nature COMMUNICATIONS

ARTICLE

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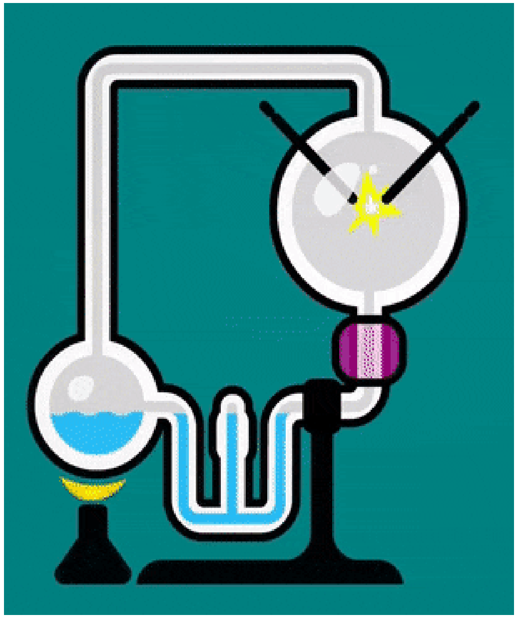
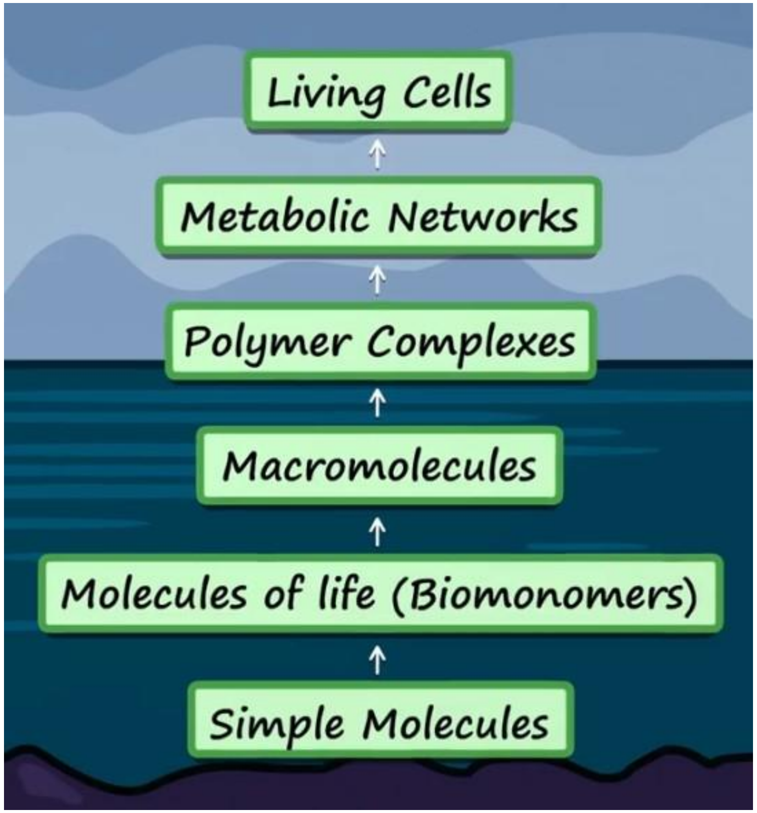
Nucleobase synthesis in interstellar ices

Yasuhiro Oba[1*], Yoshinori Takano[2,5], Hiroshi Naraoka[3,4], Naoki Watanabe[1] & Akira Kouchi[1]



https://gfycat.com/gifs/search/miller+urey



http://astropixels.com/diffusenebulae

14/11/2020

Gaurav Vishwakarma

Characterization tools: HRMS/HPLC

Orbitrap mass spectrometer
Q Exactive Plus, Thermo Fischer Scientific

High-performance liquid chromatograph (HPLC)
UltiMate 3000, Thermo Fischer Scientific

- Reversed-phase C18 separation column (1.5 × 250 mm, particle size of 3 μm, InertSustain C18, GL Science)
- Hypercarb™ separation column (4.6 × 150 mm, particle size of 5 μm, Thermo Fischer Scientific

Mass resolution of m/Δm = ~140,000 (at a m/z of 200)

Background work

Published: 28 March 2002

Amino acids from ultraviolet irradiation of interstellar ice analogues

G. M. Muñoz Caro, U. J. Meierhenrich, W. A. Schutte, B. Barbier, A. Arcones Segovia, H. Rosenbauer, W. H.-P. Thiemann, A. Brack & J. M. Greenberg

Nature **416**, 403–406(2002) | Cite this article

$H_2O:CH_3OH:NH_3:CO:CO_2$ = 2:1:1:1:1
16 amino acids

Published: 28 March 2002

Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues

Max P. Bernstein, Jason P. Dworkin, Scott A. Sandford, George W. Cooper & Louis J. Allamandola

Nature **416**, 401–403(2002) | Cite this article

$H_2O:CH_3OH:NH_3:HCN$ = 20:2:1:1

REPORT

Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs

Cornelia Meinert[1,*], Iuliia Myrgorodska[1,2], Pierre de Marcellus[3], Thomas Buhse[4], Laurent Nahon[2], Søren V. Hoffmann[5], L...
+ See all authors and affiliations

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DOI: 10.1126/science.aad8137

nature COMMUNICATIONS

ARTICLE

https://doi.org/10.1038/s41467-018-07693-x OPEN

Deoxyribose and deoxysugar derivatives from photoprocessed astrophysical ice analogues and comparison to meteorites

Michel Nuevo[1,2], George Cooper[3] & Scott A. Sandford[1] Published: 18 December 2018

RESEARCH ARTICLE

Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases

Michael P. Callahan, Karen E. Smith, H. James Cleaves II, Josef Ruzicka, Jennifer C. Stern, Daniel P. Glavin, Christopher H. House, and Jason P. Dworkin

PNAS August 23, 2011 108 (34) 13995-13998; https://doi.org/10.1073/pnas.1106493108

Edited by Mark H. Thiemens, University of California San Diego, La Jolla, CA, and approved July 12, 2011 (received for review April 25, 2011)

Astrobiology, Vol. 9, No. 7 | Research Articles

Formation of Uracil from the Ultraviolet Photo-Irradiation of Pyrimidine in Pure H_2O Ices

Michel Nuevo, Stefanie N. Milam, Scott A. Sandford, Jamie E. Elsila, and Jason P. Dworkin

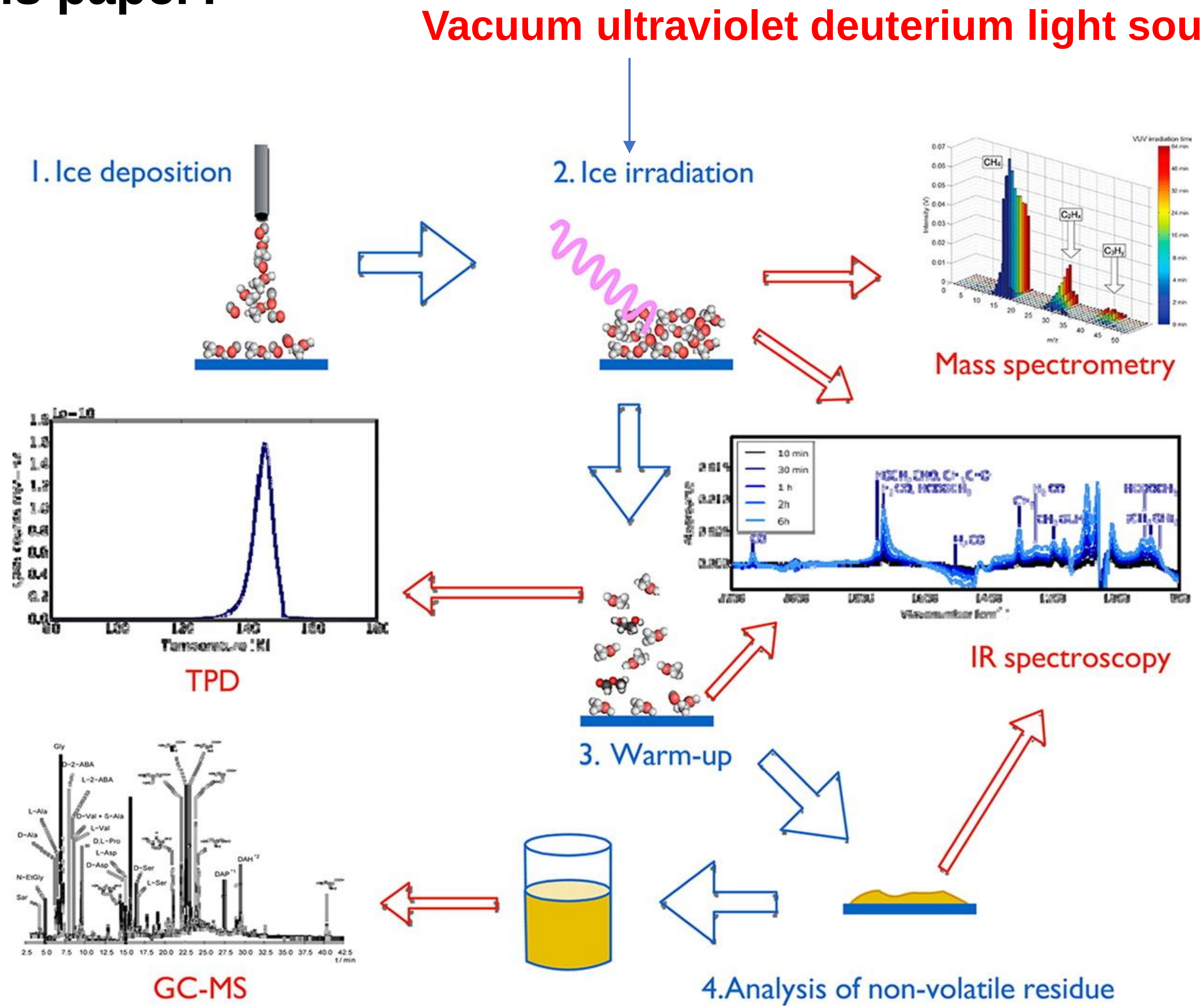
Published Online: 24 Sep 2009 | https://doi.org/10.1089/ast.2008.0324

Motivation

- Several studies reported the prebiotic synthesis of nucleobases from **formamide** (NH_2CHO) **ammonium cyanide** (NH_4CN) and **urea** ($CO(NH_2)_2$) under relatively warm conditions i.e. near or above room temperature.

- There are no reports on the formation of nucleobases from abundant molecules in interstellar ices through the combination of photolysis at astrophysically relevant low temperatures.

Why this paper?



Öberg. K. *Chem. Rev.,* **2016,** *116*, 9631−9663

Introduction

- Nucleobases play an essential role in the biology of terrestrial organisms since NBs are the basic units (of DNA/RNA) used to record genetic information.

- From the viewpoint of origins of life on the Earth, NBs have been the target for laboratory experiments on the prebiotic synthesis in terrestrial and extraterrestrial environments.

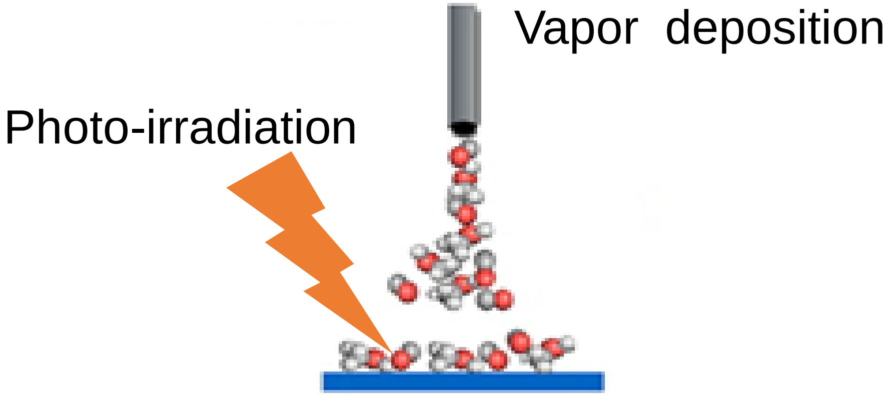
- A number of laboratory studies have been performed to gain a better understanding of the molecular evolution that takes place during the process of formation of stars (T> 100 K) from molecular clouds (T~ 10 K) abundant with molecules such as H_2O, CH_3OH and NH_3.

- Larger, more complex organic molecules such as amino acids and sugars can be produced from a mixture of those simpler molecules after exposure to ultraviolet (UV) photons and cosmic ray analogues (e.g. protons and electrons) followed by heating.

- Due to the limited number of related studies, the mechanism of formation of nitrogen-containing heterocyclic rings including purine and pyrimidine, from a mixture of abundant molecules in interstellar ices remains controversial.

Experimental procedures

Gaseous samples: H_2O, CO, NH_3, and CH_3OH
Mixing ratio: 5:2:2:2
Deposition : continuous vapor deposition
Thickness: ~3600 monolayers
Photo-irradiation time: ~200 h
Photo-irradiation temperature:10 K.



Products

Table 1 Quantification results for the nitrogen heterocyclic molecules targeted in the present study

Name of molecule	Molecular formula	Molecular structure	Mass-to-charge ratio (*m/z*) of the protonated ion	Yield (ppm)[a] by a C18 column	Yield (ppm)[a] by a Hypercarb[TM] column
Nucleobases					
Cytosine	$C_4H_5N_3O$	(1)	112.0505	2	1
Uracil	$C_4H_4N_2O_2$	(2)	113.0346	1	4
Thymine	$C_5H_6N_2O_2$	(3)	127.0502	2	<3
Adenine	$C_5H_5N_5$	(4)	136.0618	0.1	—
Hypoxanthine	$C_5H_4N_4O$	(5)	137.0458	0.06	0.2
Guanine	$C_5H_5N_5O$	(6)	152.0567	—	—
Xanthine	$C_5H_4N_4O_2$	(7)	153.0407	0.04	—
Nitrogen heterocycles					
Pyridazine	$C_4H_4N_2$	(8)	81.0447	19	31
Pyrimidine	$C_4H_4N_2$	(9)	81.0447	<1	<1
Pyrazine	$C_4H_4N_2$	(10)	81.0447	35	41
Purine	$C_5H_4N_4$	(11)	121.0509	2	5
Imidazole	$C_3H_4N_2$	(12)	69.0447	1152	1163
Pyrazole	$C_3H_4N_2$	(13)	69.0447	89	20
4-Imidazolcarboxylic acid	$C_4H_4N_2O_2$	(14)	113.0346	[b]	139
Glycine anhydride	$C_4H_6N_2O_2$	(15)	115.0502	3	42
Dihydrouracil	$C_4H_6N_2O_2$	(16)	115.0502	<1	61

For backing up the quantitative evaluation of those N-containing target molecules, we conducted the two independent chromatographic separations and co-injection determination with the corresponding authentic standard reagent (Supplementary Note 1). The small scale detection and calibration lines of the orbitrap mass spectrometry were also validated as shown in Supplementary Fig. 35

[a]Relative weight with relevance to the total deposited gas in part per million (1 ppm = 0.0001%) normalised with each carbon abundance

[b]Positively identified but not quantified

Results

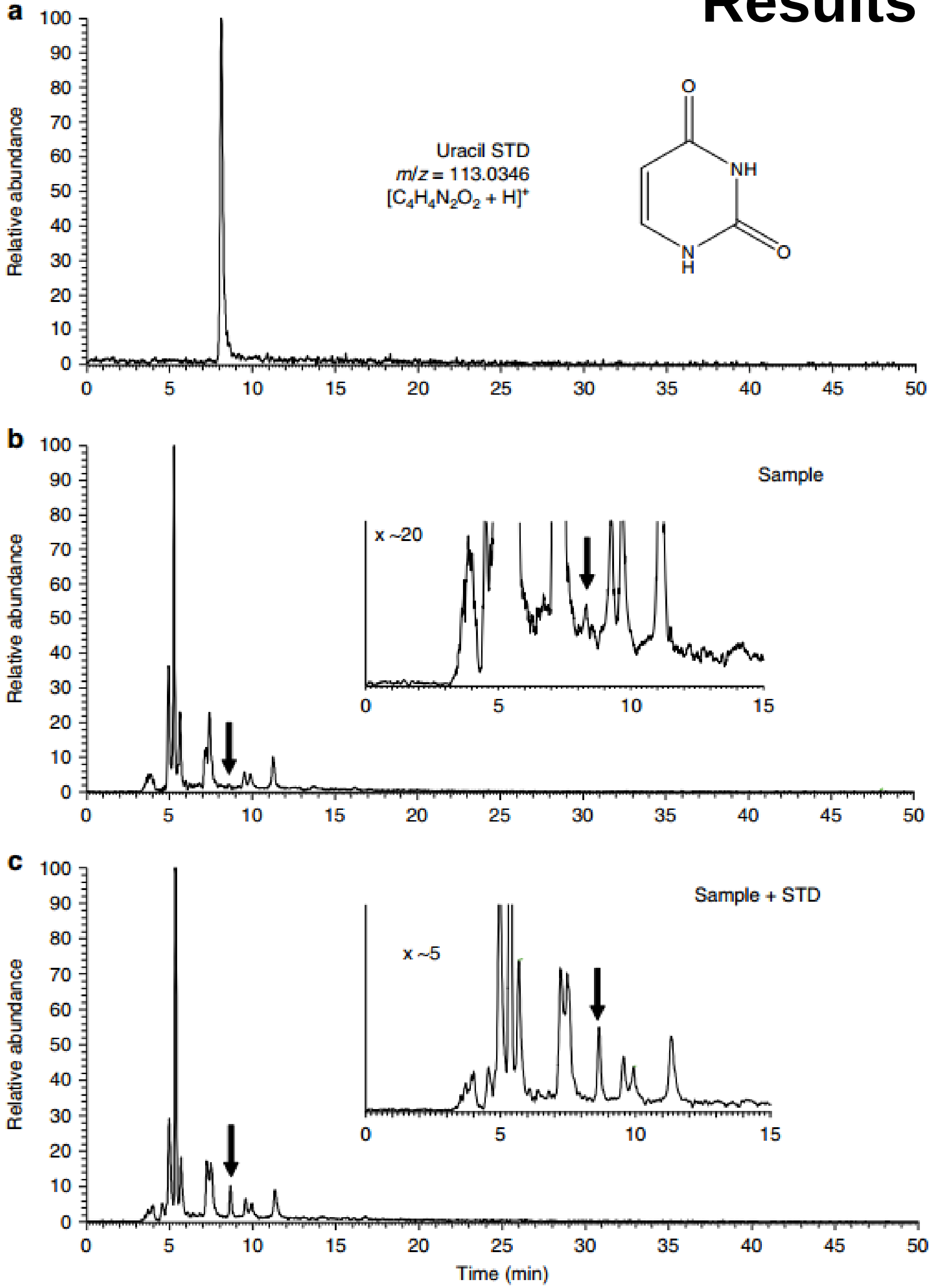


Fig. 2 Identification of uracil in the organic residues. Mass chromatograms of (**a)** the uracil standard, **(b)** the analyte sample and **(c)** the co-injected mixture of uracil standard and analyte sample at a mass-to-charge ratio (m/z) of 113.0346. A C18 separation column was used for the analysis by HPLC/HRMS. The solid arrow indicates the presence of uracil. The inset shows an enlarged spectrum from 0 to 15 min. The intensity of the peak at ~8.6 min, which is associated with uracil (panel **a**), is higher in the co-injected sample (panel **c**) than in the analyte-only sample (panel **b**)

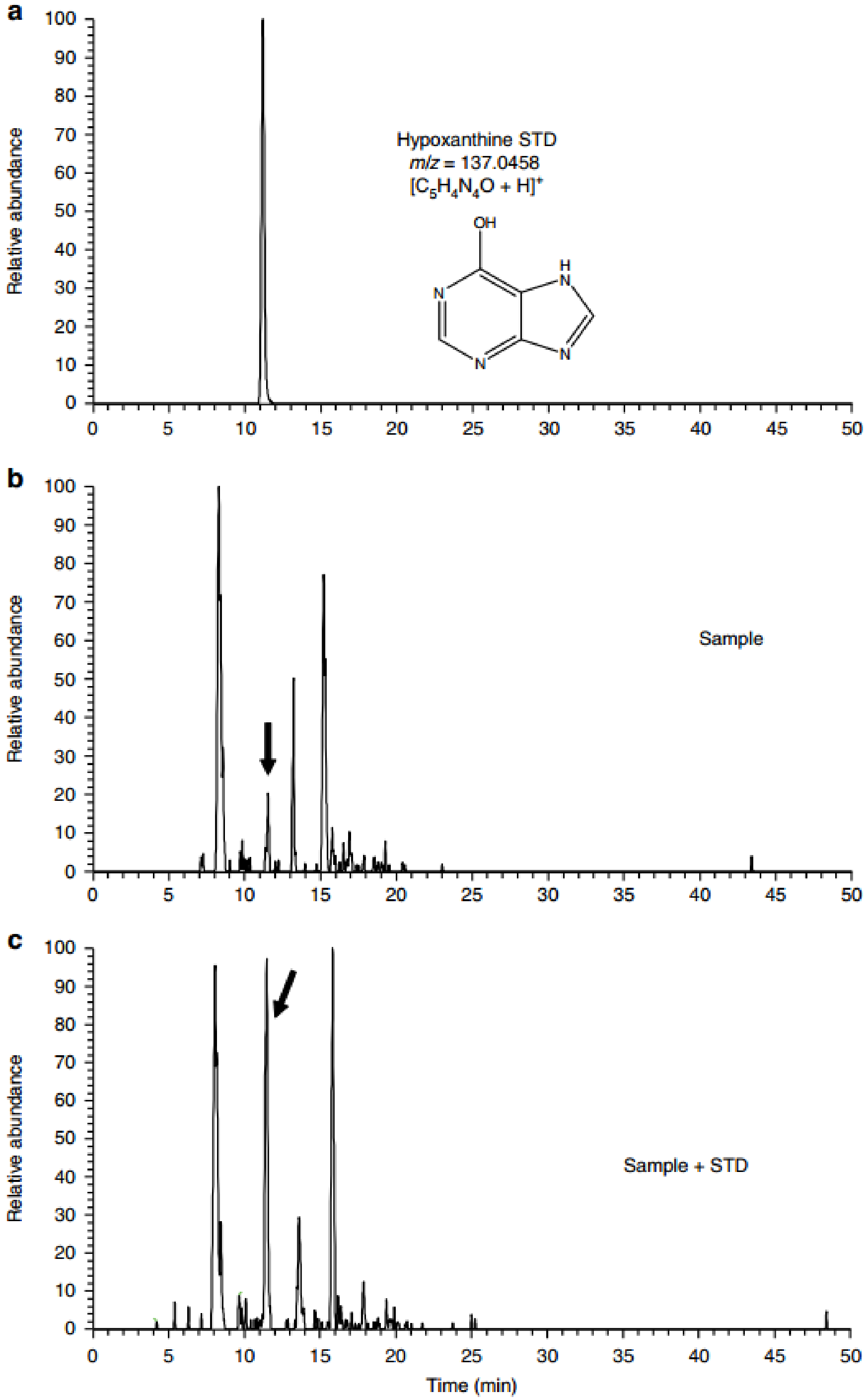
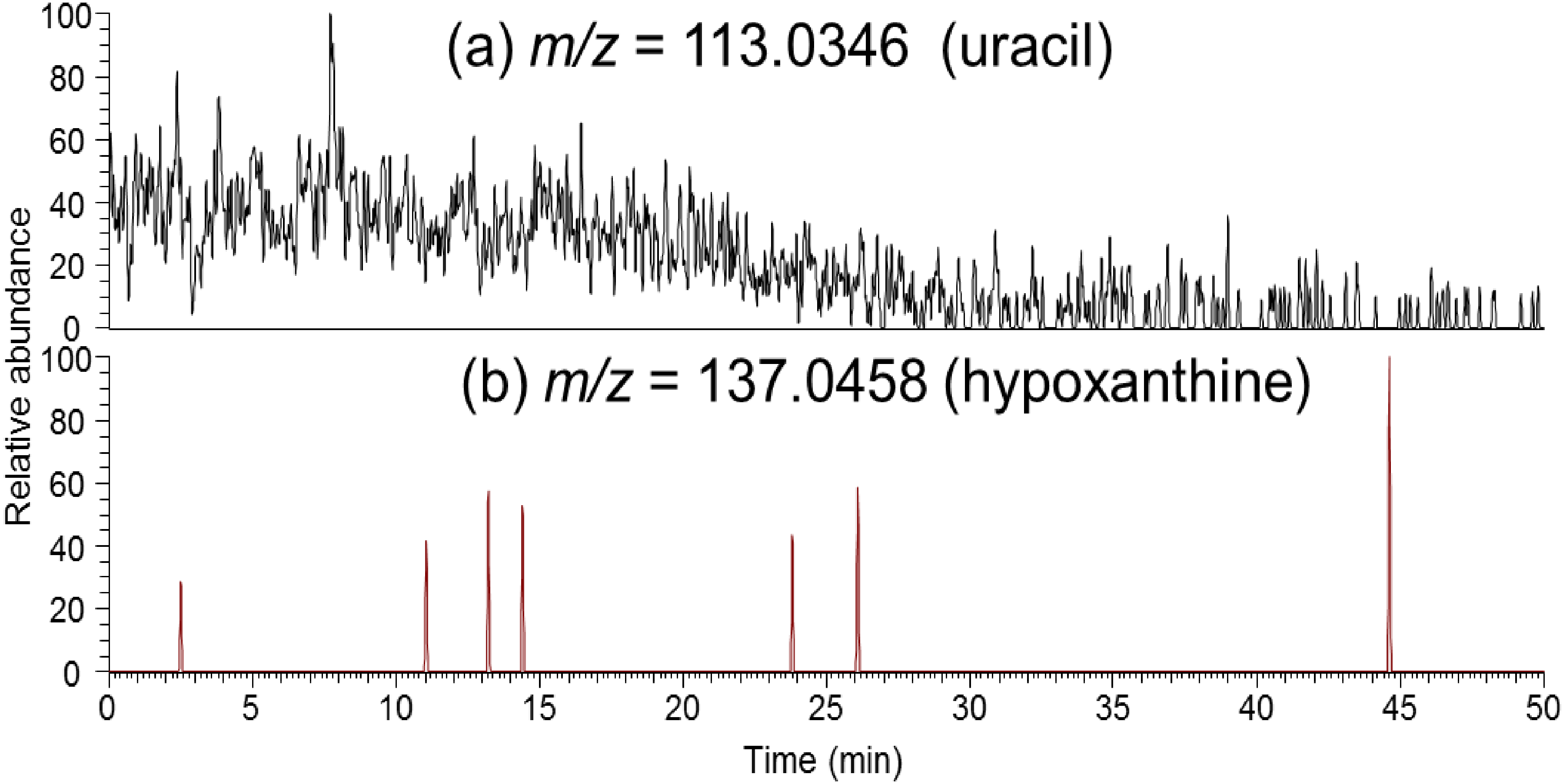


Fig. 3 Identification of hypoxanthine in the organic residues. Mass chromatograms of **(a)** the hypoxanthine standard, **(b)** the analyte sample and **(c)** the co-injected mixture of hypoxanthine standard and analyte sample at a mass-to-charge ratio (m/z) of 137.0458. A C18 separation column was used for the analysis by HPLC/HRMS. The solid arrow indicates the presence of hypoxanthine. The intensity of the peak at ~11.3 min, which is associated with hypoxanthine (panel **a**), is higher in the co-injected sample (panel **c**) than in the analyte-only sample (panel **b**)

Control Experiments



Supplementary Figure 7. Mass chromatograms of the procedural blank sample. A Hypercarb™ separation column was used for the HPLC/HRMS analysis at a mass-to-charge ratio (*m/z*) of (a) 113.0346 and (b) 137.0458. These *m/z* values are those expected for protonated uracil and hypoxanthine, respectively. No peaks derived from the target molecules are present in this study

Control Experiments

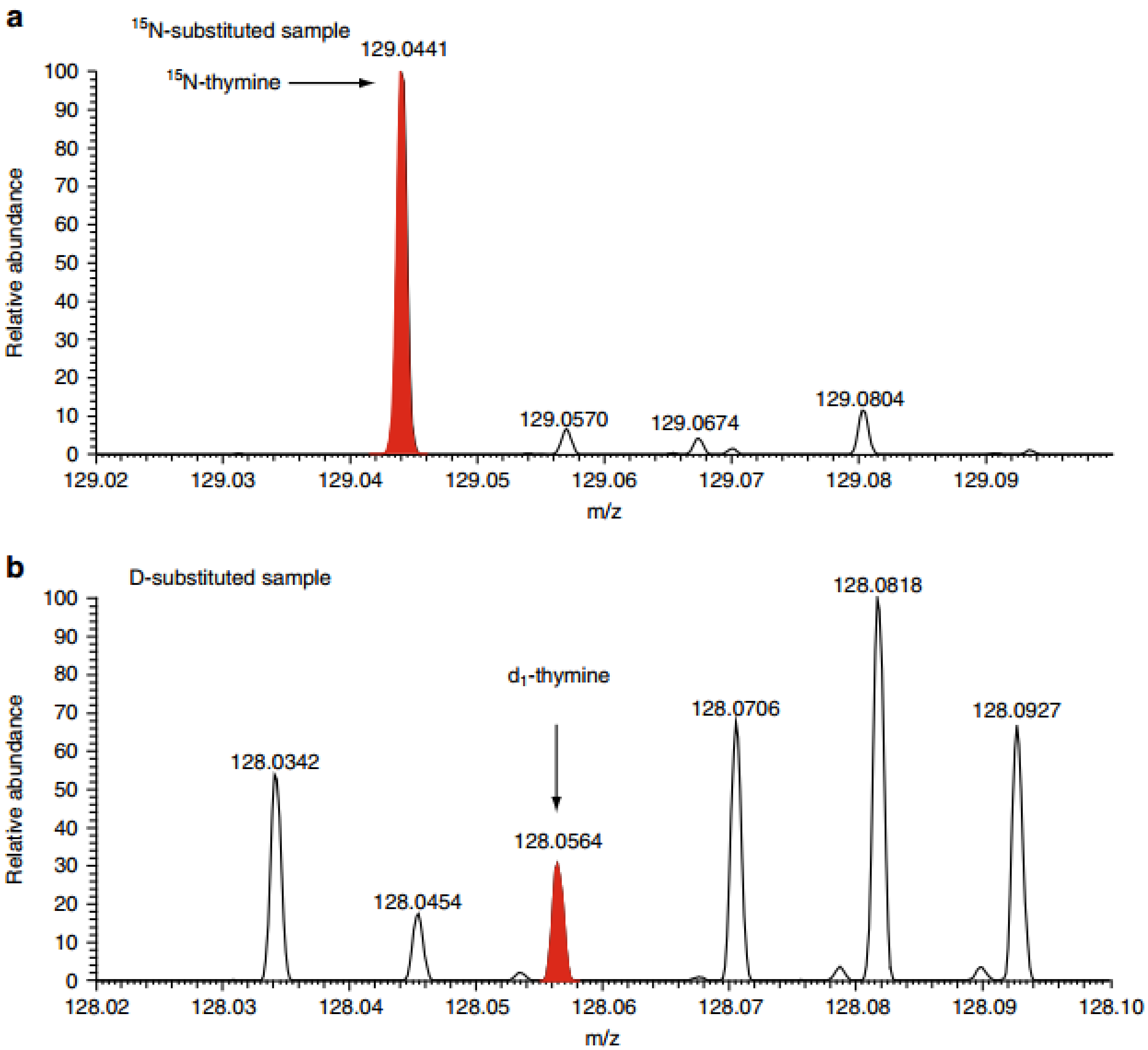


Fig. 4 Identification of thymine in the isotopically labelled organic residues. Mass spectra of thymine observed in the **(a)** ^{15}N- and **(b)** D-substituted samples at m/z from 129.02 to 129.1 and from 128.02 to 128.10, respectively. Red colored peaks at the m/z of 129.0441 in panel **(a)** and at the m/z of 128.0564 in panel **(b)** correspond to the 15N-substituted (^{15}N–) thymine ($C_5H_6{}^{15}N_2O_2$: the m/z of the protonated ion is 129.0443) and the singly deuterated (d1–) thymine ($C_5H_5DN_2O_2$: the m/z of the protonated ion is 128.0565), respectively.

Discussion/Mechanism

- **Novelty**
- **Temperature** 10 K versus >65 K
- **Possible roles for carbon monoxide in nucleobase formation**

- formation of various molecules, such as methanol (CH_3OH), formaldehyde (H_2CO) and carbon dioxide (CO_2) via surface reactions.
- thymine formation that begins with the reaction of isocyanic acid (HNCO) with propanal (CH_3CH_2CHO).

- **Mechanism** Further experimental and computational studies are highly required to decipher the formation pathways of nucleobases under interstellar conditions.

Conclusion

- They showed experimental results for the formation of nucleobases under astrophysically relevant conditions, where a mixture of simple molecules (H_2O:CO:NH_3:CH_3OH = 5:2:2:2) was exposed to UV photons on a reaction substrate at 10 K.

- In the recovered organic sample, they also detected other molecules of prebiotic interest such as nitrogen heterocycles, amino acids and dipeptides.

Thank You