

INVESTIGATING THE AMINO ACID CONTENT OF TYPE 2 CARBONACEOUS CHONDRITES. J. C. Aponte^{1,*}, H. L. McLain^{1,2}, J. E. Elsila¹, D. P. Glavin¹, and J. P. Dworkin¹, ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, ²The Catholic University of America, Washington D.C. 20064. *Email: Jose.C.Aponte@nasa.gov

Introduction: The study of meteoritic water-soluble organic compounds provides valuable insights into the available chemical inventory of the early solar system, the aqueous and thermal processing that occurred in parent bodies, and the organic chemistry preceding the origins of life in our planet [1,2]. Carbonaceous chondrite meteorites are thought to be fragments of carbon- and water-bearing asteroids. These extraterrestrial samples may contain up to 5 wt % organic carbon and are classified into eight subgroups. Among them, moderately aqueously altered CR (Renazzo-like) and CM (Mighei-like) type 2 meteorites exhibit the most abundant and diverse water-soluble organic contents [3,4].

Aliphatic amino acids have been extensively studied in CM and CR carbonaceous chondrites because of their importance and essential role on Earth's biosphere. As monomers of proteins and enzymes, the analysis of meteoritic amino acids can provide key information about their potentially universal ubiquitousness and the origins of complex organic matter under abiotic conditions [5]. Isovaline is an α -dialkyl amino acid that is not common in terrestrial biology; however, its prevalence in carbonaceous chondrites has been largely documented [6]. Indeed, isovaline L-enantiomeric excesses of up to 20% [7] have been reported in Murchison and other carbonaceous chondrites, forging a link between the origin of Earth's homochiral life and the meteoritic organic inventory.

Analytical Methods: We evaluated the amino acid abundances, and molecular diversities (including enantiomeric distributions) in thirteen type 2 carbonaceous chondrites (Table 1). Meteorite chips were separately crushed into powders using a ceramic mortar and pestle. The samples were then transferred to glass ampoules and flame-sealed for extraction at 100 °C for 24 h in 1 mL of Milli-Q ultrapure water. The water supernatants were then removed, dried under reduced pressure, and desalted using a cation-exchange resin (AG50W-X8, 100-200 mesh, hydrogen form, BIO-RAD). The isolated amino acids were derivatized before identification, quantification, and enantiomeric separation using *o*-phthalaldehyde/*N*-acetyl-L-cysteine (OPA/NAC). Amino acids were chromatographically resolved using a Waters BEH C18 column (2.1 × 50 mm, 1.7 μ m bead) and a Waters BEH phenyl column (2.1 × 150 mm, 1.7 μ m bead) in series. Both columns were maintained at 30 °C. The analyses were performed using a Waters Xevo G2-XS liquid

chromatographer with UV fluorescence and quadrupole time-of-flight mass spectrometry detection (LC-FD/Q-ToF-MS) operating in positive ion mode and following previously published methods [8].

Table 1. Meteorites analyzed in this work and enantiomeric distribution of isovaline.

Meteorite	Type [9]	β -Ala/Gly	Isovaline D/L
NWA 13456	C2	0.21	1.0
LAP 02333	CM1.5	0.16	1.0
LEW 85311	CM1.9 (CM2-an)	0.10	0.8
WIS 91600	CM2-an (oxidized) [10]	0.64	^b
Essebi	CM1.9 (heated)	1.58	^b
Nogoya	CM1.1 or CM1.6 heated	0.53	1.0
Murray	CM1.5 (heated)	0.20	1.0
Mighei	CM1.6 (heated)	0.66	1.1
GRA 98005	CM1.7 (heated)	0.53	^b
GRO 17063	CR2	^a	^b
PCA 91082	CR2.3	0.03	1.0
GRO 03116	CR2 (heated)	3.17	^b
GRA 06100	CR2 (heated)	^a	^b

^a β -alanine or glycine below detection limits (< 0.1 nmol/g meteorite).

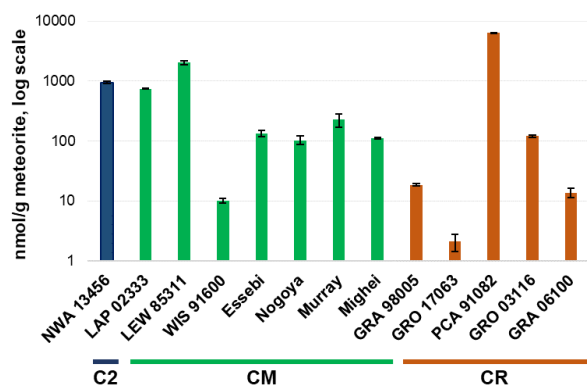
^bD- or L-Isovaline below detection limits (< 0.1 nmol/g meteorite; D/L could not be determined).

Results and Discussion. We identified and quantified two- to six-carbon amino acids, including α -H protein amino acids such as aspartic and glutamic acids, serine, threonine, alanine, valine, and their enantiomers. We also achieved enantiomeric separation of D,L-valine, D,L-isovaline, and D,L-norvaline without interferences or coelutions with other C5 amino acid isomers.

The total amino acid concentrations ranged from ~10 to 6000 nmol/g of meteorite (Figure 1). Increasing aqueous and thermal parent body alteration have been previously shown to result in lower levels of soluble organic compounds [3]. CM2 chondrites Essebi, Nogoya, and Mighei showed similar total amino acid abundances ranging from ~100 to 200 nmol/g of meteorite and a diverse molecular distribution. Other CM2 chondrites such as LAP 02333 and LEW 85311, yielded total amino acids concentrations that were three to twenty times larger than those seen in Mighei, suggesting that LAP 02333 and LEW 85311 have been altered at lower temperatures. Indeed, the amino acid abundance in WIS 91600, which experienced mild thermal processing, showed the lowest amino acid concentrations in our dataset, consistent with aqueous alteration added to sporadic episodes of high temperatures in the parent body. There are over 600 carbonaceous chondrites currently classified as CM2, however, there are only two meteorites classified as C2 that appear to be outliers from other C2 ungrouped

meteorites, NWA 13456 is one of them. The total amino acid abundance found in NWA 13456 resembles that of LAP 02333 and LEW 85311 suggesting its parent body experienced modest thermal and limited aqueous alteration.

Figure 1. Total amino acid abundances in the studied meteorites.



The amino acid abundance in CR2 chondrites we studied here seems to be very dependent on the parent body processing experienced. PCA 91082 contains the largest amino acid concentration and molecular distributions, however, GRO 03116, another CR2 chondrite, is almost fully depleted in abundances and molecular distributions (the low amino acid abundances in GRO 17063 could be due to thermal alteration [11]). These results raise questions about the nature of the parent body. Did both meteorite samples come from a single parent body that experienced localized but distinct processing? Or did they come from more than one parent body that underwent independent and separate alteration histories?

A common indicator of parent body processing is the β -alanine to glycine ratio (β -ala/gly) [8], with a high ratio typically correlating with more aqueous alteration and lower amino acid abundances. This relationship holds for LEW 85311 and PCA 91082 which show the lowest β -ala/gly and the highest amino acid concentrations among the CM and CR chondrites respectively. Similarly, GRO 03116 shows a relatively high β -ala/gly and low total amino acid abundances (Table 1). However, this correlation is not reflected when comparing other meteorites such as WIS 91600, Mighei, and Essebi. It is likely that the β -ala/gly may not be entirely caused by the degree of parent body aqueous alteration, but instead reflects the distinct chemical nature of the parent bodies themselves (e.g., different relative chemical abundances of amino acid precursors). Thus, it could be possible that other processes added to aqueous alteration, such as mild thermal processing, occurred in the parent bodies of

WIS 91600, Mighei, and Essebi and that the β -ala/gly alone cannot be used to assess their complete alteration histories.

Among the meteorites that contained D- and L-isovaline in measurable amounts (Table 1), we found these compounds were present as racemic mixtures in all samples studied except for LEW 85311, which showed an L-isovaline enantiomeric excess (*ee*) of 10.0 ± 8.9 (D/L = 0.82 ± 0.16). As previously shown for other carbonaceous chondrites [7], it seems that there is no linear relationship between a higher amino acid abundance and larger L-isovaline *ee*. Glavin and Dworkin (2009) proposed a positive correlation between meteorites that have experienced increasing levels of aqueous alteration and L-isovaline *ee* [12]. Our results suggest that this apparent correlation may be highly vulnerable to the levels of thermal metamorphism that occurred in the parent body, as can be seen for the Nogoya, Murray, and Mighei samples analyzed here and that resulted in racemic isovaline. Nonetheless, only a small fraction of all available carbonaceous chondrites has been analyzed to date and future measurements of amino acids and other soluble organics in samples with varying levels of aqueous and thermal processing are needed to validate potential relationships between synthetic pathways and parent body alterations.

Conclusions. Further analyses of meteoritic amino acids and experimental work remains to fully understand the effects of aqueous and thermal processing over the synthesis/destruction of these meteoritic organics and their potential role on the origin of life in our planet or elsewhere.

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