Prebiotic Chemistry

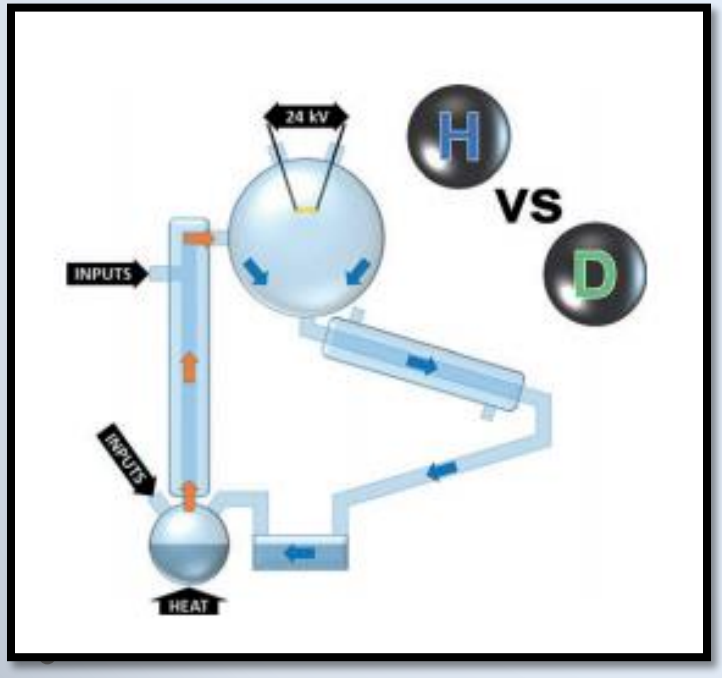
International Edition: DOI: 10.1002/anie.201610837
German Edition: DOI: 10.1002/ange.201610837

Miller–Urey Spark-Discharge Experiments in the Deuterium World

*Geoffrey J. T. Cooper, Andrew J. Surman, Jim McIver, Stephanie M. Colón-Santos, Piotr S. Gromski, Saskia Buchwald, Irene Suárez Marina, and Leroy Cronin**

[*] Dr. G. J. T. Cooper, Dr. A. J. Surman, J. McIver, S. M. Coln-Santos, Dr. P. S. Gromski, S. Buchwald, I. Suarez Marina, Prof. Dr. L. Cronin
WestCHEM, School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ (UK)

Angew. Chem. Int. Ed. 2017, 56, 1–5



H_2O (400mL)	D_2O (400mL)
H_2 (20%)	D_2 (20%)
NH_3 (40%)	ND_3 (40%)
CH_4 (40%)	CD_4 (40%)
7 Days Boiling / Recirculating	
24 kV Spark Discharge	

Gaurav Vishwakarma
27.04.2019

Background Work

A Production of Amino Acids under Possible Primitive Earth Conditions
Author(s): Stanley L. Miller
Source: *Science*, New Series, Vol. 117, No. 3046 (May 15, 1953), pp. 528-529
Published by: American Association for the Advancement of Science
Stable URL: http://www.jstor.org/stable/1680569
Accessed: 11/09/2008 17:10

A Production of Amino Acids Under Possible Primitive Earth Conditions

Stanley L. Miller[1, 2]

G. H. Jones Chemical Laboratory,
University of Chicago, Chicago, Illinois

The idea that the organic compounds that serve as the basis of life were formed when the earth had an atmosphere of methane, ammonia, water, and hydrogen instead of carbon dioxide, nitrogen, oxygen, and water was suggested by Oparin (*1*) and has been given emphasis recently by Urey (*2*) and Bernal (*3*).

In order to test this hypothesis, an apparatus was built to circulate CH_4, NH_3, H_2O, and H_2 past an electric discharge. The resulting mixture has been tested for amino acids by paper chromatography. Electrical discharge was used to form free radicals instead of ultraviolet light, because quartz absorbs wavelengths short enough to cause photo-dissociation of the gases. Electrical discharge may have played a

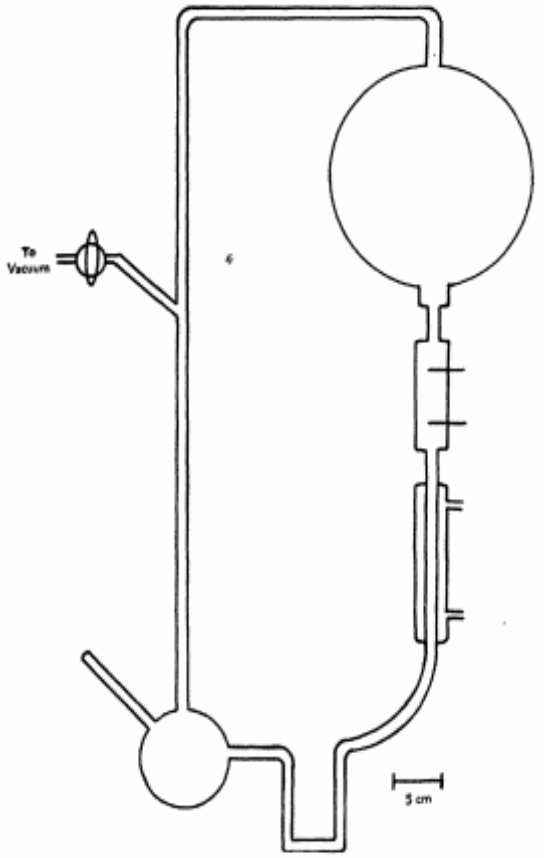


FIG. 1.

In this paper

- Deuterated and nondeuterated Miller–Urey experiments were run for seven days.
- As an initial analysis, and to align this work with that of others in the field, HPLC chromatograms were obtained with derivatization to detect primary amines (such as amino acids) by fluorescence (FLD) detection.
- By comparison with known amino acid standards, we find our mixture to contain glycine, alanine, and β-alanine, which is consistent with the previous findings of such simple spark-discharge experiments.
- Rather than specifically looking for amino acids, or indeed any specific chemical species, they wished to examine a different area of chemical space without the bias of expectation.
- Analysis of some 120 picked peaks (RT-m/z coordinates) from the HPLC-MS data reveals approximately 40 peaks that can be assigned a match in the corresponding H or D data, The remaining majority of picked peaks (80) were found only in the "hydrogenated" or "deuterated" worlds.
- Characterization and analysis- *HPLC-FLD*, *HPLC-MS*, *GC-MS*, Principal component analysis (PCA), Principal component-discriminant function analysis (PC-DFA), Formula assignment.

Relevance of this work

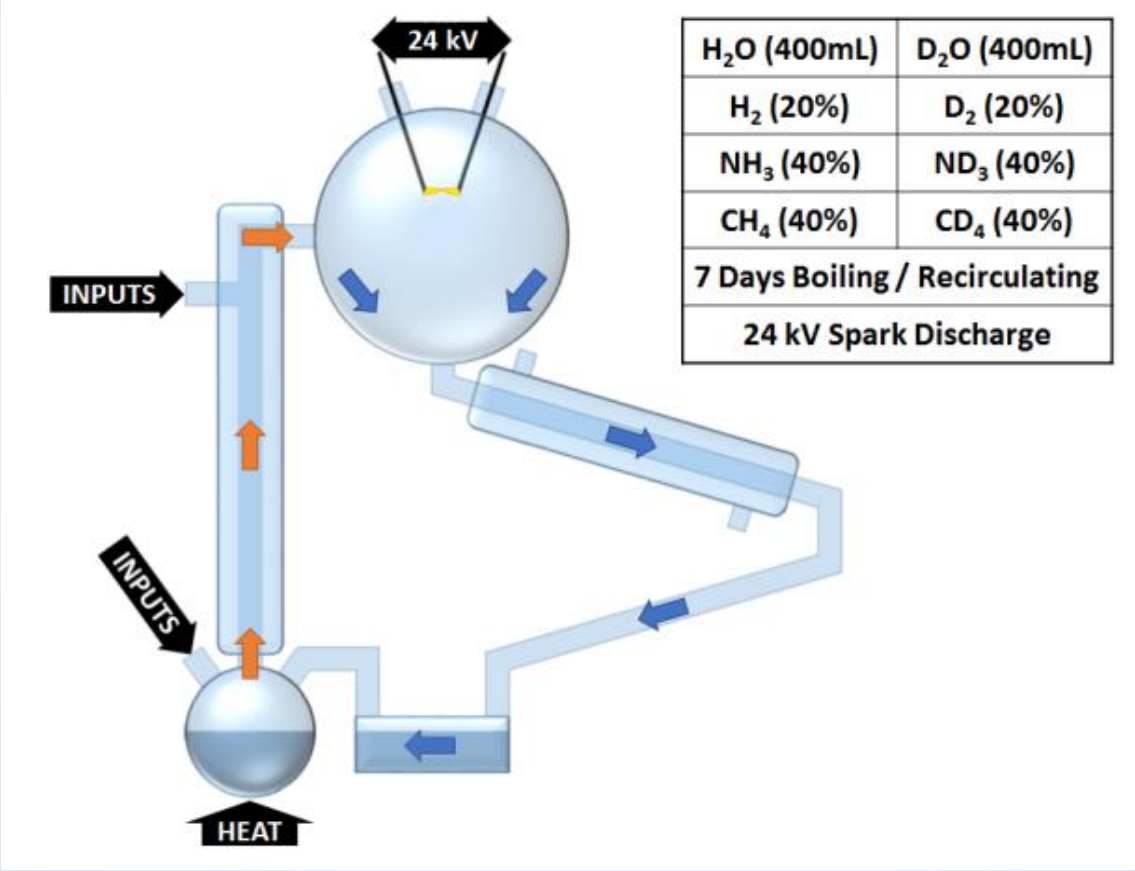
- It is interesting to note that the addition of one neutron produces such a difference under chemically identical reaction conditions.

- This choice was also inspired by the coincidence that deuterium was discovered by Urey in 1931.

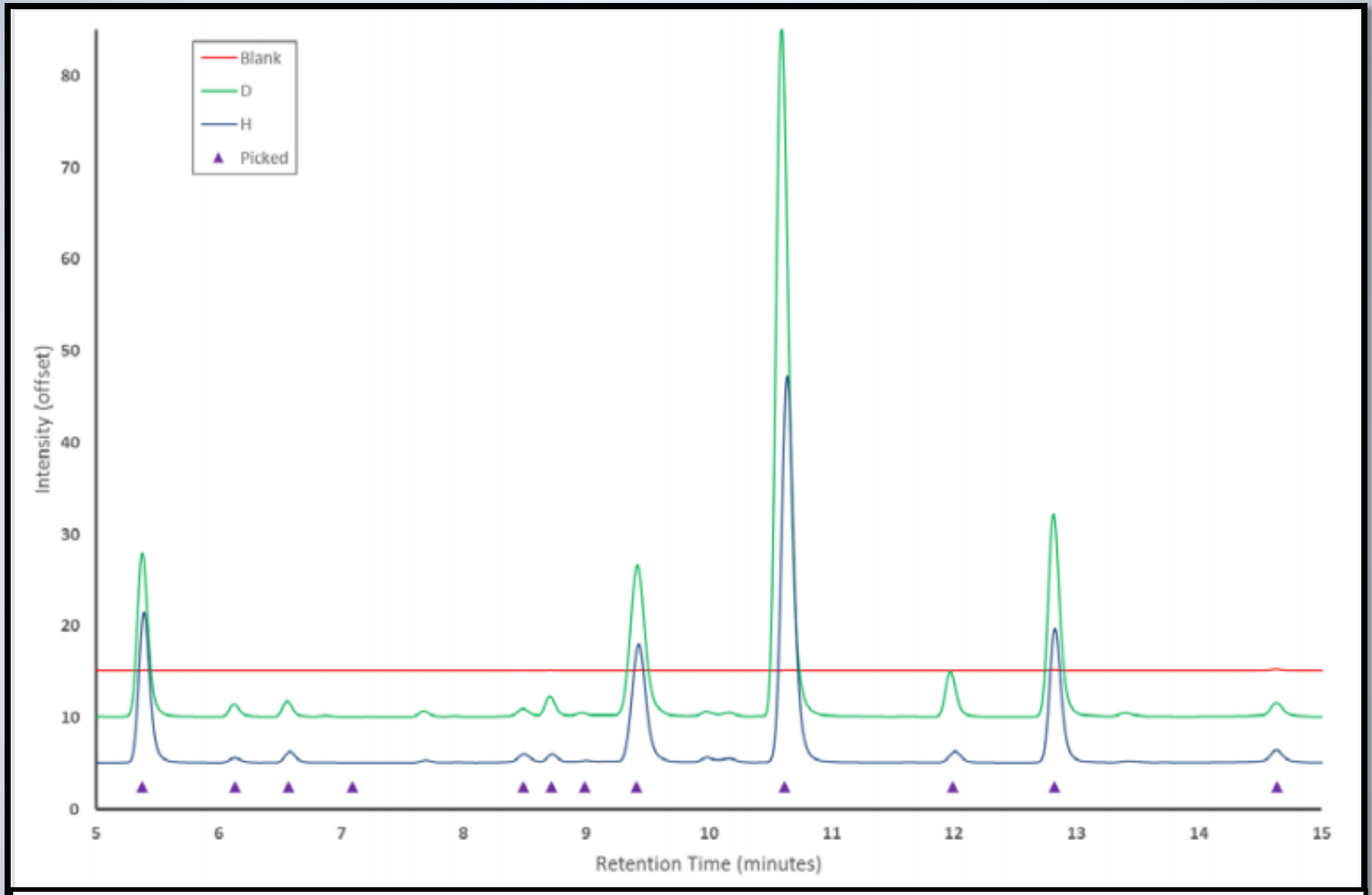
- Most of the studies were focused on very specific "prebiotically relevant" products, whereas here it is more "systems" approach.

Experimental Methods

Two sets of spark discharge apparatus were built.
The whole rig was pumped down three times and the system was pressurized to 1 atm with gas mixture (40% methane, 40% ammonia and 20% hydrogen, or their deuterated equivalents).



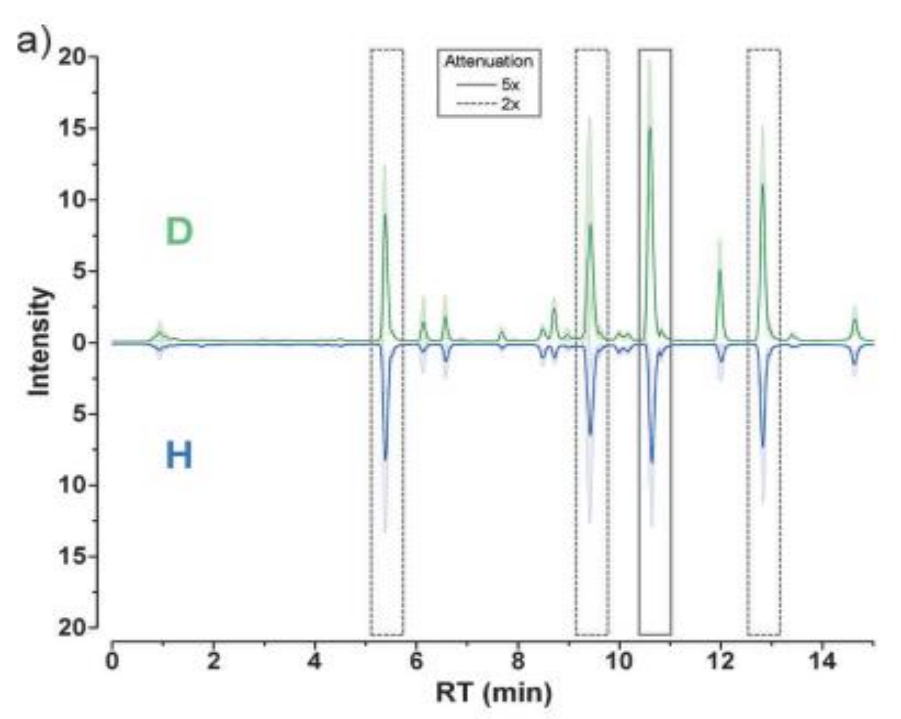
HPLC-FLD Analysis



HPLC-FLD plots averaged for deuterated vs. non-deuterated, compared to a blank run. Purple triangles show the peaks that were picked in the data analysis.

HPLC-FLD Analysis

HPLC chromatograms were obtained with derivatization of amine groups with o-phthalaldehyde (OPA)/mercaptopropionic acid (MPA) and 9- fluorenylmethyloxycarbonyl chloride (FmocCl) to allow retention of the products on a reverse phase column to detect primary amines (such as amino acids) by fluorescence (FLD) detection.



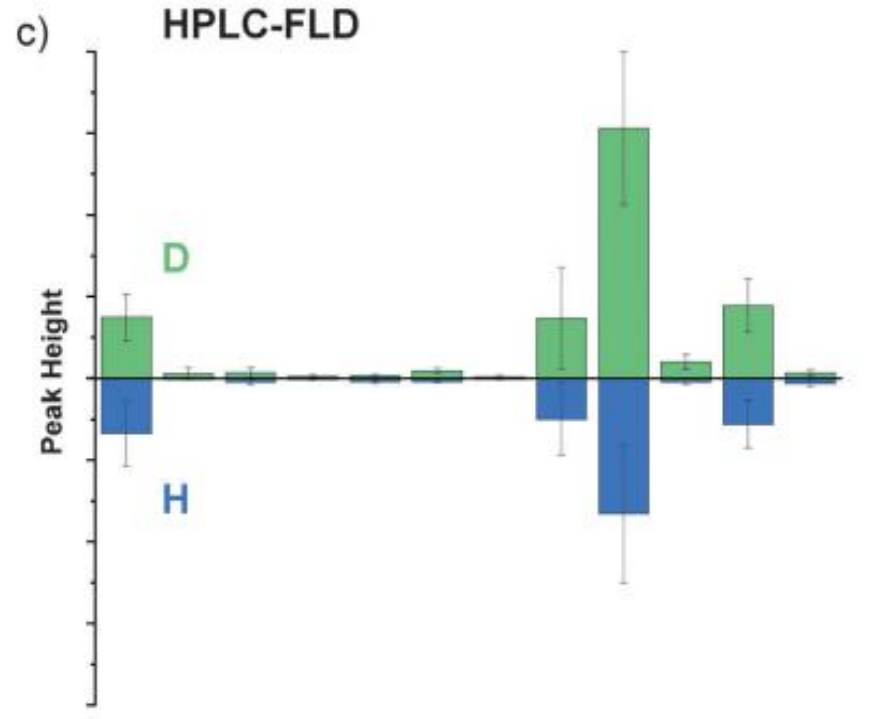
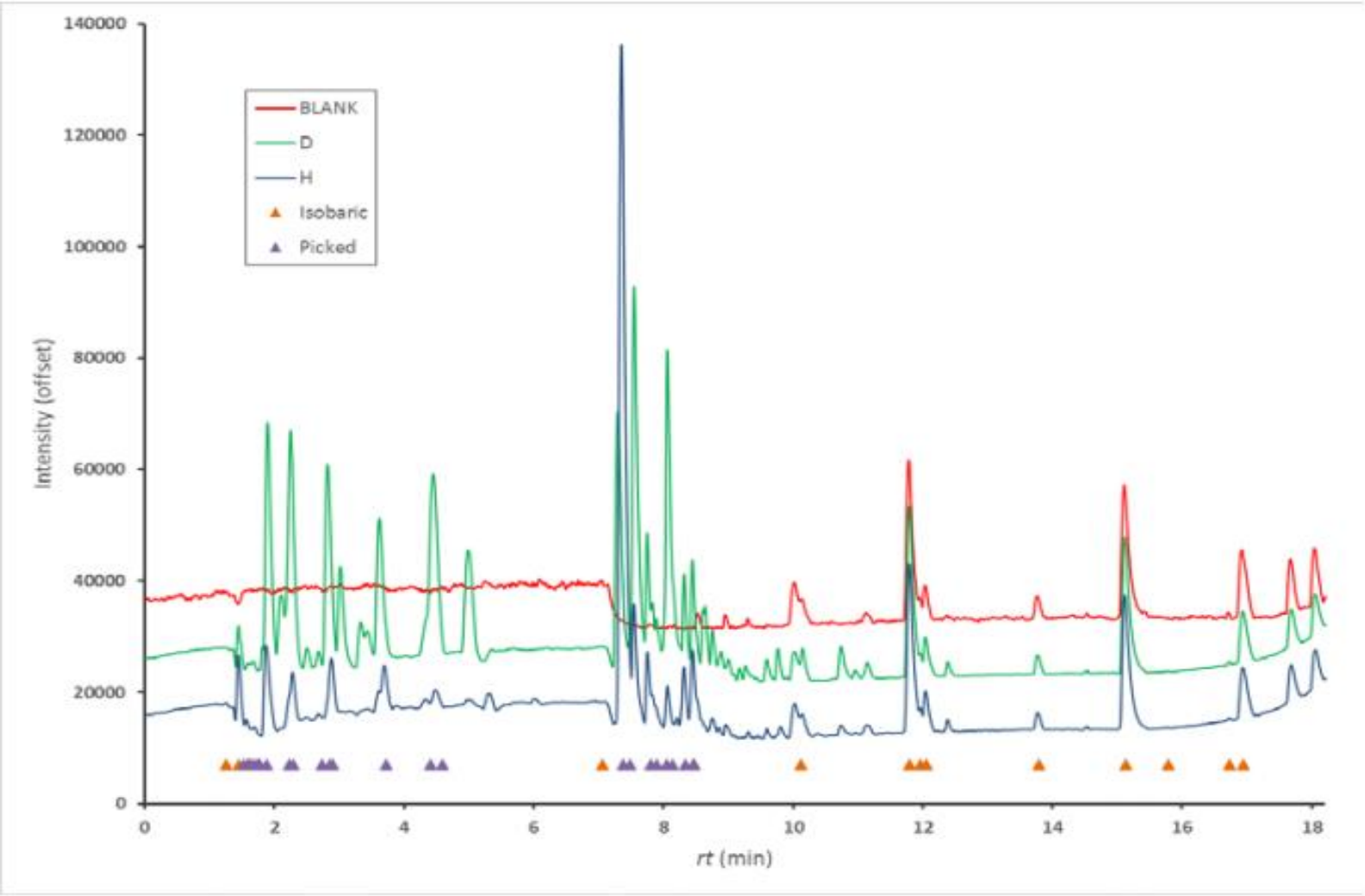


Figure- Data analysis of HPLC-FLD for the H (blue) and D (green) experiments. Plots are mirrored with D on top and H inverted below to allow easy comparison of peak position. a) HPLC-FLD chromatogram. c)Bar plot of picked peaks from HPLC-FLD data. In both sets of chromatograms, the most intense peaks are attenuated to allow smaller peaks to also be resolved.

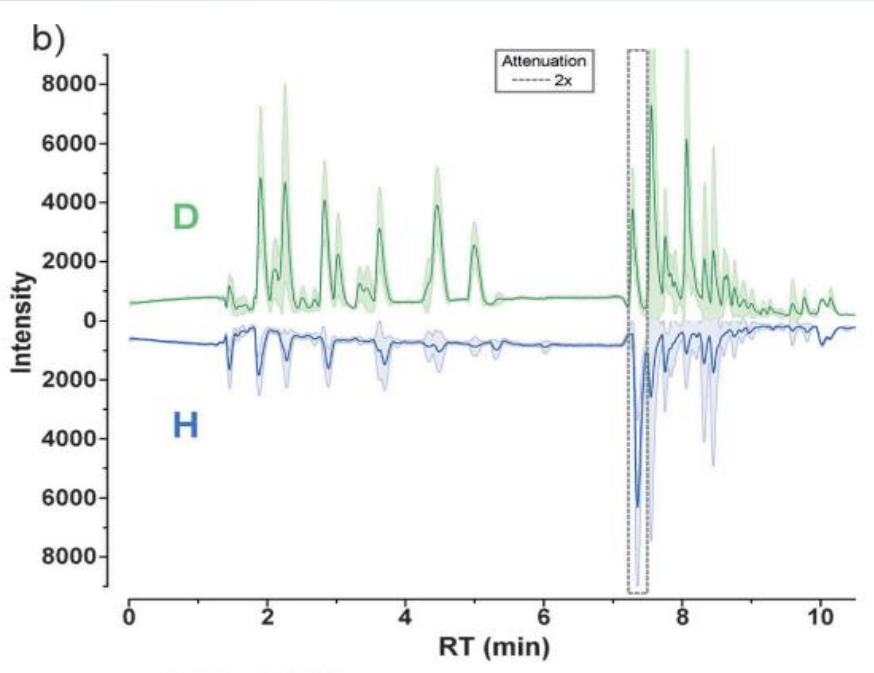
HPLC-MS Analysis



HPLC-MS BPC plots averaged for deuterated vs. non-deuterated, compared to a blank run. Purple triangles show the H peaks that were picked in the data analysis and matched to D isotopologues. Orange triangles mark peaks that were identified in both H and D but were found to have the same *m/z*.

HPLC-MS Analysis

Matched peaks corresponding to isotopologues observed in both 'H' and 'D' experiments by searching for features with matching retention times (+/- 20 s) and *m*/*z* corresponding to up to 20 H/D exchanges



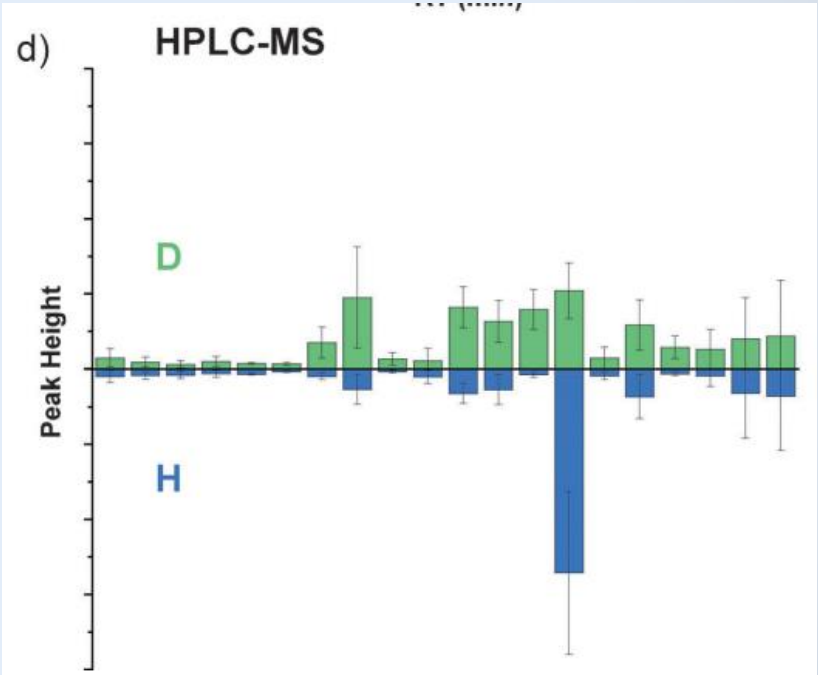
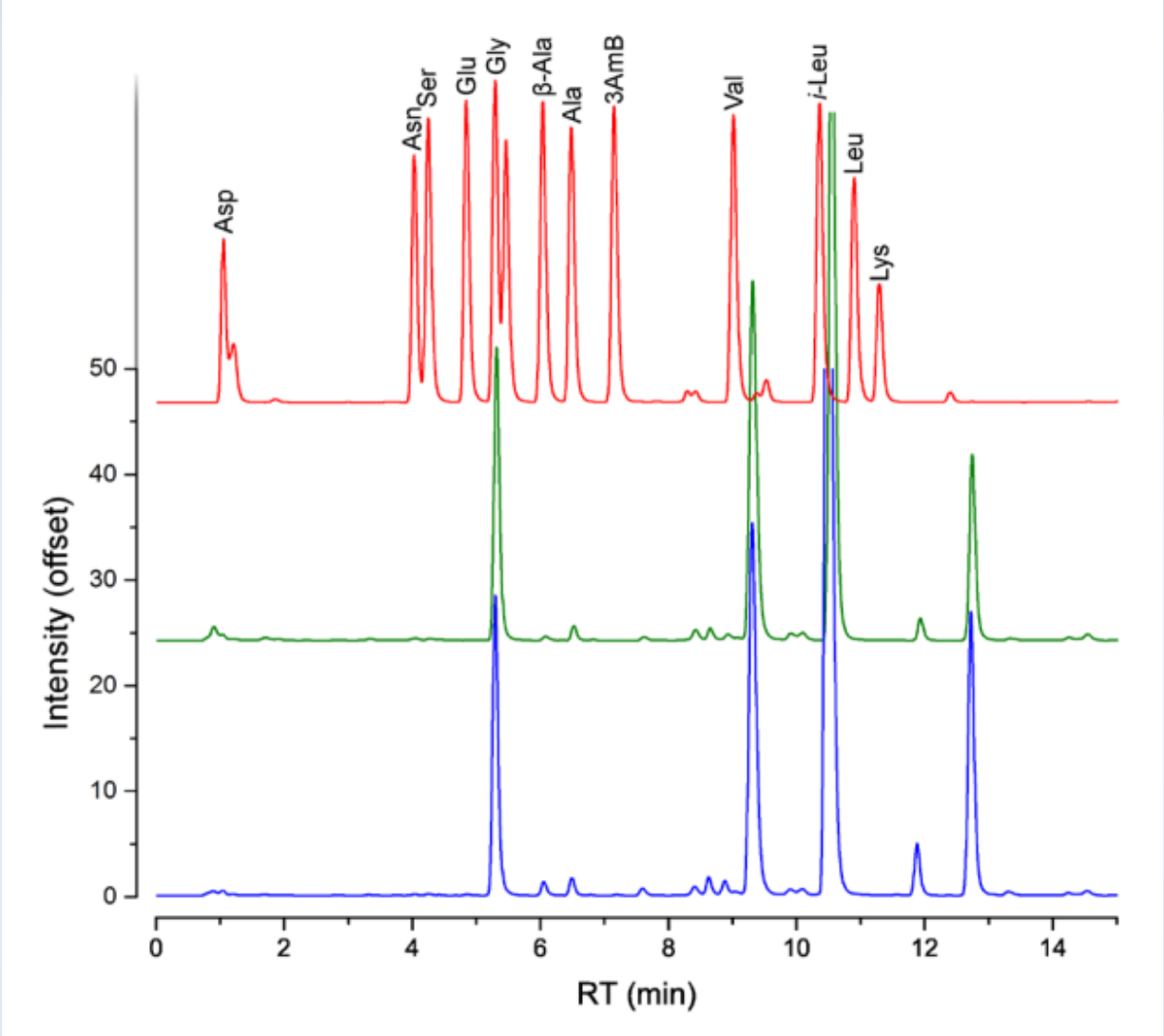


Figure. Data analysis of HPLC-MS for the H (blue) and D (green) experiments. b) HPLC-MS base peak chromatograms. d) Bar plot of picked, matched, peaks from HPLC-MS data.

Products



HPLC-FLD plots of amino acid standards (red, top), a representative deuterated run (green, middle) and a representative non-deuterated run (blue, bottom), showing positive identification of glycine and tentative identification of alanine and β-alanine. Standards of aspartic acid, asparagine, serine, glutamine, glycine, β-alanine, alanine, 3-amino butyric acid, valine, iso-leucine, leucine and lysine were made up at 2.5 mM in HPLC grade water

"Systems" Approach

Analysis of some 120 picked peaks (RT-m/z coordinates) from the HPLC-MS data reveals approximately 40 peaks that can be assigned a match in the corresponding H or D data, and the matched peaks make up the majority of large peaks

Tentative assignment of chemical formulae for peaks found in H & D experiments. Formula fitting and matching was performed using R and MS Excel.

rt /min	max. m/z	Intensity	Fitted Formula	ppm error
1.60	154.1217	3638	$C_3D_6H_4N_5O_2$	-3.82
1.70	230.0689	3128	$C_5D_4H_6N_2O_8$	-0.33
1.70	213.0998	2026	$C_{13}D_2H_9N_2O$	-0.51
1.77	118.0923	2074	$C_4D_4H_4N_3O$	-3.85
1.79	212.1819	1558	$C_8D_{10}H_6N_3O_3$	0.17
1.80	278.1210	2412	$C_8DH_{10}N_{11}O$	0.29
1.83	177.0826	8385	$C_9D_5HN_3O$	-0.72
1.83	136.0462	8452	$C_6D_3N_3O$	1.78
1.84	171.1002	19884	$C_3D_6H_3N_4O_4$	-0.93
1.88	114.0636	9227	$C_4D_2H_4N_3O$	0.36
1.91	170.1158	47524	$C_5D_7H_4N_2O_4$	0.12
1.93	171.1554	7806	$C_6D_{10}H_3N_2O_3$	-0.08
1.96	189.1260	4510	$C_5D_5H_5N_7O$	0.36
1.96	152.1610	2685	$C_6D_{10}H_2N_3O$	-1.27
2.12	236.1209	16692	$C_{13}D_5H_8NO_3$	0.12
2.22	131.0758	13895	$C_5D_4H_3N_2O_2$	0.46
2.29	241.1074	2068	$C_4D_4H_7N_7O_5$	-0.52

Conclusion

While the deuteration of the system has little effect on the distribution of amino acid products, significant differences are seen in other regions of the product-space. Not only do they observe about 120 new species, they also see significant differences in their distribution if the two hydrogen isotope worlds are compared.

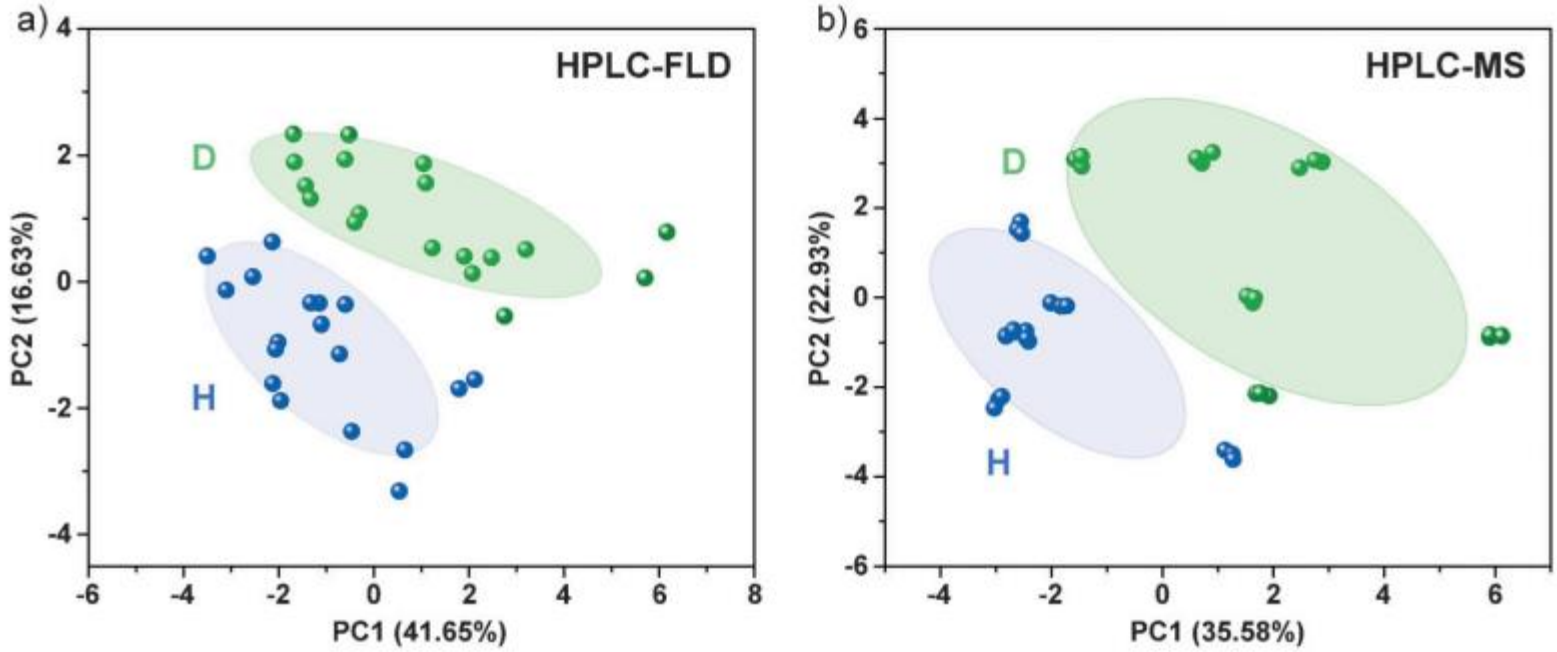


Figure 3. PCA of picked peaks from the H (blue) and D (green) experiments a) HPLC-FLD and b) HPLC-MS analysis. Confidence ellipses represent one standard deviation and loadings can be found in the Supporting Information.