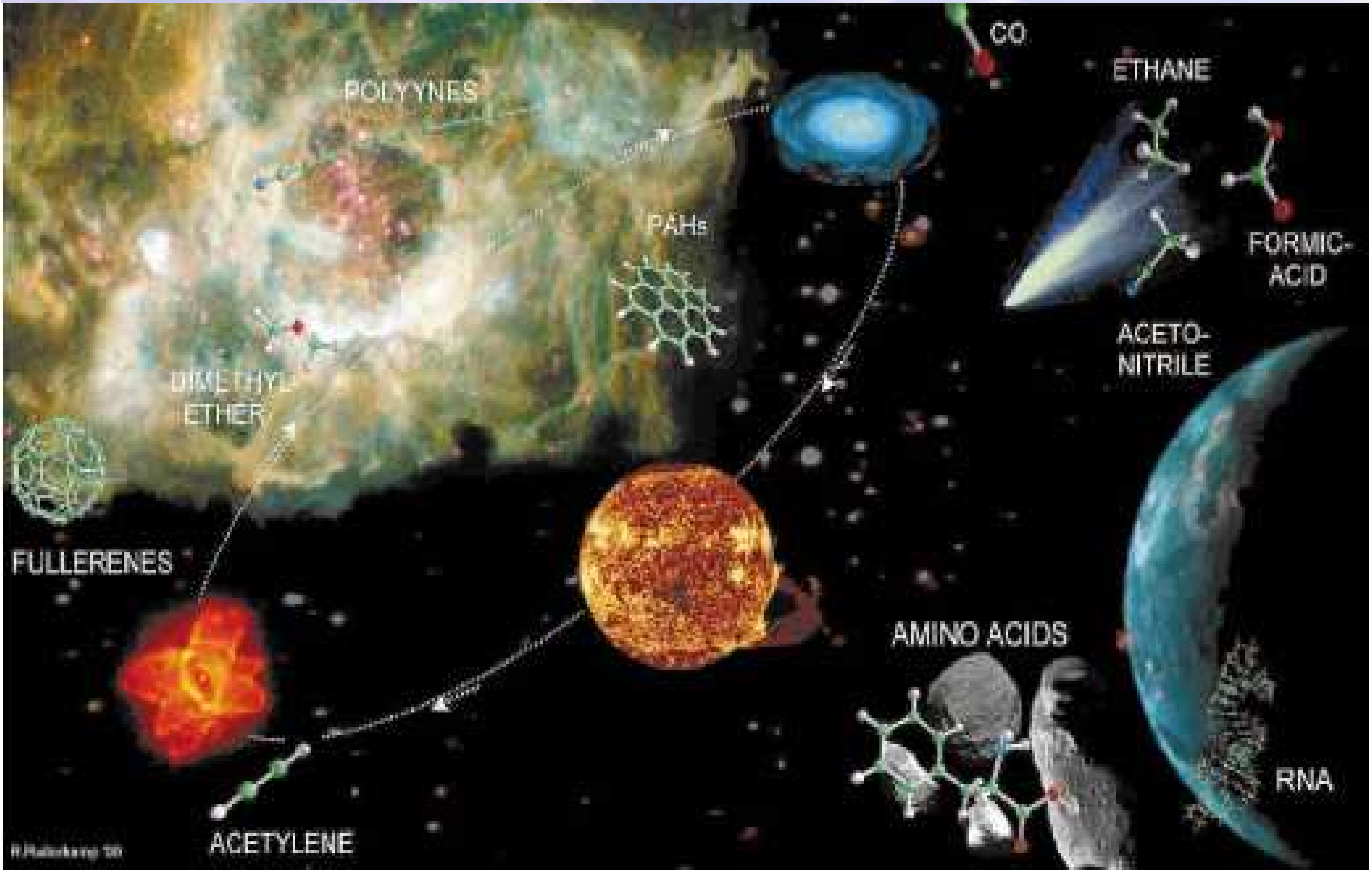
ASTROCHEMISTRY & ASTROBIOLOGY

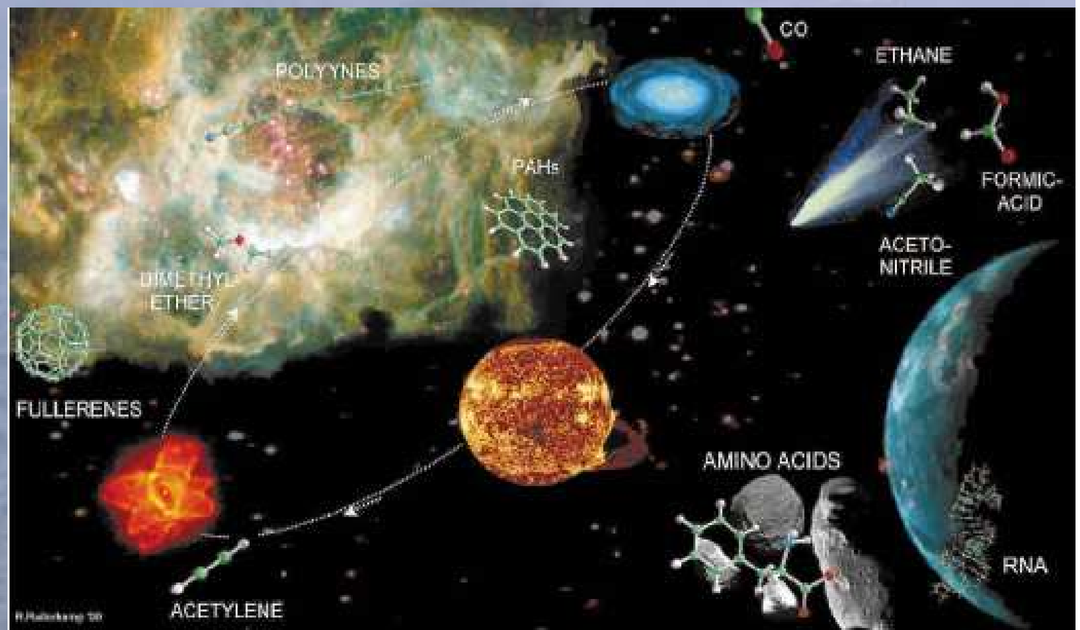


Outline

1. Astrochemistry & Meteoritic Organics

2. Extraterrestrial Delivery

3. Early Earth & Mars



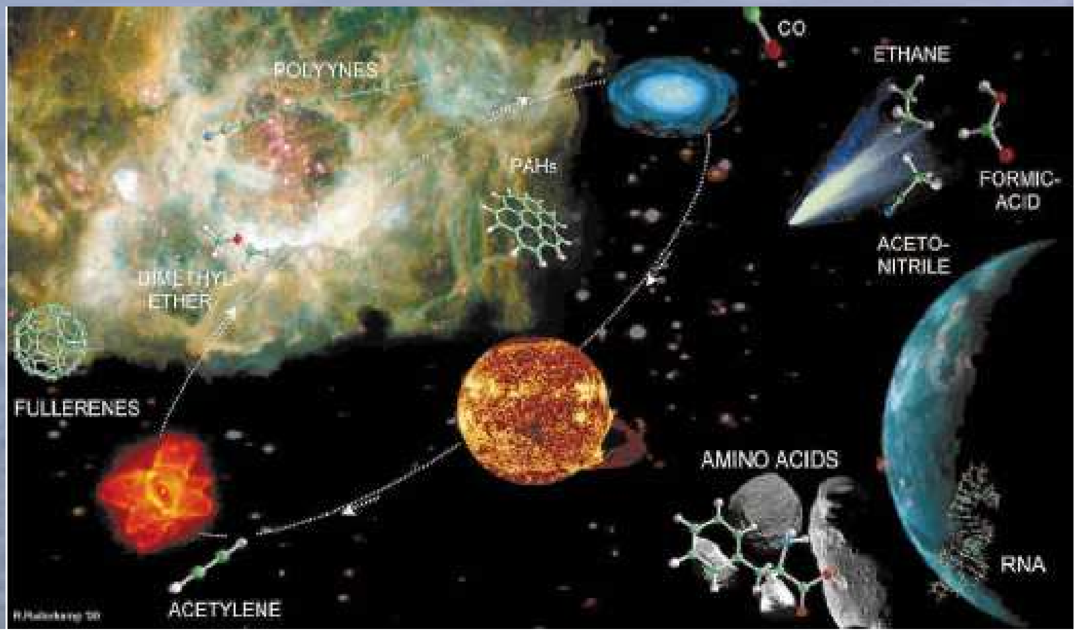
Reading

Ehrenfreund et al. (2002) Astrophysical and Astrochemical Insights into the Origin of Life, Rep. Prog. Phys., 65, 1427-1487

Cronin, J.R. & Chang, S. (1993) Organic Matter in Meteorites, in The Chemistry of Life's Origins, J.M. Greenberg et al. (eds.), Kluwer, 209-258

Botta, O. & Bada, J.M. (2002) Extraterrestrial Organic Compunds in Meteorites, Surveys in Geophysics, 23, 411-467

Sephton, M.A. (2002) Organic Compounds in Carbonaceous Meteorites, Nat. Prod. Rep., 19, 292-311



Extraterrestrial Delivery of Biogenic Molecules

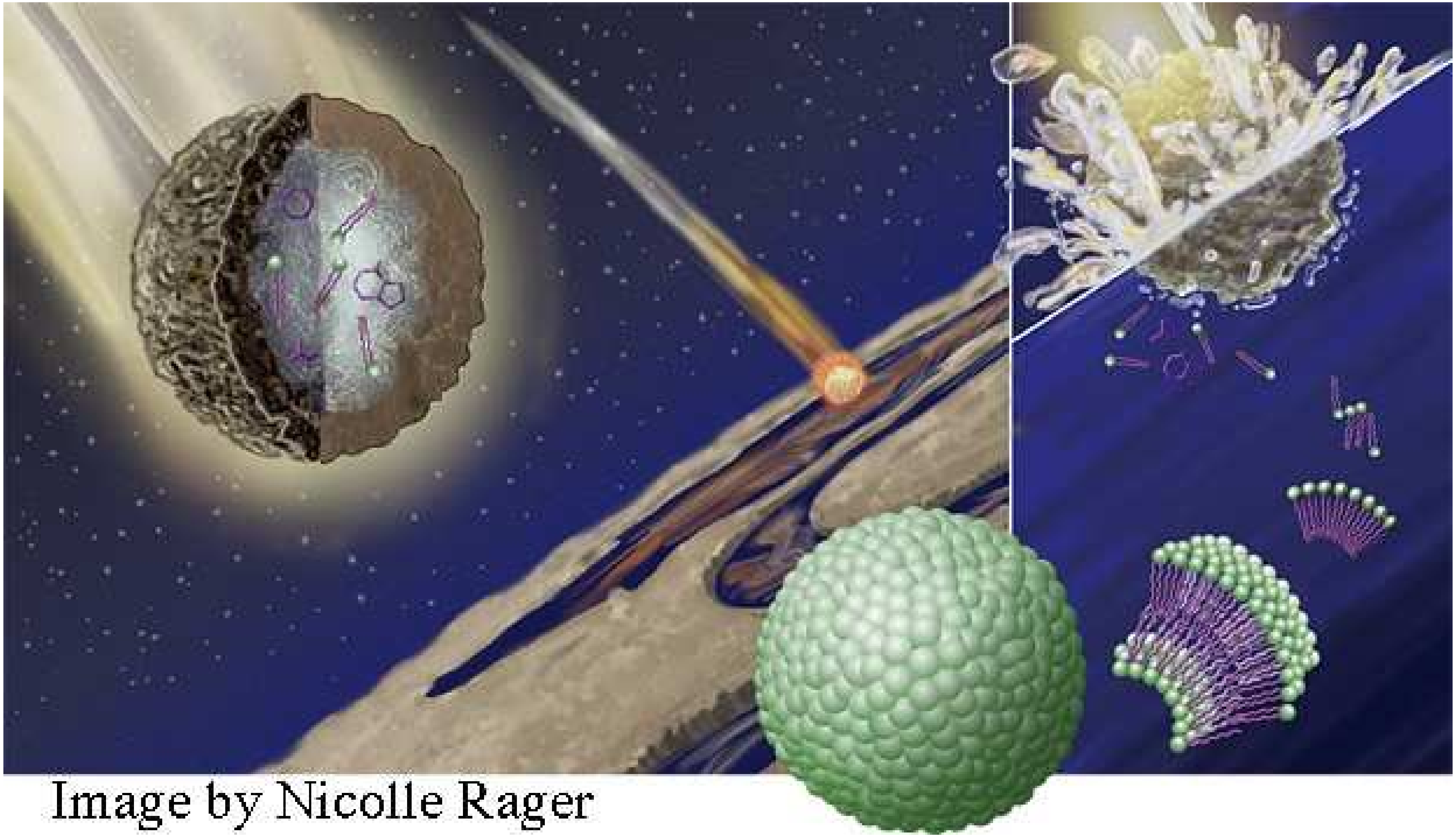


Image by Nicolle Rager

Organics Found in Meteorites

Total Carbon Content: > 3% (by weight); Soluble Fraction: < 30% of total C

COMPONENTS:

ACIDS:

- Amino acids
- Carboxylic acids
- Hydroxycarboxylic acids
- Dicarboxylic acids
- Hydroxydicarboxylic acids
- Sulfonic acids
- Phosphonic acids

HYDROCARBONS:

- non-volatile: aliphatic
  - aromatic (PAH)
  - polar
- volatile

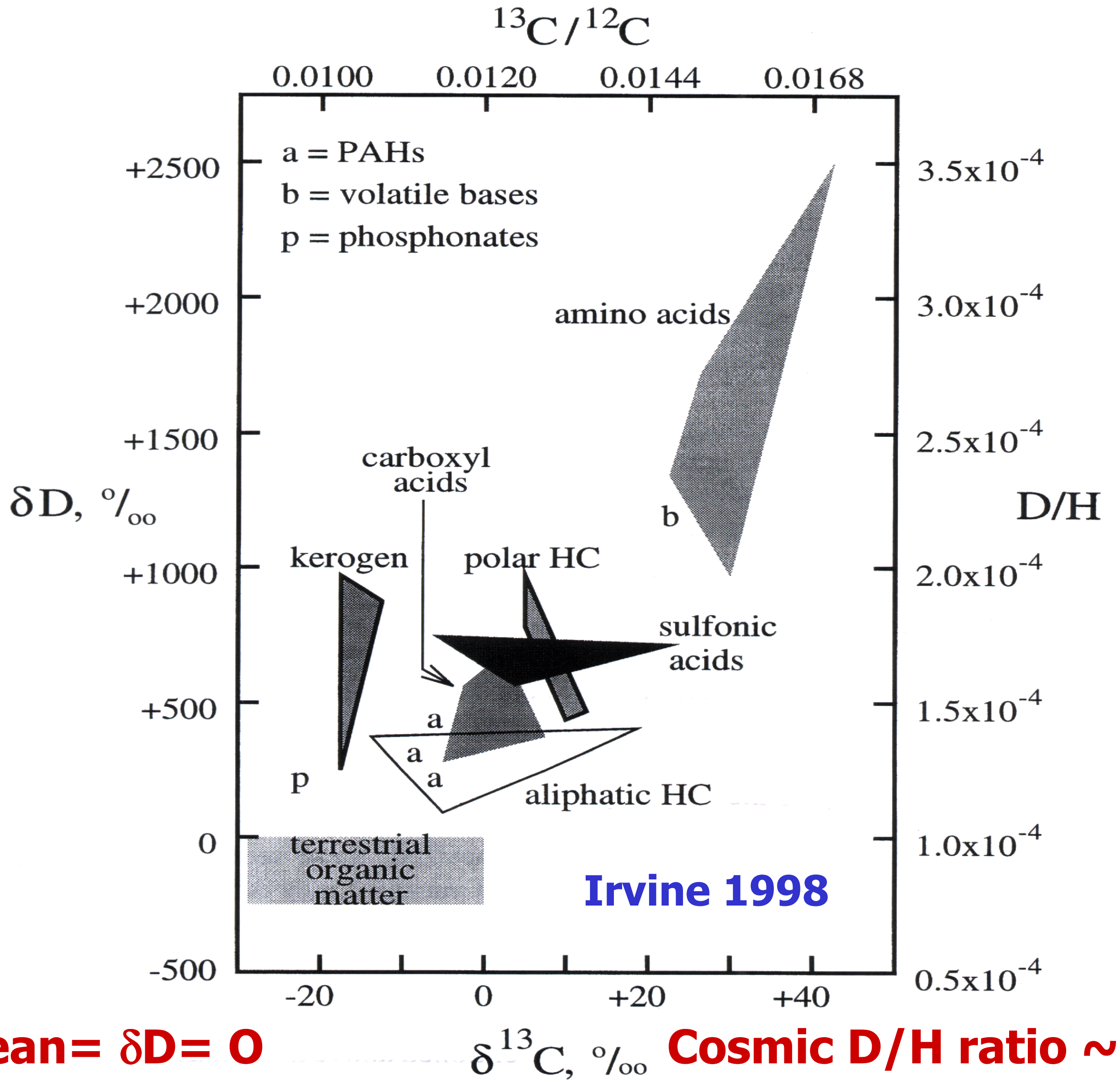
FULLERENES:

- C_{60}, C_{70}
- $He@C_{60}$
- Higher Fullerenes

OTHERS:

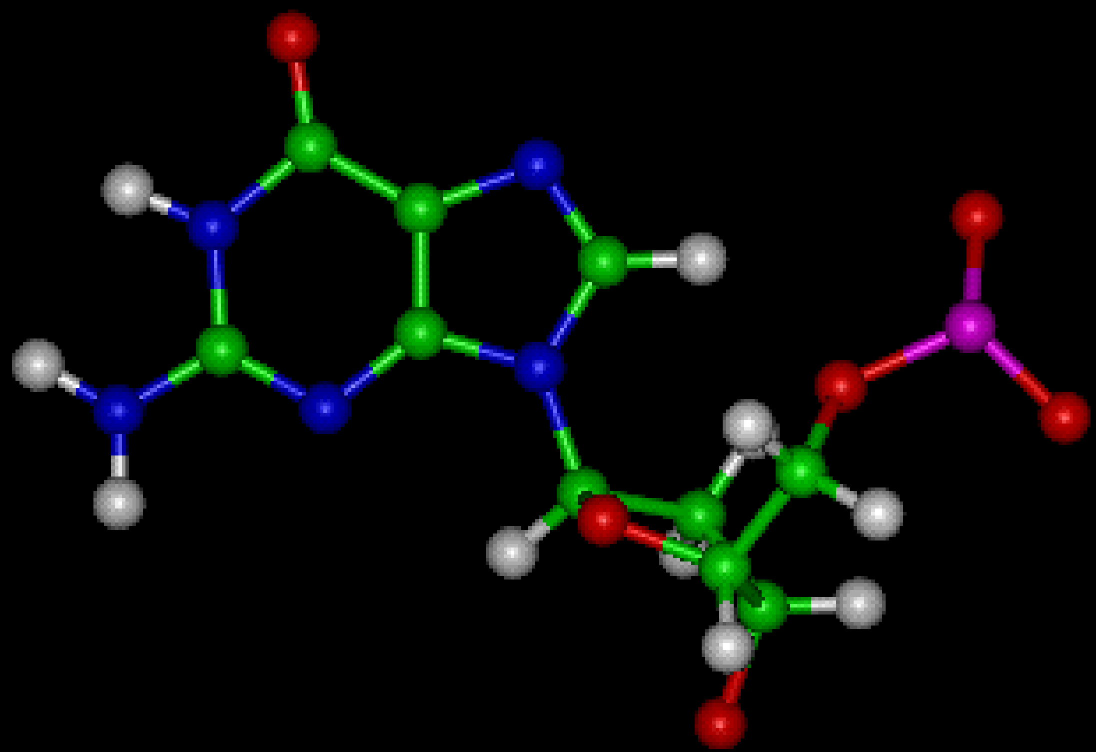
- N-Heterocycles
- Amides
- Amines
- Alcohols
- Carbonyl compounds

ISOTOPIC RATIOS FOR "C" AND "H"

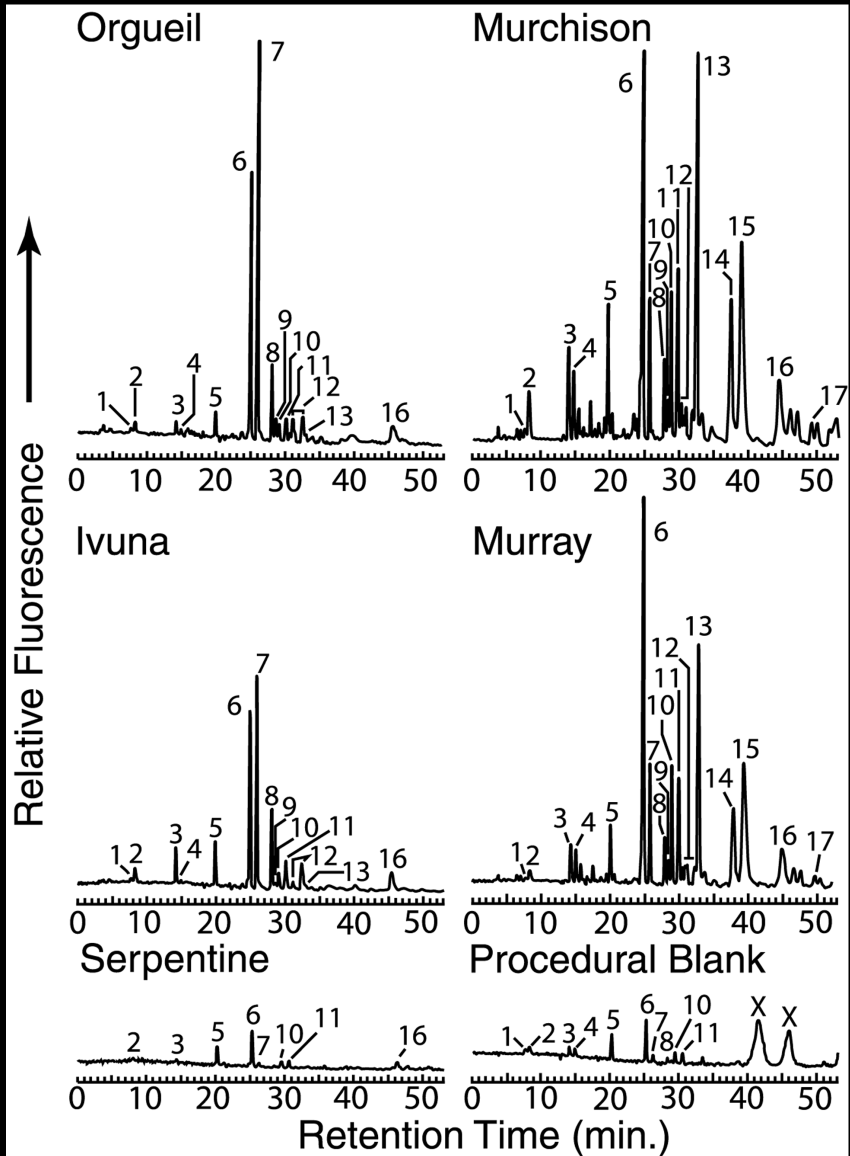


Terr.ocean= δD= O **Cosmic D/H ratio ~ 0.8-2x10^{-5}**

DNA/RNA Components



Chromatograms of Meteorite Extracts



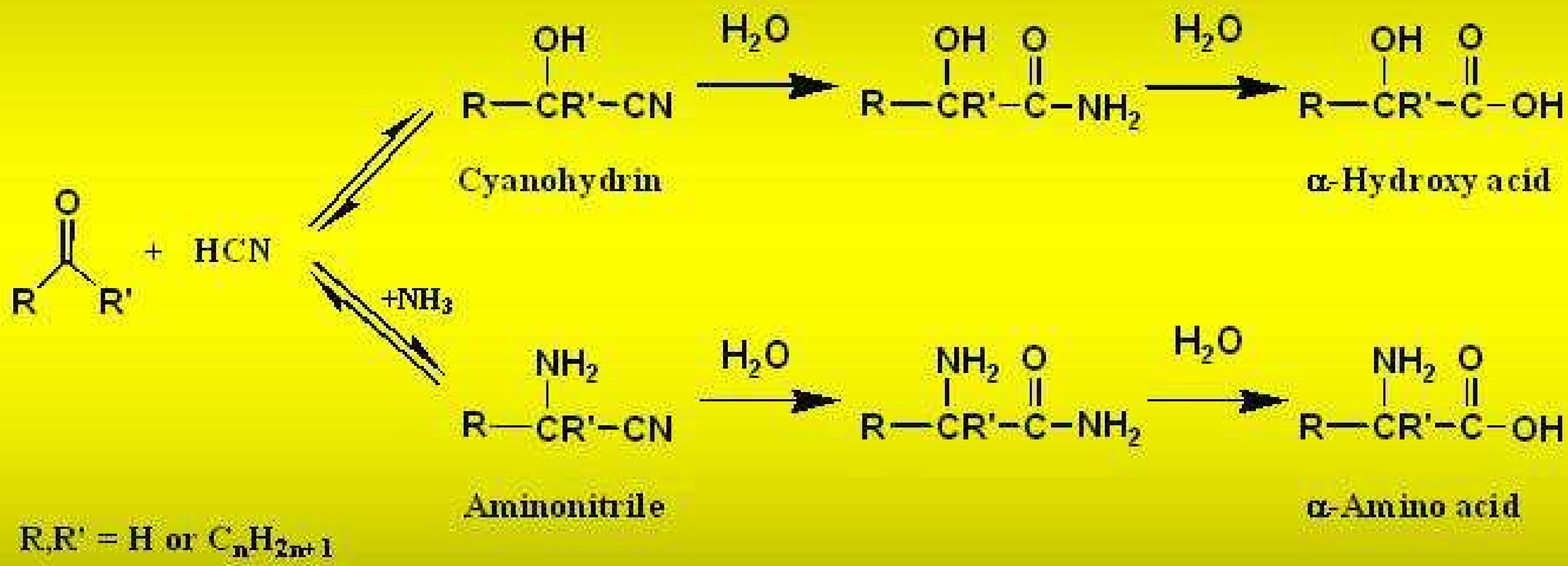
1 D-Aspartic Acid
2 L-Aspartic Acid
3 L-Glutamic Acid
4 D-Glutamic Acid
5 D,L-Serine
6 Glycine
7 β-Alanine
8 γ-Amino-*n*-butyric Acid (g-ABA)
9 D,L-b-Aminoisobutyric Acid (b-AIB)
10 D-Alanine
11 L-Alanine
12 D,L-β-Amino-n-butyric Acid (b-ABA)
13 α-Aminoisobutyric Acid (AIB)
14 D,L-α-Amino-n-butyric Acid (a-ABA)
15 D,L-Isovaline
16 L-Valine
17 D-Valine
X: unknown

Ehrenfreund *et al.*, 2001

Amino Acids in Carbonaceous Chondrites

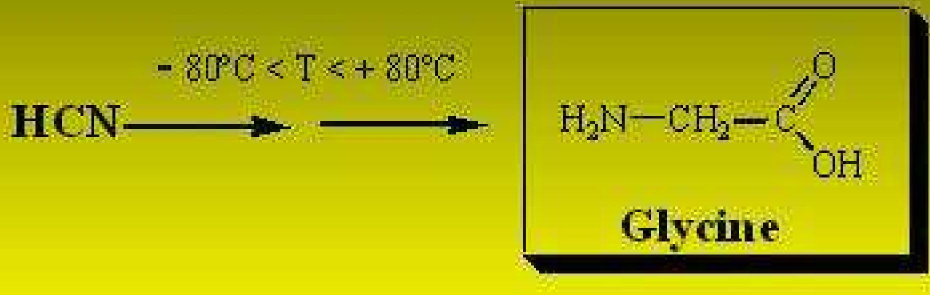
- Amino acids are readily synthesized under a variety of plausible prebiotic conditions (e.g. in the Miller-Urey Experiment).
- Amino acids are the building blocks of proteins and enzymes in life on Earth.
- Chirality (handedness) can be used to distinguish biotic vs. abiotic origins.
- Most of the amino acids found in meteorites are very rare on Earth (AIB, isovaline).

Strecker Amino Acid Synthesis in CM-type Chondrites



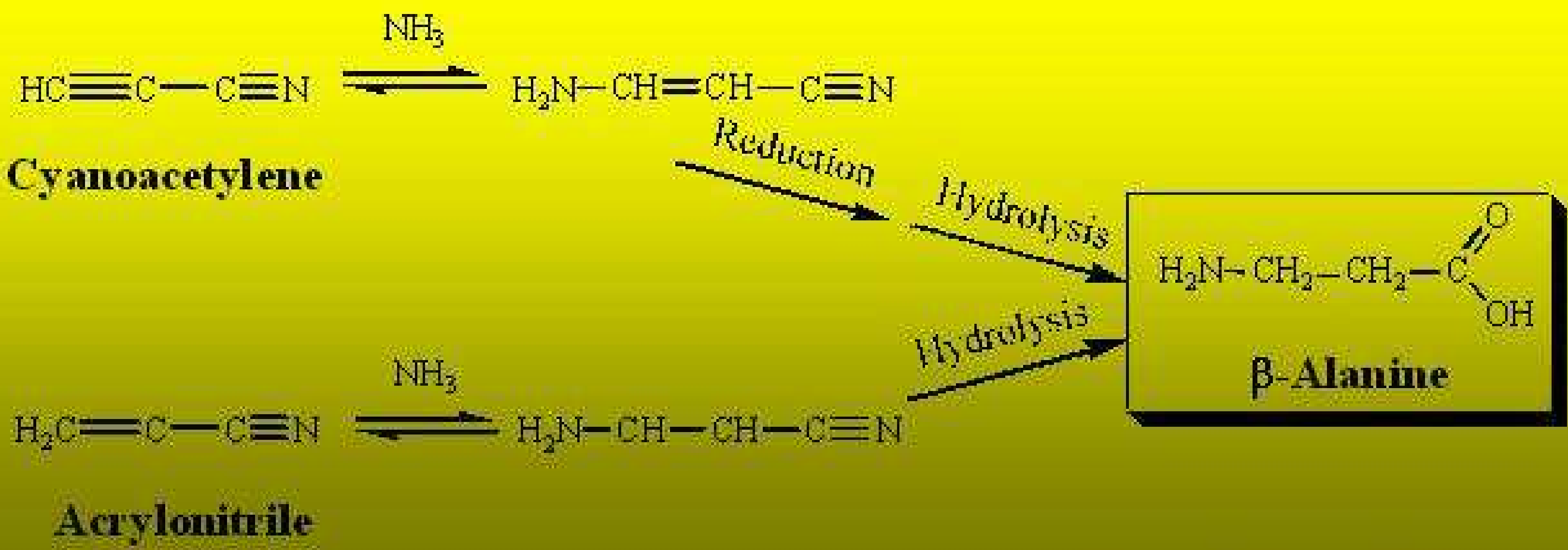
For a review: Botta and Bada, *Surv. Geophys.* 23, 411-467 (2002)

Amino Acid Synthesis in CI-type Chondrites



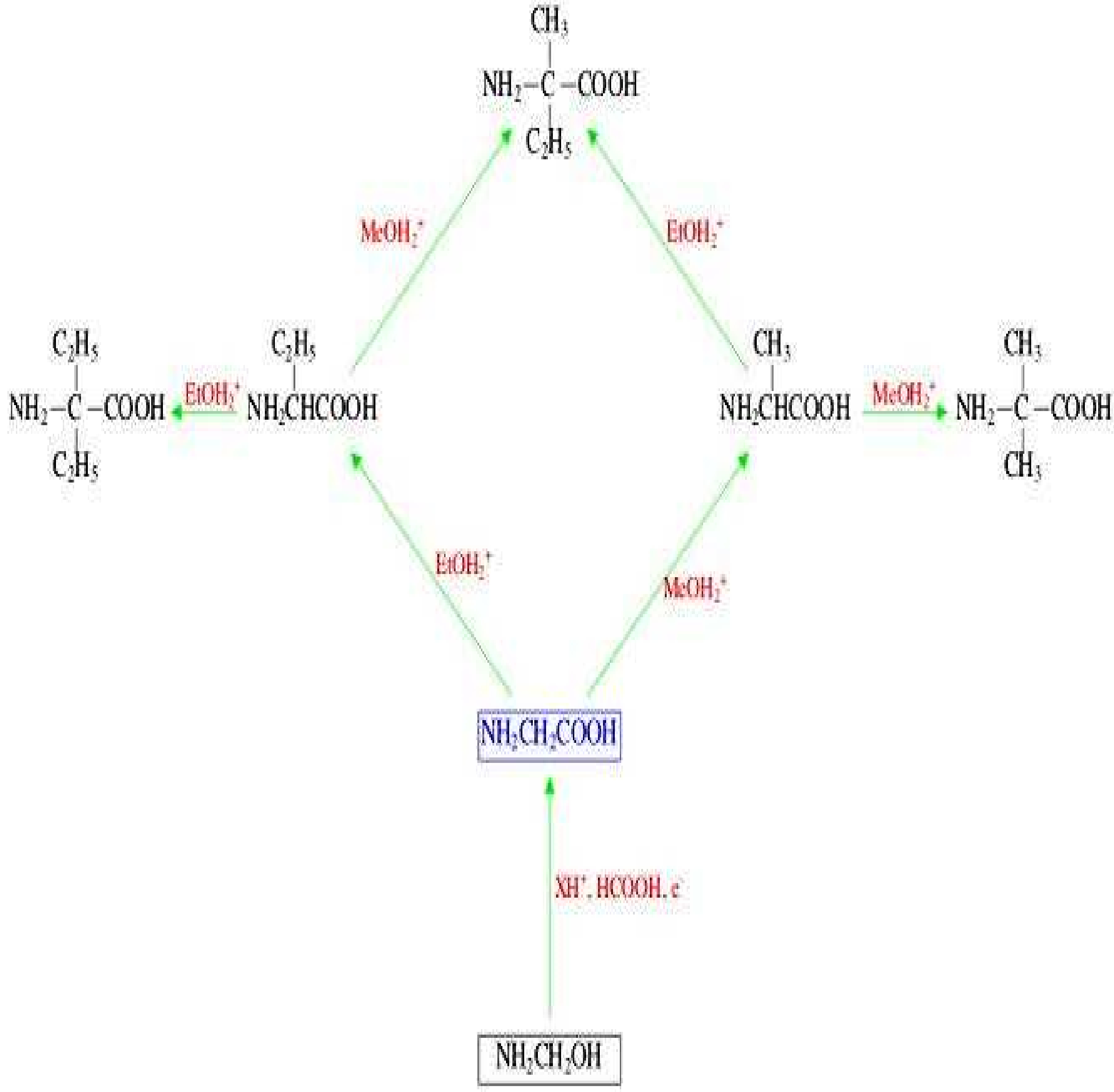
+ traces of other amino acids

Levy *et al.*, *Icarus* **145**, 609-613 (2000).

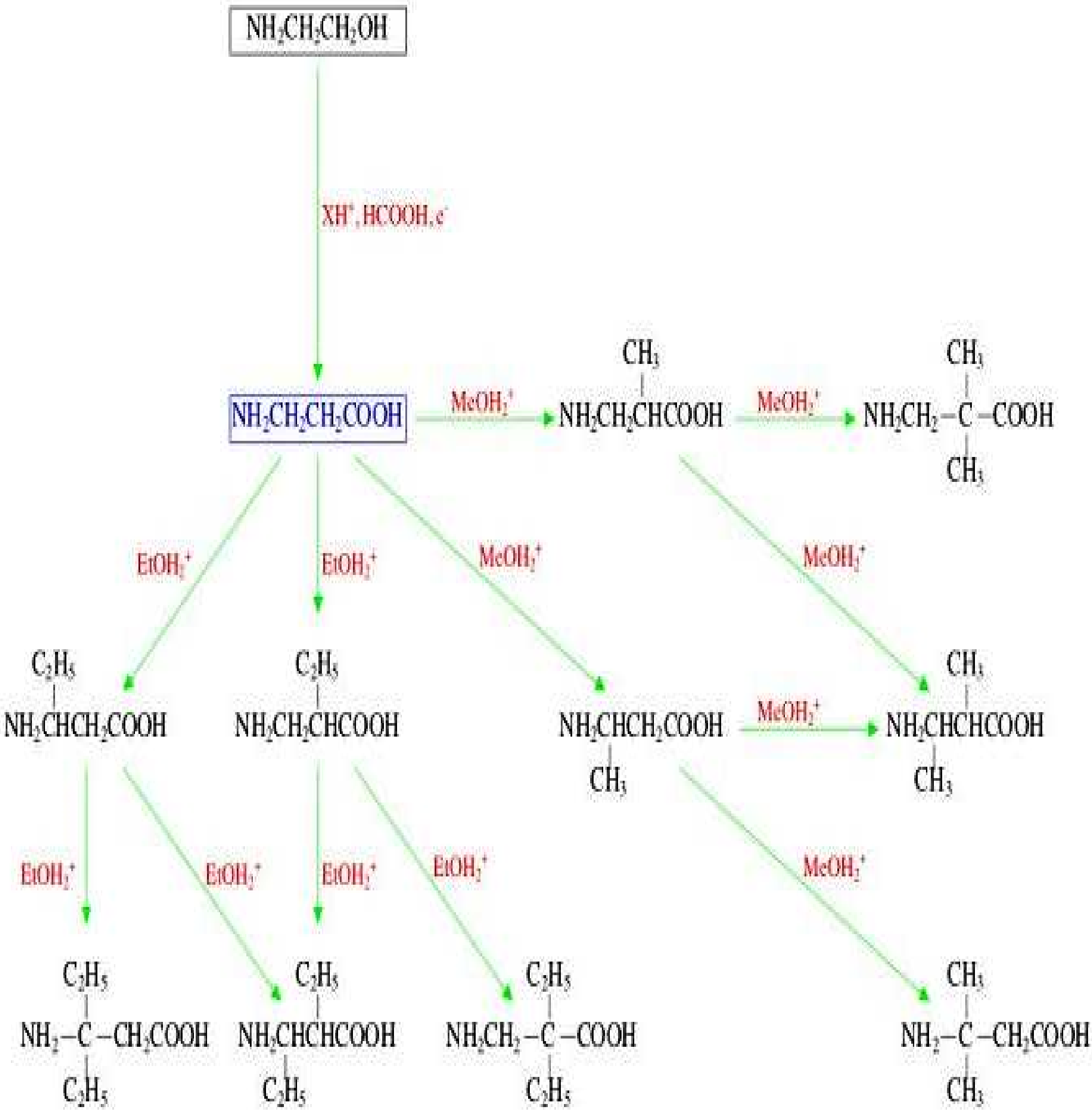


Cronin & Chang, 1993.

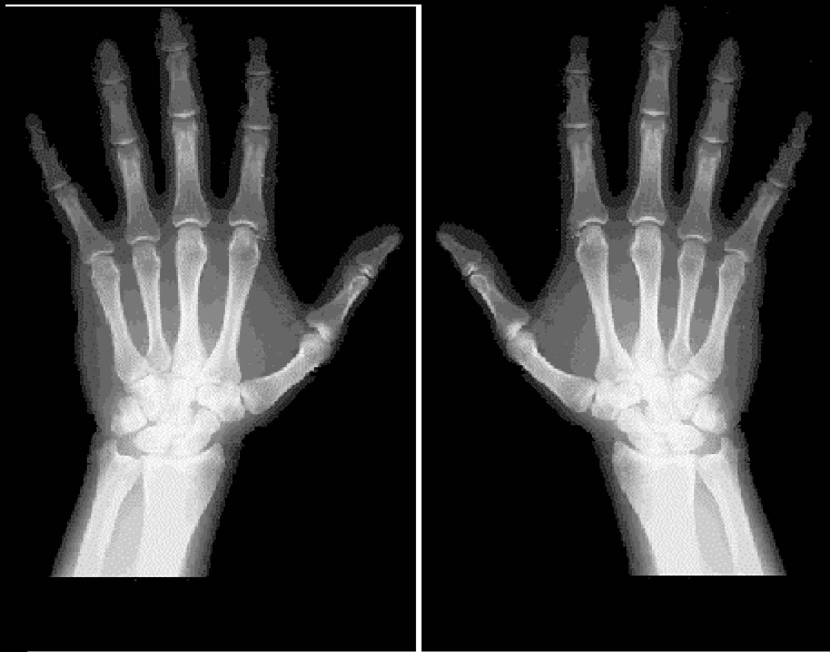
ALKYL CATION TRANSFER TO GLYCINE

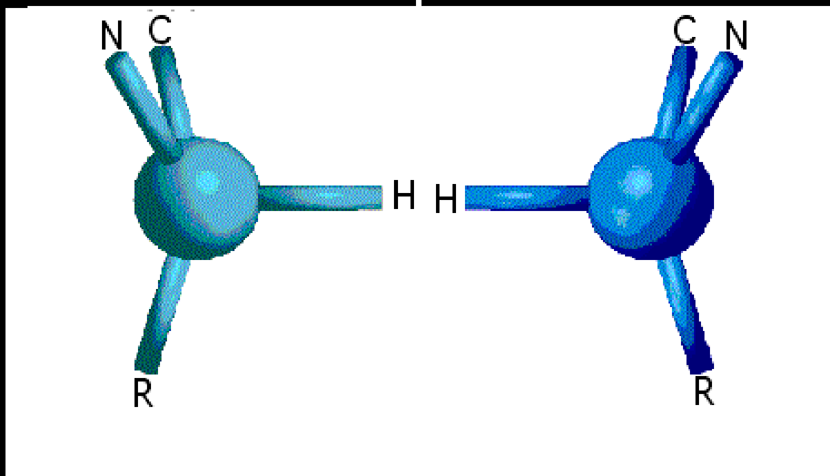


ALKYL CATION TRANSFER TO β-ALANINE



What is Chirality?





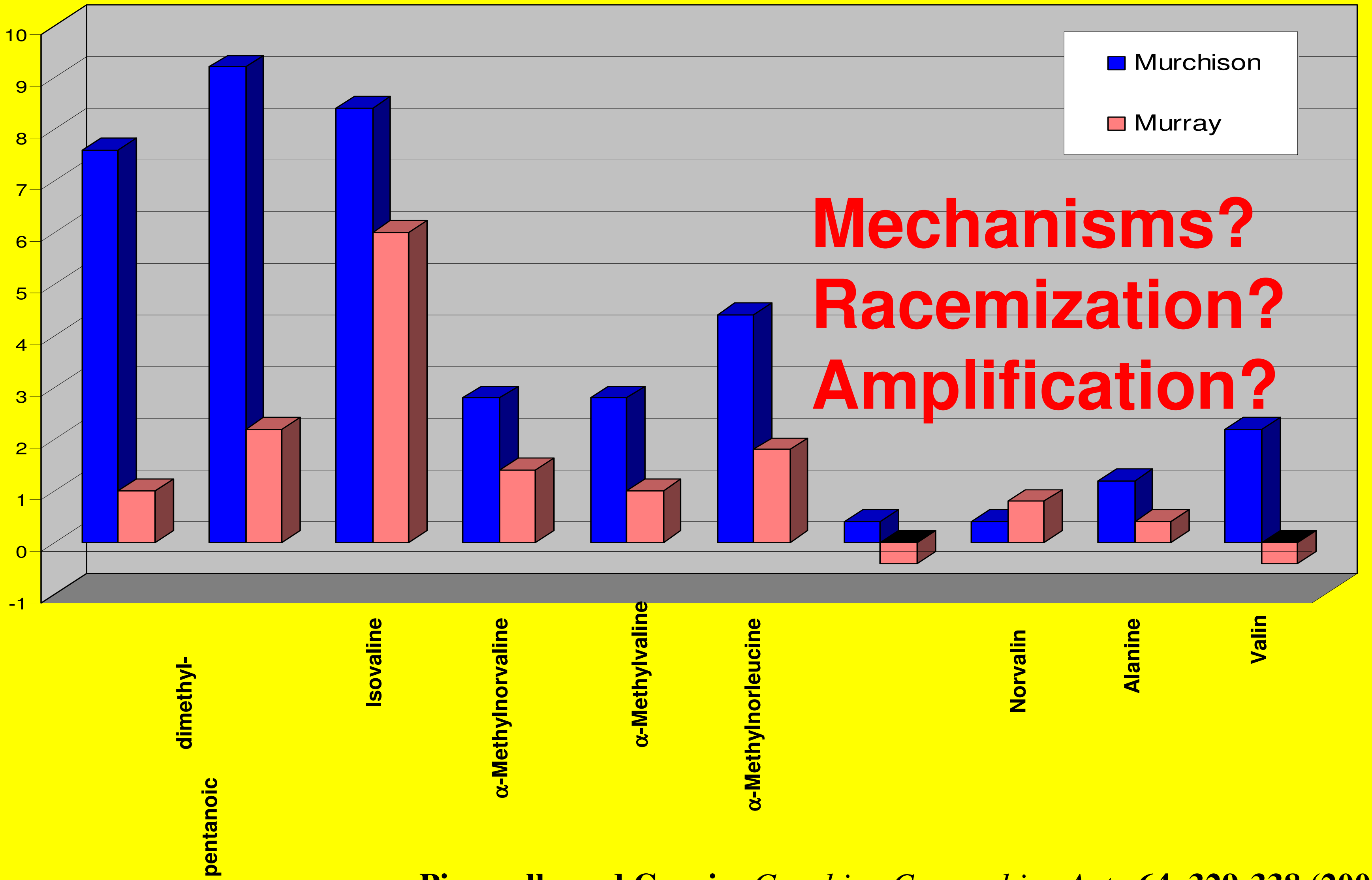
- Left- and right-handed mirror molecules are called enantiomers.
- Enantiomers possess identical physical properties (melting point *etc*.).
- They rotate the plane of planar-polarized light in opposite directions.
- They cannot be chromatographically separated on a non-chiral column.

Separation on chiral column

or

Derivatization to form diastereoisomers, separation on non-chiral column

Enantiomeric Excesses in Meteoritic Amino Acids

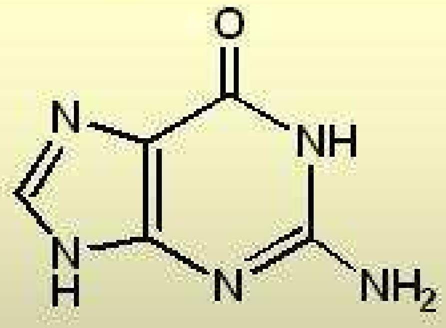


Mechanisms?
Racemization?
Amplification?

Pizzarello and Cronin, *Geochim. Cosmochim. Acta* **64, 329-338 (2000)**

Nucleobases in Carbonaceous Chondrites

Adenine



Guanine

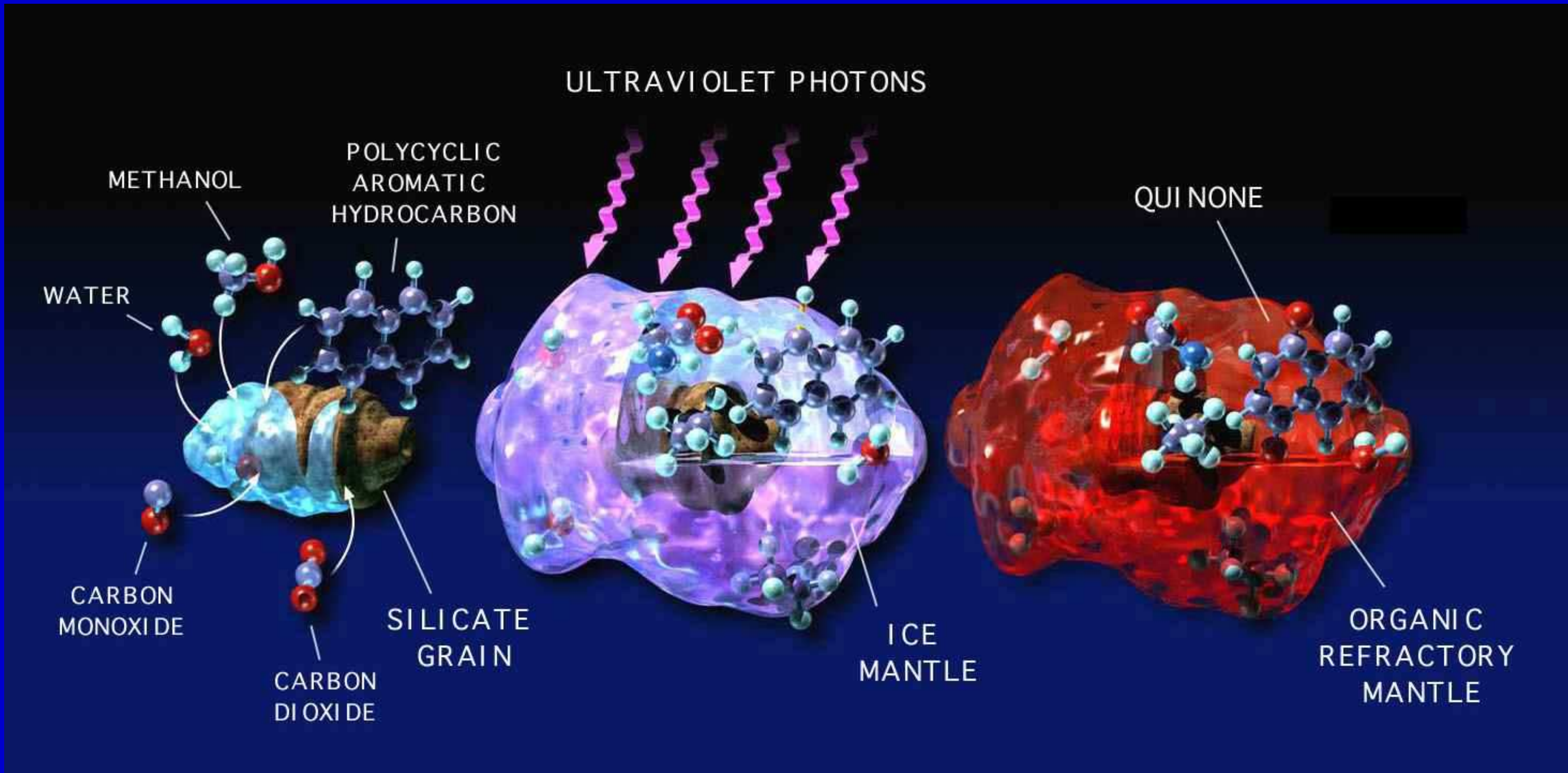
Hypoxanthine

Xanthine

Uracil

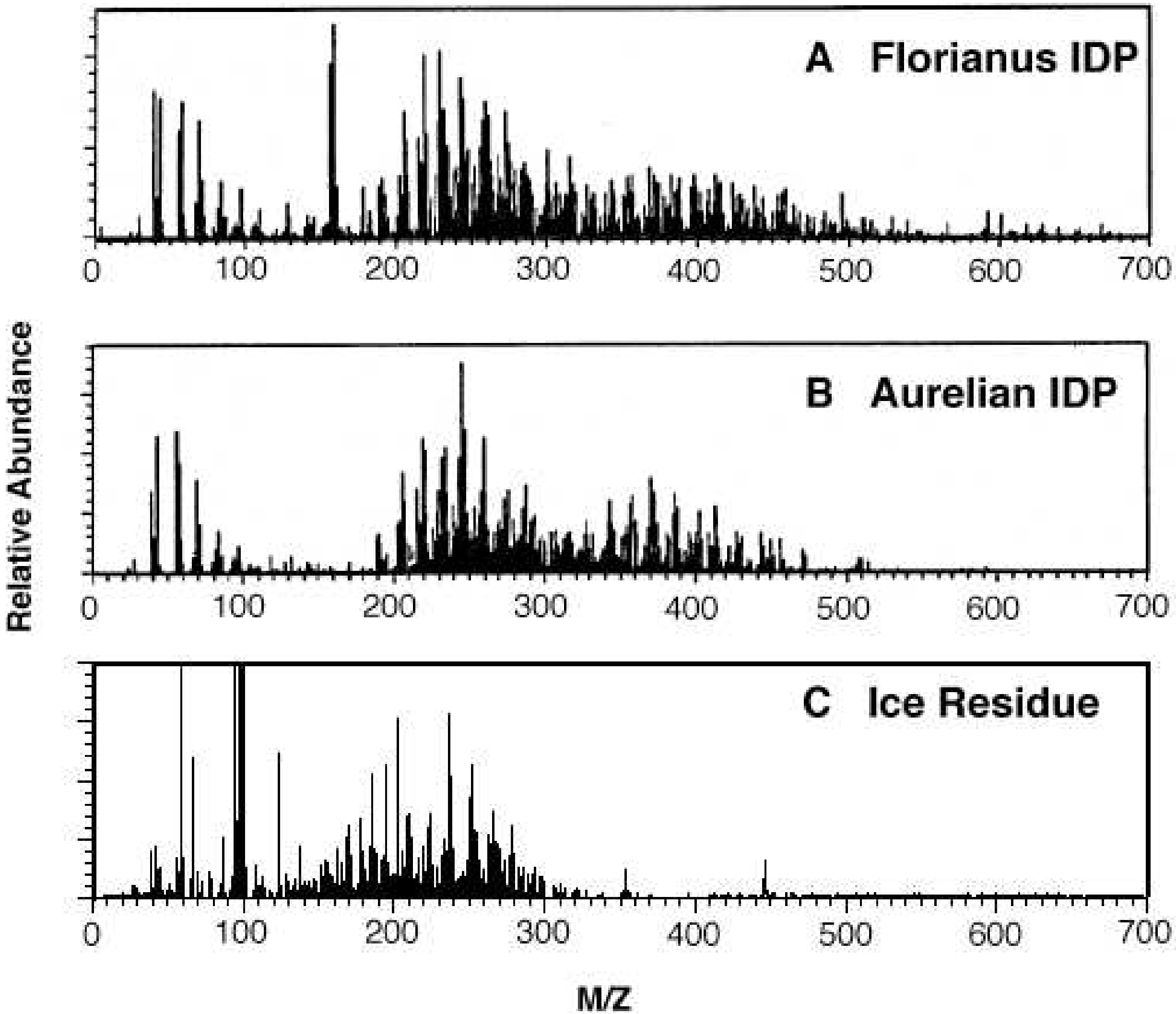
- are very important in the replicating system of all known terrestrial organisms (in DNA and RNA)
- have been detected in Murchison, Murray and Orgueil meteorites at the 200-500 ppb level (Schwartz and coworkers, 1979-1982)
- various other (non-biogenic) N-heterocycles, including a variety of alkylated pyridines, were found in meteorites
- no isotopic measurements have been reported

Interstellar Dust: ice mantle evolution



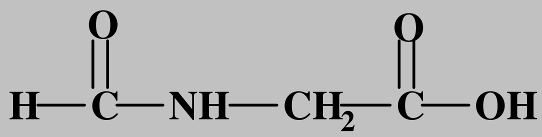
Bernstein, Sandford, Allamandola , Sci. Am. 7,1999, p26

Mass Spectrum of the Room Temperature Residue of H_2O:CH_3OH:CO:NH_3 (100:50:1:1) Ice Compared to the Mass Spectra of Two Interplanetary Dust Particles (IPDs)

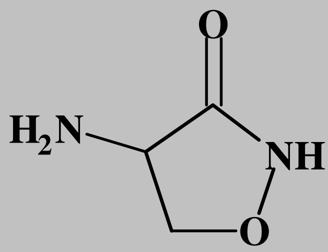


IDP Spectra - Clement et al., 1993

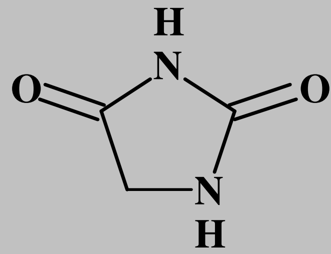
Interstellar/Precometary Ice Photolysis: Abiotic Synthesis of Important Prebiotic Organics



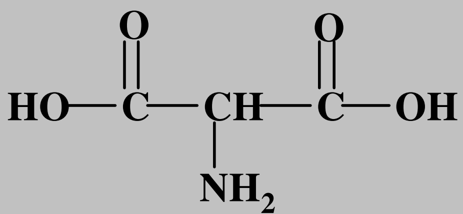
N-Formyl glycine



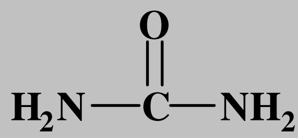
Cycloserine



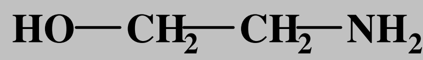
Hydantoin



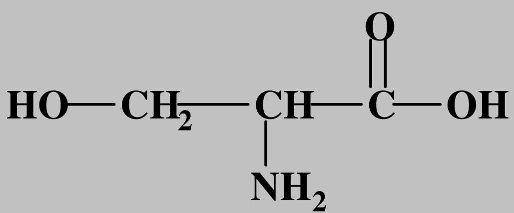
Amino malonic acid



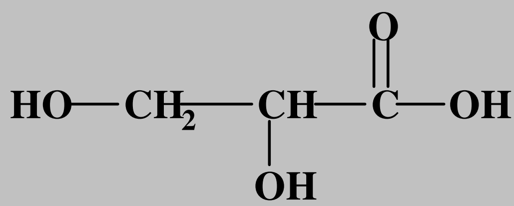
Urea



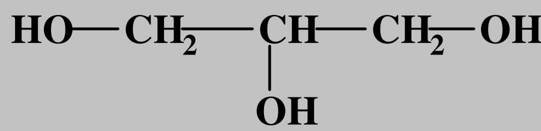
Ethanolamine



Serine



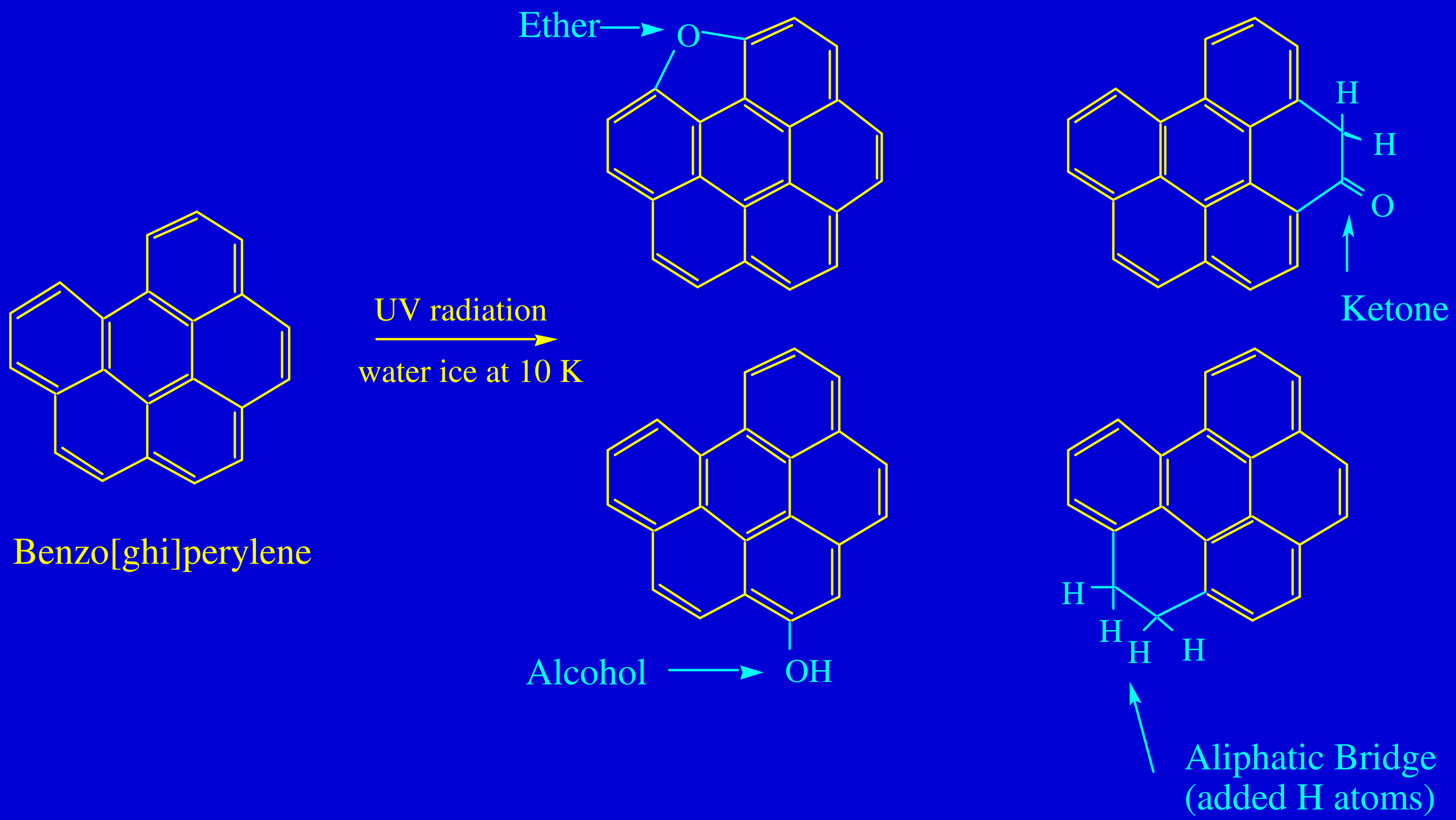
Glyceric Acid



Glycerol

Bernstein et al. (2002) Nature, 416, 401.

Photolysis of PAHs in Water Ice Produces Alkanes, Ketones, Ethers, and Alcohols.

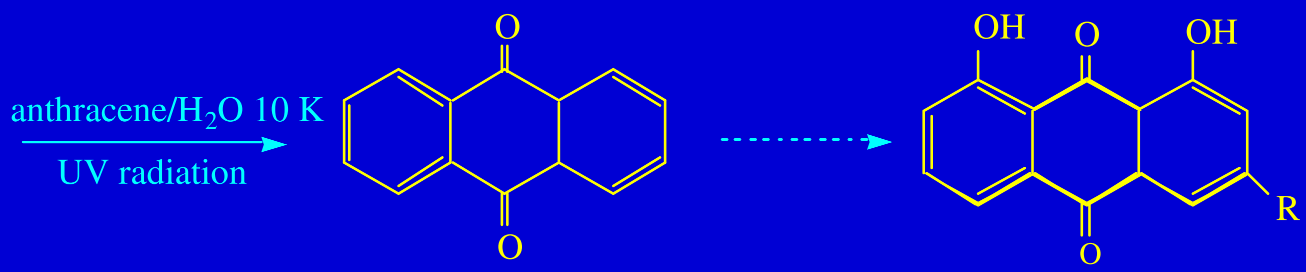


Both oxidation (alcohol, ether and ketone formation) and reduction (addition of hydrogen) reactions occur on photolysis of water ices containing PAHs. These are the same kinds of compounds observed in meteorites, fit spectra of emission objects and, in some cases, have biochemical significance.

Bernstein et al.Science 283, 1135 (1999)

Photochemistry of PAHs in Ice: Abiotic Synthesis of Biogenic Compounds

Juglone (in walnut & pecan shells)
Bull. Soc. Chim. 1, 800 (1907)



Aloe-Emodin (extract of Aloe)
Arch. Pharm. **247**, 81 (1909)

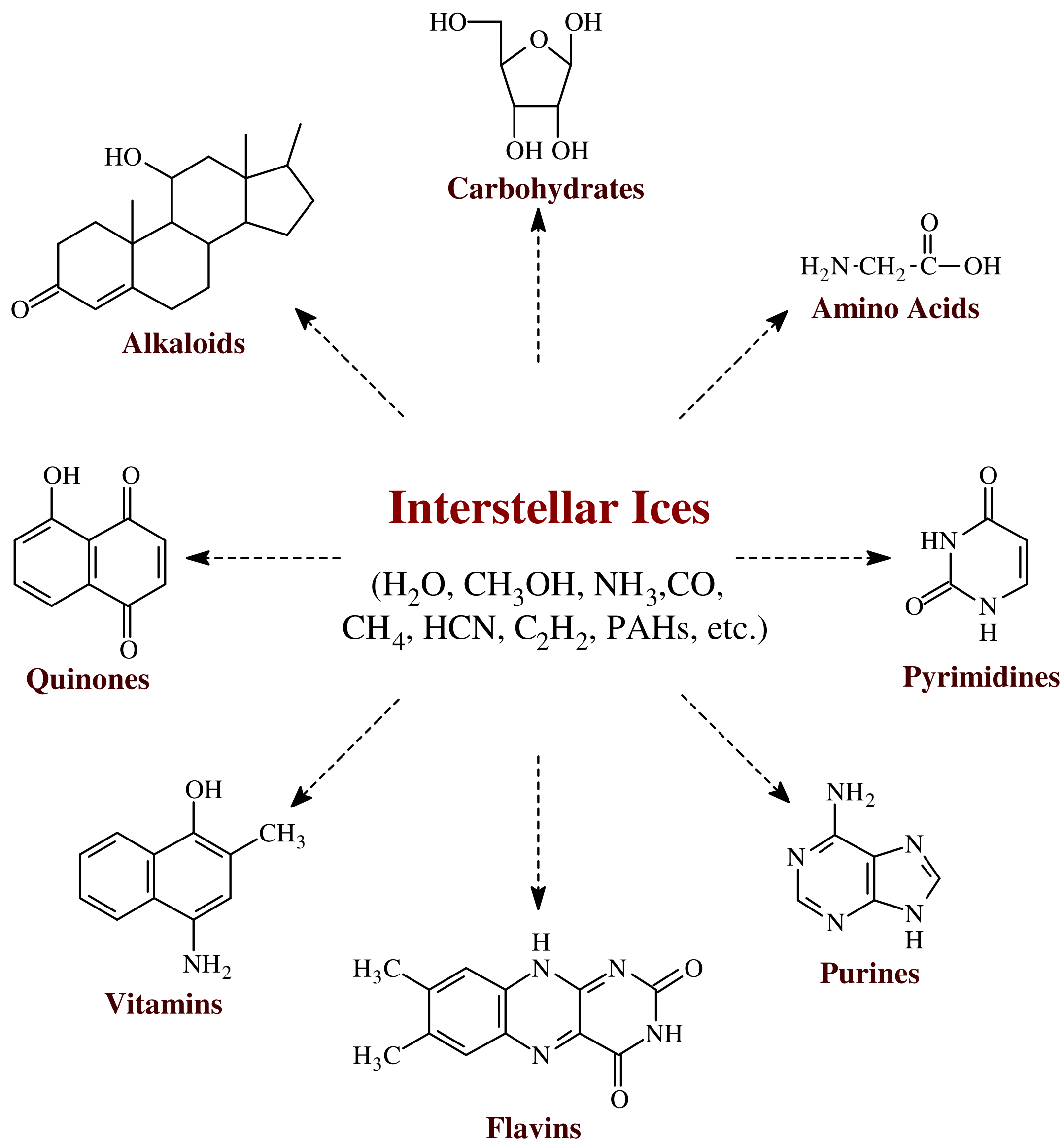
Rhein (extract of chinese rhubarb)
Ann. **50**, 196 (1844)

These quinone type structures are very important in many living systems. For example, naphthaquinones (like juglone above) are essential for electron transport in simple organisms.

Juglone: Bernstein et al.Met. & Planet. Sci. 36, 351 (2001)

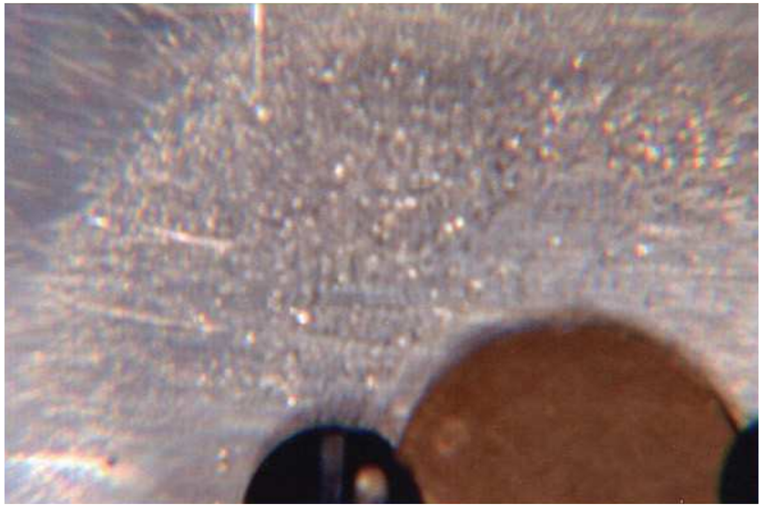
Anthroquinone: Ashbourne et al. in prep

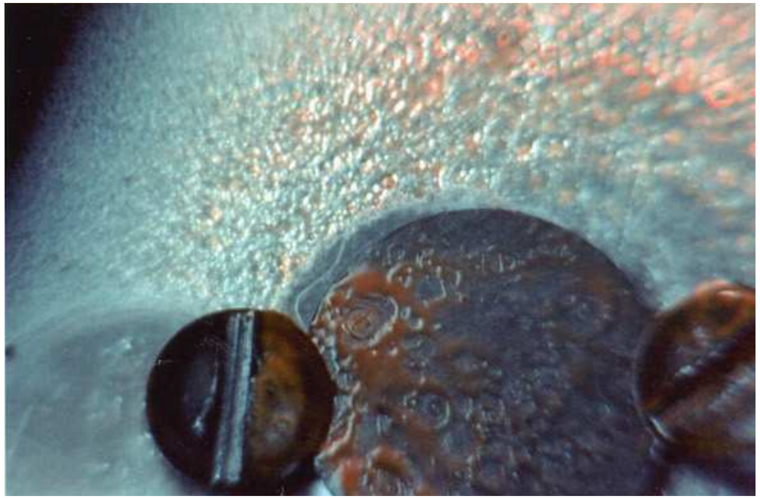
Abiotic Synthesis of Biogenically Useful Molecules in Cometary and Interstellar Ices



Courtesy Jason Dworkin

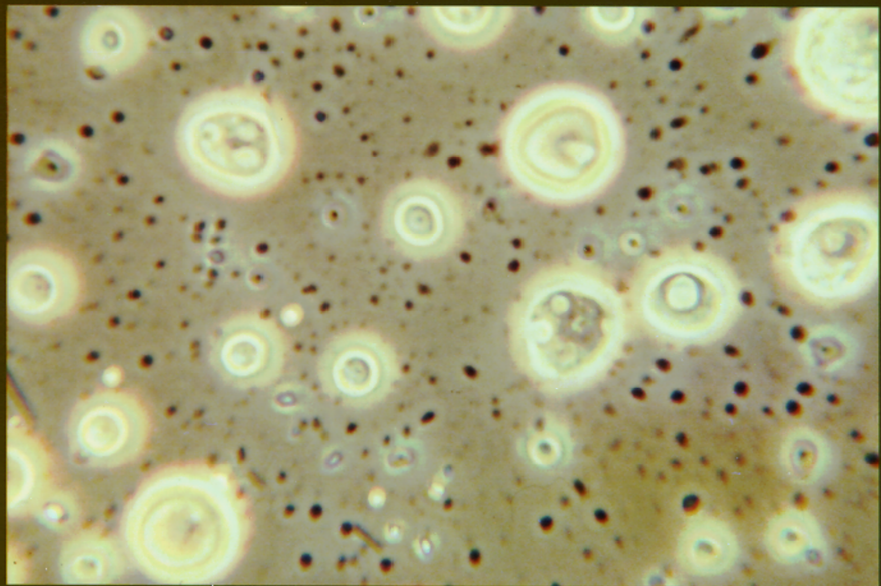
Organic Residue Remaining After the Low Temperature UV Irradiation of the Ice





SELF ORGANIZED WATER INSOLUBLE DROPLETS PRODUCED WHEN THE ORGANIC RESIDUE FROM A UV RADIATED INTERSTELLAR / PRE-COMETARY ICE ANALOG IS ADDED TO WATER

Visible Light

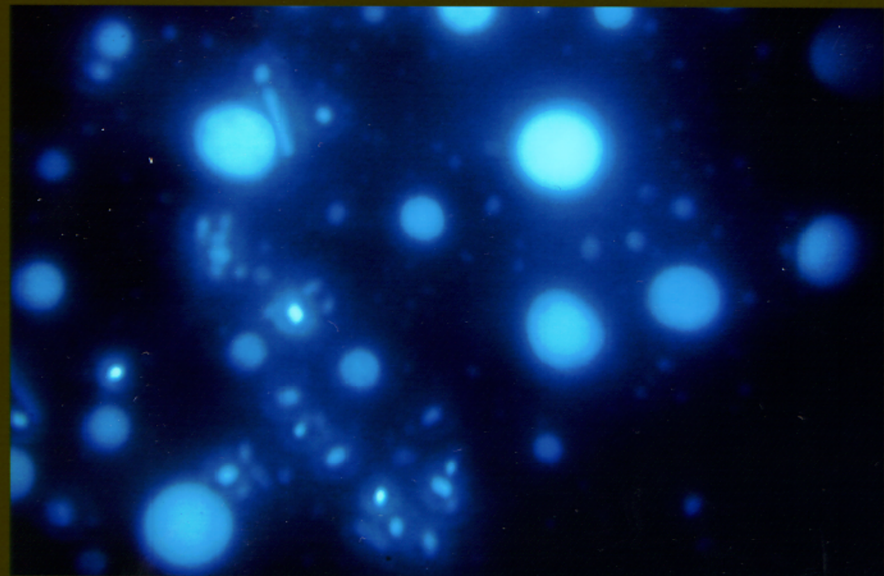


Smallest substructures are about 5 microns across

≈10 Microns

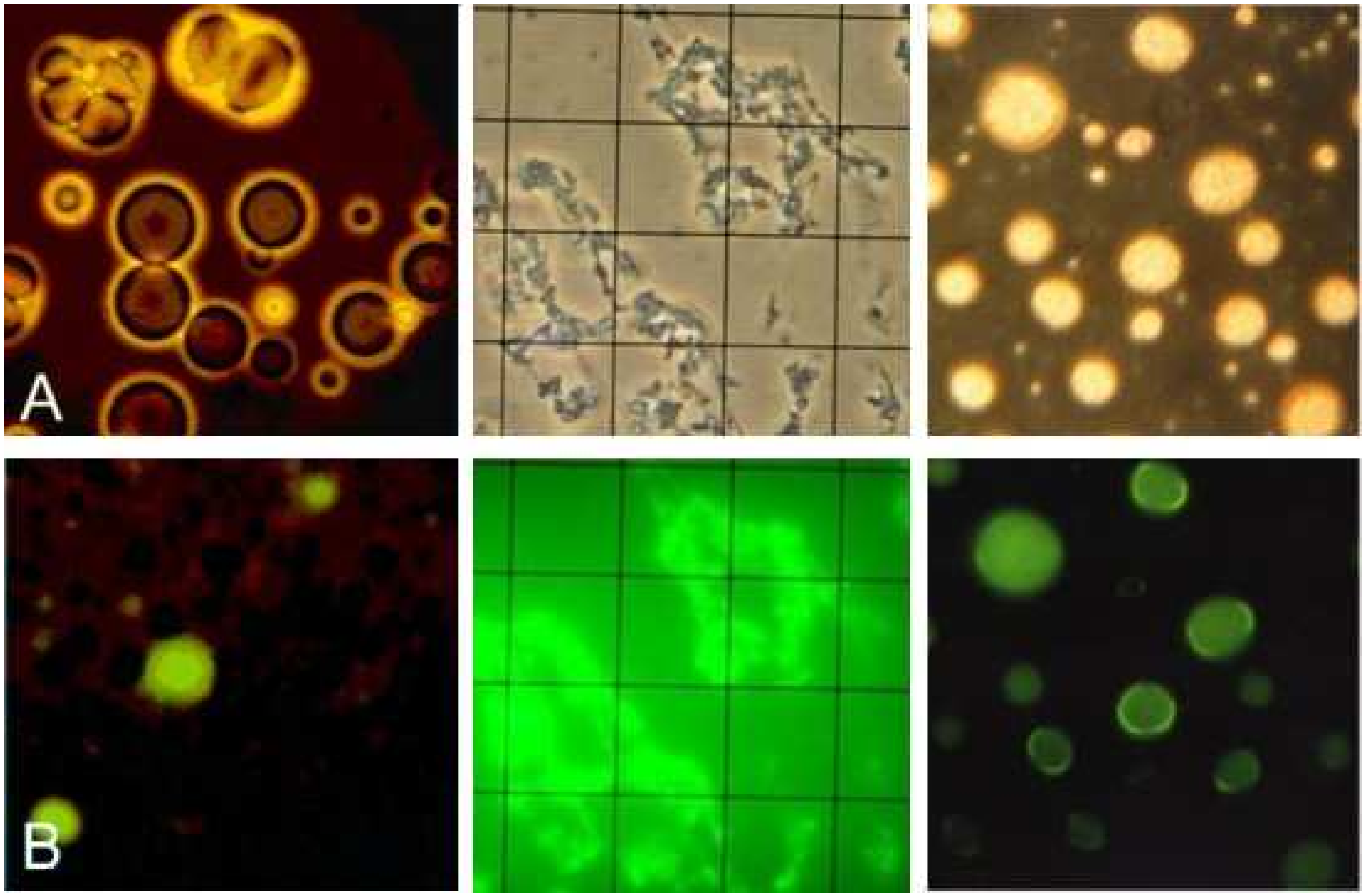
Initial Ice Composition=
$H_2O:CH_3OH:CO:NH_3$
(100:50-10:10:10)

Fluorescence ($\lambda em \approx 410nm$; $\lambda ex \approx 330nm$)



Fluorescent components have partitioned into the non-polar droplets

Formation of Various Vesicular Structures from Meteorite and Ices



Phase Contrast Microscopy

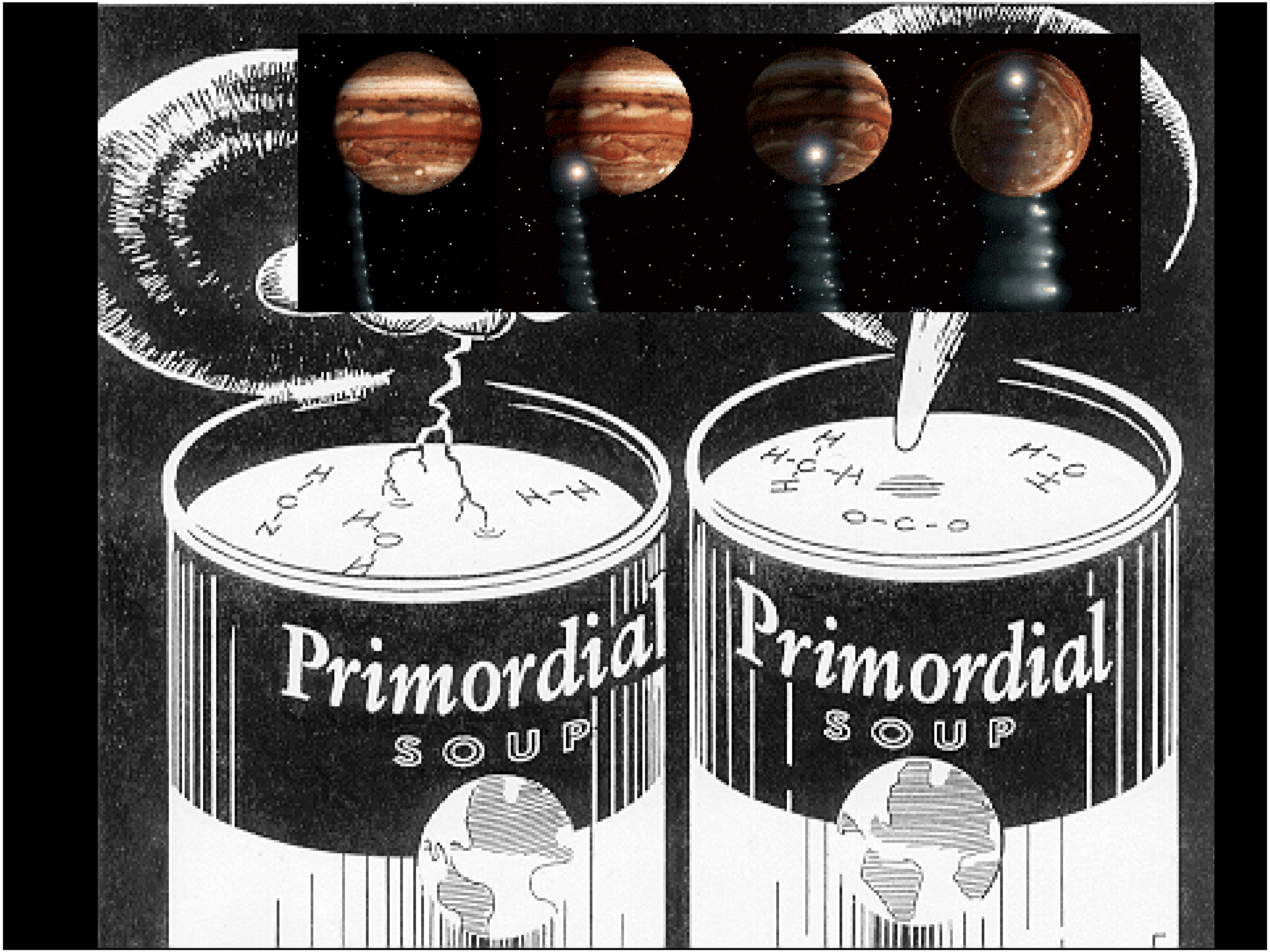
Fluorescence Microscopy

30 µm

Murchison Meteorite
Deamer et al. 2003

Proton Irradiated Ice
Dworkin &Moore
Work in progress

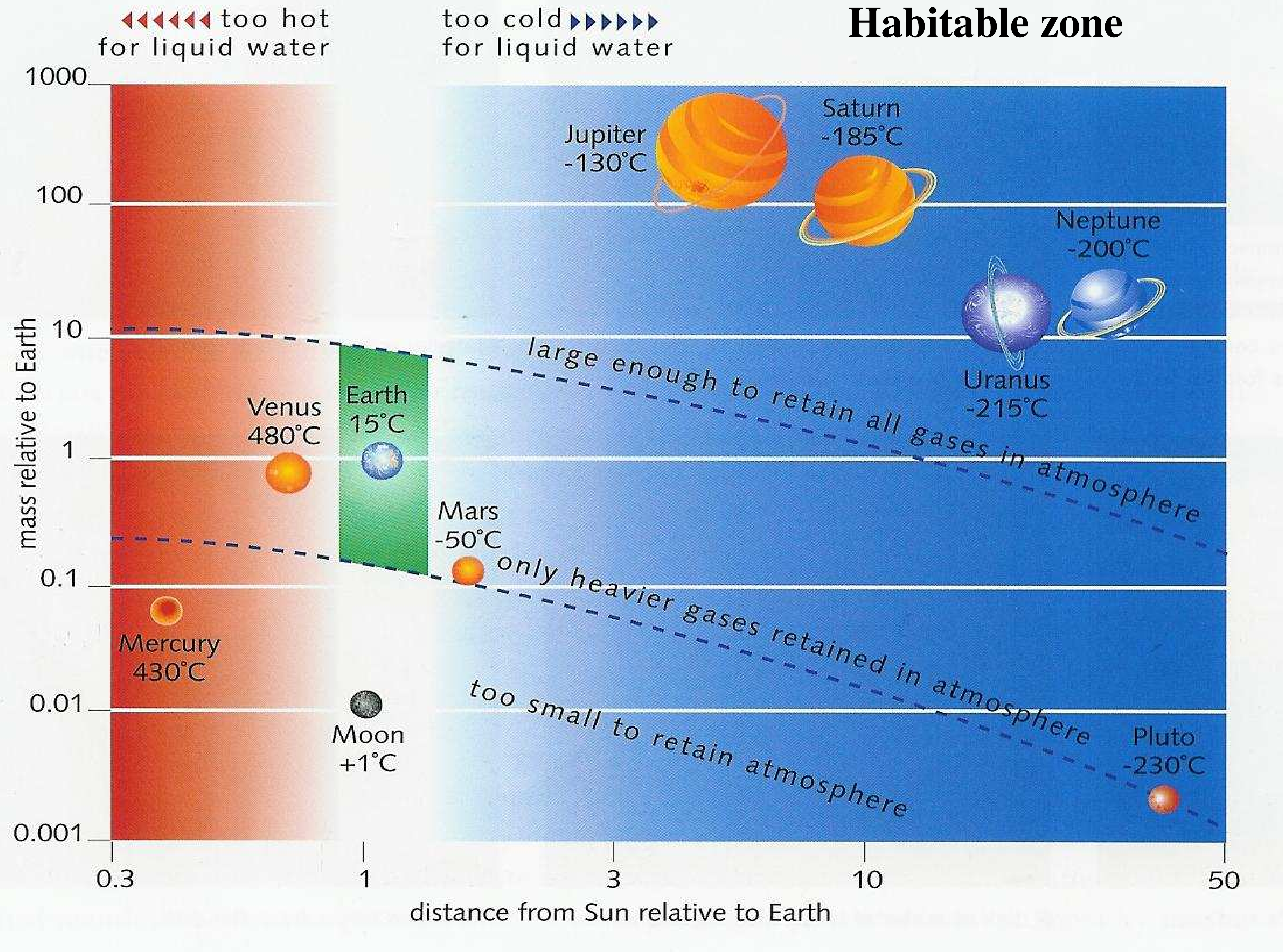
UV photolyzed Ice
Dworkin et al. 2001

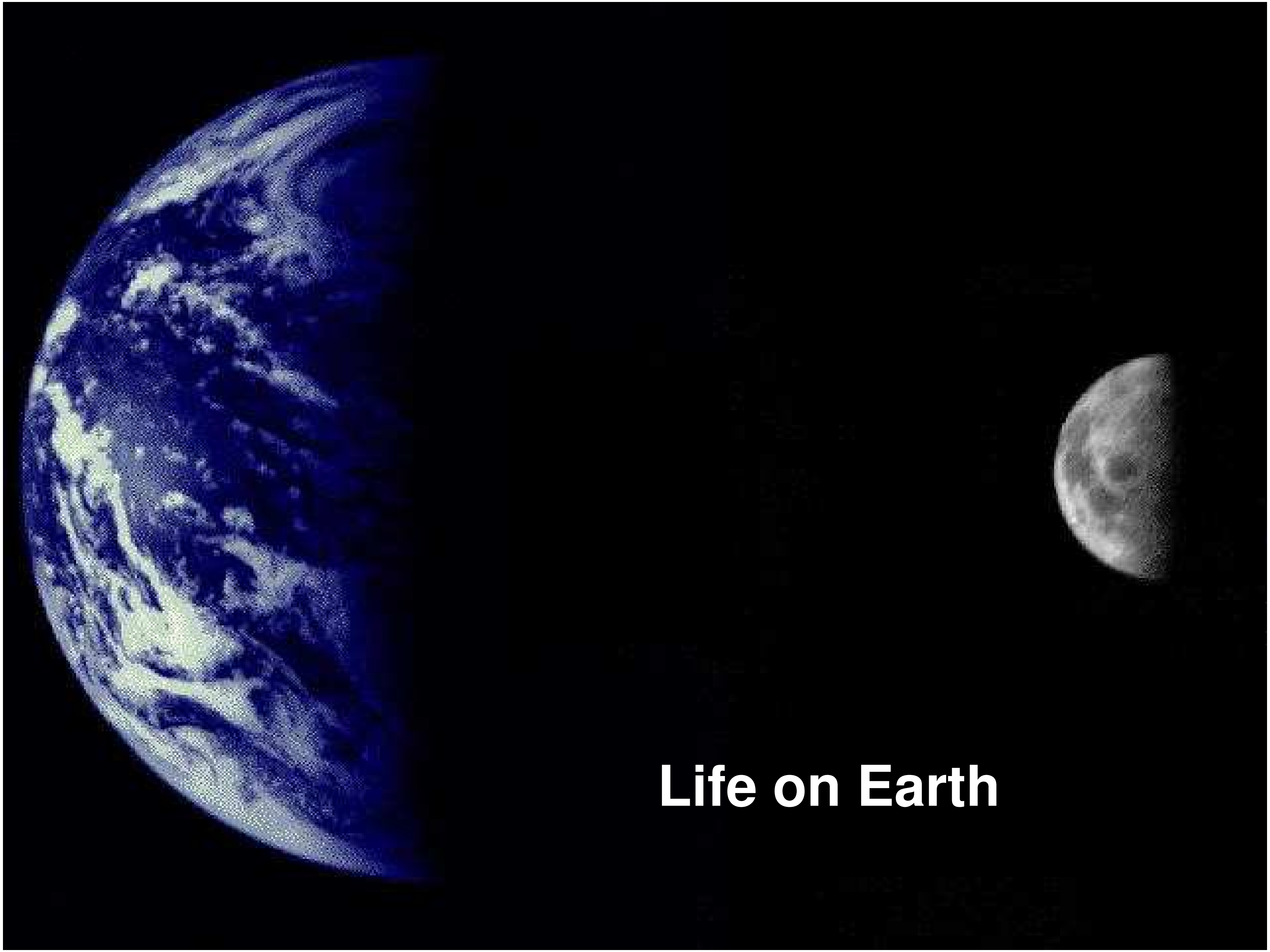

Primordial
SOUP
Primordial
SOUP

Major Sources (in kg/yr) of Prebiotic Organic Compounds in the Early Earth

Terrestrial Sources	kg/yr*
UV Photolysis	3×10^8
Electric Discharge	3×10^7
Shocks from impacts	4×10^2
Hydrothermal Vents	1×10^8
Extraterrestrial Sources	adapted from Chyba & Sagan (1992)
IDP's	2×10^8
Comets	1×10^{11}
Total	10^{11}

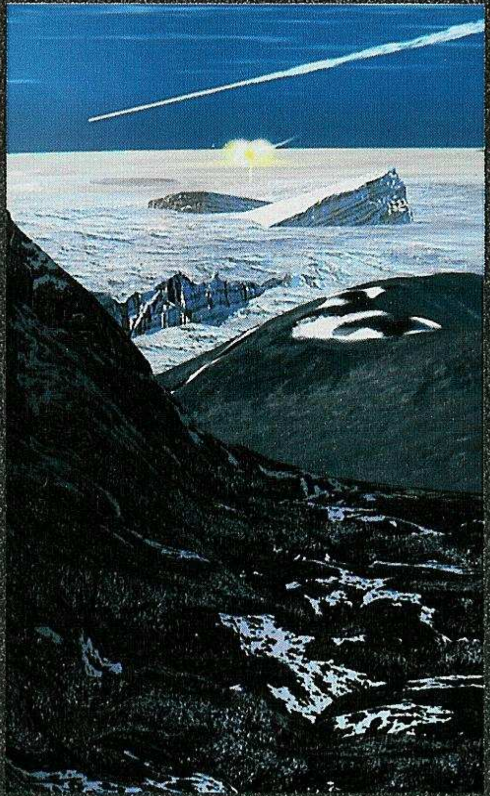
Habitable zone



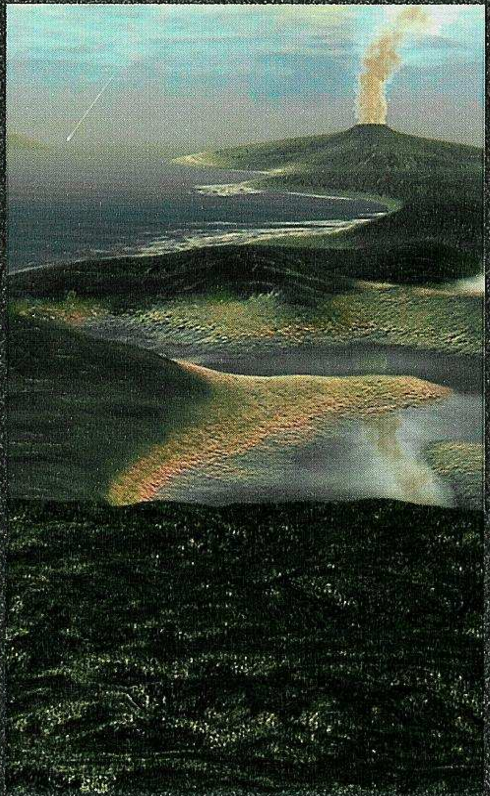

Life on Earth

EARLY EARTH

PRIMORDIAL EARTH?



FREEZING?

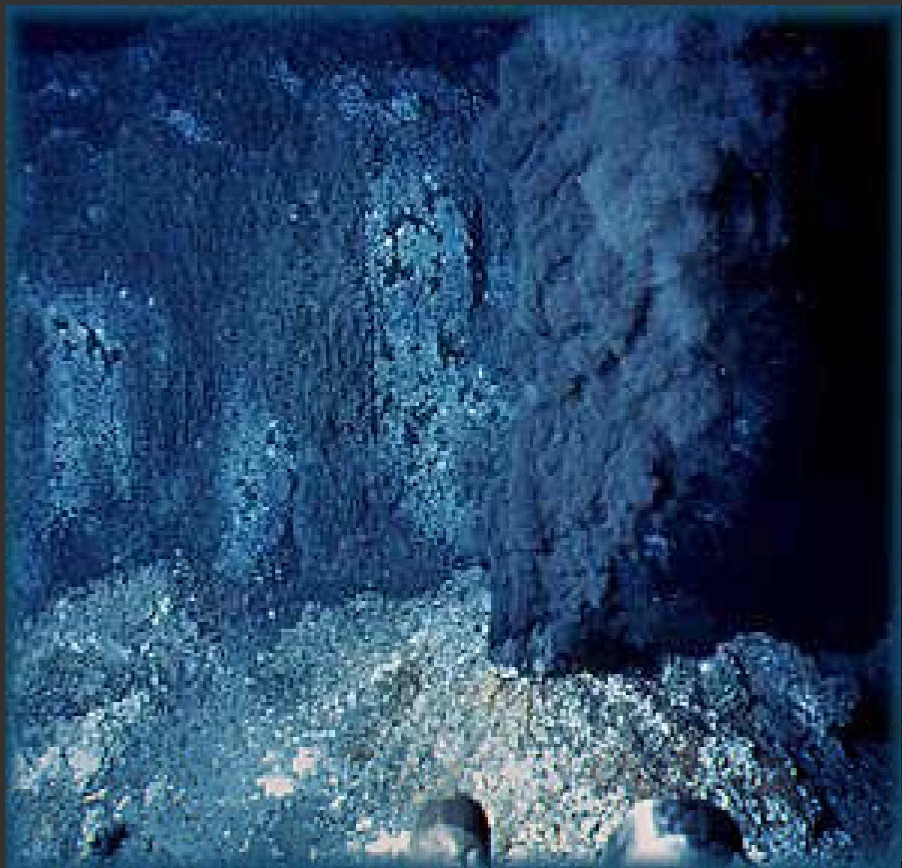


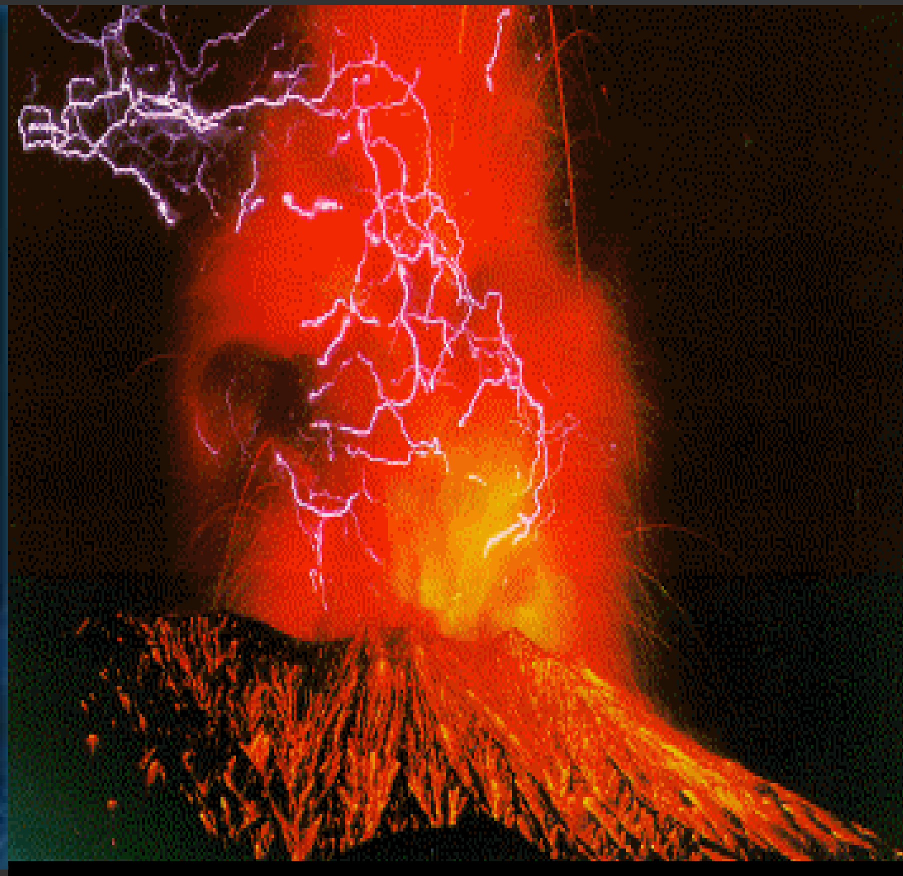
TEMPERATE?

STEAMY?

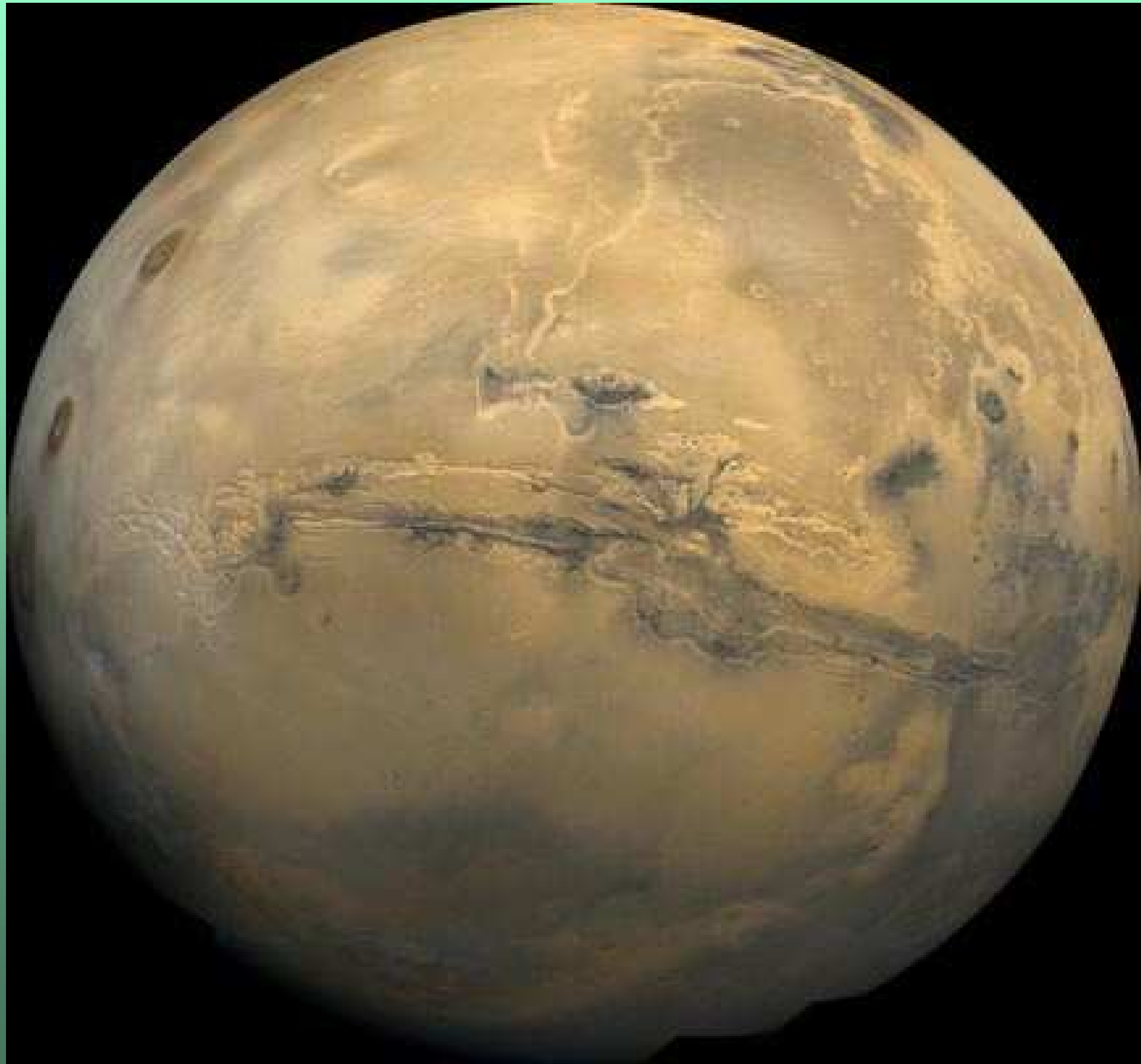
Alternative abiotic synthesis routes

- Black Smokers
- Volcanic outflows



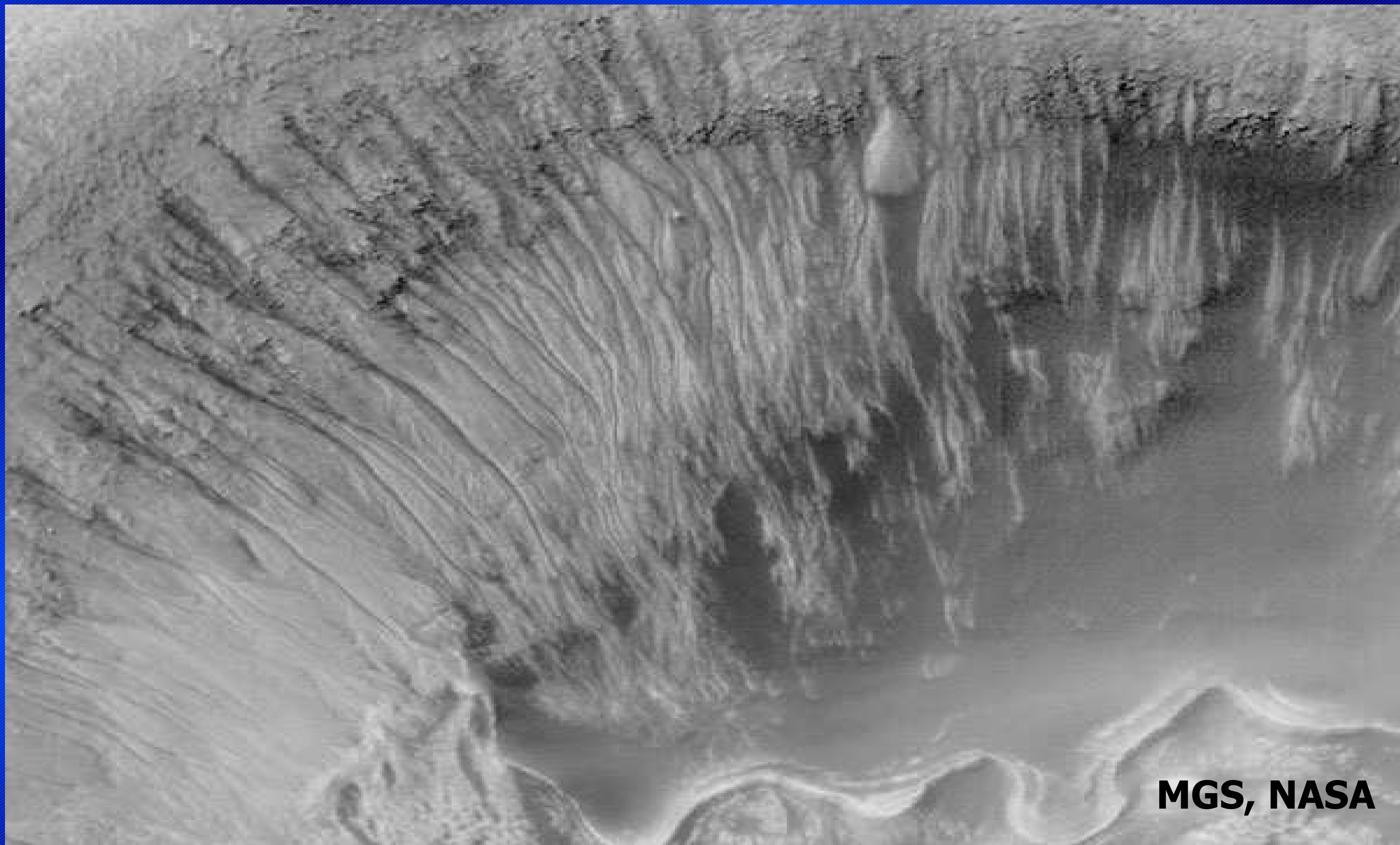


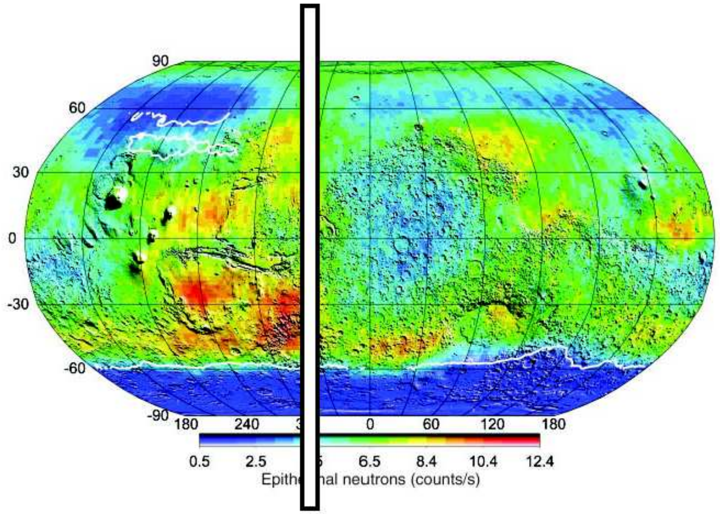
Life on Mars



Evidence for Recent Water on Mars

Many narrow channels run from top down to the crater floor in the Newton crater → outburst of subsurface water ?

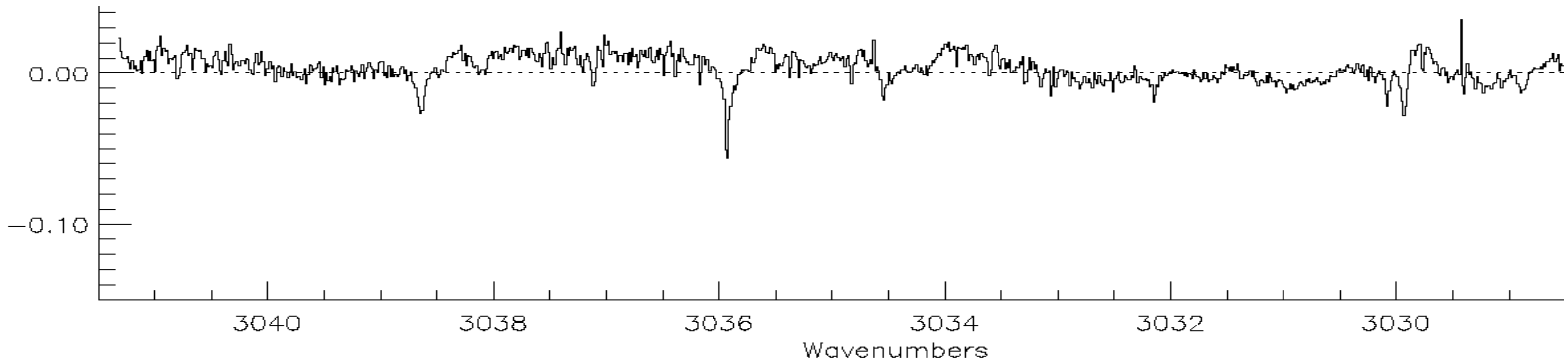




Organics and Water on Mars

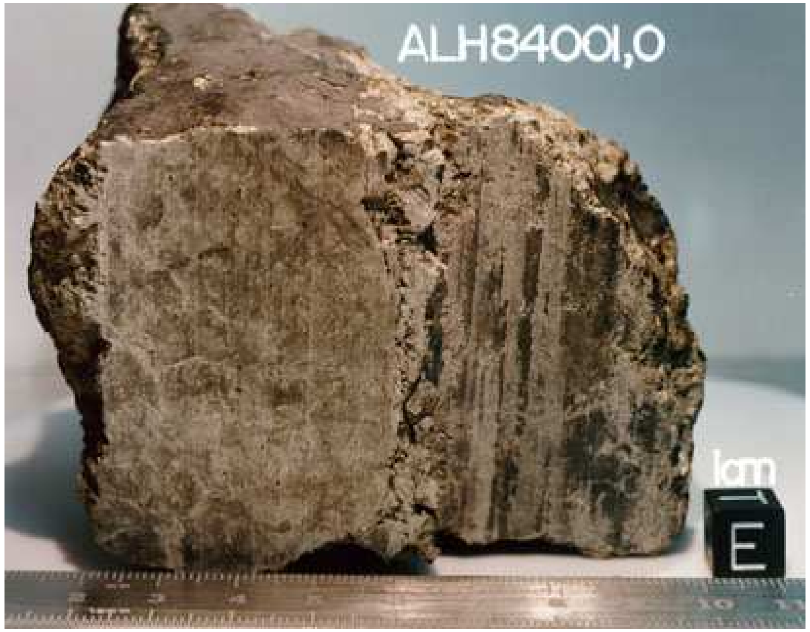
(left) sub-surface hydrogen
Mars Odyssey Boynton et al. 2002

(below) Phoenix spectra showing CH_4 and H_2O (Mumma et al. 2003)



mumma_010704.35

Organic Compounds in Martian Meteorites



- ALH84001 was reported to show evidence for past life on Mars (McKay *et al.*, 1996).
- Upon analysis, only trace amounts of amino acids were detected (few ppb).
- The identified composition showed characteristics that pointed to the majority of the amino acids being terrestrial contamination, with a (possible) Martian contribution at the sub-ppb level (Bada *et al.*, 1998).

MARS EXPLORATION ROVERS

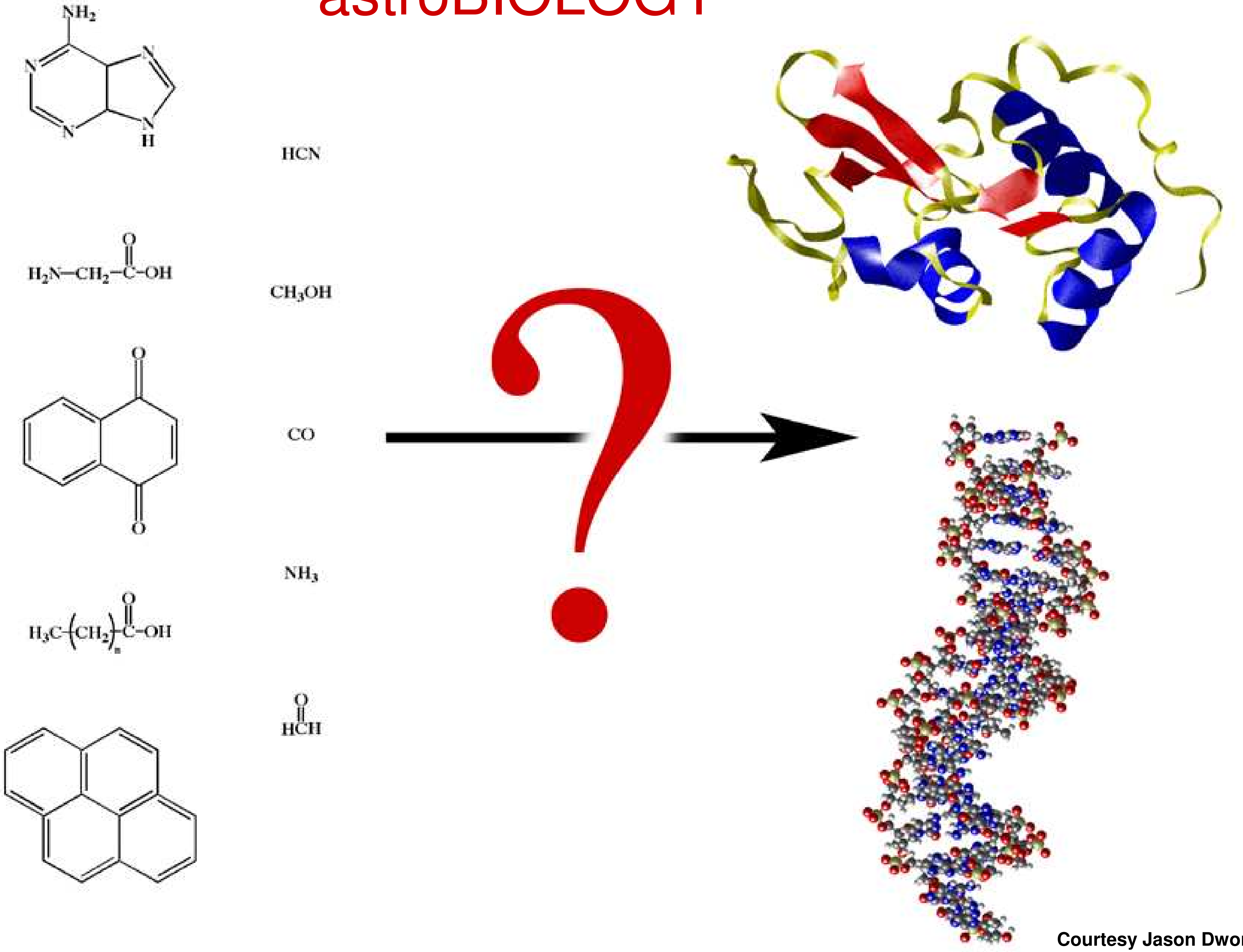
– robot rovers, 90 days mission, robots can crawl 100 m/day

ASTRObiology

Could it be that our configuration of planets is extremely rare, perhaps even unique ?

- **The right distance from the star**
- **The right mass of the central star**
- **Stable planetary orbits**
- **A Jupiter-like neighbour**
- **The right planetary mass**
- **Plate tectonics**
- **An ocean ……**

astroBIOLOGY



Courtesy Jason Dworkin


END