IV ASTRO BION
Fourth Astrobiology School at Observatório Nacional

Astrochemistry of the small bodies of the Solar System

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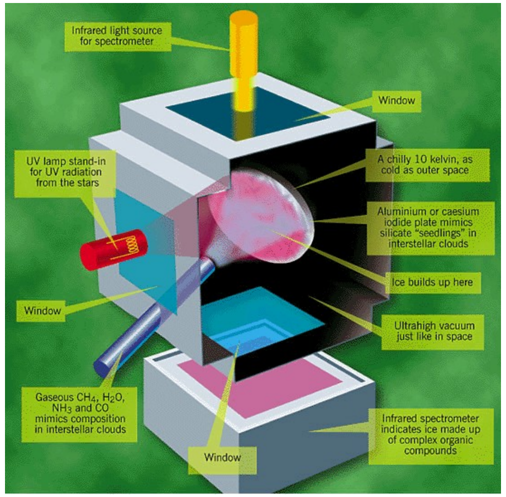

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Connaissance - Action

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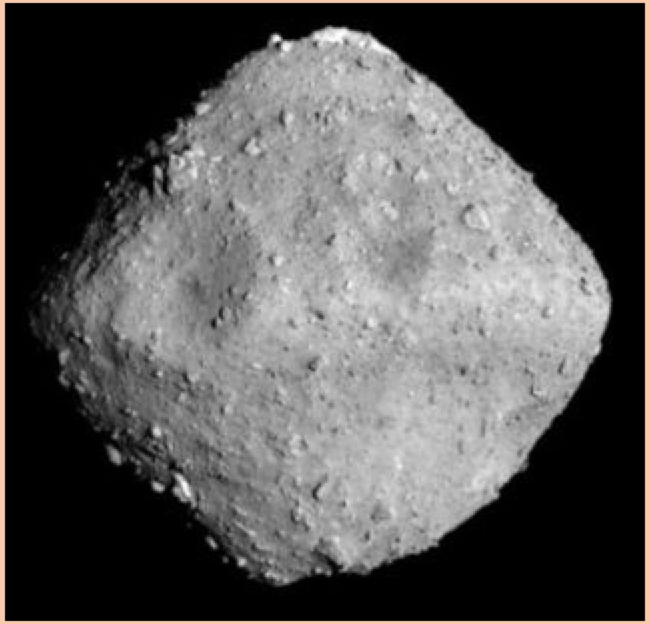
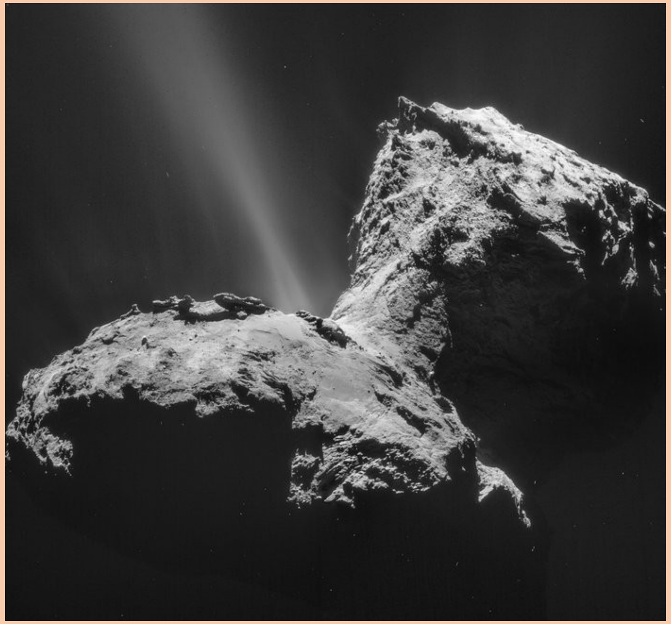
Small bodies

The sky's archives

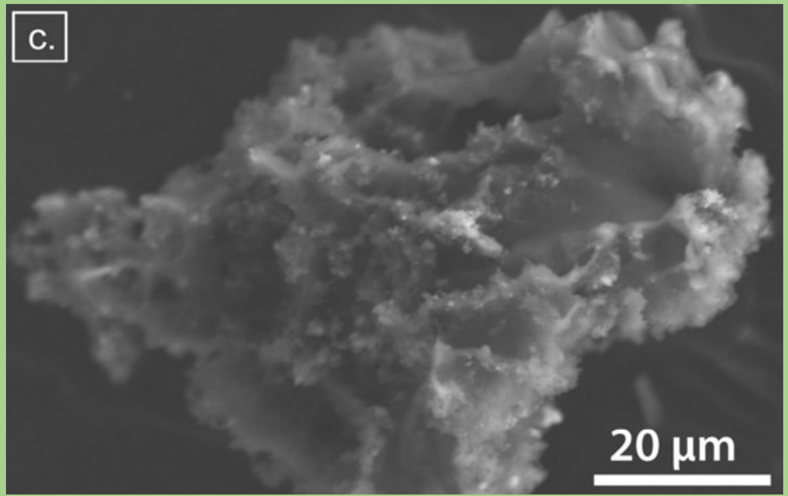


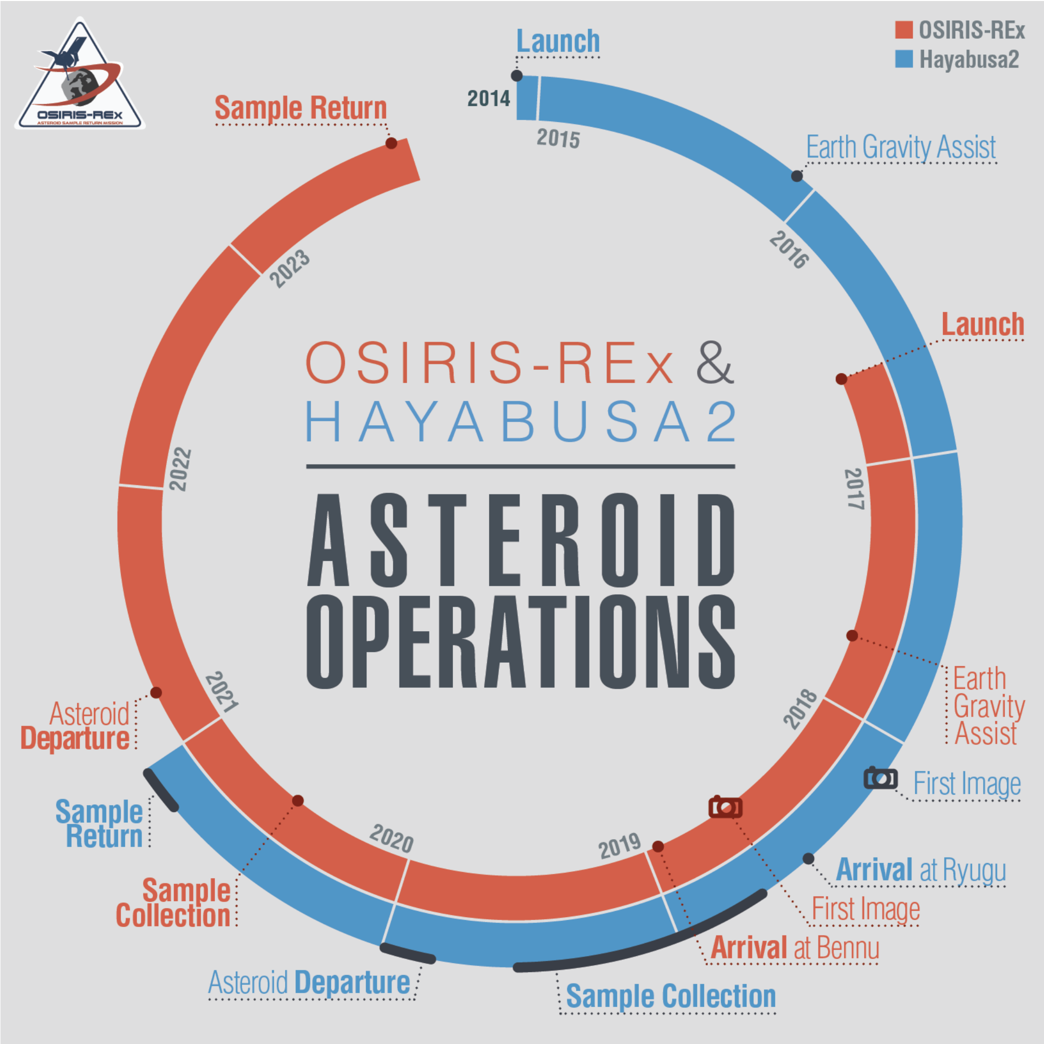


Meteorites
&
Micrometeorites

Asteroids & Comets

Trojans, centaurs, active asteroids, extinct comets, Kuiper belt and Oort clouds objects…

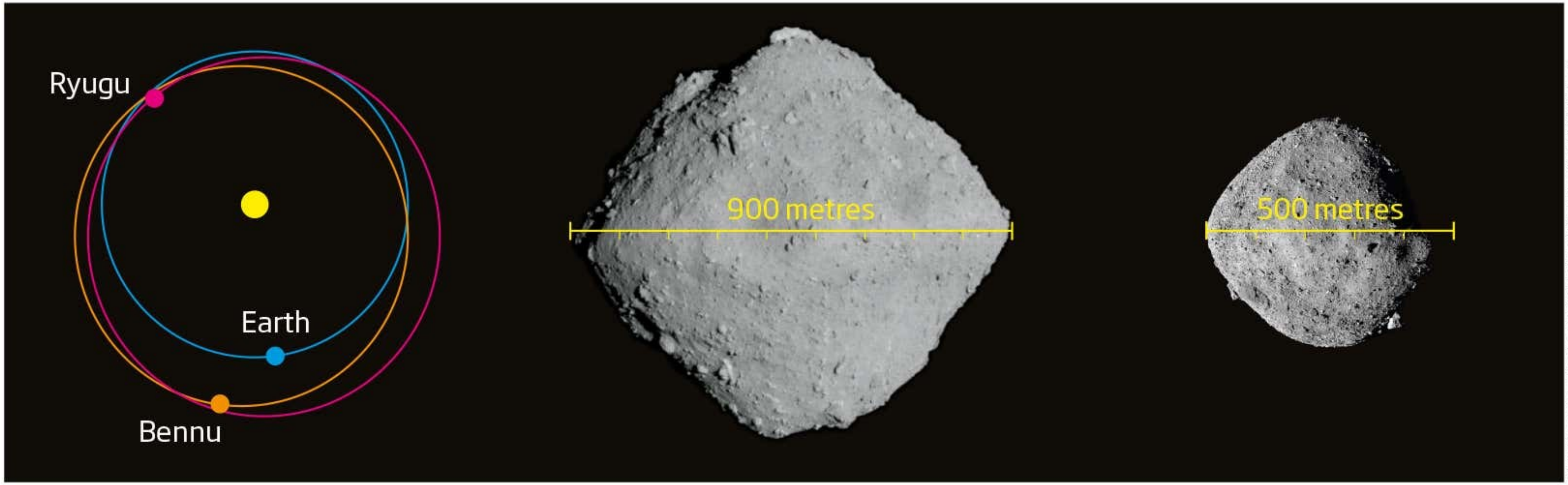




OSIRIS-REx & HAYABUSA2
ASTEROID OPERATIONS
OSIRIS-REx
Hayabusa2
OSIRIS-REx
ASTEROID SAMPLE RETURN MISSION
Launch
2014
2015
Earth Gravity Assist
2016
Launch
2017
Earth Gravity Assist
2018
First Image
Arrival at Ryugu
First Image
Arrival at Bennu
2019
Sample Collection
Asteroid Departure
2020
Sample Collection
Sample Return
Asteroid Departure
2021
2022
2023
Sample Return

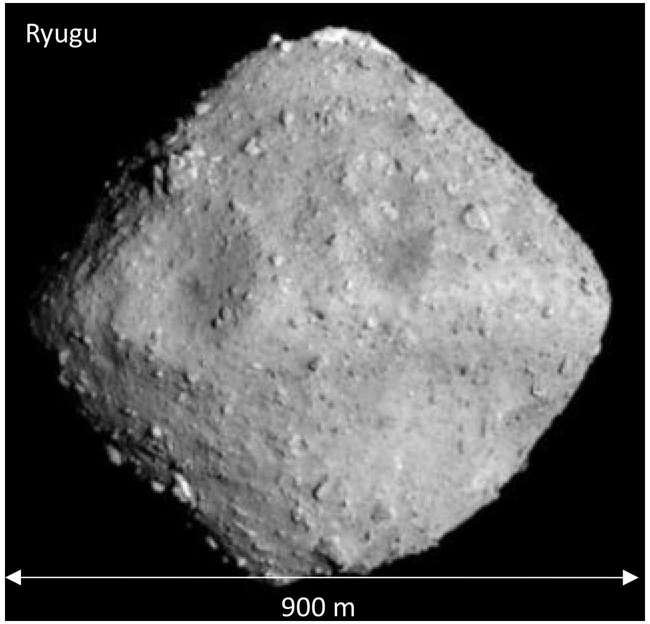
Rock collection

Ryugu and Bennu look surprisingly similar, but there are key differences



SOURCE LEFT TO RIGHT: UNIVERSITY OF ARIZONA/JAXA/NASA

	Ryugu	Bennu
Type	C-type: lots of carbon and a dark surface	B-type: bluer in colour, possibly due to more silicates and clays
Water	None detected	Water locked in molecular structure of minerals
Brightness	Mostly uniform	Light and dark spots



Video created from images captured with Hayabusa2's CAM-H at intervals between 0.5s and 5s
The first image was taken at an altitude of about 8.5m and the last is from an altitude of about 150m.
Playback speed: 10x

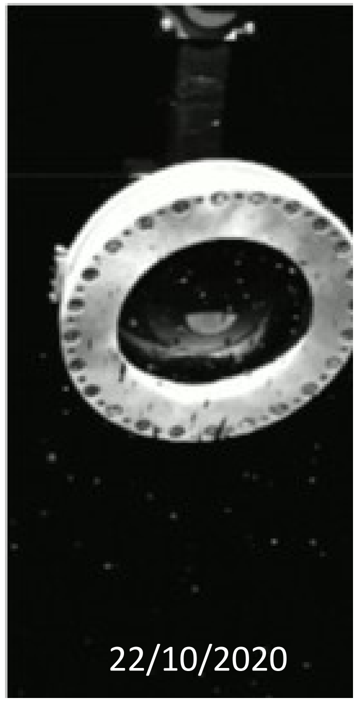
December 2014 : Launch

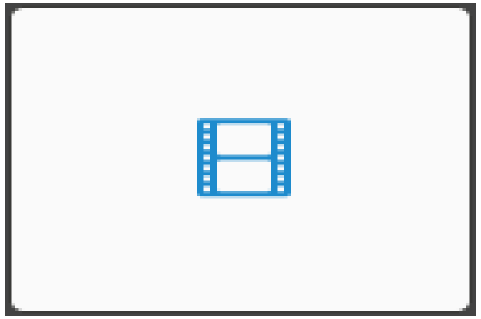
27 June 2018 : Orbit insertion at Ryugu

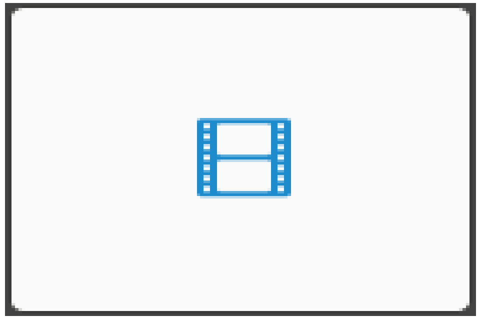
February & July 2019 : sample collection

December 2019 – December 2020 : Sample return

December 2020 : Landing
=> **5.4 g collected**





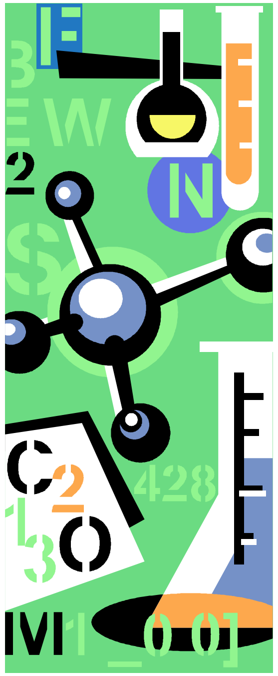


Sample return : Sept. 24th 2023

Organic matter in meteorites

Meteorites
~10 tons / year

Micrometeorites
~10 000 tons / year

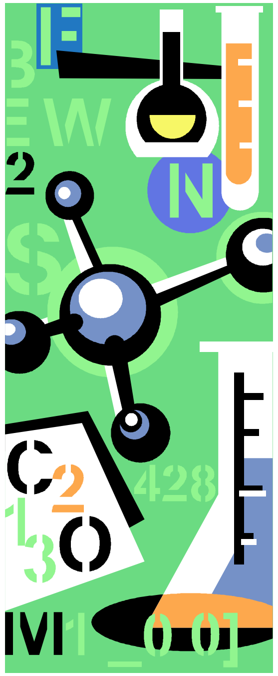


Murchison meteorite

Orgueil meteorite

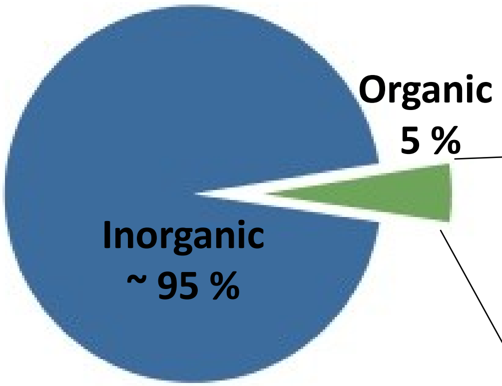
Organic matter in meteorites

Carbonaceous chondrites (CI, CM): up to 3% (mass) of C

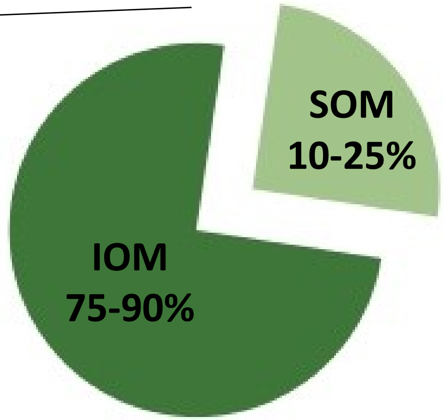


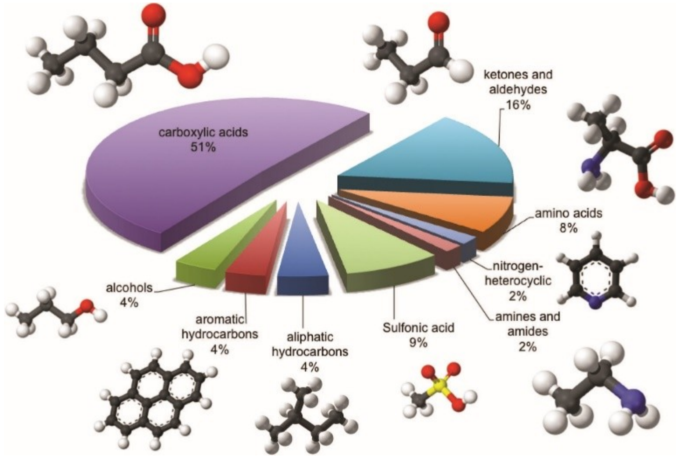
In the Murchison meteorite

More than 92 amino acids (10-100 ppm (w/w)), among them 8 proteogenic: Gly, Ala, Val, Leu, Ile, Pro, Asp, Glu

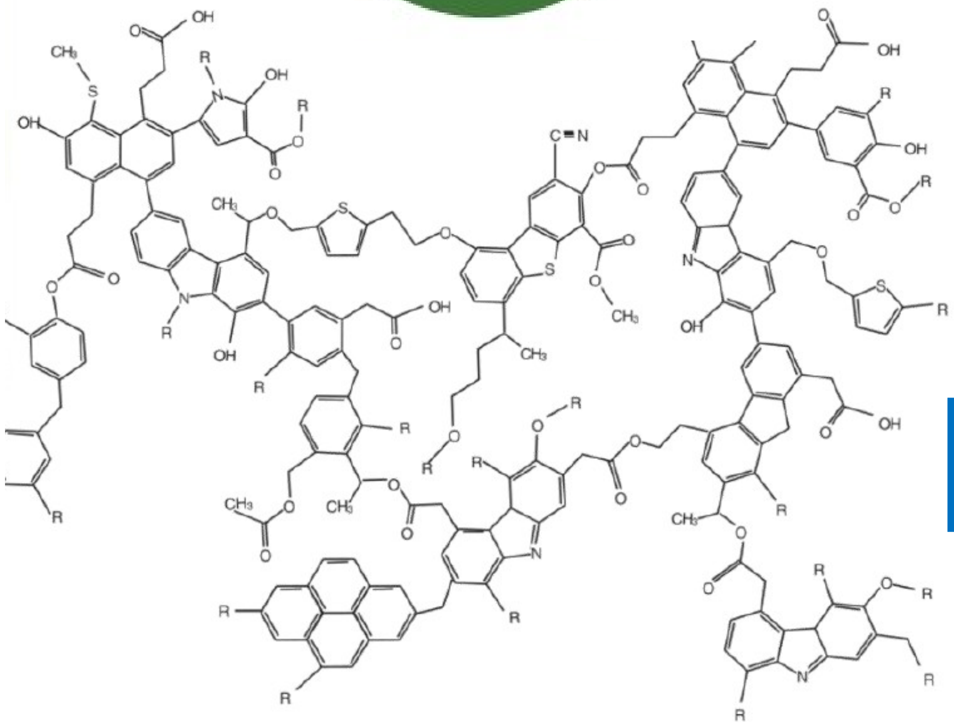


Soluble Organic Matter
SOM





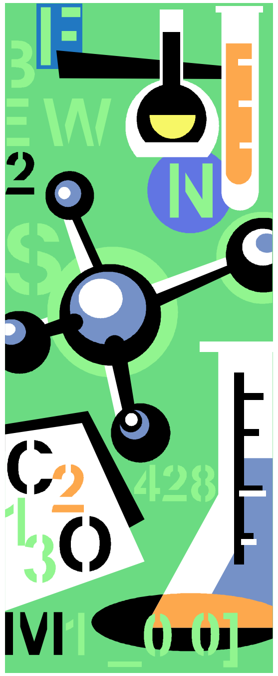
Anatomy of a carbonaceous chondrite

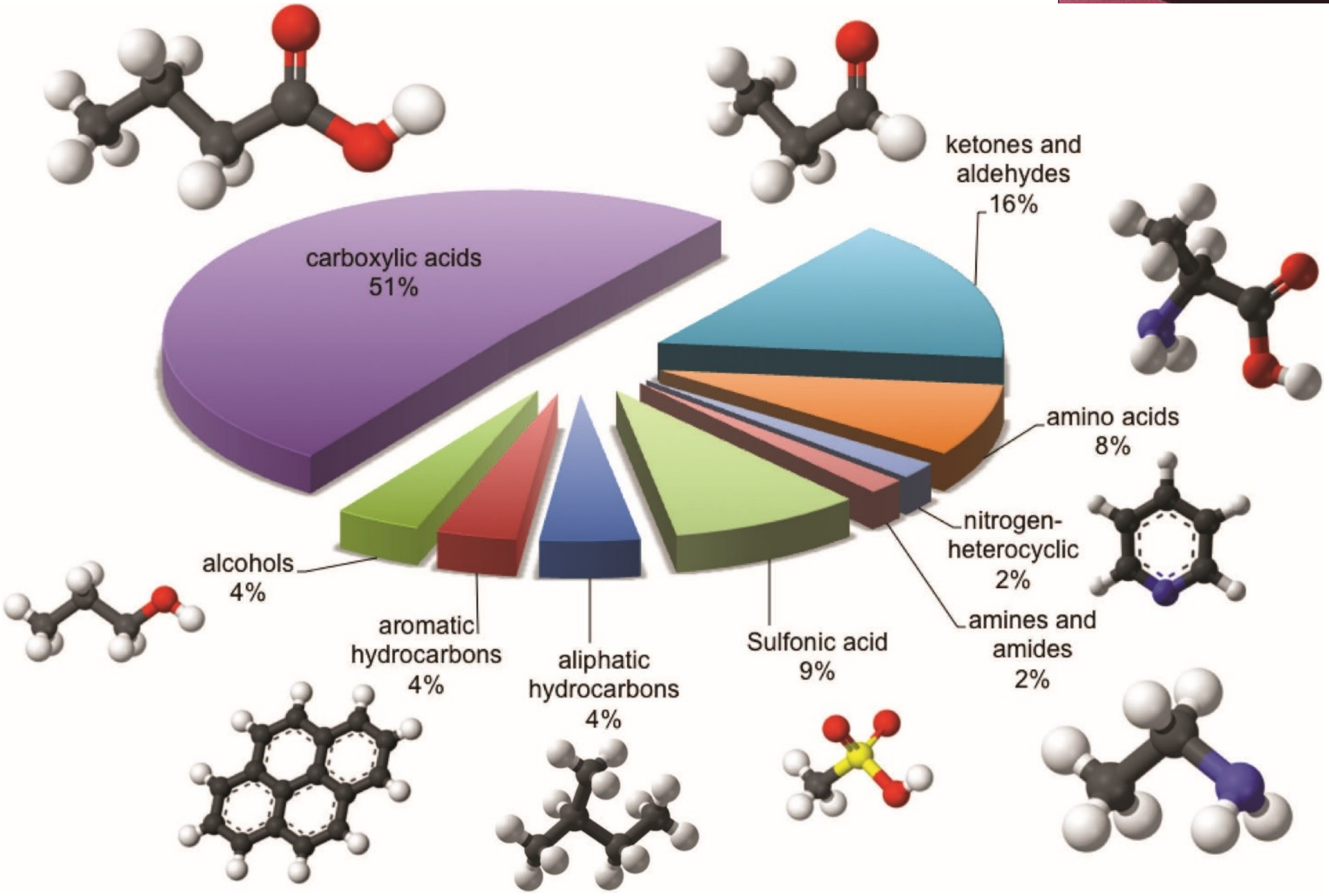


Insoluble Organic Matter (IOM)

From Derenne & Robert, MPS, 2010

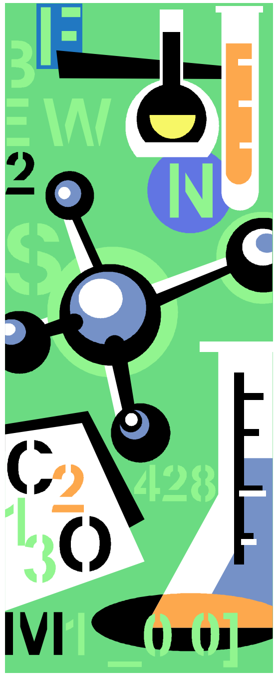
Organic matter in meteorites





Rémusat, 2015

Organic matter in meteorites

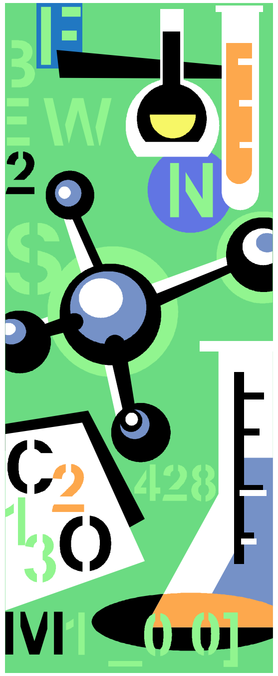


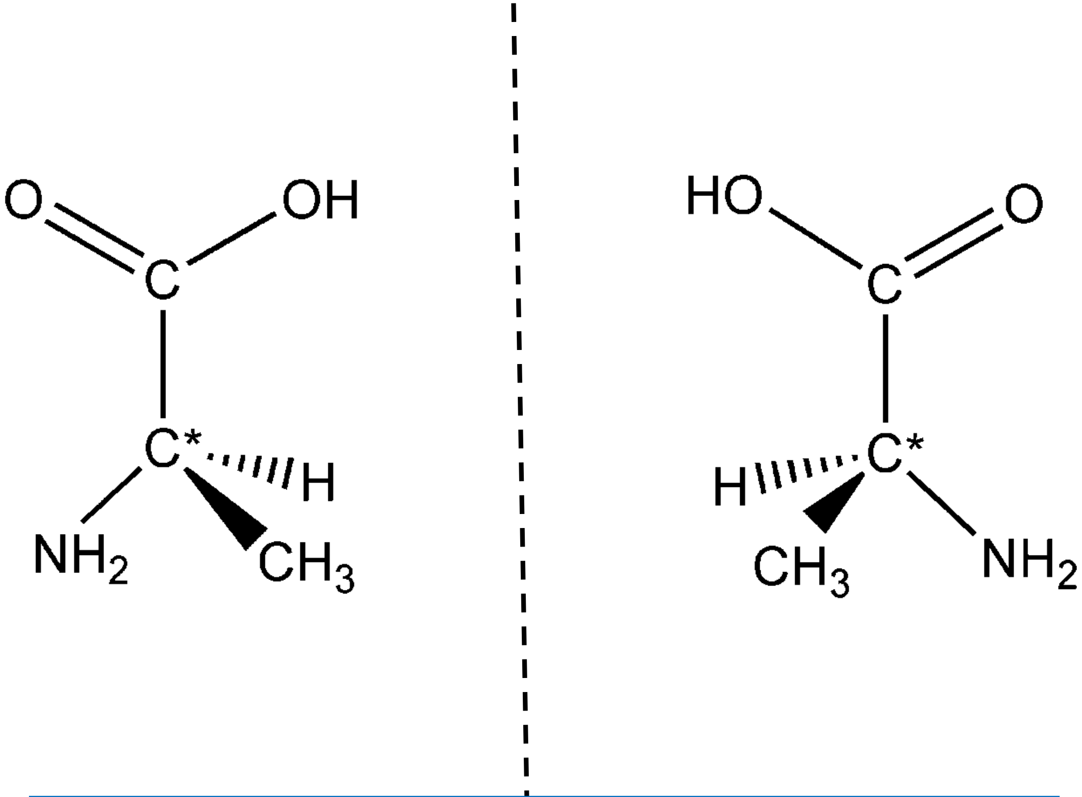
Soluble Fraction

Compounds	Abundance (ppm)
Carboxylic acids (monocarboxylic)	332
Sulphonic acids	67
Amino acids	60
Dicarboximides	> 50
Dicarboxylic acids	> 30
Urea	25
Polyols	24
Ammonia	19
Ketones	17
Hydrocarbons (aromatic)	15–28
Hydroxycarboxylic acids	15
Hydrocarbons (aliphatic)	12–35
Alcohols	11
Aldehydes	11
Amines	8
Pyridine carboxylic acid	> 7
Phosphonic acid	1.5
Purines	1.2
Diamino acids	0.4
Benzothiophenes	0.3
Pyrimidines	0.06
Basic N-heterocycles	0.05–0.5

From Cottin et al. 2017

Chirality

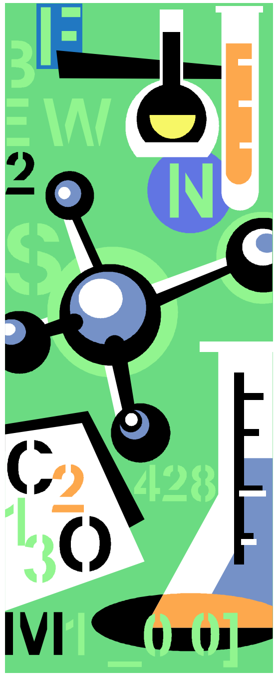


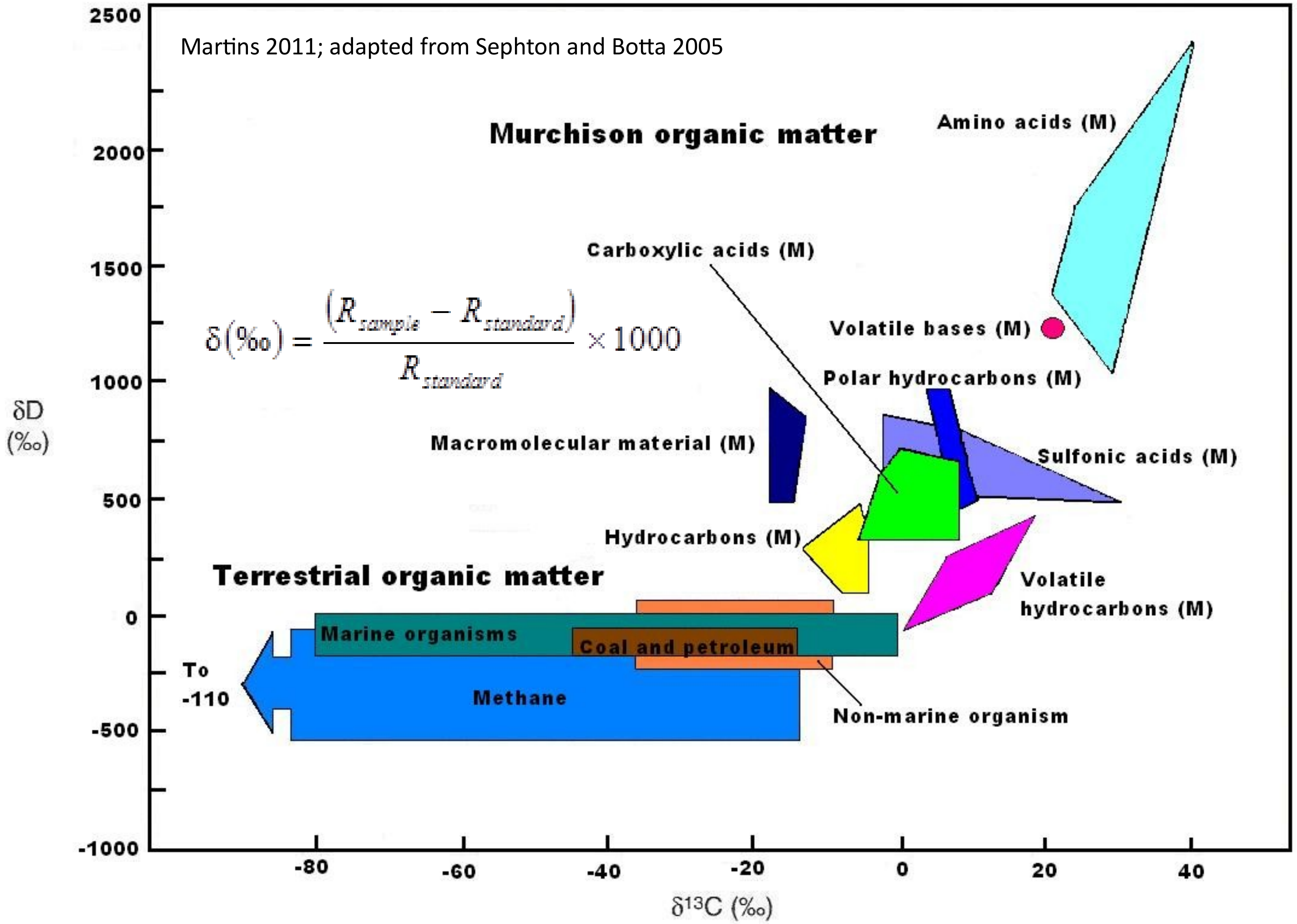


L Isovaline excess (~15%) in Murchison (Pizzarello et al. 2003; Glavin and Dworkin 2009)

Organic matter in meteorites

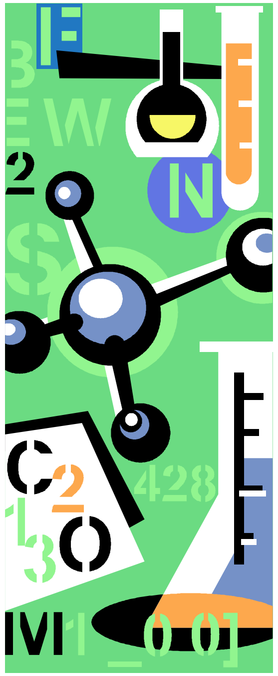
*R : D/^{1}H for hydrogen, $^{13}C/^{12}C$ for C & $^{15}N/^{14}N$ pour N.
Standards : Standard mean ocean water (SMOW) for H, Pee Dee Belemnite (PDB) for C, & air for N

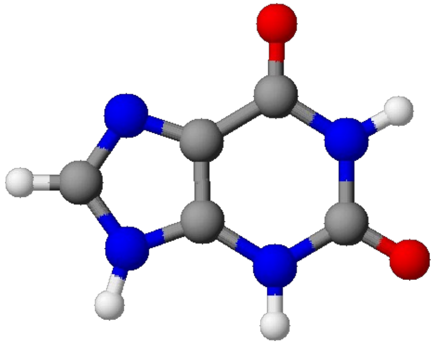


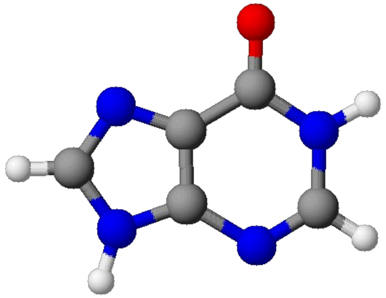


$$\delta(‰) = \frac{(R_{sample} - R_{standard})}{R_{standard}} \times 1000$$

Organic matter in meteorites



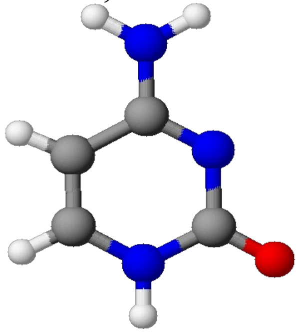




$\delta^{13}C$	Uracil	Xanthine	Thymine
Murchison	+44.5 ± 2.3	+37.7 ± 1.6	n.d.
Contrôle Sol	-10.6 ± 1.8	n.d.	-15.9 ± 1.1

Martins et al. 2008

n.d.- non mesuré, concentration trop faible



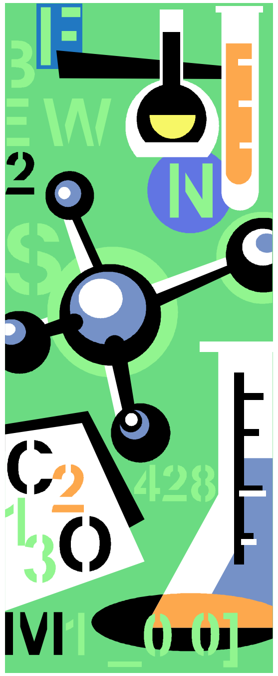
$\delta^{13}C$ (‰) of nucleobases in Murchison meteorite

Organic matter in meteorites

PNAS | February 16, 2010 | vol. 107 | no. 7 | 2763–2768

High molecular diversity of extraterrestrial organic matter in Murchison meteorite revealed 40 years after its fall

Philippe Schmitt-Kopplin[a,1,2], Zelimir Gabelica[b,1], Régis D. Gougeon[c,1], Agnes Fekete[a], Basem Kanawati[a], Mourad Harir[a], Istvan Gebefuegi[a], Gerhard Eckel[d], and Norbert Hertkorn[a,1]



Numerous descriptions of organic molecules present in the Murchison meteorite have improved our understanding of the early interstellar chemistry that operated at or just before the birth of our solar system. However, all molecular analyses were so far targeted toward selected classes of compounds with a particular emphasis on biologically active components in the context of prebiotic chemistry. Here we demonstrate that a nontargeted ultra-high-resolution molecular analysis of the solvent-accessible organic fraction of Murchison extracted under mild conditions allows one to extend its indigenous chemical diversity to tens of thousands of different molecular compositions and likely millions of diverse structures. This molecular complexity, which provides hints on heteroatoms chronological assembly, suggests that the extraterrestrial chemodiversity is high compared to terrestrial relevant biological- and biogeochemical-driven chemical space.

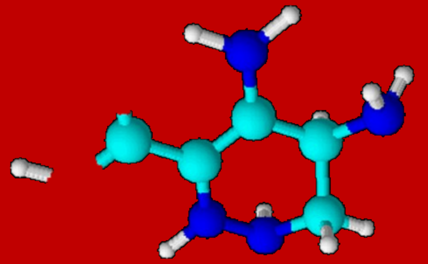
Organic matter in meteorites

^{1}H : 1.007825032 u

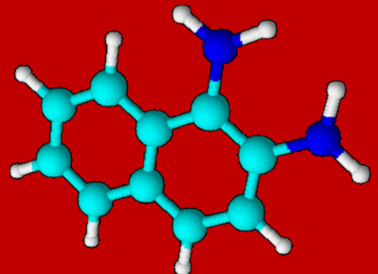
^{12}C : 12.00000000 u

^{14}N : 14.00307401 u

^{16}O : 15.99491462 u

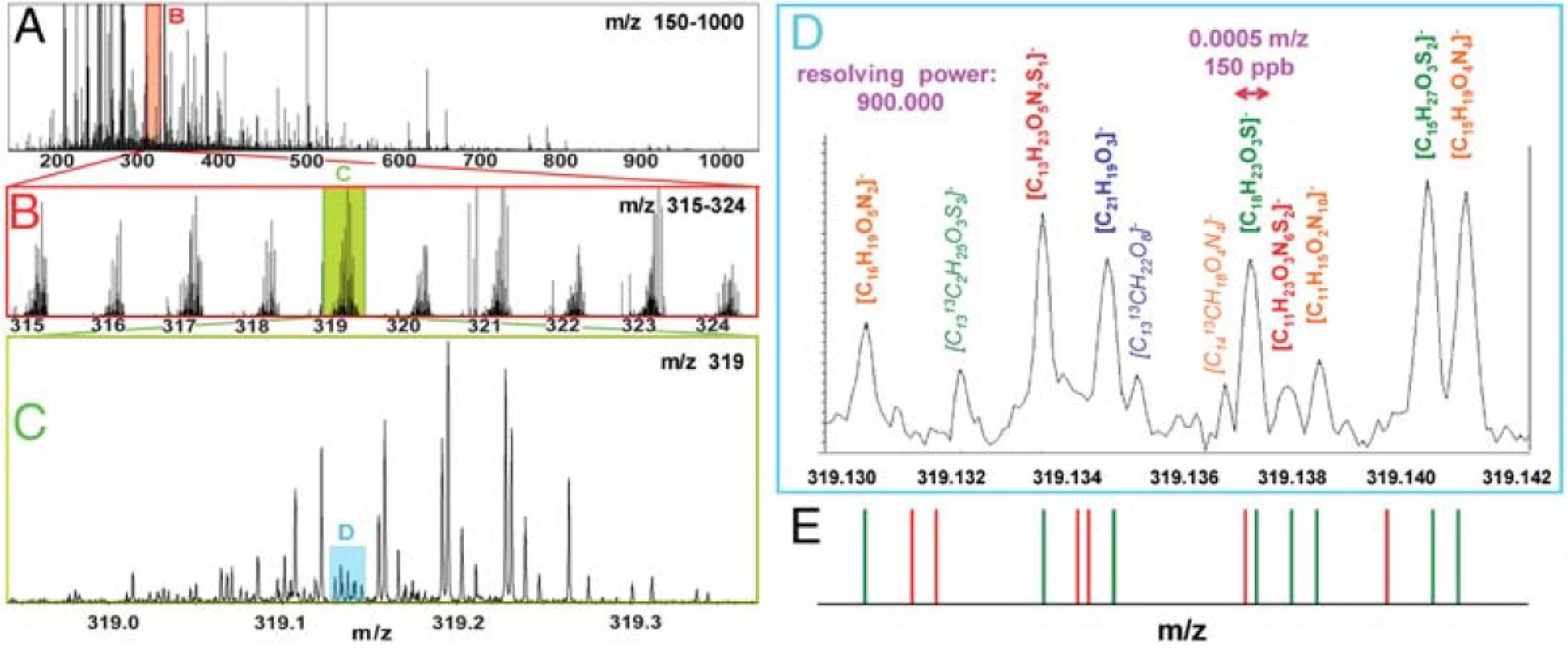


$C_5H_{10}N_4O_2$: 158.080376 u

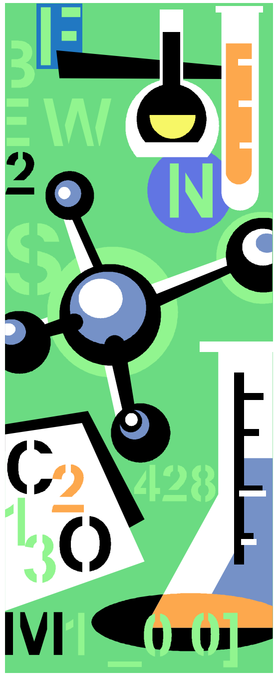


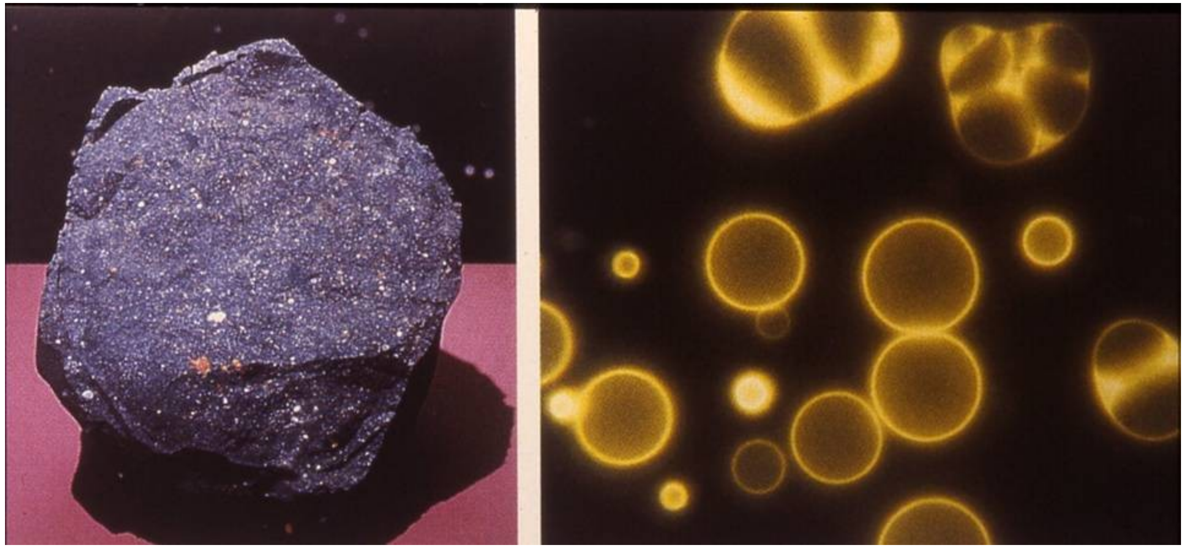
$C_{10}H_{10}N_2$: 158.084398 u

$\Delta m/m$ = 25.44 ppm, <u>required resolution : $2m/\Delta m$ ~ 80000</u>



Organic matter in meteorites





Spontaneous formation of vesicles from the meteoritic IOM

Cite as: T. Yokoyama *et al.*, *Science*
10.1126/science.abn7850 (2022).

Samples returned from the asteroid Ryugu are similar to Ivuna-type carbonaceous meteorites

Carbonaceous meteorites are thought to be fragments of C-type (carbonaceous) asteroids. Samples of the C-type asteroid (162173) Ryugu were retrieved by the Hayabusa2 spacecraft. We measure the mineralogy, bulk chemical and isotopic compositions of Ryugu samples. They are mainly composed of materials similar to carbonaceous chondrite meteorites, particularly the CI (Ivuna-type) group. The samples consist predominantly of minerals formed in aqueous fluid on a parent planetesimal. The primary minerals were altered by fluids at a temperature of 37 ± 10°C, $5.2^{+0.7}_{-0.8}$ (Stat.) $^{+1.6}_{-2.1}$ (Syst.) million years after formation of the first solids in the Solar System. After aqueous alteration, the Ryugu samples were likely never heated above ~100°C. The samples have a chemical composition that more closely resembles the Sun's photosphere than other natural samples do.

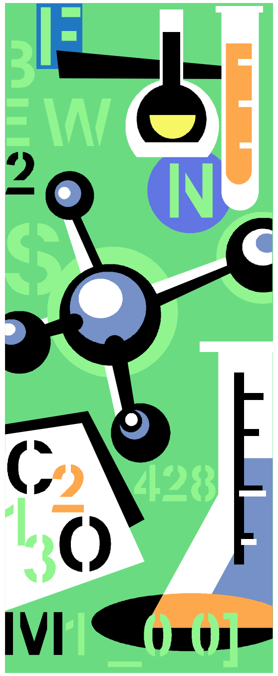
Organic/inorganic fractions for hydrogen and carbon

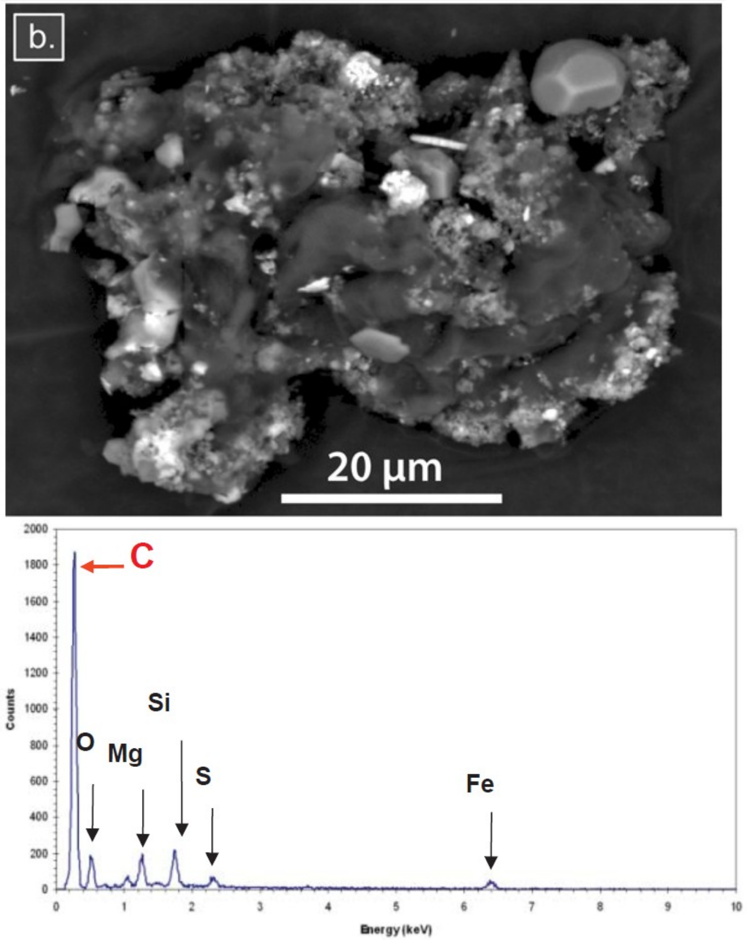
We performed an EMIA-Step analyses of the Ryugu and Ivuna samples (*12*). For Ivuna, this showed the total carbon concentration is 3.31 ± 0.33 wt.% (*12*), of which 90% is organic carbon (Fig. 7 and data S6). The total hydrogen in Ivuna is 1.59 ± 0.08 wt.%, of which 89% is inorganic hydrogen. All these values are consistent with previous measurements of the same meteorite (*44*). The total H_2O for Ivuna is 12.73 ± 0.63 wt.%, distributed as 6.58 ± 0.32 wt.% interlayer H_2O and 6.15 ± 0.30 wt.% as structural-OH or H_2O in the phyllosilicate minerals.

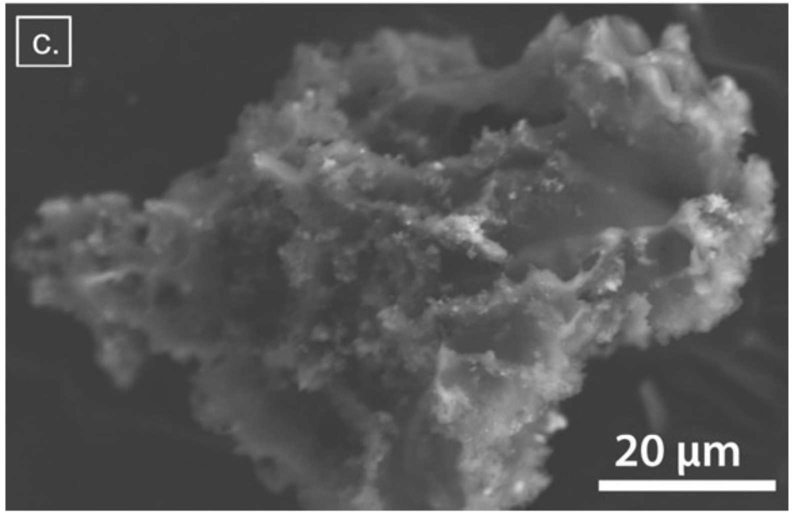
The Ryugu samples contains less H_2O than Ivuna. The total H_2O is 6.84 ± 0.34 wt.%, including 0.30 ± 0.01 wt.% interlayer H_2O and 6.54 ± 0.32 wt.% structural-OH or H_2O (data S6). The structural value is similar to Ivuna, but the interlayer water is substantially lower. The total hydrogen is 0.94 ± 0.05 wt.% for Ryugu, and the inorganic hydrogen (i.e., H_2O) comprises 81% of the total hydrogen. The amount of organic carbon in Ryugu is 3.08 ± 0.30 wt.%, indistinguishable from that in Ivuna (2.97 ± 0.29 wt.%) (Fig. 7 and data S6). This implies the inorganic/organic matter ratio is similar in the Ryugu and the Ivuna samples studied, excluding a previous proposal that Ryugu's low albedo is due to higher organic carbon contents than CI chondrites (*45*). However, the total carbon is higher in Ryugu (4.63 ± 0.23 wt.%) than in Ivuna, due to the higher abundances of carbonates in the Ryugu samples.

Organic matter in meteorites

UCAMMs
Ultra Carbonaceous Antarctic MicroMeteorites

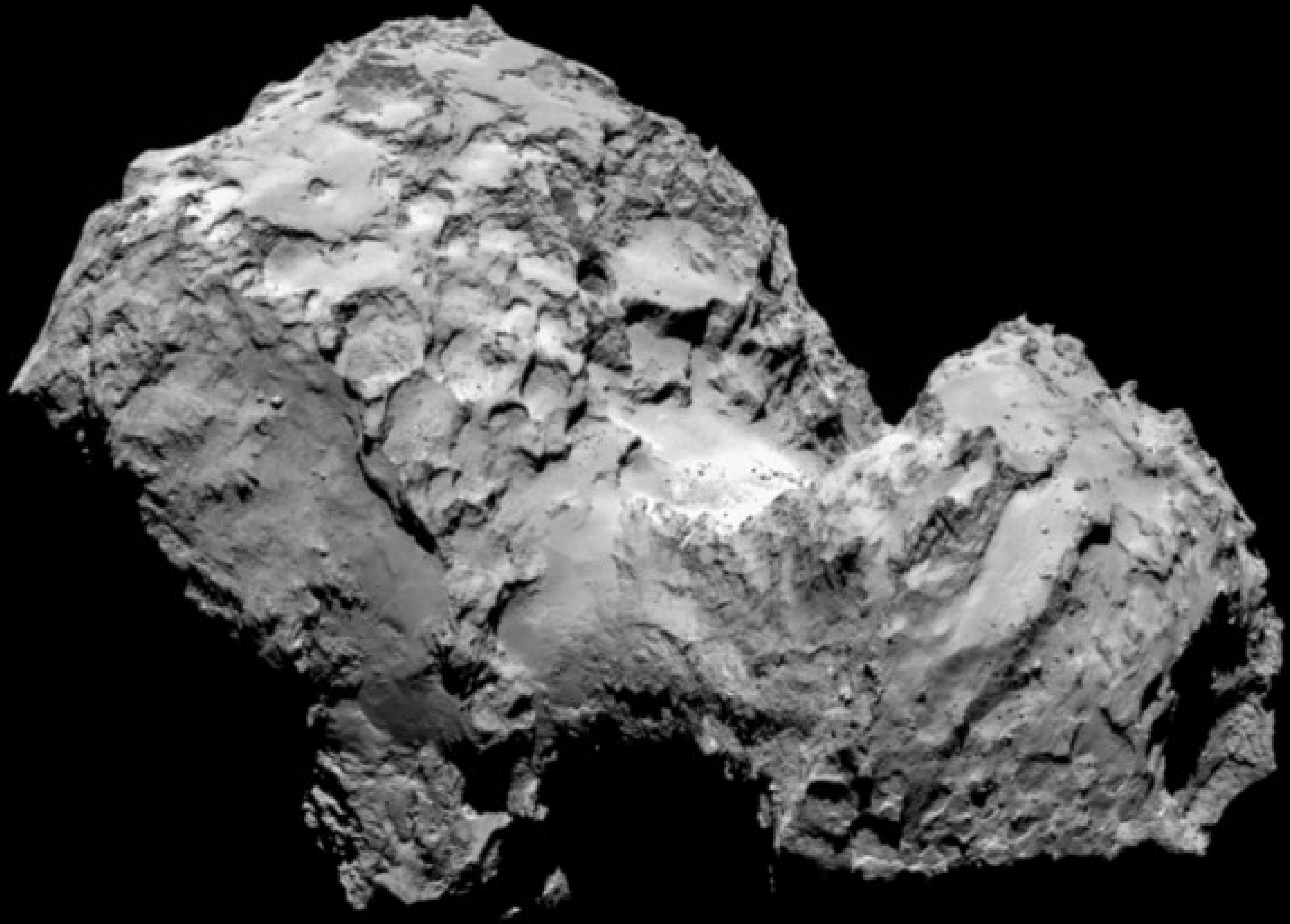






Duprat et al., 2010
Dobrica et al. 2012
Dartois et al. 2013

More than 50 % of C
High content in N



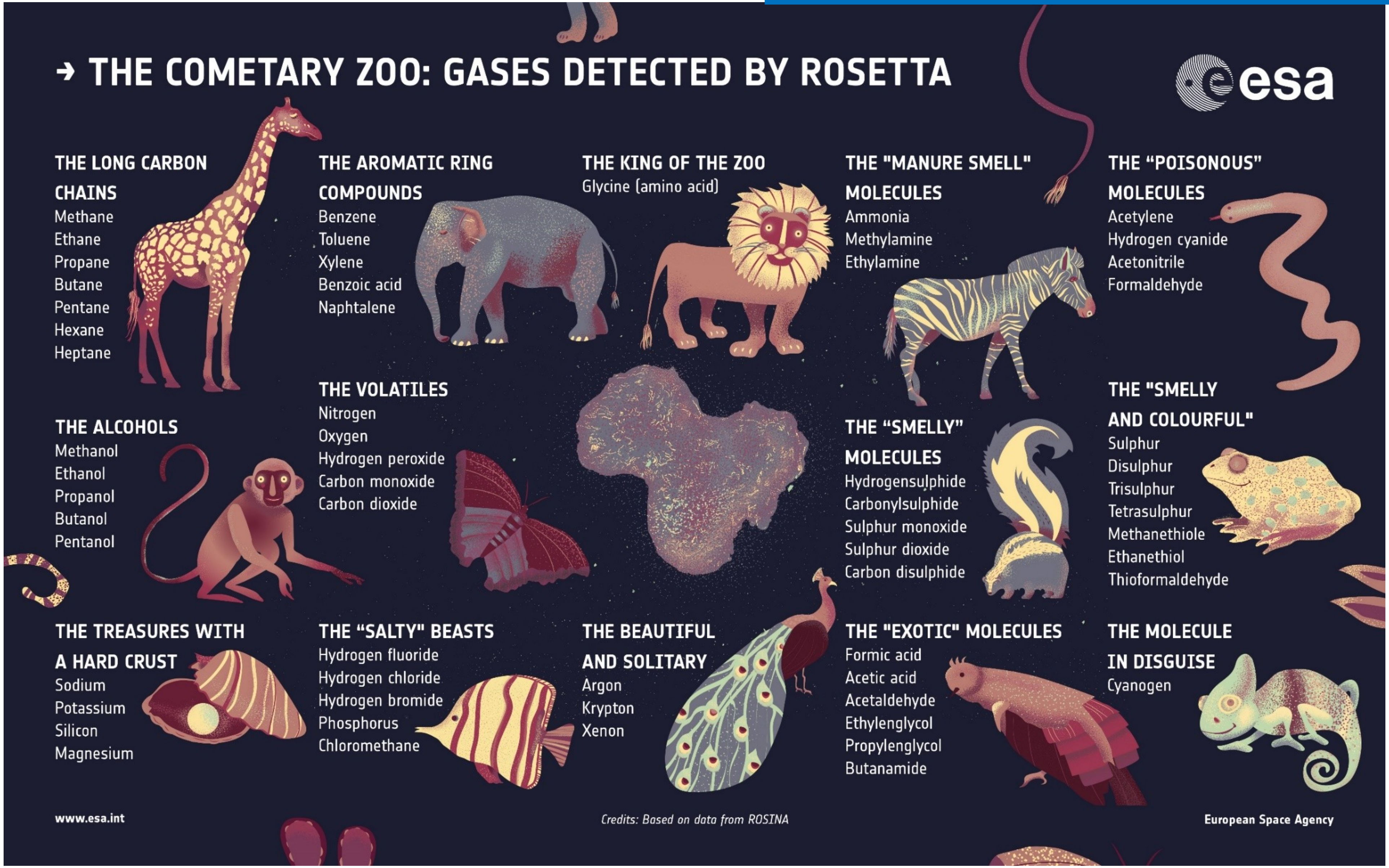
August 3rd 2014 – 285 km away from comet 67P/Churyumov-Gerasimenko

Credits: ESA/Rosetta/MPS for OSIRIS Team MPS/UPD/LAM/IAA/SSO/INTA/UPM/DASP/IDA

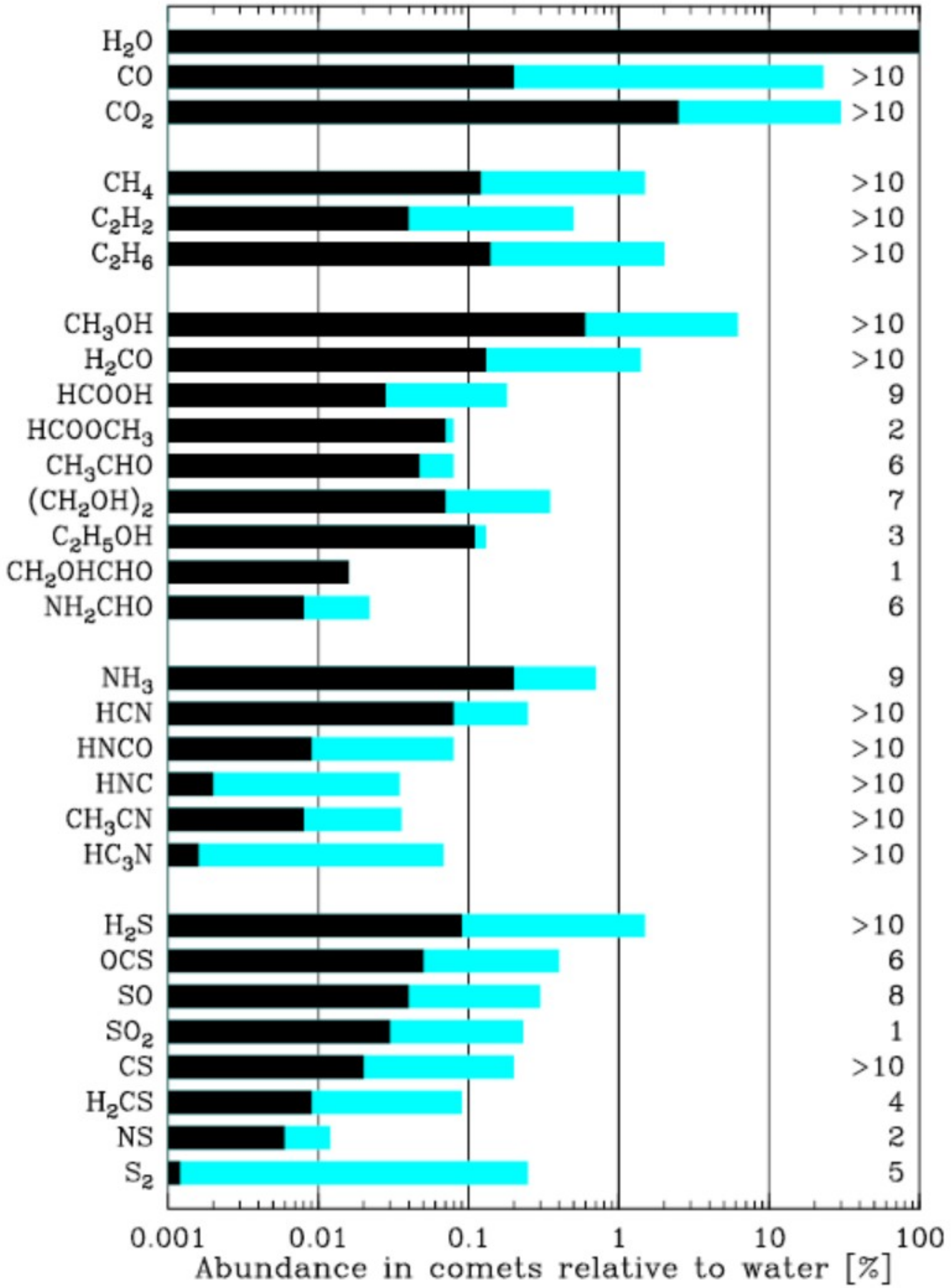
Organic matter in meteorites

ROSETTA ROSINA's ZOO

Gaseous phase, released from nucleus or shortly after dust ejection



Organic matter in comets



Inventory based on remote detections from Earth

Biver et al., 2019

An old heritage ?

Detection of organic molecules in the gaseous phase in warm regions of the interstellar medium (hot cores)

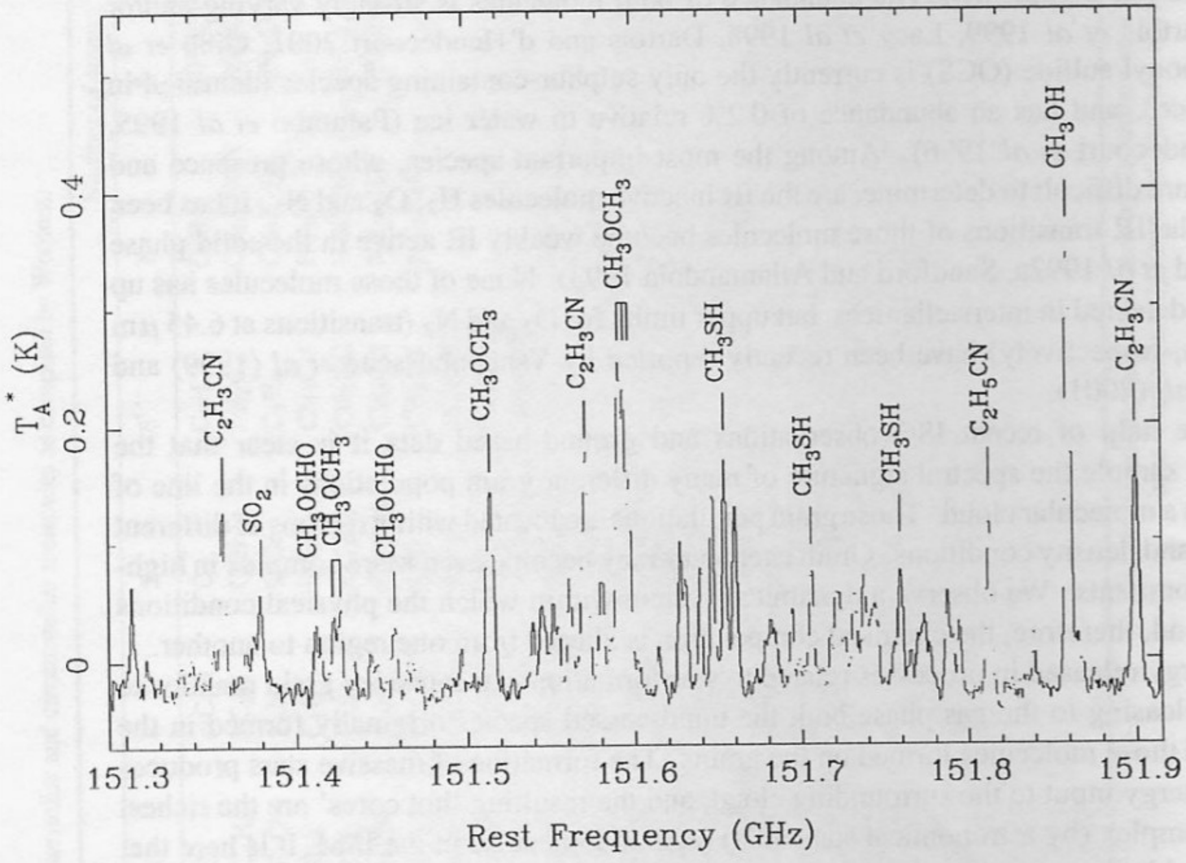
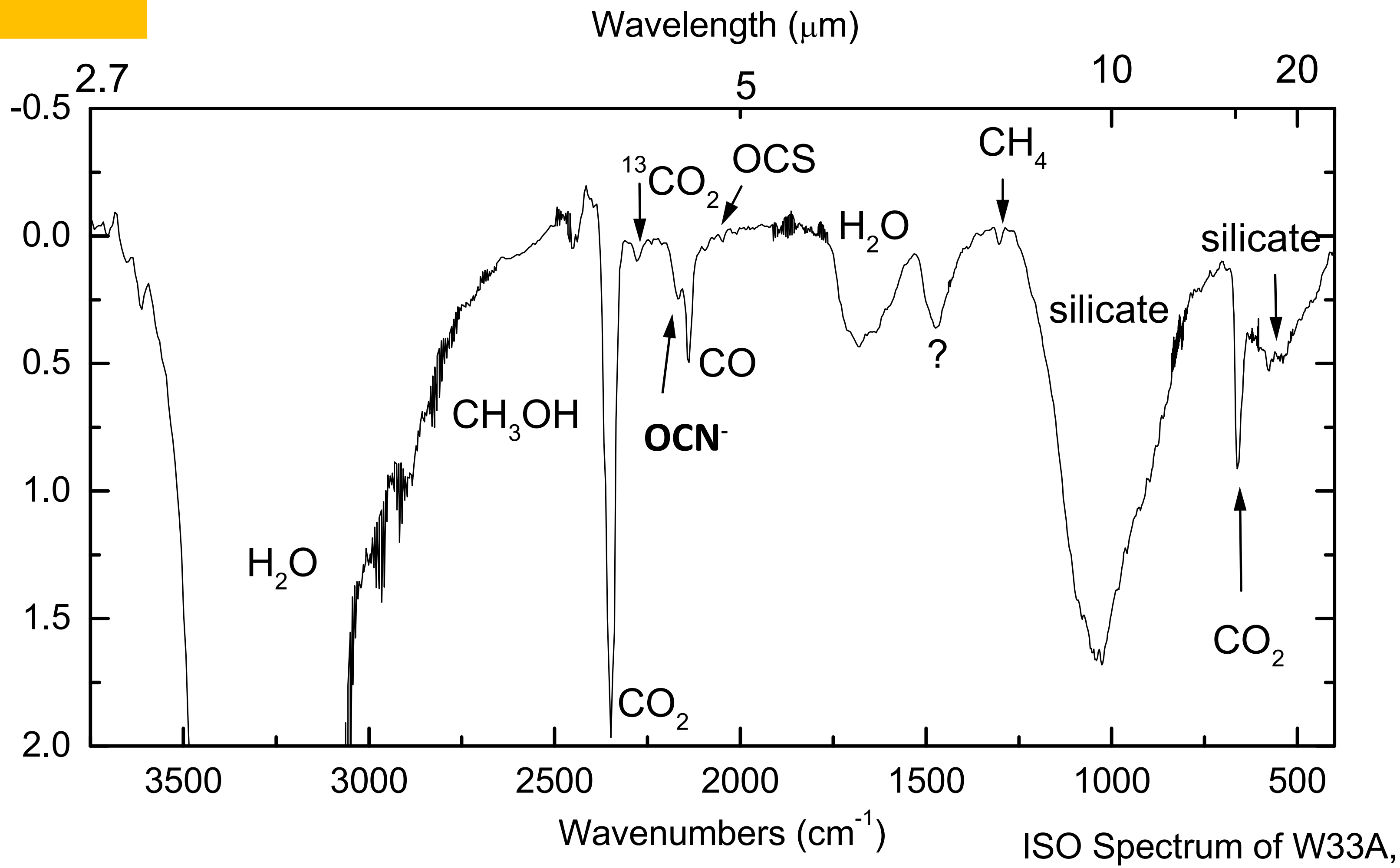


Figure 2. Observations of organic molecules toward the hot, molecular cloud core G327 around 151.6 GHz, with suggested line identifications marked. The majority of the emission lines are from organic species such as CH_3OH, CH_3OCHO, C_2H_3CN, C_2H_5CN and CH_3SH. Many of the displayed lines are unidentified to date (taken from Gibb *et al* (2000b)). Intensity is given in the radio astronomy units of antenna temperature (T_A^*, in Kelvin).

Detection of ices and silicates in cold dense cloud



ISO Spectrum of W33A,
A Protostellar Object

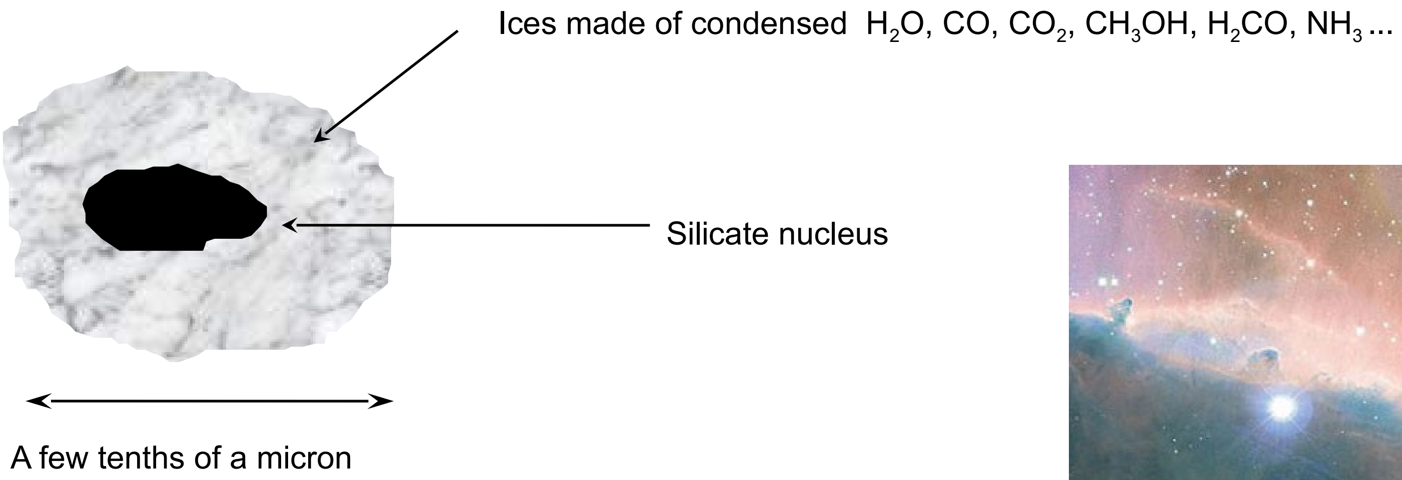
2 atomes	3 atomes	4 atomes	5 atomes	6 atomes	7 atomes	8 atomes	$\geq$ 9 atomes
CH	**H_2O**	**NH_3**	HC_3N	**CH_3OH**	CH_3CHO	$HCOOCH_3$	CH_3OCH_3
CN	HCO^+	**H_2CO**	HCOOH	CH_3CN	CH_3CCH	CH_3C_3N	CH_3CH_2OH
CH^+	HCN	HNCO	CH_2NH	NH_2CHO	CH_3NH_2	C_7H	CH_3CH_2CN
OH	**OCS**	H_2CS	NH_2CN	CH_3SH	CH_2CHCN	CH_3COOH	HC_7N
CO	HNC	C_2H_2	H_2CCO	C_2H_4	HC_5N	H_2C_6	HC_9N
H_2	H_2S	C_3N	C_4H	C_5H	C_6H	CH_2OHCHO	CH_3C_4H
SiO	N_2H^+	HNCS	SiH_4	CH_3NC	c-C_2H_4O	C_6H_2	$(CH_3)_2CO$
CS	C_2H	$HOCO^+$	c-C_3H_2	HC_2CHO	CH_2CHOH	c-C_2H_5N	C_8H
SO	SO_2	C_3O	CH_2CN	H_2CCCC	C_6H^-	CH_2CHCHO	C_6H_6
SiS	HCO	C_3H	C_5	HC_3NH^+	CH_3NCO	CH_2CCHCN	$HOCH_2CH_2OH$
NS	HNO	$HCNH^+$	SiC_4	C_5N	HC_5O	NH_2CH_2CN	CH_3CH_2CHO
C_2	**OCN^-**	H_3O^+	H_2CCC	C_4H_2	$HOCH_2CN$	*trans*-$HCOOCH_3$	CH_3CONH_2
NO	HCS^+	C_3S	**CH_4**	HC_4N	*Z*-HNCHCCH	CH_3CHNH	CH_3C_6H
HCl	HOC^+	c-C_3H	HCCNC	c-C_2H_3N	HC_4NC	CH_3SiH_3	CH_3C_5N
NaCl	c-SiC_2	HC_2N	HNCCC	c-H_2C_3O	c-C_3HCCH	$(NH_2)_2CO$	C_8H^-
AlCl	MgNC	H_2CN	H_2CO^+	CH_2CNH	H_2C5	$HCCCH_2CN$	CH_2CHCH_3
KCl	C_2S	SiC_3	C_4H^-	C_5N^-	MgC_5N	HC_5NH^+	C_2H_5OCHO
AlF	C_3	CH_3	CNCHO	*E*-HNCHCN	CH_2CCCN	CH_2CHCCH	C_3H_7CN
PN	**CO_2**	C_3N^-	HNCNH	C_5S	-	MgC_6H	C_{60}
SiC	CH_2	PH_3	CH_3O	SiH_3CN	-	$C_2H_3NH_2$	C_{70}
CP	C_2O	HCNO	NH_3D^+	*Z*-HNCHCN	-	-	$C_{14}H_{10}^+$
NH	NH_2	HOCN	H_2NCO^+	MgC_4H	-	-	C_{60}^+
SiN	NaCN	HSCN	$NCCNH^+$	CH_3CO^+	-	-	CH_3COOCH_3
SO+	N_2O	HOOH	CH_3Cl	CH_2CCH	-	-	C_6H_5OH
CO+	MgCN	$CCCH^+$	MgC_3N	H_2CCCS	-	-	CH_3CH_2SH
HF	H_3^+	HMgNC	NH_2OH	HCSCCH	-	-	C_3H_7CN
LiH	SiCN	MgCCH	HC_3O^+	C_5O	-	-	$C_2H_5OCH_3$
FeO	AlNC	NCCP	HC_3S^+	C_5H^+	-	-	CH_3CHCH_2O
N_2	SiNC	HCCO	H_2CCS	$HCCNCH^+$	-	-	CH_3NHCHO
CF^+	HCP	CNCN	C_4S	-	-	-	HC_7O
PO	CCP	*trans*-HONO	*trans*-HCOSH	-	-	-	CH_3OCH_2OH
AlO	AlOH	HCCS	HCSCN	-	-	-	c-C_6H_5CN
CN^-	H_2O^+	HNCN	HCCCO	-	-	-	CH_3COCH_2OH
OH^+	H_2Cl^+	H_2NC	-	-	-	-	c-C_5H_5CN
SH^+	KCN	$HCCS^+$	-	-	-	-	$HC_{11}N$
O_2	FeCN	-	-	-	-	-	HCCCHCHCN
HCl^+	HO_2	-	-	-	-	-	H_2CCHC_3N
SH	TiO_2	-	-	-	-	-	c-C_5H_5CN
TiO	CCN	-	-	-	-	-	$C_{10}H_7CN$ [a]
ArH^+	SiCSi	-	-	-	-	-	$H_2CCCHCCH$
NO^+	S_2H	-	-	-	-	-	c-C_5H_6
CrO	HCS	-	-	-	-	-	c-C_9H_8
NS^+	HSC	-	-	-	-	-	$NH_2CH_2CH_2OH$
VO	NCO	-	-	-	-	-	*ortho*-C_6H_4
HeH^+	CaCN	-	-	-	-	-	H_2CCCHC_3N
-	NCS	-	-	-	-	-	$C_2H_5CONH_2$
-	-	-	-	-	-	-	$C_2H_5NH_2$
-	-	-	-	-	-	-	C_2H_5NCO
-	-	-	-	-	-	-	c-C_5H_5CCH
-	-	-	-	-	-	-	C_6H_5CCH
-	-	-	-	-	-	-	CH_3C_7N
-	-	-	-	-	-	-	HC_7NH^+

How does it form ?

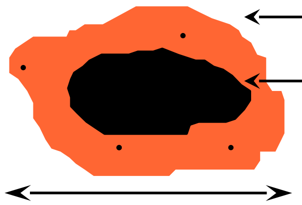
Data : http://www.astrochymist.org

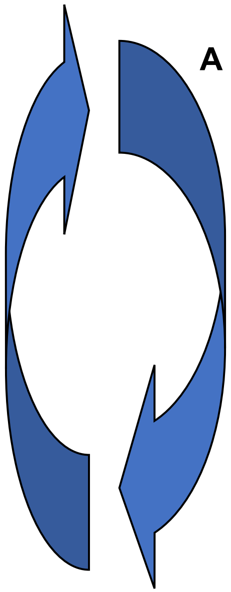
Being an interstellar dust particle

Dust particle in a diffuse interstellar environment

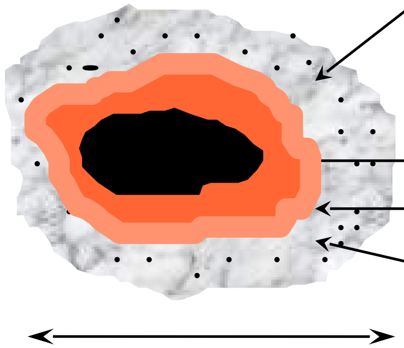


Dust particle in a molecular cloud

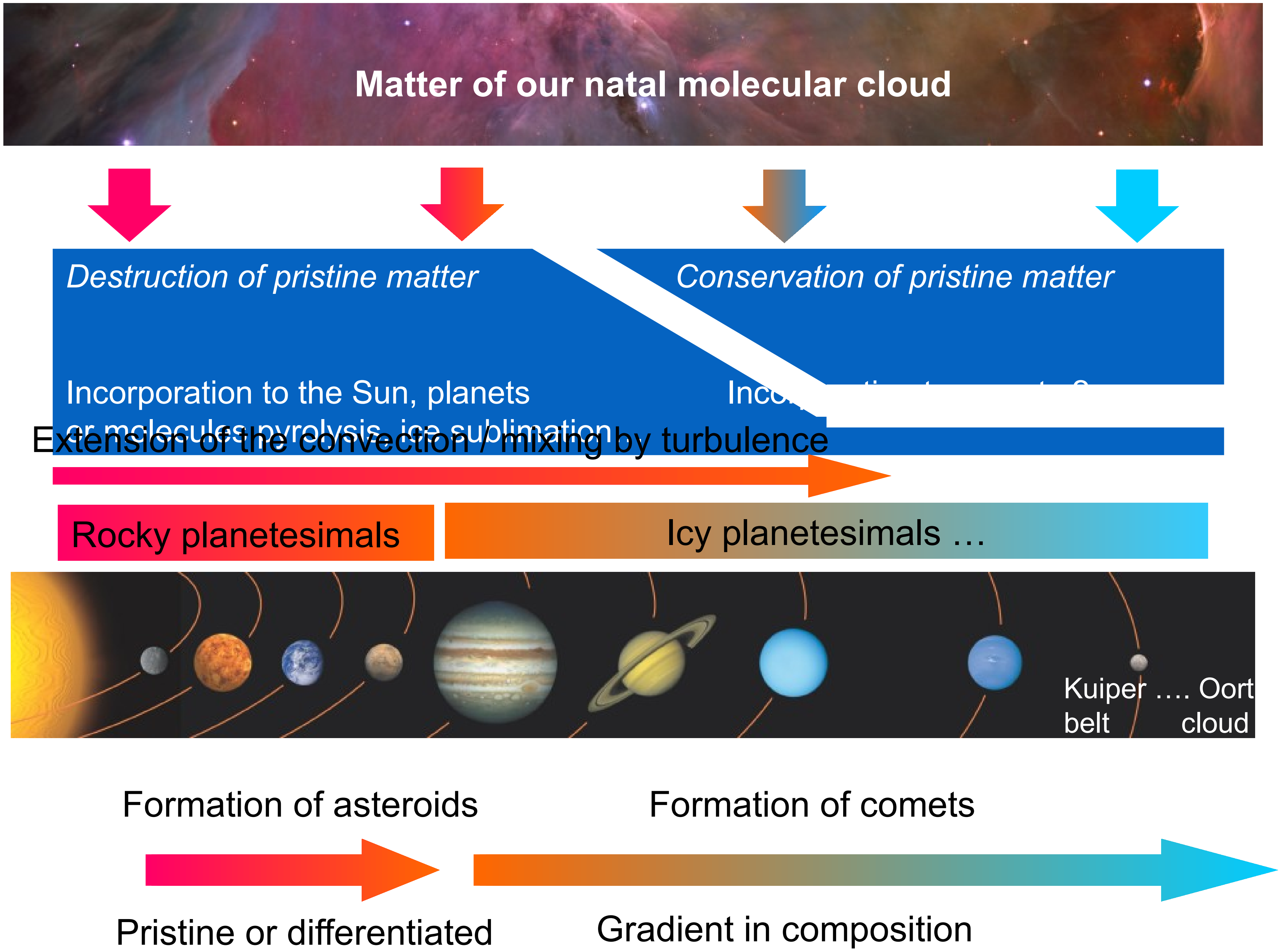


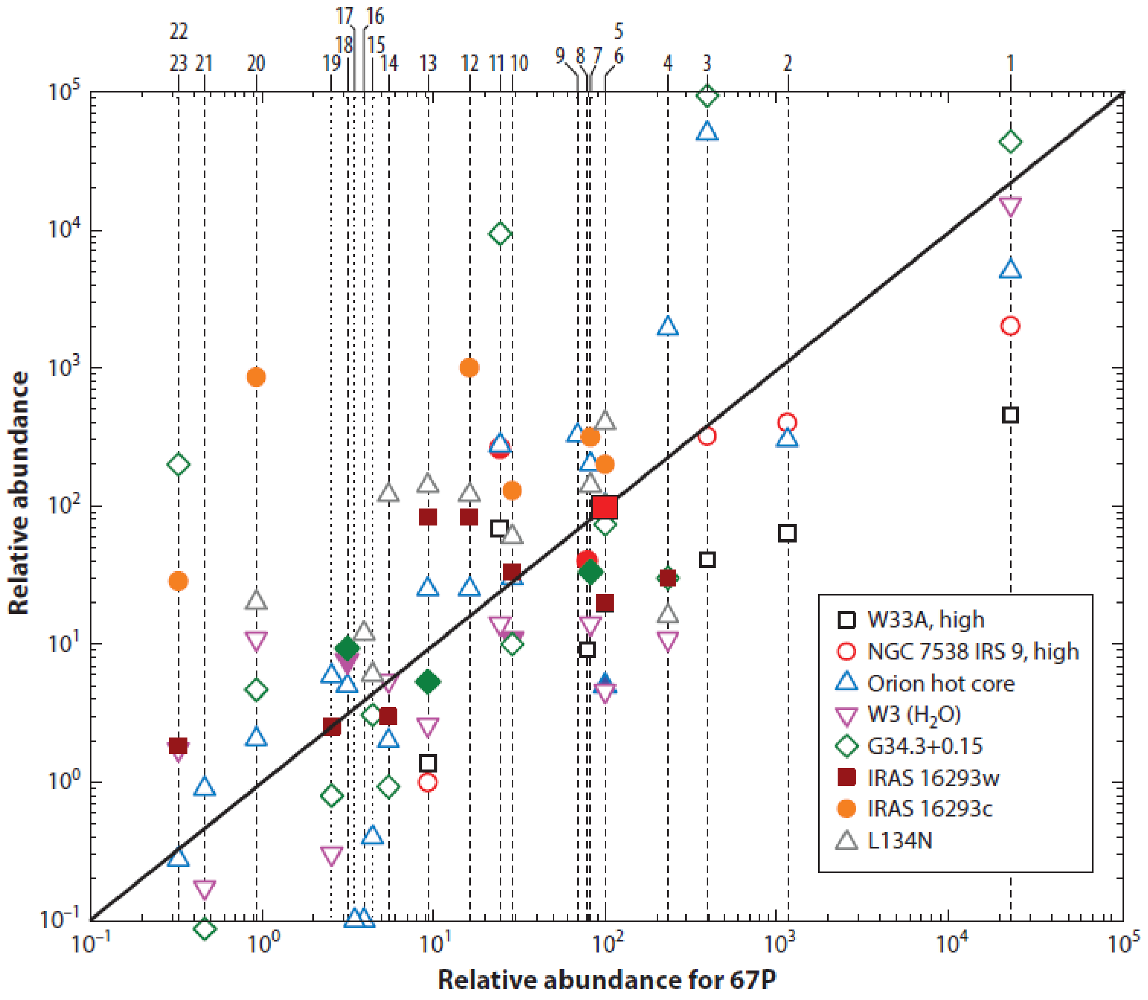


Dust particle in a diffuse interstellar environment



Dust particle in a molecular cloud


Matter of our natal molecular cloud
Destruction of pristine matter
Conservation of pristine matter
Incorporation to the Sun, planets
Extension of the convection / mixing by turbulence
Rocky planetesimals
Icy planetesimals …
Kuiper …. Oort
belt
cloud
Formation of asteroids
Formation of comets
Pristine or differentiated
Gradient in composition

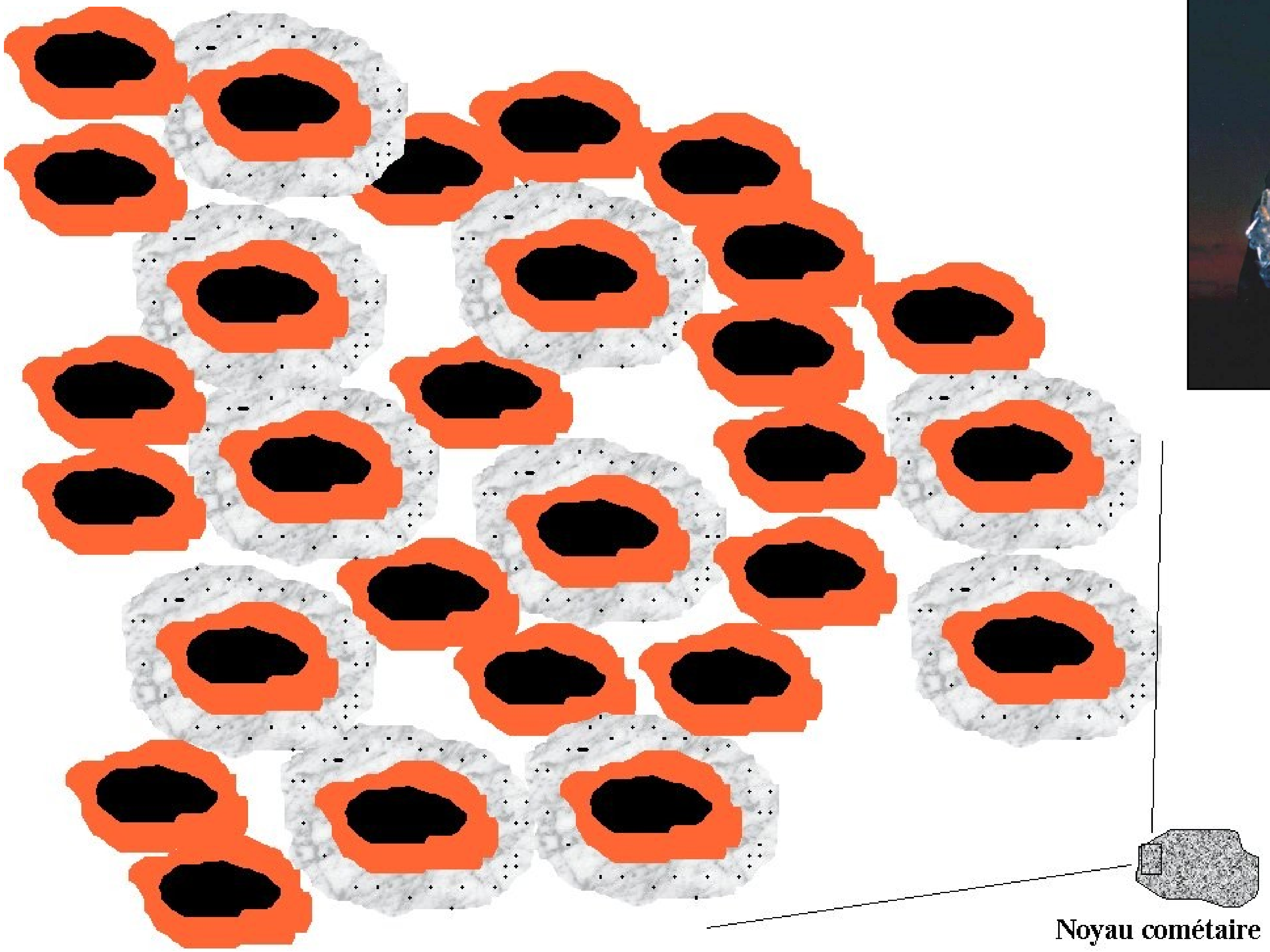


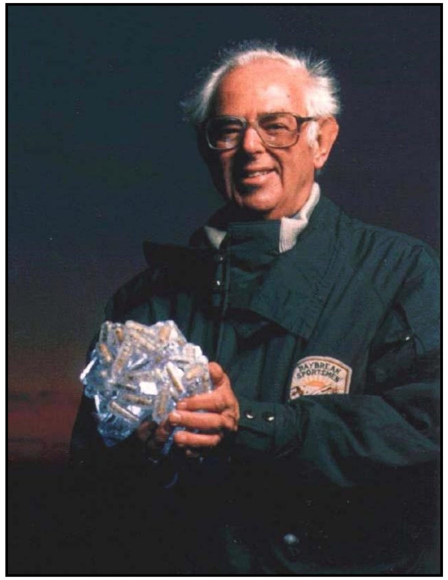
Altwegg et al., 2019

Figure 9 shows a comparison of data from 67P and from dark clouds, high- and low-mass star-forming regions, all normalized to methanol. **In general and in consideration of the uncertainties of observations, they all follow the same trend.**
There are a few outliers, namely the cooler, less dense outer part of the envelope around the low-mass protostar IRAS 16293-2422 (16293c) and the dark cloud L134N. These might be due to regions where molecules may only partly be in gas phase, especially for the warmer part of the low-mass protostar region IRAS 16293-2422 (16293w), whose **correlation with 67P is quite good**

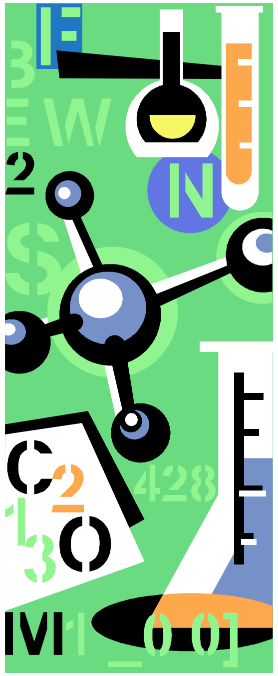
Comparison of molecular abundances relative to methanol (*red square*) in clouds of high- and low-mass protostars and 67P. A perfect match would be on the diagonal line. Numbers refer to the following molecular abundances: 1, H_2O; 2, CO_2; 3, CO; 4, H_2S; 5, H_2CO; 6, CH_3OH; 7, HCN; 8, CH_4; 9, C_2H_2; 10, SO_2; 11, NH_3; 12, SO; 13, OCS; 14, HNCO; 15, HCOOH; 16, CH_3CHO; 17, NH_2CHO; 18, $HCOOCH_3$; 19, CH_3CN; 20, CS/CS_2*; 21, HC_3N; 22, CH_3SH; 23, H_2CS. Data for astronomical bodies are from the following sources: W33A, Gibb et al. (2000b) and Keane et al. (2001); NGC 7538 IRS 9, Whittet et al. (1996), Schutte (1999), Ehrenfreund & Schutte (2000), and Keane et al. (2001); Orion hot core, Sutton et al. (1995), van Dishoeck & Blake (1998), and Irvine et al. (1999); L134N, Ohishi & Kaifu (1998), updated using values from 2000 for L134N position C; W3, Hermsen et al. (1988), Helmich et al. (1996), and Helmich & van Dishoeck (1997); G34.3+0.15, Heaton et al. (1989), Macdonald et al. (1996), Millar et al. (1997), Hatchell et al. (1998a,b,c), and Bockelée-Morvan et al. (2000). IRAS 16293w: Abundance in warm and dense inner part of the envelope 150 AU in radius around IRAS 16293–2422; data from Schöier et al. (2002). IRAS 16293c: Abundance in cooler, less dense outer part of the envelope around IRAS 16293–2422; data from Schöier et al. (2002). Data for 67P from Le Roy et al. (2015), Altwegg et al. (2017b), Calmonte et al. (2017), and Schuhmann et al. (2019). The asterisk (*) indicates that cometary data are for CS_2, whereas the other data are for the radical CS. Abbreviations: 67P, 67P/Churyumov–Gerasimenko; NGC, new galaxy catalog.

Some comets as remnants of the interstellar medium ?

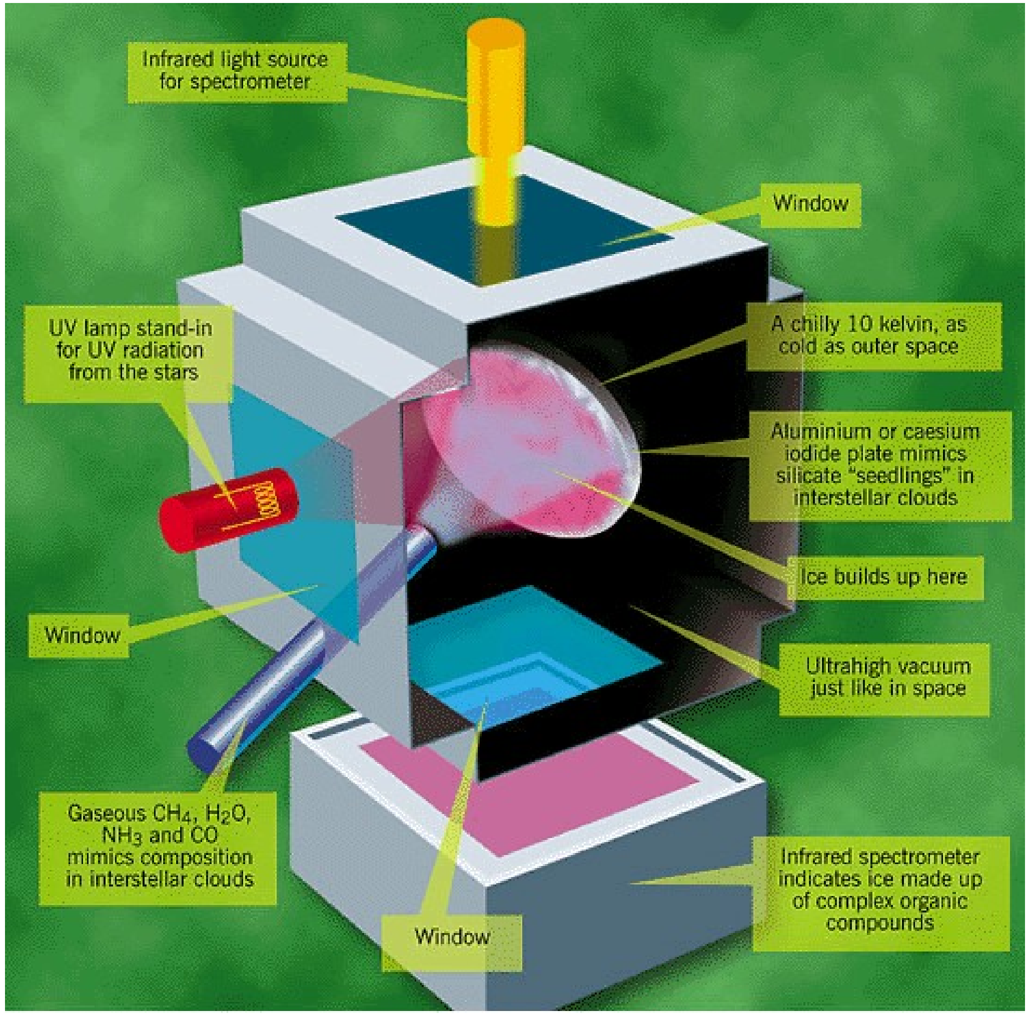




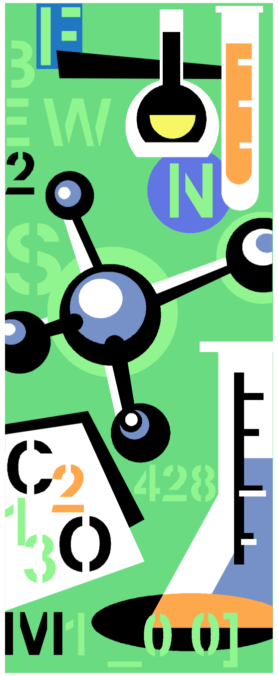
Instellar (precometary ?) ice chemistry in a laboratory



Laboratory simulation of the evolution of interstellar and/or cometary ices

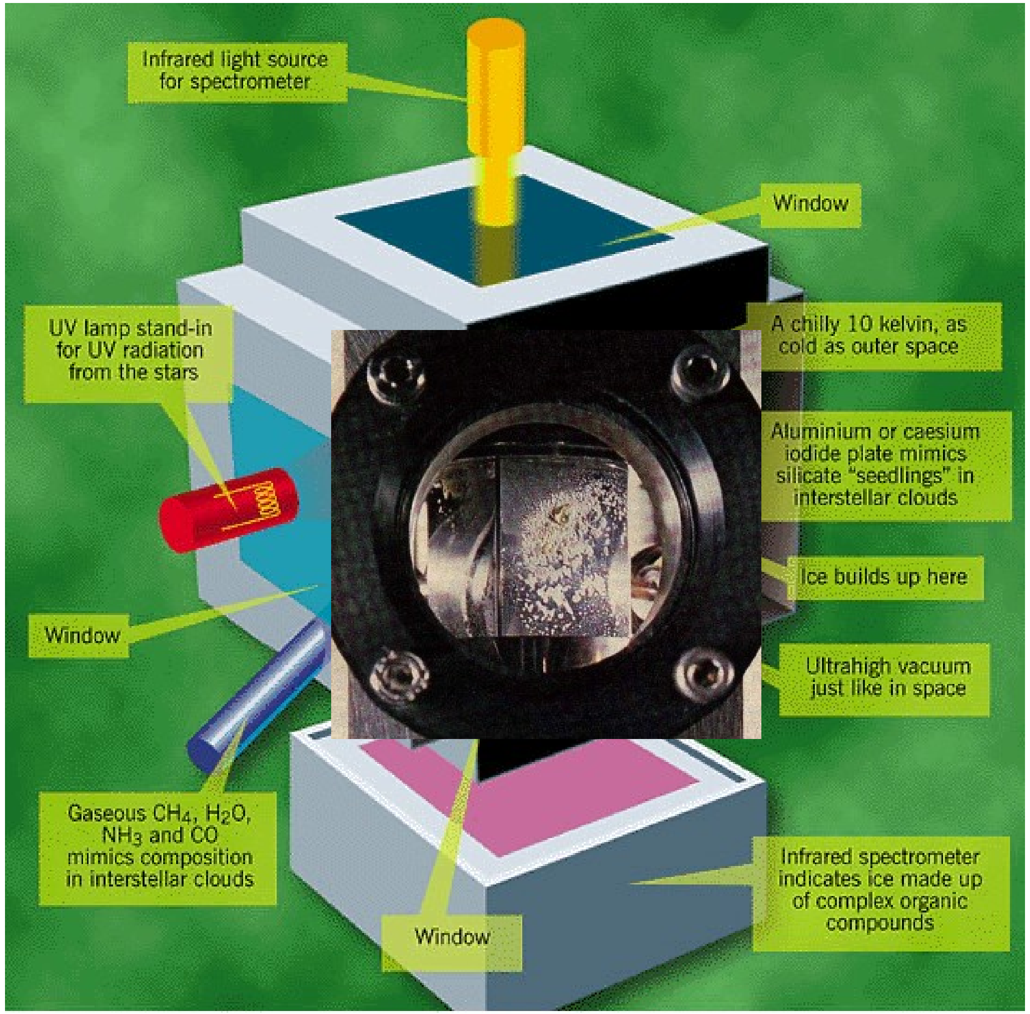


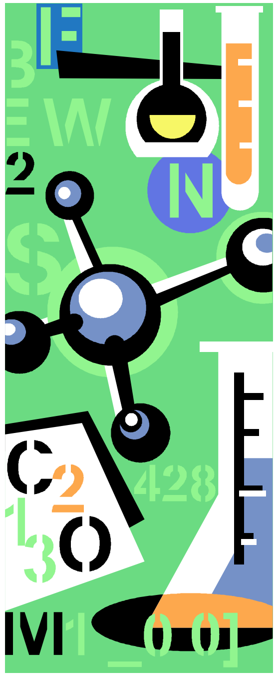
Instellar (precometary ?) ice chemistry in a laboratory

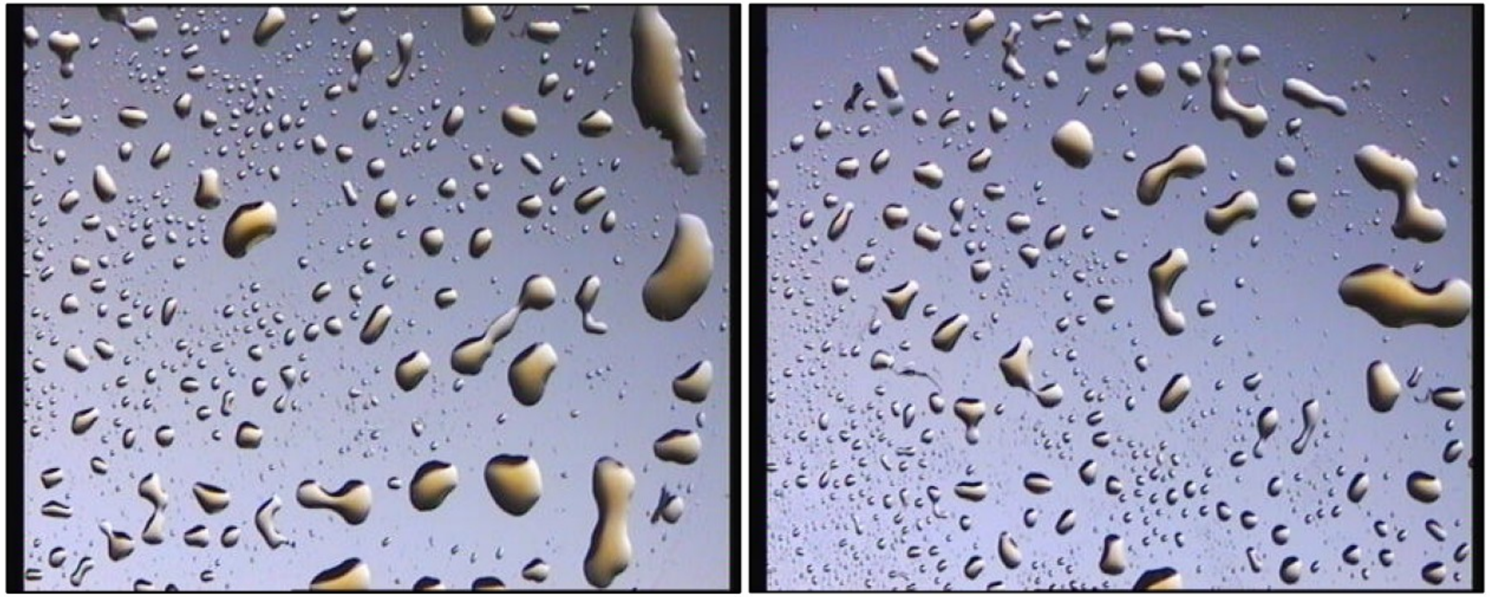


Laboratory simulation of the evolution of interstellar and/or cometary ices

Back at room T

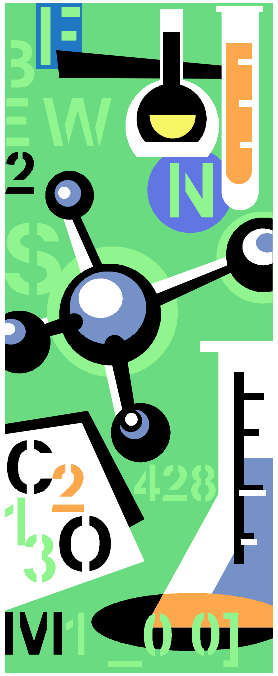






Modica et al. 2014

Incomplete list of molecules detected after ice simulations



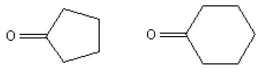
Hydrocarbons:
CH_4
C_2H_2, C_2H_4, C_2H_6
C_3H_8, C_4H_{10}
C_5H_{10}, C_5H_{12}
C_6H_{12}, C_6H_{14}
C_7H_{16}

Amides:
NH_2CHO
CH_3CONH_2
$HOCH_2CONH_2$
$NH_2(CO)_2NH_2$
$HOCH_2CH(OH)CONH_2$

Amines:
$HOCH_2CH_2NH_2$
$HCNH(NH_2)$
Diaminopyrrole
Diaminofurane
Triaminopropane
$(CH_2)_6N_4$ (HMT)

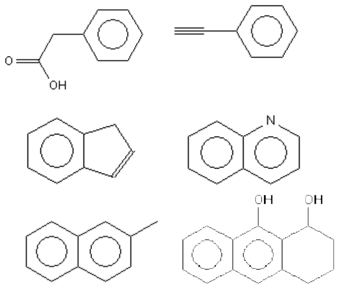
Aldehydes:
H_2CO
CH_3OCH_2CHO (t)

Ketones:
CH_3COCH_3
$HOCH_2COCH_3$
$HOCH_2CH_2COCH_3$



Carboxylic acids:
$HCOOH$
CH_3COOH (t)
$HOCH_2COOH$
$HOCH_2CH(OH)COOH$
$HOCH_2CH_2COOH$
$NH_2COCOOH$

Aromatic Compounds:



Ethers:
$CH_3OCH_2OCH_3$ (t)
$C_3H_6O_3$ (Trioxane) (t)
$(-CH_2-O-)_n$ (POM)

Alcohols:
CH_3OH
CH_3CH_2OH
$HOCH_2CH_2OH$
$HOCH_2CH(OH)CH_2OH$
$C_4H_8(OH)_2$
C_5H_9OH (t)
$C_5H_{11}OH$

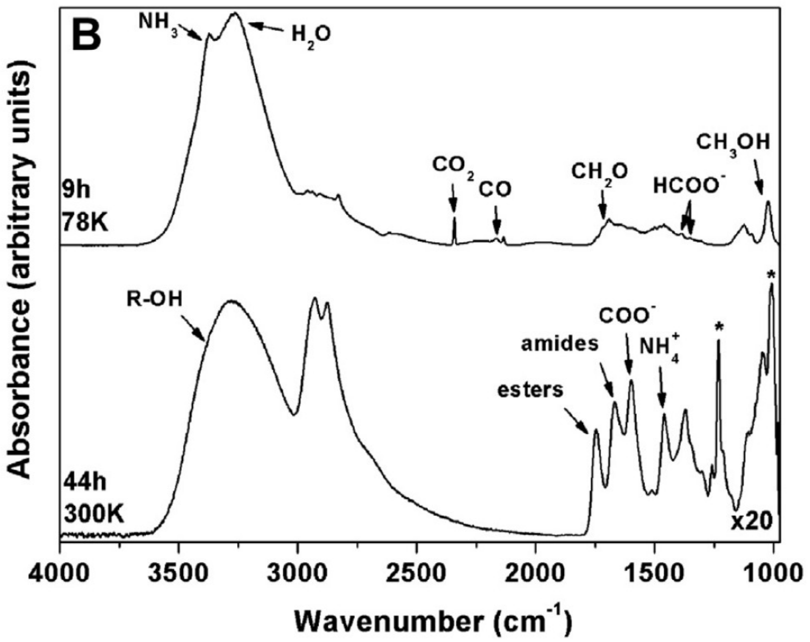
Amino Acids:
NH_2CH_2COOH (Glycine)
$NH_2CH(CH_3)COOH$ (Alanine)
$CH_3CH_2CH(NH_2)COOH$ (α ABA)
$CH_3CH(NH_2)CH_2COOH$ (β ABA)
$(CH_2NH_2)(CH_3)CHCOOH$ (AIBA)
Sarcosine
Ethylglycine
Valine, Proline, Serine
Aspartic acid
Diaminopropanoic acid
Diaminobutyric acid
Diaminopentanoic acid
Diaminohexanoic acid

Esters:
$HCOOCH_3$
CH_3COOCH_3
$CH_3CH_2COOCH_3$

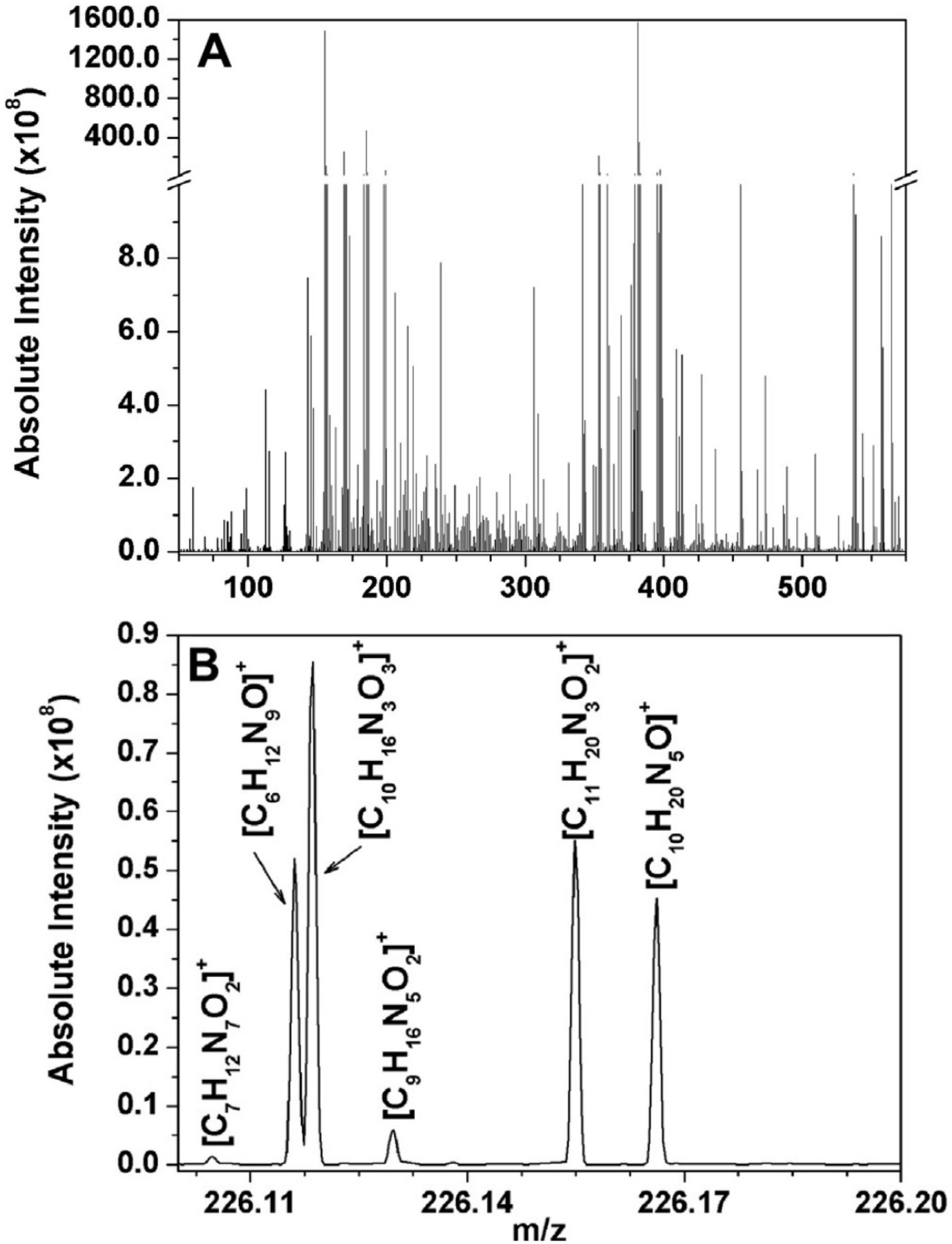
Others: CO, CO_2, C_3O_2, H_2O_2, H_2CO_3, N_2H_4, $HNCO$, NH_2CONH_2, $NH_2CONHCONH_2$

Danger et al., GCA, 2013

ESI/Orbitrap analysis of organic residue.
~ 10 000 peaks between 50 and 590 AMU.



FT-IR spectra of an ice made of H_2O: CH_3OH : NH_3 in a ratio 3:1:1 after about 9 h of UV irradiation at 78 K and resulting organic residue after about 44 h deposition and simultaneous UV irradiation at 78 K and warmed up to room temperature.



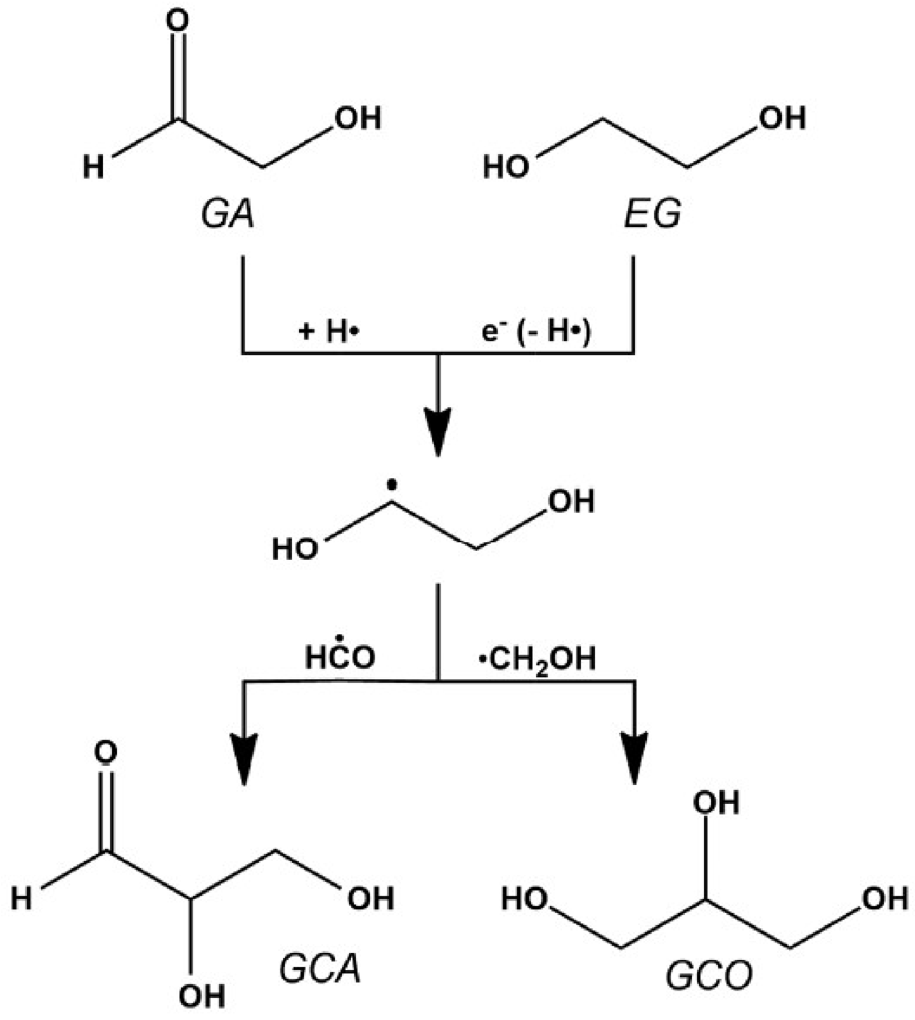
Where does it all come from ?

E.g. starting from a H_2O/CO ice

$$CO \xrightarrow{H} H^{\bullet}CO \xrightarrow{H} H_2CO \xrightarrow{H} {}^{\bullet}CH_2OH/CH_3O^{\bullet} \xrightarrow{H} CH_3OH$$

$$HO^{\bullet}CO + {}^{\bullet}H \rightarrow H_2 + CO_2$$

$$H^{\bullet}CO + {}^{\bullet}CH_2OH \rightarrow HOCH_2CHO \quad (GA)$$
$${}^{\bullet}CH_2OH + {}^{\bullet}CH_2OH \rightarrow HOCH_2CH_2OH \quad (EG)$$



Layssac et al., 2020

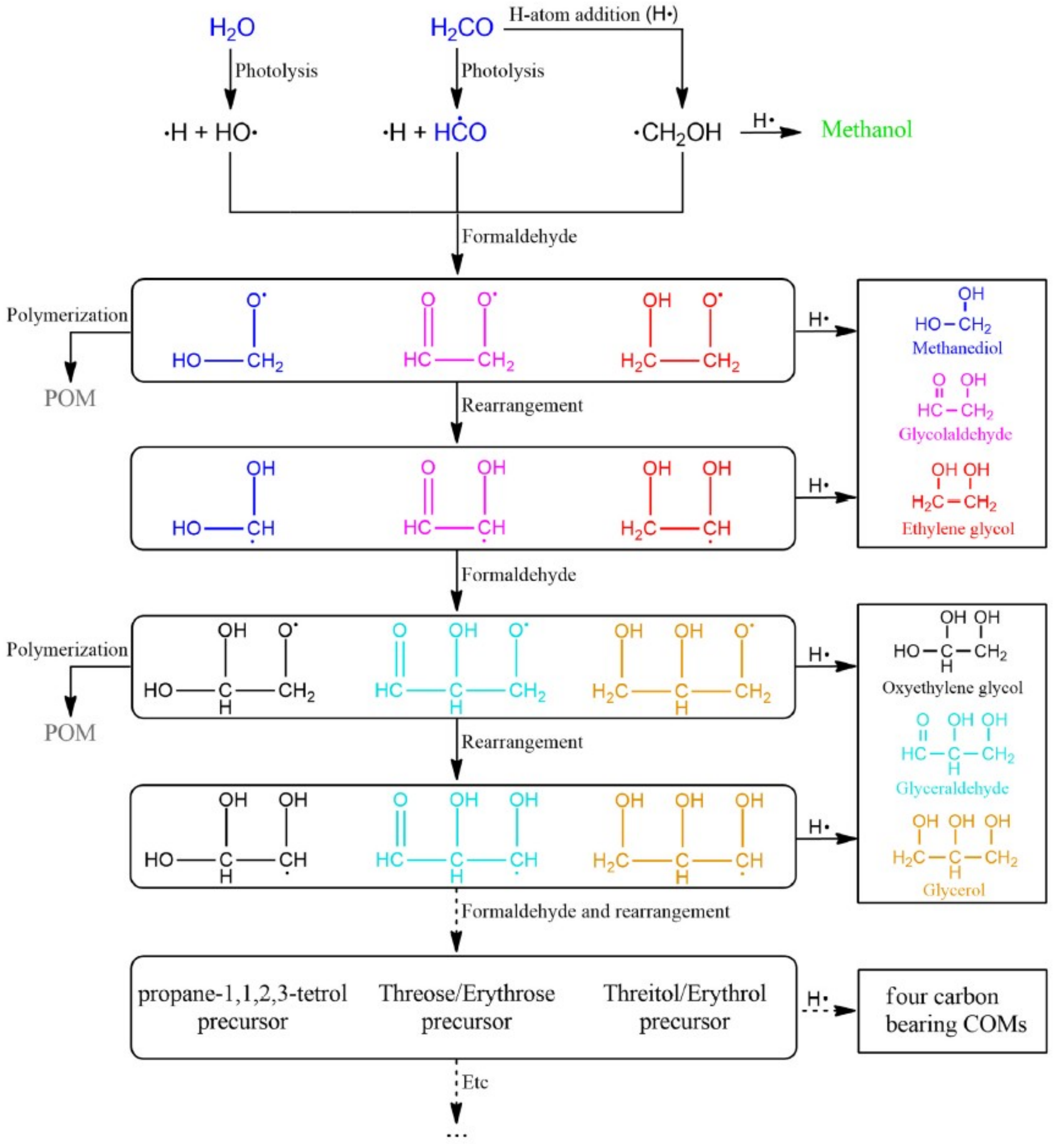
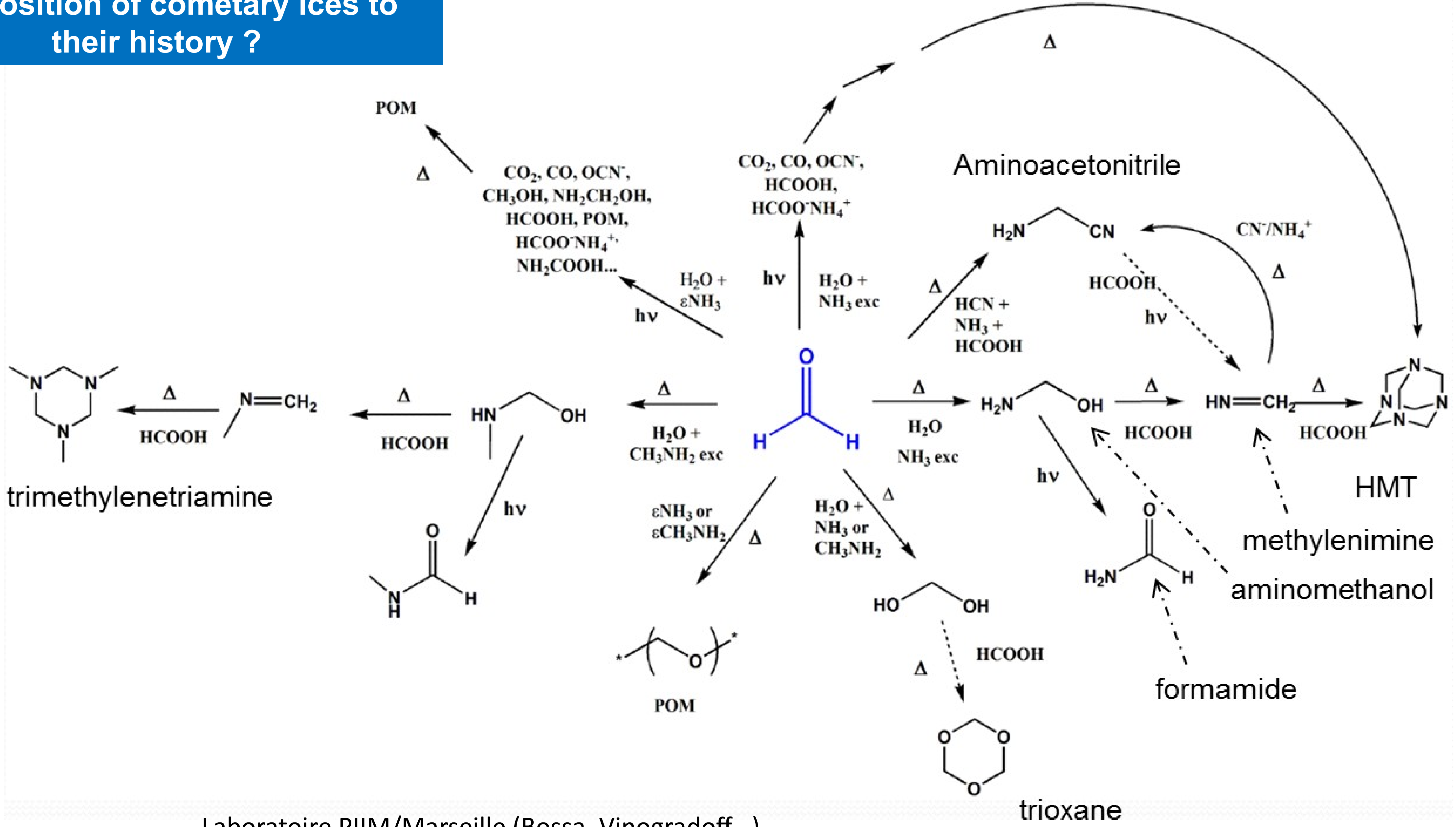


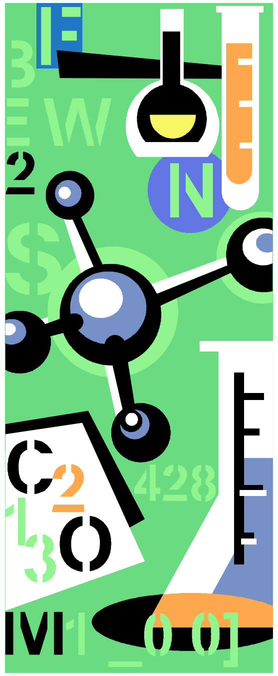
Figure 8. Proposed general formation scheme for polyols and sugars starting from formaldehyde. Molecules with vicinal diols are also displayed as OH radicals could also initiate carbon growth chain reactions. The species in black are not detected in our experiments. The only detected radical is HCO.

Layssac et al., 2020

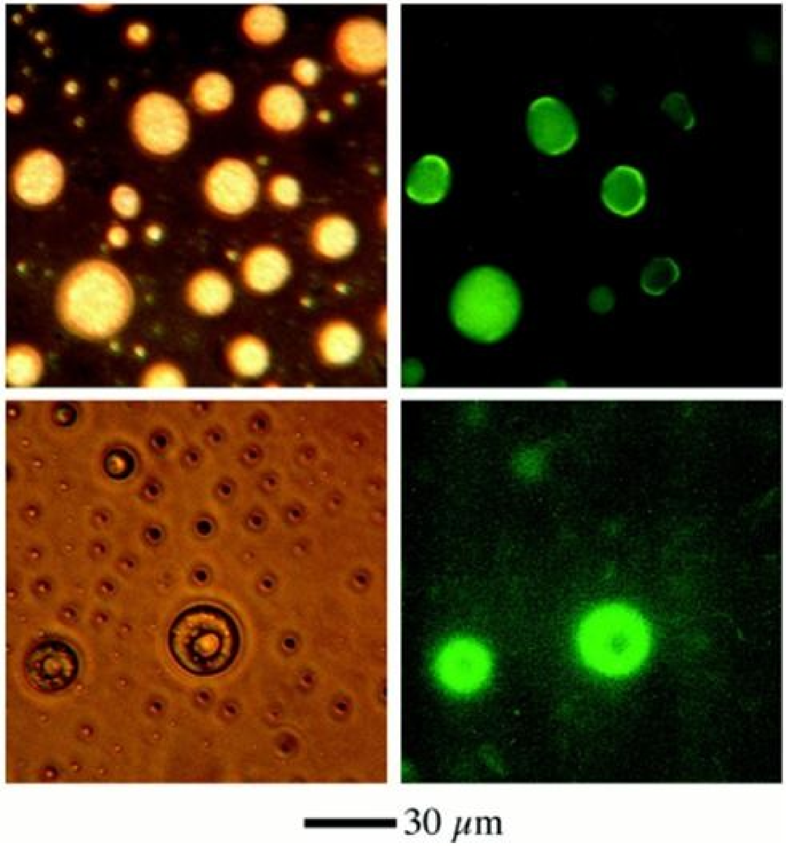
Is there a way to link the composition of cometary ices to their history ?



Laboratoire PIIM/Marseille (Bossa, Vinogradoff…)



Spontaneous formation of vesicles from the organic refractory residue



Dworkin et al. PNAS, 2001

The « iconic » case of amino acids

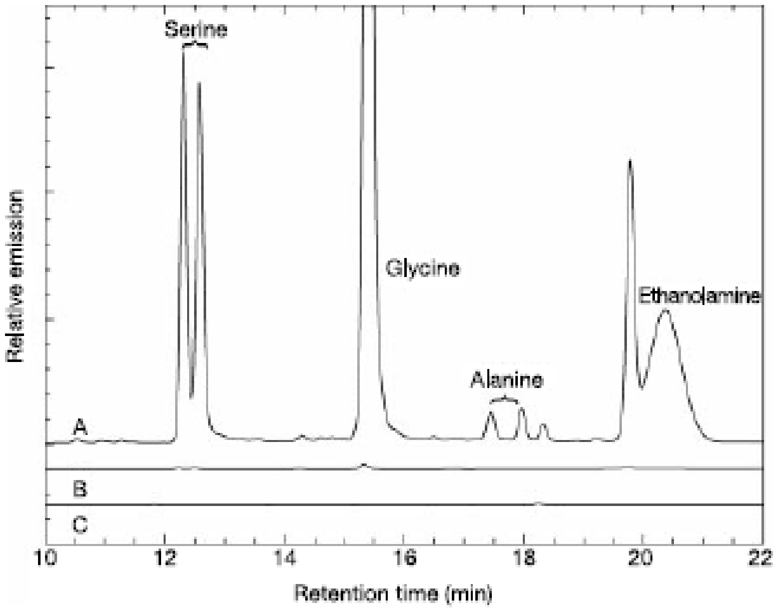
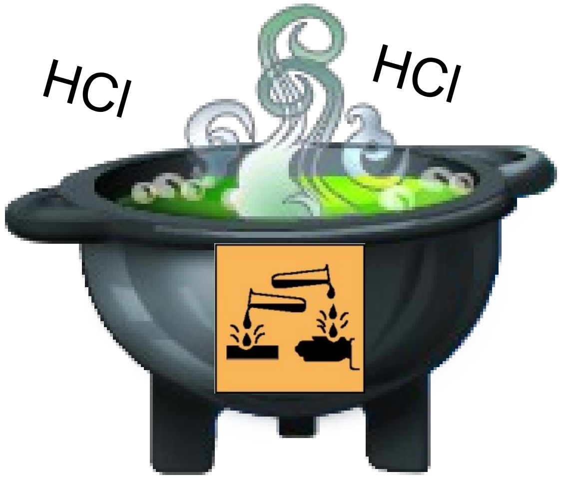
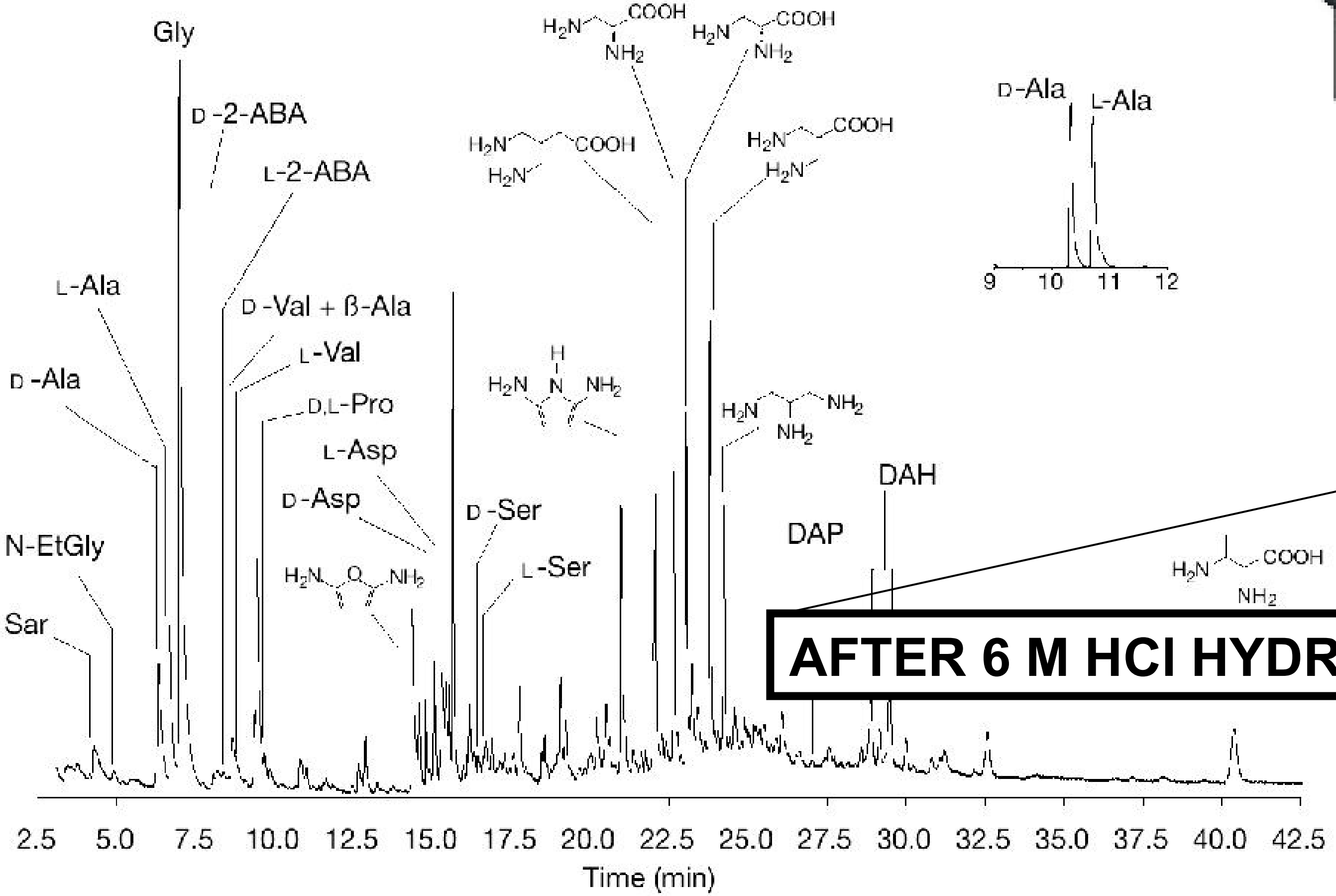


Figure 1 Amino acids are formed by the UV photolysis of a realistic interstellar ice analogue. This is demonstrated by the comparison of HPLC traces of derivatized amines resulting from: trace A, the UV photolysis of an H_2O:CH_3OH:NH_3:HCN = 20:2:1:1 ice showing that the amino acids serine, glycine and alanine, as well as other molecules, are produced; trace B, a control of the same ice with no UV photolysis; and trace C, a procedural blank. In trace A, a single peak indicates the presence of the amino acid glycine but the chiral fluorescent tag, which separates enantiomeric amines, causes the racemic serine and alanine to appear as pairs of peaks. Differing molar absorptivities of the labelled D,L serine and alanine diastereomers account for asymmetry in the peak pairs. The unlabelled peaks are unidentified amines. The racemic nature of the serine and alanine and the absence of prominent peaks in traces B and C indicate that contamination is not significant.

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

The « iconic » case of amino acids





AFTER 6 M HCl HYDROLYSIS

Gas chromatogram showing the amino acids and other compounds generated under simulated interstellar pre-cometary conditions. Data were obtained from analysis of the room temperature residue of photoprocessed interstellar medium ice analogue taken **after 6 M HCl hydrolysis** and derivatization. The inset shows the determination of alanine enantiomers in the above sample.

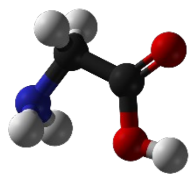
Caro et al., Nature, 416, 2002

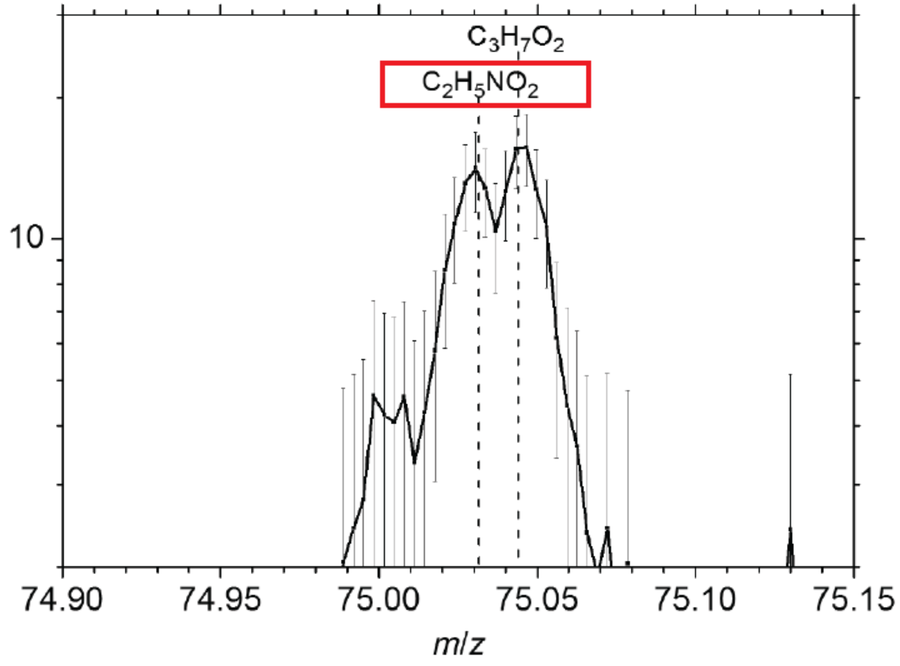
RESEARCH ARTICLE

SPACE SCIENCES

Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov-Gerasimenko

10.1126/sciadv.1600285





Glycine was also detected after analysis of samples returned from comet Wild 2 with Stardust mission

Elsila et al. 2009

Altwegg, K. *et al.* Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov-Gerasimenko. *Science Advances* **2**, doi:10.1126/sciadv.1600285 (2016).

Special Issue Article

Journal of Physical Organic Chemistry

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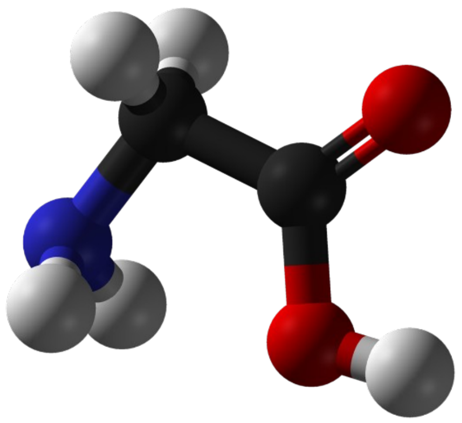
(www.interscience.wiley.com) DOI 10.1002/poc.1682

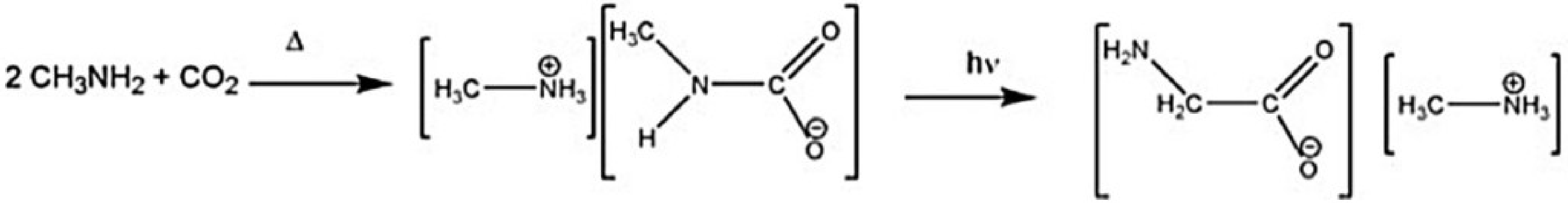
How a usual carbamate can become an unusual intermediate: a new chemical pathway to form glycinate in the interstellar medium

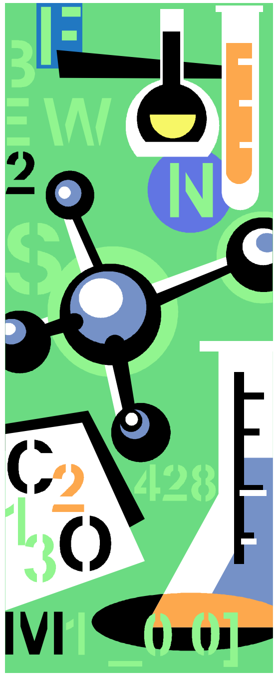
Jean-Baptiste Bossa[a], Fabien Borget[a]*, Fabrice Duvernay[a], Patrice Theulé[a] and Thierry Chiavassa[a]

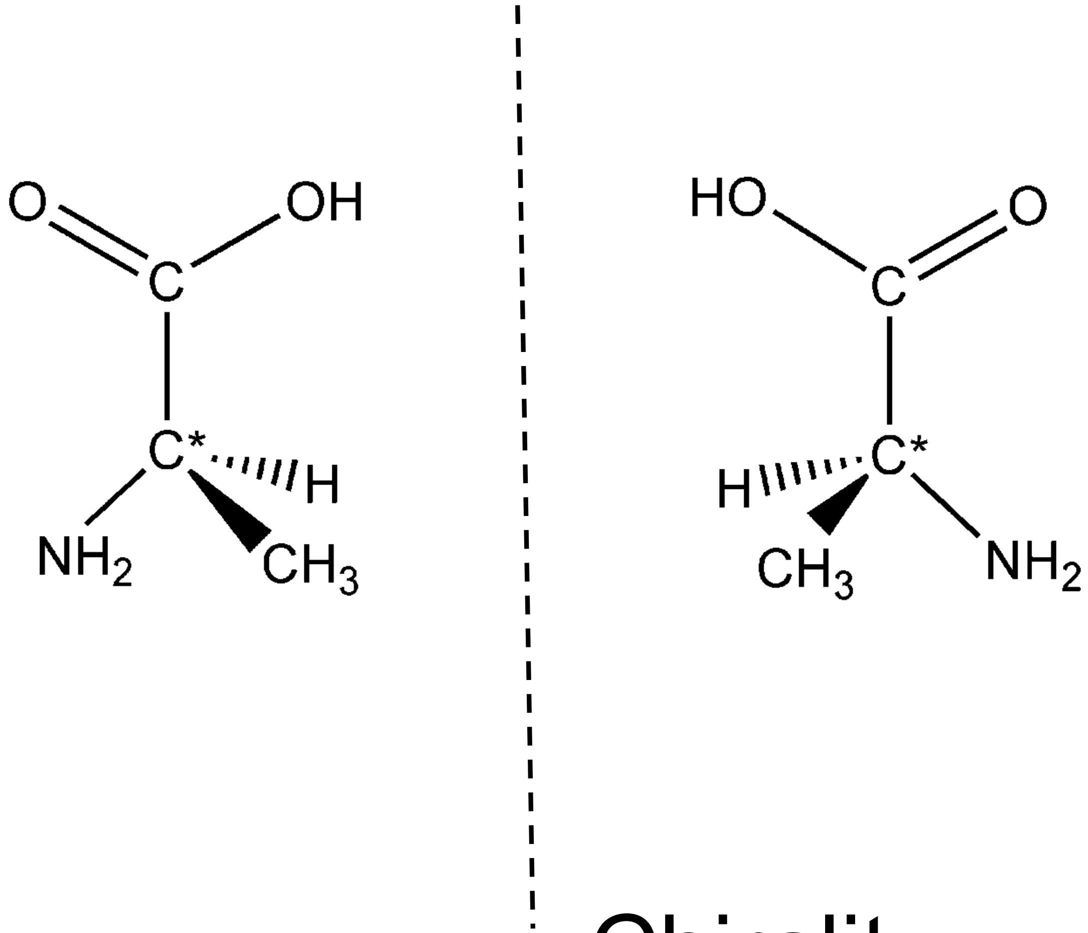
Experiments on the thermal reactivity of carbon dioxide (CO_2) and methylamine (CH_3NH_2) are reported and show methylammonium methylcarbamate (CH_3NHCOO^- $CH_3NH_3^+$) and methylcarbamic acid ($CH_3NHCOOH$) are formed at low temperature in solid environment. The VUV ($\lambda > 120$ nm) irradiation of carbamate induces the formation of methylammonium glycinate (MAG). Calculations have been performed to give an insight on the pathway for the formation of the methylcarbamic acid (MCA). These calculations show that the methylamine environment play an important role in the barrier and a cooperative effect of the methylamine molecules has to be taken into account. The implication on the interstellar reactivity is also discussed because this pathway to form glycinate can occur in interstellar ices.

Keywords: *ab initio* calculations; astrochemistry; glycinate; interstellar medium; IRTF



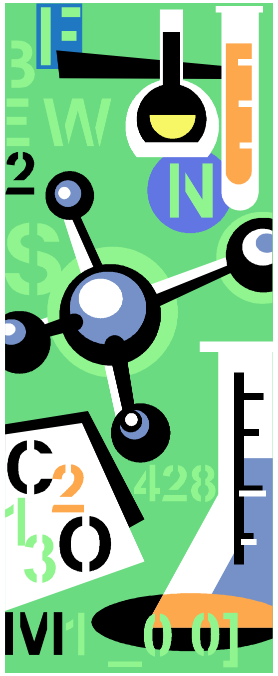






Chirality

An origin for enantiomeric excess



The Astrophysical Journal, 788:79 (11pp), 2014 June 10 doi:10.1088/0004-637X/788/1/79

ENANTIOMERIC EXCESSES INDUCED IN AMINO ACIDS BY ULTRAVIOLET CIRCULARLY POLARIZED LIGHT IRRADIATION OF EXTRATERRESTRIAL ICE ANALOGS: A POSSIBLE SOURCE OF ASYMMETRY FOR PREBIOTIC CHEMISTRY

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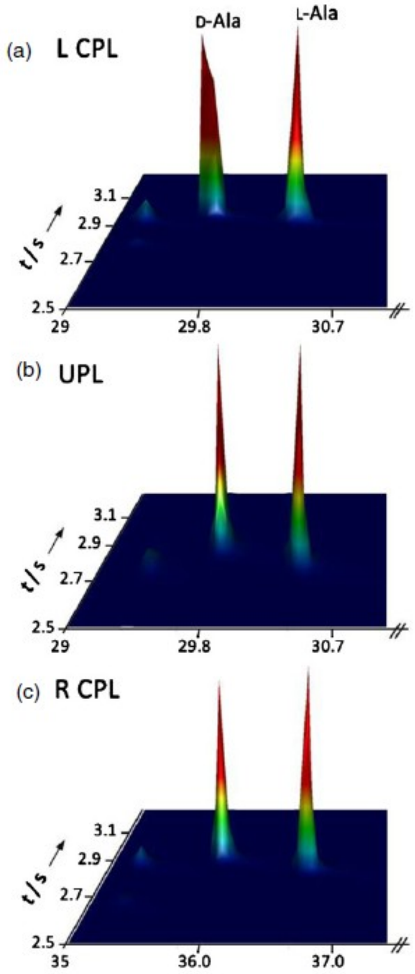
[4] CNRS, F-91404 Orsay, France; ldh@ias.u-psud.fr
Received 2014 April 3; accepted 2014 April 15; published 2014 May 23



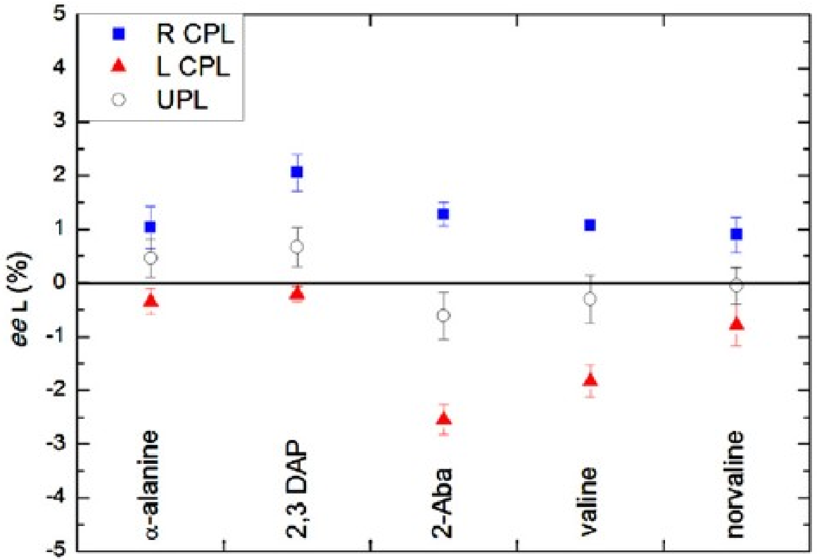


Figure 3. L-enantiomeric excess (ee_L), determined by enantioselective GC×GC-TOFMS, measured in five different amino acids labeled with ^{13}C. Experimental values are obtained from three residue-enlarged samples of initially achiral circumstellar analogs at the stage of residue irradiated by CPL at 10.2 eV. Blue squares refer to ee_L induced by R CPL, red triangles refer to ee_L induced by L CPL, and white circles refer to ee_L measured after UPL. The ee_L are of the same sign in all five amino acids for a given helicity of CPL.

What about IOM like material ?

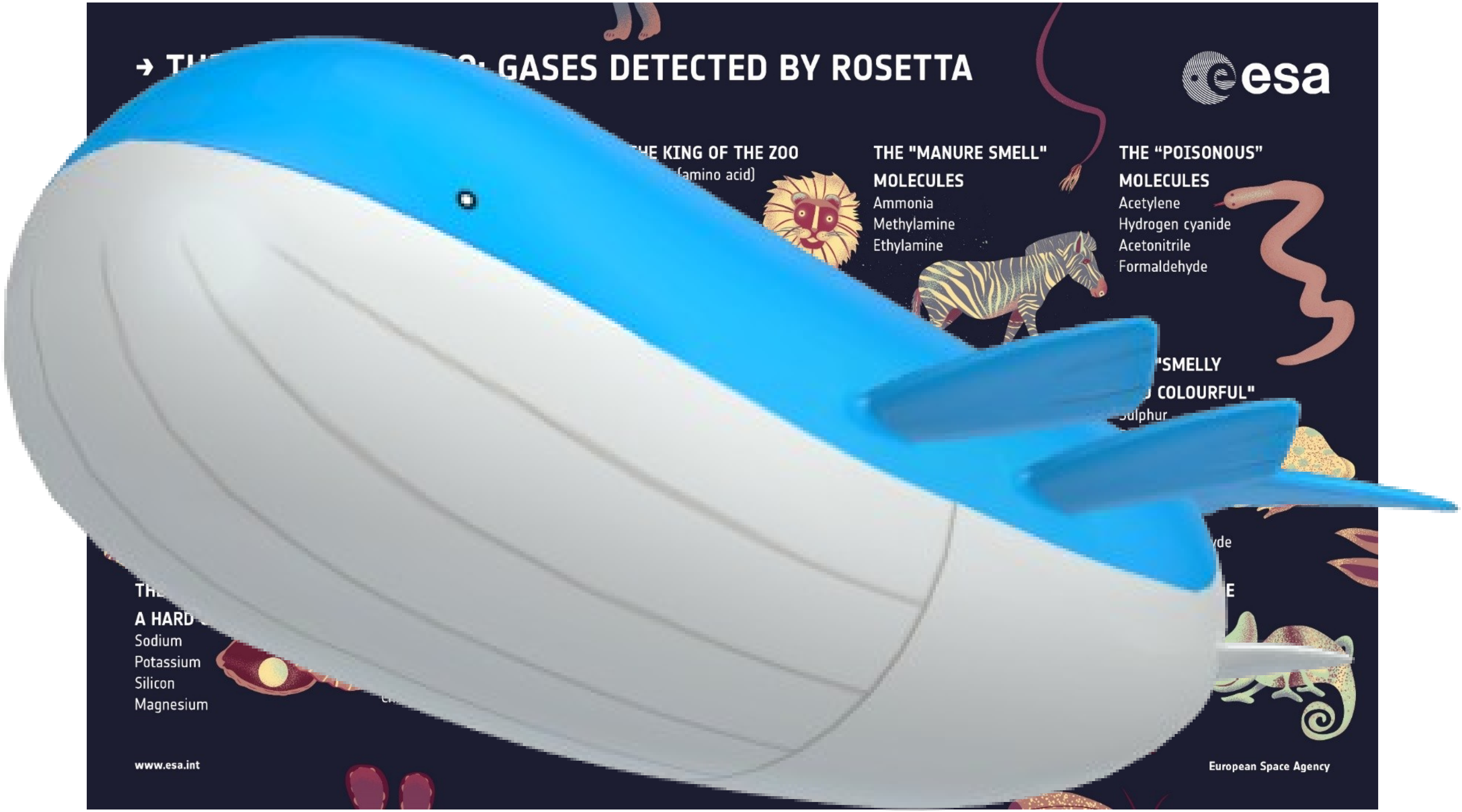


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Photo and thermochemical evolution of astrophysical ice analogues as a source for soluble and insoluble organic materials in Solar system minor bodies

Pierre de Marcellus,[1] Aurelien Fresneau,[2] Rosario Brunetto,[1] Gregoire Danger,[2★] Fabrice Duvernay,[2] Cornelia Meinert,[3] Uwe J. Meierhenrich,[3] Ferenc Borondics,[4] Thierry Chiavassa[2] and Louis Le Sergeant d'Hendecourt[1★]

Ice mixture made of $H_2O:CH_3OH:NH_3$ = 3:1:1

+ UV photolysis

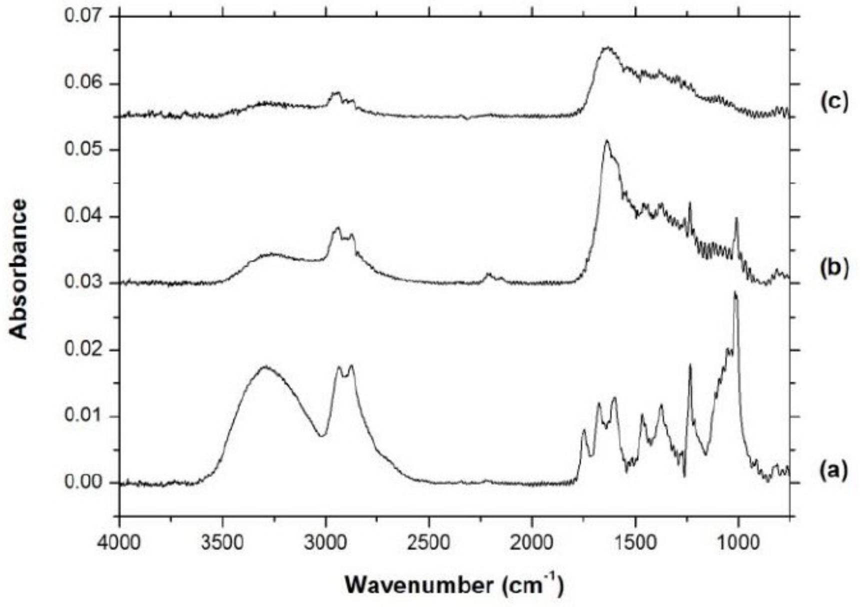


Figure 3. Infrared spectra of sample 2. **(a)** Non irradiated organic residue, much thinner than sample 1. **(b)** VUV-irradiated (73h) residue. **(c)** Photolyzed (insoluble) matter only, after liquid water extraction. The spectra were all taken within the cryogenic chamber.

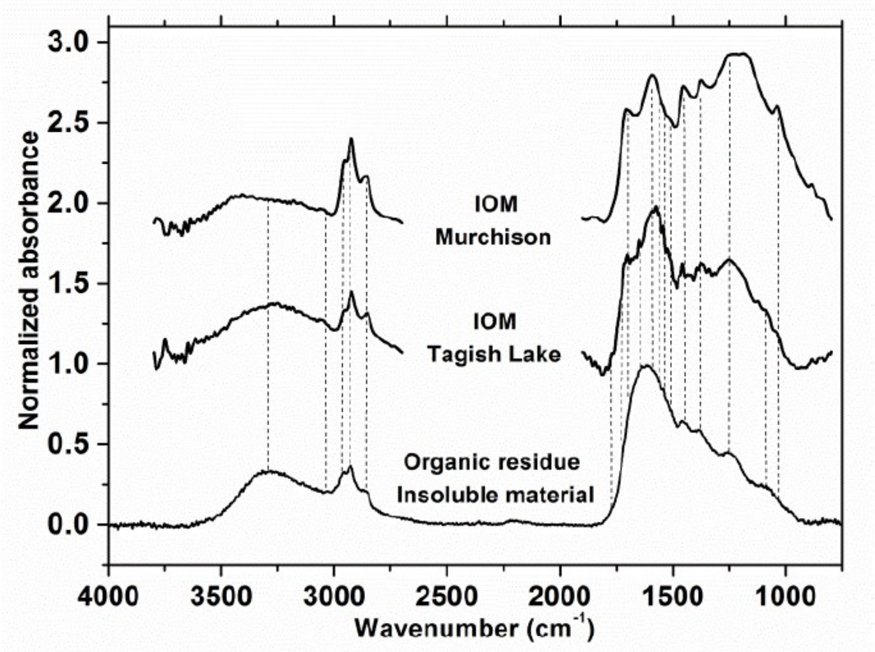


Figure 5. Comparison between the infrared spectra of our insoluble residue (bottom) with the spectra of IOM extracted from Tagish-Lake and Murchison. For meteorites, data are taken from Kebukawa et al (2011). The vertical dotted lines refer to the bands observed in the enlarged figure from the infrared spectrum of the residue (Figure 4 A and B).

The Astrophysical Journal, 673: L225–L228, 2008 February 1

A SELF-PERPETUATING CATALYST FOR THE PRODUCTION OF COMPLEX ORGANIC MOLECULES IN PROTOSTELLAR NEBULAE

Joseph A. Nuth III,[1] Natasha M. Johnson,[1,2] and Steven Manning[1,3]
Received 2007 November 19; accepted 2007 December 17; published 2008 January 8

ABSTRACT

When hydrogen, nitrogen, and CO are exposed to amorphous iron silicate surfaces at temperatures between 500 and 900 K a carbonaceous coating forms via Fischer-Tropsch-type reactions. Under normal circumstances such a coating would impede or stop further reaction. However, we find that this coating is a better catalyst than the amorphous iron silicates that initiate these reactions. Formation of a self-perpetuating catalytic coating on grain surfaces could explain the rich deposits of macromolecular carbon found in primitive meteorites and would imply that protostellar nebulae should be rich in organic material.

How do we make IOM like material ?

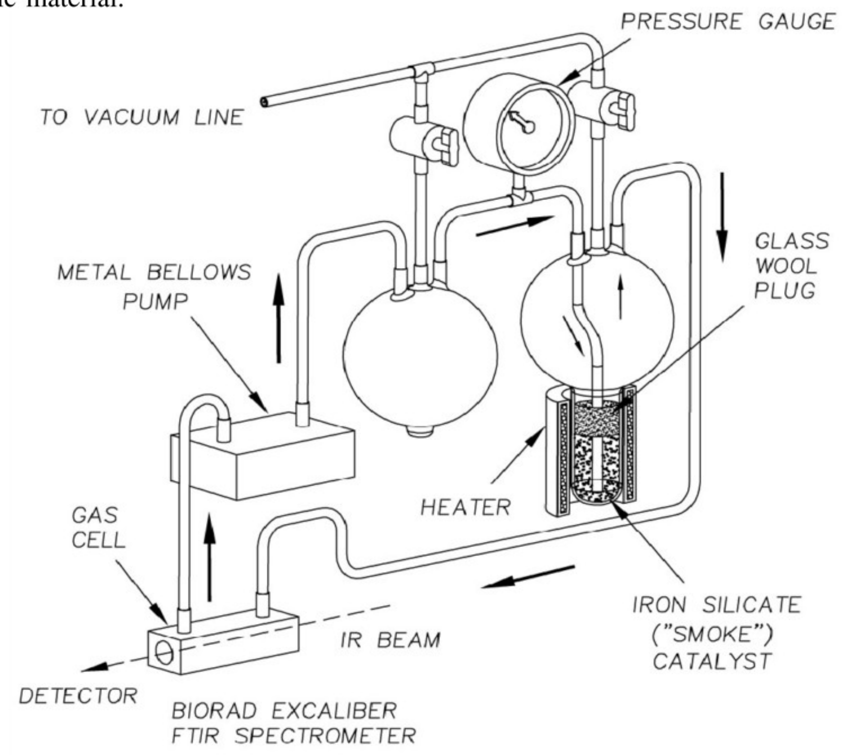


Fig. 1.—Simple experimental apparatus used to circulate reactive gas mixtures over potential catalysts at controlled temperatures and monitor the changes in the circulating gas vie infrared spectroscopy.

5. SUMMARY

Laboratory experiments have demonstrated that a macromolecular, nitrogen-rich, organic coating forms on the surfaces of many different grain types and that this coating efficiently promotes the conversion of CO, N_2, and H_2 into additional layers of organic material. Such grain coatings could have been efficiently incorporated into growing planetesimals and would then be modified by heating, hydration, and other lithification processes that produced the modern population of asteroids and meteorites. Much more experimental work is required to understand the metamorphism of the initial organic materials contained within various types of evolving planetesimal, and the analogs produced in these experiments are intended for such experiments. However, finding an organic coating that will naturally form under conditions in protostellar nebulae, and that will continue to grow as long as it is exposed to a CO, N_2, and H_2 rich gas at moderately high temperatures, adds an entirely new dimension to the chemistry of these nebulae. The organic content of protostars can no longer be modeled as the remnant organic coatings on grains from parent dark molecular clouds, even with the addition of new materials formed by similar processes in the cold dark interiors of such nebulae. One must now account for abundant organic material produced in the innermost regions of these nebulae and transported outward, possibly to the Kuiper Belt and beyond, by the same mechanisms that brought crystalline grains and fragments of chondrules and CAIs to comet Wild 2.

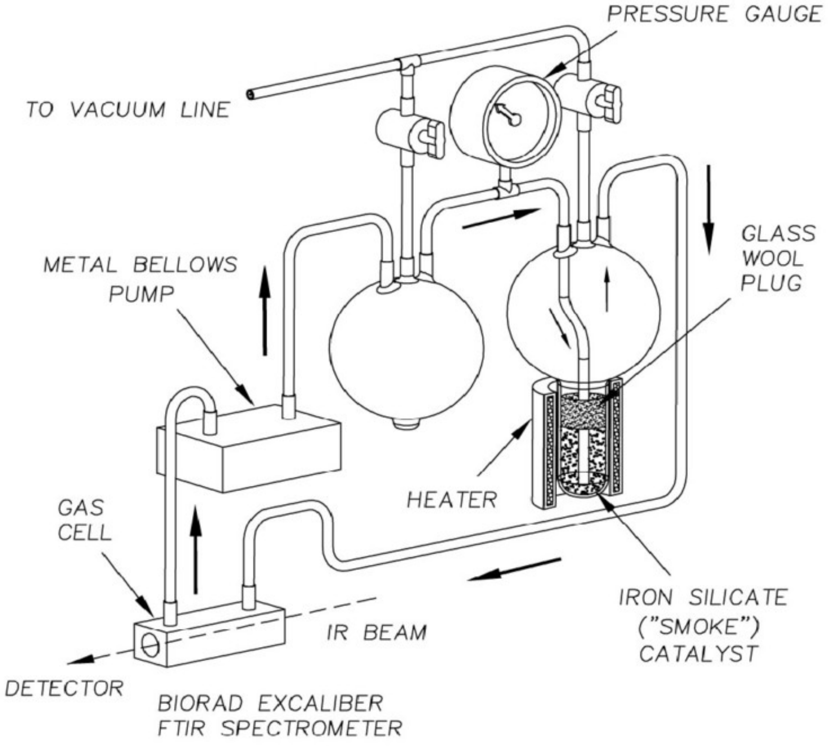
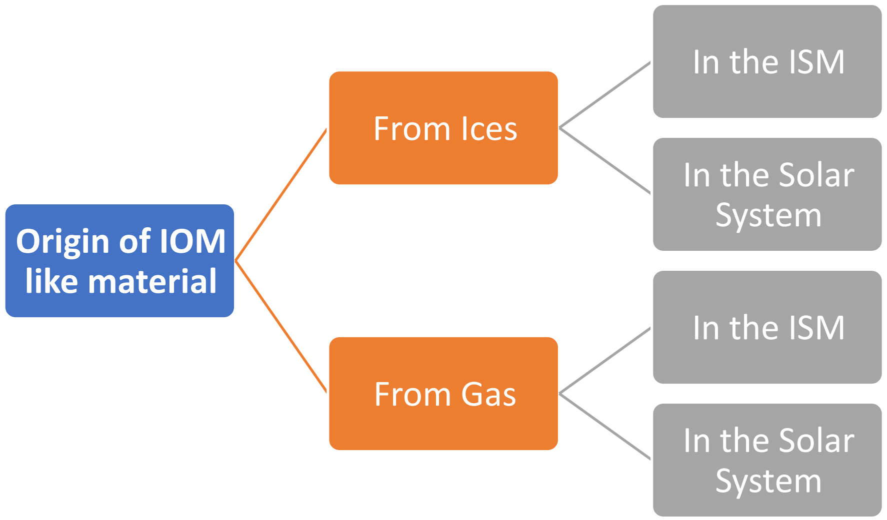


FIG. 1.—Simple experimental apparatus used to circulate reactive gas mixtures over potential catalysts at controlled temperatures and monitor the changes in the circulating gas vie infrared spectroscopy.

How do we make IOM like material ?



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Origin of insoluble organic matter in type 1 and 2 chondrites: New clues, new questions

Eric Quirico [a,*], François-Régis Orthous-Daunay [a,1], Pierre Beck [a], Lydie Bonal [a], Rosario Brunetto [b], Emmanuel Dartois [b], Thomas Pino [c], Gilles Montagnac [d], Jean-Noël Rouzaud [e], Cécile Engrand [f], Jean Duprat [f]

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The origin of organic matter (OM) in primitive chondrites has been an ongoing and open debate over the last 40 years. After the discovery of extraterrestrial amino acids in Murchison in the 70s, Fischer–Tropsch reactions in the solar nebula were invoked to account for the formation of both soluble (SOM) and insoluble (IOM) organic matter.

How do we make IOM like material ?

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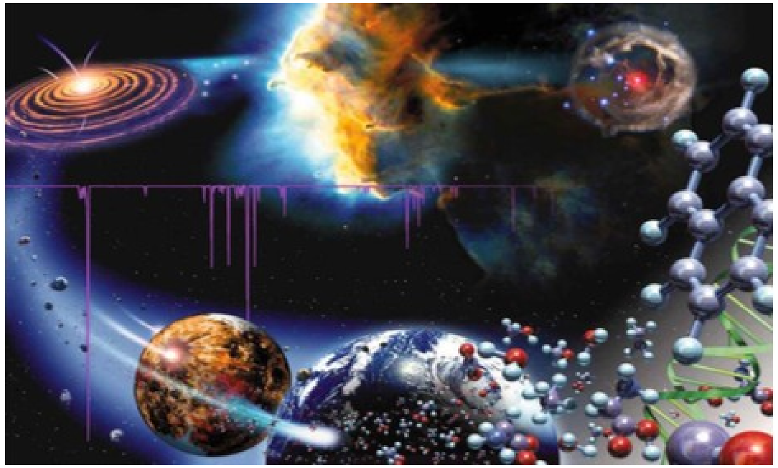
Abstract

Insoluble organic matter (IOM) extracted from primitive chondrites is a polyaromatic solid with a structure and composition resembling that of terrestrial kerogens. A survey of its composition and structure has been carried out on a series of 27 CR, CM, CI and ungrouped C2 carbonaceous chondrites (Tagish Lake, Bells, Essebi, Acfer 094) using infrared and multi-wavelength Raman micro-spectroscopy (244, 514 and 785 nm laser excitations). The results show that chondritic IOM from PCA 91008 (CM2), WIS 91600 (CM2), QUE 93005 (CM2), Tagish Lake (C2 ungrouped) and possibly Cold Bokkeveld (CM2) has been subjected to the past action of short duration thermal metamorphism, presumably triggered by impacts. The IOM in most of the CM chondrites that experienced moderate to heavy aqueous alteration may have been slightly modified by collision-induced heating. However, even IOM from chondrites that escaped significant thermal metamorphism displays Raman characteristics consistent with a formation by thermal processing, either in the protosolar disk or in the parent body. An alternative energetic process to thermal heating is ion irradiation. After thoroughly analyzing both these scenarii, no conclusion can be drawn as to which is the most plausible mechanism nor whether the heating process took place prior or after accretion. The results show for the first time that the width of the G band in spectra collected with a 514 nm excitation correlates with the O/C atomic ratio, suggesting a major role of oxygen in the cross-linking of polyaromatic units.



Astrochemistry is relying strongly on laboratory experimentation

It's a playfield for chemists, working with astrophysicists

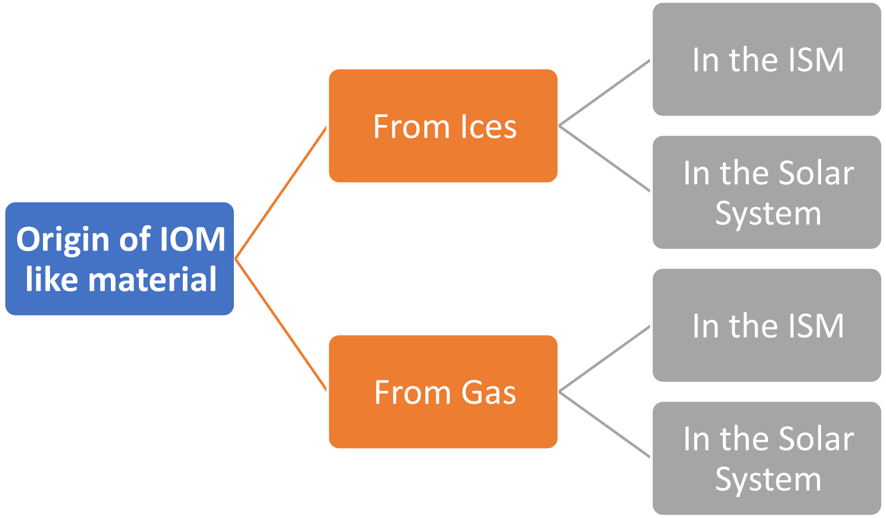
Abiotic organic chemistry in astrophysical environments produces diversity & complexity

This complexity is a challenge for analytical tools. The number of detected compounds increases as the analytical tools improve.

Life is more about organisation of this complexity. It takes much more than finding new organic compounds in astrophysical environments to study the origin of life

This image provides a steeply angled view of a region of asteroid Bennu's equator and northern hemisphere. It was taken by the PolyCam camera on NASA's OSIRIS-REx spacecraft on March 28 2019 from a distance of 3.6 km. The field of view is 52 m wide. For scale, the largest boulder in the upper left corner of the image is 14.5 m wide, which is about the length of a semi-truck trailer

How do we make IOM like material ?



Quirico et al. 2014

The detection of crystalline minerals in STARDUST grains and the ubiquitous presence of a polyaromatic solid showing strong similarities with chondritic IOM in grains of presumed cometary origin (AMMs and chondritic porous stratospheric IDPs) have challenged the idea of ISM heritage, as these crystalline minerals were definitely formed in the proto-solar disk.