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Amino acids in the Tagish Lake meteorite

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Abstract–High-performance liquid chromatography (HPLC) based amino acid analysis of a Tagish Lake meteorite sample recovered 3 months after the meteorite fell to Earth have revealed that the amino acid composition of Tagish Lake is strikingly different from that of the CM and CI carbonaceous chondrites. We found that the Tagish Lake meteorite contains only trace levels of amino acids (total abundance = 880 ppb), which is much lower than the total abundance of amino acids in the CI Orgueil (4100 ppb) and the CM Murchison (16 900 ppb). Because most of the same amino acids found in the Tagish Lake meteorite are also present in the Tagish Lake ice melt water, we conclude that the amino acids detected in the meteorite are terrestrial contamination. We found that the exposure of a sample of Murchison to cold water lead to a substantial reduction over a period of several weeks in the amount of amino acids that are not strongly bound to the meteorite matrix. However, strongly bound amino acids that are extracted by direct HCl hydrolysis are not affected by the leaching process. Thus even if there had been leaching of amino acids from our Tagish Lake meteorite sample during its 3 month residence in Tagish Lake ice and melt water, a Murchison type abundance of endogenous amino acids in the meteorite would have still been readily detectable. The low amino acid content of Tagish Lake indicates that this meteorite originated from a different type of parent body than the CM and CI chondrites. The parent body was apparently devoid of the reagents such as aldehyldes/ketones, HCN and ammonia needed for the effective abiotic synthesis of amino acids. Based on reflectance spectral measurements, Tagish Lake has been associated with P- or D-type asteroids. If the Tagish Lake meteorite was indeed derived from these types of parent bodies, our understanding of these primitive asteroids needs to be reevaluated with respect to their potential inventory of biologically important organic compounds.

INTRODUCTION

The Tagish Lake meteorite fireball was observed on 2000 January 18 throughout Yukon and the Northwest Territories, northern British Columbia and parts of Alaska. Many pieces of the meteorite were identified and collected on the Taku Arm of Tagish Lake (Brown *et al.*, 2000) soon after the fall. The cold environment of the fall site, the rapid collection and the detailed description of the curatorial procedures make the Tagish Lake meteorite especially interesting with respect to organic compound analyses. The mineralogy, oxygen isotope, and bulk chemical composition of the Tagish Lake meteorite indicate that the meteorite is an intermediate between CM and CI class chondrites (Brown *et al.*, 2000). The oxygen isotope analysis shows a high degree of sample heterogeneity and suggests a higher water to rock ratio of the Tagish Lake meteorite compared to the CM class and a lower temperature of aqueous alteration than the CI class (Brown *et al.*, 2000).

Most of the carbonaceous chondrites previously analyzed are thought to have been associated with C- and G-type asteroids on the basis of their reflectance spectra (Burbine, 1998). These types of asteroids populate the inner part of the asteroid belt. However, spectral comparison of Tagish Lake with a number of asteroid classes indicates that the best fit is with D-type asteroids (Hiroi *et al.*, 2001). These asteroids are low albedo objects that populate the outer regions of the asteroid belt and are believed to contain complex organic compounds. The possible association of the Tagish Lake meteorite with a D-type asteroid is consistent with the orbital elements calculated for the Tagish Lake fireball and indicates that this meteorite could be the first sample from this region of the asteroid belt (Brown *et al.*, 2000).

Recently it has been shown that the amino acid compositions of CM and CI class meteorites are strikingly distinct, and that amino acid chemistry can be used to constrain the nature of meteorite parent bodies (Ehrenfreund *et al.*, 2001). It has been

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suggested that CM meteorites originate from C- or G-type asteroids (Brown *et al.*, 2000; Hiroi *et al.*, 1993) while CI meteorites could be pieces of comets or extinct cometary nuclei (Campins and Swindle, 1989). In this study, we compared the amino acid composition of the Tagish Lake meteorite to the composition of the Murchison (CM) and Orgueil (CI) carbonaceous chondrites.

MATERIALS AND METHODS

The Tagish Lake meteorite sample analyzed in this study (sample 24-24) was collected ~3 months after the fall from a small puddle of water on the ice of the Taku Arm (Alan R. Hildebrand, pers. comm.). Several small meteorite fragments (1.1 g total mass) were crushed to a fine powder using a mortar and pestle in a positive pressure clean room. All glassware as well as the mortar and pestle were heat sterilized at 500 °C for 3 h. Three aliquots of the crushed Tagish Lake meteorite (203, 290, and 184 mg), pulverized interior pieces of Murchison (192, 187, and 180 mg, obtained from K. Kvenvolden), and a fragment of Orgueil (200 mg, obtained from the Musee National, Paris) were processed in parallel. As a blank control, 200 mg of a crushed serpentine sample (a hydrated magnesium silicate) that had been heated at 500 °C for 3 h was carried through the same procedure.

To evaluate possible contamination of the Tagish Lake meteorite from the Tagish Lake melt water, we also obtained 250 mL of Tagish Lake melt water from A. L. Hildebrand. The Tagish Lake melt water was dried down in a desiccator and processed in parallel with the other meteorites (hot water extraction, hydrolysis and desalting).

A set of two 180 mg Murchison samples were used to study the leaching of amino acids from carbonaceous meteorites during exposure to cold water. One Murchison sample was exposed to 3 mL of water in a test tube, the other one was kept dry. Both samples were stored in a 4 °C refrigerator for 6 weeks; the test tube with water was stirred daily.

The various samples were transferred into clean test tubes, 1 mL of double-distilled water was added and the tubes were flame sealed. After heating the samples at 100 °C for 24 h, the tubes were centrifuged and the water supernatants were removed and dried under vacuum. The residues from the dried hot water extracts were subjected to 6 M HCl vapor hydrolysis at 150 °C for 3 h (Glavin *et al.*, 1999). A 184 mg sample of the Tagish Lake meteorite and a 187 mg sample of Murchison were used to study the ratio of strongly to weakly bound amino acids in both meteorites. Both samples were dissolved in 1 mL 6 M HCl at 100 °C for 24 h. The acid-hydrolyzed hot water extracts and the direct acid-hydrolyzed HCl supernatants were dried down under vacuum and desalted using cation-exchange resin (AG50W-X8, Bio-Rad). The amino acids and their enantiomeric ratios were then analyzed by high-performance liquid chromatography (HPLC) using derivatization with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) and UV-fluorescence detection (Zhao and Bada, 1995). Peaks were identified by comparison of retention times with known standards. Amino acid standards were obtained commercially (Aldrich and Sigma) and used without further purification.

RESULTS

We found that the 6 M HCl hydrolyzed hot water extract of Tagish Lake contained only trace levels of amino acids, ranging in concentration from 11 to 306 ppb (Table 1 and Fig. 1). Direct HCl hydrolysis of a Tagish Lake meteorite sample resulted in a twofold increase in the amino acid abundance although the distribution and relative abundance of amino acids was the same as that found in the hot water extraction with subsequent hydrolysis (the same result was also obtained for the Murchison meteorite). The most predominant amino acids in Tagish Lake include L-glutamic acid, glycine, D/L-α-amino-*n*-butyric acid (α-ABA), L-aspartic acid, γ-amino-*n*-butyric acid (γ-ABA), L-alanine and β-alanine. Trace amounts D-aspartic, D-glutamic and D-alanine were detected at the 12–20 ppb level. At the low concentrations that were found, the apparent high D/L alanine ratio cannot be used as a signature of abiotic synthesis because similar alanine enantiomeric ratios in blanks carried through the same processing procedure were found. The non-protein amino acids α-aminoisobutyric acid (AIB) and isovaline, which are extremely rare on Earth, but abundant in most CM chondrites, were not detected in Tagish Lake at

TABLE 1. Summary of the blank corrected amino acid concentration in the 6 M HCl hydrolyzed hot water extracts of Orgueil (CI), Murchison (CM) and Tagish Lake meteorites.

Amino acid	Orgueil* (CI)	Tagish Lake	Murchison* (CM)
D-Asp	28 ± 16	11 ± 1	100 ± 15
L-Asp	54 ± 18	83 ± 8	342 ± 103
D-Glu	15 ± 6	16 ± 2	537 ± 117
L-Glu	61 ± 31	306 ± 48	801 ± 200
Gly	707 ± 80	147 ± 17	2919 ± 433
D-Ala	69 ± 9	20 ± 5	720 ± 95
L-Ala	69 ± 9	75 ± 18	956 ± 171
β-Ala	2052 ± 311	64 ± 10	1269 ± 202
D,L-α-ABA†	13 ± 11	84 ± 40	914 ± 189
D,L-β-ABA‡	332 ± 99	<26	708 ± 171
γ-ABA	628 ± 294	77 ± 10	1331 ± 472
AIB	39 ± 37	<27	2901 ± 328
D,L-Iva	<194	<56	3359 ± 534
Total	4100	~880	16 900

All values are given in parts per billion (ppb).
*Values taken from Ehrenfreund *et al.* (2001).
†Enantiomers could not be separated under the chromatographic conditions.
‡Optically pure standard not available for enantiomeric identification.

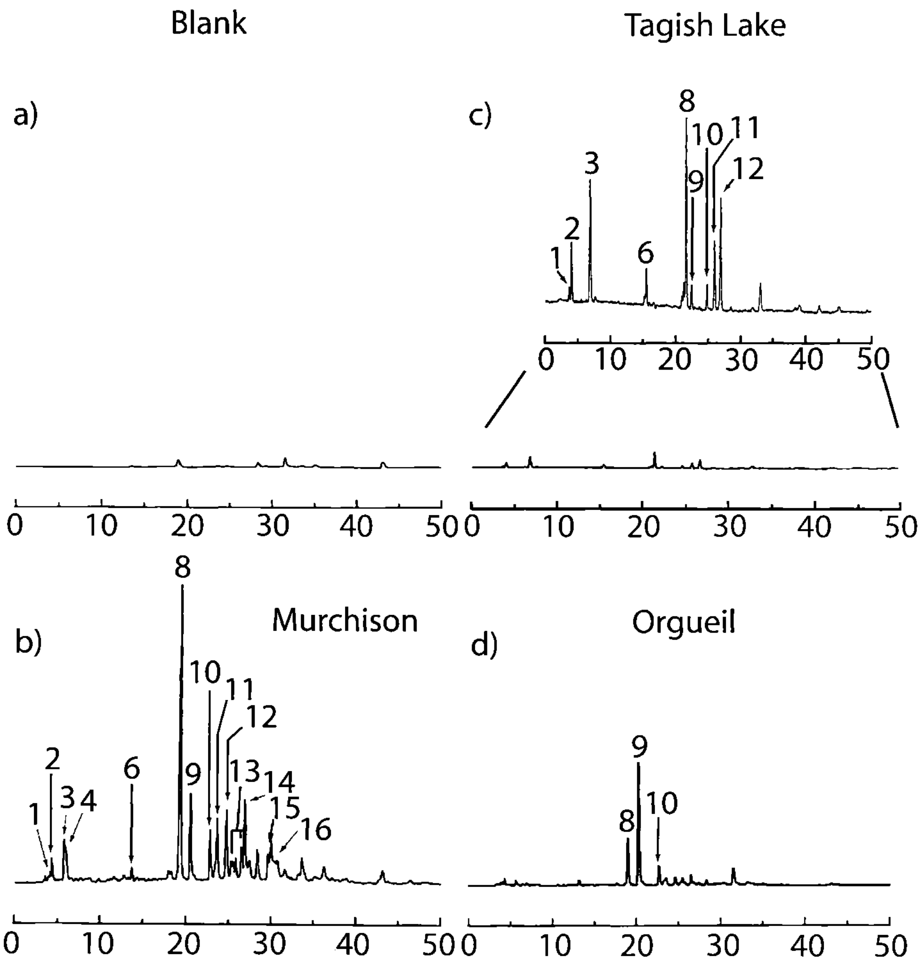

FIG. 1. HPLC chromatograms of the 1 min derivatized, 6 M HCl hydrolyzed hot water extracts of Tagish Lake, Murchison, Orgueil and a serpentine blank. All chromatograms are shown at equal attenuation for comparison. The Tagish Lake chromatogram is also expanded to show the distribution of amino acids identified in this meteorite. (1) D-aspartic acid; (2) L-aspartic acid; (3) L-glutamic acid; (4) D-glutamic acid; (5) D-serine; (6) L-serine; (7) unidentified peak; (8) glycine; (9) β-alanine; (10) γ-ABA; (11) D-alanine; (12) L-alanine; (13) D,L-β-ABA; (14) AIB; (15) D,L-α-ABA; (16) D,L-isovaline.

levels of <27 and <56 ppb, respectively (Table 1). The total abundance of amino acids in Tagish Lake (880 ppb) is much lower than the measured amino acid content of Murchison (16 900 ppb) and Orgueil (4100 ppb). The amino acid content of our Tagish Lake meteorite sample is consistent with the preliminary amino acid results reported previously for a "pristine" unleached sample (Pizzarello *et al.*, 2001).

The Tagish Lake melt water was found to have an amino acid concentration of 3.3×10^{-7} mol/L. All amino acids identified in the Tagish Lake meteorite are also found to be present in the Tagish Lake melt water (Fig. 2). The leaching experiment using the Murchison meteorite showed that it is possible to leach out ~50% of the free amino acids in 6 weeks. A mass balance of the amino acids extracted into the cold water combined with those that remained in the leached Murchison sample was found to be in excellent agreement with the total amino acids present in a Murchison sample that had not been subjected to prolonged exposure to cold water.

DISCUSSION AND CONCLUSIONS

Rapid terrestrial contamination can greatly compromise the quality of meteoritic samples with respect to organic analyses. For example, in the Martian meteorite Nakhla, which fell in the Nile Delta in 1911, the relative amino acid abundances as well as enantiomeric ratios of aspartic acid, glutamic acid and alanine are strikingly similar to those of a Nile Delta sediment sample (Glavin *et al.*, 1999). This finding is indicative of the ease in which terrestrial amino acids can become incorporated into a meteorite after its fall to Earth. In the case of the Tagish Lake meteorite, the relative abundance and the enantiomeric ratios of most of the detected amino acids are similar to the Tagish Lake melt water (Fig. 2). We estimate that the absorption of the amino acids in ~40 mL of Tagish lake melt water could account for the total amino acid abundance of 1 g of Tagish Lake meteorite. Assuming this is the case, then the slight differences in the amino acids contained in the Tagish

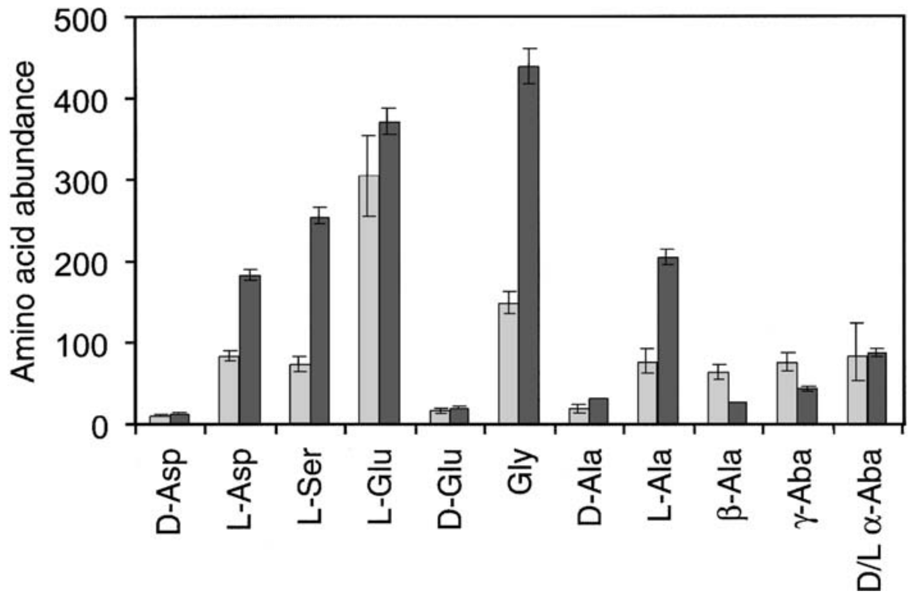

FIG. 2. Amino acid abundance in the Tagish Lake meteorite (light gray, in ppb) and the Tagish Lake melt water (dark gray). The abundance is scaled for comparison (times 5×10^9 mol/L). All the amino acids found in the Tagish Lake meteorite are present in the Tagish Lake melt water.

Lake meteorite compared to the Tagish Lake melt water (especially for L-glutamic acid, β-alanine and γ-ABA) might be due to fractional adsorption of amino acids on meteorite minerals (Mueller and Suess, 1977).

From our Murchison meteorite leaching experiment we found that there is a loss of amino acids during prolonged exposure to cold water. However, leaching of endogenous amino acids from the Tagish Lake meteorite by the surrounding melt water would not effect the amino acid abundance of the strongly bound amino acids such as those released by direct HCl acid hydrolysis. Therefore, a Murchison type amino acid abundance would have been easily recognizable even after extensive leaching of the Tagish Lake meteorite during prolonged exposure to melt water. Our conclusion is that the Tagish Lake meteorite never contained substantial endogenous amino acids prior to its exposure to the terrestrial environment.

Although most of the amino acids identified in the Tagish Lake meteorite appear to be terrestrial in origin as is indicated by the absence of the non-protein amino acids AIB, β-amino-*n*-butyric acid (β-ABA), and isovaline, and the predominance of L-amino acids, we cannot exclude the possibility of some endogenous amino acids are present at very low abundances. Carbon and nitrogen isotope analysis, which have been used to demonstrate an extraterrestrial origin of β-alanine and glycine in Orgueil (Ehrenfreund *et al.*, 2001) and of some amino acids in Murchison (Pizzarello *et al.*, 1991; Macko *et al.*, 1997) cannot be carried out for the Tagish Lake meteorite because of the low quantities of the amino acids that are present.

The Tagish Lake meteorite results are in striking contrast to the amino acid analyses of Murchison and Orgueil, which show a high complexity and abundance of amino acids as well as convincing features indicating an extraterrestrial origin (Ehrenfreund *et al.*, 2001). While spectroscopic measurements suggest that CM class meteorites are associated with C- and G-type asteroids (Burbine, 1998; Hiroi *et al.*, 1993), it has recently been suggested on the basis of amino acid chemistry that CI class meteorites could be related to comets (Campins and Swindle, 1989). The complex amino acids detected in Murchison, such as AIB and isovaline, are primarily products of the aqueous Strecker–cyanohydrin synthetic pathway, which requires the presence of hydrogen cyanide, ammonia and carbonyl compounds such as aldehydes and ketones (Cronin and Chang, 1993). For Orgueil a simple amino acid composition consisting predominantly of glycine and β-alanine has been identified indicating that HCN polymerization and Michael addition reactions could have been the dominant synthetic pathways on the CI parent body (Ehrenfreund *et al.*, 2001).

The oxygen isotope measurements of Tagish Lake suggest that the physical conditions on the Tagish Lake parent body, such as the temperature regime, were favorable for the Strecker-type synthesis of amino acids during the aqueous alteration phase (Brown *et al.*, 2000). The low amino acids abundance of Tagish Lake relative to CM and CI carbonaceous chondrites indicate that the chemical precursors for the synthesis of amino acids may have been absent on the Tagish Lake parent body.

Based on this reasoning, C- and G-type asteroids as well as comets can probably be excluded as possible parent bodies for the Tagish Lake meteorite. Spectroscopic and dynamical evidence (Brown *et al.*, 2000; Hiroi *et al.*, 2001) suggests that the Tagish Lake meteorite originated form a parent body in the outer region of the main asteroid belt, which is dominated by P- and D-type asteroids. If the Tagish Lake meteorite is a representative sample of a P- or D-type asteroid, then these objects apparently do not contain as rich a mixture of organic compounds as previously thought (Bell *et al.*, 1989). That would also mean that the planetary protection measures related to sample return from a P- or D-type asteroid might not require strict containment and handling constraints of the sample (Space Studies Board, 1998).

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