Extraterrestrial amino acids in Orgueil and Ivuna: Tracing the parent body of CI type carbonaceous chondrites

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Amino acid analyses using HPLC of pristine interior pieces of the CI carbonaceous chondrites Orgueil and Ivuna have found that β-alanine, glycine, and γ-amino-*n*-butyric acid (ABA) are the most abundant amino acids in these two meteorites, with concentrations ranging from ≈600 to 2,000 parts per billion (ppb). Other α-amino acids such as alanine, α-ABA, α-aminoisobutyric acid (AIB), and isovaline are present only in trace amounts (<200 ppb). Carbon isotopic measurements of β-alanine and glycine and the presence of racemic (D/L ≈ 1) alanine and β-ABA in Orgueil suggest that these amino acids are extraterrestrial in origin. In comparison to the CM carbonaceous chondrites Murchison and Murray, the amino acid composition of the CIs is strikingly distinct, suggesting that these meteorites came from a different type of parent body, possibly an extinct comet, than did the CM carbonaceous chondrites.

Carbonaceous chondrites provide some of the most primitive solar system material available for study and are known to contain a wide variety of organic compounds (1). In particular, one group of carbonaceous chondrites, the CIs, which have been altered extensively by water on their parent body, have been found to contain high abundances of organic carbon. Orgueil, the most well known CI carbonaceous chondrite, fell in France on May 14, 1864 at a time when organic and analytical chemistry were in their infancy. Nevertheless, by using techniques available at the time, chemists soon showed that the meteorite contained organic material probably of extraterrestrial origin (2). Some scientists even speculated that the Orgueil organic material was produced by extraterrestrial organisms and thus provided evidence for panspermia, a process wherein life on Earth was seeded by a bacterial spore from another world that had hitchhiked on a meteorite that had fallen to Earth (3). Pasteur briefly examined the Orgueil meteorite and found no evidence for bacteria, a finding that he evidently considered so unimportant that it was never published except in his notebooks (4).

The possibility that Orgueil contained evidence for extraterrestrial life resurfaced in the 1960s when Nagy and coworkers published a series of papers claiming that the meteorite contained biogenic hydrocarbons along with "organized elements" that supposedly resembled fossilized algae (5, 6). These claims generated an intense debate, and soon it was shown that the hydrocarbons were terrestrial contaminants and the organized elements were ragweed pollen (7, 8).

Because of these controversies, the CI meteorite Orgueil has seldom been studied by using the modern analytical techniques now available to investigate organic compounds in meteorites. The last amino acid analysis of Orgueil was reported in 1972 when GC analysis using a chiral derivatizing reagent showed that the meteorite contained D- and L-amino acids and other amino acids such as β-alanine, α-aminoisobutyric acid (AIB), and β-AIB, which generally are not present in terrestrial living organisms (9). Surprisingly, Ivuna, another CI carbonaceous meteorite that fell in Tanzania on December 16, 1938, has rarely been investigated for organic components, perhaps because of the controversies over Orgueil. Thus far in the only study to date, Ivuna has been found to contain a distribution of polycyclic aromatic hydrocarbons that is unique among other carbonaceous chondrites (10).

In contrast to the CIs, the CM-type chondrites Murchison and Murray, which fell in Australia in 1969 and in Kentucky in 1950, respectively, have been analyzed extensively for organic compounds by using modern techniques. Over 70 different amino acids have been detected in Murchison, the majority of which have no known terrestrial occurrence (1). The Murchison amino acids also have been shown to have unusual carbon, nitrogen, and hydrogen isotopic signatures that provide additional evidence of their extraterrestrial origin (11–13).

To enhance our knowledge of CI carbonaceous chondrites, we report here the results of amino acid analyses of Orgueil and Ivuna by using highly sensitive analytical techniques recently developed to study meteorites (14, 15).

Materials and Methods

The Meteorite Samples and Processing Procedures. A large interior chunk of the Orgueil meteorite (6.3 g obtained from the Musée National, Paris) and several small interior chips of Ivuna (0.3 g obtained from the Smithsonian National Museum of Natural History, Washington DC, USNM 6630) were crushed separately into fine powders by using a mortar and pestle in a positive-pressure (1 μm filtered air) clean room. A portion of the Orgueil (133 mg) and Ivuna (94 mg) meteorite samples then were sealed separately in clean test tubes with 1 ml of double-distilled water and boiled at 100°C for 24 h, and the water supernatants were subjected to a 6 M HCl acid vapor hydrolysis procedure as described (14).

The acid-hydrolyzed hot-water extracts of the meteorites were desalted by using cation-exchange resin (AG50W-X8, Bio-Rad), and the amino acids were then analyzed by derivatization with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine followed by HPLC coupled with UV fluorescence detection (15). For comparison, powdered samples of the CM carbonaceous chondrites Murchison (92 mg) and Murray (121 mg) were analyzed simultaneously with Orgueil and Ivuna. As controls, 108 mg of crushed serpentine (a hydrated magnesium silicate) that had been heated at 500°C for 3 h and a procedural blank were carried through the same processing procedure as the meteorite samples.

Results and Discussion

HPLC Amino Acid Analyses. We found that the 6 M HCl acid-hydrolyzed hot-water extract of Orgueil contained 2,052 ± 311

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Abbreviations: AIB, aminoisobutyric acid; ppb, parts per billion; ABA, amino-*n*-butyric acid; HCN, hydrogen cyanide.

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Table 1. Summary of the average serpentine blank-corrected amino acid concentrations in the 6 M HCl acid-hydrolyzed hot-water extracts of the CI-type carbonaceous chondrites Orgueil and Ivuna and the CM chondrites Murray and Murchison

	CI		CM	
Type	Orgueil	Ivuna	Murray	Murchison
D-Asp	28 ± 16	30 ± 2	51 ± 31*	100 ± 15
L-Asp	54 ± 18	146 ± 8	65 ± 16	342 ± 103
D-Glu	15 ± 6	8 ± 1	135 ± 50	537 ± 117
L-Glu	61 ± 31	372 ± 11	261 ± 15	801 ± 200
Gly	707 ± 80	617 ± 83	2,110 ± 144	2,919 ± 433
D-Ala	69 ± 9	82 ± 22	617 ± 79	720 ± 95
L-Ala	69 ± 9	157 ± 14	647 ± 58	956 ± 171
β-Ala	2,052 ± 311	1,401 ± 146	1,063 ± 268	1,269 ± 202
D,L-α-ABA†	13 ± 11*	12 ± 7*	463 ± 68	914 ± 189
D,L-β-ABA‡	332 ± 99	438 ± 142	424 ± 18	708 ± 171
γ-ABA	628 ± 294	≈600	717 ± 192	1,331 ± 472
AIB	39 ± 37*	46 ± 33*	1,968 ± 350	2,901 ± 328
D,L-β-AIB†	148 ± 70	84 ± 12	147 ± 88	343 ± 102
D,L-Iva†	<194 ± 230*	<163 ± 119*	2,834 ± 780	3,359 ± 534
Total	4,200	4,000	11,500	17,200

All values are reported in ppb on a bulk-sample basis. The uncertainties are based on the standard deviation of the average value of between two and five separate measurements.

*These concentrations were very similar to blank levels and therefore must be considered to be maximum values.

†Enantiomers could not be separated under the chromatographic conditions.

‡Optically pure standard not available for enantiomeric identification.

parts per billion (ppb) of β-alanine, 707 ± 80 ppb of glycine, and 628 ± 294 ppb of γ-amino-*n*-butyric acid (ABA). With the exception of 332 ± 99 ppb of β-ABA, only traces (<200 ppb) of other amino acids like aspartic and glutamic acids, alanine, α-ABA, AIB, β-AIB, and isovaline were detected in Orgueil (Table 1). High levels of β-alanine, glycine, and γ-ABA (≈600 to 1,400 ppb) were identified also in Ivuna (Table 1). Only very low levels (<10 ppb) of aspartic and glutamic acids, serine, glycine, alanine, β-alanine, and γ-ABA in the serpentine and procedural blanks could be detected by HPLC (Fig. 1). Two unknown peaks also were observed in the procedural blank (marked X in Fig. 1) but were not detected in any of the other samples.

The calculated D/L ratios in the acid-hydrolyzed hot-water extracts of Orgueil were 0.52 ± 0.34 for aspartic acid, 0.25 ± 0.16 for glutamic acid, and 1.00 ± 0.18 for alanine (Table 1). A D/L ratio of ≈1 for β-ABA in Orgueil was estimated based on the relative HPLC chromatogram peak areas (Fig. 1). The accurate determination of these enantiomeric ratios is difficult, however, given the low concentrations of these amino acids in Orgueil. The low D/L ratios of aspartic and glutamic acids in Orgueil indicate that a large fraction of these two amino acids could be terrestrial in origin, possibly derived from the meteorite fall site. However, soil samples from the Orgueil fall site could not be analyzed for the presence of these amino acids to confirm this theory. Nevertheless, the presence of racemic alanine and β-ABA in Orgueil are suggestive of an abiotic origin, a conclusion consistent with the earlier studies of amino acids in Orgueil (9). In Ivuna, we calculated a D/L ratio of 0.21 ± 0.02 for aspartic acid, 0.022 ± 0.003 for glutamic acid, and 0.52 ± 0.15 for alanine. The lower D/L ratios in Ivuna compared with Orgueil suggest that this sample of the Ivuna meteorite was subjected to a higher degree of terrestrial amino acid contamination during its residence on Earth than was our Orgueil sample.

Carbon Isotope ($\delta^{13}C$) Measurements. Additional analyses of the Orgueil acid-hydrolyzed hot-water extracts by GC combustion-isotope ratio mass spectrometry (16) yielded minimum carbon isotope values of $\delta^{13}C = +18‰$ for β-alanine and $\delta^{13}C = +22‰$ for glycine in Orgueil. These $\delta^{13}C$ values fall well outside of the terrestrial range of −20 to −35‰ (17), a finding that clearly indicates an extraterrestrial origin of these amino acids. For comparison, Pizzarello *et al.* obtained a value of $\delta^{13}C = +44‰$ from a combined glycine/alanine fraction from Murchison (11), and Engel *et al.* measured $\delta^{13}C = +22‰$ for glycine in Murchison (12). Carbon isotopic measurements of β-alanine have not been reported for Murchison and Murray. Because of the small amount of Ivuna meteorite sample allocated for this study, carbon isotopes for β-alanine and glycine could not be measured.

Amino Acid Comparison of CI- and CM-Type Carbonaceous Chondrites. The most surprising result in these analyses was the striking similarity between the amino acid compositions of the CI chondrites Orgueil and Ivuna, which were found to be distinct from the composition of the CMs (Fig. 1). The CM meteorites Murchison and Murray have been shown previously (18) to have nearly identical amino acid distributions (Fig. 1). The total abundance of amino acids detected in the CI chondrites was approximately one-third of that found in the CM chondrites (Table 1). The most notable difference in amino acid composition between the CI- and CM-type chondrites, however, was the high abundance (relative to glycine = 1.0) of β-alanine in Orgueil (2.9) and Ivuna (2.3) compared with Murchison and Murray (≈0.5). Moreover, AIB and isovaline, which are the two most abundant nonprotein amino acids found in Murchison and Murray (≈2,000 to 3,400 ppb), were present only in trace amounts (<200 ppb) in Orgueil and Ivuna (Table 1). These data suggest that the amino acids detected in the CI and CM carbonaceous chondrites were synthesized on two chemically distinct parent bodies.

Strecker Synthesis of α-Amino Acids in CM Chondrites. The most plausible synthetic pathway for the formation of the meteoritic α-amino acids detected in Murchison and Murray, including α-amino-α-alkyl acids such as AIB and isovaline, is the Strecker-

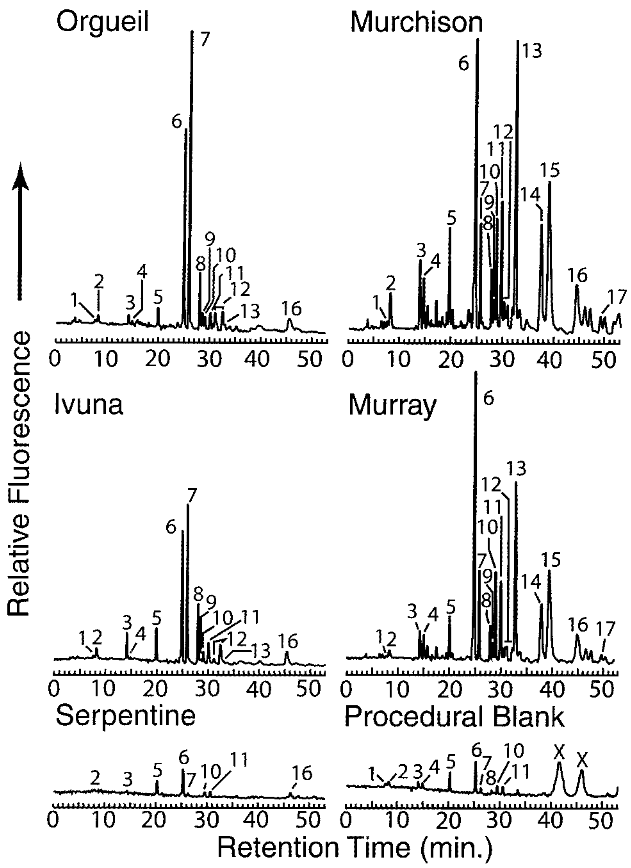

Fig. 1. The 0- to 53-min region of the HPLC chromatograms (no peaks were observed outside this time period). *o*-phthaldialdehyde/*N*-acetyl-L-cysteine derivatization (15 min) of amino acids in the 6 M HCl-hydrolyzed, hot-water extracts from the CI carbonaceous chondrites Orgueil and Ivuna, the CM chondrites Murchison and Murray, and the serpentine and procedural blanks are shown. The conditions for amino acid separations for the mobile phase at 25°C were as follows: flow rate, 1 ml/min; buffer A (50 mM sodium acetate) at pH 8.0, buffer B (methanol-optima grade); gradient, 0 to 4 min, 0% buffer B; 4 to 24 min, 0 to 30% buffer B; 24 to 54 min, 30 to 40% buffer B. Peaks were identified as follows: 1, D-aspartic acid; 2, L-aspartic acid; 3, L-glutamic acid; 4, D-glutamic acid; 5, DL-serine; 6, glycine; 7, β-alanine; 8, γ-ABA; 9, DL-β-AIB; 10, D-alanine; 11, L-alanine; 12, DL-β-ABA; 13, AIB; 14, D, L-α-ABA; 15, DL-isovaline; 16, L-valine; 17, D-valine; and X, unknown.

cyanohydrin synthesis, which is thought to take place during aqueous alteration on the CM meteorite parent body. This reaction sequence involves the formation of aminonitriles from hydrogen cyanide (HCN), ammonia, and carbonyl compounds such as aldehydes and ketones, which then would undergo hydrolysis to the corresponding amino acids (19). A variety of aldehydes and ketones such as acetaldehyde, acetone, and 2-butanone have been identified in Murchison (20) and are believed also to be present in asteroids (21). The high abundance of AIB and isovaline in Murchison and Murray indicates that Strecker synthesis was a predominant reaction on the parent bodies of these CM meteorites, because it is difficult to form these amino acids by any other synthetic pathway.

Origin of β-Alanine and Glycine in CI Chondrites. Because β-amino acids are not produced by the Strecker-cyanohydrin pathway, these amino acids must be produced by a different synthetic pathway than α-amino acids. In general, the synthesis of β-amino acids such as β-alanine could proceed by Michael addition of ammonia to α,β-unsaturated nitriles, followed by hydrolysis (22). Miller has suggested that β-alanine produced from spark-discharge experiments could be synthesized abiotically by the addition of ammonia to acrylonitrile followed by hydrolysis (22). β-alanine also could be produced by Michael addition of ammonia to cyanoacetylene.

The high relative abundance of β-alanine and the low concentrations of α-amino acids like alanine, AIB, α-ABA, and isovaline in Orgueil and Ivuna (Fig. 1) indicate that the Strecker synthetic pathway was not active on the parent bodies of these CI meteorites. Therefore, the formation of amino acids in Orgueil and Ivuna must have taken place by other processes. It has been shown that HCN polymerization reactions can proceed over a wide range of temperatures (-78°C to 100°C) to produce glycine ($\approx$1% yield from HCN) and lower yields of alanine (23). No significant amount of any other amino acid is produced from HCN polymerization. After heating a 0.1 M HCN solution at 100°C for 2 days, a synthesized glycine/alanine (G/A) ratio of $\approx$3 was measured (24). We calculate a G/A ratio of 5.1 in Orgueil and 2.6 in Ivuna (Table 1), which indicates that both glycine and alanine in these meteorites could have been produced from HCN polymerization if the CI parent body was heated to elevated temperatures. Mineralogical evidence and oxygen-isotope data suggest that the temperature of aqueous alteration on the CI parent body was higher than for CMs and could have reached 50°C (25).

Cometary vs. Asteroidal Origin of CI and CM Chondrites. Based on mineralogical and chemical evidence, including the high deuterium/hydrogen ratio of CI meteorites, it has been suggested recently that CI meteorites could be fragments of comets or extinct cometary nuclei (26, 27). Powdered samples of the CM meteorite Murchison heated up to 900°C show strong similarities in their reflectance spectra to C- and G-type asteroids, which points to an asteroidal origin for this CM meteorite (28). However, the link between CI and CM chondrites and comets and asteroids is not drawn clearly. In addition, it is unclear whether some small solar system objects such as Chiron, Wilson–Harrington, and Elst–Pizarro are comets or asteroids (29).

Observations of the recent comets Hyakutake and Hale–Bopp over the entire electromagnetic spectrum have established an inventory of cometary volatiles, including ammonia, HCN, and formaldehyde (30). Cyanoacetylene, one of the potential precursors of β-alanine, has been detected also in the coma of comet Hale–Bopp, in which its abundance is about 10% of that of HCN (30). However, a rich mixture of carbonyl compounds including ketones and aldehydes, which are necessary for Strecker chemistry to take place, has not been found in these comets (30, 31). Because only a limited number of carbonyl compounds have been detected in these comets (30, 32), it is highly unlikely that the CM meteorites Murchison and Murray originated from long-period comets. However, if Michael addition and HCN polymerization were the dominant reaction pathways on the parent bodies of Orgueil and Ivuna, the amino acid distribution that we find in these CI meteorites is consistent with the volatiles detected in the comets Hyakutake and Hale–Bopp.

Our results suggest that the amino acids in the CI chondrites Orgueil and Ivuna could have been synthesized in an early aqueous alteration phase (33) on a parent body that was rich in cometary components such as water, ammonia, HCN, and cyanoacetylene. It should be pointed out that the presence of liquid water in the interior of comets necessary for aqueous alteration has been controversial, with some of the more recent models suggesting that it is unlikely (34). After its active phase and the loss of its primordial ice, an extinct comet nuclei could have evolved into a near-Earth asteroid, fragmenting into smaller meteorites during collisions in the asteroid belt. Thus, these CI meteorites could be cometary in origin, although we cannot rule out the possibility that they originated from an asteroidal parent body that was depleted in amino acid precursor material because of more thorough aqueous processing.

On the basis of our amino acid data of CI and CM carbonaceous meteorites, organic chemistry now can be included as an additional set of criteria to constrain the nature of meteorite parent bodies. This type of amino acid analysis would be especially useful also to help classify the Tagish Lake meteorite that fell near the border of the Yukon territory and British Columbia on January 18, 2000 and has been found recently to have a mineralogy, oxygen isotope, and bulk chemical composition intermediate between CI and CM meteorites (35).

The simple amino acid mixture found in CI carbonaceous chondrites is interesting in the sense that generally it has been thought that a wide variety of amino acids were required for the origin of life. However, among the candidates for the first genetic material is peptide nucleic acid, a nucleic acid analogue in which the backbone does not contain sugar or phosphate moieties (36). For the peptide nucleic acid backbone, achiral amino acids such as glycine and β-alanine, possibly delivered by CI-type carbonaceous chondrites to the early Earth (37), may have been the only amino acids needed for the origin of life.

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