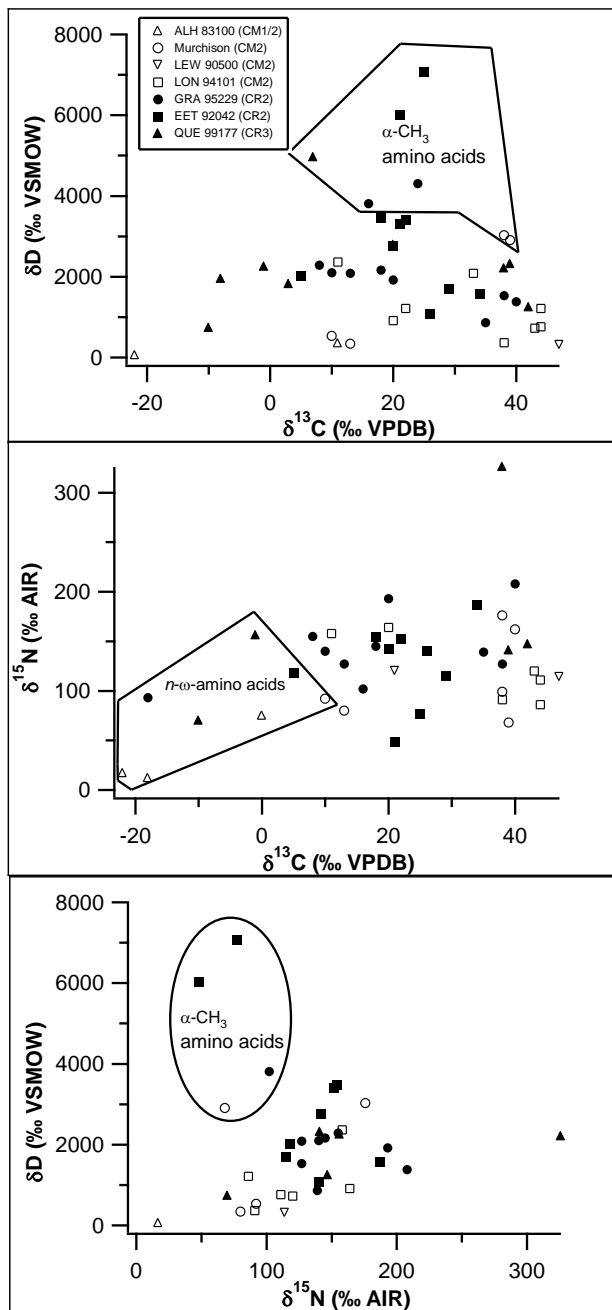
Figure 1. Isotopic data for the amino acids in the seven analyzed carbonaceous chondrites. Outlined areas highlight subsets of structurally similar compounds. Adapted from [5]. For comparison, terrestrial amino acids have $\delta^{13}C$ values ranging from -70 to +11‰ and $\delta^{15}N$ values ranging from -20 to +30 ‰, while organic hydrogen in a range of terrestrial materials has values of -270 to +66 ‰ (see [6] and references therein).

Finally, we observed that individual amino acids in the CR chondrites are consistently more enriched in D than those in the CM chondrites, with no significant

difference in $\delta^{13}C$ enrichment. This may reflect differences in reactions between amino acids and water on their respective parent bodies.

In summary, this compound-specific isotopic data of meteoritic amino acids highlights differences in formation mechanisms, precursors, and environments between different structural classes of amino acids and different carbonaceous chondrite groups and petrographic types.

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