Reports

Amino Acid Analyses of the Murchison, Murray, and Allende Carbonaceous Chondrites

Abstract. *Three carbonaceous chondrites were examined for water-extractable amino acids. The Murchison and Murray specimens were found to be of similar amino acid composition. This similarity suggests that these amino acids are indigenous to type II carbonaceous chondrites. The Allende (type III) carbonaceous chondrite was found to be essentially devoid of amino acids on the basis of an identical analysis.*

Analyses of carbonaceous chondrites for organic material have been carried out for over a century and, although the presence of certain classes of organic compounds has been firmly established, until recently there has been no accepted evidence for the presence of amino acids. Extracts of various carbonaceous chondrites have been shown to contain amino acids; however, in no case has terrestrial contamination been ruled out, and in some cases both the qualitative and quantitative results suggest contamination by handling. Much of the history of the organic analysis of carbonaceous chondrites, including the perils associated with amino acid analysis, has been described by Hayes (*1*).

The recent work of Kvenvolden and his co-workers (*2*) on the Murchison carbonaceous chondrite strongly suggests that amino acids are, in fact, constituents of this meteorite. Kvenvolden *et al.* have identified several amino acids in aqueous extracts and have found (i) that the D- and L-enantiomers of the amino acids are almost equally abundant, and (ii) that several amino acids not found in proteins are present which are unlikely terrestrial contaminants.

In view of the significance of this work and the fact that doubts (*3*) have been expressed regarding its validity, it seemed desirable to attempt an independent confirmation. The analyses reported here were carried out on material derived from a separate stone from the Murchison fall, were performed independently in a different laboratory, and were carried out with the use of somewhat different methods from those of Kvenvolden *et al.* (*2*). For comparison, identical analyses were performed on a sample of the Murray carbonaceous chondrite (type II) and the Allende carbonaceous chondrite (type III).

The samples of the carbonaceous chondrites were selected, broken, and sampled so as to minimize contamination. In each case, a complete stone was broken and crust-free fragments were selected with chemically cleaned and heat-cleaned tools. The fragments were immediately transferred to a clean diamond mortar, crushed, and then transferred to an extraction vessel containing 50 ml of water (*4*). The weights of the Murchison, Murray, and Allende samples extracted were, respectively, 2.4, 3.0, and 2.8 g. The extraction vessel was fitted with a condenser and allowed to reflux for 24 hours. The residue was collected by centrifugation, and the supernatant fluid and three 10-ml water washes of the residue were aspirated into a round-bottom flask. The water was removed on a rotary evaporator and the residue redissolved in 10 ml of water. This solution (that derived from the Murchison and Murray samples was quite yellow) was split, one-half being dried under vacuum over phosphorus pentoxide and analyzed directly. The other half was combined with an equal volume of concentrated HCl (reagent grade, 37 percent) and sealed in a vial under vacuum. The vial was kept in an oil bath at 110°C for 20 hours and the HCl-water solution was then removed under vacuum over NaOH pellets. Both the dry extracts and the dry acid-hydrolyzed extracts were taken up in 0.2*M* sodium citrate, *p*H 2.2, for amino acid analysis. Amino acid analysis was carried out with the use of an accelerated (*5*), high-sensitivity (*6*) modification of the method of Spackman *et al.* (*7*).

As can be seen in Fig. 1, the hydrolyzed Murray and Murchison extracts are qualitatively similar, both contain-

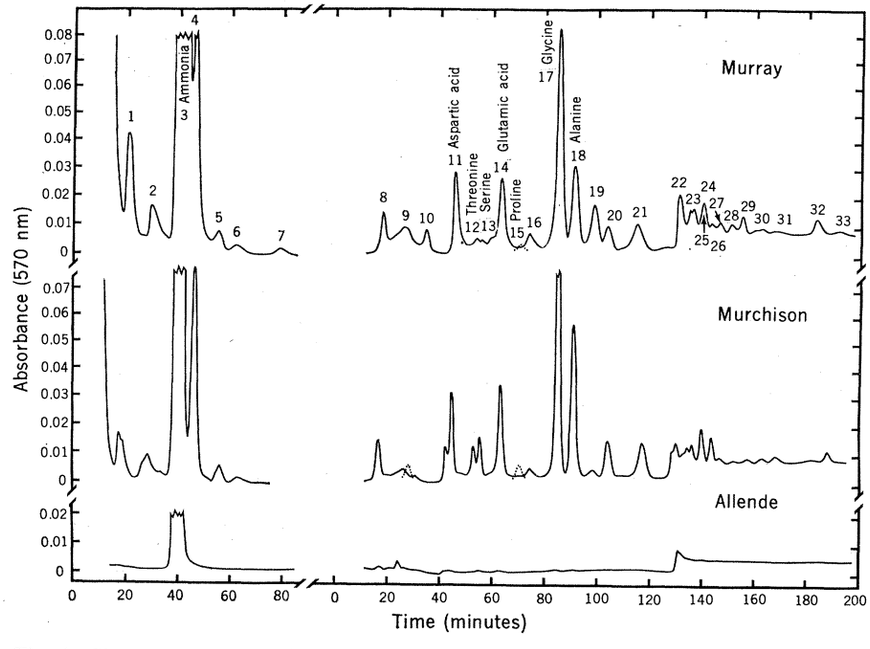

Fig. 1. Chromatograms of the hydrolyzed aqueous extracts from the Murray, Murchison, and Allende carbonaceous chondrites. The solid lines represent the long path length, 570-nm trace. The dotted lines represent the 440-nm trace where it exceeds the long path length, 570-nm trace.

Table 1. Amino acids in hydrolyzed extracts of the Murchison and Murray meteorites.

Peak	Amino acid	Murchison		Murray	
		Amount (μg/g)	Ratio (relative to glycine)	Amount (μg/g)	Ratio (relative to glycine)
	Amino acids found in proteins				
11	Aspartic acid	1.7	0.3	1.6	0.5
14	Glutamic acid	3.1	0.5	1.6	0.5
15	Proline	1.3	0.2	0.4	0.1
17	Glycine	6.1	1.0	3.0	1.0
18	Alanine	3.5	0.6	1.3	0.4
21	Valine/isovaline	1.6	0.3	0.9	0.3
	Amino acids not found in proteins				
19	α-Aminoisobutyric acid	2.5	0.4	11.4	3.8
20	α-Amino-*n*-butyric acid	1.1	0.2	0.5	0.2
32	β-Alanine	0.4	0.1	1.2	0.4
33	β-Aminoisobutyric acid	0.7	0.1	0.3	0.1

ing a large number of ninhydrin-positive components. The hydrolyzed Allende extract, on the other hand, is essentially devoid of such components. The peak and baseline shift at 130 minutes are artifacts due to a change in the eluting buffer. The ammonia peaks seen in all three chromatograms are meaningless with respect to the meteorites since no attempt was made to exclude atmospheric ammonia from the reagents used. The absence of amino acids in the Allende extracts and in the hydrolyzed extract validates the procedure employed in this laboratory for the analysis of meteoritic material for amino acids. Contamination problems, alluded to earlier, involving amino acids in extract water, in HCl, on glassware, and by retention on analyzer columns, have apparently been avoided. Contamination, if it is a factor in the Murchison and Murray data, must have occurred prior to the selection of a sample for this analysis. Furthermore, it would have been necessary for the contaminants to have permeated the stone, since interior samples were selected for analysis.

Kvenvolden *et al.* (*2*), using ion exchange chromatography, gas chromatography, and gas chromatography in conjunction with mass spectrometry, have positively identified the following protein amino acids in the Murchison meteorite: glycine (6 μg/g), alanine (3 μg/g), glutamic acid (3 μg/g), valine (2 μg/g), proline (1 μg/g), and aspartic acid; they have also positively identified the following amino acids not found in proteins: sarcosine, α-aminoisobutyric acid (2-methylalanine), β-alanine, α-amino-*n*-butyric acid, β-amino-*n*-butyric acid, γ-amino-*n*-butyric acid, isovaline, and pipecolic acid. They have tentative evidence for β-aminoisobutyric acid, norvaline, *N*-methylalanine, and *N*-ethylglycine.

In Table 1 are listed the peaks which correspond in retention time to amino acids identified or tentatively identified by Kvenvolden *et al.* (*2*). Peaks attributable to the six previously reported protein amino acids are clearly apparent both in the Murchison and Murray acid-hydrolyzed extracts. In the former, the amounts found are in agreement with the values reported by Kvenvolden *et al.* Of the 12 amino acids not found in proteins, peaks corresponding to four of them are apparent in the acid-hydrolyzed extracts from both meteorites. The remaining eight amino acids not found in proteins are not excluded on the basis of the analyses reported here, but cannot be confirmed because of incomplete resolution or low analytical sensitivity. Peak 21, for example, could include both valine and isovaline since their retention times are quite similar. Although the Murchison and Murray data are qualitatively similar, both the extract and the acid-hydrolyzed extract of the Murchison meteorite are enriched in most components by a factor of 2 to 3 relative to the Murray meteorite. The amino acids β-alanine and particularly α-aminoisobutyric acid are exceptions in this regard. The higher content of the predominant amino acids in the Murchison meteorite as compared with the Murray meteorite may be a result of variation in the degree of pulverization and hence the surface area of the two samples extracted. The effect of this variable has not as yet been determined.

Acid hydrolysis of the aqueous meteorite extracts leads to a marked increase in the amounts of most components. Glycine, for example, is found in the Murchison and Murray extracts at concentrations of 3.4 and 1.5 μg/g, respectively, whereas the acid-hydrolyzed extracts contain 6.1 and 3.0 μg/g, respectively. The amounts of the dicarboxylic amino acids aspartic acid and glutamic acid increase by a factor of 4 to 5 after acid hydrolysis. As would be expected, there are also qualitative differences between the extracts and the acid-hydrolyzed extracts. The extracts show a large 440-nm peak near peak 8 in Fig. 1 which is lost on acid hydrolysis. On the other hand, peaks 1, 6, 10, and 16 are seen only in acid-hydrolyzed extracts. Questions concerning the nature of the water-extractable material which liberates amino acids on acid hydrolysis, the state of the amino acids prior to extraction, and possible chemical reactions occurring during extraction remain to be answered.

Although the amino acid composition of the Murchison sample is in good agreement with the data of Kvenvolden *et al.* (*2*) and Oro *et al.* (*8*), amino acid compositions of the Murray sample that vary greatly from that reported here have been reported. Calvin and Vaughn (*9*), for example, found no amino acids, and Kaplan *et al.* (*10*) found 19 amino acids at a concentration exceeding 50 μg/g in total. Because the amino acid composition reported by Kaplan *et al.* agrees so well with that of fingerprints, that sample is widely held to have been contaminated by human handling (*11*). The data in best agreement with ours are those of Raia (*12*), who found amino acids totaling 37.2 μg/g in ratios to glycine very similar to those shown in Table 1. That Raia found higher absolute amounts of the amino acids may be attributable to the more stringent extraction conditions employed. Recent work by Oro *et al.* (*13*) on the enantiomeric distribution of amino acids in a Murray sample adds further support to the belief that amino acids are indigenous to this meteorite. The variability in the results reported for amino acids in the Murray meteorite are very likely a reflection of a history of handling and less than satisfactory sample selection prior to analysis. Problems of contamination by handling have been avoided in this analysis by selecting a sample taken from the interior of a single large individual stone that had been preserved intact from 20 September 1950, the date of the fall, until this sample was taken (*14*).

The extremely high content of α-aminoisobutyric acid and the generally lower content of the other amino acids in Murray extracts constitute the major

differences between this meteorite and the Murchison meteorite. Apart from these differences, a similarity in the amino acid composition of these two carbonaceous chondrites is apparent from the ratios calculated in Table 1. This compositional similarity would seem to further substantiate the conclusion that these compounds are indigenous to type II (C2) carbonaceous chondrites. The Murchison and Murray meteorites are extremely similar in their macroscopic characteristics. Both meteorites have total carbon contents of about 2.2 percent and a total nitrogen content in the range of 0.15 to 0.20 percent (by weight) (*15*). There is every reason to believe that all the C2 chondrites have a similar origin and similar chemical characteristics. The Allende chondrite, on the other hand, contains 0.25 percent carbon and only 0.006 percent nitrogen (by weight). It remains to be seen whether the amino acid composition reported for the Murchison and Murray meteorites will prove to be representative of type II and possibly type I carbonaceous chondrites.

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References and Notes

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Magnetocardiography of Direct Currents: S-T Segment and Baseline Shifts during Experimental Myocardial Infarction

Abstract. *Magnetocardiograms with a bandwidth of 0 to 40 hertz were recorded from intact dogs undergoing myocardial infarction. This was done with a superconducting magnetometer in a magnetically shielded room. The purpose was to look for the steady currents of injury from the heart which supposedly produce much of the S-T segment shifts during infarction. These heart currents cannot be measured with surface electrodes because of direct-current interference from other sources, such as from the contact potential between electrode and skin. The magnetocardiograms showed both S-T segment shifts and direct currents as a result of infarction. However, they also showed that the S-T segment shifts were not produced by the direct currents. It is unlikely that these direct currents originated from the infarcted area, and their exact origin is not yet known.*

Diagnosis of a myocardial infarction strongly depends on certain telltale signs on the electrocardiogram (ECG); one such sign is a shift of the S-T segment. Although many careful measurements have been made on exposed animal hearts in order to understand the cause of the shift, the results are not consistent and the cause is still not clear. We have started to investigate the S-T shift by using the new technique of direct-current (d-c) magnetocardiography and find that we are obtaining information not previously available. Our work is the first use of this d-c technique and we present here some of our initial results.

Magnetocardiography is the measurement of the weak magnetic field around the torso produced by natural ion currents from the heart. The currents in the torso which produce the heart's magnetic field are powered by the electrical activity of the heart muscle; it is these same currents that also produce the ECG. A record of the heart's pulsating magnetic field is called a magnetocardiogram (MCG). Because the MCG has its origins in the same currents as the ECG, the MCG has features similar to the ECG, such as the QRS complex and the T-wave. It differs from the ECG by sampling the heart currents differently, and in principle can show some heart events not detectable with the ECG (*1*). At the peak of QRS the heart's magnetic field rises to about 5×10^{-7} gauss or one-millionth of the earth's magnetic field (*2*). The first MCG was recorded by using two large coils on the chest, connected in opposition to reduce the background magnetic disturbances (*3*). Another detection scheme made use of a single, compact coil situated in a magnetically shielded room to reduce the background; with this system the heart's magnetic field was verified, the brain's alpha-rhythm field was detected at about 1×10^{-9} gauss, the heart's QRS field was mapped in detail, and a steady magnetic field of about 1×10^{-6} gauss was found at the abdomen (*4*). Recently, a more heavily shielded room was constructed at Massachusetts Institute of Technology (*5*) and a newly devel-

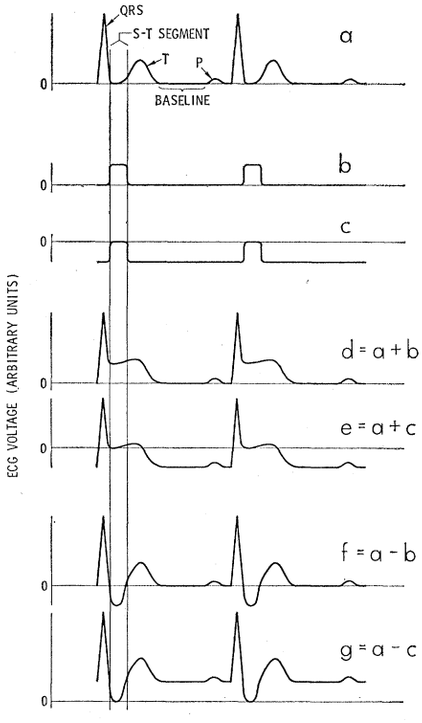

Fig. 1. Often-used explanation of the S-T segment shift on the ECG during infarction. Before infarction, the ECG is normal, as in *a*. After the start of infarction, the infarcted area generates new voltages *b* or *c*, or both; *b* can be produced by two different physiological events and *c* by yet another, third event. The lowered baseline level of *c*, which is d-c, is called the "current of injury." The various combinations of *a* with *b* and *c*, shown in *d*, *e*, *f*, and *g* appear as surface voltages. The standard ECG cannot tell the difference between *d* and *e* or between *f* and *g*.