ASTROCHEMISTRY

FROM THE BIG BANG TO LIFE

Global Astrochemistry Lecture Series (GALS) 2024

EXOGENOUS SYNTHESIS AND DELIVERY OF BIOMOLECULE PRECURSORS TO EARLY EARTH

Alexey Potapov. *Friedrich Schiller University Jena, Germany*

22.03.2024 | 15:00 - 17:00 CET

cost EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY
NanoSpace
Funded by the European Union

Outline:

Habitability

Origin of Life hypotheses

Evidence for exogenous hypothesis:
- Space
- Earth

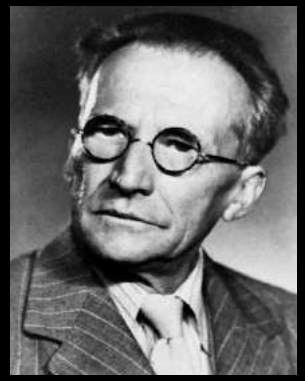
Part 1:

Habitability

What is Life?

Attempts at a definition:

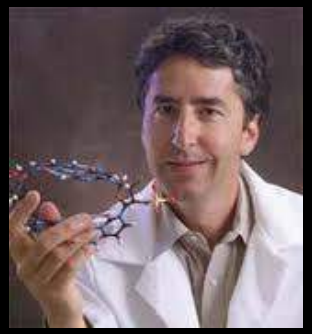
Erwin Schrödinger (physicist**)** defined life as that which resists decaying to disorder and equilibrium. This definition relates to the second law of thermodynamics, which states that closed systems will naturally gain entropy, or disorder, over time.



“Any population of entities which has the properties of multiplication, heredity, and variation.” – **John Maynard Smith** (evolutionary biologist and geneticist)



“Life is a self-sustaining system capable of Darwinian evolution.“ **- Gerald Joyce** (biochemist)



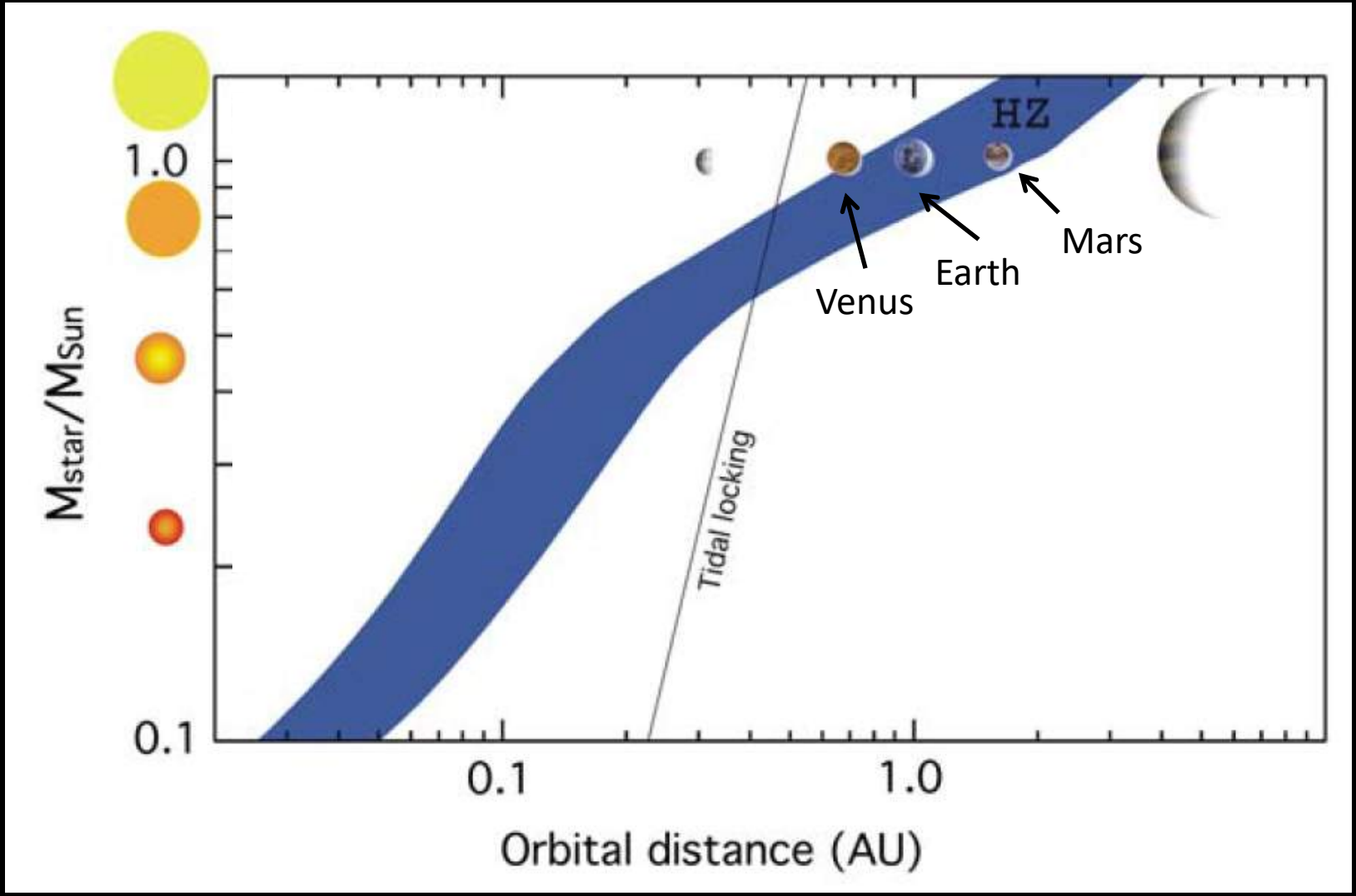
Requirements for life (as we know it) to form on a planet

A habitable planet should have:

- A solid or liquid surface
- Orbit a star that remains stable in output for billions of years
- Be at a distance from the star that results in its achieving a suitable temperature so its surface water is liquid, not frozen
- Have a circular orbit, so constant conditions prevail for its entire "year“



The Habitable Zone



H. Lammer et al. Astron. Astrophys. Rev.(2009) 17:181-249

The role of water

<u>The liquid phase facilitates chemical reactions</u>
- in a liquid reactants move freely
- liquid accumulates reactants

<u>The universal solvent</u>
- as a polar molecule, water interacts best with other polar molecules allowing for the formation of bonds
- efficient molecule, cell, drug transport in the body



<u>Chemical reactions</u>
- water molecules are involved in chemical reactions
- water is an efficient catalyst of chemical reactions
- capability to dissolve molecules providing building blocks

<u>Support of the cellular structure</u>
- water fills cells to help maintain their shape and structure
- water contributes to the formation of membranes surrounding cells

How to find signatures of life?



Earth' atmosphere:
N_2 (78.08%), O_2 (20.95%), Ar (0.93%),
CO_2, CH_4, O_3, H_2O, N_2O, He, Ne, Kr, …

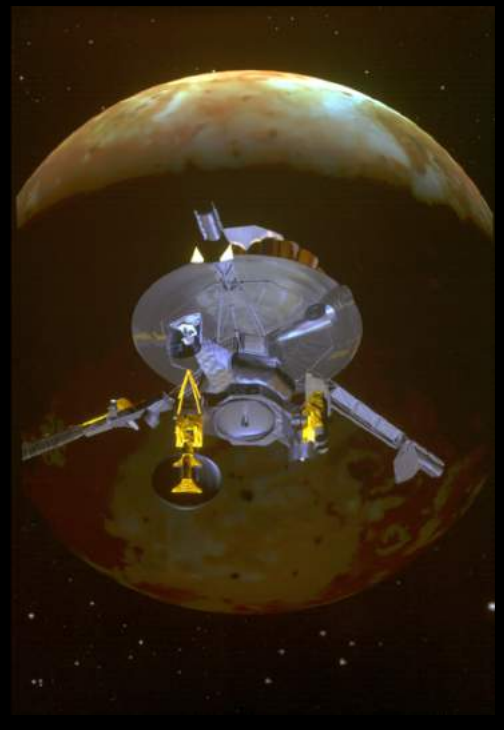
O_2 has allowed life to evolve.
H_2O, CO_2, N_2O, CH_4, O_3 – greenhouse gases (keep the surface warm enough for life to thrive).
O_3 protects us from the ultraviolet radiation.
H_2O has allowed life to appear.

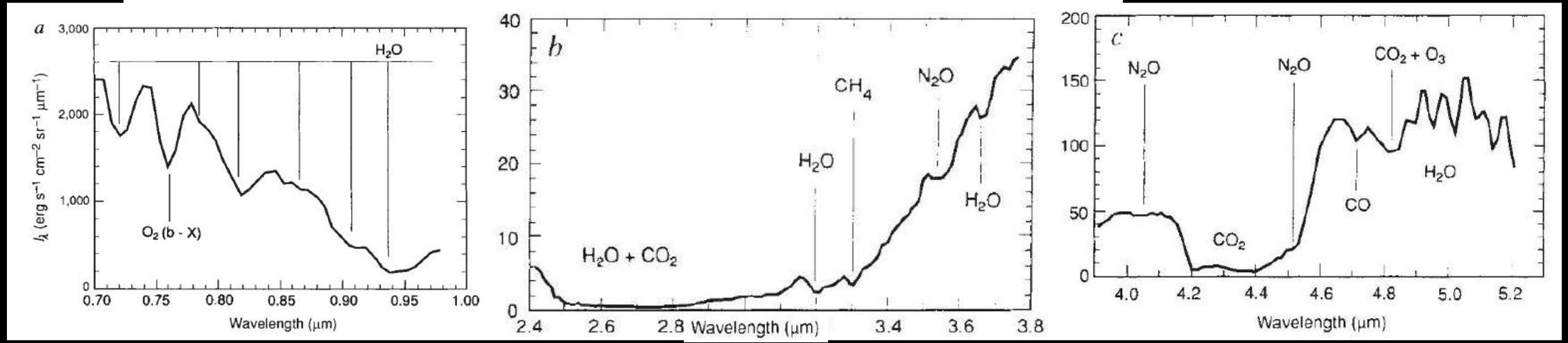
A search for life on Earth from the Galileo spacecraft

Carl Sagan*, W. Reid Thompson*, Robert Carlson†, Donald Gurnett‡ & Charles Hord§

* Laboratory for Planetary Studies, Cornell University, Ithaca, New York 14853, USA
† Atmospheric and Cometary Sciences Section, Jet Propulsion Laboratory, Pasadena, California 91109, USA
‡ Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa 52242-1479, USA
§ Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, Colorado 80309, USA

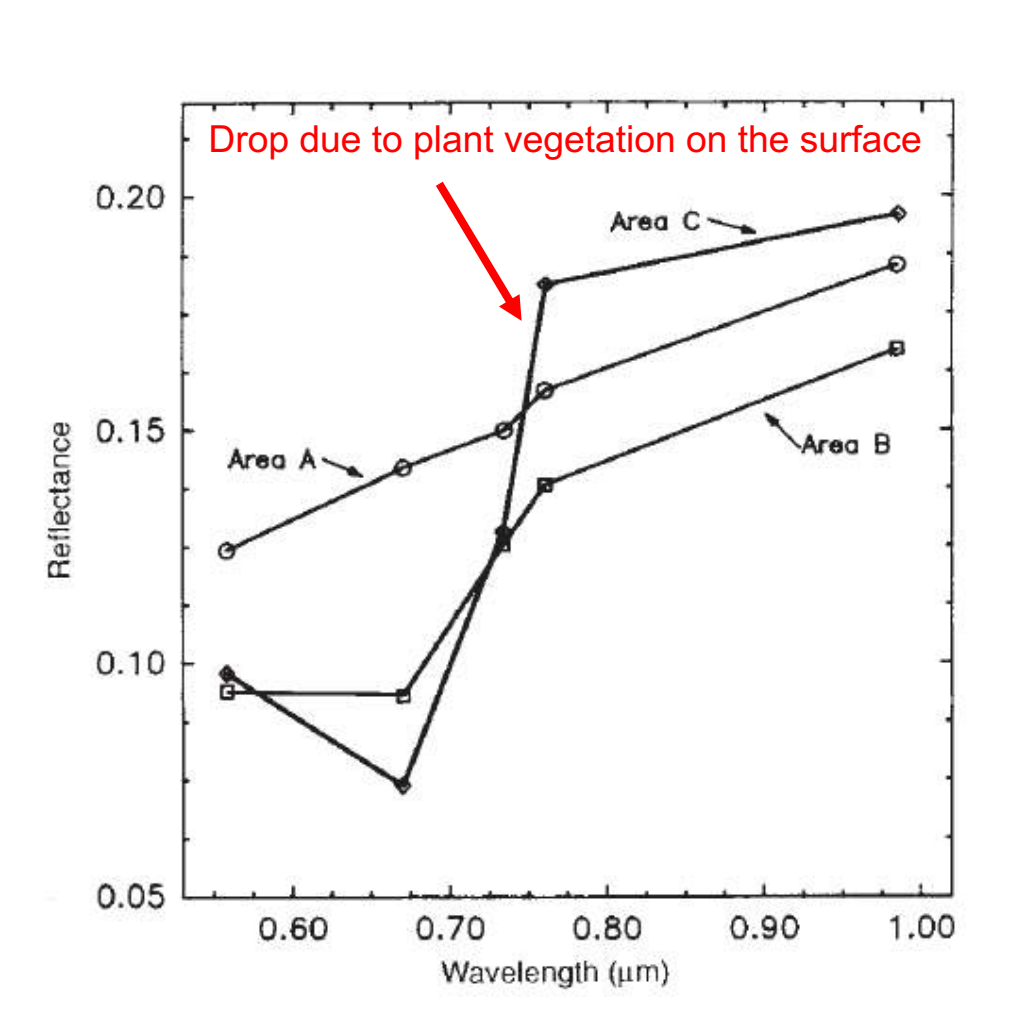
In its December 1990 fly-by of Earth, the Galileo spacecraft found evidence of abundant gaseous oxygen, a widely distributed surface pigment with a sharp absorption edge in the red part of the visible spectrum, and atmospheric methane in extreme thermodynamic disequilibrium; together, these are strongly suggestive of life on Earth. Moreover, the presence of narrow-band, pulsed, amplitude-modulated radio transmission seems uniquely attributable to intelligence. These observations constitute a control experiment for the search for extraterrestrial life by modern interplanetary spacecraft.

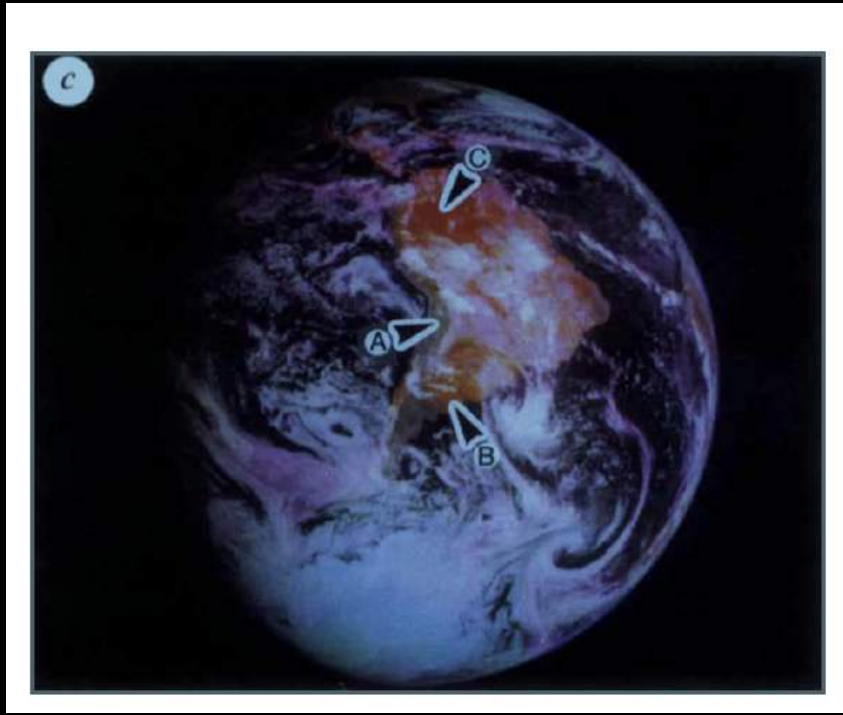




Sagan et al., Nature 365, 715 (1993)

Signs of vegetation on Earth

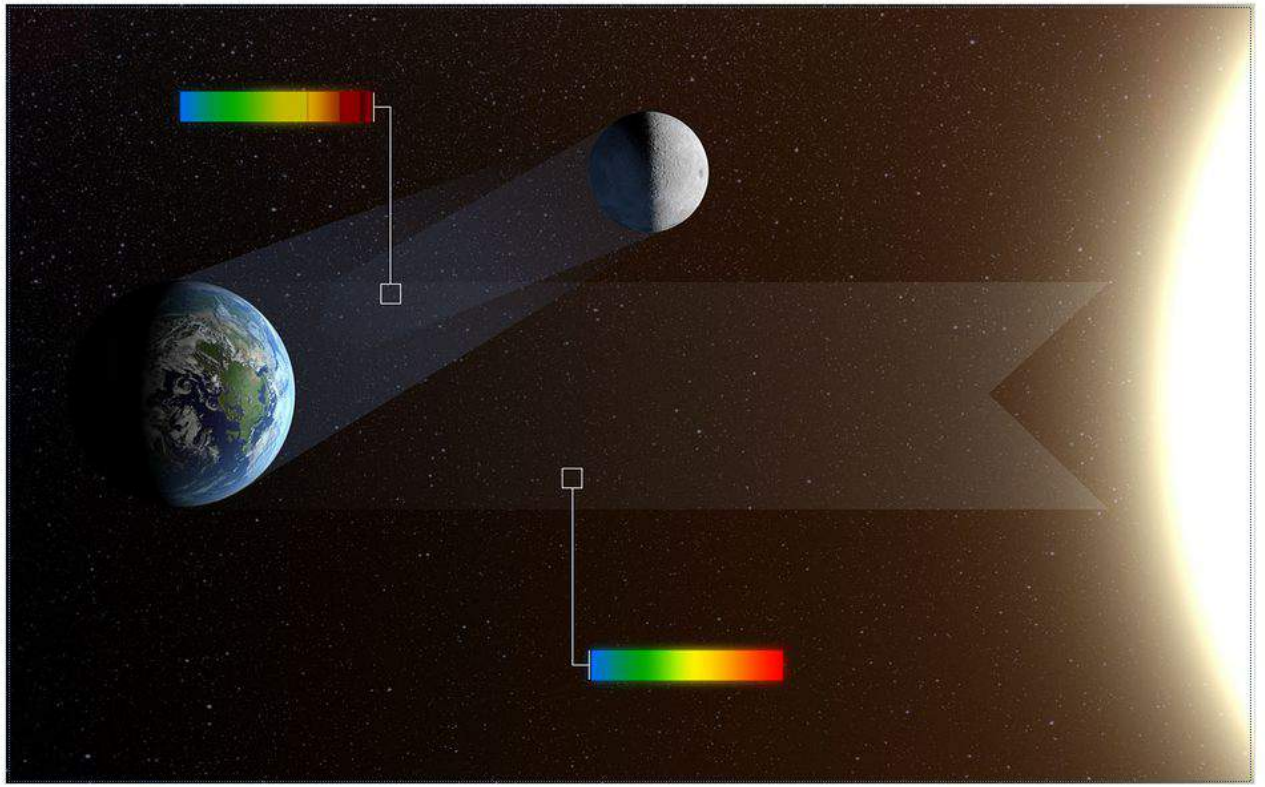




The spectrum C is inconsistent with all likely rock and soil types, and is plausibly associated with light-harvesting (photosynthetic) pigments

Sagan et al., Nature 365, 715 (1993)

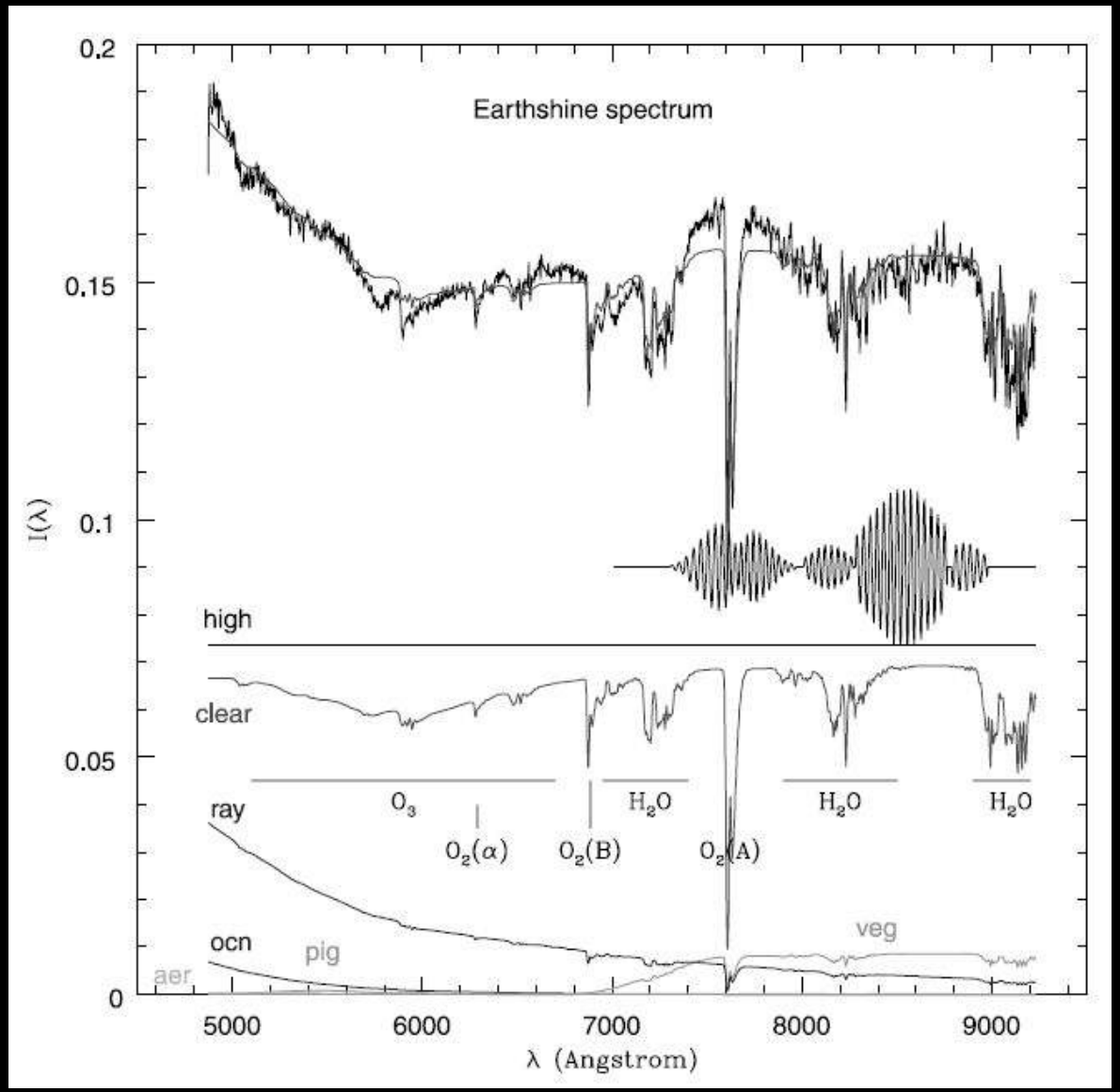
Earthshine: the Moon shining in reflected light from the Earth



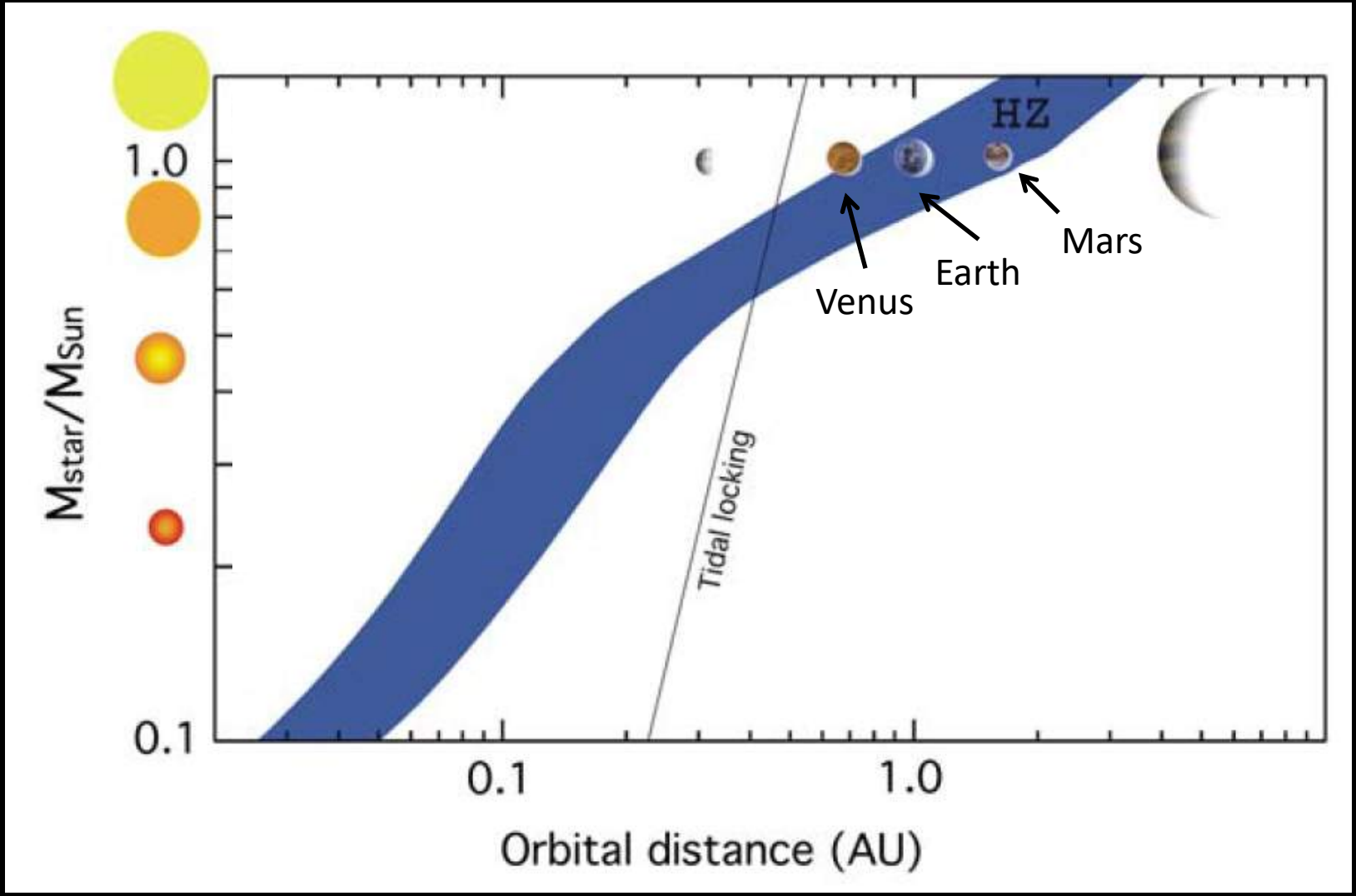
When the Moon appears as a thin crescent in the twilight skies of Earth it is often possible to see that the rest of the disc is also faintly glowing. This phenomenon is called earthshine. It is due to sunlight reflecting off the Earth and illuminating the lunar surface. After reflection from Earth the colours in the light, shown as a rainbow in this picture, are significantly changed. By observing earthshine astronomers can study the properties of light reflected from Earth as if it were an exoplanet and search for signs of life. The reflected light is also strongly polarised and studying the polarisation as well as the intensity at different colours allows for much more sensitive tests for the presence of life.

Credit: ESO/L. Calçada

Modelling the Earthshine Spectrum



The Habitable Zone



H. Lammer et al. Astron. Astrophys. Rev.(2009) 17:181-249

Life on Venus?



Venus' atmosphere:
CO_2 (96%), N_2 (3.2%), SO_2, Ar, H_2O, CO, He, O_2, Ne

Pressure: 92 bar (92 times that of the Earth)

CO_2 - strong greenhouse effect - surface temperature: about 480°C (the hottest planet in the solar system)

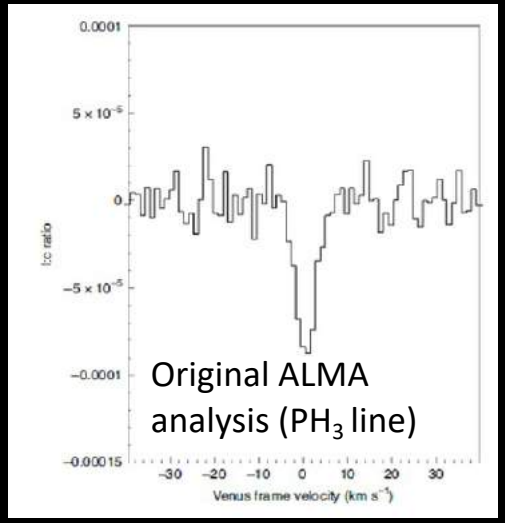
Life on Venus?

Phosphine gas in the cloud decks of Venus

Jane S. Greaves[1,2] ✉, Anita M. S. Richards[3], William Bains[4], Paul B. Rimmer[5,6,7], Hideo Sagawa[8], David L. Clements[9], Sara Seager[4,13,14], Janusz J. Petkowski[4], Clara Sousa-Silva[4], Sukrit Ranjan[4], Emily Drabek-Maunder[1,10], Helen J. Fraser[11], Annabel Cartwright[1], Ingo Mueller-Wodarg[9], Zhuchang Zhan[4], Per Friberg[12], Iain Coulson[12], E'lisa Lee[12] and Jim Hoge[12]

Measurements of trace gases in planetary atmospheres help us explore chemical conditions different to those on Earth. Our nearest neighbour, Venus, has cloud decks that are temperate but hyperacidic. Here we report the apparent presence of phosphine (PH_3) gas in Venus's atmosphere, where any phosphorus should be in oxidized forms. Single-line millimetre-waveband spectral detections (quality up to ~15σ) from the JCMT and ALMA telescopes have no other plausible identification. Atmospheric PH_3 at ~20 ppb abundance is inferred. The presence of PH_3 is unexplained after exhaustive study of steady-state chemistry and photochemical pathways, with no currently known abiotic production routes in Venus's atmosphere, clouds, surface and subsurface, or from lightning, volcanic or meteoritic delivery. PH_3 could originate from unknown photochemistry or geochemistry, or, by analogy with biological production of PH_3 on Earth, from the presence of life. Other PH_3 spectral features should be sought, while in situ cloud and surface sampling could examine sources of this gas.

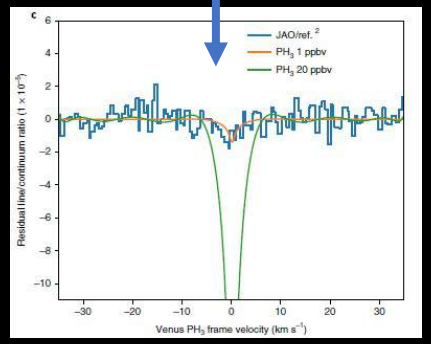
Nature Astronomy 5, 655 (2021)

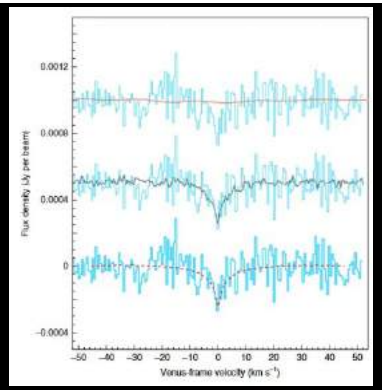


Original ALMA analysis (PH_3 line)

No evidence of phosphine in the atmosphere of Venus from independent analyses

G. L. Villanueva[1] ✉, M. Cordiner[1,2], P. G. J. Irwin[3], I. de Pater[4], B. Butler[5], M. Gurwell[6], S. N. Milam[1], C. A. Nixon[1], S. H. Luszcz-Cook[7,8], C. F. Wilson[3], V. Kofman[1,9], G. Liuzzi[1,9], S. Faggi[1,9], T. J. Fauchez[1,10], M. Lippi[1,9], R. Cosentino[1,11], A. E. Thelen[1,10], A. Moullet[12], P. Hartogh[13], E. M. Molter[4], S. Charnley[1], G. N. Arney[1], A. M. Mandell[1], N. Biver[14], A. C. Vandaele[15], K. R. de Kleer[16] and R. Kopparapu[1]





Terrestrial sources of phosphine: bacteria

After extensive criticism, and re-calibration of the ALMA data, the authors maintain that PH_3 has been detected in the atmosphere of Venus.

Life on Venus?

DETECTION OF SIMPLEST AMINO ACID *glycine* IN THE ATMOSPHERE OF VENUS

RESEARCH ARTICLE

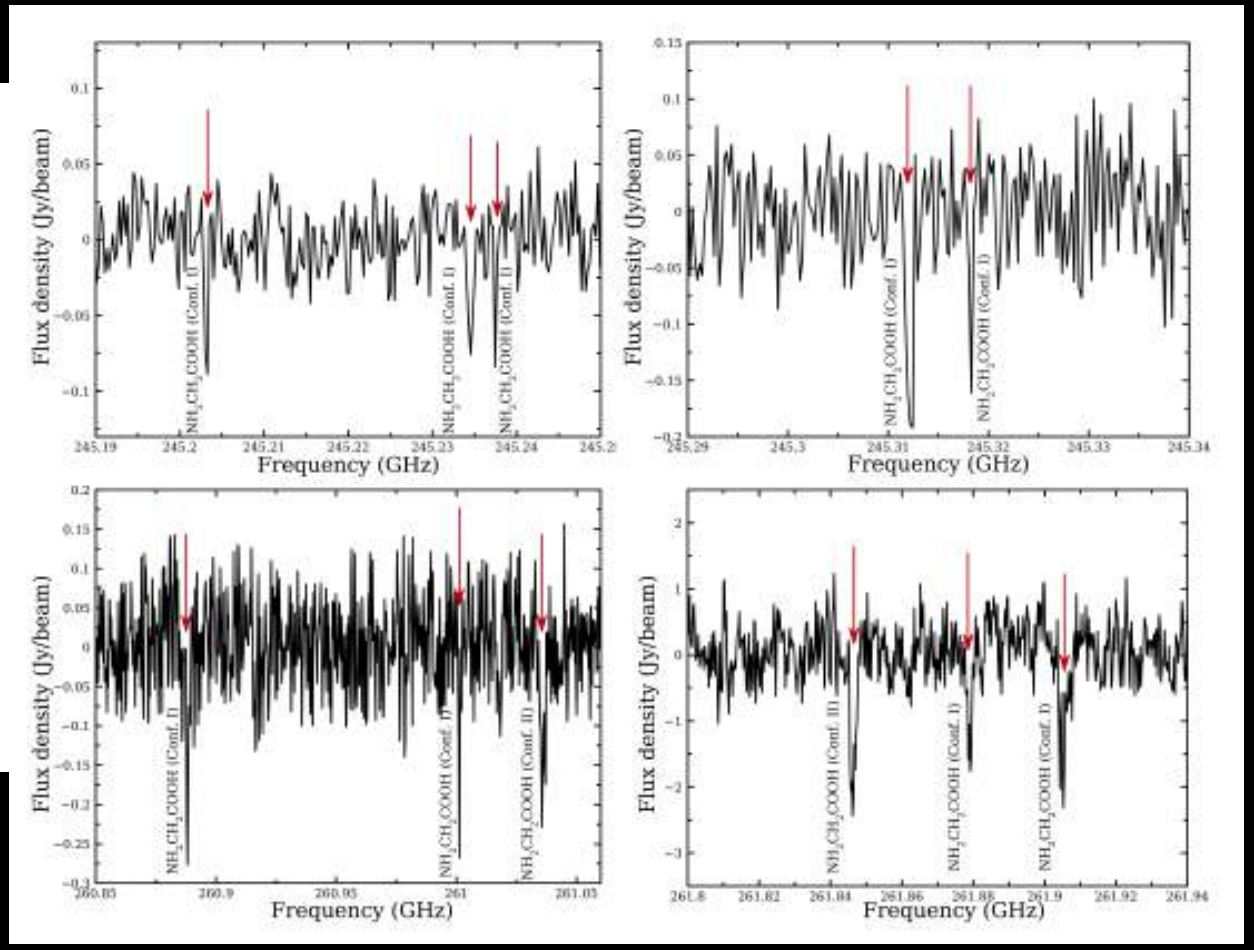
Arijit Manna
Midnapore City College
Kuturia, Bhadutala, Paschim Medinipur,
West Bengal, India 721129
Mannaarijit@hotmail.com

Sabyasachi Pal
Indian Centre for Space Physics
43 Chalantika, Garia Station Road,
Kolkata, India 700084
sabya.pal@gmail.com

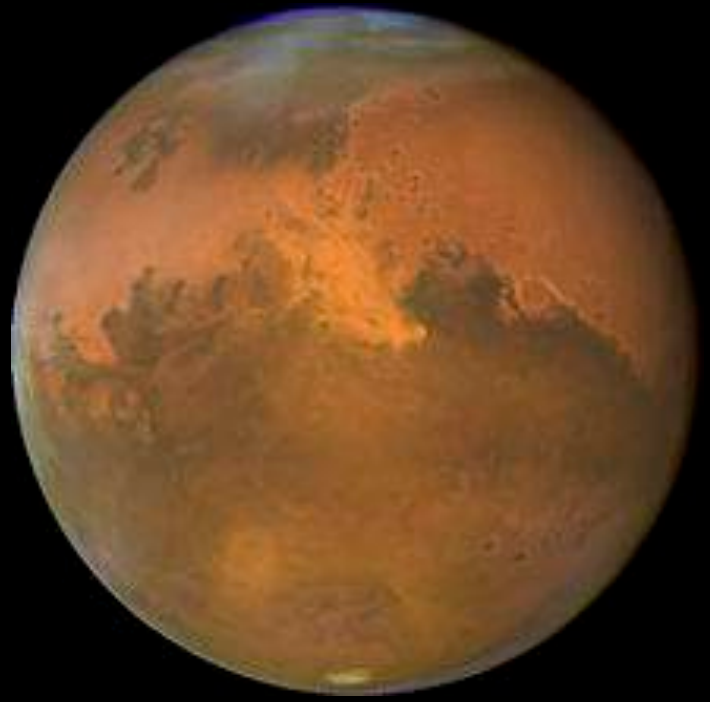
Mangal Hazra
Midnapore City College
Kuturia, Bhadutala, Paschim Medinipur,
West Bengal, India 721129
mangalkrhazra@gmail.com

April 23, 2021

https://arxiv.org/abs/2010.06211



Life on Mars?



The **Martian** atmosphere:
CO_2 (96%), N_2 (1.9%), Ar (1.9%);
Trace gases: C_2H_2, CO, CH_4, N_2O, O_2, O_3, H_2O, Kr, Ne, Xe

Pressure at the surface: 6.35 mbar
(less than 1% of the Earth's value)

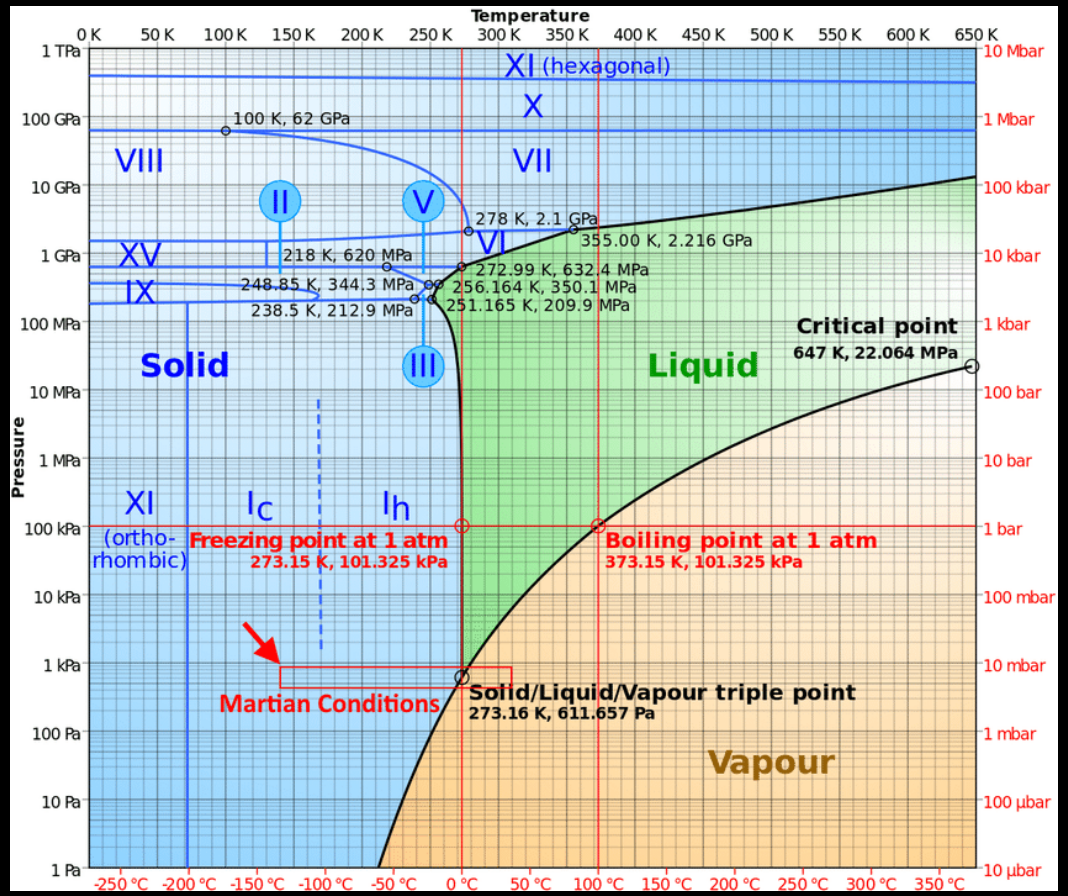
Average temperature: –60ºC (comparable to Antarctica)
Temperature ranges from –153ºC to +20ºC
(due to the low thermal inertia)

Ice caps — made of H_2O and CO_2

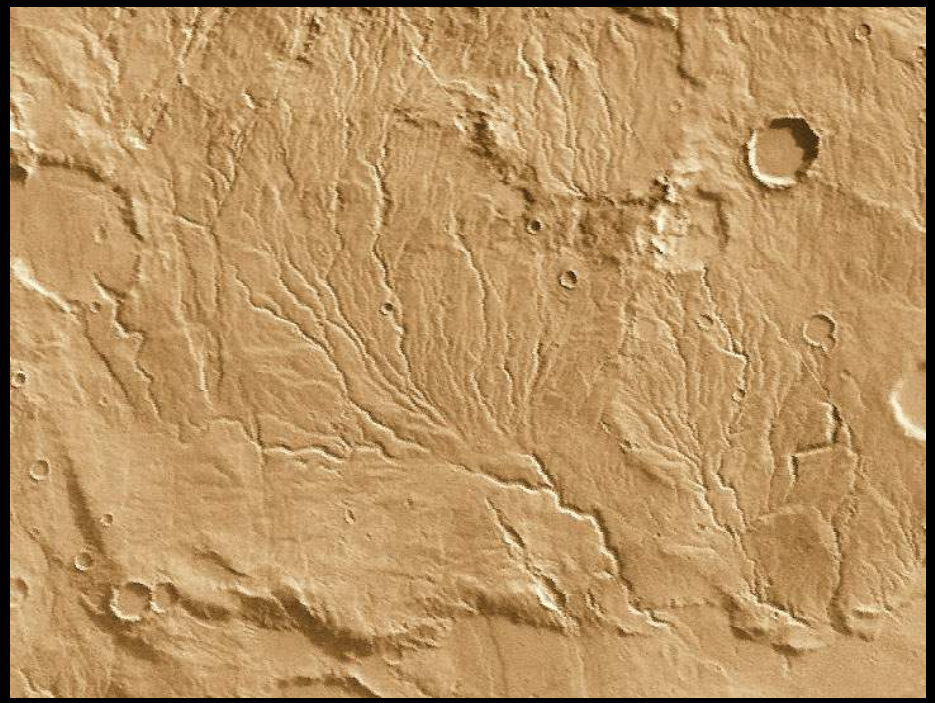
Life on Mars?

Water

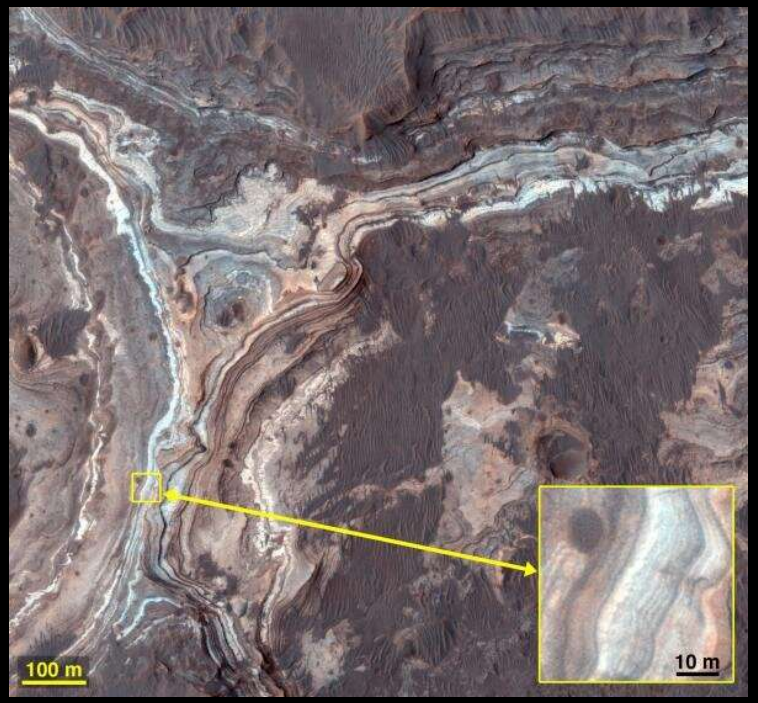
- Water can be liquid at low elevations



Life on Mars?



Valleys created by ancient river networks can be found in many places on Mars
(Photo credit: NASA)



Clay-bearing sediments created by running water on Martian surface

Weitz et al, DOI: 10.1016/j.icarus.2022.115090

Life on Mars?

Elon Musk said that he plans to send 1 million people to Mars by 2050 (Business Insider)



Part 2:

Origin of Life hypotheses

Origin of life on Earth

The main hypotheses describing the source of the organic compounds that could have served as the basis of life

Formation of prebiotic molecules under the conditions of the primitive Earth

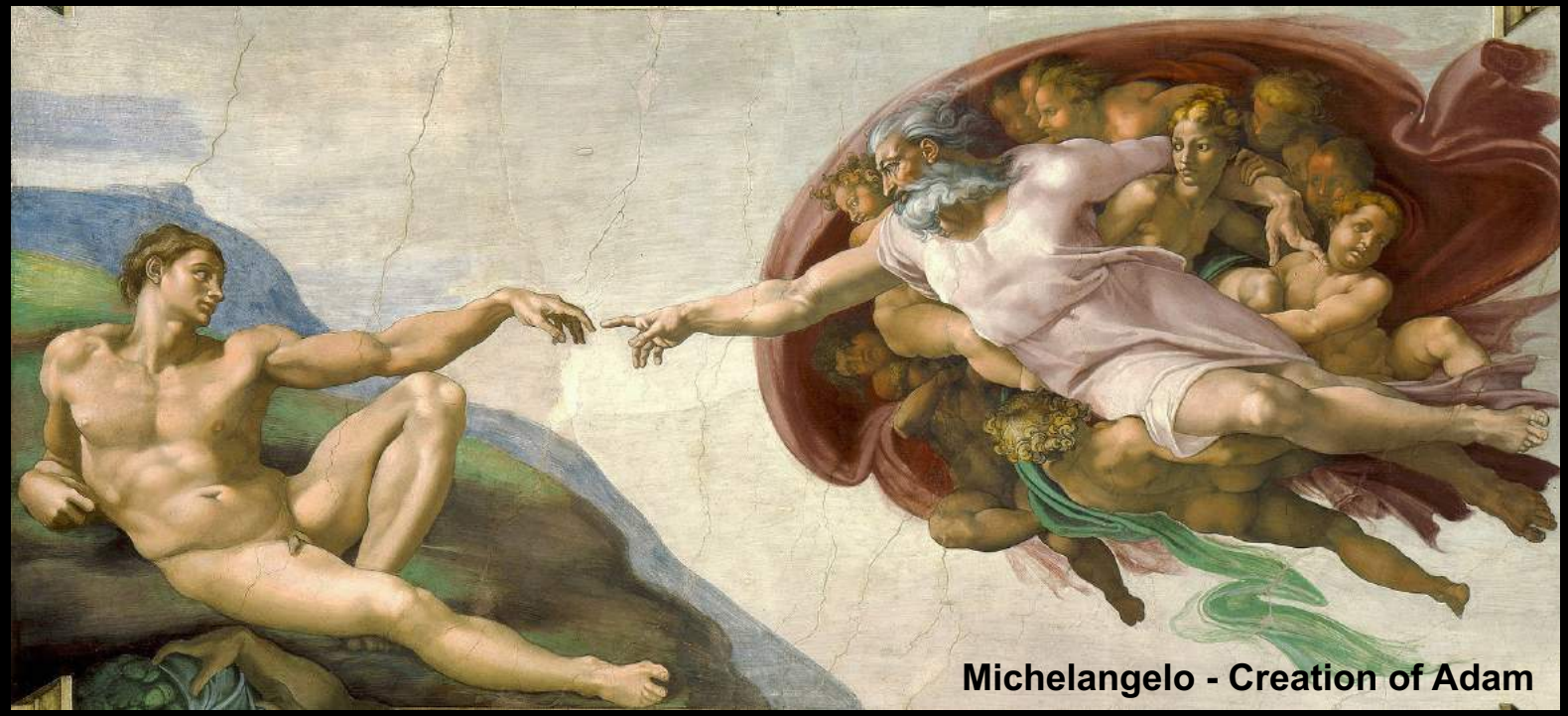


Formation of prebiotic molecules in the parent planet-forming disk or interstellar medium



Origin of life on Earth

Creationism is the religious belief that nature, and aspects such as the universe, Earth, life, and humans, originated with supernatural acts of divine creation (Wikipedia)



Michelangelo - Creation of Adam

Origin of life on Earth

Alexander Men



Science can explain practically everything but
there are 3 phenomena requiring the existence of God:

- Appearence of the universe
- Appearence of life
- Appearence of the human being

Origin of life on Earth

Spontaneous generation of life

The theory of spontaneous generation helds that living creatures could arise from nonliving matter and that such processes were commonplace and regular (Wikipedia).



Aristotle

Origin of life on Earth

Spontaneous generation of life



Van Helmont: (1600s) : He thought he could produce mice from wheat and a soiled shirt.



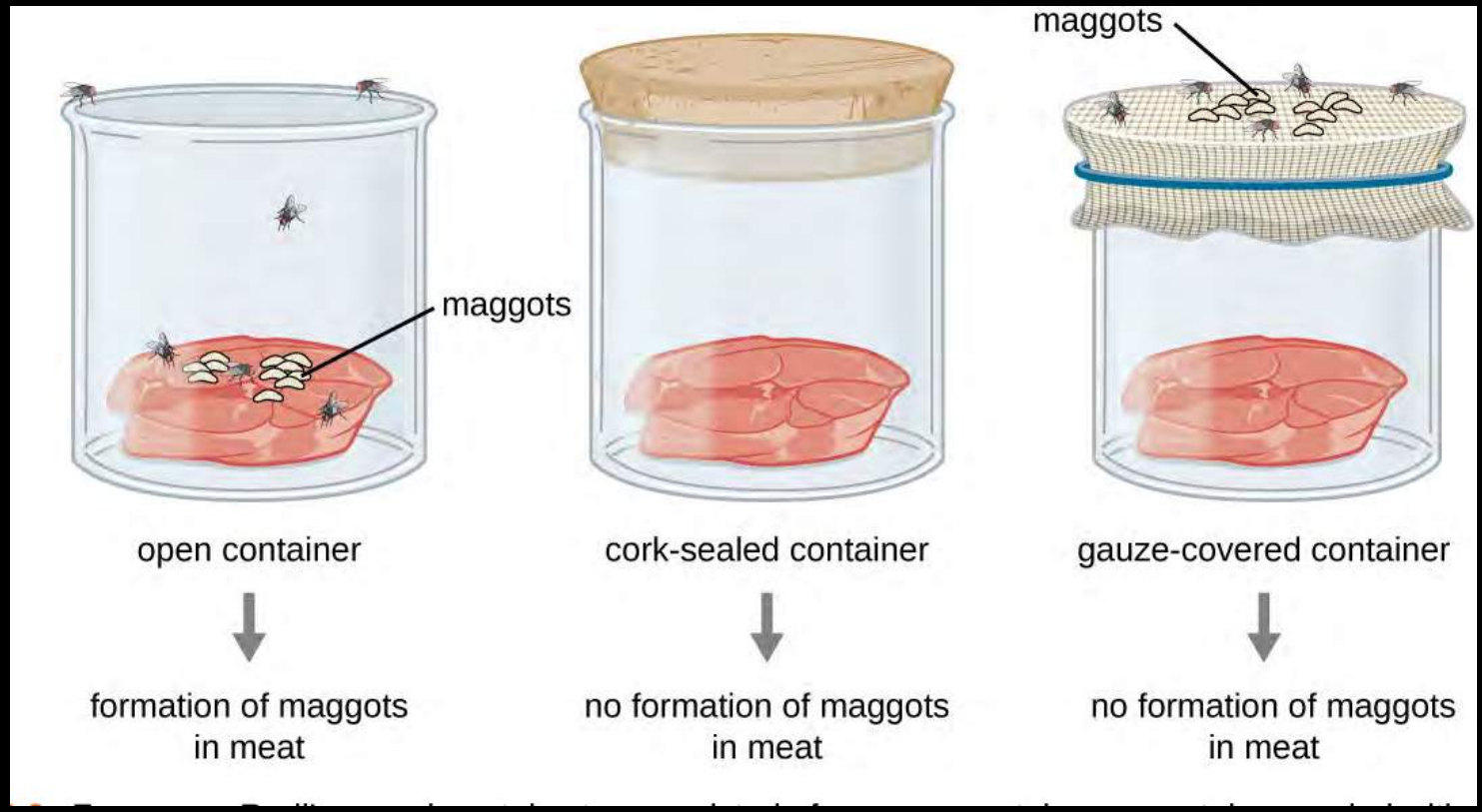


Origin of life on Earth

Spontaneous generation of life

Francesco Redi



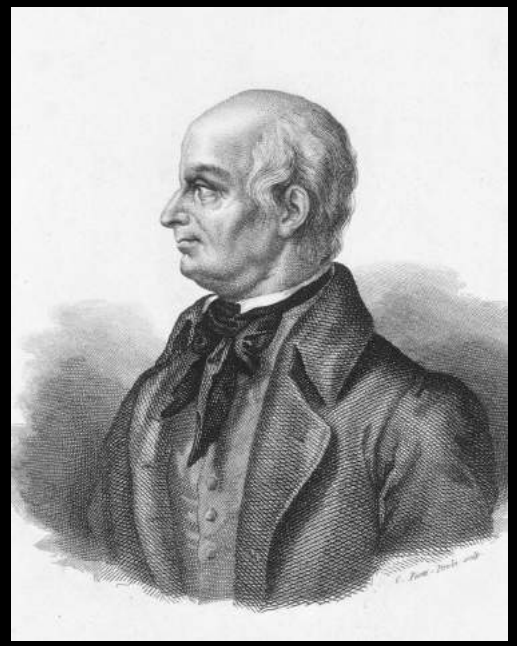


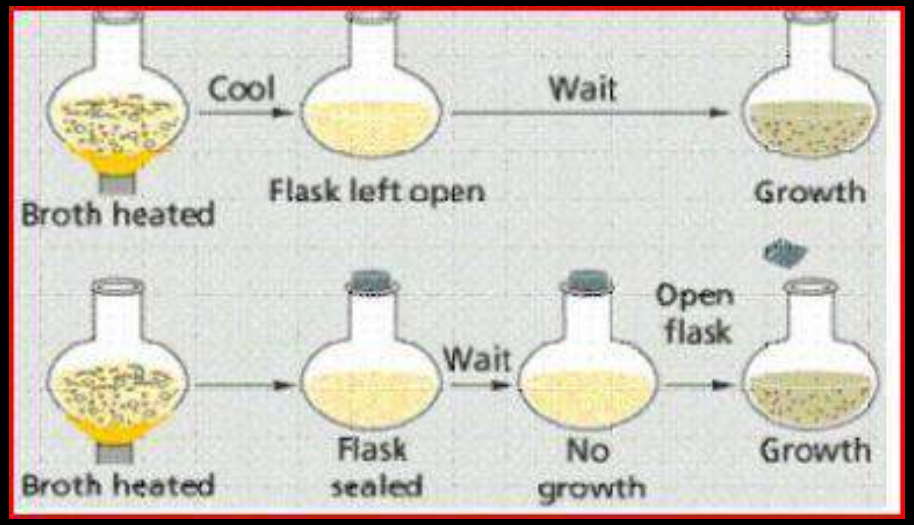
1668

Origin of life on Earth

Spontaneous generation of life

Lazzaro Spallanzani





Spontaneous generation of microorganisms?
1765



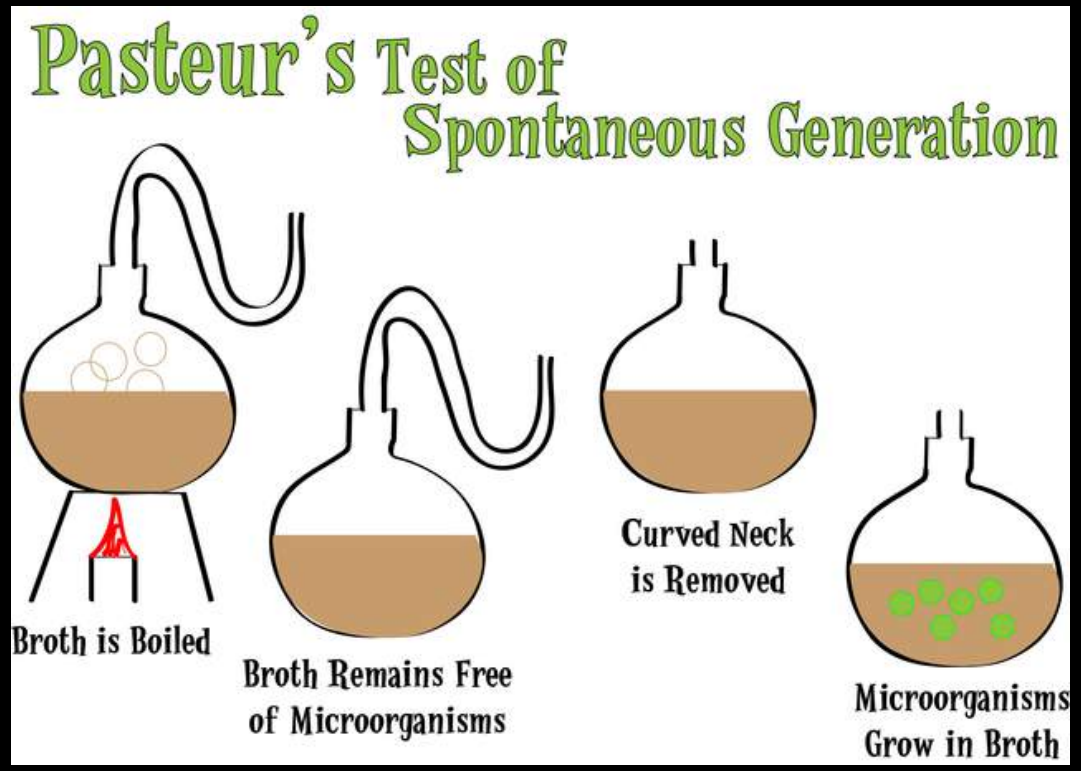
Canned food

Origin of life on Earth

Spontaneous generation of life

Louis Pasteur





Vital force in air?

1862

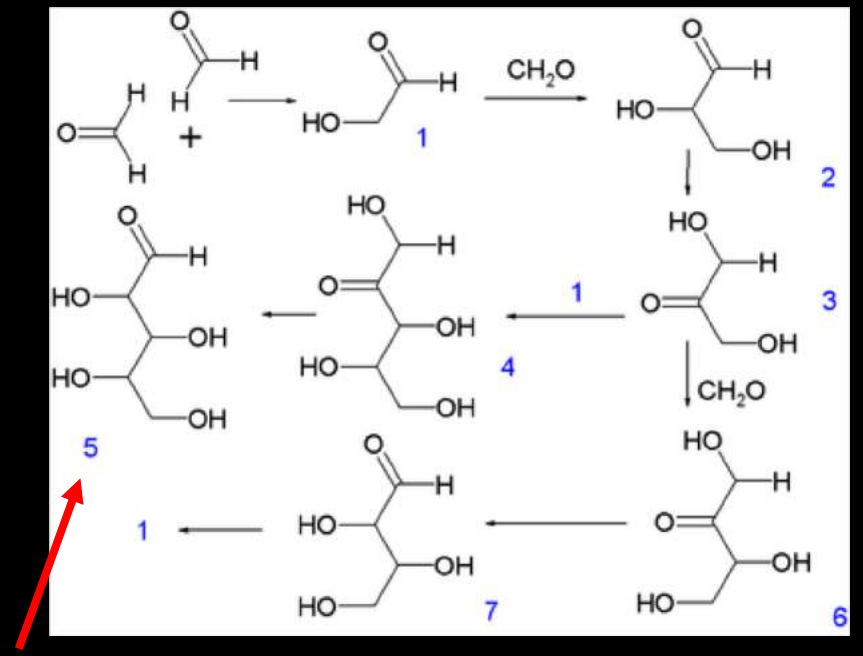
Origin of life on Earth

Abiogenesis is the natural process by which life has arisen from non-living matter, such as simple organic compounds

Alexander Butlerov



The formation of sugars from formaldehyde (1864)

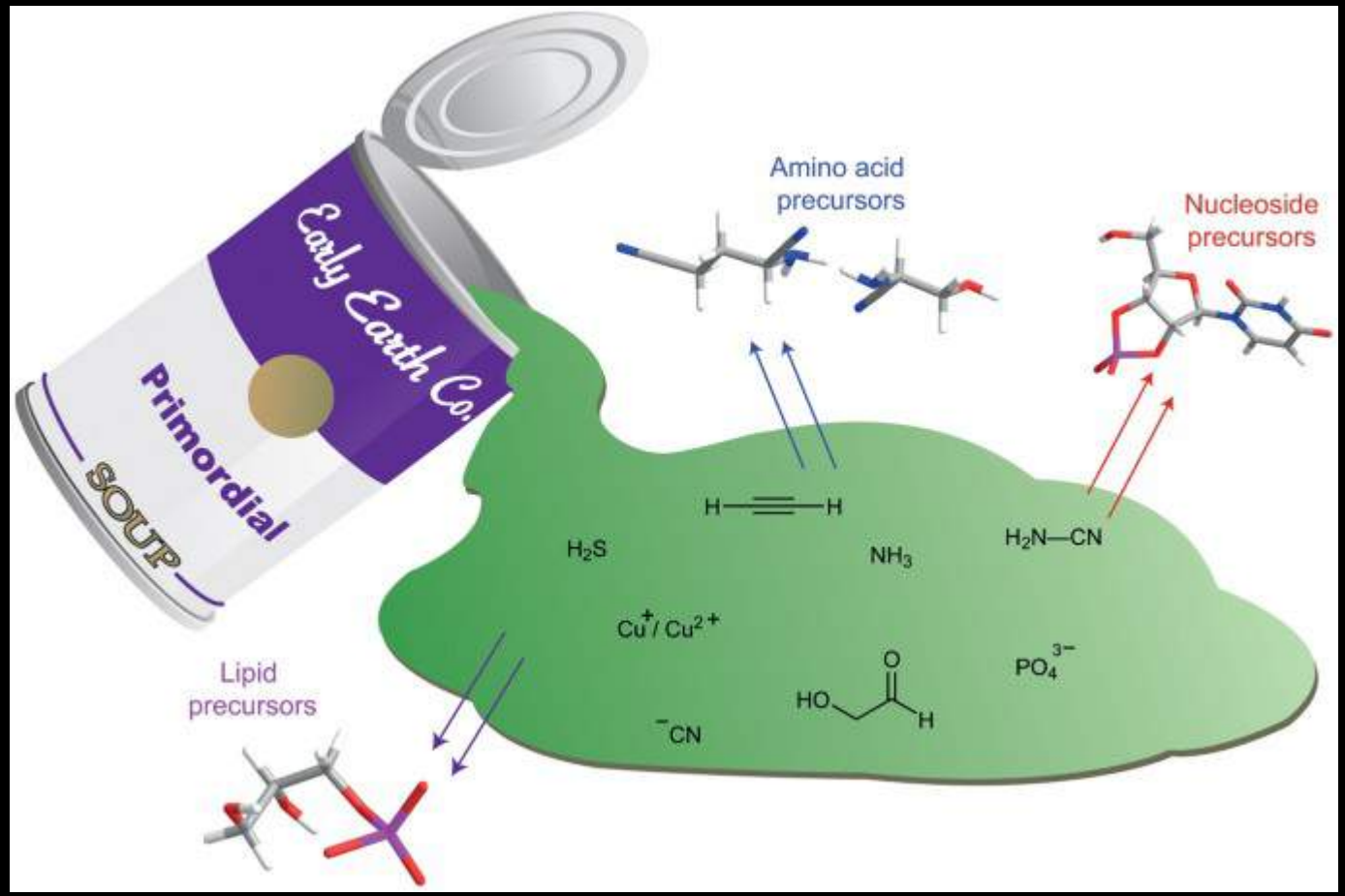


Ribose - a component of nucleotides, the basic building blocks of DNA and RNA

Origin of life on Earth



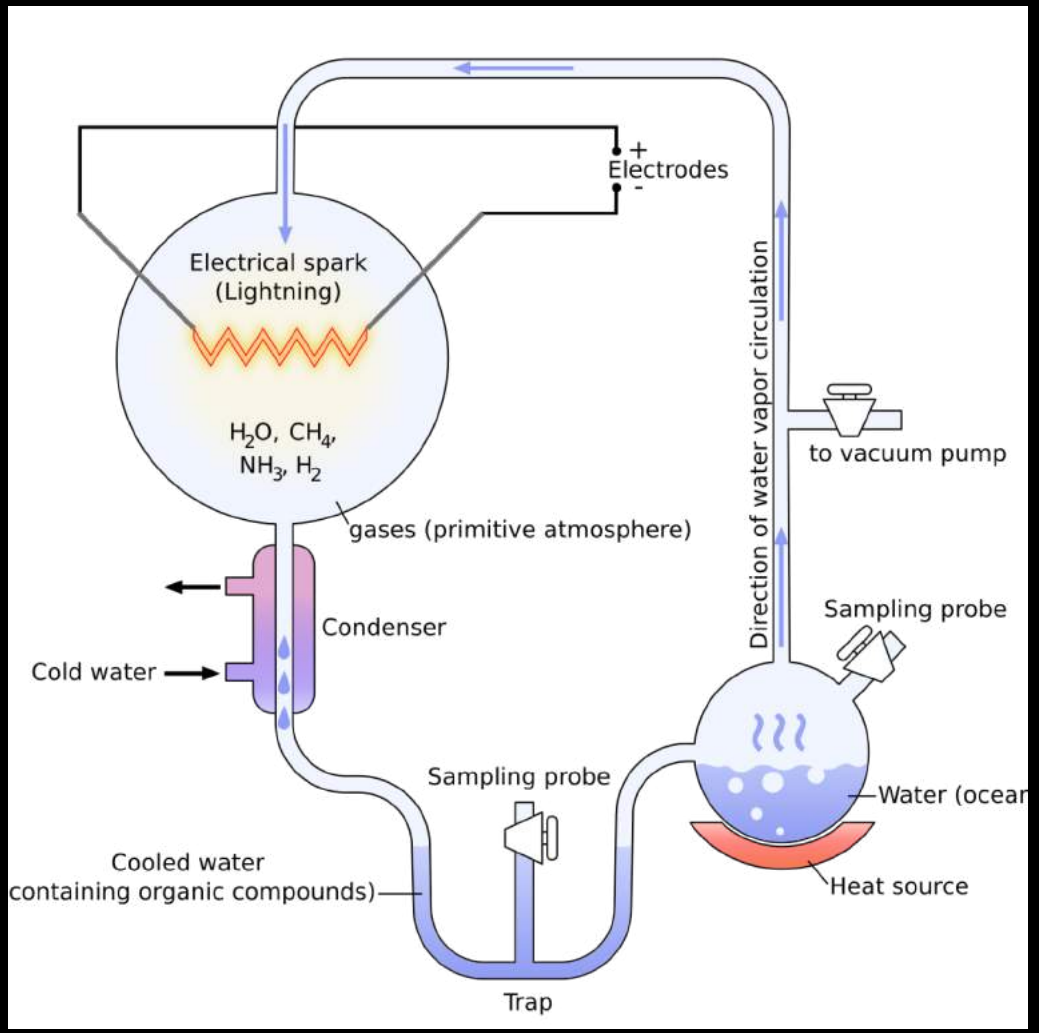
Primordial soup, or prebiotic soup, is the hypothetical set of conditions present on the Earth around 4.0 to 3.7 billion years ago. First proposed by Alexander Oparin in 1924



Origin of life on Earth



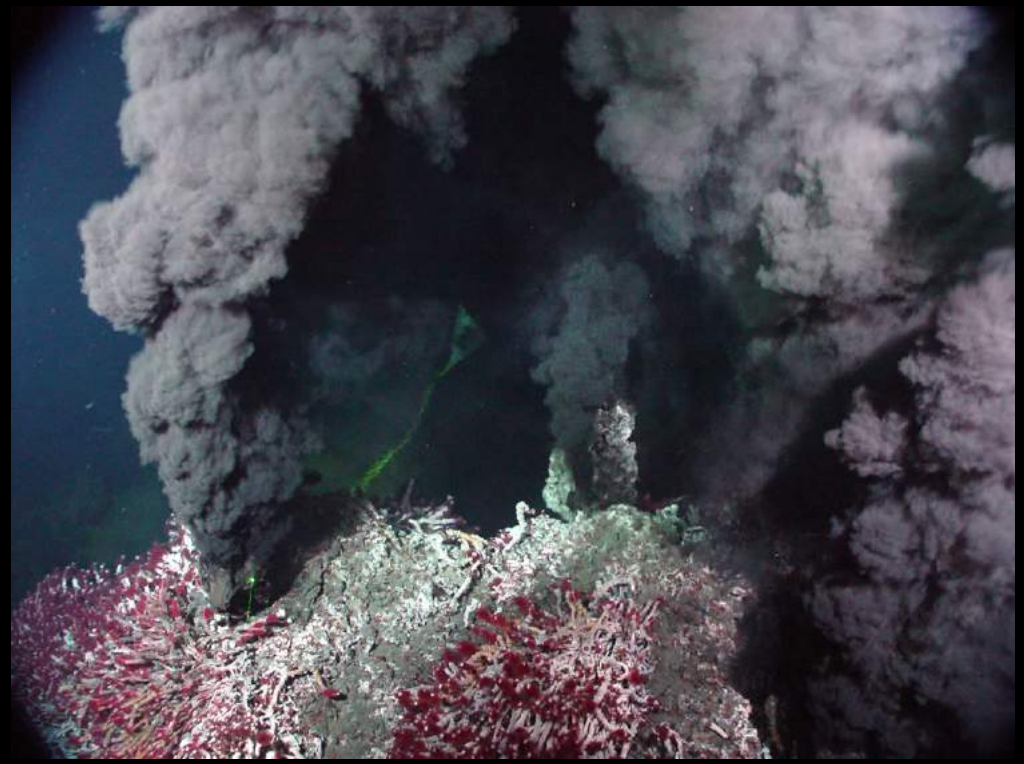
Miller experiment (Stanley Miller, 1953)



Formation of amino acids
(building blocks of proteins)

Origin of life on Earth

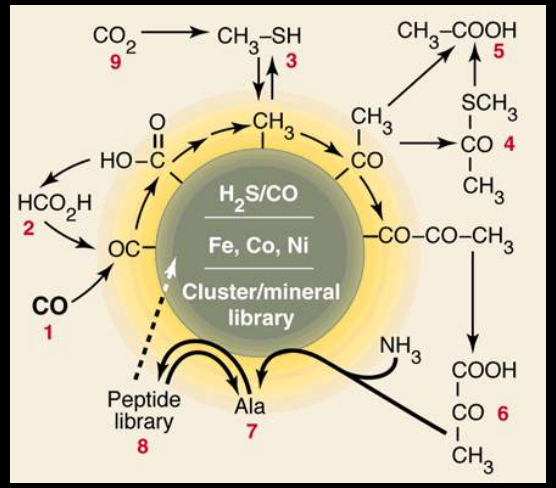
Hydrothermal vents (black and white smokers)

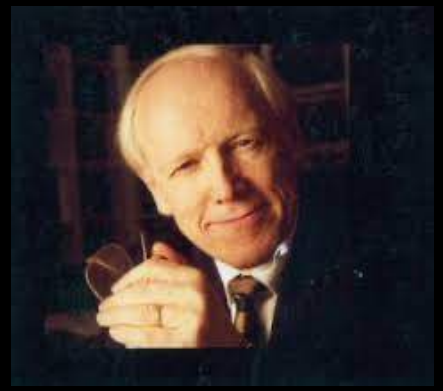




Origin of life on Earth

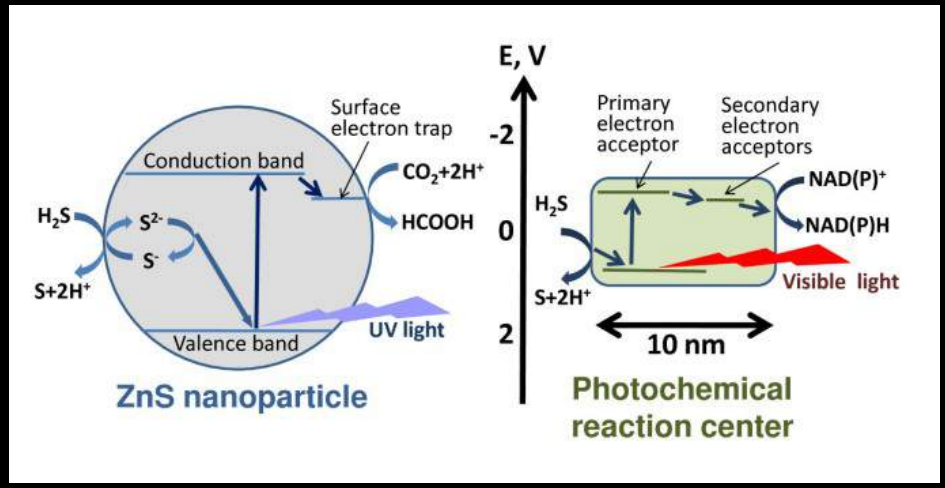
The Iron World





Günter Wächtershäuser

The Zinc World



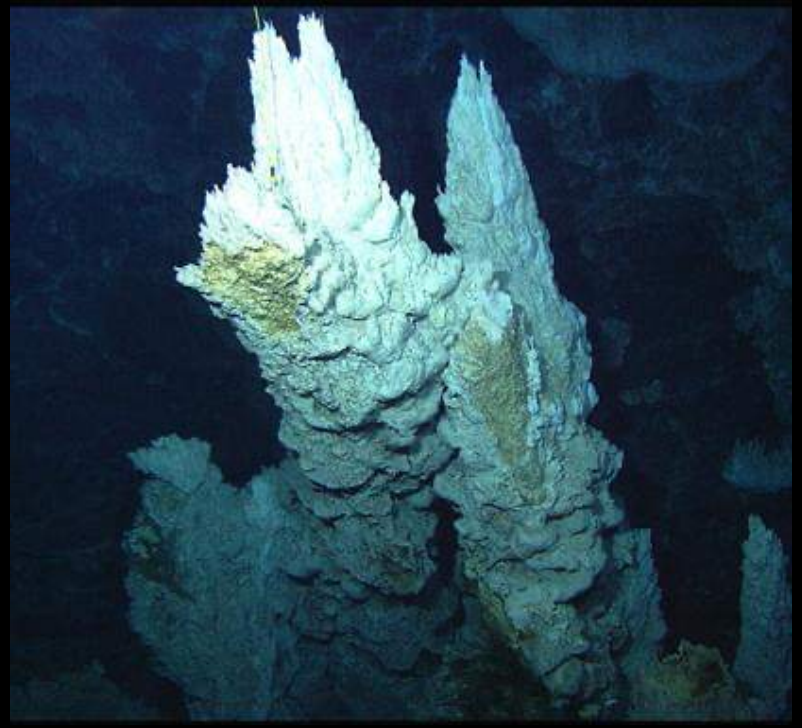


Armen Mulkidjanian

Origin of life on Earth

„Lost City“ Hydrothermal Vents







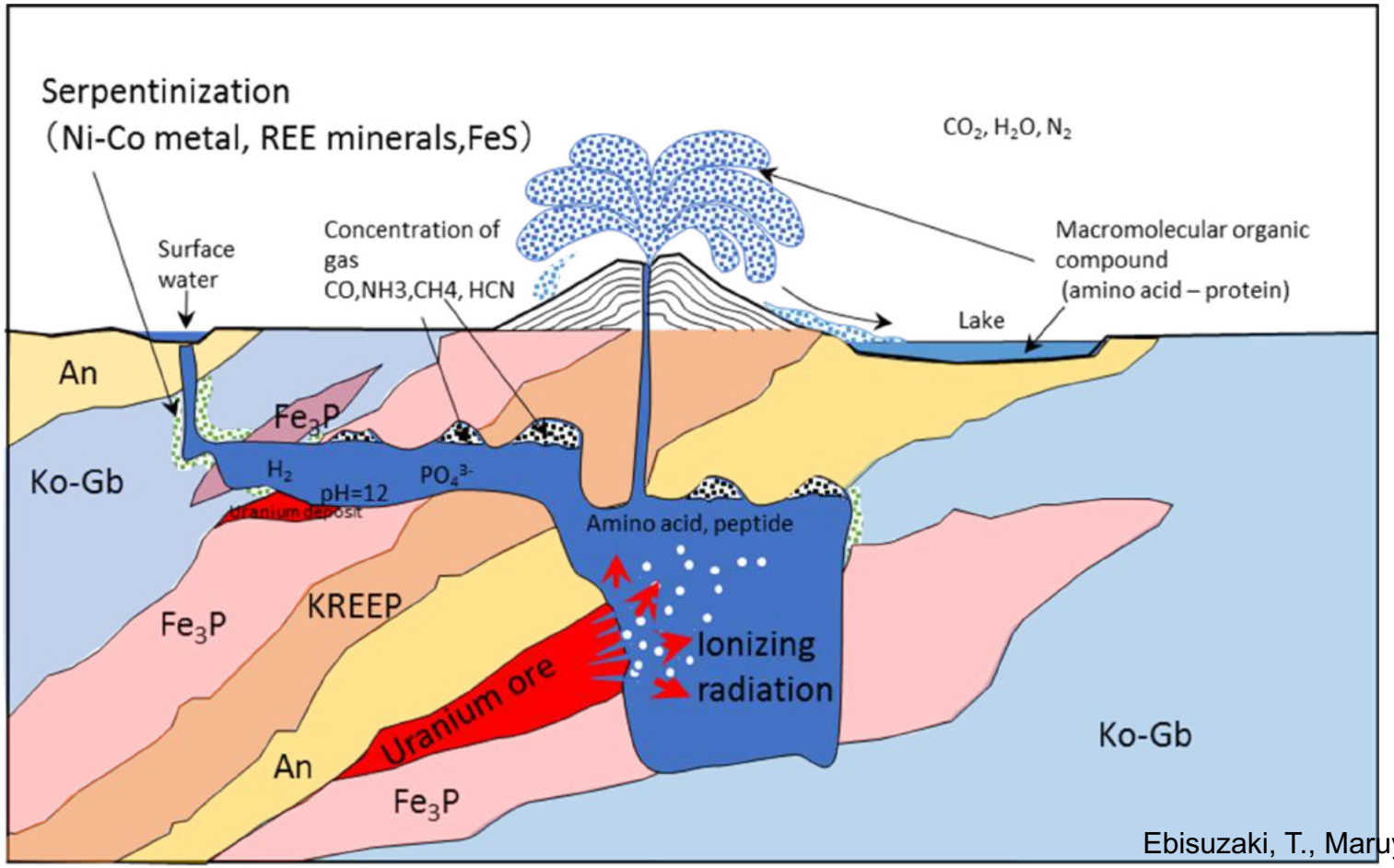
Origin of life on Earth

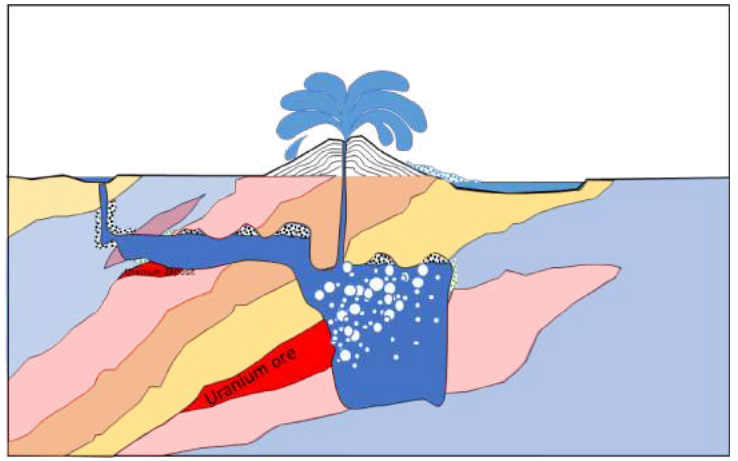
Hydrothermal fields (warm ponds, mud baths)

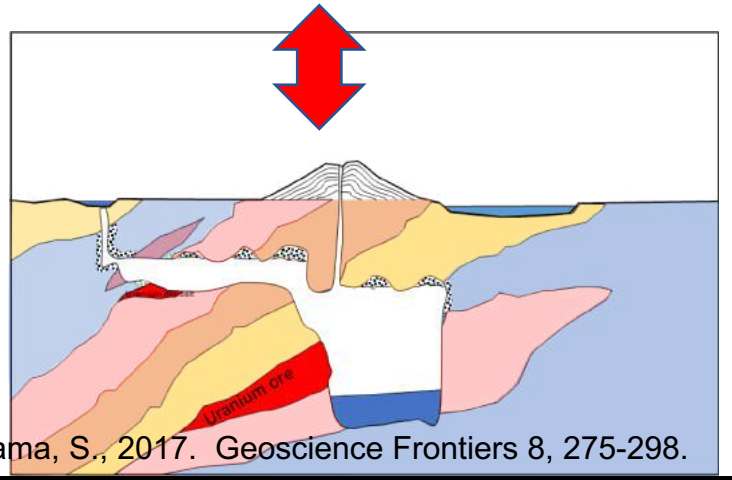


Nuclear Geyser Model

Combination of nuclear reactor and geyser
Ideal place to promote chemical reaction to emerge life







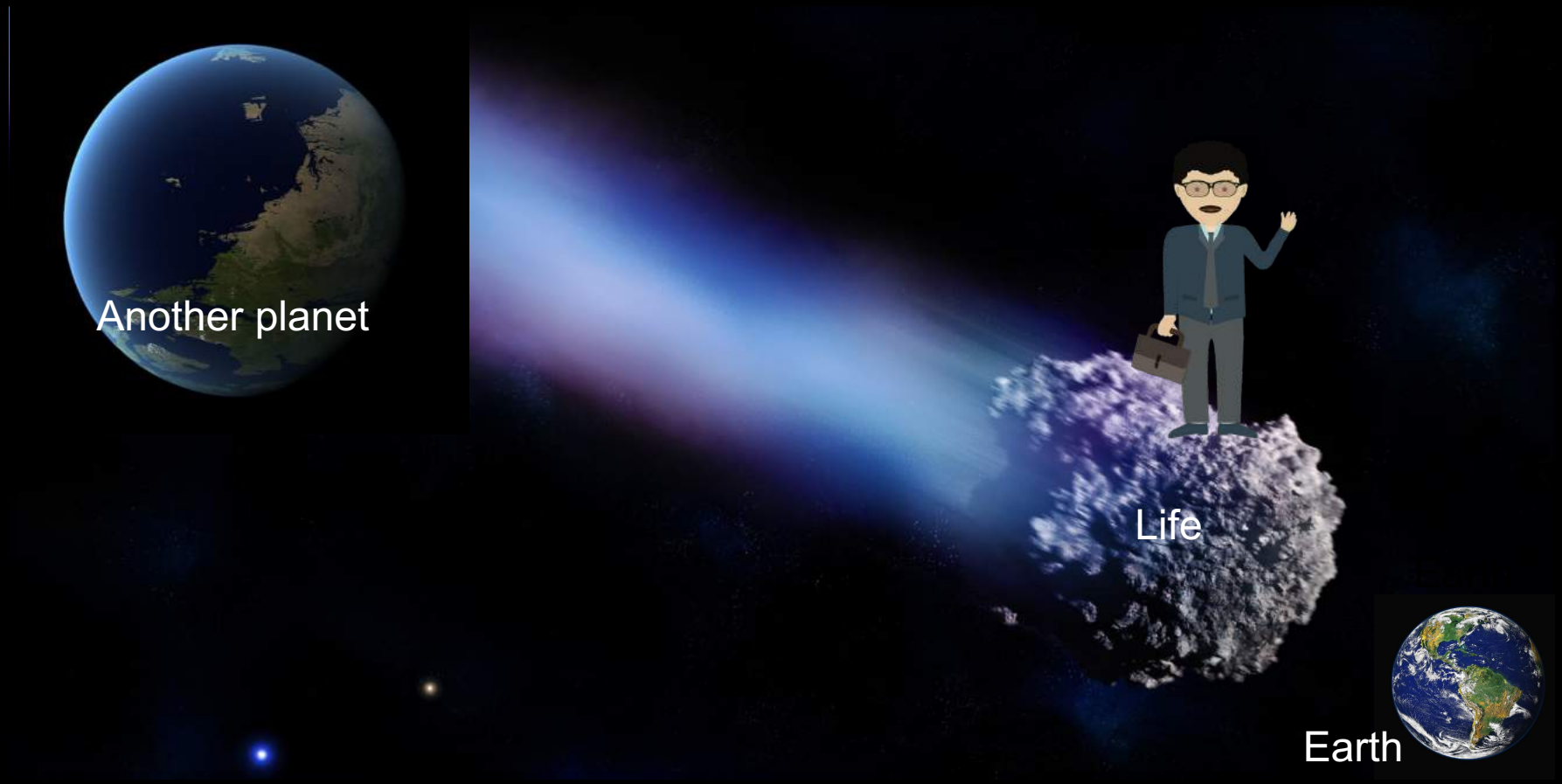
Ebisuzaki, T., Maruyama, S., 2017. Geoscience Frontiers 8, 275-298.

Nuclear Geyser system drives material circulation to mix different material (oxidized and reduced material) by connecting **different domains**.

Courtesy of Shige Maruyama

Origin of life on Earth

Panspermia is the hypothesis that life exists throughout the Universe, distributed by space dust, meteoroids, asteroids, comets, and planetoids (Wikipedia)



Origin of life on Earth



Joan Oró
1961

Abiogenesis is the natural process by which life has arisen from non-living matter, such as simple organic compounds



The interstellar medium



Prebiotic molecules



Earth

Molecules in Space. Detection history

C_2, C_3, CN and CH – in comets (19th century)

CH (1937), CN (1940), CH^+ (1941)

OH (1963), NH_3 (1968), H_2O (1969)

CO, H_2 (1970)

Until 1980th – 51 molecules

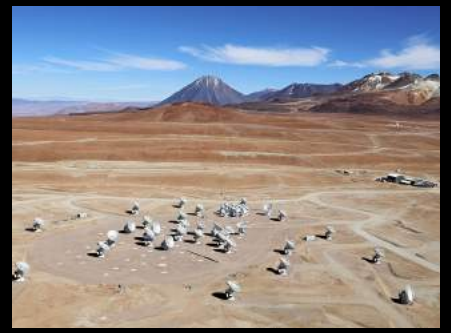
Until 1990th – 85 molecules

Until 2004 – 130 molecules

Today – > 240 molecules

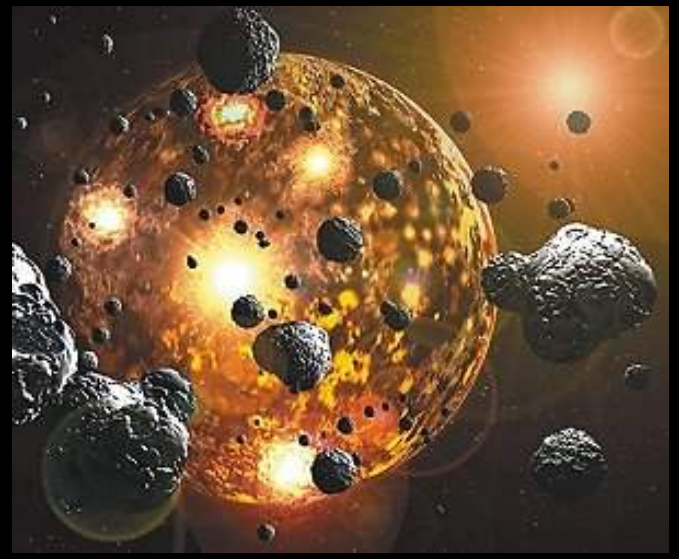






(Late Heavy) Bombardment

4.1 to 3.8 billion years ago a disproportionately large number of asteroids and comets collided with the early terrestrial planets in the inner Solar System (Wikipedia)





the delivery of organic carbon was in the order of 10^{16} kg per 100 million years

there is about 6×10^{14} kg of organic matter in the present biosphere

Asteroids versus Comets



More asteroids but less organics



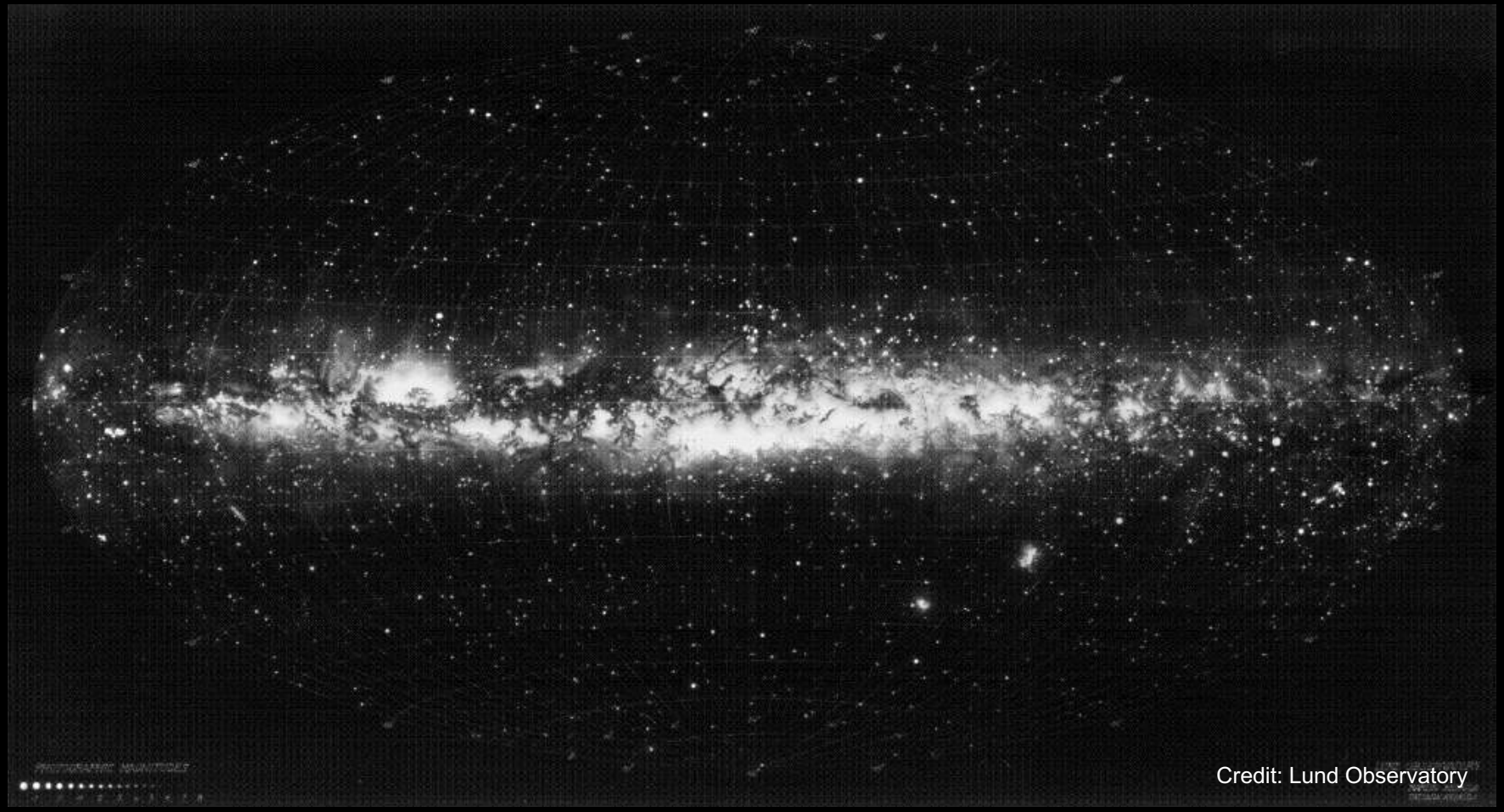
Less comets but more organics

Survival in the atmosphere and during impact?

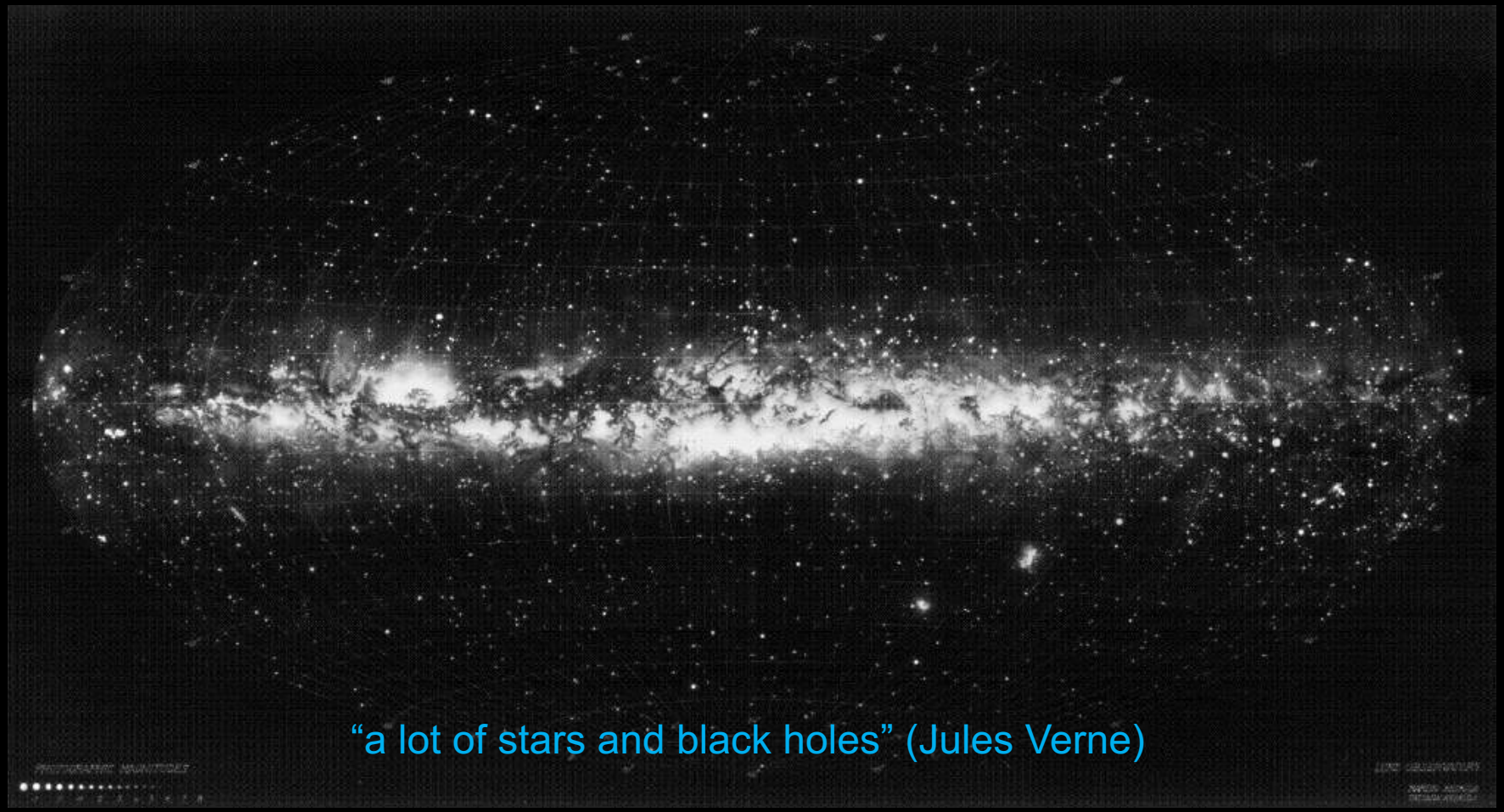
Part 3:

Evidence for exogenous hypothesis: Space

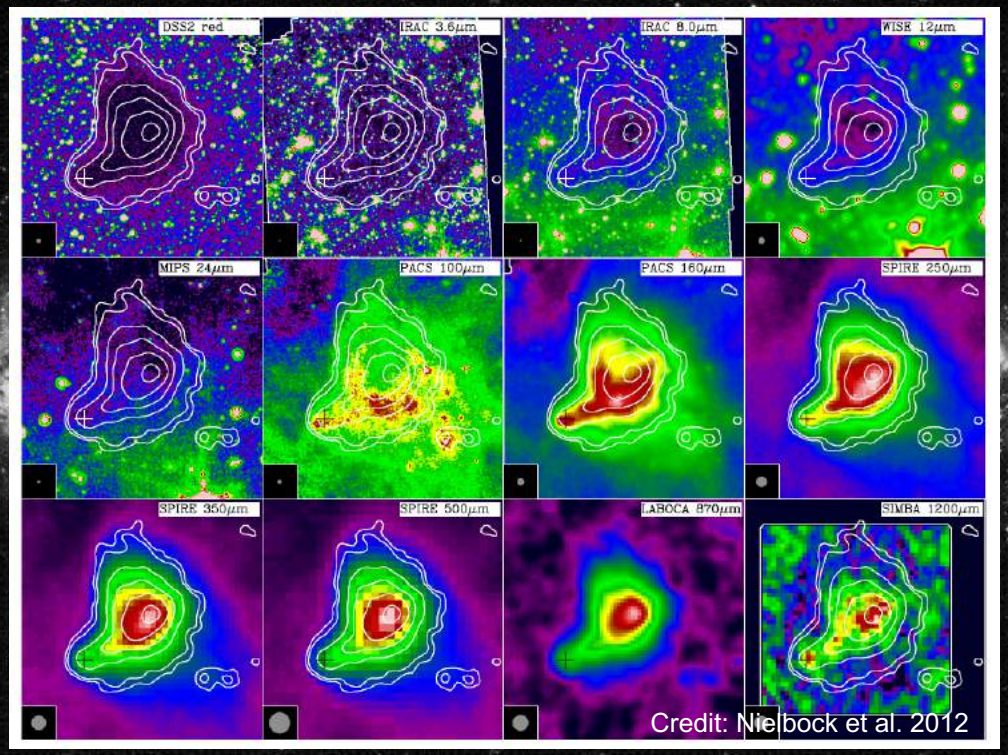
The whole sky (by eyes)



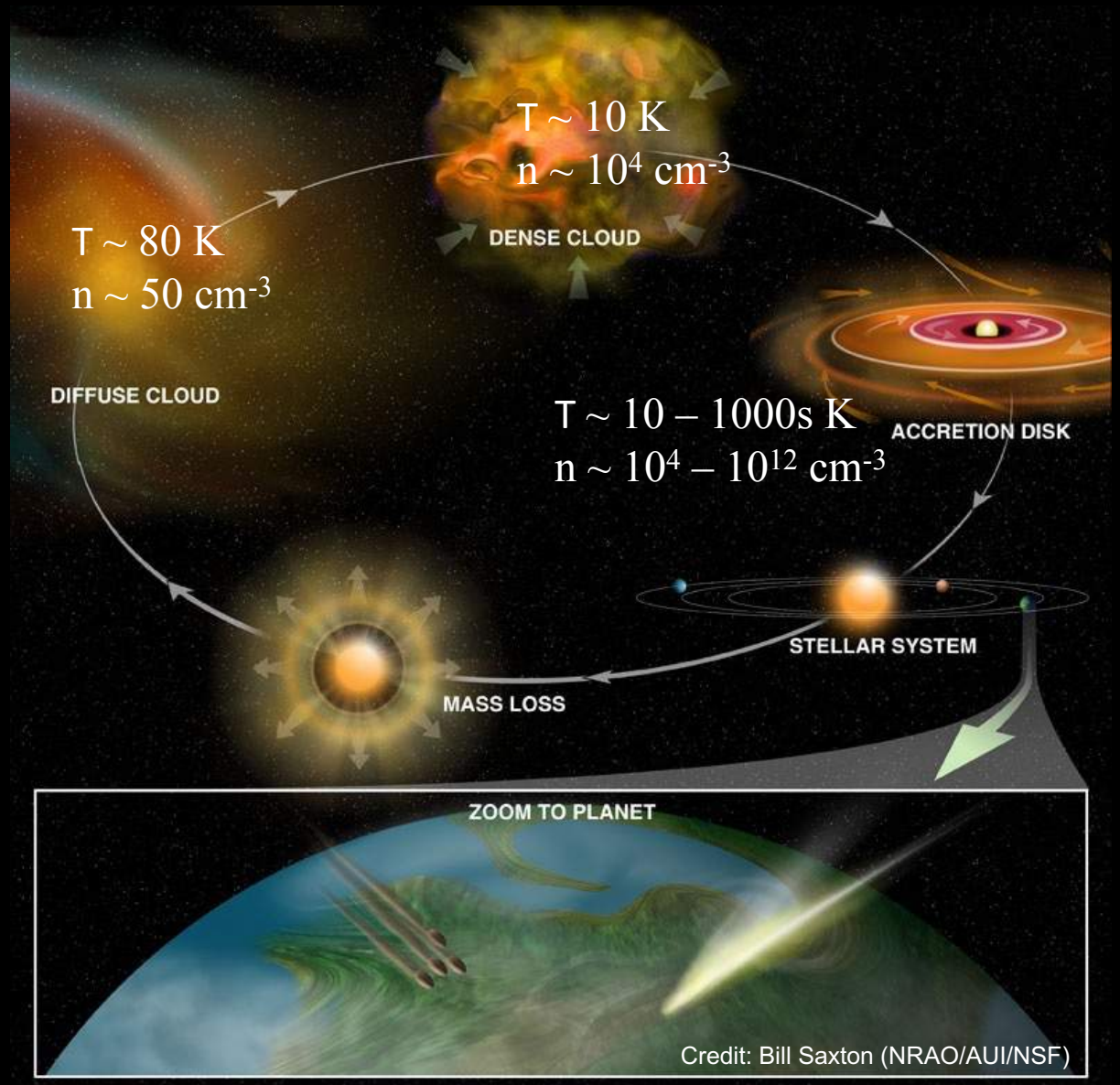
The whole sky (by eyes)



Interstellar molecular clouds



The cosmic life cycle of matter



The cosmic life cycle of matter

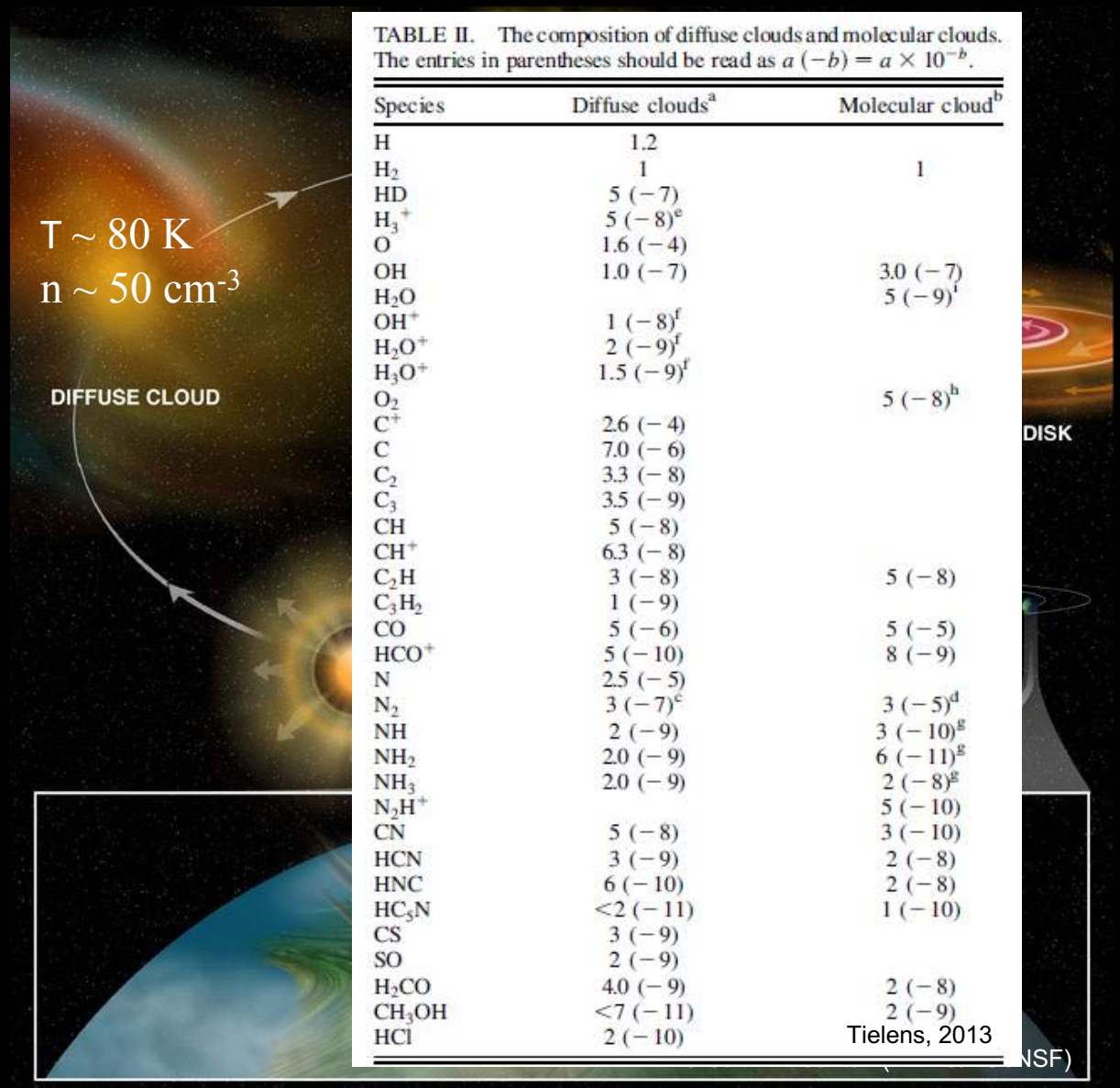


TABLE II. The composition of diffuse clouds and molecular clouds. The entries in parentheses should be read as $a\,(-b) = a \times 10^{-b}$.

Species	Diffuse clouds[a]	Molecular cloud[b]
H	1.2	
H_2	1	1
HD	5 (−7)	
H_3^+	5 (−8)[e]	
O	1.6 (−4)	
OH	1.0 (−7)	3.0 (−7)
H_2O		5 (−9)[f]
OH^+	1 (−8)[f]	
H_2O^+	2 (−9)[f]	
H_3O^+	1.5 (−9)[f]	
O_2		5 (−8)[h]
C^+	2.6 (−4)	
C	7.0 (−6)	
C_2	3.3 (−8)	
C_3	3.5 (−9)	
CH	5 (−8)	
CH^+	6.3 (−8)	
C_2H	3 (−8)	5 (−8)
C_3H_2	1 (−9)	
CO	5 (−6)	5 (−5)
HCO^+	5 (−10)	8 (−9)
N	2.5 (−5)	
N_2	3 (−7)[c]	3 (−5)[d]
NH	2 (−9)	3 (−10)[g]
NH_2	2.0 (−9)	6 (−11)[g]
NH_3	2.0 (−9)	2 (−8)[g]
N_2H^+		5 (−10)
CN	5 (−8)	3 (−10)
HCN	3 (−9)	2 (−8)
HNC	6 (−10)	2 (−8)
HC_5N	<2 (−11)	1 (−10)
CS	3 (−9)	
SO	2 (−9)	
H_2CO	4.0 (−9)	2 (−8)
CH_3OH	<7 (−11)	2 (−9)
HCl	2 (−10)	

Tielens, 2013

The cosmic life cycle of matter

Table 2
List of Detected Interstellar Molecules with Two to Seven Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

2 Atoms		3 Atoms		4 Atoms		5 Atoms		6 Atoms	7 Atoms
CH	NH	H_2O	MgCN	NH_3	SiC_3	HC_3N	C_4H^-	CH_3OH	CH_3CHO
CN	SiN	HCO^+	H_3^+	H_2CO	CH_3	HCOOH	CNCHO	CH_3CN	CH_3CCH
CH^+	SO^+	HCN	SiCN	HNCO	C_3N^-	CH_2NH	HNCNH	NH_2CHO	CH_3NH_2
OH	CO^+	OCS	AlNC	H_2CS	PH_3	NH_2CN	CH_3O	CH_3SH	CH_2CHCN
CO	HF	HNC	SiNC	C_2H_2	HCNO	H_2CCO	NH_2D^+	C_2H_4	HC_5N
H_2	N_2	H_2S	HCP	C_3N	HOCN	C_4H	H_2NCO^+	C_5H	C_6H
SiO	CF^+	N_2H^+	CCP	HNCS	HSCN	SiH_4	$NCCNH^+$	CH_3NC	c-C_2H_4O
CS	PO	C_2H	AlOH	$HOCO^+$	HOOH	c-C_3H_2	CH_3Cl	HC_2CHO	CH_2CHOH
SO	O_2	SO_2	H_2O^+	C_3O	l-C_3H^+	CH_2CN	MgC_3N	H_2C_4	C_6H^-
SiS	AlO	HCO	H_2Cl^+	l-C_3H	HMgNC	C_5	HC_3O^+	C_5S	CH_3NCO
NS	CN^-	HNO	KCN	$HCNH^+$	HCCO	SiC_4	NH_2OH	HC_3NH^+	HC_5O
C_2	OH^+	HCS+	FeCN	H_3O^+	CNCN	H_2CCC	HC_3S^+	C_5N	$HOCH_2CN$
NO	SH^+	HOC^+	HO_2	C_3S	HONO	CH_4	H_2CCS	HC_4H	HC_4NC
HCl	HCl^+	SiC_2	TiO_2	c-C_3H	MgCCH	HCCNC	C_4S	HC_4N	H_3HNH
NaCl	SH	C_2S	CCN	HC_3N	HCCS	HNCCC	CHOSH	c-H_2C_3O	c-C_3HCCH
AlCl	TiO	C_3	SiCSi	H_2CN		H_2COH^+		CH_2CNH	
KCl	ArH^+	CO_2	S_2H					C_5N^-	
AlF	NS^+	CH_2	HCS					HNCHCN	
PN	HeH^+	C_2O	HSC					SiH_3CN	
SiC	VO	MgNC	NCO					MgC_4H	
CP		NH_2	CaNC					CH_3CO^+	
		NaCN	NCS					H_2CCCS	
		N_2O						CH_2CCH	

McGuire, 2022

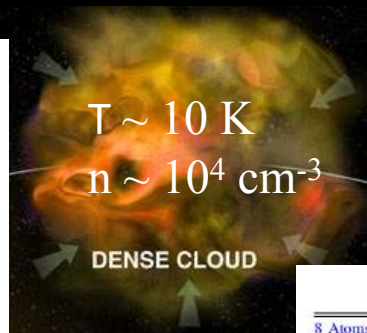


Table 3
List of Detected Interstellar Molecules with Eight or More Atoms, Categorized by Number of Atoms, and Vertically Ordered by Detection Year

8 Atoms	9 Atoms	10 Atoms	11 Atoms	12 Atoms	13 Atoms	PAHs	Fullerenes
$HCOOCH_3$	CH_3OCH_3	CH_3COCH_3	HC_9N	C_6H_6	C_6H_5CN	1-$C_{10}H_7CN$	C_{60}
CH_3C_3N	CH_3CH_2OH	$HOCH_2CH_2OH$	CH_3C_6H	n-C_3H_7CN	$HC_{11}N$	2-$C_{10}H_7CN$	C_{60}^+
C_7H	CH_3CH_2CN	CH_3CH_2CHO	C_2H_5OCHO	i-C_3H_7CN		C_9H_8	C_{70}
CH_3COOH	HC_7N	CH_3C_5N	CH_3COOCH_3	1-C_5H_5CN			
H_2C_6	CH_3C_4H	CH_3CHCH_2O	CH_3COCH_2OH	2-C_5H_5CN			
CH_2OHCHO	C_8H	CH_3CH_2OH	C_5H_6				
HC_6H	CH_3CONH_2						
CH_2CHCHO	C_8H^-						
CH_2CCHCN	CH_2CHCH_3						
NH_2CH_2CN	CH_3CH_2SH						
CH_2CHNH	HC_7O						
CH_3SiH_3	CH_3NHCHO						
NH_2CONH_2	$H_2CCCHCCH$						
$HCCCH_2CN$	HCCCHCHCN						
CH_2CHCCH	H_2CCHC_3N						

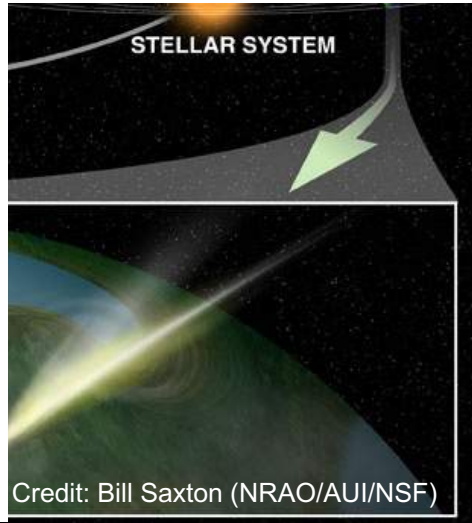
McGuire, 2022

Table 5
List of Molecules Detected in Interstellar Ices, with References to Representative Detections

Species	References
CO	1
H_2O	2
OCS	3, 4
CO_2	5
OCN^+	6
NH_3	7
H_2CO	8
HCOOH	9
CH_4	10
CH_3OH	11

OCN^-, NH_4^+, and SO_2
(JWST data - McClure, et al., 2023)

McGuire, 2022



Credit: Bill Saxton (NRAO/AUI/NSF)

The cosmic life cycle of matter

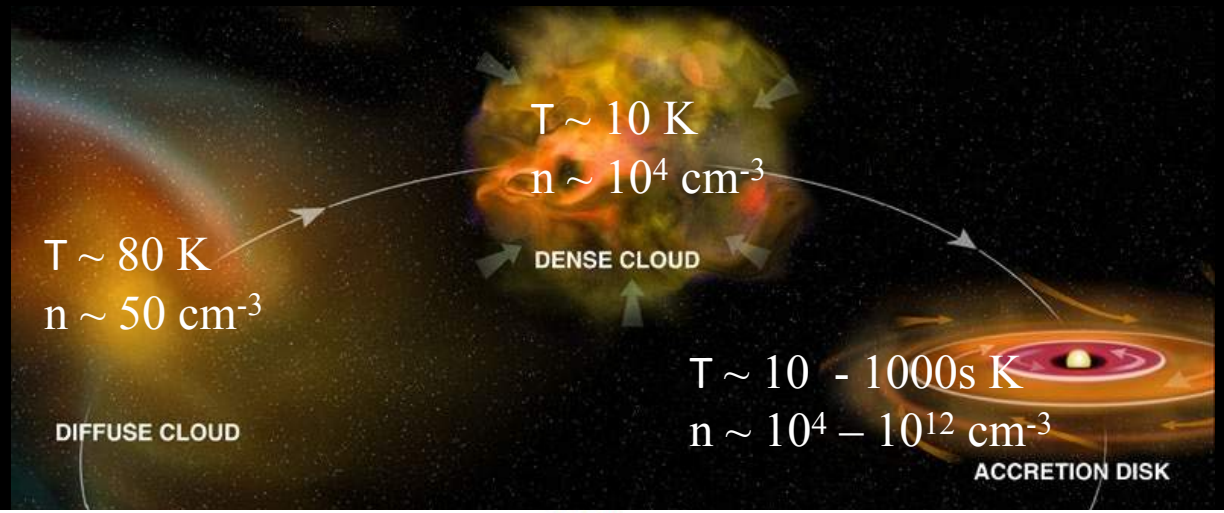


Table 6
List of Molecules, Including Rare Isotopic Species, Detected in Protoplanetary Disks, with References to Representative Detections

2 Atoms		3 Atoms		4 Atoms		5 Atoms		6 Atoms	
Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.	Species	Ref.
CN	1, 2	H_2O	3, 4, 5	NH_3	6	HC_3N	7	CH_3OH	8
$C^{15}N$	9	HCO^+	1, 2	H_2CO	2	HCOOH	10	CH_3CN	11
CH^+	12	DCO^+	13	H_2CS	14, 15	c-C_3H_2	16		
OH	17, 5	$H^{13}CO^+$	18, 13	C_2H_2	19	CH_4	20		
CO	21	HCN	1, 2						
^{13}CO	22	DCN	23						
$C^{18}O$	24	$H^{13}CN$	25						
$C^{17}O$	26, 27	$H^{15}CN$	25						
$^{13}C^{18}O$	39								
$^{13}C^{17}O$	40								
H_2	28	HNC	2						
HD	29	DNC	14						
CS	30, 31, 32	H_2S	33						
$C^{34}S$	14, 15	N_2H^+	34, 35						
^{13}CS	14, 15	N_2D^+	36						
SO	37	C_2H	2						
		C_2D	14						
		CO_2	38						

McGuire, 2022

The cosmic life cycle of matter

Table 7
List of Molecules Detected in Exoplanetary Atmospheres, with References to Representative Detections.

Species	References
OH	1
CO	2, 3, 4, 5
TiO	6, 7, 8
H_2O	9, 10, 11, 12, 13
HCN	14
CO_2	15, 2, 4
NH_3	16
C_2H_2	16
CH_4	17, 3, 18, 5

H_2S, SO_2, silicates
(new JWST data)



Molecules detected in space

Known Interstellar Molecules

Created with **ASTROMOL** v2021.1.1
bmcguir2.github.io/astromol
McGuire 2018 *ApJS* 239, 17

2 Atoms

CH, NH, CN, SiN, CH^+, SO^+, OH, CO^+, CO, HF, H_2, N_2, SiO, CF^+, CS, PO, SO, O_2, SiS, AlO, NS, CN^-, C_2, OH^+, NO, SH^+, HCl, HCl^+, NaCl, SH, AlCl, TiO, KCl, ArH^+, AlF, NS^+, PN, HeH^+, SiC, VO, CP

3 Atoms

H_2O, HCO^+, HCN, OCS, HNC, H_2S, N_2H^+, C_2H, SO_2, HCO, HNO, HCS^+, HOC^+, SiC_2, C_2S, C_3, CO_2, CH_2, C_2O, MgNC, NH_2, NaCN, N_2O, MgCN, H_3^+, SiCN, AlNC, SiNC, HCP, CCP, AlOH, H_2O^+, H_2Cl^+, KCN, FeCN, HO_2, TiO_2, CCN, SiCSi, S_2H, HCS, HSC, NCO, CaNC, NCS

4 Atoms

NH_3, H_2CO, HNCO, H_2CS, C_2H_2, C_3N, HNCS, $HOCO^+$, C_3O, *l*-C_3H, $HCNH^+$, H_3O^+, C_3S, *c*-C_3H, HC_2N, H_2CN, SiC_3, CH_3, C_3N^-, PH_3, HCNO, HOCN, HSCN, HOOH, *l*-C_3H^+, HMgNC, HCCO, CNCN, HONO, MgCCH, HCCS, HNCN

5 Atoms

HC_3N, HCOOH, CH_2NH, NH_2CN, H_2CCO, C_4H, SiH_4, *c*-C_3H_2, CH_2CN, C_5, SiC_4, H_2CCC, CH_4, HCCNC, HNCCC, H_2COH^+, C_4H^-, CNCHO, HNCNH, CH_3O, NH_3D^+, H_2NCO^+, $NCCNH^+$, CH_3Cl, MgC_3N, HC_3O^+, NH_2OH, HC_3S^+, H_2CCS, C_4S, CHOSH, HCSCN

247 Molecules

Last Updated: 28 Sep 2021

Complex organic molecules (COMs)

6 Atoms

CH_3OH, CH_3CN, NH_2CHO, CH_3SH, C_2H_4, C_5H, CH_3NC, HC_2CHO, H_2C_4, C_5S, HC_3NH^+, C_5N, HC_4H, HC_4N, *c*-H_2C_3O, CH_2CNH, C_5N^-, HNCHCN, SiH_3CN, MgC_4H, CH_3CO^+, H_2CCCS, CH_2CCH, HCSCCH

7 Atoms

CH_3CHO, CH_3CCH, CH_3NH_2, CH_2CHCN, HC_5N, C_6H, *c*-C_2H_4O, CH_2CHOH, C_6H^-, CH_3NCO, HC_5O, $HOCH_2CN$, HC_4NC, HC_3HNH, *c*-C_3HCCH, MgC_5N

8 Atoms

$HCOOCH_3$, CH_3C_3N, C_7H, CH_3COOH, H_2C_6, CH_2OHCHO, HC_6H, CH_2CHCHO, CH_2CCHCN, NH_2CH_2CN, CH_3CHNH, CH_3SiH_3, NH_2CONH_2, $HCCCH_2CN$, CH_2CHCCH, MgC_6H

9 Atoms

CH_3OCH_3, CH_3CH_2OH, CH_3CH_2CN, HC_7N, CH_3C_4H, C_8H, CH_3CONH_2, C_8H^-, CH_2CHCH_3, CH_3CH_2SH, HC_7O, $H_2CCCHCCH$, HCCCHCHCN, H_2CCHC_3N

10 Atoms

CH_3COCH_3, $HOCH_2CH_2OH$, CH_3CH_2CHO, CH_3C_5N, CH_3CHCH_2O, CH_3OCH_2OH, C_6H_4

11 Atoms

HC_9N, CH_3C_6H, C_2H_5OCHO, CH_3COOCH_3, CH_3COCH_2OH, C_5H_6, $NH_2CH_2CH_2OH$

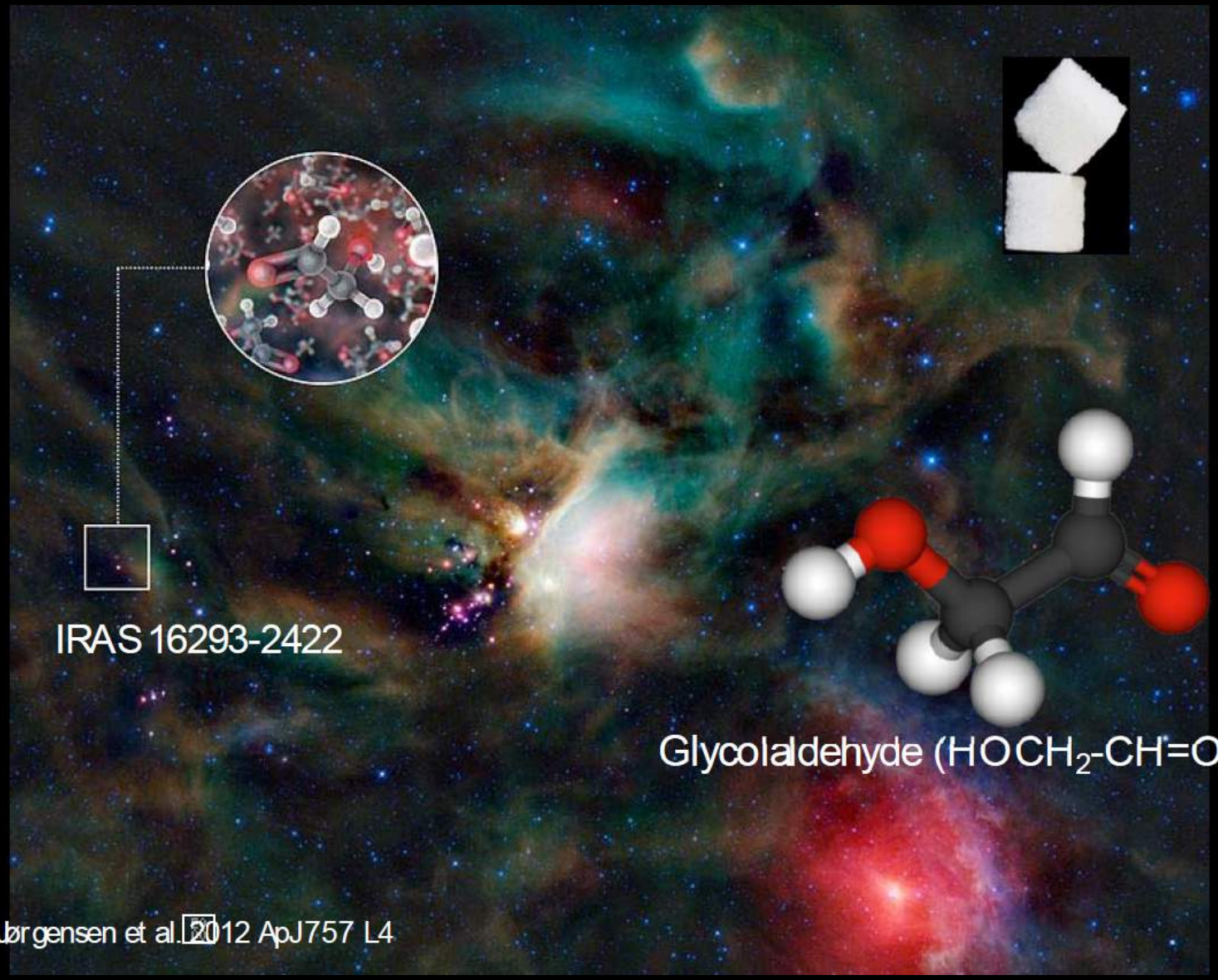
12 Atoms

C_6H_6, *n*-C_3H_7CN, *i*-C_3H_7CN, 1-C_5H_5CN, 2-C_5H_5CN

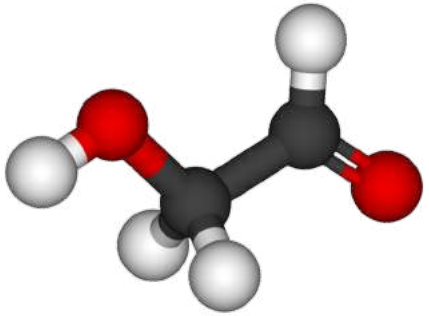
13+ Atoms

C_6H_5CN, $HC_{11}N$, 1-$C_{10}H_7CN$, 2-$C_{10}H_7CN$, C_9H_8, C_{60}, C_{60}^+, C_{70}

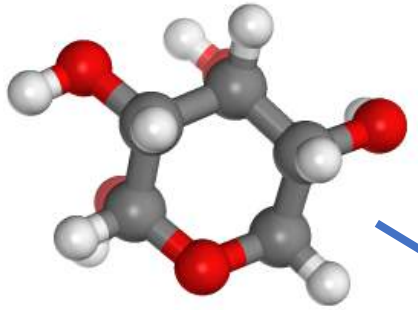
COMs in the interstellar medium



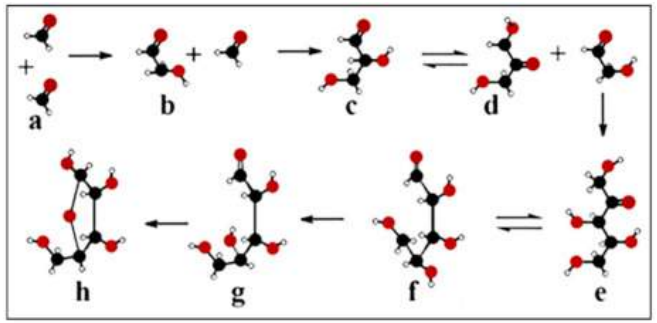
Astrochemistry – prebiotic chemistry

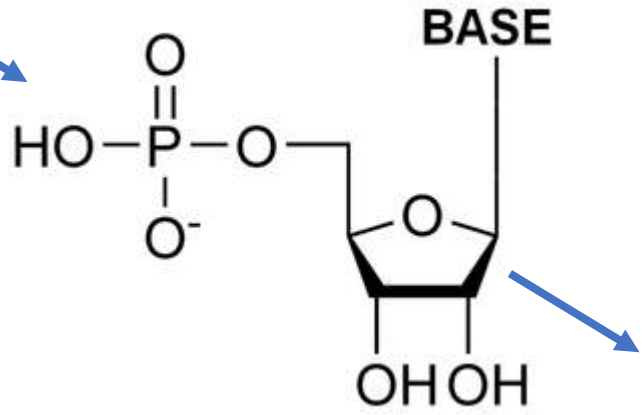


Glycolaldehyde

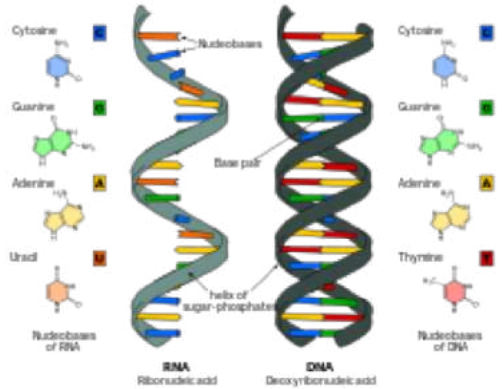


Ribose





Ribonucleotide



RNA and DNA

Astrochemistry – prebiotic chemistry

phosphorus monoxide ion (PO^+) in the ISM

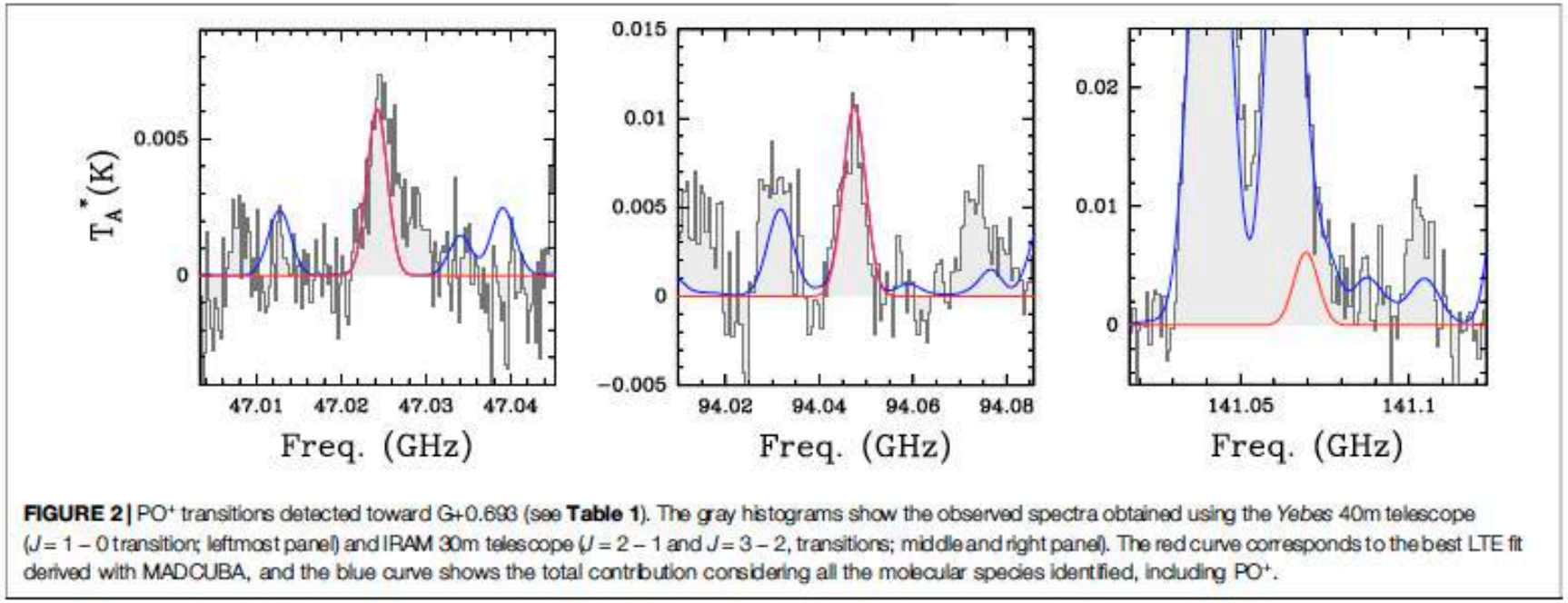


FIGURE 2 | PO^+ transitions detected toward G+0.693 (see **Table 1**). The gray histograms show the observed spectra obtained using the *Yebes* 40m telescope ($J = 1 - 0$ transition; leftmost panel) and IRAM 30m telescope ($J = 2 - 1$ and $J = 3 - 2$, transitions; middle and right panel). The red curve corresponds to the best LTE fit derived with MADCUBA, and the blue curve shows the total contribution considering all the molecular species identified, including PO^+.

Rivilla et al., 2022, doi: 10.3389/fspas.2022.829288

COMs in the interstellar medium

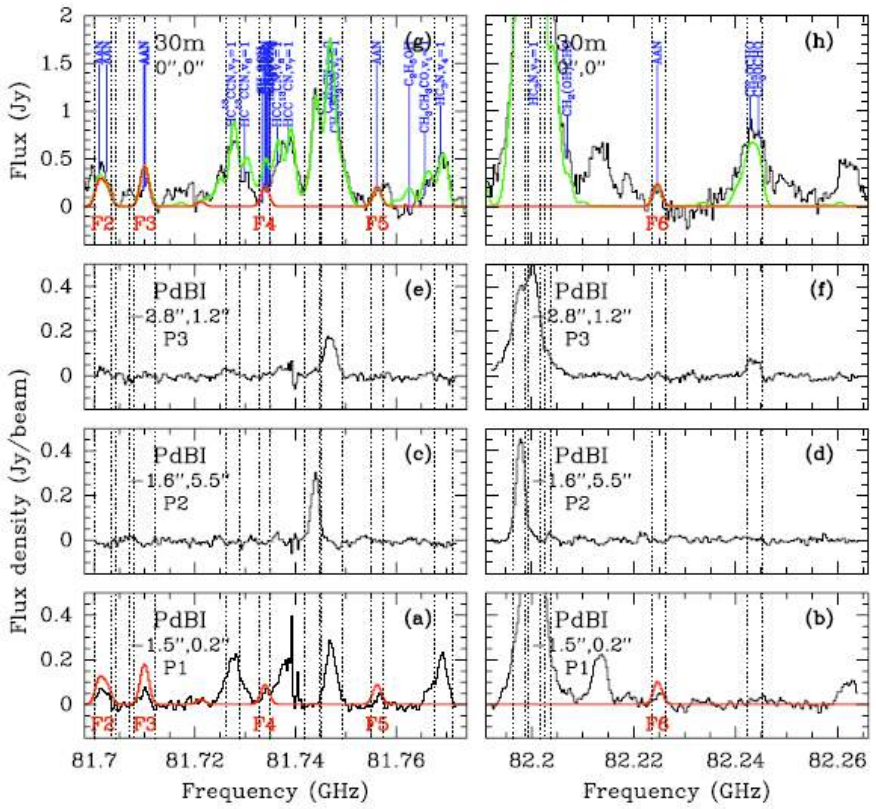
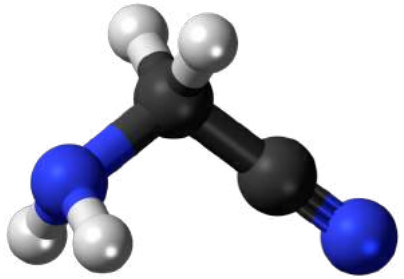


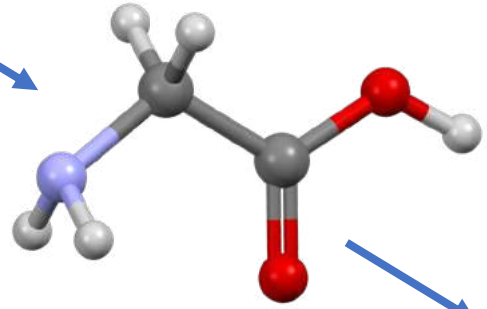
Fig. 4. Spectra obtained with the Plateau de Bure interferometer (**a**) to **f**)) and the 30 m telescope (**g**) and **h**)) toward Sgr B2(N) (in black). The dotted lines show the frequency ranges listed in Table 5. The offset position with respect to the reference position of Fig. 5 is given in each panel, along with a label (P1 to P3, see their definition in Table 6). The lines identified in our 30 m survey are labeled in blue. The red spectra show our best-fit model for amino acetonitrile (AAN) while the green spectrum corresponds to the 30 m model including all molecules. The observed lines which have no counterpart in the green spectrum are still unidentified.

Belloche et al., 2008, A&A 482, 179

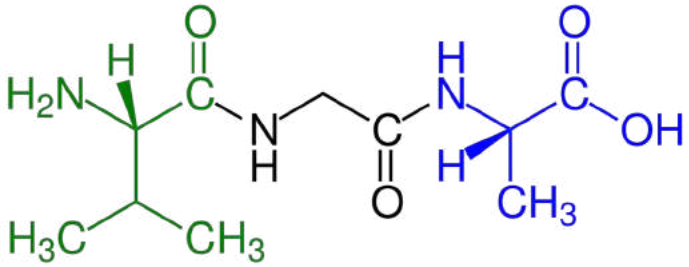
Astrochemistry – prebiotic chemistry



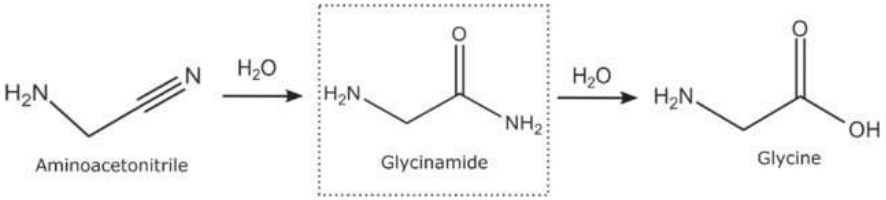
Aminoacetonitrile

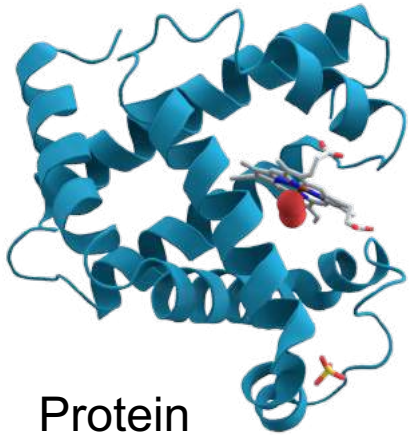


Glycine



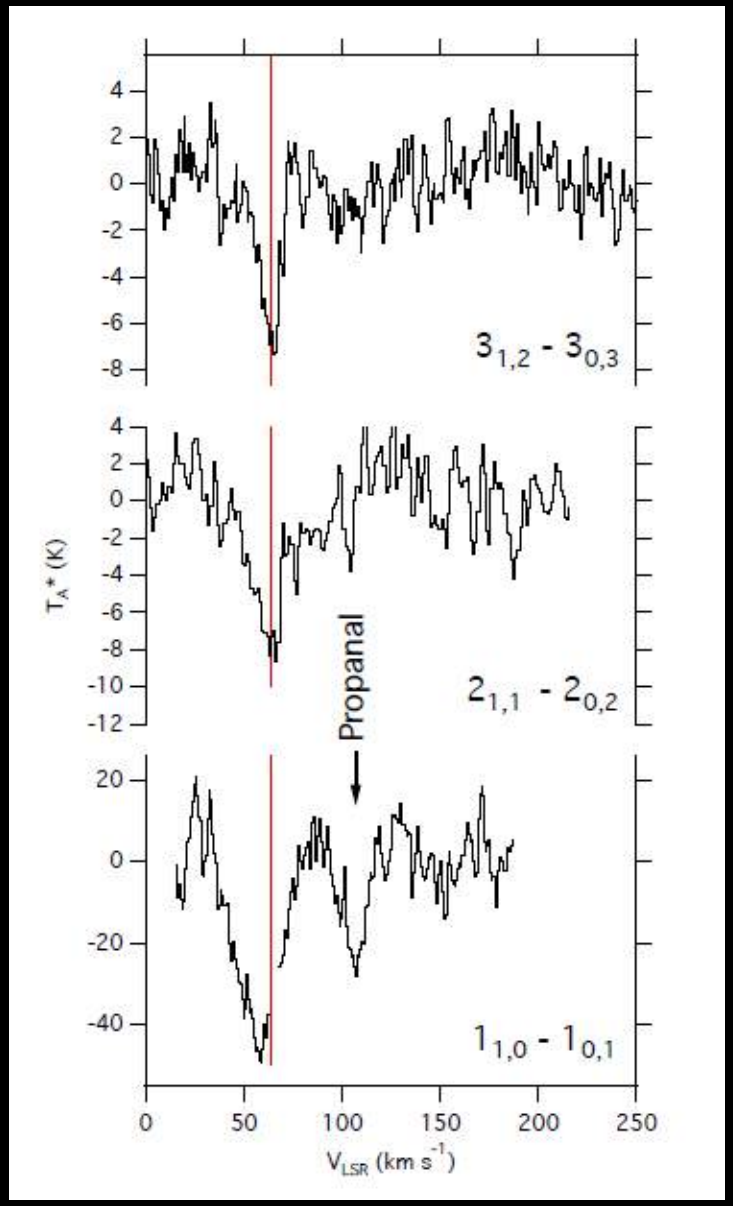
Peptide





Protein

COMs in the interstellar medium



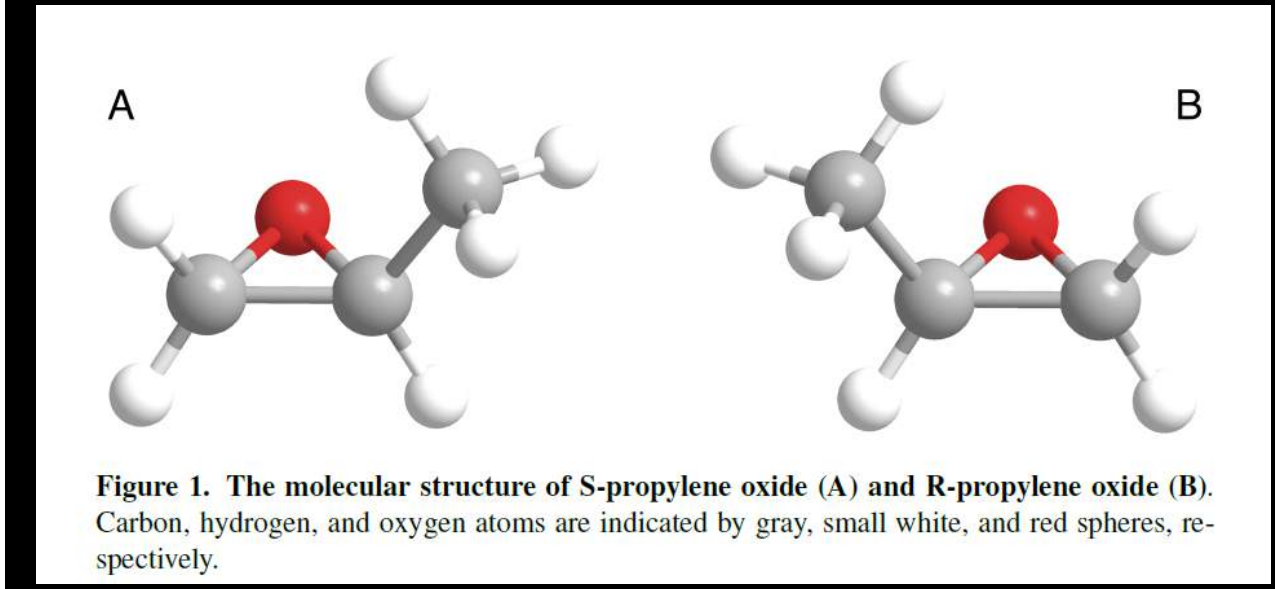


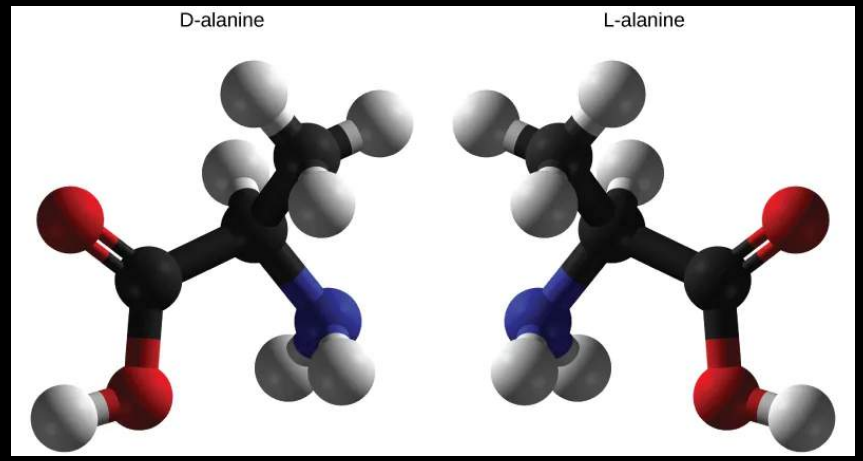
Figure 1. The molecular structure of S-propylene oxide (A) and R-propylene oxide (B). Carbon, hydrogen, and oxygen atoms are indicated by gray, small white, and red spheres, respectively.

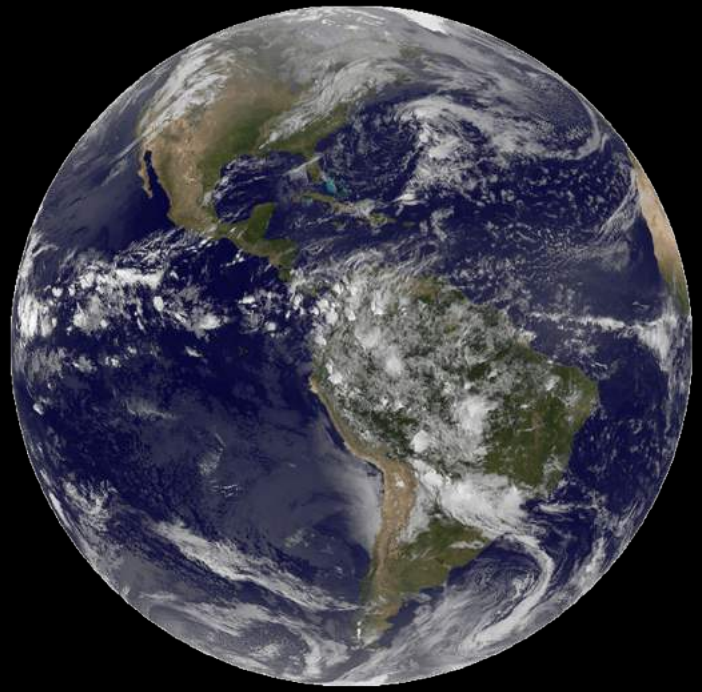
Figure 2. Observations of the 110-101 (Parkes), 211-202 (GBT), and 312-303 (GBT) transitions of propylene oxide, in absorption, toward the Galactic Center. The 64 km s^{-1} systematic velocity characteristic of Sgr B2(N) is indicated by a vertical red line.

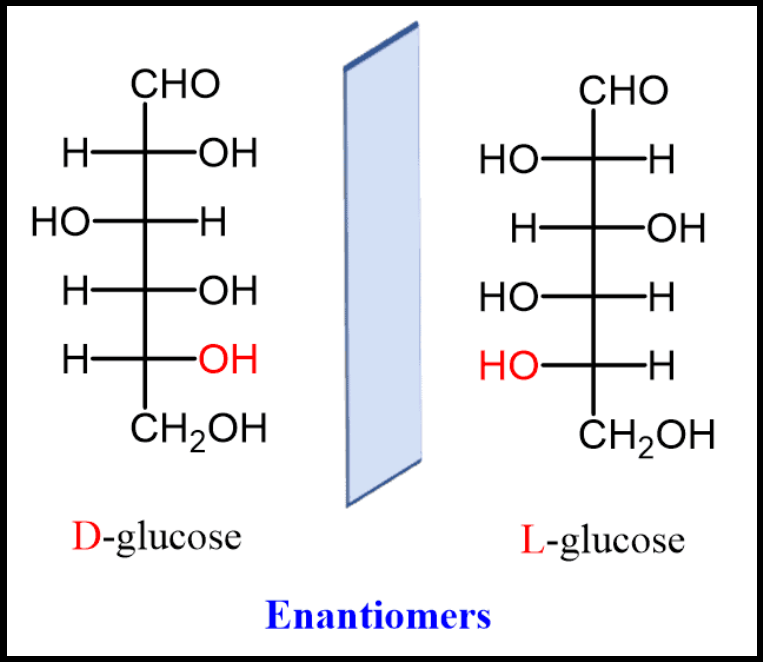
McGuire et al., 2016, Science, 352, 1449

Astrochemistry – prebiotic chemistry

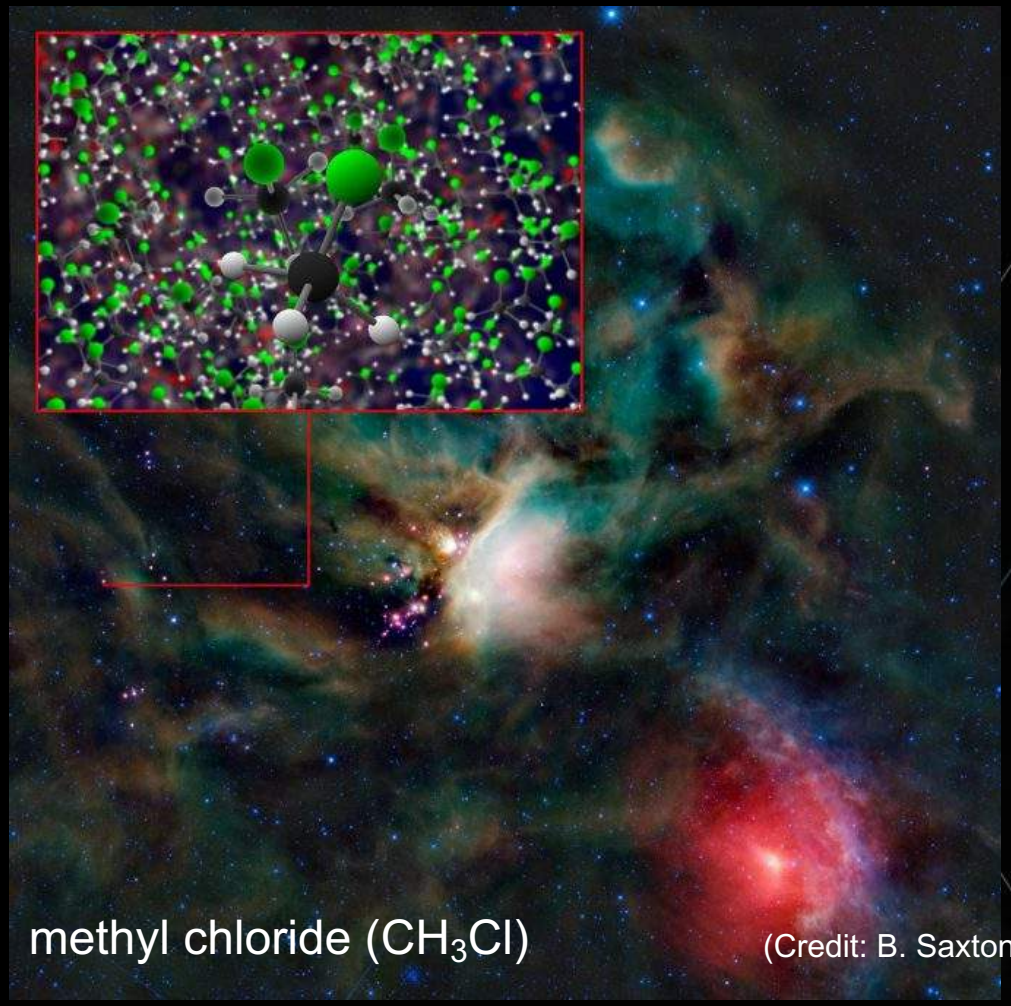
Terrestrial biochemistry is based on L-amino acids and D-sugars



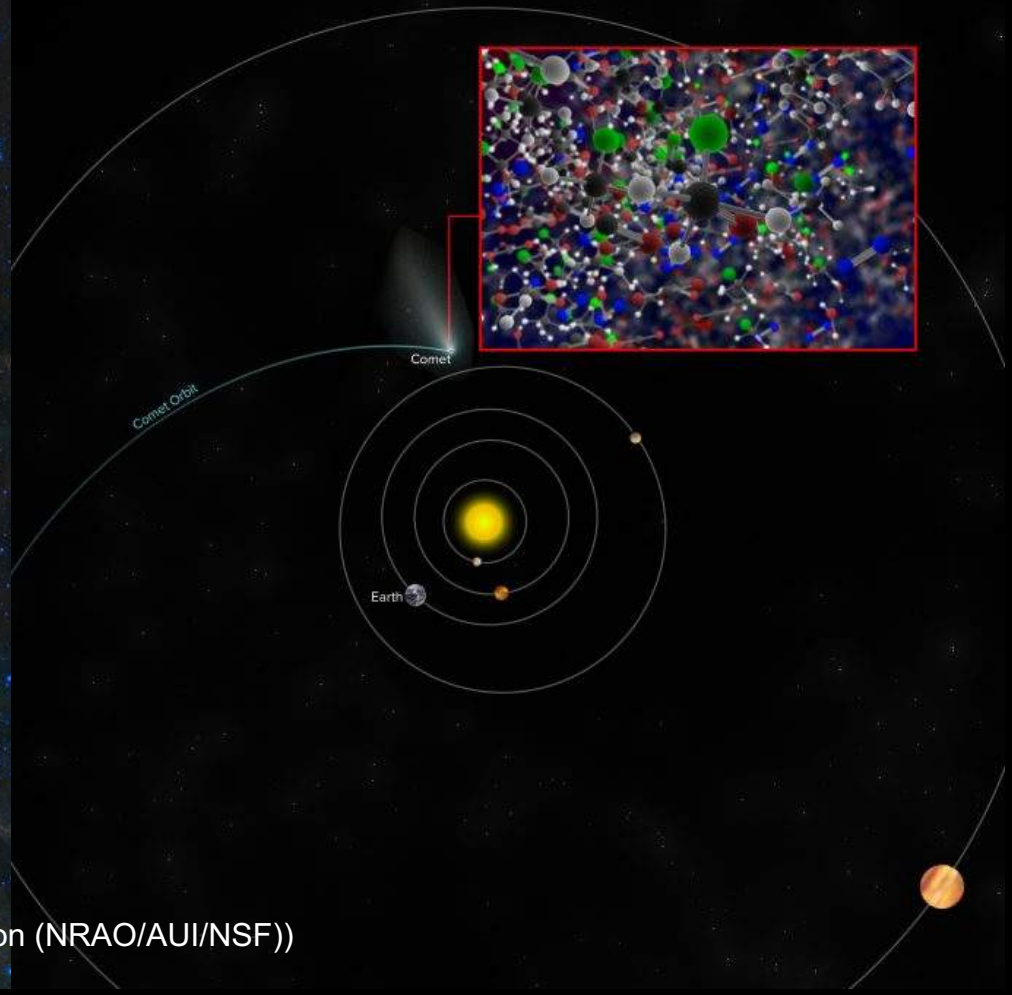




COMs in the interstellar medium



(Credit: B. Saxton (NRAO/AUI/NSF))



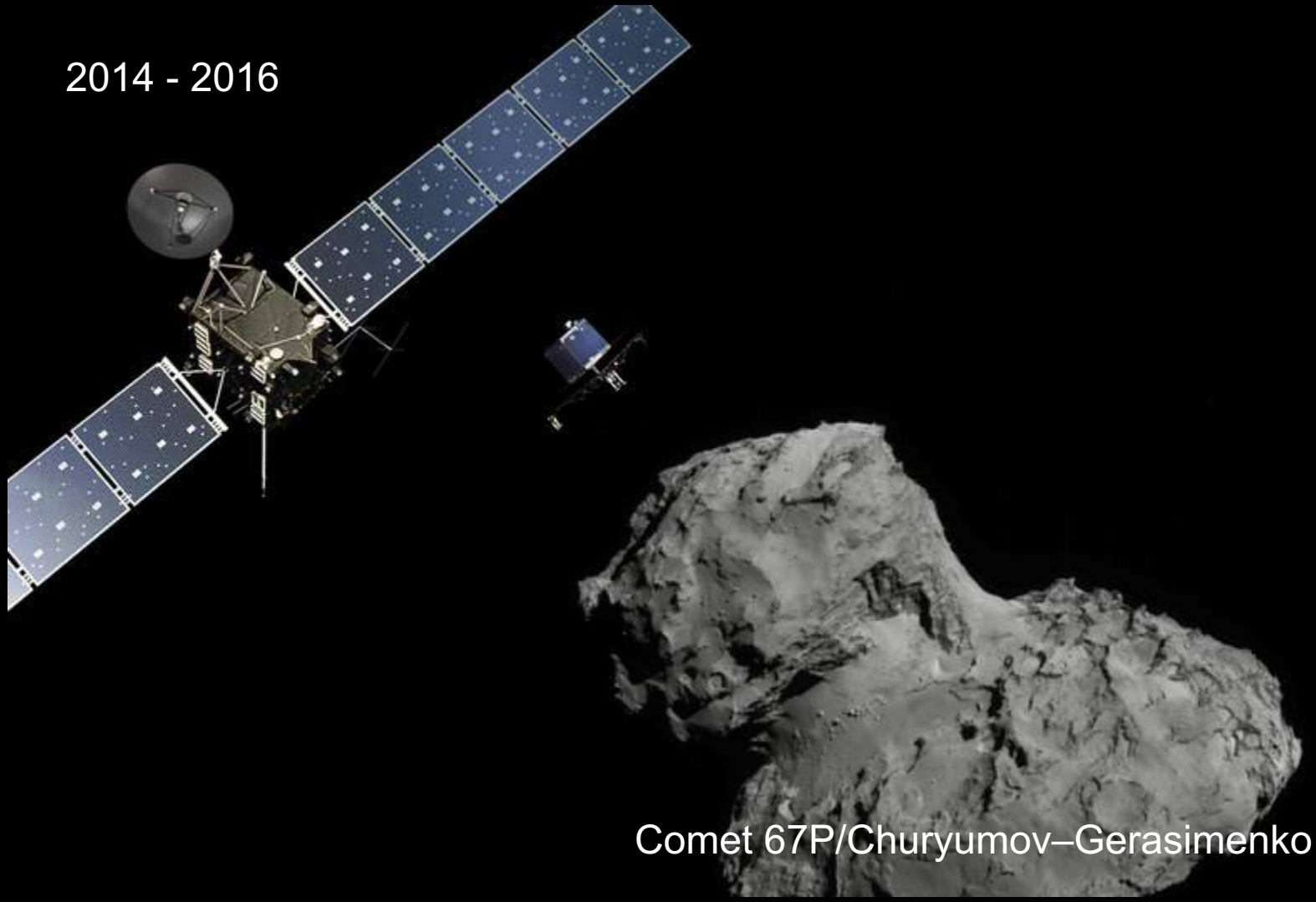
Around the infant stars in IRAS 16293-2422 by ALMA

In the atmosphere of the 67P/C-G by Rosetta

Fayolle et al., 2017, Nature Astronomy, 1, 703

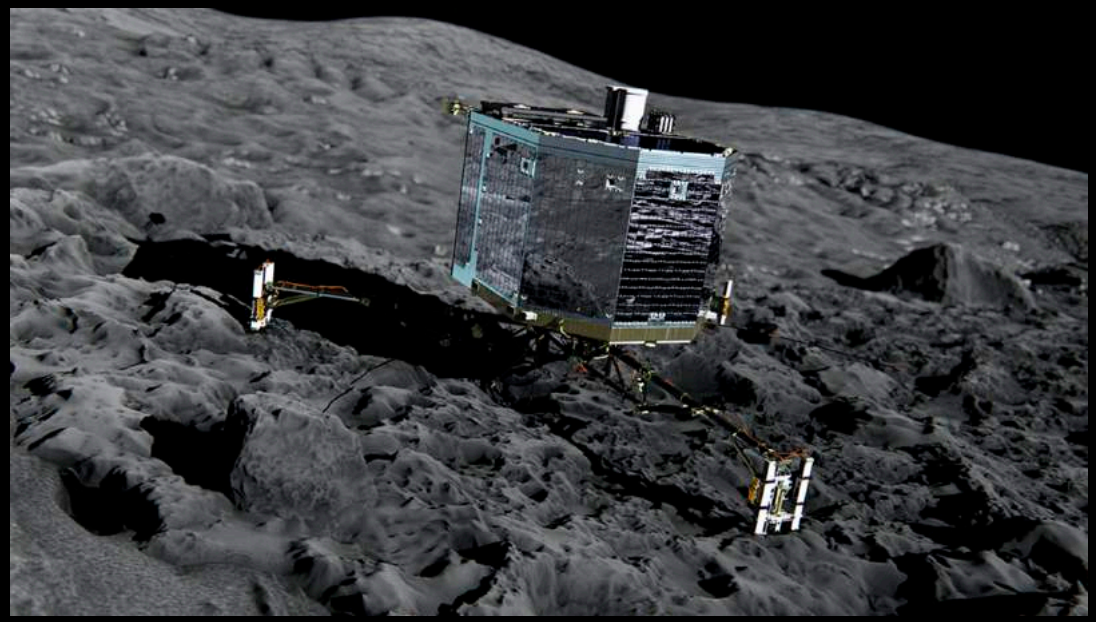
Solar system. Rosetta mission

2014 - 2016

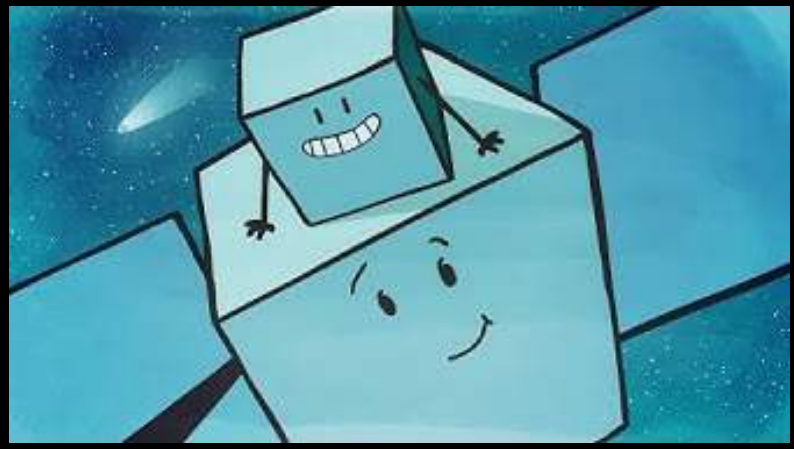


Comet 67P/Churyumov–Gerasimenko

Solar system. Rosetta mission

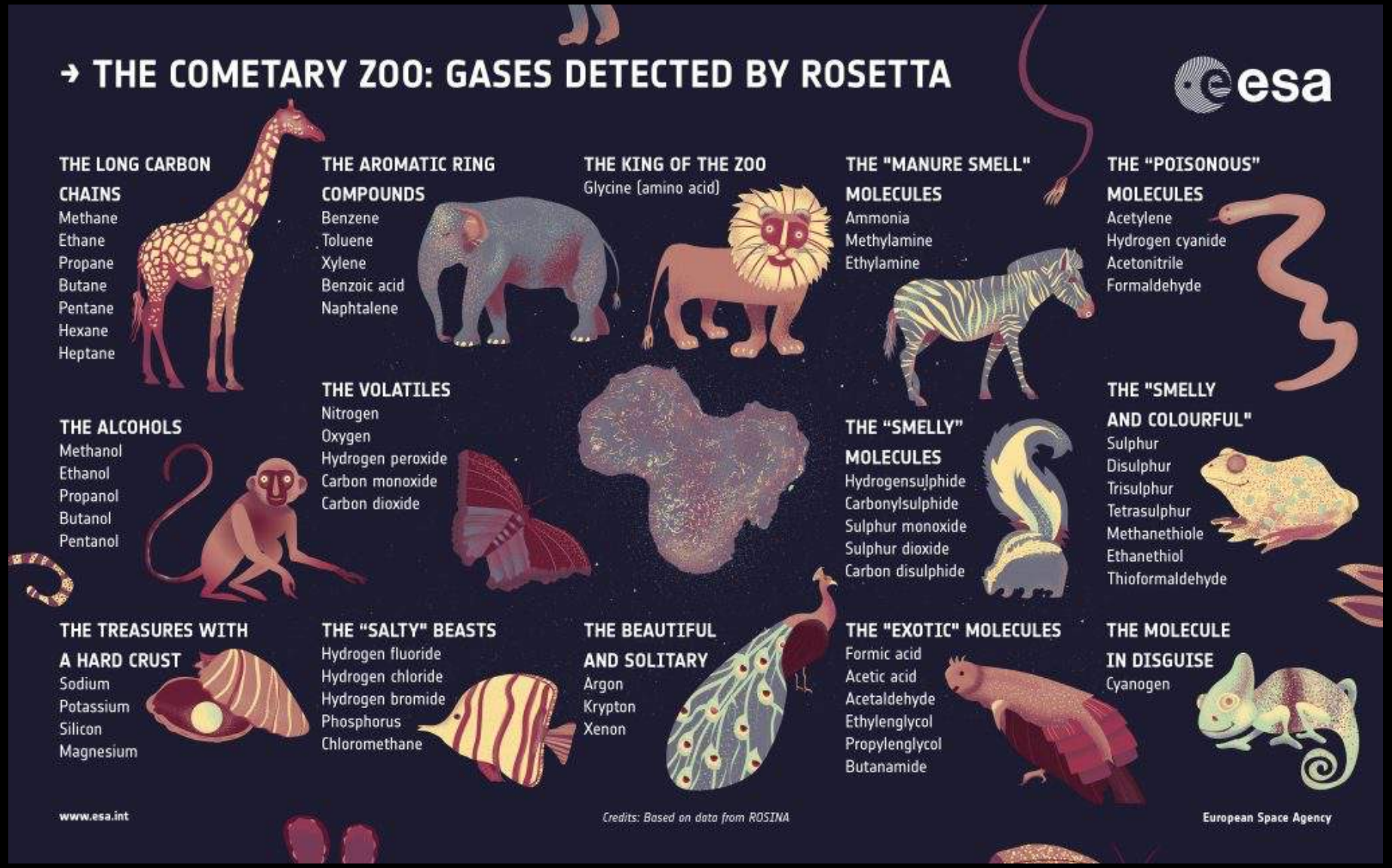


The amazing adventures of Rosetta and Philae



https://www.youtube.com/watch?v=HD2zrF3I_II

Solar system. Rosetta mission



Solar system. Rosetta mission

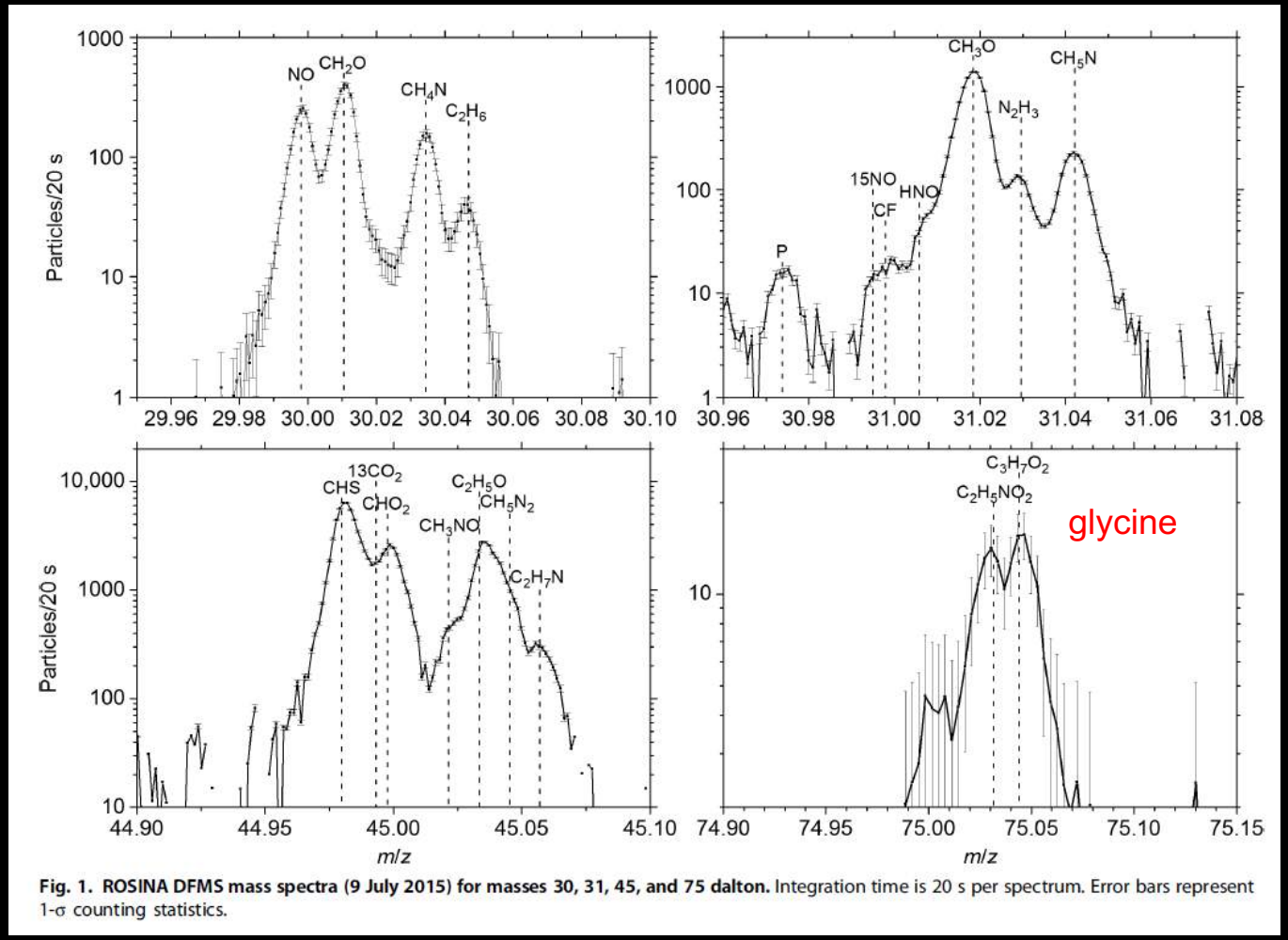
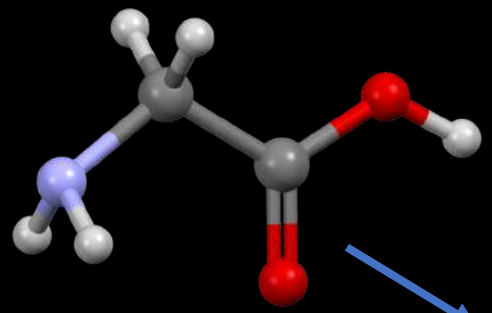


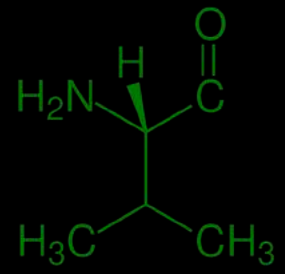
Fig. 1. ROSINA DFMS mass spectra (9 July 2015) for masses 30, 31, 45, and 75 dalton. Integration time is 20 s per spectrum. Error bars represent 1-σ counting statistics.

Altwegg et al., 2016, Science Advances, 2, e160028

Astrochemistry – prebiotic chemistry

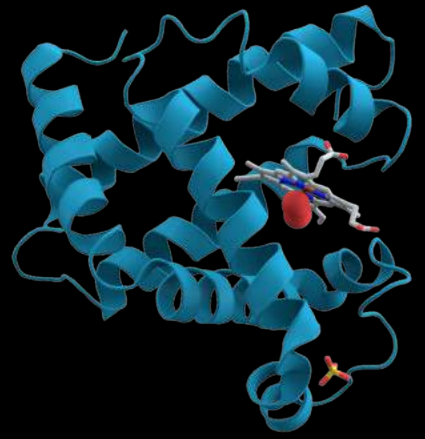


Glycine





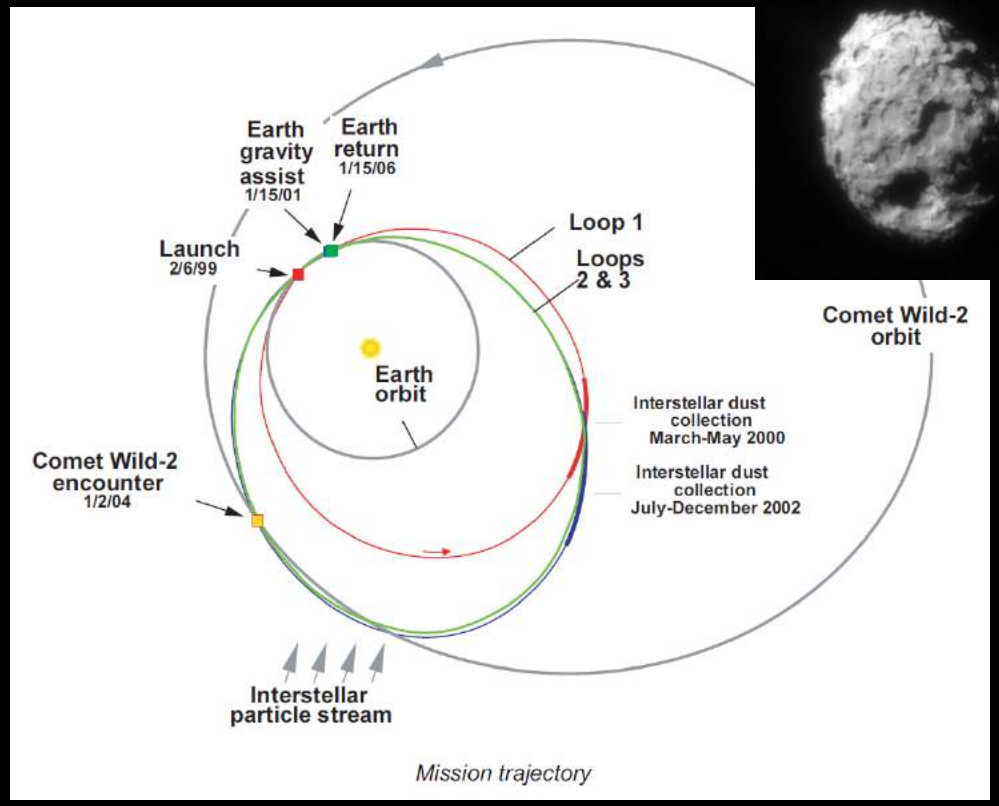
Peptide



Protein

Collecting cosmic dust





- Launch: 1999 (Delta II rocket, Florida)
- 2 ISD capture periods in 2000 & 2002
- Aerogel collector (2 sides)
- 2006: Earth return

Stardust particles

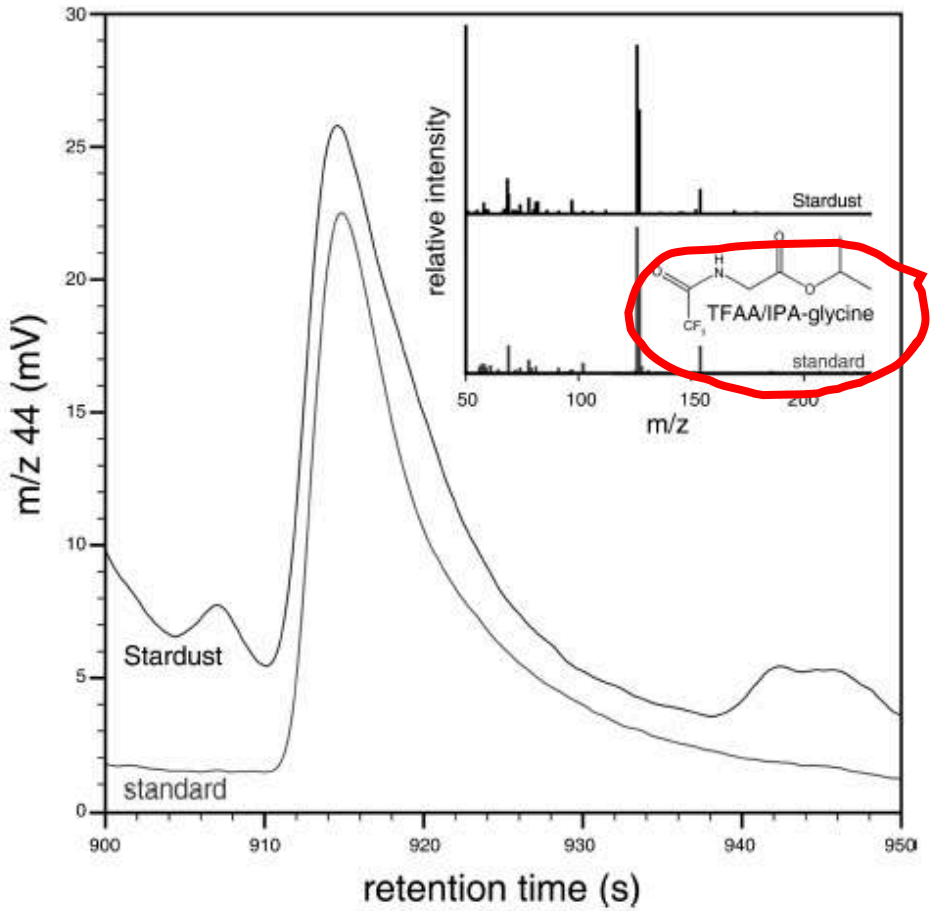
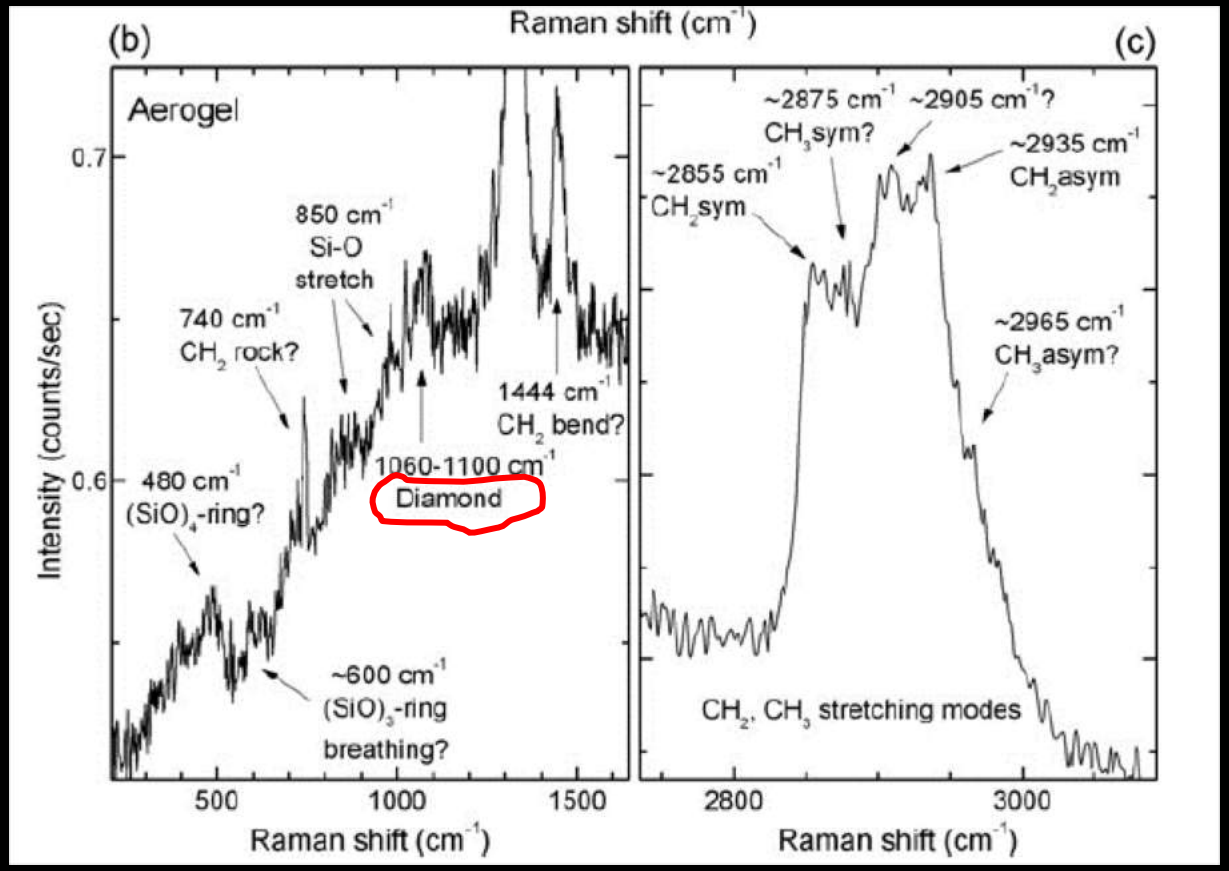


Fig. 3. GC-MS/IRMS analysis of the derivatized combined extract from four Stardust foils and of a glycine standard. The traces show the m/z 44 ($^{12}CO_2$) peak produced and measured from GC-IRMS for the peak assigned to glycine. The inset shows the simultaneously collected mass spectral fragmentation pattern for these peaks and the structure of glycine derivatized with trifluoroacetic acid/isopropanol (TFAA/IPA).

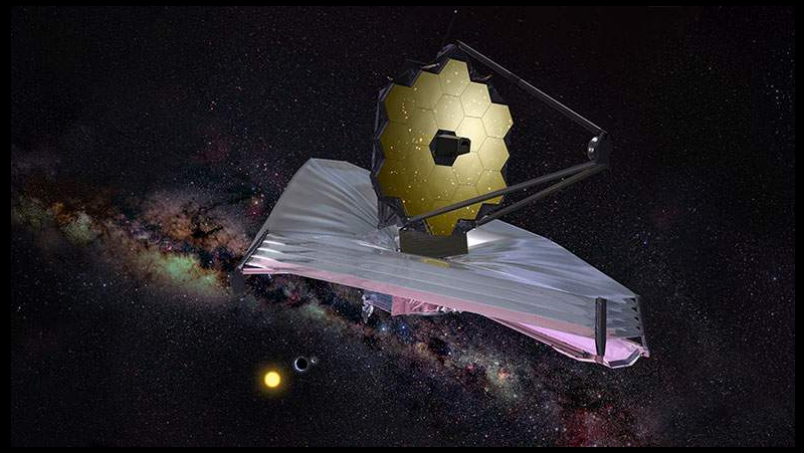
Elsila et al., 2009, Meteoritics & Planetary Science, 44, 1323

Stardust particles



Rotundi et al., 2014, Meteor. And Planet. Sci., 49, 550

Our astronomical future



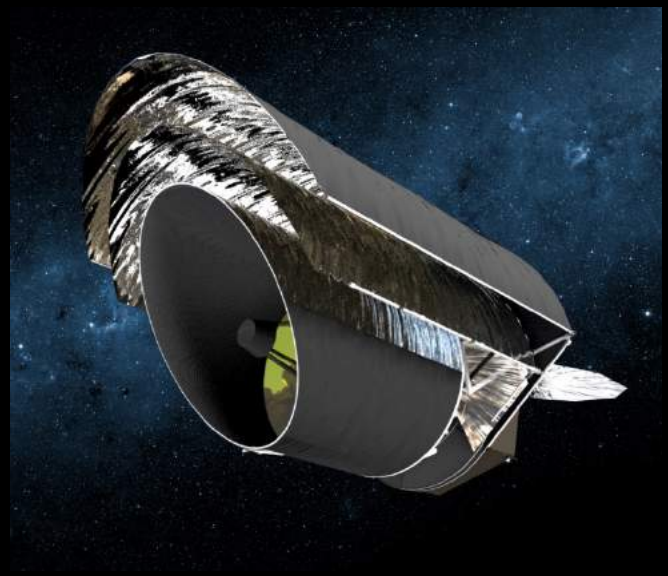
James Webb Space Telescope



Extremely Large Telescope (2027)



ARIEL Telescope (2029)



Origins Space Telescope (2035)

Part 3:

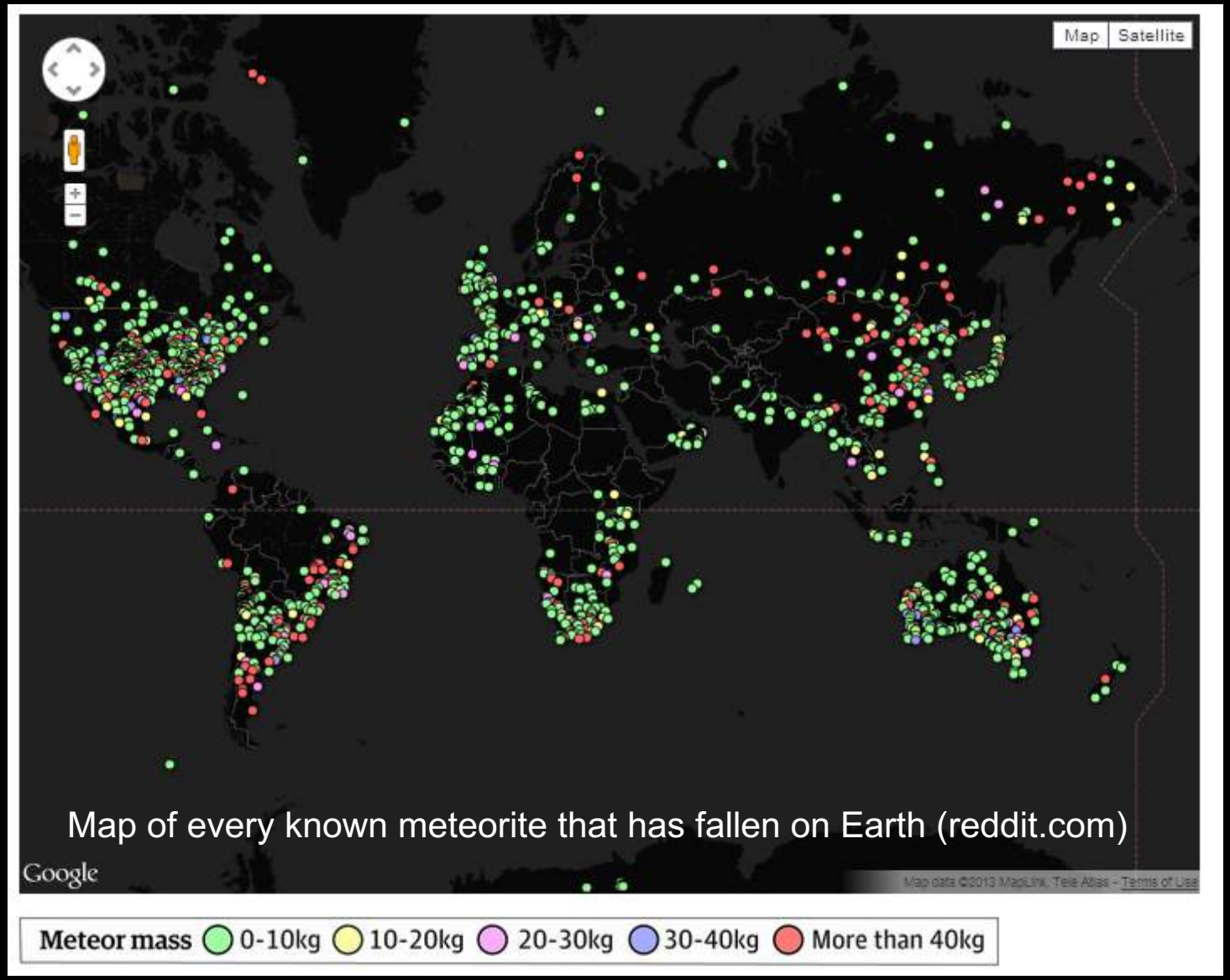
Evidence for exogenous hypothesis: Earth

Meteorites


Murchison meteorite


Paris meteorite


Northwest Africa Meteorite



Map of every known meteorite that has fallen on Earth (reddit.com)

Prebiotic molecules in meteorites

Amino acids

Table 2 Amino acids that have been detected in meteorites[4,5,8,9]

C2
Glycine
C3
Alanine
β-Alanine
Serine
Sarcosine
C4
Threonine
allo-Threonine
α-Aminobutyric acid
β-Aminobutyric acid
α-Aminoisobutyric acid
β-Aminoisobutyric acid
N-Ethylglycine
N,*N*-Dimethylglycine
N-Methylalanine
N-Methyl-β-alanine
Aspartic acid
2,3-Diaminobutanoic acid
2,4-Diaminobutanoic acid
3,3′-Diaminoisobutanoic acid
C5
Valine
Norvaline
Isovaline
3-Aminopentanoic acid
3-Amino-2-methylbutanoic acid
allo-3-Amino-2-methylbutanoic acid
3-Amino-2,2-dimethylpropanoic acid
3-Amino-2,2-dimethylpropanoic acid
3-Amino-2-ethylpropanoic acid
4-Aminopentanoic acid
4-Amino-2-methylbutanoic acid
4-Amino-3-methylbutanoic acid
5-Aminopentanoic acid
Glutamic acid
2-Methylaspartic acid
3-Methylaspartic acid
allo-3-Methylaspartic acid
N-Methylaspartic acid
4,4′-Diaminoisopentanoic acid

C6
Leucine
Isoleucine
allo-Isoleucine
Norleucine
Pseudoleucine
Cycloleucine
2-Methylnorvaline
Pipecolic acid
2-Amino-2-ethylbutanoic acid
2-Amino-2,3-dimethylbutanoic acid
3-Amino-2-ethylbutanoic acid[a]
3-Amino-2,3-dimethylbutanoic acid[a]
3-Methylamine-pentanoic acid[a]
4-Aminohexanoic acid
4-Amino-3,3-dimethylbutanoic acid[a]
4-Amino-2-methylpentanoic acid[a]
4-Amino-3-methylpentanoic acid
4-Amino-4-methylpentanoic acid
6-Aminohexanoic acid
α-Aminoadipic acid
β-Aminoadipic acid
2-Methylglutamic acid
other isomers detected, but not identified
C7
2-Amino-2,3,3-trimethylbutanoic acid
2-Amino-2-ethyl-3-methylbutanoic acid
2-Amino-2-ethylpentanoic acid
2-Amino-3-ethylpentanoic acid
2-Amino-2,3-dimethylpentanoic acid
2-Amino-2,4-dimethylpentanoic acid
2-Amino-3,3-dimethylpentanoic acid
2-Amino-3,4-dimethylpentanoic acid
2-Amino-4,4-dimethylpentanoic acid
allo-2-Amino-2,3-dimethylpentanoic acid[a]
allo-2-Amino-3,4-dimethylpentanoic acid
2-Amino-2-methylhexanoic acid
2-Amino-3-methylhexanoic acid
allo-2-Amino-3-methylhexanoic acid[a]
2-Amino-4-methylhexanoic acid
allo-2-Amino-4-methylhexanoic acid[a]
2-Amino-5-methylhexanoic acid
2-Aminoheptanoic acid
α-Aminopimelic acid
1-Aminocyclohexanecarboxylic acid
other isomers detected, but not identified
C8
Isomers detected but not identified
C9
Phenylalanine
Tyrosine
other isomers detected, but not identified

[a] Denotes compounds that were only tentatively identified.

Burton et al., 2012, Chem. Soc. Rev., 41, 5459

Prebiotic molecules in meteorites

Nucleobases

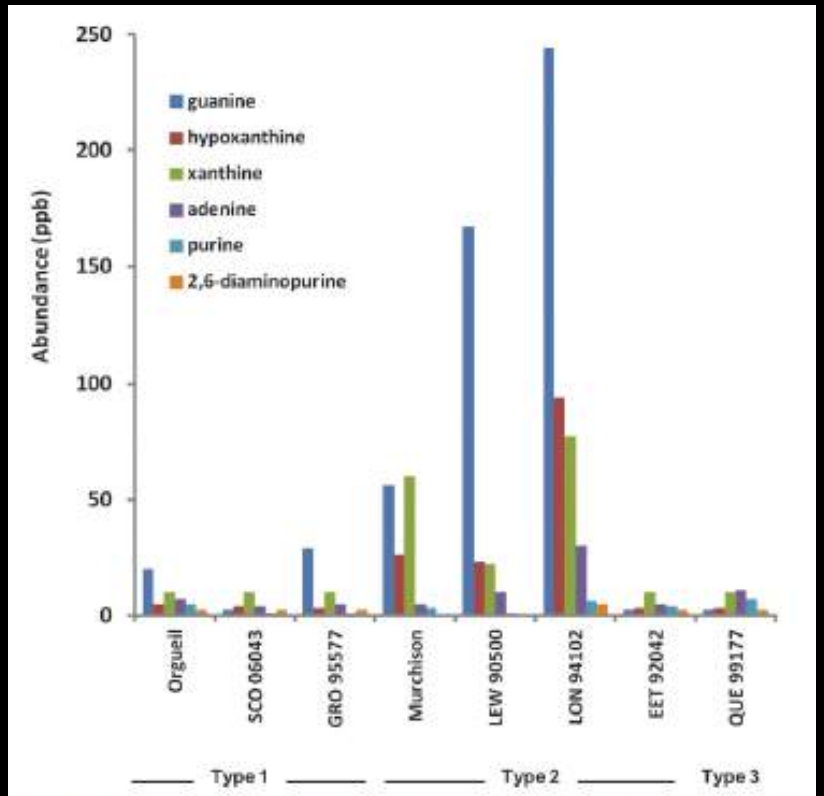
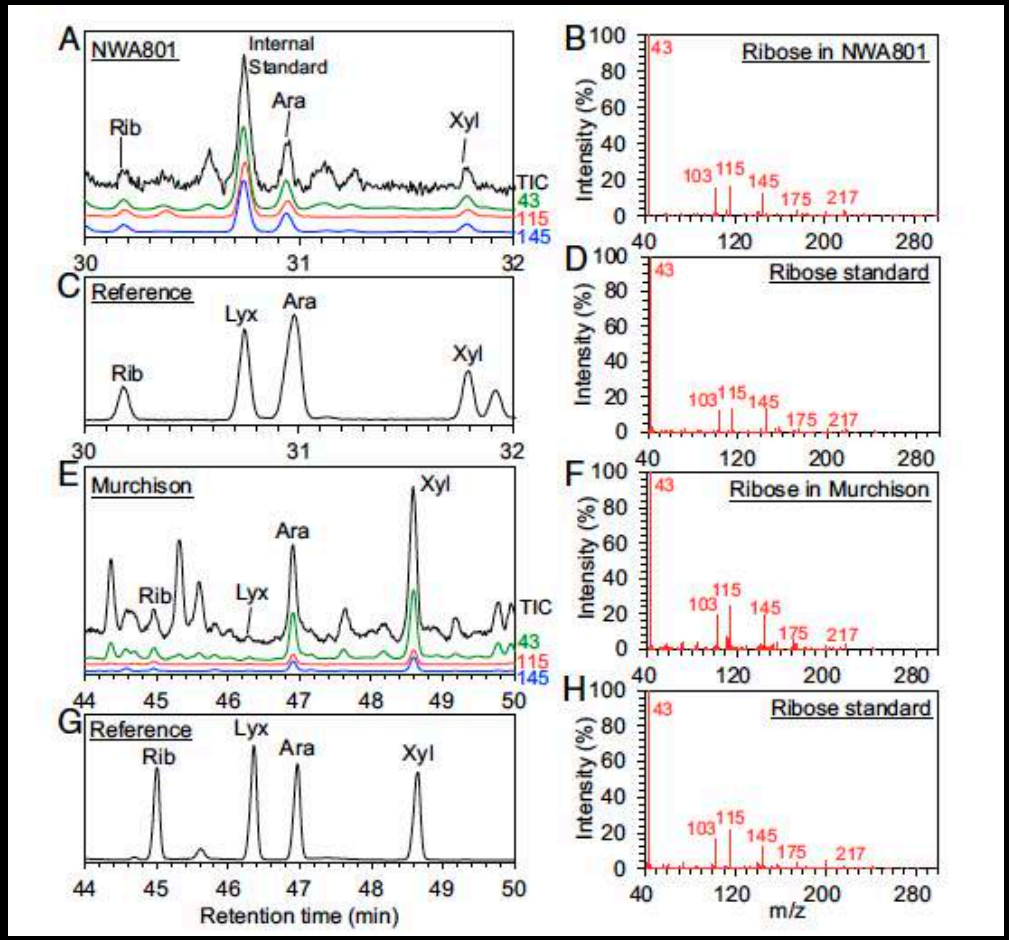


Fig. 9 Distribution of purine nucleobases in aqueously-altered carbonaceous chondrites. The meteorites are arranged from most to least aqueously altered (type 1, left, to type 3, right).

Burton et al., 2012, Chem. Soc. Rev., 41, 5459

Prebiotic molecules in meteorites

Ribose



Furukawa et al., 2019, PNAS, 116, 24440

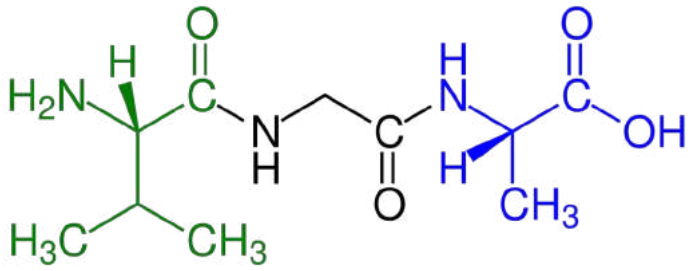
Prebiotic molecules in meteorites

Phosphates

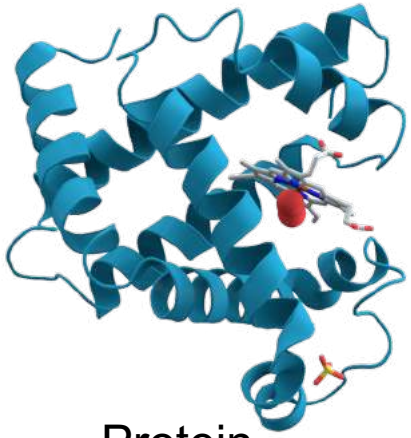
„Nine phosphate minerals are found in meteorites:
whitlockite, $Ca_3(PO_4)_2$;
chlorapatite, $Ca_5(PO_4)_3Cl$;
hydroxyapatite, $Ca_5(PO_4)_3OH$;
sarcopside, $(Fe, Mn)_3(PO_4)_2$;
graftonite, $(Fe, Mn)_3\ (PO_4)_2$;
farringtonite, $Mg_3(PO_4)_2$;
stanfieldite, $Ca_4(Mg, Fe)_5(PO_4)_6$;
brianite, $Na_2MgCa(PO_4)_2$;
panethite, $Na_2Mg_2(PO_4)_2$.
The last four have been found only in meteorites“.

Fuchs, https://link.springer.com/chapter/10.1007/978-94-010-3411-1_56

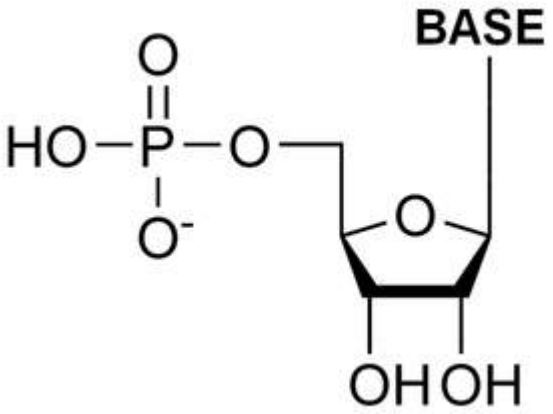
Prebiotic molecules in meteorites



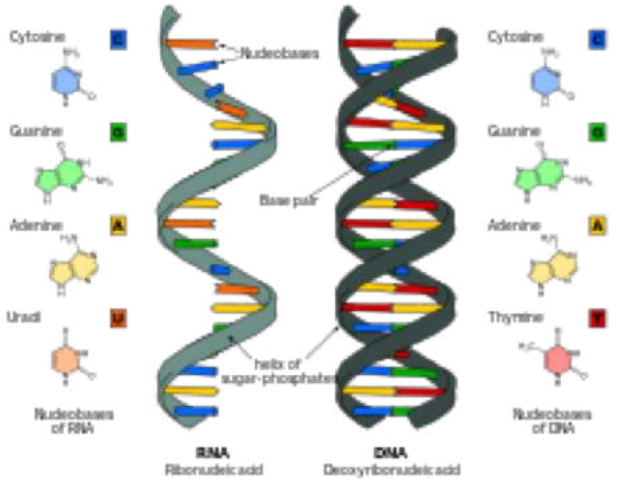
Peptide



Protein



Ribonucleotide



RNA and DNA

Prebiotic molecules in meteorites

The first proteins discovered in meteorites?????

McGeoch et al., 2020, https://arxiv.org/abs/2002.11688

Lange et al., 2020, https://chemrxiv.org/engage/chemrxiv/article-details/60c748154c89191aa0ad2e78

Lange et al., *J. Proteome Res.,* 2021, 20, 1444

Prebiotic molecules in meteorites

Chirality

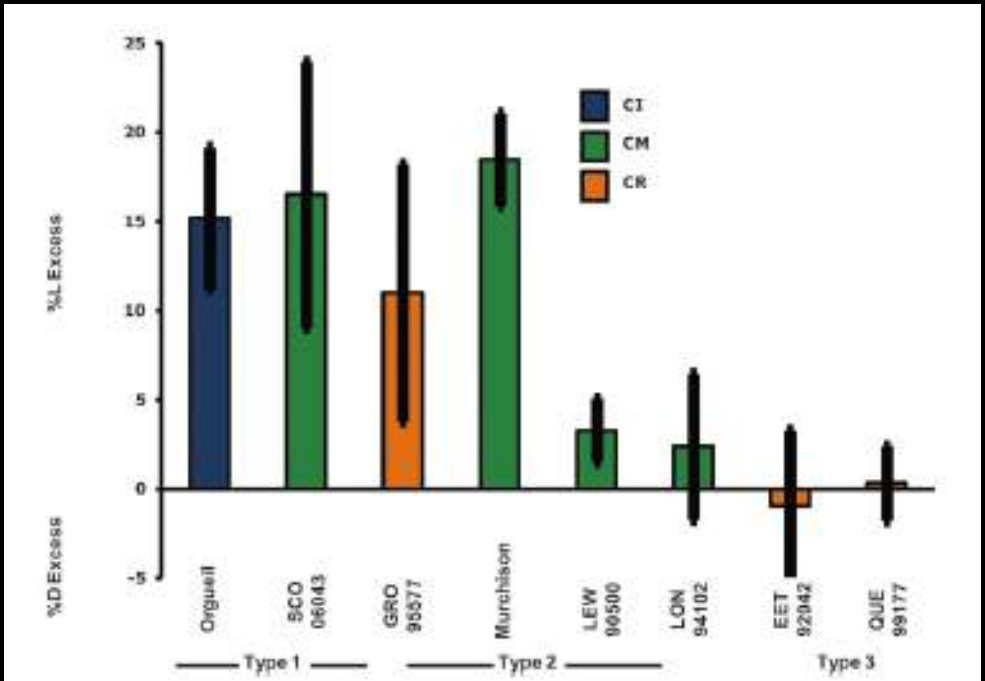


Fig. 11 Enantiomeric excesses (in percent) of isovaline measured in CI, CM, and CR carbonaceous chondrites correlate with the degree of aqueous alteration of the samples.[54]

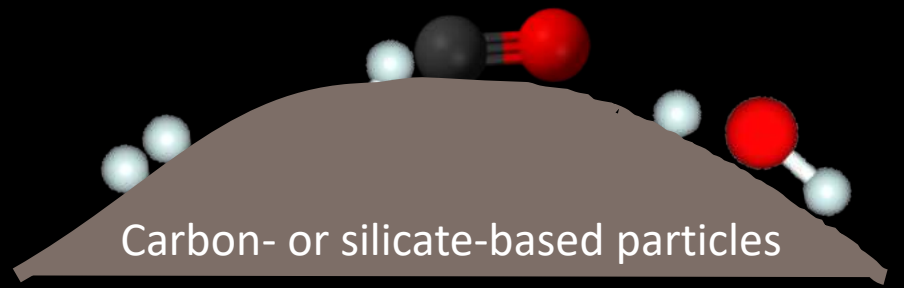
Burton et al., 2012, Chem. Soc. Rev., 41, 5459

Chemical processes leading to the formation of molecules in space

Gas phase reactions



Grain surface reactions



Surface reaction pathways lead to a greater complexity of molecular species

COMs and prebiotic molecules in models (gas-phase)

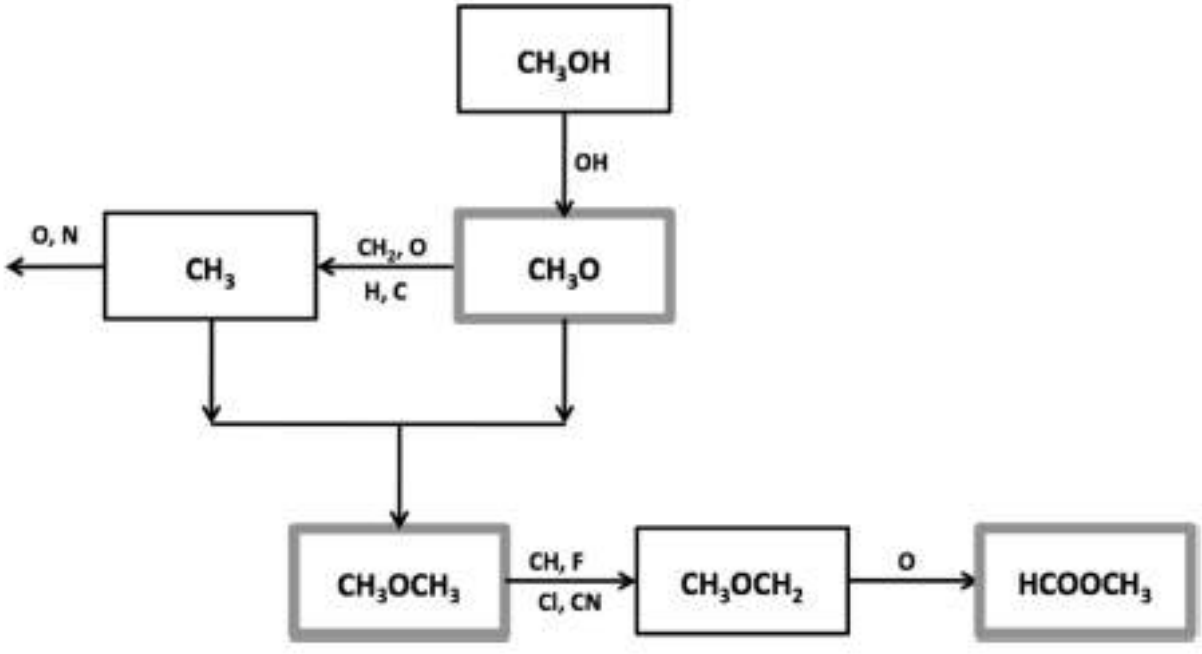


Figure 1. Scheme of the added reactions that form DME, MF and methoxy (boxes with grey large contours).

Balucani et al., 2015, MNRAS 449, L16

COMs and prebiotic molecules in models (solid state)

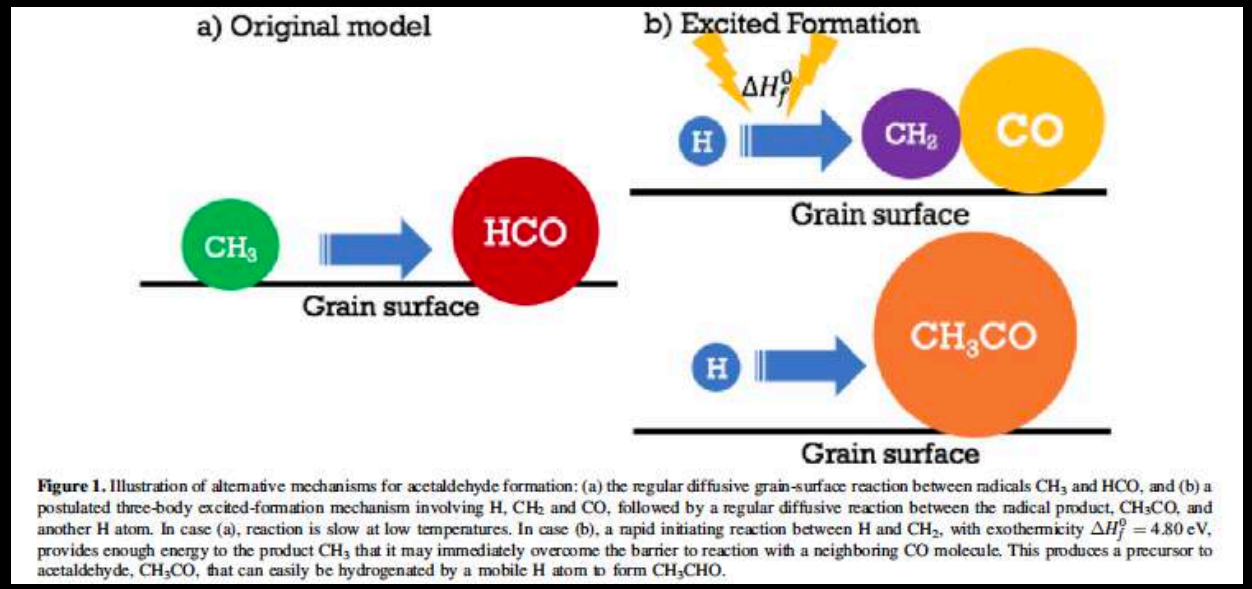


Figure 1. Illustration of alternative mechanisms for acetaldehyde formation: (a) the regular diffusive grain-surface reaction between radicals CH_3 and HCO, and (b) a postulated three-body excited-formation mechanism involving H, CH_2 and CO, followed by a regular diffusive reaction between the radical product, CH_3CO, and another H atom. In case (a), reaction is slow at low temperatures. In case (b), a rapid initiating reaction between H and CH_2, with exothermicity $\Delta H_f^0 = 4.80$ eV, provides enough energy to the product CH_3 that it may immediately overcome the barrier to reaction with a neighboring CO molecule. This produces a precursor to acetaldehyde, CH_3CO, that can easily be hydrogenated by a mobile H atom to form CH_3CHO.

Jin and Garrod, 2020, ApJ SS, 249, 26

Table 2

A Selection of Barrierless Surface/Mantle Radical-addition Reactions Relevant to Glycine or Related Species Included in the Chemical Network

Reaction		
$HOCO + CH_2NH_2$	$\rightarrow$	NH_2CH_2COOH
	$\rightarrow$	$CH_3NH_2 + CO_2$
$NH_2 + CH_2COOH$	$\rightarrow$	NH_2CH_2COOH
$OH + NH_2CH_2CO$	$\rightarrow$	NH_2CH_2COOH
$H + HNCH_2COOH$	$\rightarrow$	NH_2CH_2COOH
$CH_2OH + HNCH_2COOH$	$\rightarrow$	$NH_2CH_2COOH + H_2CO$
$CH_3O + HNCH_2COOH$	$\rightarrow$	$NH_2CH_2COOH + H_2CO$
$HCO + HNCH_2COOH$	$\rightarrow$	$NH_2CH_2COOH + CO$
$HOCO + HNCH_2COOH$	$\rightarrow$	$NH_2CH_2COOH + CO_2$
$NH + CH_2COOH$	$\rightarrow$	$HNCH_2COOH$

Garrod, 2013, ApJ, 765, 60

Chemical reaction databases

Ohio State University (OSU): 4300 reactions, 430 species, 12 elements

Manchester University (UMIST/UDFA): 4600 reactions, 420 species, 12 elements

NIST Chemical Kinetics Database: ~30,000 neutral-neutral reactions (T>300K)

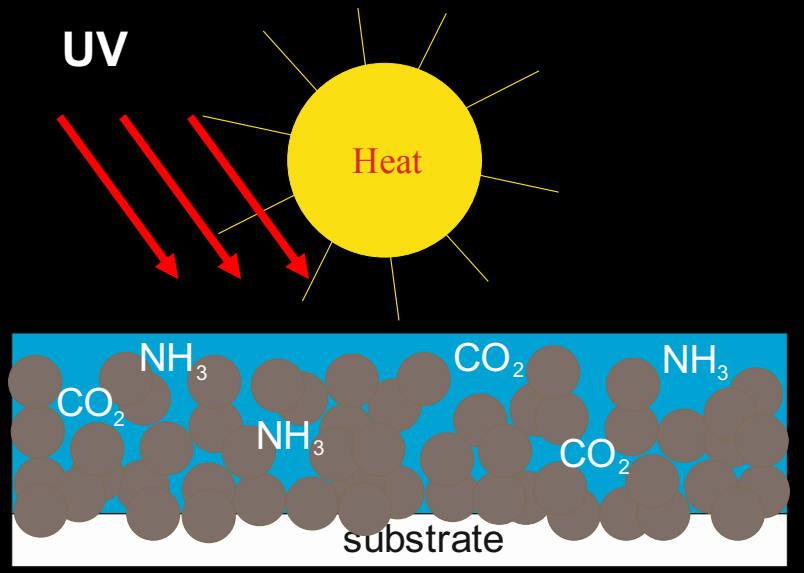
KIDA (KInetic Database for Astrochemistry): most up-to-date, 6000 reactions, 450 species, 12 elements

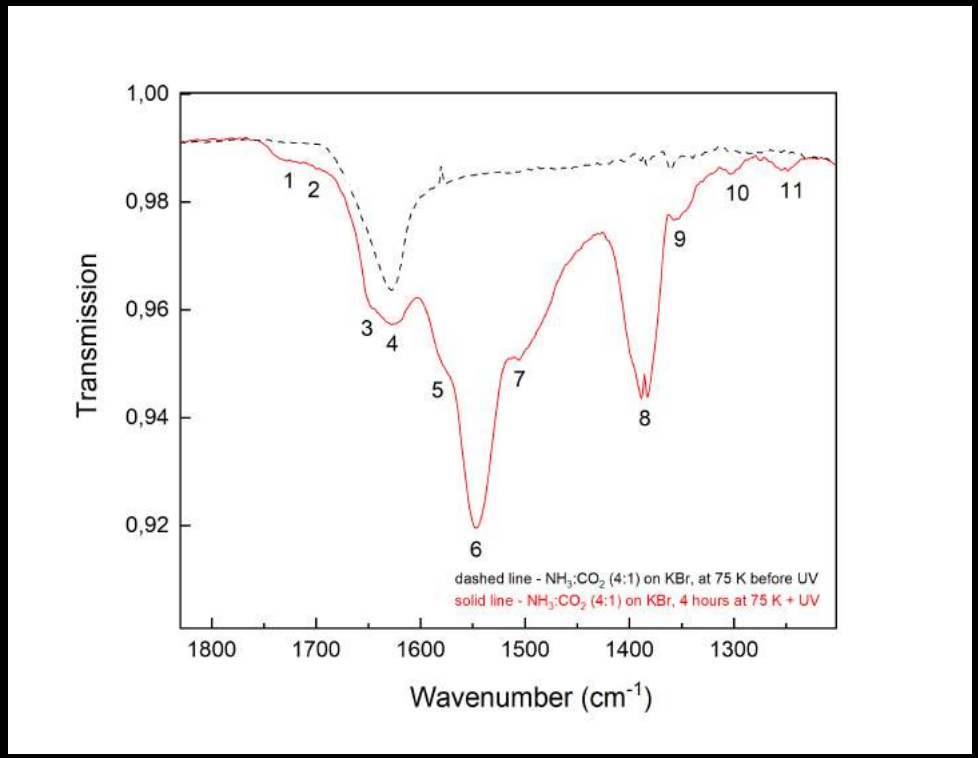
Only ~10-20% of accurate reaction rates!

Courtesy of Eric Herbst

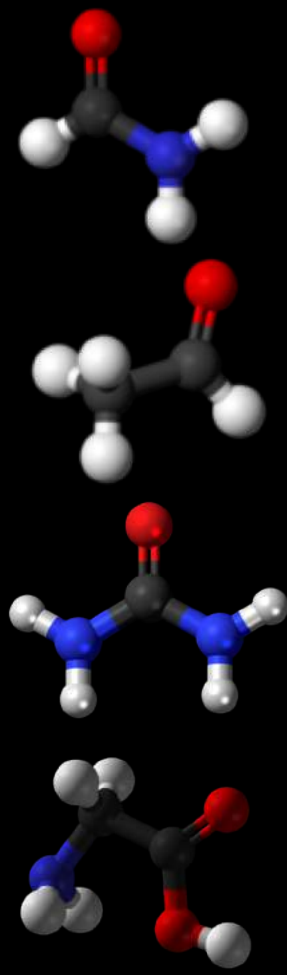
COMs and prebiotic molecules in laboratory analogues of cosmic ices

$CO_2 + NH_3$ at 75 K + UV





IR spectra before and after UV irradiation



formamide

acetaldehyde

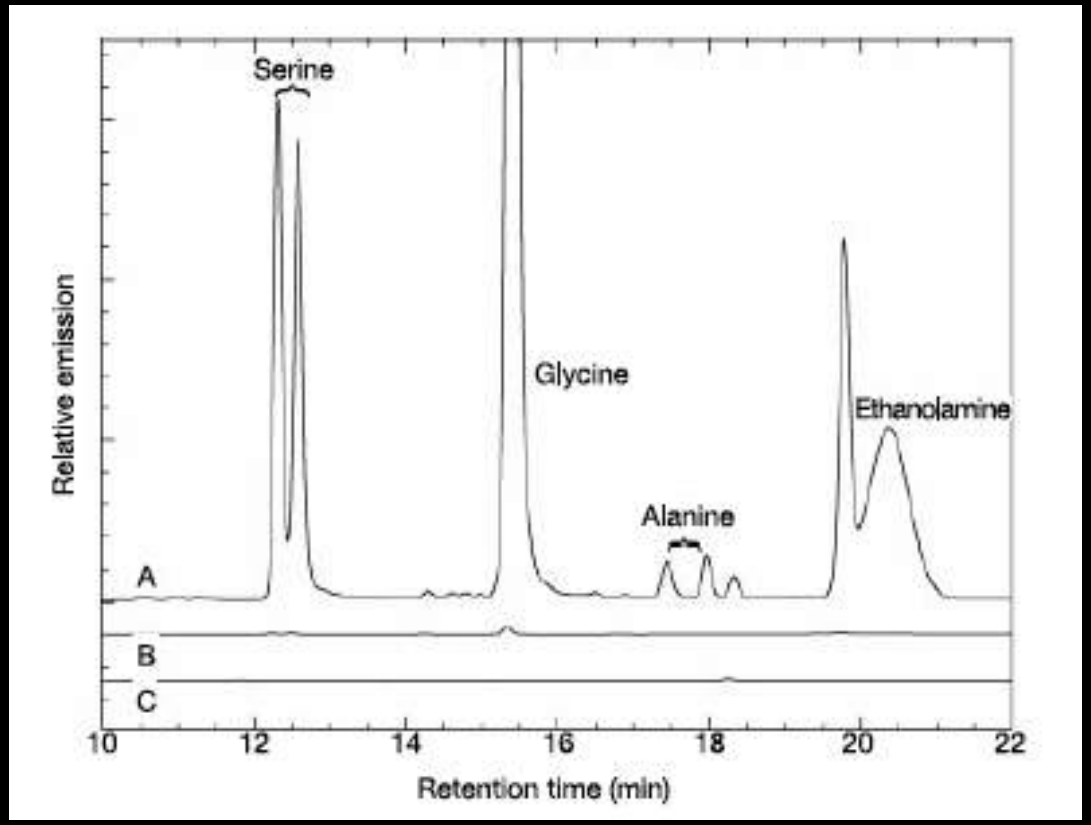
urea

glycine

Potapov et al., 2022, J. Phys. Chem. A, 126, 1627

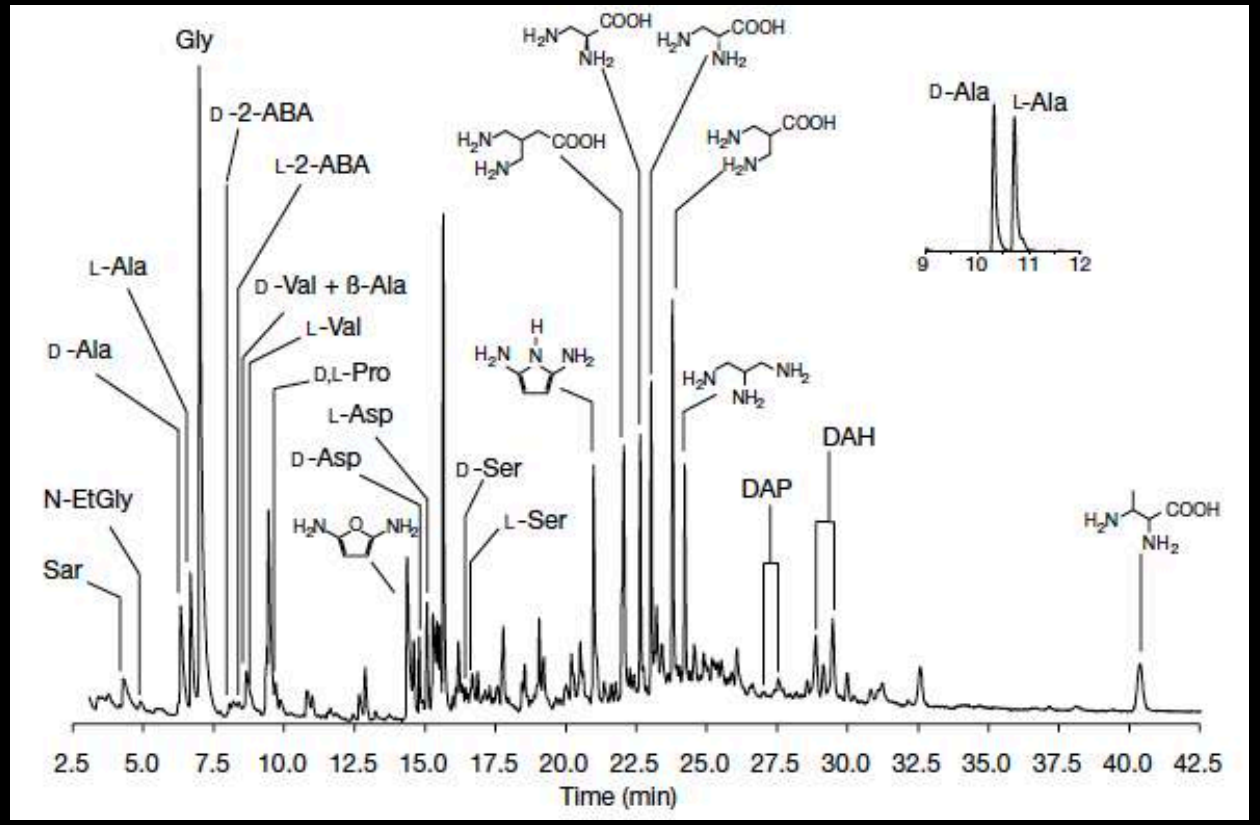
COMs and prebiotic molecules in laboratory analogues of cosmic ices

UV photolysis of an $H_2O:CH_3OH:NH_3:HCN$ ice



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

UV photolysis of an $H_2O:CH_3OH:NH_3:CO:CO_2$ ice



Munoz Caro et al., 2002, Nature, 416, 403

COMs and prebiotic molecules in laboratory analogues of cosmic ices

Species	*H_2O:Pyrimidine*[a]	*NH_3:Pyrimidine*[b]	*H_2O:NH_3:Pyrimidine*[b]
Pyrimidine	L[c]	L[*]	L[*]
2,2'-Bipyrimidine	L[*],G[*]		L[*],G[*]
1,4,5,6-Tetrahydropyrimidine		G[c,d]	G
2-Hydroxypyrimidine	G[f]		G[*,e]
4(3*H*)-Pyrimidone	L[*],G[*]	L[*,g],G[*,g]	L[*],G[*]
Pyrimidine *N*-oxide	L[*,f]		L[d]
Uracil	G[*]	G[c,g]	G[*]
4,6-Dihydroxypirimidine	G[e,f]	G[c,g]	G[e]
Barbituric acid	G[e,f]		G[d]
Isobarbituric acid			G[d,e]
2-Aminopyrimidine			G[*]
4-Aminopyrimidine		L[*],G[*]	L[*],G[*]
2,4-Diaminopyrimidine			G
4,5-Diaminopyrimidine		L,G[c,d,e]	G
2,4,6-Triaminopyrimidine			
Cytosine		G[c,d,e,g]	G[*]
Isocytosine			G
5-Aminouracil			G
6-Aminouracil			G[c,e]
2-Amino-4,6-dihydroxypyrimidine			
2,4-Diamino-6-hydroxypyrimidine			
2-Pyrimidinecarbonitrile			
Orotic acid			
2-Amino-5-nitropyrimidine			
5-Nitrouracil			
Pyridine			
Purine			
Hydantoin	G[e,f]	G[c,d,e,g]	G[*]
Urea	G[f]	G[*,g]	G[*]
Glycine	G[f]	G[c,g]	G[*]
Alanine	G[c,e,f]		G[c,d,e]
Serine			
N-Formylglycine	G[e,f]		G

UV photolysis of H_2O:NH_3:pyrimidine ice mixtures

Nuevo et al., 2012, Astrobiology, 12, 295

COMs and prebiotic molecules in laboratory analogues of cosmic ices

C + CO + NH_3 at 10 K + heat

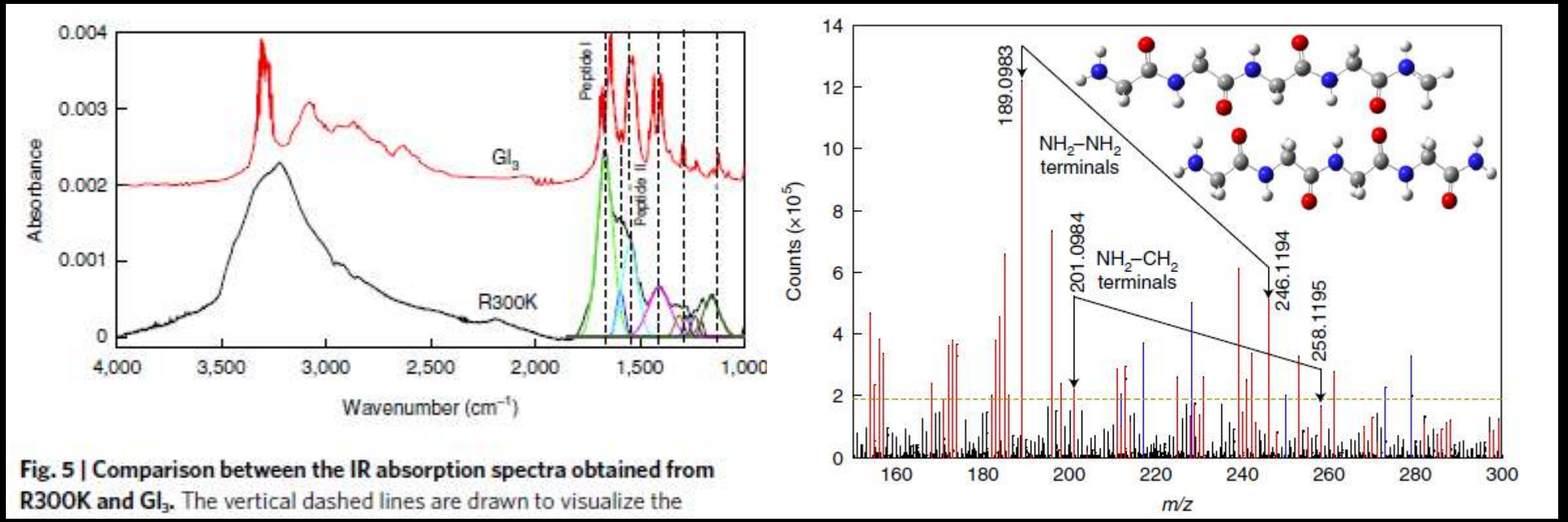
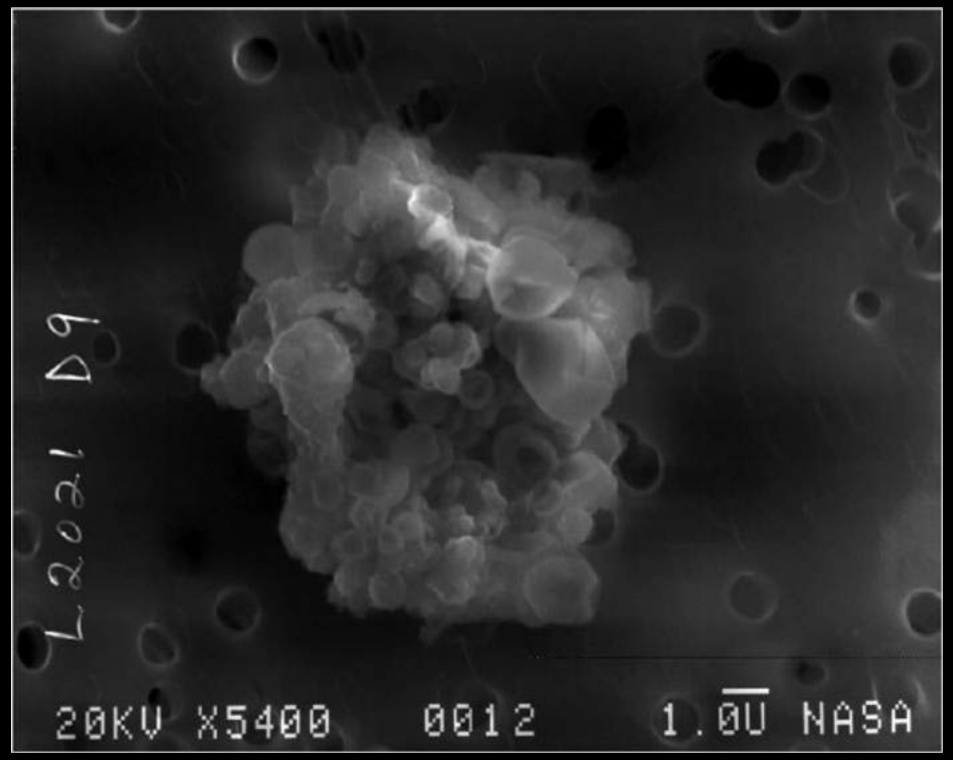


Fig. 5 | Comparison between the IR absorption spectra obtained from R300K and GI_3. The vertical dashed lines are drawn to visualize the

series of mass peaks, which are separated by the same mass of about 57.0215 amu ($NH_2CH=C=O$ molecule)

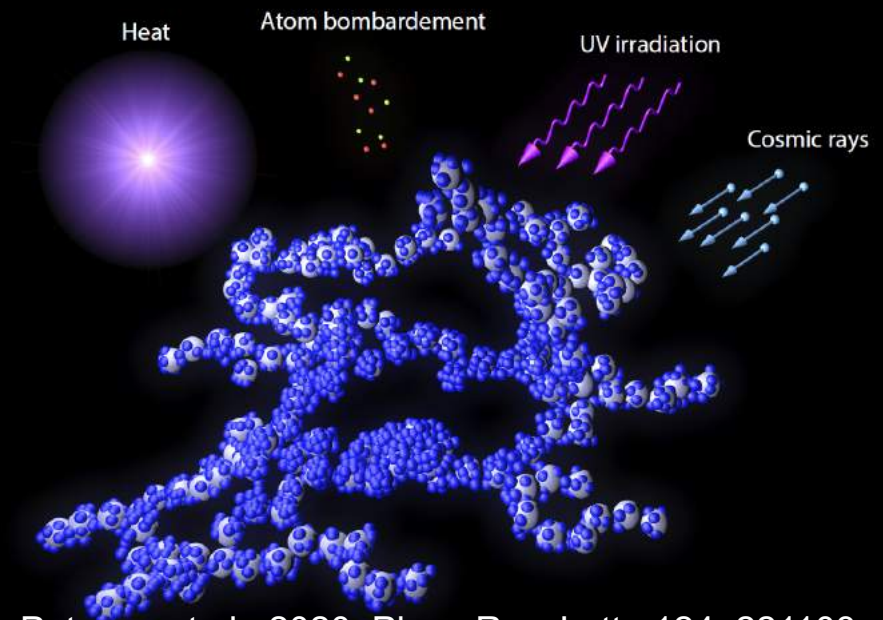
Krasnokutski et al., https://doi.org/10.1038/s41550-021-01577-9

Cosmic dust grains



- Influence the thermodynamic properties of the medium
- Participate in the formation of planets and their atmospheres
- Participate in the delivery of the chemical precursors to life to planets
- Serve as a third body and a catalyst for key chemical reactions

Role of dust grains in the chemistry on their surfaces



Potapov et al., 2020, Phys. Rev. Lett., 124, 221103

Dust grains (gray) mixed with ice molecules (blue) and the main sources of their processing

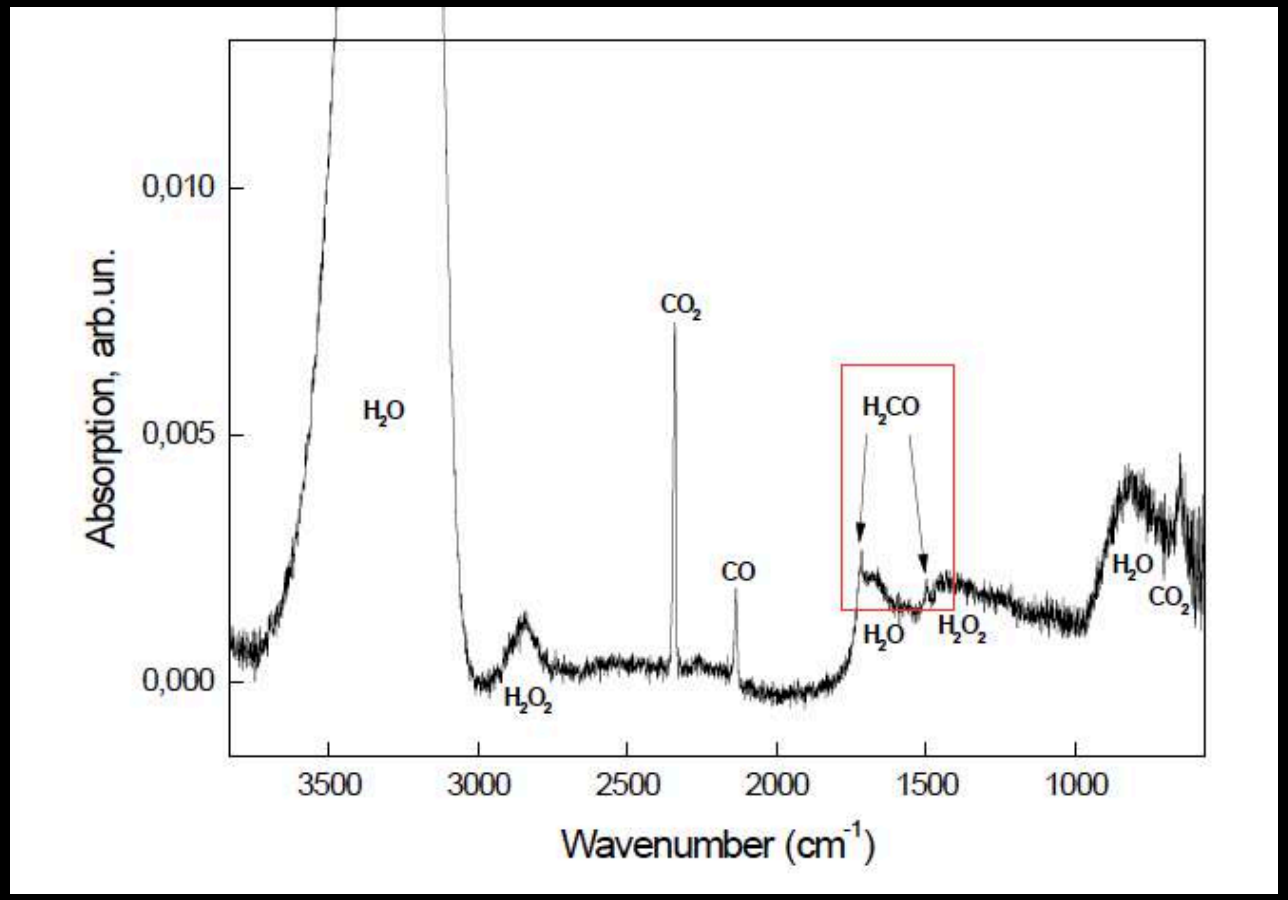
Meeting place for reactants

Dissipation of energy excess released in bond formation (third body)

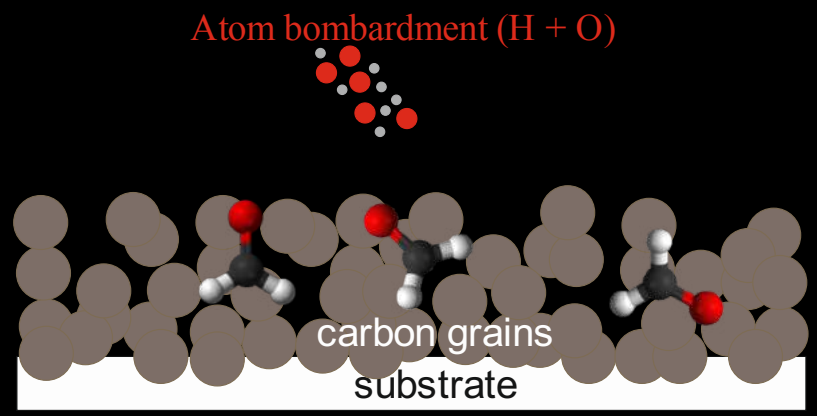
Direct participation (by atoms or functional groups) in surface reactions

Catalytic formation of molecules on dust surfaces

Direct participation of dust



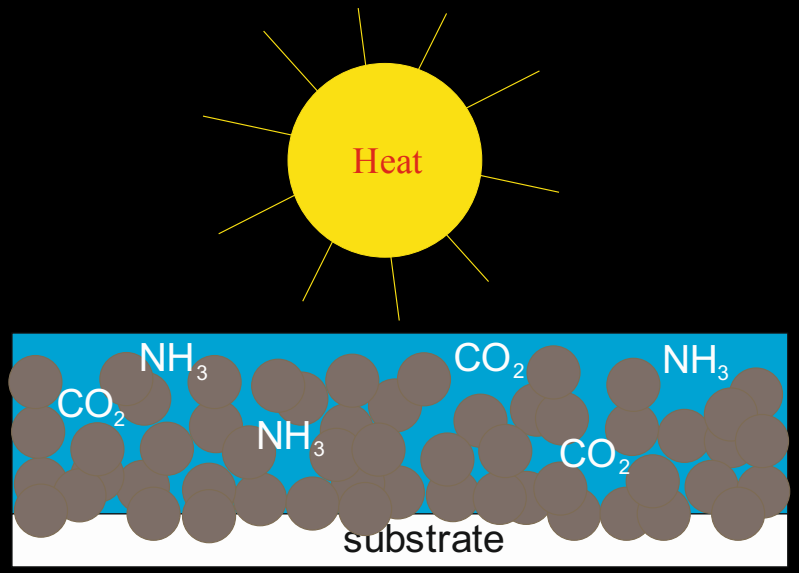
Difference IR spectrum before and after O/H bombardment of carbon grains



A new route of COM formation: <u>grain surface processes</u>

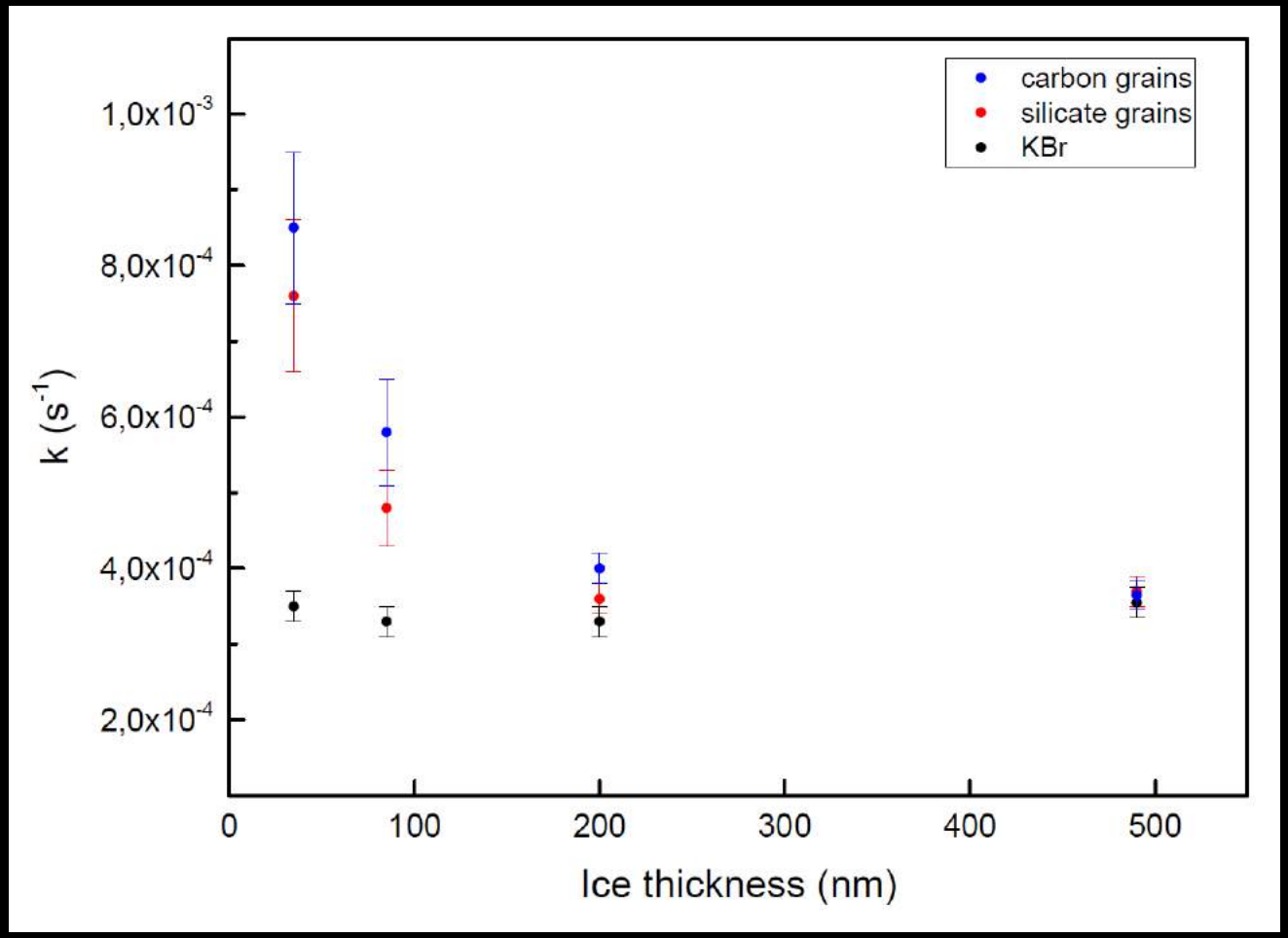
Potapov et al., ApJ, 2017, 846, 131

Catalytic effect of dust surfaces



$CO_2 + 2NH_3 \rightarrow NH_4^+NH_2COO^-$

Reduction of the reaction barrier on the dust surface

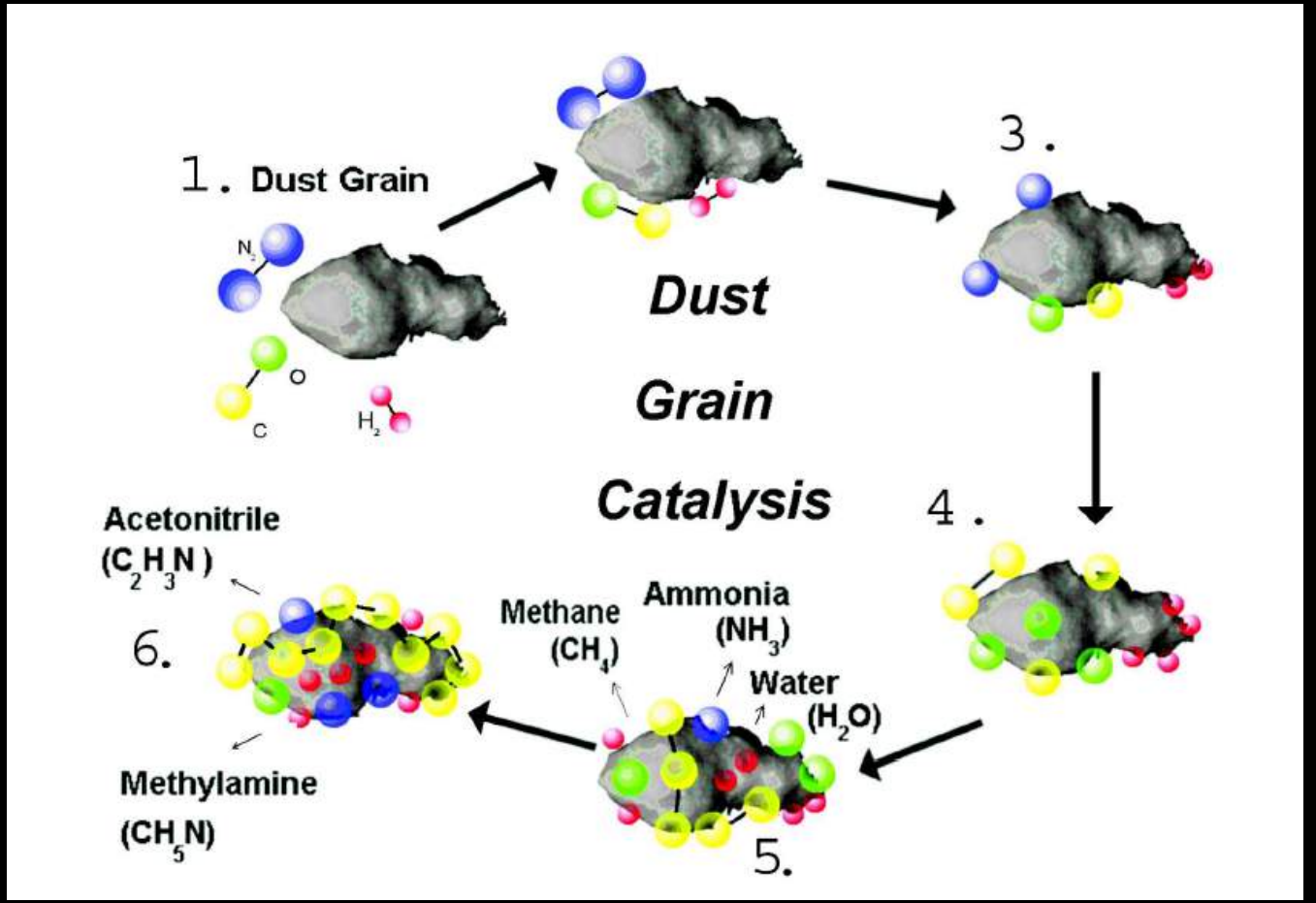


Reaction rate coefficients for various surfaces

Potapov et al., 2019, ApJ Lett., 878, L20

Catalytic formation of COMs. Exoplanets

Fischer–Tropsch and Haber–Bosch synthesis at 500 – 900 K

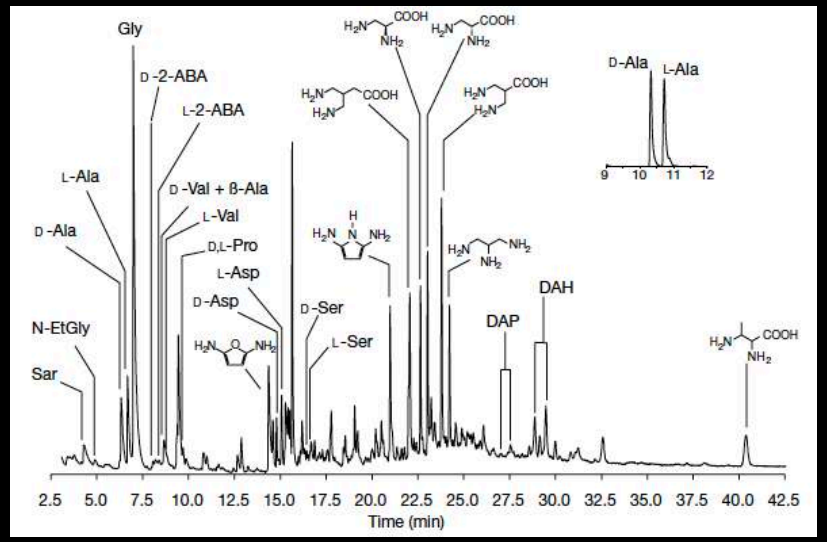


A simplified representation of the possible reaction steps on or near the catalytic surface (Hill & Nuth 2003)

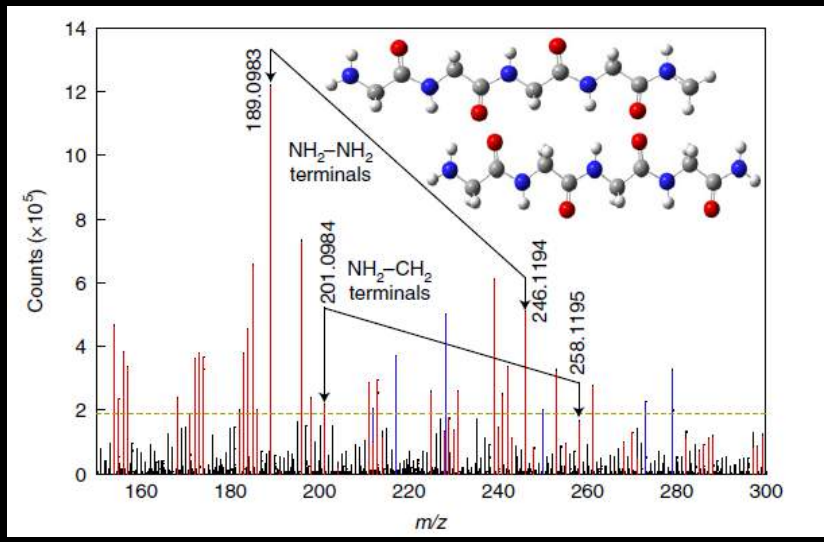
Our laboratory future

Ex situ analysis: GC-MS, HPLC-MS

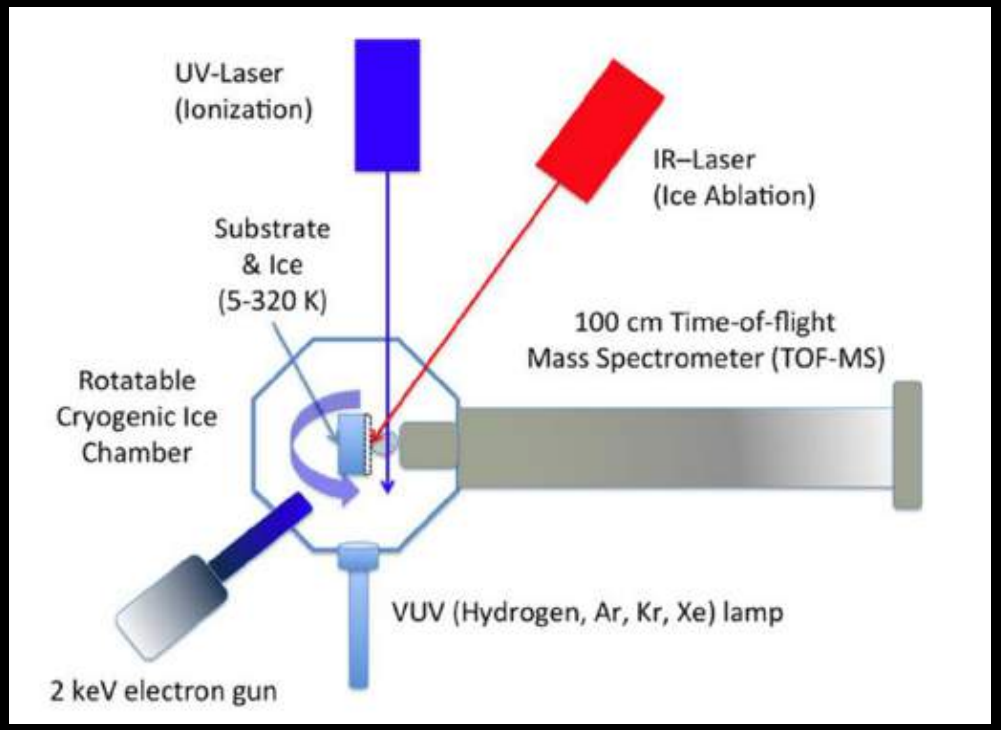
<u>Problem:</u> the direct link to astrochemical processes of interest taking place under low temperature and pressure conditions is lost.



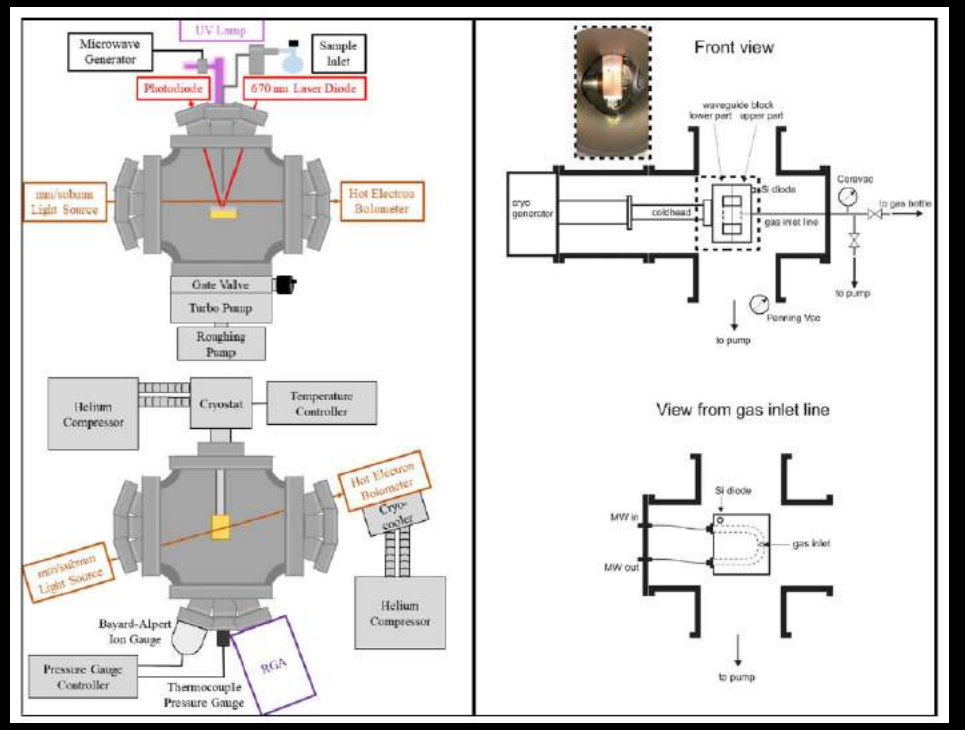
Species	*H_2O:Pyrimidine*[a]	*NH_3:Pyrimidine*[b]	*H_2O:NH_3:Pyrimidine*[b]
Pyrimidine	L[c]	L*	L*
2,2'-Bipyrimidine	L*,G*		L*,G*
1,4,5,6-Tetrahydropyrimidine		G[c,d]	G
2-Hydroxypyrimidine	G[f]		G*,e
4(3*H*)-Pyrimidone	L*,G*	L*,g,G*,g	L*,G*
Pyrimidine *N*-oxide	L*,f		L*,d
Uracil	G*	G[c,g]	G*
4,6-Dihydroxypirimidine	G*,f	G[c,g]	G*
Barbituric acid	G*,f		G*,d
Isobarbituric acid			G*,e
2-Aminopyrimidine			G*
4-Aminopyrimidine		L*,G*	L*,G*
2,4-Diaminopyrimidine			G
4,5-Diaminopyrimidine		L,G[c,d,e]	G
2,4,6-Triaminopyrimidine			
Cytosine		G[c,d,e,g]	G*
Isocytosine			G
5-Aminouracil			G
6-Aminouracil			G*,e
2-Amino-4,6-dihydroxypyrimidine			
2,4-Diamino-6-hydroxypyrimidine			
2-Pyrimidinecarbonitrile			
Orotic acid			
2-Amino-5-nitropyrimidine			
5-Nitrouracil			
Pyridine			
Purine			
Hydantoin	G*,f	G[c,d,e,g]	G*
Urea	G[f]	G*,g	G*
Glycine	G[f]	G[c,g]	G*
Alanine	G[c,e,f]		G[c,d,e]
Serine			
N-Formylglycine	G*,f		G



Our laboratory future



Gudipati and Yang, 2012, Astrophys. J. Lett., 756, L24



Yocum et al., 2019, J. Phys. Chem. A, 123, 8702
Theule, …, Potapov, 2020, ACS Earth Space Chem., 4, 86

Matrix Assisted Laser Desorption Ionization
+ high-resolution mass spectrometry

High-resolution gas-phase spectroscopy
+ surface desorption

Summary

1) Many precursors of prebiotic molecules have been detected in astrophysical environments

2) Amino acids, sugars, nucleobases have been detected in comets and meteorites

3) Results of laboratory experiments and models mimicking physico-chemical processes in astrophysical environments show that the generation of prebiotic species is possible

The role of water

<u>The liquid phase facilitates chemical reactions</u>
- in a liquid reactants move freely
- liquid accumulates reactants

<u>The universal solvent</u>
- as a polar molecule, water interacts best with other polar molecules allowing for the formation of bonds
- capability to dissolve molecules providing building blocks



<u>Chemical reactions</u>
- water molecules are involved in chemical reactions
- water is an efficient catalyst of chemical reactions

<u>Support of the cellular structure</u>
- water fills cells to help maintain their shape and structure
- water contributes to the formation of membranes surrounding cells

Origin of water on Earth and terrestrial planets

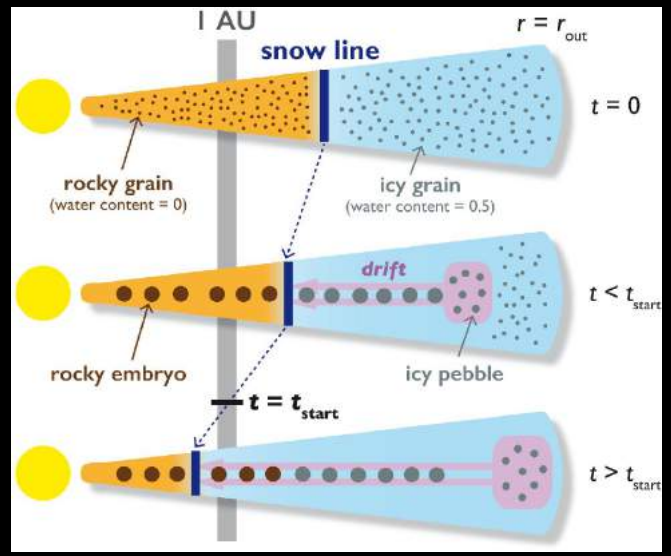
Dry scenario

delivery by water-rich asteroids and comets

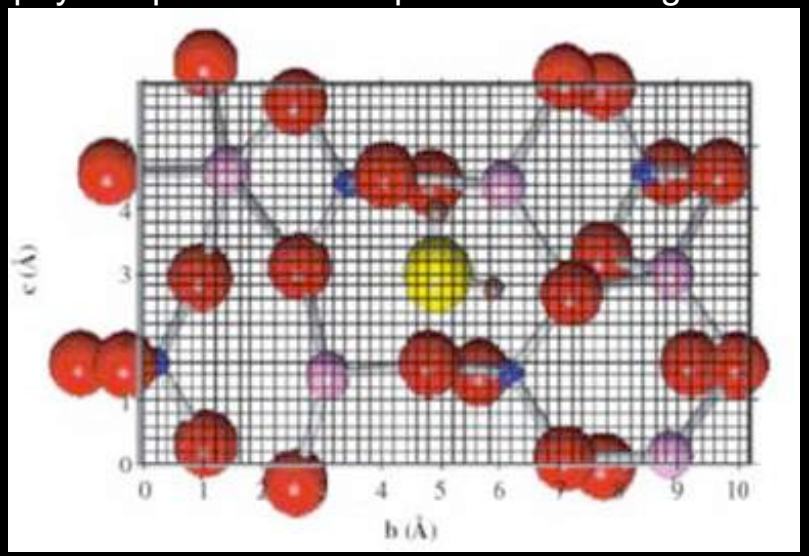


Wet scenario

time-variable location of the snowline



physisorption/chemisorption on silicate grains



Wet scenario. Water inside the snowline in disks
Gas phase

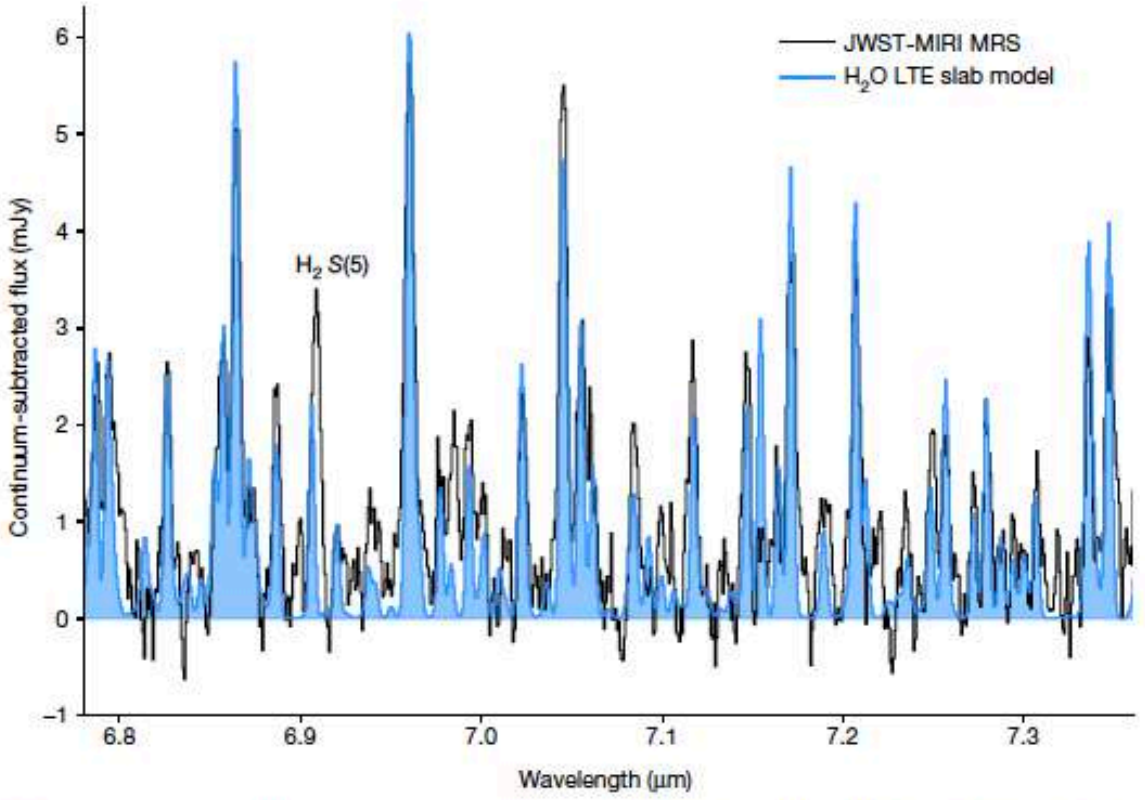
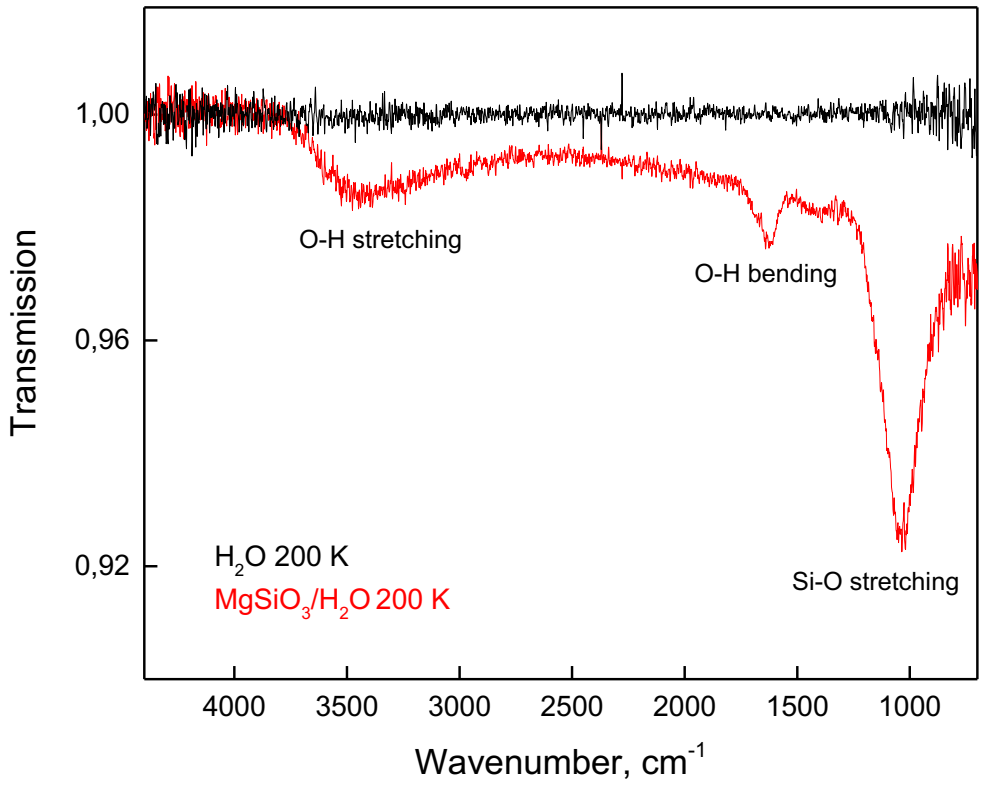
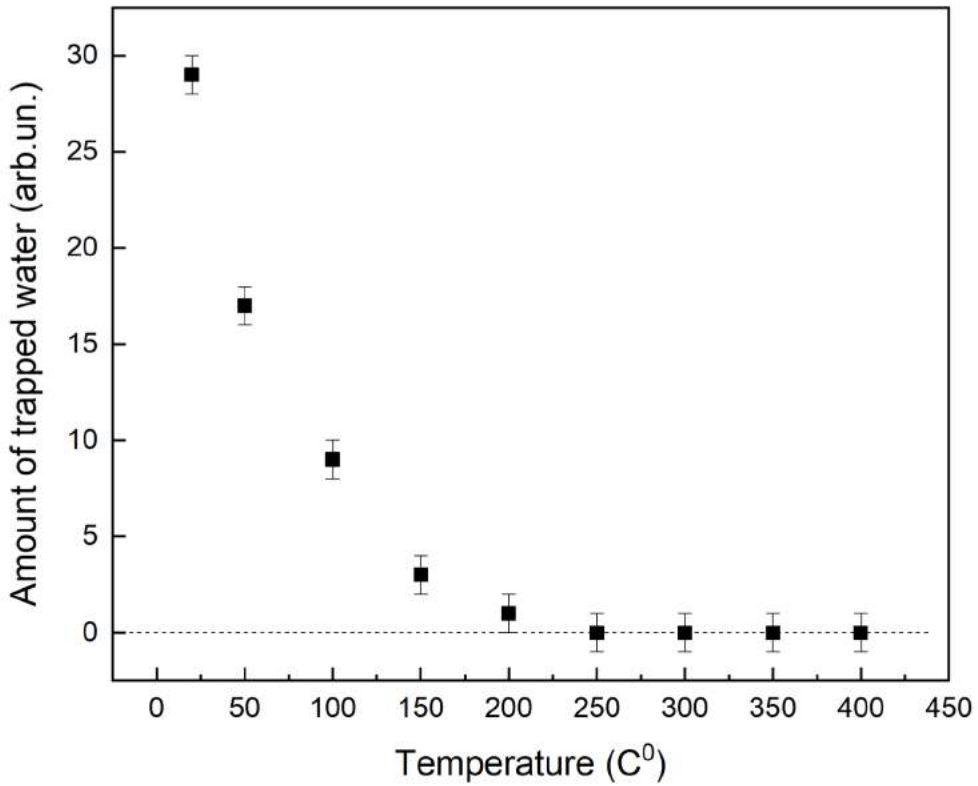


Fig. 3 | Continuum-subtracted spectrum showing H_2O emission in the 7 μm region and the best-fit LTE slab model. The best-fit model (blue) has $T = 600$ K, $N(H_2O) = 1.4 \times 10^{18}$ cm^{-2} and $R = 0.047$ AU. The molecular hydrogen H_2 S(5) line is labelled on top of the spectrum.

Perotti et al., 2023, https://doi.org/10.1038/s41586-023-06317-9

Wet scenario. Water inside the snowline in disks
Solid state





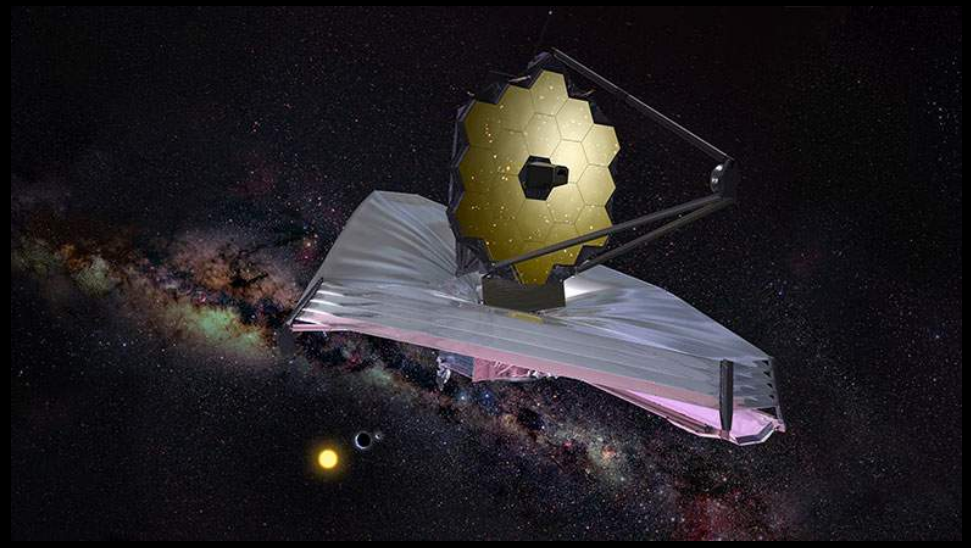
Potapov et al., ApJ, accepted, https://arxiv.org/abs/2402.13600

New data

Solid-state water inside the snowline in planet-forming disks:
exploring the origin of water on terrestrial planets

PI: Alexey Potapov

JWST Cycle 1 observations (2 disks, 14 hours)



Origin of life on Earth

Big challenges:

- We may never be able to determine the exact conditions on the early Earth
- We may reach the detection limit for exploring the molecular complexity in space
- We do not have any example of life outside Earth. No statistics

However:

- We have to try to overcome challenges
- New ideas and instiments promice a lot of exciting findings