INAF

SISSA

IS

5th Workshop of the Italian Astrobiology Society

Life in a Cosmic Context

15-17 September 2015, Trieste, Italy

Astrobiology Society - Società Italiana di Astrobiologia

The route from formamide to RNA and metabolism. Part 1

Raffaele Saladino-Università delle Tuscia (Viterbo, Italy)

PNAS
Proceedings of the National Academy of Sciences of the United States of America www.pnas.org

PNAS Celebrating 100 Years 1915-2015

Miller experiments in atomistic computer simulations

Antonino Marco Saitta[a,b,1] and Franz Saija[c,1]

[a]Sorbonne Universités, Université Pierre et Marie Curie Paris 06, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Unité Mixte de Recherche 7590, 75005 Paris, France; [b]Centre National de la Recherche Scientifique, Unité Mixte de Recherche 7590, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, 75005 Paris, France; and [c]CNR-Istituto per i Processi Chimico-Fisici, V. le F. Stagno d'Alcontres 37, 98158 Messina, Italy

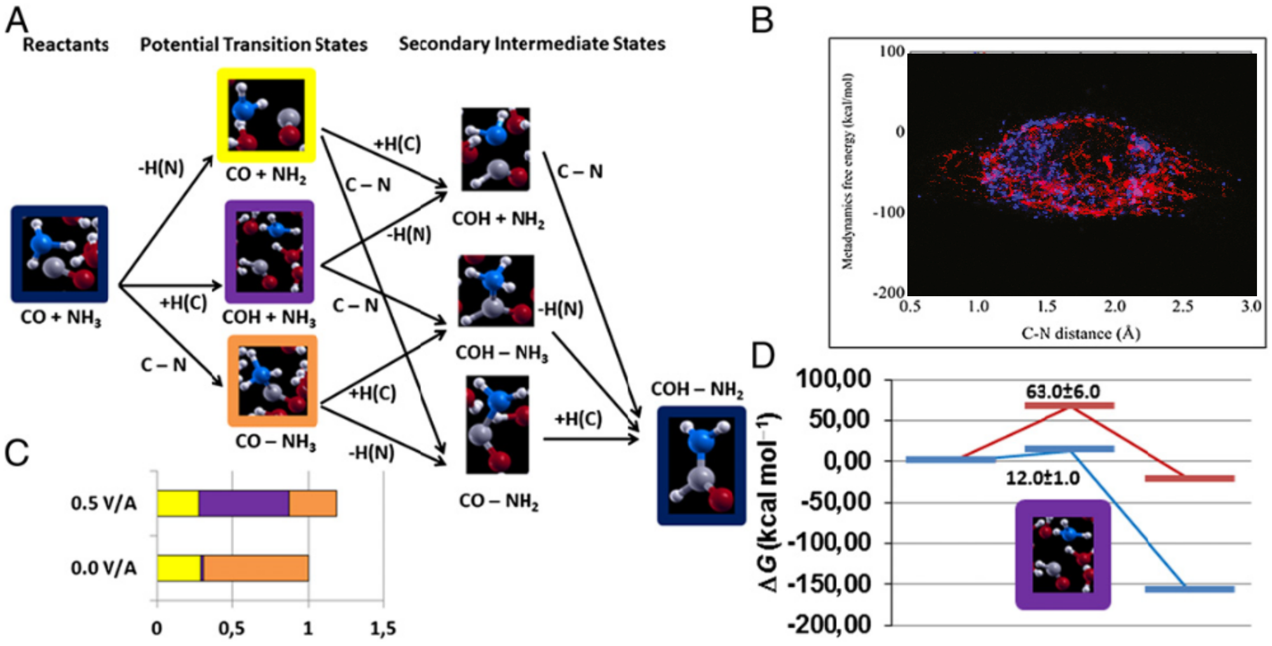
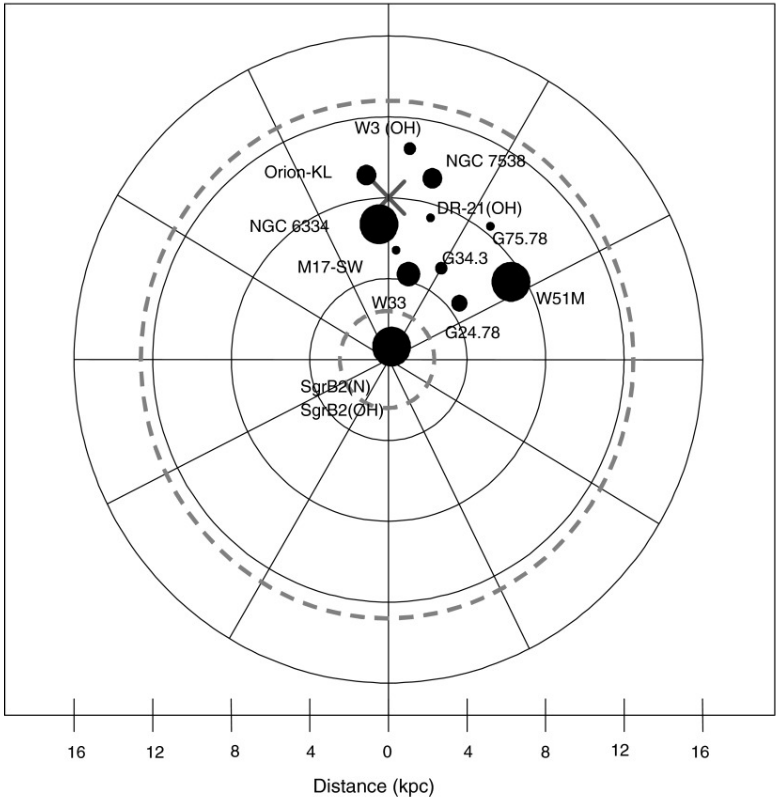


Fig. 1. Metadynamics-based analysis of the formation of formamide. (*A*) Representation of the chemical possible paths and intermediate/transition states. C–N, +H(C), and –H(N) indicate the formation of a CN bond, the formation of a CH bond, or the break of a NH bond, respectively. Secondary intermediate states are referred to in the text as SIS1, SIS2, and SIS3 from the top to the bottom, respectively. (*B*) Metadynamics-based free-energy landscape as function of the C-N distance reaction coordinate. (*C*) Statistical occurrence of the potential transition states (TS) with and without an external field, following the same color code as in *A*, and normalized with respect to the total occurrences in the fieldless case. (*D*) Energetics of the reaction with (blue line) and without (red line) the electric field, evaluated by identifying the "purple" (TS2) step as the reaction transition state as $E(TS2)=E_B+\ln(P(TS2)/\beta$, where E_B is the MetD barrier, $P(TS_x)$ is the normalized statistical occurrence of a given TS_x state, and β is the thermal term. Energy values are expressed in kilocalories per mole throughout the whole image.

Astrobiology

Observations of Interstellar Formamide: Availability of a Prebiotic Precursor in the Galactic Habitable Zone

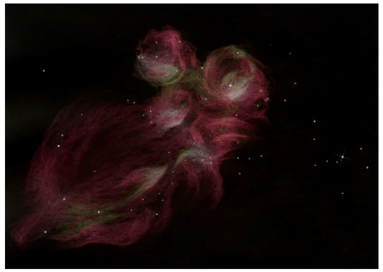
To cite this article:
Gilles R. Adande, Neville J. Woolf, and Lucy M. Ziurys. Astrobiology. May 2013, 13(5): 439-453.
doi:10.1089/ast.2012.0912.



Schematic representation of the Milky Way Galaxy. The Sun is indicated by the cross. The galactic habitable zone is indicated by the dashed, gray circles, based on work of Gowanlock *et al.* (2011). The approximate galactic positions of the molecular clouds where formamide has been detected are indicated by filled circles. The circle size indicates the relative amount of formamide. The figure summarizes the current work and past observations.

SgrB2(N)

kpc (1 kpc ~ 3259 light-years)



NGC 6334

MONTHLY NOTICES of the Royal Astronomical Society

Monthly Notices of the Royal Astronomical Society

Shedding light on the formation of the pre-biotic molecule formamide with ASAI

A. López-Sepulcre[1,2,3⋆], Ali A. Jaber[1,2,4], E. Mendoza[5], B. Lefloch[1,2], C. Ceccarelli[1,2], C. Vastel[6,7], R. Bachiller[8], J. Cernicharo[9], C. Codella[10], C. Kahane[1,2], M. Kama[11], M. Tafalla[8] †

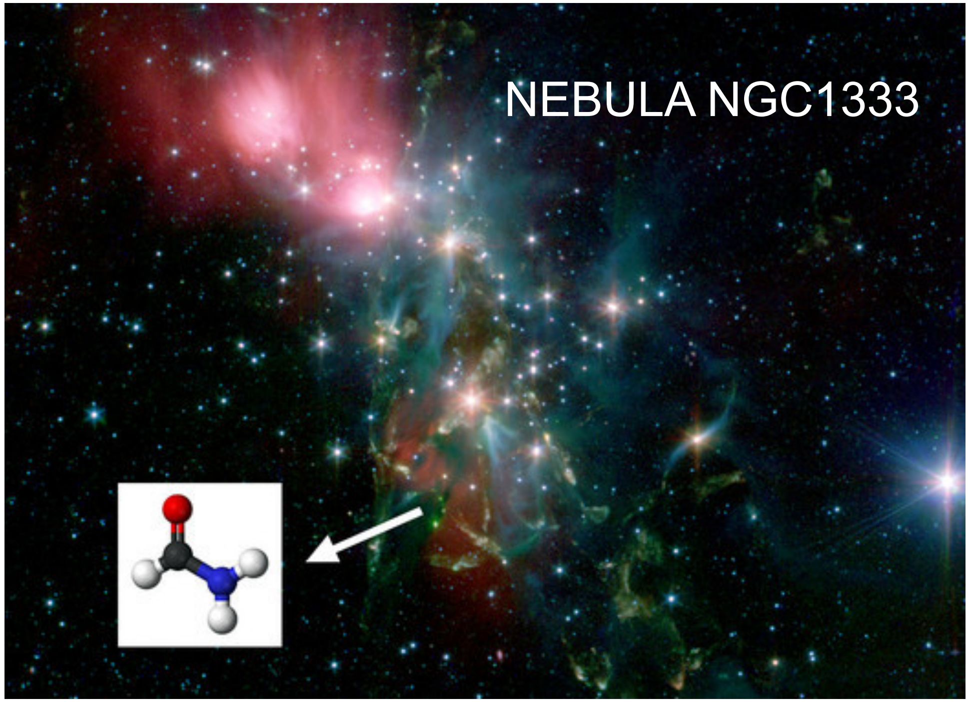
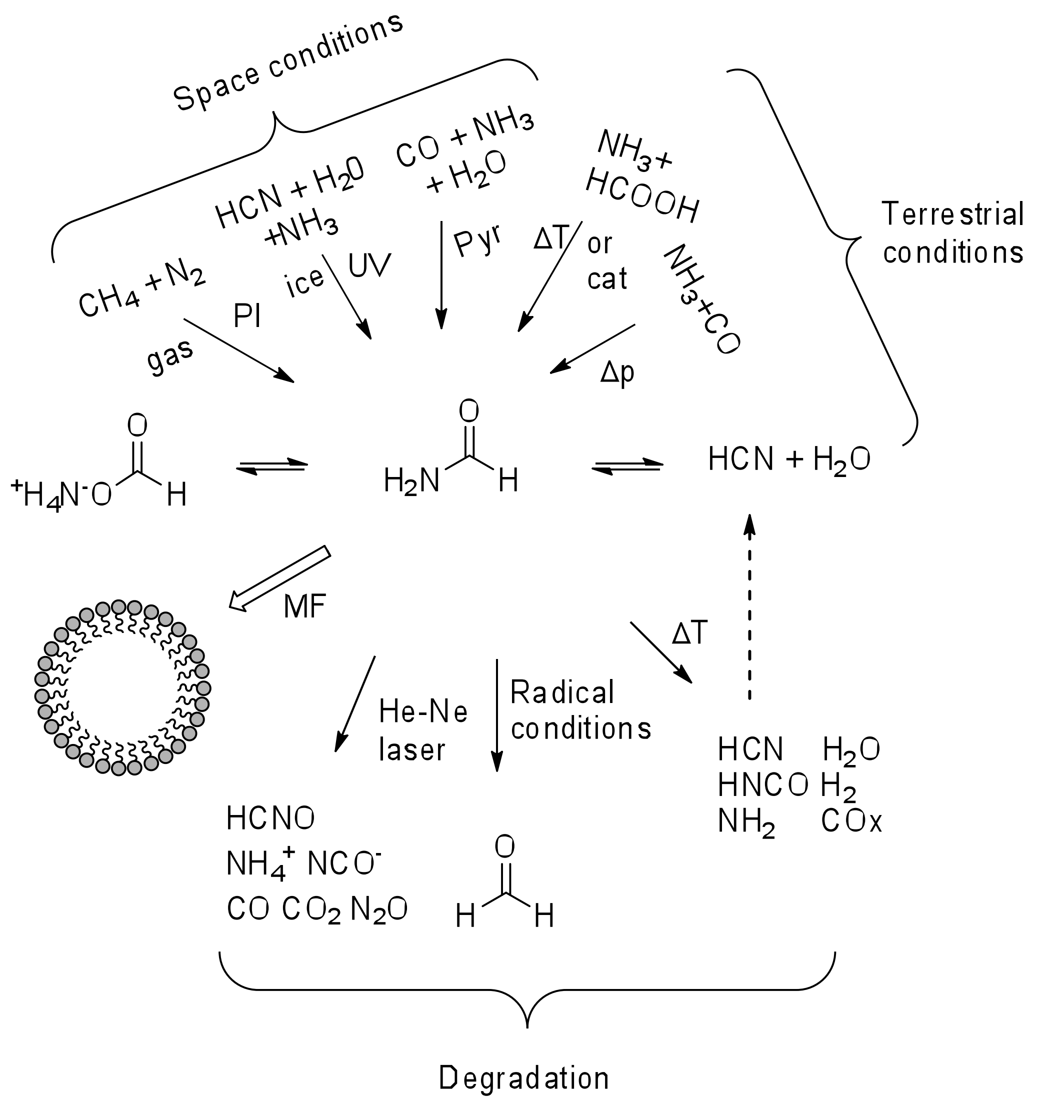


Table 2. Number of NH_2CHO and HNCO detected lines

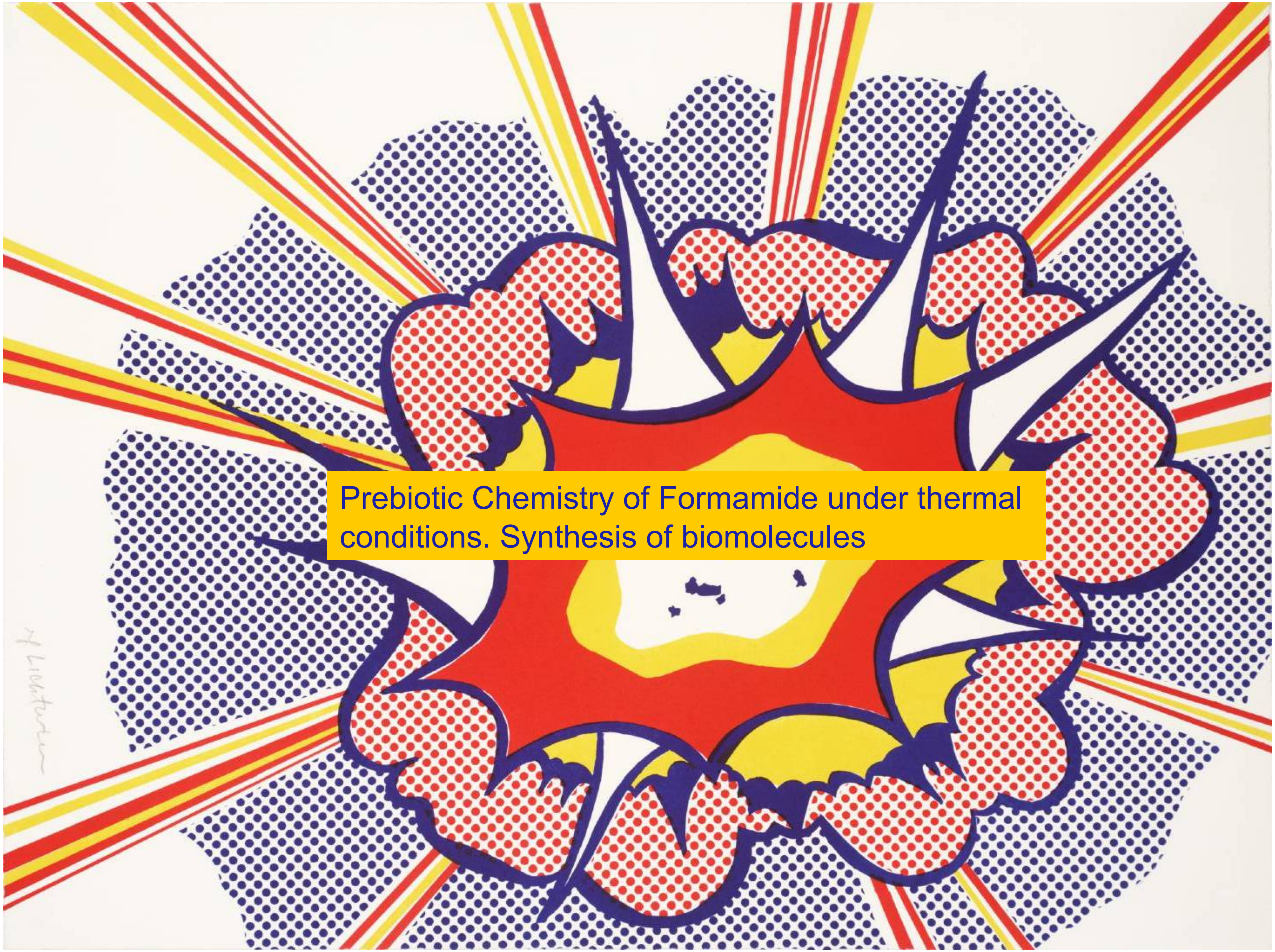
Source	NH_2CHO #	NH_2CHO E_u (K)	HNCO #	HNCO E_u (K)
L1544[a]	0	—	2	10–16
TMC1	0	—	3	10–16
B1	0	—	4	10–30
L1527	0	—	4	10–30
L1157-mm	0	—	4	10–30
IRAS 4A	7	15–70	10	10–130
SVS13A	13	15–130	19	10–130
OMC-2 FIR 4	21	10–130	9	10–100
Cep E	5	10–22	5	10–85
I16293	12	10–160	16	10–95

[a]Only 3-mm data available.

Elemental Formamide Chemistry

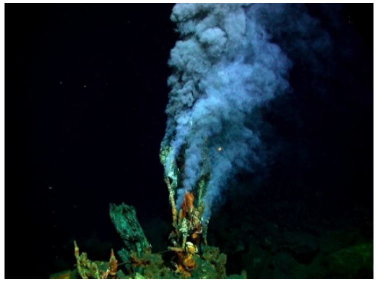


Formamide is easily produced by both space and planetary processes starting from mixtures of simple compounds. Once formed it can directly polymerize to biomolecules or it can in part degraded to other low molecular weight derivatives useful intermediates For the synthesis of biomolecules.

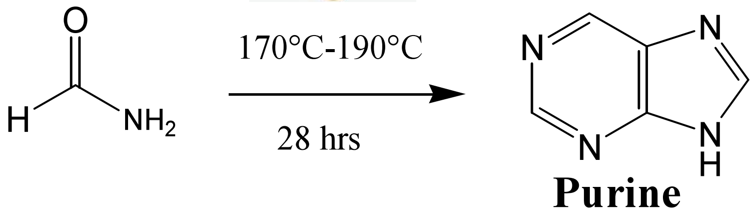


Prebiotic Chemistry of Formamide under thermal conditions. Synthesis of biomolecules

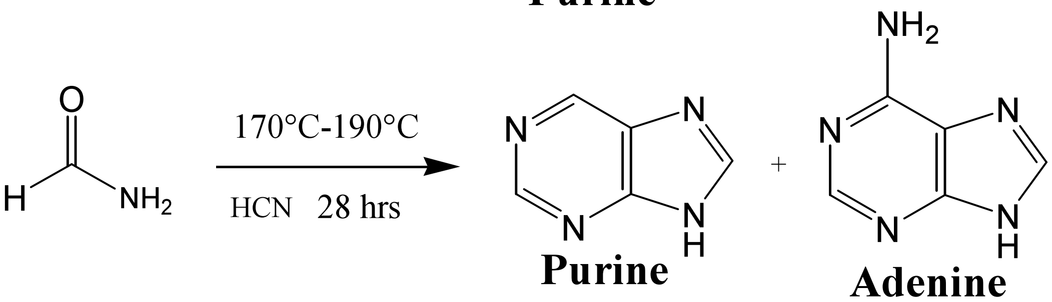
Formamide prebiotic chemistry under thermal conditions. Pioneering studies.



A)

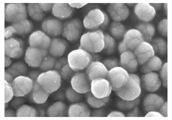


B)



Koyama, T. et al *Chem.Pharm. Bull*. **1977**, 1923.
Yamada, H. et al.*Tetrahedron Lett.* **1978**, 4039

Formamide and minerals

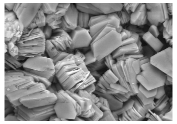


- metal oxides (impact-induced minerals)
- carbonates

2001 — CaO MnO_2 SiO MgO Al_2O_3 SiO_2 FeO CuO $CaCO_3$

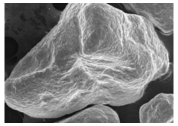
- volcanism-related minerals

2003 — TiO_2



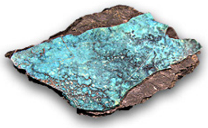
- clays

2004 — zeolites (Al,Ca,Na silicates), kaolin, montmorillonites (μcrystalline phyllosilicates) $(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6 \cdot nH_2O$



- circumstellar/cometal dusts
  silicates [(Mg,Si,Fe)O]

2005 — Fe Si Mg: olivine, fayalite, forsterite



- phosphates

2006 — phosphate minerals

- Fe/S/Cu

2008 — pirite , pirrotine, covellite, etc

- zirconium

2010 — ZrO_2 $ZrSiO_4$ $CeZrO_4$ $PbZrO_3$, etc

- boron

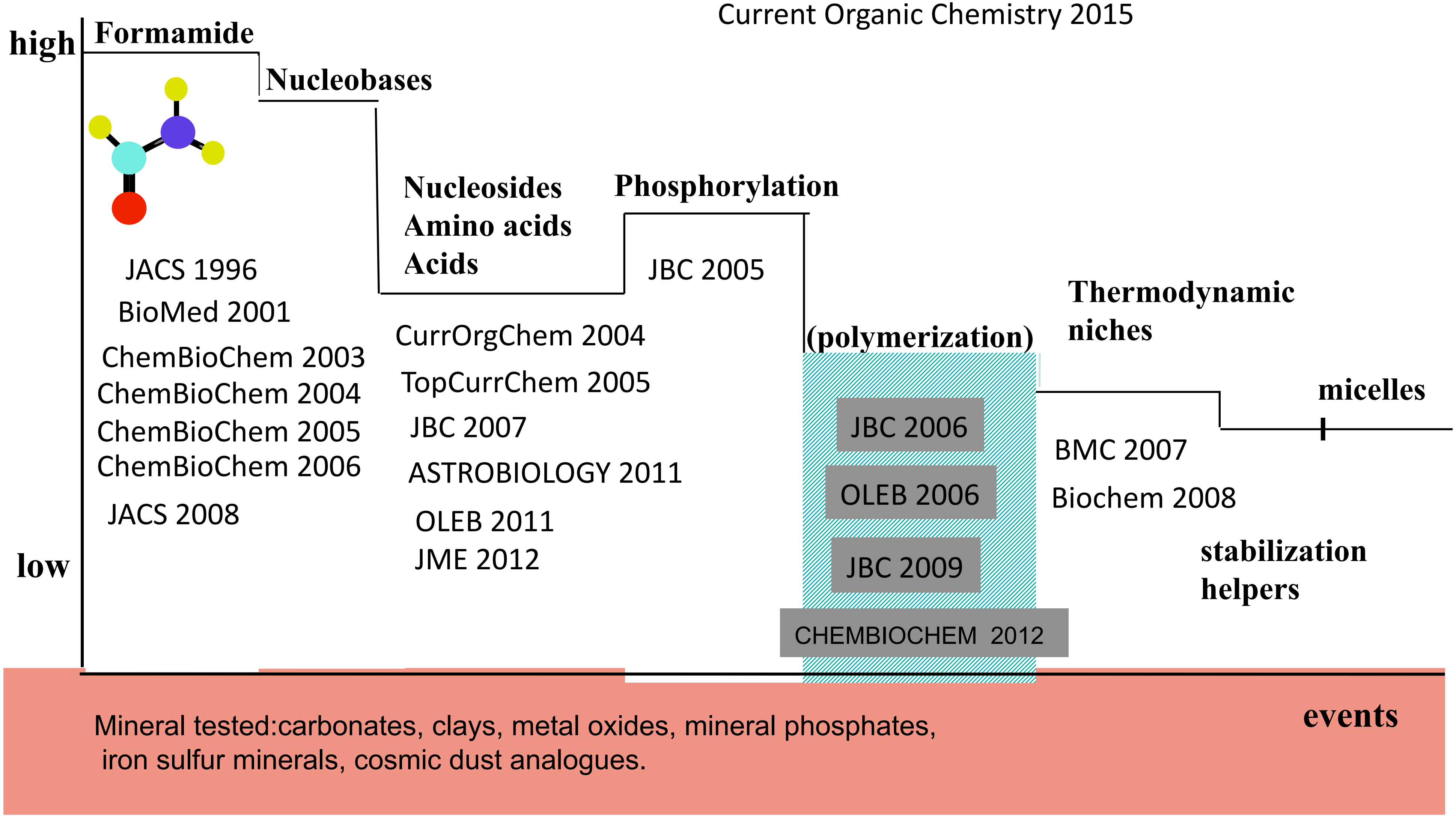
2011 — hydroboracite, ulexite, rodizite,ambersite, etc

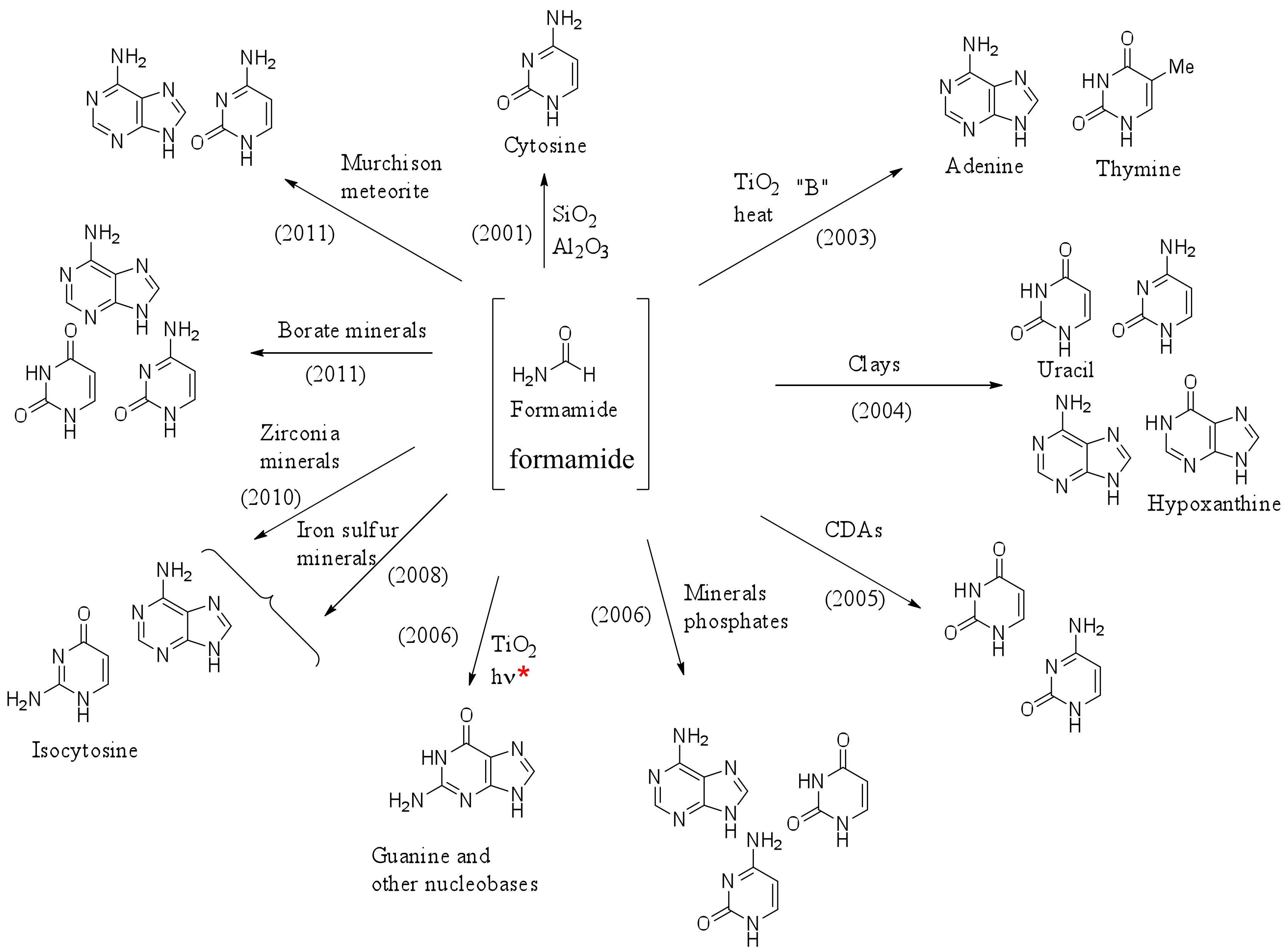
- Murchison

2011 — 

Prebiotic synthesis of biomolecules from formamide under thermal Conditions. Degree of confidence

PHYSICS OF LIFE REVIEWS 2012
ChemSocRev 2012
Current Organic Chemistry 2015





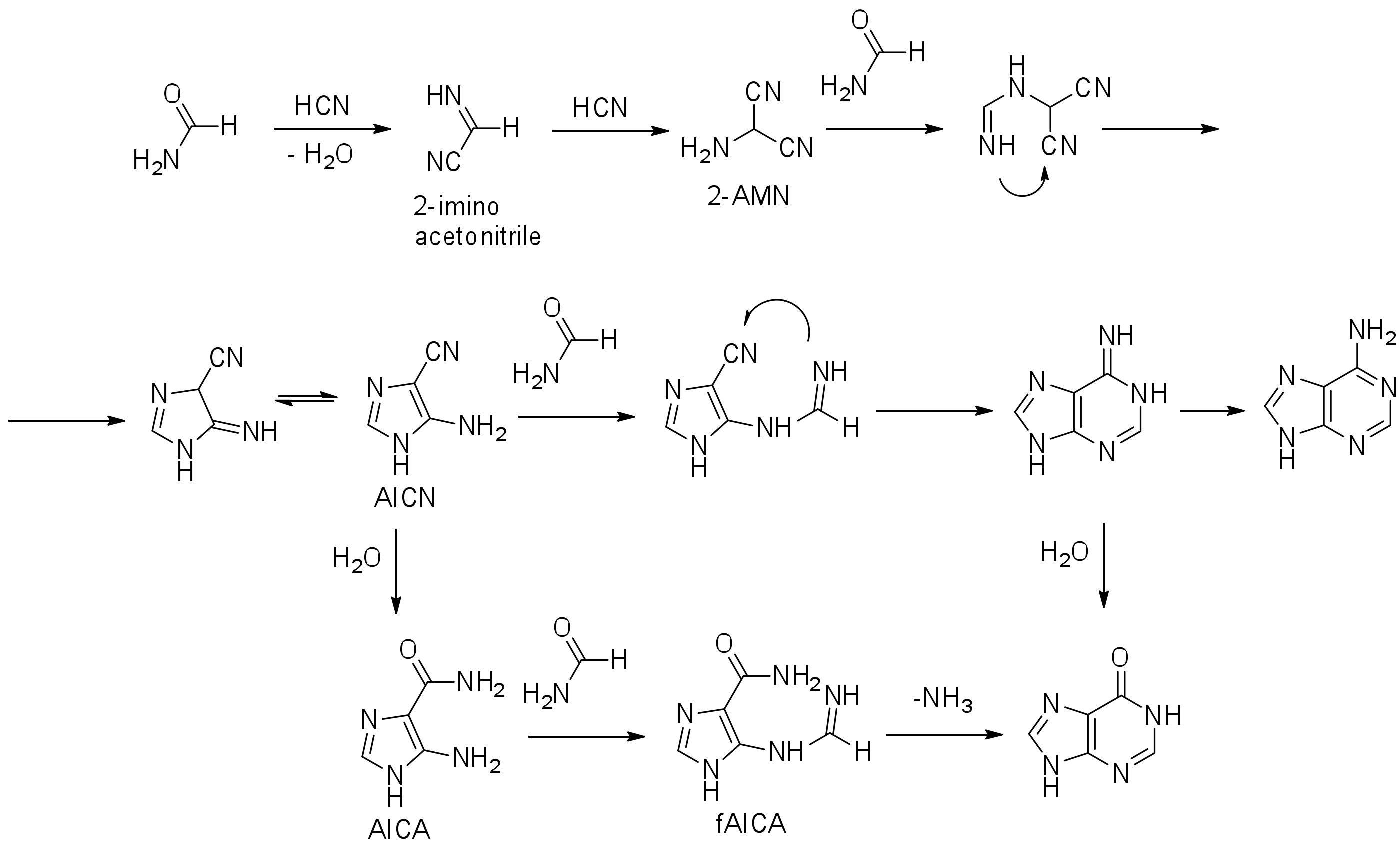
Synthesis of nucleobases from formamide metal oxides and minerals. An overview.

Angewandte Chemie International Edition
GDCh A Journal of the Gesellschaft Deutscher Chemiker

A Unified Mechanism for Abiotic Adenine and Purine Synthesis in Formamide†

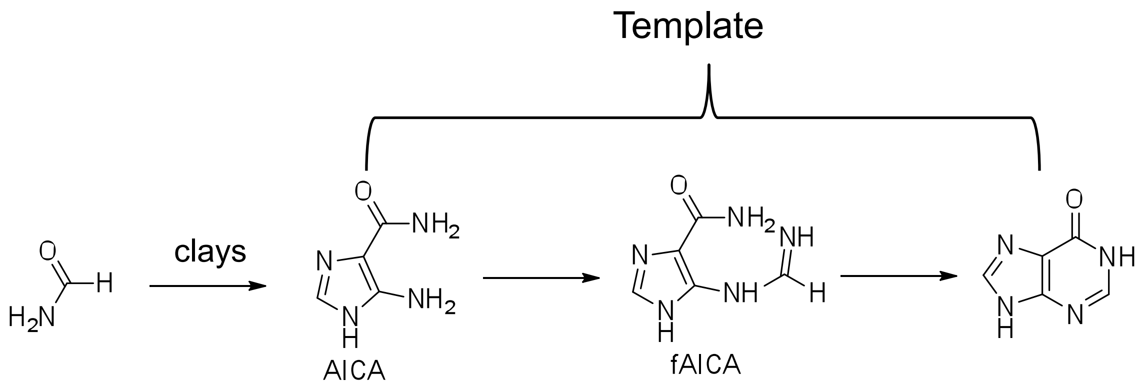
Volume 51, Issue 21
May 21, 2012
Pages 5134–5137

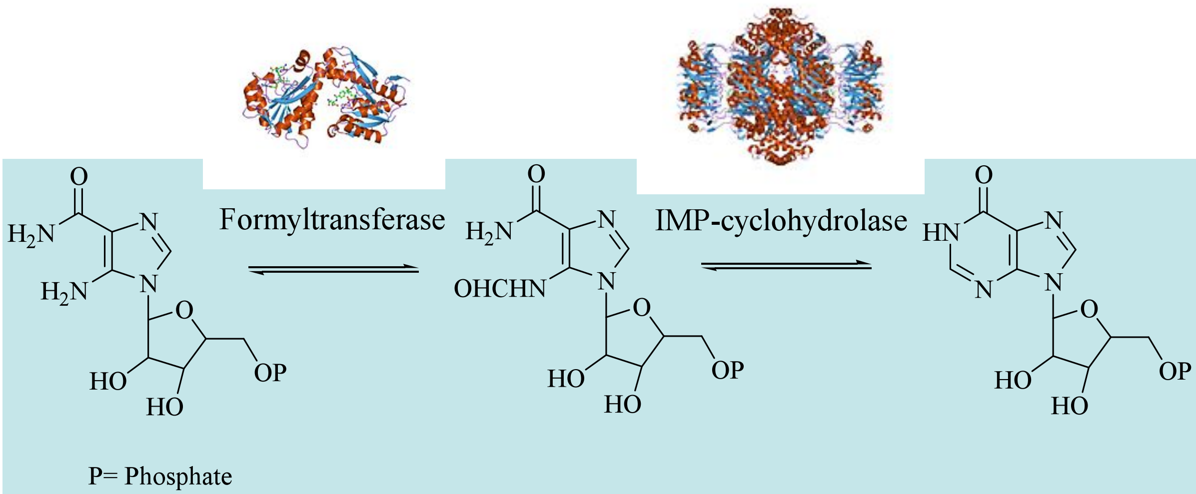
Jeremy S. Hudson, Joseph F. Eberle, Raj H. Vachhani, Luther C. Rogers, James H. Wade,
Prof. Dr. Ramanarayanan Krishnamurthy, Dr. Greg Springsteen



R. Saladino, E. Di Mauro BMC 2007
G Springsteen Angewandte Chemie 2012

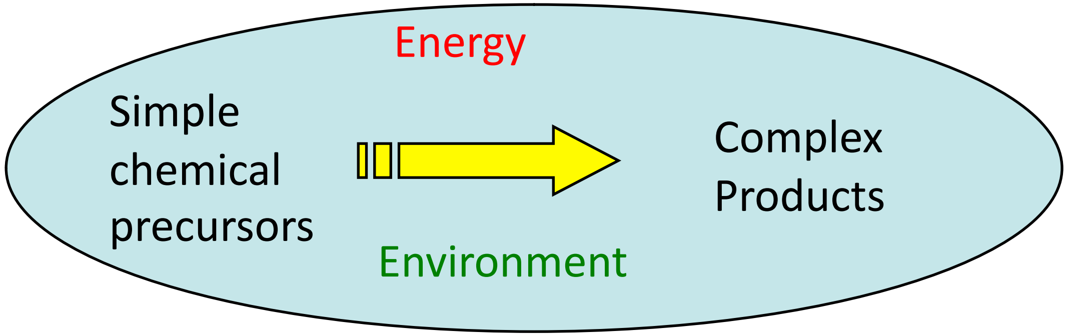
Prebiotic formyltransferase and IMP-cyclohydrolase





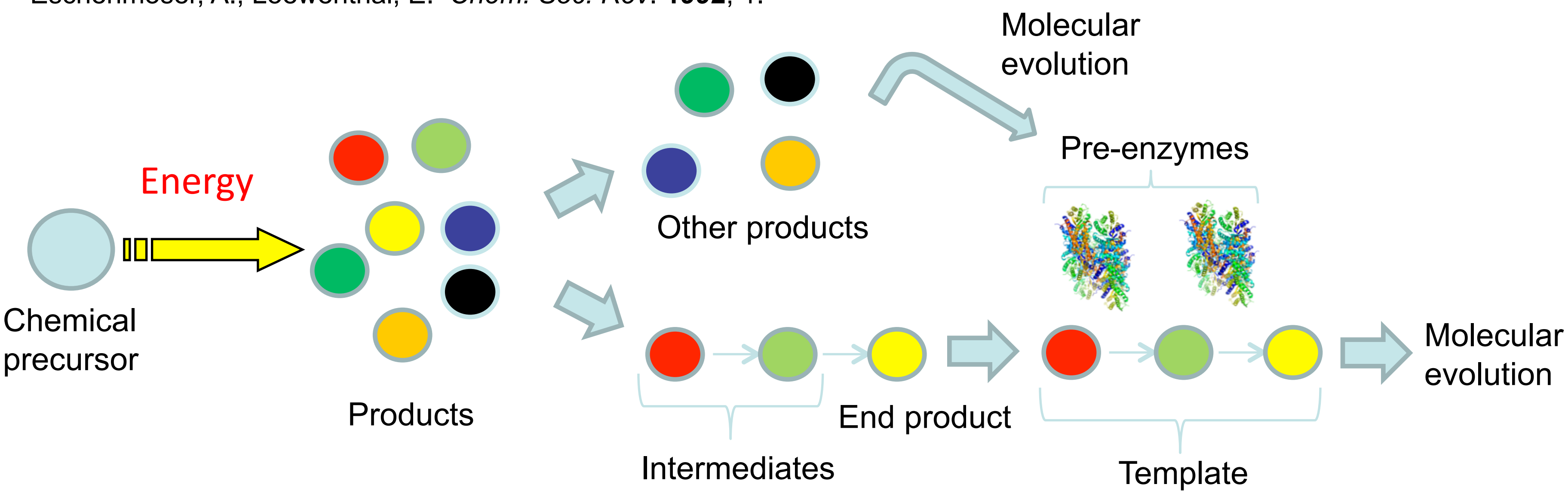
General criteria for validating a prebiotic process

Criterion of simplicity

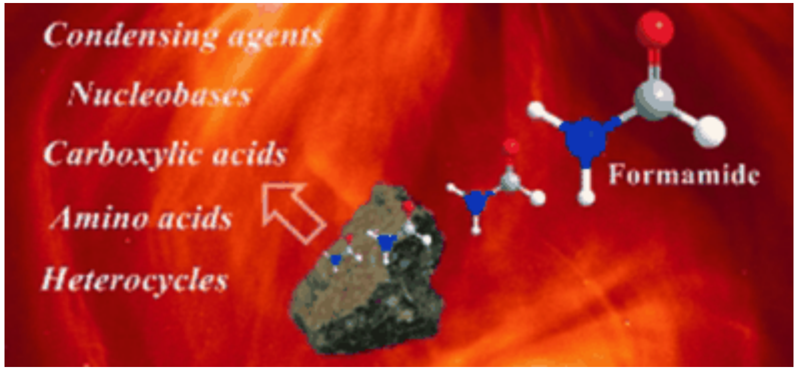


Criterion of Chemiomimesis

"*certain biosynthetic pathways can be considered as chemiomimetic of early prebiotic chemistry*"
Eschenmoser, A.; Loewenthal, E. *Chem. Soc. Rev*. **1992**, 1.

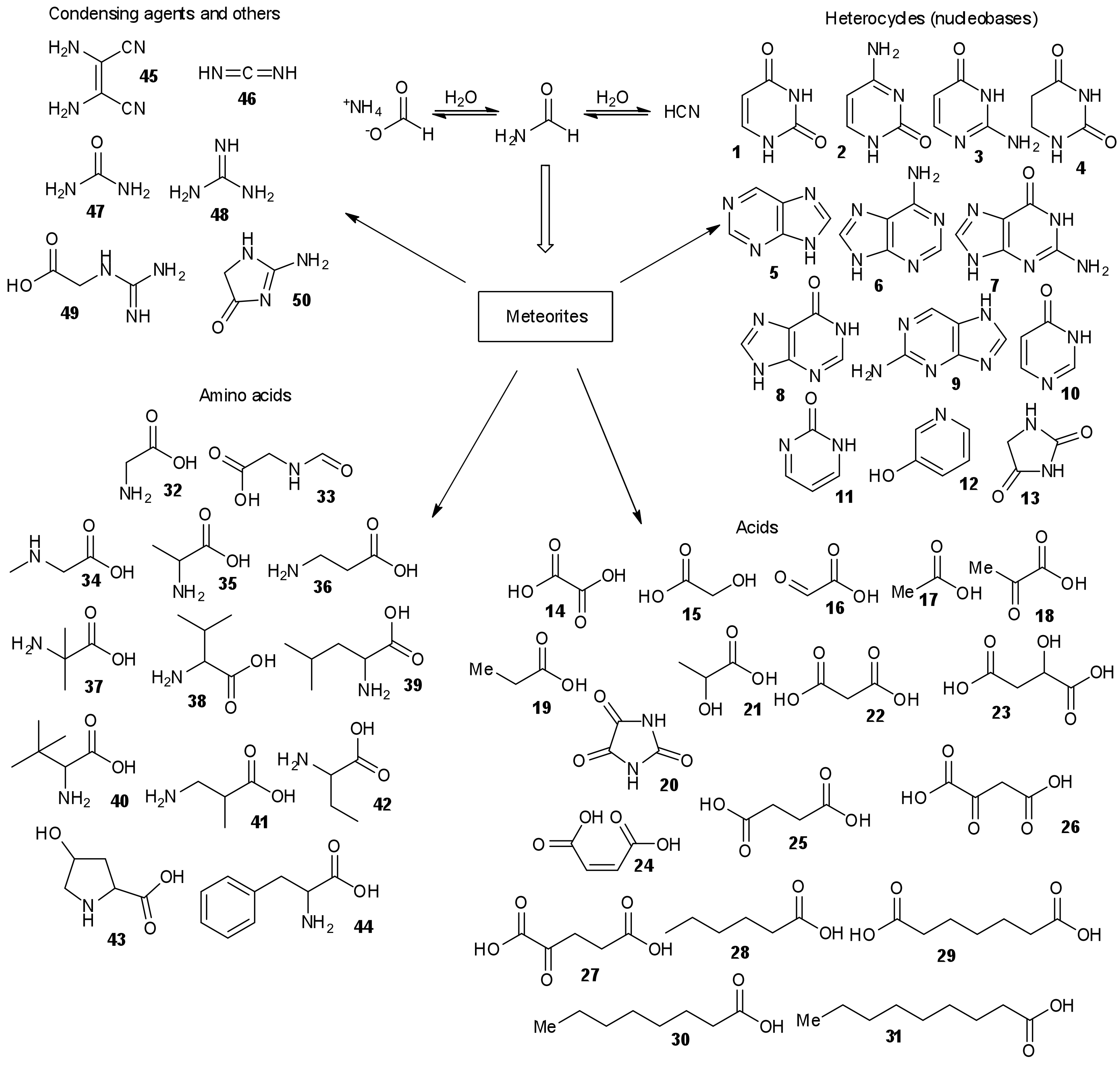


Prof. Raffaele Saladino[1,*],
Dr. Giorgia Botta[1],
Dr. Michela Delfino[1] and
Prof. Ernesto Di Mauro[2]

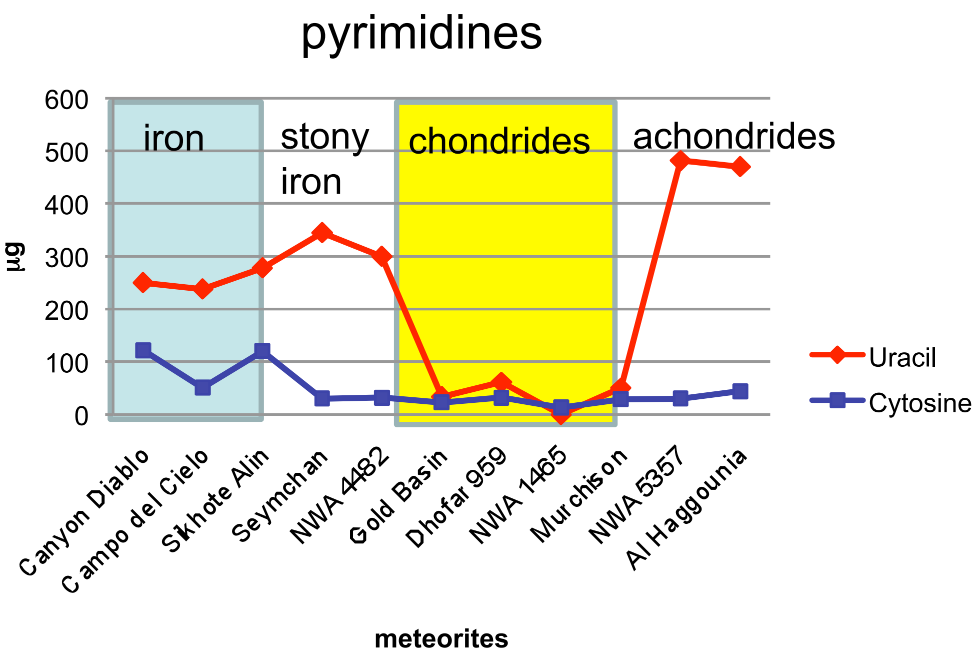


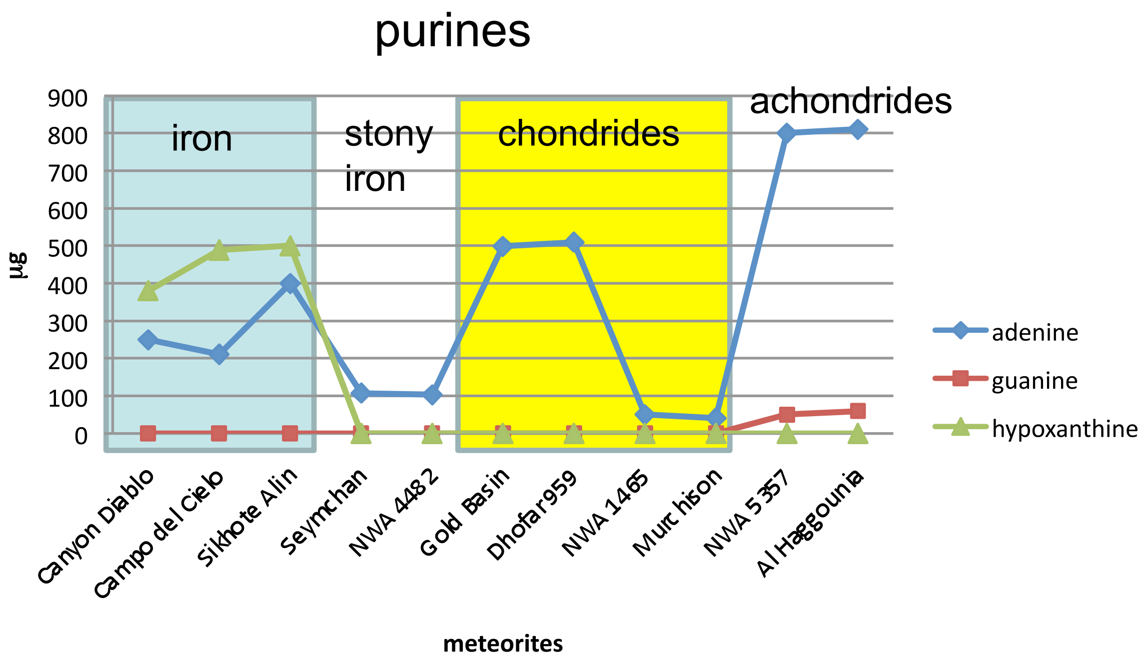
Chemistry - A European Journal
Volume 19, Issue 50,
pages 16916–16922, December 9, 2013


Iron meteorites
Canyon Diablo
Campo del Cielo
Sikhote Alin
Stony Iron meteorites
NWA 4482
Achondrites meteorites
NWA 5357
Al Haggounia
Chondrites meteorites
Gold Basin
Murchison
Dhofar 959
NWA 1465



Condensing agents and others
Heterocycles (nucleobases)
Meteorites
Amino acids
Acids
H2O
HCN


pyrimidines
600
500
400
300
200
100
0
µg
iron
stony iron
chondrides
achondrides
Canyon Diablo
Campo del Cielo
Sikhote Alin
Seymchan
NWA 4482
Gold Basin
Dhofar 959
NWA 1465
Murchison
NWA 5357
Al Haggounia
meteorites
Uracil
Cytosine


purines
900
800
700
600
500
400
300
200
100
0
µg
iron
stony iron
chondrides
achondrides
Canyon Diablo
Campo del Cielo
Sikhote Alin
Seymchan
NWA 4482
Gold Basin
Dhofar 959
NWA 1465
Murchison
NWA 5357
Al Haggounia
meteorites
adenine
guanine
hypoxanthine

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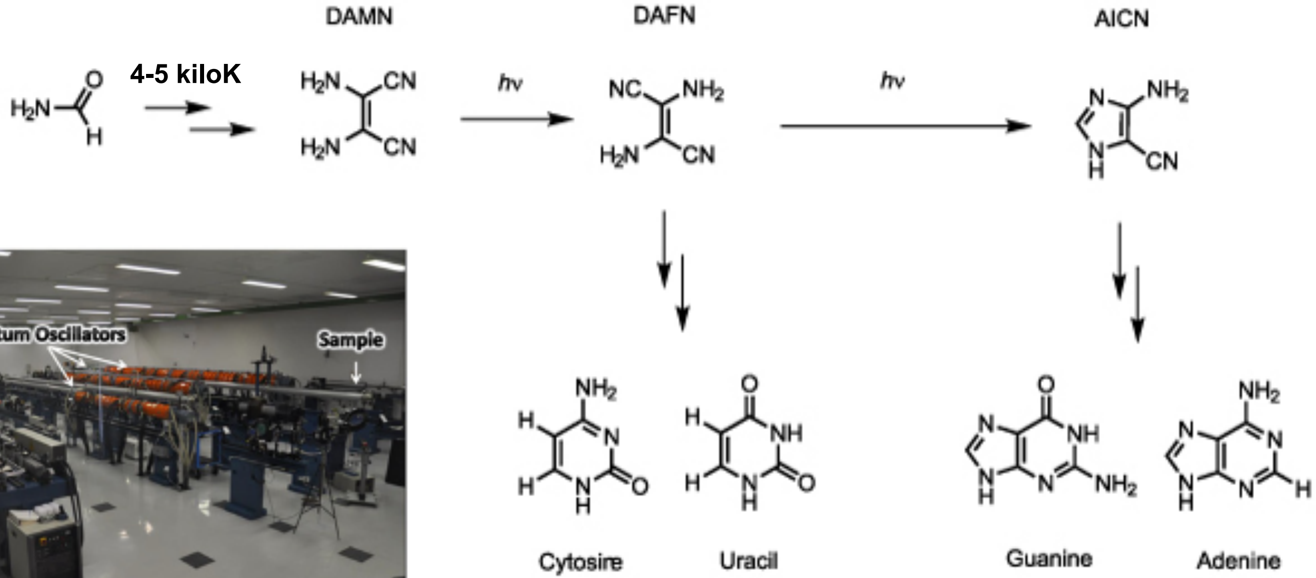
PNAS Celebrating 100 Years 1915-2015

High-energy chemistry of formamide: A unified mechanism of nucleobase formation

Martin Ferus[a,b], David Nesvorný[c], Jiří Šponer[b,d], Petr Kubelík[a,e], Regina Michalčíková[a], Violetta Shestivská[a], Judit E. Šponer[b,d,1], and Svatopluk Civiš[a,1]

[a]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic; [b]Institute of Biophysics, Academy of Sciences of the Czech Republic, 612 65 Brno, Czech Republic; [c]Department of Space Studies, Southwest Research Institute, Boulder, CO 80302; [d]Central European Institute of Technology, Masaryk University, 625 00 Brno, Czech Republic; and [e]Institute of Physics, Academy of Sciences of the Czech Republic, 182 21 Prague, Czech Republic

PNAS | **January 20, 2015** | vol. 112 | no. 3 | **657–662**



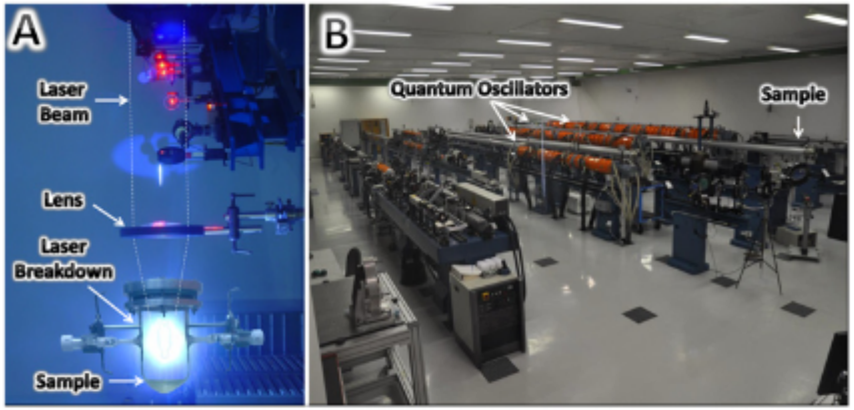
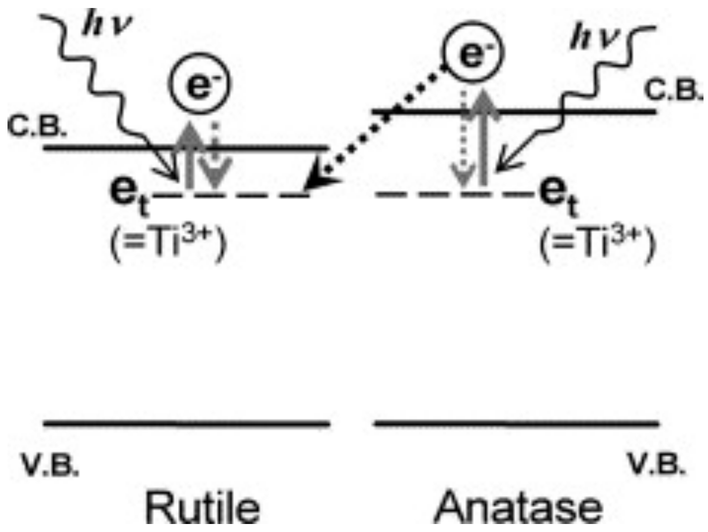
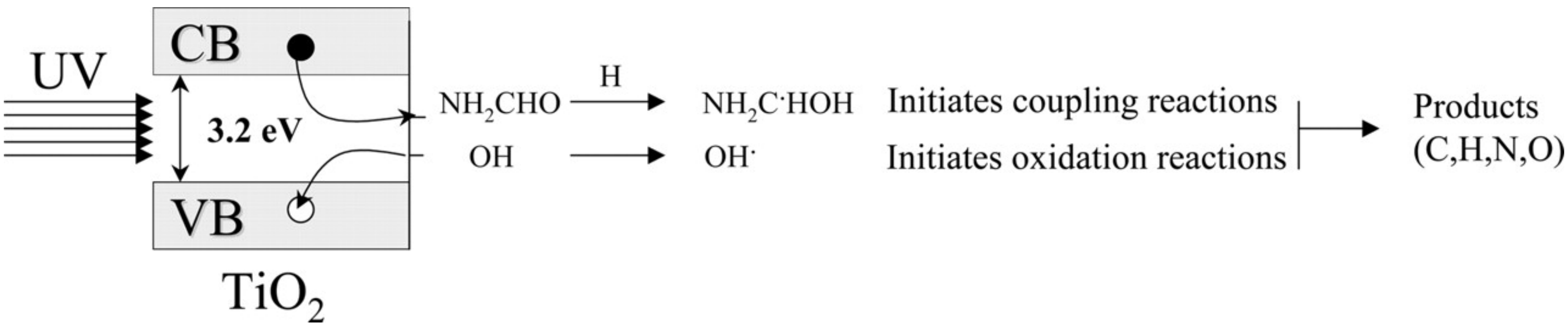


Fig. 2. (*A*) Experimental set-up used for the formamide irradiation. (*B*) Laser hall with the sample placed at the end of the beam line.

Moving towards the metabolism
Titanium dioxide, photochemical conditions

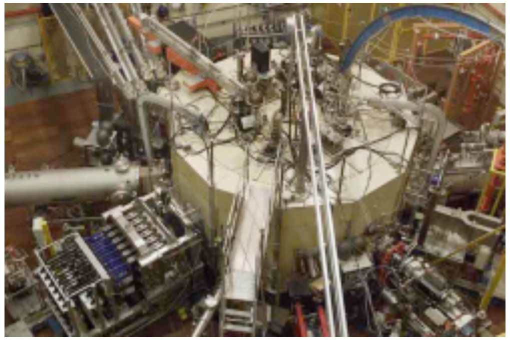

hν
e⁻
C.B.
e_t
(=Ti³⁺)
V.B.
Rutile
Anatase

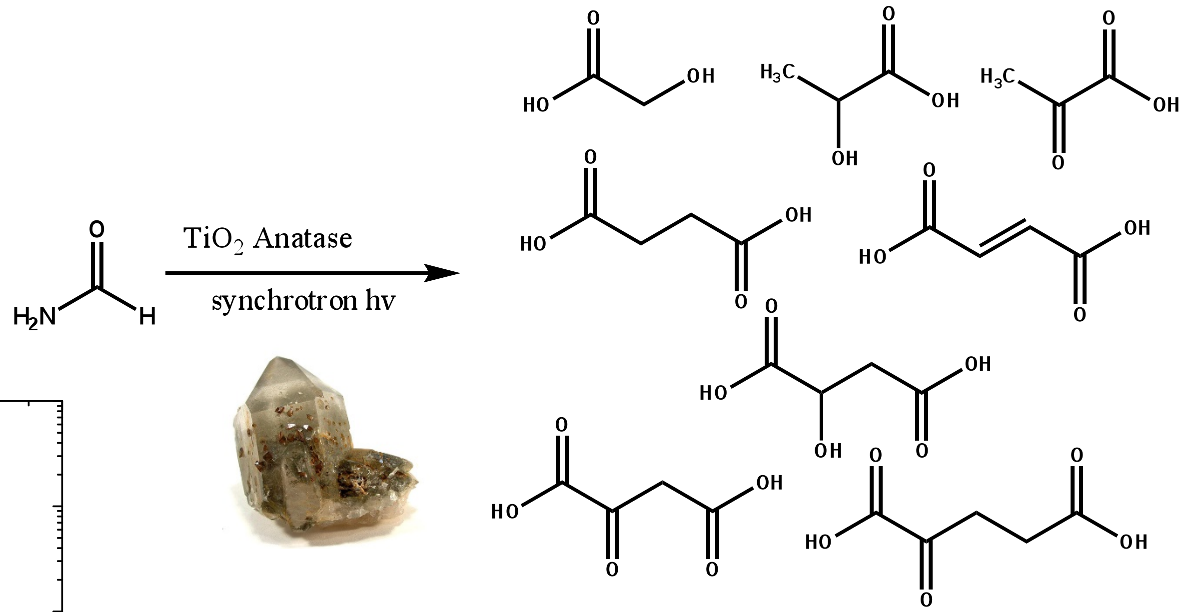

UV
CB
3.2 eV
VB
TiO2
H
NH2CHO → NH2C·HOH
OH → OH·
Initiates coupling reactions
Initiates oxidation reactions
Products
(C,H,N,O)

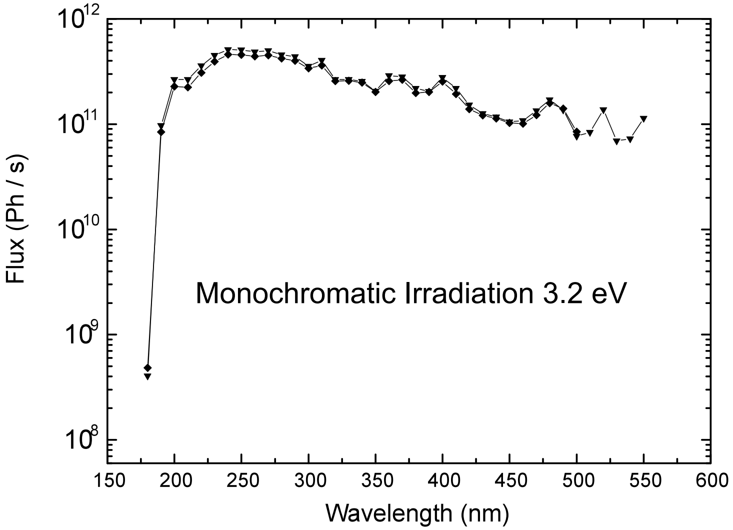
Photochemical Synthesis of Citric Acid Cycle Intermediates Based on Titanium Dioxide

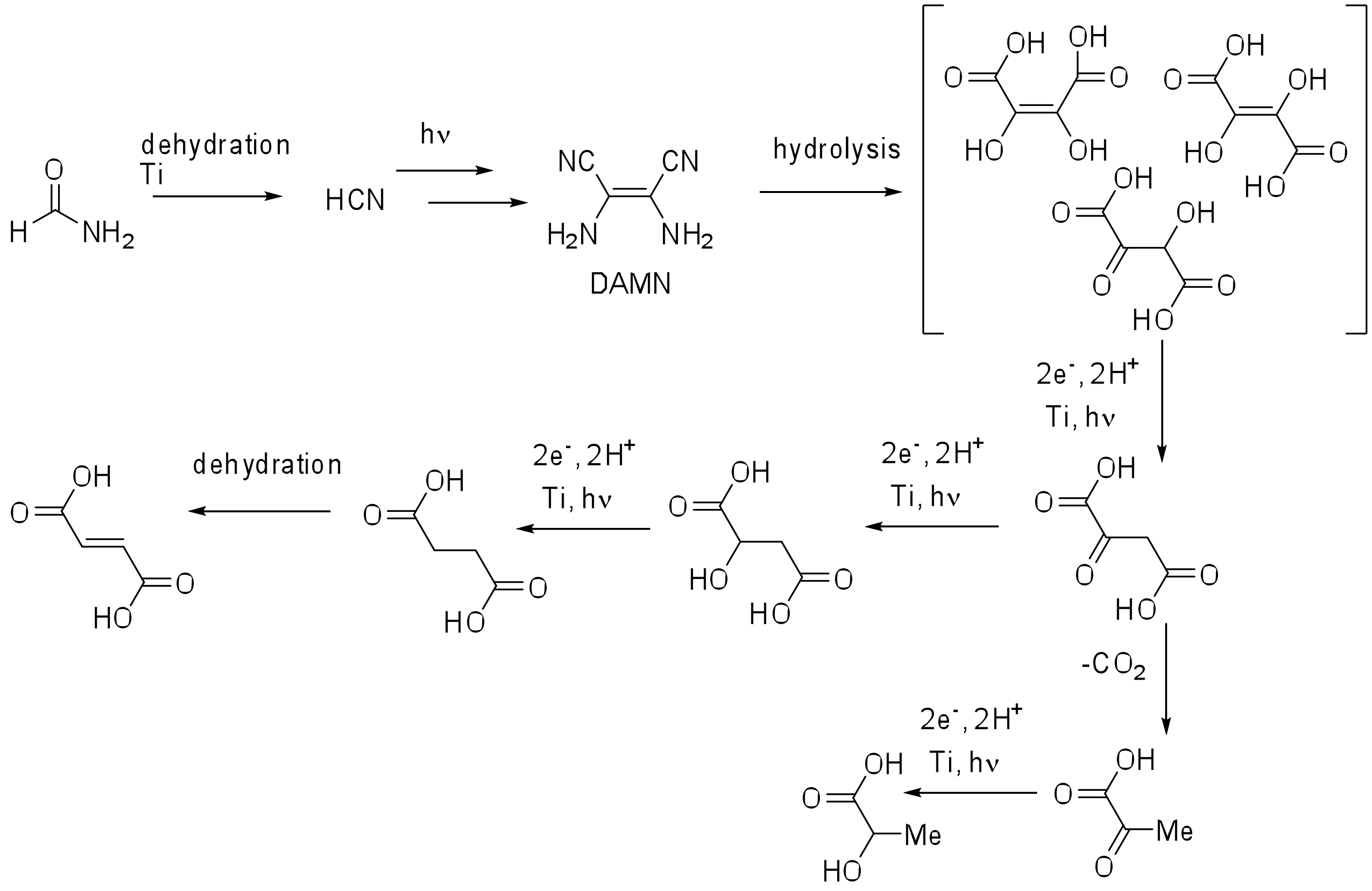
To cite this article:
Raffaele Saladino, John Robert Brucato, Antonio De Sio, Giorgia Botta, Emanuele Pace, and Lisa Gambicorti. Astrobiology. October 2011, 11(8): 815-824. doi:10.1089/ast.2011.0652.

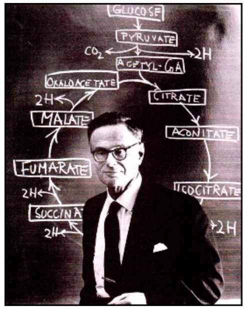
Published in Volume: 11 Issue 8: October 18, 2011



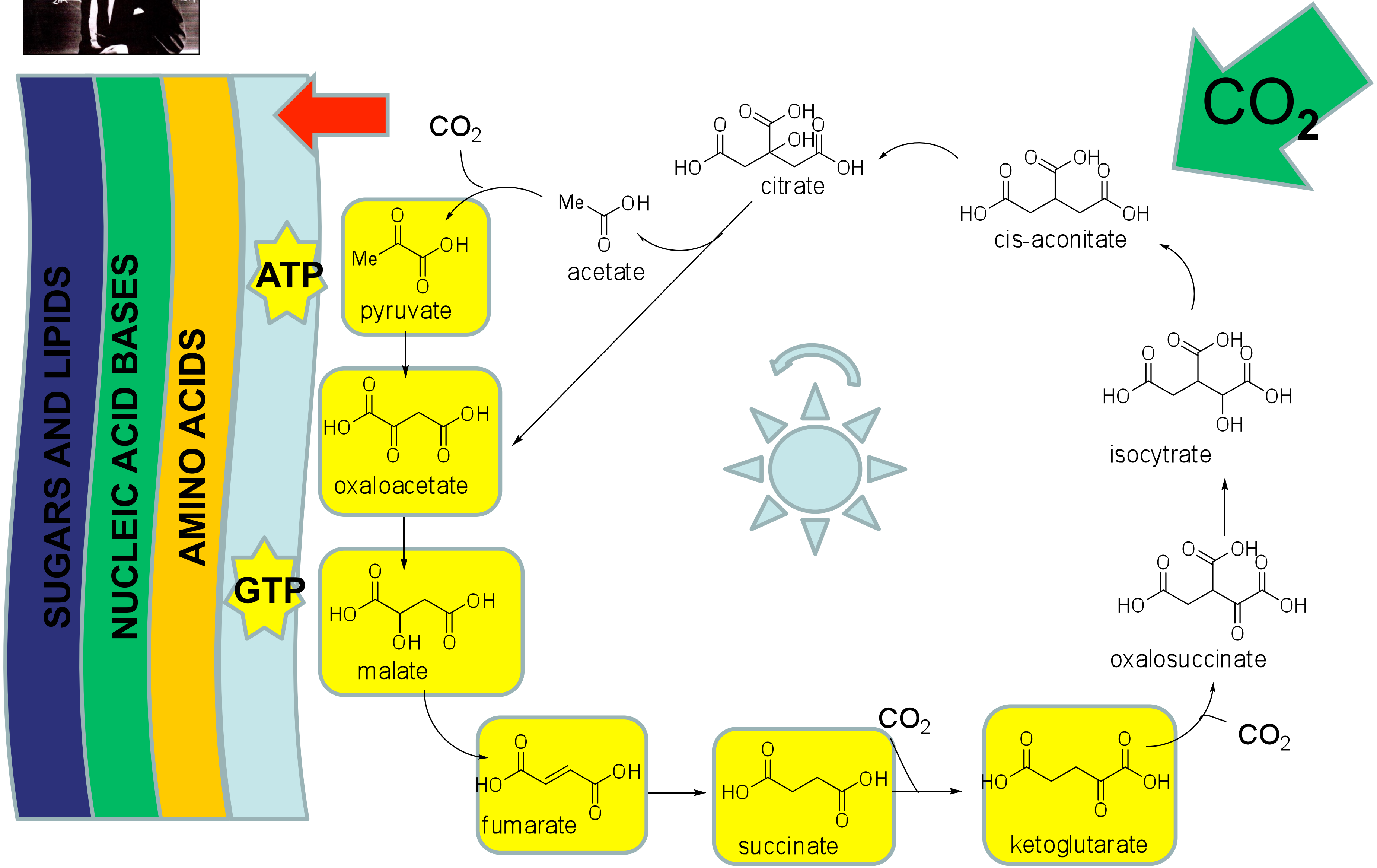


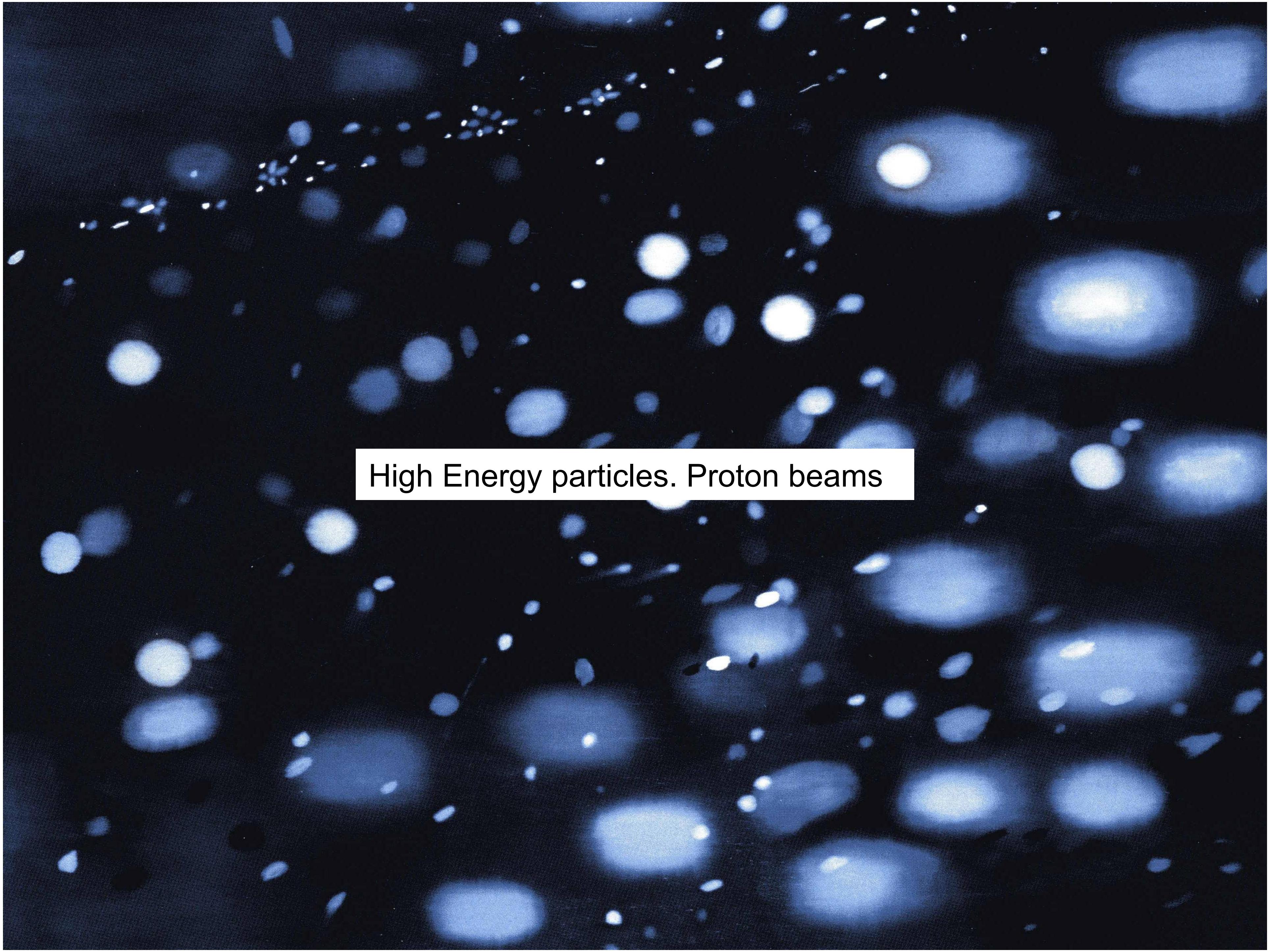



dehydration
Ti
HCN
hν
DAMN
hydrolysis
2e⁻, 2H⁺
Ti, hν
-CO2
dehydration



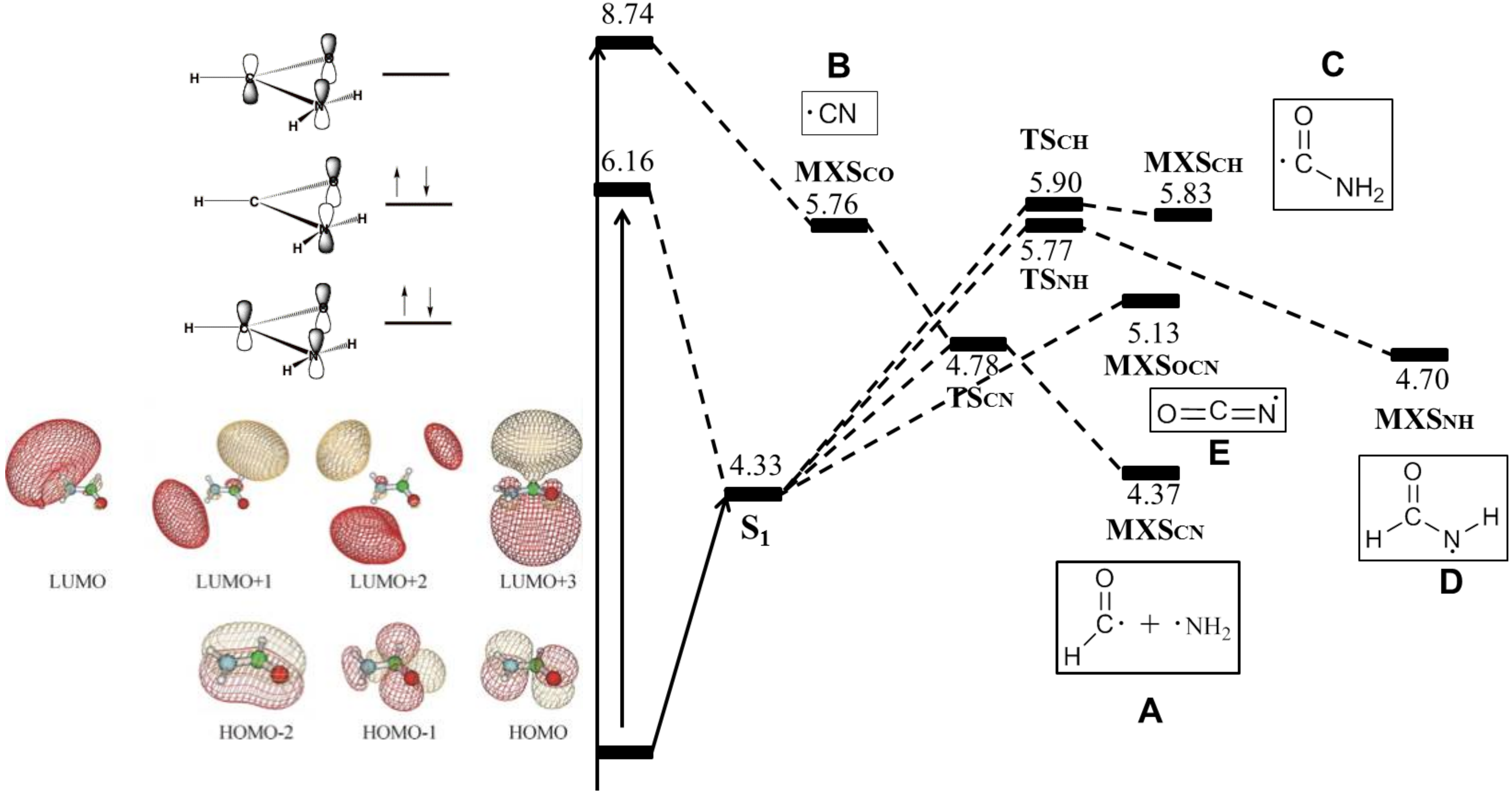
Reductive citric acid cycle





High Energy particles. Proton beams

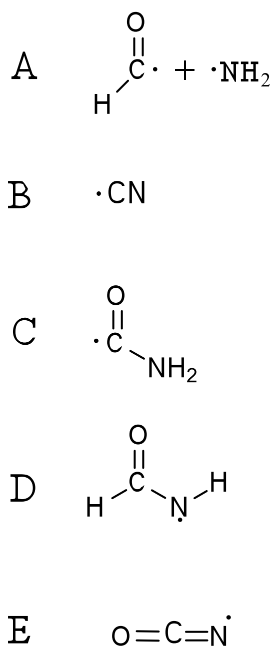
MO-π Electronic Stuctures and excited states profiles

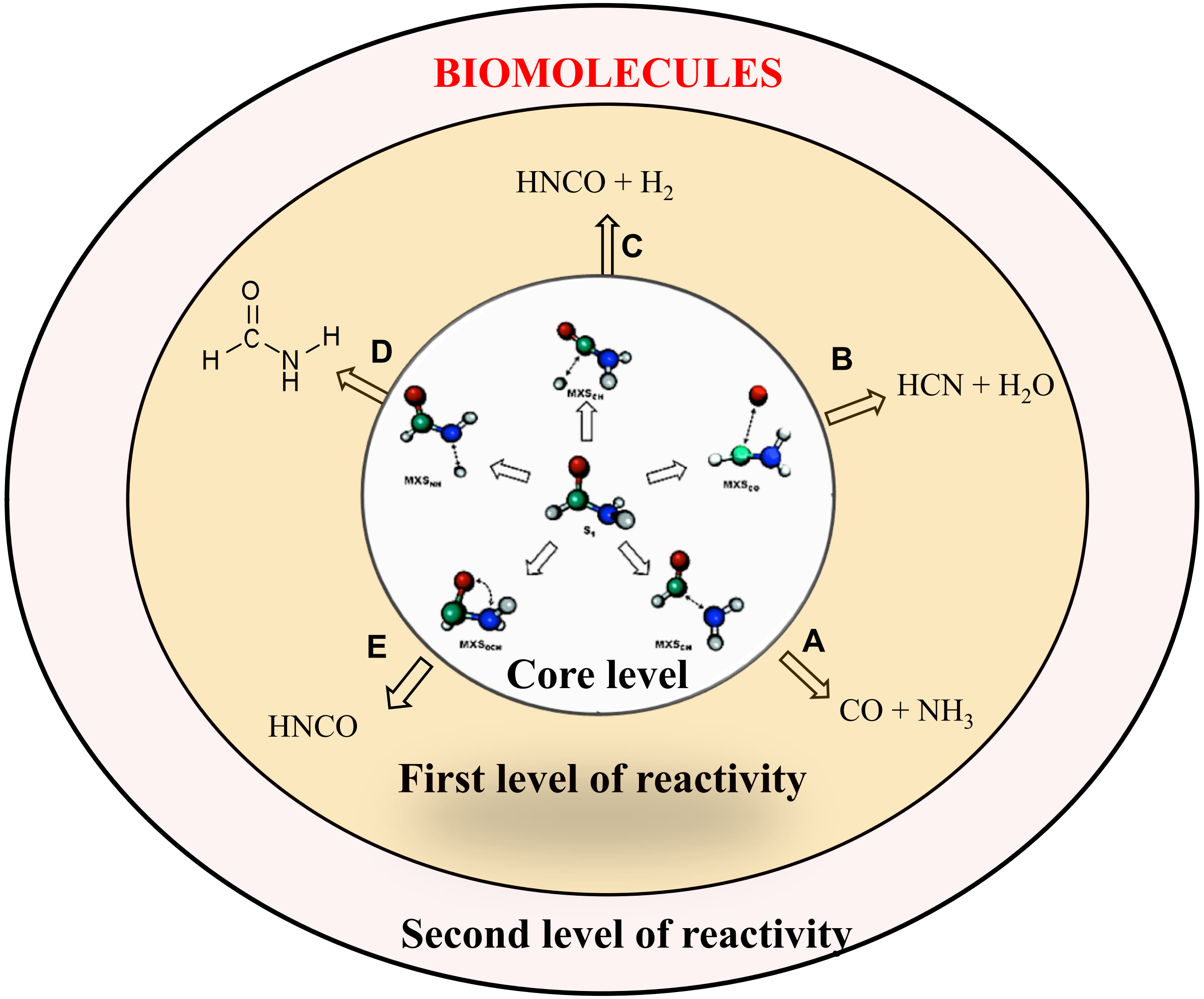


After the interaction with radiation, the formamide can be excited to high energy levels from which the molecule can be dissociated Yielding radical species, mainly centered at the N or C atoms. In figure we describes the energy profile for these processes. This is the Core of reactivity of formamide.

Formamide dissociation processes

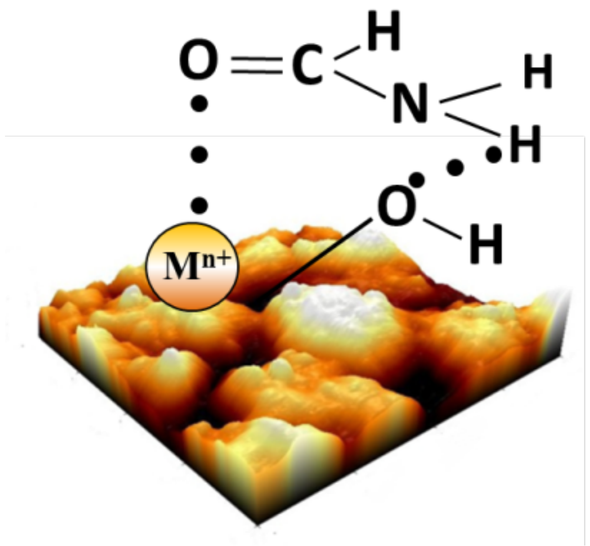
Radical Species

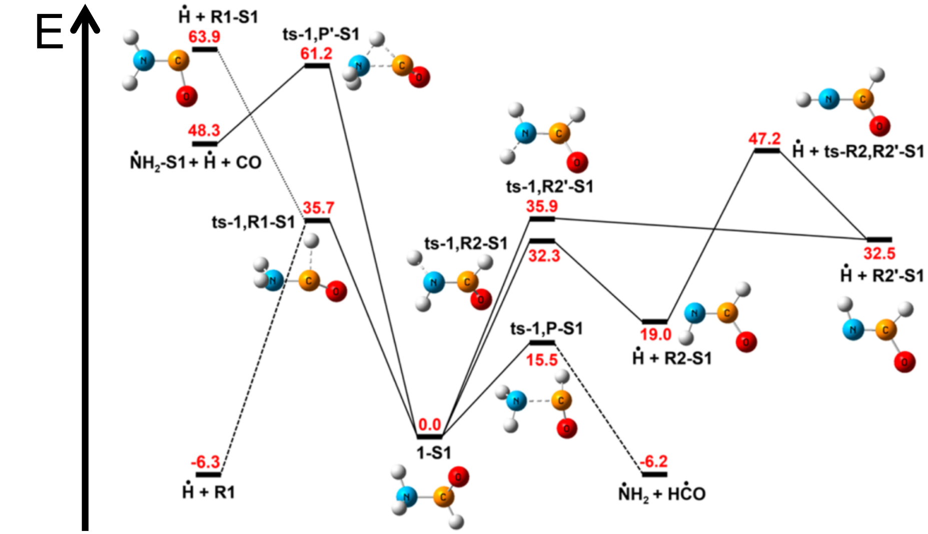


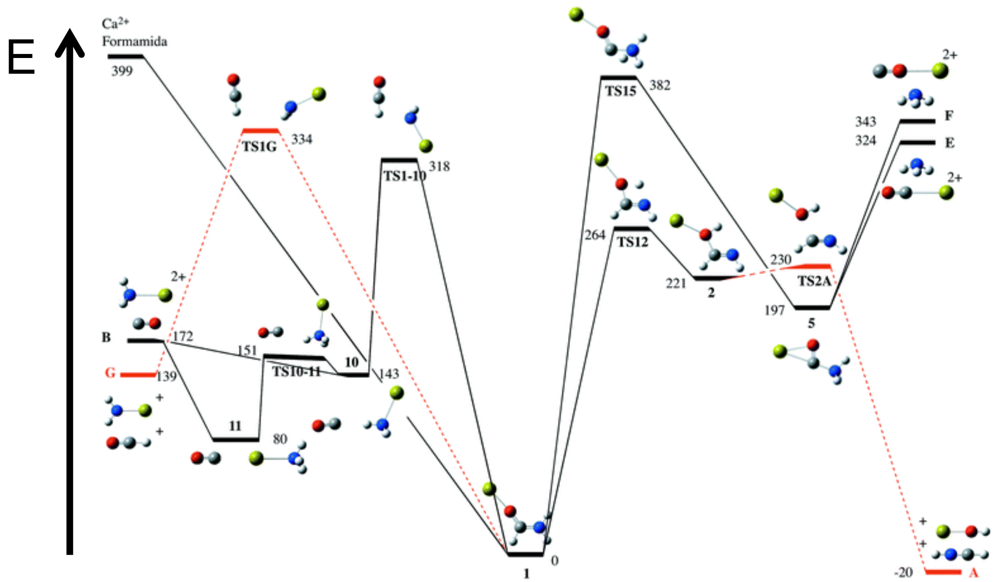


If radicals are quenched inside the first coordination sphere, as for example by hydrogen atom abstraction processes, they will produce simple compounds such as carbon monoxide (CO), hydrogen cyanide (HCN) and ammonia (NH3) which are not directly involved in the life of the cell. We can call this phenomena as the first level of reactivity of formamide.

Effect of minerals on energy profiles

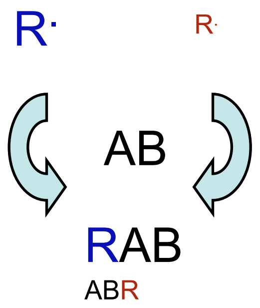




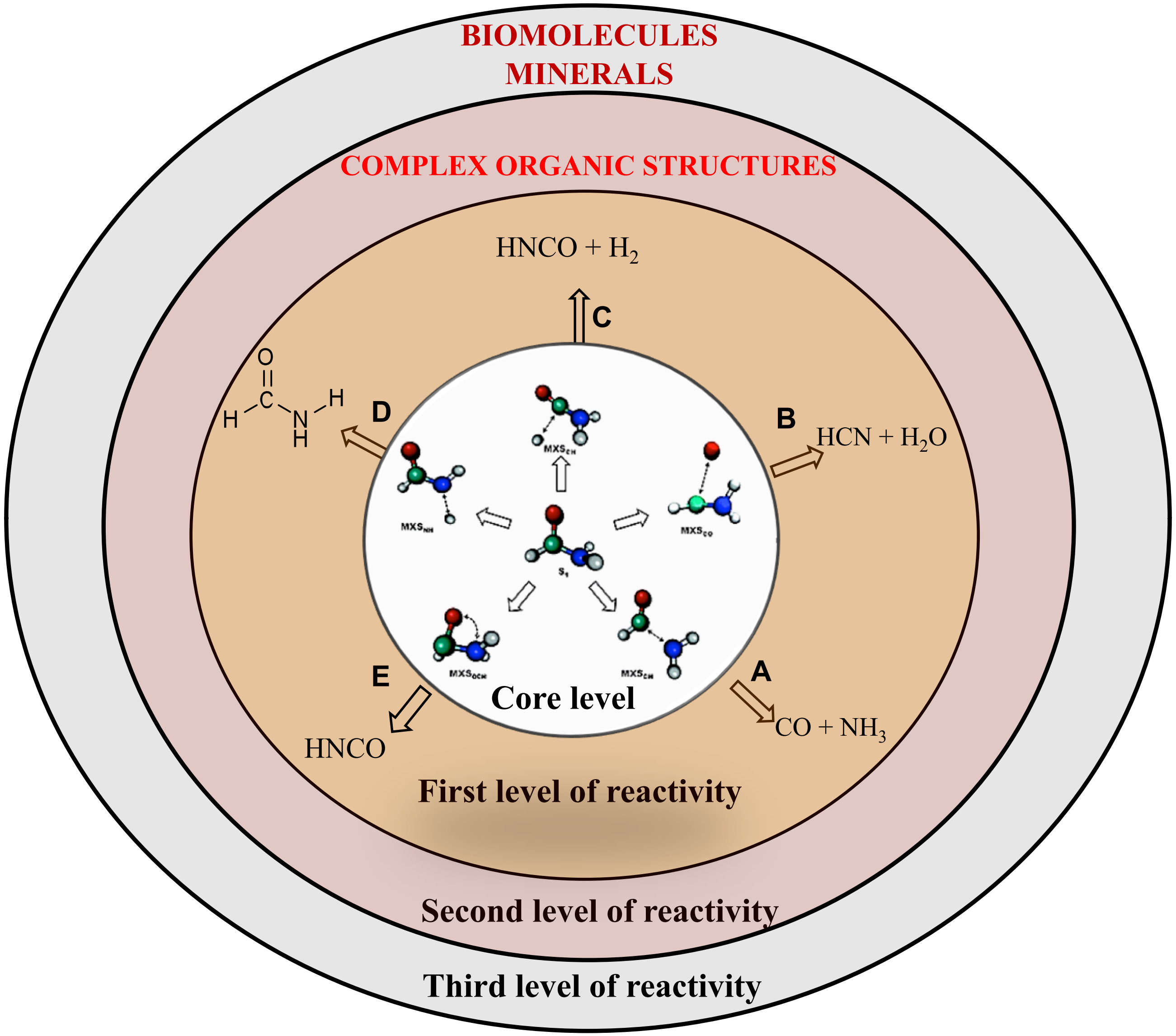


In this context it is worth to note that minerals can change the energy profiles for the formamide dissociation thus tuning the Reactivity and the selectivity of the transformations. This is the third level of reactivity for formamide, the most useful for the Formation of biomolecules.

Formamide dissociation processes



SELECTIVITY



Antol I. et al. QM/MM non-adiabatic decay dynamics of formamide in polar and non-polar solvents. Phys. Chem. Chem. Phys., 2012,14, 13262-13272

PNAS
Proceedings of the National Academy of Sciences of the United States of America www.pnas.org

PNAS Celebrating 100 Years 1915-2015

Meteorite-catalyzed syntheses of nucleosides and of other prebiotic compounds from formamide under proton irradiation

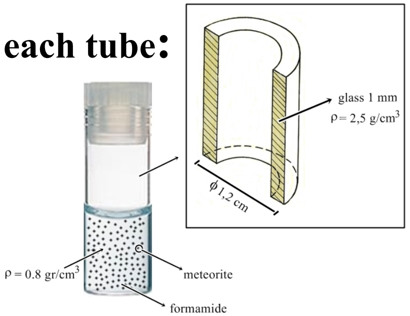
Raffaele Saladino[a,1], Eleonora Carota[a], Giorgia Botta[a], Mikhail Kapralov[b], Gennady N. Timoshenko[b], Alexei Y. Rozanov[b], Eugene Krasavin[b], and Ernesto Di Mauro[c,1]

[a]Dipartimento di Scienze Ecologiche e Biologiche, Università della Tuscia, 01100 Viterbo, Italy; [b]Laboratory of Radiation Biology, Joint Institute for Nuclear Research, 141980 Dubna, Russia; and [c]Istituto Pasteur–Fondazione Cenci Bolognetti, c/o Dipartimento di Biologia e Biotecnologie "Charles Darwin," Sapienza–Università di Roma, Rome 00185, Italy

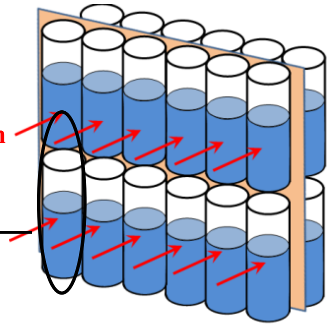
Proc. Natl. Acad. Sci. USA 2015 112 (23) 7109-7110

JINR-Phasotron

In each tube:

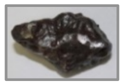


P
170 MeV
LET= 0,57 keV/µm
t= 3min
T= 25°C



	Name[a]	Class	Type
1 2	**Canyon Diablo** **Campo del Cielo**	Iron Iron	IA Hexaoctahedrite normal IAB Hexaoctahedrite coarse
3	**NWA4482**	Stony iron	Pallasite Anomalous
4 5 6 7	**NWA2828** **Gold basin** **Orgueil** **NWA1465**	Chondrite Chondrite Chondrite Chondrite	Enstatite Ordinary Carbonaceoous LV3 Anomalous
8 9	**NWA5357** **Al Haggounia**	Achondrites Achondrites	Diogenite Aubrite

Iron meteorites



Canyon Diablo

Campo del Cielo

Stony iron meteorites

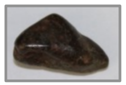
NWA 4482

Achondrites

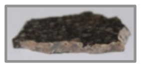
NWA 5357

Al Haggounia

Chondrites



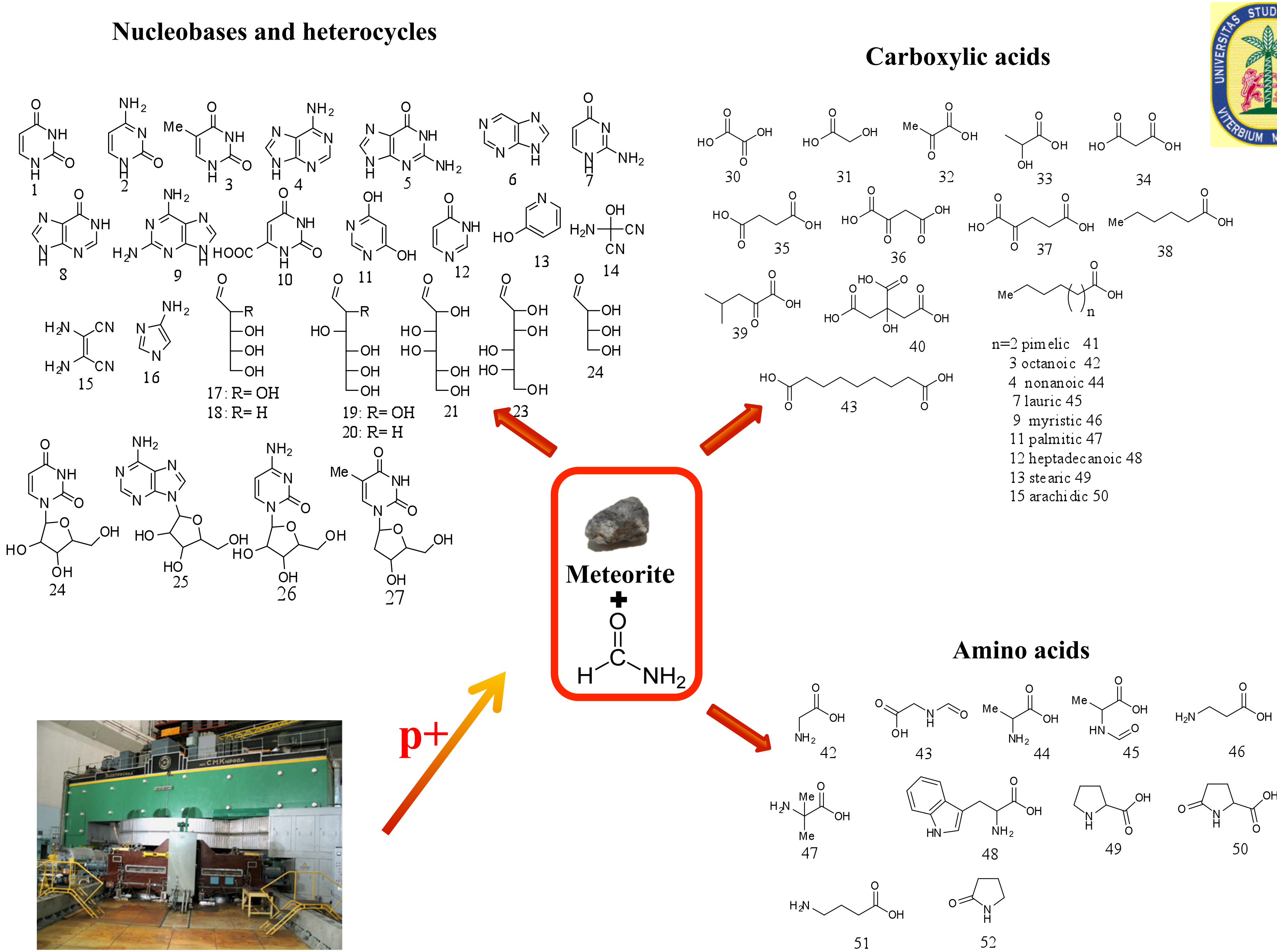
Gold Basin



NWA 1465

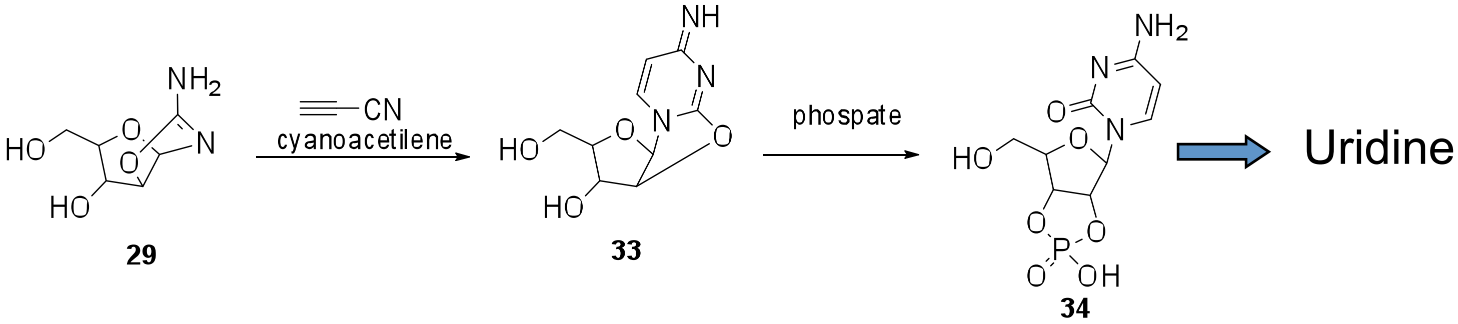
Orgueil

NWA 2828



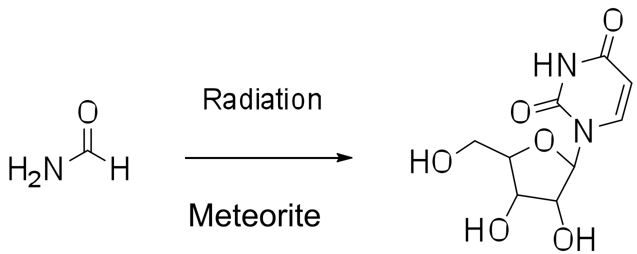
Nucleobases and heterocycles
17: R= OH
18: R= H
19: R= OH
20: R= H
Carboxylic acids
n=2 pimelic 41
3 octanoic 42
4 nonanoic 44
7 lauric 45
9 myristic 46
11 palmitic 47
12 heptadecanoic 48
13 stearic 49
15 arachidic 50
Meteorite
p+
Amino acids

Prebiotic synthesis of nucleosides



Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions
Matthew W. Powner, Béatrice Gerland & John D. Sutherland

12 steps



Only one step!

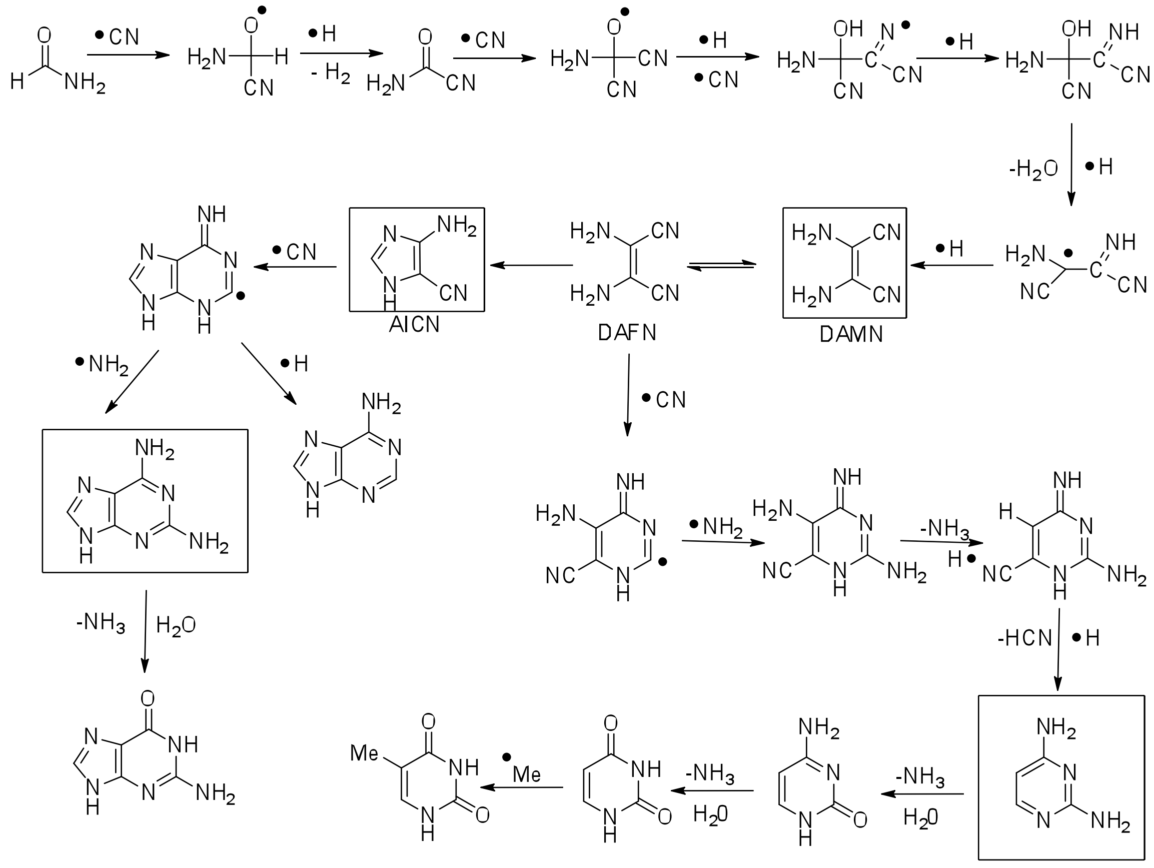
With respect to other synthesis reported in the literature, this is the most simple and direct synthesis of a nucleoside under Prebiotic conditions.

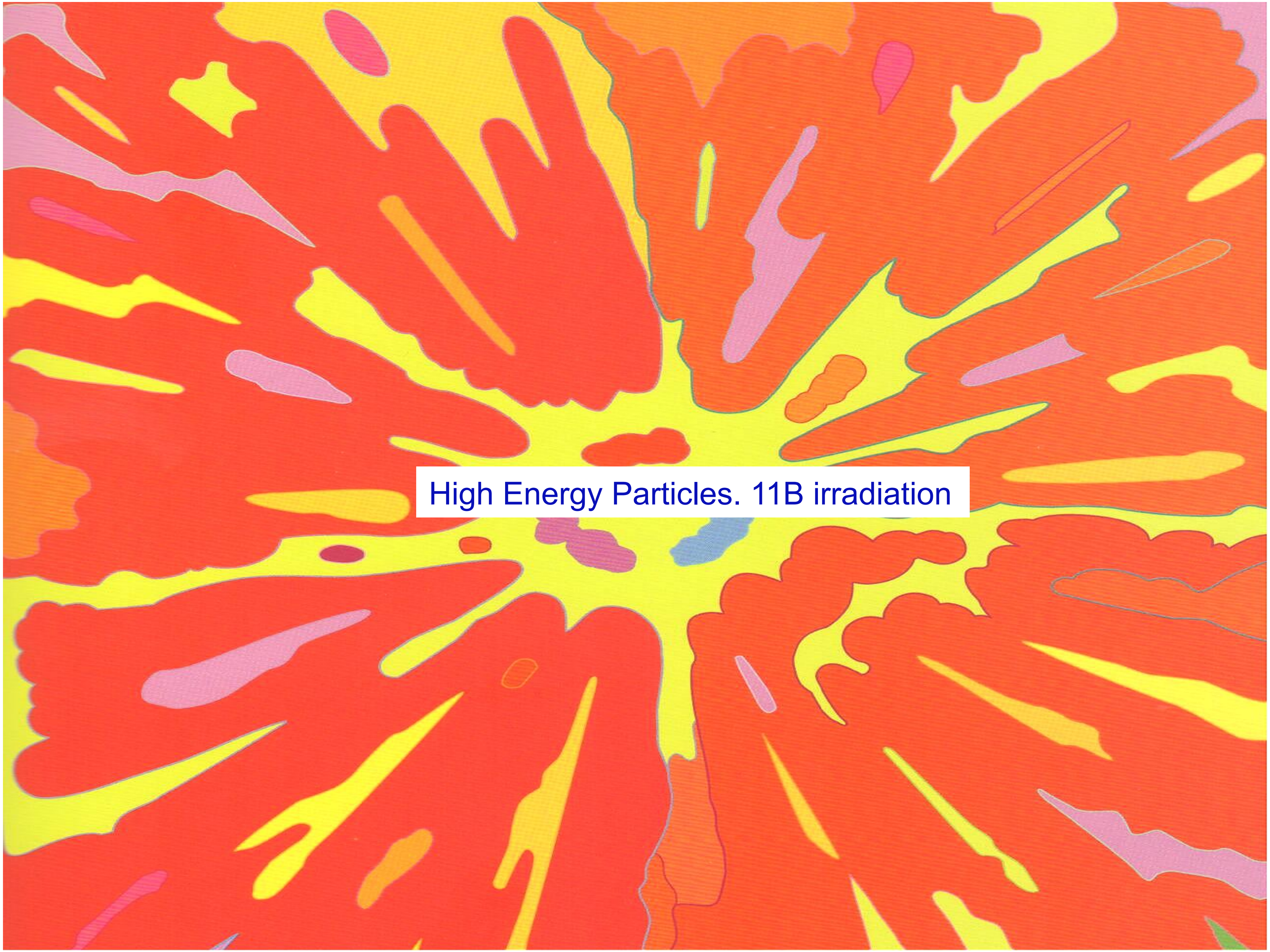
PNAS
Proceedings of the National Academy of Sciences of the United States of America www.pnas.org

PNAS Celebrating 100 Years 1915-2015

High–Energy Chemistry of Formamide: A Unified Mechanism of Nucleic Base Formation

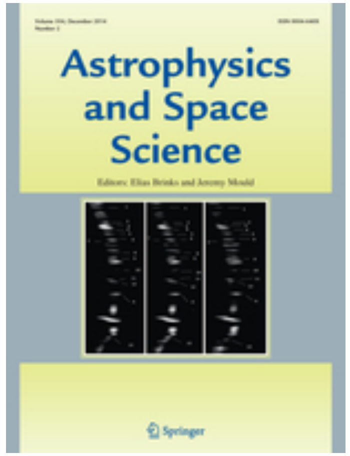
Martin Ferus,[1,2] David Nesvorný,[3] Jiří Šponer,[2,4] Petr Kubelík[1] Regina Michalčíková,[1] Violetta Shestivská,[1] Judit E. Šponer,[2,4,*] and Svatopluk Civiš [1,*]





High Energy Particles. 11B irradiation

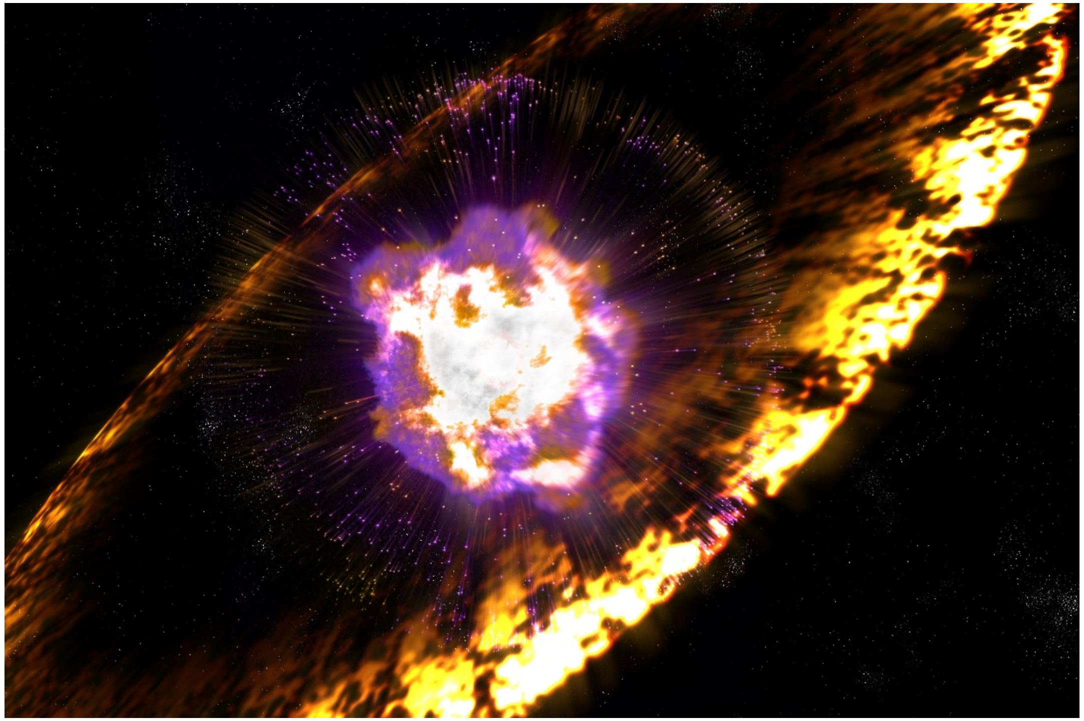
Boron as component of primary Cosmic Ray Radiation



Astrophysics and Space Science **12** (1971) 98–103.

THE RELATIVE ABUNDANCES OF THE ISOTOPES OF LITHIUM, BERYLLIUM AND BORON IN THE PRIMARY COSMIC RADIATION

N. DURGAPRASAD
Tata Institute of Fundamental Research, Bombay, India



^{11}B:^{10}B = 2.6

nature
International weekly journal of science

article

Nature **243**, 204 - 207 (25 May 1973); doi:10.1038/243204a0

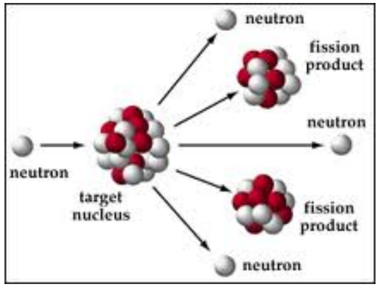
Cosmic Abundance of Boron

A. G. W. CAMERON[*], S. A. COLGATE[†] & L. GROSSMAN[‡]

[*]Belfer Graduate School of Science, Yeshiva University, New York, and Goddard Institute for Space Studies, NASA, New York
[†]New Mexico Institute of Mining and Technology, Socorro, New Mexico
[‡]Department of Geophysical Sciences, University of Chicago, Chicago, Illinois

The interstellar abudance of boron is of relevant interest for the analysis of chemical evolution in our Galaxy

A) Spallation (fission) reaction: High energy Galactic Cosmic Rays break apart heavier massive nuclei



$^{11}B:^{10}B = 2.5$

B) Fusion reaction: Low energy cosmic rays interaction with interstellar hydrogen and helium in presolar clouds

$^{11}B:^{10}B = 4.0$

Value found
In the Solar System
and meteorites

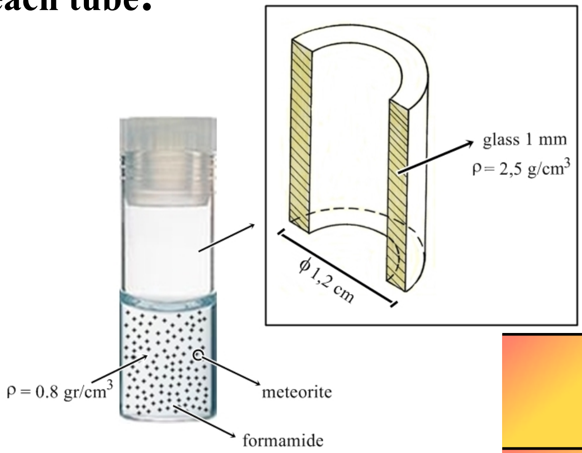
confirming the higher prevalence of ^{11}B in the pre-Solar Nebula

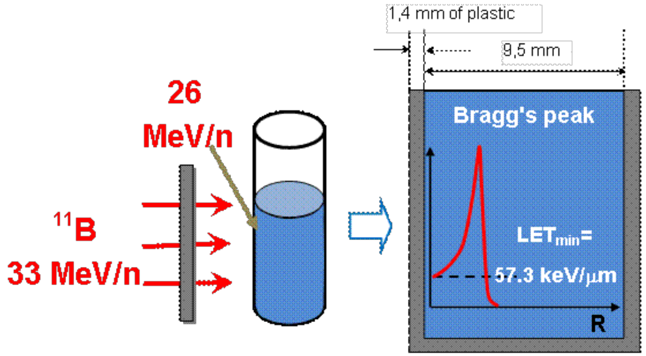
Chaussidon M, Robert F *Nature* **1995**, 374, 337-339

Formamide irradiation at U400M cyclotron

JINR-Cyclotron

In each tube:





Meteorites: Dohfar 959
Gold Basin
NWA1465
Chelyabinsk
NWA 4482

	Name[a]	Class	Type
1	**NWA4482**	Stony iron	Pallasite Anomalous
2	**NWA1465**	Chondrite	Ordinary
3	**Gold basin**	Chondrite	Ordinary
6	**Dhofar**	Chondrite	Ordinary
7	**Chelyabinsk**	Chondrite	Ordinary

Formamide irradiation at U400M cyclotron

In each tube:

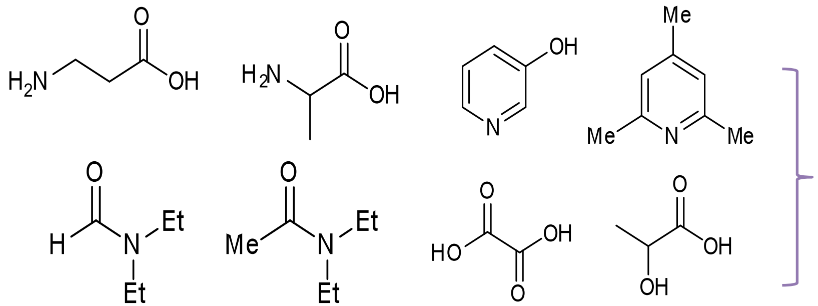
FORMAMIDE + METEORITE

Absence of RADIATION → NO PRODUCTS

FORMAMIDE ALONE

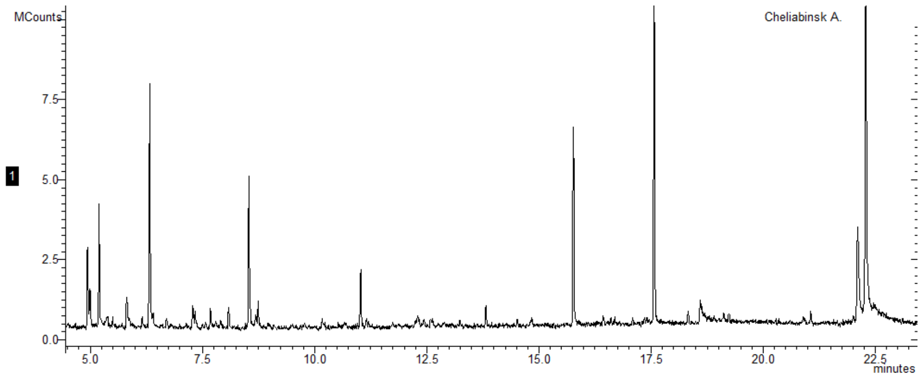
RADIATION →

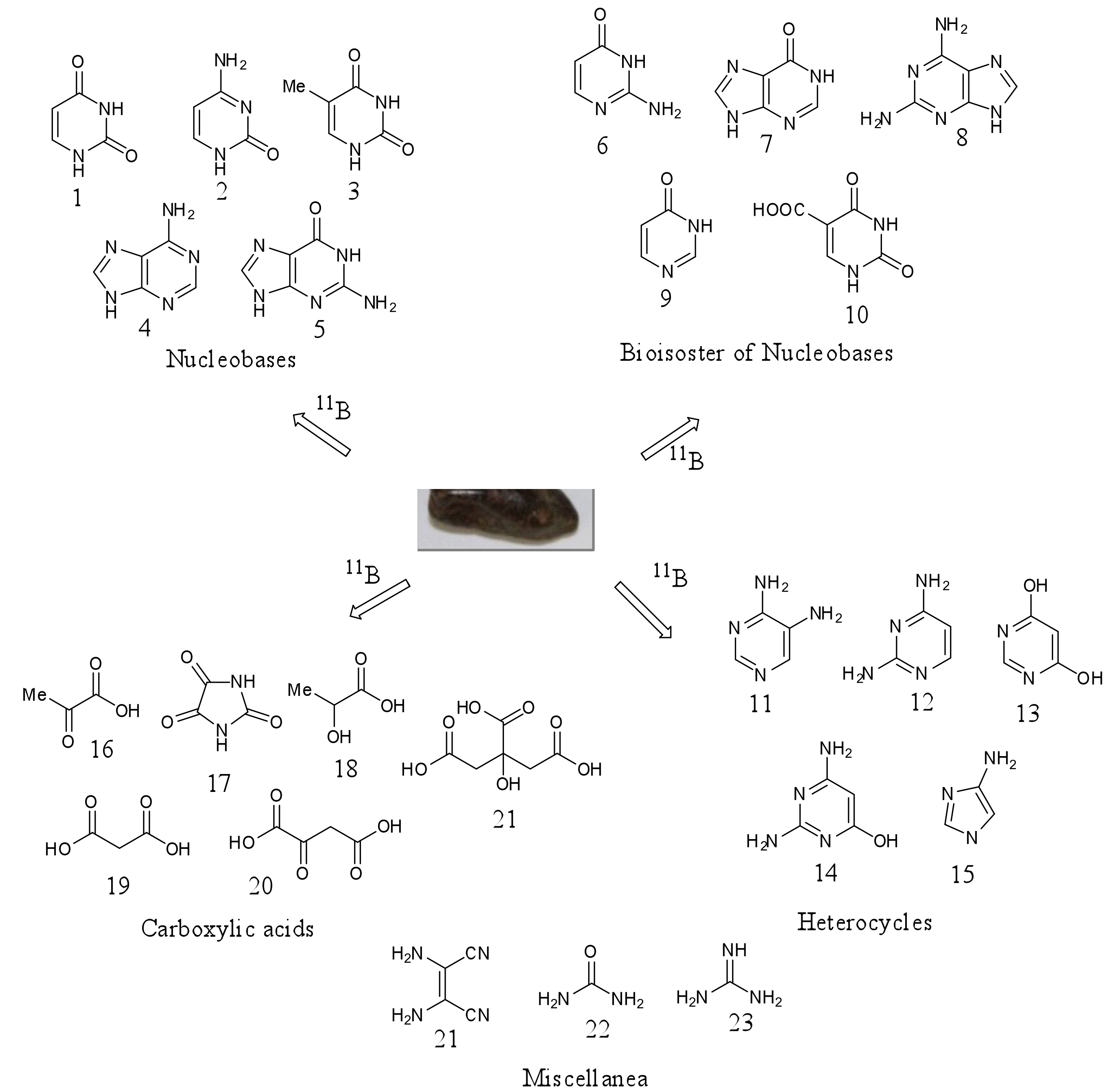
Few amounts



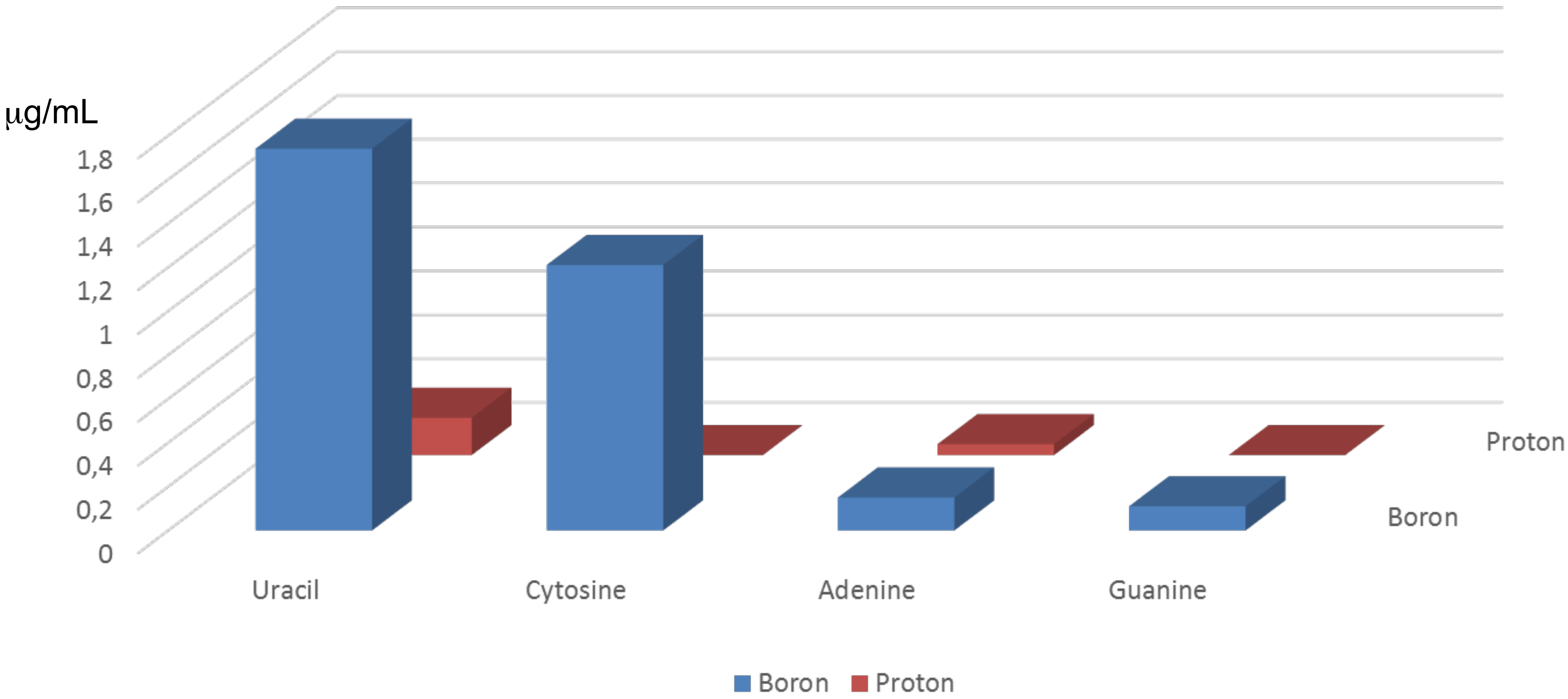
FORMAMIDE + METEORITE

RADIATION →

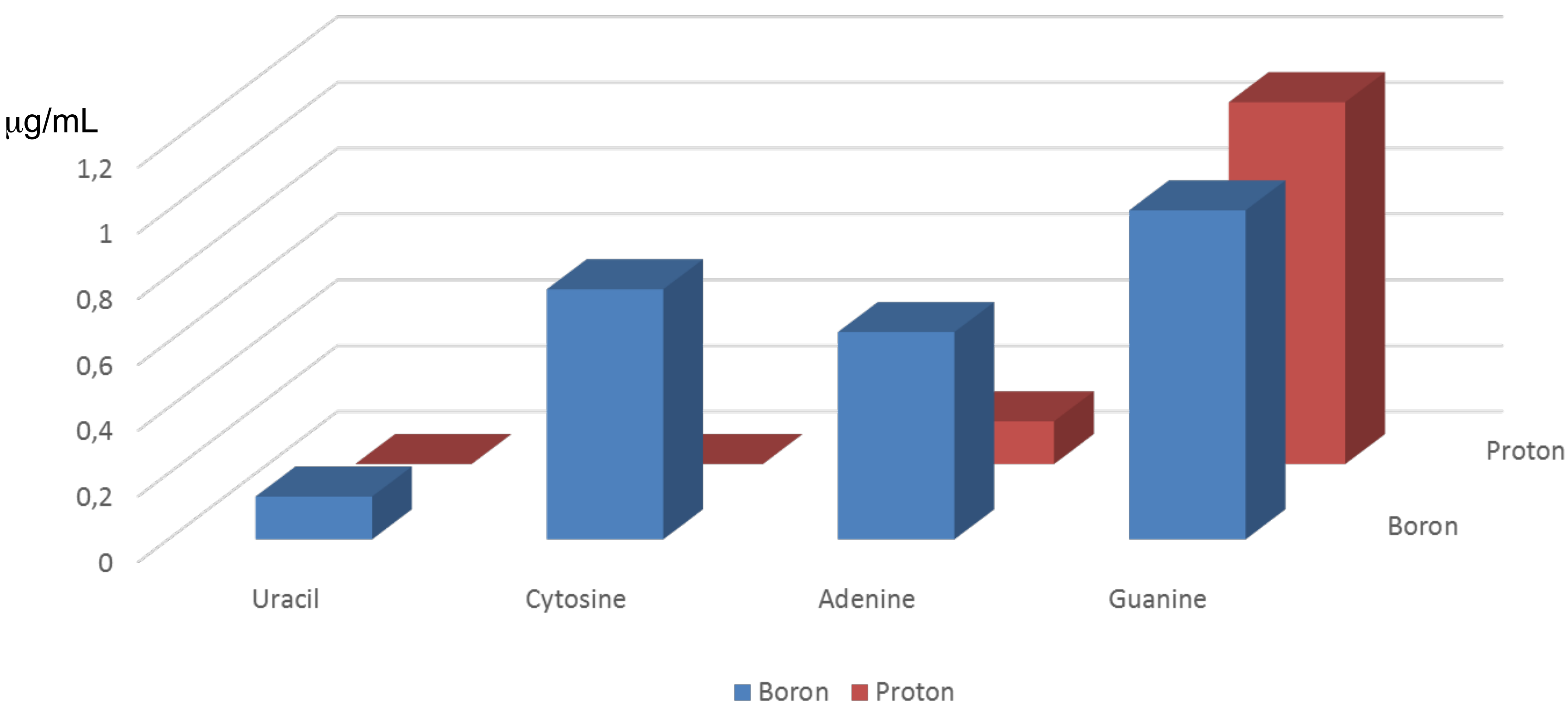



Nucleobases
Bioisoster of Nucleobases
Carboxylic acids
Heterocycles
Miscellanea
11B
11B
11B
11B

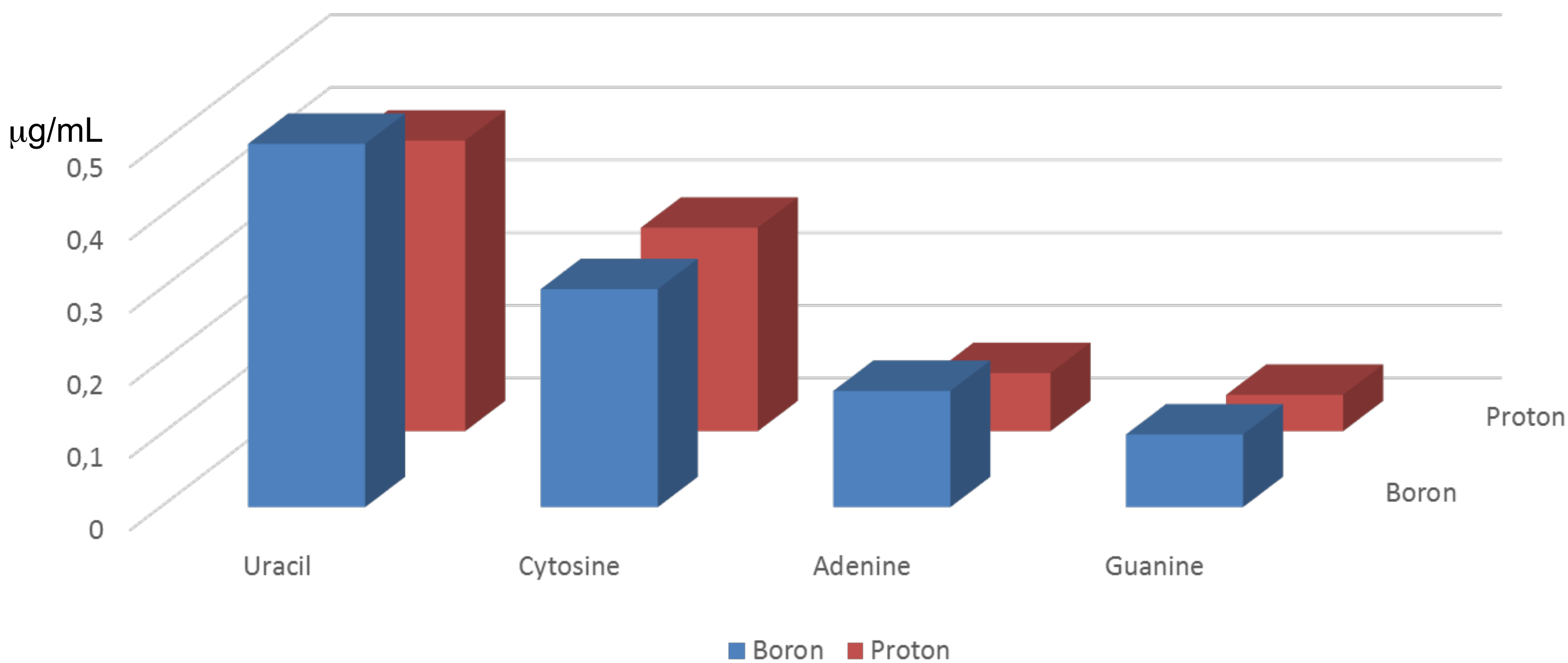
Chelyabinsk-Comparison between ^{11}B and Proton irradiation



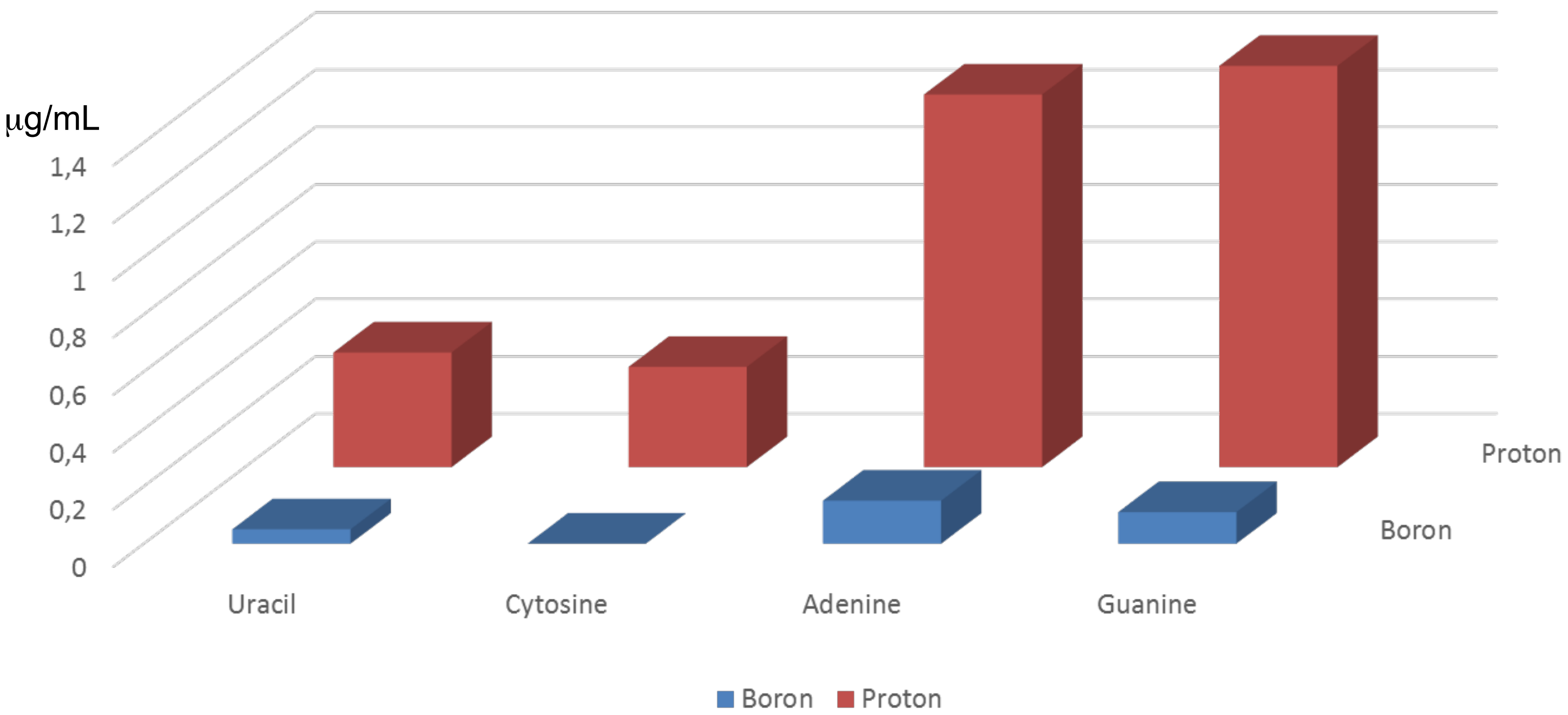
Dhofar-Comparison between ^{11}B and Proton irradiation

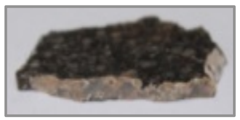


Gold Basin-Comparison between 11B and Proton irradiation



NWA 1465-Comparison between ^{11}B and Proton irradiation





Cite this: *Chem. Soc. Rev.*, 2012, **41**, 5526–5565

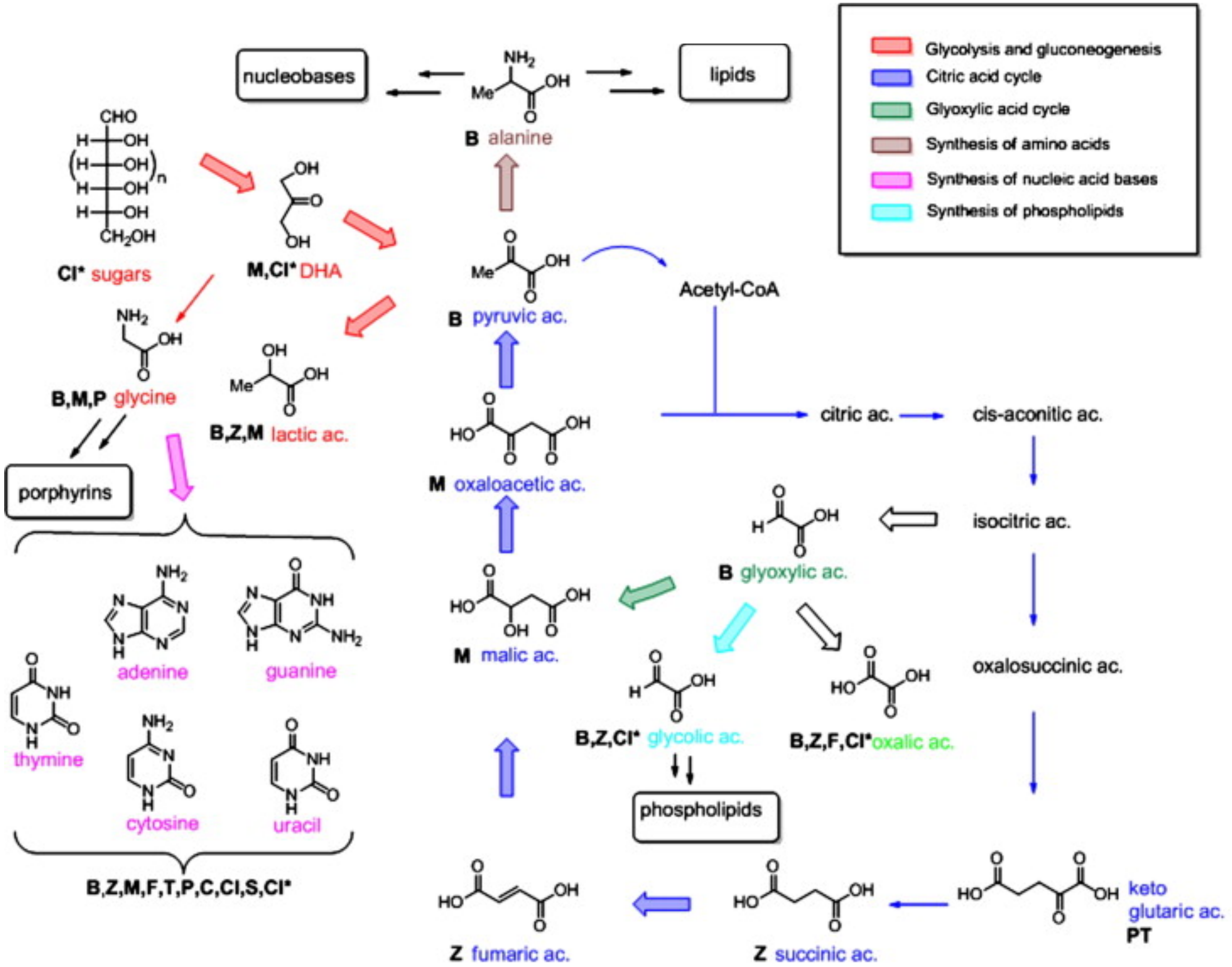
www.rsc.org/csr

CRITICAL REVIEW

Genetics first or metabolism first? The formamide clue†

Raffaele Saladino,*[a] Giorgia Botta,[a] Samanta Pino,[b] Giovanna Costanzo[c] and Ernesto Di Mauro*[d]

Received 6th March 2012
DOI: 10.1039/c2cs35066a



B= Borate minerals; Z= Zirconium minerals; M= Murchison minerals; F= Iron sulfur minerals; T= Titanium dioxide; P= Phosphate minerals; C= Cosmic dust analogues; Cl= Clays; S= Silica; Cl*= Clays/formaldehyde; PT= Photochemistry with TiO_2

Aknowledgement

E A Krasavin
G N Timoshenko
A Rozanov
M I Kapralov
E Solovoval

E Carota
G Botta
R Saladino
E Di Mauro