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Soluble Organic Compounds in the Tagish Lake Meteorite

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Abstract

The C2 ungrouped Tagish Lake meteorite preserves a range of lithologies reflecting variable degrees of parent body aqueous alteration. Here we report on soluble organic compounds, including aliphatic and aromatic hydrocarbons, monocarboxylic acids and amino acids, found within specimens representative of the range of aqueous alteration. We find that differences in soluble organic compounds among the lithologies may be explained by oxidative, fluid-assisted alteration, involving changes from one type of soluble organic compound to another, or derivation of soluble organic compounds from macromolecular material. Our results demonstrate the role of parent body alteration in the modification of organic matter in the early Solar System, and have implications for interpretation of the complement of soluble organic compounds in carbonaceous chondrites.

Introduction

The Tagish Lake meteorite is an ungrouped, type 2 carbonaceous chondrite that represents some of the most primitive, organic-rich extraterrestrial material available for study. As with other meteorites, heat during atmospheric transit only penetrated 1-2 mm into the interior (Genge and Grady, 1999), preserving the organic matter against pyrolysis. Furthermore, the collection of the ~45 specimens from the frozen surface of Tagish Lake a few days after its fall was done without direct hand contact (Hildebrand et al., 2006), and all but one specimen have been kept below 0 °C since collection. As such, the preservation of the most volatile organics is expected in these 'pristine' specimens. The Tagish Lake meteorite contains a high amount of organic carbon (~2.6 wt%; Grady et al., 2002), the characteristics of which correlate with mineralogy and petrology, providing insights into parent body alteration (Herd et al., 2011).

The first analysis of the soluble organic material in a pristine sample of the Tagish Lake meteorite was performed by Pizzarello et al. (2001). A total of approximately 100 ppm of soluble organics was found in the extracts. The suite of water soluble compounds was dominated by dicarboxylic acids, monocarboxylic acids, pyridine carboxylic acids, dicarboximides and sulfonic acids. Amino acids were also observed in the water extract, but in very low concentrations (< 0.1 ppm). For comparison, the total amino acid concentration found for pristine samples of the Murchison carbonaceous chondrite was > 15 ppm (Botta et al., 2002). Aliphatic and aromatic compounds of low polarity, such as PAHs, alkyl benzenes and n-alkanes, were detected in the benzene/methanol extract of Tagish Lake. The positive $\delta^{13}\text{C}$ values (+ 15 to +23 ‰) found for individual diacids point to an extraterrestrial origin. By contrast, the $\delta^{13}\text{C}$ values for the various n-alkanes were found to range from – 18 to – 29 ‰, which are well within the span of terrestrial reduced organics (Pizzarello et al., 2001). The authors argued that these

compounds can, nonetheless, be considered as indigenous as the insoluble macromolecular carbon inside the fragment also possesses low $\delta^{13}\text{C}$ values. Interestingly, these authors also noted that certain aliphatic compounds, such as carboxylic acids and n-alkanes showed a distinct preference for linear over branched chains, implying that the compounds were assembled via catalytic surface processes. Previous work by Kminek et al.(2002) on amino acids utilized Tagish Lake meteorite samples collected during the spring thaw (April 2000; Hildebrand et al., 2006) that were exposed to meltwater. The complement of amino acids and their relative abundances in these meteorite samples are similar to amino acids in the lakewater, and these workers conclude that the sample was contaminated. Since then, a more detailed study of amino acids in pristine Tagish Lake specimens has demonstrated that the indigenous complement of these compounds is preserved, and that variations in abundance and chirality between specimens demonstrate the role of parent body alteration in the formation of prebiotic compounds (Glavin et al., 2012).

Here we report the detailed results of soluble organic matter extraction of the same Tagish Lake specimens studied by Herd et al. (2011) and Glavin et al. (2012), including polar, non-polar and weakly polar organic molecules. Results are interpreted in the context of the established sequence of alteration ($5b < 11h < 11i \sim 11v$). [make reference to Alexander et al. (submitted) as may be appropriate]

Samples and Analytical Procedures

This study involves specimens 11v (disaggregated material), 11i, 11h and 5b (Figure 1 specimen photos), part of the pristine suite described by Herd et al. (2011). The Tagish Lake meteorite specimens were transferred from storage in a $-28\text{ }^{\circ}\text{C}$ research grade freezer held to a Styrofoam container lined with $-18\text{ }^{\circ}\text{C}$ freezer gel packs (Fisher), and then transported to a $-18\text{ }^{\circ}\text{C}$ walk in freezer for subsampling. Subsampling was carried out using sterile scalpels rinsed in

ultrapure water. Weighing was done using a balance that had been placed in the freezer for several hours to allow electronic components to equilibrate to the low temperature. The masses of the subsamples used for this study (where each mass provided was sampled on a separate date) are as follows: 1.685 g, 0.712 g, 1.485 g, and 0.558 g (11v); 0.24 g, 0.459 g and 2.020 g (11i); 1.195 g and 2.896 g (5b); 2.972 g, 0.0935 g, and 0.549 g (11h).

Weakly-polar organics extraction and analysis

Dichloromethane (CH_2Cl_2) is the solvent of choice for the extraction and solubilization of non-polar and mildly polar organic compounds. Its ability to efficiently extract both non-polar hydrocarbons and moderately polar organics, such as halogenated organics or long chain fatty acids, is due to the size of its dielectric constant, 9.1 ϵ/ϵ_0 at 20 °C, which is far below that for the highly polar solvent water, 80 ϵ/ϵ_0 at 20 °C, yet well above the values for the non-polar, hydrocarbon solvents, which range from 2-4 ϵ/ϵ_0 at 20 °C (Riddick et al., 1986). It is no surprise, therefore, that optimal extraction of non-polar, weakly polar and moderately polar solvent-soluble organic species was achieved with neat HPLC-grade dichloromethane (Fisher Scientific). A substantially smaller assortment of compounds was extracted when 50:50 (v/v) toluene-methanol solution was used and thus the use of toluene-methanol was abandoned for this study.

A typical extraction involved adding ca. 0.4 mL of ultrapure CH_2Cl_2 to ~ 0.3 g of meteorite sample at – 78 °C under Ar. If not already disaggregated, the sample was crushed with a glass rod. The mixture was warmed to room temperature and briefly swirled. The extract was then filtered through glass wool that had previously rinsed with 3 x 2 mL of HPLC grade dichloromethane. The filtrate (~ 0.2 mL) was collected and then analyzed by GC-MS using an Agilent technologies 5975-C gas chromatograph-mass spectrometer equipped with an HP-5MS column packed with (5% phenyl)methyl polysiloxane. The lower limit for the mass spectra was

30 m/z. The GC conditions used were the following: Injector temperature: 250 °C; pulsed splitless, 4 microliter manual injection; 30 psi for 0.15 min; purge flow to split vent at 0.2 min; He 0.922 mL/min. Oven temperature was held at 50 °C for 1 minute, then the temperature was ramped at 10 °C/min up to 290 °C and then held at 290 °C for 45 minutes. The solvent delay was 3.5 minutes.

FTIR analysis

Approximately 0.30 mL of ultrapure dichloromethane was added to a 0.3833-g sample of 11v at – 30 °C. The resulting slurry was warmed to room temperature, swirled gently for 5 minutes and then set aside to allow the insoluble material to settle. Approximately 0.1 mL of the yellow supernatant was cast on a sodium chloride IR plate. Evaporation of the dichloromethane solvent left two concentric rings on the plate: one pale brown (~ 3 mm diameter, 0.5 mm wide, 0.1 micron thick) and the other colorless (~ 4 mm diameter, 0.5 mm wide, 0.1 micron thick). The FTIR spectra were recorded as dichloromethane casts on a Thermo-Nicolet Nic Plan FTIR microscope attached to a Magna 760 FTIR spectrometer. For each analysis, 256 scans were collected for both the background and the sample over the range 4000-650 cm⁻¹. Omnic software (7.1) was used to collect and process the spectra. The baseline was manually corrected in all spectra. The IR spectra for these two rings are shown in Figure 2.

GC-IR-MS Analyses

The dichloromethane extracts of 11v and 11i were treated with ~ 30 x 1 mm acid-activated copper spheres to remove the elemental sulfur, which can interfere with the GC-MS analysis. Elemental sulfur, being non-polar, has a high solubility in the weakly polar solvent dichloromethane. The two x 4.0 mL 11v dichloromethane extracts (~ 8 mL total volume) were combined and concentrated down to ~150 mL by slow evaporation in a fumehood (~10 hr). The 11i dichloromethane extract (~ 4 mL) was concentrated down to ~ 300 microliters by using the

same procedure. The blank was evaporated down to ~5 microliters with a stream of dinitrogen gas. The GC-MS spectra were obtained on an Agilent Technologies 6890 GC equipped with a 5973 MSD and a GS-Q column (30 m length, 0.32 mm I.D., 0 film.) at McMaster University. The GC-MS trace for the blank contained significant quantities of the contaminants 1-chloro-2-propenol, cyclohexene, toluene, o-xylene, p-xylene and two siloxanes, which are probably column bleed. Because the blank was found to contain p-xylene, we could not justify using p-xylene as a marker compound for our comparative study of the carbon isotope ratios for the two samples. The GC-MS traces for 11v and 11i each contained significant quantities of all of the contaminants found in the blank, along with a small amount of styrene and a substantial quantity of limonene. Determinations of $\delta^{13}\text{C}$ and δD were performed on the limonene in an attempt to establish its origin. For the δD analysis, the standards and the DCM extract for 11v were run on an HP 6890 gas chromatograph and a Finnegan Delta Plus XP IRMS. The column inside the GC was a 30 m, 0.32 mm diameter GSQ. The GC conditions were the following: Injector temperature 230 °C; splitless, 3 microliter manual injection; column flow 2.0 mL/min. Oven temperature was held at 100 °C for 1 minute, then the temperature was ramped at 20 °C/min up to 220 °C and then held at 220 °C for 45 minutes. To raise the concentration of limonene in each sample up to the appropriate level for the δD GC-IR-MS work, the extracts were further concentrated by solvent evaporation with dinitrogen gas. The volume for the dark, 11v after the second evaporation procedure was ~ 3 microliters, while that for the 11v was reduced to ~ 20 microliters. A limonene standard was run to verify the retention time and the δD for the authentic toluene sample was found to be -203.9 ‰, with -1.2 % RSD for three injections. A toluene standard from Fisher was run at different amplitudes to check the reproducibility of injections.

A set of limonene standards were prepared in order to evaluate the concentration of limonene in each extract.

SPME/GC-MS/GC-IR-MS extraction of polar organics and the subsequent analysis

In a typical extraction, a ~0.70 g-subsample of a given sample was taken from storage at – 28 °C and added expeditiously to a 50 mL round-bottomed flask containing 20 mL of ultrapure deionized water. The flask and its contents were allowed to achieve ambient temperature, the meteorite material was crushed into a fine powder with a glass rod and the resulting black suspension was heated at reflux (100 °C) for 6 h. The "cooked" suspension was then cooled, filtered through glass wool that had been scrupulously washed with distilled, deionized water, and the pH of the colorless filtrate increased to ~11 via the addition of 4 drops of ultrapure 6 M NaOH(aq) (prepared from Sigma-Aldrich Traceselect sodium hydroxide monohydrate and ultrapure water). This step converts all carboxylic acids present into their corresponding, non-volatile carboxylate salts. The volume of the filtrate was then reduced to ~1 mL on a rotary evaporator operating at 75 °C. In order to regenerate the acids, the pH of the concentrate was pushed below 2 by the addition of 4 drops of ultrapure 6 M HCl(aq)(prepared from Fisher Gold Label ultrapure concentrated HCl(aq)and ultrapure water). A subsequently prepared procedural blank was found to contain trace amounts (less than 1 ppm) of formic and acetic acid. The carboxylic acids in the concentrated extracts were determined by using solid phase micro extraction (SPME) in combination with an Agilent 6890N gas chromatograph (GC) equipped with a 5973 inert mass selective detector (MS). The column used was 30m, 0.25 µm and 0.25 mm id Nukol™, with helium flow maintained at 1.1 mL/min. The GC injection port was held at 210 °C, splitless. The GC oven was programmed at 35 °C hold for 1 minute, ramp at 25 °C/minute to 135 °C, ramp at 1.5 °C/minute to 185 °C and hold for 10 minutes. A Carbowax–

Polyethylene Glycol (PEG) coated fibre, 23 gauge, 1 cm, 60 μm film thickness was used to extract the carboxylic acids from the samples and standards. All samples and standards were in a total volume of 1.5 mL and treated in the same manner. The acids were adsorbed onto the fibre for 15 minutes with stirring and then desorbed into the GC injection port for 10 minutes. The samples were quantified via external calibration. A mixed standard was prepared containing all the linear monocarboxylic acids from C_1 to C_{10} . Calibration curves were prepared for each compound using five concentration levels. For samples 11h and 5b, each compound was quantified against the corresponding calibration curve using single ion extraction and the total micrograms on the fiber were calculated. A fiber blank was run and all samples were injected at least in duplicate (11h, 11i and 11v were injected 3x while 5b was injected 2x). The concentrations for the formic and acetic acid in samples 11v and 11i were quantified by referring the peak areas to standard curves using six concentration levels. As a representative example, we have provided the standard curve constructed for formic acid in Figure 3. The concentration for each of the longer chain homologues found in samples 11v and 11i was estimated by comparison of the peak area for the acid in the meteorite extract to a single standard solution for the acid run under the same conditions.

Carbon isotope analysis of the monocarboxylic acids in the four lithologies was accomplished by using the SPME methodology with GC-IR-MS, in the manner of Huang et al. (2005). Individual acids were separated by GC(Agilent 6890N), completely burned with molecular oxygen, and the combustion product, CO_2 gas, analyzed in a Finnigan DeltaPlus XP isotope ratio mass spectrometer. The GC conditions used for the GC-IR-MS analyses were the same as those used initially to obtain the standard GC-MS spectrum of the sample, viz. 5 min desorption in the GC injection port at 210 $^{\circ}\text{C}$, followed by temperature programming from 35 to

135 °C at 25 °C/min, to 185 °C at 1.5 °C/min and held for 10 min. The $\delta^{13}\text{C}$ values for the monocarboxylic acids are quoted relative to the VPDB standard. For samples 11v, 11h and 5b, $\delta^{13}\text{C}$ values were obtained for most of the members of the homologous series of linear carboxylic acids from C_1 to C_{10} . By contrast, for 11i, $\delta^{13}\text{C}$ values were obtained for just four of the C_1 - C_{10} linear monocarboxylic acid series as these were the only acids for which concentrations were sufficiently high for C isotopic analysis.

Hydrogen isotope analyses of the individual monocarboxylic acids in 5b were performed by combining SPME (polyethylene glycol fiber) with GCIRMS(Nukol column), following the method optimized by Huang et al. (2005). The carboxylic acids were separated on 30 m x 0.25 mm x 0.25 μm NUKOL column inside an HP 6890 GC at Brown University. The separated acids were then converted to H_2 in a pyrolysis furnace. Because the concentrations of the indigenous acids were very low for GC-IR-MS, a bath of dry ice and isopropanol was applied to the outside of the column just below the injector port as a means of minimizing loss of volatile acids. Also, in order to ensure that as many acids as possible produced peaks with acceptable signal-to-noise ratios, three consecutive SPME sorption desorption cycles were performed on aqueous extract prior to transfer into the column. The sample was analyzed in duplicate. The GC conditions used for the Hydrogen Isotope GCIRMS analyses were the same as those described above for the ^{13}C GCIRMS analyses. The δD values for the monocarboxylic are quoted with respect to the VSMOW standard. Not surprisingly, owing to the low sensitivity of the deuterium isotope, we were only able to obtain δD values for seven (two branched and five linear) of the 34 identified monocarboxylic acids in the aqueous extract of 5b. Sample size and acid concentrations limited analysis of monocarboxylic acid δD values to sample 5b. It should also be mentioned here that formic and propanoic acid coelute on the Nukol column that was used for the GCIRMS

determination of δD values. The δD value found for the amalgamated peak (708 ‰) is therefore the arithmetic combination of the two individual δD values for these acids. Owing to the nature of this technique, the individual δD values cannot be extracted from the combined value.

Amino acid extraction and analysis

Ultrapure (HPLC grade, 20 mL) water was added to each sample, and the resulting suspension was refluxed for six hours. The water extract was allowed to cool to room temperature and then split, with half used for amino acid concentration analysis, and the other half set aside for compound-specific isotopic analysis (reported in Glavin et al., 2012).

Concentrations were determined using Gas Chromatograph Mass Spectrometry (GC-MS) after amino acids were derivitized to form *N*-substituted acid amide esters for each amino acid; these esters dissolved in 0.500 mL dichloromethane were analyzed on an Agilent 5975C/7890A GC-MSD with a HP-5 (5%-phenyl)methyl polysiloxane column. A standard solution was prepared and analyzed along with the unknowns. Blanks were also analyzed.

Results

Reduced organics – GC-MS: By correlating the GC-MS empirical results to a comprehensive mass spectra data base we have been able to unambiguously identify numerous reduced organic compounds in the dichloromethane extracts of the four samples. The extract for 11v displays the greatest variety of organics, and the individual compounds themselves are present in significantly higher concentrations than the organic species observed in extracts of the other three samples. Thirty-two unique organic compounds in 11v were unambiguously identified, seven of which are likely terrestrial in origin. The chromatogram for 11v is shown in Figure 4. Long-chain saturated hydrocarbons and branched alkanes dominate the suite of extraterrestrial compounds in 11v (Table 1). Alkyl substituted benzenes and low molar mass PAHs are also

relatively plentiful. Findings similar to ours were reported by Gilmour (2003), Matrajt et al. (2004) and Pizzarello et al. (2001). The most abundant terrestrial contaminant present is oleamide, a plasticizer used in the manufacture of Ziploc bags. The concentration for the oleamide in 11v, which is estimated to be ~10 ppm, was obtained by comparing the peak area for the oleamide signal to that for a 20 ppm sample of authentic oleamide in dichloromethane. Since none of the other three specimens were stored in a Ziploc bag, all of their dichloromethane extracts were free of oleamide. Phthalate esters were observed in the GC traces for 11v and 5b. Phthalates and their ester derivatives are very common industrial pollutants and thus the phthalate esters found in these two samples are likely not indigenous but rather terrestrial contaminants. By comparison with the standards, the extract for 11h had the highest limonene concentration (~5 ppm), followed by 11v (3.5 ppm), 11i (2.5 ppm) and finally 5b (<0.1 ppm).

Weakly-polar organics - FTIR: The FT-IR spectrum for the brown ring obtained for specimen 11v (Figure 4a) is virtually identical to the “typical” Tagish Lake Meteorite FT-IR spectrum of Matrajt et al. (2004). The spectrum for the brown ring contains an envelope of peaks between ca. 2800 and 3000 cm^{-1} corresponding to the aliphatic C-H absorptions for the soluble organics in the meteorite. A band for free water appears at 1630 cm^{-1} , while the broad band centred at 3385 cm^{-1} indicates hydrogen bonded O-H groups. There are also some intriguing weak bands at 1788 and ca. 2500 cm^{-1} that we believe are absorptions for some of the soluble organics extracted from the meteorite. Initially, we thought that the colourless ring (Figure 4b), like the brown ring, would be made up of soluble organics from the meteorite. However, this proved not be the case, as the colourless ring is essentially pure oleamide. Also known as slip, oleamide is an unsaturated long-chain carboxylic acid amide. Plastic bags, such as Ziploc bags, are coated in their interiors with a film of oleamide to reduce the coefficient of friction, thereby making the bags easier to pull

open. The width of the ring indicates that there are more than just trace quantities of oleamide on the IR plate. This is corroborated by the size of the oleamide peak in the chromatogram for the same sample (Figure 3).

Weakly-polar organics – GC-IR-MS: The $\delta^{13}\text{C}$ GC-IR-MS spectra for 11i and 11v each contained a well-behaved set of three peaks for limonene that was well separated from the blank impurities. In each case, a small shoulder was visible in the tail of the limonene peak (Figure?). This shoulder raises concern about the presence of a small impurity that was not visible during GC-MS analysis. The limonene peaks were manually reintegrated to ensure a consistent integration between samples and consistent inclusion of this small shoulder. Manual reintegration did not change the $\delta^{13}\text{C}$ of the 11i sample at -27.9‰. Manual reintegration did change the $\delta^{13}\text{C}$ value for 11v by up to 1 ‰. The mean $\delta^{13}\text{C}$ of three runs of 11v was -28.5 ± 0.35 ‰ (1 σ standard deviation). However, the change observed during reintegration means that accuracy and precision can be assumed to be no better than 1 ‰ in the best case scenario. The presence of the peak shoulder does raise concern about this accuracy. However, the consistency of data between the two samples and the lack of limonene in the blank do indicate that the limonene is from the meteorite and that limonene in both lithologies is indistinguishable by isotopic analysis. This suggests a common origin for the limonene. ~~This work was successful in separation and isotopic analysis of limonene from the two lithologies as was our stated goal.~~ It is possible that a new GC column could improve this, but while the peak shapes were not ideal, the separation from other compounds was excellent using this column, with the exception of the small unknown shoulder. After completion of the C GC-IR-MS study, the origin of the limonene, however, remained enigmatic as ^{13}C values of -25 ‰ have been found for both

indigenous organics in meteorites and terrestrial organics (Becker et al., 1999; Pizzarello et al., 2001).

A δD value of -97.1 ‰ with an RSD of -14.5 % was found for twelve injections. The value found for the limonene in the dichloromethane extract of 11v was -170 ± 30 ‰. The amplitude for the limonene in the sample was very low, below the lowest standard, in fact, and thus the reproducibility was poor.

SPME/GC-MS: Complete lists of all of the water soluble compounds found in the water extracts of the four specimens (11v, 11i, 11h and 5b), in order of elution, are provided in Tables 1-4, and monocarboxylic acid concentrations and isotopic compositions are provided in Tables 5-8. Chromatograms are shown in Figure 5.

Amino acids: Concentrations determined for Tagish Lake samples 11h and 5b are shown in Figure 6, with results from Kminek et al. (2002) for comparison. Unlike Kminek et al. (2002), our analysis does not discriminate between the different enantiomers; in Figure 6, the D and L enantiomers of Kminek et al. (2002) are grouped together for ease of comparison with our results. The concentrations of all amino acids analyzed in sample 11h are greater than those obtained by Kminek et al. (2002). In sample 5b, only aspartic (Asp) and glutamic (Glu) acid are lower. Kminek et al. (2002) found that the analyzed aspartic and glutamic acids had L-enantiomeric excesses, indicating that the meteorite has been contaminated from a terrestrial source. The low concentrations of the other amino acids in the Kminek et al. (2002) results likely reflect leaching by lake water.

Discussion

Weakly polar organic compounds

All four extracts were found to contain limonene. Both the $\delta^{13}\text{C}$ and δD values found for the limonene in the dichloromethane extracts of samples 11i and 11v, namely $\delta^{13}\text{C} = -28.1 \pm 1$ per mil and $\delta\text{D} = -170 \pm 30$ per mil, together point to the limonene in these samples being a terrestrial contaminant and not an indigenous compound.

With the exceptions of limonene and oleamide, no concentration estimates based on standard curves were made for any of the other organics in the four dichloromethane extracts. Nonetheless, by referring to the typical GC response factors that have been found for these compounds on the Agilent GC-MS machine equipped with an inert mass selective detector, we have concluded that the organic compounds in 11v all have concentrations below 5 ppm, with most species being present in concentrations below 1 ppm. For 11i and 11h, with the exception of limonene, all of the compounds appear to have concentrations below 1 ppm. Interestingly, reduced organics are the most scarce in 5b, with only trace quantities of organics being found (each compound < 1 ppm). In general, very few indigenous, oxygen-containing organic compounds were found in the four extracts. None were conclusively detected in 11i while only one, viz. 4,4,6-trimethyl-2-cyclohexen-1-one, an unsaturated ketone, was observed in 11v. In 11h, a long-chain carboxylic acid (nonanoic acid), an aldehyde (nonanal), a ketone (2,6-dimethyl-4-heptanone) and two alcohols (phenol and 3,3-dimethyl-2-pentanol) were found. The only oxygen-containing organic compound in 5b is nonanoic acid. No nitrogen-containing compounds were detected in any of the four extracts. Finally, it should be noted for all of the specimens investigated, the largest peak in the GC-MS trace is not an organic species, but rather extraterrestrial cyclic octatomic sulfur, or S_8 . The S_6 allotrope was also detected in the dichloromethane extracts for 11h and 11i, but in substantially smaller concentrations.

A quick scan through Tables 2-4 inclusive reveals that samples 11i and 11h have the same types of reduced organics as were found in 11v, with, of course, the exception of oleamide. In the extract for 5b, on the other hand, the only reduced organics present are low molecular weight PAHs and alkyl-substituted benzene compounds. Somewhat surprisingly, there are no alkanes present in the chromatogram for 5b. Moreover, the concentrations for the organic compounds 11h and 5b are much smaller than those in 11v and 11i.

The low concentrations found for the hydrocarbons in 5b and 11h suggests that virtually all original hydrocarbon molecules in these specimens have been oxidized, presumably by aqueous alteration pathways. Interestingly, the water extracts for 11h and 5b both contain relatively high concentrations of phenol and benzoic acid. The water extract for 5b also contains seventeen mono, di and tri-substituted alkyl phenols in its inventory. What appears to have happened in these stones is that oxidation during aqueous alteration has converted the original linear and branched alkanes into monocarboxylic acids, while the oxidation of the primordial benzene and alkylbenzenes has afforded benzoic acid, various alkylbenzoic acids, phenol and alkyl-substituted phenols, which all ended up in the water extracts. Presumably, some of the phenols and benzoic acid molecules were oxidized all the way to $(\text{CO}_3)^{2-}$, which then became incorporated into the matrix as carbonate. There are numerous reports in the literature concerning the oxidation of hydrocarbons that support this thesis. The study of the reactivity of the monocyclic aromatic compound toluene over iron oxide/iron sulfide mineral assemblages in high temperature aqueous solutions generated phenol, cresols and benzoic acid, all of which have been found in 11h and 5b [McCollum et al]. Furthermore, [Yohiro et al] were successful in oxidizing alkylbenzenes to their corresponding alkylbenzoic acids with a transition-metal oxide catalyst, while avoiding the production of dicarboxylic acids, which were absent in water extracts for 11h and 5b. McCollum et al were also

able to demonstrate that prolonged heating of benzoic acid generates CO₂ and benzene. This thermal decarboxylation reaction may well have been responsible for generating the bicarbonate which ultimately became trapped as carbonate minerals inside the Tagish Lake specimens.

It is worth noting that benzene was not observed in the DCM extracts of either 11h or 5b. Any free benzene present in these samples would have been extracted by the DCM as like DCM, benzene is only weakly polar. One possible explanation for its absence is that, once formed, any benzene would rapidly oxidize to phenol in the wet environment that lead to the formation of the benzene through the decarboxylation of the benzoic acid precursor. Interestingly, recently, [Fraga-Debruiel et al] were able to convert benzoic acid to phenol via benzene by passing hot aqueous solutions of benzoic acid over various catalytically-active metal oxide surfaces, such as NiO, CuO and Al₂O₃, mimicking what we believe has occurred inside the samples of 11h and 5b.

Taken together, the GC-MS evidence suggests that the original reduced organic compounds in 11h and 5b, viz. the alkanes, benzene and alkylbenzenes, have been sequentially oxidized, first to alcohols, then to carboxylic acids and, in some instances, ultimately to carbonate, the most highly oxidized carbon compound, thereby explaining the low abundances for hydrocarbons in these two samples. Only tiny concentrations of alkylbenzenes as well as branched and linear alkanes have been found in the most highly altered sample 11i. These compounds all have a very limited solubility in water, even above 100°C [CRC Handbook of Chemistry and Physics, 2003], and thus they are all the reduced organics that were left behind in the matrix of 11i after the pulses of hot water converted the majority of the ancestral alkylbenzenes and alkanes into benzoic acids and carboxylic acids, respectively, which, have been detected in the water extracts for 11i.

[Relationship to IOM? See Conel's paper...]

Monocarboxylic acids

It is now well established that insoluble polycyclic aromatic hydrocarbons can be readily oxidized to monocarboxylic acids and dicarboxylic acids by water when they are in contact with the surfaces of metal oxide catalysts [see for instance, [Djuricic et al, "Organic acids obtained by alkaline permanganate oxidation of kerogen from Green River (Colorado) shale", *Geochimica and Cosmochimica Acta*, Vol. 35, Issue 12, December 1971, p. 1201-1207]. More recently the oxidation of the insoluble organic matter within carbonaceous chondrites has been investigated with a view towards gaining a better understanding of the molecular architectures within these solids. Remusat et al, [*Geochimica and Cosmochimica Acta*, Vol. 69 p.4377-4388, 2005] were the first group to use RuO₄-water slurries to oxidatively degrade the aromatic cores of the IOM of the Murchison and Orgueil meteorites to a complex mixture of hydroxyl, di and tri carboxylic acids. The absence of any low molecular weight monocarboxylic acids in the product mixture was interpreted as evidence of there being very few, if any, aliphatic side chains present in the material. When Huang et al, [*Earth and Planetary Science Letters*, Vol. 259, p. 517-525 (2007) and *Geochimica and Cosmochimica Acta*, Vol. 75, p. 2309-2323, 2011] combined the RuO₄ oxidation procedure with the SPME methodology for the direct sorption of low molecular weight carboxylic acids they found that there were, indeed, aliphatic side chains in the IOM samples analyzed and that these side chains had been stripped out of the IOM and converted to monocarboxylic acids. Since other studies have found evidence of short-chain side groups in Murchison and Orgueil IOM samples, the likely reason that Resumusat et al failed to detect any short-chain carboxylic acids in their product mixtures is that they were lost during the subsequent work-up, which retains the acids in their volatile, molecular forms. The fact that both branched and linear monocarboxylic acids were found in the studies by Hunag et al indicates that the side chains themselves come in both linear and branched varieties. Most interestingly, the isotope numbers for the monocarboxylic acids derived from the oxidative cleavage of the side chains in the IOM proved to be very similar to the values found for the free, water soluble monocarboxylic acids in the meteorites. These findings do strongly suggest that either the aliphatic side chains and the monocarboxylic acids have a common chemical ancestor, or the free monocarboxylic acids within the meteorite, with the exception of formic acid, which cannot be produced by the oxidation of IOM, are the result of the oxidation of a fraction of the original aliphatic side chains.

At least eleven monocarboxylic acids have been positively identified in the aqueous extract of 11v including most of the members of the homologous series of linear, saturated monocarboxylic acids from C₁ to C₁₀, two branched, saturated monocarboxylic acids, an unsaturated, branched monocarboxylic acid and the aromatic carboxylic acids benzoic acid and 4-methylbenzoic acid (See Table 5). It is noteworthy that the concentrations of the straight-chain carboxylic acids decrease in a logarithmic manner as the carbon number grows. The only other polar, oxygen-containing organics identified in this extract were butyrolactone and the phenyl ester of carbamic acid. The N-containing ring compound 1H-pyrazole, was also found in the extract of 11v. Natural products containing the pyrazole ring are very rare, and very little 1H-pyrazole is produced industrially. Thus, it is possible that the 1H-pyrazole has an extraterrestrial origin. Comparison of the area of the peak to the signal for a 10 ppm aqueous solution of authentic pyrazole allowed us

to conclude that the pyrazole concentration in the 11v extract falls between 5 and 10 ppm. The chromatograms for the water extracts of 11i and 11h are closely comparable to that for 11v (Tables 6 and 7). In both 11i and 11h, carboxylic acids are again the dominant compounds, and, as with 11v, the straight-chain carboxylic acid abundances fall logarithmically with increasing chain length. Examples of branched and aromatic carboxylic acids are also seen in both of the extracts. As was observed for the 11v extract, the chromatograms for 11i and 11h display a clear predominance of straight-chain acids over branched isomers. Butyrolactone was identified in 11i and the contaminants found in 11i and 11h closely match those detected in 11v. The trace for the extract of 5b is markedly different from the other three (Table 8). First of all, there are more branched than linear monocarboxylic acids in the trace for 5b (17 branched versus 11 linear MCAs). In fact, owing to the large number of different types of branched isomers, it would appear that the abundances for the branched and linear carboxylic acids are comparable, which is not the case for the other three lithologies, which have linear carboxylic acids in much greater abundances. The extract for 5b is also distinct from the other three in that it contains appreciable concentrations of no less than sixteen alkyl-substituted phenols in addition to phenol itself. Neither phenol nor any of its alkyl-substituted derivatives are present in the aqueous extracts of 11i and 11v. A small amount of phenol was found in the extract for 11h. Furthermore, significantly higher concentrations and a much greater variety of monocarboxylic acids, including many branched isomers, were detected in the water extract for 5b.

The identities of most of the straight-chain monocarboxylic acids from C₁-C₁₀ and benzoic acid were unequivocally established by comparison of their mass spectra/GC retention times to those for authentic samples of the acids. In spite of its lower boiling point, formic acid has a larger retention time than acetic acid. This is caused by formic acid binding more strongly to the stationary phase than acetic acid. The concentrations of the formic and acetic in each water extract was quantified by referring the peak area to aqueous acid standard curves. We have found unusually high formic acid concentrations in the present study of Tagish Lake: (11v) 200 ppm, (11i) 120 ppm, (11h) 156 ppm and (5b) 178 ppm. It is our assertion that these anomalously large concentrations are the result of a confluence of the following factors: a) The Tagish Lake meteorite has been kept below 0°C since its recovery, which has minimized loss of volatile organics such as formic acid, and b) by analyzing an external standard mixture containing of all of the straight-chain acids present in the meteorite, and by subsequently spiking a subsample of the standard mixture with neat formic acid, we were able to ascertain that the response factor for monocarboxylic acids run on a GCMS(quadrupole) instrument increases asymptotically with increasing chain length and that the response factor for formic acid in this methodology is less than 0.01 of that for the long-chain acid nonanoic acid. Very similar GCMS(quadrupole) response factors were found by a chemical pathology research group in the U.K. during their study of short-chain monocarboxylic acids[Mills et al 1999]. The discovery that formic acid has a very low response factor when run on either a GCMS(quadrupole) or a GC-FID suggests that previous studies on carbonaceous chondrites may have dramatically underestimated the quantities of formic acid present.

For the extracts of 11v, 11h and 11i, formic acid is, by a wide margin, the most abundant monocarboxylic acid. These results are in stark contrast to all previous studies in which it was concluded that formic acid concentration was the lowest or one of the lowest of those monocarboxylic acids present in the extract[Huang et al 2001, Shimoyama et al 1986, Yuen et al, 1984, Naroka et al 1999].

The acetic acid concentration in 5b is actually slightly higher than that for formic acid, although both are present in much higher concentrations than any of the longer chain homologues. This is the second instance where 5b has displayed different concentration profiles from the other specimens, with the first being the aforementioned paucity of reduced organics in the dichloromethane extract for this lithology.

The $\delta^{13}\text{C}$ values for the monocarboxylic acids in the four lithologies show some variation, although all four specimens have a common value of ca. -20 per mil for formic acid and the higher homologues approach a constant value of ca. -25 per mil at nonanoic acid with increasing carbon number. (see Figure 8) (Insert Figure 8 here(C Isotopic Composition of Monocarboxylic Acids in the Tagish Lake meteorite.) Interestingly, for specimen 11h, the $\delta^{13}\text{C}$ decreases steadily with increasing carbon number. This trend suggests that the homologous series of carboxylic acids in 11h were formed by the sequential... **(over to you Chris)**. The acid with the greatest range of $\delta^{13}\text{C}$ values is acetic acid, which spans from + 8 per mil(11h) to -36 per mil(5b).

In spite of the fact that the $\delta^{13}\text{C}$ values fall within the range of terrestrial organics, the monocarboxylic acids in 5b, at least, are enriched in deuterium, with δD ranging from + 247 to + 581 per mil, which strongly supports an extraterrestrial origin for these compounds and indicates that contamination by terrestrial monocarboxylic acids, which have negative δD values[22, 23], has largely been avoided. In fact, large positive δD values for organics are now considered to be essentially conclusive proof of an origin beyond the earth[Huang et al 2005, 24]. In detail, specimen 5b shows some evidence of having undergone parent body processing, consistent with petrography. The isotopically light acetic acid found in this specimen is consistent with experimental studies of oxidation and hydrothermal alteration of IOM, which demonstrate that a) acetic acid is the dominant product of IOM degradation (Oba and Naraoka (Cronin et al., 1988; Oba and Naraoka, 2006) and b) MCAs derived from modification of IOM have $\delta^{13}\text{C}$ values that are significantly lighter than their IOM counterparts (Huang et al., 2007), especially for acetic acid (Oba and Naraoka, 2006).”

Amino acids [needs work, but only a little bit; refer to Glavin et al. 2012]

Notably, our samples have significant concentrations of aminoisobutyric acid (AIB) and α -amino-n-butyric acid (α -ABA), both of which are non-biological. The presence of these amino acids, our low blanks, and the overall high concentrations of amino acids strongly suggest that we have analyzed the intrinsic complement of amino acids in the Tagish Lake meteorite.

Another notable aspect of our results is that there are significant differences in concentration between samples 5b and 11h, with concentrations of all amino acids in sample 11h higher than in sample 5b with the exception of alanine (Ala). The concentration of glycine (Gly) in sample 11h is nearly three times greater than in sample 5b. The mineralogy and petrology of sample 11h may reflect a greater degree of parent body hydrothermal alteration; the observation of higher concentrations of amino acids in this lithology suggests that parent body processes play

a role in the production of amino acids, e.g., by Strecker-cyanohydrin synthesis or other parent body processes (see Botta and Bada, 2002 for a review).

The complement of Tagish Lake amino acids show similarities to results from both CI and CM chondrite meteorites. A comparison is shown in Figure 2.

In CM chondrites, glycine, AIB and isovaline are most abundant, whereas in CI chondrites, β -alanine is most abundant, followed by glycine (Ehrenfreund et al., 2001). Tagish Lake appears to be similar to both – in sample 11h (Figure 2), glycine is most abundant, followed by valine; in sample 5b, glycine is most abundant, followed by α - and β -alanine. In terms of total concentration of amino acids, Tagish Lake (4400 ppb; sample 11h) is most similar to CI chondrites, in which the total concentration is ~ 4000 ppb (Ehrenfreund et al., 2001).

The results of our analysis of amino acid concentrations in pristine Tagish Lake meteorites strongly indicate that amino acids in these samples have not been significantly affected by terrestrial contamination through exposure to meltwater. The complement of amino acids in Tagish Lake shows similarities to both CI and CM chondrites. Variations in the relative proportions and total concentrations of amino acids between two pristine samples with different mineralogical and petrological characteristics support the role of parent body alteration in the production of amino acids.

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Tables

Table 9: Selected Monocarboxylic Acids in Tagish Lake specimen 5b

Compound	C conc. (ppm)	δ $^{13}\text{C} \pm \text{S.D.}$ (per mil)	$\delta \text{ D} \pm$ S.D. (per mil)	Compound Number	Relative GC Response Factors
formic acid*	1 78	- 22 ± 1	$708 \pm$ 20	1	1
acetic acid	2 50	- 36 ± 1	$247 \pm$ 5	2	2.5
propanoic acid*	8. 2	- 24 ± 3	$708 \pm$ 20	3	5.7
isobutanoic acid	< 5	* *	$493 \pm$ 12	4	*
butanoic acid	5. 7	- 25 ± 2	$562 \pm$ 1	5	11
isopentanoic acid	* *	* *	$697 \pm$ 2	6	*
hexanoic acid	4. 5	- 29 ± 1	**	7	55
octanoic acid	1. 6	- 29 ± 1	**	8	195
nonanoic acid	0. 62	- 28 ± 5	**	9	281
decanoic acid	0. 04	- 24 ± 5	**	10	395
2- methypropanoic acid	* *	* *	**	12	**

2-methylbutanoic acid	*	*	**	13	**
3-methylbutanoic acid	*	*	**	14	**
3,3-dimethylbutanoic acid	*	*	**	15	**
2,2-dimethylbutanoic acid	*	*	**	16	**
2(E)-butenoic acid	*	*	**	17	**
2-ethylpentanoic acid	*	*	**	18	**
2-methylpentanoic acid	*	*	**	19	**
2,2-dimethylpentanoic acid	*	*	**	20	**
3-methylpentanoic acid	*	*	**	21	**
2(Z)-butenoic acid	*	*	**	22	**
4-methylpentanoic acid	*	*	**	23	**
2-ethyl, 2-methylpentanoic acid	*	*	**	24	**
2-methylhexanoic acid	*	*	**	25	**
3-methylhexanoic acid	*	*	**	26	**
4-methylhexanoic acid	*	*	**	27	**

2-ethylhexanoic acid	*	*	**	28	**
heptanoic acid	*	*	**	29	**
2-methylheptanoic acid	*	*	**	30	**
3-methylheptanoic acid	*	*	**	31	**
benzoic acid	*	*	**	32	**
2-methylbenzoic acid	*	*	**	33	**
3-methylbenzoic acid	*	*	**	34	**
4-methylbenzoic acid	*	*	**	35	**
dimethylbenzoic acid	*	*	**	36	**
benzeneacetic acid	*	*	**	37	**
ethylbenzoic acid	*	*	**	38	**
dimethylbenzoic acid	*	*	**	39	**

* = formic acid and propanoic acid coelute on the IRMS column

** = not determined

Total abundance for those MCAs in 5b whose concentrations were estimated via comparison to external standards: ca. 454 ppm.

Table 10: Selected Monocarboxylic Acids in Tagish Lake specimen 11h

Compound	Conc. (ppm)	$\delta^{13}\text{C} \pm \text{S.D.}$ (‰)	Number	Relative GC Response Factors
formic acid	155.5	-19 ± 2	1	1
acetic acid	110.4	8 ± 2	2	2.5
propanoic acid	26.1	1 ± 7	3	5.7
isobutanoic acid	*	*	4	*
butanoic acid	6	-5 ± 6	5	11
hexanoic acid	1.3	*	6	55
octanoic acid	0.8	*	7	195
nonanoic acid	0.2	-25 ± 5	8	281
decanoic acid	0.1	-2 ± 5	9	395
benzoic acid	*	*	10	*

* = not determined

Total abundance for those MCAs in 11h whose concentrations were estimated via comparison to external standards: ca. 301 ppm.

Table 11: Selected Monocarboxylic Acids in Tagish Lake specimen 11i

Compound			Number	Relative GC response factors
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	Conc. (ppm)	$\delta^{13}\text{C} \pm$ S.D. (‰)		
formic acid	120	-22 ± 1	1	1
acetic acid	42	-27 ± 4	2	2.5
propanoic acid	2	*	3	5.7
isobutanoic acid	*	*	4	*
butanoic acid	0.6	-23 ± 1	5	11
hexanoic acid	0.4	*	6	55
octanoic acid	0.1	*	7	195
nonanoic acid	0.4	-25 ± 5	8	281
decanoic acid	< 0.01	*	9	395
benzoic acid	*	*	10	*
4- methylbenzoic acid	*	*	11	*

* = not determined

Total abundance for those MCAs in 11i whose concentrations were estimated via comparison to external standards: ca. 166 ppm

Table 12: Selected Monocarboxylic Acids in Tagish Lake specimen 11v

Compound	Conc. (ppm)	$\delta^{13}\text{C} \pm$ S.D. (‰)	N umber	Relative GC Response Factors
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formic acid	200	-21 ± 2	1	1
acetic acid	46	-18 ± 4	2	2.5
propanoic acid	3.5	-15 ± 8	3	5.7
isobutanoic acid	*	*	4	*
butanoic acid	0.8	-21 ± 1	5	11
isopentanoic acid	*	*	6	*
hexanoic acid	0.4	-27 ± 5	7	55
octanoic acid	0.08	*	8	195
nonanoic acid	0.2	-27 ± 4	9	281
decanoic acid	< 0.01	-17 ± 4	10	395
benzoic acid	*	*	11	*
3-methylbenzoic acid	*	*	12	*

* = not determined

Total abundance for all linear monocarboxylic acids in 11v: ca. 251 ppm.

Table 1: Aliphatic and Aromatic Compounds(Reduced Organics) in 11v

Compound	Conc. (ppm)	Number
limonene *, ^a	3.5	1
oleamide *, ^b	ca.10	2
2-Iodo-1,3-dihydroxybenzene*	**	3
n-Hexadecanoic acid*	**	4
Diethyl Phthalate*	**	5
Benzoic acid, 2,5-dinitro-*	**	6
1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl)*	**	7
Benzene, 1,3,5-trimethyl-	**	8
Benzene, 1-ethyl-2-methyl-	**	9
Decane, 2,2,7-trimethyl-	**	10
Benzene, 1-methyl-2-(1-methylethyl)-	**	11
Undecane, 3,6-dimethyl-	**	12
Nonane, 2,2,3-trimethyl-	**	13
Cyclopentane, heneicosyl-	**	14
Hexadecane	**	15
Heptylcyclohexane	**	16
Tridecane, 5-propyl-	**	17
1,1'-Biphenyl, 2,2'-diethyl-	**	18
Tetradecane, 2,2-dimethyl-	**	19
Pentacosane	**	20
Cyclopentane, undecyl-	**	21
Tridecane, 5-propyl-	**	22
Hexadecane, 3-methyl-	**	23
Heptadecane	**	24
Cyclopentane, 1,2,3-trimethyl-	**	25
Hexacosane	**	26
n-Nonylcyclohexane	**	27
Heptane, 2,4-dimethyl-	**	28
Pentadecane, 7-methyl-	**	29
Tetradecane,	**	30
Tetratetracontane	**	31
Heptadecane, 2,6,10,14-tetramethyl-	**	32
Cyclotetradecane	**	33
Pentadecane, 2,6,10-trimethyl-	**	34
Undecane, 3,6-dimethyl-	**	35
Benzene, (1-methylpropyl)-	**	36
Decane, 2,2-dimethyl-	**	37
Benzene, 2-ethyl-1,4-dimethyl-	**	38
Undecane	**	39

Table 2: Aliphatic and Aromatic Compounds(Reduced Organics) in 11i

Compound	Conc. (ppm)	Number
limonene ^{*, a}	2.5	1
1,2-Benzenedicarboxylic acid, monobutyl ester [*]	**	2
Benzene, 1-ethyl-2,3-dimethyl-	**	3
Decane, 2,2,7-trimethyl-	**	4
p-Xylene	**	5
Ethylbenzene	**	6
2,4,4-Trimethyl-1-hexene	**	7
Octane, 2,5,6-trimethyl-	**	8
Benzene, (1-methylethyl)-	**	9
Benzene, 1,2,3-trimethyl-	**	10
Heptane, 2,2,4,6,6-pentamethyl-	**	11
Benzene, 1-ethyl-3,5-dimethyl-	**	12
Tridecane, 6-methyl-	**	13
Pentane, 2,2,3,4-tetramethyl-	**	14
Heptane, 2,2,4-trimethyl-	**	15
Decane, 3,8-dimethyl-	**	16
2-Cyclohexen-1-one, 4,4,6-trimethyl-	**	17

* = Terrestrial contaminant;

a $\delta^{13}\text{C} = -28.1 \pm 1$ per mil, $\delta\text{D} = -170 \pm 30$ per mil; ** Not determined

Table 3: Aliphatic and Aromatic Compounds (Reduced Organics) in 11h

Compound	Conc. (ppm)	Number
limonene*, ^a	ca. 5	1
Phenol	**	2
Nonanal	**	3
Nonanoic acid	**	4
3,3-Dimethyl-2-pentanol	**	5
4-Heptanone, 2,6-dimethyl-	**	6
Naphthalene	**	7
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	**	8
Pentadecane, 6-methyl-	**	9
Decane, 2,2,6-trimethyl-	**	10
Heptane, 4-ethyl-2,2,6,6-tetramethyl-	**	11
Octane, 2,6-dimethyl-	**	12
Cyclopentene, 1,2,3,3,4-pentamethyl-	**	13
Styrene	**	14
o-Xylene	**	15
p-Xylene	**	16
Benzene, propyl-	**	17
Decane, 2,6,8-trimethyl-	**	18
Benzene, 1,3,5-trimethyl-	**	19
Benzene, 1,2,3-trimethyl-	**	20
Benzene, 1-ethyl-2-methyl-	**	21
Nonane, 3-methyl-5-propyl-	**	22
Octane, 2,6-dimethyl-	**	23
Heptane, 4-ethyl-2,2,6,6-tetramethyl-	**	24
Decane, 3,7-dimethyl-	**	25

* = Terrestrial contaminant; ** Not determined

a $\delta^{13}\text{C} = -28.1 \pm 1$ per mil, $\delta\text{D} = -170 \pm 30$ per mil;

Table 4: Aliphatic and Aromatic Compounds(Reduced Organics) in 5b

Compound	Conc. (ppm)	Number
limonene*, ^a	< 0.1	1
Phthalic acid, 2-methoxyethyl undecyl ester *	**	2
Nonanoic acid	**	3
Naphthalene, 2-methyl-	**	4
Naphthalene, 1,7-dimethyl-	**	5
Naphthalene, 1,4-dimethyl-	**	6
Naphthalene, 1,8-dimethyl-	**	7
Naphthalene, 1,6-dimethyl-	**	8
Naphthalene, 2,3,6-trimethyl-	**	9
Naphthalene, 2-methyl-	**	10
Naphthalene, 1-methyl-	**	11
Naphthalene, 1-ethyl-	**	12
Naphthalene, 2,6-dimethyl-	**	13
Naphthalene,1,5-dimethyl-	**	14
Naphthalene,2,3-dimethyl-	**	15
Pyrene	**	16
Biphenyl	**	17
Fluorene	**	18
1-(2,2-Dimethylcyclopropyl)-2-phenylacetylene	**	19
Benzene, pentamethyl-	**	20
Benzocycloheptatriene	**	21
Benzene, hexamethyl-	**	22
Benzene, 1,2-bis(1-methylethyl)-	**	23
Benzene, hexamethyl-	**	24

* = Terrestrial contaminant; ** Not determined

a $\delta^{13}\text{C} = -28.1 \pm 1$ per mil, $\delta\text{D} = -170 \pm 30$ per mil;

Table 5: Complete list of water-soluble compounds extracted from 11v

Compound	Number
2-methoxyethanol*	1
2-chloroethanol*	2
acetic acid	3
formic acid	4
propanoic acid	5
2-methylpropanoic acid	6
2,2-dimethylpropanoic acid	7
butanoic acid	8
2-propenoic acid	9
butyrolactone	10
2-(2-chloroethoxy) ethanol*	11
1H-pyrazole	12
hexanoic acid	13
carbamic acid phenyl ester	14
octanoic acid	15
nonanoic acid	16
decanoic acid	17
benzoic acid	18
3-methylbenzoic acid	19
S ₆	20

* Terrestrial contaminant

Table 6: Complete list of water-soluble compounds extracted from 11i

Compound	Number
2-methoxyethanol*	1
2-chloroethanol*	2
acetic acid	3
formic acid	4
propanoic acid	5
2-methylpropanoic acid	6
2-(2-methoxyethoxy)ethanol*	7
butyrolacetone	8
2-(2-chloroethoxy)ethanol*	9
hexanoic acid	10
octanoic acid	11
nonanoic acid	12
benzoic acid	13
decanoic acid	14
4-methylbenzoic acid	15
S ₆	16

* Terrestrial contaminant

Table 7: Complete List of the Water-Soluble Compounds extracted from 11h

Compound	Number
acetic acid	1
formic acid	2
propanoic acid	3
2-methylpropanoic acid	4
butanoic acid	5
pentanoic acid	6
3,5-bis(trifluoromethyl) pyrazol	7
hexanoic acid	8
phenol	9
octanoic acid	10
nonanoic acid	11
n-decanoic acid	12
benzoic acid	13
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	14

Table 8: Complete list of the water-soluble compounds extracted from 5b

Number	Compound	Number	Compound
1	acetic acid	30	ethylphenol
2	propanoic/formic acid	31	dimethylphenol
3	2-methypropanoic acid	32	dimethylphenol
4	butanoic acid	33	4-methylphenol
5	2-methylbutanoic acid	34	3-methylphenol
6	3-methylbutanoic acid	35	nonanoic acid
7	3,3-dimethylbutanoic acid	36	2,3-dimethylphenol
8	2,2-dimethylbutanoic acid	37	2-ethyl-5-methylphenol
9	2(E)-butenoic acid	38	ethylmethylphenol
10	pentanoic acid	39	dimethylphenol
11	2-ethylbutanoic acid	40	trimethylphenol
12	2-methylpentanoic acid	41	methylethylphenol
13	2,2-dimethylpentanoic acid	42	trimethylphenol
14	3-methylpentanoic acid	43	dimethylphenol
15	2(Z)-butenoic acid	44	decanoic acid
16	4-methylpentanoic acid	45	trimethylphenol
17	2-ethyl, 2-methylpentanoic acid	46	trimethylphenol
18	1H-imidazole	47	ethylmethylphenol
19	hexanoic acid	48	tetrahydroquinoxaline
20	2-methylhexanoic acid	49	benzoic acid
21	3-methylhexanoic acid	50	2-methylbenzoic acid
22	4-methylhexanoic acid	51	3-methyl-2-thiophenecarboxylic acid
23	2-ethylhexanoic acid	52	3-methylbenzoic
24	heptanoic acid	53	4-methylbenzoic
25	2-methylheptanoic acid	54	Methyl-2-thiophenecarboxylic acid
26	3-methylheptanoic acid	55	dimethylbenzoic acid
27	2-methylphenol	56	benzeneacetic acid
28	phenol	57	ethylbenzoic
29	octanoic acid	58	dimethylbenzoic acid

Figures

Figure 1. Photos of specimens

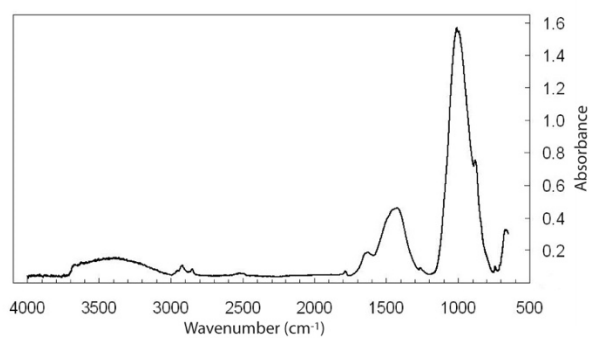


Figure 2 IR spectrum of the DCM casts of the brown ring (A) and colourless ring (B)

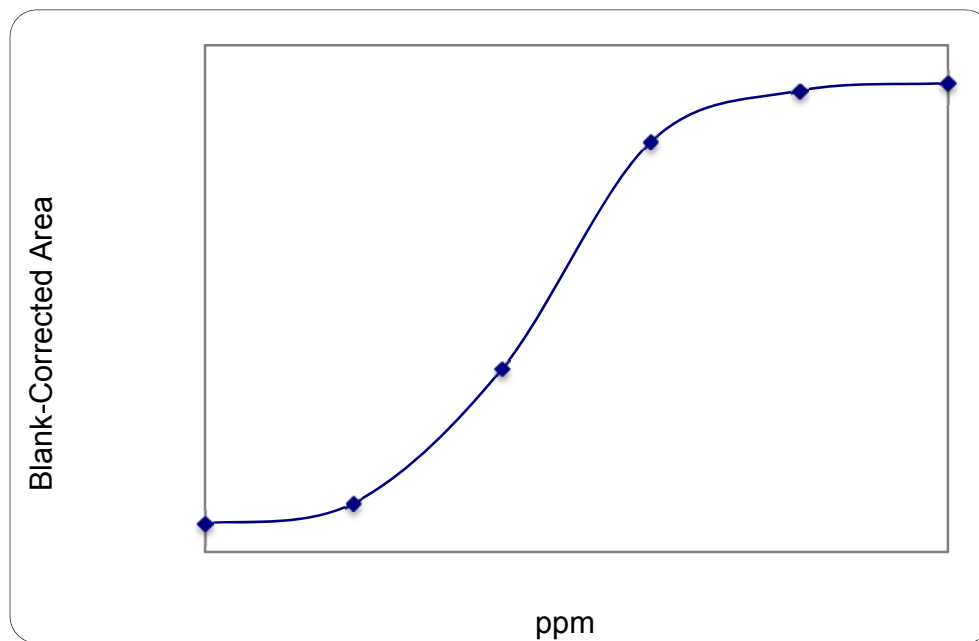


Figure 3. Blank-corrected Formic Acid Concentration Response

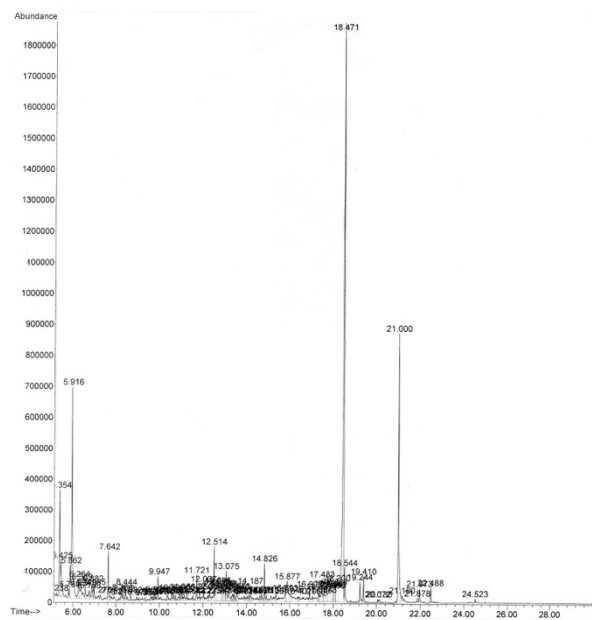


Figure 4. GC-MS trace for the DCM extract [highlight oleamide and S8].

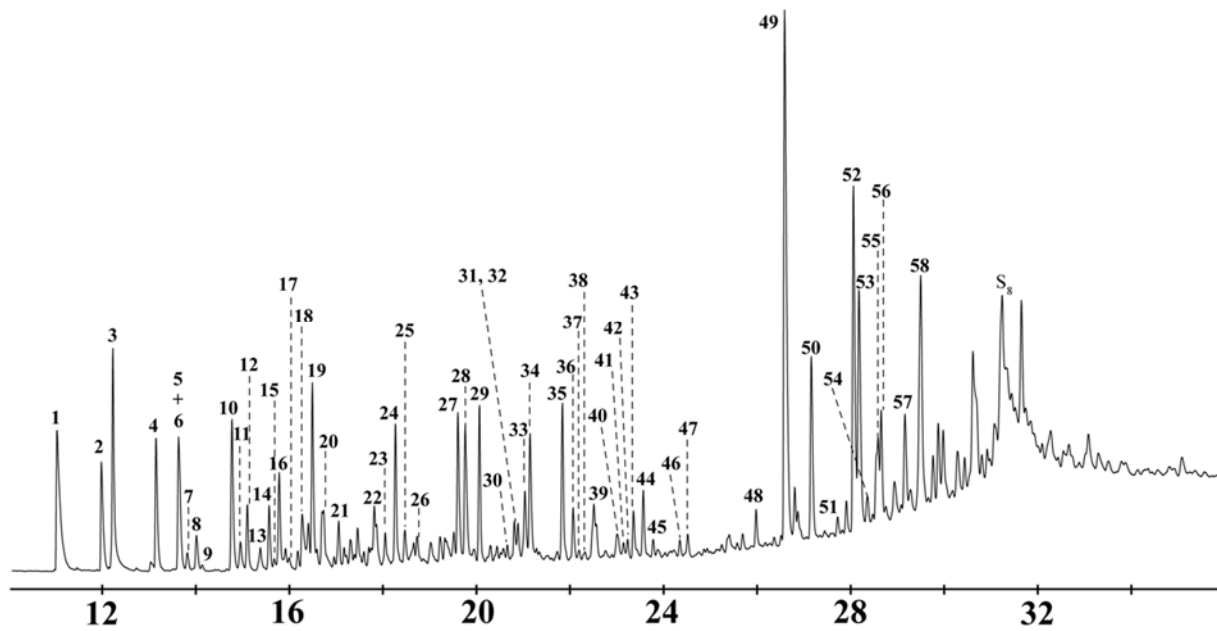


Figure 5a: GCMS (Quadrupole) Chromatogram of the Concentrated Water Extract of (5b)

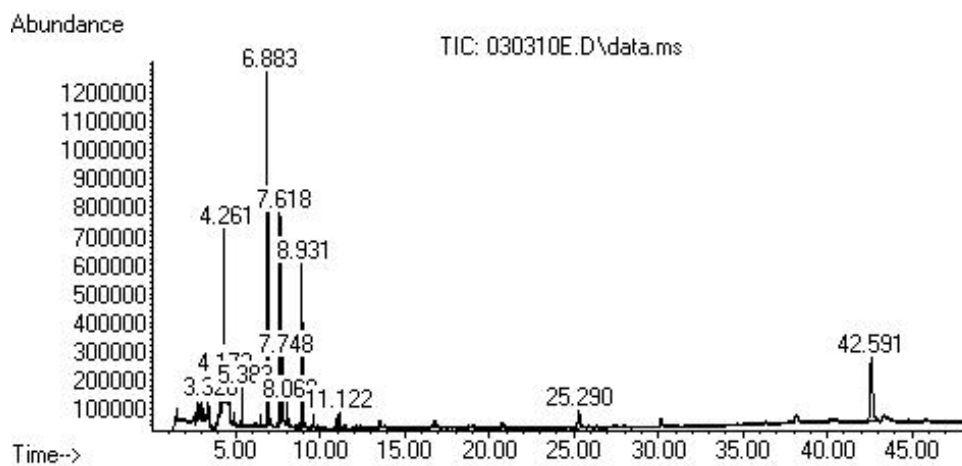


Figure 5b: GCMS (Quadrupole) Chromatogram of the Concentrated Water Extract of (11h)

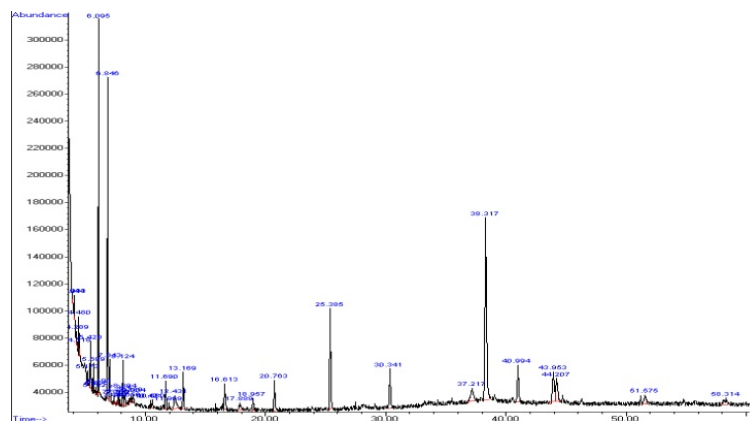


Figure 5c: GCMS (Quadrupole) Chromatogram of the concentrated water extract of (11i)

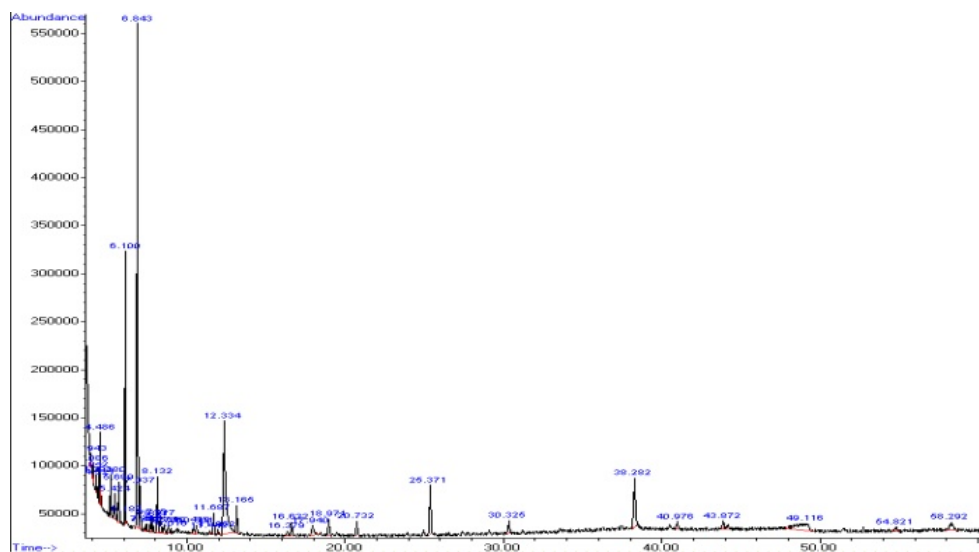


Figure 5d: GCMS (Quadrupole) Chromatogram of the Concentrated Water Extract of (11v)

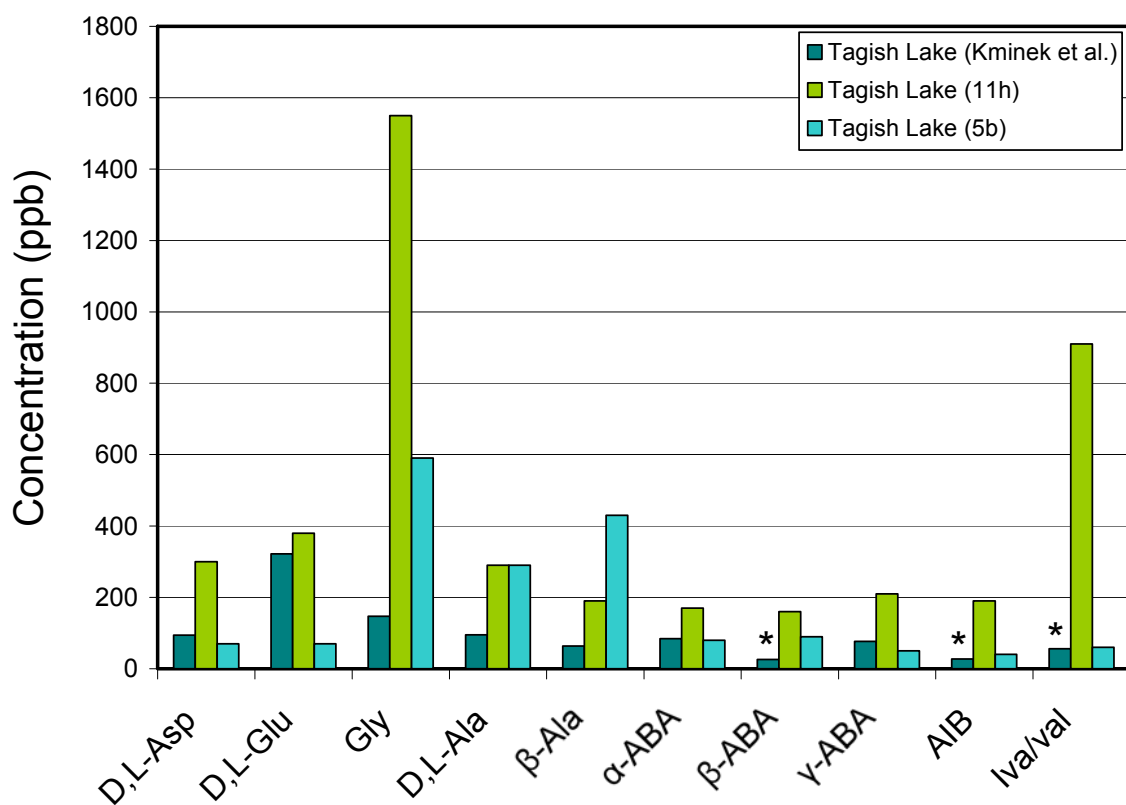


Figure 6. Amino acids abundances in the Tagish Lake meteorite. Data from Kminek et al (2002) is for meteorite material exposed to lake water. Asterisks (*) denote where concentrations are maximum values.

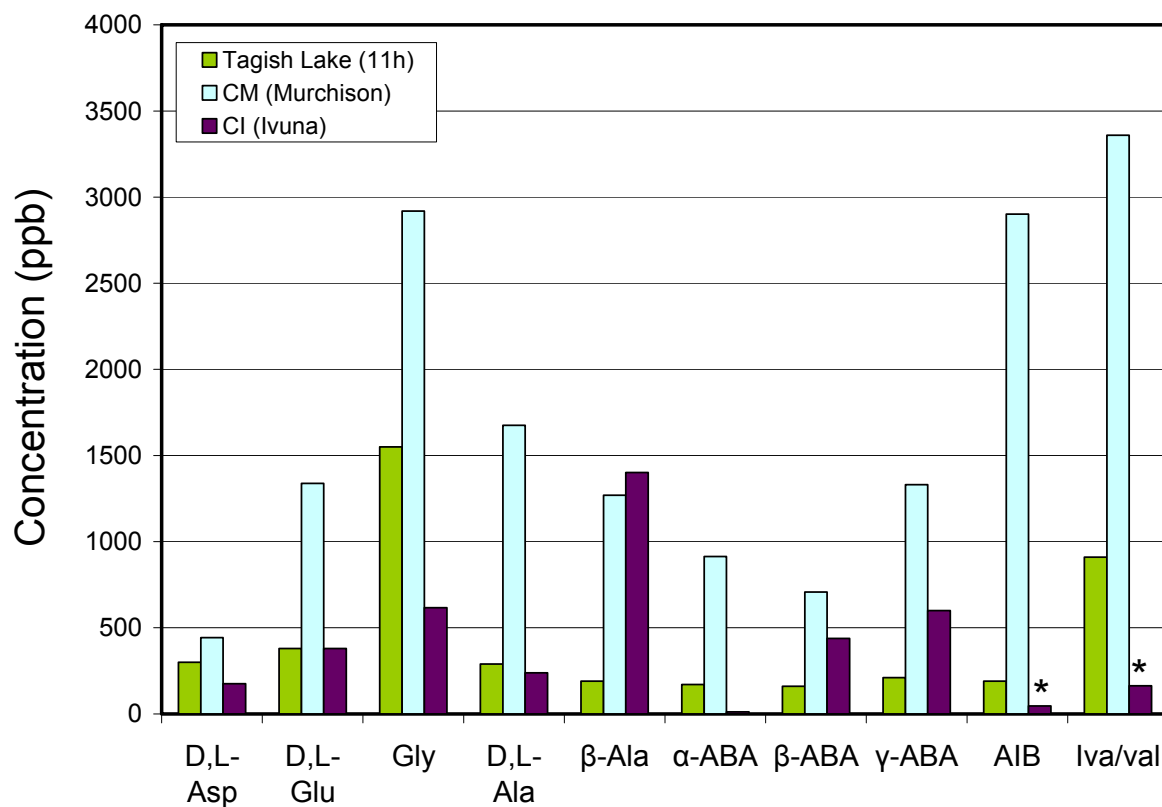


Figure 7. Results from Tagish Lake (sample 11h) with results from CM and CI meteorites for comparison (after Ehrenfreund et al., 2001). Asterisks (*) denote where concentrations are maximum values.