# The role of non terrestrial material on the prebiotic synthesis of biomolecules


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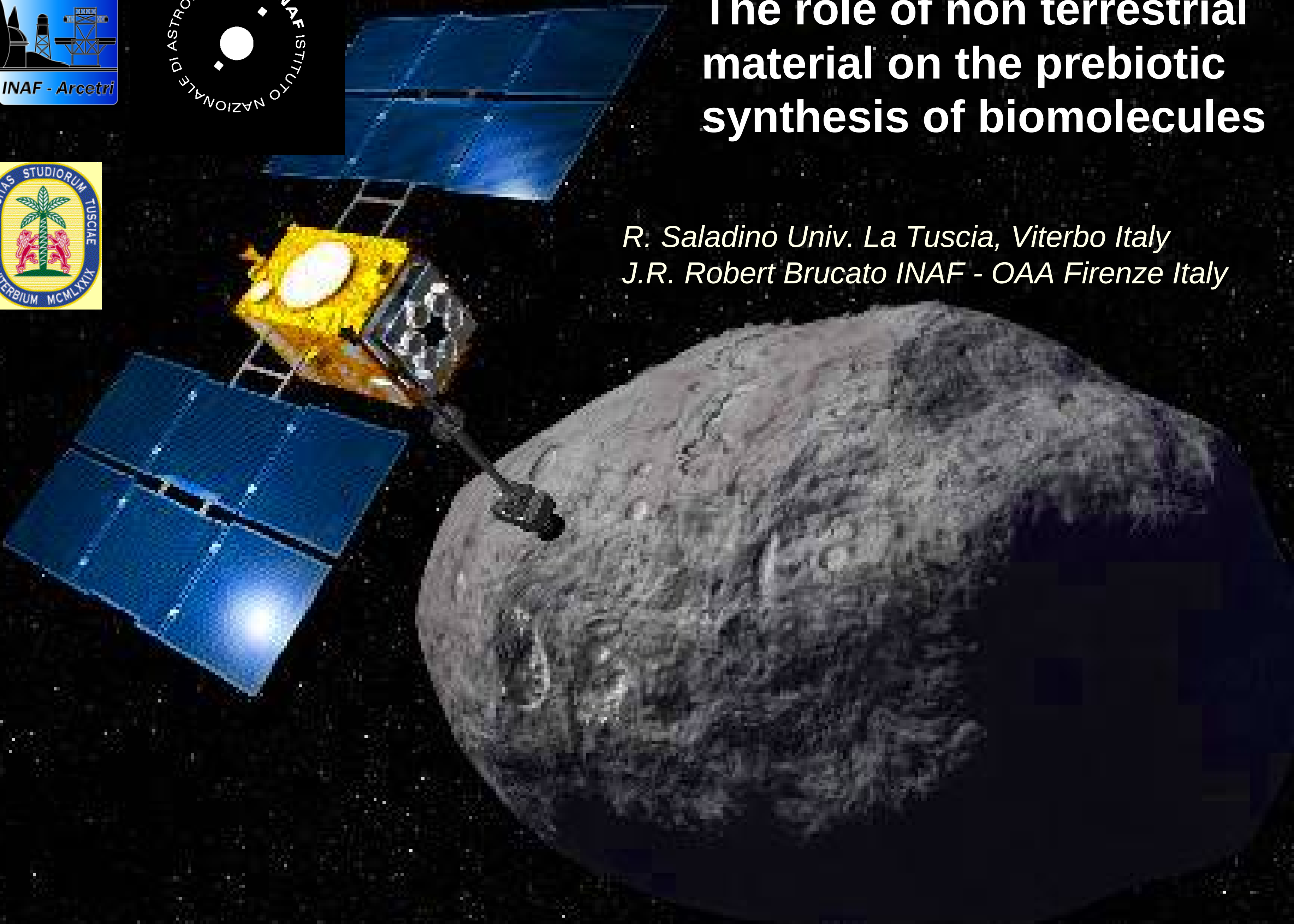
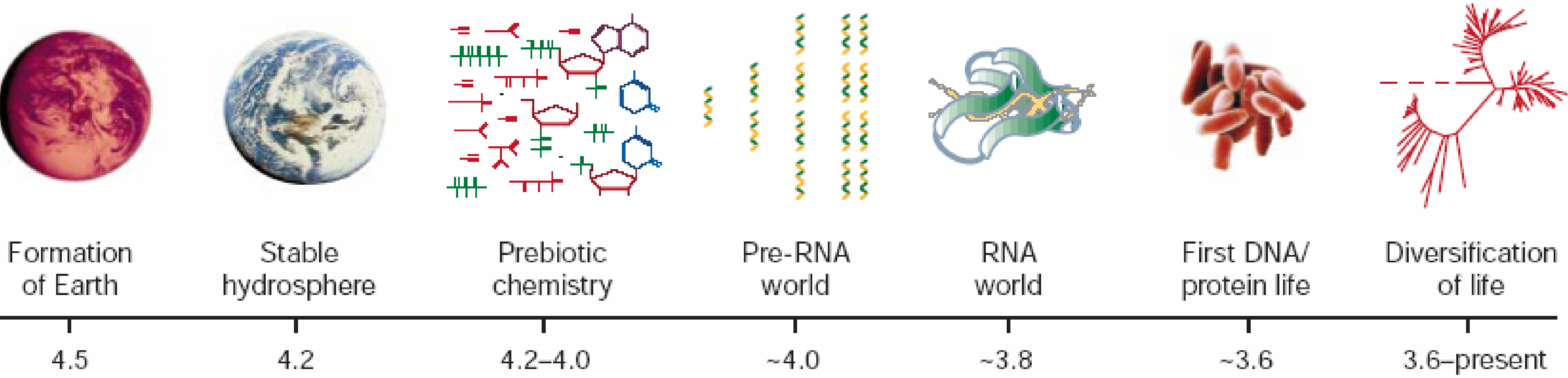


# The RNA World Hypothesis




Joyce, G.F. (2002) *Nature* **418**, 214-221.

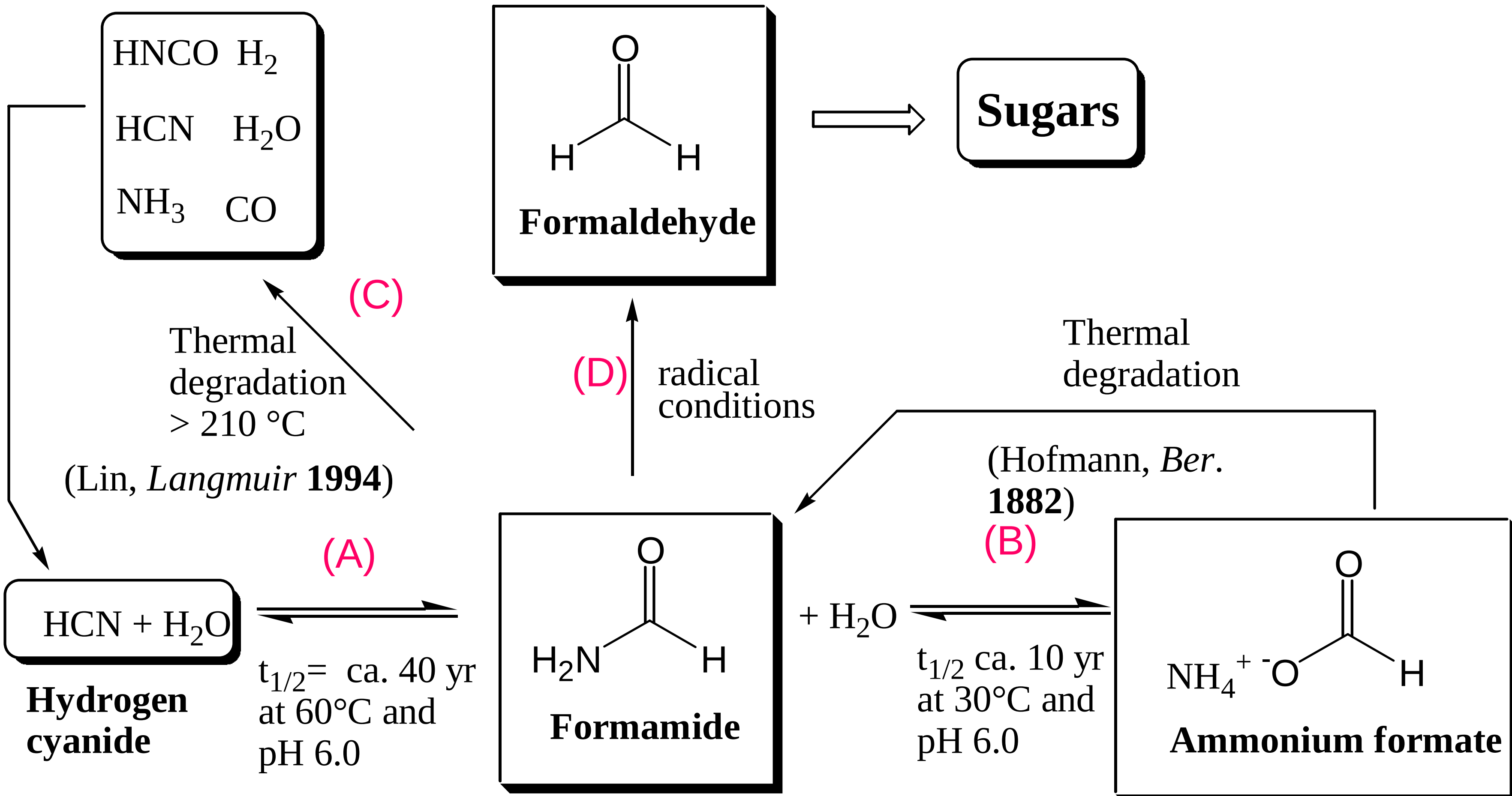
Molecular abundances of ices for comets Hyakutake and Hale-Bopp (in per cent with respect to water ice) as deduced from observations of the gas phase coma (after Bockelée-Morvan *et al* (2000) and Crovisier *et al* (2002)).

| Molecule | Hyakutake | Hale-Bopp |
|---|---|---|
| $H_2O$ | 100 | 100 |
| $H_2O_2$ | <0.04 | — |
| CO | 6–30 | 20 |
| $CO_2$ | <7 | 6 |
| $CH_4$ | 0.7 | 0.6 |
| $C_2H_2$ | ~0.5 | 0.1 |
| $C_2H_6$ | 0.4 | 0.1 |
| $CH_3C_2H$ | — | <0.045 |
| $CH_3OH$ | 2 | 2.4 |
| $H_2CO$ | 0.2–1 | 1.1 |
| HCOOH | — | 0.08 |
| $HCOOCH_3$ | — | 0.08 |
| $CH_3CHO$ | — | 0.02 |
| $H_2CCO$ | — | <0.032 |
| $C_2H_5OH$ | — | <0.05 |
| $CH_3OCH_3$ | — | <0.45 |
| $NH_3$ | 0.5 | 0.7 |
| HCN | 0.1 | 0.25 |
| HNCO | 0.07 | 0.06 |
| HNC | 0.01 | 0.04 |
| $CH_3CN$ | 0.01 | 0.02 |
| $CH_3CN$ | 0.01 | 0.02 |
| $HC_3N$ | — | 0.02 |
| $NH_2CHO$ | — | 0.01 |
| Glycine | — | <0.5 |
| $CH_2NH$ | — | <0.032 |
| $HC_5N$ | — | <0.003 |
| $H_2S$ | 0.8 | 1.5 |
| OCS | 0.1 | 0.3 |
| SO | — | 0.2–0.8 |
| $CS_2$ | 0.1 | 0.2 |
| $SO_2$ | — | 0.1 |
| $H_2CS$ | — | 0.02 |
| $S_2$ | 0.005 | — |
| NaCl | — | <0.0008 |
| NaOH | — | <0.0003 |

—[a]

Millar, 2003

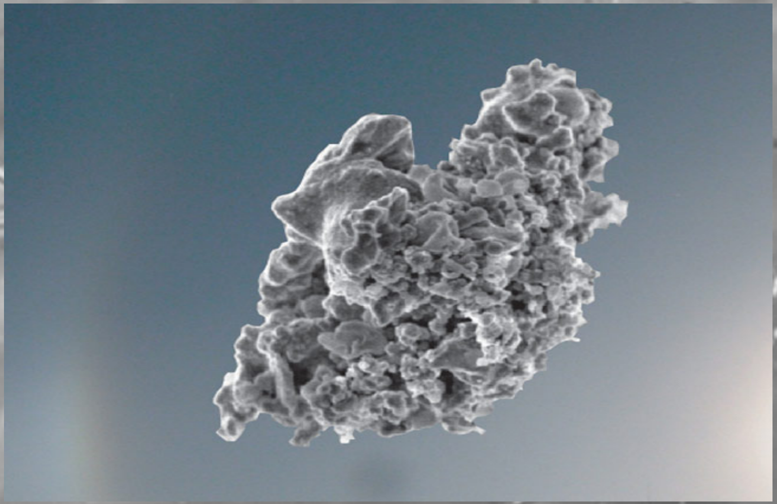
# Elemental Formamide Chemistry



## *The role of minerals and metal oxides on prebiotic processes. A general overview*

- Minerals can accumulate the prebiotic precursors (concentration effect)
- Minerals can act can act as catalytic environments, reducing the activation energy for the formation of products
- Minerals can tune the selectivity of prebiotic syntheses
- Minerals may act as a template
- Minerals are benignin environments to preserve newly formed biomolecules from degradation

# ASTEROIDS - COMETS
# METEORITES - IDPs

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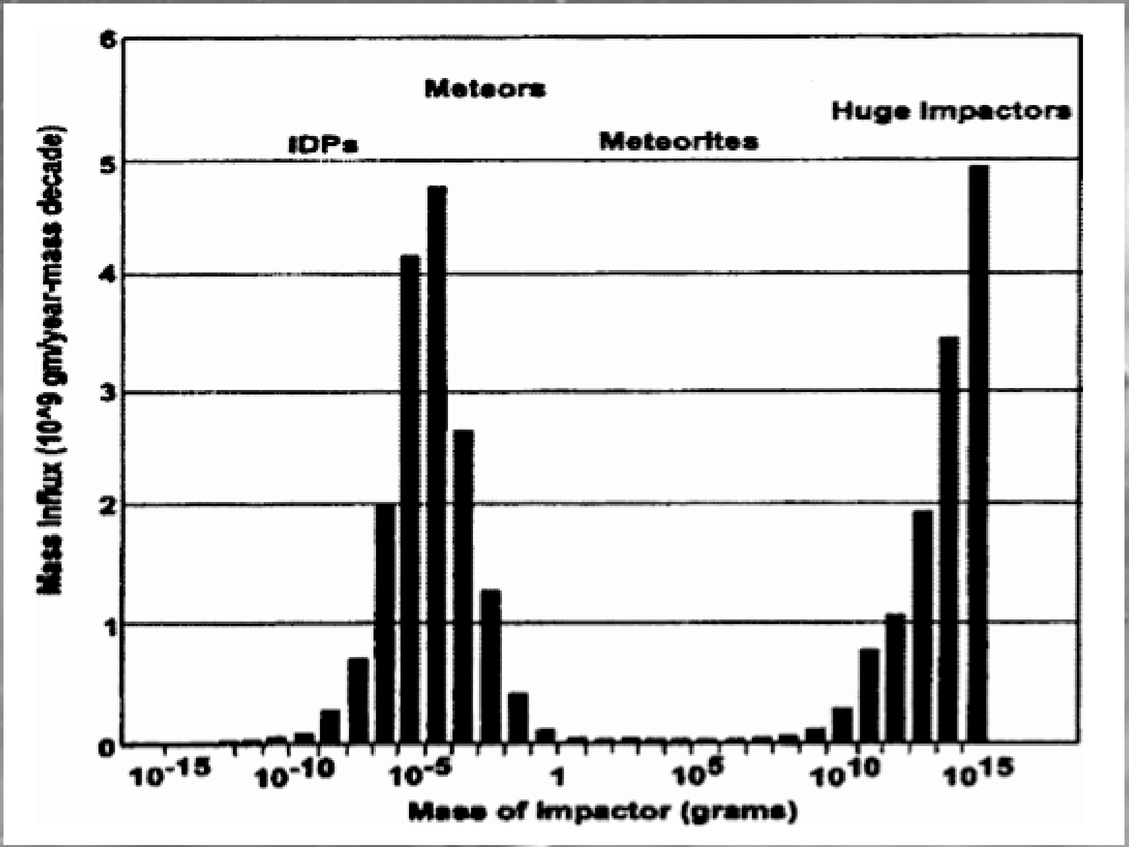
ET matter, ranging from sub-micron size dust up to objects tens of meters in size, accretes onto the Earth each year.




Impact pits on the Long Duration Exposure Facility satellite indicate that, in the present era, about 30,000 tons/year of dust accretes onto the Earth (Love and Brownlee, 1993). This dust decelerates by interacting with the Earth atmosphere. Most of the larger dust particles (>100 μm) vaporize, producing meteor trails in the atmosphere. The smaller particles ( 5–35 μm) have a large enough surface area to mass ratio that they radiate away heat rapidly. Many of them survive atmospheric deceleration without being severely heated (Brownlee, 1985). These particles, called interplanetary dust particles (IDPs), decelerate at an altitude of 90 km then settle gently on the Earth's surface (Flynn et al. 2004).

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# Meteorites and IDPs-A natural laboratory containing organic molecules that are the product of ancient chemical evolution

<u>Soluble extractable compounds</u>

*Aminoacids*

*Aromatic hydrocarbons*

*Aliphatic hydrocarbons*

*Heterocycles*

*Sulfonic and phosponic acids*

*Amines and Amides*

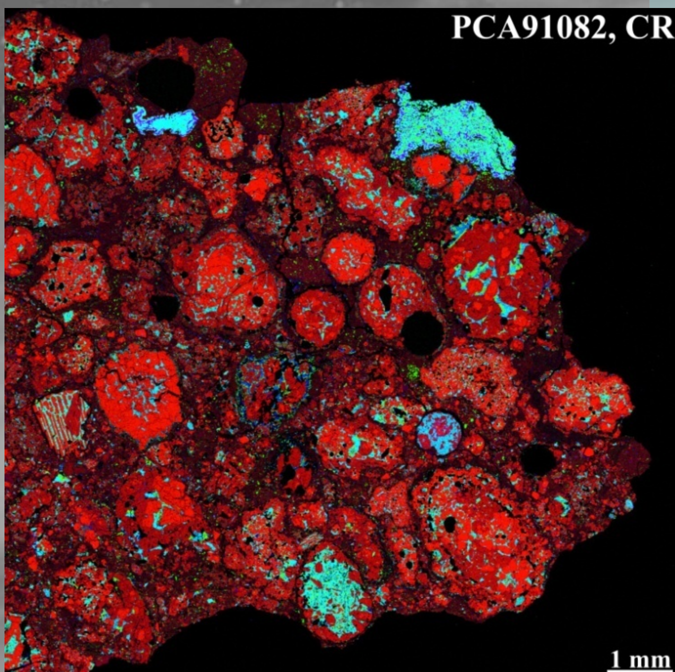
*Sugars , Alcohols, Aldehydes*

*Ketons*

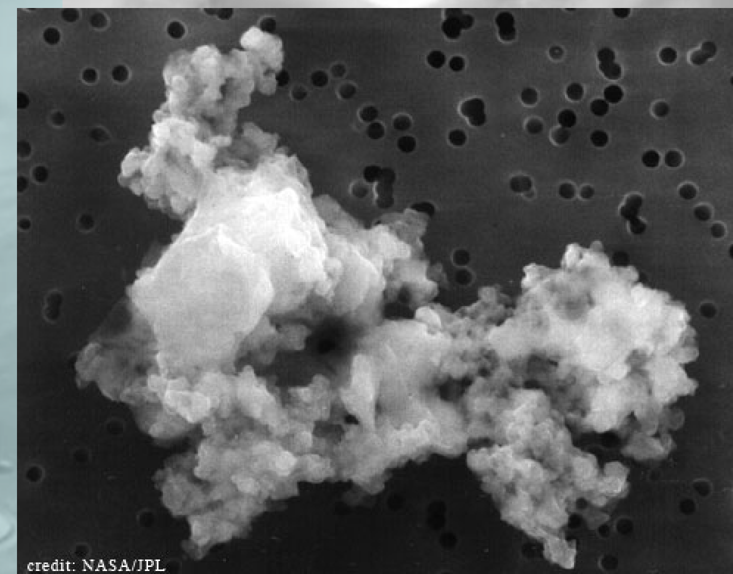
<u>Unsoluble macromolecule compounds</u>

The elemental composition of the Murchison macromolecule has been determined as $C_{100}H_{71}N_3O_{12}S_2$ based on elemental analysis (Hayatsu et al., 1977) and revised to $C_{100}H_{48}N_{1.8}O_{12}S_2$ based on pyrolytic release studies (Zinner, 1988).

# Types of minerals in Meteorites and IDPs




- Silicates
- Hydrated Silicates
- Phosphates
- Oxides
- Metals
- Carbides
- Nitrides
- Sulfides

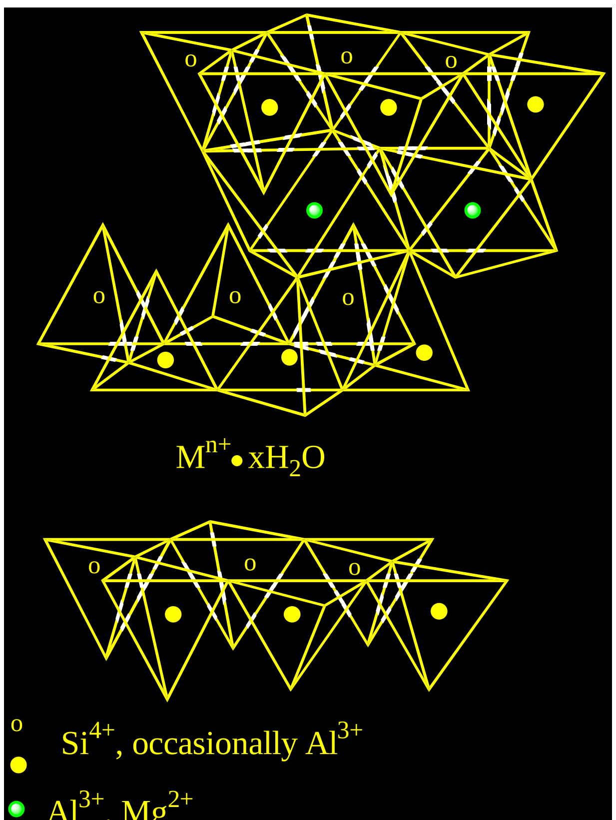


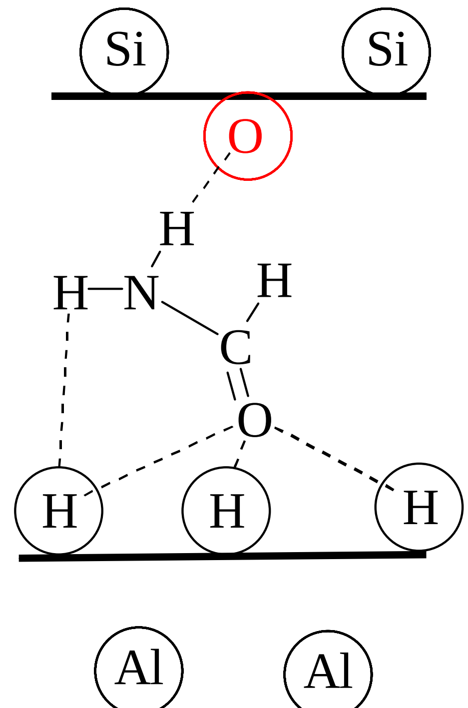

David Hardy

ChemBioChem 5 (2004) 1-9

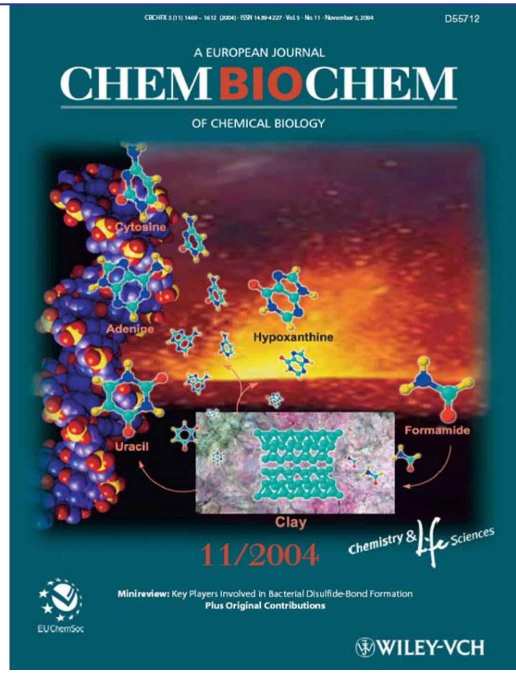
# Synthesis and Degradation of of Nucleobases and Nucleic Acids by Formamide in the Presence of Montmorillonites

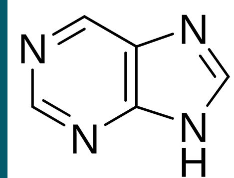
Raffaele Saladino,[a,*] Claudia Crestini, [b] Umberto Ciambecchini,[a] Fabiana Ciciriello,[c] Giovanna Costanzo,[c] and Ernesto Di Mauro [c, d]

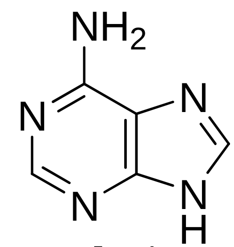


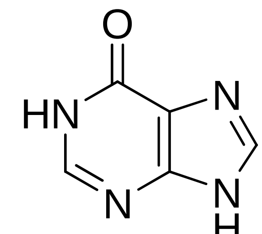



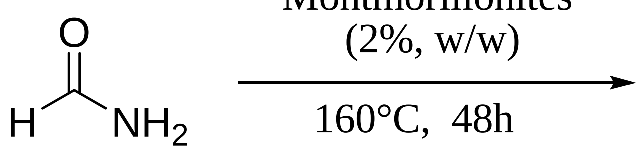

Bu, Y.; Lin, M.C. *Langmuir* **1994**

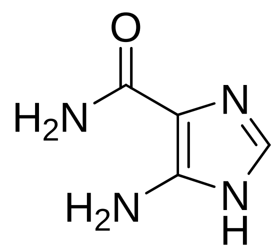


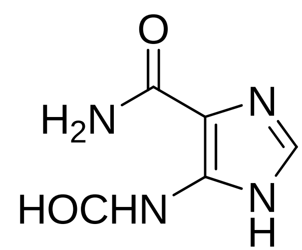


purine

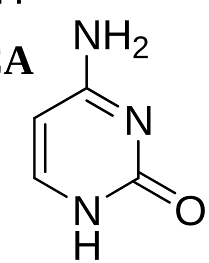

adenine

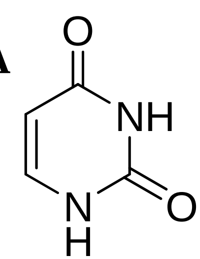

hypoxanthine





AICA

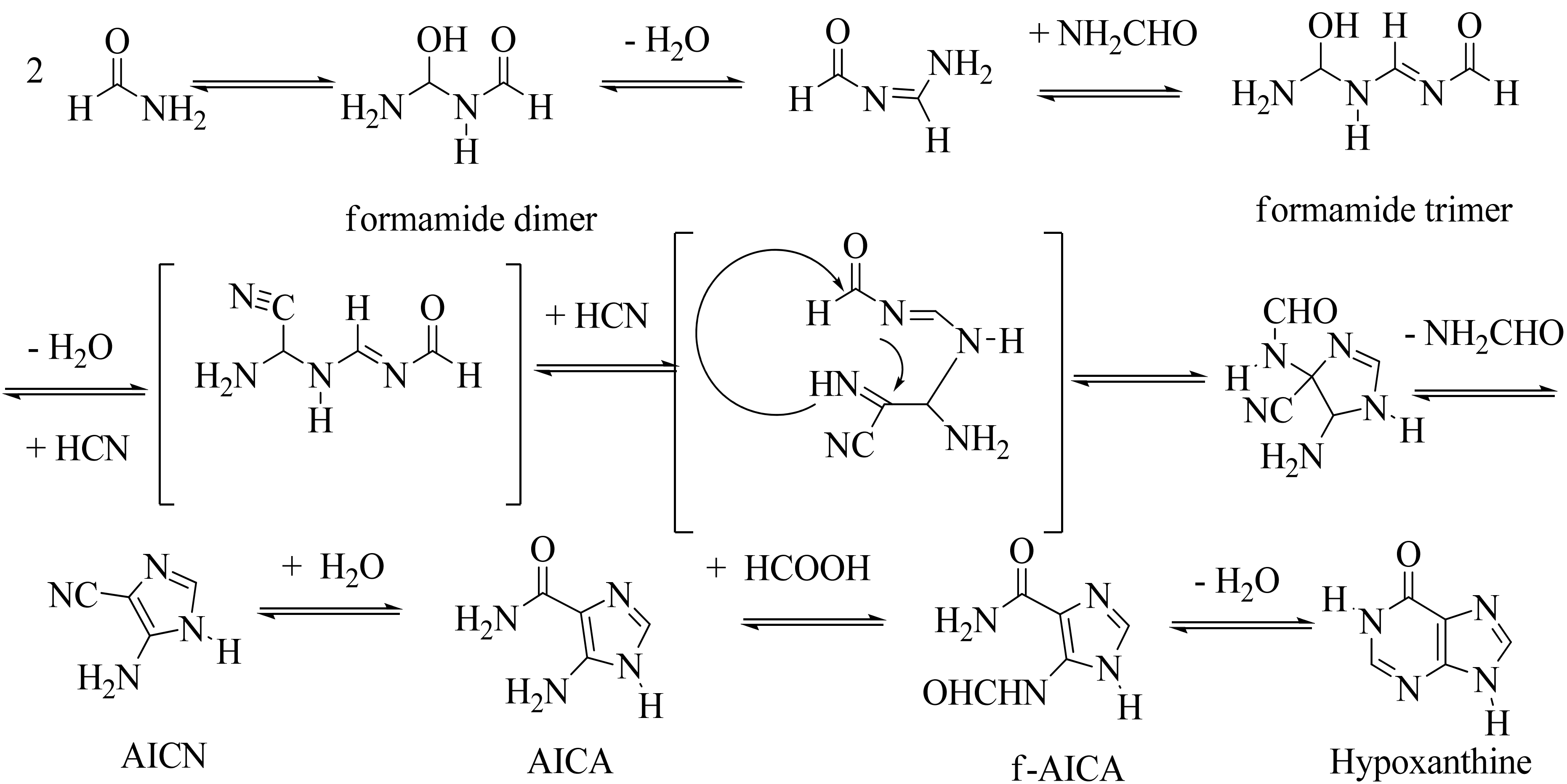

fAICA


cytosine


uracil

**AICA**: **A**mino **I**midazole **C**arboxy**A**mide
**fAICA**: **f**ormyl **A**mino **I**midazole **C**arboxy**A**mide
**fpurine**: N(9)-formyl purine

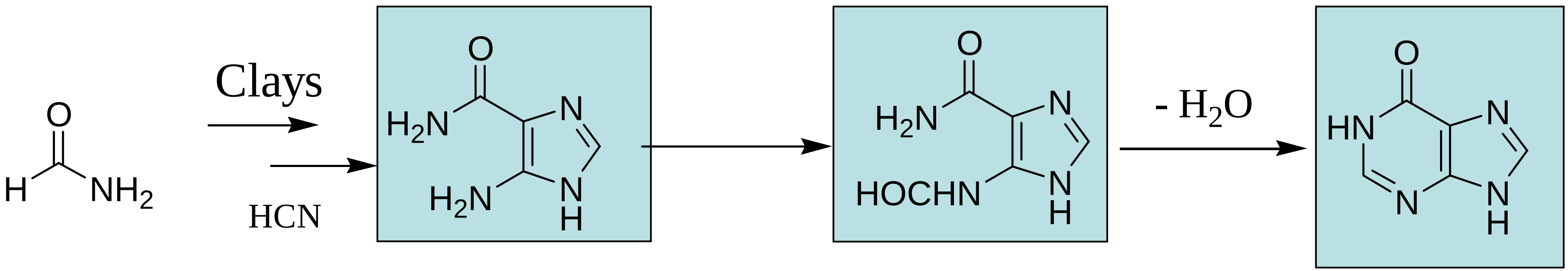
# Analyzing the reaction pathway. The"*route of the pyrimidine ring*"



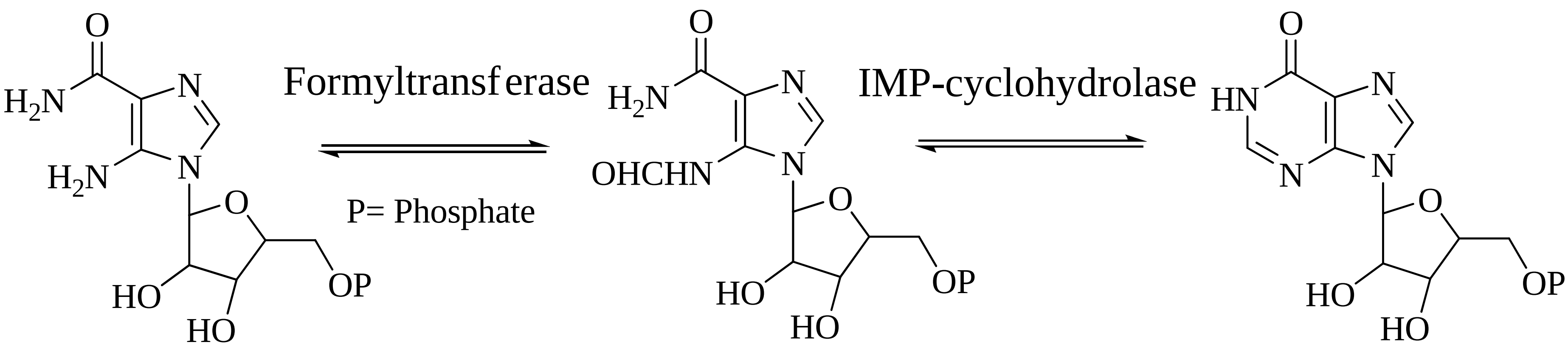
# *A novel example of Chemiomimetic pathway*

*"certain biosynthetic pathways can be considered as chemiomimetic of early prebiotic chemistry"*

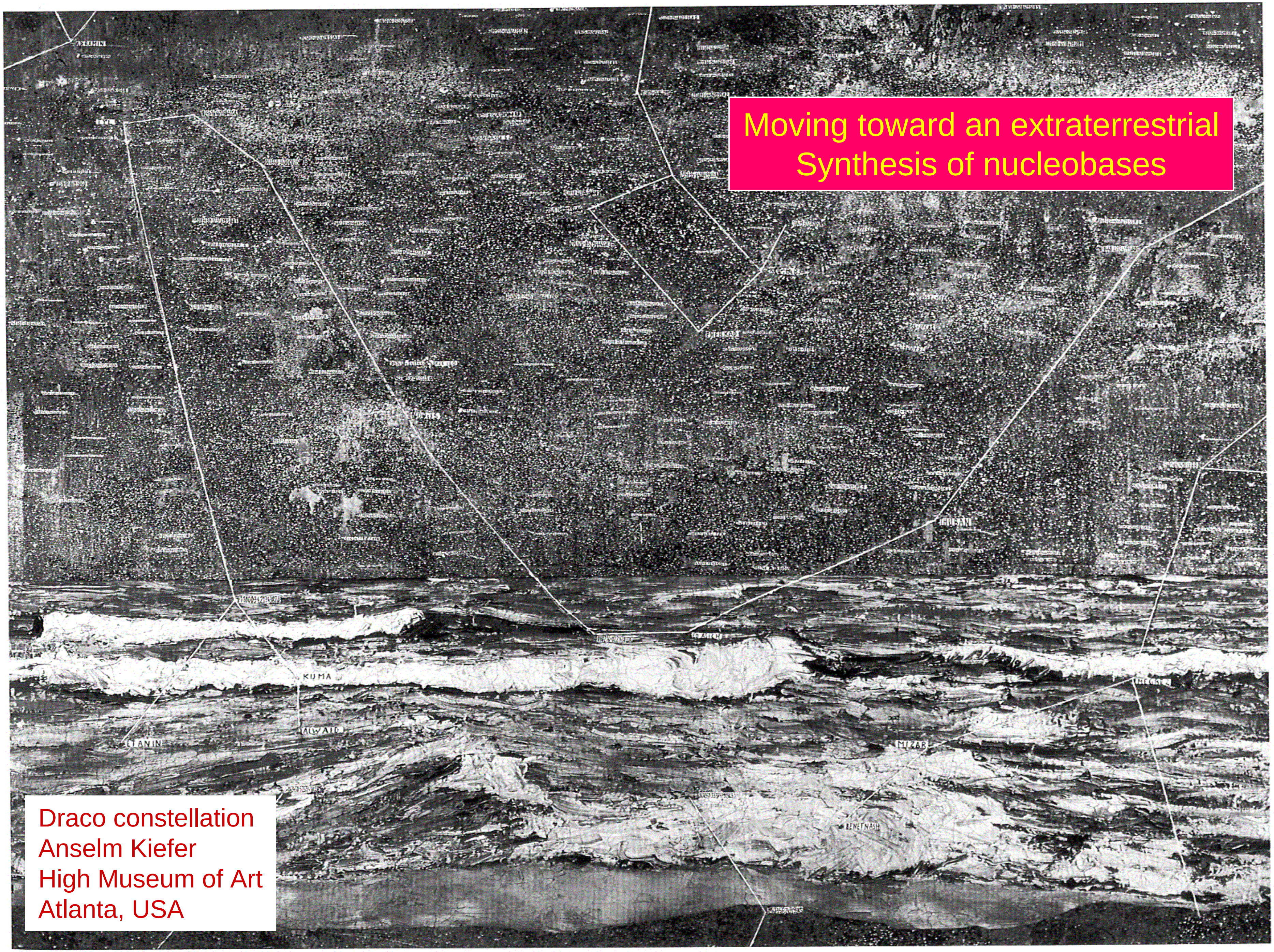
Eschenmoser, A.; Loewenthal, E. *Chem. Soc. Rev.* **1992**, 1.




In exant cell !



# Moving toward an extraterrestrial Synthesis of nucleobases



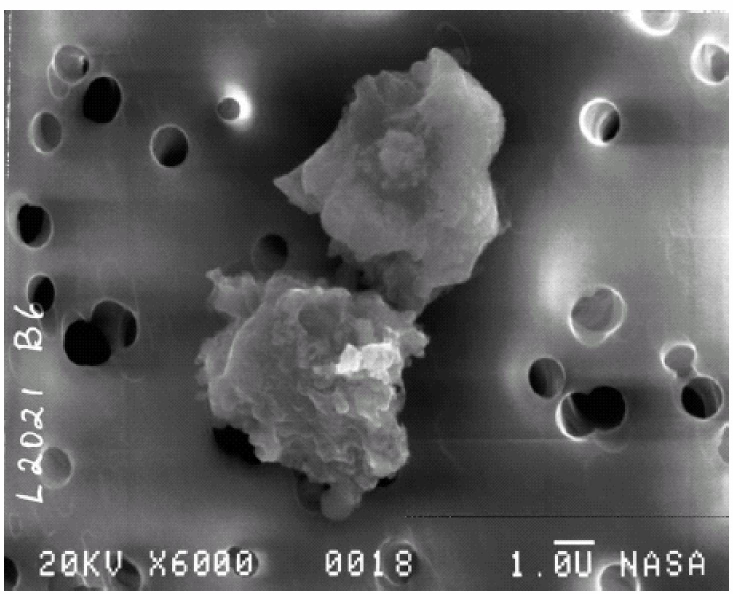
Draco constellation
Anselm Kiefer
High Museum of Art
Atlanta, USA

ChemBioChem 6 (2005) 1368-1374

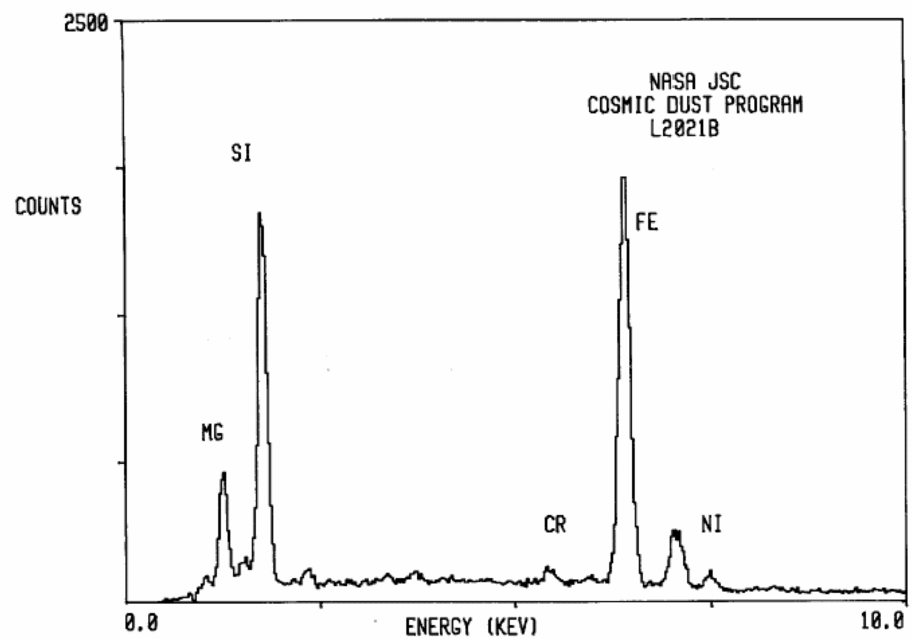
# Synthesis and Degradation of Nucleic Acid Components by Formamide and Cosmic Dust Analogues

Raffaele Saladino,[a,*] Claudia Crestini, [b] Veronica Neri,[a] John R. Brucato,[d] Luigi Colangeli,[d] Fabiana Ciciriello,[c] Giovanna Costanzo,[c] and Ernesto Di Mauro [c, d]

**L2021B6**




97E00340



# Cosmic dust analogues preparation

$SiO_2$, MgO, FeO2 → Laser Ablation

1) $Fe_2SiO_4$* (Fayalite)

2) $Mg_{0.5}Fe_{1.5}SiO_4$ *

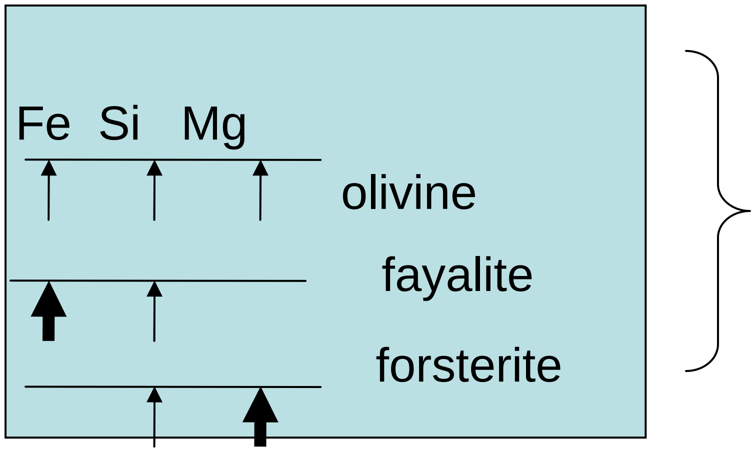
3) $MgFeSiO_4$ * (Olivine)

4) $Mg_{1.5}Fe_{0.5}$ $SiO_4$ *

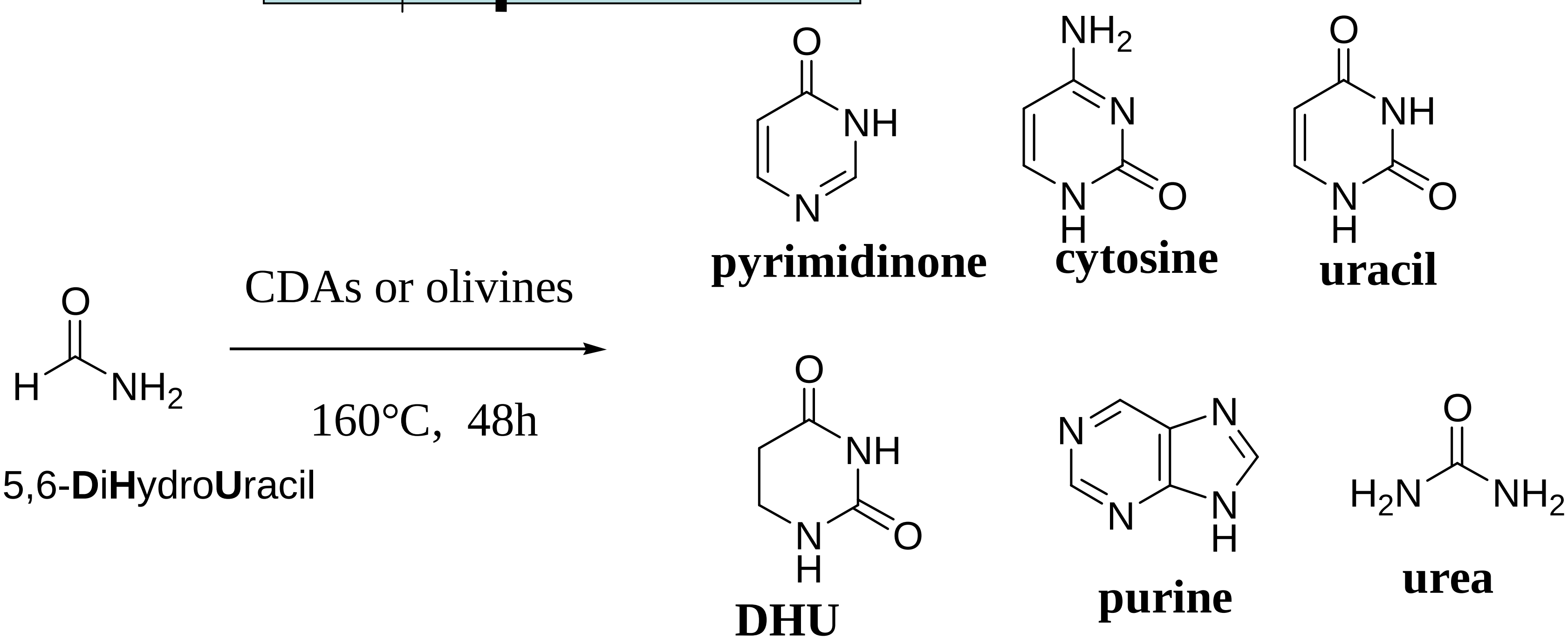
5) $Mg_2SiO_4$ * (Fosferite)

Cosmic dust analogue olivines $(Mg,Fe)_2SiO_4$ are synthesized by laser ablation technique (Nd-YAG $10^8$ $Wcm^{-2}$). Oxide pellets of MgO, $FeO_2$, $SiO_2$ are used as laser target vaporized in 10 mbar atmosphere of $O_2$.

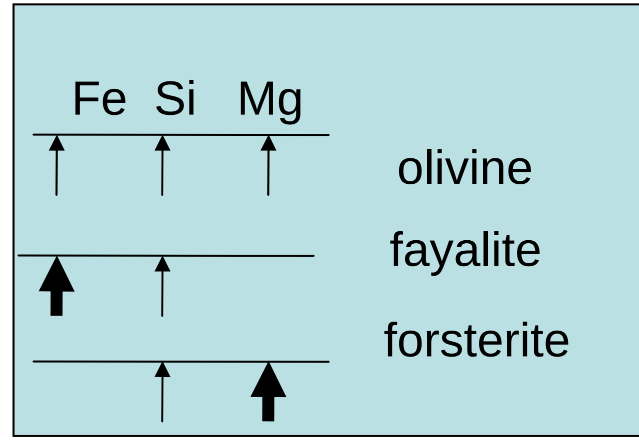
Brucato, J. R. et al in The Astronomy and Astrophysics Review, Volume 11, Issue 2-3, pp. 97-152 (**2003**)



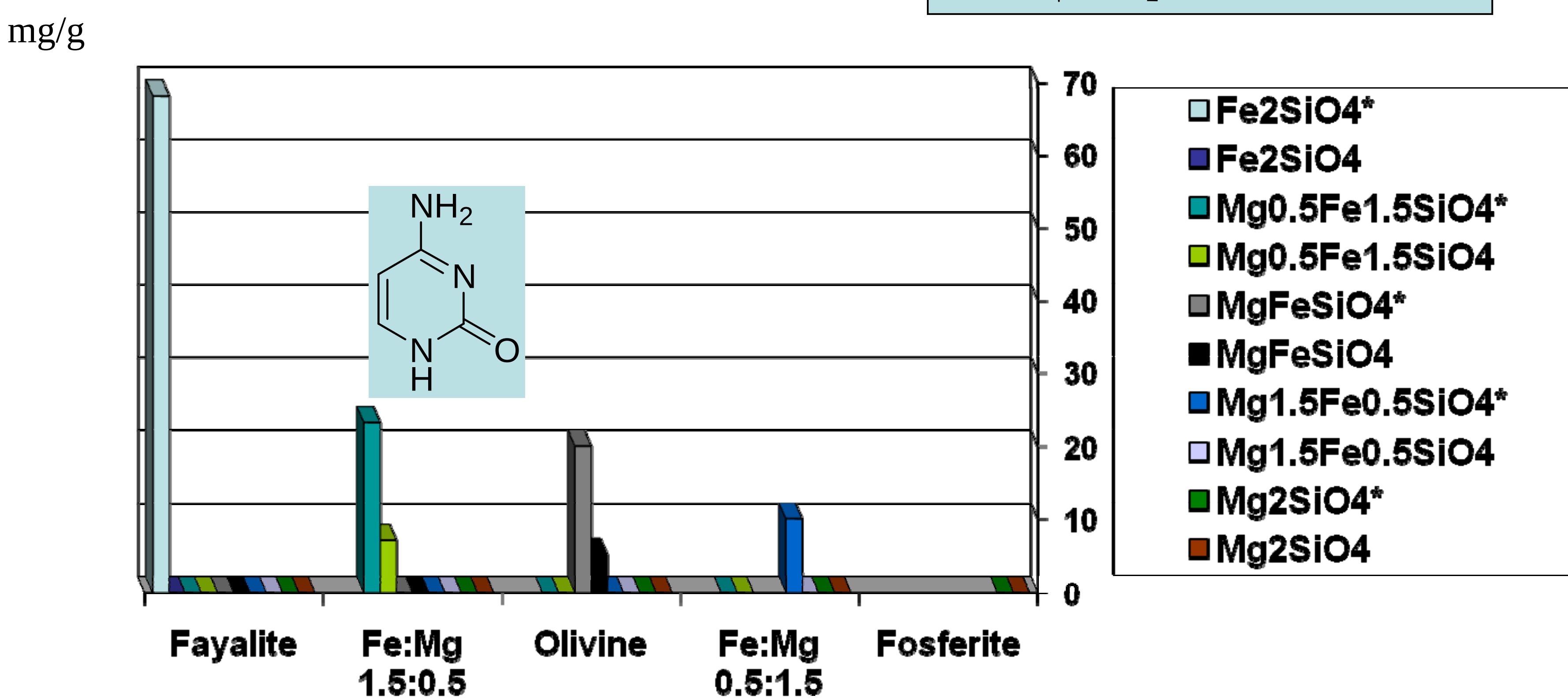

CDAs qualitative composition



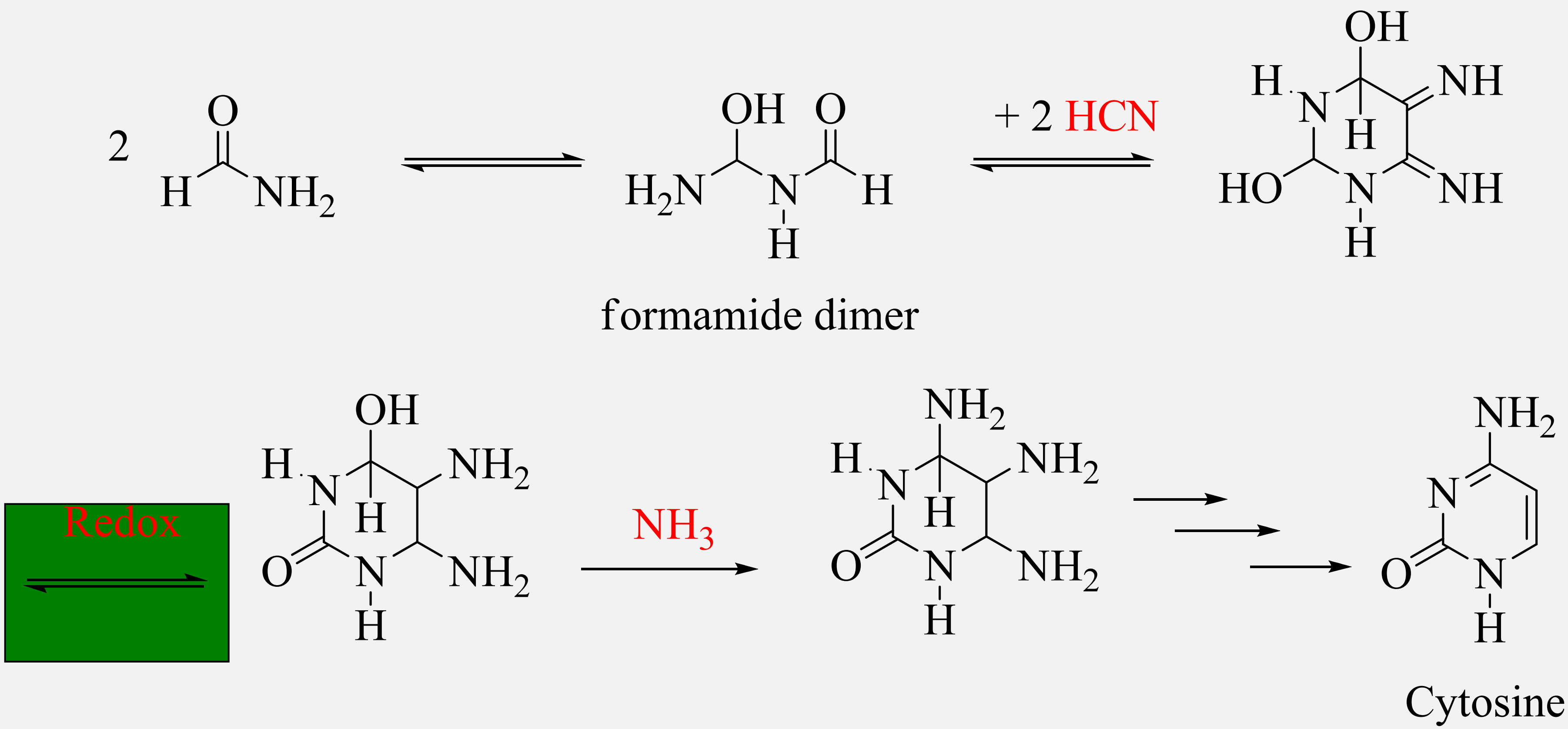

**DHU**:5,6-**D**i**H**ydro**U**racil



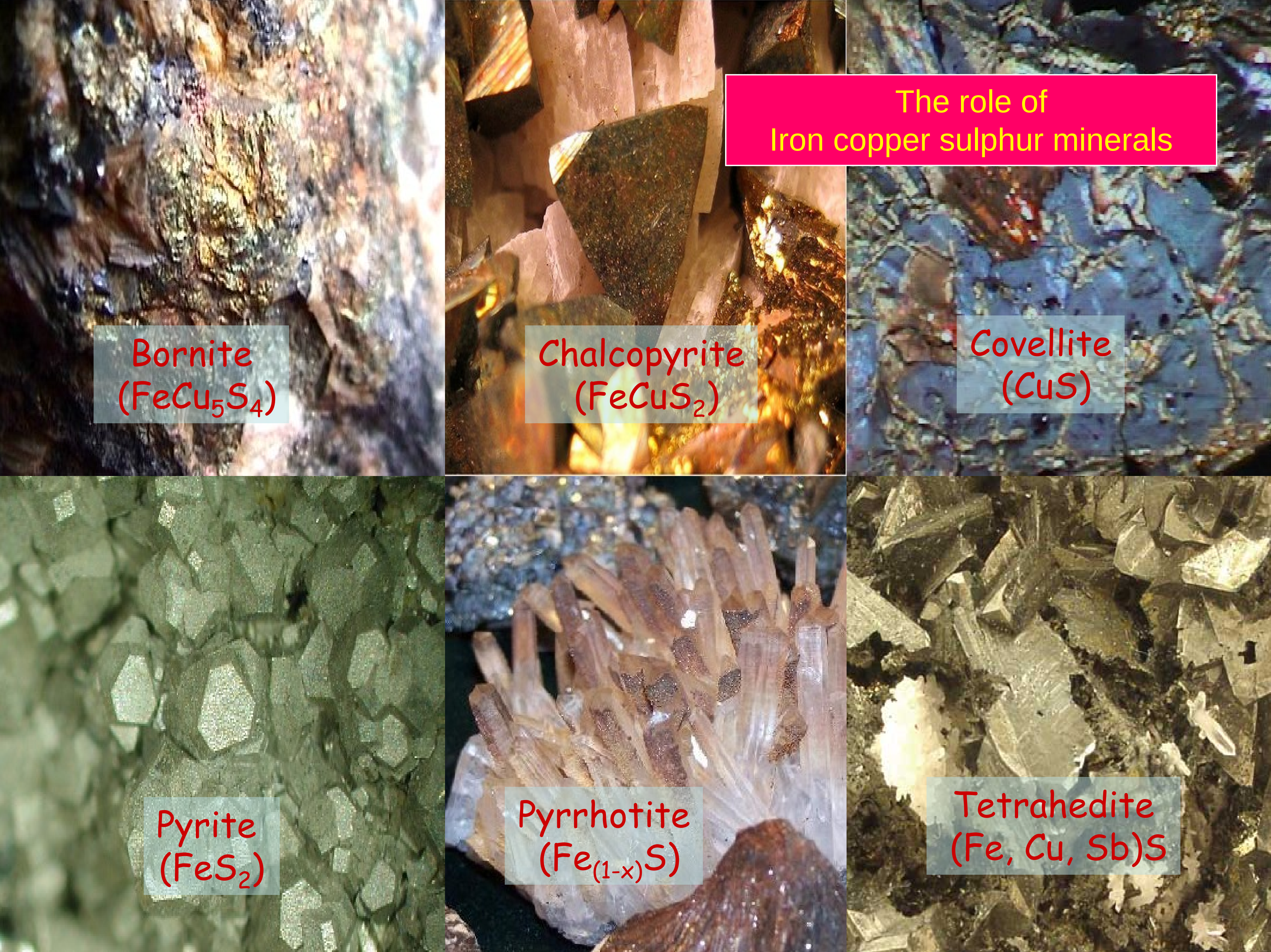

Yield defined as mg of product per gram of formamide.



# Analyzing the reaction mechanism. $^{13}C$-/$^{15}N$-NMR Experiments"*route of the pyrimidine ring*"



# The role of Iron copper sulphur minerals

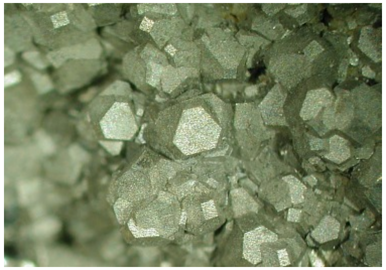


# Chemoautotrophic origin. The Wachtershauser model

$CO$ ; $CO_2$

a) $FeS + H_2S \longrightarrow FeS_2 + 2\,H^+ + 2e^-$

Pyrrothite

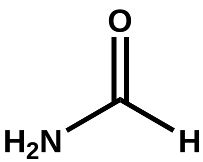


Pyrite

Reducing power

b) $CO_2 + 3\,FeS + 4\,H_2S \longrightarrow CH_3SH + 3\,FeS_2 + 2\,H_2O$

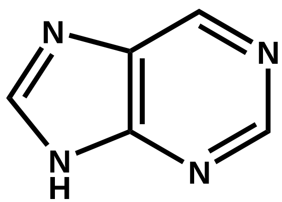
c) $CH_3SH + CO \xrightarrow{FeS/NiS} CH_3COSH$



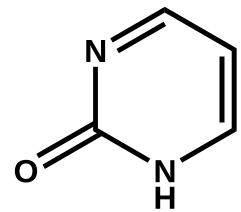
(1)

(Fe, Cu, S) mineral

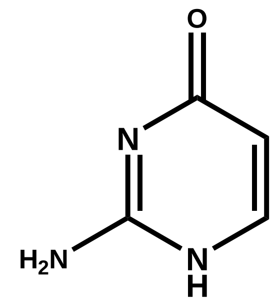
160°C



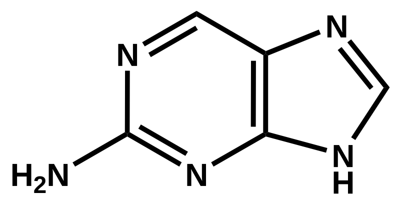
(2)



(3)



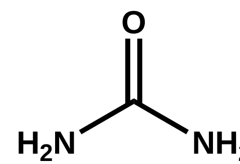
(4)



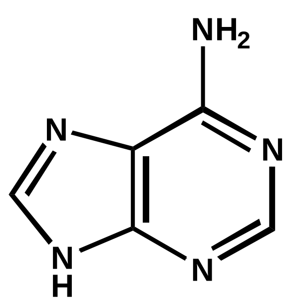
(6)

$HN{=}C{=}NH$

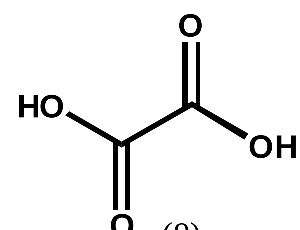
(7)



(8)



(5)



(9)

(Fe, Cu, S) mineral:

Pyrrhotite (Fe(1-x)S)

Pyrite ($FeS_2$)

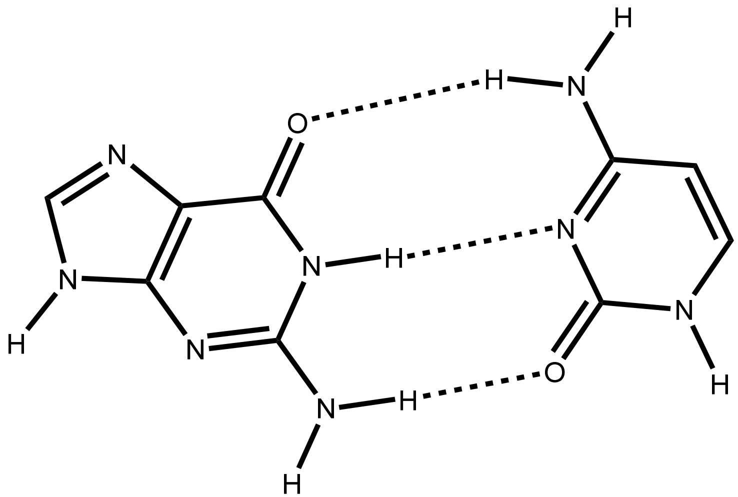
Chalcopyrite ($FeCuS_2$)

Bornite ($FeCu_5S_4$)

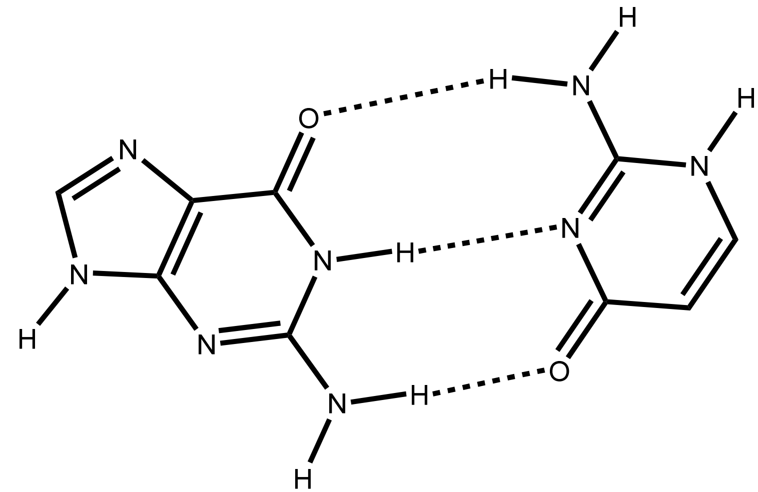
Covellite (CuS)

Tetrahedite (Fe, Cu, Sb)S

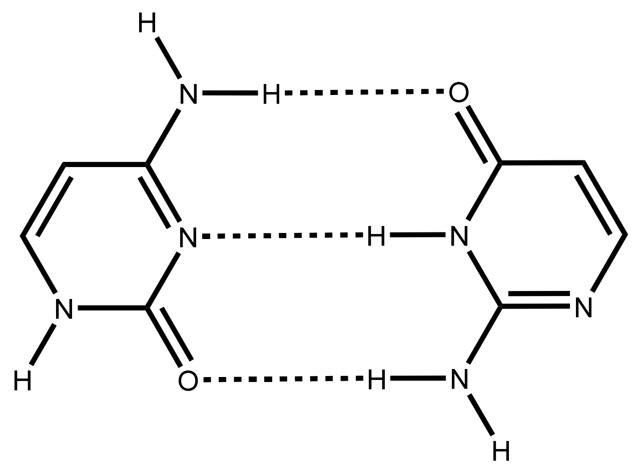
# Interaction between nucleobases



**W-C**



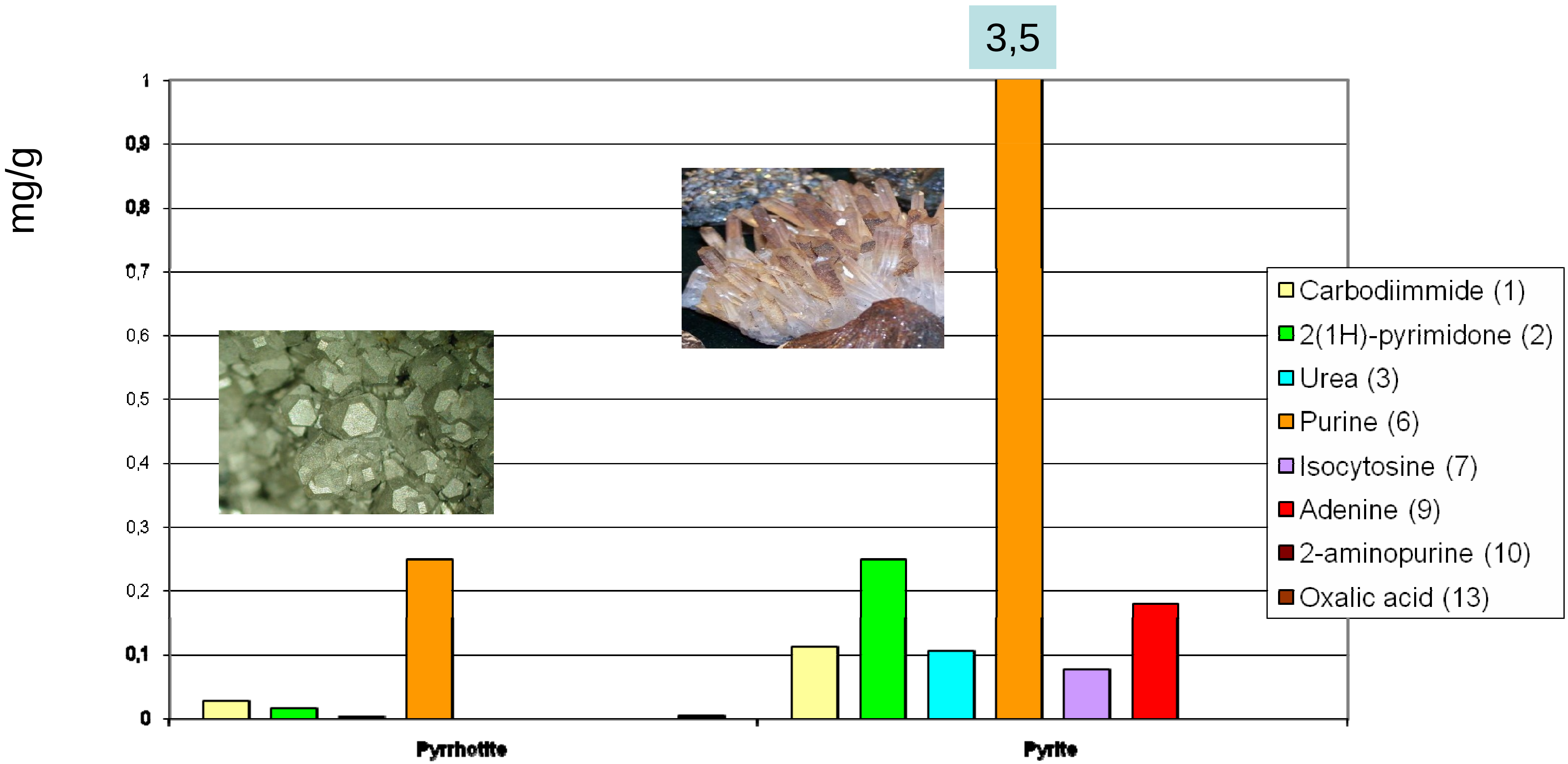
**Reversed W-C**

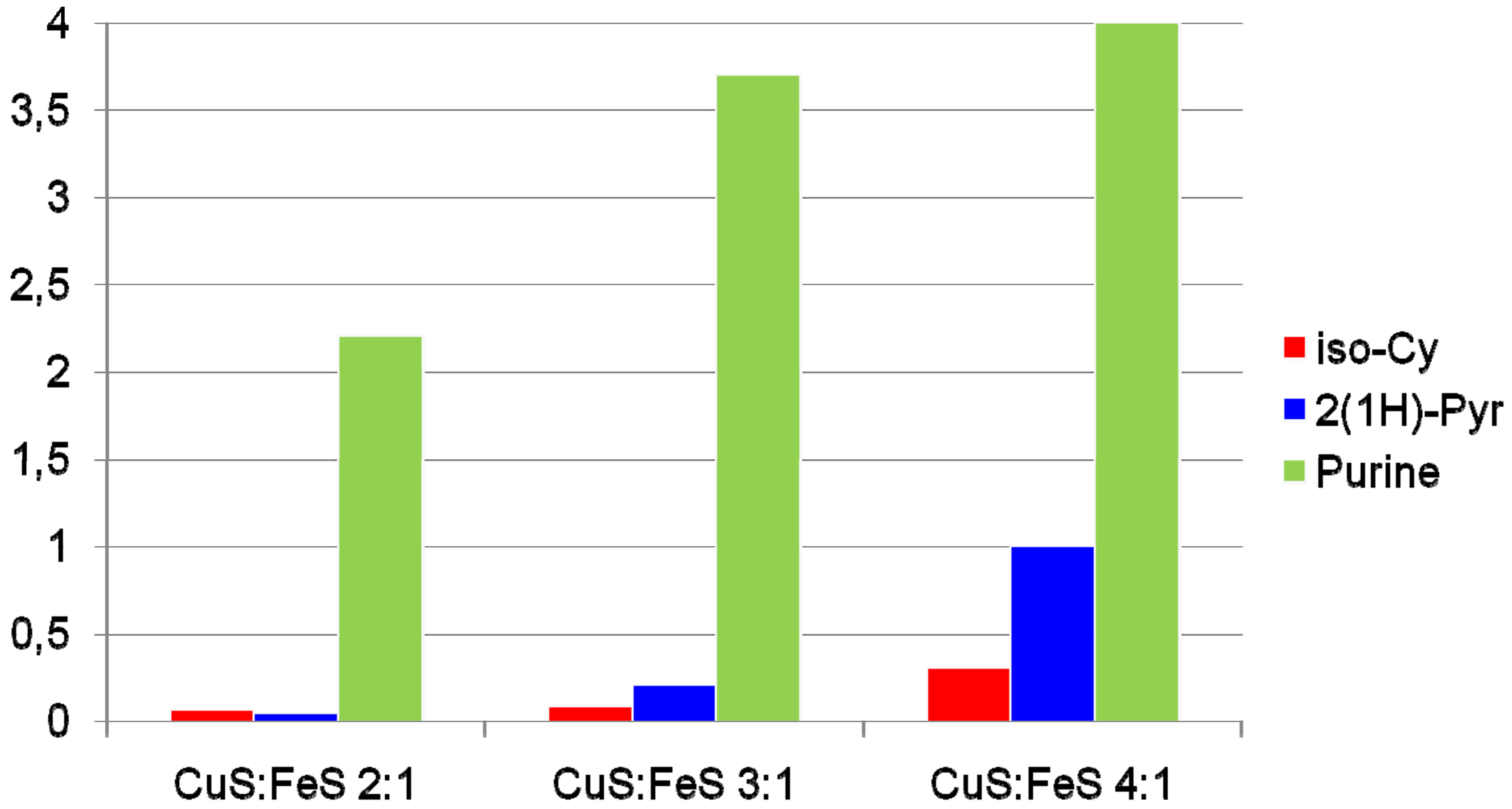


**iCC**

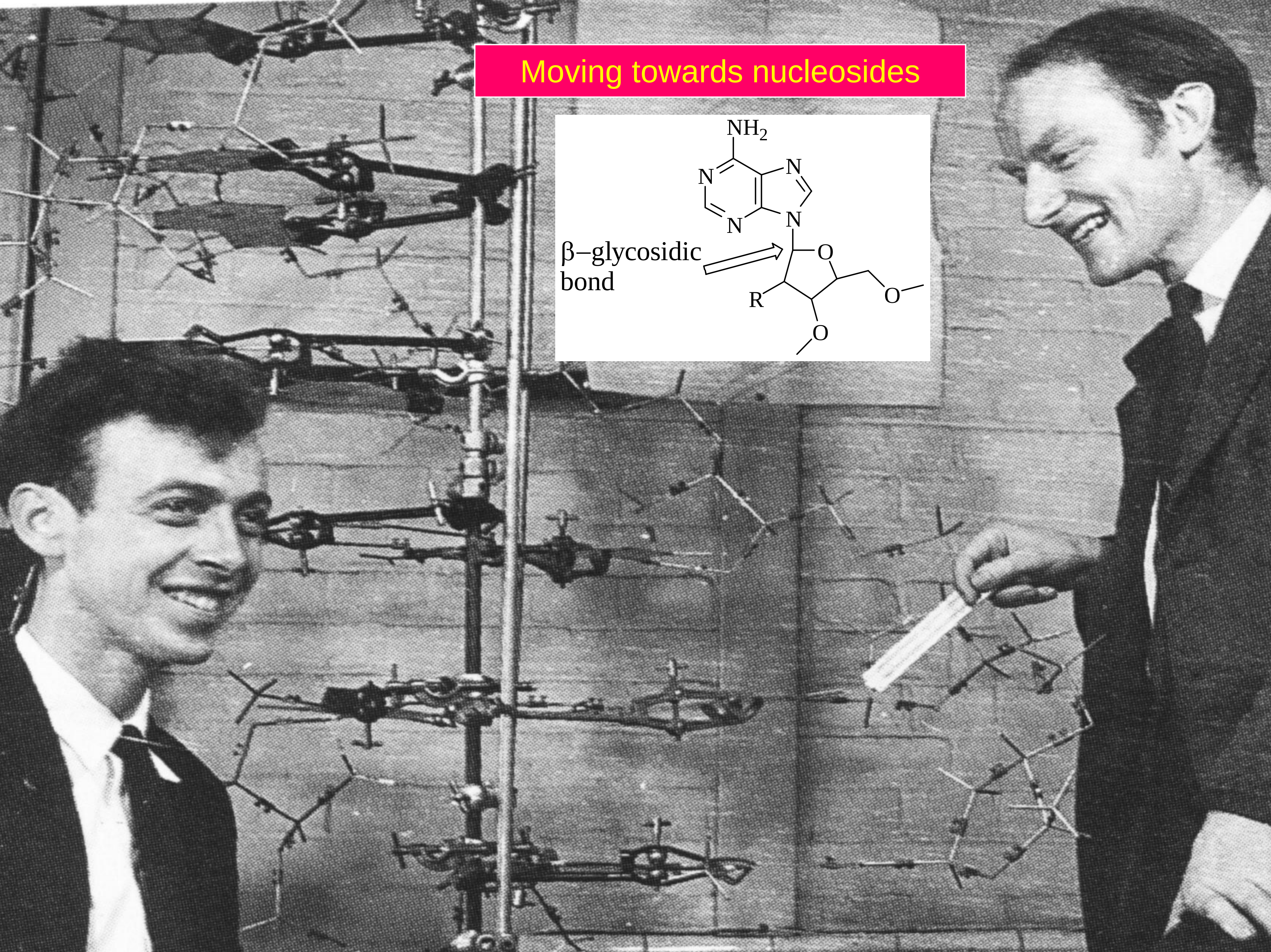
INAF Arcetri, Florence Italy-University of Tuscia, Viterbo, Italy

# Condensation of formamide with Pyrite and Pyrrhotite




4
3,5
3
2,5
2
1,5
1
0,5
0
CuS:FeS 2:1
CuS:FeS 3:1
CuS:FeS 4:1
iso-Cy
2(1H)-Pyr
Purine

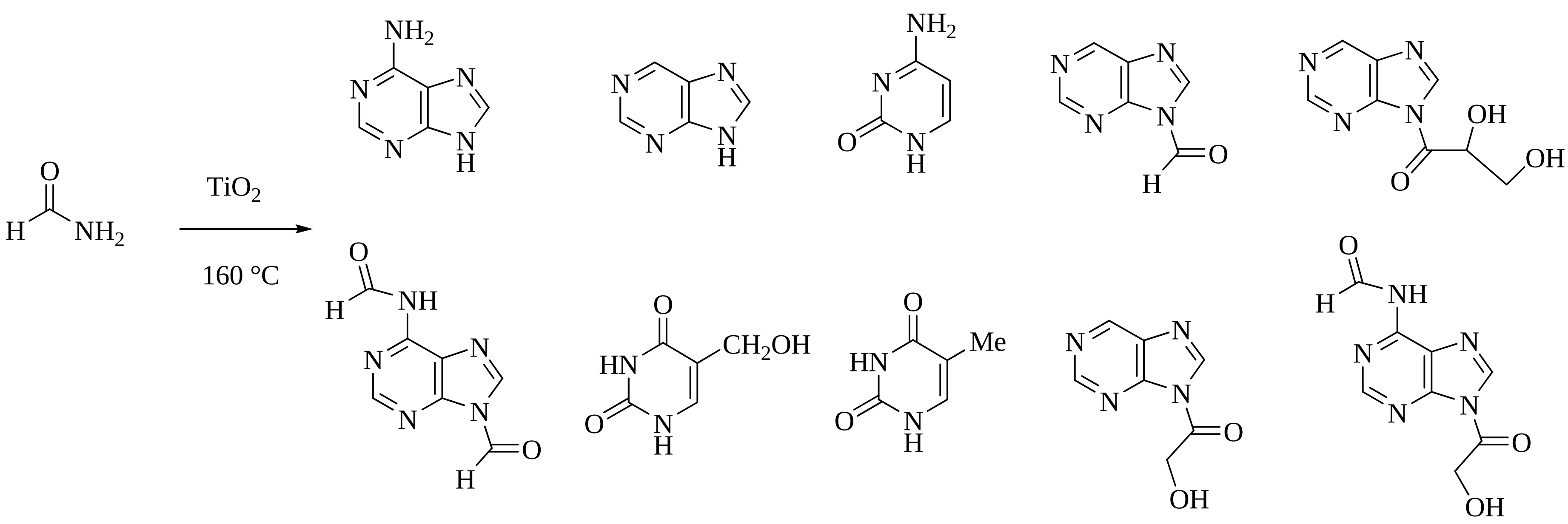
# Moving towards nucleosides



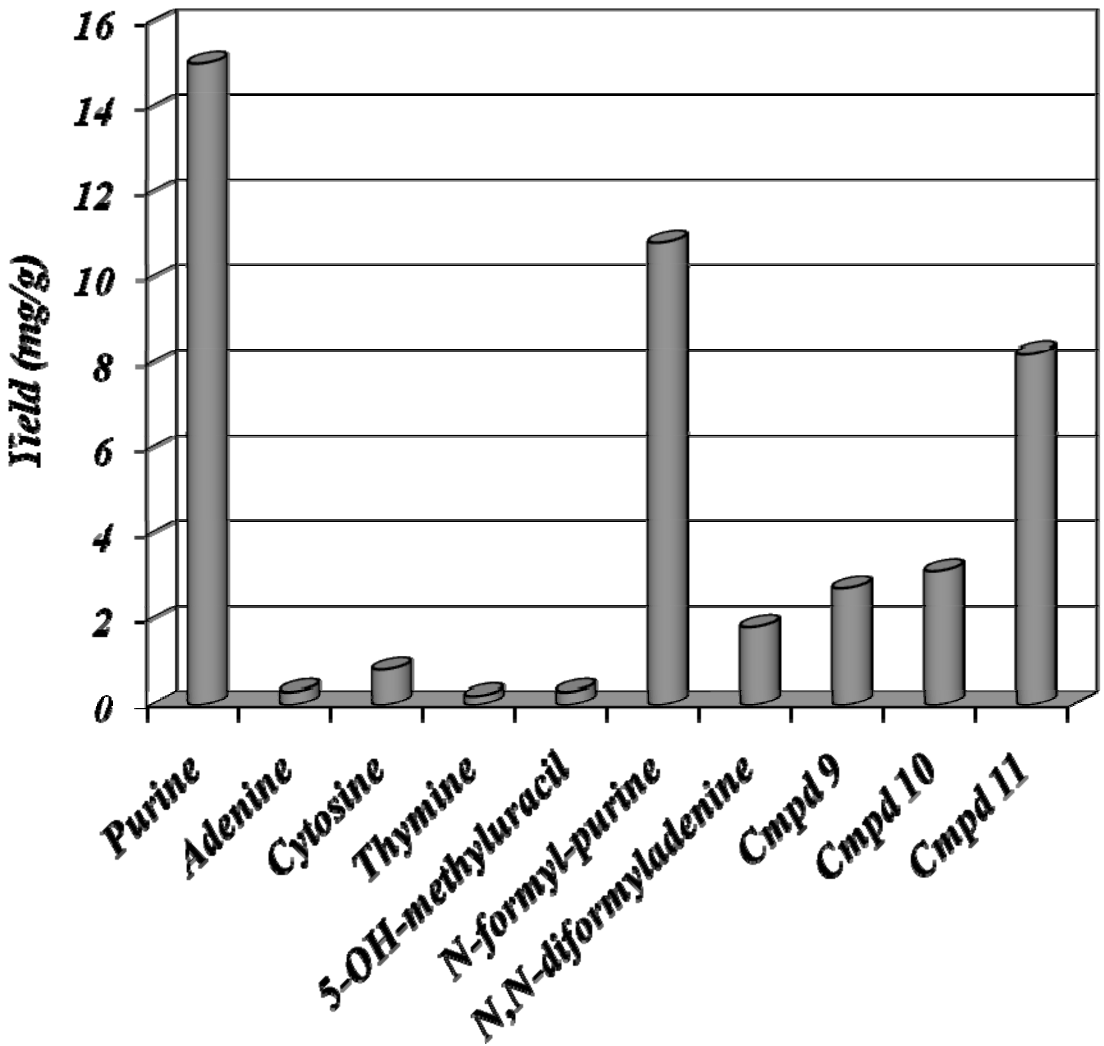
ChemBioChem 4 (2003) 514-521

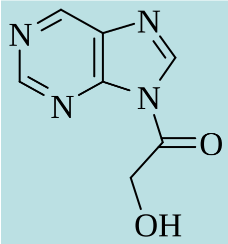
# One-pot TiO2-Catalyzed Synthesis of Nucleic Bases and Acyclonucleosides From Formamide: Implications for the Origin of Life

Raffaele Saladino,[a,*] Claudia Crestini,[b] Umberto Ciambecchini,[a] Rodolfo Negri,[c] Giovanna Costanzo,[c] Ernesto Di Mauro [c,]

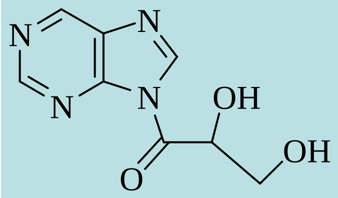


# Nucleosides from formamide

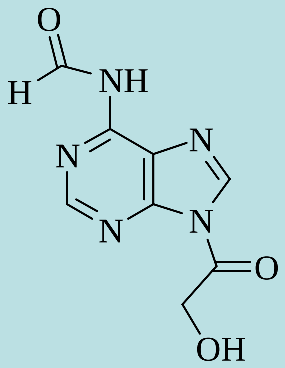


Compd 9

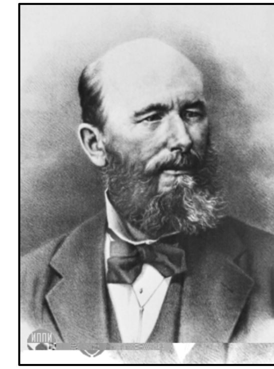


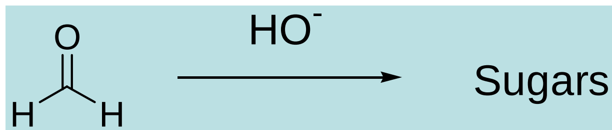
Compd 10

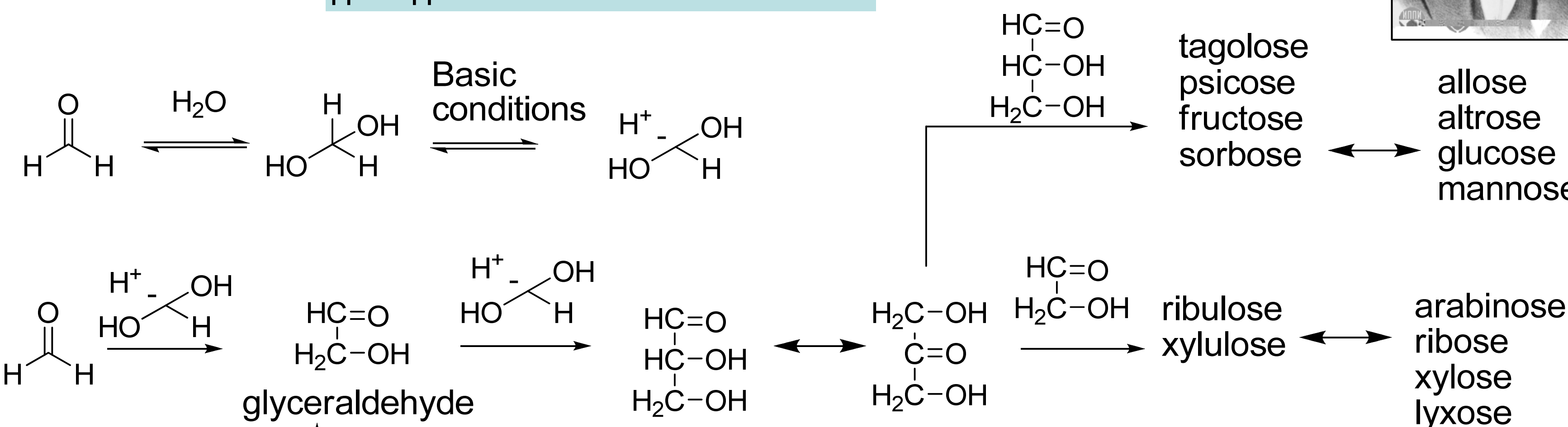


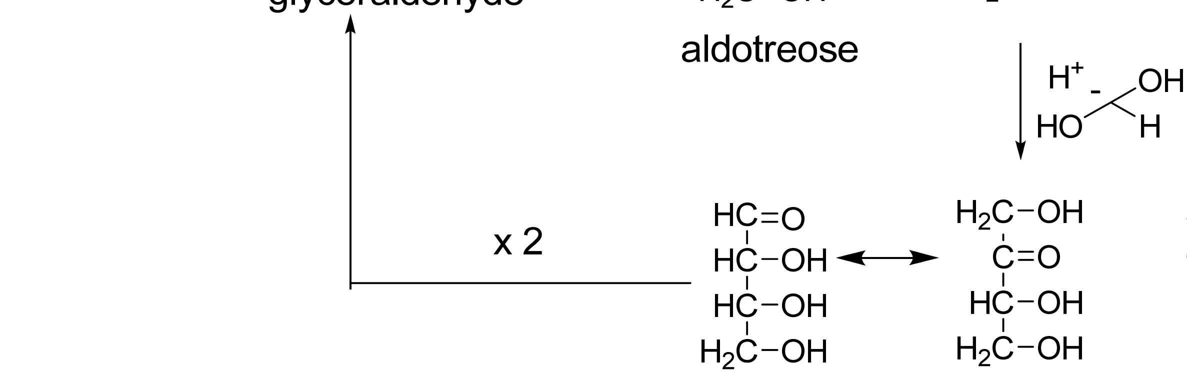
Compd 11

# Sugars synthetic pathway. The formose reaction. Butlerow, 1861.



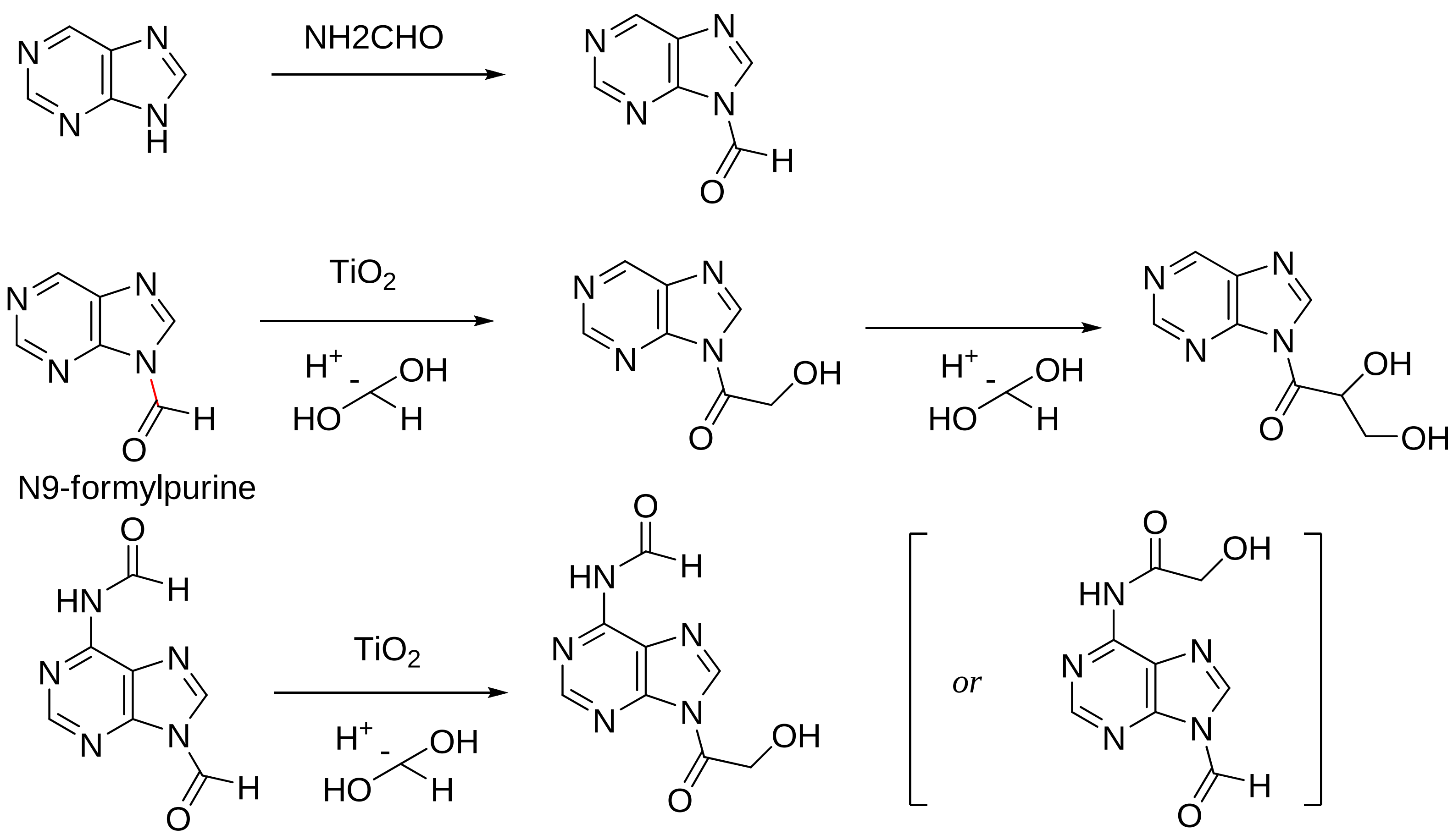



Single headed arrows represent aldol Condensations. Double-headed arrows represent enolizations. Aldotreose can undergo a reverse aldol condensation

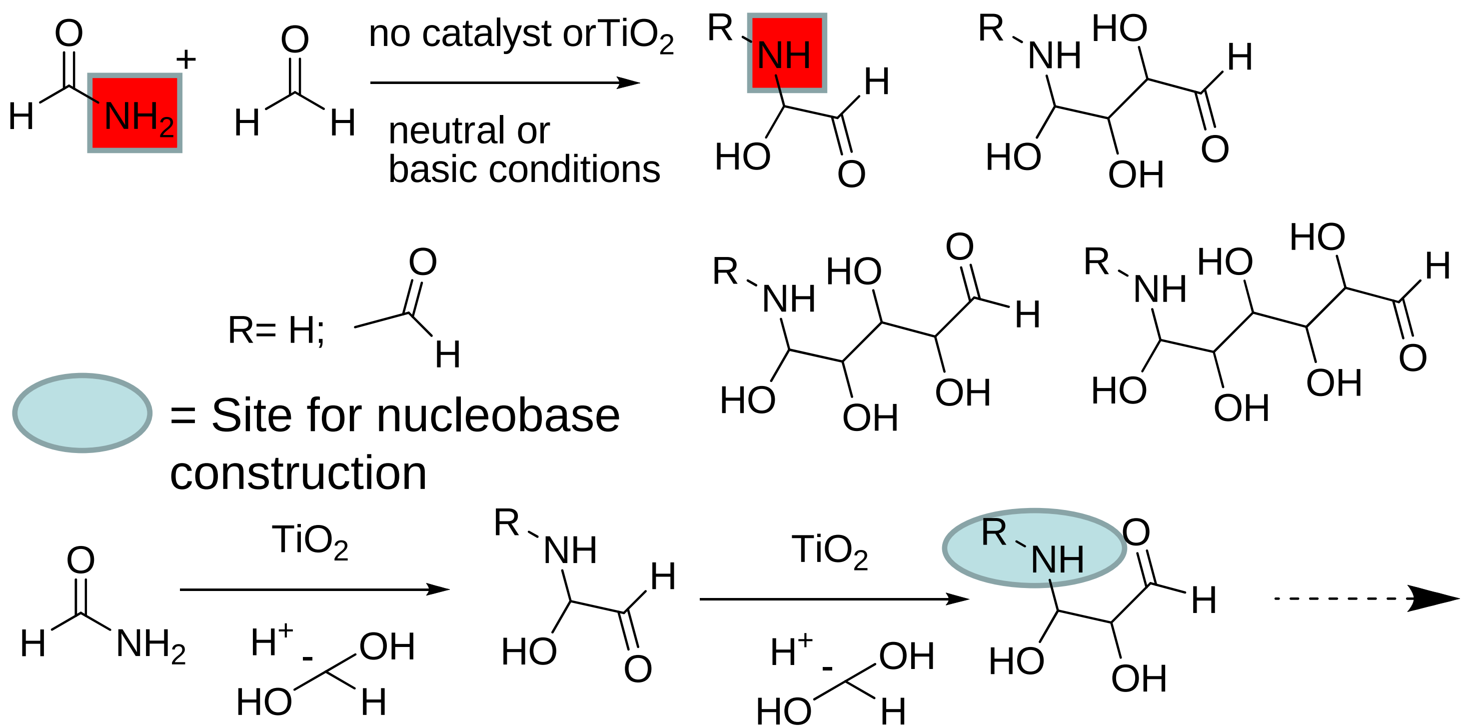
# A novel formose reaction



# The Formose condensation in the presence of Formamide

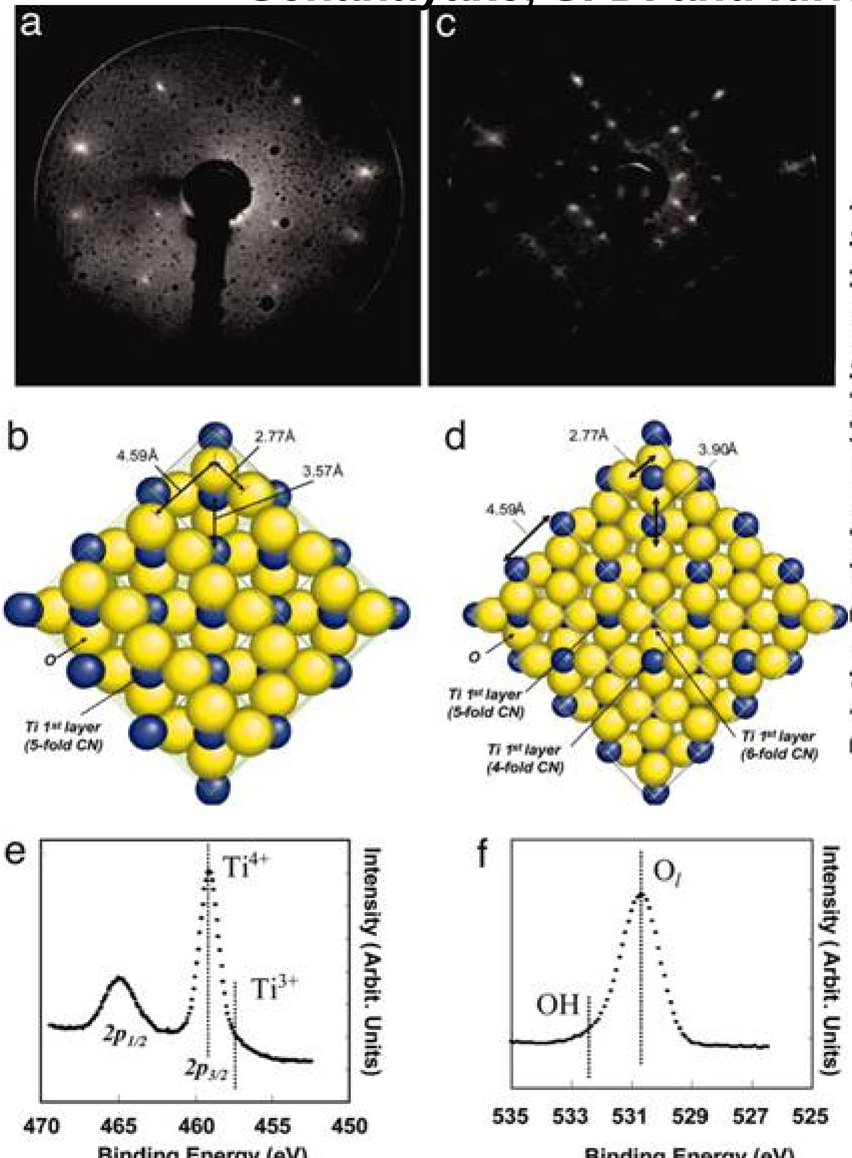
## Nucleobases

## Mixture of sugars

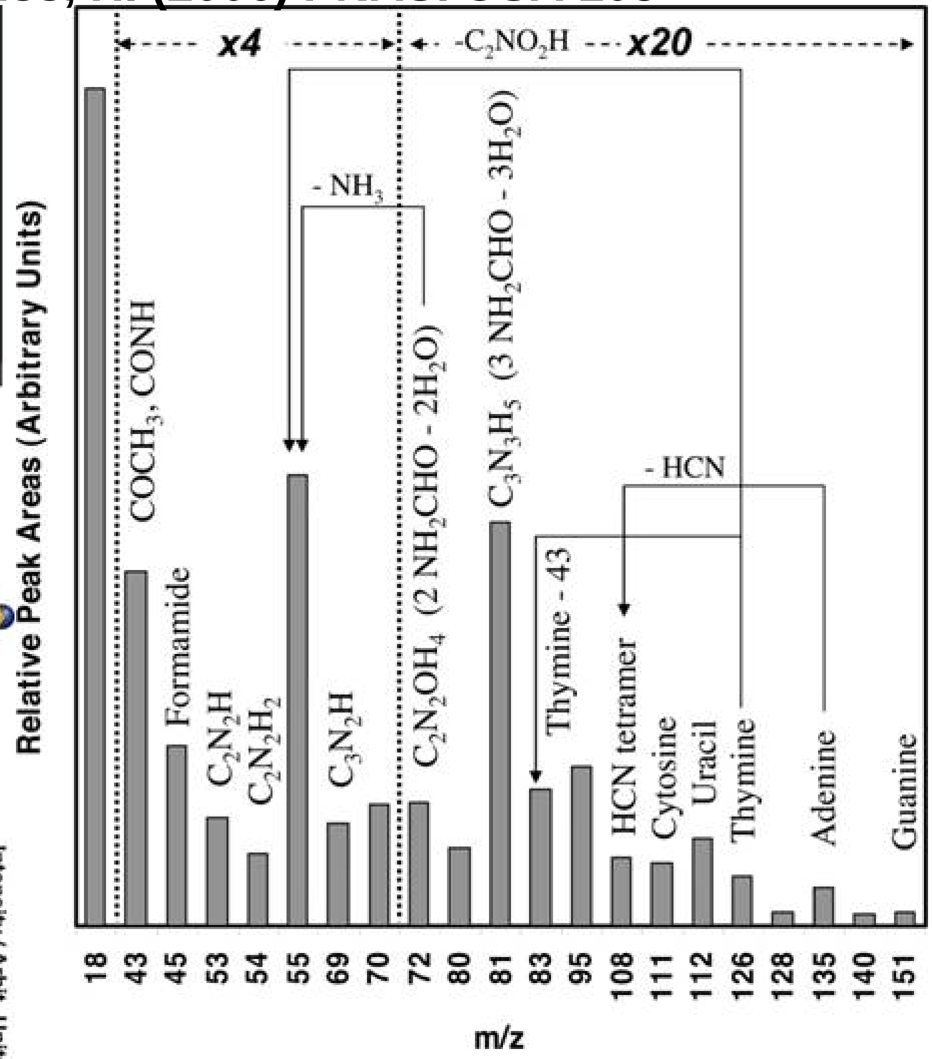


# Photocatalysis and the origin of life: Synthesis of nucleoside bases from Formamide on TiO2(001) single surface.

## Senanayake, S. D. and Idriss, H. (2006) PNAS. USA 103




The surface structures of TiO2 (001) single crystal




Uncorrected peak areas of desorbing products

PNAS

# Conclusions

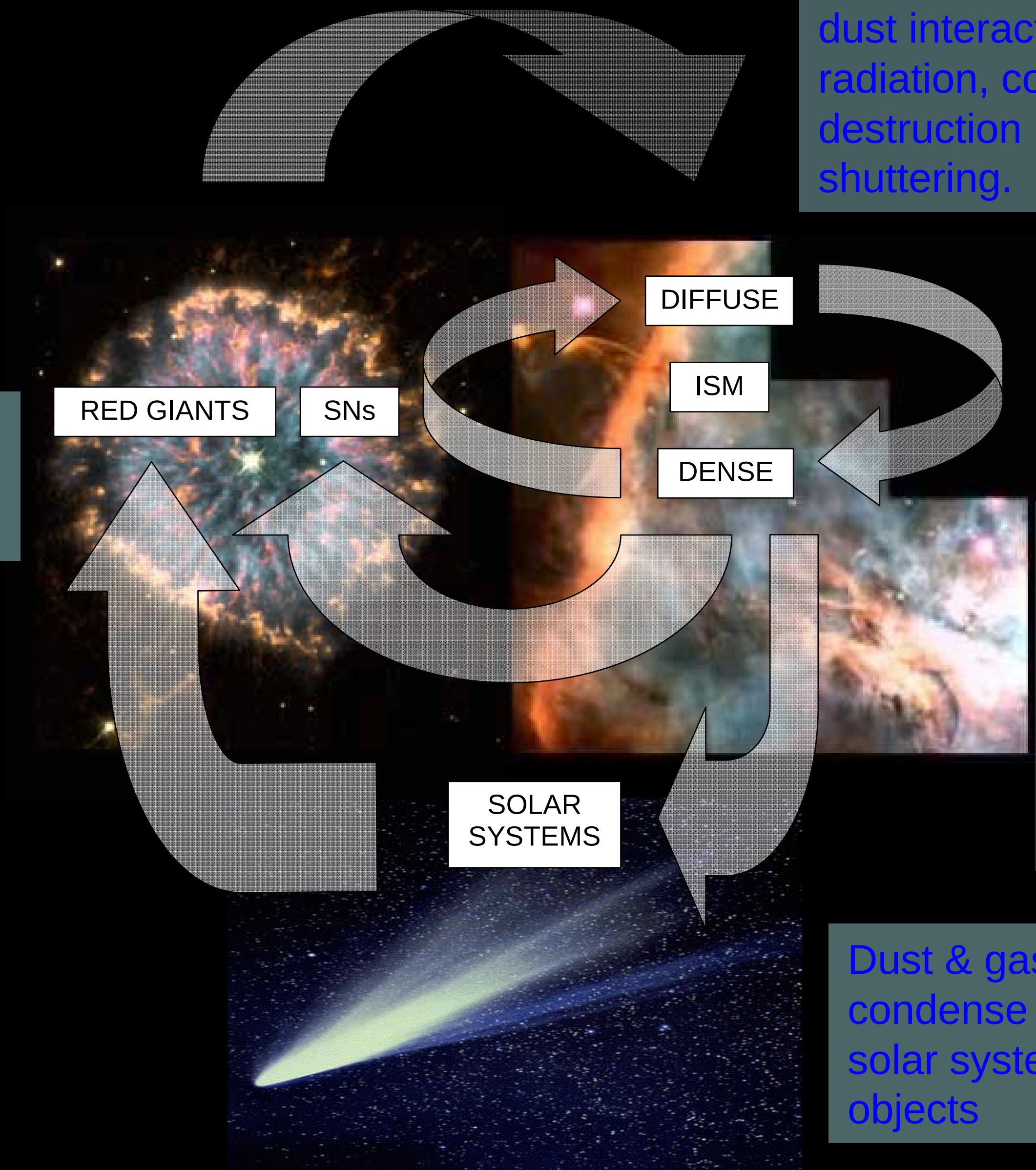
*“Understanding the role of non terrestrial minerals In the prebiotic synsthesis of biomolecules from simple chemical precursors, as well as the description of the chemical processes that led to their formation, is a primary research goal”*

David Hardy

# Infinite Cycle of Matter

In the diffuse interstellar medium dust interacts with hot gas, UV radiation, cosmic rays, undergo destruction by sputtering and shuttering.

Dust condense in cool atmosphere of evolved stars

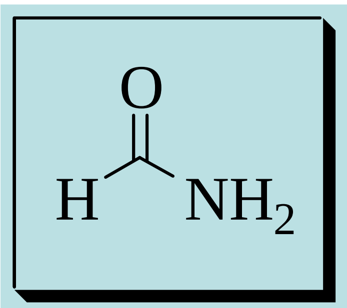



In dense interstellar medium dust growths through ice accretion and coagulation and undergo chemical evolution.

Dust & gas condense forming solar system objects


David Hardy

# Formamide as Prebiotic Probe




"*Simulations based on Density Functional Theory show that formamide is the most stable species with molecular formula "CHON*" Pauzat, F. et al. 6th EANA **2006**

"This one-carbon molecule was detected in the gas phase of interstellar medium" Crovisier, J. Astrobiology: Future Perspectives, Kluwer Eds, **2004** Chapter 8, p. 179-203.

"in the long period comet Hale-Bopp" Bockelee-Morvan,D. et al. *Astr. Astrophys.* **2000**

"and tentatively in the solid phase on grains around the young stellar object W33A " W.A. Schutte et al. *Astr. Astrophys.* **1999**

# Formamide . Physical and chemical properties

"Formamide has a high boiling point, without azeotropic effects, and a wide range of uses as a solvent. It has an efficient solubilizing effect on nucleobases, nucleosides, nucleotides, amino acids, proteins, sugars, metalsand salts"
Becker, B. *J. Chem. Eng*. **1970**

Colloids and surfacesA: Physicochem Eng. Aspects 2003
219: 281-290.
**A comparison of micelle formation of ionic surfactants in formamide, in N-methylformamide and in N, N-dimethylformamide.**
M.Salim Akhter, Sadeq M. Alawi

Langmuir. 2004 Jan 20;20(2):329-35.
**Solvation dynamics of formamide and N, N-dimethylformamide in aerosol OT reverse micelles**.
Shirota H, Segawa H.

Le slides seguenti sono un riassunto
sulle meteoriti che possono esserti utili per una tua conoscenza

# Meteorite types

About 86% of the meteorites that fall on Earth are **chondrites**, which are named for the small, round particles they contain. These particles, or chondrules, are composed mostly of silicate minerals that appear to have been melted while they were free-floating objects in space. Chondrites also contain small amounts of organic matter, including amino acids, and presolar grains. Chondrites are typically about 4.55 billion years old and are thought to represent material from the asteroid belt that never formed into large bodies. Like comets, chondritic asteroids are some of the oldest and most primitive materials in the solar system. Chondrites are often considered to be "the building blocks of the planets."

About 8% of the meteorites that fall on Earth are **achondrites**, some of which appear to be similar to terrestrial mafic igneous rocks. Most achondrites are also ancient rocks, and are thought to represent crustal material of asteroids. One large family of achondrites may have originated on the asteroid 4 Vesta. Others derive from different asteroids. Two small groups of achondrites are special, as they are younger and do not appear to come from the asteroid belt. One of these groups comes from the Moon, and includes rocks similar to those brought back to Earth by Apollo and Luna programs. The other group is almost certainly from Mars and are the only materials from other planets ever recovered by man.

About 5% of meteorites that fall are **iron meteorites** with intergrowths of iron-nickel alloys, such as kamacite and taenite. Most iron meteorites are thought to come from the core of a number of asteroids that were once molten. As on Earth, the denser metal separated from silicate material and sank toward the center of the asteroid, forming a core. After the asteroid solidified, it broke up in a collision with another asteroid.

**Stony-iron meteorites** constitute the remaining 1%. They are a mixture of iron-nickel metal and silicate minerals. One type, called pallasites, is thought to have originated in the boundary zone above the core regions where iron meteorites originated. The other major type of stony-iron meteorites is the mesosiderites.

From Wikipedia.

# Chondrites

Chondrites are stony meteorites that have not been modified due to melting or differentiation of the parent body. They formed when various types of dust and small grains that were present in the early solar system accreted to form primitive asteroids. Prominent among the components present in chondrites are the enigmatic **chondrules**, millimeter-sized objects that originated as freely floating, molten or partially molten droplets in space; most chondrules are rich in the silicate minerals olivine and pyroxene. Chondrites also contain **refractory inclusions** (including Ca-Al Inclusions), which are among the oldest objects to form in the solar system, particles rich in metallic Fe-Ni and sulfides, and isolated grains of silicate minerals. The remainder of chondrites consists of fine-grained (micrometer-sized or smaller) **dust**, which may either be present as the matrix of the rock or may form rims or mantles around individual chondrules and refractory inclusions. Embedded in this dust are **presolar grains**, which predate the formation of our solar system and originated elsewhere in the galaxy.

# Ordinary Chondrites

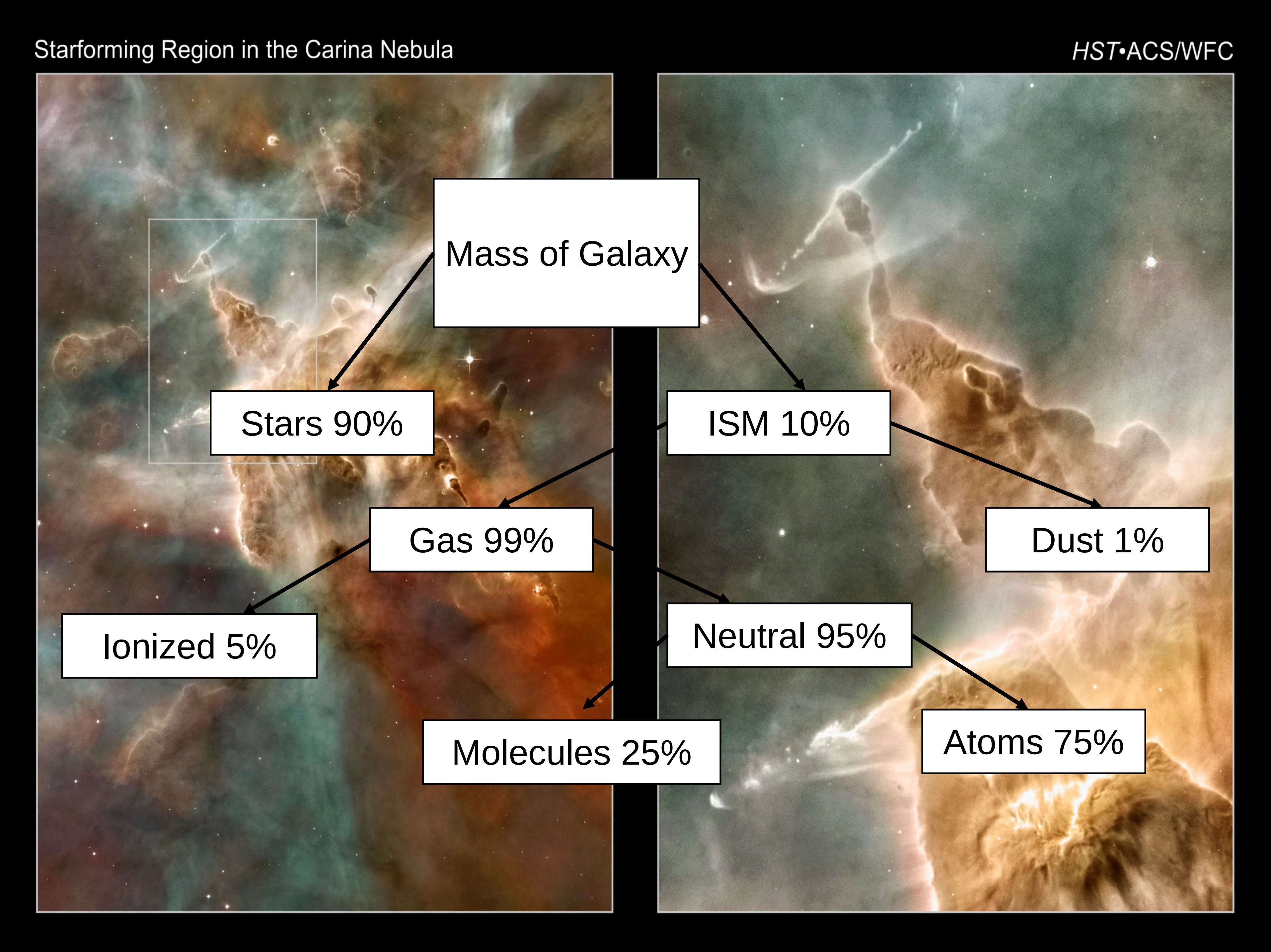
Ordinary chondrites are by far the most common type of meteorite to fall on Earth: about 80% of all meteorites and over 90% of chondrites are ordinary chondrites. They contain abundant chondrules, sparse matrix (10-15% of the rock), few refractory inclusions, and variable amounts of Fe-Ni metal and troilite (FeS). Their chondrules are generally in the range of 0.5 to 1 mm in diameter. Ordinary chondrites are distinguished chemically by their depletions in refractory lithophile elements, such as Ca, Al, Ti, and rare earths, relative to Si, and isotopically by their unusually high $^{17}O/^{16}O$ ratios relative to $^{18}O/^{16}O$ compared to Earth rocks. Most, but not all, ordinary chondrites have experienced significant degrees of metamorphism, having reached temperatures well above 500°C on the parent asteroids. They are divided into three groups, which have different amounts of metal and different amounts of total iron:

- H chondrites have High iron contents, and smaller chondrules than L and LL chondrites. ~40% of ordinary chondrite falls belong to this group.

- L chondrites have Low iron contents. About half of ordinary chondrite falls are L chondrites, which makes them the most common type of meteorite to fall on Earth.

- LL chondrites have Low iron and Low metal contents. Only 1 in 10 ordinary chondrites is LL.

From Wikipedia.


Starforming Region in the Carina Nebula
HST•ACS/WFC
Mass of Galaxy
Stars 90%
ISM 10%
Gas 99%
Dust 1%
Ionized 5%
Neutral 95%
Molecules 25%
Atoms 75%

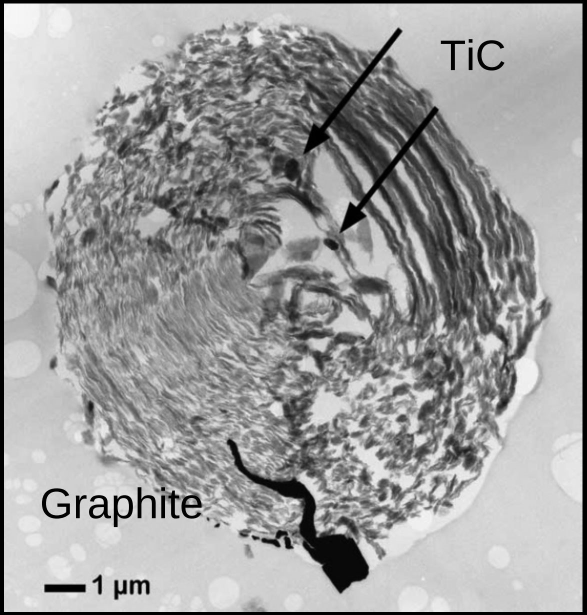
# Types of Presolar Grains in Meteorites and IDPs

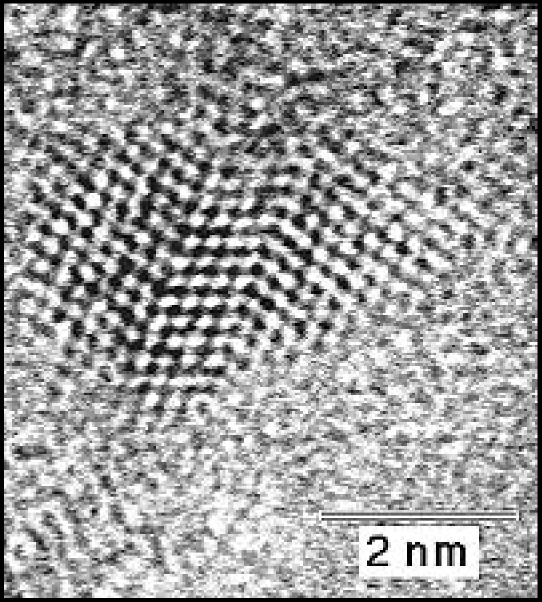
QuickTime™ e un
decompressore TIFF (Non compresso)
sono necessari per visualizzare quest'immagine.

(adapted by Zinner 1998)

SiC

QuickTime™ e un
decompressore TIFF (Non compresso)
sono necessari per visualizzare quest'immagine.

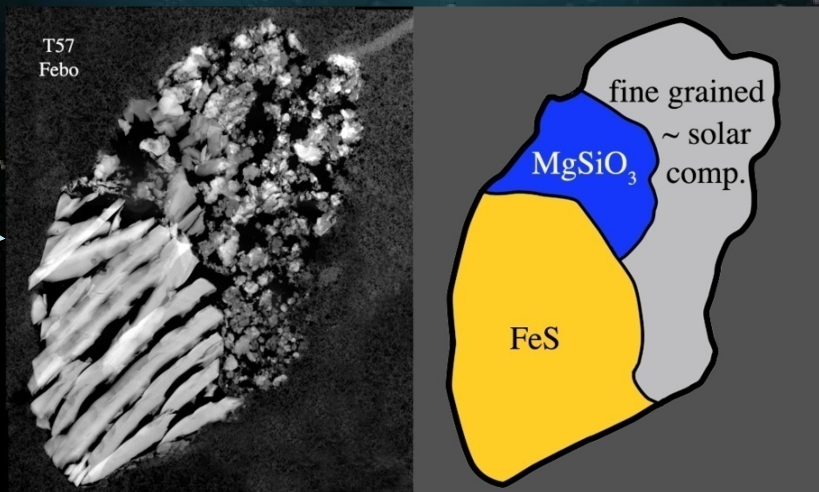


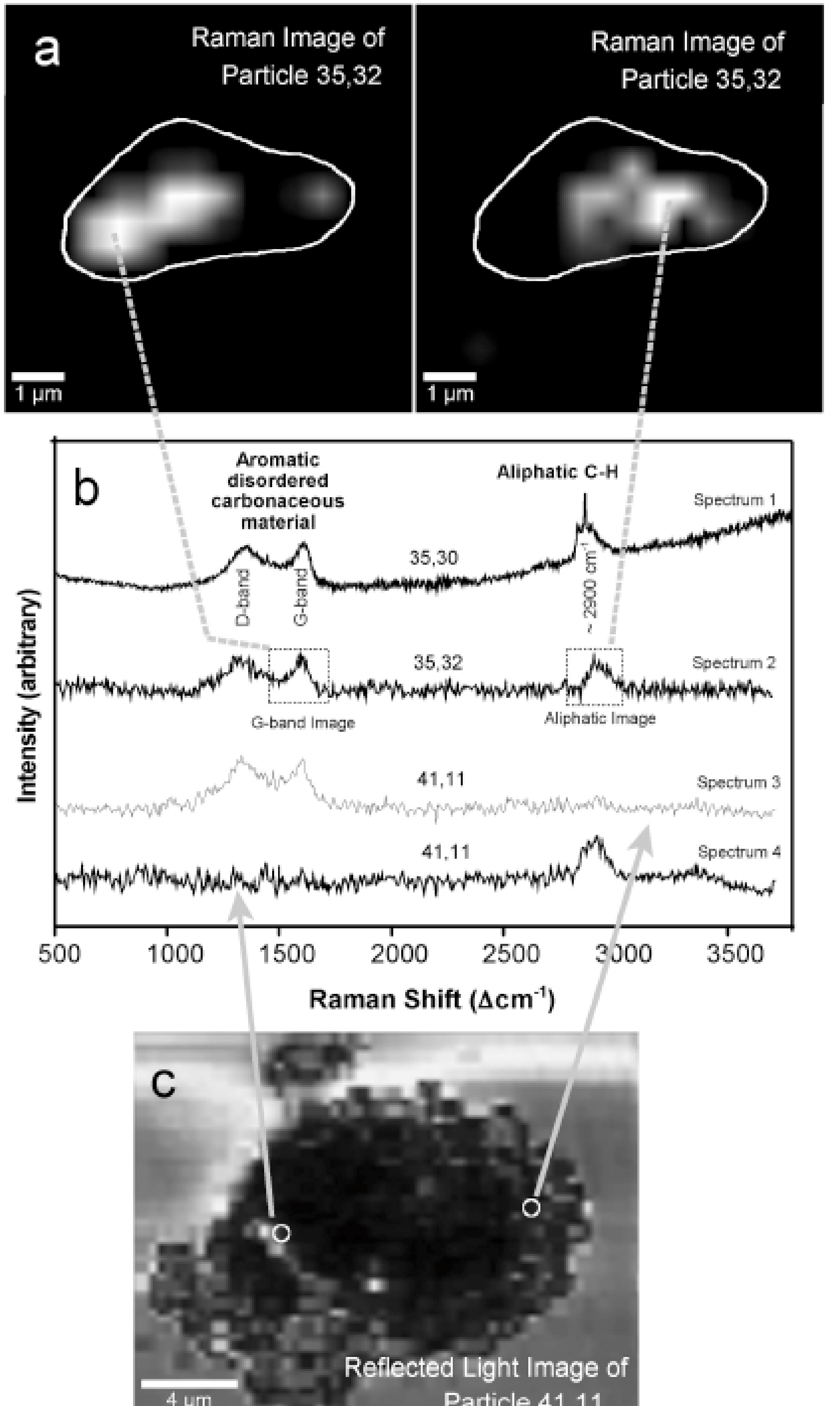



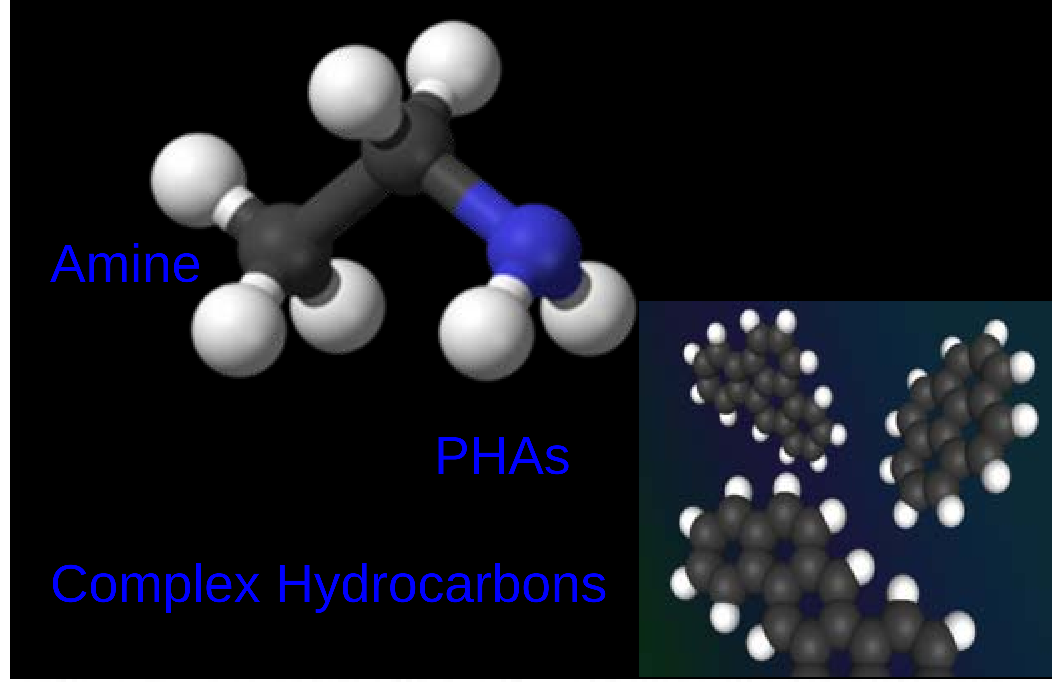

nanoDiamonds

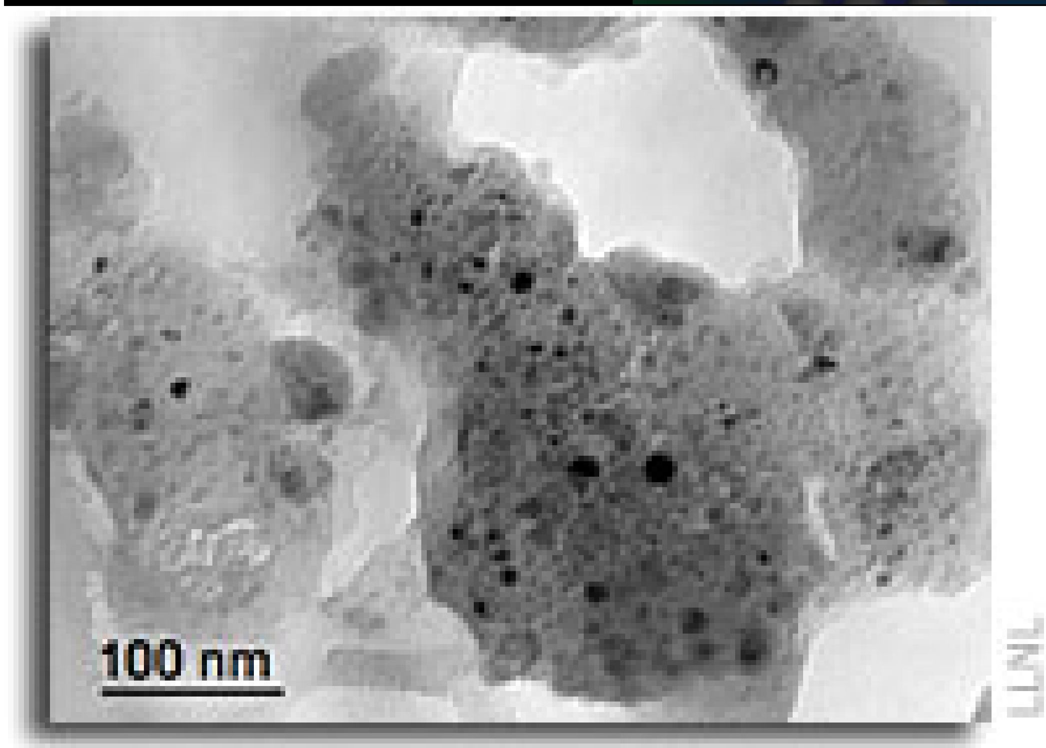
# NASA STARDUST MISSION

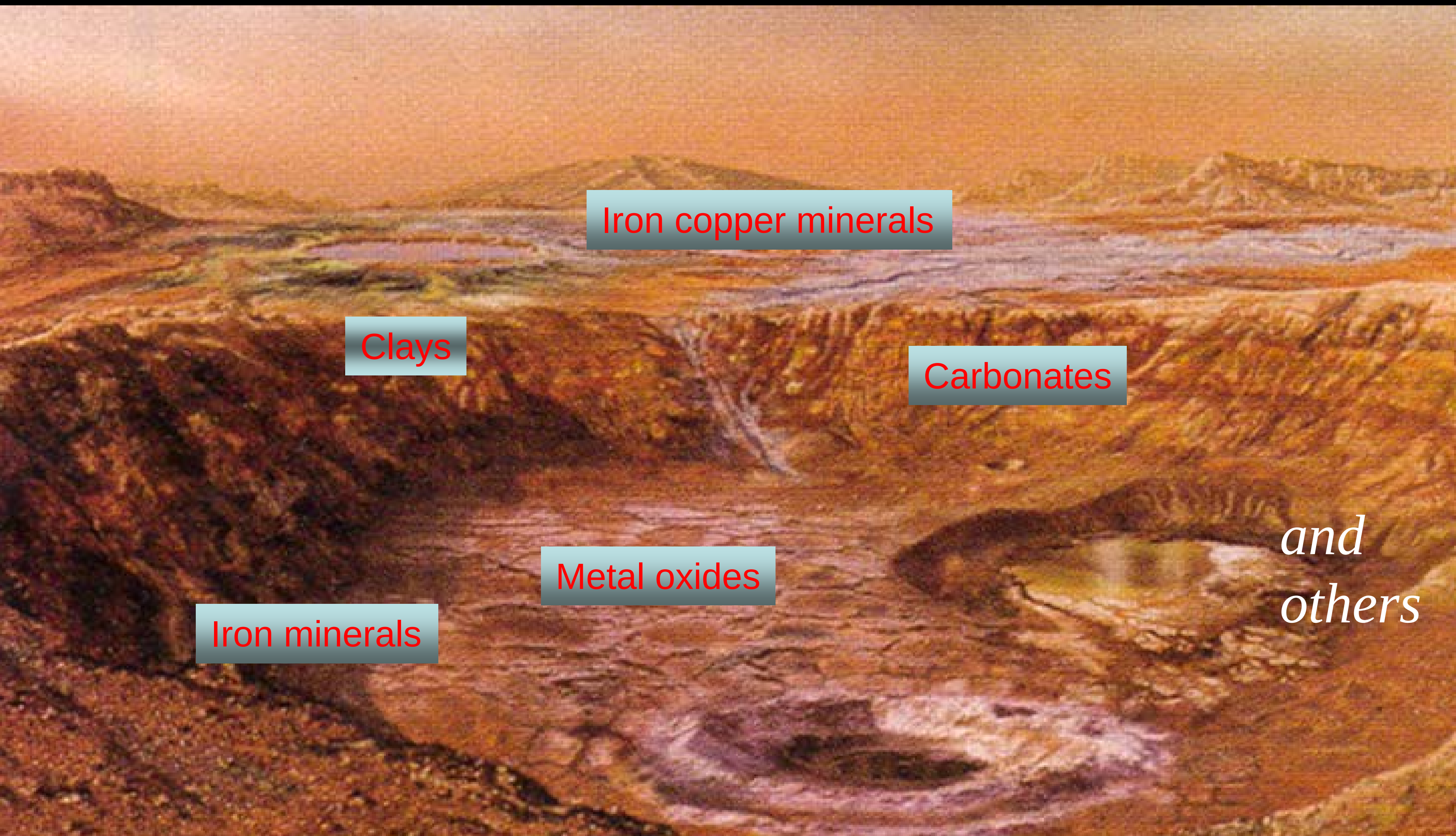
## Comet Wild2 Sample Return Mission


a
Raman Image of Particle 35,32
Raman Image of Particle 35,32
1 μm
1 μm
b
Aromatic disordered carbonaceous material
Aliphatic C-H
Spectrum 1
35,30
D-band
G-band
~ 2900 cm⁻¹
Spectrum 2
35,32
G-band Image
Aliphatic Image
Spectrum 3
41,11
Spectrum 4
41,11
Intensity (arbitrary)
500 1000 1500 2000 2500 3000 3500
Raman Shift (Δcm⁻¹)
c
4 μm
Reflected Light Image of Particle 41,11


Amine
PHAs
Complex Hydrocarbons


100 nm


Iron copper minerals
Clays
Carbonates
Metal oxides
Iron minerals
*and others*

# The effect of water