

FIRST REPORT OF ALDEHYDES AND KETONES IN THE TAGISH LAKE METEORITE: OPTIMIZED METHODOLOGY AND PRELIMINARY RESULTS. D. N. Simkus¹, R. W. Hilt², C. D. K. Herd¹, J. C. Aponte^{3,4} and J. E. Elsila³, ¹Dept of Earth & Atmospheric Sciences, University of Alberta, Edmonton, AB, Canada (simkus@ualberta.ca), ²Dept of Physical Sciences, MacEwan University, Edmonton, AB, Canada ³Solar System Exploration Division, Code 691, NASA Goddard Space Flight Center, Greenbelt, MD, USA, ⁴Catholic University of America, Washington, DC, USA.

Introduction: Aldehydes and ketones are the chemical precursors to α -amino acids in Strecker synthesis reactions. Identifying these carbonyl compounds in astromaterials can provide insight into the abiotic formation of amino acids on asteroid parent bodies. Aldehydes and ketones have been previously detected via GC-MS in a few carbonaceous chondrite meteorites, including Murchison [1,2], Bells [3] and Ivuna [3]. These studies [1,3] followed an Environmental Protection Agency (EPA) method (#556) for derivatizing aldehydes and ketones to less volatile forms using the derivatizing agent 2,3,4,5,6-pentafluorobenzyl hydroxylamine (PFBHA) (Fig. 1).

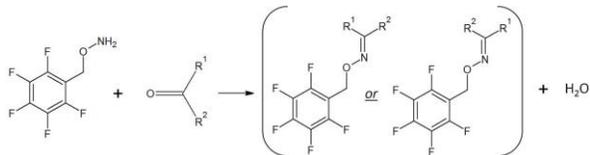


Fig. 1. PFBHA derivatization reaction. PFBHA reacts with an aldehyde or ketone to produce the (E) or (Z) N-[(pentafluorobenzyl)oxy]imine and water.

We have now modified the EPA derivatization method specifically for the analysis of astromaterials and have applied this optimized method to the analysis of aldehydes and ketones in the Tagish Lake meteorite.

Method Development: The EPA method involves derivatizing carbonyl compounds in water, by adding 1 mL of a 15 mg/mL PFBHA solution, heating the sample at 35°C for 2 hours, extracting the derivatives from the solution with hexane, and processing the extract through an acid-wash step before running the sample on the GC-MS.

Our modifications to this method include:

- Derivatizing carbonyl compounds for ≥ 24 hours to allow the reaction to go to completion (Fig. 2)
- Using dichloromethane (DCM) rather than hexane as an extraction solvent, as it produces higher yields and greater reproducibility (Fig. 3)
- Storing the derivatives in solution in cold conditions (4°C), as the derivatives degrade rapidly after evaporating the solutions to dryness, even at 4°C, but appear to remain stable if kept in solution

Advantages of using the PFBHA derivatization method are that it targets carbonyl compounds specifically and doesn't require a time-consuming clean-up step. The perfluorobenzyl moiety also allows the re-

sulting N-[(pentafluorobenzyl)oxy]imines to be easily resolved by GC-MS.

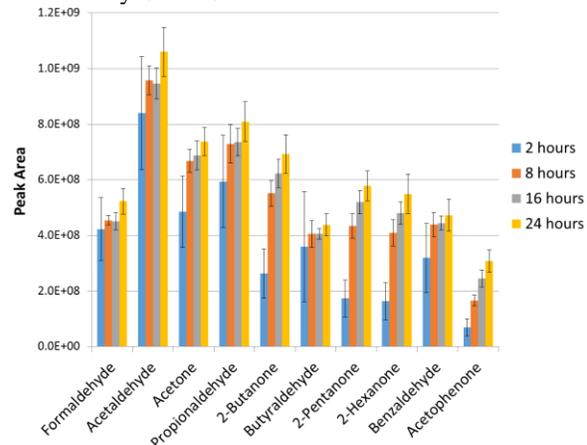


Fig. 2. Total yields (GC-MS peak areas) of aldehyde and ketone oxime derivatives from 2-, 8-, 16- and 24-hour derivatization reactions. Each bar represents 3 replicate samples and error bars represent one standard deviation from the mean.

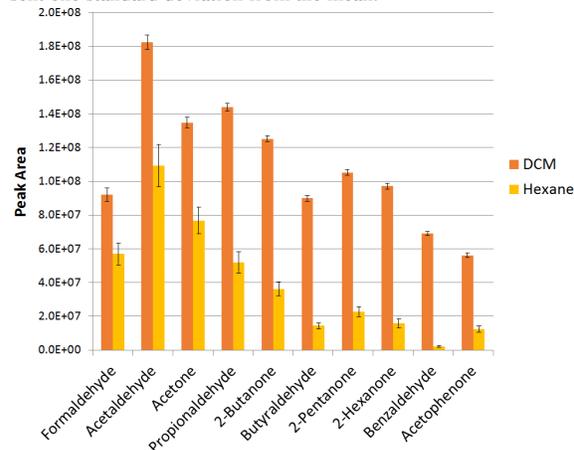


Fig. 3. Extraction efficiency of DCM vs. hexane. Each bar represents the average of 12 replicate samples and error bars represent one standard deviation from the mean.

Tagish Lake Meteorite:

Materials. The Tagish Lake (TL) carbonaceous chondrite fell onto the surface of a frozen lake, was collected shortly after its fall without direct hand contact, and has since been stored at sub-zero temperatures. TL is therefore an exceptionally pristine meteorite and molecular species with low boiling temperatures have likely been retained within the rock. Furthermore, petrologic and geochemical variations amongst different subsamples of the meteorite indicate varying degrees of aqueous alteration across the parent

body asteroid [4]. The relatively low organic content of the sample investigated, TL10a, suggests that it may be representative of a more heavily altered lithology.

Method. All glassware and tools were combusted at 450°C for > 6 hours before use. A 2.499 g subsample of TL10a was powdered in an alumina mortar and pestle within an Ar gas glovebox in a -10°C walk-in freezer. The powder was extracted in Millipore water for 24 hours at 100°C in a sealed glass ampule. The sample was centrifuged and 1 mL of the PFBHA solution (0.2 mg/mL) was added to the supernatant. After 24 hours, the reaction was quenched by adding 2 drops of 0.2 N sulfuric acid. The oxime derivatives were extracted twice from the solution using 2 mL DCM, and brought through an acid-wash step (0.2 N sulfuric acid). The DCM solution was evaporated to 50 µL under a stream of N₂ and analyzed by GC-MS. Concentrations were determined by comparison to a suite of standards prepared under the same conditions. A combusted Allende meteorite powder and a solvent blank were also processed and analyzed in the same manner.

Results and Discussion: The TL10a analysis revealed a suite of aldehydes and ketones, dominated by the low-molecular weight acetaldehyde, formaldehyde, and acetone (Fig. 4).

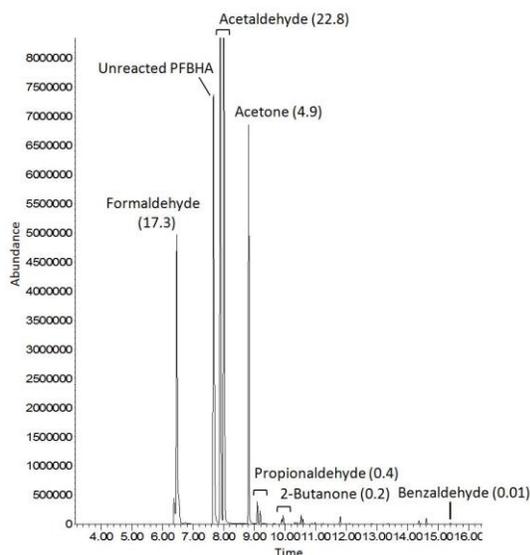


Fig. 4. GC-MS chromatogram of aldehyde and ketone derivatives in TL10a and their concentrations (nanomoles/gram of meteorite). Acetaldehyde, propionaldehyde, and 2-butanone are each composed of 2 peaks, representing their (*E*) and (*Z*) isomers. The trace only includes compounds containing the characteristic ion of N-[(pentafluorobenzyl)oxy]imines (*m/z* 181.0). Other compounds identified in the sample included trimethyl hexene, pentafluorobenzyl alcohol and inorganic sulfur.

The combusted Allende blank and the solvent blank contained small amounts of formaldehyde and acetone, indicating that a component of the carbonyl compounds in TL10a may be terrestrial. However, the relatively high abundance of acetaldehyde and other short-chain

aldehydes and ketones has been similarly observed in other meteorite samples [1,2,3]. TL10a has a much lower total abundance of aldehydes and ketones (at least 45.6 nmol/g) compared to Murchison (200 nmol/g), Bells (604 nmol/g) and Ivuna (1478 nmol/g) [1,2,3]. Whether this low abundance is a result of secondary aqueous alteration on the asteroid remains unclear until the amino acid content and degree of alteration is determined for TL10a.

The five most abundant carbonyl compounds identified in this study are the precursors to the five α -amino acids previously identified in TL samples: alanine, glycine, α -aminoisobutyric acid (AIB), isovaline and α -amino-n-butyric acid (ABA) (Fig. 5) [5]. These aldehydes and ketones could be primordial reactants that were shielded from amino acid synthesis reactions by mineral sorption or bonding with other organic compounds. Alternatively, they are products of secondary processing on the asteroid parent body. Compound-specific carbon isotope analysis of the aldehydes and ketones in TL is forthcoming, and comparing $\delta^{13}\text{C}$ compositions of aldehydes and ketones to $\delta^{13}\text{C}$ compositions of indigenous amino acids will give insight into the relationship between these two compound classes.

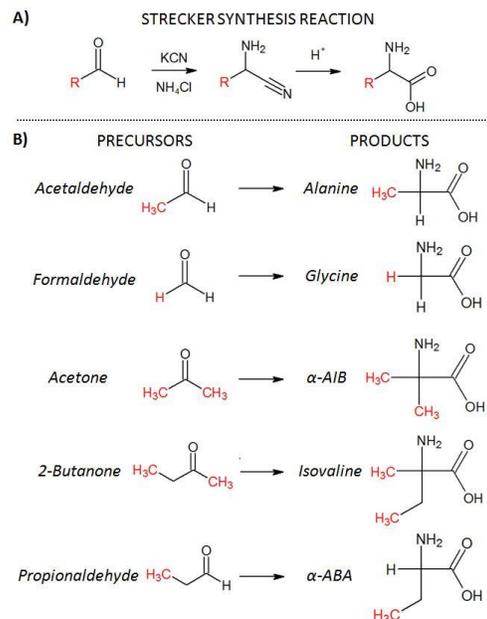


Fig. 5. (A) Strecker amino acid synthesis pathway. An aldehyde or ketone reacts with ammonium chloride in the presence of potassium cyanide to form α -aminonitrile, which is hydrolyzed to produce an amino acid. (B) Reactants (aldehyde or ketone) and expected products (amino acids) for Strecker synthesis reactions.

References:

- [1] Pizzarello S. and Holmes W. (2009) *Geochim Cosmochim Acta*, 73, 2150-2162. [2] Jungclauss G. A., et al. (1976) *Meteoritics*, 11, 231-237. [3] Monroe A. A. and Pizzarello S. (2011) *Geochim Cosmochim Acta*, 75, 7585-7595. [4] Herd, C. D. K. et al. (2011) *Science*, 332, 1304-1307. [5] Hilt, R. W. et al. (2014) *Meteor Planet Sci*, 49, 526-549.