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Unusual nonterrestrial L-proteinogenic amino acid excesses in the Tagish Lake meteorite

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Abstract–The distribution and isotopic and enantiomeric compositions of amino acids found in three distinct fragments of the Tagish Lake C2-type carbonaceous chondrite were investigated via liquid chromatography with fluorescence detection and time-of-flight mass spectrometry and gas chromatography isotope ratio mass spectrometry. Large L-enantiomeric excesses ($L_{ee} \sim 43$–59%) of the α-hydrogen aspartic and glutamic amino acids were measured in Tagish Lake, whereas alanine, another α-hydrogen protein amino acid, was found to be nearly racemic (D ≈ L) using both techniques. Carbon isotope measurements of D- and L-aspartic acid and D- and L-alanine in Tagish Lake fall well outside of the terrestrial range and indicate that the measured aspartic acid enantioenrichment is indigenous to the meteorite. Alternate explanations for the L-excesses of aspartic acid such as interference from other compounds present in the sample, analytical biases, or terrestrial amino acid contamination were investigated and rejected. These results can be explained by differences in the solid–solution phase behavior of aspartic acid, which can form conglomerate enantiopure solids during crystallization, and alanine, which can only form racemic crystals. Amplification of a small initial L-enantiomer excess during aqueous alteration on the meteorite parent body could have led to the large L-enrichments observed for aspartic acid and other conglomerate amino acids in Tagish Lake. The detection of nonterrestrial L-proteinogenic amino acid excesses in the Tagish Lake meteorite provides support for the hypothesis that significant enantiomeric enrichments for some amino acids could form by abiotic processes prior to the emergence of life.

INTRODUCTION

Meteorites provide a record of the chemical processes that occurred in the early solar system before life began on Earth. The delivery of functionalized organic compounds by carbonaceous chondrites to the early Earth and other planetary bodies could have been an important source of prebiotic compounds required for the emergence of life (Chyba and Sagan 1992). Of particular interest is the study of meteoritic amino acids and their enantiomeric compositions as these molecules are the monomers of proteins common to all life on Earth. The homochirality observed in biological molecules, so called "left-handed" (by analogy with glyceraldehyde) amino acids and "right-handed" sugars, is a property important for molecular recognition processes and is thought to be a prerequisite for life. Most amino acids (including those found in meteorites) are chiral, meaning they possess two nonsuperimposable mirror image structures, or enantiomers. In contrast to biology, which is dominated by L-amino acids, abiotic processes form racemic amino acids (equal mixtures of L- and D-enantiomers). Therefore, the questions of why and how the nearly exclusive production of one hand of

such molecules arose from what were presumably equal mixtures of L- and D-enantiomers in a prebiotic world continue to be a crucial hurdle in understanding the origin of life.

The first amino acid analysis of the Murchison meteorite shortly after its fall found that the chiral amino acids were racemic (D/L $\approx$ 1), indicating an abiotic origin with very little, if any, terrestrial amino acid contamination of the meteorite (Kvenvolden et al. 1970). However, slight to significant L-enantiomer excesses for several unusual α-dialkyl amino acids in the CM meteorites Murchison and Murray including isovaline, α-methylnorleucine, α-methylvaline, α-methylnorvaline, α-methylisoleucine, and the 2-amino-2,3-dimethylpentanoic acid diastereomers have since been discovered (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000; Pizzarello et al. 2003), with L-isovaline excesses as high as 18.5% measured in Murchison (Glavin and Dworkin 2009). An extraterrestrial origin for these α-dialkyl amino acid excesses is supported by the observation that these nonprotein amino acids are extremely rare on Earth (Cronin and Pizzarello 1997) and by compound-specific stable carbon and hydrogen isotopic measurements of D- and L-isovaline enantiomers ($\delta^{13}C \sim +12$ to $+22‰$; $\delta D \sim 3200‰$) in Murchison and Murray (Pizzarello et al. 2003; Pizzarello and Huang 2005) that are heavily enriched compared with terrestrial sources of isovaline (Elsila et al. 2011). Enantiomeric excesses of approximately 7–12% for the C_6 amino acid diastereomers L-isoleucine and D-*allo*isoleucine in the Antarctic CR meteorites GRA 95529 and LAP 02342 as well as Murchison and Murray have also been reported and are thought to be indigenous based on carbon isotope values that fall outside of the terrestrial range (Pizzarello et al. 2008). The L-isoleucine and D-alloisoleucine enantiomeric excesses are speculated to have been inherited from initial asymmetry in their chiral C_5 aldehyde precursor 2-methylbutyraldehyde (Pizzarello et al. 2008; Pizzarello and Groy 2011), although enantiomeric excesses for this aldehyde have not been reported. The original source of the hypothesized asymmetry of the aldehyde precursor remains unclear, but may have been produced by asymmetric photolytic decomposition from UV circularly polarized light (CPL) in the presolar cloud (Bonner and Rubenstein 1987; Bailey et al. 1998) prior to incorporation inside the meteorite parent body.

The origins of amino acid enantiomeric excesses in meteorites have been difficult to explain as laboratory simulations indicate that the formation of both α-hydrogen (α-H) and α-methyl amino acids from aldehyde and ketone precursors (e.g., by the Strecker-cyanohydrin pathway) on the parent bodies should have produced racemic (D = L) amino acid mixtures (Wolman et al. 1972; Miller and Orgel 1974; Bernstein et al. 2002; Muñoz Caro et al. 2002). In addition, although modest asymmetric photolytic decomposition or synthesis by UV or other circularly polarized radiation sources has been reported (De Marcellus et al. 2011), UV CPL alone cannot be used to explain the large L-isovaline excesses observed in CM and CI meteorites for two reasons: (1) the observed correlation between isovaline enantiomeric excess and relative degree of aqueous alteration places the formation of isovaline within the meteorite parent bodies, thus shielded from UV radiation (Glavin and Dworkin 2009) and (2) the most plausible ketone precursor for isovaline (2-butanone) is achiral and thus could not have been chirally biased by prior exposure to UV CPL. Other possible mechanisms for symmetry breaking and amplification of amino acid excesses in meteorites have also been proposed and are discussed in detail elsewhere (Kondepudi et al. 1990; Soai et al. 1995; Blackmond 2004; Klussman et al. 2006; Fletcher et al. 2007; Glavin et al. 2010; Pizzarello and Groy 2011). Nevertheless, the exact mechanism(s) for the formation of L-isovaline and other amino acid enantiomeric excesses found in carbonaceous meteorites remain(s) unclear.

Interpretation of L-enantiomeric excesses measured for the α-H amino acids present in Murchison and other carbonaceous meteorites has been even more problematic because unlike α-methyl amino acids, the α-H amino acids are common in biochemistry and their measurements are more susceptible to terrestrial contamination. In addition, α-H amino acids racemize (convert from one enantiomer to the other) much faster than α-methyl amino acids under aqueous or radiogenic conditions (Pollock et al. 1975; Bonner et al. 1979). Although it has been argued that racemization in an asteroid would not have completely erased any initial enantiomeric biases present in the α-H amino acids (Cohen and Chyba 2000; Cataldo et al. 2011), some racemization of the α-H amino acids will occur during parent body aqueous alteration and exposure to ionizing radiation. Engel and Nagy (1982) reported a wide range of L-enantiomer excesses ($L_{ee} \sim 25$–67%) for several common α-H protein amino acids including alanine, aspartic acid, and glutamic acid within interior fragments of the Murchison meteorite and were the first to propose that these L-excesses were not likely to be the result of terrestrial contamination after the meteorite fell to Earth as other common protein amino acids (e.g., tyrosine, phenylalanine, lysine, histidine, arginine, etc.) were absent from the meteorite. Furthermore, subsequent nitrogen isotopic measurements of D- and L-glutamic acid and D- and L-alanine detected in Murchison showed that both enantiomers for each amino acid were heavily enriched in ^{15}N relative to terrestrial amino acids and had similar $\delta^{15}N$ values ranging from $+57$ to $+60‰$, suggesting that the large L-glutamic acid and L-alanine excesses were indigenous to

the meteorite (Engel and Macko 1997, 2001). Carbon isotope measurements for D- and L-alanine in Murchison were also shown by Engel et al. (1990) to be highly enriched in ^{13}C with a $\delta^{13}C$ value of $+27‰$, similar to the carbon isotope value obtained for isovaline in the same meteorite. However, Pizzarello and Cronin (1998) argued that incomplete chromatographic resolution of L-alanine and other meteoritic amino acids could have affected both the enantiomeric ratios measured and the $\delta^{15}N$ values measured by Engel and Macko (1997).

The Tagish Lake meteorite fell the morning of January 18, 2000 after a bright fireball was observed over northwestern Canada. The first fragments were collected from the frozen surface of Taku Arm of Tagish Lake in northern British Columbia on January 25 and 26, 2000, without direct hand contact (Hildebrand et al. 2006). These "pristine" specimens have been maintained at temperatures below 0 °C since the time of their collection (Herd and Herd 2007). Tagish Lake is a type 2 carbonaceous chondrite with affinities to both CI and CM chondrites (Zolensky et al. 2002). Initial studies of organic molecules in the Tagish Lake meteorite reported only a few amino acids (Pizzarello et al. 2001) and analysis of another Tagish Lake meteorite fragment that had been exposed to the Tagish Lake meltwater showed that the sample contained predominantly L-proteinogenic amino acid contaminants derived primarily from the meltwater (Kminek et al. 2002); subsequent systematic work on distinct Tagish Lake meteorite lithologies provided a more detailed view of the variation in organic matter among the lithologies, including amino acids, demonstrating that the lithological and organic variations reflect a broad range of parent body aqueous alteration (Herd et al. 2011).

Considering the challenges associated with the analytical measurements, meteorite exposure to terrestrial contamination, and interpretation of L-enantiomeric excesses for α-H amino acids in meteorites, it is not surprising that to date there have been so few published claims of nonterrestrial proteinogenic amino acid L-excesses in meteorites. Nevertheless, given the importance of α-H amino acids to life on Earth, investigating the apparent large L-enantiomer excesses of α-H amino acids in Murchison and other carbonaceous chondrites using multiple analytical techniques is certainly warranted. Here, we report on measurements of the distribution, enantiomeric composition, and carbon isotopic ratios of amino acids in three distinct lithologies of pristine specimens of the Tagish Lake meteorite (Herd et al. 2011) by using both ultra-high-performance liquid chromatography fluorescence detection and time-of-flight mass spectrometry (LC-FD/TOF-MS) and gas chromatography mass spectrometry and isotope ratio mass spectrometry (GC-MS/IRMS) techniques.

MATERIALS AND METHODS

Chemicals and Reagents

Most of the chemicals and reagents used were purchased from Sigma-Aldrich. A stock amino acid solution (1×10^{-6} M) was prepared by mixing individual amino acid standards (97–99% purity) in Millipore Milli-Q Integral 10 (18.2 MΩ, ≤1 ppb total organic carbon) ultrapure water. All chiral amino acid standards were purchased as racemic mixtures (D = L), except for D- and L-threonine (Sigma-Aldrich, >98% purity, allo-free) and D- and L-isovaline (Acros Organics, >99% purity), which were prepared as racemic mixtures by mixing the appropriate masses of each compound in Millipore water to the standard mixture. The sources of the other C_5 amino acid standards used are detailed elsewhere (Glavin and Dworkin 2009). The details of the LC-FD/TOF-MS and GC-MS/IRMS reagents used in this study have been previously described (Glavin et al. 2010; Elsila et al. 2011).

Meteorite Samples, Controls, and Processing Procedures

All glassware and sample handling tools were heated in a furnace at 500 °C overnight. Three pristine Tagish Lake meteorite specimens (designated 5b, 11h, and 11i; the same as studied by Herd et al. 2011) were selected for detailed amino acid and compound-specific carbon isotopic analysis. Based on several petrologic differences including the relative proportions of matrix and framboidal magnetite and the replacement of chondrule glass by phyllosilicates, these three meteorite fragments represent a wide range of exposure to parent body aqueous alteration of order 5b < 11h << 11i, where 5b represents the least altered and 11i the most altered material (Herd et al. 2011). Subsamples (approximately 1–2 cm in size) of each meteorite were removed using a sterile scalpel under cold conditions (in a walk-in freezer at −20 °C), weighed (mass 5b = 2.9 g; mass 11h = 2.5 g; mass 11i = 2.0 g), transferred to round-bottom flasks, and then crushed into fine powders using a glass rod in a fume hood. As a control, a procedural blank was carried through the identical extraction procedure as the meteorite samples. In addition, a crushed serpentine (a hydrated magnesium silicate) sample that had been heated at 500 °C in air overnight was processed using the same hot water extraction, acid hydrolysis, and desalting protocol as the meteorite samples.

The powdered meteorite samples were extracted at reflux in 20 mL of Millipore water inside the round-bottom flasks at 100 °C for 6 h at University of Alberta (UA) in a chemical fume hood. After cooling to room temperature, the water supernatants were filtered

(0.2 μm) and the extracts transferred to separate round-bottom flasks and dried by rotoevaporation. At GSFC, the dried extracts of 5b, 11h, and 11i were redissolved in 5 mL of Millipore water at room temperature and one half of the water extract was transferred to a separate glass tube, dried under vacuum, and the residue was subjected to a 6 M HCl acid vapor hydrolysis procedure at 150 °C for 3 h to determine total hydrolyzable amino acid content. The acid-hydrolyzed water extracts were desalted using cation-exchange resin (AG50W-X8, 100–200 mesh, hydrogen form, BIO-RAD), and the amino acids recovered by elution with 2 M NH_4OH (prepared from Millipore water and NH_3(g) (AirProducts, *in vacuo*). The remaining half of each water extract (nonhydrolyzed fraction) was taken through the identical desalting procedure in parallel with the acid-hydrolyzed extracts to determine the free amino acid abundances in the meteorites. The amino acids in the NH_4OH eluates were dried under vacuum to remove excess ammonia; the residues were then redissolved in 100 μL of Millipore water, transferred to sterile microcentrifuge tubes, and stored at −20 °C prior to analysis. Based on our analysis of amino acid standards taken through the entire extraction and acid hydrolysis procedure, we found no evidence of significant decomposition, racemization, or thermal degradation of amino acids during the extraction.

The amino acids in the NH_4OH eluates were derivatized with OPA/NAC for 15 min at room temperature followed by separation and analysis of primary amines using a Waters ACQUITY UPLC and Waters LCT-Premier mass spectrometer. The amino acid abundances and their enantiomeric ratios in the meteorite extracts were determined by comparison of the peak areas generated from the UV fluorescence chromatograms of their OPA/NAC derivatives with the corresponding peak areas of amino acid standards under the same chromatographic conditions and included peak identification confirmation by accurate mass enumerations (TOF-MS). In addition to identifying the major fluorescent peaks present in the LC-FD/TOF-MS chromatograms by retention time, we searched for the masses of OPA/NAC derivatives corresponding to the C_2 to C_8 amino acids by plotting the mass of each primary amine derivative over the elution time. The reported amino acid abundances in parts-per-billion (ppb) are the average value of between three and ten separate LC-FD/TOF-MS measurements.

For the carbon isotopic measurements, total amino acids in the Tagish Lake 5b and 11h extracts were esterified with isopropanol and the isopropyl esters reacted with trifluoroacetic anhydride (TFAA). The $\delta^{13}C$ values of the TFAA-isopropyl derivatives were analyzed on a Thermo Trace GC and tandem DSQII MS/MAT 253 IRMS (GC-MS/IRMS), which provides compound-specific structural and isotopic information from a single sample injection. The GC-MS/IRMS instrument consists of a Thermo Trace GC whose output is split, with approximately 10% directed into a Thermo DSQII electron-impact quadrupole mass spectrometer that provides mass and structural information for each eluting peak. The remaining 90% passes through a Thermo GC-C III interface, where eluting amino acids are oxidized to form CO_2, and then is passed into a Thermo MAT 253 isotope ratio mass spectrometer (IRMS). Six pulses of high-purity CO_2 gas ($\delta^{13}C = -24.52‰$ VPDB) that had been precalibrated against two commercial reference CO_2 gases (Oztech Corporation, $\delta^{13}C = -3.61‰$ VPDB and $\delta^{13}C = -40.740‰$ VPDB) were injected into the IRMS for computation of the $\delta^{13}C$ values of the eluting derivatized amino acid standards and sample compounds. Analysis of the MAT 253 data was performed with Thermo Isodat 2.5 software. The reported $\delta^{13}C$ values for the individual amino acids in the Tagish Lake 11h and 5b meteorite extracts are the average of three separate analyses and were corrected for the carbon added during derivatization. Because of the low amino acid abundances measured in Tagish Lake meteorite 11i, there was insufficient sample available to make carbon isotope measurements of amino acids for this study. In addition, nitrogen and hydrogen isotope measurements of the amino acids in Tagish Lake samples 11h and 5b were not possible and would require at least three times the mass of meteorite sample used for the carbon isotope measurements.

RESULTS AND DISCUSSION

Amino Acid Analyses

Typical liquid chromatography UV fluorescence and TOF-MS mass chromatograms of the 6 M HCl-vapor hydrolyzed, hot-water extracts from the Tagish Lake 5b, 11h, and 11i meteorite specimens and the procedural blank show several peaks that were identified by comparison with amino acid standards, fluorescence, retention time, and mass (Figs. 1 and 2). We were able to obtain baseline separation of several α-H proteinogenic amino acids including aspartic and glutamic acids, serine, threonine, alanine, and valine and their enantiomers (Figs. 1 and 2), which was the primary focus of this study. The total procedural-blank-corrected amino acid abundances (free + bound) of identified C_2 to C_6 amino acids in the 6 M HCl-hydrolyzed, hot-water extracts of Tagish Lake were approximately 40 ppb for sample 11i, approximately 740 ppb for sample 5b, and approximately 5400 ppb for sample 11h (Tables 1 and 2). In contrast to samples 5b and 11h, the abundances of

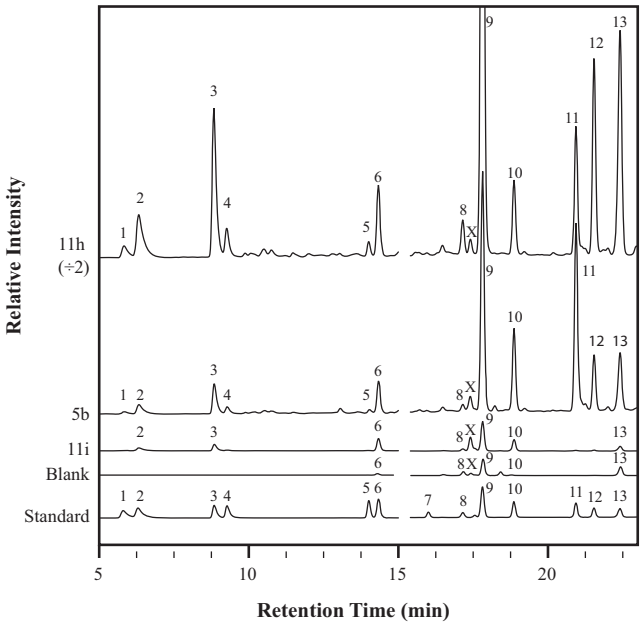

Fig. 1. The 5 to 23 min region of the LC-FD chromatograms. OPA/NAC derivatization (15 min) of amino acids in the standard mix and of the 6 M HCl-hydrolyzed, hot-water extracts of the procedural blank and Tagish Lake meteorite samples 11i, 5b, and 11h are shown. Similar chromatograms were also obtained for the nonhydrolyzed extracts. Separation was achieved for the first segment (5–15 min) of the chromatogram using a Waters BEH C18 column (2.1 × 50 mm, 1.7 μm bead) followed by a second Waters HSS T3 column (2.1 × 150 mm, 1.8 μm bead). For the second segment (15.3–23 min) of the chromatogram, the Waters HSS T3 column was replaced by a Waters BEH phenyl column (2.1 × 150 mm, 1.7 μm bead). The conditions for amino acid separations for the mobile phase at 30.0 °C for both segments were as follows: flow rate, 150 μL min^{-1}; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (0), 35 (55), 45 (100). The peaks were identified by comparison of the fluorescence retention time and molecular mass to those in the amino acid standard run on the same day. Fluorescent peaks that did not have corresponding peaks in the single ion TOF-MS chromatograms (shown in Fig. 2) with *m/z* values of the OPA/NAC amino acid derivative in the standard were not identified and quantified. Peak identifications 1) D-aspartic acid; 2) L-aspartic acid; 3) L-glutamic acid; 4) D-glutamic acid; 5) D-serine; 6) L-serine; 7) D-threonine; 8) L-threonine; 9) glycine; 10) β-alanine; 11) γ-amino-*n*-butyric acid; 12) D-alanine; and 13) L-alanine. An unidentified fluorescent desalting artifact is labeled with an X.

many amino acids in 11i were below analytical detection limits of < 0.1–1 ppb. These results are consistent with a much higher degree of aqueous alteration experienced by 11i compared with 5b and 11h as inferred from variations in mineralogy, bulk isotopes, petrology, carboxylic acid abundances, and structure of the insoluble organic matter (Herd et al. 2011). The low total amino acid abundance in 11i is similar to the abundance (< 100 ppb) previously found in another pristine Tagish Lake meteorite stone (Pizzarello et al. 2001). Overall, the amino acid abundances in the C2 Tagish Lake meteorite (approximately 40–5,400 ppb) are much lower than the levels measured in other less altered type 2 carbonaceous chondrites, but do fall within the range of amino acid concentrations measured for aqueously altered CI, CM, and CR type 1 carbonaceous chondrites (Glavin et al. 2010). The LC-TOF-MS instrument was optimized for the separation of the C_5 acyclic amino alkanoic acids and the retention times were identified based on the analysis of standards (Fig. 3). Although complete separation of all 23 possible C_5 amino acid isomers and enantiomers could not be achieved under the chromatographic conditions used, all of the C_5 amino acids were accounted for, and we observed no interference or coelution of the D- and L-enantiomers of isovaline, norvaline, valine, and 3-aminopentanoic acid (3-apa) with other C_5 amino acids (Fig. 3). Several C_6 to C_8 amino acid isomers were also detected by mass in the single ion chromatograms of the Tagish 5b and 11h meteorite extracts (Fig. 2). However, with the exception of the D,L-norleucine internal standard (Fig. 2, peak 33), the C_6 to C_8 amino acids could not be identified due to a lack of standards, low abundances, and poor chromatographic separation under the conditions employed.

A large increase in amino acid abundance (> 100% increase) in all three meteorite extracts was observed after acid hydrolysis, which indicates that most of the amino acids in the Tagish Lake specimens are present in an acid-labile or bound form (Tables 1 and 2). This observation is consistent with our amino acid analyses of CI, CM, and CR carbonaceous chondrites (Glavin et al. 2010) and was also noted by Engel and Nagy (1982) in a previous study on the isotopic composition of amino acids in Murchison. The most abundant amino acids detected and quantified by LC-FD/TOF-MS in the Tagish Lake 5b and 11h extracts were D- and L-aspartic acid, D- and L-glutamic acid, D- and L-alanine, D- and L-serine, L-threonine, β-alanine (BALA), D, L-α-amino-*n*-butyric acid (ABA), D- and L-β-ABA, γ-ABA, α-aminoisobutyic acid (AIB), D- and L-valine, D, L-norvaline, and D- and L-isovaline (Figs. 1 and 2; Tables 1 and 2). Only trace levels (< 10 ppb) of L-serine, L-threonine, glycine, β-alanine, L-alanine, and L-valine were measured by LC-FD/TOF-MS in the procedural blanks, indicating that very little amino acid contamination of the samples occurred during sample processing (Figs. 1 and 2). However, the low amino acid abundances in the procedural blanks do not rule out the possibility of amino acid contamination of the meteorites from the Tagish Lake ice, or during collection, storage, and handling of the samples. The Tagish Lake meteorite samples 11i, 5b, and 11h investigated in this study were collected at the same time directly from the surface ice

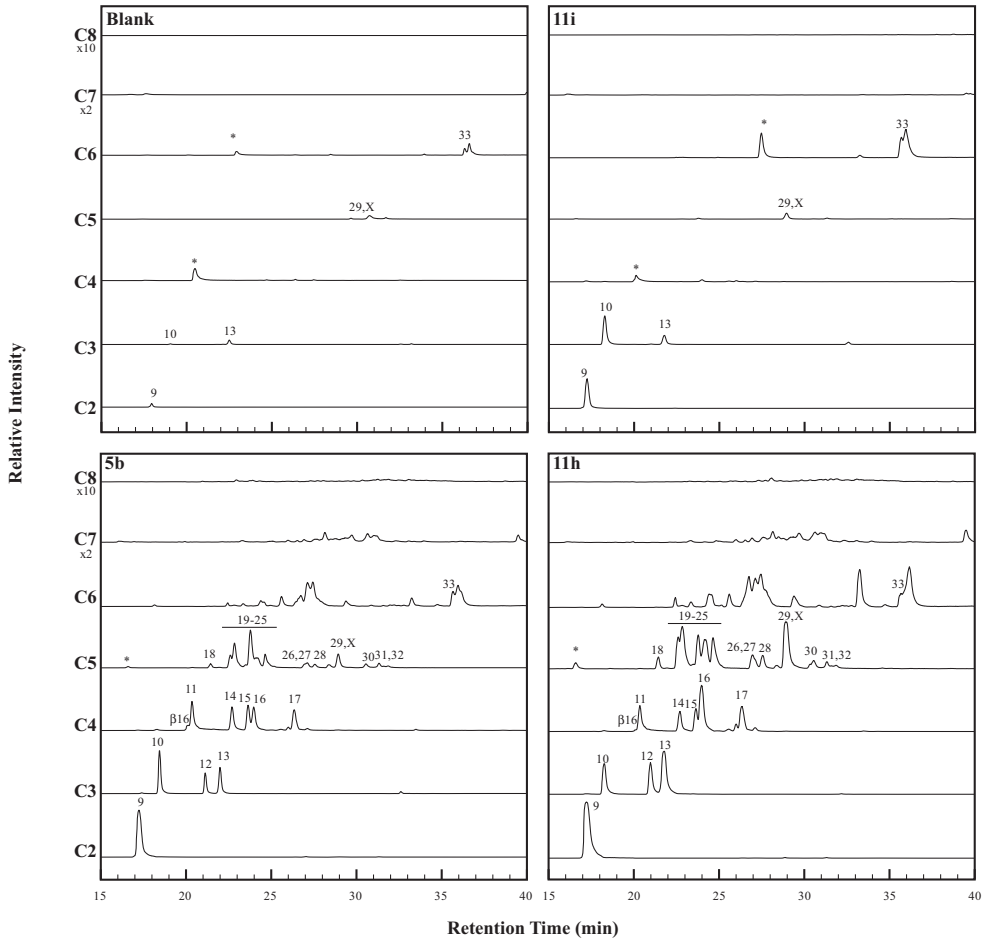

Fig. 2. The 15–40 min regions of the LC-TOF-MS single ion chromatograms (C_2: m/z = 337.09; C_3: m/z = 351.10; C_4: m/z = 365.12; C_5: m/z = 379.13; C_6: m/z = 393.15; C_7: m/z = 407.16; C_8: m/z = 421.18) in positive electrospray ionization mode. OPA/NAC derivatization (15 min) of amino acids in the 6 M HCl-hydrolyzed, hot-water extracts of Tagish Lake samples 11h, 5b, 11i, and a procedural blank are shown. Similar single ion chromatograms were obtained for the nonhydrolyzed extracts. Separation was achieved using the Waters BEH C18 column followed by the Waters BEH phenyl column using the same gradient as described in Fig. 1. Peaks were identified by comparison of the retention time and molecular mass with those in amino acid standards run on the same day. A nonfluorescent mass artifact that co-eluted with L-valine is labeled with an X. Peak identifications 9) glycine; 10) β-alanine (BALA); 11) γ-amino-*n*-butyric acid; 12) D-alanine; 13) L-alanine; 14) D-β-amino-*n*-butyric acid; 15) L-β-amino-*n*-butyric acid; 16) α-aminoisobutyric acid; 17) D, L-α-amino-*n*-butyric acid (ABA); 18–32) peak identifications for C_5 amino acids given in Fig. 3; and 33) D, L-norleucine (internal standard). Asterisks designate nonfluorescent, noninterfering mass artifacts that could not be identified.

within days after the fall and have all been kept at temperatures below 0 °C prior to extraction (Herd et al. 2011); in contrast to these specimens, a nonpristine Tagish Lake fragment (sample 24-24) that was collected from lake meltwater 3 months after the fall was found to contain a significant amount of terrestrial amino acid contamination from the lake meltwater itself (Table 1, Kminek et al. 2002).

The distributions of amino acids measured in the Tagish Lake meteorite samples 5b and 11h are clearly distinct from the Tagish Lake ice meltwater, which had higher relative abundances (normalized to glycine) of L-aspartic and L-glutamic acids, L-serine, L-alanine and D, L-α-amino-*n*-butyric acid (Fig. 4). The abundance of D-serine in the Tagish Lake ice meltwater was not reported by Kminek et al. (2002) and therefore was not included in Fig. 4. In addition, several nonprotein amino acids that are not common in terrestrial samples, including α-aminoisobutyric acid (AIB), D- and L-β-ABA, D- and L-isovaline, and D- and L-norvaline, were identified above background levels in both Tagish 5b and 11h (Tables 1 and 2), but have not been reported in the Tagish Lake meltwater or previous analyses of the Tagish Lake meteorite (Pizzarello et al. 2001; Kminek et al. 2002). The differences in relative amino acid abundances between the Tagish Lake meteorite samples 5b and 11h

Table 1. Summary of the average abundances (in ppb) of identified two- to six-carbon amino acids in the nonhydrolyzed (free) and 6 M HCl-hydrolyzed (total) hot-water extracts of the Tagish Lake meteorite measured by LC-FD/TOF-MS[a].

	This study						Previous work[b]
	Tagish Lake 11i		Tagish Lake 5b		Tagish Lake 11h		Tagish Lake 24-24
Amino acid	Free	Total	Free	Total	Free	Total	Total
D-*aspartic acid*	< 0.3	< 1	1.7 ± 0.4	8.0 ± 1.8	13.6 ± 2.5	161 ± 14	11 ± 1
L-*aspartic acid*	0.7 ± 0.2	2.6 ± 0.5	8.7 ± 0.6	20.1 ± 3.3	55.0 ± 5.6	430 ± 65	83 ± 8
D-*glutamic acid*	< 0.2	< 0.2	1.6 ± 0.2	16.4 ± 0.5	41.2 ± 1.3	244 ± 23	16 ± 2
L-*glutamic acid*	0.2 ± 0.1	5.8 ± 1.6	2.7 ± 0.6	50.6 ± 2.3	53.5 ± 13.8	844 ± 89	306 ± 48
D-*serine*	< 0.2	< 0.2	1.3 ± 0.1	1.5 ± 0.1	23.6 ± 2.3	51.8 ± 7.3	n.d.
L-*serine*	1.8 ± 0.1	2.1 ± 0.9	17.3 ± 1.5	13.9 ± 4.2	124 ± 23	181 ± 29	n.d.
D-*threonine*	< 0.1	< 0.1	< 0.1	< 0.2	< 0.2	< 0.3	n.d.
L-*threonine*	0.9 ± 0.3	1.3 ± 0.4	7.4 ± 1.8	3.5 ± 1.6	55.2 ± 5.3	97.3 ± 17.8	n.d.
glycine	2.4 ± 0.4	9.7 ± 4.2	90.0 ± 6.4	129 ± 21	619 ± 184	987 ± 257	147 ± 17
β-alanine	0.1 ± 0.1	13.5 ± 0.7	70.4 ± 14.1	82.3 ± 9.5	107 ± 19	150 ± 30	64 ± 10
γ-amino-*n*-butyric acid	0.1 ± 0.1	< 1	7.2 ± 1.0	216 ± 24	41.1 ± 2.8	374 ± 50	77 ± 10
D-*alanine*	< 0.1	< 0.5	25.7 ± 0.7	54.1 ± 3.3	252 ± 32	387 ± 25	20 ± 5
L-*alanine*	1.2 ± 1.0	1.6 ± 0.5	25.1 ± 0.7	49.7 ± 4.3	240 ± 33	363 ± 41	75 ± 18
D-β-amino-*n*-butyric acid	< 0.1	< 0.1	13.3 ± 2.0	11.5 ± 1.2	19.0 ± 3.8	36.0 ± 3.9	< 26[d]
L-β-amino-*n*-butyric acid	< 0.1	< 0.1	12.5 ± 2.0	12.8 ± 1.4	17.4 ± 4.8	38.8 ± 3.0	
α-aminoisobutyric acid (α-AIB)	0.3 ± 0.1	1.3 ± 0.2	9.2 ± 0.8	20.7 ± 2.1	161 ± 29	179 ± 23	< 27
D, L-α-amino-*n*-butyric acid[c]	< 0.1	< 0.2	10.2 ± 0.1	24.2 ± 3.9	62.1 ± 16.5	82.2 ± 15.2	84 ± 40
ε-amino-*n*-caproic acid (EACA)	< 0.2	< 0.2	< 0.2	< 0.2	< 0.3	< 0.3	n.d.
C_5 amino acids (from Table 2)	< 0.7	< 1	~40	~210	~190	~790	n.d.
Total (ppb)	~8	~40	~340	~740	~2,100	~5,400	~880

[a]Tagish Lake meteorite 11i, 5b, and 11h extracts were analyzed by OPA/NAC derivatization (15 min) and UPLC separation with UV fluorescence and time of flight mass spectrometry (TOF-MS) detection. For the LC-FD/TOF-MS data, the fluorescence peaks and the mono-isotopic masses of each protonated OPA/NAC amino acid derivative ($M + H^+$) was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The final values were normalized using the desalting and derivatization recoveries of an internal D, L-norleucine standard (recoveries ranged from 60 to 100% for the meteorite extracts). The uncertainties (δx) are based on the standard deviation of the average value of three to ten separate measurements (n) with a standard error, $\delta x = \sigma_x (n-1)^{-1/2}$. Protein amino acids are shown in italics.

[b]For comparison, HPLC-FD amino acid abundances in a nonpristine Tagish Lake meteorite sample 24-24 reported by Kminek et al. (2002).

[c]Enantiomers could not be separated under the chromatographic conditions.

[d]Upper limit for D + L enantiomers.

n.d. = not determined.

Table 2. Summary of the average five-carbon amino acid abundances (in ppb) in the nonhydrolyzed (free) and 6 M HCl-hydrolyzed (total) hot-water extracts of the Tagish Lake meteorite measured by LC-FD/TOF-MS[a].

		Tagish Lake 11i		Tagish Lake 5b		Tagish Lake 11h	
C_5	Amino acid detected	Free	Total	Free	Total	Free	Total
α	D-norvaline (D-2-apa)	< 0.2	< 0.4	2.2 ± 0.2	2.6 ± 0.2	5.4 ± 0.2	6.8 ± 0.4
	L-norvaline (L-2-apa)	< 0.2	< 0.3	1.9 ± 0.1	2.7 ± 0.1	5.6 ± 0.2	7.5 ± 0.4
	D-isovaline (D-2-a-2-mba)	< 0.2	< 0.5	2.5 ± 0.2	6.6 ± 0.2	42.7 ± 1.6	43.7 ± 1.8
	L-isovaline (L-2-a-2-mba)	< 0.2	< 0.5	3.1 ± 0.2	7.6 ± 0.2	41.9 ± 1.5	43.7 ± 1.7
	D-valine (D-2-a-3-mba)	< 0.2	< 0.4	1.9 ± 0.1	5.9 ± 0.1	7.1 ± 0.2	16.4 ± 0.5
	L-valine (L-2-a-3-mba)	< 0.7	< 1	< 4[b]	< 9[b]	< 37[b]	< 86[b]
β	D, L-3-apa[c]	< 0.2	< 0.4	12.7 ± 0.5	10.6 ± 0.4	13.4 ± 0.4	12.7 ± 0.7
	D, L- and allo-3-a-2-mba[c]	< 0.1	< 0.2	2.1 ± 0.2	2.6 ± 0.2	4.3 ± 0.2	5.4 ± 0.7
	3-a-3-mba[d]	< 0.1	< 0.1	< 0.5	< 1.5	< 2.6	< 12
	3-a-2,2-dmpa	< 0.1	< 0.1	1.5 ± 0.1	3.8 ± 0.1	9.2 ± 0.3	17.7 ± 0.6
	D, L-3-a-2-epa[e]	< 0.5	< 1	2.7 ± 0.2	10.7 ± 1.6	6.1 ± 0.2	10.2 ± 0.4
γ	D, L-4-apa[c]	< 0.1	< 0.1	1.3 ± 0.2	24.5 ± 0.8	5.3 ± 0.7	112 ± 6
	D, L-4-a-2-mba[e]	< 0.3	< 0.5	1.7 ± 0.2	34.2 ± 0.7	4.5 ± 0.3	191 ± 7
	D, L-4-a-3-mba[e]	< 0.2	< 0.3	1.0 ± 0.1	42.9 ± 1.3	4.3 ± 0.2	183 ± 5
δ	5-apa	< 0.1	< 0.2	1.2 ± 0.1	46.3 ± 1.2	2.7 ± 0.1	53.6 ± 1.1
	Total (ppb)			~40	~210	~190	~790

[a]All values are reported in parts-per-billion (ppb) on a bulk sample basis. Extracts were analyzed by OPA/NAC derivatization (15 min) and UPLC separation with UV fluorescence and time of flight mass spectrometry (TOF-MS) detection. For the LC-TOF-MS data, the mono-isotopic masses (m/z 379.13 ± 0.02) of each protonated OPA/NAC amino acid derivative ($M + H^+$) was used for quantification and final peak integrations included background level correction using a procedural blank and a comparison of the peak areas with those of an amino acid standard run on the same day. The final values were normalized using the desalting and derivatization recoveries of an internal D, L-norleucine standard (recoveries ranged from 60 to 100% for the meteorite extracts). The uncertainties (δx) are based on the standard deviation of the average value of six to eight separate measurements (n) with a standard error, $\delta x = \sigma_x (n-1)^{-1/2}$. Amino acid abbreviations are defined in Figure 3.

[b]Peak detected above blank levels; however, only upper limit reported due to unidentified coeluting peak X in LC-TOF-MS analysis of the procedural blank.

[c]Enantiomers were separated but could not be identified due to the lack of optically pure standards.

[d]3-a-3-mba co-elutes with one of the enantiomers of D, L-4-apa, therefore upper limits for 3-a-3-mba were estimated by taking the difference in peak areas of the two D, L-4-apa enantiomers.

[e]Enantiomers could not be separated under the chromatographic conditions.

(Fig. 4) and absolute abundances of both protein and nonprotein amino acids that increase in order 11i ≪ 5b < 11h (Tables 1 and 2) provide additional support that most of these amino acids are indigenous to the meteorites, as all three fragments were collected, stored, and processed in parallel under identical conditions and therefore exposed to the same terrestrial contamination environments (Herd et al. 2011). Herd et al. (2011) previously argued that differences in the absolute abundances of amino and carboxylic acids among the Tagish Lake samples are best explained by differences in the extent of aqueous alteration in the meteorite fragments on the parent body, and not terrestrial contamination.

Amino Acid Isotopic Composition and Enantiomeric Measurements

Carbon isotope measurements were made for the most abundant amino acids in the Tagish Lake meteorite extracts 5b and 11h (11i had insufficient amino acids for isotope measurements). The GC-MS/IRMS technique employed provides simultaneous compound-specific structural and carbon isotopic information from a single injection, which permitted three replicate analyses of glycine, D- and L-alanine, and β-alanine and two replicate analyses of D- and L-aspartic acid, L-glutamic acid, and γ-ABA in the meteorite extracts. We previously reported a $\delta^{13}C$ value of +19 ± 4‰ for glycine (Herd et al. 2011), the most abundant amino acid in Tagish Lake 11h, which is similar to the values previously obtained for glycine ($\delta^{13}C \sim +22$‰, Table 3) in the CM Murchison (Engel et al. 1990) and CI Orgueil meteorites (Ehrenfreund et al. 2001). The corrected $\delta^{13}C$ values for D- and L-aspartic acid peaks in 11h were +24‰ and +29‰ and were similar within a measurement error of ±4‰ (Table 3). These values fall well outside of the typical terrestrial range for organic carbon of −6‰ to −40‰ (Bowen 1988) and for aspartate (aspartic acid and asparagine) in a variety of microorganisms (−54‰ to 0‰; Scott et al. 2006) and indicate an extraterrestrial origin for both D- and L-aspartic acid. The

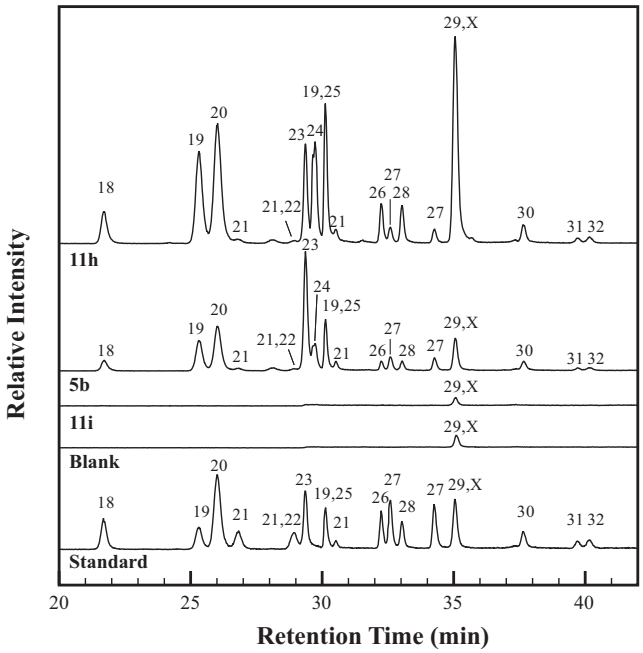

Fig. 3. The 20–42 min region of the LC-TOF-MS single ion chromatograms of the C_5 amino acids (m/z = 379.13 ± 0.02) in positive electrospray ionization mode. OPA/NAC derivatization (15 min) of amino acids in the standard mix and of the 6 M HCl-hydrolyzed, hot-water extracts of the procedural blank and the Tagish Lake meteorite samples 11i, 5b, and 11h. Similar LC-TOF-MS single ion chromatograms were obtained for the nonhydrolyzed extracts. The peaks were identified by comparison of the retention time and exact molecular mass with those in the C_5 amino acid standard run on the same day. Separation was achieved using a Waters BEH C18 column followed by a second Waters BEH phenyl column. The conditions for amino acid separations for the mobile phase at 30.0 °C were as follows: flow rate, 150 μL min^{-1}; solvent A (50 mM ammonium formate, 8% methanol, pH 8.0); solvent B (methanol); gradient, time in minutes (%B): 0 (15), 25 (20), 25.06 (35), 44.5 (40), 45 (100). The peaks were identified by comparison of the retention time and molecular mass with those in the C_5 amino acid standard run on the same day. Peak 24 (D, L-4-a-2-mba) was not present in the standard shown, but was run separately. Peak identifications: 18, 3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa); 19, D, L-4-aminopentanoic acid (D, L-4-apa); 20, D, L-4-amino-3-methylbutanoic acid (D, L-4-a-3-mba); 21, D, L-3-amino-2-methylbutanoic acid (D, L-3-a-2-mba); 22, D, L-3-amino-2-ethylpropanoic acid (D, L-3-a-2-epa); 23, 5-aminopentanoic acid (5-apa); 24, D, L-4-amino-2-methylbutanoic acid (D, L-4-a-2-mba); 25, 3-amino-3-methylbutanoic acid (3-a-3-mba); 26, D-2-amino-2-methylbutanoic acid (D-isovaline); 27, D, L-3-aminopentanoic acid (D, L-3-apa); 28, L-2-amino-2-methylbutanoic acid (L-isovaline); 29, L-2-amino-3-methylbutanoic acid (L-valine); 30, D-2-amino-3-methylbutanoic acid (D-valine); 31, D-2-aminopentanoic acid (D-norvaline); 32, L-2-aminopentanoic acid (L-norvaline); and X, nonfluorescent mass artifact.

GC-MS/IRMS data for the D- and L-aspartic acid and D- and L-alanine peaks in the combined hydrolyzed and nonhydrolyzed Tagish Lake 11h hot-water extracts are

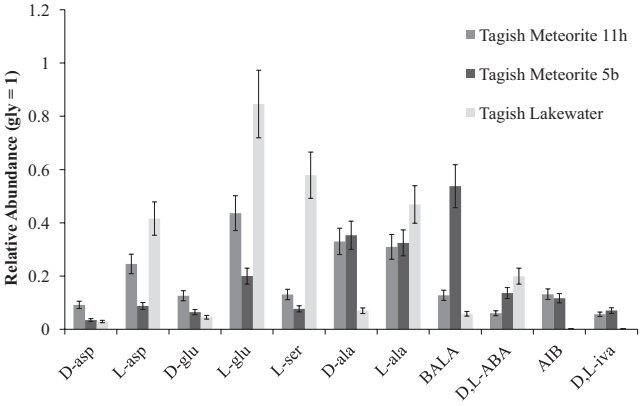

Fig. 4. A comparison of the relative molar abundances of several amino acids (glycine = 1.0) in the 6 M HCl-hydrolyzed, hot-water extracts of the Tagish Lake meteorite samples 11h and 5b and a 250 mL sample of Tagish Lake meltwater. The relative abundance data for the Tagish Lake meteorite samples were determined from the absolute abundances measured in this study. Relative amino acid abundances for the Tagish Lake water were calculated from the absolute concentrations reported in Kminek et al. (2002).

shown in Fig. 5. The abundances of amino acids in the nonhydrolyzed water extracts of the Tagish Lake meteorite were insufficient to make carbon isotope measurements of the free amino acids only. The retention times and mass spectra for both peaks in the 11h extract closely match those for the TFAA/IPA derivatives of the D- and L-aspartic acid peaks in the racemic standard (Fig. 5). We found no evidence of additional mass fragments in the mass spectra obtained for the D- and L-aspartic acid peaks in the Tagish Lake 11h extract compared with the mass spectra of the racemic aspartic acid standard that would suggest the presence of any co-eluting or interfering compounds (Fig. 5).

A corrected D/L aspartic acid ratio of 0.26 ± 0.02 was determined by GC-MS at the same time from the integrated D- and L-aspartic acid peak areas in 11h compared with the racemic aspartic acid standard and corresponds to an L-enantiomeric excess (L_{ee} = L%–D%) of 58.7 ± 1.8%. A similarly high L_{ee} in the total aspartic acid of 45.5 ± 5.2% was determined independently from the absolute abundances of D- and L-aspartic acid measured by LC-FD/TOF-MS (Table 4). If the observed L-excess for aspartic acid was due to terrestrial contamination, the measured carbon isotope value of L-aspartic acid should have been less enriched in ^{13}C compared with D-aspartic acid. For example, Pizzarello et al. (2004) measured the L- and D-aspartic acid carbon isotope ratios on a sample of Murchison with an L-enantiomer excess and reported a $\delta^{13}C$ value of −6‰ for L-aspartic acid and +25‰ for D-aspartic acid

Table 3. Summary of the $\delta^{13}C$ values (‰, VPDB) of amino acids in the 6 M HCl-acid hydrolyzed extracts of the Tagish Lake meteorite samples 5b and 11h compared with the Murchison meteorite[a].

	This study		Previous work
Amino acids	Tagish Lake 5b	Tagish Lake 11h	Murchison
D-*aspartic acid*	n.d.	+24 ± 4	+25[b]
L-*aspartic acid*	n.d.	+29 ± 4	−6[b]
D-*glutamic acid*	n.d.	n.d.	+29[b], +32[d]
L-*glutamic acid*	n.d.	−4 ± 9	+7[b], +6[c], +15[d]
glycine	+39 ± 6	+19 ± 4	+41[b], +22[c], +13[e]
D-*alanine*	+67 ± 7	+6 ± 3	+52[b], +30[c]
L-*alanine*	+55 ± 3	+16 ± 4	+38[b], +27[c], +41[e]
β-alanine	+30 ± 6	−5 ± 4	+5[b]
γ-ABA	n.d.	+4 ± 3	+18[b]

[a]For Tagish Lake meteorite sample 11h, isotope values were determined from measurements of the combined nonhydrolyzed and 6 M HCl-hydrolyzed water extracts. Protein amino acids are shown in italics. The errors in the corrected $\delta^{13}C$ values of the amino acids in the Tagish Lake meteorite samples were determined from the contributions of the errors from the carbon isotope values of both derivatized and underivatized standards and the derivatized samples (three separate analyses for glycine, D- and L-alanine, and β-alanine, and two analyses for D- and L-aspartic acid, L-glutamic acid, and γ-ABA).
[b]Data obtained from Pizzarello et al. (2004).
[c]Data obtained from Engel et al. (1990).
[d]Data obtained from Pizzarello and Cooper (2001).
[e]Data obtained from Elsila et al. (2011).
n.d. = value not determined due to low amino acid abundances and/or chromatographic interferences.

(Table 3). In that case, the depletion in $\delta^{13}C$ for the L-aspartic acid provided a clear indication that the Murchison sample contained both extraterrestrial and terrestrial sources of L-aspartic acid. This was not observed in the Tagish lake meteorite sample 11h, where L-aspartic acid nominally had a higher $\delta^{13}C$ value compared with D-aspartic acid (Table 3), which cannot be explained by terrestrial L-aspartic acid contamination. No carbon isotope fractionation or changes in the enantiomeric composition were observed in a racemic aspartic acid standard carried through the same extraction and analytical procedure. The carbon isotope values ($\delta^{13}C$) for the D- and L-aspartic acid racemic standard were identical within measurement error, as expected from a standard made from D, L-aspartic acid.

The measured $\delta^{13}C$ values for glycine, D- and L-alanine, L-glutamic acid, β-alanine, and γ-ABA in the Tagish Lake meteorite samples range from −5‰ to +67‰ (Table 3), which all fall outside of the typical terrestrial range for these amino acids. We were unable to determine the $\delta^{13}C$ value for D-glutamic acid in the Tagish Lake samples due to low D-glutamic acid abundances and a chromatographic interference. A D/L glutamic acid ratio of approximately 0.3 ($L_{ee} \sim 55\%$) was measured by LC-FD/TOF-MS in Tagish Lake 5b and 11h, which was similar to the values measured for aspartic acid in the same meteorite extracts (Tables 4 and 5). On the basis of the $\delta^{13}C$ value of −4 ± 9‰ measured for L-glutamic acid in Tagish 11h, we cannot rule out the possibility that some terrestrial L-glutamic acid contamination of the meteorite occurred, although in the absence of the D-glutamic acid carbon isotope value, we have no basis for comparison. However, if we assume that the level of L-glutamic acid contamination in 11h is similar to the total amount of L-glutamic acid measured in 11i (approximately 6 ppb, Table 1), which is a reasonable assumption as both meteorite specimens have been exposed to the same contamination environments since the time of their fall, then terrestrial L-glutamic acid contamination would represent <1% of the total L-glutamic acid in 11h (Table 1).

A similarly low D/L ratio ($D/L \sim 0.3$) for glutamic acid has previously been measured in the Murchison meteorite and was argued to be indigenous based on nonterrestrial nitrogen isotopic values for both D- and L-enantiomers that were similar (Engel and Macko 2001). However, another study of Murchison found a large L_{ee} (approximately 16–47%) of pyroglutamic acid, but with lower $\delta^{13}C$ values for the L-enantiomer compared with the D-enantiomer, pointing to a significant terrestrial contribution to the L-excesses (Pizzarello and Cooper 2001). Similar D/L ratios of aspartic and glutamic acids ($D/L \sim 0.1$–0.4) have been reported in oceanic dissolved organic matter in which the D-amino acids were attributed to peptidoglycan remnants derived from bacterial cell walls (McCarthy et al. 1998). The D/L alanine ratios measured in the same seawater samples ranged from $D/L \sim 0.3$ to 0.6 (McCarthy et al. 1998) and the Tagish Lake meltwater and a nonpristine Tagish lake meteorite sample were both reported to have D/L alanine ratios of approximately 0.2–0.3 (Kminek et al. 2002). All of these values are much lower than the racemic D/L alanine ratios found in the Tagish Lake 5b and 11h meteorite extracts measured in this study (Table 5). Therefore, it is difficult to reconcile how bacterially derived terrestrial amino acid contamination of the Tagish Lake meteorite samples 5b and 11h from the Tagish Lake ice meltwater or other sources is consistent with both the low D/L ratios of aspartic and glutamic acids and the racemic D/L alanine ratios measured in Tagish 5b and 11h (Table 5). The measured D/L ratios for aspartic and glutamic acids in the Tagish Lake meteorite are not due to the extraction procedure or LC-FD/TOF-MS analytical biases, as we observed no change in the enantiomeric ratios of a racemic aspartic and glutamic acid standard taken through the identical procedure. In addition, both aspartic and glutamic acids were found to be racemic ($D/L = 1$) within analytical

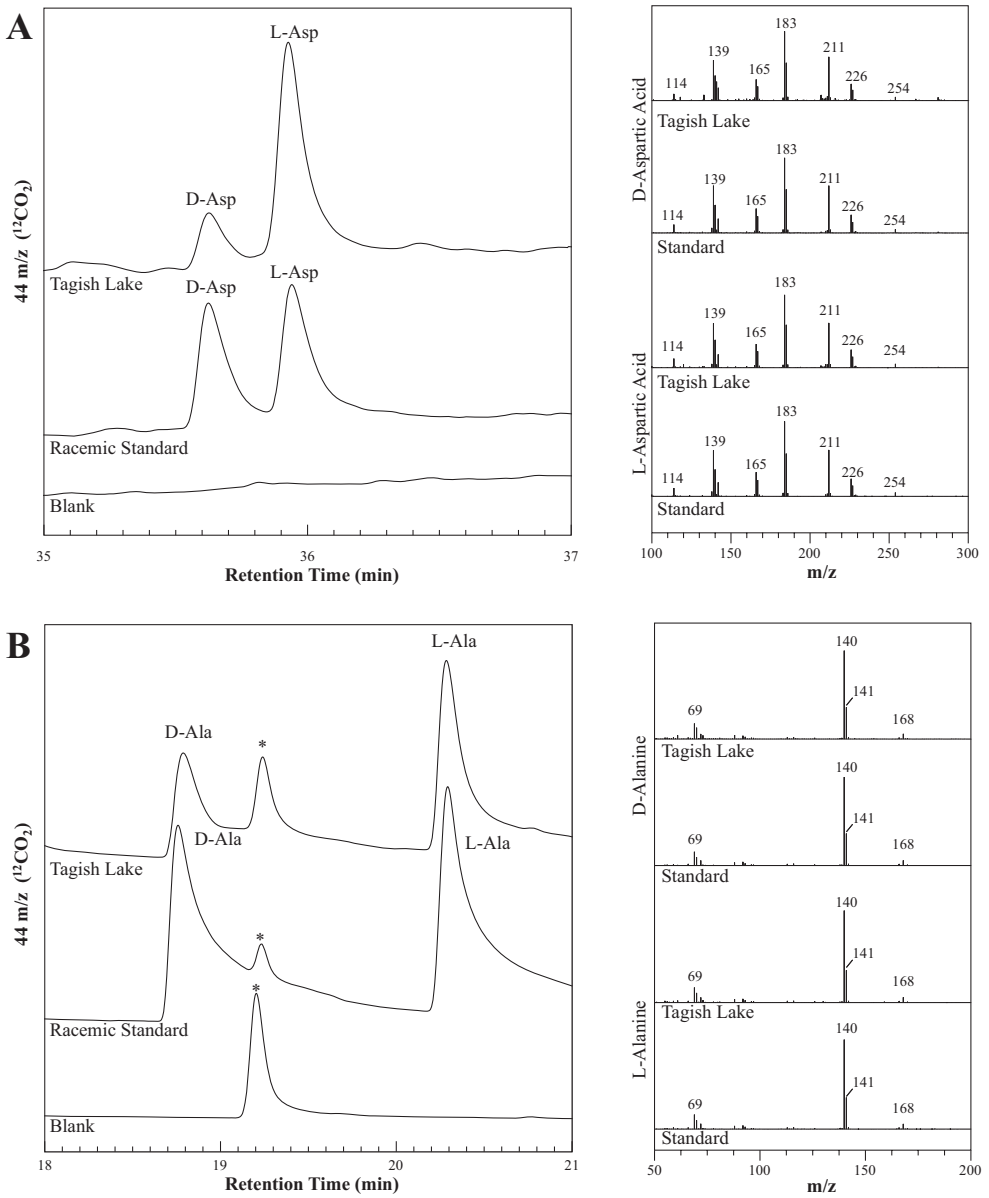

Fig. 5. Gas chromatography separation and mass spectrometry analysis of D- and L-aspartic acid (A) and D- and L-alanine (B) of the TFAA/IPA-derivatized combined 6 M HCl-hydrolyzed and nonhydrolyzed extracts of the Tagish Lake 11h meteorite and the procedural blank, and a racemic standard. The traces on the left show the *m/z* 44 ($^{12}CO_2$) peak produced and measured from GC-IRMS for the peaks assigned to D- and L-aspartic acid. The traces on the right show the simultaneously collected mass spectral fragmentation pattern for these peaks in the Tagish Lake meteorite and standard. GC separation used a 5 m base-deactivated fused silica guard column (Restek) coupled with four 25 m Chirasil L-Val columns (Restek) and the following temperature program: initial oven temperature 50 °C, ramped at 10 °C min^{-1} to 85 °C, ramped at 2 °C min^{-1} to 120 °C, ramped at 4 °C min^{-1} to 200 °C, and held for 10 min. Peaks were identified by comparison of retention time and mass spectral fragmentation with the amino acid standard run on the same day. The asterisk marks a derivatization artifact with parent mass *m/z* 97 that could not be identified.

error in the Antarctic CR meteorites EET 92042 and QUE 99177 and a sample of the CM2 Murchison meteorite using the same extraction and analytical technique (Glavin et al. 2010).

The $\delta^{13}C$ values for D- and L-alanine in the Tagish Lake meteorite were measured to be $+6 \pm 3‰$ and $+16 \pm 4‰$, respectively, for sample 11h and $+67 \pm 7‰$ and $+55 \pm 3‰$, respectively, for sample 5b (Table 3). The D/L alanine ratio of sample 11h was also measured independently by GC-MS and found to be nearly racemic (D/L $\approx$ 0.9). On the basis of observation that alanine is racemic in both meteorite samples with carbon isotope values that indicate an extraterrestrial origin, we would have expected the $\delta^{13}C$ values of D- and L-alanine in each

Table 4. Summary of the L-enantiomeric excesses measured for several amino acids in the 6 M HCl-hydrolyzed hot-water extracts of Tagish Lake meteorites 11h and 5b and racemic standards[a].

	Tagish Lake 5b		Tagish Lake 11h		Racemic Standards	
Amino acids	L_{ee} (%)	δx (n)	L_{ee} (%)	δx (n)	L_{ee} (%)	δx (n)
Aspartic acid	43.1	±8.6 (8)	45.5	±5.2 (8)	6.6	±2.9 (9)
			58.7[b]	±1.8 (3)[b]	4.7[b]	±2.3 (3)[b]
Glutamic acid	51.0	±1.5 (6)	55.1	±3.6 (6)	−2.6	±2.1 (9)
Alanine	−4.8	±5.5 (9)	−3.2	±6.7 (9)	1.0	±1.6 (9)
			7.5[b]	±1.1 (3)*	1.0[b]	±1.4 (3)[b]
Serine	80.5	±3.9 (6)	55.5	±3.6 (6)	3.3	±1.5 (9)
Threonine	89.2	±4.9 (6)	99.4	±0.3 (6)	0.3	±2.1 (9)
Valine	<19.2	±7.1 (6)	<68.2	±2.2 (8)	0.0	±0.4 (14)
β-ABA	5.3	±7.2 (6)	3.7	±6.4 (6)	0.8	±1.1 (9)
Norvaline	1.9	±4.2 (6)	4.9	±3.8 (6)	1.0	±0.8 (8)
Isovaline	7.0	±1.9 (8)	0.0	±2.8 (8)	−2.3	±1.3 (14)

[a]The standard errors (δx) for the meteorites are based on the errors given for n separate measurements propagated through the equation L_{ee} (%) = [(L−D)/(L + D)]*100. Negative % values indicate D-excesses. For the standards, the errors are based on the standard deviation of the average L_{ee} value of n separate analyses using LC-FD/TOF-MS or GC-MS. Protein amino acids are shown in italics.
[b]Values determined from the average D- and L-amino acid peak areas measured by GC-MS.

Table 5. Amino acid enantiomeric ratios (D/L) measured in the nonhydrolyzed (free) and 6 M HCl-hydrolyzed (total) hot-water extracts of the Tagish Lake meteorite[a].

	Tagish Lake 5b		Tagish Lake 11h		Tagish Lake 24-24
	This study				Previous work[b]
Amino Acids	Free	Total	Free	Total	Total
Aspartic acid	0.20 ± 0.05	0.40 ± 0.11	0.25 ± 0.05	0.37 ± 0.07	0.13 ± 0.02
				0.26 ± 0.02[c]	
Glutamic acid	0.59 ± 0.15	0.32 ± 0.02	0.77 ± 0.20	0.29 ± 0.06	0.05 ± 0.01
Serine	0.08 ± 0.01	0.11 ± 0.03	0.19 ± 0.04	0.29 ± 0.06	n.d.
Threonine	<0.01	<0.06	<0.01	<0.01	n.d.
Alanine	1.02 ± 0.04	1.09 ± 0.12	1.05 ± 0.20	1.06 ± 0.14	0.27 ± 0.09
				0.86 ± 0.02[c]	
Valine	> 0.48	> 0.65	> 0.19	> 0.19	n.d.
β-ABA	1.06 ± 0.23	0.90 ± 0.35	1.09 ± 0.37	0.80 ± 0.31	n.d.
Norvaline	1.16 ± 0.12	0.96 ± 0.08	0.96 ± 0.05	0.91 ± 0.07	n.d.
Isovaline	0.81 ± 0.08	0.87 ± 0.03	1.02 ± 0.05	1.00 ± 0.06	n.d.

[a]The uncertainties are based on the absolute errors shown in Tables 1 and 2. Protein amino acids in italics.
[b]Ratios calculated from data in Kminek et al. (2002).
[c]Values determined by GC-MS. Error based on the standard deviation of three separate measurements.
n.d. = ratio not determined due to low amino acid abundances or values that were not reported.

sample to be similar. It is possible that the slightly ^{13}C-depleted value for D-alanine in 11h is due to the isotopically light peak (indicated by an asterisk in Fig. 5) that cannot be completely resolved from the tail of the D-alanine peak. The main mass fragment of this isotopically light compound is at *m/z* 97, and we were unable to find a good match for this peak in the NIST mass spectral library. Although we did not observe *m/z* 97 mass fragments in the D- or L-alanine mass spectra of the racemic standard and Tagish Lake 11h extract (Fig. 5), it is possible that the difference in baselines between the D- and L-alanine peaks in Tagish 11h due to the presence of the artifact could explain the difference in the $\delta^{13}C$ values measured. Unfortunately, the unidentified artifact is a by-product of the TFAA/IPA derivatization reaction (see procedural blank trace in Fig. 5); therefore, additional purification of the meteorite extracts would not remove it from the sample. The D/L alanine ratio of the Tagish 11h extract and the racemic standard measured by GC-MS were not affected by the *m/z* 97 mass artifact as the *m/z* 140 mass trace was used to quantify the D- and L-alanine peak areas.

The carbon isotope values measured in Tagish Lake sample 5b for glycine, D- and L-alanine, and β-alanine were all enriched in ^{13}C compared with the same amino acids in 11h, with $\delta^{13}C$ values ranging from +30 to +67‰ (Table 3). Carbon isotope values for aspartic and glutamic acids in 5b could not be obtained due to low

amino acid abundances; however, low D/L ratios (approximately 0.3–0.4) were also measured for aspartic and glutamic acids in 5b by LC-FD/TOF-MS, corresponding to large L_{ee} of approximately 43–51% (Table 4). The relatively high $\delta^{13}C$ values in 5b indicate that these amino acids and/or their precursor materials retained a more primitive carbon isotopic signature compared with 11h, consistent with mineralogical differences and isotopic measurements of the insoluble organic matter, demonstrating that 5b has experienced less aqueous alteration compared with 11h (Herd et al. 2011). As most of the organic carbon in the Tagish Lake samples 5b and 11h is depleted with an average bulk $\delta^{13}C$ of −14‰ (Herd et al. 2011), the lighter carbon isotope values measured for the amino acids in 11h could be explained by their formation from ^{13}C-depleted precursor material during a secondary aqueous alteration stage in the parent body. We believe that the elevated abundances of α-amino acids in 11h with depleted carbon isotope ratios compared with 5b (Table 4) are best interpreted as reflecting a secondary pulse of amino acid formation in 11h during parent body alteration from ^{13}C depleted precursors by Strecker cyanohydrin synthesis (Peltzer and Bada 1978; Peltzer et al. 1984; Herd et al. 2011), although other formation mechanisms for α- and other amino acids before their incorporation in the parent body have been suggested (Elsila et al. 2007). Another possibility is that the elevated amino acid abundances and lower $\delta^{13}C$ values for the amino acids in 11h compared with 5b is an indication that 11h experienced a higher degree of terrestrial amino acid contamination than 5b. However, if we consider the differences in total abundances and carbon isotope values for L-alanine between samples 5b and 11h (Tables 1 and 4), a mass balance calculation indicates that the additional L-alanine in 11h compared with 5b (= 313 ppb, Table 1) must have an average $\delta^{13}C$ value of + 10‰ to reduce the L-alanine $\delta^{13}C$ value from + 55‰ in 5b to + 16‰ in 11h (Table 3). These $\delta^{13}C$ values are all well outside of the carbon isotope range (−3‰ to −54‰) that has been measured for alanine in a diverse set of terrestrial microorganisms (Scott et al. 2006); therefore, the elevated levels of L-alanine in 11h compared with 5b is highly unlikely to be due to terrestrial biological contamination.

Enantiomeric measurements were obtained by LC-FD/TOF-MS for several other α-H amino acids in Tagish Lake 5b and 11h including serine, threonine, and valine with L_{ee} values that range from approximately 19% for valine to > 99% for threonine (Table 4). These amino acids were not reported in previous amino acid analyses of the Tagish Lake meteorite (Pizzarello et al. 2001; Kminek et al. 2002; Herd et al. 2011). As the total abundances of these amino acids increase in the order 11i << 5b < 11h (Tables 1 and 2), it is possible that some fraction of these amino acids and their L_{ee} were formed during parent body aqueous alteration and are indigenous to the Tagish Lake meteorite. However, due to insufficient amino acid concentrations in the samples, we could not measure their carbon isotope ratios. In particular, due to the poor TFAA/IPA derivatization efficiency and higher GC-MS/IRMS detection limit for serine compared with other amino acids in the Tagish Lake meteorite present at similar abundances, we were unable to obtain the carbon isotope value for L-serine in the Tagish Lake 11h meteorite extract. In the absence of isotopic data, a case for the L-excesses of serine, threonine, and valine being extraterrestrial in origin cannot be made. In addition, due to a possible interfering mass peak in the procedural blank at the same retention time as L-valine (Figs. 2 and 3, peak X), the reported L_{ee} for valine may have been overestimated and are given as upper limits in Table 4.

In contrast to most of the α-H protein amino acids in the Tagish Lake 5b and 11h meteorite specimens that displayed large L_{ee} ranging from approximately 19 to 99%, only very small enantiomeric excesses ($L_{ee} \sim 0$–7%) were observed for the chiral nonprotein amino acids β-ABA, norvaline, and isovaline and most were racemic within analytical error (Tables 4 and 5). Although the α-methyl amino acid isovaline is highly resistant to racemization (Pollock et al. 1975; Bonner et al. 1979), β-ABA and norvaline will readily racemize on geologic time scales under aqueous conditions; therefore, it is not surprising that no enantiomeric enrichment was observed for these two nonprotein amino acids in the Tagish Lake meteorite. A slight L-isovaline excess (L_{ee} = 7.0 ± 1.9%) was measured in the Tagish 5b sample, but no L-isovaline enrichment was observed in the more aqueously altered 11h sample (L_{ee} = 0.0 ± 2.8%). These results are consistent with small L-isovaline enrichments (approximately 0–3%) that have been reported in pristine Antarctic CR carbonaceous meteorites (Pizzarello et al. 2008; Glavin and Dworkin 2009). It is possible that some radioracemization (≤5%) of isovaline from ionizing radiation produced by radioactive decay in the Tagish Lake meteorite parent body (Bonner et al. 1979) could have reduced the original L-isovaline enrichments in both Tagish Lake meteorite samples, or that a secondary pulse of amino acid formation during aqueous alteration in 11h could have overprinted any original L-isovaline excess with a racemic mixture (Herd et al. 2011). However, it is surprising that secondary aqueous alteration leading to the formation of racemic amino acids and higher amino acid abundances observed in 11h did not also reduce the L-enantiomer excesses measured for several α-H amino acids including aspartic and glutamic acids, threonine, and valine. In fact, the

L-excesses measured for these amino acids were slightly higher in 11h compared with 5b (Table 4). Given that all of these α-H amino acids will racemize under aqueous conditions, another explanation is needed for the presence of these large L-excesses, particularly for L-aspartic acid shown to be indigenous to the Tagish Lake meteorite.

Enantioenrichment by Racemization during Parent Body Alteration

The α-H amino acids alanine and aspartic acid in Tagish Lake 11h both have extraterrestrial carbon isotopic values, indicating they are indigenous to the meteorite; however, alanine is racemic, while aspartic acid shows a significant L-enantiomeric excess. One possible explanation for this disparity exists in the crystallization behavior of these two amino acids. It has been shown experimentally that aspartic acid and alanine have very different crystallization behaviors in saturated solutions—alanine preferentially forms racemic crystals (Klussman et al. 2006), while aspartic acid can form metastable conglomerate crystals in addition to racemic crystals (Viedma 2001; Viedma et al. 2008). It has also been demonstrated that saturated solutions of aspartic acid with slight enantiomeric excesses can be converted to enantiopurity under solution-phase racemizing conditions such as aldehyde-catalyzed racemization (Viedma et al. 2008). A conglomerate-forming phenylglycine derivative was also converted to enantiopurity from a slight initial excess using base-catalyzed racemization, indicating that this phenomenon is not limited to a specific racemization method (Noorduin et al. 2009). While we want to make it clear that we do not have the necessary carbon isotope data to firmly establish an extraterrestrial origin for the L-excesses measured for other α-H amino acids in Tagish Lake 11h, the tendency to form conglomerate crystals has also been observed for glutamic acid (Viedma 2001; Viedma et al. 2008) and threonine (Rodrigo et al. 2004), making it possible that L-glutamic acid and L-threonine excesses could have been formed by the same mechanism proposed for aspartic acid. It has even been suggested that spontaneous resolution of conglomerates is the most likely terrestrial mechanism for the origin of homochirality on the early Earth (Bonner 1972).

The conglomerate crystal amplification process is illustrated in Fig. 6 and is based on the observation that larger crystals are more stable than smaller crystals that preferentially dissolve in solution and begin to disappear. Over time, the major enantiomer (present in excess) will accumulate more material in the solid phase than does the minor enantiomer. This is because the minor enantiomer tends to form smaller crystals that dissolve more rapidly than larger crystals. Racemization of the minor

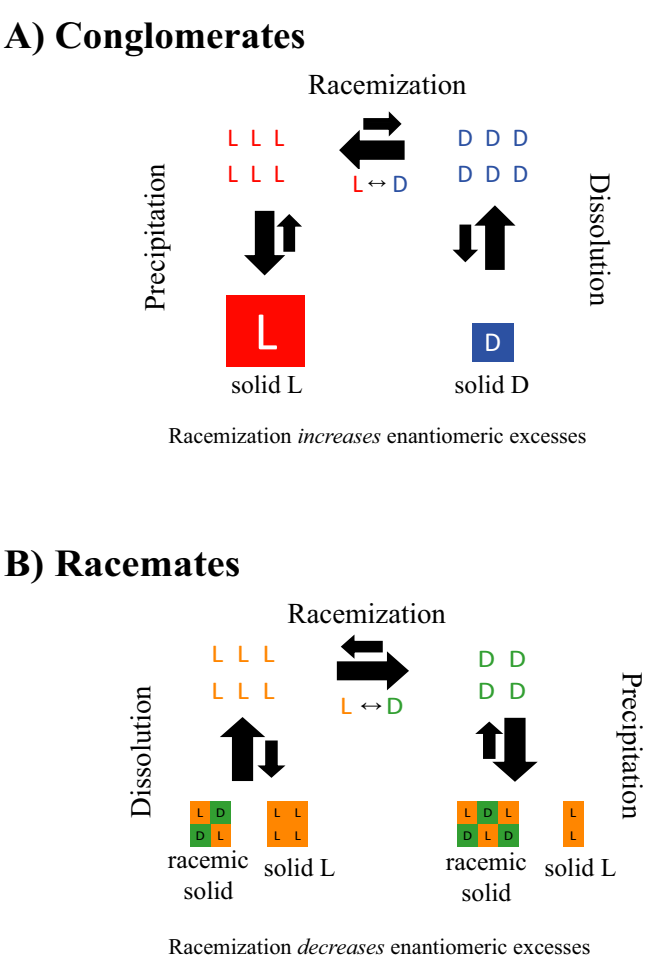

Fig. 6. Schematic illustrating the solid–liquid phase behavior of amino acids that form conglomerate (A) and racemic (B) solid crystals. For the conglomerates, amplification of the major enantiomer (in this case, the L-enantiomer) will occur through racemization and crystallization, assuming that there is a slight initial excess. For racemates, any initial excess (in this case, the L-enantiomer) will decrease over time through racemization.

enantiomer in solution will favor production of the major enantiomer, which will eventually precipitate out and help build even larger crystals of the major enantiomer (Fig. 6A). If we assume that there was a slight initial bias toward L-aspartic and L-glutamic acids on the Tagish Lake meteorite parent body generated via any of the proposed methods of breaking symmetry in amino acids or their precursors, racemization of aspartic and glutamic acids during aqueous alteration could have resulted in a large net enrichment of L- over the D-enantiomers as is observed for these two amino acids in the meteorite. The extent to which the enantioconversion occurs would be dependent on the duration of parent body aqueous alteration and the rate of racemization for the individual amino acids, with a theoretical maximum conversion of 100%, based on laboratory experiments (Viedma 2001; Viedma et al. 2008). It is likely that the interaction of amino acids with

other organic and inorganic species in the parent body would also have an effect on amplification. This is a line of research that should be explored in greater detail through laboratory crystallization experiments of free amino acids and their acid-hydrolyzable precursors under relevant parent body conditions.

Although the temperature and duration of aqueous alteration on the Tagish Lake meteorite parent body remain poorly constrained, Mn-Cr isotopic analyses of carbonate in Tagish 11h indicate that this sample experienced extensive aqueous alteration in a similar setting and timescale to the CI meteorite parent body (Blinova et al. 2011). Temperatures ranging from approximately 50 to 150 °C have been estimated previously for CI meteorites (Clayton and Mayeda 1984; Leshin et al. 1997), and aqueous alteration periods of approximately 10^2 to 10^4 yr have been estimated for CM meteorites (Zolensky and McSween 1988; Browning et al. 1996), with recent models suggesting that liquid water could have been present in asteroids for up to millions of years on CI and CM meteorite parent bodies (Cohen and Coker 2000; Palguta et al. 2010). Under these conditions, racemization of aspartic acid would have been especially rapid. For example, at a temperature of approximately 25 °C under aqueous conditions at neutral pH, the racemization half-life of aspartic acid in natural samples ranges from approximately 10^3 to 10^4 yr, and at a temperature of 100 °C, the racemization half-life of free aspartic acid in aqueous solution is only 30 days (Bada 1991). However, we note that the racemization rate of free glutamic acid is four times slower than free aspartic acid under the same conditions, and would be even slower with the formation of pyroglutamic acid (Smith and Reddy 1989). It should also be acknowledged that for metastable conglomerates such as aspartic and glutamic acids, changes in conditions on the Tagish Lake parent body such as rapid changes in temperature could trigger a shift from conglomerate crystals to racemic ones, thus stopping enantioenrichment via crystallization. This may explain why the L-aspartic and L-glutamic acid excesses measured in the Tagish Lake meteorite did not reach 100%.

For compounds that preferentially form racemic crystals, such as alanine and the majority of the chiral α-H proteinogenic amino acids (Klussman et al. 2006), as well as metastable conglomerates such as aspartic and glutamic acids that have switched to racemic crystals, racemization in the solution phase works in the opposite direction, resulting in an increase in the amount of racemic solid phase and an overall reduction in enantiomeric excess (Fig. 6B). This is because an enantiomeric excess in solution will drive racemization toward a racemic solution phase, causing more racemic crystals (with lower solubility) to precipitate. As enantiopure crystals are more soluble and will dissolve more rapidly than racemic crystals, preferential dissolution of the major enantiomer in the solid phase will drive racemization to the minor enantiomer, resulting in a net conversion of the major to the minor enantiomer and formation of racemic solid crystals. This hypothesis is consistent with racemic alanine measured in the Tagish Lake meteorite and the large L_{ee} values measured for aspartic acid, provided that there was a slight initial L-bias of aspartic acid. We also note that similarly high L-aspartic acid and L-glutamic acid excesses ($L_{ee} \sim 32$–61%) were measured in the aqueously altered type 1 CI meteorite Orgueil, while alanine was also found to be racemic (Ehrenfreund et al. 2001). Although isotopic measurements were not made for these amino acids in Orgueil, the conglomerate crystallization behavior of aspartic and glutamic acids could explain the observed L-aspartic and L-glutamic acid excesses provided that there was a slight initial L-excess.

It has been suggested previously that some amino acids formed by Strecker synthesis in meteorites could have inherited their asymmetry directly from asymmetric photolysis of aldehyde or ketone precursors that were exposed to UV circularly polarized radiation in the solar nebula prior to their incorporation inside the meteorite parent body (Pizzarello et al. 2008). For example, slight (approximately 1%) enantiomeric excesses in alanine have been produced directly from laboratory interstellar ice analogs exposed to circularly polarized UV light (De Marcellus et al. 2011). However, aspartic acid would probably not have obtained its initial asymmetry via this mechanism as its most plausible aldehyde precursor is 3-oxopropanoic acid, which is achiral. Aspartic acid could also have formed from Michael addition of ammonia to fumaric or maleic acid, although both of these precursor molecules are also achiral. Finally, the greater abundance of aspartic acid in the more aqueously altered 11h sample (approximately 600 ppb) compared with 5b (approximately 30 ppb) suggests that most of the aspartic acid was formed inside the parent body during aqueous alteration, thus shielded from any UV CPL.

CONCLUSION

Similar large enantiomeric excesses of several α-H protein amino acids reported previously in the Murchison meteorite (Engel and Nagy 1982; Engel and Macko 1997, 2001) have now been identified in two different fragments of the C2 Tagish Lake meteorite. Based on their stable carbon isotopic ratios, the amino acids observed in L-excesses are likely extraterrestrial in origin. We believe that the L-amino acid enrichment found in these meteorites can be adequately explained by their crystallization behaviors, with preferential amplification of meta-conglomerate or conglomerate

forming enantiopure crystals during parent body aqueous alteration, although future experiments are needed to confirm this hypothesis. The finding that the Tagish Lake meteorite also contains similar enrichments in L-aspartic and L-glutamic acids provides additional support that a wide variety of aqueously altered carbonaceous chondrites could have contributed nonracemic α-hydrogen amino acids leading to the origin of homochirality in life on Earth and possibly elsewhere. As suggested by others previously (Bonner 1972; Viedma 2001), similar L-enrichments of conglomerate amino acids could have occurred in ancient aqueous sedimentary environments on the Earth. As large enantiomeric excesses of conglomerate-forming α-H amino acids are apparently more easily obtained by crystallization processes than are racemic or α-methyl amino acids, conglomerate amino acids may have been more common in the first biopolymers on Earth. For example, aspartic and glutamic acids form a key part of the repetitive sequence of ferredoxin (Eck 1966), believed to be one of the first proteins formed on Earth (Hall and Rao 1971). Although amino acid homochirality can be an important signature of biological processes in the search for evidence of life elsewhere, the detection of nonterrestrial L-amino acid excesses in some carbonaceous meteorites indicates that nonbiological processes could also lead to significant enantioenrichment for some amino acids.

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