

## Amino Acids in a Carbonaceous Chondrite from Antarctica

R.K. Kotra,<sup>1</sup> Akira Shimoyama,<sup>1</sup> Cyril Ponnampereuma,<sup>1\*</sup> and P.E. Hare<sup>2</sup>

<sup>1</sup> Laboratory of Chemical Evolution, Department of Chemistry, University of Maryland, College Park, Maryland 20742,

<sup>2</sup> Carnegie Institution of Washington Geophysical Laboratory, 2801 Upton Street, N.W., Washington, D.C. 20008

**Summary.** A carbonaceous chondrite from the Antarctic, referred to as the Allan Hills meteorite 77306, appears to be free from terrestrial organic contamination. The presence of both protein and non-protein amino acids and an equal abundance of D- and L-enantiomers of amino acids, is testimony to the extraterrestrial nature of these compounds.

**Key words:** Carbonaceous chondrites — Allan Hills meteorite — Antarctic meteorites — Amino acids — D-, L-enantiomers

Recent field expeditions to the Antarctic have discovered a large number of new meteorites (Yoshida et al., 1971; Cassidy et al., 1977; Yanai, 1978). These meteorites appear to have been protected from terrestrial contaminants in the Antarctic ice since their fall. Because of their unique character, they were handled in the field and conserved in the laboratory at the NASA/Johnson Space Flight Center, in a manner similar to the lunar samples (Gibson et al., 1979). These Antarctic meteorites, therefore, provide us with new opportunities to examine extraterrestrial compounds while minimizing the possibility of terrestrial contamination.

Finding protein and non-protein amino acids and the equal abundance of enantiomers of the amino acids confirmed the abiotic extraterrestrial origin of organic compounds in the Murchison carbonaceous chondrite (Kvenvolden et al., 1970; Kvenvolden et al., 1971). These studies were subsequently extended to the Murray, Orgueil and Mighei carbonaceous chondrites (Lawless et al., 1971; Oró et al., 1971, Oró et al., 1971, Cronin and Moore, 1971; Lawless et al., 1972; Buhl, 1975). But even with these studies the number of chondrites analyzed is small. Further information is needed for a more complete understanding of primordial organic synthesis in the early solar nebula (Anders et al., 1973) and the origins of organic compounds on the primitive earth before the emergence of life (Ponnampereuma, 1972; Miller and Orgel, 1974;

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\* To whom correspondence should be addressed

Ponnamperuma, 1978). Of the extraterrestrial materials studied thus far, the lunar samples contained only a trace amount of organic matter (Gehrke et al., 1975) and the Martian soil revealed none (Biemann et al., 1976). To date, the carbonaceous chondrites provide the only available source of extraterrestrial organic compounds.

We now wish to report our finding of amino acids in a type C2 carbonaceous chondrite found at Allan Hills in Victoria Land Antarctica during the 1976-1977 field season. This sample was distributed by the Meteorite Working Group set up by the Officer of Polar Programs of the National Science Foundation. Two hundred mg of the exterior (A77306.10) and 200 mg of the interior (A77306.18) were received from the Meteorite Sample Curator at the Johnson Space Flight Center.

In a class 100 clean room, the two samples were pulverized individually in an agate mortar and treated with 2 g of water in glass vials with teflon-lined caps at 105° C for 24 h. The aqueous solutions were centrifuged and the supernatants were recovered. The residues were twice rinsed with 0.5 g of water and combined with the corresponding supernatants. The combined extracts were dried under an infrared lamp. To the dried residues 0.6 g of 6N HCl were added for hydrolysis at 105° C for 22 h. Each hydrolyzed solution was divided into two equal portions and dried. One of the dried portions was redissolved with 100  $\mu$ l water and a 10  $\mu$ l aliquot was analyzed directly on an amino acid analyzer using a fluorescence detector (Hare, 1977). The other portion was derivatized first with isopropyl alcohol -1.5N HCl and then with TFAA-CH<sub>2</sub>Cl<sub>2</sub>. The N-TFA-isopropyl esters of amino acids, thus prepared, were analyzed by a gas chromatograph equipped with a Chirasil Val glass capillary column (25m) and a nitrogen detector<sup>1</sup>. The exterior and interior samples of the Murchison meteorite and a procedure blank of a 200 mg sand sample, preheated in a furnace at 450° C for more than 24 h were processed in parallel.

The procedure blanks contained approximately 0.3 nanomoles glycine/g of sand, less than 0.06 nm alanine/g and 0.04 nm aspartic acid/g, 0.15 nm serine/g and 0.01 nm glutamic acid/g. These quantities are to be subtracted from the corresponding amino acid quantities found in the meteorite extracts.

The amino acids and their quantities in the Allan Hills and the Murchison meteorite are shown in Table 1. The two most abundant amino acids are glycine and alanine. The Allan Hills meteorite also contains the aminobutyric acids, norleucine and  $\beta$ -alanine. Thus both protein and non-protein amino acids are present in this meteorite. The quantity of the amino acids present in the Allan Hills Meteorite comprises about 1/5 to 1/10 of those in the Murchison interior sample we analyzed.

Eleven amino acids in the Allan Hills meteorite were identified by their retention times as shown in the gas chromatogram (Fig. 1). These are sarcosine, alanine,  $\alpha$ -aminobutyric acid, valine, glycine,  $\beta$ -alanine,  $\beta$ -aminobutyric acid,  $\gamma$ -aminobutyric acid, aspartic acid, glutamic acid and lysine. In the exterior portion of the Allan Hills, the enantiomers of aspartic acid, glutamic acid and lysine are present in approximately

<sup>1</sup> Chirasil Val glass capillary column purchased from Applied Science Laboratories Inc., State College, Pa. N-detector from Perkin-Elmer, Norwalk, Connecticut. Column temperature was increased from 50°C to 180°C at the rate of 1°C/min. TFAA and TFA are abbreviations for trifluoroacetic anhydride and trifluoroacetyl, respectively.

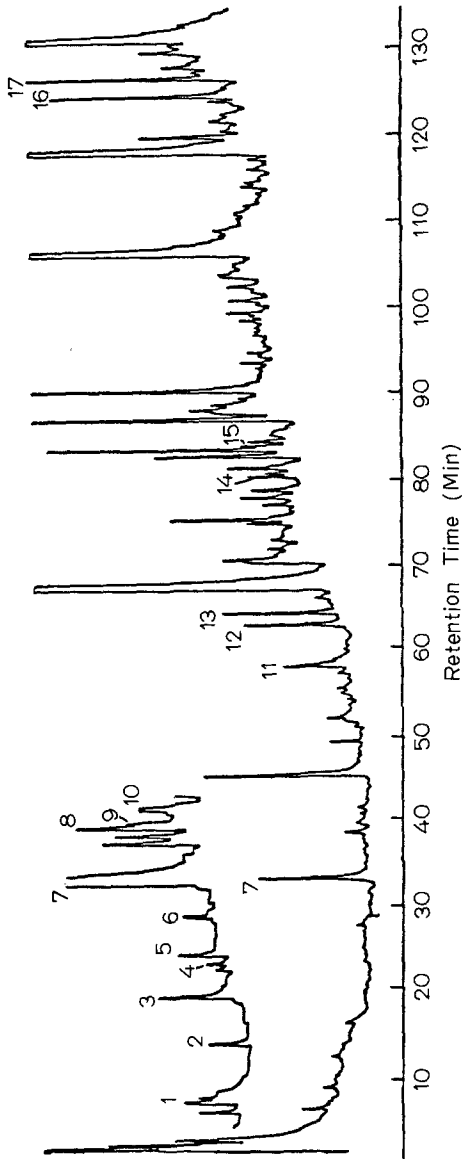


Fig. 1. Gas chromatograms of *N*-TFA-*isopropyl* esters of amino acids in the Allan Hills meteorite. Insert at top left represents interior fraction. Chromatogram below represents exterior fraction. Peaks: 1. Sacrosine, 2. D-Alanine, 3. L-Alanine, 4. D- $\alpha$ -Aminobutyric acid, 5. D-Valine, 6. L- $\alpha$ -Aminobutyric acid + L-Valine, 7. Glycine, 8.  $\beta$ -Alanine, 9. D- $\beta$ -Aminobutyric acid, 10. L- $\beta$ -Aminobutyric acid, 11.  $\gamma$ -Aminobutyric acid, 12. D-Aspartic acid, 13. L-Aspartic acid, 14. D-Glutamic acid, 15. L-Glutamic acid, 16. D-Lysine, 17. L-Lysine

1:1 ratio<sup>2</sup>. The interior portion contains alanine,  $\alpha$ -aminobutyric acid, valine,  $\beta$ -aminobutyric acid and glutamic acid in approximately equal amounts<sup>3</sup>.

<sup>2</sup> Many peaks are not resolved at the baseline. After subtracting for overlap, these amino acids appear to show equal abundances of D and L isomers.

<sup>3</sup> The more volatile amino acids either are not seen in the chromatogram or are of diminished peak size in the exterior portion because of the injection technique used. The solvent had to be evaporated at room temperature in order that larger amounts of the sample could be injected by a solids injection syringe (Scientific Glass Engineering Pvt. Ltd. Australia).

**Table 1.** Amino acid abundances in the Allan Hills and the Murchison Meteorites based on ion-exchange chromatography

Units: nanomoles/gm Amino acid	Allan Hills Exterior	Allan Hills Interior	Murchison Exterior	Murchison Interior
Aspartic acid	2.1	1.4	33.3	3.6
Threonine	0.3	0.3	13.3	1.6
Serine	0.5	0.4	14.4	1.9
Glutamic acid	1.1	1.2	48.7	13.0
Glycine	14.1	7.3	101.1	37.0
Alanine	2.8	1.8	54.1	15.2
$\alpha$ -Aminoisobutyric acid	1.3	1.4	29.0	43.1
$\alpha$ -Aminobutyric acid	5.5	0.9	16.5	7.4
Valine	0.3	0.4	28.1	10.7
Methionine	0.3	0.2	3.7	1.9
Alloisoleucine	0.6	0.5	10.6	3.3
Isoleucine	0.1	0.2	8.1	0.6
Leucine	0.2	0.2	12.0	2.0
Norleucine	0.3	0.3	0.2	0.7
Tyrosine	0.2	0.3	1.3	0.7
Phenylalanine	0.1	0.1	4.2	0.8
$\beta$ -Aminobutyric acid	1.6	1.3	5.0	3.2
$\beta$ -Alanine	3.4	1.8	14.1	7.8
$\beta$ -Aminoisobutyric acid	1.3	1.2	9.0	3.4
$\gamma$ -Aminobutyric acid	1.6	3.0	16.2	23.3

In comparison, however, the exterior of the Murchison meteorite has, among others, alanine, valine, aspartic acid, and glutamic acid with the L-enantiomers predominating. But, in the interior fraction the enantiomers are nearly equal in quantity.

Based on the ion-exchange results, the interior and exterior portions of the Allan Hills appear to contain approximately the same amounts of amino acids. This is, in general, in contrast to the Murchison meteorite and other carbonaceous chondrites where the exterior fraction usually has a greater abundance.

The similarity between the exterior and the interior of the Allan Hills has an important implication in that the Antarctic meteorites may be the least contaminated meteorites known. This conclusion is based only on one meteorite, and a more thorough analysis of the Antarctic meteorites is needed, including gas chromatography-mass spectrometry which is being pursued now in our laboratory. The presence of protein and non-protein amino acids and the enantiomer ratios lead us to the conclusion that the amino acids in the Allan Hills carbonaceous chondrite are extraterrestrial in origin.

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