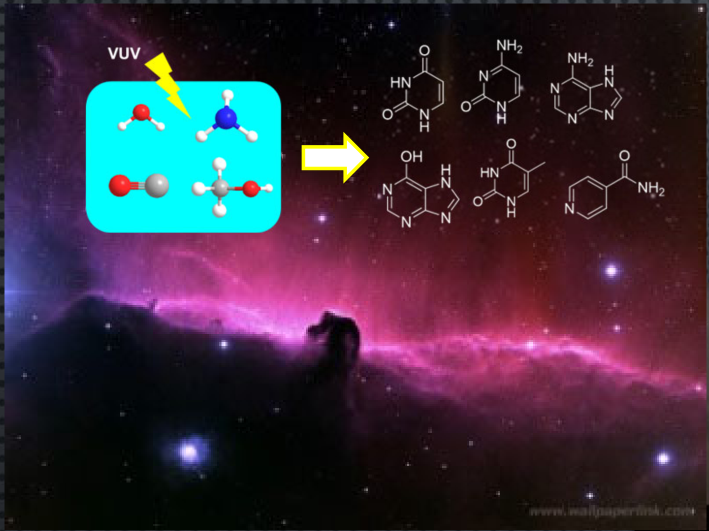
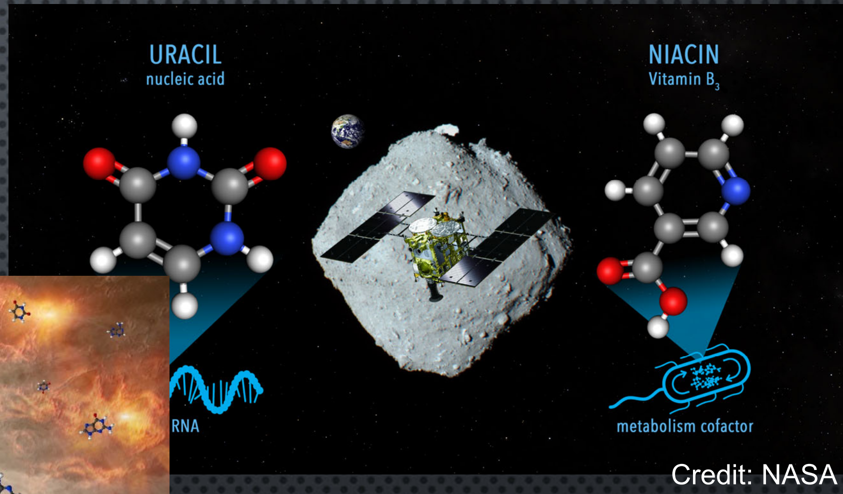
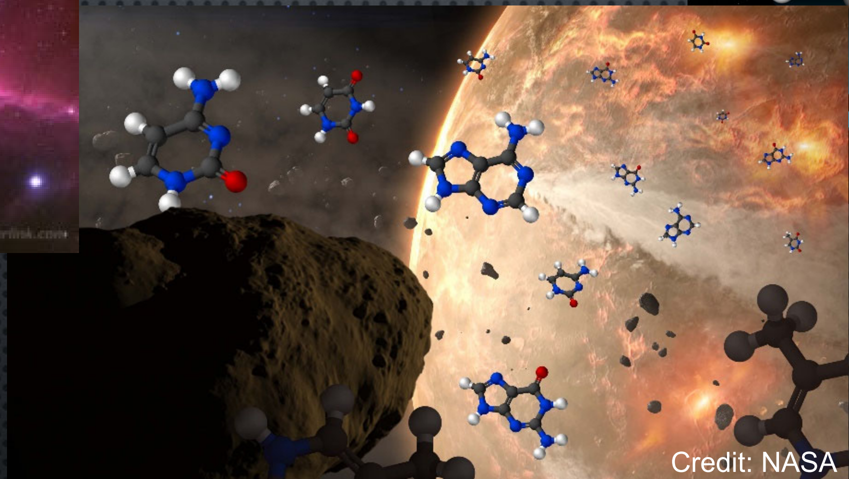
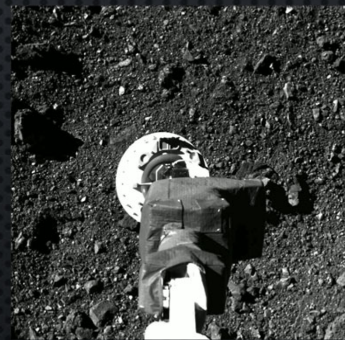
Nucleobases in the laboratory and asteroids









Yasuhiro Oba (ILTS, Hokkaido Univ., JAPAN)

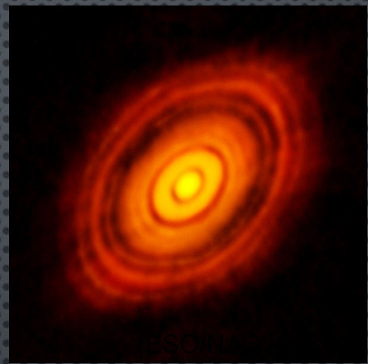
What is our origin?

Interstellar medium (ISM)

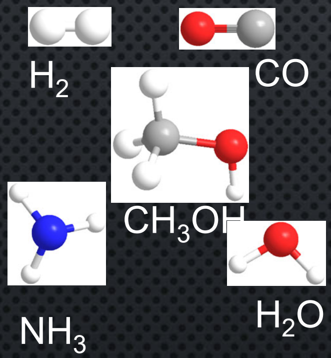
Molecular clouds (MCs)

Star-forming regions

Protoplanetary disk

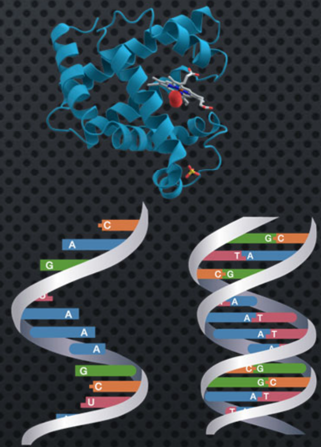


Earth
(Solar system)



Interstellar molecules
(N~200)

Gas phase reactions, Grain surface reactions,
Energetic (UV, cosmic-ray, etc.) processes,
Thermal process, Aqueous alteration, etc.



Functionalized
macromolecules

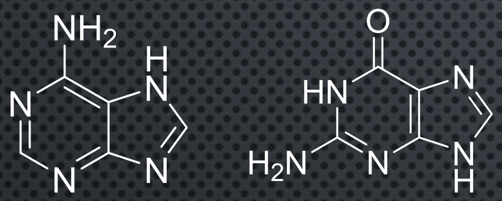
Deciphering chemical processes at each stage should be necessary to fully understand molecular evolution in space and the origin of life on Earth

What is the origin of our RNA/DNA?

Nucleobases: Key components in DNA and RNA

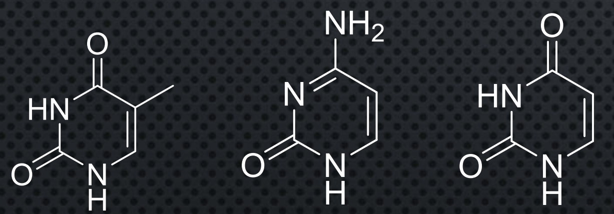
Nucleobase: Molecules having purine or pyrimidine structure

Purine bases

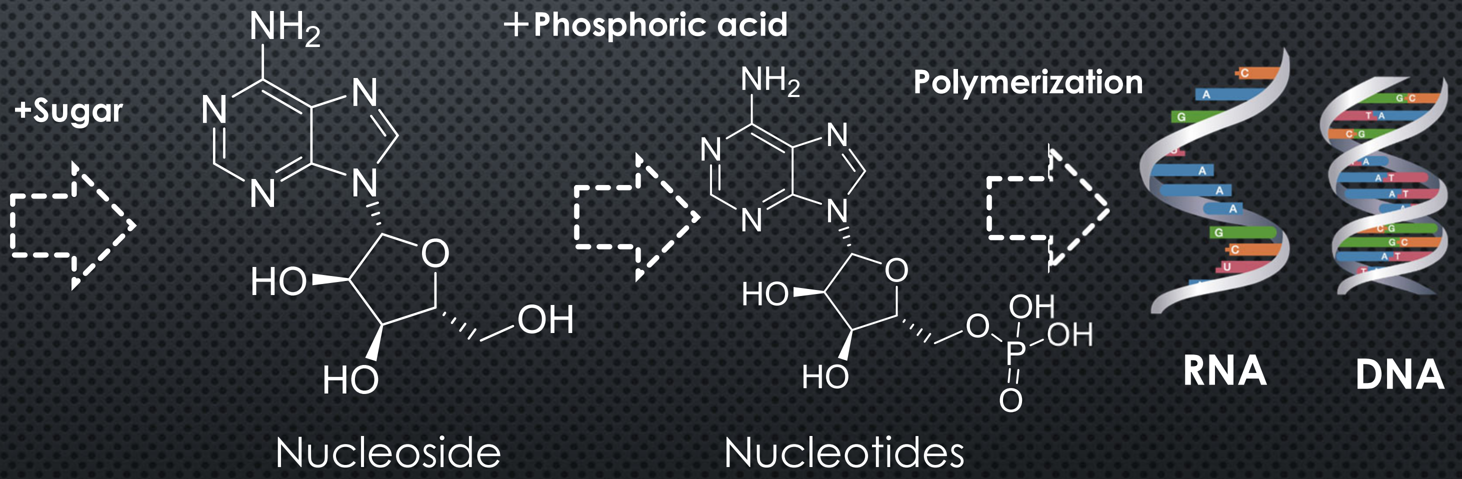


Adenine(A) **Guanine(G)**

Pyrimidine bases



Thymine(T) **Cytosine (C)** **Uracil (U)**



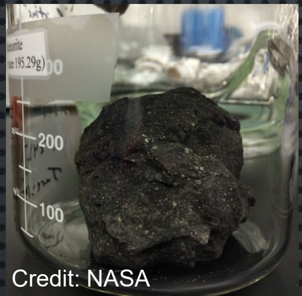
Canonical nucleobases in terrestrial biology

Source(s) of nucleobases on early Earth?

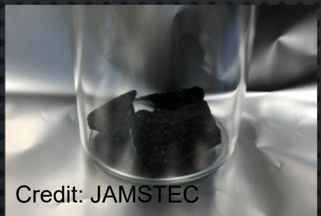
Delivery of Organic molecules from space in LHB period

©National Geographic

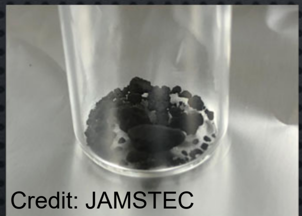
Carbonaceous meteorites: the most pristine solar system materials



Murchison



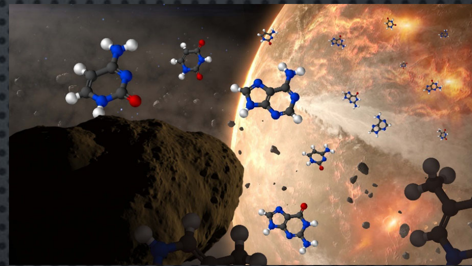
Murray



Tagish Lake

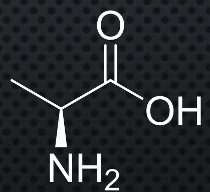
Carbonaceous meteorites

Did not significantly alter since their formation ~4.5 billion years ago

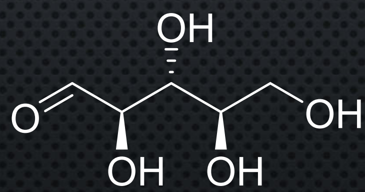


©NASA/Dan Gallagher

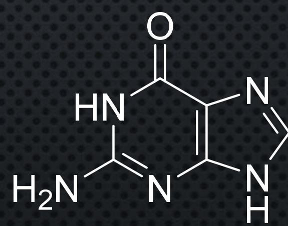
Preserve a record of organic components upon the formation of the solar system



Amino acids
(N>90)



Polyols/sugars
(e.g. Ribose)

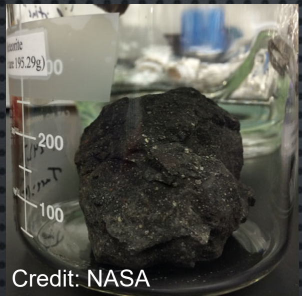


Nucleobases
(A, G, U only among canonical nucleobases)

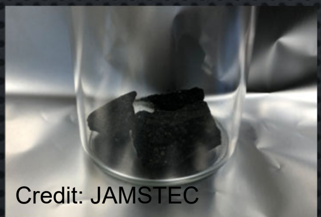
(Glavin et al. 2018; Furukawa et al. 2019)

Detailed analyses of nucleobases in carbonaceous meteorites

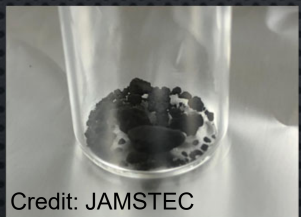
State-of-the-art analytical techniques developed by ourselves for detecting tiny amounts of nucleobases in meteorites



Murchison



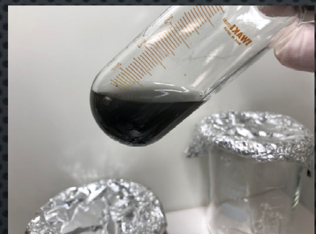
Murray



Tagish Lake

Carbonaceous meteorites
(mg to g-scale)

Extraction (& Purification)



Analysis

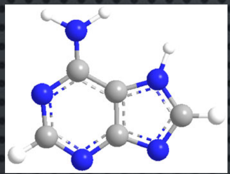
Liquid chromatography

High-resolution Mass spectroscopy (MS)

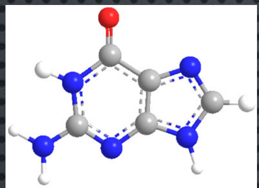
It often takes a week or so for the entire process to complete

Results: detected nucleobases and related molecules in meteorites

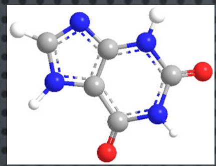
19 nucleobases including all canonical ones are found, but there are many others unidentified yet



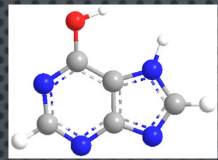
Adenine



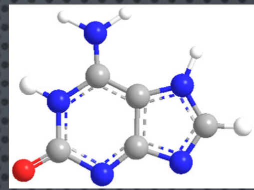
Guanine



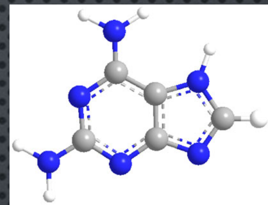
Xanthine



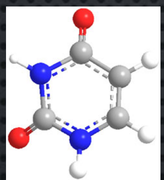
Hypoxanthine



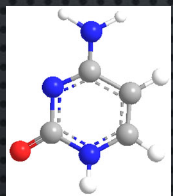
Isoguanine



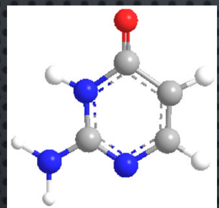
2,6-Diaminopyrine



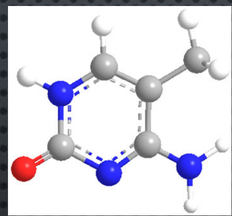
Uracil



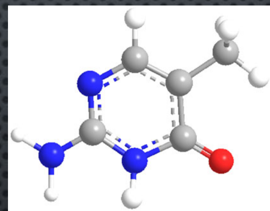
Cytosine



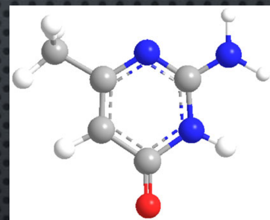
Isocytosine



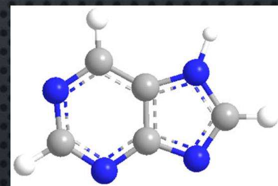
5-Methylcytosine



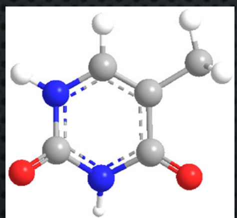
5-Methylisocytosine



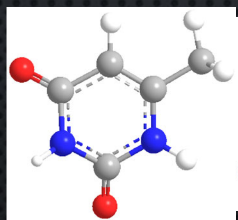
6-Methylisocytosine



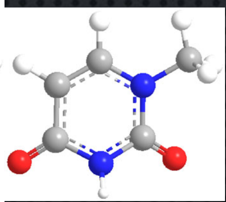
Purine



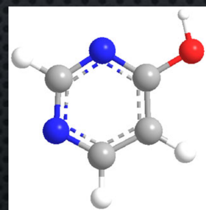
Thymine



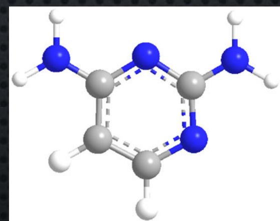
6-Methyluracil



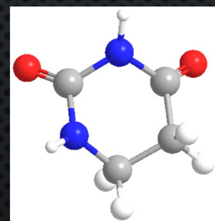
1-Methyluracil



4-Hydroxypyrimidine



2,6-Diaminopyrimidine



Dihydrouracil

Concentration: on the order of ppm or higher (10^{-6} g/g-meteorite) in total

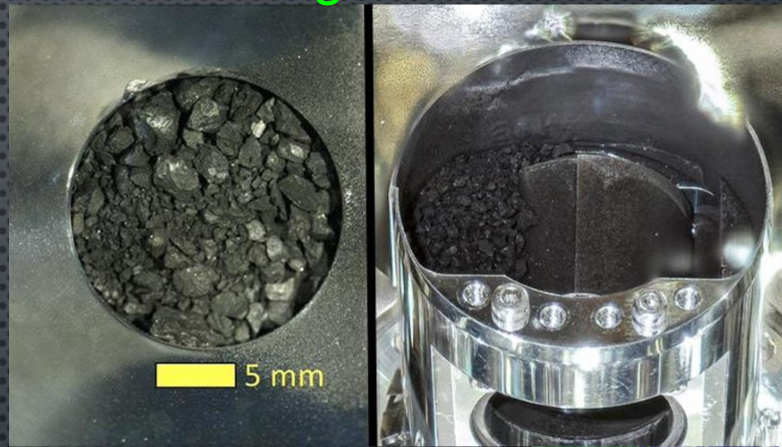
(Glavin et al. 2018; Furukawa et al. 2019; Oba et al. 2022)

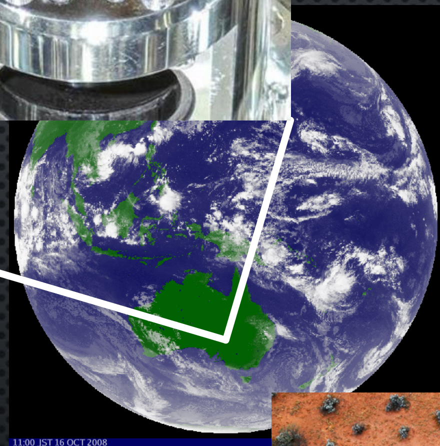
Samples returned from the asteroid Ryugu: HAYABUSA2 Project

Launched in 2014
Arrived in 2018
(0.96-1.41 AU)

Delivered to the Earth
(Dec. 2020)

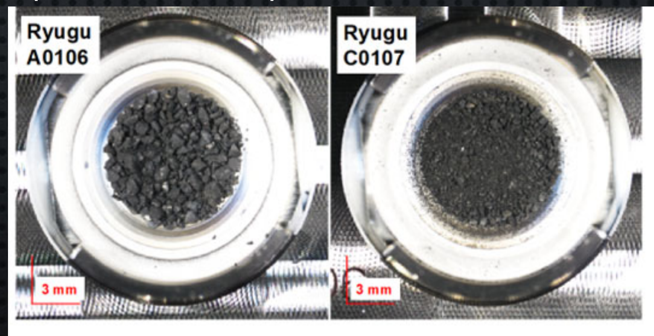
5.4 g in total





Sample A
(from surface)

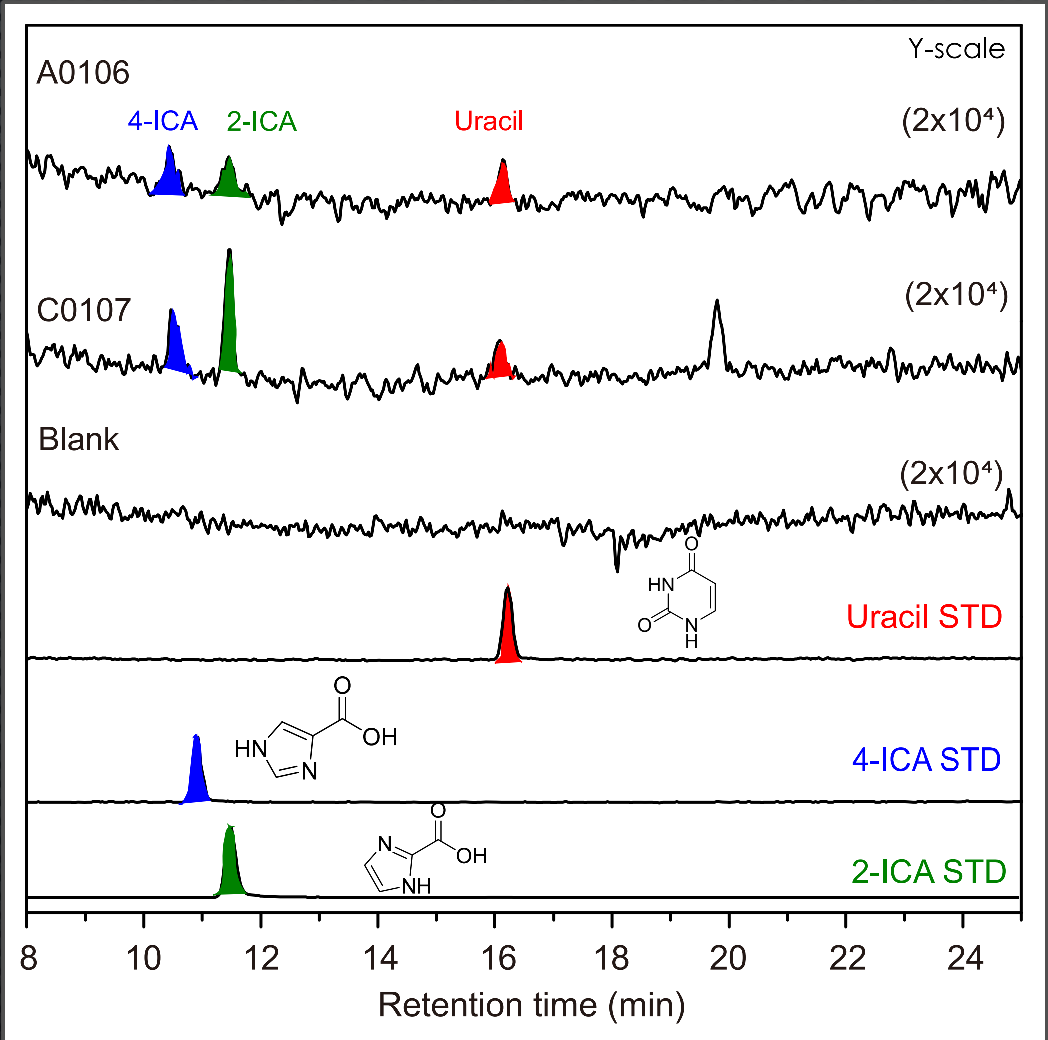
Sample C
(from sub-surface: ~1m)



Analyzed in a contamination-controlled clean laboratory

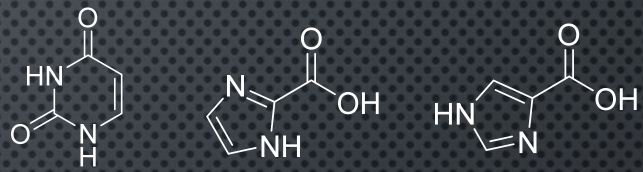
Results -Nucleobases in Ryugu samples-

High resolution mass chromatograms at m/z = 113.0346 ($C_4H_4N_2O_2+H^+$)



- 3-4 peaks detected in A0106 & C0107

  Uracil, 2-Imidazolecarboxylic acid (ICA), and 4-ICA



Uracil 2-ICA 4-ICA

- These peaks are not observed in the blank

  These 3 structural isomers are **indigenous to Ryugu**

- Concentration: 6-32 × ng/g-sample

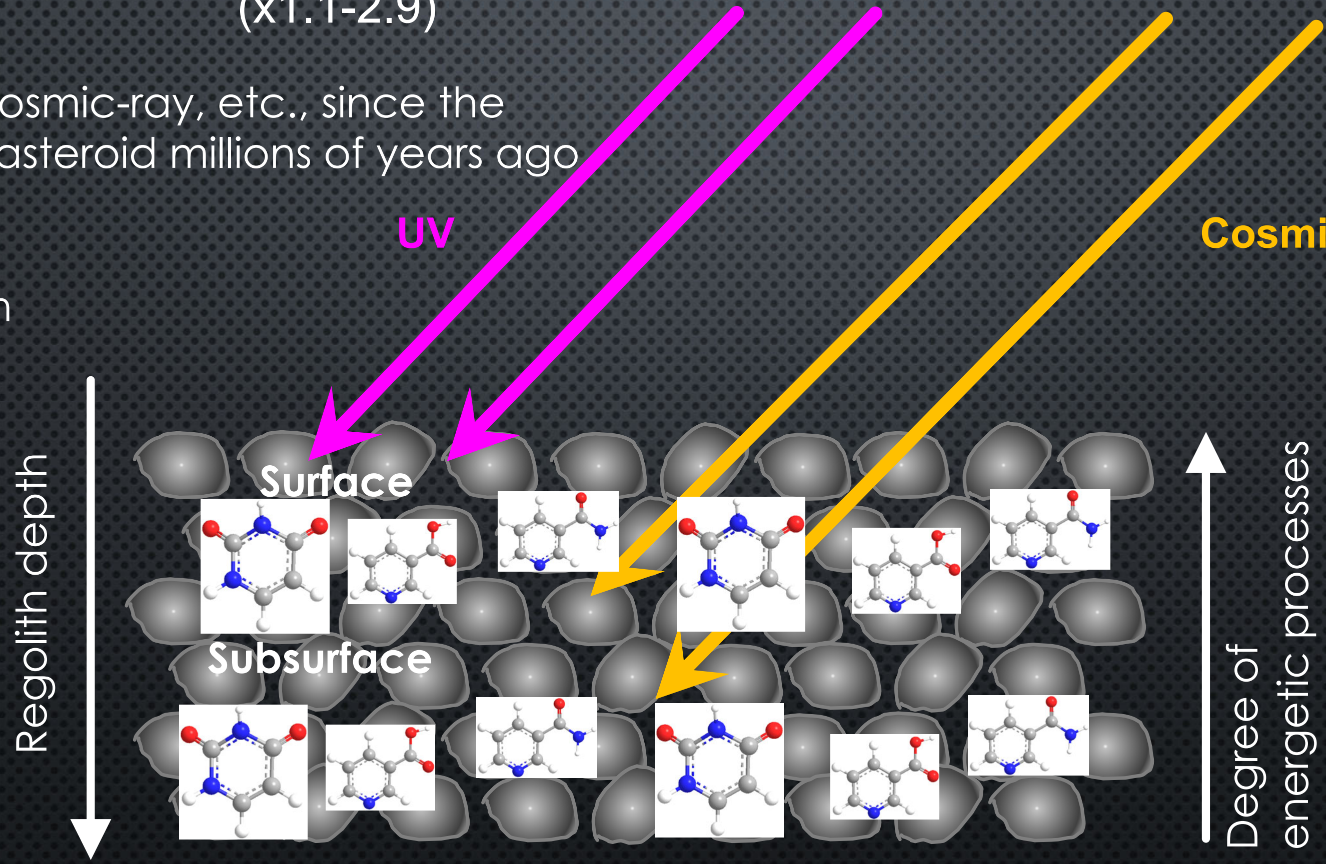
  Concentrations higher in C0107 than in A0106 (This is also true for many other molecules such as Vitamin B3 in the same samples)

Discussion –Variations in the concentration between samples

N-heterocycles are more abundant in C0107 (subsurface) than A0106 (surface) (x1.1-2.9)

Exposed to UV, cosmic-ray, etc., since the formation of the asteroid millions of years ago

cartoon



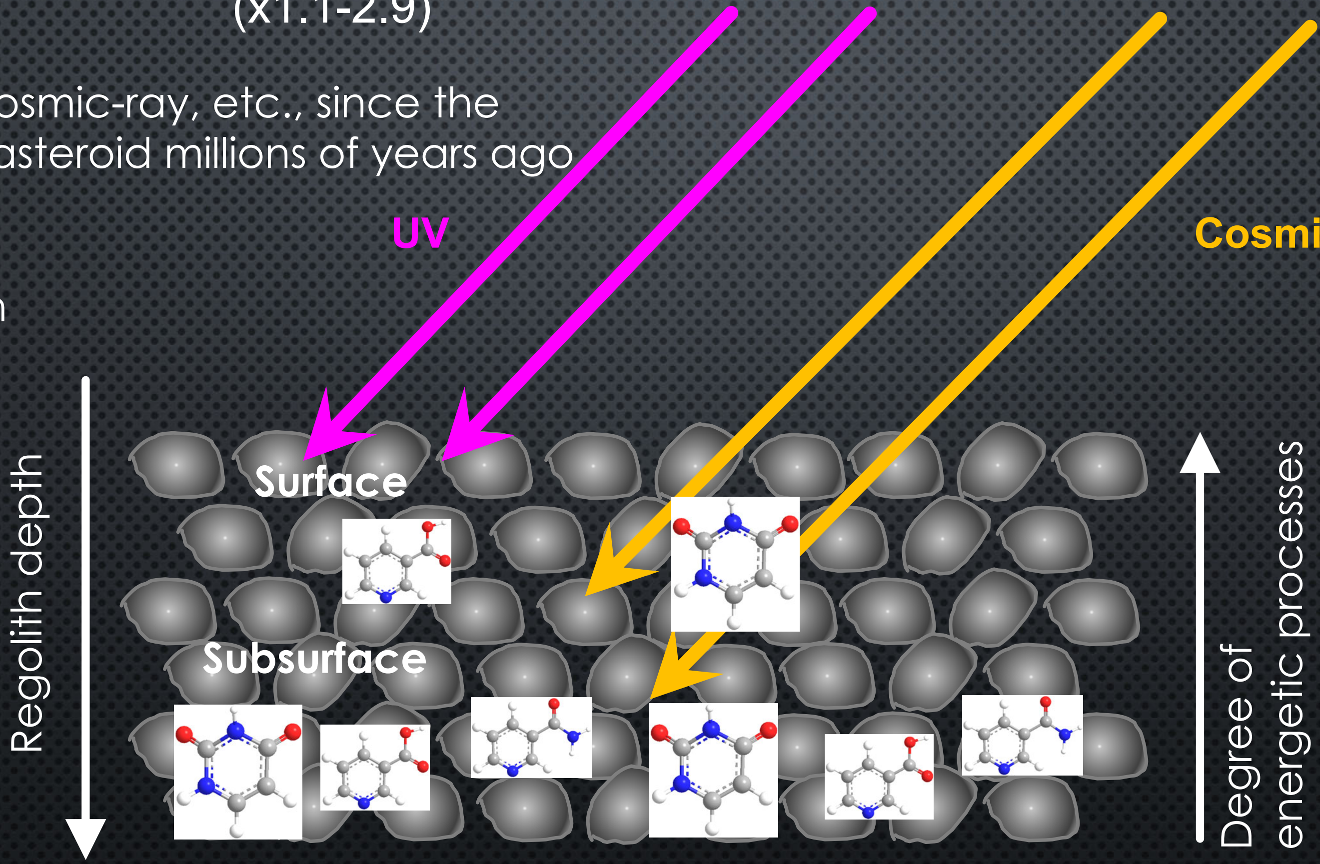
Uracil can be protected by co-existing minerals from radiolysis if it is in the subsurface (~5 cm)
(Etern et al. 2021, Icarus, 348, 114540)

Discussion –Variations in the concentration between samples

N-heterocycles are more abundant in C0107 (subsurface) than A0106 (surface) (x1.1-2.9)

Exposed to UV, cosmic-ray, etc., since the formation of the asteroid millions of years ago

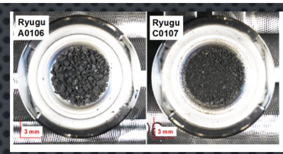
cartoon

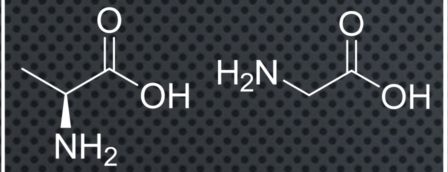


real

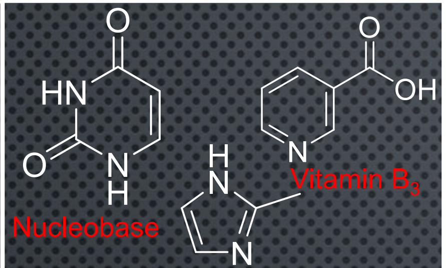
Cosmic ray-induced degradation plays a role in the distribution of nucleobases in asteroids (Ryugu & others)

Summary of individual molecules detected in Ryugu

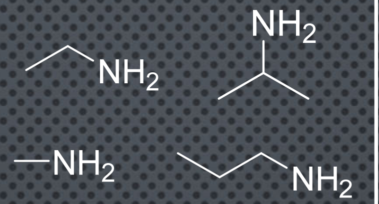




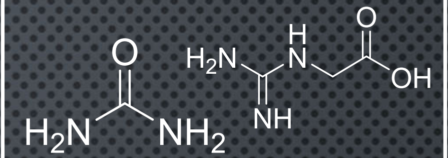
Amino acids
N>20, ~0.03-150 nmol/g
D/L ratio ~ 1
(Naraoka et al. 2023)



N-heterocycles
N>5, ~0.1-1 nmol/g
(Oba et al. 2023)
(Koga et al. in prep.)

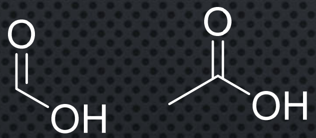


Amines
N=4, ~0.05-34.1 nmol/g
(Parker et al. 2023)

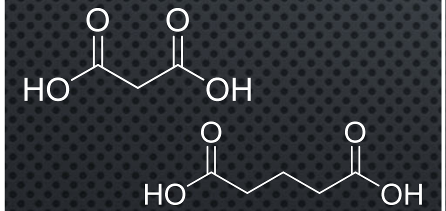


N,O-bearing (non-cyclic) molecules
N>5, ~50 nmol/g
(Takano et al. 2024)

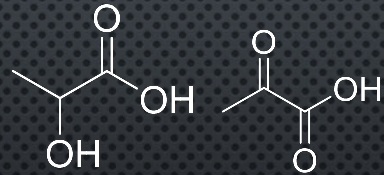
PAHs
N>5, ~10-30 nmol/g
(Aponte et al. 2023)



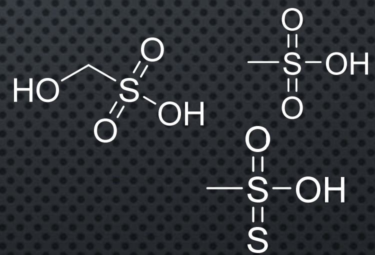
Monocarboxylic acids
N=2, ~8000 nmol/g
(Naraoka et al. 2023)



Dicarboxylic acids
N>5, ~10 nmol/g
(Takano et al. 2024)



Hydroxy/keto acids
N>10, ~0.1-10 nmol/g
(Takano et al. 2024)

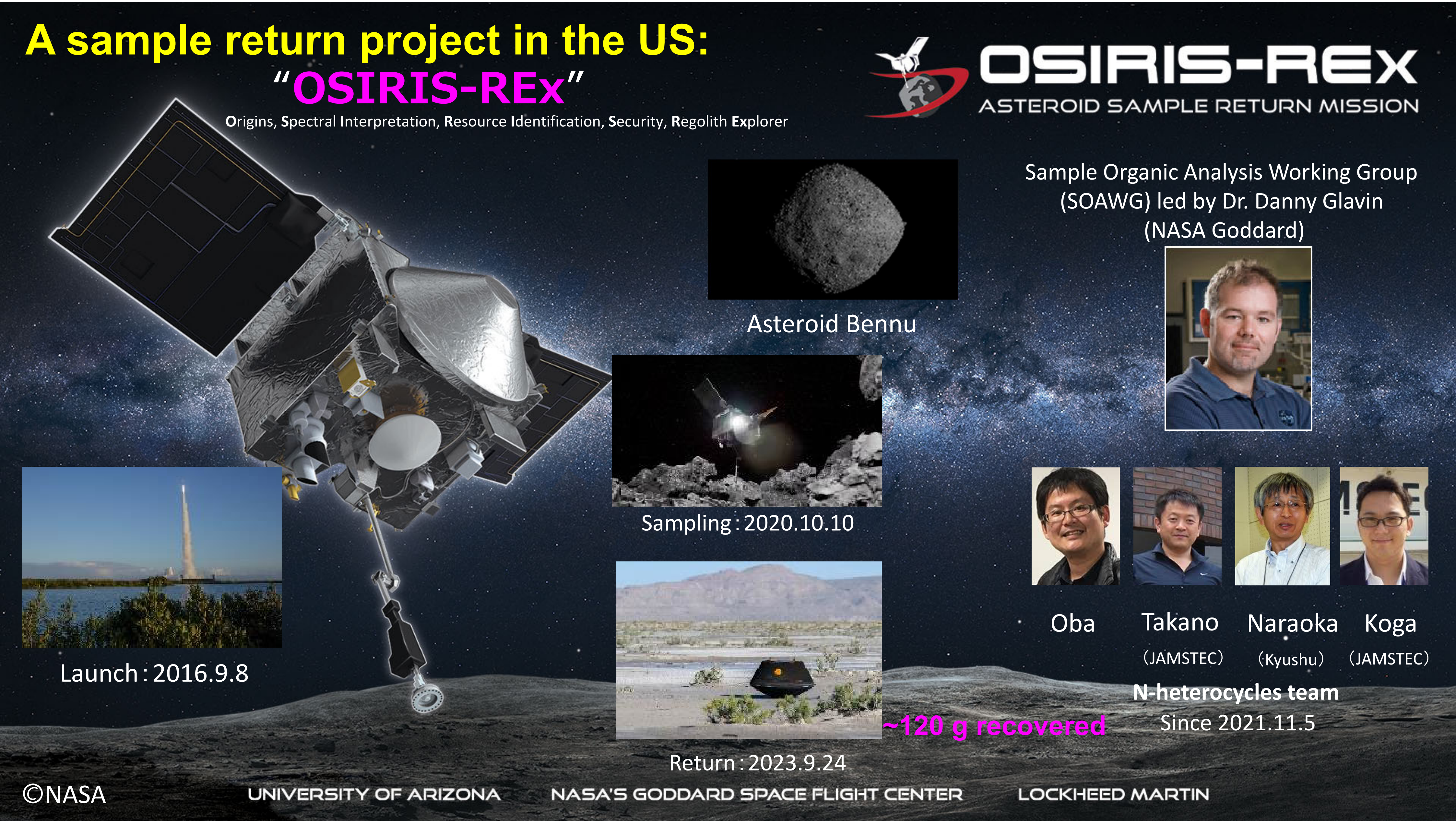


Alkylsulfonic acids
N>20, ~2500 nmol/g
(Yoshimura et al. 2023)

S^{2-} S_8 $S_5O_6^{2-}$
HSO_4^- $HS_2O_3^-$

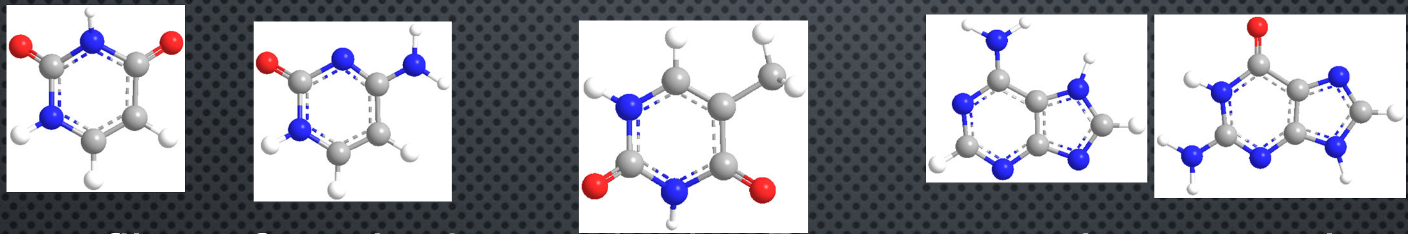
Inorganic
S-bearing species
N>7, ~84000 nmol/g
(Yoshimura et al. 2023)

--So far, at least >70 individual organic molecules have been identified in the Ryugu extract.
--A number of species must be present but have been unidentified yet. Cosmic-ray induced processes could have affected the formation/degradation of molecules in Ryugu.

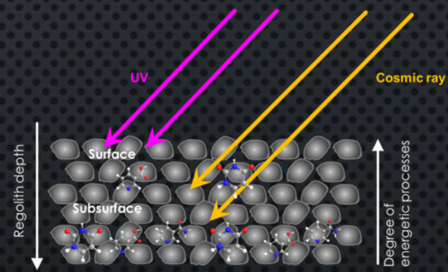

A sample return project in the US:
"OSIRIS-REx"
Origins, Spectral Interpretation, Resource Identification, Security, Regolith Explorer
OSIRIS-REx
ASTEROID SAMPLE RETURN MISSION
Asteroid Bennu
Sample Organic Analysis Working Group
(SOAWG) led by Dr. Danny Glavin
(NASA Goddard)
Sampling : 2020.10.10
Launch : 2016.9.8
Oba
Takano
(JAMSTEC)
Naraoka
(Kyushu)
Koga
(JAMSTEC)
N-heterocycles team
Since 2021.11.5
~120 g recovered
Return : 2023.9.24
©NASA
UNIVERSITY OF ARIZONA
NASA'S GODDARD SPACE FLIGHT CENTER
LOCKHEED MARTIN

Quick summary: Nucleobases in meteorites and asteroids

•All canonical nucleobases were present in meteorites and samples returned from carbonaceous asteroids Ryugu and Bennu



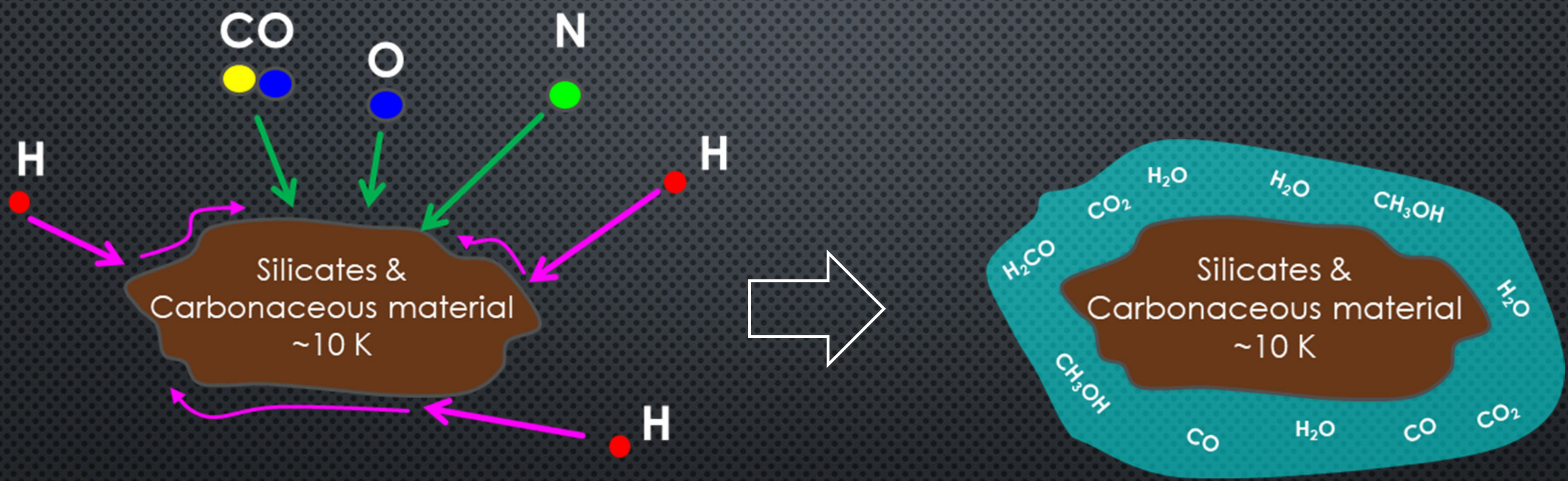
•Depth profiles of nucleobases in the Ryugu samples strongly suggest that energetic processes induced by cosmic rays, etc. caused degradation of nucleobases particularly on the topmost surface of the asteroid



•Nucleobases in extraterrestrial materials would have been provided to the early Earth during the late heavy bombardment period >4 Ga

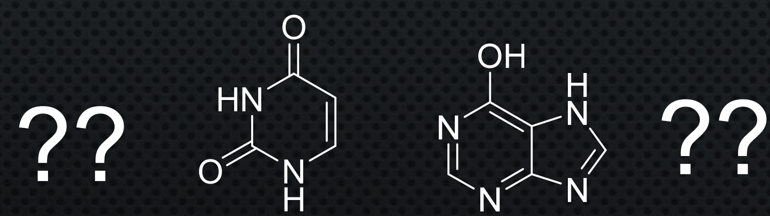
How were nucleobases formed in space?

1. Grain-surface reactions on interstellar grains at ~10 K?



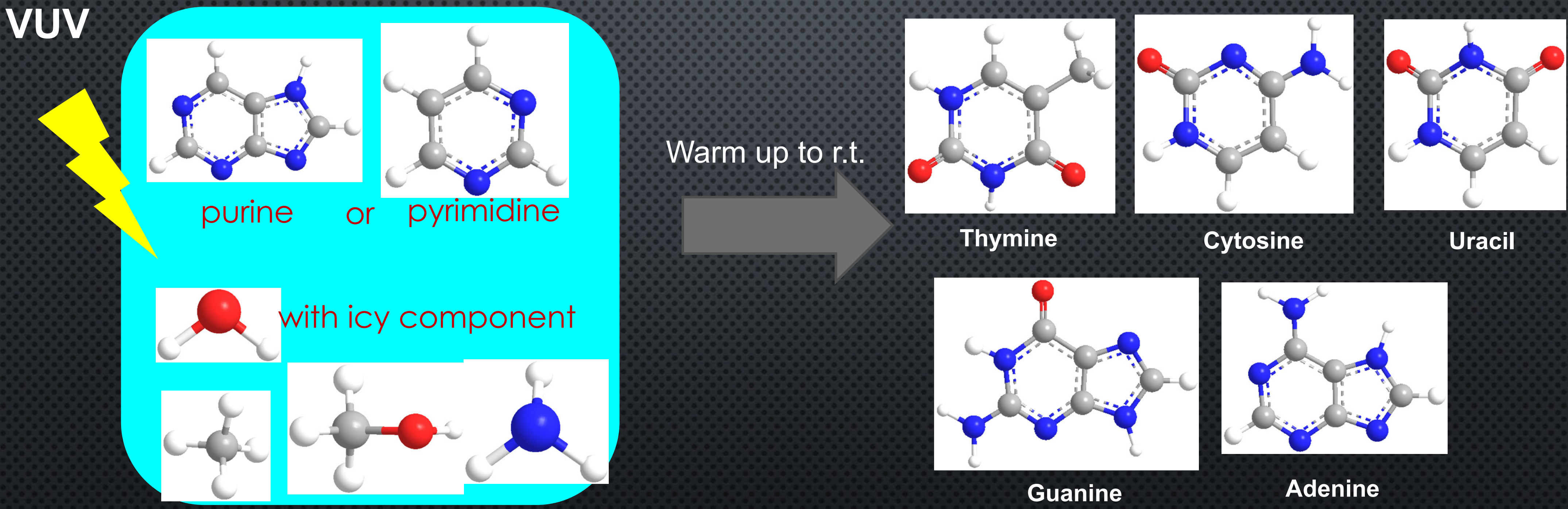
Formation of large COMs is not easy (not impossible) at 10 K

No reasonable reports on the formation of cyclic organic molecules including nucleobases



How were nucleobases formed in space?

2. (Cosmic-ray-induced) UV photons may trigger the synthesis of nucleobases: photolysis of purine or pyrimidine-containing ices



If purine or pyrimidine is present in interstellar ices, nucleobases may be produced (no detection so far)

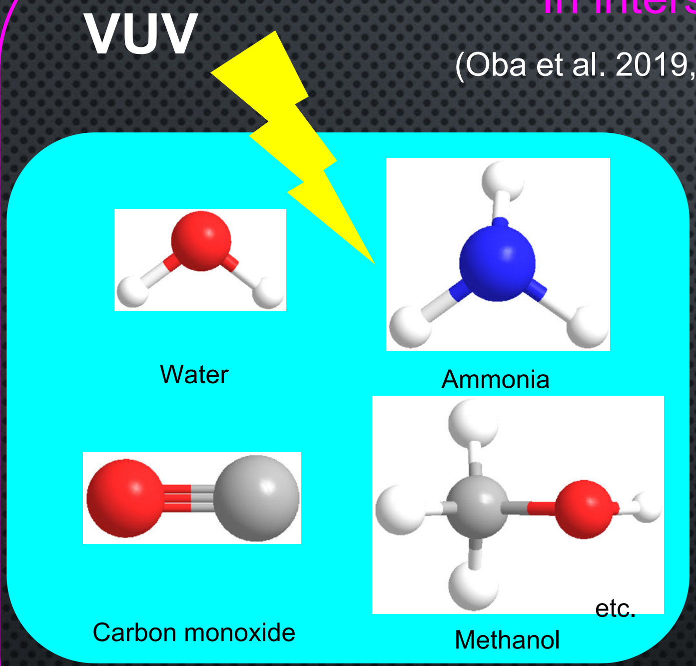
Nuevo et al. 2009, Astrobiology, 9, 683
Materese et al. 2013, Astrobiology, 13, 948
Materese et al. 2017, Astrobiology, 17, 761

How were nucleobases formed in space?

3. Photolysis of more relevant interstellar ice analogs

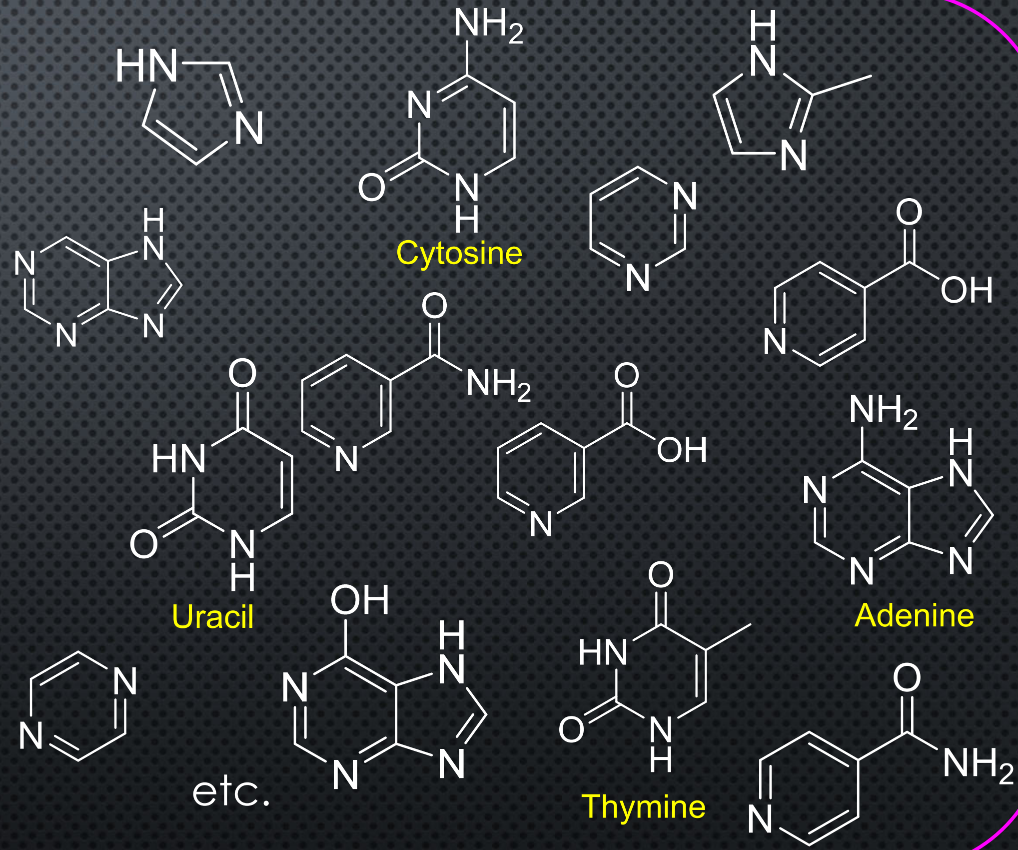
In interstellar ice analogs

(Oba et al. 2019, Nat. Commun., 10, 4413)



Interstellar ice analogs (~10 K)

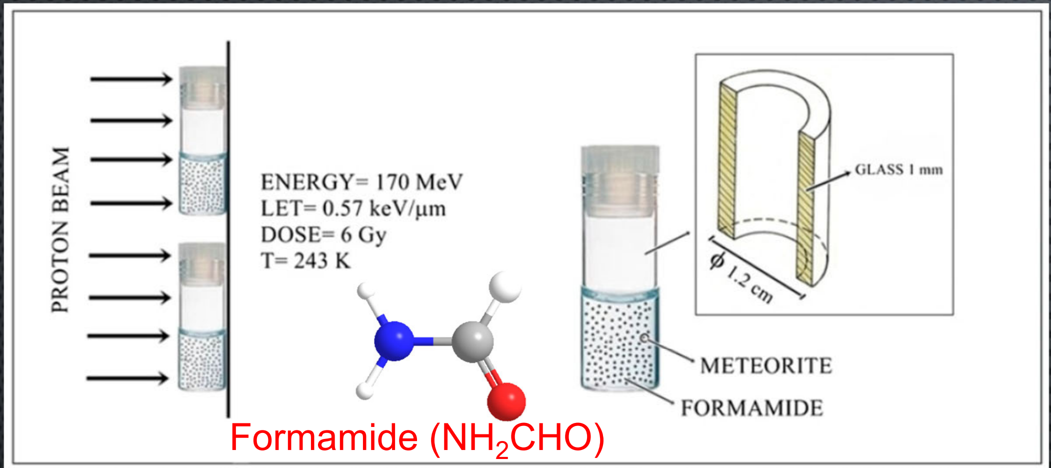
Warming up to room temperature



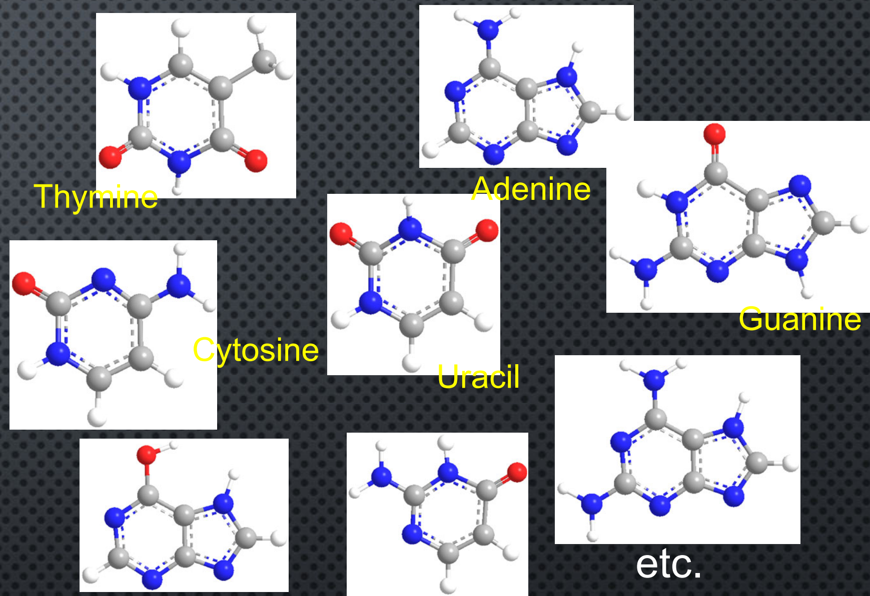
Distribution is similar to those found in asteroid Bennu (Glavin et al. accepted)

How were nucleobases formed in space?

4. Formamide (NH_2CHO) irradiated by Cosmic-ray analogs (170 MeV H^+) with meteorite powders



Experimental procedure (Saladino et al. 2015, PNAS, 112, E2746)



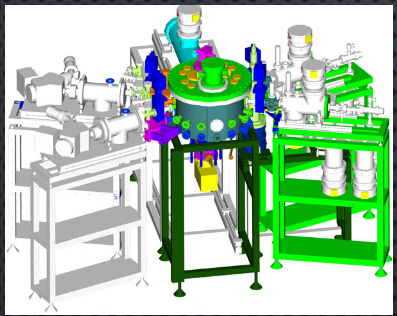
etc.

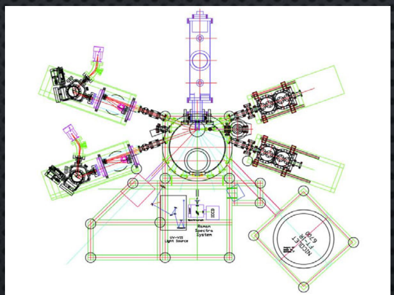
Radiolysis of formamide could have a strong potential to yield various COMs including nucleobases in space

(Although detailed formation mechanisms, the role of meteorite powders, the validity of the experimental settings, etc. need further discussion)

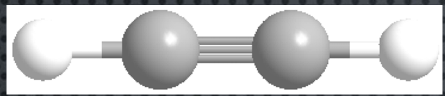
How were nucleobases formed in space?

5. Electron irradiation to acetylene + ammonia mixtures at 10 K

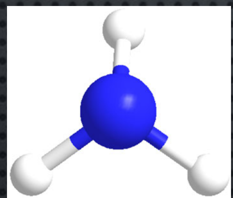




(http://uhmreactiondynamics.org/Keck.html)



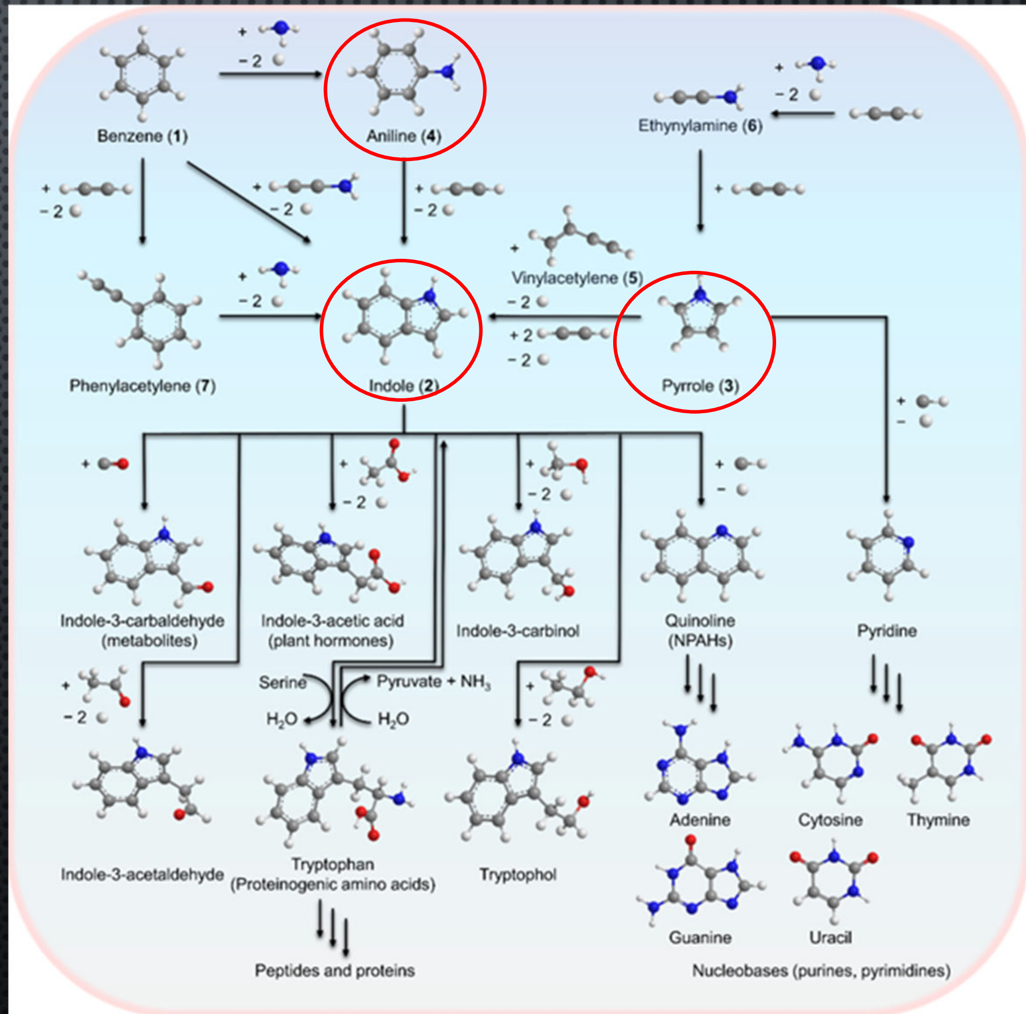
Acetylene



Ammonia

+ 5 keV electron
(at 10 K)

◯ : synthesized



(Wang et al. 2024, JACS, https://doi.org/10.1021/jacs.4c09449.)

Quick summary: Laboratory experiments on nucleobase synthesis

•The synthesis of nucleobases via non-energetic processes hardly occurs at 10 K

•Nucleobases and related N-heterocyclic molecules can be synthesized via photolysis of interstellar ice analogs at 10 K

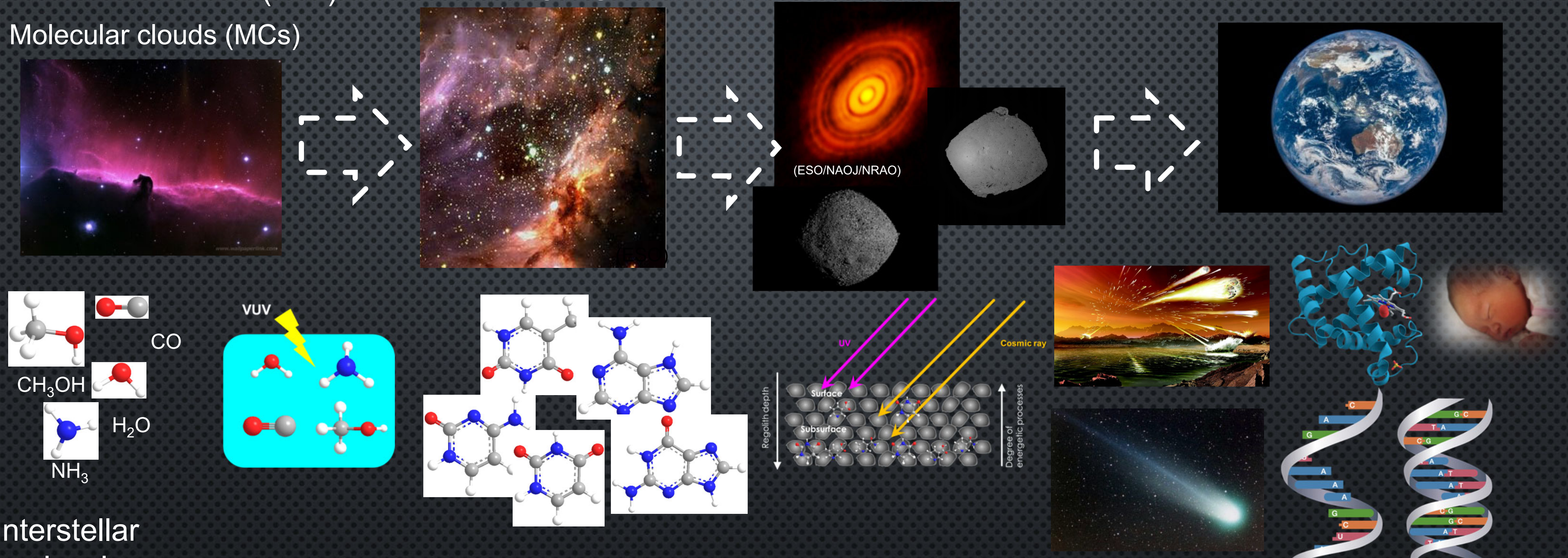
At least, cosmic-ray indirectly contributes to the synthesis of nucleobases in the interstellar medium

•Various kinds of nucleobases and their possible precursors may be synthesized from formamide (NH_2CHO) or C_2H_2/NH_3 mixed ices via its radiolysis

Not only their formation, but also their degradation should be further studied

Concluding remark

Interstellar medium (ISM) | Star-forming regions | Protoplanetary disk /Solar system | Earth (Solar system)



Interstellar molecules (N~200)

Cosmic rays would be important for the origin of life on Earth!

Functionalized macromolecules

Building blocks of life were first synthesized in molecular clouds, followed by experiencing various processes through the evolution of stars and planets, finally (somehow) resulting in the birth of the first life on Earth.