

CARBOXYLIC ACID ABUNDANCES IN THE TAGISH LAKE METEORITE: LITHOLOGICAL DIFFERENCES AND IMPLICATIONS FOR FORMIC ACID ABUNDANCES IN CARBONACEOUS CHONDRITES. R.W. HILTS¹, C.D.K. HERD², D. MORGAN³, L. EDWARDS⁴ and Y. HUANG⁴. ¹Chemistry Department, Grant MacEwan College, Edmonton, Alberta, Canada T5J 4S2 (hiltsr@macewan.ca), ²Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2E3, ³Mass Spectrometry Laboratory, Department of Chemistry, University of Alberta, ⁴Department of Geological Sciences, Brown University, Providence, Rhode Island, 02912, U.S.A.

Introduction: The most abundant soluble organic compounds in carbonaceous chondrites are typically carboxylic acids [1]. Strait-chain monocarboxylic acids up to C₁₂ have been the focus of considerable attention owing to the exciting possibility that they may have been incorporated into the molecular architecture of prebiotic protomembranes on the ancient Earth [e.g., 2]. The most abundant monocarboxylic acid in interstellar space is formic acid [e.g. 3,4]. It is generally accepted that the organic material in carbonaceous chondrites such as the Tagish Lake meteorite is derived from interstellar or nebular sources [5,6]. It is somewhat surprising, therefore, that so far only what have been described as small or moderate formic acid concentrations have been found in aqueous extracts of carbonaceous chondrites [7-12]. Previous reports have ascribed the unexpectedly low formic acid abundances to either compound loss during extraction and subsequent work up, or to depletion caused by environmental processes, such as evaporation and/or aqueous leaching of this highly volatile, highly polar compound from the meteorite upon its exposure to the Earth's hydrosphere [7,8].

Here we present our analysis of the water-soluble monocarboxylic acids in two different lithologies within the Tagish Lake meteorite using the SPME-GCMS procedures recently developed by [7] to compare the two lithologies in this respect. Our results conclusively show that formic acid is, by a wide margin, the most abundant monocarboxylic acid in both of the Tagish Lake lithologies investigated so far. This is in stark contrast to all previous studies of other meteorites in which it was concluded that the formic acid concentration was the lowest or one of the lowest of those monocarboxylic acids present in the extract [7-12]. Moreover, our serendipitous discovery that formic acid has a very low response factor when run on either GCMS (quadrupole) or GC-FID [13] instruments suggests that previous studies on carbonaceous chondrites may have dramatically underestimated the quantities of formic acid present. A close inspection of the relative abundances for the straight-chain monocarboxylic acids in each Tagish Lake lithology has led us to conclude that the overall oxidation levels for the water soluble organics from the two lithologies are different.

Methods: Two samples were analyzed: Sample 11v consists of disaggregated material composed of chondrules set in a fine-grained matrix of phyllosilicates, sulfides and abundant magnetite. It appears to be most similar to the carbonate-poor lithology of [14]. Sample 11i is an example of a "dark, dusty" lithology consisting almost entirely of fine-grained (<5 μm) material typical of matrix (incl. phyllosilicates, magnetite, and sulfides) and lacking chondrules or CAIs. In a typical extraction, a ~0.70 g-subsample of a particular lithology was taken from storage at -30°C and added expeditiously to a 50 mL round-bottomed flask containing 19 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 scrupulously washed glass wool and the pH of the colorless filtrate increased to ~11 via the addition of 4 drops of ultrapure 6 M NaOH(aq) (this step converts all carboxylic acids present into their corresponding, non-volatile carboxylate salts). The volume of the filtrate was 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). A subsequently prepared procedural blank was found to contain trace amounts (less than 1 ppm) of formic and acetic acid. The concentrated water extracts were analyzed by sorption of the monocarboxylic acids on an SPME (solid phase microextraction) fiber coated with PEG (polyethylene glycol), followed by gas chromatography with mass spectrometry (GCMS). The acids were flashed off the fiber in the hot GC port, separated on a Nukol column and finally, determined with an Agilent Technologies 5975-C GC-MS quadrupole detector.

Results: At least eleven monocarboxylic acids are present in the extract of the matrix-rich (dark, dusty) lithology (sample 11i), including most of the members of the homologous series of linear, saturated monocarboxylic acids from C₁ to C₁₀, two branched, saturated monocarboxylic acids and the aromatic carboxylic acids benzoic acid and its alkyl-substituted derivative 4-methylbenzoic acid (Figure 1).

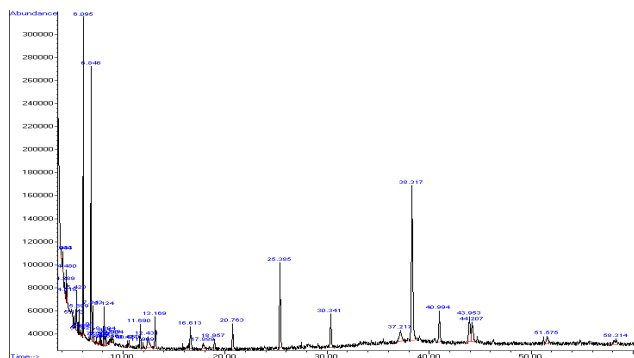


Figure 1: GCMS (Quadrupole) Chromatogram of the Concentrated Water Extract of Tagish Lake sample 11i

The chondrule-bearing material (11v) contained all of the acids detected in the matrix-rich sample (11i), along with a second branched, saturated monocarboxylic acid and the unsaturated monocarboxylic acid 2-prenopenoic acid (Figure 2).

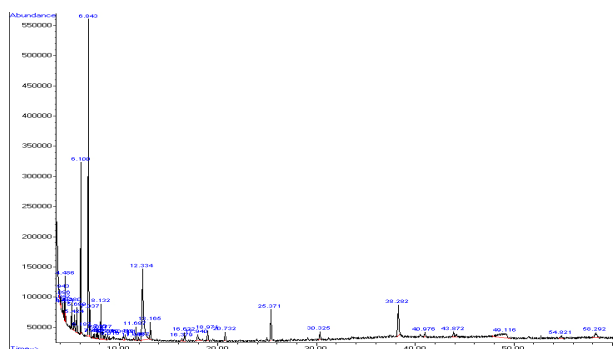


Figure 2: GCMS (Quadrupole) Chromatogram of the Concentrated Water Extract of Tagish Lake sample 11v

The identities of all of the straight-chain monocarboxylic acids (with the exception of decanoic acid) and benzoic acid were unequivocally established by comparison of their mass spectra/GC retention times to those for authentic samples of the acids. We have found unusually high formic acid concentrations in the present study of Tagish Lake, viz. more than 300 ppm for the water extract of the chondrule-bearing sample (11v) and more than 100 ppm for the water extract of the matrix-rich sample (11i) due to 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(quadropole) 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(quadropole) response factors were found by a chemical pathology research group in the U.K. during their study of short-chain monocarboxylic acids in faecal material [15]. Our GCMS results have also revealed that the formic acid to higher homologue ratios are higher for the chondrule-bearing material (11v). This implies that the chondrite-rich lithology contains a more highly oxidized suite of water soluble organics [16]. GCMS(quadropole) analyses of dichloromethane extracts for the two lithologies revealed that although both lithologies contain highly reduced organics, such as alkanes and alkyl-substituted benzenes, much higher concentrations and a greater variety of compound types were observed in the extract for the chondrule-bearing material (11v). The alkanes in this chondrule-bearing sample (11v) may very well have been formed by *in situ* hydrothermal decarboxylation of aliphatic monocarboxylic acids [17], which are clearly present in high abundance in this lithology. We will be able to give a better assessment of the origins for the monocarboxylic acids once the molecule-specific carbon and hydrogen isotope studies on the water extracts from the same Tagish Lake samples are complete.

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