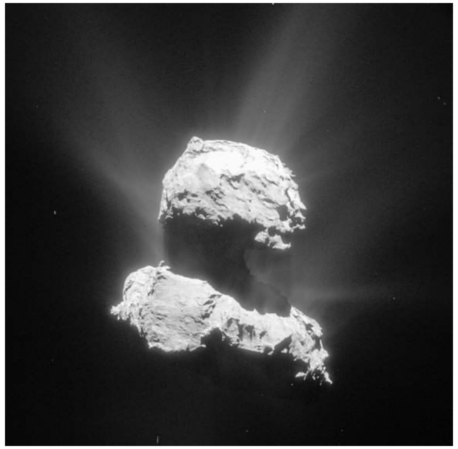

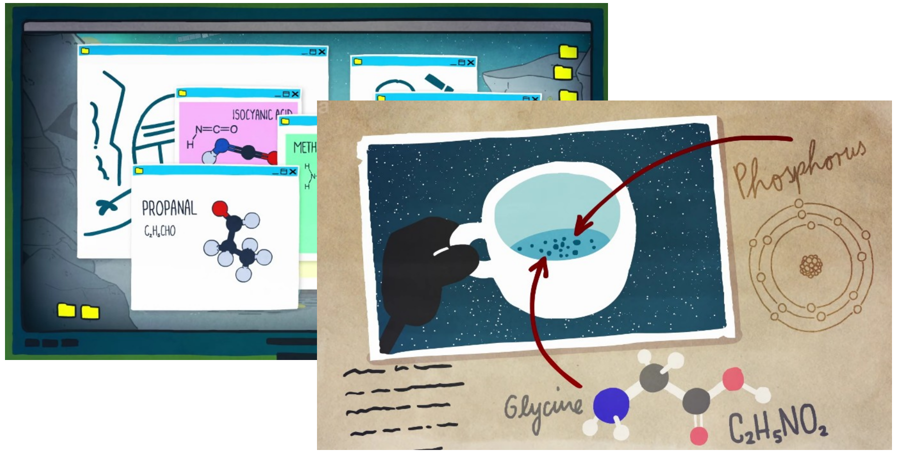

The astrobiological legacy of Rosetta

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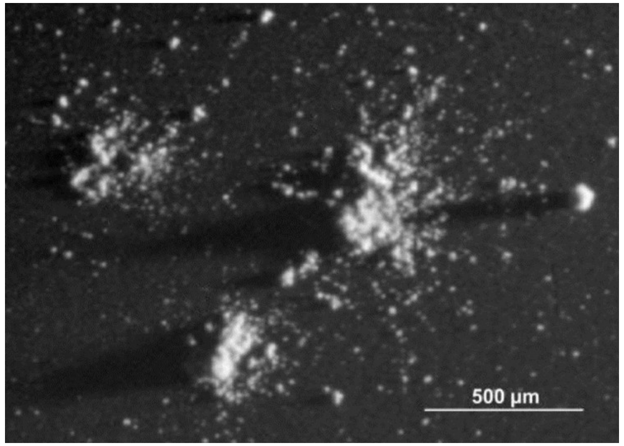

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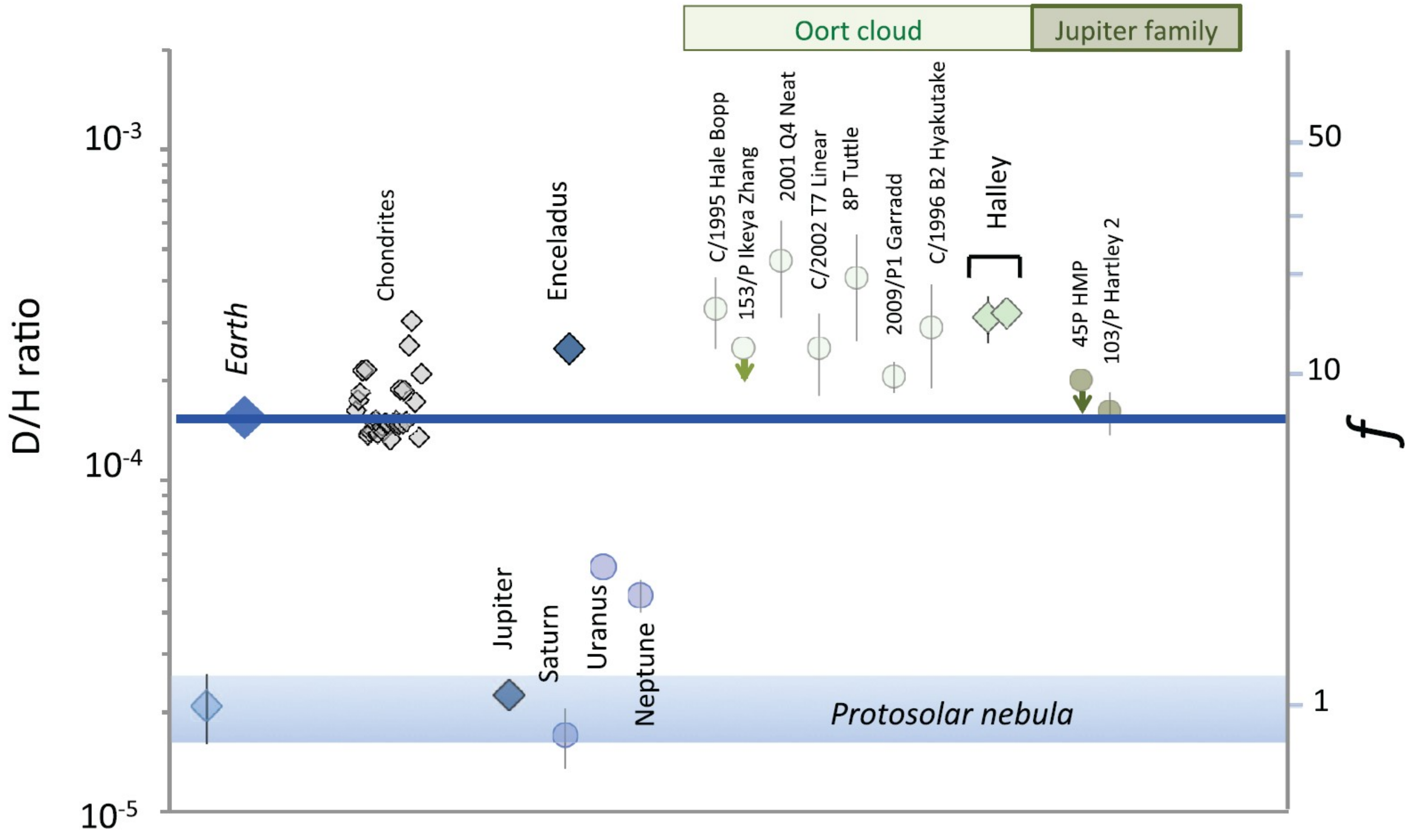
Water in comet 67P



Sciencexpress Reports

67P/Churyumov-Gerasimenko, a Jupiter family comet with a high D/H ratio

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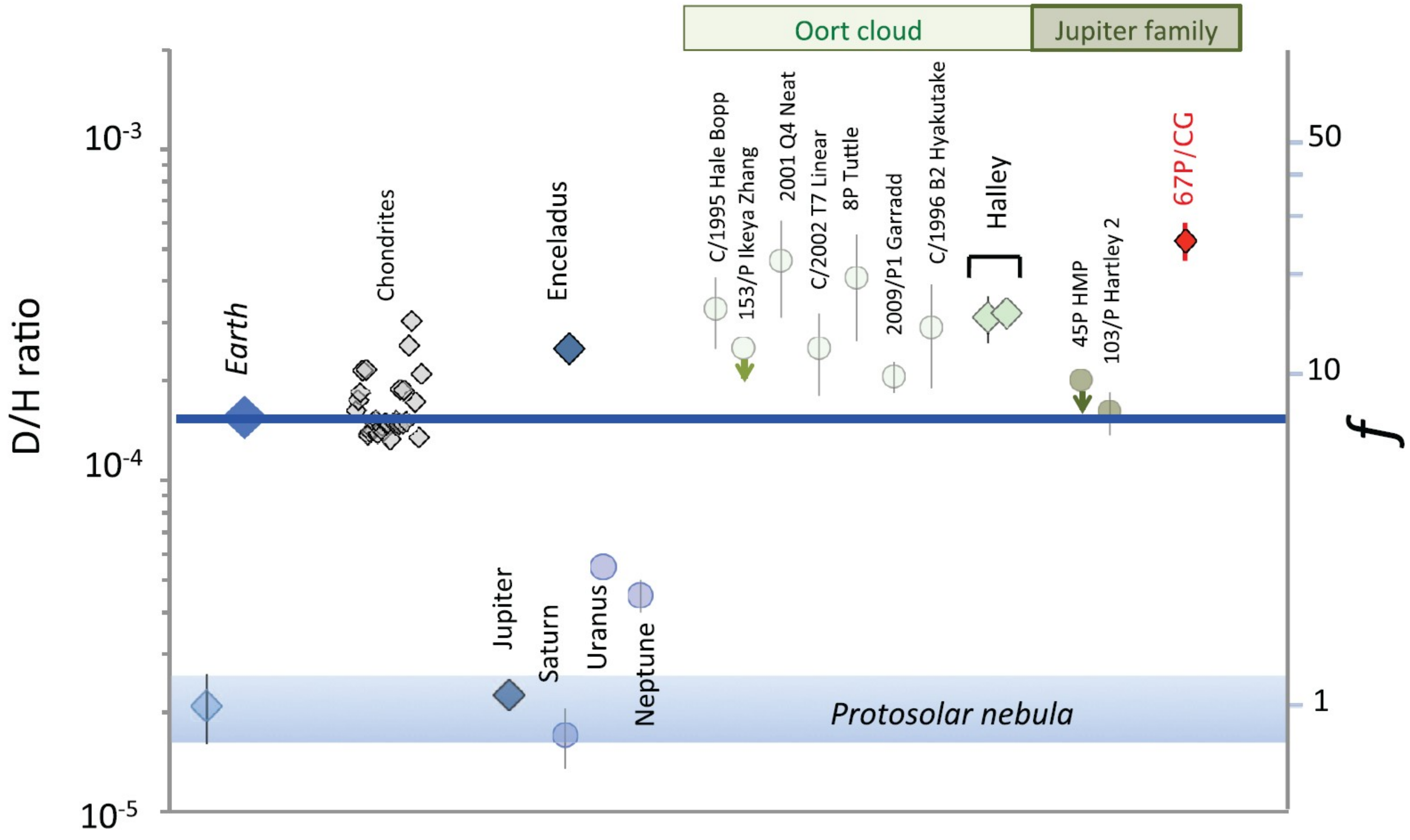
The provenance of water and organic compounds on the Earth and other terrestrial planets has been discussed for a long time without reaching a consensus. One of the best means to distinguish between different scenarios is by determining the D/H ratios in the reservoirs for comets and the Earth's oceans. Here we report the direct in situ measurement of the D/H ratio in the Jupiter family comet 67P/Churyumov-Gerasimenko by the ROSINA mass spectrometer aboard ESA's Rosetta spacecraft, which is found to be (5.3 ± 0.7) × 10^{-4}, that is, ~3 times the terrestrial value. Previous cometary measurements and our new finding suggest a wide range of D/H ratios in the water within Jupiter family objects and preclude the idea that this reservoir is solely composed of Earth ocean-like water.

the Jupiter family comet 67P/Churyumov-Gerasimenko.

The mass spectrometer ROSINA-DFMS (Rosetta Orbiter Sensor for Ion and Neutral Analysis, Double Focusing Mass Spectrometer) on the European cometary space mission Rosetta is designed to measure isotopic ratios (*8*). Its mass resolution and high dynamic range enable it to detect very rare species such as $HD^{18}O$ relative to the most abundant isotope $H_2{}^{16}O$ (*9*). ROSINA has the capability to measure all isotopic ratios in water independently (D/H, $^{17}O/^{16}O$, $^{18}O/^{16}O$) and the D/H ratio can be deduced from two different species, namely $HD^{16}O/H_2{}^{16}O$ and $HD^{18}O/H_2{}^{18}O$.

Rosetta has a neutral gaseous background due to spacecraft outgassing. The permanent particle density in the close vicinity of the spacecraft far away from the comet is around 10^6 / cm^3 consisting mostly of water, but also of organic material, fragments of hydrazine and vacuum grease (fluorine). Even after 10 years in space and after hibernation the background from Rosetta can be measured and characterized by ROSINA (*10*). The D/H ratio in water outgassed from the Rosetta spacecraft is compatible with the terrestrial value of 1.5×10^{-4} as

Water in comet 67P



Water in comet 67P

D. R. Müller et al.: High D/H ratios in water and alkanes in comet 67P

Table 1. D/H in H_2O during different mission phases and compared to previous evaluations.

Mission phase	Dates	D/H in H_2O	Heliocentric distance (au)	# of evaluated spectra
First equinox	May 2015	$(5.03 \pm 0.17) \times 10^{-4}$	1.71–1.52	44
Perihelion	August 2015	$(5.01 \pm 0.20) \times 10^{-4}$	1.24	37
Peak gas production	30 August 2015	$(4.98 \pm 0.25) \times 10^{-4}$	1.26	22
Second equinox	March 2016	$(5.02 \pm 0.17) \times 10^{-4}$	2.45–2.65	47
Relative mean ratio		$(5.01 \pm 0.10) \times 10^{-4}$		150
Absolute mean ratio		$(5.01 \pm 0.41) \times 10^{-4}$		150
Pre-first equinox [(a)]	Aug./Sep. 2014	$(5.3 \pm 0.7) \times 10^{-4}$	≈3.4	26
Pre-second equinox [(b)]	Dec. 2015/Mar. 2016	$(5.25 \pm 0.7) \times 10^{-4}$	2.0 & 2.6	18

References. [(a)] Altwegg et al. (2015). [(b)] Altwegg et al. (2017).

Muller et al. 2022

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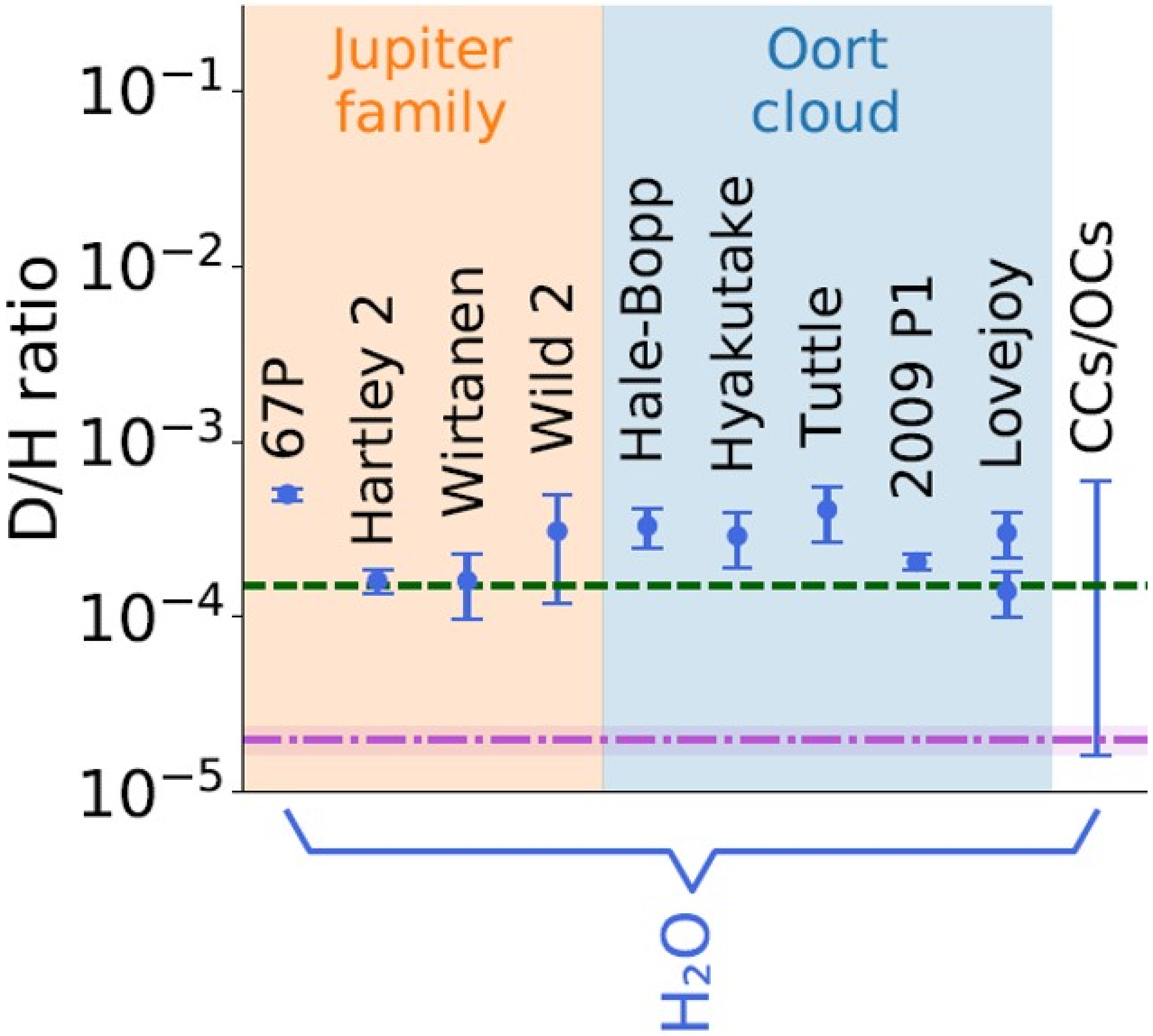

Fig. 5. D/H ratios of water and organic molecules measured in different comets compared to values from the Protosolar Nebula (purple line, Geiss & Gloeckler 2003), the Earth (green line, Wilson 1999), carbonaceous chondrites (CC), ordinary chondrites (OC), interplanetary dust particles (IDP) and ultracarbonaceous Antarctic micrometeorites (UCCAM). D/H in HDO is equal to $2 \cdot D_2O/HDO$. Full references are given in Table B.1.

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Astronomy & Astrophysics

LETTER TO THE EDITOR

Terrestrial deuterium-to-hydrogen ratio in water in hyperactive comets

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ABSTRACT

The D/H ratio in cometary water has been shown to vary between 1 and 3 times the Earth's oceans value, in both Oort cloud comets and Jupiter-family comets originating from the Kuiper belt. This has been taken as evidence that comets contributed a relatively small fraction of the terrestrial water. We present new sensitive spectroscopic observations of water isotopologues in the Jupiter-family comet 46P/Wirtanen carried out using the GREAT spectrometer aboard the Stratospheric Observatory for Infrared Astronomy (SOFIA). The derived D/H ratio of $(1.61 \pm 0.65) \times 10^{-4}$ is the same as in the Earth's oceans. Although the statistics are limited, we show that interesting trends are already becoming apparent in the existing data. A clear anti-correlation is seen between the D/H ratio and the active fraction, defined as the ratio of the active surface area to the total nucleus surface. Comets with an active fraction above 0.5 typically have D/H ratios in water consistent with the terrestrial value. These hyperactive comets, such as 46P/Wirtanen, require an additional source of water vapor in their coma, explained by the presence of subliming icy grains expelled from the nucleus. The observed correlation may suggest that hyperactive comets belong to a population of ice-rich objects that formed just outside the snow line, or in the outermost regions of the solar nebula, from water thermally reprocessed in the inner disk that was transported outward during the early disk evolution. The observed anti-correlation between the active fraction and the nucleus size seems to argue against the first interpretation, as planetesimals near the snow line are expected to undergo rapid growth. Alternatively, isotopic properties of water outgassed from the nucleus and icy grains may be different due to fractionation effects at sublimation. In this case, all comets may share the same Earth-like D/H ratio in water, with profound implications for the early solar system and the origin of Earth's oceans.

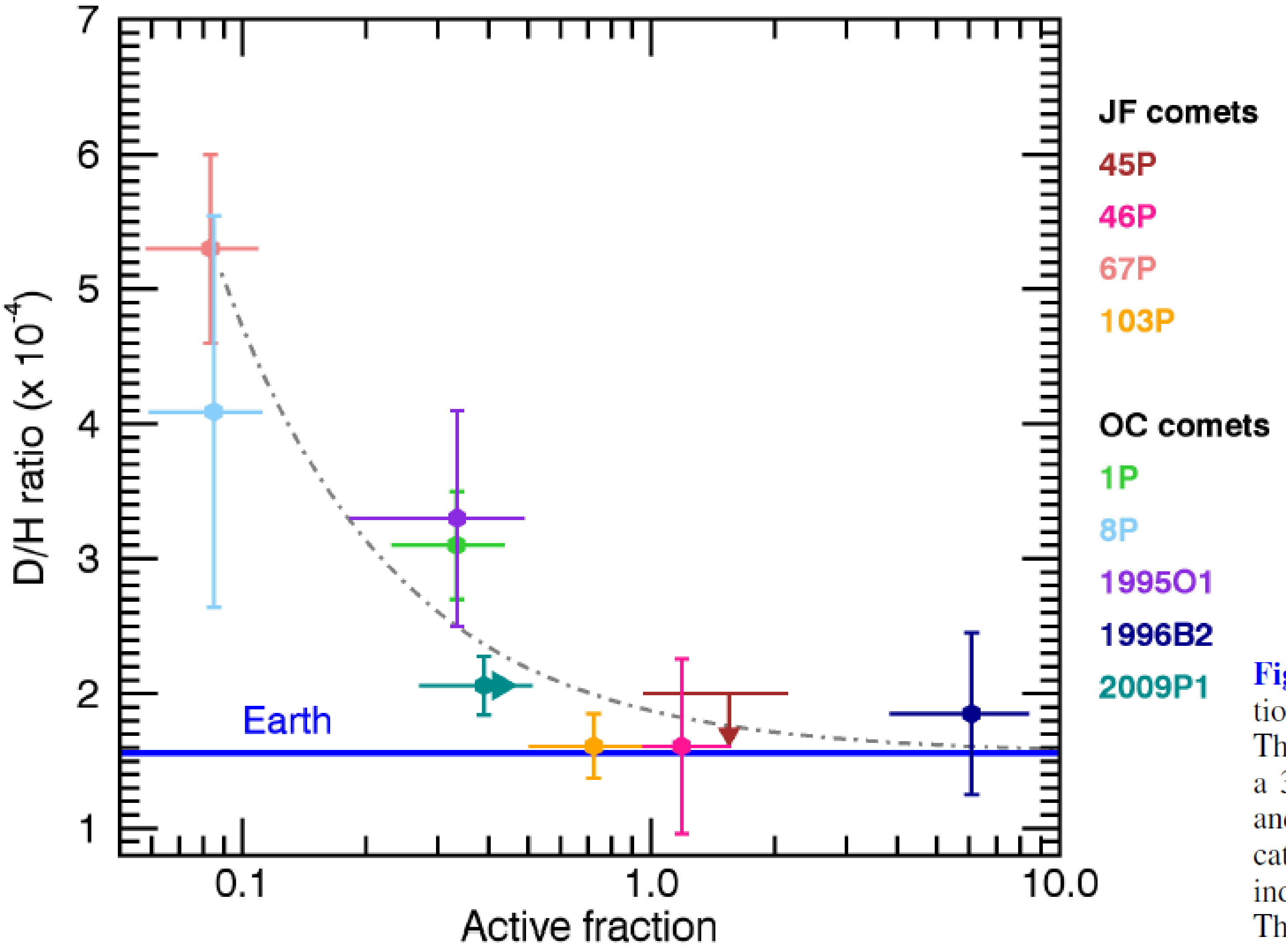
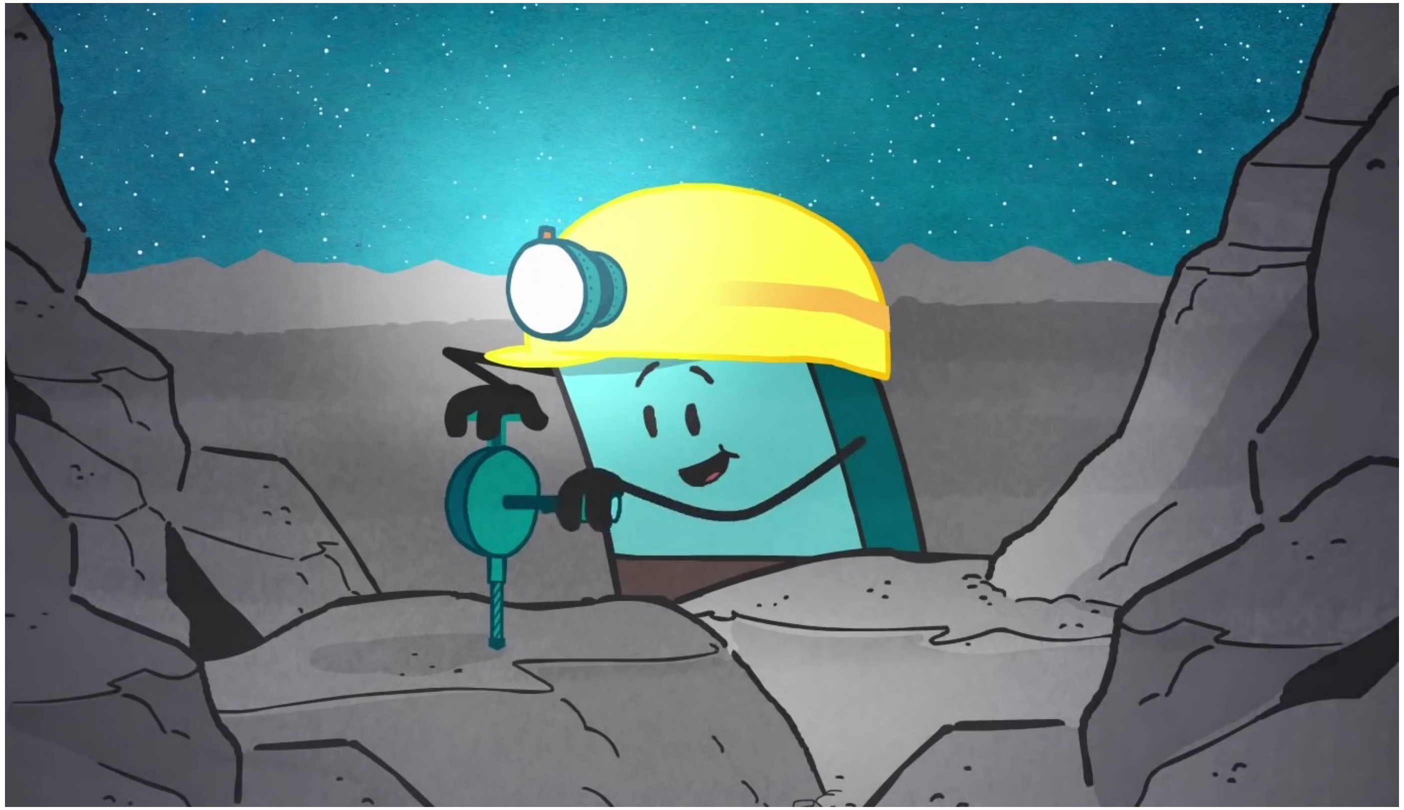


Fig. 2. D/H ratio in cometary water as a function of the active fraction computed from the water production rates measured at perihelion. The uncertainties on the active fraction (horizontal error bars) include a 30% uncertainty on the water production rates (Combi et al. 2019) and the uncertainty on the nucleus size. The color of each symbol indicates a comet; see legend at right, where the dynamical class is also indicated: Oort cloud (OC) or short-period Jupiter-family (JF) comets. The blue horizontal line corresponds to the VSMOW D/H value. The upper limit for the D/H ratio in comet 45P is indicated by a downward arrow and the lower limit for the active fraction in comet 2009P1 by a right arrow. The dash-dotted line shows the expected D/H assuming two sources of water: D-rich (3.5 × VSMOW) from the nucleus and D-poor (VSMOW). Comets with an active fraction equal to 0.08 are assumed to release only D-rich water.

A glimpse of 67P from Philae



Serendipity measurements while Philae was bouncing at the surface of 67P
PTOLEMY
COSAC

CHO-bearing organic compounds at the surface of 67P/Churyumov-Gerasimenko revealed by Ptolemy

I. P. Wright,[1*] S. Sheridan,[1] S. J. Barber,[1] G. H. Morgan,[1] D. J. Andrews,[1] A. D. Morse[1]

The surface and subsurface of comets preserve material from the formation of the solar system. The properties of cometary material thus provide insight into the physical and chemical conditions during their formation. We present mass spectra taken by the Ptolemy instrument 20 minutes after the initial touchdown of the Philae lander on the surface of comet 67P/Churyumov-Gerasimenko. Regular mass distributions indicate the presence of a sequence of compounds with additional -CH_2- and -O- groups (mass/charge ratios 14 and 16, respectively). Similarities with the detected coma species of comet Halley suggest the presence of a radiation-induced polymer at the surface. Ptolemy measurements also indicate an apparent absence of aromatic compounds such as benzene, a lack of sulfur-bearing species, and very low concentrations of nitrogenous material.

In a process guided by the pattern of peaks observed by the PICCA (Positive Ion Cluster Composition Analyzer) instrument (*11*), which identified polyoxymethylene in mass spectral measurements of coma materials from comet Halley during the Giotto mission (*12*), we superimposed mass increments of 14 and 16 (representing additions and losses of -CH_2- and -O_2-, respectively) on the mass spectra, with peaks ascribed to H_2O and CO_2 removed (Fig. 2). The data presented here do not reflect a single idealized compound polymer [e.g., $(CH_2O)_n$] with its ends terminated by H atoms. Rather, they indicate a number of different terminations, with the chain running as either -O-CH_2- or -CH_2-O- (i.e., repeating units of 16:14 or 14:16 *m/z*) (Fig. 3). In principle, such terminations result from H-, HCO-, or CH_3CO-, which can be thought of as radicals arising from hydrogen, formaldehyde, and acetaldehyde, respectively (although it depends on exactly where in the chain one considers the termination to occur). The mass spectra are consistent with the presence of formaldehyde (peaks at *m/z* 29 to 31) and acetaldehyde (peaks at *m/z* 29, 43, and 44), although Ptolemy has insuffi-

as well as H_2O and CO_2. Many of the features of the mass spectra can be explained by the presence of polyoxymethylene, but undoubtedly many other compounds are present at low concentrations. Before the Giotto encounter with Halley, researchers had already conjectured that interstellar grains may contain polyoxymethylene (*19*). The possible presence of similar materials on a comet, as postulated by a consideration of the PICCA results, raised interest in the subject of prebiotic polymers. The most immediate scientific impact of the possible presence of polyoxymethylene was that it provided an explanation for the presence of observable formaldehyde in cometary comae—that is, at distances beyond which the molecular species, if released directly from the nucleus, would be expected to survive (*20*). However, after somewhat straightforward initial interpretations (*21*), more detailed enquiries have uncovered issues that remain unresolved (*22*–*25*).

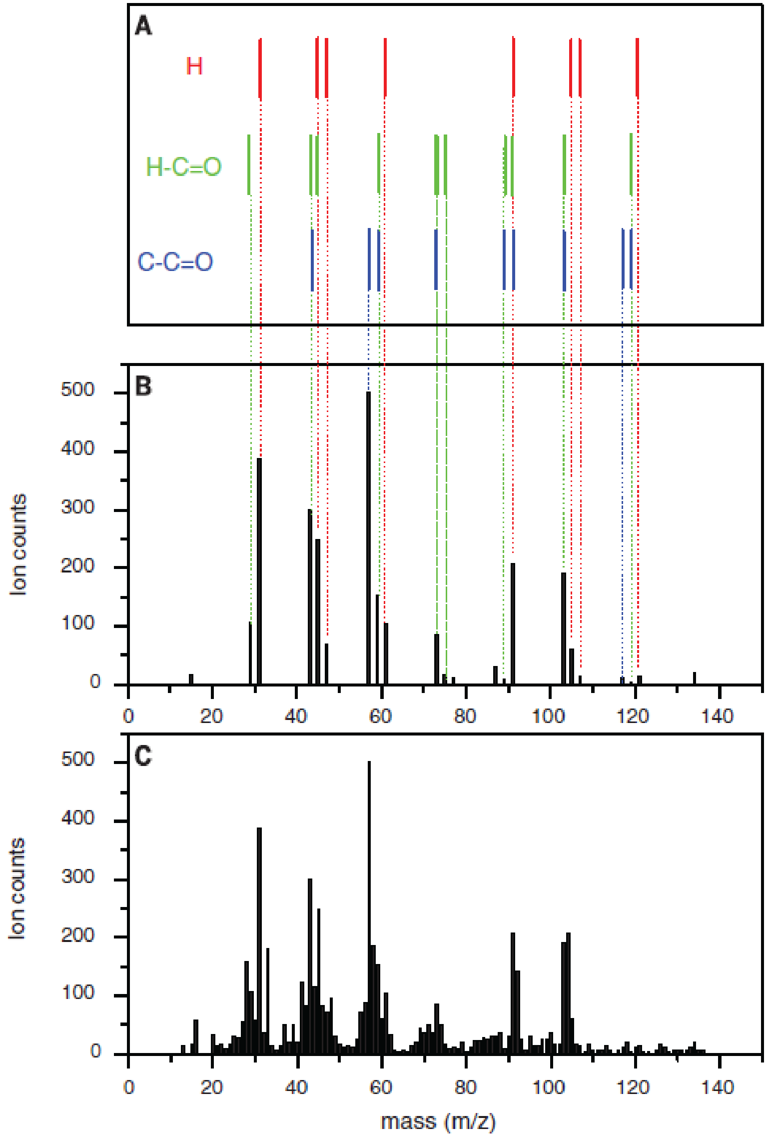


Fig. 2. Proposed polyoxymethylene fit to the Ptolemy spectra. (**A**) Schematic for proposed mass fragments of polyoxymethylene with different terminations. (**B**) Peaks that are considered to be from polyoxymethylene. (**C**) Ptolemy spectra with peaks from H_2O and CO_2 removed.

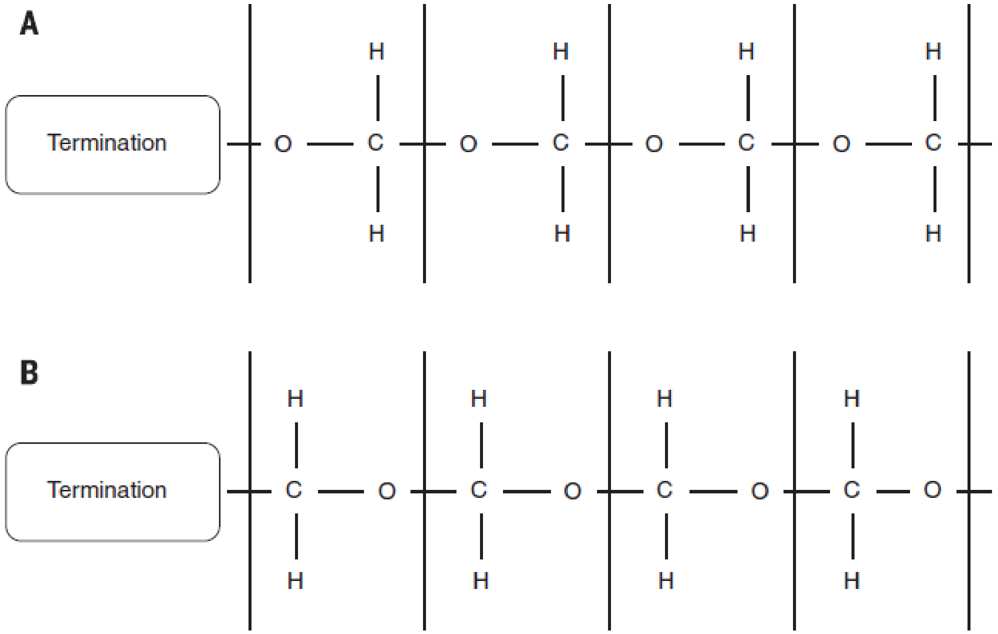


Fig. 3. Idealized polyoxymethylene chains. (**A**) Idealized polyoxymethylene chain with repeating units of 16:14 *m/z* (-O-, $-CH_2-$). For the mass spectra taken by Ptolemy, we considered three different types of termination: H-, HCO-, and CH_3CO-. The H- termination would produce peaks at 1, 17, 31, 47, 61, 77, 91, 107, and 121 *m/z*. For HCO-, peaks would occur at 29, 45, 59, 75, 89, 105, and 119. For CH_3CO-, peaks would occur at 43, 59, 73, 89, 103, and 119. Here, we consider only those peaks up to a mass of about 120. (**B**) The equivalent chain, but with repeating units in the reverse order [14:16 *m/z* ($-CH_2-$, -O-)]. In this case, the H- termination would produce peaks at 1, 15, 31, 45, 61, 75, 91, 105, and 121 *m/z*. For HCO-, peaks would occur at 29, 43, 59, 73, 89, 103, and 119. For CH_3CO-, peaks would occur at 43, 57, 73, 87, 103, and 117.

POM already suggested to interpret Giotto data at comet 1P/Halley (Huebner, 1987)

Presence of POM could be responsible of the distributed H_2CO in Halley et Hale-Bopp (Cottin et al, 2004 / Fray et al, 2006)

CH_3-CO-O -$(CH_2O)_n$- CO-CH_3

polyoxymethylene diacetate

HO -$(CH_2O)_n$- H

paraformaldehyde or polyoxymethylene

CH_3O -$(CH_2O)_n$- CH_3

polyoxymethylene dimethylether

Organic compounds on comet 67P/Churyumov-Gerasimenko revealed by COSAC mass spectrometry

Fred Goesmann,[1*] Helmut Rosenbauer,[1] Jan Hendrik Bredehöft,[2] Michel Cabane,[3] Pascale Ehrenfreund,[4,5] Thomas Gautier,[6] Chaitanya Giri,[1,7] Harald Krüger,[1] Léna Le Roy,[8] Alexandra J. MacDermott,[9] Susan McKenna-Lawlor,[10] Uwe J. Meierhenrich,[7] Guillermo M. Muñoz Caro,[11] Francois Raulin,[12] Reinhard Roll,[1] Andrew Steele,[13] Harald Steininger,[1] Robert Sternberg,[12] Cyril Szopa,[3] Wolfram Thiemann,[2] Stephan Ulamec[14]

Comets harbor the most pristine material in our solar system in the form of ice, dust, silicates, and refractory organic material with some interstellar heritage. The evolved gas analyzer Cometary Sampling and Composition (COSAC) experiment aboard Rosetta's Philae lander was designed for in situ analysis of organic molecules on comet 67P/Churyumov-Gerasimenko. Twenty-five minutes after Philae's initial comet touchdown, the COSAC mass spectrometer took a spectrum in sniffing mode, which displayed a suite of 16 organic compounds, including many nitrogen-bearing species but no sulfur-bearing species, and four compounds—methyl isocyanate, acetone, propionaldehyde, and acetamide—that had not previously been reported in comets.

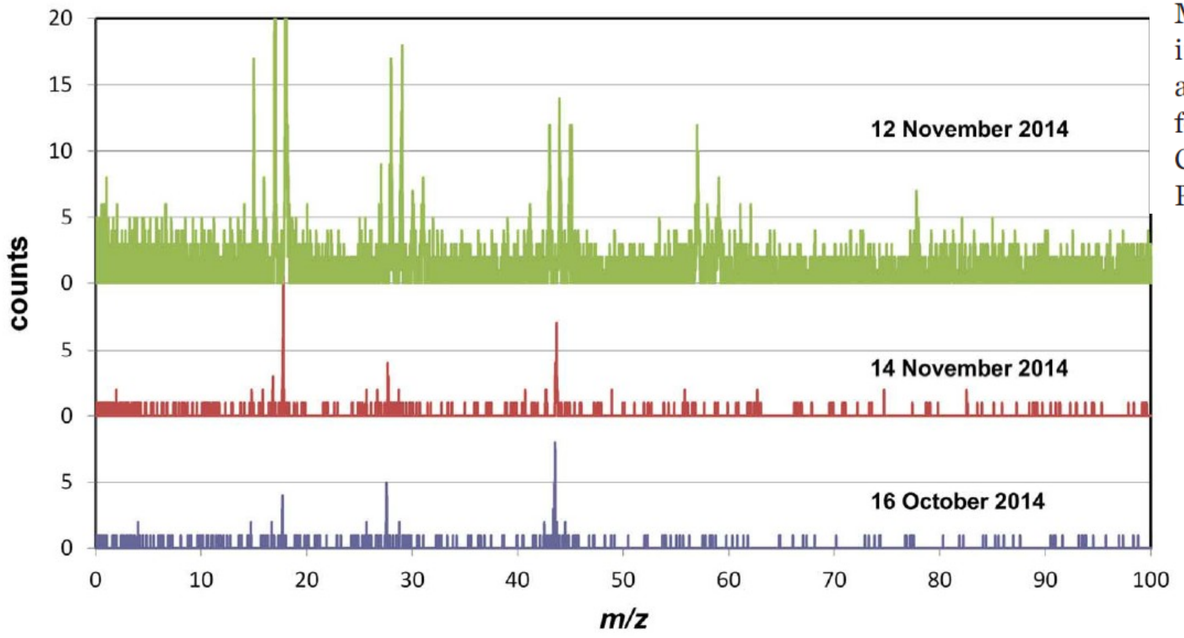


Fig. 1. Mass spectra taken by COSAC in "sniffing mode." Top (green): spectrum taken 25 min after first touchdown; the *m/z* 18 peak reached a height of 330 counts, but the spectrum is truncated to show smaller peaks more clearly; middle (red): final spectrum, taken 2 days later at the current Philae position; bottom (blue): first spectrum, obtained in orbit 27 days before landing, from a distance of 10 km.

exhaust tubes located on the bottom of the lander, where they pointed toward the surface, whereas Ptolemy sampled ambient coma gases entering exhaust tubes located on top of the lander, where they pointed toward the sky (possibly with the addition of some dust that made its way around the lander). That COSAC detected far more nitrogen-bearing compounds than Ptolemy agrees with earlier observations that nitrogen was more abundant in the dust than in the gas of comet Halley (*18*). The Ptolemy team interpret their mass spectrum as fragments of polyoxymethylene polymer, with a strong CO_2 peak of intensity 20% relative to water. COSAC did not detect ambient coma gases (which were dominated in Ptolemy data by CO_2 with a few polymer fragments). The COSAC MS maintains a constant pressure; thus, subliming gases from our ground sample pushed the ambient coma gases outside the COSAC MS. Before sublimation, the total pressure inside the COSAC MS was dominated by CO_2, in line with Ptolemy data and prelanding COSAC spectra.

Table 1. The 16 molecules used to fit the COSAC mass spectrum.

Name	Formula	Molar mass (u)	MS fraction	Relative to water
Water	H_2O	18	80.92	100
Methane	CH_4	16	0.70	0.5
Methanenitrile (hydrogen cyanide)	HCN	27	1.06	0.9
Carbon monoxide	CO	28	1.09	1.2
Methylamine	CH_3NH_2	31	1.19	0.6
Ethanenitrile (acetonitrile)	CH_3CN	41	0.55	0.3
Isocyanic acid	HNCO	43	0.47	0.3
Ethanal (acetaldehyde)	CH_3CHO	44	1.01	0.5
Methanamide (formamide)	$HCONH_2$	45	3.73	1.8
Ethylamine	$C_2H_5NH_2$	45	0.72	0.3
Isocyanomethane (methyl isocyanate)	CH_3NCO	57	3.13	1.3
Propanone (acetone)	CH_3COCH_3	58	1.02	0.3
Propanal (propionaldehyde)	C_2H_5CHO	58	0.44	0.1
Ethanamide (acetamide)	CH_3CONH_2	59	2.20	0.7
2-Hydroxyethanal (glycolaldehyde)	CH_2OHCHO	60	0.98	0.4
1,2-Ethanediol (ethylene glycol)	$CH_2(OH)CH_2(OH)$	62	0.79	0.2

The COSAC molecules form a consistent set related by plausible formation pathways (Fig. 3). A nitrogen source such as NH_3 must originally have been abundant to form the many N-bearing species, but could since have mostly evaporated or been used up in reactions. All the COSAC organics can be formed by UV irradiation and/or radiolysis of ices due to the incidence of galactic and solar cosmic rays: alcohols and carbonyls derived from CO and H_2O ices (*19*), and amines and nitriles from CH_4 and NH_3 ices (*20*). Hydrolysis of nitriles produces amides, which are linked to isocyanates by isomerization.

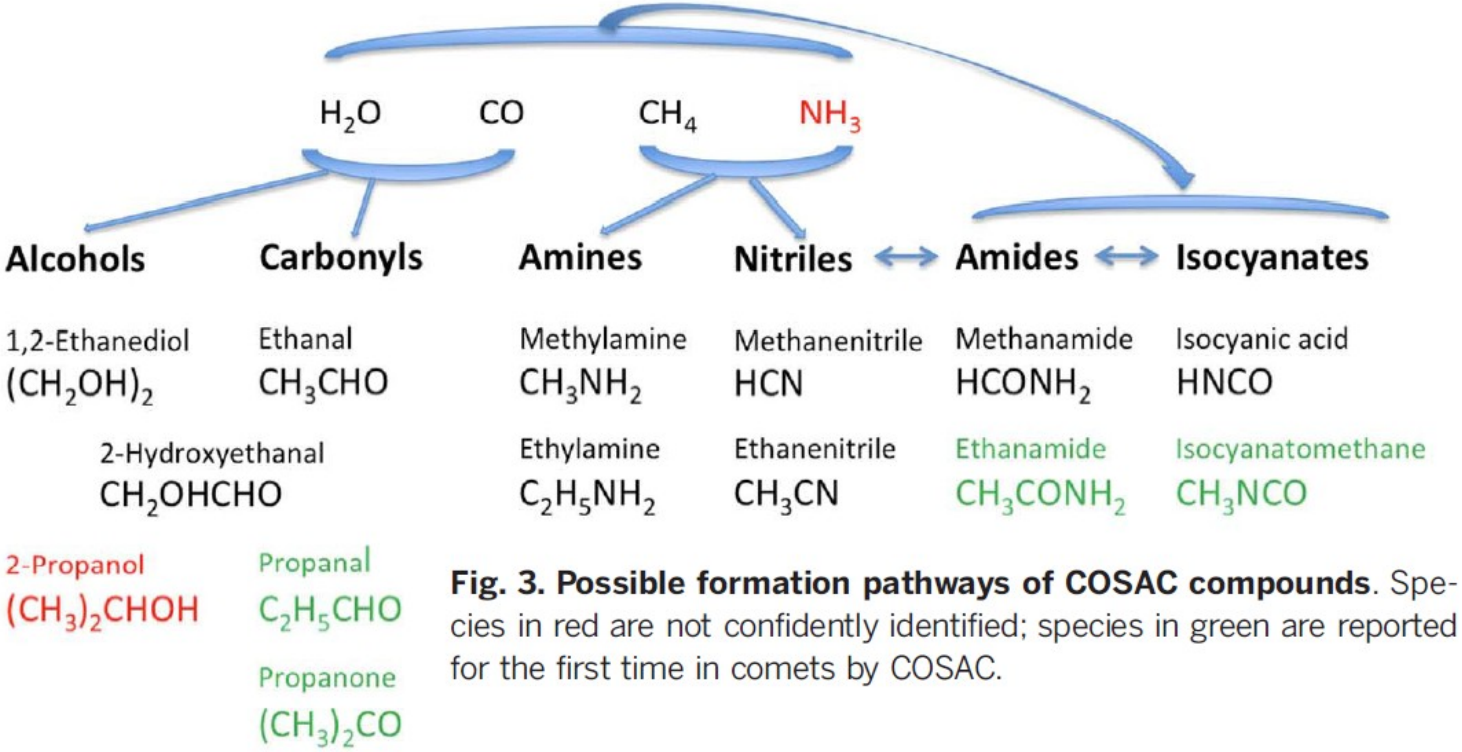


Fig. 3. Possible formation pathways of COSAC compounds. Species in red are not confidently identified; species in green are reported for the first time in comets by COSAC.

A signature of organic chemistry in ice phase (interstellar cloud / protosolar nebula) found by COSAC ?

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Astrochemistry *Very Important Paper*

ESA's Cometary Mission Rosetta—Re-Characterization of the COSAC Mass Spectrometry Results

Guillaume Leseigneur, Jan Hendrik Bredehöft, Thomas Gautier, Chaitanya Giri, Harald Krüger, Alexandra J. MacDermott, Uwe J. Meierhenrich, Guillermo M. Muñoz Caro, François Raulin, Andrew Steele, Harald Steininger, Cyril Szopa, Wolfram Thiemann, Stephan Ulamec, and Fred Goesmann*

In memory of Helmut Rosenbauer († May 5, 2016)

Abstract: The most pristine material of the Solar System is assumed to be preserved in comets in the form of dust and ice as refractory matter. ESA's mission Rosetta and its lander Philae had been developed to investigate the nucleus of comet 67P/Churyumov–Gerasimenko in situ. Twenty-five minutes after the initial touchdown of Philae on the surface of comet 67P in November 2014, a mass spectrum was recorded by the time-of-flight mass spectrometer COSAC onboard Philae. The new characterization of this mass spectrum through non-negative least squares fitting and Monte Carlo simulations reveals the chemical composition of comet 67P. A suite of 12 organic molecules, 9 of which also found in the original analysis of this data, exhibit high statistical probability to be present in the grains sampled from the cometary nucleus. These volatile molecules are among the most abundant in the comet's chemical composition and represent an inventory of the first raw materials present in the early Solar System.

Interpretation of the mass spectrum still debated… (see Altweg et al., 2017 & Leseigneur et al., 2022)

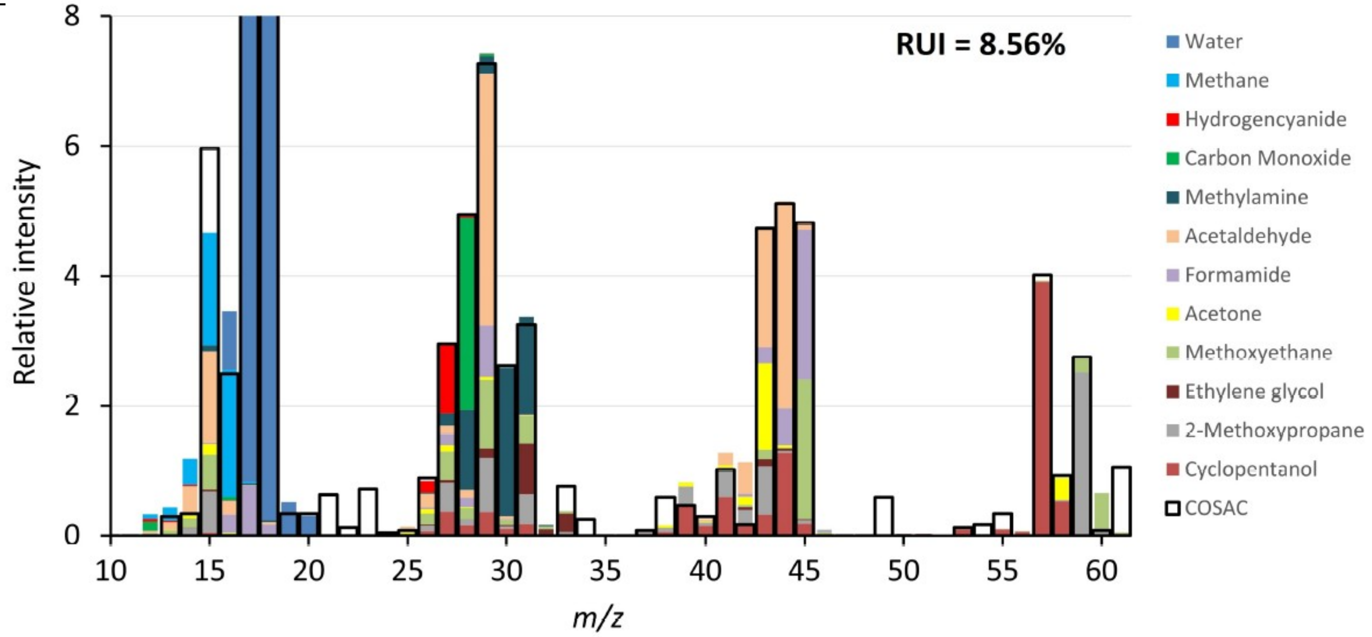
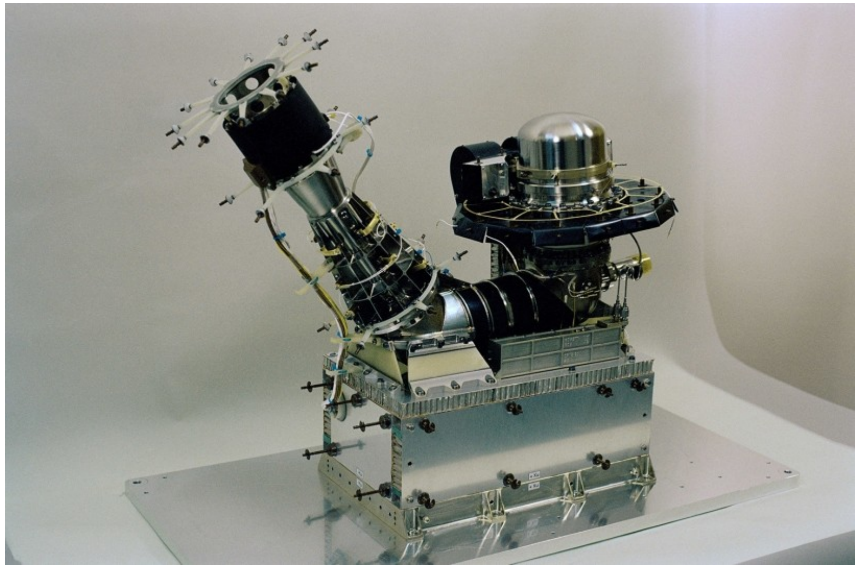
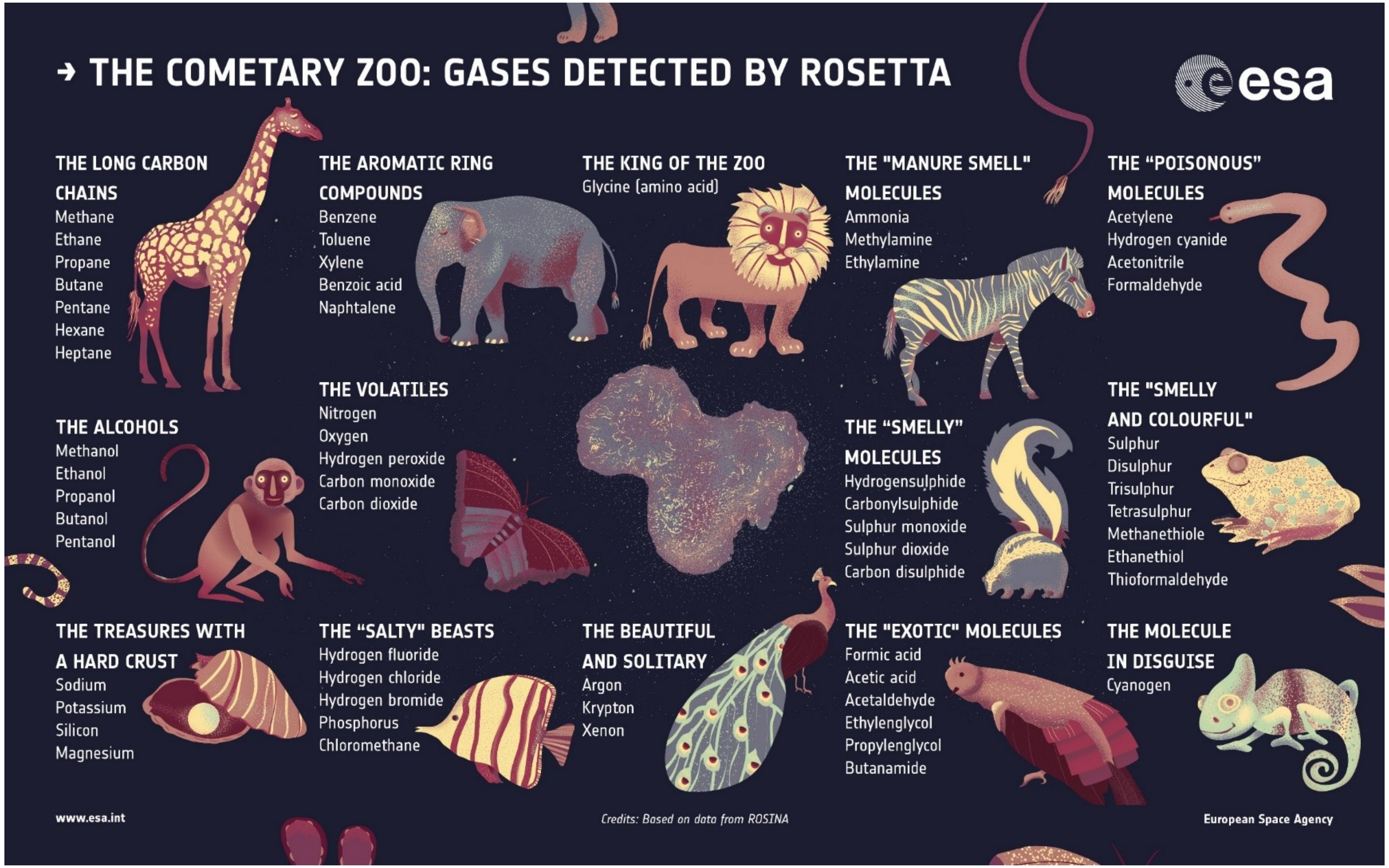


Figure 3. Individual color-coded contributions of molecules to the fitting of the CMS (black outline) when using our shortlist of 12 molecules. This is the fit without Monte Carlo iteration ($N=0$), meaning this is the exact CMS fitted by exact NIST mass spectra. The same plot comparing the CT fit, this figure, and the same one with the top 14 molecules (adding ethane and N-methylformamide) is shown in Figure S1.

Detections in the gaseous phase: large diversity but how much in abundance ?



DFMS (Double Focusing Magnetic Mass Spectrometer)



Rosetta Orbiter Spectrometer for Ion and Neutral Analysis ROSINA

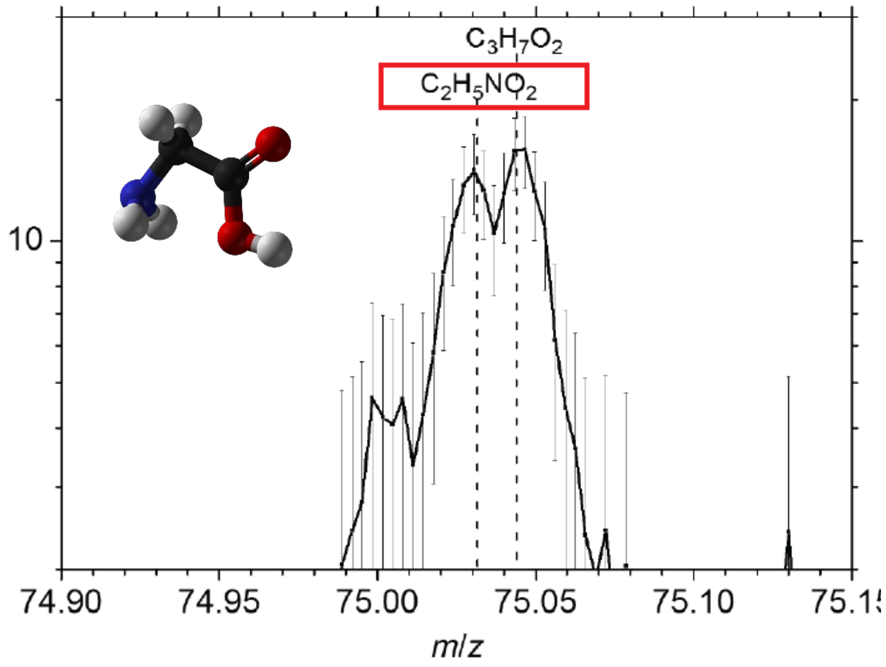
RESEARCH ARTICLE

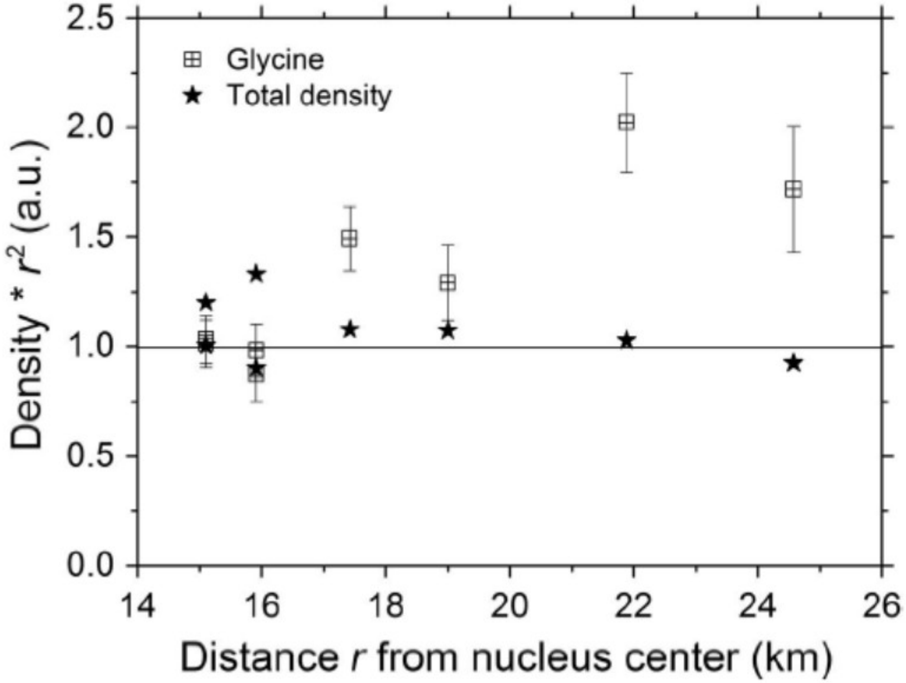
SPACE SCIENCES

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

10.1126/sciadv.1600285

Kathrin Altwegg,[1,2*] Hans Balsiger,[1] Akiva Bar-Nun,[3] Jean-Jacques Berthelier,[4] Andre Bieler,[1,5] Peter Bochsler,[1] Christelle Briois,[6] Ursina Calmonte,[1] Michael R. Combi,[5] Hervé Cottin,[7] Johan De Keyser,[8] Frederik Dhooghe,[8] Bjorn Fiethe,[9] Stephen A. Fuselier,[10] Sébastien Gasc,[1] Tamas I. Gombosi,[5] Kenneth C. Hansen,[5] Myrtha Haessig,[1,10] Annette Jäckel,[1] Ernest Kopp,[1] Axel Korth,[11] Lena Le Roy,[2] Urs Mall,[11] Bernard Marty,[12] Olivier Mousis,[13] Tobias Owen,[14] Henri Rème,[15,16] Martin Rubin,[1] Thierry Sémon,[1] Chia-Yu Tzou,[1] James Hunter Waite,[10] Peter Wurz[1]





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).

A&A 630, A32 (2019)
https://doi.org/10.1051/0004-6361/201935018

Astronomy & Astrophysics

Rosetta mission full comet phase results Special issue

Distributed glycine in comet 67P/Churyumov-Gerasimenko

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[7] Università degli Studi di Napoli Parthenope, Dipartimento di Scienze e Tecnologie, CDN IC4, 80143 Naples, Italy
[8] IRAP, Université de Toulouse, CNRS, UPS, Toulouse, France
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ABSTRACT

Most of the gaseous molecules that are detected in cometary atmospheres are produced through sublimation of nucleus ices. Distributed sources may also occur, that is, production within the coma, from the solid component of dust particles that are ejected from the nucleus. Glycine, the simplest amino acid, was observed episodically in the atmosphere of comet 67P/Churyumov-Gerasimenko (67P) by the ROSINA mass spectrometer on board the Rosetta probe. A series of measurements on 28 March 2015 revealed a distributed density profile at between 14 and 26 km away from the nucleus. We here present and discuss three study cases: (i) glycine emitted directly and only from the nucleus, (ii) glycine emitted from the sublimation of solid-state glycine on the dust particles that are ejected from the nucleus, and (iii) glycine molecules embedded in water ice that are emitted from the sublimation of this ice from the dust particles that are ejected from the nucleus. A numerical model was developed to calculate the abundance of glycine in the atmosphere of comet 67P as a function of the distance from the nucleus, and to derive its initial abundance in the lifted dust particles. We show that a good fit to the observations corresponds to a distributed source of glycine that is embedded in sublimating water ice from dust particles that are ejected from the nucleus (iii). The few hundred ppb of glycine embedded in water ice on dust particles (nominally 170 ppb by mass) agree well with the observed distribution.

Key words. comets: individual: 67P/Churyumov-Gerasimenko – astrochemistry

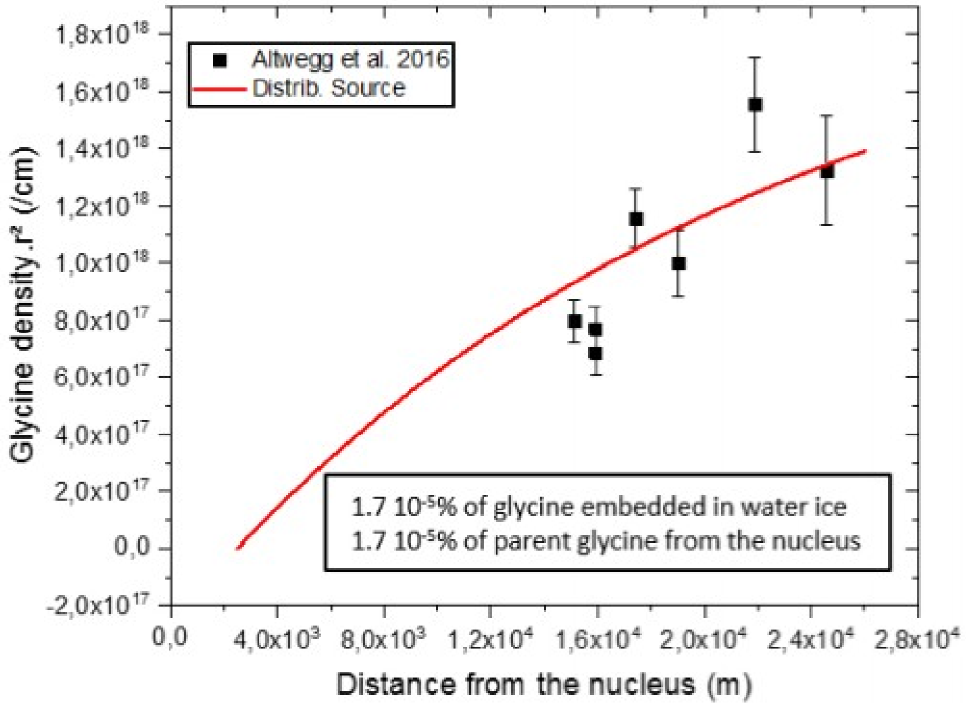
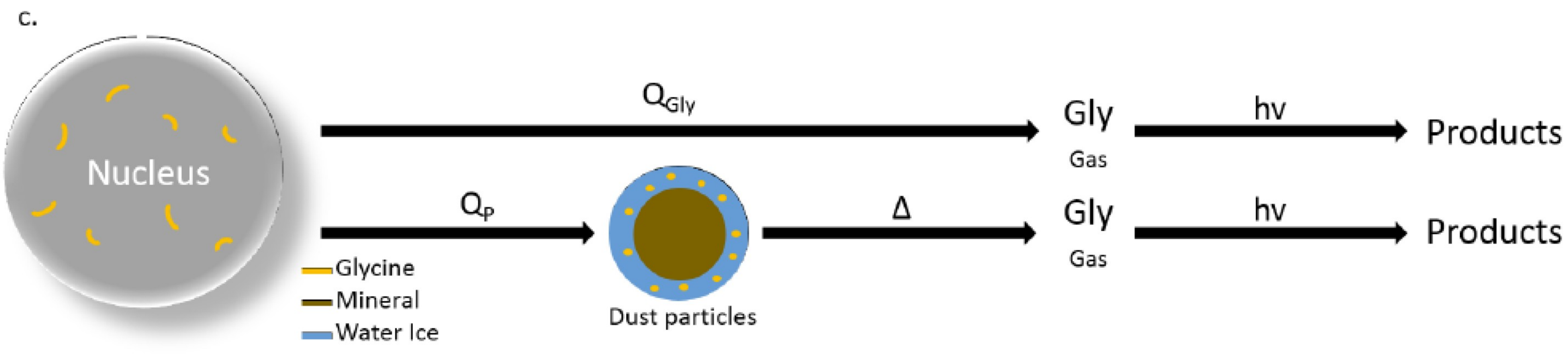
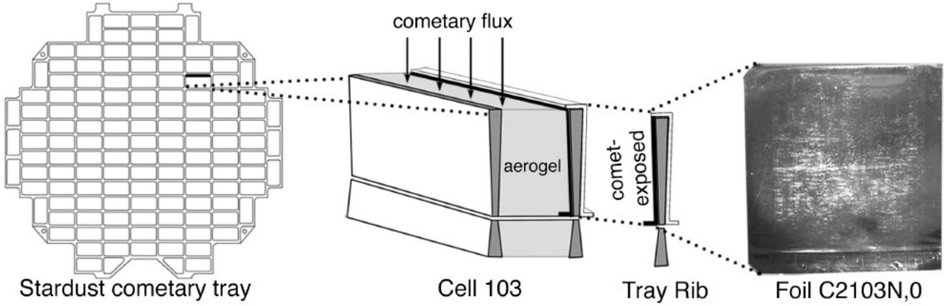


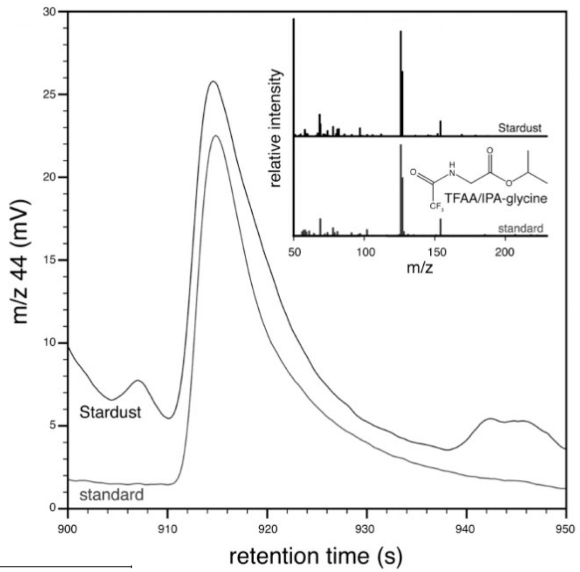
Fig. 7. Density profile of glycine as a function of the distance from the nucleus of 67P when glycine presents a distributed source for which it is embedded in water ice on particles with $1.7 \times 10^{-5}\%$ glycine, and with $1.7 \times 10^{-5}\%$ parent glycine from the nucleus.

Distributed Glycine



Elsila, J. E., Glavin, D. P., and Dworkin, J. P., 2009. Cometary Glycine Detected in Samples Returned by Stardust. *Meteoritic and Planetary Science* **44**, 1323-1330





s of the derivatized combined extract from four Stardust foils and of a
show the m/z 44 ($^{12}CO_2$) peak produced and measured from GC-IRMS for
The inset shows the simultaneously collected mass spectral fragmentation
e structure of glycine derivatized with trifluoroacetic acid/isopropanol

Amino Acid	*C2103N,0*	*C2016N,2*	*C2017N,0*	*C2078N,0*	*C2125N,2*		*C2092S,0*	
	Both sides (total)				*Aerogel side (total)*	*Metal side (total)*	*Both sides (free)*	*Both sides (total)*
Glycine	34	2	13	19	21	< 3	27	68
β-Alanine	2	1	1	3	< 2	< 2	1	7
D-Alanine	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 4
L-Alanine	2	< 1	1	1	1	< 3	6	12
EACA[b]	326	51	66	327	186	126	11	1,413

GC-MS/IRMS analysis provides compound-specific structural and isotopic information from a single injection, which permitted three replicate measurements from the 0.7 nmol of glycine and 16 nmol of EACA present in the combined foil extract. Figure 3 shows the GC-MS/IRMS data for the peak identified as glycine. The retention time and mass spectrum match that of the glycine standard, with no evidence of a coeluting compound. The $\delta^{13}C$ value for glycine was determined to be +29 ± 6‰. This value is well outside the terrestrial range for organic carbon of -6 ‰ to -40 ‰ (Bowen, 1988). The Stardust glycine $\delta^{13}C$ value falls in the range previously reported for glycine from acid-hydrolyzed hot-water extracts of the CM type carbonaceous meteorite Murchison ($\delta^{13}C$ = +22‰ to +41‰) (Engel et al., 1990; Pizzarello et al., 2004) and the CI type meteorite Orgueil ($\delta^{13}C$ = +22‰) (Ehrenfreund et al., 2001a). The value reported here may include terrestrial glycine from the non-aerogel-facing side of the foil, and should thus be viewed as a lower limit on the cometary $\delta^{13}C$ enrichment.

Detections in the gaseous phase

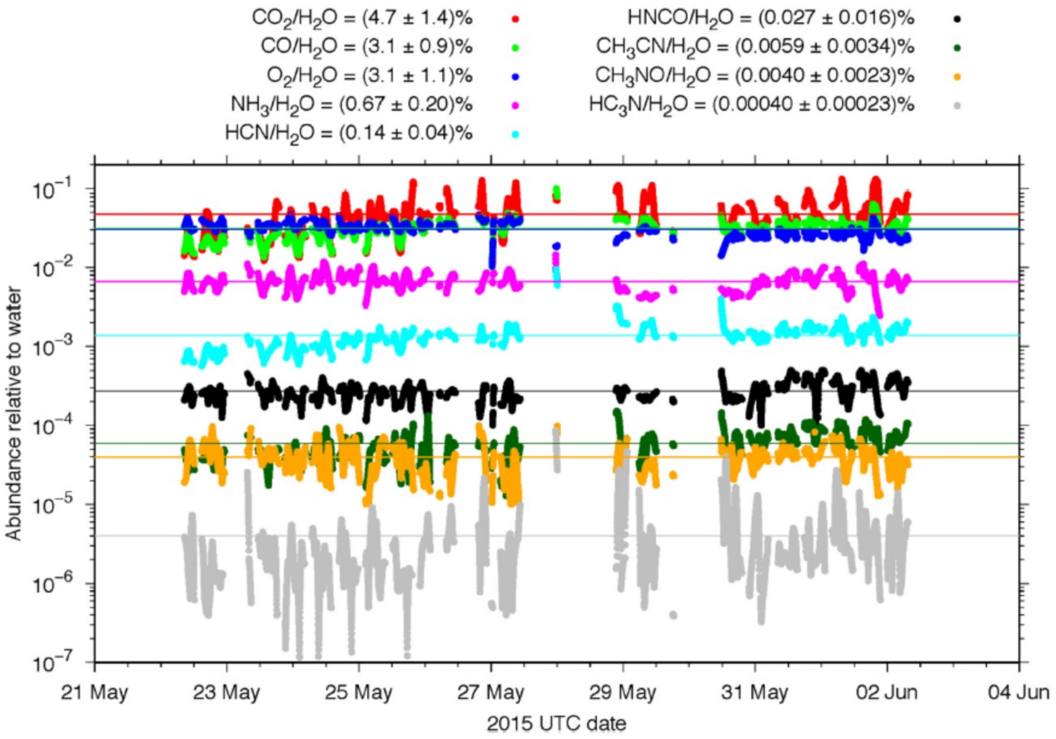


Figure 3. Measured abundances of a suite of volatile species with respect to water from the pre-perihelion period at the end of May 2015, suitable for deriving bulk abundances in the ices of comet 67P/Churyumov-Gerasimenko (Calmonte et al. 2016). The horizontal lines denote the averages for the observed period. Indicated errors represent 1σ.

Organic molecules in the COMA < 2 % (rel. water)

=> Rubin et al., MNRAS 2019

+ Glycine abundance in 67P ~ 200 ppbw in water ice (~ 4.10^{-6}% rel. water)

=> Hadraoui et al., 2019, A&A

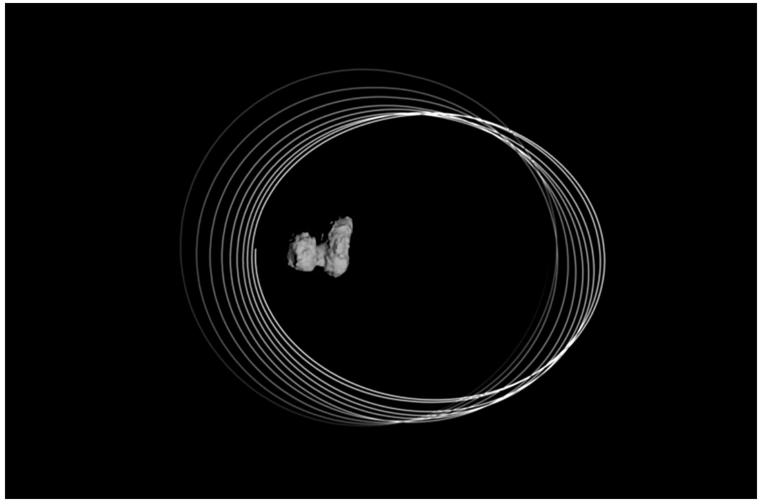
Molecule	Deduced bulk abundance	Northern versus Southern hemispheres at 3.1 au [a]
H_2O	100	100/100
CO_2	4.7 ± 1.4	2.5/80
CO	3.1 ± 0.9	2.7/20
O_2	3.1 ± 1.1	3.80 ± 0.85 [b]
CH_4	0.34 ± 0.07	0.13/0.56
C_2H_6	0.29 ± 0.06	0.32/3.3
C_3H_8	0.018 ± 0.004	
C_6H_6	0.00069 ± 0.00014	
C_7H_8	0.0062 ± 0.0012	
CH_3OH	0.21 ± 0.06	0.31/0.55
C_2H_5OH	0.039 ± 0.023	
CH_3CH_2CHO	0.0047 ± 0.0024	
H_2CO	0.32 ± 0.10	0.33/0.53
CH_3CHO	0.047 ± 0.017	0.01/0.024
HCOOH	0.013 ± 0.008	0.008/0.03
CH_3COOH	0.0034 ± 0.0020	0.004/0.023
$(CH_2OH)_2$	0.011 ± 0.007	0.0008/ < 0.0025
$CH_3(CH_2)_2CHO$	0.010 ± 0.003	
CH_3COOCH_3	0.0021 ± 0.0007	
NH_3	0.67 ± 0.20	0.06/0.15
N_2	0.089 ± 0.024	0.015 to 0.114 [a], [c]
HCN	0.14 ± 0.04	0.09/0.62
HNCO	0.027 ± 0.016	0.016/0.031
CH_3NO	0.0040 ± 0.0023	<0.0001/0.001
CH_3CN	0.0059 ± 0.0034	0.006/0.016
HC_3N	0.00040 ± 0.00023	< 0.00002/ < 0.0005

nature astronomy ARTICLES
https://doi.org/10.1038/s41550-019-0991-9

Evidence of ammonium salts in comet 67P as explanation for the nitrogen depletion in cometary comae

Kathrin Altwegg[1*], Hans Balsiger[1], Nora Hänni[1], Martin Rubin[1], Markus Schuhmann[1], Isaac Schroeder[1], Thierry Sémon[1], Susanne Wampfler[2], Jean-Jacques Berthelier[3], Christelle Briois[4], Mike Combi[5], Tamas I. Gombosi[5], Hervé Cottin[6], Johan De Keyser[7], Frederik Dhooghe[7], Björn Fiethe[8] and Steven A. Fuselier[9,10]

$NH_4^+Cl^-$ (ammoniun chloride), **$NH_4^+CN^-$** (ammonium cyanide), **$NH_4^+OCN^-$** (ammonium cyanate), **$NH_4^+HCOO^-$** (ammonium formate) et **$NH_4^+CH_3COO^-$** (ammonium acetate).



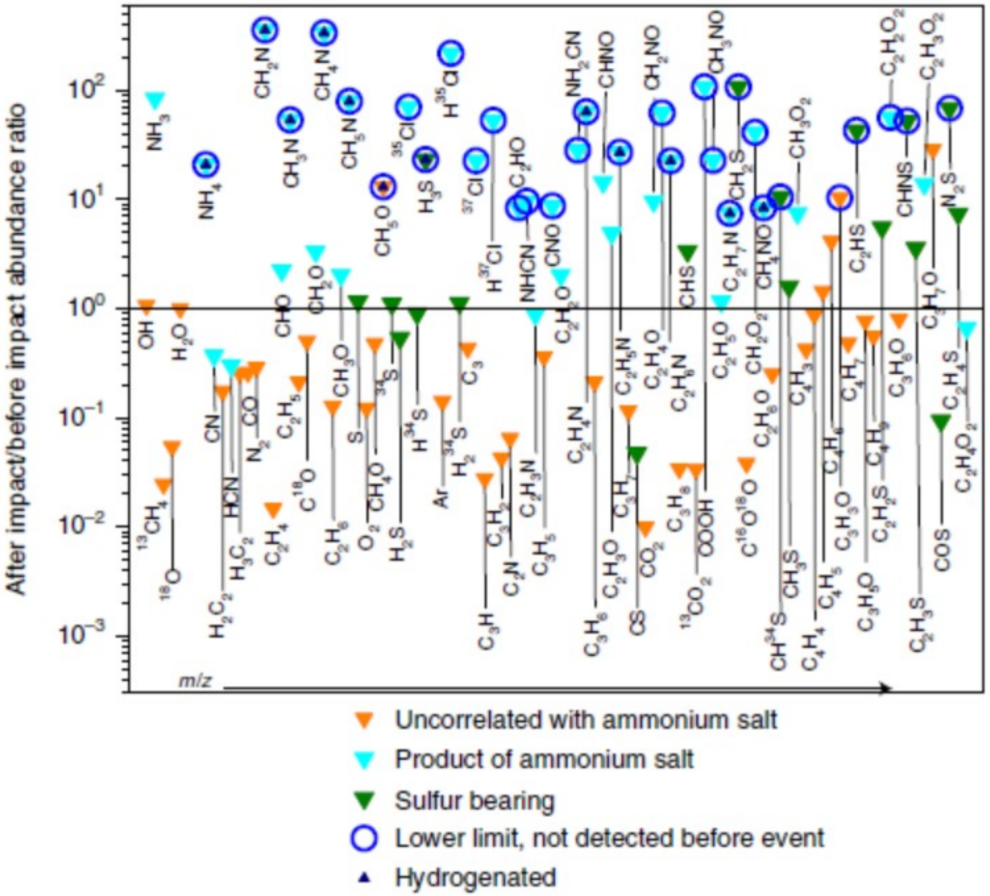


Fig. 4 | Abundance ratios normalized to H_2O. Abundance ratios for the period around 20:00 compared with 17:00 on 5 September 2016. For species not detected before impact, upper limits were derived from the noise floor of the detector, which translates into lower limits for the ratios. Sublimation of ammonium salts may produce H_2O, CO and CO_2. Their contributions to these species are small as these are the dominant species of the undisturbed coma. We consider them 'uncorrelated' to ammonium salt.

Altwegg et al. 2020

Hänni et al. 2022

nature COMMUNICATIONS

ARTICLE

https://doi.org/10.1038/s41467-022-31346-9 OPEN

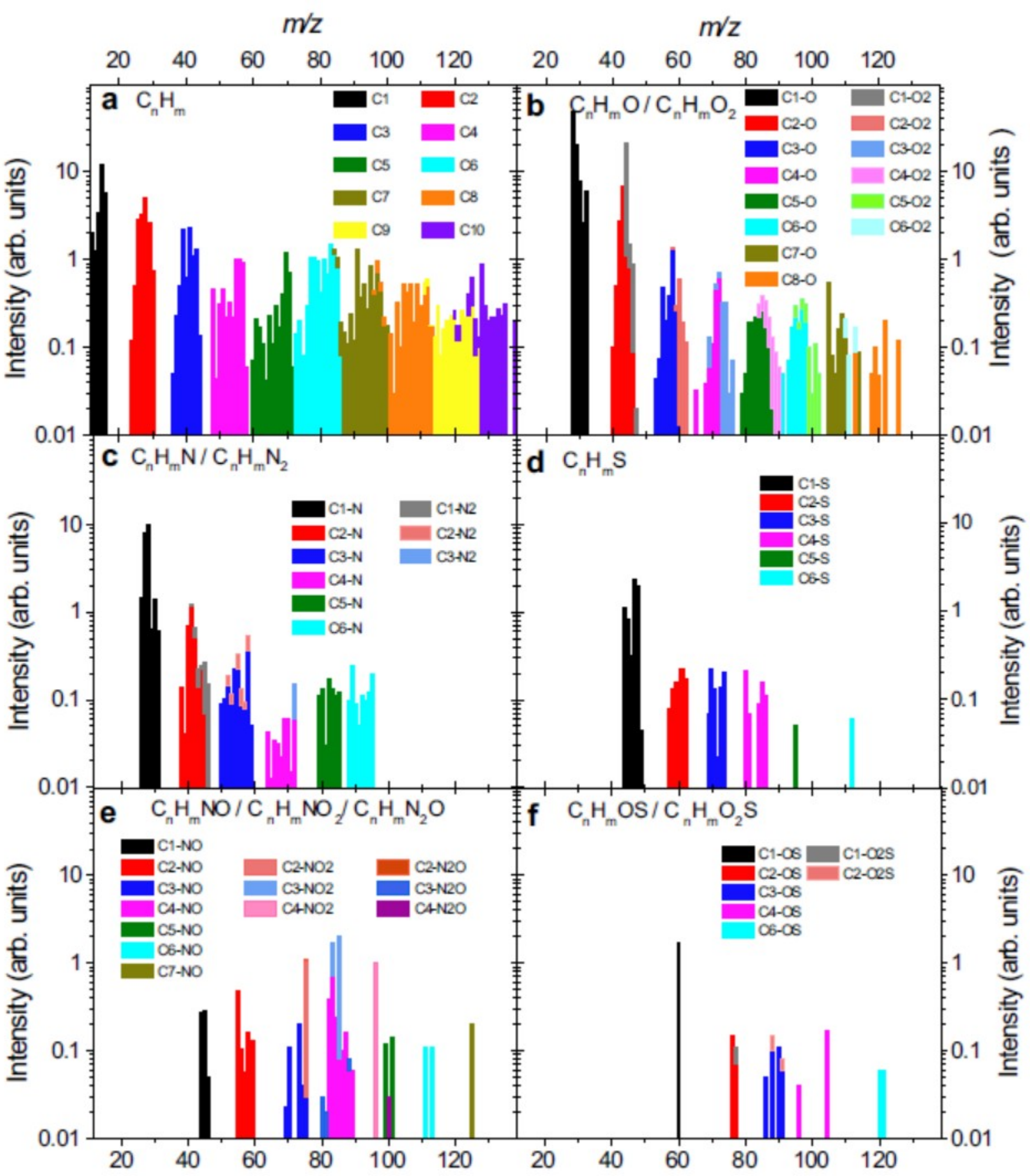
Check for updates

Identification and characterization of a new ensemble of cometary organic molecules

N. Hänni[1✉], K. Altwegg[1], M. Combi[2], S. A. Fuselier[3,4], J. De Keyser[5], M. Rubin[1] & S. F. Wampfler[6]

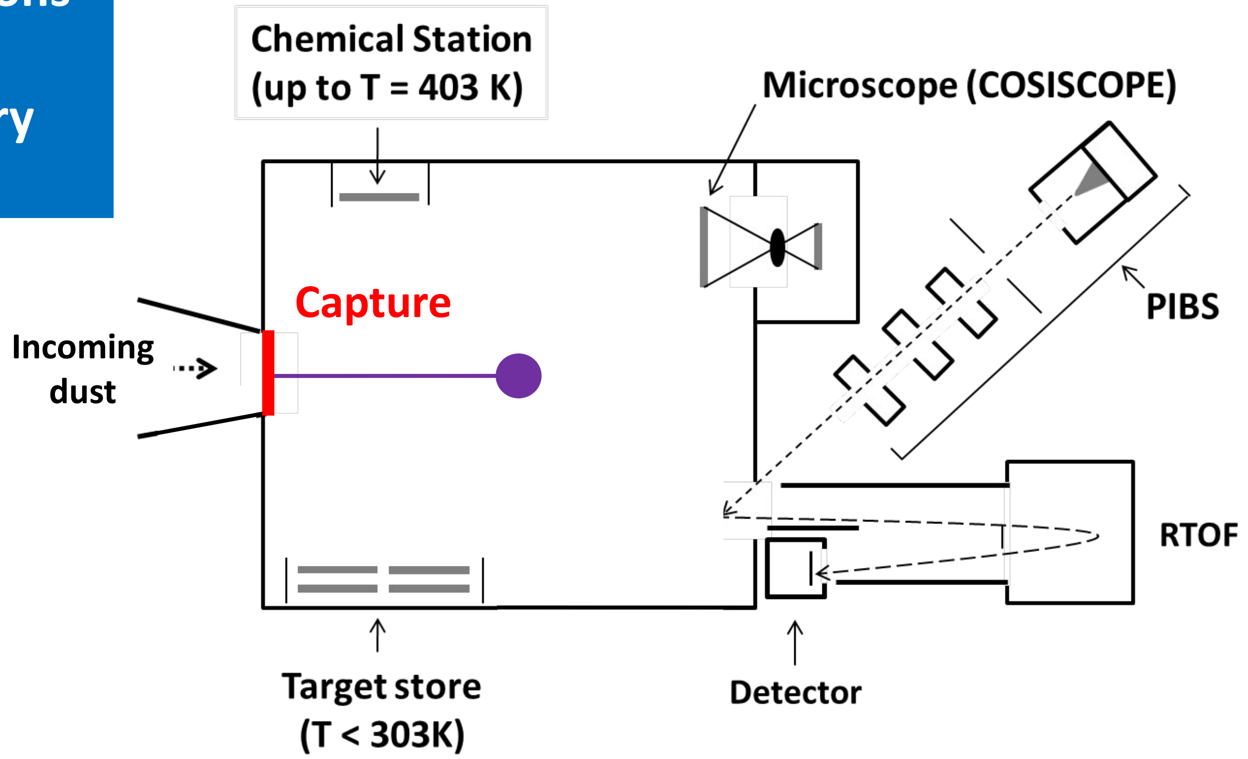
In-situ study of comet 1P/Halley during its 1986 apparition revealed a surprising abundance of organic coma species. It remained unclear, whether or not these species originated from polymeric matter. Now, high-resolution mass-spectrometric data collected at comet 67P/Churyumov-Gerasimenko by ESA's Rosetta mission unveil the chemical structure of complex cometary organics. Here, we identify an ensemble of individual molecules with masses up to 140 Da while demonstrating inconsistency of the data with relevant amounts of polymeric matter. The ensemble has an average composition of $C_1H_{1.56}O_{0.134}N_{0.046}S_{0.017}$, identical to meteoritic soluble organic matter, and includes a plethora of chain-based, cyclic, and aromatic hydrocarbons at an approximate ratio of 6:3:1. Its compositional and structural properties, except for the H/C ratio, resemble those of other Solar System reservoirs of organics—from organic material in the Saturnian ring rain to meteoritic soluble and insoluble organic matter –, which is compatible with a shared prestellar history.

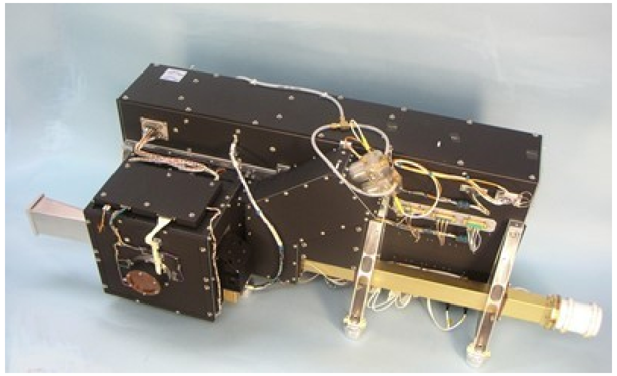
No POM, no HMT…



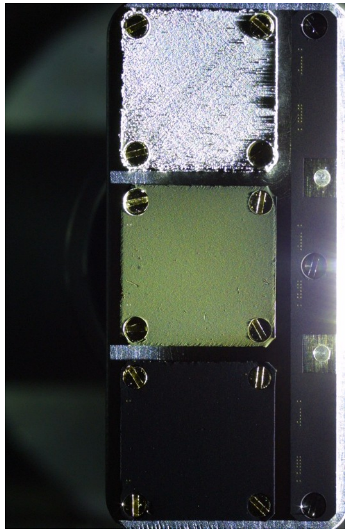
COSIMA : COmetary Secondary Ion Mass Analyzer

Observations in the refractory phase





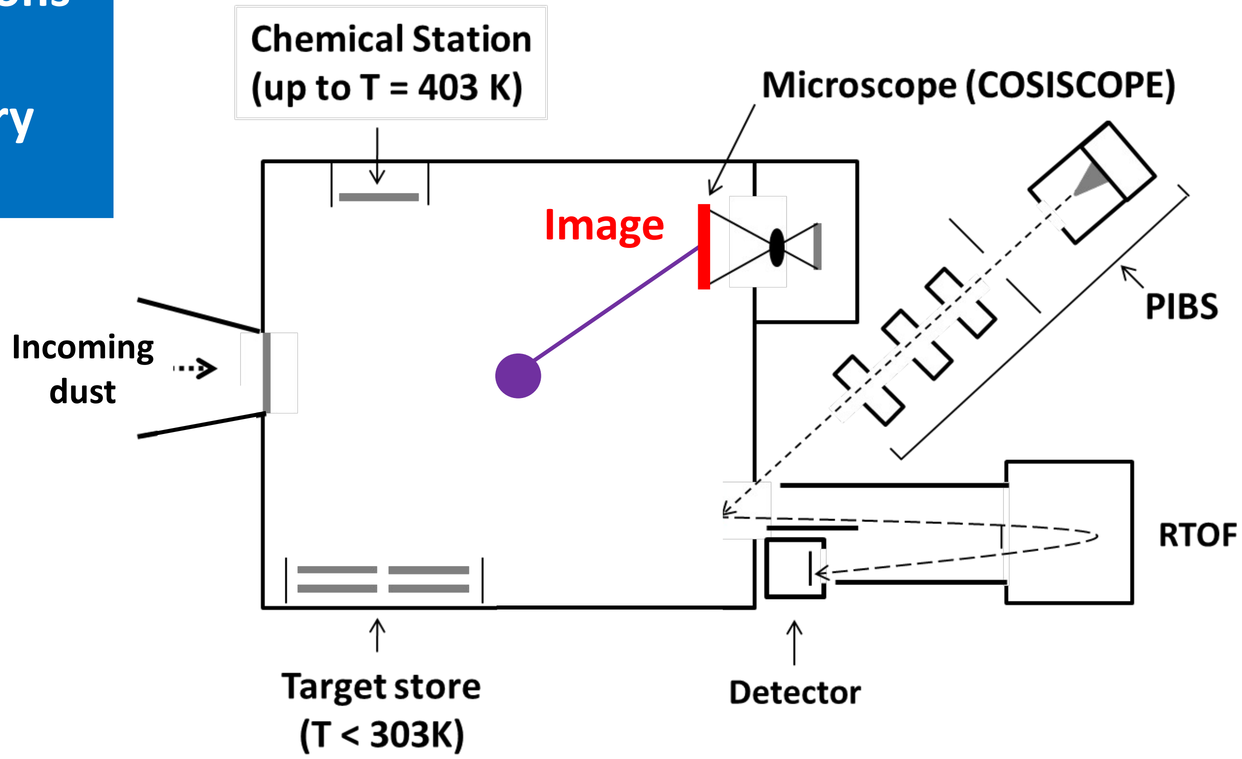
Mass: 19.9 kg
Volume (Lxlxh): 986 x 356 x362 mm^3

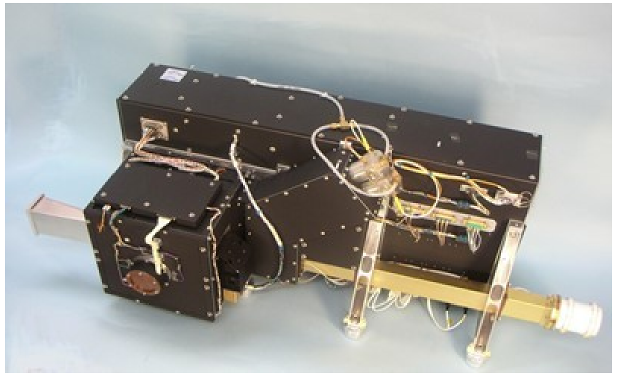


- **72 targets available**
- **Au, Ag, Pt, Pd (plain and blacks)**

COSIMA : COmetary Secondary Ion Mass Analyzer

Observations in the refractory phase



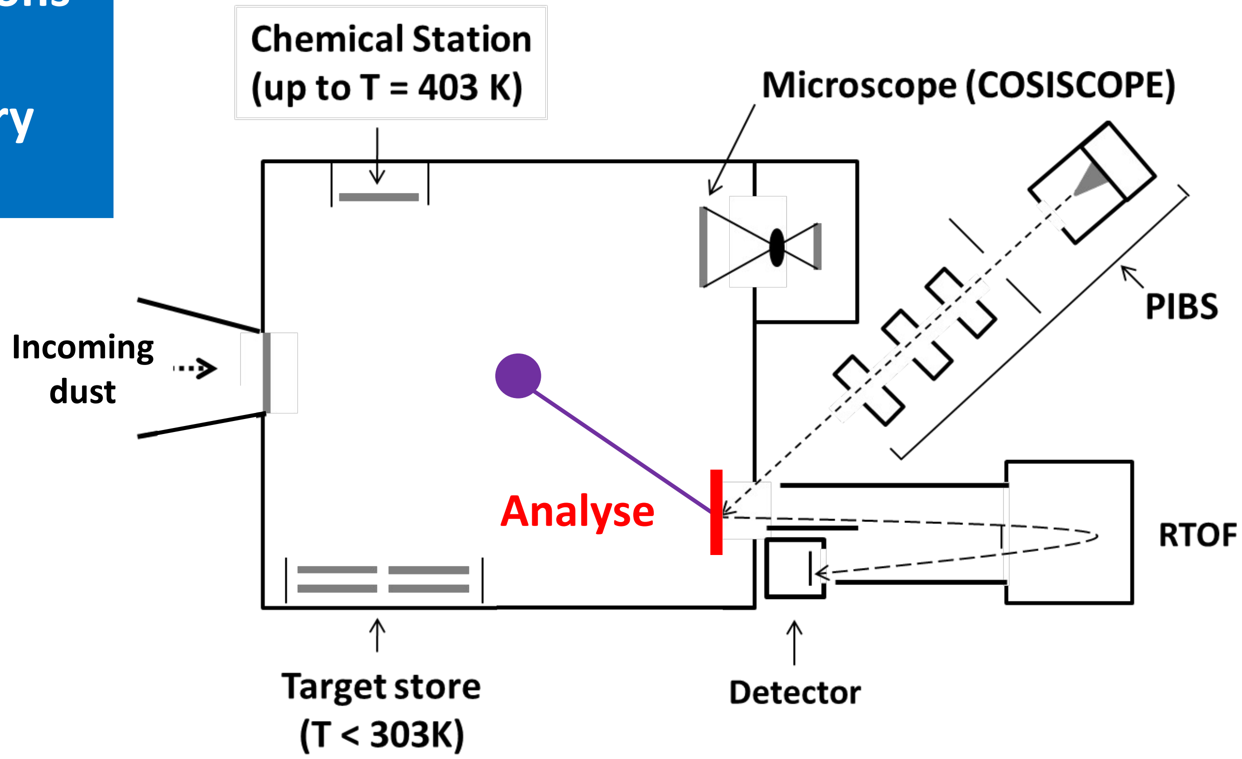


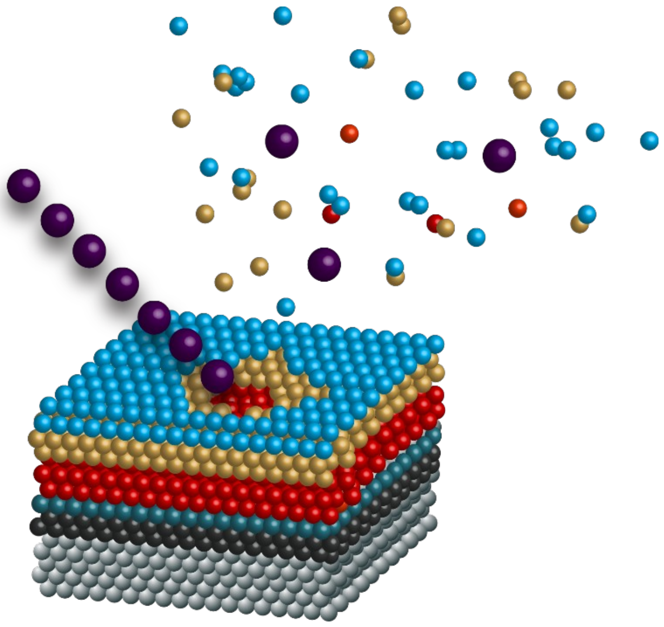
Mass: 19.9 kg
Volume (Lxlxh): 986 x 356 x362 mm^3

➢ Resolution of COSISCOPE : **14 µm/pixels**

COSIMA : COmetary Secondary Ion Mass Analyzer

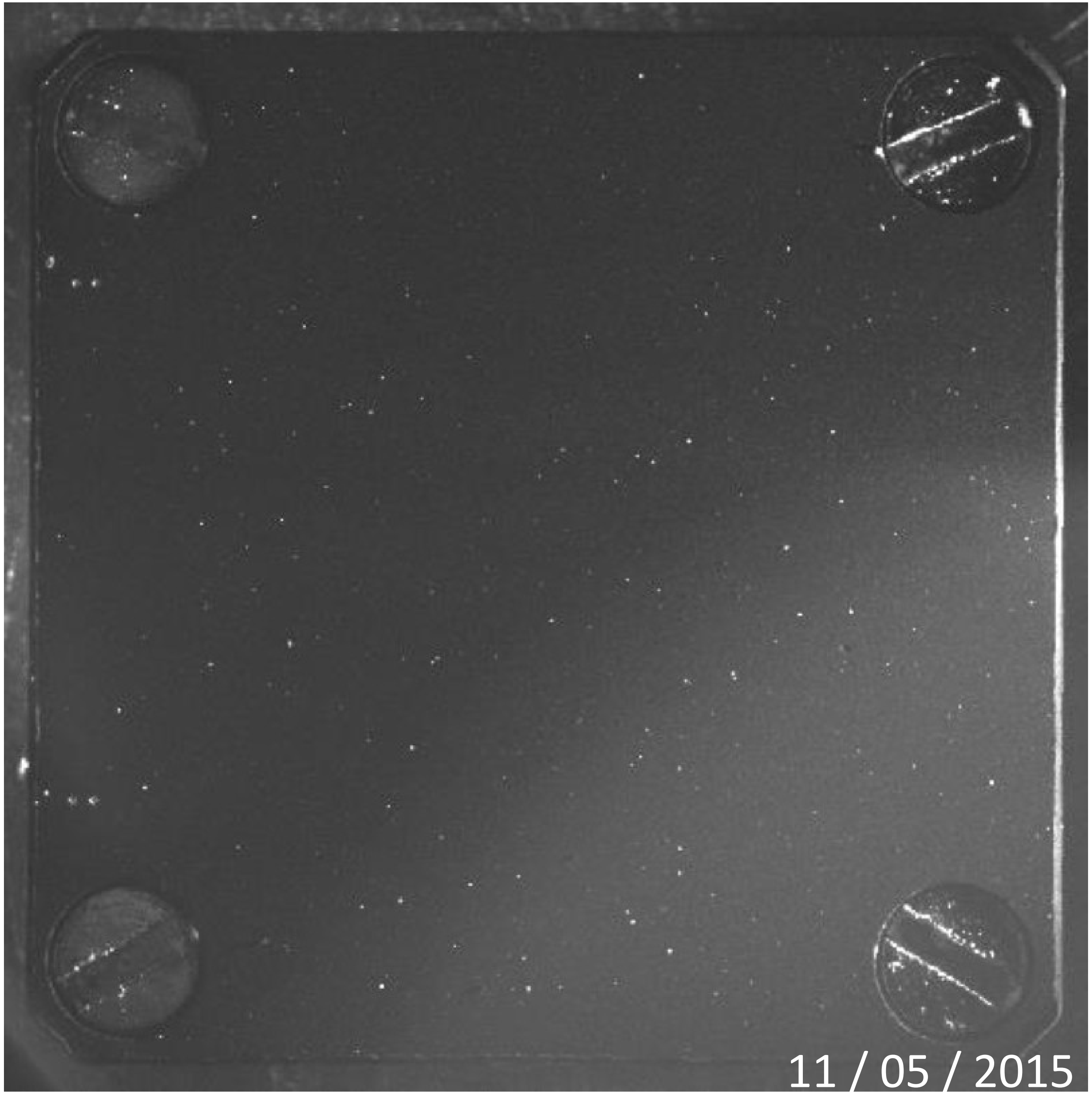
Observations in the refractory phase





- **Both positive and negative mode:** **target at ground & extractor at +/- 3 kV**
- **Footprint of the pulsed ion beam:** **35 × 50 µm²**
- **Each pulse lasts less than 3 ns**
- **With about 1000 $^{115}In^+$ ions with an energy of 8 keV**

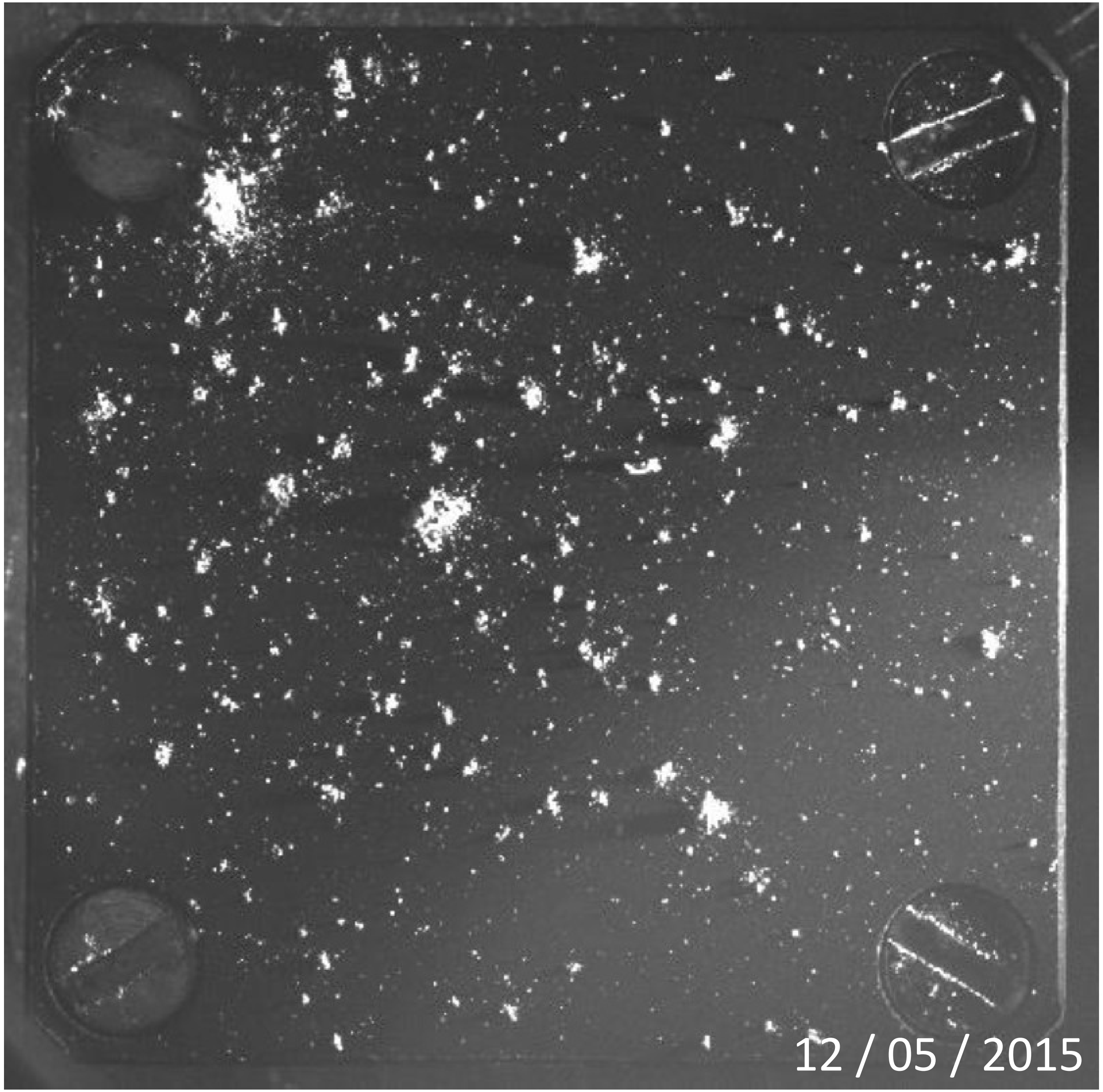
Observations in the refractory phase



Observations in the refractory phase

Velocity of the dust particles rel. to the spacecraft < 10 m.s^{-1}

Rotundi et al. 2015



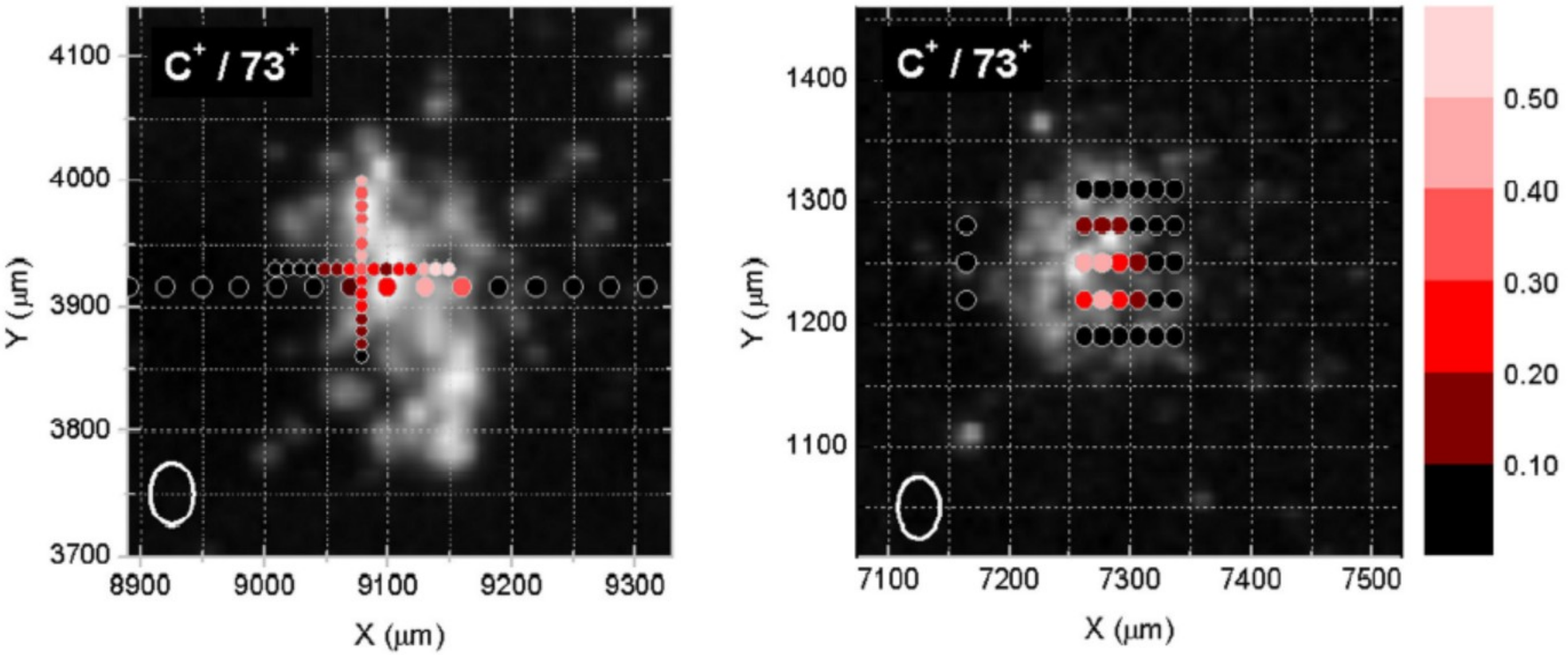
Fray et al, Nature, 2016

LETTER

doi:10.1038/nature19320

High-molecular-weight organic matter in the particles of comet 67P/Churyumov–Gerasimenko

Nicolas Fray[1]*, Anaïs Bardyn[1,2]*, Hervé Cottin[1]*, Kathrin Altwegg[3], Donia Baklouti[4], Christelle Briois[2], Luigi Colangeli[5], Cécile Engrand[6], Henning Fischer[7], Albrecht Glasmachers[8], Eberhard Grün[9], Gerhard Haerendel[10], Hartmut Henkel[11], Herwig Höfner[10], Klaus Hornung[12], Elmar K. Jessberger[13], Andreas Koch[11], Harald Krüger[7], Yves Langevin[4], Harry Lehto[14], Kirsi Lehto[15], Léna Le Roy[3], Sihane Merouane[7], Paola Modica[1,2], François-Régis Orthous-Daunay[16], John Paquette[7], François Raulin[1], Jouni Rynö[17], Rita Schulz[18], Johan Silén[17], Sandra Siljeström[19], Wolfgang Steiger[20], Oliver Stenzel[7], Thomas Stephan[21], Laurent Thirkell[2], Roger Thomas[2], Klaus Torkar[22], Kurt Varmuza[23], Karl-Peter Wanczek[24], Boris Zaprudin[14], Jochen Kissel[7] & Martin Hilchenbach[7]

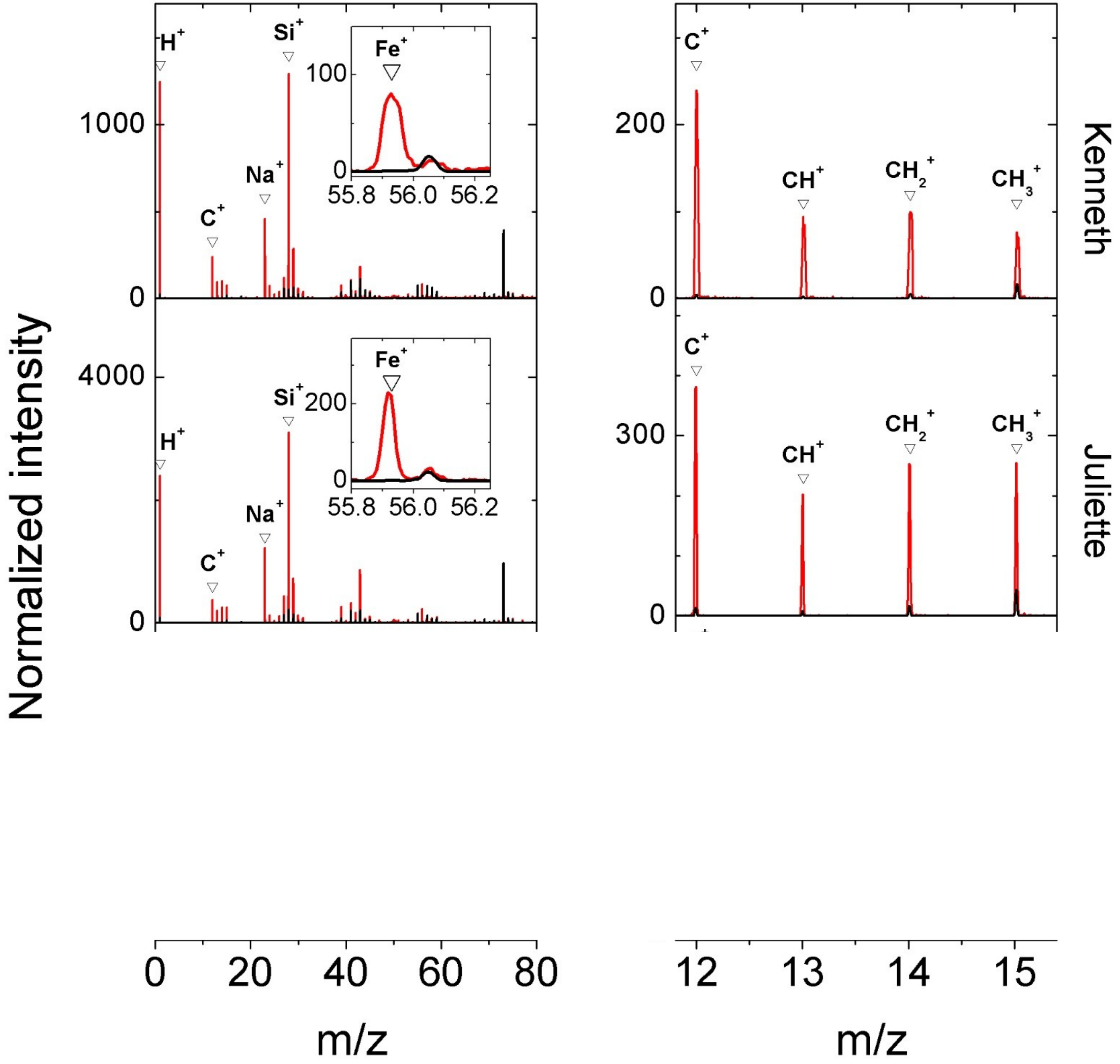


Extended Data Figure 1 | Optical images of the particles Kenneth and Juliette. These sub-pixel sampled images have an equivalent resolution of 10 µm (ref. 15). Each is the sum of two images, obtained with two grazing incidence illuminations from the left and the right. A square-root scaling has been used to bring out weakly illuminated regions. These images were acquired on 4 June 2015 (Kenneth) and 25 November 2015 (Juliette).

Detection of high molecular weight organic compounds (HMWOC) in 67P dust particles

Red: on particle
Black: off particle

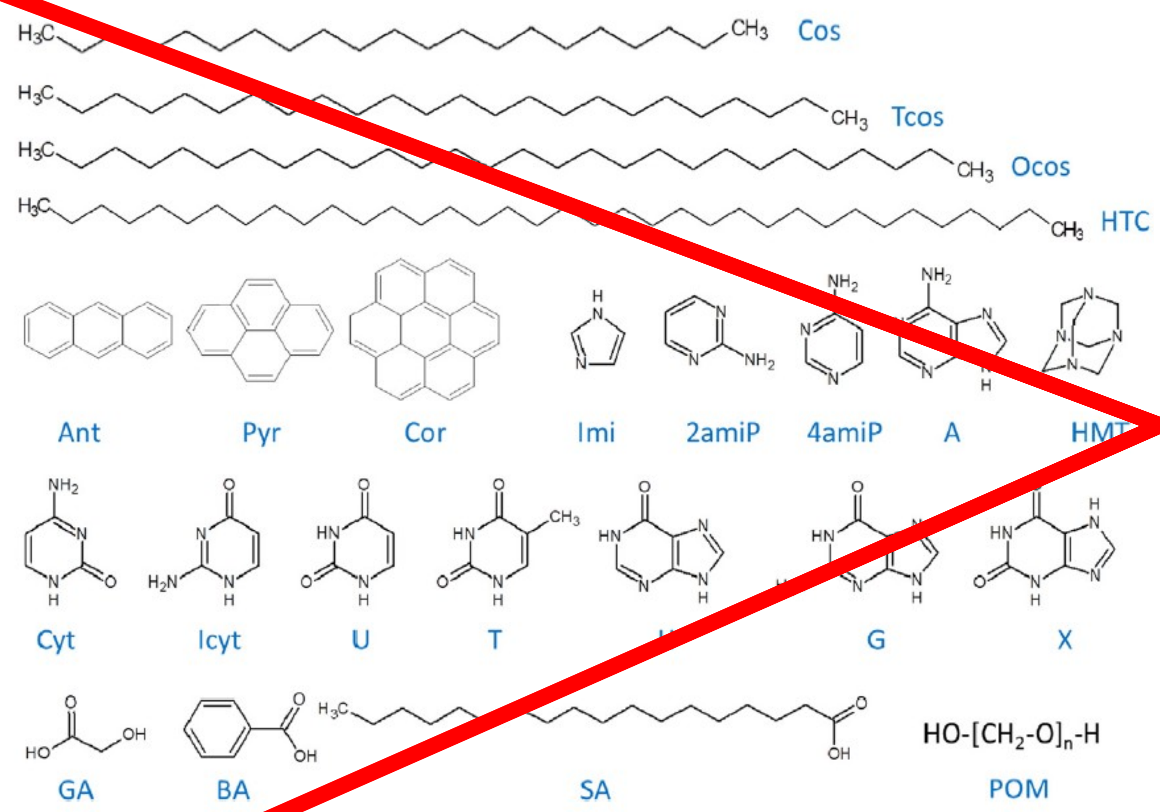
Observations in the refractory phase

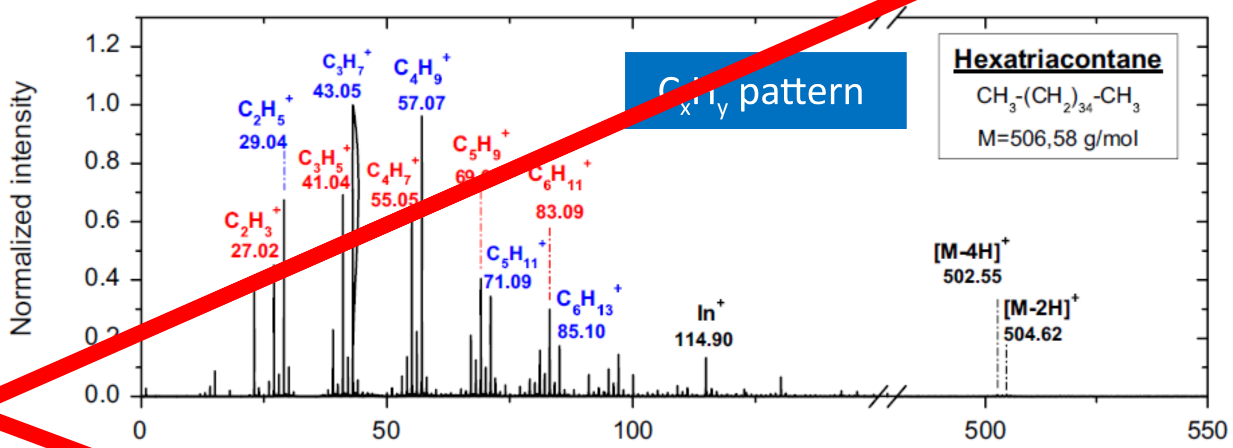


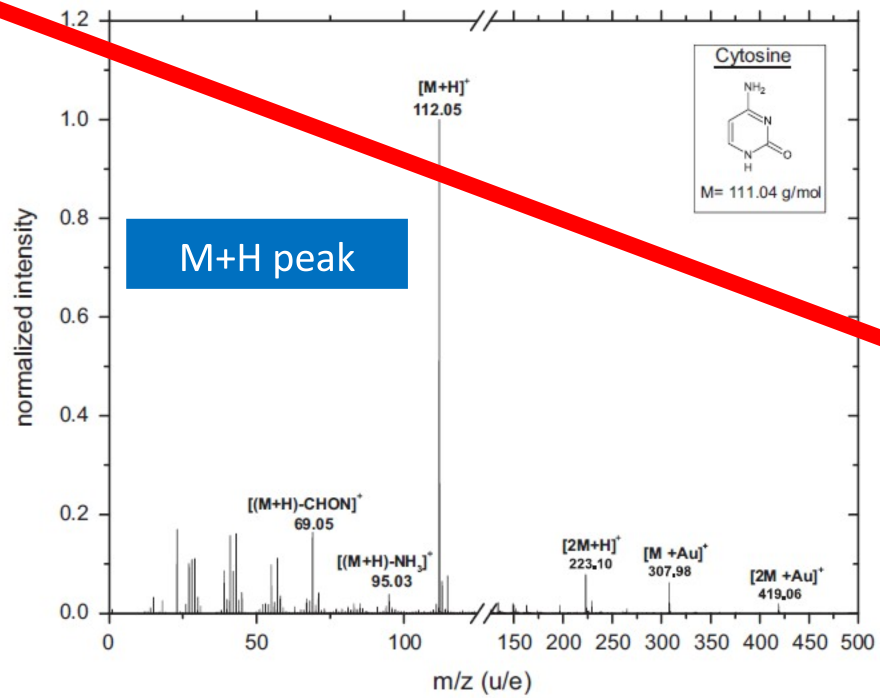
Fray et al, Nature, 2016

It's not

Something with a name, a formula with a begining and an end…
Something we actually understand…







Le Roy et al., PSS, 2015
(Calibration work : 2004-2014… and still ongoing)

It's not

Something something similar to organic residues synthesized from ice mixtures processing (at least at « standard » doses).

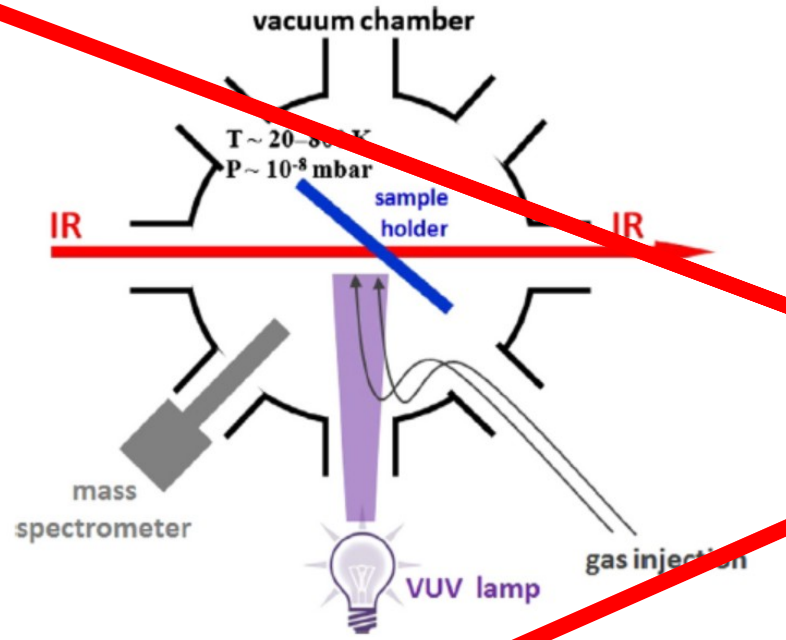
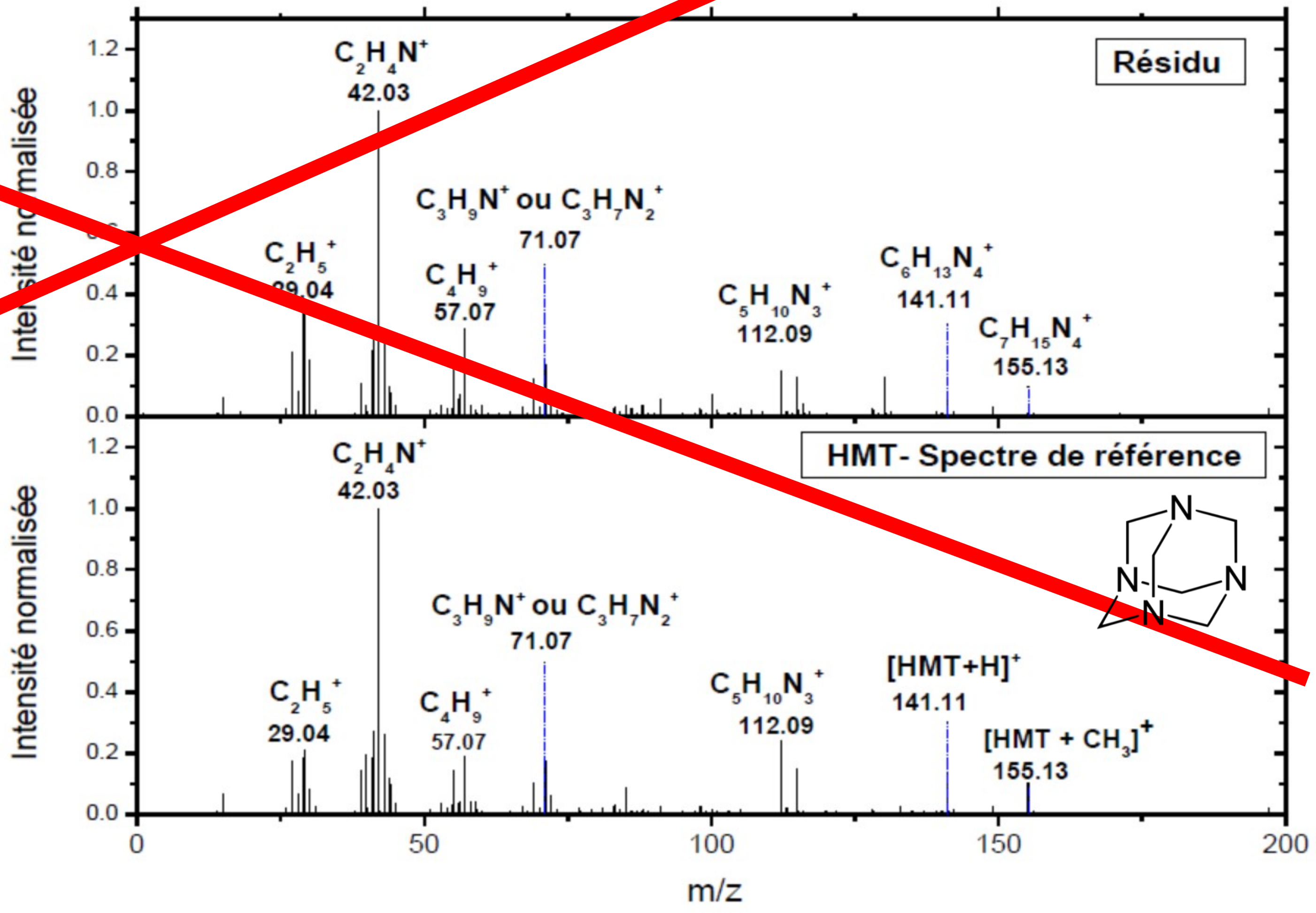


Fig. 1. Schematic representation of a horizontal section of the OREGOC experimental setup.

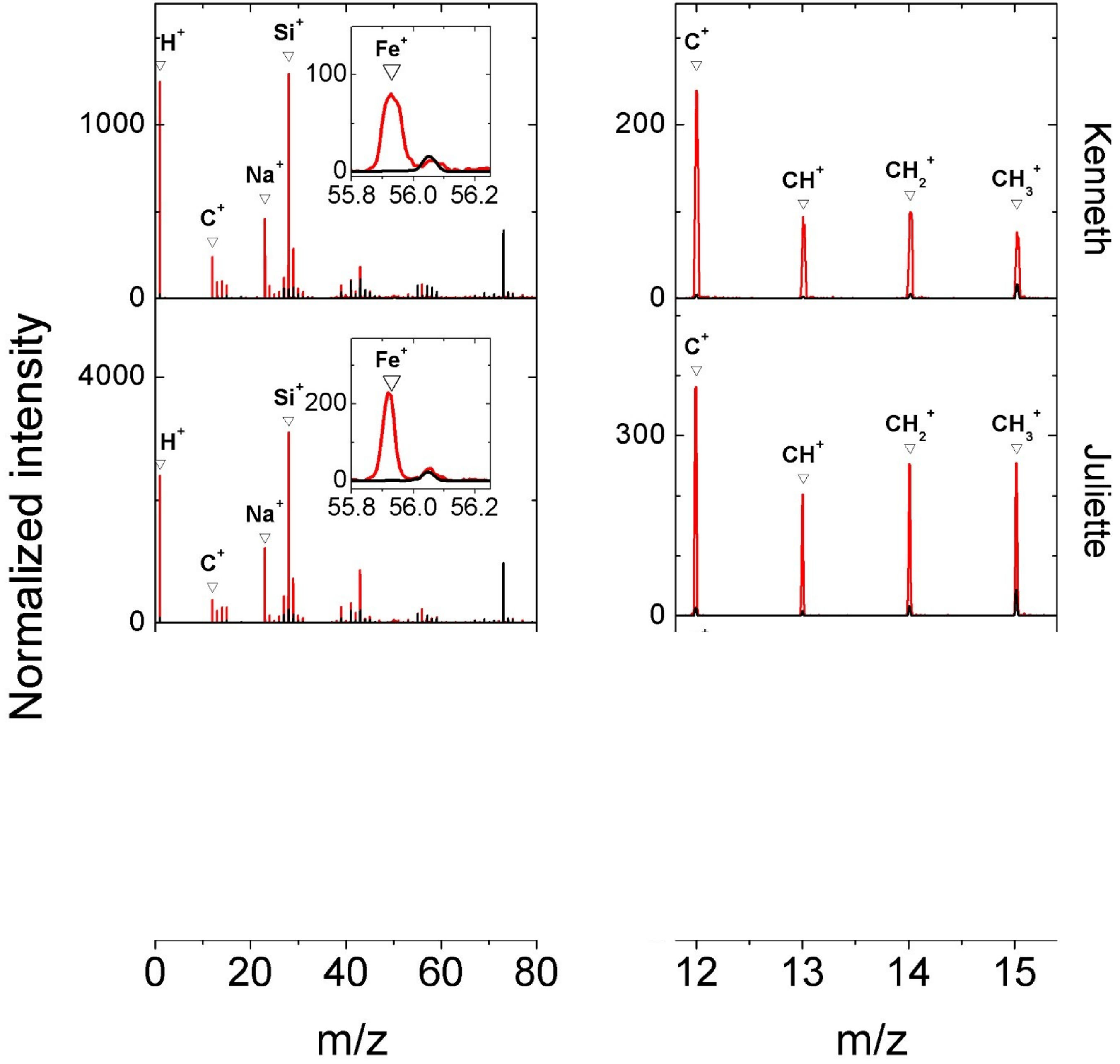


$H_2O : CH_3OH : NH_3$ (10 : 2 : 1) + hν

Detection of high molecular weight organic compounds (HMWOC) in 67P dust particles

Red: on particle
Black: off particle

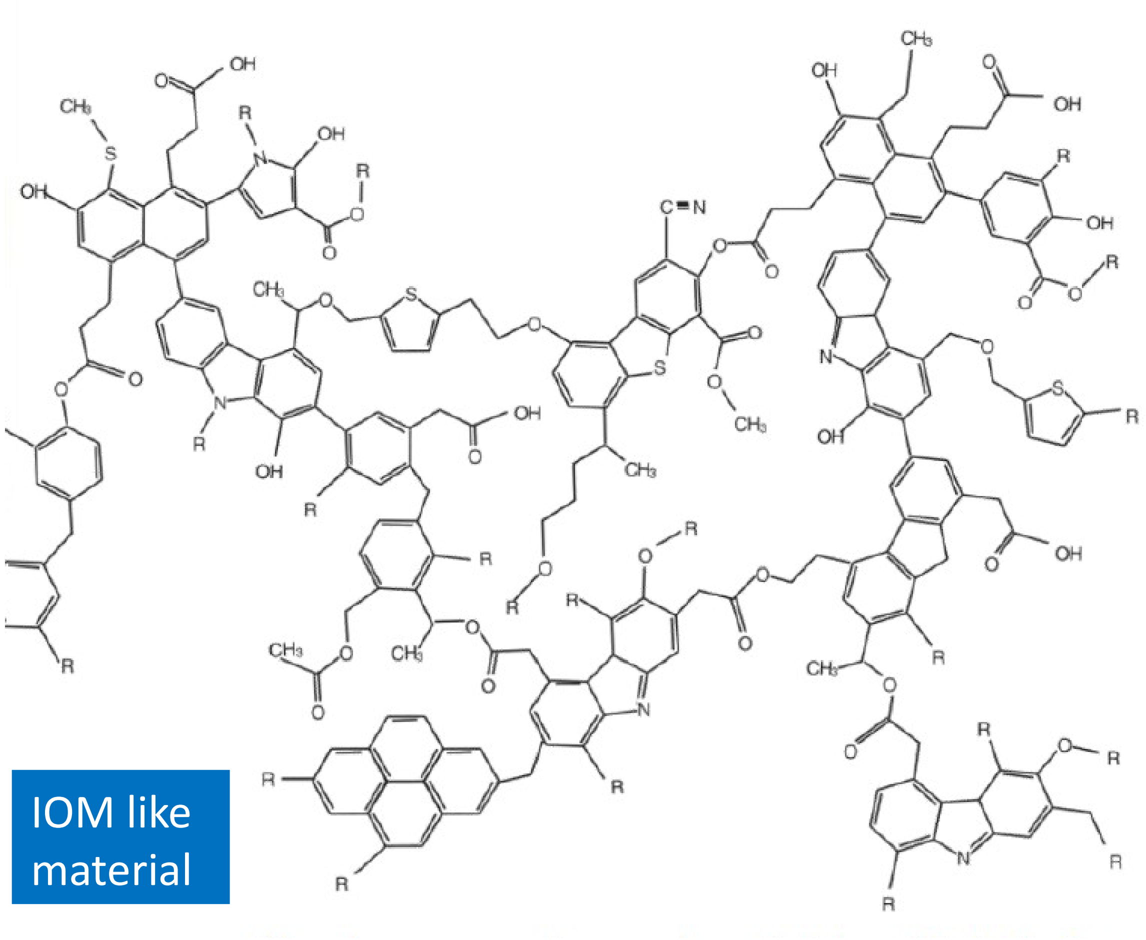
Observations in the refractory phase



Fray et al, Nature, 2016

It displays similarities with

How much ?



IOM like material

From Derenne & Robert, MPS, 2010

Solid Phase

50 Angstroms

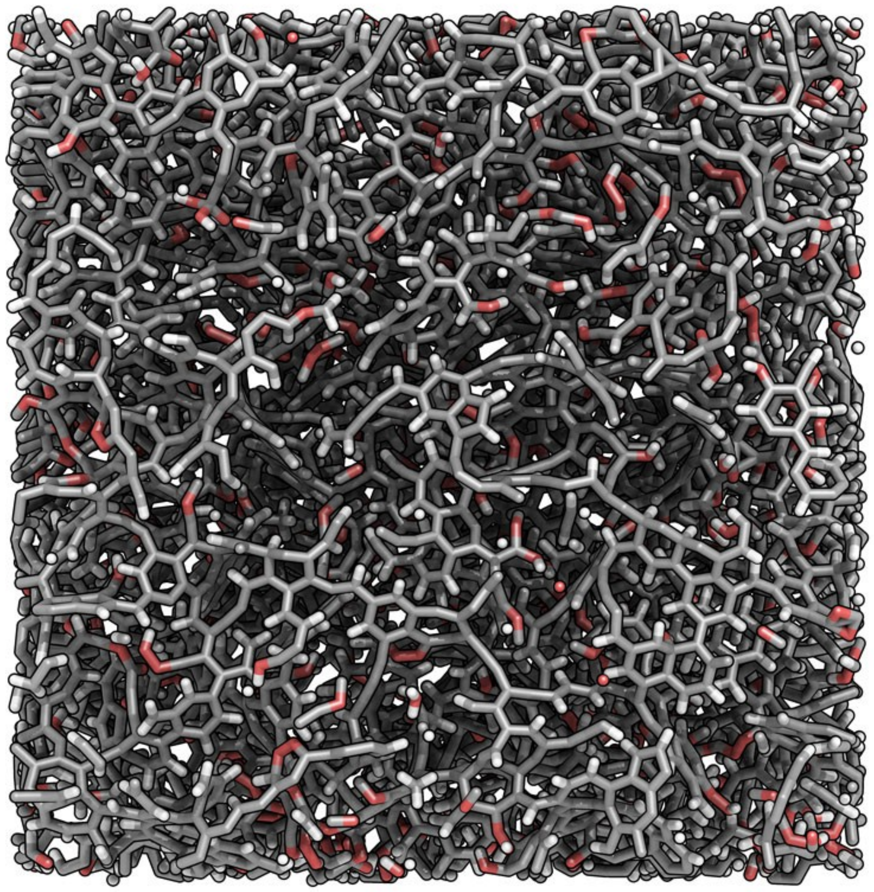
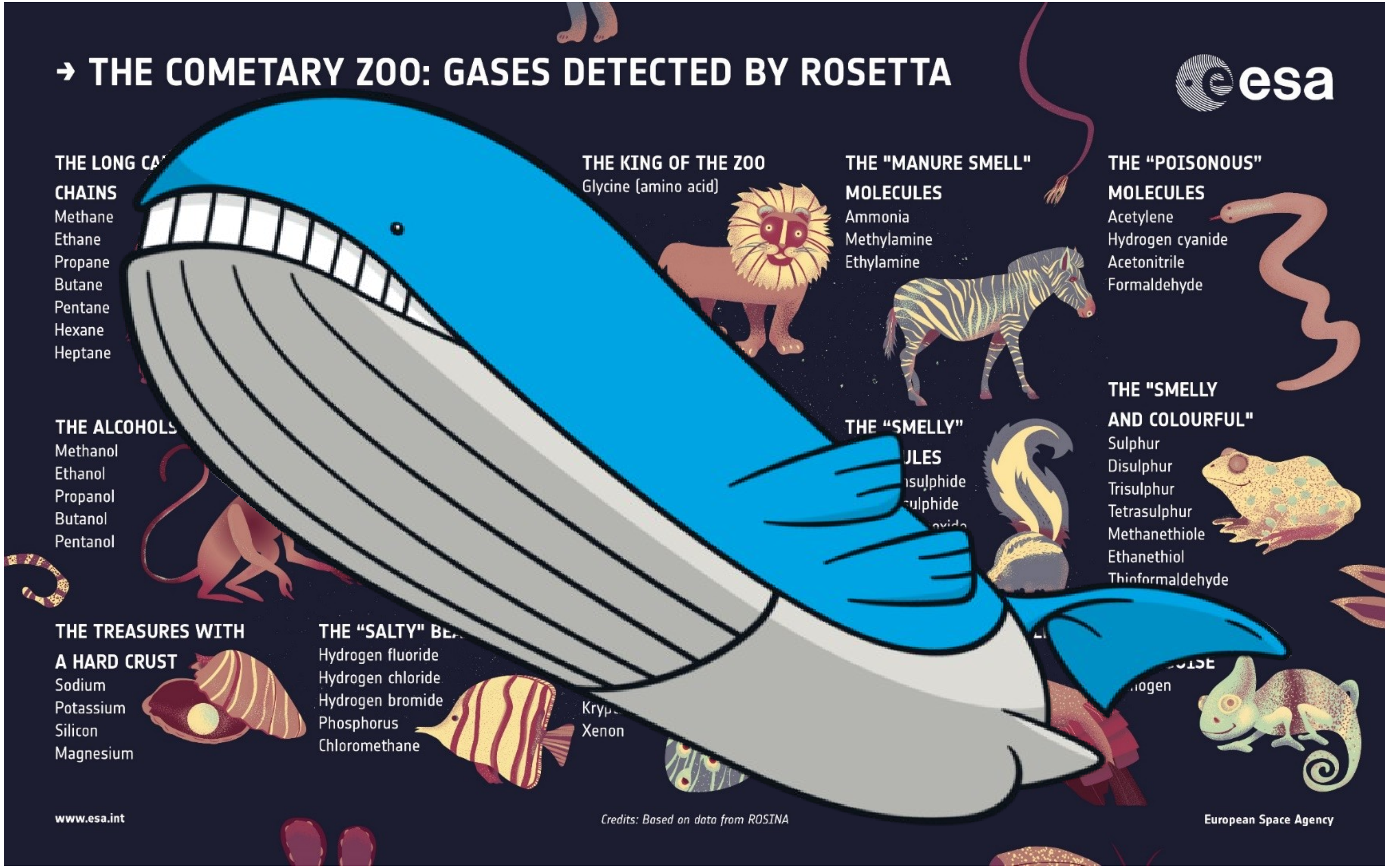


Figure (kerogen) from Bousige et al. 2016

Carbon (grey), hydrogen (white) and oxygen (red)

How much ?

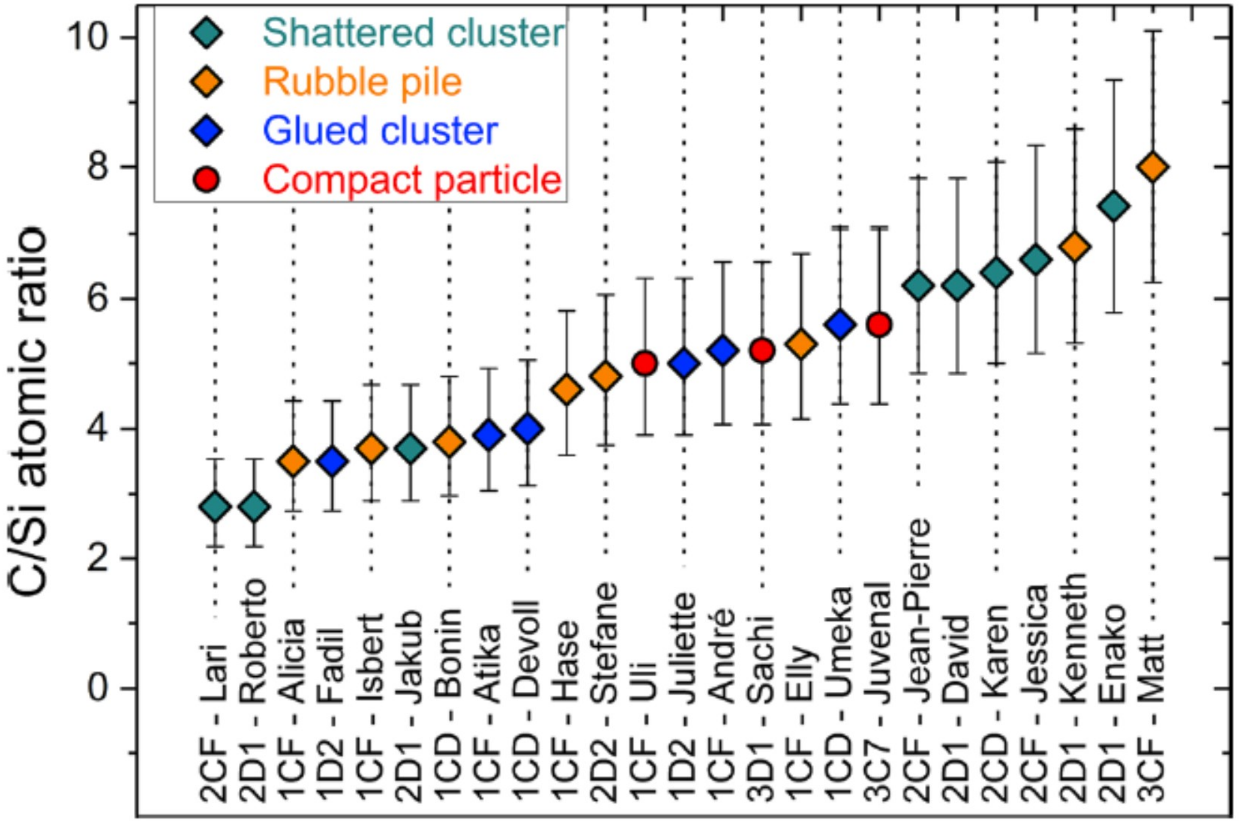


THE COMETARY ZOO: GASES DETECTED BY ROSETTA
esa
CHAINS
Methane
Ethane
Propane
Butane
Pentane
Hexane
Heptane
THE KING OF THE ZOO
Glycine (amino acid)
THE "MANURE SMELL"
MOLECULES
Ammonia
Methylamine
Ethylamine
THE "POISONOUS"
MOLECULES
Acetylene
Hydrogen cyanide
Acetonitrile
Formaldehyde
THE "SMELLY
AND COLOURFUL"
Sulphur
Disulphur
Trisulphur
Tetrasulphur
Methanethiole
Ethanethiol
Thioformaldehyde
Methanol
Ethanol
Propanol
Butanol
Pentanol
THE TREASURES WITH
A HARD CRUST
Sodium
Potassium
Silicon
Magnesium
Hydrogen fluoride
Hydrogen chloride
Hydrogen bromide
Phosphorus
Chloromethane
Xenon
www.esa.int
Credits: Based on data from ROSINA
European Space Agency

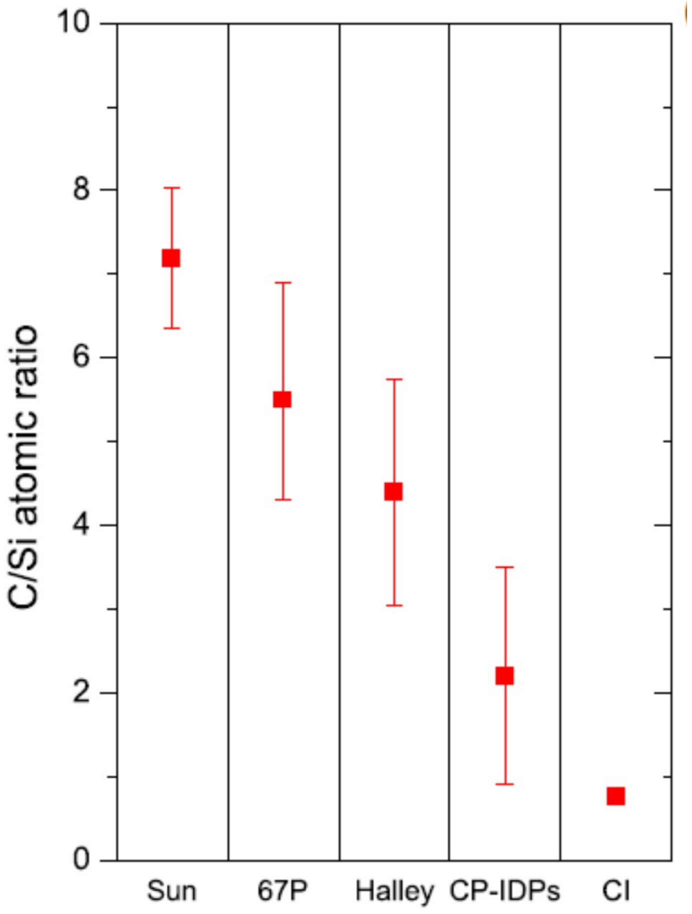
Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY
MNRAS 469, S712–S722 (2017) doi:10.1093/mnras/stx2640

Carbon-rich dust in comet 67P/Churyumov-Gerasimenko measured by COSIMA/*Rosetta*

Anaïs Bardyn,[1,2★†‡] Donia Baklouti,[3★†] Hervé Cottin,[1★] Nicolas Fray,[1] Christelle Briois,[2] John Paquette,[4] Oliver Stenzel,[4] Cécile Engrand,[5] Henning Fischer,[4] Klaus Hornung,[6] Robin Isnard,[1,2] Yves Langevin,[3] Harry Lehto,[7] Léna Le Roy,[8] Nicolas Ligier,[3] Sihane Merouane,[4] Paola Modica,[1,2] François-Régis Orthous-Daunay,[9] Jouni Rynö,[10] Rita Schulz,[11] Johan Silén,[10] Laurent Thirkell,[2] Kurt Varmuza,[12] Boris Zaprudin,[7] Jochen Kissel[4] and Martin Hilchenbach[4]



C/Si = 5.5 (+1.4/−1.2)



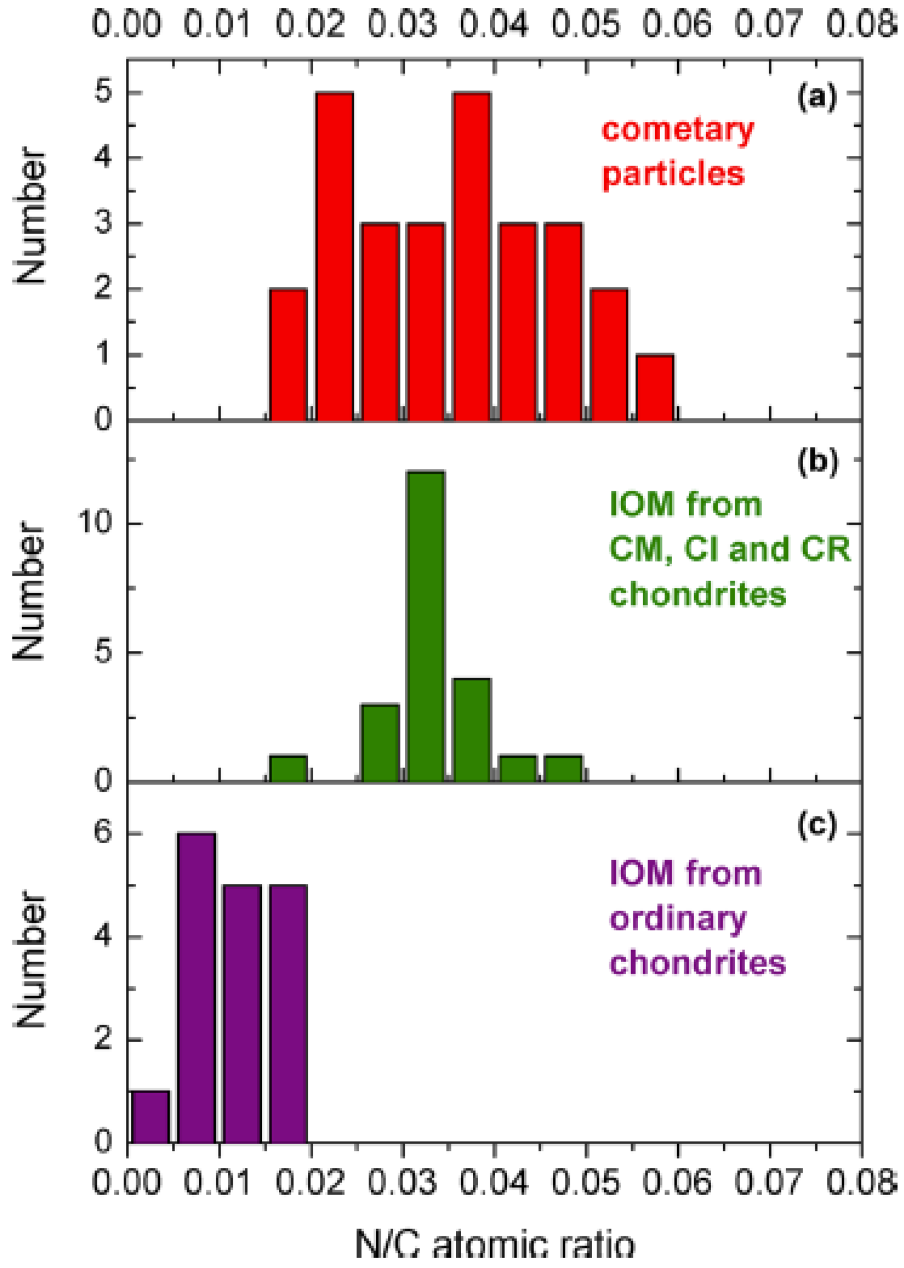
Solar value : 7.19 ± 0.83

Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY
MNRAS 469, S506–S516 (2017) doi:10.1093/mnras/stx2002
Advance Access publication 2017 August 5

Nitrogen-to-carbon atomic ratio measured by COSIMA in the particles of comet 67P/Churyumov–Gerasimenko

Nicolas Fray,[1★] Anaïs Bardyn,[1,2] Hervé Cottin,[1] Donia Baklouti,[3] Christelle Briois,[2] Cécile Engrand,[4] Henning Fischer,[5] Klaus Hornung,[6] Robin Isnard,[1,2] Yves Langevin,[3] Harry Lehto,[7] Léna Le Roy,[8] Eva Maria Mellado,[6] Sihane Merouane,[5] Paola Modica,[1,2] François-Régis Orthous-Daunay,[9] John Paquette,[5] Jouni Rynö,[10] Rita Schulz,[11] Johan Silén,[10] Sandra Siljeström,[12] Oliver Stenzel,[5] Laurent Thirkell,[2] Kurt Varmuza,[13] Boris Zaprudin,[7] Jochen Kissel[5] and Martin Hilchenbach[5]

67P dust particles : N/C = 0.035 ± 0.01



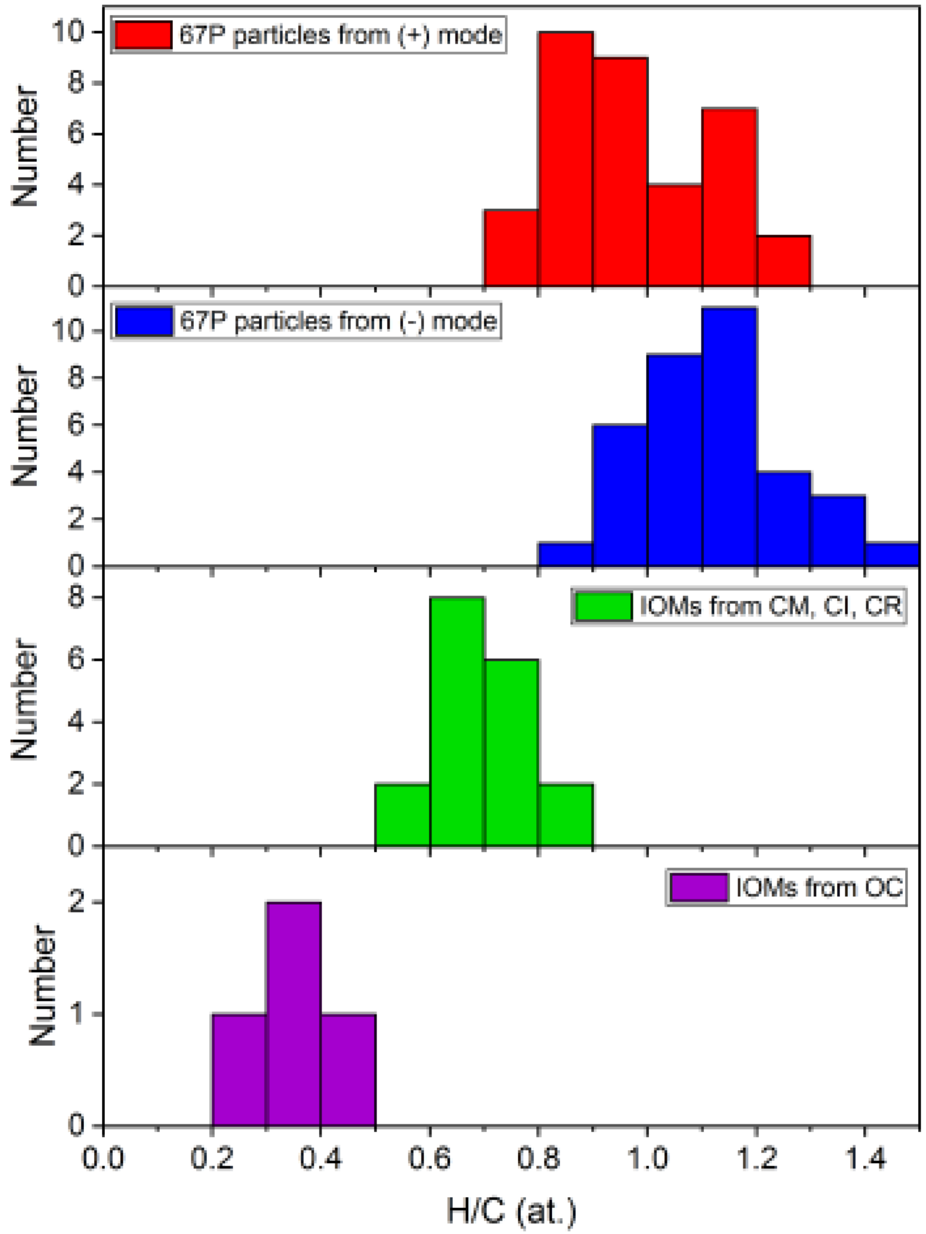
Solar value: 0.3 ± 0.1
(remaining N in salts sublimating before COSIMA analysis ?)

Astronomy & Astrophysics manuscript no. 34797corr
March 20, 2019

H/C elemental ratio of the refractory organic matter in cometary particles of 67P/Churyumov-Gerasimenko

R. Isnard[1,2], A. Bardyn[3], N. Fray[1], C. Briois[2], H. Cottin[1], J. Paquette[4], O. Stenzel[4], C. Alexander[3], D. Baklouti[5], C. Engrand[6], F-R. Orthous-Daunay[7], S. Siljeström[8], K. Varmuza[9], and M. Hilchenbach[4]

H/C = 1.040 ± 0.16



Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY
MNRAS 504, 4940–4951 (2021) doi:10.1093/mnras/stab1028
Advance Access publication 2021 April 17

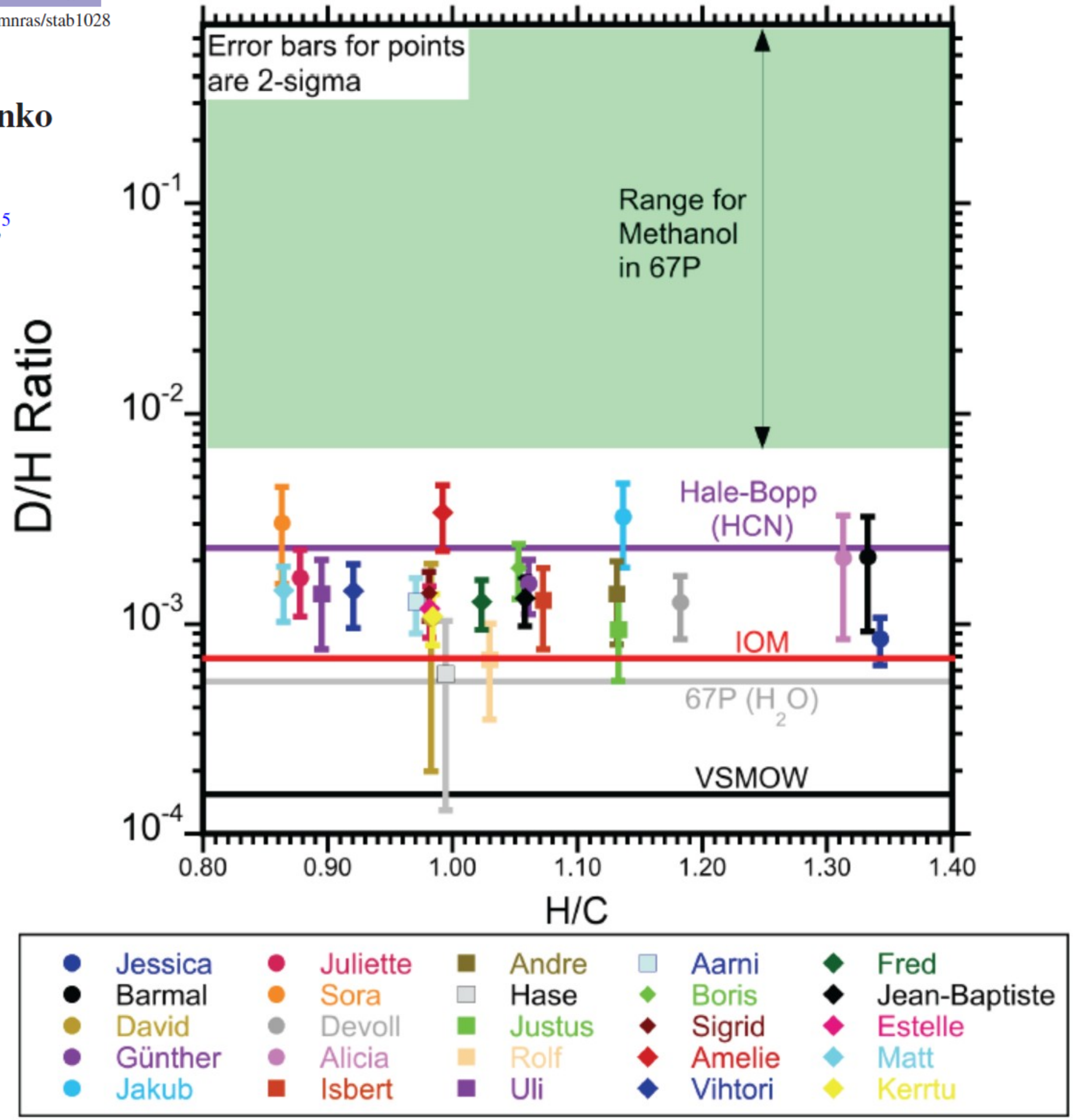
D/H in the refractory organics of comet 67P/Churyumov-Gerasimenko measured by *Rosetta*/COSIMA

J. A. Paquette[1★] N. Fray,[2] A. Bardyn,[3] C. Engrand[4] C. M. O'D. Alexander,[3] S. Siljeström,[5] H. Cottin,[2] S. Merouane,[1] R. Isnard,[2,6] O. J. Stenzel,[1] H. Fischer,[1] J. Rynö,[7] J. Kissel[1] and M. Hilchenbach[1★]

D/H = (1.57 ± 0.54) x 10^{-3}

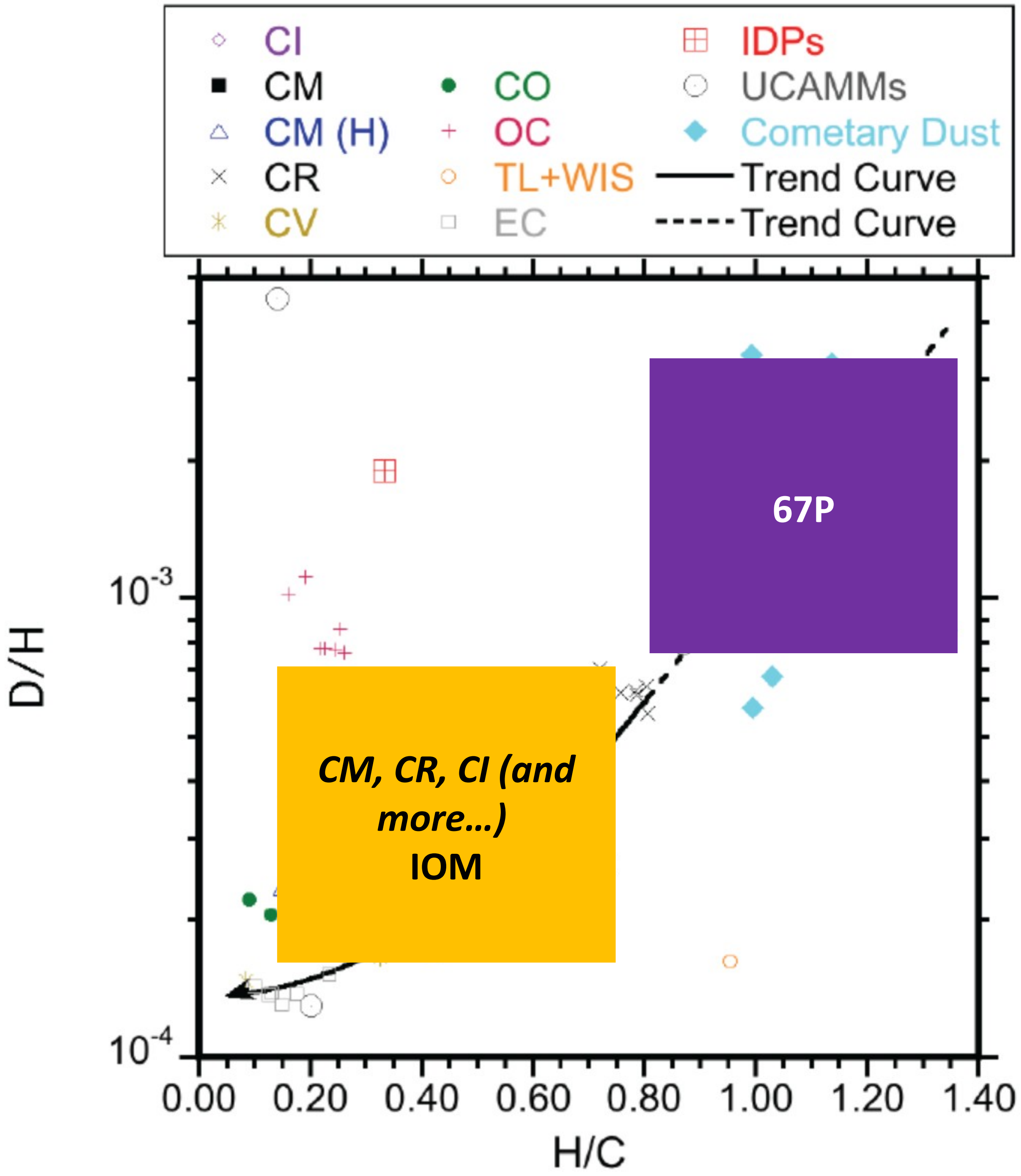
Inheritance from the presolar molecular cloud?

High averaged value suggests that refractory carbonaceous matter in comet 67P is less processed than the most primitive insoluble organic matter (IOM) in meteorites, which has a D/H ratio in the range of about 1 to 7×10^{-4}.



67P Vs Kerogens & IOMs

Paquette et al., 2021



HMWOC in 67P are less *heat /radiations* evolved organic material than IOMs and kerogens

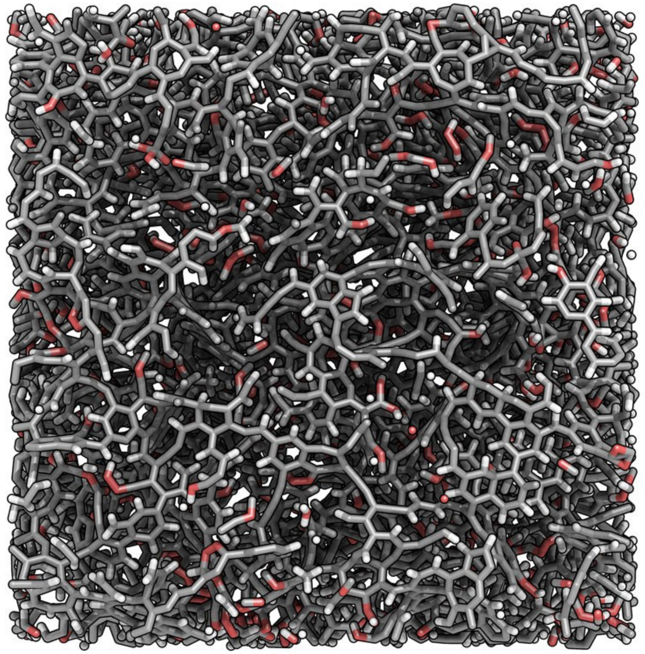
High Molecular Weight Organic Component HMWOC

C/Si = 5.5 (+1.4/−1.2)

H/C = 1.040 ± 0.16

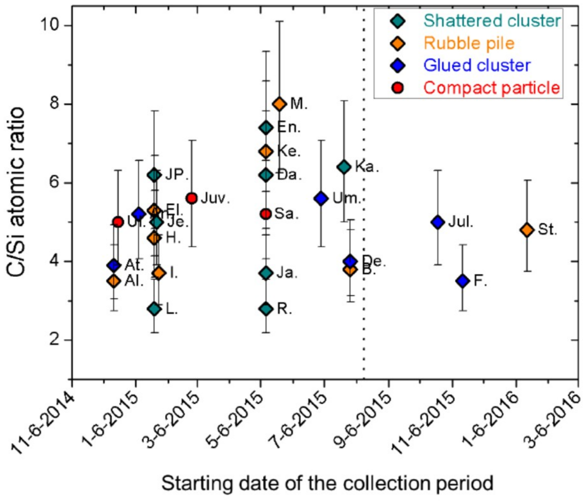
N/C = 0.035 ± 0.01

D/H = (1.57 ± 0.54) x 10^{-3}



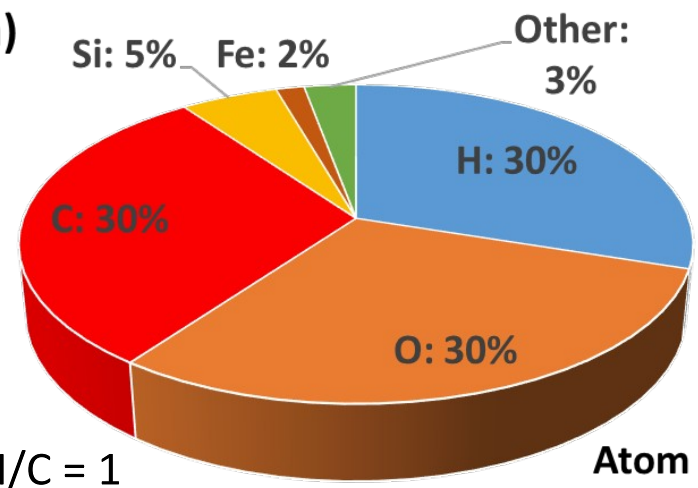
Disclaimer 1

Dust particles composition measured by COSIMA is assumed to be representative of the refractory component of the nucleus of 67P



Quantification of carbon and HMWC in 67P dust particles

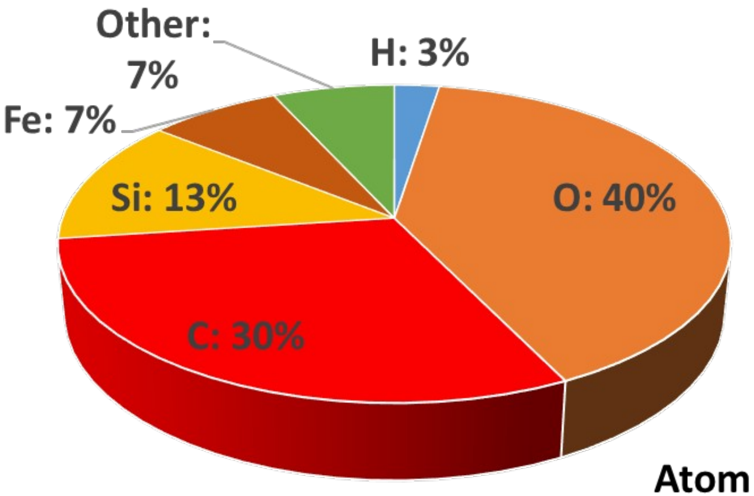
(a)



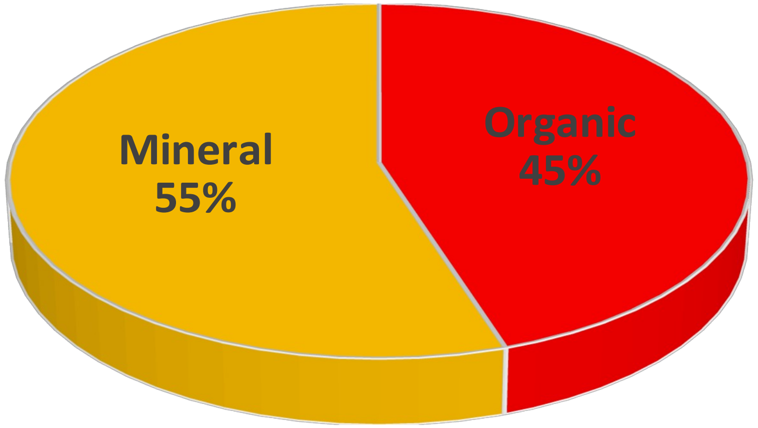
Atom number

With H/C = 1
S, Ni, … = Solar

(b)

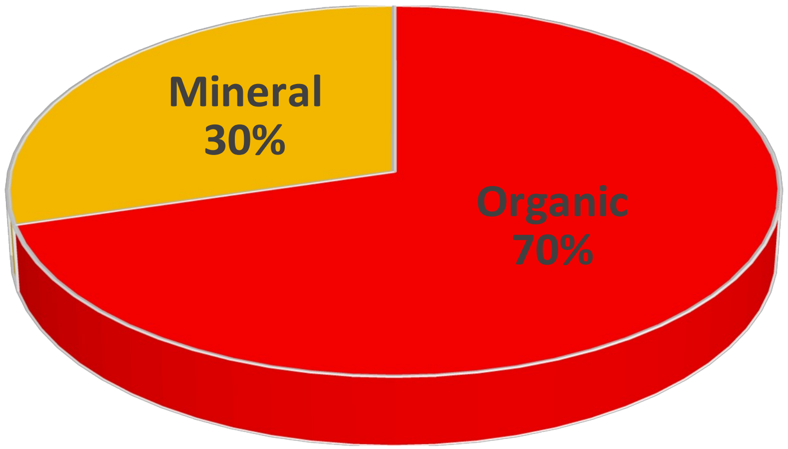


Atom mass



Abundance in Mass

With H, C, N, and some O in organic
Remaining in mineral (max O in mineral set at SiO_4)

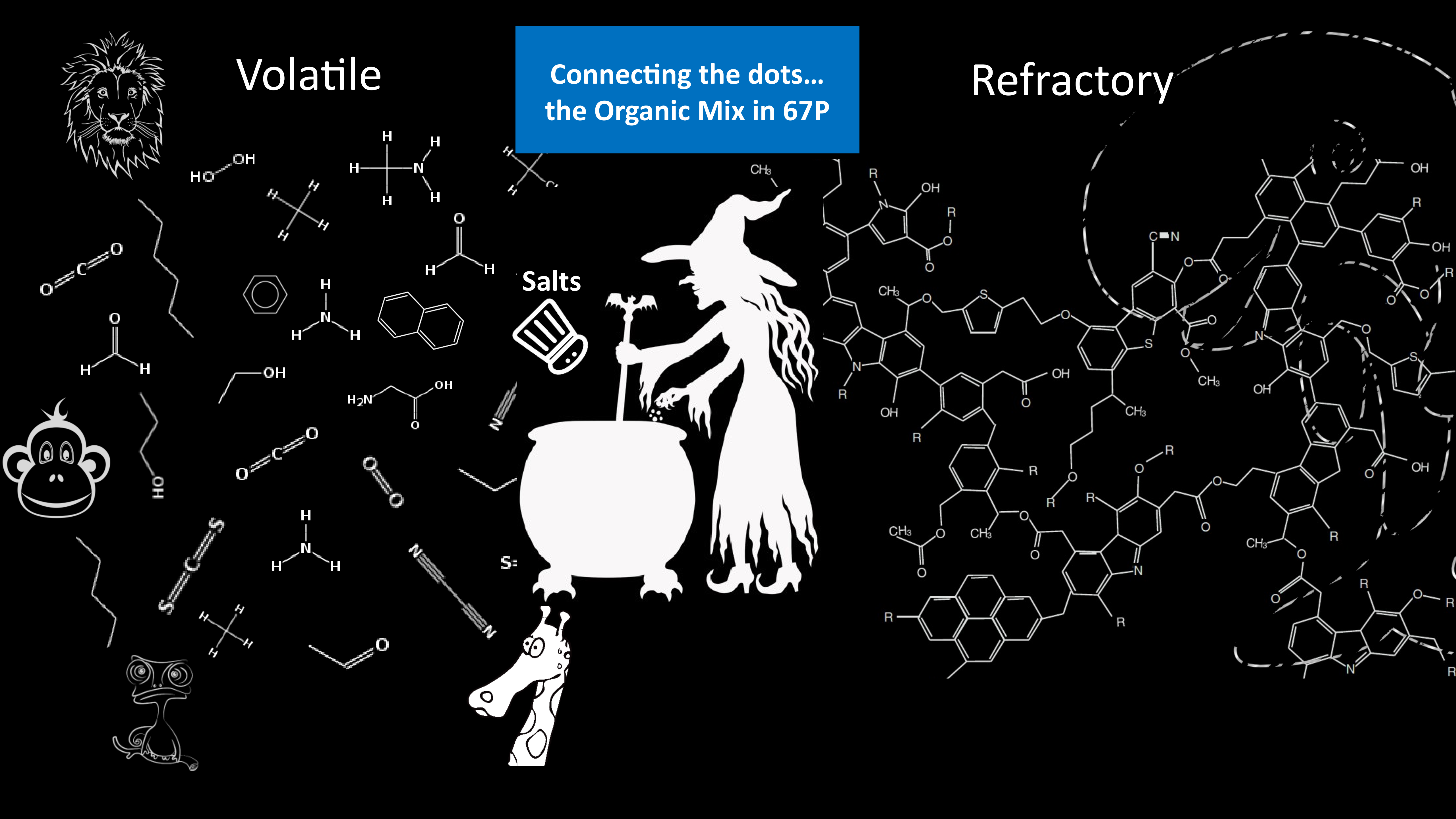


Abundance in volume

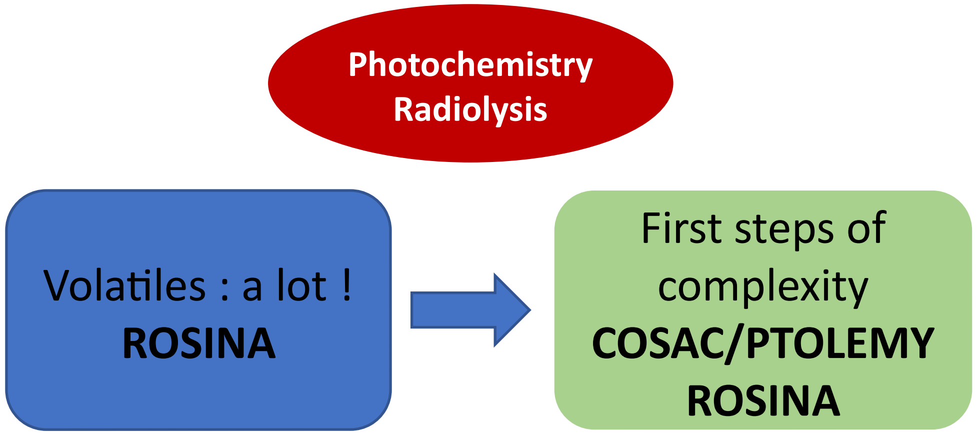
With d_{min}=3 & d_{org}=1

Bardyn et al. MNRAS, 2017

Levasseur Regourd et al., SSR, 2018


Connecting the dots…
the Organic Mix in 67P
Volatile
Refractory
Salts

Concluding remarks : the Organic Mix



Goesmann et al., Science 2015

The COSAC molecules form a consistent set related by plausible formation pathways (Fig. 3). A nitrogen source such as NH_3 must originally have been abundant to form the many N-bearing species, but could since have mostly evaporated or been used up in reactions. All the COSAC organics can be formed by UV irradiation and/or radiolysis of ices due to the incidence of galactic and solar cosmic rays: alcohols and carbonyls derived from CO and H_2O ices (*19*), and amines and nitriles from CH_4 and NH_3 ices (*20*). Hydrolysis of nitriles produces amides, which are linked to isocyanates by isomerization.

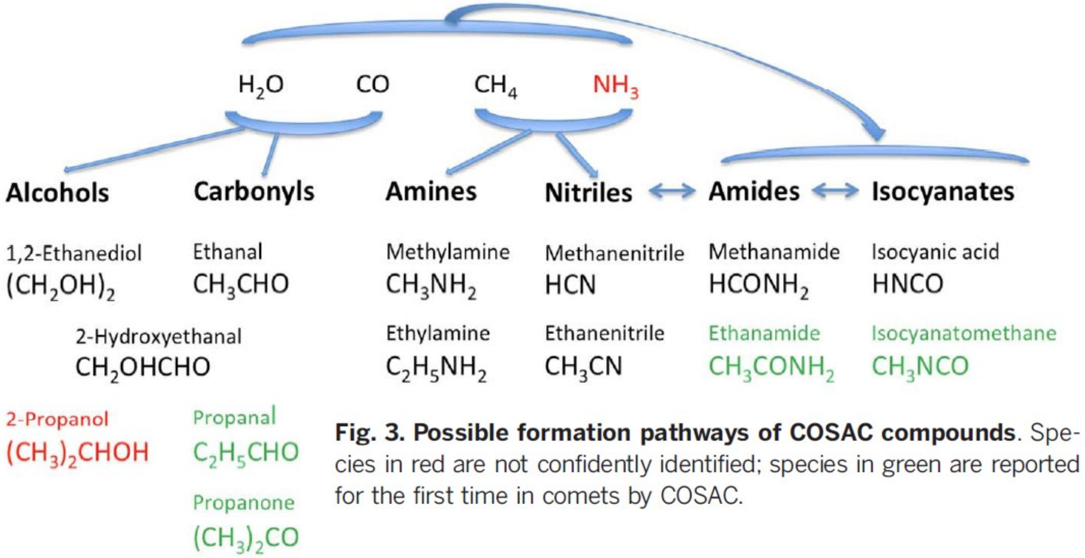


Fig. 3. Possible formation pathways of COSAC compounds. Species in red are not confidently identified; species in green are reported for the first time in comets by COSAC.

Concluding remarks : the Organic Mix

Photochemistry
Radiolysis

Photochemistry
Radiolysis
Heat

Photochemistry
Radiolysis
Heat

Volatiles : a lot !
ROSINA

→

First steps of complexity
COSAC/PTOLEMY
ROSINA

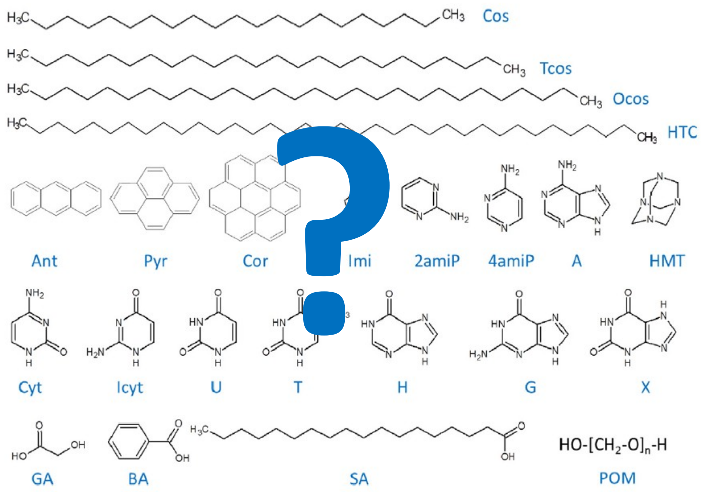
→

???
COSIMA

→

COSIMA
HMWC

Is there an equivalent of SOM found in carbonaceous chondrites ?



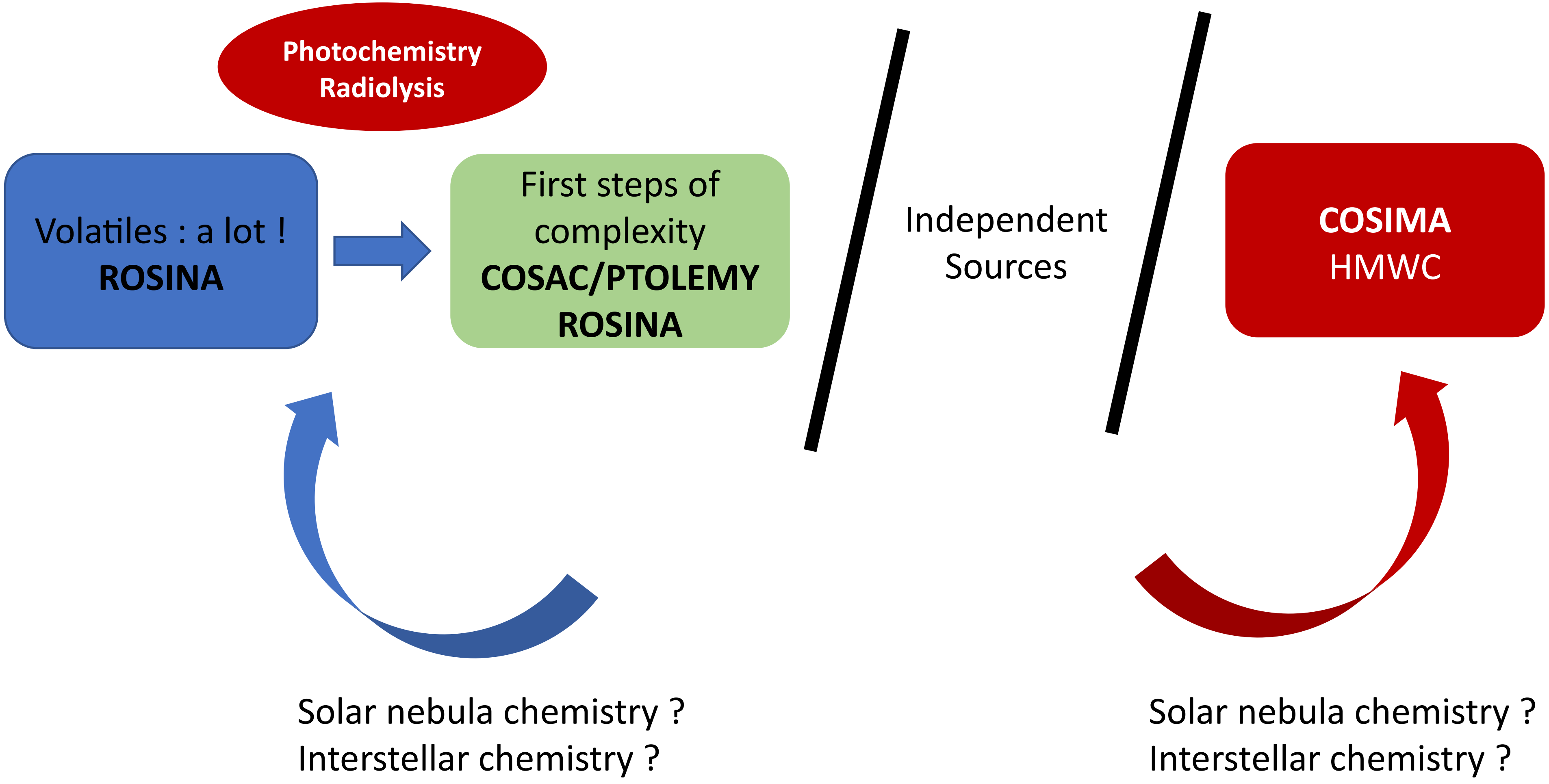
Disclaimer 2

Others molecules (smaller ones but yet refractory) might not have been detected by COSIMA either because:

1. They are below the detection limit of the instrument
2. They are not there

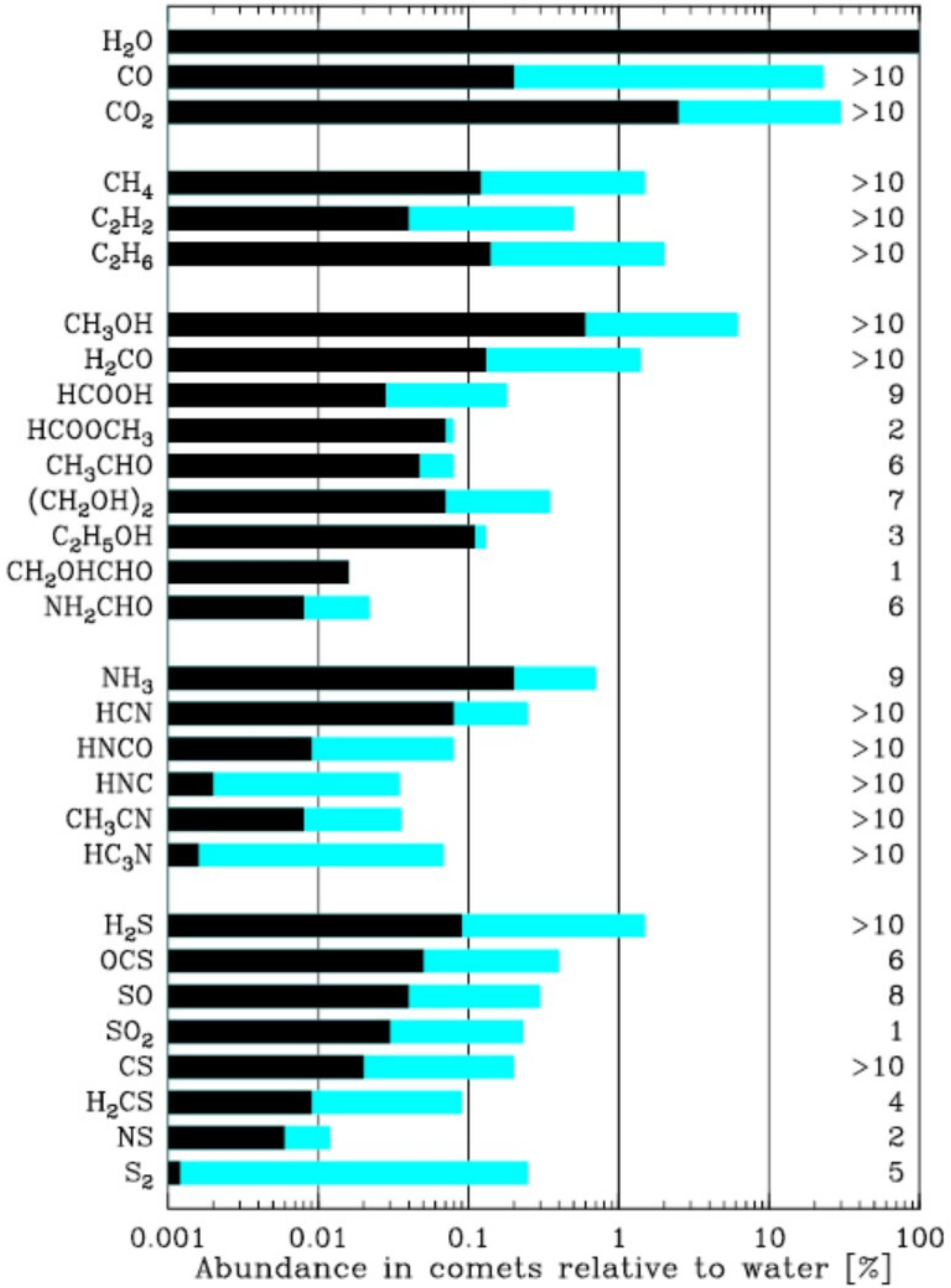
Hereafter we assume 2. (or detection limit is very low)

Concluding remarks : the Organic Mix



Organic molecules detected in comets

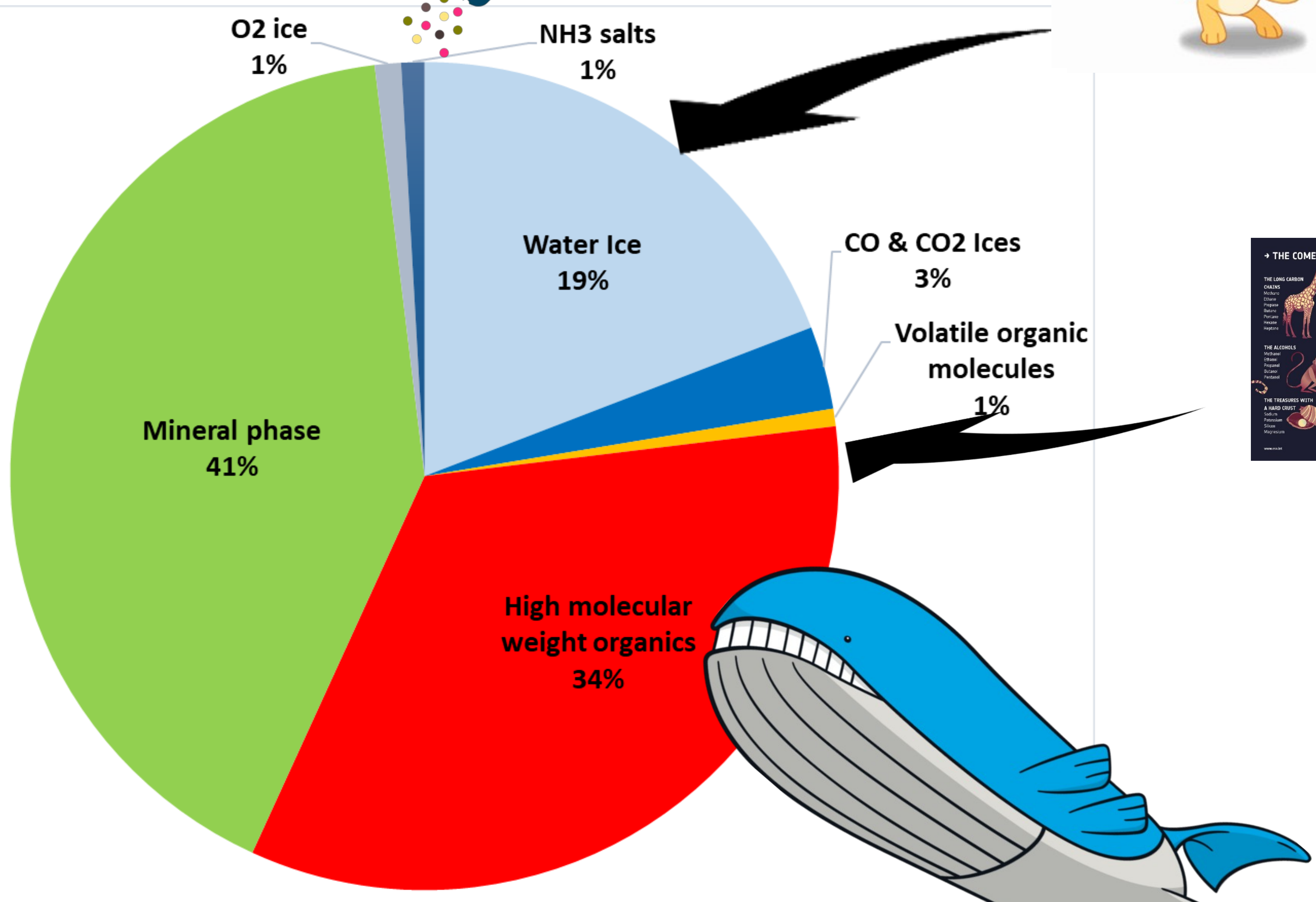
Organic molecules in the COMA :
~ 5% or less rel. to water



Inventory based on remote detections from Earth

Biver et al., ACS Earth and Space Chemistry, 2019

Composition of comet 67P

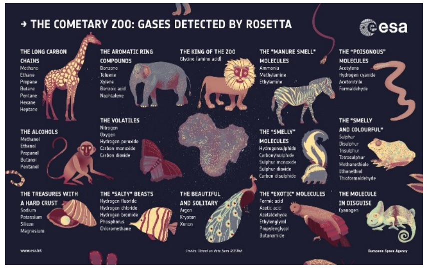


Composition of comet 67P in mass

Cottin et al., in prep

~200 ppb_w
rel. to water ice

The distributed ~~*disturbed lion*~~ glycine…



Dust = 45% organic in mass

Gas = 5% CO_2, 3% CO, 3% O_2, 2% others (CH_3OH,…)

Dust/Ice in mass = 3

For D/I see Choukroun et al., 2019

Disclaimer 3

All comets are not necessarily born equal in composition (*although they may have the same rights*)

At which extent conclusions from 67P can be generalized to all comets ? (cf. Wild 2)

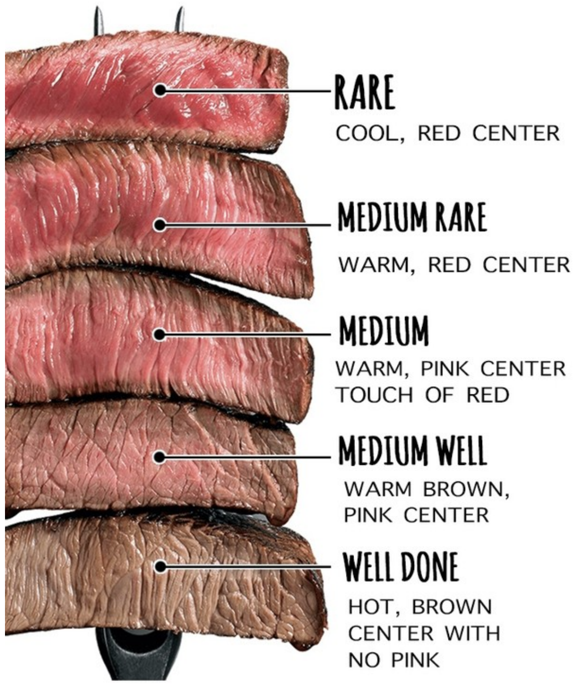
Conclusions

- Comets like 67P are an important reservoir of carbon and organic matter in the Solar System.
- The refractory organic phase in particles of comet 67P is dominated by a high molecular weight organic component (HMWOC) . This could be the parent material for IOM seen in chondrites.
- Most of the carbon of the comet is stored in the nucleus under this “complex” form.
- Glycine & other “so called” prebiotic compounds abundances are extremely low: is there enough readily available “prebiotic” ingredients ?
- The relevance for astrobiology of the cometary HMWOC has to be investigated
- Is there something missing in the whole picture ?

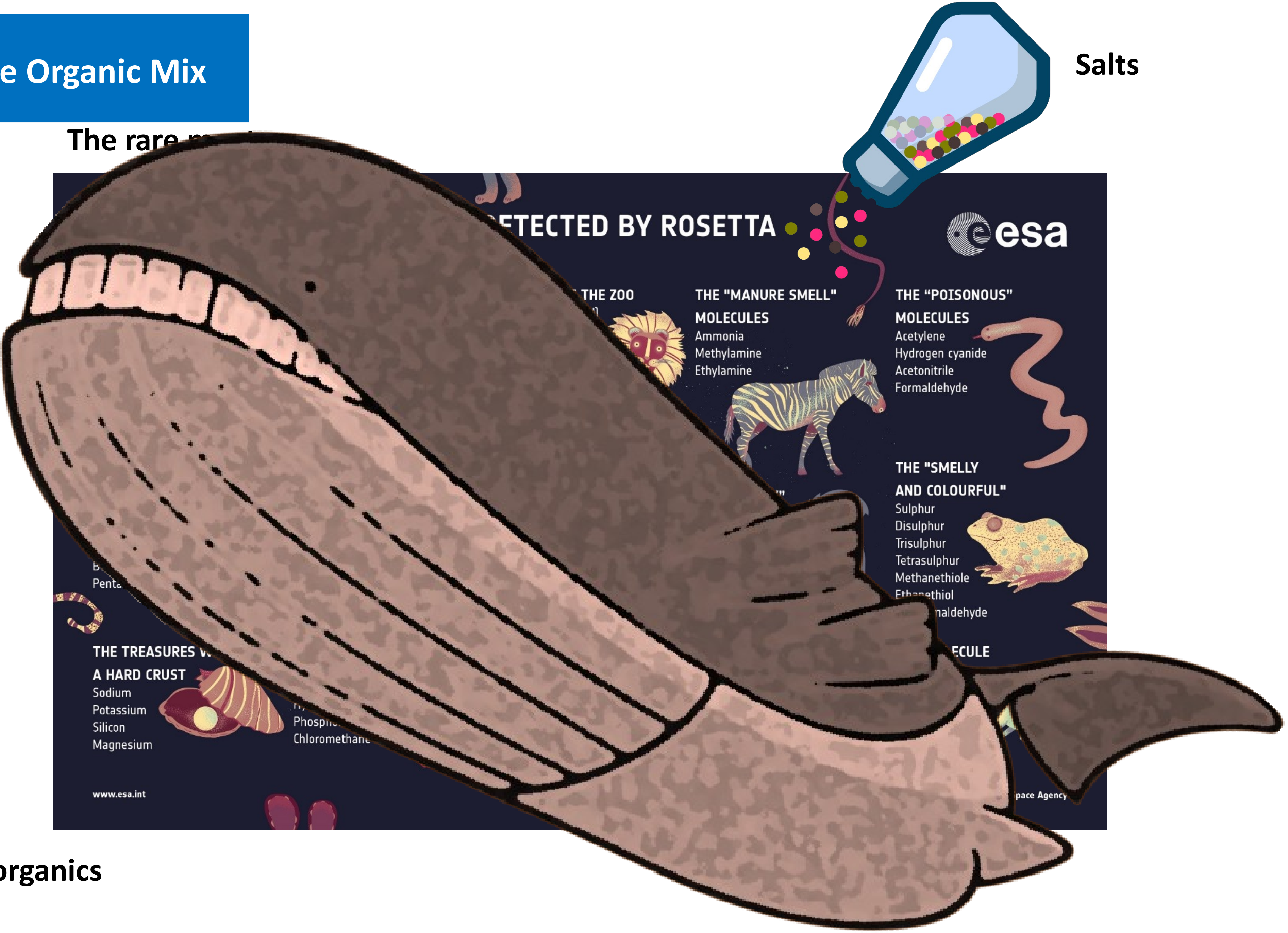
  => Recent detection of equivalent of Soluble Organic Matter from Chondritic Meterorites

Concluding remarks : the Organic Mix

The rare m



Salts



Cooking energy:

Heat or radiations

Well done HMW organics