Role of Cosmic Dust Analogues in prebiotic chemistry

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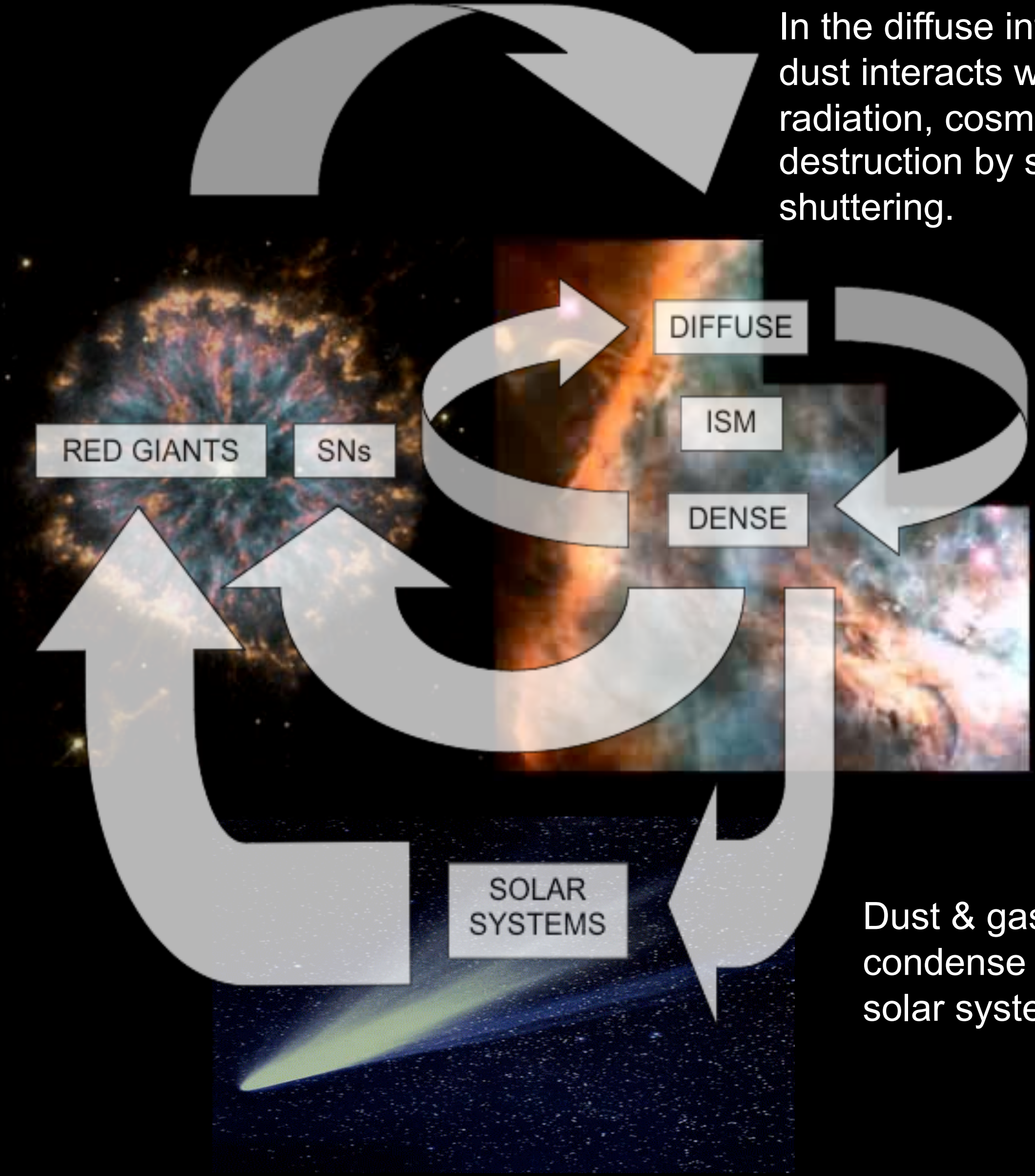
Dust is ubiquitous in Space



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

The role of dust in the universe

“The role of dust is that of observer and of catalyst”
- J. Majo Greenberg (1963)

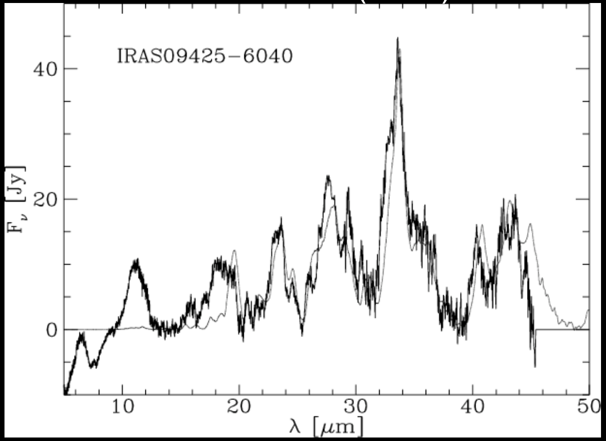
“The importance of grains in various aspects of astrochemistry is evident: they shield molecular regions from dissociating interstellar radiation, catalyze formation of molecules, and remove molecules from the gas phase”
- E.F. van Dishoeck, G.A. Blake, B.T. Draine, J.I. Lunine (1993)

“Dust is both a subject and an agent of the Galactic evolution”
- J. Dorschner and Th. Henning (1995)

“Dust does make a difference. It directly alters the way we view the universe. It also changes the nature of the universe that we see”
- P.G. Martin (2004)

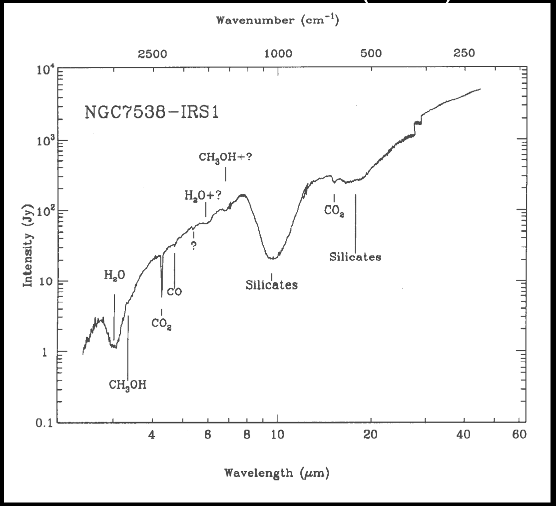
Cristalline silicates in evolved stars

Molster et al. (2002)



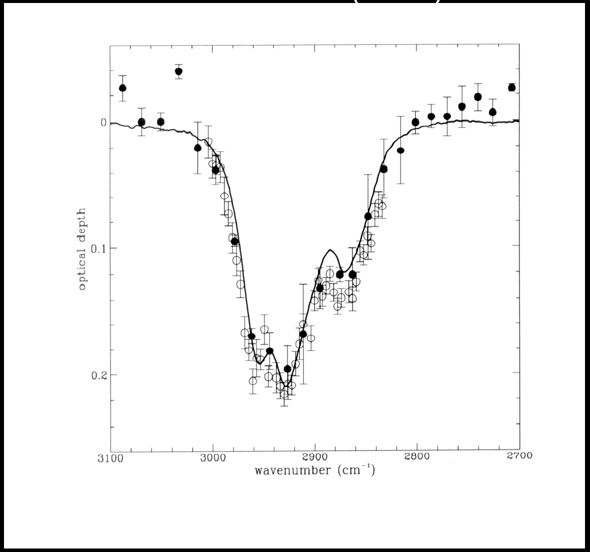
Amorphous silicates in ISM

Strazzulla et al. (1998)



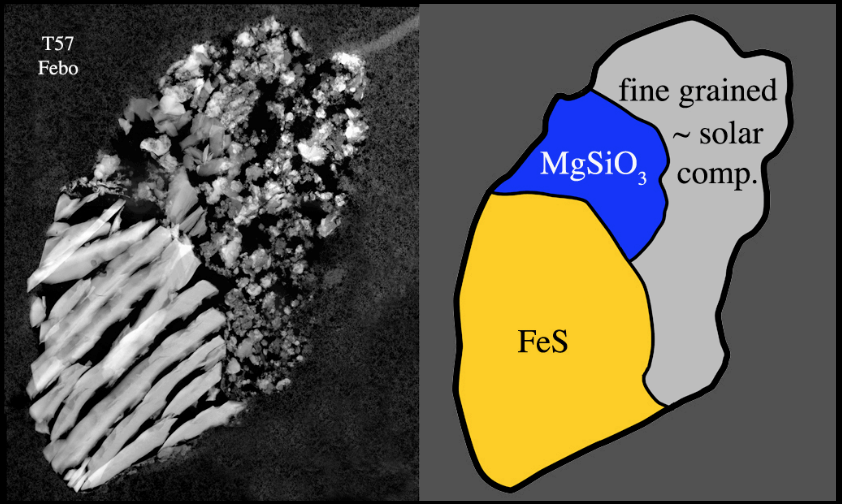
Hydrogenated a-Carbon in ISM

Mennella et al. (1999)

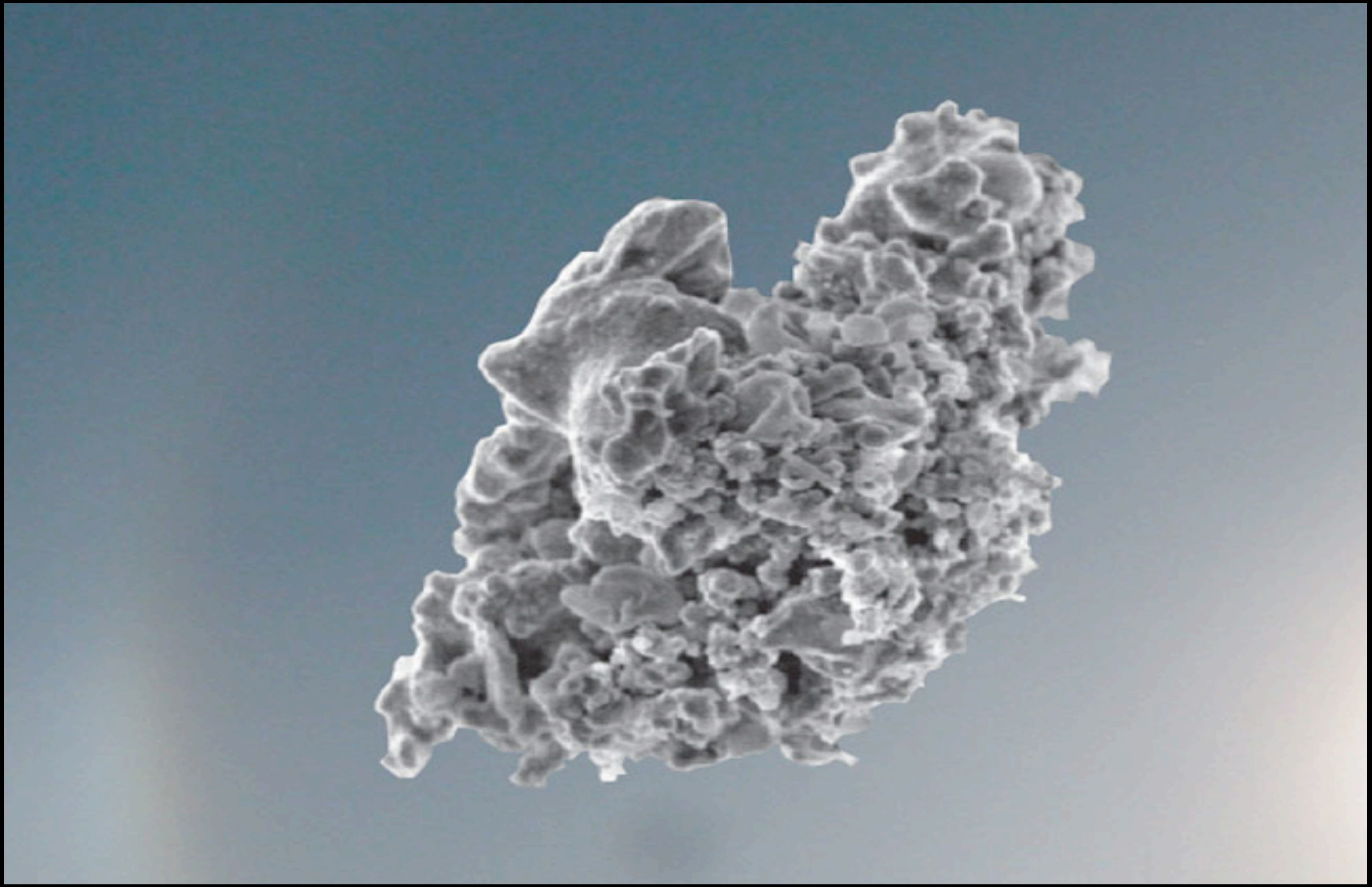


Silicate & a-carbon in comets

Brownlee et al. (2006)



IDPs Interplanetary Dust Particles



About 30,000 tons of IDPs are collected every year by Earth!

ISM, comets and Interplanetary Dust Particles inventory

Oxides:	SiO_2, MgO, FeO, Fe_2O_3, TiO_2, ZrO_2, Al_xO_y
Silicon Carbide:	SiC
a-Carbon	
Sulfides:	FeS, NiS
Silicates	Olivine: $(Mg,Fe)_2SiO_4$ Pyroxene: $(Mg,Fe)SiO_4$ Spinel: $MgAl_2O_4$ Diopsite: $CaMgSi_2O_4$ Melilite: $(Ca,Na)_2(Al,Mg)[(Si,Al)_2O_7]$
Carbonates	Calcite: $CaCO_3$ Dolomite: $CaMg(CO_3)_2$

Cosmic Dust Analogues

The use of analogues offers many advantages with respect to ET materials.

- There are no constraints to the type of measurements to be performed, thus samples can be thoroughly characterised;

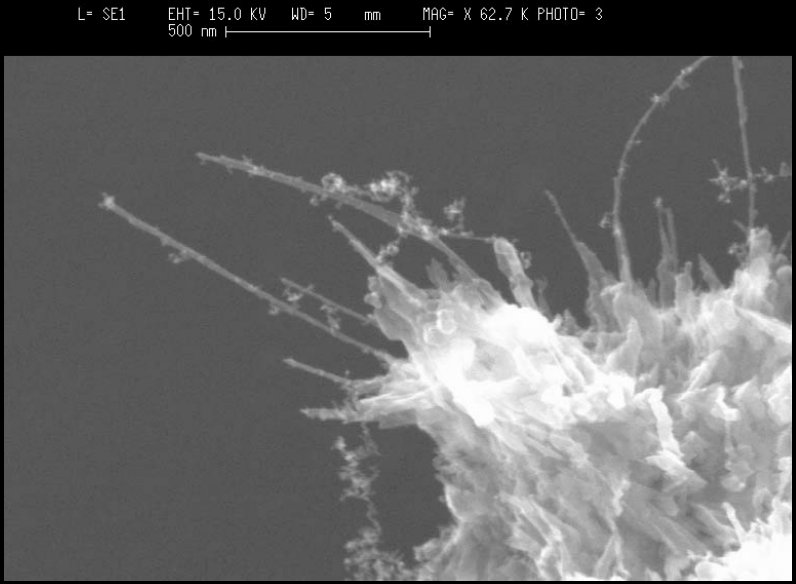
- there is wide flexibility in applying production and processing techniques capable to simulate actual space conditions and processing in order to parameterise material behaviour vs. boundary conditions;

- there is no limitation in the available amount, so that tests can be repeated

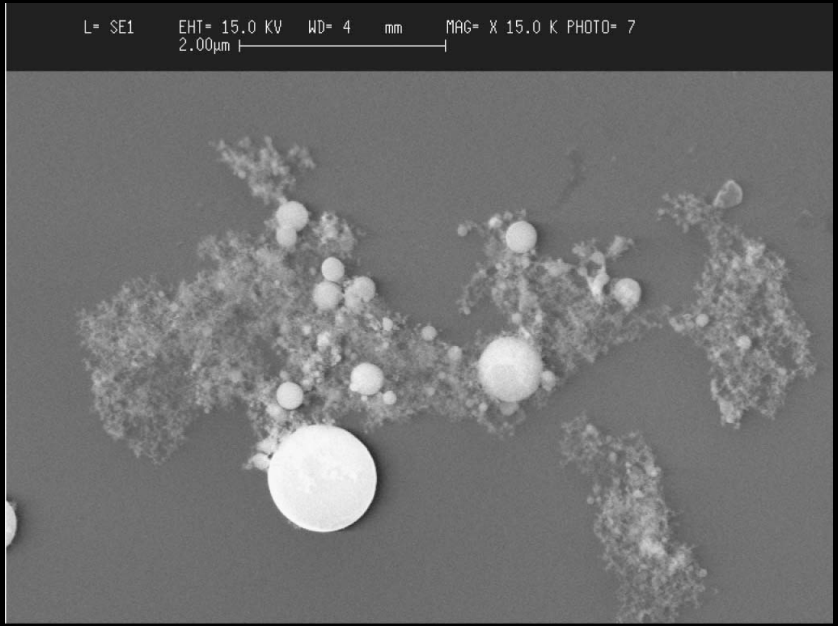
The role of minerals and metal oxides on prebiotic processes. A general overview

- Minerals can accumulate the prebiotic precursors (concentration effect)
- Minerals 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 suitable environments to preserve newly formed biomolecules from degradation

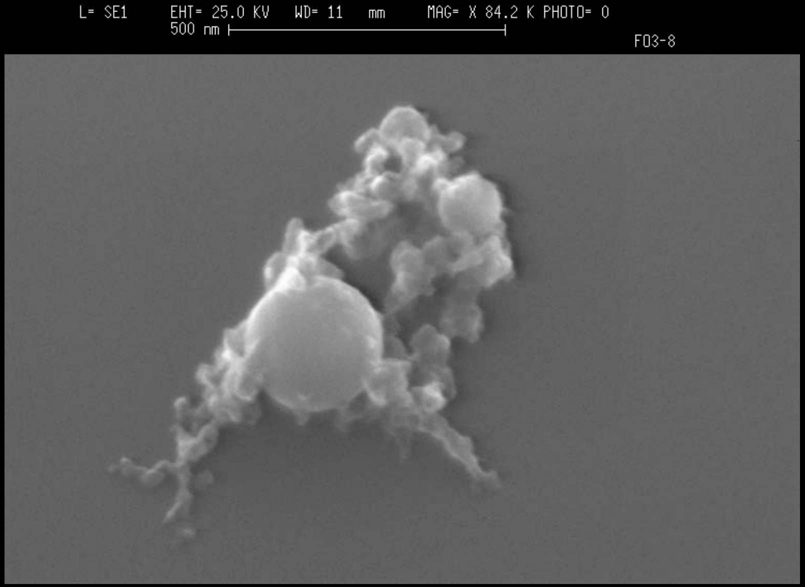
a-carbon



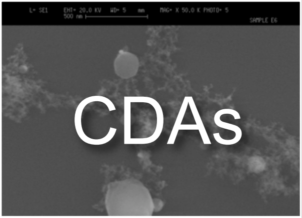
Mg-rich olivine



Mixed a-carbon & silicate



Inorganic catalysis work structure



Gas

Recombination reaction
of atoms
at 10 - 100 K

In collaboration with:
G. Vidali - Univ. Syracuse, NY

Liquid

Thermal reaction
at 160°C

In collaboration with:
R. Saladino - Univ. Viterbo
E. Di Mauro - Univ. Roma

Solid

Ion irradiation of ices
at 20 K

In collaboration with:
G. Strazzulla INAF - Catania

Gas-Solid

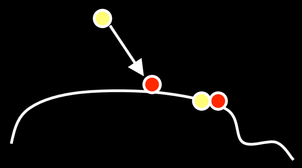
CATALYSIS

H_2 is the most abundant molecule in ISM. It plays a crucial role in the initial cooling of clouds during gravitational collapse and is involved in most reaction schemes that produce other complex molecules.

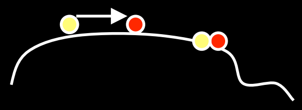
It is widely accepted that H_2 formation takes place on dust grains.

Heterogeneous catalysis ($H + H \dashrightarrow H_2$)

Eley-Rideal mechanism

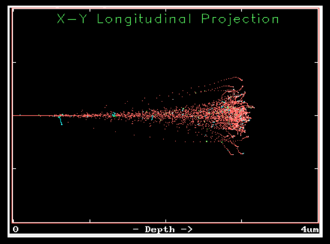


Langmuir-Hinshelwood mechanism



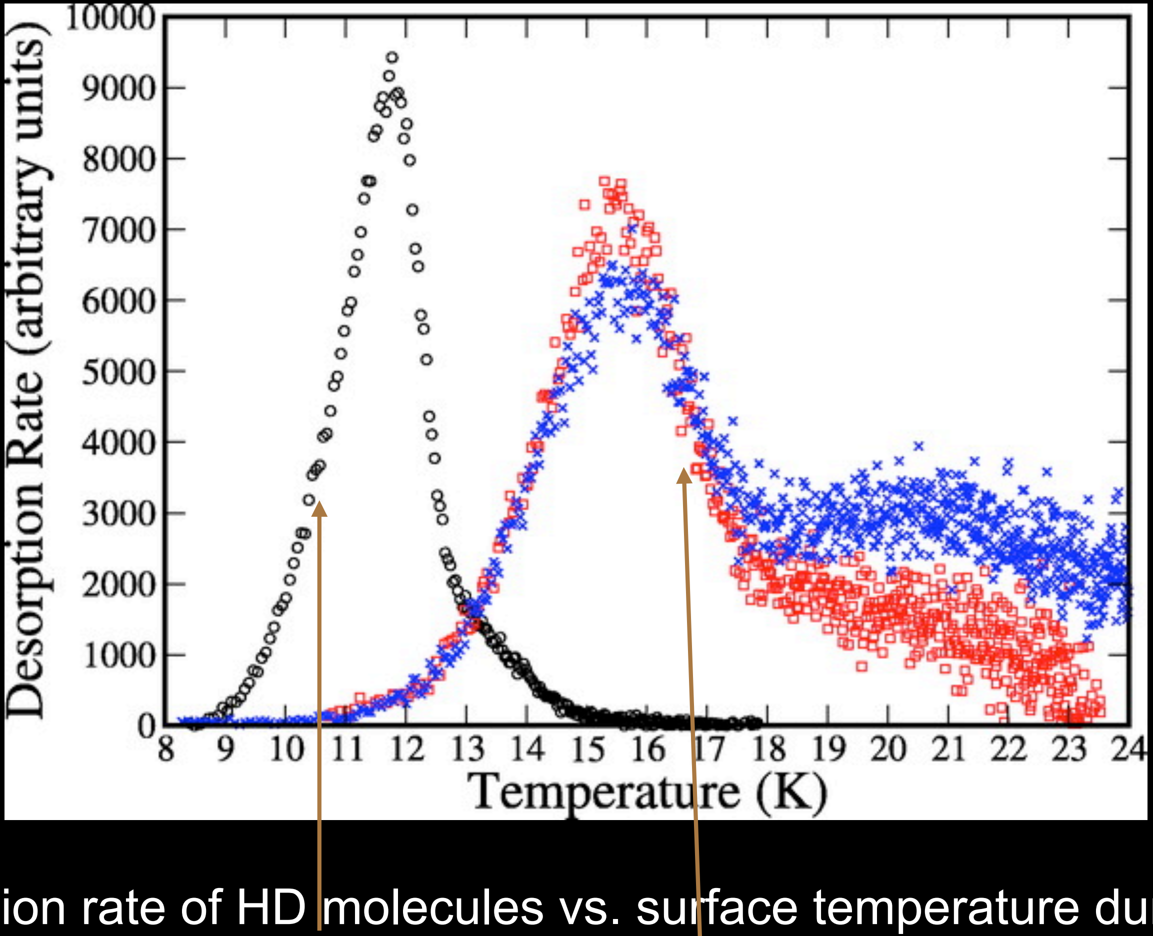
Photochemistry

Radiochemistry

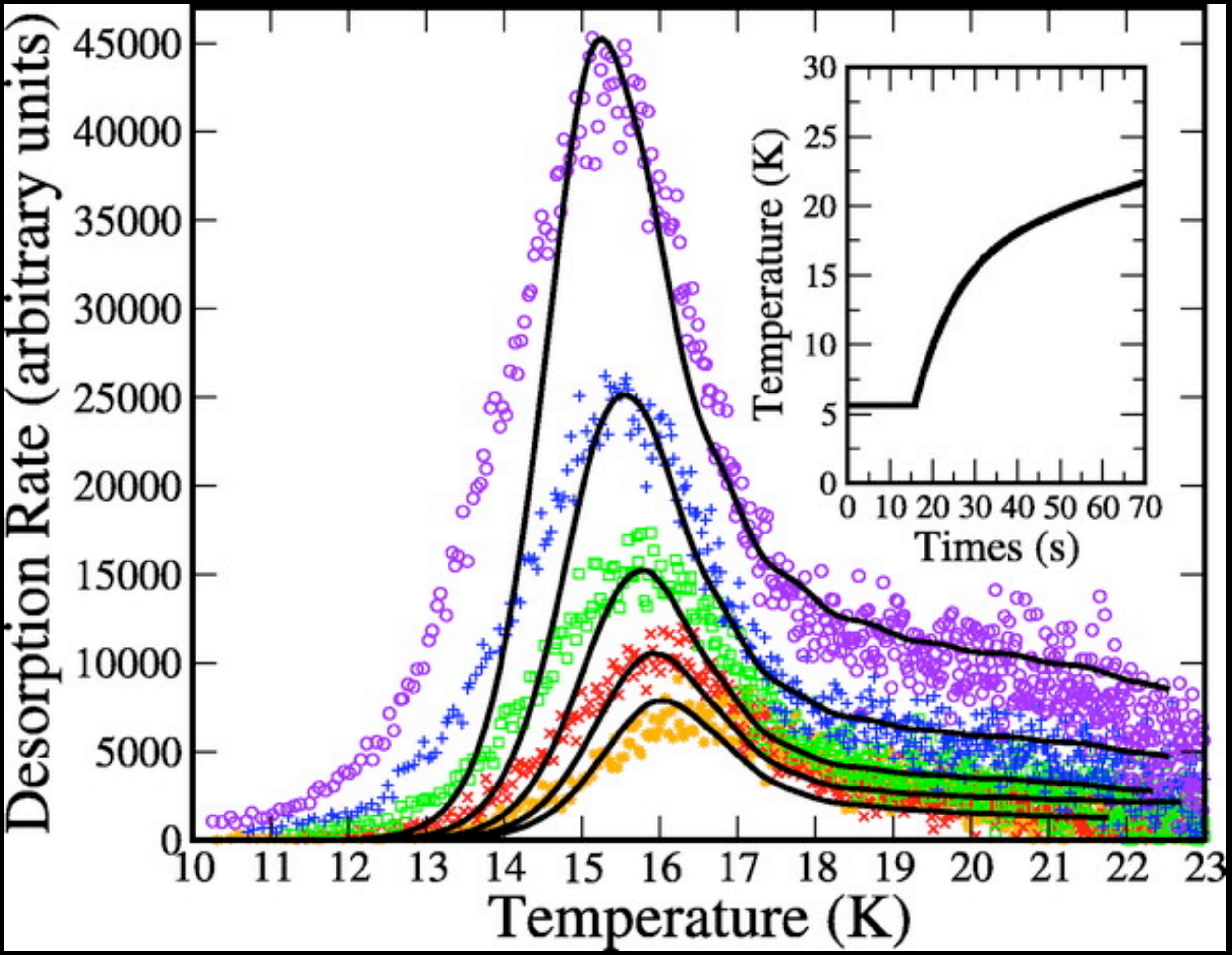


H & D beams irradiation of amorphous olivine silicate (Fe, Mg)SiO_4

(Perets et al. 2007)

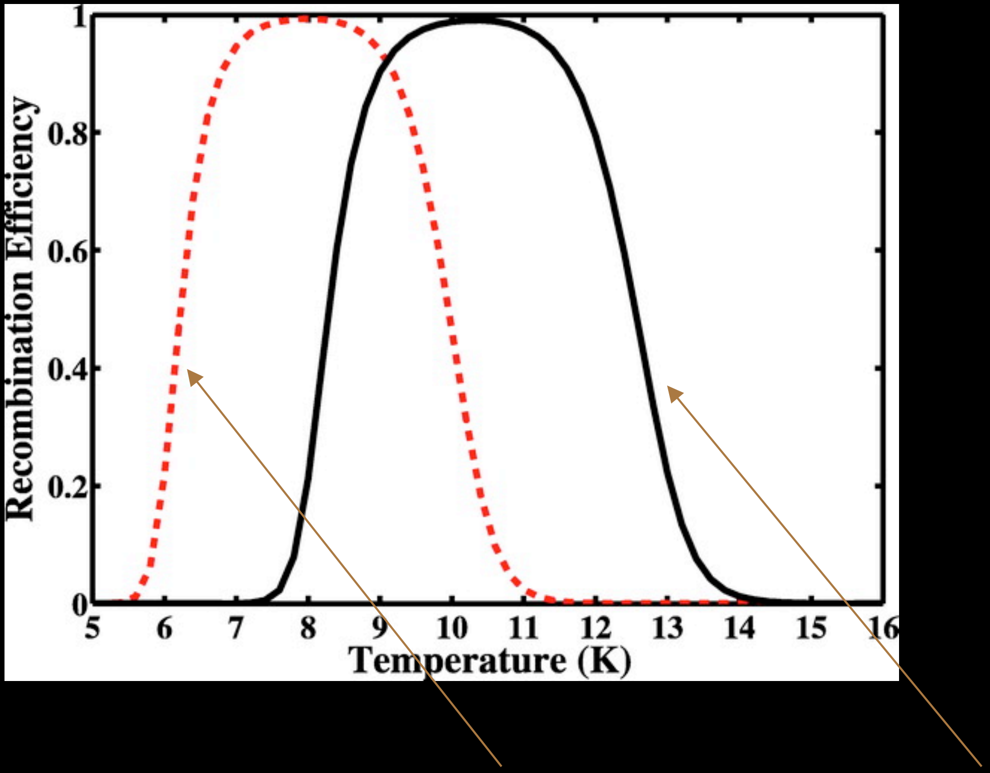


Desorpion rate of HD molecules vs. surface temperature during TDP on polycrystalline and amorphous silicates



TPD curves of HD desorption after irradiation with H+D atoms on amorphous silicates with irradiation times of 15, 30, 60, 120 and 240 s. The solid lines are fits obtaining using the rate equation model.

Molecular desorption does not occur on amorphous surface but are trapped in adsorption sites ➔ the desorbed molecules are not highly excited



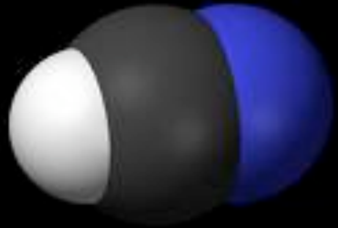
Recombination efficiency of H on polycrystalline and amorphous silicates

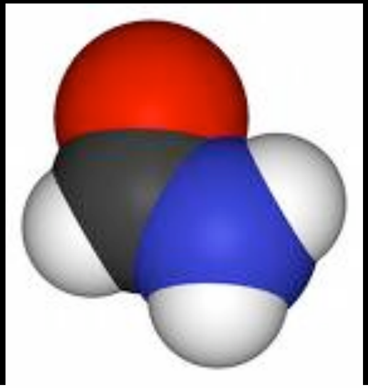
Amorphous silicates are good candidate on which H recombine with high efficiency

Solid-Solid

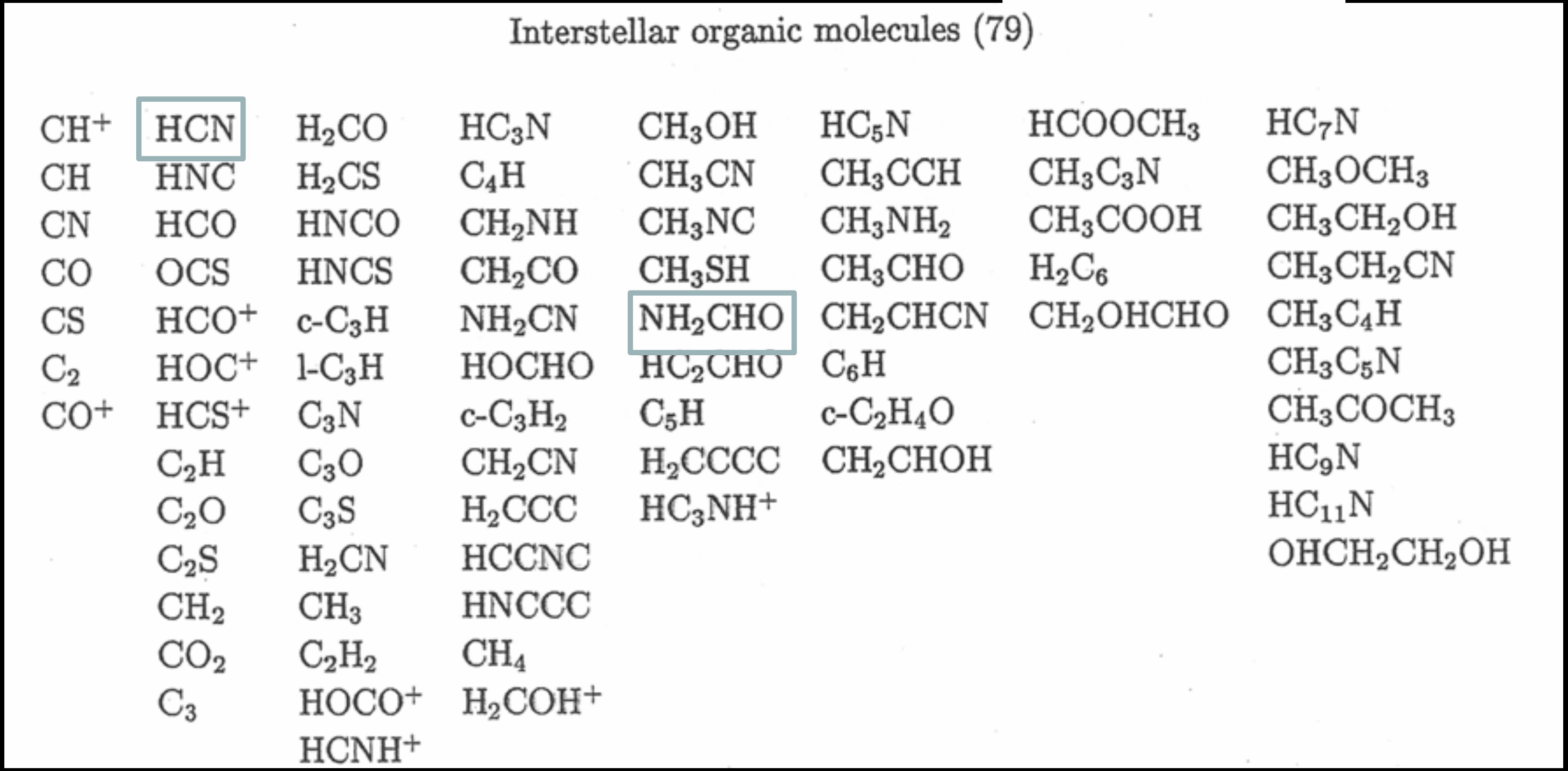
CATALYSIS

HCN





$HCONH_2$



Interstellar organic molecules (79)

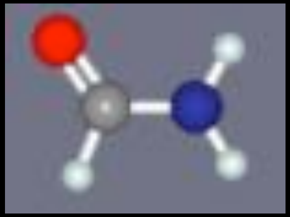
CH^+
CH
CN
CO
CS
C_2
CO^+
HCN
HNC
HCO
OCS
HCO^+
HOC^+
HCS^+
C_2H
C_2O
C_2S
CH_2
CO_2
C_3
H_2CO
H_2CS
$HNCO$
$HNCS$
c-C_3H
l-C_3H
C_3N
C_3O
C_3S
H_2CN
CH_3
C_2H_2
$HOCO^+$
$HCNH^+$
HC_3N
C_4H
CH_2NH
CH_2CO
NH_2CN
$HOCHO$
c-C_3H_2
CH_2CN
H_2CCC
$HCCNC$
$HNCCC$
CH_4
H_2COH^+
CH_3OH
CH_3CN
CH_3NC
CH_3SH
NH_2CHO
HC_2CHO
C_5H
H_2CCCC
HC_3NH^+
HC_5N
CH_3CCH
CH_3NH_2
CH_3CHO
CH_2CHCN
C_6H
c-C_2H_4O
CH_2CHOH
$HCOOCH_3$
CH_3C_3N
CH_3COOH
H_2C_6
CH_2OHCHO
HC_7N
CH_3OCH_3
CH_3CH_2OH
CH_3CH_2CN
CH_3C_4H
CH_3C_5N
CH_3COCH_3
HC_9N
$HC_{11}N$
$OHCH_2CH_2OH$

Colangeli, J.R. Brucato, A. Bar-Nun, R.L. Hudson and M.H. Moore, in Comets II, M. Festou, H.U. Keller, and H.A. Weaverin Eds., University of Arizona Press (2005).

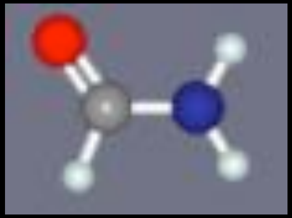
Ice	Reaction Products Identified	Least Volatile Species	Processing Experiment
H_2O	H_2O_2, HO_2[b], OH[b]	H_2O_2	Ion[a], UV[b]
CO	CO_2, C_3O_2, C_2O	C_3O_2	Ion[c], UV[b]
CO_2	CO, O_3, CO_3	H_2CO_3 (from H^+ implantation)[d]	Ion[c,d], UV[b,c]
CH_4	C_2H_2, C_2H_4, C_2H_6, C_3H_8, CH_3, C_2H_5	PAH's[e] and high molecular weight hydrocarbons	Ion[e-g], UV[b]
C_2H_2	CH_4[f], polyacetylene[h]	PAH's[e], polyacetylene[h]	Ion[e,h]
C_2H_6			
H_2CO	POM, CO, CO_2, HCO	POM	Ion[h], UV[b]
CH_3OH	CH_4, CO, CO_2, H_2CO, H_2O, $C_2H_4(OH)_2$, HCO, $HCOO^-$	$C_2H_4(OH)_2$	Ion[i,j], UV[b]
NH_3	N_2H_4[b], NH_2[b]	N_2H_4[b]	Ion[k], UV[b]
HCN	HCN oligomers	HCN oligomers	Ion[h], UV[h]
$HNCO$	NH_4^+, OCN^-, CO, CO_2	NH_4OCN	Ion[h], UV[h]
$HCOOH$			
$HC(=O)CH_3$			
$HC(=O)NH_2$			
$HC(=O)OCH_3$			
SO_2	SO_3	S_8[l]	Ion[l], UV[m]
H_2S	none reported		UV[m]
OCS			
CH_3CN	CH_4, H_2CCNH, CH_3NC		Ion[h], UV[h]
$HCCCN$			

Formamide

[a] Moore and Hudson (2000), [b] Gerakines et al. (1996), [c] Gerakines and Moore (2001), [d] Brucato et al. (1997), [e] Kaiser and Roessler (1998), [f] Mulas et al. (1998), [g] Moore and Hudson (2003), [h] Moore et al. (unpublished work), [i] Hudson and Moore (2000), [j] Palumbo et al. (1999), [k] Strazzulla and Palumbo (1998), [l] Moore (1984), [m] Salama et al. (1990).



Why Formamide?



- It’s a simple one C-bearing molecule.
- It’s active in synthesis of nucleobases.
- It’s active in selective degradation of DNA.
- It’s formed by hydrolysis of HCN.
- It’s observed in:
  - ✓ ISM (Millar 2005);
  - ✓ Hale-Bopp comet (Bockeleé-Morvan et al. 2000);
  - ✓ tentatively in young stellar object W33A (Schutte et al. 1999);
  - ✓ in dense ISM IRS9 (Raunier et al. 2000).

Environment (ice residence time in years)	Ion Processing			Photon Processing		
	Flux, 1 MeV p^+ ($eV\ cm^{-2}\ s^{-1}$)	Energy absorbed ($eV\ cm^{-2}\ s^{-1}$)[a]	Dose ($eV\ molec^{-1}$)	Flux ($eV\ cm^{-2}\ s^{-1}$)	Energy absorbed ($eV\ cm^{-2}\ s^{-1}$)	Dose ($eV\ molec^{-1}$)
Diffuse ISM $(10^5 - 10^7)$[b]	1×10^7	1.2×10^4	<1 - 30	9.6×10^8 at 10 eV[b]	5×10^8 0.02 µm ice	$10^4 - 10^6$
Dense cloud $(10^5 - 10^7)$[b]	1×10^6	1.2×10^3 0.02 µm ice	<< 1 - 3	1.4×10^4 at 10 eV	1.7×10^3 0.02 µm ice	< 1 - 4
Protoplanetary nebula $(10^5 - 10^7)$[c]	1×10^6	1.2×10^3 0.02 µm ice	<< 1 - 3	2×10^5 at 1-10 keV[d]	5×10^4 0.02 µm ice[e]	2 – 240
Oort cloud (4.6×10^9)	$\varphi(E)$[f]	f	~150 (0.1 m) ~55-5 (1-5 m) <10 (5-15 m)	9.6×10^8 at 10 eV	9.6×10^8 0.1 µm ice	2.7×10^8
Laboratory (4.6×10^{-4})[g]	8×10^{16}	2×10^{15} 1 µm ice	10	2.2×10^{15} at 7.4 eV	2.2×10^{15} 1 µm ice	10

a The absorbed energy dose from 1 MeV cosmic-ray protons assumes a 300 MeV cm2 g-1 stopping power and an H2O-ice density of 1 g cm-3. Protons deposit energy in both the entrance and exit ice layer of an ice-coated grain.

b 10eV photons = 1200 Å, vacuum UV (UV-C). Jenniskens et al., (1993).

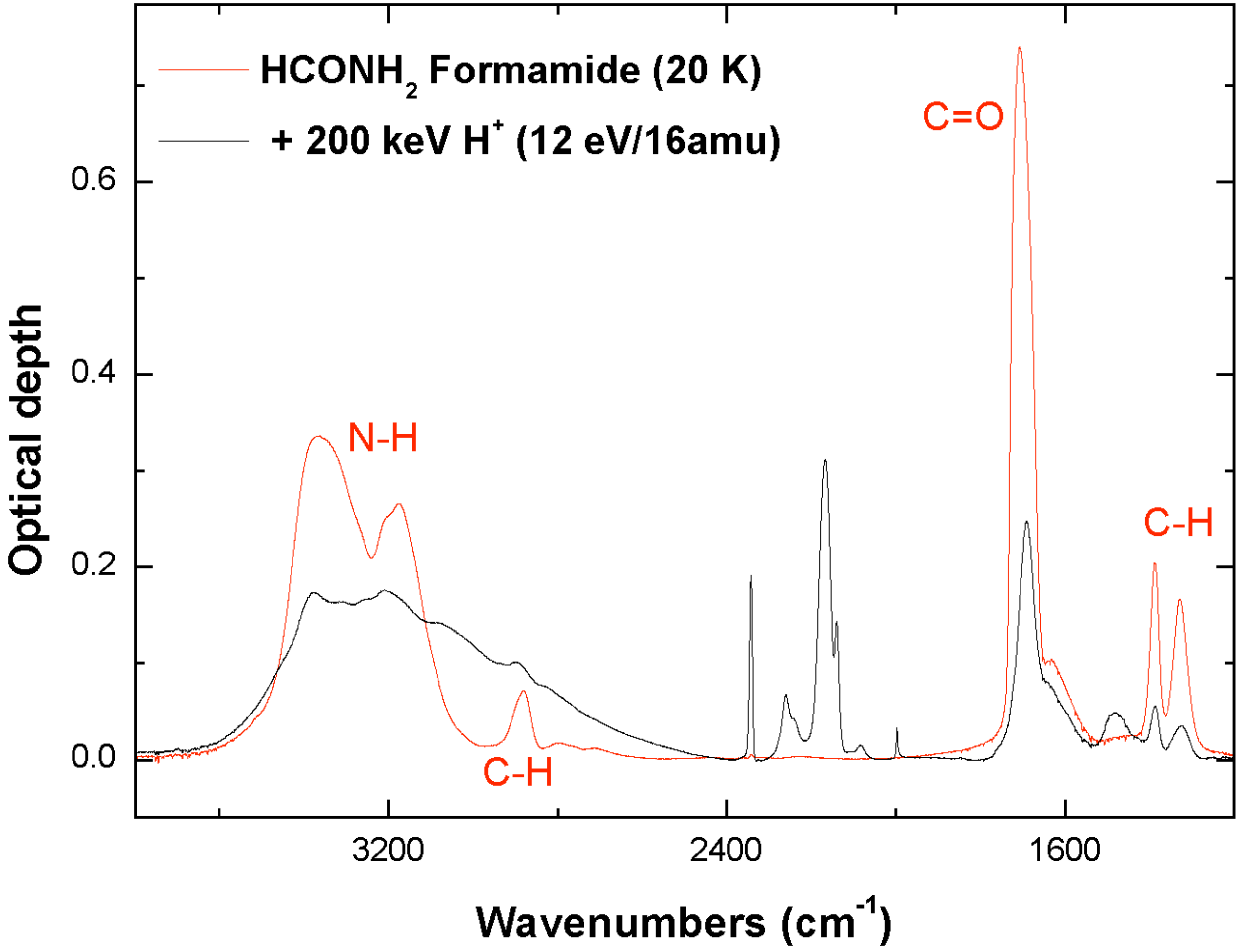
c Typical disk longevities. (Lawson et al., 1996).

d Typical flux at 0.1 pc, 1 keV photons = 12 Å, soft X-rays (Feigelson & Montmerle, 1999).

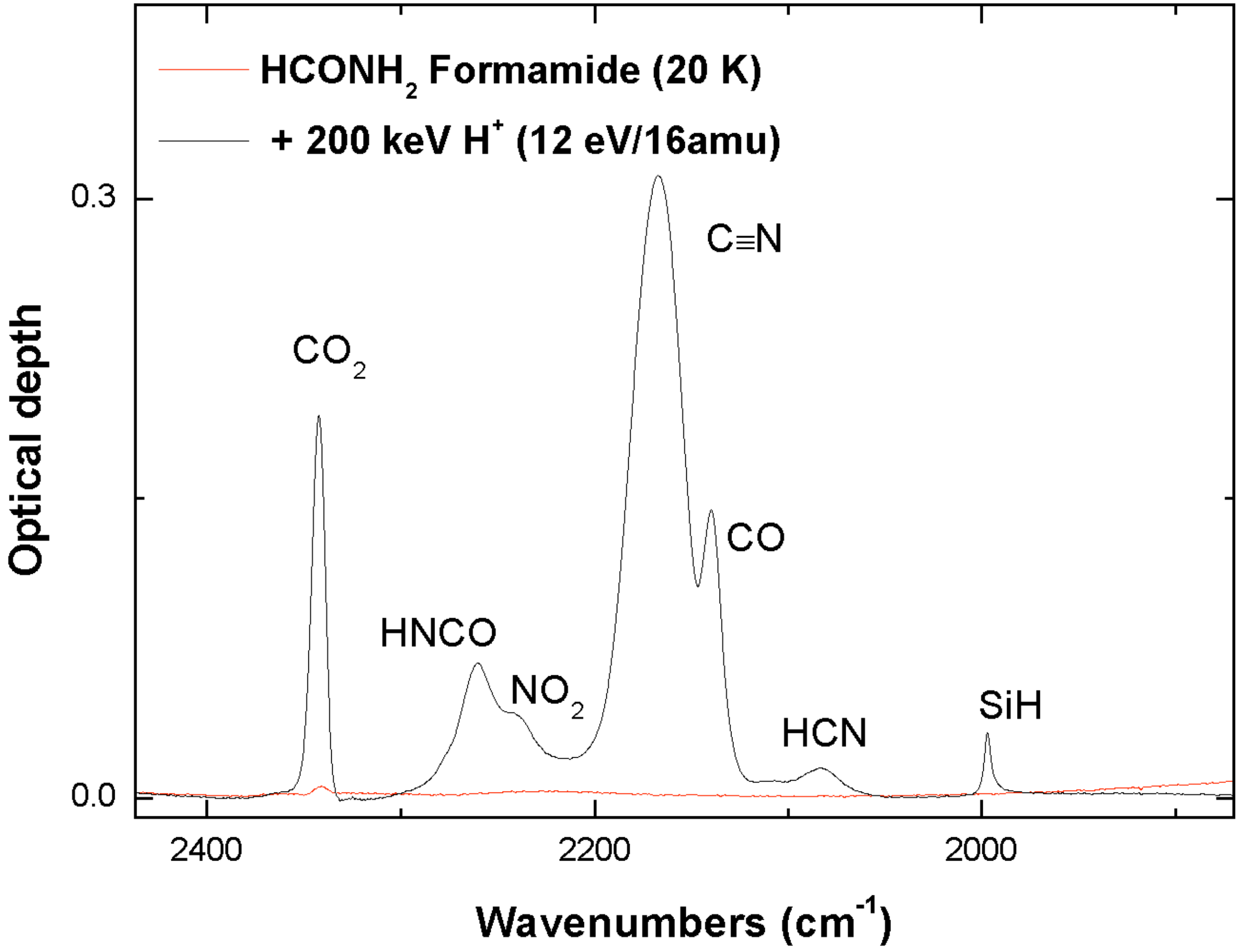
e Absorbed energy dose from 1 keV x-rays assumes a 1 keV electron production in 1 g cm-3 H2O-ice with a 127 MeV cm2 g-1 stopping power.

f An energy dependent flux, j(E), was used to calculate the resulting energy dose at different depths in a comet nucleus for an H2O-ice density of 1 g cm-3. For details see Strazzulla and Johnson (1993) and references therein.

g Typical proton and UV data from the Cosmic Ice Laboratory at NASA Goddard.

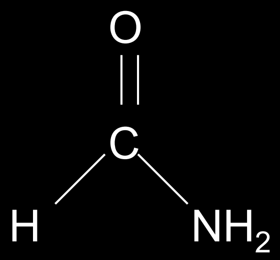


Brucato et al. 2006



Brucato et al. 2006a

Ion irradiation of pure icy Formamide



Formamide

$$\xrightarrow{\text{200 keV } H^+ \text{ at 20 K}}$$

NH_3 ammonia

CO_2

HNCO isocyanic acid

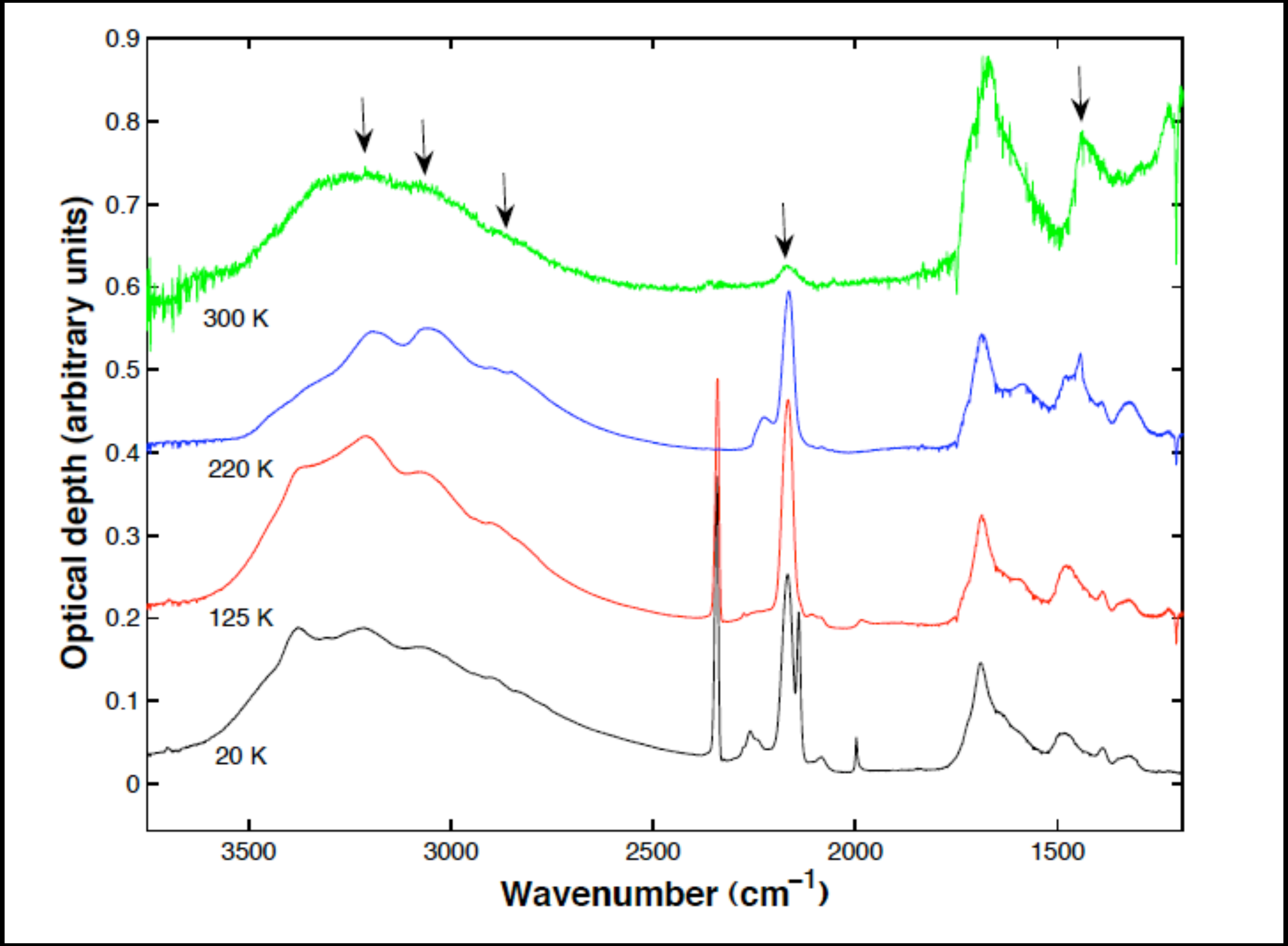
$NH_4^+OCN^-$ ammonium cyanate

HCN hydrogen cyanide

N_2O

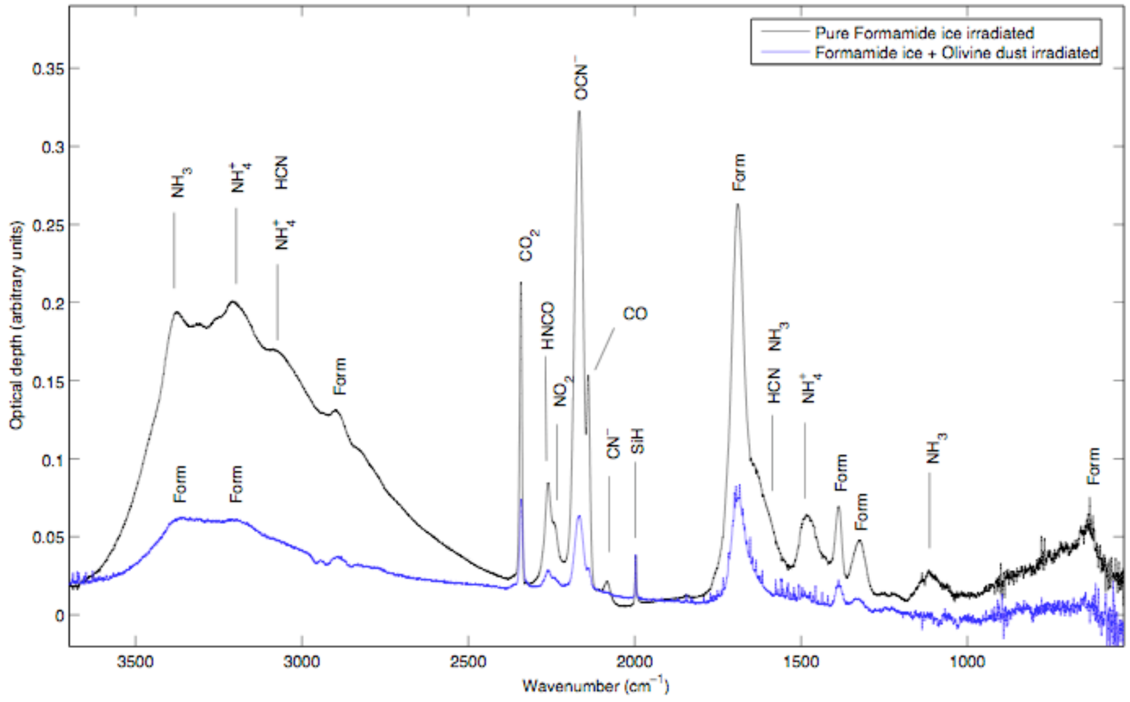
CO

Ammonium cyanide is stable at room temperature!



Brucato et al. 2006a

200 keV H+ irradiation of Formamide **with & without** a-olivine $FeMgSiO_4$



Brucato et al. 2006b

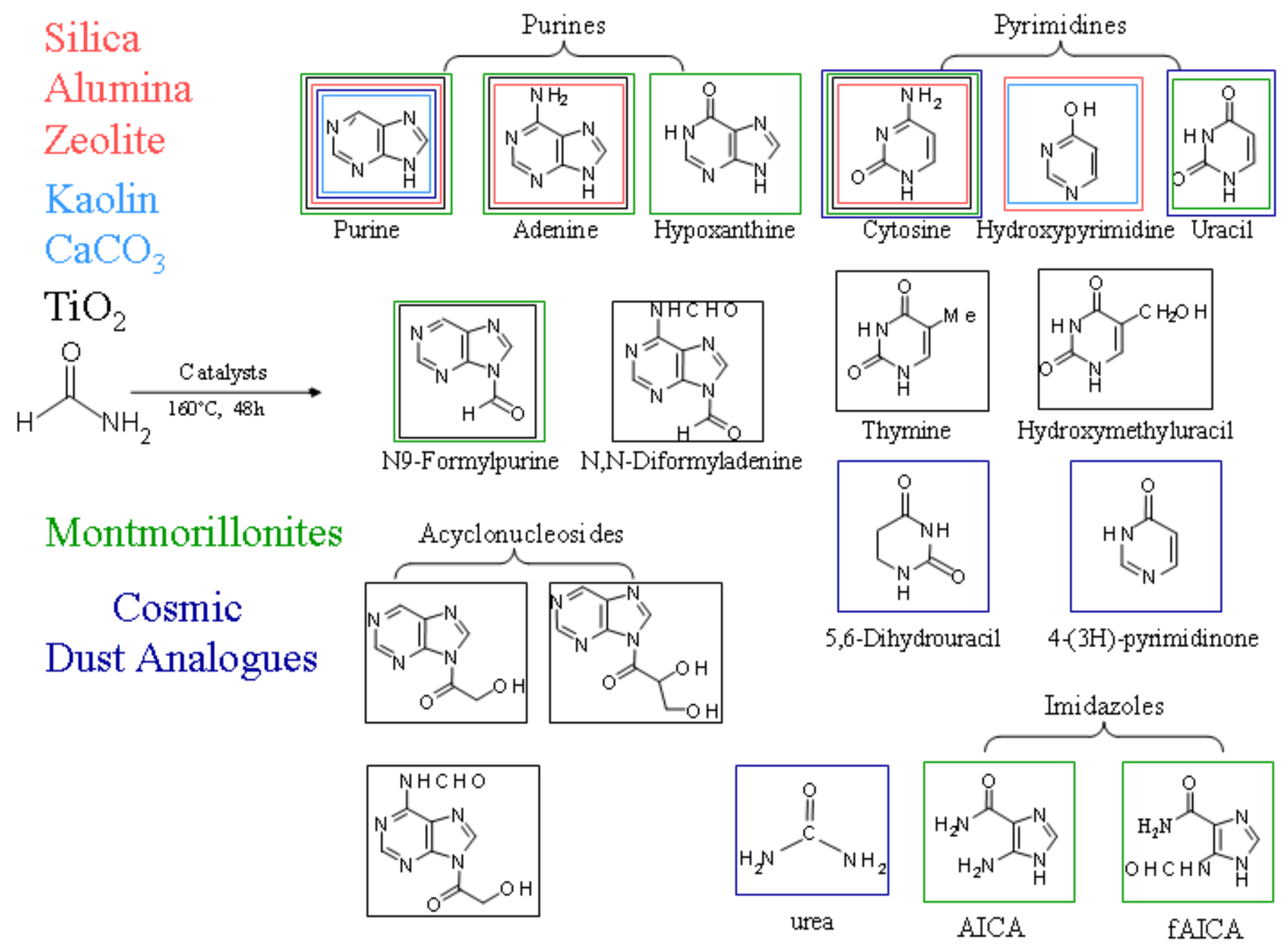
Normalized ratio of synthesized molecules
Vs.
Formamide molecules destroyed

Species	Ratio	
	Pure	CDA
NH_3	0.79	0
NH_4^-	0.56	0.47
HCN	0.44	0
CO_2	0.27	0.41
HNCO	0.14	0.10
CO	0.70	0.16
OCN^-	1	1

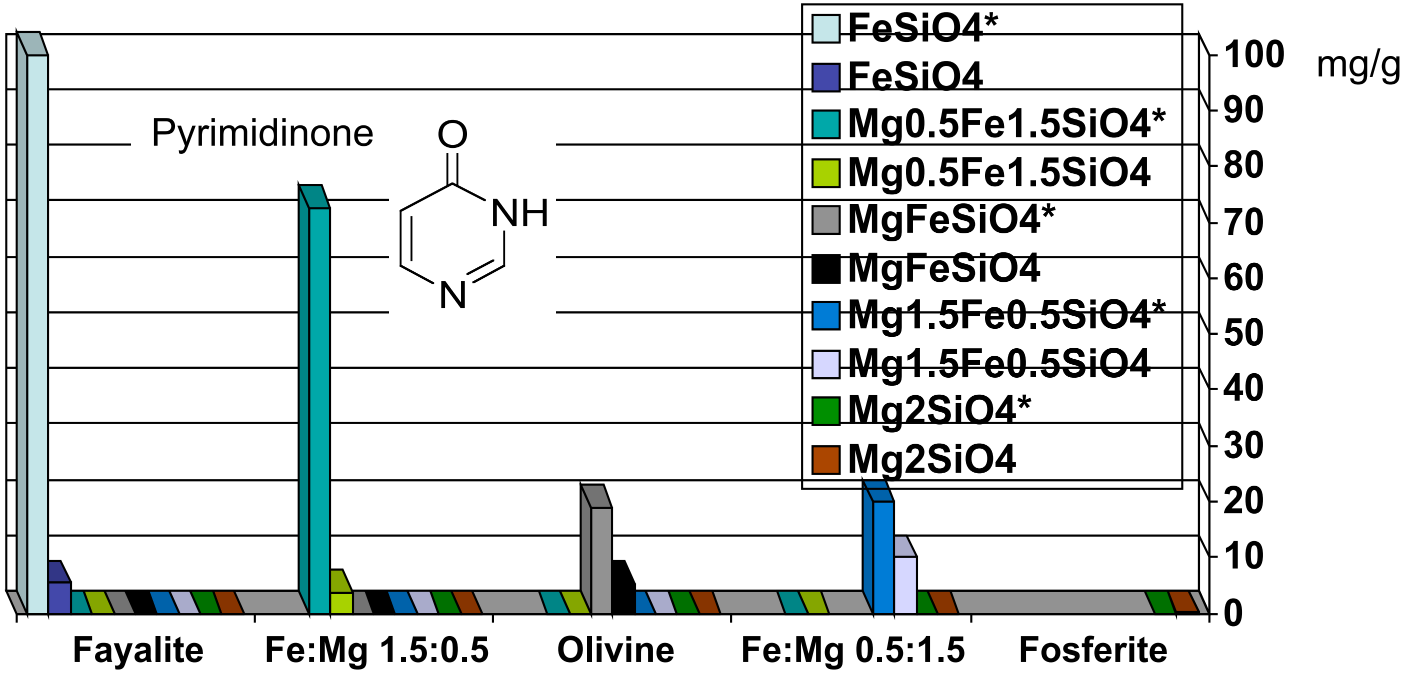
Liquid-Solid

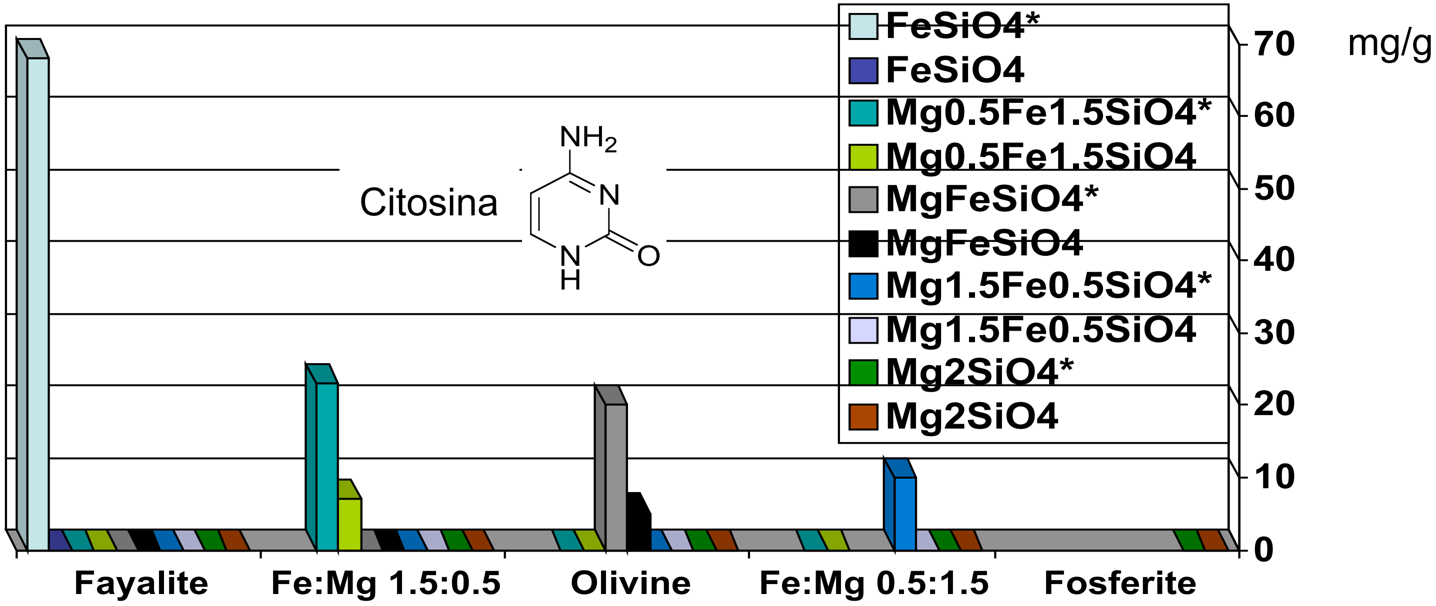
CATALYSIS

Thermal processing of *liquid* Formamide (160 °C) with & without dust

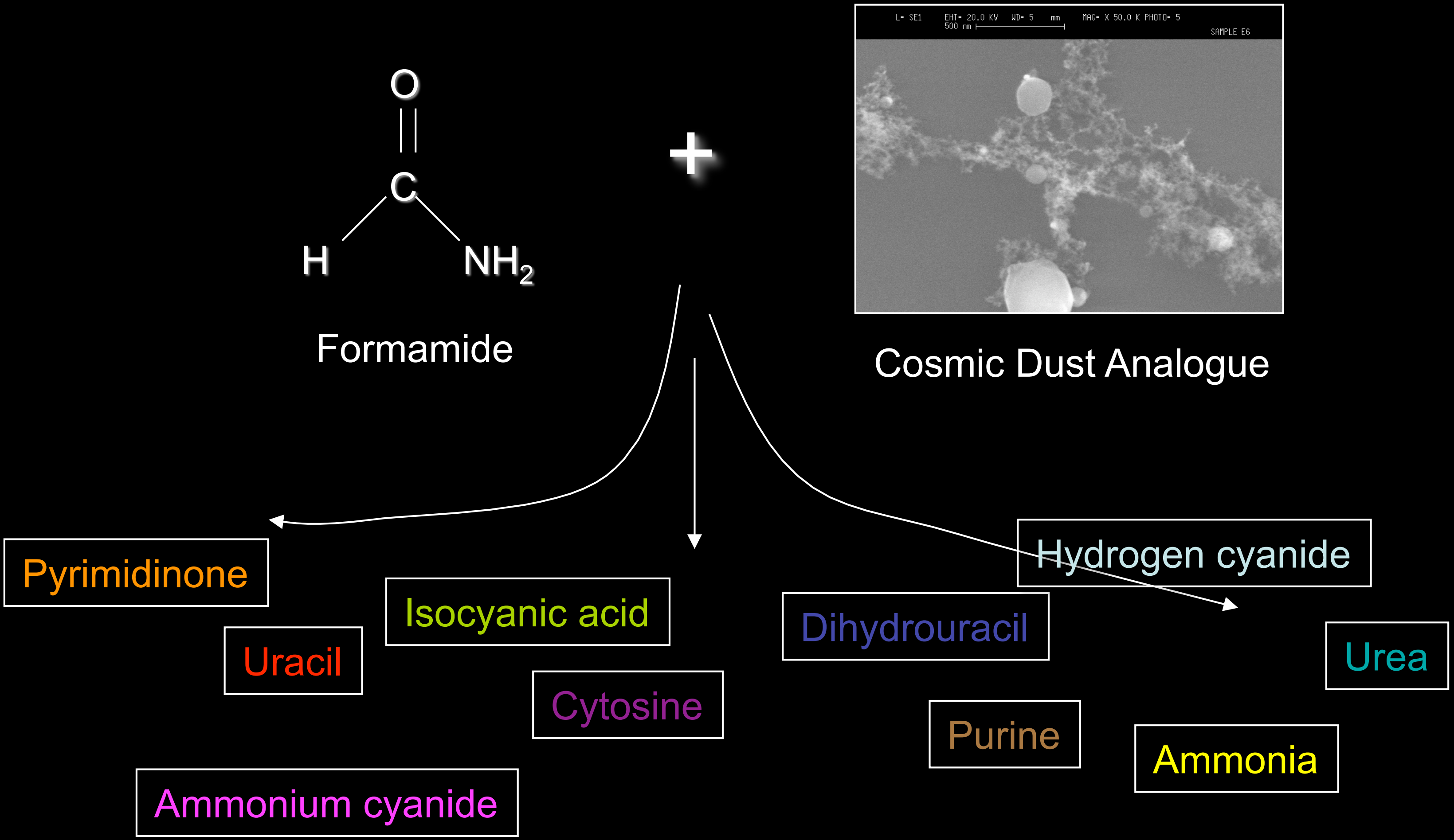


Saladino R., Crestini C., Neri C., Brucato J.R., Colangeli L. Ciciriello F., Di Mauro E., Costanzo G., *ChemBioChem* **6**, 1, 2005


Pyrimidinone
O
NH
N
FeSiO4*
FeSiO4
Mg0.5Fe1.5SiO4*
Mg0.5Fe1.5SiO4
MgFeSiO4*
MgFeSiO4
Mg1.5Fe0.5SiO4*
Mg1.5Fe0.5SiO4
Mg2SiO4*
Mg2SiO4
100
90
80
70
60
50
40
30
20
10
0
mg/g
Fayalite
Fe:Mg 1.5:0.5
Olivine
Fe:Mg 0.5:1.5
Fosferite


Citosina
NH_2
N
N
H
O
FeSiO4*
FeSiO4
Mg0.5Fe1.5SiO4*
Mg0.5Fe1.5SiO4
MgFeSiO4*
MgFeSiO4
Mg1.5Fe0.5SiO4*
Mg1.5Fe0.5SiO4
Mg2SiO4*
Mg2SiO4
70
60
50
40
30
20
10
0
mg/g
Fayalite
Fe:Mg 1.5:0.5
Olivine
Fe:Mg 0.5:1.5
Fosferite

Inorganic catalysis is an important process active for prebiotic chemistry



Formamide

Cosmic Dust Analogue

Pyrimidinone

Uracil

Isocyanic acid

Cytosine

Ammonium cyanide

Hydrogen cyanide

Dihydrouracil

Urea

Purine

Ammonia

CONCLUSION

Primitive dust condensates as observed in expanding envelopes of evolved stars, in interstellar medium, in proto solar nebulae and in planetary atmospheres are extremely interesting catalysts for prebiotic chemistry occurring in the *gas-phase*, in *liquid-phase* and in the *solid-phase*.

IN DUST WE TRUST!