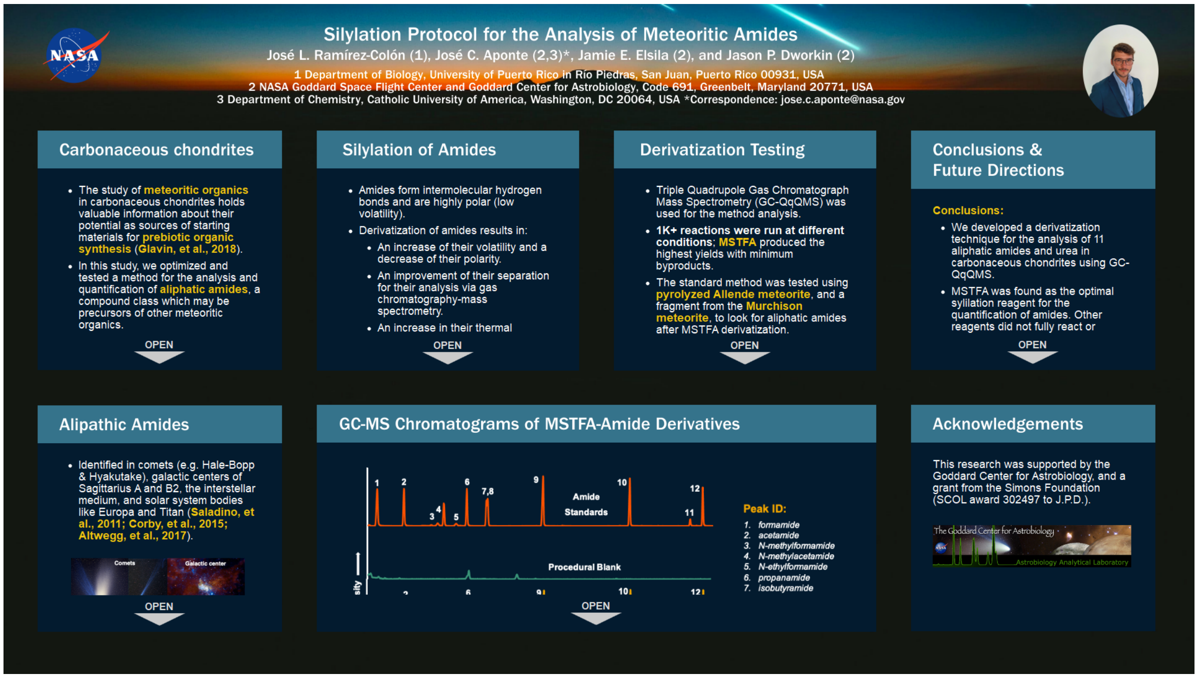
Silylation Protocol for the Analysis of Meteoritic Amides



José L. Ramírez-Colón (1), José C. Aponte (2,3)*, Jamie E. Elsila (2), and Jason P. Dworkin (2)

1 Department of Biology, University of Puerto Rico in Río Piedras, San Juan, Puerto Rico 00931, USA
2 NASA Goddard Space Flight Center and Goddard Center for Astrobiology, Code 691, Greenbelt, Maryland 20771, USA
3 Department of Chemistry, Catholic University of America, Washington, DC 20064, USA
*Correspondence: jose.c.aponte@nasa.gov

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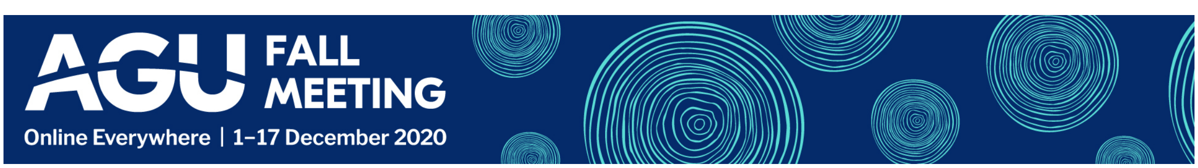
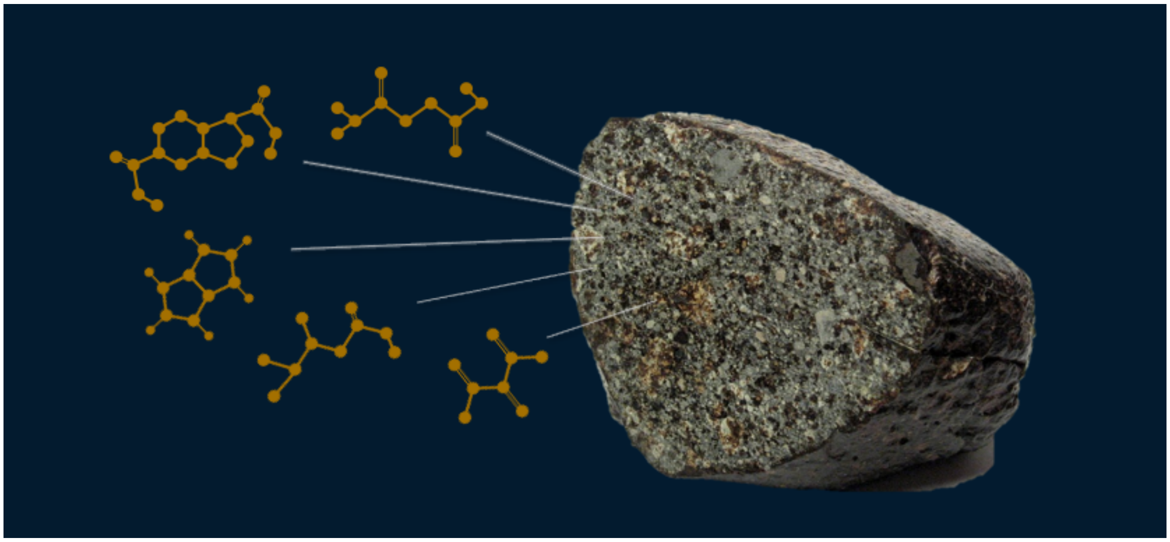


CARBONACEOUS CHONDRITES

- The study of **meteoritic organics** in carbonaceous chondrites holds valuable information about their potential as sources of starting materials for **prebiotic organic synthesis** (**Glavin, et al., 2018 (https://ntrs.nasa.gov/citations/20180004493)**).

- In this study, we optimized and tested a method for the analysis and quantification of **aliphatic amides**, a compound class which may be precursors of other meteoritic organics.



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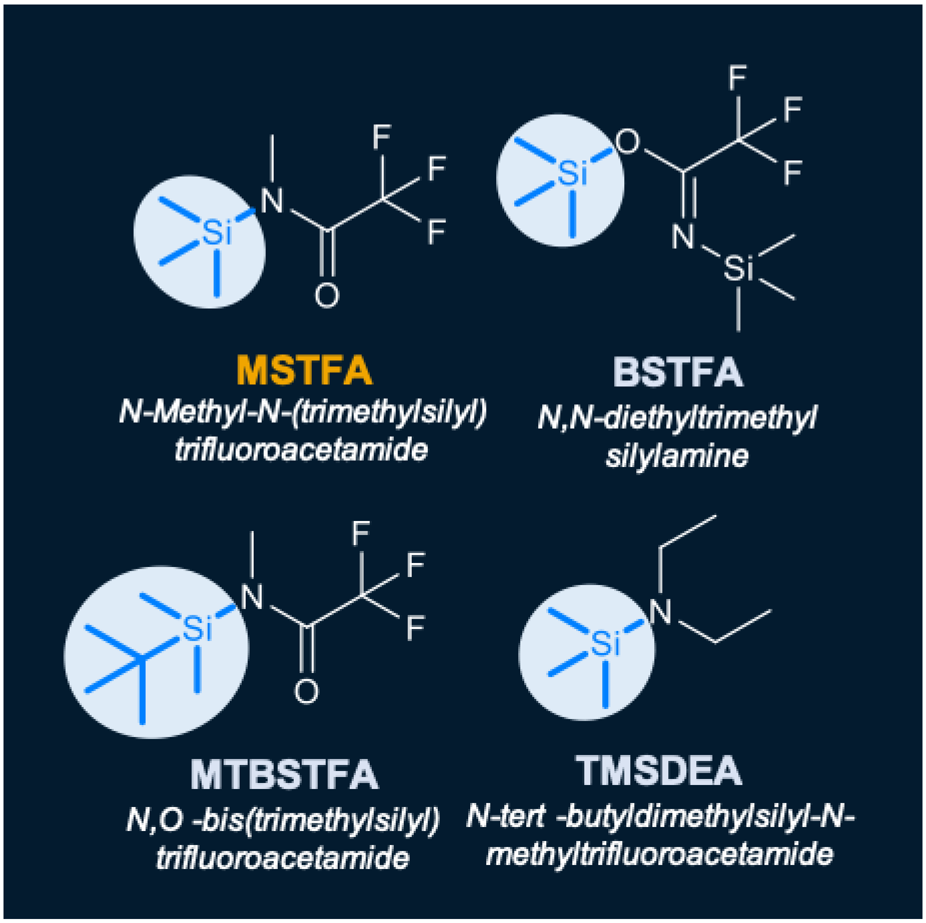
SILYLATION OF AMIDES

- Amides form intermolecular hydrogen bonds and are highly polar (low volatility).
- Derivatization of amides results in:
  - An increase of their volatility and a decrease of their polarity.
  - An improvement of their separation for their analysis via gas chromatography-mass spectrometry.
  - An increase in their thermal stability.

Reagents for Silylation:



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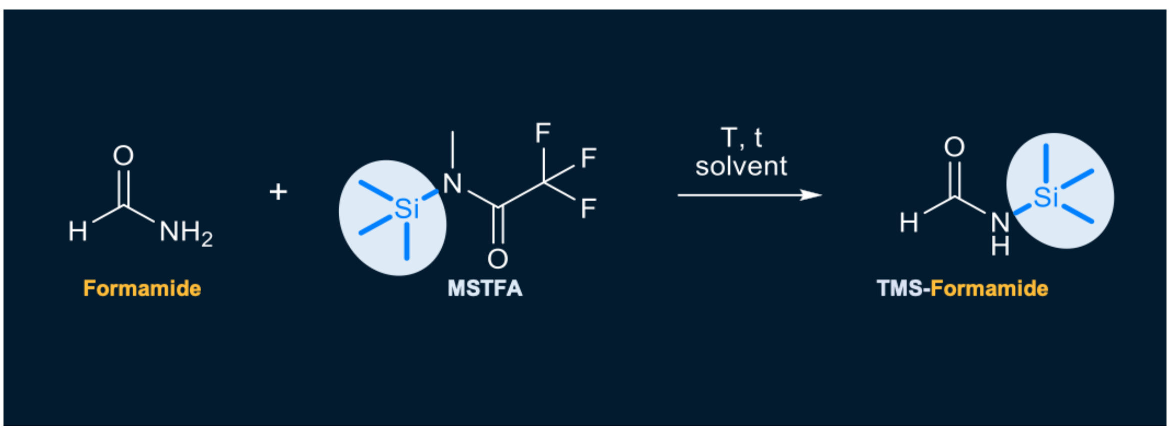
DERIVATIZATION TESTING

- Triple Quadrupole Gas Chromatograph Mass Spectrometry (GC-QqQMS) was used for the method analysis.
- **1K+ reactions were run at different conditions**; **MSTFA** produced the highest yields with minimum byproducts.
- The standard method was tested using **pyrolyzed Allende meteorite**, and a fragment from the **Murchison meteorite**, to look for aliphatic amides after MSTFA derivatization.

Conditions tested:	
Temperature / °C	60, 90, 100, 110, 130
Time / h	0.5, 1, 4, 7, 16, 24
Type of solvents	Dichloromethane, Acetonitrile, & H_2O
Volume of solvents / µL	50, 100, 200, 400, 600, 1K, 2K
Catalysts	**Bases**: Pyridine, TEA, TMA **Acids**: HCl, BF_3
Mineral analogs	Allende meteorite & Goddard Space Flight Center soil

Derivatization Reaction:



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CONCLUSIONS & FUTURE DIRECTIONS

Conclusions:

- We developed a derivatization technique for the analysis of 11 aliphatic amides and urea in carbonaceous chondrites using GC-QqQMS.
- MSTFA was found as the optimal sylilation reagent for the quantification of amides. Other reagents did not fully react or yielded substantial reaction byproducts.
- Our derivatization protocol was tested using mineral analogs and standards, showing no decomposition or byproduct formation.
- A tentative detection of meteoritic acetamide was observed from a fragment of the Murchison meteorite. However, this may be a false-positive detection as the sample may have undergone partial hydrolysis of acetonitrile either during meteorite extraction or during extract derivatization.

Future Directions:

- Additional studies are needed to understand the effects of water during extraction and derivatization of aliphatic amides. These may involve the use of Allende pyrolyzed powder impregnated with trace amounts of water in the absence and presence of aliphatic amide standards.
- Additionally, we will test: (i) molecular sieves or celite, and (ii) drying agents, to absorb water during extraction and derivatization.

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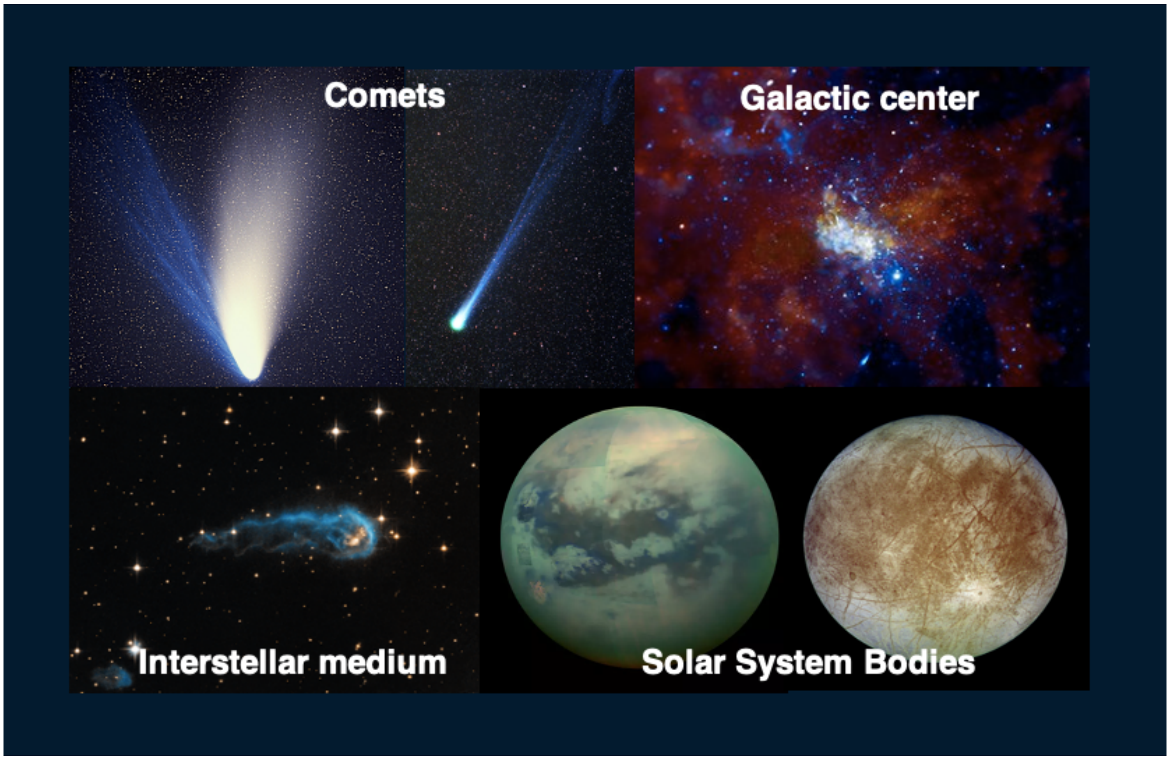
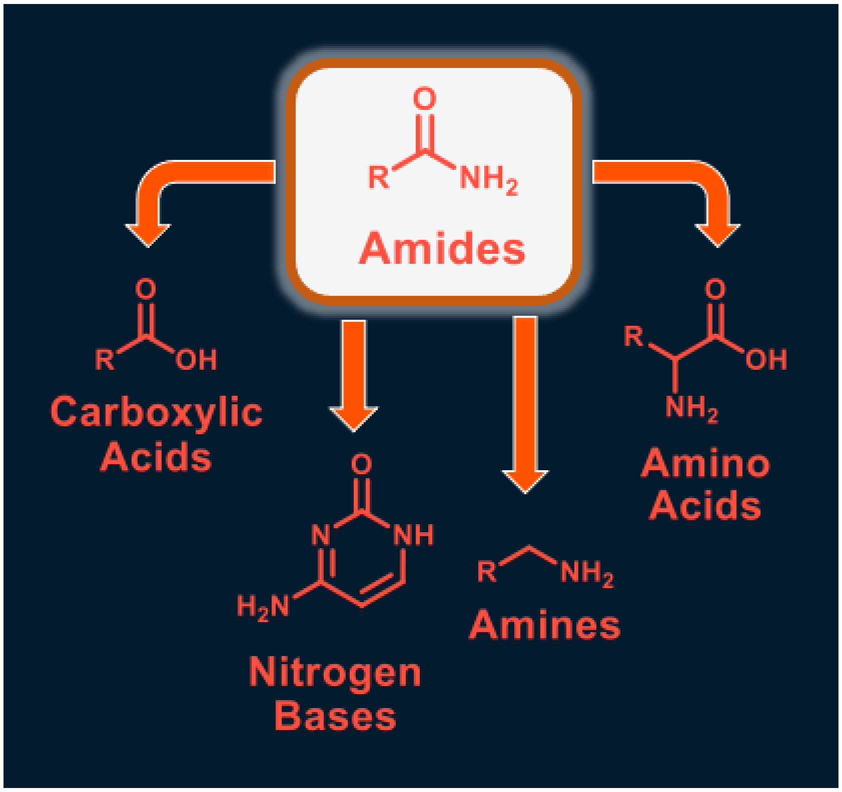
ALIPATHIC AMIDES

- Identified in comets (e.g. Hale-Bopp & Hyakutake), galactic centers of Sagittarius A and B2, the interstellar medium, and solar system bodies like Europa and Titan (**Saladino, et al., 2011 (https://www.sciencedirect.com/science/article/abs/pii/S1571064511001473?via%3Dihub); Corby, et al., 2015 (https://academic.oup.com/mnras/article/452/4/3969/1057031); Altwegg, et al., 2017 (https://academic.oup.com/mnras/article/469/Suppl_2/S130/3865958)**).



- Contain the elements required for the synthesis of biomolecules (except phosphorus & sulfur).

- Experiments using formamide mixed with metal oxides, clays, and meteorites as catalysts, proved formation of nucleobases, carboxylic acids, amino acids, and amines (**Costanzo, et al., 2007 (https://bmcevolbiol.biomedcentral.com/articles/10.1186/1471-2148-7-S2-S1); Saladino, et al., 2012 (https://pubmed.ncbi.nlm.nih.gov/22738728/)**).



Not yet been reported from meteorites

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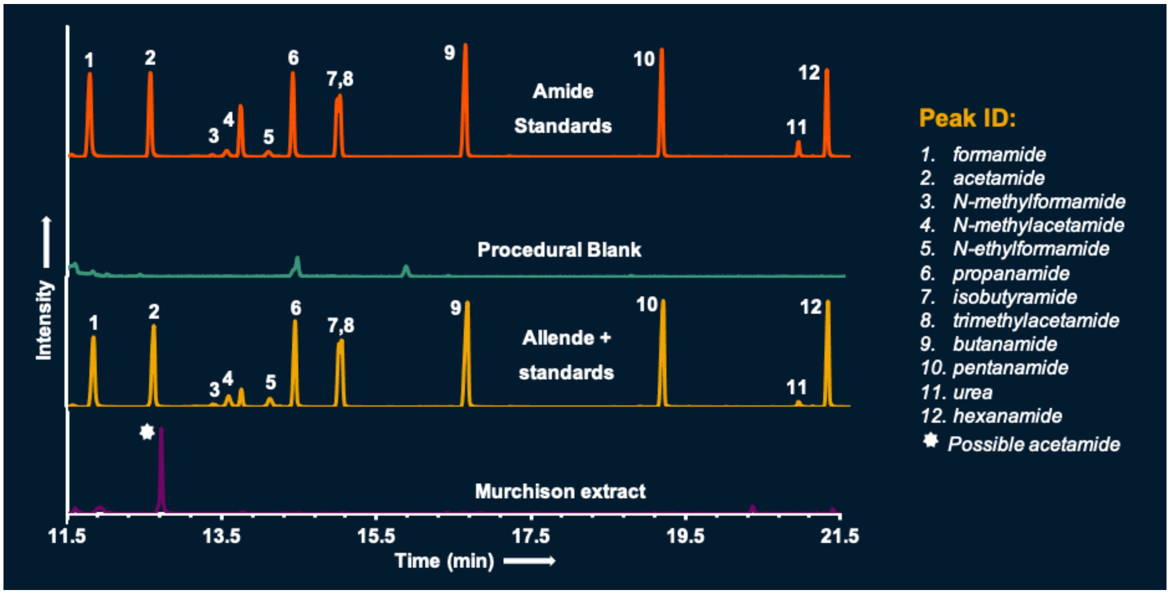
GC-MS CHROMATOGRAMS OF MSTFA-AMIDE DERIVATIVES



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ACKNOWLEDGEMENTS

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ABSTRACT

Carbonaceous chondrite meteorites are fragments of asteroids or comets, that have remained relatively unaltered since the formation of the Solar System. This extraterrestrial material contains a variety of organic compounds including amino acids, carboxylic acids, and nucleobases, among others. It has been suggested that carbonaceous chondrites may have been essential in the chemical processes that led to the origin of life on Earth (and possibly elsewhere), serving as delivery vehicles of important organic matter during Earth's early history. Based on the observed relative abundances and the different alteration processes (*i.e.*, thermal metamorphism or aqueous alteration), many synthetic mechanisms have been proposed for the origins of the organic compounds found within carbonaceous chondrites.

Among these synthetic routes, there is one mechanism involving the family of aliphatic amides, a class of substrate, with a chemical composition that includes four of the common elements required for life (C, H, O, N) which have been proposed to be important for prebiotic chemistry. The simplest, formamide, has been found in the galactic center, the interstellar medium, and comets. Experimental approaches using formamide with metal oxides, clays, phosphates, or meteorites as catalysts have formed nucleobases, carboxylic acids, amino acids, and amines. Surprisingly, neither formamide nor any other amide have been reported in meteorites. Therefore, we have developed a silylation derivatization method suitable for the identification and quantification of amides in meteoritic samples via gas chromatography mass spectrometry GC-QqQMS.

The derivatization protocol was developed using *N*-methyl-trimethylsilyl trifluoroacetamide (MSTFA) as the silylating agent for the derivatization of eleven C_1 to C_6 aliphatic amides and urea. Different temperatures, times of derivatization, solvents, volume of solvents, and acid and basic catalysts were evaluated to optimize our protocol. Finally, the optimized method was tested using pyrolyzed Allende meteorite impregnated with the amide standards as a control, and a fragment of Murchison meteorite as an analytical sample. The Allende/standard samples showed no decomposition of the tested compounds nor significant byproduct formation. In the sample of the Murchison meteorite, none of the aliphatic amides could be clearly identified, possibly due to the presence of water in the sample which could have hydrolyzed the amides during extraction or derivatization. Further studies are needed to firmly assess the presence of amides in carbonaceous chondrites either using our silylation protocol with precautions to eliminate water or with a new protocol that is less sensitive to the presence of water.