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Observations of Cometary Organics: A Post Rosetta Review

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ABSTRACT Comets are relics from the formation of the solar system. During their formation, the comets captured organics in their vicinity that may have originated in interstellar space and survived the collapse of the solar system's parent molecular cloud. The variety of organic compounds depends on the initial ingredients and formation conditions, subsequently modified through chemical processes in the solar nebula and on the comet. As a result, organic compounds record the history of their journey from interstellar space, through comets and perhaps onwards to Earth. However, because of the fragile nature of comets, the pristine organics stored on the nucleus of comets is difficult to detect directly. The composition of cometary organics has been gleaned from a variety of sources, remote sensing detection of volatiles in the coma of many comets, *in-situ* spacecraft missions of a few targeted comets, and terrestrial analysis of refractory organics in potential cometary dust arriving on Earth. The spacecraft missions providing the link between the remote sensing and terrestrial analysis. We review these observations in light of the recent completion of the Rosetta mission, with its lander Philae and long term monitoring of 67P/Churyumov-Gerasimenko, which has greatly expanded our knowledge of cometary organics.

Introduction

Comets with their diffuse coma and striking tails have been observed and recorded by humans for millennia. Ancient views on comets were often linked to omens and messengers from gods, because of their unpredictable appearance in the heavens. With the advent of the Enlightenment and the discovery that at least one comet had a predictable orbit, 1P/Halley, it was realised that comets are part of our solar system. Whipple¹, proposed that comets were a mixture of icy conglomerates, known as the "dirty snowball" hypothesis, which formed the basis of our understanding of comets. As a comet enters the inner solar system the rise in temperature causes ices to sublime to form the coma of dust and gas. The tail is formed from subsequent interaction of the coma with the solar wind.

Approximately 200 organic molecules have been detected in interstellar space². The low pressures and temperatures of their formation environment suggest that they were formed through concentration onto dust grains rather than gas phase chemistry. Laboratory simulations³⁻¹⁶ have shown that ices condensing and forming icy mantles on dust grains form a range of organic molecules in the conditions of interstellar space and star forming regions. Our solar system would have contained this material as it collapsed from the parent molecular cloud to form a proto planetary disk. An overview of the processes and conditions in the proto-planetary disk¹⁷ during the formation of comets and the planets is shown in Figure 1.

Comets are thought to be the most primitive bodies in the solar system, having formed in the solar nebula 4.6 Gy ago beyond the snowline and then dispersed by the interaction of the gas giant planets to the Oort cloud and scattered disk^{18, 19}. The chemistry of the synthesis of organic molecules is

dependent on the prevailing conditions, such as organic precursors, the prevalence of water, energy sources (e.g. UV), state (gas phase, solid-gas phase), and other physical / chemical conditions such as temperature, pressure, pH, etc.²⁰. Hence, organic molecules in comets offer a tantalising glimpse into the chemistry, conditions and evolution of the solar system. The survival for any organic molecules formed in the interstellar medium (ISM) to their detection in comets is challenging, with the molecules having to run the gauntlet of solar system formation, the frigid cometary conditions, and the sublimation processes from the comet surface to eventual detection.

Figure 1. An overview of the conditions and processes of the solar proto-planetary disk. Reproduced from Ref. ¹⁷, Copyright 2013 Chemical Reviews.

Key questions in the study of comets are: To what extent do comets record the molecular composition of the parent molecular cloud? How are the organics modified during comet formation? What organics are formed as comets enter the inner solar system? Did comets bring organic molecules to the early Earth and perhaps play a part in the emergence of life on Earth?

Ideally, studying the cometary organics would require a comet sample collected and returned to Earth for investigation by the full suite of laboratory instruments. A pristine sample would need to be collected at depth, or at a freshly exposed surface, and returned at cryogenic temperatures to maintain volatiles and limit chemical interaction. The sampling device and storage container should also maintain the sample structure (e.g. layering and porosity). Although comet sample return missions have been

proposed, technical and budgetary constraints have so far proved insurmountable. So, to determine the composition of cometary organics we have to decipher information gained from a variety of sources; remote observations, *in-situ* spacecraft missions, and laboratory analyses of cometary particles collected by space missions and on Earth; backed up with modelling and laboratory simulations.

Spectral observations of cometary organics

Remote sensing techniques

Remote sensing from telescopes on or near Earth enables observations of the coma of many comets. The spectra of the coma consist of spectral lines of the gas superimposed on the solar spectrum reflected by dust. However, the coma does not represent the pristine comet material. Solar radiation can result in the photo-ionisation and photo-dissociation of gas molecules. Close to the comet, within the collisional zone, the coma pressure is great enough for molecules and ions to collide and form new ions, radicals and molecules. The depth of the collisional zone is proportional to comet activity, and would have been a few hundred km for comet 67P/Churyumov-Gerasimenko at its peak activity of 3.5×10^{28} molecules s^{-1} .²¹ Beyond the collisional zone, photo-dissociation results in daughter and grand-daughter products. Hence, the presence of parent species has to be inferred by modelling the molecule lifetime and chemical reaction networks. Observations of parent molecules are usually made in the radio (20 – 600 GHz) and near infrared regions of the electromagnetic spectrum, occasionally in the optical and ultraviolet; the techniques are described in reviews by Bockelée-Morvan et al.²² and Cochran et al.²³.

Most observations of comets are in the visible waveband as this type of measurement has existed for much longer than in other wavebands. The visible waveband spectra typically consist of the continuum along with fluorescence emission lines from the coma gas and molecules. Observations of the coma can be made by either spectrometry or photometry. Spectrometry produces a wide spectrum where emission lines can be readily distinguished from the continuum and different emission lines are measured simultaneously so that relative abundances can be determined without concerns from temporal variability, however this technique has narrow apertures or slits and cannot cover the whole coma²³. Photometry where the coma is viewed sequentially through filters tuned to the emission bands can have larger aperture to cover the coma. However, the continuum needs to be subtracted, based on a predicted continuum, and the filters need to be swapped at a sufficient rate to minimise temporal variations.

The ultraviolet (UV) region of the electromagnetic spectrum is strongly affected by the Earth's atmosphere, so the acquiring UV comet spectra requires orbital platforms, or *in-situ* spacecraft observation. The energy of UV photons is high enough to dissociate polyatomic molecules rather than causing fluorescence. Although complex parent organics cannot be observed in the UV region, it is used to determine water and carbon monoxide production rates.

Many organic molecules are symmetric (e.g. methane, and ethane) and so they lack a permanent dipole moment making them unobservable in the visible and radio spectra. Infrared (IR) observations detect the vibrational transitions in organic molecules and so can detect both the symmetric and asymmetric

molecules. Typically, observations are made in the 1 to 5 μm region, often concentrating in the 2.5 to 5 μm region. The Earth's atmosphere is opaque in much of the IR region due to atmospheric water and carbon dioxide, so observations are restricted to windows in the atmospheric spectrum, clear of any water and carbon dioxide adsorption. Even in the clean regions IR observations require high resolution spectroscopy ($\lambda/\delta\lambda > 10^4$) and the effect of atmospheric adsorption must be removed. Comets are fainter in the IR, requiring larger telescopes and limiting observations to bright comets and close heliocentric distances.

Radio observations detect the pure rotational transitions of molecules with a permanent dipole moment. Radio spectrometers have extremely high spectral resolution ($\lambda/\delta\lambda > 10^6$) with molecules identified in several lines to remove ambiguity. A major advance is the inauguration and operation of the Atacama Large millimetre/submillimetre Array (ALMA) in 2013. ALMA is a radio interferometer consisting of 66 antennas with a baseline from 150 m to 16 km. The high spatial and spectral resolution of ALMA is capable of producing high resolution contour maps of the organics in the coma (e.g. the HCN, HNC and H₂CO coma maps of comets C/2012 F6 (Lemmon) and C/2012 S1 (ISON) ²⁴).

The majority of the coma consists of radicals and ions so observation of the less abundant parent molecules by spectral analysis requires the apparition of bright comets such as C/1995 O1 (Hale-Bopp), C/1996 B2 (Hyakutake), C1994 S4 (LINEAR), C/2012 F6 (Lemmon), C/2012 S1 (ISON), C/2013 R1 (Lovejoy), C/2013 V5 (Oukaimeden), 1P/Halley, 8P/Tuttle and 17 Holmes. Hale-Bopp was a particularly bright comet with a fortuitous apparition in 1997, just as radio and Infrared was becoming routine ²³. About half of the known organic molecules were identified for the first time in Hale-Bopp. Techniques have improved since Hale-Bopp, but detection of less abundant molecules will have to wait for the next 'comet of the century'.

Detection of organics by remote sensing

As of 2017, 18 organic molecules have been detected (reviewed by Bockelée-Morvan and Biver ²⁵), listed in Table 1 along with detection of non-organic parent molecules. The concentrations of organics relative to water vary by about a factor of 10 from comet to comet ²⁶. The ranges given in Table 1 are not errors but the range of abundances observed between comets. Typically, the make-up of the classes of organics (relative to water) is about 4% pure hydrocarbon, 2% with oxygen, 1% nitrogenous, 1% sulphurous and 0.1 % containing both oxygen and nitrogen ²⁵, with a decrease in abundance with increasing complexity. All of the organic molecules identified have been detected in the interstellar space where irradiation of CO and NH₃ in the icy mantles surrounding dust grain forms more complex organics, providing a link between interstellar and cometary organics ²⁷. The detection of ethanol (C₂H₅OH) and glycolaldehyde (HO-CH₂-CHO) in comet C2014 Q2 (Lovejoy) ²⁸ continues filling in the reaction scheme proposed by Charnley and Rodgers ²⁷.

Table 1. Molecules and their abundances relative to water (in %) from remote spectroscopic observations organised by class. Adapted from Bockelée-Morvan and Biver ²⁵.

Main compounds	Hydrocarbons	Oxygen containing organics	Nitrogen containing compounds	O & N organics	Sulphurous molecules
H ₂ O (100)	C ₂ H ₆ (0.14 – 2.0)	CH ₃ OH (0.6 – 6.2)	NH ₃ (0.3 – 0.7)	HNCO	H ₂ S (0.13 – 1.5)

CO ₂ (2.5 – 30)	CH ₄ (0.12 – 1.5)	H ₂ CO (0.13 – 1.4)	HCN (0.08 – 0.25)	NH ₂ CHO (0.009 – 0.08) (0.008 – 0.021)	OCS (0.03 – 0.40)
CO (0.23 – 23)	C ₂ H ₂ (0.04 – 0.5)	(CH ₂ OH) ₂ 0.35)	CH ₃ CN (0.008 – 0.036)	SO (0.04 – 0.30)	
		C ₂ H ₅ OH (0.12)	HC ₃ N (0.002 – 0.068)	SO ₂ (0.2)	
		HCOOCH ₃ (0.07-0.08)	HNC (0.002 – 0.035)	CS (0.02 – 0.20)	
		CH ₃ CHO (0.05 – 0.08)		H ₂ CS (0.009 – 0.09)	
		HCOOH (0.028 – 0.18)		NS (0.006 – 0.012)	
		CH ₂ OHCHO (0.016)		S ₂ (0.001 – 0.25)	

Comet Taxonomy based on remote sensing data

Observations by remote sensing can view a far greater number of comets than can ever be reached by space missions. Building a taxonomic classification system can then be used to link populations of comets with their potential formation conditions and subsequent evolution to those few individual comets visited by spacecraft ²⁹. In addition, statistical analyses of the classes and their distribution can then be used to place constraints on the dynamic evolution of the solar system based on the Nice model ³⁰.

Viewed in the visible spectrum, the main emission lines correspond to daughter products, CN, C₂, C₃, O I, OH, NH, NH₂ and CH ²³ provide evidence of the presence of organic material in the nucleus. Even early surveys of comets (e.g. Newburn and Spinrad ³¹) realised that most comets had very similar spectra, although several anomalous comets were shown to be carbon depleted with low C₂ and C₃. With this variation in the carbon content, comets are broadly categorised into two distinct groups: ‘typical’ and ‘carbon depleted’ ³². As larger surveys are being generated some complexity in taxonomy begin to appear ²⁹. Carbon depleted comets are more common in the Jupiter Family Comets (JFCs), 37% as opposed to only 18.5% of the long period comets ³³. Schleicher and Bair ³⁴ identified 7 comet groups

based on the production rate of CN, C₂ and C₃ with the majority (~70%) forming the single group classed as 'typical'.

It would seem that IR and radio observations would be more useful in identifying comet taxonomy based on the identification of the precursors that form the CN C₂ and C₃ bands. Mumma and Charnley²⁹ suggested that there were three groups, 'typical', 'organic enriched' and 'organic severely depleted'. However, there were inconsistencies such as 8P/Tuttle which is optically classified as 'typical' but in IR that it is severely depleted in C₂H₂ and HCN, low in C₂H₆ and enriched in CH₃OH. Bockelée-Morvan and Biver²⁵ noted that the histograms of each molecule showed an approximate Gaussian shaped distribution (on a log plot) with no apparent difference between JFCs, Halley type comets, long period dynamically old comets and long period dynamically new comets. A cluster analysis on 30 comets observed in high resolution IR³⁵ of eight molecular species, identified four main groups with a total of 11 sub-groups; although the division between the sub-groups was thought to be somewhat arbitrary with each comet having its own fingerprint. Overall there was a depletion in the organics relative to water for the JFCs when compared with the long period comets.

In 1995, comet 73P/Schwassmann-Wachmann, a strongly C₂ and C₃ depleted comet, split into three pieces, and those pieces continued to split and is now known to have split into over 60 objects. Observations of the fragments in visible and IR^{36,37} showed that the fragments all had identical depletions and that there had been no change in its appearance before it split³⁶. The implication is that the coma is formed from outgassing of the bulk comet which acquired its composition, in this case C₂ and C₃ depleted, during its formation. Subsequent evolution of the comet would only affect the surface layers which either have the same composition, or if different it would only be a minor contribution towards the coma composition. Additionally, any fractionation in the surface layers would preferentially enrich the less volatile species which would become concentrated until equilibrium is achieved such that the composition of the outgassing from the surface will match that of the unfractionated bulk comet.

It appears that each comet acquired its organic finger print from the local region of the solar nebula in which it formed. Subsequent evolution may have depleted the organics relative to water, but the overall composition remains unchanged. Clearly with small data sets of about 100 comets, detailed classification beyond 'typical' and 'organic depleted' is somewhat tentative. With the improvement of observing sensitivity and observation of more comets, the comet classification may become a more useful tool in constraining models of solar system formation.

In-situ observations of cometary organics

***In-situ* before Rosetta**

Here we refer to *in-situ* as measurements by spacecraft instruments within, or close to, the coma of a comet. These measurements can include remote sensing instrumentation such as spectrometers measuring the coma and surface of the comet as well as instrumentation measuring comet properties at the spacecraft such as dust detectors and mass spectrometers. To date there have been 10 spacecraft that have taken part in 13 comet encounters, with three spacecraft each encountering two comets. Mission constraints limit the comet targets to JFCs, apart from 1P/Halley which was targeted by an

armada of five spacecraft as it was inbound to its 1986 apparition. Typically, the comet encounter was a high-speed flyby, ranging from in excess of 6 km s^{-1} (Stardust) to approximately 70 km s^{-1} (missions to 1P/Halley), consequently the spacecraft was within the comet coma for only a few hours, or days at most. The exception being the Rosetta mission which remained in the vicinity of comet 67P/Churyumov-Gerasimenko from July 2014 to September 2016. The comet missions and encounter profiles are summarised in Figure 2.

Figure 2. A summary of comet missions, with mission profiles enhanced by a factor of 10 and centred on date of closest approach, which for Rosetta was the spacecraft landing on 30th September 2016. Space craft images public domain except: Giotto, Creative Commons Attribution-Share Alike 3.0 Unported license, author Andrez Mirecki; Rosetta & Philae reproduced with permission, copyright ESA/ATG medialab; Comet image: ESA/Rosetta/Navcam

The Giotto, VEGA 1 and VEGA 2 Time-of-Flight (ToF) mass spectrometers found that approximately 30% of the particles detected during the encounter with comet 1P/Halley had high amounts of carbon, hydrogen, oxygen and nitrogen (CHON)³⁸. Comparison between the mass spectra of silicate particles and CHON particles³⁹ led to the conclusion that all particles were an intimate mixture of silicates and organics on the sub-micron scale. The occurrence of silicate rich particles is probably as a result of the loss of the organics during their journey from the comet surface to the spacecraft. The Neutral Mass Spectrometer (NMS) on the Giotto spacecraft has detected seven organic molecules in the coma of Comet Halley, H₂CO, CH₃OH, C₂H₂, C₂H₄, C₂H₆ and HCN⁴⁰. Of particular interest, was that the radial distribution of both formaldehyde (H₂CO) and carbon monoxide indicated that they did not originate solely from the nucleus but were extended sources⁴¹, with the formaldehyde was solely an extended source (within errors) and its dissociation accounted for approximately 30% of the carbon monoxide. Poly-Oxy-Methylene (POM) was suggested as the most likely source⁴¹, however alternative explanations are non-uniform outgassing from the nucleus or a change in production rate a few hours before the flyby⁴².

The aim of Stardust mission was to collect and return to Earth particles from a comet and interstellar space. In 2004, the Stardust mission encountered comet 81P/Wild (also known as Wild 2) at a relative speed of 6.1 km s⁻¹ and distance of 247 km and collected particles using aerogel collectors. During the encounter, the temporal distribution of the impacting particles indicated that they consisted of conglomerates of friable particles⁴³. The Cometary and Interstellar Dust Analyzer (CIDA) ToF mass spectrometer acquired 29 mass spectra⁴⁴. The spectra showed no evidence of water and carbon monoxide, presumably having sublimed before encountering the spacecraft. The dust particles contained abundant organics, predominantly nitrogen bearing with one spectrum also indicating the presence of sulphur.

The capsule containing the aerogel returned to Earth in 2006 whilst the main spacecraft (renamed Stardust NExT) continued to an encounter with comet 9P/Tempel (also known as Tempel 1) in 2011 to the comet nucleus and the crater created by the Deep Impact mission. Particles collected by the aerogel suffered heating during their capture, similar to the heating of Interplanetary Dust Particles (IDPs) entering the Earth's atmosphere (see section 4) which would have modified the organics with the loss of light elements and potential graphitization⁴⁵. The cometary particles captured by the aerogel were an intimate mixture of organics and refractory silicates at the sub-micrometre scale. The presence of Glass Embedded Metal Sulphides (GEMS) and anhydrous silicate particles^{46, 47} indicates that some material were formed in a high temperature environment and then transported by turbulent mixing to the comet forming region. The organics associated with the particles and particle tracks were found to be a mixture of aromatic, aliphatic and polycyclic aromatic hydrocarbons (PAHs)⁴⁸. The aromatic and PAHs had not been detected in comets prior to Stardust, but Sandford et al.⁴⁸ noted that these molecules were similar to pyrolysis products of meteorite organics and so may have been produced during their capture. X-ray absorption near-edge spectroscopy (XANES), IR and Raman spectroscopy showed that the organics contained aromatic, aliphatic, carboxylic acid, ketone and nitrogen functional groups. The high CH₂/CH₃ ratios observed for the organics suggested that the aliphatic hydrocarbons were composed of longer chains than seen in the diffuse ISM, but similar to that of IDPs. The amino acid glycine and its precursor methylamine were detected in the Stardust comet-exposed aerogel and foil^{49, 50}, above background levels when compared to the unexposed foil. The glycine carbon isotopic ratio of $\delta^{13}\text{C} = +29$

$\pm 6\text{‰}$ (outside the normal terrestrial range for organic carbon of -6‰ to -40‰) is also indicative of its cometary nature ⁵⁰.

Deep Impact released a 372 kg smart impactor 24 hours before the flyby of comet 9P/Tempel at a relative speed of 10.3 km s^{-1} . The impact created a 150 m crater (as determined by the Stardust NExT spacecraft a few years later) and a large plume of material excavated from beneath the surface. The IR spectrometer on the spacecraft was low resolution but capable of detecting the broad band of C-H bond stretching of organics. The spectra of the impact plume taken by the main spacecraft showed an increase in organics, HCN abundance, and the possible detection of CH_3CN ⁵¹. Meanwhile, ground based observations indicated that most the volatile concentration was unchanged before and post impact. The exception being the $\text{C}_2\text{H}_6/\text{H}_2\text{O}$ ratio in which the ejecta had a more normal comet ratio of 0.59 ± 0.18 compared to the low pre-impact ratio of 0.194 ± 0.041 ⁵², suggesting that the surface is thermally processed with the resultant loss of hyper-volatiles C_2H_6 and CO .

Deep Impact then continued to encounter 103P/Hartley 2 in 2010. The emission of volatiles from this bi-lobed comet was highly heterogeneous with the waist emitting mainly water and the active smaller lobe emitting a high proportion of carbon dioxide and organics as well as icy grains ⁵³. A'Hearn et al. ⁵³ interpreted these results as carbon dioxide sublimed from the smaller lobe driving the release of dust, icy grains and organics whereas the waist consisted of secondary material, possibly from fallback of water ice grains and dust.

Rosetta

The Rosetta mission, launched in March 2004, aimed to catch up with comet 67P/Churyumov-Gerasimenko and make detailed close-up observations for over 2 years as the comet travelled from 3.7 AU inbound in early August 2014 to perihelion and back to 3.8 AU in September 2016. The trajectory necessitated a 10-year cruise phase involving three Earth and one Mars swing-by manoeuvres in order to match velocity with the comet. The unique mission profile of Rosetta compared to other missions is shown in Figure 2, with the spacecraft remaining within 100 km of the surface for most of the 26 months from arrival in August 2014, to comet soft impact in September 2016.

The Rosetta spacecraft had a total of 5 mass spectrometers, three on orbiter and two on the Philae lander:

1. The ROSINA - DFMS (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis – Double Focussing Mass Spectrometer) a high sensitivity high resolution mass spectrometer to measure the chemical and isotopic composition of the coma.
2. The ROSINA - RTOF (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis – Reflectron Time of Flight) high mass range and high scan rate mass spectrometer to measure the composition of the coma up to mass 3000.

3. COSIMA (COmetary Secondary Ion Mass Analyser) microscope and ion probe to analyse captured dust grains.
4. COSAC (COmetary Sampling And Composition) gas chromatography and time of flight mass spectrometer to analyse high mass organics released from a solid sample.
5. Ptolemy (no acronym, just a name) gas chromatography and ion trap mass spectrometer to measure the light element isotopic composition from a solid sample.

Two other instruments with the ability to detect organics were VIRTIS (Visual and IR Thermal Imaging Spectrometer), to map the nature of solids and temperature at the surface of the comet, and MIRO (Microwave Instrument for the Rosetta Orbiter) microwave instrument tuned to detect methanol, as well as water and ammonia. A list of Rosetta instruments with science goals to detect and measure organics is shown in Table 2, along with the instrument defining parameters.

Table 2. The list of Rosetta instruments with organic detection science goals and their defining characteristics ^{54, 55, 56, 57, 58, 59}.

Instrument	Type	Instrument parameters
ROSINA DFMS	High resolution mass spectrometer	Mass range 12 to 150, $M/\Delta M > 3000$ at 1% peak height (required for isotopic analysis), $M/\Delta M > 9000$ at FWHM peak height. Scan time 20 seconds/mass unit
ROSINA RTOF	Time of Flight mass spectrometer	Mass range 1 to 300, $M/\Delta M > 500$, 200 seconds full spectrum
COSIMA	Microscope and Ion probe	Dust collection plate with microscope 13.7 μm resolution. Ion probe micro probe, spot size 50 μm , mass range 1-3500, mass resolution (at 100 Da) 2000
Philae COSAC	Gas chromatography - Time of Flight mass spectrometer	8 GC columns High molecular mass (>600) organics. Mass range 2 to > 300 .
Philae Ptolemy	Gas chromatography - Ion Trap mass spectrometer	3 GC columns. Isotopes C, N and H. Mass range 10 to 150, Unit resolution, 2 seconds full spectrum

VIRTIS	Visible and Infrared spectrometer.	Mapping spectrometer Vis 0.25-1 μm and IR1-5 μm , resolving power 200. High resolution IR spectrometer 2.5 – 5.0 μm , resolving power 1000-2000.
MIRO	Microwave spectrometer	Frequency 188 and 562 GHz. Tuned to water, carbon monoxide, methanol, and ammonia and their hydrogen and oxygen isotopes.

Mass spectrometry directly detects molecules that enter the ion source; however, it has its own problems with identifying molecules. Molecules can have the same atomic mass e.g. N_2 and CO both mass 28 causing isobaric interferences. The gas chromatography mass spectrometry (GCMS) systems of the COSAC and Ptolemy instruments were able to separate mixtures of compounds to avoid isobaric interferences and help identify molecules. Alternatively, ROSINA DFMS used high mass resolution power to distinguish between molecules e.g. CO mass 27.9949 Da can be separated from N_2 mass 28.0061 Da with a mass resolution in excess of 3000 at FWHM (defined as $M/\Delta M$, the ability to separate a peak at mass M from an adjacent peak at $M+\Delta M$). However, mass resolution alone is often insufficient as ions fragment in the ion source e.g. CO^+ can be produced from both CO and CO_2 . In addition, molecules with the same elemental formula can have different structures and molecules of exactly the same mass can have very different chemical properties e.g. acetic acid ($\text{CH}_3\text{-COOH}$) and acetaldehyde ($\text{HO-CH}_2\text{-CHO}$), both have the same empirical formula $\text{C}_2\text{H}_4\text{O}_2$ and hence mass 60.0021 Da. To some extent, the fragmentation pattern of molecules can be used to distinguish the parent molecule, often by referring to the NIST webbook. Yet, different mass spectrometers have their own individual characteristics with both fragmentation patterns and ionisation sensitivity dependent on the instrument and its operating conditions. The ROSINA mass spectrometers had their own bespoke calibration facility, CASYMIR⁶⁰ to identify organics and determine their relative intensities. An additional complication for the Ptolemy ion trap mass spectrometer is the occurrence of ion molecule reactions especially with water to form ions with $M+1$. The Ptolemy GC was not used as a result of the non-nominal landing so the effects of ion molecule reactions are being investigated⁶¹. A further complication is that the process of ionisation in the mass spectrometer often causes the parent molecule to fragment. Hence low mass peaks can originate from low mass parent molecules or heavier molecules that have fragmented in the ion source. Interpreting a mass spectrum involves deconvoluting signals from heavier molecules, which are identified if the parent mass and all of the expected fragments are present, and removing the effect of their fragmentation from lower mass signals.

The ROSINA DFMS was extremely successful during the Rosetta mission, almost doubling the number of molecules detected in the coma to 34. A diagram of the detected molecules, often referred to by the ROSINA team as the cometary zoo, displays the molecules having similar properties grouped together and represented by an animal, see Figure 3. The current list of molecules (as of 2017) are listed by class in Table 3, although it is almost guaranteed that more will be identified as exploration of the ROSINA data set and calibration continues (e.g. Schuhmann et al.⁶²). This list of organic molecules detected by ROSINA includes all of the organic molecules previously detected by remote observation and previous space missions. Some of the newly detected species are from known classes of organics but with increasing carbon number, e.g. the carbon chain length of the alkanes has increased from 2 to 7 (ethane

to heptane) and the alcohols from 2 to 5 (ethanol to pentanol). Nevertheless, the relative abundances of the different chain lengths and structures will place constraints on the formation pathways for these molecules.

Deriving relative intensities is not straight forward as the coma is highly heterogeneous⁶³ and the derivation of relative intensities will depend upon models of the coma heterogeneity whether from insolation driven, localised active regions, or seasonal effects (cf. Reference ⁶⁴. Longer term monitoring and modelling to account for spacecraft distance, comet shape and illumination, has shown that water is more variable than CO and CO₂, possibly as it is affected more by the surface dust and recent comet history whereas CO and CO₂ sublimates from deeper layers ⁶⁵.

Figure 3. Organics identified by ROSINA DFMS in the ROSINA zoo, with each class of organic associated with its representative animal. Reproduced with permission from <http://blogs.esa.int/rosetta/2016/09/29/the-cometary-zoo/>, Copyright ESA.

Table 3. Molecules identified by ROSINA DFMS as of 2017 adapted from Altwegg et al. ⁶⁶ and references therein.

Main compounds	Hydrocarbons	Oxygen containing organics	Nitrogen containing molecules	Misc. non-organics	Sulphurous molecules
H ₂ O	Alkanes	Aldehydes	Non-organics	N ₂	Non-organics
	H-[CH ₂] _n -H	$\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R} \end{array}$			
CO	CH ₄	CH ₂ O	NH ₃	P	S

CO ₂	C ₂ H ₆	CH ₃ -CHO	N containing organics	O ₂	H ₂ S
	C ₃ H ₈	Alcohols	HCN	H ₂ O ₂	SO
	C ₄ H ₁₀	CH ₃ OH	CH ₃ NH ₂		OCS
	C ₅ H ₁₂	C ₂ H ₅ OH	C ₂ H ₃ N	Halogens	S ₂
	C ₆ H ₁₄	C ₃ H ₇ OH	C ₂ H ₅ NH ₂	HCl	SO ₂
	C ₇ H ₁₆	C ₄ H ₉ OH	C ₂ N ₂	HBr	CS ₂
Alkynes		C ₅ H ₁₁ OH		HF	S ₃
	C ₂ H ₂		O & N containing organics		S ₄
Aromatics		Carboxylic acids	C ₂ H ₅ NO ₂	Noble gases	S cont. organics
C ₆ H ₆		H-COOH	C ₄ H ₉ NO	Ar	CH ₂ S
C ₇ H ₈		CH ₃ -COOH		Kr	CH ₄ S
C ₈ H ₁₀		C ₂ H ₅ -COOH	halides	Xe	C ₂ H ₆ S
e.g.
C ₁₀ H ₈			CH ₃ Cl		
	C ₆ H ₅ -COOH

Rubin et al. ⁶⁷ measured the N₂/CO ratio of $(5.70 \pm 0.66) \times 10^{-3}$ which is depleted by a factor of 25 compared with protosolar N₂/CO ratio of 0.29 ± 0.1 (calculated from the protosolar N/C ratio of 0.29 ± 0.1 , ⁶⁸). This indicates that comet Churyumov-Gerasimenko formed at a low temperature of approximately 30 K. The D/H ratio was found to be about 4 times the terrestrial value, $(5.3 \pm 0.7) \times 10^{-4}$, which is the highest measured for a comet ⁶⁹. The D enrichment can originate either from ion molecule reactions between H₂ and H₂O, which favours larger D enrichments in the water at colder temperatures or from D rich water in-falling to the presolar nebula; both models predict an increase in D/H ratio with increasing radial distance. The high D₂O/HDO ratio of 17 ⁷⁰ indicates that a large fraction of the water formed on grains and coming unprocessed from the presolar cloud. Hence comet 67P/Churyumov-Gerasimenko appears to be a serendipitous choice as the target for the Rosetta mission was to look for pristine organic material formed at cold temperature in the outer comet forming region.

Of key note was the detection of the amino acid glycine, C₂H₅NO₂ ⁷¹. Glycine was only detected at high coma pressure when the orbiter was close to the nucleus or during dust outbursts. Concurrent with the detection of glycine was the detection of its precursor methylamine CH₅N and ethylamine C₂H₇N. The correlation of glycine with dust outbursts and glycine's relatively high sublimation temperature of about 150 °C, indicate that it was a distributed source, probably from icy mantles of dust grains released into

the coma, although direct release of glycine from the surface could not be ruled out. In the absence of aqueous water, glycine can be formed in icy mantles surrounding dust grains either by grain-surface chemical reactions⁷² or by UV irradiation⁷³. These processes could occur in the ISM or in the early solar nebula⁷⁴. A wide range of amino acids have been detected in meteorites which suggests that these amino acids formed during aqueous alteration of the parent body⁷⁵⁻⁷⁸. Altwegg et al.⁷¹ suggested that the formation of glycine and lack of other amino acids was indicative of formation on dust grains rather than through aqueous alteration.

Soluble aromatic compounds are a new class of organic molecules discovered in comets by the detection of toluene ($C_6H_5-CH_3$) reported in Altwegg et al.⁷⁹. Other aromatic compounds reported *in-situ* (but currently unpublished) are benzene, xylene, benzoic acid (C_6H_6 , $C_6H_4-[CH_3]_2$, C_6H_5-COOH) and the first PAH detected naphthalene ($C_{10}H_8$, two fused benzene rings). PAHs have been postulated as the carriers of unidentified infrared bands (UIR) in the ISM⁸⁰, although none, as yet, have been identified. Benzonitrile has recently been detected in the ISM and may be a precursor to PAHs⁸¹. Alternatively, Kwok and Zhang⁸² have suggested that the carriers of UIRs may be from mixed aromatic-aliphatic particles with aliphatic bridges between the aromatic rings. The aromatics detected in the comet could be precursor molecules to PAHs or the breakdown and fragmentation products of the mixed aromatic-aliphatic particles. The identification of aromatic compounds in comets by ROSINA opens up a new area of research in cometary organics.

The chemistry of sulphur is similar to that of oxygen with sulphur bearing organic molecules having an oxygen atom replaced by sulphur, e.g. hydrogen sulphide, H_2S , instead of water and CH_3SH instead of formaldehyde. Three sulphur bearing organics were detected CH_2S , CH_3SH and C_2H_6S , the latter two being the first detection in comets⁸³. CH_2S and CH_3SH were identified as thioformaldehyde and methanethiol. C_2H_6S has two isomers, ethanethiol (C_2H_5SH) and dimethyl sulphide (CH_3-S-CH_3) which could not be distinguished based on their mass spectrometer fragmentation pattern due to isobaric interferences from other ions and their fragments, so either or both may be present. In star forming regions sulphur is depleted by a factor of 1000 compared to its cosmic value. Irradiation by UV photons of icy mantles has been shown to destroy H_2S and lead to the formation of S_2 ⁸⁴, and then forming sulphur polymers S_n , thus acting as a sink for the observable sulphur whilst the S_n polymers remain in the grains. This model is backed up by the ROSINA detection of S_3 and S_4 ⁸³. The isotopic ratio of sulphur bearing species does not lie on either mass dependent or mass independent fractionation lines of solar values⁸⁵, pointing to non-homogenous mixing of the solar nebula.

Philae results and organics in surface dust

On 12th November 2014 the Philae lander made its first touchdown on the comet surface at the Agilkia landing site⁸⁶. Despite the 'non-nominal' landing, both of the Philae mass spectrometers, COSAC and Ptolemy, operated within 20 minutes of the touchdown and acquired mass spectra. The aim of this first measurement was to determine the background coma composition before acquisition and analysis of a surface sample. In retrospect it is apparent from the mass spectra and NavCam images of the landing that the touch down disturbed the surface producing a dust cloud, with dust or subliming molecules entering the mass spectrometers. In effect the mass spectrometers made a measurement of the surface without using the drill and sample ovens. The mass spectra from both instruments were remarkably similar as shown in Figure 4. In the earlier Ptolemy mass spectrum, only half the detected ions were

from water (m/z 17-19), indicating that the dust was relatively dry containing a high proportion of organics.

Figure

4. Comparison of the COSAC and Ptolemy mass spectra during the Philae landing

Interpretation of the mass spectra was complicated as neither instrument had sufficient resolution to unambiguously identify peaks and the organics were not separated by their respective gas chromatography columns. The COSAC team⁸⁷ used a peak fitting algorithm, starting with a list of conceivable molecules short listed based on the NIST webbook fragmentation pattern, resulting in a best fit list of molecules and their relative abundance, shown in Table 4. Their interpretation is the dust contains a high proportion of nitrogen containing organics, along with the first detection of ethanamide (CH_3CONH_2) and isocyanatomethane (CH_3NCO). The Ptolemy team⁸⁸ took a different approach as ion molecule reactions in the ion trap mass spectrometer make the use of the NIST webbook fragmentation patterns unsuitable. Instead they noted that there appeared to be peaks repeating at 14 and 16 mass units and the spectra could not be solely pure hydrocarbons, but required another element O, concluding that the dust contained a high proportion of CHO organics. These organics are likely to be built from building blocks of water and CO initially forming formaldehyde.

Table 4. Molecules identified at the surface of the comet, from Goesmann et al.⁸⁷.

Chemical name	Molecular formula	Abundance relative to water (%)
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Water	H ₂ O	100
Methane	CH ₄	0.5
Methanenitrile (hydrogen cyanide)	HCN	0.9
Carbon monoxide	CO	0.9
Methylamine	CH ₃ NH ₂	0.6
Ethanenitrile (acetonitrile)	CH ₃ CN	0.3
Isocyanic acid	HNCO	0.3
Ethanal (acetaldehyde)	CH ₃ CHO	0.5
Methanamide (formamide)	HCONH ₂	1.8
Ethylamine	C ₂ H ₅ NH ₂	0.3
Isocyanomethane (methyl isocyanate)	CH ₃ NCO	1.3
Propanone (acetone)	CH ₃ COCH ₃	0.3
Propanal (propionaldehyde)	C ₂ H ₅ CHO	0.1
Ethanamide (acetamide)	CH ₃ CONH ₂	0.7
2-Hydroxyethanal (glycolaldehyde)	CH ₂ OHCHO	0.4
1,2-Ethanediol (ethylene glycol)	CH ₂ (OH)CH ₂ (OH)	0.2

Observations of the surface by VIRTIS indicated that the surface is a mixture of opaque minerals and non-volatile macromolecular organics containing CH and CO functional groups but little N functional groups⁸⁹. A more detailed investigation indicated that carboxylic acids were a highly plausible candidate for the of the broad 3.2 μm band along with CH functional groups and ammonium⁹⁰. However, there was no indication of amines and amides. In addition, hydrated minerals were not detected, indicating no link with the carbonaceous chondrites. The macromolecular organics could be the non-volatile organics remaining once the volatiles have sublimed or material formed by exposure at the surface, aliphatic molecules losing hydrogen, forming unsaturated organics, aromatic rings and graphitisation.

The COSIMA analysis of 30 dust particles⁹¹ showed that the dust particles were a mixture of anhydrous minerals mixed with approximately 45 wt.% carbonaceous matter, regardless of grain morphology⁹²(R, G, C, S; Rubble pile, Glued cluster, Compact particle and Shattered cluster). The organics and mineral phases were not resolvable at the 40 μm scale (the COSIMA ion beam spot size) indicating an intimate mix of organics and mineral, similar to the findings of the Wild 2 captured particles³⁹. The primitive

nature of the mineral phases was supported by the detection of a calcium-aluminium-rich inclusion in a dust grain⁹³. The spectra indicated that the carbon was mostly in the form of macromolecular material similar to insoluble organic matter (IOM) found in meteorites, but having a higher hydrogen/carbon ratio and so less processed than that of meteoritic IOM⁹⁴. The lack of volatile organics may be a result of different sampling mechanisms where grains are stored on a sample plate for some time before analysis compared to the mass spectrometer instruments.

Normally ROSINA measured the volatile species in the coma however there were occasional dust impact events, identified by burst of high count rates and a mass spectra finger print similar to COSAC and Ptolemy touchdown spectra⁷⁹. The high resolution ROSINA mass spectra showed that the proportion of organics was generally $\text{CH} > \text{CHO} > \text{CHN} > \text{CHON}$ and that most of the peaks of the COSAC mass spectrum could be explained by oxygen containing organics. Also based on the fragmentation pattern methylisocyanate and acetamide were not positively identified in the ROSINA mass spectra and were only minor components of the dust at best⁷⁹. This is consistent with VIRTIS observations that the surface organics contain CH and CO functional groups but little N functional groups⁸⁹. However, the conflicting results could represent the different sampling methods between the three instruments. The Philae mass spectrometer exhaust ports, the entry point for dust into the mass spectrometers, had different geometries with COSAC's beneath the lander body pointing towards the comet surface and Ptolemy's on top of the lander body pointing away from the surface. During the landing it is possible that COSAC directly sampled the dust without exposure to solar radiation, whereas for Ptolemy (and ROSINA) the dust is exposed to space and only molecules subsequently subliming were detected. Hence it is possible that COSAC detected high concentrations of nitrogen bearing organics sampled from just beneath the surface during the touchdown impact without exposure to space. It is interesting to note that there were also discrepancies in the Stardust organics; those detected in-situ by vaporisation of particles were nitrogen rich⁴⁴, yet the organics detected in the returned aerogel samples were rich in both nitrogen and oxygen⁴⁸.

The search for Poly-Oxy-Methylene (POM)

Poly-Oxy-methylene (POM) is a polymer of formaldehyde ($\text{H}-[\text{CH}_2\text{O}]_n\text{-H}$) and its thermal breakdown has been suggested as the distributed source of formaldehyde in 1P/Halley⁴⁰. The CHON dust particles have to contain about 3% POM for it to be the source of formaldehyde detected in 1P/Halley⁹⁵. Wright et al.⁸⁸, suggested that the Ptolemy spectra was consistent with POM like material being formed from the polymerisation of formaldehyde - the masses detected at m/z 91 and 92 being possible C_3 POM fragments. Laboratory simulation of water, formaldehyde and ammonia ices have shown that POMs up to C_5 can be produced in a cometary environment³. The POM formation required low concentrations of ammonia, which is consistent with the organics on the comet having a high oxygen and low in nitrogen content based on *in-situ* analysis. However, the ROSINA DFMS high resolution mass spectra at 91 and 92 showed that the contribution from C_7H_7^+ and C_7H_8^+ (ionisation of toluene) was much larger than the postulated POM fragments $\text{C}_3\text{H}_7\text{O}_3^+$ and $\text{C}_3\text{H}_8\text{O}_3^+$ ⁷⁹. In addition, based on the mass spectra of a sample of synthetic POM analysed with the ROSINA calibration facility, the peaks larger than mass 60 were less than 0.1% of the intensity of the main peaks at masses 28 to 31. The COSIMA microprobe detected high molecular weight organics in the captured dust particles, but concluded that the organics was similar to the meteorite insoluble organic matter, albeit less altered, and did not detect any POM⁹⁴.

Terrestrial observations of cometary organics

Every year approximately 2×10^6 kg of extraterrestrial material accreted by the Earth is in the form of interplanetary dust particles (IDPs) ranging in size from 5 μm to 50 μm . With a mass of ~ 1 ng they are small enough to be decelerated by the atmosphere and survive atmospheric entry without complete vaporization or severe heating e.g., ⁹⁶. The extraterrestrial origins of IDPs has been attested by their physical, mineralogical and chemical properties, such as D/H ratios and noble gas measurements ⁹⁷⁻¹⁰².

Since 1981, NASA has used high altitude flights to collect IDPs in the stratosphere, to minimise terrestrial contamination and terrestrial alteration of the particles ¹⁰³. Two types of IDPs are present in the stratospheric collections, anhydrous chondritic porous (CP) IDPs and hydrous chondritic smooth (CS) IDPs. Most cluster particles belong to the CP class (CS:CP $\approx 1:1.2$)¹⁰⁴ likely due to their fragile nature thus prone to fragmentation during impact when captured. Hydrous CS IDPs contain minerals altered by thermal and aqueous alteration, processes that occurred on meteorite parent bodies and so they are thought to be as asteroidal origin. The low densities, high porosities and fragile microstructure of CP IDPs are consistent with the particulate material in cometary meteors ¹⁰⁵. CP IDPs have high abundances of glass with embedded metal and sulphides (GEMS) and submicrometer magnesium rich silicates such as enstatite (the magnesium-rich end-member of pyroxene) and forsterite (the magnesium-rich end-member of olivine). Comparison between CP IDPs and CS IDPs are shown in Figure 5.

With a likely cometary origin e.g., ^{105, 106}, CP IDPs have avoided parent body processes (e.g. aqueous and metamorphic activities) that are common to most other astromaterials with an asteroidal origin. Hence, CP IDPs are potentially samples that retain information about the interstellar organic matter that was present in the solar nebula, and offer insights into the nature and synthetic pathway of the first organic matter formed in our solar system.

Since 2002 NASA has flown collectors at specific times of enhanced dust infall (meteor showers) to collect material from targeted comets, such as 55P/Tempel–Tuttle, 26P/Grigg–Skjellerup, 21P/Giacobini–Zinner and Swift–Tuttle ¹⁰⁷⁻¹¹³. A summary of the targeted collections with the associated comet properties are listed in Table 5. As the collectors have also captured other background extraterrestrial material during the flight, the targeted grains cannot be connected with the targeted comets with certainty. Nevertheless, it is possible to establish a cometary origin for some of these samples by identifying unique traits, such as the mineral assemblage and very short space exposure times. In effect these targeted campaigns are comet sample return missions at very low cost.

Figure 5. Comparisons between the morphology and mineralogy of anhydrous chondritic porous CP IDP and hydrous chondritic smooth CS IDP Reproduced with permission ¹⁰⁶ Copyright 2007 Treatise on Geochemistry.

Table 5. Summary of NASA targeted IDP collection campaigns. References: ^{107, 114, 115}

Parent object		Perihelion (AU)	Eccentricity (AU)	Atmospheric entry velocity (km/sec)	Meteor shower (Date of peak)	Year of collection
Main belt asteroids				11.1		
Comets	21P/Giacobini– (perihelion <1.2 Zinner AU)	1.0	0.71	20	Draconoid (a.k.a. Giacobinids) (October 8)	2012
	26P/Grigg– Skjellerup	1.1	0.66	22	Pi Puppids (April 23)	2003
	Swift-Tuttle	1.0	0.96	61	Perseid (August 12)	
	Halley	0.6	0.97	65	Eta Aquariids (May 6)	
					Orionids (October 21)	
	55P/Tempel– Tuttle	1.0	0.91	72	Leonids (November 17)	2002

IDPs generated from comets with perihelia < 1 AU typically have higher entry velocities of > 15 km s⁻¹ than asteroidal grains. The more promising retrievable cometary materials are derived from the least luminous meteors, as they are less influenced by atmospheric entry heating. For example, the Earth-encounter velocity of comet Grigg–Skjellerup’s dust stream is ~22 km s⁻¹ ^{108, 115}. The close encounter of comet Grigg–Skjellerup with Earth has peak fluxes in April 2003 and 2004, and was predicted that at least several percent of the background interplanetary dust flux at the >40 μm size were dusts from this comet during the targeted collection ¹⁰⁸. On the contrary, dust grains associated to luminous meteor showers are derived from comets with higher eccentricity, inclination, which travel faster at perihelion, and thus arrive at the Earth’s stratosphere at higher velocities and are typically heated to a higher degree ^{114, 116, 117}. For example, the Leonid meteor shower from comet 55P/Tempel–Tuttle has an Earth-encounter velocity of 72 km s⁻¹. These grains are severely heated to melting/vaporizing stage, thus the search for surviving unmelted Tempel–Tuttle samples had been particularly challenging.

Although IDPs are often decelerated without melting, they are typically heated to elevated temperatures > 900 °C for about a second ¹¹⁸. Atmospheric entry heating of IDPs can ultimately alter the isotopic composition and the structure of the organics by modifying the relative abundance of the aliphatic and aromatic components. For instance, the preferential decomposition of the thermally labile aliphatic bridges during atmospheric entry heating could have lowered the δD values of the organics. The host of the N isotopic anomalies, such as high-mass polyaromatic hydrocarbons containing nitrogen-bearing heterocycles ¹¹⁹, are more refractory than the D-rich aliphatic material ¹¹⁹. Therefore, subjected to the loss of D-rich labile hosts, the organics in the heated IDP grains would exhibit lower δD while retaining the N isotopic anomalies.

The cometary origin of CP IDPs is further attested by their similarities to cometary dust collected/observed by the Stardust and Rosetta, shown in Figure 6. Cometary particles collected in the immediate vicinity of comet 67P/Churyumov-Gerasimenko by COSIMA exhibit extreme diversity in

typology (shattered clusters, glued clusters and rubble piles) at the 10s μm scale⁹². The IDP morphology as fine-grained aggregates of submicrometer-sized minerals is comparable to the general occurrence of cometary particle as mm-sized aggregates¹²⁰. Atomic force microscope (AFM) topographic images obtained by the Micro-Imaging Dust Analysis System (MIDAS) onboard Rosetta also revealed that cometary dust particles of comet 67P sometimes occur as large porous particles of sub-micrometre aggregates components that are built from grains smaller than 500 nm, resembling that of CP IDPs¹²¹.

Figure 6. Comparison of dust grain morphology for CP IDPs (left), 67P/Churyumov-Gerasimenko grains captured by Rosetta (middle) and 81P/Wild (Wild 2) grains captured in aerogel (right) at different scales. References from: ^{46, 92, 121-123}. Images reproduced with permission Ref. 46 Copyright Science 2008; Ref 92 Copyright Icarus 2016; Ref 121 Copyright Nature 2016; Ref. 122 Copyright Meteoritics & Planetary Science 2017; Ref. 123 Copyright Meteoritics Science 2008.

The morphology of IDPs is also comparable to the fine-grained material from comet 81P/Wild 2 returned by the Stardust mission. Terminal particles retrieved from aerogel are composed of individual grains of

<1 μm in size, and that each particle could be a fragment of a cohesive Wild 2 particle that broke apart when it decelerated in the silica aerogel capture cell ¹²⁴. The extreme composition ranges measured for the olivine and pyroxene grains of comet 81P/Wild 2 are similar to that of CP IDPs ⁴⁷, which suggest possible similar origins. The low degree of primitiveness of the amorphous carbon component of Wild 2 particles as observed by Raman spectroscopy is comparable to that observed for IDPs, suggesting that organics that are heated significantly during IDP's atmospheric entry is consistent with the expected Wild 2 particle heating on aerogel capture ¹²⁴. The submicrometer heterogeneity of primitive and processed (thermal and irradiation) carbons is also found in both IDPs and Wild 2 grains ^{48, 125, 126}, which could be a signature of cometary grains accreted in the Kuiper belt ¹²⁷.

Organics in IDPs

In the investigation of organic matter in IDPs, analytical techniques that consume a large amount of materials could not be applied due to the limited availability of IDPs. This obviates the possibility of many soluble organic analytical techniques without the required sensitivity and spatial resolution. Amino acid analysis of IDPs, for instance, is particularly challenging as it typically requires extracting and concentrating amino acids from at least 100 mg of meteorite sample as they are often present at parts-per-million (ppm) or parts-per-billion (ppb) levels in meteorites. The techniques which do offer high sensitivity and spatial resolution (e.g. FTIR, X-ray absorption near-edge structure (XANES) spectroscopy, microprobe two-step laser mass spectrometer (μL2MS)), however, are often functional group specific, rather than providing characterization of the entire organic molecule. The bias in the implementation of analytical techniques for different astromaterials results in the apparent variation in the information obtained from the study of organic matter in IDPs as compared to that obtained from the organic matter in meteorites.

Some IDPs contain a high abundance of carbon (10 wt.%) that is significantly higher than the most carbon-rich meteorites (carbonaceous chondrites contain 2–5 wt.% of carbon) ^{104, 128, 129}. The “soft-landed” IDPs are delivered to the Earth surface intact, and thus they are a crucial contributor of carbonaceous compounds to the early Earth ¹³⁰. Stratospheric IDPs retain pristine information about the exogenous carbonaceous material that are uncontaminated and relatively unaltered by terrestrial processes compared to meteorites recovered from various expeditions to hot and cold deserts.

The carbonaceous material in IDPs is often present as discrete grains or as a semicontinuous matrix of macromolecular carbonaceous material wrapping around submicrometer-sized minerals ^{102, 105}. The insoluble organic matter (IOM) component represents 5–40% of the volume of an IDP ¹³¹. Sometimes these organic components contain other carbon bearing inorganic phases such as nanodiamonds ¹³². IDPs contain highly-disordered carbon associated with amorphous aromatic units, such as PAHs and their alkylated derivatives, connected by abundant aliphatic and carbonyl (C=O) moieties as bridging material e.g., ^{100, 102, 112, 119, 133, 134}. OM in primitive anhydrous IDPs is similar to that observed in acid residues of primitive chondritic meteorites, however, the aromatic/aliphatic ratio is notably lower in the IDPs ^{100, 133}, which indicates the presence of abundant aliphatic bridges, heteroatoms, with high H/C ratios ¹³⁵. Measurements made with μL2MS by Clemett et al. ¹¹⁹ showed that two of the eight IDPs they analysed – Aurelian and Florianus – contain high-mass PAHs (500–700 Da), which could potentially reflect the presence of OM unique to IDPs, or it could be a sign of thermal alteration

(polymerization/sintering of lower molecular weight compounds) as a result of atmospheric entry heating⁹⁷.

Other than their primitive and anhydrous natures, the OM in CP-IDPs is typically enriched in the heavier stable isotopes of H and N. They display some of the largest enrichments of D measured in solar system materials (δD values up to $\sim 30000\%$)¹¹², and are accompanied by significant spatial heterogeneity of OM at micrometre-scale^{100, 136, 137}. As various astrochemical processes could lead to D enrichment, such as photodissociation of PAHs in the diffuse interstellar medium^{101, 138}, the isotopic anomalies indicate that the IDP OM contains primordial solar system materials with an origin in the interstellar medium, produced by ion–molecule reactions in cold (10–100 K) molecular clouds, and/or outer regions of the protoplanetary disk^{100, 137, 139}.

Meteorites with a possibly cometary origin

Asteroids, from which most of the Earth recovered meteorites originate, are distinguished from comets by their close to circular orbits, whereas comets have elliptical, highly inclined orbits that extend beyond Jupiter. However, the presumption that asteroids and comets are two radically different kinds of celestial bodies is challenged by the presence of various astromaterials that span a continuum between comets and asteroids^{140, 141}. Two strange meteorites – the Orgueil and Tagish Lake meteorites, shown in Figure 7, – are both classified as carbonaceous chondrites, and yet they exhibit characteristics that are not fully compatible with the majority of meteorites.

Orgueil

Tagish Lake

Murchison

Figure 7. Photos of the Orgueil, Tagish Lake and Murchison meteorites. The friable nature of the Orgueil and Tagish Lake meteorite account for their phyllosilicate-rich lithologies. Scale bars are 1 cm.

The Orgueil meteorite, which was classified as a CI carbonaceous chondrite, fell in a very well-witnessed shower in southwestern France on 14 May 1864. The rarity of CI meteorites, volatile-rich nature of Orgueil, high water-to-rock ratio, abundance of hydrated minerals ^{142, 143}, distinctive oxygen isotopes ¹⁴⁴, and the low inclination of its orbit ¹⁴¹ have led to the hypothesis that Orgueil has a cometary origin ¹⁴⁵. The low inclination of Orgueil orbit gives a Tisserand parameter (T) value of <2.8 , which is more compatible with the orbit of JFCs ($2 < T < 3$) rather than that of asteroids ($T > 3$) ^{141 and references therein}.

The carbonaceous material in Orgueil was found structurally bound to phyllosilicates ¹⁴⁶, which suggests that formation of meteoritic organics in association with clay as catalyst, and establishes that its parent body has a high water content. The striking variation between the amino acid compositions of Orgueil and the CM chondrites led to the view that Orgueil possibly derives from an extinct comet ¹⁴⁵. The high abundance of α -amino acids such as aminoisobutyric acid (AIB) and isovaline in CM chondrites suggests that the amino acids were formed via the Strecker synthesis. On the contrary, Orgueil contains predominantly β -alanine but it is depleted in α -amino acids. β -amino acids cannot be produced by Strecker synthesis, but via Michael addition of ammonia to α , β -unsaturated nitrile, followed by hydrolysis to the carboxylic acid ¹⁴⁷. The presence of phyllosilicates and the amino acid composition indicates that aqueous alteration has taken place, at odds with the lack of detection of hydrous minerals on the surface of 67P/Churymov-Gerasimenko ⁹⁰.

On January 18 2000, an exceptionally bright fireball was observed over Yukon Territory and northern British Columbia that corresponded to a huge meteoroid with an initial diameter of 4 to 6 m ¹⁴⁸. A portion of the meteorite – the Tagish Lake C2 chondrite – was recovered almost immediately from the frozen lake in January and was maintained in frozen and “pristine” states ¹⁴⁹. Although the calculated orbit for Tagish Lake is asteroidal ¹⁴⁸, its reflectance spectrum is similar to D-type asteroids that are trapped in the outer solar system beyond the main asteroid belt ¹⁵⁰⁻¹⁵². The low-albedo of Tagish Lake (~ 0.03) ¹⁵⁰ is comparable to comets (0.02 to 0.06) ¹⁵³ as well as hydrated carbonaceous chondrite (0.03 to 0.05) ¹⁵⁴. D-type asteroids are among the best candidates to be implanted cometary bodies, on the grounds of their spectral similarities with dormant cometary nuclei ¹⁵⁵⁻¹⁵⁷ and dynamic processes ¹⁵⁸⁻¹⁶¹. For example, D-type asteroids could be JFCs that had been captured in the outer asteroid belt 3.8 billion years ago ¹⁵⁹. Recently, study of the C isotopic ratio of Tagish Lake indicates that Tagish Lake ice has a $\text{CO}_2/\text{H}_2\text{O}$ ratio within the range of comets ¹⁶². These observations further strengthened the growing consensus that D-type asteroids and comets might have a common origin, and extended the possibility of a cometary origin for the Tagish Lake meteorite ¹⁵⁶.

The Tagish Lake meteorite has a mineralogy, oxygen isotope, and bulk chemical composition intermediate between CI and CM meteorites, and yet is distinct from both ^{148, 149}. It has a bulk carbon content of approximately 4 wt% of which about <2 wt% is organic matter ^{163, 164}, and it is suggested to be the most carbon-rich chondrite known ¹⁶⁵. Tagish Lake has a low H/C ratio and fractional concentration of aliphatic carbon compared to many other carbonaceous chondrites (e.g., aliphatic carbon/ total carbon of Orgueil = 0.1, Murchison > 0.1 , and Tagish Lake ~ 0.03), which reflects the degrees of parent body aqueous alteration and/or a highly special organic synthetic pathway ^{164, 166}.

The Tagish Lake meteorite contains abundant organic nanoglobules with aliphatic and oxygenated function groups that have elevated δD and $\delta^{15}N$ values, which suggests a highly primitive, possibly presolar origin for the organics, and their formation in the cold molecular clouds and the outer protosolar disk at extremely low temperatures ($<-250\text{ }^{\circ}C$)¹⁶⁷⁻¹⁷¹.

The unique organic chemistry of Tagish Lake is dissimilar to most other carbonaceous chondrites, which echoes to the distinctive nature of its mineralogy and petrology. Although the oxygen isotope measurements of Tagish Lake suggest that the physical conditions on its parent body were favourable for the formation of amino acids via the aqueous Strecker-cyanohydrin synthetic pathway¹⁴⁸, the amino acid abundance of Tagish Lake was extremely low (at the parts per billion level) and is not particularly enriched in the Strecker synthesis products such as AIB and isovaline^{75, 172, 173}. The paucity in organic matter in Tagish Lake suggests that the meteorite comes from a primitive parent body that was originally was depleted in volatile precursor molecules¹⁷², or has experienced a high degree of chemical oxidation during aqueous alteration¹⁷⁴, and the presence of clay may have protected the organic C from being completely oxidized¹⁴⁶.

Summary

Comets are enigmatic and ephemeral objects. Building a picture of their formation and record of the early solar system has involved three interlocking pieces of the puzzle; remote sensing, spacecraft missions and the laboratory analysis of their remains, the IDPs. Radio and IR observations have identified organics which show similarities with organics in interstellar space and young stellar objects. *In-situ* missions have extended the list of organic molecules, provided ground-truth data on a few individual comets, and evidences that the anhydrous IDPs collected on Earth are likely cometary. The array of instrumentation on comet mission spacecraft can provide information on the both the volatile and non-volatile character of organics as well as the dust. Since cometary IDPs and the Stardust returned samples are small fragments of cometary material that were ejected from the comet surface exposed to space, experienced a brief heating event, the organics they contain may be comparable to the processed surface material observed by VIRTIS⁸⁹ minus the heating.

Several lines of evidence suggest that comets are relatively unaltered after their formation:

1. The high abundance of volatile organics e.g methane and ethane,
2. the presence of anhydrous minerals even though they are in intimate contact with water,

3. the exposure of new cometary surfaces does not greatly affect the coma composition, as
in the case of the splitting of 73P/Schwassmann-Wachmann or deep excavation by
Deep Impact.

We do not appear to have any large cometary fragments material on Earth as they are too friable. The best contenders, Orgueil and Tagish Lake are unlikely to have a cometary origin due to the high abundances of hydrous minerals suggesting a formational environment of an extended aqueous alteration history. So, for the final part of the journey from the ISM to Earth the organics survived in the 'escape capsules' of IDPs. Perhaps in a counterintuitive fashion, ROSINA in sampling the coma detected volatiles released from a pristine source within the comet. Whereas the lander mass spectrometers, which were designed to analyse a pristine surface sample, actually measured processed material on the surface that forms the IDPs.

There are no active comet space missions and any comet sample return mission is decades from fruition at best; e.g. the proposed CAESAR (Comet Astrobiology Exploration Sample Return) spacecraft is currently planned for a launch date in the mid 2020's with a sample return in 2038. However, the future prospects for further discoveries of cometary organics is very good. Data from all the instruments of the Rosetta orbiter and Philae lander are freely available on the European Space Agency's Planetary Science Archive. As the Rosetta data is processed more molecules are bound to be identified. The operation of ALMA and continuous improvements in remote sensing techniques will improve sensitivity and spatial resolution, detecting new molecules in more comets. Meanwhile analytical laboratory techniques are always improving in sensitivity and we have the cometary IDPs and Stardust returned samples on Earth.

It is interesting to note that many of the organic molecules have been linked as possible biomarkers when searching for life ¹⁷⁵ (and the associated exoplanet database <http://seagerexoplanets.mit.edu/ASM/allmols.html>). The conditions in interstellar space and on comets are not suitable for life and they have a non-biological origin. However, it remains possible that these molecules were delivered by comets through IDPs to an early Earth and may have had a role in the emergence of life. Even if the organics didn't survive intact, comets have the common elements necessary for life, phosphorus ⁷¹ and sulphur ⁸³ as well as the CHON elements. As such, comets are no longer viewed as harbingers of doom, but are messengers from the solar system's birth and perhaps they carried ingredients for life on Earth.

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