

## Molecular and isotopic analyses of Tagish Lake alkyl dicarboxylic acids

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**Abstract**—The Tagish Lake meteorite soluble organic suite has a general composition that differs from those of both CI and CM chondrites. These differences suggest that distinct processes may have been involved in the formation of different groups of organics in meteorites. Tagish Lake alkyl dicarboxylic acids have a varied, abundant distribution and are, with carboxylated pyridines, the only compounds to have an occurrence comparable to that of the Murchison meteorite. This study has undertaken their molecular and isotopic characterization, with the aim to understand their origin and to gain insights into the evolutionary history of the meteorite parent body.

Tagish Lake alkyl dicarboxylic acids are present as a homologous series of saturated and unsaturated species with three- through ten-carbon atom chain length. Linear saturated acids are predominant and show decreasing amounts with increasing chain length. A total of 44 of these compounds were detected with the most abundant, succinic acid, present at ~40 nmol/g meteorite. Overall the molecular distribution of Tagish Lake dicarboxylic acids shows a remarkable compound-to-compound correspondence with those observed in the Murchison and Murray meteorites. In both Tagish Lake and Murchison, the imides of the more abundant dicarboxylic acids were also observed.

The hydrogen and carbon isotopic compositions of individual Tagish Lake dicarboxylic acids were determined and compared to those of the corresponding acids in the Murchison meteorite. All  $\delta D$  and  $\delta^{13}C$  values for Tagish Lake acids are positive and show a substantial isotopic enrichment.  $\delta D$  values vary from, approximately, +1120‰ for succinic acid to +1530‰ for methyl glutaric acid.  $\delta^{13}C$  values ranged from +12.6‰ for methyl glutaric acid to +22.9‰ for glutaric acid, with adipic acid having a significantly lower value (+5.5‰). Murchison dicarboxylic acid showed similar isotopic values: their  $\delta^{13}C$  values were generally higher by an average 17% and  $\delta D$  values were lower for succinic and glutaric acids, possibly due to contamination.

The molecular and isotopic data collected for these compounds restrict their possible origin to processes, either interstellar or of very cold nebular regions, that produced significant isotopic enrichments. Saturated or partially unsaturated nitriles and dinitriles appear to be good precursor candidates as their hydrolysis, upon water exposure, would produce dicarboxylic acids and other carboxylated species found in Tagish Lake. This evolutionary course could possibly include pre-accretionary processes.

### INTRODUCTION

Analyses of soluble and insoluble organics of the Tagish Lake meteorite have revealed a surprising composition that differs from those of CM and CI carbonaceous chondrites and is suggestive of distinct nebular and/or planetary processes (Pizzarello, 2001; Gilmour *et al.*, 2001a; Pizzarello *et al.*, 2001). Over 99% of the meteorite total organic carbon is represented by an acid insoluble carbonaceous residue, which is comprised of predominantly aromatic material and contrasts with the mixed alkyl and aromatic character of similar meteoritic

materials analyzed so far (Cronin *et al.*, 1987; Cody *et al.*, 1999; Gardinier *et al.*, 2000). In view of the preferred release of polycyclic aromatic hydrocarbons (PAHs) upon pyrolysis of the insoluble residue (Gilmour *et al.*, 2001b), it has been suggested that PAHs could be the major components of Tagish Lake insoluble carbon. Also, the presence in the extracts of labile compounds, as nitriles, indicates that the meteorite carbonaceous material did not undergo extensive alteration and may represent pristine early solar and presolar conditions.

The soluble organic suite extracted from Tagish Lake differs in content and distribution from those of CI and CM chondrites,

and is dominated by carboxylated species (Pizzarello *et al.*, 2001). These are the monocarboxylic acids, alkyl and aryl dicarboxylic acids, their imides and anhydrides, carboxylated quinolines, and methanesulfonic acid. Also aliphatic, aromatic and heterocyclic hydrocarbons are found in moderate abundance in this meteorite, while amino acids, amines, and other common meteoritic organics are either scarce or absent. The origin of these differences in organic composition between Tagish Lake and the other carbonaceous chondrites analyzed so far is not known. A general hypothesis of formation of the low molecular weight organics in meteorites has viewed these compounds as interstellar or as the products of parent-body aqueous processing of volatile, interstellar precursors. The Tagish Lake organic suite does not suggest that a similar mechanism of formation was predominant. For example, while the Murchison and Murray meteorites contain abundant and varied amino- and hydroxy acids, which are believed to have formed *via* the Strecker synthesis of ammonia, hydrogen cyanide, aldehydes and ketones (Peltzer and Bada, 1978; Lerner *et al.*, 1993), in Tagish Lake the amino acids are represented by few, low abundance species and hydroxy acids have not been detected. Moreover, in this meteorite some aliphatic compounds, such as the carboxylic acids and *n*-alkanes, display a definite linear chain preference. The finding contradicts the likelihood of precursor species derived from radical and ion-molecule reactions, and would point instead to some catalytic and/or other processes favoring the growth of linear hydrocarbon chain. This distribution also appears to dispute the possibility that organics similar to Murchison's were formed and lost in Tagish Lake parent body, since it is difficult to explain why the linear species would have survived over the branched ones. The findings do not exclude, however, that organic losses could have preceded the formation of the soluble organics we now find in the meteorite, nor that Tagish Lake shared with other meteorites some, if not all, of their nebular and/or planetary stages of evolution.

The latter proposition seems confirmed by the composition of Tagish Lake aliphatic dicarboxylic acids. The compounds are the most varied components of the meteorite organic suite, and an initial assessment of their occurrence and carbon isotopic content has shown that they are very similar to those observed in the Murchison meteorite (Lawless *et al.*, 1974; Cronin *et al.*, 1993; Pizzarello *et al.*, 2001), but are dissimilar from those of Orgueil. This study has undertaken the molecular and isotopic characterization of Tagish Lake alkyl dicarboxylic acids, with the aim to understand their origin, to gain possible insights into the evolutionary history of the meteorite parent body, and to ascertain the possible relationships to the formation processes of other carbonaceous chondrites.

## MATERIALS AND METHODS

Brown *et al.* (2000) describes two types of Tagish Lake (TL) stones. The "pristine" fragments were collected a week

after the fall of the meteorite, did not come above freezing temperature within that period, and have been stored frozen since. The stones of the "degraded" type were collected a few months later, after possibly being exposed to some freeze-thaw cycles in the lake in which the meteorite fell. Both types were used in this study. A 2 g sample of pristine meteorite (TLP) was taken from a fragment representing approximately half of a 10 g stone surrounded by fusion crust. This original stone was cleared of the crust and split in a clean room (kept at approximately  $-4\text{ }^{\circ}\text{C}$ ) at the Johnson Space Center, in Houston, using a nitrogen-filled glove box and instruments that had been autoclaved and ultrasonically rinsed in hexane, acetone, methanol, and ultrapure water (Steele and Zolensky, 2000, pers. comm.). The TLP samples were used for the quantitative assessment of Tagish Lake dicarboxylic acids and their carbon and hydrogen isotopic analyses. A 5.5 g sample was taken from a  $\sim 9$  g stone of degraded meteorite (TLD) and was used for the molecular characterization of the acids and the repeat analysis of their hydrogen isotopic ratios.

Two Murchison samples were used in this study and were obtained from the collection of the Center for Meteorite Studies at Arizona State University (ASU). Sample MM represented 8.5 g of mixed interior and exterior fragments, and was used for carbon isotopic analyses. Sample MI, a 3.2 g interior fragment, was used for hydrogen isotopic analyses. A 0.31 g Orgueil sample, also from the center for Meteorite Studies at ASU, was made up of three smaller fragments and powders.

## Sample Preparation

The TL meteorite samples were powdered on an agate mortar under a stream of helium, and the powders were extracted with 25 mL of water in a closed, evacuated vial, for 24 h, at  $110\text{ }^{\circ}\text{C}$ . The extracts were decanted, combined with rinses, and concentrated by rotary evaporation to  $\sim 2$  mL. They were then adjusted from the original pH (8.2) to pH 2 with 85% phosphoric acid, and applied to a cation exchange column (BIORAD AG-50, x4). The size of the columns varied for the two samples and were  $2.5 \times 5$  cm and  $2.5 \times 10$  cm for TLP and TLD, respectively. The columns were eluted with water, 40 and 100 mL, respectively, and then with equal amounts of 2 N ammonium hydroxide. The ammonium hydroxide eluate, containing basic and amphoteric compounds, was stored for future analyses. The water eluates, containing neutral and acidic compounds, were used in this study. They were adjusted to approximately pH 9 with ammonium hydroxide and concentrated.

The TLP sample (concentrated to  $\sim 1$  mL) was again acidified with two drops of 85% phosphoric acid and dried on a vacuum line, to cryogenically transfer and collect the volatile acidic compounds (Yuen *et al.*, 1984). The residue was dissolved in  $\sim 2$  mL of water and continuously extracted with distilled diethyl ether for 24 h (Cronin *et al.*, 1993). This was followed by two additional manual ether extractions of the

sample. The combined ether extracts, plus rinses, were dried by rotary evaporation and the residue esterified with isopropanol (~3 N HCl) for gas chromatography-mass spectroscopic analyses (GC-MS), and  $^{13}\text{C}$  and deuterium gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS). The MM and Orgueil samples were similarly processed, except for the cryogenic transfer step that was not included in the procedure.

The concentrated TLD and MI water eluates were stored in the freezer ( $-4\text{ }^\circ\text{C}$ ), quickly thawed for the taking of aliquots as needed for subsequent analyses, and then refrozen. All aliquots, except one, were dried and esterified as is (*i.e.*, without ether extraction) for MS analyses as TLP and MM. One fraction (about one-seventh of the sample) was dried and extracted with 2 mL of methanol at room temperature, for ~30 min, and with intermittent sonications for the analyses of alkyl dicarboximides by GC-MS.

### Gas Chromatography-Mass Spectroscopic Analyses

The gas chromatograph used for these analyses was a Hewlett Packard 5880A interfaced to a mass selective detector (HP 5970B) for mass spectrometric detection.

Either of two capillary columns were used for GC separations: one 50 m  $\times$  0.25 mm coated with Chirasil L-val and 0.16  $\mu\text{m}$  phase thickness (Chirasil-L-Val, Alltech); the other 25 m  $\times$  0.25 mm coated with a chiral  $\beta$ -hepta amylose phase of 0.7  $\mu\text{m}$  thickness (Chirasil-Dex CB, Chrompack). Typical temperature program: 70  $^\circ\text{C}$  initial temperature, 5', to 100  $^\circ\text{C}$  at 2  $^\circ\text{C}/\text{min}$  to 200  $^\circ\text{C}$  at 4  $^\circ\text{C}/\text{min}$ . Split (1:1.5) injection.

### Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometry and Gas Chromatography Thermal Conversion-Isotope Ratio Mass Spectrometry Analyses

GC-C-IRMS analyses were performed with a HP 6890 gas chromatograph connected *via* a high-temperature conversion interface III to a Finnigan Mat Delta<sup>+</sup>-XL mass spectrometer. GC separations for carbon isotope data (see below) were obtained with a Chirasil-Val column (see above) in the gas chromatograph, He as the carrier gas, and chromatographic conditions as for GC-MS, splitless injection. Comparative analyses were also performed with the Chirasil-Dex column. For  $\delta^{13}\text{C}$  measurements, individual organic compounds were oxidized into  $\text{CO}_2$  at 940  $^\circ\text{C}$  by flowing through a ceramic oxidation reactor bearing three braided NiO/CuO/Pt wires. Six pulses of standard  $\text{CO}_2$  gases, which had been pre-calibrated against a commercial reference  $\text{CO}_2$  (ZTECH Corp.,  $\delta^{13}\text{C}$ :  $-10.07\text{‰}$  PDB), were injected *via* the GC-C III interface to the IRMS for the computation of  $\delta^{13}\text{C}$  values of sample compounds. Data were analyzed using Finnigan ISODAT software and the standard deviation for duplicated analysis was less than  $\pm 0.3\text{‰}$  for peaks with intensity  $>0.5$  V. The  $\delta^{13}\text{C}$  (PDB) of isopropanol ( $-29.3\text{‰}$ ) was established by elemental

analyzer (EA)-IRMS. The EA was a Carlo Erba 1108 in the C, N mode with He as the carrier gas. Individual mass balance equations for correction of carbon contributed by derivatization reagents to the  $\delta^{13}\text{C}$  of sample diacid were:  $\delta^{13}\text{C}_{\text{diacid}} = [\delta^{13}\text{C}_{\text{der. diacid}} - \mathbf{a}(-29.3)] / \mathbf{b}$ , where **a** and **b** are the fractional carbon abundances provided to the derivatized diacid by the isopropanol and the diacid, respectively.

$\delta\text{D}$  values were measured by gas chromatography thermal conversion-isotope ratio mass spectrometry (GCTC-IRMS). The compounds were separated by GC on a Chirasil-Val column of higher capacity (50 m  $\times$  0.32 mm, 0.20 mm phase, Alltech), conveyed through a high-temperature pyrolysis reactor kept at 1440  $^\circ\text{C}$ , and quantitatively pyrolyzed to hydrogen gas and carbon monoxide or graphite (Burgoyne and Hayes, 1998). In the mass spectrometer an electrostatic filter in front of the mass-3 Faraday cup reduced the amount of scattered helium (mass-4) reaching the collector (Hilkert *et al.*, 1999), thus allowing for high-precision measurements on hydrogen isotope ratios without the interference from the helium carrier gas. A tank of ultra-high purity hydrogen gas with known  $\delta\text{D}$  values ( $\delta\text{D}_{\text{VSMOW}} = -349.76\text{‰}$ , pre-determined against commercial reference hydrogen with  $\delta\text{D}_{\text{VSMOW}} = -218.10\text{‰}$ , ZTECH Corp.) was used as isotope standard during the measurements. The  $\text{H}_3$  factor was determined daily using standard hydrogen gas introduced through a GC-C III interface. The mass spectrometer was tuned to ensure the  $\text{H}_3$  factor was  $<10$  and the daily variability was  $<0.1$ . The reproducibility and accuracy of the hydrogen isotopic analyses were evaluated routinely using laboratory isotopic standards with known isotopic values. Samples were analyzed in duplicate (Tagish Lake) and triplicates (Murchison). The  $\delta\text{D}$  of the isopropanol derivative moiety ( $-119.46\text{‰}$ ) was obtained from the GCTC-IRMS determined  $\delta\text{D}$  of an isopropyl succinate standard, by subtraction of the succinate (sodium) moiety  $\delta\text{D}$  previously obtained by EA. Individual mass balance corrections for derivatization were given by the equation:  $\delta\text{D}_{\text{diacid}} = [\delta\text{D}_{\text{der. diacid}} - \mathbf{a}(-119.46)] / \mathbf{b}$ , where **a** and **b** are the derivatized diacid fractional hydrogen abundances of isopropanol and diacids, respectively.

### Analyses of Standards and Blank

A blank sample of 100 mL of water and a 1  $\mu\text{mol}$  standard succinic acid sample were carried through the entire separatory procedure, esterified, and analyzed by GC-MS and GC-C-IRMS as the meteorite samples.

### Reagents

The water and hydrochloric acid used in the preparations were triple and double distilled, respectively, using a quartz still. Double distilled ammonium hydroxide was purchased from Aldrich Chemical Co. Concentrated phosphoric acid, 85% in water, was also obtained from Aldrich with a 99.99+%

purity. The various dicarboxylic acid standards were obtained from Aldrich and Sigma Chemical Co. A succinic disodium salt (Aldrich Chem. Co.) was used for standard isotopic analyses.

Isopropyl alcohol was purchased from Alltech and acidified with acetyl chloride (TFA-IPA amino acid kit, Alltech Assoc. Inc.).

## RESULTS

### Molecular Analyses

Alkyl dicarboxylic acids are found in Tagish Lake as a homologous series of saturated and unsaturated species with three- through ten-carbon atom chain length (Fig. 1). Linear saturated acids are predominant, show decreasing amounts with increasing chain length, and the most abundant succinic acid is present at ~40 nmol/g of meteorite (~4 ppm). A portion of these acids could be identified with reference standards (Table 1) and the remaining were recognized with good confidence on the basis of their mass spectra. A total of 44 saturated diacids were observed (*i.e.*, besides the acids listed in the table); 1 six-carbon, 6 seven-carbon, 10 eight-carbon, 7 nine-carbon and 3 ten-carbon acids were also observed. As for saturated species, few mono-unsaturated acids were positively identified, fumaric, maleic, citraconic, mesaconic, and itaconic acids, and a few more were recognized by their mass spectra. Citraconic and mesaconic acids, the five-carbon branched isomers, are the most abundant unsaturated acids. It is interesting that these compounds are both at least 3× more abundant than a, possible, straight chain isomer, suggesting a different linear-to-branched distribution between saturated and unsaturated species. The only cyclic dicarboxylic acid found was in low amount and has the stable five-carbon ring. Cyclic eight-carbon species (with a six-carbon ring) and polyene chain compounds were searched for but not found.

One diacid, 2-methyl glutaric acid, could be resolved into the D, L-enantiomers, and was found racemic in Tagish Lake (Fig. 1, insert) and the Murchison meteorite as well. Overall the molecular distribution of Tagish Lake dicarboxylic acids show a remarkable compound to compound correspondence with that observed in the Murchison meteorite samples, which were analyzed under identical procedural conditions. The similarities extend to known and unknown species of different chain length (Fig. 2) and bond saturation, the only difference being the ratios of linear to branched acids, which were consistently higher for Tagish Lake. It should be noted that the Tagish Lake fragments analyzed also showed some variability in both the absolute and relative amounts of dicarboxylic acids. For example the glutaric/methyl succinic ratios, indicative of relative abundances of linear and branched species, varied from 2.0 to 4.5; the correspondent values for the Murchison samples were 1.0 and 1.3. The degraded Tagish Lake sample yielded dicarboxylic acid in slightly larger

TABLE 1. Distribution and abundances (nmol/g)\* of alkyl dicarboxylic acids† identified in the Tagish Lake meteorite‡.

Saturated	Mono-unsaturated	Cyclic
3C: Malonic (3)		
4C: Succinic (40)	Fumaric (n.d.)§	<i>trans</i> -1,2-Pentane dicarb. (<1)
Methyl malonic (<1)	Maleic (n.d.)	
5C: Glutaric (28)	Citraconic (3.5)	
Methyl succinic (16)	Mesaconic (<1)	
	Itaconic (<1)	
6C: Adipic (19)		
D,L-2-Methyl glutaric (6)		
3-Methyl glutaric (2.5)		
2,2-Dimethyl succinic (<1)		
2,3-Dimethyl succinic (1.5)		
7C: Pimelic (1.5)		
2,2-Methyl glutaric (<1)		
2,4-Methyl glutaric (<1)		
3,3-Methyl glutaric (<1)		
3-Methyl adipic (1.5)		
8C: Suberic (<1)		
9C: Azelaic (<1)		
10C: Sebacic (<1)		

Each listing starts with the linear isomer.

\*In nanomoles/gram of meteorite.

†General formula: HOOC-R-COOH.

‡Identification based on reference standards and listed by carbon #.

§Not determined due to coelution.

amounts than the pristine samples, indicating that this fragment had not been leached of soluble organics to a significant extent.

The Orgueil meteorite also contains an abundant suite of dicarboxylic acids with compounds of up to eight-carbon chain length and with a linear to branched chain ratio very similar to those of Tagish Lake. The glutaric/methyl succinic ratios were 3.0 and 4.5 for two TLP samples, 1.8 for TLD, 1.0 and 1.3 for IM and MM, respectively, and 3.5 for Orgueil. The variability of these ratios for the different fragments of the Tagish Lake stones may indicate that this meteorite presents the same zonal variability of linear to branched species within an organic suite that has been documented for the Murchison meteorite (Cronin and Pizzarello, 1983; Pizzarello and Cronin, 2000). A difference observed between the Tagish Lake and Murchison meteorites was the abundance of imide derivatives. While in Murchison these are represented by a series of compounds whose distribution appears to parallel that of the corresponding diacids (only a few standard compounds are available for dicarboximides, also), in Tagish Lake only succinimide and

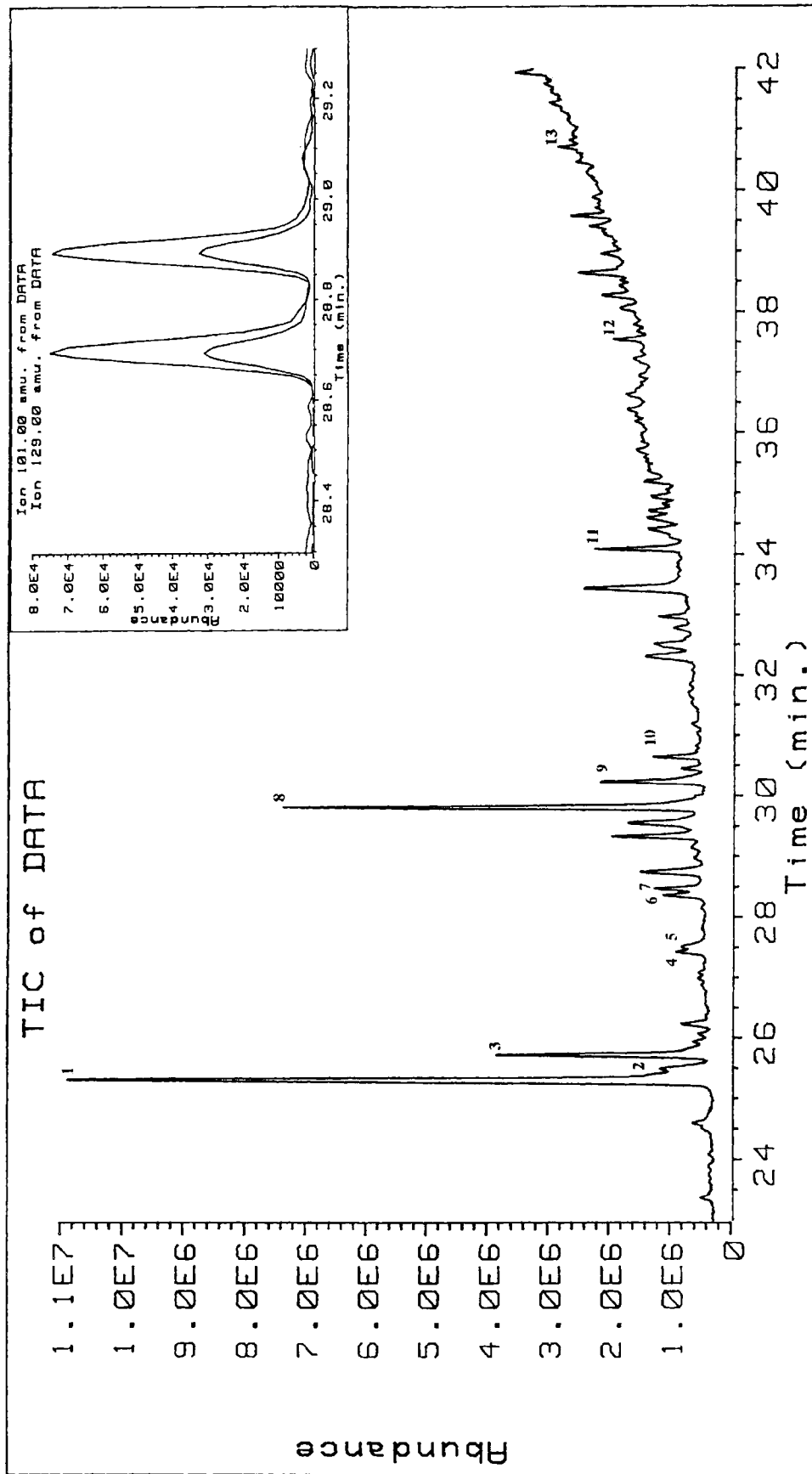


FIG. 1. GC-MS analysis of Tagish Lake dicarboxylic acids, total ion mass chromatogram (TIC) on Chirasil-Val column. Acids identified from this trace with standards: (1) succinic; (2) 2,2-dimethyl succinic; (3) methyl succinic; (4) 2,3-dimethyl succinic, (5) itaconic; (6) mesaconic; (7) citraconic; (8) glutaric; (9) 2-methyl glutaric; (10) 3-methyl glutaric; (11) adipic; (12) pimelic; (13) suberic. Inset: D,L-2-methyl glutaric acid from a Tagish Lake extract as separated on Chirasil-Dex column; m/z 129 and 101 traces.

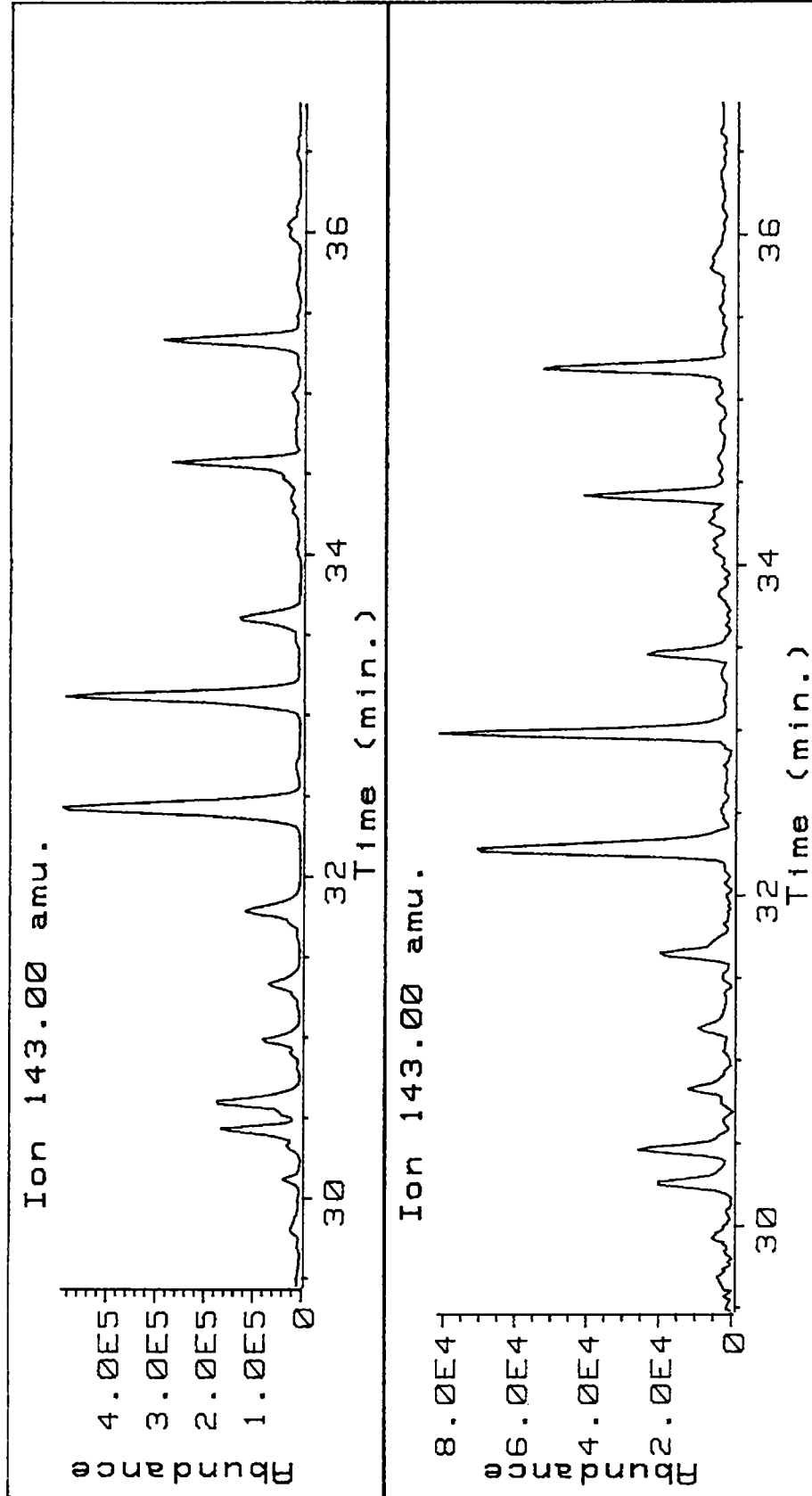


FIG. 2. Seven-carbon dicarboxylic acids from the Murchison (top) and Tagish Lake meteorites. Single ion GC-MS traces of characteristic  $m/z$  143 fragment (molecular ion minus loss of isopropoxy and isopropene). On Chirasil-Val column.

glutarimide were observed. The abundance ratios of the imides to the corresponding acids are lower in Tagish Lake than in Murchison, by about one order of magnitude.

### Isotopic Analyses

The carbon isotopic compositions of some of Tagish Lake (TLP) dicarboxylic acids were determined by GC-C-IRMS and compared to those of the corresponding compounds in the Murchison (MM) (Pizzarello *et al.*, 2001) and Orgueil meteorites (Table 2). The  $\delta^{13}\text{C}$  values of all acids from the Tagish Lake and Murchison meteorites were found positive, with  $^{13}\text{C}$  abundances in Tagish Lake acids lower than Murchison by 8% to 26%. Adipic acid was found lighter by ~60%. Also, in Tagish Lake acids the  $\delta^{13}\text{C}$  values of straight and branched chain isomers appear to differ to a small degree. All  $\delta^{13}\text{C}$  values measured for the Orgueil meteorite acids were negative and are in the general terrestrial range. These findings, and the terrestrial age of the meteorite, first suggest the possibility of contamination. Succinic acid is the intermediate in a common oxidative pathway of aerobic metabolism (the tricarboxylic acid cycle) and glutaric acid is also known in the biosphere. The other two dicarboxylic acids listed in the table, however, are far less common terrestrially and a different indigenous isotopic distribution of Orgueil diacids cannot be excluded.

The hydrogen isotopic compositions of some of the individual acids from Tagish Lake (TLP and TLD) and Murchison (IM) extracts were determined by GCTC-IRMS (Fig. 3), and their  $\delta\text{D}$  values are listed in Table 3. These should be considered minimum values as they were not corrected for hydrogen exchange, which is possible at the carbon adjacent at the carbonyl groups (Fuller and Huang, 2002). The deuterium enrichment is significant for the compounds of both meteorites, with  $\delta\text{D}$  values in the range of those determined for Murchison amino acids (Epstein *et al.*, 1987; Pizzarello *et al.*, 1991). Murchison succinic and glutaric acid values are lower than all the values measured for the other acids in both meteorites. It is possible that they are due to contamination,

since these are the acids with larger terrestrial occurrence (see above).

Overall the  $\delta^{13}\text{C}$  and  $\delta\text{D}$  values we determined for individual dicarboxylic acids exceed those obtained for Murchison by Cronin *et al.* (1993). GC-C-IRMS values are higher than those determined by class specific bulk analyses by a factor of 5 ( $\delta^{13}\text{C}$ ) to 4 ( $\delta\text{D}$ ). The difference could be attributed to either some blank interference or to a lesser isotopic enrichment of other compounds (as the hydroxydicarboxylic acid and unknowns) contained in the Cronin *et al.* samples.

### DISCUSSION

The selective distribution of soluble organics found in Tagish Lake, *i.e.*, the presence of just some suites of compounds matching those of Murchison, is suggestive of distinct pathways of organic syntheses in meteorites (Pizzarello *et al.*, 2001). It is possible that through the study and characterization of organics in Tagish Lake we may be able to single out these pathways within the multiple processes that were at work in the production of more complex organic suites and begin to elucidate the locales and time frames for this diverse evolution.

Tagish Lake alkyl dicarboxylic acids show a composition that is undoubtedly similar to that displayed by the Murchison meteorite. The similarity extends to both their molecular distribution, including the relative abundances of linear acids that is unusual for Murchison (Lawless *et al.*, 1974), and their carbon and deuterium isotopic enrichments. It appears reasonable to conclude that they had similar origins. Positive  $\delta\text{D}$  and  $\delta^{13}\text{C}$  values had been observed previously for Murchison dicarboxylic acids (Cronin *et al.*, 1993), a finding which together with the various degrees of enrichment in deuterium,  $^{13}\text{C}$ , and  $^{15}\text{N}$  of several meteoritic compounds suggested a relationship with interstellar precursors (Epstein *et al.*, 1987). Large isotopic enrichments have been spectroscopically determined for molecules in the interstellar clouds (see Sandford, 1996, for a review) where they are favored by the predominance of ion-molecule reactions and the extreme low temperatures of the medium (Sandford *et al.*, 2001). The considerable deuterium and  $^{13}\text{C}$  enrichments we have observed in Tagish Lake and Murchison dicarboxylic

TABLE 2.  $\delta^{13}\text{C}$  values (‰) of individual meteoritic alkyl dicarboxylic acids.\*

Acid	Murchison	Tagish Lake	Orgueil
Succinic	+28.1 ( $\pm 1.1$ )	+22.5 ( $\pm 0.6$ )	-23.8†
Methyl succinic	+26.5 ( $\pm 0.7$ )	+15.4 ( $\pm 3.0$ )	-19.5†
Glutaric	+26.8 ( $\pm 0.3$ )	+22.9 ( $\pm 1.5$ )	-20.4†
2-Methyl glutaric	+27.9 ( $\pm 1.0$ )	+18.6 ( $\pm 0.7$ )	-10.3†
3-Methyl glutaric	+19.1†	+12.6†	n.m.
Adipic	+21.4†	+5.5 ( $\pm 0.9$ )	n.m.

\*By GC-C-IRMS, corrected for esterification, and relative to PVDB.

†Average of two data.

n.m. = not measured.

TABLE 3.  $\delta\text{D}$  values (‰) of individual meteoritic alkyl dicarboxylic acids.\*

Acid	Tagish Lake (P)	Tagish Lake (D)	Murchison (MI)
Succinic	+1124.7	+1116.3	+389.5 $\pm$ 31.9
Methyl succinic	+1106.8	+1112.1	+1225.4 $\pm$ 43.3
Glutaric	+1387.8	+1322.1	+795.4 $\pm$ 130
2-Methyl glutaric	+1463.5	+1263.4	+1550.7 $\pm$ 26.4

\*By GCTC-IRMS, corrected for esterification and relative to VSMOW.

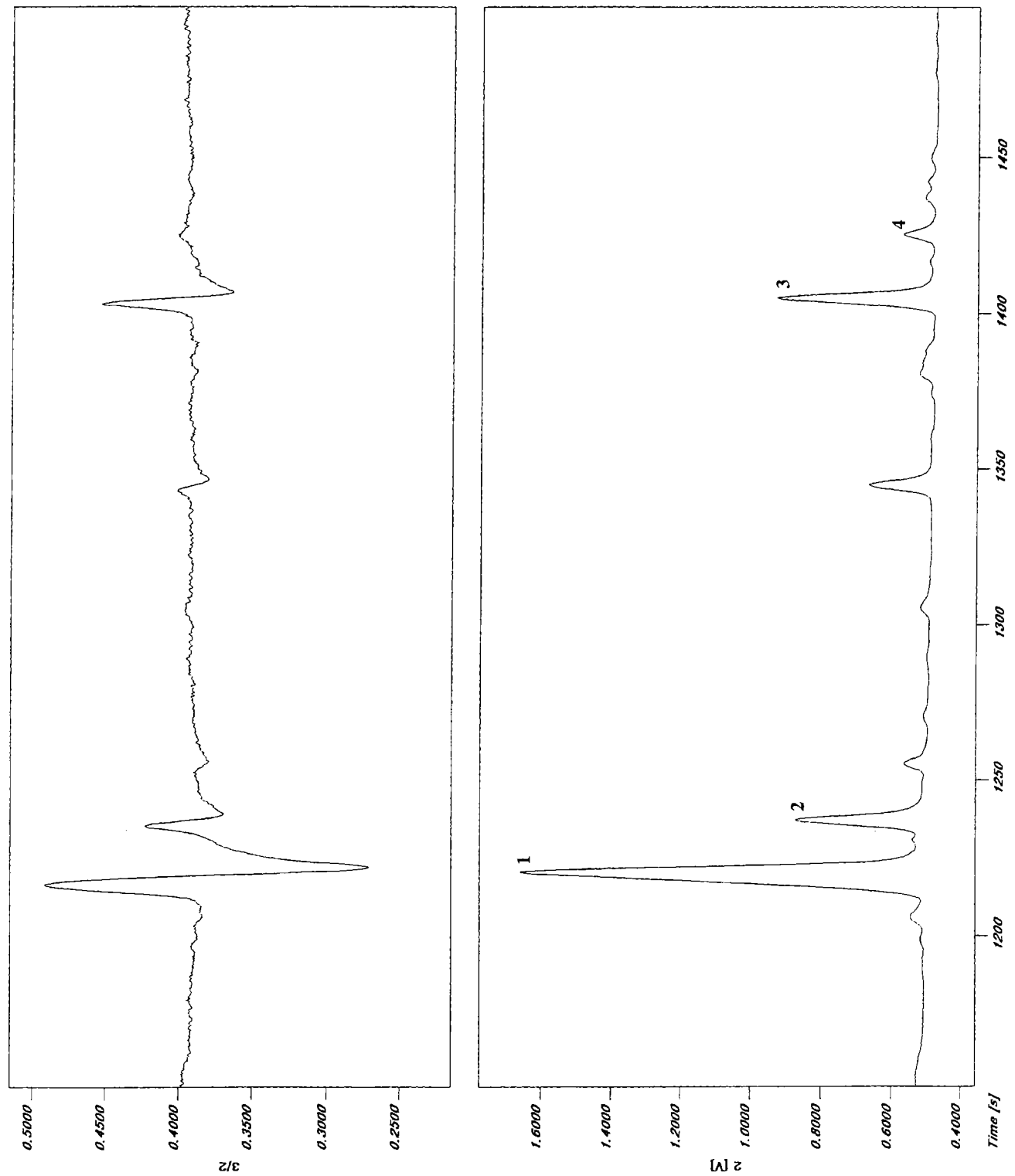


FIG. 3. GCTC-IRMS of dicarboxylic acids of the Tagish Lake meteorite. m/z 2 (bottom) and 3/2 traces. Acids analyzed: (1) succinic; (2) methyl succinic; (3) glutaric; (4) 2-methyl glutaric.



acids confirm the view that a similar low-temperature chemistry, interstellar (Wannier, 1980) or nebular (Aikawa and Herbst, 2001, and references therein), must have been at work in producing the precursors to both suites of compounds. We do not know how large the isotopic enrichments of these precursors may have been, but the data show that their isotopic signatures were not entirely altered during the later process of acids formation and were carried with similar  $\delta D$  values through at least a six-carbon chain length.

What can these data on the composition of meteoritic dicarboxylic acids tell us about their origin and distinctive history that would justify them as one of only two CM comparable suites in Tagish Lake? The isotopic values determined for both suites of acids set restrictions on the possible precursor we may suggest. Cronin and Chang (1993) proposed that interstellar grain or parent-body reactions could have yielded nitriles and dinitriles able to produce, upon hydrolysis, carboxylated and dicarboxylated compounds. Cyanopolyynes, unsaturated carbon chains of up to eleven carbon having a cyano functional group, have been observed in the interstellar medium (for a review see Ehrenfreund and Charnley, 2000) and interstellar dicyanopolyynes, while not detected so far for lack of a dipole moment, are theoretically possible. However, fully unsaturated precursors to alkyl dicarboxylic acids seem unlikely based on the molecular and isotopic data we obtained. These compounds would hydrolyze into only linear, odd carbon compounds and their hydrogenation in a parent body most probably would not have resulted in the high  $\delta D$  values of Tagish Lake and Murchison dicarboxylic acids. On the other hand, partially unsaturated nitriles, which have also been detected in the interstellar medium, should be considered good precursor candidates to diacids. Dinitriles precursors could derive from nitriles in interstellar and/or nebular and parent body environments as, for example, by HCN addition (Peltzer *et al.*, 1984).

The singularity of organics distribution in Tagish Lake would be explained if we assumed that organic compounds with different volatilities were accreted to the meteorite parent body and that, while the less volatile of these precursors produced the dicarboxylic acids and other soluble organics, the more volatiles were either lost or never accreted. Nitriles and dinitriles, as precursors to dicarboxylic acids, would satisfy the requisite of not being easily sublimed, as could have been the more volatile aldehydes and ketones, precursors to the amino acids. Succino nitrile, for example, has a boiling point at reduced pressure (20 Torr) of 158–160 °C while that of butyraldehyde is –12 °C.

The locale of meteoritic dicarboxylic acid formation is difficult to assess, given the lack of an overall consensus (Metzler *et al.*, 1992; Browning *et al.*, 2000) on the many petrological features of water alteration in carbonaceous chondrites and the possible contributions of nebular chemistry (Nakamura *et al.*, 1991; Tomeoka *et al.*, 1991; Metzler *et al.*, 1992; Ikeda and Prinz, 1993). The relation between petrology

and distribution of organics is even less clear and has never been evaluated systematically nor with specifically designed analytical tools. Cronin (1989) has made the only attempt, relating so-called "poorly characterized phases" (PCPs) to the abundance of amino acids in CM chondrites. Based on the present knowledge, we have to consider the possibility that dicarboxylic acids could have formed by parent body as well as nebular pre-accretionary processes. We can envision both nebular water alteration of interstellar grains, with their inventory of non-volatile species, and/or the processing of precursors, as unsaturated nitriles and polyynes, in regions of the nebula where energetic conditions and very cold temperatures would simulate interstellar chemistry.

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