宇宙生命計算科学連携拠点プロジェクト第2回ワークショップ
2016年4月28日＠筑波大学

模擬星間物質からのアミノ酸前駆体・核酸塩基の合成

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Outline

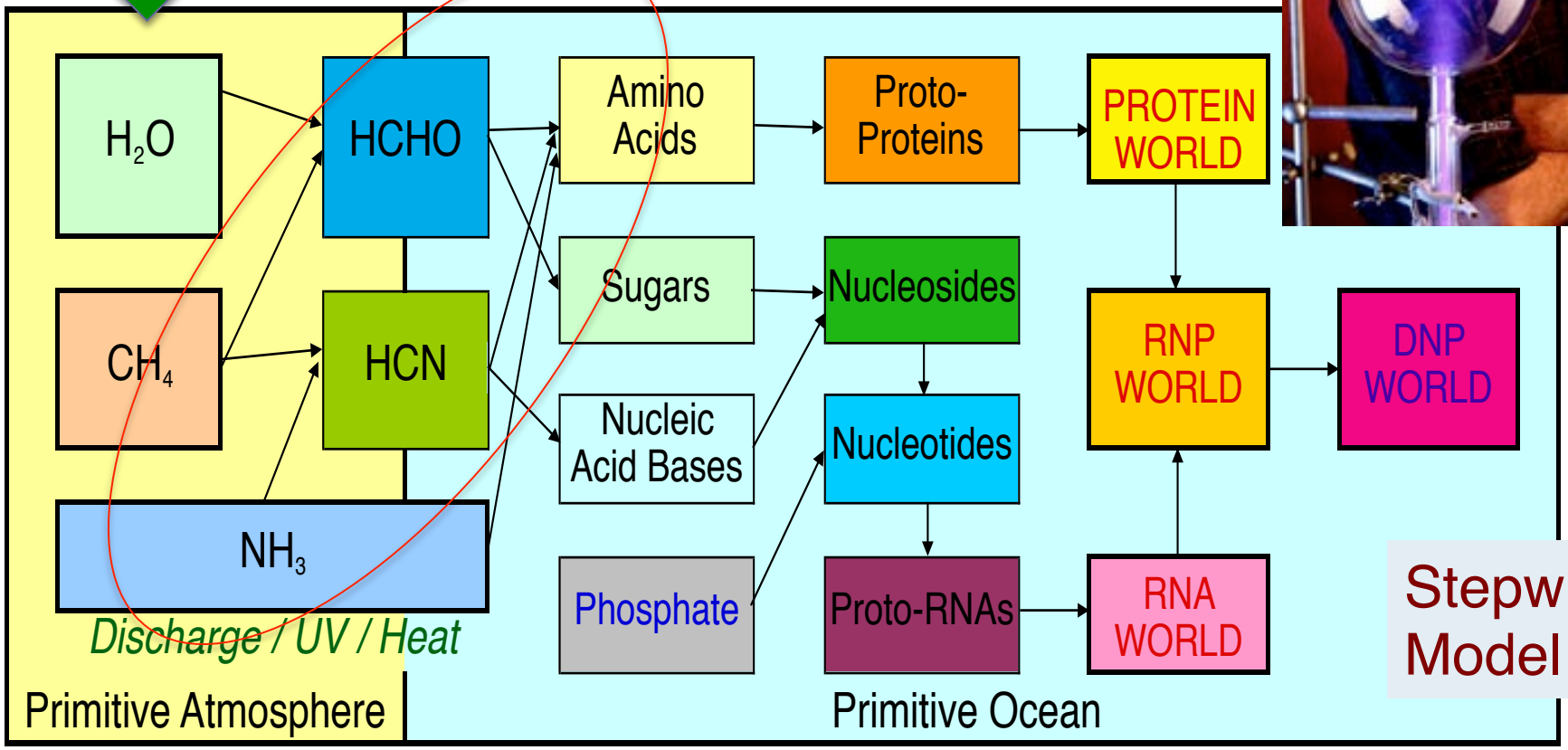
- Extraterrestrial organics and their relevance to origins of Life
- Abiotic formation of amino acid precursors from possible interstellar media
- Abiotic formation of nucleic acid bases from possible interstellar media
- Possible formation pathway of amino acid precursors and nucleic acid bases

Miller's Experiment (1953)

Experimental verification of abiotic chemistry is possible! ~~probiotic~~

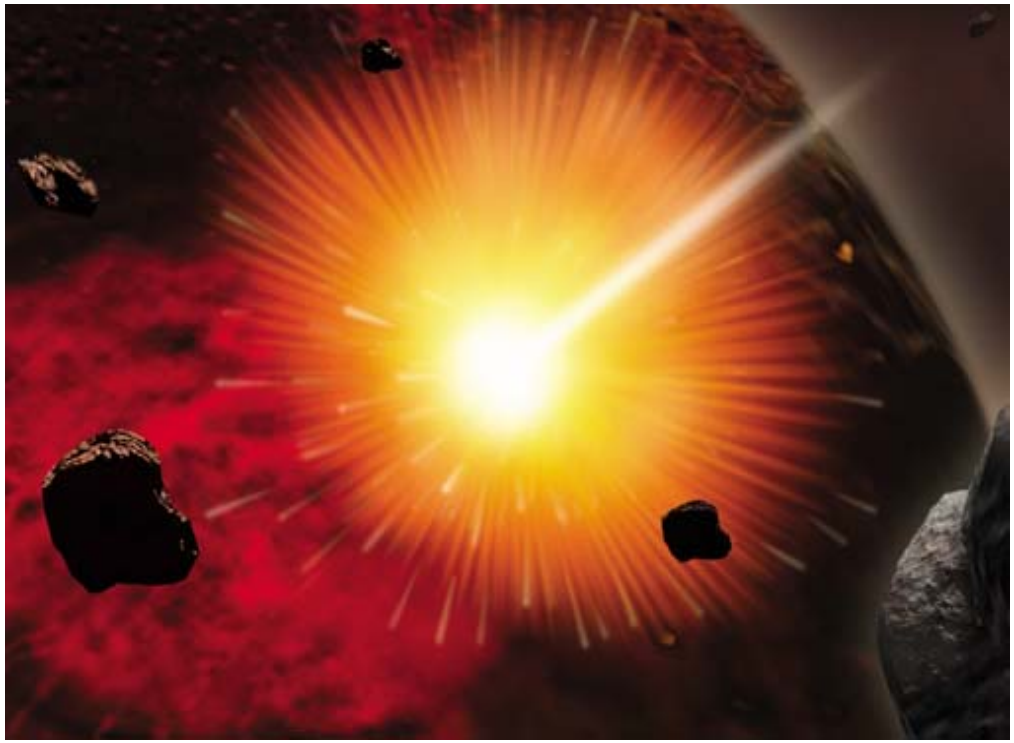
Strongly reducing atmosphere

Strecker Synthesis



Stepwise Model

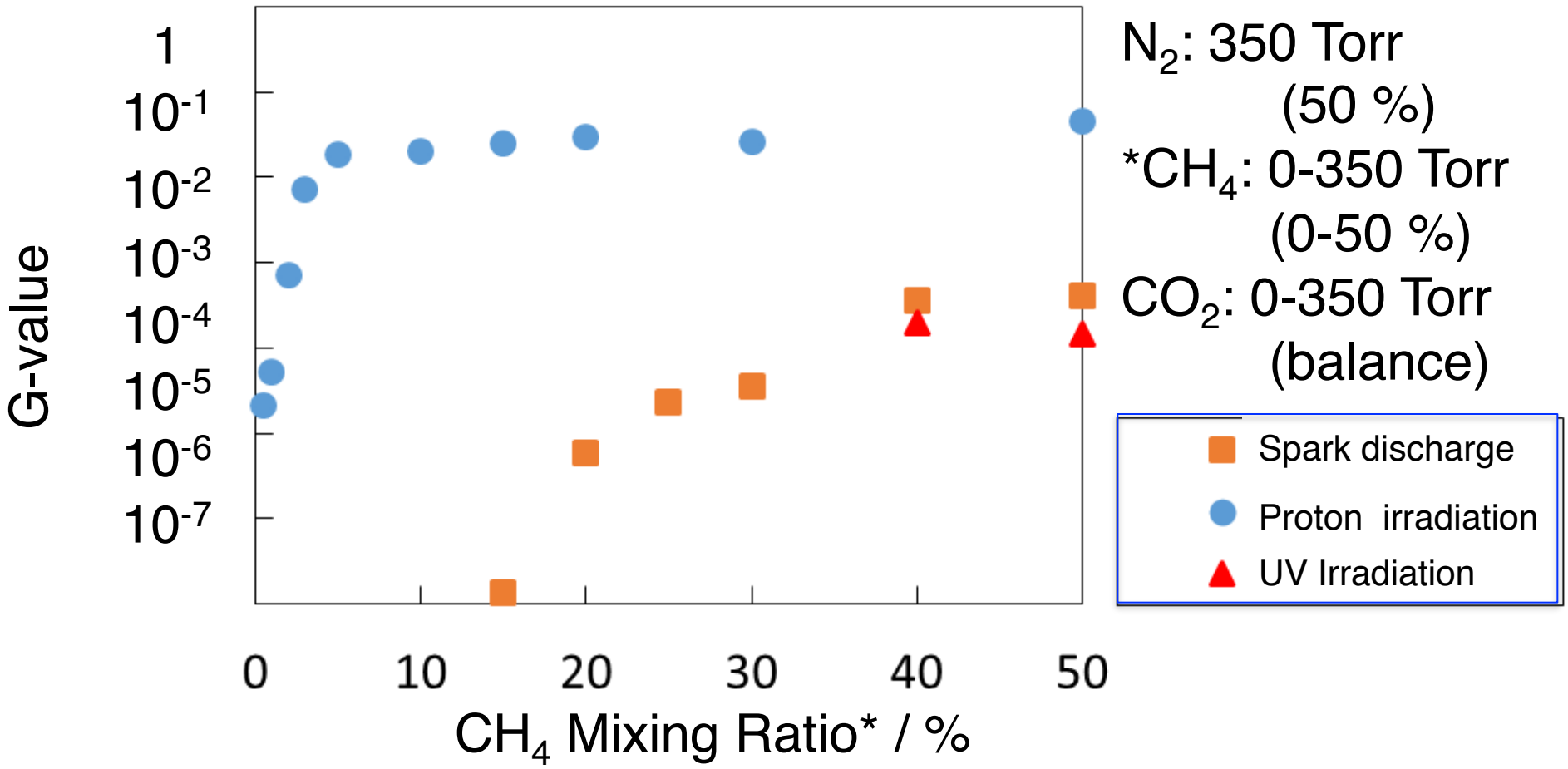
Primitive Earth Atmosphere was not Strongly-Reducing



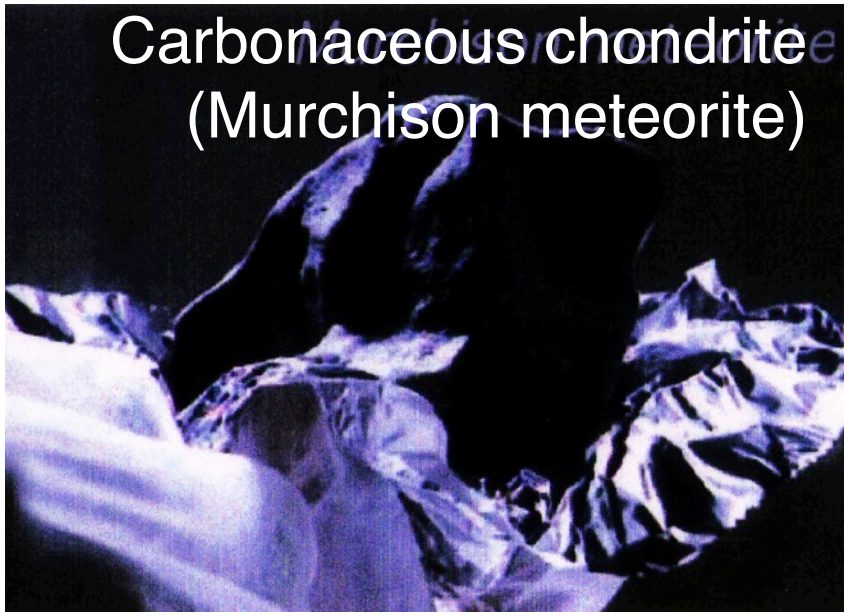
- Primitive atmosphere was only slightly-reducing
- Amino acids are hardly formed from slightly-reducing gas mixtures by UV, heat and spark discharges

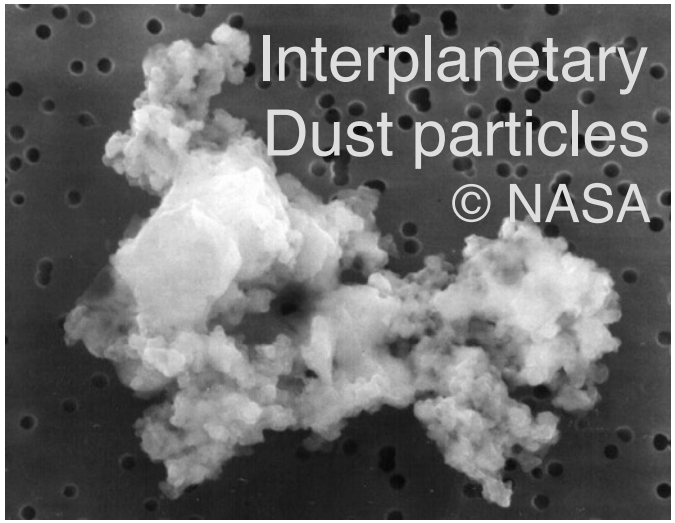
http://www.newtonpress.co.jp/search2/e_book/ebook/2002_02/mmsolarsys_0502.html

G-Values of Glycine Formed from a Mixture of CO_2, CH_4, N_2 and H_2O



Extraterrestrial Organics

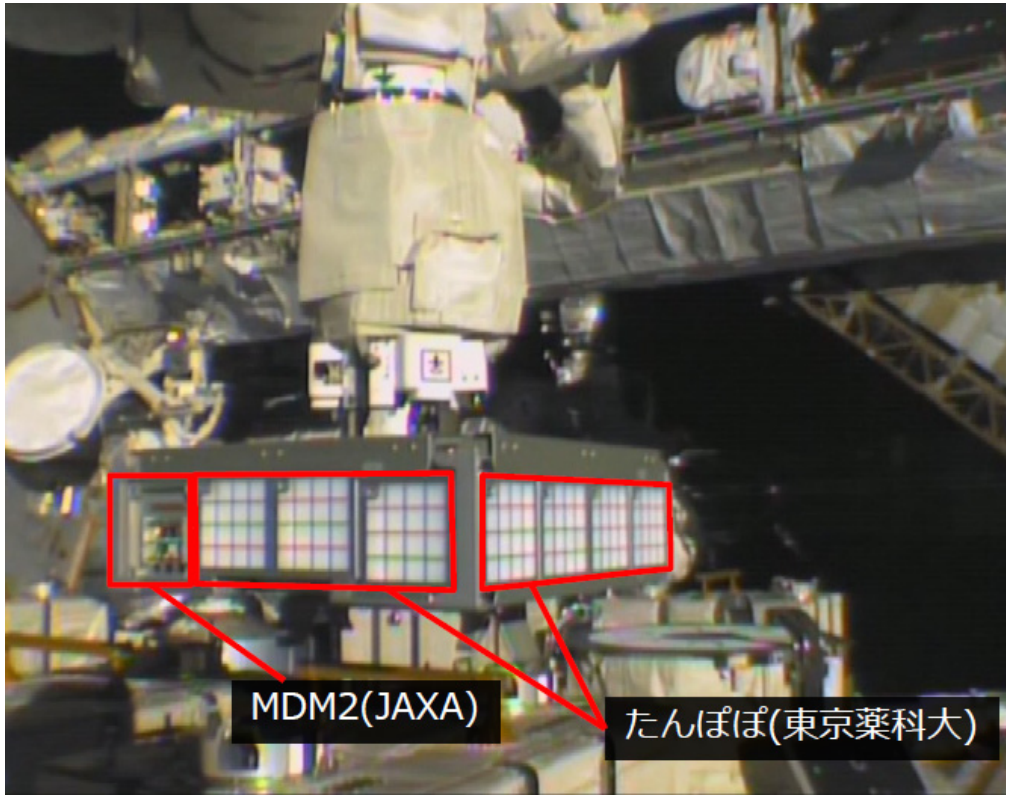




- ✓ Amino acid (precursors)
- ✓ Nucleic acid bases
- ✓ Complex organics (IOM)
- ✓ Low temperature origins

The Tanpopo Mission to Collect Cosmic Dusts in LEO Has Started

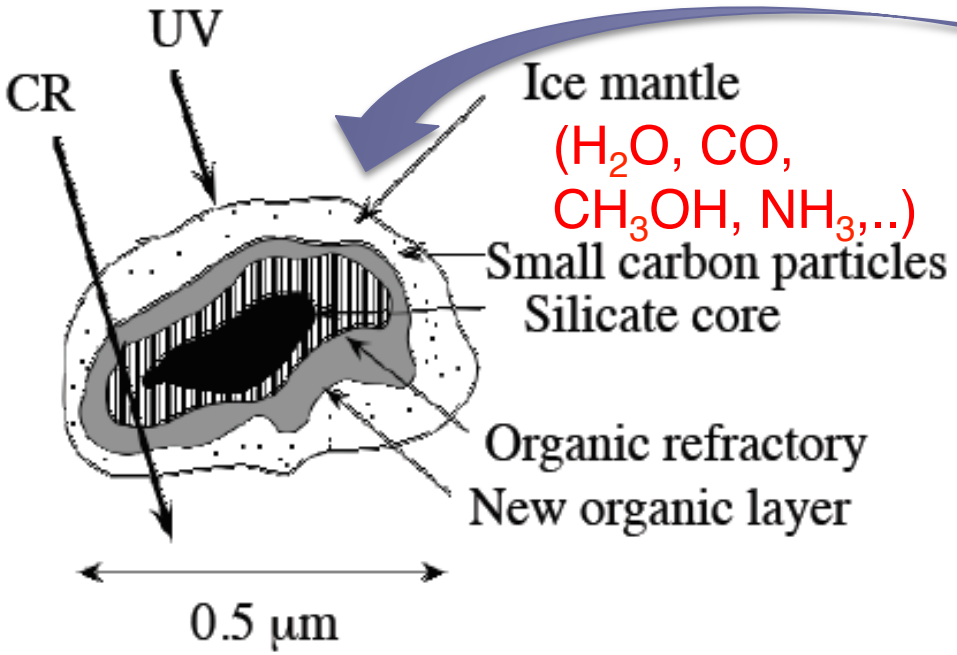
✓ Launch on April 15, 2015



✓ The apparatus was exposed on JEM-EF on May 26, 2015.

✓ The first sample will return in 2016, and the mission will last untill 2018.

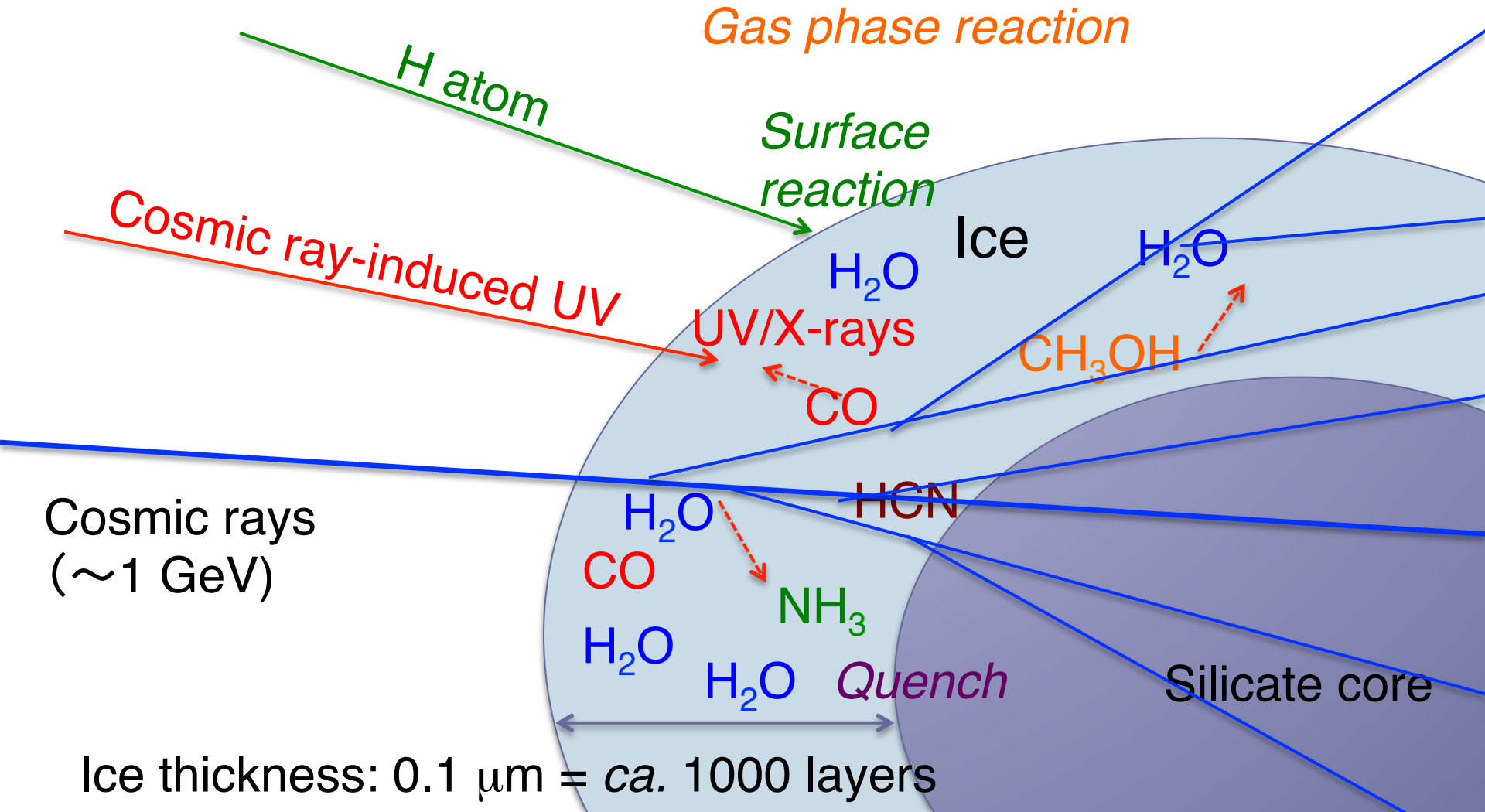
Origin of Organics in Comets and Meteorites: Formation in Molecular Clouds?



Greenberg Model：

Complex organics are formed in ice mantles of interstellar dust particles in molecular clouds

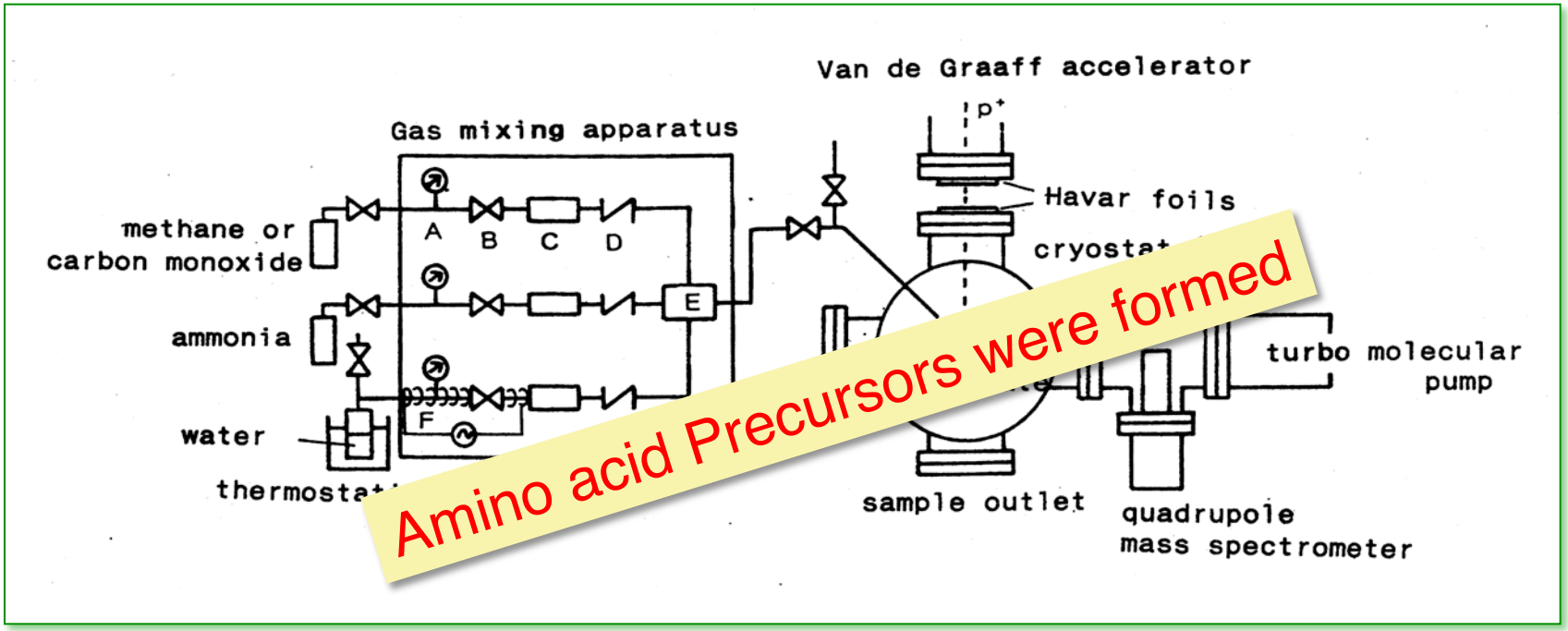
Chemical Reactions in Molecular Clouds



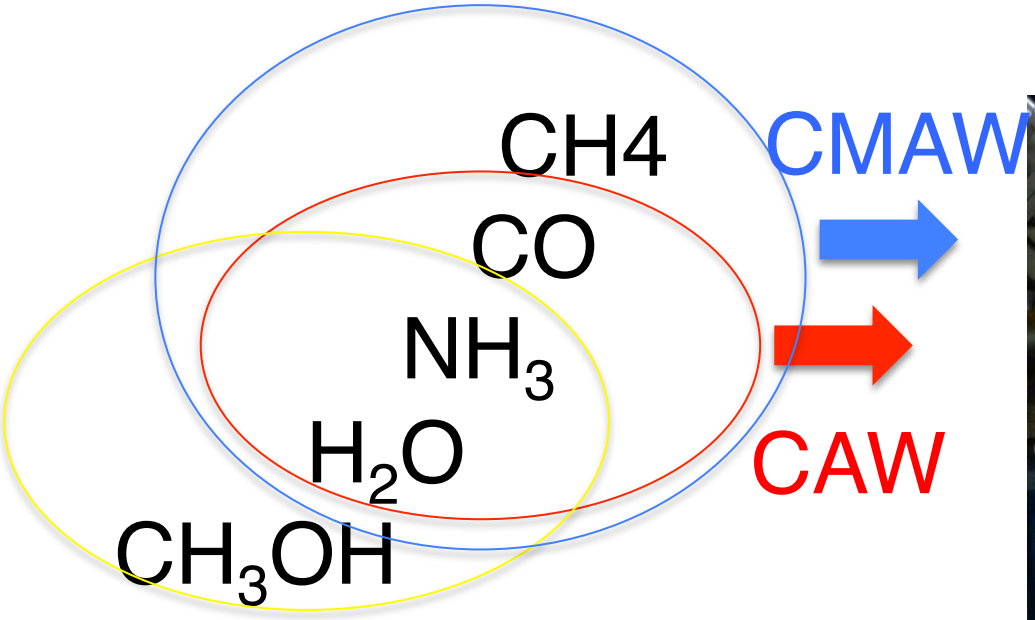
Irradiation of Simulated ISD Ices

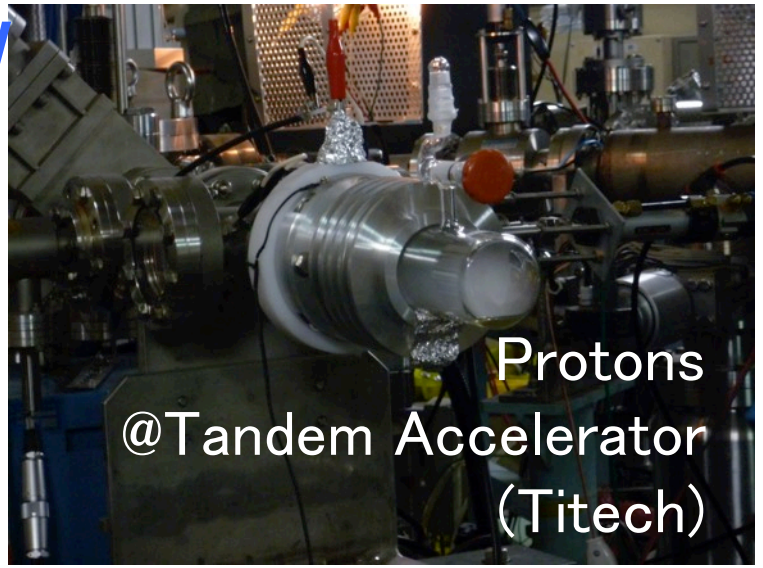
Charged Particles
- Kobayashi et al., 1995
- Kasamatsu et al., 1997
- Kobayashi et al., 2007

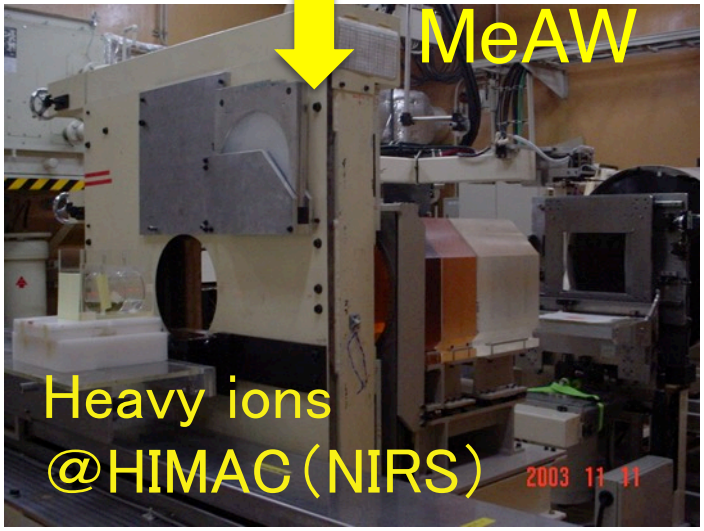
Ultraviolet Light
- Munos Caro et al., 2002
- Bernstein et al., 2002
- Takano et al., 2003



Particles Irradiation to Possible Interstelar Media

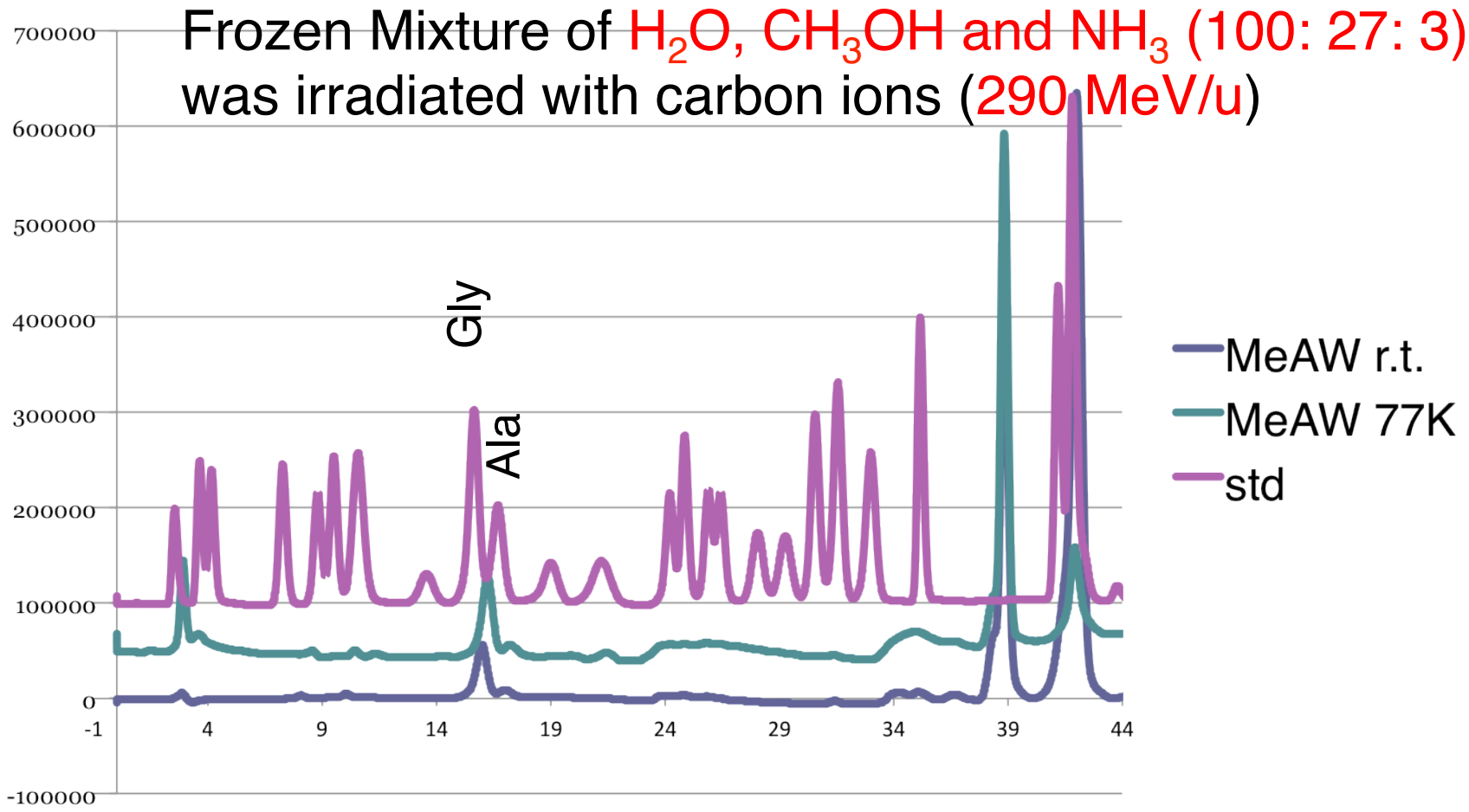




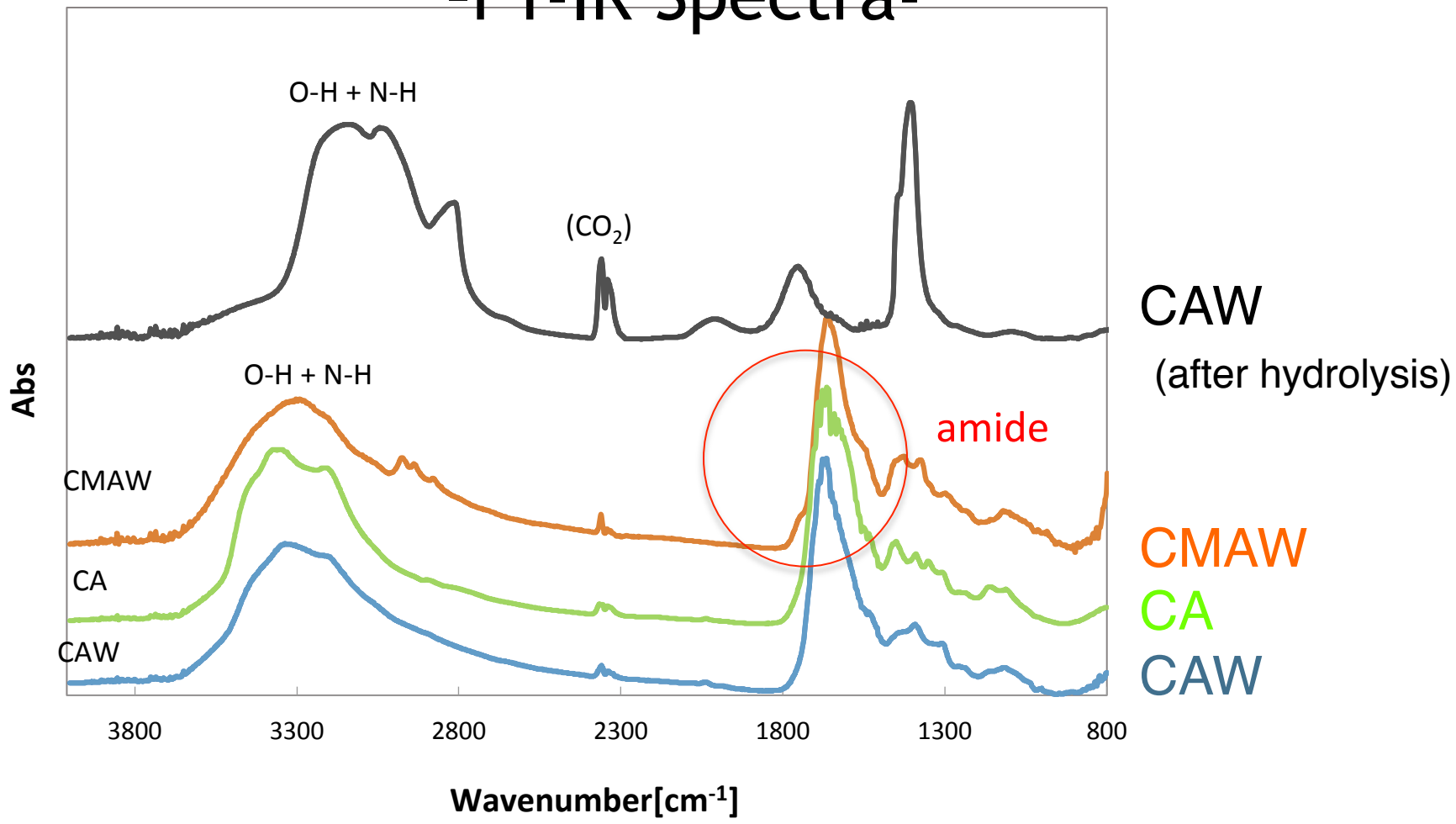


- ✓ Amino acid precursors were formed.
- ✓ No significant difference among gaseous, liquid and solid phase irradiation, except energy yields.

Ion-Exchange Chromatograms of Amino Acids Formed by Carbon Ion Bombardment (After hydrolysis)

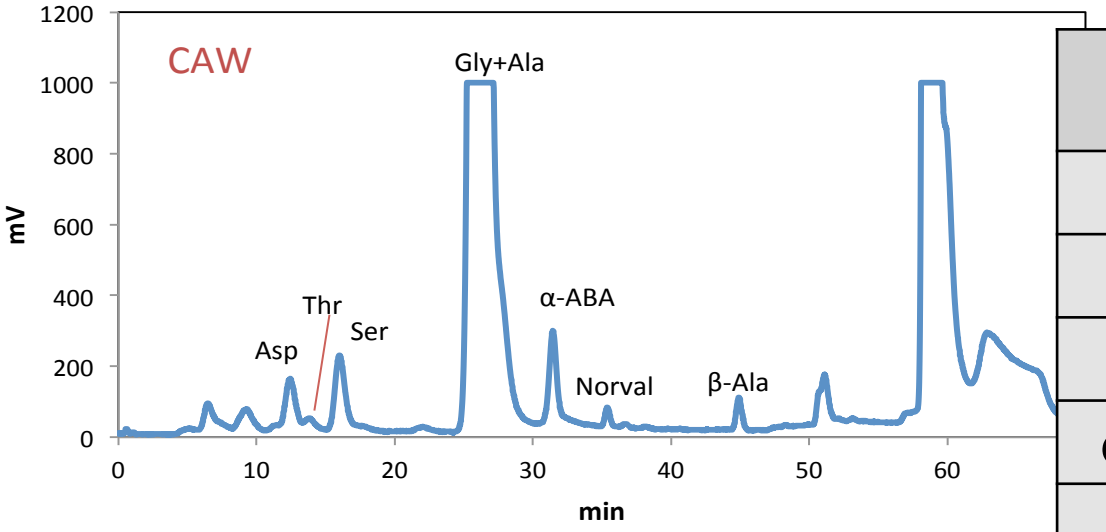


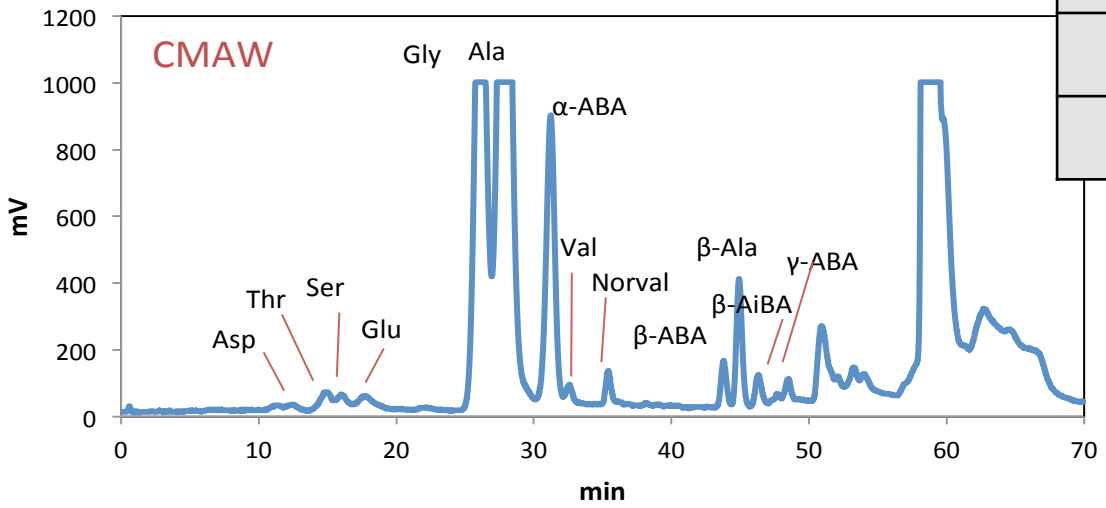
Characterization of the Irradiation Product -FT-IR Spectra-



Super-complex amino acid precursors with amide groups were over 1000 were formed.

Yields of Amino Acids in CAW & CMAW





Amino acid	CAW (µmol)	CMAW (µmol)
Asp	0.47	0.15
Ser	0.82	0.19
Gly	76 >>	6.4
α-ABA	1.4	5.7
NVal	0.05	0.12
β-Ala	0.17	0.72
Ala	0.70* <<	13

*Determined by GC/MS
ABA: Aminobutyric acid
AiBA: Aminoisobutyric acid
Nval: Norvaline

Amino acid precursors

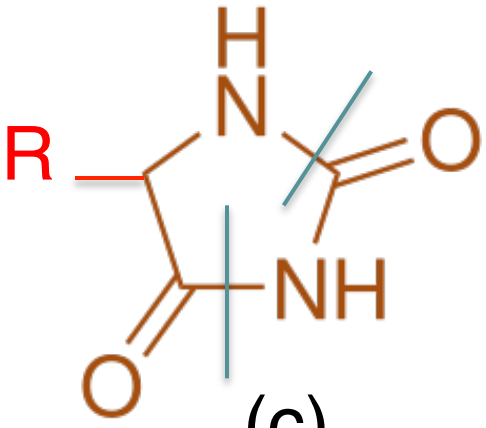
$HCN + RCHO + NH_3 \rightarrow$ $NH_2\text{-}CHR\text{-}CN$ (a)

$\downarrow H_2O$

$NH_2\text{-}CHR\text{-}CONH_2$ (b)

$\downarrow H_2O$

$NH_2\text{-}CHR\text{-}COOH + NH_3$



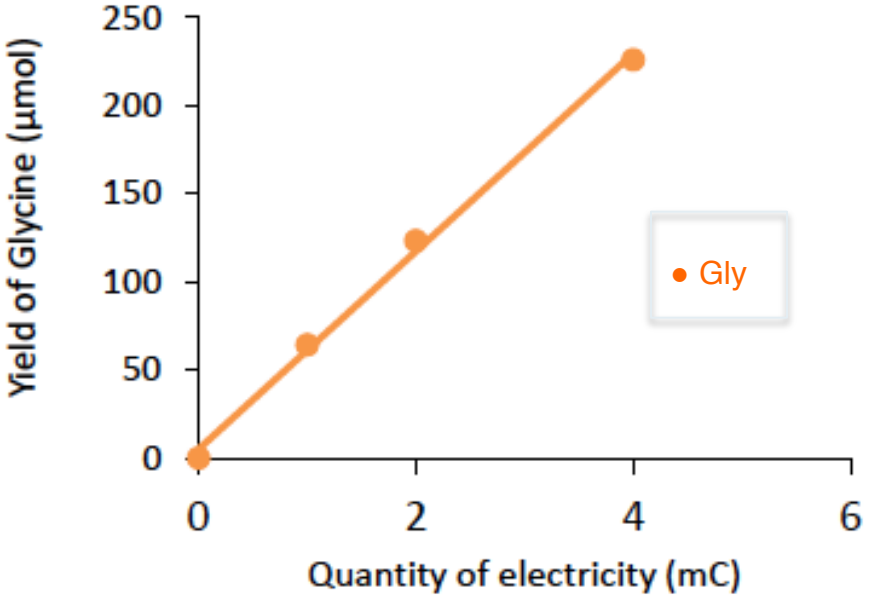
(c)

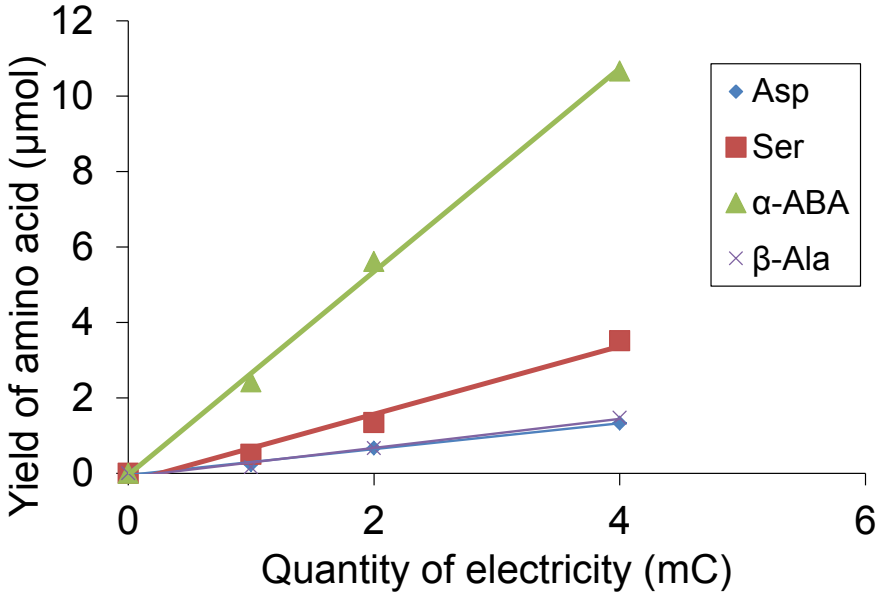
$\rightarrow NH_2\text{-}CHR\text{-}COOH + NH_3 + CO_2$

$2H_2O$

(a) aminonitriles, (b) amino acid amides, (c) hydantoins

Yields of Amino Acids in CAW





Strecker Rection: $HCN + RCHO + NH_3 \rightarrow NH_2CHRCN \rightarrow NH_2CHRCOOH + 2H_2O$

Formation of amino acids from complex organics (*Garakuta* molecules)

$CO \rightarrow C + O$

$NH_3 \rightarrow NH_2 + H$

$\downarrow$

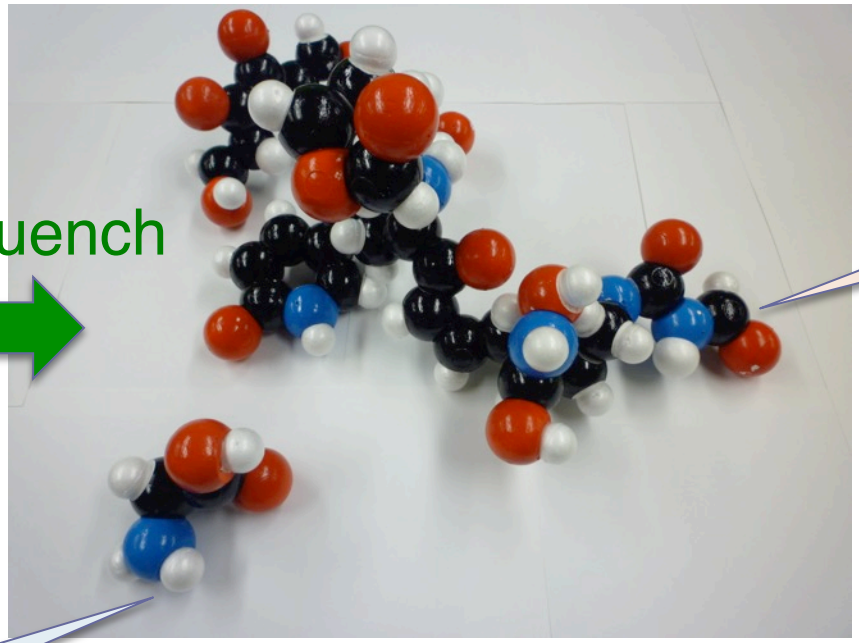
$NH + H$

$H_2O \rightarrow H + OH$

$\downarrow$

$O + H$

Quench



Garakuta Molecule (MW: ca. 1000)

Glycine (MW: 75)

…-CO-CH_2-NH-CH=C(OH)-

-CO-NH-CH_2-CO-NH-C=N-

-CH_2-CH_2-C(=NH)-O-CO-…

Hydrolysis

NH_2-CH_2-COOH

Syntheses of Nucleic Acid Bases from Simulated Primitive Atmospheres

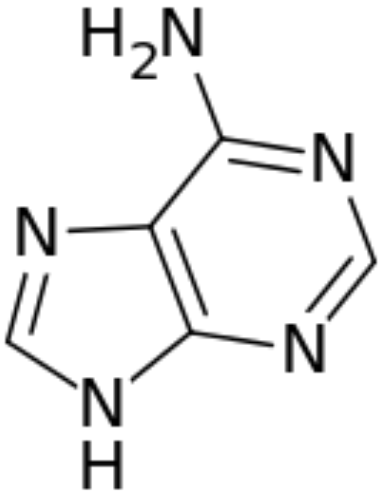
Reduced

CH_4
NH_3
H_2O

Electron Irradiation

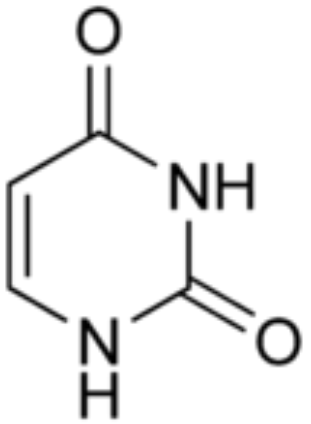
or

Spark Discharge



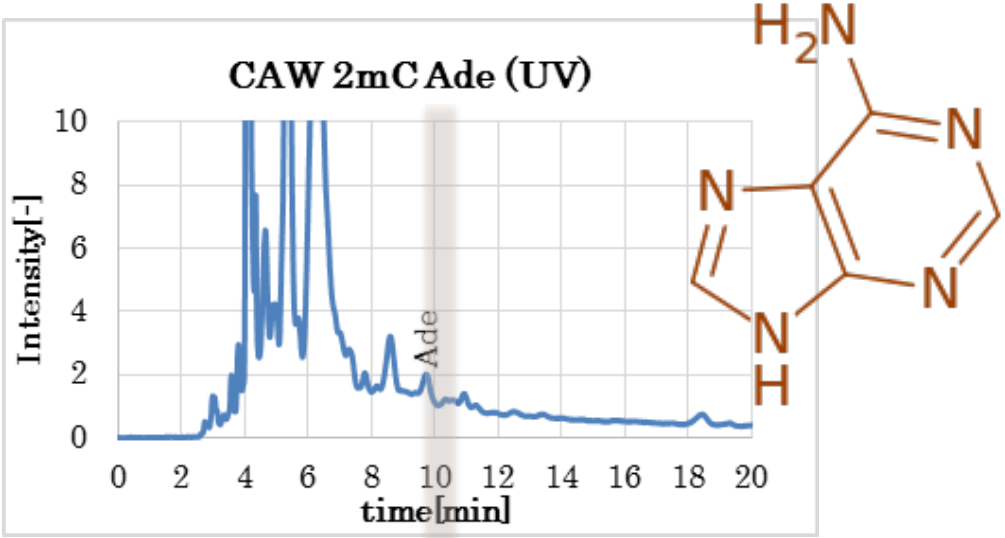
CO
N_2
H_2O

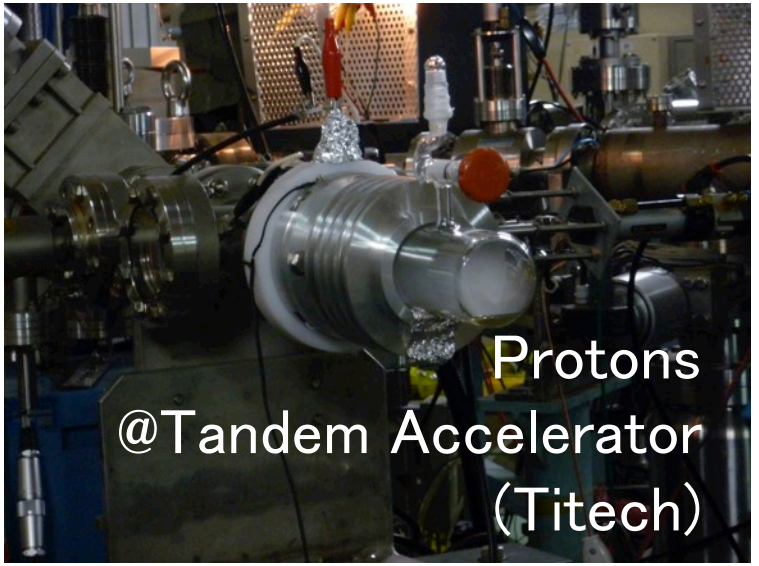
Proton Irradiation

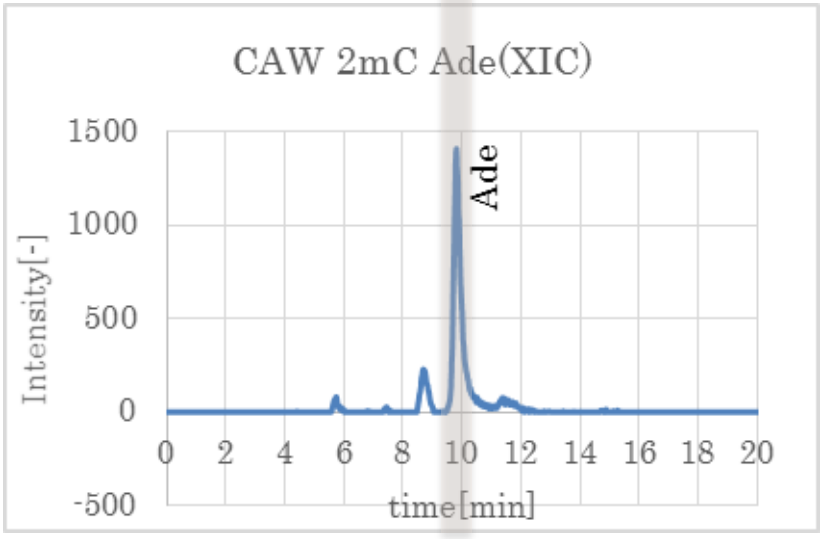


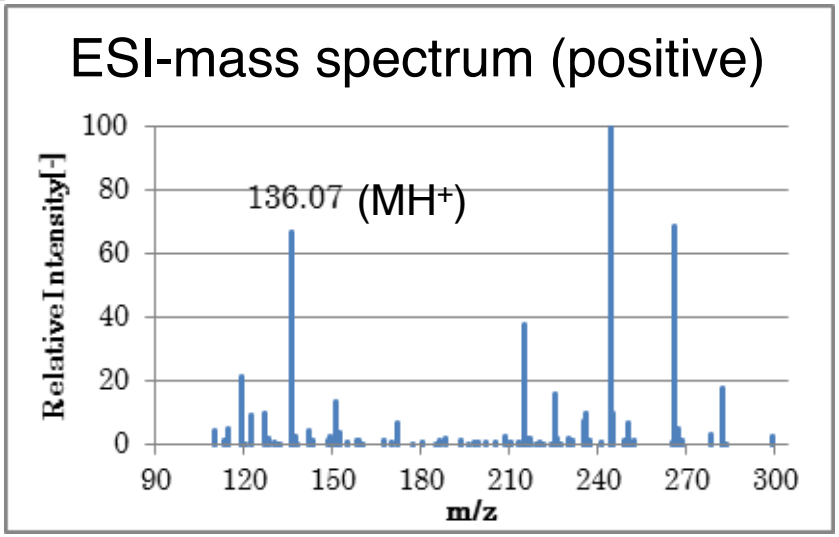
Oxidized

Identification of Adenine in CAW



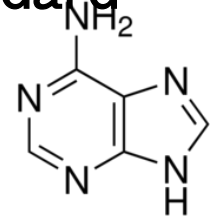






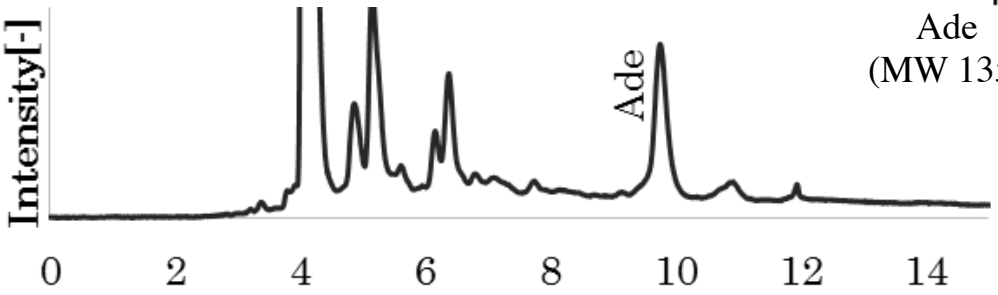
Quantitation of Nucleic Acid Bases by the Internal Standard Addition Method

^{13}CAW Sample +^{12}C-Ade **Standard**



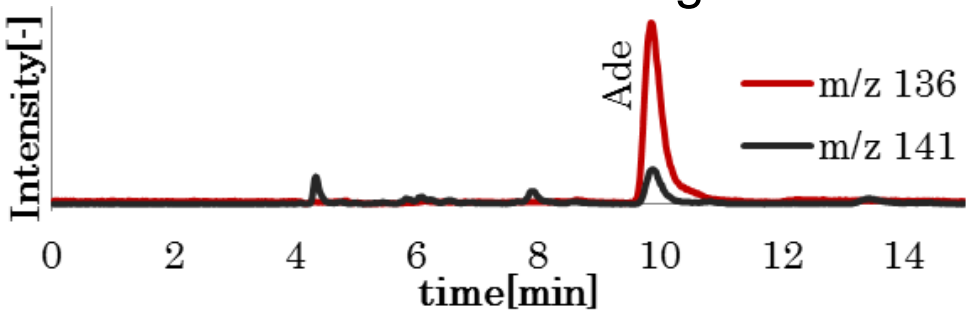
Ade
(MW 135)

UV(260 nm)
chromatogram

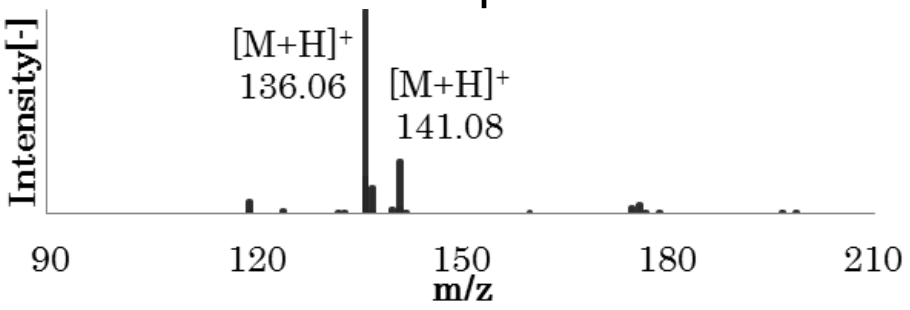


	Yields[nmol]
Ade	0.40
Ura	24
Pu	1.8
Xan	0.52
Hyp	1.3

Extracted ion chromatogram

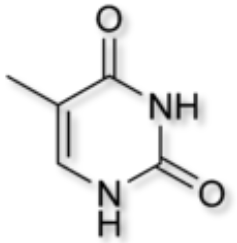


Mass spectrum

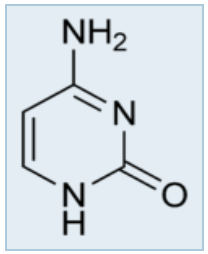


Nucleic Acid Bases Identified in CAW

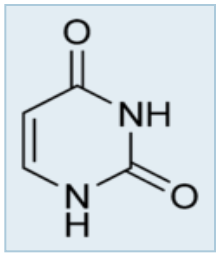
Pyrimidines



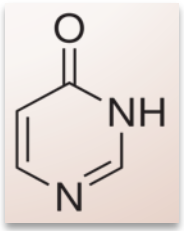
Thymine
Thy



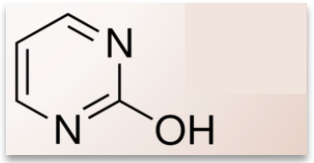
Cytosine*
Cyt



Uracil
Ura

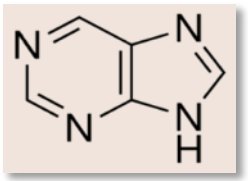


4-Hydroxy pyrimidine
4-HPy

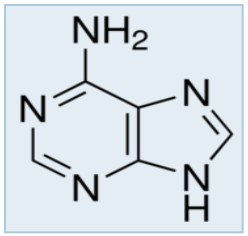


2Hydroxy pyrimidine
2-HPy

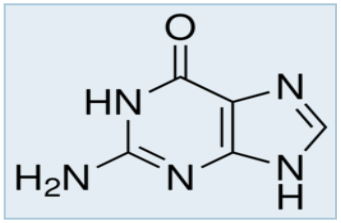
Purines



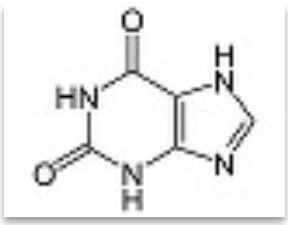
Purine
Pu



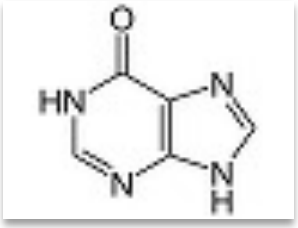
Adenine
Ade



Guanine
Gua



Xanthine
Xan



Hypoxanthine
Hyp

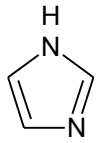
* Cytosine was identified only by GC/MS after TMS-derivatization

Composition formulae of CA and CAW before hydrolysis determined by HR-MS

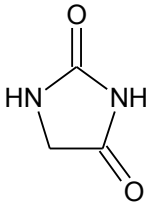
m/z	Formula	IHD*
69	$C_3H_5N_2$	2.5
86	$C_3H_8N_3$	1.5
101	$C_3H_5N_2O_2$	2.5
112	$C_4H_6N_3O$	3.5
112	$C_5H_{10}N_3$	2.5
126	$C_5H_8N_3O$	3.5
141	$C_6H_{13}N_4$	2.5
157	$C_6H_{13}N_4O$	2.5
313	$C_{12}H_{25}N_8O_2$	4.5

*IHD: Index of Hydrogen Deficiency

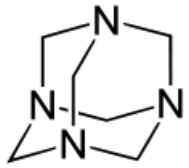
Imidazole
(M.W.: 68)



Hydantoin
(M.W.: 100)

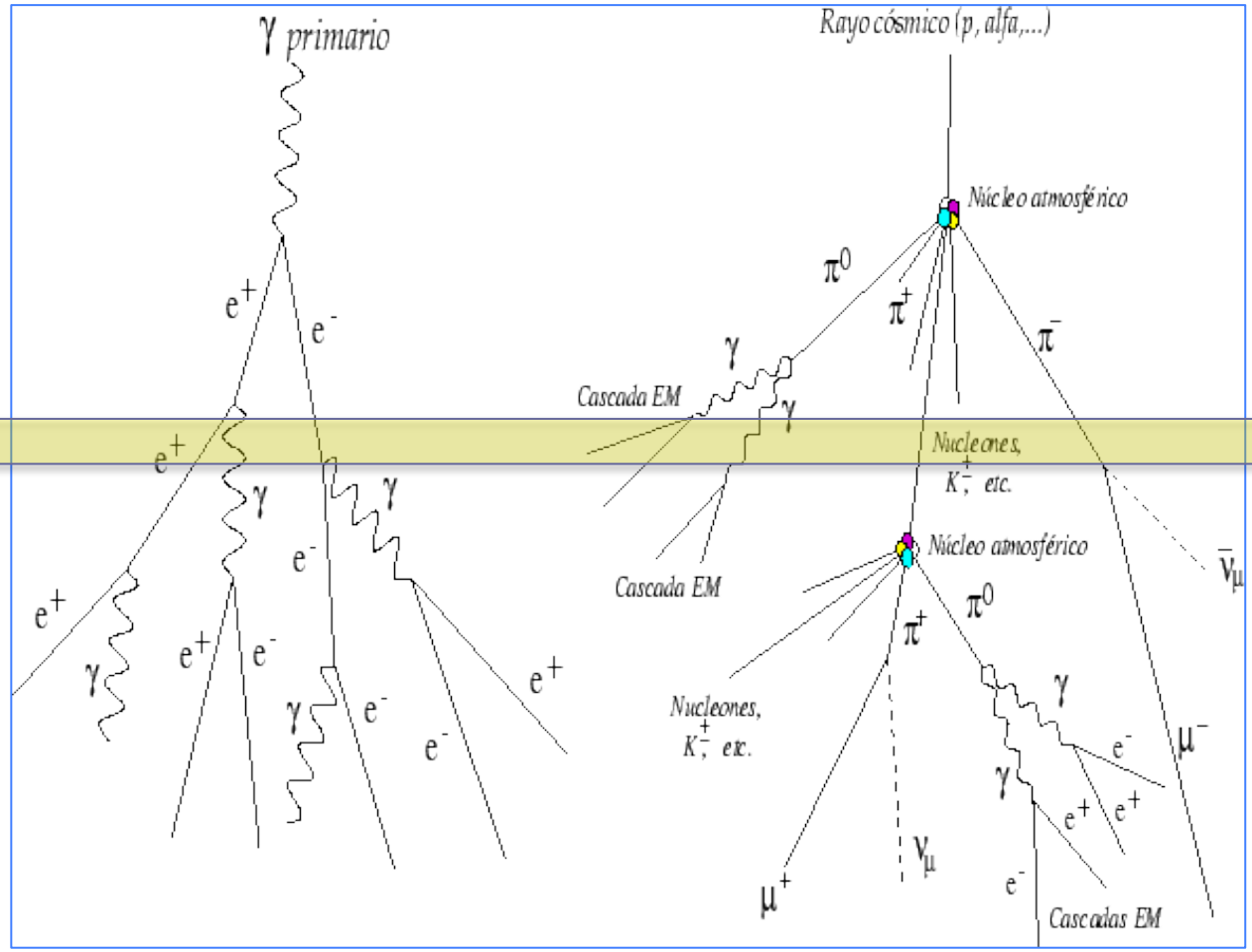


Hexamethylene-
Tetramine
(M.W.: 140)



Formation in γ-ray and Hadron showers

CO
NH_3
CH_4
CH_3OH
H_2O



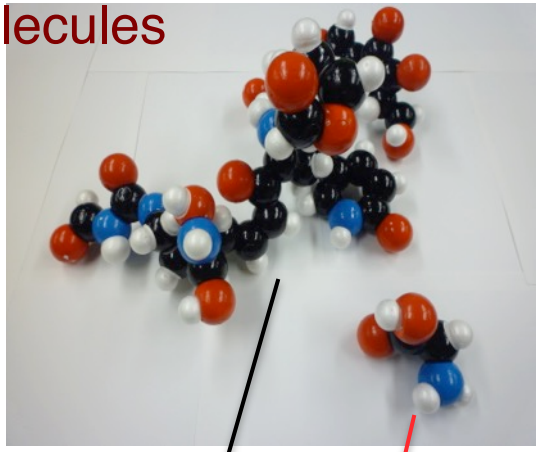
Bulk Ice

?

http://www.gae.ucm.es/~emma/docs/tesina/node8.html

Possible Reaction Mechanism

Super-complex (Garakuta) Molecules



$CO + CH_3OH + NH_3 + H_2O + CH_4$

High energy particles

$CO, CH_2, OH, NH, CH{=}CH, ..$

(Ions, radicals)

Quench

CH_4

$..\text{-}CH_2\text{-}NH\text{-}CH{=}C(OH)\text{-}CO\text{-}NH\text{-}CH_2\text{-}CO\text{-}NH\text{-}\ldots$

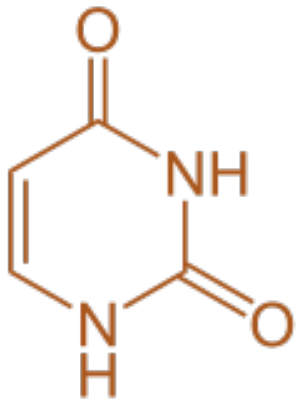
H_2O

$CO\text{-}NH\text{-}CH_2\text{-}CO\text{-}NH \rightarrow$ $NH_2\text{-}CH_2\text{-}COOH$ (Glycine)

(hydantoin)

H_2O

$CO\text{-}NH\text{-}CH{=}CH\text{-}CO\text{-}NH \rightarrow$



(uracil)

Tanpopo Mission, Meteorite analysis, Computations, …

Summary

1. Wide variety of organic compounds have been detected in extraterrestrial bodies, and some of them seemed to be formed in ice mantles of ISDs in dense clouds.
2. Amino acid precursors were formed in simulated interstellar ice by irradiation with high energy particles.
3. The amino acid precursors formed from simulated interstellar media contained hydantoins and super-complex molecules.
4. CO and CH_3OH were important to build up amino acid back bones, while CH_4 was useful to add amino acid side chains.
5. All of the nucleic acid bases could be formed from possible interstellar media by cosmic rays: Uracil was predominant.
6. 5- and 6-membered ring compounds with amide bonds were easily formed together with super-complex molecules with amide bonds.

Thank you for your attention!

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