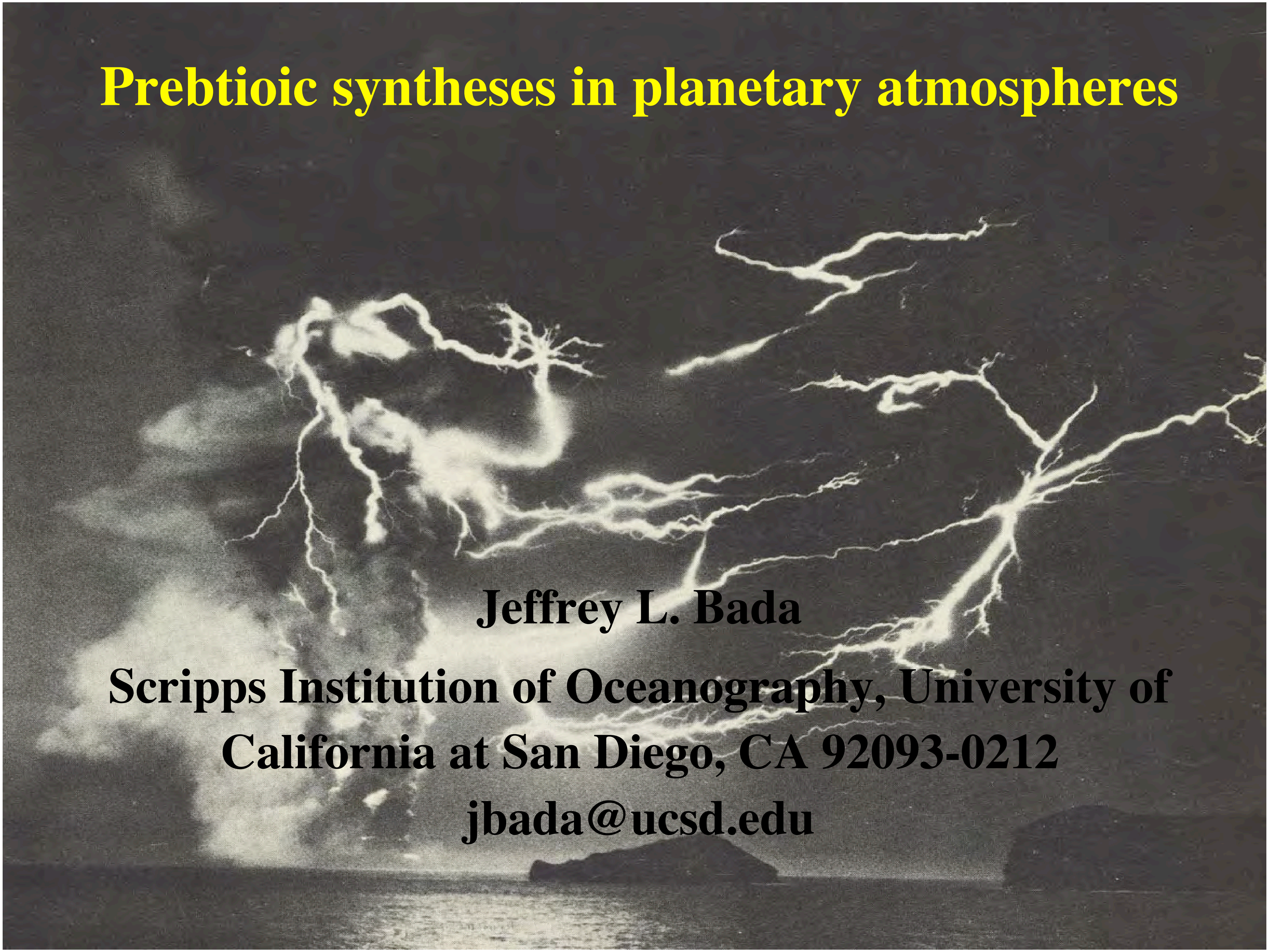
Prebtioic syntheses in planetary atmospheres



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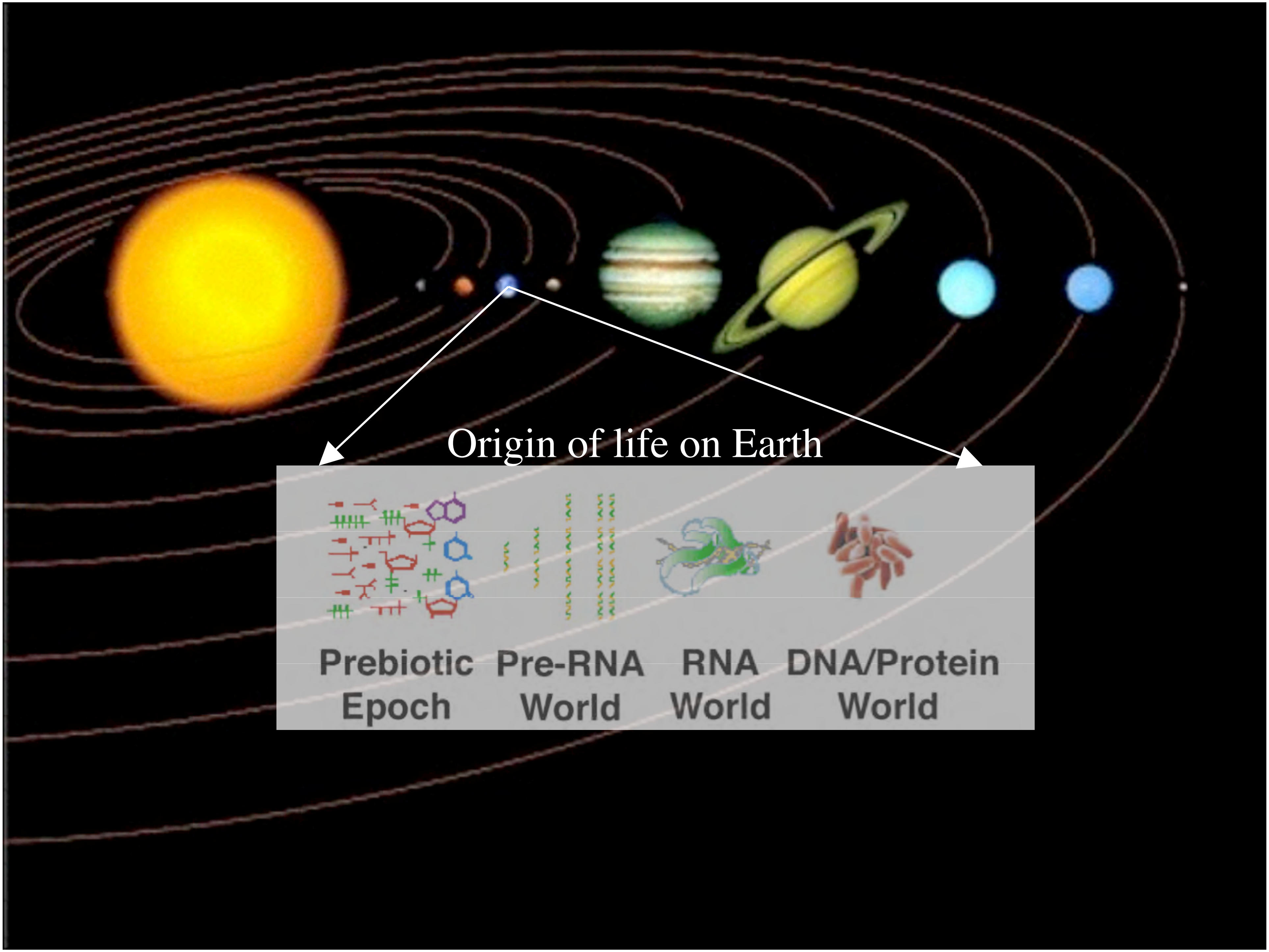
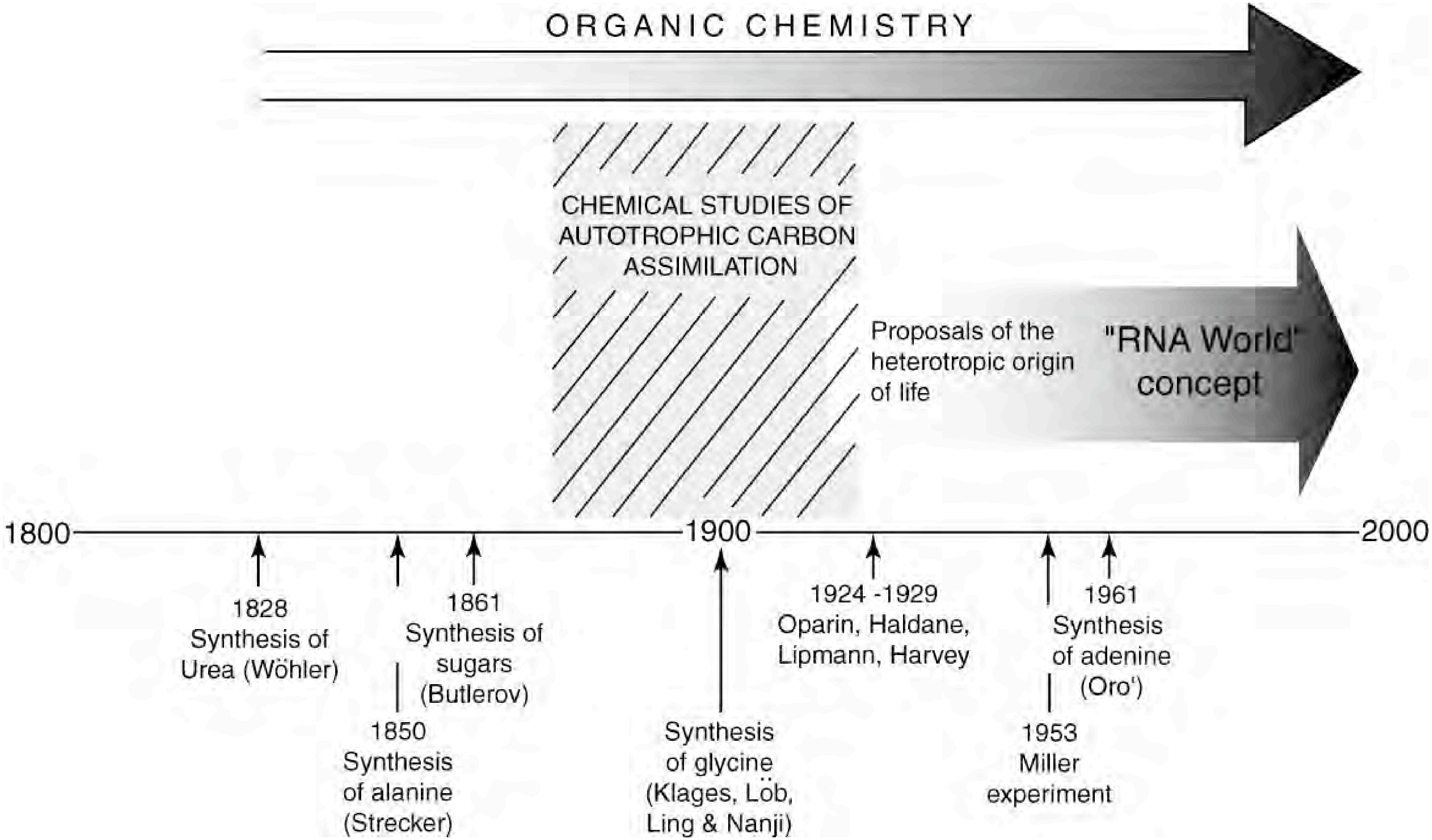

Origin of life on Earth
Prebiotic Epoch
Pre-RNA World
RNA World
DNA/Protein World

Life as we know it

There are two fundamental requirements for life as we know it, liquid water and organic polymers, such as nucleic acids and proteins. Water's unique properties (excellent solvent, exceptionally large liquid temperature range, etc.) make it an ideal medium for chemical reactions to take place. Polymers are needed to carry out the central biological functions of replication and catalysis. Without these vital components, as far as we know, life is impossible.

"There is no certainty that the existence of water means the existence of life. The other way around is probably true, though." ***David Baltimore, NY Times, March, 2004*****.**


ORGANIC CHEMISTRY
CHEMICAL STUDIES OF AUTOTROPHIC CARBON ASSIMILATION
Proposals of the heterotropic origin of life
"RNA World" concept
1800
1900
2000
1828 Synthesis of Urea (Wöhler)
1850 Synthesis of alanine (Strecker)
1861 Synthesis of sugars (Butlerov)
Synthesis of glycine (Klages, Löb, Ling & Nanji)
1924 -1929 Oparin, Haldane, Lipmann, Harvey
1953 Miller experiment
1961 Synthesis of adenine (Oro')

Organic compounds on the early Earth

- **Key ingredients such as amino acids are considered necessary for the origin of life.**
- **Deliver of key organic compounds to the Earth by interplanetary dust, meteorites, comets and asteroids.** <u>**Panspermia in its modern form!!**</u>
- **Homegrown synthesis: Miller's spark discharge experiment and others.**

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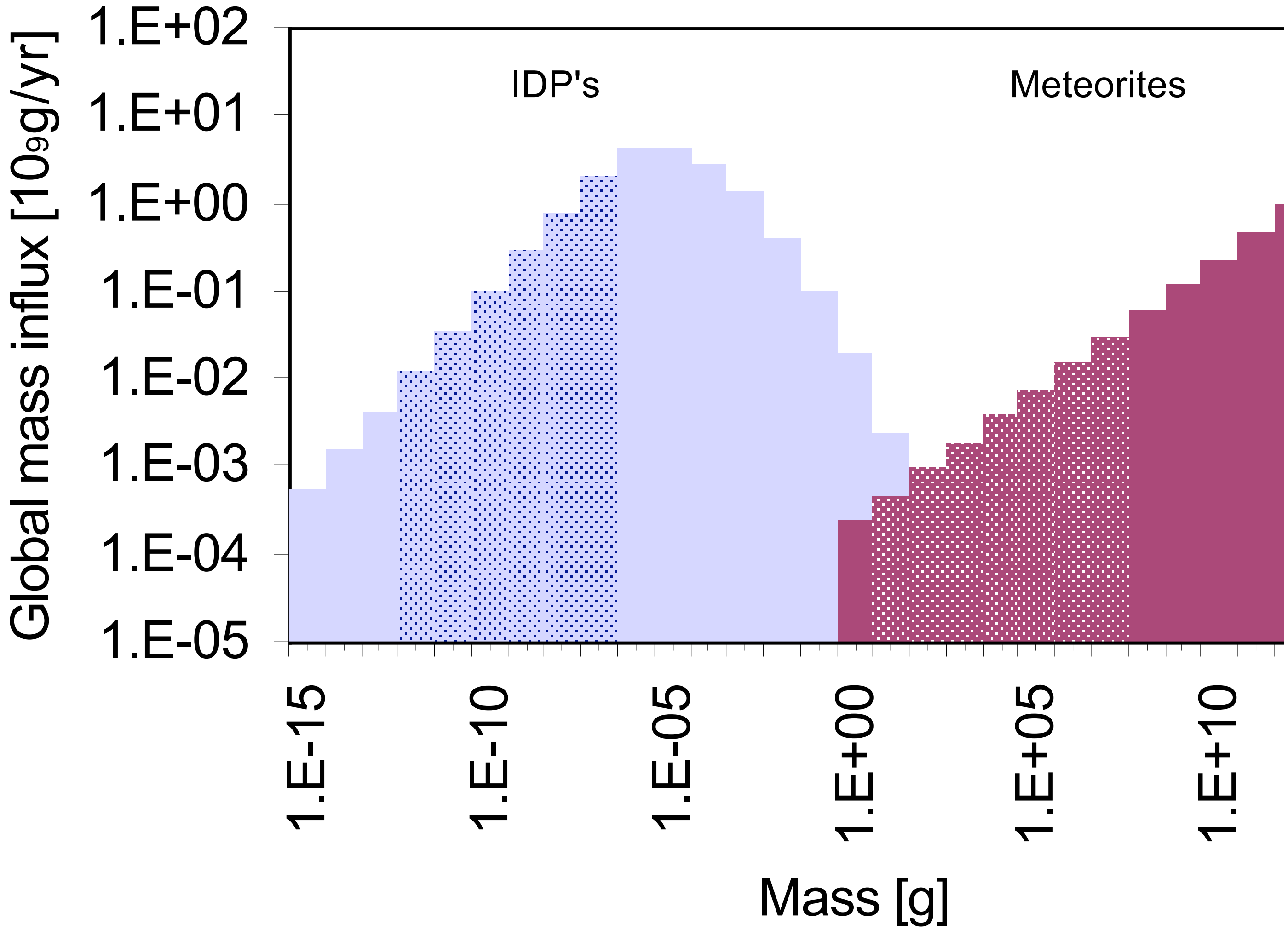
Classification of extraterrestrial bodies that could supply exogenous organic compounds based on their size and thermal histories.

Type of object	Size range (m)	Thermal history
IDPs	$<10^{-6}$	No heating
	$10^{-6} – 10^{-5}$	Full depth heating to <500ºC
	$10^{-5} – 10^{-3}$	Full depth heating up to ~1200ºC
Meteorites	$10^{-3} – 10^{2}$	Heating >600ºC up to 1 mm depth
Asteroids	$>10^{3}$	Explosive impacts: up to ~10,000ºC
Comets	$>10^{3}$	Airbursts: moderate heating

Basiuk and Douda, *Planet. Space Sci.* 47: 577-584, 1999



Global mass influx of exogenous material in the size range 10^{-6} - 10^{2} m. (Anders, *Nature*, 342: 255-257, 1989).

A summary of the abundances of individual organic compounds in CI and CM chondrites

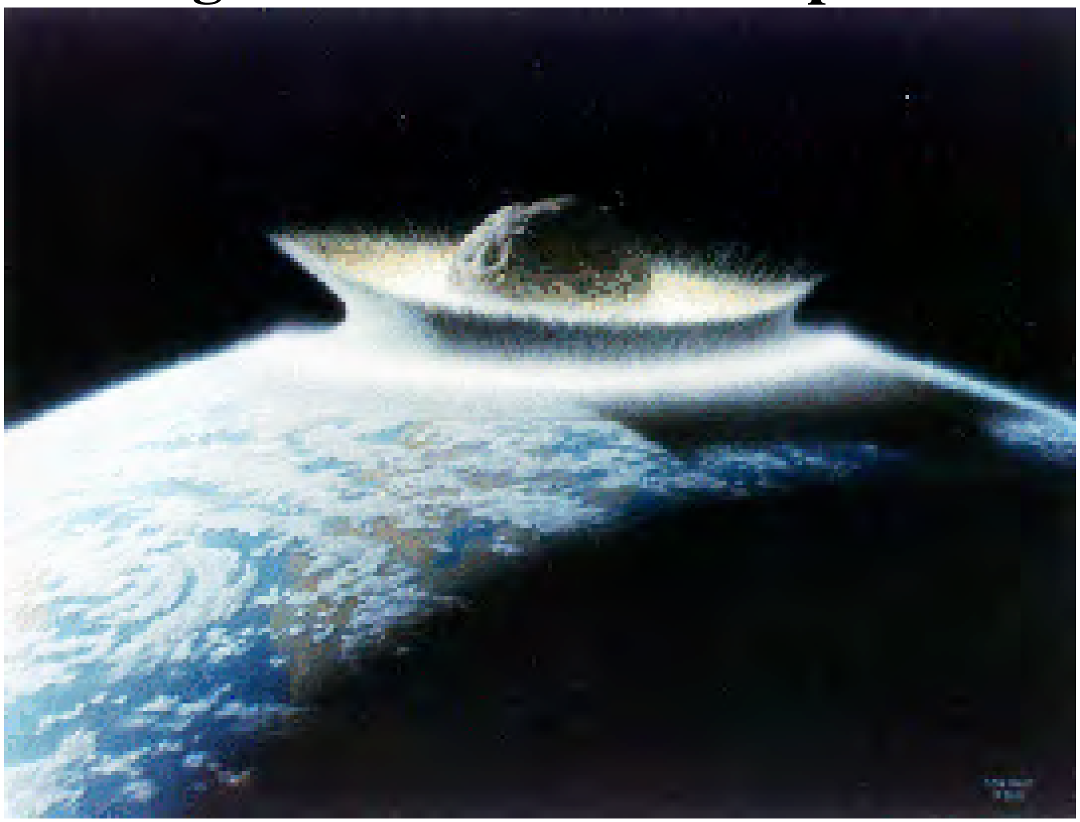
Murchison Meteorite
Australia, 1969

Compound Class		Concentration (ppm)
Amino Acids		
	CM meteorites	17-60
	CI meteorites	~ 5
Aliphatic hydrocarbons		> 35
Aromatic hydrocarbons		3300
Fullerenes		> 100
Carboxylic acids		> 300
Hydroxycarboxylic acids		15
Dicarboxylic & Hydroxydicarboxylic acids		14
Purines & Pyrimidines		1.3
Basic N-heterocycles		7
Amines		8
Amides	linear	> 70
	cyclic	> 2
Alcohols		11
Aldehydes & Ketones		27
Sulphonic acids		70
Phosphonic acids		2

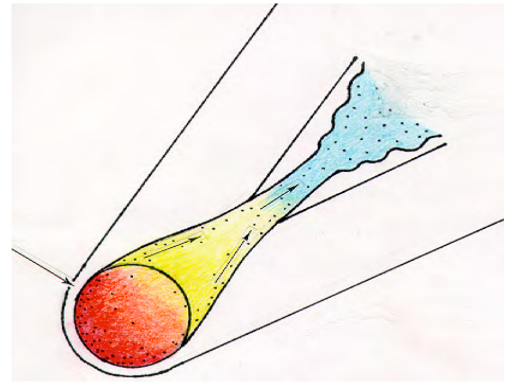
Botta and Bada, *Surv. Geophys.* 23: 411–467, 2002

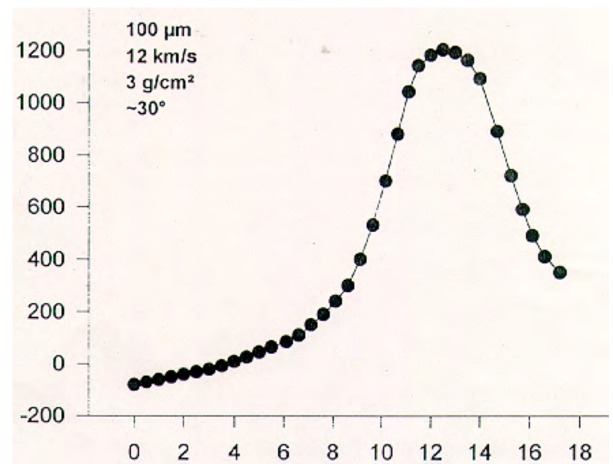
Can key organic compounds survive delivery to Earth from space?

Asteroid impacts are much more energetic than a nuclear explosion



IDPs are heated to high T





A large fraction of compounds such as amino acids would be destroyed during these processes

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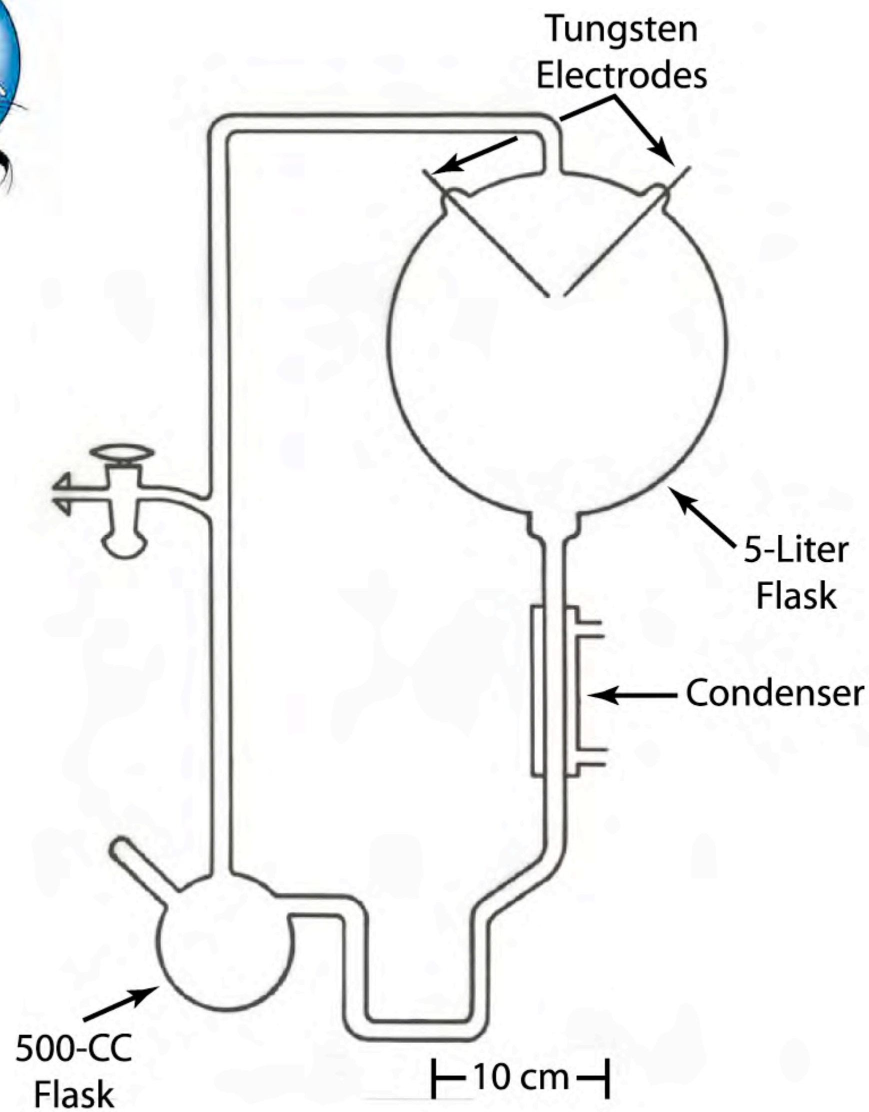
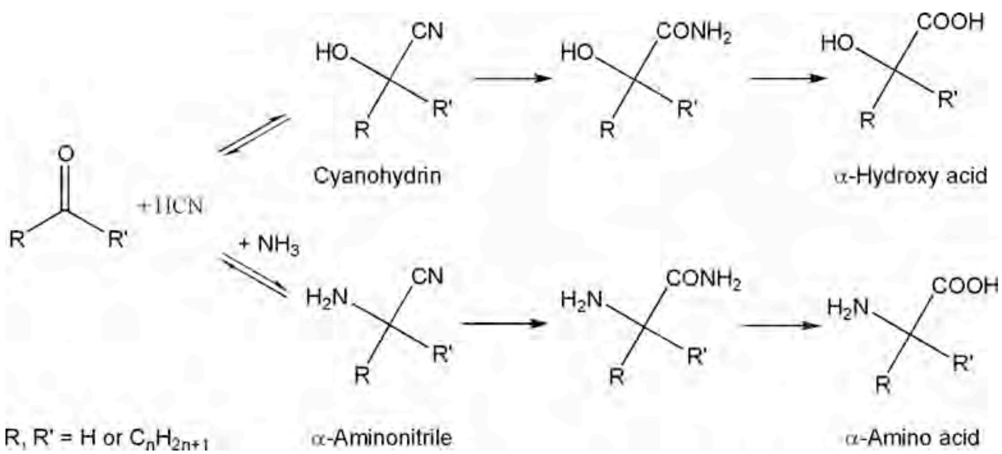
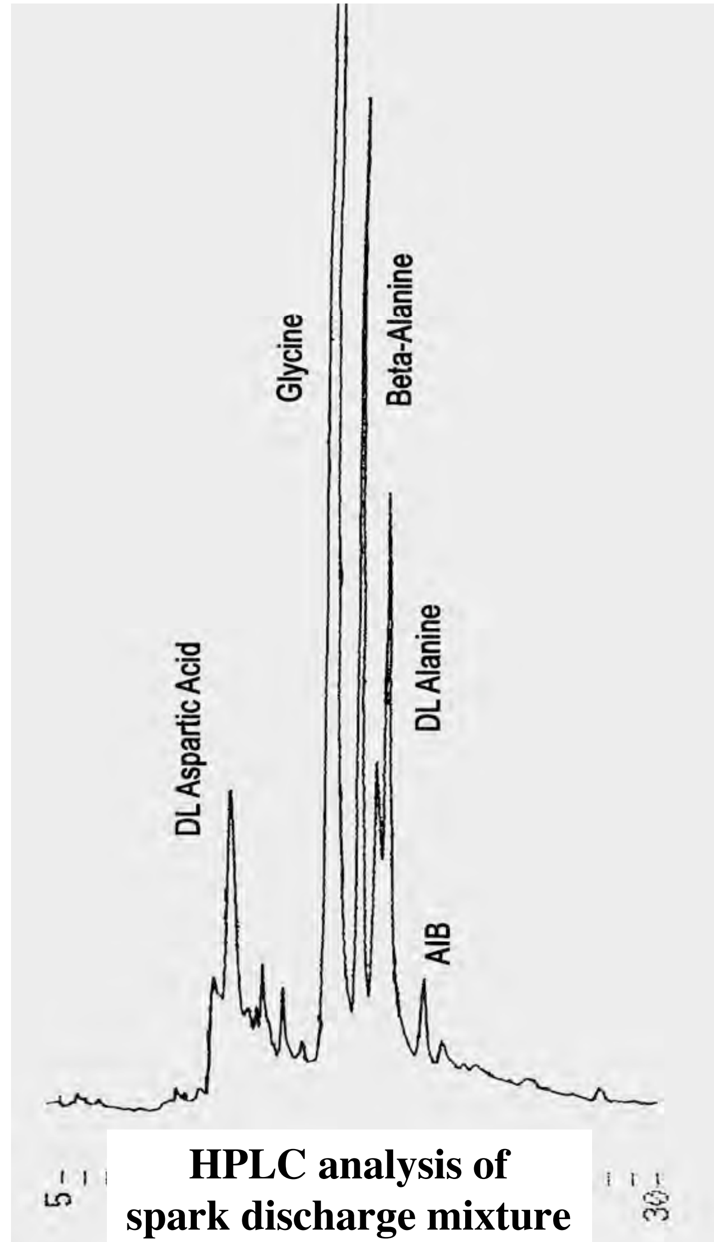


The original Miller/Urey experiment used a reducing gas mixture consisting of methane, ammonia and hydrogen

Using a reduced gas mixture a variety of organic compounds were synthesized including amino and hydroxy acids. With non-reducing mixtures, only trace quantities of these compounds were synthesized. Amino and hydroxy acids are synthesized by the reaction sequence below.

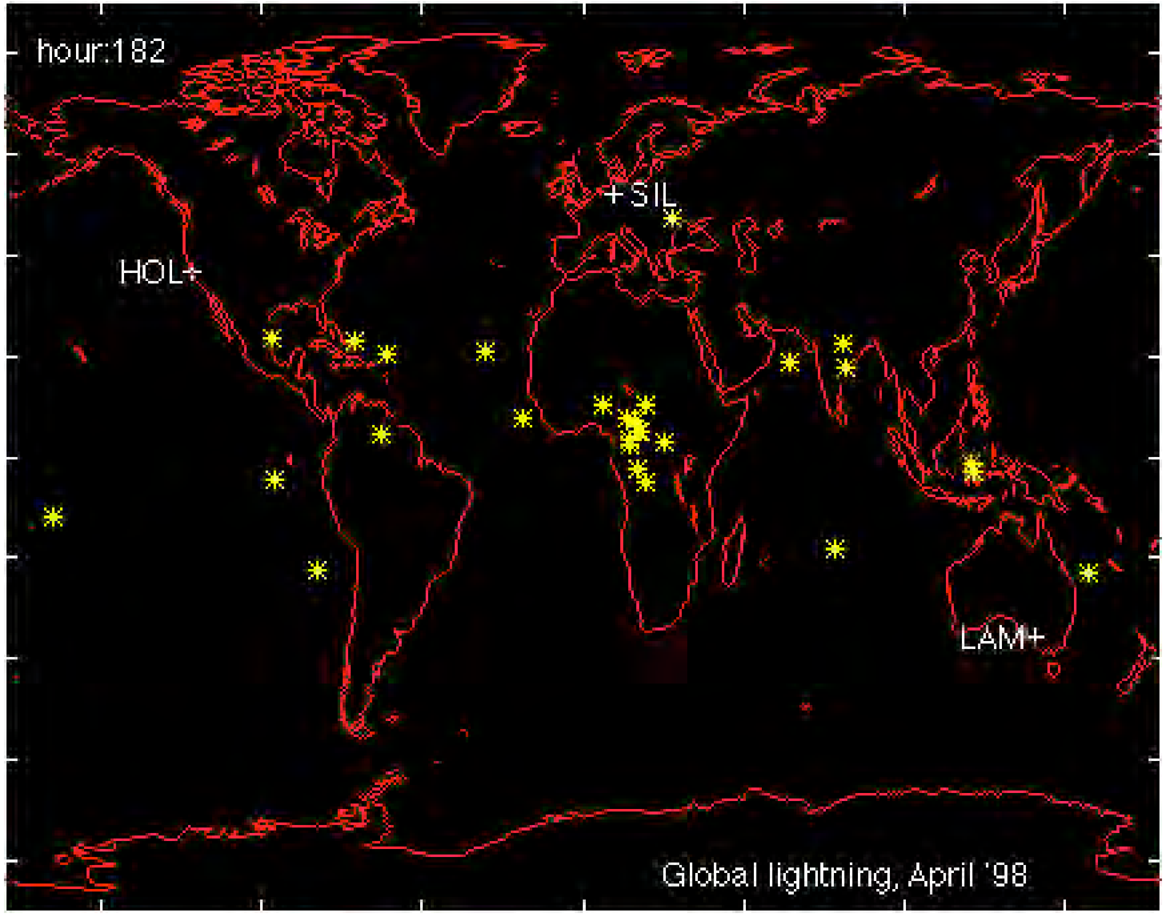


Miller-Urey Synthesis



HPLC analysis of spark discharge mixture

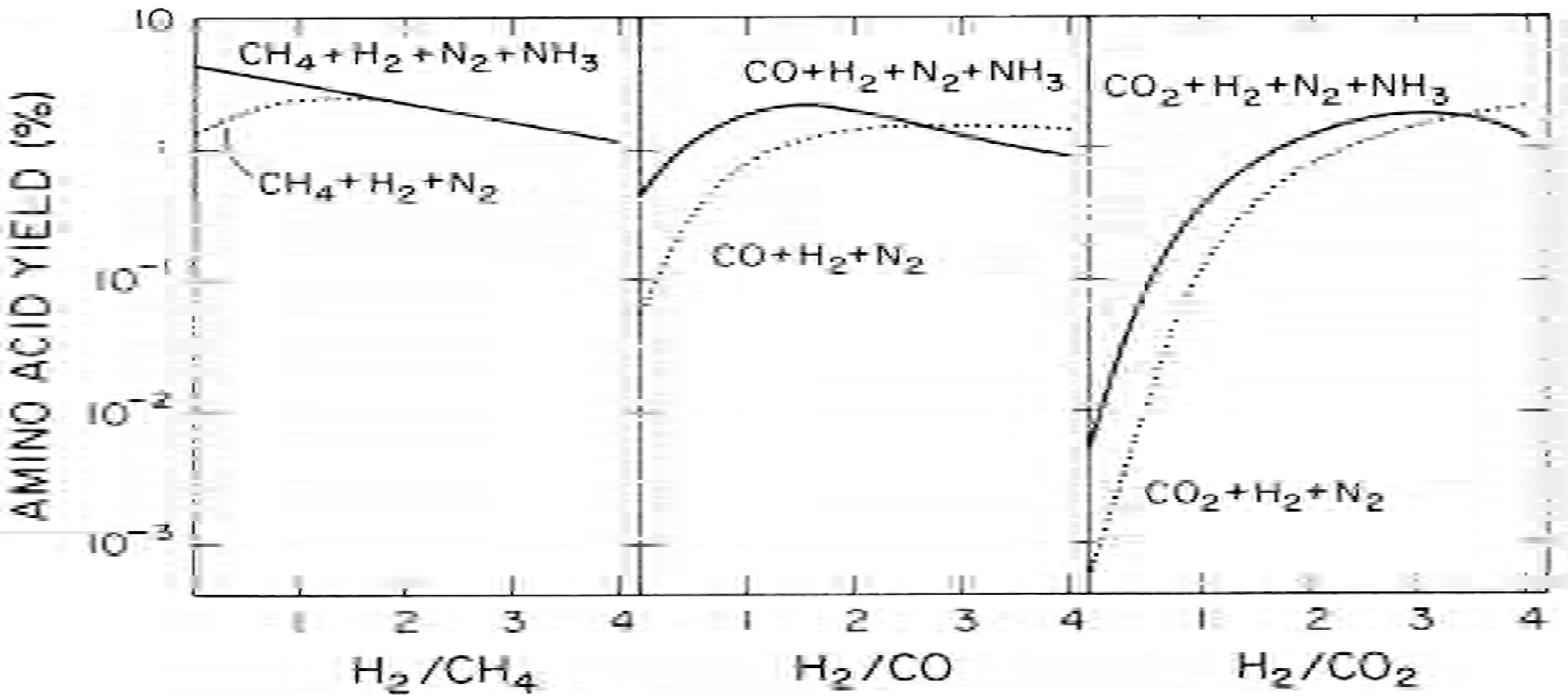
Global lightning and coronal discharges are only one possible source of energy



Other energy sources include ultraviolet radiation, cosmic rays, thermal energy and possibly radioactive decay

Atmospheric conditions are key parameters for synthesis

Schlesinger, G. & Miller, S. L., *J. Mol. Evol.* (1983) 19:376-82.



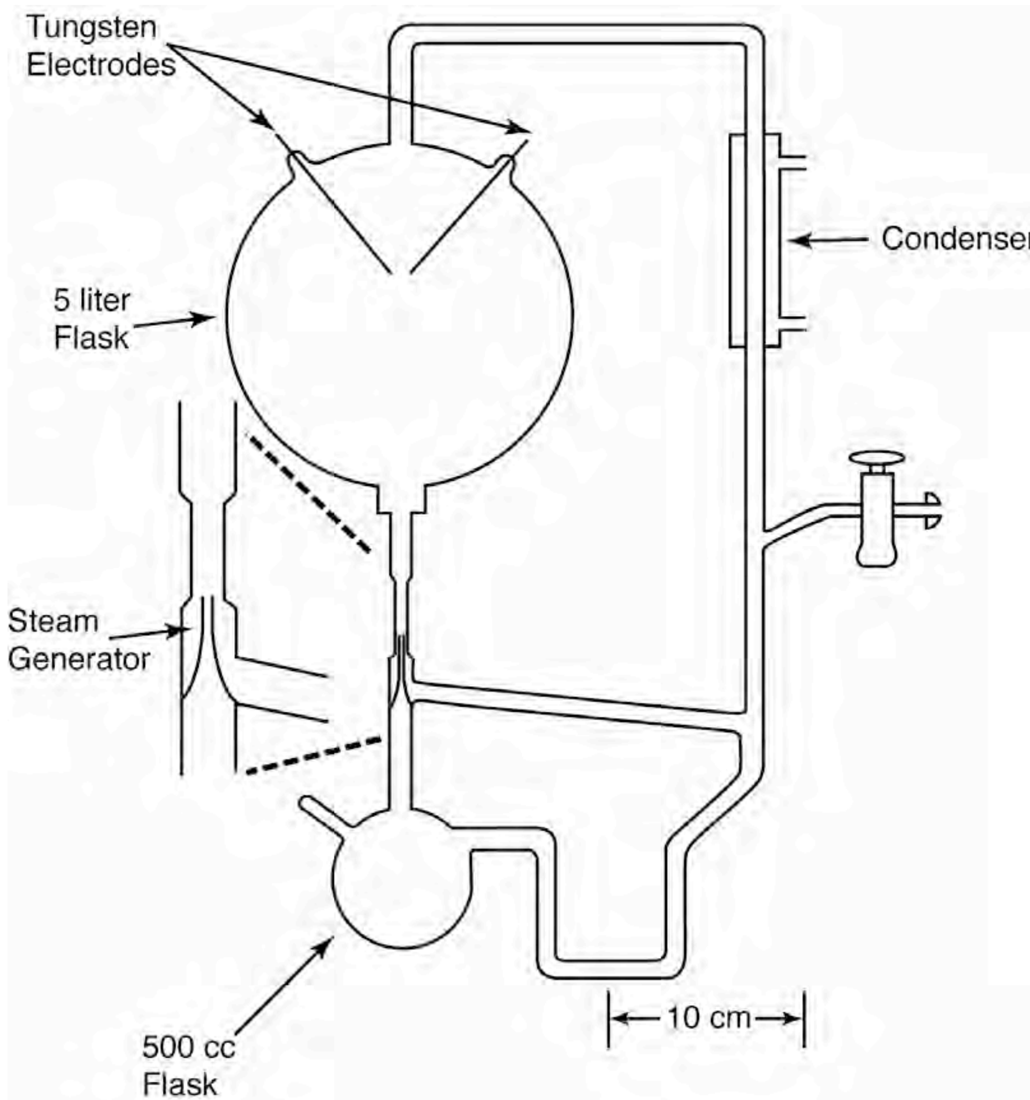
As long as hydrogen is present at sufficient levels, other reduced gases (methane, ammonia, etc.) would be present. Many geoscientists today doubt that the primitive atmosphere was hydrogen rich for more than a few 10s of millions of years.

Although reducing conditions may not have existed on a global scale, localized high concentrations of reduced gases may have existed around volcanic eruptions especially in hot-spot island-arc systems that may have been common on the early Earth. The localized release of reduced gases by volcanic eruptions on the early Earth would likely have been immediately exposed to intense lightning, which is commonly associated with volcanic eruptions today.

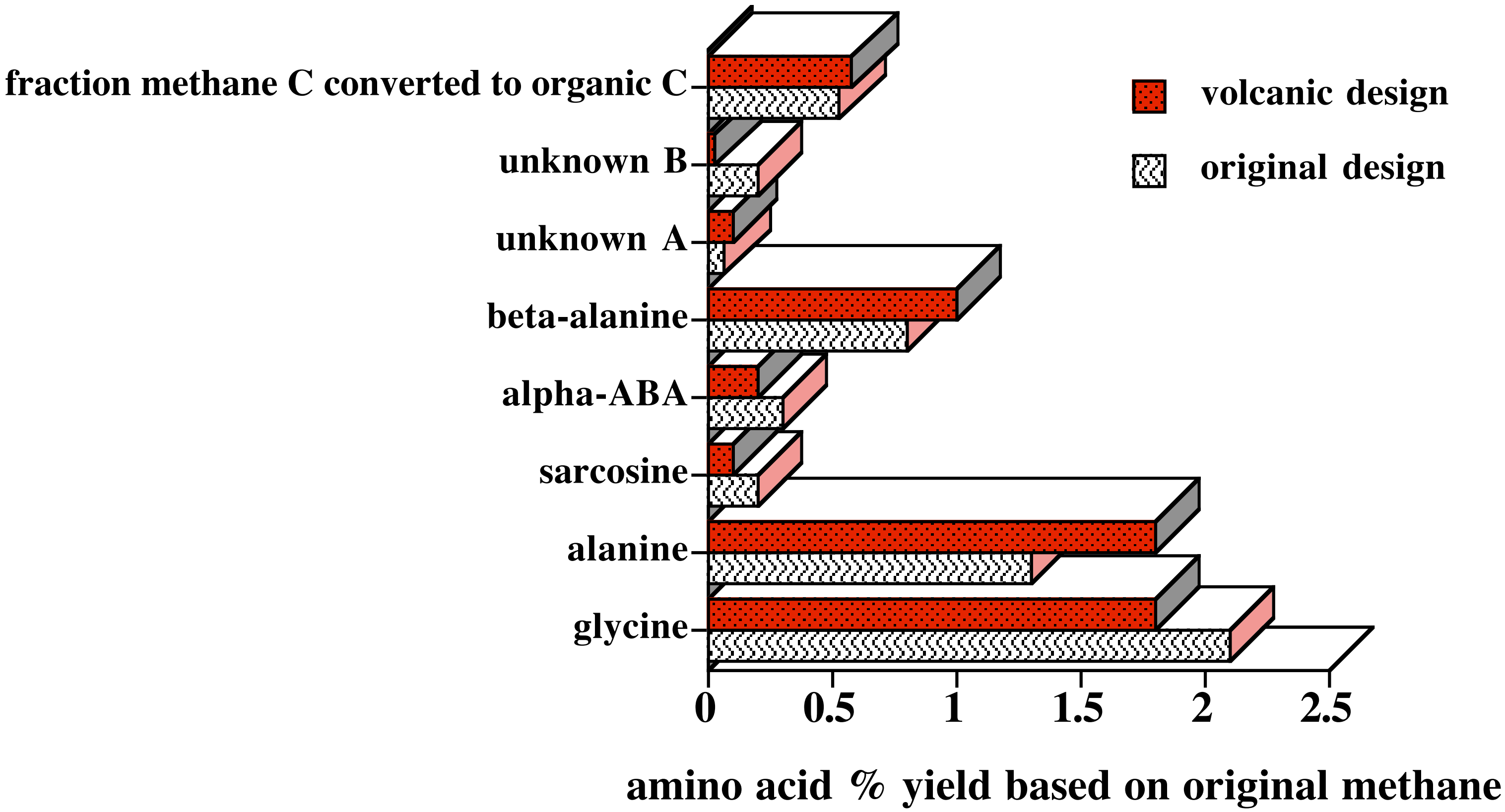
Intense volcanic lightning has been reported for nearly all historically observed volcanic eruptions, especially those on ocean islands (see S. R. McNutt, C. M. Davis, Lightning associated with the 1992 eruptions of Crater Peak, Mount Spurr Volcano, Alaska, *J. Vol. Geothermal Res.* 102 (2000), 45-65).

- **During Pliny The Elder's AD 79 observations of the Vesuvius eruption, in which he perished, intense volcanic lightning was reported.**
- **Captain MacKenzie of the *Zeeland* passed within 5 miles of the 1883 Krakatoa explosion and reported that a "black cloud rose swiftly above the mountain, with lightning flashes deep within the clouds, and a continuous crackling sound".**

Miller's other apparatus tested in the 1950s experiments mimicked lightning associated with volcanic eruptions



Yields for Miller's experiments with the original and volcanic apparatus



S. L. Miller, Production of some organic compounds under possible primitive Earth conditions, *JACS* 77, 2351-2361 (1955).

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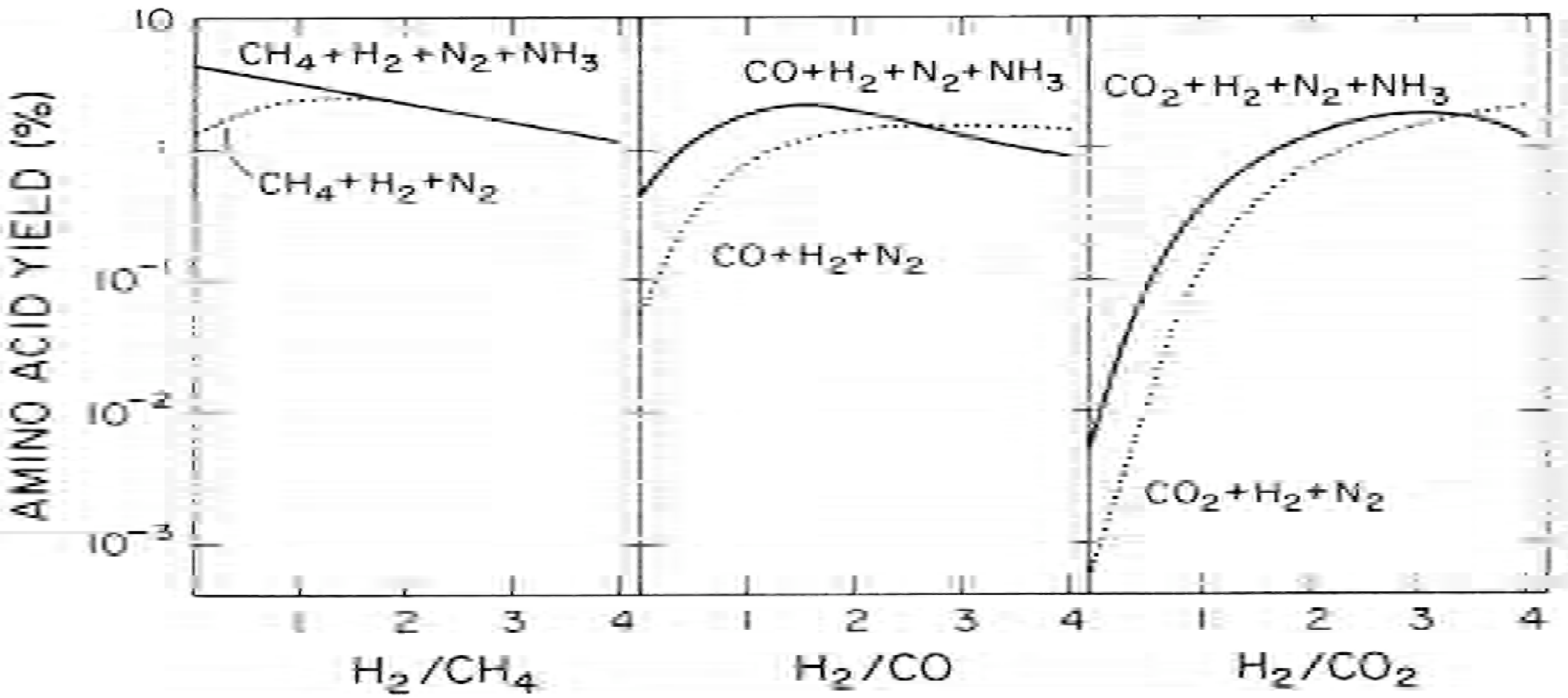
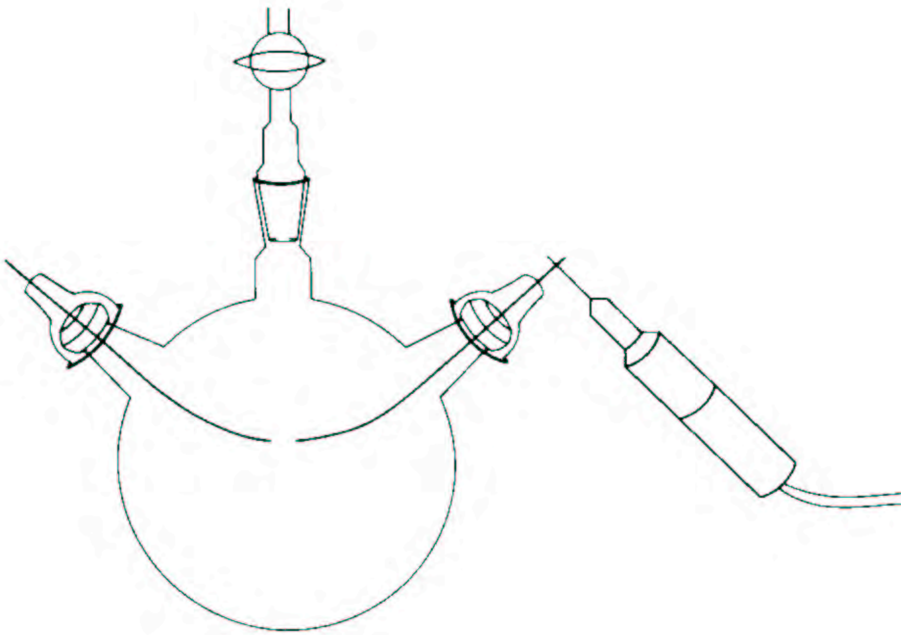


Note that with both the CO and CO_2 mixtures that even some amino acids are produced in the absence of hydrogen.

What are the actual yields with CO_2/N_2mixtures?



Experiment	Final pH	NH_3	HCN	NO^{2-}	NO^{3-}	HCHO
Schlesinger and Miller	ND	$2x10^{-3}$	0.01	ND	ND	.01
Unbuffered	3.2	0.26	$8x10^{-3}$	.02	0.33	$2x\ 10^{-4}$
Buffered	7.1	0.21	0.0	1.04	0.21	$7x\ 10^{-4}$

It is important to note that in the presence of nitrate and nitrite, when a mixture is acid hydrolyzed the amino acids are destroyed. The addition of ascorbic acid prior to hydrolysis prevents this from taking place.

Figure 1. Typical HPLC chromatograms of the OPA-NAC derivitized amino acids detected from the spark discharge reactions. Chromatograms labeled with roman numerals: I.) Amino acid standard, II.) CO_2/N_2 not sparked, III.) CO_2/N_2 + $CaCO_3$, sparked, hydrolyzed – ascorbate. IV.) CO_2/N_2, sparked, hydrolyzed - ascorbate **V.) CO_2/N_2, s parked + $CaCO_3$, h ydrolyzed + ascorbate.** Amino acids: 1.) DL aspartic Acid 2.) DL glutamic Acid 3.) DL serine 4.) glycine 5.) β-Alanine 6.) DL alanine 7.) α–amino Isobutyric acid 8.) DL norleucine (internal standard). The D and L enantiomers of glutamic acid and se rine are not separated under these chromatographic conditions.

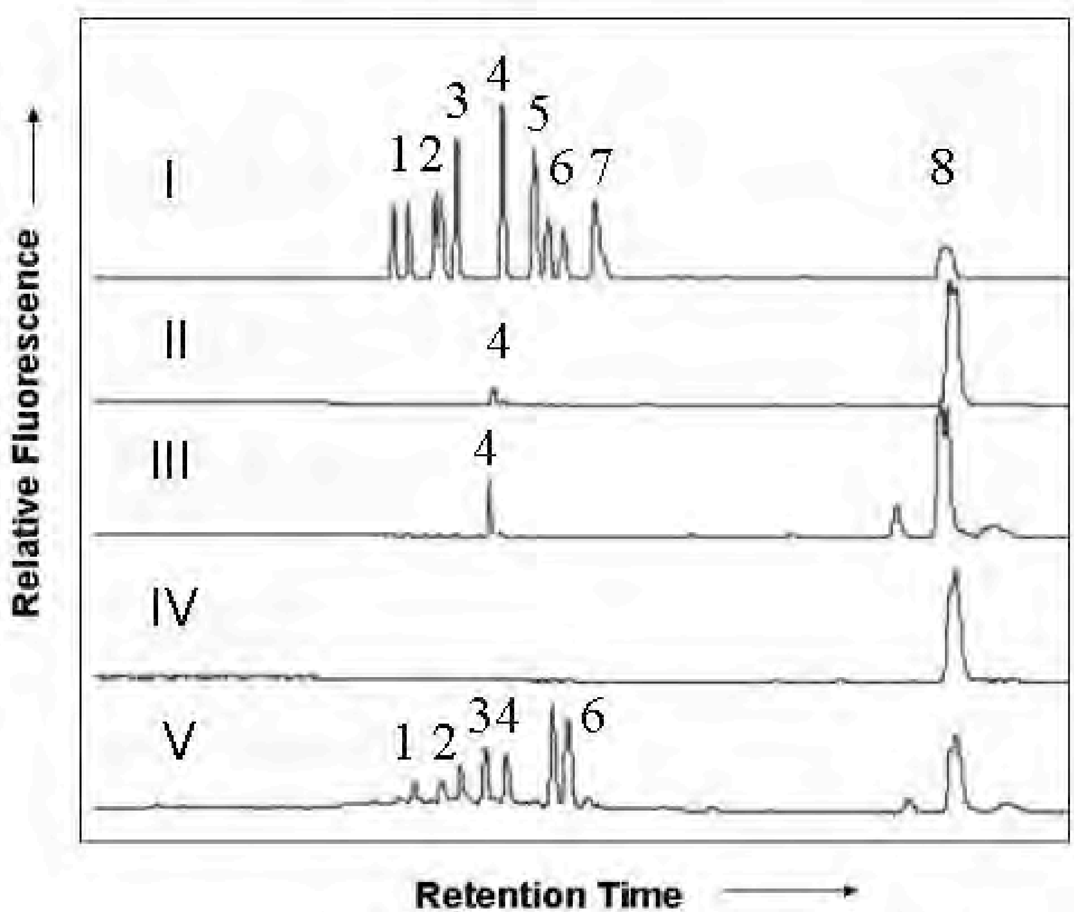


Table 1. Yields of amino acids and other small molecules from neutral atmosphere electric discharge reactions sparked 48 hours at room temperature. Yields are calculated based on input N_2 or CO_2 (for HCHO) from 100 mm CO_2, 100 mm N_2 and 100 mL H_2O with or without 2 mmoles $CaCO_3$ in a 3.1 l flask at 23° C. Yields of THAA (Total Hydrolyzable Amino Acids) are shown after hydrolysis in the absence (-) or presence (+) of ascorbate. ND = not determined.

Experiment	$pH_{initial}$/ pH_{final}	NH_3	HCN	NO_2^-	NO_3^-	HCHO	THAA -	THAA +
CO_2/N_2 Control	~6/~5	$<10^{-3}$	$<10^{-5}$	$<10^{-4}$	$<10^{-4}$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
$CO_2/N_2/CaCO_3$ Control	7.3/7.3	$<10^{-3}$	$<10^{-5}$	$<10^{-4}$	$<10^{-4}$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
CO_2/N_2	~6/3.2	0.26	0.26	0.0082	0.02	$3x10^{-4}$	0.013	1.3
$CO_2/N_2/CaCO_3$	7.3/7.1	0.21	0	1.04	0.21	$7x10^{-4}$	0.19	2.5
$CO_2/N_2/O_2$ + $CaCO_3$	7.3/7.1	ND	ND	ND	ND	ND	$8x10^{-5}$	$2x10^{-4}$

Conclusions

- **The low yields found previously were the result of oxidation of the organic compounds during hydrolytic workup by nitrite and nitrate produced in the reactions.**
- **Addition of oxidation inhibitors prior to hydrolysis results in the recovery of several hundred times more amino acids than reported previously.**
- **Organic synthesis from neutral atmospheres may thus have depended as much on oceanic conditions as on the characteristics of the primitive atmosphere itself.**
- **These findings indicate the importance of prebiotic syntheses on the primitive Earth endowed with a CO_2/N_2-rich atmosphere, even in the presence of trace amounts of oxygen.**

Where else could this happen in our solar system?

Mars, satellites of the gas giant planets?

Origin of life and evolution